



Cite this: *Green Chem.*, 2024, **26**, 8315

# Photoelectrochemical nickel-catalyzed carboacylation/silanoylation of alkenes with unactivated C/Si–H bonds†

Lanfen Wang,<sup>‡a</sup> Xiangyu Huo,<sup>‡c</sup> Xiaozhi He,<sup>a</sup> Lutz Ackermann<sup>ID</sup>\*<sup>b</sup> and Dingyi Wang<sup>ID</sup>\*<sup>a</sup>

Direct and selective installation of two different functional groups into the unsaturated bonds of alkenes constitutes a long-standing goal in organic synthesis. Herein, we first report a photoelectrochemical approach for the carboacylation/silanoylation of alkenes with unactivated alkanes/hydrosilanes *via* the LMCT process. A number of ketones with high complexity and diversity were rapidly obtained from commercially available materials in an economical and sustainable manner. Furthermore, this protocol can be scaled up to the gram-level. This paired electrocatalysis strategy features excellent regioselectivity, and ample substrate scope, is external-oxidant-free, and features a high resource economy. A series of mechanistic experiments were performed to determine the preferred pathway for the photoelectrochemical Ni(I)/Ni(II)/Ni(III) cycles in these transformations.

Received 25th October 2023,  
Accepted 12th February 2024

DOI: 10.1039/d3gc04109c

rsc.li/greenchem

## Introduction

Carbon–carbon bonds form the fundamental backbones of organic compounds, so constructing them efficiently is one of the central goals of synthetic chemistry.<sup>1</sup> Carbofunctionalization of alkenes can effectively construct carbon–carbon bonds by directly and selectively introducing two different carbon fragments into the C=C double bond.<sup>2</sup> Recently, impressive progress has been made in the radical-based carbofunctionalization of alkenes by cooperative nickel-photoredox catalysis. Many chemists have performed representative work in this field.<sup>3,4</sup> Despite the success of the direct alkene 1,2-difunctionalization process, these strategies often involve the utilization of prefunctionalized alkyl substrates, such as alkyl halides, alkyl trifluoro borates, alkyl silicates,  $\alpha$ -silyl amines, or oxalate esters, which translate into the low efficiency and low atomic economy (Scheme 1a). To overcome these major drawbacks, photochemical alkene difunctionalization by employing unactivated aliphatic C/Si–H bonds as radical precursors has been reported by Kong,<sup>5</sup> Wu,<sup>6</sup> Li,<sup>7</sup> and

our group.<sup>8</sup> Nevertheless, these methods rely heavily on the use of expensive photocatalysts, such as tetrabutylammonium decatungstates, 2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyano benzene, and [Ir(dtbbpy)[dF(CF<sub>3</sub>)ppy]<sub>2</sub>PF<sub>6</sub>], which lead to uncontrollable economic costs (Scheme 1a). Therefore, developing general and efficient synthetic strategies to achieve direct alkene 1,2-difunctionalization in an economical manner is attractive and urgently needed.

Recently, several groups have demonstrated that earth-abundant and inexpensive metal-chloride-based photocatalysts are powerful tools for versatile aliphatic C–H functionalization through the intermolecular hydrogen atom transfer (HAT) (Scheme 1b). Recent progress in this field from the groups of Rovis,<sup>9</sup> Walsh and Schelter,<sup>10</sup> Zuo,<sup>11</sup> Gong,<sup>12</sup> Zeng,<sup>13</sup> Xia,<sup>14</sup> and others<sup>15</sup> has involved the use of these metal chlorides to generate Cl radicals *via* ligand-to-metal charge transfer (LMCT). For instance, Rovis and Gong disclosed two elegant and practical CuCl<sub>2</sub>/FeCl<sub>3</sub>-catalyzed approaches for C(sp<sup>3</sup>)–H bond alkylation by using activated alkenes as alkylation reagents. However, studies on the use of these metal chlorides to difunctionalize alkenes with aliphatic C–H bonds *via* the photoinduced LMCT process has never been reported. With the rapid development of electrochemistry and photochemistry,<sup>16</sup> photoelectrocatalysis has received considerable attention from scientists. The main feature of this approach is that it combines the advantages of electrochemistry and photochemistry in the same reaction. Several groups have systematically studied photoelectrocatalysis, and provided novel synthetic strategies for organic synthetic chemistry. Representative work from the groups of Lambert,<sup>17</sup> Lin,<sup>18</sup> Lei,<sup>19</sup> Xu,<sup>20</sup> *etc.*<sup>21</sup> has proven the synthetic

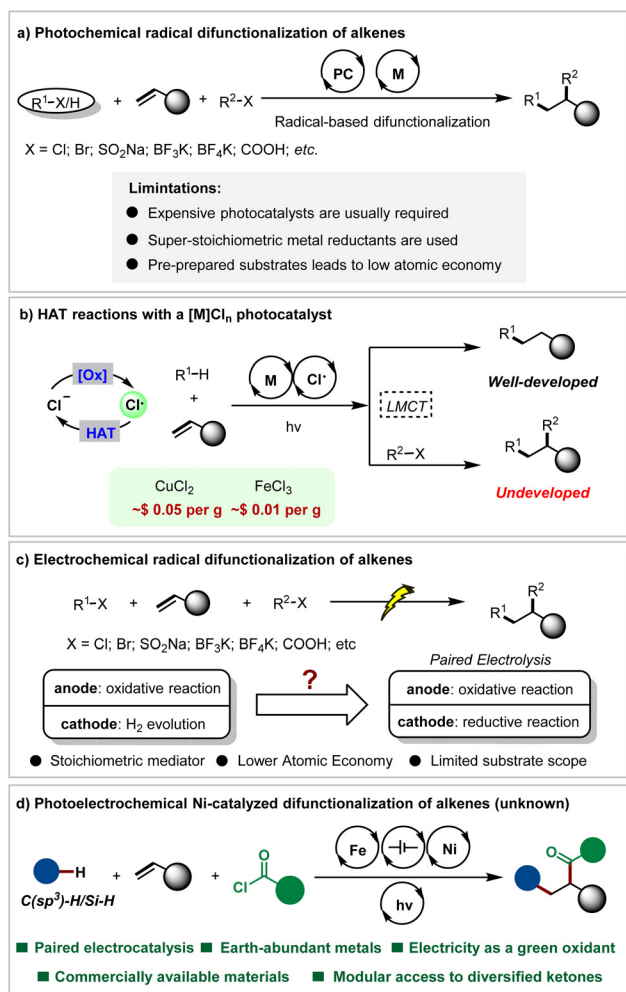
<sup>a</sup>Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, China. E-mail: wangdingyi@mail.neu.edu.cn

<sup>b</sup>Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstraße 2, Göttingen 37077, Germany. E-mail: Lutz.Ackermann@chemie.uni-goettingen.de

<sup>c</sup>State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3gc04109c>

‡ These authors have contributed equally to this paper.



**Scheme 1** Alkene functionalization via the LMCT process and the development of (photo)electrochemistry.

potential of these strategies. Although significant progress has been made, most methods have focused on two-component nonmetallic radical-mediated cross-coupling reactions or intramolecular cyclization reactions (Scheme 1b). This greatly limits the application value of these methods. In addition, in (photo)electrochemical alkene difunctionalization reactions, the anode supports the catalyst in the catalytic cycle, while the cathode merely generates hydrogen. This results in additional stages and waste creation, as well as decreased efficiency and atom economy (Scheme 1c).

In 2023, Xu and co-workers reported the photoelectrochemical asymmetric copper-catalyzed heteroarylcyanation of alkenes.<sup>22</sup> Very recently, the Lu group disclosed an elegant approach for the selective C(sp<sup>3</sup>)-H arylation/alkylation of alkanes by photoelectrocatalysis.<sup>23</sup> In this context, direct functionalization of C-H bonds, which are the most abundant chemical bonds in organic molecules, by photoelectrocatalytic strategies using inexpensive and readily available catalysts and reagents for building C-H/X bonds would be more attractive. Herein, we report a photoelectrochemical approach for the

difunctionalization of alkenes with unactivated alkanes, hydro-silanes, and a range of aryl chlorides *via* the LMCT process (Scheme 1d). In contrast to previous photochemical nickel-catalyzed alkene difunctionalizations, which require the use of noble photocatalysts, we used the cheap and readily available FeCl<sub>3</sub> as a photocatalyst. Furthermore, by combining the advantages of electrochemistry, the catalytic cycling of iron and nickel catalysts can be achieved using green electrons as oxidants. This strategy is more practical and far less economically costly than previous methods. This paired electrocatalysis strategy features excellent regioselectivity, ample substrate scope, and high resource economy.

## Results and discussion

To explore the optimal photoelectrochemical conditions for three-component alkene 1,2-difunctionalizations, we used commercially available cyclohexane (**1a**), methyl acrylate (**2a**), and *p*-toluoyl chloride (**3a**) as model substrates in the presence of dual catalysts (FeCl<sub>3</sub>·6H<sub>2</sub>O and NiBr<sub>2</sub>·DME) (Table 1). After

**Table 1** Optimization of reaction conditions<sup>a</sup>

1a + 3a + 2a → 4

FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%), NiBr<sub>2</sub>·DME (10 mol%), L<sub>1</sub> (10 mol%), LiCl (3 eq), MeCN/acetone (2/1, 3 mL), (+)GF/(-)RVC, 4 mA, 10°C, 390 nm hv

Ligands: L1, L2, L3, L4, L5, L6

Entry	Variation from "standard conditions"	Yield <sup>b</sup> (%)
1	None	71 <sup>c</sup>
2	CuCl <sub>2</sub> instead of FeCl <sub>3</sub> ·6H <sub>2</sub> O	Trace
3	CeCl <sub>3</sub> instead of FeCl <sub>3</sub> ·6H <sub>2</sub> O	Trace
4	NiCl <sub>2</sub> ·DME instead of NiBr <sub>2</sub> ·DME	62
5	NiBr <sub>2</sub> ·DME instead of NiBr <sub>2</sub>	52
6	L <sub>2</sub> -L <sub>6</sub> as ligand	0-55
7	TBACl instead of LiCl	17
8	DMF/DMA/DMSO/HFIP as solvent	0
9	MeCN/acetone (1/1)	64
10	MeCN/acetone (1/2)	55
11	(+)/GF/(-)GF	60
12	(+)/GF/(-)Ni foam	15
13	(+)/Fe/(-)RVC	<5
14	I = 6 mA	57
15	w/o NiBr <sub>2</sub> ·DME or FeCl <sub>3</sub> ·6H <sub>2</sub> O or L <sub>1</sub>	0
16	w/o light or current	0

<sup>a</sup> Reaction conditions: **1a** (3.0 mmol), **2a** (0.9 mmol), **3a** (0.3 mmol), NiBr<sub>2</sub>·DME (10 mol%), FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%), dtbbpy (10 mol%), LiCl (3.0 equiv.), MeCN/acetone (3.0 mL, 2/1), 4 mA, 24 h, 390 nm, 10 °C, nitrogen, graphite felt (GF) as an anode, reticulated vitreous carbon (RVC) as a cathode, undivided cell. <sup>b</sup> GC yields using dodecane as an internal standard. <sup>c</sup> Isolated yields.

several experiments, the electrolysis proceeded smoothly in the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as the photocatalyst,  $\text{NiBr}_2 \cdot \text{DME}$  as the nickel catalyst, and 4,4-di-*tert*-butyl bipyridine (dtbbpy) as the ligand, a mixture solvent of MeCN/acetone (2/1, 3 mL) at 10 °C in an undivided cell with a constant current (4 mA) exposed to 390 nm LEDs. Under the above conditions, the carbonylation product **4** was isolated in 71% yield with excellent regioselectivity (entry 1). When  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was replaced with other photocatalysts, such as  $\text{CuCl}_2$  and  $\text{CeCl}_3$ , the target product was detected only in trace amounts (entries 2 and 3). This is because these metal salts readily precipitate at the cathode. Switching to other nickel salts as catalysts, such as  $\text{NiCl}_2 \cdot \text{DME}$  or  $\text{NiBr}_2$ , leads to shutting down the reactivity (entries 4 and 5). Additionally, 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy) shows the best reactivity compared to the other pyridine-type ligands bearing different electronic effects, such as **L2**, **L3**, **L4**, **L5**, and **L6** (entry 6, please see the ESI†). Further studies revealed that the addition of chlorine salts increased the concentration of the anion  $[\text{FeCl}_4]^-$  and thereby improved the reaction efficiency, and LiCl shows the best outcome (entry 7). The use of other commonly used solvents, such as DMA, DMF, TFE, and HFIP, leads to completely shutting down the transformation (entry 8). It should be noted that the highest yields were obtained when the volume ratio of MeCN/acetone was set to 2 : 1, while deviations from this ratio resulted in lower reactivity (entries 9 and 10). Altering the anode or cathode exhibited lower reactivity (entries 11–13). The cascade reaction became inefficient when the current was increased from 5 to 6 mA (entry 14). Finally, control experiments indicated that this electrolysis did not occur without light irradiation, electricity, paired catalysts, or ligands (entries 15 and 16).

With the optimal reaction conditions in hand, we investigated the range of acyl chloride **3** compatible with the three-component electrophotocatalytic strategy. As shown in Scheme 2, a series of acyl chlorides bearing different groups and a range of electronic properties at the *meta*- and *para*-positions of the aromatic ring were compatible with this transformation. Electron-donating groups (Me, *t*Bu, MeO), neutral groups (H, Naphth), electron-withdrawing groups (COOMe,  $\text{CF}_3$ ), and halogens (F, Cl) all exhibited modest to good yields and high enantioselectivities (**4**–**15**). The sterically hindered *o*-toluoyl chlorides were also tolerated well, providing the corresponding product (**5**) in 62%. Notably, the method was also useful in transformations for the more challenging methyl chloride substituents of acyl chlorides (**16**). In addition to aryl chlorides, various heteroaromatic acyl chlorides, such as furans, benzofurans, and benzothiophenes, were coupled smoothly with cyclohexane **1a** and acrylic ester **2a**, furnishing the targeted dicarbofunctionalization products (**17**–**19**) in good yields. In general, electron-rich acyl chlorides exhibited higher yields than electron-deficient substrates.

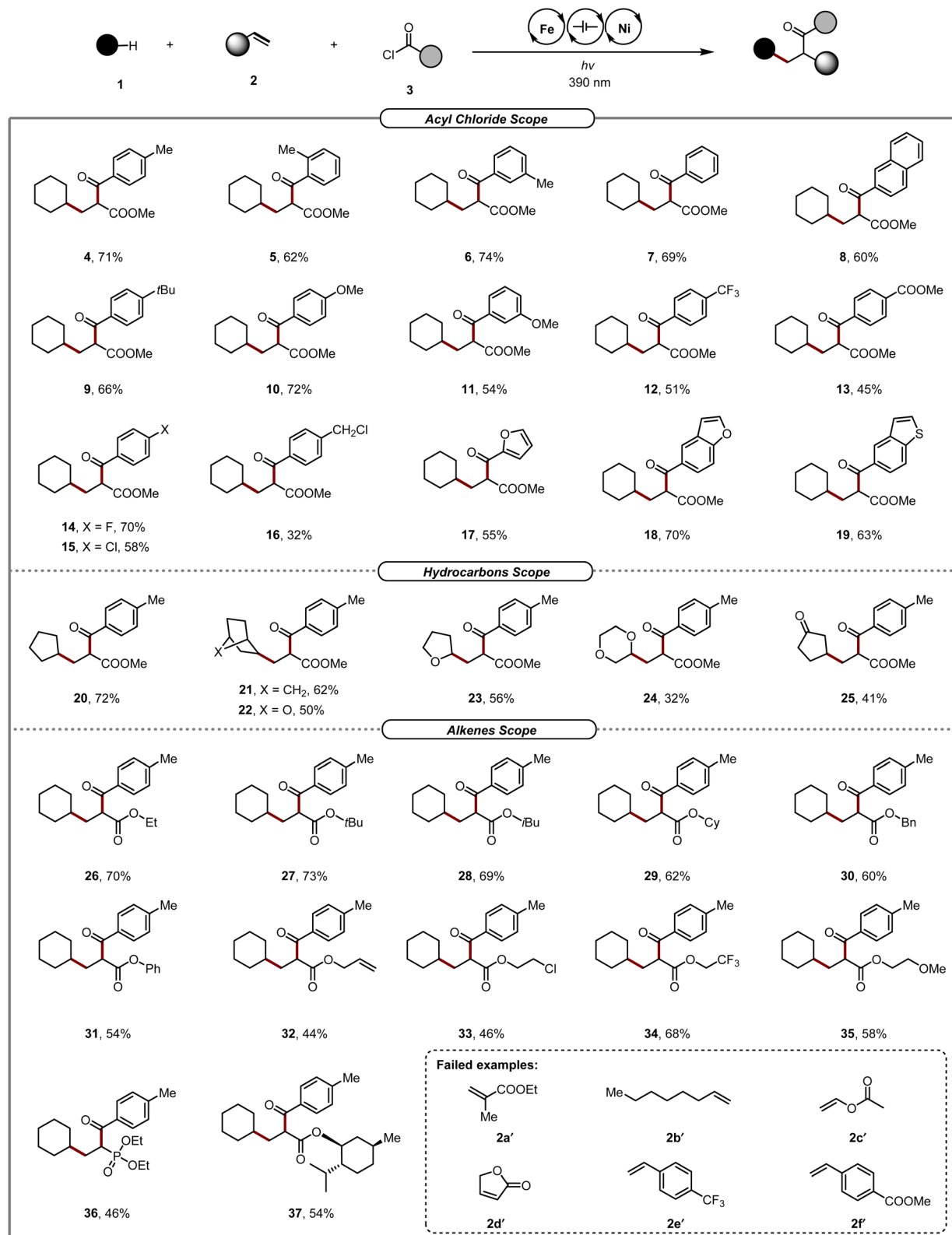
Next, the reactivities of hydrocarbons in this electrophotocatalytic system were examined. The electrophotochemical alkene difunctionalization reaction tolerated various unactivated C–H precursors with different skeletons such as cyclopentane and bicyclo[2.2.1]heptane. In addition, a number of

oxygen-containing substrates, such as (1*s*,4*s*)-7-oxabicyclo[2.2.1]heptane, tetrahydrofuran, and 1,4-dioxane, all participated smoothly in the electrophotocatalytic process, affording the target carbonyl compounds (**22**–**24**) with good yields and excellent regioselectivities. Additionally, cyclopentanone was smoothly transformed into the corresponding product **25**.

Various alkenes were studied next to further evaluate the substrate scope of this electrophotocatalytic protocol. A broad range of acrylates containing ethyl, *tert*-butyl, cyclohexyl, phenyl, benzyl, allyl, chloroalkyl, trifluoroalkyl, and alkoxy groups can be employed as effective coupling partners for these transformations. Our method was suitable not only for acrylic esters but also for other alkene acceptors. For instance, diethyl vinyl phosphonate was also well tolerated and delivered the corresponding product (**36**) in moderate yields. To our delight, this synergistic protocol was successfully applied to complex acrylate derived from natural products such as *D*-menthol (**37**). However, sterically hindered acrylates (**2a'** and **2d'**), unactivated alkenes (**2b'** and **2c'**), and styrene derivatives (**2e'** and **2f'**), were not tolerated in this transformation.

Organosilicon compounds are one of the most attractive structural motifs frequently found in the fields of agrochemistry, materials science, and medicinal chemistry, as well as serve as versatile synthetic intermediates widely used for diverse transformations in synthetic chemistry. Among the many approaches for synthesizing organosilicon compounds,<sup>24</sup> electrochemical 1,2-silylfunctionalization of alkenes by using hydrosilanes as substrates are rare. The group of Lin and He disclosed electrochemical alkene silylation reactions under metal-free conditions (Table 2a).<sup>25</sup> Since then, there have been no further reports on the silylation of alkenes utilizing hydrosilanes *via* electrochemical strategies. After the successful carboacylation of alkenes *via* a radical process, we envisioned that hydrosilanes could also be derived under standard conditions (Table 2b). To our delight, silanoylation of alkenes could be achieved under slightly modified conditions. Subsequently, various silanes and acyl chlorides with different groups were examined, and the results showed good reactivity, affording the corresponding products (**38**–**41**, **46**) without any problems. Besides, various acrylates with diverse ester O-substituents, including Bn, and alkoxy groups (**42**–**45**) are perfectly compatible with this methodology, affording the desired ketones in 47%–72% yields.

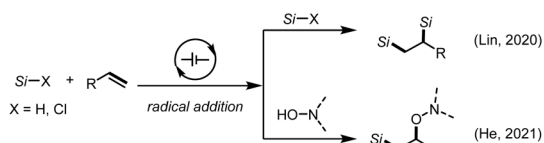
To further illustrate the outstanding potential of this approach, we conducted a gram-scale reaction under slightly modified conditions to synthesize the cascade product in good yield (Scheme 3a). A series of mechanistic experiments probing the mechanism of action have been performed. First, the addition of TEMPO (3.0 equiv.) strongly inhibited these transformations, and product **4** could not be observed. Instead, a cyclohexylated TEMPO **47** was observed by GCMS (Scheme 3b). These findings support the suggestion that this cascade reaction involved a radical mechanism. When the transformation was completed with TBABClO<sub>4</sub> to replace LiCl as the electrolyte under the standard conditions, no expected product was obtained (Scheme 3c). This finding demonstrated



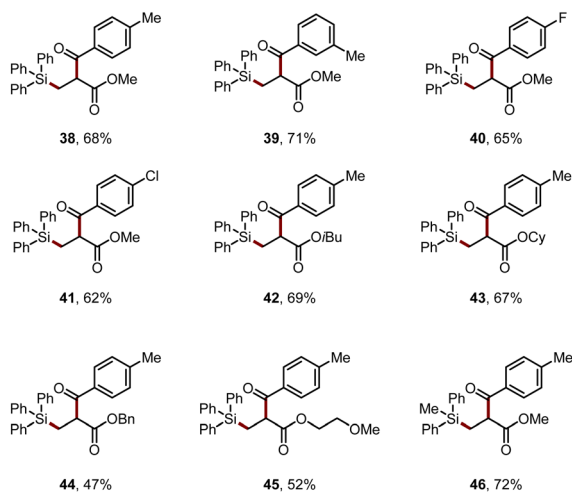
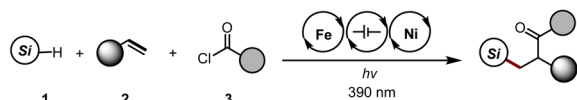
**Scheme 2** Substrate scope. Reaction conditions: **1** (3.0 mmol), **2** (0.9 mmol), **3** (0.3 mmol), NiBr<sub>2</sub>-DME (10 mol%), FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%), dtbbpy (10 mol%), LiCl (3.0 equiv.), MeCN/acetone (3.0 mL, 2/1), 4 mA, 24 h, 390 nm, 10 °C, nitrogen, GF as an anode, RVC as a cathode, undivided cell. Isolated yields.

Table 2 The substrate scope<sup>a</sup>

## a) Electrochemical nonmetallic radical-mediated cross-coupling reactions:



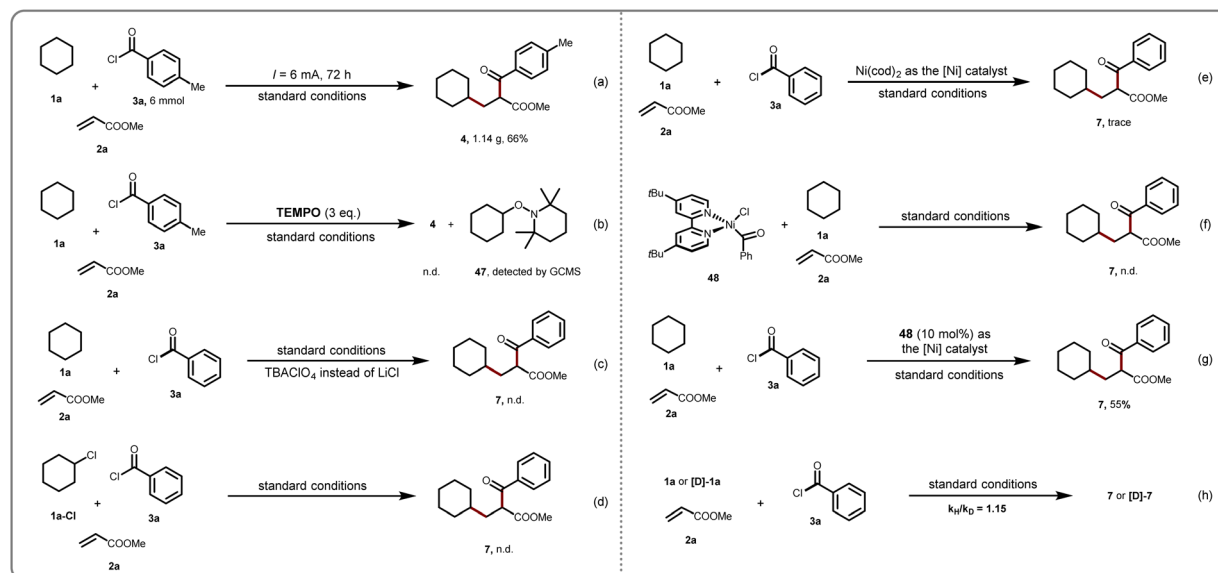
## b) Photoelectrochemical Nickel-Catalyzed Silanoylation of Alkenes (this work):



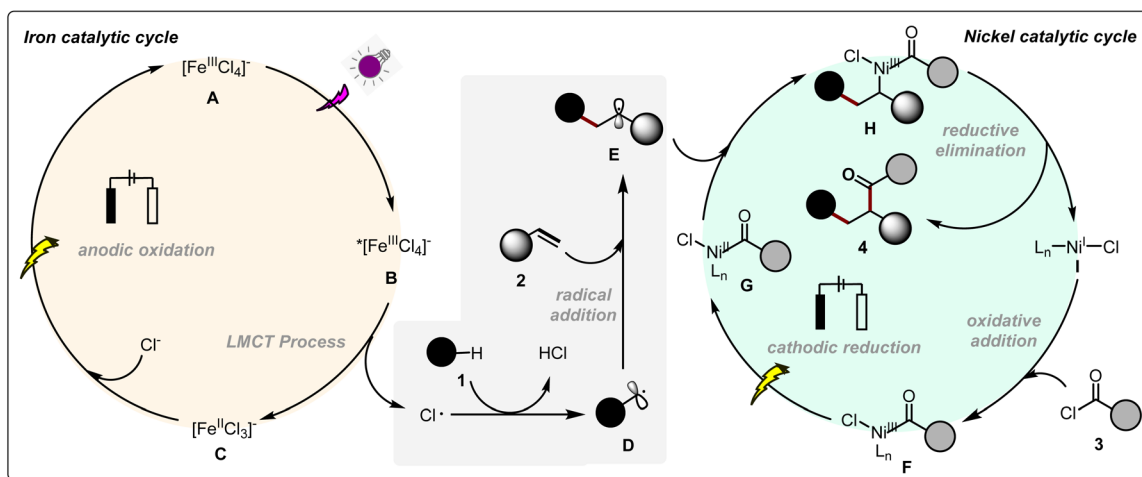
<sup>a</sup> Reaction conditions: **1** (1.5 mmol), **2** (0.9 mmol), **3** (0.3 mmol), NiBr<sub>2</sub>·DME (10 mol%), FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol%), dtbbpy (10 mol%), LiCl (3.0 equiv.), MeCN/acetone (3.0 mL, 2/1), 4 mA, 24 h, 390 nm, 25 °C, nitrogen, graphite felt (GF) as an anode, reticulated vitreous carbon (RVC) as a cathode, undivided cell. Isolated yields.

that LiCl is essential for the formation of [FeCl<sub>4</sub>]<sup>-</sup> *in situ*. The target product was not detected when the reaction was conducted by using cyclohexyl chlorides instead of cyclohexanes as substrates, indicating that the alkyl chloride is not a key intermediate in this transformation (Scheme 3d). A trace amount of additional product was obtained utilizing Ni(COD)<sub>2</sub> as a nickel catalyst, suggesting that Ni(0) species may not be involved in the main catalytic cycle (Scheme 3e). In addition, the nickel(II)-complex **48** was subjected to transformation in the presence of a catalytic photocatalyst, and no target carbonyl compound was detected (Scheme 3f). Moreover, when the reaction was performed with 10 mol% of nickel-complex **48** as the catalyst, the desired product **7** was obtained in 55% yield (Scheme 3g). Furthermore, a kinetic isotope effect (KIE) of 1.15 was observed between cyclohexane **1a** and [D]-**1a** with methyl acrylate **2a**, and benzoyl chloride **3b** from parallel reactions, suggesting that the C–H bond of the cyclohexanes cleavage step is not the turnover-determining step (Scheme 3e). Finally, cyclic voltammetry (CV) experiments further confirmed that the nickel complex (NiBr<sub>2</sub>-dtbbpy) underwent cathodic reduction at reduction potentials of Ni(II)/Ni(I) (–1.38 V vs. Fc/Fc<sup>+</sup>) and Ni(I)/Ni(0) (–1.88 V vs. Fc/Fc<sup>+</sup>) and the photocatalyst (FeCl<sub>3</sub>·H<sub>2</sub>O) underwent anodic oxidation at oxidation potentials of Fe(II)/Fe(III) (–0.09 V vs. Fc/Fc<sup>+</sup>) (please see the ESI† for details).

According to the above mechanistic studies and previous findings,<sup>20,23,26</sup> a plausible mechanism for the electrophotocatalytic alkenes carboacylation is proposed (Scheme 4). Upon visible light irradiation, [Fe<sup>III</sup>Cl<sub>4</sub>]<sup>-</sup> (**A**) is excited to generate a photoexcited state \*[Fe<sup>III</sup>Cl<sub>4</sub>]<sup>-</sup> (**B**), which could release chlorine radicals *via* the LMCT process. This highly active radical species could abstract a hydrogen atom from the C–H compound **1** to form a carbon-centered radical intermediate **D**, and the [Fe<sup>II</sup>Cl<sub>3</sub>]<sup>-</sup> (**C**) undergo anodic oxidation with chloride



Scheme 3 Gram-scale preparation and mechanistic study reactions.



**Scheme 4** Possible reaction mechanism.

ions to regenerate the  $[\text{Fe}^{\text{III}}\text{Cl}_4]^-$  (A). Concomitantly, the  $\text{Ni}^{\text{I}}$  catalyst concerted oxidative addition with acyl chlorides 3 to afford nickel<sup>III</sup> species F, which was reduced on the cathode to generate the  $\text{Ni}^{\text{II}}$  species G. Then intermediate D was added to alkenes 2 to give the secondary alkyl radical E, which could be intercepted by  $\text{Ni}^{\text{II}}$  species G to produce alkyl- $\text{Ni}^{\text{III}}$  intermediate H. The intermediate H would undergo reductive elimination to deliver the corresponding carbonyl compounds 4 and regenerate the  $\text{Ni}^{\text{I}}$  catalyst I.

## Conclusions

In summary, by combining photochemistry and electrochemistry, we have successfully developed a nickel-catalyzed three-component carboacylation/silanoylation of alkenes with acyl chlorides, hydrosilanes, and unactivated  $\text{C}(\text{sp}^3)\text{-H}$  donors. The electrophotocatalytic platform allowed the facile construction of ketones from inexpensive commercial starting materials and showed excellent enantioselectivity. In addition, a series of experimental studies revealed the key mechanistic pathway for this photoelectrocatalytic process. The use of an electrophotocatalytic strategy for developing more challenging functionalization processes of unsaturated bonds is underway in our group.

## Author contributions

D. W. and L. A. conceived and designed the study, and wrote the paper. L. W., X. H., and X. H. performed the experiments, mechanism study, and analyzed the data.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

Generous support by the National Natural Science Foundation of China (NSFC-22301032), and the DFG (Gottfried-Wilhelm Leibniz Award to L. A.) is gratefully acknowledged.

## References

- (a) J.-S. Zhang, L. Liu, T. Chen and L.-B. Han, *Chem. – Asian J.*, 2018, **13**, 2277–2291; (b) R. K. Dhungana, S. Kc, P. Basnet and R. Giri, *Chem. Rec.*, 2018, **18**, 1314–1340; (c) J. Derosa, O. Apolinar, T. Kang, V. T. Tran and K. M. Engle, *Chem. Sci.*, 2020, **11**, 4287–4296.
- (a) Y. Ping and W. Kong, *Synthesis*, 2020, 979–992; (b) X. Zhao, H.-Y. Tu, L. Guo, S. Zhu, F.-L. Qing and L. Chu, *Nat. Commun.*, 2018, **9**, 3488; (c) A. A. Kadam, T. L. Metz, Y. L. Qian and M. Stanley, *ACS Catal.*, 2019, **9**, 5651–5656; (d) L. Wang and C. Wang, *Org. Lett.*, 2020, **22**, 8829–8835; (e) M. Liu, T. Feng, Y. Wang, G. Kou, Q. Wang, Q. Wang and Y. Qiu, *Nat. Commun.*, 2023, **14**, 6467; (f) K. Yang, T. Feng and Y. Qiu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202312803.
- (a) L. Liao, R. Jana, K. B. Urkalan and M. S. Sigman, *J. Am. Chem. Soc.*, 2011, **133**, 5784–5787; (b) J.-W. Gu, Q.-Q. Min, L.-C. Yu and X. Zhang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12270–12274 (*Angew. Chem.*, 2016, **128**, 12458–12462); (c) L. Zhang, G. J. Lovinger, E. K. Edelstein, A. A. Szymaniak, M. P. Chierchia and J. P. Morken, *Science*, 2016, **351**, 70–74; (d) T. Qin, J. Cornella, C. Li, L. R. Malins, J. T. Edwards, S. Kawamura, B. D. Maxwell, M. D. Eastgate and P. S. Baran, *Science*, 2016, **352**, 801–805; (e) B. Shrestha, P. Basnet, R. K. Dhungana, S. Kc, S. Thapa, J. M. Sears and R. Giri, *J. Am. Chem. Soc.*, 2017, **139**, 10653–10656; (f) P. Gao, L. A. Chen and M. K. Brown, *J. Am. Chem. Soc.*, 2018, **140**, 10653–10657; (g) J. Derosa, R. Kleinmans, V. T. Tran, M. K. Karunananda, S. R. Wisniewski,

- M. D. Eastgate and K. M. Engle, *J. Am. Chem. Soc.*, 2018, **140**, 17878–17883; (h) P. Basnet, S. Kc, R. K. Dhungana, B. Shrestha, T. J. Boyle and R. Giri, *J. Am. Chem. Soc.*, 2018, **140**, 15586–15590; (i) M. Chierchia, P. Xu, G. J. Lovinger and J. P. Morken, *Angew. Chem., Int. Ed.*, 2019, **58**, 14245–14249 (*Angew. Chem.*, 2019, **131**, 14383–14387); (j) J. Derosa, V. T. Tran, M. N. Boulous, J. S. Chen and K. M. Engle, *J. Am. Chem. Soc.*, 2017, **139**, 10657–10660.
- 4 (a) X. Wei, W. Shu, A. García-Domínguez, E. Merino and C. Nevado, *J. Am. Chem. Soc.*, 2020, **142**, 13515–13522; (b) A. García-Domínguez, R. Mondal and C. Nevado, *Angew. Chem., Int. Ed.*, 2019, **58**, 12286–12290; (c) A. Lipp, S. O. Badir and G. A. Molander, *Angew. Chem., Int. Ed.*, 2021, **60**, 1714–1726 (*Angew. Chem.*, 2021, **133**, 1738–1750); (d) R. S. Mega, V. K. Duong, A. Noble and V. K. Aggarwal, *Angew. Chem., Int. Ed.*, 2020, **59**, 4375–4379 (*Angew. Chem.*, 2020, **132**, 4405–4409); (e) A. Dewanji, P. E. Krach and M. Rueping, *Angew. Chem., Int. Ed.*, 2019, **58**, 3566–3570 (*Angew. Chem.*, 2019, **131**, 3604–3608); (f) L. Huang and M. Rueping, *Angew. Chem., Int. Ed.*, 2018, **57**, 10333–10337 (*Angew. Chem.*, 2018, **130**, 10490–10494); (g) H. Yue, C. Zhu and M. Rueping, *Angew. Chem., Int. Ed.*, 2017, **57**, 1371–1375 (*Angew. Chem.*, 2017, **130**, 1385–1389); (h) S. Sun, Y. Duan, R. S. Mega, R. J. Somerville and R. Martin, *Angew. Chem., Int. Ed.*, 2020, **59**, 4370–4374 (*Angew. Chem.*, 2020, **132**, 4400–4404); (i) H. Jiang, X. Yu, C. G. Daniliuc and A. Studer, *Angew. Chem., Int. Ed.*, 2021, **60**, 14399–14404 (*Angew. Chem.*, 2021, **133**, 14520–14525); (j) T. Yang, X. Chen, W. Rao and M. J. Koh, *Chem*, 2020, **6**, 738–751; (k) X. Shu, L. Huan, Q. Huang and H. Huo, *J. Am. Chem. Soc.*, 2020, **142**, 19058–19064; (l) B. Maity, C. Zhu, H. Yue, L. Huang, M. Harb, Y. Minenkov, M. Rueping and L. Cavallo, *J. Am. Chem. Soc.*, 2020, **142**, 16942–16952; (m) A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath and D. W. C. MacMillan, *Chem. Rev.*, 2022, **122**, 1485–1542; (n) F.-D. Lu, J. Chen, X. Jiang, J.-R. Chen, L.-Q. Lu and W.-J. Xiao, *Chem. Soc. Rev.*, 2021, **50**, 12808–12827; (o) C. Zhu, H. Yue, L. Chu and M. Rueping, *Chem. Sci.*, 2020, **11**, 4051–4064; (p) Y.-Y. Gui, L. Sun, Z.-P. Lua and D.-G. Yu, *Org. Chem. Front.*, 2016, **3**, 522–526.
- 5 (a) S. Xu, H. Chen, Z. Zhou and W. Kong, *Angew. Chem., Int. Ed.*, 2021, **60**, 7405–7411; (b) W. Liu, C. Liu, M. Wang and W. Kong, *ACS Catal.*, 2022, **12**, 10207–10221.
- 6 J. Hou, A. Ee, H. Cao, H.-W. Ong, J.-H. Xu and J. Wu, *Angew. Chem., Int. Ed.*, 2018, **57**, 17220–17224.
- 7 M. Zheng, J. Hou, L.-L. Hua, W.-Y. Tang, L.-W. Zhan and B.-D. Li, *Org. Lett.*, 2021, **23**, 5128–5132.
- 8 D. Wang and L. Ackermann, *Chem. Sci.*, 2022, **13**, 7256–7263.
- 9 (a) S. M. Treacy and T. Rovis, *J. Am. Chem. Soc.*, 2021, **143**, 2729–2735; (b) Y. C. Kang, S. M. Treacy and T. Rovis, *ACS Catal.*, 2021, **11**, 7442–7449.
- 10 Q. Yang, Y. H. Wang, Y. Qiao, M. Gau, P. J. Carroll, P. J. Walsh and E. J. Schelter, *Science*, 2021, **372**, 847–852.
- 11 A. Hu, J. J. Guo, H. Pan and Z. Zuo, *Science*, 2018, **361**, 668–672.
- 12 Z.-Y. Dai, S.-Q. Zhang, X. Hong, P.-S. Wang and L.-Z. Gong, *Chem. Catal.*, 2022, **2**, 1211–1222.
- 13 (a) Z. Zhang, X. Li, D. Zhou, S. Ding, M. Wang and R. Zeng, *J. Am. Chem. Soc.*, 2023, **145**, 7612–7620; (b) Z. Zhang, G. Zhang, N. Xiong, T. Xue, J. Zhang, L. Bai, Q. Guo and R. Zeng, *Org. Lett.*, 2021, **23**, 2915–2920; (c) T. Xue, Z. Zhang and R. Zeng, *Org. Lett.*, 2022, **24**, 977–982.
- 14 J.-L. Tu, A.-M. Hu, L. Guo and W. Xia, *J. Am. Chem. Soc.*, 2023, **145**, 7600–7611.
- 15 (a) Y. Jin, Q. Zhang, L. Wang, X. Wang, C. Meng and C. Duan, *Green Chem.*, 2021, **23**, 6984–6989; (b) L. Troian-Gautier, M. D. Turlington, S. A. M. Wehlin, A. B. Maurer, M. D. Brady, W. B. Swords and G. J. Meyer, *Chem. Rev.*, 2019, **119**, 4628–4683; (c) L. Ding, Y. Liu, K. Niu and Q. Wang, *Chem. Commun.*, 2022, **58**, 10679–10682.
- 16 G. Yang, Y. Wang and Y. Qiu, *Chin. J. Org. Chem.*, 2021, **41**, 3935–3947.
- 17 (a) H. Huang, Z. M. Strater, M. Rauch, J. Shee, T. J. Sisto, C. Nuckolls and T. H. Lambert, *Angew. Chem., Int. Ed.*, 2019, **58**, 13318–13322; (b) H. Huang, Z. M. Strater and T. H. Lambert, *J. Am. Chem. Soc.*, 2020, **142**, 1698–1703; (c) T. Shen and T. H. Lambert, *Science*, 2021, **371**, 620–626; (d) H. Huang and T. H. Lambert, *Angew. Chem., Int. Ed.*, 2020, **59**, 658–662.
- 18 (a) H. Kim, H. Kim, T. H. Lambert and S. Lin, *J. Am. Chem. Soc.*, 2020, **142**, 2087–2092; (b) W. Zhang, K. L. Carpenter and S. Lin, *Angew. Chem., Int. Ed.*, 2020, **59**, 409–417.
- 19 (a) Z. Yang, D. Yang, J. Zhang, C. Tan, J. Li, S. Wang, H. Zhang, Z. Huang and A. Lei, *J. Am. Chem. Soc.*, 2022, **144**, 13895–13902; (b) L. Niu, C. Jiang, Y. Liang, D. Liu, F. Bu, R. Shi, H. Chen, A. D. Chowdhury and A. Lei, *J. Am. Chem. Soc.*, 2020, **142**, 17693–17702.
- 20 (a) H. Yan, Z.-W. Hou and H.-C. Xu, *Angew. Chem., Int. Ed.*, 2019, **58**, 4592–4595; (b) P. Xu, P.-Y. Chen and H.-C. Xu, *Angew. Chem., Int. Ed.*, 2020, **59**, 14275–14280; (c) Z.-W. Hou and H.-C. Xu, *ChemElectroChem*, 2021, **8**, 1571–1573; (d) H. Yan, J. Song, S. Zhu and H.-C. Xu, *CCS Chem.*, 2021, **3**, 317–325; (e) C.-Y. Cai, X.-L. Lai, Y. Wang, H.-H. Hu, J. Song, Y. Yang, C. Wang and H.-C. Xu, *Nat. Catal.*, 2022, **5**, 943–951; (f) X.-L. Lai, M. Chen, Y. Wang, J. Song and H.-C. Xu, *J. Am. Chem. Soc.*, 2022, **144**, 20201–20206.
- 21 (a) L. Zhang, L. Liardet, J. Luo, D. Ren, M. Grätzel and X. Hu, *Nat. Catal.*, 2019, **2**, 366–373; (b) H. Tateno, Y. Miseki and K. Sayama, *Chem. Commun.*, 2017, **53**, 4378–4381; (c) L. Zou, X. Wang, S. Xiang, W. Zheng and Q. Lu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202301026; (d) F. Wang and S. S. Stahl, *Angew. Chem., Int. Ed.*, 2019, **58**, 6385–6390; (e) Y. Qiu, A. Scheremetjew, L. H. Finger and L. Ackermann, *Chem. – Eur. J.*, 2020, **26**, 3241–3246.
- 22 X.-L. Lai and H.-C. Xu, *J. Am. Chem. Soc.*, 2023, **145**, 18753–18759.
- 23 L. Zou, S. Xiang, R. Sun and Q. Lu, *Nat. Commun.*, 2023, **14**, 7992.

- 24 J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15–34.
- 25 (a) L. Lu, J. C. Siu, Y. Lai and S. Lin, *J. Am. Chem. Soc.*, 2020, **142**, 21272–21278; (b) J. Ke, W. Liu, X. Zhu, X. Tan and C. He, *Angew. Chem., Int. Ed.*, 2021, **60**, 8744–8749.
- 26 (a) G. A. Dawson, E. H. Spielvogel and T. Diao, *Acc. Chem. Res.*, 2023, **56**, 3640–3653; (b) Q. Lin, Y. Fu, P. Liu and T. Diao, *J. Am. Chem. Soc.*, 2021, **143**, 14196–14206; (c) C. L. Wagner, G. Herrera, Q. Lin, C. T. Hu and T. Diao, *J. Am. Chem. Soc.*, 2021, **143**, 5295–5300; (d) G. A. Dawson, Q. Lin, M. C. Neary and T. Diao, *J. Am. Chem. Soc.*, 2023, **145**, 20551–20561; (e) M. Rafiee, D. J. Abrams, L. Cardinale, Z. Goss, A. Romero-Arenas and S. S. Stahl, *Chem. Soc. Rev.*, 2024, **53**, 566–585.