

Dimsyl Anion Enables Visible-Light-Promoted Charge Transfer in Cross-Coupling Reactions of Aryl Halides

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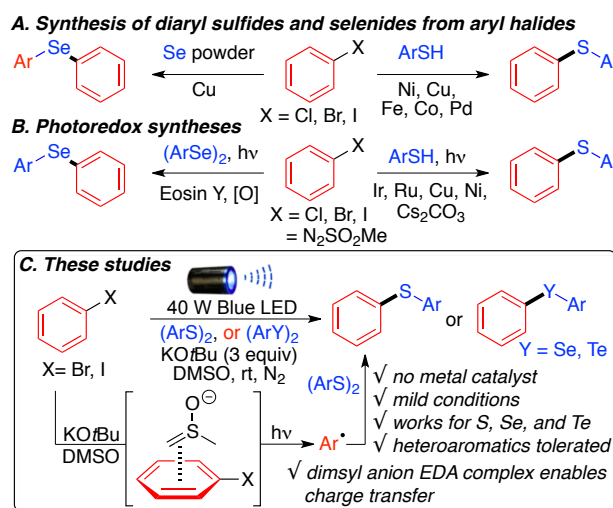
ABSTRACT: A simple and mild methodology is reported for visible-light-promoted synthesis of unsymmetrical chalconides enabled by dimsyl anion in the absence of transition-metals or photoredox catalysts. The cross-coupling reaction between aryl halides and diaryl dichalconides proceeds in good to excellent yields with electron-rich, electron-poor, and heteroaromatic moieties. Mechanistic investigations using UV-Vis spectroscopy, time-dependent density functional theory (DFT) calculations, and control reactions suggest that dimsyl anion forms an electron-donor-acceptor (EDA) complex capable of absorbing blue light, leading to a charge transfer responsible for generation of aryl radicals from aryl halides. This previously unreported mechanistic pathway may be applied to other light-induced transformations performed in DMSO in the presence of bases and aryl halides.

Diaryl sulfides, selenides, and tellurides are valuable moieties across all chemical sectors from pharmaceuticals to material sciences.¹ Consequently, the construction of these carbon-chalconide bonds has attracted significant interest.² Most methods rely on transition-metal catalysis for the cross-coupling of aryl halides^{3,4} with aryl chalconides (Scheme 1A). High temperatures and expensive ligands are often required to avoid thiolate-induced catalyst deactivation and poisoning.⁵ Additionally, the thiols and selenols used in these reactions are unstable, have strong unpleasant odors,⁶ and some derivatives, such as stannyl selenides,⁷ have increased toxicity making them unsuitable for large-scale reactions. Milder reaction conditions using photoredox strategies have been developed (Scheme 1B),^{8,9} but these methods often require the use of expensive photocatalysts. A limited number of catalyst-free photo-induced methodologies for C–S bond formation from aryl halides exist,^{2d,10} but they were not shown to work across group 16 elements.

Over the past decade, there has been an emergence of transition-metal-free cross-coupling reactions of aryl halides utilizing *tert*-butoxides (*O**t*Bu). Initial observations demonstrated that KO*t*Bu in the presence of ligands¹¹ at high temperatures enabled the direct C–H arylation of benzene with aryl halides. In the presence of visible-light, similar transformations of aryl halides have been achieved at room temperature,¹² often using dimethyl sulfoxide (DMSO) as solvent.

Tuttle and Murphy contributed significantly in elucidating the mechanism of these metal-free transformations,¹³ and it was determined that in most cases KO*t*Bu is not involved in the single electron transfer (SET) step. Instead, they identified various electron-donating species, such as the dimsyl anion, that are capable of performing a SET to aryl halides at high temperatures (135 °C).¹⁴ However, this work did not provide an explanation for the photo-induced activation of aryl halides in DMSO in the absence of additives. Recently, the Rossi group proposed that the dimsyl anion can be photo-excited to initiate a SET to alkyl halides,¹⁵ but an electron-donor-acceptor (EDA) complex was not observed.

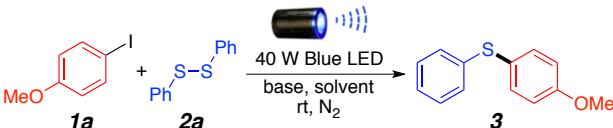
Scheme 1. Current and proposed approaches to generate diaryl sulfides and selenides



Our interest in photoinduced SET performed by KO*t*Bu, recently led us to identify a halogen-bonded EDA complex capable of C–H aminations.¹⁶ Herein, an unprecedented EDA complex between dimsyl anion and aryl halides is reported that is responsible for a photo-induced activation of aryl halides and enables a visible-light-promoted C–S, C–Se, and C–Te cross-coupling with diaryl dichalconides (Scheme 1C). The reaction proceeds at room temperature in the absence of catalysts generating the desired products in good to excellent yields across a range of substrates. The involvement of this EDA complex is supported by UV-Vis spectroscopy, time-dependent density functional theory (DFT) calculations, and experimental controls. The observation of this EDA complex provides a compelling mechanistic explanation for the SET that initiates this reaction and possibly other photo-induced transformations of aryl halides that use DMSO in the presence of base.

We selected 4-iodoanisole (**1a**) and diphenyl disulfide (**2a**) as model reagents to optimize the reaction. No product was detected in the absence of base under inert atmosphere with DMSO as the solvent (Table 1, entry 1). In the presence of three equivalents of KOtBu the reaction provided the desired product in 88% isolated yield (entry 2). Using NaOtBu or LiOtBu as base resulted in lower yields (entries 3, 4) indicating the importance of solubility of the base. Other solvents such as acetonitrile (CH₃CN) or dichloromethane (CH₂Cl₂) (entries 5, 6) also gave lower yields (see full details in the Supporting Information, S4). Inorganic and organic bases (Cs₂CO₃, DABCO, and Et₃N) were explored to further understand the potential role of the base in this transformation (Table 1, entries 7–9). Unfortunately, the yields for these reactions were low. The poor performance with Cs₂CO₃ (entry 7) further emphasizes that a different mechanism is at play compared to previously proposed transformations.^{2d} Reducing the amount of **2a** to 1.5 equivalent (entry 10) did not affect the reaction. Further reducing **2a** to 1.1 equivalent (entry 11) lowered the yield. When the reaction was performed in dark (entry 12) no product was formed, which highlighting the fundamental role of photons. Importantly, a decrease in yield was also observed when the reaction was carried out in air (entry 13). Finally, a time study showed that for the reaction was completed in 4h (entry 14).

Table 1. Optimization of reaction conditions^a



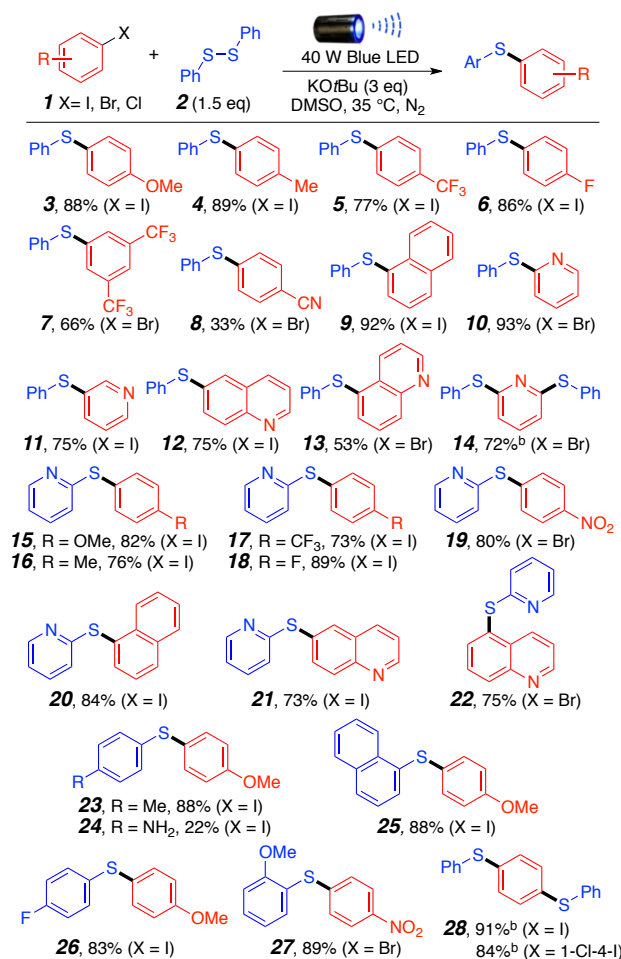
| entry | base (equiv.) | 2a (equiv.) | solvent (mL) | yield (%) ^b |
|-----------------|---------------------------------------|--------------------|---------------------------------------|------------------------|
| 1 | – | 2.0 | DMSO (1.0) | – |
| 2 ^a | KOtBu (3.0) | 2.0 | DMSO (1.0) | 85 (88) ^c |
| 3 | NaOtBu (3.0) | 2.0 | DMSO (1.0) | 76 |
| 4 | LiOtBu (3.0) | 2.0 | DMSO (1.0) | 63 |
| 5 | KOtBu (3.0) | 2.0 | CH ₃ CN (1.0) | 12 |
| 6 | KOtBu (3.0) | 2.0 | CH ₂ Cl ₂ (1.0) | – |
| 7 | Cs ₂ CO ₃ (3.0) | 2.0 | DMSO (1.0) | 35 |
| 8 | DABCO (3.0) | 2.0 | DMSO (1.0) | 38 |
| 9 | Et ₃ N (3.0) | 2.0 | DMSO (1.0) | trace |
| 10 | KOtBu (2.0) | 2.0 | DMSO (1.0) | 25 |
| 11 ^a | KOtBu (3.0) | 1.5 | DMSO (1.0) | 83 |
| 12 | KOtBu (3.0) | 1.1 | DMSO (1.0) | 59 |
| 13 ^d | KOtBu (3.0) | 1.5 | DMSO (1.0) | – |
| 14 ^e | KOtBu (3.0) | 1.5 | DMSO (1.0) | 53 |
| 15 ^f | KOtBu (3.0) | 1.5 | DMSO (1.0) | 82 |

^aConditions: **1a** (0.2 mmol), **2a**, base, solvent, room temperature around reaction flask was 35 °C (heating caused by the LED lamp), under N₂, 24h. ^bYields are based on **1a**, determined by ¹H-NMR using dibromomethane as internal standard. ^cIsolated yield. ^dThe reaction was performed in dark covered by aluminum foil. ^eThe reaction was performed in the air. ^f4h reaction.

We continued our study investigating the substrate scope for this transformation. The scope of aryl halides is quite broad (Scheme 2, products **1–14**). Both electron-donating (OMe, Me) and electron-withdrawing (CF₃, F) groups at the *para* positions afforded the desired cross-coupled products **3–6** in good to

excellent yields (77–89%). Highly electron-poor substrates such as 1-bromo-3,5-dinitrofluoromethylbenzene also gave desired product **7** albeit in slightly lower yields (66%). The presence of an aryl nitrile afforded product **8** (33%), primarily due to hydrolysis of the cyano group. Acidic or easily hydrolysable functional groups were not well tolerated. Excellent yields were obtained when 1-iodonaphthalene and 2-bromopyridine were used as coupling partners affording products **9** and **10** (92% and 93%). This promising result led us to exploration of other heteroaromatic halides, particularly those with privileged frameworks in bioactive compounds. 3-Iodopyridine and 6-iodoquinoline provided desired product **11** and **12** in good yield (75%). 5-Bromoquinoline afforded product **13** in 53% yield. Finally, 2,6-dibromopyridine was efficiently coupled at both halogen sites giving product **14** in a single step (72%).

Scheme 2. Aryl halide and aryl disulfide scope^a

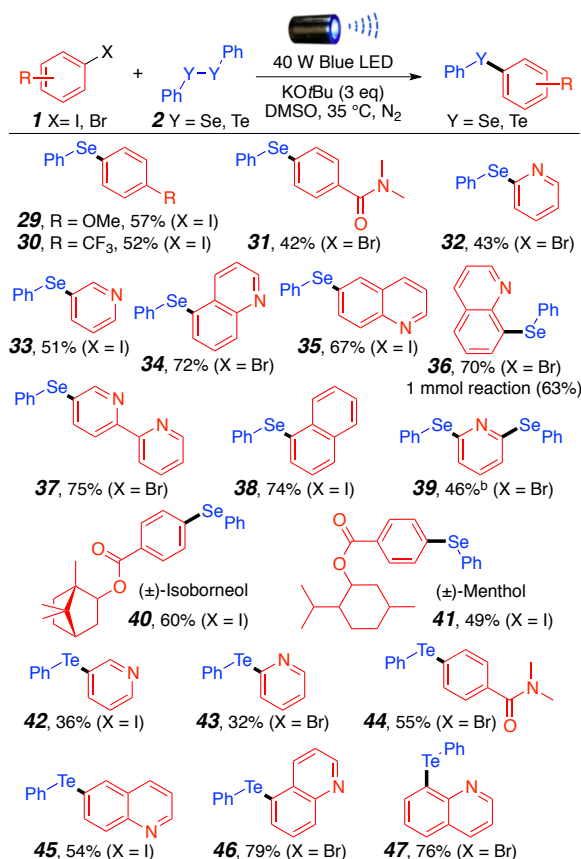


^aConditions: **1** (0.2 mmol), **2** (1.5 equiv.), KOtBu (3 equiv.), DMSO (1 mL), room temperature around reaction flask was 35 °C (heating caused by the LED lamp), under N₂, 24h. ^b**2** (3 equiv.).

Various aryl disulfides were also investigated (Scheme 2, products **15–28**). Product scope was extended to heteroaromatic moieties present on the disulfide, which complements those in the aryl halides. For example, 2,2'-dipyridyldisulfide reacted readily in good to excellent yields with both electron-rich aryl iodides (**15**, **16**) and electron-poor aryl halides (**17–19**, 73–80%) even tolerating highly electron deficient aromatic rings containing nitro (NO₂) functionalities. Having heteroaromatic moieties on both coupling partners does not negatively

affect the yield affording products **21** and **22** in 73% and 75% yields, respectively. Both electron-rich and electron-poor aromatic rings are well tolerated in the disulfide to give products **23**, **26**, and **27** (88%, 83%, and 89%). However, the presence of aniline affected product formation **24** (22%). Finally, disubstituted product **28** was generated in one step in excellent yields (91%) from 1,4-diiodobenzene, and 84% from 1-chloro-4-iodobenzene, further indicating that selected chlorinated substrates can be coupled (Scheme 2).

Scheme 3. Aryl diselenide and ditelluride scope^a



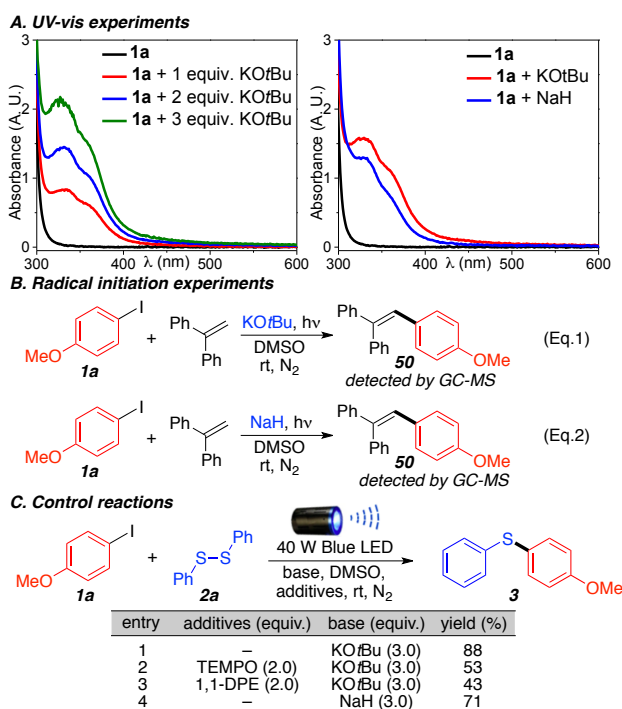
^aConditions: **1** (0.2 mmol), **2** (1.5 equiv.), KOtBu (3 equiv.), DMSO (1 mL), room temperature around reaction flask was 35 °C (heating caused by the LED lamp), under N₂, 24h. ^b**2** (3 equiv.).

Other commercially available aryl dichalcogenides (Scheme 3) were investigated. Using diphenyl diselenide, electron-rich (**29**) and electron-poor (**30**) aryl iodides were coupled in moderate (57% and 52%). Amide functionality on the *para* position was tolerated to give **31** (42%). Importantly, heteroaromatic halides also cross-coupled in moderate to good yields. Indeed 2-bromopyridine and 3-iodopyridine afforded products **32** and **33** (43% and 51%). Quinolines and bipyridines were well-tolerated affording products **34–37** in moderate to good yields, emphasizing potential application of this method to drug discovery. One-step disubstitution of 2,6-dibromopyridine also provided product **39** in moderate yield (46%). Attempting to cross-couple aryl iodides with complex ester functionalities and natural product moieties also proved to be successful, generating isoborneol (**40**) and menthol (**41**) derivatives (60% and 49%). Finally, diphenyl ditelluride was also investigated as a coupling partner and afforded desired products **42–47** (32–79%), further demonstrating that the method presented herein

works across group 16 elements. Importantly the synthesis of these diaryl tellurides tolerated heteroatoms, amide functionalities, and worked for both aryl bromides and iodides (Scheme 3).

To investigate the mechanism of this transformation we performed UV-vis spectroscopy experiments on various samples of 4-iodoanisole (**1a**) and *tert*-butoxides and NaH in DMSO (Scheme 4A, see full details in the Supporting Information S24–27). As we increased the equivalency of KOtBu in our solution of **1a** in DMSO, we observed the formation of a new peak ($\lambda_{\text{max}} = 329$ nm; shoulder: $\lambda = 360$ nm). Importantly, an identical peak was formed when KOtBu was replaced with NaH ($\lambda_{\text{max}} = 328$ nm; shoulder: $\lambda = 360$ nm) (Scheme 4A), indicating that the resulting EDA complex formed herein does not involve K⁺ or [−]OtBu. Instead, we propose that this peak results from the absorption of an EDA complex between the dimsyl anion and the aryl halide **1a**.

Scheme 4. (A) UV-vis measurements, (B) Aryl radical initiation. (C) Additional reaction screens.



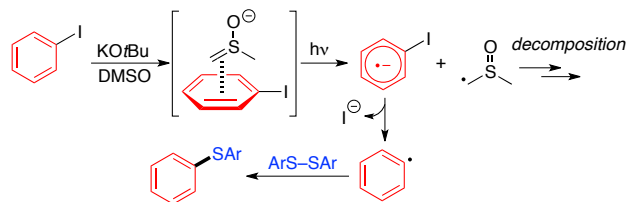
We performed additional experiments to verify that aryl halide radical initiation can take place in the absence of thiolates^{2d} or KOtBu (Scheme 4B, Eq. 1 & Eq. 2). A mixture of **1a** and KOtBu in DMSO under blue-light irradiation generates aryl radicals trapped using 1,1-diphenylethylene (1,1-DPE) to form product **50**. Replacing KOtBu by NaH under identical conditions also generated the desired aryl radicals. The use of radical quenchers, such as TEMPO and 1,1-DPE (Scheme 4C), lead to lower yields for the desired product **3**. However, using NaH as a base did not significantly affect the C–S cross-coupling reaction and afforded the desired product in 71% yield. These results further suggest that an EDA complex between dimsyl anion and aryl halide is responsible for the observed reactivity.

Finally, to support these observations, we performed time dependent-density functional theory (TD-DFT) calculations involving a π – π interaction between the dimsyl anion and the aryl halide where the shortest distance between the moieties is

3.5 Å (see Supporting Information, S28–34). Results show that the least energetic electronic transition appears at 392 nm and is responsible for the observed visible-light absorption. This transition has a charge-transfer excitation character originating from the dimsyl anion molecular orbital (MO) π_{HOMO} to the aryl halide MOs σ_{LUMO} , $\pi_{\text{LUMO}+1}$ and $\pi_{\text{LUMO}+2}$ with a 14%, 74%, and 8% contribution, respectively. Based on previous reports of KOtBu performing SET,^{11, 16} we performed various DFT calculations with analogous complexes involving [−]OtBu and aryl iodide (see supporting information S34–42). Unfortunately neither halogen-bonded intermediates nor anion– π complexes modeled in our study had charge-transfer character, further eroding a potential involvement of [−]OtBu in the SET step.

Based on the calculations and mechanistic experiments presented above, we propose that in presence of base, DMSO generates dimsyl anions capable of forming an EDA complex with the aromatic halide (Scheme 5). A charge-transfer from the dimsyl anion to the aryl halide forms aryl radical anion and dimsyl radical. Loss of iodide generates aryl radical that then couples with disulfide or thiyl radical to give the desired product. Decomposition of the dimsyl radical via reactions with *tert*-butanol, disulfide or by other processes lead to the formation of minor impurities.

Scheme 5. Proposed Mechanism



In summary, we have developed a simple and efficient visible-light-induced cross-coupling reaction between aryl halides and diaryl disulfide, diselenides, and ditellurides to form unsymmetrical chalcones without using transition-metal catalysts, a photocatalyst, or added ligands. The transformation proceeds under mild reaction conditions, exhibits good tolerance of functional groups, and can be applied to cross-couplings of heteroaromatic halides. We also have postulated a novel mechanism to account for these transformations based on control experiments, a UV-Vis spectroscopy investigation, and TD-DFT calculations. We surmise that an EDA complex between dimsyl anion and the aryl halide is formed during the reaction. Upon absorbance of visible-light, the EDA complex undergoes a charge transfer that leads to loss of halide and formation of an aryl radical. From this observation, we envision future dimsyl anion enabled cross-coupling reactions of aryl halides with different aryl radical trapping agents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written with contributions from all authors.

Notes

The authors declare no competing financial interest.

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