

# Semi-Heterogeneous Dual Nickel/Photocatalytic (Thio)Etherification using Carbon Nitrides

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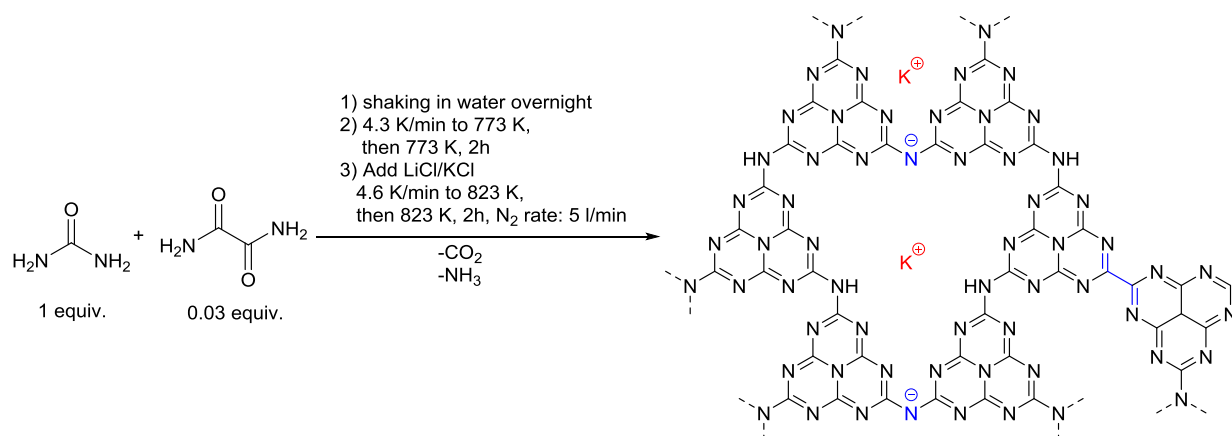
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## 1. General remarks

Substrates, reagents, and solvents were purchased from commercial suppliers and used without further purification. *N*-*tert*-butylisopropylamine (BIPA),<sup>1</sup> 6,6'-diamino-2,2'-bipyridyl,<sup>2, 3</sup> methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate,<sup>4</sup> methyl 4-(tosyloxy)benzoate,<sup>5</sup> methyl 4-(((methylsulfonyl)oxy)benzoate,<sup>6</sup> (2-bromophenoxy)ethanol,<sup>7</sup> (2-bromophenyl)propanol<sup>8</sup> and *N*-(3-hydroxy-3-phenylpropyl)-*N*-methylacetamide<sup>9</sup> were prepared according to literature procedures. <sup>1</sup>H-, <sup>13</sup>C- and <sup>19</sup>F-NMR spectra were obtained using a Varian 400 spectrometer (400 MHz, Agilent), an Ascend<sup>TM</sup> 400 spectrometer (400 MHz, cryoprobe, Bruker) and a Varian 600 spectrometer (600 MHz, Agilent) at 298 K, and are reported in ppm relative to the residual solvent peaks. Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, with coupling constants in Hz. Analytical thin layer chromatography (TLC) was performed on pre-coated TLC-sheets, ALUGRAM Xtra SIL G/UV<sub>254</sub> sheets (Macherey-Nagel) and visualized with 254 nm light or staining solutions followed by heating. Purification of final compounds was carried out by flash chromatography on the Reveleris X2 Flash Chromatography System from GRACE using prepacked columns with 40 µm silica gel. Silica 60 M (0.04-0.063 mm) silica gel (Sigma Aldrich) was used for dry loading of the crude compounds on the flash chromatography system. Centrifugation was carried out using an Eppendorf 5430 centrifuge. High-resolution mass spectral data were obtained using a HR-EI-MS (Waters Autospec Premier) and a Waters XEVO G2-XS 4K spectrometer with the XEVO G2-XS QTOF capability kit. Emission spectra of LED lamps were recorded using 10 in. (24.5 cm) integrating sphere (Labsphere, Inc. Model LMS 1050) equipped with a diode array detector (International Light, Model RPS900). The UV/Vis spectrum of Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> was recorded using a UVmini-1240 spectrometer (Shimadzu). The UV/Vis spectrum of CN-OA-m was recorded using a UV2600 spectrometer (Shimadzu) equipped with an integrating sphere. Inductively coupled plasma - optical emission spectrometry (ICP-OES) was carried out using a Horiba Ultra 2 instrument equipped with photomultiplier tube detection.

## 2. Preparation of CN-OA-m



**Scheme S1.** Synthesis of CN-OA-m

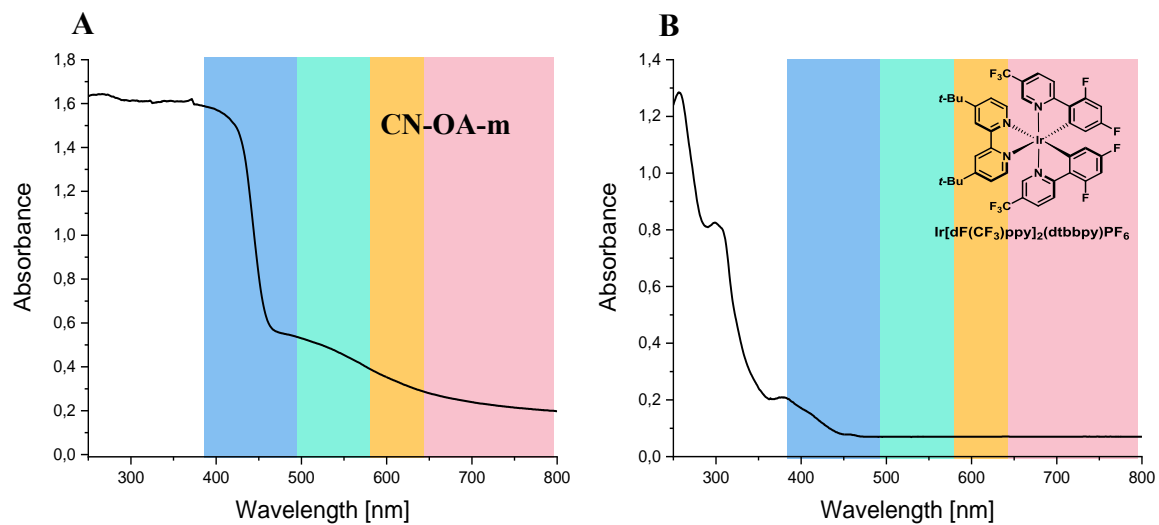
The synthesis for CN-OA-m was carried out using a slightly adapted version of the literature procedure (Scheme S1)<sup>10</sup>: for each batch of the photocatalyst, urea (10 g, 166.5 mmol) and oxamide (0.5 g, 5.7 mmol) were mixed in 10 mL of DI water to generate a homogeneous mixture. After drying at 373 K, the resulting solids were grinded, transferred into a crucible with a cover and heated up in an air-oven with a heating rate of 4.3 K/min to 773 K. After keeping the mixture for 2h at 773 K, the sample was allowed to cool to room temperature. Subsequently, KCl (3.3 g, 44.3 mmol) and LiCl (2.7 g, 63.7 mmol) were added and the solids were grinded to obtain a homogeneous mixture which was heated in an inert atmosphere (N<sub>2</sub> flow: 5 mL/min) to 823 K with a heating rate of 4.6 K/min. After keeping the mixture for 2 h at 823 K, the sample was allowed to cool to room temperature and the resulting solids were collected on a filter paper and washed with H<sub>2</sub>O (3 x 100 mL). The resulting yellow material was dried at 373 K (average yield per batch: ~400 mg).

Each batch was tested under the same set of conditions and obtaining always similar catalytic activities (+/-5% based on <sup>1</sup>H-NMR with internal standard).

The cost of CN-OA-m was calculated to be 4.2 € g<sup>-1</sup> based on the prices of urea, oxamide, LiCl and KCl from Sigma-Aldrich (Merck).<sup>11</sup> As a comparison, the price of Ir(ppy)<sub>3</sub> is 2124 € g<sup>-1</sup>.<sup>11</sup>

The UV/Vis spectrum of CN-OA-m shows a strong absorption up to ~460 nm and a comparably weaker absorption band up to ~700 nm (Figure S1, A) which are attributed to the  $\pi$ - $\pi^*$  electron transition of the sp<sup>2</sup> hybridization of C and N in the heptazine framework and n- $\pi^*$  electron transition involving the lone pairs of the edge nitrogen atoms in the heptazine units, respectively.<sup>10</sup> The capability of harvesting low energy light is therefore superior compared to Ir and Ru photocatalysts (see Figure S1, B for the UV/Vis spectrum of Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> as a representative example) which have only a low absorption band between 400 and 500 nm in the visible region, which corresponds to the metal-to-ligand charge transfer transition.



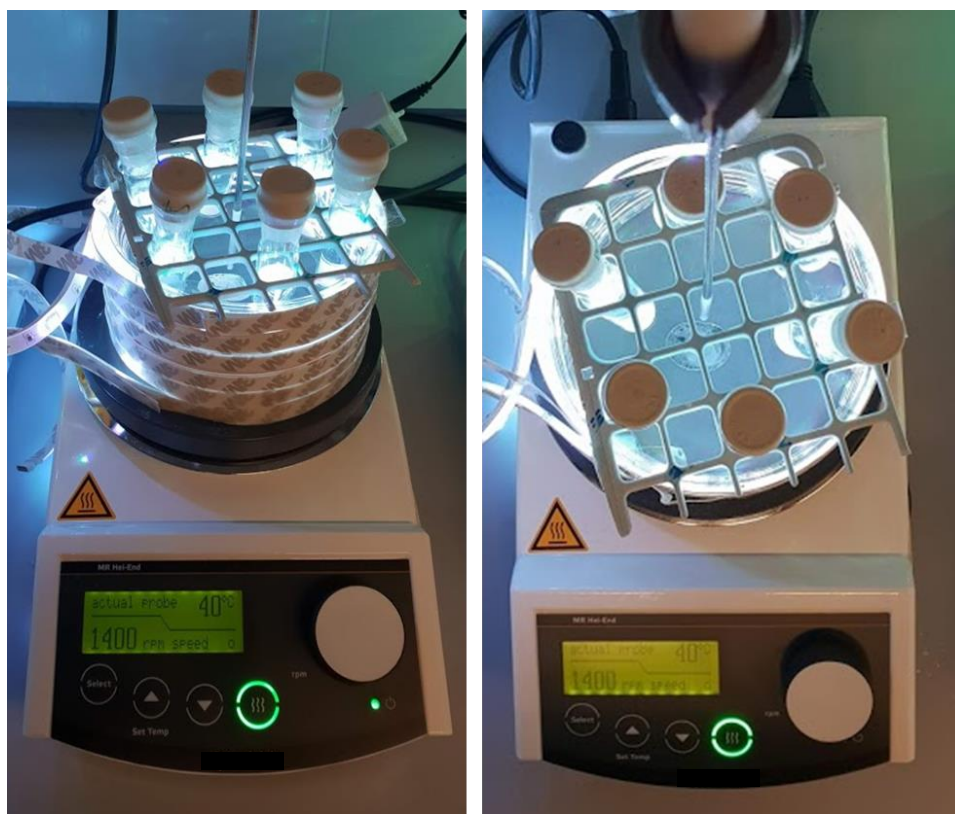


**Figure S1.** UV/Vis absorption spectra of CN-OA-m (A) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (B).

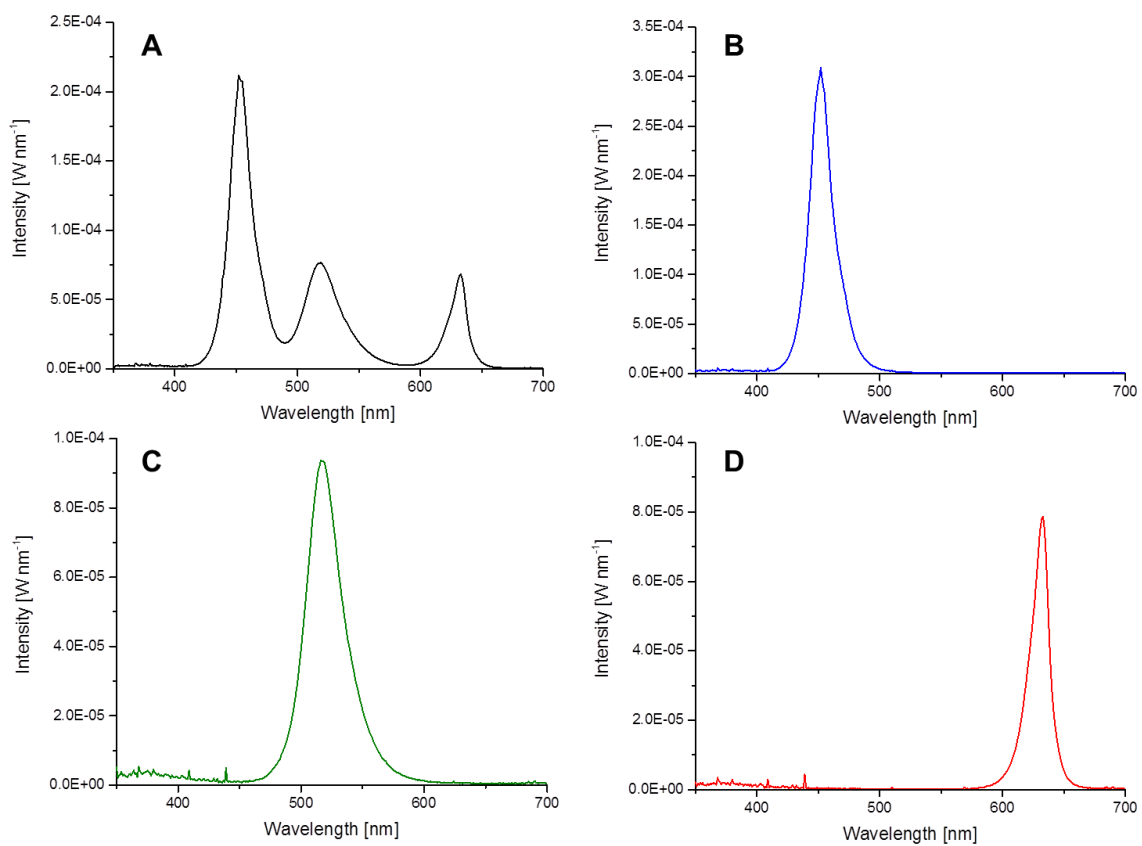
### 3. Setups for photochemical reactions

#### 3.1. RGB photoreactor (low intensity)

A flexible, red/green/blue LED strip<sup>12</sup> (RGB, 5m, 24 W/strip; Tween Light, BAHAG AG, Germany) was wrapped around a 115 mm borosilicate crystallization dish (Figure S2). White light (illumination of all three LED colors - red/green/blue) was used at full power (For emission spectra of a single diode, see Figure S3). The evaporating dish was filled with ethylene glycol and the temperature was set to 40°C to maintain a constant temperature. The sealed reaction vessels were placed at the same distance from the LED strip during all experiments (Figure S2). All reactions were performed with a stirring speed of 1400 rpm.



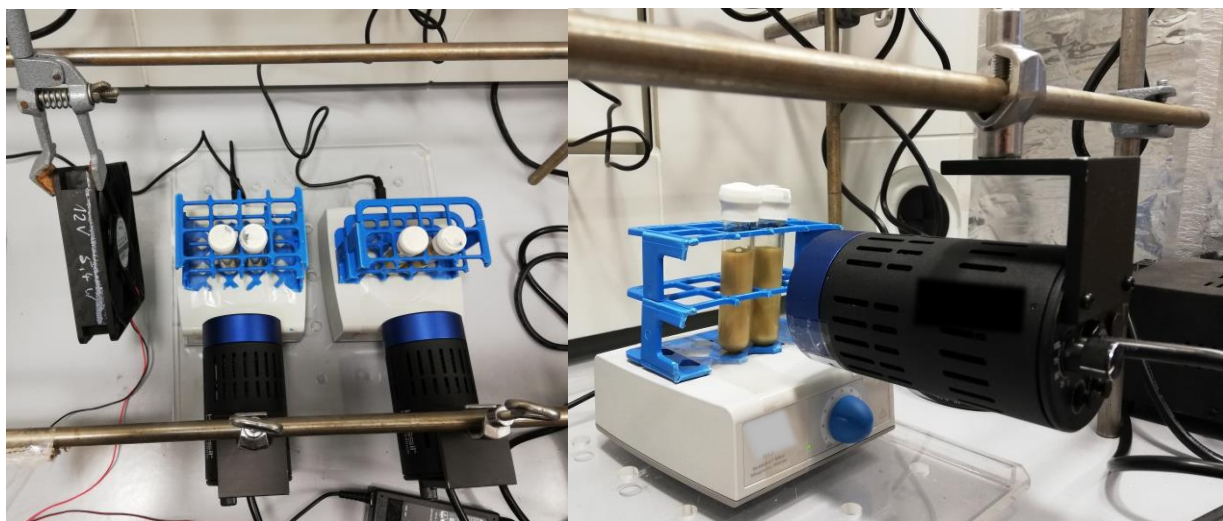
**Figure S2.** Experimental setup of the RGB photoreactor (low intensity)



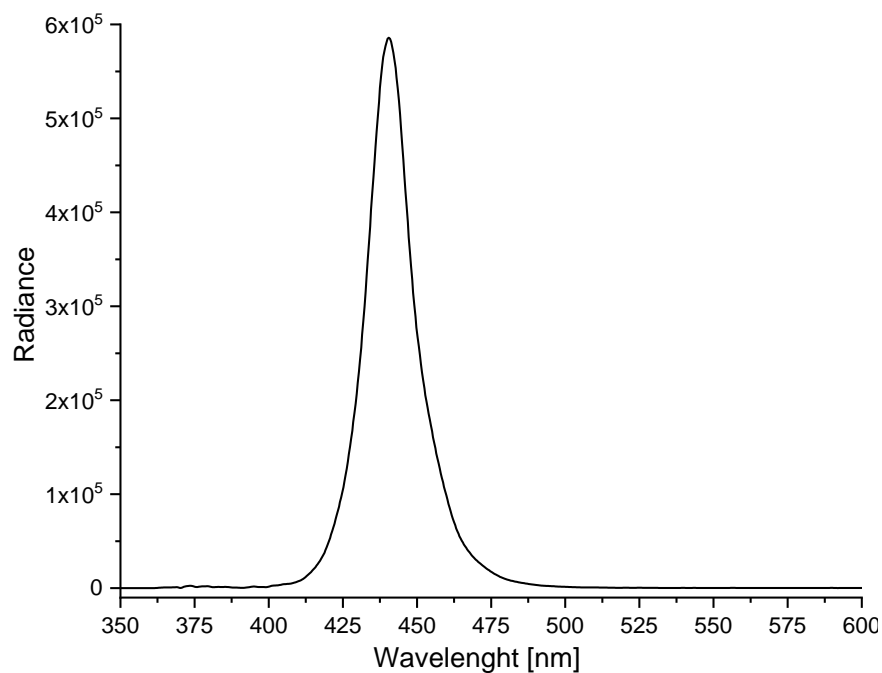
**Figure S3.** Emission spectra of the LED strips used in the RGB photoreactor (low intensity) for photochemical reactions. All experiments were carried out at maximum power. **A:** white light. **B:** blue light only. **C:** green light only. **D:** red light only.

### 3.2. 440 nm photoreactor (high intensity)

Blue LED lamps<sup>13</sup> at 50% power (440 nm, 40W, PR160, Kessil Photoredox, for emission spectrum, see Figure S5) were used for experiments on CN-OA-m recycling (Figure S4). Two sealed reaction vessels were placed on a stirring plate 4.5 cm away from a single lamp. To avoid heating of the reaction mixture, a fan was used for cooling. All reactions were performed with maximum stirring speed.



**Figure S4.** Experimental setup of the 440 nm photoreactor (high intensity).

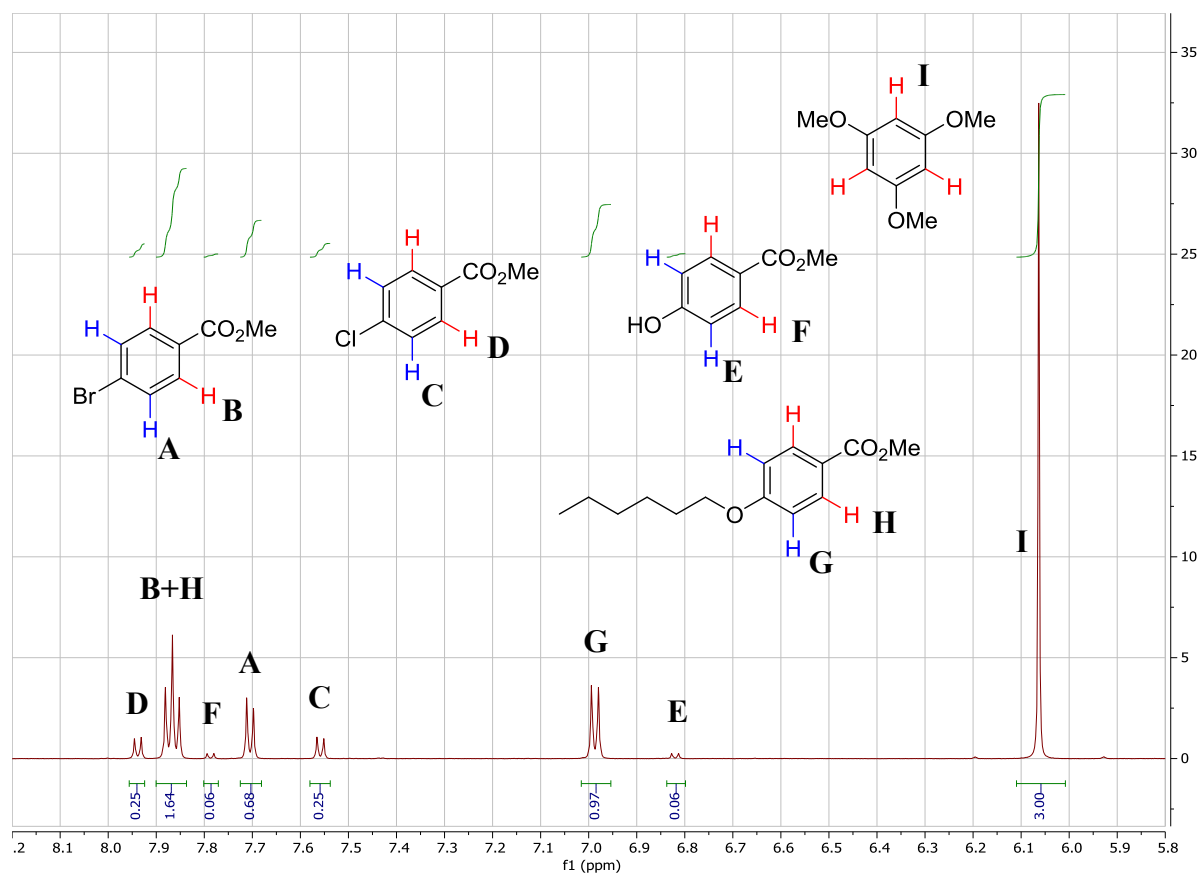
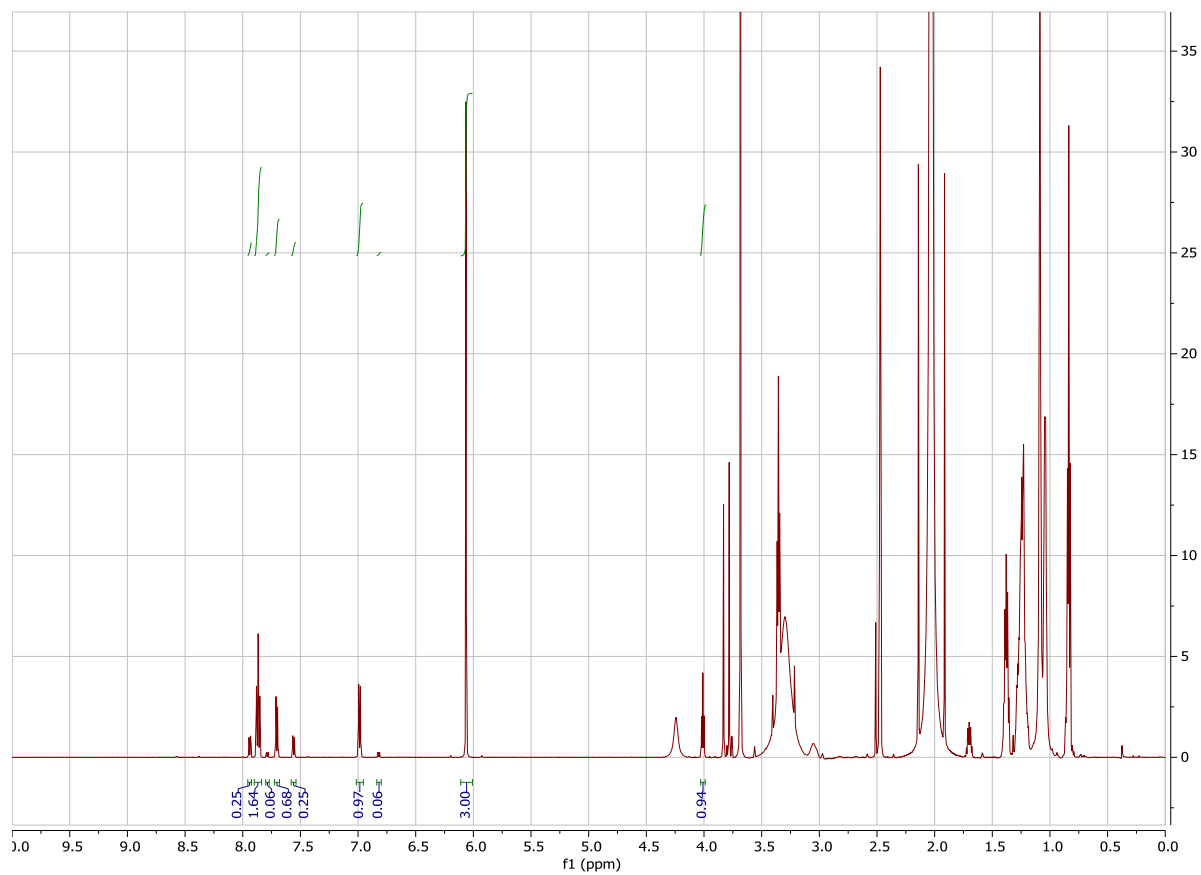


**Figure S5.** Emission spectrum of Kessil PR160-440 lamps.

## 4. Reaction optimization of the coupling of aryl bromides and alcohols

### 4.1. General experimental procedure for screening experiments

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with the Ni<sup>II</sup> source (30  $\mu$ mol, 10 mol%), the ligand (30  $\mu$ mol, 10 mol%), the CN material (10 mg) and methyl 4-bromobenzoate (64.5 mg, 0.3 mmol, 1.0 equiv). Subsequently, the solvent (3.0 mL), the base (3.0 - 5.0 equiv) and 1-hexanol (2.0 - 3.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5 - 10 min, followed by stirring for 5 min until a fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the low intensity RGB photoreactor with white light at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) was added. An aliquot of the reaction mixture (~200  $\mu$ L) was filtered, diluted with DMSO-*d*<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis. For representative NMR spectra, see Figure S6.



**Figure S6.** Example of a crude  $^1\text{H}$ -NMR spectrum of the C-O coupling of methyl 4-bromobenzoate and 1-hexanol.

## 4.2. Solvent screening

**Table S1.** Solvent screening.<sup>a</sup>

Entry	Solvent	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>	46 [%] <sup>c</sup>
1	MeCN	68	51	3	13
2	DMF	50	25	9	16
3	THF	41	22	2	17
4	Diglyme	28	11	2	15
5	DMAc	42	11	6	24
6	DMSO	15	4	5	6

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiCl<sub>2</sub>·glyme (30 μmol), dtbbpy (30 μmol), BIPA (0.9 mmol), solvent (anhydrous, 3.0 mL), white LEDs at 40 °C for 16 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Acetonitrile showed highest conversion and selectivity. HPLC grade MeCN gave identical results compared to high purity, anhydrous MeCN.

### 4.3. Screening of carbon nitride materials

**Table S2.** Screening of carbon nitride materials.<sup>a</sup>

Reaction scheme showing the conversion of methyl 4-bromobenzoate (0.1 M) and *n*-hexanol (3.0 equiv) to three products: 1 (*n*-hexyl 4-methoxycarbonylbenzoate), 2 (4-methoxycarbonylphenol), and 46 (4-chlorobenzoate). The reaction conditions are: CN (3.33 mg/mL), NiCl<sub>2</sub>·glyme (10 mol%), dtbbpy (10 mol%), BIPA (3.0 equiv), MeCN (deg.), 16 h, white LED, ~40°C.

Entry	CN material	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>	46 [%] <sup>c</sup>
1	CN-OA-m	68	51	3	13
2	CMB <sub>0.05</sub> -CN	28	18	1	9
3	mpg-CN	22	14	1	7
4	CMB <sub>0.10</sub> -CN	4	2	n.d. <sup>d</sup>	2
5	K-PHI	1	traces	n.d.	n.d.
6	CNS <sub>600</sub>	<1	n.d.	n.d.	n.d.

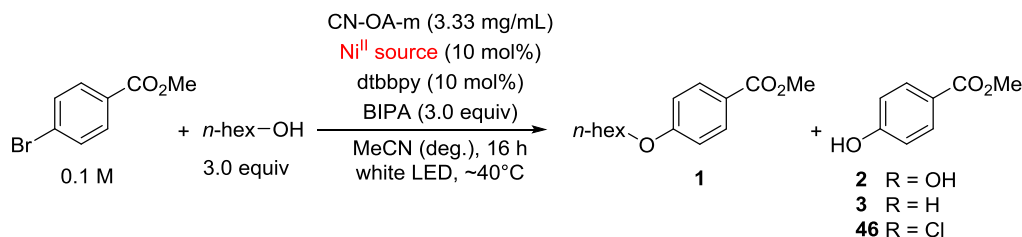
<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN material (10 mg), NiCl<sub>2</sub>·glyme (30 μmol), dtbbpy (30 μmol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.

Several carbon nitride materials were tested: mesoporous graphitic carbon nitride (mpg-CN),<sup>14</sup> two modified carbon nitrides derived from a cyanuric acid/melamide/barbituric acid complex (CMB<sub>0.05</sub>-CN and CMB<sub>0.10</sub>-CN),<sup>15</sup> a sulfur-doped material (CNS<sub>600</sub>),<sup>16</sup> a strongly oxidizing potassium poly(heptazine imide) (K-PHI),<sup>17</sup> and a carbon nitride derivative prepared *via* co-condensation of urea and oxamide followed by post-calcination in a molten salt (CN-OA-m).<sup>10</sup>



#### 4.4. Screening of Ni<sup>II</sup> sources

**Table S3.** Screening of Ni<sup>II</sup> sources.<sup>a</sup>



Entry	Ni <sup>II</sup> source	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>	3 [%] <sup>c</sup>	46 [%] <sup>c</sup>	Price [€ mol <sup>-1</sup> ] <sup>d</sup>
1	Ni(OTf) <sub>2</sub>	60	52	3	2	n.d. <sup>e</sup>	12917
2	NiCl <sub>2</sub> ·glyme	68	51	3	n.d.	13	4161
3	NiCl <sub>2</sub>	55	41	3	n.d.	11	110
4	NiBr <sub>2</sub> ·glyme	42	39	2	n.d.	n.d.	10431
5	NiBr <sub>2</sub> ·3H <sub>2</sub> O	40	36	3	n.d.	n.d.	116
6 <sup>f</sup>	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	14	5	2	3	n.d.	28
7	NiBr <sub>2</sub>	7	5	1	n.d.	n.d.	411
8	NiCl <sub>2</sub> ·6H <sub>2</sub> O	4	2	n.d.	2	n.d.	71
9	NiI <sub>2</sub>	15	14	1	n.d.	n.d.	2063
10	Ni(acac) <sub>2</sub>	4	1	n.d.	3	n.d.	620

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), Ni<sup>II</sup> source (30 μmol), dtbbpy (30 μmol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>Prices according to Sigma Aldrich (Merck).<sup>11</sup> <sup>e</sup>not detected. <sup>f</sup>methyl 4-acetoxybenzoate (4%) was formed as additional side product.

The selection of NiBr<sub>2</sub>·3H<sub>2</sub>O for further studies was based on reactivity, price (significantly cheaper compared to Ni(OTf)<sub>2</sub> and NiBr<sub>2</sub>·glyme) and selectivity (formation methyl 4-chlorobenzoate in case of NiCl<sub>2</sub>).

## 4.5. Screening of ligands

**Table S4.** Ligand screening.<sup>a</sup>

Entry	Ligand	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>
1		62	57	3
2		45	42	3
3		50	47	3
5		26	23	2
6		52	48	4
7		12	6	5

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), ligand (30 μmol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h.

<sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard.

During the study it was observed that the LED strips used in the RGB photoreactor become less efficient as they are used. As reactivity depends on the light intensity, periodic replacement of the LED strips was found to be necessary. Results reported in Table S4 were obtained right after replacing the light source, and are therefore higher than those obtained in the same conditions from the previous experiment (Table S3, entry 5).

6,6'-diamino-2,2'-bipyridyl (Entry 7) was tested because it was reported to improve the reaction when water is used as coupling partner in the nickel/photoredox catalyzed formation of phenols.<sup>18</sup>

## 4.6. Base screening

**Table S5.** Base screening.<sup>a</sup>

Entry	Base	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>	3 [%] <sup>c</sup>
1	BIPA + quinuclidine (10 mol%)	78	73	4	n.d. <sup>d</sup>
2	BIPA	62	57	3	n.d.
3	DBU <sup>e</sup>	10	4	n.d.	5
4	Et <sub>3</sub> N	23	17	2	4
5	DIPEA <sup>f</sup>	16	7	1	8
6	tetramethyguanidine	4	4	n.d.	n.d.
7	DABCO <sup>g</sup>	<1	n.d.	n.d.	n.d.
8	DMAP <sup>h</sup>	<1	n.d.	n.d.	n.d.
9	CsOAc	<1	n.d.	n.d.	n.d.
10	CsF	<1	n.d.	n.d.	n.d.
11	Cs <sub>2</sub> CO <sub>3</sub>	<1	n.d.	n.d.	n.d.
12	K <sub>2</sub> CO <sub>3</sub>	<1	n.d.	n.d.	n.d.
13	K <sub>3</sub> PO <sub>4</sub>	<1	n.d.	n.d.	n.d.

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), base (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected. <sup>e</sup>1,8-Diazabicyclo[5.4.0]undec-7-ene <sup>f</sup>*N,N*-Diisopropylethylamine. <sup>g</sup>1,4-Diazabicyclo[2.2.2]octane. <sup>h</sup>4-(dimethylamino)pyridine.

*N*-*tert*-butylisopropylamine (BIPA) performed best during the screening of different bases (Table S5). No conversion of the starting material was detected using common inorganic bases (Table S5, entries 9-13). The addition of quinuclidine (10 mol%, Sigma Aldrich, 13786 € mol<sup>-1</sup>) increased the product formation by only 15% and was therefore not used in the subsequent tests.<sup>11</sup>

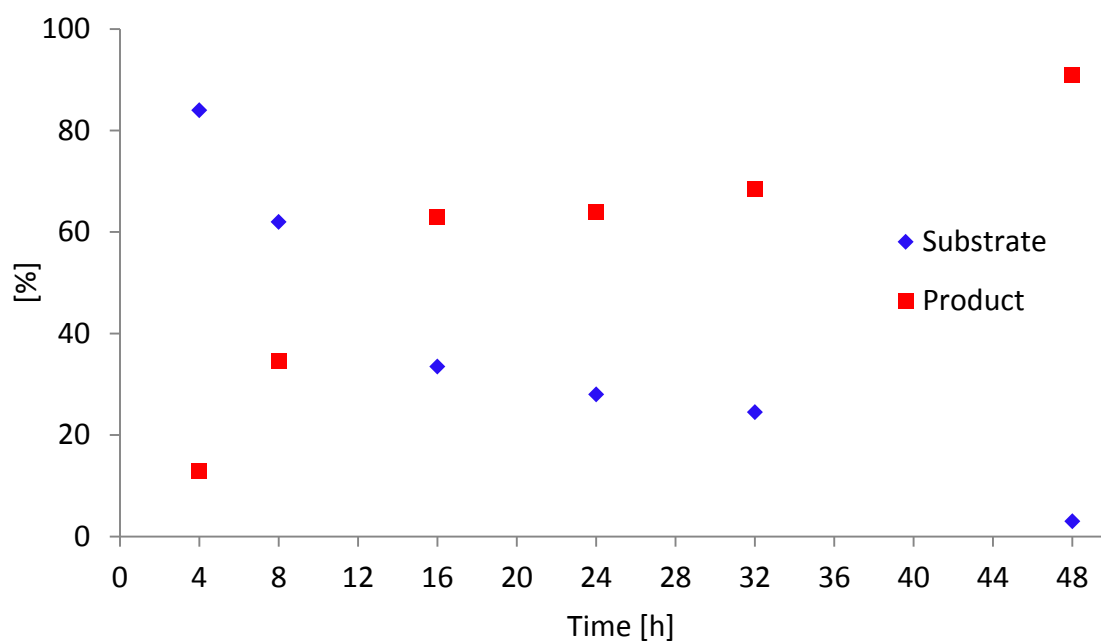
## 4.7. Screening of reaction conditions

### 4.7.1. Time

**Table S6.** Time study.<sup>a</sup>

$  \begin{array}{c}  \text{Br} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO}_2\text{Me} \\  0.1 \text{ M}  \end{array}  + n\text{-hex-OH} \xrightarrow[\text{white LED, } \sim 40^\circ\text{C}]{\begin{array}{c} \text{CN-OA-m (3.33 mg/mL)} \\ \text{NiBr}_2 \cdot 3\text{H}_2\text{O (10 mol\%)} \\ \text{dtbbpy (10 mol\%)} \\ \text{BIPA (3.0 equiv)} \\ \text{MeCN (deg.)} \end{array}}  \begin{array}{c}  n\text{-hex-O-C}_6\text{H}_4\text{---CO}_2\text{Me} \\  \mathbf{1}  \end{array}  + \begin{array}{c}  \text{HO-C}_6\text{H}_4\text{---CO}_2\text{Me} \\  \mathbf{2}  \end{array}  + \begin{array}{c}  \text{H-C}_6\text{H}_4\text{---CO}_2\text{Me} \\  \mathbf{3}  \end{array}  $					
Entry	Time [h]	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>	3 [%] <sup>c</sup>
1	4	16	13	2	n.d. <sup>d</sup>
2	8	38	35	2	n.d.
3	16	62	57	3	n.d.
4	24	70	66	4	n.d.
5	32	75	69	4	2
6	48	97	91	5	n.d.

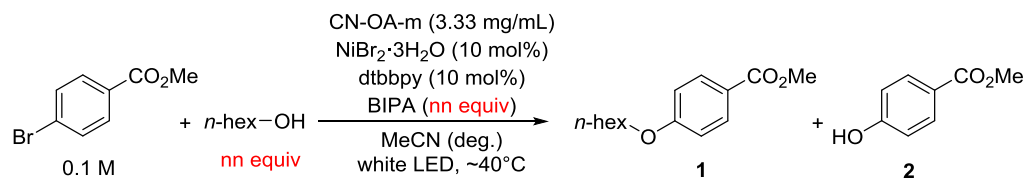
<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for the indicated time. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.



**Figure S7:** Time study (data from Table S6).

#### 4.7.2. Stoichiometry optimization

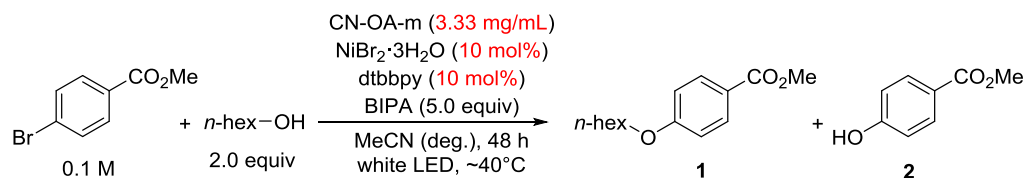
**Table S7.** Optimization of stoichiometry of alcohol and base.<sup>a</sup>



Entry	1-hexanol [equiv]	BIPA [equiv]	Time [h]	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>
1	3.0	3.0	16	62	57	3
1	3.0	3.0	24	70	66	4
1	3.0	3.0	48	97	91	5
2	2.0	3.0	16	55	51	4
3	2.0	5.0	16	65	59	5
3	2.0	5.0	24	95	86	8
4	2.0	5.0	48	>99	92	7

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 or 0.9 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), BIPA (0.9 or 1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 to 48h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.

A reduction of the amount of alcohol was realized using a higher amount of BIPA (Table S7, entry 3).

**Table S8.** Optimization of the stoichiometry of the Ni catalyst and carbon nitride material.<sup>a</sup>

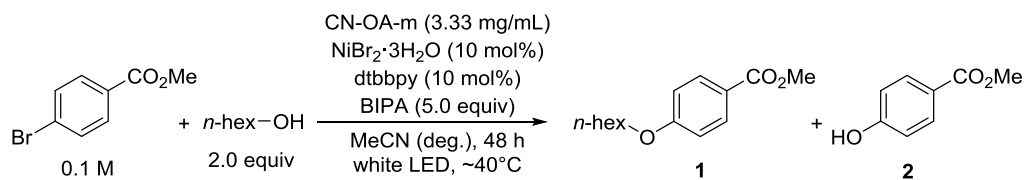
Entry	Deviation from standard conditions	Conversion [%] <sup>b</sup>	<b>1</b> [%] <sup>c</sup>	<b>2</b> [%] <sup>c</sup>
1	None	>99	92	7
2	NiBr <sub>2</sub> ·3H <sub>2</sub> O (5 mol%) with dtbbpy (5 mol%)	83	77	6
3	CN-OA-m (1.66 mg/ml)	94	90	4

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (5 or 10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (15 or 30 μmol), dtbbpy (15 or 30 μmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Reducing the amount of the Nickel catalyst resulted in significantly lower conversion within 48 hours. The CN-OA-m (Table S8, entry 3) can be reduced resulting in slightly lower yields. Since the photocatalyst is inexpensive and recyclable, 3.33 mg ml<sup>-1</sup> was maintained as loading for further experiments.

## 4.8. Control studies

**Table S9.** Control studies.<sup>a</sup>



Entry	Deviation from standard conditions	Conversion [%] <sup>b</sup>	<b>1</b> [%] <sup>c</sup>	<b>2</b> [%] <sup>c</sup>
1	None	>99	92	7
2	No CN-OA-m	<1	n.d. <sup>d</sup>	n.d.
3	No NiBr <sub>2</sub> ·3H <sub>2</sub> O	6	n.d.	n.d.
4	No dtbbpy	5	n.d.	n.d.
5	No BIPA	<1	n.d.	n.d.
6	No light	<1	n.d.	n.d.
7	No degassing	<1	n.d.	n.d.

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.

## 4.9. Screening of aryl (pseudo)halides

**Table S10.** Screening of aryl (pseudo)halides.<sup>a</sup>

COc1ccc(X)cc1 (0.1 M) +  $n$ -hex-OH (2.0 equiv)  $\xrightarrow[\text{MeCN (deg.), 48 h, white LED, } \sim 40^{\circ}\text{C}]{\text{CN-OA-m (3.33 mg/mL), NiBr}_2\cdot 3\text{H}_2\text{O (10 mol\%), dtbbpy (10 mol\%), BIPA (5.0 equiv)}}$ 
COc1ccc(OCC)cc1 (1) + COc1ccc(O)cc1 (2)

Entry	X	Conversion [%] <sup>b</sup>	1 [%] <sup>c</sup>	2 [%] <sup>c</sup>
1	Br	>99	92	7
2	I	13	13	n.d. <sup>d</sup>
3	Cl	6	4	n.d.
4	OMs	<1	n.d.	n.d.
5	OTs	<1	n.d.	n.d.
6	OTf	<1	n.d.	n.d.

<sup>a</sup>Reaction conditions: aryl (pseudo)halide (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.



## 4.10. Intramolecular etherification

**Table S11.** Intramolecular etherification for the formation of oxygen heterocycles.<sup>a</sup>

<div style="text-align: center;"> <p>             CN-OA-m (3.33 mg/mL)              NiBr<sub>2</sub>·3H<sub>2</sub>O (10 mol%)              dtbbpy (10 mol%)              BIPA (5.0 equiv)              MeCN (deg.), 168 h              white LED, ~40°C           </p> </div>			
Entry	Substrate	Product	Substrate/Product <sup>b</sup>
1 <sup>c</sup>		<b>37</b>	34/56
2			>99/0
3			>99/0

<sup>a</sup>Reaction conditions: substrate (0.6 mmol), CN-OA-m (20 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (60 μmol), dtbbpy (60 μmol), BIPA (3.0 mmol), MeCN (6.0 mL), white LEDs at 40 °C for 168 h. <sup>b</sup>Ratio calculated from <sup>1</sup>H NMR analysis. <sup>c</sup>No product formation was detected in absence of CN-OA-m, NiBr<sub>2</sub>·3H<sub>2</sub>O, dtbbpy, BIPA or light.

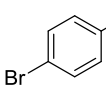

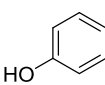
## 5. Reaction optimization for the coupling of aryl bromides and water

### 5.1. General experimental procedure for screening experiments

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (8.2 mg, 30  $\mu\text{mol}$ , 10 mol%), the ligand (8.1 mg, 30  $\mu\text{mol}$ , 10 mol%), the CN-OA-m (10 mg) and methyl 4-bromobenzoate (64.5 mg, 0.3 mmol, 1.0 equiv). Subsequently, the solvent (3.0 mL), BIPA (172.8 mg, 1.5 mmol, 5.0 equiv) and  $\text{H}_2\text{O}$  (5.4 – 108.0 mg, 0.3 – 6.0 mmol, 1 - 20 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5 - 10 min, followed by stirring for 5 min until a fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the low intensity RGB photoreactor with white light at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) was added. An aliquot of the reaction mixture (~200  $\mu\text{L}$ ) was filtered, diluted with  $\text{DMSO}-d_6$  and subjected to  $^1\text{H}$ -NMR analysis.

### 5.2. Solvent screening

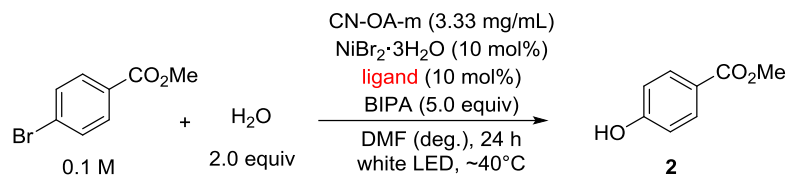
**Table S12.** Solvent screening.<sup>a</sup>

<div><div><div><div><div></div><div>0.1 M</div></div><div>+</div><div><div><div></div><div>2.0 equiv</div></div></div><div><div><div><div>CN-OA-m (3.33 mg/mL) NiBr<sub>2</sub>·3H<sub>2</sub>O (10 mol%) dtbbpy (10 mol%) BIPA (5.0 equiv) solvent (deg.), 48 h white LED, ~40°C</div><div>→</div></div></div><div><div><div><div></div><div>2</div></div></div></div></div></div></div></div>			
Entry	Solvent	Conversion [%] <sup>b</sup>	2 [%] <sup>c</sup>
1	MeCN	<1	n.d. <sup>d</sup>
2	MeCN/DMF (1:1)	23	22
3	DMF	50	49

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol),  $\text{H}_2\text{O}$  (0.6 mmol), CN-OA-m (10 mg),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (30  $\mu\text{mol}$ ), dtbbpy (30  $\mu\text{mol}$ ), BIPA (1.5 mmol), solvent (3.0 mL), white LEDs at 40 °C for 48 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by  $^1\text{H}$ -NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by  $^1\text{H}$ -NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>not detected.

### 5.3. Ligand screening

**Table S13.** Ligand screening.<sup>a</sup>

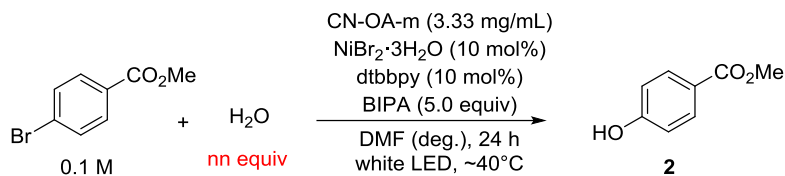


Entry	Ligand	Conversion [%] <sup>b</sup>	<b>2</b> [%] <sup>c</sup>
1		43	42
2		38	37

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (0.3 mmol),  $\text{H}_2\text{O}$  (0.6 mmol), CN-OA-m (10 mg),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (30  $\mu\text{mol}$ ), ligand (30  $\mu\text{mol}$ ), BIPA (1.5 mmol), DMF (3.0 mL), white LEDs at  $40^\circ\text{C}$  for 24 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by  $^1\text{H-NMR}$  using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by  $^1\text{H-NMR}$  using 1,3,5-trimethoxybenzene as internal standard.

## 5.4. Stoichiometry optimization

**Table S14.** Optimization of stoichiometry of water.<sup>a</sup>



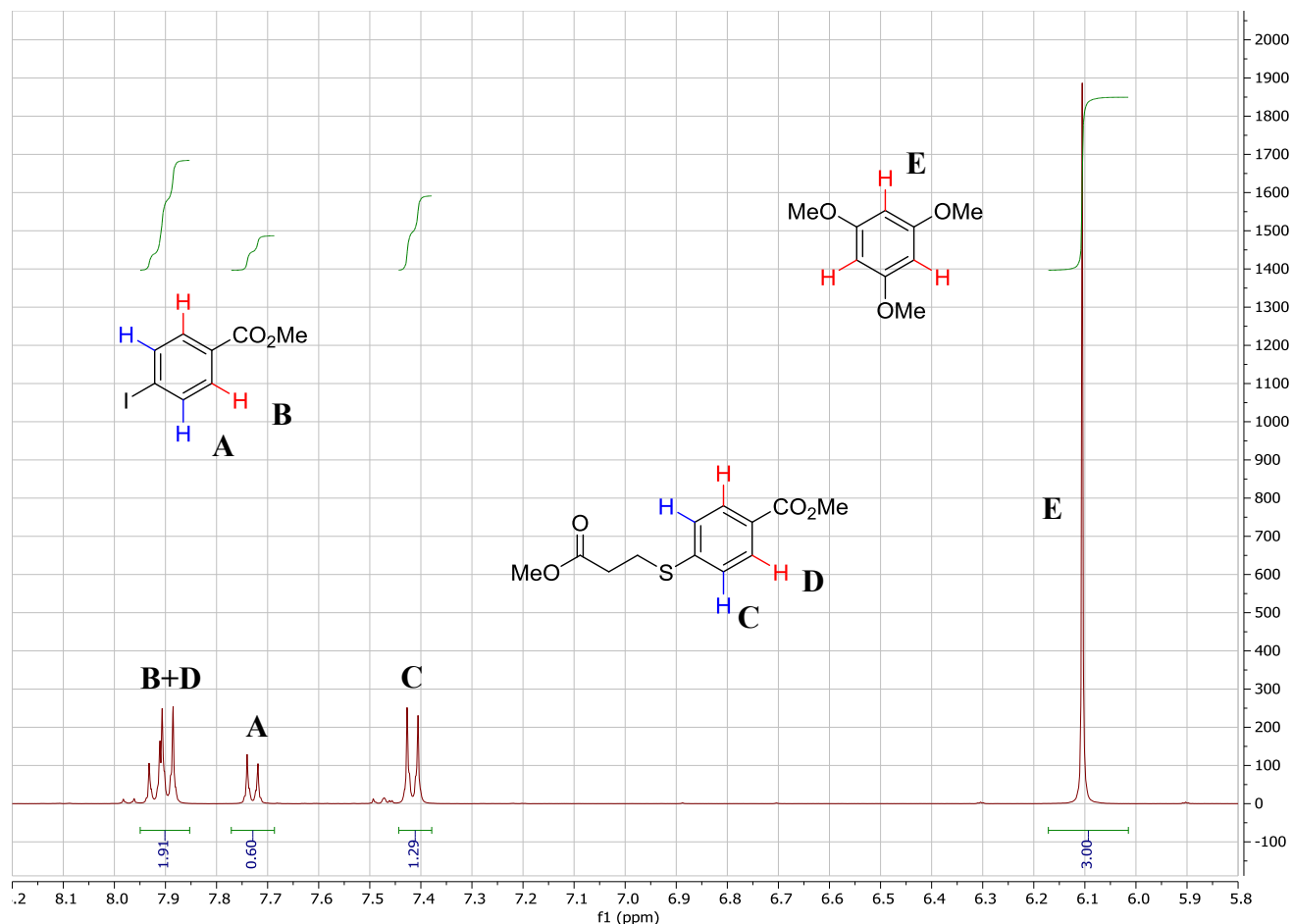
Entry	$\text{H}_2\text{O}$ [equiv]	Conversion [%] <sup>b</sup>	<b>2</b> [%] <sup>c</sup>
1	1	45	45
2	2	43	42
3	5	47	47
4	10	35	30
5	20	29	23

<sup>a</sup>Reaction conditions methyl 4-bromobenzoate (0.3 mmol),  $\text{H}_2\text{O}$  (0.3 to 6.0 mmol), CN-OA-m (10 mg),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (30  $\mu\text{mol}$ ), dtbbpy (30  $\mu\text{mol}$ ), BIPA (1.5 mmol), DMF (3.0 mL), white LEDs at  $40^\circ\text{C}$  for 24 h. <sup>b</sup>Conversion of methyl 4-bromobenzoate determined by  $^1\text{H}$ -NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup>NMR yields determined by  $^1\text{H}$ -NMR using 1,3,5-trimethoxybenzene as internal standard.

## 6. Reaction optimization for the coupling of aryl iodides and thiols

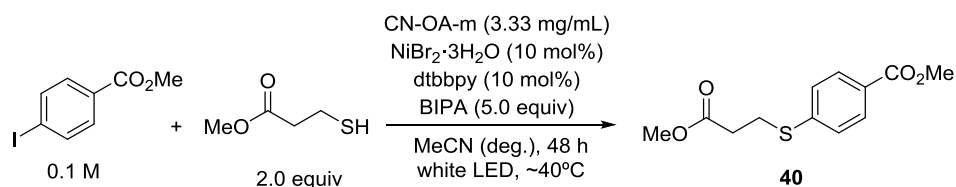
### 6.1. General experimental procedure for screening experiments

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (8.2 mg, 30  $\mu\text{mol}$ , 10 mol%), dtbbpy (8.1 mg, 30  $\mu\text{mol}$ , 10 mol%), the CN-OA-m (10 mg) and methyl 4-iodobenzoate (76.8 mg, 0.3 mmol, 1.0 equiv). Subsequently, MeCN (3.0 mL), BIPA (172.8 mg, 1.5 mmol, 5.0 equiv) and methyl 3-mercaptopropionate (72.1 mg, 0.6 mmol, 2.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5 - 10 min, followed by stirring for 5 min until a fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the low intensity RGB photoreactor with white light at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (50.5 mg, 0.3 mmol) was added. An aliquot of the reaction mixture (~200  $\mu\text{L}$ ) was filtered, diluted with  $\text{DMSO}-d_6$  and subjected to  $^1\text{H}$ -NMR analysis. For a representative NMR spectrum, see Figure S8.



**Figure S8.** Example of a crude  $^1\text{H}$ -NMR spectrum of the reaction between methyl 4-iodobenzoate and methyl 3-mercaptopropionate.

**Table S15.** Studies on the thioetherification of methyl 4-iodobenzoate and methyl 3-mercaptopropionate.<sup>a, b</sup>



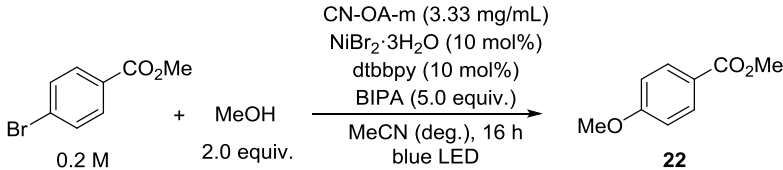
Entry	Deviation from standard conditions	Conversion [%] <sup>c</sup>	<b>40</b> [%] <sup>d</sup>
1	None	>99	94
2	Methyl 4-bromobenzoate as substrate	5	4
3	1.0 equiv of thiol	50	46
4	Pyridine (5.0 equiv) as base	43	n.d. <sup>e</sup>
5	DBU (5.0 equiv) as base	35	n.d. <sup>f</sup>
6	Reaction time 24 hours	93	92
7	Reaction time 16 hours	70	65
8	No CN-OA-m	5	3
9	No NiBr <sub>2</sub> ·3H <sub>2</sub> O	13	6
10	No dtbbpy	4	n.d.
11	No BIPA	3	n.d.
12	No light	4	1
13	No degassing	79	68

<sup>a</sup>Reaction conditions: methyl 4-iodobenzoate (0.3 mmol), methyl 3-mercaptopropionate (0.6 mmol), CN-OA-m (10 mg), NiBr<sub>2</sub>·3H<sub>2</sub>O (30 μmol), dtbbpy (30 μmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. <sup>b</sup>An unidentified side product was detected in all experiments (1 to 20%). <sup>c</sup>Conversion of methyl 4-iodobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup>NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. <sup>e</sup>not detected because overlapping with pyridine signals. <sup>f</sup>not detected.

## 7. Recycling of CN-OA-m

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with CN-OA-m (20 mg),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (32.7 mg, 120  $\mu\text{mol}$ , 10 mol%), dtbbpy (32.2 mg, 120  $\mu\text{mol}$ , 10 mol%) and methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv). Subsequently, MeCN (6 mL), BIPA (691.3 mg, 6.0 mmol, 5.0 equiv) and methanol (64.9 mg, 2.4 mmol, 2.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min, followed by stirring for 5 min until fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the high intensity 440 nm photoreactor with rapid stirring. After 16 hours, one equivalent of 1,3,5-trimethoxybenzene (201.8 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. The reaction mixture was centrifuged at 3500 rpm for 60 min and the liquid phase was carefully separated and analyzed by  $^1\text{H}$ -NMR. The solid was washed twice with MeCN (6 mL, followed by centrifugation at 3500 rpm for 30 min and separation of the liquid phase), lyophilized (overnight) and reused in the next reaction.

**Table S16.** Recycling of CN-OA-m.<sup>a</sup>

	
Cycle	Yield [%] <sup>b</sup>
1	91
2	92
3	84
4	79
5	96
6	92

<sup>a</sup>Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), methanol (2.4 mmol), CN-OA-m (20 mg),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (120  $\mu\text{mol}$ ), dtbbpy (120  $\mu\text{mol}$ ), BIPA (6.0 mmol), MeCN (6.0 mL), blue LEDs for 16 h. <sup>b</sup>NMR yields determined by  $^1\text{H}$ -NMR using 1,3,5-trimethoxybenzene as internal standard.



**Figure S9.** Fresh CN-OA-m (**A**) and CN-OA-m after six recycling experiments (**B**).

Measurement	Nickel concentration [mg/g]
1	217
2	214
3	219
Average	217

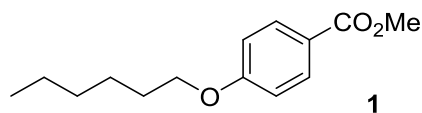
**Table S17.** ICP-OES analysis of recovered CN-OA-m after the recycling study.



## 8. Scope and Limitations

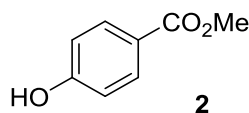
### 8.1. General procedure for the semi-heterogeneous dual nickel/photocatalytic etherification.

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with the aryl bromide (1.2 mmol, 1.0 equiv),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (32.7 mg, 120  $\mu\text{mol}$ , 10 mol%), dtbbpy (32.2 mg, 120  $\mu\text{mol}$ , 10 mol%) and CN-OA-m (20 mg). Subsequently, MeCN (6.0 mL), BIPA (691.3 mg, 6.0 mmol, 5.0 equiv) and the alcohol (2.0 – 4.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5 - 10 min followed by stirring for 5 min until a fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the low intensity RGB photoreactor with white light at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, an aliquot of the reaction mixture (~200  $\mu\text{L}$ ) was filtered, diluted with  $\text{DMSO}-d_6$  and subjected to  $^1\text{H}$ -NMR analysis. Thereafter, the NMR sample was combined with the reaction mixture, diluted with  $\text{H}_2\text{O}$  (40 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic phases were washed with aqueous NaOH (1M, 2x40 mL) and brine (40 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The product was purified by flash column chromatography ( $\text{SiO}_2$ , Hexane/EtOAc) on a Grace<sup>TM</sup> Reveleris<sup>TM</sup> system using a 12 g cartridge.



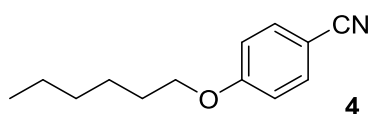
**Methyl 4-(hexyloxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 87% yield (246.0 mg, 1.04 mmol) as colorless oil using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.9 Hz, 2H), 6.89 (d,  $J$  = 8.9 Hz, 2H), 3.99 (t,  $J$  = 6.6 Hz, 2H), 3.87 (s, 3H), 1.84 – 1.74 (m, 2H), 1.51 – 1.39 (m, 2H), 1.37 – 1.28 (m, 4H), 0.97 – 0.77 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.92, 162.94, 131.55, 122.26, 114.03, 68.18, 51.84, 31.56, 29.09, 25.68, 22.61, 14.05. These data are in full agreement with those previously published in the literature.<sup>19</sup>



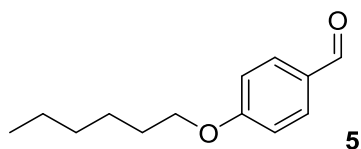
**Methyl 4-hydroxybenzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and water (108.1 mg, 6.0 mmol, 5.0 equiv), using DMF as solvent. The title compound was isolated after irradiation for 120 hours in 52% yield (93.8 mg, 0.62 mmol) as white solid using an elution gradient of 0-10% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.8 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 6.18 (s, 1H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.35, 160.13, 131.98, 122.40, 115.28, 52.12. These data are in full agreement with those previously published in the literature.<sup>18</sup>



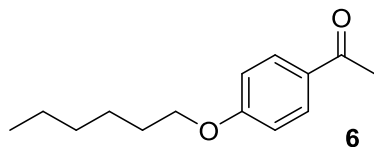
**4-(hexyloxy)benzonitrile.** From 4-bromobenzonitrile (218.4 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 91% yield (221.3 mg, 1.09 mmol) as colorless oil using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 8.8 Hz, 2H), 6.92 (d,  $J$  = 8.8 Hz, 2H), 3.98 (t,  $J$  = 6.5 Hz, 2H), 1.91 – 1.67 (m, 2H), 1.52 – 1.39 (m, 2H), 1.37 – 1.30 (m, 4H), 0.94 – 0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.45, 133.89, 119.31, 115.16, 103.53, 68.39, 31.50, 28.94, 25.61, 22.57, 14.02. These data are in full agreement with those previously published in the literature.<sup>20</sup>



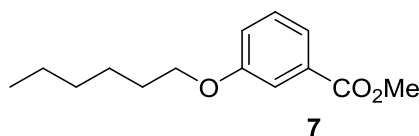
**4-(hexyloxy)benzaldehyde.** From 4-bromobenzaldehyde (222.0 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 83% yield (204.5 mg, 0.99 mmol) as yellowish oil using an elution gradient of 0-5% of ethyl acetate in hexane.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.82 (s, 1H), 7.76 (d,  $J$  = 8.8 Hz, 2H), 6.93 (d,  $J$  = 8.8 Hz, 2H), 3.98 (t,  $J$  = 6.5 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.45 – 1.38 (m, 2H), 1.34 – 1.26 (m, 4H), 0.86 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.61, 164.19, 131.87, 129.70, 114.68, 68.35, 31.47, 28.97, 25.58, 22.52, 13.95. These data are in full agreement with those previously published in the literature.<sup>21</sup>



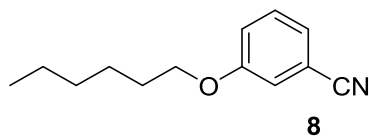
**1-(4-(hexyloxy)phenyl)ethan-1-one.** From 4-bromoacetophenone (238.9 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 90% yield (238.0 mg, 1.08 mmol) as colorless oil using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.9 Hz, 2H), 6.93 (d,  $J$  = 8.9 Hz, 2H), 4.02 (t,  $J$  = 6.6 Hz, 2H), 2.56 (s, 3H), 1.86 – 1.76 (m, 2H), 1.54 – 1.42 (m, 2H), 1.39 – 1.32 (m, 4H), 0.96 – 0.89 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.82, 163.12, 130.58, 130.05, 114.11, 68.25, 31.55, 29.07, 26.36, 25.66, 22.60, 14.05. These data are in full agreement with those previously published in the literature.<sup>19</sup>



**Methyl 3-(hexyloxy)benzoate.** From methyl 3-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 62% yield (175.4 mg, 0.74 mmol) as colorless oil using an elution gradient of 0-5% of ethyl acetate in hexane.

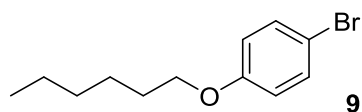
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J$  = 7.7 Hz, 1H), 7.53 (s, 1H), 7.29 (t,  $J$  = 7.9 Hz, 1H), 7.08 – 7.03 (m, 1H), 3.95 (t,  $J$  = 6.6 Hz, 2H), 3.87 (s, 3H), 1.80 – 1.71 (m, 2H), 1.48 – 1.39 (m, 2H), 1.35 – 1.29 (m, 4H), 0.89 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.92, 159.10, 131.32, 129.27, 121.70, 119.83, 114.60, 68.11, 52.03, 31.55, 29.14, 25.68, 22.59, 13.99. These data are in full agreement with those previously published in the literature.<sup>22</sup>



**3-(hexyloxy)benzonitrile.** From 3-bromobenzonitrile (218.4 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 120 hours in 85% yield (207.3 mg, 1.02 mmol) as colorless oil using an elution gradient of 0-5% of ethyl acetate in hexane.

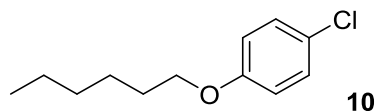
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.25 (m, 1H), 7.13 (d,  $J$  = 7.6 Hz, 1H), 7.08 – 7.03 (m, 2H), 3.89 (t,  $J$  = 6.6 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.25 (m, 4H), 0.86 (t,  $J$  = 6.8 Hz,

3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.19, 130.23, 124.07, 119.61, 118.65, 117.34, 113.08, 68.34, 31.47, 28.95, 25.58, 22.53, 13.94. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}$ : 203.1310; found: 203.1313.



**1-bromo-4-(hexyloxy)benzene.** From 1,4-dibromobenzene (283.1 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 120 hours in 80% yield (245.9 mg, 0.96 mmol) as colorless oil using an elution gradient of 0-4% of ethyl acetate in hexane.

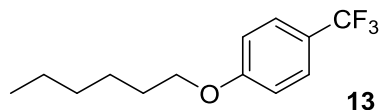
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 8.9 Hz, 2H), 6.78 (d,  $J$  = 8.9 Hz, 2H), 3.90 (t,  $J$  = 6.6 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.51 – 1.43 (m, 2H), 1.42 – 1.31 (m, 4H), 0.94 (t,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  158.29, 132.18, 116.29, 112.55, 68.23, 31.62, 29.20, 25.73, 22.65, 14.07. These data are in full agreement with those previously published in the literature.<sup>23</sup>



**1-chloro-4-(hexyloxy)benzene.** From 1-bromo-4-chlorobenzene (229.7 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 62% yield (156.5 mg, 0.74 mmol) as colorless oil using an elution gradient of 0-1% of ethyl acetate in hexane.

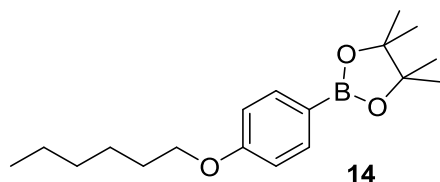
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J$  = 8.9 Hz, 2H), 6.81 (d,  $J$  = 8.9 Hz, 2H), 3.91 (t,  $J$  = 6.6 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.48 – 1.40 (m, 2H), 1.37 – 1.30 (m, 4H), 0.91 (t,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  157.75, 129.22, 125.25, 115.74, 68.31, 31.56, 29.15, 25.67, 22.58, 14.01.

These data are in full agreement with those previously published in the literature.<sup>24</sup>



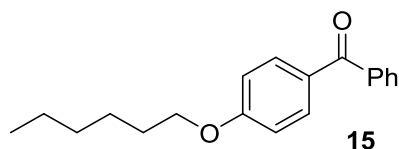
**1-(hexyloxy)-4-(trifluoromethyl)benzene.** From 4-bromobenzotrifluoride (270.0 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 79% yield (233.7 mg, 0.95 mmol) as colorless oil using an elution gradient of 0-1% of ethyl acetate in hexane.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J$  = 8.5 Hz, 2H), 6.94 (d,  $J$  = 8.5 Hz, 2H), 3.98 (t,  $J$  = 6.6 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.51 – 1.44 (m, 2H), 1.39 – 1.32 (m, 4H), 0.92 (t,  $J$  = 6.7 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  161.63, 126.77 (q,  $J$  = 3.6 Hz), 124.52 (q,  $J$  = 270.9 Hz), 122.56 (q,  $J$  = 32.6 Hz), 114.38, 68.19, 31.52, 29.04, 25.64, 22.56, 13.93.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.51. These data are in full agreement with those previously published in the literature.<sup>19</sup>



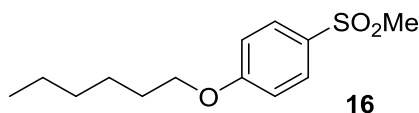
**2-(4-(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** From 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (339.6 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 82% yield (298.6 mg, 0.98 mmol) as yellowish oil using an elution gradient of 0-3% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J$  = 8.6 Hz, 2H), 6.91 (d,  $J$  = 8.6 Hz, 2H), 3.98 (t,  $J$  = 6.6 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.53 – 1.42 (m, 2H), 1.41 – 1.28 (m, 16H), 0.93 (t,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.78, 136.51, 120.33 (br s), 113.85, 83.47, 67.74, 31.61, 29.20, 25.73, 24.87, 22.63, 14.07. These data are in full agreement with those previously published in the literature.<sup>25</sup>



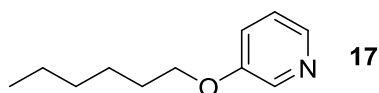
**(4-(hexyloxy)phenyl)(phenyl)methanone.** From (4-bromophenyl)(phenyl)methanone (313.3 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 84% yield (286.0 mg, 1.01 mmol) as white solid using an elution gradient of 0-3% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J$  = 8.9 Hz, 2H), 7.75 (d,  $J$  = 6.9 Hz, 2H), 7.54 (t,  $J$  = 7.4 Hz, 1H), 7.45 (t,  $J$  = 7.4 Hz, 2H), 6.94 (d,  $J$  = 8.9 Hz, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.52 – 1.41 (m, 2H), 1.40 – 1.29 (m, 4H), 0.97 – 0.88 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.42, 162.87, 138.32, 132.55, 131.84, 129.81, 129.70, 128.17, 114.00, 68.25, 31.58, 29.10, 25.70, 22.63, 14.10. These data are in full agreement with those previously published in the literature.<sup>26</sup>



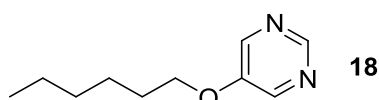
**1-(hexyloxy)-4-(methylsulfonyl)benzene.** From 1-bromo-4-(methylsulfonyl)benzene (282.1 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 120 hours in 81% yield (247.4 mg, 0.97 mmol) as white solid using an elution gradient of 0-15% of ethyl acetate in hexane.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.8 Hz, 2H), 6.97 (d,  $J$  = 8.8 Hz, 2H), 3.99 (t,  $J$  = 6.5 Hz, 2H), 2.99 (s, 3H), 1.81 – 1.73 (m, 2H), 1.47 – 1.40 (m, 2H), 1.35 – 1.28 (m, 4H), 0.88 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  163.28, 131.93, 129.46, 114.89, 68.55, 44.83, 31.45, 28.91, 25.56, 22.52, 13.97. These data are in full agreement with those previously published in the literature.<sup>19</sup>



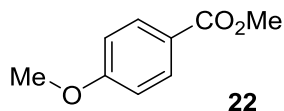
**3-(hexyloxy)pyridine.** From 3-bromopyridine (189.6 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 39% yield (84.2 mg, 0.47 mmol) as yellowish oil using an elution gradient of 0-3% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J$  = 2.6, 1.0 Hz, 1H), 8.21 (dd,  $J$  = 4.3, 1.8 Hz, 1H), 7.24 – 7.15 (m, 2H), 4.00 (t,  $J$  = 6.5 Hz, 2H), 1.89 – 1.73 (m, 2H), 1.54 – 1.42 (m, 2H), 1.41 – 1.30 (m, 4H), 0.92 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.25, 141.88, 138.04, 123.79, 120.98, 68.30, 31.55, 29.13, 25.64, 22.60, 14.05. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{18}\text{NO}$   $[(\text{M}+\text{H})^+]$  180.1388, found 180.1385.



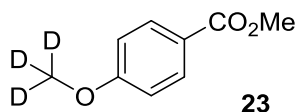
**5-(hexyloxy)pyrimidine.** From 3-bromopyrimidine (190.8 mg, 1.2 mmol, 1.0 equiv) and 1-hexanol (245.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 55% yield (118.6 mg, 0.66 mmol) as yellowish oil using an elution gradient of 0-10% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (s, 1H), 8.31 (s, 2H), 3.97 (t,  $J$  = 6.5 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.44 – 1.33 (m, 2H), 1.31 – 1.20 (m, 4H), 0.82 (t,  $J$  = 6.6 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.02, 151.20, 143.45, 68.66, 31.37, 28.89, 25.41, 22.46, 13.91. These data are in full agreement with those previously published in the literature.<sup>19</sup>



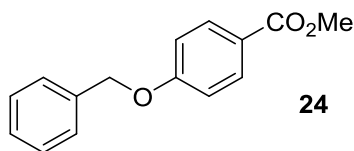
**Methyl 4-methoxybenzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and methanol (76.9 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 24 hours in 80% yield (160.1 mg, 0.96 mmol) as white solid using an elution gradient of 0-5% of ethyl acetate in hexane. The reaction can also be carried out in methanol as solvent resulting in 78 % (156.2 mg, 0.94 mmol) of the title compound after 8 hours irradiation.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J$  = 8.8 Hz, 2H), 6.87 (d,  $J$  = 8.8 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.78, 163.29, 131.53, 122.52, 113.54, 55.32, 51.77. These data are in full agreement with those previously published in the literature.<sup>27</sup>



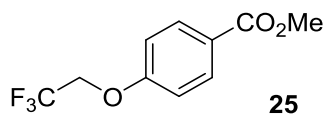
**Methyl 4-methoxybenzoate- $d_3$ .** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and methanol- $d_4$  (84.14 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 24 hours in 92% yield (185.4 mg, 1.10 mmol) as white solid using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 9.0 Hz, 2H), 6.85 (d,  $J$  = 9.0 Hz, 2H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.73, 163.29, 131.50, 122.51, 113.52, 54.47 (hept,  $J$  = 21.9 Hz), 51.70. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_9\text{H}_7\text{D}_3\text{O}_3$ : 169.0818; found: 169.0816. These data are in full agreement with those previously published in the literature.<sup>28</sup>



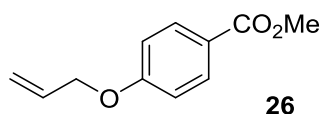
**Methyl 4-(benzyloxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and benzyl alcohol (259.5 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 92% yield (267.4 mg, 1.10 mmol) as white solid using an elution gradient of 0-5% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.9 Hz, 2H), 7.46 – 7.32 (m, 5H), 7.00 (d,  $J$  = 8.9 Hz, 2H), 5.12 (s, 2H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.83, 162.48, 136.24, 131.62, 128.69, 128.22, 127.51, 122.82, 114.46, 70.08, 51.89. These data are in full agreement with those previously published in the literature.<sup>29</sup>



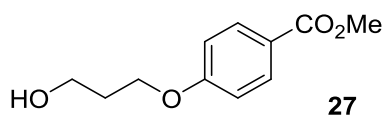
**Methyl 4-(2,2,2-trifluoroethoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (480.19 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 96 hours in 86% yield (240.4 mg, 1.03 mmol) as white solid using an elution gradient of 0-15% of ethyl acetate in hexane.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.6 Hz, 2H), 6.92 (d,  $J$  = 8.6 Hz, 2H), 4.37 (q,  $J$  = 8.0 Hz, 2H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.35, 160.68, 131.69, 124.41, 123.08 (q,  $J$  = 278.3 Hz), 114.30, 65.44 (q,  $J$  = 36.3 Hz), 51.88.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -74.01. These data are in full agreement with those previously published in the literature.<sup>30</sup>



**Methyl 4-(allyloxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and allyl alcohol (139.4 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 72 hours in 83% yield (192.1 mg, 1.00 mmol) as colorless oil using an elution gradient of 0-3% of ethyl acetate in hexane.

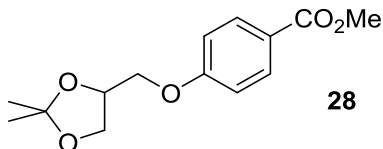
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J$  = 8.9 Hz, 2H), 6.88 (d,  $J$  = 8.9 Hz, 2H), 6.06 – 5.93 (m, 1H), 5.38 (d,  $J$  = 17.1 Hz, 1H), 5.27 (d,  $J$  = 10.6 Hz, 1H), 4.53 (d,  $J$  = 5.3 Hz, 2H), 3.84 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.72, 162.28, 132.55, 131.52, 122.64, 118.00, 114.25, 68.76, 51.78. These data are in full agreement with those previously published in the literature.<sup>31</sup>



**Methyl 4-(3-hydroxypropoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1,3-propanediol (365.3 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 24 hours in 74% yield (186.5 mg, 0.89 mmol) as colorless oil using an elution gradient of 0-35% of ethyl acetate in hexane.

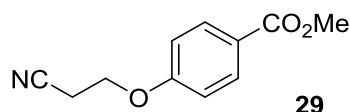
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.8 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 4.16 (t,  $J$  = 6.1 Hz, 2H), 3.91 – 3.82 (m, 5H), 2.24 – 2.19 (m, 1H), 2.10 – 2.02 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.98, 162.64, 131.61, 122.53, 114.06, 65.43, 59.77, 51.94, 31.88. HRMS-EI ( $m/z$ )  $[\text{M}^*]^+$  calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : 210.0892; found: 210.0883.





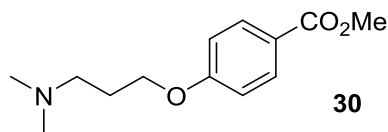
**methyl 4-((2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1,2-isopropylideneglycerol (317.2 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 88% yield (279.8 mg, 1.05 mmol) as reddish solid using an elution gradient of 0-15% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 9.0 Hz, 2H), 6.93 (d,  $J$  = 9.0 Hz, 2H), 4.49 (p,  $J$  = 5.8 Hz, 1H), 4.20 – 3.88 (m, 4H), 3.88 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.76, 162.22, 131.59, 123.02, 114.11, 109.90, 73.81, 68.79, 66.68, 51.91, 26.77, 25.32. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_5$ : 266.1154; found: 266.1152.



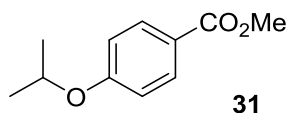
**Methyl 4-(2-cyanoethoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 3-hydroxypropanenitrile (341.2 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 72 hours in 76% yield (187.1 mg, 0.91 mmol) as white solid using an elution gradient of 0-2% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.5 Hz, 2H), 6.89 (d,  $J$  = 8.5 Hz, 2H), 4.20 (t,  $J$  = 6.3 Hz, 2H), 3.86 (s, 3H), 2.84 (t,  $J$  = 6.2 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.57, 161.31, 131.67, 123.61, 117.05, 114.14, 62.63, 51.97, 18.55. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{11}\text{H}_{11}\text{NO}_3$ : 205.0739; found: 205.0746.



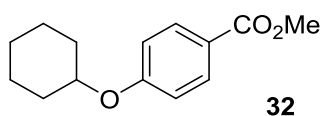
**Methyl 4-(3-(dimethylamino)propoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and *N,N'*-dimethyl-3-hydroxypropylamine (247.6 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 79% yield (224.3 mg, 0.95 mmol) as yellowish wax using an elution gradient of 0-15% of methanol in dichloromethane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J$  = 8.9 Hz, 2H), 6.88 (d,  $J$  = 8.9 Hz, 2H), 4.04 (t,  $J$  = 6.4 Hz, 2H), 3.85 (s, 3H), 2.46 (m, 2H), 2.25 (s, 6H), 1.96 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.85, 162.76, 131.53, 122.38, 114.04, 66.26, 56.13, 51.82, 45.36, 27.22. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{13}\text{H}_{19}\text{NO}_3$ : 237.1365; found: 237.1358.



**Methyl 4-isopropoxybenzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and isopropyl alcohol (288.5 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 120 hours in 84% yield (196.8 mg, 1.01 mmol) as colorless oil using an elution gradient of 0-3% of ethyl acetate in hexane.

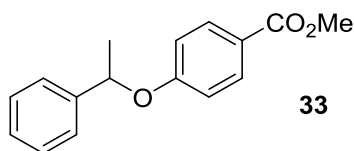
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.0 Hz, 2H), 6.84 (d,  $J$  = 8.0 Hz, 2H), 4.63 – 4.50 (m, 1H), 3.83 (s, 3H), 1.30 (d,  $J$  = 6.2 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.78, 161.77, 131.55, 122.03, 114.93, 69.89, 51.69, 21.82. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_3$ : 194.0943; found: 194.0939.



**Methyl 4-(cyclohexyloxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and cyclohexanol (480.8 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 120 hours in 82% yield (230.2 mg, 0.98 mmol) as white solid using an elution gradient of 0-4% of ethyl acetate in hexane.

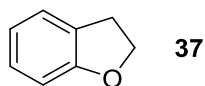
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.9 Hz, 2H), 6.89 (d,  $J$  = 8.9 Hz, 2H), 4.37 – 4.28 (m, 1H), 3.87 (s, 3H), 2.03 – 1.93 (m, 2H), 1.85 – 1.74 (m, 2H), 1.63 – 1.48 (m, 3H), 1.45 – 1.24 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.89, 161.74, 131.58, 122.01, 115.08, 75.30, 51.79, 31.58, 25.51, 23.64.

These data are in full agreement with those previously published in the literature.<sup>32</sup>



**Methyl 4-(1-phenylethoxy)benzoate.** From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1-phenylethanol (586.4 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 72 hours in 86% yield (264.8 mg, 1.03 mmol) as white solid using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 8.9 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.32 – 7.26 (m, 1H, contains residual solvent signal of  $\text{CDCl}_3$ ), 6.91 (d,  $J$  = 8.9 Hz, 2H), 5.41 (q,  $J$  = 6.4 Hz, 1H), 3.87 (s, 3H), 1.69 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.85, 161.78, 142.47, 131.49, 128.79, 127.73, 125.49, 122.43, 115.41, 76.17, 51.85, 24.49. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_3$ : 256.1099; found: 256.1091.

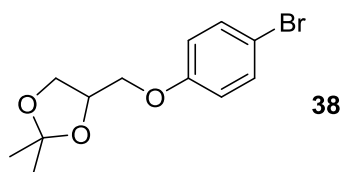


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### 2,3-dihydrobenzofuran.

From 2-(2-bromophenyl)ethanol (120.6 mg, 0.6 mmol, 1.0 equiv). The title compound was isolated after irradiation for 168 hours in 47% yield (33.4 mg, 0.28 mmol) as colorless oil using an elution gradient of 0-1% of diethyl ether in pentane.

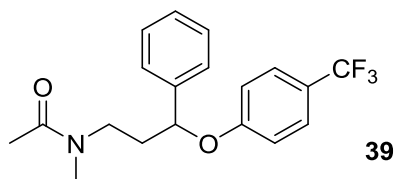
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J$  = 6.5 Hz, 1H), 7.14 (t,  $J$  = 7.7 Hz, 1H), 6.88 (t,  $J$  = 7.0 Hz, 1H), 6.83 (d,  $J$  = 8.0 Hz, 1H), 4.59 (t,  $J$  = 8.7 Hz, 2H), 3.24 (t,  $J$  = 8.7 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.00, 127.95, 126.89, 124.94, 120.35, 109.38, 71.05, 29.76. These data are in full agreement with those previously published in the literature.<sup>33</sup>



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**4-((4-bromophenoxy)methyl)-2,2-dimethyl-1,3-dioxolane.** From 1,4-dibromobenzene (283.1 mg, 1.2 mmol, 1.0 equiv) and 1,2-isopropylidenglycerol (634.4 mg, 4.8 mmol, 4.0 equiv). The title compound was isolated after irradiation for 120 hours in 61% yield (209.6 mg, 0.73 mmol) as white solid using an elution gradient of 0-10% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 8.7 Hz, 2H), 6.78 (d,  $J$  = 8.7 Hz, 2H), 4.45 (p,  $J$  = 5.9 Hz, 1H), 4.18 – 3.85 (m, 4H), 1.45 (s, 3H), 1.39 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.66, 132.27, 116.32, 113.29, 109.83, 73.88, 68.98, 66.70, 26.78, 25.34. These data are in full agreement with those previously published in the literature.<sup>34</sup>



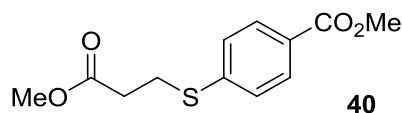
39

**N-methyl-N-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)acetamide.** From 4-bromobenzotrifluoride (270.0 mg, 1.2 mmol, 1.0 equiv) and N-(3-hydroxy-3-phenylpropyl)-N-methylacetamide (994.9 mg, 4.8 mmol, 4.0 equiv). After irradiation for 168 hours and  $^1\text{H}$  NMR analysis, the NMR sample and the reaction mixture were combined, diluted with  $\text{H}_2\text{O}$  (40 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic phases were washed with brine (40 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The title compound was isolated in 66% yield (277.8 mg, 0.79 mmol) as colorless oil using an elution gradient of 0-5% of ethyl acetate in DCM.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) rotameric mixture  $\delta$  7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H, contains residual solvent signal of  $\text{CDCl}_3$ ), 7.26 – 7.19 (m, 1H), 6.91 – 6.83 (m, 2H), 5.23 – 5.10 (m, 1H), 3.61 – 3.38 (m, 2H), 2.94 – 2.87 (m, 3H), 2.22 – 2.04 (m, 2H), 2.02 – 1.96 (m, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis  $\delta$  170.61 (170.51), 160.33 (159.94), 140.65 (139.99), (129.00) 128.76, (128.19) 127.89, (126.86 (q,  $J = 3.7$  Hz)) 126.73 (q,  $J = 3.6$  Hz), 125.72 (125.5), 124.36 (q,  $J = 271.1$  Hz) (124.26 (q,  $J = 271.3$  Hz)), 123.14 (q, 32.6 Hz) (122.76 (q,  $J = 32.6$  Hz)), 115.72 (115.64), 78.39 (minor rotamer overlapping with residual solvent signal), (47.03) 44.89, (37.31) 36.50, 36.30 (33.11), 21.84 (20.99).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis  $\delta$  -61.53 (-61.61). These data are in full agreement with those previously published in the literature.<sup>35</sup>

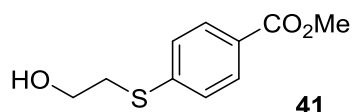
## 8.2. General procedure for the semi-heterogeneous dual nickel/photocatalytic thioetherification.

An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv),  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$  (32.7 mg, 120  $\mu\text{mol}$ , 10 mol%), dtbbpy (32.2 mg, 120  $\mu\text{mol}$ , 10 mol%) and CN-OA-m (20 mg). Subsequently, MeCN (6.0 mL), BIPA (691.3 mg, 6.0 mmol, 5.0 equiv) and the thiol (2.4 mmol, 2.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5 - 10 min, followed by stirring for 5 min until a fine dispersion of the solids was achieved. Thereafter, the mixture was degassed by bubbling argon for 10 min. The final reaction mixture was irradiated in the low intensity RGB photoreactor with white light at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, an aliquot of the reaction mixture (~200  $\mu\text{L}$ ) was filtered, diluted with  $\text{DMSO}-d_6$  and subjected to  $^1\text{H}$ -NMR analysis. Thereafter, the NMR sample was combined with the reaction mixture, diluted with  $\text{H}_2\text{O}$  (40 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic phases were washed with aqueous NaOH (1M, 2x40 mL) and brine (40 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The product was purified by flash column chromatography ( $\text{SiO}_2$ , Hexane/EtOAc) on a Grace<sup>TM</sup> Reveleris<sup>TM</sup> system using a 12 g cartridge.



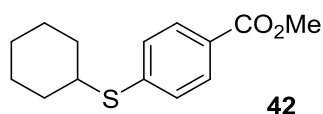
**Methyl 4-((3-methoxy-3-oxopropyl)thio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and methyl 3-mercaptopropionate (288.4 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 79% yield (242.1 mg, 0.95 mmol) as white solid using an elution gradient of 0-5% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.6 Hz, 2H), 7.31 (d,  $J$  = 8.6 Hz, 2H), 3.89 (s, 3H), 3.69 (s, 3H), 3.25 (t,  $J$  = 7.4 Hz, 2H), 2.68 (t,  $J$  = 7.4 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.90, 166.67, 142.61, 130.07, 127.24, 126.99, 52.12, 51.99, 33.68, 27.21. HRMS-EI ( $m/z$ ) [ $\text{M}^*$ ] $^+$  calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_4\text{S}$ : 254.0613; found: 254.0605.



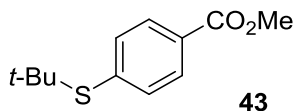
**Methyl 4-((2-hydroxyethyl)thio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and 2-mercaptoethanol (187.5 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 48 hours in 60% yield (152.9 mg, 0.72 mmol) as white solid using an elution gradient of 0-25% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 7.9 Hz, 2H), 7.33 (d,  $J$  = 7.9 Hz, 2H), 3.90 (s, 3H), 3.83 (m, 2H), 3.19 (t,  $J$  = 6.2 Hz, 2H), 2.66 – 2.56 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.83, 142.69, 130.05, 127.15, 127.06, 60.46, 52.20, 35.20. These data are in full agreement with those previously published in the literature.<sup>36</sup>



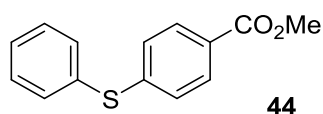
**Methyl 4-(cyclohexylthio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and cyclohexanethiol (278.9 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 96 hours in 53% yield (157.8 mg, 0.63 mmol) as colorless oil using an elution gradient of 0-5% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J$  = 8.1 Hz, 2H), 7.34 (d,  $J$  = 8.1 Hz, 2H), 3.90 (s, 3H), 3.36 – 3.21 (m, 1H), 2.12 – 1.96 (m, 2H), 1.86 – 1.72 (m, 2H), 1.68 – 1.58 (m, 1H), 1.51 – 1.19 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.80, 143.08, 129.88, 128.37, 127.03, 52.06, 44.96, 33.07, 25.95, 25.70. These data are in full agreement with those previously published in the literature.<sup>37</sup>



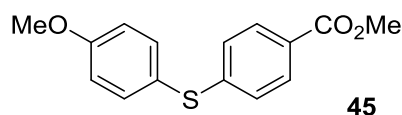
**Methyl 4-(tert-butylthio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and 2-methylpropanethiol (216.4 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 96 hours in 43% yield (117.3 mg, 0.52 mmol) as colorless oil using an elution gradient of 0-2% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.5 Hz, 2H), 7.59 (d,  $J$  = 8.5 Hz, 2H), 3.92 (s, 3H), 1.31 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.72, 138.96, 136.83, 130.05, 129.45, 52.23, 46.74, 31.06. These data are in full agreement with those previously published in the literature.<sup>37</sup>



**Methyl 4-(phenylthio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and thiophenol (264.4 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 144 hours in 33% yield (98.4 mg, 0.40 mmol) as white solid using an elution gradient of 0-5% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J$  = 8.6 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.45 – 7.36 (m, 3H), 7.23 (d,  $J$  = 8.6 Hz, 2H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.72, 144.46, 133.77, 132.31, 130.12, 129.69, 128.72, 127.52, 127.43, 52.14. These data are in full agreement with those previously published in the literature.<sup>38</sup>



**Methyl 4-((4-methoxyphenyl)thio)benzoate.** From methyl 4-iodobenzoate (314.4 mg, 1.2 mmol, 1.0 equiv) and 4-methoxybenzenethiol (336.5 mg, 2.4 mmol, 2.0 equiv). The title compound was isolated after irradiation for 168 hours in 41% yield (134.2 mg, 0.49 mmol) as white solid using an elution gradient of 0-4% of ethyl acetate in hexane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.6 Hz, 2H), 7.49 (d,  $J$  = 8.8 Hz, 2H), 7.10 (d,  $J$  = 8.6 Hz, 2H), 6.97 (d,  $J$  = 8.8 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.81, 160.61, 146.45, 136.81, 129.97, 126.67, 125.76, 121.52, 115.35, 55.43, 52.06. These data are in full agreement with those previously published in the literature.<sup>39</sup>

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## 10. Copies of NMR spectra of isolated compounds

