Supplementary Information

Photoredox catalysis under shear using thin film vortex fluidics

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General

The design and operation of the vortex fluidic device (VFD) used herein is detailed elsewhere.¹ All starting materials were obtained commercially and used without further purification unless otherwise stated. Thin layer chromatography (TLC) was conducted on Merck Kieselgel 60 F254 plates and products were visualised under shortwave UV light (254 nm). ¹H- and ¹³C nuclear magnetic resonance spectra were obtained using a Bruker AV-500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C) or Bruker Avance 600 spectrometer (600 MHz for ¹H and 150 MHz for ¹³C). Each sample was dissolved in d-chloroform and each spectrum was calibrated using the residual solvent peak (δ 7.26 for ¹H and δ 77.0 for ¹³C). Mass spectra were recorded with a Waters LCT Premier XE spectrometer, run in positive ionisation W-mode, using the electrospray ionisation technique.

Optimisation of reaction conditions for the coupling of *N***phenyltetrahydroisoquinoline and nitromethane with Rose Bengal**

A 10 mm NMR tube was charged with *N*-phenyltetrahydroisoquinoline (0.075 mmol), Rose Bengal (3.80 mg, 5 mol%) and nitromethane (1 mL). The tube was capped tightly then rotated in the VFD at 2000, 4000 or 7000 rpm with a tilt angle of 15, 45 or 75° for 90 minutes in the presence of green LEDs at a distance of 3 cm. The mixture was then diluted with EtOAc (2-3 mL) transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto silica gel and subsequent flash chromatography (EtOAc:hexanes, 1:9) gave the desired compound.

General procedure for photoredox aza-Henry reactions with Rose Bengal

A 10 mm NMR tube was charged with the appropriate tetrahydroisoquinoline (0.075 mmol), Rose Bengal (0.76 mg, 1 mol%), the appropriate nitro compound (0.4 mL) and water/MeCN (0.05 mL/0.55 mL). The tube was capped tightly then rotated in the VFD at 4000 rpm with a tilt angle of 45° for 75 minutes in the presence of green LEDs at a distance of 3 cm. The mixture was then diluted with EtOAc (2-3 mL) and transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto silica gel and subsequent flash chromatography (EtOAc:hexanes, 1:9) gave the desired compounds.

1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (80%). ¹H and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.16 (m, 6H), 7.03-7.00 (m, 2H), 6.91-6.87 (m, 1H), 5.56 (t, *J* = 7.5 Hz, 1H), 4.90 (dd, *J* = 7.5, 11.5 Hz, 1H), 4.57 (dd, *J* = 7.5, 11.5 Hz, 1H), 3.73-3.63 (m, 2H), 3.15-3.09 (m, 1H), 2.82 (dt, *J* = 5.0, 16 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 148.40, 135.25, 132.91, 129.48, 129.16, 128.09, 126.98, 126.68, 119.41, 115.09, 78.76, 58.17, 42.06, 26.44.

2-(4-Methylphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 1)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (79%). ¹H and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.26-7.16 (m, 4H), 7.09-7.07 (m, 2H), 6.91-6.88 (m, 2H), 5.50 (t, *J* = 7.0 Hz, 1H), 4.85 (dd, *J* = 7.0, 12.0 Hz, 1H), 4.56 (dd, *J* = 7.0, 12.0 Hz, 1H), 3.67-3.56 (m, 2H), 3.10-3.03 (m, 1H), 2.79-2.73 (m, 1H), 2.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 146.35, 135.32, 132.93, 129.95, 129.25, 129.10. 127.97, 126.94, 126.59, 115.89, 78.81, 58.36, 42.30, 26.22, 20.32.

2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 2)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (81%). ¹H and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.13 (m, 4H), 6.93-6.91 (m, 2H), 6.83-6.81 (m, 2H), 5.39 (dd, *J* = 4.0, 8.5 Hz, 1H), 4.83 (dd, *J* = 8.5, 12.0 Hz, 1H), 4.56 (dd, *J* = 8.5, 12.0 Hz, 1H), 3.75 (s, 3H), 3.61-3.52 (m, 2H), 3.05-2.98 (m, 1H), 2.73-2.68 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 153.98, 143.04, 135.41, 132.88, 129.43, 127.87. 126.89, 126.60, 118.84, 114.69, 78.94, 58.89, 55.56, 43.13, 25.80.

2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 3)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (83%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.33 (m, 2H), 7.28-7.12 (m, 4H), 6.87-6.83 (m, 2H), 5.49 (t, *J* =

7.0 Hz, 1H), 4.85 (dd, J = 8.0, 12.0 Hz, 1H), 4.57 (dd, J = 8.0, 12.0 Hz, 1H), 3.68-3.59 (m, 2H), 3.10-3.04 (m, 1H), 2.82-2.77 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 147.48, 135.01, 132.45, 132.21, 129.27, 128.26. 126.95, 126.82, 116.78, 111.58, 78.61, 58.09, 42.10, 26.19.

1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 4)

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (78%). ¹H and ¹³C NMR spectra were consistent with literature values.³ d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.12 (m, 6H), 7.05-7.00 (m, 2H), 6.87-6.83 (m, 1H), 5.30-5.25 (m, 1H), 5.11-5.05 (m, 0.6H, major isomer), 4.95-4.89 (m, 0.3H, minor isomer), 3.89-3.84 (m, 0.6H), 3.65-3.59 (m, 1.4H), 3.11-3.05 (m, 1H), 2.99-2.89 (m, 1H), 1.73 (d, *J* = 7.0 Hz, 1.2H, minor isomer), 1.54 (d, *J* = 7.0 Hz, 2.6H, major isomer); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 149.15*, 148.87, 135.61, 134.75*, 133.81*, 132.02, 129.42*, 129.30 (major and minor isomers), 129.09*, 128.70*, 128.33, 128.19, 127.25*, 126.59*, 126.12, 119.33, 118.78*, 115.43, 114.50*, 88.94*, 85.42, 62.73, 61.15*, 43.55*, 42.69, 26.74*, 26.40, 17.42*, 16.37.

2-(4-Methylphenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 5)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (72%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ d.r. = 1:1.5; ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.00 (m, 6H), 6.91-6.88 (m, 1H), 5.18 (m, 1H), 5.06-5.00 (m, 0.6H, major isomer), 4.91-4.85 (m, 0.3H, minor isomer), 3.84-3.79 (m, 0.6H), 3.59-3.51 (m, 1.4H), 3.06-3.00 (m, 1H), 2.90-2.81 (m, 1H), 2.27 (s, 1.2H), 2.24 (s, 1.8H), 1.70 (d, *J* = 7.0 Hz, 1.2H, minor isomer), 1.54 (d, *J* = 7.0 Hz, 1.8H, major isomer); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 149.13*, 148.78, 135.71, 134.86*, 133.78*, 132.04, 129.90*, 129.80 (major and minor isomers), 129.12*, 128.91*, 128.77, 128.40, 128.35*, 128.07*, 127.23, 126.51, 126.04, 116.07, 115.20*, 88.94*, 85.50, 62.89, 61.43*, 43.88*, 43.02, 26.53*, 26.27, 20.30*, 20.25, 17.35*, 16.40.

2-(4-Methoxyphenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 6)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (74%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.10 (m, 4H), 6.93-6.91 (m, 2H), 6.83-6.78 (m, 2H), 5.06-4.98 (m, 1.6H), 4.89-4.84 (m, 0.4H, minor isomer), 3.80-3.74 (m, 4H), 3.53-3.47 (m, 1.4H), 3.01-2.94 (m, 1H), 2.85-2.75 (m, 1H), 1.68 (d, *J* = 7.0 Hz, 1.2H, minor isomer), 1.54 (d, *J* = 7.0 Hz, 1.8H, major isomer); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 153.82, 153.57*, 143.90*, 143.51, 135.82, 135.02*, 133.67*, 132.07, 129.25, 128.95*, 128.36*, 128.01, 127.97*, 127.19*, 126.51*, 126.03, 118.91, 118.25, 114.70*, 114.58, 88.81*, 85.75, 63.46, 62.17*, 55.60*, 55.55, 45.03*, 44.03, 26.26*, 17.09*, 16.56.

2-(4-Bromophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 7)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (76%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ d.r. = 1:2.2; ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.00 (m, 6H), 6.86-6.81 (m, 2H), 5.20 (d, *J* = 9.0 Hz, 0.4H, minor isomer), 5.15 (d, *J* = 9.0 Hz, 0.6H, major isomer) 5.03-4.98 (m, 0.6H), 4.89-4.84 (m, 0.4H), 3.84-3.78 (m, 0.6H), 3.59-3.48 (m, 1.4H), 3.06-3.00 (m, 1H), 2.95-2.88 (m, 1H), 1.67 (d, *J* = 6.5 Hz, 1.2H, minor isomer), 1.54 (d, *J* = 6.5 Hz, 1.8H, major isomer); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 148.15*, 147.88, 135.30, 134.49*, 133.46*, 132.13, 132.01 (minor and major isomers), 131.74, 129.14, 128.71*, 128.40, 128.32, 127.22*, 126.76*, 126.26, 116.98, 116.02*, 111.43, 110.81*, 88.76*, 85.40, 62.72, 61.05*, 43.74*, 42.75, 26.69*, 26.20, 17.33*, 16.57.

1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 8)

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (71%). ¹H and ¹³C NMR spectra were consistent with literature values.³ d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.13 (m, 6H), 7.00-6.92 (m, 2H), 6.83-6.77 (m, 1H), 5.23 (d, *J* = 9.5 Hz, 0.4H, minor isomer), 5.12 (d, *J* = 9.5 Hz, 0.6H, major isomer), 4.87 (m, 0.6H, major isomer), 4.68 (m, 0.4H, minor isomer), 3.85 (m, 0.6H, major isomer), 3.69-3.50 (m, 2H), 3.10-3.02 (m, 1H), 2.92-2.84 (m, 1H), 2.20-2.09 (m, 1.7H), 1.86-1.79 (m, 0.7H), 0.96-0.91 (m, 3H); ¹³C NMR (125 MHz, CDCl₃, minor isomer

marked*) δ 149.07, 148.99*, 135.56, 134.68*, 133.91*, 132.57, 129.42, 129.32, 129.18 (major and minor isomers), 128.68, 128.59*, 128.22*, 128.17, 127.23*, 126.64*, 125.90 (major and minor isomers), 119.40, 118.58*, 115.83, 114.13*, 96.16*, 93.05, 62.18, 60.70*, 43.54*, 42.33, 26.83*, 25.74, 25.00*, 24.62, 10.69 (major and minor isomers).

2-(4-Methylphenyl)-1-(1-nitropropyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 9)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (76%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.00 (m, 4H), 7.00-6.98 (m, 2H), 6.89-6.86 (m, 0.8H), 6.84-6.82 (m, 1.2H), 5.15 (d, *J* = 9.5 Hz, 0.4H, minor isomer), 5.04 (d, *J* = 9.5 Hz, 0.6H, major isomer), 4.84 (m, 0.6H, major isomer), 4.68 (m, 0.4H, minor isomer), 3.82 (m, 0.6H, major isomer), 3.64-3.50 (m, 2H), 3.05-3.00 (m, 1H), 2.84-2.80 (m, 1H), 2.25 (s, 1.2H) 2.21 (s, 1.8H), 2.20-2.08 (m, 1.7H), 1.86-1.80 (m, 0.6H), 0.95-0.91 (m, 3H); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 146.98, 146.94*, 135.64, 134.76*, 133.89*, 132.56, 129.89, 129.68, 129.35 (major and minor isomers), 128.95, 128.71*, 128.65*, 128.11, 128.06*, 127.22*, 126.55 (major and minor isomers), 125.82, 116.41, 114.69*, 96.15*, 93.11, 62.36, 60.91*, 43.78*, 42.61, 26.63*, 25.55, 24.98*, 24.61, 20.30, 20.23*, 10.69.

2-(4-Methoxyphenyl)-1-(1-nitropropyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 10)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (77%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.12 (m, 4H), 6.91-6.74 (m, 4H), 5.02 (d, *J* = 9.0 Hz, 0.4H, minor isomer), 4.92 (d, *J* = 9.0 Hz, 0.6H, major isomer), 4.84 (m, 0.6H, major isomer), 4.67 (m, 0.4H, minor isomer), 3.82 (m, 1H), 3.75 (s, 1.2H), 3.72 (s, 1.8H), 3.60-3.42 (m, 1.4H), 3.05-2.96 (m, 1H), 2.82-2.75 (m, 1H), 2.19-2.08 (m, 1.4H), 1.86-1.80 (m, 0.6H), 0.96-0.92 (m, 3H); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 153.77, 153.27*, 143.68 (major and minor isomers), 135.73, 134.85*, 133.77*, 132.52, 129.43, 128.83*, 128.73, 128.01, 128.20*, 126.53*, 125.84, 119.10, 117.47*, 114.72*, 114.46, 96.01*, 93.28, 62.95, 61.55*, 55.62*, 55.52, 44.66*, 43.53, 26.25*, 25.31, 24.93*, 24.63, 10.70, 10.63*.

2-(4-Bromophenyl)-1-(1-nitropropyl)-1,2,3,4-tetrahydroisoquinoline (Table 2, Entry 11)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (74%). ¹H and ¹³C NMR spectra were consistent with literature values.⁴ d.r. = 1:1.6; ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.00 (m, 6H), 6.85-6.82 (m, 0.8H), 6.80-6.78 (m, 1.2H), 5.19 (d, *J* = 9.0 Hz, 0.4H, minor isomer), 5.05 (d, *J* = 9.0 Hz, 0.6H, major isomer), 4.81 (m, 0.6H, major isomer), 4.67 (m, 0.4H, minor isomer), 3.82 (m, 0.6H), 3.62-3.55 (m, 1H), 3.49-3.45 (m, 0.4H), 3.10-3.02 (m, 1H), 2.95-2.86 (m, 1H), 2.20-2.00 (m, 1.4H), 1.86-1.78 (m, 0.6H), 0.95-0.91 (m, 3H); ¹³C NMR (125 MHz, CDCl₃, minor isomer marked*) δ 148.05, 147.99*, 135.26, 134.40*, 133.57*, 132.23, 132.10, 131.91, (major and minor isomers), 129.34, 128.61, 128.41, 128.39, 127.19*, 126.79*, 126.08, 117.33, 115.65*, 111.46, 110.57*, 95.95*, 92.95, 62.13, 60.65*, 43.70*, 42.45, 26.77*, 25.66, 24.94*, 24.68, 10.63.

General procedure for photoredox cyanation with Rose Bengal

A 10 mm NMR tube was charged with the appropriate tetrahydroisoquinoline (0.075 mmol), Rose Bengal (0.76 mg, 1 mol%), TMSCN (0.05 mL, 0.375 mmol) and water/MeCN (0.08 mL/0.87 mL). The tube was capped tightly then rotated in the VFD at 4000 rpm with a tilt angle of 45° for 75 minutes in the presence of green LEDs at a distance of 3 cm. The mixture was then diluted with EtOAc (2-3 mL) transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto silica gel and subsequent flash chromatography (EtOAc:hexanes, 1:9) gave the desired compounds.

2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (Table 2, Entry 12)

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (83%). ¹Hand ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.20 (m, 6H), 7.05-7.03 (m, 2H), 6.99-6.97 (m, 1H), 5.48 (s, 1H), 3.73 (dddd, *J* = 1.0, 3.0, 6.0, 12.0 Hz, 1H), 3.48-3.42 (m, 1H), 3.16-3.11 (m, 1H), 2.93 (dt, J = 3.5, 16.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 148.36, 134.59, 129.57, 129.55, 129.33, 128.74, 127.03, 126.83, 121.88, 117.71, 117.58, 53.20, 44.16, 28.51.

2-(4-Methylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (Table 2, Entry 13)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (81%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.21 (m, 4H), 7.08-7.04 (m, 2H), 6.99-6.97 (m, 2H), 5.44 (s, 1H), 3.68 (dddd, *J* = 1.5, 2.5, 6.0, 12.5 Hz, 1H), 3.45-3.40 (m, 1H), 3.17-3.10 (m, 1H), 2.92 (dt, *J* = 3.0, 16.0 Hz, 1H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 146.25, 134.51, 131.80, 130.07, 129.65, 129.37, 128.66, 127.05, 126.74, 118.29, 117.68, 54.07, 44.35, 28.56, 20.56.

2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (Table 2, Entry 14)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (69%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.21 (m, 4H), 7.09-7.07 (m, 2H), 6.92-6.90 (m, 2H), 5.36 (s, 1H), 3.80 (s, 3H), 3.68 (m, 1H), 3.46-3.41 (m, 1H), 3.19-3.13 (m, 1H), 2.95-2.90 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 155.69, 142.57, 134.33, 129.68, 129.44, 128.64, 127.06, 126.68, 120.99, 117.57, 114.78, 55.57, 55.52, 44.89, 28.68.

2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (Table 2, Entry 15)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (87%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.45 (m, 2H), 7.34-7.24 (m, 4H), 6.97-6.95 (m, 2H), 5.46 (s, 1H), 3.73 (m, 1H), 3.50-3.45 (m, 1H), 3.18-3.12 (m, 1H), 2.98 (dt, J = 3.5, 16.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 147.38, 134.39, 132.43, 129.33, 129.17, 128.91, 127.02, 126.98, 119.08, 117.42, 114.34, 52.85, 44.21, 28.39.

General procedure for Mannich reactions under photoredox conditions with Rose Bengal

A 10 mm NMR tube was charged with the appropriate tetrahydroisoquinoline (0.075 mmol), Rose Bengal (0.76 mg, 1 mol%), diethylmalonate (0.4 mL) and water/MeCN (0.05 mL/0.55 mL). The tube was capped tightly then rotated in the VFD at 4000 rpm with a tilt angle of 45° for 75 minutes in the presence of green LEDs at a distance of 3

cm. The mixture was then diluted with EtOAc (2-3 mL) transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto silica gel and subsequent flash chromatography (EtOAc:hexanes, 1:9) gave the desired compounds.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonic acid diethyl ester (Table 2, Entry 16)

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (81%). ¹Hand ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.08 (m, 6H), 6.99-6.97 (m, 2H), 6.75-6.73 (m, 1H), 5.71 (d, *J* = 9.0 Hz, 1H), 4.19-3.97 (m, 4H), 3.90 (d, *J* = 9.0 Hz, 1H), 3.71-3.50 (m, 2H), 3.11-3.03 (m, 1H), 2.91-2.85 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.95, 167.13, 148.85, 135.95, 134.80, 129.04, 128.86, 127.48, 127.17, 125.99, 118.43, 115.08, 61.56, 61.55, 59.54, 57.86, 42.27, 26.12, 13.91, 13.86.

2-[2-(4-Methylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]malonic acid diethyl ester (Table 2, Entry 17)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (74%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.26-7.00 (m, 6H), 6.89-6.87 (m, 2H), 5.63 (d, *J* = 9.5 Hz, 1H), 4.19-4.00 (m, 4H), 3.90 (d, *J* = 9.5 Hz, 1H), 3.71-3.59 (m, 2H), 3.11-3.02 (m, 1H), 2.84-2.78 (m, 1H), 2.23 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.99, 167.19, 146.81, 135.79, 134.80, 129.55, 128.95, 127.97, 127.38, 127.22, 125.88, 115.74, 61.50, 59.53, 58.28, 42.32, 25.81, 20.28, 13.92, 13.90.

2-[2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]malonic acid diethyl ester (Table 2, Entry 18)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (77%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.07 (m, 4H), 6.89-6.87 (m, 2H), 6.76-6.74 (m, 2H), 5.49 (d, *J* = 9.0 Hz, 1H), 4.12-4.00 (m, 4H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.70 (s, 3H), 3.68-3.62 (m, 1H), 3.56-3.50 (m, 1H), 3.00-2.95 (m, 1H), 2.76-2.72 (m, 1H), 1.14-1.08 (m,

6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.98, 167.23, 153.10, 143.51, 135.61, 134.79, 129.04, 127.34, 127.22, 125.88, 118.05, 114.39, 61.47, 61.44, 59.52, 58.86, 55.55, 43.01, 25.57, 13.96, 13.88.

2-[2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]malonic acid diethyl ester (Table 2, Entry 19)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (78%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.10 (m, 6H), 6.85-6.83 (m, 2H), 5.65 (d, *J* = 9.5 Hz, 1H), 4.16-3.94 (m, 4H), 3.85 (d, *J* = 9.5 Hz, 1H), 3.71-3.64 (m, 1H), 3.59-3.53 (m, 1H), 3.09-3.01 (m, 1H), 2.94-2.89 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.78, 166.96, 147.80, 135.69, 134.54, 131.74, 128.82, 127.69, 127.10, 126.16, 116.38, 110.29, 61.65, 59.43, 57.79, 42.48, 26.11, 13.90.

General procedure for phosphonylation reactions under photoredox conditions with Rose Bengal

A 10 mm NMR tube was charged with the appropriate tetrahydroisoquinoline (0.075 mmol), Rose Bengal (0.76 mg, 1 mol%), diethylphosphite (0.05 mL, 0.38 mmol) and water/MeCN (0.08 mL/0.87 mL). The tube was capped tightly then rotated in the VFD at 4000 rpm with a tilt angle of 45° for 75 minutes in the presence of green LEDs at a distance of 3 cm. The mixture was then diluted with EtOAc (2-3 mL) transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto silica gel and subsequent flash chromatography (EtOAc:hexanes, 1:9) gave the desired compounds.

Diethyl 2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-yl-phosphonate (Table 2, Entry 20)

Using *N*-phenyltetrahydroisoquinoline² the title compound was obtained (81%). ¹Hand ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.38 (m, 1H), 7.27-7.15 (m, 5H), 6.99-6.98 (m, 2H), 6.82-6.79 (m, 1H), 5.18 (d, *J* = 20.0 Hz, 1H), 4.20-3.89 (m, 5H), 3.68-3.61 (m, 1H), 3.11-2.98 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 149.37 (d, *J* = 5.8 Hz), 136.42 (d, *J* = 5.5 Hz), 130.65, 129.10, 128.71 (d, *J* = 2.6 Hz), 128.09 (d, *J* = 4.6 Hz), 127.39 (d, *J* = 3.4 Hz), 125.83 (d, *J* = 2.8 Hz), 118.43, 114.75, 63.26 (d, *J* = 7.2 Hz), 62.28 (d, *J* = 7.6 Hz), 58.80 (d, *J* = 159.3 Hz), 43.45, 26.73, 16.42 (d, *J* = 5.4 Hz), 16.34 (d, *J* = 5.4 Hz).

Diethyl 2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-yl-phosphonate (Table 2, Entry 21)

Using *N*-(4-methylphenyl)tetrahydroisoquinoline² the title compound was obtained (82%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.37 (m, 1H), 7.20-7.12 (m, 4H), 7.08-7.05 (m, 2H), 6.90-6.87 (m, 2H), 5.12 (d, *J* = 20.5 Hz, 1H), 4.13-3.90 (m, 5H), 3.63-3.58 (m, 1H), 3.00-2.98 (m, 2H), 2.25 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 147.38 (d, *J* = 7.0 Hz), 136.42 (d, *J* = 5.6 Hz), 130.59, 129.61, 128.77 (d, *J* = 2.5 Hz), 128.10 (d, *J* = 4.4 Hz), 127.93, 127.26 (d, *J* = 3.4 Hz), 125.75 (d, *J* = 2.9 Hz), 115.29 (d, *J* = 1.0 Hz), 63.29 (d, *J* = 7.2 Hz), 62.22 (d, *J* = 7.6 Hz), 59.00 (d, *J* = 158.5 Hz), 43.78, 26.39, 20.25, 16.45 (d, *J* = 5.4 Hz), 16.33 (d, *J* = 5.4 Hz).

Diethyl 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-yl-phosphonate (Table 2, Entry 22)

Using *N*-(4-methoxyphenyl)tetrahydroisoquinoline² the title compound was obtained (84%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.37 (m, 1H), 7.20-7.12 (m, 3H), 6.92-6.90 (m, 2H), 6.83-6.80 (m, 2H), 5.03 (d, *J* = 20.5 Hz, 1H), 4.13-3.93 (m, 5H), 3.75 (s, 3H), 3.55-3.53 (m, 1H), 2.94-2.91 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 153.08, 144.15 (d, *J* = 8.2 Hz), 136.38 (d, *J* = 5.7 Hz), 130.50, 128.87 (d, *J* = 2.5 Hz), 128.14 (d, *J* = 4.4 Hz), 127.23, (d, *J* = 3.5 Hz), 125.77 (d, *J* = 2.9 Hz), 117.55, 114.48, 63.29 (d, *J* = 7.1 Hz), 62.19 (d, *J* = 7.6 Hz), 59.45 (d, *J* = 157.4 Hz), 55.61, 44.62, 26.10, 16.44 (d, *J* = 5.4 Hz), 16.33 (d, *J* = 5.4 Hz).

Diethyl 2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl-phosphonate (Table 2, Entry 23)

Using *N*-(4-bromophenyl)tetrahydroisoquinoline² the title compound was obtained (71%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.31 (m, 3H), 7.22-7.15 (m, 3H), 6.86-6.84 (m, 2H), 5.10 (d, *J* = 19.0 Hz, 1H), 4.10-3.85 (m, 5H), 3.58-3.61 (m, 1H), 3.20-3.12 (m, 1H), 3.02-2.94 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.27 (d, *J* = 4.8 Hz), 136.25 (d, *J* = 4.8 Hz), 131.75, 130.37, 128.62 (d, *J* = 2.6 Hz), 128.08 (d, *J* = 4.7 Hz), 127.61 (d, *J* = 3.5 Hz), 125.98 (d, *J* = 2.8 Hz), 116.08, 110.25, 63.22 (d, *J* = 7.2 Hz), 62.41 (d, *J* = 7.6 Hz), 58.72 (d, *J* = 158.6 Hz), 43.59, 26.89, 16.42 (d, *J* = 5.4 Hz), 16.33 (d, *J* = 5.4 Hz).

General procedure for photoredox aza-Henry reactions with Rose Bengal under flow conditions

A 10 mm NMR tube was fed at a specific flow rate with a mixed working solution (25 ml) of *N*-phenyltetrahydroisoquinoline² (1.88 mmol), Rose Bengal (19 mg, 1 mol%), the appropriate coupling partner (for nitromethane/diethylmalonate, 10 mL and for TMSCN/diethylphosphite, 1.25 mL) and water/MeCN (for nitromethane/diethylmalonate, 1.25 mL/13.75 mL and for TMSCN/diethylphosphite, 2mL/21.75mL). The tube was then rotated in the VFD at 4000 rpm with a tilt angle of 45° in the presence of green LEDs at a distance of 3 cm. The solution that was liberated from the tube was collected in 2 ml aliquots and these were diluted with EtOAc (5 mL) transferred to a round bottom flask and evaporated to dryness and the residue assayed by ¹H nmr for conversion.

General procedure for Ugi-type multicomponent photoredox reactions with Rose Bengal

A 10 mm NMR tube was charged with the appropriate amine (0.15 mmol), isocyanide (0.075 mmol), Rose Bengal (0.76 mg, 1 mol%), and water/MeCN (0.08 mL/0.87 mL). The tube was capped tightly then rotated in the VFD at 4000 rpm with a tilt angle of 45° for 12 hours in the presence of green LEDs at a distance of 3 cm. The mixture was then diluted with EtOAc (2-3 mL) transferred to a round bottom flask and evaporated to dryness. The residue was then redissolved in EtOAc and adsorbed onto

silica gel and subsequent flash chromatography (EtOAc:hexanes, 2:3) gave the desired compounds.

2-(Methyl(phenyl)amino)-*N*-(tosylmethyl)acetamide (Table 3, Entry 1)

Using *N*,*N*-dimethylaniline and 4-toluenesulfonylmethyl isocyanide the title compound was obtained (83%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.33-7.25 (m, 4H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.67 (d, *J* = 7.0 Hz, 2H), 3.74 (s, 2H), 2.98 (s, 3H), 2.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.28, 148.95, 145.53, 133.73, 129.91, 129.43, 128.80, 119.22, 113.40, 59.81, 58.49, 40.01, 21.75.

2-(Methyl(4-methylphenyl)amino)-*N*-(tosylmethyl)acetamide (Table 3, Entry 2)

Using 4,*N*,*N*-Trimethylaniline and 4-toluenesulfonylmethyl isocyanide the title compound was obtained (72%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.42-7.40 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.67 (d, *J* = 7.0 Hz, 2H), 3.69 (s, 2H), 2.94 (s, 3H), 2.45 (s, 3H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.48, 146.93, 145.47, 133.75, 129.89, 129.88, 128.80, 128.64, 113.72, 59.82, 58.79, 40.28, 21.73, 20.26.

2-((4-Bromophenyl)(methyl)amino)-*N*-(tosylmethyl)acetamide (Table 3, Entry 3)

Using 4-bromo-*N*,*N*-dimethylaniline and 4-toluenesulfonylmethyl isocyanide the title compound was obtained (79%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (600 MHz, CDCl₃) δ 7.69 (d, *J* = 7.0 Hz, 2H), 7.34-7.32 (m, 4H), 7.26-7.24 (m, 1H), 6.51 (d, *J* = 7.5 Hz, 2H), 4.67 (d, *J* = 6.0 Hz, 2H), 3.71 (s, 2H), 2.96 (s, 3H), 2.46 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.78, 147.92, 145.62, 133.69, 132.12, 129.94, 128.71, 114.95, 113.34, 59.81, 58.24, 40.14, 21.76.

N-Butyl-2-(methyl(phenyl)amino)acetamide (Table 3, Entry 4)

Using *N*,*N*-dimethylaniline and butyl isocyanide the title compound was obtained (44%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.25 (m, 2H), 6.84-6.82 (t, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.57 (br s, 1H), 3.84 (s, 2H), 3.26 (q, *J* = 7.0 Hz, 2H), 2.99 (s, 3H), 1.46-1.42

(m, 2H), 1.29-1.25 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.17, 149.29, 129.33, 118.60, 113.11, 58.94, 39.69, 38.88, 31.60, 19.93, 13.65.

N-Butyl-2-(methyl(4-methylphenyl)amino)acetamide (Table 3, Entry 5)

Using 4,*N*,*N*-Trimethylaniline and butyl isocyanide the title compound was obtained (53%). ¹H NMR (500 MHz, CDCl₃) δ 7.08-7.06 (m, 2H), 6.65-6.64 (m, 3H), 3.79 (s, 2H), 3.26 (q, *J* = 6.5 Hz, 2H), 2.96 (s, 3H), 2.26 (s, 3H), 1.46-1.41 (m, 2H), 1.29-1.25 (m, 2H), 0.88 (t, J = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.38, 147.28, 129.80, 127.99, 113.37, 59.26, 39.91, 38.83, 31.60, 20.18, 19.93, 13.64. HRMS calculated for C₁₄H₂₂N₂ONa [M+Na] 257.1630 found 257.1639.

N-Butyl-2-(methyl(4-bromophenyl)amino)acetamide (Table 3, Entry 6)

Using 4-bromo-*N*,*N*-dimethylaniline and butyl isocyanide the title compound was obtained (48%). ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.31 (m, 2H), 6.59-6.56 (m, 2H), 6.44 (br s, 1H), 3.80 (s, 2H), 3.26 (q, *J* = 7.0 Hz, 2H), 2.98 (s, 3H), 1.46-1.40 (m, 2H), 1.29-1.23 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.60, 148.18, 132.00, 114.64, 110.74, 58.70, 39.86, 38.91, 31.56, 19.91, 13.63. HRMS calculated for C₁₃H₁₉BrN₂ONa [M+Na] 321.0578 found 321.0573.

Methyl 2-(2-(methyl(phenyl)amino)acetamido)acetate (Table 3, Entry 7)

Using *N*,*N*-dimethylaniline and methyl isocyanoacetate the title compound was obtained (80%). ¹H- and ¹³C NMR spectra were consistent with literature values. ³ ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.06 (br s, 1H), 6.85-6.75 (m, 3H), 4.06 (d, *J* = 5.5 Hz, 2H), 3.89 (s, 2H), 3.72 (s, 3H), 3.03 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.03, 169.98, 149.26, 129.33, 118.76, 113.30, 58.72, 52.31, 40.74, 39.69.

Methyl 2-(2-(methyl(4-methylphenyl)amino)acetamido)acetate (Table 3, Entry 8)

Using 4,*N*,*N*-Trimethylaniline and methyl isocyanoacetate the title compound was obtained (73%). ¹H- and ¹³C NMR spectra were consistent with literature values.⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.13 (br s, 1H), 7.09-7.07 (m, 2H), 6.70-6.68 (m, 2H), 4.06 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 2H), 3.73 (s, 3H), 2.99 (s, 3H), 2,26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.23, 170.00, 147.25, 129.80, 128.17, 113.60, 59.07, 52.28, 40.71, 39.93, 20.21.

Methyl 2-(2-(methyl(4-bromophenyl)amino)acetamido)acetate (Table 3, Entry 9)

Using 4-bromo-*N*,*N*-dimethylaniline and methyl isocyanoacetate the title compound was obtained (70%). ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.33 (m, 2H), 6.94 (br s, 1H), 6.64-6.61 (m, 2H), 4.06 (d, *J* = 5.5 Hz, 2H), 3.87 (s, 2H), 3.73 (s, 3H), 3.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.48, 169.95, 148.19, 132.02, 114.88, 110.96, 58.51, 52.38, 40.75, 39.85. HRMS calculated for C₁₂H₁₅BrN₂O₃Na [M+Na] 337.0164 found 337.0173.

N-Benzyl-2-(methyl(phenyl)amino)acetamide (Table 3, Entry 10)

Using *N*,*N*-dimethylaniline and benzyl isocyanide the title compound was obtained (41%). ¹H- and ¹³C NMR spectra were consistent with literature values.³ ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.24 (m, 5H), 7.21-7.19 (m, 2H), 6.95 (br s, 1H), 6.86-6.83 (m, 1H), 6.75-6.73 (m, 2H), 4.48 (d, *J* = 6.0 Hz, 2H), 3.92 (s, 2H), 3.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.40, 149.20, 137.93, 129.33, 128.61, 127.44, 127.40, 118.69, 113.19, 58.92, 43.04, 39.84.

N-Benzyl-2-((4-methylphenyl)(methyl)amino)acetamide (Table 3, Entry 11)

Using 4,*N*,*N*-Trimethylaniline and benzyl isocyanide the title compound was obtained (52%). ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.20 (m, 5H), 7.09-7.06 (m, 2H), 7.02 (br s, 1H), 6.68-6.66 (m, 2H), 4.48 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 2H), 2.96 (s, 3H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.57, 147.22, 138.02, 129.80, 128.58, 128.12, 127.43, 127.35, 113.52, 59.23, 43.02, 40.08, 20.19. HRMS (ESI) calculated for C₁₇H₂₀N₂ONa [M+Na] 291.1473 found 291.1471.

N-Benzyl-2-((4-bromophenyl)(methyl)amino)acetamide (Table 3, Entry 12)

Using 4-bromo-*N*,*N*-dimethyl aniline and benzyl isocyanide the title compound was obtained (50%). ¹H- and ¹³C NMR spectra were consistent with literature values. ⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.24 (m, 5H), 7.19-7.17 (m, 2H), 6.87 (br s, 1H), 6.59-6.57 (m, 2H), 4.46 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 2H), 2.98 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.80, 148.16, 137.85, 132.03, 128.67, 127.51, 127.45, 114.80, 110.91, 58.73, 43.14, 40.03.

Supporting Figure



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195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm























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