

## **Supporting Information**

### **Investigation into the Rate of Photoreductive Alkyl Radical Generation**

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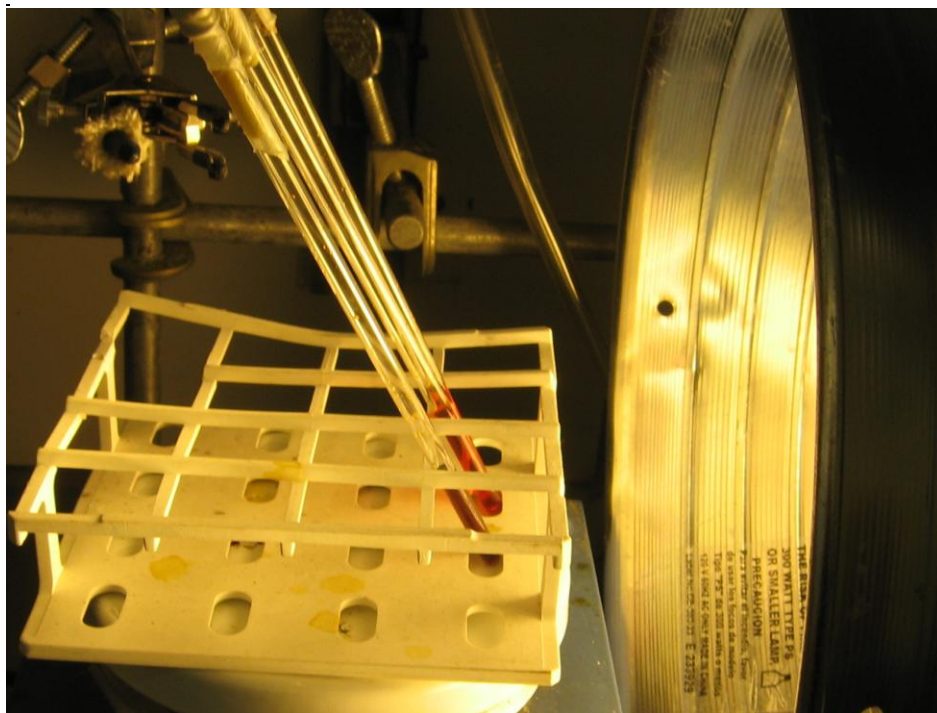
## **Experimental Section**

**General.** All reagents were reagent grade quality and used as received from Aldrich or Acros unless otherwise indicated. All reactions were conducted under inert conditions (Ar or N<sub>2</sub>) using flame dried or oven dried glassware cooled under inert atmosphere unless otherwise indicated. Anhydrous acetonitrile (MeCN or CD<sub>3</sub>CN) and N,N-diisopropylethylamine (EtN<sup>i</sup>Pr<sub>2</sub>) were distilled from CaH<sub>2</sub> prior to use.  $\alpha$ -D-glucopyranosyl bromide tetrabenzoate (**1**) was synthesized according to a literature procedure.<sup>1</sup> Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and Ru(dmb)<sub>3</sub>Cl<sub>2</sub> were synthesized by reported procedures,<sup>2</sup> and Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and Ru(dmb)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> were synthesized in an analogous manner to reported anion metatheses.<sup>3</sup> All NMR spectra were recorded on Bruker Avance 600 MHz with Cryoqnp probe, a Bruker 500 MHz with bbo probe, or a 400 MHz with bbfo probe using Topshim at STP. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc, unless otherwise noted. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts are reported in  $\delta$  units, parts per million (ppm) relative to the chemical shift of residual solvent or an external standard. Reference peaks for chloroform-*d* in <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. The reference peak for acetonitrile-*d*<sub>3</sub> in <sup>1</sup>H NMR was set at 1.94 ppm. Reaction vessels were covered in foil to protect them from light during manipulations prior to irradiation.

#### *Reaction apparatuses.*

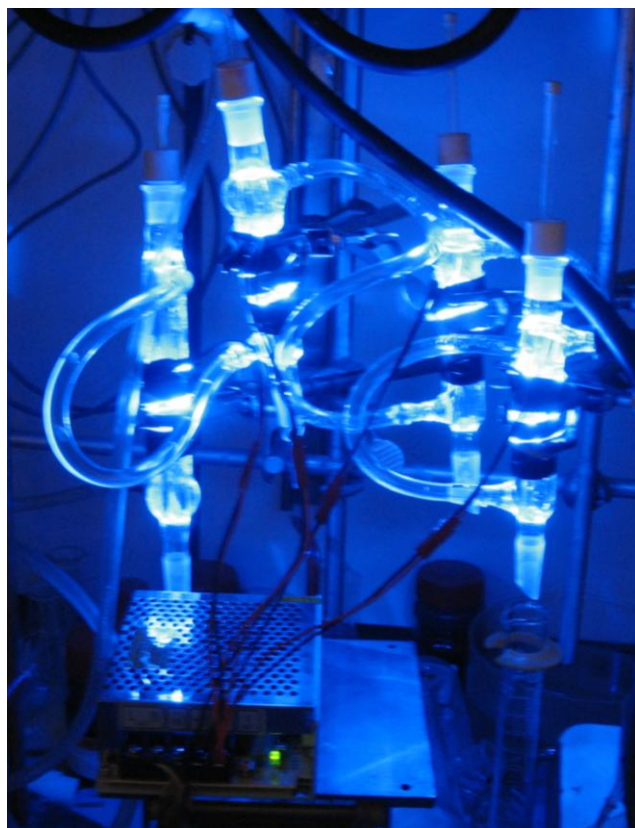
Compact fluorescent light bulb (14 W):

NMR tubes were placed approximately 8-10 cm away from a 14 W CFL with a focusing cone (see image below).



Blue LEDs:

NMR tubes were placed inside a reflux condenser around which 12 inch blue LED light strips (from [www.creativelightings.com](http://www.creativelightings.com)) were wrapped in a 5 cm vertical span (see image below). Four of these reflux condensers were placed in serial, and water was used to keep the reactions at room temperature ( $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ ), as the LED strips generated significant amounts of heat. The flow of the water was regulated to keep the temperature between the first and fourth reflux condensers within  $1\text{ }^{\circ}\text{C}$  of each other.



### *Procedures.*

#### ***Varying concentration of <sup>t</sup>BuSH:***

A 10 mL round bottom flask under Ar was charged with **1** (201 mg, 0.305 mmol), EtN<sup>i</sup>Pr<sub>2</sub> (160  $\mu$ L, 0.915 mmol, 3 eq), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mmol), 1,3,5-trimethoxybenzene (41.6 mg as an internal standard), and 2.5 mL CD<sub>3</sub>CN. 500  $\mu$ L of this solution was transferred to oven dried NMR tubes containing 7  $\mu$ L, 14  $\mu$ L, 34  $\mu$ L, and 68  $\mu$ L of 2-methyl-2-propanethiol, each. The NMR tubes were degassed by three freeze-pump-thaw cycles, and the reactions were irradiated with a 14 W compact fluorescent light bulb for 3 hours. <sup>1</sup>H NMR monitoring (d<sub>1</sub> = 5  $\mu$ sec) before and after the reaction was used to determine the % conversion.

[ <sup>t</sup> BuSH] (mM)	0.12	0.24	0.57	1.06
% Conversion of <b>1</b>	<b>49</b>	<b>51</b>	<b>48</b>	<b>47</b>

Average % conversion: 48.8  $\pm$  3.5%

***Varying concentration of 1:***

A 10 mL round bottom flask under Ar was charged with 2-methyl-2-propanethiol (69  $\mu$ L, 0.61 mmol) EtN<sup>i</sup>Pr<sub>2</sub> (160  $\mu$ L, 0.915 mmol, 3 eq), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (13 mg, 0.015 mmol), 1,3,5-trimethoxybenzene (42.1 mg as an internal standard), and 2.5 mL CD<sub>3</sub>CN. 500  $\mu$ L of this solution was transferred to oven dried NMR tubes containing 10.1 mg, 19.7 mg, 40.4 mg, and 82.0 mg of **1**, each. The NMR tubes were degassed by three freeze-pump-thaw cycles, and the reactions were irradiated with a 14 W compact fluorescent light bulb for 3 hours. <sup>1</sup>H NMR monitoring (d<sub>1</sub> = 5  $\mu$ sec) before and after the reaction was used to determine the % conversion.

[1] (mM)	0.031	0.060	0.122	0.249
mmol of <b>1</b> consumed	<b>0.014</b>	<b>0.020</b>	<b>0.026</b>	<b>0.041</b>

***Varying concentration of EtN<sup>i</sup>Pr<sub>2</sub>:***

**1** (809.7 mg, 1.228 mmol), 2-methyl-2-propanethiol (275  $\mu$ L, 2.44 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (51.0 mg, 0.059 mmol), and 1,3,5-trimethoxybenzene (~200 mg as an internal standard) was brought to a final volume of 5 mL in CD<sub>3</sub>CN. Oven dry NMR tubes were charged with 250  $\mu$ L of this stock solution and 10  $\mu$ L, 32  $\mu$ L, 65  $\mu$ L, and 100  $\mu$ L of EtN<sup>i</sup>Pr<sub>2</sub>. The reactions were then diluted to a final volume of 0.5 mL with CD<sub>3</sub>CN, and the solutions were degassed by three freeze-pump-thaw cycles. The reactions were then irradiated with a 14 W compact fluorescent light for 3 hours. <sup>1</sup>H NMR monitoring (d<sub>1</sub> = 5  $\mu$ sec) before and after the reaction was used to determine the % conversion.

[EtN <sup>i</sup> Pr <sub>2</sub> ] (mM)	0.12	0.37	0.75	1.15
% conversion of <b>1</b> (CFL)	<b>37.6</b>	<b>54.5</b>	<b>63.3</b>	<b>65.5</b>

***Varying amount of cosolvent:***

**1** (809.2 mg, 1.228 mmol), EtN<sup>i</sup>Pr<sub>2</sub> (638  $\mu$ L, 3.66 mmol), 2-methyl-2-propanethiol (275  $\mu$ L, 2.44 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (51.0 mg, 0.059 mmol), and 1,3,5-trimethoxybenzene (~200 mg as an internal standard) was brought to a final volume of 5 mL in CD<sub>3</sub>CN. Oven dry NMR tubes were charged with 250  $\mu$ L of this stock solution and 10  $\mu$ L, 25  $\mu$ L, 50  $\mu$ L, and 100  $\mu$ L of cosolvent was added (see table below). The reactions were then diluted to a final volume of 0.5 mL with CD<sub>3</sub>CN, and the solutions were degassed by three freeze-pump-thaw cycles. The reactions

were then irradiated with blue LEDs for 3 hours.  $^1\text{H}$  NMR monitoring ( $d_1 = 5 \mu\text{sec}$ ) before and after the reaction was used to determine the % conversion.

**Table 1: % Conversion of 1 for various cosolvent concentrations**

Cosolvent	2% cosolvent	5% cosolvent	10% cosolvent	20% cosolvent
MeOH	<b>23.3</b>	<b>23.0</b>	<b>22.4</b>	<b>26.3</b>
DMSO	<b>23.9</b>	<b>23.5</b>	<i>a</i>	<i>a</i>
Ethylene Glycol	<b>28.3</b>	<b>29.1</b>	<b>ND</b>	<b>37.4</b>
H <sub>2</sub> O	<b>33.2</b>	<b>43.5</b>	<b>55.7</b>	<i>b</i>

ND: Not determined. *a*: At higher concentrations of DMSO, the reaction suffered from hydrolysis of the substrate, and conversion was not determined for these concentrations. *b*: **1** was insoluble in >10% aqueous acetonitrile.

***Varying concentration of catalyst under anhydrous conditions (representative example):***

**1** (807.2 mg, 1.22 mmol), EtN<sup>i</sup>Pr<sub>2</sub> (638  $\mu\text{L}$ , 3.66 mmol), 2-methyl-2-propanethiol (275  $\mu\text{L}$ , 2.44 mmol), and 1,3,5-trimethoxybenzene (~200 mg as an internal standard) was brought to a final volume of 5 mL in CD<sub>3</sub>CN. Oven dry NMR tubes were charged with 250  $\mu\text{L}$  of this stock solution and varying amounts of a stock solution of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> was added (see manuscript for final concentrations). The reactions were then diluted to a final volume of 0.5 mL with CD<sub>3</sub>CN, and the solutions were degassed by three freeze-pump-thaw cycles. The reactions were then irradiated with a 14 W compact fluorescent light bulb or blue LEDs for 3 hours.  $^1\text{H}$  NMR monitoring ( $d_1 = 5 \mu\text{sec}$ ) before and after the reaction was used to determine the % conversion.

***Varying concentration of catalyst under aqueous conditions:***

**1** (801.6 mg, 1.215 mmol), EtN<sup>i</sup>Pr<sub>2</sub> (638  $\mu\text{L}$ , 3.66 mmol), 2-methyl-2-propanethiol (275  $\mu\text{L}$ , 2.44 mmol), and 1,3,5-trimethoxybenzene (~200 mg as an internal standard) was brought to a final volume of 5 mL in CD<sub>3</sub>CN. Oven dry NMR tubes were charged with 250  $\mu\text{L}$  of this stock solution, and varying amounts of a stock solution of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> was added (see manuscript for final concentrations and results). The reactions were then diluted to a final volume of 0.5 mL with CD<sub>3</sub>CN, and an additional 50  $\mu\text{L}$  of H<sub>2</sub>O was added. The solutions were degassed by three freeze-pump-thaw cycles. The reactions were then irradiated with a 14 W compact fluorescent light bulb or

blue LEDs for 3 hours.  $^1\text{H}$  NMR monitoring ( $d_1 = 5 \mu\text{sec}$ ) before and after the reaction was used to determine the % conversion.

***Blue LED apparatus control experiment:***

To determine the consistency of the LED apparatus (see picture above), 4 trial experiments were conducted, one in each of the LED “chambers”. A 10 mL round bottom flask under Ar was charged with **1** (204 mg, 0.309 mmol), 2-methyl-2-propanethiol (69  $\mu\text{L}$ , 0.61 mmol),  $\text{EtN}^i\text{Pr}_2$  (160  $\mu\text{L}$ , 0.915 mmol),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (12.8 mg, 0.015 mmol), 1,3,5-trimethoxybenzene (43.4 mg as an internal standard), and 2.5 mL  $\text{CD}_3\text{CN}$ . 500  $\mu\text{L}$  of this solution was transferred to oven dried NMR tubes, which were then degassed by three freeze-pump-thaw cycles, and the reactions were irradiated with blue LEDs for 3 hours.  $^1\text{H}$  NMR monitoring ( $d_1 = 5 \mu\text{sec}$ ) before and after the reaction was used to determine the % conversion.

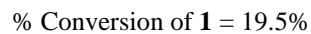
Trial #	1	2	3	4
% Conversion of <b>1</b>	<b>59.8</b>	<b>60.8</b>	<b>61.3</b>	<b>60.8</b>

Average % conversion:  $60.7 \pm 1.1\%$

***Radical coupling with electron-deficient alkenes (representative procedure):***

A dry 10 mL Schlenk tube under Ar was charged with **4** (50 mg, 0.12 mmol),  $\text{RuL}_3(\text{PF}_6)_2$  (0.006 mmol), diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HEH, 34 mg, 0.134 mmol) and 1 mL MeCN (for anhydrous reactions) or 0.9 mL MeCN and 0.1 mL  $\text{H}_2\text{O}$  (for aqueous reactions).  $\text{EtN}^i\text{Pr}_2$  (64  $\mu\text{L}$ , 0.37 mmol) was added, and the heterogeneous solution was degassed by three freeze-pump-thaw cycles. Methyl acrylate (22  $\mu\text{L}$ , 0.24 mmol) was added, and the vessels were irradiated with blue LEDs. Anhydrous reactions were quenched by passing the reaction through a plug of silica in ether and concentrated *in vacuo*. Aqueous reactions were transferred to a separatory funnel with 10 mL EtOAc and 10 mL  $\text{H}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted 3 x EtOAc. The combined organic layers were successively rinsed 1 x HCl (1M), 1 x sat.  $\text{NaHCO}_3(\text{aq})$ , 1 x brine, dried with  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. 1,3,5-trimethoxybenzene was added as a quantitative internal  $^1\text{H}$  NMR standard for determination of yield and conversion ( $d_1 = 5 \mu\text{sec}$ ).

**Initial spectrum (CD<sub>3</sub>CN, 400 MHz):**



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- <sup>1</sup> Dowlut, M.; Hall, D. G.; Hindsgaul, O. *J. Org. Chem.* **2005**, *70*, 9809.  
<sup>2</sup> Broomhead, J. A.; Young, C. G. *Inorg. Synth.* **1990**, *28*, 338.  
<sup>3</sup> Masui, H.; Murray, R. W. *Inorg. Chem.* **1997**, *36*, 5118.