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Aliphatic aldehydes as CO surrogates *via* photocatalyzed hydrogen atom transfer

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The search for safe and practical carbon monoxide (CO) surrogates is central to unlocking the full potential of carbonylation chemistry in academic settings. Herein, we propose aliphatic aldehydes as a convenient class of CO photosurrogates under photocatalyzed decarbonylative Hydrogen Atom Transfer (HAT) conditions. Compared to previously reported surrogates, whose synthesis is often a daunting task, these carbonyl compounds are inexpensive, commercially available, and already present in standard laboratory inventories. From a conceptual standpoint, this light-mediated approach overcomes a longstanding limitation in the use of aldehydes as CO surrogates, namely the reliance on expensive noble metal catalysis under forcing conditions to enable CO release.

Green foundation

1. Reported CO surrogates suffer from low atom economy, high environmental factors, and require lengthy synthetic procedures or forcing conditions to trigger CO release. This work proposes aliphatic aldehydes as CO photosurrogates *via* decarbonylative photocatalyzed hydrogen atom transfer. These carbonyl compounds are cheap, widely available feedstock chemicals and show a high CO content. This enables fast, on-demand CO release under mild conditions and avoids hazardous reagents and byproducts, using light as a clean energy source.
2. Compared to traditional surrogates, photosurrogates offer precise temporal control over CO release *via* light modulation, improving safety. This method delivers up to 95% CO release yield and a CO weight percentage of 33%, significantly outperforming benchmarks like SilaCOgen (11%) in atom economy and environmental impact.
3. Future work should aim to enhance catalytic efficiency, develop greener photocatalysts, and expand surrogate design for high-pressure carbonylation reactions.

Introduction

The introduction of a carbonyl group, *i.e.* one of the most prevalent and versatile functionalities in organic chemistry, enables smooth access to a wide plethora of bulk chemicals such as ketones, amides and esters.[1,2] The use of CO gas is ideal for large-scale carbonylation in industry, where infrastructure enables its safe and efficient handling.[3] In contrast, academic research prioritizes flexibility for generating diverse compound libraries, but often lacks the expertise and equipment to safely manage even small amounts of this lethal gas (Scheme 1A).

A controlled release of carbon monoxide is possible thanks to CO surrogates,[4–7] *i.e.* relatively stable molecules that liberate carbon monoxide only upon judicious chemical. Albeit a few cases demonstrate experimentally viable conditions for this approach,[8–10] in most synthetic contexts, such activation still requires stringent conditions—such as high temperatures (>100 °C), strong acids or bases, or expensive transition metals —often in combination (Scheme 1B). These conditions not only limit practicality but also prevent controlled CO release, as CO evolution and the associated catalytic cycles cannot be halted once initiated.

An elegant solution to this impasse is offered by CO photosurrogates (aka photoCORMs,[11] CORMs: CO releasing molecules), where photons deliver the energy needed to liberate carbon monoxide from the surrogate. In fact, this strategy offers the ability to precisely dose and regulate the production of CO in time literally with the flip of a switch. Recent efforts have been focused on designing or constructing metal-free photosurrogates. In 2017, Li and co-workers suggested *N*,*N*-dimethylformamide (DMF) as a surrogate for a carbonylative

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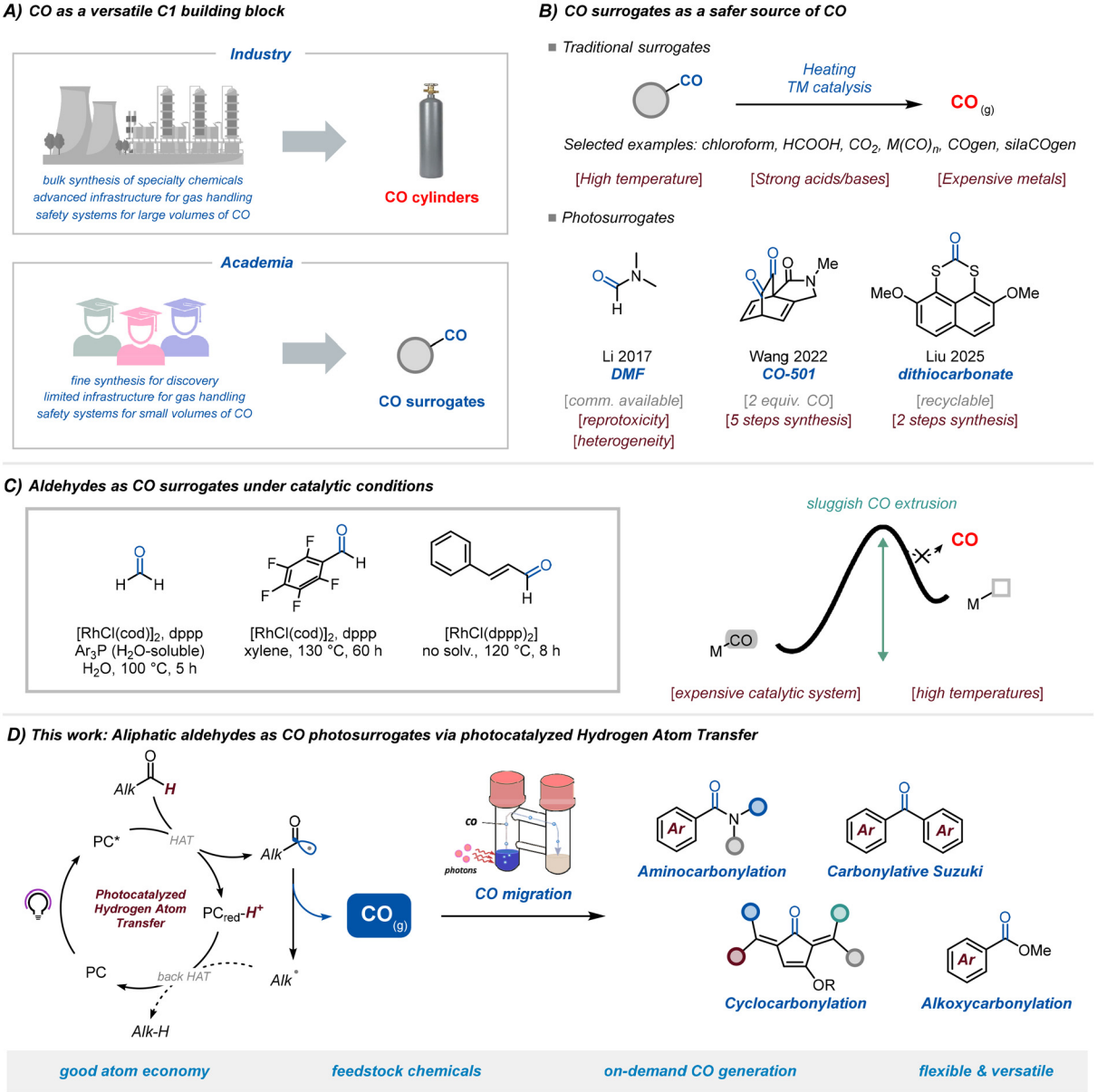


Scheme 1 (A) CO as a versatile C1 building block: industry *vs.* academia. (B) CO surrogates as a safer alternative to CO gas. (C) The use of aldehydes as CO surrogates *via* traditional transition-metal catalysis. (D) This work: aliphatic aldehydes as CO photosurrogates *via* photocatalyzed Hydrogen Atom Transfer (HAT).

Suzuki reaction in the presence of TiO_2 as heterogeneous photocatalyst.[12] In 2022, Wang and co-workers developed CO-501 to deliver CO upon photolysis with blue light irradiation.[13] During the preparation of this manuscript, the group of Liu has proposed the class of 1,8-naphthylene dithiocarbonates as a new class of recyclable CO photosurrogates (Scheme 1B).[14] Despite their groundbreaking contributions, these strategies are hindered by significant limitations: (i) the low CO weight percentage of most surrogates undermines the sustainability of the process; (ii) the surrogates themselves often require time-consuming, multi-step syntheses; (iii) in heterogeneous systems, uneven irradiation can lead to delayed CO release, which in turn compromises reaction selectivity and reproducibility, (iv) photocatalytic methods for CO release are underrepresented. Overall, the field continues to present significant opportunities for innovation and improvement.

Due to their known propensity for decarbonylation to release CO under metal-catalyzed conditions, aldehydes have attracted interest as commercially available surrogates (Scheme 1C). However, this strategy typically requires harsh conditions—high temperatures and noble metal catalysts—to facilitate the extrusion of a CO molecule from a metallocarbonyl intermediate.[15,16] Prompted to address this mechanistic limitation, we were inspired by photocatalyzed Hydrogen Atom Transfer (HAT).[17–25] In fact, it is well known that the formyl C(sp^2)–H bonds of alkyl aldehydes can be activated *via* photocatalyzed HAT to give acyl radicals.[26]

The latter intermediates undergo rapid decarbonylation if the resulting alkyl radical is stabilized enough (*e.g.*, tertiary or benzylic radicals),[27–31] making aliphatic aldehydes ideal CO photosurrogates *via* HAT.

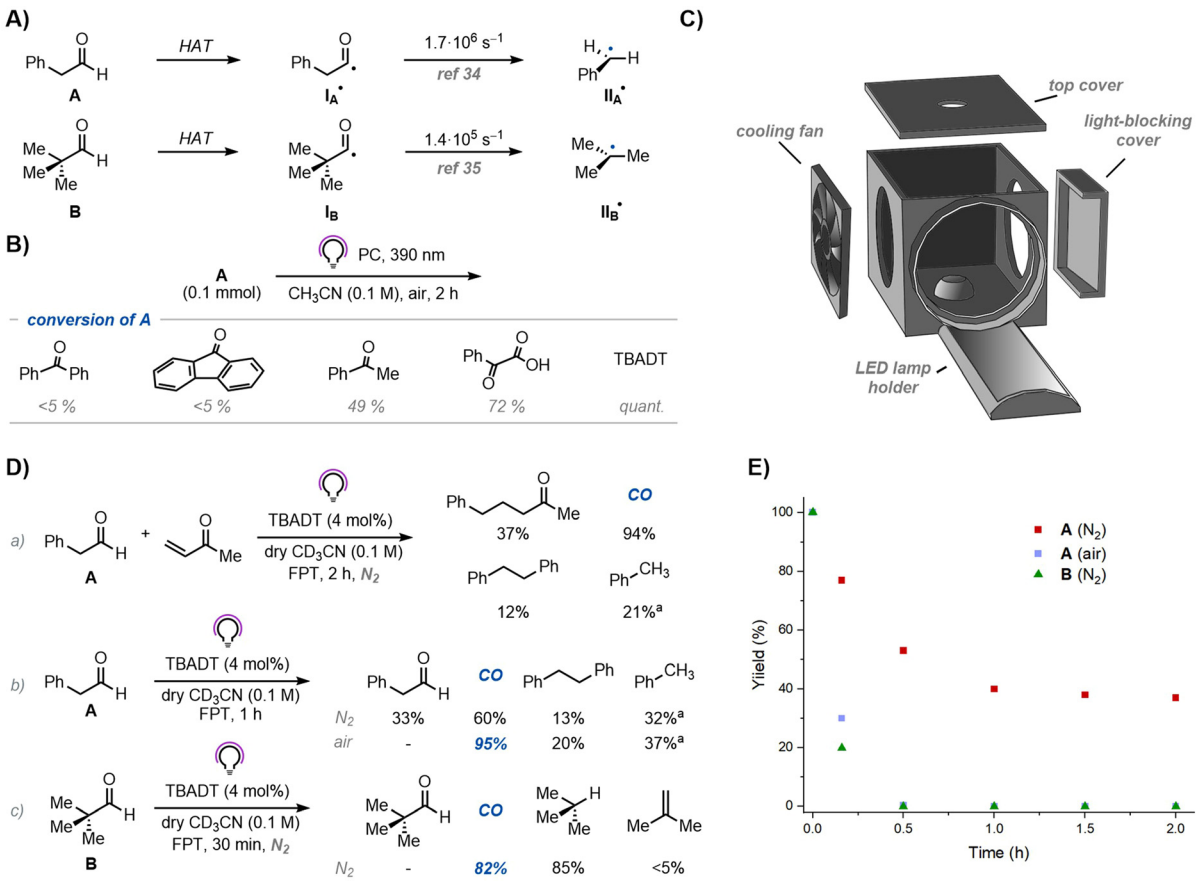
In this work, we propose a catalytic method for leveraging light aliphatic aldehydes as CO surrogates *via* photocatalyzed HAT (Scheme 1D).[32] These compounds are commercially available, inexpensive and avoid lengthy synthesis. Importantly, this approach would allow on-demand CO release with minimal delay in initiation or termination. This method compares profitably with established manifolds as it enables quantitative CO release with improved atom economy and diminished environmental factor.

Results and discussion

At the outset of our study, we selected phenylacetaldehyde **A** and pivalaldehyde **B** as aliphatic aldehydes for our purposes (see section 4.3 in the SI for further discussion). The choice was based on the following criteria: (i) they are cheap and commercially available (0.10 and 1.16 € per mmol,[33] respectively); (ii) the acyl radical generated *via* HAT undergoes relatively rapid decarbonylation in both cases (Scheme 2A, $k_d = 1.7 \times 10^6$ s^{-1} for **A**[34] and 1.4×10^5 s^{-1} for **B**[35]); (iii) any by-products formed upon CO release should be easily removed, leaving no traces behind.

Thus, in an ideal scenario (Scheme 2A), the photocatalyst (PC) absorbs light and initiates a HAT event from the aliphatic aldehyde, generating acyl radical **I**$^{\bullet}$. This intermediate then undergoes decarbonylation to yield radical **II**$^{\bullet}$, completing the HAT–decarbonylation sequence. Both for **A** and **B**, **II**$^{\bullet}$ is stabilized, making it susceptible to two main fates: back-HAT with the reduced photocatalyst (PC_{red}–H^+) to afford the corresponding hydrocarbon, or dimerization and other side reactions. Notably, the latter pathways can negatively impact the turnover number of the photocatalyst.

Our investigation started by identifying the most effective HAT photocatalyst to realize our strategy (Scheme 2B). Thus, we irradiated 0.1 M air-equilibrated solutions of aldehyde **A** in



Scheme 2 Preliminary results and implementation. (A) Elementary steps involved in the use of aliphatic aldehydes as CO photosurrogates *via* HAT. Phenylacetaldehyde (**A**) and pivalaldehyde (**B**) were selected as aldehydes for this work. (B) Preliminary tests for the decomposition of aldehydes with different photocatalysts. (C) Schematic of the CO-box$_\alpha$ reactor used for the decarbonylation studies. (D) Experiments conducted for the determination of the efficiency of CO generation. (E) Kinetic profile for experiments reported in Scheme Db and c. Procedures adopted for analysis are described in detail in section 4.5 and 4.6 in the SI. [a] Minor amounts of benzaldehyde and phenylacetic acid were detected (10% overall). PC: photocatalyst. FPT: freeze–pump–thaw.

CH_3CN using a 390 nm LED lamp at full intensity, in the presence of various photocatalysts, and monitored aldehyde consumption as a proxy for CO release. Aromatic ketones, phenylglyoxylic acid, and tetrabutylammonium decatungstate (TBADT, $(n\mathrm{Bu}_4\mathrm{N})_4[\mathrm{W}_{10}\mathrm{O}_{32}]$) were tested in the role of photocatalysts.[24] We found that, after 2 h of irradiation, only TBADT could promote complete conversion of **A**[36] and, accordingly, we selected it for its better catalytic performance (see section 4.4 in the SI).

With this initial combination of aldehyde and photocatalyst (**A** and TBADT), we moved to evaluate the efficiency of CO generation. In recognizing the importance of a standardized geometry of irradiation for conducting reproducible measurements, we designed and 3D-printed a reactor in PLA (CO-box$_\alpha$, see Scheme 2C and section 4.1 of the SI for the detailed description).[37] To validate the experimental setup, we performed the decarbonylative Giese-type reaction[28] shown in Scheme 2Da while monitoring the volume of CO released *via* a water volumeter (see section 4.2 in the SI). The mass balance, determined by comparing the amount of CO released to the quantity of tolyl-containing products formed, showed consistent results with a margin of error of approximately 5% (see section 4.2 in the SI).

The calculated CO release efficiency (η_{CO}) was 94%.

In a second experiment where we removed the electron-poor olefin (Scheme 2Db) to avoid any possible interference with the catalytic cycle, the conversion of **A** dropped to 60%, suggesting inhibited turnover of the catalyst. A persistent blue colour after irradiation hinted accumulation of the reduced form of TBADT.[38] For this reason, we hypothesized that air-equilibrated conditions could promote TBADT reoxidation, thus promoting turnover. While this approach led to the formation of ~15% unidentified byproducts, it successfully restored a η_{CO} = 95%. Also in this case, the major byproducts were toluene and biphenyl, accounting for 77% total yield.

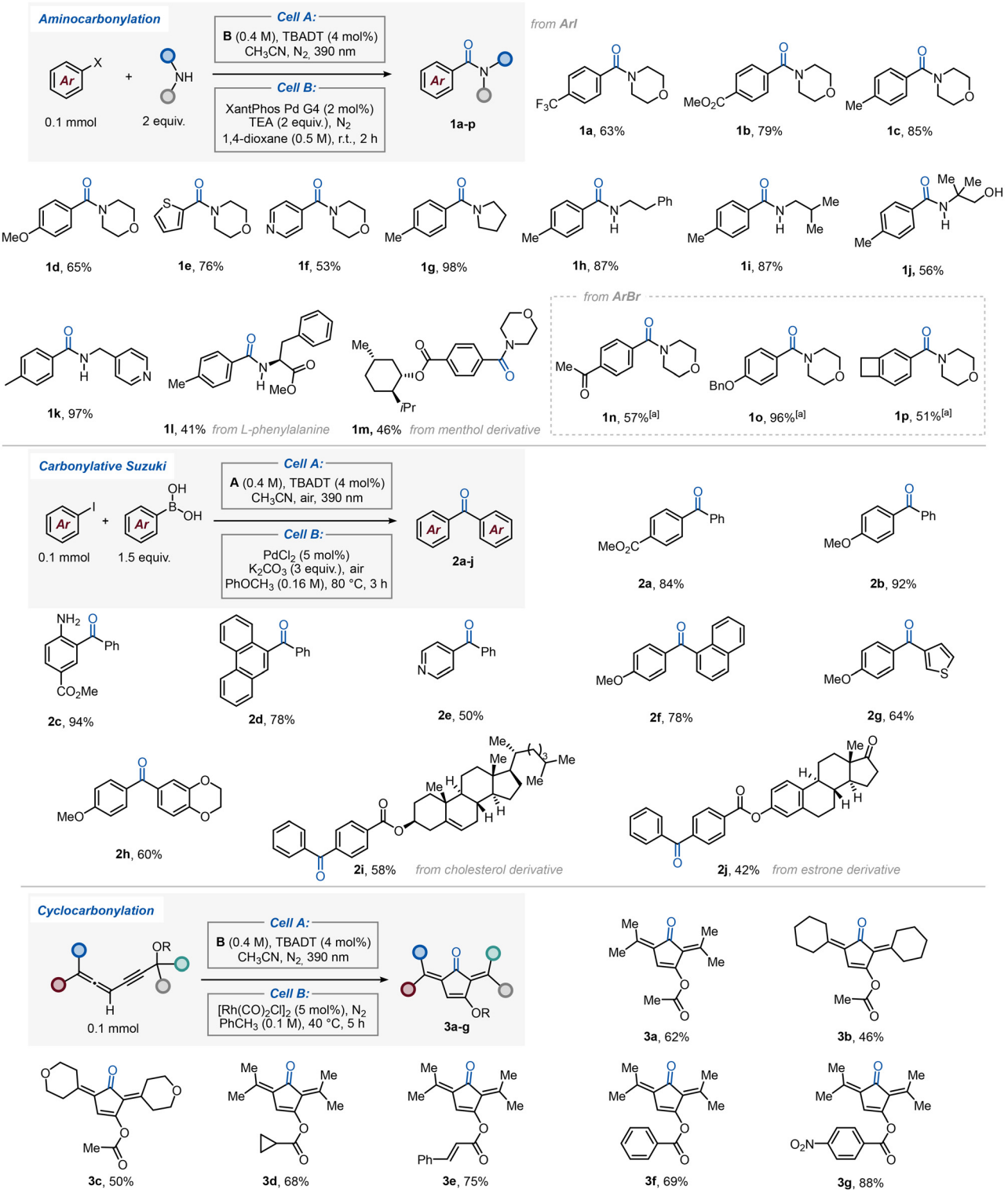
Intriguingly, when we conducted a similar investigation for pivalaldehyde (**B**), we observed that complete aldehyde consumption could be observed under N_2 atmosphere (Scheme 2Dc). In this case, the major byproduct observed was isobutane, in accordance with the literature.[39] Owing to the gaseous nature of the byproducts generated in the HAT-decarbonylation sequence, we performed GC-TCD analysis, which revealed a 2 : 1 ratio of CO to isobutane. As detailed in section 4.7 in the SI, this corresponds to η_{CO} = 82%. It is important to stress here that **B** offers a reliable entry point for those carbonylation reactions that require strictly inert conditions, where the use of **A** under air-equilibrated conditions would be problematic. Finally, an analysis of the decarbonylation reaction in time (Scheme 2E) showed that in all cases mentioned above, CO evolution was complete within 1 h of irradiation with a LED lamp (λ = 390 nm, full intensity).

Next, we moved to evaluate the applicability of our photosurrogates **A** and **B** in different classes of carbonylation reactions: a Pd-catalyzed aminocarbonylation, a Pd-catalyzed carbonylative Suzuki coupling, a Rh-catalyzed cyclocarbonylation and a Co-catalyzed (Scheme 3) photo-alkoxycarbonylation. Reactions were performed in a standardized glassware (so-called COware) developed by the Skrydstrup group,[7] featuring two connected chambers: Cell A, for CO release, and Cell B, for CO-consuming reactions. Only Cell A is irradiated (irradiation time: 1 h, after which the lamp is switched off), while Cell B operates under conditions specific to the carbonylation reaction. As mentioned above, the geometry of irradiation is crucial to achieve reproducibility, which led us to develop a dedicated 3D-printed reactor to accommodate the COware (CO-box$_\beta$, see section 4.1 in the SI).

First, we evaluated the performance of our system in the context of Pd-catalyzed aminocarbonylation, where XantPhos Pd G4[40] was used to promote the formation of amides from a variety of commercially available aryl iodides.[41] Cell A was loaded with an oxygen-free solution of aldehyde **B** (0.4 M) and TBADT (4 mol%) in CH_3CN, while Cell B was charged with a 1,4-dioxane solution of the desired amine, aryl iodide, Pd catalyst and triethylamine (TEA) under inert atmosphere. The cell was placed in the CO-box$_\beta$ and irradiation of Cell A was started (λ = 390 nm). After two hours, the content of Cell B was withdrawn and purified to isolate the desired amide. Starting from variously substituted aryl iodides, and using morpholine as model amine, we obtained the desired products **1a–1f** in good to excellent yields. The reaction worked well both with electron-withdrawing (**1a–1b**, 63–79%) and electron-donating groups (**1c–1d**, 65–85%), as well as in the presence of heterocycles such as thiophene (**1e**, 76%) and pyridine (**1f**, 53%). Subsequently, different amine moieties were investigated. By employing primary and secondary amines, we obtained the desired aminocarbonylated products **1g–1k** in good to high yield after isolation (56–98%). The robustness of our approach was demonstrated by its compatibility with biorelevant motifs, including a C-protected amino acid (L-phenylalanine methyl ester) as the amine component and menthyl 4-iodobenzoate as the aryl iodide, affording the corresponding amides **1l** and **1m** in synthetically useful yields. Finally, we also proved that the methodology can be expanded to aryl bromides (**1n–1p**) in good yields (>51%), even though longer reaction times were typically required (16 hours) in Cell B.

Second, we focused on an air-tolerant carbonylative Suzuki coupling strategy to synthesize unsymmetrical aromatic ketones.[42] As inert atmosphere was not required for this transformation, we selected aldehyde **A** as surrogate for this methodology. Thus, Cell A was loaded with an air-equilibrated solution of aldehyde **A** (0.4 M) and TBADT (4 mol%) in CH_3CN, while Cell B was charged with an anisole solution of the desired aryl boronic acid, aryl iodide, Pd catalyst and K_2CO_3 as the base. The reaction was carried out as described for the aminocarbonylation (3 h reaction time), and Cell B was heated at 80 °C. In all cases, full conversion of the aryl iodide was achieved. Both electron-deficient and electron-rich aryl iodides were well tolerated (**2a–2d**, 78–94%), affording the expected ketones in high yields, even in the presence of unprotected aniline groups (**2c**, 94%), indicating minimal interference from the free amine, or starting from the iodopyridine (**2e**,

50%). Comparable yields were obtained with diverse boronic acids, including heteroaryl (*e.g.*, thiophene, **2g**, 64%) and electron-rich protected catechols (**2h**, 60%). In this case, to prove the flexibility of our approach, we subjected cholesterol and estrone derivatives to our conditions and obtained the desired products **2i** and **2j** with 58% and 42%, respectively.



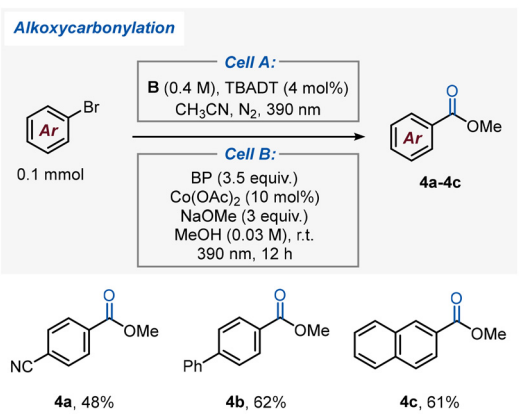
Scheme 3 Substrate scope of carbonylation reactions using aldehydes **A** and **B** as CO photosurrogates. All reactions were conducted in the COware mounted on the CO-box$_\beta$ reactor equipped with a LED lamp (λ = 390 nm, full intensity). See SI for further details. TEA: triethylamine. [a] Reaction time: 16 h.

Third, we challenged our strategy with a rhodium-catalyzed carbocyclization of 1,4-allenynes recently reported by us, which proceeds through a [2 + 2 + 1] cycloaddition pathway.[43]

By exploiting the Rh-1,3 acyloxy migration, and subsequent CO insertion into the Rh-diallene intermediate, we were able to obtain the cyclopentenones **3** in good to excellent yields (46–88%). In this case, Cell A was loaded with an oxygen-free solution of aldehyde **B** (0.4 M) and TBADT (4 mol%) in CH_3CN, while Cell B was charged with a toluene solution of the desired conjugated allenyne and the Rh catalyst. The reaction was carried out as described for the aminocarbonylation (5 hours reaction time), by applying gentle heating (40 °C) to Cell B.

Finally, we decided to challenge our system by conducting a photochemical reaction with our photosurrogates. With this aim, inspired by the Co-catalyzed photochemical alkoxycarbonylation protocol already reported by Jia and Yin,[44,45] we decided to carry out the reaction using two parallel CO-box$_\alpha$ setups, in order to maximize the irradiation in the two separated Schlenk tubes (see sections 4.1 and 5.6 in the SI). Thus, starting from aryl bromides and using benzophenone (3.5 equiv.) as photosensitizer and $Co(OAc)_2$ (10 mol%), with MeOH as solvent (Scheme 4), we were able to achieve the desired ester derivatives **4a–4c** with 48–62% yield of the isolated product, supporting the idea that our approach offers applicability also for dual-photochemical systems.

Finally, a comparison in terms of sustainability with state-of-the-art CO surrogates is in order. Metallocarbonyl complexes have long served as benchmarks in this field; however, their volatility and metal content raise serious environmental and health concerns, conflicting with the principles of safer chemical synthesis (Principle 3). Among the most widely used alternatives are COgen and SilaCOgen, developed by the Skrydstrup group,[46,47] which deliver carbon monoxide in a controlled fashion but contain only ~11% CO by mass, compromising atom economy (Principle 2). As a comparison, CO weight percentage for **A** and **B** are 23% and 33%, respectively.



Scheme 4 The use of aldehydes as photosurrogates to conduct a photochemical alkoxycarbonylation. The reactions were conducted in a dual CO-box$_\alpha$ reactor (see section 5.6 in the SI).

More recent developments, such as photoactivatable surrogates like CO-501[13] and dithiocarbonates,[14] offer precise temporal control over CO release, enhancing safety and process efficiency. While these methods align well with Green Chemistry in terms of real-time control and accident prevention (Principle 12), their low CO content by mass (9% and 28%, respectively), along with the need for elaborate synthetic preparation, limit their overall sustainability (Principle 8: reduce derivatives).

Lighter CO releasing molecules such as CO_2, chloroform, DMF, and formates have been explored as well,[48] broadening the landscape of safer carbonylation methods. In this context, aliphatic aldehydes emerge as highly competitive candidates. In fact, our method leverages these feedstocks to generate CO *in situ* under mild conditions, without the need for pressurized gases, toxic intermediates, or harsh reagents. This aligns with several Green Chemistry principles, including safer solvents and auxiliaries (Principle 5), energy efficiency (Principle 6), and waste prevention (Principle 1).

Conclusions

In conclusion, we have demonstrated the effective use of aliphatic aldehydes, specifically phenylacetaldehyde and pivalaldehyde, as versatile CO photosurrogates. Under photocatalyzed hydrogen atom transfer (HAT) conditions, these compounds rapidly generate CO *via* catalytic decarbonylative HAT. This strategy offers several compelling advantages over existing approaches. First, these aldehydes are commercially available and cheap, and do not require any laborious synthesis. Second, the high CO weight percentage significantly improves the atom economy compared to reported alternatives. Third, temporal control is easily achieved: CO release can be started and stopped instantly with light, providing a level of precision and safety rarely accessible with traditional surrogates.

We have validated the broad applicability of this approach across a range of synthetically valuable carbonylation reactions, including aminocarbonylation, carbonylative Suzuki coupling, cyclocarbonylation, and a photochemical alkoxycarbonylation.

One area for future development is the use of CO photosurrogates in high-pressure carbonylation, which currently represents a clear limitation of surrogates-based carbonylation reactions. Furthermore, in the context of scale-up, the cost of photons[49] will require careful evaluation. We are confident that the simplicity, tunability, and operational safety of this method will make it a valuable tool for sustainable synthesis.‡

Conflicts of interest

There are no conflicts to declare.

‡ It is worth noting that the efficacy of aldehydes as CO surrogates has been very recently demonstrated in biological settings.[50]

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: additional experimental procedures, characterization data for synthesized compounds, NMR spectra, and photographs of the experimental setup. See DOI: https://doi.org/10.1039/d5gc03981a.

Additionally, the .stl files for the 3D-printing of CO-box reactors (both model alpha and beta) are available at Zenodo at https://doi.org/10.5281/zenodo.17064424.

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