Electronic Supplementary Information

Chiral Lewis acid-catalyzed enantioselective cyclopropanation and C-H insertion reactions of vinyl ketones with \( \alpha \)-diazoesters

Peng Zhao, Simeng Wu, Chaoqi Ke, Xiaohua Liu,* Xiaoming Feng*

* Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

* liuxh@scu.edu.cn

* xmfeng@scu.edu.cn

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1. General remarks

Reactions were carried out using commercially available reagents in oven-dried apparatus. CH\textsubscript{2}Cl\textsubscript{2} was dried over K\textsubscript{2}CO\textsubscript{3} and distilled under nitrogen just before use. Enantiomeric excess (ee) were determined by HPLC analysis using the corresponding commercially chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 nm. Optical rotations were reported as follows: [\alpha]D\textsuperscript{T} (c g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI source). \textsuperscript{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Spectra were reported as follows: chemical shift (\delta ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz), integration and assignment. \textsuperscript{13}C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. \textsuperscript{19}F NMR spectra were collected on commercial instruments (376 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. IR spectra was recorded on SHIMADZU UV-2600 UV-vis spectrophotometer in a 10.0 mm quartz cuvette. Chromatography: Silica gel (HG/T2354-2010) made in Qingdao Haiyang Chemical Co., Ltd.

2. Preparation of the starting materials

All the \(\alpha\)-substituted vinyl ketones were prepared by the similar procedure in the literature: \([1]\)

![Chemical reaction diagram]

Experimental procedure of step 1: a mixture of substituted phenylacetonitrile and phenylboronic acid (2 equiv) and Pd(OAc)\textsubscript{2} (5 mol%), 2,2'-dipyridine (10 mol%), TFA (10 equiv), THF (0.5 M), and H\textsubscript{2}O (0.4 mL/mmol) was reflux at 80 °C under nitrogen atmosphere for 36 h. The residue was dissolved in AcOEt and washed with water. The aqueous phase was washed with AcOEt and the organic layers were combined, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo, which was further purified by silica gel chromatography.

Experimental procedure of step 2: to a solution of the products from step 1 and formaldehyde
(4 equiv), piperidine (0.1 equiv), AcOH (0.2 equiv) and MeOH (5 M) was reflux for 6 h. After completion of this reaction, water was added after evaporation of MeOH. Then, the residue was washed with CH$_2$Cl$_2$ and the organic layer were combined, washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo, which was further purified by silica gel chromatography. $\alpha$-Alkyl-$\alpha$-diazoesters synthesized according the previous report. [2]

3. General procedure for chiral $N,N'$-dioxides preparation

The $N,N'$-dioxide ligands were prepared by the similar procedure in the literature.[3]

Figure S1 Structures of $N,N'$-dioxide ligands.

4. General procedure for the preparation of the racemic products

To an oven-dried reaction tube were added Sc(OTf)$_3$ (10 mol %), rac-$L$-$PiMe_3$ (10 mol %), and THF (0.5 mL). The suspensions were stirred at 30 °C for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone (0.1 mmol), $\alpha$-diazoester (0.15 mmol) and CH$_2$Cl$_2$ (0.5 mL) were added at 0 °C. Then the solutions were stirred at 0 °C for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether: petroleum ether = 1:15-1:40) to provide the desired products, respectively.

5. General procedure for the catalytic asymmetric transformation

General Procedure: To an oven-dried reaction tube were added Sc(OTf)$_3$ (10 mol %), $L_2$-$PiMe_3$ (10 mol %), and THF (0.5 mL). The suspensions were stirred at 30 °C for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone 2 (0.1 mmol), $\alpha$-diazoester 1 (0.15 mmol) and CH$_2$Cl$_2$ (0.5 mL) were added at 0 °C. Then the solutions were stirred at 0 °C for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether: petroleum ether = 1:15-1:40) to afford the corresponding product 3 and 4, respectively.
6. Experimental procedure for the gram-scale reaction

\[
\begin{align*}
\text{N}_2 \quad \text{N}^+\text{CO}_2\text{Me} & \quad + \quad \text{Ph} \quad \text{Br} \quad \text{Sc(OTf)}_3 \quad \text{L}_2\text{-PiMe}_3 \quad \text{CH}_2\text{Cl}_2, \; 0 \; ^\circ\text{C}, \; 72 \; \text{h} \\
1a & \quad 0.995 \; \text{g} \quad 3.46 \; \text{mmol} \\
2i & \quad 3.830 \; \text{g} \quad 53\% \; \text{yield} \\
3ai & \quad 0.830 \; \text{g} \quad 53\% \; \text{yield} \\
4ai & \quad 0.721 \; \text{g} \quad 48\% \; \text{yield}
\end{align*}
\]

To an oven-dried 50 mL round-bottomed flask were added Sc(OTf)\(_3\) (10 mol%), \text{L}_2\text{-PiMe}_3 (10 mol%), and THF (25 mL). The suspensions were stirred at 30 °C for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone 2i (3.46 mmol), α-diazoester 1 (5.19 mmol) and CH\(_2\)Cl\(_2\) (25 mL) were added at 0 °C. Then the solutions were stirred at 0 °C for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether:petroleum ether = 1:15) to afford the corresponding product 3ai and 4ai, respectively.

7. Experimental procedure for the synthesis of 5aa

Experimental procedure for the synthesis of 5aa: An oven-dried test tube was charged with 3aa (0.10 mmol, 37.0 mg) and MeOH (1.0 mL). The tube was sealed with a stopper. Then, TsNHNH\(_2\) (0.20 mmol, 37.2 mg) was added under stirring, and the mixture was stirred at the 60 °C for 3 h before it was directly purified by flash chromatography on silica gel (eluent : petroleum ether : EtOH = 5:1) to afford the desired product 5aa in 64% yield.

8. Optimization of the conditions

\textit{Table S1.} Optimization of the conditions.
Unless otherwise noted, the reactions were performed with 10 mol% metal salt, 10 mol% ligand, 1a (0.15 mmol) and 2a (0.1 mmol) in solvent (0.5 mL) under N₂ for 24 h. a Isolated yield by silica gel chromatography. b Determined by chiral HPLC analysis (Chiralcel IB).

9. Operando IR experiments
The analytical and spectral characterization data of the products

Methyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate(3a)

White powder, m.p. 86 - 90 °C, 46% yield, ee = 99%, \([\alpha]^{19}_D = +29.9\) (c = 0.68, in CH\(_2\)Cl\(_2\)). **HPLC** (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, \(t_R\) (major) = 5.54 min, \(t_R\) (minor) = 6.01 min. **H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 8.11 – 8.04 (m, 2H), 7.50 (ddd, \(J = 7.1, 3.5, 1.5\) Hz, 3H), 7.43 (t, \(J = 7.4\) Hz, 2H), 7.27 – 7.15 (m, 8H), 3.94 (dd, \(J = 14.9, 1.4\) Hz, 1H), 3.31 (s, 3H), 2.47 (dd, \(J = 5.5, 1.4\) Hz, 1H), 2.23 (d, \(J = 14.9\) Hz, 1H), 1.97 (d, \(J = 5.5\) Hz, 1H). **C NMR** (101 MHz, CDCl\(_3\)) \(\delta\) 196.1, 170.7, 138.9, 135.8, 133.2, 129.9, 129.6, 128.6, 128.5, 128.4, 127.6, 126.5, 51.8, 45.7, 38.1, 37.6, 21.8. **IR** (film): \(\nu (\text{cm}^{-1})\) 2968, 1726, 1669, 1448, 1282, 705. **HRMS** (FTMS + ESI) calcd for C\(_{25}\)H\(_{22}\)NaO\(_3\)\(^+\) ([M]+Na\(^+\)) = 393.1461 found 393.1462.
Methyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4aa)

Colorless oil, 45% yield, ee = 90%, $[\alpha]^6_D = -74.0$ ($c = 0.70$, in CH$_2$Cl$_2$). HPLC (Chiral IB column) $^1$PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 9.26 min, $t_R$ (minor) = 10.11 min. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.66 – 7.59 (m, 2H), 7.55 – 7.48 (m, 1H), 7.43 – 7.35 (m, 2H), 7.31 (d, $J = 2.0$ Hz, 3H), 7.28 (d, $J = 1.7$ Hz, 1H), 7.27 – 7.24 (m, 2H), 7.04 – 6.96 (m, 4H), 6.28 (d, $J = 10.6$ Hz, 1H), 3.73 – 3.66 (m, 1H), 3.69 (s, 3H), 3.16 (dd, $J = 13.7$, 6.1 Hz, 1H), 2.87 (dd, $J = 13.7$, 9.0 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.5, 172.9, 144.0, 138.2, 137.7, 137.5, 135.1, 132.4, 129.9, 129.2, 129.1, 128.5, 128.3, 128.3, 127.9, 126.8, 52.3, 47.4, 38.5, 29.7. IR (film): $\nu$ (cm$^{-1}$) 2936, 1740, 1634, 1354, 698.

HRMS (FTMS + ESI) caled for C$_{25}$H$_{22}$NaO$_5$ $^+([M]+Na^+)=393.1461$, found 393.1462.
Ethyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate (3ba)

White powder, m.p. 98 - 104 °C, 53% yield, ee = 99%, $[\alpha]^{19}_D = +35.7 \ (c = 1.00, \ \text{in} \ \text{CH}_2\text{Cl}_2)$. HPLC (Chiral IC column) ‘PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 11.45 min, $t_R$ (major) = 15.53 min. $^1\text{H NMR}$ (400 MHz, Chloroform-\text{d}) $\delta$ 8.08 (dd, $J = 7.3, 1.7$ Hz, 2H), 7.59 – 7.48 (m, 3H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.28 – 7.19 (m, 6H), 7.18 – 7.10 (m, 2H), 3.95 (d, $J = 14.9$ Hz, 1H), 3.87 – 3.64 (m, 2H), 2.55 – 2.45 (m, 1H), 2.23 (d, $J = 14.9$ Hz, 1H), 1.95 (d, $J = 5.5$ Hz, 1H), 0.84 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 196.2, 170.1, 139.0, 135.9, 135.7, 133.1, 130.1, 129.6, 128.7, 128.5, 128.4, 128.3, 127.6, 126.4, 60.9, 45.6, 38.2, 37.4, 21.8, 13.7. IR (film): $\nu$(cm$^{-1}$) 2910, 2378, 1726, 1649, 1271, 694.

HRMS (FTMS + ESI) calcd for C$_{26}$H$_{24}$NaO$_3$ $^{[\text{M+Na}^+] = 407.1618}$ found 407.1609.
Ethyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4ba)

Colorless oil, 43% yield, ee = 90%, $[\alpha]_D^{16} = -90.1$ ($c = 0.64$, in CH$_2$Cl$_2$). HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 19.94 min, $t_R$ (major) = 24.03 min. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.72 – 7.60 (m, 2H), 7.52 (td, $J = 7.4$, 1.5 Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.22 (m, 3H), 7.11 – 6.88 (m, 4H), 6.29 (d, $J = 10.6$ Hz, 1H), 4.14 (dt, $J = 8.3$, 6.6 Hz, 2H), 3.74 – 3.60 (m, 1H), 3.13 (d, $J = 6.2$ Hz, 1H), 2.87 (dd, $J = 13.7$, 9.0 Hz, 1H), 1.23 (td, $J = 7.2$, 1.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.6, 172.4, 143.8, 138.6, 137.7, 137.6, 135.1, 132.4, 129.9, 129.2, 129.2, 128.5, 128.3, 128.2, 127.9, 126.8, 61.2, 47.5, 38.5, 14.2. IR (film): $\nu$(cm$^{-1}$) 2978, 1741, 1651, 1446, 1282, 1174, 711. HRMS (FTMS + ESI) calcd for C$_{26}$H$_{24}$NaO$_3$+ ([M]+Na$^+$) = 407.1618 found 407.1625.

Isopropyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate (3ca)
White powder, m.p. 103 - 108 °C, 62% yield, ee = 99%, [α]D = +44.3 (c = 0.45, in CH2Cl2). HPLC (Chiral IC column) PrOH / Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (minor) = 9.69 min, tR (major) = 13.89 min. 1H NMR (400 MHz, Chloroform-d) δ 8.14 – 8.01 (m, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 4.6 Hz, 6H), 7.20 – 7.13 (m, 2H), 4.59 (p, J = 6.2 Hz, 1H), 3.94 (d, J = 14.9 Hz, 1H), 2.55 (d, J = 14.9 Hz, 1H), 2.24 (d, J = 14.9 Hz, 1H), 1.91 (d, J = 5.4 Hz, 1H), 0.95 (d, J = 6.3 Hz, 3H), 0.72 (d, J = 6.3 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 196.2, 169.5, 139.1, 135.9, 135.5, 133.1, 130.2, 129.6, 128.7, 128.5, 128.4, 128.3, 127.6, 126.4, 68.5, 45.2, 38.5, 37.4, 21.9, 21.7, 21.0. IR (film): ν(cm⁻¹) 2987, 1722, 1660, 1435, 1278, 1116. HRMS (FTMS + ESI) calcd for C27H26NaO3⁺ ([M]+Na⁺) = 421.1774 found 421.1768.

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Isopropyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4ca)

Colorless oil, 25% yield, ee = 90%, [α]D = −95.6 (c = 0.37, in CH2Cl2). HPLC (Chiral IC column) PrOH / Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (minor) = 16.05 min, tR (major) = 18.41 min. 1H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.63 (m, 2H), 7.55 – 7.50 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (dd, J = 5.2, 1.8 Hz, 3H), 7.25 (t, J = 4.7 Hz, 3H), 7.07 – 6.89 (m, 4H), 6.29 (d, J = 10.5 Hz, 1H), 5.01 (p, J = 6.3 Hz, 1H), 3.62 (ddd, J = 10.6, 8.9, 6.2 Hz, 1H), 3.13 (dd, J = 13.7, 6.3 Hz, 1H), 2.85 (dd, J = 13.7, 8.9 Hz, 1H).
1H), 1.24 (d, J = 6.2 Hz, 3H), 1.18 (d, J = 6.3 Hz, 3H). $^1$H NMR (101 MHz, CDCl$_3$) δ 196.6, 171.9, 143.7, 138.9, 137.8, 137.6, 135.1, 132.4, 129.9, 129.2, 129.2, 128.4, 128.2, 127.8, 126.7, 68.6, 47.7, 38.4, 21.8, 21.7. IR (film): ν(cm$^{-1}$) 2978, 1728, 1647, 1261, 1163, 1087, 698. HRMS (FTMS + ESI) calcd for C$_{27}$H$_{26}$NaO$_3^+$ ([M]+Na$^+$) = 421.1774 found 421.1776.

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**Tert-butyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate (3da)**

White powder, m.p. 126 - 130 °C, 62% yield, ee = 98%, [α]$^D_{16}$ = +61.9 (c = 1.15, in CH$_2$Cl$_2$). HPLC (Chiral IA column) PrOH/*Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 8.17 min, $t_R$ (minor) = 15.23 min. $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.19 – 7.92 (m, 2H), 7.71 – 7.56 (m, 2H), 7.55 – 7.46 (m, 1H), 7.43 (d, J = 7.9 Hz, 2H), 7.24 (t, J = 3.5 Hz, 6H), 7.21 – 7.09 (m, 2H), 3.89 (dd, J = 15.0, 1.3 Hz, 1H), 2.56 (dd, J = 5.4, 1.4 Hz, 1H), 2.24 (d, J = 15.0 Hz, 1H), 1.85 (d, J = 5.4 Hz, 1H), 1.02 (s, 9H). $^1$C NMR (101 MHz, CDCl$_3$) δ 196.3, 168.4, 139.4, 139.4, 135.4, 135.4, 133.1, 130.3, 129.6, 128.7, 128.5, 128.3, 128.2, 127.5, 126.3, 81.0, 44.7, 38.9, 37.9, 27.5, 22.1. IR (film): ν(cm$^{-1}$) 2987, 2927, 1722, 1668, 1161, 690. HRMS (FTMS + ESI) calcd for C$_{28}$H$_{28}$NaO$_3^+$ ([M]+Na$^+$) = 435.1921 found 435.1930.
**Retention Time** | **Area** | **% Area**
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1 8.217 | 7621736 | 48.24
2 15.138 | 8176795 | 51.76

**Retention Time** | **Area** | **% Area**
--- | --- | ---
1 8.169 | 25209381 | 99.21
2 15.227 | 200284 | 0.79

**Tert-butyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4da)**

Colorless oil, 26% yield, ee = 94%, $[\alpha]^{15}_D = -116.5$ (c = 0.16, in CH$_2$Cl$_2$). HPLC (Chiral IA column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 11.00 min, $t_R$ (major) = 11.60 min. **$^1$H NMR** (400 MHz, Chloroform-$d$) $\delta$ 7.68 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.32 (d, $J = 2.1$ Hz, 1H), 7.31 (d, $J = 1.9$ Hz, 2H), 7.28 – 7.23 (m, 3H), 7.06 – 6.99 (m, 4H), 6.26 (d, $J = 10.6$ Hz, 1H), 3.62 – 3.52 (m, 1H), 3.10 (dd, $J = 13.8$, 6.3 Hz, 1H), 2.83 (dd, $J = 13.8$, 8.9 Hz, 1H), 1.43 (s, 9H). **$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 196.6, 171.5, 143.5, 139.4, 138.0, 137.7, 135.2, 132.4, 129.9, 129.3, 129.2, 128.4, 128.2, 127.8, 126.7, 81.6, 48.5, 38.4, 28.0. **IR** (film): $\nu$ (cm$^{-1}$) 2981,1724, 1676, 1446, 1367, 1276, 1155. **HRMS (FTMS + ESI)** calcd for C$_{25}$H$_{28}$NaO$_3^+$ ([M]+Na$^+$) = 435.1921 found 435.1931.

**Retention Time** | **Area** | **% Area**
--- | --- | ---
1 10.999 | 9531170 | 97.15
2 11.599 | 279585 | 2.85
White powder, m.p 64 - 70 °C, 45% yield, ee = 98%, [$\alpha$]$^{16}_D$ = +8.6 (c = 0.23, in CH$_2$Cl$_2$) HPLC (Chiral IA column) 'PrOH/Hexane = 5/95. Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 8.80 min, $t_R$ (minor) = 15.23 min,

**1H NMR** (400 MHz, Chloroform- $d$) δ 8.07 (d, $J$ = 7.3 Hz, 2H), 7.50 (s, 1H), 7.43 (t, 2H), 7.38 (d, $J$ = 8.1 Hz, 1H), 7.22 (dd, $J$ = 12.5, 6.2 Hz, 5H), 7.04 (d, $J$ = 8.0 Hz, 2H), 3.92 (d, $J$ = 14.9 Hz, 1H), 3.35 (s, 3H), 2.43 (d, $J$ = 5.3 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 1H), 1.95 (d, $J$ = 5.4 Hz, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 196.1, 170.8, 138.9, 137.4, 135.9, 133.1, 132.7, 129.8, 129.6, 129.2, 128.6, 128.4, 126.5, 51.8, 45.5, 38.1, 37.5, 21.7, 21.1. **IR** (film): v(cm$^{-1}$) 2951, 1762, 1668, 1475, 1286, 698. **HRMS** (FTMS + ESI) calcd for C$_{26}$H$_{25}$O$_3$+ ([M]+H$^+$) = 385.1798 found 385.1808.

**Methyl 2-benzoyl-1-(2-methylbenzyl)-2-phenylcyclopropane-1-carboxylate (3ea)**

![Chemical structure](image)

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**Methyl (E)-2-(2-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ea)**

Colorless oil, 47% yield, ee = 82%, [$\alpha$]$^{16}_D$ = -88.6 (c = 0.22, in CH$_2$Cl$_2$) HPLC (Chiral IA column) 'PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 8.79 min, $t_R$ (major) = 10.26 min. **1H NMR** (400 MHz, Chloroform-$d$) δ 7.62 (d, $J$ = 8.1 Hz, 2H), 7.50 (s, 1H), 7.38 (d, $J$ = 7.5 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.12 (d, $J$ = 7.7 Hz,
2H), 7.03 (d, J = 7.2 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H), 6.24 (d, J = 10.5 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.68 (s, 3H), 3.15 (dd, J = 13.7, 6.1 Hz, 1H), 2.90 (dd, J = 8.9 Hz, 1H), 2.34 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 196.8, 172.9, 144.0, 137.8, 137.6, 137.6, 132.4, 132.1, 129.8, 129.2, 129.1, 128.5, 128.4, 128.2, 126.8, 52.2, 47.3, 38.6, 21.3. IR (film): ν(cm⁻¹) 2949, 1741, 1651, 1261, 1149, 715.

HRMS (FTMS + ESI) calcd for C26H24NaO3⁺ ([M]+Na⁺) = 407.1618 found 407.1613.

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**Retention Time**

**Area**

**% Area**

Methyl 2-benzoyl-1-(2-fluorobenzyl)-2-phenylcyclopropane-1-carboxylate (3fa)

White powder, m.p. 80 - 84 °C, 42% yield, ee = 97%, [α]D = +37.8 (c = 0.25, in CH2Cl2) HPLC (Chiral IB column) PrOH/Hexane = 2/98, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 6.59 min, tR (minor) = 7.21 min. 1H NMR (400 MHz, Chloroform-d) δ 7.70 (d, J = 8.2 Hz, 2H), 7.48 (m, 1H), 7.41 (t, J = 7.6 Hz, 2H). 7.28 (m, 3H), 7.22 (d, J = 7.6 Hz, 1H), 7.01 (m, 2H), 6.92 (m, 3H), 6.31 (d, J = 10.6 Hz, 1H), 3.72 (d, J = 3.0 Hz, 1H), 3.69 (s, 3H), 3.10 (dd, J = 6.0, 6.0 Hz, 1H), 2.86 (dd, J = 13.7, 9.0 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 196.4, 172.7, 144.2, 137.8, 137.5, 134.8, 132.4, 131.4 (d, J = 4.5 Hz), 131.4, 129.8, 129.1, 128.8, 128.7, 128.3, 127.9, 124.8, 124.6, 124.1, 124.0, 115.5, 115.3, 52.3, 46.0, 31.7, 29.7. 19F NMR (376 MHz, CDCl3) δ = -113.3 (s, 1F).

IR (film): ν(cm⁻¹) 2935, 1741, 1664, 1500, 1257, 696. HRMS (FTMS + ESI) calcd for C25H23NaFO3⁺ ([M]+Na⁺) = 411.1367 found 411.1378.
Retention Time | Area     | % Area
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Methyl (E)-2-(2-fluorobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4fa)

Colorless oil, 46% yield, ee = 92%, [α]D = −105.1 (c = 0.29, in CH2Cl2) 
HPLC (Chiral IC column) PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, tR (minor) = 12.39 min, tR (major) = 13.80 min.

1H NMR (400 MHz, Chloroform-d) δ 7.73 – 7.66 (m, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.25 – 7.19 (m, 1H), 7.03 (dd, J = 7.1, 1.7 Hz, 2H), 6.97 (dd, J = 6.6, 2.9 Hz, 2H), 6.32 (d, J = 10.6 Hz, 1H), 3.79 – 3.71 (m, 1H), 3.69 (s, 3H), 3.14 (dd, J = 13.7, 6.0 Hz, 1H), 2.96 (dd, J = 13.7, 9.0 Hz, 1H).

13C NMR (101 MHz, CDCl3) δ 196.4, 172.7, 161.2 (d, J = 245.8 Hz), 144.2, 137.8, 137.5, 134.8, 132.4, 131.4 (d, J = 4.5 Hz), 129.8, 129.1, 128.7 (d, J = 8.1 Hz), 128.3, 127.9, 124.7 (d, J = 15.5 Hz), 124.1 (d, J = 3.4 Hz), 115.4 (d, J = 21.9 Hz), 52.3, 46.1, 31.7, 29.7. IR (film): ν(cm⁻¹) 2927, 1757, 1639, 1502, 1392, 1261, 773. 19F NMR (376 MHz, CDCl3) δ = −117.3 (s, 1F).

Methyl 2-benzoyl-1-(3-methylbenzyl)-2-phenylcyclopropane-1-carboxylate (3ga)

White powder, m.p. 80 - 86 °C, 49% yield, ee = 99%, [α]D = +36.4 (c = 0.31, in CH₂Cl₂); HPLC (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, tR (major) = 5.07 min, tR (minor) = 5.63 min.

1H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.0 Hz, 3H), 7.43 (t, J = 7.3 Hz, 2H), 7.28 - 7.20 (m, 2H), 7.20 - 7.08 (m, 2H), 7.04 - 6.94 (m, 3H), 3.90 (d, J = 14.9 Hz, 1H), 3.33 (s, 3H), 2.45 (d, J = 5.5 Hz, 1H), 2.28 (s, 3H), 1.96 (d, J = 14.9 Hz, 1H), 2.19 (d, J = 14.9 Hz, 1H), 1.96 (d, J = 5.5 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 196.1, 170.8, 138.8, 137.9, 135.9, 135.9, 133.1, 130.0, 129.6, 129.5, 128.5, 128.4, 128.3, 127.6, 127.3, 125.6, 51.8, 45.8, 38.0, 37.6, 29.7, 21.7, 21.4. IR (film): ν(cm⁻¹) 2944, 1741, 1638, 1184, 1135, 711. HRMS (FTMS + ESI) calcld for C₂₆H₂₄NaO₃⁺ ([M]+Na⁺) = 407.1618 found 407.1615.
Methyl (E)-2-(3-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ga)

Colorless oil, 45% yield, ee = 92%, [α]D = −48.2 (c = 0.29, in CH2Cl2).

**HPLC** (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 8.23 min, tR (minor) = 9.08 min.

**'H NMR** (400 MHz, Chloroform-d) δ 7.63 (d, J = 7.1 Hz, 2H), 7.53 (s, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.32 (dd, J = 5.0, 1.8 Hz, 3H), 7.17 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.97 (dd, J = 6.4, 3.1 Hz, 2H), 6.88 – 6.77 (m, 2H), 6.27 (d, J = 10.6 Hz, 1H), 3.70 (s, 3H), 3.14 (dd, J = 13.7, 5.7 Hz, 1H), 2.83 (dd, J = 13.7, 9.4 Hz, 1H), 2.31 (s, 3H).

**'C NMR** (101 MHz, CDCl3) δ 196.6, 172.9, 143.9, 138.4, 138.1, 137.6, 137.6, 135.1, 132.4, 129.8, 129.2, 128.4, 128.2, 127.8, 127.6, 126.2, 52.3, 52.2, 47.3, 38.4, 21.4. **IR** (film): ν (cm⁻¹) 2945, 1732, 1653, 1206, 1164, 704. **HRMS** (FTMS + ESI) calcd for C26H24NaO3+ ([M]+Na⁺) = 407.1618 found 407.1614.
Methyl 2-benzyloxy-1-(3-methoxybenzyl)-2-phenylcyclopropane-1-carboxylate (3ha)

White powder, 51% yield, ee = 99%, [α]D 20 = +48.4 (c = 0.27, in CH2Cl2) HPLC (Chiral IA column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 9.73 min, tR (minor) = 18.82 min. 1H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 3H), 7.25 (d, J = 7.1 Hz, 2H), 7.20 – 7.12 (m, 2H), 6.87 – 6.62 (m, 3H), 3.92 (d, J = 15.0 Hz, 1H), 3.76 (s, 3H), 3.33 (s, 3H), 2.48 (d, J = 5.5 Hz, 1H), 2.20 (d, J = 15.0 Hz, 1H), 1.96 (d, J = 5.5 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 196.1, 170.7, 159.6, 140.4, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 29.7, 21.8. IR (film): ν(cm⁻¹) 2924, 1730, 1452, 1271, 702. HRMS (FTMS + ESI) calcd for C26H24NaO4⁺ ([M]+Na⁺) = 423.1567 found 423.1563.

Methyl (E)-2-(3-methoxybenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ha)

Colorless oil, 46% yield, ee = 95%, [α]D 20 = -88.2 (c = 0.26, in CH2Cl2) HPLC (Chiral ADH column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 11.65 min, tR (minor) = 12.48 min. 1H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 7.2 Hz, 2H), 7.51 (dd, J = 6.4, 2.4 Hz, 3H), 7.44 (d, J = 7.8 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.19 – 7.09 (m, 2H), 6.85 – 6.67 (m, 3H), 3.92 (d, J = 15.0 Hz, 1H), 3.75 (s, 3H), 3.32 (s, 3H), 2.48 (d, J = 6.4 Hz, 1H), 2.21 (d, J = 15.0 Hz, 1H), 1.96 (d, J = 5.5 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 196.1, 170.7, 159.6, 140.4, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 29.7, 21.8.
MHz, CDCl3) δ 196.1, 170.7, 159.6, 140.5, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 21.8. IR (film): ν(cm⁻¹) 2920, 1737, 1658, 1454, 1261, 1170. HRMS (FTMS + ESI) calcd for C₂₆H₂₄NaO₄⁺ ([M]+Na⁺) = 423.1567 found 423.1575.

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Methyl 2-benzoyl-1-(4-methylbenzyl)-2-phenylcyclopropane-1-carboxylate (3ia)

Colorless oil, 49% yield, ee = 94%, [α]D = 28.4 (c = 0.37, in CH₂Cl₂).

HPLC (Chiral IB column) PrOH/ Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 5.46 min, tR (minor) = 6.10 min., ¹H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 8.6 Hz, 2H), 7.49 (td, J = 5.2, 4.7, 1.5 Hz, 3H), 7.43 (t, J = 7.3 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 7.01 (m, 4H), 3.90 (d, J = 14.8 Hz, 1H), 3.32 (s, 2H), 2.44 (d, J = 5.5 Hz, 1H), 2.27 (s, 3H), 2.18 (d, J = 14.9 Hz, 1H), 1.96 (d, J = 5.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.1, 170.8, 136.0, 135.9, 135.8, 133.1, 123.0, 129.6, 129.2, 129.1, 128.5, 128.4, 128.3, 128.6, 118.3, 51.8, 45.8, 37.8, 21.7, 21.0. IR (film): ν(cm⁻¹) 2980, 1726, 1097, 1060, 902. HRMS (FTMS + ESI) calcd for C₂₆H₂₄NaO₄⁺ ([M]+Na⁺) = 407.1618 found 407.1616.

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Methyl (E)-2-(4-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ia)

Colorless oil, 45% yield, ee = 90%, [α]\textsubscript{D} = −57.0 (c = 0.36, in CH\textsubscript{2}Cl\textsubscript{2}). HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, \(t_R\) (major) = 9.22 min, \(t_R\) (minor) = 10.49 min.

\textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.68 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, \(J = 7.6\) Hz, 2H), 7.31 (dd, \(J = 5.3, 1.9\) Hz, 3H), 7.08 (d, \(J = 7.7\) Hz, 2H), 7.03 – 6.98 (m, 2H), 6.90 (d, \(J = 7.8\) Hz, 2H), 6.29 (d, \(J = 10.5\) Hz, 1H), 3.68 (s, 3H), 3.11 (dd, \(J = 13.7, 6.2\) Hz, 1H), 2.84 (dd, \(J = 13.8, 8.8\) Hz, 1H), 2.33 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 196.6, 172.9, 143.8, 138.4, 137.6, 136.4, 135.1, 134.5, 132.4, 129.9, 129.2, 129.0, 128.3, 128.2, 127.9, 52.2, 47.5, 38.2, 21.1. IR (film): ν(cm\textsuperscript{-1}) 2941, 1745, 1662, 1446, 1257. HRMS (FTMS + ESI) calcd for C\textsubscript{26}H\textsubscript{24}NaO\textsubscript{3} \([\text{M}+\text{Na}]^+\) = 407.1618 found 407.1626.

Methyl 2-benzoyl-1-(4-fluorobenzyl)-2-phenylcyclopropane-1-carboxylate (3ja)
White powder, m.p. 80 - 88 °C, 48% yield, ee = 98%, [α]^{16}D = +28.2 (c = 0.57, in CH$_2$Cl$_2$).**HPLC** (Chiral IA column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_h$ (minor) = 5.69 min, $t_h$ (major) = 10.87 min. **1H NMR** (400 MHz, Chloroform-d) δ 8.12 - 8.03 (m, 2H), 7.50 (d, $J$ = 7.0 Hz, 3H), 7.45 (d, $J$ = 7.7 Hz, 2H), 7.28 - 7.20 (m, 2H), 7.20 - 7.13 (m, 3H), 6.93 (t, $J$ = 8.7 Hz, 2H), 3.91 (d, $J$ = 14.9 Hz, 1H), 3.31 (s, 3H), 2.46 (d, $J$ = 1.3 Hz, 1H), 2.19 (d, $J$ = 14.9 Hz, 1H), 1.95 (d, $J$ = 5.5 Hz, 1H). **13C NMR** (101 MHz, CDCl$_3$) δ 195.9, 170.6, 162.9, 160.4, 135.7 (d, $J$ = 6.4 Hz), 134.5 (d, $J$ = 3.2 Hz), 133.2, 130.1 (d, $J$ = 7.9 Hz), 129.9, 129.6, 128.5 (d, $J$ = 8.9 Hz), 127.7, 115.3, 115.1, 51.8, 45.7, 37.6, 37.4, 21.7. **19F NMR** (376 MHz, CDCl$_3$) δ = −116.6 (s, 1F). **IR** (film): ν (cm$^{-1}$) 2954, 1730, 1678, 1467, 1282, 786. **HRMS** (FTMS + ESI) calcd for C$_{25}$H$_{21}$NaFO$_3$ ([(M]+Na$^+$)) = 389.1547 found 389.1540.

**Methyl (E)-2-(4-fluorobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ja)**

Colorless oil, 46% yield, ee = 86%, [α]^{16}D = −123.7 (c = 0.38, in CH$_2$Cl$_2$). **HPLC** (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_h$ (minor) = 19.72 min, $t_h$ (major) = 25.67 min. **1H NMR** (400 MHz, Chloroform-d) δ 7.71 - 7.63 (m, 2H), 7.57 - 7.48 (m, 1H), 7.45 - 7.37 (m, 2H), 7.35 - 7.30 (m, 3H), 7.03 (dd, $J$ = 7.4,
2.2 Hz, 2H), 6.97 – 6.91 (m, 4H), 6.28 (d, J = 10.6 Hz, 1H), 3.69 (s, 3H), 3.68 – 3.61 (m, 1H), 1.11 (dd, J = 13.8, 6.2 Hz, 1H), 2.84 (dd, J = 13.8, 8.7 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 196.3, 172.7, 161.8 (d, J = 245.1 Hz), 144.1, 137.5 (d, J = 20.0 Hz), 135.0, 133.4 (d, J = 3.3 Hz), 132.6, 130.6, 130.5, 129.8, 129.1, 128.4, 128.3, 115.3 (d, J = 21.3 Hz), 52.3, 47.4, 37.7, 29.7. 19F NMR (376 MHz, CDCl3) δ = −116.0 (s, 1F). IR (film): ν(cm⁻¹) 2920, 1735, 1666, 1519, 1224, 694. HRMS (FTMS + ESI) calcd for C25H21NaFO3⁺ ([M]+Na⁺) = 411.1367 found 411.1372.

**Retention Time** | **Area** | **% Area**
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2 | 25.818 | 17558281 | 43.61

**Methyl 2-benzoyl-1-(4-bromobenzyl)-2-phenylcyclopropane-1-carboxylate(3ka)**

White powder, m.p. 94 - 102 °C, 50% yield, ee = 99%. [α]D = +26.3 (c = 0.32, in CH2Cl2). HPLC (Chiral IA column) PrOH / Hexane = 10/90. Flow rate: 1.0 mL/min, 254 nm, tR (major) = 10.15 min, tR (minor) = 21.83 min. 1H NMR (400 MHz, Chloroform-d) δ 8.06 (d, J = 7.2 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.45 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.18 (d, J = 7.2 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 3.89 (d, J = 14.9 Hz, 1H), 2.48 (d, J = 6.4 Hz, 1H), 2.17 (d, J = 15.0 Hz, 1H), 1.94 (d, J = 5.5 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 195.9, 170.5, 137.9, 135.7, 135.6, 133.2, 131.5, 130.4, 129.9, 129.6, 128.5, 128.4, 127.7, 120.4, 51.9, 45.6, 37.6, 37.3, 21.7. IR (film): ν(cm⁻¹) 2954, 1734, 1678, 1448, 1274, 1182. HRMS (FTMS + ESI) calcd for C25H21NaBrO3⁺ ([M]+Na⁺) = 471.0566 and 473.0546 found 471.0563 and 473.0543.
Methyl (E)-2-(4-bromobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ka)

Colorless oil, 48% yield, ee = 72%, \( [\alpha]^{D}_{D} = -46.4 \) (c = 0.27, in CHCl \textsubscript{3}) HPLC (Chiral IA column) PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, \( t_R \) (major) = 9.61 min, \( t_R \) (minor) = 11.23 min. \( ^{1}H \) NMR (400 MHz, Chloroform-d) \( ^{1}H \) NMR (400 MHz, Chloroform-d) \( \delta 7.70 – 7.63 \) (m, 2H), 7.54 – 7.49 (m, 1H), 7.41 (d, \( J = 7.8 \) Hz, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 (d, \( J = 4.4 \) Hz, 1H), 7.03 (dd, \( J = 7.4, 2.1 \) Hz, 2H), 6.87 (d, \( J = 8.2 \) Hz, 2H), 6.25 (d, \( J = 10.5 \) Hz, 1H), 3.70 (s, 3H), 3.68 – 3.63 (m, 1H), 3.09 (dd, \( J = 13.8, 6.2 \) Hz, 1H), 2.82 (dd, \( J = 13.8, 8.7 \) Hz, 1H). \( ^{13}C \) NMR (101 MHz, CDCl \textsubscript{3}) \( \delta 196.3, 172.6, 144.2, 137.3, 136.7, 134.9, 132.6, 131.6, 130.8, 129.8, 129.1, 128.4, 128.3, 128.0, 120.7, 52.4, 47.1, 37.8, 29.7. IR (film): \( \nu(\text{cm}^{-1}) \) 2916, 1741, 1668, 1498, 1396, 1253, 1087, 702. HRMS (FTMS + ESI) calcd for C\textsubscript{25}H\textsubscript{22}NaBrO\textsubscript{3} \* ([M]+Na\textsuperscript{+}) = 471.0566 and 473.0546 found 471.0563 and 473.0548.
Methyl 2-benzoyl-2-phenyl-1-propylcyclopropane-1-carboxylate (3a)

Colorless oil, 61% yield, ee = 96%, [α]D19 = +24.3 (c = 0.55, in CH2Cl2) HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, τr (minor) = 7.22 min, τr (major) = 9.38 min. 1H NMR (400 MHz, Chloroform-d) δ 8.07 – 7.97 (m, 2H), 7.49 – 7.37 (m, 5H), 7.21 (dd, J = 8.3, 6.6 Hz, 2H), 7.17 – 7.11 (m, 1H), 3.42 (s, 3H), 2.64 – 2.52 (m, 1H), 2.29 (dd, J = 5.3, 1.5 Hz, 1H), 1.70 (d, J = 5.3 Hz, 1H), 1.47 – 1.32 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H), 0.82 – 0.75 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 196.3, 171.4, 136.1, 135.9, 132.9, 130.0, 129.6, 128.4, 128.3, 127.5, 51.8, 45.8, 37.0, 34.9, 21.3, 21.1, 14.0. IR (film): ν(cm⁻¹) 2960, 1741, 1672, 1436, 1261, 1170. HRMS (FTMS + ESI) calcd for C23H22NaO3⁺ ([M]+Na⁺) = 345.1461 found 345.1456.

Methyl (E)-5-oxo-4,5-diphenyl-2-propylpent-3-enoate (4a)

Colorless oil, 34% yield, ee = 85%, [α]D19 = -101.1 (c = 0.37, in CH2Cl2) HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, τr (minor) = 14.09 min, τr (major) = 17.25 min. 1H NMR (400 MHz, Chloroform-d) δ 7.83 (d, J = 7.4 Hz, 2H), 7.49 – 7.37 (m, 5H), 7.21 (dd, J = 7.2 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.1 Hz, 1H), 7.33 – 7.25 (m, 3H), 6.36 (d, J = 10.6 Hz, 1H), 3.72 (s, 3H), 3.35-3.45 (m, 7.6 Hz, 1H), 1.84 – 1.69 (m, 1H), 1.58 – 1.50 (m, 1H), 1.30 (dd, J =
= 17.4, 7.4 Hz, 1H), 1.23 – 1.13 (m, 1H), 0.80 (t, J = 7.3 Hz, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.6, 173.7, 143.1, 139.7, 137.7, 135.3, 132.4, 129.9, 129.3, 128.4, 128.3, 127.9, 52.1, 52.1, 45.4, 34.8, 20.3, 13.7. IR (film): \(\nu\) (cm\(^{-1}\)) 2964, 1737, 1651, 1450, 1388, 1276. HRMS (FTMS + ESI) calcd for C\(_{21}\)H\(_{22}\)NaO\(_3\)\(^+\) ([M]+Na\(^+\)) = 359.1618 found 359.1627.

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Methyl 2-benzoyl-1-butyl-2-phenylcyclopropane-1-carboxylate (3ma)

Colorless oil, 49% yield, ee = 98%. \([\alpha]\)\(^D\) = +20.9 (c = 0.72, in CH\(_2\)Cl\(_2\))

HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, \(t_R\) (minor) = 6.86 min, \(t_R\) (major) = 8.71 min. \(^1H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.08 – 7.94 (m, 2H), 7.52 – 7.36 (m, 5H), 7.21 (dd, \(J = 8.2, 7.1\) Hz, 2H), 7.17 – 7.09 (m, 1H), 3.42 (s, 3H), 2.65 – 2.52 (m, 1H), 2.29 (dt, \(J = 5.3, 1.3\) Hz, 1H), 1.69 (dd, \(J = 5.2, 0.9\) Hz, 1H), 1.44 – 1.20 (m, 4H), 0.91 – 0.74 (m, 4H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.3, 171.4, 136.1, 136.0, 132.9, 130.0, 129.5, 128.4, 128.3, 127.5, 51.8, 46.0, 37.2, 32.7, 30.1, 22.6, 21.2, 14.0. IR (film): \(\nu\) (cm\(^{-1}\)) 2960, 2856, 1751, 1674, 1456, 1263, 704 HRMS (FTMS + ESI) calcd for C\(_{22}\)H\(_{22}\)NaO\(_3\)\(^+\) ([M]+Na\(^+\)) = 359.1618 found 359.1614.
Methyl (E)-2-(3-oxo-2,3-diphenylprop-1-en-1-yl) hexanoate(4ma)

Colorless oil, 41% yield, ee = 77%, [α]D = −99.7 (c = 0.41, in CH2Cl2)

HPLC (Chiral IC column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (minor) = 17.47 min, tR (major) = 21.18 min. 1H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.80 (m, 2H), 7.53 (d, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.1 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.36 (d, J = 10.6 Hz, 1H), 3.72 (s, 3H), 3.53 – 3.26 (m, 1H), 1.89 – 1.69 (m, 1H), 1.59 (s, 2H), 1.24-1.15 (m, 3H), 0.83 (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 196.6, 173.7, 143.1, 139.8, 137.7, 135.3, 132.5, 129.9, 129.3, 128.4, 128.3, 127.9, 100.0, 52.1, 45.6, 32.4, 29.1, 22.3, 13.8. IR (film): ν(cm⁻¹) 2956, 1737, 1668, 1450, 1253, 723. HRMS (FTMS + ESI) calcd for C22H24NaO3⁺ ([M]+Na⁺) = 359.1618 found 359.1619.
Methyl 2-benzoyl-1-benzyl-2-(2-bromophenyl) cyclopropane-1-carboxylate(3ab)

Colorless oil, 73% yield, ee = 98%, [α]^{16}_{D} = +76.7 (c = 0.99, in CH₂Cl₂) HPLC (Chiral IC column) PrOH/Hexane = 2/98, Flow rate: 1.0 mL/min, 254 nm, tᵣ (major) = 13.23 min, tᵣ (minor) = 14.53 min. \(^{1}H\) NMR (400 MHz, Chloroform-d) \(\delta\) 8.06 (d, \(J = 8.4\) Hz, 2H), 7.56 – 7.47 (m, 3H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.36 (d, \(J = 8.0\) Hz, 2H), 7.28 – 7.20 (m, 2H), 7.18 (t, \(J = 7.3\) Hz, 1H), 7.09 (d, \(J = 8.2\) Hz, 2H), 3.89 (d, \(J = 5.5\) Hz, 1H), 3.30 (s, 3H), 2.48 (d, \(J = 5.5\) Hz, 1H), 2.17 (d, \(J = 5.5\) Hz, 1H), 1.94 (d, \(J = 5.5\) Hz, 1H). \(^{13}C\) NMR (101 MHz, CDCl₃) \(\delta\) 195.9, 170.5, 137.9, 135.7, 135.6, 133.2, 131.5, 130.4, 129.9, 129.6, 128.5, 128.4, 127.7, 120.4, 51.9, 45.6, 37.6, 21.7. IR (film): \(\nu (cm^{-1})\) 2951, 1739, 1666, 1436, 1257, 759, 704. HRMS (FTMS + ESI) calcd for C₂₅H₂₁NaBrO₃ \(^{+}\) ([M]+Na\(^{+}\)) = 471.0566 and 473.0546 found 471.0563 and 473.0544.

Methyl (E)-2-benzyl-4-(2-bromophenyl)-5-oxo-5-phenylpent-3-enoate (4ab)

Colorless oil, 24% yield, ee = 60%, [α]^{16}_{D} = −28.4 (c = 0.26, in CH₂Cl₂) HPLC (Chiral IA column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tᵣ (major) = 13.70 min, tᵣ (minor) = 14.88 min. \(^{1}H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.70 – 7.61 (m, 2H), 7.54 – 7.50 (m, 1H), 7.43 – 7.35 (m, 4H), 7.33 (d, \(J = 6.9\) Hz, 3H), 7.03 (dd, \(J = 7.5, 2.0\) Hz, 2H), 6.89 – 6.82 (m, 2H), 6.26 (d, \(J = 10.5\) Hz, 1H), 3.78 – 3.71 (m, 1H), 3.70 (s, 3H), 3.09 (dd, \(J = 13.8, 6.2\) Hz, 1H), 2.82 (dd, \(J = 13.8, 8.7\) Hz, 1H). \(^{13}C\) NMR (101 MHz, CDCl₃) \(\delta\) 196.3, 172.6, 144.2, 141.9, 137.4, 137.3, 137.2, 136.7, 134.9, 132.6, 131.6, 131.6, 130.9, 130.8, 129.8, 129.1, 128.4, 128.3, 128.0, 120.7, 52.4,
47.1, 37.8. IR (film): ν (cm⁻¹) 2912, 1741, 1654, 1446, 1269, 1031. HRMS (FTMS + ESI) calced for C₂₅H₂₁NaBrO₃⁺ ([M]+Na⁺) = 471.0566 and 473.0546 found 471.0559 and 473.0540.

Retention Time | Area  | % Area
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1 | 13.753 | 48.32
2 | 14.906 | 51.68

Methyl 2-benzoyl-1-benzyl-2-(2-methoxyphenyl) cyclopropane-1-carboxylate (3ac)

White powder, m.p.84 - 90 °C, 50% yield, ee = 97%, [α]D = −76.6 (c = 0.86, in CH₂Cl₂) HPLC (Chiral IA column) PrOH/ Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, tₑ (major) = 8.41 min, tₑ (minor) = 11.42 min. ¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 8.1 Hz, 2H), 7.46-7.38 (m, 7.9 Hz, 4H), 7.24 (d, J = 4.5 Hz, 4H), 7.21-7.10 (m, 2H), 6.83 (d, J = 7.5 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 3.81 (d, 1H), 3.79 (s, 3H), 3.41 (s, 1H), 2.40 (d, J = 14.8 Hz, 1H), 2.25 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 197.6, 171.4, 158.6, 139.3, 137.5, 132.3, 131.6, 129.0, 12.0, 128.8, 128.30, 128.0, 126.3, 124.7, 120.3, 110.8, 55.1, 51.8, 42.8, 38.6, 36.5, 23.2. IR (film): ν (cm⁻¹) 2960, 1730, 1685, 1508, 1271, 754. HRMS (FTMS + ESI) calced for C₂₆H₂₄NaO₄⁺ ([M]+Na⁺) = 423.1567 found 423.1558.

Retention Time | Area  | % Area
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1 | 8.403 | 48.10
2 | 11.753 | 51.90
Methyl (E)-2-benzyl-4-(2-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4ac)

Colorless oil. 44% yield, ee = 89%, [α]D = -83.7 (c = 0.63, in CH2Cl2) HPLC (Chiral IA column) THF/H2O = 10/90, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 10.66 min, tR (minor) = 13.72 min. 1H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.57 (m, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.26 – 7.21 (m, 3H), 7.05 – 6.94 (m, 4H), 6.82 (d, J = 8.2 Hz, 1H), 6.28 (d, J = 10.5 Hz, 1H), 3.77 – 3.70 (m, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 3.14 (dd, J = 13.8, 6.4 Hz, 1H), 2.88 (dd, J = 13.8, 8.7 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 197.2, 173.0, 156.7, 141.2, 138.9, 138.1, 137.8, 131.9, 131.2, 129.9, 129.8, 129.0, 128.4, 127.9, 126.6, 124.8, 120.5, 110.7, 55.2, 52.1, 47.5, 38.6, 25.4. IR (film): ν/cm⁻¹ 2927, 1737, 1716, 1651, 1556, 1261. HRMS (FTMS + ESI) calcd for C26H24NaO4⁺ ([M]+Na⁺) = 423.1567 found 423.1558.
White powder, m.p. 60 - 64 °C, 46% yield, ee = 98%, [α]^{16}_{D} = +24.3 (c = 0.40, in CH₂Cl₂). HPLC (Chiral IA column) PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.08 min, t_R (minor) = 17.59 min.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 – 8.02 (m, 2H), 7.54 – 7.48 (m, 3H), 7.43 (dd, J = 8.3, 6.6 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 6.82 – 6.70 (m, 3H), 3.92 (dd, J = 15.0, 1.3 Hz, 1H), 3.75 (s, 3H), 3.66 (q, J = 6.0 Hz, 1H), 3.14 (dd, J = 13.6, 5.9 Hz, 1H), 2.84 (dd, J = 13.6, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ 196.0, 170.7, 159.6, 140.5, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 21.8. IR (film): ν (cm⁻¹) 2974, 1737, 1683, 1589, 1269, 1097, 1055, 871. HRMS (FTMS + ESI) calcd for C₂₆H₂₄NaO₄⁺ ([M]+Na⁺) = 423.1567 found 423.1571.

Methyl (E)-2-benzyl-4-(3-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4ad)

Colorless oil, 46% yield, ee = 88%, [α]^{16}_{D} = −39.2 (c = 0.33, in CH₂Cl₂) HPLC (Chiral ID column) PrOH/Hexane = 15/85, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 17.20 min, t_R (minor) = 18.30 min. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.61 (m, 2H), 7.51 (d, J = 7.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 – 7.29 (m, 3H), 7.20 (t, J = 7.9 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.79 (dd, J = 8.3, 2.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 6.54 (t, J = 1.9 Hz, 1H), 6.27 (d, J = 10.6 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.66 (q, J = 6.0 Hz, 1H), 3.14 (dd, J = 13.6, 5.9 Hz, 1H), 2.84 (dd, J = 13.6, 9.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ 196.5, 172.8, 159.7, 144.0, 139.2, 138.1, 137.5, 135.08, 132.5, 129.9, 129.5, 129.2, 128.8, 128.6, 128.3.
128.3, 127.9, 121.5, 114.5, 112.5, 55.1, 52.3, 47.3, 38.6. \textbf{IR} (film): \(\nu (\text{cm}^{-1})\) 2993, 1741, 1643, 1363, 1244, 1182, 1031, 702.

HRMS (FTMS + ESI) calcd for C_{26}H_{24}NaO_3^+ ([M]+Na^+) = 423.1567 found 423.1570.

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Methyl 2-benzoyl-1-benzyl-2-(p-tolyl)cyclopropane-1-carboxylate (3ae)

Colorless oil, 45% yield, ee = 99%, \([\alpha]^{14}D = +39.4 (c = 0.21, \text{in CH}_2\text{Cl}_2)\)

\textbf{HPLC} (Chiral IB column) \textit{PrOH} / \textit{Hexane} = 5/95, Flow rate: 1.0 mL/min, 254 nm, \(t_R\) (major) = 5.45 min, \(t_R\) (minor) = 6.06 min. \textbf{1H NMR} (400 MHz, Chloroform-\(d\))

8.10 – 8.05 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 (t, \(J = 7.3\) Hz, 2H), 7.38 (d, \(J = 7.9\) Hz, 2H), 7.27 – 7.17 (m, 5H), 7.04 (d, \(J = 7.9\) Hz, 2H), 3.92 (d, \(J = 14.9\) Hz, 1H), 3.35 (s, 3H), 2.43 (d, \(J = 6.8\) Hz, 1H), 2.23 (s, 3H), 1.95 (d, \(J = 5.4\) Hz, 1H). \textbf{13C NMR} (101 MHz, \textit{CDCl}_3) \(\delta\)

161.1, 170.8, 138.9, 137.4, 136.9, 135.3, 132.7, 129.8, 129.6, 129.2, 128.6, 128.5, 128.4, 126.5, 51.9, 45.5, 38.1, 37.5, 21.8, 21.1. \textbf{IR} (film): \(\nu (\text{cm}^{-1})\) 3021, 2947, 2735, 1761, 1631, 1358, 1084, 704. \textbf{HRMS} (FTMS + ESI) calcd for C_{26}H_{24}NaO_3^+ ([M]+Na^+) = 407.1618 found 407.1619.

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Methyl (E)-2-benzyl-5-oxo-5-phenyl-4-(p-tolyl)pent-3-enoate (4ac)

Colorless oil, 53% yield, ee = 99%, [α]¹⁶β = −40.6 (c = 0.31, in CH₂Cl₂)

HPLC (Chiral IB column) ³PrOH/ ⁴Hexane = 5/95, Flow rate: 1.0 mL/min,
254 nm, tₗ (major) = 9.22 min, tₗ (minor) = 10.49 min. ¹H NMR (400 MHz,
Chloroform-d) δ 7.62 (dd, J = 8.1, 1.4 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.37 (t,
J = 7.6 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.12 (d, J = 7.7 Hz, 2H), 7.06 – 7.01
(m, 2H), 6.88 (d, J = 7.7 Hz, 2H), 6.24 (d, J = 10.5 Hz, 1H), 3.68 (s, 3H).
³¹C NMR (101 MHz, CDCl₃) δ 196.8, 172.9, 144.0, 137.8, 137.7, 137.6, 137.6, 133.1, 132.4, 132.1, 129.8, 129.2, 129.1, 128.5, 128.2,
126.8, 124.9, 52.2, 47.3, 38.6, 21.3. IR (film): ν(cm⁻¹) 3035, 1737, 1654, 1465, 1276. HRMS (FTMS +

Methyl 2-benzoyl-1-benzyl-2-(4-methoxyphenyl) cyclopropane-1-carboxylate (3af)
Colorless oil, 42% yield, ee = 97%, [α]_{D}^{16} = −70.5 (c = 0.26, in CH₂Cl₂)

HPLC (Chiral IA column) PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, tₘ (major) = 8.53 min, tₘ (minor) = 26.30 min. \(^1\)H NMR (400 MHz, Chloroform-d) δ 7.62 (d, J = 7.3 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.06 – 6.99 (m, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.88 – 6.80 (m, 2H), 6.23 (d, J = 10.5 Hz, 1H), 3.81 (s, 3H), 3.77 – 3.70 (m, 1H), 3.69 (s, 3H), 3.16 (dd, J = 13.7, 6.1 Hz, 1H), 2.87 (dd, J = 13.7, 9.0 Hz, 1H). \(^1\)H NMR (101 MHz, CDCl₃) δ 196.9, 172.9, 159.2, 143.6, 137.7, 137.6, 132.4, 130.4, 129.8, 129.1, 128.5, 128.2, 127.4, 126.8, 113.8, 55.3, 55.2, 52.2, 47.4, 38.6. IR (film): ν(cm\(^{-1}\)) 2949, 1737, 1672, 1512, 1253, 1178.

HRMS (FTMS + ESI) calcd for C\(_{26}\)H\(_{25}\)O\(_4\) \([\text{M}+\text{H}]+\) = 401.1747 found 401.1750.

**Retention Time** | **Area** | **% Area**
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2 | 26.272 | 7737130 | 51.93

Methyl (E)-2-benzyl-4-(4-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4af)

Colorless oil, 57% yield, ee = 91%, [α]_{D}^{16} = +161.0 (c = 0.29, in CH₂Cl₂)

HPLC (Chiral IA column) PrOH/Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, tₘ (major) = 12.95 min, tₘ (minor) = 14.09 min. \(^1\)H NMR (400 MHz, Chloroform-d) δ 8.08 – 8.04 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (dd, J = 14.8, 8.1 Hz, 4H), 7.25 (d, 1H), 7.24-7.19 (m, 4H), 6.76 (d, J = 8.8 Hz, 2H), 3.92 (d, J = 14.9 Hz, 1H), 3.72 (s, 3H), 3.36 (s, 3H), 2.41 (d, J = 5.4 Hz, 1H), 2.21 (d, J = 14.9 Hz, 1H), 1.94 (d, J = 5.4 Hz, 1H). \(^1\)C NMR (101 MHz,
CDCl$_3$ $\delta$ 196.2, 170.8, 158.9, 139.0, 135.9, 133.0, 131.1, 129.6, 128.6, 128.5, 127.6, 126.5, 113.8, 55.1, 51.9, 45.0, 38.1, 37.6, 21.8.  

HRMS (FTMS + ESI) calcd for C$_{26}$H$_{24}$NaO$_{4}$+ ([M]+Na$^+$) = 423.1567 found 423.1564.

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Methyl 2-benzoyl-1-benzyl-2-(4-fluorophenyl) cyclopropane-1-carboxylate (3ag)

White powder, m.p. 70 - 78 °C, 46% yield, ee = 98%, $[\alpha]^{16}_{D}$ = +30.0 (c = 0.32, in CH$_2$Cl$_2$) HPLC (Chiral IB column) PrOH/ nHexane = 5/95, Flow rate: 1.0 mL/min, $t_R$ (major) = 5.81 min, $t_R$ (minor) = 6.74 min.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.05 (d, $J$ = 7.1 Hz, 2H), 7.53 (d, $J$ = 7.2 Hz, 1H), 7.46 (t, $J$ = 7.4 Hz, 2H), 7.30 (d, $J$ = 7.7 Hz, 1H), 7.28 - 7.10 (m, 7H), 6.93 - 6.80 (m, 1H), 3.91 (d, $J$ = 14.9 Hz, 1H), 3.37 (s, 3H), 2.46 (d, $J$ = 4.6 Hz, 1H), 2.22 (d, $J$ = 15.0 Hz, 1H), 1.98 (d, $J$ = 5.5 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.6, 170.4, 163.7, 138.3 (d, $J$ = 7.5 Hz), 138.3, 135.6, 133.4, 129.9 (d, $J$ = 8.4 Hz), 128.6 (d, $J$ = 3.6 Hz), 128.6, 128.4, 126.6, 125.6, 117.0 (d, $J$ = 22.1 Hz), 114.9, 114.7, 52.0, 45.2, 37.9 (d, $J$ = 28.6 Hz), 21.9.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = −113.9 (s, 1F).

IR (film): $\nu$(cm$^{-1}$) 2935, 1745, 1685, 1423, 1286, 1165. HRMS (FTMS + ESI) calcd for C$_{26}$H$_{24}$NaFO$_{3}$+ ([M]+Na$^+$) = 411.1367 found 411.1366.
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Methyl (E)-2-benzyl-4-(4-fluorophenyl)-5-oxo-5-phenylpent-3-enoate (4ag)

Colorless oil, 46% yield, ee = 89%, [α]D = −13.9 (c = 0.07, in CH₂Cl₂)

**HPLC (Chiral IB column)**: PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 
254 nm, tR (major) = 5.81 min, tR (minor) = 6.68 min.

**1H NMR** (400 MHz, Chloroform-d)
δ 7.65 – 7.60 (m, 2H), 7.56 – 7.50 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.27 (dd, J = 8.4, 6.7 Hz, 3H), 7.04 – 6.98 (m, 4H), 6.94 – 6.89 (m, 2H), 6.30 (d, J = 10.6 Hz, 1H), 3.70 (s, 3H), 3.63 (dd, J = 5.7, 1.2 Hz, 1H), 3.17 (dd, J = 13.7, 5.7 Hz, 1H), 2.85 (dd, J = 13.7, 9.4 Hz, 1H).

**13C NMR** (101 MHz, CDCl₃)
δ 196.3, 172.6, 140.9 (d, J = 422.2 Hz), 137.5 (d, J = 21.1 Hz) 132.5, 131.0 (d, J = 8.2 Hz), 129.80 129.5, 129.1, 128.6, 128.4, 128.3, 126.9, 115.3 (d, J = 21.5 Hz), 52.3, 47.5, 38.4.

**19F NMR** (376 MHz, CDCl₃)
δ = −113.9 (s, 1F)

**IR** (film): ν(cm⁻¹) 2953, 1741, 1654, 1593, 1512, 1454, 1220, 1141.

**HRMS (FTMS + ESI)** calcd for C₂₅H₂₁NaFO₃⁺ ([M]+Na⁺) = 389.1547 found 389.1552.
Methyl 2-benzoyl-1-benzyl-2-(4-chlorophenyl) cyclopropane-1-carboxylate (3ah)

Colorless oil, 45% yield, ee = 98%, [α]$_{D}^{16}$ = +17.1 (c = 0.80, in CH$_2$Cl$_2$) HPLC (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 5.32 min, $t_R$ (minor) = 6.25 min. $^1$H NMR (400 MHz, Chloroform-d) δ 8.06–8.00 (m, 2H), 7.54–7.50 (m, 1H), 7.48–7.42 (m, 4H), 7.25–7.24 (m, 1H), 7.22 (d, $J = 1.7$ Hz, 2H), 7.20 (d, $J = 2.7$ Hz, 3H), 7.18 (d, $J = 1.6$ Hz, 1H), 3.92 (d, $J = 14.9$ Hz, 1H), 3.36 (s, 3H), 2.44 (dd, $J = 5.6, 1.4$ Hz, 1H), 2.22 (d, $J = 14.9$ Hz, 1H), 1.98 (d, $J = 5.6$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.7, 170.5, 138.6, 135.7, 134.4, 133.7, 133.3, 131.3, 129.5, 128.7, 128.6, 128.5, 128.4 128.4, 126.6, 52.0, 45.0, 38.0, 37.7, 21.8. IR (film): ν(cm$^{-1}$) 2953, 1737, 1675, 1498, 1450, 1261, 1101, 694. HRMS (FTMS + ESI) calcd for C$_{25}$H$_{21}$NaClO$_3$ + ([M]+Na$^+$) = 427.1071 and 429.1042 found 427.1079 and 429.1051.
Colorless oil, 47% yield, ee = 87%, [α]°D = −50.7 (c = 0.29, in CH₂Cl₂) HPLC (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.35 min, t_R (minor) = 10.21 min. ¹H NMR (400 MHz, Chloroform-d) δ 7.62 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.02 (d, J = 6.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.31 (d, J = 10.7 Hz, 1H), 3.70 (s, 3H), 3.65 – 3.57 (m, 1H), 3.18 (dd, J = 13.7, 5.6 Hz, 1H), 2.86 (dd, J = 13.7, 9.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.1, 172.6, 142.9, 139.0, 137.5, 137.3, 134.0, 133.4, 132.6, 130.6, 129.8, 129.6, 129.4, 129.2, 128.7, 128.6, 128.5, 128.3, 128.1, 126.9, 52.4, 47.6, 38.4. IR (film): ν (cm⁻¹) 2956, 1745, 1639, 1494, 1265, 1101. HRMS (FTMS + ESI) calcd for C₂₅H₂₁NaClO₃⁺ ([M⁺Na⁺]) = 427.1071 and 429.1042 found 427.1078 and 429.1049.

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Methyl 2-benzoyl-1-benzyl-2-(4-bromophenyl) cyclopropane-1-carboxylate (3ai)

Colorless oil, 46% yield, ee = 98%, [α]°D = −12.8 (c = 0.26, in CH₂Cl₂) HPLC (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.53 min, t_R (minor) = 6.64 min. ¹H NMR (400 MHz, Chloroform-d) ¹H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.58 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.38 (m, 4H), 7.29 – 7.23 (m, 3H), 7.04 – 7.00 (m, 2H), 6.82 – 6.78 (m, 2H), 6.31 (d, J = 10.7 Hz, 1H), 3.68 (s, 3H), 3.63 – 3.57 (m, 1H), 3.17 (dd, J = 13.7, 5.6 Hz, 1H), 2.85 (dd, J = 13.7, 9.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 195.6, 170.5, 138.6, 135.6, 134.9, 133.4, 131.6, 131.6, 129.5, 128.6, 128.4, 126.6, 121.9, 52.0, 45.1, 38.0, 37.7, 21.8.
IR (film): ν (cm⁻¹) 2920, 1745, 1651, 1384, 1276, 1068. HRMS (FTMS + ESI) calcd for C_{25}H_{21}NaBrO_{3}⁺ ([M]+H⁺) = 471.0566 and 473.0546 found 471.0570 and 473.0551.

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HRMS (FTMS + ESI) calcd for C_{25}H_{21}NaBrO_{3}⁺ ([M]+H⁺) = 471.0566 and 473.0546 found 471.0570 and 473.0551.

Methyl (E)-2-benzyl-4-(4-bromophenyl)-5-oxo-5-phenylpent-3-enoate (4ai)

Colorless oil, 46% yield, ee = 83%, [α]^{D}_{D} = -44.0 (c = 0.22, in CH_2Cl_2)

HPLC (Chiral IB column) \^1PrOH/\^Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.65 min, t_R (minor) = 10.45 min.

\^1H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.58 (m, 2H), 7.56 – 7.51 (m, 1H), 7.42 (dd, J = 8.1, 6.2 Hz, 4H), 7.28 (dd, J = 9.0, 7.4 Hz, 3H), 7.05 – 6.99 (m, 2H), 6.79 (d, J = 8.1 Hz, 2H), 6.31 (d, J = 10.7 Hz, 1H), 3.70 (s, 3H), 3.65 – 3.55 (m, 1H), 3.17 (dd, J = 13.7, 5.5 Hz, 1H), 2.85 (dd, J = 13.7, 9.5 Hz, 1H).

\^13C NMR (101 MHz, CDCl_3) δ 196.0, 172.6, 143.0, 139.0, 137.5, 137.3, 133.9, 132.6, 131.4, 130.9, 129.8, 129.2, 128.6, 128.3, 127.0, 122.2, 52.4, 47.6, 38.4, 36.6, 24.7.

IR (film): ν (cm⁻¹) 2974, 1734, 1654, 1462, 1093, 1055, 891. HRMS (FTMS + ESI) calcd for C_{25}H_{21}NaBrO_{3}⁺ ([M]+H⁺) = 471.0566 and 473.0546 found 471.0562 and 473.0543.

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Methyl 2-benzyloxy-1-benzyl-2-(naphthalen-2-yl) cyclopropane-1-carboxylate (3aj)

White powder, m.p.96 - 102 °C, 50% yield, ee = 98%, [α]D = +25.6 (c = 0.19, in CH2Cl2) HPLC (Chiral IB column) PrOH/ n-Hexane = 2/98, Flow rate: 1.0 mL/min, tR (major) = 6.08 min, tR (minor) = 7.25 min. 1H NMR (400 MHz, Chloroform-d) δ 8.17 – 8.08 (m, 2H), 7.97 (d, J = 1.9 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.74 – 7.69 (m, 2H), 7.61 (dd, J = 8.6, 1.9 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.38 (m, 4H), 7.26 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 4.00 (dd, J = 14.9, 1.4 Hz, 1H), 3.27 (s, 3H), 2.57 (dd, J = 5.4, 1.4 Hz, 1H), 2.29 (d, J = 14.9 Hz, 1H), 2.07 (d, J = 5.4 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 196.0, 170.8, 138.8, 135.8, 133.3, 133.2, 132.6, 129.6, 129.4, 128.6, 128.5, 128.4, 128.1, 127.9, 127.6, 127.2, 126.5, 126.3, 126.2, 100.0, 51.9, 45.9, 38.1, 37.7, 21.9. IR (film): ν (cm⁻¹) 2935, 1734, 1653, 1278, 742, 702. HRMS (FTMS + ESI) calcd for C29H25O3+ ([M]+H⁺) = 421.1798 found 421.1801.
Methyl (E)-2-benzyl-4-(naphthalen-2-yl)-5-oxo-5-phenylpent-3-enoate (4aj)

Colorless oil, 45% yield, ee = 92%, $[\alpha]_D^{16} = -24.1$ (c = 0.63, in CH$_2$Cl$_2$)

**HPLC** (Chiral IC column) iPrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, $t_R$ (minor) = 32.48 min, $t_R$ (major) = 34.89 min.

**$^1$H NMR** (400 MHz, Chloroform-d) $\delta$ 7.84 – 7.80 (m, 1H), 7.78 (d, $J$ = 8.3 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.53 – 7.50 (m, 1H), 7.48 (dd, $J$ = 6.2, 3.3 Hz, 2H), 7.41 (d, $J$ = 7.7 Hz, 2H), 7.34 (s, 1H), 7.28 (d, $J$ = 2.3 Hz, 2H), 7.23 – 7.13 (m, 2H), 7.10 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.03 (dd, $J = 6.7, 2.9$ Hz, 2H), 6.37 (d, $J = 10.7$ Hz, 1H), 3.81 – 3.72 (m, 1H), 3.16 (d, $J = 5.7$ Hz, 1H), 2.99 – 2.68 (m, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 196.6, 172.8, 144.1, 138.4, 137.7, 133.0, 132.8, 132.5, 129.9, 129.3, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 126.9, 126.3, 126.2, 52.3, 52.3, 47.5, 38.6, 29.7.

**IR** (film): $\nu$ (cm$^{-1}$) 2949, 1741, 1662, 1446, 1261, 698.

**HRMS** (FTMS + ESI) calcd for C$_{29}$H$_{24}$NaO$_3$+ ([M]+Na$^+$) = 443.1618 found 443.1615.

Methyl 1-benzyl-2-(4-methylbenzoyl)-2-(p-tolyl) cyclopropane-1-carboxylate (3ak)

Colorless oil, 45% yield, ee = 95%, $[\alpha]_D^{16} = +12.8$ (c = 0.88, in CH$_2$Cl$_2$)

**HPLC** (Chiral IB column) iPrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, $t_R$ (major) = 5.25 min, $t_R$ (minor) = 5.84 min.

**$^1$H NMR** (400 MHz, Chloroform-d) $\delta$ 8.00 (d, $J$ = 8.2 Hz, 2H), 7.38 (d, $J$ = 8.2 Hz, 2H), 7.27 – 7.15 (m, 7H), 7.03 (d, $J$ = 8.0 Hz, 2H), 3.91 (d, $J = 14.9$ Hz, 1H), 3.35 (s, 3H), 2.44 – 2.39 (m, 1H), 2.36 (s, 3H), 2.10 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.03 (dd, $J = 6.7, 2.9$ Hz, 2H), 6.37 (d, $J = 10.7$ Hz, 1H), 3.81 – 3.72 (m, 1H), 3.16 (d, $J = 5.7$ Hz, 1H), 2.99 – 2.68 (m, 1H).

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Methyl 1-benzyl-2-(4-methylbenzoyl)-2-(p-tolyl) cyclopropane-1-carboxylate (3ak)
2.23 (s, 3H), 2.19 (d, J = 15.0 Hz, 1H), 1.93 (d, J = 5.3 Hz, 1H). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 195.6, 170.9, 144.0, 139.0, 137.3, 133.2, 132.9, 130.0, 129.8, 129.7, 129.2, 129.2, 128.6, 128.4, 127.0, 126.4, 51.8, 45.5, 38.2, 37.3, 21.8, 21.7, 21.7, 21.1. IR (film): \(\nu (\text{cm}^{-1})\) 3030, 1741, 1658, 1600, 1446, 1276, 1170. HRMS (FTMS + ESI) calcd for C\(_{27}\)H\(_{26}\)NaO\(_3\) \(([\text{M}]+\text{Na}^+) = 421.1774\) found 421.1766.

### Methyl (E)-2-benzyl-5-oxo-4,5-di-p-tolypent-3-enoate(4ak)

Colorless oil, 54% yield, ee = 90%, \([\alpha]\)^{19}D = \(-84.5\) (c = 0.26, in CH\(_2\)Cl\(_2\)) HPLC (Chiral IA column) PrOH/\(n\)Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, \(t_R\) (major) = 15.03 min, \(t_R\) (minor) = 21.26 min. \(^1\text{H NMR}\) (400 MHz, Chloroform-d) \(\delta\) 7.55 (d, J = 8.1 Hz, 2H), 7.26 (q, J = 6.1, 4.9 Hz, 3H), 7.18 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 6.6 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.20 (d, J = 10.6 Hz, 1H), 3.72 (ddd, J = 10.6, 9.0, 6.3 Hz, 1H), 3.68 (s, 3H), 3.15 (dd, J = 13.7, 6.2 Hz, 1H), 2.88 (dd, J = 13.7, 8.9 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 196.5, 173.0, 144.0, 143.2, 137.8, 137.6, 136.7, 134.8, 132.3, 130.1, 129.2, 129.0, 128.9, 128.5, 126.8, 52.2, 47.3, 38.6, 21.6, 21.3. IR (film): \(\nu (\text{cm}^{-1})\) 3035, 1745, 1658, 1265, 1174, 759. HRMS (FTMS + ESI) calcd for C\(_{27}\)H\(_{26}\)NaO\(_3\) \(([\text{M}]+\text{Na}^+) = 421.1774\) found 421.1770.

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Methyl 1-benzyl-2-(4-fluorophenyl)-2-(4-methylbenzoyl) cyclopropane-1-carboxylate (3al)

Colorless oil, 43% yield, ee = 99%, $[\alpha]^\text{D} = +20.6$ (c = 0.79, in CH$_2$Cl$_2$) HPLC (Chiral IB column) PrOH/ Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 5.32 min, $t_R$ (minor) = 6.10 min. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.97 (d, $J$ = 8.2 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.28 – 7.21 (m, 4H), 7.18 (d, $J$ = 7.0 Hz, 3H), 6.92 (t, $J$ = 8.7 Hz, 2H), 3.92 (dd, $J$ = 15.0, 1.3 Hz, 1H), 3.34 (s, 3H), 2.44 (dd, $J$ = 5.5, 1.4 Hz, 1H), 2.38 (s, 3H), 2.20 (d, $J$ = 15.0 Hz, 1H), 1.95 (d, $J$ = 5.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.4, 170.7, 162.0 (d, $J$ = 247.2 Hz), 144.3, 138.8, 133.0, 131.8 (d, $J$ = 3.2 Hz), 131.6 (d, $J$ = 8.2 Hz), 129.7, 129.3, 128.6, 128.4, 126.5, 115.4 (d, $J$ = 21.6 Hz), 51.9, 44.8, 38.2, 37.5, 22.0, 21.7. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = −114.1 (s, 1F). IR (film): $\nu$(cm$^{-1}$) 2956, 1737, 1724, 1647, 1552, 1498. HRMS (FTMS + ESI) calcd for C$_{26}$H$_{24}$FO$_3$+ ([M]+H$^+$) = 403.1704 found 403.1710.
Methyl (E)-2-benzyl-4-(4-fluorophenyl)-5-oxo-5-(p-tolyl)pent-3-enoate (4al)

Colorless oil, 55% yield, ee = 90%. \([\alpha]_{D}^{16} = -61.5\) (c = 0.64, in CH$_2$Cl$_2$)

**HPLC** (Chiral IA column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 13.31 min, $t_R$ (minor) = 21.25 min.

**$^1$H NMR** (400 MHz, Chloroform-$d$) $\delta$ 7.60 – 7.51 (m, 2H), 7.28 (dd, $J$ = 7.2, 2.2 Hz, 2H), 7.20 (d, $J$ = 8.1 Hz, 2H), 7.07 – 6.99 (m, 3H), 6.96 (s, 2H), 6.93 (d, $J$ = 2.4 Hz, 2H), 6.25 (d, $J$ = 10.6 Hz, 1H), 3.70 (s, 2H), 3.66 – 3.61 (m, 1H), 3.16 (dd, $J$ = 13.7, 5.7 Hz, 1H), 2.85 (dd, $J$ = 13.7, 9.3 Hz, 1H), 2.41 (s, 3H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 196.0, 172.8, 162.4 (d, $J$ = 247.0 Hz), 143.3 (d, $J$ = 38.3 Hz), 137.7 (d, $J$ = 13.1 Hz), 134.6, 131.6, 131.1, 132.0, 130.9, 130.3, 130.0, 129.7, 129.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 127.2, 126.9, 116.3, 116.1, 115.3 (d, $J$ = 21.3 Hz), 52.3, 47.4, 38.4, 21.7.

**$^{19}$F NMR** (376 MHz, CDCl$_3$) $\delta$ = −114.0 (s, 1F).

**IR** (film): $\nu$(cm$^{-1}$) 2953, 1737, 1668, 1610, 1508, 1224.

**HRMS (FTMS + c ESI)** calcd for C$_{26}$H$_{23}$NaFO$_3$ $^+ ([M]+Na^-)$ = 425.1523 found 425.1523.

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Methyl (3E,5Z)-2-benzyl-4,5-diphenyl-5-(2-tosylhydrazono) pent-3-enoate (5)

**Retention Time** | **Area** | **% Area**
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2 | 21.248 | 5.25

42
White powder, m.p. 125 - 128 °C, 64% yield, ee = 90%, [α]D^26 = -26.0 (c = 0.68, in CH₂Cl₂) HPLC (Chiral ADH column) \(^{3}\)PrOH/ Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 11.10 min, tR (minor) = 12.85 min. \(^{1}\)H NMR (400 MHz, Chloroform-d) δ 7.49 (dd, J = 5.2, 1.9 Hz, 3H), 7.38 – 7.28 (m, 4H), 7.25 – 7.15 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 7.07 – 6.99 (m, 2H), 6.83 (dd, J = 6.5, 3.0 Hz, 2H), 6.77 – 6.64 (m, 2H), 5.47 (d, J = 10.5 Hz, 1H), 3.57 (s, 3H), 3.43 – 3.27 (m, 1H), 2.92 (dd, J = 13.4, 6.0 Hz, 1H), 2.62 (dd, J = 13.5, 9.0 Hz, 1H), 2.41 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ 173.2, 156.3, 143.9, 143.7, 137.8, 136.0, 134.9, 130.6, 123.0, 129.8, 129.6, 129.4, 128.2, 128.0, 127.6, 127.1, 126.5, 52.0, 47.6, 38.6, 21.6. IR (film): ν (cm⁻¹) 1737, 1670, 1444, 1444, 1261, 1230, 1298. HRMS (FTMS + c ESI) calcd for C₃₂H₃₀Na₂O₄S⁺ ([M]+Na⁺) = 561.1818 found 561.1825.

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Methyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate-3,3-d₂ (D-3aa)

White powder, m.p. 94 - 100 °C, 45% yield, ee = 99%, [α]D^26 = +27.6 (c = 0.60, in CH₂Cl₂) HPLC (Chiral IB column) \(^{3}\)PrOH/ Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, tR (major) = 5.49 min, tR (minor) = 5.97 min. \(^{1}\)H NMR (400 MHz, Chloroform-d) δ 8.13 – 8.00 (m, 2H), 7.50 (d, J = 7.6 Hz, 3H), 7.43 (dd, J = 8.2, 6.4 Hz, 2H), 7.30 – 7.08 (m, 84H), 3.93 (d, J = 14.9 Hz, 1H), 3.31 (s, 3H), 2.23 (d, J = 15.0 Hz, 1H). \(^{13}\)C
NMR (101 MHz, CDCl₃) δ 196.1, 170.7, 138.9, 135.9, 135.8, 133.1, 129.6, 128.6, 128.5, 128.4, 127.6, 126.5, 51.8, 45.6, 38.0, 37.4. IR (film): ν(cm⁻¹) 1734, 1656, 1448, 1259. HRMS (FTMS + c ESI) calcd for C₃₂H₃₀NaN₂O₄S⁺ ([M]+Na⁺) = 395.1587 found 395.1587.

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Methyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate-2,3-d₂ (D-4aa)

Colorless oil, 44% yield, ee = 93%. [α]₆₀°D = +61 (c = 0.56, in CH₂Cl₂) HPLC (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm. tᵣ (major) = 9.40 min, tᵣ (minor) = 10.32 min. ¹H NMR (400 MHz, Chloroform-d) δ 7.64 (dd, J = 8.2, 1.4 Hz, 1H), 7.55 – 7.48 (m, 0H), 7.39 (t, J = 7.7 Hz, 1H), 7.31 (td, J = 4.7, 1.5 Hz, 2H), 7.28 (s, 0H), 7.26 (d, J = 2.6 Hz, 1H), 7.06 – 6.93 (m, 2H), 3.68 (s, 2H), 3.15 (d, J = 13.7 Hz, 1H), 2.87 (d, J = 13.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.50, 172.85, 143.87, 137.65, 137.54, 135.04, 132.44, 129.84, 129.18, 129.12, 128.50, 128.29, 128.25, 127.88, 126.82, 126.28, 52.25, 38.45, 29.71. IR (film): ν(cm⁻¹) 1734, 1662, 1591, 1492, 1444,1261, 1230. HRMS (FTMS + c ESI) calcd for C₃₂H₃₀NaN₂O₄S⁺ ([M]+Na⁺) = 395.1587 found 395.1582.

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11. Limitation of scope with cyclopropanation and C-H insertion reaction of enones

Table S2. Optimization of the conditions use chalcone as substrate *
**Figure S2** Structures of substrates with no reactions

**Methyl 5-benzoyl-3-benzyl-4-phenyl-4,5-dihydro-3H-pyrazole-3-carboxylate**

Colorless oil, 30% yield, ee = 69%, dr > 20:1, **HPLC** (Chiral IB column) PrOH/Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 13.19 min, t_R (minor) = 17.23 min. **^1H NMR** (400 MHz, Chloroform-d) δ 8.15 – 8.08 (m, 2H), 7.55 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 7.31 – 7.25 (m, 7H), 7.23 – 7.19 (m, 3H), 7.17 – 7.09 (m, 2H), 6.68 (s, 1H), 4.59 (s, 1H), 3.46 (d, J = 13.3 Hz, 1H), 3.24 (s, 3H), 3.08 (d, J = 13.3 Hz, 1H). **^13C NMR** (101 MHz, CDCl_3) δ 170.0, 151.0, 135.9, 134.4, 132.5, 130.8, 130.0, 129.8, 129.0, 128.8, 128.6, 128.1, 128.1, 127.8, 127.7, 106.0, 59.5, 51.9, 43.6. **HRMS** (FTMS + e ESI) calcd for C_{25}H_{23}NaN_2O_3^+ ([M]+Na^+) = 421.1523 found 421.1519.
12. X-ray crystallography data

(a) The absolute configuration of 3aa was determined by X-ray chromatography analysis.

Single crystal of the cyclopropanation product 3aa [C_{25}H_{22}O_3] was obtained from the mixed solvents of petroleum ether, ethyl acetate. The absolute configuration of 3aa is (1S, 2R). CCDC 1843744 contains
the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

(b) The absolute configuration of 5aa was determined by X-ray chromatography analysis. The carbon insertion product 4aa can be converted to the product 5aa. Single crystal of the product 5aa ([C₃H₈N₂O₄S₁] was obtained from the mixed solvents of petroleum ether, ethyl acetate. The absolute configuration of 5aa is (S, E). CCDC 1843745 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

13. reference
14. Copies of NMR spectra for substrates and products