Overriding Cage Effect in Electron Donor-Acceptor Photoactivation of Diaryliodonium Reagents: Synthesis of Chalcogenides

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Abstract

In recent times, diaryliodonium reagents (DAIRs) have witnessed a resurgence as an arylating agent, especially under photoinduced conditions. However, reactions proceeding through electron donor-acceptor (EDA) complex formation with DAIRs are restricted to electron-rich reacting partners serving as donors due to the well-known cage effect. We discovered a visible-light-induced convenient and practical EDA platform to activate DAIRs for generating and concomitant utilization of resulting aryl radicals for synthesizing organic chalcogenides that are prevalent in natural products and biologically active compounds. In this process, an array of DAIRs and dichalcogenides react in the presence of 1,4 diazabicyclo[2.2.2]octane (DABCO) as a cheap and readily available donor, furnishing a diverse variety of di(hetero)aryl and aryl/alkyl chalcogenides in good yields. The method is scalable, features a broad scope with good yields, and operates under open-to-air conditions. The photoinduced chalcogenation technology is suitable for late-stage functionalizations and disulfide bioconjugations and facilitates access to biologically relevant thioesters, dithiocarbamates, sulfoximines, and sulfones. Moreover, the discovered method applies to synthesizing diverse pharmaceuticals, such as vortioxetine, promazine, mequitazine, and dapsone, under amenable conditions.

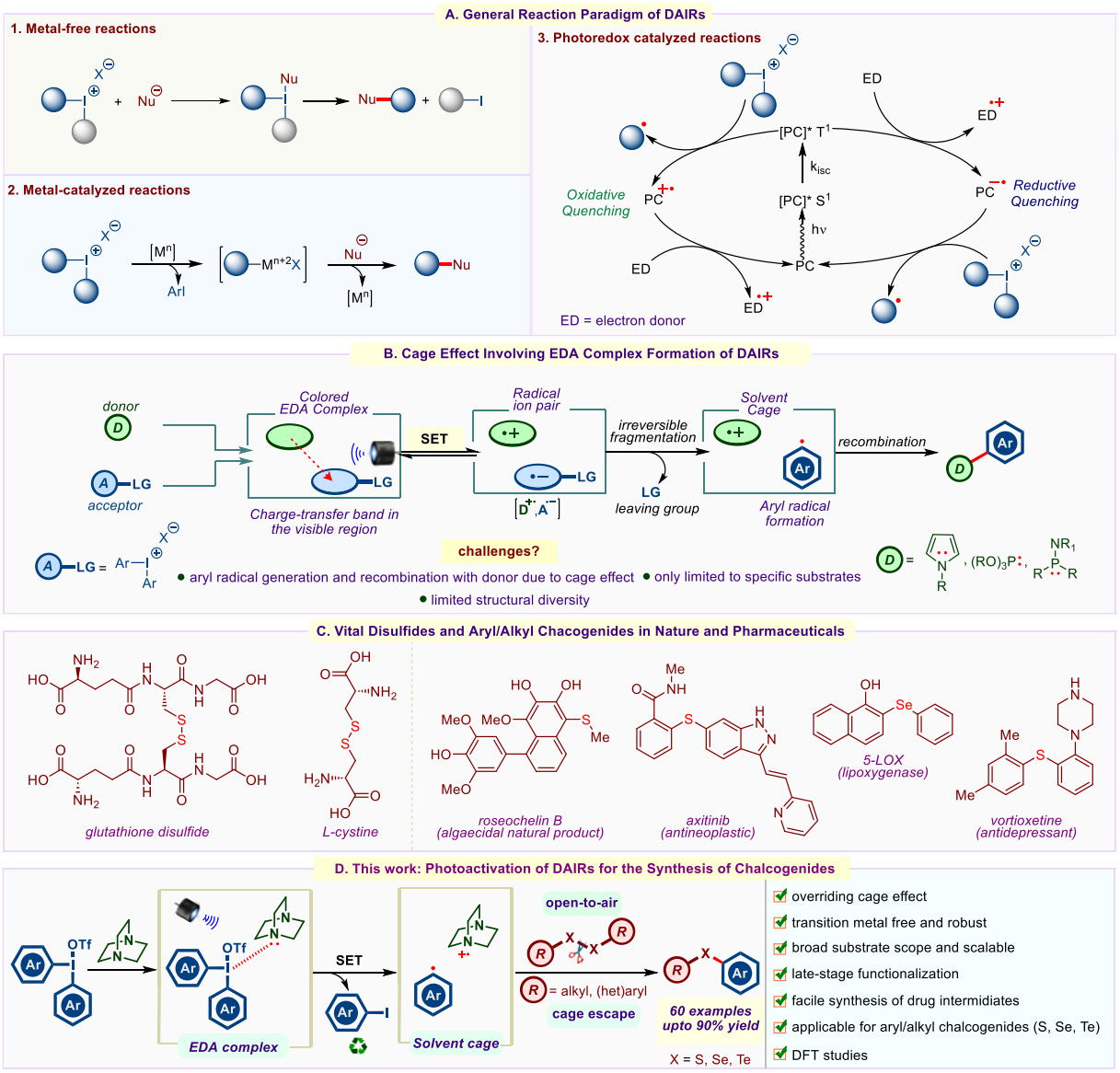
Introduction

Hypervalent iodine(III) reagents have witnessed tremendous applications in an array of synthetic transformations, and they have contributed significantly to the synthesis of natural products, pharmaceutically relevant compounds, and polymeric materials.[1] Diaryliodonium reagents (DAIRs) belong to the category of iodine(III) reagents and have received reinvigorated interest as an arylating agent in recent times.[2] The popularity of DAIRs is due to their ease of preparation, bench stability, non-toxicity, and high functional group tolerance. They have been utilized as electrophilic reagents in various carbon-carbon and carbon-heteroatom bond-forming reactions under transition metal-free and metal-catalyzed conditions. More recently, with the emergence of visible-light-induced synthetic transformations,[3] DAIRs have also served as aryl radical precursors under photocatalytic approaches, proceeding through either oxidative or reductive quenching of the photocatalyst (Scheme 1A).[4] In this regard, the electron donor-acceptor (EDA) complex-driven photoactivation platform has intrinsic advantages regarding sustainability, as it operates under mild and exogenous photocatalyst-free conditions and enables selective formation of radicals under visible light irradiation.[5] However, reports on using DAIRs as aryl radical progenitors under visible light-induced electron donor-acceptor (EDA) conditions are restricted.[6] The limited reports utilize reacting partners as donor-acceptor pairs; hence, generation and recombination of aryl radical dominates due to radical cage effects (Scheme 1B).[7] Furthermore, these methods are limited regarding the type of donor substrates and their structural diversity. Hence, curating suitable donor systems and reaction conditions to override this radical cage effect would create new opportunities and enable the development of new reactions involving DAIRs as aryl radical precursors under photoinduced EDA conditions.

Organosulfur compounds, such as aryl thioethers and disulfides, are rich in biology and medicines and ubiquitous throughout the planet's history.[8] Disulfides like cystine and glutathione disulfide play vital roles in cell signaling, protein conformation, and cellular redox homeostasis (Scheme 1C).[9] They represent one of the most dynamic bonds and are responsive to various stimuli, including free radicals, as observed in disulfide metathesis reactions. On the other hand, aryl sulfides are present as principal moieties in a variety of biologically active compounds, natural products, pharmaceuticals, and organic materials, manifesting diverse medicinal properties (Scheme 1C).[10] Accordingly, we wondered if the aryl radicals generated from DAIRs under photocatalyst-free suitable EDA conditions could be reacted with disulfides much like radical disulfide exchange reactions to provide biologically relevant aryl sulfides under metal-free conditions. Such a method could, in principle, be extended to the synthesis of other aryl chalcogenides as well. To the best of our knowledge, such a general strategy allowing access to an array of simple or complex bioactive di(hetero)aryl or aryl/alkyl chalcogenides under green and sustainable conditions is unknown.

Various methods for constructing carbon-chalcogenide bonds have been developed, given their importance across different chemical sectors.[11] Traditional methods mainly rely on transition metal-catalyzed cross-couplings involving aryl thiols, diaryl dichalcogenides, or other functionalized chalcogenide precursors.[12] Despite significant progress, these methods often require precious metal catalysts, air-sensitive ligands, and harsh conditions. Moreover, commonly used thiols and selenols in these

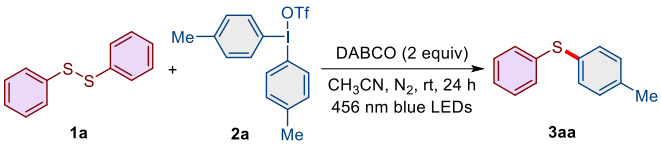
transformations are relatively unstable, induce catalyst poisoning, have unpleasant odors, and some organometallic chalcogenide derivatives encounter toxicity, making them unsuited for industrial applications.[13] To curtail these issues, several photoinduced synthetic strategies have been developed. The photoredox methods mainly utilize precious metal-based photocatalysts,[14] and photoinduced methods often require super-stoichiometric strong inorganic bases, high energy UV light, and excess of reacting partners.[11b,15] Moreover, these methods mostly were not extended to aryl/alkyl chalcogenides. In this regard, developing a transition metal-free, sustainable, and general platform for synthesizing a variety of di(hetero)aryl and aryl/alkyl chalcogenides is of utmost importance. In conjunction with our interest in visible-light-induced synthetic transformations[16] and hypervalent iodine chemistry,[1e,1f,4e-g,6b,17] we report a transition-metal and photocatalyst-free, convenient, and practical photoinduced approach for the synthesis of a variety of organic chalcogenides from DAIRs and di-aryl/alkyl dichalcogenides using 1,4 diazabicyclo[2.2.2]octane (DABCO) as a cheap and readily available donor (Scheme 1c).



Scheme 1. A. Reaction paradigm of DAIRs under metal-free, transition metal-catalyzed, and photoredox-catalyzed conditions. B. Cage-effect involving DAIRs under EDA conditions. C. Important disulfides and aryl/alkyl chalcogenides in nature and pharmaceuticals. D. Present work on the synthesis of di(hetero)aryl and aryl/alkyl chalcogenides.

Results and Discussion

Table 1. Optimization of reaction conditions.[a]



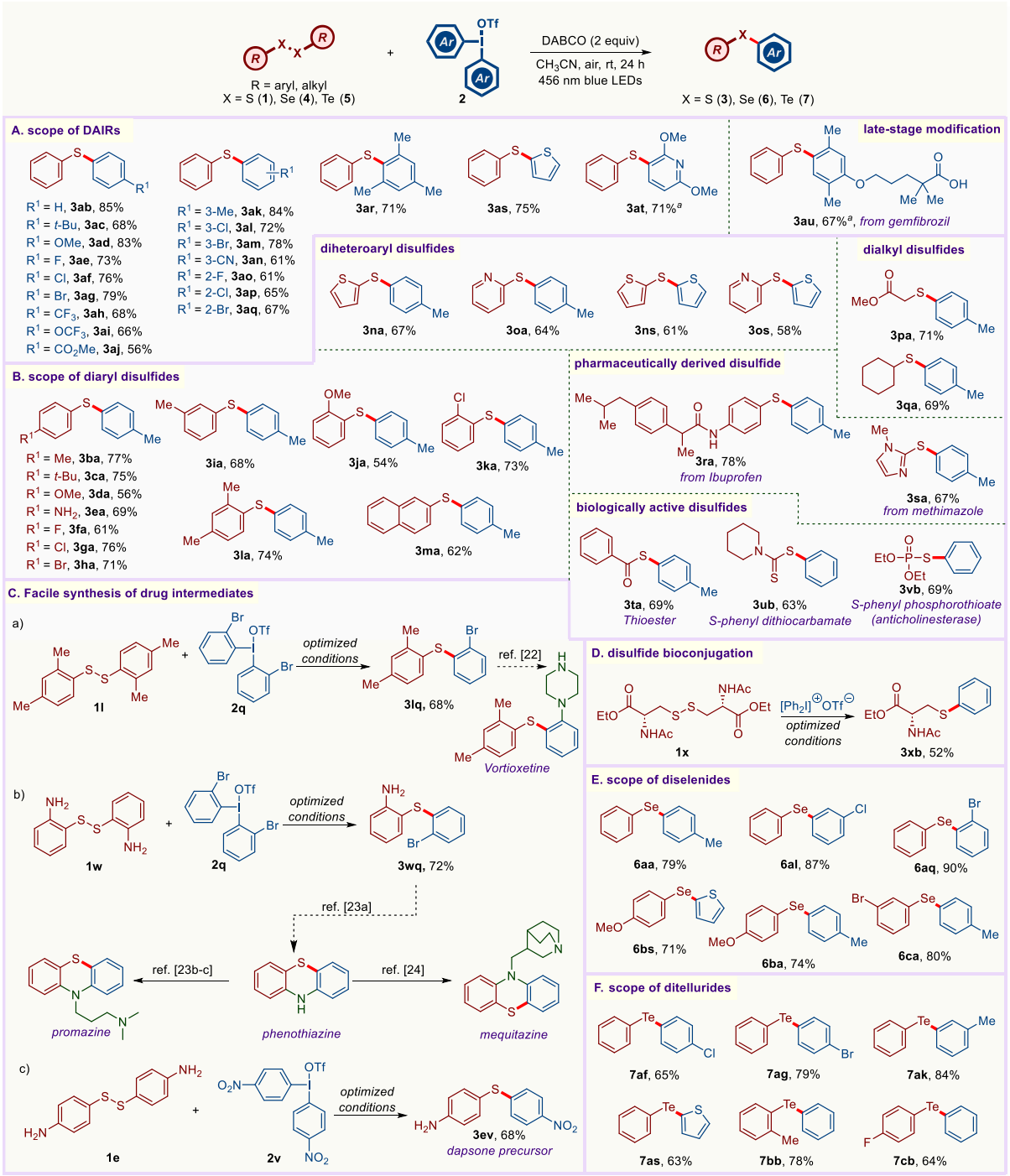
Entry	Deviation from Above	Yield **3aa** [%][b]
1	None	85
2	DBU or DMAP instead of DABCO	50, 70
3	PPh_3 or K_2CO_3 instead of DABCO	35, 65
4	1,4-dioxane or THF instead of CH_3CN	45, 40
5	DMF or DMAc instead of CH_3CN	30, 35
6	Without DABCO	Trace
7	Without irradiation	N.D.
8	Under air	85
9	1.5 or 1.01 equiv of **2a**	85, 75
10	1.2 or 1.5 equiv of DABCO	60, 75
11	440 nm or 467 nm instead of 456 nm blue LEDs	80, 60

[a]Reaction conditions: **1a** (0.15 mmol, 1 equiv), **2a** (1.1 equiv), DABCO (2 equiv), and CH_3CN (1.5 mL) under nitrogen atmosphere using Blue LEDs (456 nm) for 24 h. [b]Isolated yield. N.D. = not detected.

To assess the feasibility of the stated hypothesis, we initiated our study by irradiating a solution of diphenyl disulfide **1a** (0.15 mmol, 1 equiv), di(4-tolyl) iodonium triflate **2a** (1.1 equiv), and DABCO (2 equiv) in acetonitrile (CH_3CN) using blue LEDs (456 nm) and under nitrogen atmosphere (Table 1 and Table S1 in the SI). To our delight the reaction went to completion in 24 h to furnish the desired diaryl sulfide **3aa** in 85% yield (entry 1). Replacing DABCO with other sacrificial donors, such as DBU, DMAP, PPh_3, and K_2CO_3, led to inferior yields (entries 2-3). Evaluation of a spectrum of different solvents revealed that other polar aprotic solvents, such as 1,4-dioxane, THF, DMF, or DMA, are less effective as compared to acetonitrile (entries 4-5). Control experiments disclosed that trace or no product formation was detected in the absence of DABCO or irradiation (entries 6-7). These findings ruled out the possibility of an EDA formation between **1a** and **2a** under the reaction conditions. Notably, the reaction could also be carried out under open air without an inert atmosphere, providing identical results (entry 8). Further screening of reactant and reagent concentrations was not beneficial (entries 9-10). Evaluation of different light sources established that 456 nm blue LEDs was the most effective (entry 11).

Having optimized the reaction conditions, we explored the scope of DAIRs **2** by reacting with diphenyl disulfide **1a** (Scheme 2A). Delightfully, DAIRs with a variety of electron-donating (*t*-Bu, OMe) and electron-withdrawing (F, Cl, Br) substituents at the *para*-position of the phenyl ring participated in the chalcogenation to provide respective diaryl thioethers (**3ab-3ag**) in moderate to excellent yields (68-85%). Pleasingly, DAIRs embedded with sensitive functional groups (4-CF_3, 4-OCF_3, 4-CO_2Me) afforded corresponding products (**3ah-3aj**) in moderate yields. Importantly, DAIRs with electronically diverse *meta*-substituents (**3ak-3an**) and sterically demanding ortho-substitution pattern (**3ao-3aq**) underwent a smooth transformation to provide the desired products in moderate to high yields (61-84%). Since, halogen substituents (Cl, Br) survived under our reaction conditions to afford chlorinated and brominated sulfides, this method can complement other thioether synthesis approaches proceeding via generation of aryl radicals through reduction of the C-X bond. Notably, DAIRS with sterically congested mesityl group and electron-rich thiophene could be accommodated under the reaction conditions providing (**3ar-3as**) in good yields (71-75%). In corroboration with earlier reports,[6b,18] we found that 3,5-dimethyl-4-isoxazolyl (DMIX) serves as a perfect dummy ligand and facilitates the transfer of the aryl counterpart from the corresponding non-symmetrical iodonium salt. Accordingly, 2,4-dimethoxy

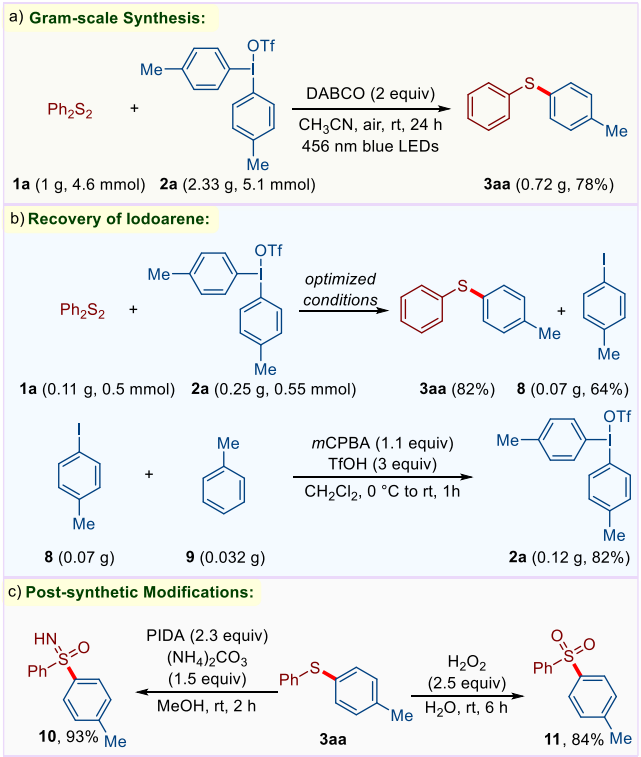
pyridine (**3at**, 71%) and gemfibrozil (**3au**, 67%), a triglyceride-lowering drug, were selectively transferred from the DMIX-derived non-symmetric DAIRs en route to the synthesis of corresponding diaryl sulfides. Overall, these conditions tolerated sensitive functional groups and enabled late-stage modification of drug molecules, such as gemfibrozil, thereby showcasing the robustness and practicality of the method. Subsequently, we explored the scope of various disulfides (Scheme 2B). Pleasingly, an array of diaryl disulfides having electron-donating (CH_3, *t*-Bu, OMe, NH_2), and electron-withdrawing (F, Cl, Br) substituents at the para-position of the phenyl ring reacted with DAIR **2a** to provide corresponding products (**3ba-3ha**) in good yields (56-77%). Other than *para*, aryl disulfides with *meta* and *ortho*-substitution patterns and naphthyl disulfides were well accommodated (**3ia-3ma**, 54-74%). Gladly, disulfides with heteroaromatic rings also participated in the process, enabling the synthesis of heteroaryl/aryl (**3na-3oa**) and diheteroaryl sulfides (**3ns-3os**) in moderate yields (58-67%). Most importantly, aliphatic disulfides, including the ones with sensitive functional groups, successfully reacted with DAIR **2a** to afford the corresponding products (**3pa-3qa**) in good yields (69-71%). Notably, the preparation of aliphatic/aromatic sulfides was outside the purview of most of the earlier photoinduced methods.[15b,15d]



Scheme 2. Scope of the photoinduced chalcogenation method. Reaction conditions: **1/4/5** (0.25 mmol, 1 equiv), **2** (1.1 equiv), DABCO (2 equiv), and CH_3CN (2.5 mL) under open air using blue LEDs (456 nm) for 24 h. [a]Corresponding 3,5-dimethyl-4-isoxazolyl (DMIX)-substituted non-symmetrical iodonium salt was used.

Emboldened by these exciting results, we examined the method's applicability in the synthesis and functionalization of biologically active compounds, pharmaceuticals, and complex molecules. Gratifyingly, ibuprofen-derived aryl disulfide underwent a facile transformation to provide **3ra** in 78% yield. It is reported in the literature that the conversion of methimazole to methimazole disulfide is responsible for the anti-thyroid activity of methimazole.[19] Interestingly, our method allowed efficient conversion of methimazole disulfide to S-phenyl methimazole **3sa** in 67% yield. On the other hand, dibenzoyl disulfide successfully reacted with DAIR **2a** under the optimized conditions to afford thioester **3ta** in 69% yield. Notably, the thioester unit is frequently encountered in various physiologically active substances and agrochemicals and serves as synthons in organic synthesis.[20] The method was also amenable to the synthesis of biologically relevant S-phenyl dithiocarbamate **3ub** (63%) and O,O-diethyl S-phenyl phosphorothiolate **3vb** (69%).[21] The practicality and synthetic applicability of our protocol were further demonstrated through an efficient synthesis of key intermediates (**3lq**, **3wq**, **3ev**) of several pharmaceuticals, such as vortioxetine (antidepressant),[22] promazine (antipsychotic drug),[23] mequitazine (antihistaminic drug),[23a,24] and dapsone (used to treat skin diseases)[25] under mild and metal-free conditions (Scheme 2C). Finally, we were intrigued to explore the possibility of cleaving a cysteine-derived disulfide through our method, which in turn may provide a new way of labeling peptides and proteins.[26] Accordingly, a reaction between cysteine derivative **1x** and DAIR **2b** provided the desired bioconjugated thioether **3xb** in 52% yield (Scheme 2D). The method was successfully extended to the preparation of other diaryl chalcogenides. A variety of differently substituted diaryl diselenides and ditellurides having electron-donating and electron-withdrawing groups on the phenyl ring coupled with electronically diverse DIARs to afford the respective diaryl selenides (Scheme 2E) and diaryl tellurides (Scheme 2F) in moderate to excellent yields (64-90%).

The scalability and commercial prospects of the photoinduced method were realized by reacting 1 g of diphenyl disulfide **1a** with DAIR **2a** under the optimized protocol. To our delight, the efficacy of the process was retained to provide the desired diaryl sulfide **3aa** in 78% yield (Scheme 3a). Moreover, as shown in Scheme 3b, the released iodoarene **8** in the reaction between **1a** and **2a** was recovered in 64% yield, and recycled to prepare DAIR **2a** (82%).[27] This experiment explicitly portrays the sustainability aspect of the process. Notably, final thioethers are amenable to further synthetic modifications, leading to valuable building blocks and potentially bioactive compounds. Accordingly, diaryl sulfide **3aa** was converted to corresponding NH-sulfoximine **10** (93%)[28] and sulfone **11** (84%)[29] derivatives under convenient oxidative conditions (Scheme 3c).



Scheme 3. Scale-up experiment, recycling of iodoarene and post-synthetic modifications.

Finally, detailed mechanistic studies were carried out to understand the mechanism of this photoinduced chalcogenation process (Figure 1 and SI). The inhibition of model reaction between **1a** and **2a** in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl) or BHT (2,6-di-*tert*-butyl-4-methylphenol) as radical scavengers under standard reaction conditions and detection of the corresponding TEMPO and BHT adducts **12** and **13** by high-resolution mass spectrometry (HRMS) established the intermediacy of aryl radicals in this photoinduced process (Figure 1a). The UV/Vis absorption spectra analysis of individual and combined reaction components in CH_3CN evidenced the formation of an EDA complex between DAIR **2a** and DABCO (Figure 1b and SI). While DAIR **2a** and DABCO individually presented an absorption band in the near UV region, their mixture displayed a significant bathochromic shift with visible-light absorption. On the contrary, no such red-shift was noticed when disulfide **1a** was mixed with either DAIR **2a** or DABCO, confirming no involvement of disulfide in the EDA formation. This set of observations is in agreement with the visual appearance of each solution. The solution developed an intense yellow color when DAIR **2a** was mixed with DABCO, whereas it remained colorless in all other cases (Figure 1b). The formation of an EDA complex was further established by the Job plot, where a 0.35:0.65 stoichiometric relation between DAIR **2a** and DABCO was confirmed (Figure 1c). Furthermore, "light/dark" experiments and calculation of photochemical quantum yield (Φ = 1.02) of the model reaction between **1a** and **2a** indicated the indispensability of constant irradiation and ruled out the possibility of a radical chain mechanism.

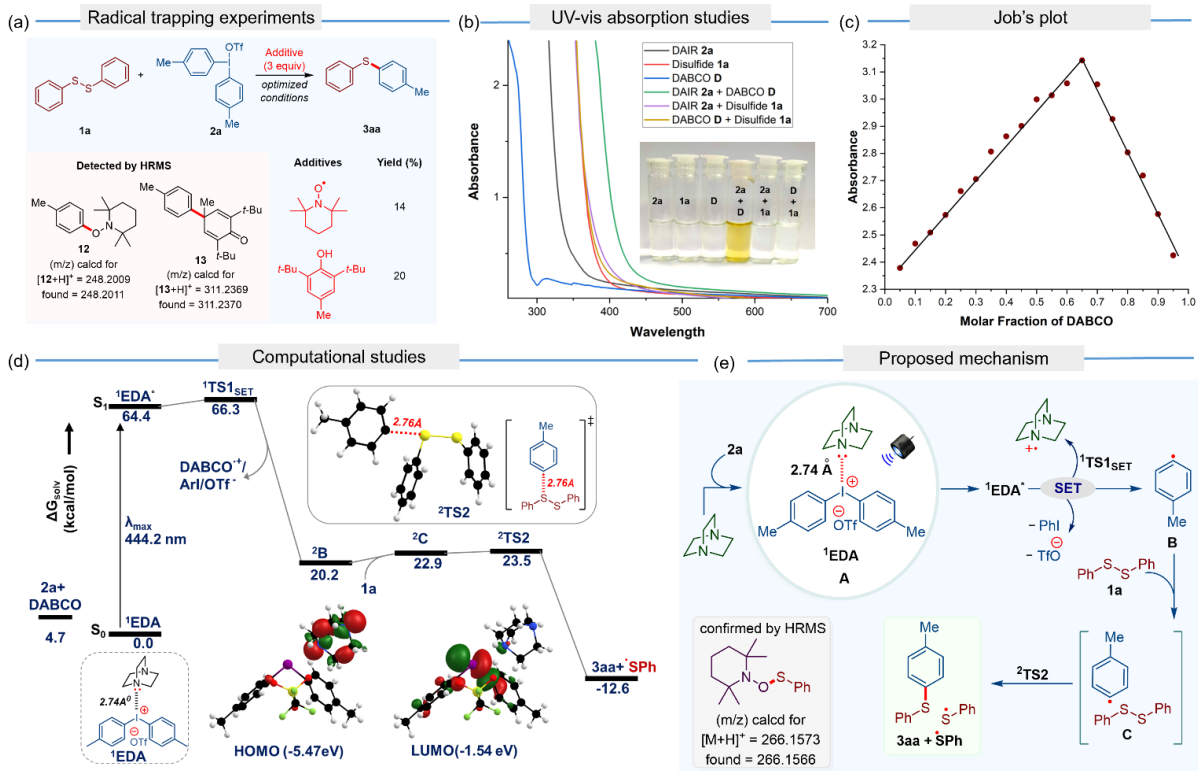
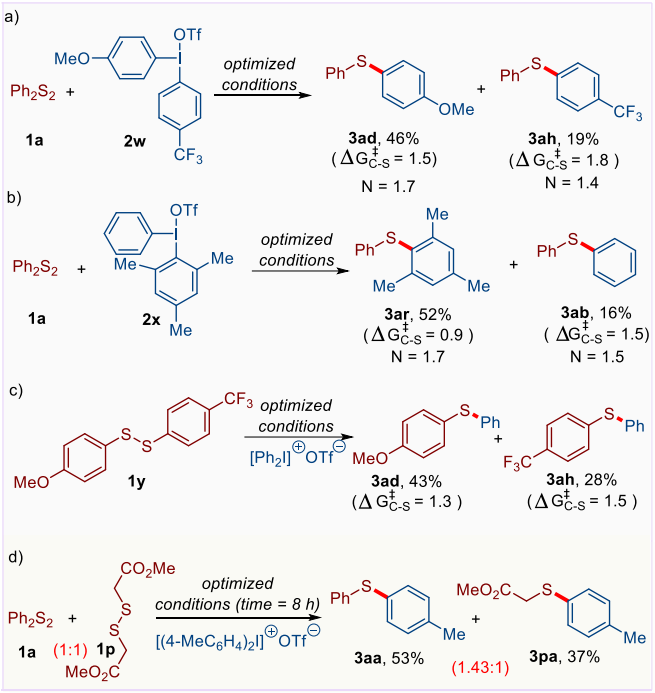


Figure 1. Mechanistic studies. (a) radical trapping experiments. (b) UV-Vis absorption studies with DAIR **2a**. (c) Stern-Volmer plot. (d) computational studies. (e) proposed mechanism.

Consequently, to get an in-depth insight into the mechanism, we conducted density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations at B3LYP-D3(BJ)/SMD(Acetonitrile)/6-311+G(d,p) and M06L/SMD(Acetonitrile)/6-311+G(d,p), in a respective manner. The corresponding free energy profile is depicted in Figure 1d, and an overall mechanistic picture is shown in Figure 1e based on the reaction between **1a** and **2a** under the optimized conditions (see SI for computational details). Our computational study predicted that an electron-donor acceptor complex, ^{1}**EDA** (ΔG= -4.7 kcal/mol), is formed by non-covalent interactions between DABCO and **2a** at 2.74 Å, where the nitrogen lone pairs of DABCO (HOMO) is the donor and primarily C(aryl)-I based vacant σ* orbital (LUMO) is the acceptor (Figure 1d). This favored arrangement induces the photoexcitation of ^{1}**EDA** (S_0) to ^{1}**EDA*** (S_1) at a predicted absorption wavelength of λ_{calc} = 444.2 nm, with the highest absorption intensity of f = 0.0492. Interestingly, photoexcitation to ^{1}**EDA*** leads to a single-electron transfer (SET) from the donor (DABCO) to the acceptor (**2a**) through ^{1}**TS1**$_{SET}$ at an energy barrier of 66.3 kcal/mol. This triggers cleavage of the C(aryl)-I bond to generate an unconfined tolyl radical (^{2}**B**), separated from the rest of the components (DABCO$^{•+}$/ArI/OTf$^-$) of the EDA complex.

Interaction of the disulfide substrate (**1a**) with this radical (**^{2}B**) initially generates a slightly endergonic reactant complex **^{2}C** (ΔG= 2.7 kcal/mol w.r.t **^{2}B** + **1a**), followed by a transition state, **^{2}TS2,** featuring C-S bonding at 2.76 Å and a minimal energetic expense of 3.3 kcal/mol. This is followed by the generation of the desired product **3aa** along with weakly interacting •SPh radical. Notably, the formation of •SPh radical was confirmed by detecting the corresponding radical trapping adduct with TEMPO by HRMS (Figure 1e).

Subsequently, we synthesized unsymmetrical DAIRs (**2w** and **2x**) and reacted them with disulfide **1a** under the established conditions to evaluate if a chemoselective transfer of one aryl moiety over the other is possible or not (Scheme 4). This study is pertinent considering the paucity of reports in the literature on the selective transfer of a particular aryl moiety from unsymmetrical DAIRs under photoinduced EDA conditions. In the case of DAIR **2w**, a selective transfer of electron-rich aryl group providing corresponding compounds **3ad** (46%) and **3ah** (19%) was observed (Scheme 4a). On the other hand, the predominant transfer of the sterically more demanding mesityl group was observed (**3ar**, 52%) when mesityliodonium salt **2x** was employed (Scheme 4b). Interestingly, as per the literature, electron-deficient and sterically less-hindered aryl groups are generally transferred selectively under photoredox-catalyzed conditions.[4e, 4h, 6d] We resorted to computational studies to understand the unprecedented chemoselectivity trend under EDA conditions. The calculations reaffirmed our experimental findings and predicted the C-S bond-forming step outcome with similar preferences in both cases. The C-S bond-forming transition states corresponding to products **3ad** and **3ah** shows $\Delta\Delta G^{\ddagger}$ = 0.3 kcal/mol, at a computed **3ad**:**3ah** ratio of 1.7:1 (Scheme 4a). Notably, the $\Delta\Delta G^{\ddagger}$ of the C-S bond forming step for **3ab** and **3ar** is comparatively higher and turned out to be 0.6 kcal/mol, manifesting **3ar**:**3ab** = 2.7:1 as shown in Scheme 4b. A careful computational analysis further shows that the nucleophilicity index (N) of the anisole radical leading to product **3ad** is slightly greater than that of the trifluoromethylphenyl radical leading to **3ah**. A similar preference for the greater nucleophilic aryl radical towards the C-S bond formation step is also predicted for **3ar** over **3ab**. These findings certainly indicate that electron-donating substituents leading to greater nucleophilicity of the aryl radical would be decisive in chemoselectivity trends under photoinduced EDA conditions. Further, we evaluated the selectivity in the case of nonsymmetrical diaryl disulfide as well. A preferred transfer of electron-rich phenyl ring containing –OMe group (**3ad**, 43%) over the electron-deficient one (**3ah**, 28%) with $\Delta\Delta G^{\ddagger}$ = 0.1 kcal/mol corresponding to the computed ratio of **3ad** and **3ah** as 1.2:1 was observed (Scheme 4c). Subsequently, relative alkyl and aryl disulfide consumption rates were evaluated by reacting a 1:1 mixture of diaryl disulfide **1a** and dialkyl disulfide **1p** with DAIR **2a** for 8 h under the optimized conditions (Scheme 4d). A product ratio of phenyl thioether **3aa** and alkyl thioether **3pa** (**3aa**:**3pa** = 1.43:1) manifested a slightly higher rate of consumption of diaryl disulfide.



Scheme 4. Unsymmetrical studies. Relative free energy barriers are in units of kcal/mol. N denotes the computed nucleophilicity index in units of eV^{-1} of the aryl radical.

Conclusion

In summary, we demonstrated a general strategy for generating aryl radicals from DAIRs under photoinduced EDA conditions using DABCO as a cheap and commercially available donor. In this process, following the generation, aryl radicals can escape the solvent cage and be captured by dichalcogenides en route to the synthesis of organic chalcogenides. In general, a variety of structurally and electronically diverse DAIRs were cross-coupled with an array of diaryl chalcogenides to furnish a plethora of unsymmetrical di(hetero)aryl chalcogenides in moderate to excellent yields without the need for any transition metal, precious external ligand or photocatalyst. The method was successfully extended to dialkyl disulfides to prepare aryl alkyl thioethers. Gratifyingly, a wide range of sensitive functional groups, including $–NO_2$, $-CF_3$, $-OCF_3$, -CN, $-CO_2Me$, $-CO_2H$, and $–NH_2$ were accommodated in the reaction, thus reinforcing appreciable functional group tolerance of the protocol. Moreover, the method enabled the incorporation of sulfide moiety on the backbone of densely functionalized pharmaceuticals. The developed photoinduced chalcogenation platform provided a new mode of disulfide bioconjugation. It facilitated access to an array of biologically relevant substrate classes, such as thioesters, dithiocarbamates, sulfoximines, and sulfones, as well as pharmaceuticals, such as vortioxetine, promazine, mequitazine, and dapsone under mild conditions. Detailed mechanistic investigations comprising control experiments, photophysical studies, and computational calculations indicated a charge transfer interaction mechanism. Given the mild conditions and ability to perform (hetero)aryl/alkyl chalcogenation on a variety of electron-rich and electron-deficient arenes and heteroarenes, it is anticipated that the presented method will open new avenues in the synthesis of pharmaceutical drugs and natural products.

Acknowledgements

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