Supporting Information

Visible Light C-H Amidation of Heteroarenes with Benzoyl Azides

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1) General Information

$^1$H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer in CDCl$_3$ or acetone-d$_6$ solution with internal solvent signal as reference. $^{13}$C NMR were recorded on a 75 MHz spectrometer in CDCl$_3$ or acetone-d$_6$ solution and referenced to the internal solvent signal. $^1$H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), and coupling constants (Hz) and number of protons. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F$_{254}$; visualization was accomplished with short wavelength UV light (254 nm) and/or staining with appropriate stains (anisaldehyde, orthophosphomolybdic acid). Standard flash chromatography was performed using silica gel of particle size 40–63 μm. Ru(bipy)$_3$Cl$_2$·$6$H$_2$O was purchased from Sigma Aldrich. All other commercially available reagents and solvents were used without further purification. The blue light irradiation was performed using high-power LEDs (Philips LUXEON® Rebel (1W, $\lambda_{Ex}$ = 455 ± 15 nm, 3.5 V, 145 lm, 700mA)).

2) General Procedures

a) Preparation and characterization of acyl azides

General procedure for the preparation of acylazides.

\begin{equation*}
\text{R-} \overset{\text{H}^+}{\underset{\text{H}^-}{\text{C}l}} \xrightarrow{\text{Na}_2\text{N}_3 \text{Acetone/Water 1/1}} \text{R-} \overset{\text{H}^+}{\underset{\text{H}^-}{\text{O}}} \overset{\text{N}_3}{\underset{\text{N}_3}{\text{O}}}
\end{equation*}

The appropriate benzoyl chloride (5 mmol, 1 equiv) was dissolved in 7 mL of acetone. After cooling the reaction mixture to 0 °C (using an ice bath) sodium azide (5.5 mmol, 1.1 equiv) in 7 mL of water was added dropwise at 0 °C. The resulting mixture was stirred for 2 hours. The resulting mixture was then transferred to a separating funnel and the organic layer was collected, dried over magnesium sulfate and evaporated (note that the temperature of the heating bath should not exceed 30 °C) to give the corresponding acyl azide. **Caution: It is known that these reagents are potential explosives and must be therefore handled with care and stored in a fridge. It is also recommended to prepare acyl azides at a maximum of 10 mmol scale to avoid risks.**

**Compound 1a: Benzoyl azide**

\begin{equation*}
\overset{\text{N}_3}{\underset{\text{N}_3}{\text{O}}}
\end{equation*}

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 8.07 – 7.97 (m, 2H), 7.78 – 7.66 (m, 1H), 7.61 – 7.50 (m, 2H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 172.89, 135.39, 131.54, 130.03, 129.77.
**Compound 1b: 4-Methoxybenzoyl azide**

\[ \text{MeO} \quad \text{N}_3 \]

\(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\) 7.96 (d, \(J = 9.0\) Hz, 2H), 7.05 (d, \(J = 9.0\) Hz, 2H), 3.90 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\) 171.90, 165.77, 132.35, 123.83, 115.00, 56.10.

**Compound 1c: 1-Naphthoyl azide**

\[ \text{MeO} \quad \text{N}_3 \]

\(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\) 8.06 (dd, \(J = 5.1\), 4.4 Hz, 1H), 7.90 (dd, \(J = 7.0\), 2.3 Hz, 1H), 7.75 (d, \(J = 8.0\) Hz, 1H), 7.62 – 7.49 (m, 2H), 7.45 – 7.34 (m, 2H); \(^{13}\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\) 161.34, 136.10, 135.06, 132.22, 129.03, 127.66, 127.57, 126.88, 126.56, 123.17, 123.02.

**Compound 1d: 3,4,5-Trimethoxybenzoyl azide**

\[ \text{MeO} \quad \text{N}_3 \quad \text{MeO} \]

Colorless solid; m.p. = 85-87°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\) 7.27 (s, 2H), 3.89 (s, 6H), 3.82 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\) 172.13, 154.29, 144.75, 126.30, 107.41, 60.76, 56.57.

**Compound 1e: 4-Cyanobenzoyl azide**

\[ \text{N} = \text{C} \quad \text{N}_3 \]

Colorless solid; m.p. = 82-84°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\) 8.17 (d, \(J = 8.7\) Hz, 2H), 7.98 (d, \(J = 8.6\) Hz, 2H); \(^{13}\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\) 171.92, 135.12, 133.66, 130.60, 118.41, 118.20.

**Compound 1f: Methyl 3-(azidocarbonyl)benzoate**

\[ \text{MeO}_2\text{C} \quad \text{N}_3 \]

\(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\) 8.56 (t, \(J = 1.5\) Hz, 1H), 8.33 – 8.26 (m, 1H), 8.26 – 8.18 (m, 1H), 7.71 (t, \(J = 7.8\) Hz, 1H), 3.94 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\) 172.23, 166.16, 135.67, 134.13, 132.02, 131.90, 130.63, 130.36, 52.79.
Compound 1g: 4-Chlorobenzoyl azide

\[
\begin{align*}
\text{CH} & \text{Cl} \\
\text{N} & \text{O} \\
\text{N} & \text{3}
\end{align*}
\]

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 8.00 (d, $J = 8.8$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 172.00, 141.18, 131.71, 130.26, 130.01.

Compound 1h: Thiophene-3-carbonyl azide

\[
\begin{align*}
\text{S} & \text{H} \\
\text{O} & \text{N} \\
\text{N} & \text{3}
\end{align*}
\]

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 8.61 – 7.99 (m, 1H), 7.77 – 7.20 (m, 2H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 167.81, 135.67, 135.23, 128.60, 127.97.

Compound 1i: 2-Phenylacetyl azide

\[
\begin{align*}
\text{S} & \text{H} \\
\text{O} & \text{N} \\
\text{N} & \text{3}
\end{align*}
\]

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 7.35 – 7.24 (m, 1H), 4.38 (d, $J = 6.2$ Hz, 1H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 156.98, 139.59, 129.28, 128.30, 128.05, 45.14.

Compound 1j: Cinnamoyl azide

\[
\begin{align*}
\text{S} & \text{H} \\
\text{O} & \text{N} \\
\text{N} & \text{3}
\end{align*}
\]

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 7.85 – 7.68 (m, 1H), 7.56 – 7.34 (m, 1H), 6.59 (d, $J = 15.9$ Hz, 1H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 172.34, 147.36, 134.83, 132.01, 129.93, 129.61, 119.89.

Compound 1k: 4-Methylbenzenesulfonyl azide

\[
\begin{align*}
\text{S} & \text{H} \\
\text{O} & \text{N} \\
\text{N} & \text{3}
\end{align*}
\]

$^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 7.91 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 2.50 (s, 2H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 147.52, 136.40, 131.39, 128.33, 21.62.
b) General procedure for the reaction of acyl azide with heteroarenes

In a 5 mL snap vial equipped with magnetic stirring bar Ru(bipy)$_3$Cl$_2$.6H$_2$O, (0.025 equiv), benzoyl azide (1 equiv), H$_3$PO$_4$ (2 equiv) and the heteroarene (5 equiv) were dissolved in dry DMSO (0.09 mmol/mL) and the resulting mixture was degassed by “pump-freeze-thaw” cycles (×2) via a syringe needle and filled with nitrogen. The vial was irradiated through the vial’s plane bottom side using blue LEDs. After complete conversion of the starting material (monitored by TLC) the pressure inside the vial was released by a syringe needle and the reaction mixture was transferred into a separating funnel, diluted with ethyl acetate and washed with 15 mL of water. The aqueous layer was washed three times with ethyl acetate. The combined organic layers were dried over MgSO$_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate as eluent. NMR spectra of the compounds were typically recorded in acetone-d$_6$, because of their limited stability in CDCl$_3$.

**Compound 3a: N-(1-Methyl-1H-pyrrol-2-yl)benzamide**

65%, $R_f = 0.30$ (PE:EA, 7:3); viscous oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 7.3$ Hz, 2H), 7.61 – 7.53 (m, 2H), 7.48 (t, $J = 7.4$ Hz, 1H), 6.58 (m, 1H), 6.12 (t, $J = 3.3$ Hz, 1H), 6.05 (m, 1H), 3.52 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.55, 133.75, 132.24, 128.89, 127.43, 124.84, 120.19, 106.78, 104.11, 33.12; HR-MS (ESI): m/z calculated for C$_{12}$H$_{13}$N$_2$O 201.1028 obtained 201,1024.

**Compound 3b: 4-Methoxy-N-(1-methyl-1H-pyrrol-2-yl)benzamide**

71%, $R_f = 0.25$ (PE:EA, 7:3); colorless solid; m.p. = 109-111°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.3$ Hz, 2H), 7.47 (brs, 1H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.57 (m, 1H), 6.11 (t, $J = 3.3$ Hz, 1H), 6.03 (m, 1H), 3.87 (s, 3H), 3.51 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.03, 162.78, 129.36, 125.05, 120.14, 114.06, 106.75, 104.09, 55.61, 33.13; HR-MS (ESI): m/z calculated for C$_{13}$H$_{15}$N$_2$O$_2$ 231,1128 obtained 231,1124.
Compound 3c: N-(1-Methyl-1H-pyrrol-2-yl)-1-naphthamide

47%, R$_f$ = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 150-152°C; $^1$H NMR (300 MHz, Aceton) $\delta$ 9.16 (brs, 1H), 8.47 – 8.40 (m, 1H), 8.09 – 7.96 (m, 2H), 7.89 (d, $J$ = 6.8 Hz, 1H), 7.65 – 7.52 (m, 3H), 6.62 (s, 1H), 6.06 (s, 1H), 6.01 (t, $J$ = 3.3 Hz, 1H), 3.65 (s, 3H); $^{13}$C NMR (75 MHz, acetone) $\delta$ 169.30, 134.69, 131.41, 131.34, 130.72, 129.15, 127.74, 127.19, 127.05, 126.50, 126.47, 125.69, 119.95, 106.73, 103.80, 33.28; HR-MS (ESI): m/z calculated for C$_{16}$H$_{15}$N$_2$O 251.1179 obtained 251.1178.

Compound 3d: 3,4,5-Trimethoxy-N-(1-methyl-1H-pyrrol-2-yl)benzamide

54%, R$_f$ = 0.15 (PE:EA, 7:3); colorless solid; m.p. = 200-202°C; $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 9.89 (s, 1H), 7.32 (s, 2H), 6.74 – 6.57 (m, 1H), 6.00 – 5.94 (m, 1H), 5.87 (dd, $J$ = 3.4, 1.9 Hz, 1H), 3.85 (s, 6H), 3.72 (s, 3H), 3.42 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 165.85, 152.69, 140.36, 128.78, 125.94, 119.44, 105.73, 105.19, 103.24, 60.14, 56.05, 32.62; HR-MS (ESI): m/z calculated for C$_{15}$H$_{19}$N$_2$O$_4$ 291.1339 obtained 291.1340.

Compound 3e: 4-Cyano-N-(1-methyl-1H-pyrrol-2-yl)benzamide

63%, R$_f$ = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 215-217°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.40 (brs, 1H), 8.19 (d, $J$ = 8.4 Hz, 2H), 7.95 (d, $J$ = 8.5 Hz, 2H), 6.72 – 6.47 (m, 1H), 6.14 – 5.75 (m, 2H), 3.54 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 165.98, 164.36, 139.18, 133.28, 129.34, 120.24, 118.78, 115.79, 106.78, 104.02, 33.16; HR-MS (ESI): m/z calculated for C$_{13}$H$_{12}$N$_3$O 226.0981 obtained 226.0975.

Compound 3f: Methyl 3-((1-methyl-1H-pyrrol-2-yl)carbamoyl)benzoate

46%, R$_f$ = 0.22 (PE:EA, 7:3); colorless solid; m.p. = 197-199°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.42 (brs, 1H), 8.63 (s, 1H), 8.27 (m, 1H), 8.22 – 8.13 (m, 1H), 7.67 (t, $J$ = 7.8 Hz, 1H), 6.66 – 6.46 (m, 1H), 5.98 (t, $J$ = 3.3 Hz, 1H), 5.94 (m, 1H), 3.92 (s, 3H), 3.53 (s, 3H); $^{13}$C NMR (75 MHz,
acetone-d$_6$) $\delta$ 166.66, 166.56, 135.64, 133.08, 132.87, 131.45, 129.77, 129.31, 126.72, 120.14, 106.70, 104.04, 52.62, 33.15; HR-MS (ESI): m/z calculated for C$_{14}$H$_{13}$N$_2$O$_3$ 259,1077 obtained 259,1079.

**Compound 3g: 4-Chloro-N-(1-methyl-1H-pyrrol-2-yl)benzamide**

![Structure](image)

61%, $R_f = 0.25$ (PE:EA, 7:3); colorless solid; m.p. = 186-188$^\circ$C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.3$ Hz, 2H), 7.73 (brs, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 6.56 (m, 1H), 6.10 (t, $J = 3.2$ Hz, 1H), 6.02 (m, 1H), 3.47 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.63, 138.51, 132.02, 129.11, 128.92, 124.55, 120.28, 106.82, 104.22, 33.09; HR-MS (ESI): m/z calculated for C$_{12}$H$_{12}$ClN$_2$O 235,0637 obtained 235,0633.

**Compound 3h: N-(1-Methyl-1H-pyrrol-2-yl)thiophene-3-carboxamide**

![Structure](image)

49%, $R_f = 0.23$ (PE:EA, 7:3); colorless solid; m.p. = 157-159$^\circ$C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.04 (s, 1H), 8.32 – 8.15 (m, 1H), 7.64 (m, 1H), 7.56 (dd, $J = 5.0$, 2.9 Hz, 1H), 6.64 – 6.49 (m, 1H), 5.96 (t, $J = 3.3$ Hz, 1H), 5.88 (ddd, $J = 3.6$, 1.9, 0.6 Hz, 1H), 3.49 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 163.00, 138.32, 129.91, 127.90, 127.35, 126.77, 120.05, 106.65, 104.09, 33.09; HR-MS (ESI): m/z calculated for C$_{10}$H$_{11}$N$_2$OS 207,0587 obtained 207,0588.

**Compound 3j: N-(4-Acetyl-1-methyl-1H-pyrrol-2-yl)benzamide**

![Structure](image)

65%, $R_f = 0.25$ (PE:EA, 7:3); colorless solid; m.p. = 124-126$^\circ$C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.85 (s, 1H), 8.08 (dd, $J = 6.9$, 1.6 Hz, 2H), 7.69 – 7.50 (m, 3H), 6.67 (d, $J = 3.3$ Hz, 1H), 6.53 (d, $J = 3.3$ Hz, 1H), 3.62 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 194.11, 167.06, 134.65, 133.09, 132.87, 129.59, 128.58, 120.55, 115.82, 108.75, 34.77, 27.70; HR-MS (ESI): m/z calculated for C$_{14}$H$_{14}$N$_2$O$_2$ 243,1128 obtained 243,1129.
Compound 3k: 4-Methoxy-N-(1-phenyl-1H-pyrrol-2-yl)benzamide

![Structure of Compound 3k](image)

72%, $R_f = 0.25$ (PE:EA, 7:3); colorless solid; m.p. = 183-185°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 8.95 (brs, 1H), 7.86 (d, $J = 8.5$ Hz, 2H), 7.46 – 7.35 (m, 4H), 7.33 – 7.25 (m, 1H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.89 – 6.77 (m, 1H), 6.21 (t, $J = 3.4$ Hz, 1H), 6.17 (d, $J = 1.1$ Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 167.09, 163.37, 137.46, 130.21, 129.96, 127.61, 127.44, 125.69, 120.23, 114.44, 108.56, 107.01, 106.15, 55.82; HR-MS (ESI): m/z calculated for C$_{18}$H$_{17}$N$_2$O$_2$ 293.1285 obtained 293,1284.

Compound 3l: 4-Methoxy-N-(1H-pyrrol-2-yl)benzamide

![Structure of Compound 3l](image)

69%, $R_f = 0.10$ (PE:EA, 7:3); colorless solid; m.p. = 179-181°C; $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 10.75 (brs, 1H), 10.42 (brs, 1H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 8.9$ Hz, 2H), 6.64 – 6.21 (m, 1H), 5.93 (dd, $J = 5.6$, 2.6 Hz, 1H), 5.83 (d, $J = 1.4$ Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 163.44, 161.86, 129.32, 128.13, 126.20, 113.71, 112.63, 106.30, 96.06, 55.45; HR-MS (ESI): m/z calculated for C$_{12}$H$_{13}$N$_2$O$_2$ 217.0972 obtained 217,0975.

Compound 3m: 4-Methoxy-N-(1-(4-methoxybenzoyl)-1H-pyrrol-2-yl)benzamide

![Structure of Compound 3m](image)

64%, $R_f = 0.30$ (PE:EA, 7:3); colorless solid; m.p. = 151-153°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 11.09 (s, 1H), 7.92 (d, $J = 8.9$ Hz, 2H), 7.77 (d, $J = 8.9$ Hz, 2H), 7.04 – 6.92 (m, 5H), 6.68 (dd, $J = 3.6$, 1.7 Hz, 1H), 6.24 (t, $J = 3.6$ Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 171.58, 163.45, 163.12, 162.65, 132.22, 129.11, 126.26, 125.47, 117.48, 114.11, 114.03, 111.98, 111.97, 101.60, 55.72, 55.57; HR-MS (ESI): m/z calculated for C$_{20}$H$_{19}$N$_2$O$_4$ 351,1339 obtained 351,1339.

Compound 3n: 4-Methoxy-N-(5-methylfuran-2-yl)benzamide

![Structure of Compound 3n](image)

49%, $R_f = 0.25$ (PE:EA, 7:3); colorless solid; m.p. = 122-124°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.89 (brs, 1H), 8.03 (d, $J = 8.9$ Hz, 2H), 7.19 – 6.92 (m, $J = 8.9$ Hz, 2H), 6.24 (d, $J = 3.1$ Hz, 1H), 6.00 (d, $J = 2.9$, 1H), 3.88 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 163.61, 163.49, 146.18,
145.31, 130.28, 126.95, 114.50, 107.61, 96.68, 55.83, 13.20; HR-MS (ESI): m/z calculated for C_{13}H_{14}NO_{3} 232.0968 obtained 232.0969.

**Compound 3o:** N-(Benzofuran-2-yl)-4-methoxybenzamide

![Structure of Compound 3o]

15%, R_f = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 145-147°C; \(^1\)H NMR (300 MHz, acetone-\textit{d}_6) \(\delta\) 7.94 (d, \(J = 9.0\) Hz, 2H), 7.59 – 7.52 (m, 1H), 7.36 – 7.27 (m, 1H), 7.05 – 6.94 (m, 3H), 6.89 (d, \(J = 8.2\) Hz, 1H), 6.73 (d, \(J = 6.7\) Hz, 1H), 6.27 (d, \(J = 6.7\) Hz, 1H), 3.86 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\textit{d}_6) \(\delta\) 164.76, 163.87, 163.63, 130.57, 129.00, 128.52, 126.51, 126.06, 124.02, 123.34, 120.88, 114.66, 110.78, 90.47, 55.91; HR-MS (ESI): m/z calculated for C_{16}H_{14}NO_{4} 268,0968 obtained 268,0968.

**Compound 3p:** N-(1-(Dimethylamino)-1H-pyrrol-2-yl)-4-methoxybenzamide

![Structure of Compound 3p]

59% (75mg), R_f = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 117-119°C; \(^1\)H NMR (300 MHz, acetone-\textit{d}_6) \(\delta\) 9.05 (brs, 1H), 7.91 (d, \(J = 8.8\) Hz, 2H), 7.04 (d, \(J = 8.8\) Hz, 2H), 6.90 (dd, \(J = 3.3, 1.9\) Hz, 1H), 6.23 (dd, \(J = 3.8, 1.8\) Hz, 1H), 6.02 (t, \(J = 3.6\) Hz, 1H), 3.87 (s, 3H), 2.82 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\textit{d}_6) \(\delta\) 163.24, 162.95, 129.79, 127.75, 127.43, 114.58, 108.53, 106.54, 94.59, 55.82, 47.72; HR-MS (ESI): m/z calculated for C_{14}H_{18}N_{3}O_{2} 260,1394 obtained 260,1399.

**Compound 3q:** N-(4-Acetyl-1-methyl-1H-pyrrol-2-yl)-4-chlorobenzamide

![Structure of Compound 3q]

46%, R_f = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 163-165°C; \(^1\)H NMR (300 MHz, acetone-\textit{d}_6) \(\delta\) 9.85 (brs, 1H), 8.09 (d, \(J = 8.6\) Hz, 2H), 7.61 (d, \(J = 8.6\) Hz, 2H), 6.68 (d, \(J = 3.3\) Hz, 1H), 6.53 (d, \(J = 3.3\) Hz, 1H), 3.61 (s, 3H), 2.30 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-\textit{d}_6) \(\delta\) 194.04, 166.15, 138.68, 133.38, 132.34, 130.41, 129.72, 120.63, 116.05, 108.82, 34.65, 27.73; HR-MS (ESI): m/z calculated for C_{14}H_{14}ClN_{2}O_{2} 277,0738 obtained 277,0741.
Compound 3r: 4-Chloro-\(N\)-(1-phenyl-1H-pyrrol-2-yl)benzamide

\[
\begin{align*}
\text{Cl} & \quad \text{N} \quad \text{O} \\
\text{C} & \quad \text{H} & \quad \text{N}
\end{align*}
\]

88\%, \(R_f = 0.38\) (PE:EA, 7:3); colorless solid; m.p. = 195-197°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\)
9.22 (s, 1H), 7.88 (d, \(J = 8.5\) Hz, 3H), 7.49 (d, \(J = 8.5\) Hz, 3H), 7.42 (d, \(J = 4.4\) Hz, 6H), 7.31 (dd, \(J = 8.5, 4.3\) Hz, 2H), 6.92 – 6.82 (m, 2H), 6.27 – 6.17 (m, 3H); \(^1\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\)
166.66, 140.09, 138.07, 133.95, 130.16, 130.04, 129.46, 127.75, 126.24, 125.70, 120.50, 108.66, 107.07; HR-MS (ESI): m/z calculated for C\(_{17}\)H\(_{14}\)ClN\(_2\)O 277.0789 obtained 277.0788.

Compound 3s: 4-Chloro-\(N\)-(1-methyl-1H-indol-2-yl)benzamide

\[
\begin{align*}
\text{Cl} & \quad \text{N} \quad \text{O} \\
\text{C} & \quad \text{H} & \quad \text{N}
\end{align*}
\]

59\%, \(R_f = 0.25\) (PE:EA, 7:3); colorless solid; m.p. = 190-192°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\)
9.74 (brs, 1H), 8.09 (d, \(J = 8.5\) Hz, 2H), 7.59 (d, \(J = 8.6\) Hz, 2H), 7.52 (d, \(J = 7.9\) Hz, 2H), 7.37 (d, \(J = 8.2\) Hz, 1H), 7.19 – 7.10 (m, 1H), 7.09 – 6.99 (m, 1H), 6.50 (s, 1H), 3.72 (s, 3H); \(^1\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\)
166.01, 143.07, 138.36, 135.90, 133.74, 130.46, 129.53, 127.92, 121.76, 120.77, 120.30, 110.05, 95.58, 29.53; HR-MS (ESI): m/z calculated for C\(_{16}\)H\(_{14}\)ClN\(_2\)O 287.0764 obtained 287.0764.

Compound 3t: 4-Chloro-\(N\)-(5-methylthiophen-2-yl)benzamide

\[
\begin{align*}
\text{Cl} & \quad \text{N} \quad \text{O} \\
\text{C} & \quad \text{H} & \quad \text{N}
\end{align*}
\]

35\%, \(R_f = 0.29\) (PE:EA, 7:3); colorless solid; m.p. = 167-169°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\)
10.64 (brs, 1H), 8.01 (d, \(J = 8.6\) Hz, 2H), 7.55 (d, \(J = 8.6\) Hz, 2H), 6.67 (d, \(J = 3.7\) Hz, 1H), 6.54 (d, \(J = 3.6\) Hz, 1H), 2.40 (s, 3H); \(^1\)C NMR (75 MHz, acetone-\(d_6\)) \(\delta\)
162.85, 138.45, 138.13, 133.29, 131.78, 130.09, 129.54, 122.56, 112.66, 14.74; HR-MS (ESI): m/z calculated for C\(_{12}\)H\(_{11}\)ClNOS 252.0244 obtained 252.0249.

Compound 3u: 4-Cyano-\(N\)-(1,3-dimethyl-1H-indol-2-yl)benzamide

\[
\begin{align*}
\text{NC} & \quad \text{N} \quad \text{O} \\
\text{C} & \quad \text{H} & \quad \text{N}
\end{align*}
\]

61\%, \(R_f = 0.22\) (PE:EA, 7:3); colorless solid; m.p. = 199-201°C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)) \(\delta\)
9.78 (brs, 1H), 8.28 (d, \(J = 8.5\) Hz, 2H), 7.99 (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 7.9\) Hz, 1H), 7.36 (d, \(J =

S-10
8.2 Hz, 1H), 7.23 – 7.11 (m, 1H), 7.06 (dd, J = 11.0, 4.0 Hz, 1H), 3.66 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) δ 166.16, 138.85, 135.82, 133.39, 130.23, 129.49, 127.92, 122.30, 119.62, 119.29, 118.76, 116.06, 109.98, 104.28, 30.35, 8.51; HR-MS (ESI): m/z calculated for C$_{18}$H$_{16}$N$_3$O 290.1288 obtained 290.1284.

**Compound 3v:** 4-Cyano-N-(5-methylfuran-2-yl)benzamide

![Image of compound 3v](image)

44%, R$_f$ = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 139-141°C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.42 (brs, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 6.33 (d, J = 2.7 Hz, 1H), 5.99 (d, J = 2.1 Hz, 1H), 2.23 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.78, 146.13, 142.85, 137.43, 132.74, 127.98, 117.99, 115.71, 107.42, 97.68, 13.42; HR-MS (ESI): m/z calculated for C$_{12}$H$_{12}$N$_2$O$_2$ 227.0742 obtained 227.0744.

**Compound 3w:** N-(1-Phenyl-1H-pyrrol-2-yl)cinnamamide

![Image of compound 3w](image)

55%, R$_f$ = 0.25 (PE:EA, 7:3); colorless solid; m.p. = 213-215°C; $^1$H NMR (300 MHz, acetone-d$_6$) δ 8.80 (brs, 1H), 7.58 (dd, J = 9.8, 5.8 Hz, 2H), 7.49 – 7.30 (m, 9H), 6.84 – 6.70 (m, 2H), 6.27 (d, J = 1.6 Hz, 1H), 6.20 (t, J = 3.4 Hz, 1H); $^{13}$C NMR (75 MHz, acetone-d$_6$) δ 165.42, 143.01, 141.64, 139.89, 135.93, 130.52, 130.11, 129.74, 128.61, 127.80, 125.87, 121.88, 119.81, 108.64, 105.56; HR-MS (ESI): m/z calculated for C$_{19}$H$_{17}$N$_2$O 289,1335 obtained 289,1336.

**Compound 3x:** 4-Methyl-N-(1-methyl-1H-pyrrol-2-yl)benzenesulfonamide

![Image of compound 3x](image)

52%, R$_f$ = 0.23 (PE:EA, 7:3); colorless solid; m.p. = 157-159°C; $^1$H NMR (300 MHz, acetone-d$_6$) δ 9.04 (s, 1H), 8.32 – 8.15 (m, 1H), 7.64 (m, 1H), 7.56 (dd, J = 5.0, 2.9 Hz, 1H), 6.64 – 6.49 (m, 1H), 5.96 (t, J = 3.3 Hz, 1H), 5.88 (ddd, J = 3.6, 1.9, 0.6 Hz, 1H), 3.49 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) δ 163.00, 138.32, 129.91, 127.90, 127.35, 126.77, 120.05, 106.65, 104.09, 33.09; HR-MS (ESI): m/z calculated for C$_{12}$H$_{15}$N$_2$O$_2$S 251,0849 obtained 251,0850.
Compound 6: 4-Chloro-N-(3-methyl-1-phenyl-1H-indol-2-yl)benzamide

65%, R$_f$ = 0.70 (PE:EA, 7:3); colorless solid; m.p. = 213-215°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.51 (brs, 1H), 7.91 (d, $J$ = 8.5 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.53 – 7.33 (m, 7H), 7.24 – 7.10 (m, 3H), 2.27 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 166.58, 143.84, 138.24, 137.95, 136.08, 133.63, 131.90, 130.22, 130.14, 129.49, 128.47, 128.15, 127.98, 123.20, 120.69, 119.62, 110.67, 108.17, 8.55; HR-MS (ESI): m/z calculated for C$_{22}$H$_{18}$ClN$_2$O 363.1081 obtained 363,1084.

Compound 8: 2-(4-Chlorophenyl)-4-methyl-4-phenyl-4,5-dihydrooxazole

55%, R$_f$ = 0.35 (PE:EA, 7:3); colorless oil, $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 8.08 (d, $J$ = 8.7 Hz, 2H), 7.58 (d, $J$ = 8.8 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.39 (m, 2H), 7.38 – 7.30 (m, 1H), 4.20 (d, $J$ = 14.9 Hz, 1H), 4.11 (d, $J$ = 14.9 Hz, 1H), 1.82 (s, 3H); $^{13}$C NMR (101 MHz, acetone-d$_6$) $\delta$ 162.04, 146.75, 137.71, 130.53, 129.55, 129.41, 128.18, 128.10, 125.11, 87.84, 69.76, 28.48; HR-MS (ESI): m/z calculated for C$_{16}$H$_{15}$ClNO 273,0869 obtained 273,0875.

Compound 9: 2-(4-Methoxyphenyl)-3a,8b-dihydrobenzofuro[2,3-d]oxazole

35%, R$_f$ = 0.7 (PE:EA, 7:3); colorless solid; m.p. = 150-152°C; $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 7.94 (d, $J$ = 9.0 Hz, 2H), 7.63 – 7.48 (m, 1H), 7.39 – 7.25 (m, 1H), 7.06 – 6.94 (m, 3H), 6.89 (d, $J$ = 8.2 Hz, 1H), 6.73 (d, $J$ = 6.7 Hz, 1H), 6.27 (d, $J$ = 6.7 Hz, 1H), 3.86 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 167.50, 163.93, 160.01, 132.48, 131.46, 127.85, 124.89, 121.95, 120.01, 114.77, 111.48, 105.55, 83.63, 55.85; HR-MS (ESI): m/z calculated for C$_{16}$H$_{14}$NO$_3$ 269,1001 obtained 269,1001.
3) Proton and carbon NMR spectra of prepared compounds
Compound 1a: benzoyl azide
Compound 1b: 4-methoxybenzoyl azide
Compound 1c: 1-naphthoyl azide
Compound 1d: 3,4,5-trimethoxybenzoyl azide
Compound 1e: 4-cyanobenzoyl azide
Compound 1f: methyl 3-(azidocarbonyl)benzoate
Compound 1h: thiophene-3-carbonyl azide
Compound 1i: 2-phenylacetyl azide
Compound 1j: cinnamoyl azide
Compound 1k: 4-methylbenzenesulfonyl azide
Compound 3a: N-(1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3b: 4-methoxy-N-(1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3c: N-(1-methyl-1H-pyrrol-2-yl)-1-naphthamide
Compound 3d: 3,4,5-trimethoxy-N-(1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3e: 4-cyano-N-(1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3f: methyl 3-((1-methyl-1H-pyrrol-2-yl)carbamoyl)benzoate
Compound 3g: 4-chloro-N-(1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3h: N-(1-methyl-1H-pyrrolo-2-yl)thiophene-3-carboxamide
Compound 3j: N-(4-acetyl-1-methyl-1H-pyrrol-2-yl)benzamide
Compound 3k: 4-methoxy-N-(1-phenyl-1H-pyrrol-2-yl)benzamide
Compound 3l: 4-methoxy-N-(1H-pyrrol-2-yl)benzamide
Compound 3m: 4-methoxy-N-(1-(4-methoxybenzoyl)-1H-pyrrol-2-yl)benzamide
Compound 3n: 4-methoxy-N-(5-methylfuran-2-yl)benzamide
Compound 3o: N-(benzofuran-2-yl)-4-methoxybenzamide
Compound 3p: N-(1-(dimethylamino)-1H-pyrrol-2-yl)-4-methoxybenzamide
Compound 3q: N-(4-acetyl-1-methyl-1H-pyrrol-2-yl)-4-chlorobenzamide
Compound 3r: 4-chloro-N-(1-phenyl-1H-pyrrol-2-yl)benzamide
Compound 3s: 4-chloro-N-(1-methyl-1H-indol-2-yl)benzamide
Compound 3t: 4-chloro-N-(5-methylthiophen-2-yl)benzamide
Compound 3u: 4-cyano-N-(1,3-dimethyl-1H-indol-2-yl)benzamide
Compound 3v: 4-cyano-N-(5-methylfuran-2-yl)benzamide
Compound 3w: N-(1-phenyl-1H-pyrrol-2-yl)cinnamamide
Compound 3x: 4-methyl-N-(1-methyl-1H-pyrrol-2-yl)benzenesulfonamide
Compound 6: 4-chloro-N-(3-methyl-1-phenyl-1H-indol-2-yl)benzamide
Compound 8: 2-(4-chlorophenyl)-4-methyl-4-phenyl-4,5-dihydrooxazole
Compound 9: 2-(4-methoxyphenyl)-3a,8b-dihydrobenzofuro[2,3-d]oxazole
## Crystallographic data

### Compound 8

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<td>Correction method</td>
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Data completeness = 0.967 θ(max) = 63.480
R(reflections) = 0.0366 (3356) wR2(reflections) = 0.1027 (3758)
S = 1.040 Npar = 367
5) Cyclic voltammetry of compound 1b

Measurements were carried out with an Autolab PGSTAT302N Metrohm

Working electrode: Glassy Carbon
Counter electrode: Platinum wire
Pseudo reference electrode: Silver wire
Supporting electrolyte: Tetrabutylammonium tetrafluoroborate Fluka 0.1 M
Solvent: DMSO

DMSO was degassed with argon prior to the measurements. All experiments were performed under argon atmosphere. Ferrocene was used as an internal reference for the reduction and oxidation potentials.
Reduction and oxidation potentials of compound 1b (DMSO)

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<th>Without Acid</th>
<th>With Acid</th>
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<td>$E_{\text{Ox(DMSO)}} = +0.37$ V vs. Fe$^+/\text{Fe}$</td>
<td>$E_{\text{Ox(DMSO)}} = +0.90$ V vs. Fe$^+/\text{Fe}$</td>
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<tr>
<td>$E_{\text{Red(DMSO)}} = -1.87$ V vs. Fe$^+/\text{Fe}$</td>
<td>$E_{\text{Red(DMSO)}} = -1.87$ V vs. Fe$^+/\text{Fe}$</td>
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</tbody>
</table>
6) Stern-Volmer analysis for \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} + \text{compound 1b} \)

Left figure: Changes in the fluorescence spectra (in this case intensity) of \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) upon successive addition of 4-chlorobenzoyl azide.

Right figure: Changes in the fluorescence spectra (in this case intensity) of \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) upon successive addition of 4-chlorobenzoyl azide in the presence of \( \text{H}_3\text{PO}_4 \) (19.1 mg/mL).

Emission quenching of \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) in the presence of increasing amounts of compound 1g in DMSO at 25 °C. The concentration of \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) was 0.05 mM and the concentration of 1g was increased from 0 to 0.25 mM. Excitation wavelength was 455 nm.

Stern-Volmer plot for \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} + \text{compound 1g} \) in DMSO at 25 °C. The concentration of \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) was 0.05 mM. Excitation wavelength was 455 nm. 19.1 mg/mL \( \text{H}_3\text{PO}_4 \).

Fluorescence emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer. Solutions containing \( \text{Ru(bpy)}_3\text{Cl}_2 \times 6\text{H}_2\text{O} \) with varying concentrations of the quencher were excited at...
455 nm and the emission intensities at ca. 620 nm were determined. DMSO was degassed before measurements. $I_0$ and $I$ represent the intensities of the emission in the absence and presence of the quencher at ca. 620 nm.

The triplet energy of acyl azides is reported to be ~ 41 kcal/mol. The triplet energy of phenyl azide is estimated to be 68 kcal/mol.
7) Time profile of the reaction of 1b with 2a with and without blue light irradiation.

We performed an experiment with “on-off” switching of the light source in the reaction of compound 1b and 2a under standard condition with mesitylene as internal standard. The internal standard was added to the reaction mixture with the substrates. We start with 30 min of irradiation followed by 30 min stirring in the dark. Next, 1 hour of irradiation followed by 1 hour of stirring in the dark. One additional hour of irradiation is needed to complete the reaction in this case. Without light the reaction conversion stops immediately. The conversion of 1b was determined by GC using mesitylene as the internal standard. The results indicate that the reaction is not a radical chain process and the conversion requires the light excitation.

![Conversion of 1b](image-url)
8) GC-MS analysis of crude reaction mixtures

Reaction conditions: Compound 1b, N-methylpyrrole, Ru(bpy)$_3$Cl$_2$ · 6 H$_2$O in DMSO under N$_2$. Blue LED ($\lambda_{Ex} = 455$ nm) irradiation for 1.5 hours.
Reaction conditions: Compound 1b and Ru(bpy)$_3$Cl$_2$·6 H$_2$O were irradiated in DMSO under N$_2$ with a blue LED ($\lambda_{ex} = 455$ nm) for 1.5 hours.
Reaction conditions: Compound 1b, N-methylpyrrole, Ru(bpy)$_3$Cl$_2$. 6 H$_2$O and H$_3$PO$_4$ in DMSO under N$_2$. Irradiation by blue LED ($\lambda_{ex} = 455$ nm) for 1.5 hours.
Reaction conditions: Compound 1b, N-methylpyrrole, Ru(bpy)$_3$Cl$_2$, 6 H$_2$O and H$_3$PO$_4$ in DMSO under N$_2$. Irradiation by blue LED ($\lambda_{Ex} = 455$ nm) for 1.5 hours.
9) References