Supporting Information

Photoinduced Olefin Diamination with Alkylamines

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2 General Experimental Details

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. THF was distilled from sodium/benzophenone, CH₂Cl₂ and was distilled from CaH₂. CH₃CN was distilled from activated 4Å molecular sieves, Et₃N was distilled over KOH. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to CHCl₃ (7.27 and 77.0 ppm for ¹H and ¹³C respectively). ¹H NMR coupling constants are reported in Hertz and refer to apparent multiplicities and not true coupling constants. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, sx = sextet, sp = septet, m = multiplet, dd = doublet of doublets, etc.), proton assignment (determined by 2D NMR experiments: COSY, HSQC and HMBC) where possible. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ES). Infra-red spectra were recorded using a JASCO FT/IR 410 spectrometer, ATI Mattson Genesis Series FTIR or Bruker Alpha-P spectrometer as evaporated films or liquid films. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in ninhydrin stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. UV/Vis spectra were obtained using an Agilent 6453 spectrometer and 1 mm High Precision Cell made of quartz from Hellma Analytics. The LEDs used are Kessil H150-blue. All the reactions were conducted in CEM 10 mL glass microwave tubes.
3 Starting Material Synthesis

*N*-Methoxy-*N*-methylpent-4-enamide (S1)

A mixture of 100 mL *N*,*O*-dimethylhydroxylamine hydrochloride (0.90 g, 9.27 mmol, 1.1 equiv.), CH₂Cl₂ (20 mL) and pyridine (1.70 mL, 21.0 mmol, 2.5 equiv.) was cooled to 0 °C, treated with pent-4-enoyl chloride (1.0 g, 8.43 mmol, 1.0 equiv.), warmed to room temperature and stirred for 4 h. The mixture was diluted with EtOAc (30 mL), and washed with 2 N aqueous HCl (20 mL) and brine (20 mL). The organic layer was dried (MgSO₄), filtered and evaporated to give S1 (1.15 g, 95%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ 5.82 (1H, ddt, *J* = 17.2, 10.0, 6.4 Hz), 5.03 (1H, ddt, *J* = 17.2, 1.7, 1.6 Hz), 4.95 (1H, ddt, *J* = 10.0, 1.6, 1.4 Hz), 3.65 (3H, s), 3.14 (3H, s), 2.49 (2H, t, *J* = 7.6 Hz), 2.40–2.29 (2H, m). Data in accordance with literature.[¹]

Pent-4-en-1-yl Benzoate (S2)

A solution of 4-pentenol (0.6 g, 7.0 mmol, 1.0 equiv.) and TMEDA (0.6 mL, 4.17 mmol, 0.6 equiv.) in CH₂Cl₂ (20 mL) was cooled to −78 °C, treated with BzCl (0.90 mL, 7.65 mmol, 1.1 equiv.) and allowed to warm to room temperature overnight. Aqueous 1 M KOH (20 mL) was added, the layers were separated and the aqueous layer was extracted with CH₂Cl₂ (10 mL x 3). The combined organic layers were dried (MgSO₄), filtered and evaporated. Purification by column chromatography on silica gel eluting petrol–EtOAc (99:1) gave S2 (0.96 g, 75%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ 8.14–7.96 (2H, m), 7.63–7.50 (1H, m), 7.49–7.40 (2H, m), 5.85 (1H, ddt, *J* = 16.9, 10.2, 6.6 Hz), 5.08 (1H, ddt, *J* = 17.1, 1.6, 1.4 Hz), 5.02 (1H, ddt, *J* = 10.2, 1.6, 1.4 Hz), 4.34 (2H, t, *J* = 6.6 Hz), 2.32–2.15 (2H, m), 1.94–1.80 (2H, m). Data in accordance with literature.[²]

*N*-Allyl-4-methylbenzenesulfonamide (S3)

A solution of TsCl (1.05 g, 5.5 mmol, 1.1 equiv.) in CH₂Cl₂ (5 mL) was cooled to 0 °C and treated with Et₃N (0.74 mL, 5.3 mmol, 1.05 equiv.) and allylamine (0.37 mL, 5.0 mmol, 1.0 equiv.). The mixture was allowed to warm to room temperature overnight.
Aqueous 1 M HCl (5 mL) was added and the layers were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL x 3). The combined organic layers were dried (MgSO$_4$), filtered and evaporated to give S3 (1.1 g, quantitative) as a solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85–7.68 (2H, m), 7.41–7.20 (2H, m), 5.85–5.64 (1H, m), 5.26–5.05 (2H, m), 4.62 (1H, br s), 3.67–3.58 (2H, m), 2.61–2.22 (3H, m). Data in accordance with literature.[3]

**Benzyl (S)-2-(((benzyl)oxy)carbonyl)amino)pent-4-enoate (S4)**

A solution of L-allyl glycine (0.50 g, 4.34 mmol, 1.0 equiv.), and NaHCO$_3$ (1.02 g, 12.1 mmol, 2.8 equiv.) in H$_2$O (10 mL) was treated with CbzCl (0.93 mL, 6.51 mmol, 1.5 equiv.) and stirred for 4 h. Et$_2$O (10 mL) was added and the layers were separated. The aqueous layer was acidified with 1 N aqueous HCl (20 mL) and extracted with Et$_2$O (30 mL x 3). The combined organic layers were dried (MgSO$_4$), filtered and evaporated to give S4 (0.62 g, 56%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.72 (1H, br s), 7.44–7.27 (5H, m), 5.72 (1H, ddt, $J$ = 16.9, 10.3, 7.2 Hz), 5.36 (1H, d, $J$ = 8.2 Hz), 5.23–5.05 (4H, m), 4.50 (1H, dt, $J$ = 8.0, 5.8 Hz), 2.71–2.38 (2H, m). Data in accordance with literature.[4]

**Benzyl (S)-2-(((benzyl)oxy)carbonyl)amino)pent-4-enoate (S5)**

A solution of S4 (0.62 g, 2.49 mmol, 1.0 equiv.) and K$_2$CO$_3$ (0.516 g, 3.75 mmol, 1.5 equiv.) in DMF (5 mL) was treated with BnBr (0.44 mL, 3.75 mmol, 1.5 equiv.) and heated under reflux for 18 h. The mixture was cooled to room temperature and diluted with H$_2$O (10 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine (10 mL), dried (MgSO$_4$), filtered and evaporated. Purification by column chromatography on silica gel, eluting with petrol–EtOAc (9:1), gave S5 (0.66 g, 79%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47–7.27 (10H, m), 5.64 (1H, ddt, $J$ = 17.5, 10.6, 7.2 Hz), 5.32 (1H, d, $J$ = 8.2 Hz), 5.25–5.12 (2H, m), 5.13–5.02 (4H, m), 4.51 (1H, dt, $J$ = 8.2, 5.8 Hz), 2.67–2.41 (2H, m). Data in accordance with literature.[5]
(R)-Quinolin-4-yl((1S,2R,4S,5R)-5-vinlynuclidin-2-yl)methyl Benzoate (S6)

![Chemical Structure](image)

A solution of cinchonidine (2.0 g, 6.8 mmol, 1.0 equiv.) and TMEDA (0.61 mL, 4.10 mmol, 0.6 equiv.) in CH₂Cl₂ (40 mL) was cooled to –78 °C, treated with BzCl (0.87 mL, 7.5 mmol, 1.1 equiv.) and allowed to warm to room temperature overnight. The mixture was diluted with aqueous 1 M KOH (20 mL), the layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried (MgSO₄), filtered and evaporated. Purification by column chromatography on silica gel, eluting with CH₂Cl₂–MeOH–37% aq. NH₃ (97:3:0.5), gave S6 (2.2 g, 81%) as a foam. Rf 0.40 [CH₂Cl₂:MeOH 97:3]; FT-IR: νmax (film)/cm⁻¹ 2940, 2862, 1718, 1266; ¹H NMR (500 MHz, CDCl₃) δ 8.87 (1H, d, J = 4.5 Hz), 8.33 (1H, d, J = 8.5 Hz), 8.14 (1H, d, J = 8.4 Hz), 8.12–8.06 (2H, m), 7.72 (1H, ddd, J = 8.4, 6.7, 1.3 Hz), 7.63 (1H, ddd, J =8.4, 6.7, 1.4 Hz), 7.60–7.55 (1H, m), 7.47 (3H, dd, J = 8.7, 6.4 Hz), 6.80 (1H, d, J = 6.8 Hz), 5.84 (1H, ddd, J = 17.5, 10.3, 7.4 Hz), 5.05–4.95 (2H, m), 3.50 (1H, q, J = 7.5 Hz), 3.22 (1H, ddd, J = 13.4, 10.3, 5.5, 2.5 Hz), 3.07 (1H, dd, J = 13.9, 10.1 Hz), 2.72–2.59 (2H, m), 2.35–2.22 (1H, m), 2.00–1.92 (1H, m), 1.91–1.86 (1H, m), 1.81–1.66 (2H, m), 1.57 (1H, dddt, J = 13.4, 11.0, 5.6, 2.9 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 165.6, 150.1, 148.8, 145.5, 141.8, 133.5, 130.6, 129.9, 129.8, 129.3, 128.7, 127.0, 126.1, 123.4, 118.6, 114.6, 74.8, 60.1, 56.9, 42.6, 39.8, 28.0, 27.8, 24.4; HRMS (ESI⁺): Found M⁺ 398.1986, [C₂₆H₂₆N₂O₂]⁺ requires 398.1994.

1-(3-(Allyloxy)propyl)-4-chlorobenzene (S7)

![Chemical Structure](image)

A suspension of NaH (0.47 g, 11.7 mmol, 2.0 equiv., 60% wt. in mineral oil) in THF (10 mL) was cooled to 0 °C and treated with 3-(4-chlorophenyl)propanol (1.0 g, 5.86 mmol, 1.0 equiv.). The mixture was stirred for 1 h and, treated with allyl bromide (0.60 mL, 7.0 mmol, 1.2 equiv.) and allowed to warm to room temperature overnight. The mixture was cooled to 0 °C and diluted with saturated aqueous NH₄Cl (10 mL). Et₂O (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et₂O (10 mL x 3). The combined organic layers were dried (MgSO₄), filtered and
evaporated S7 (1.14 g, 93%) as an oil. FT-IR: \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2935, 2857, 1491, 1090; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29–7.21 (2H, m), 7.16–7.07 (2H, m), 5.93 (1H, ddt, \(J = 17.2, 10.3, 5.6\) Hz), 5.28 (1H, ddt, \(J = 17.2, 1.7, 1.6\) Hz), 5.18 (1H, ddt, \(J = 10.4, 1.6, 1.5\) Hz), 3.96 (2H, dt, \(J = 5.6, 1.4\) Hz), 3.43 (2H, t, \(J = 6.3\) Hz), 2.68 (2H, t, \(J = 7.5\) Hz), 1.96–1.79 (2H, m); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.5, 135.0, 131.6, 130.0, 128.5, 117.0, 72.0, 69.3, 31.8, 31.4; HRMS (ESI\(^+\)): found MH\(^+\) 211.0882, \([\text{C}_{12}\text{H}_{16}\text{ClO}]^+\) requires 211.0982.

1-(4-(tert-Butyl)phenyl)but-3-en-1-ol (S8)

A solution of tert-butyl benzaldehyde (1.67 mL, 10.0 mmol, 1.0 equiv.) in THF (25 mL) was cooled to 0 °C and treated with allyl–MgBr (12.0 mL, 12.0 mmol, 1.2 equiv., 1 M in Et\(_2\)O). The mixture was allowed to warm to room temperature overnight, quenched with saturated aqueous NH\(_4\)Cl solution (20 mL) and extracted with Et\(_2\)O (30 mL x 3). The organic phase was dried (MgSO\(_4\)), filtered and evaporated to give S8 (2.1 g, quantitative) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43–7.35 (2H, m), 7.33–7.28 (2H, m), 5.84 (1H, ddt, \(J = 17.2, 10.2, 7.1\) Hz), 5.25–5.04 (2H, m), 4.78–4.62 (1H, m), 2.59–2.45 (2H, m), 2.04 (1H, br s), 1.33 (9H, s). Data in accordance with literature.\(^{[6]}\)

1-(4-(tert-Butyl)phenyl)but-3-en-1-yl Benzoate (S9)

A solution of S8 (719 mg, 3.52 mmol, 1.0 equiv.) and TMEDA (0.32 mL, 2.11 mmol, 0.6 equiv.) in CH\(_2\)Cl\(_2\) (5 mL) was cooled to –78 °C and treated with BzCl (0.60 mL, 3.87 mmol, 1.1 equiv.). The mixture was allowed to warm to room temperature overnight. Aqueous 1 M KOH (5 mL) was added, the layers were separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (5 mL x 3). The combined organic layers were dried (MgSO\(_4\)), filtered and evaporated. Purification by column chromatography on silica gel eluting with petrol–EtOAc (98:2) gave S9 (0.80 g, 74%) as an oil. FT-IR: \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2961, 1716, 1266; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (2H, d, \(J = 7.5\) Hz), 7.56 (1H, t, \(J = 7.3\) Hz), 7.43 (2H, t, \(J = 7.6\) Hz), 7.42–7.35 (4H, m), 6.06 (1H, dd, \(J = 7.9, 5.6\) Hz), 5.81 (1H, ddt, \(J = 17.1, 10.2, 6.9\) Hz), 5.15 (1H, dd, \(J = 17.4, 1.5\) Hz),
5.07 (1H, dd, J = 10.3 Hz, 1.1 Hz), 2.89–2.76 (1H, m), 2.75–2.66 (1H, m), 1.31 (9H, s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 165.8, 150.9, 137.2, 133.6, 133.0, 130.6, 129.7, 128.4, 126.3, 125.5, 118.1, 75.7, 41.0, 34.6, 31.4. HRMS (ESI\(^{+}\)): found M\(^{+}\) 308.1757, [C\(_{21}\)H\(_{24}\)O\(_2\)]\(^{+}\) requires 308.1776.

1-(4-Fluorophenyl)but-3-en-1-ol (S10)

\[
\begin{align*}
\text{F} & \quad \text{OH} \\
\text{H} & \quad \text{H}
\end{align*}
\]

A solution of 4-fluorobenzaldehyde (0.87 mL, 8.0 mmol, 1.0 equiv.) in THF (10 mL) was cooled to 0 °C and treated with allyl-MgCl (5.0 mL, 10.0 mmol, 1.25 equiv., 2 M in THF). The mixture was allowed to warm to room temperature and monitored by TLC until completion (2 h). Saturated aqueous NH\(_4\)Cl solution (10 mL) and Et\(_2\)O (20 mL) were added. The layers were separated and the aqueous layer was extracted with Et\(_2\)O (3 x 20 mL). The combined organic layers were dried (MgSO\(_4\)), filtered and evaporated. Purification by column chromatography on silica gel eluting with petrol–EtOAc (97:3) gave S10 (1.2 g, 86%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.44–7.29 (2H, m), 7.19–6.97 (2H, m), 5.79 (1H, dddd, J = 17.0, 10.5, 7.6, 6.6 Hz), 5.21–5.15 (1H, m), 5.14 (1H, d, J = 1.2 Hz), 4.73 (1H, dd, J = 7.7, 5.4 Hz), 2.61–2.39 (3H, m). Data in accordance with literature.\(^7\)

1-(4-Fluorophenyl)but-3-en-1-one (S11)

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

To a solution of S10 (482 mg, 2.9 mmol) in CH\(_2\)Cl\(_2\) (15 mL) was added Celite (0.8 g) followed by PCC (935 mg, 4.35 mmol, 1.5 equiv.). The mixture was stirred at room temperature for 4 h, and then filtered through a short pad Celite washing with CH\(_2\)Cl\(_2\) (20 mL). The combined filtrates were evaporated and the residue was purified by column chromatography on silica gel eluting petrol–EtOAc (90:10) to give S11 (341 mg, 73%) as an oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.07–7.93 (2H, m), 7.21–7.05 (2H, m), 6.07 (1H, ddt, J = 17.0, 10.3, 6.7 Hz), 5.32–5.15 (2H, m), 3.82–3.65 (2H, m). Data in accordance with literature.\(^7\)
**7-Allyl-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (S12)**

A suspension of theophylline (810 mg, 4.5 mmol, 1.0 equiv.) and K₂CO₃ (700 mg, 5.0 mmol, 1.1 equiv.) in DMF (8 mL, 0.6 M) was treated with allyl bromide (430 µL, 5.0 mmol, 1.1 equiv.) at room temperature. The mixture was warmed to 40 °C, stirred for 4 h and then cooled to room temperature. The crude was diluted with EtOAc (20 mL) and H₂O (20 mL). The layers were separated and the aqueous layer was washed with EtOAc (3 x 20 mL). The combined organic layers were dried (MgSO₄), filtered and evaporated to give S12 (600 mg, 60%) as a solid. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (1H, s), 6.05 (1H, ddt, J = 16.4, 11.0, 5.8 Hz), 5.42–5.15 (2H, m), 4.95 (2H, d, J = 5.9 Hz), 3.60 (3H, s), 3.41 (3H, s). Data in accordance with literature.⁸

**1-(Allyloxy)-2-benzylbenzene (101)**

A suspension of 2-benzylphenol (1.00 g, 5.43 mmol, 1.0 equiv.) and K₂CO₃ (2.25 g, 16.28 mmol, 3.0 equiv.) in acetone (40 mL) was stirred at room temperature for 30 min, treated with allyl bromide (0.70 mL, 8.15 mmol, 1.5 equiv.) and heated under reflux for 12 h. The mixture was evaporated, diluted with EtOAc (20 mL) and aqueous 1 M KOH (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and evaporated to give 101 (1.22 g, quantitative) as an oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.21 (4H, m), 7.29–7.20 (2H, m), 7.08 (1H, dd, J = 7.5, 1.7 Hz), 6.92–6.79 (2H, m), 6.01 (1H, ddt, J = 17.3, 10.3, 5.0 Hz), 5.36 (1H, dd, J = 17.3, 1.8 Hz), 5.23 (1H, dd, J = 10.5, 1.7 Hz), 4.52 (2H, d, J = 5.1), 4.00 (2H, s). Data in accordance with literature.⁹
4 Olefin Aminochlorination

4.1 Reaction Optimization

A tube equipped with a stirring bar was charged with Ru(bpy)$_3$(PF$_6$)$_2$ (1.0 mg, 1.0 μmol, 1 mol%) and N-chlorosuccinimide (NCS). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). Piperidine 1 (12 μL, 0.12 mmol, 1.2 equiv.) and the solvent (0.5 mL, 0.2 M, dry and degassed by bubbling through with N$_2$ for 20 min) were added and the mixture was stirred in the dark for 1 h at room temperature. 4-Phenyl-1-butene 10 was added along with an additional 0.5 mL of the same solvent, followed by the acid. The blue LEDs were immediately switched on and the mixture was stirred under irradiation for 1 h. KOH (1.0 M, 3 mL) and EtOAc (3 mL) were added and the mixture was shaken vigorously. 1,3,5-Trimethoxybenzene (17 mg, 0.1 mmol, 1.0 equiv.) was added and the layers were separated. The aqueous layer was extracted with EOAc (x3), the combined organic layers were dried (MgSO$_4$), filtered and evaporated. CDCl$_3$ (0.4 mL) was added and the mixture was analysed by $^1$H NMR spectroscopy to determine the NMR yield. Table S1 reports all the experiments performed.

Table S1.

| Entry | Bronsted acid (equiv.) | Solvent | Yield (%) |
|-------|------------------------|---------|-----------|
| 1     | HClO$_4$               | CH$_2$Cl$_2$ | 89        |
| 2     | HClO$_4$               | HFIP    | –         |
| 3     | TFA                    | CH$_2$Cl$_2$ | 96        |
| 4     | AcOH                   | CH$_2$Cl$_2$ | –         |
| 5     | TFA                    | CH$_2$Cl$_2$ | 92        |
| 6     | TFA                    | CH$_2$Cl$_2$ | 48        |
| 7     | –                      | CH$_2$Cl$_2$ | –         |
| 8$^a$ | TFA                    | CH$_2$Cl$_2$ | 37        |
| 9$^b$ | TFA                    | CH$_2$Cl$_2$ | –         |

a) Reaction was run without Ru(bpy)$_3$(PF$_6$). b) Reaction was run in the dark.
4.2 Substrate Scope

General Procedure for the Olefin Aminochlorination Using Free Amines – GP1

A dry tube equipped with a stirring bar was charged with NCS (1.0 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%) and the amine if solid (1.2 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). CH$_2$Cl$_2$ (0.2 M) (dry and degassed by bubbling through with N$_2$ for 20 min) and the amine (1.2 equiv.) if liquid were added and the mixture was stirred for 1 h at room temperature. The mixture was cooled to 0 °C and a solution of the olefin (1.0 equiv.) in CH$_2$Cl$_2$ (0.2 M) and TFA (6 equiv.) were added. The LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 °C. Aqueous 1 M KOH and EtOAc were added and the mixture was shaken vigorously. The aqueous layer was extracted with EOAc (x 3), the combined organic layers were dried (MgSO$_4$), filtered and evaporated. Purification by flash column or preparative thin-layer chromatography on silica gel gave the products.

General Procedure for the Olefin Aminochlorination Using Ammonium Salts – GP2

A dry tube equipped with a stirring bar was charged with NCS (1.0 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%) and the ammonium salt (1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). CH$_2$Cl$_2$ (0.2 M) (dry and degassed by bubbling through with N$_2$ for 20 min) and (i-Pr)$_2$NEt (1.1 equiv.) were added and the mixture was stirred for 60 min in the dark. The mixture was cooled to 0 °C and a solution of the olefin (1.0 equiv.) in CH$_2$Cl$_2$ (0.2 M) and TFA (6 equiv.) were added. The LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 °C. Aqueous 1 M KOH and EtOAc were added and the mixture was shaken vigorously. The aqueous layer was extracted with EOAc (x 3), the combined organic layers were dried (MgSO$_4$), filtered
and evaporated. Purification by flash column or preparative thin-layer chromatography on silica gel gave the products.

1-(2-Chloro-4-phenylbutyl)piperidine (11)

Following GP1, 1 (12 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 11 (23 mg, 91%) as an oil. R_f 0.60 [petrol:EtOAc (8:2)]; FT-IR ν_max (film)/cm⁻¹ 2938, 2859, 2651, 2341, 1495, 1454, 1303, 1259, 1156, 1029; ¹H NMR (500 MHz, CDCl₃) δ 7.33–7.27 (2H, m), 7.24–7.18 (3H, m), 3.95 (1H, dddd, J = 11.0, 9.6, 4.0, 3.5 Hz), 2.93 (1H, ddd, J = 14.1, 9.5, 4.8 Hz), 2.75 (1H, ddd, J = 13.8, 9.3, 7.2 Hz), 2.64 (1H, dd, J = 13.1, 6.5 Hz), 2.52 (1H, dd, J = 13.1, 7.3 Hz), 2.38 (4H, br s), 2.33–2.17 (1H, m), 1.92 (1H, dtd, J = 14.3, 9.4, 4.9 Hz), 1.55 (4H, p, J = 5.6 Hz), 1.47–1.34 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 141.4, 128.7, 128.5, 126.1, 66.0, 59.5, 55.1, 38.0, 32.5, 26.0, 24.4; HRMS (HESI): found MH⁺ 252.1512, [C₁₅H₂₃NCl]⁺ requires 252.1514.

1-(2-Chloro-4-phenylbutyl)-2,6-syn-dimethylpiperidine (12)

Following GP1, (2S,6R)-2,6-dimethylpiperidine (16 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 12 (15 mg, 55%) as an oil. R_f 0.40 [petrol:EtOAc (8:2)]; FT-IR ν_max (film)/cm⁻¹ 2359, 2341, 1455, 1258, 1086, 1019; ¹H NMR (500 MHz, CDCl₃) δ 7.28 (2H, t, J = 7.3 Hz), 7.20 (3H, dd, J = 18.1, 7.6 Hz), 3.89–3.82 (1H, m), 2.96 (1H, dd, J = 14.0, 9.3, 4.4 Hz), 2.87 (1H, dd, J = 15.1, 5.8 Hz), 2.82–2.66 (2H, m), 2.57–2.49 (1H, m), 2.50–2.42 (1H, m), 2.38–2.28 (1H, m), 1.79 (1H, dtd, J = 14.4, 9.9, 4.3 Hz), 1.67–1.60 (1H, m), 1.50–1.42 (2H, m), 1.38–1.28 (1H, m), 1.28–1.17 (2H, m), 1.06 (3H, d, J = 6.2 Hz), 1.01 (3H, d, J = 6.3 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 141.4, 128.7, 128.5, 126.1, 62.8, 58.5, 57.9, 38.0, 33.1, 24.6, 22.2, 22.1; HRMS (ASAP): Found MH⁺ 280.1822, [C₁₇H₂₇NCl]⁺ requires 280.1827.
1-(2-Chloro-4-phenylbutyl)-2,2,6,6-tetramethylpiperidine (13)

Following **GP1**, 2,2,6,6-tetramethylpiperidine (20 μL, 0.12 mmol) and **10** (10 μL, 0.1 mmol) gave 13 (6.5 mg, 21%) as an oil. Rf 0.35 [petrol:EtOAc (8:2)]; FT-IR ν\text{max} (film)/cm\(^{-1}\) 2926, 2359, 1455, 1381, 1258, 1174, 1089, 1021; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.32–7.27 (2H, m), 7.24–7.15 (3H, m), 3.93–3.84 (1H, m), 2.99 (1H, ddd, J = 13.7, 9.2, 4.3 Hz), 2.89 (1H, dd, J = 15.6, 5.4), 2.79–2.61 (2H, m), 2.58–2.43 (1H, m), 1.82–1.65 (1H, m), 1.55 (1H, br s), 1.51 (1H, br s), 1.38 (4H, t, J = 6.0 Hz), 1.00 (6H, s), 0.92 (6H, s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 141.6, 128.7, 128.5, 126.0, 65.7, 55.0, 52.5, 41.4, 37.2, 33.5, 25.8, 17.9; HRMS (ASAP): Found MH\(^+\) 308.2133 C\(_{19}\)H\(_{31}\)NCl requires 308.2140.

1-(2-Chloro-4-phenylbutyl)piperidin-3-ol (14)

Following **GP2**, adding NaCl (6 mg, 0.1 mmol) to the reaction mixture, 3-hydroxypiperidine hydrochloride (16 mg, 0.12 mmol) and **10** (10 μL, 0.1 mmol) gave 14 (12 mg, 45%) as an oil. dr: 1:1. Rf 0.20 [petrol:EtOAc (8:2)]; FT-IR ν\text{max} (film)/cm\(^{-1}\) 3334, 2359, 2341, 1634, 1260, 1017; \(^1\)H NMR (500 MHz, CDCl\(_3\), diastereomers) δ 7.30 (2H, t, J = 7.5 Hz), 7.23–7.19 (3H, m), 3.96–3.87 (1H, m), 3.85–3.72 (1H, m), 2.92 (1H, ddd, J = 14.0, 9.2, 4.9 Hz), 2.75 (1H, dt, J = 13.9, 8.1 Hz), 2.71–2.61 (1H, m), 2.61–2.54 (1H, m), 2.54–2.44 (3H, m), 2.29 (1H, q, J = 10.0, 9.5 Hz), 2.24–2.15 (1H, m), 1.99–1.85 (1H, m), 1.83–1.72 (1H, m), 1.61–1.53 (2H, m), 1.63–1.45 (1H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\), diastereomers) δ 141.2 (x 2), 128.6 (x 2), 126.2 (x 2), 66.2, 66.1, 65.0, 64.8, 61.1, 60.7, 59.5, 59.2, 54.3, 54.1, 37.9 (x 2), 32.5 (x 2), 31.5 (x 2), 21.7, 21.6; HRMS (ASAP): Found MH\(^+\) 268.1460 C\(_{15}\)H\(_{23}\)NOCl requires 268.1463.

4-Azido-1-(2-chloro-4-phenylbutyl)piperidine (15)

Following **GP2**, 4-azidopiperidine hydrochloride (15 mg, 0.12 mmol) and **10** (10 μL, 0.1 mmol) gave 15 (23 mg, 79%) as an oil. Rf 0.50 [petrol:EtOAc (8:2)]; FT-IR ν\text{max}
(film)/cm⁻¹ 2847, 2360, 1644, 1259, 1015; ¹H NMR (500 MHz, CDCl₃) δ 7.30 (2H, t, J = 7.6 Hz), 7.25–7.18 (3H, m), 3.90 (1H, dtd, J = 9.7, 7.0, 3.0 Hz), 3.42–3.34 (1H, m), 2.93 (1H, ddd, J = 13.9, 9.2, 4.8 Hz), 2.80–2.70 (3H, m), 2.67 (1H, dd, J = 13.3, 6.5 Hz), 2.56 (1H, dd, J = 13.2, 7.2 Hz), 2.32–2.13 (3H, m), 1.97–1.89 (1H, m), 1.90–1.82 (2H, m), 1.65 (2H, dtt, J = 15.8, 9.6, 4.9 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 141.1, 128.5, 128.5, 126.1, 64.8, 59.2, 57.5, 51.9, 51.4, 37.8, 32.4, 30.8, 30.7; HRMS (ASAP): Found MH⁺ 293.1522 C₁₅H₂₂N₄Cl requires 293.1528.

1-(1-(2-Chloro-4-phenylbutyl)-4-phenylpiperidin-4-yl)ethan-1-one (16)

Following GP2, 4-acetyl-4-phenylpiperidine hydrochloride (29 mg, 0.12 mmol) and 10 (10 µL, 0.1 mmol) gave 16 (21 mg, 56%) as an oil. R₇ 0.60 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2925, 2341, 1702, 1599, 1494, 1446, 1353, 1259, 1202, 1028; ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.34 (2H, m), 7.33–7.27 (5H, m), 7.25–7.18 (3H, m), 3.98–3.87 (1H, m), 2.93 (1H, ddd, J = 14.0, 9.3, 4.9 Hz), 2.82–2.73 (1H, m), 2.73–2.62 (3H, m), 2.54 (1H, dd, J = 13.1, 7.1 Hz), 2.48–2.39 (2H, m), 2.37–2.18 (3H, m), 2.14–2.01 (2H, m), 1.99–1.86 (1H, m), 1.91 (3H, s); ¹³C NMR (126 MHz, CDCl₃) δ 209.6, 141.7, 141.3, 129.0, 128.7, 128.6, 127.3, 126.5, 126.2, 65.2, 59.3, 54.6, 51.4, 51.3, 38.0, 32.9, 32.8, 32.5, 25.8; HRMS (HESI): Found MH⁺ 370.1926 C₂₃H₂₉NOCl requires 370.1932.

N-(1-(2-Chloro-4-phenylbutyl)piperidin-4-yl)-N-cyclopropyl-3-(trifluoromethyl)benzene-sulfonamide (17)

Following GP1, N-cyclopropyl-N-(piperidin-4-yl)-3-(trifluoromethyl)benzenesulfonamide (42 mg, 0.12 mmol) and 10 (10 µL, 0.1 mmol) gave 17 (31 mg, 60%) as an oil. R₇ 0.40 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2951, 2838, 2359, 2341, 1651, 1404, 1260, 1104, 1013; ¹H NMR (500 MHz, CDCl₃) δ 8.12 (1H, s), 8.05 (1H, d, J = 7.9 Hz), 7.84 (1H, d, J = 7.9 Hz), 7.67 (1H, t, J = 7.8 Hz), 7.29 (2H, t, J = 7.5 Hz), 7.20 (3H, d, J = 7.3 Hz), 4.15–3.64 (2H, m), 2.91 (1H, ddd, J = 14.1, 9.3, 4.9 Hz), 2.87 –
2.78 (2H, m), 2.73 (1H, dt, \(J = 14.0, 8.2\) Hz), 2.64 (1H, dd, \(J = 13.2, 6.8\) Hz), 2.52 (1H, dd, \(J = 13.2, 6.8\) Hz), 2.25–2.14 (2H, m), 2.13–2.02 (1H, m), 2.00–1.85 (4H, m), 1.48 (2H, d, \(J = 11.5\) Hz), 1.03–0.92 (2H, m), 0.78 (2H, q, \(J = 6.3\) Hz); \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta 141.3, 141.2, 131.8\) (q, \(J = 33.4\) Hz), 130.6, 129.9, 129.2 (q, \(J = 3.3\) Hz), 128.6, 128.5, 126.2, 124.6 (q, \(J = 3.6\) Hz), 123.3 (q, \(J = 272.9\) Hz), 64.9, 59.3, 59.0, 54.1, 53.8, 38.0, 32.5, 31.0, 30.9, 26.2, 7.8; \(^{19}\text{F NMR}\) (471 MHz, CDCl\(_3\)) \(\delta 62.81;\)

HRMS (ASAP): Found MH\(^+\) 515.1738 C\(_{25}\)H\(_{31}\)N\(_2\)O\(_2\)ClSF\(_3\) requires 515.1741.

1-(2-Chloro-4-phenylbutyl)-4-(4-chlorophenyl)piperidin-4-ol (18)

Following GP1, 4-(4-chlorophenyl)-4-hydroxypiperidine (25 mg, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 18 (34 mg, 91%) as an oil. \(R_f\) 0.40 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 3322, 2960, 2918, 2849, 1637, 1493, 1454, 1398, 1258, 1090, 1012; \(^{1}\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta 7.43 (2H, d, J = 8.6\) Hz), 7.36–7.28 (4H, m), 7.25–7.18 (3H, m), 4.02–3.94 (1H, m), 2.95 (1H, ddd, \(J = 14.0, 9.4, 4.9\) Hz), 2.84–2.67 (4H, m), 2.63 (1H, dd, \(J = 13.2, 6.8\) Hz), 2.58–2.43 (2H, m), 2.31–2.20 (1H, m), 2.15–2.04 (2H, m), 1.96 (1H, ddd, \(J = 14.2, 9.3, 4.9\) Hz), 1.73–1.63 (2H, m), 1.56 (1H, br s); \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta 146.9, 141.3, 132.9, 128.7, 128.5, 126.2, 71.0, 65.3, 59.4, 50.0, 49.8, 38.5, 38.0, 32.5; HRMS (ASAP): Found MH\(^+\) 378.1382 C\(_{21}\)H\(_{26}\)NOCl\(_2\) requires 378.1386.

1-(2-Chloro-4-phenylbutyl)-4-(4-(trifluoromethoxy)phenoxy)piperidine (19)

Following GP1, 4-[4-(trifluoromethoxy)phenoxy]piperidine (31 mg, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 19 (36 mg, 84%) as an oil. \(R_f\) 0.40 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2951, 2359, 2341, 1503, 1454, 1261, 1238, 1194, 1159, 1042; \(^{1}\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta 7.30 (2H, t, J = 7.4\) Hz), 7.24–7.19 (3H, m), 7.12 (2H, d, \(J = 8.5\) Hz), 6.87 (2H, d, \(J = 8.5\) Hz), 4.31–4.21 (1H, m), 4.01–3.87 (1H, m), 2.94 (1H, ddd, \(J = 14.1, 9.3, 4.8\) Hz), 2.77 (1H, dd, \(J = 14.4, 7.7\) Hz), 2.74–2.66 (3H, m), 2.59 (1H, dd, \(J = 13.2, 7.2\) Hz), 2.42–2.19 (3H, m), 2.05–1.85 (3H, m), 1.84–1.74 (2H, m); \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta 156.1, 142.8\) (q, \(J\)
= 2.1 Hz), 141.3, 128.7, 128.6, 126.2, 122.6, 120.7 (q, J = 256.1 Hz), 116.9, 73.1, 65.1, 59.4, 51.2, 50.8, 37.9, 32.5, 30.9, 30.8; \(^{19}F\) NMR (471 MHz, CDCl\(_3\)) \(\delta -58.4\); HRMS (ASAP): Found MH\(^+\) 428.1588 C\(_{22}\)H\(_{26}\)NO\(_2\)ClF requires 428.1599.

2-((1-(2-Chloro-4-phenylbutyl)piperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (20)

Following GP2, desbenzyl donepezil hydrochloride (39 mg, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 20 (36 mg, 79%) as an oil. d.r. 1:1. R\(_f\) 0.20 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2960, 2359, 2341, 1693, 1590, 1499, 1455, 1313, 1258, 1016; \(^1\)H NMR (500 MHz, CDCl\(_3\), diasteromers) \(\delta\) 7.29 (2H, t, \(J = 7.5\) Hz), 7.24–7.18 (3H, m), 7.17 (1H, s), 6.85 (1H, s), 3.96 (3H, s), 4.00–3.92 (1H, m), 3.90 (3H, s), 3.23 (1H, dd, \(J = 17.5, 8.0\) Hz), 2.92 (1H, ddd, \(J = 14.0, 9.4, 4.8\) Hz), 2.88–2.79 (2H, m), 2.78–2.72 (1H, m), 2.72–2.62 (3H, m), 2.59–2.52 (1H, m), 2.32–2.20 (1H, m), 2.12–1.84 (4H, m), 1.75–1.57 (2H, m), 1.52–1.43 (1H, m), 1.41–1.22 (3H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\), diasteromers) \(\delta\) 207.7 (x 2), 155.5 (x 2), 149.4 (x 2), 148.7 (x 2), 141.2 (x 2), 129.3 (x 2), 128.5 (x 2), 128.4 (x 2), 126.0 (x 2), 107.3 (x 2), 104.4 (x 2), 65.4 (x 2), 59.3 (x 2), 56.3, 56.2, 56.1, 56.0, 54.6 (x 2), 54.0 (x 2), 45.4 (x 2), 38.7 (x 2), 37.9 (x 2), 34.3 (x 2), 33.3 (x 2), 33.1, 32.9, 32.4 (x 2), 31.8, 31.7; HRMS (ASAP): Found MH\(^+\) 456.2293 C\(_{27}\)H\(_{35}\)NO\(_3\)NCl requires 456.2300.

4-(2-Chloro-4-phenylbutyl)morpholine (21)

Following GP1, morpholine (10 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 21 (22 mg, 86%) as an oil. R\(_f\) 0.20 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2957, 2853, 2810, 2359, 2341, 1495, 1454, 1360, 1259, 1207, 121116, 1069, 1008; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.27 (2H, m), 7.24–7.17 (3H, m), 4.01–3.87 (1H, m), 3.75–3.63 (4H, m), 2.93 (1H, ddd, \(J = 14.0, 9.2, 4.9\) Hz), 2.81–2.71 (1H, m), 2.68 (1H, dd, \(J = 13.1, 6.8\) Hz), 2.56 (1H, dd, \(J = 13.1, 7.0\) Hz), 2.48–2.40 (4H, m), 2.30–2.19 (1H, m), 1.94 (1H, dtd, \(J = 14.2, 9.2, 4.9\) Hz); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 141.2, 128.7,
128.6, 126.2, 67.0, 65.6, 58.7, 54.0, 37.9, 32.5; HRMS (ASAP): Found MH\(^+\) 254.1302
\(\text{C}_{14}\text{H}_{21}\text{NOCl}\) requires 254.1306.

4-(2-Chloro-4-phenylbutyl)-2,6-syn-dimethylmorpholine (22)

Following GP1, cis-2,6-dimethylmorpholine (15 \(\mu\)L, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 22 (31 mg, 81%) as an oil. R\(_f\) 0.20 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2931, 2858, 2815, 2360, 2342, 1495, 1454, 1374, 1322, 1225, 1178, 1143, 1085, 1049, 1030; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.25 (2H, m), 7.24–7.17 (3H, m), 3.93 (1H, dtd, \(J = 9.8, 6.8, 3.1\) Hz), 3.65 (2H, dqd, \(J = 16.4, 8.7, 4.4\) Hz), 2.93 (1H, ddd, \(J = 13.9, 9.2, 4.9\) Hz), 2.75 (1H, dt, \(J = 13.8, 8.2\) Hz), 2.69–2.48 (4H, m), 2.30–2.19 (1H, m), 1.99–1.87 (1H, m), 1.79 (2H, dt, \(J = 20.5, 10.5\) Hz), 1.13 (3H, t, \(J = 6.7\) Hz), 1.12 (3H, t, \(J = 6.4\) Hz); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 141.1, 128.5, 128.5, 126.1, 71.6, 71.5, 59.8, 59.6, 58.6, 37.8, 32.3, 19.1 (x 2); HRMS (ASAP): Found MH\(^+\) 282.1617 \(\text{C}_{16}\text{H}_{25}\text{NOCl}\) requires 282.1619.

Benzyl 4-(2-Chloro-4-phenylbutyl)piperazine-1-carboxylate (23)

Following GP1, 1-Cbz-piperazine (23 \(\mu\)L, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 23 (29 mg, 75%) as an oil. R\(_f\) 0.60 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2960, 2359, 2341, 1699, 1496, 1454, 1428, 1361, 1257, 1237, 1079, 1015; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39–7.27 (7H, m), 7.23–7.18 (3H, m), 5.13 (2H, s), 3.92 (1H, dtd, \(J = 9.8, 6.7, 3.1\) Hz), 3.49 (4H, t, \(J = 5.0\) Hz), 2.92 (1H, ddd, \(J = 13.9, 9.1, 4.9\) Hz), 2.81–2.72 (1H, m), 2.70 (1H, dd, \(J = 13.4, 7.0\) Hz), 2.59 (1H, dd, \(J = 13.2, 6.8\) Hz), 2.42 (4H, br s), 2.30–2.18 (1H, m), 2.01–1.86 (1H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 155.1, 141.0, 136.7, 128.55 (x 2), 128.5, 128.0, 127.9, 126.1, 67.2, 64.9, 58.6, 53.1, 43.7, 37.7, 32.3; HRMS (ASAP): Found MH\(^+\) 387.1826 \(\text{C}_{22}\text{H}_{28}\text{ClN}_{3}\text{O}_{2}\) requires 387.1834.
**1-(2-Chloro-4-phenylbutyl)pyrrolidine (24)**

Following **GP1** but adding NaCl (6 mg, 0.1 mmol) to the reaction mixture, pyrrolidine (10 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 24 (22 mg, 91%) as an oil. \( R_f 0.40 \) [petrol:EtOAc (8:2)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.34–7.24 \) (2H, m), 7.23–7.17 (3H, m), 4.01–3.85 (1H, m), 2.93 (1H, ddd, \( J = 14.2, 9.4, 4.9 \) Hz), 2.86–2.65 (3H, m), 2.52 (4H, br s), 2.29–2.17 (1H, m), 1.95 (1H, dtd, \( J = 10.7, 9.2, 8.6, 4.8 \) Hz), 1.76 (4H, br s); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \( \delta 141.1, 128.5, 128.4, 126.0, 63.3, 60.5, 54.4, 37.9, 32.4, 23.5 \). Data in accordance with the literature.\(^{[10]}\)

**1-(2-Chloro-4-phenylbutyl)azepane (25)**

Following **GP1**, hexamethyleimine (13.5 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 25 (19 mg, 74%) as an oil. \( R_f 0.60 \) [petrol:EtOAc (8:2)]; FT-IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\) 2359, 2341, 1652, 1459, 1454, 1258, 1017; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.34–7.27 \) (2H, m), 7.24–7.16 (3H, m), 3.90–3.80 (1H, m), 2.93 (1H, ddd, \( J = 14.1, 9.5, 4.8 \) Hz), 2.85 (1H, dd, \( J = 13.4, 5.8 \) Hz), 2.75 (1H, dd, \( J = 14.9, 7.3 \) Hz), 2.72–2.67 (1H, m), 2.66 (4H, br s), 2.37–2.25 (1H, m), 1.90 (1H, dtd, \( J = 14.2, 9.3, 4.6 \) Hz), 1.65–1.50 (8H, m); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \( \delta 141.5, 128.7, 128.5, 126.1, 64.5, 60.7, 55.9, 37.7, 32.6, 28.5, 27.3 \); HRMS (ASAP): Found MH\(^+\) 266.1668 C\(_{16}\)H\(_{25}\)NCl requires 266.1670.

**1-(2-Chloro-4-phenylbutyl)azetidine (26)**

Following **GP2** but using 2.0 equiv. of the olefin, azetidine hydrochloride (11 mg, 0.12 mmol) and 10 (20 μL, 0.2 mmol) gave 26 (17 mg, 76%) as an oil. \( R_f 0.50 \) [petrol:EtOAc (8:2)]; FT-IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\) 2959, 2359, 2341, 1715, 1455, 1259, 1179, 1028; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.32–7.25 \) (2H, m), 7.23–7.14 (3H, m), 3.84–3.73 (1H, m), 3.26 (4H, t, \( J = 7.1 \) Hz), 2.89 (1H, ddd, \( J = 14.0, 9.3, 4.9 \) Hz), 2.79–2.61 (3H, m), 2.19–2.01 (3H, m), 1.92 (1H, dtd, \( J = 14.2, 9.3, 4.9 \) Hz); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \( \delta 141.2, 128.7, 128.6, 126.2, 66.6, 60.5, 56.4, 38.0, 32.6, 18.2 \); HRMS (ASAP): Found MH\(^+\) 224.1199 C\(_{13}\)H\(_{19}\)NCl requires 224.1201.
6-(2-Chloro-4-phenylbutyl)-2-oxa-6-azaspiro[3.3]heptane (27)

Following GP2 but using 3.0 equiv. of the olefin, 2-oxa-6-azaspiro[3.3]heptane oxalate (23 mg, 0.12 mmol) and 10 (30 μL, 0.3 mmol) gave 27 (12 mg, 45%) as an oil. Rf 0.20 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2961, 2360, 2341, 1259, 1028; ¹H NMR (500 MHz, CDCl₃) δ 7.33–7.26 (2H, m), 7.24–7.12 (3H, m), 4.72 (4H, s), 3.78–3.70 (1H, m), 3.41 (4H, s), 2.87 (1H, ddd, J = 14.0, 9.0, 5.0 Hz), 2.72 (1H, dd, J = 15.0, 6.5 Hz), 2.66 (1H, br s), 2.65 (1H, br s), 2.14–1.99 (1H, m), 1.92 (1H, dtd, J = 14.3, 9.2, 5.0 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 141.0, 128.6, 128.6, 126.2, 81.4, 66.1, 65.0, 60.5, 39.7, 37.9, 32.5; HRMS (HESI): Found MH⁺ 266.1295 C₁₅H₂₁NOCl requires 266.1293.

2-Chloro-N,N-dimethyl-4-phenylbutan-1-amine (28)

Following GP2, Me₂NH•HCl (10 mg, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 29 (19 mg, 91%) as an oil. Rf 0.60 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2960, 2919, 2849, 2360, 1634, 1455, 1258, 1018; ¹H NMR (500 MHz, CDCl₃) δ 7.34–7.25 (2H, m), 7.25–7.17 (3H, m), 3.97–3.85 (1H, m), 2.93 (1H, ddd, J = 14.1, 9.4, 4.9 Hz), 2.76 (1H, ddd, J = 13.7, 9.2, 7.2 Hz), 2.64 (1H, dd, J = 12.9, 7.5 Hz), 2.51 (1H, dd, J = 12.9, 6.2 Hz), 2.26 (6H, s), 2.23–2.15 (1H, m), 1.93 (1H, dtd, J = 14.3, 9.4, 4.9 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 141.2, 128.7, 128.6, 126.2, 66.5, 59.4, 45.8, 38.0, 32.5; HRMS (ASAP): Found MH⁺ 212.1203 C₁₂H₁₉NCl requires 212.1201.

2-Chloro-N,N-diethyl-4-phenylbutan-1-amine (29)

Following GP1, 8 (46 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 29 (15 mg, 62%) as an oil. Rf 0.20 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2359, 2341, 1635, 1495, 1454, 1258, 1015; ¹H NMR (500 MHz, CDCl₃) δ 7.35–7.27 (2H, m), 7.24–7.16 (3H, m), 4.05–3.71 (1H, m), 2.94 (1H, ddd, J = 14.1, 9.6, 4.7 Hz), 2.80–2.68 (2H, m), 2.62 (1H, ddd, J = 13.6, 7.7 Hz), 2.58–2.44 (4H, m), 2.36–2.18 (1H, m), 1.87 (1H, dtd, J = 14.2, 9.5, 4.7 Hz), 0.98 (6H, t, J = 7.1 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 141.5, 128.7,
128.5, 126.1, 61.1, 60.7, 48.1, 37.8, 32.7, 12.1; HRMS (HESI): Found MH\(^+\) 240.1509 C\(_{14}\)H\(_{23}\)NCl requires 240.1514.

**2-((2-Chloro-4-phenylbutyl)(methyl)amino)ethan-1-ol (30)**

Following GP1, 2-(methylamino)ethanol (10 \(\mu\)L, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 30 (15 mg, 64\%) as an oil. \(R_f\) 0.20 [petrol:EtOAc (8:2)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 3378, 2922, 2852, 2358, 2342, 2170, 2343, 2170, 1973, 1454, 1199, 1031; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.32–7.28 (2H, m), 7.24–7.17 (3H, m), 3.98–3.90 (1H, m), 3.62–3.53 (2H, m), 2.93 (1H, ddd, \(J = 14.0, 9.3, 5.0\) Hz), 2.80–2.69 (2H, m), 2.68–2.59 (2H, m), 2.58–2.52 (1H, m), 2.28 (3H, s), 2.18–2.07 (1H, m), 1.94 (1H, dtd, \(J = 14.2, 9.3, 5.0\) Hz); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 141.0, 128.7, 128.6, 126.3, 64.5, 60.1, 59.5, 58.6, 42.3, 37.9, 32.5; HRMS (ASAP): Found MH\(^+\) 242.1305 C\(_{13}\)H\(_{21}\)NOCl requires 242.1306.

**N-(2-Chloro-4-phenylbutyl)cyclohexanamine (32)**

Following GP1 but adding KPF\(_6\) (18 mg, 0.1 mmol) to the reaction mixture, cyclohexylamine (14 \(\mu\)L, 0.12 mmol) and 10 (10 \(\mu\)L, 0.1 mmol) gave 32 (17 mg, 65\%)

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SI-20
as an oil. R_f 0.40 [petrol:EtOAc (8:2)]; FT-IR ν_max (film)/cm⁻¹ 2961, 2926, 2854, 1410, 1258, 1018; ¹H NMR (500 MHz, CDCl₃) δ 7.28 (2H, t, J = 7.9 Hz), 7.23–7.16 (3H, m), 4.04–3.97 (1H, m), 2.96–2.81 (3H, m), 2.75 (1H, dt, J = 13.2, 8.2 Hz), 2.46–2.37 (1H, m), 2.13–1.98 (2H, m), 1.85 (2H, d, J = 11.8 Hz), 1.72 (2H, d, J = 12.7 Hz), 1.61 (1H, d, J = 12.6 Hz), 1.27–1.01 (6H, m); ¹³C NMR (126 MHz, CDCl₃) δ 140.9, 128.5, 128.5, 126.1, 63.2, 56.3, 53.4, 38.0, 33.6, 33.4, 32.6, 26.1, 25.0, 24.9; HRMS (ASAP): Found MH⁺ 266.1666 C₁₆H₂₅NCl requires 266.1670.

N-(tert-Butyl)-2-chloro-4-phenylbutan-1-amine (33)

Following GP1, t-BuNH₂ (13 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 34 (20 mg, 85%) as an oil. R_f 0.50 [petrol:EtOAc (8:2)]; FT-IR ν_max (film)/cm⁻¹ 2839, 2360, 2341, 1645, 1404, 1260, 1014; ¹H NMR (500 MHz, CDCl₃) δ 7.27 (2H, t, J = 7.1 Hz), 7.22–7.14 (3H, m), 4.04–3.87 (1H, m), 2.94–2.85 (1H, m), 2.83–2.76 (2H, m), 2.79–2.70 (1H, m), 2.18–1.97 (2H, m), 1.31 (1H, br s), 1.09 (9H, s); ¹³C NMR (126 MHz, CDCl₃) δ 140.9, 128.5, 128.5, 126.1, 63.2, 56.3, 53.4, 38.0, 33.6, 33.4, 32.6, 26.1, 25.0, 24.9; HRMS (ASAP): Found MH⁺ 240.1512 C₁₄H₂₃NCl requires 240.1514.

N-(2-chloro-4-phenylbutyl)adamantan-1-amine (34)

Following GP1, 1-adamantylamine (12 mg, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 34 (29 mg, 91%) as an oil. R_f 0.40 [petrol:EtOAc (8:2)]; FT-IR ν_max (film)/cm⁻¹ 2961, 2909, 2852, 2359, 2341, 1456, 1259, 1029; ¹H NMR (500 MHz, CDCl₃) δ 7.32–7.26 (2H, m), 7.23–7.16 (3H, m), 4.00–3.90 (1H, m), 3.00–2.80 (3H, m), 2.80–2.70 (1H, m), 2.17–1.97 (5H, m), 1.73–1.49 (12H, m); ¹³C NMR (126 MHz, CDCl₃) δ 141.1, 128.7, 128.6, 126.2, 64.0, 50.5, 49.7, 38.2, 32.7, 29.1; HRMS (ASAP): Found MH⁺ 318.1969 C₂₀H₂₉NCl requires 318.1983.
(1S,2R)-2-((2-Chloro-4-phenylbutyl)amino)-1-phenylpropan-1-ol (35)

Following GP1 but using 10.0 equiv. of TFA, (1S,2R)-(+) -norephedrine (18 mg, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 35 (6 mg, 20%) as an oil. d.r. 1:1. Rf 0.70 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2960, 2924, 2360, 2341, 1455, 1257, 1016; ¹H NMR (500 MHz, CDCl₃, diastereomers) δ 7.38–7.27 (6.5H, m), 7.24–7.18 (3.5H, m), 4.72 (0.5H, d, J = 3.8 Hz), 4.70 (0.5H, d, J = 3.9 Hz), 4.06–3.94 (1H, m), 3.06 (0.5H, dd, J = 13.0, 3.9 Hz), 2.97–2.89 (2.5H, m), 2.82–2.71 (1H, m), 2.15–2.03 (2H, m), 1.31 (1H, br s), 1.29–1.22 (1H, m), 0.85 (1.5H, d, J = 3.3 Hz), 0.83 (1.5H, d, J = 3.4 Hz); ¹³C NMR (126 MHz, CDCl₃, diastereomers) δ 141.2, 141.1, 140.9, 140.8, 128.7 (x 2), 128.6 (x 2), 128.3, 128.2, 127.2 (x 2), 126.4 (x 2), 126.2 (x 2), 73.5, 73.4, 63.1, 62.5, 58.4, 58.0, 54.0, 53.4, 38.0, 37.7, 32.8, 32.6, 15.0, 14.8; HRMS (ASAP): Found MH⁺ 318.1612 C₁₉H₂₅NOCl requires 318.1619.

2-Chloro-N-(((1S,2R,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4-phenylbutan-1-amine (36)

Following GP1, (−)-cis-myrtanylamine (20 μL, 0.12 mmol) and 10 (10 μL, 0.1 mmol) gave 36 (10 mg, 30%) as an oil. d.r:1:1. Rf 0.50 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2959, 2359, 2341, 1455, 1258, 1020; ¹H NMR (500 MHz, CDCl₃) δ 7.34–7.24 (2H, m), 7.24–7.14 (3H, m), 4.09–3.96 (1H, m), 2.90 (1H, ddd, J = 14.2, 8.6, 5.7 Hz), 2.86–2.78 (1H, m), 2.80–2.69 (1H, m), 2.67–2.47 (2H, m), 2.39–2.29 (1H, m), 2.22–2.13 (1H, m), 2.09–1.99 (2H, m), 1.95–1.86 (4H, m), 1.77–1.63 (1H, m), 1.56 (1H, br s), 1.50–1.38 (1H, m), 1.34–1.27 (1H, m), 1.18 (3H, s), 0.97 (3H, s), 0.93–0.87 (1H, m); ¹³C NMR (126 MHz, CDCl₃, diastereomers) δ 142.1, 141.1, 128.7, 128.6, 128.6, 128.4, 126.2, 125.9, 62.9, 62.8, 56.5, 56.4, 56.0, 55.9, 44.6, 44.5, 41.8, 41.7, 41.6, 38.8 (x 2), 38.0 (x 2), 33.6 (x 2), 32.7 (x 2), 28.3, 28.2, 26.4, 26.3, 23.5(x2), 20.8, 20.7; HRMS (ASAP): Found MH⁺ 320.2136 C₂₀H₃₁NCl requires 320.2140.
1-(2-Chloro-4-methylpentyl)piperidine (37)

Following GP1, 1 (48 µL, 0.48 mmol) and 4-methylpent-1-ene (34 mg, 0.4 mmol) gave 37 (68 mg, 83%) as an oil. Rf 0.30 [petrol:EtOAc (95:5)]; 1H NMR (500 MHz, CDCl3) δ 4.02 (1H, dtd, J = 10.3, 6.7, 3.7 Hz), 2.62 (1H, dd, J = 13.1, 6.8 Hz), 2.47 (1H, dd, J = 13.2, 6.5 Hz), 2.45–2.33 (4H, m), 1.99–1.81 (1H, m), 1.67–1.51 (6H, m), 1.41 (2H, p, J = 5.7 Hz), 0.94 (3H, d, J = 6.7 Hz), 0.89 (3H, d, J = 6.6 Hz); 13C NMR (125 MHz, CDCl3) δ 66.8, 58.6, 55.1, 45.7, 26.0, 25.3, 24.4, 23.5, 21.2. HRMS (ESI+): found MH⁺ 204.1516, [C11H23ClN]⁺ requires 204.1520.

1-(2-Chloro-2-cyclohexylethyl)piperidine (38)

Following GP1, 1 (48 µL, 0.48 mmol) and vinylcyclohexane (56 µL, 0.4 mmol) gave 38 (79 mg, 86%) as an oil. Rf 0.30 [petrol:EtOAc (95:5)]; FT-IR vmax (film)/cm⁻¹: 2960, 2926, 1259, 800; 1H NMR (400 MHz, CDCl3) δ 3.96 (1H, td, J = 6.7, 3.0 Hz), 2.60 (2H, d, J = 6.7 Hz), 2.41 (4H, t, J = 5.4 Hz), 1.83–1.62 (6H, m), 1.57 (4H, p, J = 5.7 Hz), 1.44–1.38 (2H, m), 1.37–1.26 (2H, m); 1.24–1.07 (3H, m). 13C NMR (101 MHz, CDCl3) δ 65.5, 63.7, 54.9, 42.2, 30.5, 27.0, 26.4, 26.3, 26.1, 25.8, 24.2; HRMS (ESI+): found MH⁺ 230.1666, [C13H25ClN]⁺ requires 230.1676.

Methyl 3-chloro-4-(piperidin-1-yl)pentanoate (39)

Following GP1, 1 (12 µL, 0.12 mmol) and methyl 4-pentenoate (12 µL, 0.1 mmol) gave 39 (20 mg, 93%) as an oil. Rf 0.30 [petrol:EtOAc (90:10)]; FT-IR vmax (film)/cm⁻¹ 1 2361, 2341, 1733; 1H NMR (500 MHz, CDCl3) δ 4.03 (1H, dddd, J = 9.5, 7.7, 6.2, 3.2 Hz), 3.68 (3H, s), 2.66–2.27 (9H, m), 1.92–1.80 (1H, m), 1.63–1.50 (4H, m), 1.41 (2H, p, J = 6.0 Hz); 13C NMR (126 MHz, CDCl3) δ 173.7, 66.0, 59.2, 55.1, 51.8, 31.5, 30.9, 26.1, 24.4; HRMS (ESI+): found MH⁺ 234.1246, [C11H21ClNO₂]⁺ requires 234.1262.
4-Chloro-5-(piperidin-1-yl)pentanenitrile (40)

Following GP1, 1 (12 μL, 0.12 mmol) and 4-pentenenitrile (10 μL, 0.1 mmol) gave 40 (18 mg, 90%) as an oil. Rf 0.30 [petrol:EtOAc (95:5)]; ¹H NMR (500 MHz, CDCl₃) δ 4.02–4.03 (1H, m), 2.69–2.32 (9H, m), 1.90 (1H, m), 1.60–1.49 (4H, m), 1.41 (2H, p, J = 6.0 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 119.2, 65.3, 57.6, 55.2, 32.1, 26.1, 24.2, 14.7; HRMS (ESI⁺): found MH⁺ 201.1150, [C₁₀H₁₈ClN₂]⁺ requires 201.1159.

4-Chloro-N-methoxy-N-methyl-5-(piperidin-1-yl)pentanamide (41)

Following GP1, 1 (24 μL, 0.24 mmol) and S1 (18 μL, 0.2 mmol) gave 41 (14 mg, 64%) as an oil. Rf 0.30 [petrol:EtOAc:NH₃aq. (60:40:0.5)]; FT-IR νmax (film)/cm⁻¹: 2957, 1659, 1172, 802; ¹H NMR (400 MHz, CDCl₃) δ 4.10 (1H, dtd, J = 9.9, 6.8, 2.8 Hz), 3.69 (3H, s), 3.17 (3H, s), 2.75–2.60 (3H, m), 2.59–2.28 (6H, m), 1.87–1.75 (1H, m), 1.56 (4H, p, J = 5.6 Hz), 1.47–1.34 (2H, m); ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 66.1, 61.4, 59.6, 55.0, 32.3, 31.2, 28.7, 25.9, 24.3; HRMS (ESI⁺): found MH⁺ 263.1509, [C₁₂H₂₄ClN₂O₂]⁺ requires 263.1529.

4-Chloro-5-(piperidin-1-yl)pentyl benzoate (42)

Following GP1, 1 (48 μL, 0.48 mmol) and S2 (76 mg, 0.4 mmol) gave 42 as an oil (124 mg, quantitative). Rf 0.30 [petrol:EtOAc (85:15)]; ¹H NMR (500 MHz, CDCl₃) δ 8.09–8.01 (2H, m), 7.58–7.52 (1H, m), 7.48–7.40 (2H, m), 4.36 (2H, t, J = 6.2 Hz), 4.12–3.97 (1H, m), 2.65 (1H, dd, J = 13.1, 6.4 Hz), 2.52 (1H, dd, J = 13.1, 7.5 Hz), 2.48–2.33 (4H, m), 2.21–2.03 (2H, m), 1.98–1.85 (1H, m), 1.82–1.71 (1H, m), 1.55 (2H, p, J = 5.8 Hz), 1.40 (2H, p, J = 6.0 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 133.0, 130.4, 129.7, 128.5, 66.0, 64.5, 59.6, 55.1, 32.9, 26.0, 25.7, 24.3; HRMS (ESI): found M⁺ 309.1490, [C₁₇H₂₄ClNO₂]⁺ requires 309.1496.
Following **GP1**, 1 (48 μL, 0.48 mmol) and **S3** (62 mg, 0.4 mmol) gave **43** (120 mg, 91%) as an oil. $R_f$ 0.30 [petrol:EtOAc (8:2)]; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (2H, d, $J = 8.2$ Hz), 7.32 (2H, d, $J = 7.9$ Hz), 6.93 (1H, br s), 3.96 (1H, tt, $J = 9.1, 4.5$ Hz), 3.42 (1H, dd, $J = 12.8, 4.9$ Hz), 3.21 (1H, ddd, $J = 12.9, 8.2, 1.3$ Hz), 2.67 (1H, dd, $J = 12.9, 4.3$ Hz), 2.54 (1H, d, $J = 11.3$ Hz), 2.51–2.42 (2H, m), 2.44 (3H, s), 2.35–2.23 (2H, m), 1.58 (4H, p, $J = 5.7$ Hz), 1.48–1.38 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 143.6, 137.3, 129.9, 127.1, 65.7, 55.1, 53.8, 50.2, 26.1, 24.0, 21.7; HRMS (ESI+): found MH$^+$ 331.1233, [C$_{15}$H$_{24}$ClN$_2$O$_2$S]$^+$ requires 331.1248.

**syn-1-(2-Chlorocyclohexyl)piperidine (44)** and **anti-1-(2-Chlorocyclohexyl)piperidine (44’)**

Following **GP1**, 1 (48 μL, 0.48 mmol) and cyclohexene (41 μL, 0.4 mmol, 1.0 equiv.) gave **44** and **44’** (70% crude NMR yield). **44:44’** = 1:2:1. **44’** decomposes on silica.

Following **GP1** but using 1.5 equiv. of piperidine and 1.6 equiv. of NCS gave **44** as an oil (42 mg, 52%). Data for **44**: $R_f$ 0.40 [petrol:EtOAc:aq. NH$_3$ 37% (40:60:0.5)]; $^1$H NMR (500 MHz, CDCl$_3$) δ 4.65–4.56 (1H, m), 2.71–2.57 (4H, m), 2.42 (1H, d, $J = 11.6$), 2.04–2.00 (1H, m), 1.84–1.77 (2H, m), 1.77–1.53 (8H, m), 1.48–1.41 (3H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 66.9, 60.5, 50.8, 34.4, 26.0, 25.5, 24.5, 24.0, 19.8; HRMS (ESI+): Found MH$^+$ 202.1357, [C$_{11}$H$_{21}$ClN]+ requires 202.1363.

**Tert-butyl 3-chloro-3-(piperidin-1-ylmethyl)azetidine-1-carboxylate (45)**

Following **GP1**, 1 (14 μL, 0.14 mmol) and tert-butyl 3-methyleneazetidine-1-carboxylate (19 μL, 0.12 mmol) gave **45** (85%) as an oil. $R_f$ 0.60 [petrol:EtOAc (80:20)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2361, 2339, 1554, 1260, 1080; $^1$H NMR (500 MHz, CDCl$_3$) δ 4.13 (2H, d, $J = 9.3$ Hz), 4.04 (2H, d, $J = 9.3$ Hz), 2.69 (2H, s), 2.50 (4H, t, $J = 5.2$ Hz), 1.59–1.50 (4H, m), 1.42 (9H, s), 1.41–1.35 (2H, m); $^{13}$C NMR (126 MHz,
CDCl\textsubscript{3} \(\delta\) 156.2, 80.0, 65.8, 62.8, 61.7, 55.9, 28.4, 26.1, 24.0; HRMS (ESI): Found MH\textsuperscript{+} 289.1681, \(C_{14}H_{26}N_2O_2Cl\) requires 289.1683.

**Benzyl (2S)-2-(((benzyloxy)carbonyl)amino)-4-chloro-5-(piperidin-1-yl)pentanoate (46)**

![Formula](attachment:image.png)

Following **GP1**, 1 (48 \(\mu\)L, 0.48 mmol) and S5 (184 mg, 0.4 mmol, 1.00 equiv.) gave 46 as an oil (130 mg, 96%). d.r. 1:1.

Data for the first eluting isomer: R\textsubscript{f} 0.4 [petrol:EtOAc:NH\textsubscript{3} aq. 37% (70:30:05)]; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.47–7.27 (10H, m), \(\delta\) 5.96 (1H, d, \(J = 8.1\) Hz), 5.30–4.98 (4H, m), 4.53 (1H, m), 3.95 (1H, m), 2.73–2.43 (2H, m), 2.43–2.15 (6H, m), 1.70–1.45 (4H, m), 1.45–1.28 (2H, m); \(^{13}\text{C} \text{NMR}\) (101 MHz, CDCl\textsubscript{3}) \(\delta\) 171.9, 156.3, 136.6, 135.5, 128.7, 128.5, 128.5, 128.3, 128.2, 128.2, 67.3, 67.0, 65.9, 54.9, 54.1, 51.9, 40.0, 25.3, 24.0; HRMS (ESI\textsuperscript{+}): found MH\textsuperscript{+} 459.2024, \([C_{25}H_{32}ClN_2O_4]\textsuperscript{+}\) requires 459.2045.

Data for the second eluting isomer: R\textsubscript{f} 0.35 [petrol:EtOAc:NH\textsubscript{3} aq. 37% (70:30:0.5)]; \(^1\text{H} \text{NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.40–7.27 (10H, m), 6.00 (1H, br s), 5.28–5.02 (4H, m), 4.74–4.58 (1H, m), 4.05–4.96 (1H, m), 2.64 (1H, dd, \(J = 13.1, 5.4\) Hz), 2.51 (1H, dd, \(J = 13.1, 8.7\) Hz), 2.53–2.24 (5H, m), 2.23–2.05 (1H, m), 1.64–1.47 (4H, m), 1.46–1.33 (2H, m); \(^{13}\text{C} \text{NMR}\) (126 MHz, CDCl\textsubscript{3}) \(\delta\) 172.1, 156.3, 136.3, 135.4, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 67.4, 67.4, 67.2, 65.7, 65.7, 55.4, 55.1, 52.4, 39.1, 25.8, 24.2; HRMS (ESI\textsuperscript{+}): found M\textsuperscript{–} 458.1972, \([C_{25}H_{32}ClN_2O_4]\textsuperscript{–}\) requires 458.1972.

(R)-((1S,2R,4S,5R)-5-(1-Chloro-2-(piperidin-1-yl)ethyl)quinuclidin-2-yl)(quinolin-4-yl)methyl Benzoate (47)

![Formula](attachment:image.png)

Following **GP1** but using 8.0 equivalents of TFA, 1 (48 \(\mu\)L, 0.48 mmol) and S6 (159 mg, 0.4 mmol) gave 47 (124 mg, 60%) as an oil. R\textsubscript{f} 0.60 [CH\textsubscript{2}Cl\textsubscript{2}:/i-PrOH (97:3)]; \(^1\text{H} \text{NMR}\) (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.87 (1H, d, \(J = 4.5\) Hz), 8.31 (1H, d, \(J = 8.5\) Hz), 8.14 (1H, dd, \(J = 8.5, 1.3\) Hz), 8.12–8.06 (2H, m), 7.74 (1H, ddd, \(J = 8.4, 6.8, 1.3\) Hz), 7.65 (1H,
ddd, $J = 8.3, 6.8, 1.4$ Hz), 7.62–7.55 (1H, m), 7.51–7.44 (3H, m), 6.82 (1H, d, $J = 6.3$ Hz), 3.95 (1H, dt, $J = 9.6, 6.1$ Hz), 3.53 (1H, dt, $J = 9.8, 7.0$ Hz), 3.19 (1H, dddd, $J = 13.2, 10.3, 5.1, 2.4$ Hz), 3.07 (1H, dd, $J = 14.2, 9.8$ Hz), 2.78 (1H, ddd, $J = 13.2, 10.3, 5.1, 2.4$ Hz), 2.58 (2H, d, $J = 6.2$ Hz), 2.49–2.31 (4H, m), 2.12–2.06 (1H, m), 1.97–1.84 (2H, m), 1.83–1.66 (2H, m), 1.59–1.46 (5H, m), 1.44–1.34 (2H, m);

$13^C$ NMR (126 MHz, CDCl$_3$) $\delta$ 165.6, 150.1, 148.8, 145.3, 133.6, 130.7, 129.8, 129.4, 128.8, 127.2, 126.0, 123.4, 74.8, 65.3, 64.8, 60.1, 60.1, 56.7, 55.3, 42.6, 42.2, 28.7, 26.0, 25.8, 24.4, 24.3; HRMS (ESI$^+$): found MH$^+$ 518.2562, [C$_{31}$H$_{37}$ClN$_3$O$_2$]$^+$ requires 518.2575.

$(5R$)-5-(2-Chloro-1-(piperidin-1-yl)propan-2-yl)-2-methylcyclohex-2-en-1-one (48)

Following GP1, 1 (24 µL, 0.24 mmol) and (R)-carvone (18 µL, 0.2 mmol) gave 48 (45 mg, 83%) as an oil. d.r. 1:1. R$_f$ 0.20 [petrol:EtOAc (9:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2933, 1669, 800; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.79–6.67 (1H, m), 2.79–2.31 (11H, m), 1.80–1.74 (3H, m), 1.62–1.43 (7H, m), 1.41–1.31 (2H, m); $^13^C$ NMR (126 MHz, CDCl$_3$, diastereomers) $\delta$ 199.7 (A), 199.6 (B), 144.9 (A), 144.7 (B), 135.2 (A), 135.2 (B), 76.8 (A), 76.7 (B), 67.6 (A), 67.3 (B), 56.9 (A), 56.8 (B), 43.1 (A), 42.7 (B), 40.4 (AB), 39.9 (AB), 39.9, 28.2 (AB), 27.7 (AB), 26.8 (A), 26.6 (B), 26.4 (AB), 24.1 (A), 24.0 (B), 15.7 (AB); HRMS (ESI$^+$): found MH$^+$ 270.1612, [C$_{15}$H$_{25}$CINO]$^+$ requires 270.1625.

1-(2-Chloro-3-(3-(4-chlorophenyl)propoxy)propyl)piperidine (49)

Following GP1, 1 (48 µL, 0.48 mmol) and S7 (84 mg, 0.4 mmol) gave 49 (131 mg, 99%) as an oil. R$_f$ 0.30 [petrol:EtOAc 9:1]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2933, 2854, 1116, 1091; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26–7.22 (2H, m), 7.15–7.10 (2H, m), 4.13–4.03 (1H, m), 3.72 (1H, dd, $J = 10.5, 4.4$ Hz), 3.59 (1H, dd, $J = 10.5, 6.2$ Hz), 3.54–3.41 (2H, m), 2.71–2.64 (3H, m), 2.59 (1H, dd, $J = 13.3, 6.5$ Hz), 2.52–2.33 (4H, m), 1.88
(2H, dq, $J = 9.3, 6.9$ Hz), 1.56 (4H, p, $J = 5.6$ Hz), 1.47–1.37 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.4, 131.6, 130.0, 128.5, 73.4, 70.2, 62.7, 57.8, 55.2, 31.7, 31.2, 26.1, 24.3; HRMS (ESI$^+$): found MH$^+$ 330.1370, [C$_{17}$H$_{26}$Cl$_2$NO]$^+$ requires 330.1392.

1-(4-(tert-Butyl)phenyl)-3-chloro-4-(4-(hydroxydiphenylmethyl)piperidin-1-yl)butyl benzoate (50)

Following GP2, $\alpha,\alpha$-diphenyl-4-piperidinomethanol hydrochloride (36 mg, 0.12 mmol) and S9 (61 mg, 0.1 mmol) gave 50 (37 mg, 60%) as an oil. d.r. 1:1. R$_f$ 0.40 [petrol:EtOAc (8:2)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2961, 2359, 2341, 1716, 1489, 1447, 1314, 1258, 1093, 1066, 1024; $^1$H NMR (500 MHz, CDCl$_3$, diastereomers) δ 8.14–7.95 (2H, m), 7.55 (1H, t, $J = 7.5$ Hz), 7.49 (4H, t, $J = 7.0$ Hz), 7.46–7.40 (2.5H, m), 7.40–7.35 (3H, m), 7.35–7.27 (4H, m), 7.23–7.16 (2.5H, m), 6.31 (0.5H, dd, $J = 10.3, 2.9$ Hz), 6.26 (0.5H, t, $J = 7.4$ Hz), 4.35–4.01 (0.5H, m), 3.83–3.63 (0.5H, m), 3.03–2.83 (1.5H, m), 2.83–2.72 (0.5H, m), 2.72–2.58 (3H, m), 2.50–2.33 (1.5H, m), 2.31–2.13 (2H, m), 2.13–2.00 (1H, m), 1.95 (0.5H, td, $J = 11.0, 3.9$ Hz), 1.65–1.41 (4H, m), 1.30 (4.5H, s), 1.29 (4.5H, s); $^{13}$C NMR (126 MHz, CDCl$_3$, diastereomers) δ 165.6, 165.5, 151.3, 151.0, 145.9 (x 2), 137.3 (x 2), 136.1 (x 2), 133.0, 132.9, 130.4, 130.3, 129.7, 129.6, 128.4, 128.3, 128.2 (x 2), 128.2, 128.1, 126.7 (x 2), 126.6, 126.5, 126.4, 126.0 (x 2), 125.8, 125.7, 125.6, 125.5, 79.6, 79.5, 77.3, 74.6, 73.5, 65.1, 55.7, 55.5, 55.1, 53.8, 53.6, 44.0, 43.9, 43.5, 42.6, 34.6, 34.6, 31.3, 31.3, 29.7, 26.5, 26.5, 26.3, 26.2; HRMS (ASAP): Found MH$^+$ 610.3057 C$_{39}$H$_{45}$NO$_3$Cl requires 610.3082.

3-Chloro-4-(4-(4-chlorophenyl)-4-hydroxypiperidin-1-yl)-1-(4-fluorophenyl)butan-1-one (51)

Following GP1 in CD$_2$Cl$_2$ without adding KOH at the end of the reaction, 4-(4-chlorophenyl)-4-hydroxypiperidine (25 mg, 0.12 mmol) and S11 (16 mg, 0.1 mmol) and gave 51 (30 mg, 73%) as an oil. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.99 (2H, dd, $J =$
8.7, 5.4 Hz), 7.44 (2H, d, J = 8.9 Hz), 7.37 (2H, d, J = 8.5 Hz), 7.25–7.15 (2H, m), 4.94 (1H, p, J = 6.4 Hz), 3.89–3.77 (2H, m), 3.75 (1H, dd, J = 18.3, 5.4 Hz), 3.70 (2H, t, J = 5.9 Hz), 3.67–3.58 (2H, m), 3.56 (1H, dd, J = 18.3, 7.3 Hz), 2.64–2.56 (2H, m), 2.18–2.05 (2H, m); \textsuperscript{13}C NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 195.3, 167.14 (d, J = 256.5 Hz), 144.1, 132.5 (d, J = 2.9 Hz), 131.65 (d, J = 9.8 Hz), 129.4, 126.5, 126.4, 116.73 (d, J = 22.0 Hz), 69.7, 63.2, 51.9, 49.9, 49.7, 45.2, 35.7, 35.1; \textsuperscript{19}F NMR (471 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ –76.31. LC-MS expected: 410.31; found: 410.1.

\textbf{7-(2-Chloro-3-((2-hydroxyethyl)(methyl)amino)propyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (52)}

Following GP\textsubscript{1} but adding KPF\textsubscript{6} (18 mg, 0.1 mmol) to the reaction mixture and using HClO\textsubscript{4} instead of TFA, 2-(methylamino)ethanol (10 μL, 0.12 mmol) and S12 (22 mg, 0.1 mmol) and gave 52 (20 mg, 62%) as an oil. R\textsubscript{f} 0.50 [petrol:EtOAc (8:2)]; FT-IR ν\textsubscript{max} (film)/cm\textsuperscript{-1} 3444, 2952, 2360, 1699, 1651, 1604, 1547, 1437, 1456, 1428, 1408, 1377, 1259, 1234, 1191, 1027; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.68 (1H, s), 5.17 (1H, dd, J = 14.3, 2.5 Hz), 4.42–4.33 (1H, m), 4.05 (1H, dd, J = 14.2, 10.0 Hz), 3.65 (2H, br s), 3.60 (3H, s), 3.39 (3H, s), 3.12 (1H, br s), 2.86 (1H, dd, J = 13.4, 5.9 Hz), 2.81–2.68 (2H, m), 2.60 (1H, dt, J = 13.0, 4.9 Hz), 2.40 (3H, s) 1.83 (1H, br s); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 155.4, 151.5, 149.3, 142.6, 106.4, 62.4, 59.8, 59.1, 58.6, 51.9, 42.6, 29.9, 28.1; HRMS (HESI): Found MNa\textsuperscript{+} 352.1135 C\textsubscript{13}H\textsubscript{20}N\textsubscript{5}O\textsubscript{3}ClNa requires 352.1147.

\textbf{1-(3-(2-Benzylphenoxy)-2-chloropropyl)piperidine (102)}

Following GP\textsubscript{1}, 1 (12 μL, 0.12 mmol) and 1-(allyloxy)-2-benzylbenzene 100 (22 mg, 0.1 mmol, 1.00 equiv.) gave 102 as an oil (34 mg, quantitative). R\textsubscript{f} = 0.8 [petrol:EtOAc (8:2)]; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.27–7.20 (4H, m), 7.20–7.13 (2H, m), 7.11 (1H, d, J = 7.5 Hz), 6.90 (1H, t, J = 7.4 Hz), 6.85 (1H, d, J = 8.2 Hz), 4.29–4.13 (3H, m), 4.01 (2H, s), 2.71 (1H, dd, J = 13.3, 6.8 Hz), 2.61 (1H, dd, J = 13.3, 5.5 Hz), 2.47–2.28
(4H, m), 1.53 (4H, p, $J = 5.6$ Hz), 1.40 (2H, p, $J = 6.0$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 156.2, 141.1, 130.8, 130.1, 129.1, 128.4, 127.6, 125.9, 121.1, 111.6, 70.3, 62.4, 56.8, 55.2, 36.3, 26.1, 24.3. HRMS (ESI$^+$): found MH$^+$ 344.1775, [C$_{21}$H$_{27}$ClNO]$^+$ requires 344.1775.
4.3 Mechanistic Considerations

4.3.1 Protonation of N-Chloropiperidine

A solution on N-chloropiperidine (12 mg, 0.1 mmol, 1.0 equiv.) in CD$_2$Cl$_2$ in a dry NMR tube was treated with the acid (0.6 mmol, 6.0 equiv.) and the sample was immediately analysed by $^1$H NMR spectroscopy.

This study demonstrated that AcOH is not able to protonate N-chloropiperidine.

![Figure 1](image-url)
4.3.2 Quantum Yield Determination

The quantum yield was determined using the method reported by Yoon\textsuperscript{[11]} at three different times. Since the reaction is fully complete after 10 s, this indicates $\Phi > 200$ in CH$_2$Cl$_2$ and supports a radical chain mechanism. All yields were determined by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard.

| Entry | Reaction time (s) | 11 (%) | 10 (%) | $\Phi$ |
|-------|------------------|--------|--------|--------|
| 1     | 5                | 3      | 95     | >200   |
| 2     | 10               | 100    | –      | >200   |
| 3     | 30               | 100    | –      | >200   |
5 Aziridinium Formation and Ring-Opening Studies

5.1 Aziridinium Formation

A stock solution of 11 (126 mg, 0.5 mmol, 1.0 equiv.) and 1,3-dinitrobenzene (84 mg, 0.5 mmol, 1.0 equiv.) as the internal standard in CD$_3$CN (2.5 mL) was prepared and was added to five NMR tubes (3 x 500 μL):

A. Tube 1: nothing else added.
B. Tube 2: 1.5 equiv. of NaI (23 mg, 0.15 mmol, 1 M solution in CD$_3$CN)
C. Tube 3: 3.0 equiv. of NaI (45 mg, 0.30 mmol, 1 M solution in CD$_3$CN)
D. Tube 4: 5.0 equiv. of NaI (75 mg, 0.50 mmol, 1 M solution in CD$_3$CN)
E. Tube 5: 1.5 equiv. of AgBF$_4$ (29 mg, 0.15 mmol, 1.5 equiv.)

$^1$H NMR spectra were acquired at regular intervals (Figure 2).

![Figure 2.](image-url)
Data for 59: $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 7.34 (2H, dd, $J = 8.0, 6.7$ Hz), 7.31–7.21 (3H, m), 3.22 (1H, dt, $J = 12.9, 6.4$ Hz), 3.13–2.99 (3H, m), 2.98–2.79 (4H, m), 2.64 (1H, dd, $J = 7.4, 3.7$ Hz), 2.40–2.22 (1H, m), 2.07–1.97 (1H, m), 1.86–1.65 (5H, m); 13C NMR (101 MHz, CD$_3$CN) $\delta$ 141.0, 129.7, 129.5, 127.6, 61.5, 53.8, 53.2, 43.6, 33.0, 28.1, 23.9, 23.7, 22.2.

The putative $\beta$-iodoamine intermediate S13 involved in the formation of 59 was detected by positive ESI MS analysis of the mixture in the NMR tube in the presence of 1% HCOOH (Figure 3).
5.2 Aziridinium Ring-Opening

A CD$_3$CN solution of 59 was treated with Et$_2$NH (5.0 equiv.) and an $^1$H NMR spectrum was recorded after 5 minutes showing complete conversion into the diamine 60 (Figure 4).

![Figure 4](image_url)
6 Olefin Diamination

6.1 Reaction Optimization

An oven-dried tube equipped with a stirring bar was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N₂ (x3) and charged with piperidine 1 (10 μL, 0.1 mmol, 1.0 equiv.). Ru(bpy)_3(PF_6)_2 (0.4 mg, 0.5 μmol, 0.5 mol%) and NCS (15 mg, 0.11 mmol, 1.1 equiv.) as a stock solution in CH_2Cl_2 (0.5 mL, dry and degassed by bubbling through with N₂ for 20 min). The mixture was stirred for 1 h at room temperature. The mixture was cooled to 0 ºC and 4-Phenylbutene 10 (15 μL, 0.1 mmol, 1.0 equiv.) was added as a solution in CH_2Cl_2 (0.5 mL) followed by TFA (46 μL, 0.6 mmol, 6 equiv.). The blue LEDs were switched on and the mixture was stirred under irradiation for 1 h at 0 ºC. The base (10.0 equiv.) was added and the reaction was warmed to room temperature and stirred for 30 minutes. A solution of NaI (75 mg, 0.5 mmol, 5.0 equiv) and tert-butylamine in CH_3CN (0.5 mL) was added and the mixture was stirred for 18 h at room temperature. Aqueous 1 M KOH (3 mL), EtOAc (3 mL) and 1,3,5-trimethoxybenzene (17 mg, 0.1 mmol, 1.0 equiv.) were added and the layers were separated. The aqueous layer was extracted with EOAc (3 x 3 mL), the combined organic layers were dried (MgSO_4), filtered and evaporated. CDCl_3 (0.4 mL) was added and the mixture was analysed by ^1H NMR spectroscopy to determine the NMR yield.

Table S3 reports all the experiments performed. The conditions of entry 8 were chosen to run all one-pot diamination reactions.

| Entry | base         | t-BuNH₂ (equiv.) | Yield (%) |
|-------|--------------|-----------------|-----------|
| 1     | –            | 2.5             | –         |
| 2     | –            | 10              | 87        |
| 3     | HMDS         | 2.5             | –         |
| 5     | DIPEA        | 2.5             | 78        |
| 6     | DIPEA        | 5.0             | 86        |
6.2 Reaction Scope

General Procedure for the Olefin Diamination Using Free Amines – GP3

A dry tube equipped with a stirring bar was charged with NCS (1.0 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%) and the amine if solid (1.2 equiv.). The tube was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). CH$_2$Cl$_2$ (0.2 M) (dry and degassed by bubbling through with N$_2$ for 20 min) and the amine (1.2 equiv.) if liquid were added and the mixture was stirred for 1 h at room temperature. The mixture was cooled to 0 ºC and a solution of the olefin (1.0 equiv.) in CH$_2$Cl$_2$ (0.2 M) and TFA (6.0 equiv.) were added. The LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 ºC. (i-Pr)$_2$NEt (10.0 equiv.) was added and the mixture stirred at room temperature for 30 min. As solution of the second amine (5.0 equiv.) and NaI (5.0 equiv.)$^1$ in CH$_3$CN (1 M) was added and the mixture was stirred at room temperature for 18 h. Aqueous 1 M KOH (3 mL) and EtOAc (3 mL) were added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were dried (MgSO$_4$), filtered and evaporated. Purification by flash column or preparative TLC chromatography on silica gel gave the products.

While this procedure afforded the desired products in all instances, in a few cases we have slightly modified the elaboration of the intermediate N-chloroamine to improve the reaction yield.

Alternative General Procedure for the Olefin Diamination Using Free Amines – GP3'

A dry tube equipped with a stirring bar was charged with NCS (1.0 equiv.), Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%) and the amine if solid (1.2 equiv.). The tube was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl), evacuated and refilled with

1 If the amine is available as a hydrochloride salt, the amount of NaI should be adjusted to account for the precipitation of insoluble NaCl.
N₂ (x 3). CH₂Cl₂ (0.2 M) (dry and degassed by bubbling through with N₂ for 20 min) and the amine (1.2 equiv.) if liquid were added and the mixture was stirred for 1 h at room temperature. The mixture was cooled to 0 °C and a solution of the olefin (1.0 equiv.) in CH₂Cl₂ (0.2 M) and TFA (6 equiv.) were added. The LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 °C. Aqueous 1 M KOH (3 mL) and EtOAc (3 mL) were added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were dried (MgSO₄), filtered and evaporated. The crude was dissolved in CH₃CN (0.1 M, 1.0 mL), the second amine (5.0 equiv.) and NaI (5.0 equiv.) were added and the mixture was stirred at room temperature for 18 h. Aqueous 1 M KOH (3 mL) and EtOAc (3 mL) were added. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 3 mL). Purification by flash column or preparative TLC chromatography on silica gel gave the products.

**N,N-Diethyl-4-phenyl-2-(piperidin-1-yl)butan-1-amine (60)**

Following GP3, 1 (10 µL, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and Et₂NH (52 µL, 0.5 mmol, 5.0 equiv.) gave 60 (23 mg, 78%) as an oil. Rf 0.15 [CH₂Cl₂:MeNO₂:MeOH (3:1:1)]; FT-IR νₘₐₓ (film)/cm⁻¹: 2928, 2852, 2794, 1453, 1381; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (2H, t, J = 7.4 Hz), 7.22–7.18 (2H, m), 7.18–7.11 (1H, m), 2.82–2.37 (12H, m), 2.22 (1H, dd, J = 12.6, 7.2 Hz), 1.80–1.66 (2H, m), 1.62–1.48 (4H, m), 1.47–1.36 (2H, m), 0.99 (6H, t, J = 7.1 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 128.6, 128.3, 125.6, 62.1, 53.0, 49.8, 47.7, 33.6, 31.9, 26.8, 25.3, 11.8; HRMS (ESI⁺): found MH⁺ 289.2628, [C₁₉H₃₈N₂]⁺ requires 289.2644.

**4-(4-Phenyl-2-(piperidin-1-yl)butyl)morpholine (61)**

Following GP3, 1 (10 µL, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and morpholine (44 µL, 0.5 mmol, 5.0 equiv.) gave 61 (29 mg, quantitative) as an oil. Rf 0.63 [CH₂Cl₂:MeNO₂:MeOH (8:1:1)]; FT-IR νₘₐₓ (film)/cm⁻¹ 2929, 2850, 1453, 1116;
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.24 (2H, m), 7.24–7.13 (3H, m), 3.66 (4H, t, $J = 4.7$ Hz), 2.82–2.61 (5H, m), 2.59–2.41 (5H, m), 2.40–2.32 (2H, m), 2.19 (1H, dd, $J = 12.5$, 6.9 Hz), 1.92–1.77 (1H, m), 1.74–1.65 (1H, m), 1.65–1.51 (4H, m), 1.46 (2H, p, $J = 5.8$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.8, 128.7, 128.4, 125.8, 67.3, 60.6, 59.2, 54.3, 50.0, 33.4, 32.2, 26.6, 25.0; HRMS (ESI$^+$): found MNa$^+$ 325.2239, [C$_{19}$H$_{30}$N$_2$ONa]$^+$ requires 325.2250.

*N-(tert-Butyl)-4-phenyl-2-(piperidin-1-yl)butan-1-amine (62)*

Following GP3, 1 (10 $\mu$L, 0.1 mmol, 1.0 equiv.), 10 (15 $\mu$L, 0.1 mmol, 1.0 equiv.) and tert-butylamine (53 $\mu$L, 0.5 mmol, 5.0 equiv.) gave 62 as an oil (25 mg, 86%). $R_f$ 0.3 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (3:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2929, 2852, 2799, 1495, 1452, 1441; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 (2H, d, $J = 6.3$ Hz), 7.21–7.11 (3H, m), 2.72–2.45 (7H, m), 2.39–2.27 (2H, m), 2.26–1.98 (1H, br s), 1.92 (1H, ddd, $J = 16.8$, 9.4, 5.1 Hz), 1.62–1.51 (2H, m), 1.51–1.35 (5H, m), 1.12 (9H, s); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.7, 128.5, 128.4, 125.9, 64.0, 50.2, 49.3, 42.6, 34.1, 29.2, 29.0, 27.0, 25.2; HRMS (ESI$^+$): found MH$^+$ 289.2628, [C$_{19}$H$_{33}$N$_2$]$^+$ requires 289.2644.

4-Phenyl-2-(piperidin-1-yl)-N-(2,2,2-trifluoroethyl)butan-1-amine (63) and 4-phenyl-1-(piperidin-1-yl)-N-(2,2,2-trifluoroethyl)butan-2-amine (63’)

Following GP3, 1 (10 $\mu$L, 0.1 mmol, 1.0 equiv.), 10 (15 $\mu$L, 0.1 mmol, 1.0 equiv.) and 2,2,2-trifluoroethan-1-amine (39 $\mu$L, 0.5 mmol, 5.0 equiv.) gave a mixture of 63 and 63 (21 mg, 68%) as an oil. $63:63' = 3:1$.

Data for 63: $R_f$ 0.50 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (10:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 3335, 2929, 2853, 2802, 1142; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.26 (2H, m), 7.22–7.14 (3H, m), 3.18 (2H, q, $J = 11.1$, 10.0 Hz), 2.74–2.66 (2H, m), 2.66–2.47 (6H, m), 2.38–2.28 (2H, m), 1.97–1.85 (1H, m), 1.61–1.47 (3H, m), 1.47–1.35 (4H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.4, 128.5, 128.4, 126.0 ($q$, $J = 279.8$ Hz), 126.0, 63.7, 50.9 ($q$, $J =
30.7 Hz), 49.6, 49.5, 33.9, 28.7, 26.9, 25.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –71.4; HRMS (ESI$^+$): found MH+ 315.2035, [C$_{17}$H$_{26}$F$_3$N$_2$]$^+$ requires 315.2043.

$N$-(4-phenyl-2-(piperidin-1-yl)butyl)aniline (64) and $N$-(4-phenyl-1-(piperidin-1-yl)butan-2-yl)aniline (64')

Following GP3, 1 (10 µL, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and aniline (48 µL, 0.5 mmol, 5.0 equiv.) gave a mixture of 64 and 64' (1.7:1) (19 mg, 60%) as oils. 64:64' = 1.7:1.

Data for 64: $R_f$ 0.56 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (10:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 3354, 2926, 2850, 1602, 1505; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33–7.26 (2H, m), 7.23–7.15 (5H, m), 6.69 (1H, t, $J$ = 7.3 Hz), 6.64 (2H, d, $J$ = 7.9 Hz), 3.20 (1H, dd, $J$ = 11.2, 4.7 Hz), 2.86 (1H, t, $J$ = 10.7 Hz), 2.77–2.66 (2H, m), 2.63–2.53 (3H, m), 2.42–2.30, (2H, m), 2.05–1.94 (1H, m), 1.64–1.48 (6H, m), 1.46–1.40 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 149.0, 142.3, 129.4, 128.6, 128.4, 126.1, 117.1, 113.2, 63.0, 49.2, 44.0, 38.8, 28.7, 27.0, 25.1; HRMS (ESI$^+$): found MH+ 309.2320, [C$_{21}$H$_{29}$N$_2$]$^+$ requires 309.2325.

Data for 64': $R_f$ 0.40 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (10:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 3354, 2926, 2850, 1602, 1505; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25–7.18 (2H, m), 7.15–7.09 (3H, m), 7.10–7.04 (2H, m), 6.65–6.58 (1H, m), 6.55–6.47 (2H, m), 4.48–3.91 (1H, br s), 3.49–3.28 (1H, m), 2.65 (2H, dd, $J$ = 9.4 Hz, 7.1 Hz), 2.53–2.43 (1H, m), 2.42–2.23 (5H, m), 1.89–1.79 (1H, m), 1.60–1.41 (4H, m), 1.41–1.31 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 148.3, 142.1, 129.2, 128.5, 128.4, 125.9, 117.2, 113.4, 62.2, 54.7, 49.7, 35.4, 31.9, 25.9, 24.2; HRMS (ESI$^+$): found MH$^+$ 309.2320, [C$_{21}$H$_{29}$N$_2$]$^+$ requires 309.2325.

$N$-(4-phenyl-2-(piperidin-1-yl)butyl)-2,3-dihydrobenzo[d]thiazol-2-amine (65)

Following GP3', 1 (10 µL, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and 2-aminobenzothiazole (75 mg, 0.5 mmol, 5.0 equiv.) gave 65 (28 mg, 77%) as an oil.
Rf 0.25 [CH₂Cl₂:MeNO₂:MeOH (10:1:1)]; FT-IR ν max (film)/cm⁻¹ 3331, 2929, 2851, 1605, 1117; ¹H NMR (500 MHz, CDCl₃) δ 7.25–7.18 (3H, m), 7.18–7.10 (4H, m), 6.96 (1H, t, J = 7.6 Hz), 6.80 (1H, d, J = 8.1 Hz), 4.05–3.94 (2H, m), 3.08–2.99 (1H, m), 2.78–2.69 (1H, m), 2.69–2.56 (5H, m), 1.98–1.87 (1H, m), 1.73–1.62 (1H, m), 1.60–1.46 (5H, m), 1.46–1.38 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 162.4, 142.6, 141.2, 128.5, 128.4, 126.1, 125.7, 121.5, 121.4, 109.9, 60.9, 49.9, 33.4, 31.1, 30.9, 26.9, 25.1; HRMS (ESI⁺): found MH⁺ 366.2005, [C₂₂H₂₈N₃S]⁺ requires 366.1998.

1-(4-phenyl-1-(1H-pyrazol-1-yl)butan-2-yl)piperidine (66)

Following GP3, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 10 (15 μL, 0.1 mmol, 1.0 equiv.) and pyrazole (34.0 mg, 0.5 mmol, 5.0 equiv.) gave 66 (12 mg, 43%) as an oil. Rf 0.62 [CH₂Cl₂:MeNO₂:MeOH (10:1:1)]; FT-IR ν max (film)/cm⁻¹: 2931, 2852, 2801, 1512, 749; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (1H, d, J = 1.8 Hz), 7.39 (1H, d, J = 2.2 Hz), 7.28–7.22 (2H, m), 7.18–7.10 (3H, m), 6.22 (1H, t, J = 2.1 Hz), 4.28 (1H, dd, J = 13.7, 6.9 Hz), 4.00 (1H, dd, J = 13.7, 6.8 Hz), 2.98–2.92 (1H, m), 2.73–2.63 (1H, m), 2.57–2.44 (5H, m), 1.89–1.76 (1H, m), 1.57–1.46 (5H, m), 1.46–1.38 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 142.5, 139.1, 130.0, 128.6, 128.4, 125.8, 105.4, 64.1, 52.2, 49.5, 33.1, 31.0, 26.9, 25.1; HRMS (ESI⁺): found MH⁺ 284.2116, [C₁₈H₂₆N₃]⁺ requires 284.2120.

4-Phenyl-1-(4-phenyl-2-(piperidin-1-yl)butyl)pyridin-1-ium iodide (67)

Following GP3', 1 (10 μL, 0.1 mmol, 1.0 equiv.), 10 (15 μL, 0.1 mmol, 1.0 equiv.) and 4-phenylpyridine (78 mg, 0.5 mmol, 5.0 equiv.) gave 67 (29 mg, 79%) as a solid. Rf 0.73 [CH₂Cl₂:MeNO₂:MeOH (10:1:1)]; FT-IR ν max (film)/cm⁻¹ 2930, 2852, 1636, 1452; ¹H NMR (500 MHz, CDCl₃) δ 9.12 (2H, d, J = 6.6 Hz), 8.05 (2H, d, J = 6.6 Hz), 7.73 (2H, d, J = 6.9 Hz), 7.60–7.51 (3H, m), 7.28–7.22 (5H, m), 5.03 (1H, dd, J = 13.3, 3.5 Hz), 4.64–4.55 (1H, m), 2.91–2.84 (1H, m), 2.85–2.74 (4H, m), 2.24–2.18 (2H, m), 2.07–1.97 (1H, m), 1.70–1.65 (1H, m), 1.39–1.35 (6H, m); ¹³C NMR (126 MHz, CDCl₃) δ 156.2, 145.5, 141.3, 133.8, 132.5, 130.1, 128.7, 128.6, 127.9, 126.3, 123.7. 
66.0, 60.7, 49.9, 33.5, 28.6, 26.7, 24.6; HRMS (ESI\(^+\)): found M+ 371.2499, \([C_{26}H_{31}N_2]^+\) requires 371.2482.

**8-(2-(Azepan-1-yl)-4-phenylbutyl)-8-azabicyclo[3.2.1]octan-3-one (68)**

Following GP3 but warming the reaction to 60 °C after the addition of NaI (10.0 equiv.) and the second amine, azepane (11 µL, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and nortropinone hydrochloride (81 mg, 0.5 mmol, 5.0 equiv.) gave 68 (32 mg, 90%) as an oil. R\(_f\) 0.41 \([CH_2Cl_2:MeNO_2:MeOH (10:1:1)]\); FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\): 2923, 2852, 1713, 1452; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30–7.26 (2H, m), 7.24–7.20 (2H, m), 7.17 (1H, t, \(J = 7.2\) Hz), 3.43 (2H, d, \(J = 16.8\) Hz), 2.93–2.77 (3H, m), 2.74–2.66 (2H, m), 2.67–2.48 (5H, m), 2.36–2.28 (1H, m), 2.36–2.28 (2H, m), 2.05–1.81 (4H, m), 1.71–1.54 (10H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 207.3, 143.1, 128.6, 128.4, 125.7, 64.3, 59.6, 51.7, 48.2, 47.9, 33.5, 30.5, 28.4, 27.8, 27.2 (the following signals were missing in the \(^{13}\)C NMR and were identified by analysing the \(^1\)H–\(^{13}\)C HMBC (500 MHz, CDCl\(_3\)) \(\delta\) 207.3, 143.1, 130.5); HRMS (ESI\(^+\)): found MH\(^+\) 355.2731, \([C_{23}H_{35}N_2O]^+\) requires 355.2744.

**5-(tert-Butylamino)-4-(2,6-syn-dimethylmorpholino)pentanenitrile (69)**

Following GP3 but on the compound purified by flash chromatography and warming the reaction to 60 °C, 2,6-syn-dimethylmorpholine (12.5 µL, 0.1 mmol, 1.0 equiv.), pent-4-enenitrile (10 µL, 0.1 mmol, 1.0 equiv.) and tert-butylamine (53 µL, 0.5 mmol, 5.0 equiv.) gave 69 (27 mg, quant.) as an oil. dr 1:1. R\(_f\) 0.4 [CH\(_2\)Cl\(_2\):acetone (1:1)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\): 2965, 2866, 1453, 1362, 1322, 1259, 1230, 1143, 1084, 1028; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.64–3.54 (2H, m), 2.70 (1H, dd, \(J = 11.1, 7.3\) Hz), 2.64–2.43 (4H, m), 2.42 (2H, t, \(J = 7.4\) Hz), 2.14 (2H, q, \(J = 10.0\) Hz), 2.10 (1H, br s), 1.88–1.78 (1H, m), 1.78–1.68 (1H, m), 1.14 (6H, d, \(J = 6.2\) Hz), 1.09 (9H, s); \(^{13}\)C NMR (126
MHz, CDCl$_3$) $\delta$ 120.0, 72.4, 72.4, 63.2, 54.7, 54.6, 50.7, 41.5, 29.0, 24.5, 19.2, 19.2, 15.1; HRMS (ASAP): found MH$^+$ 268.2383, C$_{13}$H$_{30}$N$_3$O requires 268.2383.

5-(**tert**-Butylamino)-4-(diethylamino)pentanenitrile (70)

Following **GP3** at 60 ºC, diethylamine (10.5 µL, 0.1 mmol, 1.0 equiv.), pent-4-enenitrile (10 µL, 0.1 mmol, 1.0 equiv.) and **tert**-butylamine (53 µL, 0.5 mmol, 5.0 eq.) gave 70 (12 mg, 52%) as an oil. R$_f$ 0.6 [CH$_2$Cl$_2$:acetone (1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$: 2870, 2243, 1702, 1474, 1447, 1381, 1299, 1259, 1232, 1205, 1059; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.81 (1H, p, $J$ = 6.8 Hz), 2.63 (1H, dd, $J$ = 11.1, 8.1 Hz), 2.59–2.53 (1H, m), 2.51 (2H, q, $J$ = 7.1 Hz), 2.47 (2H, q, $J$ = 7.0 Hz), 2.45–2.38 (2H. m), 1.89–1.77 (1H, m), 1.77–1.65 (1H, m), 1.15 (9H, s), 1.04 (6H, t, $J$ = 7.1 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 120.1, 58.9, 51.6, 43.3, 42.1, 28.7, 25.1, 15.2, 15.0; HRMS (ASAP): found MH$^+$ 226.2279 C$_{13}$H$_{28}$N$_3$ requires 226.2278.

$N,N$-Dimethyl-4-phenyl-1-thiomorpholinobutan-2-amine (71)

Following **GP3** but warming the reaction to 60 ºC after the addition of NaI (6.0 equiv.) and the second amine, dimethylamine hydrochloride (8 mg, 0.1 mmol, 1.0 equiv.), 10 (15 µL, 0.1 mmol, 1.0 equiv.) and thiomorpholine (50 µL, 0.5 mmol, 5.0 equiv.) gave 71 (22 mg, 80%) as an oil. R$_f$ 0.34 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (10:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2924, 2852, 1670, 1454; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31–7.26 (2H, m), 7.23–7.15 (3H, m), 2.73–2.61 (10H, m), 2.61–2.50 (2H, m), 2.31 (6H, s), 2.21–2.14 (1H, m), 1.82–1.71 (1H, m), 1.66 (1H, ddt, $J$ = 13.7, 9.5, 6.3 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.2, 128.6, 128.5, 126.0, 60.3, 59.3, 55.8, 40.8, 33.3, 31.5, 28.1 (the following signal was missing in the $^{13}$C NMR and were identified by analysing the $^1$H–$^{13}$C HMBC (500 MHz, CDCl$_3$) 142.2; HRMS (ESI$^+$): found MH$^+$ 279.1879, [C$_{16}$H$_{27}$N$_2$S]$^+$ requires 279.1889.
Methyl 5-morpholino-4-(piperidin-1-yl)pentanoate (72)

Following GP3 but warming the reaction to 60 °C after the addition of NaI and the second amine, 1 (10 µL, 0.1 mmol, 1.0 equiv.), methyl pent-4-enoate (12 µL, 0.1 mmol, 1.0 equiv.) and morpholine (45 µL, 0.5 mmol, 5.0 equiv.) gave 72 (26 mg, 92 %) as an oil. Rf 0.50 [CH$_2$Cl$_2$:MeNO$_2$:MeOH (10:1:1)]; FT-IR $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2930, 2851, 1737, 1440, 1118; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.73–3.62 (7H, m), 2.72–2.62 (2H, m), 2.61–2.54 (1H, m), 2.53–2.43 (4H, m), 2.43–2.31 (5H, m), 2.13 (1H, dd, J = 12.3, 7.9 Hz), 1.80–1.67 (2H, m), 1.55–1.44 (4H, m), 1.44–1.37 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.9, 67.2, 60.8, 59.1, 54.4, 51.5, 49.8, 31.9, 26.8, 25.7, 25.1; HRMS (ESI$^+$): found MH+ 285.2161, [C$_{15}$H$_{29}$N$_2$O$_3$]$^+$ requires 285.2173.

N-(3-(Azetidin-1-yl)-2-(piperidin-1-yl)propyl)-4-methylbenzenesulfonamide (73)

Following GP3 but using 10 equiv. of NaI and 15 equiv. of (i-Pr)$_2$NEt, 1 (10 µL, 0.1 mmol, 1.0 equiv.), S3 (33 mg, 0.1 mmol, 1.0 equiv.) and azetidine hydrochloride (47 mg, 0.5 mmol, 5.0 equiv.) gave 73 (19 mg, 55%) as an oil. Rf 0.15 [CH$_2$Cl$_2$:MeOH:MeNO$_2$ (3:1:1)]; $^1$H NMR (500 MHz, CDCl$_3$, NH missing) $\delta$ 7.76 (2H, d, J = 8.2 Hz), 7.30 (2H, d, J = 8.1 Hz), 3.21 (4H, t, J = 6.9 Hz), 2.92 (1H, m), 2.81 (1H, dd, J = 12.4, 4.0 Hz), 2.53 (1H, dd, J = 12.4, 7.2 Hz), 2.41 (3H, s), 2.31–2.23 (2H, m), 2.13–2.00 (4H, m), 1.96 (2H, dd, J = 11.1, 5.8 Hz), 1.34 (6H, br s); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.4, 136.6, 129.7, 127.5, 62.0, 60.3, 56.5, 54.3, 49.4, 26.1, 24.2, 21.7, 18.1. HRMS (ESI$^+$): found MH$^+$ 352.2053, [C$_{18}$H$_{30}$N$_3$O$_3$S]$^+$ requires 352.2053.
2,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)-N-(4-phenyl-2-(piperidin-1-yl)butyl)tetrahydro-2H-pyran-3-amine (74)

Following GP3 but using 7.5 equiv. NaI, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 10 (15 μL, 0.1 mmol, 1.0 equiv.) and 2-amino-2-deoxy-3,4,6-tri-O-benzyl-β-D-glucopyranoside hydrochloride (144 mg, 0.25 mmol, 2.5 equiv.) gave 74 (61 mg, 81%) as an oil. d.r. 1:1. \( R_f \) 0.50 [CH\(_2\)Cl\(_2\):MeNO\(_2\):MeOH (10:1:1)]; FT-IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\): 2930, 2853, 1453, 1095, 697; \(^1\)H NMR (500 MHz, CDCl\(_3\), diastereomers) \( \delta \) 7.44–7.27 (15H, m), 7.25–7.19 (5H, m), 7.19–7.14 (2H, m), 7.13–7.10 (1H, m), 7.07 (1H, d, \( J = 7.6 \) Hz), 7.02 (1H, d, \( J = 7.5 \) Hz), 5.00 (1H, d, \( J = 13.6 \) Hz), 4.95 (1H, d, \( J = 13.6 \) Hz), 4.87–4.72 (2H, m), 4.67 (1H, dd, \( J = 12.2, 4.4 \) Hz), 4.64–4.60 (2H, m), 4.57 (1H, dd, \( J = 10.5, 5.3 \) Hz), 4.45 (0.5H, d, \( J = 7.8 \) Hz), 4.40 (0.5H, d, \( J = 7.8 \) Hz), 3.81–3.65 (3H, m), 3.58–3.47 (2H, m), 3.21–3.08 (0.5H, d, \( J = 7.8 \) Hz), 2.96 (0.5H, dd, \( J = 11.9, 4.4 \) Hz), 2.71–2.62 (1.5H, m), 2.56–2.42 (4.5H, m), 2.42–2.30 (2H, m), 2.27–2.19 (2.5H, m), 1.86–1.73 (1.5H, m), 1.41–1.29 (4H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\), diastereomers) \( \delta \) 142.8, 142.7, 138.7, 138.5, 138.4 (x 2), 138.2, 138.0, 137.8, 137.4, 128.7–128.5(16C), 128.4–128.3(10C), 128.2 (x 2), 128.1 (x 2), 128.0 (x 2), 127.9(7C), 127.8(3C), 127.7, 127.6, 127.5 (x 2), 127.3 (x 2), 125.3, 125.7, 104.6, 102.5, 86.1, 83.7, 79.1 (x 2), 75.4 (x 2), 75.2, 75.1, 75.0, 74.9, 73.7 (x 2), 71.4, 71.1, 69.1 (x 2), 64.4 (x 2), 64.1, 63.9, 49.9, 49.6, 49.2(4C), 33.9, 33.8, 28.8, 28.5, 26.5(4C), 25.2, 25.1; HRMS (ESI\(^+\)): found MH+ 755.4437, \([\text{C}_{49}\text{H}_{59}\text{N}_{2}\text{O}_{5}]^+\) requires 755.4418.

Methyl (4-Phenyl-2-(piperidin-1-yl)butyl)prolinate (75)

Following GP3 but using 10 equiv. of NaI, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 10 (15 μL, 0.1 mmol, 1.0 equiv.) and L-Pro-OMe hydrochloride (83 mg, 0.5 mmol, 5.0 equiv.) gave 75 (25 mg, 73%) as an oil. d.r. 1:1. \( R_f \) 0.30 [CH\(_2\)Cl\(_2\):MeNO\(_2\):MeOH (10:1:1)]; FT-IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\): 2926, 2852, 2803, 1664, 1496; \(^1\)H NMR (400 MHz, CDCl\(_3\),
diastereomers) δ 7.29–7.23 (2H, m), 7.23–7.11 (3H, m), 3.68 (3H, s), 3.29–3.19 (1H, m), 3.15–3.06 (1H, m), 2.75–2.67 (1.5H, m), 2.67–2.48 (5H, m), 2.47–2.36 (2H, m), 2.13–1.97 (1.5H, m), 1.95–1.80 (3H, m), 1.80–1.70 (3H, m), 1.60–1.47 (4H, m), 1.47–1.36 (2H, m); 13C NMR (126 MHz, CDCl3, diastereomers) δ 175.3, 174.9, 143.3, 143.1, 128.7, 128.6, 128.4, 125.7, 125.6, 66.3, 66.2, 63.1, 62.5, 54.9, 54.7, 54.1, 53.4, 51.8, 51.7, 49.7, 49.5, 33.7, 33.4, 31.5, 31.0, 30.0, 29.9, 29.1, 26.8, 26.8, 25.2, 23.6, 23.3; HRMS (ESI+): found MH+ 345.2534, [C21H33N2O2]+ requires 345.2537.

tert-Butyl-3-(((S,4S)-2-oxa-5-azabicyclo[2.2.1]heptan-5-yl)methyl)-3-(piperidin-1-yl)azetidine-1-carboxylate (76)

Following GP3 but using AgBF4 (1.5 equiv.) in place of NaI, 1 (10 µL, 0.1 mmol, 1.0 equiv.) and (S,4S)-2-oxa-5-azabicyclo[2.2.1]heptane hydrochloride (68 mg, 0.5 mmol, 5.0 equiv.) gave 76 (17.5 mg, 50%) as an oil. Rf 0.40 [CH2Cl2:acetone (7:3)]; FT-IR νmax (film)/cm–1 2933, 1700, 1399, 1366, 1258, 1031; 1H NMR (500 MHz, CDCl3) δ 4.32 (1H, s), 3.91 (1H, d, J = 7.6 Hz), 3.68–3.61 (3H, m), 3.57 (2H, d, J = 7.5 Hz), 3.38 (1H, s), 2.99 (1H, d, J = 9.5 Hz), 2.81 (1H, d, J = 13.8 Hz), 2.75 (1H, d, J = 13.8 Hz), 2.56 (1H, d, J = 9.6 Hz), 2.50–2.40 (4H, m), 1.72 (1H, d, J = 9.3 Hz), 1.64 (1H, d, J = 9.5 Hz), 1.47 (4H, p, J = 5.4 Hz), 1.42–1.33 (2H, m), 1.36 (9H, s); 13C NMR (126 MHz, CDCl3 conformers) δ 156.7, 79.2, 77.5, 70.1, 64.1, 63.6, 60.2, 57.1, 56.7, 55.8, 55.2, 55.0, 46.9, 36.4, 28.5, 26.6, 24.8; HRMS (HESI): found MNa+ 374.2400, C19H33N3O3Na requires 374.2414.

1,3-Dimethyl-7-(((trans-2-phenylcyclopropyl)amino)-2-(piperidin-1-yl)propyl)-3,7-dihydro-1H-purine-2,6-dione (77)

Following GP3 but warming the reaction to 60 ºC after the addition of NaI (10.0 equiv.) and the second amine, 1 (10 µL, 0.1 mmol, 1.0 equiv.), S12 (22 mg, 0.1 mmol, 1.0 equiv.) and trans-2-phenylcyclopropan-1-amine hydrochloride (75 mg, 0.5 mmol, 5.0
equiv.) gave 77 (17.5 mg, 40%) as an oil. d.r. 1:1. R$_f$ 0.50 [acetone:CH$_2$Cl$_2$ (7:3)]; FT-IR $v_{\text{max}}$ (film)/cm$^{-1}$ 2930, 1700, 1650, 1551, 1434, 1259, 1030; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.58 (1H, br s), 7.27–7.19 (2H, m), 7.16–7.11 (1H, m), 7.07–6.94 (2H, m), 4.47–4.22 (2H, m), 3.59 (1H, s), 3.58 (1.5H, s), 3.40 (1.5H, s), 3.38 (1.5H, s), 3.14–3.00 (1H, m), 2.92–2.84 (1H, m), 2.74–2.62 (2H, m), 2.63–2.46 (3H, m), 2.41–2.28 (1H, m), 1.95–1.81 (1H, m), 1.52 (4H, br s), 1.44 (2H, br s), 1.09 (0.5H, dt, $J = 9.5$, 4.8 Hz), 1.05 (0.5H, dt, $J = 9.5$, 4.8 Hz), 1.00–0.91 (1H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.3, 155.2, 151.8, 151.7, 148.9 (x2), 142.4, 142.3, 142.2, 142.1, 128.4, 128.3, 125.9, 125.8, 125.6 (x 2), 106.9 (x 2), 63.4, 64.1, 53.9, 50.0, 49.9, 46.9, 46.7, 45.6 (x 2), 41.8, 41.7, 29.9, 29.8, 29.4, 28.1, 26.8, 25.1, 25.0, 24.8 (x 2), 17.4 (x 2); HRMS (ESI): found MH$^+$ 437.2641, C$_{24}$H$_{33}$N$_6$O$_2$ requires 437.2660.

**Benzyl 4-(1-((IR,5S)-8-Oxo-1,5,6,8-tetrahydro-2H-1,5-methanopyrido[1,2-a][1,5]diazocin-3(4H)-yl)-4-phenylbutan-2-yl)piperazin-1-ylcarboxylate (78)**

Following GP3’ but warming the reaction to 60 °C after the addition of NaI and the second amine, benzyl piperazine-1-carboxylate (19 µL, 0.1 mmol, 1.0 equiv.) and cytisine (95 mg, 0.5 mmol, 5.0 equiv.) gave 78 (31 mg, 57%) as an oil. d.r. 1:1. R$_f$ 0.50 [CH$_2$Cl$_2$:acetone (1:1)]; FT-IR $v_{\text{max}}$ (film)/cm$^{-1}$ 29339, 2805, 2360, 1697, 1651, 1565, 1545, 1495, 1492, 1356, 1209, 1257, 1240, 1139, 1058, 1026; $^1$H NMR (500 MHz, CDCl$_3$, diasteromers) $\delta$ 7.43–7.26 (5H, m), 7.23 (2H, t, $J = 8.4$ Hz), 7.19–7.00 (4H, m), 6.34 (0.5H, d, $J = 9.0$ Hz), 6.30 (0.5H, d, $J = 9.0$ Hz), 5.90 (0.5H, d, $J = 7.6$ Hz), 5.89 (0.5H, d, $J = 7.5$ Hz), 5.13 (1H, s), 5.12 (1H, s), 4.06–3.93 (1H, m), 3.91–3.77 (1H, m), 3.52–3.15 (4H, m), 2.96–2.70 (3H, m), 2.60–2.45 (2H, m), 2.45–2.31 (4H, m), 2.32–2.21 (3H, m), 2.21–2.11 (2H, m), 2.05–1.94 (1H, m), 1.85 (1H, d, $J = 12.9$ Hz), 1.73 (1H, d, $J = 12.9$ Hz), 1.63–1.45 (1H, m), 1.45–1.32 (1H, m); $^{13}$C NMR (126 MHz, CDCl$_3$, diasteromers) $\delta$ 163.5, 163.4, 155.3, 155.2, 151.4, 151.3, 142.5, 142.4, 138.6, 138.4, 137.0, 136.9, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 125.7, 125.6, 125.6, 116.7, 116.6, 116.5, 104.5, 104.4, 67.1, 67.0, 61.3, 61.2, 61.0, 60.1, 60.0, 58.4, 58.0, 50.1, 50.0, 49.2, 48.4, 48.1, 47.4, 44.6,
35.7, 32.8, 32.7, 32.0, 31.9, 28.2, 28.1, 26.0; HRMS (ESI): found MNa\(^+\) 563.2976, C\(_{33}\)H\(_{40}\)N\(_4\)O\(_3\)Na requires 563.2993.
7 Aminohydroxylation and Diamination of Styrenes

7.1 Aminohydroxylation – Substrate Scope

General Procedure for the Aminohydroxylation of Styrenes – GP4

A tube equipped with a stirring bar was charged with NCS (1.0 equiv.) and Ru(bpy)$_3$(PF$_6$)$_2$ (1 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). The amine (1.0 equiv.) and CH$_2$Cl$_2$ (0.2 M, dry and degassed by bubbling through with N$_2$ for 20 min) were added and the mixture was stirred for 1 h in the dark. The mixture was cooled to 0 ºC then the styrene (1.0 equiv.) and TFA (3.0 equiv.) were added, and the blue LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 ºC. Na$_2$CO$_3$ (10.0 equiv.) and H$_2$O (1 mL) were added and the resulting heterogeneous mixture was stirred vigorously for 30 minutes. The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (x 2). The combined organic layers were dried (MgSO$_4$), filtered and evaporated. Purification by preparative TLC chromatography on silica gave the products.

1-Phenyl-2-(piperidin-1-yl)ethan-1-ol (55)

Following GP4, 1 (10 μL, 0.1 mmol, 1.0 equiv.) and 53 (13 μL, 0.1 mmol, 1.0 equiv.) gave 55 (13 mg, 65%) as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37–7.24 (5H, m), 4.69 (1H, dd, $J$ = 10.6 Hz, 3.5 Hz), 2.66 (2H, br s), 2.45 (1H, dd, $J$ = 12.4 Hz, 3.6 Hz), 2.40–2.34 (3H, m), 1.67–1.45 (6H, m); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.6, 128.4, 127.5,126.0, 68.9, 67.2, 54.6, 26.3, 24.4. Data in accordance with the literature.$^{[12]}$

2-(pyrrolidin-1-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (56)

Following GP4, pyrrolidine (8.5 μL, 0.1 mmol, 1.0 equiv.) and 1-(trifluoromethyl)-4-vinylbenzene (15 μL, 0.1 mmol, 1.0 equiv.) gave 56 (13 mg, 51%) as an oil. R$_f$ 0.50
2-(Azepan-1-yl)-1-(3-bromophenyl)ethan-1-ol (57)

Following GP4, azepane (11.5 μL, 0.1 mmol, 1.0 equiv.) and 1-bromo-3-vinylbenzene (13 μL, 0.1 mmol, 1.0 equiv.) gave 57 (24 mg, 82%) as an oil. Rf 0.50 [Et2O:CH2Cl2 (6:4)]; FT-IR v_max (film)/cm⁻¹ 3400, 2924, 2853, 1595, 1568, 1471, 1426, 1400, 1323, 1258, 1195, 1066; ¹H NMR (400 MHz, CDCl3) δ 7.54 (1H, s), 7.38 (1H, d, J = 7.8 Hz), 7.28 (1H, d, J = 7.8 Hz), 4.57 (1H, dd, J = 10.6, 3.6 Hz), 4.39 (1H, br s), 2.88–2.78 (2H, m), 2.78 (1H, dd, J = 12.6, 3.6 Hz), 2.67 (1H, dd, J = 13.1, 7.2 Hz), 2.72–2.63 (1H, m), 2.37 (1H, dd, J = 12.5, 10.5 Hz, 1H), 1.79–1.55 (8H, m); ¹³C NMR (126 MHz, CDCl3) δ 145.1, 130.5, 130.0, 129.0, 124.6, 122.6, 68.9, 66.2, 55.7, 28.7, 27.1; HRMS (ASAP): Found MH⁺ 298.0809 C₁₄H₁₇NOBr requires 298.0801.

2-(Diisopropylamino)-1-phenylethan-1-ol (58)

Following GP4, i-PrNH₂ (14 μL, 0.1 mmol, 1.0 equiv.) and 53 (13 μL, 0.1 mmol, 1.0 equiv.) gave 58 (5 mg, 22%) as an oil. ¹H NMR (400 MHz, CDCl3) δ 7.40–7.23 (5H, m), 4.56 (1H, dd, J = 10.5, 3.9 Hz), 3.15 (2H, hept, J = 6.6 Hz), 2.74 (1H, dd, J = 13.4, 3.9 Hz), 2.36 (1H, dd, J = 13.4, 10.6 Hz), 1.14 (6H, d, J = 6.7 Hz), 1.03 (6H, d, J = 6.6 Hz). Data in accordance with the literature.¹³
7.2 Diamination – Substrate Scope

General Procedure for the Diamination of Styrenes – GP5

\[ R^1NHR^3 + \begin{align*}
\text{NCS (1.0 equiv.)} & \quad \text{Ru(bpy)}_3(PF_6)_2 (1 \text{ mol%}) \\
\text{CH}_2Cl_2 (0.2 M) & \quad 1 \text{ h}
\end{align*} \]

then HClO\textsubscript{4} 70% (3.0 equiv.), blue LEDs, 0 °C, 30 min
then R^2RNH (3.0 equiv.), Na_2CO_3 (5.0 equiv.), r.t., 1 h

A tube equipped with a stirring bar was charged with NCS (1.0 equiv.) and Ru(bpy)_3(PF_6)_2 (1 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N\textsubscript{2} (x 3). The amine (1.0 equiv.) and CH\textsubscript{2}Cl\textsubscript{2} (0.1 M, dry and degassed by bubbling through with N\textsubscript{2} for 20 min) were added and the mixture was stirred for 1 h in the dark. The mixture was cooled to 0 °C then the styrene (1.0 equiv.) and HClO\textsubscript{4} 70% (3.0 equiv.) were added, and the blue LEDs were immediately switched on. The mixture was stirred under irradiation for 1 h at 0 °C. The second amine (3.0 equiv.) was added, followed by Na\textsubscript{2}CO\textsubscript{3} (5.0 equiv.). The mixture was stirred for 1 h at room temperature, then H\textsubscript{2}O (2 mL) was added and the mixture was shaken vigorously. The layers were separated and the aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (x 2). The combined organic layers were dried (MgSO\textsubscript{4}), filtered and evaporated. Purification by preparative TLC chromatography on silica gave the products.

4-(1-Phenyl-2-(piperidin-1-yl)ethyl)morpholine (79)

Following GP5, 1 (9μL, 0.1 mmol, 1.0 equiv.), 53 (13μL, 0.1 mmol, 1.0 equiv.) and morpholine (26μL, 0.3 mmol, 3.0 equiv.) gave 79 (23 mg, 83%) as an oil. R\textsubscript{f} 0.50 [CH\textsubscript{2}Cl\textsubscript{2}:acetone (6:4)]; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.33–7.26 (2H, m), 7.26–7.19 (3H, m), 3.65 (4H, t, J = 4.7 Hz), 3.52 (1H, t, J = 6.1 Hz), 2.87 (1H, dd, J = 13.1, 6.4 Hz), 2.57 (1H, dd, J = 13.1, 5.7 Hz), 2.61–2.51 (2H, m), 2.47–2.33 (6H, m), 1.49 (4H, p, J = 5.6 Hz), 141–1.32 (2H, m). Data in accordance with literature. \textsuperscript{144}
**N,N-Diethyl-1-phenyl-2-(piperidin-1-yl)ethan-1-amine (80)**

Following **GP5**, Et₂NH (10.5 μL, 0.1 mmol, 1.0 equiv.), 53 (13 μL, 0.1 mmol, 1.0 equiv.) and 1 (30 μL, 0.3 mmol, 3.0 equiv.) gave 80 (8.5 mg, 33%) as an oil. ¹H NMR (500 MHz, CDCl₃) δ 7.15–7.55 (5H, m), 3.54 (1H, t, J = 6.4 Hz), 2.96 (1H, dd, J = 13.1, 5.4 Hz), 2.82 (1H, dd, J = 13.1, 5.5 Hz), 2.46–2.70 (4H, m), 2.39 (4H, br s), 1.42–1.75 (4H, m), 1.22–1.42(2H, m), 0.95 (6H, t, J = 7.1 Hz). Data in accordance with literature.[¹⁵]

**Benzyl 4-(1-Phenyl-2-(piperidin-1-yl)ethyl)piperazine-1-carboxylate (81)**

Following **GP5**, 1 (9 μL, 0.1 mmol, 1.0 equiv.), 53 (13 μL, 0.1 mmol, 1.0 equiv.) and 1-Cbz-piperazine (58 μL, 0.3 mmol, 3.0 equiv.) gave 81 (29 mg, 72%) as an oil. Rₜ 0.50 [CH₂Cl₂:acetone (6:4)]; FT-IR νₘₐₓ (film)/cm⁻¹ 2341, 2256, 1635, 1463, 1374, 1258, 1037, 920; ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.24 (7H, m), 7.24–7.09 (3H, m), 5.05 (2H, s), 3.58 (1H, t, J = 6.1 Hz), 3.50–3.38 (4H, m), 2.82 (1H, dd, J = 13.2, 6.6 Hz), 2.56 (1H, dd, J = 13.2, 5.5 Hz), 2.51–2.43 (2H, m), 2.36 (6H, br s), 1.47 (4H, p, J = 5.6 Hz), 1.39–1.29 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 155.3, 140.3, 136.9, 128.6, 128.5, 128.2, 128.0, 127.9, 127.2, 67.2, 67.1, 62.6, 55.2, 50.4, 44.3, 26.1, 24.4; HRMS (ASAP): Found MH⁺ 408.2636 C₂₅H₃₄N₃O₂ requires 408.2646.

**1-Phenyl-2-(piperidin-1-yl)-N-((tetrahydrofuran-3-yl)methyl)ethan-1-amine (82)**

Following **GP5**, 1 (9 μL, 0.1 mmol, 1.0 equiv.), 53 (13 μL, 0.1 mmol, 1.0 equiv.) and 3-(aminomethyl)tetrahydrofuran (30 μL, 0.3 mmol, 3.0 equiv.) gave 82 (22 mg, 76%) as an oil. d.r. 1:1. Rₜ 0.50 [CH₂Cl₂:acetone (6:4)]; FT-IR νₘₐₓ (film)/cm⁻¹ 2934, 2359, 1504, 1260, 1242, 1197, 1163, 1096, 1040; ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.27 (4H, m), 7.23 (1H, t, J = 7.4 Hz), 3.88 (1H, dt, J = 15.9, 7.8 Hz), 3.84–3.74 (1H, m), 3.77–3.66 (2H, m), 3.48–3.40 (1H, m), 2.54 (2H, br s), 2.50–2.43 (2H, m), 2.40 (2H,
td), 2.33–2.18 (3H, m), 2.02 (1H, tdd, \(J = 13.3, 7.6, 5.5\) Hz), 1.68–1.51 (5H, m), 1.50–1.32 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\), diastereomers) \(\delta 143.2\) (x 2), 128.3 (x 2), 127.3 (x 2), 127.1 (x 2), 72.3, 72.0, 67.9, 67.8, 66.5 (x 2), 60.3 (x 2), 54.6 (x 2), 51.7, 51.4, 39.6 (x 2), 30.8 (x 2), 26.2 (x 2), 24.5 (x 2); HRMS (ASAP): Found MH\(^+\) 289.2268 C\(_{18}\)H\(_{29}\)N\(_2\)O requires 289.2274.

1-(1-Phenyl-2-(piperidin-1-yl)ethyl)pyridin-1-i um perchlorate (83)

Following GP5 but letting the reaction stir overnight upon addition of the second amine, 1 (9 \(\mu\)L, 0.1 mmol, 1.0 equiv.) and pyridine (24 \(\mu\)L, 0.3 mmol) gave 83 (13 mg, 50%) as a solid. \(R_f\) 0.51 [CH\(_2\)Cl\(_2\):MeNO\(_2\):MeOH (20:1:1)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 2934, 2852, 1710, 1092; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.90\) (2H, d, \(J = 5.7\) Hz), 8.42 (1H, t, \(J = 7.7\) Hz), 7.99 (2H, t, \(J = 7.1\) Hz), 7.57 (2H, dd, \(J = 6.5, 2.9\) Hz), 7.47 (3H, dd, \(J = 5.1, 1.9\) Hz), 6.06 (1H, dd, \(J = 11.3, 3.4\) Hz), 3.33–3.22 (1H, m), 3.14 (1H, dd, \(J = 14.2, 3.3\) Hz), 2.82–2.68 (2H, m), 2.27 (2H, dt, \(J = 10.7, 4.4\) Hz), 1.55–1.34 (6H, m) \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 145.6, 144.2, 133.5, 130.7, 130.0, 128.9, 127.8, 72.6, 61.5, 54.7, 26.1, 24.0\); HRMS (ESI\(^+\)): found M+ 267.1844, [C\(_{18}\)H\(_{23}\)N\(_2\)]\(^+\) requires 267.1856.

1-(4-Methoxyphenyl)-N,N-dimethyl-2-(piperidin-1-yl)ethan-1-amine (84)

Following GP5, 1 (9 \(\mu\)L, 0.1 mmol, 1.0 equiv.) and 1-methoxy-4-vinylbenzene (13 \(\mu\)L, 0.1 mmol, 1.0 equiv.) and Et\(_2\)NH (38 \(\mu\)L, 0.3 mmol, 40% wt solution in H\(_2\)O) gave 84 (16 mg, 60%) as an oil. \(R_f\) 0.50 [CH\(_2\)Cl\(_2\):acetone (6:4)]; FT-IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1610, 1465, 1456, 1245, 1038; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.13\) (2H, d, \(J = 8.6\) Hz), 6.85 (2H, d, \(J = 8.7\) Hz), 3.80 (3H, s), 3.49 (1H, t, \(J = 6.3\) Hz), 2.85 (1H, dd, \(J = 13.0, 6.3\) Hz), 2.56 (1H, dd, \(J = 13.0, 6.3\) Hz), 2.37 (4H, br s), 2.17 (6H, s), 1.52-1.47 (4H, m), 1.36 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 158.6, 131.8, 129.8, 113.3, 66.8, 62.7, 55.3, 55.3, 42.6, 26.1, 24.5\); HRMS (HESI): Found MH\(^+\) 263.2212 [C\(_{16}\)H\(_{27}\)N\(_2\)O]\(^+\) requires 263.2210.
2-((1-(4-Methoxyphenyl)-2-(piperidin-1-yl)ethyl)(methyl)amino)ethan-1-ol (85)

Following GP5, 1 (9 μL, 0.1 mmol, 1.0 equiv.), 1-methoxy-4-vinylbenzene (13 μL, 0.1 mmol, 1.0 equiv.) and 2-(methylamino)ethanol (30.5 μL, 0.3 mmol, 3.0 equiv.) gave 85 (15 mg, 51%) as an oil. Rf 0.40 [CH2Cl2:acetone (6:4)]; FT-IR νmax (film)/cm⁻¹ 3345, 1498, 1442, 1440, 1258, 1025, 862; ¹H NMR (500 MHz, CDCl3) δ 7.13 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 3.87 (1H, dd, J = 11.9, 4.6 Hz), 3.80 (3H, s), 3.71–3.60 (1H, m), 3.48 (1H, dt, J = 10.7, 3.0 Hz), 3.14–2.94 (2H, m), 2.63 (2H, br s), 2.35 (2H, br s), 2.29–2.18 (2H, m), 2.24 (3H, s), 1.71–1.57 (4H, m), 1.51–1.40 (2H, m); ¹³C NMR (126 MHz, CDCl3) δ 159.0, 130.7, 129.3, 113.7, 62.7, 60.6, 60.0, 55.3, 54.1, 52.4, 40.4, 25.7, 24.5; HRMS (HESI): Found MH⁺ 293.2212 C₁₇H₂₉N₂O₂ requires 293.2224.

N,N-dimethyl-2-(piperidin-1-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-amine (86)

Following GP5, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 1-(trifluoromethyl)-4-vinylbenzene (15 μL, 0.1 mmol) and Me₂NH (38 μL, 0.3 mmol, 3.0 equiv., 40% wt solution in H₂O) gave 86 (17 mg, 57%) as an oil. Rf 0.50 [CH₂Cl₂:acetone (6:4)]; FT-IR νmax (film)/cm⁻¹ 2359, 2341, 1325, 1259, 1032, 860; ¹H NMR (500 MHz, CDCl₃) δ 7.57 (2H, d, J = 8.1 Hz), 7.35 (2H, d, J = 8.0 Hz), 3.55 (1H, t, J = 6.4 Hz), 2.84 (1H, dd, J = 13.0, 6.1 Hz), 2.57 (1H, dd, J = 13.0, 6.8 Hz), 2.46–2.30 (4H, m), 2.19 (6H, s), 1.48 (4H, p, J = 5.5 Hz), 1.42–1.31 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 144.5, 129.2 (q, J = 32.4 Hz), 128.8, 124.9 (q, J = 3.9 Hz), 124.4 (q, J = 271.9 Hz), 67.4, 62.2, 55.3, 42.9, 26.0, 24.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3; HRMS (ASAP): Found MH⁺ 301.1881 C₁₆H₂₄N₂F₃ requires 301.1886.
5,6-Dimethoxy-2-((1-(2-(piperidin-1-yl)-1-(2-(trifluoromethyl)phenyl)ethyl) piperidin-4-yl)methyl)-2,3-dihydro-1H-inden-1-one (87)

Following GP5, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 1-(trifluoromethyl)-2-vinylbenzene (15 μL, 0.1 mmol, 1.0 equiv.) and desbenzyl donepezil hydrochloride (98 mg, 0.3 mmol, 3.0 equiv.) gave 87 (41 mg, 76%) as an oil. dr 1:1. Rf 0.50 [CH$_2$Cl$_2$:acetone (6:4)]; FT-IR v$_{max}$ (film)/cm$^{-1}$ 2923, 2850, 2359, 2341, 1698, 1591, 1500, 1456, 1361, 1311, 1260, 1223, 1154, 1118, 1034; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.74 (1H, d, $J$ = 7.9 Hz), 7.59 (1H, d, $J$ = 7.9 Hz), 7.49 (1H, t, $J$ = 7.6 Hz), 7.30 (1H, t, $J$ = 7.6 Hz), 7.16 (1H, s), 6.84 (1H, d, $J$ = 1.6 Hz), 3.95 (3H, s), 3.90 (3H, s), 3.87 (1H br s), 3.51 (1H, t, $J$ = 11.7 Hz), 3.21 (1H, dd, $J$ = 17.3, 7.8 Hz), 2.74 (1H, dd, $J$ = 13.9, 8.0 Hz), 2.73–2.61 (2H, m), 2.56 (1H, t, $J$ = 11.6 Hz), 2.40 (2H, br s), 2.31 (1H, dd, $J$ = 13.5, 3.8 Hz), 2.25 (2H, br s), 2.12 (1H, tt, $J$ = 12.1, 2.9 Hz), 1.98 (1H, t, $J$ = 11.4 Hz), 1.94–1.74 (2H, m), 1.72–1.54 (1H, m), 1.52–1.41 (6H, m), 1.39–1.28 (4H, m); $^{13}$C NMR (126 MHz, CDCl$_3$, diastereomers) δ 208.0, 207.9, 155.4 (x 2), 149.4 (x 2), 148.8 (x 2), 143.5 (x 2), 131.6 (x 2), 129.3 (x 2), 128.2 (x 2, q, $J$ = 29.4 Hz), 126.4 (x 2), 125.31(2C, q, $J$ = 5.6 Hz), 124.6(2C, q, $J$ = 274.0 Hz), 107.3 (x 2), 104.4 (x 2), 64.8 (x 2), 61.6 (x 2), 56.2 (x 2), 56.1 (x 2), 55.0 (x 2), 52.7 (x 2), 51.7 (x 2), 45.5 (x 2), 38.7 (x 2), 34.8 (x 2), 33.7, 33.6, 33.2 (x 2), 32.3, 32.1, 26.1 (x 2), 24.4 (x 2); $^{19}$F NMR (376 MHz, CDCl$_3$, diastereomers) δ −57.2, −57.25; HRMS (HESI): Found MH$^+$ 545.2983 C$_{31}$H$_{40}$N$_2$O$_3$F$_3$ requires 545.2986.
1-(1-(3-Bromophenyl)-2-(piperidin-1-yl)ethyl)-4-(4-(trifluoromethoxy)phenoxy) piperidine (88)

Following **GP5**, 1 (10 μL, 0.1 mmol, 1.0 equiv.), 1-bromo-3-vinylbenzene (13 μL, 0.1 mmol, 1.0 equiv.) and 4-[4-(trifluoromethoxy)phenoxy]piperidine (78 mg, 0.3 mmol, 3.0 equiv.) gave 88 (49 mg, 94%) as an oil. R_{f} 0.50 [CH\textsubscript{2}Cl\textsubscript{2}:acetone (6:4)]; FT-IR ν\textsubscript{max} (film)/cm\textsuperscript{-1} 2934, 2359, 1504, 1260, 1242, 1197, 1163, 1096, 1040; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.42 (1H, s), 7.37 (1H, dt, J = 6.0, 2.4 Hz), 7.22–7.16 (2H, m), 7.09 (2H, d, J = 8.7 Hz), 6.83 (2H, d, J = 9.1 Hz), 4.15 (1H, tt, J = 8.2, 3.9 Hz), 3.61 (1H, t, J = 6.2 Hz), 2.79 (1H, dd, J = 13.2, 6.2 Hz), 2.88–2.69 (2H, m), 2.57 (1H, dd, J = 13.1, 6.3 Hz), 2.49–2.32 (4H, m), 2.31–2.21 (2H, m), 2.05–1.86 (2H, m), 1.75 (2H, ddp, J = 13.2, 8.8, 4.9, 4.3 Hz), 1.56–1.42 (4H, m), 1.42–1.34 (2H, m); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 156.1, 143.4, 142.7, 131.4, 130.0, 129.6, 127.1, 122.5, 122.4, 120.69 (q, J = 256.1 Hz), 116.9, 74.0, 66.6, 62.1, 55.3, 48.2, 47.4, 31.4, 31.3, 26.2, 24.5; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ –58.4; HRMS (HESI): Found MH\textsuperscript{+} 527.1513 C\textsubscript{25}H\textsubscript{31}N\textsubscript{2}O\textsubscript{2}BrF\textsubscript{3} requires 527.1521.

Methyl-4-(1-(4-(4-chlorophenyl)-4-hydroxypiperidin-1-yl)-2-(pyrrolidin-1-yl)ethyl) benzoate (89)

Following **GP5**, pyrrolidine (10 μL, 0.1 mmol, 1.0 equiv.), methyl 4-vinylbenzoate (16 mg, 0.1 mmol, 1.0 equiv.) and 4-(4-chlorophenyl)piperidin-4-ol (63 mg, 0.3 mmol, 3.0 equiv.) gave 89 (25 mg, 57%) as an oil. R_{f} 0.50 [CH\textsubscript{2}Cl\textsubscript{2}:acetone (1:1)]; FT-IR ν\textsubscript{max} (film)/cm\textsuperscript{-1} 3381, 2952, 2821, 2358, 1720, 1609, 1489, 1435, 1387, 1280, 1185, 1109, 1042, 1012; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3} and MeOH) δ 7.90 (2H, d, J = 8.1 Hz), 7.37–
7.25 (4H, m), 7.16 (2H, d, $J = 8.5$ Hz), 3.81 (3H, s), 3.68–3.62 (1H, m), 3.01 (1H, dd, $J = 12.4$, 5.3 Hz), 2.87 (1H, dd, $J = 12.5$, 7.7 Hz), 2.80–2.72 (1H, m), 2.59–2.50 (1H, m), 2.50–2.40 (2H, m), 2.40–2.31 (2H, m), 2.31–2.16 (2H, m), 2.00 (1H, td, $J = 12.8$, 4.5 Hz), 1.89 (1H, td, $J = 12.8$, 4.4 Hz), 1.68–1.53 (4H, m), 1.58–1.50 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$ and MeOH) $\delta$ 167.3, 147.2, 144.0, 132.2, 129.2, 128.9, 128.8, 128.0, 126.0, 70.4, 68.6, 58.5, 54.9, 52.0, 47.9, 44.5, 38.1, 38.0, 23.0; HRMS (APCI): Found MH$^+$ 443.2089 C$_{25}$H$_{32}$N$_2$O$_3$Cl requires 443.2096.
8 Olefin Aziridination

8.1 Substrate Scope

General Procedure for the Olefin Aziridination – GP6

A dry tube equipped with a stirring bar was charged with NCS (13 mg, 0.1 mmol, 1.0 equiv.) and Ru(bpy)$_3$(PF$_6$)$_2$ (0.7 mg, 0.01 mmol, 1 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N$_2$ (x 3). CH$_2$Cl$_2$ (0.5 mL) (dry and degassed by bubbling through with N$_2$ for 20 min) and the amine (0.1 mmol, 1.2 equiv.), were added and the mixture was stirred for 1 h in the dark. The mixture was cooled to 0 ºC and then a solution of the olefin (0.1 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (0.5 mL) and TFA (46 μL, 0.6 mmol, 6.0 equiv.) were added. The blue LEDs were immediately switched on and the mixture was stirred under irradiation at 0 ºC for 1 h. NaOH (1.0 M in MeOH) was added and the mixture was stirred for 1 h at 60 ºC. The mixture was allowed to cool to room temperature, diluted with H$_2$O (10 mL) and the layers were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were dried (MgSO$_4$), filtered and evaporated. Purification by flash column chromatography or preparative TLC chromatography on silica gel gave the products.

1-Cyclohexyl-2-phenethylaziridine (90)

Following GP6 but adding adding KPF$_6$ (18 mg, 0.1 mmol, 1.0 equiv.) to the reaction mixture, cyclohexylamine (14 μL, 0.12 mmol, 1.2 equiv.) and 10 (15 μL, 0.1 mmol, 1.0 equiv.) gave 90 (11.5 mg, 50%) as an oil.  

$R_f$ 0.50 [petrol:EtOAc (8:2)]; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2362, 1259, 1029, 861; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 (2H, t, $J = 7.5$ Hz), 7.24–7.13 (3H, m), 2.83 (1H, ddd, $J = 13.8$, 10.2, 5.8 Hz), 2.70 (1H, ddd, $J = 13.8$, 10.1, 6.0 Hz), 1.90–1.77 (3H, m), 1.81–1.70 (2H, m), 1.66–1.52 (2H, m), 1.51 (1H, d, $J = 3.5$ Hz), 1.45–1.28 (3H, m), 1.25 (1H, d, $J = 6.3$ Hz), 1.21–1.10 (3H, m), 1.03 (1H, tt, $J = 10.7$, 3.9 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$
142.2, 128.5, 128.4, 125.9, 69.1, 38.2, 35.3, 34.3, 33.3, 32.7, 26.3, 25.2; HRMS (HESI): Found MH$^+$ 230.1893 C$_{16}$H$_{24}$N requires 230.1903.

1-*(tert-Butyl)-2-phenethylaziridine (91)

Following GP6, tert-butylamine (13 μL, 0.12 mmol, 1.2 equiv.) and 10 (15 μL, 0.1 mmol) gave 91 (11 mg, 56%) as an oil. R$_f$ 0.50 [petrol:EtOAc (8:2)]; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2360, 2341, 2156, 1260, 1089, 1030; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32–7.23 (2H, m), 7.23–7.14 (3H, m), 2.89–2.76 (1H, m), 2.74–2.61 (1H, m), 1.86–1.73 (1H, m), 1.70–1.54 (2H, m), 1.48 (1H, d, $J$ = 5.7 Hz), 1.29 (1H, s), 0.98 (9H, s); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.3, 128.5, 128.4, 125.8, 52.6, 35.6, 34.4, 32.0, 26.9, 26.8; HRMS (HESI): Found MH$^+$ 204.1741 C$_{14}$H$_{22}$N requires 204.1747.

1-*(Adamantan-1-yl)-2-phenethylaziridine (92)

Following GP6, 1-adamantylamine (12 mg, 0.12 mmol, 1.2 equiv.) and 10 (15 μL, 0.1 mmol, 1.0 equiv.) gave 92 (24 mg, 87%) as an oil. R$_f$ 0.50 [petrol:EtOAc (8:2)]; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2851, 2360, 2342, 1258, 1088, 1027; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (2H, t, $J$ = 7.4 Hz), 7.25–7.13 (3H, m), 2.86–2.79 (1H, m), 2.72–2.64 (1H, m), 2.07 (3H, br s), 1.86–1.73 (2H, m), 1.74–1.63 (4H, m), 1.62–1.56 (4H, m), 1.54 (7H, s); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.3, 128.5, 128.4, 125.8, 52.2, 40.7, 36.9, 35.8, 34.4, 29.9, 29.6, 24.9; HRMS (HESI): Found MH$^+$ 282.2207 C$_{20}$H$_{28}$N requires 282.2216.

cis-7-phenethyl-7-azabicyclo[4.1.0]heptane (93)

Following GP6, 2-phenylethan-1-amine (15 μL, 0.12 mmol, 1.2 equiv.) and cyclohexene (10 μL, 0.10 mmol, 1.0 equiv.) and 10 (15 μL, 0.1 mmol) gave 93 (8 mg, 40%) as an oil. R$_f$ 0.60 [petrol:EtOAc (8:2)]; FT-IR $\nu_{max}$ (film)/cm$^{-1}$ 2359, 2341, 2257, 1635, 1373, 1260, 1035; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33–7.22 (2H, m), 7.22–7.16
(3H, m), 2.87 (2H, t, $J = 7.8$ Hz), 2.47 (2H, t, $J = 7.9$ Hz), 1.83–1.66 (2H, m), 1.74–1.66 (2H, m), 1.43 (2H, br s), 1.38–1.29 (2H, m), 1.21–1.09 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.5, 129.0, 128.4, 126.1, 63.3, 38.5, 36.6, 24.6, 20.7; HRMS (HESI): Found MH$^+$ 202.1583 $C_{14}H_{20}N$ requires 202.1590. Data in accordance with the literature.$^{[16]}$
9 Diversification of β-Chloroamines

9.1 Substrate Scope

General Procedure for the Derivatization of β-Chloroamines – GP7

A tube equipped with a stirring bar was charged with NaI (5.0 equiv.), and the appropriate nucleophile as the sodium salt (5.0 equiv). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N₂ (x 3). A solution of 11 (1.0 equiv.) in DMF (0.25 M) was added and the mixture was stirred at 60 °C for 16 h. After cooling the reaction at room temperature, H₂O was added and the layer was separated. The aqueous layer was extracted with CH₂Cl₂ (x 3). The combined organic layers were dried (MgSO₄), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products.

1-(1-Methoxy-4-phenylbutan-2-yl)piperidine (94) and 1-(2-methoxy-4-phenylbutyl)piperidine (94‘)

Following GP7, 11 (25 mg, 0.1 mmol) and NaOMe (solution 24% in MeOH, 118 μL, 0.5 mmol, 5.0 equiv.) gave 94 and 94‘ (15 mg, 59%) as an oil. 94:94‘ = 3:1.

Data for 94: Rf 0.60 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2961, 2359, 2341, 1734, 1652, 1558, 1539, 1456, 1259, 1035; ¹H NMR (500 MHz, CDCl₃) δ 7.43–7.32 (2H, m), 7.33–7.20 (3H, m), 3.72–3.59 (1H, m), 3.45–3.28 (1H, m), 3.41 (3H, s), 2.90–2.62 (5H, m), 2.61–2.48 (2H, m), 1.97–1.72 (2H, m), 1.73–1.59 (4H, m), 1.57–1.48 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 142.9, 128.6, 128.4, 125.8, 72.8, 63.4, 59.0, 50.5, 33.3, 33.2, 30.6, 25.1; HRMS (ASAP): Found MH⁺ 248.2007 C₁₆H₂₆NO requires 248.2009.
4-Phenyl-1-(piperidin-1-yl)butan-2-ol (95)

Following GP7, 11 (25 mg, 0.1 mmol, 1.0 equiv.) and KOH (0.5 mL, 1M, 5.0 equiv.)
gave 95 (21 mg, 89%) as an oil. Rf 0.53 [CH₂Cl₂:MeNO₂:MeOH (4:1:1)]; FT-IR νmax
(film)/cm⁻¹ 3349, 2932, 1453, 698; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.27 (2H, m),
7.25–7.17 (3H, m), 4.11 (1H, tdd, J = 9.3, 6.3, 3.4 Hz), 2.93 (1H, ddd, J = 13.9, 9.2, 4.8
Hz), 2.80 (1H, dd, J = 13.1, 6.2 Hz), 2.71 (1H, ddd, J = 13.8, 9.0, 7.3 Hz), 2.60 (1H,
dd, J = 13.1, 8.8 Hz), 2.38–2.30 (4H, m), 2.31–2.21 (1H, m), 2.05 (1H, dtd, J = 14.2,
9.2, 4.7 Hz), 1.88–1.70 (1H, m), 1.59–1.48 (4H, m), 1.46–1.34 (2H, m); ¹³C NMR (126
MHz, CDCl₃) δ 141.2, 128.7, 128.5, 126.2, 67.8, 54.7, 39.1, 35.4, 35.1, 26.0, 24.4 (the
following signal was missing in the ¹³C NMR and were identified by analysing the ¹H–
¹³C HMBC (500 MHz, CDCl₃) 35.1); HRMS (ESI⁺): found MNa⁺ 256.1660,
[C₁₅H₂₃NONa]⁺ requires 256.1672.

1-(1-Azido-4-phenylbutan-2-yl)piperidine (96) and 1-(2-azido-4-
phenylbutyl)piperidine (96')

Following GP7, 11 (25 mg, 0.1 mmol) and NaN₃ (16 mg, 0.25 mmol) gave 96 and 96'
(26 mg, 99%) as an oil. 94:94' = 3:1. Rf 0.60 [petrol:EtOAc (8:2)]; FT-IR νmax
(film)/cm⁻¹ 2961, 2359, 2341, 1716, 1489, 1447, 1314, 1258, 1093, 1066, 1024; ¹H
NMR (500 MHz, CDCl₃) δ 7.34–7.24 (4H, m), 7.24–7.14 (6H, m), 3.48 (1H, m), 3.41
(1H, dd, J = 12.7, 7.6 Hz), 3.07 (1H, dd, J = 12.6, 5.2 Hz), 2.81 (1H, ddd, J = 14.5, 9.6,
5.4 Hz), 2.73–2.61 (4H, m), 2.60–2.50 (4H, m), 2.49–2.41 (2H, m), 2.40–2.31 (3H, m),
1.91–1.73 (3H, m), 1.73–1.63 (2H, m), 1.62–1.51 (8H, m), 1.49–1.39 (4H, m); ¹³C
NMR (126 MHz, CDCl₃, mixture of isomers) δ 142.1, 141.3, 128.5, 128.4, 128.4,
128.0, 125.8, 63.6, 63.5, 59.1, 55.0, 50.9, 49.8, 34.4, 33.2, 32.4, 30.2, 26.5, 26.0,
25.0, 24.3; HRMS (ASAP): Found MH⁺ 259.1917 C₁₅H₂₃N₄ requires 259.1911.
5-Phenyl-3-(piperidin-1-yl)pentanenitrile (97)

Following GP7, 11 (25 mg, 0.1 mmol) and NaCN (12 mg, 0.25 mmol) gave 97 (23 mg, 95%) as an oil. Rf 0.60 [petrol:EtOAc (8:2)]; FT-IR νmax (film)/cm⁻¹ 2933, 2853, 2359, 2341, 1495, 1454, 1259, 1035; ¹H NMR (500 MHz, CDCl₃) δ 7.31–7.26 (2H, m), 7.23–7.17 (3H, m), 2.85–2.78 (1H, m), 2.78–2.65 (2H, m), 2.64–2.53 (2H, m), 2.46 (1H, dd, J = 16.8, 5.5 Hz), 2.39–2.33 (2H, m), 2.30 (1H, dd, J = 16.9, 7.1 Hz), 2.00–1.89 (1H, m), 1.89–1.78 (1H, m), 1.69–1.51 (4H, m), 1.49–1.39 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 141.8, 128.6, 128.5, 126.1, 119.5, 60.5, 49.4, 33.1, 32.5, 26.5, 24.9, 16.9; HRMS (ASAP): Found MH⁺ 243.1857 C₁₆H₂₃N₂ requires 243.1856.

1-(2-Fluoro-4-phenylbutyl)piperidine (98)

A tube equipped with a stirring bar was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N₂ (x 3). A solution of 11 (48 μL, 0.2 mmol, 1.0 equiv.) in CHCl₃ (0.2 mL, 1.0 M) was added followed by Et₃N•3HF (228 μL, 1.4 mmol, 7.0 equiv.). The mixture was stirred at 60 °C for 16 h. After cooling to room temperature, H₂O (10 mL) was added and the layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were dried (MgSO₄), filtered and evaporated. Purification by flash column chromatography on silica gel gave 98 (7.5 mg, 32%) as an oil. Rf 0.40 [CH₂Cl₂:acetone (99:1)]; FT-IR νmax (film)/cm⁻¹ 2961, 2359, 2341, 1716, 1489, 1447, 1314, 1258, 1093, 1066, 1024; ¹H NMR (500 MHz, CDCl₃) δ 7.32–7.26 (2H, m), 7.23–7.16 (3H, m), 4.68 (1H, dddd, J = 50.2, 11.3, 7.3, 3.3 Hz), 2.82 (1H, dddd, J = 14.7, 9.8, 5.3 Hz), 2.70 (1H, ddd, J = 13.1, 9.2, 6.7 Hz), 2.65–2.53 (1H, m), 2.50–2.34 (5H, m), 2.05–1.76 (2H, m), 1.58 (4H, p, J = 5.6 Hz), 1.50–1.38 (2H, m); ¹³C NMR (126 MHz, CDCl₃) δ 141.5, 128.6, 128.6, 126.1, 91.7 (d, J = 169.7 Hz), 63.5 (d, J = 21.0 Hz), 55.3, 35.7 (d, J = 21.0 Hz), 31.4 (d, J = 4.6 Hz), 26.0, 24.3; ¹⁹F NMR (376 MHz, CDCl₃) δ –181.5; HRMS (ASAP): Found MH⁺ 236.1814, C₁₅H₂₃NF requires 236.1809.
1-(4-Phenylbutan-2-yl)piperidine (99)

A tube equipped with a stirring bar was charged with NaI (75 mg, 0.5 mmol, 5.0 equiv.) and then capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N₂ (x 3). A solution of 11 (25 mg, 0.1 mmol, 1.0 equiv.) in CH₃CN (0.5 mL) was added and the mixture was stirred at room temperature for 18 h. The mixture was cooled to 0 °C, treated with LiAlH₄ (0.10 mL, 0.1 mmol, 1.0 equiv., 1.0 M in THF) and stirred for 5 minutes. H₂O (0.04 mL) and 1 M NaOH (0.04 mL) were added. The mixture was stirred for 15 minutes and diluted with 1 M KOH (3 mL) and EtOAc (3 mL). The layers were separated and the organic layer was dried (MgSO₄), filtered and evaporated to give 99 (21 mg, 96%) as an oil. FT-IR νmax (film)/cm⁻¹ 2359, 2342; ¹H NMR (500 MHz, CDCl₃) δ 7.29–7.23 (2H, m), 7.22–7.12 (3H, m), 2.71–2.52 (3H, m), 2.51–2.44 (2H, m), 2.42–2.31 (2H, m), 1.90–1.80 (1H, ddt, J = 13.4, 10.1, 5.9 Hz), 1.62–1.48 (5H, m), 1.42 (2H, p, J = 5.9 Hz), 0.98 (3H, d, J = 6.6 Hz). ¹³C NMR (126 MHz, CDCl₃) δ 143.1, 128.6, 128.4, 125.7, 59.0, 49.4, 35.7, 33.4, 26.7, 25.2, 13.9; HRMS (ESI⁺): found MH⁺ 218.1895, [C₁₅H₂₄N]⁺ requires 218.1909. Data in accordance with literature.[¹⁷]

1-(1-(2-Benzylphenoxy)propan-2-yl)piperidine (103)

A tube equipped with a stirring bar was charged with NaI (75 mg, 0.5 mmol, 5.0 equiv.) and then capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N₂ (x 3). A 0.1 M solution of 102 (35 mg, 0.1 mmol, 1.00 equiv.) in CH₃CN (1.0 mL) was added and the mixture was stirred at room temperature for 18 h. The mixture was cooled to 0 °C, treated with LiAlH₄ (0.10 mL, 0.1 mmol, 1.0 equiv., 1.0 M in THF) and stirred for 5 minutes. H₂O (0.04 mL) and 1 M NaOH (0.04 mL) were added. The mixture was stirred for 15 minutes and diluted with 1 M KOH (3 mL) and EtOAc (3 mL). The layers were separated and the organic layer was dried (MgSO₄), filtered and evaporated to give 103 as an oil (15 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.00 (7H, m), 6.94–6.79 (2H, m), 4.09–4.03 (1H, m), 3.98 (2H,
s), 3.08–2.98 (1H, m), 2.64–2.50 (4H, m), 1.62–1.53 (4H, m), 1.46–1.36 (2H, m), 1.14 (3H, d, $J = 6.8$ Hz). Data in accordance with literature.$^{[18]}$
10 Olefin Aminochlorination Scale-Up by Batch-to-Flow

10.1 General Experimental Details

The flow process was performed with the set-up shown in (Figure ) on a Masterflex L/R model 77200-60 pump connected with a photochemical 450 nm LED reactor (PennOC photoreactor M1, Figure ) containing Aldtech FT tubing (1.6 mm internal diameter). The calculated volume of solvent in the reactor was 6.66 mL.
10.2 General Flow Procedure

To a 250 mL flask charged with a stirring bar, was added NCS (9.310 g, 70 mmol, 1.0 equiv.), Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (26.2 mg, 0.35 mmol 0.05 mol%) and CH$_2$Cl$_2$ (120 mL, 0.58 M). The heterogeneous solution was sonicated for 5 minutes until complete solubilisation of NCS, then cooled to 0 °C. 1 (7 mL, 70 mmol, 1.0 equiv.) was then added dropwise over 10 minutes under vigorous stirring. The solution was then allowed to warm to room temperature stirring for 1 h. TFA (32 mL, 420 mmol, 6.0 equiv.) was then added giving a homogeneous bright orange solution which was divided in three fractions. Each fraction was poured in a 100 mL flask (approx. 53 mL of crude in each flask). Prior to the pumping of the reaction, the reactor was fully liquid filled with CH$_2$Cl$_2$ from the solvent reservoir. 10 (31.5 mL, 70 mmol, 1.0 equiv.) was divided in three portions (10.5 mL, 23.33 mmol, 0.33 equiv. each) and added sequentially in each of the three flasks under vigorous stirring, pumping the solution into the system at the end of every addition. Once the entire content of the three flasks was pumped through the reactor (approx. 3-4 minutes into the system), CH$_2$Cl$_2$ was allowed to flush from the solvent reservoir, until all the reaction solution had been collected (approx. 2 minutes). The reaction solution was pumped at 46 mL/min resulting in a theoretical residence time of 8.7 s within the photochemical reactor. The collected homogeneous orange solution was added dropwise over 30 min to a 0 °C solution of 3.5 M sodium hydroxide (200 mL, 10 equiv.). The organic phase was collected, and the aqueous phase extracted with CH$_2$Cl$_2$ (50 mL x 3). The combined organic phases were dried (MgSO$_4$), filtered, and evaporated to give an oil. The crude was then purified by column chromatography on silica gel eluting cyclohexane:EtOAc (9:1) to give 11 as an oil (8.44 g, 48%). Low yield was the result of the partial evaporation of the product under the high vacuum used. The reaction was repeated on the same scale adding 1,3,5-trimethoxybenzene as internal standard. The yield in this case was 87% (17 mmol min$^{-1}$).
Figure 5.

Figure 6.
11 NMR Spectra

S6 – $^1$H NMR (500 MHz, CDCl$_3$)

\[
\text{NMR Spectra}
\]

\[
\text{S6 – }^{13}\text{C NMR (125 MHz, CDCl}_3\text{)}
\]
S7 – $^1$H NMR (400 MHz, CDCl$_3$)

S7 – $^{13}$C NMR (100 MHz, CDCl$_3$)
S9 - $^1$H NMR (400 MHz, CDCl$_3$)

S9 - $^{13}$C NMR (125 MHz, CDCl$_3$)
11 – $^1$H NMR (500 MHz, CDCl$_3$)

11 – $^{13}$C NMR (126 MHz, CDCl$_3$)
12 – $^1$H NMR (500 MHz, CDCl$_3$)

12 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$^{13}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{14}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

SI-75
$^{15}_{-}^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{15}^{13}C$ NMR (126 MHz, CDCl$_3$)
16 – $^1$H NMR (500 MHz, CDCl$_3$)

16 – $^{13}$C NMR (126 MHz, CDCl$_3$)
17 $^1$H NMR (500 MHz, CDCl$_3$)
$^{17}$-$^{19}$F NMR (471 MHz, CDCl$_3$)
19 – $^1$H NMR (500 MHz, CDCl$_3$)

![NMR spectrum of 19](image)

19 – $^{13}$C NMR (126 MHz, CDCl$_3$)

![NMR spectrum of 19](image)
$^{19}$F NMR (471 MHz, CDCl$_3$)
20 – $^1$H NMR (500 MHz, CDCl$_3$)

20 – $^{13}$C NMR (126 MHz, CDCl$_3$)
\[21 \text{ - } ^1\text{H NMR (500 MHz, CDCl}_3\text{)}\]

\[\text{O} \quad \text{Cl} \quad \text{Ph}\]

\[21 \text{ - } ^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}\]
22 – $^1$H NMR (500 MHz, CDCl$_3$)

22 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
25 - $^1$H NMR (500 MHz, CDCl$_3$)

25 - $^{13}$C NMR (126 MHz, CDCl$_3$)
26 – $^1$H NMR (500 MHz, CDCl$_3$)

26 – $^{13}$C NMR (126 MHz, CDCl$_3$)
27 – $^1$H NMR (500 MHz, CDCl$_3$)

27 – $^{13}$C NMR (126 MHz, CDCl$_3$)
28 – $^1$H NMR (500 MHz, CDCl$_3$)

28 – $^{13}$C NMR (126 MHz, CDCl$_3$)
29 $^1$H NMR (500 MHz, CDCl$_3$)

29 $^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

HO\[N-\text{Cl} / \text{Ph}\]

$^{13}$C NMR (126 MHz, CDCl$_3$)
31 – $^1$H NMR (500 MHz, CDCl$_3$)

31 – $^{13}$C NMR (126 MHz, CDCl$_3$)
32 – $^1$H NMR (500 MHz, CDCl$_3$)

32 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, $\text{CDCl}_3$)

$^{13}C$ NMR (126 MHz, $\text{CDCl}_3$)

SI-95
$\text{SI-96}$
$^{35}$ - $^1$H NMR (500 MHz, CDCl$_3$, diastereomers)

$^{35}$ - $^{13}$C NMR (126 MHz, CDCl$_3$)

SI-97
36 – $^1$H NMR (500 MHz, CDCl$_3$, diastereomers)

![NMR spectrum](image)

36 – $^{13}$C NMR (126 MHz, CDCl$_3$)

![NMR spectrum](image)
37 – $^1$H NMR (500 MHz, CDCl$_3$)

37 – $^{13}$C NMR (125 MHz, CDCl$_3$)
38 – $^{1}H$ NMR (400 MHz, CDCl$_3$)

![NMR Spectrum](image)

38 – $^{13}C$ NMR (100 MHz, CDCl$_3$)

![NMR Spectrum](image)
39 – $^1$H NMR (500 MHz, CDCl$_3$)

![NMR spectrum for compound 39]

39 – $^{13}$C NMR (125 MHz, CDCl$_3$)

![NMR spectrum for compound 39]
40 – $^1$H NMR (500 MHz, CDCl$_3$)

40 – $^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H\text{ NMR (}400\text{ MHz, CDCl}_3)$

$^{13}C\text{ NMR (}100\text{ MHz, CDCl}_3)$
42 – $^1$H NMR (500 MHz, CDCl$_3$)

42 – $^{13}$C NMR (125 MHz, CDCl$_3$)
43 – $^1$H NMR (400 MHz, CDCl$_3$)

43 – $^{13}$C NMR (125 MHz, CDCl$_3$)
44 – $^1$H NMR (500 MHz, CDCl$_3$)

44 – $^{13}$C NMR (125 MHz, CDCl$_3$)
45 - $^1$H NMR (500 MHz, CDCl$_3$)

45 - $^{13}$C NMR (126 MHz, CDCl$_3$)
46 (second eluting isomer) – $^1$H NMR (400 MHz, CDCl$_3$)

46 (second eluting isomer) – $^{13}$C NMR (125 MHz, CDCl$_3$)
47 – $^1$H NMR (500 MHz, CDCl$_3$)

47 – $^{13}$C NMR (125 MHz, CDCl$_3$)
48 – $^1$H NMR (500 MHz, CDCl$_3$)

48 – $^{13}$C NMR (125 MHz, CDCl$_3$, diastereomers)
49 – $^1$H NMR (400 MHz, CDCl$_3$)

49 – $^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
51 – $^1$H NMR (500 MHz, CD$_2$Cl$_2$, reaction crude due to product decomposition)

51 – $^{13}$C NMR (126 MHz, CDCl$_3$, reaction crude)
$-^{19}\text{F NMR (471 MHz, CDCl}_3\text{, reaction crude)}$
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
102 – $^1$H NMR (500 MHz, CDCl$_3$)

102 – $^{13}$C NMR (125 MHz, CDCl$_3$)
56 – $^1$H NMR (500 MHz, CDCl$_3$)

56 – $^{13}$C NMR (126 MHz, CDCl$_3$)
55 – $^{19}$F NMR (471 MHz, CDCl$_3$)
$57 - ^1\text{H NMR (500 MHz, CDCl}_3\text{)}$

$57 - ^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$
59 – $^1$H NMR (400 MHz, CD$_3$CN)

\[
\text{[Structure image]}
\]

59 – $^{13}$C NMR (100 MHz, CD$_3$CN)

\[
\text{[NMR spectrum image]}
\]
60 – $^1$H NMR (500 MHz, CDCl$_3$)

![H NMR spectrum](image)

60 – $^{13}$C NMR (125 MHz, CDCl$_3$)

![C NMR spectrum](image)
61 – $^1$H NMR (500 MHz, CDCl$_3$)

61 – $^{13}$C NMR (126 MHz, CDCl$_3$)
62 – $^1$H NMR (500 MHz, CDCl$_3$)

62 – $^{13}$C NMR (125 MHz, CDCl$_3$)
63 – $^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$
64 – $^1$H NMR (500 MHz, CDCl$_3$)

64 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$64^\circ$ – $^1$H NMR (500 MHz, CDCl$_3$)

![H NMR spectrum]

$64^\circ$ – $^{13}$C NMR (125 MHz, CDCl$_3$)

![C NMR spectrum]
65 – $^1$H NMR (500 MHz, CDCl$_3$)

65 – $^{13}$C NMR (126 MHz, CDCl$_3$)
66 – $^1$H NMR (500 MHz, CDCl$_3$)

66 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$67 - ^1\text{H} \text{NMR} \ (500 \text{ MHz, CDCl}_3)$

$67 - ^{13}\text{C} \text{NMR} \ (126 \text{ MHz, CDCl}_3)$
68 – $^1$H NMR (500 MHz, CDCl$_3$)

68 – $^{13}$C NMR (126 MHz, CDCl$_3$)
69 – $^1$H NMR (500 MHz, CDCl$_3$)

69 – $^{13}$C NMR (126 MHz, CDCl$_3$)
**70 - $^1$H NMR (500 MHz, CDCl$_3$)**

![NMR spectrum image]

**70 - $^{13}$C NMR (126 MHz, CDCl$_3$)**

![NMR spectrum image]
71 – $^1$H NMR (500 MHz, CDCl$_3$)

71 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$^1\text{H} - ^{13}\text{C}$ HMBC (500 MHz, CDCl$_3$)
$^72$ – $^1$H NMR (500 MHz, CDCl$_3$)

$^72$ – $^{13}$C NMR (126 MHz, CDCl$_3$)
73 – $^1$H NMR (500 MHz, CDCl$_3$)

73 – $^{13}$C NMR (125 MHz, CDCl$_3$)

SI-137
74 – $^1$H NMR (500 MHz, CDCl$_3$)

74 – $^{13}$C NMR (126 MHz, CDCl$_3$)
75 – $^1$H NMR (500 MHz, CDCl$_3$)

75 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$\text{H NMR (500 MHz, CDCl}_3\text{)}$

$\text{76 – } ^1\text{H NMR (500 MHz, CDCl}_3\text{)}$

$\text{76 – } ^1\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^1$H NMR (500 MHz, CDCl$_3$)
$\textbf{78} - ^1\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
82 - $^1$H NMR (500 MHz, CDCl$_3$)

82 - $^{13}$C NMR (126 MHz, CDCl$_3$)
83 – \(^1\)H NMR (500 MHz, CDCl\(_3\))

83 – \(^{13}\)C NMR (126 MHz, CDCl\(_3\))
$^1$H NMR (500 MHz,CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

SI-146
85 – $^1$H NMR (500 MHz, CDCl$_3$)

85 – $^{13}$C NMR (126 MHz, CDCl$_3$)
86 – $^1$H NMR (500 MHz, CDCl$_3$)

86 – $^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$F NMR (471 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)
$$88 - ^1\text{H NMR (500 MHz, CDCl}_3\text{)}$$

$$88 - ^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$$
$\text{SI-153}$
$^1$H NMR (500 MHz, CDCl$_3$–CD$_3$OD)

$^{13}$C NMR (126 MHz, CDCl$_3$–CD$_3$OD)
$90 - ^1H$ NMR (500 MHz, CDCl$_3$)

$90 - ^{13}C$ NMR (126 MHz, CDCl$_3$)
91 - $^1$H NMR (500 MHz, CDCl$_3$)

91 - $^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{1} $H NMR (500 MHz, CDCl$_{3}$)

![NMR spectrum](image)

$^{13} $C NMR (126 MHz, CDCl$_{3}$)

![NMR spectrum](image)
94 – $^{1}H$ NMR (500 MHz, CDCl$_3$)

94 – $^{13}C$ NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1\text{H} - ^{13}\text{C}$ HSQC (500–125 MHz, CDCl$_3$)
96 – $^1$H NMR (500 MHz, CDCl$_3$)

96 – $^{13}$C NMR (126 MHz, CDCl$_3$)
97 – $^1$H NMR (500 MHz, CDCl$_3$)

97 – $^{13}$C NMR (126 MHz, CDCl$_3$)
**98** – $^1$H NMR (500 MHz, CDCl$_3$)

![NMR Spectrogram](image)

**98** – $^{13}$C NMR (126 MHz, CDCl$_3$)

![NMR Spectrogram](image)
$^1$H NMR (471 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (500 MHz, CDCl$_3$)
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