

# **A modular, self-assembling metallaphotocatalyst for cross couplings using the full visible-light spectrum**

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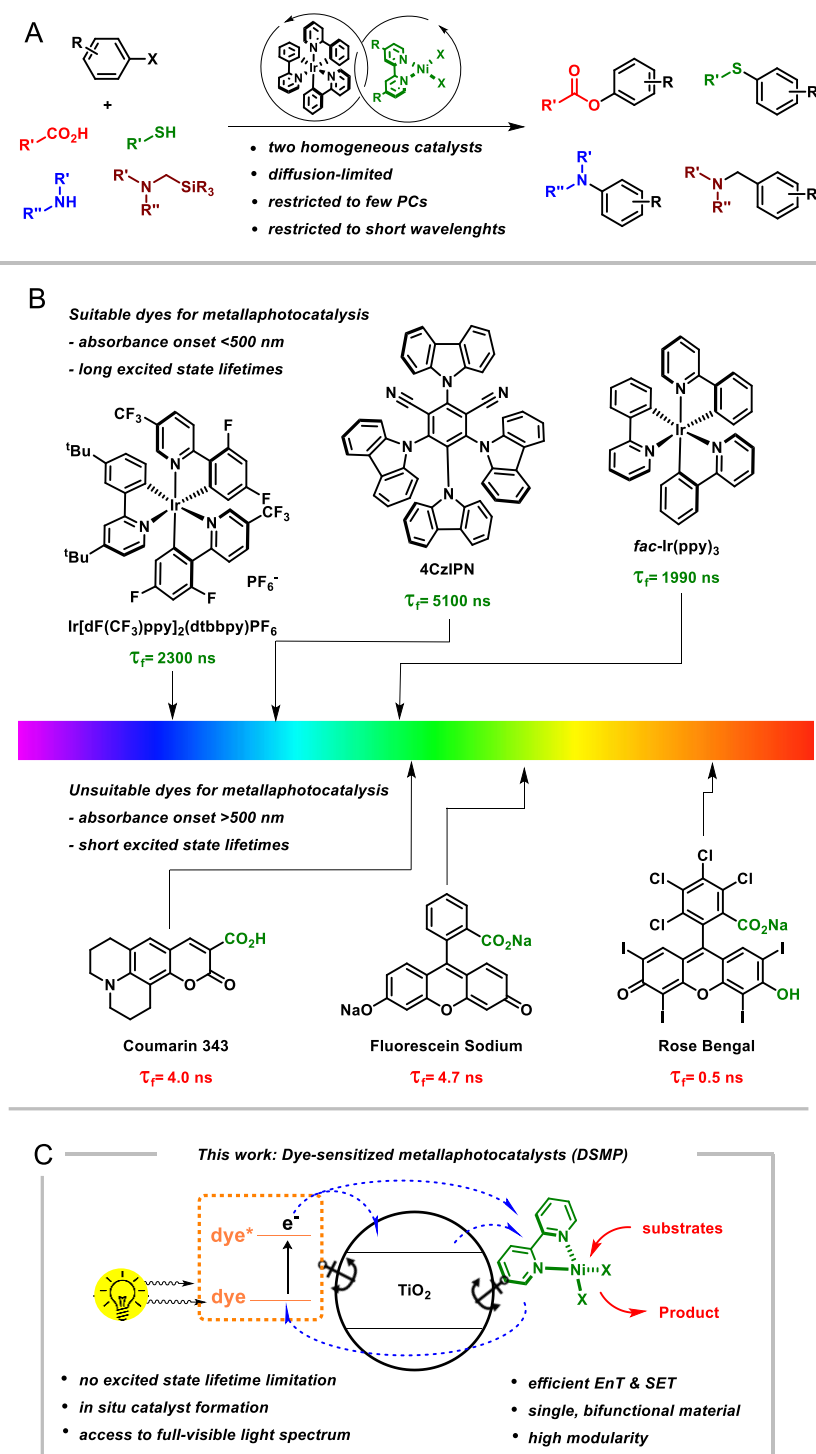
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**Abstract:** The combination of nickel- and photocatalysis has unlocked a variety of cross couplings. These protocols rely on a few photocatalysts that can only convert a small portion of visible light (<500 nm) into chemical energy. Many dyes that absorb a much broader spectrum of light are not applicable due to their short-lived excited states. Here we describe a self-assembling catalyst system that overcomes this limitation. The modular approach combines nickel catalysis with dye-sensitized titanium dioxide and can be used to catalyze various bond formations.

The combination of photo- and nickel catalysis (metallaphotocatalysis) has emerged as a powerful strategy for carbon–carbon and carbon–heteroatom cross couplings (Fig. 1A) (1-3). Key to the success are redox or photosensitization events between a nickel- and a photocatalyst (PC). Applicable PCs are iridium and ruthenium polypyridyl complexes (2), or carbazolyl dicyanobenzenes (4), with tailored redox potentials or triplet energies, and long-lived excited states (Fig. 1B). These PCs are limited to short excitation wavelengths that can cause unwanted side-reactions (5). These could be avoided in a metallaphotocatalytic system that harvests longer wavelengths. Current approaches towards photocatalysis with low photon energies require complex catalytic cocktails that enable photon upconversion (6), osmium complexes as PCs (7), or multi-photon excitation processes (5).

The use of abundant dyes that absorb broadly across the visible-light spectrum is highly desirable. The redox potentials and triplet energies of many commodity chemicals, such as fluorescein, rose bengal, or coumarins are in theory suitable for metallaphotocatalysis (8), but their short excited state lifetime render a diffusion-limited interaction with a nickel catalyst in a homogeneous solution unlikely (Fig. 1B). These dyes are, however, able to sensitize metal oxide semiconductors, such as TiO<sub>2</sub>, in dye-sensitized solar cells (DSSCs) (9), or dye-sensitized photocatalysts (DSPs) for light-driven H<sub>2</sub> production (10). The carboxylic acid groups of the dyes bind to the surface hydroxyl groups of TiO<sub>2</sub>. This facilitates electron injection into the conduction band of the semiconductor upon photoexcitation. This results in a charge-separated species that is sustained for several microseconds (11).

We wondered whether immobilization of a suitable nickel complex on dye-sensitized TiO<sub>2</sub> accesses a bifunctional material that serves as metallaphotocatalyst (Fig. 1 C). We hypothesized that such a system overcomes limitations related to short excited state lifetimes and diffusion-controlled energy or single electron transfer events due to the close spatial proximity between the PC and the nickel catalyst. The proposed, modular design of dye-sensitized metallaphotocatalysts (DSMPs) allows selecting dyes/wavelengths and nickel complexes depending on the respective application.

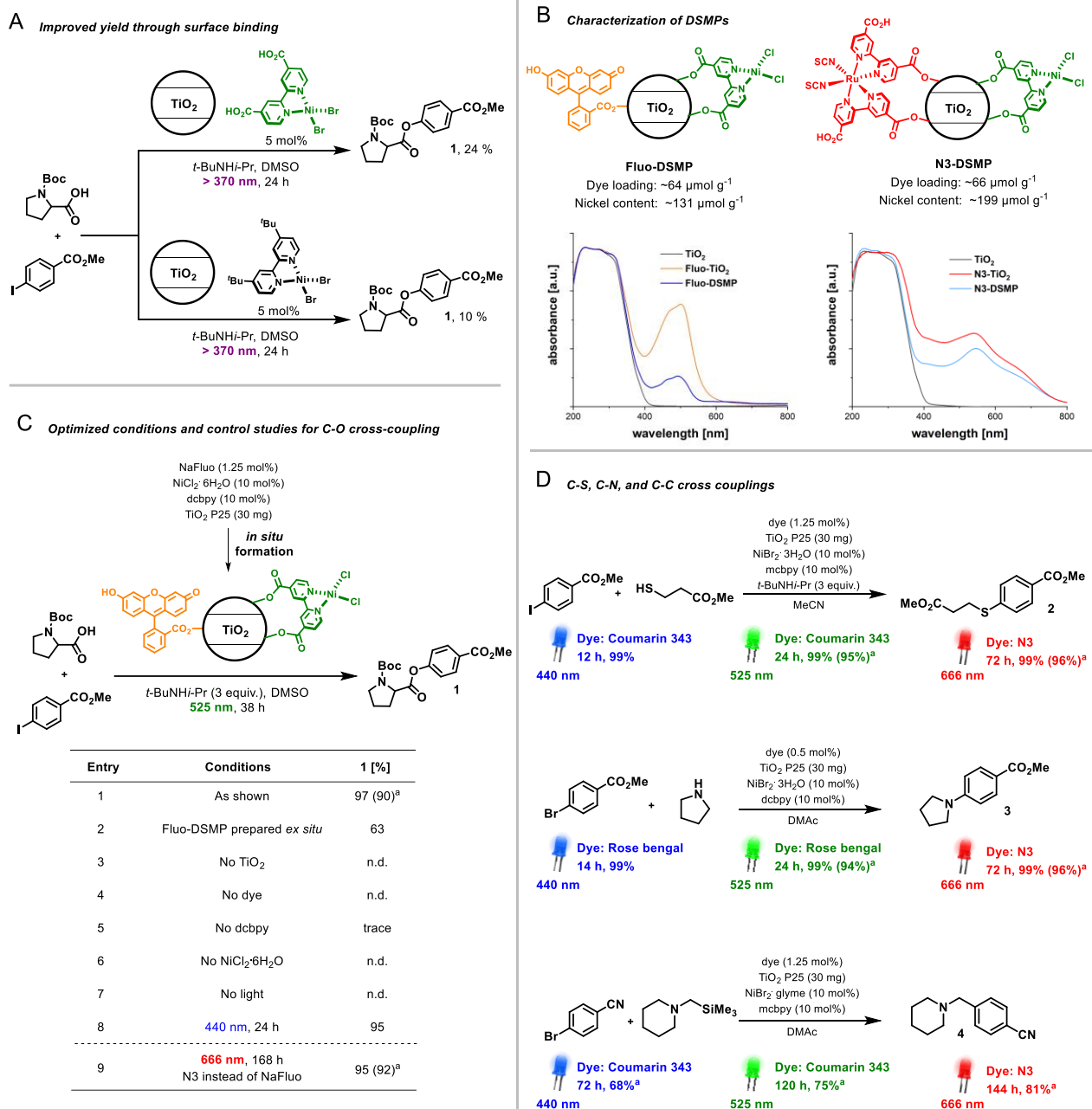


**Fig. 1. Working hypothesis towards a modular, heterogeneous metallaphotocatalyst.** Cross-coupling reactions using homogeneous metallaphotocatalysis (A). Onset of absorption of photocatalysts. The suitability for homogeneous metallaphotocatalysis depends on excited state lifetime (B). Dye-sensitized metallaphotocatalysts (DSMP) are proposed to overcome excited state lifetime limitations (C).

Our investigations started with the *O*-arylation of carboxylic acids that was reported using the PC Ir(ppy)<sub>3</sub> (ppy = 2-phenylpyridine) and a nickel bipyridine complex. The cross-coupling proceeds *via* an energy transfer (EnT) mechanism (12), and is feasible using semiconductors that absorb blue light (13, 14), but does not work using simple organic dyes (4). We first tested if anchoring of a nickel complex on TiO<sub>2</sub> P25 results i) in an active, heterogeneous metallaphotocatalyst, and ii) improves the reaction yield due to permanent spatial proximity of the PC and the nickel catalyst using near-UV light. A ligand equipped with carboxylic acid groups (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid) indeed gave a higher yield of the C–O cross coupling product **1** than a ligand that lacks functionalities capable of binding to the semiconductor's surface (dtbbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl) (Fig. 2A). Next, dyes that contain a suitable anchoring group were studied as sensitizers using green light (525 nm). Fluorescein sodium (NaFluo) showed the best results (see Supplementary Information). The C–O coupling was also feasible at higher wavelengths (666 nm) using the ruthenium dye N3 that has an excited state lifetime of 20 ns (9). The DSMPs self-assemble *in situ*. An *ex situ* preparation of the DSMPs was carried out to characterize the bifunctional materials (Fig. 2B). The UV–Vis spectra of the materials confirmed immobilization of the dyes on the metal oxide, and inductively coupled plasma - optical emission spectrometry (ICP-OES) corroborated anchoring of the nickel complex.

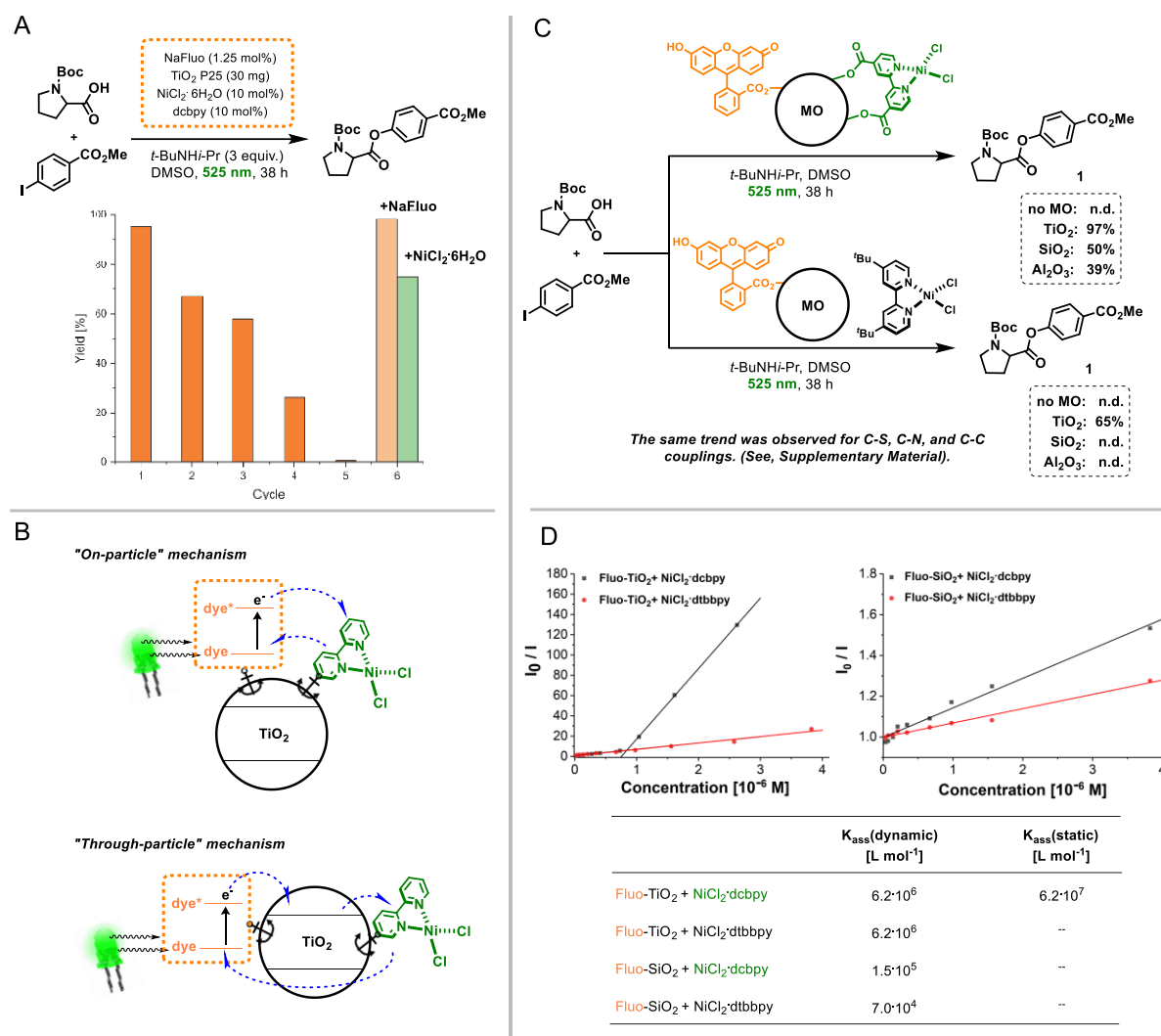
Optimization of all reaction parameters using the *in situ* DSMP approach resulted in a highly selective formation of **1** using blue (440 nm), green (525 nm), or red (666 nm) light (Fig. 2C). The highest activities were obtained when the amount of dye (1.25 mol%) and NiCl<sub>2</sub>·dcbpy (10 mol%) exceeded the loading that was determined using *ex situ* DSMP preparation. This is rationalized by a dynamic equilibrium between immobilized and unbound NiCl<sub>2</sub>·dcbpy as well as dye molecules, which also contribute to productive catalysis in the course of the bulk experiment (10). No product formation was observed in the absence TiO<sub>2</sub> P25, the dye, dcbpy, nickel salt, or light.

The DSMP approach also enabled metallaphotocatalyzed C–S (15), C–N (16), and C–C (17) bond formations that proceed *via* single electron transfer processes (SET) (Fig. 2D). The modular design principle and the self-assembling strategy facilitated a straightforward optimization of dyes, nickel salts, and ligands resulting in selective cross-couplings using blue (440 nm), green (525 nm), and red (666 nm) light. With regards to the C–C coupling, 68% of the desired product (**4**) were obtained using blue light, which is similar to the homogeneous metallaphotocatalysis system (17). Reactions at higher wavelengths, not accessible with the original, homogeneous approach, resulted in a higher selectivity.



**Fig. 2. Self-assembling, modular metallaphotocatalysts enable cross-couplings using the entire visible-light spectrum.** Anchoring of nickel complexes on TiO<sub>2</sub> P25 improves yield due to permanent spatial proximity (A). UV-Vis spectra and nickel/dye loadings of two representative DSMPs (B). Optimized conditions and control experiments for the *O*-arylation of carboxylic acids using DSMPs. (D) C-S, C-N, and C-C cross coupling catalyzed by DSMPs using blue, green, or red light. Yields were determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard if not stated otherwise. <sup>a</sup>Isolated yields. DSMP = dye-sensitized metallaphotocatalyst n.d. = not detected. dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid. mcbpy = 4'-methyl-2,2'-bipyridine-4-carboxylic acid. glyme = 1,2-dimethoxyethane. NaFluo = fluorescein sodium

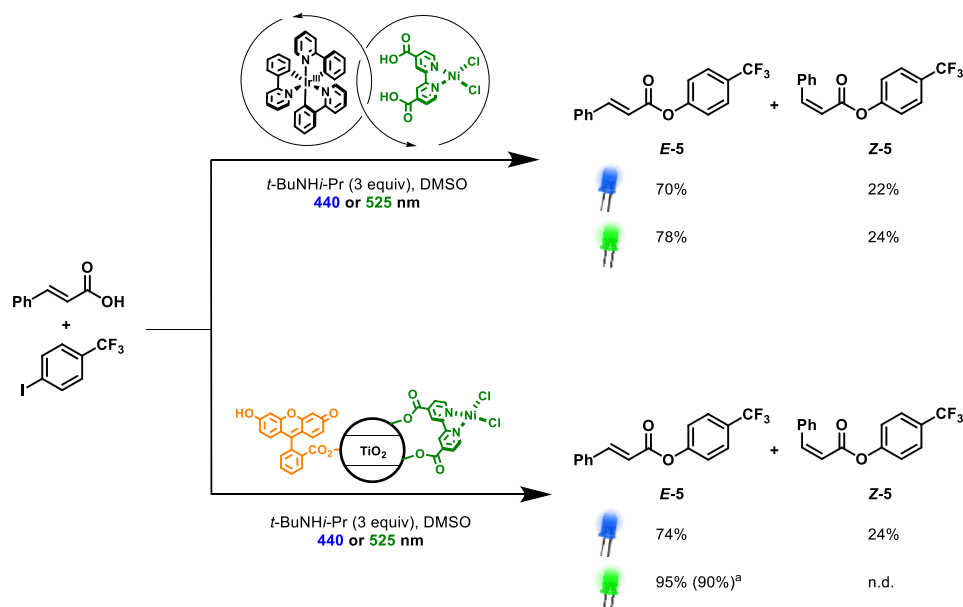
The dynamic equilibrium between immobilized and unbound molecules is responsible for leaching of nickel and fluorescein during catalyst recycling studies and caused a gradual decrease of the yield of **1** (Fig. 3A). Addition of either NaFluo or the nickel salt restored the catalytic activity. This indicated that the amount of immobilized dye molecules and nickel complexes have to be above a certain limit to observe catalytic activity. We therefore questioned if only the close proximity of the dye molecules and the nickel complex is responsible for productive catalysis, and TiO<sub>2</sub> P25 only acts as support. In other words, an “on-particle” rather than a “through-particle” mechanism could be responsible for overcoming the short excited state lifetime (Fig. 3B). To test this hypothesis, we substituted TiO<sub>2</sub> P25 with the insulating metal oxides (MO) SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> that only enable binding of the dye and the nickel complex and observed product formation for all cross-couplings, but with significantly lower efficiency compared to TiO<sub>2</sub> P25 (Fig. 3C). A second set of experiments was carried out using a nickel complex that is not able to bind to the surface of metal oxides. Here, only experiments with the semiconductor TiO<sub>2</sub> P25 gave productive catalysis. This confirms that dye sensitization leads to a charge-separated species that is sufficiently long-lived to turn over a homogeneous nickel catalyst in a semi-heterogeneous, diffusion-controlled reaction. Spectrophotometric titrations unveiled the electronic communication between the excited dye and the immobilized nickel complex “through” a semiconductor. Static fluorescence quenching of fluorescein-sensitized TiO<sub>2</sub> P25 was observed with a nickel complex that binds to the semiconductor’s surface (NiCl<sub>2</sub>·dcbpy). NiCl<sub>2</sub>·dtbbpy showed solely dynamic quenching (Fig. 3D). Titration experiments with fluorescein bound to SiO<sub>2</sub> instead of TiO<sub>2</sub> P25 displayed dynamic quenching behavior in case of both nickel complexes, and significantly lower quenching rates. Taking all results together, we assumed that a combination of “on-particle” and “through-particle” processes is responsible for the high catalytic activity of DSMPs with TiO<sub>2</sub> P25.



**Fig. 3. Mechanistic investigations.** (A) Recycling experiments showed that catalytic inactive materials still contain nickel complexes and dye molecules. (B) DSMPs might work *via* an “on-particle” and/or “through-particle” mechanism. (C) Experiments using insulating metal oxides and diffusion controlled metallaphotocatalysis. (D) Spectrophotometric titrations show static quenching for DSMPs, whereas solely dynamic quenching was observed in other systems. MO = metal oxide. dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid. dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine. Fluo = fluorescein.

In addition, we sought to compare the selectivity of DSMPs with homogenous metallaphotocatalysis systems in the C–O arylation of (*E*)-cinnamic acid with 4-iodobenzotrifluoride (Figure 4). The resulting coupling product (*E*-5) is prone to subsequent photocatalytic isomerization or cycloadditions that could lead to low selectivities (18, 19). We indeed observed significant amounts of the undesired *Z*-isomer (*Z*-5) when Ir(ppy)<sub>3</sub> was used as PCs using 440 nm irradiation. Other Ir complexes gave even worse results (see Supplementary Information). Control experiments showed that *E*-5 is also slowly converted to *Z*-5 at 440 nm in the absence of a PC (see Supplementary Information). The selectivity was,

however, not improved using Ir(ppy)<sub>3</sub> and 525 nm irradiation, because the triplet energy of the PC is not wavelength-dependent. The *E-Z* isomerization was also observed when the reaction was catalyzed by a DSMP at 440 nm, but was totally suppressed by switching to higher wavelengths, resulting in a selective formation of *E-5*.



**Figure 4. C–O arylation of (*E*)-cinnamic acid with 4-iodobenzotrifluoride with different metallaphotocatalyst systems.** Yields were determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard if not stated otherwise. <sup>a</sup>Isolated yield in parentheses.

The DSMP concept overcomes the constraint of long excited state lifetimes of PCs for metallaphotocatalysis and unlocks the potential of many dyes that were previously unsuitable. Many cross couplings can be carried out using the entire visible light spectrum and selectivity issues can be tackled strategically. The simplicity and modularity of DSMPs suggest that the present approach will complement existing methods.

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