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General information

Purification of reaction products was carried out by flash column chromatography using silica gel (40 – 63 µm), unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on aluminum or glass, cut to size. Visualization was accomplished with UV light followed by staining with a potassium permanganate or ninhydrin solution and heating. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AVANCE 300 MHz, 400 MHz, and 500 MHz spectrometers at ambient temperature, unless otherwise indicated. Spectral data was reported in ppm using solvent as the reference (CDCl$_3$ at 7.26 ppm, CD$_3$OD at 3.31 ppm, or benzene-$d_6$ at 7.16 ppm for $^1$H NMR and CDCl$_3$ at 77.0 ppm or CD$_3$OD at 49.0 ppm for $^{13}$C NMR). $^1$H NMR data was reported as: multiplicity (ap = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextuplet, sept = septuplet, m = multiplet), integration and coupling constant(s) in Hz. $^{13}$C NMR is reported indicating information from distortionless enhancement by polarization Transfer (DEPT) experiments. Infrared (IR) spectra were obtained on an Attenuated Total Reflectance Fourier Transform Infrared spectrometer (ATR – FTIR). High – resolution mass spectroscopy (HRMS) was performed on a mass spectrometer with an electron beam of 70 eV (EI) or Micromass Q-TOF I - Time of flight Electrospray Ionisation mass spectrometer (ESI).

Materials

Unless otherwise noted, all commercially available materials were purchased from commercial sources and used without further purification.
Additional optimization data

Original optimization of the reported hydroamination reaction sequence used tertiary amine $S5a$ to prevent over-oxidation of the amine. The resulting N-oxide $S6a$ can undergo Cope elimination of acrylonitrile to yield hydroxylamine $2a$. A stronger oxidant, mCPBA, can be used for tertiary amine reagents since over-oxidation is not an issue. There are different chemoselectivity issues for the reduction step of this sequence when using this approach ($N$-oxide $S6a$ vs. $3a$), and therefore different reductants were also optimal for this approach vs. the secondary amine approach reported.

Table S1: Optimization of hydroamination cascade from tertiary amines$^a$

| Entry | Equiv amine | Equiv mCPBA | Boron Reductant (equiv) | Temp ($^\circ$C) | Yield 3a (%)$^b$ | Yield 4a (%)$^b$ |
|-------|-------------|-------------|-------------------------|------------------|------------------|------------------|
| 1     | 1.1         | 1.0         | none                    | 70               | 75               | 0                |
| 2     | 1.1         | 1.0         | $B_3$pin$_2$ (1.1)      | 70               | 0                | 60               |
| 3     | 1.1         | 1.0         | none                    | 50               | 93               | 0                |
| 4     | 1.1         | 1.0         | $B_3$pin$_2$ (1.1)      | 50               | 0                | 34               |
| 5     | 1.1         | 1.0         | $ArB(OH)_2$ A (1.1)     | 50               | 46               | 52               |
| 6     | 1.2         | 1.0         | $ArB(OH)_2$ A (1.2)     | 50               | 44               | 52               |
| 7     | 1.0         | 1.1         | $ArB(OH)_2$ A (1.1)     | 50               | 25               | 39               |
| 8     | 1.0         | 1.1         | $ArB(OH)_2$ A (1.5)     | 50               | 17               | 45               |
| 9     | 1.0         | 1.5         | $ArB(OH)_2$ A (1.5)     | 50               | 8                | 23               |

(a) Conditions: amine $1a$ in CHCl$_3$ (0.1 M), then mCPBA added, stirred at 0 °C, 30 min. Reductant then added, stirred at given temperature, 4 h. (b) $^1$H NMR yield of $4a$ using 1,3,5-trimethoxybenzene as an internal standard. Bpin = B(pinacolato) = B(O$_2$C$_2$(CH$_3$)$_4$)
**Boron reductants**

![Image of boron reductants](image)

**Table S2: Solvent scan for hydroamination using tertiary amine starting materials**

![Diagram of reaction](image)

| Entry | Solvent    | Yield 3a (%)<sup>b</sup> | Yield 4a (%)<sup>b</sup> |
|-------|------------|--------------------------|--------------------------|
| 1     | CDCl<sub>3</sub> | 40                       | 42                       |
| 2     | MeCN       | 47                       | 13                       |
| 3     | t-BuOH     | 6                        | trace                    |
| 4     | Cyclohexane | 0                        | 0                        |
| 5     | DCE        | 43                       | 40                       |
| 6     | PhCF<sub>3</sub> | 34                  | 23                       |
| 7     | Dioxane    | 22                       | 19                       |

(a) Conditions: amine 1<sub>a</sub> (1.2 equiv) in solvent (0.1 M), then mCPBA (1.0 equiv) added, stirred at 0 °C, 30 min. 2-Methylphenyl boronic acid (ArB(OH)<sub>2</sub> A) then added (1.2 equiv), stirred at 50 °C, 4 h. (b) <sup>1</sup>H NMR yield of 4<sub>a</sub> using 1,3,5-trimethoxybenzene as an internal standard.
Table S3: Boron reductant scan for hydroamination using tertiary amine starting materials

| Entry | Boron Reductant | Temp (°C) | Time (h) | Yield 3a (%)<sup>b</sup> | Yield 4a (%)<sup>b</sup> |
|-------|-----------------|-----------|----------|--------------------------|--------------------------|
| 1     | B(C₆F₅)₃        | 50        | 4        | 0                        | 0                        |
| 2     | B(C₆F₅)₃        | rt        | 4        | 0                        | 13                       |
| 3     | HOB(tol)        | 50        | 4        | 0                        | 8                        |
| 4     | HOB(tol)₄       | rt        | 4        | 20                       | 0                        |
| 5     | Et₃SiBpin       | 50        | 4        | 12                       | 20                       |
| 6     | Et₃SiBpin       | rt        | 4        | 30                       | 43                       |
| 7     | ArB(OR)₂ A      | 50        | 24       | 100                      | trace                    |
| 8     | ArB(OR)₂ B      | 50        | 24       | 100                      | trace                    |
| 9     | ArB(OH)₂ A      | 50        | 4        | 44                       | 52                       |
| 10    | ArB(OH)₂ B      | 50        | 4        | 73                       | 22                       |
| 11    | ArB(OH)₂ C      | 50        | 24       | 100                      | trace                    |
| 12    | ArB(OH)₂ D      | 50        | 24       | 100                      | trace                    |
| 13    | ArB(OH)₂ E      | 50        | 4        | 75                       | 25                       |
| 14    | ArB(OH)₂ F      | 50        | 4        | 83                       | 10                       |
| 15    | ArB(OH)₂ G      | 50        | 4        | 95                       | 0                        |
| 16    | ArB(OH)₂ H      | 50        | 4        | 55                       | 36                       |
| 17    | ArB(OH)₂ I      | 50        | 4        | 69                       | 19                       |
| 18    | ArB(OH)₂ J      | 50        | 4        | 98                       | trace                    |
| 19    | ArB(OH)₂ K      | 50        | 24       | 99                       | trace                    |
| 20    | ArB(OH)₂ L      | 50        | 24       | 58                       | 30                       |

(a) Conditions: amine 1a (1.2 equiv) in CHCl₃ (0.1 M), then mCPBA (1.0 equiv) added, stirred at 0 °C, 30 min. Reductant then added (1.2 equiv), stirred at given temperature, 4 – 24 h. (b) <sup>1</sup>H NMR yield of 4a using 1,3,5-trimethoxybenzene as an internal standard.
Table S4: Optimization of the oxidation and hydroamination of secondary amines

Additional optimization data for the solvent and oxidant choice for the oxidation/Cope-type hydroamination steps of the reported reaction sequence are included. Diboron species (B$_2$pin$_2$ or B$_2$(OH)$_4$) were determined to be optimal reductants and were not evaluated within the following entries.

![Chemical structure](image)

| Entry | Solvent (M)                  | Oxidant (equiv) | Temp (°C) | Yield 3a (%)$^b$ |
|-------|------------------------------|-----------------|-----------|------------------|
| 1     | TFE (0.1)                    | UHP (1.2)       | 50        | 92               |
| 2     | TFE (0.2)                    | UHP (1.2)       | 50        | 91               |
| 3     | MeOH/HFIP 3:1 (0.1)          | UHP (1.2)       | 50        | 52               |
| 4     | MeOH/HFIP 1:1 (0.1)          | UHP (1.2)       | 50        | 79               |
| 5     | MeOH                         | UHP (1.2)       | 50        | 30               |
| 6     | EtOH (0.1)                   | UHP (1.2)       | 50        | 22               |
| 7     | i-PrOH (0.1)                 | UHP (1.2)       | 50        | 16               |
| 8     | t-BuOH (0.1)                 | UHP (1.2)       | 50        | 18               |
| 9     | HFIP (0.1)                   | UHP (1.2)       | 50        | 70               |
| 10    | i-PrOH/TFE 10:1 (0.1)        | UHP (1.2)       | 50        | 27               |
| 11    | i-PrOH/HFIP 10:1 (0.1)       | UHP (1.2)       | 50        | 36               |
| 12    | TFE (0.1)                    | 30% aq. H$_2$O$_2$ (1.2) | 50  | 42               |
| 13    | TFE (0.1)                    | 30% aq. H$_2$O$_2$ (1.5) | 50  | 84               |
| 14    | TFE (0.1)                    | H$_2$O$_2$ (1.5) | rt       | 62               |
| 15    | TFE (0.1)                    | UHP (1.2)       | rt        | 33               |

(a) Conditions: amine 1a (1.0 equiv) in solvent, then oxidant added, stirred at given temperature, 16 h. (b) $^1$H NMR yield of 3a using 1,3,5-trimethoxybenzene as an internal standard. UHP = urea hydrogen peroxide adduct; TFE = 2,2,2-trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoroisopropanol.

General procedures

**General procedure A: Synthesis of secondary amines**

To a round bottom flask was added 5-bromopent-1-ene (1.0 equiv) followed by dilution in EtOH (2.5 M). A primary amine (5.0 equiv) and NaI (0.05 equiv) were added, and the mixture was heated to reflux for 4 h. Upon completion, the reaction was concentrated via rotary evaporation. The reaction mixture was diluted with DCM and was extracted using 1M KOH (x1), then water (x1), and then brine (x1). The organic phase was dried with Na$_2$SO$_4$ and filtered. The filtrate was concentrated via rotary evaporation and the product was isolated using silica-gel flash column chromatography.
General procedure B: Redox–enabled hydroamination sequence

To a clean dry microwave vial was added the corresponding secondary amine 1 (1.0 equiv) followed by dilution with TFE (0.1 M). UHP was then added (1.2 equiv). The vial was sealed then stirred at 50 °C for 16 h. The reaction vessel was opened and B$_2$(OH)$_4$ (1.2 equiv for alkyl–substituted amines or 2.2 equiv for Lewis–base–substituted amines) was added. The vial was resealed then stirred at 50 °C for 1 h. The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1M HCl was added, and the phases were separated. 15 mL of 1M KOH was added to the aqueous phase, which was then extracted with DCM twice (50 mL each). The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, then filtered before concentration via rotary evaporation. The crude product did not require any further purification.

General procedure C: Robustness screen

To a clean dry microwave vial was added additive (0.1 mmol, 1.0 equiv), followed by amine 1a (17.5 mg, 0.1 mmol) in a solution of TFE (0.1 M). UHP was then added (11.3 mg, 0.12 mmol). The vial was sealed then stirred at 50 °C for 16 h. The reaction vessel was opened and B$_2$(OH)$_4$ (10.8 mg, 0.12 mmol) was added. The vial was resealed then stirred at 50 °C for 1 h. The crude reaction mixture was concentrated via rotary evaporation, then 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) in a solution of CDCl$_3$ (0.2 M) was added to the crude reaction mixture. $^1$H NMR spectra were obtained and the integration of diagnostic signals for the additive and for pyrrolidine 4a were attained to find the amount (%) of both species. When the additive was volatile and no signals for this species could be observed, no amount remaining is reported. However, when the additive was somewhat volatile and signals for this species could be observed, likely in reduced quantities due to evaporation, the amount remaining is reported.

Characterization data

N-Benzylpent-4-en-1-amine 1a

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.49 g, 10.0 mmol), benzyamine (5.50 mL, 50.0 mmol), sodium iodide (0.075 g, 0.05 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes to 40% EtOAc/Hexanes) to yield the title compound as a yellow oil (1.28 g, 73%). Characterization data is in good agreement with previously reported data.

TLC Rf: 0.52 in 10% MeOH/DCM

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1 K. D. Collins and F. Glorius, Nat. Chem. 2013, 5, 597.
2 Y.-H. Wang, J.-L. Ye, A.-E. Wang and P.-Q. Huang, Org. Biomol. Chem. 2012, 10, 6504.
\[ \text{N-(4-Methylbenzyl)pent-4-en-1-amine 1b} \]

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.01 g, 6.80 mmol), \( p \)-tolylmethanamine (4.33 mL, 34.0 mmol), sodium iodide (0.102 g, 0.680 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% Et\(_3\)N) to yield the title compound as a yellow oil (1.09 g, 85%).

**TLC Rf:** 0.28 in 30% EtOAc/Hexanes

\[ \text{^1H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 7.12 (m, 2H), 7.05 (m, 2H), 5.73 (ddt, } J = 16.9, 10.1, 2.2, 1.3 \text{ Hz, 1H), 3.66 (s, 2H), 2.60 – 2.52 (m, 2H), 2.25 (s, 3H), 2.06 – 1.97 (m, 2H), 1.52 (p, } J = 7.3 \text{ Hz, 2H), 1.21 (br s, 1H).} \]

**13C NMR (125 MHz, CDCl\(_3\)):** \( \delta \) 138.6 (CH), 137.6 (C), 136.4 (C), 129.1 (CH), 128.1 (CH), 114.6 (CH\(_2\)), 53.8 (CH\(_2\)), 48.9 (CH\(_2\)), 31.6 (CH\(_2\)), 29.4 (CH\(_2\)), 21.1 (CH\(_3\)).

**IR (FTIR):** 3316, 3001, 2922, 1639, 1513, 1448, 1113, 908, 802 cm\(^{-1}\).

**HRMS (EI):** Exact mass calcd for C\(_{13}\)H\(_{19}\)N [M]+ 189.1517. Found: 189.1515.

\[ \text{N-Phenethylpent-4-en-1-amine 1c} \]

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (2.51 g, 16.8 mmol), 2-phenylethane-1-amine (10.6 mL, 84.2 mmol), sodium iodide (0.252 g, 1.68 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% Et\(_3\)N) to yield the title compound as a yellow oil (0.59 g, 61%).

**TLC Rf:** 0.43 in 10% MeOH/DCM

\[ \text{^1H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 7.29 – 7.15 (m, 2H), 7.18 – 7.09 (m, 3H), 5.72 (ddt, } J = 16.9, 10.1, 6.7 \text{ Hz, 1H), 4.95 – 4.88 (m, 1H), 4.86 (ddt, } J = 10.2, 2.2, 1.2 \text{ Hz, 1H), 2.85 – 2.68 (m, 4H), 2.62 – 2.50 (m, 2H), 2.04 – 1.91 (m, 2H), 1.49 (p, } J = 7.4 \text{ Hz, 2H), 1.26 (s, 1H).} \]
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 140.1 (C), 138.4 (CH), 128.7 (CH), 128.5 (CH), 126.2 (CH), 114.67 (CH\(_2\)), 51.2 (CH\(_2\)), 49.3 (CH\(_2\)), 36.4 (CH\(_2\)), 31.6 (CH\(_2\)), 29.2 (CH\(_2\)).

IR (FTIR): 3030, 3021, 2917, 2801, 1636, 1464, 1451, 1126, 906, 742, 696 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{19}\)N [M]+ 189.1517. Found: 189.1535.

\textbf{N-Isobutylpent-4-en-1-amine 1d}

The title compound was synthesized according to \textbf{general procedure A} using 5-bromopent-1-ene (1.01 g, 6.80 mmol), isobutylamine (3.38 mL, 34.0 mmol), sodium iodide (0.102 g, 0.680 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20\% EtOAc/Hexanes + 1\% Et\(_3\)N) to yield the title compound as a yellow oil (0.59 g, 61\%).

TLC R\(_f\): 0.30 in 30\% EtOAc/Hexanes

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 5.82 – 5.70 (m, 1H), 4.95 (dq, \(J = 17.1, 1.6\) Hz, 1H), 4.88 (ddt, \(J = 10.1, 2.3, 1.3\) Hz, 1H), 2.53 (td, \(J = 7.3, 1.9\) Hz, 2H), 2.34 (dt, \(J = 6.8, 1.3\) Hz, 2H), 2.07 – 1.98 (m, 2H), 1.68 (dpd, \(J = 13.4, 6.7, 1.7\) Hz, 1H), 1.52 (pd, \(J = 7.4, 1.8\) Hz, 2H), 1.31 (br s, 1H), 0.83 (dt, \(J = 6.5, 1.3\) Hz, 6H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.6 (CH), 114.6 (CH\(_2\)), 58.1 (CH\(_2\)), 49.6 (CH\(_2\)), 31.6 (CH\(_2\)), 29.3 (CH\(_2\)), 28.3 (CH), 20.7 (CH\(_3\)).

IR (FTIR): 3325, 3074, 2952, 2869, 1640, 1465, 1126, 990, 908, 734 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_9\)H\(_{18}\)N [M – H]+ 140.1439. Found: 140.1432.

\textbf{N-(Cyclohexylmethyl)pent-4-en-1-amine 1e}

The title compound was synthesized according to \textbf{general procedure A} using 5-bromopent-1-ene (1.49 g, 10.0 mmol), cyclohexylmethanamine (6.51 mL, 50.0 mmol), sodium iodide (0.150 g, 1.00 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (80\% EtOAc/Hexanes) to yield the title compound as a yellow oil (1.75 g, 96\%).

TLC R\(_f\): 0.33 in 30\% EtOAc/Hexanes
\(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta \) 5.75 (ddt, \(J = 16.9, 10.2, 6.6\) Hz, 1H), 4.95 (dq, \(J = 17.1, 1.7\) Hz, 1H), 4.88 (ddt, \(J = 10.2, 2.3, 1.3\) Hz, 1H), 2.56 – 2.49 (m, 2H), 2.36 (d, \(J = 6.7\) Hz, 2H), 2.06 – 1.98 (m, 2H), 1.71 – 1.55 (m, 5H), 1.52 (p, \(J = 7.4\) Hz, 2H), 1.44 – 1.32 (m, 1H), 1.25 – 1.01 (m, 4H), 0.83 (qd, \(J = 12.5, 3.8\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta \) 138.6 (CH), 114.6 (CH\(_2\)), 56.9 (CH\(_2\)), 49.7 (CH\(_2\)), 38.0 (CH), 31.7 (CH\(_2\)), 31.5 (CH\(_2\)), 29.3 (CH\(_2\)), 26.7 (CH\(_2\)), 26.1 (CH\(_2\)).

IR (FTIR): 3081, 2919, 2848, 1639, 1445, 1127, 909 cm\(^{-1}\).

HRMS (ESI): Exact mass calcd for C\(_{12}\)H\(_{24}\)N [M+H]+ 182.1909. Found: 182.1903.

\(N\)-\((1\)-Phenylethyl\))pent-4-en-1-amine 1f

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.49 g, 10.0 mmol), 1-phenylethanamine (6.40 mL, 50.0 mmol), sodium iodide (0.075 g, 0.50 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (60% EtOAc/Hexanes) to yield the title compound as a yellow oil (1.76 g, 93%).

TLC R\(_f\): 0.37 in 60% EtOAc/Hexanes

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.37 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 5.78 (ddt, \(J = 16.9, 10.2, 6.6\) Hz, 1H), 4.98 (ap dq, \(J = 17.2, 1.7\) Hz, 1H), 4.92 (ddt, \(J = 10.2, 2.2, 1.3\) Hz, 1H), 3.75 (q, \(J = 6.6\) Hz, 1H), 2.52 (ddd, \(J = 11.4, 7.9, 6.3\) Hz, 1H), 2.43 (ddd, \(J = 11.4, 7.9, 6.8\) Hz, 1H), 2.05 (dddt, \(J = 10.8, 5.6, 2.8, 1.4\) Hz, 2H), 1.64 – 1.47 (m, 2H), 1.35 (d, \(J = 6.6\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 145.8 (C), 138.5 (CH), 128.4 (CH), 126.8 (CH), 126.5 (CH), 114.5 (CH\(_2\)), 58.3 (CH), 47.3 (CH\(_2\)), 31.6 (CH\(_2\)), 29.4 (CH\(_2\)), 24.4 (CH\(_3\)).

IR (FTIR): 3027, 3017, 2956, 2931, 2805, 1637, 1456, 1447, 1132, 910, 761, 697 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{18}\)N [M-H]+ 188.1439. Found: 188.1449.

\((R)\)-\((1\)-Phenylethyl\))pent-4-en-1-amine 1g

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (0.745 g, 5.00 mmol), \((R)\)-phenylethanamine (3.22 mL, 25.0 mmol), sodium iodide (0.038
g, 0.25 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (25% EtOAc/Hexanes + 1% NEt₃) to yield the title compound as a yellow oil (0.830 g, 88%).

TLC Rf: 0.30 in 20% EtOAc/Hexanes + 1% NEt₃

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H), 5.78 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (ap dq, J = 17.1, 1.7 Hz, 1H), 4.93 (ddt, J = 10.2, 2.3, 1.3 Hz, 1H), 3.75 (q, J = 6.6 Hz, 1H), 2.52 (ddd, J = 11.4, 7.9, 6.3 Hz, 1H), 2.43 (ddd, J = 11.4, 7.9, 6.8 Hz, 1H), 2.14 – 1.98 (m, 2H), 1.62 – 1.50 (m, 2H), 1.35 (d, J = 6.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 145.8 (C), 138.5 (CH), 128.4 (CH), 126.8 (CH), 126.5 (CH), 114.5 (CH₂), 58.3 (CH), 47.3 (CH₂), 31.5 (CH₂), 29.5 (CH₂), 24.4 (CH₃).

IR (FTIR): 3028, 2956, 2915, 2810, 1637, 1447, 1124, 906, 761, 697 cm⁻¹.

HRMS (EI): Exact mass calcd for C₁₃H₁₈N [M – H]+ 188.1439. Found: 188.1418.

\[
\text{N-Benzylhex-5-en-2-amine 1h}
\]

To a vial was added a solution of hex-5-en-2-one (1.0 mL, 8.6 mmol) and TFE (17 mL), which was stirred at rt for 18 h. Then, benzylamine (1.0 mL, 9.5 mmol) was added and the mixture vigorously stirred overnight. Then, NaBH₄ (0.39 g, 10 mmol) was added. After completion of the reaction, as monitored by TLC, the reaction mixture was filtered, washing with TFE (17 mL). The filtrate was concentrated via rotary evaporation, and the crude product was purified using silica-gel flash column chromatography (20% EtOAc/petroleum ether + 1% NEt₃) to yield the title compound as a yellow oil (0.90 g, 55% over 2 steps). Characterization data is in good agreement with previously reported data.³

TLC Rf: 34 in 20% EtOAc/Petroleum ether + 1% NEt₃

¹H NMR (500 MHz, CDCl₃): δ 7.31 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 5.74 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.06 – 4.74 (m, 2H), 3.76 (d, J = 12.9 Hz, 1H), 3.67 (d, J = 13.0 Hz, 1H), 2.64 (h, J =

³ C. Quinet, P. Jourdain, C. Hermans, A. Ates, I. Lucas and I. E. Markó, Tetrahedron 2008, 64, 1077-1087.
6.3 Hz, 1H), 2.03 (dddddd, J = 15.7, 13.2, 8.0, 6.6, 1.4 Hz, 2H), 1.57 – 1.46 (m, 1H), 1.36 (m, 2H), 1.03 (d, J = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, CDCl₃) δ 140.8 (C), 138.8 (CH), 128.4 (CH), 128.2 (CH), 126.9 (CH), 114.5 (CH₂), 52.1 (CH), 51.4 (CH₂), 36.2 (CH₂), 30.3 (CH₂), 20.3 (CH₃).

![N-Benzyl-4-methylpent-4-en-1-amine 1i](image)

Ethyl 4-methylpent-4-enoate was prepared using a literature procedure. The obtained crude product (2.10 g, 98%) was used next step without further purification.⁴ To a vial was added benzylamine (0.60 mL, 5.50 mmol) and 1M DIBAL in THF solution (1.0 mL, 1.0 mmol), which was stirred at rt. After 5 minutes, ethyl 4-methylpent-4-enoate (0.711 g, 5 mmol) was added and the mixture was vigorously stirred at 80 °C for 24 h. Upon completion by TLC, the mixture was transferred to a 100 mL round bottomed flask and the vial was rinsed with additional THF (15 mL) and cooled to 0 °C. LiAlH₄ was added slowly to the flask. The reaction mixture was allowed to warm to room temperature, then was and stirred overnight at 60 °C. The reaction was quenched by cooling to 0 °C and adding sequentially water (1 mL per g LiAlH₄), then 15% aqueous NaOH (1 mL per g LiAlH₄), then water (3 mL per g LiAlH₄), then saturated Rochelle’s solution (50 mL). The solution was allowed to stir for 1 h then filtered, washing with EtOAc. The filtrate was added into an extraction funnel and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, then dried over Na₂SO₄, and concentrated via rotary evaporation. The crude product was purified by alumina column chromatography (20% EtOAc/hexanes + 1% NEt₃) to yield the title compound as a yellow oil (0.53 g, 56% over 3 steps). Characterization data is in good agreement with previously reported data.⁵

TLC Rf: 0.2 in 20% EtOAc/Petroleum ether + 1% NEt₃

^{1}H NMR (300 MHz, CDCl₃) δ 7.30 – 7.22 (m, 4H), 7.22 – 7.12 (m, 1H), 4.67 – 4.56 (m, 2H), 3.71 (s, 2H), 2.62 – 2.48 (m, 2H), 2.04 – 1.92 (m, 2H), 1.64 (s, 3H), 1.64 – 1.52 (m, 2H).

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⁴ L. A. Adrio, L. S. Quek, J. G. Taylor and K. K. Hii, *Tetrahedron* 2009, **65**, 10334-10338.

⁵ A. J. Musacchio, B. C. Lainhart, X. Zhang, S. G. Naugib, T. C. Sherwood and R. R. Knowles, *Science* 2017, **355**, 727.
The title compound was synthesized according to a two-step procedure. To a round bottom flask was added \((Z)-\text{hex}-4\text{-en}-1\text{-ol}\) (1.00 g, 10.0 mmol) followed by dilution in THF (0.2 M). \(\text{PPh}_3\) (3.15 g, 12.0 mmol), then imidazole (2.04 g, 30.0 mmol) were added, and the mixture was cooled to 0 °C. Iodine (2.79 g, 11.0 mmol) was then added. The reaction mixture was stirred at 0 °C for 30 min then rt for 30 min. Upon completion, the reaction was concentrated via rotary evaporation. The reaction mixture was diluted with EtOAc and was extracted using water (x1) and then brine (x1). The organic phase was dried with Na\(_2\)SO\(_4\) and filtered. The filtrate was concentrated via rotary evaporation and \(\text{OPPh}_3\) was removed from the mixture via precipitation using Et\(_2\)O/hexanes. The filtrate was concentrated, and this product was used without further purification. Then, the amine was alkylated according to a modified \textbf{general procedure A} using the crude 6-iodohex-2-ene, \(N\)-benzylamine (5.50 mL, 50.0 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% NEt\(_3\)) to yield the title compound as a yellow oil (0.397 g, 21% over two steps).

**TLC Rf:** 0.38 in 20% EtOAc/Hexanes + 1% NEt\(_3\)

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.37 – 7.30\) (m, 4H), 7.29 – 7.20 (m, 1H), 5.52 – 5.32 (m, 2H), 3.79 (s, 2H), 2.65 (dd, \(J = 7.2\) Hz, 2H), 2.14 – 2.04 (m, 2H), 1.64-1.53 (m, 5H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 140.5\) (C), 130.1 (CH), 128.4 (CH), 128.1 (CH), 126.8 (CH), 124.2 (CH), 54.1 (CH\(_2\)), 49.1 (CH\(_2\)), 29.9 (CH\(_2\)), 24.6 (CH\(_2\)), 12.7 (CH\(_3\)).

IR (FTIR): 3012, 2923, 2807, 1653, 1494, 1452, 1117, 1028 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for \(C_{13}H_{19}N\) [M]+ 189.1517. Found: 189.1503.
**E-N-Benzylhex-4-en-1-amine 1j''**

The title compound was synthesized according to a two-step procedure. To a round bottom flask was added (E)-hex-4-en-1-ol (1.50 g, 15.0 mmol) followed by dilution in THF (0.2 M). PPh<sub>3</sub> (4.72 g, 18.0 mmol), then imidazole (3.06 g, 45.0 mmol) were added, and the mixture was cooled to 0 °C. Iodine (4.18 g, 16.5 mmol) was then added. The reaction mixture was stirred at 0 °C for 30 min then rt for 30 min. Upon completion, the reaction was concentrated via rotary evaporation. The reaction mixture was diluted with EtOAc and was extracted using water (x1) and then brine (x1). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated via rotary evaporation and OPPh<sub>3</sub> was removed from the mixture via recrystallization using Et<sub>2</sub>O/hexanes. The filtrate was concentrated, and this product was used without further purification.

Then, the amine was alkylated according to a modified general procedure A using the crude 6-iodohex-2-ene, N-benzylamine (8.20 mL, 75.0 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% NEt<sub>3</sub>) to yield the title compound as a yellow oil (1.17 g, 41% over two steps).

**TLC Rf:** 0.75 in 10% MeOH/DCM

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.35 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 5.49 – 5.32 (m, 2H), 3.78 (s, 2H), 2.63 (t, J = 7.1 Hz, 2H), 2.05 – 1.99 (m, 2H), 1.63 (dt, J = 4.8, 1.2 Hz, 3H), 1.57 (p, J = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 140.5 (C), 130.9 (CH), 128.4 (CH), 128.1 (CH), 126.9 (CH), 125.1 (CH), 54.0 (CH<sub>2</sub>), 48.9 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 17.0 (CH<sub>3</sub>).

**IR (FTIR):** 3022, 2916, 2851, 2810, 1602, 1494, 1452, 1116, 1028, 963 cm<sup>−1</sup>.

**HRMS (EI):** Exact mass calcd for C<sub>13</sub>H<sub>19</sub>N [M]+ 189.1517. Found: 189.1508.

**N-(Pent-4-en-1-yl)aniline 1k**

The title compound was synthesize according to general procedure A using 5-bromopent-1-ene (0.745 g, 5.0 mmol), aniline (2.3 mL, 25.0 mmol), sodium iodide (0.38 g, 0.25 mmol) in EtOH (2.5 M). The product was purified using silica gel flash column chromatography (5%
EtOAc/Hexanes) to yield the title compound as a yellow oil (0.667 g, 83%). Characterization data is in good agreement with previously reported data.\(^6\)

TLC Rf: 0.39 in 5% EtOAc/Hexanes

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.22 - 7.11\) (m, 2H), \(6.72 - 6.68\) (m, 1H), \(6.63 - 6.58\) (m, 2H), \(5.85\) (ddt, \(J = 16.9, 10.2, 6.6\) Hz, 1H), \(4.98 - 5.14\) (m, 2H), \(3.64\) (br s, 1H), \(3.15\) (t, \(J = 7.1\) Hz, 2H), \(2.31 - 2.08\) (m, 2H), \(1.73\) (p, \(J = 7.2\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 148.4\) (C), \(138.1\) (CH), \(129.3\) (CH), \(117.2\) (CH), \(115.1\) (CH\(_2\)), \(112.8\) (CH), \(43.4\) (CH\(_2\)), \(31.3\) (CH\(_2\)), \(28.7\) (CH\(_2\)).

3,5-Dimethyl-N-(pent-4-en-1-yl)aniline 1l

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.19 g, 8.00 mmol), 3,5-dimethylaniline (5.00 mL, 40.0 mmol), sodium iodide (0.600 g, 0.400 mmol) in EtOH (2.5 M). The product was purified using silica gel flash column chromatography (5% EtOAc/Hexanes) to yield the title compound as an orange-brown oil (1.13 g, 75%).

TLC Rf: 0.37 in 5% EtOAc/Hexanes

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 6.37\) (s, 1H), \(6.26\) (s, 1H), \(5.85\) (ddt, \(J = 16.9, 10.2, 6.6\) Hz, 1H), \(5.13 - 4.94\) (m, 2H), \(3.12\) (t, \(J = 7.1\) Hz, 2H), \(2.25\) (s, 6H), \(2.21 - 2.15\) (m, 2H), \(1.72\) (p, \(J = 7.2\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 148.4\) (C), \(138.9\) (C), \(138.1\) (CH), \(119.3\) (CH), \(115.0\) (CH\(_2\)), \(110.8\) (CH), \(43.5\) (CH\(_2\)), \(31.3\) (CH\(_2\)), \(28.7\) (CH\(_2\)), \(21.5\) (CH\(_3\)).

IR (FTIR): 3396, 3014, 2917, 2854, 1599, 1513, 1472, 1337, 1185, 990, 908, 818 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{19}\)N [M]+ 189.1517. Found: 189.1488.

\(^6\) T. Brown, M. Cumbes, L. J. Diorazio, G. J. Clarkson and M. Wills, J. Org. Chem. 2017, 82, 10489.
2-Allyl-N-benzylaniline 1m

To a clean dry microwave vial was added a solution of benzaldehyde (0.3 mL, 3 mmol) and TFE (6 mL) and was magnetically stirred at RT. After 5 minutes, the respective o-allylaniline (3 mmol) was added and the mixture vigorously stirred. After stirring for overnight, NaBH₄ (0.14 g, 3.6 mmol) was added. After completion of the reaction, as monitored by TLC, the mixture was filtered, washing with TFE (6 mL). The filtrate was concentrated via rotary evaporation and the crude product was purified using silica-gel flash column chromatography (30% toluene/petroleum ether) to yield the title compound as a yellow oil (0.30 g, 44% over 2 steps). Characterization data is in good agreement with previously reported data.⁷

TLC Rf: 0.38 in 30% Toluene/Petroleum ether

¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.24 (m, 4H), 7.20 (tdd, J = 10.0, 4.2, 2.7 Hz, 1H), 7.11 – 6.95 (m, 2H), 6.64 (td, J = 7.4, 1.2 Hz, 1H), 6.59 – 6.49 (m, 1H), 5.88 (ddt, J = 16.6, 10.3, 6.2 Hz, 1H), 5.10 – 4.94 (m, 2H), 4.27 (s, 2H), 4.07 (br s, 1H), 3.24 (dt, J = 6.2, 1.7 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 146.1 (C), 139.4 (C), 136.0 (CH), 129.8 (CH), 128.6 (CH), 127.7 (CH), 127.4 (CH), 127.2 (CH), 123.6 (C), 117.4 (CH), 116.4 (CH₂), 110.8 (CH), 48.2 (CH₂), 36.6 (CH₂).

N-(Pyridin-2-ylmethyl)pent-4-enum-1-amine 1n

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.49 g, 10.0 mmol), pyridine-2-ylmethanamine (5.20 mL, 50.0 mmol), sodium iodide (0.075 g, 0.50 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (8% MeOH/DCM to 12% MeOH/DCM) to yield the title compound as an orange oil (1.39 g, 79%).

TLC Rf: 0.40 in 10% MeOH/DCM

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⁷ H. Shen, Q. Deng, R. Liu, Y. Feng, C. Zheng and Y. Xiong, Org. Chem. Front. 2017, 4, 1806-1811.
**N-(Thiophen-2-ylmethyl)pent-4-en-1-amine 1o**

To a round bottom flask was added 5-bromopent-1-ene (1.01 g, 6.8 mmol) followed by dilution in DMSO (1 M). NaN₃ (0.771 g, 11.9 mmol) was added and the mixture was stirred at room temperature for 3 h until the solution gets cloudy. Upon completion, the reaction mixture was poured into water (50 mL) and extracted with Et₂O (50 mL x 2), then the organic layer was dried through Na₂SO₄. PPh₃ (3.56 g, 13.6 mmol) and thiophene – 2 – carbaldehyde (0.76 g, 6.8 mmol) were added to the ether solution and the mixture was stirred over night at room temperature. The reaction mixture was concentrated via rotary evaporation and added MeOH (20 mL) followed by NaBH₄ (0.308 g, 8.13 mmol). The mixture was stirred at room temperature for 1h. Upon completion, HCl 1 M (20 mL) and H₂O (30 mL) were added, the slurry mixture was filtered to remove phosphine-based by-products. The acidic solution was extracted with Et₂O (50 mL) to remove other impurities and then basified by NaOH 1M (25 mL). The basic solution was extracted by DCM (50 mL x 2), then the DCM layer was rinsed with water (x1), and then brine (x1). The organic phase was dried with Na₂SO₄ and filtered. The filtrate was concentrated via rotary evaporation. The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% Et₃N) to yield the title compound as a yellow oil (0.43 g, 37%).

TLC Rf: 0.44 in 30% EtOAc/Hexanes
3.91 (d, J = 0.8 Hz, 2H), 2.72 – 2.50 (m, 2H), 2.03 (dtt, J = 7.9, 6.6, 1.4 Hz, 2H), 1.63 – 1.46 (m, 2H), 1.31 (br s, 1H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ 144.3 (C), 138.4 (CH), 126.5 (CH), 124.6 (CH), 124.2 (CH), 114.6 (CH\(_2\)), 48.5 (CH\(_2\)), 48.3 (CH\(_2\)), 31.4 (CH\(_2\)), 29.1 (CH\(_2\)).

IR (FTIR): 3309, 3070, 2919, 2812, 1639, 1437, 1108, 908, 691 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{10}\)H\(_{15}\)NS [M]+ 181.0925. Found: 181.0940.

\(N-(2\text{-Methoxybenzyl})\text{pent-4-en-1-amine 1p}\)

The title compound was synthesized according to \textit{general procedure A} using 5-bromopent-1-ene (1.013 g, 6.80 mmol), (2-methoxyphenyl)methanamine (4.44 mL, 34.0 mmol), sodium iodide (0.102 g, 0.680 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% Et\(_3\)N) to yield the title compound as a yellow oil (0.904 g, 65%).

TLC R\(_f\): 0.25 in 30% EtOAc/Hexanes

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.20 – 7.12 (m, 2H), 6.84 (td, J = 7.4, 1.1 Hz, 1H), 6.79 (dd, J = 8.6, 1.1 Hz, 1H), 5.74 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.93 (dq, J = 17.1, 1.7 Hz, 1H), 4.87 (ddt, J = 10.2, 2.3, 1.3 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.54 (m, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ 157.7 (C), 138.7 (CH), 129.8 (CH), 128.6 (C), 128.1 (CH), 120.4 (CH), 114.5 (CH\(_2\)), 110.2 (CH), 55.2 (CH\(_3\)), 49.4 (CH\(_2\)), 48.8 (CH\(_2\)), 31.6 (CH\(_2\)), 29.3 (CH\(_2\)).

IR (FTIR): 3332, 3074, 2926, 2835, 1639, 1600, 1490, 1237, 1029, 908, 749 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{19}\)NO [M]+ 205.1467. Found: 205.1459.

\(N-(3\text{-Methoxybenzyl})\text{pent-4-en-1-amine 1q}\)

The title compound was synthesized according to \textit{general procedure A} using 5-bromopent-1-ene (1.01 g, 6.80 mmol), (3-methoxyphenyl)methanamine (4.35 mL, 34.0 mmol), sodium iodide (0.102 g, 0.680 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (20% EtOAc/Hexanes + 1% Et\(_3\)N) to yield the title compound as a yellow oil (0.904 g, 65%).

TLC R\(_f\): 0.25 in 30% EtOAc/Hexanes

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.20 – 7.12 (m, 2H), 6.84 (td, J = 7.4, 1.1 Hz, 1H), 6.79 (dd, J = 8.6, 1.1 Hz, 1H), 5.74 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.93 (dq, J = 17.1, 1.7 Hz, 1H), 4.87 (ddt, J = 10.2, 2.3, 1.3 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.54 (m, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ 157.7 (C), 138.7 (CH), 129.8 (CH), 128.6 (C), 128.1 (CH), 120.4 (CH), 114.5 (CH\(_2\)), 110.2 (CH), 55.2 (CH\(_3\)), 49.4 (CH\(_2\)), 48.8 (CH\(_2\)), 31.6 (CH\(_2\)), 29.3 (CH\(_2\)).

IR (FTIR): 3332, 3074, 2926, 2835, 1639, 1600, 1490, 1237, 1029, 908, 749 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{19}\)NO [M]+ 205.1467. Found: 205.1459.
chromatography (20% EtOAc/Hexanes + 1% Et$_3$N) to yield the title compound as a yellow oil (0.97 g, 69%).

TLC R$_f$: 0.3 in 30% EtOAc/Hexanes

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.19 – 7.12 (m, 1H), 6.85 – 6.79 (m, 2H), 6.71 (ddd, $J = 8.2, 2.6, 1.0$ Hz, 1H), 5.74 (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 4.94 (dq, $J = 17.1, 1.7$ Hz, 1H), 4.87 (ddt, $J = 10.2, 2.3, 1.3$ Hz, 1H), 3.73 (s, 3H), 3.69 (s, 2H), 2.60 – 2.53 (m, 2H), 2.07 – 1.99 (m, 2H), 1.54 (p, $J = 7.4$ Hz, 2H), 1.20 (s, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.8 (C), 142.3 (C), 138.6 (CH), 129.4 (CH), 120.4 (CH), 114.6 (CH$_2$), 113.6 (CH), 112.4 (CH), 55.2 (CH$_3$), 54.0 (CH$_2$), 49.0 (CH$_2$), 31.6 (CH$_2$), 29.3 (CH$_2$).

IR (FTIR): 3310, 3075, 2925, 2831, 1584, 1451, 1260, 1152, 1042, 908, 775, 691 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{13}$H$_{19}$NO [M]+ 205.1467. Found: 205.1489.

![Structure](image)

N-((Tetrahydrofuran-2-yl)methyl)pent-4-en-1-amine 1r

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.49 g, 10.0 mmol), (tetrahydrofuran-2-yl)methanamine (5.20 mL, 50.0 mmol), sodium iodide (0.075 g, 0.50 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (12% MeOH/DCM) to yield the title compound as a pale yellow oil (1.03 g, 61%).

TLC R$_f$: 0.31 in 10% MeOH/DCM

$^1$H NMR (400 MHz, CDCl$_3$): δ 5.80 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 1H), 5.00 (ap dq, $J = 17.1, 1.7$ Hz, 1H), 4.94 (ddt, $J = 10.2, 2.2, 1.3$ Hz, 1H), 4.00 (qd, $J = 7.3, 3.9$ Hz, 1H), 3.84 (dt, $J = 8.4, 6.7$ Hz, 1H), 3.73 (dt, $J = 8.3, 6.8$ Hz, 1H), 2.72 – 2.56 (m, 4H), 2.13 – 2.03 (m, 2H), 1.96 (dddd, $J = 11.5, 8.5, 6.7, 5.1$ Hz, 1H), 1.91 – 1.82 (m, 2H), 1.65 – 1.43 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.5 (CH), 114.5 (CH$_2$), 78.2 (CH), 67.8 (CH$_2$), 54.4 (CH$_2$), 49.6 (CH$_2$), 31.5 (CH$_2$), 29.3 (CH$_2$), 29.2 (CH$_2$), 25.7 (CH$_2$).

IR (FTIR): 3054, 2959, 2912, 2847, 1637, 1462, 1129, 1056, 996, 905, 737 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{10}$H$_{18}$NO [M – H]$^+$ 168.1388. Found: 168.1387.
3-(Pent-4-en-1-ylamino)propan-1-ol 1s

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (1.01 g, 6.80 mmol), (3-methoxyphenyl)methanamine (2.59 mL, 34.0 mmol), sodium iodide (0.102 g, 0.680 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (40% MeOH/DCM + 1% NH₄OH) to yield the title compound as a yellow oil (0.45 g, 46%).

TLC Rf: 0.32 in 40% MeOH/DCM + 1% NH₄OH

^1^H NMR (500 MHz, CDCl₃): δ 5.79 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (dq, J = 17.1, 1.7 Hz, 1H), 4.96 (dq, J = 10.1, 1.4 Hz, 1H), 3.83 – 3.77 (m, 2H), 3.07 (br s, 2H), 2.90 – 2.84 (m, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.69 (p, J = 5.5 Hz, 2H), 1.57 (p, J = 7.3 Hz, 2H).

^1^3^C NMR (125 MHz, CDCl₃): δ 138.2 (CH), 114.9 (CH₂), 64.6 (CH₂), 50.2 (CH₂), 49.2 (CH₂), 31.4 (CH₂), 30.6 (CH₂), 29.0 (CH₂).

IR (FTIR): 3268, 3071, 2924, 2833, 1639, 1437, 1114, 1060, 907 cm⁻¹.

HRMS (ESI): Exact mass calcd for C₁₉H₁₈NO [M+H]^+ 144.1388. Found: 144.1360.

(R)-2-(Pent-4-en-1-ylamino)-2-phenylethanol 1t

The title compound was synthesized according to general procedure A using 5-bromopent-1-ene (0.745 g, 5.00 mmol), (R)-2-amino-2-phenylethanol (3.43 g, 25.0 mmol), sodium iodide (0.038 g, 0.025 mmol) in EtOH (2.5 M). The product was purified using silica-gel flash column chromatography (70% EtOAc/Hexanes) to yield the title compound as a pale yellow oil (0.615 g, 60%).

TLC Rf: 0.35 in 70% EtOAc/Hexanes

^1^H NMR (500 MHz, CDCl₃): δ 7.40 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 5.78 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (ap dq, J = 17.1, 1.7 Hz, 1H), 4.94 (ddt, J = 10.2, 2.3, 1.4 Hz, 1H), 3.75 (dd, J = 8.5, 4.5 Hz, 1H), 3.70 (dd, J = 10.5, 4.5 Hz, 1H), 3.52 (dd, J = 10.5, 8.5 Hz, 1H), 2.59 (dt, J = 11.5, 7.1 Hz, 1H), 2.49 (dddd, J = 11.5, 7.6, 6.5 Hz, 1H), 2.19 – 1.99 (m, 2H), 1.58 (dddd, J = 12.8, 11.2, 9.3, 6.5 Hz, 2H).
\[^{13}\text{C NMR (125 MHz, CDCl\textsubscript{3})}\]: \(\delta\) 140.9 (C), 138.4 (CH), 128.6 (CH), 127.6 (CH), 127.0 (CH), 114.7 (CH\textsubscript{2}), 66.5 (CH\textsubscript{2}), 64.5 (CH), 46.8 (CH\textsubscript{2}), 31.4 (CH\textsubscript{2}), 29.4 (CH\textsubscript{2}).

IR (FTIR): 3336, 3053, 2908, 2823, 1643, 1472, 1449, 1041, 916, 753, 699 cm\(^{-1}\).

HRMS (ESI): Exact mass calcd for \(\text{C}_{13}\text{H}_{20}\text{NO}[\text{M+H}]^+\) 206.1545. Found: 206.1555.

\[\text{N-}(2\text{-Morpholinoethyl})\text{pent-4-en-1-amine 1u}\]

The title compound was synthesized according to \textbf{general procedure A} using 5-bromopent-1-ene (1.49 g, 10.0 mmol), 2-morpholinoethanamine (6.60 mL, 50.0 mmol), sodium iodide (0.075 g, 0.50 mmol) in EtOH (2.5 M). The product was adequately pure with further purification yielding the title compound as a yellow oil (1.62 g, 82%).

TLC \(R_f\): 0.50 in 10% MeOH/DCM

\(^1\text{H NMR (400 MHz, CDCl\textsubscript{3})}\): \(\delta\) 5.81 (ddt, \(J = 16.9, 10.1, 6.7\) Hz, 1H), 5.01 (ap dq, \(J = 17.1, 1.7\) Hz, 1H), 4.94 (ddt, \(J = 10.1, 2.3, 1.2\) Hz, 1H), 3.77 – 3.62 (m, 4H), 2.69 (dd, \(J = 6.6, 5.6\) Hz, 2H), 2.65 – 2.58 (m, 2H), 2.48 (dd, \(J = 6.6, 5.7\) Hz, 2H), 2.45 – 2.35 (m, 4H), 2.15 – 2.03 (m, 2H), 1.65 – 1.49 (m, 2H).

\[^{13}\text{C NMR (100 MHz, CDCl\textsubscript{3})}\]: \(\delta\) 138.4 (CH), 114.6 (CH\textsubscript{2}), 67.0 (CH\textsubscript{2}), 58.3 (CH\textsubscript{2}), 53.7 (CH\textsubscript{2}), 49.4 (CH\textsubscript{2}), 46.0 (CH\textsubscript{2}), 31.5 (CH\textsubscript{2}), 29.1 (CH\textsubscript{2}).

IR (FTIR): 3085, 2915, 2846, 2813, 1636, 1450, 1270, 1118, 907, 758 cm\(^{-1}\).

HRMS (ESI): Exact mass calcd for \(\text{C}_{11}\text{H}_{23}\text{N}_{2}\text{O}[\text{M+H}]^+\) 199.1810. Found: 199.1818.
2-Allylaniline 1v

The title compound was prepared using a modified literature procedure to yield the title compound as a yellow oil (0.57 g, 57%). Characterization data is in good agreement with previously reported data.\(^8\)

TLC Rf: 0.38 in 10% EtOAc/Petroleum ether

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.05 – 6.91 (m, 2H), 6.67 (tt, \(J = 7.4, 1.3\) Hz, 1H), 6.59 (d, \(J = 7.8\) Hz, 1H), 5.97 – 5.77 (m, 1H), 5.10 – 4.94 (m, 2H), 3.62 – 3.53 (m, 2H), 3.22 (dd, \(J = 6.0, 1.6\) Hz, 2H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.8 (C), 136.0 (CH), 130.2 (CH), 127.6 (CH), 124.0 (C), 118.9 (CH), 116.1 (CH\(_2\)), 115.8 (CH), 36.5 (CH\(_2\)).

1-Benzyl-2-methylpyrrolidine 4a

The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1a (0.105 g, 0.60 mmol), B\(_2\)(OH)\(_4\) (0.064 g, 0.72 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a pale yellow oil (0.090 g, 85%). Characterization data is in good agreement with previously reported data.\(^9\)

TLC Rf: 0.45 in 10% MeOH/DCM

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.34 – 7.29 (m, 4H), 7.25 – 7.22 (m, 1H), 4.02 (d, \(J = 12.8\) Hz, 1H), 3.14 (d, \(J = 12.8\) Hz, 1H), 2.91 (td, \(J = 10.8, 2.6\) Hz, 1H), 2.39 (dq, \(J = 13.5, 6.2\) Hz, 1H), 2.10 (q, \(J = 9.0\) Hz, 1H), 1.94 (dddd, \(J = 12.5, 9.7, 7.3, 5.3\) Hz, 1H), 1.76 – 1.67 (m, 1H), 1.64 (dddd, \(J = 13.8, 8.7, 6.3, 3.3\) Hz, 1H), 1.46 (dddd, \(J = 12.5, 10.8, 8.6, 5.8\) Hz, 1H), 1.18 (d, \(J = 6.0\) Hz, 3H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 139.6 (C), 129.1 (CH), 128.2 (CH), 126.8 (CH), 59.6 (CH), 58.4 (CH\(_2\)), 54.1 (CH\(_2\)), 32.8 (CH\(_2\)), 21.5 (CH\(_2\)), 19.2 (CH\(_3\)).

\(^8\) S. Fu, S.; H. Yang, G. Li, Y. Deng, H. Jiang and W. Zeng, Org. Lett. 2015, 17, 1018–1021.
\(^9\) J. Zhang and S. Chang, J. Am. Chem. Soc. 2020, 142, 12585.
2-Methyl-1-(4-methylbenzyl)pyrrolidine 4b
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1b (0.114 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1 M HCl was added, and the phases were separated. Additional 20 mL of water was added into DCM layer, the aqueous phases were separated and combined. The product was isolated after basic extraction to yield the title compound as a yellow oil (0.076 g, 67%).

TLC Rf: 0.39 in 5% MeOH/DCM + 0.5% NH$_4$OH

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.15 – 7.10 (m, 2H), 7.09 – 6.99 (m, 2H), 3.90 (d, $J = 12.7$ Hz, 1H), 3.05 (d, $J = 12.8$ Hz, 1H), 2.82 (ddd, $J = 9.4$, 8.1, 2.6 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.25 (s, 3H), 2.02 (q, $J = 9.0$ Hz, 1H), 1.85 (ddddd, $J = 12.5$, 9.7, 7.4, 5.3 Hz, 1H), 1.69 – 1.57 (m, 1H), 1.57 – 1.48 (m, 1H), 1.38 (ddddd, $J = 12.3$, 10.8, 8.6, 5.8 Hz, 1H), 1.09 (d, $J = 6.0$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 136.4 (C), 136.2 (C), 129.1 (CH), 128.9 (CH), 59.6 (CH$_3$), 57.9 (CH$_2$), 53.9 (CH$_2$), 32.8 (CH$_2$), 21.5 (CH$_2$), 21.1 (CH), 19.1 (CH$_3$).

IR (FTIR): 3004, 2960, 2779, 1513, 1373, 1138, 1100, 804 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{13}$H$_{19}$N [M]+ 189.1517. Found: 189.1515.

2-Methyl-1-phenethylpyrrolidine 4c
The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.085 g, 0.90 mmol), amine 1c (0.114 g, 0.60 mmol), B$_2$(OH)$_4$ (0.081 g, 0.90 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a pale yellow oil (0.078 g, 68%).

TLC Rf: 0.45 in 10% MeOH/DCM
\[ ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 7.32} - 7.25 (m, 2H), 7.22 - 7.15 (m, 3H), 3.26 (td, } J = 8.7, 2.7 \text{ Hz, 1H), 3.03 (td, } J = 11.5, 5.8 \text{ Hz, 1H), 2.83 (pd, } J = 13.0, 5.6 \text{ Hz, 2H), 2.37 - 2.26 (m, 2H), 2.20 (q, } J = 8.8 \text{ Hz, 1H), 1.93 (dddd, } J = 12.3, 9.7, 7.2, 5.2 \text{ Hz, 1H), 1.82 (dddd, } J = 17.3, 10.8, 8.5, 5.2 \text{ Hz, 1H), 1.71 (dddd, } J = 12.5, 11.4, 6.0, 2.7 \text{ Hz, 1H), 1.45 (dddd, } J = 12.3, 10.6, 8.7, 6.0 \text{ Hz, 1H), 1.12 (d, } J = 6.1 \text{ Hz, 3H).} \]

\[ ^{13}\text{C NMR (125 MHz, CDCl}_3\text{): } \delta \text{ 140.7 (C), 128.6 (CH), 128.3 (CH), 126.0 (CH), 60.0 (CH), 56.1 (CH}_2\text{), 54.0 (CH}_2\text{), 35.5 (CH}_2\text{), 32.7 (CH}_2\text{), 21.7 (CH}_2\text{), 18.93 (CH}_3\text{).} \]

IR (FTIR): 3029, 2953, 2775, 1600, 1457, 1451, 1373, 1134, 743, 695 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_{13}\)H\(_{19}\)N [M]+189.1517. Found: 189.1495.

\[ \text{1-Isobutyl-2-methylpyrrolidine hydrochloride 4d} \]

The title compound was synthesized according to \textit{general procedure B} using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1d (0.114 g, 0.60 mmol), B\(_2\)(OH)\(_4\) (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1M HCl was added, and the phases were separated. Additional 20 mL of water was added into DCM layer, the aqueous phases were separated and combined. The product was isolated after basic extraction and direct salt formation in DCM by HCl/dioxane 4 M solution (0.2 mL, 0.8 mmol) to yield the title compound as a white solid (0.079 g, 74%).

TLC R\(_f\): 0.18 in 5% MeOH/DCM + 0.5% NH\(_4\)OH

\[ ^1\text{H NMR (500 MHz, CD}_3\text{OD): } \delta \text{ 3.75 (ddd, } J = 11.6, 7.9, 5.5 \text{ Hz, 1H), 3.48 (dt, } J = 9.9, 6.5 \text{ Hz, 1H), 3.24 - 3.11 (m, 2H), 2.93 (dd, } J = 12.8, 5.2 \text{ Hz, 1H), 2.31 (dtd, } J = 13.0, 7.5, 5.0 \text{ Hz, 1H), 2.10 (dqt, } J = 12.0, 8.6, 3.6 \text{ Hz, 4H), 1.82 (dq, } J = 13.1, 9.2 \text{ Hz, 1H), 1.49 (d, } J = 6.5 \text{ Hz, 3H), 1.10 (d, } J = 6.6 \text{ Hz, 3H), 1.06 (d, } J = 6.7 \text{ Hz, 3H).} \]

\[ ^{13}\text{C NMR (125 MHz, CD}_3\text{OD): } \delta \text{ 65.8 (CH), 61.1 (CH}_2\text{), 53.9 (CH}_2\text{), 30.8 (CH}_2\text{), 25.5 (CH), 21.0 (CH}_2\text{), 19.8 (CH}_3\text{), 19.2 (CH}_3\text{), 14.6 (CH}_3\text{).} \]

IR (FTIR): 3398, 2964, 2873, 2592, 1420, 1047 cm\(^{-1}\).

HRMS (EI): Exact mass calcd for C\(_9\)H\(_{19}\)N [M]+ 141.1517. Found: 141.1533.
1-(Cyclohexylmethyl)-2-methylpyrrolidine 4e
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1e (0.109 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1M HCl was added, and the phases were separated. Additional 20 mL of water was added into DCM layer, the aqueous phases were separated and combined. The product was isolated after basic extraction to yield the title compound as a yellow oil (0.070 g, 64%).

TLC R$_f$: 0.38 in 5% MeOH/DCM + 0.5% NH$_4$OH

$^1$H NMR (500 MHz, CDCl$_3$): δ 3.07 (td, J = 8.7, 2.8 Hz, 1H), 2.44 (dd, J = 11.9, 9.4 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.97 (q, J = 8.9 Hz, 1H), 1.92 – 1.75 (m, 3H), 1.75 – 1.53 (m, 6H), 1.43 – 1.29 (m, 2H), 1.24 – 1.01 (m, 3H), 1.00 (d, J = 6.1 Hz, 3H), 0.89 – 0.72 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 61.8 (CH$_2$), 60.8 (CH), 54.6 (CH$_2$), 37.1 (CH), 32.6 (CH$_2$), 32.5 (CH$_2$), 32.0 (CH$_2$), 26.8 (CH$_2$), 26.3 (CH$_2$), 26.1 (CH$_2$), 21.8 (CH$_2$), 19.0 (CH$_3$).

IR (FTIR): 2958, 2918, 2849, 2779, 1447, 1374, 1170, 1118 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{12}$H$_{23}$N [M]+ 181.1830. Found: 181.1821.

2-Methyl-1-(1-phenylethyl)pyrrolidine 4f
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1f (0.114 g, 0.60 mmol), B$_2$(OH)$_4$ (0.065 g, 0.72 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a 2.2:1 diastereomeric mixture and a pale yellow oil (0.098 g, 86%).

TLC R$_f$: 0.40 in 10% MeOH/DCM
1H NMR (500 MHz, CDCl3): δ (major) 7.38 – 7.20 (m, 5H), 3.86 (q, J = 6.9 Hz, 1H), 2.86 (td, J = 8.5, 3.3 Hz, 1H), 2.55 (ap h, J = 6.3 Hz, 1H), 2.41 (q, J = 8.2 Hz, 1H), 1.82 (ddt, J = 11.8, 9.0, 7.3 Hz, 1H), 1.74 (tdd, J = 9.3, 7.4, 4.4 Hz, 1H), 1.61 – 1.54 (m, 1H), 1.47 (d, J = 6.9 Hz, 3H), 1.43 – 1.39 (m, 1H), 1.11 (d, J = 6.1 Hz, 3H). δ (minor) 7.38 – 7.20 (m, 5H), 3.68 (q, J = 6.7 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.77 (dt, J = 9.1, 3.7 Hz, 1H), 2.46 (q, J = 8.8 Hz, 1H), 1.92 (ddt, J = 12.3, 9.2, 7.7 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.66 (ddd, J = 16.0, 7.8, 3.7 Hz, 1H), 1.43 – 1.39 (m, 1H), 1.36 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.2 Hz, 3H).

13C NMR (125 MHz, CDCl3): δ (major) 140.2 (C), 128.1 (CH), 127.9 (CH), 126.8 (CH), 58.7 (CH), 54.9 (CH), 48.2 (CH2), 32.5 (CH2), 21.8 (CH2), 19.4 (CH3), 18.4 (CH3). δ (minor) 141.9 (C), 128.0 (CH), 127.7 (CH), 126.6 (CH), 60.4 (CH), 56.2 (CH), 49.8 (CH2), 32.9 (CH2), 22.3 (CH2), 21.8 (CH3), 19.0 (CH3).

IR (FTIR): 3019, 2965, 2875, 2777, 1456, 1449, 1367, 1153, 757, 698 cm⁻¹.

HRMS (EI): Exact mass calcd for C13H19N [M]+ 189.1517. Found: 189.1532.

2-Methyl-1-((R)-1-phenylethyl)pyrrolidine 4g

The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1g (0.114 g, 0.60 mmol), B2(OH)4 (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.067 g, 59%).

TLC Rf: 0.40 in 10% MeOH/DCM

1H NMR (500 MHz, CDCl3): δ (major) 7.38 – 7.20 (m, 5H), 3.86 (q, J = 6.9 Hz, 1H), 2.86 (td, J = 8.3, 3.4 Hz, 1H), 2.54 (ap h, J = 6.3 Hz, 1H), 2.40 (q, J = 8.1 Hz, 1H), 1.82 (ddt, J = 11.8, 9.0, 7.3 Hz, 1H), 1.74 (tdd, J = 9.3, 7.4, 4.4 Hz, 1H), 1.61 – 1.54 (m, 1H), 1.46 (d, J = 6.9 Hz, 3H), 1.43 – 1.39 (m, 1H), 1.10 (d, J = 6.1 Hz, 3H). δ (minor) 7.38 – 7.20 (m, 5H), 3.67 (q, J = 6.6 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.77 (dt, J = 8.7, 3.7 Hz, 1H), 2.45 (q, J = 8.8 Hz, 1H), 1.92 (ddt, J = 12.2, 9.2, 7.7 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.66 (ddd, J = 16.0, 7.8, 3.7 Hz, 1H), 1.43 – 1.39 (m, 1H), 1.36 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.2 Hz, 3H).

13C NMR (125 MHz, CDCl3): δ (major) 140.9 (C), 128.1 (CH), 127.9 (CH), 126.8 (CH), 58.7 (CH), 54.9 (CH), 48.2 (CH2), 32.5 (CH2), 21.8 (CH2), 19.4 (CH3), 18.4 (CH3). δ (minor) 141.9 (C), 128.0 (CH), 127.7 (CH), 126.6 (CH), 60.4 (CH), 56.2 (CH), 49.9 (CH2), 32.9 (CH2), 22.3 (CH2), 21.7 (CH3), 19.0 (CH3).
IR (FTIR): 3018, 2957, 2865, 2779, 1456, 1450, 1367, 1155, 763, 699 cm$^{-1}$.

HRMS (ESI): Exact mass calcd for C$_{13}$H$_{20}$N [M+H]$^+$ 190.1596. Found: 190.1591.

\[
\begin{array}{c}
\text{IR (FTIR): 3018, 2957, 2865, 2779, 1456, 1450, 1367, 1155, 763, 699 cm}^{-1}. \\
\text{HRMS (ESI): Exact mass calcd for C$_{13}$H$_{20}$N [M+H]$^+$ 190.1596. Found: 190.1591.}
\end{array}
\]

1-Benzyl-2,5-dimethylpyrrolidine 4h
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1h (0.134 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1 M HCl was added, and the phases were separated. 15 mL of 1 M KOH and 100 mL of brine were added. The product was isolated after 3 x 50 mL DCM extractions to yield the title compound as a 6.8:1 diastereomeric mixture as a pail yellow oil (0.089 g, 78%). Characterization data is in good agreement with previously reported data.$^3$

TLC Rf: 0.48 in 5% MeOH/DCM + 1% NEt$_3$

$^1$H NMR (500 MHz, CDCl$_3$) δ (cis) 7.25 – 7.09 (m, 5H), 3.65 (s, 2H), 2.55 – 2.44 (m, 2H), 1.74 – 1.64 (m, 2H), 1.34 – 1.23 (m, 2H), 0.97 (d, J = 6.1 Hz, 6H). δ (trans) 7.41 – 7.00 (m, 5H), 3.75 (d, J = 13.8 Hz, 1H), 3.43 (d, J = 13.8 Hz, 1H), 2.99 – 2.86 (m, 2H), 1.97 – 1.84 (m, 2H), 1.34 – 1.23 (m, 2H), 0.89 (d, J = 6.3 Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (cis) 139.3 (C), 129.3 (CH), 128.0 (CH), 126.7 (CH), 59.7 (CH), 55.2 (CH$_2$), 31.3 (CH$_2$), 20.7 (CH$_3$). δ (trans) 140.4 (C), 128.6 (CH), 128.1 (CH), 126.5 (CH), 55.1 (CH), 51.7 (CH$_2$), 31.0 (CH$_2$), 17.1 (CH$_3$).

1-Benzyl-2,2-dimethylpyrrolidine 4i
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1i (0.114 g, 0.60 mmol), B$_2$(OH)$_4$ (0.065 g, 0.72 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1 M HCl was added, and the phases were
separated. The product was isolated after basic extraction to yield the title compound as a yellow oil (0.077 g, 68%). Characterization data is in good agreement with previously reported data.\textsuperscript{10}

TLC Rf: 0.34 in 5\% MeOH/DCM + 1\% NEt$_3$

$^1$H NMR (300 MHz, CDCl$_3$)  $\delta$ 7.30 –  7.06 (m, 5H), 3.42 (s, 2H), 2.60 –  2.45 (m, 2H), 1.73 –  1.52 (m, 4H), 1.01 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.0 (C), 128.6 (CH), 128.2 (CH), 126.6 (CH), 60.2 (C), 53.2 (CH$_2$), 50.9 (CH$_2$), 40.0 (CH$_2$), 23.1 (CH$_3$), 20.5 (CH$_2$).

![Structure](image)

1-Benzyl-2-ethylpyrrolidine 4j

The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1j$'$ (0.114 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.053 g, 47%). Characterization data is in good agreement with previously reported data.\textsuperscript{5}

TLC Rf: 0.34 in 10\% MeOH/DCM

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.39 –  7.25 (m, 5H), 4.05 (d, J = 12.9 Hz, 1H), 3.17 (d, J = 12.9 Hz, 1H), 2.93 (ddd, J = 9.1, 7.3, 2.4 Hz, 1H), 2.29 (qd, J = 8.1, 3.1 Hz, 1H), 2.12 (q, J = 9.0 Hz, 1H), 1.93 (ddd, J = 12.3, 9.5, 7.8, 6.0 Hz, 1H), 1.79 (dq, J = 13.2, 7.5, 3.3 Hz, 1H), 1.72 –  1.59 (m, 2H), 1.51 (ddd, J = 13.2, 10.2, 8.0, 5.3 Hz, 1H), 1.43 –  1.27 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 139.1 (C), 129.1 (CH), 128.2 (CH), 126.8 (CH), 65.8 (CH), 58.5 (CH$_2$), 54.2 (CH$_2$), 29.8 (CH$_2$), 26.5 (CH$_2$), 21.8 (CH$_2$), 10.5 (CH$_3$).

![Structure](image)

2-Methyl-1-phenylpyrrolidine 4k

The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1k (0.097 g, 0.60 mmol), B$_2$(OH)$_4$ (0.645 g, 0.72 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title

\textsuperscript{10} A. Agosti, S. Britto and P. Renaud, Org. Lett. 2008, 10, 1417-1420.
compound as a brown oil (0.049 g, 51%). Characterization data is in good agreement with previously reported data.\textsuperscript{11}

TLC Rf: 0.91 in 40% EtOAc/Hexanes

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta 7.25 - 7.19 \) (m, 2H), 6.67 – 6.59 (m, 1H), 6.61 – 6.52 (m, 2H), 3.88 (pd, \( J = 6.2 \), 1.6 Hz, 1H), 3.42 (ddd, \( J = 9.2 \), 7.6, 2.6 Hz, 1H), 3.16 (td, \( J = 8.9 \), 6.8 Hz, 1H), 2.13 – 2.01 (m, 2H), 1.97 (ddddd, \( J = 10.0 \), 7.4, 5.1, 3.0 Hz, 1H), 1.71 (ddddd, \( J = 10.3 \), 7.8, 6.5, 2.3 Hz, 1H), 1.17 (d, \( J = 6.2 \) Hz, 3H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta 147.2 \) (C), 129.1 (CH), 115.1 (CH), 111.7 (CH), 53.6 (CH), 48.1 (CH\textsubscript{2}), 33.1 (CH\textsubscript{2}), 23.3 (CH\textsubscript{2}), 19.4 (CH\textsubscript{3}).

1-(3,5-Dimethylphenyl)-2-methylpyrrolidine 4I

The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1I (0.114 g, 0.60 mmol), \( \text{B}_2\text{O}_4\text{H}_4 \) (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and brine (50 mL), and the phases were separated. The aqueous phase was then extracted with DCM (50 mL). The combined organic phases were dried over Na\textsubscript{2}SO\textsubscript{4}, then filtered before concentration via rotary evaporation. The crude reaction mixture was purified by silica plug (100% DCM) to yield the title compound a viscous orange oil (0.054 g, 47%). Characterization data is in good agreement with previously reported data.\textsuperscript{12}

TLC Rf: 0.84 in 20% EtOAc/Hexanes

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta 6.32 \) (s, 1H), 6.23 (s, 2H), 3.92 – 3.79 (m, 1H), 3.41 (t, \( J = 7.7 \) Hz, 1H), 3.19 – 3.09 (m, 1H), 2.27 (s, 6H), 2.10 – 1.90 (m, 3H), 1.73 – 1.63 (m, 1H), 1.17 (d, \( J = 6.3 \) Hz, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta 147.4 \) (C), 138.7 (C), 117.2 (CH), 109.7 (CH), 53.5 (CH), 48.2 (CH\textsubscript{2}), 33.0 (CH\textsubscript{2}), 23.2 (CH\textsubscript{2}), 21.7 (CH\textsubscript{3}), 19.5 (CH\textsubscript{3}).

\textsuperscript{11} M. T. La, S. Kang and H.-K. Kim, J. Org. Chem. 2019, \textbf{84}, 6689.
\textsuperscript{12} V. H. Tran, M. T. La, S. Kang and H.-K. Kim, Org. Biomol. Chem. \textbf{2020}, \textit{18}, 5008-5016.
**1-Benzyl-2-methylindoline 4m**
The title compound was synthesized according to a modified **general procedure B** using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1m (0.134 g, 0.60 mmol), B$_2$(OH)$_4$ (0.065 g, 0.72 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, and it was purified by column chromatography (20% toluene/petroleum ether) to yield the title compound as a yellow oil (0.043 g, 32%). Characterization data is in good agreement with previously reported data.$^{13}$

TLC Rf: 0.3 in 20% Toluene/Petroleum ether

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.25 (m, 2H), 7.22 (dd, $J$ = 8.5, 6.8 Hz, 2H), 7.18 – 7.12 (m, 1H), 6.96 (dd, $J$ = 7.1, 1.3 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.54 (td, $J$ = 7.3, 1.0 Hz, 1H), 6.23 (d, $J$ = 7.8 Hz, 1H), 4.27 (d, $J$ = 16.1 Hz, 1H), 4.11 (d, $J$ = 16.1 Hz, 1H), 3.64 (ddq, $J$ = 9.5, 8.6, 6.1 Hz, 1H), 3.08 (dd, $J$ = 15.5, 8.6 Hz, 1H), 2.59 (ddt, $J$ = 15.5, 9.5, 1.1 Hz, 1H), 1.21 (d, $J$ = 6.1 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.8 (C), 139.3 (C), 128.9 (C), 128.5 (CH), 127.4 (CH), 127.4 (CH), 126.9 (CH), 124.2 (CH), 117.4 (CH), 106.9 (CH), 60.6 (CH), 51.2 (CH$_2$), 37.5 (CH$_2$), 19.7 (CH$_3$).

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**2-((2-Methylpyrrolidin-1-yl)methyl)pyridine 4n**
The title compound was synthesized according to a modified **general procedure B** using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1n (0.106 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as an orange oil (0.070 g, 66%).

TLC Rf: 0.29 in 10% MeOH/DCM

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.53 (ddd, $J$ = 5.0, 1.9, 0.9 Hz, 1H), 7.63 (td, $J$ = 7.6, 1.8 Hz, 1H), 7.14 (dd, $J$ = 7.9, 4.6 Hz, 1H), 7.41 (d, $J$ = 7.8 Hz, 1H), 4.11 (d, $J$ = 13.6 Hz, 1H), 3.38 (d, $J$ = 13.6 Hz, 1H), 2.97 (ddd, $J$ = 10.6, 8.4, 2.8 Hz, 1H), 2.50 (td, $J$ = 12.3, 4.9 Hz, 1H), 2.22 (q, $J$ = 8.9 Hz, 3H).

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$^{13}$ A. F. G. Maier, S. Tussing, T. Schneider, U. Flörke, Z.-W. Qu, S. Grimme and J. Paradies, *Angew. Chem. Int. Ed.* 2016, **10**, 12219–12223.
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1o (0.109 g, 0.60 mmol), Bu(OH)₂ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.071 g, 65%).

TLC Rf: 0.46 in 5% MeOH/DCM + 0.5% NH₄OH

1H NMR (500 MHz, CDCl₃): δ 7.11 (dd, J = 5.1, 1.3 Hz, 1H), 6.85 (dd, J = 5.1, 3.4 Hz, 1H), 6.84 – 6.80 (m, 1H), 4.04 (dd, J = 14.0, 1.0 Hz, 1H), 3.48 (d, J = 14.0 Hz, 1H), 2.95 (td, J = 8.7, 2.7 Hz, 1H), 2.40 – 2.28 (m, 1H), 2.16 (q, J = 8.9 Hz, 1H), 1.84 (dddd, J = 12.5, 9.6, 7.3, 5.2 Hz, 1H), 1.67 (dddd, J = 17.3, 10.8, 8.5, 5.2 Hz, 1H), 1.61 – 1.46 (m, 1H), 1.38 (dddd, J = 12.4, 10.8, 8.6, 6.0 Hz, 1H), 1.08 (d, J = 6.1 Hz, 3H).

13C NMR (125 MHz, CDCl₃): δ 142.1 (C), 126.4 (CH), 125.8 (CH), 124.6 (CH), 58.7 (CH), 53.7 (CH₂), 51.6 (CH₂), 32.8 (CH₂), 21.5 (CH₂), 19.0 (CH₃).

IR (FTIR): 3064, 2959, 2780, 1457, 1374, 1172, 852, 690 cm⁻¹.

HRMS (EI): Exact mass calcd for C₁₃H₁₅NS [M]+ 181.0925. Found: 181.0908.
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1p (0.123 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.077 g, 63%).

TLC R$_f$: 0.29 in 5% MeOH/DCM + 0.5% NH$_4$OH

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.26 (dd, $J = 7.4$, 1.8 Hz, 1H), 7.13 (td, $J = 7.8$, 1.8 Hz, 1H), 6.83 (td, $J = 7.4$, 1.1 Hz, 1H), 6.77 (dd, $J = 8.2$, 1.1 Hz, 1H), 3.91 (d, $J = 13.5$ Hz, 1H), 3.73 (s, 3H), 3.24 (d, $J = 13.4$ Hz, 1H), 2.94 (ddd, $J = 9.3$, 8.1, 2.5 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.09 (q, $J = 9.0$ Hz, 1H), 1.84 (ddd, $J = 12.5$, 9.7, 7.3, 5.2 Hz, 1H), 1.73 – 1.58 (m, 1H), 1.60 – 1.46 (m, 1H), 1.37 (ddd, $J = 12.3$, 10.8, 8.7, 5.9 Hz, 1H), 1.11 (d, $J = 6.0$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 157.7 (C), 130.8 (CH), 127.9 (CH), 127.5 (C), 120.2 (CH), 110.4 (CH), 59.6 (CH), 55.4 (CH), 54.2 (CH$_2$), 51.5 (CH$_2$), 32.8 (CH$_2$), 21.7 (CH$_2$), 19.2 (CH$_3$).

IR (FTIR): 3033, 2960, 2873, 1589, 1490, 1237, 1030, 750 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{13}$H$_{19}$NO [M]+ 205.1467. Found: 205.1450.

The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1q (0.123 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.083 g, 67%).

TLC R$_f$: 0.32 in 5% MeOH/DCM + 0.5% NH$_4$OH

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.12 (t, $J = 7.8$ Hz, 1H), 6.85 – 6.79 (m, 2H), 6.69 (ddd, $J = 8.2$, 2.7, 1.0 Hz, 1H), 3.90 (d, $J = 12.9$ Hz, 1H), 3.71 (s, 3H), 3.04 (d, $J = 12.9$ Hz, 1H), 2.84 (ddd, $J = 9.1$, 8.7, 1.0 Hz, 1H), 2.56 (ddd, $J = 12.5$, 9.7, 7.2 Hz, 1H), 2.09 (q, $J = 9.0$ Hz, 1H), 1.84 (ddd, $J = 12.5$, 9.7, 7.3, 5.2 Hz, 1H), 1.73 – 1.58 (m, 1H), 1.60 – 1.46 (m, 1H), 1.37 (ddd, $J = 12.3$, 10.8, 8.7, 5.9 Hz, 1H), 1.11 (d, $J = 6.0$ Hz, 3H).
8.0, 2.6 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.02 (q, J = 9.0 Hz, 1H), 1.84 (dddd, J = 12.5, 9.7, 7.3, 5.3 Hz, 1H), 1.68 – 1.58 (m, 1H), 1.58 – 1.49 (m, 1H), 1.37 (dddd, J = 12.4, 10.8, 8.6, 5.9 Hz, 1H), 1.08 (d, J = 6.0 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.6 (C), 141.3 (C), 129.1 (CH), 121.5 (CH), 114.6 (CH), 112.2 (CH), 59.7 (CH), 58.4 (CH$_2$), 55.2 (CH$_3$), 54.1 (CH$_2$), 32.8 (CH$_2$), 21.6 (CH$_2$), 19.2 (CH$_3$).

IR (FTIR): 3009, 2957, 2779, 1585, 1486, 1260, 1148, 1042, 770, 692 cm$^{-1}$.

HRMS (EI): Exact mass calcd for C$_{13}$H$_{19}$NO [M]+ 205.1467. Found: 205.1439.

2-Methyl-1-((tetrahydrofuran-2-yl)methyl)pyrrolidine 4r

The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.068 g, 0.72 mmol), amine 1r (0.102 g, 0.60 mmol), B$_2$(OH)$_4$ (0.118 g, 1.32 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a 1.1:1 diastereomeric mixture and a yellow oil (0.081 g, 80%).

Note: No common NMR solvents tested gave adequately resolved $^1$H NMR signals for unambiguous structural determination of the major and minor diastereomers. In CDCl$_3$, one signal was well – resolved: (minor) 2.91 (dd, J = 12.6, 8.1 Hz, 1H) and (major) 2.81 (dd, J = 12.4, 5.7 Hz, 1H). In benzene-$d_6$, three signals were well – resolved: (major) 4.05 (p, J = 6.5 Hz, 1H) and (minor) 3.96 (p, J = 4.8 Hz, 1H), (major) 3.30 (ddd, J = 9.8, 7.9, 2.8 Hz, 1H) and (minor) 3.22 (ddd, J = 8.9, 7.7, 3.0 Hz, 1H), (major) 2.76 (dd, J = 12.1, 6.5 Hz, 1H) and (minor) 2.85 (dd, J = 12.9, 5.8 Hz, 1H).

TLC Rf: 0.26 in 10% MeOH/DCM

$^1$H NMR (500 MHz, benzene-$d_6$): δ (major) 4.05 (p, J = 6.5 Hz, 1H), 3.77 – 3.72 (m, 1H), 3.63 – 3.53 (m, 1H), 3.30 (ddd, J = 9.8, 7.9, 2.8 Hz, 1H), 2.76 (dd, J = 12.1, 6.5 Hz, 1H), 2.38 – 2.27 (m, 1H), 2.27 – 2.18 (m, 1H), 2.15 (q, J = 8.8 Hz, 1H), 1.79 – 1.42 (m, 7H), 1.35 – 1.27 (m, 1H), 1.06 (dd, J = 6.0 Hz, 3H). δ (minor) 3.96 (p, J = 4.8 Hz, 1H), 3.77 – 3.72 (m, 1H), 3.63 – 3.53 (m, 1H), 3.22 (ddd, J = 8.9, 7.7, 3.0 Hz, 1H), 2.85 (dd, J = 12.9, 5.8 Hz, 1H), 2.38 – 2.27 (m, 2H), 2.27 – 2.18 (m, 1H), 1.79 – 1.42 (m, 7H), 1.35 – 1.27 (m, 1H), 1.05 (dd, J = 6.0 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ (1:1 mix of two diastereomers) 78.5 (CH), 77.5 (CH), 68.0 (CH$_2$), 67.8 (CH$_2$), 60.5 (CH, two overlapping signals), 58.9 (CH$_2$), 58.7 (CH$_2$), 54.9 (CH$_2$), 54.6 (CH$_2$), 32.4 (CH$_2$), 32.3 (CH$_2$), 30.5 (CH$_2$), 30.3 (CH$_2$), 25.5 (CH$_2$), 25.3 (CH$_2$), 21.9 (CH$_2$), 21.8 (CH$_2$), 19.0 (CH$_3$), 18.9 (CH$_3$).
IR (FTIR): 2953, 2859, 2777, 1545, 1376, 1168, 1056 cm⁻¹.

HRMS (EI): Exact mass calcd for C₁₀H₁₉NO [M]+ 169.1467. Found: 169.1477.

3-(2-Methylpyrrolidin-1-yl)propan-1-ol 4s
The title compound was synthesized according to general procedure B using urea hydrogen peroxide (0.0677 g, 0.72 mmol), amine 1s (0.086 g, 0.60 mmol), B₂(OH)₄ (0.118 g, 1.32 mmol) in TFE (0.1 M). The crude reaction mixture was concentrated via rotary evaporation, then diluted with DCM (50 mL) and water (50 mL). 10 mL of 1M HCl was added, and the phases were separated. 15 mL of 1M KOH and excessive amount of NaCl were added to saturate the acidic solution. The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.053 g, 62%).

TLC Rf: 0.46 in 40% MeOH/DCM + 1% NH₄OH

¹H NMR (500 MHz, CDCl₃) δ 4.69 (s, 1H), 3.78 – 3.68 (m, 2H), 3.26 (ddd, J = 9.4, 7.9, 3.2 Hz, 1H), 2.93 (td, J = 11.7, 4.1 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.30 – 2.20 (m, 1H), 2.04 (q, J = 8.8 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.74 – 1.54 (m, 2H), 1.49 (dp, J = 14.7, 3.8 Hz, 1H), 1.33 (ddddd, J = 12.5, 10.3, 8.5, 6.2 Hz, 1H), 1.08 (d, J = 6.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 64.6 (CH₂), 60.4 (CH), 54.2 (CH₂), 54.0 (CH₂), 32.6 (CH₂), 29.1 (CH₂), 21.6 (CH₂), 18.9 (CH₃).

IR (FTIR): 3335, 2955, 2868, 2796, 1374, 1061 cm⁻¹.

HRMS (EI): Exact mass calcd for C₈H₁₇NO [M]+ 143.1310. Found: 143.1330.

(2R)-2-(2-methylpyrrolidin-1-yl)-2-phenylethanol 4t
The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.055 g, 0.60 mmol), amine 1t (0.102 g, 0.50 mmol), B₂(OH)₄ (0.099 g, 1.10 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title
The title compound was synthesized according to a modified **general procedure B** using urea hydrogen peroxide (0.124 g, 1.32 mmol), amine 1u (0.119 g, 0.60 mmol), B$_2$(OH)$_4$ (0.172 g, 1.92 mmol) in TFE (0.1 M). The product was isolated after aqueous extraction to yield the title compound as a yellow oil (0.055 g, 46%).

**TLC Rf:** 0.25 in 10% MeOH/DCM

$^1$H NMR (500 MHz, CDCl$_3$): δ (major) 3.71 (t, J = 4.7 Hz, 4H), 3.17 (td, J = 8.7, 2.8 Hz, 1H), 2.97 (ddd, J = 11.7, 8.9, 6.5 Hz, 1H), 2.56 – 2.45 (m, 6H), 2.29 (dt, J = 8.5, 6.3 Hz, 1H), 2.19 (ddd, J = 11.7, 8.5, 6.4 Hz, 1H), 2.11 (q, J = 8.9 Hz, 1H), 1.90 (ddddd, J = 12.4, 9.7, 7.2, 5.2 Hz, 1H), 1.77 (ddddd, J = 17.3, 10.8, 8.5, 5.1 Hz, 1H), 1.69 (ddddd, J = 12.5, 9.6, 6.3, 3.2 Hz, 1H), 1.41 (ddddd, J = 12.4, 10.6, 8.7, 6.1 Hz, 1H), 1.10 (d, J = 6.1 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 66.9 (CH$_2$), 60.5 (CH), 58.1 (CH$_2$), 54.4 (CH$_2$), 54.2 (CH$_2$), 51.2 (CH$_2$), 32.4 (CH$_2$), 21.7 (CH$_2$), 18.9 (CH$_3$).

IR (FTIR): 2936, 2915, 2863, 1637, 1452, 1124, 994, 906, 763, 697 cm$^{-1}$.

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4-(2-(2-Methylpyrrolidin-1-yl)ethyl)morpholine 4u

The title compound was synthesized according to a modified **general procedure B** using urea hydrogen peroxide (0.081 g, 79%). Characterization data is in good agreement with previously reported data for the major diastereomer.$^{14}$

**TLC Rf:** 0.31 and 0.53 in 10% MeOH/DCM

$^1$H NMR (500 MHz, benzene-$d_6$): δ (major) 7.15 – 7.10 (m, 3H), 6.95 – 6.88 (m, 2H), 3.98 – 3.84 (m, 2H), 3.68 (dd, J = 9.7, 4.5 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.43 (ap h, J = 6.0 Hz, 1H), 2.02 (q, J = 8.5 Hz, 1H), 1.48 – 1.39 (m, 2H), 1.20 – 1.07 (m, 2H), 1.00 (d, J = 6.0 Hz, 3H). δ (minor) 7.31 – 7.20 (m, 2H), 7.15 – 7.10 (m, 3H), 3.98 – 3.84 (m, 1H), 3.75 (dd, J = 10.8, 5.7 Hz, 1H), 3.59 (t, J = 6.0 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.78 – 2.73 (m, 1H), 2.50 (dt, J = 9.1, 7.6 Hz, 1H), 1.63 – 1.48 (m, 2H), 1.37 – 1.27 (m, 1H), 1.20 – 1.07 (m, 1H), 0.83 (d, J = 6.2 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ (major) 134.9 (C), 129.2 (CH), 128.1 (CH), 127.8 (CH), 67.5 (CH), 62.0 (CH), 60.9 (CH$_2$), 54.5 (CH$_2$), 32.0 (CH$_2$), 21.5 (CH$_2$), 19.1 (CH$_3$). δ (minor) 138.4 (C), 129.0 (CH), 128.4 (CH), 127.8 (CH), 77.2 (CH), 63.4 (CH$_2$), 55.3 (CH), 52.5 (CH$_2$), 33.0 (CH$_2$), 22.4 (CH$_2$), 20.2 (CH$_3$).

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$^{14}$ J. M. Andres, I. Herraiz-Sierra, R. Pedrosa and A. Perez-Encabo, *Eur. J. Org. Chem.* 2000, **9**, 1719.
HRMS (EI): Exact mass calcd for C₁₁H₂₂N₂O [M]+ 198.1732. Found: 198.1760.

Gram – scale reaction

1-Benzyl-2-methylpyrrolidine 4a
The title compound was synthesized according to a modified general procedure B using urea hydrogen peroxide (0.678 g, 7.20 mmol), amine 1a (1.05 g, 6.00 mmol), B₂(OH)₄ (0.646 g, 7.20 mmol) in TFE (55 mL, 0.11 M). The reaction was stirred in a 55 mL volume screw cap vial (no headspace). The product was isolated after aqueous extraction to yield the title compound as a pale yellow oil (0.904 g, 86%). Characterization data is in good agreement with previously reported data.¹⁵

¹H NMR (500 MHz, CDCl₃): δ 7.34 – 7.29 (m, 4H), 7.25 – 7.22 (m, 1H), 3.96 (d, J = 12.8 Hz, 1H), 3.08 (d, J = 12.8 Hz, 1H), 2.85 (td, J = 10.8, 2.6 Hz, 1H), 2.32 (dq, J = 13.5, 6.2 Hz, 1H), 2.04 (q, J = 9.0 Hz, 1H), 1.88 (ddddd, J = 12.5, 9.7, 7.3, 5.3 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.64 (ddddd, J = 13.8, 8.7, 6.3, 3.3 Hz, 1H), 1.40 (ddddd, J = 12.5, 10.8, 8.6, 5.8 Hz, 1H), 1.11 (d, J = 6.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 131.2 (CH), 130.0 (C), 129.0 (CH), 128.9 (CH), 62.6 (CH), 55.6 (CH₂), 52.4 (CH₂), 31.3 (CH₂), 20.9 (CH₃), 15.8 (CH₃).

1-Benzyl-2-methylpyrrolidine 4a-HCl
To a stirred solution of pyrrolidine 4a in 10 mL ether was added 1.4 mL of 4M HCl in dioxane dropwise and solids precipitated immediately. The product was isolated after filtration, washing with hexanes, to yield the title compound as a 9.5:1 diastereomeric mixture as a white solid (0.931 g, 73%).

TLC Rf: 0.31 in 10% MeOH/DCM

¹H NMR (500 MHz, CDCl₃): δ (major) 12.45 (br s, 1H), 7.61 – 7.57 (m, 2H), 7.47 – 7.41 (m, 3H), 4.33 (dd, J = 13.2, 4.5 Hz, 1H), 4.06 (dd, J = 13.3, 5.4 Hz, 1H), 3.62 (dq, J = 11.7, 6.8, 5.1 Hz, 1H), 3.23 (p, J = 7.4 Hz, 1H), 2.83 (p, J = 8.5 Hz, 1H), 2.26 – 2.14 (m, 2H), 2.11 – 2.03 (m, 1H), 1.86 (tt, J = 13.8, 8.7 Hz, 1H), 1.86 (tt, J = 13.8, 8.7 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ (major) 131.2 (CH), 130.0 (C), 129.29 (CH), 128.9 (CH), 62.6 (CH), 55.6 (CH₂), 52.4 (CH₂), 31.3 (CH₂), 20.9 (CH₃), 15.8 (CH₃).

¹⁵ J. Zhang and S. Chang, J. Am. Chem. Soc. 2020, 142, 12585.
4a (gram-scale)
4a-HCl
(gram-scale)