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Aryldiazonium salts can serve as nitrogen-based Lewis acid catalysts and their applications in the formation of photoactive charge transfer complexes

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ABSTRACT

We report the Lewis acid catalysis of aryldiazonium salts, and their Lewis acidity applications in photogeneration of aryl radicals under additive-, photocatalyst- and transition metal-free conditions. In this visible light-mediated transformation, the Lewis acidic character of aryldiazonium salts enables access to the photoactive charge transfer complex with dichalcogenides. The usefulness and versatility of this new protocol are demonstrated through the chalcogenation of a variety of aryldiazonium salts.

Aryl chalcogen-containing compounds [1–5] which are present in a wide range of pharmaceuticals, agrochemicals and functional materials have always been an inspiration for chemists to design novel strategies for their preparation [6–13]. Traditional methods of forming arylsulfides include the Stadler-Ziegler reaction, which involves the reaction of diazonium salts and thiolates [14–16]. Recently, photoinduced single electron transfer (SET) process has proven useful for the generation of aryl radicals from aryldiazonium salts [17–21]. In the context of the photosynthesis of aryl chalcogenides from aryldiazonium salts and dichalcogenides/thiols, so far photocatalysts, oxidants [22–26] or pre-activation [27,28] of aryldiazonium salts are usually required (Scheme 1A). On the other hand, the Lewis acidity of aryldiazonium salts enables to form Lewis adducts with various nucleophiles and Lewis bases (Scheme 1B) [29–31]. Given the dearth of nitrogen-based Lewis acid catalysts [32–36] and our ongoing research in main-group Lewis acid−base interaction enabled photoreactions [37,38], we set out to explore the possibility of developing Lewis acid catalysis of aryldiazonium salts, and Lewis acidity of aryldiazonium salts enabled the synthesis of aryl chalcogen-containing compounds without using photocatalysts and pre-activation (Scheme 1C). During our preparation of the manuscript, Molander and co-workers reported an interesting electron donor-acceptor (EDA) complex photoactivation strategy for the synthesis of various aryl-aryl sulfides from thianthrenium salts and (hetero)aryl thiols in the presence of potassium carbonate (Scheme 1D) [39].

We recently discovered that the diselenides can serve as good chalcogen bonding donors to interact with alkynyl sulfonium salts for the formation of charge-transfer complexes [40]. Guided by this study and our hypothesis, we began our research by investigating the N···Se interaction between aryldiazonium salts and diselenides. Firstly, the electrostatic potential surface (EPS) study of aryldiazonium salt **1** demonstrates that the electron-deficient region is located around of middle nitrogen atom (Fig. 1A). We then carried out non-covalent interaction (NCI) plot index to further analyze the N···Se complex (Fig. 1B) [41,42]. The NCI analysis indicates the attractive interaction in ^{1}**IM1** is of noncovalent nature (green surface). Congruent with this view, the binding of diphenyl diselenide **2** to **1** revealed a weak bond (3.39 Å), shorter than the sum of Van der Waals radius (3.45 Å), and a negative charge (0.04 e) is transferred from **DSe** to **1** component (Fig. 1C). In addition, the quantum theory of atoms (AIM) in molecules provides a way to study chemical bonding [43], in which the chemical bonding generally consists of bond critical points (BCPs) along with the electron density (ρ), Laplacian ($\nabla^2\rho$), and energy density (H) at BCPs. A small electron density, together with positive Laplacian and energy densities, is widely accepted as a characteristic of donor-accept interaction. For the ^{1}**IM1**, the electron density (ρ) of 0.0080 a.u. indicates incipient

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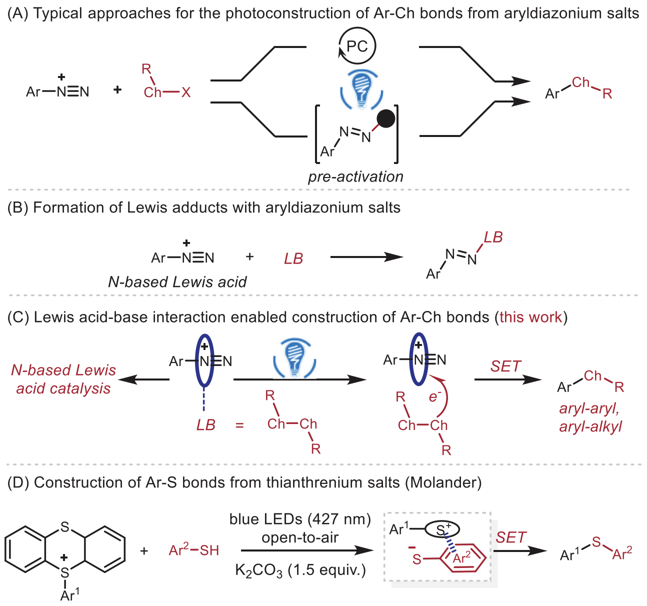


Scheme 1. Typical approaches for the photoconstruction of C–Ch bonds from aryldiazonium salts or thianthrenium salts *vs.* our approach.

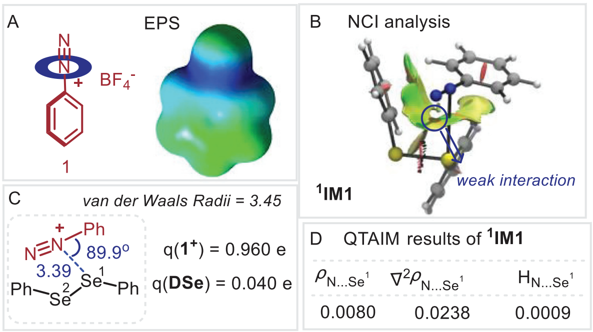


Fig. 1. Computational results.

chemical bonding in the range of noncovalent bonding between the practical boundary of a molecule ($\rho \approx 0.001$ a.u.) and covalent bonding ($\rho > 0.1$ a.u.). The positive Laplacian ($\nabla^2\rho$) of +0.0238 a.u. is also indicative of electron density donation. Moreover, the positive value of H (+0.0009) means the interaction is electrostatic dominant (Fig. 1D). All these results are consistent with the occurrence of weak bonding.

We subsequently assessed the feasibility of the proposed interaction to undergo SET process. To this end, we subjected aryldiazonium salt **1** to diphenyl diselenide **2** under blue light irradiation (12 W). To our delight, the desired product **3** was obtained in 70% yield. In the absence of light, only traces of product **3** were observed. To examine the generality of this reactivity mode. The reaction scope was subsequently conducted and the results are presented in Scheme 2A. Both electron-withdrawing (4-CO_2Me, 4-F, 4-Cl, 4-CN and 4-CF_3) and electron-donating (4-OCF_3, 4-OMe, 4-*t*Bu and 4-Me) groups on the phenyl ring of diselenides were tolerable and provided the desired products **4**–**12** in moderate to good yields. The *meta*-(3-Me, 3-OMe and 3-Cl) and *ortho*-substituents (2-Me and 2-Cl) were also effective (**13**–**17**). That was also true for the disubstituted substrates (**18**–**22**). Notably, dialkyl diselenides were also transformed to the corresponding products **23** and **24** under these conditions. Then a variety of substituted aryldiazonium salts was evaluated. As expected, substituents changing from single substitution to double or triple substitutions all worked well

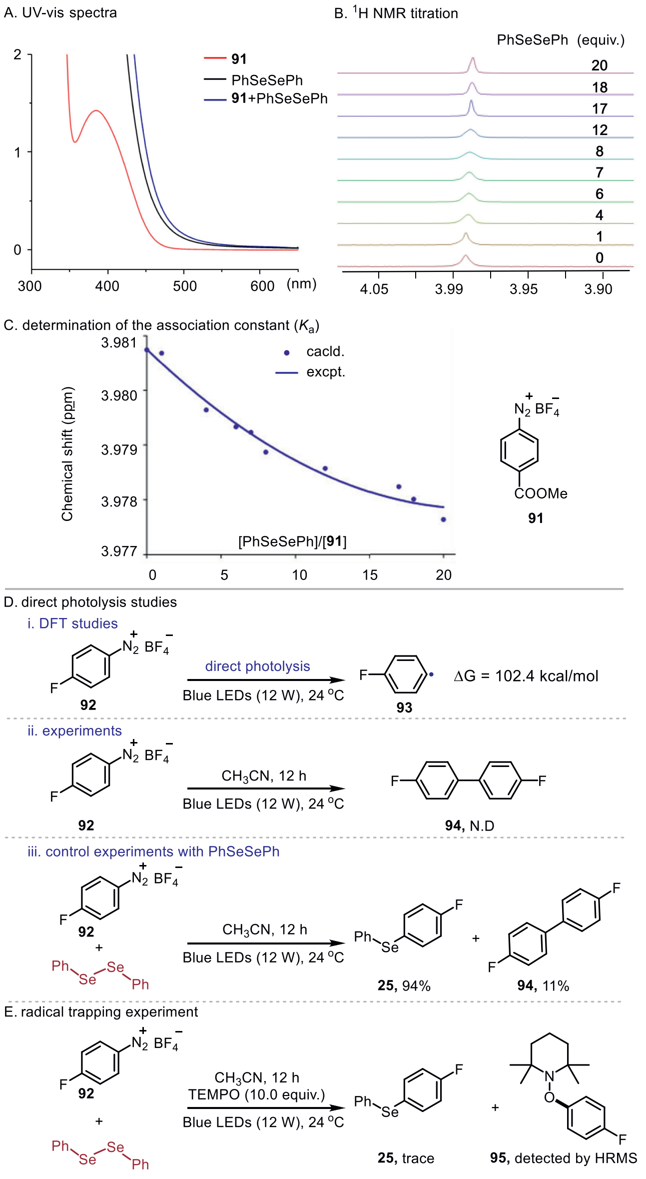
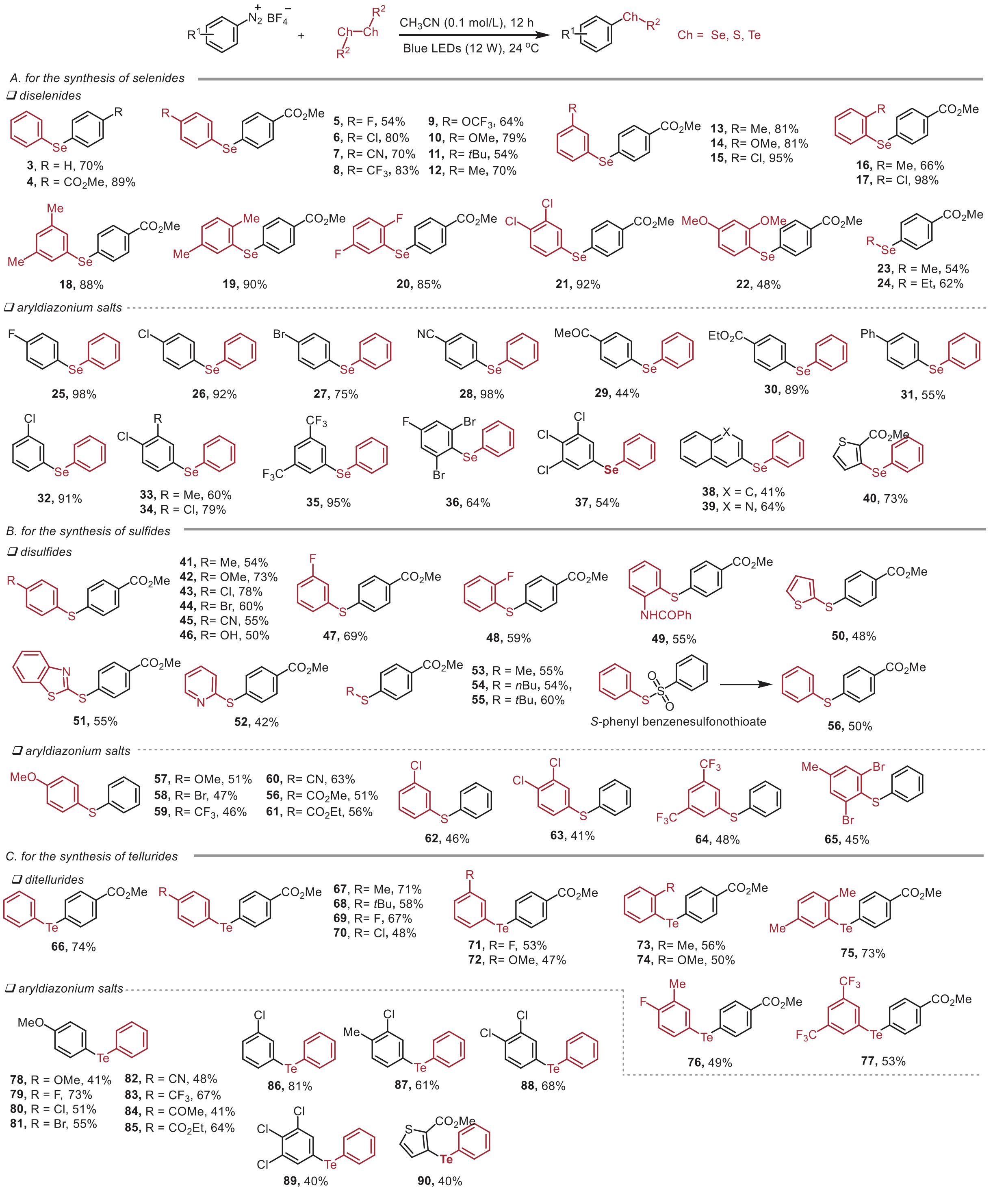


Fig. 2. Mechanistic studies.

to give the targeted molecules with satisfactory results (**25**–**37**). In addition, naphthalene-, quinoline- and thiophene-substituted diazonium salts also delivered the corresponding products **38**–**40** in 41%–73% yields.

Given the medical applications of sulfides, a convenient protocol for the synthesis of the sulfides was also achieved (Scheme 2B). The electronic properties of the substituents (4-Me, 4-OMe, 4-Cl, 4-Br, 4-CN, 4-OH, 3-F, 2-F and 2-NHCOPh) at disulfides had a limited effect on the yields (**41**–**49**). Thiophene-, benzothiazole- and pyridine-substituted disulfides proceeded smoothly to afford the desired products in moderate yields (**50**–**52**). The condition was also suitable for dialkyl disulfides (**53**–**55**). Notably, S-phenyl benzenesulfonothioate can also be employed in this methodology, affording diphenyl sulfide **56** in 50% yield. Further exploration of the reaction scope showed that various aryldiazonium salts with 4-OMe, 4-Br, 4-CF_3, 4-CN, 4-CO_2Et, 4-CO_2Me and 3-Cl substituents were suitable reaction partners (**57**–**62**). Multi-substituted disulfides were also allowed to deliver the target products (**63**–**65**).

To demonstrate the synthetic utility of this new strategy, a range of tellurides was then prepared (Scheme 2C). A series



Scheme 2. Reaction scope. Yields of isolated products are given.

of ditellurides bearing electron-donating (Me, *t*Bu and OMe) or electron-withdrawing substituents (F, Cl) at the *para*-, *meta*-, or *ortho*-positions of the benzene ring reacted smoothly and gave the desired products **66**–**74** in good yields. The reaction of disubstituted ditellurides proceeded well without apparent change in the yields (**75**–**77**). The scope of the reaction with respect to the aryldiazonium salts was also examined and different substituted substrates delivered the desired products in moderate to good yields (**78**–**90**).

To shed light on the reaction mechanism, we first carried out UV–vis experiments. Upon mixing **91** and **2**, a color change from light yellow to orange was observed, and a new absorption band appeared (Fig. 2A), indicating a weak interaction between them. In addition, ^{1}H NMR titration also suggested a weak interaction between **91** and **2**, and their association constant (*K*a) was calculated as 15.2 L/mol in CD_3CN (Figs. 2B and C). Furthermore, we conducted DFT and direct photolysis studies to determine if diazonium salts can photolyze to produce aryl radicals. The DFT studies

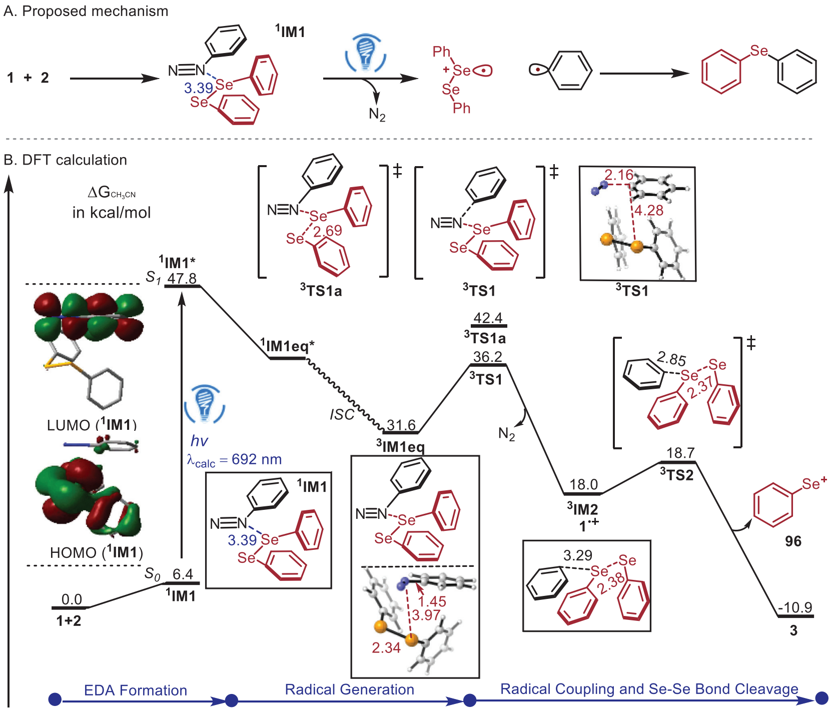


Fig. 3. Computational results.

showed that a minimum of 102.4 kcal/mol of energy is required for **92** to undergo C–N bond homolysis to produce aryl radical. In addition, the calculated maximum absorption wavelength of **92** is 315 nm. In agreement with this view, direct photolysis of aryldiazonium salt **92** does not lead to dimerization product **94**, however, dimerization product **94** is obtained in 11% yield in the presence of diselenide (Fig. 2D). Based on these results, it was unlikely that diazonium salts would undergo direct photolysis in this system. Additionally, the radical trapping reaction indicated that an aryl radical had been generated (Fig. 2E). These control experiments revealed that aryl radicals were generated by a weak interaction between diselenides and aryldiazonium salts.

Next, we carried out density functional theory time-dependent DFT (TDDFT) calculations (see Supporting information for computational details) to obtain the reaction pathway using the reaction of **1** with **2** as a representative (Fig. 3). **IM1** was predicted to have a maximum absorption wavelength of 695 nm. Thus, irradiation of visible light excites the ground-state **IM1** to the first singlet excited state **^{1}IM1***. The examination of HOMO and LUMO of **IM1** indicates that the excitation results in the single-electron transfer (SET) from Se to N. Then **^{1}IM1*** relaxes to an equilibrium structure **^{1}IM1eq*** in the first excited state. Alternatively, **^{1}IM1eq*** may convert to the triplet **^{3}IM1eq** via an intersystem crossing. Subsequently, the C–N bond cleavage of **^{3}IM1eq** *via* **^{3}TS1** with a low barrier of 4.6 kcal/mol gives phenyl radical **^{3}IM2** and $\mathbf{1}^{\bullet+}$ ($PhSeSePh^{\bullet+}$), which is more favorable than Se-Se bond cleavage (**^{3}TS1a**). The resultant radical **^{3}IM2** attacks $\mathbf{1}^{\bullet+}$ (**^{2}TS2**) with a barrier of 0.7 kcal/mol, generating positive ion **96**$^{+}$ and affording product **3**. The intermediate **96**$^{+}$ may react with CH_3CN to convert into the by-product.

Inspired by the above studies, aryldiazonium salt **91** was investigated as a potential Lewis acid catalyst for the bromination of anisole [44] with NBS by using catalyst loadings of 40 mol% (Fig. 4A). After two hours at room temperature, 87% yield of **97** was observed. Similar reactivity was also observed for the bromolactonization of unsaturated carboxylic acid [44] with NBS, affording the desired product **98** in 86% yield within 2 h (Fig. 4B). In addition, the reaction of quinoline with a Hantzsch ester [45] yielded the transfer hydrogenation product **99** in 40% yield (Fig. 4C). For nitro-Michael addition reaction [46], a catalyst loading of 20 mol% led to the corresponding product **100** in 75% yield (Fig. 4D).

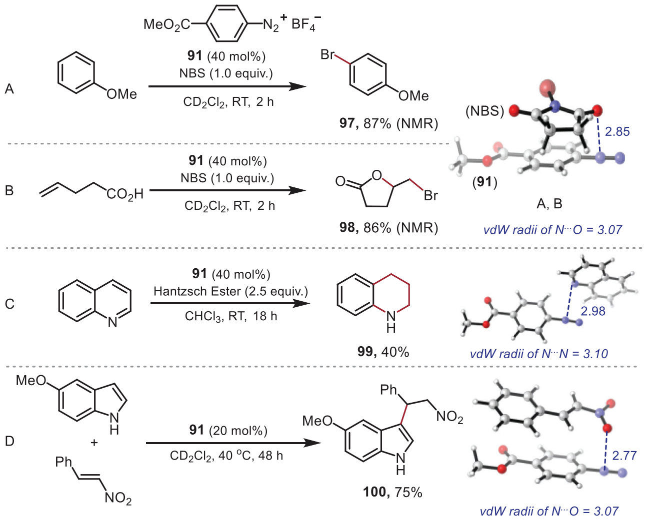


Fig. 4. Reactivity investigations using aryldiazonium salt as Lewis acid catalyst.

In conclusion, various aryl chalcogen-containing compounds can be easily obtained under photoinduced simple and additive-free conditions from aryldiazonium salts and dichalcogenides. In addition, we have extended the nitrogen-containing Lewis acid catalyst club by exploration of the performance of aryldiazonium salts for four benchmark catalytic reactions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.107821.

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