Supporting Information for


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1. General Information

All reactions were performed in flame-dried reaction vessels under an argon atmosphere, unless otherwise stated. Anhydrous solvents were obtained from MBRAUN SP-5 solvent purification system and were dried by passage through double filtration columns under nitrogen. Anhydrous benzylamine (≥99.5%, purified by redistillation) was purchased from Sigma Aldrich. All other reagents were acquired from Sigma Aldrich, Fluorochem, Acros Organics, Alfa Aesar or TCI and used without further purification. Brine refers to a saturated aqueous solution of NaCl.

Reactions were monitored by TLC using Merck Silicagel 60 F\textsubscript{254} aluminium-backed silica plates (particle size 0.20 mm) and visualised by exposure to UV light ($\lambda = 254$ nm) and/or staining and heating with phosphomolybdic acid, vanillin or potassium permanganate as appropriate. Flash column chromatography was performed using Merck Geduran\textsuperscript{®} Silicagel 60 (40–63 μm) according to the method of Still and co-workers.\textsuperscript{1} The required solvent system is specified in parentheses and where mixtures of solvents are described, the ratios are given as volume:volume. N-Benzyl piperidine and pyrrolidine products were purified on pre-basified silica (as noted in General Procedure A and B) which was prepared as follows; silica (400 g), pentane (250 mL), Et\textsubscript{2}O (250 mL) and triethylamine (5 mL) were combined in a 1 L beaker and stirred for 15 minutes. The solvent was allowed to evaporate overnight, and the resulting silica could be stored in a sealed bottle for a few weeks.

Nuclear magnetic resonance (NMR) spectra were recorded on 400 or 500 MHz spectrometers at ambient temperature, unless otherwise stated. $^1$H and $^{13}$C spectra were referenced to residual solvent peaks. Chemical shifts (δ) are recorded in parts per million (ppm) to the nearest 0.01 ppm for $^1$H NMR or 0.1 ppm for $^{13}$C and $^{19}$F NMR, except where additional precision was required to distinguish two close peaks. Coupling constants (J) are measured in hertz (Hz) and quoted to the nearest 0.1 Hz. Peaks are assigned as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), heptet (hept), multiplet (m), broad (br.) or a combination such as doublet of doublets (dd), doublet of triplets (dt) etc. Multiplicities are based on appearance rather than interpretation. For cyclic compounds, the abbreviation ‘ax’ denotes the axial proton and ‘eq’ the equatorial proton. For diastereotopic CH\textsubscript{2} groups in acyclic molecules or in cases where it was not possible to definitively assign axial vs equatorial environments, the CH\textsubscript{2} protons are labelled ‘a’ and ‘b’. $^1$H NMR yields were calculated by integration with respect to an internal standard (1,1,2,2-tetrachloroethane) run with an extended relaxation delay of 25 seconds.

Chiral phase HPLC was performed on an Agilent 1260 Series HPLC unit equipped with UV-vis diode-array detector, fitted with the appropriate Daicel Chiralpak column (dimensions: 0.46 cm ø x 25 cm)
along with the corresponding guard column (0.4 cm \( \times \) 1 cm). Wavelengths (\( \lambda \)) are reported in nm, retention times (\( t_R \)) are reported in minutes and solvent flow rates are reported in mL min\(^{-1}\). The Cbz-protected saturated heterocycles are extremely non-polar and we observed significant variation in their retention times from day to day. It was therefore essential to run enantiopure samples back to back with the corresponding authentic racemic sample.

Fourier-transformed infrared (FT-IR) spectra were recorded as a thin film or solid on a Bruker Tensor 27 FT-IR spectrometer equipped with a Pike Miracle Attenuated Total Reflectance sampling accessory. Absorption maxima are quoted in wavenumbers (cm\(^{-1}\)). The abbreviation br. denotes a broad peak.

Electrospray ionisation (ESI) HRMS were recorded on a Thermo Exactive orbitrap spectrometer equipped with a Waters Equity LC system, with a flow rate of 0.2 mL/min using water:methanol:formic acid (10:89.9:0.1) as eluent. The system uses a heated electrospray ionisation (HESI-II) probe for ESI\(^+\) and has a resolution of 50,000 FWHM under conditions for maximum sensitivity, with an accuracy of better than 5 ppm for 24 h following external calibration on the day of analysis. The mass reported is that containing the most abundant isotopes, with each value rounded to 4 decimal places and within 5 ppm of the calculated mass.

Melting point analysis was carried out using a Lecia VMTG heated-stage microscope equipped with a Testo 720 thermometer.

Optical rotations were recorded on a Schmidt Haensch Unipol L2000 polarimeter in a cell with a path length of 1 dm (using the sodium D line, 589 nm). Concentrations are reported in g/100 mL. Temperatures are reported in °C.
## 2. Extended Optimization Table for Enantiospecific Annulation

![Diagram](image)

**Entry** | **Base** | **Solvent** | **T / °C** | **Yield / %** | **er**
--- | --- | --- | --- | --- | ---
1 | - | Toluene | 110 | (54) | 57:43
2 | NaHCO₃ | Toluene | 110 | 92(80) | 71:29
3 | KHCΟ₃ | Toluene | 110 | 85 | 73:27
4 | CsHCO₃ | Toluene | 110 | 98 | 74:26
5 | NaOAc | Toluene | 110 | 90(86) | 62:38
6 | KOAc | Toluene | 110 | 95 | 54:46
7 | Na₂CO₃ | Toluene | 110 | 94 | 67:33
8 | K₂CO₃ | Toluene | 110 | 61 | 54:46
9 | Cs₂CO₃ | Toluene | 110 | 21 | 78:22
10 | NaOH | Toluene | 110 | 94 | 76:24
11 | KOH | Toluene | 110 | 92 | 71:29
12 | CsOH.xH₂O | Toluene | 110 | n.r. | -
13 | tBuOK | Toluene | 110 | 88 | 69:31
14 | tBuOK (5 mol%) | Toluene | 110 | n.r. | -
15 | tBuOK (10 mol%) | Toluene | 110 | n.r. | -
16 | CsHCO₃ | Heptane | 110 | 82 | 76:24
17 | CsHCO₃ | tBuOH | 110 | 84 | 76:24
18 | CsHCO₃ | TFE | 110 | 69 | 56:44
19 | CsHCO₃ | 1,4-dioxane | 110 | 85 | 79:21
20 | CsHCO₃ | CPME | 110 | 81 | 80:20
21 | CsHCO₃ | - | 110 | 93 | 82:18
22 | CsHCO₃ | Water | 110 | 79 | 84:16
23 | - | Water | 110 | 79 | 83:17
24 | - | Brine | 110 | 81 | 65:35
25 | CsHCO₃ | 1:1 Water:CPME | 110 | 95 | 81:19
26 | - | Water | 65 | 11 | 80:20
27 | - | Water | 70 | 41 | 85:15
28 | - | Water | 75 | 61 | 88:12
29 | - | Water | 80 | 69(72) | 90:10
30 | - | Water | 90 | 78 | 86:14
31 | - | Water | 100 | 82 | 85:15

(a) Reaction conditions: diol (–)-2i (1 equiv), benzylamine (1.5 equiv), [Cp*IrCl₂]₂ (1 mol%), base (2 mol%), solvent (2 M), 65-110 °C, 16 h. (b) Yields determined by ¹H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. Yields in parentheses refer to isolated material after column chromatography. (c) Enantiomeric purity determined after conversion to the corresponding Cbz-protected amine by HPLC using a chiral stationary phase (see Experimental Procedures for details).
3. General Procedures

3.1 General procedure A: Hydrogen borrowing alkylation of amines with diols in toluene
To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added the appropriate alcohol substrate (1.0 equiv.), [IrCp*Cl₂]₂ (1.0 mol%) and NaHCO₃ (2.0 mol%). The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum), evacuated under vacuum and refilled with argon three times. Anhydrous toluene (2 M) was added via syringe, followed by the appropriate amine (1.5 equiv.). The vial was sealed with Parafilm®, placed in a preheated oil bath and stirred at 110 °C for 16 hours. The reaction mixture was cooled to room temperature and concentrated under a flow of nitrogen. Purification by column chromatography (SiO₂ was basified with Et₃N prior to use, see General Information for details) afforded the piperidine product.

3.2 General procedure B: Hydrogen borrowing alkylation of amines with diols in water
To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added the appropriate alcohol substrate (1.0 equiv.) and [IrCp*Cl₂]₂ (1.0 mol%). The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum), evacuated under vacuum and refilled with argon three times. Deionised water (2 M) was added via syringe, followed by the appropriate amine (1.5 equiv.). The vial was sealed with Parafilm®, placed in a preheated oil bath and stirred at the appropriate temperature for 16 hours. The reaction mixture was cooled to room temperature and extracted with CH₂Cl₂ (3 × 10 mL). The organic phase was dried over MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (SiO₂ was basified with Et₃N prior to use, see General Information for details) afforded the title compound.

3.3 General procedure C: Carboxybenzyl (Cbz) protection for HPLC analysis
To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added the appropriate N-benzyl substrate (1.0 equiv.). Benzyl chloroformate (3 M in toluene, 6.0 equiv.) was added slowly via syringe. The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum) and equipped with a balloon (caution: gas evolution!). The reaction mixture was stirred at 80 °C for 2 hours. The reaction mixture was cooled to room temperature and transferred directly onto a silica column. Purification by column chromatography (SiO₂) afforded the title compound.
4. Experimental Procedures

4.1 Synthesis of Starting Materials

2-Benzylpentane-1,5-diol, rac-2k

LiAlH₄ (1.20 g, 38.0 mmol) was suspended in anhydrous THF (150 mL) at 0 °C and a solution of 3-benzyltetrahydro-2H-pyran-2-one (2.00 g, 10.5 mmol) in anhydrous THF (25 mL) added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 hour. The reaction was cooled to 0 °C, diluted with a further portion of THF (100 mL) and quenched with dropwise addition of water (1.2 mL) followed by 15% aq. NaOH (1.2 mL) and water (3.6 mL). The mixture was warmed to room temperature and stirred for 10 minutes after which MgSO₄ was added, and the mixture was stirred for a further 30 minutes at room temperature. The mixture was filtered through Celite® eluting with Et₂O and concentrated in vacuo. Purification by column chromatography (CH₂Cl₂:MeOH 95:5) afforded diol rac-2k as a viscous, colourless oil (1.74 g, 85%).

¹H NMR (500 MHz, CDCl₃) δ = 7.30-7.26 (2H, m, ArH), 7.21-7.17 (3H, m, ArH), 3.66-3.55 (3H, m, CH₂-1a and CH₂-5), 3.50 (1H, dt, J = 10.7, 5.3 Hz, CH₂-1b), 2.67-2.59 (2H, m, CH₂-6), 2.03-2.01 (1H, m, OH), 2.00-1.98 (1H, m, OH), 1.86-1.79 (1H, m, CH-2), 1.67-1.54 (2H, m, CH₂-4), 1.52-1.45 (1H, m, CH₂-3a), 1.41-1.34 (1H, m, CH₂-3b).

¹³C NMR (101 MHz, CDCl₃) δ = 140.8, 129.2, 128.4, 126.0, 64.5, 63.0, 42.3, 37.9, 29.8, 26.9.

The data are consistent with the literature.³

(S)-2-Phenylpentane-1,5-diol, (+)-2j

Racemic: LiAlH₄ (1.45 g, 38.3 mmol) was suspended in anhydrous THF (50 mL) at 0 °C and 2-phenylglutaric anhydride (2.43 g, 12.8 mmol) was added portionwise. The reaction mixture was warmed to room temperature and then heated at reflux, with stirring, for 4 hours. The reaction was cooled to 0 °C, diluted with a further portion of THF (50 mL) and quenched with dropwise addition of water (1.5 mL) followed by 15% aq. NaOH (1.5 mL), and water (4.5 mL). The mixture was warmed to room temperature and stirred for 10 minutes after which MgSO₄ was added and the mixture stirred for a further 30 minutes. The mixture was filtered through Celite® (eluting with Et₂O) and
concentrated in vacuo. Purification by column chromatography (CH$_2$Cl$_2$:MeOH 95:5) afforded the title compound rac-2j (1.70 g, 74%) as a viscous, colourless oil.

**Enantioenriched:** (+)-2j (>99:1 e.r.) was prepared by preparative SFC separation of racemic diol rac-2j using a Chiralpak® ID column, 80:20 CO$_2$:MeOH, 10 mL min$^{-1}$, 260 nm, 35°C, 20 μL injections of 100 mg/mL diol rac-2j in MeOH; $t_\text{r}$ (S) = 4.3 min, $t_\text{r}$ (R) = 5.0 min. Absolute configuration was determined to be (S) by comparison of the optical rotation value with literature data.$^4$

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.35-7.19 (5H, m, ArH), 3.80-3.71 (2H, m, CH$_2$-1), 3.63-3.56 (2H, m, CH$_2$-5), 2.84-2.76 (1H, m, CH-2), 1.87-1.79 (1H, m, CH$_2$-3a), 1.70-1.19 (5H, m, CH$_2$-3b, CH$_2$-4, 2 × OH).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 142.3, 128.8, 128.2, 126.9, 67.6, 62.8, 48.5, 30.5, 28.3. These spectral data are consistent with the literature.$^5$

Enantiomeric excess was determined by SFC; Chiralpak® ID column (5-50% MeOH:CO$_2$ gradient over 3.5 min, 2 mL min$^{-1}$, DAD 210-400 nm, 40 °C):

(5)-2-Isobutylbutane-1,4-diol, (−)-2al

**Racemic:** LiAlH$_4$ (661 mg, 17.4 mmol) was suspended in anhydrous THF (40 mL) at 0 °C and a solution of isobutylsuccinic acid (1.01 g, 5.80 mmol) in anhydrous THF (15 mL) was added dropwise. The reaction mixture was warmed to room temperature and then heated to 70 °C for 16 hours. The reaction was then cooled to 0 °C, diluted with Et$_2$O (50 mL) and quenched by dropwise addition of water (0.66 mL) followed by 15% aq. NaOH (0.66 mL) and water (2.0 mL). The mixture was warmed
to room temperature and stirred for 10 minutes after which MgSO₄ was added, and the mixture was
stirred for a further 30 minutes at room temperature. The mixture was filtered through Celite®
eluting with Et₂O and concentrated in vacuo. Purification by column chromatography (CH₂Cl₂:MeOH
95:5) afforded diol rac-2al as a viscous, colourless oil (671 mg, 79%).

**Enantioenriched:** LiAlH₄ (678 mg, 17.9 mmol) was suspended in anhydrous THF (40 mL) at 0 °C and a
solution of (S)-(−)-2-isobutylsuccinic acid 1-methyl ester (1.12 g, 5.95 mmol) in anhydrous THF
(15 mL) was added dropwise. The reaction mixture was warmed to room temperature and then
heated to 70 °C for 16 hours. The reaction was then cooled to 0 °C, diluted with Et₂O (50 mL) and
quenched by dropwise addition of water (0.68 mL) followed by 15% aq. NaOH (0.68 mL) and water
(2.1 mL). The mixture was warmed to room temperature and stirred for 10 minutes after which
MgSO₄ was added, and the mixture was stirred for a further 30 minutes at room temperature. The
mixture was filtered through Celite® eluting with Et₂O and concentrated in vacuo. Purification by
column chromatography (CH₂Cl₂:MeOH 95:5) afforded diol (−)-2al as a viscous, colourless oil (691
mg, 79%).

1H NMR (400 MHz, CDCl₃) δ = 3.75 (1H, ddd, J = 10.7, 6.4, 4.4 Hz, CH₂-4α), 3.66 – 3.58 (4H, m,
CH₂-4β, CH₂-1α and 2 x OH), 3.41 (1H, dd, J = 10.5, 7.3 Hz, CH₂-1β), 1.76 – 1.47 (4H, m, CH-2, CH-6, CH₂-3), 1.15
(1H, dt, J = 13.9, 7.0 Hz, CH₂-5α), 1.06 (1H, dt, J = 13.9, 7.1 Hz, CH₂-5β), 0.88 (3H, d, J = 6.4 Hz, CH₃-7a),
0.86 (3H, d, J = 6.4 Hz, CH₃-7b).

13C NMR (101 MHz, CDCl₃) δ = 66.6, 61.2, 41.3, 37.2, 36.2, 25.4, 23.0, 22.8.

HRMS: ESI+ found [M+H]+ = 147.1380, C₈H₁₉O₂ requires 147.1380, Δ = 0.20 ppm.

FTIR (film): v_max = 3286 (br), 2954, 1466, 1367, 1036 cm⁻¹.

[α]D²⁵ = −12.6 (c = 1.0, CHCl₃).

(R)-2-Isopropylbutane-1,4-diol, (−)-2am

LiAlH₄ (1.64 g, 43.1 mmol) was suspended in anhydrous THF (100 mL) at 0 °C and a solution of (R)-2-
isopropylsuccinic acid-1-methyl ester (2.50 g, 14.4 mmol) in anhydrous THF (30 mL) was added
dropwise. The reaction mixture was warmed to room temperature and then heated to 70 °C for
16 hours. The reaction was then cooled to 0 °C, diluted with Et₂O (100 mL) and quenched by
dropwise addition of water (1.6 mL) followed by 15% aq. NaOH (1.6 mL) and water (4.9 mL). The
mixture was warmed to room temperature and stirred for 10 minutes after which MgSO₄ was added,
and the mixture was stirred for a further 30 minutes at room temperature. The mixture was filtered
through Celite® eluting with Et₂O and concentrated in vacuo. Purification by column chromatography (CH₂Cl₂:MeOH 95:5) afforded diol (−)-2am as a viscous, colourless oil (1.53 g, 81%). The corresponding racemic diol rac-2am was prepared by an identical procedure starting from racemic 2-isobutylsuccinic acid 1-methyl ester.

1H NMR (400 MHz, CDCl₃) δ = 3.77 (1H, ddd, J = 10.7, 6.3, 4.3 Hz, CH₂-4a), 3.71 – 3.63 (3H, m, CH₂-1a and 2 x OH), 3.60 (1H, ddd, J = 10.4, 8.1, 4.1 Hz, CH₂-α), 3.51 (1H, dd, J = 10.2, 7.8 Hz, CH₂-1b), 1.79 – 1.65 (2H, m, CH₂-3a and CH-5), 1.55 (1H, dt, J = 14.3, 8.3, 4.1 Hz, CH₂-3b), 1.45 (1H, dddd, J = 11.7, 8.3, 4.8, 3.2 Hz, CH-2), 0.89 (3H, d, J = 7.0 Hz, CH₃-6a), 0.87 (3H, d, J = 7.4 Hz, CH₃-6b).

13C NMR (101 MHz, CDCl₃) δ = 65.1, 62.0, 45.7, 33.1, 29.8, 20.0, 19.5.

HRMS: ESI+ found [M+H]+ = 133.1223, C₇H₁₇O₂ requires 133.1223, Δ = −0.17 ppm.

FTIR (film): νmax = 3296 (br), 2957, 1465, 1387, 1369, 1023 cm⁻¹.

[α]D²⁵ = −20.1 (c = 1.0, CHCl₃).

(2R,5R)-2-methylhexane-1,5-diol, (+)-2o

Racemic: We have previously reported the synthesis of diol rac-2o (12:88 d.r.).⁵

Enantioenriched: According to a modified literature procedure,⁷ to a pre-cooled vial at 0 °C was added (S)-(−)-α,α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (1.00 g, 3.10 mmol), methyl-3,4-dihydroxybenzoate (1.90 g, 12.3 mmol), propanal (4.43 mL, 61.4 mmol) and methyl vinyl ketone (7.48 mL, 92.2 mmol). The vial was sealed and stirred at 0 °C for 24 hours. The reaction solution was transferred into pre-cooled ethanol (500 mL) at 0 °C via syringe and sodium borohydride (11.6 g, 0.31 mol) was added portionwise. The reaction mixture was allowed to warm to room temperature and stirred for a further 16 hours. The mixture was poured onto ice and allowed to warm to room temperature. The solution was concentrated in vacuo to remove the majority of the EtOH and then extracted with Et₂O (3 × 400 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (CH₂Cl₂:MeOH 95:5) afforded diol (+)-2o (1.23 g, 15%, ~53:47 dr,* 94:6 er) as a colourless oil and an inseparable mixture of diastereomers. The enantiomeric purity of (+)-2o was determined by chiral HPLC analysis after conversion to the corresponding dibenzoyl ester (see below).

* It was not possible to calculate dr of the crude reaction mixture or purified compound due to overlapping peaks in the 1H NMR spectrum, but a dr of ~53:47 was estimated by HPLC for the benzoyl ester derivative S1. N.B. the major diastereoisomer of racemic and enantioenriched diols were opposite.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 3.81-3.77\) (1H, m, CH-5), 3.49-3.43 (2H, m, CH-2), 2.29-1.39 (6H, m, 2 \(\times\) OH, CH-2, CH-3, and CH-4\(_b\)), 1.29-1.11 (1H, m, CH-4\(_a\)), 1.19 (3H, d, \(J = 6.2\) Hz, CH-6), 0.94-0.90 (3H, m, CH-7). N.B. no separate signals were observed for the minor diastereoisomer.

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 68.6, 68.1, 36.6, 35.9, 29.2, 23.7, 16.8\). N.B. the minor diastereoisomer displays signals at \(\delta = 68.3, 68.2, 36.3, 35.6, 29.0, 23.8, 16.7\).

HRMS: ESI+ found [M+Na]\(^+\) = 155.1040, C\(_7\)H\(_{16}\)O\(_2\)Na requires 155.1043, Δ = –1.69 ppm.

FTIR (film): \(\nu_{\max} = 3318, 2927, 2872, 1459, 1374, 1112, 1021, 984, 943\) cm\(^{-1}\).

\([\alpha]_D^{25} = +11.0\) (c = 1.0, CHCl\(_3\)).

\((2R,5R)-2\)-Methylhexane-1,5-diyldibenzoate, S1

To a solution of \((2R)-2\)-Methylhexane-1,5-diol (+)-2o (26 mg, 0.20 mmol, ~53:47 d.r.) in anhydrous CH\(_2\)Cl\(_2\) (5 mL) was added pyridine (0.05 mL, 0.60 mmol) and benzoyl chloride (0.06 mL, 0.50 mmol).

The resulting solution was stirred at room temperature for 2 hours before addition of saturated aqueous NH\(_4\)Cl solution (10 mL). The mixture was extracted with CH\(_2\)Cl\(_2\) (3 \(\times\) 10 mL) and the combined organic phases dried over MgSO\(_4\), filtered and concentrated in vacuo.

Purification by column chromatography (CH\(_2\)Cl\(_2\)) afforded diester S1 (9.5 mg, 14%, ~53:47 dr, *94:6 er) as a colourless oil and an inseparable mixture of diastereomers. The corresponding racemic diester rac-S1 (~13:87 d.r.) was prepared by an identical procedure starting from rac-2o.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.04-8.00\) (4H, m, Ar), 7.57-7.52 (2H, m, Ar), 7.43-7.38 (4H, m, Ar), 5.22-5.13 (1H, m, CH-5), 4.22-4.13 (2H, m, CH-2), 2.03-1.94 (1H, m, CH-2), 1.90-1.56 (3H, m, CH-3 and CH-4\(_a\)), 1.45-1.28 (1H, m, CH-4\(_b\)), 1.36 (3H, d, \(J = 6.3\) Hz, CH-7), 1.05 (3H, d, \(J = 6.8\) Hz, CH-6).

N.B. no separate signals were observed for the minor diastereoisomer.

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 166.7, 166.3, 133.0, 132.9, 130.9, 130.5, 129.6\) (two overlapping signals), 128.5, 128.4, 71.5, 69.5, 33.6, 33.8, 29.4, 20.3, 17.2. N.B. the minor diastereoisomer displays signals at \(\delta = 166.7, 166.3, 133.0, 132.9, 130.9, 130.5, 129.6\) (two overlapping signals), 128.5, 128.4, 71.7, 69.6, 33.4, 33.7, 29.2, 20.3, 17.0.

HRMS: ESI+ found [M+H]\(^+\) = 341.1749, C\(_{21}\)H\(_{25}\)O\(_4\) requires 341.1747, Δ = 0.47.

FTIR (film): \(\nu_{\max} = 1714, 1451, 1314, 1272, 1109, 1070, 1026, 710\) cm\(^{-1}\).

\([\alpha]_D^{25} = +1.6\) (c = 0.79, CHCl\(_3\)).

* It was not possible to calculate dr of the crude reaction mixture or purified compound due to overlapping peaks in the \(^1\)H NMR spectrum, but a dr of ~53:47 was estimated by HPLC.
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (99.7:0.3 hexane:IPA, 1.0 mL min$^{-1}$, 210 nm, room temperature), ~53:47 dr; major diastereomer $t_r$ (major) = 33.6 min, $t_r$ (minor) = 50.0 min, 94:6 er; minor diastereomer $t_r$ (minor) = 31.0 min, $t_r$ (major) = 42.3 min; 94:6 er. [N.B. racemate with ~13:87 d.r.].

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4.2 Hydrogen Borrowing Annulation

N-Benzyl-4-methylpiperidine, 3a

Commercially available 4-methylpentane-1,5-diol 2a (118 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et\(_2\)O 50:50) afforded piperidine 3a (182 mg, 96%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.32-7.21 (5H, m, ArH), 3.48 (2H, s, NC\(\text{H}_2\)Ph), 2.87-2.82 (2H, m, 2\(\times\)C\(\text{H}_2\)-2m), 1.93 (2H, td, \(J = 11.5, 2.4\) Hz, 2\(\times\)CH\(_2\)-2a), 1.62-1.56 (2H, m, 2\(\times\)CH\(_2\)-3a), 1.41-1.30 (1H, m, CH-4), 1.29-1.19 (2H, m, 2\(\times\)CH\(_2\)-3b), 0.91 (3H, d, \(J = 6.2\) Hz, CH\(_3\)).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 138.9, 129.4, 128.2, 127.0, 63.7, 54.1, 34.5, 30.9, 22.1.

The data are consistent with the literature.\(^8\)

N-Benzyl-4-phenylpiperidine, 3b

3-Phenylpentane-1,5-diol\(^6\) 2b (180 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et\(_2\)O 60:40) afforded piperidine 3b (208 mg, 83%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.18-7.39 (10H, m, ArH), 3.58 (2H, s, NCH\(_2\)Ph), 3.06-3.01 (2H, m, 2\(\times\)CH\(_2\)-2a), 2.58-2.46 (1H, m, CH-4), 2.16-2.08 (2H, m, 2\(\times\)CH\(_2\)-2b), 1.86-1.80 (4H, m, 2\(\times\)CH\(_2\)-3).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 146.7, 138.7, 129.4, 128.5, 128.3, 127.1, 127.0, 126.2, 63.7, 54.4, 42.9, 33.7.

HRMS: ESI\(^+\) found [M+H]\(^+\)\(^\text{ESI}\) = 252.1742, C\(_{18}\)H\(_{22}\)N requires 252.1747, \(\Delta = -2.09\) ppm.

FTIR (film): \(\nu_{\max} = 3027, 2934, 2798, 2750, 1493, 1452, 1366, 991, 735, 696\) cm\(^{-1}\).
3-(4-Fluorophenyl)-pentane-1,5-diol$^6$ 2c (198 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl$_2$]$_2$ (8.0 mg, 1.0 mol%), NaHCO$_3$ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et$_2$O 60:40) afforded piperidine 3c (215 mg, 80%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.37-7.31 (4H, m, ArH), 7.29-7.24 (1H, m, ArH), 7.21-7.15 (2H, m, ArH), 7.01-6.94 (2H, m, ArH), 3.55 (2H, s, NC$_2$H$_2$Ph), 3.05-2.98 (2H, m, 2 x CH$_2$-2eq), 2.48 (1H, tt, $J$ = 10.3, 5.2 Hz, CH$_4$-4ax), 2.08 (2H, td, $J$ = 11.2, 3.7 Hz, 2 x CH$_2$-2ax), 1.83-1.75 (4H, m, 2 x CH$_2$-3).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 161.3 (d, $J$ = 243.3 Hz), 142.2 (d, $J$ = 3.1 Hz), 138.4, 129.3, 128.2, 127.0, 115.1 (d, $J$ = 20.9 Hz), 63.5, 54.2, 42.0, 33.7.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -117.5.

HRMS: ESI$^+$ found [M+H]$^+$ = 270.1651, C$_{18}$H$_{21}$FN requires 270.1653, $\Delta$ –0.46 ppm.

FTIR (film): $\nu_{\text{max}}$ = 2935, 2800, 1604, 1509, 1453, 1366, 1342, 1223, 1159, 1031, 992, 832, 795, 773, 737, 698, 613 cm$^{-1}$.

$N$-Benzyl-4-(4-methoxyphenyl)piperidine, 3d

3-(4-Methoxyphenyl)-pentane-1,5-diol$^6$ 2d (198 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl$_2$]$_2$ (8.0 mg, 1.0 mol%), NaHCO$_3$ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et$_2$O 50:50) afforded piperidine 3d (258 mg, 92%) as a colourless solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.80-7.31 (4H, m, ArH), 7.29-7.24 (1H, m, ArH), 7.18-7.14 (2H, m, ArH), 6.87-6.83 (2H, m, ArH), 3.79 (3H, s, OCH$_3$), 3.56 (2H, s, NCH$_2$Ph), 3.04-2.98 (2H, m, 2 x CH$_2$-2eq), 2.46 (1H, tt, $J$ = 10.9, 3.8 Hz, 2 x CH$_2$-2ax), 2.08 (2H, td, $J$ = 10.9, 3.8 Hz, 2 x CH$_2$-2ax), 1.83 – 1.70 (4H, m, 2 x CH$_2$-3).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 157.9, 138.8, 138.5, 129.3, 128.2, 127.7, 127.0, 113.8, 63.6, 55.3, 54.4, 41.8, 33.8.
HRMS: ESI+ found [M+H]⁺ = 282.1851, C₁₉H₂₃NO requires 282.1852, Δ −0.54 ppm.
FTIR (film): ν_max = 2941, 2795, 2752, 1608, 1512, 1467, 1365, 1327, 1244, 1176, 1146, 1115, 1033, 989, 833, 808, 766, 739, 696, 613 cm⁻¹.
Melting point = 68–71 °C.

_N-Benzyl-4-(naphthalen-2-yl)piperidine, 3e_

![Chemical Structure](image)

3-(Naphthalene-1-yl)-pentane-1,5-diol⁶ 2e (230 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 60:40) afforded piperidine 3e (261 mg, 87%) as a colourless solid.

³¹H NMR (400 MHz, CDCl₃) δ = 8.11 (1H, d, J = 8.4 Hz, ArH), 7.87 (1H, dd, J = 7.6, 2.0 Hz, ArH), 7.72 (1H, dd, J = 6.8, 2.6 Hz, ArH), 7.55-7.33 (8H, m, ArH), 7.31-7.27 (1H, m, ArH), 3.63 (2H, s, NC₆H₄Ph), 3.34 (1H, tt, J = 10.7, 5.2 Hz, CH-4₃), 3.15-3.07 (2H, m, 2 x CH₂-2₃), 2.27 (2H, td, J = 11.1, 4.2 Hz, 2 x CH₂-2₃), 2.03-1.92 (4H, m, 2 x CH₂-3).

¹³C NMR (101 MHz, CDCl₃) δ = 142.2, 138.5, 133.9, 131.4, 129.3, 129.0, 128.2, 127.0, 126.5, 125.7, 125.3, 123.0, 122.5, 63.6, 54.6, 37.6, 33.2.

HRMS: ESI+ found [M+H]⁺ = 302.1902, C₂₂H₂₄N requires 302.1903, Δ −0.44 ppm.
FTIR (film): ν_max = 3048, 2936, 2799, 1597, 1494, 1453, 1396, 1366, 1343, 1144, 988, 778, 737, 699 cm⁻¹.
Melting point = 76–78 °C.

_N-Benzyl-4-(trifluoromethyl)piperidine, 3f_

![Chemical Structure](image)

4-(Trifluoromethyl)-pentane-1,5-diol⁹ 2f (172 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine 3f (192 mg, 79%) as a pale yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.36-7.24 (5H, m, ArH), 3.51 (2H, s, NCH$_2$Ph), 2.97 (2H, m, 2 $\times$ CH$_2$-2$_{ax}$), 2.05-1.91 (3H, m, CH-4 and 2 $\times$ CH$_2$-2$_{eq}$), 1.85-1.78 (2H, m, 2 $\times$ CH$_2$-3$_{eq}$), 1.64 (2H, qd, $J$ = 12.7, 3.9 Hz, 2 $\times$ CH$_2$-3$_{ax}$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 138.3, 129.2, 128.4, 127.7 ($q$, $J$ = 278.4 Hz), 127.2, 63.2, 52.5, 40.5 ($q$, $J$ = 27.1 Hz), 24.8.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -73.7

The data are consistent with the literature.$^{10}$

**N-Benzylmorpholine, 3g**

![N-Benzylmorpholine structure](image)

Commercially available diethylene glycol 2g (106 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl$_2$]$_2$ (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 110 °C. Purification by column chromatography (pentane:Et$_2$O 80:20) afforded piperazine 3g as a colourless oil (74 mg, 35%) as an inseparable mixture with dibenzylamine (14 mol%, the spectral data for dibenzylamine are consistent with the literature$^{12}$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.36-7.24 (5H, m, ArH), 3.72-3.70 (4H, m, 2 $\times$ CH$_2$-2), 3.50 (2H, s, NCH$_2$Ph), 2.46-2.43 (4H, m, 2 $\times$ CH$_2$-1).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 137.9, 129.3, 128.4, 127.3, 67.2, 63.6, 53.8.

The data are consistent with the literature.$^{11}$

**N, N’-Dibenzypiperazine, 3h**

![N, N’-Dibenzypiperazine structure](image)

Commercially available N-benzyldiethanolamine 2h (195 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl$_2$]$_2$ (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 110 °C. Purification by column chromatography (pentane:Et$_2$O 80:20) afforded piperazine 3h (48 mg, 16%) as a pale yellow solid as an inseparable mixture with dibenzylamine (15 mol%, the spectral data for dibenzylamine are consistent with the literature$^{12}$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.35-7.22 (10H, m, ArH), 3.51 (4H, s, 2 $\times$ NCH$_2$Ph), 2.48 (8H, br. s, 4 $\times$ CH$_2$-2).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 138.3, 129.4, 128.3, 127.1, 63.2, 53.2.

The data are consistent with the literature.$^{13}$
1-Benzyl-3-methylpiperidine, 3i

![Structure of 1-Benzyl-3-methylpiperidine]

2-Methylhexane-1,5-diol\(^6\) \textit{rac}-2i (118 mg, 1.0 mmol, >99:1 er), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}]_2\) (8.0 mg, 1.0 mol%) and anhydrous toluene (0.5 mL) were subjected to \textbf{general procedure A}. Purification by column chromatography (pentane:Et\(_2\)O 90:10) afforded piperidine 3i (122 mg, 64%) as a colourless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.33-7.22\) (5H, m, ArH), 3.48 (2H, s, NCH\(_2\)Ph), 2.79 (2H, m, CH\(_2\)-2\(_a\) and CH\(_2\)-6\(_{eq}\)), 1.85 (1H, td, \(J = 11.1, 3.7\) Hz, CH\(_2\)-6\(_{ax}\)), 1.72-1.51 (5H, m, CH\(_2\)-2\(_b\), CH\(_3\)-3, CH\(_2\)-4\(_a\) and CH\(_2\)-5), 0.90-0.86 (1H, m, CH\(_2\)-4\(_b\)), 0.83 (3H, d, \(J = 6.4\) Hz, CH\(_3\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 138.8, 129.3, 128.2, 126.9, 63.8, 62.1, 54.1, 33.2, 31.3, 25.7, 19.9.

HRMS: ESI+ found [M+H]\(^+\) = 190.1590, C\(_{13}\)H\(_{20}\)N requires 190.1590, \(\Delta = -0.04\) ppm.

FTIR (film): \(\nu_{\text{max}} = 2927, 2794, 2756, 1454, 1346, 1120, 1073, 1028, 976, 737, 698\) cm\(^{-1}\).

\(N\)-Benzyl-3-phenylpiperidine, 3j

![Structure of \(N\)-Benzyl-3-phenylpiperidine]

2-Phenylpentane-1,5-diol\(^6\) \textit{rac}-2j (180 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}]_2\) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to \textbf{general procedure A}. Purification by column chromatography (pentane:Et\(_2\)O 90:10) afforded piperidine 3j (162 mg, 64%) as a colourless solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.39-7.22\) (10H, m, ArH), 3.55 (2H, s, NCH\(_2\)Ph), 3.01 (1H, ddt, \(J = 11.0, 3.6, 1.7\) Hz, CH\(_2\)-2\(_{eq}\)), 2.96-2.91 (1H, m, CH\(_2\)-6\(_{eq}\)), 2.85 (1H, tt, \(J = 11.6, 3.7\) Hz, CH\(_2\)-3\(_{eq}\)), 2.05 (1H, t, \(J = 11.1\) Hz, CH\(_2\)-2\(_{ax}\)), 2.03-1.90 (2H, m, CH\(_2\)-6\(_b\) and CH\(_2\)-4\(_a\)), 1.81-1.67 (2H, m, CH\(_2\)-5), 1.51-1.41 (1H, m, CH\(_2\)-4\(_b\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 145.0, 138.5, 129.3, 128.4, 128.3, 127.4, 127.0, 126.4, 63.7, 61.2, 53.9, 43.1, 31.8, 25.9.

Melting point = 45–47 °C.
1,3-Dibenzylpiperidine, 3k

2-Benzylpentane-1,5-diol rac-2k (194 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine 3k (208 mg, 78%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ = 7.34-7.13 (10H, m, ArH), 3.57-3.40 (2H, m, C₆H₂-7), 2.81 (1H, dd, J = 10.9, 3.0 Hz, C₆H₂-2a), 2.76 (1H, d, J = 11.0 Hz, C₆H₂-6a), 2.61-2.43 (2H, m, C₆H₂-8), 1.96-1.86 (2H, m, CH-3 and CH-6b), 1.79 (1H, t, J = 10.4 Hz, CH₂-2a), 1.71-1.61 (2H, m, CH₂-4a and CH₂-5a), 1.56-1.45 (1H, m, CH₂-4b), 1.00-0.92 (1H, m, CH₂-5b).

The data are consistent with the literature.¹⁴

N-Benzyl-3-methylpyrrolidine, 3l

2-Methylpentane-1,4-diol rac-2l (104 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), NaHCO₃ (1.7 mg, 2.0 mol%), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10) afforded pyrrolidine 3l (74 mg, 42%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.21 (5H, m, ArH), 3.63-3.56 (2H, m, NCH₃Ph), 2.82 (1H, dd, J = 9.0, 7.4 Hz, CH₂-2a), 2.70 (1H, ddd, J = 9.2, 8.0, 5.4 Hz, CH₂-5a), 2.45 (1H, td, J = 8.8, 6.4 Hz, CH₂-5b), 2.32-2.19 (1H, m, CH-3), 2.07-1.96 (2H, m, CH₂-2a and CH₂-4a), 1.34 (1H, dddd, J = 12.6, 8.5, 6.3, 5.4 Hz, CH₂-4b), 1.01 (3H, d, J = 6.8 Hz, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ = 139.6, 129.0, 128.3, 126.9, 62.4, 61.0, 54.3, 32.8, 32.0, 20.6.

HRMS: ESI⁺ found [M+H]⁺ = 176.1434, C₁₂H₁₈N requires 176.1434, Δ = -0.03 ppm.

FTIR (film): νₚₐₓ = 2955, 2783, 1453, 1375, 1155, 1136, 1124, 1029, 907, 739, 698 cm⁻¹.
**rac-(2R,3R)-1-Benzyl-2,3-dimethylpiperidine, 3m**

4-methylhexane-1,5-diol \(^6\) *rac-2m* (132 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([IrCp^*Cl_2]_2\) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to **general procedure A**. NMR analysis of the crude reaction mixture indicated the presence of two diastereomers in 89:11 dr. Purification by column chromatography (pentane:Et\(_2\)O 90:10) afforded piperidine 3\(_m\)\(_{\text{maj}}\) (132 mg, 65%, >95:5 d.r.) as a colourless oil and piperidine 3\(_m\)\(_{\text{min}}\) (20 mg, 10%, >95:5 d.r.) as a colourless oil. The relative stereochemistry was determined by \(J\)-coupling constant analysis.

**Data for the major diastereoisomer:**

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.37-7.20 \) (5H, m, ArH), 3.66-3.50 (2H, m, NC\(_2\)H\(_2\)), 2.77 (1H, qd, \( J = 6.7, 4.0 \) Hz, CH\(_2\)), 2.45 (1H, ddd, \( J = 11.7, 9.9, 3.9 \) Hz, CH\(_2\)-6\(_{\text{eq}}\)), 2.32 (1H, dt, \( J = 11.7, 4.1 \) Hz, CH\(_2\)-6\(_{\text{ax}}\)), 2.32 (1H, dt, \( J = 11.7, 4.1 \) Hz, CH\(_2\)-6\(_{\text{ax}}\)), 1.89 (1H, dqt, \( J = 10.9, 7.0, 4.0 \) Hz, CH-3), 1.61-1.40 (3H, m, CH\(_2\)-4 and CH\(_2\)-5\(_{\text{eq}}\)), 1.32-1.21 (1H, m, CH\(_2\)-5\(_{\text{ax}}\)), 0.90 (3H, d, \( J = 6.7 \) Hz, CH\(_3\)-7), 0.86 (3H, d, \( J = 7.0 \) Hz, CH\(_3\)-8).

\( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta = 140.5, 128.7, 128.2, 126.7, 59.3, 57.8, 46.8, 35.1, 28.1, 25.2, 18.1, 6.7.

HRMS: ESI+ found [M+H]\(^+\) = 204.1747, C\(_{14}\)H\(_{22}\)N requires 204.1747, \( \Delta = 0.26 \) ppm.

FTIR (film): \( \nu_{\text{max}} = 2926, 2793, 1494, 1452, 1373, 1142, 1122, 1090, 1027, 955, 731, 697 \) cm\(^{-1}\).

**Data for the minor diastereoisomer:**

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.34-7.21 \) (5H, m, ArH), 3.99 (1H, d, \( J = 13.6 \) Hz, NCH\(_2\)Ph), 3.28 (1H, d, \( J = 13.6 \) Hz, NCH\(_2\)Ph), 2.75 (1H, dtd, \( J = 11.6, 3.9, 1.5 \) Hz, CH\(_2\)-6\(_{\text{eq}}\)), 2.07-1.96 (2H, m, CH-2 and CH\(_2\)-6\(_{\text{eq}}\)), 1.71-1.64 (1H, m, CH\(_2\)-4\(_{\text{eq}}\)), 1.54-1.48 (2H, m, CH\(_2\)-5\(_{\text{eq}}\)), 1.44-1.35 (1H, m, CH-3), 1.21 (3H, d, \( J = 6.1 \) Hz, CH\(_2\)-7), 1.09-0.97 (1H, m, CH\(_2\)-4\(_{\text{ax}}\)), 0.95 (3H, d, \( J = 6.6 \) Hz, CH\(_3\)-8).

\( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta = 139.9, 129.2, 128.2, 126.7, 62.8, 58.1, 52.3, 37.0, 33.1, 24.8, 20.1, 17.0.

HRMS: ESI+ found [M+H]\(^+\) = 204.1747, C\(_{14}\)H\(_{22}\)N requires 204.1747, \( \Delta = 0.11 \) ppm.

FTIR (film): \( \nu_{\text{max}} = 2928, 2787, 1494, 1454, 1368, 1119, 1028, 733, 698 \) cm\(^{-1}\).
rac-(2S,4S)-1-Benzyl-2,4-dimethylpiperidine, 3n

3-Methylhexane-1,5-diol\textsuperscript{6} rac-2n (132 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp^*Cl\textsubscript{2}]\textsubscript{2} (8.0 mg, 1.0 mol%), NaHCO\textsubscript{3} (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to \textbf{general procedure A} at 110 °C. Purification by column chromatography (pentane:Et\textsubscript{2}O 75:25) afforded piperidine 3n (126 mg, 62%, 82:18 d.r.) as a colourless oil as a mixture of diastereoisomers. The relative stereochemistry was determined by J-coupling constant analysis. A small quantity of diastereoisomerically pure cis-3n (34 mg, >95:5 d.r.) was isolated by column chromatography (pentane:Et\textsubscript{2}O 85:15).

HRMS: ESI+ found [M+H]\textsuperscript{+} = 204.1747, C\textsubscript{14}H\textsubscript{22}N requires 204.1747, \(\Delta = 0.26\) ppm.

FTIR (film): \(\nu_{\text{max}}\) = 2949, 2916, 1494, 1453, 1373, 1328, 1192, 1135, 1123, 1065, 1029, 730, 697 cm\textsuperscript{-1}.

Data for the major diastereoisomer:

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.30 – 7.11\) (5H, m, ArH), 4.03 (1H, d, \(J = 13.3\) Hz, NCH\textsubscript{2}Ph), 3.03 (1H, d, \(J = 13.3\) Hz, NCH\textsubscript{2}Ph), 2.71 (1H, ddd, \(J = 11.6, 3.9, 2.8\) Hz, CH\textsubscript{2}-6\textsubscript{eq}), 2.11 (1H, ddd, \(J = 12.0, 6.0, 2.7\) Hz, CH-2), 1.81 (1H, ddd, \(J = 12.5, 11.6, 2.6\) Hz, CH\textsubscript{2}-6\textsubscript{ax}), 1.56 – 1.25 (3H, m, CH\textsubscript{2}-3\textsubscript{eq}, CH\textsubscript{2}-5\textsubscript{eq}, CH-4), 1.13 (3H, d, \(J = 6.1\) Hz, CH\textsubscript{3}-7), 1.04 (1H, dd, \(J = 12.6, 3.8\) Hz, CH\textsubscript{2}-5\textsubscript{ax}), 0.97 (1H, q, \(J = 12.0\) Hz, CH\textsubscript{2}-3\textsubscript{ax}), 0.81 (3H, d, \(J = 6.6\) Hz, CH\textsubscript{3}-8).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 139.6, 129.3, 128.2, 126.7, 58.3, 57.0, 53.2, 44.1, 34.6, 31.5, 22.2, 21.6.

Data for the minor diastereoisomer:

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.30 – 7.11\) (5H, m, ArH), 3.55 (1H, d, \(J = 13.5\) Hz, NCH\textsubscript{2}Ph), 3.45 (1H, d, \(J = 13.5\) Hz, NCH\textsubscript{2}Ph), 2.93 – 2.85 (1H, m, CH-2), 2.44 – 2.31 (2H, m, CH\textsubscript{2}-6), 1.70 – 1.58 (1H, m, CH-4), 1.56 – 1.25 (3H, m, CH\textsubscript{2}-3 and CH\textsubscript{2}-5), 1.15 – 1.09 (1H, m, CH\textsubscript{2}-5\textsubscript{ax}), 0.95 (3H, d, \(J = 6.7\) Hz, CH\textsubscript{3}-7), 0.84 – 0.81 (3H, m, CH\textsubscript{3}-8).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 140.2, 128.9, 128.2, 126.7, 59.2, 52.0, 45.9, 40.7, 34.1, 25.2, 21.8, 11.9.

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rac-\((2R,5R)\)-N-Benzyl-2,5-dimethylpiperidine, 3o

2-Methylhexane-1,5-diol\(^6\) rac-2o (132 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to \textit{general procedure A} at 110 °C. \(^1\)H NMR analysis of the crude reaction mixture indicated the presence of two diastereomers in 71:29 dr. Purification by column chromatography (pentane:Et\(_2\)O 90:10) afforded piperidine 3o (138 mg, 68%, 72:28 d.r.) as a colourless oil as a mixture of diastereoisomers. An small quantity of each diastereoisomer was obtained by column chromatography (pentane:Et\(_2\)O 90:10). The relative stereochemistry was determined by a combination of \(J\)-coupling constant and nOe analysis. 

HRMS: ESI+ found [M+H]\(^+\) = 204.1748, C\(_{14}\)H\(_{22}\)N requires 204.1747, Δ = 0.63 ppm.

FTIR (film): \(\nu_{\text{max}}\) = 2925, 1494, 1454, 1370, 1144, 1125, 1064, 732, 697 cm\(^{-1}\).

Data for the major diastereomer:

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 7.34-7.21 (5H, m, ArH), 4.07 (1H, d, \(J = 13.5\) Hz, NCH\(_2\)Ph), 3.14 (1H, d, \(J = 13.5\) Hz, NCH\(_2\)Ph), 2.74-2.70 (1H, m, CH\(_2\)-6\(a\)), 2.12 (1H, dqq, \(J = 12.0, 6.1, 2.7\) Hz, CH\(_2\)-2\(ax\)), 1.70-1.33 (5H, m, CH\(_2\)-3, CH\(_2\)-4\(a\), CH\(_5\), and CH\(_2\)-6\(b\)), 1.21 (3H, d, \(J = 6.1\) Hz, CH\(_3\)-7), 0.96-0.85 (1H, m, CH\(_2\)-4\(b\)), 0.76 (3H, d, \(J = 6.2\) Hz, CH\(_3\)-8).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 139.5, 129.3, 128.2, 126.7, 61.1, 58.3, 56.7, 35.3, 33.7, 31.4, 22.3, 19.9.

Data for the minor diastereomer:

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 7.37-7.21 (5H, m, ArH), 3.66-3.46 (2H, m, NCH\(_2\)Ph), 2.81-2.88 (1H, m, CH-2), 2.34 (1H, dd, \(J = 11.6, 4.2\) Hz, CH\(_2\)-6\(b\)), 2.17 (1H, dd, \(J = 11.6, 9.0\) Hz, CH\(_2\)-6\(a\)), 1.81-1.61 (2H, m, CH\(_2\)-4\(a\) and CH-5), 1.55-1.44 (2H, m, CH\(_2\)-3\(a\) and CH\(_2\)-4\(b\)), 1.30-1.16 (1H, m, CH\(_2\)-3\(b\)), 1.01 (3H, d, \(J = 6.6\) Hz, CH\(_3\)-7), 0.87 (3H, d, \(J = 6.7\) Hz, CH\(_3\)-8).
**rac-\{(2R,6S)-1-Benzyl-2,6-dimethylpiperidine, 3p**

Heptane-2,6-diol \(6 \) rac-\(2p \) (132 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([IrCp^*Cl_2]_2 \) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to **general procedure A**. Purification by column chromatography (pentane:Et\(_2\)O 60:40) afforded piperidine \(3p \) (135 mg, 66%, 80:20 dr) as an orange oil as an inseparable mixture of diastereoisomers. The major diastereomer was identified as **cis** by comparison with literature data.\(^{16}\)

HRMS: ESI+ found [M+H]\(^+\) = 207.1747, C\(_{14}\)H\(_{22}\)N requires 204.1747, \(\Delta = 0.03\) ppm.

FTIR (film): \(\nu_{\text{max}}\) = 2927, 1494, 1453, 1374, 1340, 1312, 1201, 1121, 1094, 1056, 1028, 943, 753, 723, 696 cm\(^{-1}\).

Data for the major diastereomer:

\[^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 7.42-7.37 \) (2H, m, ArH), 7.33-7.25 (2H, m, ArH), 7.24-7.18 (1H, m, ArH), 3.82 (2H, s, NCH\(_2\)Ph), 2.54-2.45 (2H, m, 2 x CH-2), 1.69-1.51 (3H, 2 x CH-3 and CH-4), 1.39-1.26 (3H, 2 x CH-3 and CH-4), 1.09 (6H, d, J = 6.3 Hz, 2 x CH\(_3\)).

\[^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta = 142.7, 128.7, 128.5, 126.7, 58.0, 54.3, 35.4, 25.0, 22.9\).}

Data for the minor diastereomer:

\[^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 7.42-7.37 \) (2H, m, ArH), 7.33-7.25 (2H, m, ArH), 7.24-7.18 (1H, m, ArH), 3.93 (1H, d, J = 13.8 Hz, NCH\(_2\)Ph), 3.42 (1H, d, J = 13.9 Hz, NCH\(_2\)Ph), 2.92-2.82 (2H, m, CH-2 and CH-6), 1.69-1.51 (3H, 2 x CH-3 and CH-4), 1.39-1.26 (3H, 2 x CH-3 and CH-4), 1.02 (6, d, J = 6.5 Hz, 2 x CH\(_3\)).

\[^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta = 142.7, 129.0, 128.7, 126.9, 54.0, 50.3, 33.5, 20.1, 16.6\).}

**N-Benzyl-4,4-dimethylpiperidine, 3q**

3,3-Dimethylpentane-1,5-diol\(^6\) \(2q \) (132 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([IrCp^*Cl_2]_2 \) (8.0 mg, 1.0 mol%), NaHCO\(_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to **general procedure A**. Purification by column chromatography (pentane:Et\(_2\)O 80:20) afforded piperidine \(3q \) (149 mg, 73%) as a colourless oil.
1H NMR (400 MHz, CDCl₃) δ = 7.35-7.21 (5H, m, ArH), 3.51 (2H, s, NCH₂Ph), 2.40-2.37 (4H, m, 2 × CH₂-2), 1.41-1.38 (4H, m, 2 × CH₂-3), 0.92 (6H, s, 2 × CH₃).

13C NMR (101 MHz, CDCl₃) δ = 138.9, 129.4, 128.2, 127.0, 63.7, 50.2, 38.9, 28.6, 28.4 (br).

HRMS: ESI+ found [M+H]+ = 204.1749, C₁₄H₂₂N requires 204.1747, Δ = 0.85 ppm.

FTIR (film): νmax = 2948, 2910, 2803, 2760, 1473, 1454, 1385, 1118, 1028, 988, 919, 736 cm⁻¹.

8-Benzyl-8-azaspiro[4.5]decane, 3r

2,2’-(Cyclopentane-1,1-diyl)bis(ethan-1-ol) 2r (158 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O:Et₃N 79.5:19.5:1) afforded piperidine 3r (170 mg, 74%) as a pale yellow oil.

1H NMR (500 MHz, CDCl₃) δ = 7.33-7.22 (5H, m, ArH), 3.48 (2H, s, NCH₂Ph), 2.37 (4H, br. s, 2 × CH₂-2), 1.59-1.55 (4H, m, 2 × CH₂-6), 1.49-1.46 (4H, m, 2 × CH₂-3), 1.41-1.38 (4H, m, 2 × CH₂-5).

13C NMR (125 MHz, CDCl₃) δ = 138.9, 129.4, 128.2, 127.0, 63.8, 51.6, 40.9, 38.2 (br), 37.8, 24.5.

HRMS: ESI+ found [M+H]+ = 230.1905, C₁₆H₂₄N requires 230.1903, Δ = 0.65 ppm.

FTIR (film): νmax = 2940, 2917, 2867, 2801, 2759, 1468, 1366, 1342, 1122, 735, 697 cm⁻¹.

3-Benzyl-3-azaspiro[5.5]undecane, 3s

2,2’-(Cyclohexane-1,1-diyl)bis(ethan-1-ol) 2s (172 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 80:20) afforded piperidine 3s (166 mg, 68%) as a pale yellow solid.

1H NMR (500 MHz, CDCl₃) δ = 7.33-7.22 (5H, m, ArH), 3.50 (2H, s, NCH₂Ph), 2.37 (4H, t, J = 5.6 Hz, 2 × CH₂-2), 1.46 (4H, t, J = 5.7 Hz, 2 × CH₂-3), 1.42-1.39 (6H, m, 2 × CH₂-6 and CH₂-7), 1.33-1.31 (4H, m, 2 × CH₂-5).

13C NMR (125 MHz, CDCl₃) δ = 138.8, 129.4, 128.2, 127.0, 63.8, 49.5, 36.8 (br), 36.4, 30.9, 27.0, 21.7.

HRMS: ESI+ found [M+H]+ = 244.2058, C₁₇H₂₆N requires 244.2060, Δ = -0.72 ppm.

FTIR (film): νmax = 2919, 2848, 2802, 2763, 1450, 1125, 987, 914, 736, 697 cm⁻¹.
Melting point = 44–46 °C.

\((15,6S)-3\text{-benzyl}-6\text{-isopropyl}-2\text{-methyl}-3\text{-azabicyclo[4.1.0]heptane, 3t}\)

2-\((15S,2S)-2\text{-}(1\text{-hydroxyethyl})\text{-}1\text{-isopropylcyclopentyl}ethan-1\text{-ol}\) \(2t\) (172 mg, 1.0 mmol), anhydrous benzylamine (0.16 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]\) (8.0 mg, 1.0 mol%), \(\text{NaHCO}_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to \textbf{general procedure A}. Purification by column chromatography (pentane:EtO 90:10) afforded piperidine \(3t\) (174 mg, 71%, 62:38 dr) as an orange oil as an inseparable mixture of diastereoisomers. The relative stereochemistry was assigned by nOe analysis.

\textbf{FTIR (film)}: \(c_m = 3061, 2955, 2793, 1494, 1452, 1365, 1156, 1028, 734, 698 \text{ cm}^{-1}\).

\textbf{HRMS: ESI+} found [M+H]^+ = 244.2060, \(\text{C}_{19}\text{H}_{26}\text{N}\) requires 244.2060, \(\Delta = 0.07 \text{ ppm}\).

\([\alpha]_D^{25} = +19.8 \text{ (c = 1.0, CHCl}_3\text{)}.\)

\textbf{Data for the major diastereomer:}

\(\text{\textsuperscript{1}H NMR} (500 \text{ MHz, CDCl}_3) \delta = 7.34\text{-}7.19\) (5H, m, ArH), 3.69 (1H, d, \(J = 14.0 \text{ Hz, NCH}_3\text{Ph})\), 3.34 (d, \(J = 13.9 \text{ Hz, NCH}_3\text{Ph})\), 2.83 (1H, q, \(J = 6.4 \text{ Hz, CH-2})\), 2.51\text{-}2.39 (1H, m, CH-6a), 1.95 (1H, ddd, \(J = 12.2\), 7.1, 5.3 Hz, CH-2b), 1.72\text{-}1.59 (1H, m, CH-5a), 1.54 (1H, ddd, \(J = 12.8, 6.9, 5.3 \text{ Hz, CH-5b})\), 1.24\text{-}1.18 (3H, m, CH-7), 1.04\text{-}0.81 (7H, m, CH-9, CH-10, CH-11), 0.56\text{-}0.49 (2H, m, CH-3 and CH-8a), 0.36\text{-}0.32 (1H, m, CH-8b).

\(\text{\textsuperscript{13}C NMR} (125 \text{ MHz, CDCl}_3) \delta = 140.2, 128.5, 128.0, 126.5, 57.6, 54.1, 43.6, 37.5, 25.8, 24.6, 23.6, 19.1, 18.4, 18.1, 16.4\).

\textbf{Data for the major diastereomer:}

\(\text{\textsuperscript{1}H NMR} (500 \text{ MHz, CDCl}_3) \delta = 7.34\text{-}7.19\) (5H, m, ArH), 3.99 (1H, d, \(J = 14.0 \text{ Hz, NCH}_3\text{Ph})\), 3.04 (d, \(J = 14.0 \text{ Hz, NCH}_3\text{Ph})\), 2.62 (1H, qd, \(J = 6.0, 4.1 \text{ Hz, CH-2})\), 2.51\text{-}2.39 (1H, m, CH-6a), 1.77 (1H, td, \(J = 11.7, 4.6 \text{ Hz, CH-6b})\), 1.72\text{-}1.59 (1H, m, CH-5a), 1.47\text{-}1.39 (1H, m, CH-5b), 1.24\text{-}1.18 (3H, m, CH-7), 1.04\text{-}0.81 (7H, m, CH-9, CH-10, CH-11), 0.71 (1H, ddd, \(J = 9.4, 5.5, 4.3 \text{ Hz, CH-3})\), 0.56\text{-}0.49 (1H, m, CH-8a), 0.25 (1H, dd, \(J = 9.0, 3.7 \text{ Hz, CH-8b})\).

\(\text{\textsuperscript{13}C NMR} (125 \text{ MHz, CDCl}_3) \delta = 140.3, 128.6, 128.0, 126.5, 58.5, 53.8, 50.5, 37.8, 26.7, 25.1, 23.5, 20.0, 18.9, 18.2, 14.4\).
3-Benzyl-3-azabicyclo[3.3.1]nonane, 3u

\[(1R,3S)-\text{Cyclohexane-1,3-diyldimethanol}\] 2u (144 mg, 1.0 mmol), benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl]2 (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 98:2) afforded piperidine 3u (162 mg, 75%) as a colourless oil.

\(1^H\) NMR (400 MHz, CDCl₃) δ = 7.36-7.28 (4H, m, ArH), 7.26-7.20 (1H, m, ArH), 3.37 (2H, s, NCH₂Ph), 2.88 (2H, d, J = 11.3 Hz, 2 x CH₂-2), 2.74 (1H, qt, J = 12.7, 6.1 Hz, CH₂-5α), 2.22 (2H, d, J = 10.9 Hz, 2 x CH₂-2b), 1.83-1.47 (9H, m, 2 x CH₃-4, 2 x CH₂-5, CH₂-5b).

\(13C\) NMR (101 MHz, CDCl₃) δ = 139.9, 128.7, 128.1, 126.5, 64.2, 59.9, 34.4, 31.5, 29.7, 22.6.

HRMS: ESI⁺ found [M+H]⁺ = 216.1746, \(C_{18}H_{22}N\) requires 216.1747, Δ = −0.32 ppm.

FTIR (film): \(\nu_{max} = \) 3387, 2909, 1644, 1495, 1454, 1391, 1250, 1146, 1073, 1017, 968, 830, 764, 728, 698 cm⁻¹.

\(\alpha\) \[\text{D}^2\] = +37.5 (c = 1.0, CHCl₃).

(1R,5S)-3-Benzyl-1,8,8-trimethyl-3-azabicyclo[3.2.1]octane, 3v

\[(1R,3S)-1,2,2\text{-Trimethylcyclopentane-1,3-diyldimethanol}\] 2v (172 mg, 1.0 mmol), benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine 3v (163 mg, 67%) as a yellow oil.

\(1^H\) NMR (400 MHz, CDCl₃) δ = 7.36-7.20 (5H, m, ArH), 3.55 (2H, s, NCH₂Ph), 2.59 (1H, dd, J = 10.5, 2.3 Hz, CH₂-6a), 2.45 (1H, dd, J = 10.5, 3.7 Hz, CH₂-6b), 2.35 (1H, d, J = 10.5 Hz, CH₂-2a), 2.17 (1H, d, J = 10.5 Hz, CH₂-2b), 1.84-1.65 (3H, m, CH₂-7a and CH₂-8), 1.61-1.49 (2H, m, CH₂-7b and CH-5), 0.91 (3H, s, CH₃-11), 0.86 (3H, s, CH₃-10), 0.76 (3H, s, CH₃-9).

\(13C\) NMR (101 MHz, CDCl₃) δ = 139.9, 128.6, 128.1, 126.6, 61.9, 61.2, 54.6, 46.1, 42.8, 41.7, 35.6, 26.8, 24.4, 18.3, 17.9.

HRMS: ESI⁺ found [M+H]⁺ = 244.2058, \(C_{19}H_{26}N\) requires 244.2060, Δ = −0.87 ppm.

FTIR (film): \(\nu_{max} = \) 2952, 2803, 1653, 1454, 1366, 1343, 1276, 1097, 1028, 799, 746, 727, 698 cm⁻¹.

\[\alpha\] \[\text{D}^2\] = +37.5 (c = 1.0, CHCl₃).
**N-Methyl-1-(4-(trifluoromethyl)benzyl)piperidine, 3w**

3-Methylpentane-1,5-diol 2a (118 mg, 1.0 mmol), p-(trifluoromethyl)benzylamine (0.21 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine 3w (220 mg, 86%) as a pale yellow oil.

**1H NMR (400 MHz, CDCl₃)** \(\delta = 7.57-7.54 \text{ (2H, m, ArH), 7.45-7.42 \text{ (2H, m, ArH), 3.52 \text{ (2H, s, NCΗ₂Ph), 2.83-2.78 \text{ (2H, m, 2 × CH₂-2α), 1.95 \text{ (2H, td, J = 11.5, 2.5 Hz, 2 × CH₂-3β), 1.42-1.31 \text{ (1H, m, CH-4), 1.29-1.19 \text{ (2H, m, 2 × CH₂-3β), 0.92 \text{ (3H, d, J = 6.4 Hz, CH₃).}}}}\)

**13C NMR (101 MHz, CDCl₃)** \(\delta = 143.4, 129.3, 129.2 \text{ (q, J = 32.4 Hz), 125.2 \text{ (q, J = 3.9 Hz), 124.5 \text{ (q, J = 271.7 Hz), 63.1, 54.2, 34.5, 30.9, 22.1.}}\)

**19F NMR** (376 MHz, CDCl₃) \(\delta = -62.3\).

HRMS: ESI+ found [M+H]+ = 258.1466, C₁₄H₁₉F₃N requires 258.1475, \(Δ = -3.61 \text{ ppm.}\)

FTIR (film): \(ν_{max} = 2924, 2797, 1324, 1161, 1123, 1102, 1066, 847, 812 \text{ cm}^{-1}.\)

**N-(4-Fluorobenzyl)-4-phenylpiperidine, 3x**

3-Phenylpentane-1,5-diol 6 2b (180 mg, 1.0 mmol), p-fluorobenzylamine (0.17 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%), NaHCO₃ (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to general procedure A. Purification by column chromatography (pentane:Et₂O 90:10 → 80:20) afforded piperidine 3x (167 mg, 62%) as a colourless solid.

**1H NMR (400 MHz, CDCl₃)** \(\delta = 7.34-7.28 \text{ (4H, m, ArH), 7.25-7.18 \text{ (3H, m, ArH), 7.05-6.99 \text{ (2H, m, ArH), 3.52 \text{ (2H, s, NCH₂Ar), 3.02-2.97 \text{ (2H, m, 2 × CH₂-2α), 2.56-2.45 \text{ (1H, m, CH-4), 2.12-2.05 \text{ (2H, m, 2 × CH₂-3β), 1.85-1.72 \text{ (4H, m, 2 × CH₂-3).}}}}\)

**13C NMR (126 MHz, CDCl₃)** \(\delta = 163.1 \text{ (d, J = 244.6 Hz), 146.6, 134.3 \text{ (d, J = 3.0 Hz), 130.8 \text{ (d, J = 8.0 Hz) 128.5, 127.0, 126.2, 115.1 \text{ (d, J = 21.1 Hz), 62.8, 54.4, 42.8, 33.6.}}\)

**19F NMR (376 MHz, CDCl₃)** \(\delta = -116.13\).

HRMS: ESI+ found [M+H]+ = 270.1651, C₁₈H₂₁F₂N requires 270.1653, \(Δ = -0.67 \text{ ppm.}\)

FTIR (film): \(ν_{max} = 2936, 2795, 2756, 1603, 1507, 1221, 1154, 1090, 992, 835, 755, 699 \text{ cm}^{-1}.\)

Melting point = 69–70 °C.
**N-(4-Methoxybenzyl)-4-phenylpiperidine, 3y**

3-Phenylpentane-1,5-diol\(^6\) 2b (180 mg, 1.0 mmol), \(\textit{para}\)-methoxybenzylamine (0.20 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]\) \((8.0 \text{ mg}, 0.1 \text{ mol%})\), NaHCO\(_3\) \((1.7 \text{ mg}, 2.0 \text{ mol%})\) and anhydrous toluene \((0.5 \text{ mL})\) were subjected to \textbf{general procedure A}. Purification by column chromatography (pentane:Et\(_2\)O 60:40) afforded piperidine 3y \((95 \text{ mg}, 34\%)\) as a colourless oil.

\(^1\)H NMR \((400 \text{ MHz, CDCl}_3\) \(\delta = 7.30-7.15 \text{ (7H, m, ArH)}, 6.88-6.84 \text{ (2H, m, ArH)}, 3.80 \text{ (3H, s, OCH}_3\)), 3.48 \text{ (2H, s, NC}_2\text{H}_5\text{Ph)}, 3.02-2.97 \text{ (2H, m, 2} \times \text{CH}_2-2a), 2.51-2.44 \text{ (1H, m, CH}-4\)), 2.08-2.02 \text{ (2H, m, 2} \times \text{CH}_2-2b), 1.81-1.76 \text{ (4H, m, 2} \times \text{CH}_2-3\).

\(^{13}\)C NMR \((125 \text{ MHz, CDCl}_3\) \(\delta = 158.8, 146.7, 130.6, 128.5, 127.0, 126.2, 113.7, 63.0, 55.4, 54.3, 42.9, 33.7\).

HRMS: ESI+ found [M+H\(^+\)] = 282.1847, C\(_{19}\)H\(_{24}\)NO requires 282.1852, \(\Delta = -1.76 \text{ ppm}\).

FTIR (film): \(\nu_{\text{max}}\) = 2933, 2796, 2754, 1611, 1510, 1453, 1243, 833, 757, 699 cm\(^{-1}\).

**N-(Naphthalen-1-ylmethyl)-4-phenylpiperidine, 3z**

3-Phenylpentane-1,5-diol\(^6\) 2b (180 mg, 1.0 mmol), 1-naphthylethylamine (0.22 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]\) \((8.0 \text{ mg}, 0.1 \text{ mol%})\), NaHCO\(_3\) \((1.7 \text{ mg}, 2.0 \text{ mol%})\) and anhydrous toluene \((0.5 \text{ mL})\) were subjected to \textbf{general procedure A}. Purification by column chromatography (pentane:Et\(_2\)O 95:5) afforded piperidine 3z \((137 \text{ mg}, 45\%)\) as a colourless solid.

\(^1\)H NMR \((400 \text{ MHz, CDCl}_3\) \(\delta = 8.38-8.36 \text{ (1H, m, ArH)}, 7.87 \text{ (1H, d, J = 7.8 Hz, ArH)}, 7.79 \text{ (1H, d, J = 7.8 Hz, ArH)}, 7.57-7.42 \text{ (4H, m, ArH)}, 7.32-7.17 \text{ (5H, m, ArH)}, 3.96 \text{ (2H, s, NCH}_2\text{Ar)}, 3.09 \text{ (2H, dt, J = 11.0, 3.6 Hz, 2} \times \text{CH}_2-2a), 2.55 \text{ (1H, tt, J = 10.8, 5.6 Hz, CH}-4\)), 2.23-2.16 \text{ (2H, m, 2} \times \text{CH}_2-2b), 1.85-1.74 \text{ (4H, m, 2} \times \text{CH}_2-3\).

\(^{13}\)C NMR \((101 \text{ MHz, CDCl}_3\) \(\delta = 146.8, 134.8, 134.0, 132.8, 128.52, 128.48, 127.9, 127.4, 127.0, 126.2, 125.8, 125.7, 125.3, 125.0, 61.6, 54.8, 43.0, 33.8\).

HRMS: ESI+ found [M+H\(^+\)] = 302.1901, C\(_{23}\)H\(_{24}\)N requires 302.1903, \(\Delta = -0.67 \text{ ppm}\).

FTIR (film): \(\nu_{\text{max}}\) = 1598, 1493, 1452, 1365, 1334, 1167, 1108, 988, 784, 699cm\(^{-1}\).

Melting point = 106–107 °C.
4-Phenyl-N-(1-phenylethyl)piperidine, 3aa

3-Phenylpentane-1,5-diol\(^6\) **2b** (180 mg, 1.0 mmol), α-methylbenzylamine (0.19 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]\) (8.0 mg, 1.0 mol%), \(\text{NaHCO}_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to **general procedure A**. Purification by column chromatography (pentane:Et\(_2\)O 60:40) afforded piperidine **3aa** (184 mg, 65%) contaminated with 8% *meso*-bis(1-phenylethyl)amine **S2** as a yellow oil.

**Data for 3aa:**
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.33-7.05\) (10H, m, ArH), 3.40 (1H, q, \(J = 6.8\) Hz, NCH(\(\text{CH}_3\))Ph), 2.86 (1H, dtt, \(J = 11.3, 3.4, 2.0, \text{CH}_2\)-eq), 2.40-2.32 (1H, m, CH-4), 2.06-1.97 (1H, m, CH\(_2\)-ax), 1.88 (1H, td, \(J = 11.2, 3.4\) Hz, CH\(_2\)-6), 1.81-1.51 (6H, m, CH\(_2\)-2 and CH\(_2\)-5), 1.34 (3H, d, \(J = 6.5\) Hz, CH\(_3\)).
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 146.8, 144.0, 128.5, 128.1, 127.8, 126.9, 126.8, 126.0, 65.1, 51.4, 51.3, 43.1, 33.9, 33.8, 19.7.

HRMS: ESI\(^+\) found [M+H]\(^+\) = 266.1904, \(\text{C}_{19}\text{H}_{24}\text{N}\) requires 266.1903, \(\Delta = 0.27\) ppm.

FTIR (film): \(\nu_{\text{max}} = 3026, 2932, 2796, 1493, 1451, 1129, 1022, 756, 699\) cm\(^{-1}\).

**Data for S2:**
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 3.69\) (2H, q, \(J = 6.5\) Hz, NCH(\(\text{CH}_3\))Ph), 1.28 (6H, d, \(J = 6.6\) Hz, CH\(_3\)).
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta = 146.1, 128.6, 127.0, 126.7, 55.0, 23.3.

*The data are consistent with the literature.*\(^{17}\)

4-Phenyl-N-(2-phenylpropan-2-yl)piperidine, 3ab

3-Phenylpentane-1,5-diol\(^6\) **2b** (180 mg, 1.0 mmol), cumylamine (0.22 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]\) (8.0 mg, 1.0 mol%), \(\text{NaHCO}_3\) (1.7 mg, 2.0 mol%) and anhydrous toluene (0.5 mL) were subjected to **general procedure A**. Purification by column chromatography (pentane:Et\(_2\)O 95:5) afforded piperidine **3ab** (185 mg, 66%) as a colourless solid.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.60$-$7.57$ (2H, m, ArH), $7.35$-$7.17$ (8H, m, ArH), $2.95$-$2.93$ (2H, m, $2 \times$ CH$_2$-2eq), $2.47$ (1H, tt, $J = 11.8$, 4.3 Hz, CH$_4$-2ax), $2.22$ (2H, td, $J = 11.4$, 2.7 Hz, $2 \times$ CH$_2$-2eq), $1.82$-$1.68$ (4H, m, $2 \times$ CH$_2$-3), $1.39$ (6H, s, $2 \times$ CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 150.0, 147.1, 128.5, 128.1, 127.1, 126.2, 126.13, 126.08, 60.1, 47.3, 43.5, 34.6, 24.5.

HRMS: ESI+ found [M+H]$^+$ = 280.2060, C$_{20}$H$_{26}$N requires 280.2060, $\Delta = 0.17$ ppm.

FTIR (film): $\nu_{\text{max}} =$ 2972, 2930, 1493, 1446, 1271, 1177, 1073, 1024, 959, 759, 698 cm$^{-1}$.

Melting point = 101–102 °C.

(2S,4S)-1-Benzyl-2-methyl-4-phenylpiperidine, (+)-3ac

(3S)-3-Phenylhexane-1,5-diol$^6$ (−)-2ac (110 mg, 0.56 mmol, 60:40 d.r., >99:1 e.r.), anhydrous benzyllamine (0.09 mL, 0.84 mmol), [IrCp*Cl$_2$]$_2$ (4.5 mg, 1.0 mol%), NaHCO$_3$ (0.9 mg, 2.0 mol%) and anhydrous toluene (0.28 mL, 2 M) were subjected to general procedure A. Purification by column chromatography afforded piperidine (+)-3ac as a colourless oil as an inseparable mixture of diastereoisomers (169 mg, 64%, 80:20 d.r., >99:1 e.r.). The corresponding racemic piperidine $\text{rac}$-3ac was prepared by an identical procedure starting from $\text{rac}$-2ac.$^6$ The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyll carbamate (see below).

HRMS: ESI+ found [M+H]$^+$ = 266.1902, C$_{19}$H$_{24}$N requires 266.1903, $\Delta = 0.32$ ppm.

FTIR (film): $\nu_{\text{max}} =$ 3027, 2931, 2790, 1602, 1494, 1451, 1374, 1329, 1137, 1066, 1028, 756, 732, 698 cm$^{-1}$.

$[^{[\alpha]}]_{D}^{25} = +45.3$ (c = 1.00, CH$_2$Cl$_2$).

Data for the major diastereomer:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.38$-$7.17$ (10H, m, ArH), 4.17 (1H, d, $J = 13.4$ Hz, NCH$_2$Ph), 3.21 (1H, d, $J = 13.3$ Hz, NCH$_2$Ph), 2.94 (1H, dt, $J = 11.7$, 3.4 Hz, CH$_2$-6eq), 2.58 (1H, tt, $J = 12.0$, 4.1 Hz, CH$_4$-4eq), 2.37 (1H, dqd, $J = 12.1$, 5.9, 2.6 Hz, CH-2eq), 2.07 (1H, td, $J = 11.6$, 3.4 Hz, CH$_2$-6ax), 1.87-1.82 (1H, m, CH$_2$-3eq), 1.78-1.65 (2H, m, CH$_2$-S), 1.60 (1H, td, $J = 12.8$, 10.9 Hz, CH$_2$-3eq), 1.28 (3H, d, $J = 6.1$ Hz, CH$_3$).
\( ^{13} \text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta = 146.6, 139.3, 129.4, 128.5, 128.3, 126.94, 126.89, 126.2, 58.2, 57.3, 53.4, 43.2, 43.1, 33.5, 21.5. 

Data for the minor diastereomer:

\( ^{1} \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta = 7.39 \ (2 \text{H}, \text{d, } J = 7.5 \text{ Hz, ArH}), 7.34-7.17 \ (8 \text{H, m, ArH}), 3.70-3.54 \ (2 \text{H, m, NCH}_2\text{Ph}), 3.24-3.19 \ (1 \text{H, m, CH-2eq}), 2.88-2.81 \ (1 \text{H, m, CH-4ax}), 2.64-2.61 \ (2 \text{H, m, CH-6}), 2.03 \ (1 \text{H, td, } J = 12.7, 4.8 \text{ Hz, CH-3ax}), 1.78-1.74 \ (7 \text{H, m, CH-5a}), 1.68 \ (1 \text{H, dt, } J = 12.9, 3.1 \text{ Hz, CH-3eq}), 1.12 \ (3 \text{H, d, } J = 6.7 \text{ Hz, CH}_3). 

\( ^{13} \text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta = 146.9, 140.0, 128.8, 128.5, 127.1, 126.9, 126.1, 59.3, 52.2, 45.8, 39.5, 36.6, 33.6, 10.0. 

Benzyl (2S,4S)-2-methyl-4-phenylpiperidine-1-carboxylate, S3

(2S,4S)-1-Benzyl-2-methyl-4-phenylpiperidine (+)-3ac (30 mg, 0.11 mmol, 80:20 d.r.) and benzyl chloroformate (3 M in toluene, 0.23 mL, 0.68 mmol) were subjected to general procedure C. Purification by column chromatography (80:20 pentane:Et\(_2\)O) afforded Cbz-piperidine S3 (34 mg, 97%, 76:24 dr, >99:1 e.r.) as a colourless oil. The corresponding racemic piperidine rac-S3 was prepared by an identical procedure starting from rac-3ac.

\( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta = 7.42 - 7.17 \ (10 \text{H, m, ArH}), 5.21 - 5.13 \ (2 \text{H, m, NCH}_2\text{Ph}), 4.05 \ (1 \text{H, dp, } J = 10.2, 6.4 \text{ Hz, CH-2}), 3.89 \ (1 \text{H, dddd, } J = 13.9, 7.6, 3.3, 0.7 \text{ Hz, CH-6a}), 3.34 \ (1 \text{H, ddd, } J = 13.9, 9.8, 6.4 \text{ Hz, CH-6b}), 2.77 \ (1 \text{H, dddd, } J = 12.9, 10.4, 7.6, 3.3 \text{ Hz, CH-4}), 2.18 \ (1 \text{H, ddtd, } J = 13.5, 9.9, 7.6, 1.4 \text{ Hz, CH-5a}), 1.94 \ (1 \text{H, dddd, } J = 13.5, 6.3, 3.3, 1.4 \text{ Hz, CH-5b}), 1.74 - 1.55 \ (2 \text{H, m, CH-3a and CH-3b}), 1.24 \ (3 \text{H, d, } J = 6.4 \text{ Hz, CH}_3). \) The minor diastereoisomer displays diagnostic signals at \( \delta = 4.72 - 4.55 \) (1H, m, CH-2), 4.30 – 4.10 (1H, m, CH-6a), 3.15 – 3.01 (1H, m, CH-6b), 2.98 – 2.85 (1H, m, CH-4).

\( ^{13} \text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta = 155.8, 145.8, 137.1, 128.5, 128.5, 127.9, 127.8, 126.8, 126.2, 66.8, 50.5, 38.0, 38.0, 37.0, 31.2, 19.9.

HRMS: ESI+ found [M+Na]\(^+\) = 332.1620, \( C_{20}H_{25}O_2NNa \) requires 332.1621, \( \Delta = -0.16 \) ppm.

FTIR (film): \( \nu_{\max} = 2970, 1696, 1454, 1421, 1334, 1281, 1243, 1212, 1140, 1066, 1029, 757, 699 \text{ cm}^{-1}. \)

\( [\alpha]_D^{25} = +42.1 \) (c = 1.0, CHCl\(_3\)).
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (99.5:0.5 hexane:IPA, 1.0 mL min⁻¹, 210 nm, room temperature), major diastereomer tᵣ (major) = 42.1 min, tᵣ (minor) = 47.2 min, >99:1 er; minor diastereomer tᵣ (major) = 44.2 min, tᵣ (minor) = 52.4 min; >99:1 er.

(S)-1-Benzyl-3-methylpiperidine, (+)-3i

(S)-2-Methylpentane-1,5-diol⁶ (–)-2i (132 mg, 1.0 mmol, >99:1 er), anhydrous benzylamine (0.16 mL, 1.5 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine (+)-3i (136 mg, 72%, 90:10 er) as a colourless oil. The spectral data was identical to that of the corresponding racemate described above.

\[ \alpha_D^{25} = +8.9 \ (c = 1.0, \text{CHCl}_3). \]

The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

Benzyl (S)-3-methylpiperidine-1-carboxylate, S₄

(S)-1-Benzyl-3-methylpiperidine (+)-3i (26 mg, 0.14 mmol) and benzyl chloroformate (3 M in toluene, 0.5 mL, 1.5 mmol) were subjected to general procedure C. Purification by column chromatography (75:25 pentane:Et₂O) afforded piperidine S₄ (27 mg, 82%, 90:10 er) as a colourless oil. The
corresponding racemic Cbz-piperidine rac-S4 was prepared by an identical procedure starting from rac-3i.

1H NMR (400 MHz, CDCl₃, 298 K) δ = 7.36-7.28 (5H, m, ArH), 5.13 (2H, s, OCH₂Ph), 4.10-4.02 (1H, m, CH₂-6eq), 3.99-3.92 (1H, m, CH₂-2eq), 2.76 (1H, td, J = 12.9, 3.0 Hz, CH₂-6ax), 2.50-2.36 (1H, m, CH₂-2ax), 1.82-1.75 (1H, m, CH₂-4eq), 1.66-1.54 (2H, m, CH₂-5a and CH-3), 1.49-1.40 (1H, m, CH₂-5b) 1.11-1.01 (1H, m, CH₂-4a), 0.88 (3H, d, J = 6.6 Hz, CH₃).

13C NMR (101 MHz, CDCl₃, 298 K) δ = 155.4, 137.2, 128.6, 128.0, 127.9, 67.0, 51.5, 44.5, 33.1, 31.1, 25.3 (br), 19.0.

The data are consistent with the literature.¹⁸

¹H NMR (500 MHz, d₈-toluene, 363 K) δ = 5.11-5.06 (2H, m, OCH₂Ph), 3.97-3.92 (2H, m, CH₂-2eq and CH₂-6eq), 2.55 (1H, ddd, J = 13.1, 11.2, 3.5 Hz, CH₂-6ax), 2.25 (1H, dd, J = 13.0, 10.1 Hz, CH₂-2ax), 1.45-1.41 (1H, m, CH₂-4a), 1.37-1.16 (3H, m, CH-3, CH-5), 0.78-0.70 (1H, m, CH₂-4a), 0.63 (3H, d, J = 6.6 Hz, CH₃). Signals corresponding to the aromatic protons are obscured by the d₈-toluene solvent signals. The aromatic signals can be clearly observed in the room temperature CDCl₃ data above.

¹³C NMR (125 MHz, d₈-toluene, 363 K) δ = 155.3, 138.3, 128.6, 128.3, 128.0, 67.1, 51.8, 44.8, 33.4, 31.2, 25.4, 18.8.

HRMS: ESI+ found [M+H]⁺ = 234.1491, C₁₄H₂₀NO₂ requires 234.1489, Δ = 1.08 ppm.

FTIR (film): νmax = 2929, 2852, 1697, 1428, 1257, 1235, 1154, 1097, 972 cm⁻¹.

[α]D²⁵ = +19.1 (c = 1.7, CHCl₃).

HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min⁻¹, 210 nm, room temperature):
(S)-3-Methyl-1-(4-(trifluoromethyl)benzyl)piperidine, (+)-3ad

(S)-2-Methylhexane-1,5-diol\textsuperscript{6} 2i (118 mg, 1.0 mmol, >99:1 er), \textit{para}-(trifluoromethyl)benzylamine (0.21 mL, 1.5 mmol), [IrCp*Cl\textsubscript{2}]\textsubscript{2} (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to \textbf{general procedure B} at 80 °C. Purification by column chromatography (pentane:Et\textsubscript{2}O 90:10) afforded piperidine (+)-3ad (166 mg, 65\%, 91:9 er) as a colourless oil.

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.57-7.55\) (2H, m, ArH), 7.45-7.43 (2H, m, ArH), 3.51 (2H, s, NC\textsubscript{H}\textsubscript{2}Ph), 2.79-2.71 (2H, m, CH\textsubscript{2}-2a and CH\textsubscript{2}-6\textsubscript{eq}), 1.89 (1H, td, \(J = 11.1, 3.4\) Hz, CH\textsubscript{2}-6\textsubscript{ax}), 1.73-1.51 (5H, m, CH\textsubscript{2}-2b, CH-3, CH\textsubscript{2}-4\textsubscript{a}, CH-5), 0.92-0.84 (1H, m, CH\textsubscript{2}-4\textsubscript{b}), 0.84 (3H, d, \(J = 6.3\) Hz, CH\textsubscript{3}).

\textbf{13C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta = 143.4, 129.3, 129.2\) (q, \(J = 32.4\) Hz), 125.2 (q, \(J = 3.8\) Hz), 124.5 (q, \(J = 272.1\) Hz), 63.2, 62.2, 54.2, 33.1, 31.3, 25.7, 19.8.

\textbf{19F NMR} (376 MHz, CDCl\textsubscript{3}) \(\delta = -62.3\).

HRMS: ESI\textsuperscript{+} found [M+H]\textsuperscript{+} = 258.1463, C\textsubscript{14}H\textsubscript{19}F\textsubscript{3}N requires 258.1464, \(\Delta = -0.31\) ppm.

FTIR (film): \(\nu_{\text{max}} = 2930, 1323, 1162, 1123, 1103, 1066, 1019, 836, 819\) cm\textsuperscript{-1}.

\([\alpha]_{D}^{25} = +6.7\) (\(c = 1.0,\) CHCl\textsubscript{3}).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding \(N\)-Cbz compound S4 (synthesised using \textbf{general procedure C}, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak\textsuperscript{®} IC column (99:1 hexane:IPA, 0.7 mL min\textsuperscript{-1}, 210 nm, room temperature):

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\textbf{Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min\textsuperscript{-1}, 210 nm, room temperature):}
(S)-1-(4-Fluorobenzyl)-3-methylpiperidine, (+)-3ae

(S)-2-Methylhexane-1,5-diol\textsuperscript{6} 2i (118 mg, 1.0 mmol, >99:1 er), 4-fluorobenzylamine (0.17 mL, 1.5 mmol), [IrCp*Cl\textsubscript{2}]\textsubscript{2} (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et\textsubscript{2}O 90:10) afforded piperidine (+)-3ae (150 mg, 72%, 90:10 er) as a colourless oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 7.29-7.21 \) (2H, m, ArH), 7.01-6.96 (2H, m, ArH), 3.43 (2H, s, NCH\textsubscript{2}Ph), 2.79-2.71 (2H, m, CH\textsubscript{2}-2\textsubscript{a} and CH\textsubscript{2}-6\textsubscript{eq}), 1.84 (1H, td, \( J = 11.2, 3.3 \) Hz, CH\textsubscript{2}-6\textsubscript{ax}), 1.72-1.49 (5H, m, CH\textsubscript{2}-2\textsubscript{b}, CH-3, CH\textsubscript{2}-4\textsubscript{b}, CH\textsubscript{2}-5), 0.91-0.82 (1H, m, CH\textsubscript{2}-4\textsubscript{a}), 0.84 (3H, d, \( J = 6.4 \) Hz, CH\textsubscript{3}).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta = 162.0 \) (d, \( J = 244.0 \) Hz), 134.6 (d, \( J = 3.2 \) Hz), 130.7 (d, \( J = 7.9 \) Hz), 115.0 (d, \( J = 20.8 \) Hz), 62.9, 62.0, 54.1, 33.2, 31.3, 25.7, 19.9.

\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \( \delta = -116.40 \).

HRMS: ESI\textsuperscript{+} found [M+H]\textsuperscript{+} = 208.1497, C\textsubscript{13}H\textsubscript{19}FN requires 208.1496, \( \Delta = 0.48 \) ppm.

FTIR (film): \( \nu_{\text{max}} = 2928, 1604, 1508, 1465, 1458, 1356, 1293, 1221, 1154, 1120, 1091, 1078, 1039, 844, 822 \) cm\textsuperscript{-1}.

\( [\alpha]_{D}^{25} = +8.7 \) (c = 1.0, CHCl\textsubscript{3}).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min\textsuperscript{-1}, 210 nm, room temperature):
(S)-1-(3,5-Difluorobenzyl)-3-methylpiperidine, (+)-3af

(S)-2-Methylhexane-1,5-diol\(^6\) 2i (118 mg, 1.0 mmol, >99:1 er), 3,5-difluorobenzylamine (0.18 mL, 1.5 mmol), [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et\(_2\)O 95:5) afforded piperidine (+)-3af (152 mg, 67%, 93:7 er) as a colourless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 6.90-6.84\) (2H, m, ArH), 6.66 (1H, tt, \(J = 9.0\), 2.4 Hz, ArH), 3.42 (2H, s, NCH\(_2\)Ph), 2.77-2.69 (2H, m, CH\(_2\)-2\(_a\) and CH\(_2\)-6\(_{eq}\)), 1.89 (1H, td, \(J = 11.1\), 3.4 Hz, CH\(_2\)-6\(_{eq}\)), 1.72-1.52 (5H, m, CH\(_2\)-2\(_b\), CH-3, CH-4\(_a\), CH-5), 0.92-0.82 (1H, m, CH\(_2\)-4\(_b\)), 0.85 (3H, d, \(J = 6.2\) Hz, CH\(_3\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 162.1\) (dd, \(J = 247.8\), 12.7 Hz), 142.7 (1H, td, \(J = 9.7\) Hz), 110.5-110.3 (m), 101.2 (t, \(J = 25.6\) Hz), 61.8 (t, \(J = 1.9\) Hz), 61.1, 53.2, 32.0, 30.3, 24.7, 18.8.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -110.9\).

HRMS: ESI+ found [M+H]\(^+\) = 226.1403, C\(_{13}\)H\(_{18}\)F\(_2\)N requires 226.1402, \(\Delta = 0.61\) ppm.

FTIR (film): \(\nu_{\text{max}} = 2930, 1626, 1597, 1458, 1438, 1346, 1346, 1115, 976, 965, 846\) cm\(^{-1}\).

\([\alpha]_{D}^{25} = +11.5\) (c = 1.0, CHCl\(_3\)).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min\(^{-1}\), 210 nm, room temperature):
(S)-3-Methyl-1-(3,4,5-trifluorobenzyl)piperidine, (+)-3ag

(S)-2-Methylhexane-1,5-diol\(^6\) 2i (118 mg, 1.0 mmol, >99:1 er), 3,4,5-trifluorobenzyl nitrite (0.19 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]_2\) (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et\(_2\)O 90:10) afforded piperidine (+)-3ag (137 mg, 56%, 90:10 er) as a colourless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.00\)–6.92 (2H, m, ArH), 3.47 (2H, s, NC\(_2\)H\(_2\)Ph), 2.75–2.66 (2H, m, CH\(_2\)-2\(_a\) and CH\(_2\)-6\(_{eq}\)), 1.88 (1H, td, \(J = 11.1, 3.2\) Hz, CH\(_2\)-6\(_{ax}\)), 1.73–1.49 (5H, m, CH\(_2\)-2\(_b\), CH-3, CH\(_2\)-4\(_a\), CH\(_2\)-5), 0.92–0.83 (1H, m, CH\(_2\)-4\(_b\)), 0.84 (3H, d, \(J = 6.3\) Hz, CH\(_3\)).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 151.2\) (ddd, \(J = 249.4, 10.1, 4.0\) Hz), 138.6 (dt, \(J = 249.6, 15.4\) Hz), 135.9 (td, \(J = 6.8, 4.6\) Hz), 112.4 (d, \(J = 20.8\) Hz), 62.4, 62.0, 54.1, 33.0, 31.3, 25.6, 19.8.

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = –135.3, –163.6\).

HRMS: ESI+ found [M+H]\(^+\) = 244.1308, C\(_{13}\)H\(_{17}\)F\(_3\)N requires 244.1308, \(\Delta = 0.34\) ppm.

FTIR (film): \(\nu_{\text{max}} = 2930, 1621, 1526, 1445, 1372, 1360, 1350, 1231, 1131, 1122, 1039, 980\) cm\(^{-1}\).

\([\alpha]^{D}_{25} = +10.4\) (c = 1.0, CHCl\(_3\)).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min\(^{-1}\), 210 nm, room temperature):
(S)-1-(4-Methoxybenzyl)-3-methylpiperidine, (+)-3ah

(S)-2-Methylhexane-1,5-diol\(^6\) 2i (118 mg, 1.0 mmol, >99:1 er), \(p\)-methoxybenzylamine (0.20 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]_2\) (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et\(_2\)O 75:25) afforded piperidine (+)-3ah (148 mg, 67%, 72:28 er) as a colourless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.24-7.20 (2H, \text{m, ArH}), 6.87-6.83 (2H, \text{m, ArH}), 3.80 (3H, s, \text{OC}\text{H}_3), 3.42 (2H, s, \text{NC}\text{H}_2\text{Ph}), 2.82-2.74 (2H, \text{m, CH}_2\text{-2a and CH}_2\text{-6eq}), 1.83 (1H, td, \text{J} = 11.2, 3.5 Hz, \text{CH}_2\text{-6ax}), 1.72-1.49 (5H, m, \text{CH}_2\text{-2b, CH}-3, \text{CH}_2\text{-4a, CH}_2\text{-5}), 0.89-0.80 (1H, m, \text{CH}_2\text{-4b}), 0.83 (3H, d, \text{J} = 6.4 Hz, \text{CH}_3).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 158.7, 130.8, 130.5, 113.6, 63.1, 62.0, 55.4, 54.0, 33.3, 31.3, 25.7, 19.9.

HRMS: ESI+ found [M+H]\(^+\) = 220.1696, \(C_{14}H_{22}NO\) requires 220.1696, \(\Delta = 0.12\) ppm.

FTIR (film): \(\nu_{\text{max}} = 2927, 1613, 1511, 1464, 1300, 1243, 1179, 1121, 1038, 830, 815\) cm\(^{-1}\).

\([\alpha]_D^{25} = +5.2\) (c = 1.0, CHCl\(_3\)).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding \(N\)-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak\textsuperscript{®} IC column (99:1 hexane:IPA, 0.7 mL min\(^{-1}\), 210 nm, room temperature):

(S)-1-(Benzo[\(\alpha\])[1,3]dioxol-5-ylmethyl)-3-methylpiperidine, (+)-3ai

(S)-2-Methylhexane-1,5-diol\(^6\) 2i (118 mg, 1.0 mmol, >99:1 er), piperonylamine (0.19 mL, 1.5 mmol), \([\text{IrCp}^*\text{Cl}_2]_2\) (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B
at 80 °C. Purification by column chromatography (pentane:EtO 50:50) afforded piperidine (±)-3ai (68 mg, 29%, 64:36 er) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 6.85 (1H, t, $J$ = 1.0 Hz, ArH), 6.74-6.72 (2H, m, ArH), 5.93 (2H, s, OCH$_2$O), 3.38 (2H, s, NCH$_2$Ph), 2.81-2.73 (2H, m, CH$_2$-2 and CH$_2$-6eq), 1.83 (1H, td, $J$ = 11.2, 3.4 Hz, CH$_2$-6ax), 1.72-1.49 (5H, m, CH$_2$-2b, CH$_2$-3, CH$_2$-4a, CH$_2$-5), 0.89-0.83 (1H, m, CH$_2$-4b), 0.83 (3H, d, $J$ = 6.4 Hz, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 147.6, 146.5, 132.8, 122.3, 109.7, 107.9, 100.9, 63.5, 62.0, 54.0, 33.2, 31.3, 25.7, 19.9.

HRMS: ESI+ found [M+H]$^+$ = 234.1488, C$_{14}$H$_{20}$NO$_2$ requires 234.1489, $\Delta$ = -0.03 ppm.

FTIR (film): $\nu_{\text{max}}$ = 2927, 2762, 1502, 1488, 1440, 1369, 1339, 1240, 1181, 1159, 1112, 1039, 932 cm$^{-1}$.

$[\alpha]_D^{25}$ = +3.9 (c = 1.0, CHCl$_3$).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min$^{-1}$, 210 nm, room temperature):

(S)-3-Methyl-1-(naphthalen-1-ylmethyl)piperidine, (+)-3aj

(S)-2-Methylhexane-1,5-diol $^6$ 2i (118 mg, 1.0 mmol, >99:1 er), naphthalene-1-ylmethanamine (0.22 mL, 1.5 mmol), [IrCp$^*$Cl$_2$]$_2$ (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:EtO 90:10) afforded piperidine (±)-3aj (82 mg, 34%, 73:27 er) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.35-8.32 (1H, m, ArH), 7.86-7.84 (1H, m, ArH), 7.77 (1H, dt, $J$ = 7.9, 1.1 Hz, ArH), 7.54-7.39 (4H, m, ArH), 3.92-3.80 (2H, m, NCH$_2$Ph), 2.89-2.83 (2H, m, CH$_2$-2a and CH$_2$-6eq),
1.97 (1H, td, J = 11.1, 3.4 Hz, CH2-6ax), 1.73-1.49 (5H, m, CH2-2b, CH-3, CH2-4b, CH2-5), 0.96-0.82 (1H, m, CH2-4b), 0.85 (3H, d, J = 6.1 Hz, CH3).

13C NMR (101 MHz, CDCl3) δ = 135.0, 134.0, 132.8, 128.5, 127.7, 127.2, 125.7, 125.6, 125.0, 62.5, 61.8, 54.5, 33.3, 31.3, 25.8, 19.9.

HRMS: ESI+ found [M+H]+ = 240.1746, C17H22N requires 240.1747, Δ = 0.48 ppm.

FTIR (film): νmax = 2926, 2801, 2756, 1509, 1465, 1457, 1370, 1341, 1168, 1126, 1117, 975, 791, 783, 772 cm⁻¹.

[α]D²⁵ = +10.1 (c = 1.0, CHCl₃).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S4 (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S4, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min⁻¹, 210 nm, room temperature):

(S)-3-Methyl-1-((R)-1-phenylethyl)piperidine, (+)-3ak

(S)-2-Methylhexane-1,5-diol⁶ 2i (118 mg, 1.0 mmol, >99:1 er), (R)-α-methylbenzylamine (0.19 mL, 1.5 mmol), [IrCp*Cl₂] (8.0 mg, 1.0 mol%) and deionised water (0.5 mL) were subjected to general procedure B at 80 °C. Analysis of the crude reaction mixture by 1H NMR indicated a dr of 83:17. Purification by column chromatography (pentane:Et₂O 80:20) afforded piperidine (+)-3ak (161 mg, 79%, 76:24 er, 85:15 dr) as a colourless oil.

1H NMR (400 MHz, CDCl3) δ = 7.35-7.21 (5H, m, ArH), 3.41 (1H, q, J = 6.8 Hz, NCH(CH3)Ph), 2.98-2.88 (1H, m, CH2-6eq), 2.76-2.70 (1H, m, CH2-2eq), 1.85 (1H, td, J = 11.1, 3.3 Hz, CH2-6ax), 1.70-1.51 (4H, m, CH-3, CH2-4b, CH2-5), 1.45 (1H, t, J = 10.6 Hz, CH2-2ax), 1.37 (3H, d, J = 7.0 Hz, CH3-8), 0.87-0.74 (1H, m, CH2-4b), 0.78 (3H, d, J = 6.4 Hz, CH3-7). The minor diastereomer displays diagnostic signals at δ = 3.50
(1H, q, J = 6.8 Hz, NCH(CH₃)Ph), 1.76 (1H, td, J = 11.3, 3.0 Hz, CH₇-6H), 1.27 (3H, d, J = 6.7 Hz, CH₈-8), 0.68 (3H, d, J = 6.3 Hz, CH₉-7).

¹³C NMR (101 MHz, CDCl₃) δ = 144.1, 128.1, 127.9, 126.8, 65.0, 59.0, 51.1, 33.4, 31.5, 26.0, 20.0, 19.5. Not all of the signals for the minor diastereoisomer could be distinguished, but peaks were observed at δ = 65.1, 59.2, 51.1, 33.4, 25.6, 19.5, 20.0.

HRMS: ESI+ found [M+H]⁺ = 204.1748, C₁₄H₂₂N requires 204.1747, Δ = 0.78 ppm.

FTIR (film): ν̇max = 2927, 1492, 1453, 1373, 1125, 1081, 760, 700 cm⁻¹.

[α]D²⁵ = +38.9 (c = 1.0, CHCl₃).

HPLC: Enantiomeric excess was determined by chiral HPLC analysis of the corresponding N-Cbz compound S₄ (synthesised using general procedure C, analytic sample isolated by preparative TLC. For full characterisation data for this compound, see S₄, page S31). Chiralpak® IC column (99:1 hexane:IPA, 0.7 mL min⁻¹, 210 nm, room temperature):

![HPLC chromatogram](image)

**HPLC**

(5)-N-Benzyl-3-phenylpiperidine, (−)-3j

(5)-2-Phenylpentane-1,5-diol (+)-2j (144 mg, 0.8 mmol, >99:1 er), anhydrous benzylamine (0.13 mL, 1.2 mmol), [IrCp*Cl₂]₂ (6.3 mg, 1 mol%) and water (0.4 mL) were subjected to general procedure B at 80 °C. Purification by column chromatography (pentane:Et₂O 90:10) afforded piperidine (−)-3j (107 mg, 43%, 67:33 er) as a colourless solid. The spectral data was identical to that of the corresponding racemate described above.

[α]D²⁵ = −10.6 (c = 1.0, CHCl₃).

The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

**Benzyl (5)-3-phenylpiperidine-1-carboxylate, S₅**
(S)-N-Benzyl-3-phenylpiperidine (−)-3j (30 mg, 0.12 mmol) and benzyl chloroformate (3 M in toluene, 0.5 mL, 1.5 mmol) were subjected to general procedure C. Purification by column chromatography (pentane:Et₂O 75:25) afforded piperidine S5 (36 mg, 99%, 67:33 er) as a colourless oil. The corresponding racemic piperidine rac-S5 was prepared by an identical procedure starting from rac-3j. The data is consistent with the literature.¹⁹

¹H NMR (400 MHz, CDCl₃) δ = 7.37-7.21 (10H, m, ArH), 5.16 (2H, s, OC₂H₅), 4.38-4.20 (2H, br. m, CH₂-2a and CH₂-6a), 2.89-2.66 (3H, br. m, CH₂-2b, CH-3 and CH₂-6b), 2.07-2.02 (1H, m, CH-4a), 1.84-1.55 (3H, m, CH₂-4b and CH₂-5). Some of the signals appear broad due to the rotameric nature of the carbamate.

¹³C NMR (101 MHz, CDCl₃) δ = 155.4, 143.4, 137.1, 128.7, 128.6, 128.1, 128.0, 127.2, 126.8, 67.2, 50.8, 44.5, 42.8, 31.9, 25.6. Some of the signals appear broad due to the rotameric nature of the carbamate.

[α]₂⁰⁰ = −18.8 (c = 1.0, CHCl₃).

HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IB-N column (99:1 hexane:IPA, 1.0 mL min⁻¹, 210 nm, room temperature):

(R)-N-Benzyl-3-methylpyrrolidine, (−)-3l

To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added (R)-2-methylpentane-1,4-diole²⁰ (R)-2l (104 mg, 1.0 mmol, >99:1 er), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%) and CsHCO₃ (3.9 mg, 2.0 mol%). The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum), evacuated under vacuum and refilled with argon three times. Cyclopentyl methyl ether (0.5 mL) was
added via syringe, followed by anhydrous benzylation (0.16 mL, 1.5 mmol). The vial was sealed with Parafilm®, placed in a preheated oil bath and stirred at 110 °C for 24 hours. The reaction mixture was cooled to room temperature and concentrated under a flow of nitrogen. Purification by column chromatography (pentane:Et₂O 80:20, SiO₂ was basified with Et₃N prior to use, see General Information for details) afforded pyrrolidine (−)-3I (126 mg, 72%, 94:6 er) as a colourless oil. The spectral data was identical to that of the corresponding racemate described above. 
\[ \alpha ]_{D}^{25} = -5.2 \text{ (c = 1.0, CHCl}_3). 

The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

**Benzyl (R)-3-methylpyrrolidine-1-carboxylate, S6**

(R)-N-benzyl-3-methylpyrrolidine (−)-3I (19 mg, 0.08 mmol) and benzyl chloroformate (3 M in toluene, 0.5 mL, 1.5 mmol) were subjected to general procedure C. Purification by column chromatography (pentane:Et₂O 80:20) afforded pyrrolidine S6 (28 mg, 38%, 94:6 er) as a colourless oil. The corresponding racemic Cbz-pyrrolidine rac-S6 was prepared by an identical procedure starting from rac-3I. The data are consistent with the literature.²¹

¹H NMR (400 MHz, CDCl₃) δ = 7.39-7.26 (5H, m, ArH), 5.13 (2H, s, OCH₂Ph), 3.63-3.50 (2H, m, CH₂-2a and CH₂-5a), 3.40-3.30 (1H, m, CH₂-5b), 2.98-2.85 (1H, m, CH₂-2b), 2.31-2.17 (1H, m, CH-3), 2.02-1.94 (1H, m, CH-4a), 1.55-1.45 (1H, m, CH₂-4b), 1.05 (3H, m, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ = 155.0, 137.3, 128.6, 128.0, 127.9, 66.72, 66.69, 53.4, 53.0, 46.2, 45.8, 33.8, 33.7, 33.0, 32.9, 17.8. N.B. The majority of the signals are doubled due to the rotameric nature of the carbamate.

HRMS: ESI+ found [M+Na]+ = 242.1153, C₁₃H₁₇NO₂Na requires 242.1152, Δ = 0.54 ppm.

FTIR (film): νmax = 2959, 2874, 1702, 1419, 1358, 1216, 1177, 1149, 1133, 1103, 1074 cm⁻¹.

\[ \alpha ]_{D}^{25} = +18.5 \text{ (c = 1.0, CHCl}_3).
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IB-N column (99:1 hexane:IPA, 1.0 mL min⁻¹, 210 nm, room temperature):

\[
\begin{array}{cccccccc}
\text{#} & \text{Time} & \text{Type} & \text{Area} & \text{Height} & \text{Width} & \text{Area%} & \text{Symmetry} \\
1 & 42.03 & R & 1552 & 25.3 & 0.720 & 49.630 & 0.993 \\
2 & 42.03 & R & 1553 & 25.4 & 1.050 & 30.130 & 0.993 \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{#} & \text{Time} & \text{Type} & \text{Area} & \text{Height} & \text{Width} & \text{Area%} & \text{Symmetry} \\
1 & 42.83 & R & 1117 & 121.1 & 0.225 & 50.054 & 0.528 \\
2 & 42.83 & R & 1117 & 121.1 & 0.225 & 50.054 & 0.528 \\
\end{array}
\]

(S)-1-Benzyl-3-isobutylpyrrolidine, (+)-3al

To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added (S)-2-isobutylbutane-1,4-diol (−)-2al (146 mg, 1.0 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%) and CsHCO₃ (3.9 mg, 2.0 mol%). The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum), evacuated under vacuum and refilled with argon three times. Cyclopentyl methyl ether (0.5 mL) was added via syringe, followed by anhydrous benzylamine (0.16 mL, 1.5 mmol). The vial was sealed with Parafilm®, placed in a preheated oil bath and stirred at 110 °C for 24 hours. The reaction mixture was cooled to room temperature and concentrated under a flow of nitrogen. Purification by column chromatography (pentane:Et₂O 75:25, SiO₂ was basified with Et₃N prior to use, see General Information for details) afforded pyrrolidine (+)-3al (169 mg, 78%, 89:11 er) as a colourless oil. The corresponding racemic pyrrolidine rac-3al was prepared by an identical procedure starting from rac-2al.

\(^1\)H NMR (400 MHz, CDCl₃) δ = 7.35 – 7.21 (5H, m, ArH), 3.61 (1H, d, J = 12.8 Hz, NCH₂Ph), 3.57 (1H, d, J = 12.8 Hz, NCH₂Ph), 2.84 (1H, dd, J = 9.0, 7.4 Hz, CH₂-2₃), 2.72 (1H, ddd, J = 9.2, 8.0, 5.2 Hz, CH₂-5₃), 2.39 (1H, td, J = 8.9, 6.5 Hz, CH₂-5₄), 2.31 – 2.18 (1H, m, CH-3), 2.04 – 1.94 (2H, m, CH₂-2₅ and CH₂-4₅), 1.60 – 1.45 (1H, nonet, J = 6.7 Hz, CH-7), 1.36 (1H, ddd, J = 12.2, 8.6, 6.7, 5.3 Hz, CH₂-4ₕ), 1.24 (2H, t, J = 7.2 Hz, CH₂-6), 0.87 (3H, d, J = 6.6 Hz, CH₃-8a), 0.85 (3H, d, J = 6.6 Hz, CH₃-8b).

\(^13\)C NMR (101 MHz, CDCl₃) δ = 139.6, 129.0, 128.3, 126.9, 61.1, 61.0, 54.1, 45.2, 35.5, 31.1, 26.9, 22.9, 22.9.

HRMS: ESI+ found [M+H]⁺ = 218.1904, C₁₅H₂₄N requires 218.1903, Δ = 0.26 ppm.

FTIR (film): \( v_{\max} \) = 2954, 2783, 1467, 1454, 1382, 1351, 1155, 1132, 738, 698 cm⁻¹.
\([\alpha]_{D}^{25} = +10.2\) (c = 1.0, CHCl\(_3\)).

The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

**Benzyl (S)-3-isobutylpyrrolidine-1-carboxylate, S7**

![Image](https://via.placeholder.com/150)

(S)-1-Benzyl-3-isobutylpyrrolidine (+)-3al (30 mg, 0.14 mmol) and benzyl chloroformate (3 M in toluene, 0.28 mL, 0.83 mmol) were subjected to **general procedure C**. Purification by column chromatography afforded piperidine S7 (19 mg, 53%, 89:11 e.r.). The corresponding racemic Cbz-pyrrolidine rac-S7 was prepared by an identical procedure starting from rac-3al.

**1H NMR** (400 MHz, CDCl\(_3\)) \(\delta = 7.40 – 7.27\) (5H, m, ArH), 5.13 (2H, s, OCH\(_3\)Ph), 3.67 – 3.47 (2H, m, CH\(_2\)-2\(_a\) and CH\(_2\)-5\(_b\)), 2.96 – 2.83 (1H, m, CH\(_2\)-2\(_b\)), 2.29 – 2.12 (1H, m, CH-3), 2.06 – 1.93 (1H, m, CH\(_2\)-4\(_a\)), 1.64 – 1.39 (2H, m, CH-7 and CH\(_2\)-4\(_b\)), 1.31 – 1.21 (2H, m, CH\(_2\)-6), 0.95 – 0.86 (6H, m, 2 x CH\(_3\)-8).

**13C NMR** (101 MHz, CDCl\(_3\)) \(\delta = 155.0, 137.3, 128.6, 128.0, 128.0, 127.9, 66.7, 66.7, 52.1, 51.7, 46.2, 45.7, 42.6, 42.6, 37.2, 36.3, 32.3, 31.5, 26.9, 26.8, 23.0, 22.9, 22.8, 22.8. N.B. The majority of the signals are doubled due to the rotameric nature of the carbamate.

**HRMS**: ESI+ found [M+Na]\(^+\) = 284.1621, C\(_{16}\)H\(_{23}\)O\(_2\)NNa requires 284.1621, \(\Delta = -0.08\) ppm.

**FTIR** (film): \(\nu_{\text{max}} = 2955, 1704, 1418, 1359, 1109, 768, 697\) cm\(^{-1}\).

\([\alpha]_{D}^{25} = -21.4\) (c = 1.0, CHCl\(_3\)).

**HPLC**: Enantiomeric excess was determined by HPLC with a Chiralpak\textsuperscript{®} IA column (99:1 hexane:IPA, 1.0 mL min\(^{-1}\), 210 nm, room temperature):

<table>
<thead>
<tr>
<th>#</th>
<th>Time</th>
<th>Type</th>
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<th>Height</th>
<th>Width</th>
<th>Area%</th>
<th>Symmetry</th>
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<tr>
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<td>BP</td>
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<td>107.8</td>
<td>0.8072</td>
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<tr>
<td>2</td>
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<td>PP</td>
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<td>50.6</td>
<td>0.4961</td>
<td>49.869</td>
<td>0.728</td>
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</thead>
<tbody>
<tr>
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<td>21.922</td>
<td>BP</td>
<td>678.1</td>
<td>275.1</td>
<td>0.4453</td>
<td>89.369</td>
<td>0.597</td>
</tr>
<tr>
<td>2</td>
<td>23.922</td>
<td>BP</td>
<td>610.2</td>
<td>27.6</td>
<td>0.4544</td>
<td>10.631</td>
<td>0.542</td>
</tr>
</tbody>
</table>
To a 2-5 mL Biotage® microwave vial equipped with a stirrer bar was added (R)-2-isopropylbutane-1,4-diol (–)-2am (132 mg, 1.0 mmol), [IrCp*Cl₂]₂ (8.0 mg, 1.0 mol%) and CsHCO₃ (3.9 mg, 2.0 mol%). The vial was sealed with a microwave vial crimp cap (containing a Reseal® septum), evacuated under vacuum and refilled with argon three times. Cyclopentyl methyl ether (0.5 mL) was added via syringe, followed by anhydrous benzylamine (0.16 mL, 1.5 mmol). The vial was sealed with Parafilm®, placed in a preheated oil bath and stirred at 110 °C for 24 hours. The reaction mixture was cooled to room temperature and concentrated under a flow of nitrogen. Purification by column chromatography (pentane:Et₂O 75:25, SiO₂ was basified with Et₃N prior to use, see General Information for details) afforded pyrrolidine (+)-3am (155 mg, 76%, 92:8 er) as a colourless oil. The corresponding racemic pyrrolidine rac-3am was prepared by an identical procedure starting from rac-2am.

**1H NMR (400 MHz, CDCl₃)** \( \delta = 7.29 – 7.13 \) (5H, m, ArH), 3.54 (1H, d, \( J = 12.8 \) Hz, NC₃H₂Ph), 3.49 (1H, d, \( J = 12.8 \) Hz, NCH₂Ph), 2.74 (1H, dd, \( J = 9.0, 7.4 \) Hz, CH₃-2a), 2.71 – 2.63 (1H, m, CH₂-5b), 2.28 (1H, td, \( J = 8.9, 6.2 \) Hz, CH₂-5a), 1.98 (1H, t, \( J = 8.6 \) Hz, CH₂-2b), 1.92 – 1.72 (2H, m, CH₂-4a and CH-3), 1.45 – 1.31 (2H, m, CH₂-4b and CH-6), 0.81 (3H, d, \( J = 6.6 \) Hz, CH₃-7a), 0.77 (3H, d, \( J = 6.6 \) Hz, CH₃-7b).

**13C NMR (101 MHz, CDCl₃)** \( \delta = 139.6, 129.0, 128.3, 126.9, 61.2, 59.2, 54.4, 45.6, 33.2, 29.2, 21.5, 21.3.\)

HRMS: ESI+ found [M+H]⁺ = 204.1747, C₁₄H₂₂N requires 204.1747, \( \Delta = 0.33 \) ppm.

**FTIR (film)**: \( \nu_{\text{max}} = 2956, 2784, 1453, 1377, 1154, 737, 698 \text{ cm}^{-1}.\)

\( [\alpha]_{D}^{25} = +5.5 \) (c = 1.0, CHCl₃).

The enantiomeric purity was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

**Benzyl (R)-3-isopropylpyrrolidine-1-carboxylate, S8**

(R)-1-Benzyl-3-isopropylpyrrolidine (+)-3am (30 mg, 0.15 mmol) and benzyl chloroformate (3 M in toluene, 0.29 mL, 0.89 mmol) were subjected to general procedure C. Purification by column
chromatography afforded piperidine \textbf{S8} (13 mg, 36%, 92:8 e.r.). The corresponding racemic Cbz-pyrrolidine \textbf{rac-S8} was prepared by an identical procedure starting from \textbf{rac-3am}.

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.41 - 7.27 (5\text{H}, m, Ar^H), 5.13 (2\text{H}, s, OCH\textsubscript{2}Ph), 3.70 - 3.52 (2\text{H}, m, CH\textsubscript{2}-2\text{z} and CH\textsubscript{2}-5\text{z}), 3.34 - 3.24 (1\text{H}, m, CH\textsubscript{2}-2\text{b}), 2.99 - 2.89 (1\text{H}, m, CH\textsubscript{2}-2\text{b}), 2.06 - 1.95 (1\text{H}, m, CH\textsubscript{2}-4\text{z}), 1.90 - 1.74 (1\text{H}, m, CH-3), 1.57 - 1.41 (2\text{H}, m, CH-6 and CH\textsubscript{2}-4\text{b}), 0.95 - 0.89 (6\text{H}, 2 \times CH\textsubscript{3}-7).

\textbf{13C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta = 155.0, 137.3, 128.6, 128.1, 128.0, 128.0, 66.7, 66.7, 50.9, 50.4, 46.9, 46.7, 46.3, 32.1, 30.6, 29.8, 21.3, 21.3, 21.3. \textit{N.B. The majority of the signals are doubled due to the rotameric nature of the carbamate.}

HRMS: ESI+ found [M+H]\textsuperscript{+} = 248.1646, C\textsubscript{15}H\textsubscript{22}O\textsubscript{2}N requires 248.1645, Δ = 0.55 ppm.

\textbf{FTIR} (film): \(\nu_{\text{max}} = 2959, 1703, 1418, 1359, 1106, 798, 697 \text{ cm}^{-1}.

\([\alpha]_D^{25} = -32.4 \ (c = 1.0, \text{ CHCl}_{3}).

\textbf{HPLC:} Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (99:1 hexane:IPA, 1.0 mL min\textsuperscript{-1}, 210 nm, room temperature):

\(\begin{array}{cccccccc}
\text{#} & \text{Time} & \text{Type} & \text{Area} & \text{Height} & \text{Width} & \text{Area% Symmetry} \\
1 & 22.59 & FP & 2629.4 & 96.4 & 0.644 & 69.47 & 0.722 \\
2 & 27.07 & FP & 2699.5 & 77.6 & 0.378 & 50.67 & 0.418 \\
\end{array}\)

\(\begin{array}{cccccccc}
\text{#} & \text{Time} & \text{Type} & \text{Area} & \text{Height} & \text{Width} & \text{Area% Symmetry} \\
1 & 22.671 & 66 & 5085.3 & 118.8 & 0.447 & 92.37 & 0.301 \\
2 & 26.879 & 66 & 744.7 & 23.7 & 0.312 & 7.426 & 0.405 \\
\end{array}\)

\(\begin{array}{cccccccc}
\text{(2R,5R)-1-Benzyl-2,5-dimethylpiperidine, 3o}
\end{array}\)

\(\begin{array}{cccccccc}
\text{(2R,5R)-2-Methylhexane-1,5-diol (+)-2o} & (132 mg, 1.0 mmol, \sim53:47 \text{ dr, 94:6 er}), \text{ anhydrous benzyamine (0.16 mL, 1.5 mmol), [IrCp*Cl}_2] (8.0 mg, 1.0 mol%) and water (0.5 mL) were subjected to \textbf{general procedure B} at 110 °C. \textbf{1H NMR} analysis of the crude reaction mixture indicated the presence of two diastereomers in 63:37 dr. Purification by column chromatography (pentane:Et\textsubscript{2}O 95:5) afforded piperidine (−)-\textbf{3omajor} (105 mg, 52%, >95:5 dr, 75:25 er) as a colourless oil and piperidine (+)-\textbf{3ominor} (50 mg, 25%, >95:5 dr, 75:25 er) as a colourless oil. The spectral data for both diastereoisomers was identical to that of the corresponding racemate described above.

(−)-\textbf{3omajor}: \([\alpha]_D^{25} = -65.2 \ (c = 2.1, \text{ CHCl}_{3})).

(+)-\textbf{3ominor}: \([\alpha]_D^{25} = +2.4 \ (c = 0.7, \text{ CHCl}_{3}).

\[45\]
The enantiomeric purity of each diastereoisomer was determined by chiral HPLC analysis after conversion to the corresponding benzyl carbamate (see below).

**Benzyl (2R,5R)-2,5-dimethylpiperidine-1-carboxylate, S9**

\[
\text{N-benzyl-(2R,5R)-2,5-dimethylpiperidine (–)-30}_{\text{major}} \text{ (26 mg, 0.13 mmol) and benzyl chloroformate (3 M in toluene, 0.5 mL, 1.5 mmol) were subjected to general procedure C. Purification by column chromatography afforded piperidine S9 (31 mg, 98%, 75:25 er, >95:5 dr). The corresponding racemic piperidine rac-S9 was prepared by an identical procedure starting from rac-30}_{\text{major}}.}
\]

\[\begin{align*}
\text{H NMR (400 MHz, CDCl}_3) & \delta = 7.37-7.28 (5H, m, ArH), 5.16-5.10 (2H, m, OC\text{H}_2\text{Ph}), 4.46-4.39 (1H, m, CH-2), 3.73 (1H, dt, J = 13.6, 2.3 Hz, CH}_2-6\text{a}), 3.13 (1H, dd, J = 13.5, 3.4 Hz, CH}_2-6\text{b}), 1.96-1.78 (3H, m, CH}_2-3\text{a}, CH}_2-4\text{a} \text{ and CH}_2-5), 1.32-1.25 (2H, m, CH}_2-3\text{b} \text{ and CH}_2-4\text{b}), 1.13 (3H, d, J = 6.9 Hz, CH}_3-7), 0.98 (3H, d, J = 6.9 Hz, CH}_3-8). \\
\text{C NMR (101 MHz, CDCl}_3) & \delta = 156.1, 137.3, 128.6, 127.9, 127.8, 66.9, 46.8, 44.0, 27.8, 24.9, 24.8, 16.7, 16.3. \\
\text{HRMS: ESI+ found [M+H]^+} = 248.1646, \text{C}_{15}\text{H}_{22}\text{O}_2\text{N requires 248.1645, \Delta = 0.24 ppm.} \\
\text{FTIR (film): } \nu_{\text{max}} = 2936, 1693, 1423, 1355, 1336, 1308, 1260, 1244, 1159, 1076, 1029, 697 \text{ cm}^{-1}. \\
[\alpha]_D^{25} = -14.2 \text{ (c = 1.4, CHCl}_3). \\
\text{HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (99:1 hexane:IPA, 1.0 mL min}^{-1}, 210 \text{ nm, room temperature):}
\end{align*}\]
Benzyl (25,5R)-2,5-dimethylpiperidine-1-carboxylate, S10

\[
\begin{align*}
\text{PH} & \quad \text{O} \\
\text{N} & \quad \text{2Me} \\
\text{3} & \quad \text{Me} \\
\text{4} & \quad \text{7Me} \\
\end{align*}
\]

\(N\)-benzyl-(25,5R)-2,5-dimethylpiperidine (+)-30\text{minor} (25 mg, 0.12 mmol) and benzyl chloroformate (3M in toluene, 0.5 mL, 1.5 mmol) were subjected to general procedure C. Purification by column chromatography afforded piperidine S10 (29 mg, 95%, 75:25 er, >95:5 dr). The corresponding racemic piperidine rac-S10 was prepared by an identical procedure starting from rac-30\text{minor}.

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.39-7.28 (5\text{H}, \text{m, ArH}), 5.13 \ (2\text{H}, \text{s, OCH}_2\text{Ph}), 4.53-4.40 \ (1\text{H}, \text{m, CH-2}), 4.02-3.86 \ (1\text{H}, \text{m, CH}_2\text{-6a}), 2.53-2.43 \ (1\text{H}, \text{m, CH}_2\text{-6b}), 1.74-1.63 \ (1\text{H}, \text{m, CH}_2\text{-3a}), 1.60-1.44 \ (3\text{H}, \text{m, CH}_2\text{-3b, CH}_2\text{-4a and CH-5}), 1.30-1.19 \ (1\text{H}, \text{m, CH}_2\text{-4b}), 1.13 \ (3\text{H}, \text{d, J = 7.0 Hz, CH}_3\text{-7}), 0.89 \ (3\text{H}, \text{d, J = 6.3 Hz, CH}_3\text{-8}).

\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta = 156.1, 137.3, 128.6, 128.0, 127.9, 67.0, 45.8, 31.5, 30.2, 27.6, 19.4, 16.2. \text{N.B. the carbonyl peak was not observed presumably due to restricted N-CO bond rotation on the NMR timescale.}

HRMS: ESI+ found [M+H]\(^+\) = 248.1646, \(C_{15}H_{22}O_2N\) requires 248.1645, \(\Delta = 0.55 \text{ ppm.}

FTIR (film): \(\nu_{\text{max}} = 2936, 1693, 1423, 1336, 1308, 1260, 1244, 1159, 1146, 1076, 1029, 697 \text{ cm}^{-1}.

\([\alpha]_D^{25} = +5.0 \ (c = 1.6, \text{CHCl}_3).\n
HPLC: Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (99:1 hexane:IPA, 1.0 mL min\(^{-1}\); 210 nm, room temperature):
4.3 Resubjection Experiment

To test whether the saturated aza-heterocycle products can undergo epimerization under the reaction conditions, isomerically pure cis-3n was resubjected to the optimized reaction conditions:

**Procedure:** 3,3-Dimethylpentane-1,5-diol\(^6\) 2q (15 mg, 0.12 mmol), cis-3n (35 mg, 0.17 mmol, >95:5 d.r.), [IrCp*Cl\(_2\)]\(_2\) (0.9 mg, 1.0 mol%), NaHCO\(_3\) (0.2 mg, 2.0 mol%) and anhydrous toluene (0.06 mL) were subjected to general procedure A at 110 °C. Purification by column chromatography (pentane:Et\(_2\)O 75:25) afforded piperidine cis-3n (28 mg, 80%, >95:5 d.r.) as a colourless oil. The spectral data of cis-3n (>95:5 d.r.) was identical to that described above. No signals corresponding to the minor diastereoisomer were observed in the \(^1\)H-NMR spectra of either the purified material or the crude reaction mixture. Additionally, no formation of crossover product 3q was observed. These results imply that epimerization of the products does not occur under the reaction conditions via reversible amine dehydrogenation.
5. References

6. NMR Spectra

![NMR Spectra Image]

**Formula:** HO-\(\text{Ph}\)-OH

**Spectrum Details:**
- **Chemical Shifts:**
  - 8.0 ppm
  - 7.5 ppm
  - 7.0 ppm
  - 6.5 ppm
  - 6.0 ppm
  - 5.5 ppm
  - 5.0 ppm
  - 4.5 ppm
  - 4.0 ppm
  - 3.5 ppm
  - 3.0 ppm
  - 2.5 ppm
  - 2.0 ppm
  - 1.5 ppm
  - 1.0 ppm
  - 0.5 ppm
  - 0.0 ppm

**Peak Assignments:**
- 4.3 ppm
- 4.8 ppm
- 5.4 ppm
- 6.3 ppm

**Additional Notes:**
- The spectrum shows multiple peaks indicating the presence of different chemical environments.
- The peaks are labeled with their respective chemical shifts for analysis.
3b
Ph
\[
\begin{align*}
&\text{N} \\
&\text{Ph} \\
&\text{F}
\end{align*}
\]

3c

F (ppm)

-180 -170 -160 -150 -140 -130 -120 -110 -100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0

59
3y
(+)-3ac (80:20 d.r.)
(+)-3ad

[Chemical structure image]
(+)-3ah
cis-3n (>95.5 d.r.)

from resubjection experiment