Supporting Information

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1. General information.

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents before use were dried and degassed by standard methods and stored under argon. All reactions were monitored by TLC with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. 1H and 13C NMR (300 and 75 MHz, respectively) spectra were recorded in CDCl₃. ¹H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃, δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ¹³C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl₃, δ = 77.0 ppm). ESI HRMS spectra were recorded on BioTOF Q. HPLC analysis was performed on SHIMADZU (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AD column and Chiralcel OJ column were purchased from Daicel Chemical Industries (Hong Kong, China). Chiralcel OD column (Sino-chiral® OD) was purchased from Funsea Technology Inc. (Beijing, China). Optical rotations were measured on a Perkin-Elmer 341 Polarimeter at λ = 589 nm (c g/100ml). All enantiomer ratios have been controlled by co injections of the pure sample with the racemic substrates.

2. General procedure for preparation of α-substituted-β-enamino esters 1a-1p[1]

To a solution of ester 8 (20 mmol) in anhydrous ethyl ether was added ethyl formate (3.2 mL, 40 mmol) at 0°C. Then sodium (0.92 g, 40 mmol) was added slowly. The reaction mixture was stirred at room temperature. After completion of the reaction, the mixture was poured into ice water and extracted with Et₂O (3×30 mL). The aqueous phase was acidified with a solution of 2N HCl to PH 3. Followed an extraction with Et₂O (3×30 mL) and the organic layers were combined, dried over Na₂SO₄, filtered and concentrated in vacuum, leading to aldehyde 9 as a yellow oil.
which was used in the next step without further purification. Then 9 was dissolved in anhydrous dichloromethane and \( p \)-methoxyaniline (2.95 g, 24 mmol) was added, the reaction mixture was stirred overnight at room temperature, the solvent was evaporated and the residue was subjected to chromatography to afford \( \beta \)-enaminoo ester 1.

**(Z)-ethyl 3-(4-methoxyphenylamino)-2-phenylacrylate (1a):** 1H NMR (300 MHz, CDCl\(_3\)): \( \delta = 10.31 \) (d, \( J = 12.8 \) Hz, 1H), 7.23-7.38 (m, 6H), 6.98 (d, \( J = 8.9 \) Hz, 2H), 6.88 (d, \( J = 8.9 \) Hz, 2H), 4.28 (q, \( J = 7.0 \) Hz, 2H), 3.80 (s, 3H), 1.32 (t, \( J = 7.1 \) Hz, 3H) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 169.3, 155.5, 144.8, 138.1, 134.3, 129.4, 127.9, 125.8, 117.1, 114.9, 101.7, 59.7, 55.5, 14.4 \) ppm. ESI HRMS exact mass calcd. For \((C_{18}H_{19}NO_3 + H)^+\) requires m/z 298.1443, found m/z 298.1444.

**(Z)-ethyl 2-(4-methoxyphenyl)-3-(4-methoxyphenylamino)acrylate (1b):** 1H NMR (300 MHz, CDCl\(_3\)): \( \delta = 10.23 \) (d, \( J = 12.7 \) Hz, 1H), 7.27-7.32 (m, 3H), 6.85-6.98 (m, 6H), 4.27 (q, \( J =7.0 \) Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 1.31 (t, \( J = 7.0 \) Hz, 3H) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 169.4, 157.9, 155.4, 144.2, 134.5, 130.5, 117.0, 114.9, 113.3, 101.2, 59.6, 55.5, 55.2, 14.4 \) ppm. ESI HRMS exact mass calcd. For \((C_{19}H_{21}NO_4 + H)^+\) requires m/z 328.1549, found m/z 328.1551.

**(Z)-ethyl 2-(2-methoxyphenyl)-3-(4-methoxyphenylamino)acrylate (1c):**

1H NMR (300 MHz, CDCl\(_3\)): \( \delta = 10.17 \) (d, \( J = 12.7 \) Hz, 1H), 7.20-7.32 (m, 3H), 6.84-6.94 (m, 6H), 4.22 (q, \( J =7.1 \) Hz, 2H), 3.82 (s, 3H), 3.78 (s, 1H), 1.25 (t, \( J = 7.1 \)Hz, 3H) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 169.6, 157.8, 155.2, 144.2, 134.5, 131.5, 128.0, 127.1, 120.3, 116.8, 114.8, 110.4, 97.7, 55.4, 55.3, 14.4 \) ppm. ESI HRMS exact mass calcd. For \((C_{19}H_{21}NO_4 + H)^+\) requires m/z 328.1549, found m/z 328.1550.

**(Z)-ethyl 2-(3-methoxyphenyl)-3-(4-methoxyphenylamino)acrylate (1d):** 1H NMR (300 MHz, CDCl\(_3\)): \( \delta = 10.35 \) (d, \( J = 12.8 \) Hz, 1H), 7.21-7.35 (m, 6H), 6.86-6.94 (m, 6H), 4.23 (d, \( J = 7.0 \) Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.32 (t, \( J = 7.1 \) Hz, 3H) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 169.3, 157.9, 155.4, 144.2, 134.5, 130.5, 117.0, 114.9, 113.3, 101.2, 59.6, 55.5, 55.2, 14.4 \) ppm. ESI HRMS exact mass calcd. For \((C_{19}H_{21}NO_4 + H)^+\) requires m/z 328.1549, found m/z 328.1550.
Hz, 1H), 7.40 (d, J = 12.8, 1H), 7.27 (t, J = 8.14Hz, 1H), 6.96-6.99 (m, 4H), 6.80-6.87 (m, 3H), 4.30 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 1.34 (t, J = 7.1Hz, 3H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 169.1, 159.0, 155.5, 144.7, 139.4, 131.1, 128.6, 121.7, 117.0, 115.1, 114.7, 111.0, 59.6, 55.3, 54.9, 14.3\) ppm. ESI HRMS exact mass calcd. For \((C_{19}H_{21}NO_4 + H)^+\) requires m/z 328.1549, found m/z 328.1551.

\((Z)\)-ethyl 2-(3,4-dimethoxyphenyl)-3-(4-methoxyphenylamino) acrylate (1e): \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.22 (d, J = 12.7\) Hz, 1H), 7.31 (d, J = 12.8 Hz, 1H), 6.93- 6.96 (m, 3H), 6.81-6.87 (m, 4H ), 4.25 (q, J = 7.1 Hz, 2H), 3.88 (s, 6H), 3.76 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 169.3, 155.5, 148.1, 147.4, 144.3, 134.4, 130.9, 121.3, 117.0, 114.9, 113.5, 110.8, 101.3, 59.6, 55.8, 55.7, 55.5, 14.4\) ppm. ESI HRMS exact mass calcd. For \((C_{20}H_{23}NO_5 + H)^+\) requires m/z 358.1654, found m/z 358.1662.

\((Z)\)-ethyl 2-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenylamino) acrylate (1f): \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.22 (d, J = 12.8\) Hz, 1H), 7.29 (d, J = 12.8 Hz, 1H), 6.95 (d, J = 8.9 Hz, 2H), 6.80-6.86 (m, 3H), 6.74-6.77 (m, 2H), 5.95 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.31 (t, J = 7.1Hz, 3H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 169.3, 155.4, 147.0, 145.8, 144.4, 134.3, 132.0, 122.3, 117.0, 114.8, 110.4, 107.7, 101.2, 100.8, 59.7, 55.4, 14.4\) ppm. ESI HRMS exact mass calcd. For \((C_{19}H_{19}NO_5 + H)^+\) requires m/z 342.1341, found m/z 342.1340.

\((Z)\)-ethyl 2-(4-fluorophenyl)-3-(4-methoxyphenylamino) acrylate (1g): \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.24 (d, J = 12.5\) Hz, 1H), 7.26-7.30 (m, 3H), 6.94-7.04 (m, 4H), 6.85-6.88 (m, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 169.2, 163.0, 159.7, 155.7, 144.7, 134.3, 134.0 (J = 3.2 Hz), 131.0 (J = 7.7 Hz), 117.2, 114.9, 114.7 (J = 21.1 Hz), 100.7, 59.8, 55.5, 14.4\) ppm. ESI HRMS exact mass calcd. For \((C_{18}H_{18}FNO_3 + H)^+\) requires m/z 316.1349, found m/z 316.1352.
(Z)-ethyl 3-(4-methoxyphenylamino)-2-(2,4,5-trifluorophenyl)acrylate (1h): $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 10.29$ (d, $J = 12.8$ Hz, 1H), 7.26 (d, $J = 12.9$ Hz, 1H), 7.06-7.11 (m, 1H), 6.85-6.97 (m, 5H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 168.5$, 156.0, 145.8, 133.9, 119.7 (d, $J = 4.1$ Hz), 119.5 (d, $J = 4.4$ Hz), 117.5, 114.9, 105.5, 105.1 (d, $J = 8.6$ Hz), 104.8, 59.8, 55.4, 14.2 ppm. ESI HRMS exact mass calcd. For (C$_{18}$H$_{16}$F$_3$NO$_3$ + H)$^+$ requires m/z 352.1161, found m/z 352.1163.

(Z)-ethyl 2-(4-chlorophenyl)-3-(4-methoxyphenylamino)acrylate (1i): $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 10.31$ (d, $J = 12.8$ Hz, 1H), 7.25-7.33 (m, 5H), 6.96 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 168.9$, 155.7, 144.7, 136.6, 134.1, 131.5, 130.6, 127.9, 117.2, 114.9, 100.5, 59.8, 55.5, 14.3 ppm. ESI HRMS exact mass calcd. For (C$_{18}$H$_{18}$ClNO$_3$ + H)$^+$ requires m/z 332.1053, found m/z 332.1053.

(Z)-ethyl 2-(2-chlorophenyl)-3-(4-methoxyphenylamino)acrylate (1j): $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 10.22$ (d, $J = 12.7$ Hz, 1H), 7.40-7.43 (m, 1H), 7.20-7.28 (m, 4H), 6.95 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 168.9$, 155.6, 144.9, 136.7, 135.7, 134.2, 132.5, 129.3, 128.0, 126.5, 117.3, 117.2, 114.9, 99.3, 59.7, 55.5, 14.3 ppm. ESI HRMS exact mass calcd. For (C$_{18}$H$_{18}$ClNO$_3$ + H)$^+$ requires m/z 332.1053, found m/z 332.1052.

(Z)-ethyl 2-(3-chlorophenyl)-3-(4-methoxyphenylamino)acrylate (1k): $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 10.34$ (d, $J = 12.8$ Hz, 1H), 7.19-7.35 (m, 5H), 6.97 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.79 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 2H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 168.8$, 155.7, 145.1, 139.9, 134.0, 133.5, 129.2, 129.0, 127.5, 125.7, 117.3, 114.9, 100.4, 59.8, 55.5, 14.3 ppm. ESI HRMS exact mass calcd. For (C$_{18}$H$_{18}$ClNO$_3$ + H)$^+$ requires m/z 332.1053, found m/z
(Z)-ethyl 2-(4-bromophenyl)-3-(4-methoxyphenylamino)acrylate (1l): 1H NMR (300 MHz, CDCl₃): δ = 10.30 (d, J = 12.8 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 12.8 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl₃): δ = 168.9, 155.8, 144.8, 137.1, 134.2, 131.0, 119.6, 117.3, 115.0, 59.8, 55.5, 14.4 ppm. ESI HRMS exact mass calcd. For (C₁₈H₁₈BrNO₃ + H)⁺ requires m/z 376.0548, found m/z 376.0550.

(Z)-ethyl 2-(4-phenylphenyl)-3-(4-methoxyphenylamino)acrylate (1m): 1H NMR (300 MHz, CDCl₃): δ = 10.39 (d, J = 12.8 Hz, 1H), 7.60 (d, J = 12.8 Hz, 1H), 7.18-7.20 (m, 16H), 7.00-7.02 (m, 2H), 6.98 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl₃): δ = 169.3, 155.6, 144.7, 140.9, 138.5, 137.2, 134.3, 129.6, 128.7, 127.0, 126.9, 126.6, 117.2, 114.9, 101.2, 59.8, 55.5, 14.4 ppm. ESI HRMS exact mass calcd. For (C₂₄H₂₃NO₃ + H)⁺ requires m/z 374.1756, found m/z 374.1760.

(Z)-ethyl 3-(4-methoxyphenylamino)-2-(naphthalen-2-yl)acrylate (1n): 1H NMR (300 MHz, CDCl₃): δ = 10.41 (d, J = 12.8 Hz, 1H), 7.81-7.87 (m, 3H), 7.76 (s, 1H), 7.60 (dd, J = 8.5 Hz, 1H), 7.02 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.83 (s, 6H), 3.76 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl₃): δ = 169.3, 155.6, 145.0, 135.9, 134.3, 133.5, 131.8, 128.8, 127.6, 127.4, 126.9, 126.8, 125.8, 125.3, 117.2, 114.9, 101.7, 59.7, 55.5, 14.4 ppm. ESI HRMS exact mass calcd. For (C₂₂H₂₁NO₃ + H)⁺ requires m/z 348.1600, found m/z 348.1602.

(E)-ethyl 3-(4-methoxyphenylamino)-2-(thiophen-2-yl)acrylate (1o): 1H NMR (300 MHz, CDCl₃): δ = 10.41 (d, J = 12.8 Hz, 1H), 7.81-7.87 (m, 3H), 7.81-7.87 (m, 3H),
7.76 (s, 1H), 7.60 (dd, \( J = 8.5 \text{ Hz}, 1.6 \text{ Hz} \), 1H), 7.02 (d, \( J = 8.9 \text{ Hz} \), 2H), 6.90 (m, d, \( J = 8.9 \text{ Hz} \), 2H), 4.33 (q, \( J = 7.1 \text{ Hz} \), 2H), 3.83 (s, 6H), 3.76 (s, 3H), 1.35 (t, \( J = 7.1 \text{ Hz} \), 3H) ppm. \(^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)): \( \delta = 168.3, 155.6, 144.1, 140.4, 133.7, 126.4, 123.5, 123.1, 117.2, 114.7, 95.1, 59.9, 55.2, 14.2 \) ppm. ESI HRMS exact mass calcd. For \((\text{C}16\text{H}19\text{NO}3\text{S} + \text{H})^+\) requires m/z 306.1164, found m/z 306.1166.

(Z)-ethyl 2-benzyl-3-(4-methoxyphenylamino)acrylate (1p): \(^{1}\text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta = 9.89 \) (d, \( J = 12.4 \text{ Hz} \), 1H), 7.18-7.33 (m, 5H), 7.11 (d, \( J = 12.5 \text{ Hz} \), 1H), 6.84-6.91 (m, 4H), 4.19 (q, \( J = 7.1 \text{ Hz} \), 2H), 3.78 (s, 3H), 3.57 (s, 2H), 1.25 (t, \( J = 7.1 \text{ Hz} \), 3H) ppm. \(^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)): \( \delta = 170.0, 155.1, 143.2, 141.7, 134.8, 128.4, 128.1, 125.7, 116.6, 114.9, 98.0, 59.4, 55.5, 36.0, 14.3 \) ppm. ESI HRMS exact mass calcd. For \((\text{C}19\text{H}21\text{NO}3 + \text{H})^+\) requires m/z 312.1600, found m/z 312.1608.

(Z)-ethyl 2-isopropyl-3-(4-methoxyphenylamino)acrylate (1q): \(^{1}\text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta = 9.86 \) (d, \( J = 12.3 \text{ Hz} \), 1H), 7.08 (d, \( J = 12.4 \text{ Hz} \), 1H), 6.81-6.89 (m, 6H), 4.21 (q, \( J = 7.1 \text{ Hz} \), 2H), 3.76 (s, 3H), 2.73-2.82 (m, 1H), 1.31 (t, \( J = 7.1 \text{ Hz} \), 3H), 1.13 (d, \( J = 6.9 \text{ Hz} \), 6H) ppm. \(^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)): \( \delta = 170.2, 154.9, 140.2, 116.6, 114.8, 104.9, 59.2, 55.5, 27.8, 22.5, 14.4 \) ppm. ESI HRMS exact mass calcd. For \((\text{C}15\text{H}21\text{NO}3 + \text{H})^+\) requires m/z 264.1600, found m/z 264.1611.

(E)-ethyl 2-benzamido-3-(4-methoxyphenylamino)acrylate (1r): \(^{1}\text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta = 8.76 \) (d, \( J = 11.8 \text{ Hz} \), 1H), 8.24 (s, 1H), 7.89 (d, \( J = 7.2 \text{ Hz} \), 2H), 7.66 (d, \( J = 12.1 \text{ Hz} \), 1H), 7.46-7.57 (m, 3H), 6.99 (d, \( J = 8.8 \text{ Hz} \), 2H), 6.87 (d, \( J = 8.8 \text{ Hz} \), 2H), 4.28 (q, \( J = 7.1 \text{ Hz} \), 2H), 3.79 (s, 3H), 1.34 (t, \( J = 7.1 \text{ Hz} \), 3H) ppm. \(^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)): \( \delta = 166.1, 165.4, 155.4, 135.0, 134.0, 131.9, 131.0, 128.8, 127.2, 117.2, 114.8, 102.0, 60.9, 55.6, 14.5 \) ppm. ESI HRMS exact mass calcd. For \((\text{C}18\text{H}21\text{N}2\text{O}4 + \text{H})^+\) requires m/z 341.1501, found m/z 341.1510.

3. Preparation and characterization of the Lewis base catalysts

Catalysts (3-7) were prepared according to the literatures. [2-5]
Synthesis of (3\textit{R}, 5\textit{S})-1-(4-chloropicolinoyl)-5-(hydroxydiphenylmethyl)pyrrolidin-3-yl pivalate (3i):

To a solution of 4-chloropicolinic acid (157 mg, 1 mmol) and triethylamine (0.30 mL, 2 mmol) in dry dichloromethane (25 mL) was added ethyl chloroformate (0.2 mL, 2 mmol) in dry dichloromethane (2 mL) at 0\textdegree C in 15mins. The result mixture was stirred for an addition 1 hour. Then a solution of (3\textit{R},5\textit{S})-5-(hydroxydiphenylmethyl)pyrrolidin-3-ol (269 mg, 1mmol) in dry dichloromethane (10 mL) was added dropwise to the mixture. After stirring at 0\textdegree C for 1h, the ice bath was removed. The mixture was stirred at room temperature overnight. The reaction was quenched with water, extracted with EtOAc (3\times15 mL), and dried over MgSO\textsubscript{4} for 2h. The solvent was evaporated on rotovap. The residue was dissolved in dry dichloromethane (10 mL) and pyridine (5 mL), then pivaloyl chloride (145 mg, 1.2 mmol) in dry dichloromethane (2 mL) was added dropwise at 0\textdegree C. The reaction mixture was stirred at room temperature for 4 hours. The reaction was quenched with 1N HCl solution, extracted with dichloromethane (3\times15 mL), dried and concentrated. The residue was subject to flash chromatography to give 330 mg (67% yield) white powder. \textsuperscript{1}H NMR (300MHz, CDCl\textsubscript{3}): \(\delta = 8.24-8.44 \text{ (m, 1H)}, 7.30-7.63 \text{ (m, 10H)}, 6.96-7.00 \text{ (m, 2H)}, 5.5-5.63 \text{ (m, 1H)}, 4.87-5.25 \text{ (m, 1H)}, 4.01 \text{ (brs, 1H)}, 3.43-3.73 \text{ (m, 1H)}, 2.17-2.60 \text{ (m, 2H)}, 1.11 \text{ (s, 9H) ppm.} \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 178.1, 154.6, 149.3, 147.2, 145.1, 144.6, 127.9, 127.5, 127.1, 125.1, 81.9, 72.8, 69.3, 56.4, 54.4, 38.5, 36.2, 35.4, 29.7, 27.0 \text{ ppm.} [\alpha]_{D}^{20} = +23 \text{ (c = 0.5, CHCl\textsubscript{3})}. \) ESI HRMS exact mass calcd. For (C\textsubscript{28}H\textsubscript{29}ClN\textsubscript{2}O\textsubscript{4} + H)\textsuperscript{+} requires m/z 493.1894, found m/z 493.1901.

4. Asymmetric hydrosilylation of \textit{a}-substituted-\textit{\beta}-enamino esters:

General procedure: A solution of trichlorosilane (41 \mu L, 0.3 mmol, 2.0 equiv.) in 160 \mu L of dichloromethane was added to a stirred solution of the corresponding \textit{a}-substituted-\textit{\beta}-enamino ester (0.20 mmol) and the catalyst (0.020 mmol) in dichloromethane (2.0 mL) at -10 \textdegree C. The
mixture was stirred at the same temperature until the reaction was completed. Then the reaction was quenched with a saturated aqueous solution of NaHCO₃ and was extracted with dichloromethane. The combined organic layer was washed with brine, and dried over anhydrous Na₂SO₄ and the solvents were evaporated. Purification by column chromatography (silica gel, hexane/EtOAc = 10/1) afforded the products. The ee values were determined using established HPLC techniques with chiral stationary phases.

Racemates: All the racemic products were prepared by using DMF (0.1 equiv.) as a catalyst and trichlorosilane as hydrosilylation reagent.

**ethyl 3-(4-methoxyphenylamino)-2-phenylpropanoate (2a):** ¹H NMR (300 MHz, CDCl₃): δ = 7.30-7.39 (m, 5H), 6.80 (d, J = 7.5 Hz, 2H), 6.60 (d, J = 7.5 Hz, 2H), 4.11-4.19 (m, 2H), 3.92 (t, J = 8.0 Hz, 1H), 3.84 (s, 1H), 3.66 (s, 1H), 3.80 (s, 3H), 3.66 (brs, 1H), 3.43 (q, J = 6.1 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 172.8, 152.3, 141.3, 136.8, 128.8, 128.0, 127.6, 114.9, 114.5, 60.9, 55.7, 50.8, 47.9, 14.0 ppm. ESI HRMS exact mass calcd. For (C₁₈H₂₁NO₃ + H)+ requires m/z 300.1600, found m/z 300.1605. [α]D²⁰ = +92 (c = 0.50, CHCl₃). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, tᵣ = 8.2, 9.5.

**ethyl 2-(4-methoxyphenyl)-3-(4-methoxyphenylamino)propanoate (2b):** ¹H NMR (300 MHz, CDCl₃): δ = 7.26 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 9.0 Hz, 2H), 4.10-4.19 (m, 2H), 3.73-3.89 (m, 8H), 3.62 (brs, 1H), 3.39 (q, J = 6.3 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 173.1, 159.0, 152.3, 141.5, 129.0, 128.8, 114.9, 114.6, 114.2, 60.8, 55.7, 55.2, 50.0, 47.9, 14.0 ppm. ESI HRMS exact mass calcd. For (C₁₉H₂₃NO₄ + H)+ requires m/z 330.1705, found m/z 330.1693. [α]D²⁰ = +84 (c = 0.50, CHCl₃). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, tᵣ = 13.6, 19.6.

**ethyl 2-(4-methoxyphenyl)-3-(4-methoxyphenylamino)propanoate (2c):** ¹H NMR (300 MHz, CDCl₃): δ = 7.26-7.30 (m, 1H), 7.18 (d, J = 7.4 Hz, 1H),
ethyl 2-(3-methoxyphenyl)-3-(4-methoxyphenylamino)propanoate (2d): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.25-7.31 (m, 1H), 6.78-6.90 (m, 5H), 6.59 (d, $J$ = 8.9 Hz, 2H), 4.10-4.18 (m, 2H), 3.86-3.91 (m, 1H), 3.76-3.81 (m, 7H), 3.41 (q, $J$ = 6.0 Hz, 1H), 1.21 (t, $J$ = 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.7, 159.8, 152.3, 149.1, 148.4, 141.4, 129.8, 129.8, 120.3, 114.8, 114.6, 113.7, 112.9, 61.0, 55.7, 55.1, 47.8, 14.0 ppm. ESI HRMS exact mass calcd. For (C$_{19}$H$_{23}$NO$_4$ + H)$^+$ requires m/z 330.1705, found m/z 330.1693. $[\alpha]_D^{20}$ = +158 (c = 0.50, CHCl$_3$). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 10.5, 12.5.

ethyl 2-(3,4-dimethoxyphenyl)-3-(4-methoxyphenylamino)propanoate (2d): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 6.72-6.83 (m, 5H), 6.56-6.60 (m, 2H), 5.95 (s, 2H), 6.58 (d, $J$ = 9.0 Hz, 2H), 4.10-4.17 (m, 2H), 3.70-3.84 (m, 5H), 3.75-3.81 (m, 4H), 3.61 (brs, 1H), 3.37 (q, $J$ = 6.1 Hz, 1H), 1.23 (t, $J$ = 9.7 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.8, 152.3, 147.9, 141.3, 130.5, 121.5, 114.9, 111.9, 55.7, 55.4, 46.4, 44.8, 14.0 ppm. ESI HRMS exact mass calcd. For (C$_{20}$H$_{25}$NO$_5$ + H)$^+$ requires m/z 360.1811, found m/z 330.1804. $[\alpha]_D^{20}$ = +112 (c = 0.50, CHCl$_3$). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 16.7, 17.9.

ethyl 2-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenylamino)propanoate (2f): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 6.72-6.83 (m, 5H), 6.56-6.60 (m, 2H), 5.95 (s, 2H), 6.58 (d, $J$ = 9.0 Hz, 2H), 4.10-4.17 (m, 2H), 3.70-3.84 (m, 5H), 3.75-3.81 (m, 4H), 3.61 (brs, 1H), 3.37 (q, $J$ = 6.1 Hz, 1H), 1.23 (t, $J$ = 9.7 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.8, 152.3, 147.9, 141.3, 130.5, 121.5, 114.9,
ethyl 2-(4-fluorophenyl)-3-(4-methoxyphenylamino)propanoate (2g):

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta = 7.26-7.30 (m, 2H), 7.04 (t, J = 8.6 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 4.11-4.20 (m, 2H), 3.90 (t, J = 7.8 Hz, 1H), 3.75-3.81 (m, 4H), 3.60 (brs, 1H), 3.39 (q, J = 6.3 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm. \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta = 172.7, 163.8, 160.5, 152.4, 141.2, 132.6 (J = 3.2 Hz), 129.6 (J = 3.2 Hz), 115.7 (J = 21.3), 114.7 (J = 25.9), 61.0, 55.7, 50.1, 47.9, 14.0 ppm. \]

ESI HRMS exact mass calcd. For \((\text{C}_{18}\text{H}_{20}\text{FNO}_4 + \text{H})^+\) requires m/z 318.1505, found m/z 318.1496. 

\[ [\alpha]_D^{20} = +102 \text{ (c = 0.50, CHCl}_3\text{). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, t_r = 8.0, 9.1.} \]

ethyl 3-(4-methoxyphenylamino)-2-(2,4,5-trifluorophenyl)propanoate (2h):

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta = 7.15-7.21 (m, 1H), 6.92-7.00 (m, 1H), 7.42-7.50 (m, 3H), 6.79 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 4.14-4.21 (m, 3H), 3.69-3.77 (m, 5H), 3.40 (q, J = 5.6 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H) ppm. \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta = 171.7, 157.3, 154.0 (d, J = 12.0Hz), 152.5, 151.0 (t, J = 12.5 Hz), 148.5 (dd, J = 12.5 Hz, 3.6 Hz), 147.7 (t, J = 12.5 Hz), 145.3 (dd, J = 12.6 Hz, 3.7 Hz), 120.6 (d, J = 11.8 Hz), 117.1 (dd, J = 19.8 Hz, 4.3 Hz), 114.7 (d, J = 38.9 Hz), 61.4, 55.7, 46.9, 43.4, 14.0 ppm. \]

ESI HRMS exact mass calcd. For \((\text{C}_{18}\text{H}_{19}\text{F}_3\text{NO}_3 + \text{H})^+\) requires m/z 354.1317, found m/z 330.1317. 

\[ [\alpha]_D^{20} = +78 \text{ (c = 0.50, CHCl}_3\text{). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, t_r = 8.9, 10.4.} \]

ethyl 2-(4-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (2i):

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta = 7.33 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 6.58 (d, J = 9.0 Hz, 2H), 4.11-4.18 (m, 2H), 3.89 (t, J = 9.0, 1H), 3.75-3.81 (m, 4H), 3.63 (brs, 1H), 3.40 (q, J = 6.3 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm. \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{): } \delta = 172.5, 152.4, 148.5 (dd, J = 12.5 Hz, 3.6 Hz), 147.7 (t, J = 12.5 Hz), 145.3 (dd, J = 12.6 Hz, 3.7 Hz), 120.6 (d, J = 11.8 Hz), 117.1 (dd, J = 19.8 Hz, 4.3 Hz), 114.7 (d, J = 38.9 Hz), 61.4, 55.7, 46.9, 43.4, 14.0 ppm. \]

ESI HRMS exact mass calcd. For \((\text{C}_{18}\text{H}_{18}\text{ClNO}_3 + \text{H})^+\) requires m/z 330.1317, found m/z 316.1317. 

\[ [\alpha]_D^{20} = +78 \text{ (c = 0.50, CHCl}_3\text{). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, t_r = 8.9, 10.4.} \]
ethyl 2-(2-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (2j): 

1H NMR (300 MHz, CDCl3): δ = 7.40-7.44 (m, 1H), 7.23-7.32 (m, 3H), 6.79 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.45 (q, J = 5.4 Hz, 1H), 4.17 (q, J = 6.9 Hz, 2H), 3.75 (s, 3H), 3.69 (s, 1H), 3.41-3.47 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 172.6, 152.3, 141.2, 134.9, 133.9, 129.9, 128.9, 128.7, 127.2, 114.9, 114.5, 61.2, 55.7, 47.5, 46.8, 14.0 ppm. ESI HRMS exact mass calcd. For (C18H20ClNO3 + H)+ requires m/z 334.1210, found m/z 334.1197. [α]D20 = +58 (c = 0.50, CHCl3). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, tR = 7.9, 9.0.

ethyl 2-(2-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (2k):

1H NMR (300 MHz, CDCl3): δ = 7.26-7.30 (m, 3H), 7.16-7.19 (m, 1H), 6.79 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 4.11-4.19 (m, 2H), 3.86-3.90 (m, 1H), 3.74-3.81 (m, 4H), 3.40 (q, J = 6.0 Hz, 1H), 2.64 (brs, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 172.3, 152.4, 141.1, 138.8, 134.6, 130.1, 128.2, 127.9, 126.3, 114.9, 114.6, 61.2, 55.7, 50.5, 47.8, 14.0 ppm. ESI HRMS exact mass calcd. For (C18H20ClNO3 + H)+ requires m/z 334.1210, found m/z 334.1210. [α]D20 = +121 (c = 0.50, CHCl3). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, tR = 8.5, 10.8.

ethyl 2-(4-bromophenyl)-3-(4-methoxyphenylamino)propanoate (2l):

1H NMR (300 MHz, CDCl3): δ = 7.48 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 6.57 (d, J = 8.9 Hz, 2H), 4.10-4.17 (m, 2H), 3.88 (t, J = 8.0, 1H), 3.74-3.81 (m, 4H), 3.64 (brs, 1H), 3.39 (q, J = 6.3 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 172.4, 152.4, 141.1, 135.8, 131.9, 129.8, 121.6, 114.9, 114.6, 61.1, 55.7, 50.3, 47.7, 14.0 ppm. ESI HRMS exact mass calcd. For (C18H20BrNO3 + H)+ requires m/z 378.0705, found m/z 378.0673. [α]D20 = +122 (c = 0.50, CHCl3). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, tR = 9.0, 9.7.
ethyl 2-(4-phenylphenyl)-3-(4-methoxyphenylamino)propanoate (2k): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.61 (d, $J$ = 8.1 Hz, 2H), 7.35-7.49 (m, 5H), 6.83 (d, $J$ = 8.9 Hz, 2H), 6.64 (d, $J$ = 8.9 Hz, 2H), 4.15-4.23 (m, 2H), 3.97 (t, $J$ = 7.5 Hz, 1H), 3.85-3.90 (m, 1H), 3.78 (s, 1H), 3.71 (bs, 1H), 3.49 (q, $J$ = 6.2 Hz, 1H), 1.25 (t, 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.8, 152.4, 141.4, 140.5, 135.9, 128.7, 128.4, 127.5, 127.0, 114.9, 114.6, 61.0, 55.7, 50.5, 47.9, 14.1 ppm. ESI HRMS exact mass calcd. For (C$_{24}$H$_{25}$NO$_3$ + H)$^+$ requires m/z 376.1913, found m/z 376.1908. $\left[\alpha\right]_{D}^{20} = +128$ (c = 0.50, CHCl$_3$). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 19.8, 27.4.

ethyl 3-(4-methoxyphenylamino)-2-(naphthalen-2-yl)propanoate (2n): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.76-7.86 (m, 3H), 7.51 (s, 1H), 7.42-7.50 (m, 3H), 6.80 (d, $J$ = 8.9 Hz, 2H), 6.61 (d, $J$ = 8.9 Hz, 2H), 4.08-4.20 (m, 3H), 3.87-3.90 (m, 1H), 3.77 (s, 3H), 3.63 (bs, 1H), 3.52 (q, $J$ = 6.6 Hz, 1H), 1.20 (t, $J$ = 7.1 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.8, 152.3, 141.3, 139.9, 134.2, 133.4, 132.7, 128.9, 127.8, 127.6, 127.1, 126.3, 126.1, 125.7, 117.0, 114.9, 114.6, 61.1, 55.7, 50.9, 47.8, 14.1 ppm. ESI HRMS exact mass calcd. For (C$_{22}$H$_{23}$NO$_3$ + H)$^+$ requires m/z 350.1756, found m/z 350.1758. $\left[\alpha\right]_{D}^{20} = +143$ (c = 0.50, CHCl$_3$). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 13.0, 18.0.

ethyl 3-(4-methoxyphenylamino)-2-(thiophen-2-yl)propanoate (2o): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.24-7.27 (m, 1H), 6.99 (d, $J$ = 7.0 Hz), 6.81 (d, $J$ = 10.0 Hz), 6.60 (d, $J$ = 9.0 Hz), 4.17-4.24 (m, 3H), 3.77-3.81 (m, 2H), 3.75 (s, 1H), 3.49 (q, $J$ = 6.5 Hz, 1H), 1.23 (t, $J$ = 4.8 Hz) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 172.0, 152.4, 141.0, 138.6, 126.8, 126.0, 125.1, 114.9, 114.6, 61.3, 55.7, 48.7, 46.2, 14.0 ppm. ESI HRMS exact mass calcd. For (C$_{16}$H$_{19}$NO$_3$S + H)$^+$ requires m/z 306.1164, found m/z 306.1161. $\left[\alpha\right]_{D}^{20} = +76$ (c = 0.50, CHCl$_3$). AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 9.0, 10.8.
ethyl 2-((4-methoxyphenylamino)methyl)-3-phenylpropanoate (2p): 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.19-7.33 (m, 5H), 6.76 (d, $J$ = 8.7 Hz, 2H), 6.50 (d, $J$ = 8.7 Hz, 2H), 4.12 (q, $J$ = 7.1 Hz, 2H), 3.75 (s, 1H), 3.65 (brs, 1H), 3.34-3.38 (m, 1H), 3.21-3.26 (m, 1H), 2.96-3.07 (m, 2H), 2.93 (q, $J$ = 6.6 Hz, 1H), 1.19 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 174.4, 152.2, 141.8, 138.7, 128.9, 128.5, 126.5, 114.8, 114.3, 60.6, 55.7, 46.9, 45.9, 36.1, 14.1 ppm. ESI HRMS exact mass calcd. For (C$_{19}$H$_{23}$NO$_3$ + H)$^+$ requires m/z 314.1756, found m/z 314.1761. [$\alpha$]$_D^{20}$ = -93 (c = 0.50, CHCl$_3$).

AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 10.8, 12.4.

ethyl 2-benzamido-3-(4-methoxyphenylamino)propanoate (2r): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.77 (d, $J$ = 7.3 Hz, 2H), 7.40-7.54 (m, 3H), 7.04 (d, $J$ = 6.9 Hz, 1H), 6.76 (d, $J$ = 8.7 Hz, 2H), 6.64 (d, $J$ = 8.7 Hz, 2H), 4.95-4.99 (m, 1H), 4.20-4.28 m, 1H), 3.73 (s, 1H), 3.63-3.69 (m, 1H), 1.30 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 171.3, 167.3, 152.6, 141.6, 131.9, 128.6, 127.1, 114.8, 114.7, 76.6, 62.0, 55.7, 53.1, 46.9, 14.2 ppm. ESI HRMS exact mass calcd. For (C$_{19}$H$_{22}$N$_2$O$_4$ + H)$^+$ requires m/z 343.1658, found m/z 343.1661. [$\alpha$]$_D^{20}$ = -59 (c = 0.50, CHCl$_3$).

AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, $t_r$ = 13.8, 19.5.

References:


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