A New Synthetic Route for Axially Chiral Secondary Amines with Binaphthyl Backbone and Their Applications in Asymmetric Michael Reaction of Aldehydes to Nitroalkenes

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Supporting Information

1. General procedures
2. Synthesis and characterization of chiral secondary amine catalysts
3. Typical procedure for the Michael reaction of aldehydes to nitroolefins
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1. General procedures

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200-300 mesh). $^1$H NMR spectra were recorded on a Bruker XL 400 (400 MHz) spectrometer and the spectra were referenced internally to the residual proton resonance in CDCl$_3$ ($\delta = 7.26$ ppm), or with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the $\delta$ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). $^{13}$C NMR spectra were recorded on Bruker (400 MHz) spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference (CDCl$_3$, $\delta = 77.0$ ppm). HPLC analyses were conducted on an Agilent instrument using Daicel Chiralcel OD-H, Chiralpak AD-H or AS-H columns (0.46 cm diameterx25 cm length). Optical rotations were recorded on a Perkin-Elmer polarimeter (Model 341). High Resolution Mass was recorded on an ESI-ion trap mass spectrometer (Shimadzu, LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Synthesis and characterization of chiral secondary amine catalysts

(R)-Ethyl 2,2'-bis(methoxymethoxy)-1,1'-binaphthyl-3-carboxylate 11a

To a solution of 10 (15 g, 40 mmol) in THF (600 mL), n-BuLi (24 mL, 2.5 M in hexane, 60 mmol) was added dropwise at -78 °C under argon atmosphere. The mixture was stirred for 6 hours under -78 °C and ethyl carbonochloridate (5.5 mL, 60 mmol) was added dropwise. Then the reaction mixture was stirred overnight under -78 °C and warmed to room temperature, water was carefully added. After removal of THF under vacuum, the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na$_2$SO$_4$ and then concentrated. The residue was purified by flash column chromatography on silica gel (eluting with hexane/ethyl
acetate 10:1) to give the desired compound 11a (80% yield; \(\delta^\text{H}_{\text{D}}\) : +93.0 (c 0.70, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.44\) (3H, t, \(J = 7.1\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 3.56 (3H, s, -O-CH\(_3\)), 3.17 (3H, s, -O-CH\(_3\)), 4.45 (2H, q, \(J = 7.1\) Hz, -O-CH\(_2\)-O-), 4.78 (2H, dd, \(J = 5.6, 11.9\) Hz, -O-CH\(_2\)-O-), 5.01 (1H, d, \(J = 6.9\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 5.15 (1H, d, \(J = 6.9\)Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 7.16 (1H, d, Ar-H, \(J = 8.4\) Hz), 7.20 (1H, d, Ar-H, \(J = 8.5\) Hz), 7.29-7.36 (3H, m, Ar-H), 7.44 (1H, t, \(J = 7.0\) Hz, Ar-H), 7.58 (1H, d, \(J = 9.1\) Hz, Ar-H), 7.86 (1H, d, \(J = 8.1\) Hz, Ar-H), 7.96 (2H, d, \(J = 9.2\) Hz, Ar-H), 8.49 (1H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 14.4\), 55.9, 56.1, 61.3, 94.9, 100.0, 116.4, 120.3, 124.1, 125.6, 125.7, 126.0, 126.7, 127.7, 127.8, 128.2, 128.9, 129.6, 129.9, 132.7, 134.1, 135.6, 151.1, 153.0, 166.5; HRMS (ESI-TOF) m/z: calculated for [M+Na]\(^+\) C\(_{27}\)H\(_{30}\)O\(_4\)Na 469.1627; found: 469.1635.

**(R)-Diethyl 2,2'-bis(methoxymethoxy)-1,1'-binaphthyl-3,3'-dicarboxylate 11b**

11b was prepared in a similar manner with 11a, using 3 equiv. of n-BuLi and 4 equiv. of ethyl carbonochloridate, 75% yield; \(\delta^\text{H}_{\text{D}}\) : +41.9 (c 0.94, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.44\) (6H, t, \(J = 7.1\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 2.48 (6H, s, -O-CH\(_3\)), 4.44 (4H, q, \(J = 7.1\) Hz, -O-CH\(_2\)-O-), 4.80 (2H, d, \(J = 6.0\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 4.86 (2H, d, \(J = 6.0\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 7.20 (2H, d, \(J = 8.5\) Hz, Ar-H), 7.36 (2H, t, \(J = 7.7\) Hz, Ar-H), 7.46 (2H, t, \(J = 7.5\) Hz, Ar-H), 7.96 (2H, d, \(J = 8.1\) Hz, Ar-H), 8.53 (2H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 14.3\), 56.0, 61.4, 100.2, 125.3, 125.7, 126.4, 127.3, 128.4, 128.8, 129.6, 133.2, 135.7, 151.7, 166.3; HRMS (ESI-TOF) m/z: calculated for [M+Na]\(^+\) C\(_{30}\)H\(_{32}\)O\(_4\)Na 541.1838; found: 541.1845.

**(R)-Ethyl 2,2'-dihydroxy-1,1'-binaphthyl-3-carboxylate 12a**

Demethoxymethylation of 11a (14.2 g, 32 mmol) was carried out with 6 M HCl (80 mL) in THF (200 mL) at 60 °C for 2 hours. After being cooled to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic extract was washed with brine and dried over Na\(_2\)SO\(_4\). Evaporation of the solvent gave 12a (92% yield), which was directly used for the following reaction; \(\delta^\text{H}_{\text{D}}\) : +43.2 (c 0.65, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.51\) (3H, t, \(J = 6.0\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 4.52 (2H, q, \(J = 7.1\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 4.97 (1H, s, Ar-OH), 7.07 (1H, d, \(J = 8.3\) Hz, Ar-H), 7.16-7.25 (2H, m, Ar-H), 7.29-7.38 (4H, m, Ar-H), 7.86 (1H, d, \(J = 8.0\) Hz, Ar-H), 7.90-7.95 (2H, m, Ar-H), 9.73 (1H, s, Ar-H), 10.92 (1H, s, Ar-OH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 14.3\), 62.3, 114.2, 114.7, 114.7, 117.9, 123.5, 124.5, 124.7, 124.9, 126.7, 127.4, 128.4, 129.4, 129.9, 130.1, 130.3, 133.7, 133.8, 137.5, 151.6, 155.1, 170.0; HRMS (ESI-TOF) m/z: calculated for [M-H]\(^-\) C\(_{23}\)H\(_{21}\)O\(_6\) 357.1127; found: 357.1128.

**(R)-Diethyl 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate 12b**

12b was prepared in a similar manner with 12a, 95% yield; \(\delta^\text{H}_{\text{D}}\) : +168.5 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.50\) (6H, t, \(J = 7.1\) Hz, -CO\(_2\)CH\(_2\)CH\(_3\)), 4.50-4.54 (4H, m, -CO\(_2\)CH\(_2\)CH\(_3\)), 7.15 (2H, qd, \(J = 3.1, 6.6\) Hz, Ar-H), 7.33 (4H, qd, \(J = 3.4, 6.7\) Hz, Ar-H), 7.93 (2H, dd, \(J = 3.2, 6.3\) Hz, Ar-H), 8.69 (2H, s, Ar-H), 10.81 (2H, s, Ar-OH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 14.3\), 62.0, 114.5, 117.0, 124.0, 124.7, 127.2, 129.4, 129.8, 132.8, 137.2, 154.2, 170.2; HRMS (ESI-TOF) m/z: calculated for [M-H]\(^-\) C\(_{28}\)H\(_{21}\)O\(_6\) 429.1338; found: 429.1347.
(R)-Ethyl 2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl-3-carboxylate 13a

To a solution of 12a (10.5 g, 29.4 mmol) and DMAP (0.72 g, 5.9 mmol) in pyridine (80 mL), Ti(O-i-Pr)4 (15 mL, 88.2 mmol) was added dropwise at 0 °C. Then the reaction mixture was stirred at room temperature for 4 hours and cooled to 0 °C. The solution was carefully poured into cool water and extracted with ethyl ether. The organic extract was washed with 2M HCl and dried over Na2SO4. Evaporation of solvent afforded 13a (98% yield), which was directly used for the following reaction: \([\alpha]_{D}^{27} = -146.9\) (c 0.74, CH2Cl2); \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 1.45\) (3H, t, \(J = 7.1\) Hz, -CO2CH2CH3); 4.39-4.47 (1H, m, -CO2CHCH2CH3); 4.51-4.59 (1H, m, -CO2CHCH2CH3); 7.24 (2H, d, \(J = 8.6\) Hz, Ar-H); 7.40 (1H, t, \(J = 7.7\) Hz, Ar-H); 7.47 (1H, t, \(J = 7.7\) Hz, Ar-H); 7.58 (1H, t, \(J = 7.6\) Hz, Ar-H); 7.63-7.65 (2H, m, Ar-H); 8.16 (1H, d, \(J = 9.1\) Hz, Ar-H); 8.01 (1H, d, \(J = 8.3\) Hz, Ar-H); 8.08 (1H, d, \(J = 8.2\) Hz, Ar-H); 8.72 (1H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl3): \(\delta = 13.9, 62.3, 119.3, 123.0, 123.9, 125.1, 127.0, 127.1, 127.3, 128.0, 128.1, 128.4, 129.4, 129.7, 131.3, 132.3, 133.2, 134.6, 135.2, 142.6, 145.6, 164.6; HRMS (ESI-TOF) m/z: calculated for [M+Na]+ C25H16F6O8S2Na 645.0088; found: 645.0098.

(R)-Diethyl 2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl-3,3′-dicarboxylate 13b

13b was prepared in a similar manner with 13a, 92% yield; \([\alpha]_{D}^{27} = -159.2\) (c 1.0, CH2Cl2); \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 1.47\) (6H, t, \(J = 7.1\) Hz, -CO2CH2CH3); 4.39-4.47 (2H, m, -CO2CH2CH3); 4.54-4.62 (2H, m, -CO2CH2CH3); 7.19 (2H, d, \(J = 8.6\) Hz, Ar-H); 7.44-7.48 (2H, m, Ar-H); 7.62-7.66 (2H, m, Ar-H); 8.09 (2H, d, \(J = 8.2\) Hz, Ar-H); 8.75 (2H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl3): \(\delta = 14.0, 62.4, 116.2, 119.4, 123.9, 124.8, 127.5, 128.1, 129.4, 129.6, 131.3, 134.7, 135.5, 142.5, 164.4, 219.5; HRMS (ESI-TOF) m/z: calculated for [M+Na]+ C25H20F6O8S2Na 717.0300; found: 717.0294.

(R)-Ethyl 2,2′-dimethyl-1,1′-binaphthyl-3-carboxylate 14a

ZnMe2 (72 mL, 1.2 M in toluene, 86.4 mmol) was added dropwise to a solution of 13a (17.9 g, 28.8 mmol) in DMF (115 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred overnight at 120 °C, then carefully poured into ice-cooled 3 N HCl solution and filtered to remove the catalyst. The filtrate was extracted with ether. The combined organic extract was washed with brine and dried over Na2SO4. Evaporation of solvent and purification of the residue by column chromatography on silica gel (eluting with hexane/ethyl acetate 10:1) gave 14a (95% yield); \([\alpha]_{D}^{27} = +57.0\) (c 0.64, CH2Cl2); \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 1.47\) (3H, t, \(J = 7.1\) Hz, -CO2CH2CH3); 2.01 (3H, s, Ar-CH3); 2.22 (3H, s, Ar-CH3); 4.46 (2H, q, \(J = 7.1\) Hz, -CO2CH2CH3); 7.00 (2H, t, \(J = 8.6\) Hz, Ar-H); 7.20 (1H, t, \(J = 7.6\) Hz, Ar-H); 7.24-7.29 (1H, m, Ar-H); 7.37-7.45 (2H, m, Ar-H); 7.50 (1H, d, \(J = 8.4\) Hz, Ar-H); 7.88 (2H, d, \(J = 8.5\) Hz, Ar-H); 7.95 (1H, d, \(J = 8.2\) Hz, Ar-H); 8.50 (1H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl3): \(\delta = 14.4, 17.8, 20.1, 61.1, 125.0, 125.6, 125.8, 125.8, 126.2, 127.7, 128.0, 128.2, 128.7, 129.0, 129.8, 130.8, 131.1, 132.2, 132.7, 133.6, 134.1, 134.5, 134.8, 137.1, 168.6; HRMS (ESI-TOF) m/z: calculated for [M+Na]+ C25H22O2Na 377.1518; found: 377.1514.

(R)-Diethyl 2,2′-dimethyl-1,1′-binaphthyl-3,3′-dicarboxylate 14b
14b was prepared in a similar manner with 14a, 89% yield; \([\alpha]_{D}^{25}\) : +74.2 (c 0.76, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 1.38 (6H, t, J = 7.1 Hz, -CO₂CH₂CH₃), 2.13 (6H, s, Ar-CH₃), 4.37 (4H, q, J = 7.1 Hz, -CO₂CH₂CH₃), 6.88 (2H, d, J = 8.5 Hz, Ar-H), 7.19 (2H, t, J = 7.7 Hz, Ar-H), 7.35 (2H, t, J = 7.5 Hz, Ar-H), 7.88 (2H, d, J = 8.1 Hz, Ar-H), 8.44 (2H, s, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.4, 17.9, 61.2, 125.7, 125.9, 128.4, 129.0, 129.8, 131.1, 133.8, 134.1, 136.8, 168.5; HRMS (ESI-TOF) m/z: calculated for [M+Na⁺] C₂₂H₂₂O₂Na 449.1729; found: 449.1727.

(R)-Ethyl 2,2'-bis(bromomethyl)-1,1'-binaphthyl-3,3'-dicarboxylate 15a

A mixture of 14a (9.6 g, 29.3 mmol), N-bromosuccinimide (NBS) (10.7 g, 60.1 mmol), and 2,2'-azobisisobutyronitrile (AIBN) (0.45 g, 2.7 mmol) in cyclohexane (75 mL) was heated to reflux for 3 hours. After being cooled to room temperature, the mixture was poured into water and extracted with diethyl ether. The organic extract was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate 40:1) to afford 15a (88% yield); \([\alpha]_{D}^{12}\) : +149.0 (c 0.82, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 1.51 (3H, t, J = 7.1 Hz, -CO₂CH₂CH₃), 4.19 (1H, d, J = 10.3 Hz, Ar-CH₂Br), 4.35 (1H, d, J = 10.4 Hz, Ar-CH₂Br), 4.52 (2H, q, J = 7.1 Hz, -CO₂CH₂CH₃), 4.58 (1H, d, J = 10.0 Hz, Ar-CH₂Br), 4.86 (1H, d, J = 9.7 Hz, Ar-CH₂Br), 7.03-7.07 (2H, m, Ar-H), 7.29 (1H, d, J = 8.1 Hz, Ar-H), 7.36 (1H, t, J = 7.7 Hz, Ar-H), 7.50 (1H, t, J = 7.7 Hz, Ar-H), 7.55 (1H, t, J = 7.6 Hz, Ar-H), 7.76 (1H, d, J = 8.6 Hz, Ar-H), 7.93 (1H, d, J = 8.2 Hz, Ar-H), 8.01 (1H, d, J = 8.2 Hz, Ar-H), 8.04 (1H, d, J = 8.6 Hz, Ar-H), 8.65 (1H, s, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.3, 30.2, 32.5, 61.7, 126.7, 126.9, 127.0, 127.2, 127.7, 127.8, 128.1, 128.4, 128.8, 129.0, 129.6, 132.2, 132.3, 133.2, 133.6, 133.8, 134.3, 136.4, 167.4; HRMS (ESI-TOF) m/z: calculated for [M+Na⁺] C₂₂H₂₂Br₂O₂Na 532.9728; found: 532.9732.

(R)-Diethyl 2,2'-bis(bromomethyl)-1,1'-binaphthyl-3,3'-dicarboxylate 15b

15b was prepared in a similar manner with 15a, 98% yield; \([\alpha]_{D}^{25}\) : +96.7 (c 0.64, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 1.44 (6H, t, J = 7.1 Hz, -CO₂CH₂CH₃), 4.45 (4H, q, J = 7.1 Hz, -CO₂CH₂CH₃), 4.59 (2H, d, J = 9.8 Hz, Ar-CH₂Br), 4.72 (2H, d, J = 9.7 Hz, Ar-CH₂Br), 6.95 (2H, d, J = 8.4 Hz, Ar-H), 7.27-7.31 (2H, m, Ar-H), 7.49 (2H, t, J = 7.5 Hz, Ar-H), 7.94 (2H, d, J = 8.1 Hz, Ar-H), 8.59 (2H, s, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ=13.3, 29.1, 60.7, 126.1, 126.7, 127.5, 127.9, 128.1, 131.2, 132.3, 132.4, 133.2, 134.9, 166.3; HRMS (ESI-TOF) m/z: calculated for [M+Na⁺] C₂₂H₂₂Br₂O₂Na 604.9939; found: 604.9926.

(R)-Ethyl 4-allyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine-2-carboxylate 8a

Allylamine (5.4 mL, 72 mmol) was added to a solution of 15a (12.2 g, 24 mmol) in acetonitrile (75 mL) at 0 °C. The mixture was heated to 50 °C for 5 hours, then poured into water. The solution was extracted with CH₂Cl₂, the organic layer was combined and dried over Na₂SO₄. Evaporation of the solvent and purification of the residue by column chromatography on silica gel (eluting with hexane/ethyl acetate 5:1) gave 8a (75% yield); \([\alpha]_{D}^{25}\) : -322.1 (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 1.46 (3H, t, J = 7.1 Hz, -CO₂CH₂CH₃), 3.00-3.04 (2H, m, -CH₂N-), 3.14 (1H, d, J = 12.4 Hz, -NCH(N)CH₃), 3.24 (1H, dd, J = 6.6, 13.4 Hz, -NCH₂CH₃), 3.75 (1H, d, J = 12.4 Hz, -CH₂H(N)), 4.46 (2H, q, J = 7.1 Hz, -CO₂CH₂CH₃), 4.78 (1H, d, J = 12.8 Hz, -CH₂H(N)), 5.15-5.21.
(2H, m, -CH=CH₂), 5.94-6.05 (1H, m, -CH=CH₂), 7.25-7.27 (1H, m, Ar-H), 7.32-7.34 (2H, m, Ar-H), 7.37 (1H, d, J = 8.3 Hz, Ar-H), 7.43-7.51 (2H, m, Ar-H), 7.53 (1H, d, J = 8.3 Hz, Ar-H), 7.96 (2H, t, J = 8.1 Hz, Ar-H), 8.00 (1H, d, J = 8.1 Hz, Ar-H), 8.56 (1H, s, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.4, 49.9, 54.7, 58.7, 61.5, 117.6, 125.5, 125.9, 126.3, 127.2, 127.5, 127.6, 127.8, 128.4, 128.7, 129.2, 131.4, 131.6, 131.8, 132.0, 132.7, 133.1, 133.3, 134.5, 136.3, 137.4, 168.1; HRMS (ESI-TOF) m/z: calculated for [M+H]+ C₂₈H₂₆N₂O₂ 408.1964; found: 408.1955.

**(R)-Diethyl 4-allyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine-2,6-dicarboxylate 8b**

8b was prepared in a similar manner with 8a, 75% yield; [α]₁⁰⁰₁⁰⁰⁰ D ≈ -431.5 (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 1.47 (6H, t, J = 7.1 Hz, -CO₂CH₂CH₂), 2.91-2.93 (1H, m, -NCH₂CH=), 2.97 (2H, d, J = 12.9 Hz, Ar-CH₂), 3.30 (1H, dd, J = 6.0, 13.5 Hz, -NCHHCH=), 4.47 (4H, q, J = 7.1 Hz, -CO₂CH₂CH₂), 4.79 (2H, d, J = 12.9 Hz, Ar-CH₂), 5.14-5.14 (2H, m, -CH=CH₂), 5.94-6.00 (1H, m, -CH=CH₂), 7.24 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, t, J = 7.6 Hz, Ar-H), 7.50 (2H, t, J = 7.4 Hz, Ar-H), 8.01 (2H, d, J = 8.2 Hz, Ar-H), 8.58 (2H, s, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.4, 49.7, 58.3, 61.5, 117.1, 126.3, 127.2, 128.0, 128.9, 129.3, 131.7, 131.9, 132.7, 136.4, 136.9, 168.0; HRMS (ESI-TOF) m/z: calculated for [M+H]+ C₃₁H₂₆O₄ 480.2175; found: 480.2174.

**(R)-(4-Allyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepin-2-yl)bis(3,5-dimethylphenyl)methanol 16c**

3,5-dimethyl phenyl lithium (1.5 mL, 2 M in diethyl ether solution, 3.0 mmol) was added to a solution of 8a (407 mg, 1 mmol) in Et₂O (10 mL) at -78 °C. The mixture was stirred for 2 hours at -78 °C, then saturated NH₄Cl was carefully added dropwise. After extracted with ethyl acetate, the organic layer was combined and washed with brine, dried over Na₂SO₄ and concentrated. The resulting residue was recrystallized from CH₂Cl₂/hexane to give 16c (440 mg, 0.85 mmol, 85% yield); [α]₁⁰⁰₁⁰⁰⁰ D ≈ +144.3 (c 0.86, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 2.22 (6H, s, Ar-CH₃), 2.25 (1H, overlap of peaks, ArCH₂), 2.32 (6H, s, Ar-CH₃), 2.81 (1H, dd, J = 6.4, 12.7 Hz, -NCHHCH=), 3.11 (1H, dd, J = 6.3, 12.7 Hz, -NCHHCH=), 3.54 (1H, d, J = 13.9 Hz, ArCH₂), 3.65 (1H, d, J = 14.1 Hz, ArCH₂), 3.72 (1H, d, J = 11.5 Hz, ArCH₂), 5.01-5.08 (2H, m, -CH=CH₂), 5.84-5.94 (1H, m, -CH=CH₂), 6.82 (1H, s), 6.96 (1H, s), 7.07-7.13 (4H, m, Ar-H), 7.17-7.23 (2H, m, Ar-H), 7.36-7.39 (4H, m, Ar-H), 7.49 (1H, t, J = 7.4 Hz), 7.70 (2H, t, J = 7.7 Hz), 7.84 (2H, m, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.5, 21.7, 51.8, 54.6, 58.1, 83.2, 118.0, 125.2, 125.6, 125.8, 125.9 (two peaks overlap), 126.6, 127.1, 127.9, 128.0, 128.3, 128.4 (two peaks overlap), 128.8, 129.1, 129.6, 130.5, 131.1, 131.5, 132.3, 133.2, 133.8, 135.5 (two peaks overlap), 137.0,
137.1, 137.4, 144.9, 146.6, 148.6, 219.5; HRMS (ESI-TOF) m/z: calculated for [M-H] C_{32}H_{35}NO 572.2953; found: 572.2962.

16a and 16b were prepared in a similar manner with 16c. For 16a 6 equiv. of phenyl lithium was used.

(R)-(4-Allyl-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine-2,6-diyil)-bis(diphenylmethanol)

16a

Yield: 82%; \([\alpha]^D_{D} = +151.4\) (c 1.0, CH_2Cl_2); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta = 2.51\) (1H, dd, \(J = 8.7, 12.7\) Hz, -NCHHHCH-), 2.78 (2H, d, \(J = 13.1\) Hz, -CHHN-), 3.23 (1H, d, \(J = 11.6\) Hz, -NCHHHCH-), 4.00 (2H, d, \(J = 13.1\) Hz, -CHHN-), 4.76 (1H, d, \(J = 17.0\) Hz, -CH=CHH), 4.86 (1H, d, \(J = 9.8\) Hz, -CH=CHH), 5.68-5.82 (1H, m, -CH=CH_2), 7.13-7.33 (8H, m), 7.29-7.41 (20H, m), 7.63 (2H, d, \(J = 8.1\) Hz), \(^1^3\)C NMR (100 MHz, CDCl_3): \(\delta = 48.2, 51.4, 83.1, 117.4, 125.7, 126.1, 126.9, 127.1, 127.2, 127.9, 128.4, 128.9, 130.8, 131.5, 132.8, 136.1, 138.0, 143.4, 146.6, 159.0; HRMS (ESI-TOF) m/z: calculated for [M+H]^+ C_{51}H_{42}NO 700.3216; found: 700.3217.

(R)-(4-Allyl-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepin-2-yl)diphenylmethanol

16b

Yield: 87%; \([\alpha]^D_{D} = +86.9\) (c 0.8, CH_2Cl_2); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta = 2.28\) (1H, dd, \(J = 11.6\) Hz, ArCH_2), 2.81 (1H, dd, \(J = 6.3, 13.1\) Hz, -NCHHHCH-), 3.07 (dd, 1H, \(J = 6.9, 13.1\) Hz, -NCHHHCH-), 3.53 (1H, d, \(J = 14.0\) Hz, ArCH_2), 3.67 (2H, d, \(J = 13.5\) Hz, ArCH_2), 5.04-5.09 (2H, m, -CH=CH_2), 5.84-5.89 (1H, m, -CH=CH_2), 7.17 (1H, s, Ar-H), 7.17-7.21 (2H, m, Ar-H), 7.28-7.55 (14H, m, Ar-H), 7.65 (1H, d, \(J = 7.7\) Hz, Ar-H), 7.71 (1H, d, \(J = 8.5\) Hz, Ar-H), 7.95 (2H, dd, \(J = 4.2, 8.1\) Hz, Ar-H); \(^1^3\)C NMR (100 MHz, CDCl_3): \(\delta = 52.0, 54.1, 57.9, 83.3, 118.3, 125.7, 125.9, 126.1, 126.9, 127.1, 127.4, 127.8, 128.1, 128.0, 128.3, 128.5, 128.8, 129.0, 129.7, 130.5, 131.0, 131.4, 132.2, 133.2, 133.5, 135.3, 135.4, 137.6, 144.4, 146.8, 148.8; HRMS (ESI-TOF) m/z: calculated for [M+H]^+ C_{39}H_{35}NO 518.2494; found: 518.2493.

(R)-(4,5-Dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepin-2-yl)bis(3,5-dimethylphenyl)methanol

6c

A mixture of (R)-16c (440 mg, 0.85 mmol), N,N-dimethylbarbituric acid (NDMBA) (398 mg, 2.55 mmol), Pd(OAc)_2 (18 mg, 0.08 mmol), and triphenylphospine (84 mg, 0.32 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 4 hours under argon atmosphere. After addition of CH_2Cl_2, the organic layer was washed with saturated NaHCO_3, dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography on silica gel (eluting with CH_2Cl_2/MeOH/NH_3/H_2O = 20:1:0.1) to give 6c (381 mg, 0.8 mmol, 94% yield); \([\alpha]^D_{D} = -32.4\) (c 0.68, CH_2Cl_2); \(^1\)H NMR (400 MHz, CDCl_3): \(\delta = 2.22\) (6H, s, Ar-CH_2), 2.31 (6H, s, Ar-CH_3), 2.97 (1H, d, \(J = 12.2\) Hz, Ar-CH_2), 3.44 (1H, d, \(J = 13.0\) Hz, Ar-CH_2), 3.81 (1H, d, \(J = 13.1\) Hz, Ar-CH_2), 4.07 (1H, d, \(J = 12.2\) Hz, Ar-CH_2), 6.86 (1H, s, Ar-H), 6.97 (1H, s, Ar-H), 7.05 (4H, d, \(J = 7.3\) Hz, Ar-H), 7.19-7.23 (1H, m, Ar-H), 7.26 (1H, s, Ar-H), 7.33 (2H, d, \(J = 8.2\) Hz, Ar-H), 7.39 (1H, t, \(J = 7.5\) Hz, Ar-H), 7.47-7.49 (2H, m, Ar-H), 7.59 (1H, d, \(J = 8.4\) Hz, Ar-H), 7.71 (1H, d, \(J = 8.1\) Hz, Ar-H), 7.93 (2H, d, \(J = 8.2\) Hz, Ar-H); \(^1^3\)C NMR (100 MHz, CDCl_3): \(\delta = 21.6, 21.7, 44.7, 48.5, 83.1, 125.4, 125.6, 125.8, 125.9, 126.1, 126.4, 127.0, 127.1, 127.6, 128.4, 128.7, 128.9, 129.0, 129.2, 130.0, 130.6, 131.4, 132.1, 133.2, 135.2, 137.2, 137.3, 137.4, 144.1, 146.9, 148.2; HRMS (ESI-TOF) m/z: calculated for [M-H]^+ C_{39}H_{35}NO 532.2640; found: 532.2642.
6a, 6b were prepared in a similar manner with 6c.

(R)-(4,5-Dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine-2,6-diyl)bis(diphenylmethanol) 6a

Yield: 91%; \( \left[ \alpha \right]_{D}^{25} = +30.7 \) (c 1.0, CH\(_{2}\)Cl\(_{2}\)); \(^{1}\)H NMR (400 MHz, CDCl\(_{3}\)): \( \delta = 2.80 \) (2H, d, \( J = 12.4 \) Hz, -CHNH-), 4.00 (2H, d, \( J = 12.8 \) Hz, -CH\(_{2}\)N-), 7.24-7.41 (28H, m, Ar-\( \text{H} \)), 7.64 (2H, d, \( J = 8.1 \) Hz, Ar-\( \text{H} \)); \(^{13}\)C NMR (100 MHz, CDCl\(_{3}\)): \( \delta = 44.9, 83.2, 125.7, 126.1, 127.0, 127.2, 127.6, 127.9, 128.0, 128.3, 128.9, 130.0, 130.9, 131.7, 137.7, 143.0, 146.9, 147.9; \) HRMS (ESI-TOF) m/z: calculated for [M+H]\(^{+}\)\( \text{C}_{60}\text{H}_{58}\text{NO}_{2} \) 660.2903; found: 660.2895.

(R)-(4,5-Dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepin-2-yl)diphenylmethanol 6b

Yield: 95%; \( \left[ \alpha \right]_{D}^{26} = -20.7 \) (c 1.0, CH\(_{2}\)Cl\(_{2}\)); \(^{1}\)H NMR (400 MHz, CDCl\(_{3}\)): \( \delta = 2.96 \) (d, 1H, \( J = 12.1 \) Hz, Ar-\( \text{CH}_{2}\)), 3.47 (1H, d, \( J = 13.2 \) Hz, Ar-\( \text{CH}_{2}\)), 3.85 (1H, d, \( J = 13.3 \) Hz, Ar-\( \text{CH}_{2}\)), 4.07 (1H, d, \( J = 12.1 \) Hz, Ar-\( \text{CH}_{2}\)), 7.19-7.24 (4H, m, Ar-\( \text{H} \)), 7.28-7.39 (9H, m, Ar-\( \text{H} \)), 7.45-7.48 (4H, m, Ar-\( \text{H} \)), 7.57 (1H, d, \( J = 8.5 \) Hz, Ar-\( \text{H} \)), 7.64 (1H, d, \( J = 8.1 \) Hz, Ar-\( \text{H} \)), 7.92 (2H, d, \( J = 8.2 \) Hz, Ar-\( \text{H} \)); \(^{13}\)C NMR (100 MHz, CDCl\(_{3}\)): \( \delta = 44.5, 48.4, 83.1, 125.6, 125.9, 126.0, 125.4, 126.2, 126.9, 127.0, 127.1, 127.5, 127.6, 127.9, 128.0, 128.3, 128.6, 128.9, 129.3, 130.1, 130.6, 131.3, 132.1, 133.2, 135.1, 137.7, 143.6, 146.9, 148.1; \) HRMS (ESI-TOF) m/z: calculated for [M+H]\(^{+}\)\( \text{C}_{68}\text{H}_{38}\text{NO} \) 478.2171; found: 478.2163.

(R)-2-(Bis(3,5-dimethylphenyl)(trimethylsilyloxy)methyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine 7c

To a CH\(_{2}\)Cl\(_{2}\) (3 mL) solution of 6c (381 mg, 0.8 mmol) was added Et\(_{3}\)N (0.17 mL, 1.2 mmol) and TMSOTf (0.19 mL, 1.0 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature and quenched with aq. NH\(_{4}\)Cl and the organic materials were extracted with ethyl acetate. The organic layer was washed with saturated NaHCO\(_{3}\), dried over anhydrous Na\(_{2}\)SO\(_{4}\) and concentrated under vacuum. Purification by neutral aluminum oxide column chromatography (ethyl acetate: hexane 1:20) gave 7c (395 mg, 0.72 mmol, 90% yield); \( \left[ \alpha \right]_{D}^{25} = -209.1 \) (c 1.0, CH\(_{2}\)Cl\(_{2}\)); \(^{1}\)H NMR (400 MHz, CDCl\(_{3}\)): \( \delta = -0.08 \) (9H, s, SiCH\(_{3}\)), 2.25 (6H, s, ArCH\(_{3}\)), 2.32 (6H, s, ArCH\(_{3}\)), 2.95 (1H, d, \( J = 14.9 \) Hz, ArCH\(_{2}\)), 3.19 (1H, d, \( J = 10.3 \) Hz, ArCH\(_{2}\)), 3.52 (1H, d, \( J = 10.3 \) Hz, ArCH\(_{2}\)), 4.34 (1H, d, \( J = 14.5 \) Hz, ArCH\(_{2}\)), 6.88 (1H, s, Ar-H), 6.94 (1H, s, Ar-H), 7.01 (2H, s, Ar-H), 7.08 (2H, s, Ar-H), 7.21-7.23 (2H, m, Ar-H), 7.29 (1H, d, \( J = 8.2 \) Hz, Ar-H), 7.36 (1H, d, \( J = 8.4 \) Hz, Ar-H), 7.43 (2H, t, \( J = 7.4 \) Hz, Ar-H), 7.51 (1H, d, \( J = 8.3 \) Hz, Ar-H), 7.83 (1H, d, \( J = 8.1 \) Hz, Ar-H), 7.91 (2H, d, \( J = 8.2 \) Hz, Ar-H), 7.94 (1H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl\(_{3}\)): \( \delta = 2.2, 21.4, 21.5, 45.3, 48.1, 86.0, 125.0, 125.0, 125.3, 125.4, 125.8, 126.9, 127.1, 127.3, 128.2, 128.4, 128.5, 128.6, 128.7, 129.5, 130.8, 131.1, 131.3, 132.9, 134.4, 135.6, 135.9, 136.7, 136.8, 137.2, 142.6, 145.6, 148.2; \) HRMS (ESI-TOF) m/z: calculated for [M-H-OTMS]\( \text{C}_{39}\text{H}_{33}\text{N} \) 516.2691; found: 516.2684.

7a, 7b were prepared in a manner similar to that described above.

(R)-2,6-Bis(diphenyl(trimethylsilyloxy)methyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine 7a
Yield: 90%; \([\alpha]_{D}^{20} : -103.5 (c 0.66, \text{CH}_{2} \text{Cl}_{2})\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -0.11 (18\text{H}, \text{s}, \text{SiCH}_3)\), 2.82 (2H, d, \(J = 12.8\text{ Hz}, -\text{CHCH}_2\)), 4.01 (2H, d, \(J = 12.9\text{ Hz}, -\text{CHCH}_2\)), 7.11 (2H, d, \(J = 8.4\text{ Hz}, \text{Ar-H}\)), 7.16-7.20 (2H, m, Ar-H), 7.25-7.42 (22H, m, Ar-H), 7.78 (2H, d, \(J = 8.1\text{ Hz}, \text{Ar-H}\)), 7.89 (2H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 2.2, 45.0, 86.2, 125.1, 125.7, 126.8, 127.0, 127.1, 127.6, 127.7, 128.3, 128.6, 128.7, 129.5, 131.1, 131.1, 135.2, 137.6, 142.3, 146.5, 147.2; HRMS (ESI-TOF) m/z: calculated for [M+H]\(^+\)\(\text{C}_{65}\text{H}_{39}\text{NO}_3\text{Si}\): 804.3693; found: 804.3699.

\((R)-(4,5\text{-Dihydro}-3\text{H}-\text{dienaphtho[2,1-c:1',2'-e]azepin}-2\text{-yl})\text{diphenylmethanol}\) 7b

Yield: 87%; \([\alpha]_{D}^{20} : -155.0 (c 1.0, \text{CH}_{2} \text{Cl}_{2})\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.07 (9\text{H}, \text{s}, \text{SiCH}_3)\), 2.97 (1H, d, \(J = 14.6\text{ Hz}, \text{Ar-CH}_2\)), 3.19 (1H, d, \(J = 10.4\text{ Hz}, \text{Ar-CH}_2\)), 3.51 (1H, d, \(J = 10.4\text{ Hz}, \text{Ar-CH}_2\)), 4.34 (1H, d, \(J = 14.5\text{ Hz}, \text{Ar-CH}_2\)), 7.20-7.22 (2H, m, Ar-H), 7.27-7.38 (8H, m, Ar-H), 7.42-7.52 (7H, m, Ar-H), 7.81 (1H, d, \(J = 8.1\text{ Hz}, \text{Ar-H}\)), 7.92 (2H, d, \(J = 8.3\text{ Hz}, \text{Ar-H}\)), 7.95 (1H, s, Ar-H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 2.2, 45.2, 48.1, 86.3, 125.1, 125.5, 125.5, 126.0, 127.1, 127.2, 127.3, 127.5, 127.7, 127.9, 128.2, 128.6, 128.7, 129.1, 129.5, 130.9, 131.1, 131.3, 133.0, 134.5, 135.6, 136.9, 142.2, 144.7, 147.7; HRMS (ESI-TOF) m/z: calculated for [M-H-OTMS] \(\text{C}_{35}\text{H}_{28}\text{N}\): 460.2065; found: 460.2051.

3. Typical procedure for the Michael reaction of aldehydes to nitroolefins

Propanal (0.36 mL, 5.0 mmol) was added to a solution of (E)-(2-nitrovinyl)-benzene (75 mg, 0.5mmol), PhCOOH (6 mg, 0.05 mmol) and catalyst 7c (30 mg, 0.05 mmol) in \(\text{CH}_2\text{Cl}_2\) (2.0 mL) at room temperature. After the reaction mixture had been stirred for 3 hours at that temperature, it was concentrated under vacuum and the crude mixture was purified by flash chromatography to afford the Michael adduct as clear oil (121 mg, 87% yield). Assignment of the stereoisomers was performed by comparison with literature data. The value of \(\text{syn/anti}\) ratio was determined by \(^1\)H NMR by comparing different integrations of hydrogens of the aldehyde group. The enantiomeric excess was measured by HPLC with Chiralcel OD-H columns.

4. Characterization of Michael adducts

\((2S,3R)-2\text{-Methyl}-4\text{-nitro}-3\text{-phenylbutanal} (17a)^{[1]}\)

Prepared from (E)-(2-nitrovinyl)-benzene and propanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; \(ee > 99\%\); The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column (\(\lambda = 208\text{ nm, hexane/i-PrOH = 85:15, 0.8 mL-min}^{-1}\)), \(t_f = 21.08\text{ min (major)}, t_b = 28.48\text{ min (minor)}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.00 (3\text{H}, \text{d}, \(J = 7.3\text{ Hz}\)), 2.78-2.84 (1\text{H}, \text{m}), 3.70-3.76 (1\text{H}, \text{m}), 4.66-4.71 (1\text{H}, \text{m}), 4.77-4.82 (1\text{H}, \text{m}), 7.16-7.22 (2\text{H}, \text{m}), 7.29-7.37 (3\text{H}, \text{m}), 9.71 (1\text{H}, \text{d}, \(J = 1.7\text{ Hz})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 12.1, 44.1, 48.4, 78.1, 128.1, 129.1, 136.6, 202.3.\)
(2S,3R)-3-(4-Bromophenyl)-2-methyl-4-nitrobutanal (17b)[1]

Prepared from (E)-1-bromo-4-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 94%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 230 nm, hexane/i-PrOH = 85:15, 0.8 mL·min⁻¹), tₘ = 19.95 min (major), tₘ = 14.84 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 1.01 (3H, d, J = 7.3 Hz), 2.71-2.82 (1H, m), 3.75-3.84 (1H, m), 4.62-4.67 (1H, m), 4.77-4.81 (1H, m), 7.05-7.07 (2H, m), 7.47-7.49 (2H, m), 9.70 (1H, d, J = 1.5 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 12.2, 43.5, 48.2, 77.8, 122.2, 129.8, 132.3, 135.7, 201.8.

(2S,3R)-3-(4-Methoxyphenyl)-2-methyl-4-nitrobutanal (17c)[1]

Prepared from (E)-1-methoxy-4-(2-nitrovinyl)-benzene and propanal according to the general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee > 99%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AS-H column (λ = 208 nm, hexane/i-PrOH = 85:15, 1.0 mL·min⁻¹), tₘ = 19.14 min (major), tₘ = 25.64 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 1.00 (3H, d, J = 7.3 Hz), 2.69-2.77 (1H, m), 3.74-3.77 (1H, m), 3.79 (3H, s), 4.59-4.66 (1H, m), 4.73-4.77 (1H, m), 6.85-6.88 (2H, m), 7.07-7.09 (2H, m), 9.71 (1H, d, J = 1.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 12.0, 43.4, 48.6, 55.2, 78.3, 114.4, 128.3, 129.1, 129.2, 202.5.

(2S,3R)-2-Methyl-3-(naphthalen-1-yl)-4-nitrobutanal (17d)[1]

Prepared from (E)-1-(2-nitrovinyl)-naphthalene and propanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 92%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 220 nm, hexane/i-PrOH = 99.2:0.8, 1.0 mL·min⁻¹), tₘ = 37.09 min (major), tₘ = 33.05 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 0.98 (3H, d, J = 7.3 Hz), 2.97-3.02 (1H, m), 4.87-4.95 (3H, m), 7.37 (1H, d, J = 7.2 Hz), 7.57-7.62 (3H, m), 7.82 (1H, d, J = 8.2 Hz), 7.90 (1H, d, J = 8.1 Hz), 8.13-8.17 (1H, m), 9.76 (1H, d, J = 1.7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 12.5, 37.4, 49.2, 78.0, 122.5, 124.1, 125.4, 126.1, 126.9, 128.7, 129.4, 131.2, 133.5, 134.2, 202.5.
(2S,3S)-3-(Furan-2-yl)-2-methyl-4-nitrobutanal (17e)

Prepared from (E)-2-(2-nitrovinyl)-furan and propanal at 0 °C according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 98%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 210 nm, hexane/i-PrOH = 99:1, 1.0 mL·min⁻¹), tR = 28.35 min (major), tR = 24.81 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 1.07 (3H, d, J = 7.3 Hz), 2.79-2.83 (1H, m), 4.06-4.12 (1H, m), 4.71-4.75 (2H, m), 6.18 (1H, d, J = 3.3 Hz), 6.30-6.31 (1H, m), 7.36 (1H, s). 13C NMR (100 MHz, CDCl₃): δ = 11.0, 37.7, 47.1, 75.8, 108.7, 110.4, 142.7, 149.9, 201.6.

(2S,3S)-2-Methyl-4-nitro-3-(2-thiophyl)-butanal (17f)

Prepared from (E)-2-(2-nitrovinyl)-thiophene and propanal at 0 °C according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 97%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 238 nm, hexane/i-PrOH = 99:1, 1.0 mL·min⁻¹), tR = 41.27 min (major), tR = 30.26 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (3H, d, J = 7.3 Hz), 2.78-2.84 (1H, m), 4.23-4.28 (1H, m), 4.67-4.80 (2H, m), 6.90-6.91 (1H, m), 6.96-6.97 (1H, m), 7.21-7.27 (1H, m), 9.71 (1H, d, J = 1.1 Hz); 13C NMR (100 MHz, CDCl₃): δ = 11.5, 39.4, 48.8, 78.4, 125.3, 126.7, 127.1, 138.9, 201.8.

(2S,3S)-2,5-Dimethyl-3-(nitromethyl)hexanal (17g)

Prepared from (E)-4-methyl-1-nitropent-1-ene and propanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 95%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 208 nm, hexane/i-PrOH = 99:1, 1.0 mL·min⁻¹), tR = 9.51 min (major), tR = 7.65 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 0.90-0.94 (6H, m), 1.14 (3H, d, J = 7.1 Hz), 1.16-1.24 (2H, m), 1.53-1.64 (1H, m), 2.54-2.60 (1H, m), 2.81-2.89 (1H, m), 4.36-4.41 (1H, m), 4.46-4.50 (1H, m), 9.90 (1H, s); 13C NMR (100 MHz, CDCl₃): δ = 8.8, 21.8, 23.0, 25.3, 35.1, 37.5, 47.1, 77.1, 202.6.

(2S,3R)-2-Ethyl-4-nitro-3-phenylbutanal (17h)
Prepared from (E)-(2-nitrovinyl)-benzene and butyraldehyde according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 97%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column ($\lambda = 208$ nm, hexane/i-PrOH = 85:15, 0.8 mL-min$^{-1}$), $t_R = 18.08$ min (major), $t_S = 21.53$ min (minor). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.84$ (3H, t, $J = 7.5$ Hz), 1.48-1.53 (2H, m), 2.65-2.71 (1H, m), 3.76-3.82 (1H, m), 4.60-4.75 (2H, m), 7.16-7.19 (2H, m), 7.30-7.35 (3H, m), 9.72 (1H, d, $J = 2.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 10.6$, 20.3, 42.7, 55.0, 78.6, 128.0, 128.2, 129.1, 136.9, 203.4.

(S)-2-((R)-2-nitro-1-phenylethyl)pentanal (17i)$^{[1]}$

Prepared from (E)-(2-nitrovinyl)-benzene and $n$-pentanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 97%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column ($\lambda = 208$ nm, hexane/i-PrOH = 85:15, 0.8 mL-min$^{-1}$), $t_R = 16.03$ min (major), $t_S = 19.59$ min (minor). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.80$ (3H, t, $J = 7.1$ Hz), 1.13-1.37 (4H, m), 2.67-2.74 (1H, m), 3.75-3.81 (1H, m), 4.62-4.73 (2H, m), 7.17-7.19 (2H, m), 7.30-7.35 (3H, m), 9.71 (1H, d, $J = 2.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.9$, 19.8, 29.5, 43.2, 53.8, 78.4, 128.0, 128.2, 129.1, 136.8, 203.3.

(S)-2-((R)-2-Nitro-1-phenylethyl)hexanal (17j)$^{[4]}$

Prepared from (E)-(2-nitrovinyl)-benzene and $n$-hexanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 95%. The enantiomeric excess was determined by HPLC using Daicel Chiralcel OD-H column ($\lambda = 208$ nm, hexane/i-PrOH = 85:15, 0.8 mL-min$^{-1}$), $t_R = 14.67$ min (major), $t_S = 17.27$ min (minor). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.78$ (3H, t, $J = 6.9$ Hz), 1.14-1.25 (4H, m), 1.25-1.36 (2H, m), 2.66-2.73 (1H, m), 3.75-3.81 (1H, m), 4.64-4.72 (2H, m), 7.16-7.19 (2H, m), 7.30-7.36 (3H, m), 9.71 (1H, d, $J = 2.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.6$, 22.5, 27.0, 28.5, 43.1, 53.9, 78.4, 128.0, 128.1, 129.1, 136.9, 203.3.

(2S,3R)-2-Isopropyl-4-nitro-3-phenylbutanal (17k)$^{[4]}$
Prepared from (E)-(2-nitrovinyl)-benzene and 3-methylbutanal according to general procedure. Purified by preparative chromatography on silica gel (petroleum ether/ethyl acetate 20:1); Colorless oil; ee = 94%. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column (λ = 208 nm, hexane/i-PrOH = 85:15, 0.8 mL·min⁻¹), tᵣ = 5.74 min (major), tᵣ = 5.23 min (minor). ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (3H, d, J = 7.0 Hz), 1.10 (3H, d, J = 7.2 Hz), 1.69-1.76 (1H, m), 2.21-2.36 (1H, m), 2.75-2.79 (1H, m), 4.55-4.69 (2H, m), 7.18-7.20 (2H, m), 7.29-7.37 (3H, m), 9.93 (1H, d, J = 2.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 17.0, 21.7, 27.9, 41.9, 58.8, 79.0, 128.0, 128.1, 129.2, 137.1, 204.4.

Reference


5. NMR spectra of compounds

¹H and ¹³C NMR spectra of 11a
¹H and ¹³C NMR spectra of 12a
¹H and ¹³C NMR spectra of 13a
¹H and ¹³C NMR spectra of 14a
¹H and ¹³C NMR spectra of 15a
¹H and ¹³C NMR spectra of 8a
¹H and ¹³C NMR spectra of 11b
¹H and ¹³C NMR spectra of 12b
¹H and ¹³C NMR spectra of 13b
¹H and ¹³C NMR spectra of 14b
¹H and ¹³C NMR spectra of 15b
¹H and ¹³C NMR spectra of 8b
¹H and ¹³C NMR spectra of 16a
¹H and ¹³C NMR spectra of 16b
¹H and ¹³C NMR spectra of 16c
¹H and ¹³C NMR spectra of 6a
¹H and ¹³C NMR spectra of 6b
¹H and ¹³C NMR spectra of 6c
¹H and ¹³C NMR spectra of 7a
¹H and ¹³C NMR spectra of 7b
¹H and ¹³C NMR spectra of 7c
Compound 11a
Compound 12a

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Compound 13a

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Compound 15a
Compound 8a

[Diagram of compound 8a]

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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Compound 11b

[Chemical structure images and spectra]

Bruker

[Additional chemical structure images and spectra]
Compound 13b
Compound 14b
Compound 15b
Compound 16a
Compound 16c
Compound 6b
Compound 6c
Compound 7a
Compound 7c