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Article

Photo-induced versatile aliphatic C–H functionalization via electron donor–acceptor complex

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ABSTRACT

The ability to selectively introduce diverse functionality onto hydrocarbons is of substantial value in the synthesis of both small molecules and pharmaceuticals. In this endeavour, as a photocatalyst- and metal-free process, the electron donor–acceptor (EDA) strategy has not been well explored. Here we report an approach to aliphatic carbon-hydrogen bond diversification through an EDA complex constituted by HCl and S^{IV}=O groups. As an efficient hydrogen atom transfer (HAT) reagent, chlorine radical can be produced via a proton-coupled electron transfer process in this system. Based on this unusual path, a photo-promoted versatile aliphatic C–H functionalization is developed without photo- and metal-catalysts, including thiolation, arylation, alkynylation, and allylation. This conversion has concise and ambient reaction conditions, good functional group tolerance, and substrate diversity, and provides an alternative solution for the high value-added utilization of bulk light alkanes.

1. Introduction

With the ever-increasing demand for the sustainable development of chemical synthesis, direct functionalization of C(sp^3)–H bonds that can provide practical solutions to upgrade abundant hydrocarbon feedstocks into valued chemicals has drawn significant research attention [1–4]. In this context, compared to activated C(sp^3)–H bonds adjacent to a heteroatom or π-system, the selective modification of unactivated C(sp^3)–H bonds presents a remarkable challenge due to their high bond dissociation energies (BDEs), low acidities, and unreactive molecular orbital profiles (Fig. 1a) [5,6]. In response to these challenges, various valuable technologies have been developed for the functionalization of unactivated C(sp^3)–H bonds. As an attractive strategy, the direct hydrogen atom transfer (HAT) enabling diversification of aliphatic C–H bonds has become an emerging trend through the common generated alkyl radicals with different coupling modules (Fig. 1b) [7–9]. Compared to the one-to-one mode, this strategy can achieve the economical, shortcut, and diverse C(sp^3)–H modification, and the introduction of diverse functional groups can provide more opportunities for drug screening without resorting to *de novo* synthesis [4,9–14].

Recently, chlorine radical mediated HAT has become an attractive research hotspot in C(sp^3)–H functionalization field [15–18]. Due to the abundance and inexpensive nature of chloride salts and the high bond dissociation energy of HCl (BDE = 103 kcal/mol), chlorine radical is naturally considered as an effective HAT reagent [19]. Overcoming the high oxidation potentials (E^{ox} (Cl^-/Cl·) = +2.03 V vs. saturated calomel electrode (SCE)), few strategies have been reported for the efficient generation of Cl· from Cl^-, including the ligand-to-metal charge transfer (LMCT) from metal chloride [15,20–27], the single electron transfer (SET) by photoredox catalysis [28], and others [29–33] (Fig. 1c). However, as a photocatalyst- and metal-free process, the electron donor–acceptor (EDA) strategy has not been well explored.

Based on the current research status, we found a novel approach for generating the chlorine radical through an EDA complex constituted by HCl and S^{IV}=O groups of sulfinates (Fig. 1d). The electron rich nature of the sulfinates usually renders it an electron donor in photocatalyst-free conversions [34–36], but it has not been well explored as an electron acceptor. Under visible light irradiation, a proton-coupled electron transfer (PCET) [37] process could be achieved between chloride anions and S^{IV}=O groups to produce the chlorine radicals, which could effectively activate the various C(sp^3)–H bonds to give the corresponding alkyl radicals owing to the strong hydrogen atom affinity. Herein, based on the novel chlorine radical generation strategy, we report a photo-promoted versatile aliphatic C–H functionalization of inert alkanes

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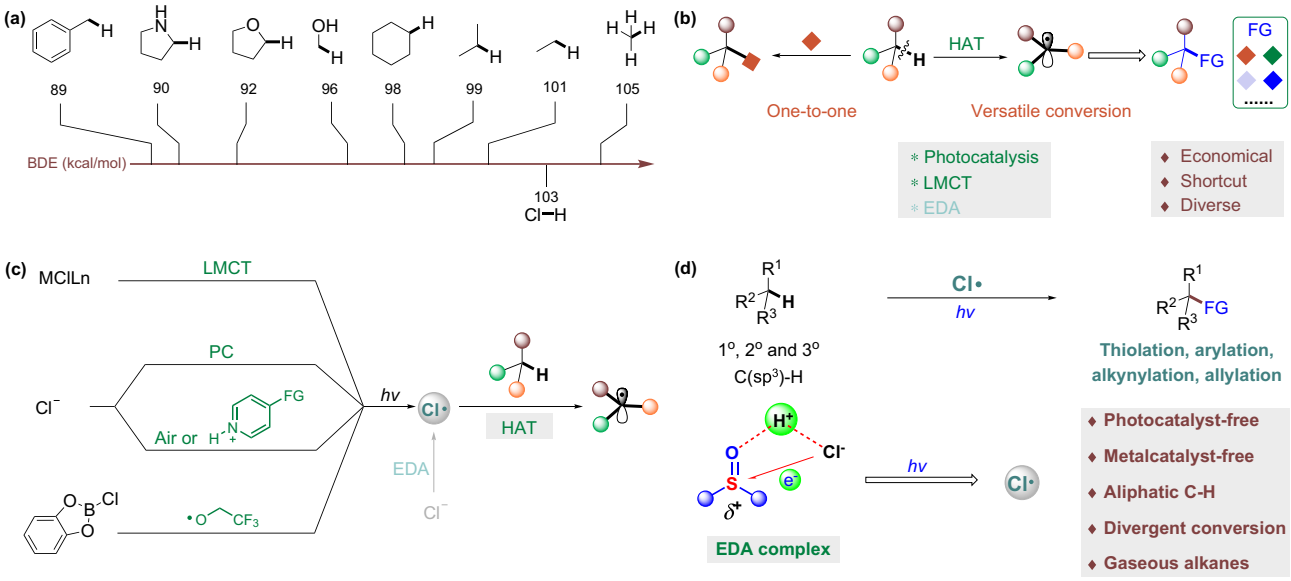


Fig. 1. (Color online) (a) Common bond dissociation energies of C(sp^3)–H. (b) C(sp^3)–H diversification strategy. (c) Chlorine radical generation strategy in HAT conversions. (d) EDA enabling aliphatic C–H diversification.

without photo- and metal-catalysts, including thiolation, arylation, alkynylation, and allylation. This conversion has concise and ambient reaction conditions, good functional group tolerance, and substrate diversity, and provides an alternative solution for high value-added utilization of bulk light alkanes (mainly including C2–C6) [38,39].

2. Materials and methods

2.1. General procedure for liquid alkanes with sodium arylsulfites

The sodium arylsulfite **2** (0.2 mmol) was added to a test tube (10 mL) charged with a magnetic stir bar. The tube was purged with Ar for four times, followed by addition of **1** (2.0 mmol), HCl (conc.) (84.0 μL, 1.0 mmol), and MeCN (2.0 mL). The reaction mixture was stirred with 6 W LED lamp (420–430 nm) irradiation at 38–40 °C for 24 h. Then the reaction solution was diluted with ethyl acetate, filtered, concentrated in vacuo, and purified by flash chromatography on silica gel to obtain product **3**.

2.2. General procedure for liquid alkanes with sodium sulfites

The sodium sulfite (25.2 mg, 0.2 mmol) was added to a test tube (10 mL) charged with a magnetic stir bar. The tube was purged with Ar for four times, followed by addition of **1** (2.0 mmol), HCl (conc.) (67.2 μL, 0.8 mmol), MeCN (1.5 mL), and ethyl acetate (0.5 mL). The reaction mixture was stirred with 6 W LED lamp (420–430 nm) irradiation at 38–40 °C for 24 h. Then the reaction solution was diluted with ethyl acetate, filtered, concentrated in vacuo, and purified by flash chromatography on silica gel to obtain product **4**.

2.3. General procedure for liquid alkanes with heteroarenes

The heteroarene **11** (0.2 mmol) was added to a test tube (10 mL) charged with a magnetic stir bar. The tube was purged with Ar for four times, followed by addition of **1** (2.0 mmol), dimethyl sulfoxide (DMSO, 17.0 μL, 0.24 mmol), HCl (conc.) (50.4 μL, 0.6 mmol), and MeCN (2.0 mL). The reaction mixture was stirred with 6 W LED lamp (420–430 nm) irradiation at 38–40 °C for 24 h. Then the Na_2CO_3 (100 mg) was added and the reaction solution was diluted with ethyl acetate, stirred for 5 min, filtered, concentrated in vacuo, and purified by flash chromatography on silica gel to obtain product **12**.

2.4. General procedure for allylation

The allyl sulfone **13** (0.1 mmol) was added to a test tube (10 mL) charged with a magnetic stir bar. The tube was purged with Ar for four times, followed by addition of **1** (2.0 mmol), DMSO (21.3 μL, 0.3 mmol), HCl (conc.) (33.6 μL, 0.4 mmol), and MeCN (2.0 mL). The reaction mixture was stirred with 6 W LED lamp (420–430 nm) irradiation at 38–40 °C for 24 h. Then the Na_2CO_3 (50 mg) was added, and the reaction solution was diluted with ethyl acetate, stirred for 5 min, filtered, concentrated in vacuo, and purified by flash chromatography on silica gel to obtain product **15**.

2.5. General procedure for alkynylation

The alkynyl sulfone **14** (0.1 mmol) was added to a test tube (10 mL) charged with a magnetic stir bar. The tube was purged with Ar for four times, followed by addition of **1** (2.0 mmol), DMSO (14.2 μL, 0.2 mmol), HCl (conc.) (4.2 μL, 0.05 mmol), and MeCN (2.0 mL). The reaction mixture was stirred with 6 W LED lamp (420–430 nm) irradiation at 38–40 °C for 24 h. Then the Na_2CO_3 (50 mg) was added, and the reaction solution was diluted with ethyl acetate, stirred for 5 min, filtered, concentrated in vacuo, and purified by flash chromatography on silica gel to obtain product **16**.

3. Results and discussion

In our initial evaluation, we began our investigation with sodium benzenesulfinate **2a** and cyclohexane **1a** as the template substrates. After screening, we found that the C–H thio product **3a** was formed in 81% isolated yield only using hydrochloric acid as the additive under the optimized conditions. Changing the sol-

vents to ethyl acetate or acetone decreased the efficiency of this transformation (Table 1, entries 2–3). Decreasing the concentration of hydrochloric acid greatly reduced the yield to 25% (Table 1, entry 4). The HCl was essential to the conversion, and no thioether products were detected with other Brønsted acids (H_2SO_4 (conc.), trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (*p*-TsOH), AcOH, and HBr) (Table 1, entry 5). Increasing or reducing the wavelength of the lamp had no booster effect on yields (Table 1, entries 6 and 7). Adding photocatalysts, such as *fac*-[Ir(ppy)$_3$], Ir[dF(CF$_3$)ppy]$_2$-(bpy)PF$_6$, Ru(bpy)$_3$(PF$_6$)$_2$, and 4CzIPN, seriously inhibited this process (Table 1, entry 8). Thioether **3a** was obtained in moderate yield under air atmosphere suggesting that the reaction was not sensitive to oxygen (Table 1, entry 9). The control experiments revealed that both hydrochloric acid and light were essential for this protocol (Table 1, entry 10).

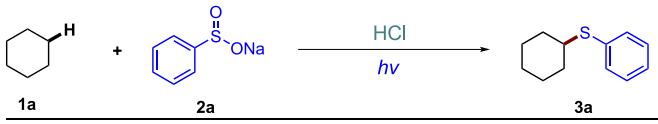
After obtaining the optimal reaction conditions, we approached the substrate scope to different C(sp^3)–H species using sodium benzenesulfinate **2a** as the coupling partner. As shown in Fig. 2, a diverse array of organic frameworks were proved to be competent coupling partners for the C(sp^3)–H thiolation protocol [40,41]. Cycloalkanes with different ring sizes readily underwent the C–H thiolation to give the products in moderate to good yields (**3a**–**3f**). Linear aliphatic systems gave the corresponding coupling products with a greater-than-statistical preference observed at the large steric secondary carbon positions (**3g**–**3i**). The regioselectivity is similar to regular reports on the chlorine radical dominating C(sp^3)–H conversion [22,42]. The active allylic C–H bonds could be also thiolated in good yields (**3j**). For linear alkanes bearing chlorine or nitrile, this conversion showed good regioselectivity at the secondary carbon positions far away from the substituent groups (**3k**–**3l**, 57%–73% selectivity). As an uncommon substrate, tetraethylsilane could be selectively converted to a single thio product **3m** at the end site in 35% yield. It was important to note that this transformation was not limited to the unactivated C(sp^3)–H systems. The 1,4-dioxane with activated C–H bonds could be smoothly converted into the desired product with a good yield (**3n**). Moreover, bridged alkane norbornane gave the *exo*-product **3o** with high stereoselectivity [43,44].

Gaseous alkanes, as abundant and cheap bulk industrial raw materials, are generally used as a source of energy for heating, propulsion, or electricity generation. In addition, its high value-added conversion has always been the research focus in science and industry [45,46]. The key challenges are related to the high bond dissociation energies and the high requirements for reaction devices. Encouragingly, using typical gaseous alkanes, such as propane (BDE = 99–101 kcal/mol) and ethane (BDE = 101 kcal/mol), the desired products were successfully generated in moderate yields (**3p**–**3u**) (Fig. 2). Unfortunately, we have carried out a series of explorations on methane with the higher bond energy (BDE = 105 kcal/mol), but no satisfactory results were obtained.

Subsequently, we focused on the scope of arylsulfinate coupling partners (Fig. 2). A broad range of alkyl and phenyl phenylsulfinates provided the thioether products smoothly (**3v**–**3x**). Then, substrates bearing halogens in different positions underwent the thiolation as well, especially the iodine group could be retained under light conditions (**3y**–**3ad**) [47]. With different electron-donating groups, such as methoxy, benzyloxy, trifluoromethoxy, and acetamido, the desired products could be successfully generated in moderate to good yields (**3ae**–**3ah**). Of course, the electron-deficient phenylsulfinates containing trifluoromethyl, ester, cyano, or sulfone afforded the corresponding thioethers smoothly as well (**3ai**–**3al**). Moreover, the polysubstituted phenylsulfinates were effective substrates (**3am**–**3ar**). Furthermore, sulfinates substituted with naphthalene and thiophene provided the sulfide products with moderate yields (**3as**–**3at**).

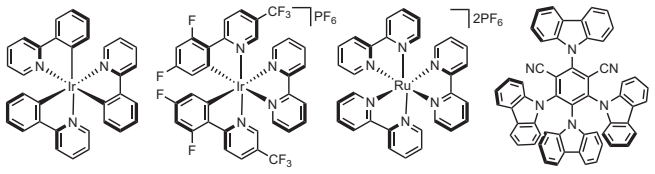
Interestingly, when we tried this conversion using the inorganic sodium sulfites, the *S*-alkyl alkanesulfonothiolates were obtained as the major products through activating the strong aliphatic C–H bonds (Fig. 2). A wide range of cyclic alkanes successfully provided the desired products in moderate to good yields (**4a**–**4e**).

Table 1
(Color online) Optimization of the reaction conditions.



1a 2a 3a

Entry	Deviation from standard conditions[a]	Yield (%)[b]
1	None	85(81)[c]
2	AcOEt instead of CH_3CN	35
3	Acetone instead of CH_3CN	45
4	HCl (6 N) instead of HCl (conc.)	25
5	H_2SO_4, TFA, *p*-TsOH, AcOH, or HBr instead of HCl	0
6	460–470 nm	4
7	400–410 nm	64
8[d]	PC 1, PC 2, PC 3, or PC 4 added	<12
9	Air	53
10	No light or no HCl	0



PC 1 PC 2 PC 3 PC 4

[a] Reactions were carried out with **1a** (2.0 mmol), **2a** (0.2 mmol), HCl (conc.) (1.0 mmol), and CH_3CN (2.0 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere.
[b] Yields determined by ^{1}H NMR using dibromomethane as an external standard.
[c] Isolated yield.
[d] With 6 W LED lamp (460–470 nm).

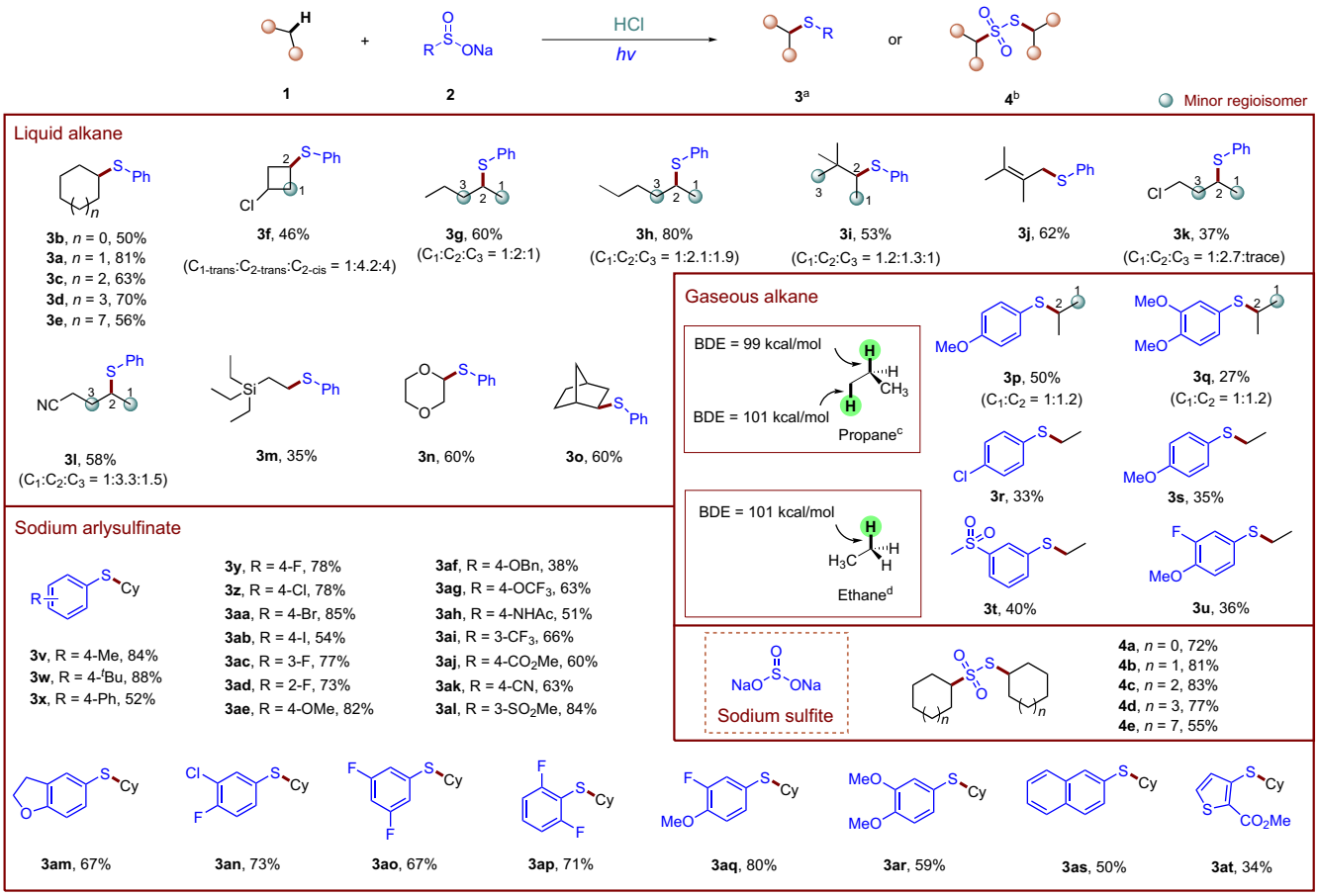


Fig. 2. (Color online) Direct thiolation of strong aliphatic C–H bonds. [a] Condition 1: **1a** (2.0 mmol), sodium arylsulfinate (0.2 mmol), HCl (conc.) (1.0 mmol), and CH_3CN (2.0 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere. [b] Condition 2: **1a** (2.0 mmol), sodium sulfite (0.2 mmol), HCl (conc.) (0.8 mmol), and CH_3CN/EtOAc (1.5/0.5 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere. [c] Propane (0.9 MPa). [d] Ethane (4.0 MPa). The yield of **4** is based on the amount of sulfur atom. Isolated yields. Bright green circles denote sites where notable amounts of other regioisomers are observed.

This protocol established a connecting channel between the inorganic and organic world and achieved the efficient conversion from inexpensive inorganic sulfur sources to high-value-added organic sulfur chemicals [48].

In order to understand this transformation more deeply, a series of mechanistic experiments were conducted (See Section 5 in Supplementary materials (online) for details). By monitoring the conversion, other thio byproducts **5** and **6** were detected in addition to the thioether **3a**, and its content increased firstly, then decreased with the extension of reaction times (Fig. 3a). So, we speculated that the sulfoxide **5** and thiosulfonate **6** might be the important reaction intermediates. Then, we used **5** and **6** instead of the sodium phenylsulfite **2a** to react under standard conditions, and obtained **3a** in different yields (Fig. 3b). Meanwhile, we found that the thiosulfonate **6** easily decomposed under light conditions [49], and few thioethers **3a** were produced from the sulfoxide **5** without light [50]. These results showed that light could significantly promote the conversion. In addition, the chlorocyclohexane **7** was also detected by gas chromatography-mass spectrometer (GC–MS) in the template reaction [17,18]. Subsequently, using the byproduct **7** instead of cyclohexane **1a** under the standard conditions failed to provide thioether **3a**. Based on these results, we speculated that chlorocyclohexane **7** was only a byproduct rather than a reaction intermediate, and the cyclohexane might play dual roles of reducing agents and coupling substrates. Furthermore, hydrogen chloride was demonstrated to play an essential role in this system through the control assays.

Adding 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) to the reaction mixtures, the thiolation was significantly inhibited, and the binding products **8** by **1a** with TEMPO were produced in high yields, indicating the existence of cyclohexyl radicals (Fig. 3c). Then, adding 1,1-diphenylethylene to this system, the *anti*-Markovnikov's chlorinated product **9** was detected, suggesting the generation of chlorine radicals, which was also proved by chlorocyclohexane **7** detected in the template reactions (Fig. 3d).

Using sulfuric acid or tetrabutylammonium chloride (TBAC) alone to replace the proton or chloride anion in hydrogen chloride correspondingly, the desired thioether **3a** was not obtained, meaning that the proton and chloride anion might act synergistically in the system (Fig. 3e). With excess protons, a significant positive correlation existed between the yields of **3a** and the amount of chloride anions, showing that the chloride anions were not catalytic. In addition to the thioethers, almost equal amounts of chlorocyclohexanes **7** were obtained, suggesting the final destination of chlorine. Besides, the competing kinetic isotope effects were examined, giving k_H/k_D = 1.38. This suggested that the cleavage of C–H bonds might not be the rate-determining step (Fig. 3f).

In the UV–Vis absorption spectrum experiments, adding the hydrochloric acids to $PhSO_2H$ could enable an obvious bathochromic shift (Fig. 3g). The setting employed for the light source has an

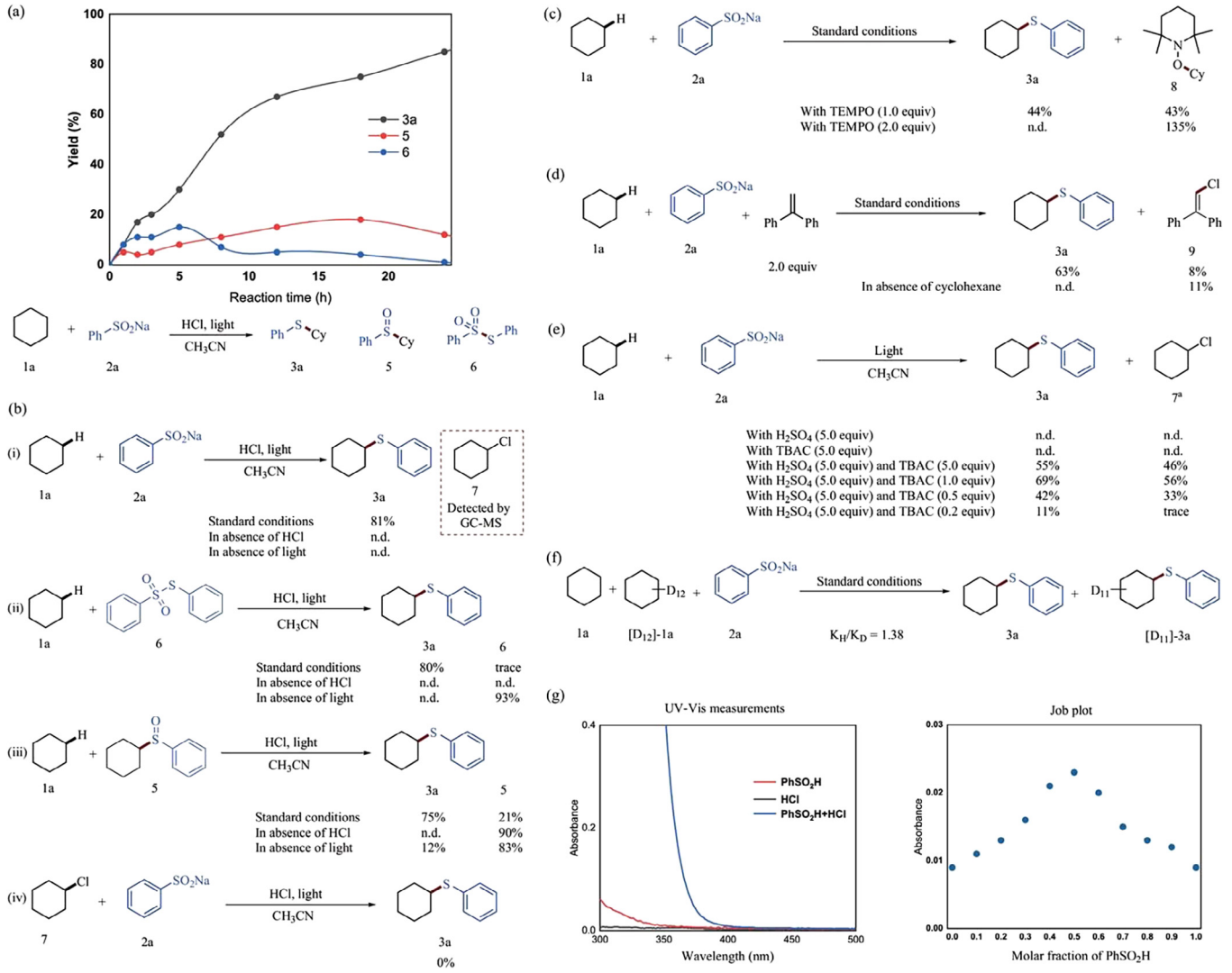


Fig. 3. (Color online) Studies for the reaction mechanism. (a) Reaction time curve. (b) Control experiment. (c) Alkyl radical trapping. (d) Chlorine radical trapping. (e) The flow trace of chlorine atoms. (f) Kinetic isotope effect. (g) Absorption spectra. [a] GC yields. The yield involving **6** is based on the amount of sulfur atom.

emission spectrum with a small peak at 385–395 nm (Fig. S6 online), which has a partial intersection with the absorption range of this system. All these results showed that there might be an EDA complex between the $PhSO_2H$ and hydrochloric acids. Meanwhile, the association constant of the EDA complex and analysis via Job's method demonstrated a 1:1 molar stoichiometry.

Based on the mechanistic studies above, we proposed a plausible reaction mechanism. The corresponding density functional theory (DFT) calculations were also carried out at M06-2X-D3/Def2-SVP/IEFPCM (acetonitrile) level of theory (see Section 8 in Supplementary materials (online) for details). As described in Fig. 4, the $PhSO_2H$ can be formed by $PhSO_2Na$ under acid conditions, and construct the EDA complex **IM1** with HCl through electrostatic effect. Then, the chlorine radical and **IM2** are given through the PCET process under visible light irradiation. The **IM2** would derive into the sulfonyl radical **IM3** after dehydration under acid conditions, which furtherly gives the thiosulfonate **6** through the dimerization and rearrangement [51]. Meanwhile, the cyclohexane undergoes the HAT process with chlorine radical providing cyclohexyl radical, which couples with chlorine radical in the system to give the byproduct **7.** Now, there are two possible ways to the thioether **3a**: (1) The sulfonyl radical **IM3** would couple with cyclohexyl radical to afford the sulfoxide **5**. After the coupling phase, sulfoxide **5** recarries out the PCET process with HCl to provide the chlorine radical and **IM5**, which can be transformed to **IM6** after dehydration under acid conditions [52–54]. Finally, the thioether **3a** is generated from **IM6** through the SET process with Cl^-. (2) As a good radical acceptor, the thiosulfonate **6** can directly give the thioether **3a** by coupling with the cyclohexyl radical [55]. Meanwhile, the generated sulfonyl radical **IM7** would furtherly derive into the benzenesulfonic acid via the HAT process with HCl. In the Fig. 3b(ii), no thioether products were obtained in the absence of HCl, suggesting that neither **IM7** nor $PhS^{\cdot}$ produced by photolysis could give cyclohexyl radicals through HAT with cyclohexane. But the conversion carried out smoothly using the $PhSO_2SPh$ under standard conditions. Furthermore, the path through $Cl^{\cdot}$ had the lower energy than the HAT process with cyclohexane in the DFT calculations (Fig. S14 online). So, the HAT process between cyclohexane and **IM7** was naturally excluded.

Based on the mechanism studies above, the PCET process could also occur between the sulfoxide and HCl, which laid a foundation for further aliphatic C–H divergent conversions. Furthermore, an EDA complex between the sulfoxide and hydrochloric acids was also revealed through the UV–Vis absorption spectrum experiments (Fig. S5 online) and ^1H nuclear magnetic

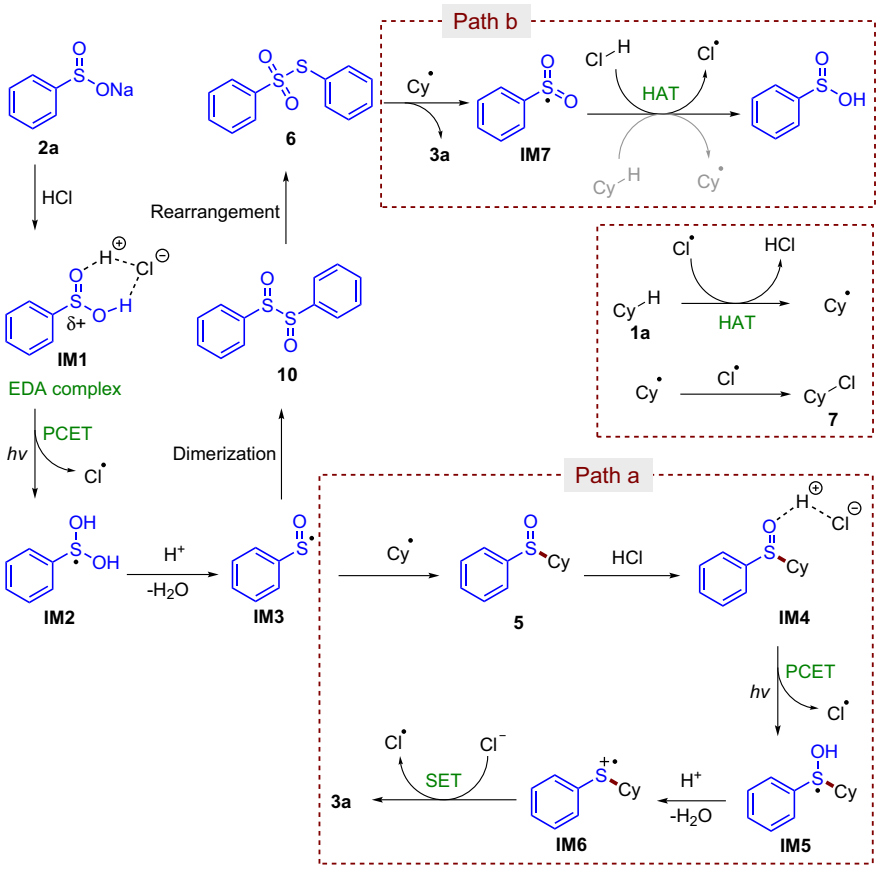


Fig. 4. (Color online) Proposed mechanism for C(sp^3)–H thiolation.

resonance (NMR) spectrum experiments (Fig. S7 online). In this system, the sulfoxide can effectively avoid coupling with alkyl radicals, but only act as an electron transfer acceptor. Herein, using DMSO as the green oxidant, we developed aliphatic C–H arylation with the electron-deficient heteroarenes [56–59]. As shown in Fig. 5, with the different substituent groups (fluorine, chlorine, bromine, methyl, trifluoromethyl, cyano, phenyl, ester), quinolines and isoquinolines could obtain the desired coupling products in moderate to excellent yields (**12a**–**12m**). Furthermore, pyridines and pyrimidines could be successfully modified in moderate yields as well (**12n**–**12s**), and good regioselectivity at the 4-position was given for the pyrimidine (**12s**–**1**). The polyalkylated products were smoothly generated using excess alkanes (**12t**–**12v**). Surprisingly, our method was suitable for hydroquinine with a complex skeleton, showing excellent functional group tolerance (**12w**).

Then, we approached the substrate scopes to different C(sp^3)–H species using 4-chloroquinoline as the coupling partner. A set of simple cyclic alkanes provided the corresponding alkylated heteroarenes in excellent yields (**12x**–**12aa**). The arylation of linear alkanes also occurred with high selectivity at the polysubstituted carbon position (**12ab**–**12ad**). Fortunately, unusual alkyl silanes could achieve the C(sp^3)–H arylation by our method, and so did the bridged alkanes norbornane and adamantane (**12ae**–**12ag**). It was important to note that this transformation was not limited to the unactivated C(sp^3)–H systems. Indeed, various activated C(sp^3)–H bonds adjacent to a heteroatom or π-system were also readily modified. The benzylic C–H abstractions of methylbenzene derivatives gave benzylated heteroarenes with good to excellent yields (**12ah**–**12aj**). For most alcohols and ethers, the conversion was achieved successfully at the α-site of the oxygen atom (**12ak**–**12aq**). It was not surprising that the ethylated quinoline was obtained as the minor product through C–O cleavage using diethyl ether as the alkane source [30]. Moreover, cyclohexane d_{12} could react in an analogous fashion (**12ar**). For the gaseous alkanes with stronger C–H bonds, our method was also applicable. Using the typical gaseous alkanes propane and ethane, the desired coupling products were successfully generated in moderate to good yields (**12as**–**12aw**). This conversion showed obvious regioselectivity at the methylene position using the propane.

Next, the direct allylation [28] and alkynylation [60,61] of the strong aliphatic C–H bonds were achieved by a similar strategy. As shown in Fig. 6, a series of simple cyclic alkanes provided the corresponding alkenyl esters in moderate yields (**15a**–**15d**). Using the ether and methylbenzene with activated C(sp^3)–H bonds, the conversions were carried out successfully as well (**15e**–**15g**). In the alkynylation transformation, the simple cyclic alkanes could give the desired products in 41% to 80% yields (**16a**–**16e**). For the alcohol, ether, and methylbenzene with the activated C(sp^3)–H bonds, the alkynylation products could be generated at the activated site successfully (**16f**–**16j**). When the aromatic rings bear functional groups with different electrical properties, the conversion was not significantly affected (**16k**–**16p**).

4. Conclusion

In summary, with the detailed mechanism verification and theoretical calculation, a novel generation path of chlorine radicals was revealed through an EDA complex constituted by HCl and S^{IV}=O groups. In this system, the chloride anions could be oxidated to chlorine radicals via a PCET process with S^{IV}=O groups under visible light irradiation. The aliphatic hydrocarbons could be activated

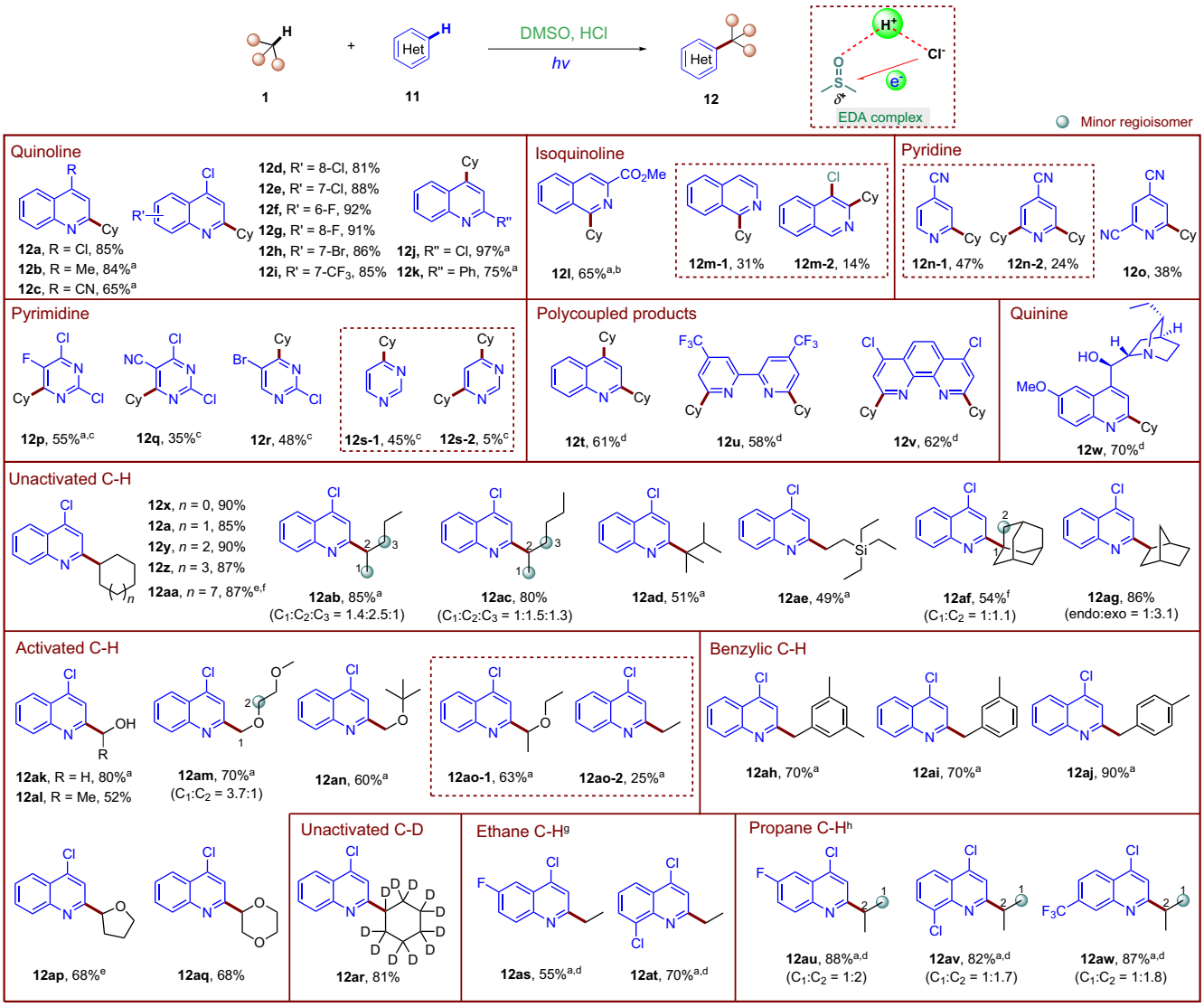


Fig. 5. (Color online) Direct arylation of strong aliphatic C–H bonds. Condition: **1** (2.0 mmol), **11** (0.2 mmol), DMSO (0.24 mmol), HCl (conc.) (0.6 mmol), and CH_3CN (2.0 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere. Isolated yield. [a] DMSO (0.3 mmol) was used. [b] CH_3CN (3.0 mL) was used. [c] HCl (0.8 mmol) was used. [d] **11** (0.1 mmol) was used. [e] Acetone (2.0 mL) instead of CH_3CN. [f] **1** (1.0 mmol) was used. [g] Ethane (4.0 MPa). [h] Propane (0.9 MPa). Bright green circles denote sites where notable amounts of other regioisomers are observed.

by the generated chlorine radicals through the HAT process, and subsequently coupled with the different radical acceptors. Even the gaseous alkanes with high bond energies could be modified by this protocol. Finally, a photo-promoted versatile aliphatic C–H functionalization was completed without photo- and metal-catalysts, including thiolation, arylation, alkynylation, and allylation. What's more, this EDA strategy provides a new path for the generation and application of chlorine radicals in the versatile C(sp^3)–H functionalization field.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Zemin Wang designed and performed the experiments. Chao-Xian Yan performed the DFT calculations. Dayong Shi directed the project. Ruihua Liu, Xiaowei Li, Jiajia Dai, and Xiangqian Li discussed the results and revised the manuscript. Zemin Wang wrote the manuscript with input from all authors.

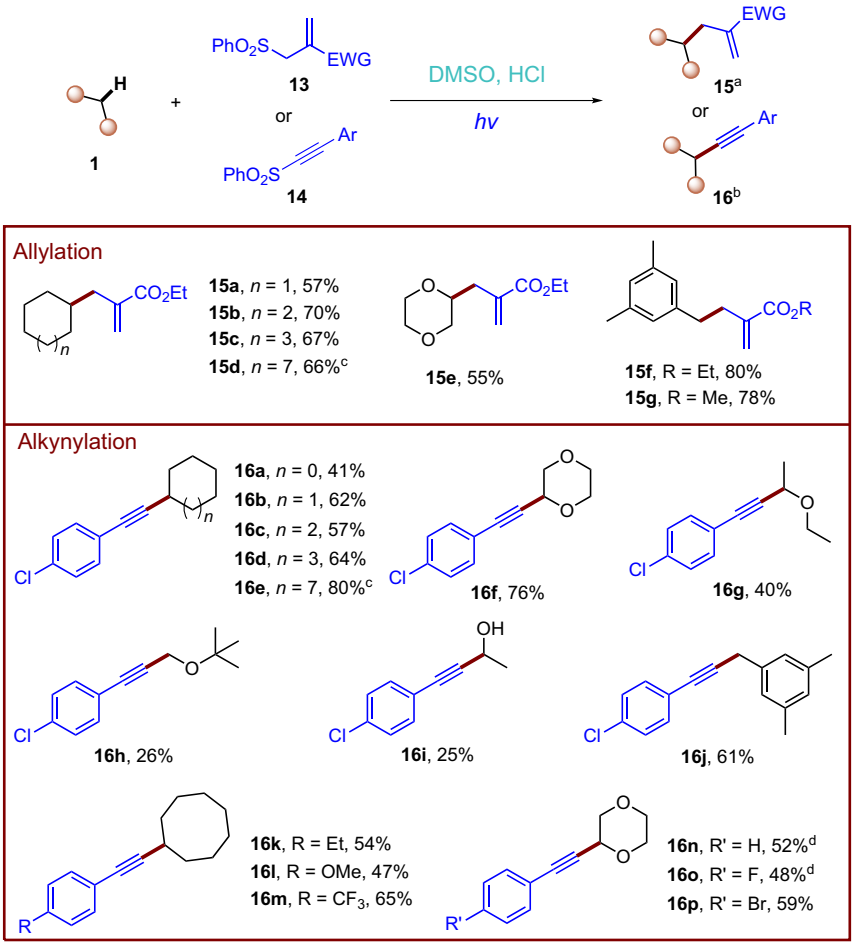

Fig. 6. (Color online) Direct allylation and alkynylation of strong aliphatic C–H bonds. [a] Condition 1: **1** (2.0 mmol), **13** (0.1 mmol), DMSO (0.3 mmol), HCl (conc.) (0.4 mmol), and CH_3CN (2.0 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere. [b] Condition 2: **1** (2.0 mmol), **14** (0.1 mmol), DMSO (0.2 mmol), HCl (conc.) (0.05 mmol), and CH_3CN (2.0 mL) at the temperature of 38–40 °C with 6 W LED lamp (420–430 nm) irradiation for 24 h under argon atmosphere. Isolated yield. [c] **1** (1.0 mmol) was used. [d] HCl (0.2 mmol) was used.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2023.11.048.

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