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An on/off photocatalytic switch: from a carbon monoxide surrogate to controlled carbonylations

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ABSTRACT

Carbon monoxide surrogates have become valuable tools in carbonylation chemistry, enabling safer and more practical access to carbonylated products while avoiding the direct handling of toxic CO gas. We report a visible-light-controlled *ex situ* system for carbon monoxide generation using triphenylacetyl chloride as a structurally simple CO surrogate. Under photocatalytic conditions, the precursor undergoes rapid decarbonylation, enabling CO release to be switched on and off by irradiation. The generated CO was delivered in a two-chamber setup and applied to several transition-metal-catalyzed carbonylations, including oxidative carbonylative cyclizations, aminocarbonylations, alkoxycarbonylations, and carbonylative Suzuki couplings. CO formation was monitored using deoxyhemoglobin trapping and ^{13}C NMR analysis, while Stern–Volmer experiments and DFT calculations support a mechanism involving initial reduction of the acyl chloride followed by rapid decarbonylation of the resulting acyl radical. This *PhotoCOgen* platform provides a practical and controllable approach for laboratory-scale carbonylation chemistry without direct handling of gaseous CO.

1. Introduction

Carbonylation is a cornerstone transformation in synthetic chemistry [1,2]. The breadth of methods developed for its implementation reflects the pervasive importance of the carbonyl functional group in natural products [3–5] and industrially relevant molecules [6–9]. Despite this, the use of carbon monoxide remains challenging: CO displays a substantial activation barrier [2] and, more critically, poses significant safety concerns due to its high toxicity (Fig. 1A). As a result, carbonylations often require dedicated equipment that is not routinely available in many academic or industrial laboratories. These limitations have fueled intense efforts toward CO surrogates that enable tailored CO release, ultimately converging into two major operational formats for carbonylation chemistry (Fig. 1B) [10–19]. In the first approach, *in situ* CO generation, the gas is produced in the same vessel where the carbonylation takes place (Fig. 1B, *in situ*). Pioneering contributions by Manabe [20], Wu [21], Yudin [22], and others have convincingly demonstrated how CO substitutes can unlock efficient *in situ* carbonylations. However, the broader adoption of these methods is often dictated by practical constraints, including surrogate cost, synthetic complexity, and the need for thermal or chemical activation, features that can translate into uncontrolled CO release (Fig. 1C, *left*). Moreover, although *in situ* protocols can in principle be run with standard glassware, they require stringent compatibility between the CO-releasing manifold and the carbonylation reaction: the CO-generation conditions must be inert toward the reagents and catalysts of the downstream transformation. In addition, stoichiometric additives used to trigger CO release can introduce separation and purification issues, thereby restricting the overall versatility of the methodology. In this context, Wu's *in/ex tube* reactor represents an elegant approach to addressing incompatibilities between CO generation and the carbonylation step [23].

The second format relies on *ex situ* CO generation, in which CO is produced in a dedicated compartment and subsequently delivered to the carbonylation chamber (Fig. 1B, *ex situ*). A key advance in this area was

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introduced by Skrydstrup, who developed a practical two-chamber system (*COware*) that leverages versatile CO surrogates such as *COgen* and *SilaCOgen* [24–27]. These precursors enable operationally simple *ex situ* CO formation for a broad range of carbonylative transformations and can also support the installation of $^{13}C/^{14}C$-labelled carbonyl groups [28]. More generally, multiple CO-releasing reagents can be adapted to two-chamber platforms, including $Mo(CO)_6$ as demonstrated by Larhed [29].

Against this background, photo-induced (or photocatalytic) decarbonylation offers a compelling alternative to purely thermal activation by enabling on-demand CO generation under mild conditions, typically at room temperature, simply by toggling light exposure. Numerous photodecarbonylation reactions of organic and organometallic substrates have been reported [30–45]. For example, photocatalysis has been used to decarbonylate dimethylformamide [35], cyclopropenones [36], alkyloxalyl chlorides [37], and aldehydes [38–40]. Complementarily, acyl radicals can be accessed *via* single-electron transfer processes from carboxylic-acid derivatives (e.g., thio-/selenoesters and acyl chlorides), followed by decarbonylation [41]. However, these transformations typically proceed with slow kinetics, often requiring hours to days for full substrate consumption, which limits their utility for fast and controlled CO production. In a few notable examples, including the elegant contributions from Yang, Wang and Corcè among others, CO can be generated upon photo(catalytic) activation of dedicated precursors and successfully applied to *in situ* or *ex situ* carbonylations (Fig. 1C, *right*) [42–45]. While these studies clearly validate the power of light as an external trigger for CO delivery, they also leave substantial room for improvement from a practical standpoint. In particular, the required precursors often involve laborious multistep syntheses and may display limited chemical stability, which reduces their appeal for routine use. Moreover, CO release is not always straightforward to implement, as activation can depend on specific irradiation setups or carefully optimized conditions, which may limit operational simplicity and broader adoption. These observations highlight that, despite significant progress, important challenges remain, including the need for more accessible surrogates, lower synthetic and operational complexity, and improved control over CO-release rates in practical *ex situ* carbonylation platforms. Addressing these issues would move the field closer to an ideal surrogate: inexpensive, readily available, structurally simple, regenerable, and capable of rapid, light-controlled CO generation on demand.

We herein report a general photoredox strategy for efficient *ex situ* CO generation (Fig. 1D). The *PhotoCOgen* method enables rapid, on-demand delivery of CO, which can then be readily trapped in a range of standard carbonylation reactions using a simple two-chamber setup. Importantly, the transformation can also be driven with inexpensive, readily available blue LED strip lights in a simple setup, avoiding the need for specialized photochemical equipment. The process relies on the use of the simple triphenylacetyl chloride for photocatalytic CO generation, offering several notable advantages: (a) it is commercially available or can be readily synthesized from inexpensive precursors; (b) it displays substantial resistance to moisture, enabling practical long-term storage; (c) CO extrusion from the corresponding acyl radical is strongly favored due to the stability and persistence of the trityl radical; and (d) the surrogate can be easily regenerated, further enhancing the synthetic appeal of the approach. In contrast to methods where CO release is

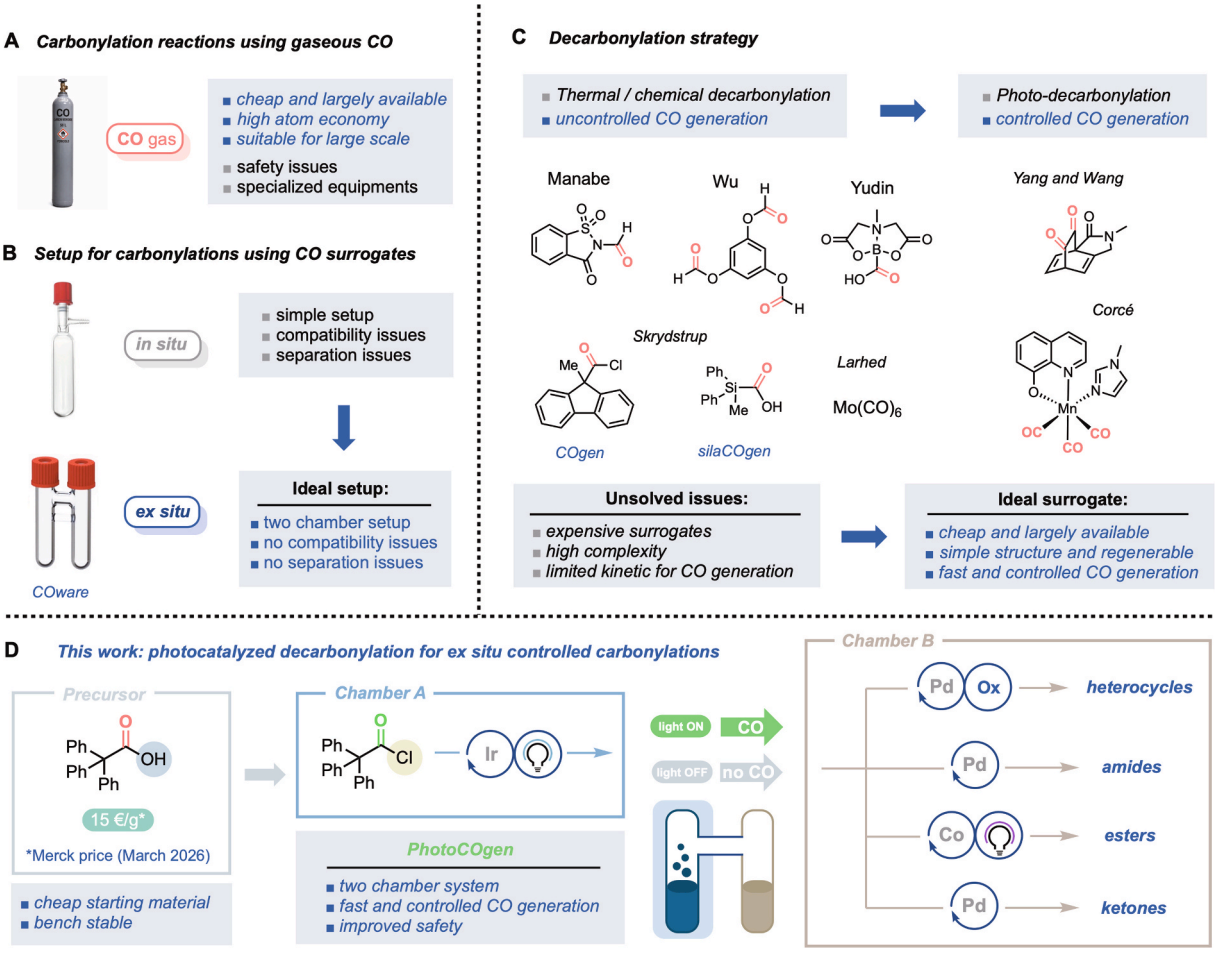


Fig. 1. A) Carbonylation reactions using CO gas; B) Setup for carbonylation reactions using CO surrogates; C) Decarbonylation strategy; D) *This work*: photocatalyzed decarbonylation for *ex situ* controlled carbonylation (*PhotoCOgen*).

triggered by chemical and/or thermal stimuli, photocatalytic CO generation follows a digital logic, as the light source provides a precisely controllable on/off switch. This feature affords direct temporal control over the kinetics of CO release, maximizing safety and minimizing the risk of undesired leakages.

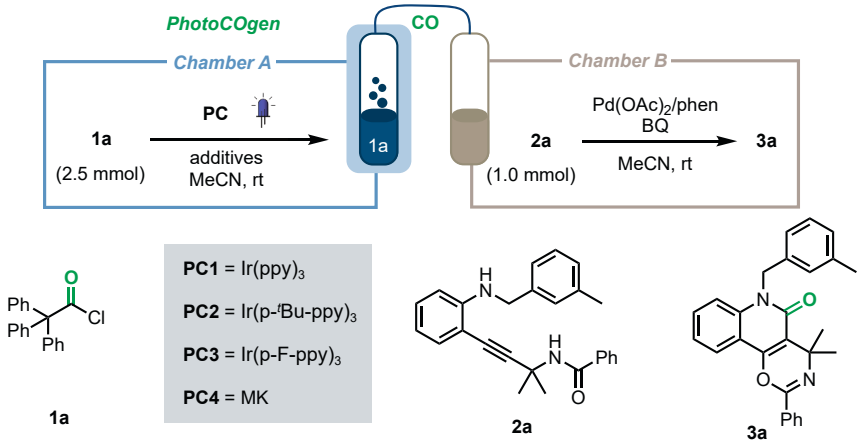
2. Results and discussion

2.1. Design and optimization of the PhotoCOgen surrogate system

Building on prior literature [30–43] and on our group's experience in photocatalytic CO generation [44], we set out to develop a complementary strategy based on the formation of an acyl radical, followed by rapid decarbonylation to deliver CO and a more stable carbon-centered radical intermediate. In this context, acyl chlorides have emerged as attractive, structurally simple precursors that are readily accessible and well suited for radical-generation manifolds. We therefore focused on promoting a single-electron-transfer (SET) reduction of acyl chlorides under photocatalytic conditions, while accounting for their energetically demanding reduction potentials [46,47]. For instance, triphenylacetyl chloride **1a** displays a reduction potential of ca. −1.96 V vs SCE [48]. Initial attempts using organic super-reducing systems [49–51] proved unproductive, and approaches relying on solvated electrons [52–54] were likewise unsuccessful. Encouraging reactivity was eventually observed with electron-rich tris-cyclometallated Ir(III) photocatalysts, such as $Ir(ppy)_3$ ($E_{1/2}$ Ir(IV)/Ir*(III) = −1.73 V *vs* SCE) and its analogues [55], as well as with Michler's ketone (E^{T1}_{red} PC^+/PC^* = -1.84 V *vs* SCE) [56]. To evaluate the efficiency of CO generation, we implemented a two-chamber setup, coupling CO photogeneration in chamber A with a mild carbonylation reaction developed in our laboratory in chamber B (Table 1 and Table S1, Section 4 in SI) [57,58]. In this arrangement, the yield of product **3a** obtained from carbonylation of 2-ethynylaniline **2a** served as a practical readout of the effectiveness of CO production under the selected conditions.

Specifically, 2-ethynylaniline **2a** undergoes a Pd-catalyzed carbonylative cascade to deliver polycycle **3a**. When a degassed MeCN solution of **1a** (2.5 equiv relative to **2a**) and $Ir(ppy)_3$ (1 mol%) was irradiated in *Chamber A* with a 22 W LED strip (λ_max = 456 nm), we were pleased to observe formation of **3a** in 22% yield in *Chamber B* (Table 1, entry 1). This result unequivocally confirmed that CO was generated under the photochemical conditions. Solvent screening revealed a strong dependence on medium. Switching from MeCN to chlorobenzene, dichloroethane (DCE), or 1,4-dioxane decreased the efficiency, while the process was completely suppressed in toluene or trifluorotoluene (Table 1, entries 2–3). Highly polar solvents such as DMF and DMSO instead promoted hydrolysis of **1a**, leading to quantitative formation of triphenylacetic acid. The addition of DIPEA proved beneficial, with the best outcome obtained using 2 equiv of the amine (Table 1, entries 4–5). Other aliphatic amines were less effective (Table 1, entry 6), and no reaction was observed with pyridine. Replacing $Ir(ppy)_3$ (PC1) with PC2, a stronger reductant bearing *tert*-butyl substituents on the phenylpyridinate ligands ($E^1/_2$ Ir(IV)/Ir*(III) = −1.90 V vs SCE), led to an increased yield of **3a** (Table 1, entry 7) [55]. In contrast, PC3, featuring electron-withdrawing fluorine atoms on its ancillary ligands, furnished **3a** in lower yield (Table 1, entry 8); consistent with its weaker reducing power relative to PC1 ($E^1/_2$} Ir(IV)/Ir*(III) = −1.60 V vs SCE) [59]. Using Michler's ketone (PC4) also afforded the carbonylation product, albeit in 55% yield (Table 1, entry 9), possibly reflecting the short triplet-state lifetime of this photocatalyst. Unexpectedly, the addition of 1 equiv of water markedly improved the CO photogeneration, boosting

Table 1
Optimization of reaction conditions for the CO generation.[a]



Entry	PC	Deviation from initial conditions	Yield of **3a** (%)[b]
1	PC1	-	22
2	PC1	in dioxane, chlorobenzene, dichloroethane (DCE)	9-12
3	PC1	in PhMe, $PhCF_3$, DMF or DMSO	-
4	PC1	DIPEA (2 equiv)	62
5	PC1	DIPEA (1 equiv)	39
6	PC1	TEA or Cy_2NEt (2 equiv)	24
7	PC2	DIPEA (2 equiv)	65
8	PC3	DIPEA (2 equiv)	29
9	PC4[c,d]	DIPEA (2 equiv)	55
10	PC2	DIPEA (2 equiv), H_2O (1 equiv)	94[e]
11	PC2	with pivaloyl chloride or diphenylacetyl chloride	-
12	PC2	with 2,2-diphenylpropanoyl chloride	42

[a] Reaction conditions for the CO generation (*Chamber A*): **1a** (0.25 mmol, 77 mg), PC (2.5 μmol) in dry MeCN (0.1 M, 2.5 mL), under blue LED irradiation (λ_{max} = 456 nm); for the Pd-catalyzed carbonylation (*Chamber B*): **2a** (0.1 mmol, 38 mg), $Pd(OAc)_2$ (5 μmol, 1.1 mg), 1,10-phenanthroline monohydrate (5 μmol, 1 mg), 1,4-benzoquinone (0.13 mmol, 14 mg) in dry MeCN (0.1 M, 1 mL); [b] NMR yield using CH_2Br_2 as internal standard; [c] 2 mol%; [d] irradiating with violet LED (λ_{max} = 396 nm); [e] yield of the compound after isolation.

the yield of **3a** to 94% (Table 1, entry 10). Notably, direct hydrolysis of **1a** to triphenylacetic acid was not observed under these conditions; instead, triphenylmethanol (72%) and triphenylmethane (26%) were observed at the end of the reaction, with both yields calculated relative to the initial amount of **1a** (see Section 5.2 in the SI). No formation of **3a** was detected when **1a** was replaced with either pivaloyl chloride or diphenylacetyl chloride (Table 1, entry 11), likely due to a less efficient decarbonylation step. Employing 2,2-diphenylpropanoyl chloride, which more closely resembles the structure of the *COgen* reagent [27], enabled formation of **3a**, but in diminished yield (Table 1, entry 12), as this acyl chloride underwent partial hydrolysis under the optimized conditions. Finally, CO generation failed entirely in the absence of either light or the photocatalyst, and no traces of **3a** were observed.

2.2. Synthetic applications of the PhotoCOgen system

Having established the optimal conditions for CO generation, we next broadened the substrate scope of the carbonylative cyclization of **2**. Under the optimized *PhotoCOgen* protocol, a range of substrates smoothly delivered the corresponding products **3b–e** in consistently high yields (82–95%, Fig. 2A). Overall, these outcomes underscore that the present *ex situ* CO-release strategy can reach an efficiency comparable to that of widely adopted catalytic systems that employ CO balloons, while offering a more practical and potentially safer alternative to handling gaseous CO directly [57]. Encouraged by these results, we turned our attention to the aminocarbonylation of aryl halides, a cornerstone transformation in synthetic chemistry for the preparation of amide derivatives (Fig. 2B). The reactions were carried out using a XantPhos-ligated Buchwald-type precatalyst, a class of catalysts known for their excellent performance and broad functional-group tolerance under mild conditions [60]. When the *PhotoCOgen* method was paired with this aminocarbonylation manifold, the desired arylamides **4a–e** were obtained in good to excellent isolated yields (74–99%) starting from the corresponding aryl iodides [61]. Notably, the reactions proceeded cleanly at room temperature, highlighting the mildness of the overall process. Moreover, synthetically valuable functional groups were well tolerated, a substrate bearing a bromide substituent can be converted efficiently without undesired side reactivity, enabling the isolation of product **4b** and leaving a handle for further downstream diversification. To further probe the practicality of the approach, the synthesis of **4a** was successfully scaled up to 1 mmol without any observable loss in yield, thus demonstrating that the method is not limited to small-scale experiments and has clear potential for preparative applications. We then explored whether *PhotoCOgen* could be integrated with a distinct carbonylation platform, namely the cobalt-catalyzed alkoxycarbonylation of aryl bromides, which operates in the presence of benzophenone under light irradiation (Fig. 2C) [62]. In this case, a variety of aryl bromides was subjected to carbonylation using methanol as both the solvent and the nucleophile, enabling straightforward access to methyl ester products. Electron-rich substrates bearing donating substituents such as *tert*-butyl or methoxy groups performed particularly well, affording esters **5a** and **5d** in excellent yields (81–90%). In contrast, electron-deficient arenes and fused aromatic systems generally gave slightly lower yields, consistent with the diminished reactivity often observed for these classes of substrates in related carbonylation manifolds. Nevertheless, the overall trend confirmed that *PhotoCOgen* can supply CO at a rate and concentration compatible with this cobalt/photochemical regime.

Finally, we assessed a palladium-catalyzed carbonylative Suzuki coupling, a powerful transformation for the assembly of unsymmetrical ketones from readily available building blocks (Fig. 2D). Using the corresponding aryl bromides in combination with aryl boronic acids, a

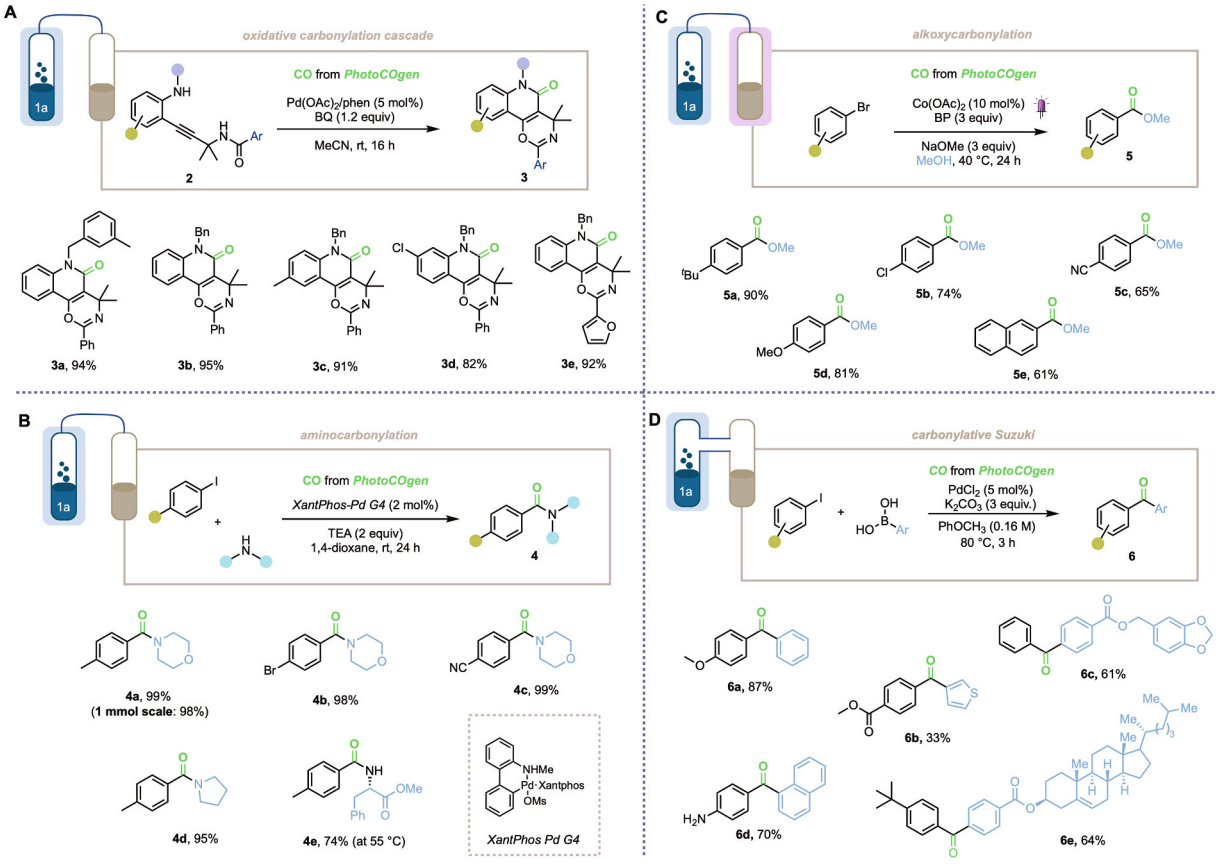


Fig. 2. Catalytic applications of the *PhotoCOgen* system (conditions from Table 1, entry 10): A) Pd-catalyzed oxidative carbonylation cascade; B) Pd-catalyzed aminocarbonylation; C) Co-photocatalyzed alkoxy-carbonylation; D) Pd-catalyzed carbonylative Suzuki (*COware*). Reported yields after isolation.

series of ketones **6a–e** was obtained in generally good yields, with the *COware* setup showing slightly better performance than the setup used previously (33–87%) [63]. While some substrate combinations led to more modest efficiency, the reaction proved successful across a representative range of examples, further highlighting the breadth of the approach. Taken together, these studies demonstrate that our *ex situ* CO-generation method is broadly compatible with multiple, conceptually different carbonylation catalytic systems, spanning cyclizations, aminocarbonylations, alkoxycarbonylations, and cross-coupling manifolds, and, importantly, can match the performance typically achieved when gaseous CO is supplied directly.

2.3. Light-controlled CO release and mechanistic investigations

To demonstrate the underlying *switch on–off* principle and to quantify both the amount of CO produced and its release kinetics, the rapid reaction between deoxyhemoglobin and carbon monoxide was harnessed (Fig. 3A). Specifically, we exploited the significant change in the visible region (450–750 nm) of Hb's absorption spectrum in the presence of CO, forming carbonmonoxy Hb (HbCO) (Fig. S10, SI). Spectral analysis allowed to quantify HbCO and thus determine the amount of CO produced [64,65]. To monitor the kinetics of CO production, the reaction mixture was irradiated with blue light following three successive cycles, each consisting of two steps: 10 minutes with the light on and 30 minutes with the light off. At the end of each step, the CO concentration was quantified (Fig. 3A). The results show that CO is selectively produced when the mixture is irradiated with blue light, whereas no gas production occurs in the absence of light (i.e., the amounts of CO produced in the two steps of each cycle are comparable). Moreover, the production kinetics displayed in Fig. 3A indicate that the

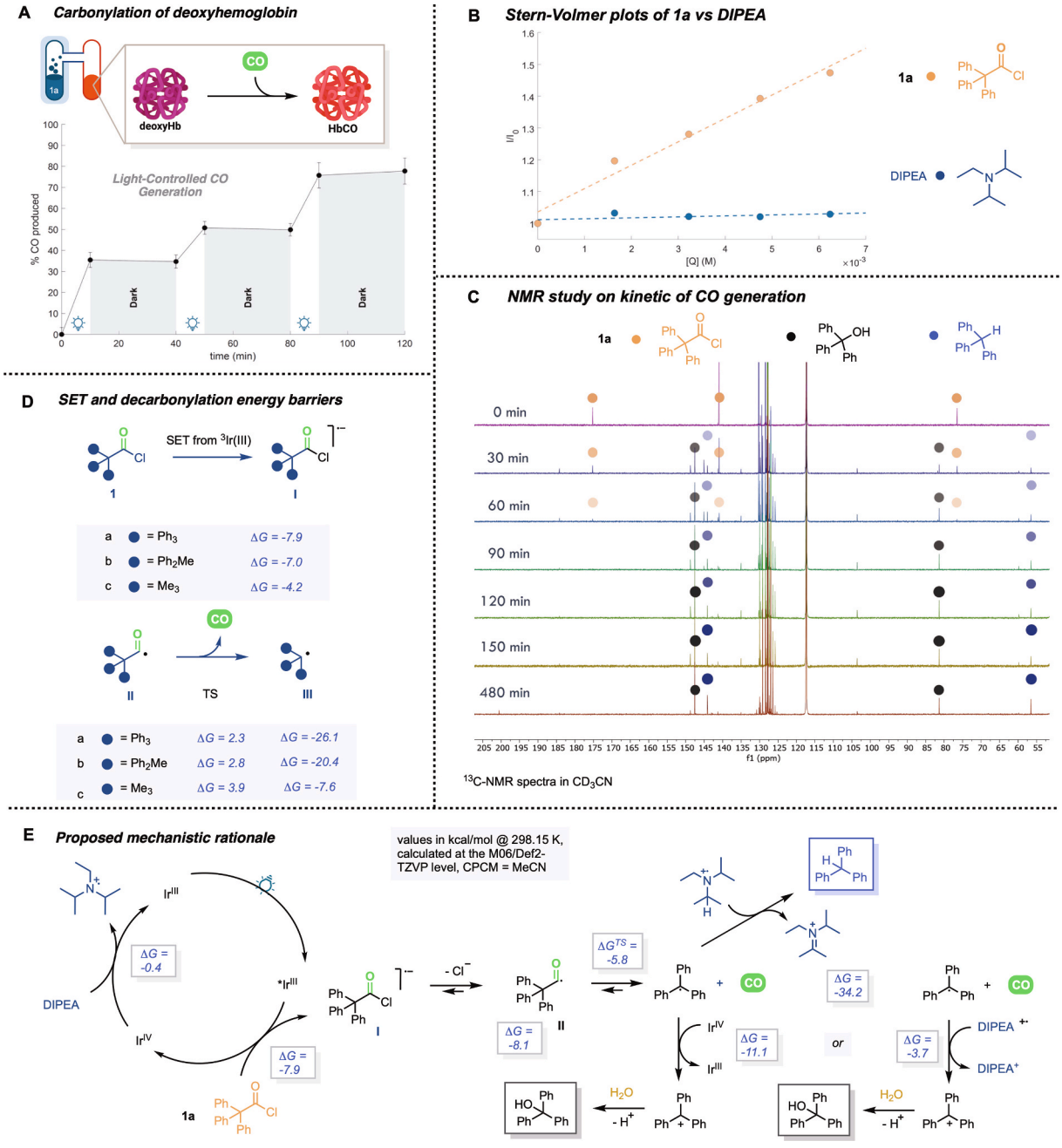


Fig. 3. A) Carbonylation of deoxyhemoglobin; B) Phosphorescence quenching studies and corresponding Stern-Volmer plot; C) NMR study (in CD_3CN) on the kinetic of the photocatalytic CO generation; D) Comparative energy barriers for acyl chlorides a, b and c; E) Proposed mechanistic rationale.

amount of product after 30 minutes of blue light irradiation (i.e., the last measured point) ranges between 70% and 80% of the reagent used. This finding is fully consistent with NMR analyses (*vide infra*), which reveal that the reagent is completely consumed within the first 60 minutes of the reaction.

Experiments were then carried out to rationalize the mechanism of the photocatalytic system. The redox potential of PC2 is compatible with either the oxidation of DIPEA or the reduction of **1a**. Phosphorescence quenching measures were performed to establish which species reacts initially with the photoexcited complex (Fig. 3B). The tertiary amine is a very poor quencher, while a clear decay of the phosphorescence band is observed by adding a solution of **1a** to the excited PC2. These results were confirmed deriving the corresponding Stern-Volmer plot, in which the slope of the two linear regressions indicated that **1a** reacts faster with the photoredox catalyst (K_{sv} = 74 and 2 mol^{-1}, respectively). The data strongly suggests that the reaction that generates CO begins with the reduction of **1a**.

We next examined the kinetics of the triphenylacetyl chloride decarbonylation by ^{13}C-NMR to assess the rate of CO generation (Fig. 3C). The optimized conditions (Table 1, entry 10) were replicated in deuterated acetonitrile. The mixture was irradiated with blue light for thirty minutes between each collection of a spectrum. The conversion of the acyl chloride **1a** is remarkably fast, and the substrate is consumed upon one hour of irradiation. For sake of comparison, it is worth noting that commonly-observed radical decarbonylations have significantly slower kinetics [30–41] and that the *COgen* surrogate requires 1.5 hours to thermally release CO in the presence of a palladium catalyst [27]. The two species that are observed upon the consumption of **1a** are triphenylmethanol and triphenylmethane [66]. Both can be recovered almost quantitatively by chromatography, and could be reacted separately to regenerate **1a** [67].

In order to provide a more comprehensive understanding of the decarbonylation process, comparative energy barriers for various acyl chlorides (a–c) have been meticulously modeled (Fig. 3D). Accordingly, a similar reaction involving 2,2-diphenylpropanoyl chloride is less favorable, and the SET on pivaloyl chloride even less so (Fig. 3D, −7.0 and −4.2 kcal/mol in ΔG, respectively). Similarly, the calculated barrier for the decarbonylation of these three model compounds indicate that the most favorable process involves the formation of the trityl radical, while the process generating the *tert*-butyl radical is the more energetically costly of the series (ΔG = +2.3, +2.8 and +3.9 kcal/mol in ΔG, respectively). This trend is consistent with the experimental results presented in Table 1 (entries 10-12), which indicated that an efficient generation of CO occurred using **1a**, for which the energetic convenience of the calculated reaction is higher, a less efficient process using 2,2-diphenylpropanoyl chloride, and poor performances using pivaloyl chloride.

The proposed mechanism for CO generation is finally depicted in Fig. 3E and is based on density functional theory (DFT) calculations performed at the M06/Def2-TZVP level (see Section 8 in SI for details). The photoexcited PC2 can reduce **1a**, affording the radical anion **I** and an Ir(IV) species (ΔG = −7.9). The former can collapse, delivering **II** and liberating a chloride anion. The acyl radical can then release CO through a low barrier (ΔG = 2.3), generating the trityl radical. The latter could be oxidized to the corresponding cation by Ir(IV) (ΔG = −11.1), regenerating the ground-state of the PC. Alternatively, the photoredox cycle can be closed by DIPEA (ΔG = −0.4). We speculate that the latter pathway easily took place in the initial stages of the reaction, in which the concentration of the amine largely exceeds that of the trityl radical. The radical cation of DIPEA could be responsible for the formation of triphenylmethane *via* intermolecular HAT. The redox between this radical cation and the trityl radical is similarly feasible according to DFT (ΔG = −3.7). Eventually, the formation of triphenylmethanol can be accounted for by the reaction of the trityl cation with water. The unexpected positive effect of a few microliters of water on the photocatalytic generation of CO could be due to its ability to trap the trityl cation. This, in turn, could push the equilibria involving the latter and its parent trityl radical, avoiding their accumulation in solution. Alternatively, water could reversibly hydrolyze the iminium cation that is formed together with triphenylmethane. The hydrolysis would avoid that **1a** faces a possible competitor for its initial reduction by the excited PC because iminium cations have reduction potentials similar to those of acyl chlorides.

In summary, we developed a system for the controlled photocatalytic generation of CO driven by LED irradiation. The rapid decarbonylation of a suitable acyl chloride enables precise regulation of carbon monoxide production by adjusting the irradiation time and the amount of substrate. The *PhotoCOgen* system efficiently supplied CO to several model carbonylation reactions, ranging from amino- and alkoxycarbonylations to carbonylative Suzuki couplings and carbonylation cascade processes. We anticipate broad adoption of this photocatalytic generation approach because it relies on structurally simple reagents and a practical setup, ensuring wide applicability in laboratory research.

CRediT authorship contribution statement

Aleksandr Voronov: Methodology, Investigation, Formal analysis, Data curation. **Maurizio Chiminelli:** Methodology, Formal analysis. **Luna Raineri:** Methodology, Data curation. **Omar De Bei:** Formal analysis, Data curation. **Luca Ronda:** Validation, Formal analysis, Data curation. **Bartolo Gabriele:** Writing – review & editing, Validation. **Raffaella Mancuso:** Writing – review & editing, Validation. **Giovanni Maestri:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **Nicola Della Ca:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2026.117037.

Data availability

Data will be made available on request.

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