Supporting Information

for

Organocatalytic asymmetric nitroso aldol reaction of α-substituted malonamates

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Detailed experimental procedures, complete characterization data for all compounds, single-crystal X-ray data of 4a, copies of NMR spectra, and HPLC chromatograms
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General experimental information:

Unless otherwise specified, all reactions were carried out under air atmosphere in oven-dried round-bottomed flasks. The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Flash chromatography was performed on 100–200 mesh silica gel using the gradient system ethyl acetate/hexane. NMR data were recorded with a Bruker AV 400 MHz spectrometer in CDCl₃ using as internal standards the residual CHCl₃ signal for ¹H NMR (δ = 7.26 ppm) and the deuterated solvent signal for ¹³C NMR (δ = 77.16 ppm). Coupling constants are given in hertz (Hz) and the standard abbreviations are used to describe the signal multiplicities. Melting points were measured with a Büchi B-540 melting point apparatus and are uncorrected. High resolution mass spectra were obtained using a Q-TOF mass spectrometer. The ee values were determined on a Waters Standard HPLC System using chiral column with hexane and ethanol as eluent, wavelength = 254 nm. All commercially available reagents were used as received. α-Methylmalonamates 1a–u were synthesized following a literature procedure.¹
Characterization data for compounds 4a–y and 5

(S)-Methyl 3-((4-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4a)

Following the general procedure, treatment of methyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1a, 57 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4a as white solid (71 mg, 90%). RF(EtOAc/hexane 3:7) = 0.20. Mp 115-117 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.5 (C), 167.0 (C), 147.1 (C), 136.5 (C), 132.1 (CH), 132.1(CH), 128.9 (CH), 128.9 (CH), 126.1 (CH), 122.2 (CH), 122.2 (CH), 121.6 (CH), 121.6 (CH), 117.4 (C), 76.8 (C), 53.5 (CH3), 17.9 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 9.04 (s, 1H), 7.47-7.44 (m, 5H), 7.31-7.26 (m, 2H), 7.20-7.14 (m, 3H), 3.81 (s, 3H), 1.59 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τ minor = 13.0 min, τ major = 13.9 min, 90% ee). HRMS for C17H17BrN2O4+: calcd. [M+Na]+: 415.0264, found: 415.0278, [M+2+Na]+: 417.0257.

(S)-Methyl 2-(hydroxy(phenyl)amino)-2-methyl-3-(p-tolylamino)propanoate (4b)

Following the general procedure, treatment of methyl 2-methyl-3-oxo-3-(p-tolylamino)propanoate (1b, 44 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4b as white solid (62 mg, 95%). RF(EtOAc/hexane 3:7) = 0.28. Mp 149-151 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.7 (C), 166.5 (C), 147.3 (C), 134.9 (C), 134.4 (C), 129.6 (CH), 129.6 (CH), 128.8 (CH), 128.8 (CH), 125.7 (CH), 121.9 (CH), 121.9 (CH), 120.0 (CH), 120.0 (CH), 77.2 (C), 53.3 (CH3), 20.9 (CH3), 17.6 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 9.04 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.45 (s, 1H), 7.34-7.26 (m, 4H), 7.17 (d, J = 8.0, 3H), 3.85 (s, 3H), 2.36 (s, 3H), 1.65 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τ minor = 28.9 min, τ major = 32.8 min, 84% ee). HRMS for C18H20N2NaO4+: calcd. [M+Na]+: 351.1315, found: 351.1323.
(5)-Methyl 3-((4-chlorophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4c)

Following the general procedure, treatment of methyl 3-((4-chlorophenyl)amino)-2-methyl-3-oxopropanoate (1c, 48 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4c as white solid (66 mg, 95%). Rf (EtOAc/hexane 3:7) = 0.5. Mp 134-136 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.6 (C), 167.0 (C), 147.1 (C), 136.0 (C), 129.8 (C), 129.2 (CH), 129.2 (CH), 129.0 (CH), 129.0 (CH), 126.1 (CH), 122.2 (CH), 122.2 (CH), 121.3 (CH), 121.3 (CH), 76.8 (C), 53.5 (CH3), 18.1 (CH3).1H NMR (400 MHz, δ ppm/CDCl3): 9.03 (s, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.39 (s, 1H), 7.31-7.28 (m, 4H), 7.21-7.15 (m, 3H), 3.82 (s, 3H), 1.60 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, tminor = 6.7 min, tmajor = 7.2 min, 83% ee). HRMS for C17H17ClN2O4+: calcd. [M+H]+: 349.0950, found: 349.0940, [M+2+H]+: 351.0910.

(5)-Methyl 3-((4-fluorophenyl)amino)-2-(hydroxy(phenyl)aminomethyl)-3-oxopropanoate (4d)

Following the general procedure, treatment of methyl 3-((4-fluorophenyl)amino)-2-methyl-3-oxopropanoate (1d, 45 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4d as white solid (61 mg, 92%). Rf (EtOAc/hexane 3:7) = 0.45. Mp 116-118°C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.7 (C), 167.0 (C), 159.7 (d, J = 242.7 Hz, C), 147.1 (C), 133.5 (C), 128.9 (CH), 128.9 (CH), 126.0 (CH), 122.1 (CH), 122.1 (CH), 121.9 (d, J = 7.8 Hz, CH), 121.9 (d, J = 7.8 Hz, CH), 115.8 (d, J = 22.4 Hz, CH), 115.5 (d, J = 22.4 Hz, CH), 76.7 (C), 53.4 (CH3), 18.0 (CH3).1H NMR (400 MHz, δ ppm/CDCl3): 8.98 (s, 1H), 7.55-7.51 (m, 2H), 7.33-7.20 (m, 5H), 7.17 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 8.8 Hz, 2H), 3.84 (s, 3H), 1.61 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, tminor = 27.4 min, tmajor = 30.9 min, 79% ee). HRMS for C17H17FN2O4+: calcd. [M+Na]+: 355.1065, found: 355.1063.
(S)-Methyl 3-((4-acetylphenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropionate (4e)

Following the general procedure, treatment of methyl 3-((4-acetylphenyl)amino)-2-methyl-3-oxopropionate (1e, 50 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4e as white solid (53 mg, 75%). Rf (EtOAc/hexane 3:7) = 0.39. Mp 130-132 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 197.4 (C), 171.1 (C), 167.4 (C), 147.1 (C), 141.9 (C), 133.2 (C), 129.9 (CH), 129.9 (CH), 128.9 (CH), 128.9 (CH), 126.2 (CH), 122.4 (CH), 122.4 (CH), 119.3 (CH), 119.3 (CH), 77.1 (C), 53.4 (CH3), 26.5 (CH3), 17.7 (CH3).

1H NMR (400 MHz, δ ppm/CDCl3): 9.27 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.4 Hz, 3H), 7.28-7.18 (m, 4H), 7.13 (t, J = 7.0 Hz, 1H), 3.77 (s, 3H), 2.52 (s, 3H), 1.57 (s, 3H).

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 19.0 min, τmajor = 21.1 min, 75% ee). HRMS for C19H20N2NaO5+: calcd. [M+Na]+: 379.1264, found: 379.1288.

(5)-Methyl 2-(hydroxy(phenyl)amino)-2-methyl-3-((4-nitrophenyl)amino)-3-oxopropionate (4f)

Following the general procedure, treatment of methyl 2-methyl-3-((4-nitrophenyl)amino)-3-oxopropionate (1f, 51 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4f as a yellow solid (68 mg, 95%). Rf (EtOAc/hexane 3:7) = 0.33. Mp 161-163 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 170.8 (C), 167.7 (C), 146.7 (C), 144.0 (C), 143.3 (C), 129.1 (CH), 129.1 (CH), 126.6 (CH), 125.3 (CH), 125.3 (CH), 122.5 (CH), 122.5 (CH), 119.6 (CH), 119.6 (CH), 76.8 (C), 53.6 (CH3), 18.4 (CH3).

1H NMR (400 MHz, δ ppm CDCl3): 9.39 (s, 1H), 8.23 (d, J = 9.2 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.35-7.26 (m, 3H), 7.22 (d, J = 8.4 Hz, 3H), 3.85 (s, 3H), 1.62 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 10.3 min, τmajor = 11.5 min, 85% ee). HRMS for C17H17N3NaO6+: calcd. [M+Na]+: 382.1010, found: 382.1002.
Following the general procedure, treatment of methyl 3-((3-bromophenyl)amino)-2-methyl-3-oxopropanoate (1g, 57 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4g as white solid (74 mg, 95%). Rf (EtOAc/hexane 3:7) = 0.26. Mp 145-147 °C. 

\[ \text{13C NMR (100 MHz, } \delta \text{ ppm/CDCl}_3): 171.5 (C), 167.1 (C), 147.0 (C), 138.7 (C), 130.5 (CH), 129.0 (CH), 129.0 (CH), 127.8 (CH), 126.1 (CH), 123.0 (CH), 122.8 (C), 122.2 (CH), 122.2 (CH), 118.5 (CH), 76.8 (C), 53.5 (CH\_3), 18.0 (CH\_3). \]

\[ \text{1H NMR (400 MHz, } \delta \text{ ppm/CDCl}_3): 9.05 (s, 1H), 7.86 (s, 1H), 7.47 (d, } J = 7.6 \text{ Hz, 1H), 7.33-7.28 (m, 3H), 7.22-7.16 (m, 5H), 3.83 (s, 3H), 1.60 (s, 3H). \]

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 24.8 \text{ min, } \tau_{\text{major}} = 27.6 \text{ min, 63% ee). HRMS for } C_{17}H_{17}BrN_2O_4^+: \text{ calcd. } [M+Na]^+: 415.0264, \text{ found: 415.0252}, [M+2+Na]^+: 417.0229. \]

(5)-Methyl 2-((hydroxy(phenyl)amino)-3-((3-methoxyphenyl)amino)-2-methyl-3-oxopropanoate (4h)

Following the general procedure, treatment of methyl 3-((3-methoxyphenyl)amino)-2-methyl-3-oxopropanoate (1h, 47 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4h as a red solid (52 mg, 75%). Rf (EtOAc/hexane 3:7) = 0.30. Mp 135-137 °C. 

\[ \text{13C NMR (100 MHz, } \delta \text{ ppm/CDCl}_3): 171.7 (C), 166.8 (C), 160.4 (C), 147.1 (C), 138.7 (C), 129.8 (CH), 128.9 (CH), 126.0 (CH), 122.1 (CH), 122.1 (CH), 112.1 (CH), 111.0 (CH), 111.0 (CH), 105.5 (CH), 77.2 (C), 55.5 (CH\_3), 53.5 (CH\_3), 17.9 (CH\_3). \]

\[ \text{1H NMR (400 MHz, } \delta \text{ ppm/CDCl}_3): 9.01 (s, 1H), 7.36-7.16 (m, 8H), 7.03 (d, } J = 7.6 \text{ Hz, 1H), 6.70 (d, } J = 7.6 \text{ Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.61 (s, 3H). \]

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 35.3 \text{ min, } \tau_{\text{major}} = 37.5 \text{ min, 80% ee). HRMS for } C_{18}H_{20}N_2O_5^+: \text{ calcd. } [M+Na]^+: 367.1264, \text{ found: 367.1269.} \]
(S)-Methyl 2-(hydroxy(phenyl)amino)-2-methyl-3-((3-nitrophenyl)amino)-3-oxopropanoate (4i)

Following the general procedure, treatment of methyl 2-methyl-3-((3-nitrophenyl)amino)-3-oxopropanoate (1i, 51 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4i as a yellow solid (68 mg, 95%). \( R_f \) (EtOAc/hexane 3:7) = 0.33. Mp 155-157 °C. \( ^{13} \)C NMR (100 MHz, δ ppm/CDCl\(_3\)): 171.3 (C), 167.7 (C), 148.8 (C), 146.8 (C), 138.6 (C), 130.0 (CH), 129.0 (CH), 129.0 (CH), 126.4 (CH), 125.7 (CH), 122.5 (CH), 122.5 (CH), 119.3 (CH), 114.9 (CH), 76.8 (C), 53.6 (CH\(_3\)), 18.4 (CH\(_3\)). \( ^1 \)H NMR (400 MHz, δ ppm/CDCl\(_3\)): 9.30 (s, 1H), 8.48 (s, 1H), 7.97 (t, \( J = 8.8 \) Hz, 2H), 7.51 (t, \( J = 8.0 \) Hz, 1H), 7.43 (s, 1H), 7.33-7.17 (m, 5H), 3.84 (s, 3H), 1.62 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{minor} = 19.6 \) min, \( \tau_{major} = 20.3 \) min, 41% ee). HRMS for C\(_{17}\)H\(_{17}\)N\(_3\)NaO\(_6\): calcd. [M+Na\(^+\)]: 382.1010, found: 382.1032.

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{minor} = 19.6 \) min, \( \tau_{major} = 20.3 \) min, 41% ee). HRMS for C\(_{17}\)H\(_{17}\)N\(_3\)NaO\(_6\): calcd. [M+Na\(^+\)]: 382.1010, found: 382.1032.

(5)-Methyl 3-((2-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4j)

Following the general procedure, treatment of methyl 3-((2-bromophenyl)amino)-2-methyl-3-oxopropanoate (1j, 57 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4j as white solid (71 mg, 90%). \( R_f \) (EtOAc/hexane 3:7) = 0.34. Mp 125-127 °C. \( ^{13} \)C NMR (100 MHz, δ ppm/CDCl\(_3\)): 171.1 (C), 167.1 (C), 147.1 (C), 135.6 (C), 132.5 (CH), 128.9 (CH), 128.9 (CH), 128.5 (CH), 126.3 (CH), 125.6 (CH), 122.8 (CH), 122.8 (CH), 122.0 (CH), 114.0 (C), 76.8 (C), 53.4 (CH\(_3\)), 18.0 (CH\(_3\)). \( ^1 \)H NMR (400 MHz, δ ppm/CDCl\(_3\)): 9.67 (s, 1H), 8.32 (d, \( J = 8 \) Hz, 1H), 7.57 (d, \( J = 8 \) Hz, 1H), 7.33-7.18 (m, 6H), 7.10 (s, 1H), 7.01 (t, \( J = 7.2 \) Hz, 1H), 3.84 (s, 3H), 1.63 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{minor} = 14.0 \) min, \( \tau_{major} = 15.1 \) min, 54% ee). HRMS for C\(_{17}\)H\(_{17}\)BrN\(_2\)NaO\(_4\): calcd. [M+Na\(^+\)]: 415.0264, found: 415.0242, [M+2+Na\(^+\)]: 417.0226.
(S)-Methyl 3-((2,5-dimethylphenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (1C less) (4k)

Following the general procedure, treatment of methyl 3-((2,5-dimethylphenyl)amino)-2-methyl-3-oxopropanoate (1k, 47 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4k as white solid (65 mg, 95%). Rf (EtOAc/hexane 3:7) = 0.50. Mp 123-125 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.9 (C), 166.7 (C), 147.3 (C), 136.6 (C), 135.2 (C), 130.3 (CH), 128.8 (CH), 128.8 (CH), 125.9 (CH), 125.6 (CH), 122.7 (CH), 121.8 (CH), 76.6 (C), 53.3 (CH3), 21.2 (CH3), 17.9 (CH3), 17.1 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 9.01 (s, 1H), 7.77 (s, 1H), 7.51 (s, 1H), 7.32-7.22 (m, 4H), 7.15 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.82 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H), 1.66 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 95:5 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 26.6 min, τmajor = 27.9 min, 85% ee). HRMS for C19H22N2O4+: calcd. [M+Na]+: 365.1472, found: 365.1445.

(S)-Methyl 3-((3,4-dimethoxyphenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4l)

Following the general procedure, treatment of methyl 3-((3,4-dimethoxyphenyl)amino)-2-methyl-3-oxopropanoate (1l, 50 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 4 h followed by column chromatography afforded the product 4l as white solid (61 mg, 82%). Rf (EtOAc/hexane 3:7) = 0.16. Mp 143-145 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 171.8 (C), 166.6 (C), 149.3 (C), 147.2 (C), 146.2 (C), 131.2 (C), 128.9 (CH), 128.9 (CH), 125.9 (CH), 122.1 (CH), 122.1 (CH), 111.8 (CH), 111.5 (CH), 104.7 (CH), 76.7 (C), 56.3 (CH3), 56.1 (CH3), 53.4 (CH3), 17.9 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 8.93 (s, 1H), 7.40-7.28 (m, 4H), 7.23-7.21 (m, 2H), 7.15 (t, J = 7.2 Hz, 1H), 6.94 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 1.61 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 16.3 min, τmajor = 17.5 min, 91% ee). HRMS for C19H23N2O6+: calcd. [M+H]+: 375.1551, found: 375.1554.
(S)-Methyl 2-(hydroxy(phenyl)amino)-2-methyl-3-((4-methylthiazol-2-yl)amino)-3-oxopropanoate (4m)

Following the general procedure, treatment of methyl 2-methyl-3-((4-methylthiazol-2-yl)amino)-3-oxopropanoate (1m, 45 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4m as white solid (44 mg, 66%). Rf (EtOAc/hexane 3:7) = 0.50. Mp 133-135 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 170.2 (C), 167.2 (C), 157.3 (C), 147.4 (C), 147.4 (C), 128.8 (CH), 128.8 (CH), 126.3 (CH), 122.9 (CH), 122.9 (CH), 108.7 (CH), 76.8 (C), 53.4 (CH3), 17.5 (CH3), 17.0 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 7.26-7.20 (m, 3H), 7.16-7.15 (m, 2H), 7.10 (t, J = 5.8 Hz, 1H), 6.50 (s, 1H), 3.70 (s, 3H), 2.30 (s, 3H), 1.57 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 9.1 min, τmajor = 9.8 min, 62% ee). HRMS for C15H18N3O4S+: calcd. [M+H]+: 336.1013, found: 336.1010.

(5)-Methyl 3-(tert-butylamino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4n)

Following the general procedure, treatment of methyl 3-(tert-butylamino)-2-methyl-3-oxopropanoate (1n, 34 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4n as white solid (50 mg, 85%). Rf (EtOAc/hexane 3:7) = 0.50. Mp 144-146 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 172.4 (C), 167.9 (C), 147.5 (C), 128.6 (CH), 128.6 (CH), 125.0 (CH), 121.3 (CH), 121.3 (CH), 76.1 (C), 53.1 (CH3), 51.5 (C), 28.5 (CH3), 28.5 (CH3), 18.2 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 7.42 (s, 1H), 7.30-7.26 (m, 2H), 7.18-7.16 (m, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.98 (s, 1H), 3.80 (s, 3H), 1.56 (s, 3H), 1.36 (s, 9H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, τminor = 13.6 min, τmajor = 14.5 min, 71% ee). HRMS for C15H23N2O4+: calcd. [M+H]+: 295.1652, found: 295.1653.
(S)-Ethyl 3-((4-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4o)

Following the general procedure, treatment of ethyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1o, 60 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4o as white solid (54 mg, 66%). \( R_f \) (EtOAc/hexane 3:7) = 0.22. *Mp* 122-124 °C. **\( ^{13} \text{C} \) NMR** (100 MHz, δ ppm/CDCl\(_3\)): 171.0 (C), 167.0 (C), 147.2 (C), 136.5 (C), 132.1 (CH), 132.1 (CH), 128.8 (CH), 128.8 (CH), 126.0 (CH), 122.1 (CH), 122.1 (CH), 121.6 (CH), 121.6 (CH), 117.3 (C), 76.8 (C), 62.8 (CH\(_2\)), 17.6 (CH\(_3\)), 14.0 (CH\(_3\)). **\( ^1 \text{H} \) NMR** (400 MHz, δ ppm/CDCl\(_3\)): 9.02 (s, 1H), 7.50-7.44 (m, 4H), 7.32-7.26 (m, 2H), 7.22-7.16 (m, 3H), 4.31 (q, \( J = 7.2 \) Hz, 2H), 1.60 (s, 3H), 1.29 (t, \( J = 7.2 \) Hz, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 95:5 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 10.6 \) min, \( \tau_{\text{major}} = 13.2 \) min, 76% ee). **HRMS** for C\(_{18}\)H\(_{19}\)BrN\(_2\)NaO\(_4\): calcd. [M+Na]\(^+\): 429.0420, found: 429.0476, [M+2+Na]\(^+\): 431.0422.

(5)-Ethyl 3-((3,4-dimethoxyphenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4p)

Following the general procedure, treatment of ethyl 3-((3,4-dimethoxyphenyl)amino)-2-methyl-3-oxopropanoate (1p, 56 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4p as white solid (51 mg, 66%). \( R_f \) (EtOAc/hexane 3:7) = 0.22. *Mp* 132-134 °C. **\( ^{13} \text{C} \) NMR** (100 MHz, δ ppm/CDCl\(_3\)): 171.3 (C), 166.7 (C), 149.2 (C), 147.3 (C), 146.2 (C), 131.2 (C), 128.8 (CH), 128.8 (CH), 125.8 (CH), 122.0 (CH), 122.0 (CH), 111.8 (CH) 111.5 (CH), 104.7 (CH), 76.6 (C), 62.8 (CH\(_2\)), 56.2 (CH\(_3\)), 56.0 (CH\(_3\)), 17.7 (CH\(_3\)), 14.0 (CH\(_3\)). **\( ^1 \text{H} \) NMR** (400 MHz, δ ppm/CDCl\(_3\)): 8.91 (s, 1H), 7.39 (d, \( J = 2.0 \) Hz, 1H), 7.34-7.29 (m, 3H), 7.24-7.22 (m, 2H), 7.16 (t, \( J = 5.8 \) Hz, 1H), 6.96 (dd, \( J = 6.8, 2.0 \) Hz, 1H), 6.83 (d, \( J = 6.8 \) Hz, 1H), 4.32-4.30 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 1.62 (s, 3H), 1.30 (t, \( J = 5.8 \) Hz, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 36.3 \) min, \( \tau_{\text{major}} = 40.1 \) min, 80% ee). **HRMS** for C\(_{20}\)H\(_{24}\)N\(_2\)O\(_6\): calcd. [M+Na]\(^+\): 411.1527, found: 411.1540.
(S)-Ethyl 2-(hydroxy(phenyl)amino)-2-methyl-3-((4-nitrophenyl)amino)-3-oxopropanoate (4q)

Following the general procedure, treatment of ethyl 2-methyl-3-((4-nitrophenyl)amino)-3-oxopropanoate (1q, 53 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4q as white solid (52 mg, 70%). 

\[ R_f (\text{EtOAc/hexane} \ 3:7) = 0.22. \] 

\[ \text{Mp} \ 115-117 °C. \]

\[ ^{13}C \text{ NMR} \ (100 \text{ MHz}, \delta \text{ ppm/CDCl}_3): 170.7 \ (C), \ 167.8 \ (C), \ 146.9 \ (C), \ 143.9 \ (C), \ 129.0 \ (CH), \ 129.0 \ (CH), \ 126.4 \ (CH), \ 125.2 \ (CH), \ 125.2 \ (CH), \ 122.5 \ (CH), \ 119.5 \ (CH) \ 119.5 \ (CH), \ 119.5 \ (CH), \ 76.8 \ (C), \ 63.0 \ (CH), \ 18.0 \ (CH), \ 14.0 \ (CH). \]

\[ ^1H \text{ NMR} \ (400 \text{ MHz}, \delta \text{ ppm/CDCl}_3): 9.42 \ (s, \ 1H), \ 8.20 \ (d, \ J = 8.8 \text{ Hz}, \ 2H), \ 7.74 \ (d, \ J = 8.8 \text{ Hz}, \ 2H), \ 7.60 \ (s, \ 1H), \ 7.32-7.26 \ (m, \ 2H), \ 7.22-7.16 \ (m, \ 3H), \ 4.29 \ (Q, \ J = 7.0 \text{ Hz}, \ 2H), \ 1.60 \ (s, \ 3H), \ 1.28 \ (t, \ J = 7.2 \text{ Hz}, \ 3H). \]

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 12.8 \text{ min}, \tau_{\text{major}} = 24.8 \text{ min}, 67\% \text{ ee})). \ HRMS for C_{18}H_{19}N_{3}NaO_{6}^{+}: \text{calcd.} \ [\text{M+Na}^{+}]: 396.1166, \text{found:} 396.1168.

(S)-tert-Butyl 3-((3,4-dimethoxyphenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4r)

Following the general procedure, treatment of t-butyl 3-((3,4-dimethoxyphenyl)amino)-2-methyl-3-oxopropanoate (1r, 62 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 6 h followed by column chromatography afforded the product 4r as a red solid (42 mg, 50%). 

\[ R_f (\text{EtOAc/hexane} \ 3:7) = 0.28. \] 

\[ \text{Mp} \ 96-98 °C. \]

\[ ^{13}C \text{ NMR} \ (100 \text{ MHz}, \delta \text{ ppm/CDCl}_3): 170.6 \ (C), \ 167.2 \ (C), \ 149.3 \ (C), \ 147.5 \ (C), \ 146.2 \ (C), \ 131.3 \ (C), \ 128.8 \ (CH), \ 128.8 \ (CH), \ 125.7 \ (CH), \ 122.2 \ (CH), \ 122.2 \ (CH), \ 112.0 \ (CH), \ 111.6 \ (CH), \ 104.9 \ (CH), \ 84.5 \ (C), \ 77.2 \ (C), \ 56.3 \ (CH_3), \ 56.1 \ (CH_3), \ 28.0 \ (CH_3), \ 28.0 \ (CH_3), \ 28.0 \ (CH_3), \ 18.3 \ (CH_3). \]

\[ ^1H \text{ NMR} \ (400 \text{ MHz}, \delta \text{ ppm/CDCl}_3): 8.90 \ (s, \ 1H), \ 7.54 \ (s, \ 1H), \ 7.36-7.26 \ (m, \ 5H), \ 7.15 \ (t, \ J = 7.2 \text{ Hz}, \ 1H), \ 6.96 \ (dd, \ J = 8.4, 2.4 \text{ Hz}, \ 1H), \ 6.82 \ (d, \ J = 8.4 \text{ Hz}, \ 1H), \ 3.89 \ (s, \ 3H), \ 3.86 \ (s, \ 3H), \ 1.56 \ (s, \ 3H), \ 1.50 \ (s, \ 9H). \]

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 24.0 \text{ min}, \tau_{\text{major}} = 24.9 \text{ min}, 84\% \text{ ee})). \ HRMS for C_{22}H_{29}N_{2}O_{6} : \text{calcd.} \ [\text{M+H}^{+}]: 417.2020, \text{found:} 417.2018.
(S)-tert-Butyl 2-(hydroxy(phenyl)amino)-2-methyl-3-((4-nitrophenyl)amino)-3-oxopropanoate (4s)

Following the general procedure, treatment of tert-butyl 2-methyl-3-((4-nitrophenyl)amino)-3-oxopropanoate (1s, 59 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4s as a yellow solid (48 mg, 60%). $R_f$ (EtOAc/hexane 3:7) = 0.23. Mp 115-117 °C. $^{13}$C NMR (100 MHz, δ ppm/CDCl$_3$): 170.0 (C), 168.3 (C), 146.9 (C), 143.9 (C), 143.4 (C), 128.9 (CH), 128.9 (CH), 126.4 (CH), 125.2 (CH), 125.2 (CH), 122.6 (CH), 122.6 (CH), 119.5 (CH), 119.5 (CH), 85.0 (C), 77.2 (C), 28.0 (CH$_3$), 28.0 (CH$_3$), 18.8 (CH$_3$). $^1$H NMR (400 MHz, δ ppm/CDCl$_3$): 9.36 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 9.2 Hz, 2H), 7.73 (s, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.25-7.18 (m, 3H), 1.56 (s, 3H), 1.50 (s, 9H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 95:5 V/V, flow rate 1.0 mL/min, 254 nm, $\tau_{\text{minor}}$ = 11.3 min, $\tau_{\text{major}}$ = 12.5 min, 82% ee). HRMS for C$_{20}$H$_{23}$N$_3$NaO$_6$: calcd. [M+Na]$^+$: 424.1479, found: 424.1486.

(5)-4-Methoxybenzyl 3-((4-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4t)

Following the general procedure, treatment of 4-methoxybenzyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1t, 78 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4t as white solid (75 mg, 75%). $R_f$ (EtOAc/hexane 3:7) = 0.22. Mp 145-147 °C. $^{13}$C NMR (100 MHz, δ ppm/CDCl$_3$): 170.6 (C), 166.7 (C), 160.0 (C), 147.1 (C), 136.5 (C), 132.1 (CH), 132.1 (CH), 130.3 (CH), 130.3 (CH), 128.9 (CH), 128.9 (CH), 126.8 (C), 125.9 (CH), 122.0 (CH), 122.0 (CH), 121.6 (CH), 121.6 (CH), 117.3 (C), 114.1 (CH), 114.1 (CH), 77.0 (C), 68.2 (CH$_2$), 55.4 (CH$_3$), 17.4 (CH$_3$). $^1$H NMR (400 MHz, δ ppm/CDCl$_3$): 8.94 (s, 1H), 7.44-7.37 (m, 4H), 7.26-7.22 (m, 5H), 7.14-7.13 (m, 3H), 6.82 (d, J = 8.4 Hz, 2H), 5.23-5.16 (m, 2H), 3.79 (s, 3H), 1.58 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 95:5 V/V, flow rate 1.0 mL/min, 254 nm, $\tau_{\text{minor}}$ = 7.5 min, $\tau_{\text{major}}$ = 8.2 min, 82% ee). HRMS for C$_{24}$H$_{23}$BrN$_2$NaO$_5$: calcd. [M+Na]$^+$: 521.0683, found: 521.0705, [M+2+Na]$^+$: 415.0264.
(S)-4-Methoxybenzyl 2-(hydroxy(phenyl)amino)-3-((4-methoxyphenyl)amino)-2-methyl-3-oxopropanoate (4u)

Following the general procedure, treatment of 4-methoxybenzyl 3-((4-methoxyphenyl)amino)-2-methyl-3-oxopropanoate (1u, 69 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4u as white solid (63 mg, 70%). Rf (EtOAc/hexane 3:7) = 0.22. Mp 155-157 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 170.7 (C), 166.3 (C), 159.9 (C), 156.6 (C), 147.3 (C), 130.5 (C), 130.2 (CH), 130.2 (CH), 128.7 (CH), 128.7 (CH), 126.9 (C), 125.5 (CH), 121.7 (CH), 121.7 (CH), 121.7 (CH), 121.7 (CH), 114.2 (CH), 114.2 (CH) 114.0 (CH), 114.0 (CH), 114.0 (CH), 76.8 (C), 68.0 (CH2), 55.5 (CH3), 55.3 (CH3) 17.2 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 8.85 (s, 1H), 7.47-7.42 (m, 2H), 7.26-7.14 (m, 8H), 6.89-6.85 (m, 4H), 5.27-5.20 (m, 2H), 3.82 (s, 6H), 1.63 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, tmin = 15.6 min, tmaj = 16.9 min, 81% ee). HRMS for C25H28N2O6+: calcd. [M+H]+: 451.1864, found: 451.1855.

(S)-3-Methoxybenzyl 3-((4-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4v)

Following the general procedure, treatment of 3-methoxybenzyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1v, 78 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4v as white solid (77 mg, 77%). Rf (EtOAc/hexane 3:7) = 0.22. Mp 135-137 °C. 13C NMR (100 MHz, δ ppm/CDCl3): 170.6 (C), 166.8 (C), 159.9 (C), 147.1 (C), 136.5 (C), 136.3 (C), 132.1 (CH), 132.1 (CH), 129.9 (CH), 128.9 (CH), 128.9 (CH), 126.0 (CH), 122.1 (CH), 122.1 (CH), 121.7 (CH), 121.7 (CH), 120.4 (CH), 117.4 (C), 114.3 (CH), 113.6 (CH), 77.0 (C), 68.1 (CH2), 55.3 (CH3), 17.5 (CH3). 1H NMR (400 MHz, δ ppm/CDCl3): 9.00 (s, 1H), 7.44-7.39 (m, 4H), 7.30 (s, 1H), 7.25-7.22 (m, 3H), 7.16-7.13 (m, 3H), 6.87-6.82 (m, 3H), 5.20 (d, J = 2.4 Hz, 2H), 3.73 (s, 3H), 1.61 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IA column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 235 nm), minor enantiomer tR = 15.9 min, major enantiomer tR = 13.8 min, 83% ee. HRMS for C24H24BrN2O5+: calcd. [M+H]+: 499.0863, found: 499.0873, [M+2+H]+: 501.0848.
(S)-3,4,5-Trimethoxybenzyl 3-((4-bromophenyl)amino)-2-(hydroxy(phenyl)amino)-2-methyl-3-oxopropanoate (4w)

Following the general procedure, treatment of 3,4,5-trimethoxybenzyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1w, 90.0 mg, 0.20 mmol) with nitrosobenzene (2a, 26 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4w as white solid (73 mg, 65%). Rf (EtOAc/hexane 3:7) = 0.10. Mp 140-142 °C.

13C NMR (100 MHz, δ ppm/CDCl3): 170.4 (C), 166.9 (C), 153.3 (C), 153.3 (C), 153.3 (C), 147.1 (C), 138.1 (C), 136.5 (C), 132.1 (CH), 132.1 (CH), 132.1 (CH), 130.4 (C), 128.8 (CH), 125.9 (CH), 122.1 (CH), 121.5 (CH), 121.5 (CH), 117.3 (CH), 105.2 (CH), 105.2 (CH), 77.2 (C), 68.2 (CH2), 60.9 (CH3), 56.1 (CH3), 56.1 (CH3), 17.7 (CH3).

1H NMR (400 MHz, δ ppm/CDCl3): 9.05 (s, 1H), 7.42 (s, 4H), 7.24-7.20 (m, 2H), 7.16-7.14 (m, 3H), 6.49 (s, 2H), 5.17 (s, 2H), 3.81 (s, 3H), 3.75 (s, 6H), 1.62 (s, 3H).

Enantiomeric excess was determined by HPLC on Chiralpak IA column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 235 nm), minor enantiomer tR = 19.4 min, major enantiomer tR = 16.8 min, 39% ee. HRMS for C26H28BrN2O7+: calcd. [M+Na]+: 581.0894, found: 581.0901, [M+2+Na]+: 583.0881.

(S)-Methyl 3-((4-bromophenyl)amino)-2-(hydroxy(o-tolyl)amino)-2-methyl-3-oxopropanoate (4x)

Following the general procedure, treatment of methyl 3-((4-bromophenyl)amino)-2-methyl-3-oxopropanoate (1a, 57 mg, 0.20 mmol) with 2-methylnitrosobenzene (2b, 29 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 3 h followed by column chromatography afforded the product 4x as white solid (25 mg, 31%). Rf (EtOAc/hexane 3:7) = 0.50. Mp 145-147 °C.

13C NMR (100 MHz, δ ppm/CDCl3): 173.2 (C), 166.7 (C), 144.2 (C), 136.7 (C), 132.2 (CH), 132.2 (CH), 131.6 (C), 128.1 (CH), 127.0 (CH), 123.0 (CH), 123.0 (C), 121.7 (CH), 121.7 (CH), 117.3 (CH), 74.7 (C), 53.4 (CH3), 20.9 (CH3), 18.8 (CH3).

1H NMR (400 MHz, δ ppm/CDCl3): 9.22 (s, 1H), 7.81 (s, 1H), 7.54-7.39 (m, 4H), 7.26-7.16 (m, 4H), 3.93 (s, 3H), 2.49 (s, 3H), 1.51 (s, 3H).

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 95:5 V/V, flow rate 1.0 mL/min, 254 nm, tminor = 6.6 min, tmajor = 8.4 min, 30% ee). HRMS for C18H19BrN2O4: calcd. [M+Na]+: 429.0420, found: 429.0410, [M+2+Na]+: 431.0264.
(S)-Methyl 3-((3,4-dimethoxyphenyl)amino)-2-(hydroxy(o-tolyl)amino)-2-methyl-3-oxopropanoate (4y)

Following the general procedure, treatment of methyl 3-((3,4-dimethoxyphenyl)amino)-2-methyl-3-oxopropanoate (1I, 57 mg, 0.20 mmol) with 2-methylnitrosobenzene (2b, 29 mg, 0.24 mmol) in the presence of (R,R)-TUC (3a, 17 mg, 0.04 mmol) in toluene (3 mL) at 0 °C for 4 h followed by column chromatography afforded the product 4y (27 mg, 35%). \( R_f \) (EtOAc/hexane 3:7) = 0.42. \( \text{Mp} \) 129-131 °C. \( ^{13} \text{C NMR} \) (100 MHz, δ ppm/CDCl\(_3\)): 173.4 (C), 168.4 (C), 149.4 (C), 146.2 (C), 144.4 (C), 136.8 (C), 131.5 (CH), 131.4 (C), 127.9 (CH), 127.0 (CH), 123.0 (CH), 111.9 (CH), 111.6 (CH), 104.9 (CH), 74.7 (C), 56.3 (CH\(_3\)), 56.1 (CH\(_3\)), 53.3 (CH\(_3\)), 21.0 (CH\(_3\)), 18.8 (CH\(_3\)). \( ^1\text{H NMR} \) (400 MHz, δ ppm/CDCl\(_3\)): 9.12 (s, 1H), 7.84 (s, 1H), 7.49 (s, 1H), 7.26-7.18 (m, 4H), 6.91-6.83 (m, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 2.50 (s, 3H), 1.52 (s, 3H).

Enantiomeric excess was determined by HPLC on Chiralpak IC column (Hexane/Ethanol 90:10 V/V, flow rate 1.0 mL/min, 254 nm, \( \tau_{\text{minor}} = 16.5 \text{ min}, \tau_{\text{major}} = 23.0 \text{ min}, 30\% \text{ ee} \)). \( \text{HRMS} \) for C\(_{20}\)H\(_{24}\)N\(_2\)O\(_6\)\(\text{Na}^+\): calcd. [M+H]\(^+\): 411.1527, found: 411.1527.

Synthesis of methyl-3-((4-bromophenyl)amino)-2-methyl-3-oxo-2-(phenylamino)propanoate (5)

To a 10 mL round-bottomed flask charged with 4a (78 mg, 0.20 mmol, 1 equiv) were added Zn dust (260 mg, 4.0 mmol, 20 equiv) and acetic acid (2 mL). This reaction mixture was stirred at 25 °C for 2 h. After the completion of the reaction, as indicated by TLC, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layer was washed with saturated solution of NaHCO\(_3\) and brine. After drying over anhydrous Na\(_2\)SO\(_4\) the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (100–200 mesh silica gel) using ethyl acetate as the eluent to afford compound 5 as white solid (70 mg, 93%). \( R_f \) (ethyl acetate/hexane 15:85) = 0.35. \( \text{Mp} \) 183-185 °C. \( ^{13} \text{C NMR} \) (100 MHz, δ ppm/CDCl\(_3\)): 172.1 (C), 167.6 (C), 142.9 (C), 136.5 (C), 132.1 (CH), 132.1(CH), 129.6 (CH), 129.6 (CH), 121.5 (CH), 121.5 (CH), 120.5 (CH), 117.4 (C), 116.6 (CH), 116.6 (CH), 66.0 (C), 54.1 (CH\(_3\)), 18.9 (CH\(_3\)). \( ^1\text{H NMR} \) (400 MHz, δ ppm/CDCl\(_3\)): 8.90 (s, 1H), 7.42 (s, 4H), 7.20 (t, \( J = 8.0 \text{ Hz}, 2H \)), 6.90 (t, \( J = 7.2 \text{ Hz}, 1H \)), 6.65 (d, \( J = 7.6 \text{ Hz}, \))
2H), 5.12 (s, 1H), 3.85 (s, 3H), 1.76 (s, 3H). Enantiomeric excess was determined by HPLC on Chiralpak IA column (Hexane/Ethanol 92:8 V/V, flow rate 1.0 mL/min, 251 nm, $\tau_{\text{minor}} = 24.9$ min, $\tau_{\text{major}} = 15.9$ min, 49% ee). **HRMS** for $\text{C}_{17}\text{H}_{18}\text{BrN}_2\text{O}_3^+$: calcd. [M+H]$^+$: 377.0495, found: 377.0498, [M+2+H]$^+$: 379.0477.

**X-ray data of compound 4a**

**X-ray data collection and structure refinement details of compound 4a**

A good quality colorless single crystal of size 0.28 × 0.22 × 0.19 mm, was selected under a polarizing microscope and mounted on a glass fiber for data collection. Single crystal X-ray data for compound 4a were collected on a Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4 × 4 bin mode using the monochromated MoKα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5° steps at 293(2) K. Cell determination, data collection, and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b242 software. Structure solution and refinement were performed by using SHELXTL-NT.3 Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

**Figure S1**: ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of chiral compound 4a determined at 293 K. The absolute configuration of C7 is S.
Table S1: Crystal data and structure refinement details for compound 4a.

| Compound | 4a |
|----------|----|
| Empirical formula | C\textsubscript{17} H\textsubscript{17} Br N\textsubscript{2} O\textsubscript{4} |
| Formula weight | 393.24 |
| Crystal System | Orthorhombic |
| Space group | \( P 2_1 2_1 2_1 \) |
| \( a \) (Å) | 10.151(3) |
| \( b \) (Å) | 12.755(3) |
| \( c \) (Å) | 14.560(4) |
| \( \alpha \) (°) | 90.00 |
| \( \beta \) (°) | 90.00 |
| \( \gamma \) (°) | 90.00 |
| \( V \) (Å\textsuperscript{3}) | 1885.2(9) |
| \( Z \) | 4 |
| \( D_c \) (g/cm\textsuperscript{3}) | 1.386 |
| \( F_{000} \) | 800 |
| \( \mu \) (mm\textsuperscript{-1}) | 2.201 |
| \( \theta_{\text{max}} \) (°) | 25.36 |
| Total reflections | 12849 |
| Unique reflections | 3413 |
| Reflections \([I > 2\sigma(I)]\) | 1773 |
| Parameters | 217 |
| \( R_{\text{int}} \) | 0.0488 |
| Goodness-of-fit | 0.959 |
| \( R \) \([F^2 > 2\sigma(F^2)]\) | 0.0488 |
| \( wR \) \((F^2\text{, all data})\) | 0.1242 |
| CCDC No. | 1898632 |

References

1. R. A. Dhokale, P. R. Thakare, S. B. Mhaske, *Org. Lett.* **2012**, *14*, 3994.
2. CrystalClear 2.1, Rigaku Corporation, Tokyo, Japan.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
Copies of $^1$H and $^{13}$C NMR spectra for all compounds
400 MHz/CDCl₃

100 MHz/CDCl₃
400 MHz/CDCl₃

100 MHz/CDCl₃
HPLC chromatograms of all compounds

| Sr. No. | Component Name | Ret. Time | Area \( \mu \text{volt sec} \) | Height \( \mu \text{volt} \) | Area % | Height % | ID |
|---------|----------------|-----------|-------------------------------|--------------------------|-------|----------|----|
| 1       |                | 12.96     | 33221.54                      | 1217                     | 54.82 | 53.65    | U  |
| 2       |                | 13.87     | 27374.23                      | 1051                     | 45.18 | 46.35    | U  |
|         |                |           |                               |                          | 60595.77 | 2268     | 100.00 | M  |

Area % Height %

| Sr. No. | Component Name | Ret. Time | Area \( \mu \text{volt sec} \) | Height \( \mu \text{volt} \) | Area % | Height % | ID |
|---------|----------------|-----------|-------------------------------|--------------------------|-------|----------|----|
| 1       |                | 12.89     | 3523.49                       | 154                      | 3.51  | 5.00     | U  |
| 2       |                | 13.89     | 96969.54                      | 2931                     | 96.49 | 95.00    | U  |
|         |                |           |                               |                          | 100493.03 | 3085      | 100.00 | M  |
### Peak Results

| Name | RT  | Area  | Height | % Area |
|------|-----|-------|--------|--------|
| 1    | 19.418 | 5025795 | 1503003 | 61.24 |
| 2    | 21.330 | 53403309 | 1326406 | 48.76 |

### Peak Results

| Name | RT  | Area  | Height | % Area |
|------|-----|-------|--------|--------|
| 1    | 19.034 | 39931666 | 93706 | 12.64 |
| 2    | 21.080 | 27565429 | 729079 | 87.36 |
| Sr. No. | Component Name | Ret. Time | Area μ volt sec | Height μ volt | Area % | Height % | ID |
|--------|----------------|-----------|-----------------|--------------|--------|----------|----|
| 1      | 4f             | 10.30     | 39617.03        | 1217         | 47.63  | 50.24    | U  |
| 2      | 4f             | 11.60     | 43557.03        | 1205         | 52.37  | 49.76    | M  |

**Area % Height %**

| Sr. No. | Component Name | Ret. Time | Area μ volt sec | Height μ volt | Area % | Height % | ID |
|--------|----------------|-----------|-----------------|--------------|--------|----------|----|
| 1      | 4f             | 11.47     | 127287.94       | 3645         | 93.13  | 92.20    | U  |
| 2      | 4f             | 136680.69 | 3954            | 100.00       | 100.00 | 100.00   | M  |
Peak Results

| Name | RT  | Area   | Height | % Area |
|------|-----|--------|--------|--------|
| 1    | 8.942 | 18685037 | 1528419 | 49.08  |
| 2    | 9.424 | 19389232 | 1450639 | 50.92  |

Peak Results

| Name | RT  | Area   | Height | % Area |
|------|-----|--------|--------|--------|
| 1    | 9.127 | 5766116 | 365250 | 18.85  |
| 2    | 9.789 | 22285109 | 1551883 | 81.15  |
Peak Results

| Name | RT  | Area  | Height | % Area |
|------|-----|-------|--------|--------|
| 1    | 11.308 | 41880293 | 1541295 | 49.57  |
| 2    | 12.551 | 42608916 | 1767799 | 50.43  |

Peak Results

| Name | RT  | Area  | Height | % Area |
|------|-----|-------|--------|--------|
| 1    | 11.340 | 1876471 | 85359  | 9.20   |
| 2    | 12.454 | 18519793 | 664953 | 90.80  |
