Supporting Information

Regio- and Stereoselective Syntheses of Chiral α-Quaternary (Z)-Trisubstituted Allylic Amino Acids via Synergistic Pd/Cu Catalysis

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1. General information

All reactions were accomplished in Schlenk tube and round flask. Column chromatograph was performed over silica gel (200-300 mesh). $^1$H NMR spectra were recorded on a Bruker AM400 spectrometer, chemical shifts (in ppm) were referred to CDCl$_3$ ($\delta = 7.26$ ppm). $^{13}$C NMR spectrum were obtained by using the same NMR spectrometer and were calibrated with CDCl$_3$ ($\delta = 77.0$ ppm). The following abbreviations have been used to illuminate the diversities: $\delta =$ chemical shifts, $J =$ coupling constant, s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet. HRMS were recorded on a Bruker microTOF spectrometer (ESI). Ee values were determined by Agilent high-performance liquid chromatograph (HPLC). All anhydrous solvents were dried by the standard treated method. Vinylethylene carbonates$^1$ and aldimine ester$^2$ were synthesized according to known references. All materials were obtained by commercial suppliers, unless otherwise notice, and most stating materials were purchased from Adamas, Bide and Energy Chemical. PE = petroleum ether, DCM = dichloromethane, MeOH = methanol, EA = ethyl acetate.

2. Procedure for the synthesis chiral $\alpha$-quaternary ($Z$)-trisubstituted allylic amino acids

The preparation of Cu catalyst: Cu(CH$_3$CN)$_4$PF$_6$ (5 mol%), L1 (6 mol%) were stirred in DCE (0.5 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

Method A: To a Schlenk tube with prepared Cu catalyst were added Cs$_2$CO$_3$ (32.6 mg, 0.1 mmol), aldimine Schiff base (0.1 mmol, 1.0 equiv), vinylethylene carbonates (24.7 mmol, 1.3 equiv), Pd catalyst (4 mol%) and DCE (0.5 mL) under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 4 h. To the reaction mixture was added dry MeOH (1 mL) and NaBH$_3$CN (31.4mg, 5.0 equiv) at 0 °C and the mixture was stirred for 2 h. Then the crude products were purified by SiO$_2$ column chromatography (PE/EA = 3:1) to give the desired products. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.
3. Results and discussion

3.1 Optimization of reaction conditions

Table S1. Screening of reaction conditions.  

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<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ee (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Z/E&lt;sup&gt;d&lt;/sup&gt;</th>
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<td>91</td>
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<sup>a</sup> Reaction conditions: 1a (0.1 mmol), 2a (0.12 mmol), Pd(PPh$_3$)$_4$ (5 mol%), Cu (10 mol%), L (12 mol%), base (1.5 equiv.), solvent (1 mL), NaBH$_4$ (5 equiv.), MeOH (1 mL), N$_2$, 9 h, r.t.  
<sup>b</sup> Determined by 1H NMR using CHBr$_2$ as internal standard.  
<sup>c</sup> Determined by HPLC using chiral column.  
<sup>d</sup> LiAlH$_4$ (4 equiv.).  
<sup>e</sup> NaBH(OAc)$_2$ (4 equiv.).  
<sup>f</sup> NaBH$_4$CN (4 equiv.).  
<sup>g</sup> 40 °C.  
<sup>h</sup> 40 °C.  
<sup>i</sup> 1b (0.1 mmol).  
<sup>j</sup> 1c (0.1 mmol).  
<sup>k</sup> 1d (0.1 mmol).  
<sup>l</sup> 1b (0.1 mmol), 2a (0.13 mmol), Pd(PPh$_3$)$_4$ (4 mol%), Cu(CH$_3$CN)$_2$PF$_6$ (5 mol%), L1 (6 mol%), Cs$_2$CO$_3$ (1 equiv.), DCE (1 mL), NaBH$_4$CN (5 equiv.), MeOH (1.0 mL), N$_2$, 6 h, 40 °C.  

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3.2 Stereocontrol experiments

Scheme S1. Stereocontrol experiments

3.3 Reaction mechanism

Scheme S2. A plausible mechanism
3.4. Characterization of trisubstituted allylic amino acids

3ba (30.7mg, 86% yield, PE/EA=3:1, 92% ee, Z/E >20:1) was synthesized in method A afforded 86% isolated yield as a colorless oil. 

[α]D =+4 (c=0.60, CHCl₃). **1H NMR (400 MHz, CDCl₃)** δ 7.35 (d, J = 7.3 Hz, 2H), 7.22 (ddd, J = 10.0, 8.0, 4.9 Hz, 5H), 7.02 – 6.84 (m, 2H), 5.72 (dd, J = 9.4, 7.4 Hz, 1H), 4.34 (dd, J = 52.1, 12.3 Hz, 2H), 3.70 (s, 3H), 3.55 (dd, J = 36.3, 11.7 Hz, 2H), 2.59 (ddd, J = 21.2, 13.9, 8.4 Hz, 2H), 2.33 (bs, 2H), 1.39 (s, 3H). **13C NMR (100 MHz, CDCl₃)** δ 176.5, 162.1 (d, J = 245.0 Hz), 144.6, 141.6, 134.9 (d, J = 3.1 Hz), 130.0 (d, J = 8.1 Hz), 128.4, 127.3, 126.2, 124.8, 115.4 (d, J = 21.4 Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.7. HRMS (ESI) m/z: [M + H]+ Calcd for C₂₁H₂₄FNO₃ 358.1813; found: 358.1839. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; t_R = 8.65 min (major), 9.87 min (minor).
3bb (32.1 mg, 87% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 87% isolated yield as a colorless oil. [α]D = +16 (c=0.64, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.27 – 7.17 (m, 4H), 7.05 (d, J = 7.9 Hz, 2H), 6.97 – 6.86 (m, 2H), 5.68 (dd, J = 9.4, 7.4 Hz, 1H), 4.32 (dd, J = 57.3, 12.3 Hz, 2H), 3.70 (s, 3H), 3.55 (dd, J = 41.4, 11.7 Hz, 2H), 2.81 (bs, 1H), 2.58 (ddd, J = 21.1, 13.9, 8.5 Hz, 3H), 2.26 (s, 3H), 1.39 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 176.4, 162.1 (d, J = 245.4 Hz), 144.5, 138.7, 137.1, 134.7 (d, J = 2.7 Hz), 130.1 (d, J = 8.0 Hz), 129.1, 126.0, 123.9, 115.4 (d, J = 21.2 Hz), 61.9, 59.8, 52.4, 48.2, 39.4, 21.6, 21.0. HRMS (ESI) m/z: [M + H]+ Calcd for C22H26FNO3: 372.1969; found: 372.1989. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; tR = 7.99 min (major), 9.19 min (minor).
3bc (25.3 mg, 61% yield, PE/EA=3:1, 84% ee, Z/E >20:1) was synthesized in method A afforded 61% isolated yield as a colorless oil. $[\alpha]_D^{25} = +12$ (c=0.51, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.25 (m, 4H), 7.23 – 7.17 (m, 2H), 6.97 – 6.85 (m, 2H), 5.78 – 5.60 (m, 1H), 4.33 (dd, $J = 56.9, 12.3$ Hz, 2H), 3.70 (s, 3H), 3.54 (dd, $J = 40.3, 11.6$ Hz, 2H), 2.81 (bs, 1H), 2.58 (ddd, $J = 21.0, 13.8, 8.7$ Hz, 2H), 1.39 (s, 3H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, $J = 245.3$ Hz), 150.3, 144.4, 138.6, 134.8 (d, $J = 3.1$ Hz), 130.1 (d, $J = 8.1$ Hz), 125.8, 125.3, 124.0, 115.4 (d, $J = 21.4$ Hz), 61.9, 59.8, 52.4, 48.2, 39.5, 34.4, 31.3, 21.6. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{25}$H$_{32}$FNO$_3$ 414.2439; found: 414.2465. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R = 10.49$ min (major), 11.23 min (minor).
3bd (25.0 mg, 65% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method A afforded 65% isolated yield as a colorless oil. $[\alpha]_{25}^{D}=21+$ (c=0.50, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 6.96 – 6.86 (m, 2H), 6.83 – 6.71 (m, 2H), 5.63 (dd, $J = 9.5, 7.3$ Hz, 1H), 4.31 (dd, $J = 55.3, 12.3$ Hz, 2H), 3.72 (s, 3H), 3.70 (s, 3H), 3.54 (dd, $J = 39.9, 11.6$ Hz, 2H), 2.86 (bs, 1H), 2.56 (ddd, $J = 21.2, 13.9, 8.4$ Hz, 2H), 1.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.5, 162.1 (d, $J = 245.5$ Hz), 159.0, 144.0, 134.8 (d, $J = 3.2$ Hz), 134.1, 130.1 (d, $J = 8.1$ Hz), 127.3, 123.1, 115.4 (d, $J = 21.4$ Hz), 113.7, 61.9, 59.8, 55.3, 52.4, 48.2, 39.4, 21.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{26}$FNO$_4$ 388.1919; found: 388.1943. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; t$_R$ =13.20 min (major), 14.96 min (minor).
3be (26.9 mg, 67% yield, PE/EA=3:1, 92% ee, Z/E >20:1) was synthesized in method A afforded 67% isolated yield as a colorless oil. [$\alpha$]$_D^{25}$=+17 (c=0.42, CHCl$_3$). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 2H), 7.16 – 7.08 (m, 2H), 6.98 – 6.78 (m, 2H), 5.69 (dd, $J$ = 9.5, 7.3 Hz, 1H), 4.30 (dd, $J$ = 57.1, 12.3 Hz, 2H), 3.71 (s, 3H), 3.54 (dd, $J$ = 40.5, 11.6 Hz, 2H), 2.93 (s, 1H), 2.57 (dd, $J$ = 21.2, 13.9, 8.5 Hz, 2H), 2.40 (s, 3H), 1.39 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, $J$ = 245.3 Hz), 144.1, 138.4, 137.5, 134.7 (d, $J$ = 8.1 Hz), 144.1, 126.5, 126.5, 124.2, 115.4 (d, $J$ = 21.3 Hz), 61.9, 59.6, 52.4, 48.2, 39.4, 21.5, 15.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{26}$FNO$_3$S 404.1690; found:404.1715. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$=12.40 min (major), 13.82 min (minor).
3bf (31.6 mg, 72% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 72% isolated yield as white solid. 

$[\alpha]_{25}^D = +9$ (c=0.40, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 7.8$ Hz, 1H), 7.61 – 7.49 (m, 7H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.37 – 7.28 (m, 3H), 7.02 (t, $J = 8.5$ Hz, 2H), 5.87 (dd, $J = 9.2$, 7.5 Hz, 1H), 4.45 (dd, $J = 55.9$, 12.2 Hz, 2H), 3.80 (s, 3H), 3.64 (dd, $J = 41.5$, 11.5 Hz, 2H), 3.15 (bs, 1H), 2.70 (ddd, $J = 21.1$, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, $J = 245.3$ Hz), 144.3, 140.6, 140.5, 140.2, 137.5, 134.6 (d, $J = 1.9$ Hz), 132.4, 130.1 (d, $J = 8.1$ Hz), 130.0, 128.7, 128.2, 127.3, 127.1, 127.0, 126.5, 124.7, 115.5 (d, $J = 21.4$ Hz), 62.0, 59.7, 52.4, 48.3, 39.4, 21.5.

HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{27}$H$_{28}$FNO$_3$ 434.2126; found: 434.2153. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; $t_R$ = 15.88 min (major), 17.03 min (minor).
3bg (24.9 mg, 66% yield, PE/EA=3:1, 92% ee, Z/E > 20:1) was synthesized in method A afforded 66% isolated yield as a colorless oil. \( [\alpha]_{25}^{D} = +20 \) (c=0.50, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.43 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.07 – 6.93 (m, 4H), 5.72 (dd, \( J = 9.5, 7.3 \) Hz, 1H), 4.37 (dd, \( J = 62.0, 12.3 \) Hz, 2H), 3.79 (s, 3H), 3.63 (dd, \( J = 42.7, 11.3 \) Hz, 2H), 3.07 (bs, 1H), 2.65 (ddd, \( J = 21.2, 13.9, 8.5 \) Hz, 2H), 1.48 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 176.3, 163.4 (d, \( J = 6.5 \) Hz), 161.0 (d, \( J = 5.7 \) Hz), 143.9, 137.7 (d, \( J = 3.0 \) Hz), 134.5 (d, \( J = 2.5 \) Hz), 130.2 (d, \( J = 8.1 \) Hz), 127.8 (d, \( J = 7.9 \) Hz), 124.5, 115.5 (d, \( J = 21.4 \) Hz), 115.2 (d, \( J = 21.4 \) Hz), 62.0, 52.5, 48.3, 39.2, 21.4. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{21}\)H\(_{23}\)F\(_2\)NO\(_3\): 376.1719; found: 376.1739. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25 min; \( t_R = 9.18 \) min (major), 10.55 min (minor).
3bh (25.7 mg, 66% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method A afforded 66% isolated yield as a colorless oil. \([\alpha]_D^{25} = +10\) (c=0.51, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 4H), 6.99 – 6.87 (m, 2H), 5.70 (dd, J = 9.4, 7.4 Hz, 1H), 4.28 (dd, J = 54.5, 12.3 Hz, 2H), 3.71 (s, 3H), 3.53 (dd, J = 38.1, 11.5 Hz, 2H), 2.80 (bs, 1H), 2.56 (ddd, J = 21.2, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 176.4, 162.1 (d, J = 245.6 Hz), 143.6, 140.1, 134.7 (d, J = 3.2 Hz), 133.1, 130.1 (d, J = 8.1 Hz), 128.4, 127.4, 125.3, 115.45 (d, J = 21.3 Hz), 61.9, 59.6, 52.4, 48.2, 39.2, 21.5. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C₂₁H₂₃ClFNO₃ 392.1423; found: 392.1448. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 7.24\) min (major), 7.81 min (minor).
3bi (25.3 mg, 58% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method A afforded 58% isolated yield as a colorless oil. $[\alpha]_{D}^{25} = +6$ (c=0.51, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.40 (m, 2H), 7.34 – 7.23 (m, 4H), 7.06 – 6.93 (m, 2H), 5.77 (dd, $J = 9.6$, 7.3 Hz, 1H), 4.36 (dd, $J = 62.4$, 12.3 Hz, 2H), 3.79 (s, 3H), 3.63 (dd, $J = 43.0$, 11.5 Hz, 2H), 2.65 (ddd, $J = 21.2$, 13.9, 8.6 Hz, 2H), 2.12 (bs, 1H), 1.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.2, 162.2 (d, $J = 245.6$ Hz), 143.9, 140.6, 134.3 (d, $J = 5.2$ Hz), 131.4, 130.2 (d, $J = 8.0$ Hz), 127.8, 125.2, 121.3, 115.5 (d, $J = 21.3$ Hz), 62.0, 59.5, 52.5, 48.3, 39.2, 21.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{21}$H$_{23}$BrFNO$_3$ 436.0918; found: 436.0944. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 8.17 min (major), 9.08 min (minor).
3bj (29.9 mg, 70% yield, PE/EA=3:1, 86% ee, Z/E >20:1) was synthesized in method A afforded 70% isolated yield as a colorless oil. \([\alpha]_D^{25} = +17\ (c=0.30, \text{CHCl}_3)\). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 – 7.50 (m, 4H), 7.32 – 7.26 (m, 2H), 7.05 – 6.97 (m, 2H), 5.86 (dd, \(J = 9.4, 7.4\) Hz, 1H), 4.39 (dd, \(J = 58.0, 12.3\) Hz, 2H), 3.79 (s, 3H), 3.62 (dd, \(J = 40.7, 11.5\) Hz, 2H), 2.75 (bs, 1H), 2.68 (ddd, \(J = 21.2, 13.9, 8.5\) Hz, 2H), 1.48 (s, 3H). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 162.2 (d, \(J = 245.7\) Hz), 145.2, 143.9, 134.4 (d, \(J = 3.0\) Hz), 130.2 (d, \(J = 8.1\) Hz), 129.3 (q, \(J = 32.5\) Hz), 126.8, 126.4, 125.3 (q, \(J = 3.7\) Hz), 124.2 (q, \(J = 270.3\) Hz), 115.5 (d, \(J = 21.3\) Hz), 62.0, 59.5, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{22}\)H\(_{23}\)F\(_4\)NO\(_3\) 426.1687; found: 426.1713. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 8.42\) min (major), 9.26 min (minor).
3bk (16.7 mg, 44% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 44% isolated yield as a colorless oil. $[\alpha]_D^{25} = +11$ (c=0.29, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.50 (m, 2H), 7.48 – 7.43 (m, 2H), 7.23 – 7.16 (m, 2H), 7.00 – 6.89 (m, 2H), 5.83 (dd, $J = 9.1$, 7.8 Hz, 1H), 4.29 (dd, $J = 51.7$, 12.3 Hz, 2H), 3.73 (s, 3H), 3.55 (dd, $J = 37.5$, 11.5 Hz, 2H), 2.87 (s, 1H), 2.60 (ddd, $J = 21.3$, 13.9, 8.5 Hz, 2H), 1.41 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.2, 162.1 (d, $J = 245.8$ Hz), 146.2, 143.5, 134.3 (d, $J = 2.9$ Hz), 132.2, 130.1 (d, $J = 8.1$ Hz), 127.8, 126.7, 118.9, 115.6, 115.4, 110.7, 61.9, 59.2, 52.6, 48.3, 39.1, 21.4. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{23}$FN$_2$O$_3$ 383.1765; found: 383.1801. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 40 min; $t_R$ =28.08 min (major), 31.53 min (minor).
3bl (25.6 mg, 69% yield, PE/EA=3:1, 93% ee, Z/E >20:1) was synthesized in method A afforded 69% isolated yield as a colorless oil. [α]D25 =+18 (c=0.27, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.33 – 7.27 (m, 2H), 7.25 (s, 1H), 7.23 – 7.19 (m, 2H), 7.10 – 7.07 (m, 1H), 7.03 – 6.98 (m, 2H), 5.77 (dd, J = 9.6, 7.3 Hz, 1H), 4.40 (dd, J = 57.6, 12.3 Hz, 2H), 3.78 (s, 3H), 3.63 (dd, J = 41.1, 11.5 Hz, 2H), 3.13 (bs, 1H), 2.66 (dd, J = 21.1, 13.9, 8.5 Hz, 2H), 2.35 (s, 3H), 1.45 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 176.4, 162.1 (d, J = 245.5 Hz), 144.9, 141.6, 138.0, 134.7 (d, J = 2.5 Hz), 130.1 (d, J = 8.1 Hz), 128.3, 128.1, 126.9, 124.5, 123.2, 115.4 (d, J = 21.4 Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.6, 21.4. HRMS (ESI) m/z: [M + H]+ Calcd for C22H26FNO3 372.1969; found:372.1991. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; tR = 8.14 min (major), 9.28 min (minor).
3bm (30.4 mg, 78% yield, PE/EA=3:1, 85% ee, Z/E >20:1) was synthesized in method A afforded 78% isolated yield as a colorless oil. $[\alpha]_D^{25} = +15$ (c=0.38, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.31 (m, 1H), 7.25 – 7.14 (m, 6H), 6.98 – 6.88 (m, 2H), 5.73 (dd, $J = 9.3$, 7.5 Hz, 1H), 4.29 (dd, $J = 54.7$, 12.3 Hz, 2H), 3.72 (s, 3H), 3.55 (dd, $J = 39.3$, 11.5 Hz, 2H), 2.81 (bs, $J = 76.5$ Hz, 1H), 2.58 (dd, $J = 21.2$, 13.9, 8.5 Hz, 3H), 1.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.1, 162.2 (d, $J = 245.6$ Hz), 143.7, 143.5, 134.35 (d, $J = 3.0$ Hz), 134.3, 130.2 (d, $J = 8.1$ Hz), 129.6, 127.3, 126.3, 125.8, 124.4, 115.5 (d, $J = 21.3$ Hz), 62.1, 59.5, 52.5, 48.2, 39.0, 21.5. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{21}$H$_{23}$ClFNO$_3$ 382.1423; found: 382.1447. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R = 9.50$ min (minor), 10.15 min (major).
3bn (30.3 mg, 70% yield, PE/EA=3:1, 94% ee, Z/E >20:1) was synthesized in method A afforded 70% isolated yield as a colorless oil. [α]$^D_{25}$ =+23 (c=0.28, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.53 (m, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.20 – 7.15 (m, 1H), 7.06 – 6.97 (m, 2H), 5.79 (dd, $J$ = 9.5, 7.4 Hz, 1H), 4.35 (dd, $J$ = 55.8, 12.3 Hz, 2H), 3.79 (s, 3H), 3.62 (dd, $J$ = 39.7, 11.6 Hz, 2H), 2.95 (bs, 1H), 2.65 (ddd, $J$ = 21.2, 13.9, 8.5 Hz, 2H), 1.47 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.3, 162.1 (d, $J$ = 245.6 Hz), 143.9, 143.7, 134.5 (d, $J$ = 1.9 Hz), 130.2 (d, $J$ = 6.0 Hz), 130.1, 129.9, 129.2, 126.0, 124.8, 122.5, 115.5 (d, $J$ = 21.3 Hz), 62.0, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{21}$H$_{23}$BrFNO$_3$ 436.0918; found: 436.0945. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =15.99 min (minor), 17.09 min (major).
3bo (22.7 mg, 53% yield, PE/EA=3:1, 91% ee, Z/E >20:1) was synthesized in method A afforded 53% isolated yield as a colorless oil. 

$[\alpha]^2_D = +10$ (c=0.45, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 – 7.32 (m, 1H), 7.24 – 7.18 (m, 2H), 6.99 – 6.89 (m, 2H), 5.77 (dd, $J = 9.4$, 7.4 Hz, 1H), 4.32 (dd, $J = 56.1$, 12.3 Hz, 2H), 3.73 (s, 3H), 3.56 (dd, $J = 40.1$, 11.6 Hz, 2H), 2.89 (bs, 1H), 2.60 (ddd, $J = 21.3$, 13.9, 8.5 Hz, 2H), 1.41 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.3, 162.2 (d, $J = 245.6$ Hz), 143.8, 142.5, 134.5 (d, $J = 2.6$ Hz), 130.7 (q, $J = 64.3$, 32.3 Hz), 130.1 (d, $J = 8.1$ Hz), 129.5, 128.8, 126.4, 124.1 (q, $J = 270.8$ Hz), 123.9 (q, $J = 3.6$ Hz), 122.9 (q, $J = 3.7$ Hz), 115.5 (d, $J = 21.3$ Hz), 62.0, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{23}$F$_4$NO$_3$ 426.1687; found: 426.1712. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R = 5.95$ min (minor), 6.64 min (major).
**3bp** (21.6 mg, 56% yield, PE/EA=3:1, 88% ee, Z/E >20:1) was synthesized in method A afforded 56% isolated yield as a colorless oil. 

$\left[\alpha\right]_D^{25} = +16 \,(c=0.43, \text{CHCl}_3).$ 

**1H NMR** (400 MHz, CDCl$_3$) δ 7.29 – 7.21 (m, 2H), 7.20 – 7.13 (m, 1H), 7.0 – 6.99 (m, 1H), 6.97 – 6.89 (m, 2H), 6.84 (t, $J = 7.4$ Hz, 1H), 6.77 (d, $J = 8.2$ Hz, 1H), 5.50 (dd, $J = 9.0, 7.1$ Hz, 1H), 4.25 (dd, $J = 44.8, 12.4$ Hz, 2H), 3.69 (s, 3H), 3.65 (s, 3H), 3.60 (dd, 2H), 2.70 (bs, 1H), 2.63 (ddd, $J = 21.2, 14.2, 8.1$ Hz, 2H), 1.39 (s, 3H). 

**13C NMR** (100 MHz, CDCl$_3$) δ 176.4, 162.0 (d, $J = 244.9$ Hz), 156.2, 143.2, 135.4 (d, $J = 3.0$ Hz), 131.9, 130.1, 129.9 (d, $J = 8.0$ Hz), 128.6, 127.1, 120.8, 115.2 (d, $J = 21.2$ Hz), 110.4, 61.8, 61.0, 55.3, 52.2, 47.9, 38.3, 21.9. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{26}$FNO$_4$: 388.1919; found: 388.1940. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; $t_R = 13.05$ min (minor), 14.46 min (major).
3bq (22.8 mg, 61% yield, PE/EA=3:1, 86% ee, Z/E >20:1) was synthesized in method A afforded 61% isolated yield as a colorless oil. \([\alpha]_D^{25} = +23\) (c=0.46, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27 – 7.12 (m, 5H), 7.04 – 6.99 (m, 1H), 6.98 – 6.91 (m, 3H), 5.64 (dd, \(J = 9.4, 7.2\) Hz, 1H), 4.30 (dd, \(J = 62.7, 12.6\) Hz, 2H), 3.71 (s, 3H), 3.57 (dd, \(J = 36.5, 11.6\) Hz, 2H), 2.74 (bs, 1H), 2.62 (ddd, \(J = 21.2, 14.0, 8.3\) Hz, 2H), 1.41 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 163.3, 159.6 (d, \(J = 246.0\) Hz), 140.1 (d, \(J = 0.8\) Hz), 134.8 (d, \(J = 2.8\) Hz), 130.1 (d, \(J = 3.8\) Hz), 130.0 (d, \(J = 8.1\) Hz), 129.7 (d, \(J = 14.4\) Hz), 128.9 (d, \(J = 8.3\) Hz), 128.2 (d, \(J = 2.5\) Hz), 124.1 (d, \(J = 3.4\) Hz), 115.7, 115.4 (d, \(J = 21.2\) Hz), 61.8, 60.5, 52.4, 48.1, 38.8, 21.6. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{21}\)H\(_{23}\)F\(_2\)NO\(_3\) 376.1719; found: 376.1741. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 10.99\) min (minor), 12.02 min (major).
3br (33.5 mg, 86% yield, PE/EA=3:1, 88% ee, Z/E >20:1) was synthesized in method A afforded 86% isolated yield as a colorless oil. 

$[^{[\alpha]}]_{D}^{25} = +16$ (c=0.53, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.30 (m, 3H), 7.21 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 7.06 – 6.97 (m, 2H), 5.46 (dd, J = 9.7, 7.1 Hz, 1H), 4.33 (dd, J = 82.0, 13.1 Hz, 2H), 3.78 (s, 3H), 3.74 – 3.59 (m, 2H), 2.74 (ddd, J = 20.6, 13.6, 9.1 Hz, 2H), 1.51 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, J = 245.5 Hz), 143.6, 143.5, 134.6 (d, J = 3.3 Hz), 134.2, 130.1 (d, J = 8.1 Hz), 129.6, 127.3, 126.3, 126.0, 124.3, 115.5 (d, J = 21.3 Hz), 61.9, 59.6, 52.5, 48.3, 39.2, 21.5. HRMS (ESI) m/z: [M + H]$^+$ Calcld for C$_{21}$H$_{23}$ClFNO$_3$ 392.1423; found: 392.1447. HPLC conditions: OZ-H column, 254 nm, 30 ℃, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 13.31 min (minor), 15.60 min (major).
3bs (29.4 mg, 72% yield, PE/EA=3:1, 92% ee, Z/E >20:1) was synthesized in method A afforded 72% isolated yield as a colorless oil. \( \alpha \) \( \delta \) \( \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.21 (d, \( J = 7.8 \text{ Hz}, 2\text{H} \)), 7.07 – 6.81 (m, 4H), 6.74 (d, \( J = 7.8 \text{ Hz}, 1\text{H} \)), 5.64 (dd, \( J = 11.1, 4.5 \text{ Hz}, 1\text{H} \)), 4.31 (dd, \( J = 56.6, 12.0 \text{ Hz}, 2\text{H} \)), 3.80 (s, 6H), 3.71 (s, 3H), 3.55 (dd, \( J = 39.4, 11.5 \text{ Hz}, 2\text{H} \)), 2.61 (bs, 1H), 2.70 – 2.46 (m, 2H), 1.40 (s, 3H). \( \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 176.4, 162.1 (d, \( J = 245.5 \text{ Hz} \)), 148.7, 148.5, 144.4, 134.8 (d, \( J = 2.7 \text{ Hz} \)), 134.7, 130.1 (d, \( J = 8.0 \text{ Hz} \)), 123.4, 118.5, 115.4 (d, \( J = 21.3 \text{ Hz} \)), 110.9, 109.4, 62.0, 59.9, 55.9, 55.8, 52.4, 48.2, 39.4, 21.6. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{23}\)H\(_{28}\)FNO\(_5\) 418.2024; found: 418.2048. HPLC conditions: OD-H column, 254 nm, 30 \( \degree \text{C} \), flow rate: 1.3 mL/min, Hex:IPA = 92:8. 30min; \( t_R = 21.79 \text{ min} \) (minor), 24.15 min (major).
3bt (26.7 mg, 63% yield, PE/EA=3:1, 89% ee, Z/E >20:1) was synthesized in method A afforded 63% isolated yield as a colorless oil. 

\[ \alpha \] = +7 (c=0.53, CHCl₃).

**¹H NMR** (400 MHz, CDCl₃) δ 7.44 (d, J = 2.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.23 – 7.18 (m, 3H), 7.00 – 6.88 (m, 2H), 5.74 (dd, J = 9.3, 7.5 Hz, 1H), 4.26 (dd, J = 52.5, 12.3 Hz, 2H), 3.72 (s, 3H), 3.54 (dd, J = 38.8, 11.5 Hz, 2H), 3.02 (bs, 1H), 2.57 (ddd, J = 21.3, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H).  

**¹³C NMR** (100 MHz, CDCl₃) δ 176.3, 162.1 (d, J = 245.6 Hz), 142.8, 141.7, 134.5 (d, J = 2.7 Hz), 132.4, 131.1, 130.2, 130.1, 128.0, 126.3, 125.5, 115.5 (d, J = 21.4 Hz), 61.9, 59.3, 52.5, 48.3, 39.1, 21.4.  

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₁H₂₂Cl₂FNO₃ 426.1034; found: 426.1058. HPLC conditions: OJ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \( t_R \) = 16.07 min (major), 21.58 min (minor).
3bu (17.6 mg, 44% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 44% isolated yield as a colorless oil. 

\([\alpha]^{25}_{D} = +20 \text{ (c=0.30, CHCl}_3)\).  

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.26 (m, 2H), 7.05 – 6.95 (m, 2H), 6.94 – 6.87 (m, 2H), 6.75 (d, $J = 7.9$ Hz, 1H), 5.94 (s, 2H), 5.68 (dd, $J = 9.5, 7.3$ Hz, 1H), 4.35 (dd, $J = 56.5, 12.3$ Hz, 2H), 3.78 (s, 3H), 3.62 (dd, $J = 41.3, 11.6$ Hz, 2H), 2.65 (bs, 1H), 2.62 (ddd, $J = 21.2, 13.9, 8.5$ Hz, 2H), 1.46 (s, 3H).  

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, $J = 245.4$ Hz), 147.7, 146.9, 144.3, 135.9, 134.7 (d, $J = 3.1$ Hz), 130.1 (d, $J = 8.1$ Hz), 123.6, 119.7, 115.5 (d, $J = 21.3$ Hz), 108.1, 106.8, 101.0, 62.0, 59.9, 52.4, 48.3, 39.3, 21.5.  

HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{24}$FNO$_5$ 402.1711; found: 402.1733.  

HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R = 18.19$ min (minor), 19.40 min (major).
3bv (21.5 mg, 48% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 48% isolated yield as white solid. 

\([\alpha]_D^{25} = +9\) (c=0.43, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (dd, $J = 18.3, 7.7$ Hz, 2H), 7.63 (s, 1H), 7.54 (d, $J = 7.3$ Hz, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 7.3$ Hz, 1H), 7.34–7.27 (m, 3H), 7.02 (t, $J = 8.6$ Hz, 2H), 5.86 (dd, $J = 9.2, 7.6$ Hz, 1H), 4.47 (dd, $J = 52.4, 12.3$ Hz, 2H), 3.89 (s, 2H), 3.80 (s, 3H), 3.64 (dd, $J = 39.7, 11.6$ Hz, 2H), 3.04 (bs, 1H), 2.69 (ddd, $J = 21.2, 13.9, 8.5$ Hz, 2H), 1.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.5, 162.1 (d, $J = 245.4$ Hz), 145.0, 143.5, 143.4, 141.3, 141.0, 140.3, 134.7 (d, $J = 3.0$ Hz), 130.1 (d, $J = 8.1$ Hz), 126.7, 126.6, 125.0, 124.9, 124.4, 122.8, 119.8, 119.7, 115.4 (d, $J = 21.4$ Hz), 62.0, 60.0, 52.4, 48.3, 39.5, 36.9, 21.6.

HRMS (ESI) $m/z$: [M + H]$^+$ Calcld for C$_{28}$H$_{28}$FNO$_3$ 446.2126; found: 446.2154. HPLC conditions: AS-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R = 12.35$ min (major), 18.12 min (minor).
3bw (16.9 mg, 42% yield, PE/EA=3:1, 92% ee, Z/E >20:1) was synthesized in method A afforded 42% isolated yield as a colorless oil. \([\alpha]_D^{25} = 13\) (c=0.34, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (dd, \(J = 12.2, 8.4\) Hz, 2H), 7.68 (d, \(J = 8.2\) Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 7.04 – 6.91 (m, 2H), 5.54 (dd, \(J = 10.0, 6.9\) Hz, 1H), 4.32 (dd, \(J = 110.5, 12.5\) Hz, 2H), 3.69 (s, 3H), 3.61 (dd, \(J = 48.6, 9.0\) Hz, 2H), 3.04 (bs, 1H), 2.71 (ddd, \(J = 20.6, 13.7, 8.5\) Hz, 2H), 1.47 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 162.2 (d, \(J = 245.5\) Hz), 145.8, 140.7, 134.8 (d, \(J = 3.0\) Hz), 133.5, 131.2, 130.2 (d, \(J = 8.1\) Hz), 128.3, 127.7, 127.2, 126.0, 125.9, 125.7, 125.6, 125.3, 115.5 (d, \(J = 21.3\) Hz), 61.6, 61.3, 52.4, 48.2, 39.6, 21.8. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{25}\)H\(_{26}\)FNO\(_3\) 408.1969; found: 408.1993. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; \(t_R = 11.85\) min (minor), 14.83 min (major).
3bx (23.3 mg, 57% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 57% isolated yield as a colorless oil. 

$[\alpha]_{D}^{25}$ = +12 (c = 0.30, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (s, 1H), 7.85 – 7.76 (m, 3H), 7.61 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.35 – 7.28 (m, 2H), 7.07 – 6.98 (m, 2H), 5.95 (dd, $J$ = 9.4, 7.4 Hz, 1H), 4.52 (dd, $J$ = 49.0, 12.3 Hz, 2H), 3.80 (s, 3H), 3.65 (dd, $J$ = 40.2, 11.6 Hz, 2H), 3.10 (bs, 1H), 2.73 (ddd, $J$ = 21.2, 13.9, 8.5 Hz, 2H), 1.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.4, 162.1 (d, $J$ = 245.5 Hz), 144.7, 138.8, 134.7 (d, $J$ = 2.8 Hz), 133.3, 132.6, 130.1 (d, $J$ = 8.1 Hz), 128.1, 127.9, 127.5, 126.2, 125.8, 125.3, 124.7, 124.5, 115.4 (d, $J$ = 21.3 Hz), 62.0, 59.8, 52.5, 48.3, 39.4, 21.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{25}$H$_{26}$FNO$_3$ 408.1969; found: 408.1992.

HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 10.35 min (major), 11.36 min (minor).
**3by** (21.4 mg, 49% yield, PE/EA=3:1, 91% ee, Z/E >20:1) was synthesized in method A afforded 49% isolated yield as a colorless oil. \([\alpha]_D^{25} = +11\) (c=0.36, CHCl₃). 

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 7.82 (s, 1H), 7.74 – 7.66 (m, 2H), 7.56 – 7.51 (m, 1H), 7.34 – 7.27 (m, 2H), 7.15 – 7.09 (m, 2H), 7.05 – 6.97 (m, 2H), 5.90 (dd, \(J = 9.4, 7.4\) Hz, 1H), 4.50 (dd, \(J = 49.9, 12.3\) Hz, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.71 – 3.57 (m, 2H), 3.02 (bs, 1H), 2.71 (ddd, \(J = 21.2, 13.9, 8.5\) Hz, 2H), 1.50 (s, 3H). 

**13C NMR** (100 MHz, CDCl₃) \(\delta\) 176.4, 162.1 (d, \(J = 245.4\) Hz), 157.6, 144.6, 136.6, 134.7 (d, \(J = 1.5\) Hz), 133.8, 130.1 (d, \(J = 8.1\) Hz), 129.6, 128.8, 126.8, 125.0, 124.6, 124.4, 119.0, 115.4 (d, \(J = 21.3\) Hz), 105.4, 62.0, 59.8, 55.3, 52.4, 48.3, 39.5, 21.6. HRMS (ESI) \(m/z\): [M + H]* Calcd for C₂₆H₂₈FNO₄ 438.2075; found: 438.2100. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 16.74\) min (major), 18.87 min (minor).
3bz (21 mg, 64% yield, PE/EA=3:1, 92% ee, E/Z >20:1) was synthesized in method A afforded 64% isolated yield as a colorless oil. \([\alpha]_D^{25}=+22\) (c=0.22, CHCl₃). **H NMR** (400 MHz, CDCl₃) \(\delta\) 7.31 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 6.97 – 6.87 (m, 2H), 6.33 – 6.28 (m, 2H), 6.02 (dd, \(J = 9.5, 7.7\) Hz, 1H), 4.26 (dd, \(J = 39.4, 12.4\) Hz, 2H), 3.72 (s, 3H), 3.55 (dd, \(J = 38.3, 11.6\) Hz, 2H), 2.59 (ddd, \(J = 21.5, 14.0, 8.8\) Hz, 3H), 1.40 (s, 3H). **C NMR** (100 MHz, CDCl₃) \(\delta\) 176.5, 162.1 (d, \(J = 245.0\) Hz), 144.6, 141.6, 134.9 (d, \(J = 3.1\) Hz), 130.0 (d, \(J = 8.1\) Hz), 128.4, 127.3, 126.2, 124.8, 115.4 (d, \(J = 21.4\) Hz), 61.9, 59.9, 52.4, 48.2, 39.4, 21.7. HRMS (ESI) \(m/z\): [M + H]⁺ Calcd for C₁⁹H₂₂FNO₄ 348.1606; found: 348.1627. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 9.72\) min (major), 10.91 min (minor).
3baa (25.7 mg, 74% yield, PE/EA=3:1, 92% ee, E/Z >20:1) was synthesized in method A afforded 74% isolated yield as a colorless oil. \([\alpha]_D^{25}=+20\) (c=0.40, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.23 – 7.19 (m, 2H), 7.09 – 7.06 (m, 1H), 7.06 – 7.02 (m, 1H), 6.96 – 6.89 (m, 3H), 5.87 (dd, \(J = 9.3, 7.6\) Hz, 1H), 4.34 (dd, \(J = 34.4, 12.4\) Hz, 2H), 3.72 (s, 3H), 3.54 (dd, \(J = 37.5, 11.6\) Hz, 2H), 2.82 (bs, 1H), 2.57 (ddd, \(J = 21.5, 14.0, 8.4\) Hz, 2H), 1.38 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.3, 162.1 (d, \(J = 244.0\) Hz), 144.9, 138.1, 134.7 (d, \(J = 2.9\) Hz), 130.1 (d, \(J = 8.1\) Hz), 127.6, 124.1, 123.6, 123.0, 115.5 (d, \(J = 21.1\) Hz), 62.2, 59.5, 52.4, 48.2, 38.8, 21.4. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{19}\)H\(_{22}\)FNO\(_3\)S 364.1377; found: 364.1397. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 10.92\) min (major), 14.75 min (minor).
3bab (20.2 mg, 57% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 57% isolated yield as a colorless oil. 

\([\alpha]_D^{25} = +17 \, (c=0.32, \, \text{CHCl}_3)\). 

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 – 7.17 (m, 4H), 7.14 – 7.10 (m, 1H), 6.96 – 6.90 (m, 2H), 5.82 (dd, \(J = 9.4, 7.5\) Hz, 1H), 4.31 (dd, \(J = 41.7, 12.3\) Hz, 2H), 3.71 (s, 3H), 3.54 (dd, \(J = 38.2, 11.6\) Hz, 2H), 2.60 (bs, 1H), 2.57 (dd, \(J = 21.4, 14.0, 8.4\) Hz, 2H), 1.38 (s, 3H). 

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 176.4, 162.1 (d, \(J = 245.5\) Hz), 142.3, 139.2, 134.7 (d, \(J = 3.1\) Hz), 130.1 (d, \(J = 8.1\) Hz), 125.7, 125.6, 123.0, 120.5, 115.4 (d, \(J = 21.3\) Hz), 62.1, 59.5, 52.4, 48.2, 38.8, 21.5. 

HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{19}\)H\(_{22}\)FNO\(_3\)S 364.1377; found: 364.1396. 

HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 10.15\) min (major), 12.48 min (minor).
3ea (29.2 mg, 79% yield, PE/EA=3:1, 92% ee, Z/E >20:1) was synthesized in method A afforded 79% isolated yield as a colorless oil. 

$[\alpha]_D^{25} = +15$ (c=0.36, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.33 (m, 2H), 7.27 – 7.18 (m, 5H), 6.98 – 6.86 (m, 2H), 5.72 (dd, $J = 9.4$, 7.5 Hz, 1H), 4.33 (dd, $J = 52.9$, 12.3 Hz, 2H), 4.22 – 4.12 (m, 2H), 3.55 (dd, $J = 37.4$, 11.5 Hz, 2H), 2.74 (bs, 1H), 2.58 (ddd, $J = 21.2$, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.9, 162.1 (d, $J = 245.4$ Hz), 144.7, 141.7, 134.8 (d, $J = 3.0$ Hz), 130.1 (d, $J = 8.1$ Hz), 128.4, 127.3, 126.1, 124.8, 115.4 (d, $J = 21.3$ Hz), 61.8, 61.4, 59.8, 48.2, 39.4, 21.5, 14.3. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{22}$H$_{26}$FNO$_3$ 372.1969; found: 372.1993. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ = 7.57 min (major), 10.07 min (minor).
**3fa** (17.5 mg, 54% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method A afforded 54% isolated yield as a colorless oil. \([\alpha]_{D}^{25} =+13 \text{ (c=0.36, CHCl}_3\text{).}^{1} \) **H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.32 (m, 2H), 7.27 – 7.16 (m, 6H), 6.98 – 6.89 (m, 2H), 5.73 (dd, \(J = 9.3, 7.6\) Hz, 1H), 4.33 (dd, \(J = 53.9, 12.2\) Hz, 2H), 3.55 (dd, \(J = 37.6, 11.4\) Hz, 2H), 2.96 (bs, 1H), 2.55 (ddd, \(J = 21.1, 13.8, 8.5\) Hz, 2H), 1.44 (s, 9H), 1.35 (s, 3H). \(^{13}C\) **NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 175.1, 162.1 (d, \(J = 245.3\) Hz), 144.6, 141.8, 134.8, 130.1 (d, \(J = 8.0\) Hz), 128.4, 127.2, 126.1, 125.0, 115.5 (d, \(J = 21.3\) Hz), 81.8, 62.1, 59.8, 48.3, 39.4, 28.1, 21.4. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{24}\)H\(_{30}\)FNO\(_3\) 400.2282; found: 400.2309. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 10min; \(t_R = 4.44\) min (major), 6.14 min (minor).
3\textsuperscript{ga} (28.0 mg, 73% yield, PE/EA=3:1, 91% ee, Z/E >20:1) was synthesized in method A afforded 73% isolated yield as a colorless oil. 

\[ \alpha \] \textsuperscript{D} \text{=} +7 (c=0.56, CHCl\textsubscript{3}), \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.38 – 7.32 (m, 2H), 7.27 – 7.17 (m, 5H), 6.98 – 6.87 (m, 2H), 5.72 (dd, \textit{J} = 9.5, 7.3 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.34 (dd, \textit{J} = 55.2, 12.3 Hz, 2H), 3.56 (dd, \textit{J} = 39.0, 11.5 Hz, 2H), 2.99 (bs, 1H), 2.59 (ddd, \textit{J} = 21.2, 13.9, 8.5 Hz, 2H), 1.39 (s, 3H), 1.22 (d, \textit{J} = 6.3 Hz, 6H).\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 175.2, 162.2 (d, \textit{J} = 245.5 Hz), 144.6, 141.7, 134.7 (d, \textit{J} = 1.1 Hz), 130.1 (d, \textit{J} = 8.1 Hz), 128.4, 127.3, 126.1, 124.8, 115.5 (d, \textit{J} = 21.4 Hz), 69.0, 61.9, 59.8, 48.2, 39.2, 21.9, 21.8, 21.4. HRMS (ESI) \textit{m/z}: [M + H]\textsuperscript{+} Calcd for C\textsubscript{23}H\textsubscript{28}FNO\textsubscript{3} 386.2126; found: 386.2153. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 15min; \textit{t}_R = 6.21 min (major), 10.51 min (minor)
5ba (12.5 mg, 35% yield, PE/EA=3:1, 86% ee, Z/E >20:1) was synthesized in method A afforded 35% isolated yield as a colorless oil. $[\alpha]_D^{25} = +33$ (c=0.20, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 – 7.16 (m, 7H), 6.97 – 6.92 (m, 2H), 6.03 (t, $J = 6.9$ Hz, 1H), 4.09 (ddd, $J = 85.9$, 13.2, 6.9 Hz, 2H), 3.50 (dd, $J = 48.7$, 11.2 Hz, 2H), 3.07 (s, 3H), 3.02 (s, 2H), 1.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.5, 162.2 (d, $J = 244.0$ Hz), 142.0, 139.1, 134.78 (d, $J = 3.1$ Hz), 132.9, 130.2 (d, $J = 8.1$ Hz), 128.2, 127.4, 126.7, 115.5 (d, $J = 21.2$ Hz), 60.5, 58.3, 51.7, 48.3, 41.7, 22.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{21}$H$_{24}$FNO$_3$ 358.1813; found: 358.1836. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =17.21 min (minor), 20.28 min (major).
**5bb** (14.4 mg, 33% yield, PE/EA=3:1, 85% ee, Z/E >20:1) was synthesized in method A afforded 33% isolated yield as white solid. 

\([\alpha]_D^{25} = +24 \ (c=0.29, \text{CHCl}_3)\). **1H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.45 (m, 4H), 7.38 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 – 7.17 (m, 2H), 6.98 – 6.92 (m, 2H), 6.09 (t, \(J = 6.9\) Hz, 1H), 4.11 (ddd, \(J = 83.5, 13.2, 6.9\) Hz, 2H), 3.51 (dd, \(J = 50.5, 11.2\) Hz, 2H), 3.10 (s, 3H), 3.05 (s, 2H), 1.39 (s, 3H).

**13C NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 175.6, 162.17 (d, \(J = 245.5\) Hz), 140.9, 140.4, 140.2, 138.6, 134.8 (d, \(J = 3.0\) Hz), 132.9, 130.2 (d, \(J = 8.1\) Hz), 128.8, 127.4, 127.1, 126.9, 126.8, 115.54 (d, \(J = 21.3\) Hz), 60.6, 58.3, 51.8, 48.3, 41.6, 22.5.

**HRMS (ESI) m/z:** [M + H]\(^+\) Calcd for C\(_{27}\)H\(_{34}\)FNO\(_3\) 434.2126; found: 434.2155.

**HPLC conditions:** OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; \(t_R = 10.99\) min (major), 12.17 min (minor).
5bc (12.1 mg, 33% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method A afforded 33% isolated yield as a colorless oil. \([\alpha]^2_D = +11 (\text{c}=0.24, \text{CHCl}_3)\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.21 – 7.17 \text{ (m, 2H)}, 7.12 – 7.08 \text{ (m, 1H)}, 6.99 – 6.92 \text{ (m, 5H)}, 6.03 \text{ (t, } J = 6.9 \text{ Hz, 1H)}, 4.08 \text{ (ddd, } J = 87.3, 13.1, 6.9 \text{ Hz, 2H)}, 3.50 \text{ (dd, } J = 48.3, 11.3 \text{ Hz, 2H)}, 3.10 \text{ (s, 3H)}, 3.00 \text{ (d, } J = 3.0 \text{ Hz, 2H)}, 2.26 \text{ (s, 3H)}, 1.37 \text{ (s, 3H)}. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 175.5, 162.2 \text{ (d, } J = 244.1 \text{ Hz)}, 141.9, 139.2, 137.7, 134.7 \text{ (d, } J = 2.3 \text{ Hz)}, 132.6, 130.2 \text{ (d, } J = 8.1 \text{ Hz)}, 128.2, 128.1, 127.3, 123.8, 115.5 \text{ (d, } J = 21.3 \text{ Hz)}, 60.6, 58.2, 51.7, 48.3, 41.5, 22.5, 21.4\). HRMS (ESI) \(m/z\): [M + H]^+ Calcd for C\(_{22}\)H\(_{26}\)FNO\(_3\) 372.1969; found: 372.1994. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \(t_R = 9.53 \text{ min (minor), 10.31 min (major)}\).
5bd (10.1 mg, 28% yield, PE/EA=3:1, 80% ee, Z/E >20:1) was synthesized in method A afforded 28% isolated yield as a colorless oil. \([\alpha]_D^{25} =+17 \) (c=0.20, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.21 - 7.17 \) (m, 2H), 7.15 – 7.11 (m, 1H), 6.96 – 6.92 (m, 2H), 6.78 – 6.76 (m, 1H), 6.72 – 6.71 (m, 2H), 6.08 (t, \(J = 6.9\) Hz, 1H), 4.08 (ddd, \(J = 85.2, 13.1, 7.0\) Hz, 2H), 3.72 (s, 3H), 3.50 (dd, \(J = 47.5, 11.2\) Hz, 2H), 3.15 (s, 3H), 3.00 (s, 2H), 1.37 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 175.5, 162.2 (d, \(J = 244.0\) Hz), 159.5, 143.4, 139.0, 134.8 (d, \(J = 1.7\) Hz), 132.8, 130.2 (d, \(J = 8.0\) Hz), 129.2, 119.1, 115.5 (d, \(J = 21.4\) Hz), 112.8, 112.4, 60.6, 58.1, 55.3, 51.8, 48.3, 41.6, 22.4. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C\(_{22}\)H\(_{26}\)FNO\(_4\) 388.1919; found: 388.1944. HPLC conditions: AD-H column, 254 nm, 30 \(^\circ\)C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25 min; \(t_R\) =11.53 min (major), 12.86 min (minor).
5be (6.2 mg, 16% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method A afforded 16% isolated yield as a colorless oil. \([\alpha]_D^{25} = +21 \) (c=0.12, CHCl$_3$). \( ^1H\) NMR (400 MHz, CDCl$_3$) \( \delta \) 7.32 – 7.18 (m, 6H), 7.16 – 7.11 (m, 1H), 7.04 – 7.00 (m, 2H), 6.12 (t, \( J = 6.7 \) Hz, 1H), 4.16 (ddd, \( J = 79.4, 13.3, 6.8 \) Hz, 2H), 3.57 (dd, \( J = 48.9, 11.2 \) Hz, 2H), 3.25 (s, 3H), 3.06 (q, \( J = 13.8 \) Hz, 2H), 1.45 (s, 3H). \( ^13C\) NMR (100 MHz, CDCl$_3$) \( \delta \) 175.3, 162.2 (d, \( J = 245.2 \) Hz), 143.8, 137.6, 134.5 (d, \( J = 3.5 \) Hz), 134.1, 134.0, 130.3 (d, \( J = 8.0 \) Hz), 129.6, 127.4, 126.6, 125.0, 115.6 (d, \( J = 21.4 \) Hz), 60.5, 58.2, 51.9, 48.3, 41.4, 22.4. HRMS (ESI) \( m/z \): [M + H]$^+$ Calcd for C$_{21}$H$_{23}$ClFNO$_3$ 392.1423; found: 392.1447. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; \( t_R \) =12.58 min (minor), 14.32 min (major).
5bf (16.3 mg, 40% yield, PE/EA=3:1, 80% ee, Z/E >20:1) was synthesized in method A afforded 40% isolated yield as a colorless oil. $[\alpha]_D^{25} = +49$ (c=0.33, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.76 (m, 3H), 7.71 – 7.69 (m, 1H), 7.48 – 7.38 (m, 3H), 7.27 – 7.22 (m, 2H), 7.04 – 6.94 (m, 2H), 6.26 (t, $J$ = 6.9 Hz, 1H), 4.22 (ddd, $J$ = 82.7, 13.2, 6.9 Hz, 2H), 3.57 (dd, $J$ = 54.3, 11.3 Hz, 2H), 3.21 (q, $J$ = 13.8 Hz, 2H), 2.98 (s, 3H), 1.47 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.5, 162.2 (d, $J$ = 245.4 Hz), 139.2, 138.9, 134.7 (d, $J$ = 3.2 Hz), 133.4, 133.4, 133.1, 132.7, 130.2 (d, $J$ = 8.2 Hz), 128.0, 127.9, 127.5, 126.3, 125.9, 125.7, 125.1, 115.5 (d, $J$ = 21.3 Hz), 60.7, 58.3, 51.7, 48.3, 41.5, 22.5. HRMS (ESI) $m/z$: [M + H]$^+$ Calcd for C$_{25}$H$_{26}$FNO$_4$ 408.1919; found: 408.1998. HPLC conditions: OD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 25min; $t_R$ =13.14 min (major), 15.66 min (minor).
5bg (10.1 mg, 30% yield, PE/EA=3:1, 28% ee, Z/E >20:1) was synthesized in method A afforded 30% isolated yield as a colorless oil. \([\alpha]_D^{25} = +4\) (c=0.20, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.28 – 7.21 (m, 2H), 7.03 – 6.99 (m, 2H), 5.73 (t, \(J = 7.0\) Hz, 1H), 3.95 (dd, \(J = 83.0, 12.7, 7.0\) Hz, 2H), 3.78 (s, 3H), 3.63 (dd, \(J = 24.1, 11.2\) Hz, 2H), 2.59 (dd, \(J = 75.2, 13.6\) Hz, 2H), 1.92 – 1.78 (m, 2H), 1.46 (s, 3H), 1.37 – 1.24 (m, 4H), 0.86 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\) 176.9, 162.2 (d, \(J = 245.4\) Hz), 138.8, 134.8 (d, \(J = 2.8\) Hz), 130.3 (d, \(J = 8.1\) Hz), 129.5, 115.51 (d, \(J = 21.4\) Hz), 60.5, 57.8, 52.2, 48.4, 41.7, 36.9, 30.3, 22.6, 22.3, 13.89. HRMS (ESI) \(m/z\): [M + H]\(^+\) Calcd for C₁₉H₂₈FNO₃ 338.2128; found: 338.2146. HPLC conditions: OZ-H column, 220 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 10min; \(t_R = 4.72\) min (major), 5.17 min (minor).
**5bh** (18.8 mg, 67% yield, PE/EA=3:1, 54% ee, Z/E >20:1) was synthesized in method A afforded 67% isolated yield as a colorless oil. \([\alpha]_D^{25} = +5\) (c=0.37, CHCl<sub>3</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) \(\delta\) 7.25 – 7.19 (m, 2H), 6.98 – 6.86 (m, 2H), 5.73 – 5.45 (m, 2H), 4.00 (d, \(J = 5.2\) Hz, 2H), 3.66 (s, 3H), 3.53 (q, \(J = 11.9\) Hz, 2H), 2.37 (qd, \(J = 14.1, 7.1\) Hz, 2H), 1.86 (s, 2H), 1.27 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl<sub>3</sub>) \(\delta\) 176.4, 162.0 (d, \(J = 244.9\) Hz), 135.7 (d, \(J = 3.0\) Hz), 133.5, 129.9 (d, \(J = 8.0\) Hz), 126.2, 115.2 (d, \(J = 21.3\) Hz), 63.2, 62.3, 52.0, 47.7, 41.5, 22.0. HRMS (ESI) \(m/z\): [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>FNO<sub>3</sub> 282.1500; found: 282.1515. HPLC conditions: AD-H column, 220 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 95:5, 25min; \(t_R = 10.93\) min (major), 11.59 min (minor).
3.5 Gram-scale reaction for compound 3ba.

\[
\text{Ar} - \text{N} - \text{COOMe} \quad 1b + \quad \text{O} - \text{O} - \text{Ph} \quad 2a \rightarrow \quad \text{Ph} \quad \text{COOMe} \quad 3ba
\]

\[
Pd(PPh_3)_4 (4 \text{ mol\%}), \quad \text{Cu(CH_3CN)_4PF_6 (5 \text{ mol\%})/L1 (6 \text{ mol\%})/Cs_2CO_3 (1.0 \text{ equiv}), DCE (1 mL)}
\]

1) NaBH_3CN (5 equiv), MeOH (1 mL)

83% yield, 90% ee >20:1 Z/E

The preparation of Cu catalyst: Cu(CH_3CN)_4PF_6 (5 mol\%), L (6 mol%) were stirred in DCE (20 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

Method: A flame-dried Schlenk tube was cooled to r.t. and prepared with Cu catalyst. To this flask were added Cs_2CO_3 (1.17g, 3.6 mmol), aldimine Schiff base 1b (3.6 mmol, 1.0 equiv) and vinylene carbonate 2a (4.68 mmol, 1.3 equiv), Pd catalyst (4 mol\%) and DCE (20 mL) was then added. The reaction mixture was stirred at 40 °C for 4 h. To the reaction mixture was added dry MeOH (40 mL) and NaBH_3CN (1.2g, 5.0 equiv) at 0 °C and the mixture was stirred for 2 h. Extracted with EtOAc (5 mL x 3). The combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was then purified by SiO_2 column chromatography (PE/EA = 3:1) to give the desired products. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

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3.6 The method for the synthesis of 6aa

\[
\text{Ar} - \text{N} - \text{COOMe} \quad 1b + \quad \text{O} - \text{O} - \text{Ph} \quad 2a \rightarrow \quad \text{Ph} \quad \text{COOMe} \quad 6aa
\]

\[
Pd(PPh_3)_4 (4 \text{ mol\%}), \quad \text{Cu(CH_3CN)_4PF_6 (5 \text{ mol\%})/L1 (6 \text{ mol\%})/Cs_2CO_3 (1.0 \text{ equiv}), DCE (1 mL)}
\]

1) 2M HCl

6aa, 45% yield, 90% ee >20:1 Z/E
The preparation of Cu catalyst: Cu(CH$_3$CN)$_4$PF$_6$ (5 mol%), L (6 mol%) were stirred in THF (0.5 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 30 min.

Method B: A flame-dried Schlenk tube was cooled to r.t. and prepared with Cu catalyst. To this flask were added Cs$_2$CO$_3$ (32.6 mg, 0.1 mmol), aldimine Schiff base (0.1 mmol, 1.0 equiv) and vinylethylene carbonates (24.7 mmol, 1.3 equiv) and DCE (0.5 mL) was then added. The reaction mixture was stirred at 40 °C for 4 h. To the reaction mixture was added HCl (2.0 M, 2.0 mL) at 0 °C and the mixture was stirred for 2 h. Adjust pH to 7-8 by NaHCO$_3$, extracted with DCM (5 mL x 3). The combined extracts were dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was then purified by SiO$_2$ column chromatography (PE/EA = 1:2) to give the desired product. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

6aa (11.2 mg, 45% yield, PE/EA=3:1, 90% ee, Z/E >20:1) was synthesized in method B afforded 45% isolated yield as a colorless oil. [α]$_D^{25}$ = -29 (c=0.22, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.35 (m, 2H), 7.29 – 7.18 (m, 3H), 5.69 (dd, $J$ = 9.2, 7.7 Hz, 1H), 4.35 (dd, $J$ = 65.4, 12.1 Hz, 2H), 3.69 (s, 3H), 2.59 (ddd, $J$ = 30.8, 18.3, 10.2 Hz, 6H), 1.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.3, 145.3, 142.0, 128.3, 127.2, 126.1, 125.2, 59.8, 56.8, 52.7, 39.9, 26.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{19}$O$_3$ 250.1438; found: 250.1443. HPLC conditions: OJ-H column, 254 nm, 30 °C, flow rate: 1.2 mL/min, Hex:IPA = 95:5, 25min; $t_R$ =20.34 min (minor), 21.59 min (major).
3.7 The method for the synthesis of 6ab and 6ac.

**Method C:** A flame-dried Schlenk tube was cooled to rt and filled with N₂. To this flask were added 3ba (0.5 mmol, 1.0 equiv), I₂ (1.0 mmol, 2.0 equiv), NaHCO₃ (84.0 mg, 1.0 mmol) and dry MeCN at 0 °C for 30 min, then warm up to rt for 12h. The reaction mixture was quenched by Na₂S₂O₃(aq.) and extracted with EA, then concentrated in vacuo. The residue was then purified by SiO₂ column chromatography (PE/EA = 15:1) to give the desired products. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

**Method D:** A flame-dried Schlenk tube was cooled to rt and filled with N₂. To this flask were added 3ba (0.1 mmol, 1.0 equiv), PBr₃ (0.05 mmol, 0.5 equiv) and dry DCM at 0 °C for 2 hours, then add DIPEA (0.1 mmol) at 0 °C for 24 h. The reaction mixture was extracted with EA, then concentrated in vacuo. The residue was then purified by SiO₂ column chromatography (PE/EA = 20:1) to give the desired products. The ee value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.

**6ab** (118.9 mg, 49% yield, PE/EA=3:1, 87% ee, Z/E >20:1) was synthesized in method C afforded 49% isolated yield as a yellow oil. \([\alpha]_D^{25} = +5 \text{ (c}=1.20, \text{ CHCl}_3)\). **¹H NMR** (400 MHz, CDCl₃) δ 7.46 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 – 7.25 (m, 2H), 6.95 – 6.80 (m, 4H), 4.56 (t, J = 11.8 Hz, 1H), 4.36 (dd, J = 12.9, 7.3 Hz, 1H), 4.29 (d, J = 12.1 Hz, 1H), 3.80 – 3.68 (m, 3H), 3.61 (s, 3H), 3.03 (t, J = 12.6 Hz, 1H), 2.33 (dd, J = 12.1, 7.4 Hz, 1H), 1.57 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 177.5, 162.1 (d, J = 245.9 Hz), 140.4, 133.6 (d, J = 3.1 Hz),
131.2 (d, J = 8.1 Hz), 128.6, 127.7, 127.0, 114.9 (d, J = 21.2 Hz), 73.1, 68.4, 67.6, 52.8, 49.5, 49.2, 33.9, 22.5. HRMS (ESI) m/z: [M + H]^+ Calcd for C_{21}H_{23}FNO_3 484.0779; found: 484.0798. HPLC conditions: OZ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 92:8, 15 min; t_R = 5.77 min (major), 6.75 min (minor).

6ac (12.5 mg, 37% yield, PE/EA=20:1, 87% ee, Z/E >20:1) was synthesized in method D afforded 37% isolated yield as a colorless oil. [α]_D^{25} = +16 (c=0.25, CHCl_3). ^{1}H NMR (400 MHz, CDCl_3) δ 7.35 – 7.25 (m, 2H), 7.23 – 7.05 (m, 5H), 7.03 – 6.80 (m, 2H), 6.01 (s, 1H), 3.78 (dd, J = 151.7, 14.0 Hz, 5H), 3.52 – 3.25 (m, 2H), 2.91 – 2.23 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.0, 161.9 (d, J = 244.3 Hz), 139.2, 135.7 (d, J = 2.9 Hz), 134.4, 129.8 (d, J = 7.9 Hz), 128.3, 127.1, 124.8, 120.2, 115.0 (d, J = 21.2 Hz), 61.3, 54.7, 51.8, 49.6, 36.5, 22.8. HRMS (ESI) m/z: [M + H]^+ Calcd for C_{21}H_{22}FNO_2 340.1707;
found: 340.1726. HPLC conditions: OJ-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 90:10, 15min; \( t_R = 7.05 \) min (minor), 7.89 min (major).

3.8 HPLC spectrum of compounds (\( R \))-3ga, (\( S \))-3ga, (\( S \))-1g', and (\( R \))-1g'

\[ \begin{align*}
\text{(rac)-1g} & \quad + \quad \text{2a} \\
\text{(R,R)-L1} & \quad \text{standard conditions} \\
& \quad \text{then NaBH}_3\text{CN, 2 h} \\
\rightarrow & \quad \text{(R)-3ga, 52% yield, 93% ee}
\end{align*} \]
1g’ (12.9 mg, 54% recovered, PE/EA=20:1, 19% ee) was colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.13 (m, 2H), 7.08 – 6.82 (m, 2H), 5.30 – 4.69 (m, 1H), 3.62 (dd, J = 57.8, 12.7 Hz, 2H), 3.24 (q, J = 7.0 Hz, 1H), 1.79 (s, 1H), 1.52 – 0.89 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 162.0 (d, J = 244.7 Hz), 135.5 (d, J = 3.0 Hz), 129.8 (d, J = 8.0 Hz), 115.2 (d, J = 21.2 Hz), 68.2, 56.0, 51.2, 21.9, 21.8, 19.1. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₃H₁₈FNO₂ 240.1394; found: 240.1411. HPLC conditions: AD-H column, 254 nm, 30 °C, flow rate: 1.3 mL/min, Hex:IPA = 97:3, 15 min; tᵣ = 3.61 min, 4.07 min.
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(R)-1g + O

standard conditions, 10 min
then NaBH₃CN, 2 h

3ga, 87% yield, 95% ee

(R)-1g', trace
4. References


5. Copies of $^1$H and $^{13}$C spectrum of trisubstituted allylic amino acids

$^1$H NMR spectrum of 3ba in CDCl$_3$

$^{13}$C NMR spectrum of 3ba in CDCl$_3$
$^1$H NMR spectrum of 3bb in CDCl$_3$

$^{13}$C NMR spectrum of 3bb in CDCl$_3$
$^1$H NMR spectrum of 3bc in CDCl$_3$

$^{13}$C NMR spectrum of 3bc in CDCl$_3$
$^1$H NMR spectrum of 3bd in CDCl$_3$

$^{13}$C NMR spectrum of 3bd in CDCl$_3$
$^1$H NMR spectrum of 3be in CDCl$_3$

$^{13}$C NMR spectrum of 3be in CDCl$_3$
$^{1}H$ NMR spectrum of 3bf in CDCl$_3$

$^{13}C$ NMR spectrum of 3bf in CDCl$_3$
$^1$H NMR spectrum of 3bg in CDCl$_3$

$^{13}$C NMR spectrum of 3bg in CDCl$_3$
\(^1\)H NMR spectrum of 3bh in CDCl\(_3\)

\(^{13}\)C NMR spectrum of 3bh in CDCl\(_3\)
$^1$H NMR spectrum of 3bi in CDCl$_3$

$^{13}$C NMR spectrum of 3bi in CDCl$_3$
$^1\text{H NMR}$ spectrum of 3bj in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of 3bj in CDCl$_3$
$^1$H NMR spectrum of 3bk in CDCl₃

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$^1$H NMR spectrum of 3bl in CDCl$_3$

$^{13}$C NMR spectrum of 3bl in CDCl$_3$
\(^1\text{H NMR}\) spectrum of 3bm in CDCl\(_3\)

\[^{13}\text{C NMR}\) spectrum of 3bm in CDCl\(_3\)
$^1$H NMR spectrum of 3bn in CDCl$_3$

$^{13}$C NMR spectrum of 3bn in CDCl$_3$
$^1$H NMR spectrum of 3bo in CDCl$_3$

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$^1$H NMR spectrum of 3bs in CDCl$_3$

$^{13}$C NMR spectrum of 3bs in CDCl$_3$
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$^{13}C$ NMR spectrum of 3bt in CDCl$_3$
$^1\text{H NMR}$ spectrum of $3\text{bu}$ in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of $3\text{bu}$ in CDCl$_3$
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13C NMR spectrum of 3bz in CDCl$_3$
\(^1\)H NMR spectrum of 3baa in CDCl\(_3\)

\(^{13}\)C NMR spectrum of 3baa in CDCl\(_3\)
$^1$H NMR spectrum of 3bab in CDCl$_3$

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