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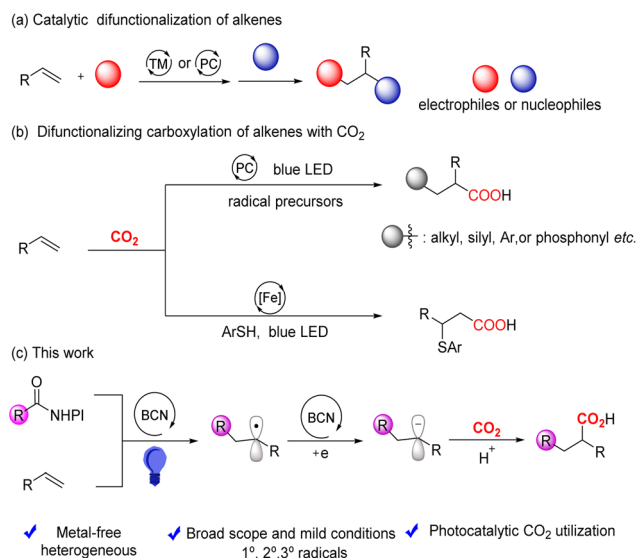
Metal-free semiconductors for visible-light-induced carbocarboxylation of styrenes with aliphatic redox-active esters and CO₂[†]Hao Hou,^a Meizhen Luo,^a Senmao Zhai,^a Tao Yuan,^{a,b} Meifang Zheng ^{*a} and Sibow Wang ^{*a}

A sustainable system for the carbocarboxylation of olefins with redox-active esters and CO₂ via visible-light-induced photoredox catalysis has been developed using metal-free boron carbonitride (BCN) as the photocatalyst. The scheme introduces versatile alkyl groups (including primary, secondary, and tertiary) and CO₂ into the C–C double bond in a fully regioselective manner to produce valuable carboxylic derivatives with excellent yields.

The vicinal difunctionalization of olefins has emerged as a powerful synthetic method as it enables the increase of molecular complexity from readily available building blocks in one step.¹ Versatile electrophilic and nucleophilic reagents have been forged to form new C–C or C–X bonds in molecules by transition metal-catalyzed difunctionalization reactions (Scheme 1a).² The incorporation of carbon dioxide (CO₂) into olefins to generate value-added chain carboxylic acids is a hot research topic, because CO₂ is a sustainable, low-cost, abundant and non-toxic C1 synthon (Scheme 1b).^{3,4} The boom is assisting the development of photochemistry, which enables previously redox-challenging reactions *via* a single electron transfer (SET) process with visible light.⁵ Recently, the groups of Yu, Martin, Wu, *etc.*^{6–9} have developed the regioselective carbonylation of activated alkenes with transition metal-containing complexes or organic dyes as photosensitizers, and introduced CO₂ and diverse radical precursors, including aryl halides, H–P(O) compounds, alkyl silicon reagents, *etc.*, into the alkenes forming valuable carboxylic derivatives.

The recycling and cost issues of those homogeneous photosensitizers inspire the idea of heterogeneous photocatalysis, which emerges as a growing technique for organic synthesis and exhibits superior advantages such as recyclability, good stability, and facile separation of the products from the reac-

tion mixture.¹⁰ Therefore, efforts have been dedicated to building Earth-abundant element-containing heterogeneous semiconductor systems for catalysis and organic synthesis.¹¹ Metal-free semiconductors, including graphitic carbon nitrides (g-CN),¹² covalent organic frameworks (COFs),¹³ and conjugated microporous polymers (CMPs),¹⁴ could function as photocatalysts for cycloaddition, cross-coupling, hydrogenation and so on.^{15–17} Boron carbonitrides (BCNs) are non-metallic two-dimensional semiconductor materials, composed of the elements boron, carbon and nitrogen, featuring the advantages of easily available precursors, simple synthetic operation, and a large open surface area with abundant active sites for catalysis performance.^{18,19} They are visible light-responsive with a tunable band gap (0–5.5 eV), which depends on the carbon content incorporated into the boron nitride (BN) frameworks, allowing extended utilization of light energy for artificial photosynthesis.^{20–23} To date, they have rarely been



Scheme 1 Difunctionalization of alkenes.

^aState Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, P. R. China.

E-mail: mfzheng@fzu.edu.cn, sibowang@fzu.edu.cn

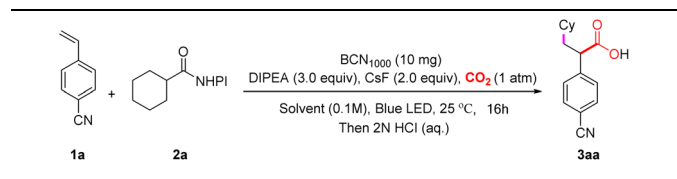
^bCollege of Chemical Engineering, Fuzhou University, Fuzhou 350116, P. R. China[†]Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3gc04450e>

used in direct carboxylation with CO₂, with just one exception of hydrocarboxylation of alkenes.²⁴ Therefore, we herein design the carbocarboxylation of alkenes using the surface catalytic process of BCN (Scheme 1c).

The reaction started with 4-cyanostyrene **1a** and cyclohexyl *N*-(acyloxy)phthalimide **2a** as the model substrates under atmospheric pressure of CO₂ with 450 nm LEDs at 25 °C in the solvent *N,N*-dimethylacetamide (DMA) (Table 1, entry 1). Metal-based Ru(bpy)₃Cl₂·6H₂O and *fac*-Ir(ppy)₃ were less efficient than BCN for this transformation (entries 2 and 3). Other solvents depressed the yield of **3aa** (entries 4 and 5). The yield of **3aa** declined when using Et₃N and DABCO instead of DIPEA as the sacrificial agent (entries 6 and 7). We also screened a range of bases, among which CsF gave the optimal yield of 78% (Table S1 in the ESI†). Notably, product **3aa** was not detected in the absence of either BCN or light, indicating the necessity of these factors (entries 9 and 10). Gratifyingly, when recycled BCN was tested under the standard reaction conditions, it exhibited conserved catalytic performance (Scheme 2a and b), which demonstrated good stability of the BCN photocatalyst during prolonged light exposure. It was further verified by the similar patterns of XRD, DRS, SEM, and TEM characterization studies of fresh and used BCN (Fig. S13 and S14†).

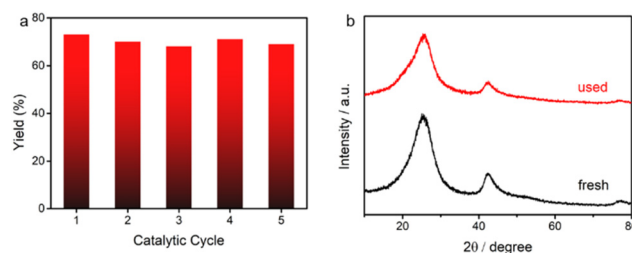
Having identified the optimized reaction conditions, we then surveyed the reaction scope of aliphatic *N*-(acyloxy)phthalimide redox-active esters (RAEs) **2** with **1a** (Table 2). A variety of secondary aliphatic acid esters were efficient substrates to afford the desired products. Specifically, the generation of secondary alkyl radicals from cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl RAEs formed the desired products in moder-

Table 1 Screening of the optimal reaction conditions^a



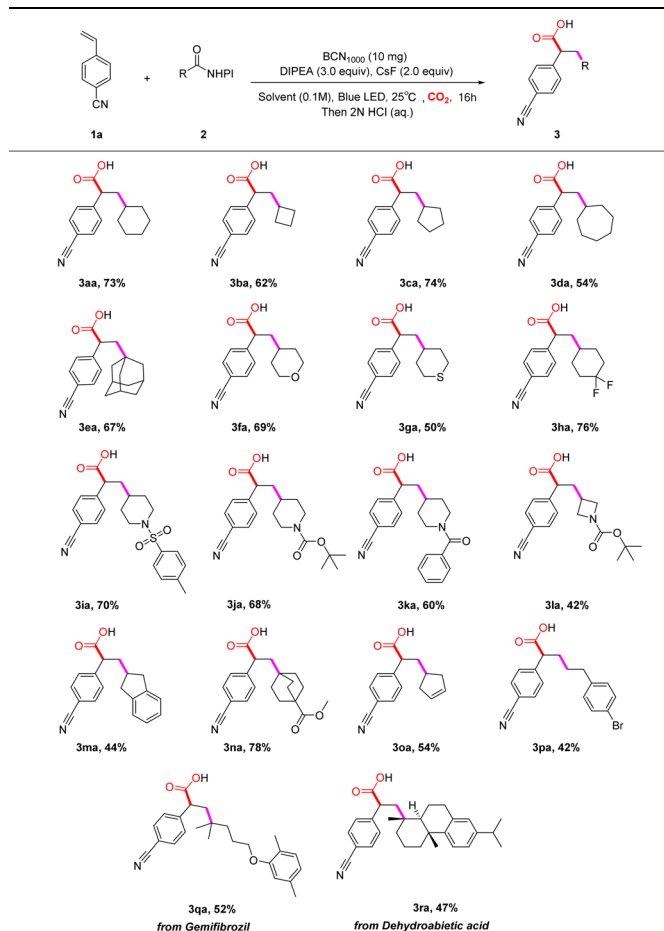
Entry	Variation from standard conditions	Yield of 3aa ^b [%]
1	None	78 (73 ^c)
2	Ru(bpy) ₃ Cl ₂ ·6H ₂ O used as the PC	14
3	<i>fac</i> -Ir(ppy) ₃ used as the PC	28
4	DMF instead of DMA	54
5	MeCN instead of DMA	N.D.
6	DABCO instead of DIPEA	14
7	Et ₃ N instead of DIPEA	32
8	Without CsF	30
9	Without light	N.D.
10	Without PC	N.D.
11	Without DIPEA	N.D.
12	Without CO ₂	Trace

^a Standard conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), BCN₁₀₀₀ (10 mg), CsF (0.2 mmol), DIPEA (0.3 mmol), DMA (1.0 mL), CO₂ (1 atm), 450 nm blue LEDs, 25 °C, quenched with 2N HCl (aq.). "N.D." is short for "not detected". ^b Yield was determined by ¹H NMR with dibromomethane as the internal standard. ^c Isolated yield.



Scheme 2 (a) Activity test with recycled BCN. (b) XRD patterns of fresh and used BCN.

Table 2 Scope of alkyl esters^a



^a Standard conditions: **1a** (0.1 mmol), **2** (0.15 mmol), BCN₁₀₀₀ (10 mg), CsF (0.2 mmol), DIPEA (0.3 mmol), DMA (1.0 mL), CO₂ (1 atm), 450 nm blue LEDs, 25 °C, for 16 h, quenched with 2N HCl (aq.). Isolated yields.

ate to good yields (**3aa–3da**). The reaction with a sterically-hindered tertiary adamantanyl RAE was feasible with a 67% yield of **3ea**. In addition, secondary alkyl RAEs containing biologically-active pyran, thiane, and piperidine motifs²⁵ underwent the reaction smoothly, affording the corresponding products in moderate yields (**3fa**, **3ga** and **3ia–3la**). Furthermore, RAE derivatives with difluoromethyl or alkenyl substituents were

also well tolerated under the reaction conditions, delivering the desired products **3ha** and **3oa** smoothly. Of note, tertiary aliphatic esters could also benefit from the established strategy. The protocol is also feasible for a polycyclic [2.2.2]bicyclooctane-containing ester (**3na**). In particular, the primary alkyl derivative could undergo the photocatalytic SET process forming a primary alkyl radical and the subsequent corresponding products (**3pa**). The heterogeneous photocatalysis system could be applied to the derivatives of RAEs containing a gemfibrozil fragment or an abietic acid fragment, for this transformation, producing the products **3qa** and **3ra**.

We further screened the scope of alkenes (Table 3). A series of substituted styrenes with sensitive substituents, such as the trifluoromethyl group, cyano group and ester group, could be accommodated and they afforded the corresponding products in moderate to good yields (**3aa–3af**). Notably, polyfluorine-substituted styrene could also be converted to difunctionalized product **3ag** with a yield of 70%. 1,1-Diarylethylenes and α -substituted styrenes could also result in the target compounds (**3ah**, **3ak** and **3al**) with quaternary carbon centers under the standard reaction conditions. Remarkably, unconjugated alkenyl and alkynyl substitutions were compatible in this protocol (**3ai** and **3aj**). Cyclodecanal-derived styrene

underwent the process smoothly with moderate yield (**3am**). Satisfactorily, isobornyl and menthol derivatives underwent the carbocarboxylation successfully, giving the products in moderate yields (**3an** and **3ao**). Moreover, methacrylate could also be converted to the corresponding product (**3ap**).

Additional experiments were performed to gain insight into the mechanism (Scheme 3). The Stern–Volmer quenching plots exhibited that the excited BCN was quenched by RAE **2a** or DIPEA rather than 4-cyanostyrene **1a** (see the ESI, Fig. S6–S9†). With the addition of 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO), **3aa** was not detected (Scheme 3a), and the cyclohexyl radical–TEMPO adduct **4** was detected. Furthermore, the radical clock experiment of (1-(2-phenylcyclopropyl)vinyl) benzene **7** with **2a** resulted in the ring-opening product **8**, verifying the formation of the carbon radical intermediate in the process (Scheme 3d).⁹ When D₂O was added, up to 75% deuterium incorporation of **3aa'** was observed (Scheme 3b). Furthermore, the *gem*-difluoro alkene **6** was detected when using trifluoromethylalkenes **5** and cyclohexyl RAE **2a** as the substrates, which was consistent with the radical/polar cross-over defluorinative alkylation pathway (Scheme 3c). The results indicate the existence of a benzylic carbon anion intermediate. Since **3aa** was not detected when **3aa'** was used, the possibility that **3aa'** was the intermediate was ruled out (Scheme 3e).

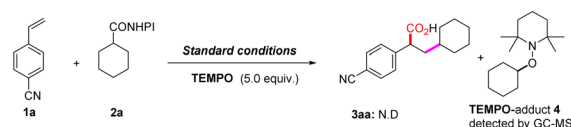
Based on the mechanistic studies and literature precedents,²⁶ a mechanism for BCN-catalyzed carbocarboxylation of alkenes was proposed (Scheme 4). Initially, a photogenerated electron–hole pair is generated from the excited state BCN upon visible light irradiation. *N*-Hydroxyphthalimide esters **2** are then reduced by the photogenerated electron

Table 3 Scope of alkenes^a

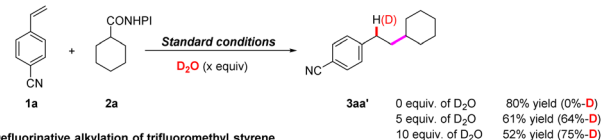
R_1 R_2		Cy-NHPI	BCN ₁₀₀₀ (10 mg) DIPEA (3.0 equiv), CsF (2.0 equiv) Solvent (0.1 M), Blue LED, 25 °C, CO ₂ , 16 h Then 2N HCl (aq.)	R_1 R_2
1		2a		3
3aa, 73%	3ab, 48%	3ac, 64%	3ad, 65%	
3ae, 54%	3af, 54%	3ag, 70%	3ah, 41%	
3ai, 64%	3aj, 50%	3ak, 44%	3al, 40%	
3am, 48%	3an, 61% From Isoborneol	3ao, 56% From Menthol	3ap, 44%	

^a Standard conditions: **1** (0.1 mmol), **2a** (0.15 mmol), BCN₁₀₀₀ (10 mg), CsF (0.2 mmol), DIPEA (0.3 mmol), DMA (1.0 mL), CO₂ (1 atm), 450 nm blue LEDs, 25 °C, for 16 h, quenched with 2N HCl (aq.). Isolated yields.

a. Radical trapping experiment



b. Isotope labeling experiments with D₂O



c. Defluorinative alkylation of trifluoromethyl styrene



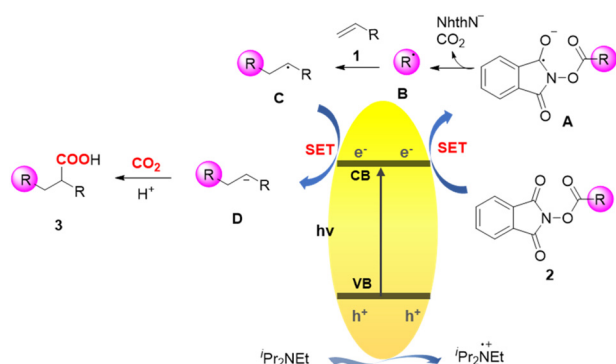
d. Radical clock reaction



e. Direct carboxylation of the hydroalkylation product



Scheme 3 Mechanistic studies.



Scheme 4 Proposed mechanism.

forming the phthalimide ester radical, which decomposes to the NHPI anion, CO_2 , and alkyl radical **B**. Meanwhile, the photogenerated hole is consumed by DIPEA. The following radical addition of intermediate **B** to alkene **1** affords benzylic radical **C**, which subsequently is reduced by the photogenerated electron to give the benzylic carbanion **D** through the single electron transfer pathway. Nucleophilic addition of intermediate **D** to CO_2 and subsequent protonation furnish the final carboxylic product **3**.

Conclusions

In summary, a ternary metal-free heterogeneous photoredox system was introduced into the carbocarboxylation of olefins with CO_2 and aliphatic redox-active esters in one pot with visible light. This strategy has the advantages of wide substrate scope, mild reaction conditions, low photocatalyst loading and recyclability. The protocol presented the potential practicality of CO_2 fixation in fine chemical synthesis *via* heterogeneous catalysis.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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