Visible Light-Promoted Alkylation of Imines Using Potassium Organotrifluoroborates

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**General Information**

Unless otherwise noted, all reagents were purchased from commercial sources and used as received. \(N\)-(Benzyldiene)aniline (2a) was prepared according to the method of Bigelow and Eatough.\(^1\) Solvents were degassed and dried using a PureSolv Solvent Purification System by Innovative Technology. Melting points were measured on an Electrothermal IA9100 digital melting point apparatus and are uncorrected. \(^1\)H NMR spectra were obtained at 300 MHz or 400 MHz; \(^{13}\)C NMR spectra were obtained at 75 MHz or 100 MHz. Chemical shifts are reported in parts per million (δ) using the solvent residual proton or carbon signal (CDCl\(_3\): δH 7.26 ppm, δC 77.3 ppm; d6-DMSO: δH 2.50 ppm, δC 39.5 ppm) as an internal reference. FTIR spectra were recorded on a ThermoScientific Nicolet iS10 or Avatar 370 spectrometer. GC/EI-MS analyses were performed on an Agilent Technologies 7890 GC equipped with 30 m x 0.32 mm Agilent HP-5 column coupled to an Agilent Technologies 5975C MSD. Flash column chromatography was carried out using silica gel (grade 60, 230 – 400 mesh). Feit 16 W PAR 38 blue LED reflector floodlights were purchased from Amazon.com; the emission spectrum was measured with an Ocean Optics Red Tide USB650 spectrophotometer.

**General Procedure for Visible Light-Promoted Alkylation of Imines.**

An appropriate potassium organotrifluoroborate (1, 0.38 mmol), 2a (0.25 mmol), \(\text{Ir-dF(CF}_3\text{-dtb})\) (7.1 mg, 0.0063 mmol, 2.5 mol %), and \(\text{CH}_2\text{Cl}_2\) (5 mL) were added to an oven dried 25 mL Schlenk tube equipped with a Teflon stir bar and rubber septum. The solution was sparged with argon for 15 minutes, and then placed between two Feit 16 W blue LED floodlights (~9 cm away, Figure S1; emission spectrum shown in Figure S2). Unless otherwise indicated, the solution was illuminated with stirring for 46 h; the temperature was maintained at approximately 30 °C by a fan blowing across the reaction vessel. The reaction mixture was quenched with saturated aqueous \(\text{NH}_4\text{Cl}\) (20 mL), and extracted with (3 x 10 mL) of \(\text{CH}_2\text{Cl}_2\). The combined organic layers were dried (\(\text{Na}_2\text{SO}_4\)), evaporated, and purified by flash column chromatography (hexanes/ethyl acetate) to give the product.
Figure S1

Feit 16W Blue LED Floodlight Emission Spectrum

Figure S2
**Compound Data for Amines (3)**

**\(N-(1,2\text{-Diphenylethyl})\text{aniline (3a)}\)**

\[
\text{Ph} \quad \text{Ph} \\
\text{NHPh} \\
\text{Ph} \quad \text{Ph}
\]

Pale yellow oil. Yield: 70%. \(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.38-7.19 (m, 8H), 7.18-7.11 (m, 2H), 7.10-7.02 (m, 2H), 6.68-6.61 (m, 1H), 6.51-6.44 (m, 2H), 4.62-4.56 (m, 1H), 4.12 (br s, 1H), 3.20-2.97 (m, 2H). \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz): \(\delta\) 147.4, 143.5, 137.8, 129.3, 129.1, 128.7, 128.6, 127.1, 126.8, 126.5, 117.6, 113.7, 59.3, 45.3. EI-MS: \(m/z\) 273 (M\(^+\), 1), 183 (32), 182 (100), 180 (20), 104 (30), 91 (17), 77 (49). These data are in agreement with reported literature data.\(^2\)

**\(N-(1\text{-Phenyl-3-buten-1-yl})\text{aniline (3b)}\)**

\[
\text{Ph} \quad \equiv \quad \text{Ph}
\]

Orange oil. Yield: 70%. \(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.49-7.20 (m, 5H), 7.16-7.04 (m, 2H), 6.72-6.61 (m, 1H), 6.56-6.46 (m, 2H), 5.86-5.68 (m, 1H), 5.26-5.12 (m, 2H), 4.45-4.36 (m, 1H), 4.18 (br s, 1H), 2.69-2.42 (m, 2H). \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz): \(\delta\) 147.4, 143.6, 134.7, 129.1, 128.7, 127.1, 126.4, 118.4, 117.4, 113.6, 57.2, 43.4. IR (ATR): 3407 cm\(^{-1}\) (N-H). EI-MS: \(m/z\) 223 (M\(^+\), 2), 183 (18), 182 (100), 104 (23), 77 (39). These data are in agreement with reported literature data.\(^2\)\(^5\)

**\(N-(1\text{-Cyclohexyl-1-phenylmethyl})\text{aniline (3c)}\)**

\[
\text{Ph} \quad \text{NPh} \\
\text{Ph}
\]

Orange oil. Yield: 72%. \(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.31-7.16 (m, 5H), 7.10-7.01 (m, 2H), 6.64-6.56 (m, 1H), 6.52-6.45 (m, 2H), 5.86-5.68 (m, 1H), 4.15 (br s, 1H), 4.11 (d, \(J = 6.3\) Hz, 1H), 4.18 (br s, 1H), 1.94-1.44 (m, 6H), 1.30-0.94 (m, 5H). \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz): \(\delta\) 147.8, 142.7, 129.1, 128.3, 127.3, 126.8, 117.0, 113.2, 63.5, 45.0, 30.3, 29.5, 26.5, 26.4. IR (ATR): 3422 cm\(^{-1}\) (N-H). EI-MS: \(m/z\) 265 (M\(^+\), 3), 183 (18), 182 (100), 104 (15), 91 (13), 77 (25). These data are in agreement with reported literature data.\(^3\)
N-(1-Cyclobutyl-1-phenylmethyl)aniline (3e); N-(2,2-dichloro-1-phenylethyl)aniline (4)

Pale yellow oil. Isolated as an inseparable mixture of compounds 3e and 4. The ratio of 3e:4 was determined by NMR integration of the signals at 2.58 (3e, integration 1 H) and 6.07 (4, integration 0.08 H) and to be 12:1; reported percent yields are calculated based on this ratio.

\[
\text{NMPHP} \quad (3e)
\]

Compound 3e: Yield: 48%. $^1$H-NMR (CDCl$_3$, 400 MHz): δ 7.40-7.46 (m, 4H), 7.20 (t, J = 7.0 Hz, 1H), 7.05 (t, J = 7.6 Hz, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 7.7 Hz, 2H), 4.16 (d, J = 8.8 Hz, 1H), 4.01 (br s, 1H), 2.59-2.46 (m, 1H), 2.19-2.07 (m, 1H), 1.96-1.73 (m, 5H). $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 147.8, 142.6, 129.1, 128.5, 127.0, 126.6, 117.2, 113.4, 63.8, 42.6, 26.2, 25.6, 17.6. IR (ATR): 3410 cm$^{-1}$ (N-H). EI-MS: m/z 237 (M$^+$, 6), 183 (14), 182 (100), 144 (12), 129 (17), 115 (20), 104 (12), 91 (25), 77 (30). HRMS calculated for C$_{17}$H$_{20}$N (M + H): 238.1590, found: 238.1590.

\[
\text{NMPHP} \quad \text{Cl} \quad \text{Cl} \quad (4)
\]

Compound 4: Yield: 4%. EI-MS: m/z 265 (M$^+$, 2), 267 (M+2, 3), 193 (6), 183 (15), 182 (100), 104 (15), 91 (6), 77 (22). HRMS calculated for C$_{14}$H$_{14}$Cl$_2$N (M + H): 266.0498, found: 266.0499.

N-(1,3-Diphenylpropyl)aniline (3f)

Illuminated for 168 h. Yellow oil. Yield: 41%. $^1$H-NMR (CDCl$_3$, 300 MHz): δ 7.37-7.13 (m, 10H), 7.08 (t, J = 7.5 Hz, 2H), 6.64 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 8.5 Hz, 2H), 4.35 (t, J = 6.8 Hz, 1H), 4.12 (br s, 1H), 2.80-2.62 (m, 2H), 2.24-2.04 (m, 2H). $^{13}$C-NMR (CDCl$_3$, 75 MHz): δ 147.2, 143.8, 141.5, 129.2, 128.7, 128.6, 128.5, 127.1, 126.6, 126.1, 117.5, 113.5, 57.9, 40.2, 32.7. IR (ATR): 3409 cm$^{-1}$ (N-H). EI-MS: m/z 287 (M$^+$, 4), 194 (16), 183 (18), 182 (100), 115 (15), 104 (20), 93 (17), 91 (55), 77 (32). These data are in agreement with reported literature data.$^4$
**N-(2,2-Dimethyl-1-phenylpropyl)aniline (3g)**

![Structure of 3g]

Yellow oil. Yield: 60%. $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 7.35-7.17 (m, 5H), 7.06 (t, $J = 7.4$ Hz, 2H), 6.61 (t, $J = 7.4$ Hz, 1H), 6.51 (d, $J = 7.7$ Hz, 2H), 4.28 (br s, 1H), 4.06 (s, 1H), 1.01 (s, 9H). $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 147.5, 141.0, 129.1, 128.6, 127.8, 126.9, 117.3, 113.6, 67.6, 35.0, 27.2. IR (ATR): 3438 cm$^{-1}$ (N-H). EI-MS: m/z 239 (M$^+$, 3), 183 (22), 182 (100), 181 (36), 180 (47), 104 (24), 77 (55). These data are in agreement with reported literature data.$^5$

**N-(2-Phenoxy-1-phenylethyl)aniline (3h)**

![Structure of 3h]

Yellow oil. Yield: 61%. $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 7.45-7.22 (m, 10H), 7.05 (t, $J = 8.0$ Hz, 2H), 6.67 (t, $J = 7.3$ Hz, 2H), 6.52 (d, $J = 7.7$ Hz, 2H), 4.83-4.49 (m, 4H), 3.74 (dd, $J = 10.0$, 4.0 Hz, 1H), 3.59 (t, $J = 9.2$ Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 147.4, 140.6, 137.9, 129.1, 128.8, 128.6, 127.9, 127.8, 127.0, 118.0, 114.3, 74.4, 73.1, 58.5. IR (ATR): 3391 cm$^{-1}$ (N-H). EI-MS: m/z 303 (M$^+$, 5), 183 (37), 182 (100), 180 (13), 104 (34), 91 (45), 77 (50). HRMS calculated for C$_{21}$H$_{22}$NO (M + H): 304.1696, found: 304.1697.
Light-Dark Experiment.

Potassium benzyltrifluoroborate (1a, 54.5 mg, 0.38 mmol), benzalaniline (2a, 45.4 mg, 0.25 mmol), \textit{Ir-dF(CF}_3\textit{)-dtb} (7.1 mg, 0.0063 mmol, 2.5 mol %), and CH$_2$Cl$_2$ (5 mL) were added to an oven dried 25 mL Schlenk tube equipped with a Teflon stir bar and rubber septum. Decane (145 µL) was added as an internal standard. The solution was sparged with argon for 15 minutes, then placed between two 16 W blue LEDs (~9 cm away, Figure S1). The solution was illuminated with stirring for a period of time (usually 10 min), and sampled for GC/MS analysis at the end of the illumination period. The solution was stirred in the dark (kept in a sealed cardboard box, usually 30 min), and sampled for GC/MS analysis at the end of the “dark” stir period. Progress of the reaction was measured by the ratio of GC area of product 3a to GC area of decane (IS). Results are tabulated below.

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<tr>
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References

COMPOUND SPECTRA

2a (300 MHz, CDCl₃)

2a (75 MHz, CDCl₃)
NHPh

3b (300 MHz, CDCl₃)

NHPh

3b (75 MHz, CDCl₃)
3f (300 MHz, CDCl₃)

3f (75 MHz, CDCl₃)
3g (300 MHz, CDCl₃)

3g (75 MHz, CDCl₃)
NHPh
Ph
O
Ph

3h (300 MHz, CDCl₃)

NHPh
Ph
O
Ph

3h (100 MHz, CDCl₃)