Asymmetric reduction of ketimines with trichlorosilane employing an imidazole derived organocatalyst

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Ethyl 1-methylimidazole-2-carboxylate^1

A solution of 1-methylimidazole (100 mmol, 8.21 g) and triethylamine (30 cm³) in acetonitrile (50 cm³) was cooled to 0 ºC with an ice bath. Ethyl chloroformate (150 mmol, 14 cm³) was added dropwise. The mixture was warmed up to room temperature slowly and stirred overnight. The yellow solution was filtered and the residue was dissolved in water (250 cm³), extracted with CH₂Cl₂ (2 × 100 cm³) and the combined organic phases were evaporated under reduced pressure. The resulting yellow oil was purified by dry flash chromatography on silica gel (AcOEt), yielding a pale yellow oil (6.22 g, 40% yield) which crystallised almost immediately upon exposure to air. m.p. 43 – 45 ºC (lit. 2 44 ºC from Et₂O/hexane); δ_H (250 MHz, CDCl₃) 1.41 (t, 3H, J 7.2 Hz, OCH₂CH₃), 4.00 (s, 3H, NCH₃), 4.39 (q, 2H, J 7.2 Hz, OCH₂CH₃), 7.02 (s, 1H, ArC), 7.12 (s, 1H, ArCH); δ_C (63 MHz, CDCl₃) 14.1 (OCH₂CH₃), 35.6 (NCH₃), 61.1 (OCH₂CH₃), 126.2 (ArCH), 129.1 (ArCH), 136.5 (ArC), 159.0 (C=O); Data was in accordance with literature.

2-Hydroxymethyl-1-methylimidazole^3

Paraformaldehyde (330 mmol, 9.95 g) and 1-methylimidazole (120 mmol, 9.6 cm³) were introduced into a round-bottom flask and heated at 160 ºC for 1 hr. The hot plate was removed, MeOH (12 cm³) was immediately added and the mixture stirred until it had cooled to RT, filtered, and cooled to 0 ºC, causing the formation of crystals, which were isolated and recrystallised from CH₂Cl₂ to afford the title compound (1.99 g, 14%). m.p. 86 – 90 ºC (from CH₂Cl₂, lit. 3 110 ºC); δ_H (250 MHz, CDCl₃) 3.69 (s, 3H, NCH₃), 4.58 (s, 2H, CH₂O), 6.27 (br s, 1H, OH), 6.77 (d, 1H, J 1.7 Hz, ArCH), 6.80 (d, 1H, J 1.7 Hz, ArCH); δ_C (63 MHz, CDCl₃) 32.7 (CH₃), 55.4 (CH₂O), 121.4 (ArCH), 126.4 (ArCH), 148.1 (ArC). Data was in accordance with literature.
2-Chloromethyl-1-methylimidazole hydrochloride

\[ \text{N} \text{N} \text{Cl} \cdot \text{HCl} \]

Thionyl chloride (83 mmol, 6.0 cm³) and CH₂Cl₂ (10 cm³) were introduced into a round-bottom flask and cooled to 0 ºC. 2-Hydroxymethyl-1-methylimidazole (24 mmol, 2.66 g) was added dropwise as a solution in CH₂Cl₂ (20 cm³) and the mixture was heated to reflux and stirred for 15 min. The solvent was evaporated, the concentrate was dissolved in ethanol and heated at reflux for 15 min. Solvent was evaporated, and the resulting was recrystallised from to afford the title compound as beige crystals (2.17 g, 55%). m.p. 153 – 157 ºC (from CH₂Cl₂, lit.3 174 ºC); \( \delta_{\text{H}} \) (250 MHz, d⁶-DMSO) 3.88 (NCH₂), 5.20 (CH₂Cl), 7.72 (d, 1H, J 1.9 Hz, ArCH₂), 7.79 (d, 1H, J 1.9 Hz, ArCH); \( \delta_{\text{C}} \) (63 MHz, d⁶-DMSO) 31.5 (CH₂), 34.2 (CH₃), 119.1 (ArCH), 124.7 (ArCH), 141.4 (ArC). Data was in accordance with literature.

N-[(S)-1-Hydroxymethyl-2-methyl]propyl 1-methylimidazole-2-carboxamide

\[ \text{O} \text{N} \text{N} \text{H} \text{Pr} \]

Sodium hydride (60% dispersion in mineral oil, 8.5 mmol, 339 mg) was introduced into a two-necked flask and washed twice with petroleum ether 40-60 ºC. (S)-Valinol (7.8 mmol, 805 mg) and toluene (20 cm³) were introduced and the mixture was stirred for 1 hr, then cooled to 0 ºC. Ethyl 1-methylimidazole-2-carboxylate (7.8 mmol, 1.20 g) was added as a solution in toluene (20 cm³). The mixture was warmed to room temperature and stirred for 48 hr. Water (10 cm³) was added, the mixture was stirred for 10 min, and phases were separated. The aqueous phase was extracted with CH₂Cl₂ (3 × 50 cm³), the combined organic phases were dried over magnesium sulfate, filtered on an alumina plug, evaporated and dried under vacuum to afford the title compound as yellow crystals (709 mg, 43%). m.p. 100 – 110 ºC (from AcOEt); [α]D -52.0 (c 1.0 in CHCl₃); \( \nu_{\text{max}} \) cm⁻¹ 3475, 3202, 1643, 1565, 1473, 1412 and 1282; \( \delta_{\text{H}} \) (250 MHz, CDCl₃) 0.99 (3H, d, J 6.7 Hz, CH₃CH), 1.00 (3H, d, J 6.7 Hz, CH₃CH), 1.98 [1H, m, (CH₃)₂CH], 3.10 (1H, br s, OH), 3.67 – 3.89 [3H, m, (CH₃)₂CHCH, HOCH₂], 4.02 (3H, s, CH₃N), 6.93 (1H, s, ArCH), 6.96 (1H, s, ArCH), 7.50 (1H, br d, J 7.6 Hz, NH); \( \delta_{\text{C}} \) (63 MHz, CDCl₃) 18.7 (CH₃CH), 19.6 (CH₃CH), 29.2 [(CH₃)₂CH],

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35.6 (CH\textsubscript{3}N), 56.9 (CHN), 63.6 (CH\textsubscript{2}OH), 125.4 (ArCH), 127.4 (ArCH), 139.0 (ArC), 159.6 (CO); m/z (ES) 212.1396 (100%, MH\textsuperscript{+} C\textsubscript{10}H\textsubscript{18}N\textsubscript{3}O\textsubscript{2} requires 212.1399).

(S)-4, 5-Dihydro-4-(1-methylethyl)-2-(1-methyl-1\textsubscript{H}-imidazol-2-yl) oxazole\textsuperscript{4}

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THF (25 cm\textsuperscript{3}), N-[(S)-1-hydroxymethyl-2-methyl]propyl 1-methylimidazole-2-carboxamide (4.7 mmol, 1.0 g), titanium tert-butoxide (0.24 mmol, 0.1 cm\textsuperscript{3}) and triethylamine (7.1 mmol, 1 cm\textsuperscript{3}) were introduced into a round-bottom flask, followed by diphenylphosphoryl chloride (4.7 mmol, 0.98 cm\textsuperscript{3}). The mixture was stirred for 2 hr, while disappearance of starting material was checked by TLC. The mixture was cooled to 0 °C, potassium tert-butoxide (23.7 mmol, 2.65 g) was added progressively and the mixture was stirred for 1 hr at 0 °C then 1 hr at RT. The mixture was filtered through a plug of silica gel, and the plug was washed with AcOEt (100 cm\textsuperscript{3}). The combined organic phases were evaporated and dried to yield the title compound as pale yellow crystals (0.70 g, 77%). mp 100 – 102 °C (from AcOEt); [\(\alpha\)]\textsubscript{D} -46.0 (c 1.0 in CHCl\textsubscript{3}); (Found; C, 62.2; H, 7.9; N, 21.5. C\textsubscript{10}H\textsubscript{15}N\textsubscript{3}O requires C, 62.2; H, 7.8; N, 21.7); \(\nu\)max/cm\textsuperscript{-1} 1655, 1478, 1437, 1288 and 1245; \(\delta\)\textsubscript{H} (250 MHz, CDCl\textsubscript{3}) 0.87 (3H, d, \(J\) 6.7, CH\textsubscript{3}CH), 0.96 (3H, d, \(J\) 6.7, CH\textsubscript{3}CH), 1.65 – 1.85 (1H, m, CH\textsubscript{3}CH), 3.96 (3H, s, CH\textsubscript{3}N), 4.03 – 4.10 (2H, m, CH\textsubscript{3}CH\textsubscript{2}CH, OCH\textsubscript{2}), 4.24 – 4.39 (1H, m, OCH\textsubscript{2}), 6.92 (1H, s, ArCH\textsubscript{2}), 7.04 (1H, s, ArCH\textsubscript{2}); \(\delta\)\textsubscript{C} (63 MHz, CDCl\textsubscript{3}) 17.9 (CH\textsubscript{3}CH), 18.3 (CH\textsubscript{3}CH), 32.4 [(CH\textsubscript{3})\textsubscript{2}CH], 35.0 (CH\textsubscript{3}N), 69.7 (CH\textsubscript{2}OH), 72.7 (CHN), 124.2 (ArCH), 128.5 (ArCH), 135.6 (ArC), 155.0 (C=N); m/z (EI) 387 [8%, (M)\textsubscript{2}H\textsuperscript{+}], 216 (40, M\textsubscript{2}Na\textsuperscript{+}), 194.1294 (100, MH\textsuperscript{+} C\textsubscript{10}H\textsubscript{15}N\textsubscript{3}O requires 194.1293).

(S)-N-Ethoxycarbonylproline methyl ester\textsuperscript{5}

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To a solution of L-proline (100 mmol, 11.58g) in methanol (200 cm\textsuperscript{3}) was added potassium carbonate (100 mmol, 13.82 g). The solution was cooled down to 0 °C and ethyl chloroformate (220 mmol, 21 cm\textsuperscript{3}) was added dropwise. The mixture was allowed to warm to room temperature and was stirred overnight. Methanol was
evaporated under reduced pressure, and the residual oil was dissolved in water. This solution was extracted with chloroform (3 × 100 cm³), the combined organic phases washed with brine (100 cm³), dried over magnesium sulfate and filtered. Subsequent concentration under reduced pressure and drying on Schlenk line yielded the product as a thick, pale yellow oil (20.17 g, quantitative). δH (400 MHz, CDCl₃, mixture of rotamers) 1.21 (t, 3H, J 7.1 Hz, CH₂C₃H₃), 1.28 (t, 3H, J 7.1 Hz, CH₂C₃H₃), 1.85 – 2.30 (m, 8H, pyrrolidine ring), 3.41 – 3.64 (m, 4H, CH₂N), 3.73 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 4.04 – 4.26 (m, 4H, CH₂CH₃), 4.31 (dd, 1H, J 3.6, 8.7 Hz, CHN), 4.38 (dd, 1H, J 3.6, 8.7 Hz, CHN); δC (100.6 MHz, CDCl₃, mixture of rotamers) 14.6 (CH₂C₃H₃), 14.7 (CH₂C₃H₃), 23.5 (CH₂), 24.3 (CH₂), 29.9 (CH₂), 30.9 (CH₂), 46.3 (CH₂N), 46.7 (CH₂N), 52.1 (OCH₃), 52.2 (OCH₃), 58.8 (CHN), 59.0 (CHN), 61.2 (OCH₂), 61.4 (OCH₂), 154.6 [NC(O)], 155.2 [NC(O)], 173.3 [OC(O)], 173.4 [OC(O)]. Data was in accordance with literature.

(S)-N-Ethoxycarbonyl-α,α-diphenylprolinol

Magnesium turnings (9.84 g, 0.4 mol) were introduced into a 250 cm³ two-necked flask fitted with a dropping funnel and stirred for 5 min. Bromobenzene (0.2 mol, 21 cm³) and THF (100 cm³) were introduced into the dropping funnel and added dropwise over 1 hr. The mixture was stirred for 30 min afterwards. (S)-N-Ethoxycarbonylproline methyl ester (0.05 mol, 10.8 g) was introduced into a 500 cm³ 3-necked round bottomed flask fitted with a dropping funnel, followed by THF (100 cm³). The mixture was cooled down to 0º C and the solution of phenylmagnesium bromide was transferred via cannula to the dropping funnel, then added dropwise over 2 hr. After addition was completed, the reaction mixture was warmed to room temperature and stirred overnight. Saturated aqueous ammonium chloride (50 cm³) was added dropwise (vigorous gas evolution occured), and a white precipitate formed. The mixture was extracted with CH₂Cl₂ (2 × 200 cm³), the combined organic phases washed with brine (100 cm³) and concentrated under reduced pressure. Dry flash chromatography yielded the title compound as a yellow solid (6.61 g, 40%), m.p. 112 – 113 ºC (from petroleum ether 60 – 80 ºC, lit. 6115 – 116.5 ºC from hexane); [α]D -144.7 (c 1.03 in CHCl₃, lit. 6 -146, c 1.04 in CHCl₃); δH (400 MHz, CDCl₃) 0.81 (bs,
1H, ring), 1.26 (t, 3H, J 6.8 Hz, OCH₂CH₃), 1.46 – 1.56 (m, 1H, ring), 1.93 – 2.00 (m, 1H, ring), 2.08 – 2.17 (m, 1H, ring), 2.97 (bs, 1H, ring), 3.43 (q, 1H, J 9.1 Hz, ring), 4.02 – 4.23 (m, 2H, OCH₂CH₃), 4.95 (dd, 1H, J 3.4, 8.8 Hz, CHN), 6.11 (bs, 1H, OH), 7.28 – 7.44 (m, 10H, ArCH); δC (100 MHz, CDCl₃) 14.7 (OCH₂CH₃), 23.0 (CH₂), 29.7 (CH₂), 47.8 (NCH₂), 61.9 (OCH₂CH₃), 65.9 (CHN), 81.6 (Ph₂COH), 127.1 (ArCH), 127.2 (ArCH), 127.5 (ArCH), 127.6 (ArCH), 127.9 (ArCH), 128.2 (ArCH), 143.7 (ArC), 146.4 (CO). Data was in accordance with the literature.

(S)-α,α-Diphenylprolinol

(S)-N-Ethoxycarbonyl-α,α-diphenylprolinol (5.12 g, 17 mmol) was introduced into a round-bottom flask fitted with a condenser, methanol (70 cm³) and potassium hydroxide (205 mmol, 11.5 g) were added and the mixture was refluxed for 36 hr. Methanol was evaporated under reduced pressure, water (100 cm³) and CH₂Cl₂ were added and the phases were separated. The remaining oil was extracted with CH₂Cl₂ (4 × 50 cm³), the combined organic phases washed with brine (100 cm³) and concentrated under reduced pressure to yield (S)-α,α-diphenylprolinol as brown crystals (3.36 g, 78% yield). m.p. 63 – 65 °C (from petroleum 40 – 60 °C, lit.⁷ 79 – 79.5 °C from hexane); [α]D -68.8 (c 0.305 in MeOH, lit.⁷ -54.3, c 0.261 in MeOH); δH (250 MHz, CDCl₃) 1.55 – 1.81 (m, 4H, CH₂), 2.91 – 3.10 (m, 2H, CH₂N), 4.28 (t, 1H, J 7.5 Hz, CHN), 7.16 – 7.35 (m, 6H, ArCH), 7.50 – 7.61 (m, 4H, ArCH); δC (63 MHz, CDCl₃) 25.5 (CH₂), 26.3 (CH₂), 46.8 (CH₂N), 64.5 (CHN), 77.1 (CPh₂OH) 125.6 (ArCH), 125.9 (ArCH), 126.3 (ArCH), 126.4 (ArCH), 128.0 (ArCH), 128.2 (ArCH), 145.4 (ArC), 148.2 (ArC). Data was in accordance with literature.

(S)-N-Ethoxycarbonyl-α,α-dinaphth-2-ylprolinol

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Magnesium turnings (2.9 g, 0.12 mol) were introduced into a 250 cm³ two-necked flask fitted with a dropping funnel and stirred for 10 min. 2-Bromonaphthalene (0.06 mol, 12.52 g) and THF (100 cm³) were introduced into the dropping funnel and added dropwise over 1 hr. The mixture was heated to reflux and stirred for 20 min afterwards. (S)-N-Ethoxycarbonylproline methyl ester (0.03 mol, 5.45 g) was introduced into a 500 cm³ 3-necked round bottomed flask fitted with a dropping funnel, followed by THF (50 cm³). The mixture was cooled to 0º C and the solution of 2-naphthylmagnesium bromide was transferred via cannula to the dropping funnel, then added dropwise over 1 hr. After addition was completed, the reaction mixture was stirred for 3 hr at 0 ºC, then warmed to room temperature and stirred overnight. Saturated aqueous ammonium chloride (50 cm³) was added dropwise (vigorous gas evolution occurred), and a white precipitate formed. The mixture was extracted with CH₂Cl₂ (2 × 200 cm³). The combined organic phases were washed with brine (100 cm³) and concentrated under reduced pressure. Dry flash chromatography (petroleum ether 40 – 60 ºC/AcOEt) yielded the title compound as a glassy yellow solid (2.54 g, 20%). m.p. 103 – 104 ºC (lit.⁸ 105 – 106 ºC); [α]D -187.0 (c 1.05 in CHCl₃, lit.⁸ - 222.0, c 1.0 in CHCl₃); ν (thin film, cm⁻¹) 3370, 2981, 1664, 1423, 1381, 1335, 1197, 1127; δH (400 MHz, CDCl₃) 0.78 (bs, 1H, CH₂), 1.24 – 1.30 (m, 3H, CH₃CH₂O), 1.48 – 1.52 (m, 1H, CH₂), 2.12 – 2.30 (m, 2H, CH₂), 3.00 (bs, 1H, CH₂), 3.44 – 3.47 (m, 1H, CH₂), 4.12 – 4.17 (m, 2H, CH₃CH₂O), 5.18 (dd, 1H, J 3.5, 8.8 Hz, CHN), 7.48 – 7.59 (m, 6H, ArCH), 7.79 – 7.91 (m, 8H, ArCH); δC (100 MHz, CDCl₃) 14.6 (CH₃CH₂O), 23.2 (CH₂), 29.8 (CH₂), 47.8 (CH₂), 62.0 (CH₃CH₂O), 66.2 (CHN), 81.9 (CAr₂OH), 125.2 (ArCH), 125.9 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 126.5 (ArCH), 127.0 (ArCH), 127.2 (ArCH), 127.3 (ArCH), 127.5 (ArCH), 127.9 (ArCH), 128.4 (ArCH), 132.7 (ArC), 132.8 (ArC), 141.1 (ArC), 143.7 (CO). Data was in accordance with literature.

[(S)-2-(Hydroxydiphenylmethyl)-pyrrolidin-1-yl]-(1-methyl-1H-imidazol-2-yl)-methanone

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Sodium hydride (60% dispersion in mineral oil, 12 mmol, 0.48 g) was introduced into a two-necked flask and washed twice with petroleum ether. Toluene (5 cm³) and (S)-α,α-diphenylprolinol (2.33 g, 9.2 mmol) were introduced and the solution was stirred at room temperature for 30 min. Ethyl 1-methylimidazole-2-carboxylate (1.53 g, 11 mmol) was added and the mixture was heated at 70 ºC, stirred for 40 hr and cooled to RT. Water (5 cm³) was added, the mixture extracted with CH₂Cl₂ (4 × 20 cm³, the combined organic phases were washed with brine (20 cm³), dried over sodium sulfate and evaporated. The remaining oil was purified by flash chromatography (AcOEt, silica gel) to yield the product as white crystals that were recrystallised from CH₂Cl₂ and petroleum ether 40 – 60 ºC (1.29 g, 39% yield); m.p. 143 – 145 ºC; [α]₀ -88 (c 0.5 in CHCl₃); (Found: C 72.78; H 6.60; N 11.66; C₂₂H₂₃N₃O₂ requires C 73.11; H 6.41; N 11.63); ν (thin film, cm⁻¹) 3387, 1613, 1458; δH (500 MHz, d⁶-DMSO, 101.3 ºC) 1.64 – 1.86 (m, 2H, CH₂CH₂), 1.94 – 2.00 (m, 1H, CH₂CH₂N), 2.07 – 2.15 (m, 1H, CH₂CH₂N), 2.96 (s, 3H, NH₃), 3.49 (ddd, 1H, J 6.7, 9.1, 11.6 Hz, CH₂N), 3.93 (ddd, 1H, J 5.1, 9.1, 11.6 Hz, CH₂N), 5.84 (s, 1H, CHN), 6.16 (bs, 1H, OH), 6.86 (d, 1H, J 1.1 Hz, ArCH), 6.98 (s, 1H, ArCH), 7.04 – 7.09 (m, 3H, ArCH), 7.14 (bd, 2H, J 6.4 Hz, ArCH), 7.21 – 7.25 (m, 1H, ArCH), 7.30 – 7.34 (m, 2H, ArCH), 7.45 – 7.47 (m, 2H, ArCH); δC (126 MHz, d⁶-DMSO, 101.3ºC) 22.2 (CH₂), 27.2 (CH₂), 33.7 (CH₂), 47.5 (CH), 63.5 (CH₃), 80.8 (Ph₂COH), 123.2 (ArCH), 125.4 (ArCH), 125.5 (ArCH), 126.03 (ArCH), 126.06 (ArCH), 126.1 (ArCH), 126.5 (ArCH), 127.1 (ArCH), 140.2 (ArC), 145.3 (ArC), 145.4 (ArC), 159.0 (CO); m/z (ES) 344 (37%), 356 (73), 362 (30), 370 (36), 384 (5), 452 (100), 362.1872 (MH⁺ C₂₂H₂₄N₃O₂ requires 362.1869).

\[(S)-2-(Hydroxymethyl)-pyrrolidin-1-yl)-(1-methyl-1H-imidazol-2-yl)-methanone\]

Procedure was the same as above, except starting material was commercial (S)-prolinol (1.01 g, 10 mmol). Title compound was isolated by flash chromatography (95/5 CH₂Cl₂/MeOH, silica gel) as a yellow oil (690 mg, 33%). [α]₀ -12.6 (c 3.49, CHCl₃); ν (thin film, cm⁻¹) 3415, 1616, 1461; δH (500 MHz, d⁶-DMSO, mixture of rotamers) 1.75 – 1.95 (m, 8H, prolinol ring), 3.21 [dd, 2H, J 6.8, 10.4 Hz, (CH₂)₂CH₃N], 3.40 – 3.47 (m, 4H, CH₂N), 3.57 – 3.64 (m, 2H, CH₂OH), 3.79 – 3.85
Supporting information

(m, 6H, NCH₃), 4.17 (heptet, 1H, J 3.6 Hz, CH₂OH), 4.74 (bs, 1H, OH), 4.81 (t, 1H, J 5.7 Hz, CH₂OH), 5.16 (bs, 1H, OH), 6.97 (s, 1H, ArCH), 6.98 (s, 1H, ArCH), 7.29 (s, 2H, ArCH); δ C (126 MHz, d⁶-DMSO, mixture of rotamers) 21.0 (C₂H), 24.0 (C₂H), 26.4 (CH₂), 27.6 (CH₂), 34.5 (NCH₂), 34.9 (NCH₂), 45.9 (CHN), 49.4 (CHN), 59.2 (NCH₃), 60.9 (CH₂OH), 62.5 (CH₂OH), 124.2 (ArCH), 124.5 (ArCH), 126.4 (ArCH), 126.7 (ArCH), 140.2 (ArC), 140.4 (ArC), 158.7 (CO), 158.8 (CO); m/z (ES) 210 (40%), 232.1069 (MNa⁺ C₁₀H₁₅N₃O₂Na requires 232.1062).

(S)-1-(1-Methyl-1H-imidazol-2-ylmethyl)-pyrrolidine-2-carboxylic acid methyl ester

L-Proline (29 mmol, 3.32 g) was dissolved in methanol (50 cm³), and thionyl chloride (43 mmol, 3.20 cm³) was added dropwise. The mixture was stirred for 3.5 hr at RT and concentrated under reduced pressure. The resulting yellow was dissolved in DMF (20 cm³), potassium carbonate (15 g) was added, followed by 2-chloromethyl-1-methylimidazole hydrochloride (9 mmol, 1.51 g). The mixture was stirred at RT for 24 hr, dissolved in water (100 cm³) and extracted with CH₂Cl₂ (3 × 100 cm³). The organic phases were combined, dried over sodium sulfate, concentrated under reduced pressure and co-evaporated with toluene. The desired compound was obtained as a yellow oil (1.23 g, 61%). [α]D -71.7 (c 0.6, CHCl₃); ν (thin film, cm⁻¹) 2818, 1734, 1651, 1503, 1439, 1284, 1203, 1175; ¹H NMR (250 MHz, CDCl₃) δH 1.73 – 1.97 (m, 3H, CH₂), 2.10 – 2.23 (m, 1H, CH₂), 2.43 (app. q, 1H, J 8.5 Hz, NCH₂), 2.89 – 2.97 (m, 1H, NCH₂), 3.23 (dd, 1H, J 6.4, 9.2 Hz, MeOOCCHN), 3.63 (d, 1H, J 13.1 Hz, NCH₂Ar), 3.64 (s, 3H, NCH₃), 3.75 (s, 3H, OCH₃), 3.93 (d, 1H, J 13.1 Hz, NCH₂Ar), 6.81 (d, 1H, J 1.2 Hz, ArCH), 6.88 (d, 1H, J 1.2 Hz, ArCH); δC 23.1 (CH₂), 29.4 (CH₂), 32.7 (NCH₃), 50.7 (CH₃O), 51.6 (CH₂N), 53.6 (ArCH₂N), 65.1 (CHN), 121.4 (ArCH), 126.9 (ArCH), 145.2 (ArC), 174.3 (CO); m/z (ES) 224.1396 (MH⁺ C₁₁H₁₈N₃O₂ requires 224.1399).
Magnesium turnings (441 mg, 18 mmol) were introduced into a 100 cm³ two-necked flask fitted with a nitrogen inlet, a condenser and a dropping funnel. After stirring for 5 min, and a solution of bromobenzene (1.75 cm³, 16.5 mmol) in diethyl ether (20 cm³) was added progressively. After addition was completed, diethyl ether (10 cm³) was added, and the mixture was stirred for 30 min, then cooled to 0 ºC. (S)-1-(1-Methyl-1H-imidazol-2-ylmethyl)-pyrrolidine-2-carboxylic acid methyl ester (1.07 g, 4.8 mmol) was added dropwise as a solution in diethyl ether (10 cm³). After addition was completed, diethyl ether (10 cm³) was added and the mixture was stirred at RT for 48 hr. It was then cooled down to 0ºC and saturated aqueous ammonium chloride (50 cm³) was added. The phases were separated and aqueous phase was extracted with ether (2 × 50 cm³) and ethyl acetate (2 × 50 cm³). The combined organic phases were washed with brine (2 × 100 cm³), dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was dried on a Schlenk line, and the desired compound was isolated by flash chromatography (95/5 \( \text{CH}_2\text{Cl}_2 \)/methanol) as pale yellow crystals (1.03 g, 54% yield). m.p. 139 – 140 ºC; \([\alpha]_D\) -9.5 (c 1.48, CHCl₃); (Found: C 76.01; H 7.32; N 11.65; \( \text{C}_{22}\text{H}_{25}\text{N}_{3}\text{O} \) requires C 76.05; H 7.25; N 12.09); ν (thin film, cm⁻¹) 3419, 1644; δH (500 MHz, d⁶-DMSO) 1.60 – 1.72 (m, 3H, \( \text{C}_2\text{H}_2\text{C}_2\text{H}_2 \)), 1.87 – 1.95 (m, 1H, \( \text{C}_2\text{H}_2\text{CH}_2 \)), 2.67 – 2.77 (m, 2H, \( \text{CH}_2\text{N} \)), 3.16 (s, 3H, \( \text{NCH}_3 \)), 3.35 (d, 1H, AB, \( J 13.2 \text{ Hz}, \text{NCH}_2\text{Ar} \)), 3.42 (d, 1H, AB, \( J 13.2 \text{ Hz}, \text{NCH}_2\text{Ar} \)), 4.08 (dd, 1H, \( J 4.8, 9.0 \text{ Hz}, \text{HOPh}_2\text{CCHN} \)), 6.69 (s, 1H, ArCH)), 6.84 (s, 1H, ArCH)), 7.11 – 7.15 (m, 2H, ArCH), 7.25 – 7.28 (m, 4H, ArCH)), 7.55 (dd, 2H, \( J 1.2, 8.2 \text{ Hz}, \text{ArCH} \)), 7.74 (dd, 2H, \( J 1.2, 8.2 \text{ Hz}, \text{ArCH} \)); δC (127 MHz, CDCl₃) 23.9 (CH₃), 29.6 (CH₂), 32.6 (NCH₃), 52.3 (NCH₂), 55.4 (NCH₂Ar), 70.8 (CHN), 77.8 (Ar₂COH), 121.2 (ArCH), 125.1 (ArCH), 125.7 (ArCH), 126.2 (ArCH), 126.6 (ArCH), 127.0 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 145.5 (ArC), 146.6 (ArC), 148.1 (ArC); m/z (ES) 330 (28%), 348.2085 (MH⁺ \( \text{C}_{22}\text{H}_{26}\text{N}_{3}\text{O} \) requires 348.2076).
Supporting information

[(S)-2-(Hydroxynaphth-2-ylmethyl)-pyrrolidin-1-yl]-[1-methyl-1H-imidazol-2-yl]-methanone

(S)-N-Ethoxycarbonyl-α,α-dinaphth-2-ylprolinol (2.54 g, 6 mmol) was introduced in a round-bottom flask fitted with a condenser (the reaction was carried out under open atmosphere), MeOH (30 cm³), potassium hydroxide (205 mmol, 11.5 g) were added and the mixture was refluxed for 6 hr. The solvent was evaporated under reduced pressure, and the remaining oil was extracted with CH₂Cl₂ (3 × 70 cm³). The combined organic phases were washed with brine (50 cm³), dried over magnesium sulfate, concentrated under reduced pressure and dried on Schlenk line, to yield (S)-α,α-dinaphth-2-ylprolinol as brown crystals (523 mg, 28% yield), which were used in the next step without further purification.

Sodium hydride (60% dispersion in mineral oil, 3 mmol, 120 mg) was introduced into a two-necked flask and washed twice with petroleum ether. Toluene (5 cm³) and (S)-α,α-dinaphth-2-ylprolinol were introduced and the solution was stirred at room temperature for 30 min. Ethyl 1-methylimidazole-2-carboxylate (347 mg, 2.25 mmol) was added and the mixture was stirred at RT for 40 hr. Water (25 cm³) was added, the solution was extracted with CH₂Cl₂ (3 × 25 cm³). The combined organic phases were washed with brine (20 cm³), dried over sodium sulfate, filtered and evaporated. The remaining oil was purified by flash chromatography (ethyl acetate) to yield the product as white crystals that were recrystallised from petroleum ether 40 – 60 ºC (169 mg, 24% yield). m.p. 140 – 145 ºC (AcOEt/petroleum ether 40-60 ºC); [α]D -102.1 (c 0.48, CHCl₃); (Found: C 77.68; H 5.84; N 9.02; C₂₀H₂₇N₃O₂ requires C 78.07; H 5.90; N 9.10); ν (thin film, cm⁻¹) 3421, 3056, 2980, 1614, 1506, 1458, 1359, 1281, 1203, 1148, 1123; δH (500 MHz, d⁶-DMSO, 101.4 ºC) 1.72 – 1.81 (m, 1H, CH₂), 1.85 – 1.93 (m, 1H, CH₂), 2.12 – 2.18 (m, 1H, CH₂), 2.23 – 2.31 (m, 1H, CH₂), 2.96 (d, 3H, J 1.6 Hz, NCH₃), 3.60 (ddd, 1H, J 6.8, 9.2, 11.6 Hz, NCH₂), 3.96 (ddd, 1H, J 5.0, 9.0, 11.6 Hz, NCH₂), 6.13 (d, 1H, J 0.7 Hz, NCH), 6.43 (br s, 1H, OH), 6.77 (s, 1H, ArCH), 6.84 (d, 1H, J 1.1 Hz, ArCH),
7.17 (d, 1H, *J* 8.4 Hz, ArCH), 7.38 – 7.44 (m, 2H, ArCH), 7.47 – 7.52 (m, 3H, ArCH), 7.62 (dd, 1H, *J* 1.9, 8.7 Hz, ArCH), 7.71 – 7.75 (m, 2H, ArCH), 7.82 – 7.87 (m, 3H, ArCH), 7.91 – 7.93 (m, 1H, ArCH), 8.06 (d, 1H, *J* 1.3 Hz, ArCH); δC (125 MHz, d⁶-DMSO, 101.4 ºC) 23.3 (CH₂), 28.2 (CH₂), 33.8 (CH₃), 48.5 (CH₂N), 63.3 (CHN), 81.3 (Ar₂COH), 123.2 (ArCH), 124.3 (ArCH), 124.9 (ArCH), 125.0 (ArCH), 125.1 (ArCH), 125.2 (ArCH), 125.4 (ArCH), 125.5 (ArCH), 126.4 (ArCH), 126.6 (ArCH), 126.7 (ArCH), 127.6 (ArCH), 127.7 (ArCH), 131.3 (ArC), 131.5 (ArC), 131.7 (ArC), 132.1 (ArC), 139.0 (ArC), 142.8 (ArC), 142.9 (ArC), 158.0 (CO); m/z (ES) 444 (18%), 462.2166 (MH⁺ C₃₀H₂₈N₃O₂ requires 462.2182).

**General procedure A for the preparation of imines from their ketone precursor**
Activated 4Å molecular sieve (40 g), toluene (80 cm³), ketone (100 mmol) and aniline or *p*-anisidine (130 mmol) were introduced into a 250 cm³ two-necked flask. The mixture was stirred at RT for 20 hr and filtered. The title compound was afforded by distillation or crystallisation from petroleum ether 40 – 60 ºC.

**General procedure B for the preparation of imines from their ketone precursor**
Ketone (20 mmol), amine (aniline or *p*-anisidine, 22 mmol) and activated 4Å molecular sieves (4 g) were introduced in a Smith Process Vial™ containing a small stirrer bar. The vial was sealed and heated with a microwave reactor. The desired imine was isolated by crystallisation (and further purified by recrystallisation from petroleum ether) or by Kugelrohr distillation.

**General procedure C for the preparation of imines from their ketone precursor**
Ketone (1 eq.), *p*-anisidine (1.1 eq.), *p*-toluene sulfonic acid (0.01 eq.) and toluene (100 cm³) were introduced in a round-bottom flask and heated overnight under Dean-Stark conditions. The imine crystallised after partial evaporation of toluene and was isolated by filtration. Recrystallisation from toluene was performed when necessary.

![1-Phenylethylidene]-phenylamine
Prepared according to general procedure A from acetophenone and aniline, purified by distillation under reduced pressure. Pale yellow crystals (64%). m.p. 42 – 43 ºC (from petroleum ether 40 – 60 ºC, lit.9 39 – 40 ºC); δ\textsubscript{H} (250 MHz, CDCl\textsubscript{3}) 2.23 (3H, s, CH\textsubscript{3}), 6.80 (app. dd, 2H, J 1.2, 7.3 Hz, ArCH\textsubscript{2}), 7.09 (app. t, 1H, J 7.3 Hz, ArCH), 7.35 (app. t, 2H, J 7.8 Hz, ArCH\textsubscript{2}), 7.42 – 7.48 (m, 3H, ArCH\textsubscript{2}), 7.95 – 8.00 (m, 2H, ArCH\textsubscript{2}); δ\textsubscript{C} (62.9 MHz, CDCl\textsubscript{3}) 17.4 (CH\textsubscript{3}), 119.4 (ArCH), 123.3 (ArCH), 127.2 (ArCH), 128.4 (ArCH), 129.0 (ArCH), 130.5 (ArCH), 139.5 (ArC), 151.7 (ArC), 165.5 (C=N). Data was in accordance with the literature.

[1-(4-Chlorophenyl)ethylidene]-phenylamine

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{phenyl} & \quad \text{Ar}
\end{align*}
\]

Prepared according to general procedure A from 4-chloroacetophenone and aniline, purified by crystallisation from petroleum ether 40 – 60 ºC (yellow needles, 79%). m.p. 93 – 94 ºC (from petroleum ether 40 – 60 ºC); (Found C, 73.04; H, 5.10; N, 6.05; Cl, 15.49; C\textsubscript{14}H\textsubscript{12}NCl requires C, 73.20; H 5.27; N 6.10; Cl 15.43); ν (thin film, cm\textsuperscript{-1}) 3425, 1634, 1592; δ\textsubscript{H} (250 MHz, CDCl\textsubscript{3}) 2.21 (s, 3H, CH\textsubscript{3}), 6.75 – 6.80 (m, 2H, ArCH\textsubscript{2}), 7.06 – 7.13 (m, 1H, ArCH\textsubscript{2}), 7.31 – 7.43 (m, 4H, ArCH\textsubscript{2}), 7.89 – 7.94 (m, 2H, ArCH\textsubscript{2}); δ\textsubscript{C} (63 MHz, CDCl\textsubscript{3}) 17.2 (CH\textsubscript{3}), 119.3 (ArCH), 123.4 (ArCH), 128.6 (ArCH), 129.0 (ArCH), 136.6 (ArC), 137.9 (ArC), 151.4 (ArC), 164.2 (C=N); m/z (EI) 77 (78%), 118 (22), 214 (100), 216 (46), 229 (70), 229.0668 (M\textsuperscript{+} C\textsubscript{14}H\textsubscript{12}NCl requires 229.0658).

[1-Phenylpropylidene]-phenylamine\textsuperscript{11}

\[
\begin{align*}
\text{phenyl} & \quad \text{N} \\
\text{isopropyl} & \quad \text{Ar}
\end{align*}
\]

Prepared using general procedure B from propiophenone, isolated by crystallisation from petroleum ether. Yellow crystals (12%); δ\textsubscript{H} (250 MHz, CDCl\textsubscript{3}, isomer ratio 91/9) 1.08 (t, 3H, J 7.6 Hz, CH\textsubscript{3}CH\textsubscript{3}, major), 1.23 (t, 3H, J 7.3 Hz, CH\textsubscript{2}CH\textsubscript{3}, minor), 2.66...
Supporting information

(q, 2H, J 7.6 Hz, CH₂CH₃, major), 2.80 (q, 2H, J 7.3 Hz, CH₂CH₃, minor), 6.63 (app. d, 2H, J 8.5 Hz, ArH, minor), 6.80 (app. dd, 2H, J 1.1, 8.4 Hz, ArH, major), 6.88 (app. t, 1H, J 7.3 Hz, ArH, minor), 7.08 (app. tt, 1H, J 1.1, 7.3 Hz, ArH, major), 7.18 – 7.23 (m, 3H, ArH, minor), 7.35 (app. tt, 2H, J 1.9, 7.9 Hz, ArH), 7.43 – 7.48 (m, 3H, ArH), 7.91 – 7.95 (m, 2H, ArH); δC (62.9 MHz, CDCl₃) 10.9 (CH₃, minor), 12.9 (CH₃, major), 23.5 (CH₂, major), 34.4 (CH₂, minor), 119.1 (ArCH), 120.9 (ArCH), 123.0 (ArCH), 127.6 (ArCH), 127.8 (ArCH), 128.0 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 129.0 (ArCH), 130.3 (ArCH), 138.1 (ArC), 151.6 (ArC), 170.7 (C=N). Data was in accordance with literature.

[3,4-Dihydro-2H-naphthalenylidene]-phenylamine¹⁰

Prepared using general procedure B from α-tetralone and aniline, isolated by flash chromatography (90/10 petroleum ether 60 – 80 °C/AcOEt). Orange crystals (52%). m.p. 73 °C (lit.¹⁰ 74 – 75 °C); δH (250 MHz, CDCl₃) 1.91 (p, 2H, J 6.2 Hz, ArCH₂CH₂), 2.51 (t, 2H, J 6.2 Hz, ArCH₂CH₂), 2.90 (t, 2H, J 6.2 Hz, CH₂C=N), 6.79 (d, 2H, J 8.2 Hz, ArCH), 7.06 (t, 1H, J 7.3 Hz, ArCH), 7.18 – 7.39 (m, 5H, ArH), 8.30 (d, 1H, J 7.6 Hz, ArH); δC (62.8 MHz, CDCl₃) 23.1 (CH₂), 29.9 (CH₂), 30.0 (CH₂), 119.6 (ArCH), 123.1 (ArCH), 126.4 (ArCH), 126.5 (ArCH), 128.8 (ArCH), 129.0 (ArCH), 129.1 (ArCH), 130.7 (ArCH), 130.8 (ArCH), 134.0 (ArC), 141.4 (ArC), 151.8 (ArC), 165.6 (C=N). Data was in accordance with literature.

[1-Phenylethylidene]-(4-methoxyphenyl)-amine¹¹

Prepared according to general procedure A from acetophenone and p-anisidine, purified by crystallisation from petroleum ether 60 – 80 °C (yellow crystals, 52%). m.p. 86 °C (lit.¹² 84 – 85 °C); δH (250 MHz, CDCl₃) 2.25 (s, 3H, CH₃C=N), 3.81 (s,
Supporting information

3H, OCH₃), 6.75 [(AX)₂, 2H, ArCH], 6.90 [(AX)₂, 2H, ArCH], 7.40 – 7.47 (m, 3H, ArCH), 7.93 – 7.98 (m, 2H, ArCH); δC (63 MHz, CDCl₃) 17.3 (CH₃C=N), 55.5 (CH₃O), 114.2 (ArCH), 120.7 (ArCH), 127.1 (ArCH), 128.3 (ArCH), 130.3 (ArCH), 139.8 (ArC), 144.8 (ArC), 155.9 (ArC), 165.7 (C=N). Data was in accordance with literature.

[1-Phenylpropylidene]-(4-methoxyphenyl)-amine¹³

Prepared according to general procedure B from propiophenone, purified by recrystallisation from petroleum ether 40 – 60 °C (Brown crystals, 33%). m.p. 102 – 103 °C (lit.¹³ 101 – 103 °C); δH (250 MHz, CDCl₃, isomer ratio 88/12) 1.08 (t, 3H, J 7.6 Hz, CH₂CH₃, major), 1.20 (t, 3H, J 7.6 Hz, CH₂CH₃, minor), 2.68 (q, 2H, J 7.6 Hz, CH₂CH₃, major), 2.79 (q, 2H, J 7.6 Hz, CH₂CH₃, minor), 3.70 (s, 3H, OCH₃, minor), 3.81 (s, 3H, OCH₃, major), 6.52 – 6.68 (m, 4H, ArCH, minor), 6.74 [(AX)₂, 2H, ArCH major], 6.91 [(AX)₂, 2H, ArCH, major], 7.05 – 7.08 (m, 2H, ArCH, minor), 7.19 – 7.23 (m, 3H, ArCH, minor), 7.41 – 7.49 (m, 3H, ArCH, major), 7.88 – 7.96 (m, 2H, ArCH, major); δC (63 MHz, CDCl₃) 11.0 (CH₂CH₃, minor), 12.9 (CH₂CH₃, major), 23.3 (CH₂CH₃, major), 34.6 (CH₂CH₃, minor), 55.3 (OCH₃, minor), 55.5 (OCH₃, major), 113.8 (ArCH, minor), 114.3 (ArCH, major), 120.3 (ArCH, major), 122.3 (ArCH, minor), 127.6 (ArCH, major), 127.8 (ArCH, minor), 128.1 (ArCH, minor), 128.2 (ArCH, minor), 128.5 (ArCH, major), 130.2 (ArCH, major), 138.3 (ArC) 144.8 (ArC), 155.8 (ArC), 171.4 (C=N). Data was in accordance with literature.

[3,4-Dihydro-2H-naphthalenylidene]-(4-methoxyphenyl)-amine¹⁴

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Prepared according to general procedure A from $\alpha$-tetralone and $p$-anisidine. Purified by recrystallisation from petroleum ether 60 – 80 ºC. Dark brown crystals (67%). m.p. 115 – 116 ºC (lit.\textsuperscript{14} 109 – 112 ºC); $\delta$\textsubscript{H} (250 MHz, CDCl\textsubscript{3}) 1.91 (p, 2H, $J$ 6.5 Hz, ArCH\textsubscript{2}CH\textsubscript{2}), 2.56 (t, 2H, $J$ 6.5 Hz, ArCH\textsubscript{2}), 2.90 (t, 2H, $J$ 6.5 Hz, CH\textsubscript{2}C=N), 3.81 (s, 3H, OCH\textsubscript{3}), 6.76 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{2}], 6.91 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{2}], 7.19 (d, 1H, $J$ 8.9 Hz, ArCH), 7.23 – 7.40 (m, 2H, ArCH), 8.31 (dd, 1H, $J$ 1.5, 7.6 Hz, ArCH); $\delta$\textsubscript{C} (63 MHz, CDCl\textsubscript{3}) 23.1 (CH\textsubscript{n}), 29.9 (CH\textsubscript{n}), 30.0 (CH\textsubscript{n}), 55.5 (OCH\textsubscript{3}), 114.3 (ArCH), 120.9 (ArCH), 126.3 (ArCH), 126.4 (ArCH), 128.7 (ArCH), 130.5 (ArCH), 134.1 (ArC), 141.2 (ArC), 144.7 (ArC), 155.8 (ArC), 165.9 (C=N). Data was in accordance with literature.

\textbf{[1-Cyclohexylethylidene]- (4-methoxyphenyl)-amine\textsuperscript{15}}

Prepared using general procedure B from cyclohexyl methyl ketone, isolated by Kugelrohr distillation. Yellow oil (43%). $\delta$\textsubscript{H} (250 MHz, CDCl\textsubscript{3}, isomer ratio 80/20) 1.25 – 1.47 (m, 6H, cyclohexyl ring), 1.71 (s, 3H, CH\textsubscript{3}C=N, minor), 1.73 (s, 3H, CH\textsubscript{3}C=N, major), 1.79 – 1.92 (m, 4H, cyclohexyl ring), 2.22 – 2.33 (m, 1H, CHCNCH\textsubscript{3}), 3.76 (s, 3H, OCH\textsubscript{3}, major), 3.78 (s, 3H, OCH\textsubscript{3}, minor), 6.60 [(AX)\textsubscript{2}, 2H, ArCH], 6.82 [(AX)\textsubscript{2}, 2H, ArCH]; $\delta$\textsubscript{C} (63 MHz, CDCl\textsubscript{3}) 17.5 (CH\textsubscript{3}CN, major), 22.4 (CH\textsubscript{3}CN, minor), 25.5 (CH\textsubscript{2}, minor), 26.2 (CH\textsubscript{2}), 30.3 (CH\textsubscript{2}), 42.3 (CH, minor), 49.5 (CH, major), 55.4 (OCH\textsubscript{3}), 114.1 (ArCH, major), 115.9 (ArCH, minor), 120.3 (ArCH, major), 120.5 (ArCH, minor), 144.9 (ArC), 155.6 (ArC), 176.1 (C=N); Data was in accordance with literature.

\textbf{(4-Methoxy-phenyl)-[1-naphthalen-1-yl-ethylidene]-amine\textsuperscript{16}}
Prepared using general procedure C. Yellow solid, m.p. 72 – 75 °C (from CH₂Cl₂/petroleum ether 40 – 60 °C, not reported previously); ν (thin film, cm⁻¹) 3055, 2999, 2951, 2833, 1640, 1503, 1464, 1440, 1363, 1292, 1242, 1208, 1180, 1104, 1035; δ_H (400 MHz, CDCl₃, isomer ratio 60/40) 2.36 (s, 3H, C₅H₃C=N, major), 2.60 (s, 3H, C₅H₃C=N, minor), 3.58 (s, 3H, OCH₃, minor), 3.84 (s, 3H, OCH₃, major), 6.47 – 6.52 (m, ArCH), 6.58 – 6.63 (m, ArCH), 6.89 – 7.01 (m, ArCH), 7.13 – 7.18 (m, ArCH), 7.31 – 7.37 (m, ArCH), 7.41 – 7.62 (m, ArCH), 7.70 – 7.80 (m, ArCH), 7.86 – 7.90 (m, ArCH), 8.32 – 8.36 (m, ArCH); δ_C (100 MHz, CDCl₃) 22.0 (C₅H₃C=N), 29.9 (C₅H₃C=N), 55.1 (OCH₃), 55.5 (OCH₃), 113.6 (ArC₅H), 114.5 (ArC₅H), 120.9 (ArCH), 121.8 (ArCH), 124.7 (ArCH), 125.1 (ArCH), 125.2 (ArCH), 125.4 (ArCH), 126.1 (ArCH), 126.2 (ArCH), 126.6 (ArCH), 126.8 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 129.2 (ArC), 129.4 (ArCH), 130.3 (ArC), 133.3 (ArC), 134.1 (ArC), 137.9 (ArC), 139.6 (ArC), 143.5 (ArC), 144.3 (ArC), 156.0 (ArC), 156.3 (ArC), 169.7 (C=N), 170.2 (C=N); m/z (EI) 69 (26%), 77 (15), 92 (12), 127 (16), 152 (11), 153 (14), 217 (15), 260 (98), 261 (26), 274 (83), 275 (100), 275.1301 (M⁺ C₁₉H₁₇NO requires 275.1310). Data was in accordance with literature.

(4-Methoxy-phenyl)-[1-naphthalen-2-yl-ethylidene]-amine

Prepared using general procedure C (63%), but crystallised directly out of solution. Yellow crystals, m. p. 148 – 150 °C (from petroleum ether 40 – 60 °C, none reported in literature); δ_H (400 MHz, CDCl₃) 2.41 (s, 3H, C₅H₃C=N), 3.86 (s, 3H, CH₃O), 6.83 [(AX)₂, 2H, ArCH], 6.96 [(AX)₂, 2H, ArCH], 7.53 – 7.59 (m, 2H, ArCH), 7.89 – 7.97 (m, 3H, ArCH), 8.25 (dd, J 1.6, 8.6 Hz, ArCH), 8.33 (s, 1H, ArCH); δ_C (100.6 MHz, CDCl₃) 17.3 (H₃CC=N), 55.5 (CH₃O), 114.3 (ArCH), 120.8 (ArCH), 124.3 (ArCH), 126.3 (ArCH), 127.1 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 128.0 (ArCH), 128.9 (ArCH), 133.0 (ArC), 134.4 (ArC), 137.1 (ArC), 144.9 (ArC), 156.0 (ArC), 165.5 (C=N). Data was in accordance with literature.
Supporting information

[1-(4-Methoxyphenyl)ethylidene]-(4-methoxyphenyl)-amine\(^{17}\)

Prepared using general procedure C (79%). Purified by crystallisation from toluene. Yellow crystals, m.p. 132 – 134 °C (from petroleum ether 40 – 60 °C, lit.\(^{17}\) 126 °C); \(\delta_H\) (400 MHz, CDCl\(_3\)) 2.21 (s, 3H, CH\(_3\)C=N), 3.81 (s, 3H, OCH\(_3\)), 3.86 (s, 3H, OCH\(_3\)), 6.74 [(AX)\(_2\), 2H, ArCH], 6.92 [(AX)\(_2\), 2H, ArCH], 6.97 [(AX)\(_2\), 2H, ArCH], 7.93 [(AX)\(_2\), 2H, ArCH]; \(\delta_C\) (100 MHz, CDCl\(_3\)) 17.1 (CH\(_3\)C=N), 55.4 (OCH\(_3\)), 55.5 (OCH\(_3\)), 113.6 (ArCH), 114.2 (ArCH), 120.9 (ArCH), 128.7 (ArCH), 132.5 (ArC), 145.1 (ArC), 155.8 (ArC), 161.4 (ArC), 164.8 (C=N). Data were in accordance with literature.

[1-(4-Trifluoromethylphenyl)ethylidene]-(4-methoxyphenyl)-amine

Prepared using general procedure C (44%). Purified by crystallisation from toluene. Yellow crystals, m.p. 106 – 108 °C (from petroleum ether 40 – 60 °C); (Found C, 65.35; H, 4.68; N, 4.64; C\(_{16}\)H\(_{14}\)F\(_3\)NO requires C, 65.52; H, 4.81; N, 4.78); \(\nu\) (thin film, cm\(^{-1}\)) 3430, 1636, 1135; \(\delta_H\) (250 MHz, CDCl\(_3\)) 2.28 (s, 3H, CH\(_3\)C=N), 3.82 (s, 3H, OCH\(_3\)), 6.76 [(AX)\(_2\), 2H, ArCH], 6.92 [(AX)\(_2\), 2H, ArCH], 7.69 (d, 2H, J 8.1 Hz, ArCH), 8.07 (d, 2H, J 8.1 Hz, ArCH); \(\delta_C\) (62.9 MHz, CDCl\(_3\)) 17.3 (CH\(_3\)C=N), 55.5 (OCH\(_3\)), 114.4 (ArCH), 121.9 (ArCH), 124.1 (q, J\(_{C-F}\) 272 Hz, CCF\(_3\)), 125.2 (ArCH), 127.5 (ArCH), 131.9 (q, J\(_{C-F}\) 32.6 Hz, CCF\(_3\)), 143.0 (ArC), 144.2 (ArC), 156.3 (ArC), 164.3 (C=N); \(\delta_F\) (235 MHz, CDCl\(_3\)) -62.7; \(m/z\) (EI) 64 (26%), 77 (34), 92 (30), 148 (25), 235 (19), 278 (100), 279 (31), 293 (83), 293.1030 (M\(^+\) C\(_{16}\)H\(_{14}\)F\(_3\)NO requires 293.1027).

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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[1-(4-Nitrophenyl)ethyldene]-(4-methoxyphenyl)-amine\textsuperscript{18}

\[ \text{O} \]

\[ \text{N} \]

\[ \text{Me} \]

\[ \text{O} \]

\[ \text{N} \]

\[ \text{Me} \]

Prepared using general procedure C (48%). Purified by crystallisation from toluene. Yellow crystals, m.p. 90 – 92 °C (from petroleum ether 40 – 60 °C, lit.\textsuperscript{18} 93 – 95.5 °C from hexane); \( \nu \) (thin film, cm\textsuperscript{-1}) 3660, 3440, 3102, 2954, 2836, 1629, 1598, 1506, 1444, 1347, 1320, 1245, 1213, 1169, 1104, 1037; \( \delta \)\(_{\text{H}} \) (250 MHz, CDCl\textsubscript{3}) 2.34 (s, 3H, CH\textsubscript{3}C=N), 3.85 (s, 3H, OCH\textsubscript{3}), 6.80 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{i}], 6.96 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{i}], 8.15 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{i}], 8.31 [(AX)\textsubscript{2}, 2H, ArCH\textsubscript{i}]; \( \delta \)\(_{\text{C}} \) (63 MHz, CDCl\textsubscript{3}) 17.4 (CH\textsubscript{3}C=N), 55.5 (OCH\textsubscript{3}), 114.4 (ArCH), 120.8 (ArCH), 123.5 (ArCH), 128.1 (ArCH), 143.8 (ArC), 145.3 (ArC), 148.9 (ArC), 156.7 (ArC), 163.5 (C=N). Data was in accordance with literature.

**General procedure D for the reduction of imines with trichlorosilane**

Imine (1 mmol), catalyst (0.01 mmol) and dry CH\textsubscript{2}Cl\textsubscript{2} (1 cm\textsuperscript{3}) were introduced into an oven-dried 50 cm\textsuperscript{3} two-necked flask or an oven-dried carousel tube. The mixture was stirred until complete dissolution, then cooled to 0 °C and trichlorosilane (2 mmol, 0.2 cm\textsuperscript{3}) was added by syringe over five to ten seconds. The reaction was left to stir for the desired time. Hydrochloric acid (1 M, \textit{ca.} 2 cm\textsuperscript{3}) was added, which led to strong gas evolution and precipitation, followed by CH\textsubscript{2}Cl\textsubscript{2} (20 cm\textsuperscript{3}) and aqueous sodium hydroxide (1 M, 20 cm\textsuperscript{3}). This mixture was stirred until the precipitate was completely dissolved. The phases were separated and the aqueous phase was extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 × 20 cm\textsuperscript{3}). The combined organic phases were combined, washed with brine (20 cm\textsuperscript{3}) and dried over magnesium sulfate. The product was isolated by concentration under reduced pressure. Racemic samples of compound were obtained by this procedure, using \( N \)-formylpyrrolidine (5%) as catalyst. Characterisation of the chiral amines was made from their racemic samples.
Supporting information

N-Phenyl-1-phenylethanamine

Prepared according to general procedure D (77%, e.e. 86%). Yellow oil. $t_R = 4.9 \text{ min.}$ ($S$ isomer), 6.1 min. ($R$ isomer) (3-Cellucoat, 95/5 hexane/propan-2-ol); $[\alpha]_D^{\text{19}} +13.9$ (c 1 in MeOH, 86% e.e. from HPLC); lit.\textsuperscript{19} +17.0 (c 1 in MeOH, pure $S$ isomer); $\delta_H$ (250 MHz, CDCl$_3$) 1.51 (d, 3H, $J_{CH} = 6.7$ Hz, $C_H_3CHN$), 4.03 (bs, 1H, $NH$), 4.48 (q, 1H, $J_{CH} = 6.7$ Hz, $CH_3CN$), 6.50 (d, 2H, $J_{Ar} = 7.6$ Hz, Ar$CH$), 6.63 (t, 1H, $J_{Ar} = 7.3$ Hz, Ar$CH$), 7.08 (t, 2H, $J_{Ar} = 7.3$ Hz, Ar$CH$), 7.20 – 7.39 (m, 5H, Ar$CH$); $\delta_C$ (62.9 MHz, CDCl$_3$) 25.1 (CH$_3$), 53.5 (CH), 113.4 (Ar$CH$), 117.3 (Ar$CH$), 125.9 (Ar$CH$), 126.9 (Ar$CH$), 128.7 (Ar$CH$), 129.2 (Ar$CH$), 145.3 (ArC), 147.4 (ArC). Data was in accordance with literature.

N-Phenyl-1-(4-chlorophenyl)ethanamine

Prepared according to general procedure D (77%, e.e. 87%). Yellow oil. $t_R = 8.2 \text{ min.}$ (major), 10.0 min. (minor) (3-Cellucoat, 98/2 hexane/propan-2-ol); $[\alpha]_D^{\text{21}} -3.0$ (c 1 in CHCl$_3$, 85% e.e. from HPLC); lit.\textsuperscript{21} -17 (c 1.7 in CH$_2$Cl$_2$, 90% e.e. from HPLC, absolute configuration was not determined), $\delta_H$ (400 MHz, CDCl$_3$) 1.52 (d, 3H, $J_{CH} = 6.9$ Hz, CHN$CH_3$), 4.04 (br. s, 1H, NH), 4.48 (q, 1H, $J_{CH} = 6.9$ Hz, CHN$CH_3$), 6.51 (d, 2H, $J_{Ar} = 7.8$ Hz, Ar$CH$), 6.69 (t, 1H, $J_{Ar} = 7.3$ Hz, Ar$CH$), 7.13 (app. t, 2H, $J_{Ar} = 7.8$ Hz, Ar$CH$), 7.28 – 7.35 (m, 4H, Ar$CH$); $\delta_C$ (100 MHz, CDCl$_3$) 25.2 (CHN$CH_3$), 53.4 (CHN$CH_3$), 113.7 (Ar$CH$), 117.9 (Ar$CH$), 127.7 (Ar$CH$), 129.2 (Ar$CH$), 129.6 (Ar$CH$), 132.8 (ArC), 144.2 (ArC), 147.4 (ArC); $m/z$ (ES) 139 (100%), 141 (23), 232 (21), 234 (2); $m/z$ (ES) 232.0887 (MH$^+$ C$_{14}$H$_{15}$NCl requires 232.0893). Data was in accordance with literature.
**N-Phenyl-1-phenylpropanamine**

Prepared according to general procedure D (59%, e.e. 79%). Yellow oil. $t_R = 4.1$ min. (major), 4.6 min. (minor) (3-Cellucoat, 95/5 hexane/propan-2-ol); $[\alpha]_D$ -4.8 (c 1.04 in MeOH, 80% e.e. from HPLC); lit. -6.79 (c 1.06 in MeOH, 87% e.e., absolute configuration is not conclusively determined); $\delta_H$ (250 MHz, CDCl$_3$) 0.96 (t, 3H, $J$ 7.3 Hz, CH$_2$CH$_3$), 1.74 – 1.91 (m, 2H, CH$_2$CH$_3$), 4.07 (bs, 1H, NH), 4.22 (t, 1H, $J$ 6.7 Hz, CHN), 6.51 (d, 2H, $J$ 8.9 Hz, ArCH$_2$), 6.62 (t, 1H, $J$ 7.3 Hz, ArCH$_2$), 7.08 (t, 2H, $J$ 7.3 Hz, ArCH$_2$), 7.18 – 7.36 (m, 5H, ArCH$_2$); $\delta_C$ (63 MHz, CDCl$_3$) 10.9 (CH$_3$CH$_2$), 31.8 (CH$_3$CH$_2$), 59.8 (CHN), 113.4 (ArCH), 117.2 (ArCH), 126.6 (ArCH), 127.0 (ArCH), 128.1 (ArCH), 128.7 (ArCH), 129.2 (ArCH), 133.0 (ArCH), 144.1 (ArC), 147.7 (ArC). Data was in accordance with literature.

**N-Phenyl-(1,2,3,4-tetrahydronaphthalen-1-yl)amine**

Prepared according to general procedure D (42%, e.e. 19%). Yellow oil. $t_R = 5.1$ min. (minor), 5.4 min. (major) (Chiralpak AD, 95/5 hexane/propan-2-ol); $[\alpha]_D$ -2.0 (c 1 in MeOH, 19% e.e. from HPLC); lit. $[\alpha]_D$ +1.46, (c 0.89 in MeOH, 12% e.e. from HPLC, absolute configuration was not determined); $\delta_H$ (250 MHz, CDCl$_3$) 1.75 – 2.02 (m, 4H, CHNCH$_2$CH$_2$), 2.70 – 2.91 (m, 2H, ArCH$_2$), 3.88 (bs, 1H, NH), 4.63 (s, 1H, CHNH), 6.66 – 6.73 (m, 3H, ArCH), 7.10 – 7.23 (m, 5H, ArCH), 7.38 – 7.42 (m, 1H, ArCH); $\delta_C$ (63 MHz, CDCl$_3$) 19.5 (CH$_2$), 28.8 (CH$_2$), 29.4 (CH$_2$), 51.2 (CHN), 113.0 (ArCH), 117.2 (ArCH), 126.2 (ArCH), 127.2 (ArCH), 129.1 (ArCH), 129.4 (ArCH), 129.5 (ArCH), 137.7 (ArC), 138.3 (ArC), 147.5 (ArC). Data was in accordance with literature.
**N-(4-Methoxyphenyl)-1-phenylethanamine**

Prepared according to general procedure D (95%, e.e. 87%). Yellow oil. $t_R = 7.9$ min. ($R$ isomer), 8.6 min. ($S$ isomer) (Chiralpak AD, 95/5 hexane/propan-2-ol); [$\alpha]_D$ -5.6 (c 0.54 in CHCl$_3$, 87% e.e. from HPLC); lit.$^{25}$ -4.0 (c 1.0 in CHCl$_3$, 81% e.e., major isomer $S$); $\delta_H$ (250 MHz, CDCl$_3$) 1.49 (d, 3H, $J = 6.7$ Hz, CD$_3$CHN), 3.68 (s, 3H, OCH$_3$), 3.78 (bs, 1H, NH), 4.41 (q, 1H, $J = 6.7$ Hz, CH$_3$CHN), 6.46 [(AX)$_2$, 2H, ArCH], 6.68 [(AX)$_2$, 2H, ArCH], 7.18 – 7.38 (m, 5H, ArCH); $\delta_C$ (62.9 MHz, CDCl$_3$) 25.2 (CH$_3$CHN), 54.3 (CH$_3$CHN), 55.8 (CH$_3$O), 114.6 (ArCH), 114.8 (ArCH), 125.9 (ArCH), 126.8 (ArCH), 141.6 (ArC), 145.5 (ArC), 151.9 (ArC). Data was in accordance with literature.

**N-(4-Methoxyphenyl)-(1,2,3,4-tetrahydronaphthalen-1-yl)amine**

Prepared according to general procedure D (41%, e.e. 22%). Yellow oil. $t_R = 9.4$ min. (minor), 10.2 min. (major) (3-Cellucoat, 99.5/0.5 hexane/propan-2-ol); [$\alpha]_D$ +3.0 (c 1.0 in CHCl$_3$, 22% e.e. from HPLC); lit.$^{16}$ -22.0 (c 1.0 in CHCl$_3$, 91% e.e. from HPLC, absolute configuration was not determined); $\delta_H$ (250 MHz, CDCl$_3$) 1.73 – 1.98 (m, 4H, CH$_2$CH$_2$), 2.75 – 2.83 (m, 2H, CH$_2$), 3.60 ( bs, 1H, NH), 3.76 (s, 3H, OCH$_3$), 4.52 – 4.56 (m, 1H, CH$_2$CHNH), 6.64 [(AX)$_2$, 2H, ArCH], 6.80 [(AX)$_2$, 2H, ArCH], 7.09 – 7.19 (m, 3H, ArCH), 7.40 – 7.43 (m, 1H, ArCH); $\delta_C$ (62.9 MHz, CDCl$_3$) 19.3 (CH$_2$), 28.9 (CH$_2$), 29.4 (CH$_2$), 52.2 (CHN), 55.9 (CH$_3$O), 114.5 (ArCH), 115.0 (ArCH), 126.1 (ArCH), 127.1 (ArCH), 129.0 (ArCH), 129.3 (ArCH), 137.6 (ArC), 138.3 (ArC), 152.0 (ArC). Data were in accordance with literature.
**Supporting information**

*N-(4-Methoxyphenyl)-1-phenylpropanamine*\(^{16}\)

![N-(4-Methoxyphenyl)-1-phenylpropanamine](image)

Prepared according to general procedure D (95%, e.e. 84%). Yellow oil. \(t_R = 9.2\) min. (minor), 10.3 min. (major) (Chiralpak AD, 98/2 hexane/propan-2-ol); \([\alpha]_D\) -26.9 (c 1.0 in CHCl\(_3\), 84% e.e. from HPLC,) lit.\(^{16}\) -24.2, (c 0.5 in CHCl\(_3\), 92% e.e., absolute configuration was not determined); \(\delta_H\) (250 MHz, CDCl\(_3\)) 0.94 (t, 3H, J 7.3 Hz, CH\(_2\)CH\(_3\)), 1.71 – 1.90 (m, 2H, CH\(_2\)CH\(_3\)), 3.68 (s, 3H, OCH\(_3\)), 3.82 (bs, 1H, NH), 4.15 (t, 1H, J 6.7 Hz, CHNH), 6.46 [(AX)\(_2\), 2H, ArCH], 6.68 [(AX)\(_2\), 2H, ArCH], 7.17 – 7.35 (m, 5H, ArH); \(\delta_C\) (63 MHz, CDCl\(_3\)) 10.8 (CH\(_3\)CH\(_2\)), 31.7 (CH\(_3\)CH\(_2\)), 55.8 (OCH\(_3\)), 60.6 (CHN), 114.5 (ArCH), 114.8 (ArCH), 126.6 (ArCH), 126.9 (ArCH), 128.5 (ArCH), 141.8 (ArC), 144.2 (ArC), 151.9 (ArC). Data was in accordance with literature.

*N-(4-Methoxyphenyl)-1-cyclohexylethanamine*\(^{15}\)

Prepared according to general procedure D (85%, e.e. 73%). Yellow oil. \(t_R = 9.6\) min. (minor), 10.4 min. (major) (Chiralpak AD, 99.5/0.5 hexane/propan-2-ol). \([\alpha]_D\) +10.5 (c 0.44 in CHCl\(_3\), 73% e.e. from HPLC); lit.\(^{15}\) +18.2 (c 0.99 in CHCl\(_3\), absolute configuration not determined but assumed to be (S) isomer in analogy with other compounds prepared); \(\delta_H\) (250 MHz, CDCl\(_3\)) 1.07 (d, 3H, J 6.4 Hz, CHNCH\(_3\)), 1.14 – 1.28 (m, 5H, cyclohexyl ring), 1.39 – 1.50 [m, 1H, CHCH(NH)CH\(_3\)], 1.60 – 1.82 (m, 5H, cyclohexyl ring), 3.19 – 3.26 (m, 2H, CHNH), 3.73 (s, 3H, OCH\(_3\)), 6.53 [(AX)\(_2\), 2H, ArCH], 6.75 [(AX)\(_2\), 2H, ArCH]; \(\delta_C\) (63 MHz, CDCl\(_3\)) 17.4 (CH\(_3\)), 26.4 (CH\(_2\)), 26.5 (CH\(_2\)), 26.7 (CH\(_2\)), 28.3 (CH\(_2\)), 29.7 (CH\(_2\)), 42.9 (CH), 54.1 (CH), 55.9 (OCH\(_3\)), 114.5 (ArCH), 115.0 (ArCH), 142.3 (ArC), 151.6 (ArC). Data was in accordance with literature.
N-(4-Methoxyphenyl)-1-naphth-1-ylethanamine\textsuperscript{16}

\[ \text{HN} \quad \text{OMe} \]

Prepared according to general procedure D (71%, e.e. 74%). Yellow crystals. m.p. 61 °C (not reported in literature). \( t_R = 9.2 \text{ min. (minor), 12.4 \text{ min. (major)}} \) (Chiralpak AD, 95/5 hexane/propan-2-ol); [\( \alpha \)]\textsubscript{D} +123.8 (c 0.44 in CHCl\textsubscript{3}, 74% e.e. from HPLC); lit.\textsuperscript{16} +80.2 (c 0.44 in CHCl\textsubscript{3}, 98% e.e., absolute configuration not determined); \( \delta \text{H} \) (250 MHz, CDCl\textsubscript{3}) 1.65 (d, 3H, \( J \) 6.6 Hz, \( \text{CH}_{3}\text{CHN} \)), 3.67 (s, 3H, \( \text{OC}_{\text{H}} \)), 3.93 (bs, 1H, \( \text{NH} \)), 5.22 (q, 1H, \( J \) 6.6 Hz, \( \text{CH}_{3}\text{CHN} \)), 6.44 [(AX)\textsubscript{2}, 2H, \( \text{ArCH} \)], 6.67 [(AX)\textsubscript{2}, 2H, \( \text{ArCH} \)], 7.42 (t, 1H, \( J \) 7.8 Hz, \( \text{ArH} \)), 7.48 – 7.60 (m, 2H, \( \text{ArCH} \)), 7.66 (d, 1H, \( J \) 7.0 Hz, \( \text{ArCH} \)), 7.75 (d, 1H, \( J \) 8.2 Hz, \( \text{ArCH} \)), 7.89 – 7.93 (m, 1H, \( \text{ArCH} \)), 8.18 (d, 1H, \( J \) 7.9 Hz, \( \text{ArCH} \)); \( \delta \text{C} \) (63 MHz, CDCl\textsubscript{3}) 23.8 (\( \text{CH}_{3}\text{CHN} \)), 50.1 (\( \text{CH}_{3}\text{CHN} \)), 55.8 (\( \text{CH}_{3}\text{O} \)), 114.3 (\( \text{ArCH} \)), 114.9 (\( \text{ArCH} \)), 122.4 (\( \text{ArCH} \)), 122.7 (\( \text{ArCH} \)), 125.5 (\( \text{ArCH} \)), 126.0 (\( \text{ArCH} \)), 126.1 (\( \text{ArCH} \)), 127.4 (\( \text{ArCH} \)), 129.2 (\( \text{ArCH} \)), 130.8 (\( \text{ArC} \)), 134.2 (\( \text{ArC} \)), 140.3 (\( \text{ArC} \)), 141.5 (\( \text{ArC} \)), 151.9 (\( \text{ArC} \)). Data was in accordance with literature.

N-(4-Methoxyphenyl)-1-naphth-2-ylethanamine\textsuperscript{25}

\[ \text{HN} \quad \text{OMe} \]

Prepared according to general procedure D (86%, e.e. 86%). Yellow crystals. m.p. 95 – 96 °C (not reported in literature). \( t_R = 19.5 \text{ min. (S isomer), 22.4 \text{ min. (R isomer)}} \) (Chiralpak AD, 99/1 hexane/propan-2-ol); [\( \alpha \)]\textsubscript{D} -26.0 (c 1.0 in CHCl\textsubscript{3}, 86% e.e. from HPLC); lit.\textsuperscript{25} -23.2 (c 1.0 in CHCl\textsubscript{3}, 96% e.e., S major isomer); \( \delta \text{H} \) (400 MHz, CDCl\textsubscript{3}) 1.60 (d, 3H, \( J \) 6.6 Hz, \( \text{CHNCH}_{3} \)), 3.70 (s, 3H, \( \text{OCH}_{3} \)), 3.92 (bs, 1H, \( \text{NH} \)), 4.60 (q, 1H, \( J \) 6.6 Hz, \( \text{CHNCH}_{3} \)), 6.54 [(AX)\textsubscript{2}, 2H, \( \text{ArCH} \)], 6.70 [(AX)\textsubscript{2}, 2H, \( \text{ArCH} \)], 7.44 – 7.51 (m, 2H, \( \text{ArH} \)), 7.53 (dd, 1H, \( J \) 1.5, 8.6 Hz, \( \text{ArH} \)), 7.81 – 7.85 (m, 4H, \( \text{ArH} \)); \( \delta \text{C} \) (100 MHz, CDCl\textsubscript{3}) 25.2 (\( \text{CHNCH}_{3} \)), 54.5 (\( \text{CHNCH}_{3} \)), 55.8 (\( \text{OCH}_{3} \)), 114.7 (\( \text{ArCH} \)), 114.8 (\( \text{ArCH} \)), 124.3 (\( \text{ArCH} \)), 124.5 (\( \text{ArCH} \)), 125.5 (\( \text{ArCH} \)), 126.0 (\( \text{ArCH} \)), 127.7 (\( \text{ArCH} \)), 127.7 (\( \text{ArCH} \)).
127.8 (ArCH), 128.5 (ArCH), 132.8 (ArC), 133.6 (ArC), 141.6 (ArC), 143.1 (ArC), 152.0 (ArC). Data was in accordance with literature.

N-(4-Methoxyphenyl)-1-(4-methoxyphenyl)ethanamine\textsuperscript{25}

Prepared according to general procedure D (81%, e.e. 85%). Yellow oil. \( t_{R} = 23.9 \) min. (minor), 27.1 min. (major) (Chiralcel OD, 99/1 hexane/propan-2-ol); \([\alpha]_{D} \) -15.5 (c 1.1 in CHCl\(_3\), 85% e.e. from HPLC); lit.\textsuperscript{25} -17.8 (c 1.0 in CHCl\(_3\), 94% e.e. for the (S)-enantiomer); \( \delta_{H} \) (400 MHz, CDCl\(_3\)) 1.48 (d, 3H, \( J \) 6.6 Hz, CHNC\(_3\)), 3.70 (s, 3H, O\( \text{C} \)H\(_3\)), 3.79 (s, 3H, O\( \text{C} \)H\(_3\)), 4.38 (q, 1H, \( J \) 6.6 Hz, CHNCH\(_3\)), 6.49 [(AX)\(_2\), 2H, ArC\( \text{H} \)], 6.70 [(AX)\(_2\), 2H, ArCH\(_2\)], 6.86 [(AX)\(_2\), 2H, ArCH\(_2\)], 7.28 [(AX)\(_2\), 2H, ArCH\(_2\)]; \( \delta_{C} \) (100 MHz, CDCl\(_3\)) 25.0 (CH\(_3\)), 53.6 (CHNH), 55.2 (O\( \text{C} \)H\(_3\)), 55.7 (O\( \text{C} \)H\(_3\)), 113.9 (ArCH), 114.6 (ArCH), 114.7 (ArCH), 126.9 (ArCH), 137.4 (ArC), 141.5 (ArC), 151.9 (ArC), 158.4 (ArC). Data was in accordance with literature.

N-(4-Methoxyphenyl)-1-(4-trifluoromethylphenyl)ethanamine\textsuperscript{25}

Prepared according to general procedure D (72%, e.e. 82%). Yellow oil. \( t_{R} = 29.1 \) min. (minor), 40.1 min. (major) (Chiralcel OD, 99/1 hexane/propan-2-ol); \([\alpha]_{D} \) +6.3 (c 0.32 in CHCl\(_3\), 82% e.e. from HPLC); lit.\textsuperscript{25} +6.5 (c 1, CHCl\(_3\), 81% e.e. for (S)-enantiomer); \( \delta_{H} \) (250 MHz, CDCl\(_3\)) 1.53 (d, 3H, \( J \) 6.9 Hz, CHNCH\(_3\)), 3.72 (s, 3H, O\( \text{C} \)H\(_3\)), 3.88 (bs, 1H, NH), 4.48 (q, 1H, \( J \) 6.9 Hz, CHNCH\(_3\)), 6.45 [(AX)\(_2\), 2H, ArCH\(_2\)], 6.71 [(AX)\(_2\), 2H, ArCH\(_2\)], 7.50 (d, 2H, \( J \) 8.2 Hz, ArCH\(_2\)), 7.59 (d, 2H, \( J \) 8.2 Hz, ArCH\(_2\)); \( \delta_{F} \) (235 MHz, CDCl\(_3\)) -62.3; \( \delta_{C} \) (62.9 MHz, CDCl\(_3\)) 25.1 (CHNCH\(_3\)), 54.1 (CHNCH\(_3\)), 55.7 (O\( \text{C} \)H\(_3\)), 114.6 (ArCH), 114.9 (ArCH), 124.3 (q, \( J_{C-F} \) 272 Hz, CF\(_3\)), 125.7 (ArCH), 126.3 (ArCH), 129.2 (q, \( J_{C-F} \) 33 Hz, ArCCF\(_3\)), 141.1 (ArC), 149.8 (ArC), 152.3 (ArC). Data was in accordance with literature.
**Supporting information**

*N-(4-Methoxyphenyl)-1-(4-nitrophenyl)ethanamine*\(^\text{27}\)

![Chemical structure](image)

Prepared according to general procedure D (85%, e.e. 86%). Dark yellow oil. \(t_R = 43.2\) min. (major), 50.9 min. (minor) (Chiralpak AD, 98/2 hexane/propan-2-ol); \([\alpha]_D\) -25.9 (c 0.54 in CHCl\(_3\), 86% e.e. from HPLC); lit.\(^\text{27}\) +29.8 (c 0.2, CHCl\(_3\), 95% e.e. for \((R)\)-enantiomer); \(\delta_H\) (400 MHz, CDCl\(_3\)) 1.55 (d, 3H, \(J\) 6.6 Hz, CHNCH\(_3\)), 3.71 (s, 3H, OCH\(_3\)), 3.91 (br. s, 1H, NH), 4.52 (q, 1H, \(J\) 6.6 Hz, CHNCH\(_3\)), 6.43 [(AX\(_2\), 2H, ArCH\(_2\)], 6.71 [(AX\(_2\), 2H, ArCH\(_2\)], 7.57 [(AX\(_2\), 2H, ArCH\(_2\)], 8.19 [(AX\(_2\), 2H, ArCH\(_2\)]; \(\delta_C\) (100 MHz, CDCl\(_3\)) 25.0 (CH\(_3\)CHN), 54.0 (CHNH), 55.7 (OCH\(_3\)), 114.6 (ArCH), 114.7 (ArCH), 124.0 (ArCH), 126.8 (ArCH), 140.8 (ArC), 147.0 (ArC), 152.3 (ArC), 153.6 (ArC). Data was in accordance with literature.

**References**