Supporting Information

Discovery of an Iridacycle Catalyst with Improved Reactivity and Enantioselectivity in the Hydrogenation of Dialkyl Ketimines

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General Information

Working Techniques:

All chemicals were purchased from Acros Organics, Sigma-Aldrich, Fluka, Merck Molecula or Strem Chemicals and used as received, unless otherwise noted. Anhydrous solvents were obtained in sure-seal bottles from Aldrich or Fluka, collected from a purification column system (PureSolv, Innovative Technology Inc.) or purified using standard methods (distillation of potassium/benzophenone or CaH2). Air sensitive reactions were carried out in an atmosphere of purified nitrogen by using a glovebox and/or standard Schlenk techniques under argon. Column chromatographic purifications were performed on Merck silica gel 60 (particle size 40-63 nm). The eluents were of technical grade and distilled prior to use. The hydrogenation experiments were prepared under purified nitrogen in a glove box (MBraun Labmaster 130) and the dichloromethane was purchased from Aldrich (≥ 99.5%, over molecular sieves).

Analytical Methods:

Melting Points (m.p.): Melting points were determined on a Büchi 535 and Büchi 545 apparatus. The Büchi 545 apparatus was calibrated with benzoic acid.

Thin Layer Chromatography (TLC): TLC plates were obtained from Machrey-Nagel (Polygram SIL/UV254, 0.2 mm silica with fluorescence indicator). UV light (254 nm) or or stain solutions (KMnO4, Ce(SO4)2, Ninhydrine) were used to visualize the respective compounds.

NMR-Spectroscopy (NMR): NMR spectra were measured either on a Bruker Avance 400 (1H: 400 MHz, 13C: 100.6 MHz) or a Bruker Avance 500 (1H: 500 MHz, 13C: 125.8 MHz) spectrometer. The chemical shifts (δ) are given in ppm. The chemical shift δ values were corrected to the signal of the deuterated solvents: 7.26 ppm (1H-NMR) and 77.16 ppm (13C{1H}-NMR) for CDCl3; 5.32 ppm (1H-NMR) and 53.5 ppm (13C{1H}-NMR) for CD2Cl2. 31P{1H}-NMR spectra are calibrated relative to 85% phosphoric acid (δ = 0 ppm) and 19F-NMR spectra relative to CFCl3 (δ = 0 ppm) as external standards. 13C and 31P spectra were recorded 1H-decoupled. The assignment of 1H and 13C signals was accomplished, when needed by two-dimensional correlation experiments (COSY and HSQC). Multiplets are assigned as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sex (sextet), sept (septet) and m (multiplet). Broad signals are assigned with: br (broad).

Infrared Spectroscopy (IR): Infrared spectra were collected on a Shimadzu FTIR-8400S spectrometer. The compounds were measured as pure substance via Specac ATR attachment. The absorption bands are given in wave numbers (ν [cm⁻¹]). The peak intensity is described by: s (strong), m (medium), w (weak).

Mass Spectroscopy (MS): Mass spectra were measured by Dr. H. Nadig (Departement of Chemistry, University of Basel) on a VG70-250 spectrometer (electron ionization (EI)) or on a MAR 312 spectrometer (fast atom bombardement (FAB)). FAB was performed with 3-nitrobenzyl alcohol (NBA)) as matrix. The signals are given in mass-to-charge ratios (m/z). The fragments and relative intensities are given in brackets.

Optical Rotations ([α]D): Optical rotations were measured on a Perkin Elmer Polarimeter 341 (in a cuvette (l = 1 dm)) at 20 °C at 589 nm. The concentration (c) is given in g/100 mL.
**Elemental Analysis (EA):** Elemental analyses were measured by Mr. W. Kirsch (department of Chemistry, University of Basel) and by M. Schneider (Microanalytical Laboratory of the Department of Organic Chemistry at the ETH Zurich) on a Leco CHN-900 (C-, H-, N-detection). The data are indicated in mass percent.

**High Resolution Mass Spectrometry (HRMS):** Performed by Dr. H. Nadig (Departement of Chemistry, University of Basel) on a Bruker maXis 4G and by the Laboratory of Mass Spectroscopy of the Department of Organic Chemistry at the ETH Zurich on a Bruker Daltonics maXis (UHR-TOF) and Bruker solariX 94 ESI/MALDI-FT-ICR spectrometer.

**High Performance Liquid Chromatography (HPLC):** HPLC analyses were performed on Shimadzu systems with SLC-10A/SIL-20AHT system controller, CTO-10AC/AS column oven, LC10-AD/20-AD pump system, DGU-14A/20AD3 degasser and SPD-M10A/M20A diode array- or UV/VIS detector. Chiral columns Chiracel AD-H, AS-H, OB-H, OD-H, OJ or OJ-H (0.46 x 250 mm) from Daicel Chemical Industries were used.

**Gas Chromatography (GC):** Gas chromatograms were recorded on Carlo Erba HRGC Mega2 Series 800 (HRGS Mega2), on CarboErga GC8000Top and on Shimadzu GC-2010 plus instruments. Separations on achiral phases were performed on a Restek Rtx-1701 (30 m x 0.25 mm x 0.25 μmol) or a Macherey-Nagel Optima 5-Amin (0.25 mm x 0.25 μm x 30 m) column. Separations of enantiomers were achieved on a ChiralSolv γ-cyclodextrin TFA G-TA (30 m x 0.25 mm x 0.12 μm) or a Brechbühler β-cyclodextrin DEtTBuSil (SE54), (0.25 mm x 0.25 μm x 25 m) column.

**Gas Chromatography / Mass Spectroscopy (GC-MS):** GC-MS analysis was performed on open-source 5890 Series II (GC-columns : Macherey-Nagel OPTIMA1 Me2Si, 25 m x 0.2 mm, 0.35 um, 20 psi, split ca. 20:1, carrier gas : 1 mL/min helium, 5971 series mass selective detector (El) ; Macherey-Nagel Optima5 5% PhMeSi, 25 m 0.2 mm, 0.35 um, 20 psi, split ca 20:1, carrier gas : 1 mL/min helium, 5970A series mass selective detector (El)) and Shimadzu GC 2010 plus with GCMS-QP2010 SE mass detectors. The signals are given in mass-to-charge ratios (m/z) with the relative intensity in brackets.
Synthetic Procedures

1-Cyclopentylethanone (15)

Into a 25 mL two-necked round-bottom flask was placed a magnetic stirrer, the flask was closed with a stopper, and dried with a Bunsen burner while evacuating. After cooling to room temperature, the flask was purged with argon three times and cyclopentanoic acid (1 g, 8.85 mmol, 1.0 eq.) was added and dissolved in dry diethylether (8 mL). The reaction mixture was cooled to -78 °C with the aid of a dry ice / acetone bath and a solution of MeLi (1.6 M, 12.5 mL, 20.11 mmol, 2.3 eq.) was added dropwise via syringe over a period of 15 minutes. The reaction was allowed to warm to room temperature while stirring overnight. After quenching with saturated NH₄Cl solution (8 mL) the mixture turned clear and layers were separated. The organic layer was washed with water (10 mL) and the aqueous layer washed with ether (10 mL). The combined organic phases were dried over MgSO₄, filtered and solvents removed under reduced pressure to afford 0.5 g (4.4 mmol, 50%) of 15 as a clear oil.

C₇H₁₂O (112.17 g/mol):

$^1$H-NMR (400 MHz, CDCl₃, δ/ppm) δ 2.94 – 2.78 (m, 1H, CH), 2.16 (s, 3H, CH₃), 1.88 – 1.45 (m, 10H, CH₂). $^{13}$C($^1$H)-NMR (101 MHz, CDCl₃) δ 211.44 (C=O), 52.40 (CH), 28.95 (CH₂CH₂CH), 28.86 (CH₂CH₂CH), 26.10 (CH₃). GC-MS: (Rtx-5MS, 100.2/10.270/10): t_R = 3.3 min, m/z = 113 ([M+1]^+).

4-Bromo-2,6-diisopropylaniline (16)

In a 500 mL round-bottom flask was placed 2,6-diisopropylaniline (6 mL, technical, ~90%, ~30 mmol) and dissolved in CH₂Cl₂ (250 mL). Tetrabutylammonium tribromide (15.4 g, 32 mmol) was added in one go. The reaction was stirred for 30 minutes before the solvent was removed under reduced pressure. The residue was redissolved in diethyl ether (250 mL), washed with NaOH (0.5 M, 150 mL), water (2 x 150 mL), dried over MgSO₄, filtered and solvents removed under reduced pressure to afford 7.6 g (29.7 mmol, 98%) of 16 as a yellow oil.

C₁₂H₁₈BrN (256.18 g/mol):

$^1$H-NMR (400 MHz, CDCl₃, δ/ppm) δ 7.11 (s, 2H, CH₆), 3.70 (s, 2H, NH₂), 2.95 – 2.81 (m, 2H, CH(CH₃)₂), 1.25 (d, J = 6.8 Hz, 12H, CH₃).
1-Bromo-3,5-diisopropylbenzene (17)²

In a 500 mL round-bottom flask was placed 16 (7.6 g, 29.7 mmol, 1.0 eq.) and suspended in HCl (2 M, 70 mL). The reaction mixture was cooled to -5 °C and sodium nitrite (5.12 g, 74 mmol, 1.05 eq) was added portionwise. After addition the reaction was stirred for 30 minutes before H₃PO₄ (50% in water, 35 mL, 300 mmol, 4.0 eq.) was added. The mixture was stirred at 4 °C overnight. Ether (100 mL) was added and layers were separated. The aqueous layer was washed with ether (2 x 100 mL) and the combined organic layers were dried over MgSO₄, filtered and solvents removed under reduced pressure. Purification by distillation (115 °C, 0.15 mbar) afforded 4.0 g (16.6 mmol, 56%) of 17 as a yellow oil.

C₁₂H₁₇Br (241.17 g/mol):
b.p.: 115°C at 0.1 torr; ¹H-NMR (400 MHz, CDCl₃, δ/ppm) δ 7.18 (d, J = 1.5 Hz, 2H, CH₂BrCBrCH₂Ar), 6.98 (s, 1H, CH₂Ar), 2.92 – 2.77 (m, 2H, CH(CH₃)₂), 1.23 (d, J = 6.9 Hz, 12H, CH₃).

3,5-Di-isopropylbenzaldehyde (18)²

In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet, thermometer and a stopper was placed 17 (4.0 g, 16.6 mmol, 1.0 eq.) and cooled to -78 °C with the aid of a dry ice / acetone bath. n-BuLi (1.6 M, 18.26 mmol, 1.1 eq.) was added dropwise via syringe and the resultant suspension was stirred for 20 minutes at -78 °C. Then DMF (1.33 g, 18.26 mmol, 1.1 eq.) was added dropwise via syringe, the mixture stirred for 10 minutes being allowed to warm to -10 °C. The reaction was quenched with water (12 mL) at -10 °C and the mixture warmed to room temperature. Layers were separated and the aqueous layer washed with ether (100 mL). Organic layers were combined and solvents removed under reduced pressure. The residue was purified by flash chromatography (SiO₂, 18 x 4.5 cm, cyclohexane/EtOAc 20:1) to afford 2.05 g (10.77 mmol, 65%) of 18 as a clear oil.

C₁₃H₁₈O (190.28 g/mol):
Rᵣ (SiO₂, n-pentane/AcOEt 10:1, UV, Ce(SO₄)₂) = 0.63; ¹H-NMR (400 MHz, CDCl₃, δ/ppm) δ 9.99 (s, 1H, CHO), 7.57 (d, J = 1.7 Hz, 2H, CH₃CHOCH₂Ar), 7.35 (s, 1H, CH₂Ar), 3.04 – 2.90 (m, 2H, CH(CH₃)₂), 1.29 (dd, J = 6.9, 1.8 Hz, 12H, CH₃).
1-(3,5-Di-isopropylphenyl)ethanol (19)

In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet and a stopper was placed 18 (2.05 g, 10.77 mmol, 1.0 eq.) and dissolved in dry diethyl ether (40 mL). The solution was cooled to 0 °C and MeMgBr (3.0 M, 16.2 mmol, 1.5 eq.) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 15 minutes before being allowed to warm to room temperature and stirred for 2 hours. The mixture was cooled to 0 °C again and quenched with sat. NH₄Cl (40 mL) and water (20 mL). After warming to room temperature, layers were separated and the aq. layer was extracted with EtOAc (3 x 60 mL). The combined organic layers were dried over MgSO₄, filtered and solvents removed under reduced pressure. The residue was purified via flash chromatography (SiO₂, 15 x 3 cm, cyclohexane/EtOAc 5:1) to afford 1.89 g (9.16 mmol, 85%) of 19 as an orange viscous oil.

C₁₄H₂₂O (206.32 g/mol):

1H-NMR (400 MHz, CDCl₃, δ/ppm) δ 7.06 (d, J = 1.6 Hz, 2H, CH₂Ar), 7.01 (d, J = 6.9 Hz, 2H, CH(CH₃)₂), 4.87 (qd, J = 6.4, 3.6 Hz, 1H, CH(OH)), 2.90 (hept, J = 6.9 Hz, 2H, CH(CH₃)₂), 1.51 (d, J = 6.4 Hz, 3H, CH(CH₃)OH), 1.26 (d, J = 6.9 Hz, 12H, CH(CH₃)₂).

13C{¹H}-NMR (101 MHz, CDCl₃) δ 149.30 (C=CH(CH₃)₂), 145.89 (C=CH(OH)), 124.12 (CH₂ArCH(CH₃)₂CH(OH)), 70.98 (CH(OH)), 34.40 (CH(CH₃)₂), IR (neat, ATR) ν/cm⁻¹ = 3340 (m br), 2961 (s), 2929 (m), 2887 (m), 2868 (m), 1603 (w), 1467 (m), 1459 (m), 1450 (m), 1382 (w), 1363 (m), 1176 (w), 1112 (w), 1073 (w), 1020 (w), 873 (w), 716 (m);

GC-MS: (Rtx-5MS, 100.2/10.270/10): t_R = 11.8 min, m/z = 206 ([M]+).

1-(3,5-Di-isopropylphenyl)ethanone (20)

In a 100 mL round-bottom flask was placed 19 (1.0 g, 4.5 mmol, 1.0 eq.) and dissolved in CH₂Cl₂ (50 mL). Dess-Martin Periodane (2.7 g, 6.37 mmol, 1.4 eq.) was added in one portion and the resultant mixture stirred for one hour at room temperature. The reaction mixture was poured into a solution of pentane/EtOAc (4:1, 80 mL) and a white precipitate was formed. The suspension was filtered over a frit (SiO₂) and a yellow solution was obtained. The fritt was rinsed with more pentane/EtOAc (4:1, 100 mL) and solvents were removed under reduced pressure. The residue was purified by flash chromatography (SiO₂, 18 x 3 cm, cyclohexane/EtOAc 20:1) to afford 1.0 g (4.31 mmol, 96%) of 20 as an orange oil.

C₁₄H₂₀O (204.31 g/mol):

1H-NMR (400 MHz, CDCl₃, δ/ppm) δ 7.64 (d, J = 1.7 Hz, 2H, CH₂Ar), 7.29 (t, J = 1.6 Hz, 1H, CH₂Ar), 3.03 – 2.86 (m, 2H, CH(CH₃)₂), 2.60 (s, 3H, CH₃C=O), 1.28 (d, J = 6.9 Hz, 12H, CH(CH₃)₂), 13C{¹H}-NMR (101 MHz, CDCl₃) δ 198.83 (C=O), 149.46 (CH(CH₃)₂), 137.59 (C=O), 129.93 (CH₂Ar), 124.07 (2 CH₂Ar), 34.32 (CH(CH₃)₂), 26.92 (C=OCH₃), 24.12 (CH(CH₃)₂).


1-(3,5-Di-tert-butylphenyl)ethanol (21)\(^4\)

In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet and a stopper was placed 3,5-di-tert-butylbenzaldehyde (1.0 g, 4.5 mmol, 1.0 eq.) and dissolved in dry diethyl ether (18 mL). The solution was cooled to 0 °C and MeMgBr (3.0 M, 6.82 mmol, 1.5 eq.) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 15 minutes before being allowed to warm to room temperature and stirred for 2 hours. The mixture was cooled to 0°C again and quenched with sat. NH\(_4\)Cl (40 mL) and water (20 mL). After warming to room temperature, layers were separated and the aq. layer was extracted with EtOAc (3 x 60 mL). The combined organic layers were dried over MgSO\(_4\), filtered and solvents removed under reduced pressure to afford 1.05 g (4.47 mmol, 96%) of 21 as a white solid.

C\(_{16}\)H\(_{26}\)O (234.38 g/mol):

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \(\delta/\text{ppm}\)) \(\delta 7.36\) (t, \(J = 1.8\) Hz, 1H, CH\(_{Ar}\)), 7.23 (d, \(J = 1.7\) Hz, 2H, CH\(_{Ar}\)), 4.90 (q, \(J = 6.4\) H, 1H, CHOH), 1.77 (s\(\text{br}\), 1H, OH), 1.52 (d, \(J = 6.5\) Hz, 3H, CH\(_3\)), 1.34 (s, 18H, C(CH\(_3\))\(_3\)).

1-(3,5-Di-tert-butylphenyl)ethanone (22)\(^5\)

In a 100 mL round-bottom flask was placed 21 (1.05 g, 4.47 mmol, 1.0 eq.) and dissolved in CH\(_2\)Cl\(_2\) (50 mL). Dess-Martin Periodane (2.5 g, 5.9 mmol, 1.32 eq.) was added in one portion and the resultant mixture stirred for one hour at room temperature. The reaction mixture was poured into a solution of pentane/EtOAc (4:1, 80 mL) and a white precipitate was formed. The suspension was filtered over a fritt (SiO\(_2\)) and a yellow solution was obtained. The frit was rinsed with more pentane/EtOAc (4:1, 100 mL) and solvents were removed under reduced pressure. The residue was purified by flash chromatography (SiO\(_2\), 18 x 3 cm, cyclohexane/EtOAc 20:1) to afford 1.0 g (4.31 mmol, 96%) of 22 as a clear oil.

C\(_{16}\)H\(_{24}\)O (232.36 g/mol):

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \(\delta/\text{ppm}\)) \(\delta 7.81\) (d, \(J = 1.8\) Hz, 2H, CH\(_{Ar}\)), 7.65 (t, \(J = 1.8\) Hz, 1H, CH\(_{Ar}\)), 2.62 (s, 3H, C=OC\(_{CH_3}\)), 1.36 (s, 18H, C(CH\(_3\))\(_3\)); \(^{13}\)C\(^{(1}\)H)-NMR (101 MHz, CDCl\(_3\)) \(\delta 199.04\) (C=O), 151.36 (C\(_{Ar}\)C(CH\(_3\))\(_3\)), 137.04 (C\(_{Ar}\)C=O), 127.50 (1 CH\(_{Ar}\)), 122.66 (2 CH\(_{Ar}\)), 35.13 (C(CH\(_3\))\(_3\)), 31.54 (C(CH\(_3\))\(_3\)), 27.07 (C=OCH\(_3\)).

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(S)-1-phenyl-N-(1-phenylethylidene)ethanamine ((S)-23)\(^6\)

By general method acetophenone (1.96 g, 16.32 mmol, 1.2 eq.) and (S)-1-phenylethanamine (1.65 g, 13.6 mmol, 1.0 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (135 °C at 0.15 mbar) afforded (S)-23 (1.92 g, 8.6 mmol, 63 %) as a clear oil.

\(\text{C}_{16}\text{H}_{17}\text{N} (223.31 \text{ g/mol})\):

- **b.p.:** 135 °C (0.15 mbar); 10:1 \(E/Z\) mixture, major: \(^1\text{H}-\text{NMR} (500 \text{ MHz}, \text{CDCl}_3) \delta: 7.84 (m, 2H, CH\text{Ar}CH\text{Ar}C=\text{N}), 7.47 (d, \text{J} = 7.8 \text{ Hz}, 2H, CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}), 7.39 (m, 3H, CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}) and CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}), 7.33 (t, \text{J} = 7.5 \text{ Hz}, 2H, CH\text{Ar}CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}), 7.23 (t, \text{J} = 7.7 \text{ Hz}, 1H, CH\text{Ar}CH\text{Ar}CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}), 4.84 (q, \text{J} = 6.5 \text{ Hz}, 1H, CH\text{Ar}CH\text{Ar}CH\text{Ar}C=\text{N}), 2.27 (s, 3H, CH\text{Ar}CH\text{Ar}C=\text{N}), 1.54 (d, \text{J} = 6.5 \text{ Hz}, 3H, CH\text{Ar}CH\text{Ar}C=\text{N}); \(^{13}\text{C}\{^1\text{H}\}-\text{NMR} (126 \text{ MHz}, \text{CDCl}_3) \delta: 163.68 \text{ (C=\text{N})}, 146.37 \text{ (C=\text{N})}, 141.68 \text{ (C=\text{N})}, 129.56 \text{ (C=\text{N})}, 128.51 \text{ (C=\text{N})}, 128.33 \text{ (C=\text{N})}, 126.82 \text{ (C=\text{N})}, 126.67 \text{ (C=\text{N})}, 125.25 \text{ (CH(CH}_3\text{)N)}, 15.78 \text{ (C=NCH}_3\text{)}; \text{Optical Rotation: } [\alpha]^{20}_{D} = 92.5 \text{ (c 0.75 in CHCl}_3, \text{0.75% EtOH)} \text{ (Lit. +97.7 (c 1.8 in CCl}_4)}\).\n
(R)-1-phenyl-N-(1-phenylethylidene)ethanamine ((R)-23)\(^6\)

By general method acetophenone (0.98 g, 8.16 mmol, 1.2 eq.) and (R)-1-phenylethanamine (0.824 g, 6.8 mmol, 1.0 eq.) were dissolved in dry benzene (10 mL). Purification by Kugelrohr distillation (135 °C at 0.15 mbar) afforded (R)-23 (0.925 g, 4.14 mmol, 61 %) as a clear oil.

\(\text{C}_{16}\text{H}_{17}\text{N} (223.31 \text{ g/mol})\):

\(^1\text{H}-\text{NMR} (500 \text{ MHz}, \text{CDCl}_3) \delta: 7.84 (m, 2H, CH\text{Ar}CH\text{Ar}C=\text{N}), 7.47 (d, \text{J} = 7.8 \text{ Hz}, 2H, CH\text{Ar}CH\text{Ar}C=\text{N}), 7.39 (m, 3H, CH\text{Ar}CH\text{Ar}C=\text{N}) and CH\text{Ar}CH\text{Ar}C=\text{N}), 7.33 (t, \text{J} = 7.5 \text{ Hz}, 2H, CH\text{Ar}CH\text{Ar}C=\text{N}), 7.23 (t, \text{J} = 7.7 \text{ Hz}, 1H, CH\text{Ar}CH\text{Ar}C=\text{N}), 4.84 (q, \text{J} = 6.5 \text{ Hz}, 1H, CH\text{Ar}CH\text{Ar}C=\text{N}), 2.27 (s, 3H, CH\text{Ar}CH\text{Ar}C=\text{N}), 1.54 (d, \text{J} = 6.5 \text{ Hz}, 3H, CH\text{Ar}CH\text{Ar}C=\text{N}); \(^{13}\text{C}\{^1\text{H}\}-\text{NMR} (126 \text{ MHz}, \text{CDCl}_3) \delta: 163.68 \text{ (C=\text{N})}, 146.37 \text{ (C=\text{N})}, 129.56 \text{ (C=\text{N})}, 128.33 \text{ (C=\text{N})}, 126.82 \text{ (C=\text{N})}, 126.67 \text{ (C=\text{N})}, 125.25 \text{ (CH(CH}_3\text{)N)}, 15.78 \text{ (C=NCH}_3\text{)}; \text{Optical Rotation: } [\alpha]^{20}_{D} = -94.0 \text{ (c 0.75 in CHCl}_3, \text{0.75% EtOH)} \text{ (Lit. -97.7 (c 1.8 in CCl}_4)}\).\n
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2-(1-aminoethyl)phenol (24)\(^7\)

In a 500 mL three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser was inserted 2-methoxybenzonitrile (4.50 g, 33.8 mmol, 1.0 eq), CuBr (98.0 mg, 0.683 mmol, 0.02 eq) and dissolved in dry THF (75 mL). A solution of MeMgCl in THF (3M, 21.4 mL, 4.81 g MeMgCl, 64.3 mmol, 1.9 eq) was added and the resultant mixture heated to reflux for 16 hours. A short reaction control via TLC depicted all the starting material had not been consumed and therefore again a solution of MeMgCl in THF (3M, 5.00 mL, 1.12 g, 15.0 mmol, 0.4 eq; total 5.93 g MeMgCl) was added and refluxing continued for further 5 hours. Afterwards the reaction mixture was allowed to cool to room temperature. A mechanical stirrer, a ammonia condensation vessel and washing bottles were mounted and the mixture cooled to -78 °C. Subsequently ammonia (approx. 200 mL) was condensed into the reaction mixture. Lithium (1.19 g, 169 mmol, 5.0 eq) was added in small pieces until the reaction mixture turned blue. The cooling bath was removed and the reaction mixture was allowed to warm up overnight while stirring and evaporating all ammonia. tert-Butylmethylether (MTBE) was added to the mixture, cooled to 0 °C and titrated with concentrated HCl to pH 8. The organic layer was separated, the aqueous layer salted out and extracted with MTBE (3 x 100 mL). The combined organic layers were washed with brine (100 mL), 0.5 M HCl (3 x 150 mL) and the acidic aqueous phase extracted with MTBE (3 x 50 mL). The combined organic layers were dried over MgSO\(_4\), solvents removed under reduced pressure and the residue was purified via distillation (60-65 °C at 0.08 mbar). 24 was obtained as a greenish oil (1.03 g, 7.5 mmol, 22%). The product contained 1-(2-Methoxyphenyl)ethanamine as an impurity (0.265 g, 1.8 mmol, 4%).

C\(_8\)H\(_{11}\)NO (137.18 g/mol):

\[ \text{b.p.: } 65^\circ\text{C} (0.08 \text{ mbar}); \text{\( ^1\)H-NMR (400 MHz, CDCl}_3) \delta 7.15 (\text{td, } ^3J = 7.9 \text{ Hz, } ^4J = 1.7 \text{ Hz, } 1\text{H}, \text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}(\text{NH}_2); 6.97 (\text{dd, } ^3J = 7.5 \text{ Hz, } ^4J = 1.5 \text{ Hz, } 1\text{H}, \text{CH}_2\text{C}_6\text{H}_4(\text{OH}); 6.84 (\text{dd, } ^3J = 8.1 \text{ Hz, } \text{CH}_2\text{CH}_2\text{C}_6\text{H}_4(\text{OH}); 6.78 (\text{td, } ^3J = 7.4 \text{ Hz, } ^4J = 1.1 \text{ Hz, } 1\text{H}, \text{CH}_2\text{C}_6\text{H}_4\text{CH}(\text{OH}); 4.33 (\text{q, } J = 6.6 \text{ Hz, } 1\text{H}, \text{CH}(\text{NH}_2)(\text{CH}_3); 3.85 (\text{s, } 2\text{H, } \text{NH}_2); 1.48 (\text{d, } J = 6.7 \text{ Hz, } 3\text{H, } \text{CH}_3); ^13\text{C}(\text{H})-\text{NMR (126 MHz, CDCl}_3) \delta 157.76 (\text{C}_6\text{H}_4(\text{OH}), 128.59 (\text{C}_6\text{H}_4(\text{CH}); 128.23 (\text{CH}_2); 127.31 (\text{CH}_2); 119.13 (\text{CH}_2); 117.35 (\text{CH}_2); 51.87 (\text{CH}(\text{NH}_2)(\text{CH}_3)); 24.01 (\text{CH}_3).\]

\[\text{N-1-(2-hydroxyphenyl)ethylbenzamide (25)}\]

In a 25 mL two-neck round bottom flask equipped with a magnetic stirrer and a septum was placed crude 24 (1.295 g, 9.3 mmol, 1.24 eq), dissolved in CH\(_2\)Cl\(_2\) (10 mL) and cooled to 0 °C. Benzoylchloride (1.05 g, 7.50 mmol, 1.0 eq) and triethylamine (0.833 g, 8.25 mmol, 1.1 eq) were added via syringe pump over a period of 5 minutes. After another 10 minutes the cooling bath was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. Solvents were removed at the rotavap and the crude was purified via elution chromatography (7 cm x 4 cm, SiO\(_2\), EtOAc) to give 25 as a yellow oil. The product contained N-(1-(2-Methoxyphenyl)ethyl)benzamide as an impurity of about 25%. Thus, the crude product was transferred to an

25 mL oven-dried argon-purged two-neck round bottom flask, dissolved in 5 mL CH₂Cl₂ and cooled to -78 °C. A solution of BBr₃ (1M in CH₂Cl₂) was added dropwise via syringe and the resultant mixture stirred for 15 minutes. The cooling bath was removed and reaction mixture allowed to warm to room temperature overnight. 10% NaOH (10 mL) were added dropwise and the resultant mixture stirred for 10 minutes. Layers were separated and the aqueous layer was acidified with 1M HCl (25 mL), set to pH 8 via addition of saturated NaHCO₃ solution and extracted with CH₂Cl₂ (2 x 25 mL). The combined organic layers were dried over MgSO₄, solvents removed under reduced pressure and 25 obtained as a yellow oil (1.54 g, 6.4 mmol, 85%). Enantiomers were separated by semipreparative HPLC. 25 was dissolved in a mixture of heptane/2-propanol (9:1) to a concentration of 0.3 g mL⁻¹. Daicel Chiralcel OD (2 cm x 25 cm), n-hexane : 2-propanol (90:10), 6 mL min⁻¹, 40 °C, 0.25 mL injection volume, tᵣ = 41.0 min (S)-(+) tᵣ = 49.0 min (R)-(−)

C₁₃H₁₅NO₂ (241.29 g/mol):

m.p.: 131-133 °C; ¹H-NMR (500 MHz, CDCl₃) δ 9.23 (s, 1H, C₆(OH)), 7.75 (m, 2H, CH₆C₆C=O), 7.51 (m, 1H, CH₆CH₆CH₆C₆C=O), 7.43 (m, 2H, CH₆CH₆C₆C=O), 7.28 (dd, 3J = 7.7, 4J = 1.7 Hz, 1H, CH₆CH₆CH₆(C₆H)), 7.20 (ddd, 3J = 8.1, 7.3, 4J = 1.7 Hz, 1H, CH₆CH₆C₆C₆H), 6.97 (dd, 3J = 8.1, 4J = 1.3 Hz, 1H, CH₆C₆C₆H), 6.53 (dd, 3J = 8.5 Hz, 1H, NH), 5.51 (dq, 3J = 8.6, 7.1 Hz, 1H, CH₆NH), 1.73 (d, 3J = 7.0 Hz, 3H, CH₆); ¹³C(¹H)-NMR (101 MHz, CDCl₃) δ 168.73 (C=O); 155.47 (C₆(OH)); 133.12 (C₆C=O); 132.31 (CH₆CH₆CH₆C₆C=O); 129.48 (CH₆CH₆C₆C₆H); 128.82 (CH₆CH₆C₆C₆H₆); 128.57 (C₆(C₆H)); 127.26 (CH₆C₆C₆H); 125.91 (C₆C₆C₆H); 120.39 (CH₆C₆C₆C₆H); 118.60 (CH₆C₆C₆H); 43.64 (CH₆NH); 19.79 (CH₆); IR (neat, ATR) ν/cm⁻¹ = 3350 (m), 3065 (w), 2933 (w), 2733 (w), 2677 (w), 2620 (w), 1623 (m), 1568 (w), 1538 (s), 1488 (s), 1409 (m), 1349 (m), 1277 (m), 1232 (s), 1188 (m), 1132 (m), 1102 (m), 1019 (w), 928 (w), 872 (w), 838 (m), 765 (s), 705 (s), 696 (s); MS (EI, 70 eV): 241.1 (45.8%, [M]+), 168.7 (26.5) (c 0.75 in CHCl₃, 0.75% EtOH); Optical Rotation (S)-isomer: [α]²⁶ = +24.8 (c 0.75 in CHCl₃, 0.75% EtOH).

4-Methyl-2-phenyl-4H-benzo[e][1,3]oxazine (26)

In a 10 mL 2-neck round bottom flask was placed (R)-25 (61.3 mg, 0.254 mmol, 1.0 eq.), dissolved in CH₂Cl₂ (2 mL) and cooled to -40 °C. POCl₃ (0.63 mL of a 0.4M solution, 0.254 mmol, 1.0 eq.) was added and the reaction mixture stirred for 30 minutes. Then pyridine (125 µL, 120 mg, 1.524 mmol, 6.0 eq) was added and stirring continued for 15 minutes. Afterwards the cooling bath was removed and the mixture allowed to warm to room temperature while stirring overnight. Reaction was quenched with 1M NaOH (2.5 mL), extracted with diethyl ether (2 x 5 mL) and solvents removed under reduced pressure. Purification via flash chromatography (SiO₂, 18 x 2.5 cm, 7 mL frctns, cyclohexane/EtOAc 10:1, frctns 12-14) gave (R)-26 as a clear oil (1.3 mg, 0.0058 mmol, 2%). With the identical procedure, (S)-25 (58.9 mg, 0.244 mmol, 1.0 eq.) gave (S)-26 (3.3 mg, 0.015 mmol, 6%) as a clear oil.

C₁₃H₁₃NO (223.27 g/mol):

¹H-NMR (400 MHz, CDCl₃) δ 8.10 (m, 2H, CH₆C₆C₆=N), 7.47 (m, 3H, CH₆CH₆C₆C₆=N and CH₆CH₆CH₆C₆C₆=N), 7.23 (m, 1H, CH₆CH₆C₆C₆-O), 7.14 (m, 2H, CH₆C₆C₆CH(CH₃)N and...
CH₄CH₂C₆H₄CH(CH₃)N, 7.04 (d, J = 8.0 Hz, 1H, CH₃C₆H₄-O), 4.83 (q, J = 6.9 Hz, 1H, CH(CH₃)N), 1.58 (d, J = 6.9 Hz, 3H, CH(CH₃)N); \(^{13}\text{C}\text{H}-\text{NMR}\) (101 MHz, CDCl₃) \(\delta\) 151.72 (O-C=N), 148.97 (C₆H₄-O), 132.55 (C₆H₄C=N), 131.05 (CH₃CH₂CH₂CH₆H₄C=N), 128.36 (CH₃CH₂CH₂CH₆H₄C=N), 128.04 (CH₃CH₂CH₂CH₆H₄C=N), 127.55 (CH₃CH₂CH₂CH₆H₄C=N), 126.12 (CH₃CH₂CH₂CH₆H₄N), 124.89 (CH₃CH₂CH₂CH₆H₄N), 115.62 (CH₃C₆H₄-O), 50.16 (CH₃CH₂N), 25.51 (CH₃); \text{IR}\) (neat, ATR) \(\nu\) = 3059 (w), 2964 (m), 2925 (m), 2854 (w), 1670 (s), 1585 (w), 1488 (m), 1462 (w), 1449 (m), 1347 (m), 1289 (w), 1275 (s), 1198 (s); \text{Optical Rotation}\) (R)-isomer: \([\alpha]_{D}^{20}\) = -8.6 (c 0.13 in CHCl₃, 0.75% EtOH); \text{Optical Rotation}\) (S)-isomer: \([\alpha]_{D}^{20}\) = +10.3 (c 0.165 in CHCl₃, 0.75% EtOH).

**1-(2-methoxyphenyl)-2-methylpropan-1-amine (27)**

![Image](426x653 to 433x658)

In a 500 mL three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser was inserted 2-methoxybenzonitrile (4.50 g, 33.8 mmol, 1.0 eq) and dissolved in dry THF (75 mL). A solution of isopropyl magnesium chloride in THF (2 M, 32 mL, 6.61 g PrMgCl, 64.27 mmol, 1.9 eq) was added and the resultant mixture heated to reflux for 16 hours. Afterwards the reaction mixture was allowed to cool to room temperature. A mechanical stirrer, a ammonia condensation vessel and washing bottles were mounted and the mixture cooled to -78 °C. Subsequently ammonia (approx. 200 mL) was condensed into the reaction mixture. Lithium (735 mg, 105 mmol, 3.1 eq) was added in small pieces until the reaction mixture turned blue. The cooling bath was removed and the reaction mixture was allowed to warm up overnight while stirring and evaporating all ammonia. \textit{Tert}-butylmethyl ether (MTBE) was added to the mixture, cooled to 0 °C and titrated with concentrated HCl to pH 8. The organic layer was separated and the aqueous layer salted out and extracted with MTBE (3 x 100 mL). The combined organic layers were washed with brine (100 mL), 0.5 M HCl (3 x 150 mL) and the acidic aqueous phase extracted with MTBE (3 x 50 mL). The acidic aqueous layer was set to pH 11 with 10% NaOH (10%), salted out and extracted with MTBE (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO₄, solvents removed at the rotavap and the residue was purified via distillation (63 °C at 0.08 mbar) to afford 27 (5.21 g, 29 mmol, 86%) as a yellow oil.

**C₇H₁₄NO** (179.26 g/mol); \text{b.p.}: 65 °C at 0.08 mbar; \text{H-NMR}\) (400 MHz, CDCl₃) \(\delta\) 7.24 (m, 1H, CH₃C₆H₄CH(NH₂)), 7.19 (m, 1H, CH₃C₆H₄CH(NH₂)), 6.93 (t, J = 7.5, 1H, CH₃CH₂C₆H₄C(OCH₃)), 6.85 (d, J = 8.2 Hz, 1H, CH₃C₆H₄C(OCH₃)), 3.88 (d, J = 7.6 Hz, 1H, CH(CH₃)₂), 3.82 (s, 3H, OCH₃), 1.97 (m, 1H, CH(CH₃)₂), 1.50 (s, 2H, NH₂), 0.99 (d, J = 6.7 Hz, 3H, CH(CH₃)₂), 0.79 (d, J = 6.8 Hz, 3H, CH(CH₃)₂).

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\[ N-(1-(2\text{-hydroxyphenyl})-2\text{-methylpropyl})\text{benzamide (28)} \]

\[
\begin{align*}
\text{In a 25 mL round-bottom flask was placed 27 (1.0 g, 5.59 mmol, 1.0 eq.) and cooled to 0 °C. Benzyol chloride (782 mg, 5.59 mmol, 1.0 eq.) and triethylamine (621 mg, 6.15 mmol, 1.1 eq.) were added dropwise and the reaction mixture was stirred at room temperature for 24 hours. Elution chromatography (SiO}_2, \text{EtOAc}) and removal of solvents under reduced pressure afforded } N-(1-(2-methoxyphenyl)-2-methylpropyl)\text{benzamide (1.52 g, 5.36 mmol, 96 %) which was dissolved in dry dichloromethane (12 mL) and cooled to} -78 °C. \text{Boron tribromide (1.0 M in CH}_2\text{Cl}_2, 16.1 mmol, 3.0 eq.) was added dropwise, the cooling bath removed and the reaction mixture allowed to warm up to room temperature while stirring overnight. It was then cooled to 0 °C and quenched by addition NaOH (10% w/w, 30 mL). After seizure of gas evolution layers were separated and the aqueous layer acidified with concentrated HCl (8 mL). It was then basified to pH of 8 by addition of NaHCO}_3 (150 mL) and extracted with CH}_2\text{Cl}_2 (2 x 25 mL). The combined organic layers were dried over anhydrous MgSO}_4, filtered and solvents removed under reduced pressure. The residue was dried \textit{in vacuo} to afford 28 (1.2 g, 4.46 mmol, 83 %) as a white solid. Enantiomers were separated via semipreparative HPLC (Daicel Chiralcel AD (2 cm x 25 cm), \textit{n}-hexane : 2-propanol (90:10), 6 mL min^{-1}, 25 °C, 0.4 mL injection volume, \textit{t}_R = 43.0 \text{min (+), } \textit{t}_S = 52.0 \text{min (-)}, 28 \text{ was dissolved in a mixture of heptane/2-propanol (9:1) to a concentration of 0.3 g mL}^{-1}. C_{17}H_{19}NO_2 (269.34 g/mol):
\]
\[ \text{m.p.: 138 °C; } ^1\text{H-NMR (500 MHz, CDCl}_3) \delta 8.56 (s, 1H, OH), 7.75 (m, 2H, CH}_2\text{Ar}, C=O), 7.48 (m, 1H, CH}_2\text{ArCH}_2\text{CH}=C(OH), 7.39 (m, 2H, CH}_2\text{ArCH}=C(OH), 7.17 (dd, J = 7.6, 1.6 Hz, 1H, CH}_2\text{Ar}, C=O(NH)), 7.02 (d, J = 9.1 Hz, 1H, NH), 6.94 (dd, J = 8.1, 1.2 Hz, 1H, CH}_2\text{Ar(OH)), 6.87 (td, J = 7.5, 1.2 Hz, 1H, CH}_2\text{ArCH}_2\text{ArCNHNH), 4.91 (dd, J = 10.3, 9.1 Hz, 1H, CH=O), 2.43 (dhept, J = 10.3, 6.6 Hz, 1H, CH(CH}_3)_2), 1.18 (d, J = 6.6 Hz, 3H, CH}_3), 0.87 (d, J = 6.6 Hz, 3H, CH}_3); ^13\text{C}(^1\text{H})\text{-NMR (101 MHz, CDCl}_3) \delta 168.46 (C=O), 155.22 (C=O), 133.87 (C=O), 131.96 (CH}_2\text{ArCH}_2\text{CH}=C(OH), 128.85 (CH}_2\text{ArCH}=C(OH), 128.75 (CH}_2\text{Ar}, C=O), 128.14 (CH}_2\text{ArCNHNH, 127.44 (C=O), 127.19 (CH}_2\text{Ar}, C=O), 120.54 (CH}_2\text{ArCH}=C(OH), 118.02 (CH}_2\text{Ar}, C=O), 56.86 (CH=O), 31.32 (CH(CH}_3)_2), 20.61 (CH}_3), 20.51 (CH}_3); \text{IR (neat, ATR) } \nu/cm}^{-1} = 3401 (m), 3155 (w), 3103 (w), 3076 (w), 2955 (w), 2870 (w), 1633 (s), 1576 (m), 1487 (m), 1453 (s), 1380 (m), 1311 (m), 1259 (m), 1252 (m), 1188 (m), 1130 (m), 1104 (w), 1040 (m), 930 (m), 857 (m), 756 (s), 704 (s), 685 (s); \text{MS (EI, 70 eV): 269.1 (3.4%, [M]^+), 226.1 (49%, [M-CH}_3]^+); HRMS: calculated: 269.1411; found: 269.1413; EA: calculated: C, 75.81; H, 7.11; N, 5.20; found: C, 74.60, H, 7.13; N, 5.13; Optical Rotation (R)-isomer: \[
[a]^{26}_{D} = -24.3 \ \text{(c 0.75 in CHCl}_3, 0.75\% \text{ EtOH)}; \quad \text{Optical Rotation (S)-isomer: } [a]^{26}_{D} = +25.7 \ \text{(c 0.75 in CHCl}_3, 0.75\% \text{ EtOH)}. \]
4-Isopropyl-2-phenyl-4H-benzo[e][1,3]oxazine (29)

In a 10 mL Schlenk vial was placed (R)-28 (100 mg, 0.37 mmol, 1.0 eq.) and dissolved in CH$_2$Cl$_2$ (1 mL). The solution was cooled to -40 °C with the aid of a cryostat. Then a solution of POCl$_3$ (0.4 M in CH$_2$Cl$_2$, 1 mL, 0.4 mmol, 1.08 eq.) was added dropwise. The reaction mixture was stirred at -40 °C for 2 hours. Pyridine (176 mg, 2.23 mmol, 6.0 eq.) was added dropwise and stirring continued for one hour. The cryostat was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. It was then cooled to 0 °C and quenched with NaOH solution (1 M, 5 mL, 5 mmol). After ether extraction (3 x 25 mL) the combined organic layers were dried over MgSO$_4$, filtered and solvents removed under reduced pressure. The residue was purified by flash chromatography to afford (R)-28 (39 mg, 0.155 mmol, 42%) as an off-white oil. Identical to the procedure above, (S)-28 (538 mg, 2.0 mmol, 1.0 eq.) , a solution of POCl$_3$ (306 mg, 2.0 mmol, 1.0 eq.) and pyridine (949 mg, 12 mmol, 6.0 eq.) gave (S)-29 (114 mg, 0.45 mmol, 23%) as a clear oil.

C$_{17}$H$_{17}$NO (251.32 g/mol):

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (m, 2H, H12), 7.46 (m, 3H, H13 and H14), 7.25 (td, $J$ = 7.7, 1.8 Hz, 1H, H7), 7.14 (td, $J$ = 7.4, 1.2 Hz, 1H, H6), 7.09 (dd, $J$ = 7.5, 1.7 Hz, 1H, H5), 7.04 (dd, $J$ = 8.1, 1.0 Hz, 1H, H8), 4.67 (d, $J$ = 3.9 Hz, 1H, H3), 2.14 (m, 1H, H2), 1.09 (d, $J$ = 6.8 Hz, 3H, H1), 0.86 (d, $J$ = 6.8 Hz, 3H, H1'); $^{13}$C{H}$^1$-NMR (101 MHz, CDCl$_3$) $\delta$ 152.10 (C10), 149.90 (C9), 132.53 (C11), 131.04 (C14), 128.36 (C13), 127.96 (C7), 127.62 (C12), 124.56 (C6), 122.50 (C4), 115.39 (C8), 60.06 (C3), 36.56 (C2), 18.93 (C1), 17.20 (C1'); IR (neat, ATR) v/cm$^{-1}$ = 3066 (w), 3044 (w), 2959 (m), 2928 (w), 2871 (w), 1675 (s), 1586 (w), 1486 (m), 1458 (m), 1355 (m), 1291 (m), 1243 (m), 1224 (s), 1194 (m), 1063 (m), 1028 (w); HRMS: calculated: 251.1305; found: 251.1308; EA: calc. C, 81.24; H, 8.24; N, 5.57; O, 6.97; found: C, 80.91; H, 7.48; N, 5.20; Optical Rotation (R)-isomer: $\left[\alpha\right]_{D}^{20}$ = -44.4 (c 1.65 in CHCl$_3$, 0.75% EtOH); Optical Rotation (S)-isomer: $\left[\alpha\right]_{D}^{20}$ = + 20.4 (c 0.75 in CHCl$_3$, 0.75% EtOH).

N-(2-methoxybenzylidene)-1-phenylmethanamine (30)$^9$

A 50 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge was set under argon atmosphere and charged with 4 Å molecular sieves (4.00 g). Benzylamine (8.0 mL, 73.4 mmol, 1.0 eq) was added and dissolved in CH$_2$Cl$_2$ (19 mL). To the stirred mixture was added a solution of 2-methoxybenzaldehyde (10.0 g, 73.4 mmol, 1.0 eq) in CH$_2$Cl$_2$ (4.3 mL) and stirring continued for three hours. The reaction mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. Distillation (0.09-0.10 mbar, 136-138 °C) of the filtrate gave 30 (14.5 g, 64.4 mmol, 88%) as a colourless oil.

C₈H₁₅NO (225.29 g/mol):
\textbf{b.p.:} 136-138 °C at 0.09-0.10 mbar; \textbf{¹H-NMR} (400 MHz, CDCl₃) δ 8.85 (s, 1H, CH=N), 8.01 (dd, 3\(J = 7.7\) Hz, \(4J = 1.6\) Hz, 1H, CH₂CH₂C₆H₅CH=N), 7.39 (m, 1H, CH₃CH₂CH₂CH₃C₆H₅(COCH₃)), 7.33 (m, 4H, CH₂CH₂CH₂ and CH₂CH₂CH₂CH₂), 7.24 (m, 1H, CH₃CH₂CH₂CH₂CH₂), 6.98 (t, \(5J = 7.5\) Hz, 1H, CH₂CH₂C₆H₅(OCH₃)), 6.92 (d, \(J = 8.3\) Hz, 1H, CH₂CH₂CH₂C₆H₅(CH=CH)), 4.82 (s, 2H, CH₂), 3.88 (s, 3H, OCH₃); \textbf{GC-MS} (EI, 70 eV, PhMeSi, 100.2/10.270/10): \(t_r = 16.9\) min, \(m/z = 224\) ([M-H]$^+$).

\begin{center}
\textbf{N-benzyl-1-(2-methoxyphenyl)-2,2-dimethylpropan-1-amine (31)$^9$

\begin{center}
\includegraphics[width=0.2\textwidth]{image1}
\end{center}
\end{center}

A 250 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge was set under argon atmosphere and charged with \textit{tert}-BuLi (22 mL of a 1.7 M solution in pentane, 37.8 mmol, 1.7 eq). The solution was cooled to -30 °C and via a cooling trap the solvent was removed \textit{in vacuo}. The resulting colourless solid was cooled to -78 °C and \textit{tert}-BuLi (22 mL of a 1.7 M solution in pentane, 37.8 mmol, 1.0 eq) was added over a period of two hours using a syringe pump and causing the mixture to turn purple. After three hours h the mixture was allowed to warm to 0 °C and stirring was continued overnight. A saturated aqueous solution of NH₄Cl (11 mL) was added and the mixture turned yellow. Layers were separated, the aqueous layer was extracted with Et₂O (2 x 20 mL), the combined organic layers were dried over Na₂SO₄ and solvent was removed under reduced pressure. Distillation (0.06-0.08 mbar, 131-142 °C) of the residue gave 31 (4.82 g, 17.0 mmol, 77%) as a yellow oil.

C₁₉H₂₃NO (283.41 g/mol):
\textbf{b.p.:} 131-142 °C at 0.06-0.08 mbar; \textbf{¹H-NMR} (400 MHz, CDCl₃) δ 7.45 (d, \(J = 7.3\) Hz, 1H, CH₂CH₂C₆H₅CH(=N)), 7.18 (m, 4H, CH₂CH₂C₆H₅CH₂ and CH₂CH₂CH₂CH₂), 7.21 (m, 2H, CH₂CH₂C₆H₅CH₂CH₂ and CH₂CH₂CH₂CH₂CH₂), 6.97 (t, \(J = 7.2\) Hz, 1H, CH₂CH₂CH₂C₆H₅(OCH₃)), 6.87 (d, \(J = 8.1\) Hz, 1H, CH₂CH₂C₆H₅(OCH₃)), 4.06 (s, 1H, CH₂NH), 3.77 (s, 3H, OCH₃), 3.55 (d, \(J = 13.2\) Hz, 1H, CH₂), 3.39 (d, \(J = 13.2\) Hz, 1H, CH₂), 0.89 (s, 9H, C(CH₃)₃).

\begin{center}
\textbf{1-(2-methoxyphenyl)-2,2-dimethylpropan-1-amine (32)$^9$

\begin{center}
\includegraphics[width=0.2\textwidth]{image2}
\end{center}
\end{center}

A 50 mL round-bottom flask equipped with a stirring bar and an argon tube was charged with Pd/C (Degussa type 101 NE/W, 0.343 g), 31 (4.82 g, 17.0 mmol, 1.0 eq) and EtOH (15 mL). The mixture was degassed performing three “freeze-pump-thaw” cycles purging with hydrogen each time. Afterwards the mixture was heated to 60 °C and stirred for 26 hours under ambient hydrogen pressure. After cooling to room temperature the mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. Distillation (0.06-0.08 mbar, 82-85 °C) of the residue gave 32 (2.93 g, 15.2 mmol, 89%). Enantiomers were separated by recrystallisation. A 25 mL round-bottom flask equipped with a stirring bar and a reflux condenser was charged with 32 (2.93 g, 15.2 mmol, 1.0 eq), (S)-mandelic acid (2.31 g, 15.2 mmol, 1.0 eq) and AcOEt (4.5 mL). The mixture was heated to reflux until all the solid was dissolved and the stirring bar was removed from
the hot solution. After 22 hours the mother liquor was decanted and the remaining crystals were washed with Et$_2$O and n-pentane and dried in vacuo. Afterwards the obtained (R,S)-salt was recrystallized twice as follows. A 50 mL round-bottom flask with a stirring bar was charged with the (R,S)-salt (1.95 g, 5.64 mmol), AcOEt (14.5 mL) and EtOH (1.16 mL). The mixture was heated until all salt dissolved and the stirring bar was removed. After 40 hours the mother liquor was decanted and the precipitated crystals were washed with Et$_2$O and n-pentane and dried in vacuo. A diastereomeric excess >96% was detected by $^1$H-NMR. The enantiomerically enriched (R,S)-salt (0.980 g, 2.84 mmol) was put into a separating funnel and washed with 10% aqueous NaOH (2 x 20 mL). The combined aqueous layers were extracted with TBME (40 mL) and washed with 10% aqueous NaOH (2 x 20 mL). The combined aqueous layers were extracted with TBME (3 x 40 mL). The combined organic layers were dried over Na$_2$SO$_4$ and evaporation of the solvent gave already partially enantiomerically enriched (S)-32 (2.37 g, 12.3 mmol). A 50 mL round-bottom flask was charged with partially enantiomerically enriched (S)-32, (R)-mandelic acid (1.86 g, 12.3 mmol), AcOEt (26.3 mL) and EtOH (0.7 mL) and the mixture was heated until all salt dissolved and the stirring bar was removed. After 20 hours the mother liquor was decanted and the crystals were washed with Et$_2$O and n-pentane. This recrystallisation procedure was repeated once. A diastereomeric excess >96% was detected by $^1$H-NMR. The free amine was obtained from the (S,R)-salt (0.727 g, 2.11 mmol) by addition of 10% aqueous NaOH and subsequent extraction with AcOEt as described above to afford (S)-32 (0.381 g, 1.97 mmol, 26%) as a colourless oil.

C$_{12}$H$_{19}$NO (193.29 g/mol):

b.p.: 82-85 °C at 0.06-0.08 mbar; $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.34 (mbr, 1H, CH$_A$C$_A$CHNH$_2$), 7.19 (t, $J = 7.8$ Hz, 1H, CH$_A$C$_A$C$_A$CHNH$_2$), 6.93 (t, $J = 7.4$ Hz, 1H, CH$_A$C$_A$C$_A$(OCH$_3$)), 6.84 (d, $J = 8.2$ Hz, 1H, CH$_A$C$_A$(OCH$_3$)), 4.26 (s, 1H, CHNH$_2$), 3.79 (s, 3H, OCH$_3$), 3.39 (s, 3H, OCH$_3$), 1.52 (sbr, 2H, NH$_2$), 0.91 (s, 9H, C(CH$_3$)$_3$); GC-MS (EI, 70 eV, PhMeSi, 100.2/10.270/10): t$_R$ = 10.3 min, m/z = 136 ([M-(C(CH$_3$)$_3$)]$^+$). Optical Rotation (R)-isomer: $[\alpha]^{20}_D = +37.0$ (c 2.02 in EtOH); Optical Rotation (S)-isomer: $[\alpha]^{20}_D = -37.1$ (c 2.02 in EtOH).

(R)-(−)-2-(1-amino-2,2-dimethylpropyl)phenol (33)$^9$

In a 25 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge (R)-32 (0.537 g, 2.78 mmol, 1.0 eq) was dissolved in CH$_2$Cl$_2$ (4.7 mL) and cooled to -78 °C. BBr$_3$ (7.5 mL of a 1 M solution in CH$_2$Cl$_2$) was added dropwise and the mixture was stirred overnight. The reaction mixture was poured on a saturated aqueous solution of NaHCO$_3$ (20 mL) and ice. Additional NaHCO$_3$ solution was added until a pH at 9 was observed. Phase separation, extraction with CH$_2$Cl$_2$ (3 x 30 mL), drying over Na$_2$SO$_4$ and evaporation of the solvent gave crude (R)-33 (511 mg, 2.78 mmol, 99%) as a brown solid.

C$_{11}$H$_{17}$NO (179.26 g/mol):

$^1$H-NMR (250 MHz, CDCl$_3$) δ 7.14 (t, $J = 7.3$ Hz, 1H, CH$_A$C$_A$C$_A$CH(NH$_2$)), 6.90 (d, $J = 7.1$ Hz, 1H, CH$_A$C$_A$C$_A$CH(NH$_2$)), 6.81 (d, $J = 8.0$ Hz, 1H, CH$_A$C$_A$(OH)), 6.74 (t, $J = 7.2$ Hz, 1H, CH$_A$C$_A$C$_A$(OH)), 3.87 (s, 1H, CH(NH$_2$)), 0.96 (s, 9H, C(CH$_3$)$_3$); Optical Rotation (R)-isomer: $[\alpha]^{20}_D = -37.6$ (c 2.06 in CDCl$_3$, 0.75% EtOH).
(R)-(−)-N-((1-(2-hydroxyphenyl)-2,2-dimethylpropyl)benzamide (34)\textsuperscript{10}

\[ \text{In a 25 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge a solution of crude (R)-33 (0.470 g, 2.62 mmol, 1.0 eq) in CH}_2\text{Cl}_2 (7.5 mL) was cooled to 0 °C and benzoyl chloride (0.33 mL, 2.88 mmol, 1.1 eq) and triethylamine (0.44 mL, 3.15 mmol, 1.2 eq) were added. The cooling bath was removed after 5 min. and the mixture was stirred at room temperature for 18 hours. Elution of the reaction mixture with AcOEt through a short silica gel column gave (R)-34 (435 mg, 1.54 mmol, 59%) as a grey solid.}

C\textsubscript{18}H\textsubscript{21}NO\textsubscript{2} (283.36 g/mol): m.p.: 151-152 °C; \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.23 (d, \( J \) = 7.2 Hz, 1H, NH), 7.80 (d, \( J \) = 6.9 Hz, 2H, CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 7.52 (t, \( J \) = 7.7 Hz, 1H, CH\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 7.40 (t, \( J \) = 7.7 Hz, 2H, CH\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 7.13 (t, \( J \) = 7.3 Hz, 1H, CH\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 6.89 (t, \( J \) = 7.5 Hz, 1H, CH\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 6.78 (d, \( J \) = 8.1 Hz, 1H, CH\textsubscript{Ar}CH\textsubscript{Ar}C=O), 5.25 (d, \( J \) = 9.9 Hz, 1H, CHNH), 1.06 (s, 9H, C(C\textsubscript{3}H\textsubscript{3})); IR (neat, ATR) v/cm\textsuperscript{-1} = 3395 (m), 3236 (w), 3185 (w), 2961 (m), 2866 (w), 1639 (s), 1625 (s), 1600 (m), 1531 (s), 1487 (m), 1453 (s), 1356 (m), 1245 (m), 1208 (m), 1174 (m), 1110 (m), 1063 (m), 1024 (m), 838 (m), 751 (s), 704 (s), 691 (s); MS (EI, 70 eV): 283.1 (1.4%, [M]+). 226.1 (100%, [M-C\textsubscript{4}H\textsubscript{9}]+); Optical Rotation \((R)\)-isomer: \( [\alpha]_D^{20} \) = -114.0 (c 3.26 in EtOH).

(R)-(−)-4-(tert-butyl)-2-phenyl-4H-benzo[e][1,3]oxazine (35)\textsuperscript{10}

\[ \text{In a 10 mL Schlenk vial was placed (R)-34 (75 mg, 0.265 mmol, 1.0 eq.) and dissolved in CH}_2\text{Cl}_2 (2.6 mL). The solution was cooled to -40 °C with the aid of a cryostat. Then a solution of POCl\textsubscript{3} (40 mg, 0.265 mmol, 1.0 eq.) was added dropwise. The reaction mixture was stirred at -40 °C for 30 minutes. Pyridine (126 mg, 1.59 mmol, 6.0 eq.) was added dropwise and stirring continued for one hour. The cryostat was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. It was then cooled to 0 °C and quenched with NaOH solution (1 M, 5 mL, 5 mmol). After ether extraction (3 x 25 mL) the combined organic layers were dried over MgSO\textsubscript{4}, filtered and solvents removed under reduced pressure. The residue was purified by flash chromatography (SiO\textsubscript{2}, cyclohexane/EtOAc 20:1, 20x2 cm, 7 mL fractions) to afford (R)-35 (20 mg, 0.073 mmol, 28%) as a clear oil.}

C\textsubscript{18}H\textsubscript{19}NO (265.35 g/mol): \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.13 (m, 2H, H12), 7.50 (m, 1H, H14) 7.47 (m, 2H, H13), 7.30 (m, 1H, H7), 7.16 (m, 1H, H6), 7.13 (m, 1H, H5), 7.08 (d, \( J \) = 7.9 Hz, 1H, H8), 4.46 (s, 1H, H3), 0.99 (s, 9H, H1); \textsuperscript{13}C\textsuperscript{(1)}H-NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 152.32 (C10), 150.39 (C9), 132.37 (C11), 131.12 (C14), 128.68 (C5), 128.40 (C13), 128.02 (C7), 127.79 (C12), 123.96 (C6), 121.61 (C4), 115.50 (C8), 64.71 (C3), 38.88 (C2), 10.83 (C15), 1.06 (9H, C(C\textsubscript{3}H\textsubscript{3})); IR (neat, ATR) v/cm\textsuperscript{-1} = 3395 (m), 3236 (w), 3185 (w), 2961 (m), 2866 (w), 1639 (s), 1625 (s), 1600 (m), 1531 (s), 1487 (m), 1453 (s), 1356 (m), 1245 (m), 1208 (m), 1174 (m), 1110 (m), 1063 (m), 1024 (m), 838 (m), 751 (s), 704 (s), 691 (s); MS (EI, 70 eV): 283.1 (1.4%, [M]+). 226.1 (100%, [M-C\textsubscript{4}H\textsubscript{9}]+); Optical Rotation \((R)\)-isomer: \( [\alpha]_D^{20} \) = -114.0 (c 3.26 in EtOH).

26.18 C(1); **IR** (neat, ATR) ν/cm⁻¹ = 3058 (w), 3032 (w), 2950 (m), 2930 (w), 2905 (m), 1667 (s), 1583 (w), 1494 (m), 1486 (m), 1477 (m), 1458 (m), 1449 (m), 1391 (w), 1363 (m), 1348 (s), 1287 (w), 1244 (s), 1221 (s), 1193 (s), 1177 (m), 1091 (s), 1066 (s), 1023 (m); **HRMS:** calculated: 265.1462; found: 265.1464; **Optical Rotation** (R)-isomer: [α]D²⁰ = -11.0 (c 1.1 in CHCl₃, 0.75% EtOH).
Synthesis of Complexes

General method: An 8 mL oven-dried glass vial was equipped with a magnetic stirrer and closed with a septum. It was evacuated while cooling to room temperature and purged with argon three times. \([\text{Ir}(\text{L})(\text{COD})]\)BArF and the corresponding imine were placed into the vial and the vial was closed again. After evacuation and purging with hydrogen gas via balloon three times, freshly distilled dry THF (2 mL) was added and the reaction mixture was stirred at room temperature for 4 hours. A distinct colour change from red/orange to bright yellow was observed in all cases. The solvent was evaporated via a N\textsubscript{2} stream and LiCl (100 mg) and SiO\textsubscript{2} (100 mg) were added and suspended in EtOAc (2 mL). The vial was closed again and stirred overnight at room temperature. The solvent was evaporated via a N\textsubscript{2} stream and the residue was suspended in Pentane/TBME (1:1) where the yellow band was collected. The solvent was removed under reduced pressure and the residue triturated with pentane to give a yellow solid.

\([\text{Ir}((S)-\text{Pr-PHOX})(\text{I1})(\text{H})(\text{THF})]\)BArF (2)

In the glove box, 3 (10 mg, 0.0126 mmol, 1.0 eq.) and NaBArF (11.1 mg, 0.0126 mmol, 1.0 eq.) were added to a young’s NMR tube and dissolved in THF-d\textsubscript{8} at room temperature. The mixture was shaken until it turned homogenous and NMR spectra were recorded.

\(\text{C}_{74}\text{H}_{57}\text{BF}_{24}\text{IrN}_{2}\text{O}_{2}\text{P} (\text{M}_{\text{W}} = 1696.34 \text{ g/mol}):\)

\(^1\text{H}-\text{NMR}\) (500 MHz, THF) \(\delta\) 7.68 (s, 8H), 7.59 – 7.50 (m, 3H), 7.46 (s, 4H), 7.44 (d, \(J = 2.9 \text{ Hz}, 1\text{H}\)), 7.35 – 7.28 (m, 3H), 7.24 (d, \(J = 18.7 \text{ Hz}, 4\text{H}\)), 7.19 (d, \(J = 7.9 \text{ Hz}, 1\text{H}\)), 6.98 (t, \(J = 7.4 \text{ Hz}, 1\text{H}\)), 6.92 (t, \(J = 7.4 \text{ Hz}, 1\text{H}\)), 6.83 (t, \(J = 7.1 \text{ Hz}, 2\text{H}\)), 6.81 – 6.76 (m, 1H), 6.64 (d, \(J = 7.3 \text{ Hz}, 1\text{H}\)), 6.52 (t, \(J = 7.4 \text{ Hz}, 1\text{H}\)), 6.41 (t, \(J = 9.0 \text{ Hz}, 3\text{H}\)), 5.83 (d, \(J = 7.2 \text{ Hz}, 1\text{H}\)), 5.30 – 5.17 (m, 1H), 4.16 (dd, \(J = 8.6, 4.5 \text{ Hz}, 1\text{H}\)), 3.87 (t, \(J = 9.4 \text{ Hz}, 1\text{H}\)), 2.72 – 2.63 (m, 1H), 2.14 (s, 3H), 0.68 (d, \(J = 7.1 \text{ Hz}, 3\text{H}\)), -0.09 (d, \(J = 6.9 \text{ Hz}, 3\text{H}\)), -18.30 (d, \(J = 20.7 \text{ Hz}, 1\text{H}\)); \(^{31}\text{P}^{(1)}\text{H}-\text{NMR}\) (202 MHz, THF) \(\delta\) 0.80 (d, \(J = 19.8 \text{ Hz}\).
[Ir((S)-iPr-PHOX(II)(H)(Cl)) (3)]

By general method [Ir((S)-iPr-PHOX)(COD)]BArF (100 mg, 0.065 mmol, 1.0 eq.) and II (25.3 mg, 0.13 mmol, 2.0 eq.) afforded 24 mg (0.03 mmol, 46%) of 3 as a yellow solid.

C₃₈H₃₇ClIrN₂OP (796.36 g/mol):

1H-NMR (400 MHz, CD₂Cl₂) δ 7.70 – 7.61 (m, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 (d, J = 7.4 Hz, 1H), 7.36 (m, 6H), 7.12 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.96 (td, J = 8.0, 2.4 Hz, 2H), 6.86 – 6.80 (m, 1H), 6.72 (m, 2H), 6.62 (t, J = 7.1 Hz, 1H), 6.49 (dd, J = 11.3, 7.8 Hz, 2H), 5.88 (d, J = 7.2 Hz, 1H), 5.26 (ddd, J = 10.0, 4.2, 3.1 Hz, 1H), 4.22 (dd, J = 8.8, 4.5 Hz, 1H), 4.02 – 3.94 (m, 1H), 2.76 – 2.66 (m, 1H), 2.28 (s, 3H), 0.81 (d, J = 7.1 Hz, 3H), -0.03 (d, J = 6.8 Hz, 3H), -18.21 (d, J = 20.7 Hz, 1H); 31P{1H}-NMR (162 MHz, CD₂Cl₂) δ 2.63 (d, J = 14.5 Hz).
[Ir((S)-iPr-PHOX)(11)(H)(THF)]PF$_6$ (5)

In the glove box, [Ir((S)-iPr-PHOX)(COD)]PF$_6$ (100 mg, 0.122 mmol, 1.0 eq.) and 11 (47 mg, 0.241 mmol, 2.0 eq.) was weighed into a schlenk tube and dissolved in dry THF (3 mL). The tube was brought outside of the box and cooled to 0°C. The stopper was replaced with a septum and a long cannula was passed through into the solution. Hydrogen gas was bubbled through the stirring solution for 90 minutes at 0°C. The needle was pulled out and the resultant orange solution was degassed by freezing the solution in liquid nitrogen and evacuating while warming up in total three times. The solution was layered with dry pentane (5 mL) and placed in the freezer overnight. The solution was carefully decanted and the precipitate was rinsed with pentane (5 mL) and dried in vacuo to give 5 as a yellow amorphous solid. NMR’s were recorded at this stage. X-Ray quality crystals were obtained by redissolving the precipitate in THF and slow diffusion of diethyl ether into the solution. A total of three crystallisation cycles was required to obtain X-Ray quality crystals.
C₄₃H₄₅F₃IrN₂O₂P₂ (977.97 g/mol):

¹H-NMR (500 MHz, CD₂Cl₂) δ -21.57 (d, J = 17.0 Hz, 1H); ³¹P{¹H}-NMR (202 MHz, CD₂Cl₂) δ -4.45 (s), -149.15 (m, PF₆).

By general method [Ir((S)-iPr-SimplePHOX)(I1)(H)(Cl)]BArF (50 mg, 0.03 mmol, 1.0 eq.) and I1 (13 mg, 0.06 mmol, 2.0 eq.) afforded 18 mg (0.03 mmol, 76%) of 7 as a yellow solid.

X-Ray quality crystals were obtained by redissolving the precipitate in CH₂Cl₂ and layering with pentane. After evaporation of solvents an oil was observed which solidified into a crystalline material in the course of a few weeks.

C₃₅H₅₁ClIrN₂O₂P (790.44 g/mol):
\( ^1H\)-NMR (500 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 7.72 (s, 1H), 7.68 – 7.61 (m, 1H), 7.56 – 7.49 (m, 1H), 7.36 (s, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.94 (dd, J = 8.3, 4.4 Hz, 2H), 6.90 (s, 1H), 5.13 (d, J = 9.3 Hz, 1H), 4.28 (dd, J = 8.7, 3.1 Hz, 1H), 3.83 (t, J = 9.1 Hz, 1H), 2.90 – 2.69 (m, 1H), 2.42 (s, 3H), 2.32 (d, J = 7.7 Hz, 1H), 2.16 (d, J = 12.1 Hz, 1H), 1.91 – 1.45 (m, 10H), 1.35 – 1.18 (m, 6H), 1.15 (s, 6H), 0.90 (d, J = 7.1 Hz, 3H), 0.69 (d, J = 6.9 Hz, 3H), -19.50 (d, J = 24.3 Hz, 1H); \( ^{31}P\{^1H\}\)-NMR (202 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 101.41 (d, J = 21.9 Hz).

By general method [Ir(PHOX)(COD)]BA\( _{12} \)F (75 mg, 0.05 mmol, 1.0 eq.) and (S)-9 (22.3 mg, 0.1 mmol, 2.0 eq.) afforded 33 mg (0.042 mmol, 83%) of 10 as a yellow solid.

\( ^1H\)-NMR (500 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) -18.25 (d, J = 22.7 Hz, 1H), -19.47 (d, J = 21.7 Hz, 1H); \( ^{31}P\{^1H\}\)-NMR (202 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 5.25 (d, J = 20.2 Hz), 3.50 (d, J = 19.8 Hz).
[Ir(PHOX)((S)-9)(H)(CH₂Cl₂)]BARF (11)

In the glove box, 10 (5 mg, 0.0063 mmol, 1.0 eq.) and NaBARF (6 mg, 0.0068 mmol, 1.08 eq.) were added to a young’s NMR tube and dissolved in CD₂Cl₂ (0.4 mL) at room temperature. The mixture was shaken until it turned homogenous and NMR spectra of 11 were recorded.

C₇₀H₄₉BCl₂F₁₂IrN₂OP (1694.23 g/mol):

¹H-NMR (500 MHz, CD₂Cl₂) δ 8.23 – 8.17 (m, 1H), 7.87 (dd, J = 12.1, 7.7 Hz, 2H), 7.77 (dt, J = 5.1, 2.3 Hz, 13H), 7.75 – 7.69 (m, 2H), 7.67 (dd, J = 8.4, 6.4 Hz, 1H), 7.61 (s, 6H), 7.56 (ddt, J = 10.5, 7.8, 3.8 Hz, 4H), 7.43 (d, J = 7.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 6.42 (d, J = 8.1 Hz, 1H), 5.35 – 5.29 (m, 1H), 4.14 – 4.03 (m, 1H), 3.97 (dt, J = 10.8, 8.6 Hz, 1H), 3.01 (dd, J = 10.8, 11.0, 8.6 Hz, 1H), 2.77 (s, 3H), 1.76 (d, J = 6.6 Hz, 3H), 1.47 (dt, J = 13.6, 10.3 Hz, 1H), -16.85 (d, J = 14.6 Hz, 1H); ³¹P{¹H}-NMR (202 MHz, CD₂Cl₂) δ 10.28 (d, J = 5.7 Hz).
By general method [Ir(PHOX)(COD)]BAR$_F^-$ (25 mg, 0.017 mmol, 1.0 eq.) and (S)-26 (3 mg, 0.013 mmol, 0.8 eq.) afforded 6 mg (0.008 mmol, 59%) of 12 as a yellow solid.

C$_{36}$H$_{31}$ClIrN$_2$O$_2$P (782.29 g/mol):

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.89 (dd, $J = 7.7$, 3.2 Hz, 1H), 7.73 (dd, $J = 11.4$, 7.3 Hz, 2H), 7.57 – 7.08 (m, 21H), 6.93 (dd, $J = 11.1$, 6.9 Hz, 2H), 6.66 (t, $J = 7.4$ Hz, 1H), 6.59 (d, $J = 7.9$ Hz, 1H), 6.38 – 6.30 (m, 1H), 5.77 (dd, $J = 12.4$, 5.9 Hz, 1H), 4.52 – 4.39 (m, 2H), 4.29 (ddd, $J = 16.4$, 12.9, 10.0 Hz, 2H), 4.17 (dt, $J = 17.7$, 8.9 Hz, 1H), 3.60 (ddd, $J = 13.6$, 11.1, 8.5 Hz, 2H), 1.58 (d, $J = 6.6$ Hz, 3H), -19.09 (d, $J = 15.9$ Hz, 1H); $^{31}$P($^1$H)-NMR (162 MHz, CD$_2$Cl$_2$) δ 12.44 (s$_{br}$).
By general method [Ir(PHOX)(COD)][BArF] (25 mg, 0.017 mmol, 1.0 eq.) and (S)-29 (10.5 mg, 0.042 mmol, 2.5 eq.) afforded 10.4 mg (0.013 mmol, 75%) of 13 as a yellow solid.

C$_{38}$H$_{35}$ClIrN$_2$O$_2$P (810.34 g/mol):

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) δ 7.88 (dd, $J = 6.9$, 3.5 Hz, 1H), 7.75 (dd, $J = 11.4$, 7.4 Hz, 2H), 7.55 – 7.38 (m, 5H), 7.34 (td, $J = 7.6$, 2.0 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.25 – 7.09 (m, 5H), 6.98 – 6.86 (m, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.59 (d, $J = 7.9$ Hz, 1H), 6.34 (td, $J = 7.7$, 1.6 Hz, 1H), 5.59 – 5.51 (m, 1H), 4.44 (dd, $J = 13.6$, 10.9, 9.4 Hz, 1H), 4.31 – 4.22 (m, 1H), 4.14 (dt, $J = 10.9$, 9.0 Hz, 1H), 3.57 (ddd, $J = 13.6$, 11.1, 8.3 Hz, 1H), 2.96 – 2.84 (m, 1H), 0.94 (d, $J = 7.1$ Hz, 3H), 0.56 (d, $J = 6.9$ Hz, 3H), -19.19 (d, $J = 15.9$ Hz, 1H); $^3$P($^1$H)-NMR (162 MHz, CD$_2$Cl$_2$) δ 12.49 (s).
By general method [Ir(PHOX)(COD)]BAr₆ (50 mg, 0.0334 mmol, 1.0 eq.) and (S)-35 (17.2 mg, 0.067 mmol, 2.0 eq.) afforded 15.1 mg (0.018 mmol, 55%) of 14 as a yellow solid. C₃₀H₃₇ClIrN₃O₂P (824.37 g/mol):

^1H-NMR (500 MHz, CD₂Cl₂) δ 7.80 (dd, J = 11.6, 7.6 Hz, 2H), 7.73 (dd, J = 8.0, 3.7 Hz, 1H), 7.55 – 7.33 (m, 8H), 7.33 – 7.10 (m, 8H), 6.94 (dd, J = 11.2, 7.5 Hz, 2H), 6.63 (dd, J = 8.1, 5.3 Hz, 2H), 6.33 (t, J = 7.5 Hz, 1H), 5.75 (d, J = 2.5 Hz, 1H), 4.27 (ddd, J = 13.8, 11.0, 8.7 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.96 (dt, J = 11.1, 8.5 Hz, 1H), 3.03 (ddd, J = 13.7, 10.9, 8.6 Hz, 1H), 1.01 (s, 9H), -19.44 (d, J = 16.7 Hz, 1H); ^31P{1H}-NMR (202 MHz, CD₂Cl₂) δ 12.41 (d, J = 10.9 Hz).
Synthesis of Imines

General Method:
A 25mL oven-dried two-neck round-bottom flask equipped with a stirrer, reflux condenser and a stopper was evacuated and purged with Argon gas three times. Freshly activated 4Å mol sieves were added under an argon counterflow. The stopper was replaced with a septum and ketone, aniline and solvent were added. A spatula tip of p-toluenesulfonic acid was added. The septum was replaced by a stopper and the solution was heated to reflux for 24 to 48 hours. After cooling to room temperature under argon the solution was filtered through a paper filter and rinsed with toluene. The solvent was removed under reduced pressure and the product was purified by Kugelrohr distillation.

Compounds I111, I1912, I2013, I2112 had been prepared previously in our laboratories.

N-(1-(4-methoxyphenyl)ethylidene)aniline (I2)14

By general method 4-methoxyacetophenone (2.7 g, 18 mmol, 1.0 eq.) and aniline (2 g, 21.9 mmol, 1.21 eq.) were dissolved in dry benzene (7.5 mL). Purification by Kugelrohr distillation (110-180 °C at 0.07 mbar) afforded 3.4 g (15.1 mmol, 83%) of I2 as a yellow solid.

C15H15NO (225.29 g/mol):

m.p.: 91-92 °C (Lit. 92-94°C); 1H-NMR (500 MHz, CDCl3): 7.85 (d, J = 8.6 Hz, 2H, CHArCHArC=N), 7.25 (t, J = 7.7 Hz, 2H, CHArCHArC=N), 6.98 (t, J = 7.4 Hz, 1H, CHArCHArCHArArC=N), 6.86 (d, J = 8.6 Hz, 2H, CHArCHArArC=OMe), 6.70 (d, J = 7.7 Hz, 2H, CHArArArC=N), 3.77 (s, 3H, OC6H3), 2.11 (s, 3H, C6H3C=N);

13C{1H}-NMR (126 MHz, CDCl3) δ 164.65 (C=O), 161.62 (C=O), 151.99 (C=O), 132.30 (C=O), 129.02 (CHArCHArArC=N), 128.94 (CHArArArC=N), 123.12 (CHArCHArArC=O), 119.71 (CHArArArC=N), 113.70 (CHArArArC=O), 55.51 (OCH3), 17.30 (CH3C=N).

N-(1-cyclohexylethylidene)aniline (I3)15

By general method 1-Cyclohexylethan-1-one (1.83 g, 14.53 mmol, 1.0 eq.) and aniline (1.49 g, 15.98 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (130 °C at 0.15 mbar) afforded 1.30 g (6.44 mmol, 44%) of I3 as a colourless oil.

C14H19N (201.31 g/mol):

1H-NMR (400 MHz, CDCl3) δ 7.32 – 7.22 (m, 2H), 7.05 – 6.98 (m, 1H), 6.71 – 6.63 (m, 2H), 2.30 (ttt, J = 11.5, 3.2 Hz, 1H), 1.93 (dd, J = 6.7, 5.5 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.74 – 1.70 (m, 3H), 1.49 – 1.16 (m, 6H); 13C{1H}-NMR (101 MHz, CDCl3) δ 175.75, 151.94, 128.96, 122.91, 119.52, 113.70, 111.36, 109.04, 108.78, 108.51, 95.76, 88.80, 81.34, 70.97, 67.28, 65.34, 59.76, 53.89, 31.14, 28.47, 26.53, 23.12, 19.01, 18.78.

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14 D. Pei, Z. Wang, S. Wei, Y. Zhang, J. Sun, Org. Lett. 2006, 8, 5913-5915
49.53, 30.39, 26.30, 26.28, 17.81; GC (Machary-Nagel Optima-5-Amin (0.50 μm x 0.25 μm x 30 m), 60 kPa H2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): tR = 18.5 min; HRMS: calculated: 201.1512; found: 201.1512

N-(1-(o-toly)ethylidene)aniline (I4)

By general method acetophenone (2.29 g, 17 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.3 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (100-160 °C at 0.1 mbar) afforded 2.74 g (13.1 mmol, 77%) of I4 as a yellow oil.

C13H15N (209.29 g/mol):

major: 1H-NMR (500 MHz, CDCl3) δ 7.419 (m, 1H, CHArC=N), 7.392 (m, 2H, CH2ArCH2C=N), 7.297 (m, 1H, CH2ArCH2C=N), 7.280 (m, 1H, CH2ArCH2C=N), 7.278 (m, 1H, CH2ArCH2C=N), 7.127 (m, 1H, CH2ArCH2C=N), 6.876 (m, 2H, CH2ArC=N), 2.543 (s, 3H, C6H5CH3), 2.18 (s, 3H, CH3C=N); 13C{1H}-NMR (126 MHz, CDCl3) δ 170.036 (C=N), 151.291 (C=N), 141.571 (C=N), 135.04 (C=N), 131.111 (C=N), 129.103 (C=N), 128.683 (C=N), 127.183 (C=N), 125.849 (C=N), 123.459 (C=N), 119.303 (C=N), 21.23 (C=N), 20.51 (C=N).

minor: 1H-NMR (500 MHz, CDCl3) δ 7.122 (m, 1H, CHArCH2C=N), 7.115 (m, 1H, CHArCH2C=N), 7.107 (m, 2H, CHArCH2C=N), 7.052 (m, 1H, CHArC=N), 7.036 (m, 1H, CHArC=N), 6.906 (m, 1H, CHArCH2C=N), 6.687 (m, 2H, CHArC=N), 2.493 (s, 3H, CH3C=N); 13C{1H}-NMR (126 MHz, CDCl3) δ 171.106 (C=N), 150.290 (C=N), 139.050 (C=N), 133.01 (C=N), 130.208 (C=N), 128.251 (C=N), 128.162 (C=N), 127.069 (C=N), 125.379 (C=N), 123.498 (C=N), 120.841 (C=N), 29.32 (C=N), 21.33 (C=N).

GC-MS: (Optima-5-Amine, 100.2/10.270/10): tR = 14.6 min, m/z = 209 ([M]+1), 194 ([M-CH3]+1), 118 ([M-NPh]+1).

N-(1-(2-fluorophenyl)ethylidene)aniline (I5)

By general method 2-fluoroacetophenone (2.5 g, 18.1 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.2 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (110-160 °C at 0.1 mbar) afforded 3.08 g (14.5 mmol, 80%) of I5 as a yellow oil.

C14H12F (213.25 g/mol):

E/Z mixture 7:1, signals overlapping, only major isomer characterised: 1H-NMR (500 MHz, CDCl3) δ 7.85 (tt, J = 7.7, 1.9 Hz, 1H, CHArC=N), 7.41 (ddddd, 1H, J = 8.2, 7.1, 5.1, 1.8 Hz, CH2ArCHArF), 7.37 (t, J = 7.7 Hz, 2H, CH2ArCHArF), 7.22 (t, J = 7.5 Hz, 1H, CH2ArCH2ArF), 7.15 (m, 1H, CHArC=F), 7.12 (m, 1H, CH2ArC=F), 6.83 (d, J = 7.7 Hz, 2H, CHArC=N), 2.25 (d, J = 3.5 Hz, 3H, CH3C=N); 13C{1H}-NMR (126 MHz, CDCl3): 165.37 (C=N), 161.22 (d, J = 250.6 Hz, C-Ar-F), 150.85 (C-Ar-N), 131.70 (d, J = 8.6 Hz, C-Ar-F).

By general method 3-nitroacetophenone (0.5 g, 3 mmol, 1.0 eq.) and aniline (0.33 g, 3.6 mmol, 1.2 eq.) were dissolved in dry toluene (10 mL). Purification by recrystallisation from ethanol afforded 0.291 g (1.02 mmol, 43%) of I6 as a yellow solid.

C_{12}H_{12}N_2O_2 (240.26 g/mol):

**m.p.:** 96 °C; **^1H-NMR** (400 MHz, CDCl₃) δ 8.89 – 8.70 (m, 1H, CH₃C₆ArNO₂), 8.44 – 8.22 (m, 2H, CH₃CH₂C₆ArNO₂&CH₃C₆ArC=N), 7.64 (t, J = 8.0 Hz, 1H, CH₃CH₂CH₆ArC=N), 7.38 (t, J = 7.8 Hz, 2H, CH₃CH₂C₆ArC=N), 7.13 (t, J = 7.4 Hz, 1H, CH₃CH₂CH₆ArC=N), 6.80 (d, J = 7.3 Hz, 2H, CH₃C₆ArC=N), 2.30 (s, 3H, CH₃C=N); **^{13}C[^1H]-NMR** (101 MHz, CDCl₃) δ 163.33 (C=N), 150.91 (C₆Ar=N), 141.21 (C₆Ar=N), 133.10 (CH₃C₆ArC=N), 129.51 (C₆Ar=NC₆H₃C₆ArNO₂), 129.24 (CH₃CH₂C₆ArC=N), 125.12 (CH₃CH₂CH₆ArC=N), 124.01 (CH₃C₆ArNO₂), 119.31 (CH₃C₆ArC=N), 17.50 (CH₃C=N); **IR** (neat, ATR) ν/cm⁻¹ = 3114 (w), 3099 (w), 3076 (w), 3070 (w), 3017 (w), 1623 (m), 1593 (m), 1576 (m), 1525 (s), 1483 (s), 1473 (s), 1432 (m), 1368 (m), 1345 (s), 1317 (m), 1286 (m), 1258 (m), 1213 (m), 1170 (w), 1111 (m), 1060 (m), 1024 (w), 900 (m), 818 (m), 744 (m), 735 (s), 693 (s); **MS** (EI, 70 eV): 240.1 (82.4%), 225.1 (100%), 179.1 (42.5%); **HRMS** calculated: 240.0894; found: 240.0900; **EA:** calc. C, 69.99; H, 5.03; N, 11.66; found: C, 69.81; H, 5.14; N, 11.56
1209 (m), 1169 (w), 1144 (m), 1100 (w), 1073 (m), 910 (m), 903 (m), 810 (m), 795 (m), 753 (s), 728 (s), 654 (s); MS (EI, 70 eV): 285.1 (100%), 270.1 (82.8%), 224.1 (18.1%), 178.1 (24.1%); HRMS: calculated: 285.0744; found: 285.0740; EA: calc. C, 58.93; H, 3.89; N, 14.73; found: C, 58.93; H, 3.99; N, 14.64

N-(1-(3,5-dimethylphenyl)ethylidene)aniline (I8)

By general method 3,5-dimethylacetophenone (0.3 g, 2.2 mmol, 1.1 eq.) was dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (160 °C at 0.08 mbar) afforded 0.310 g (1.11 mmol, 45%) of I9 as a yellow oil.

C_{18}H_{25}N (279.42 g/mol):
E/Z mixture 8:1, signals overlapping; major: ¹H-NMR (500 MHz, CDCl₃) δ: 7.65 (d, J = 4.0 Hz, 2H, CH₃CH₃C=Ar-N), 7.35 (t, J = 7.7 Hz, 2H, CH₃CH₃C=Ar-N), 7.09 (d, J = 7.0 Hz, 2H, CH₃CH₃C=Ar-N), 7.02 (s, 1H, CH₃CH₃C=Ar-N), 7.02 (s, 1H, CH₃CH₃C=Ar-N), 6.98 (d, J = 6.9 Hz, 2H, CH₃CH₃C=Ar-N), 2.23 (d, J = 7.0 Hz, 3H, CH₃C=Ar-N), 1.30 (d, J = 7.1 Hz, 12H, CH₃CH₃C=Ar-N); ¹³C(¹H)-NMR (125 MHz, CDCl₃) δ: 166.23 (C=Ar-N), 152.10 (C=Ar-N), 149.18 (C=Ar-N), 139.68 (C=Ar-N), 127.05 (CH₃CH₃C=Ar-N), 123.19 (CH₃CH₃C=Ar-N), 119.54 (CH₃CH₃C=Ar-N), 117.30 (CH₃CH₃C=Ar-N), 67.09 (CH₃CH₃C=Ar-N), 11.59 (CH₃CH₃C=Ar-N), 10.38 (CH₃CH₃C=Ar-N).
N-(1-(3,5-di-tert-butylphenyl)ethylidene)aniline (I10)

By general method 15 (0.5 g, 2.15 mmol, 1.0 eq.) and aniline (0.25 g, 2.8 mmol, 1.3 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (170 °C at 0.1 mbar) afforded 0.368 g (1.2 mmol, 56%) of I10 as a yellow-white solid.

\[ C_{23}H_{29}N \] (307.47 g/mol):
- **m.p.:** 86-90 °C;
- **\[^1\]H-NMR** (500 MHz, CDCl\(_3\)) \( \delta \): 7.84 (s, 2H, CH\(_3\)ArC=Ar=N), 7.58 (s, 1H, C\(_6\)H\(_5\)C(CH\(_3\))\(_3\)CH\(_3\)ArC=Ar=N), 7.36 (t, \( J = 7.7 \) Hz, 2H, CH\(_3\)ArCH\(_3\)Ar=N), 7.09 (t, \( J = 7.5 \) Hz, 1H, CH\(_3\)ArCH\(_3\)Ar=N), 6.82 (d, \( J = 7.7 \) Hz, 2H, CH\(_3\)ArC=Ar=N), 1.40 (s, 18H, C(C(CH\(_3\))\(_3\))), 31.63 (C(CH\(_3\))\(_3\)), 17.92 (CH\(_3\)C=); **IR** (neat, ATR) \( \nu \) cm\(^{-1} \): 3061 (w), 2961 (m), 2934 (w), 2905 (w), 2865 (w), 1685 (w), 1636 (m), 1590 (m), 1477 (m), 1447 (m), 1393 (w), 1362 (m), 1232 (m), 1247 (m), 1212 (s), 1168 (m), 1068 (m), 1024 (m), 903 (m), 879 (m), 798 (m), 755 (s), 751 (s); **HRMS** (EI, 70 eV): 307.2 (52.7%), 292.2 (100%), 276.1 (12.6%); **HRMS** calculated: 307.2295; found: 307.2294;
- **EA:** calc. C, 85.94; H, 9.49; N, 4.56; found: C, 85.93; H, 9.49; N, 4.44.

N-(1-(4-(tert-butyl)phenyl)ethylidene)aniline (I11)

By general method 4-tert-butyl acetophenone (0.48 g, 2.72 mmol, 1.0 eq.) and aniline (0.35 g, 3.93 mmol, 1.44 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125 °C at 0.08 mbar) afforded 0.28 g (1.11 mmol, 41%) of I11 as yellow-white solid.

\[ C_{18}H_{21}N \] (251.37 g/mol):
- **b.p.:** 125 °C at 0.08 mbar;
- **m.p.:** 63-64 °C;
- **\[^1\]H-NMR** (400 MHz, CDCl\(_3\)) \( \delta \): 7.93 (d, \( J = 8.5 \) Hz, 2H, CH\(_3\)ArC=Ar=N), 7.48 (d, \( J = 8.5 \) Hz, 2H, CH\(_3\)ArC=Ar=N), 7.35 (t, \( J = 7.8 \) Hz, 2H, CH\(_3\)ArCH\(_3\)Ar=N), 7.08 (t, \( J = 7.4 \) Hz, 1H, CH\(_3\)ArCH\(_3\)Ar=N), 6.79 (t, \( J = 7.4 \) Hz, 2H, CH\(_3\)ArC=Ar=N), 2.22 (s, 3H, CH\(_3\)C=); 1.36 (s, 9H, C(CH\(_3\))\(_3\)); **\[^13\]C\(^{\text{\[^{1}\]H}}\)-NMR** (101 MHz, CDCl\(_3\)) \( \delta \): 165.31 (C=); 154.01 (CH\(_3\)ArC=); 152.01 (C=Ar-N), 139.13 (CCH\(_3\)); **IR** (neat, ATR) \( \nu \) cm\(^{-1} \): 3053 (w), 2971 (w), 2952 (m), 2902 (w), 2864 (w), 1623 (m), 1601 (m), 1589 (m), 1560 (m), 1509 (w), 1478 (m), 1434 (m), 1360 (m), 1312 (w), 1290 (m), 1216 (m), 1199 (m), 1126 (m), 1024 (m), 1011 (m), 852 (m), 824 (s), 699 (s); **MS** (EI, 70 eV): 251.2 (46.7%), 236.1 (100%); **HRMS** calculated: 251.1669; found: 251.1670;
- **EA:** calc. C, 86.01; H, 8.42; N, 5.57; found: C, 85.83; H, 8.49; N, 5.59.

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N-(1-(p-tolyl)ethylidene)aniline (I12)\(^{17}\)

By general method 4-methyl acetophenone (1.3 mL, 10 mmol, 1 eq.) and aniline (1.1 mL, 12 mmol, 1.2 eq.) were dissolved in dry benzene (5 mL). Purification by Kugelrohr distillation (130 °C at 0.08 mbar) afforded 1.67 g (7.98 mmol, 79 %) of I12 as a yellow oil.

\[ \text{C}_{15}H_{15}N (209.29 \text{ g/mol}): \]
\[ \text{m.p.}: 130 \text{ °C} ( \text{Lit. 130-135 °C}); \]
\[ ^1H-\text{NMR} (400 MHz, CD}_2\text{Cl}_2): 7.90 \text{ (d, } J = 7.25 \text{ Hz, 2H, CH}_Ar\text{CH}_Ar\text{C=C=N); 7.67 } (\text{t, } J = 7.25 \text{ Hz, 2H, CH}_Ar\text{CH}_Ar\text{C=C=N); 7.10 } (\text{t, } J = 7.25 \text{ Hz, 1H, CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N}); \]
\[ ^{13}C\{^1H\}-\text{NMR} (100 MHz, CD}_2\text{Cl}_2): 164.9 \text{ (C=N); 152.0 } (\text{C}_Ar\text{CH}_3); 140.7 \text{ (C}_Ar\text{C=C=N); 128.9 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 128.8 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 127.0 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 122.9 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 119.3 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 21.1 } (\text{CH}_3\text{C=N}). \]

N-(1-(4-chlorophenyl)ethylidene)aniline (I13)\(^{18}\)

By general method 1-(4-chlorophenyl)ethanone (1.3 mL, 10 mmol, 1 eq.) and aniline (1.1 mL, 12 mmol, 1.2 eq.) were dissolved in dry benzene (5 mL). Purification by Kugelrohr distillation (145 °C at 0.08 mbar) afforded 1.87 g (8.1 mmol, 81 %) of I13 as a yellow solid.

\[ \text{C}_{14}H_{12}ClN (229.70 \text{ g/mol}): \]
\[ \text{m.p.}: 93 \text{ °C} ( \text{Lit. 93-95 °C}); \]
\[ ^1H-\text{NMR} (600 MHz, CD}_2\text{Cl}_2): 7.95 \text{ (d, } J = 8.0 \text{ Hz, 2H, CH}_Ar\text{CH}_Ar\text{C=C=N); 7.45 } (\text{d, } J = 8.0 \text{ Hz, 2H, CH}_Ar\text{CH}_Ar\text{C=C=N); 7.38 } (\text{t, } J = 7.25 \text{ Hz, 1H, CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 6.79 } (\text{d, } J = 7.75 \text{ Hz, 2H, CH}_Ar\text{CH}_Ar\text{C=C=N); 2.21 } (\text{s, 3H, CH}_3\text{C=N); 13}^{1}C\{^1H\}-\text{NMR} (100 MHz, CD}_2\text{Cl}_2): 163.88 \text{ (C=N); 151.40 } (\text{C}_Ar\text{C=N); 137.87 } (\text{C}_Ar\text{C=C=N); 128.91 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 128.81 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 127.0 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 122.9 } (\text{CH}_Ar\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 119.3 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 21.1 } (\text{CH}_3\text{C=N).} \]

N-(1-(4-fluorophenyl)ethylidene)aniline (I14)\(^{15}\)

By general method 1-(4-fluorophenyl)ethanone (2.517 g, 18.22 mmol, 1 eq.) and aniline (2 g, 21.9 mmol, 1.2 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (120-160 °C at 0.1 mbar) afforded 3.21 g (15 mmol, 82 %) of I14 as an off-white solid.

\[ \text{C}_{14}H_{12}FN (213.25 \text{ g/mol}); \]

\[ ^1H-\text{NMR} (500 MHz, CD}_2\text{Cl}_2): 7.90 \text{ (d, } J = 8.0 \text{ Hz, 2H, CH}_Ar\text{C=C=N); 7.37 } (\text{t, } J = 7.25 \text{ Hz, 2H, CH}_Ar\text{C=C=N); 7.28 } (\text{d, } J = 7.75 \text{ Hz, 2H, CH}_Ar\text{C=C=N); 7.10 } (\text{t, } J = 7.25 \text{ Hz, 1H, CH}_Ar\text{C=C=N); 6.81 } (\text{d, } J = 7.75 \text{ Hz, 2H, CH}_Ar\text{C=C=N); 2.43 } (\text{s, 3H, CH}_3\text{C=N); 2.27 } (\text{s, 3H, CH}_3\text{C=N); 13}^{1}C\{^1H\}-\text{NMR} (100 MHz, CD}_2\text{Cl}_2): 164.98 \text{ (C=N); 152.0 } (\text{C}_Ar\text{C=C=N); 140.7 } (\text{C}_Ar\text{C=C=N); 128.91 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 128.81 } (\text{CH}_Ar\text{CH}_Ar\text{C=C=N); 127.0 } (\text{CH}_Ar\text{C=C=N); 122.9 } (\text{CH}_Ar\text{C=C=N); 119.3 } (\text{CH}_Ar\text{C=C=N); 21.1 } (\text{CH}_3\text{C=N).} \]

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**N-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline (I15)**

By general method 1-(4-(trifluoromethyl)phenyl)ethanone (1.135 g, 6.03 mmol, 1.0 eq.) and aniline (0.67 g, 7.2 mmol, 1.2 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (100-150 °C at 0.07 mbar) afforded 0.456 g (1.89 mmol, 63 %) of I15 as a yellow white solid.

C13H12F3N (263.26 g/mol):

**m.p.:** 72-74 °C (Lit. 75-77°C); **1H-NMR** (400 MHz, CD2Cl2) δ 8.13 (d, J = 8.0 Hz, 2H, CH3C6H4C=N), 7.73 (d, J = 8.0 Hz, 2H, CH3C6H4C=N), 7.39 (t, J = 7.5 Hz, 2H, CH3C6H4C=N), 7.13 (t, J = 7.2 Hz, 1H, CH3C6H4C6H4C=N), 6.82 (t, J = 7.0, 2H, CH3C6H4C=N), 2.27 (s, 3H, CH3)=N; **13C{1H}-NMR** (126 MHz, CD2Cl2) δ 164.61 (C=N), 151.72 (C6H4C=N), 143.24 (C6H4C=N), 131.98 (q, J = 32.5 Hz, C6H4-CF3), 129.41 (CH3C6H4C=N), 127.98 (CH3C6H4C=N), 125.62 (q, J = 3.8 Hz, CH3C6H4-CF3), 123.90 (CH3C6H4C6H4C=N), 119.52 (CH3C6H4C=N), 17.57 (CH3C=N); **19F{1H}-NMR** (376 MHz, CD2Cl2) δ -64.16.

**N-(1-(4-nitrophenyl)ethylidene)aniline (I16)**

By general method 4-nitroacetophenone (0.5 g, 3.03 mmol, 1.0 eq.) and aniline (0.33 g, 3.55 mmol, 1.2 eq.) were dissolved in dry toluene (10 mL). Purification by recrystallisation from ethanol and pentane-washing afforded 0.456 g (1.89 mmol, 63 %) of I16 as an orange solid.

C13H12NO2 (240.26 g/mol):

**m.p.:** 110-114 °C (Lit. 113-115°C); **1H-NMR** (400 MHz, CDCl3) δ 8.30 (d, J = 8.8 Hz, 2H, CH3C6H4C=N), 8.14 (d, J = 8.8 Hz, 2H, CH3C6H4C=N), 7.38 (t, J = 7.7 Hz, 2H, CH3C6H4C=N), 7.14 (t, J = 7.4 Hz, 1H, CH3C6H4C6H4C=N), 6.80 (d, J = 7.5 Hz, 2H, CH3C6H4C=N), 2.29 (s, 3H, CH3C=N); **13C{1H}-NMR** (101 MHz, CDCl3) δ 163.77 (C=N), 150.93 (C6H4-N), 149.12 (C6H4-NO2), 145.10 (C6H4-C=N), 129.25 (CH3C6H4C6H4C=N), 128.29 (CH3C6H4C=N), 124.10 (CH3C6H4C6H4C=N), 123.70 (CH3C6H4C=N), 119.21 (CH3C6H4C=N), 17.67 (CH3C=N).
**N-(2-bromophenyl)-1-(p-tolyl)ethan-1-imine (I17)**

![N-(2-bromophenyl)-1-(p-tolyl)ethan-1-imine](image)

By general method 4- Me-acetophenone (1.0 g, 7.45 mmol, 1.0 eq.) and 2-bromoaniline (1.28 g, 7.45 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (190 °C at 0.1 mbar) afforded 0.678 g (3.24 mmol, 76 %) of **I17** as yellow oil.

C_{18}H_{14}BrN (287.03 g/mol):
- b.p.: 190 °C at 0.1 mbar; ¹H-NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 8.1 Hz, 2H, CH₂Ar C=Br), 7.59 (d, J = 8.0 Hz, 1H, CH₂Ar C=Br), 7.28 (m, 1H, CH₂ArC₆H₄C=Br), 7.26 (d, J = 8.0 Hz, CH₂ArC₆H₄C=Br), 6.94 (t, J = 7.7 Hz, 1H, CH₂ArC₆H₄C=Br), 6.79 (d, J = 7.8 Hz, 1H, CH₂ArC₆H₄C=Br), 2.42 (s, 3H, CH₃)
- ¹³C¹H-NMR (126 MHz, CDCl₃) δ 167.29 (C=Br), 150.27 (CAr-N), 141.31 (CAr-CH₃), 136.32 (CAr-C=Br), 132.97 (CH₂Ar-Br), 129.27 (CH₂Ar-Br), 128.09 (CH₂ArC₆H₄C=Br), 127.54 (CH₂ArC₆H₄C=Br), 124.44 (CH₂CH₂ArC₆H₄C=Br), 120.64 (CH₂CH₂ArC₆H₄C=Br), 114.01 (CAr-Br), 21.58 (CAr-CH₃), 18.16 (CH₃C=Br); GC-MS: (EI, 70 eV, PhMeSi, 100.2/10.27): tR = 17.8 min, m/z = 287 [M⁺]

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**2-Methyl-N-(1-phenylethylidene)aniline (I18)**

![2-Methyl-N-(1-phenylethylidene)aniline](image)

By general method acetophenone (0.515 g, 4.29 mmol, 1.15 eq.) and o-toluidine (0.4 g, 3.74 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125 °C at 0.08 mbar) afforded 0.678 g (3.24 mmol, 76 %) of **I18** as yellow oil.

C_{19}H_{15}N (209.29 g/mol):
- b.p.: 125°C at 0.08 mbar; ¹H-NMR (400 MHz, CDCl₃) δ 8.09 – 7.91 (m, 2H, CH₆ArCC=N), 7.45 (m, 3H, CH₂Ar & CH₂CH₂C₆H₄C=N), 7.19 (m, 2H, C₆H₄CH₂CH₂C₆H₄C=N), 7.00 (t, J = 7.4 Hz, 1H, C₆H₄CH₂CH₂C₆H₄C=N), 6.65 (d, J = 7.7 Hz, 1H, CH₂ArC=N), 2.16 (s, 3H, C₆H₄CH₂), 2.10 (s, 3H, C₆H₄C=NCH₂).

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**N-(1-phenylethylidene)-4-(trifluoromethyl)aniline (I22)**

![N-(1-phenylethylidene)-4-(trifluoromethyl)aniline](image)

By general method acetophenone (0.373 g, 3.1 mmol, 1.0 eq.) and 4-(trifluoromethyl)aniline (0.5 g, 3.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (150 °C at 0.2 mbar) afforded 0.056 g (0.21 mmol, 6 %) of **I22** as yellow-orange solid.

C_{19}H_{12}F₃N (263.26 g/mol):
- ¹H-NMR (500 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H, CH₆ArCC=N), 7.61 (d, J = 8.3 Hz, 2H, CH₂ArC(CF₃)), 7.54 – 7.42 (m, 3H, CH₂Ar & CH₂CH₂CH₂ArC₆H₄C=N), 6.88 (d, J = 8.2 Hz, 2H, CH₂ArC=N), 2.24 (s, 3H, CH₃C=N); ¹³C¹H-NMR (126 MHz, CDCl₃) δ 166.34 (s, C=Br), 154.98 (s, CAr-N), 138.98 (s, CAr-C=Br), 131.06 (s, 1CH₂Ar), 128.62 (s, 2CH₂Ar), 127.40 (s, 2CH₂CC=N), 126.42 (d, J =

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3.7 Hz, CH$_A$C(CF$_3$)), 125.66 (d, $J = 13.5$ Hz, CC(CF$_3$)), 124.45 (q, $J = 225.2$ Hz, CF$_2$), 119.54 (s, CH$_A$C-N), 17.75 (s, CH$_2$C-N); GC-MS: (Rtx-5MS, 100.2/10.270/10): $t_R = 21.2$ min, $m/z = 263$ ([M]$^+$); m.p.: 51-52 °C (Lit. 80-81 °C)

### 2-Isopropyl-N-(1-phenylethylidene)aniline (I23)

By general method acetophenone (0.515 g, 4.29 mmol, 1.4 eq.) and 2-isopropylaniline (0.418 g, 3.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (138 °C at 0.1 mbar) afforded 0.654 g (2.76 mmol, 89%) of I23 as yellow oil.

C$_{17}$H$_{19}$N (237.34 g/mol):

**b.p.:** 138 °C at 0.1 mbar; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.08 – 7.96 (m, 2H CH$_A$CC=N), 7.56 – 7.42 (m, 3H, CH$_A$&CH$_A$CHCC=N), 7.32 (dd, $J = 7.6$, 1.2 Hz, 1H, C$_A$(CH$_2$CH$_3$)$_2$CH$_A$), 7.18 (td, $J = 7.5$, 1.5 Hz, 1H, C$_A$(CH$_2$CH$_3$)$_2$CH$_A$CH$_A$), 7.10 (td, $J = 7.5$, 1.3 Hz, 1H, C$_A$(CH$_3$)$_2$CH$_A$CH$_A$CH$_A$), 6.61 (dd, $J = 7.7$, 1.3 Hz, 1H, C$_A$-NCH$_A$), 3.09 – 2.92 (m, 1H, C$_A$-N), 1.79 (s, 3H, CH$_2$N); IR (neat, ATR) v/cm$^{-1}$: 3060 (w), 3021 (w), 2959 (m), 2925 (w), 2866 (w), 1645 (m), 1633 (s), 1594 (m), 1578 (m), 1480 (m), 1447 (m), 1365 (m), 1287 (m), 1220 (m), 1192 (w), 1084 (w), 1033 (w), 753 (m), 692 (m); MS (EI, 70 eV): 237.1 (16.5%), 222.1 (100%), 207.1 (1.4%); HRMS: calculated: 237.1512; found: 237.1515; 13C($^1$H)-NMR (101 MHz, CDCl$_3$) $\delta$: 164.66 (C=N), 149.16 (C$_A$-N), 139.66 (C$_A$C=N), 138.27 (C$_A$CH$_2$CH$_3$), 130.50 (C$_A$CH$_2$CH$_A$C$_A$C=N), 128.51 (C$_A$CH$_2$C$_A$C=N), 127.28 (C$_A$CH$_A$C$_A$=N), 126.19 (C$_A$CH$_A$CH$_A$C$_A$C$_A$C=N), 125.76 (C$_A$CH$_2$CH$_A$C$_A$CH$_2$), 125.76 (C$_A$CH$_2$CH$_A$C$_A$CH$_2$), 123.78 (C$_A$CH$_A$CH$_2$CH$_2$), 118.78 (C$_A$CH$_2$C$_A$CH$_A$), 28.48 (C$_A$CH$_2$CH$_2$), 22.97 (C$_A$CH$_2$CH$_2$), 17.71 (CH$_3$C=N); m.p.: 51-52 °C (Lit. 80-81 °C)

### 2,6-Dimethyl-N-(1-phenylethylidene)aniline (I24)$^{20}$

By general method acetophenone (0.98 g, 8.1 mmol, 1.0 eq.) and 2,6-dimethylaniline (0.98 g, 8.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (137.5 °C at 0.1 mbar) afforded 0.4 g (1.8 mmol, 21%) of I24 as yellow-white solid.

C$_{19}$H$_{17}$N (291.31 g/mol):

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$: 8.08 – 7.99 (m, 2H, CH$_A$CC=N), 7.54 – 7.42 (m, 3H, CH$_A$&CH$_A$CH$_A$C$_A$C=N), 7.06 (d, $J = 7.5$ Hz, 2H, C$_A$CH$_2$C$_A$(CH$_3$)), 6.92 (t, $J = 7.5$ Hz, 1H, C$_A$(CH$_2$CH$_3$)CH$_A$CH$_A$), 2.07 (s, 3H, C=NCH$_3$), 2.03 (s, 6H, C$_A$(CH$_3$)); $^{13}$C($^1$H)-NMR (126 MHz, CDCl$_3$) $\delta$: 165.39 (C=N), 149.13 (C$_A$-N), 139.27 (C$_A$C=N), 130.60 (CH$_A$), 128.54 (CH$_A$), 127.96 (CH$_A$), 127.22 (CH$_A$), 125.88 (CH$_A$), 122.88 (CH$_A$), 18.11 (C$_A$(CH$_3$)), 17.63(CH$_3$C=N); m.p.: 61-62 °C (Lit. 59-60 °C)

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**N-(3-methylbutan-2-ylidene)aniline (I25)**

By general method 3-methyl-2-butanone (2.11 g, 24.5 mmol, 1.14 eq.) and aniline (2.0 g, 21.5 mmol, 1.0 eq.) were dissolved in dry benzene (6 mL). Purification by Kugelrohr distillation (75 °C at 0.15 mbar) afforded 2.01 g (12.47 mmol, 58%) of I25 as a colourless oil.

C11H15N (161.24 g/mol; calculated: C, 82.23; H, 9.60; N, 8.32; found: C, 81.84; H, 9.60; N, 8.32) by GC-MS (EI, 70 eV, PhMeSi, 80.2/10.270/10): tR = 9.2 min, m/z = 161 ([M]+), 146, 118 ([M-(C(CH3)3]+); HRMS: calculated: 161.1199; found: 161.1200

**N-(4-methylpentan-2-ylidene)aniline (I26)**

By general method 4-Methyl-2-pentanone (3.0 g, 30 mmol, 1.0 eq.) and aniline (2.79 g, 30 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (95 °C at 0.1 mbar) afforded 1.14 g (6.55 mmol, 21%) of I26 as a colourless oil.

C12H17N (175.27 g/mol; calculated: C, 81.78; H, 10.97; N, 7.25; found: C, 81.91; H, 10.84; N, 7.35) by GC-MS (EI, 70 eV, PhMeSi, 80.2/10.270/10): tR = 8.8 min, m/z = 175 ([M]+), 160, 132, 118, 104, 92; EA: calc. C, 82.23; H, 9.78; N, 7.99; found: C, 81.84; H, 9.60; N, 8.32
**N-(1-phenylpropan-2-ylidene)aniline (127)**

By general method Phenylacetone (2.7 g, 20 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.1 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (125 °C at 0.1 mbar) afforded 1.58 g (7.55 mmol, 38%) of 127 as a yellow-orange clear oil.

C_{12}H_{13}N (209.29 g/mol):
E/Z mixture 3:1, major: \(^1\)H-NMR (400 MHz, CD_2Cl_2) \(\delta\) 7.42 – 7.28 (m, 7H), 7.10 – 7.04 (m, 1H), 6.73 (d, \(J = 7.7\) Hz, 2H), 3.74 (s, 2H), 1.74 (s, 3H); \(^{13}\)C\(^{(1)}\)H-NMR (126 MHz, CD_2Cl_2) \(\delta\) 170.63, 151.93, 137.74, 129.63, 129.23, 128.93, 127.02, 123.34, 119.70, 48.73, 19.02; minor: \(^1\)H-NMR (400 MHz, CD_2Cl_2) \(\delta\) 7.14 (d, \(J = 7.5\) Hz, 1H), 6.81 (d, \(J = 7.7\) Hz, 1H), 3.51 (s, 1H), 2.07 (s, 2H).

Other signals overlayed by major isomer: \(^{13}\)C\(^{(1)}\)H-NMR (126 MHz, CD_2Cl_2) \(\delta\) 169.58, 151.60, 137.27, 129.41, 129.38, 129.02, 126.87, 119.82, 115.15, 40.65, 25.99; GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): \(t_R = 20.2\) min; GC-MS (Rtx-5MS, 50.2/30.2/50.5): \(t_R = 8.9\) min, \(m/z = 209 ([M]^+)\), 193, 167, 118, 91, 77.

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**N-(pentan-2-ylidene)aniline (128):**

By general method 2-pentanone (1.62 g, 18.8 mmol, 1.0 eq.) and aniline (2 g, 21.5 mmol, 1.14 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (75 °C at 0.1 mbar) afforded 1.16 g (7.2 mmol, 38%) of 128 as a colourless oil.

C_{11}H_{15}N (161.24 g/mol):
3:1 E/Z mixture, major: \(^1\)H-NMR (400 MHz, CDCl_3) \(\delta\) 7.30 (m, 2H, CH_2Ch_3Ar-N), 7.03 (t, \(J = 7.4\) Hz, 1H, CH_2Ch_3Ar-N), 6.68 (d, \(J = 7.3\) Hz, 2H, CH_2Ch_3Ar-N), 2.41 (t, \(J = 7.5\) Hz, 2H, CH_2Ch_2CH_2C=N); \(^{13}\)C\(^{(1)}\)H-NMR (101 MHz, CDCl_3) \(\delta\) 172.12 (C=N), 151.77 (C_1Ar-N), 128.96 (CH_2Ch_3Ar-N), 123.05 (CH_2Ch_3CH_2Ch_3Ar-N), 119.64 (CH_2Ch_3Ar-N), 43.74 (CH_2C=N), 19.83 (CH_2C=N), 19.52 (CH_2CH_2C=N), 13.91 (CH_2CH_2CH_2C=N); minor: \(^1\)H-NMR (400 MHz, CD_2Cl_2) \(\delta\) 7.30 (m, 2H, CH_2Ch_3Ar-C_1Ar-N), 7.03 (t, \(J = 7.4\) Hz, 1H, CH_2Ch_3Ar-C_1Ar-N), 6.66 (d, \(J = 7.2\) Hz, 2H, CH_2Ch_3Ar-N), 2.15 (s, 3H, CH_3C=N), 2.11 (dd, \(J = 8.7, 6.9\) Hz, 2H, CH_2C=N), 1.52 (qt (m), 2H, CH_2CH_2CH_2C=N), 0.83 (t, \(J = 7.4\) Hz, 3H, CH_3CH_2CH_2C=N); \(^{13}\)C\(^{(1)}\)H-NMR (101 MHz, CDCl_3) \(\delta\) 173.64 (C,N), 151.21 (C_1Ar-N), 129.39 (CH_2Ch_3Ar-C_1Ar-N), 122.94 (CH_2Ch_3CH_2Ch_3Ar-N), 115.20 (CH_2Ch_3Ch_2C=N), 36.12 (CH_2C=N), 25.97 (CH_3C=N), 20.39 (CH_2CH_2CH_2C=N), 14.14 (CH_2CH_2CH_2C=N); IR (neat, ATR) v/cm\(^{-1}\) = 3075 (w), 3060 (w), 3028 (w), 3018 (w), 2959 (m), 2931 (w), 2872 (w), 1658 (s), 1594 (s), 1483 (m), 1366 (m), 1252 (m), 1225 (w), 1186 (m), 1168 (w), 1093 (w), 1071 (m), 900 (w), 797 (m), 746 (m), 698 (s); GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H_2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): \(t_R = 12.7\) min; GC-MS (EI, 70 eV, PhMeSi, 100.2/10.270/10): \(t_R = 7.1\) min, \(m/z = 161 ([M]^+)\); EA: calc. C, 81.94; H, 9.38; N, 8.69; found: C, 81.72; H, 9.33; N, 8.65.

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N-(6-methylhept-5-en-2-ylidene)aniline (I29)

By general method 6-methylhept-5-en-2-one (1.71 g, 13.55 mmol, 1.0 eq.) and aniline (1.26 g, 13.55 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (112.5°C at 0.1 mbar) afforded 600 mg (3.0 mmol, 22%) of I29 as a yellow clear oil.

C14H19N (201.31 g/mol): E/Z mixture 3:1, major: 1H-NMR (400 MHz, CDCl3) δ 7.33 – 7.28 (m, 2H), 7.05 (tt, J = 7.5, 1.2 Hz, 1H), 6.70 (dd, J = 8.4, 1.1 Hz, 2H), 5.22 (dddt, J = 6.8, 5.3, 2.8, 1.4 Hz, 1H), 2.48 – 2.43 (m, 2H), 2.42 – 2.37 (m, 2H), 1.79 (s, 3H), 1.74 (d, J = 1.2 Hz, 3H), 1.68 (d, J = 1.2 Hz, 3H); 13C{1H}-NMR (101 MHz, CDCl3) δ 171.71, 151.63, 132.37, 128.86, 123.28, 122.95, 119.51, 41.59, 25.77, 25.04, 19.66, 17.79; minor: 1H-NMR (400 MHz, CDCl3) δ 7.31 – 7.27 (m, 2H), 7.06 – 7.02 (m, 1H), 6.72 – 6.68 (m, 2H), 4.97 (dddt, J = 7.0, 5.5, 3.0, 1.5 Hz, 1H), 2.47 – 2.45 (m, 2H), 2.39 – 2.36 (m, 2H), 2.18 (s, 3H), 1.67 (d, J = 1.1 Hz, 3H), 1.53 (d, J = 1.2 Hz, 3H); 13C{1H}-NMR (101 MHz, CDCl3) δ 172.26, 151.09, 132.91, 128.79, 122.85, 122.66, 119.51, 34.02, 26.04, 25.64, 25.43, 17.56; GC (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H2, 100°C/2 min, 10°C/min, 250°C/10 min): tR = 17.2 min; GC-MS (Rtx-5MS, 50.2/10.250/10): tR = 8.1 min, m/z = 201 ([M]+), 186, 158, 144, 132, 118, 109, 93, 77; IR (neat, ATR) ν/cm–1 = 3072 (w), 3057 (w), 3022 (w), 2966 (m), 2914 (m), 2854 (m), 1663 (s), 1593 (m), 1483 (m), 1443 (w), 1367 (w), 1246 (w), 1169 (w); EA: calculated: C, 83.53; H, 9.51; N, 6.96, found: C, 83.45; H, 9.31; N, 6.87.

N-(octan-2-ylidene)aniline (I30)

By general method 2-Octanone (1.64 g, 12.8 mmol, 1.0 eq.) and aniline (1.19 g, 12.8 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125°C at 0.1 mbar) afforded 847 mg (4.17 mmol, 32%) of I30 as a slightly yellowish clear oil.

C14H21N (203.32 g/mol): E/Z mixture 3:1, major: 1H-NMR (400 MHz, CDCl3) δ 7.30 (m, 2H), 7.05 (m, 1H), 6.70 (m, 2H), 2.42 (m, 2H), 1.79 (s, 3H), 1.69 (m, 2H), 1.41 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H); 13C{1H}-NMR (101 MHz, CDCl3) δ 172.35, 151.77, 128.96, 123.03, 119.65, 41.88, 31.83, 29.16, 26.48, 22.73, 19.55, 14.22; minor: 1H-NMR (400 MHz, CDCl3) δ 7.30 (m, 2H), 7.05 (m, 1H), 6.70 (m, 2H), 2.17 (s, 3H), 2.14 (m, 2H), 1.49 (m, 2H), 1.18 (m, 4H), 1.26 (m, 2H), 0.86 (m, 3H); 13C{1H}-NMR (101 MHz, CDCl3) δ 172.89, 151.77, 128.91, 122.95, 119.63, 34.21, 31.52, 29.27, 27.00, 26.05, 22.55, 14.13; GC (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H2, 100°C/2 min, 10°C/min, 250°C/10 min): tR = 17.3 min; GC-MS (Rtx-5MS, 100.2/10.270/10): tR = 13.3 min, m/z = 203 ([M]+), 188, 174, 160, 146, 132, 118, 92, 77.

N-(1-cyclopentylethyldiene)aniline (I31)

By general method 8 (0.34 g, 3.125 mmol, 1.0 eq.) and aniline (0.32 g, 3.43 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (100°C at 0.15 mbar) afforded 0.25 g (1.33 mmol, 42%) of I31 as a colourless oil.

C14H17N (187.28 g/mol): calculated: 175.1356; found: 175.1357.

By general method Pinacolone (2.15 g, 21.4 mmol, 1.0 eq.) and aniline (2.0 g, 21.5 mmol, 1.0 eq.) were dissolved in dry benzene (6 mL). Purification by Kugelrohr distillation (100-150°C at 0.07 mbar) afforded 1.5 g (8.56 mmol, 40%) of I32 as a colourless oil.

C16H17N (177.27 g/mol): calculated: 177.2656; found: 177.2657.

N-(3,3-dimethylbutan-2-ylidene)aniline (I32) 23

N-(1-cyclohexylethylidene)-1-phenylmethanamine (I33)\(^{24}\)

By general method cyclohexylmethylketone (1.09 g, 8.6 mmol, 1.0 eq.) and benzylamine (1.02 g, 9.5 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125° C at 0.1 mbar) afforded 0.84 g (3.9 mmol, 45%) of I33 as a colourless clear oil.

C\(_{15}\)H\(_{21}\)N (215.33 g/mol):

1H-NMR (400 MHz, CDCl\(_3\)) \(\delta 7.31\) (m, 5H, C\(_H\)Ar), 4.49 (s, 2H, C\(_H\)2), 2.25 (tt, J = 11.6, 3.3 Hz, 1H, C\(_H\)C=N), 1.84 (s, 3H, C\(_H\)3), 1.77 (m, 4H, C\(_H\)Aliph), 1.32 (m, 6H, C\(_H\)Aliph);

GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 20.6\) min (I34);

GC-MS (Rtx-5MS, 100.2/10.270/10): \(t_R = 16.8\) min, m/z = 215 ([M]+), 200, 186, 174, 160, 147, 124, 91.

N-(1-cyclohexylethylidene)butan-1-amine (I34)

By general method cyclohexylmethylketone (0.92 g, 7.27 mmol, 1.0 eq.) and \(n\)-butylamine (1.6 g, 21.8 mmol, 3.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (87° C at 0.15 mbar) afforded 0.75 g (4.11 mmol, 56%) of I34 as a colourless clear oil.

C\(_{12}\)H\(_{23}\)N (181.32 g/mol):

1H-NMR (400 MHz, CDCl\(_3\)) \(\delta 3.23\) (t, \(J = 7.3\) Hz, 2H), 2.17 (ddt, \(J = 11.3, 6.6, 3.3\) Hz, 1H), 1.83 – 1.73 (m, 4H), 1.76 (s, 3H), 1.72 – 1.66 (m, 1H), 1.60 (p, \(J = 7.4\) Hz, 2H), 1.39 – 1.34 (m, 2H), 1.30 (ddd, \(J = 12.3, 7.4, 3.4\) Hz, 1H), 0.94 (t, \(J = 7.3\) Hz, 3H);

13C{\(^1\)H}-NMR (101 MHz, CDCl\(_3\)) \(\delta 173.36, 51.07, 50.87, 33.20, 30.32, 26.31, 26.29, 29.87, 14.91, 14.19;

GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/10 min): \(t_R = 13.8\) min (I35);

GC-MS (Rtx-5MS, 50.2/30.250/5): \(t_R = 7.0\) min, m/z = 181 ([M]+), 166, 152, 126, 98; IR (neat, ATR) \(\nu/cm^{-1} = 2955\) (s), 2924 (s), 2851 (s), 1663 (m), 1643 (w), 1447 (m), 1369 (w), 1248 (w), 1198 (w);

EA: calculated: C, 79.49; H, 12.79; N, 7.72, found: C, 79.61; H, 12.63; N, 7.76.

N-(1-cyclohexylethylidene)propan-2-amine (I35)

By general method cyclohexylmethylketone (0.92 g, 7.27 mmol, 1.0 eq.) and isoproylamine (2.15 g, 36.33 mmol, 5.0 eq.) were dissolved in dry toluene (10 mL) and stirred at room temperature for four days. Purification by Kugelrohr distillation (100° C at 0.15 mbar) afforded 0.52 g (3.1 mmol, 43%) of I35 as a colourless clear oil.

C\(_{11}\)H\(_{21}\)N (167.29 g/mol):

E/Z mixture 16:1, major: 1H-NMR (400 MHz, CDCl\(_3\)) \(\delta 3.60\) (hept, \(J = 6.3\) Hz, 1H), 2.16 (td, \(J = 9.6, 8.9, 4.8\) Hz, 1H), 1.75 (s, 3H), 1.81 – 1.65 (m, 6H), 1.36 – 1.25 (m, 4H), 1.10 (s, 3H), 1.09 (s,

\(^{13}\text{C}\{^1\text{H}\}\text{-NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 170.70, 51.16, 49.81, 30.25, 26.26, 26.20, 23.63, 13.78; GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/10 min): \(t_R = 10.8 \text{ min}\); GC-MS (Rtx-5MS, 50.2/30.250/5): \(t_R = 6.0 \text{ min}\), \(m/z = 167 ([M]^+)\), 152, 126, 112, 99, 84; IR (neat, ATR) \(\nu/cm^{-1} = 2964 \text{ (m)}, 1924 \text{ (s)}, 1853 \text{ (m)}, 1663 \text{ (m)}, 1643 \text{ (m)}, 1448 \text{ (m)}, 1373 \text{ (w)}, 1364 \text{ (w)}, 1246 \text{ (w)}, 1202 \text{ (w)}, 1159 \text{ (w)}, 808 \text{ (w)}; EA: calculated: C, 78.97; H, 12.65; N, 8.37, found: C, 78.44; H, 12.50; N, 8.34.

\(N\)-(1-cyclohexylethylidene)cyclohexanamine (I36)

By general method cyclohexylmethylketone (1.834 g, 14.53 mmol, 1.0 eq.) and cyclohexylamine (1.439 g, 14.53 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (100 °C at 0.1 mbar) afforded 1.153 g (5.56 mmol, 38%) of I36 as a colourless clear oil. C\(_{14}\)H\(_{25}\)N (207.35 g/mol):

\(^1\text{H}\text{-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 3.22 (m, 1H, CHC-N), 2.19 – 2.12 (m, 1H, \(CHC=\text{N}\)), 1.82 – 1.61 (m, 11H), 1.61 – 1.54 (m, 2H), 1.45 – 1.13 (m, 10H); \(^{13}\text{C}\{^1\text{H}\}\text{-NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 171.13, 58.93, 51.29, 33.85, 30.41, 26.36, 26.30, 25.99, 25.33, 14.01; GC (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/10 min): \(t_R = 17.4 \text{ min}\); GC-MS (Rtx-5MS, 100.2/10.270/10): \(t_R = 13.2 \text{ min}\), \(m/z = 207 ([M]^+)\), 192, 178, 166, 152, 126, 124, 83; IR (neat, ATR) \(\nu/cm^{-1} = 2922 \text{ (s)}, 2851 \text{ (s)}, 1657 \text{ (m)}, 1447 \text{ (m)}, 1369 \text{ (w)}, 1358 \text{ (w)}, 1240 \text{ (w)}, 1196 \text{ (w)}, 1028 \text{ (w)}, 889 \text{ (w)}, 843 \text{ (w)}; EA: calculated: C, 81.09; H, 12.15; N, 6.75, found: C, 80.69; H, 12.04; N, 6.94.
Hydrogenations

All hydrogenation reactions were carried out in anhydrous crown-cap dichloromethane, which was used without further purification.

Procedure for the hydrogenation at elevated pressure:
Imine (0.1 mmol), catalyst (2 µmol), additive (2 µmol), and a stir bar were added to an oven-dried glass vial that had been placed in an autoclave (60 mL) and purged with argon for 5 min. Anhydrous CH₂Cl₂ (1 mL) was added by syringe under a stream of argon and the autoclave was closed. For reactions at low temperature the autoclave was immersed in a cooling bath for 60 min before starting the reaction. The autoclave was pressurized with hydrogen gas, hydrogen was released and the autoclave pressurized again. It was then placed on a stirring plate for the time indicated. After pressure release the solvent was evaporated under a stream of nitrogen.

Procedure for the hydrogenation at atmospheric pressure:
Same procedure as above, but the vials were placed in a flask equipped with 24/40 joint which was closed with a rubber septum. The flask was evacuated and purged with hydrogen gas via H₂-filled balloon (Dräger 1.5 L) three times. The solvent (1 mL) was added via syringe and the flask placed on a stirring plate for the time indicated.

The residue was suspended in pentane/ether (5:1) and filtered through a short elution plug (cotton bottom, 40x5 mm silica gel). The crude filtrate was analysed by GC for conversion before being purified by flash chromatography (SiO₂, pentane/ether 20:1, 15x2 cm) and analysed by HPLC on a chiral stationary phase for determination of the enantiomeric excess.

Derivatization for the determination of enantiomeric excess:
A35 was dissolved in CH₂Cl₂ (1 mL) before acetic anhydride and triethylamine (4 drops each) were added. The solution was stirred for 30 minutes at room temperature and solvents evaporated by a stream of nitrogen. The residue was suspended in pentane/ether (5:1) and filtered through a CHROMAPHIL HPLC filter prior to GC analysis.
A33 and A36 was dissolved in CH₂Cl₂ (1 mL) before 1-naphtoyl chloride and triethylamine (4 drops each) were added. The solution was stirred for 30 minutes at room temperature. The product was purified by flash chromatography prior to HPLC analysis.

\[
\text{N-(1-phenylethyl)aniline (A1)}^{11}
\]

\[
\begin{align*}
\text{C}_{14}\text{H}_{15}\text{N} & \quad (197.28 \text{ g/mol)}; \\
\text{GC} & \quad (\text{Machary-Nagel Optima-5-Amin (0.50 } \mu\text{m x 0.25 } \mu\text{m x 30 m)}, 60 \text{ kPa He, 150 °C min, } 7^\circ\text{C/min, 250 °C/10 min): } t_R = 12.8 \text{ min}; \\
\text{HPLC} & \quad (\text{Daicel Chiral OD-H (2.6 x 250 mm), n-heptane/iso-propanol 99:1, 0.5 mL/min, 20 °C, 210 nm): } t_R = 24.6 \text{ min ((S)-A1), } t_R = 33.0 \text{ min ((R)-A1).}
\end{align*}
\]
\[ N-(1-(4-methoxyphenyl)ethyl)aniline (A2) \]

\[ \text{C}_{13}\text{H}_{17}\text{NO} \ (227.31 \text{ g/mol}): \]
\[ \text{GC (Machary-Nagel Optima-5-Amin (0.50} \ \mu\text{m x 0.25} \ \mu\text{m x 30 m), 60 kPa He, 150 °C min, 7°C/min, 250 °C/10 min): } t_R = 19.6 \text{ min.} \]

\[ (R)(-)-N-(1-cyclohexylethyl)aniline (A3) \]

\[ \text{C}_{14}\text{H}_{21}\text{N} \ (203.32 \text{ g/mol}): \]
\[ ^1\text{H-NMR (400 MHz, CDCl}_3\text{): } \delta 7.19 – 7.10 \text{ (m, 2H), 6.64 (t, } J = 7.3 \text{ Hz, 1H), 6.57 (d, } J = 7.7 \text{ Hz, 2H), 3.48 (s, 1H), 3.39 – 3.25 \text{ (m, 1H), 1.88 – 1.61 (m, 5H), 1.51 – 1.39 (m, 1H), 1.32 – 1.15 (m, 3H), 1.12 (d, } J = 6.5 \text{ Hz, 3H), 1.10 – 0.99 \text{ (m, 2H); } ^{13}\text{C}\{^1\text{H}\}-\text{NMR (101 MHz, CDCl}_3\): } \delta 148.10, 129.40, 116.63, 113.07, 53.10, 29.93, 28.54, 26.79, 26.63, 26.49, 17.55; \text{ GC (Machary-Nagel Optima-5-Amin (0.50} \ \mu\text{m x 0.25} \ \mu\text{m x 30 m), 60 kPa H}_2\text{, 100 °C/2 min, 10°C/min, 250 °C/10 min): } t_R = 19.6 \text{ min; } \text{GC-MS (Rtx-5MS, 100.2/10.270/10): } t_R = 15.7 \text{ min, } m/z = 203 \text{ ([M]^+), 120; HPLC (Daicel Chiracel OJ-H, n-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): } t_R = 21.0 \text{ min ((R)(-)-A3), } t_R = 24.0 \text{ min ((S)(-)-A3); Optical Rotation: } [\alpha]_D^{20} = -19.0 \text{ (c 1.0 in CHCl}_3\text{, 0.75% EtOH).} \]

\[ (R)(-)-N-(3-methylbutan-2-yl)aniline (A25) \]

\[ \text{C}_{11}\text{H}_{17}\text{N} \ (163.26 \text{ g/mol}): \]
\[ ^1\text{H-NMR (400 MHz, CDCl}_3\): } \delta 7.16 \text{ (t, } J = 7.9 \text{ Hz, 2H), 6.65 (t, } J = 7.3 \text{ Hz, 1H), 6.58 (d, } J = 7.8 \text{ Hz, 2H), 3.48 (s, 1H), 3.42 – 3.27 \text{ (m, 1H), 1.93 – 1.77 (m, 1H), 1.10 (d, } J = 6.4 \text{ Hz, 3H), 0.98 (d, } J = 6.9 \text{ Hz, 3H), 0.92 (d, } J = 6.8 \text{ Hz, 3H); } ^{13}\text{C}\{^1\text{H}\}-\text{NMR (101 MHz, CDCl}_3\): } \delta 147.98, 129.41, 116.75, 113.18, 53.55, 32.35, 19.34, 17.65, 16.71; \text{ GC-MS (EI, 70 eV, PhMeSi, 80.2/10.270/10): } t_R = 10.4 \text{ min, } m/z = 163 \text{ ([M]^+), 120 ([M-(C(CH}_3)_2])^+, \text{ GC (Machary-Nagel Optima-5-Amin (0.50} \ \mu\text{m x 0.25} \ \mu\text{m x 30 m), 60 kPa H}_2\text{, 100 °C/2 min, 10°C/min, 250 °C/7 min): } t_R = 13.3 \text{ min; HPLC (Daicel Chiracel OJ, n-heptane/iso-propanol 100:0, 0.5 mL/min, 25 °C, 247/297 nm): } t_R = 31.2 \text{ min ((R)(-)-A25), } t_R = 36.1 \text{ min ((S)(-)-A25); Optical Rotation: } [\alpha]_D^{20} = -49.4 \text{ (c 1.0 in CHCl}_3\text{, 0.75% EtOH).} \]
(-)-N-(4-methylpentan-2-yl)aniline (A26)\textsuperscript{25}

\[
\text{C}_{12}\text{H}_{19}\text{N} (177.29 	ext{ g/mol}):
\]

\(^1\text{H}-\text{NMR}\ (400 \text{ MHz, CDCl}_3) \delta 7.16 (t, J = 7.9 \text{ Hz, 2H}), 6.66 (t, J = 7.3 \text{ Hz, 1H}), 6.58 (d, J = 7.8 \text{ Hz, 2H}), 3.60 - 3.47 (m, 1H), 3.36 (s, 1H), 1.84 - 1.68 (m, 1H), 1.48 (dt, J = 14.0, 7.1 \text{ Hz, 1H}), 1.26 (dt, J = 13.7, 6.9 \text{ Hz, 1H}), 1.16 (d, J = 6.2 \text{ Hz, 3H}), 0.95 (d, J = 6.6 \text{ Hz, 3H}), 0.91 (d, J = 6.6 \text{ Hz, 3H}); \(\text{^13}\text{C}\{^1\text{H}\}-\text{NMR}\ (101 \text{ MHz, CDCl}_3) \delta 147.85, 129.42, 116.86, 113.15, 47.07, 46.58, 25.23, 23.10, 22.72, 21.21; \text{GC-MS}\): (Rtx-5MS, 100.2/10.270/10): \(t_R = 9.8 \text{ min, } m/z = 177 ([M]^+)\), 162, 120; \text{GC (Machary-Nagel Optima-5-Amin (0.50 \mu m x 0.25 \mu m x 30 m), 60 kPa H}_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 14.4 \text{ min}; \text{HPLC (Daicel Chiral OJ-H, n-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): } t_R = 19.6 \text{ min ((+)-A26), } t_R = 22.5 \text{ min ((-)-A26); Optical Rotation: } [\alpha]_D^{20} = -24.6 (c 1.10 \text{ in CHCl}_3 0.75% EtOH), 69\% \text{ ee.}

\]

N-(1-phenylpropan-2-yl)aniline (A27)\textsuperscript{23}

\[
\text{C}_{13}\text{H}_{17}\text{N} (211.30 	ext{ g/mol}):
\]

\(^1\text{H}-\text{NMR}\ (400 \text{ MHz, CDCl}_3) \delta 7.30 (m, 2H, CH\_Ar), 7.20 (m, 5H, CH\_Ar), 6.69 (t, J = 7.3 \text{ Hz, 1H, CH\_ArCH\_ArCH\_Ar-N}), 6.63 (dd, J = 8.5, 0.9 \text{ Hz, 2H, CH\_ArN}), 3.77 (qdd (m), 1H, 1H, CH\_N), 3.53 (s, 1H, NH), 2.95 (dddd, J = 13.4, 4.7 \text{ Hz, 1H, CHPh}), 2.70 (dd, J = 13.4, 7.3 \text{ Hz, 1H, CHPh}), 1.16 (d, J = 6.4 \text{ Hz, 3H, CH2CHCHN}); \text{GC-MS}: (Rtx-5MS, 100.2/10.270/10): \(t_R = 17.3 \text{ min, } m/z = 211 ([M]^+)\), 120, 103, 91; \text{GC (Machary-Nagel Optima-5-Amin (0.50 \mu m x 0.25 \mu m x 30 m), 60 kPa H}_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 21.1 \text{ min; HPLC (Daicel Chiral OJ-H, n-heptane/iso-propanol 97:3, 0.5 mL/min, 25 °C, 208/243 nm): } t_R = 21.2 \text{ min ((+)-A27), } t_R = 23.2 \text{ min ((-)-A27); Optical Rotation: } [\alpha]_D^{20} = +1.3 (c 0.65 \text{ in CHCl}_3 0.75% EtOH), 72\% \text{ ee.}

\]

(-)-N-(pentan-2-yl)aniline (A28)\textsuperscript{25}

\[
\text{C}_{14}\text{H}_{17}\text{N} (163.26 	ext{ g/mol}):
\]

\(^1\text{H}-\text{NMR}\ (400 \text{ MHz, CDCl}_3) \delta 7.21 - 7.11 (m, 2H), 6.69 - 6.63 (m, 1H), 6.61 - 6.55 (m, 2H), 3.48 (qd, J = 21.1, 5.9 \text{ Hz, H}), 3.42 (s, 1H), 1.60 - 1.51 (m, 1H), 1.48 - 1.36 (m, 3H), 1.18 (d, J = 6.3 \text{ Hz, 3H}), 0.94 (dd, J = 7.1, 4.1, 3.2 \text{ Hz, 3H}); \(\text{^13}\text{C}\{^1\text{H}\}-\text{NMR}\ (101 \text{ MHz, CDCl}_3) \delta 147.87 (C\_ArN), 129.41 (CH\_ArCH\_Ar-N), 116.86 (CH\_ArCH\_ArCH\_Ar-N), 113.18 (CH\_Ar-N), 48.30 (CH\_N), 39.60 (CH\_CH\_N), 20.92 (CH\_CH\_CH\_N), 19.47 (CH\_CH\_N), 14.27 (CH\_CH\_2); \text{GC-MS}: (EI, 70 eV, PhMeSi, 100.2/10.270/10): \(t_R = 7.9 \text{ min, } m/z = 163 ([M]^+)\), 148, 132, 120; \text{GC (Machary-Nagel Optima-5-Amin (0.50 \mu m x 0.25 \mu m x 30 m), 60 kPa H}_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 13.6 \text{ min; HPLC (Daicel Chiral OJ-H, n-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): } t_R = 19.1 \text{ min ((+)-A28), } t_R = 21.6 \text{ min ((-)-A28); Optical Rotation: } [\alpha]_D^{20} = -14.5 (c 2.565 \text{ in CHCl}_3 0.75% EtOH), 40\% \text{ ee.}


45
N-((6-methylhept-5-en-2-yl)aniline (A29)\textsuperscript{26}

\[
\text{C}_{18}\text{H}_{21}\text{N} (203.32 \text{ g/mol}): \quad \text{\^{1}H-NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta \ 7.16 \ (t, J = 7.7 \text{ Hz}, 2\text{H}), 6.68 - 6.63 \ (m, 1\text{H}), 6.60 - 6.55 \ (m, 2\text{H}), 3.46 \ (dt, J = 12.6, 6.2 \text{ Hz}, 1\text{H}), 3.43 - 3.37 \ (m, 1\text{H}), 1.62 - 1.52 \ (m, 1\text{H}), 1.47 - 1.34 \ (m, 3\text{H}), 1.34 - 1.24 \ (m, 6\text{H}), 1.17 \ (d, J = 6.2 \text{ Hz}, 3\text{H}), 0.92 - 0.85 \ (m, 3\text{H}); \ \text{\^{13}C\textsuperscript{\{H\}}-NMR} \quad (101 \text{ MHz, CDCl}_3) \ \delta \ 147.85, \ 129.40, \ 116.85, \ 113.19, \ 48.59, \ 37.38, \ 32.00, \ 29.52, \ 26.29, \ 22.78, \ 20.93, \ 14.25; \ \text{GC-MS} \quad (\text{Rtx-5MS, 100.2/10.270/10}): \ \text{t}_{R} = 14.2 \text{ min, } m/z = 205 \ ([M]^+) \text{, 189, 190, 132, 120; GC} \quad \text{Machary-Nagel Optima-5-Amin} \ (0.50 \mu \text{m} \times 0.25 \mu \text{m} \times 30 \text{m}), \ 60 \text{ kPa H}_2, \ 100 ^\circ \text{C/2 min}, \ 10^\circ \text{C/min}, \ 250 ^\circ \text{C/7 min}); \ \text{t}_{R} = 18.07 \text{ min; HPLC} \quad \text{(Daicel Chiracel OJ-H, n-heptane/iso-propanol 99:1, 0.5 mL/min, 25 } ^\circ \text{C}, \ 247/297 \text{ nm): } \text{t}_{R} = 9.97 \text{ min} \ ((\pm)-(\pm)-A30), \ \text{t}_{R} = 10.71 \text{ min} \ ((S)-(\pm)-A30); \ \text{Optical Rotation: } [\alpha]_{D}^{20} = +14.8 \text{ (c 1.0 in CHCl}_3, 0.75\% \text{ EtOH), 50\% ee.}

\[\text{(S)-(\pm)-N-(octan-2-yl)aniline (A30)\textsuperscript{27}}\]

\[
\text{C}_{18}\text{H}_{23}\text{N} (205.34 \text{ g/mol}): \quad \text{\^{1}H-NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta \ 7.19 - 7.13 \ (m, 2\text{H}), 6.68 - 6.63 \ (m, 1\text{H}), 6.60 - 6.55 \ (m, 2\text{H}), 3.46 \ (dt, J = 12.6, 6.2 \text{ Hz}, 1\text{H}), 3.43 - 3.37 \ (m, 1\text{H}), 1.62 - 1.52 \ (m, 1\text{H}), 1.47 - 1.34 \ (m, 3\text{H}), 1.34 - 1.24 \ (m, 6\text{H}), 1.17 \ (d, J = 6.2 \text{ Hz}, 3\text{H}), 0.92 - 0.85 \ (m, 3\text{H}); \ \text{\^{13}C\textsuperscript{\{H\}}-NMR} \quad (101 \text{ MHz, CDCl}_3) \ \delta \ 147.85, \ 129.40, \ 116.85, \ 113.19, \ 48.59, \ 37.38, \ 32.00, \ 29.52, \ 26.29, \ 22.78, \ 20.93, \ 14.25; \ \text{GC-MS} \quad (\text{Rtx-5MS, 100.2/10.270/10}): \ \text{t}_{R} = 14.2 \text{ min, } m/z = 205 \ ([M]^+) \text{, 190, 132, 120; GC} \quad \text{Machary-Nagel Optima-5-Amin} \ (0.50 \mu \text{m} \times 0.25 \mu \text{m} \times 30 \text{m}), \ 60 \text{ kPa H}_2, \ 100 ^\circ \text{C/2 min}, \ 10^\circ \text{C/min}, \ 250 ^\circ \text{C/7 min}); \ \text{t}_{R} = 18.07 \text{ min; HPLC} \quad \text{(Daicel Chiracel OJ-H, n-heptane/iso-propanol 99:1, 0.5 mL/min, 40 } ^\circ \text{C}, \ 247/297 \text{ nm): } \text{t}_{R} = 9.97 \text{ min} \ ((R)-(\pm)-A30), \ \text{t}_{R} = 10.71 \text{ min} \ ((S)-(\pm)-A30); \ \text{Optical Rotation: } [\alpha]_{D}^{20} = +14.8 \text{ (c 1.0 in CHCl}_3, 0.75\% \text{ EtOH).}

\[\text{(-)-N-(1-cyclopentylethyl)aniline (A31)}\]

\[
\text{C}_{13}\text{H}_{19}\text{N} (189.30 \text{ g/mol}): \quad \text{\^{1}H-NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta \ 7.15 \ (t, J = 7.9 \text{ Hz}, 2\text{H}), 6.64 \ (t, J = 7.3 \text{ Hz}, 1\text{H}), 6.58 \ (d, J = 7.7 \text{ Hz}, 2\text{H}), 3.47 \ (s, 1\text{H}), 3.32 \ (s, 1\text{H}), 1.92 \ (dq, J = 16.3, 8.0 \text{ Hz}, 1\text{H}), 1.86 - 1.70 \ (m, 2\text{H}), 1.69 - 1.48 \ (m, 4\text{H}), 1.37 - 1.23 \ (m, 2\text{H}), 1.16 \ (d, J = 6.2 \text{ Hz}, 3\text{H}); \ \text{\^{13}C\textsuperscript{\{H\}}-NMR} \quad (101 \text{ MHz, CDCl}_3) \ \delta \ 148.10, \ 129.39, \ 116.73, \ 113.14, \ 53.07, \ 46.80, \ 29.91, \ 29.62, \ 25.84, \ 25.65, \ 19.49; \ \text{IR} \quad \text{(neat, ATR) v/cm}^{-1} = \]

\[\text{26} \quad \text{C. Li, B. Villa-Marcos, J. Xiao, J. Am. Chem. Soc. 2009, 131, 6967-6969} \]
\[\text{27} \quad \text{P. Yin and T.-P. Loh, Org. Lett. 2009, 11, 3791-3793} \]
(R)-(-)-N-(3,3-dimethylbutan-2-yl)aniline (A32)\textsuperscript{23}

\begin{center}
\includegraphics[width=0.3\textwidth]{structure1}
\end{center}

C\textsubscript{12}H\textsubscript{19}N (177.29 g/mol):

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.15 (t, \( J = 7.9 \) Hz, 2H, \( CH\textsubscript{Ar}CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 6.63 (t, \( J = 7.4 \) Hz, 1H, \( CH\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 6.59 (d, \( J = 8.5 \) Hz, 2H, \( CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 3.24 (q, \( J = 6.5 \) Hz, 1H, \( CH\textsubscript{3}C\textsubscript{H}3\)), 1.09 (d, \( J = 6.4 \) Hz, 3H, \( CH\textsubscript{3}CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 3.39 (s \( \text{br} \)), 1H, \( NH\)), 1.09 (d, \( J = 6.4 \) Hz, 3H, \( CH\textsubscript{3}CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 0.96 (s, 9H, \( C(CH\textsubscript{3})\textsubscript{3}\)), 1.03 (d, \( J = 6.5 \) Hz, 3H, \( CH\textsubscript{3}CH\textsubscript{Ar}C\textsubscript{Ar}-N)), 48.63 (C\textsubscript{Ar}-N), 129.40 (C\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C\textsubscript{Ar}-N), 116.65 (C\textsubscript{Ar}CH\textsubscript{Ar}CH\textsubscript{Ar}C\textsubscript{Ar}-N), 113.13 (C\textsubscript{Ar}CH\textsubscript{Ar}C\textsubscript{Ar}-N), 57.32 (CHNH), 34.92 (C(CH\textsubscript{3})\textsubscript{3}), 15.98 (CH\textsubscript{3}CHNH); GC-MS: (Rtx-5MS, 100.2/10.270/10): \( t_R = 9.3 \) min, \( m/z = 177 \) ([M\textsuperscript{+}]), 120; GC (Machary-Nagel Optima-5-Amin (0.50 \( \mu \)m x 0.25 \( \mu \)m x 30 m), 60 kPa H\textsubscript{2}, 100 °C/2 min, 10°C/min, 250 °C/10 min): \( t_R = 14.1 \) min; HPLC (Daicel Chiracel OJ-H, n-heptane/isopropanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): \( t_R = 15.1 \) min ((R)-(A32), \( t_R = 18.4 \) min (S)-(A32)); Optical Rotation: \( [\alpha]_D^{26} = -0.5 \) (c 0.05 in CHCl\textsubscript{3} 0.75% EtOH), 76% ee.

(R)-N-benzyl-1-cyclohexylethanamine (A33)\textsuperscript{28}

\begin{center}
\includegraphics[width=0.3\textwidth]{structure2}
\end{center}

C\textsubscript{15}H\textsubscript{23}N (217.35 g/mol):

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 3.84 (d, \( J = 13.1 \) Hz, 1H), 3.71 (d, \( J = 13.1 \) Hz, 1H), 2.50 (p, \( J = 6.3 \) Hz, 1H), 1.80 – 1.62 (m, 5H), 1.36 (t(d,t), \( J = 11.5 \), 5.6, 3.1 Hz, 1H), 1.30 – 1.19 (m, 2H), 1.19 – 1.10 (m, 2H), 1.03 (m, 2H), 1.03 (d, \( J = 6.5 \) Hz, 3H); GC (Machary-Nagel Optima-5-Amin (0.50 \( \mu \)m x 0.25 \( \mu \)m x 30 m), 60 kPa H\textsubscript{2}, 100 °C/2 min, 10°C/min, 250 °C/7 min): \( t_R = 20.0 \) min (A34); GC-MS: (Rtx-5MS, 100.2/10.270/10): \( t_R = 16.2 \) min, \( m/z = 202 \) ([M-CH\textsubscript{3}\textsuperscript{+}]), 134 ([M-C\textsubscript{6}H\textsubscript{11}\textsuperscript{+}]), 91; HPLC (Daicel Chiracel OD-H, n-heptane/isopropanol 95:5, 0.8 mL/min, 25 °C, 225/287 nm): \( t_R = 15.9 \) min ((R)-A33-1-naphtamide), \( t_R = 19.9 \) min ((S)-A33-1-naphtamide); Optical Rotation: \( [\alpha]_D^{26} = -23.7 \)° (c 1.0 in CHCl\textsubscript{3} 0.75% EtOH).

(R)-N-(1-cyclohexylethyl)butan-1-amine (A34)

\[
\text{C}_{12}\text{H}_{25}\text{N} \quad (183.33 \text{ g/mol})
\]

\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 2.63 (dt, \(J = 13.9, 7.3\) Hz, 1H), 2.50 (dt, \(J = 11.3, 7.2\) Hz, 1H), 2.42 (p, \(J = 6.2\) Hz, 1H), 1.75 (dt, \(J = 12.4, 3.4\) Hz, 2H), 1.71 – 1.61 (m, 3H), 1.45 (p, \(J = 7.1\) Hz, 2H), 1.34 (h, \(J = 7.5\) Hz, 3H), 1.27 – 0.98 (m, 5H), 0.97 (d, \(J = 6.6\) Hz, 3H), 0.91 (t, \(J = 7.1\) Hz, 3H), 0.81 (s, 1H, NH); \(^{13}\text{C}^{(1)}\text{H}-\text{NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 58.03, 47.54, 43.06, 32.79, 30.18, 28.10, 26.85, 26.69, 20.76, 16.98, 14.19; \(\text{IR}\) (neat, ATR) \(\nu /\text{cm}^{-1}\) = 2956 (m), 2920 (s), 2851 (s), 2809 (w), 1463 (w), 1447 (w), 1370 (m), 1154 (w), 1124 (w), 890 (w), 834 (w); \(\text{GC}\) (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 13.7\) min (A35); \(\text{GC-MS}\): (Rtx-5MS, 100.2/10.270/10): \(t_R = 6.1\) min, \(m/z = 154\) (\([\text{M} - \text{CH}_3]^+\)), 86; \(\text{GC}\) (MEGA Diethyl-terbutylsilyl-b-086 (0.25 \(\mu\)m x 0.25 mm x 25 m), 60 kPa H\(_2\), 90 °C/10 min, 1°C/min to 120°C, 10°C/min to 180°C, 10 min): \(t_R = 21.7\) min ((S)-A34), \(t_R = 22.1\) min ((R)-A34); \(\text{HRMS}\): calc. 183.1987, found: 184.2062 (M+H); \(\text{Optical Rotation}\): \([\alpha]_D^{26} = -12.2°\) (c 1.0 in CHCl\(_3\) 0.75% EtOH)

(R)-N-(1-cyclohexylethyl)propan-2-amine (A35)

\[
\text{C}_{11}\text{H}_{23}\text{N} \quad (169.31 \text{ g/mol})
\]

\(^1\text{H-NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 2.84 (hept, \(J = 6.3\) Hz, 1H), 2.48 (p, \(J = 6.3\) Hz, 1H), 1.73 (dt, \(J = 11.8, 3.5\) Hz, 2H), 1.64 (q, \(J = 11.4\) Hz, 3H), 1.28 (ddd, \(J = 11.3, 3.4, 1\) Hz, 1H), 1.20 (ddd, \(J = 15.9, 9.7, 5.1, 3.3\) Hz, 2H), 1.16 – 1.08 (m, 1H), 1.02 (d, \(J = 6.3\) Hz, 3H), 0.99 (d, \(J = 6.2\) Hz, 3H), 0.97 (m, 1H), 0.96 (m, H), 0.94 (d, \(J = 6.5\) Hz, 3H), 0.63 (s, 1H, NH); \(^{13}\text{C}^{(1)}\text{H}-\text{NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 54.64, 45.69, 43.23, 30.33, 27.93, 26.97, 26.86, 26.67, 23.99, 23.27, 17.54; \(\text{GC-MS}\): (Rtx-5MS, 100.2/10.270/10): \(t_R = 6.1\) min, \(m/z = 154\) (\([\text{M} - \text{CH}_3]^+\)), 86; \(\text{GC}\) (Machary-Nagel Optima-5-Amin (0.50 \(\mu\)m x 0.25 \(\mu\)m x 30 m), 60 kPa H\(_2\), 100 °C/2 min, 10°C/min, 250 °C/7 min): \(t_R = 11.1\) min; \(\text{GC}\) (MEGA Diethyl-terbutylsilyl-b-086 (0.25 \(\mu\)m x 0.25 mm x 25 m), 60 kPa H\(_2\), 100 °C/2 min, 1°C/min to 135°C, 10°C/min to 180°C, 10 min): \(t_R = 32.4\) min ((S)-A35-acetamide), \(t_R = 32.1\) min ((R)-A35-acetamide); \(\text{IR}\) (neat, ATR) \(\nu /\text{cm}^{-1}\) = 2959 (m), 2921 (s), 2851 (s), 1465 (m), 1377 (m), 1336 (w), 1168 (m), 1134 (w), 890 (w), 834 (w), 713 (m); \(\text{HRMS}\): calc. 169.1830, found: 170.1901 (M+H); \(\text{Optical Rotation}\): \([\alpha]_D^{26} = -13.6°\) (c 1.0 in CHCl\(_3\) 0.75% EtOH)

(R)-N-(1-cyclohexylethyl)cyclohexanamine (A36)

\[
\text{C}_{14}\text{H}_{27}\text{N} \quad (209.37 \text{ g/mol})
\]

\(^1\text{H-NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 2.59 – 2.49 (m, 1H), 2.49 – 2.38 (m, 1H), 1.83 (t, \(J = 14.5\) Hz, 2H), 1.77 – 1.55 (m, 8H), 1.33 – 0.96 (m, 11H), 0.95 (d, \(J = 6.5\) Hz, 3H), 0.66 (s, 1H); \(^{13}\text{C}^{(1)}\text{H}-\text{NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 54.23, 54.09, 43.36, 34.79, 34.05, 30.32, 28.10, 26.96, 26.84, 26.67, 26.40, 25.51, 25.35, 17.85; \(\text{GC-MS}\) (Rtx-5MS, 50.2/30.250/5): \(t_R = 8.2\) min, \(m/z = 209\) (\([\text{M}]^+\)), 194, 166,
127, 126, 44; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H₂, 100 °C/2 min, 10°C/min, 250 °C/7 min): \( t_R = 17.6 \) min; **HPLC** (Daicel Chiracel OD-H, n-heptane/isopropanol 97:3, 0.5 mL/min, 40 °C, 225/284 nm): \( t_R = 19.2 \) min ((S)-A36-1-naphtamide), \( t_R = 21.3 \) min ((R)-A36-1-naphtamide); **IR** (neat, ATR) \( \nu/cm^{-1} = 2919 \) (s), 2848 (s), 1463 (m), 1447 (m), 1371 (m), 1155 (w), 1115 (w), 888 (w), 843 (w); **HRMS**: calc. 209.2143, found: 210.2217 (M+H); **Optical Rotation**: \([\alpha]_{D}^{28} = -17.3\) (c 1.0 in CHCl₃ 0.75% EtOH).
**Crystal Structures**

Single crystals were obtained by layering a solution of 5 in THF with diethylether and 7 in CH$_2$Cl$_2$ with pentane. The crystals were mounted with an oil drop on a glass fiber and frozen in the cold gas stream of a CRYOstream cooler. Data collection was carried out at 173 K using the “Collect” data collection software (Nonius BV, 2002). The structure were solved with SIR92 or SIR97 and refined with CRYSTALS. The plots have been created using the program Mercury.

The structure of 7 presented very big problems on various levels. The best crystals that could be obtained after numerous crystallization experiments were far from optimal for a structure determination. Apart from the fact that diffraction stopped to be observable at quite low Theta values it also seems that they were multiply twinned. The triclinic unit cell did not permit transformation to higher symmetry, even if the structure vaguely suggested the presence of a 3$_1$ axes as a symmetry element. Attempts to use alternative methods to determine the unit cell, for instance the program “cell_now”, always confirmed the strange unit cell with two axes a and b of approximately the same dimension and the angle $\gamma$ of about 120 degrees, but angles $\alpha$ and $\beta$ far away from 90 degrees which makes transformation to a higher symmetry impossible.

The Z value of the structure is 12. The data quality did not permit to locate all atoms, and like that the refinement finished at some intermediate state. Nevertheless the structure seems to demonstrate that all 12 complex molecules have the same configuration. While all peripheral groups are fuzzy the coordination sphere seems to be determined well enough to identify the compound and confirm its main geometrical features.

Nevertheless the refinement could, even with big efforts, not be brought to a level that would permit the deposition with the CCDC. For this reason the structure is mentioned here as unfinished work.
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**Ligand Screening**

![Chemical reaction diagram](image)

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Competition experiment

Throughout the catalytic reaction, neither imine I1 nor amine A1 can be observed by GC analysis. However, once the substrate is fully reduced, a new peak at $t_R = 23$ min appears and rises at the end of the reaction to about 2%. This decomposition product has not been identified or further investigated.

Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2013
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Total: 294097  44004
Decomposition product (ca. 2%)
Concentration series

To an equimolar mixture of I2 and A2 was added I1 and A1 in different concentrations to detect the minimal threshold in GC analysis of these substrates. They can already be detected at concentrations as low as 0.1 mol%.

0.1 mol%

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Method Name: D:\DATA\York\Methoden Line 2 amine_mittelhang_methoxyimin.gcm

**Intesity**

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ISTD Amount : 

Data Name : D:\DATA\York\YSIV743_0.5mol%.gcm
Method Name : D:\DATA\York\Method Line 2 amine_mittelang_methoxymin.gcm

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**Intensity**

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Assignment of the absolute configuration:

The absolute configuration of \( \text{A3, A28, A30 and A32} \) was assigned by comparison of the chiral stationary phase GC or HPLC data obtained after conducting a Buchwald-Hartwig amination.\(^{29}\)

\[
\text{Cl} + \begin{array}{c}
\text{NH}_2 \\
\text{R}^*
\end{array} \xrightarrow{\text{Pd(OAc)}_2, \text{CyPF}^4\text{Bu, NaO}^+\text{Bu}} \begin{array}{c}
\text{HN} \\
\text{R}^*
\end{array}
\text{MeO(CH}_2\text{)}_2\text{OMe, 100 °C, 48 h}
\]

The absolute configuration of \( \text{A33 to A36} \) was assigned by comparison of the chiral stationary phase GC or HPLC data obtained after condensation of \((R)-\text{cyclohexylethylamine}\) with the corresponding aldehyde and subsequent reduction with NaBH\(_4\) or LiAlH\(_4\).

\[
\text{NH}_2 + \begin{array}{c}
\text{K}
\end{array} \xrightarrow{1) \text{MS 4A, toluene, 23 °C, 48 h}} \begin{array}{c}
\text{HN}
\end{array} \\
1) \text{MS 4A, toluene, 23 °C, 48 h} \xrightarrow{2) \text{NaBH}_4/\text{LiAlH}_4, 0 °C to 23 °C, 24 h} \begin{array}{c}
\text{R}^*
\end{array}
\]

HN

```
PDA Multi 2 297nm,4nm

mAU

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PDA Multi 2 297nm,4nm

mAU

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The image contains a chemical structure with the formula: \( \text{HN} \) connected to the aromatic ring. Below the structure, there is a chromatogram with two peaks labeled as PDA Multi 2 297nm.4nm.

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