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Photo-induced carboxylation of $C(sp^2)-S$ bonds in aryl thiols and derivatives with CO_2

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Aryl thiols have proven to be a useful class of electron donors and hydrogen atom sources in photochemical processes. However, the direct activation and functionalization of $C(sp^2)-S$ bonds in aryl thiols remains elusive in the field of photochemistry. Herein, a photochemical carboxylation of $C(sp^2)-S$ bonds in aryl thiols with CO_2 is reported, providing a synthetic route to important aryl carboxylic acids. Moreover, different kinds of aryl thiol derivatives, benzeneselenol and diphenyl diselenide also show moderate-to-high reactivity in this transformation. Mechanistic studies, including DFT calculations, suggest that the in situ generated carbon dioxide radical anion ($CO_2^{\bullet-}$) and disulfide might be the key intermediates, which undergo radical substitution to yield products. This reaction features mild and catalyst-free conditions, good functional group tolerance and wide substrate scope. Furthermore, the efficient degradation of polyphenylene sulfide highlights the usefulness of this methodology.

Photochemistry has experienced significant renaissance over past decades and enabled transformations that are inconceivable or even impossible by alternative means[1–11]. The importance of light-induced processes is also reflected in diverse fields such as biology, material science, and medicine. It is preferable for reagents used in photochemistry to be cost-effective, function well under mild reaction conditions, and possess unique properties suitable for various types of reactions. In this context, aryl thiols have recently proven to be powerful reagents with multidimensional features that can serve various types of reactions in different ways (Fig. 1a)[12–16]. Firstly, aryl thiols are well-known to serve as polarity reversal catalysts in the hydrogen atom transfer (HAT) process, especially in photoredox/HAT synergistic catalysis[17–20]. Meanwhile, aryl thiols and corresponding thiolates can readily quench the excited photocatalyst to generate thiyl radicals, which are employed for the construction of organosulfur compounds in addition to function as HAT reagents[21,22]. Moreover, the aryl thiolates can form the electron-donor-acceptor (EDA) complexes with substrates bearing the appropriate π acceptor (e.g., aryl, vinyl)[23–26], or act directly as a photocatalyst for inert bond activation[27,28]. However, to the best of our knowledge, the photochemical activation and functionalization of $C(sp^2)-S$ bonds in aryl thiols have not been reported yet.

In the pursuit of producing cleaner fuels, continuous efforts have been directed towards the elimination of sulfur from petroleum fractions by cleaving the carbon–sulfur (C–S) bond in organosulfur compounds[29–31]. Meanwhile, organosulfur compounds have been emerging as the surrogate for conventional organo halides in organic synthesis. In particular, transformations of the $C(sp^2)-S$ bonds in thiophenol derivatives, including thioethers, sulfoxides, sulfones, and sulfonium salts, are of particular interest and offer a plethora of promising synthetic methods for the construction of C–C and C–heteroatom bonds via transition metal catalysis[32–37], photocatalysis[38–41] or electrochemistry[42]. So far, the direct activation and functionalization of $C(sp^2)-S$ bonds in aryl thiols are still elusive (Fig. 1b), with only a few cases reported under harsh reaction conditions or using stoichiometric metal reagents[43–45]. This is due to both

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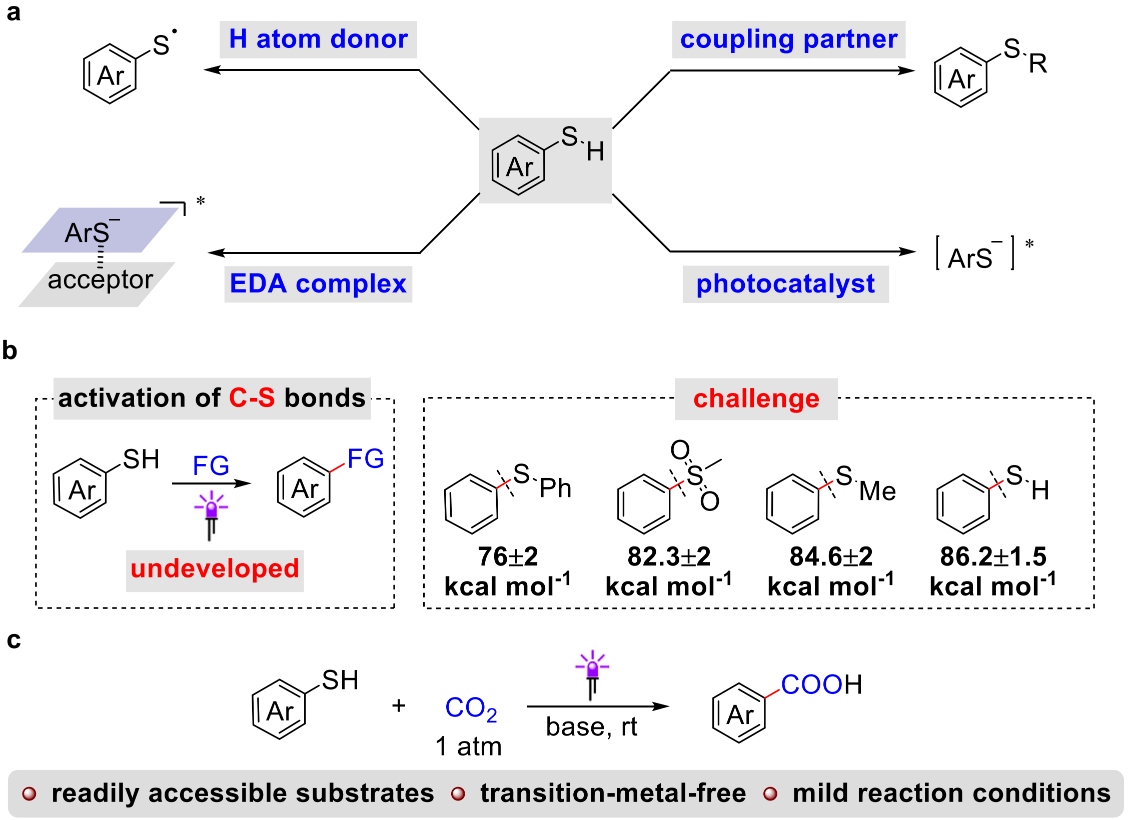


Fig. 1 | Photochemical strategies for transformations of aryl thiols. FG = functional group. a Recent advances of aryl thiols in photochemical organic synthesis. **b** The challenge of the photo-induced functionalization of C–S bonds in aryl thiols. **c** Photo-induced carboxylation of C–S bonds in aryl thiols with CO_2.

the inherent strong C(sp^2)–S bonds in thiophenol (BDE = 86 kcal mol^{-1})[46] and corresponding thiolates compared to thiophenol derivatives, as well as the catalyst-deactivating properties of both thiolates and sulfide leaving groups that are formed after the cleavage of C–S bonds[47].

Given our ongoing interest in the activation and utilization of carbon dioxide (CO_2)[48–59], we wondered if it was possible that aryl thiolates could directly activate CO_2 under photochemical conditions and the carbon dioxide radical anion ($CO_2^{\bullet-}$)[24,26,60–63], produced through single electron transfer (SET) reduction, was expected to achieve a direct carboxylation of C(sp^2)–S bonds. However, this transformation is fraught with challenges. Although CO_2 is an abundant, non-toxic, and renewable C1 source, its thermodynamic and kinetic stability make the coupling of these two relatively inert units difficult[49–57]. Furthermore, carboxylation of C(sp^2)–S bonds in aryl thiols with CO_2 has not been reported, and the mechanistic studies in this field are blank. In addition, competing side reactions, such as Kolbe-Schmitt type reactions[64] and hydrodesulfurization[44], are possible. Herein, we present a photo-induced carboxylation of C(sp^2)–S bonds in aryl thiols with CO_2 (Fig. 1c). A variety of aryl thiols and derivatives undergo this carboxylation reaction smoothly in the absence of transition metals.

Results

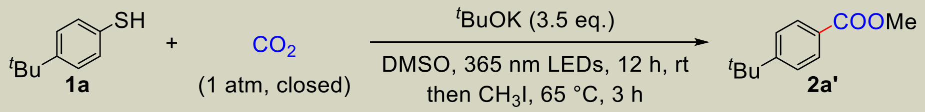
Screening of reaction conditions

In our previous research on thiolate-catalyzed carboxylation of C(sp^2)–H bonds with CO_2[26], we investigated the impact of various wavelengths of light on the reaction. During further exploration, we observed the production of aryl carboxylic acids as byproducts derived from aryl thiols under CO_2 atmosphere. Based on the preliminary result, 4-*tert*-butylthiophenol **1a** was employed as the model substrate, reacting with one atmospheric pressure of CO_2 under 30 W 365 nm light-emitting diodes (LEDs) irradiation at room temperature (rt) (Table 1). After an extensive investigation of the reaction conditions, the desired carboxylation product **2a'** was obtained with 82% yield in the presence of ᵗBuOK as the base and dimethyl sulfoxide (DMSO) as the solvent (entry 1). Control experiments revealed that the light source, base, and CO_2 all played vital roles in this transformation (entries 2-4). Decreasing the reaction time and reducing the quantity of alkali both resulted in lower yields (entries 5-6). Other bases and solvents led to lower yields (entries 7-12). Light sources with other wavelengths gave poor results (entries 13-15).

Substrate scope

With the optimal reaction conditions in hand, we first examined the scope of aryl thiols with different substituents. As shown in Fig. 2, a broad range of *para*- and *meta*-substituted aryl thiols (**1a**-**1q**) were effectively transformed with CO_2, producing the desired carboxylic acids **2a**-**2q** in moderate to good yields (41%-87%), and the carboxylation of **1a** with CO_2 can be easily scaled up to afford **2a** in 78 % yield. Notably, diverse functional groups, including ether (**1e**), amide (**1f**), boronic ester (**1g**), ester (**1h, 1j**, and **1k**), thioether (**1i**), silyloxy (**1l**), trimethylsilyl (**1n**), and even unprotected hydroxy group (**1m**), were well tolerated in the reaction, demonstrating the application practicability of this methodology. It is noteworthy that the aryl thiol **1q** bearing an unactivated vinyl group was competent for this carboxylation reaction, with the vinyl group remaining intact, affording desired product **2q** in a satisfactory yield. The sterically hindered aryl thiol **1r** bearing *ortho* methyl group could also undergo carboxylation with high efficiency. Beyond mono-substituted aryl thiols, disubstituted aryl thiols bearing methyl (**1s**-**1t**), and heterocycle (**1u**) were also amenable to this transformation, furnishing the desired carboxylic acids **2s**-**2u** in 67-94% yields. Additionally, tri-substituted aryl thiols were successfully converted into the corresponding

Table. 1 | Optimization of reaction conditions[a]



Entry	Variations	Yield of 2a′ (%)[b]
1	none	82% (84%)[c]
2	w/o light	n.d.
3	w/o ^{t}BuOK	n.d.
4	w/o CO_2	n.d.
5	^{t}BuOK (2.0 eq.)	73%
6	6 h instead of 12 h	71%
7	^{t}BuONa instead of ^{t}BuOK	65%
8	^{t}BuOLi instead of ^{t}BuOK	68%
9	Cs_2CO_3 instead of ^{t}BuOK	58%
10	NMP instead of DMSO	66%
11	DMF instead of DMSO	61%
12	DMAc instead of DMSO	69%
13	450 nm instead of 365 nm	trace
14	415 nm instead of 365 nm	24%
15	395 nm instead of 365 nm	25%

[a]Conditions: **1a** (0.2 mmol), ^{t}BuOK (3.5 eq.), DMSO (2.0 mL), 1 atm of CO_2, 365 nm LEDs, rt, 12 h, then CH_3I (5.0 eq.), 65 °C, 3 h. [b]Determined by GC with dodecane as the internal standard. [c]Isolated yield of corresponding carboxylic acid **2a**. n.d. = not detected. DMF = *N*,*N*-dimethylformamide. DMAc = *N*,*N*-dimethylacetamide. NMP = *N*-methyl-2-pyrrolidone.

carboxylic acids **2v**-**2w**. Furthermore, aryl thiols derived from biologically active molecules including derivatives from borneol (**1x**), menthol (**1y**), and cholesterol (**1z**) were compatible in this reaction, yielding the desired products in good yields.

Encouraged by the above success, we further expanded the substrate scope to arylthiol derivatives. To our delight, a variety of aryl thioethers, which are challenging substrates in previous photo-induced selective cleavage of C–S bonds, underwent smooth carboxylation with CO_2 under the optimized reaction conditions (Fig. 3). Different alkylthioarenes bearing primary (**3a, 3b**), secondary (**3c, 3d**), and tertiary (**3e**) alkyl groups were selectively transformed to **2a** in 53-95% yields. It is worth noting that a thiophenol-derived alkene **3f** is compatible under the present conditions. Next, diaryl sulfide **3g** was tested to afford the carboxylic product **2a** in 68% yield. Moreover, thioesters (**3h, 3i**) were successfully subjected to the reaction conditions, leading to the corresponding products in good yields. Notably, thiocarbamates **3j** and **3k** could also undergo the C(sp^2)–S bond carboxylation smoothly, yielding the corresponding products in 95% and 58% yields, respectively.

Synthetic applications

To further underscore the practicality of this strategy, carboxylation of analogues of aryl thiols were carried out (Fig. 4). For instance, the carboxylation of benzeneselenol **4** was performed to provide the corresponding carboxylic acid **5**, albeit in a moderate yield (Fig. 4a). Interestingly, diphenyl diselenide, a commonly used radical scavenger, was found to be amenable to Se–Se bond cleavage and carboxylation of C(sp^2)–Se bond with CO_2 (Fig. 4b)[58,65].

Polyphenylene sulfide (PPS) is a high-performance engineering plastic that is extensively utilized in the fields of flame retardancy, heat insulation, and dielectric insulation[66,67]. PPS possesses many desirable characteristics, such as excellent high-temperature stability, flame retardant properties, chemical corrosion resistance, as well as good mechanical, and electrical properties. However, the degradation of PPS typically requires intense conditions. In light of above progress, we wonder whether we could extend this photochemical strategy to the degradation of PPS. To our delight, when PPS was subjected to the similar reaction conditions, it could be degraded into product **8** effectively (Fig. 5).

Mechanistic investigations

To gain more insights into the reaction mechanism, a series of mechanistic studies were conducted (Fig. 6). Firstly, the control experiments demonstrated that both light and ^{t}BuOK were crucial for the cleavage of C–S bonds in aryl thioether **3c**. (Fig. 6a, entries 2–4). The formation of **9** and **10** was determined by GC, suggesting that the cleavage of the alkyl C–S bond in thioether and the generation of a corresponding alkyl radical were involved in this transformation[68]. We further conducted the ultraviolet-visible spectroscopic measurements (Fig. 6b). Compared to the spectrum of thioether **3a**, a bathochromic shift was observed for the mixture of **3a** and ^{t}BuOK. These results suggested the formation of an electron donor-acceptor (EDA) complex between thioether **3a** and ^{t}BuOK. After that, the photo-induced carboxylation was obviously suppressed in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), indicating the involvement of a radical process (Fig. 6c). Next, the generation of formate (HCO_2^-) was detected only in the presence of thiolates and CO_2, indicating that $CO_2^{\cdot-}$ might be generated from the SET between CO_2 and photoactivated thiolate (Fig. 6d). The reaction profile demonstrated the formation of disulfide **12** and the anionic species *p*-^{t}BuC$_6$H$_4$SS$^-$, which reacted with iodoethane to produce **13** during the reaction (Fig. 6e). Compounds **12** and **13** were then subjected to standard reaction conditions, resulting in 77% and 80% yields of the desired acid **2a**, respectively. These results indicated that **12** and *p*-^{t}BuC$_6$H$_4$SS$^-$ act as the potential intermediates in this transformation (Fig. 6f, g).

To have a better understanding of this process, computational studies were performed to investigate the cleavage of C–S bond and subsequent carboxylation with CO_2.[24,26] According to the experimental observations (Fig. 6c, d), $CO_2^{\cdot-}$ and a thiyl radical are very likely generated as the key intermediates in this reaction. Preliminary

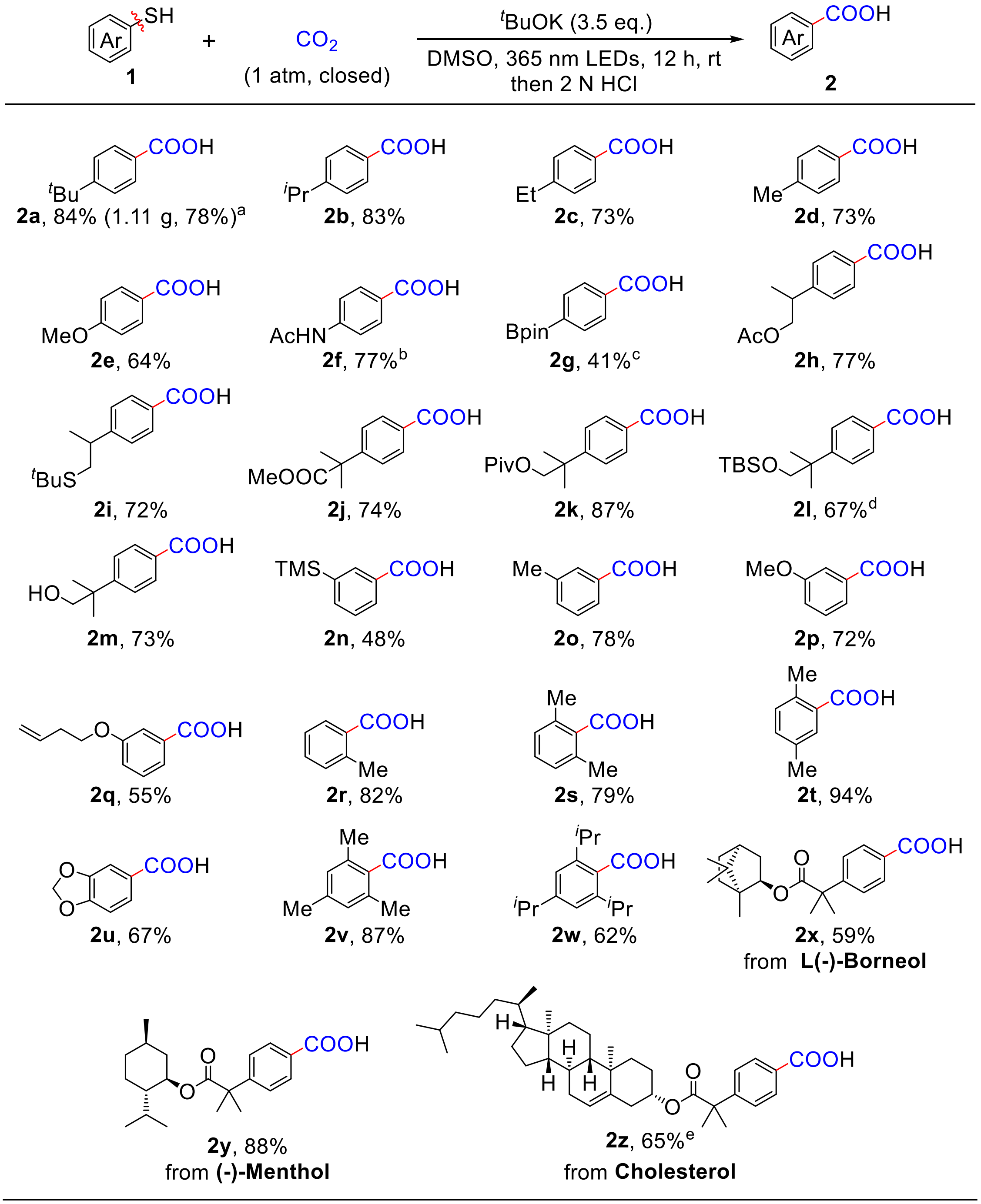


Fig. 2 | Photo-induced carboxylation of C(sp^2)–S Bonds in aryl thiols with CO_2. Reaction Conditions: **1a** (0.2 mmol), ^{t}BuOK (3.5 eq.), DMSO (2.0 mL), 1 atm of CO_2, 365 nm LEDs, rt, 12 h, then 2 N HCl. Yields of isolated products. ^{a}Gram-scale reaction, 36 h. $^{b t}$BuOK (5.0 eq.). ^{c}Cs_2CO_3 (3.5 eq.). $^{d t}$BuOLi (3.5 eq.). ^{e}DMSO/THF (2:1, v/v, 3 mL).

calculations were carried out using thiyl radical **1-IN** as the starting zero point (Fig. 7). **1-IN** can undergo a kinetically favored radical dimerization to form disulfide intermediate **2-IN** (-29.2 kcal mol^{-1}). The carbon atom of $CO_2^{\bullet-}$ exhibits strong nucleophilicity[69], which might react with disulfide **2-IN** via radical-type nucleophilic substitution to realize the cleavage of C–S bond[70]. The DFT calculation clearly reveals that the substitution of $CO_2^{\bullet-}$ on the phenyl ring in **2-IN** via transition state **3-TS** requires an energy barrier of 6.3 kcal mol^{-1}, which is 11.8 kcal mol^{-1} lower than that at sulfur atom via transition state **6-TS**, suggesting that the reaction via **6-TS** could be kinetically excluded. The geometry structure in **3-TS** shows that the length of C1–C2 and C1–S1 bonds are 2.01 Å and 1.83 Å, respectively. As a result, the carboxylate intermediate **4-IN** was generated via nucleophilic aromatic substitution transition state **3-TS** by the release of disulfur radical **5-IN**, formation of C(sp^2)–COO bond and the cleavage of C(sp^2)–S bond. The radical-type substitution to cleavage S–S bond via transition state **3-TSa** is also considered (Please see more information in supporting information (SI)), which would result in the generation of thiyl radical **1-IN** and unstable thiocarbonate **4-INa**. However, the computational results reveal an invalid conversion process, which can be neglected. Further DFT calculation demonstrates that disulfur radical **5-IN** could preferentially undergo reduction, S–S bond dissociation[71] to fulfill the carboxylation transformation of a molecule of C–S bond (Please see more information in SI).

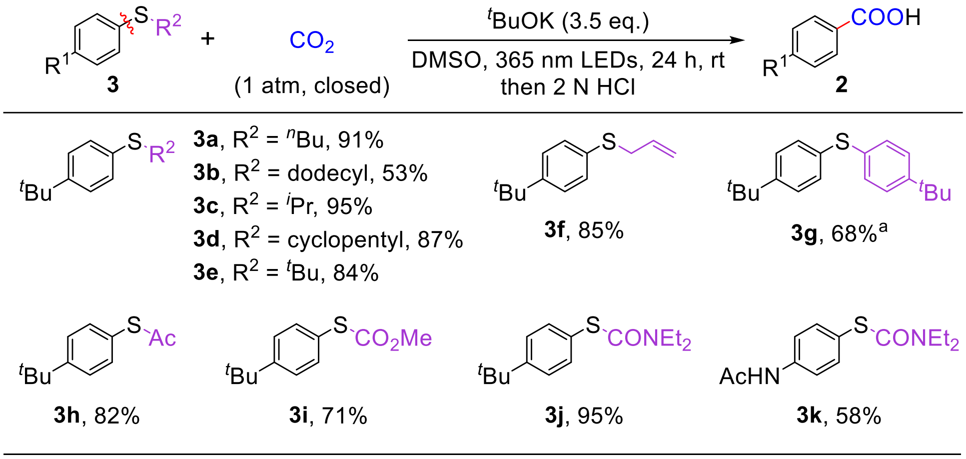


Fig. 3 | Photo-induced carboxylation of C(sp^2)–S bonds in arylthiol derivatives with CO_2. Reaction Conditions: **3** (0.2 mmol), ^{t}BuOK (3.5 eq.), DMSO (2.0 mL), 1 atm of CO_2, 365 nm LEDs, rt, 24 h, then 2 N HCl. Yields of isolated products. [a]72 h, the isolated yield is on phenyl group basis.

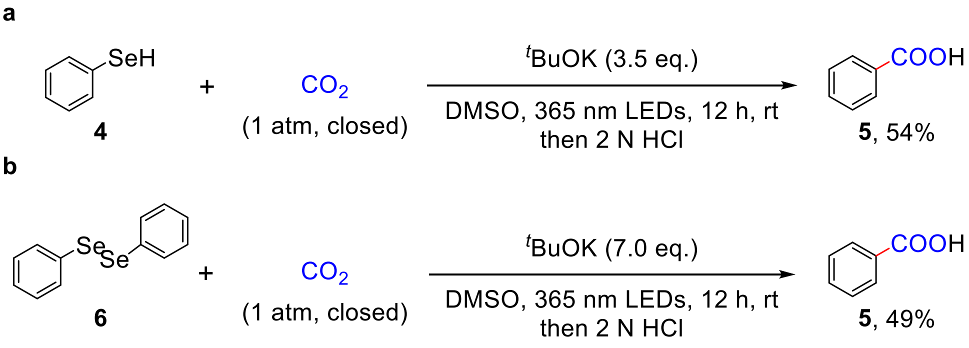


Fig. 4 | Carboxylation of C(sp^2)–Se bonds with CO_2. a Carboxylation of C(sp^2)–Se bond in benzeneselenol. **b** Carboxylation of C(sp^2)–Se bond in diphenyl diselenide.

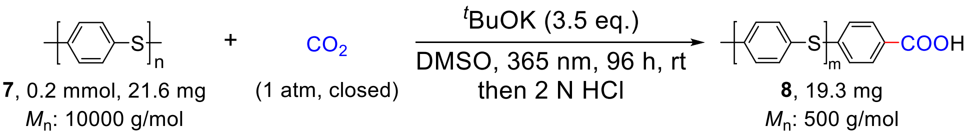


Fig. 5 | Degradation and carboxylation of polyphenylene sulfide with CO_2. Reaction Conditions: **7** (0.2 mmol), ^{t}BuOK (3.5 eq.), DMSO (2.0 mL), 1 atm of CO_2, 365 nm LEDs, rt, 96 h, M_n: Number-average molecular weight.

Based on the mechanistic studies and previous reports[24,26], a plausible pathway for the cleavage and carboxylation of C(sp^2)–S bonds in aryl thiols with CO_2 is proposed (Fig. 8). Initially, upon the irradiation with 365 nm light, a single electron transfer event between the excited thiolate **II** and CO_2 would occur to afford $CO_2^{\bullet-}$ and thiyl radical **III**. The thiyl radical **III** then undergoes dimerization to form the disulfide intermediate **12**. Subsequently, the radical addition of $CO_2^{\bullet-}$ to disulfide **12** would generate the desired carboxylate **IV** and radical intermediate **V**. Intermediate **V** is then reduced by $CO_2^{\bullet-}$ via a SET process to produce intermediate **VI**, which can be trapped by EtI. Finally, intermediate **VI** would be converted to thiolate **I** under strong basic conditions. At this stage, we could not exclude other reaction pathways. Further mechanistic studies to elucidate and refine the intricacies of the mechanism are undergoing in our laboratory.

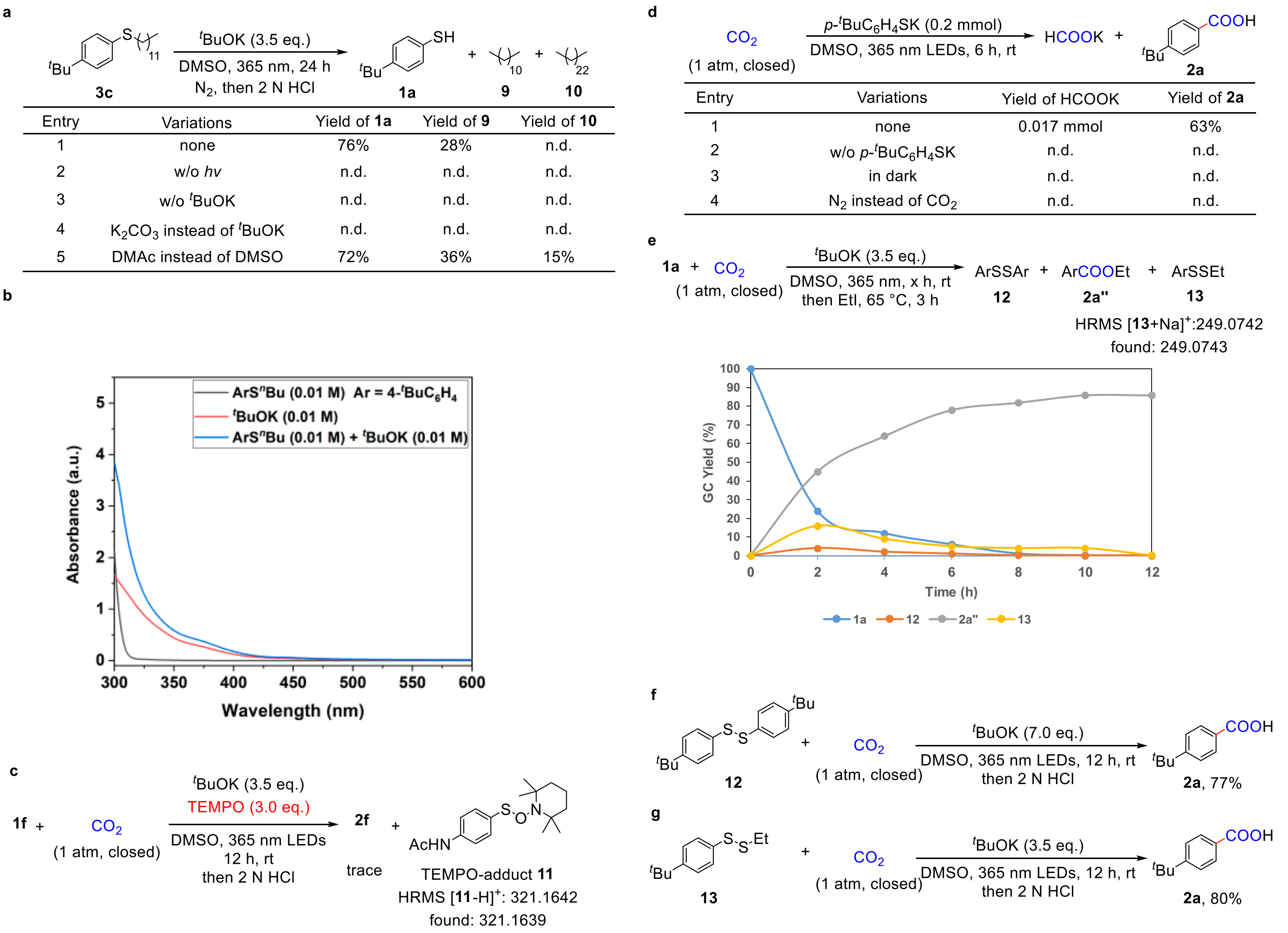
Discussion

In summary, we have developed a photochemical carboxylation of C(sp^2)–S bonds in thiols with CO_2. A diverse array of readily accessible aryl thiols and derivatives were successfully converted into the corresponding carboxylic acids with high yields. Notably, the carboxylation of C(sp^2)–Se bonds in benzeneselenol and diphenyl diselenide with CO_2 was also achieved. This transition-metal-free and operationally simple reaction process features a broad substrate scope and good functional group tolerance. Furthermore, the degradation of PPS demonstrates the potential applications of this method in material science.

Methods

General procedure for the synthesis of 2a–2z from 1

To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with arylthiols **1** (0.2 mmol, 1.0 eq. for solid substrates). Then, the tube was transferred to glovebox to add ^{t}BuOK (0.7 mmol, 78.6 mg, 3.5 eq.). After being taken out of the glovebox, the tube was then evacuated and back-filled with CO_2 atmosphere three times. Anhydrous DMSO (2 mL) was added under CO_2 atmosphere followed by liquid arylthiols **1**, and the tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W 365 nm LEDs lamp (0.5 cm away, with a cooling fan to keep the reaction temperature at 25-30 °C and keeping the reaction region located in the center of LEDs lamp) for



Entry	Variations	Yield of **1a**	Yield of **9**	Yield of **10**
1	none	76%	28%	n.d.
2	w/o *hν*	n.d.	n.d.	n.d.
3	w/o ^{t}BuOK	n.d.	n.d.	n.d.
4	K_2CO_3 instead of ^{t}BuOK	n.d.	n.d.	n.d.
5	DMAc instead of DMSO	72%	36%	15%

Entry	Variations	Yield of HCOOK	Yield of **2a**
1	none	0.017 mmol	63%
2	w/o p-^{t}BuC$_6$H$_4$SK	n.d.	n.d.
3	in dark	n.d.	n.d.
4	N_2 instead of CO_2	n.d.	n.d.

Fig. 6 | Mechanistic investigations. a Study of C–S bond cleavage of **3c**. **b** UV-vis spectroscopic measurement in DMSO. **c** Radical inhibition experiment. **d** Detection of potassium formate. **e** Reaction profile of aryl thiol **1a** with CO_2. **f** Identification of possible intermediate **12**. **g** Identification of possible intermediate derivative **13**.

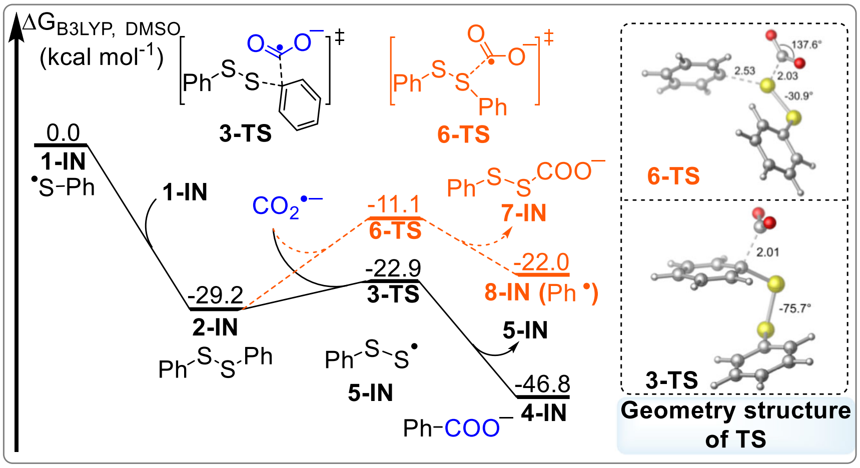


Fig. 7 | Free energy profiles of carboxylation of C(sp^2)–S bonds in disulfide with CO_2. Calculations were performed using Gaussian 16 at the M06/6-311 + G(d,p)/SMD(DMSO)//B3LYP/6-31 + G(d)/SMD(DMSO) level of theory. All energies are in kcal mol^{-1} and bond lengths are shown in angstroms (Å).

12 hours. Upon completion of the reaction, the reaction mixture was diluted with 2 mL EA and quenched by 7 mL 2 N HCl. The mixture was extracted with EA four times and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (PE/EA/AcOH 30/1/0 ~ 7/1/0.2%) to give the pure desired products **2**.

General procedure for the synthesis of 2 from 3

To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with thioesters **3** (0.2 mmol, 1.0 eq. for solid substrates). Then, the tube was transferred to glovebox to add ^{t}BuOK (0.7 mmol, 78.6 mg, 3.5 eq.). After being taken out of the glovebox, the tube was then evacuated and back-filled with CO_2

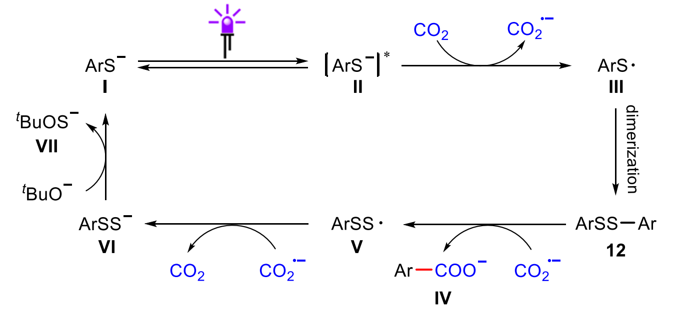


Fig. 8 | Proposed mechanism. Plausible reaction mechanism of CO_2 and aryl thiols in the presence of base and light.

atmosphere three times. Anhydrous DMSO (2 mL) was added under CO_2 atmosphere followed by arylthiol derivatives **3**, and the tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W 365 nm LEDs lamp (0.5 cm away, with a cooling fan to keep the reaction temperature at 25-30 °C and keeping the reaction region located in the center of LEDs lamp for 24 hours). Upon completion of the reaction, the reaction mixture was diluted with 2 mL EA and quenched by 7 mL 2 N HCl. The mixture was extracted with EA four times and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (PE/EA/AcOH 30/1/0 ~ 7/1/0.2%) to give the pure desired products **2**.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files. B3LYP geometries for all the optimized structures and transition states are provided in the source date file. Source data are provided with this paper. Extra data are available from the author upon request.

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Author contributions

D.G.Y. and J.H.Y. conceived and designed the study. J.L., W.W., L.L.L.,W.Z., J.P.Y., Y.L. & X.W.C. performed the experiments, mechanistic studies and wrote the manuscript. All authors contributed to the analysis and interpretation of the data.

Competing interests

The authors declare no competing interests.

Additional information

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