

Supporting Information

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I. General Information

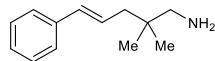
All reactions were performed under an N₂ atmosphere unless otherwise stated. All glassware was dried in an oven at 120 °C for at least 2 h prior to use and allowed to cool in a desiccator cabinet. Reactions carried out below 0 °C employed an acetone/dry ice bath or a cryocool equipped with an acetone bath. MeCN, THF, Et₂O, DMF, toluene, and CH₂Cl₂ were purified by elution through alumina as described by Grubbs.¹ Cu(TFA)₂•H₂O was either used as purchased from Alfa-Aesar or prepared from CuCO₃ and TFA as described in Section IV. All other chemicals were purchased from commercial suppliers and used as received.

Flash column chromatography was performed with normal phase SiO₂ (Sigma-Aldrich or Macherey-Nagel, 60 Å pore size, 230-400 mesh, 40-63 µm particle size) according to the method of Still.² Reactions were monitored by thin-layer chromatography (Silicycle, 250 µm thickness), and visualization was accomplished with a 254 nm UV light or by staining with KMnO₄ solution (3.0 g of KMnO₄ and 20.0 g of K₂CO₃ in 5 mL of 5% aq. NaOH and 300 mL H₂O).

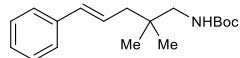
¹H and ¹³C{¹H} NMR data for all previously uncharacterized compounds were obtained using a Bruker AVANCE-400 or Bruker AVANCE-500 spectrometer with DCH, Prodigy, or BBFO+ probes. ¹H spectra were internally referenced to tetramethyl silane (0.00 ppm) or the residual protio-solvent peak in DMSO-*d*₆. ¹³C{¹H} spectra were internally referenced to CDCl₃ (77.16 ppm) or DMSO-*d*₆ (39.52 ppm). ¹H NMR spectra were tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant(s), and number of protons. ¹³C NMR spectra were tabulated by observed peak. The spectrometers used for this work are supported by the NIH (S10 OD012245) and a generous gift from Paul J. and Margaret M. Bender. Mass spectrometry was performed with a Thermo Q ExactiveTM Plus. This instrument is supported by the NIH (S10 OD020022) and the University of Wisconsin. IR spectra were obtained using a Bruker Alpha Platinum FTIR spectrometer equipped with an attenuated total reflectance (ATR) sampling head. Melting points were obtained using a Stanford Research Systems DigiMelt apparatus.

II. Synthesis of Oxyamination Substrates

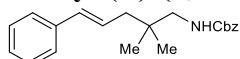
(4E)-2,2-Dimethyl-5-phenylpent-4-enitrile (S1, S1). Synthesized according to the method of Hampel and coworkers. All spectral data were in agreement with previously reported values.³



***tert*-Butyl (E)-(2,2-dimethyl-5-phenylpent-4-en-1-yl)carbamate (Table 1, 5a).** Synthesized according to the method of Nicewicz and coworkers. All spectral data were in agreement with previously reported values.⁴

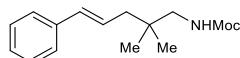


Benzyl (E)-(2,2-dimethyl-5-phenylpent-4-en-1-yl)carbamate (Scheme 3, 5b). A solution of **S1** (0.101 g, 0.511 mmol) and Et₃N (0.220 mL, 1.53 mmol) in CH₂Cl₂ (2.50 mL) was treated dropwise via syringe with benzyl chloroformate (0.080 mL, 0.56 mmol). The resulting solution was allowed to stir at rt for 20 h. The reaction mixture was diluted with H₂O (20 mL) and CH₂Cl₂ (20 mL), and the layers were separated. The aqueous phase was extracted with CH₂Cl₂ (2 x 20 mL), and the combined organic extracts were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give a yellow oil/solid mixture. The residue was purified by chromatography on SiO₂ (20% EtOAc in hexanes) to give **5b** (0.076 g, 0.23 mmol, 46%) as a clear, colorless oil.

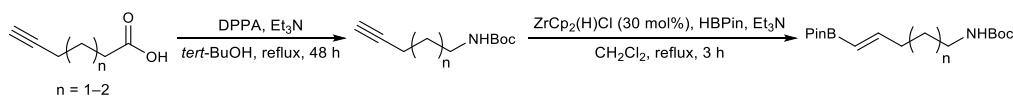


IR (ATR): ν 3350.5, 3024.5, 2957.6, 1693.6, 1597.0, 1532.7, 1236.6 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.39–7.26 (m, 9 H), 7.23–7.16 (m, 1 H), 6.38 (d, J = 15.7 Hz, 1 H), 6.23 (dt, J = 15.5, 7.5 Hz, 1 H), 5.10 (s, 2 H), 4.82 (br. s, 1 H), 3.08 (d, J = 6.6 Hz, 2 H), 2.12 (d, J = 7.4 Hz, 2 H), 0.93 (s, 6 H); **¹³C NMR** (100 MHz, CDCl₃): δ 156.8, 137.6, 136.7, 132.8, 128.7, 128.6, 128.3, 128.3, 127.2, 126.6, 126.2, 66.9, 51.1, 43.5, 35.6, 25.0; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₂₁H₂₆NO₂]⁺ required 324.1958 m/z , found 324.1957 m/z .

Methyl N-[(4E)-2,2-dimethyl-5-phenylpent-4-en-1-yl]carbamate (Scheme 3, 5c). A solution of **S1** (0.099 g, 0.50 mmol) and Et₃N (0.220 mL, 1.53 mmol) in CH₂Cl₂ (2.50 mL) was treated dropwise via syringe with methyl chloroformate (0.045 mL, 0.56 mmol). The resulting solution was allowed to stir at rt for 20 h. The reaction mixture was diluted with H₂O (20 mL) and CH₂Cl₂ (20 mL), and the layers were separated. The aqueous phase was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic extracts were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give a yellow oil. The oil was purified by chromatography on SiO₂ (25% EtOAc in hexanes) to give **5c** (0.057 g, 0.23 mmol, 46%) as a clear, colorless oil.



IR (ATR): ν 3351.7, 3022.4, 2956.9, 1692.8, 1533.4, 1237.3 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.38–7.27 (m, 4 H), 7.24–7.16 (m, 1 H), 6.39 (d, J = 15.7 Hz, 1 H), 6.23 (dt, J = 15.4, 7.5 Hz, 1 H), 4.73 (br. s, 1 H), 3.67 (s, 3 H), 3.07 (d, J = 6.6 Hz, 2 H), 2.12 (d, J = 7.4 Hz, 2 H), 0.93 (s, 6 H); **¹³C NMR** (100 MHz, CDCl₃): δ 157.5, 137.6, 132.8, 128.6, 127.2, 126.7, 126.2, 52.3, 51.1, 43.5, 35.6, 25.0; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₅H₂₂NO₂]⁺ required 248.1645 m/z , found 248.1646 m/z .



tert-Butyl pent-4-yn-1-ylcarbamate (S2). A solution of 5-hexynoic acid (10.0 mL, 90.6 mmol), diphenylphosphoryl azide (23.1 mL, 107 mmol), and Et₃N (24.9 mL, 178 mmol) in *tert*-BuOH (89 mL) was stirred at reflux for 48 h. The reaction mixture was cooled to rt and diluted with Et₂O (100 mL) and H₂O (100 mL). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 100 mL). The combined organic extracts were washed with H₂O (2 x 200 mL) and brine (2 x 200 mL), dried over MgSO₄, and filtered. The solvent was evaporated under reduced pressure to give an orange oil. The oil was purified by chromatography on SiO₂ (15% EtOAc in hexanes) to give **S2** (13.96 g, 76.18 mmol, 85%) as a clear, colorless oil. All spectral data were in agreement with reported values.⁵

tert-Butyl-(E)-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)carbamate

(S3). To a solution of **S2** (6.36 g, 34.7 mmol), Et₃N (4.84 mL, 34.7 mmol), and pinacolborane (7.55 mL, 52.1 mmol) in CH₂Cl₂ (35 mL) was added ZrCp₂(H)Cl (2.64 g, 10.2 mmol) in a single portion and the resulting mixture was stirred at reflux for 3 h while shielded from light. The reaction mixture was cooled to rt and quenched by slow, dropwise addition of MeOH. The solvent was evaporated under reduced pressure and the residue was taken up in Et₂O and filtered through a thin pad of boron-doped SiO₂.⁶ The solvent was evaporated under reduced pressure. The volatile components were removed via Kugelrohr distillation (0.5 torr, 80-90 °C, 1 h) to give **S3** (7.768 g, 24.96 mmol, 72%) as a pale yellow oil.

IR (ATR): ν 3319.4, 2974.0, 2932.3, 1678.3, 1640.7, 1520.9 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 6.60 (dt, J = 18.0, 6.4 Hz, 1 H), 5.45 (d, J = 18.0 Hz, 1 H), 4.58 (br. s, 1 H), 3.12 (app. d, J = 6.8 Hz, 2 H), 2.22–2.16 (m, 2 H), 1.61 (p, J = 7.3 Hz, 2 H), 1.44 (s, 9 H), 1.26 (s, 12 H); **¹³C NMR** (125 MHz, CDCl₃): 155.9, 153.2, 119.4 (br), 83.1, 79.0, 40.2, 33.0, 28.5, 28.4, 24.8; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₆H₃₀BNO₄Na]⁺ required 333.2196 m/z , found 333.2192 m/z .

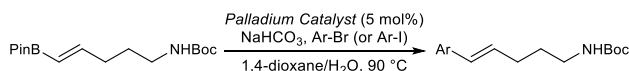
tert-Butyl hex-5-yn-1-ylcarbamate (S4). A solution of 6-heptynoic acid (0.800 mL, 6.32 mmol), diphenylphosphoryl azide (1.65 mL, 7.66 mmol), and Et₃N (1.75 mL, 12.6 mmol) in *tert*-BuOH (6.3 mL) was stirred at reflux for 48 h. The reaction mixture was cooled to rt and diluted with Et₂O (50 mL) and H₂O (50 mL). The layers were separated and the aqueous phase was extracted with Et₂O (2 x 50 mL). The combined organic extracts were washed with H₂O (100 mL) and brine (100 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give a dark yellow oil. The oil was purified by chromatography on SiO₂ (15% EtOAc in hexanes) to give **S4** (0.871 g, 4.42 mmol, 70%) as a clear, colorless oil. All spectral data were in agreement with reported values.⁷

tert-Butyl (E)-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)carbamate (S5).

A solution of **S4** (0.860 g, 4.36 mmol), ZrCp₂(H)Cl (0.341 g, 1.32 mmol), Et₃N (0.610 mL, 4.38 mmol), and HBPIn (0.950 mL, 6.55 mmol) in CH₂Cl₂ (4.40 mL) was stirred at reflux for 3 h. The reaction mixture was cooled to rt and quenched by dropwise addition of MeOH (5.0 mL). The organic solvents were evaporated under reduced pressure to give a cloudy white oil which was taken up in Et₂O (50 mL) and filtered through a thin pad of boron-doped SiO₂.⁶ The solvent was evaporated under reduced pressure to give a clear,

colorless oil. The volatile components were evaporated via Kugelrohr distillation (90-100 °C, 0.5 torr, 45 min) to give **S5** (1.077 g, 3.311 mmol, 76%) as a pale yellow oil.

IR (ATR): ν 3361.4, 2976.6, 2930.9, 2865.0, 1696.6, 1638.5, 1516.9 cm^{-1} . **^1H NMR** (500 MHz, CDCl_3): δ 6.60 (dt, $J = 17.9, 6.4$ Hz, 1 H), 5.43 (d, $J = 17.9$ Hz, 1 H), 4.49 (br. s, 1 H), 3.13–3.09 (m, 2 H), 2.21–2.10 (m, 2 H), 1.52–1.44 (m, 4 H), 1.44 (s, 9 H), 1.26 (s, 12 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 155.9, 153.9, 119.0, 83.0, 79.0, 40.4, 35.3, 29.6, 28.4, 25.4, 24.8; **HRMS** (ESI^+): $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{17}\text{H}_{32}\text{BNO}_4\text{Na}]^+$ required 347.2353 m/z , found 347.2353 m/z .



General Procedure for the Synthesis of Styrene Substrates: A solution of vinyl boronate (**S3** or **S5**, 1 equiv), aryl halide (1 equiv), NaHCO_3 (4 equiv), and palladium catalyst (0.05 equiv, 5 mol%) in 1,4-dioxane (10 mL/mmol boronate ester) and H_2O (4 mL/mmol boronate ester) was stirred at 90 °C until the reaction was complete as indicated by thin-layer chromatography. The reaction mixture was cooled to rt and diluted with EtOAc and H_2O . The layers were separated and the organic phase was washed with H_2O (2x) and brine (2x), dried over MgSO_4 , and filtered. The solvent was evaporated under reduced pressure. The residue was purified by chromatography on SiO_2 to afford pure styrene.

tert-Butyl (E)-(5-phenylpent-4-en-1-yl)carbamate (S6). Synthesized according to the general procedure using **S3** (0.499 g, 1.60 mmol), bromobenzene (0.170 mL, 1.60 mmol), NaHCO_3 (0.542 g, 6.45 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (0.062 g, 0.076 mmol). After chromatography on SiO_2 (10% EtOAc in hexanes), **S6** was isolated as a white solid (0.296 g, 1.13 mmol, 70%). All spectral data were in agreement with reported values.⁸

tert-Butyl (E)-(5-(p-tolyl)pent-4-en-1-yl)carbamate (S7). Synthesized according to the general procedure using **S3** (0.398 g, 1.28 mmol), iodotoluene (0.279 g, 1.28 mmol), NaHCO_3 (0.434 g, 5.17 mmol), and $\text{Pd}(\text{Bu}_3\text{P})_2$ (0.033 g, 0.065 mmol). After chromatography on SiO_2 (15% EtOAc in hexanes), **S7** was isolated as a white solid (0.298 g, 1.08 mmol, 84%).

Mp 53–55 °C; **IR** (ATR): ν 3364.2, 3018.9, 2977.3, 2936.5, 2868.2, 1680.2, 1511.3 cm^{-1} ; **^1H NMR**: (400 MHz, CDCl_3): δ 7.23 (d, $J = 8.1$ Hz, 2 H), 7.10 (d, $J = 8.0$ Hz, 2 H), 6.36 (d, $J = 15.7$ Hz, 1 H), 6.14 (dt, $J = 15.8, 6.9$ Hz, 1 H), 4.54 (br s, 1 H), 3.17 (app. d, $J = 6.9$ Hz, 2 H), 2.32 (s, 3 H), 2.22 (m, 2 H), 1.65 (p, $J = 7.3$ Hz, 2 H), 1.45 (s, 9 H); **^{13}C NMR**: (125 MHz, CDCl_3): δ 156.1, 136.8, 134.9, 130.4, 129.3, 128.8, 126.0, 79.2, 40.3, 30.4, 29.9, 28.6, 21.3; **HRMS** (ESI^+): $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{17}\text{H}_{25}\text{NO}_2\text{Na}]^+$ required 298.1778 m/z , found 298.1774 m/z .

tert-Butyl (E)-(5-(4-fluorophenyl)pent-4-en-1-yl)carbamate (S8). Synthesized according to the general procedure using **S3** (0.511 g, 1.64 mmol), 1-bromo-4-fluorobenzene (0.180 mL, 1.64 mmol), NaHCO_3 (0.544 g, 6.48 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (0.060 g, 0.073 mmol). After chromatography on SiO_2 (10% EtOAc in hexanes), **S8** was isolated as a white crystalline solid (0.300 g, 1.07 mmol, 66%).

Mp 59–60 °C; **IR** (ATR): ν 3316.3, 2979.1, 2932.7, 2861.2, 1675.9 cm^{-1} ; **^1H NMR**: (400 MHz, CDCl_3) δ 7.28 (m, 2 H), 6.98 (m, 2 H), 6.35 (d, J = 15.7 Hz, 1 H), 6.10 (dt, J = 15.8, 6.9 Hz, 1 H), 4.59 (br s, 1 H), 3.17 (app. d, J = 6.8 Hz, 2 H), 2.23 (m, 2 H), 1.65 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **^{13}C NMR**: (100 MHz, CDCl_3) δ 161.9 (d, J = 245.8 Hz), 156.0, 133.7 (d, J = 3.3 Hz), 129.5 (d, J = 2.3 Hz), 129.3, 127.4 (d, J = 7.9 Hz), 115.3 (d, J = 21.5 Hz), 79.1, 40.2, 30.2, 29.7, 28.4; **HRMS** (ESI^+): $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{16}\text{H}_{22}\text{FNO}_2\text{Na}]^+$ required 302.1527 m/z , found 302.1522 m/z .

tert-Butyl (E)-(5-(4-methoxyphenyl)pent-4-en-1-yl)carbamate (S9). Synthesized according to the general procedure using **S3** (0.505 g, 1.62 mmol), 4-bromoanisole (0.200 mL, 1.60 mmol), NaHCO_3 (0.544 g, 6.59 mmol), and $\text{Pd}(\text{tBu}_3\text{P})_2$ (0.042 g, 0.082 mmol). After chromatography on SiO_2 (35% Et_2O in hexanes), **S9** was isolated as a white crystalline solid (0.281 g, 0.964 mmol, 60%).

Mp 68–70 °C; **IR** (ATR): ν 3335.5, 2968.7, 2927.8, 2865.4, 1685.6, 1603.5, 1533.4, 1605.9 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.29–7.24 (m, 2 H), 6.86–6.79 (m, 2 H), 6.34 (d, J = 15.8 Hz, 1 H), 6.05 (dt, J = 15.7, 6.9 Hz, 1 H), 4.54 (br. s, 1 H), 3.80 (s, 3 H), 3.17 (q, J = 6.8 Hz, 2 H), 2.27–2.15 (m, 2 H), 1.65 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 158.9, 156.1, 130.6, 130.0, 127.7, 127.2, 114.0, 79.3, 55.4, 40.4, 30.4, 30.0, 28.6; **HRMS** (ESI^+): $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{17}\text{H}_{25}\text{NO}_3\text{Na}]^+$ required 314.1727 m/z , found 314.1722 m/z .

tert-Butyl (E)-(5-(4-chlorophenyl)pent-4-en-1-yl)carbamate (S10). Synthesized according to the general procedure using **S3** (0.400 g, 1.29 mmol), 1-bromo-4-chlorobenzene (0.255 g, 1.33 mmol), NaHCO_3 (0.442 g, 5.26 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.082 g, 0.071 mmol). After chromatography on SiO_2 (15% EtOAc in hexanes), **S10** was isolated as a white powder (0.289 g, 0.997 mmol, 76%).

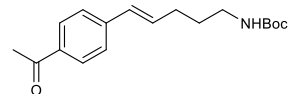
Mp 72–73 °C; **IR** (ATR): ν 3379.5, 2979.9, 2934.9, 2851.3, 1684.9 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.26–7.23 (m, 4 H), 6.34 (d, J = 15.8 Hz, 1 H), 6.17 (d, J = 15.7, 6.9, 1 H), 4.60 (br. s, 1 H), 3.17 (app. d, J = 6.8 Hz, 2 H), 2.28–2.16 (m, 2 H), 1.65 (p, J = 7.3 Hz, 2 H), 1.44 (s, 9 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 156.0, 136.1, 130.6, 129.3, 128.6, 127.2, 125.5, 79.1, 40.2, 30.3, 29.7, 28.5; **HRMS** (ESI^+): $[\text{M}+\text{Na}]^+$ calculated for $[\text{C}_{16}\text{H}_{22}\text{ClNO}_2\text{Na}]^+$ required 318.1231 m/z , found 318.1226 m/z .

tert-Butyl (E)-(5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl)carbamate (S11). Synthesized according to the general procedure using **S3** (0.498 g, 1.60 mmol), 4-trifluoromethyl-1-bromobenzene (0.225 mL, 1.61 mmol), NaHCO_3 (0.541 g, 6.44 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (0.059 g, 0.072 mmol). After chromatography on SiO_2 (30% Et_2O in hexanes), **S11** was isolated as a white solid (0.318 g, 0.966 mmol, 60%).

Mp 87–88 °C; **IR** (ATR): ν 3376.0, 2982.6, 2922.3, 2859.8, 1683.8, 1612.8, 1520.9 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.53 (d, J = 8.2 Hz, 2 H), 7.41 (d, J = 8.1 Hz, 2 H), 6.43 (d, J = 15.9 Hz, 1 H), 6.31 (dt, J = 15.8, 6.8 Hz, 1 H), 4.58 (br. s, 1 H), 3.18 (app. d, J = 6.7 Hz, 2 H), 2.33–2.15 (m, 2 H), 1.68 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 156.1, 141.2, 132.8,

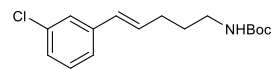
129.5, 128.9 (q, $J = 32.4$ Hz), 126.2, 125.6 (q, $J = 3.8$ Hz), 124.4 (q, $J = 271.7$ Hz), 79.3, 40.3, 30.5, 29.7, 28.6; **HRMS** (ESI⁺): $[M+Na]^+$ calculated for $[C_{17}H_{22}F_3NO_2Na]^+$ required 352.1495 m/z , found 352.1495 m/z .

tert-Butyl (E)-(5-(4-acetylphenyl)pent-4-en-1-yl)carbamate (S12). Synthesized according to the general procedure using **S3** (0.509 g, 1.64 mmol), 4'-bromoacetophenone (0.321 g, 1.61 mmol), NaHCO₃ (0.544 g, 6.48 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.059 g, 0.072 mmol). After chromatography on SiO₂ (20% EtOAc in hexanes), **S12** was isolated as a white powder (0.356 g, 1.17 mmol, 72%).



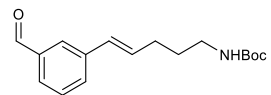
Mp 70–72 °C; **IR** (ATR): ν 3372.1, 2988.5, 2966.1, 2915.3, 2853.1, 1679.9, 1599.4, 1559.0 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.89 (d, $J = 8.4$ Hz, 2 H), 7.40 (d, $J = 8.4$ Hz, 2 H), 6.44 (d, $J = 16.0$ Hz, 1 H), 6.35 (dt, $J = 15.8, 6.6$ Hz, 1 H), 4.60 (br. s, 1 H), 3.18 (app. q, $J = 6.8$ Hz, 2 H), 2.58 (s, 3 H), 2.28 (q, $J = 6.8$ Hz, 2 H), 1.69 (p, $J = 7.4$ Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.6, 156.0, 142.3, 135.6, 133.0, 129.7, 128.8, 126.0, 79.2, 40.2, 30.4, 29.6, 28.4, 26.6; **HRMS** (ESI⁺): $[M+Na]^+$ calculated for $[C_{18}H_{25}NO_3Na]^+$ required 326.1727 m/z , found 326.1725 m/z .

tert-Butyl (E)-(5-(3-chlorophenyl)pent-4-en-1-yl)carbamate (S13). Synthesized according to the general procedure using **S3** (0.400 g, 1.28 mmol), 1-bromo-3-chlorobenzene (0.150 mL, 1.28 mmol), NaHCO₃ (0.438 g, 5.21 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.050 g, 0.061 mmol). After chromatography on SiO₂ (40% Et₂O in hexanes), **S13** was isolated as a white solid (0.244 g, 0.825 mmol, 64%).



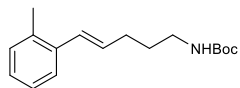
Mp 47–50 °C; **IR** (ATR): ν 3365.3, 2978.4, 2934.9, 2869.2, 1678.7, 1590.7, 1562.8, 1525.7 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.33–7.29 (m, 1 H), 7.25–7.11 (m, 3 H), 6.33 (d, $J = 15.8$ Hz, 1 H), 6.21 (dt, $J = 15.8, 6.8$ Hz, 1 H), 4.58 (br. s, 1 H), 3.17 (app. q, $J = 6.8$ Hz, 2 H), 2.27–2.21 (m, 2 H), 1.66 (p, $J = 7.3$ Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 156.1, 139.6, 134.5, 131.5, 129.8, 129.4, 127.0, 126.0, 124.3, 79.3, 40.3, 30.4, 29.7, 28.5; **HRMS** (ESI⁺): $[M+Na]^+$ calculated for $[C_{16}H_{22}ClNO_2Na]^+$ required 318.1321 m/z , found 318.1231 m/z .

tert-Butyl (E)-(5-(3-formylphenyl)pent-4-en-1-yl)carbamate (S14). Synthesized according to the general procedure using **S3** (0.501 g, 1.61 mmol), 3-bromobenzaldehyde (0.190 mL, 1.63 mmol), NaHCO₃ (0.540 g, 6.43 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.061 g, 0.075 mmol). After chromatography on SiO₂ (50% Et₂O in hexanes), **S14** was isolated as a yellow oil (0.260 g, 0.899 mmol, 56%).



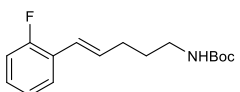
IR (ATR): ν 3349.5, 2971.5, 2925.9, 2855.2, 2728.7, 1692.1, 1587.3, 1516.9 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 10.00 (s, 1 H), 7.83 (s, 1 H), 7.70 (d, $J = 7.5$ Hz, 1 H), 7.58 (d, $J = 7.7$ Hz, 1 H), 7.45 (d, $J = 7.6$ Hz, 1 H), 6.45 (d, $J = 15.9$ Hz, 1 H), 6.32 (dt, $J = 15.8, 6.9$ Hz, 1 H), 4.71 (s, 1 H), 3.19 (app. d, $J = 6.8$ Hz, 2 H), 2.28 (app. q, $J = 7.5$ Hz, 2 H), 1.69 (p, $J = 7.3$ Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 192.5, 156.0, 138.6, 136.7, 132.0, 131.9, 129.2, 129.2, 128.3, 126.9, 79.2, 40.2, 30.3, 29.7, 28.5; **HRMS** (ESI⁺): $[M+Na]^+$ calculated for $[C_{17}H_{23}NO_3Na]^+$ required 312.1570 m/z , found 312.1570 m/z .

tert-Butyl (E)-(5-(*o*-tolyl)pent-4-en-1-yl)carbamate (S15). Synthesized according to the general procedure using **S3** (0.399 g, 1.28 mmol), 2-bromotoluene (0.155 mL, 1.29 mmol), NaHCO₃ (0.433 g, 5.15 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.049 g, 0.060 mmol). After chromatography on SiO₂ (35% Et₂O in hexanes), **S15** was isolated as an off-white, crystalline solid (0.213 g, 0.770 mmol, 60%).



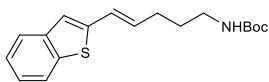
Mp 43–44 °C; **IR** (ATR): ν 3383.8, 3052.0, 2974.9, 2940.4, 2913.5, 1685.1 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.39 (d, J = 6.3 Hz, 1 H), 7.18–7.09 (m, 3 H), 6.59 (dt, J = 15.7, 1.6 Hz, 1 H), 6.06 (dt, J = 15.6, 6.9 Hz, 1 H), 4.57 (br. s, 1 H), 3.19 (app. d, J = 6.8 Hz, 2 H), 2.32 (s, 3 H), 2.30–2.20 (m, 2 H), 1.67 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 156.0, 136.7, 134.9, 131.1, 130.2, 128.4, 126.9, 126.0, 125.5, 79.1, 40.2, 30.7, 29.9, 28.5, 19.9; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₇H₂₅NO₂Na]⁺ required 298.1778 m/z , found 298.1774 m/z .

tert-Butyl (E)-(5-(2-fluorophenyl)pent-4-en-1-yl)carbamate (S16). Synthesized according to the general procedure using **S3** (0.403 g, 1.29 mmol), 1-bromo-2-fluorobenzene (0.140 mL, 1.28 mmol), NaHCO₃ (0.437 g, 5.20 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.048 g, 0.059 mmol). After chromatography on SiO₂ (35% Et₂O in hexanes), **S16** was isolated as a colorless oil that solidified upon standing (0.207 g, 0.741 mmol, 57%).



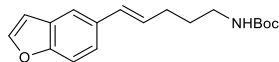
Mp 38–40 °C; **IR** (ATR): ν 3385.9, 3044.9, 2977.3, 2936.8, 2856.5, 1685.0, 1519.1 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.41 (td, J = 7.7, 1.8 Hz, 1 H), 7.16 (tdd, J = 7.3, 5.1, 1.8 Hz, 1 H), 7.10–6.97 (m, 2 H), 6.55 (d, J = 16.0 Hz, 1 H), 6.28 (dt, J = 16.0, 6.9 Hz, 1 H), 4.55 (br. s, 1 H), 3.18 (app. d, J = 6.8 Hz, 2 H), 2.39–2.14 (m, 2 H), 1.68 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 159.9 (d, J = 248.2 Hz), 155.9, 132.5 (d, J = 4.5 Hz), 128.1 (d, J = 8.2 Hz), 127.1 (d, J = 3.9 Hz), 125.3 (d, J = 12.3 Hz), 124.0 (d, J = 3.5 Hz), 122.9 (d, J = 3.3 Hz), 115.6 (d, J = 22.1 Hz), 79.2, 40.2, 30.7, 29.6, 28.4; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₅H₂₂FN₂O₂Na]⁺ required 302.1527 m/z , found 302.1525 m/z .

tert-Butyl (E)-(5-(benzo[*b*]thiophen-2-yl)pent-4-en-1-yl)carbamate (S17). Synthesized according to the general procedure using **S3** (0.500 g, 1.61 mmol), 2-bromobenzothiophene (0.342 g, 1.61 mmol), NaHCO₃ (0.539 g, 6.42 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.059 g, 0.072 mmol). After chromatography on SiO₂ (15% EtOAc in hexanes), **S17** was isolated as a yellow solid (0.181 g, 0.570 mmol, 35%).



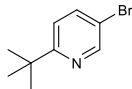
Mp 91–93 °C; **IR** (ATR): ν 3354.2, 2975.4, 2982.4, 1684.1, 1527.1 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.73 (dd, J = 7.6, 1.4 Hz, 1 H), 7.65 (dd, J = 6.9, 1.5 Hz, 1 H), 7.32–7.22 (m, 2 H), 7.05 (s, 1 H), 6.62 (d, J = 15.6 Hz, 1 H), 6.13 (dt, J = 15.5, 6.9 Hz, 1 H), 4.56 (br. s, 1 H), 3.18 (app. q, J = 6.9 Hz, 2 H), 2.31–2.20 (m, 2 H), 1.68 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 155.9, 142.8, 140.2, 138.5, 132.5, 124.5, 124.3, 123.2, 122.1, 121.5, 79.2, 40.2, 30.2, 29.5, 28.4; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₈H₂₄NO₂S]⁺ required 318.1522 m/z , found 318.1522 m/z .

***tert*-Butyl (*E*)-(5-(benzofuran-5-yl)pent-4-en-1-yl)carbamate (S18).** Synthesized according to the general procedure using **S3** (0.499 g, 1.60 mmol), 5-bromobenzofuran (0.200 mL, 1.60 mmol), NaHCO₃ (0.541 g, 6.44 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.063 g, 0.077 mmol). After chromatography on SiO₂ (30% Et₂O in hexanes), **S18** was isolated as clear, colorless oil (0.248 g, 0.823 mmol, 51%).

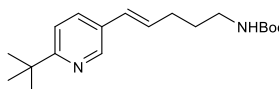


IR (ATR): ν 3353.8, 2974.3, 2930.2, 1689.0, 1512.8 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.58 (d, *J* = 2.2 Hz, 1 H), 7.52 (d, *J* = 1.7 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 1 H), 7.30 (dd, *J* = 8.6, 1.7 Hz, 1 H), 6.72 (d, *J* = 2.1 Hz, 1 H), 6.48 (d, *J* = 15.7 Hz, 1 H), 6.16 (dt, *J* = 15.8, 6.9 Hz, 1 H), 4.58 (br. s, 1 H), 3.21–3.15 (m, 2 H), 2.30–2.16 (m, 2 H), 1.67 (p, *J* = 7.0 Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 155.9, 154.3, 145.3, 132.7, 130.6, 128.6, 127.7, 122.5, 118.5, 111.2, 106.6, 79.1, 40.2, 30.3, 29.8, 28.4; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₈H₂₄NO₃]⁺ required 302.1751 *m/z*, found 302.1749 *m/z*.

5-bromo-2-(*tert*-butyl)pyridine (SI, S19). Synthesized according to the method of Cossy and coworkers. All spectral data were in agreement with reported values.⁹

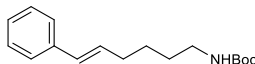


***tert*-Butyl (*E*)-(5-(6-(*tert*-butyl)pyridin-3-yl)pent-4-en-1-yl)carbamate (S20).** Synthesized according to the general procedure using **S3** (0.380 g, 1.22 mmol), **S19** (0.260 g, 1.21 mmol), NaHCO₃ (0.404 g, 4.81 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.052 g, 0.064 mmol). After chromatography on SiO₂ (30% EtOAc in hexanes), **S20** was isolated as a yellow oil (0.209 g, 0.656 mmol, 54%).

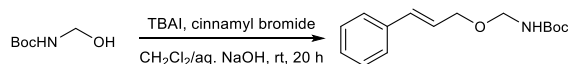


IR (ATR): ν 3341.8, 2963.3, 2868.7, 1692.2, 1516.8 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 8.49 (d, *J* = 2.3 Hz, 1 H), 7.59 (dd, *J* = 8.3, 2.4 Hz, 1 H), 7.26 (d, *J* = 8.2 Hz, 1 H), 6.37 (d, *J* = 15.9 Hz, 1 H), 6.21 (dt, *J* = 15.9, 6.8 Hz, 1 H), 4.56 (br. s, 1 H), 3.17 (q, *J* = 6.8 Hz, 2 H), 2.32–2.20 (m, 2 H), 1.73–1.61 (m, 2 H), 1.44 (s, 9 H), 1.35 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 168.0, 156.1, 146.9, 132.8, 131.4, 130.2, 127.2, 118.9, 79.3, 40.3, 37.3, 30.5, 30.3, 29.8, 28.6; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₉H₃₁N₂O₂]⁺ required 319.2380 *m/z*, found 319.2374 *m/z*.

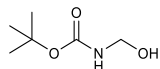
***tert*-Butyl (*E*)-(6-phenylhex-5-en-1-yl)carbamate (S21).** Synthesized according to the general procedure using **S5** (0.500 g, 1.54 mmol), bromobenzene (0.165 mL, 1.54 mmol), NaHCO₃ (0.521 g, 6.20 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.055 g, 0.067 mmol). After chromatography on SiO₂ (25% Et₂O in hexanes), **S21** was isolated as an off-white solid (0.248 g, 0.901 mmol, 58%).



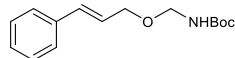
Mp 50–51 °C; **IR** (ATR): ν 3377.9, 2977.4, 2934.0, 2860.2, 1683.1, 1514.3 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.35–7.31 (m, 2 H), 7.32–7.25 (m, 2 H), 7.21–7.16 (m, 1 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 6.19 (dt, *J* = 15.8, 6.9 Hz, 1 H), 4.51 (br. s, 1 H), 3.14 (q, *J* = 6.4 Hz, 2 H), 2.23 (qd, *J* = 7.0, 1.5 Hz, 2 H), 1.57–1.48 (m, 4 H), 1.44 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 156.0, 137.7, 130.4, 130.2, 128.5, 126.9, 125.9, 79.1, 40.4, 32.6, 29.6, 28.4, 26.5; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₇H₂₆NO₂]⁺ required 276.1958 *m/z*, found 276.1956 *m/z*.



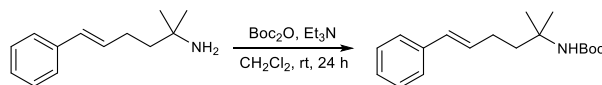
tert-Butyl ((hydroxymethyl)carbamate (S22). Synthesized according to the procedure of del Pozo and coworkers. All spectral data were in agreement with reported values.¹⁰



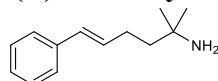
tert-Butyl ((cinnamyloxy)methyl)carbamate (S23). To a solution of **S22** (0.100 g, 0.679 mmol) in CH₂Cl₂ (6.8 mL) was added 20% aq. NaOH (6.8 mL), tetrabutylammonium iodide (0.752 g, 2.04 mmol), and cinnamyl bromide (0.454 g, 2.30 mmol) sequentially and the resulting mixture was stirred at rt for 20 h. The reaction mixture was extracted with CH₂Cl₂ (3 x 20 mL) and the combined organic extracts were washed with brine (50 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to a green-yellow oil/solid mixture. This residue was purified by chromatography on SiO₂ (20% EtOAc in hexanes) to give **S23** (0.083 g, 0.315 mmol, 46%) as a clear, colorless oil.



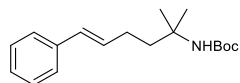
IR (ATR): ν 3379.6, 2977.5, 2928.5, 1698.0, 1506.8 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.41–7.36 (m, 2 H), 7.33–7.27 (m, 2 H), 7.25–7.20 (m, 1 H), 6.62 (d, J = 16.0 Hz, 1 H), 6.28 (dt, J = 15.9, 6.0 Hz, 1 H), 5.36 (s, 1 H), 4.69 (d, J = 7.2 Hz, 2 H), 4.20 (dd, J = 6.0, 1.5 Hz, 2 H), 1.47 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 155.6, 136.7, 132.4, 128.5, 127.7, 126.5, 125.7, 80.1, 71.6, 68.7, 28.3; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₅H₂₁NO₃Na]⁺ required 286.1414 m/z , found 286.1414 m/z .



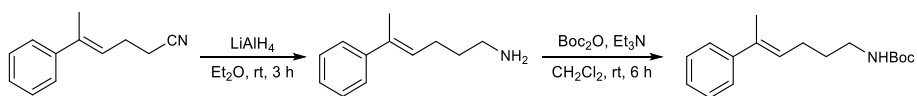
(E)-2-Methyl-6-phenylhex-5-en-2-amine (S24). Synthesized according to the method of Denmark and coworkers. All spectral data were in agreement with reported values.⁸



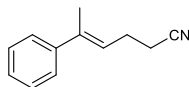
tert-Butyl (E)-(2-methyl-6-phenylhex-5-en-2-yl)carbamate (S25). A solution of **S24** (0.175 g, 0.924 mmol) and Et₃N (0.385 mL, 2.77 mmol) in CH₂Cl₂ (4.5 mL) at 0 °C was treated dropwise via syringe with Boc₂O (0.425 mL, 1.85 mmol) and the resulting solution was stirred at rt for 24 h. The reaction mixture was diluted with CH₂Cl₂ (20 mL), washed with H₂O (2 x 20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give a yellow oil. The oil was purified by chromatography on SiO₂ (5% Et₂O in hexanes) to give **S25** (0.189 g, 0.653 mmol, 71%) as a white, crystalline solid.



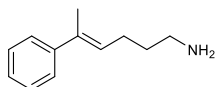
Mp 44–46 °C; **IR** (ATR): ν 3362.4, 2972.8, 2922.4, 1689.8, 1513.7 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.35–7.24 (m, 4 H), 7.21–7.14 (m, 1 H), 6.38 (dt, J = 15.8, 1.4 Hz, 1 H), 6.21 (dt, J = 15.8, 6.8 Hz, 1 H), 4.44 (br. s, 1 H), 2.24–2.12 (m, 2 H), 1.87–1.73 (m, 2 H), 1.44 (s, 9 H), 1.28 (s, 6 H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.5, 137.9, 130.8, 129.9, 128.6, 126.9, 126.0, 78.8, 52.4, 39.8, 28.6, 28.1, 27.4; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₈H₂₈NO₂]⁺ required 290.2115 m/z , found 290.2109 m/z .



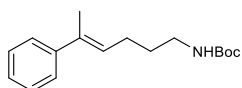
(E)-5-Phenylhex-4-enitrile (S26). Synthesized according to the method of Knowles and coworkers. All spectral data were in agreement with reported values.¹¹



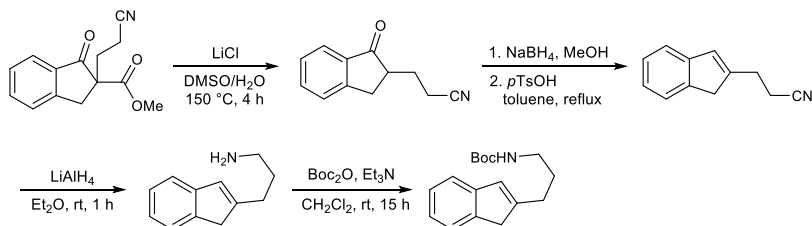
(E)-5-Phenylhex-4-en-1-amine (S27). To a suspension of LiAlH₄ (0.681 g, 17.9 mmol) in Et₂O (60 mL) at 0 °C was added dropwise via syringe a solution of **S26** (1.51 g, 8.82 mmol) in Et₂O (18 mL) and the resulting solution was stirred at rt for 3 h. The reaction mixture was cooled to 0 °C and quenched by slow addition of H₂O (5 mL). The mixture was filtered through Celite and concentrated under reduced pressure to give **S27** (1.500 g) as a pale yellow oil which was used without further purification.



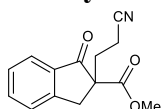
tert-Butyl (E)-(5-phenylhex-4-en-1-yl)carbamate (S28). A solution of **S27** (1.500 g) and Et₃N (2.10 mL, 15.0 mmol) in CH₂Cl₂ (37 mL) at 0 °C was treated dropwise via syringe with Boc₂O (1.90 mL, 8.27 mmol) and the resulting solution was stirred at rt for 6 h. The reaction mixture was diluted with H₂O (100 mL) and the layers separated. The aqueous phase was extracted with CH₂Cl₂ (2 x 50 mL) and the combined organic extracts were washed with brine (100 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give a white solid/oil mixture. This residue was purified by chromatography on SiO₂ (20% EtOAc in hexanes) to give **S28** (1.77 g, 6.43 mmol, 73% over 2 steps).



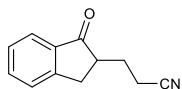
Mp 50–52 °C; **IR** (ATR): ν 3323.4, 3047.4, 2973.6, 2935.9, 2866.6, 1682.4, 1529.1 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.38–7.34 (m, 2 H), 7.31–7.28 (m, 2 H), 7.24–7.18 (m, 1 H), 5.74 (app. td, J = 7.2, 1.4 Hz, 1 H), 4.55 (s, 1 H), 3.23–3.12 (m, 2 H), 2.23 (q, J = 7.4 Hz, 2 H), 2.03 (d, J = 1.3 Hz, 3 H), 1.65 (p, J = 7.3 Hz, 2 H), 1.45 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 155.9, 143.8, 135.5, 128.1, 127.3, 126.6, 125.6, 79.1, 40.4, 29.9, 28.4, 26.1, 15.8; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₇H₂₆NO₂]⁺ required 276.1958 m/z , found 276.1958 m/z .



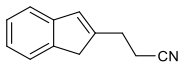
Methyl 2-(2-cyanoethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S29). Prepared according to the method of Colombo and coworkers. All spectral data were in agreement with reported values.¹²



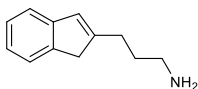
3-(1-Oxo-2,3-dihydro-1H-inden-2-yl)propanenitrile (S30). A solution of **S29** (0.747 g, 3.07 mmol) and LiCl (0.147 g, 3.47 mmol) in a mixture of DMSO (4.5 mL) and H₂O (0.080 mL) was stirred at 150 °C for 4 h. The reaction mixture was cooled to rt and diluted with H₂O (100 mL). The aqueous solution was extracted with CH₂Cl₂ (3 x 50 mL) and the combined organic extracts were washed with H₂O (2 x 100 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give crude **S30** as an orange oil. The oil was purified by chromatography on SiO₂ (25% EtOAc in hexanes) to give **S30** (0.390 g, 2.11 mmol, 69%) as a yellow oil. All spectral data were in agreement with previously reported values.¹³



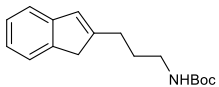
3-(1H-Inden-2-yl)propanenitrile (S31). To a solution of NaBH₄ (0.162 g, 4.28 mmol) in MeOH (2 mL) at 0 °C was added dropwise via syringe a solution of **S30** (0.390 g, 2.11 mmol) in MeOH (1.8 mL) and the resulting solution was stirred at rt for 2 h. The solvent was evaporated under reduced pressure and the residue taken up in 1 M aq. HCl (50 mL). The aqueous solution was extracted with Et₂O (3 x 50 mL) and the combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure to give a yellow-green oil (0.348 g) which was used without further purification. The oil was taken up in toluene (13.2 mL) and *p*-toluenesulfonic acid (0.038 g, 0.22 mmol) was added. The resulting solution was stirred at 90 °C for 20 min. The reaction mixture was cooled to rt and the solvent was evaporated under reduced pressure. The residue was taken up in Et₂O (20 mL) and the solution was filtered through a thin pad of SiO₂. The solvent was evaporated under reduced pressure to give **S31** (0.266 g, 1.57 mmol, 75% over 2 steps) as a green oil. All spectral data were in agreement with previously reported values.¹⁴



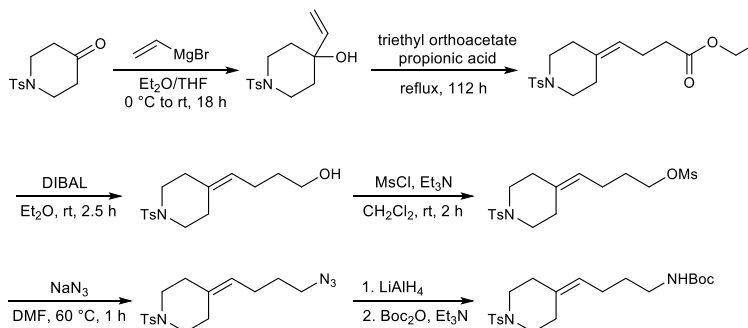
3-(1H-Inden-2-yl)propan-1-amine (S32). To a suspension of LiAlH₄ (0.117 g, 3.08 mmol) in Et₂O (2 mL) at 0 °C was added dropwise via syringe a solution of **S31** (0.266 g, 1.57 mmol) in Et₂O (3.2 mL) and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of H₂O (1 mL). The suspension was stirred for 20 min, diluted with Et₂O (50 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give **S32** (0.222 g) as a green oil which was used without further purification.



***tert*-Butyl (3-(1H-inden-2-yl)propyl)carbamate (S33).** A solution of **S32** (0.222 g) and Et₃N (0.540 mL, 3.84 mmol) in CH₂Cl₂ (6.4 mL) at 0 °C was treated dropwise via syringe with Boc₂O (0.590 mL, 2.56 mmol) and the resulting solution was stirred at rt for 15 h. The solvent was evaporated under reduced pressure to give crude **S33** as a yellow oil. The oil was purified by chromatography on SiO₂ (10% EtOAc in hexanes) to give **S33** (0.265 g, 0.969 mmol, 62% over 2 steps).



Mp 72–74 °C; **IR** (ATR): ν 3356.5, 2974.8, 2930.2, 1684.3, 1517.3 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.37 (d, *J* = 7.4 Hz, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1 H), 6.52 (s, 1 H), 4.57 (br. s, 1 H), 3.30 (s, 2 H), 3.19 (q, *J* = 6.8 Hz, 2 H), 2.51 (t, *J* = 7.6 Hz, 2 H), 1.80 (p, *J* = 7.4 Hz, 2 H), 1.44 (s, 9 H); **¹³C NMR** (125 MHz, CDCl₃): δ 156.1, 149.6, 145.6, 143.2, 126.8, 126.4, 123.9, 123.6, 120.1, 79.3, 41.2, 40.6, 29.6, 28.6, 28.6; **HRMS** (ESI⁺): [M+NH₄]⁺ calculated for [C₁₇H₂₇N₂O₂]⁺ required 291.2067 *m/z*, found 291.2059 *m/z*.



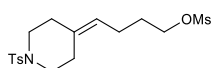
1-Tosyl-4-vinylpiperidin-4-ol (S34). A solution of 1-(4-methylbenzenesulfonyl)piperidin-4-one (0.202 g, 0.797 mmol) in Et₂O (2.8 mL) at 0 °C was treated dropwise via syringe with a solution of vinyl magnesium bromide (1.03 mL, 1.03 mmol, 1 M in THF) and the resulting solution was stirred at 0 °C for 1 h and then at rt for 18 h. The reaction mixture was diluted with Et₂O (20 mL) and sat. aq. NH₄Cl (20 mL) and the layers separated. The organic phase was washed with brine (20 mL), dried over Na₂SO₄, filtered, and the solvent evaporated under reduced pressure to give a clear, colorless oil. The oil was purified by chromatography on SiO₂ (50% EtOAc in hexanes) to give **S34** (0.143 g, 0.508 mmol, 64%) as a white, crystalline solid. All spectral data were in agreement with that previously reported.¹⁵

Ethyl 4-(1-tosylpiperidin-4-ylidene)butanoate (S35). A solution of **S34** (2.10 g, 7.46 mmol) and propionic acid (0.560 mL, 7.46 mmol) in triethyl orthoacetate (16.4 mL, 89.6 mmol) was stirred at reflux for 112 h. The reaction mixture was cooled to rt and diluted with Et₂O (200 mL). The organic phase was washed with H₂O (100 mL) and sat. aq. NaHCO₃ (100 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give an orange oil. The oil was purified by chromatography on SiO₂ (25% EtOAc in hexanes) to give **S35** (1.044 g) as a pale yellow oil which was used without further purification.

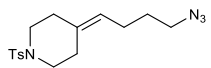
4-(1-Tosylpiperidin-4-ylidene)butan-1-ol (S36). To a solution of **S35** (1.044 g) in Et₂O (13 mL) at 0 °C was added dropwise via syringe a solution of DIBAL (7.11 mL, 7.11 mmol, 1 M in hexanes) and the resulting solution was stirred at rt for 2.5 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of H₂O (5 mL) and 1 M aq. NaOH (5 mL). The reaction mixture was stirred for 15 min and MgSO₄ was added slowly at 0 °C. The suspension was filtered through Celite and the filtrate was concentrated under reduced pressure to give crude **S36** as a clear, colorless oil. The oil was purified by chromatography on SiO₂ (50% EtOAc in hexanes) to give **S36** (0.323 g, 1.04 mmol, 14% over 3 steps) as a clear, colorless oil.

IR (ATR): ν 3396.6, 2930.9, 2848.3, 1328.25, 1160.8 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.63 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 5.17 (t, J = 7.4 Hz, 1 H), 3.59 (t, J = 6.5 Hz, 2 H), 3.05–2.94 (m, 4 H), 2.42 (s, 3 H), 2.33 (t, J = 5.6 Hz, 2 H), 2.25 (t, J = 5.6 Hz, 2 H), 2.03 (q, J = 7.4 Hz, 2 H), 1.59–1.51 (m, 2 H), 1.29 (br. s, 1 H); **¹³C NMR** (100 MHz, CDCl₃): δ 143.6, 134.0, 133.5, 129.8, 127.8, 124.2, 62.4, 48.1, 47.4, 35.4, 32.8, 27.7, 23.5, 21.7; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₆H₂₃NO₃Na]⁺ required 332.1291 m/z , found 332.1287 m/z .

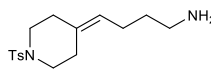
4-(1-Tosylpiperidin-4-ylidene)butyl methanesulfonate (S37). A solution of **S36** (0.320 g, 1.03 mmol) and Et₃N (0.175 mL, 1.24 mmol) in CH₂Cl₂ (2 mL) at 0 °C was treated dropwise via syringe with methanesulfonyl chloride (0.095 mL, 1.24 mmol) and the resulting solution was stirred at rt for 2 h. The reaction mixture was quenched by dropwise addition of sat. aq. NaHCO₃ (2 mL) and diluted with H₂O (50 mL). The aqueous solution was extracted with CH₂Cl₂ (3 x 50 mL) and the combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure to give **S37** (0.410 g) as a cloudy white oil which was used without further purification.



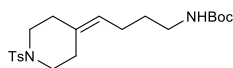
4-(4-Azidobutylidene)-1-tosylpiperidine (S38). A suspension of **S37** (0.410 g) and NaN₃ (0.199 g, 3.06 mmol) in DMF (3.7 mL) was stirred at 60 °C for 1 h. The reaction mixture was cooled to rt, diluted with H₂O (50 mL), and extracted with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were washed with H₂O (2 x 50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to give **S38** (0.220 g) as a clear, colorless which was used without further purification.



4-(1-Tosylpiperidin-4-ylidene)butan-1-amine (S39). To a suspension of LiAlH₄ (0.054 g, 1.42 mmol) in Et₂O (10 mL) at 0 °C was added dropwise via syringe a solution of **S38** (0.220 g) in Et₂O (3.2 mL) and the resulting solution was stirred at rt for 1 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of H₂O (2 mL) and 1 M aq. NaOH (4 mL). The suspension was stirred for 15 min and MgSO₄ was added slowly at 0 °C. The mixture was filtered through Celite and concentrated under reduced pressure to give **S39** (0.111 g) as a cloudy white oil which was used without further purification.

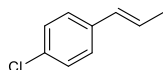


tert-Butyl (4-(1-tosylpiperidin-4-ylidene)butyl)carbamate (S40). A solution of **S39** (0.111 g) and Et₃N (0.150 mL, 1.08 mmol) in CH₂Cl₂ (1.80 mL) at 0 °C was treated dropwise via syringe with Boc₂O (0.165 mL, 0.720 mmol) and the resulting solution was stirred at rt for 16 h. The solvent was evaporated under reduced pressure to give a clear, colorless oil. The oil was purified by chromatography on SiO₂ (30% EtOAc in hexanes) to give **S40** (0.113 g, 0.277 mmol, 27% over 4 steps) as a clear, colorless oil.



IR (ATR): ν 3396.0, 2971.0, 2930.0, 2851.4, 1696.4, 1159.2 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.56–7.48 (m, 2 H), 7.35–7.27 (m, 2 H), 5.14 (t, J = 7.3 Hz, 1 H), 4.48 (br. s, 1 H), 3.12–2.92 (m, 6 H), 2.42 (s, 3 H), 2.30 (t, J = 5.6 Hz, 2 H), 2.24 (t, J = 5.6 Hz, 2 H), 1.96 (q, J = 7.4 Hz, 2 H), 1.50 (p, J = 7.3 Hz, 2 H), 1.42 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃): δ 156.0, 143.6, 134.0, 133.5, 129.8, 127.8, 124.0, 79.3, 48.1, 47.3, 40.3, 35.4, 30.3, 28.5, 27.7, 24.5, 21.7; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₂₁H₃₃N₂O₄S]⁺ required 409.2156 m/z , found 409.2152 m/z .

(E)-1-Chloro-4-(prop-1-en-1-yl)benzene (SI, S41). Synthesized according to the method of Xu and coworkers. All spectral data were in agreement with previously reported values.¹⁶



III. Optimization Studies for Oxyamination

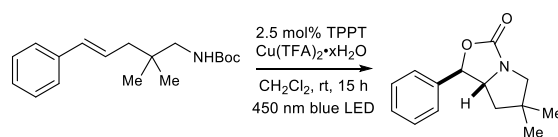
Table S1. Oxidant screen

2.5 mol% TPPT
3 equiv. oxidant
CH₂Cl₂, rt, 15 h
450 nm blue LED

entry ^a	oxidant	% yield (d.r.)
1	air	0%
2	DDQ	0%
3	PIDA	8%
4	TEMPO	trace
5	TBHP	0%
6	CAN	4%
7	MnO ₂	trace
8	FeCl ₃	3%
9	Cu(TFA) ₂ ·xH ₂ O	58% (>20:1)

^aYields were determined by ¹H NMR analysis of the unpurified reaction mixtures using phenanthrene as an internal standard.

Table S2. Optimization of oxyamination



^astandard conditions^a

entry	variation from “standard conditions”	% yield (d.r.) ^a
1	None	82% (>20:1)
2	Cu(TFA) ₂ ·xH ₂ O prepared from basic CuCO ₃ and trifluoroacetic acid	77% (>20:1)
3	Cu(OAc) ₂ ·xH ₂ O instead of Cu(TFA) ₂ ·xH ₂ O	7% (n.d.)
4	Cu(EH) ₂ instead of Cu(TFA) ₂ ·xH ₂ O	7% (n.d.)
5	Cu(OTf) ₂ instead of Cu(TFA) ₂ ·xH ₂ O	24% (>20:1)
6	CuCl ₂ instead of Cu(TFA) ₂ ·xH ₂ O	5% (n.d.)
7	Ru(bpz) ₃ (BAr ^F) ₂ instead of TPPT	trace
8	[Ir(dF-CF ₃ -ppy) ₂ (dtbbpy)]PF ₆ instead of TPPT	5% (n.d.)
9	9,10-anthracenedicarbonitrile instead of TPPT	2% (n.d.)
10	MesAcrMe ⁺ instead of TPPT	72% (>20:1)
11	MeCN instead of CH ₂ Cl ₂	32% (<20:1)
12	DMF instead of CH ₂ Cl ₂	0%
13	no Cu(TFA) ₂ ·xH ₂ O	trace
14	no TPPT	1% (n.d.)
15	no light	0%

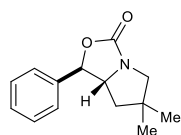
^aYields were determined by ¹H NMR analysis of the unpurified reaction mixtures using phenanthrene as an internal standard.

IV. Photocatalytic Oxyamination of Styrenes

A. Preparation of $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$:¹⁷ A solution of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (2.23 g, 10.1 mmol) in water (3 mL) was placed in a round-bottomed flask and treated with trifluoroacetic acid (3.06 mL, 40.0 mmol). The reaction mixture was stirred at ambient temperature until effervescence ceased (ca. 1 h). The resulting solution was then filtered through Celite and concentrated under reduced pressure to give a light blue gum. Further drying under high vacuum at 60 °C gave $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (4.631 g, 16.00 mmol, 79%) as a blue solid.

B. General procedure for intramolecular oxyamination of styrenes: A solution of alkene (1 equiv), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (1.2 equiv by anhydrous molecular mass), and TPPT (0.025 equiv, 2.5 mol%) in CH_2Cl_2 (0.1 M) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution stirred for the indicated time at rt under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with EtOAc, filtered through a thin pad of SiO_2 (eluting with EtOAc), and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 to afford pure product.

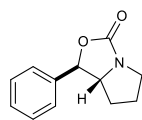
6,6-Dimethyl-1-phenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Table 1, **6**). Synthesized according to the general procedure using **5a** (0.101 g, 0.349 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiating for 18 h. After chromatography on SiO_2 (35% EtOAc in hexanes), **6** was isolated as a white solid (0.058 g, 0.25 mmol, 72%).



1 gram scale: A solution of **5a** (1.01 g, 3.50 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (1.22 g, 4.20 mmol), and TPPT (0.035 g, 0.088 mmol) in CH_2Cl_2 (35 mL) was degassed (freeze-pump-thaw, 5 cycles of 5 min each) and the resulting solution was stirred at rt for 48 h under irradiation by two 15 W blue LED flood lamps. The reaction mixture was concentrated under reduced pressure to give a brown oil which was taken up in Et_2O (10 mL), filtered through a thin pad of SiO_2 (Et_2O), and concentrated under reduced pressure to give a green oil. The oil was purified by chromatography on SiO_2 (35% EtOAc in hexanes) to give **6** as a clear oil that solidified upon standing (0.679 g, 2.94 mmol, 84%).

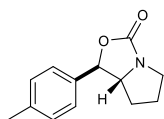
Mp 67–68 °C; **IR** (ATR): ν 2959.4, 2925.0, 2860.2, 2164.8, 1729.6, 1455.0 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.45–7.32 (m, 5 H), 5.25 (d, J = 5.0 Hz, 1 H), 4.00 (ddd, J = 9.0, 6.4, 5.0 Hz, 1 H), 3.45 (AXq, J = 11.1 Hz, 1 H), 2.98 (AXq, J = 11.1 Hz, 1 H), 1.88 (dd, J = 12.3, 6.4 Hz, 1 H), 1.58 (dd, J = 12.3, 9.0 Hz, 1 H), 1.22 (s, 3 H), 1.13 (s, 3 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 160.9, 139.2, 129.0, 128.9, 125.7, 82.7, 66.7, 59.2, 46.2, 41.7, 28.4, 27.7; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}_2]^+$ required 232.1332 m/z , found 232.1328 m/z .

1-Phenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **8**). Synthesized according to the general procedure using **S6** (0.091 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiating for 18 h. After chromatography on SiO_2 (35% EtOAc in hexanes), **8** was isolated as a pale yellow oil which solidified upon standing (0.058 g, 0.29 mmol, 82%).



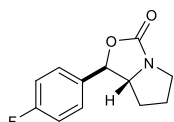
Mp 73–75 °C; **IR** (ATR): ν 2973.0, 1735.8, 1453.8, 1393.8 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.44–7.32 (m, 5 H), 5.25 (d, J = 4.2 Hz, 1 H), 3.81 (ddd, J = 9.2, 6.1, 4.2 Hz, 1 H), 3.70 (dt, J = 11.2, 7.6 Hz, 1 H), 3.20 (ddd, J = 11.3, 8.9, 4.5 Hz, 1 H), 2.23–2.06 (m, 2 H), 2.01–1.86 (m, 1 H), 1.74–1.60 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 161.1, 193.2, 129.0, 128.8, 125.7, 81.8, 67.1, 45.8, 31.1, 25.8; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{12}\text{H}_{14}\text{NO}_2]^+$ required 204.1019 m/z , found 204.1021 m/z .

1-(*p*-Tolyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **9**). Synthesized according to the general procedure using **S7** (0.095 g, 0.34 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (40% EtOAc in hexanes), **9** was isolated as a clear, colorless oil which solidified upon standing (0.053 g, 0.24 mmol, 71%).



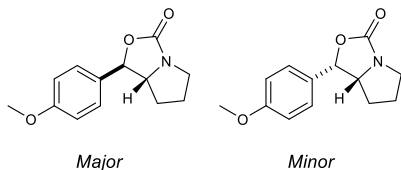
Mp 62–64 °C; **IR** (ATR): ν 2965.1, 2909.8, 2871.9, 1740.9 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.29–7.23 (m, 2 H), 7.23–7.17 (m, 2 H), 5.21 (d, J = 4.2 Hz, 1 H), 3.80 (ddd, J = 9.1, 6.1, 4.2 Hz, 1 H), 3.70 (dt, J = 11.7, 7.4 Hz, 1 H), 3.20 (ddd, J = 11.4, 8.9, 4.5 Hz, 1 H), 2.36 (s, 3 H), 2.21–2.05 (m, 2 H), 2.01–1.85 (m, 1 H), 1.73–1.58 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 161.2, 138.7, 136.3, 129.6, 125.8, 81.9, 67.2, 45.8, 31.1, 25.6, 21.3; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_2]^+$ required 218.1176 m/z , 218.1175 m/z .

1-(4-Fluorophenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **10**). Synthesized according to the general procedure using **S8** (0.098 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (70% Et_2O in hexanes), **10** was isolated as a clear, colorless oil that solidified upon standing (0.059 g, 0.27 mmol, 77%).



Mp 53–55 °C; **IR** (ATR): ν 2969.0, 2908.4, 1743.9, 1508.8 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.39–7.34 (m, 2 H), 7.13–7.06 (m, 2 H), 5.23 (d, J = 4.1 Hz, 1 H), 3.79 (ddd, J = 9.2, 6.1, 4.1 Hz, 1 H), 3.71 (dt, J = 11.2, 7.5 Hz, 1 H), 3.21 (ddd, J = 11.3, 9.0, 4.5 Hz, 1 H), 2.23–2.09 (m, 2 H), 2.02–1.89 (m, 1 H), 1.72–1.62 (m, 1 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 163.0 (d, J = 247.7 Hz), 160.9, 135.1 (d, J = 3.2 Hz), 127.8 (d, J = 8.3 Hz), 116.0 (d, J = 21.8 Hz), 81.3, 67.2, 45.9, 31.1, 25.8; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{12}\text{H}_{13}\text{FNO}_2]^+$ required 222.0925 m/z , found 222.0925 m/z .

1-(4-Methoxyphenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **11**). Synthesized according to the general procedure using **S9** (0.102 g, 0.350 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.123 g, 0.425 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 24 h. After chromatography on SiO_2 (35–70% Et_2O in hexanes), **11major** and **11minor** were isolated as clear, colorless oils that solidified upon standing (0.037 g, 0.16 mmol, 45%, 4:1 major:minor).



Major Diastereomer (11major)

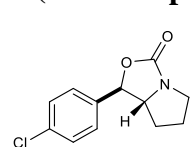
Mp 60–63 °C; **IR** (ATR): ν 2922.1, 2854.1, 1752.6, 1510.1 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.34–7.28 (m, 2 H), 6.95–6.90 (m, 2 H), 5.19 (d, J = 4.2 Hz, 1 H), 3.82 (s, 3 H), 3.84–3.78 (m, 1 H), 3.70 (dt, J = 11.3, 7.4 Hz, 1 H), 3.21 (ddd, J = 11.3, 8.9, 4.5 Hz, 1 H), 2.20–2.06 (m, 2 H),

2.01–1.87 (m, 1 H), 1.71–1.59 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 161.2, 160.1, 131.3, 127.5, 114.4, 82.0, 67.2, 55.5, 45.9, 31.2, 25.9; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_3]^+$ required 234.1125 m/z , found 234.1122 m/z .

Minor Diastereomer (11minor)

Mp 81–82 °C; **IR** (ATR): ν 2968.4, 2924.2, 2849.9, 1743.5, 1514.1 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.25–7.18 (m, 2 H), 6.94–6.89 (m, 2 H), 5.77 (d, $J = 7.8$ Hz, 1 H), 4.11 (ddd, $J = 10.3, 7.8, 5.8$ Hz, 1 H), 3.82 (s, 3 H), 3.71 (dt, $J = 11.4, 8.0$ Hz, 1 H), 1.94 (dtdd, $J = 12.6, 8.5, 3.9, 2.3$ Hz, 1 H), 1.79 (dddt, $J = 13.0, 10.7, 9.4, 7.3$ Hz, 1 H), 1.38 (dddd, $J = 12.8, 7.6, 5.9, 2.4$ Hz, 1 H), 1.13 (dtd, $J = 12.6, 10.6, 8.6$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 161.6, 159.6, 128.0, 126.5, 114.2, 76.8, 64.7, 55.4, 46.5, 26.7, 25.2; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_3]^+$ required 234.1125 m/z , found 234.1123 m/z .

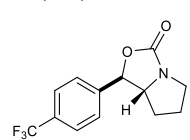
1-(4-Chlorophenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **12**).



Synthesized according to the general procedure using **S10** (0.106 g, 0.358 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.124 g, 0.428 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (30% EtOAc in hexanes), **12** was isolated as an off-white solid (0.074 g, 0.31 mmol, 87%).

Mp 78–80 °C; **IR** (ATR): ν 2970.6, 2898.8, 1744.9, 1486.8 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.41–7.35 (m, 2 H), 7.35–7.28 (m, 2 H), 5.22 (d, $J = 4.1$ Hz, 1 H), 3.76 (ddd, $J = 9.3, 6.1, 4.1$ Hz, 1 H), 3.71 (dt, $J = 11.1, 7.4$ Hz, 1 H), 3.21 (ddd, $J = 11.3, 9.0, 4.5$ Hz, 1 H), 2.23–2.08 (m, 2 H), 2.02–1.89 (m, 1 H), 1.74–1.62 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.9, 137.8, 134.8, 129.3, 127.2, 81.1, 67.2, 45.9, 31.2, 25.9; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{12}\text{H}_{13}\text{ClNO}_2]^+$ required 238.0629 m/z , found 238.0626 m/z .

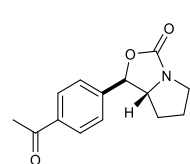
1-(4-(Trifluoromethyl)phenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **13**).



Synthesized according to the general procedure using **S11** (0.117 g, 0.355 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 24 h. After chromatography on SiO_2 (75% Et₂O in hexanes), **13** was isolated as a white powder (0.053 g, 0.20 mmol, 56%).

Mp 117–119 °C; **IR** (ATR): ν 2965.8, 2905.6, 1775.9, 1459.7, 1402.9 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.68 (d, $J = 8.1$ Hz, 2 H), 7.51 (d, $J = 8.0$ Hz, 2 H), 5.32 (d, $J = 4.1$ Hz, 1 H), 3.77 (ddd, $J = 9.3, 6.1, 4.1$ Hz, 1 H), 3.72 (ddd, $J = 11.4, 8.1, 7.1$ Hz, 1 H), 3.21 (ddd, $J = 11.3, 9.0, 4.5$ Hz, 1 H), 2.27–2.11 (m, 2 H), 2.02–1.90 (m, 1 H), 1.78–1.67 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.7, 143.3 (app. d, $J = 1.4$ Hz), 131.1 (q, $J = 32.6$ Hz), 126.1 (q, $J = 3.8$ Hz), 126.0, 124.0 (q, $J = 270.0$ Hz), 80.9, 67.1, 45.9, 31.2, 25.9; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{13}\text{F}_3\text{NO}_2]^+$ required 272.0893 m/z , found 272.0891 m/z .

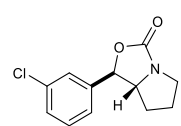
1-(4-Acetylphenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **14**). Synthesized



according to the general procedure using **S12** (0.106 g, 0.350 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (55% EtOAc in hexanes), **14** was isolated as an off-white solid (0.061 g, 0.25 mmol, 72%).

Mp 108–110 °C; **IR** (ATR): ν 2965.0, 2914.8, 1745.0, 1672.1 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 8.00 (d, J = 8.3 Hz, 2 H), 7.48 (d, J = 8.3 Hz, 2 H), 5.33 (d, J = 4.1 Hz, 1 H), 3.78 (ddd, J = 9.8, 6.1, 4.2 Hz, 1 H), 3.71 (dt, J = 11.4, 7.7 Hz, 1 H), 3.21 (ddd, J = 11.2, 9.0, 4.4 Hz, 1 H), 2.62 (s, 3 H), 2.28–2.10 (m, 2 H), 2.04–1.89 (m, 1 H), 1.79–1.65 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 197.6, 160.8, 144.3, 137.4, 129.1, 125.7, 81.0, 67.1, 45.9, 31.2, 26.8, 25.8; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{14}\text{H}_{16}\text{NO}_3]^+$ required 246.1125 m/z , found 246.1120 m/z .

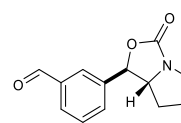
1-(3-Chlorophenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **15**).



Synthesized according to the general procedure using **S13** (0.105 g, 0.355 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.123 g, 0.425 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (70% Et_2O in hexanes), **15** was isolated as a clear, colorless oil that solidified upon standing (0.048 g, 0.20 mmol, 57%).

Mp 49–51 °C; **IR** (ATR): ν 2984.3, 2917.7, 2872.7, 1747.2 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.40–7.36 (m, 1 H), 7.38–7.30 (m, 2 H), 7.29–7.23 (m, 1 H), 5.23 (d, J = 4.1 Hz, 1 H), 3.77 (ddd, J = 9.3, 6.1, 4.1 Hz, 1 H), 3.70 (dt, J = 11.3, 7.6 Hz, 1 H), 3.20 (ddd, J = 11.2, 9.0, 4.4 Hz, 1 H), 2.25–2.08 (m, 2 H), 2.02–1.89 (m, 1 H), 1.74–1.62 (m, 1 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 160.8, 141.3, 135.0, 130.4, 129.0, 125.9, 123.8, 80.8, 67.0, 45.8, 31.1, 25.8; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{12}\text{H}_{13}\text{ClNO}_2]^+$ required 238.0629 m/z , found 238.0626 m/z .

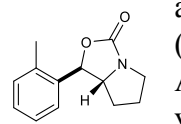
3-(3-Oxotetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-yl)benzaldehyde (Scheme 2, **16**).



Synthesized according to the general procedure using **S14** (0.102 g, 0.349 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (60% EtOAc in hexanes), **16** was isolated as a pale yellow oil (0.040 g, 0.17 mmol, 49%).

IR (ATR): ν 2969.1, 1743.5, 1691.7, 1600.3 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 10.05 (s, 1 H), 7.92–7.85 (m, 2 H), 7.72–7.65 (m, 1 H), 7.64–7.57 (m, 1 H), 5.35 (d, J = 4.1 Hz, 1 H), 3.82 (ddd, J = 9.8, 6.1, 4.1 Hz, 1 H), 3.73 (dt, J = 11.5, 7.7 Hz, 1 H), 3.23 (ddd, J = 11.3, 9.0, 4.4 Hz, 1 H), 2.29–2.10 (m, 2 H), 2.06–1.89 (m, 1 H), 1.80–1.65 (m, 1 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 191.8, 160.8, 140.6, 137.0, 131.6, 130.4, 129.9, 126.6, 80.9, 67.1, 45.9, 31.2, 25.8; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{14}\text{NO}_3]^+$ required 232.0968 m/z , found 232.0964 m/z .

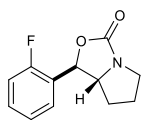
1-(*o*-Tolyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **17**). Synthesized



according to the general procedure using **S15** (0.096 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.421 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (70% Et_2O in hexanes), **17** was isolated as a pale yellow oil which solidified upon standing (0.056 g, 0.26 mmol, 74%).

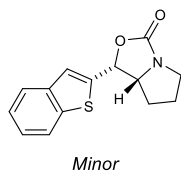
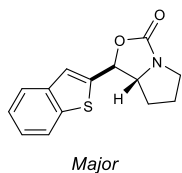
Mp 83–85 °C; **IR** (ATR): ν 2974.9, 2910.3, 2866.4, 1740.7 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.48–7.43 (m, 1 H), 7.29–7.22 (m, 2 H), 7.21–7.16 (m, 1 H), 5.48 (d, J = 3.9 Hz, 1 H), 3.77–3.59 (m, 2 H), 3.18 (ddd, J = 11.2, 9.1, 4.3 Hz, 1 H), 2.32 (s, 3 H), 2.24–2.09 (m, 2 H), 1.99–1.87 (m, 1 H), 1.76–1.67 (m, 1 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 161.3, 137.4, 134.1, 130.8, 128.5, 126.7, 124.7, 79.1, 66.7, 45.7, 31.5, 25.8, 19.2; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_2]^+$ required 218.1176 m/z , found 218.1173 m/z .

1-(2-Fluorophenyl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **18**). Synthesized according to the general procedure using **S16** (0.099 g, 0.35 mmol), Cu(TFA)₂·xH₂O (0.125 g, 0.432 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO₂ (45% Et₂O in hexanes), **18** was isolated as a clear, colorless oil that solidified upon standing (0.042 g, 0.19 mmol, 54%).



Mp 60–62 °C; **IR** (ATR): ν 3073.7, 2965.4, 1749.9, 1487.4 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.52 (td, *J* = 7.6, 1.8 Hz, 1 H), 7.34 (tdd, *J* = 7.5, 5.4, 1.8 Hz, 1 H), 7.24–7.17 (m, 1 H), 7.13–7.05 (m, 1 H), 5.55 (d, *J* = 4.3 Hz, 1 H), 3.83–3.76 (m, 1 H), 3.69 (dt, *J* = 11.3, 7.3 Hz, 1 H), 3.19 (ddd, *J* = 11.3, 9.0, 4.5 Hz, 1 H), 2.25 (dtd, *J* = 13.0, 6.7, 3.1 Hz, 1 H), 2.19–2.09 (m, 1 H), 2.01–1.89 (m, 1 H), 1.73 (dq, *J* = 12.3, 9.2 Hz, 1 H); **¹³C NMR** (125 MHz, CDCl₃): δ 160.8, 159.6 (d, *J* = 246.1 Hz), 130.2 (d, *J* = 8.2 Hz), 126.8 (d, *J* = 12.8 Hz), 126.5 (d, *J* = 3.7 Hz), 124.7 (d, *J* = 3.5 Hz), 115.5 (d, *J* = 20.4 Hz), 76.3 (d, *J* = 3.7 Hz), 66.8 (d, *J* = 1.6 Hz), 45.8, 31.1, 25.9; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₂H₁₃FN₂O₂]⁺ required 222.0925 *m/z*, found 222.0921 *m/z*.

1-(Benzo[*b*]thiophen-2-yl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **19**). Synthesized according to the general procedure using **S17** (0.111 g, 0.350 mmol), Cu(TFA)₂·xH₂O (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO₂ (75% Et₂O in hexanes), **19major** and **19minor** were isolated as clear, colorless oils which solidified upon standing (0.044 g, 0.17 mmol, 48%, 5:1 major:minor).



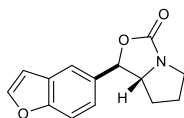
Major Diastereomer (**19major**)

Mp 91–92 °C; **IR** (ATR): ν 2922.1, 1742.8, 757.0 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.86–7.80 (m, 1 H), 7.79–7.72 (m, 1 H), 7.41–7.31 (m, 3 H), 5.55 (d, *J* = 4.1 Hz, 1 H), 4.03 (ddd, *J* = 9.2, 6.1, 4.1 Hz, 1 H), 3.73 (dt, *J* = 11.4, 7.6 Hz, 1 H), 3.24 (ddd, *J* = 11.3, 8.9, 4.6 Hz, 1 H), 2.27–2.08 (m, 2 H), 2.06–1.90 (m, 1 H), 1.75–1.60 (m, 1 H); **¹³C NMR** (100 MHz, CDCl₃): 160.4, 142.1, 139.9, 139.1, 125.2, 124.8, 124.1, 122.7, 122.7, 78.1, 66.9, 46.0, 30.8, 25.8; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₄H₁₄NO₂S]⁺ required 260.0740 *m/z*, found 260.0735 *m/z*.

Minor Diastereomer (**19minor**)

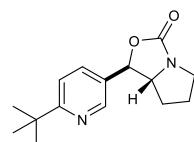
Mp 113–115 °C; **IR** (ATR): ν 2922.1, 2855.3, 1742.2, 1384.3 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 7.7 Hz, 1 H), 7.41–7.29 (m, 3 H), 6.03 (d, *J* = 7.9 Hz, 1 H), 4.19 (ddd, *J* = 10.3, 7.9, 5.8 Hz, 1 H), 3.73 (dt, *J* = 11.5, 8.0 Hz, 1 H), 3.25 (ddd, *J* = 11.4, 9.3, 3.9 Hz, 1 H), 2.07–1.96 (m, 1 H), 1.93–1.79 (m, 1 H), 1.71–1.59 (m, 1 H), 1.48–1.34 (m, 1 H); **¹³C NMR** (100 MHz, CDCl₃): δ 160.6, 139.4, 139.2, 138.9, 124.9, 124.8, 123.9, 122.5, 121.7, 74.7, 64.4, 46.5, 26.8, 25.4; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₄H₁₄NO₂S]⁺ required 260.0740 *m/z*, found 260.0736 *m/z*.

1-(Benzofuran-5-yl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **20**). Synthesized according to the general procedure using **S18** (0.103 g, 0.342 mmol), Cu(TFA)₂·xH₂O (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO₂ (70% Et₂O in hexanes), **20** was isolated as a light green oil (0.057 g, 0.23 mmol, 69%).



IR (ATR): ν 3111.1, 2957.2, 2904.0, 1737.7 cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3): δ 7.66 (d, J = 2.2 Hz, 1 H), 7.64 (d, J = 1.8 Hz, 1 H), 7.53 (dt, J = 8.5, 0.8 Hz, 1 H), 7.31 (dd, J = 8.5, 1.9 Hz, 1 H), 5.35 (d, J = 4.2 Hz, 1 H), 3.86 (ddd, J = 9.1, 6.1, 4.2 Hz, 1 H), 3.73 (dt, J = 11.3, 7.5 Hz, 1 H), 3.23 (ddd, J = 11.3, 8.9, 4.4 Hz, 1 H), 2.24–2.08 (m, 2 H), 2.02–1.88 (m, 1 H), 1.77–1.63 (m, 1 H); **^{13}C NMR** (100 MHz, CDCl_3): δ 161.2, 155.1, 146.1, 134.0, 127.9, 122.2, 118.9, 112.0, 106.8, 82.3, 67.6, 45.9, 31.2, 25.9; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{14}\text{H}_{14}\text{NO}_3]^+$ required 244.0968 m/z , found 244.0965 m/z .

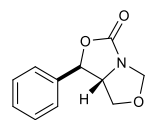
1-(6-(*tert*-Butyl)pyridin-3-yl)tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (Scheme 2, **21**).



Synthesized according to the general procedure using **S20** (0.090 g, 0.28 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.098 g, 0.34 mmol), and TPPT (0.0028 g, 0.0071 mmol) and irradiated for 48 h. After chromatography on SiO_2 (50% EtOAc in hexanes), **21** was isolated as a clear, colorless oil (0.018 g, 0.069 mmol, 24%).

IR (ATR): ν 2959.9, 2870.5, 1749.4 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 8.54 (d, J = 2.4 Hz, 1 H), 7.69 (dd, J = 8.3, 2.5 Hz, 1 H), 7.40 (d, J = 8.3 Hz, 1 H), 5.27 (d, J = 4.2 Hz, 1 H), 3.82 (ddd, J = 10.0, 6.1, 4.3 Hz, 1 H), 3.72 (dt, J = 11.2, 7.5 Hz, 1 H), 3.22 (ddd, J = 11.3, 8.9, 4.5 Hz, 1 H), 2.24–2.10 (m, 2 H), 2.03–1.91 (m, 1 H), 1.70 (dq, J = 12.3, 9.2 Hz, 1 H), 1.37 (s, 9 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 170.5, 160.8, 146.5, 133.8, 131.5, 119.5, 79.7, 66.8, 45.9, 37.6, 31.1, 30.2, 25.9; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2]^+$ required 261.1598 m/z , found 261.1596 m/z .

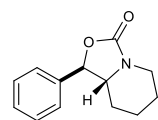
1-Phenyldihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazol-3-one (Scheme 2, **22**). Synthesized



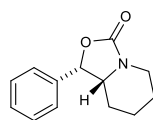
according to the general procedure using **S23** (0.092 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (50% Et_2O in hexanes), **22** was isolated as an off-white solid (0.030 g, 0.15 mmol, 42%).

Mp 94–97 $^\circ\text{C}$; **IR** (ATR): ν 3037.7, 2962.7, 2899.3, 1749.6 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.46–7.38 (m, 5 H), 5.35 (d, J = 5.7 Hz, 1 H), 5.33 (d, J = 3.2 Hz, 1 H), 4.42 (d, J = 5.7 Hz, 1 H), 4.13–4.04 (m, 2 H), 3.80 (dd, J = 8.2, 5.7 Hz, 1 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 161.8, 138.0, 129.4, 129.3, 126.0, 81.4, 80.7, 69.5, 64.5; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{11}\text{H}_{12}\text{NO}_3]^+$ required 206.0812 m/z , found 206.0810 m/z .

1-Phenylhexahydro-3*H*-oxazolo[3,4-*a*]pyridin-3-one (Scheme 2, **23**). Synthesized according to



Major



Minor

the general procedure using **S21** (0.097 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.123 g, 0.425 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (60% Et_2O in hexanes), **23major** and **23minor** were isolated as clear, colorless oils which solidified upon standing (0.057 g, 0.262 mmol,

75%, 2.7:1 d.r.).

Major Diastereomer (23major)

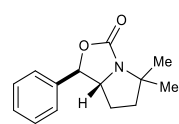
Mp 89–92 $^\circ\text{C}$; **IR** (ATR): ν 2940.4, 2856.4, 1731.1, 1419.5 cm^{-1} ; **^1H NMR** (CDCl_3 , 400 MHz): δ 7.44–7.31 (m, 5 H), 5.00 (d, J = 7.4 Hz, 1 H), 3.92 (dd, J = 13.0, 5.0 Hz, 1 H), 3.41 (ddd, J = 11.1, 7.4, 3.3 Hz, 1 H), 2.82 (td, J = 12.7, 3.4 Hz, 1 H), 2.03–1.88 (m, 2 H), 1.78–1.67 (m, 1 H), 1.56–

1.27 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.6, 138.1, 128.9, 128.9, 125.7, 82.1, 62.5, 41.5, 30.2, 24.3, 22.7; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_2]^+$ required 218.1176 m/z , found 218.1173 m/z .

Minor Diastereomer (23minor)

Mp 88–90 °C; **IR** (ATR): ν 2929.4, 2852.5, 1730.4 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 7.41–7.31 (m, 3 H), 7.30–7.27 (m, 2 H), 5.61 (d, J = 8.2 Hz, 1 H), 4.01–3.90 (m, 1 H), 3.86 (ddd, J = 11.9, 8.2, 3.5 Hz, 1 H), 2.96–2.82 (m, 1 H), 1.84–1.74 (m, 1 H), 1.65–1.58 (m, 1 H), 1.39–1.30 (m, 2 H), 1.16–1.06 (m, 1 H), 0.92–0.75 (m, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 157.2, 135.4, 128.6, 128.4, 125.9, 77.8, 59.1, 42.3, 26.9, 24.2, 23.1; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_2]^+$ required 218.1176 m/z , found 218.1172 m/z .

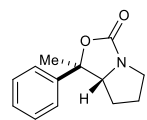
5,5-Dimethyl-1-phenyltetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (Scheme 2, **24**).



Synthesized according to the general procedure using **S25** (0.102 g, 0.352 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.122 g, 0.420 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 48 h. After chromatography on SiO_2 (15% EtOAc in hexanes), **24** was isolated as a yellow oil (0.065 g, 0.28 mmol, 80%).

IR (ATR): ν 2969.7, 2934.9, 2876.0, 1742.4 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 7.43–7.31 (m, 5 H), 5.17 (d, J = 8.5 Hz, 1 H), 4.10 (ddd, J = 9.6, 8.5, 5.3 Hz, 1 H), 2.16–1.94 (m, 3 H), 1.92–1.80 (m, 1 H), 1.55 (s, 3 H), 1.42 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 155.6, 138.2, 128.9, 128.8, 125.7, 83.6, 68.6, 59.6, 44.3, 29.3, 28.3, 25.1; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}_2]^+$ required 232.1332 m/z , found 232.1328 m/z .

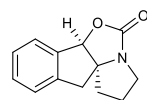
1-Methyl-1-phenyltetrahydro-1H,3H-pyrrolo[1,2-c]oxazol-3-one (Scheme 2, **25**). Synthesized



according to the general procedure using **S28** (0.096 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.121 g, 0.418 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 18 h. After chromatography on SiO_2 (70% Et_2O in hexanes), **25** was isolated as a clear, colorless oil (0.033 g, 0.15 mmol, 43%).

IR (ATR): ν 2980.3, 2915.8, 2858.4, 1736.4, 1249.9 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 7.43–7.36 (m, 4 H), 7.33–7.28 (m, 1 H), 3.92 (dd, J = 10.2, 5.4 Hz, 1 H), 3.67 (dt, J = 11.2, 7.9 Hz, 1 H), 3.15 (ddd, J = 11.2, 9.2, 3.5 Hz, 1 H), 2.20–2.10 (m, 1 H), 2.03–1.86 (m, 2 H), 1.77–1.68 (m, 1 H), 1.67 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 160.5, 145.4, 128.8, 127.9, 124.0, 82.9, 70.5, 45.6, 27.1, 25.9, 24.6; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_2]^+$ required 218.1176 m/z , found 218.1173 m/z .

2,3,6a,11-Tetrahydro-1H,5H-indeno[2,1-d]pyrrolo[1,2-c]oxazol-5-one (Scheme 2, **26**).

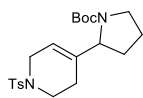


Synthesized according to the general procedure using **S33** (0.096 g, 0.35 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.124 g, 0.428 mmol), and TPPT (0.0035 g, 0.0088 mmol) and irradiated for 72 h. After chromatography on SiO_2 (30% EtOAc in hexanes), **26** was isolated as a light yellow solid (0.045 g, 0.21 mmol, 60%).

Mp 168–170 °C; **IR** (ATR): ν 2958.3, 2925.3, 2832.9, 1734.7, 1359.1 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 7.48 (d, J = 7.5 Hz, 1 H), 7.37–7.34 (m, 1 H), 7.32–7.29 (m, 1 H), 7.24 (d, J = 7.5 Hz, 1 H), 5.68 (s, 1 H), 3.70 (ddd, J = 11.4, 8.4, 6.8 Hz, 1 H), 3.28 (d, J = 16.6 Hz, 1 H), 3.25 (ddd,

$J = 11.3, 8.6, 4.1$ Hz, 1 H), 2.97 (d, $J = 16.6$ Hz, 1 H), 2.25–2.14 (m, 1 H), 2.14–2.03 (m, 2 H), 2.03–1.94 (m, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 160.8, 140.8, 138.9, 130.2, 127.8, 126.1, 125.4, 86.0, 75.6, 45.0, 43.3, 34.8, 25.7; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{14}\text{NO}_2]^+$ required 216.1019 m/z , found 216.1017 m/z .

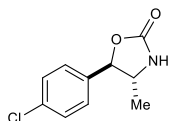
***tert*-Butyl 2-(1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)pyrrolidine-1-carboxylate** (Scheme 2, **27**). Synthesized according to the general procedure using **S40** (0.100 g, 0.245 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.084 g, 0.29 mmol), and TPPT (0.0024 g, 0.0061 mmol) and irradiated for 18 h. After chromatography on SiO_2 (30% EtOAc in hexanes), **27** was isolated as a clear, colorless oil (0.038 g, 0.093 mmol, 38%).



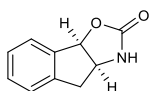
IR (ATR): ν 2970.5, 2924.4, 1686.6, 1598.5, 1391.2, 1158.6 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 353 K): δ 7.65 (d, $J = 8.3$ Hz, 2 H), 7.42 (d, $J = 8.0$ Hz, 2 H), 5.37–5.26 (m, 1 H), 4.04 (dd, $J = 8.2, 4.0$ Hz, 1 H), 3.57–3.53 (m, 2 H), 3.33 (td, $J = 10.6, 7.4$ Hz, 1 H), 3.23 (ddd, $J = 10.6, 7.4, 5.4$ Hz, 1 H), 3.20–3.10 (m, 2 H), 2.40 (s, 3 H), 2.03–1.96 (m, 2 H), 1.91 (dq, $J = 12.3, 8.0$ Hz, 1 H), 1.74–1.64 (m, 2 H), 1.51 (dtd, $J = 12.2, 6.0, 4.2$ Hz, 1 H), 1.32 (s, 9 H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, 353 K): δ 153.0, 142.9, 137.1, 133.6, 129.3, 126.8, 115.1, 77.7, 60.7, 46.1, 43.9, 42.2, 30.2, 27.7, 24.3, 22.4, 20.5; HRMS (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_4\text{S}]^+$ required 407.1999 m/z , found 407.1997 m/z .

C. General procedure for intermolecular oxyamination of styrenes: A solution of alkene (1 equiv), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (1.2 equiv), BocNH_2 (3 equiv), and TPPT (0.025 equiv, 2.5 mol%) in CH_2Cl_2 (0.1 M) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was allowed to stir for the indicated time at rt under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with EtOAc, filtered through a thin pad of SiO_2 (eluting with EtOAc), and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 to afford pure product(s).

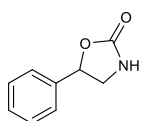
5-(4-Chlorophenyl)-4-methyloxazolidin-2-one (Scheme 2, **28**). Synthesized according to the general procedure using **S41** (0.038 g, 0.25 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.088 g, 0.30 mmol), BocNH_2 (0.089 g, 0.75 mmol), and TPPT (0.0025 g, 0.0063 mmol) and irradiated for 40 h. After chromatography on SiO_2 (60% EtOAc in hexanes), **28** was isolated as an off-white solid (0.027 g, 0.13 mmol, 51%, 7:1 *trans:cis*). All spectral data were in agreement with previously reported values.¹⁸



3,3a,4,8b-Tetrahydro-2H-indeno[2,1-d]oxazol-2-one (Scheme 2, **29**). Synthesized according to the general procedure using indene (0.029 mL, 0.25 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.087 g, 0.30 mmol), BocNH_2 (0.088 g, 0.75 mmol), and TPPT (0.0025 g, 0.0063 mmol) and irradiated for 7 d. After chromatography on SiO_2 (50% EtOAc in hexanes), **29** was isolated as an off-white solid (0.017 g, 0.097 mmol, 39%, >20:1 d.r.). All spectral data were in agreement with previously reported values.¹⁹



5-Phenyloxazolidin-2-one (Scheme 2, **30**). Synthesized according to the general procedure using styrene (0.029 mL, 0.25 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.087 g, 0.30 mmol), BocNH_2 (0.088 g, 0.75 mmol), and TPPT (0.0025 g, 0.0063 mmol) and irradiated for 40 h. After chromatography on SiO_2 (70% EtOAc in hexanes), **30** was isolated as a light



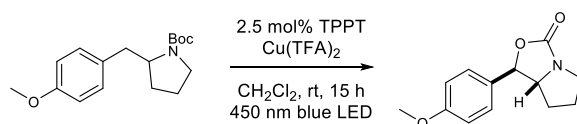
brown solid (0.012 g, 0.074 mmol, 29%). All spectral data were in agreement with previously reported values.²⁰

Methyl 2-oxo-5-phenyloxazolidine-4-carboxylate (Scheme 2, **31**). Synthesized according to the general procedure using methyl *trans*-cinnamate (0.040 g, 0.25 mmol), Cu(TFA)₂·xH₂O (0.089 g, 0.31 mmol), BocNH₂ (0.088 g, 0.75 mmol), and TPPT (0.0025 g, 0.0063 mmol) and irradiated for 72 h. After chromatography on SiO₂ (50% EtOAc in hexanes), **31** was isolated as a yellow oil (0.013 g, 0.059 mmol, 24 %, >20:1 d.r.). All spectral data were in agreement with previously reported values.²¹

V. Mechanistic Experiments

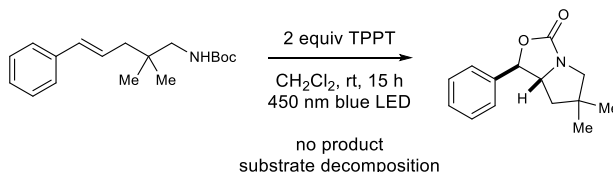
Experiment 1: Generation of benzylic radical intermediate via arene oxidation

tert-Butyl-2-(4-methoxybenzyl)pyrrolidine-1-carboxylate (Scheme 3, **32**). A solution of **S9** (0.105 g, 0.36 mmol), thiophenol (0.035 mL, 0.34 mmol), and Ru(bpz)₃(BAR^F)₂ (0.041 g, 0.018 mmol) in MeNO₂ (1.70 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 18 h under irradiation by a 26 W CFL bulb. The reaction mixture was concentrated under reduced pressure to give crude **32** as a red oil. The oil was purified by chromatography on SiO₂ (20% EtOAc in hexanes) to give **32** (0.048 g, 0.17 mmol, 46%) as a yellow oil. All spectral data were in agreement with previously reported values.²²



A solution of **32** (0.045 g, 0.15 mmol), Cu(TFA)₂·xH₂O (0.053 g, 0.18 mmol), and TPPT (0.0015 g, 0.0039 mmol) in CH₂Cl₂ (1.5 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 15 h under irradiation by a 450 nm blue LED. The reaction mixture was diluted with Et₂O (10 mL), filtered through a thin pad of SiO₂ (Et₂O), and concentrated under reduced pressure to give a yellow oil (0.063 g). ¹H NMR analysis of the unpurified residue using phenanthrene as an internal standard showed a 14% yield of **11** (4:1 d.r.).

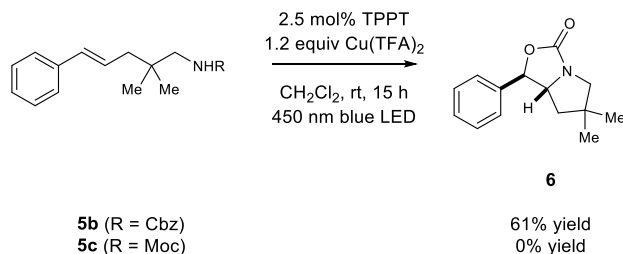
Experiment 2: Stoichiometric TPPT in the absence of Cu(TFA)₂·xH₂O



A solution of **5a** (0.029 g, 0.10 mmol) and TPPT (0.078 g, 0.20 mmol) in CH₂Cl₂ (0.960 mmol) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 15 h under irradiation by a 450 nm blue LED. The reaction mixture was diluted with Et₂O (10 mL), filtered through a thin pad of SiO₂ (Et₂O), and concentrated under reduced pressure to

give a light yellow solid (0.008 g). ^1H NMR analysis of the unpurified residue using phenanthrene as an internal standard showed 0% yield of **6** and 0% remaining starting material.

Experiment 3: Different carbamate protecting groups



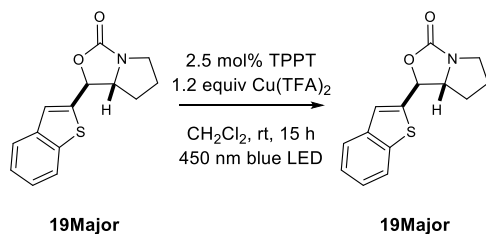
Reaction of **5b** under photocatalytic oxyamination conditions:

A solution of **5b** (0.114 g, 0.352 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.124 g, 0.428 mmol), and TPPT (0.0035 g, 0.0088 mmol) in CH_2Cl_2 (3.5 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 18 h under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with EtOAc, filtered through a thin pad of SiO_2 (eluting with EtOAc), and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (30% EtOAc in hexanes) to give **6** (0.050 g, 0.22 mmol, 61%) as a clear, colorless oil that solidified upon standing.

Reaction of **5c** under photocatalytic oxyamination conditions:

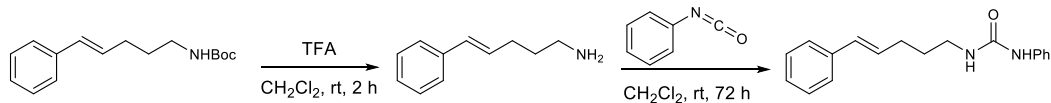
A solution of **5c** (0.024 g, 0.097 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.087 g, 0.30 mmol), and TPPT (0.0010 g, 0.0025 mmol) in CH_2Cl_2 (1 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 15 h under irradiation by a 450 nm blue LED. The reaction mixture was diluted with EtOAc (10 mL), filtered through a thin pad of SiO_2 (EtOAc), and concentrated under reduced pressure to give a pale yellow oil (0.028 g). ^1H NMR analysis of the oil using phenanthrene as an internal standard revealed 0% yield of **6** and 15% remaining starting material.

Experiment 4: Resubjection of oxazolidone product with electron-rich aromatic ring to the reaction conditions



A solution of **19Major** (0.024 g, 0.093 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (0.032 g, 0.11 mmol), and TPPT (0.00093 g, 0.0023 mmol) in CH_2Cl_2 (0.93 mL) was degassed (freeze-pump-thaw, 3 cycles of 5 min each) and the resulting solution was stirred at rt for 15 h under irradiation by a 450 nm blue LED. The reaction mixture was diluted with Et_2O (10 mL), filtered through a thin pad of SiO_2 (Et_2O), and concentrated under reduced pressure to give a clear, colorless oil (0.026 g). ^1H NMR analysis of the oil using phenanthrene as an internal standard revealed no isomerization of **19Major** to **19Minor** and 68% remaining starting material.

VI. Synthesis of Diamination Substrates



General procedure for synthesis of substituted ureas: A solution of *N*-Boc amine (1 equiv), trifluoroacetic acid (TFA, 0.86 M), and CH₂Cl₂ (0.45 M) was stirred at room temperature for 2 h. The reaction mixture was diluted with CH₂Cl₂ (10 mL), and 6 M NaOH was added until a pH of 11 was attained. The resulting solution was washed with NaOH (6 M, 3 x 25 mL) and water (3 x 25 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure to afford the primary amine, which was subsequently converted to the desired urea using a known procedure.²³ A solution of the unpurified primary amine in CH₂Cl₂ (0.9 M) was treated with phenyl isocyanate (1 equiv), and the resulting solution was stirred at room temperature for 72 h. The reaction mixture was diluted with CH₂Cl₂, washed with 1 M HCl (3 x 20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on SiO₂ to give pure urea.

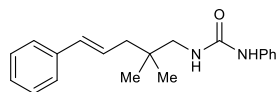
(*E*)-1-Phenyl-3-(5-phenylpent-4-en-1-yl)urea (S42). Synthesized according to the general procedure using **S6** (1.23 g, 4.9 mmol), TFA (5.7 mL), and CH₂Cl₂ (10.9 mL) to afford the corresponding primary amine. The amine was subjected to phenyl isocyanate (0.60 mL) in CH₂Cl₂ (9.8 mL). After chromatography on SiO₂ (60% Et₂O in hexanes), **S42** was isolated as a white solid (0.742 g, 2.65 mmol, 54%).

Mp 90–91 °C; **IR** (ATR): ν 3313.8, 2929.0, 2861.5, 1629.5, 1594.9, 1550.8 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.32–7.25 (m, 9 H), 7.22–7.16 (m, 1 H), 7.07 (tt, *J* = 5.9, 2.6 Hz, 1 H), 6.63 (br. s, 1 H), 6.39–6.34 (m, 1 H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1 H), 5.03 (bs, 1 H), 3.28 (t, *J* = 7.2 Hz, 2 H), 2.23 (t, *J* = 8.4 Hz, 2 H), 1.68 (p, *J* = 7.3 Hz, 2 H). **¹³C NMR** (125 MHz, CDCl₃): δ 155.9, 138.5, 137.5, 130.5, 129.6, 129.3, 128.5, 127.0, 126.0, 124.0, 121.4, 40.0, 30.4, 29.7; **HRMS** (ESI⁺): [M+H]⁺ calculated for [C₁₈H₂₀N₂OH]⁺ required 281.1648 *m/z*, found 281.1647 *m/z*.

(*E*)-1-Phenyl-3-(5-(*p*-tolyl)pent-4-en-1-yl)urea (S43). Synthesized according to the general procedure using **S7** (0.6601 g, 2.23 mmol), TFA (2.54 mL), and CH₂Cl₂ (5.0 mL) to afford the corresponding primary amine. The amine was subjected to phenyl isocyanate (0.24 mL) in CH₂Cl₂ (4.42 mL). After chromatography on SiO₂ (80% Et₂O in hexanes), **S43** was isolated as a white solid (0.360 g, 1.14 mmol, 52%).

Mp 102–104 °C; **IR** (ATR): ν 3315, 3026, 2929, 2861, 1944, 1873, 1796, 1629, 1595, 1558 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.33–7.25 (m, 6 H), 7.23–7.19 (m, 2 H), 7.11–7.07 (m, 3 H), 6.41 (s, 1 H), 6.34 (d, *J* = 15.8 Hz, 1 H), 6.12 (dt, *J* = 15.7, 6.9 Hz, 1 H), 4.87 (bs, 1 H), 3.29 (t, *J* = 7.1 Hz, 2 H), 2.32 (s, 3 H), 2.27–2.20 (m, 2 H), 1.69 (p, *J* = 7.3 Hz, 2 H); **¹³C NMR** (CDCl₃, 126 MHz): δ 155.8, 138.4, 136.7, 134.7, 130.4, 129.3, 129.2, 128.6, 125.8, 124.1, 121.5, 40.0, 30.4, 29.8, 21.1; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₁₉H₂₂N₂O₂Na]⁺ required 317.1624 *m/z*, found 317.1622 *m/z*.

(E)-1-(2,2-Dimethyl-5-phenylpent-4-en-1-yl)-3-phenylurea (S44). A solution of **S1** (2.01 g, 10.6 mmol) in CH₂Cl₂ (11 mL) at 0 °C was treated dropwise via syringe with phenyl isocyanate (1.15 mL, 10.6 mmol) and the resulting solution was stirred at rt for 24 h. The reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with 1 M aq. HCl (50 mL), dried over MgSO₄, and concentrated under reduced pressure to give crude **S44** (1.312 g) as a brown oil. The oil was purified by chromatography on SiO₂ (50% Et₂O in hexanes) to give a white solid which was recrystallized from hexanes layered over CH₂Cl₂ to give **S44** as a white powder (1.325 g, 4.30 mmol, 41%).



Mp 155–156 °C; **IR** (ATR): ν 3362.8, 3316.7, 2958.4, 2913.9, 1646.4, 1598.7, 1544.1 cm⁻¹; **¹H NMR** (CDCl₃, 500 MHz): δ 7.36–7.30 (m, 4 H), 7.30–7.27 (m, 2 H), 7.23–7.18 (m, 1 H), 7.15–7.10 (m, 1 H), 6.34 (d, J = 15.8 Hz, 1 H), 6.29–6.20 (m, 1 H), 6.14 (bs, 1 H), 4.73 (t, J = 6.2 Hz, 1 H), 3.15 (d, J = 6.3 Hz, 2 H), 2.13 (dd, J = 7.5, 1.1 Hz, 2 H), 1.55 (s, 3 H), 0.95 (s, 3 H). **¹³C NMR** (CDCl₃, 125 MHz): δ 155.8, 138.3, 137.4, 132.6, 129.5, 128.5, 127.1, 126.6, 126.1, 124.5, 122.0, 50.0, 43.7, 35.6, 25.1; **HRMS** (ESI⁺): [M+Na]⁺ calculated for [C₂₀H₂₄N₂ONa]⁺ required 309.1961 m/z , found 309.1958 m/z .

VII. Optimization Studies for Diamination

General Procedure for Diamination Optimization Studies: A solution of alkene (1 equiv, 0.89 mmol), oxidant, photocatalyst, and other additives as indicated in solvent was degassed (freeze-pump-thaw, 4 cycles of 5 min each), and the resulting solution was stirred under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with EtOAc, filtered through a thin pad of SiO₂ (eluting with EtOAc), and concentrated under reduced pressure. Yields were determined by ¹H NMR analysis of the unpurified reaction mixtures using phenanthrene as an internal standard.

Table S3. Optimization of Cu(II) source

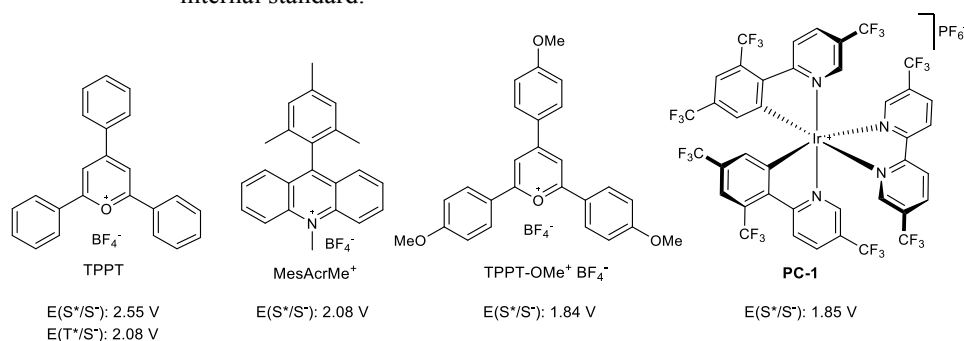
entry	[Cu]	yield A ^a	yield B ^a	RSM ^a
1	Cu(OTf) ₂	15%	0%	31%
2	CuCl ₂	1%	4%	37%
3	CuBr ₂	0%	0%	21%
4	Cu(NO ₃) ₂	trace	trace	trace
5	Cu(TFA) ₂ ·xH ₂ O	0%	10%	0%
6	CuSO ₄	0%	0%	81%
7	Cu(OAc) ₂ ·xH ₂ O	22%	0%	14%
8	Cu(EH) ₂	trace	0%	65%
9	Cu(OBz) ₂	17%	0%	0%
10	Cu(OH) ₂	0%	0%	87%

^aYields were determined by ¹H NMR analysis of the unpurified reaction mixture using phenanthrene as an internal standard.

Table S4. Optimization of photocatalyst

entry	catalyst	% yield ^a	RSM ^a
1	TPPT	22%	15%
2	MesAcrMe ⁺	56%	0%
3	TPPT-OMe ⁺ BF ⁻	23%	20%
4	PC1	11%	0%

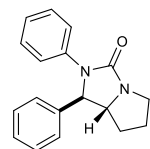
^aYields were determined by ¹H NMR analysis of the unpurified reaction mixture using phenanthrene as an internal standard.



VIII. Photocatalytic Diamination of Styrenes

General procedure for diamination of styrenes: A solution of alkene (1 equiv, 0.350 mmol), Cu(OAc)₂·xH₂O (1.2 equiv by anhydrous molecular mass), and MesAcrMe⁺ (0.001 equiv, 1 mol%) in CH₂Cl₂ (0.1 M) was degassed (freeze-pump-thaw, 4 cycles of 5 min each) and the resulting solution was stirred at rt for 36 h under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with EtOAc, filtered through a thin pad of SiO₂ (eluting with EtOAc), and concentrated under reduced pressure. The residue was purified by chromatography on SiO₂ to afford pure product.

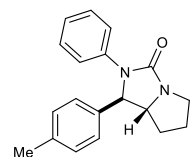
1,2-Diphenylhexahydro-3H-pyrrolo[1,2-c]imidazol-3-one (Scheme 4b, **34**). Synthesized according to the general procedure using **34** (0.098 g, 0.35 mmol), Cu(OAc)₂·xH₂O (0.076 g, 0.42 mmol), and MesAcrMe⁺ (0.0014 g, 0.0035 mmol) and irradiated for 36 h. After chromatography on SiO₂ (gradient from 0% to 10% Et₂O in DCM), **34** was isolated as a white solid (0.051 g, 0.18 mmol, 52%).



Mp 163–165 °C; **IR** (ATR): ν 3061.3, 3029.9, 2961.7, 2914.5, 2896.5, 1686.3, 1597.0, 1498.1 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 7.50–7.44 (m, 2 H), 7.36–7.31 (m, 4 H), 7.28–7.19 (m, 4 H), 6.96 (td, *J* = 7.4, 1.1 Hz, 1 H), 5.06 (d, *J* = 2.4 Hz, 1 H), 3.84 (dt, *J* = 11.5, 7.9 Hz, 1 H), 3.54 (ddd, *J* = 9.6, 5.9, 2.4 Hz, 1 H), 3.15 (ddd, *J* = 11.4, 9.2, 4.2 Hz, 1 H), 2.18 (dddd, *J* = 13.0, 8.0, 6.1, 2.5 Hz, 1 H), 2.03 (dtdd, *J* = 12.8, 8.5, 4.2, 2.5 Hz, 1 H), 1.83 (dddt, *J* = 12.8, 10.2, 9.0, 7.3 Hz, 1 H), 1.66–1.53 (m, 1 H); **¹³C NMR** (125 MHz, CDCl₃): δ 161.5, 140.9, 139.0, 129.1, 128.7, 128.0,

126.1, 123.1, 119.8, 65.5, 63.7, 45.5, 31.3, 24.5; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{18}\text{H}_{18}\text{N}_2\text{OH}]^+$ required 279.1492 m/z , found 279.1490 m/z .

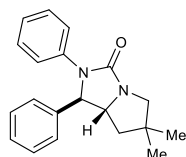
2-Phenyl-1-(*p*-tolyl)hexahydro-3*H*-pyrrolo[1,2-*c*]imidazol-3-one (Scheme 4b, **35**). Synthesized



according to the general procedure using **S42** (0.103 g, 0.350 mmol), $\text{Cu}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ (0.076 g, 0.42 mmol), and MesAcrMe^+ (0.0014 g, 0.0035 mmol) and irradiated for 36 h. After chromatography on SiO_2 (gradient from 0% to 5% Et_2O in CH_2Cl_2), **35** was isolated as a white solid (0.067 g, 0.24 mmol, 66%).

Mp 149–153 °C; **IR** (ATR): ν 3297.8, 3051.2, 3966.1, 2904.0, 1687.5, 1595.1, 1560.2, 1499.5; **^1H NMR** (500 MHz, CDCl_3) δ 7.49–7.44 (m, 2 H), 7.23–7.18 (m, 4 H), 7.12 (d, $J = 7.8$ Hz, 2 H), 6.98–6.93 (m, 1 H), 5.02 (d, $J = 2.3$ Hz, 1 H), 3.83 (dt, $J = 11.5, 7.8$ Hz, 1 H), 3.52 (ddd, $J = 9.6, 5.9, 2.5$ Hz, 1 H), 3.14 (ddd, $J = 11.5, 9.2, 4.2$ Hz, 1 H), 2.29 (s, 3 H), 2.20–2.12 (m, 1 H), 2.07–2.98 (m, 1 H), 1.88–1.77 (m, 1 H), 1.62–1.52 (m, 1 H); **^{13}C NMR** (CDCl_3 , 125 MHz) δ 160.5, 137.9, 136.8, 128.7, 127.6, 125.0, 122.0, 118.9, 64.6, 62.5, 44.4, 30.2, 23.5, 23.5, 20.1; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{OH}]^+$ required 293.1648 m/z , found 293.1646 m/z .

6,6-Dimethyl-1,2-diphenylhexahydro-3*H*-pyrrolo[1,2-*c*]imidazol-3-one (Scheme 4b, **36**).

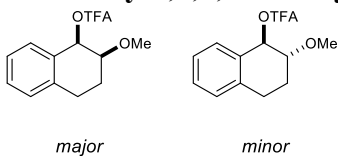


Synthesized according to the general procedure using **S43** (0.108 g, 0.350 mmol), $\text{Cu}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ (0.076 g, 0.42 mmol), and MesAcrMe^+ (0.0014 g, 0.0035 mmol) and irradiated for 36 h. After chromatography on SiO_2 (gradient from 0% to 5% Et_2O in DCM), **36** was isolated as a white solid (0.044 g, 0.15 mmol, 41%).

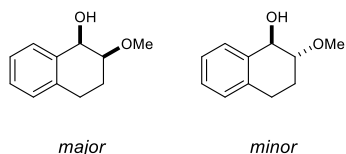
Mp 129–132 °C; **IR** (ATR): ν 3033.8, 2955.6, 2875.4, 2243.1, 1696.9, 1596.7, 1546.0 cm^{-1} ; **^1H NMR** (500 MHz, CDCl_3): δ 7.46–7.42 (m, 2H), 7.32 (d, $J = 6.1$ Hz, 4 H), 7.23 (dtd, $J = 24.2, 7.2, 6.4, 2.0$ Hz, 4 H), 6.96 (td, $J = 7.3, 1.1$ Hz, 1 H), 5.04 (d, $J = 3.0$ Hz, 1 H), 3.76 (ddd, $J = 9.5, 6.1, 3.1$ Hz, 1 H), 3.59 (d, $J = 11.3$ Hz, 1 H), 2.94 (d, $J = 11.3$ Hz, 1 H), 1.96 (dd, $J = 12.1, 6.1$ Hz, 1 H), 1.66–1.55 (m, 2 H), 1.18 (s, 3 H), 1.11 (s, 3 H); **^{13}C NMR** (125 MHz, CDCl_3): δ 160.3, 139.9, 137.9, 128.1, 127.6, 127.0, 125.1, 122.0, 118.9, 76.3, 76.0, 75.7, 63.9, 63.4, 58.3, 45.6, 38.9, 27.6, 26.9; **HRMS** (ESI^+): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{20}\text{H}_{22}\text{N}_2\text{OH}]^+$ required 307.1805 m/z , found 307.1802 m/z .

IX. Photocatalytic Dioxygenation of Styrenes

General procedure for dioxygenation of styrenes: A solution of 1,2-dihydronaphthalene (1 equiv, 0.350 mmol), $\text{Cu}(\text{TFA})_2 \cdot x\text{H}_2\text{O}$ (1.2 equiv by anhydrous molecular mass), alcohol (4 equiv) and TPPT (0.0025 equiv, 2.5 mol%) in CH_2Cl_2 (0.05 M) was degassed (freeze-pump-thaw, 5 cycles of 5 min each) and the resulting solution was stirred at rt for the indicated period of time under irradiation by a 15 W blue LED flood lamp. The reaction mixture was diluted with Et_2O , filtered through a thin pad of SiO_2 (Et_2O), and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 to afford pure products. For ease of purification, the products were hydrolyzed to the corresponding free alcohols and then separated.

2-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl 2,2,2-trifluoroacetate (Scheme 4c, **37**).

Synthesized according to the general procedure using 1,2-dihydronaphthalene (0.091 mL, 0.70 mmol), Cu(TFA)₂·xH₂O (0.244 g, 0.843 mmol), MeOH (0.113 mL, 2.80 mmol), and TPPT (0.0069 g, 0.018 mL) and irradiated for 18 h. After chromatography on SiO₂ (10% EtOAc in hexanes), **37** was isolated as an inseparable mixture of diastereomers (0.099 g, 0.36 mmol, 52%, 1.6:1 *cis:trans*).

2-Methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (S45). A solution of **37** (0.094 g, 0.34 mmol) and

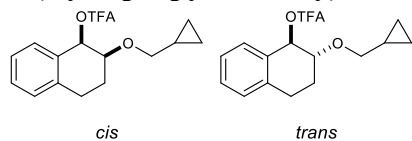
Na₂CO₃ (0.182 g, 1.71 mmol) in MeOH (7.6 mL) and H₂O (4 mL) was stirred at rt for 5 h. The volatile solvent was evaporated under reduced pressure and the resulting solution was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure to give crude **S45** (0.080 g) as an orange oil. The oil was purified by chromatography on SiO₂ (50% Et₂O in hexanes) to give **S45** (0.041 g, 0.23 mmol, 68%, 1.5:1 *cis:trans*) as a mixture of diastereomers. Analytically pure samples of both diastereomers can be obtained by chromatography on SiO₂ (25% Et₂O in hexanes).

Major Diastereomer (S45Major, cis)

IR (ATR): ν 3445.3, 2929.1, 1457.6, 1103.2 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.54–7.45 (m, 1 H), 7.24–7.17 (m, 2 H), 7.15–7.05 (m, 1 H), 4.78 (t, *J* = 4.8 Hz, 1 H), 3.66 (ddd, *J* = 9.0, 3.7, 2.7 Hz, 1 H), 3.49 (s, 3 H), 2.95 (dt, *J* = 17.0, 6.1 Hz, 1 H), 2.74 (ddd, *J* = 16.9, 8.1, 6.1 Hz, 1 H), 2.64 (d, *J* = 5.9 Hz, 1 H), 2.17 (dddd, *J* = 13.6, 9.0, 8.2, 5.7 Hz, 1 H), 1.95–1.84 (m, 1 H); **¹³C NMR** (125 MHz, CDCl₃): δ 136.7, 136.6, 129.8, 128.5, 127.9, 126.4, 78.5, 68.5, 56.5, 26.5, 22.8; **HRMS** (ESI): [M+Na]⁺ calculated for [C₁₁H₁₄O₂Na]⁺ required 201.0886 *m/z*, found 201.0884 *m/z*.

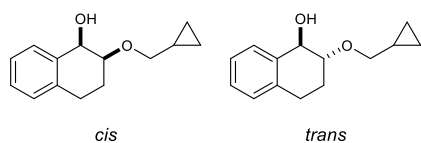
Minor Diastereomer (S45Minor, trans)

IR (ATR): ν 3418.6, 2925.6, 1457.6, 1098.8 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.55 (d, *J* = 7.5 Hz, 1 H), 7.27–7.16 (m, 2 H), 7.09 (d, *J* = 7.2 Hz, 1 H), 4.67 (dd, *J* = 7.5, 3.2 Hz, 1 H), 3.50 (s, 3 H), 3.45 (ddd, *J* = 10.4, 7.4, 3.3 Hz, 1 H), 2.90 (m, 2 H), 2.56 (d, *J* = 3.6 Hz, 1 H), 2.24 (dtd, *J* = 13.5, 5.2, 3.3 Hz, 1 H), 1.75 (dtd, *J* = 13.1, 10.0, 5.9 Hz, 1 H); **¹³C NMR** (125 MHz, CDCl₃): δ 136.8, 135.7, 128.3, 127.7, 127.5, 126.5, 82.1, 72.6, 56.8, 27.3, 24.3; **HRMS** (ESI): [M+Na]⁺ calculated for [C₁₁H₁₄O₂Na]⁺ required 201.0886 *m/z*, found 201.0883 *m/z*.

2-(Cyclopropylmethoxy)-1,2,3,4-tetrahydronaphthalen-1-yl 2,2,2-trifluoroacetate (Scheme

4c, **38**). Synthesized according to the general procedure using 1,2-dihydronaphthalene (0.046 mL, 0.35 mmol), Cu(TFA)₂·xH₂O (0.123 g, 0.425 mmol), cyclopropanemethanol (0.113 mL, 1.40 mmol), and TPPT (0.0035 g, 0.0089 mmol) and irradiated for 18 h. After chromatography on SiO₂ (5-10% EtOAc in hexanes), **38** was isolated as an inseparable mixture of diastereomers (0.047 g, 0.16 mmol, 45%, 1:1 *trans:cis*).

2-(Cyclopropylmethoxy)-1,2,3,4-tetrahydronaphthalen-1-ol (S46).

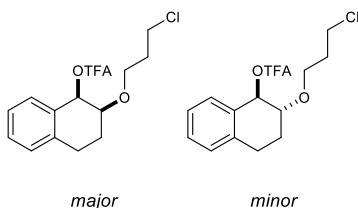


A solution of **38** (0.064 g, 0.20 mmol) and Na₂CO₃ (0.106 g, 1.00 mmol) in MeOH (4.4 mL) and H₂O (2.4 mL) was stirred at rt for 1 h. The volatile solvents were evaporated under reduced pressure and the resulting solution was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure to give crude **S46** (0.050 g) as a milky, pale yellow oil. The oil was purified by chromatography on SiO₂ (30% Et₂O in hexanes) to give **S46** (0.035 g, 0.16 mmol, 80%) as clear, colorless oils. Analytically pure samples of *cis*-**S46** can be obtained by chromatography on SiO₂ (15% Et₂O in hexanes). Unfortunately, an analytically pure sample of *trans*-**S46** could not be obtained.

***cis*-S46**

IR (ATR): ν 3472.8, 3008.0, 2925.1, 2862.4, 1457.7, 1090.2 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.52–7.42 (m, 1 H), 7.25–7.17 (m, 2 H), 7.14–7.06 (m, 1 H), 4.76 (t, *J* = 4.6 Hz, 1 H), 3.78 (ddd, *J* = 9.2, 3.8, 2.8 Hz, 1 H), 3.55–3.35 (m, 2 H), 2.96 (dt, *J* = 16.9, 5.9 Hz, 1 H), 2.80 (d, *J* = 5.4 Hz, 1 H), 2.74 (ddd, *J* = 16.8, 8.0, 5.2 Hz, 1 H), 2.22–2.10 (m, 1 H), 1.87 (dtd, *J* = 12.6, 6.0, 2.7 Hz, 1 H), 1.15–1.04 (m, 1 H), 0.61–0.49 (m, 2 H), 0.29–0.17 (m, 2 H); **¹³C NMR** (125 MHz, CDCl₃): δ 136.8, 136.4, 130.0, 128.5, 127.9, 126.4, 76.7, 73.7, 68.5, 26.9, 23.6, 11.1, 3.4, 3.2; **HRMS** (ESI): [M+H]⁺ calculated for [C₁₄H₁₉O₂]⁺ required 219.1380 *m/z*, found 219.1379 *m/z*.

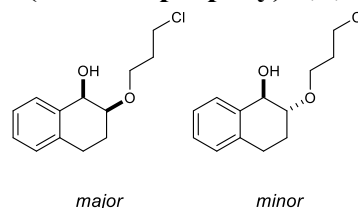
2-(3-Chloropropoxy)-1,2,3,4-tetrahydronaphthalen-1-yl 2,2,2-trifluoroacetate (39).



mmol, 39%, 1.7:1 *cis:trans*).

Synthesized according to the general procedure using 1,2-dihydronaphthalene (0.046 mL, 0.35 mmol), Cu(TFA)₂·xH₂O (0.123 g, 0.425 mmol), 3-chloro-1-propanol (0.117 mL, 1.40 mmol), and TPPT (0.0035 g, 0.0089 mmol) and irradiated for 48 h. After chromatography on SiO₂ (1-3% Et₂O in hexanes), **39** was isolated as an inseparable mixture of diastereomers (0.046 g, 0.14

2-(3-Chloropropoxy)-1,2,3,4-tetrahydronaphthalen-1-ol (S47).



A solution of **39** (0.020 g, 0.059 mmol) and Na₂CO₃ (0.031 g, 0.30 mmol) in MeOH (1.3 mL) and H₂O (0.7 mL) was stirred at rt for 1 h. The volatile solvents were evaporated under reduced pressure and the resulting solution was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure to give crude **S47** as a clear, colorless oil. The oil was purified by chromatography on SiO₂ (40% Et₂O in hexanes) to give **S47major** and **S47minor** (0.013 g total, 0.054 mmol, 92%, 1.5:1 *cis:trans*) as oils.

Major Diastereomer (S47major)

IR (ATR): ν 3452.5, 2927.0, 2876.7, 1452.7, 1106.8 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃): δ 7.52–7.42 (m, 1 H), 7.25–7.19 (m, 2 H), 7.13–7.07 (m, 1 H), 4.77 (t, *J* = 4.7 Hz, 1 H), 3.84–3.70 (m, 3 H), 3.67 (td, *J* = 6.4, 1.8 Hz, 2 H), 2.96 (dt, *J* = 16.9, 6.1 Hz, 1 H), 2.75 (ddd, *J* = 16.9, 8.2, 5.9 Hz, 1 H), 2.61 (d, *J* = 5.8 Hz, 1 H), 2.18 (dtd, *J* = 13.6, 8.5, 5.6 Hz, 1 H), 2.11–2.02 (m, 2 H), 1.89

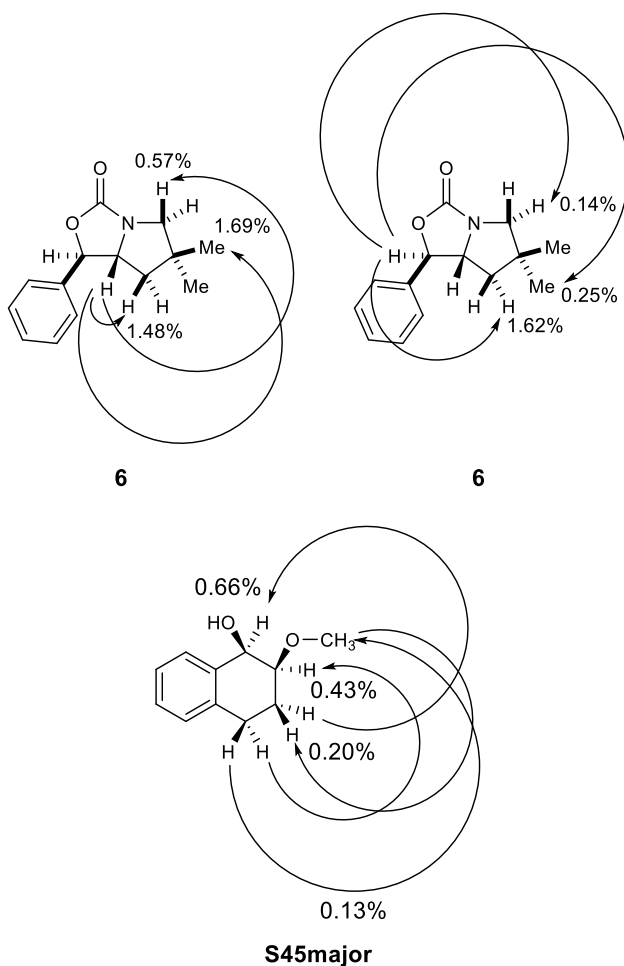
(dtd, $J = 12.9, 6.2, 2.7$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 136.7, 136.4, 129.8, 128.5, 127.9, 126.4, 68.7, 65.1, 52.1, 32.8, 26.6, 23.3; **HRMS** (ESI): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{18}\text{ClO}_2]^+$ required 241.0990 m/z , found 241.0989 m/z .

Minor Diastereomer (S47minor)

IR (ATR): ν 3418.5, 2925.0, 2872.1, 1451.3, 1106.7 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.55 (d, $J = 7.5$ Hz, 1 H), 7.27–7.16 (m, 2 H), 7.09 (d, $J = 7.4$ Hz, 1 H), 4.67 (dd, $J = 7.4, 3.4$ Hz, 1 H), 3.86 (ddd, $J = 9.5, 6.4, 5.4$ Hz, 1 H), 3.72–3.62 (m, 3 H), 3.54 (ddd, $J = 10.4, 7.4, 3.3$ Hz, 1 H), 2.97–2.78 (m, 2 H), 2.53 (d, $J = 3.7$ Hz, 1 H), 2.21 (dtd, $J = 13.6, 5.2, 3.3$ Hz, 1 H), 2.11–2.02 (m, 2 H), 1.78 (dtd, $J = 13.1, 10.0, 6.0$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 136.9, 135.7, 128.3, 127.7, 127.5, 126.5, 80.9, 72.7, 65.4, 42.1, 32.9, 27.4, 25.1; **HRMS** (ESI): $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{18}\text{ClO}_2]^+$ required 241.0990 m/z , found 241.0989 m/z .

X. Assignment of Relative Stereochemistry by 1D NOESY Experiments

Figure S1. Observed NOE enhancements



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