A carbon nitride material can be combined with homogeneous nickel catalysts for light-mediated cross-couplings of aryl bromides with alcohols under mild conditions. The metal-free heterogeneous semiconductor is fully recyclable and couples a broad range of electron-poor aryl bromides with primary and secondary alcohols as well as water. The application for intramolecular reactions and the synthesis of active pharmaceutical ingredients was demonstrated. The catalytic protocol is applicable for the coupling of aryl iodides with thiols as well.
Semi-Heterogeneous Dual Nickel/Photocatalytic (Thio)Etherification using Carbon Nitrides

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ABSTRACT: A carbon nitride material can be combined with homogeneous nickel catalysts for light-mediated cross-couplings of aryl bromides with alcohols under mild conditions. The metal-free heterogeneous semiconductor is fully recyclable and couples a broad range of electron-poor aryl bromides with primary and secondary alcohols as well as water. The application for intramolecular reactions and the synthesis of active pharmaceutical ingredients was demonstrated. The catalytic protocol is applicable for the coupling of aryl iodides with thiols as well.

Alkyl aryl ethers are a common structural motif in many active pharmaceutical ingredients (APIs), such as Fluoxetine, Ketoconazole, Raloxifene and Flecainide (Figure 1).1,2

Figure 1. Examples of APIs containing the alkyl aryl ether motif.

Nucleophilic substitution of alkyl halides with phenolates (Williamson ether synthesis) traditionally used to synthesize these scaffolds, suffers from functional group incompatibilities due to the harsh conditions it requires. Catalytic strategies for the synthesis of ethers were developed to overcome these drawbacks. Copper can catalyze the coupling of phenols and aryl halides (Ullmann-type reaction),4,5 as well as aryl boronic acids and alcohols (Chan-Evans-Lam coupling).6 Palladium catalyzed O-arylations of alcohols via Buchwald–Hartwig type cross-coupling reactions broaden the substrate scope.7,8 Strongly basic conditions and well-designed bipyridine ligands are required for efficient cross-coupling reactions.9 Nickel catalysis gained increasing interest due to its significantly higher abundance compared to noble metals,10,11 The low electronegativity of Ni enables facile oxidative addition into carbon–halide bonds, whereas reductive elimination, especially in case of C–O couplings, is difficult.12,13 Thermolysis of Ni(II) oxametallacycles, for example, results in β-hydride elimination of undesired carbonyl compounds, whereas oxidation to Ni(III) complexes via single electron transfer (SET) with stoichiometric oxidants can induce reductive elimination resulting in C–O bond formation.14 Combining nickel with photoredox catalysis,15,16,18 enables the coupling of aryl bromides with alcohols19,20 or water21 without stoichiometric SET oxidants.

Photoredox catalysis is dominated by expensive, homogenous iridium and ruthenium complexes. Noble-metal-free, homogeneous photoredox catalysts, such as borondipyromethene derivatives (BODIPY),21 require tedious purification procedures and are prone to degradation.22 Heterogeneous semiconductors are a recyclable alternative to common homogeneous photoredox catalysts.23–26 CdSe quantum dots27 and CdS28 were used for carbon-heteratom couplings via the dual nickel/photoredox catalytic approach. Cadmium, however, is among the most toxic elements29 and strictly regulated.30 Its application in the synthesis of APIs is therefore not desirable.

Carbon nitride (CN) materials, a class of stable and metal-free semiconductors with low toxicity31 that can be easily made from commodity chemicals, are able to activate Ni complexes via photosensitization.32 Here, we show that these materials
are also able to catalyze alkyl aryl ether synthesis, likely by triggering reductive elimination via SET modification of the oxidation state of Ni complexes.\textsuperscript{19}

The etherification of methyl 4-bromobenzoate with 1-hexanol served as a model reaction for initial studies (Table 1). A careful optimization of all reaction parameters showed that a carbon nitride material prepared by polymerization of urea and oxamide (CN-OA-m)\textsuperscript{22} in combination with catalytic amounts of NiBr\textsubscript{2}-3H\textsubscript{2}O and di-\textit{tert}-butylbipyridyl (dtbbpy) results the selective synthesis of the desired ether (I) after 48 h irradiation with white LEDs in acetonitrile under mildly basic conditions (entry 1-2). The only side-products were small amounts of the corresponding phenol (2) from the cross-coupling with water, and dehalogenated methyl benzoate (3). In homogenous dual catalysis, the addition of catalytic amounts of quinuclidine was reported to accelerate the reaction.\textsuperscript{19, 20} For similar reasons, an amine-modified organonickel complex was used in combination with photoredox catalysis for the synthesis of phenols from aryl halides and water.\textsuperscript{21} The semi-heterogeneous protocol did not result in significant rate enhancement when 10 mol\% quinuclidine were added (entries 3-4). The utilization of 6,6’-diamino-2,2’-bipyridyl instead of dtbbpy drastically reduced the efficacy of the C–O coupling in our model system (see Table S4 in the Supporting Information). A reaction with methyl 4-chlorobenzoate as substrate resulted in very low amounts of the desired ether product under optimized conditions (Table 1, entry 5). No reaction was detected in case of the mesylate, triflate or tosylate derivatives (see Table S10 in the Supporting Information). Control experiments proved that light, CN-OA-m, NiBr\textsubscript{2}-3H\textsubscript{2}O, dtbbpy, \textit{N-t}ert-butylisopropylamine (BIPA) and oxygen-free conditions are essential for successful C–O cross-couplings (entries 6-11).

With the optimized conditions in hand, the versatility of the semi-heterogeneous cross-coupling was investigated (Scheme 1). Aryl bromides substituted with electron withdrawing groups in \textit{para}-position were generally isolated in good to excellent yields. A broad range of functional groups including esters (I), nitriles (4), aldehydes (5), ketones (6, 15), phenylboronic acid pinacol esters (14), chlorides (10), and trifluoromethyl- (13) as well as methylsulfonyl-groups (16) were tolerated. Substrates with electron withdrawing \textit{meta}-substituents (7, 8) did also yield the desired products, although with lower efficiency. \textit{Ortho}-substituted aryl bromides (11, 12) resulted in a drastically decreased reactivity. Coupling of 1,4-dibromobenzene with 1-hexan gave a selective mono-etherification as the resulting aryl alkyl ether (9) deactivates the second bromide functionality. Heteroaryl bromides (17, 18) were successfully coupled under these conditions. Substrates lacking a strong electron withdrawing group gave very low amounts of the desired C–O coupling products (20, 21) within 48 hours.

While electronic effects dictate the reactivity of aryl bromides, steric effects are responsible for the scope and limitations of aliphatic alcohols (Scheme 2). Coupling of methyl 4-bromobenzoate with methanol (22) was completed within 24 hours under standard conditions and within 8 hours when MeOH was used as solvent (see the Supporting Information). The semi-heterogeneous methodology provides an effective method to prepare deuterium labeled anisoles (23) in excellent yield. Primary alcohols with benzyl (24), allyl (26), nitrile (29), trifluormethyl (25), and tertiary amine (30) groups were coupled with high selectivity. The secondary alcohols isopropanol (31), cyclohexanol (32) and 1-phenylethanol (33) reacted efficiently as well. Sterically encumbered secondary (34, 35) and tertiary (36) alcohols resulted in low amounts of the desired ether products within 48 hours. Formation of diaryl ethers from the reaction of aryl bromides and phenols was not observed, presumably due to the low nucleophilicity of aromatic alcohols.

Coupling of methyl 4-bromobenzoate with water as nucleophile gave phenol 2 in moderate isolated yield by switching to DMF as a solvent (for details, see Table S12 in the Supporting Information). The \textit{ortho}-substituted, electron-rich aryl bromide 2-(2-bromophenyl)ethanol did undergo an intramolecular C–O coupling, resulting in 2,3-dihydrobenzofuran (37).\textsuperscript{34} An analogous preparation of chromane and 1,4-benzodioxane was not feasible (see Table S11 in the Supporting Information). The reason for this remains unclear, especially because chromanes were previously synthesized by reductive elimination from the corresponding nickel(II) oxametalacycles.\textsuperscript{35} The semi-heterogeneous dual catalytic reaction of 1,4-dibromobenzene and isopropylideneglycol afforded 38, a potential intermediate for the preparation of ketoconazole (Figure 1), itraconazole, terconazole and their derivatives.\textsuperscript{35} The antidepressant Fluoxetine can be synthesized using this method. N-protected 3-methylamino-1-phenylpropanol reacted with 1-bromo-4-(trifluoromethyl)benzene resulting in N-acetyl fluoxetine (39) in 66%.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{entry} & \textbf{conditions} & \textbf{1} & \textbf{2} & \textbf{3} \\
\hline
1 & as shown & 96 & 3 & 1 \\
2 & CN-OA-m (1.66 mg mL\textsuperscript{-1})  & 90 & 6 & n.d. \\
3 & 24 h & 55 & 3 & n.d. \\
4 & 24 h with 10 mol% quinuclidine & 61 & 2 & n.d. \\
5 & methyl 4-chlorobenzoate & 4 & n.d. & n.d. \\
6 & no light & n.d. & n.d. & n.d. \\
7 & no CN-OA-m & n.d. & n.d. & n.d. \\
8 & no NiBr\textsubscript{2}-3H\textsubscript{2}O & n.d. & n.d. & n.d. \\
9 & no dtbbpy & n.d. & n.d. & n.d. \\
10 & no BIPA & n.d. & n.d. & n.d. \\
11 & no degassing & n.d. & n.d. & n.d. \\
\hline
\end{tabular}
\caption{Optimized conditions and control experiments\textsuperscript{[a]}}
\end{table}

\textsuperscript{[a]}\textsuperscript{Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (10 mg), NiBr\textsubscript{2}-3H\textsubscript{2}O (30 \mu mol), dtbbpy (30 \mu mol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. Determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. n.d. = not detected.}
Scheme 1. Scope and limitations of the semi-heterogeneous etherification

Reaction conditions: aryl bromide (1.2 mmol), alcohol (2.4 - 4.8 mmol), CN-OA-m (20 mg), NiBr₂·3H₂O (120 µmol), dtbbpy (120 µmol), BIPA (6.0 mmol), MeCN (6.0 mL), white LEDs at 40 °C.

48 hours resulting in 79% isolated yield of the desired thioether (40). When 2-mercaptoethanol was used, a selective C–S bond formation (41), with no detectable amount of the corresponding etherification product was obtained. In contrast to the C–O coupling, the semi-heterogeneous C–S bond formation is not limited to primary and secondary thiols (40–42). Tertiary (43) and aromatic thiols (44, 45) also gave the desired thioethers in moderate isolated yields. This finding can be rationalized by the formation of highly reactive thyl radicals which are proposed to add to Ni(I) intermediates in the dual catalytic thioether synthesis.

Scheme 2. Scope of semi-heterogeneous thioetherification

Reaction conditions: methyl 4-iodobenzoate (1.2 mmol), thiol (2.4 mmol), CN-OA-m (20 mg), NiBr₂·3H₂O (120 µmol), dtbbpy (120 µmol), BIPA (6.0 mmol), MeCN (6.0 mL), white LEDs at 40 °C.

The reaction rate was significantly increased by using blue LEDs with higher light intensity (for details, see Supporting Information). The coupling of methyl 4-bromobenzoate and methanol, for example, was complete after 16 hours instead of 24 (Figure 1) using a modified setup. These intensified conditions were used for studying the recyclability of the heterogeneous carbon nitride material (Figure 2). CN-OA-m was recycled six times, without losing its catalytic activity (Figure 2), proving its high potential for sustainable photocatalysis.

Figure 2. Recycling of CN-OA-m in the semi-heterogeneous etherification.

"Reaction conditions: aryl bromide (1.2 mmol), alcohol (2.4 - 4.8 mmol), CN-OA-m (20 mg), NiBr₂·3H₂O (120 µmol), dtbbpy (120 µmol), BIPA (6.0 mmol), MeCN (6.0 mL), white LEDs at 40 °C.

°Determined by ¹H-NMR using 1,3,5-trimethoxybenzene as internal standard.°DMF was used as solvent.

The same catalytic system was evaluated for the coupling of thiols with aryl halides. The reaction of aryl bromides and thiols usually requires strongly reducing photoredox catalysts, whereas aryl iodides can be successfully coupled using weaker reductants. When the optimized semi-heterogeneous protocol (the conduction band minimum of CN-OA-m was reported to be at -1.6 V vs. Ag/AgCl) was applied on the reaction of methyl 4-bromobenzoate with methyl 3-mercaptopropionate, only 4% of the desired thioether were formed after 48 hours (Table S15). The analogous reaction using methyl 4-iodobenzoate went to completion within 48 hours resulting in 79% isolated yield of the desired thioether (40).
In conclusion, a dual Ni/photocatalytic C–O coupling was developed using a carbon nitride semiconductor as recyclable photocatalyst with low toxicity. The semi-heterogeneous nickel/carbon nitride catalysis is an inexpensive, sustainable alternative to homogeneous protocols. The method selectively couples a broad range of electron-poor aryl bromides with primary and secondary alcohols as well as water in good to excellent isolated yields. The application of this protocol for intramolecular reactions and API synthesis was demonstrated. The same catalytic protocol can be utilized to couple aryl iodides with thiols.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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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), 6,6’-diamino-2,2’-bipyridyl, 3 methyl 4-((trifluoromethyl)sulfonyl)oxy)benzoate, methyl 4-(tosyloxy)benzoate, methyl 4-((methylsulfonyl)oxy)benzoate, (2-bromophenoxy)ethanol, (2-bromophenyl)propanol and N-(3-hydroxy-3-phenylpropyl)-N-methylacetamide were prepared according to literature procedures. 1H-, 13C- and 19F-NMR spectra were obtained using a Varian 400 spectrometer (400 MHz, Agilent), an Ascend 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/UV254 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(CF3)ppy]2(dtbbpy)PF6 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

The synthesis for CN-OA-m was carried out using a slightly adapted version of the literature procedure (Scheme S1)\(^\text{10}\): 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\(_2\) 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\(_2\)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 \(^1\)H-NMR with internal standard).

The cost of CN-OA-m was calculated to be 4.2 € g\(^{-1}\) based on the prices of urea, oxamide, LiCl and KCl from Sigma-Aldrich (Merck).\(^\text{11}\) As a comparison, the price of Ir(ppy)\(_3\) is 2124 € g\(^{-1}\).\(^\text{11}\)

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\(^2\) 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.\(^\text{10}\) 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\(_3\))ppy]\(_2\)(dtbbpy)PF\(_6\) 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(CF₃)ppy]₂(dtbbpy)PF₆ (B).
3. Setups for photochemical reactions

3.1. RGB photoreactor (low intensity)

A flexible, red/green/blue LED strip\textsuperscript{12} (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)]](image-url)
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\textsuperscript{13} 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.

\textbf{Figure S4.} Experimental setup of the 440 nm photoreactor (high intensity).

\textbf{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^{II} source (30 µmol, 10 mol%), the ligand (30 µmol, 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 intensitiy 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 µL) was filtered, diluted with DMSO-d$_6$ and subjected to $^1$H-NMR analysis. For representative NMR spectra, see Figure S6.
**Figure S6.** Example of a crude $^1$H-NMR spectrum of the C-O coupling of methyl 4-bromobenzoate and 1-hexanol.

S10
4.2. Solvent screening

Table S1. Solvent screening.\textsuperscript{a}

| Entry | Solvent | Conversion [%]\textsuperscript{b} | 1 [%]\textsuperscript{c} | 2 [%]\textsuperscript{c} | 46 [%]\textsuperscript{c} |
|-------|---------|---------------------------------|----------------|----------------|----------------|
| 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               |

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

| Entry | CN material        | Conversion [%] | 1 [%] | 2 [%] | 46 [%] |
|-------|--------------------|----------------|-------|-------|--------|
| 1     | CN-OA-m            | 68             | 51    | 3     | 13     |
| 2     | CMB$_{0.05}$-CN    | 28             | 18    | 1     | 9      |
| 3     | mpg-CN             | 22             | 14    | 1     | 7      |
| 4     | CMB$_{0.10}$-CN    | 4              | 2     | n.d.  | 2      |
| 5     | K-PHI              | 1              | traces| n.d.  | n.d.   |
| 6     | CNS$_{600}$        | <1             | n.d.  | n.d.  | n.d.   |

---

aReaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN material (10 mg), NiCl$_2$·glyme (30 µmol), dtbbpy (30 µmol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h. Contributes of methyl 4-bromobenzoate determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. NMR yields determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. n.d. not detected.

Several carbon nitride materials were tested: mesoporous graphitic carbon nitride (mpg-CN), two modified carbon nitrides derived from a cyanuric acid/melamine/barbituric acid complex (CMB$_{0.05}$-CN and CMB$_{0.10}$-CN), a sulfur-doped material (CNS$_{600}$), a strongly oxidizing potassium poly(heptazine imide) (K-PHI), and a carbon nitride derivative prepared via co-condensation of urea and oxamide followed by post-calcination in a molten salt (CN-OA-m).
### 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>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.\(^a\)

| Entry | Ligand | Conversion [%]\(^b\) | 1 [%]\(^c\) | 2 [%]\(^c\) |
|-------|--------|-----------------------|------------|------------|
| 1     | ![Ligand 1](image1.png) | 62                    | 57         | 3          |
| 2     | ![Ligand 2](image2.png) | 45                    | 42         | 3          |
| 3     | ![Ligand 3](image3.png) | 50                    | 47         | 3          |
| 5     | ![Ligand 5](image4.png) | 26                    | 23         | 2          |
| 6     | ![Ligand 6](image5.png) | 52                    | 48         | 4          |
| 7     | ![Ligand 7](image6.png) | 12                    | 6          | 5          |

\(^a\)Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiBr\(_2\)-3H\(_2\)O (30 \(\mu\)mol), ligand (30 \(\mu\)mol), BIPA (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h.

\(^b\)Conversion of methyl 4-bromobenzoate determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard.

\(^c\)determined by \(^1\)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.\(^{18}\)
### 4.6. Base screening

Table S5. Base screening.$^a$

| Entry | Base                                | Conversion [%]$^b$ | 1 [%]$^c$ | 2 [%]$^c$ | 3 [%]$^c$ |
|-------|-------------------------------------|--------------------|-----------|-----------|-----------|
| 1     | BIPA + quinuclidine (10 mol%)       | 78                 | 73        | 4         | n.d.      |
| 2     | BIPA                               | 62                 | 57        | 3         | n.d.      |
| 3     | DBU$^e$                            | 10                 | 4         | n.d.      | 5         |
| 4     | Et$_3$N                            | 23                 | 17        | 2         | 4         |
| 5     | DIPEA$^f$                          | 16                 | 7         | 1         | 8         |
| 6     | tetramethyguanidine                | 4                  | 4         | n.d.      | n.d.      |
| 7     | DABCO$^g$                          | <1                 | n.d.      | n.d.      | n.d.      |
| 8     | DMAP$^h$                           | <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$_2$CO$_3$                        | <1                 | n.d.      | n.d.      | n.d.      |
| 12    | K$_2$CO$_3$                        | <1                 | n.d.      | n.d.      | n.d.      |
| 13    | K$_3$PO$_4$                        | <1                 | n.d.      | n.d.      | n.d.      |

$^a$Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.9 mmol), CN-OA-m (10 mg), NiBr$_2$·3H$_2$O (10 mol%), dtbbpy (30 µmol), base (0.9 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 16 h.$^b$Conversion of methyl 4-bromobenzoate determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. $^c$NMR yields determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. $^d$not detected. $^e$1,8-Diazabicyclo[5.4.0]undec-7-ene $^f$N,N-Diisopropylethylamine. $^g$1,4-Diazabicyclo[2.2.2]octane. $^h$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$^{-1}$) increased the product formation by only 15% and was therefore not used in the subsequent tests.$^{11}$
4.7. Screening of reaction conditions

4.7.1. Time

Table S6. Time study.\textsuperscript{a}

| Entry | Time [h] | Conversion [%]\textsuperscript{b} | 1 [%]\textsuperscript{c} | 2 [%]\textsuperscript{c} | 3 [%]\textsuperscript{c} |
|-------|----------|----------------------------------|----------------|----------------|----------------|
| 1     | 4        | 16                               | 13             | 2              | n.d.\textsuperscript{d} |
| 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.            |

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

Figure S7: Time study (data from Table S6).
4.7.2. Stoichiometry optimization

Table S7. Optimization of stoichiometry of alcohol and base.\textsuperscript{a}

| Entry | 1-hexanol [equiv] | BIPA [equiv] | Time [h] | Conversion [%]\textsuperscript{b} | 1 [%]\textsuperscript{c} | 2 [%]\textsuperscript{c} |
|-------|-------------------|-------------|----------|---------------------------------|--------------------|-----------------|
| 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               |

\textsuperscript{a} Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 or 0.9 mmol), CN-OA-m (10 mg), NiBr\textsubscript{2}·3H\textsubscript{2}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 48 h. \textsuperscript{b} Conversion of methyl 4-bromobenzoate determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. \textsuperscript{c} NMR yields determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. \textsuperscript{d} 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.\textsuperscript{a}

![Chemical reaction diagram]

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

\textsuperscript{a}Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (5 or 10 mg), NiBr\textsubscript{2}·3H\textsubscript{2}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. \textsuperscript{b}Conversion of methyl 4-bromobenzoate determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. \textsuperscript{c}NMR yields determined by \textsuperscript{1}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\textsuperscript{-1} was maintained as loading for further experiments.
4.8. Control studies

Table S9. Control studies.\(^a\)

| Entry | Deviation from standard conditions | Conversion [%]\(^b\) | 1 [%]\(^c\) | 2 [%]\(^c\) |
|-------|-----------------------------------|---------------------|---------|---------|
| 1     | None                             | >99                 | 92      | 7       |
| 2     | No CN-OA-m                       | <1                  | n.d.\(^d\) | n.d.   |
| 3     | No NiBr\(_2\)·3H\(_2\)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.    |

\(^a\)Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (10 mg), NiBr\(_2\)·3H\(_2\)O (30 µmol), dtbbpy (30 µmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. \(^b\)Conversion of methyl 4-bromobenzoate determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard. \(^c\)NMR yields determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard. \(^d\)not detected.
## 4.9. Screening of aryl (pseudo)halides

### Table S10. Screening of aryl (pseudo)halides.\(^a\)

| Entry | X      | Conversion [%] | 1 [%] | 2 [%] |
|-------|--------|----------------|-------|-------|
| 1     | Br     | >99            | 92    | 7     |
| 2     | I      | 13             | 13    | n.d.  |
| 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.  |

\(^a\)Reaction conditions: aryl (pseudo)halide (0.3 mmol), 1-hexanol (0.6 mmol), CN-OA-m (10 mg), NiBr\(_2\)·3H\(_2\)O (30 \(\mu\)mol), dtbbpy (30 \(\mu\)mol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. \(^b\)Conversion of methyl 4-bromobenzoate determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard. \(^c\)NMR yields determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard. \(^d\)not detected.
4.10. Intramolecular etherification

Table S11. Intramolecular etherification for the formation of oxygen heterocycles.\(^a\)

| Entry | Substrate | Product | Substrate/Product\(^b\) |
|-------|-----------|---------|--------------------------|
| 1\(^c\) | ![Substrate Image] | ![Product Image] (37) | 34/56 |
| 2     | ![Substrate Image] | ![Product Image] | >99/0 |
| 3     | ![Substrate Image] | ![Product Image] | >99/0 |

\(^a\)Reaction conditions: substrate (0.6 mmol), CN-OA-m (20 mg), NiBr\(_2\)-3H\(_2\)O (60 µmol), dtbbpy (60 µmol), BIPA (3.0 mmol), MeCN (6.0 mL), white LEDs at 40 °C for 168 h. \(^b\)Ratio calculated from \(^1\)H NMR analysis. \(^c\)No product formation was detected in absence of CN-OA-m, NiBr\(_2\)-3H\(_2\)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 NiBr$_2$·3H$_2$O (8.2 mg, 30 µmol, 10 mol%), the ligand (8.1 mg, 30 µmol, 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 H$_2$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 µL) was filtered, diluted with DMSO-$d_6$ and subjected to $^1$H-NMR analysis.

5.2. Solvent screening

Table S12. Solvent screening.$^a$

| Entry | Solvent       | Conversion [%]$^b$ | 2 [%]  |
|-------|---------------|--------------------|--------|
| 1     | MeCN          | <1                 | n.d.$^d$ |
| 2     | MeCN/DMF (1:1)| 23                 | 22     |
| 3     | DMF           | 50                 | 49     |

$^a$Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), H$_2$O (0.6 mmol), CN-OA-m (10 mg), NiBr$_2$·3H$_2$O (30 µmol), dtbbpy (30 µmol), BIPA (1.5 mmol), solvent (3.0 mL), white LEDs at 40 °C for 48 h. $^b$Conversion of methyl 4-bromobenzoate determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. $^c$NMR yields determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal standard. $^d$not detected.
5.3. Ligand screening

Table S13. Ligand screening. 

\[
\begin{array}{ccc}
\text{Entry} & \text{Ligand} & \text{Conversion [%]} \quad \text{[%]} \quad \text{2 [%]} \\
1 & \begin{array}{c}
\text{Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), H}_2\text{O (0.6 mmol), CN-OA-m (10 mg), NiBr}\text{2·3H}_2\text{O (30 µmol), ligand (30 µmol), BIPA (1.5 mmol), DMF (3.0 mL), white LEDs at 40 °C for 24 h.} \\
\text{Conversion of methyl 4-bromobenzoate determined by } ^1\text{H-NMR using 1,3,5-trimethoxybenzene as internal standard. NMR yields determined by } ^1\text{H-NMR using 1,3,5-trimethoxybenzene as internal standard.}
\end{array}
\end{array}
\]
5.4. Stoichiometry optimization

**Table S14.** Optimization of stoichiometry of water.\(^a\)

| Entry | H\(_2\)O [equiv] | Conversion [%]\(^b\) | 2 [%]\(^c\) |
|-------|------------------|-----------------------|------------|
| 1     | 1                | 45                    | 45         |
| 2     | 2                | 43                    | 42         |
| 3     | 5                | 47                    | 47         |
| 4     | 10               | 35                    | 30         |
| 5     | 20               | 29                    | 23         |

\(^a\)Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), H\(_2\)O (0.3 to 6.0 mmol), CN-OA-m (10 mg), NiBr\(_2\)-3H\(_2\)O (30 µmol), dtbbpy (30 µmol), BIPA (1.5 mmol), DMF (3.0 mL), white LEDs at 40 °C for 24 h. \(^b\)Conversion of methyl 4-bromobenzoate determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal standard. \(^c\)NMR yields determined by \(^1\)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 NiBr$_2$·3H$_2$O (8.2 mg, 30 µmol, 10 mol%), dtbbpy (8.1 mg, 30 µmol, 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 µL) was filtered, diluted with DMSO-$d_6$ and subjected to $^1$H-NMR analysis. For a representative NMR spectrum, see Figure S8.

![Figure S8. Example of a crude $^1$H-NMR spectrum of the reaction between methyl 4-iodobenzoate and methyl 3-mercaptopropionate.](image-url)
Table S15. Studies on the thioetherification of methyl 4-iodobenzoate and methyl 3-mercaptopropionate.\textsuperscript{a, b}

| Entry | Deviation from standard conditions | Conversion [%]\textsuperscript{c} | 40 [%]\textsuperscript{d} |
|-------|-----------------------------------|---------------------------------|-----------------|
| 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.o.\textsuperscript{e} |
| 5     | DBU (5.0 equiv) as base            | 35                              | n.d.\textsuperscript{f} |
| 6     | Reaction time 24 hours             | 93                              | 92              |
| 7     | Reaction time 16 hours             | 70                              | 65              |
| 8     | No CN-OA-m                         | 5                               | 3               |
| 9     | No NiBr\textsubscript{2}·3H\textsubscript{2}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              |

\textsuperscript{a}Reaction conditions: methyl 4-iodobenzoate (0.3 mmol), methyl 3-mercaptopropionate (0.6 mmol), CN-OA-m (10 mg), NiBr\textsubscript{2}·3H\textsubscript{2}O (30 µmol), dtbbpy (30 µmol), BIPA (1.5 mmol), MeCN (3.0 mL), white LEDs at 40 °C for 48 h. \textsuperscript{b}An unidentified side product was detected in all experiments (1 to 20%). \textsuperscript{c}Conversion of methyl 4-iodobenzoate determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. \textsuperscript{d}NMR yields determined by \textsuperscript{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. \textsuperscript{e}not detected because overlapping with pyridine signals. \textsuperscript{f}not detected.
An oven dried vial (19 x 100 mm) equipped with a stir bar was charged with CN-OA-m (20 mg), NiBr$_2$·3H$_2$O (32.7 mg, 120 µmol, 10 mol%), dtbbpy (32.2 mg, 120 µmol, 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 $^{1}$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.**

| Cycle | Yield [%]$^b$ |
|-------|---------------|
| 1     | 91            |
| 2     | 92            |
| 3     | 84            |
| 4     | 79            |
| 5     | 96            |
| 6     | 92            |

$^a$Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), methanol (2.4 mmol), CN-OA-m (20 mg), NiBr$_2$·3H$_2$O (120 µmol), dtbbpy (120 µmol), BIPA (6.0 mmol), MeCN (6.0 mL), blue LEDs for 16 h. $^b$NMR yields determined by $^1$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), NiBr₂·3H₂O (32.7 mg, 120 µmol, 10 mol%), dtbbpy (32.2 mg, 120 µmol, 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 µL) was filtered, diluted with DMSO-d₆ and subjected to ¹H-NMR analysis. Thereafter, the NMR sample was combined with the reaction mixture, diluted with H₂O (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 Na₂SO₄ and concentrated. The product was purified by flash column chromatography (SiO₂, Hexane/EtOAc) on a Grace™ Reveleris™ 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.

¹H NMR (400 MHz, CDCl₃) δ 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).

¹³C NMR (101 MHz, CDCl₃) δ 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.
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.

$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.

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.

$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.

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.

$^1$H NMR (600 MHz, 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). $^{13}$C NMR (151 MHz, 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.
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.

$^1$H NMR (400 MHz, 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).

$^{13}$C NMR (101 MHz, 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.$^{19}$

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.

$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.$^{22}$

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.

$^1$H NMR (600 MHz, 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).
13C NMR (151 MHz, CDCl₃) δ 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-ESI (m/z) [M⁺] calcd for C₁₃H₁₇NO: 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.

¹H NMR (600 MHz, CDCl₃) δ 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). ¹³C NMR (151 MHz, CDCl₃) δ 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.

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.

¹H NMR (600 MHz, CDCl₃) δ 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). ¹³C NMR (151 MHz, CDCl₃) δ 157.75, 132.18, 116.29, 112.55, 68.31, 31.62, 29.20, 25.73, 22.58, 14.01. These data are in full agreement with those previously published in the literature.

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.
$^1$H NMR (600 MHz, 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). $^{13}$C NMR (151 MHz, 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. $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -61.51. These data are in full agreement with those previously published in the literature.$^{19}$

![Image](14)

**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.

$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.$^{25}$

![Image](15)

**26 (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.

$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.$^{26}$
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.

$^1$H NMR (600 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 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. $^{19}$

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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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 C$_{11}$H$_{18}$NO [(M+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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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. $^{19}$
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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 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.

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.

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

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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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.
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.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 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).\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 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. \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) δ -74.01. These data are in full agreement with those previously published in the literature.\(^{30}\)

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.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 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).\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 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.\(^{31}\)

Methyl 4-(3-hydroxypropoxy)benzoate. From methyl 4-bromobenzoate (258.0 mg, 1.2 mmol, 1.0 equiv) and 1,3-propandiole (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.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 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).\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ
166.98, 162.64, 131.61, 122.53, 59.77, 51.94, 31.88. HRMS-EI (m/z) [M^+] calcd for C_{11}H_{14}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-isopropylidenglycerol (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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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) [M^+] calcd for C$_{14}$H$_{18}$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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.57, 161.31, 131.67, 123.61, 117.05, 114.14, 62.63, 51.97, 18.55. HRMS-EI (m/z) [M^+] calcd for C$_{11}$H$_{11}$NO$_3$: 205.0739; found: 205.0746.

**Methyl 4-(3-(dimethylamino)prooxy)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.
\(^1\)H NMR (400 MHz, 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).\(^{13}\)C NMR (101 MHz, 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) [M\(^+\)] calcd for C\(_{13}\)H\(_{19}\)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.

\(^1\)H NMR (400 MHz, 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). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.78, 161.77, 131.55, 122.03, 114.93, 69.89, 51.69, 21.82. HRMS-EI (m/z) [M\(^+\)] calcd for C\(_{11}\)H\(_{14}\)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.

\(^1\)H NMR (400 MHz, 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). \(^{13}\)C NMR (101 MHz, 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.\(^{32}\)

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.
1H NMR (400 MHz, CDCl₃) δ 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 CDCl₃), 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). 13C NMR (101 MHz, CDCl₃) δ 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-ESI (m/z) [M⁺] calcd for C₁₆H₁₆O₃: 256.1099; found: 256.1091.

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.

1H NMR (400 MHz, CDCl₃) δ 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). 13C NMR (101 MHz, CDCl₃) δ 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.³³

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-isopropylidene glycerol (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.

1H NMR (400 MHz, CDCl₃) δ 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). 13C NMR (101 MHz, CDCl₃) δ 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.³⁴
**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 $^1$H NMR analysis, the NMR sample and the reaction mixture were combined, diluted with H$_2$O (40 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic phases were washed with brine (40 mL), dried over Na$_2$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.

$^1$H NMR (600 MHz, CDCl$_3$) rotamer mixture $\delta$ 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H, contains residual solvent signal of 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). $^{13}$C NMR (151 MHz, CDCl$_3$) rotamer 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). $^{19}$F NMR (564 MHz, CDCl$_3$) rotamer 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.$^{35}$

**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), NiBr$_2$·3H$_2$O (32.7 mg, 120 µmol, 10 mol%), dtbbpy (32.2 mg, 120 µmol, 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 µL) was filtered, diluted with DMSO-$_d_6$ and subjected to $^1$H-NMR analysis. Thereafter, the NMR sample was combined with the reaction mixture, diluted with H$_2$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 Na₂SO₄ and concentrated. The product was purified by flash column chromatography (SiO₂, Hexane/EtOAc) on a Grace™ Reveleris™ 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.

\[ \text{MeO} \rightleftharpoons \text{S} \rightleftharpoons \text{CO}_2\text{Me} \]

\[ \delta 7.93 (d, J = 8.6 \text{ Hz}, 2H), 7.31 (d, J = 8.6 \text{ Hz}, 2H), 3.89 (s, 3H), 3.69 (s, 3H), 3.25 (t, J = 7.4 \text{ Hz}, 2H), 2.68 (t, J = 7.4 \text{ Hz}, 2H). \]

\[ ^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.93 (d, J = 8.6 \text{ Hz}, 2H), 7.31 (d, J = 8.6 \text{ Hz}, 2H), 3.89 (s, 3H), 3.69 (s, 3H), 3.25 (t, J = 7.4 \text{ Hz}, 2H), 2.68 (t, J = 7.4 \text{ Hz}, 2H). \]

\[ ^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 171.90, 166.67, 142.61, 130.07, 127.24, 126.99, 52.12, 51.99, 33.68, 27.21. \]

HRMS-El (m/z) [M*]^+ calcd for C₁₂H₁₄O₄S: 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.

\[ \text{HO} \rightleftharpoons \text{S} \rightleftharpoons \text{CO}_2\text{Me} \]

\[ ^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.91 (d, J = 7.9 \text{ Hz}, 2H), 7.33 (d, J = 7.9 \text{ Hz}, 2H), 3.90 (s, 3H), 3.69 (s, 3H), 3.25 (t, J = 7.4 \text{ Hz}, 2H), 2.68 (t, J = 7.4 \text{ Hz}, 2H). \]

\[ ^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 166.83, 142.69, 130.05, 127.15, 127.06, 60.46, 52.20, 35.20. \]

These data are in full agreement with those previously published in the literature.

**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.
$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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.$^{37}$

**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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 3.92 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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.$^{37}$

**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.

$^1$H NMR (400 MHz, CDCl$_3$) δ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 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.$^{38}$

**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.
$^1$H NMR (400 MHz, 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). $^{13}$C NMR (101 MHz, 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.$^{39}$
10. Copies of NMR spectra of isolated compounds
