SUPPORTING INFORMATION

Bifunctional Copper-Based Photocatalyst for Reductive Pinacol-Type Couplings.

Antoine Caron, Émilie Morin and Shawn K. Collins*

Département de Chimie, Centre for Green Chemistry and Catalysis, Université de Montréal, CP 6128 Station Downtown, Montréal, Québec H3C 3J7 CANADA

SUPPORTING INFORMATION

TABLE OF CONTENTS:

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>GENERAL</td>
<td>S2</td>
</tr>
<tr>
<td>EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA</td>
<td>S3</td>
</tr>
<tr>
<td>REACTION OPTIMIZATION</td>
<td>S15</td>
</tr>
<tr>
<td>ABSORBANCE/EMISSION DATA</td>
<td>S16</td>
</tr>
<tr>
<td>EXCITED STATE LIFETIME DATA</td>
<td>S19</td>
</tr>
<tr>
<td>ELECTROCHEMICAL DATA</td>
<td>S21</td>
</tr>
<tr>
<td>CATALYST STABILITY</td>
<td>S23</td>
</tr>
<tr>
<td>QUENCHING DATA</td>
<td>S26</td>
</tr>
<tr>
<td>NMR DATA FOR ALL NEW COMPOUNDS</td>
<td>S29</td>
</tr>
</tbody>
</table>
GENERAL:

All reactions that were carried out under anhydrous conditions were performed under an inert argon or nitrogen atmosphere in glassware that had previously been dried overnight at 120 °C or had been flame dried and cooled under a stream of argon or nitrogen. All chemical products were obtained from Milipore Sigma Chemical Company, Alfa Aesar or Oakwood Chemical and were reagent quality. Technical solvents were obtained from ACP Chemicals Inc or Fisher Scientific. Anhydrous solvents (CH₂Cl₂, Et₂O, THF, DMF, toluene, and n-hexane) were dried and deoxygenated using a GlassContour system (Irvine, CA). Isolated yields reflect the mass obtained following flash column silica gel chromatography. Organic compounds were purified using the method reported by W. C. Still and using silica gel obtained from Silicycle Chemical division (40-63 nm; 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed on glass-backed silica gel 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F₂₅₄). Visualization of TLC plate was performed by UV (254 nm), KMnO₄ or p-anisaldehyde stains. All mixed solvent eluents are reported as v/v solutions. Concentration refers to removal of volatiles at low pressure on a rotary evaporator. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ¹H NMR. NMR spectra were taken in deuterated CDCl₃ using Bruker AV-300, AV-400 and AV-500 instruments unless otherwise noted. Signals due to the solvent served as the internal standard (CHCl₃: δ 7.27 for ¹H, δ 77.0 for ¹³C). The acquisition parameters are shown on all spectra. The ¹H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list ofcouplings constants (J) corresponds to the order of the multiplicity assignment. High resolution mass spectroscopy (HRMS) was done by the Centre régional de spectrométrie de masse at the Département de Chimie, Université de Montréal from an Agilent LC-MSD TOF system using ESI mode of ionization unless otherwise noted.
EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA

SYNTHESIS OF LIGANDS AND CATALYSTS

3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (S1): A mixture of 2-acetylpyridine (1.12 mL, 10 mmol, 1 eq.) and N,N-dimethylformamide dimethylacetal (3.00 mL, 3.3 M) was refluxed for 18 h, then concentrated in vacuo. The crude mixture was solubilised in a minimum amount of CHCl₃ and addition of pentane produced a yellow precipitate that was filtered to afford a yellow/brown solid (769 mg, 44 %). Spectral data were in accordance with previous reports.¹

2-(1H-pyrazol-3-yl)pyridine (pypz, S2): Hydrazine (65% in H₂O, 0.95 mL, 12.7 mmol, 3 eq.) was added to an ethanol solution (3 M) of 3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (747 mg, 4.24 mmol, 1 eq.). The mixture was stirred at reflux for 30 min. The reaction was then cooled down to room temperature, extracted with water/AcOEt. The organic phases were washed with brine and dried over Na₂SO₄. Flash chromatography (1 % MeOH in CH₂Cl₂) afforded a beige solid (589 mg, 96 %). Spectral data were in accordance with previous reports.¹

3-Oxo-3-(pyridin-2-yl)propanenitrile (S3): To a stirred suspension of NaH (60%, 3.98 g, 99.2 mmol, 1 eq.) in toluene (0.68 M) under an inert atmosphere (N₂), is added dropwise a solution of ethyl picolinate (13.4 mL, 99.2 mmol, 1 eq.) in MeCN (5.2 mL, dried over 4 Å molecular sieves). The mixture was left to stir at 65 °C over 48 h. The reaction was cooled down to room temperature and then slowly quenched with water. Et₂O is added and the phases separated. The organic phases were washed with water. The aqueous phases were slowly acidified until precipitation occurred. The solid was filtered and washed with water to afford a pink/brown solid (4.82 g, 33 %). Spectral data were in accordance with previous reports.²

3-(Pyridin-2-yl)-1H-pyrazol-5-amine (pypza, S4): Hydrazine (65% in H₂O, 7.38 mL, 99 mmol, 3 eq.) was added to an ethanol solution (0.3 M) of 3-oxo-3-(pyridin-2-yl)propanenitrile (4.82 g, 33 mmol, 1 eq.). The mixture was stirred at reflux for 24 h. The reaction was then cooled down to room temperature, extracted with water/AcOEt. The organic phases were washed with brine and dried over Na₂SO₄. Flash chromatography (2 % MeOH in CH₂Cl₂) afforded a beige solid (3.57 g, 68 %). Spectral data were in accordance with previous reports.²

4-Fluoro-N-(3-(pyridin-2-yl)-1H-pyrazol-5-yl)benzenesulfonamide (pypzs, S5): 3-(Pyridin-2-yl)-1H-pyrazol-5-amine (329 mg, 206 mmol, 1 eq.) was dissolved in anhydrous THF (0.2 M) under a nitrogen atmosphere. Then, 4-fluorophenyl sulfonyl chloride (399 mg, 2.06 mmol, 1 eq.) was added in one portion followed by pyridine (332μL, 4.12 mmol, 2 eq.). After stirring for 2h, the reaction mixture was filtered and washed with AcOEt. The resulting filtrate was reduced under vacuum and the crude material purified by flash chromatography (2 % MeOH in CH₂Cl₂) to yield afford a white solid (250 mg, 38 %).¹

¹H NMR (400 MHz, Acetone-d6): δ = 12.18 (br s, 1H), 9.29 (br s, 1H), 8.58-8.57 (d, J = 4 Hz, 1H), 7.97-7.93 (m, 2H), 7.87-7.84 (m, 2H); 7.34-7.28 (m, 3H); 6.76 (s 1H); ¹³C NMR (75 MHz, Acetone-d6) δ = 205.3, 149.5, 137.1, 136.8, 3, 130.2, 130.0, 123.1, 119.9, 116.1, 115.8, 95.9, 61.6; HRMS (ESI⁺): calcd. for C₁₄H₁₂N₄FNa (M+Na)⁺ 341.0479; found 341.0491.

Cu(pypz)(BINAP)BF₄ (3): To a stirred solution of [Cu(MeCN)₄](BF₄) (50 mg, 0.159 mmol, 1.0 eq.) in anhydrous THF (0.005 M) was added BINAP (104 mg, 0.167 mmol, 1.05 eq.). The reaction was stirred at room temperature for one hour. Then, to the reaction mixture was added the pypz (24 mg, 0.167 mmol, 1.05 eq.). The reaction mixture was stirred for an additional hour. The reaction mixture was evaporated under vacuum to approximately a tenth of the original volume and Et₂O was added to precipitate the product. Filtration afforded the desired complex as yellow solid (138 mg, 95 %).¹H NMR (400 MHz, CDCl₃, 5 °C): δ = 12.84 (br s, 1H), 8.10 (d, J = 4.9 Hz, 1H), 8.01 (d, J = 1.9 Hz, 1H), 7.95 (ddd, J = 7.9, 1.0 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.80-7.70 (m, 1H), 7.63-7.54 (m, 2H), 7.54-7.41 (m, 4H), 7.41-7.28 (m, 9H), 7.26-7.18 (m, 2H) 7.18-
7.01 (m, 4H), 6.98-6.76 (m, 6H), 6.75-6.69 (m, 5H); Note that the $^{13}$C NMR spectra for the catalysts are complex, with multiple overlapping signals. Possible explanations include the coupling of various carbon signals with phosphorus, or the formation of mixtures of diastereomeric-at-copper complexes. Where possible, all the signals observed have been reported below. $^{13}$C NMR (100 MHz, CDCl$_3$, 5 °C) δ = 149.8, 149.5, 148.6, 139.25, 139.23, 139.10, 139.07, 138.4, 138.34, 138.29, 138.2, 134.4, 134.3, 133.9, 133.8, 133.7, 133.4, 133.2, 133.1, 132.7, 130.4, 130.2, 129.3, 129.2, 128.9, 128.1, 127.8, 127.50, 127.46, 127.4, 126.5, 126.4, 126.3, 126.1, 124.0, 121.4, 102.7; HRMS (ESI$^+$): calcd. for C$_{52}$H$_{39}$Cu$_3$N$_3$P$_2^{2+}$ (M$^+$) 830.1915; found 830.1917.

Cu(pypza)(BINAP)BF$_4$ (4): To a stirred solution of [Cu(MeCN)$_4$](BF$_4$) (50 mg, 0.159 mmol, 1.0 eq.) in anhydrous THF (0.005 M) was added BINAP (104 mg, 0.167 mmol, 1.05 eq.). The reaction was stirred at room temperature for one hour. Then, to the reaction mixture was added the pypza (27 mg, 0.167 mmol, 1.05 eq.). The reaction mixture was stirred for an additional hour. The reaction mixture was evaporated under vacuum to approximately a tenth of the original volume and Et$_2$O was added to precipitate the product. Filtration afforded the desired complex as yellow solid (140 mg, 93 %). Peaks of residual THF and Et$_2$O are visible in both NMR spectra $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 5 °C): δ = 11.63 (br s, 1H), 8.15-8.05 (m, 1H), 7.97-7.87 (m, 1H), 7.84-7.71 (m, 2H), 7.69-7.61 (m, 1H), 7.61-7.53 (m, 2H), 7.53-7.40 (m, 5H), 7.40-7.23 (m, 9H), 7.22-7.09 (m, 4H), 7.09-7.01 (m, 1H), 6.98-6.86 (m, 3H), 6.85-6.75 (m, 2H), 6.73-6.63 (m, 3H), 6.63-6.47 (m, 2H), 6.12-6.04 (m, 1H), 4.76 (br s, 2H); Note that the $^{13}$C NMR spectra for the catalysts are complex, with multiple overlapping signals. Possible explanations include the coupling of various carbon signals with phosphorus, or the formation of mixtures of diastereomeric-at-copper complexes. Where possible, all the signals observed have been reported below. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 5 °C) δ = 150.9, 150.3, 149.6, 149.4, 139.5, 139.4, 138.24, 138.15, 138.1, 138.64, 134.62, 134.5, 134.4, 134.2, 134.1, 133.6, 133.5, 133.4, 133.2, 132.9, 130.4, 130.3, 129.3, 129.22, 129.17, 129.1, 128.9, 128.8, 128.2, 127.8, 127.6, 127.5, 126.7, 126.4, 126.33, 126.27, 123.9, 121.4, 85.5; HRMS (ESI$^+$): calcd. for C$_{52}$H$_{40}$Cu$_4$N$_4$P$_2^{2+}$ (M$^+$) 845.2097; found 845.2022.

Cu(pypzs)(BINAP)BF$_4$ (5): To a stirred solution of [Cu(MeCN)$_4$](BF$_4$) (246 mg, 0.782 mmol, 1.0 eq.) in anhydrous CH$_2$Cl$_2$ (0.005 M) was added BINAP (482 mg, 0.782 mmol,
The reaction was stirred at room temperature for one hour. Then, to the reaction mixture was added the pypzs (246 mg, 0.782 mmol, 1 eq.). The reaction mixture was stirred for an additional hour. The reaction mixture was evaporated under vacuum to approximately a tenth of the original volume and Et₂O was added to precipitate the product. Filtration afforded the desired complex as yellow solid (683 mg, 80 %). 

\[ \text{H NMR (400 MHz, CDCl}_3\text{:} \delta = 12.28 (s, 1H), 9.03 (s, 1H), 8.16-8.15 (d, J = 6Hz, 1H), 7.98-7.93 (m, 4H), 7.72-6.59 (m 37H): Note that the }^{13}\text{C NMR spectra for the catalysts are complex, with multiple overlapping signals. Possible explanations include the coupling of various carbon signals with phosphorus, or the formation of mixtures of diastereomeric-at-copper complexes. Where possible, all the signals observed have been reported below. }^{13}\text{C NMR (100 MHz, THF:CDCl}_3\text{9:1, 5 °C)} \delta = 165.90, 163.36, 148.97, 140.26, 138.81, 138.23, 137.51, 134.70, 133.98, 133.57, 133.43, 132.87, 132.72, 132.57, 134.45, 132.33, 130.74, 129.72, 129.63, 129.38, 128.59, 128.46, 128.38, 128.19, 128.09, 127.44, 127.17, 126.89, 126.58, 125.89, 125.69, 125.62, 125.50, 124.37, 123.84, 121.74, 115.67, 115.45, 94.97; HRMS (ESI\text{+}): \text{calcd. for } C_{58}H_{43}CuFN_4O_2P_2S (M) \text{+ 1003.1857; found 1003.1887.}

**GENERAL PROCEDURE FOR PCET REACTIONS**

To an oven dried screw cap vial was added Cu(ppyzs)(BINAP)BF₄ (2 mol %) and Hantzsch ester (HEH, 2 eq.). Anhydrous, degassed THF was added (0.05 M) followed by the substrate. The reaction vessel was sealed with a cap having a septum and further degassed for 5 minutes. The vial was placed into the center of a blue LED reactor and irradiated overnight. The LED reactor was an aluminum cylinder in which the interior was lined with a light-emitting diode (LED) strip connected to a power source. LED strips were purchased from Creative Lightings (https://www.creativelightings.com/). Note that no temperature regulation of the reactions was necessary. Following the reaction time, silica gel was added and vigorously stirred. The solvent was then evaporated under vacuum and the resulting dry crude reaction mixture was purified via flash chromatography to afford the desired product.

**Ketones :**

**2,3-Diphenylbutane-2,3-diol (1):** Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 85:15) to afford the product as a
white solid (90 %). Spectral data for the product was in accordance with what was previously reported.\textsuperscript{3}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image1.png}
\caption{Structure of 2,3-Di(1,1'-biphenyl)-4-yl)butane-2,3-diol (6).}
\end{figure}

**2,3-Di(1,1'-biphenyl)-4-yl)butane-2,3-diol (6):** Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 85:15) to afford the product as a white solid (90 %). Spectral data for the product was in accordance with what was previously reported.\textsuperscript{4}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image2.png}
\caption{Structure of 2,3-Bis(3-bromophenyl)butane-2,3-diol (7).}
\end{figure}

**2,3-Bis(3-bromophenyl)butane-2,3-diol (7):** Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 85:15) to afford the product as a white solid (96 %).\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) (peaks are reported for the mixture of both the \textit{meso} and \textit{dl} isomers): $\delta = 7.46$-7.38 (m, 7H), 7.22-7.04 (m, 8H), 2.53 (br s, 2H), 2.17 (br s, 2H), 1.54 (s, 6H), 1.49 (s, 6H); \textsuperscript{13}C NMR (300 MHz, CDCl\textsubscript{3}) $\delta =$146.0, 145.4, 130.6, 130.3, 130.3, 130.1, 128.8, 128.7, 126.0, 125.6, 121.8, 121.7, 78.5, 78.2, 25.1, 24.8; HRMS (ESI\textsuperscript{+}): calcd. for C\textsubscript{16}H\textsubscript{16}Br\textsubscript{2}O\textsubscript{2}Na (M+Na)$^+$ 420.9409; found 420.9390.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image3.png}
\caption{Structure of 2,3-Bis(4-bromophenyl)butane-2,3-diol (8).}
\end{figure}

**2,3-Bis(4-bromophenyl)butane-2,3-diol (8):** Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the

\textsuperscript{3} Guo, H.; Zhang, Y. \textit{J. Chem. Research} 2000, 284–286
product as a white solid (90 %). Spectral data for the product was in accordance with what was previously reported.²

2,3-Bis(3-bromo-4-fluorophenyl)butane-2,3-diol (9): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (74 %).¹ H NMR (400 MHz, CDCl₃) (peaks are reported for the mixture of both the meso and dl isomers): δ = 7.52-7.50 (d, J = 6.4 Hz, 2H), 7.40-7.39 (d, J = 6.4 Hz, 2H), 7.20-7.16 (m, 2H), 7.02-6.98 (m, 6H), 1.52 (s, 6H), 1.49 (s, 6H); ¹³C NMR (300 MHz, CDCl₃) δ = 159.9, 159.8, 156.6, 156.5, 141.1, 140.6, 140.5, 132.4, 128.0, 127.9, 127.8, 127.7, 115.3, 115.2, 115.0, 114.9, 108.2, 108.1, 107.9, 107.8, 78.2, 77.9, 25.2, 24.8; HRMS (ESI⁺): calcd. for C₁₆H₁₄Br₂F₂O₂Na (M+Na)⁺ 456.9221; found 456.9201.

2,3-Bis(2-chlorophenyl)butane-2,3-diol (10): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (99 %).¹ H NMR (400 MHz, CDCl₃) (peaks are reported for the mixture of both the meso and dl isomers): δ = 7.51-7.49 (m, 2H), 7.24-7.07 (m, 14H), 3.99 (s, 2H) 3.80 (s, 2H) 1.84 (s, 6H), 1.81 (s, 6H); ¹³C NMR (300 MHz, CDCl₃) δ = 139.8, 139.8, 133.0, 132.6, 131.8, 131.8, 131.3, 128.8, 128.7 126.3, 126.0, 82.5, 82.0, 26.0, 25.6; HRMS (ESI⁺): calcd. for C₁₄H₁₆Cl₂O₂Na⁺ (M+Na)⁺ 333.0405; found 333.0420.

2,3-Bis(4-(pyridin-3-yl)phenyl)butane-2,3-diol (11): Following the general procedure described above, the product was isolated by chromatography (DCM/MeOH 95:5) to afford the product as a white solid (58 %).¹ H NMR (400 MHz, CDCl₃) (peaks are reported
for the mixture of both the meso and dl isomers): \( \delta = 8.867-8.862 \) (d, \( J = 2 \text{ Hz}, \) 2H) 8.60-8.59 (m, 2H) 7.92-7.89 (m, 2H) 7.52-7.50 (m, 4H) 7.39-7.36 (m, 6H), 1.60 (s, 6H); \(^{13}\text{C}\) NMR (300 MHz, DMSO-D6) \( \delta = 207.1, 206.7, 176.7, 148.6, 147.9, 146.8, 135.9, 134.7, 134.1, 128.6, 125.0, 77.7, 60.2; \) HRMS (ESI\(^{+}\)): calcd. for C\(_{26}\)H\(_{25}\)N\(_{2}\)O\(_{2}\) (M+H\(^{+}\))\(^{+}\) 397.1911; found 397.1914.

Dimethyl -4'-(2,3-dihydroxybutane-2,3 diyl)dibenzoate (12): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (46 %). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) (peaks are reported for the mixture of both the meso and dl isomers): \( \delta = 7.93-7.89 \) (m, 4H), 7.62-7.24 (m, 4H), 3.94 (s, 6H), 2.60 (brs, 2H), 1.55 (s, 6H); \(^{13}\text{C}\) NMR (300 MHz, CDCl\(_3\)) \( \delta = 148.3, 129.0, 128.5, 127.5, 127.1, 78.8, 52.1, 24.8; \) HRMS (ESI\(^{+}\)): calcd. for C\(_{20}\)H\(_{26}\)NO\(_6\) (M+NH\(_4\))\(^{+}\) 376.1755; found 376.1761

2,3-Bis(4-(methylthio)phenyl)butane-2,3-diol (13): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10 : 90) to afford the product as a white solid (62 %). Spectral data for the product was in accordance with what was previously reported.\(^5\)

2,3-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butane-2,3-diol (14): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (75%). $^1$H NMR (400 MHz, CDCl$_3$) (peaks are reported for the mixture of both the *meso* and *dl* isomers): $\delta = 7.71-7.67$ (m, 8H), 7.31-7.29 (d, $J = 8.4$ Hz, 4H), 7.20-7.18 (d, $J = 8.2$ Hz, 4H, 1.55 (s, 6H), 1.49 (s, 6H), 1.36 (s, 48H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta = 146.9, 146.4, 133.9, 133.6, 126.8, 126.3, 83.8, 78.9, 78.7, 77.2, 25.2, 24.9, 24.9; HRMS (ESI$^+$): calcd. for C$_{28}$H$_{44}$B$_2$N$_4$O$_6$ (M+NH$_4^+$) 512.3349; found 512.3342.

1,1,2,2-Tetra-p-tolylethane-1,2-diol (15): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (58 %). Spectral data for the product was in accordance with what was previously reported.$^6$

1,2-Di(thiophen-2-yl)-1,2-di-p-tolylethane-1,2-diol (16): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (62%). Spectral data for the product was in accordance with what was previously reported.$^7$

Aldehydes:


1,2-Diphenylethane-1,2-diol (17): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (99 %). Spectral data for the product was in accordance with what was previously reported.\(^3\)

1,2-Bis(2-chlorophenyl)ethane-1,2-diol (18): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (93 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) (peaks are reported for the mixture of both the meso and dl isomers): \(\delta = 7.71-7.69\) (d, \(J = 7.6\) Hz, 2H), 7.34-7.18 (m, 14H), 5.64 (s, 2H), 5.40 (s ,2H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta = 137.3, 136.4, 133.4, 132.7, 129.5, 129.2, 129.1, 128.9, 128.9, 128.7, 126.9, 126.5, 73.0, 42.2\); HRMS (ESI\(^+\)):
calcd. for C\(_{14}\)H\(_{16}\)Cl\(_2\)NO\(_2\) (M+NH\(_4\))^+ 300.0541; found 300.0553.

1,2-Bis(4-bromophenyl)ethane-1,2-diol (19): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 15:85) to afford the product as a white solid (99 %). Spectral data for the product was in accordance with what was previously reported.\(^8\)

1,2-Bis(3-bromophenyl)ethane-1,2-diol (20): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (99%). Spectral data for the product was in accordance with what was previously reported.\(^7\)

![Structure 1](image1)

1,2-Bis(4-methoxyphenyl)ethane-1,2-diol (21): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (66%). Spectral data for the product was in accordance with what was previously reported.\(^9\)

![Structure 2](image2)

1,2-Bis(2-hydroxyphenyl)ethane-1,2-diol (22): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (74%). Spectral data for the product was in accordance with what was previously reported.\(^10\)

![Structure 3](image3)

1,2-Bis(4-ethylphenyl)ethane-1,2-diol (23): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (85%). Spectral data for the product was in accordance with what was previously reported.\(^4\)


1,2-Di(naphthalen-1-yl)ethane-1,2-diol (24): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 20:80) to afford the product as a white solid (57 %). Spectral data for the product was in accordance with what was previously reported.³

1,2-Di(pyridin-2-yl)ethane-1,2-diol (25): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 50 : 50) to afford the product as a white solid (82 %). Spectral data for the product was in accordance with what was previously reported.¹¹

1,2-Di(quinolin-4-yl)ethane-1,2-diol (26): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 10:90) to afford the product as a white solid (68 %). ¹H NMR (400 MHz, CDCl₃) (peaks are reported for the mixture of both the meso and dl isomers): δ = 8.92 (m, 1H), 8.19-8.16 (d, J = 8.4 Hz, 1H), 8.0-7.97 (d, J = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.62-7.57 (m, 2H), 5.27 (s, 2H); ¹³C NMR (300 MHz, CDCl₃) δ =150.2, 147.6, 129.9, 129.4, 126.8, 125.8, 122.9, 118.2, 77.2, 61.6 ; HRMS (ESI⁺): calcd. for C₂₀H₁₇N₂O₂ (M+H)⁺ 317.1204; found 317.1291.

1,2-Bis(3-methylbenzo[b]thiophen-2-yl)ethane-1,2-diol (28): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 70:30) to afford the product as a white solid (82 %). $^1$H NMR (400 MHz, CDCl$_3$) ($meso$ and $dl$): $\delta$ = 7.83-7.81 (m, 4H), 7.69-7.67 (d, $J$ = 7.2 Hz, 8H), 7.47-7.30 (m, 10H), 5.42 (s, 2H), 5.33 (s, 2H), 2.39 (s, 6H), 1.76 (s, 6H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ =140.3, 140.1, 139.1, 137.1, 130.5, 130.2, 124.5, 124.0, 123.9, 122.5, 121.9, 121.8, 73.4, 72.9, 12.2, 11.3; HRMS (ESI$^+$): calcd. for C$_{20}$H$_{18}$O$_2$S$_2$Na (M+Na)$^+$ 377.0640; found 377.0624.

1,2-Di(thiophen-2-yl)ethane-1,2-diol (27): Following the general procedure described above, the product was isolated by chromatography (hexane/AcOEt 50:50) to afford the product as a white solid (54 %). $^1$H NMR (400 MHz, CDCl$_3$) (peaks are reported for the mixture of both the $meso$ and $dl$ isomers): $\delta$ = 7.32-7.31 (d, $J$ = 4.8, 2H), 7.28-7.27 (d, $J$ = 7.2 Hz, 2H), 7.06-7.05 (d, $J$ = 3.2 Hz 2H), 5.42 (s, 2H), 7.02-6.99 (m, 2H), 6.94-6.92 (m, 2H), 6.86-6.85 (m, 2H), 5.15 (s, 2H), 5.08 (s, 2H), 3.01 (br s, 2H), 2.50 (br s, 2H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ =142.8, 142.5, 126.6, 126.0, 125.9, 125.6, 125.4, 75.0, 74.5; HRMS (ESI$^+$): calcd. for C$_{10}$H$_{10}$O$_2$S$_2$Na (M+Na)$^+$ 249.0014; found 249.0002.
REACTION OPTIMIZATION

Table S1. Pinacol-Type Coupling Employing Bifunctional Cu-Based Photocatalysts in Different Solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Notes</th>
<th>Yield I (%) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>PhMe</td>
<td>HEH poorly soluble</td>
</tr>
<tr>
<td>5</td>
<td>CH(_3)CN</td>
<td>HEH poorly soluble</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yields. 1:1 ratio of diastereomers observed in all cases.

Table S2. Pinacol-Type Coupling Employing Bifunctional Cu-Based Photocatalysts with Different H-Atom Donors.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Yield I (%) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEH</td>
<td>76</td>
</tr>
<tr>
<td>Et(_3)SiH</td>
<td>0</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0</td>
</tr>
<tr>
<td>Sodium Formate</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yields. 1:1 ratio of diastereomers observed in all cases.
Absorbance UV-Vis spectra were recorded with Varian Cary 5000 UV-Vis-NIR Spectrophotometer in a quartz cuvette.

**Figure S1:** UV-visible absorption spectrum of Cu(diamine)(BINAP)BF₄ recorded at ambient temperature in CH₂Cl₂ (5.0·10⁻⁵M).
Emission spectra were recorded with the Varian Cary Eclipse Fluorescence Spectrophotometer/Fluorometer in a quartz cuvette.

**Figure S2:** Emission spectrum of Cu(pypz)(BINAP)BF$_4$ excited at 395 nm, recorded at ambient temperature in CH$_2$Cl$_2$ ($5.0 \cdot 10^{-3}$M).

**Figure S3:** Emission spectrum of Cu(pypza)(BINAP)BF$_4$ excited at 395 nm, recorded at ambient temperature in CH$_2$Cl$_2$ ($5.0 \cdot 10^{-3}$M).
Figure S4: Emission spectrum of Cu(pypzs)(BINAP)BF₄ excited at 395 nm, recorded at ambient temperature in CH₂Cl₂ (5.0·10⁻³M).
EXCITED STATE LIFETIME DATA

Lifetime measurements were done with an Edinburgh Instruments FLS-920 fluorimeter with an EPL 375 laser (exciting at 375 nm).

Figure S5: Life time spectrum of Cu(pypz)(BINAP)BF$_4$ excited at 375 nm, recorded at ambient temperature in CH$_2$Cl$_2$ (1.25·10$^{-5}$M).

Figure S6: Life time spectrum of Cu(pypza)(BINAP)BF$_4$ excited at 375 nm, recorded at ambient temperature in CH$_2$Cl$_2$ (1.25·10$^{-5}$M).
Figure S7: Life time spectrum of Cu(pypzs)(BINAP)BF₄ excited at 375 nm, recorded at ambient temperature in CH₂Cl₂ (1.25×10⁻³ M).
ELECTROCHEMICAL DATA

Cyclic voltammetry measurements in dry acetonitrile (MeCN) with tetra-\(n\)-butylammonium hexafluorophosphate (TBAPF\(_6\)) as the supporting electrolyte were performed using a standard three-electrode cell, consisting of a silver wire pseudo-reference electrode, a platinum wire counter electrode and a platinum working electrode with a BioLogic SP-50 potentiostat. The solutions were degassed with a flow of argon for 5 minutes prior to the measurements. All measurements were carried out at 22 °C. All potentials were reported to the mid-point potential of the ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple which was determined in the aforementioned electrolyte.

\[ \text{Figure S8: Cyclic voltammogram of Cu(pypz)(BINAP)BF}_4 \text{ in MeCN (1 mM) using TBAPF}_6 \text{ (100 mM) as supporting electrolyte at a scan rate of 50 mV s}^{-1}. \]
Figure S9: Cyclic voltammogram of Cu(pypza)(BINAP)BF₄ in MeCN (1 mM) using TBAPF₆ (100 mM) as supporting electrolyte at a scan rate of 50 mV s⁻¹.

Figure S10: Cyclic voltammogram of Cu(pypzs)(BINAP)BF₄ in MeCN (1 mM) using TBAPF₆ (100 mM) as supporting electrolyte at a scan rate of 50 mV s⁻¹.
CATALYST STABILITY

Catalyst Cu(pypz)(BINAP)BF$_4$ was stored as a solid with no precautions to exclude light, air or humidity. Below are $^1$H NMR spectra of the same batch of catalyst taken after $\sim$9 months.

Figure S11: Catalyst stability in the solid state examined by $^1$H NMR.
Catalyst Cu(pypzs)(BINAP)BF₄ was dissolved in THF and then irradiated with blue LEDs for 24 hours. The solvent was then evaporated and the sample analyzed by ¹H NMR (CDCl₃) and UV-vis spectroscopy.

Figure S12: Catalyst before irradiation (top) and after irradiation bottom.
**Figure S13:** Catalyst before irradiation (blue) and after irradiation (orange) (a) above UV-vis and (b) below emission.
QUENCHING DATA
Quenching experiments were performed by examining the effect on the excited state lifetime through the addition of either HEH or acetophenone. Lifetime measurements were done with an Edinburgh Instruments FLS-920 fluorimeter with an EPL 375 laser (exciting at 375 nm). The lifetime data are summarized in a table below and the life time spectra are shown below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Excited State Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pypz)(BINAP)BF$_4$</td>
<td>8.79 ns</td>
</tr>
<tr>
<td>Cu(pypz)(BINAP)BF$_4$ + Acetophenone</td>
<td>13.18 ns</td>
</tr>
<tr>
<td>Cu(pypz)(BINAP)BF$_4$ + HEH</td>
<td>0.21 ns</td>
</tr>
</tbody>
</table>

Figure S14: Life time spectra of Cu(pypz)(BINAP)BF$_4$ excited at 375 nm, recorded at ambient temperature in CH$_2$Cl$_2$ (5·10$^{-4}$M).
Figure S15: Life time spectra of Cu(pypzs)(BINAP)BF$_4$ with acetophenone, excited at 375 nm, recorded at ambient temperature in CH$_2$Cl$_2$ (5 $\times$ 10$^{-4}$M).

Figure S16: Life time spectra of Cu(pypzs)(BINAP)BF$_4$ with HEH, excited at 375 nm, recorded at ambient temperature in CH$_2$Cl$_2$ (5 $\times$ 10$^{-4}$M).
$k_q = 4.25 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$

**Figure S15**: Stern-Volmer Quenching Studies of Cu(pypzs)(BINAP)BF$_4$ by the Hantzsch ester (HEH).
NMR DATA