Advanced Synthesis & Catalysis

Accepted Article

Title: 2-Azaallyl anions as light-tunable super-electron-donors: coupling with aryl fluorides, chlorides, and bromides

Authors: Qianmei Wang, Michal Poznik, Minyan Li, Patrick J. Walsh, and Jason Chruma

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800396

Link to VoR: http://dx.doi.org/10.1002/adsc.201800396

10.1002/adsc.201800396

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

2-Azaallyl anions as light-tunable super-electron-donors: coupling with aryl fluorides, chlorides, and bromides

Qianmei Wang[a], Michal Poznik[b]*, Minyan Li,[b] Patrick J. Walsh,[b] Jason J. Chruma[a]*

[a] Key Laboratory of Green Chemistry & Technology, College of Chemistry and Sino-British Materials Research Institute, College of Physical Science & Technology, Sichuan University, Chengdu, Sichuan 610064, P. R. China, E-mail: poznik@scu.edu.cn; chruma@scu.edu.cn

[b] Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States.

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. Herein, we present 2-azaallyl anions as colored super-electron-donors capable of reducing a collection of aryl halides via a single electron transfer and coupling with the corresponding radicals to forge new C-C bonds. This offers a robust approach for the arylation of 2-azaallyls. Mechanistic studies demonstrate that the reactions proceed via either a radical pathway for aryl bromides and chlorides or a S_NAr mechanism for activated aryl fluorides. Moreover, we demonstrate that irradiation of the colored 2-azaallyl anions with visible light can further extend their reducing power, enabling radical-mediated coupling with otherwise unreactive electron-rich aryl halides. Isolated yields up to 94% are obtained and the overall relevance and utility is demonstrated by the derivatization of both a known pharmaceutical agent and a popular fluorophore.

Keywords: electron transfer; 2-azaallyl; organic reductants; photochemistry; visible light

Introduction

The formation of C–C bonds is arguably one of the most desired transformations in synthetic organic chemistry. Very recently, there has been a substantial thrust to identify unique transition-metal-free strategies for forging C-C bonds.[1] One such popular approach involves utilizing radicals as active intermediates.[2] An advantage of this tactic is that it readily allows for coupling to C(sp^3) centers. Several strategies for generating and recombining C-centered radicals have been reported, with light-initiated processes receiving growing attention.[3] In such processes, single-electron transfer (SET) to or from an excited state catalyst is frequently employed to generate a radical species, which then undergoes further transformations.[3c, 4] The redox potential of these photocatalysts is, therefore, one of the key features regarding their potencies. An alternative approach for the generation of radical species is to use organic compounds, termed super-electron-donors (SEDs), which are capable of directly performing SET. The redox potentials for known neutral SEDs can be as low as -1.5 V (vs. SCE).[5] Another photochemical approach for reducing aryl halides to aryl radicals is via visible light irradiation of electron donor-acceptor (EDA) complexes.[6]

As part of a larger research program focused on the generation and functionalization of 2-azaallyl anions,[7] it was recently discovered that these anionic species can couple with vinyl bromides under transition-metal-free conditions (Figure 1a).[7h] Computational studies and EPR measurements suggested the presence of radical species, possibly 2-azaallyl radicals, in the reaction. The intermediacy of 2-azaallyl radicals was confirmed in later studies where 2-azaallyl anions acted as SEDs to reduce and couple with aryl iodides and alkyl iodides/bromides (Figure 1b).[8] The resulting diarylmethylamine derivatives are of importance to the pharmaceutical industry.[9].

In this work, we build on the concept of 2-azaallyl anions as SEDs in the absence of added transition-metals for their coupling with a collection of previously unreactive electron-deficient aryl bromides, chlorides, and fluorides (Figure 1c). Most significantly, we capitalize on an often overlooked feature of 2-azaallyl anions, their beautiful deep reddish-purple color, which opens the door to excited state reactivity mediated by visible light. Specifically, we discovered that photoexcitation of 2-azaallyl anions using green or blue LEDs enhanced their reactivity sufficiently to perform reductive C–C couplings with otherwise unreactive electron-rich aryl bromides and chlorides. Mechanistic investigations strongly suggest that 2-azaallyl anions are indeed capable of performing SET with aryl halides to create transient aryl radicals, which can then react with the resultant 2-azaallyl radicals.[10] A slightly different

radical pathway ($S_{RN}1$) cannot be ruled out at this time for electron-deficient aryl bromides/chlorides. Activated aryl fluorides, on the other hand, follow the classic S_NAr mechanism. Overall, these studies make evident that 2-azaallyl anions are powerful SEDs with very high and light-tunable redox potentials capable of reducing most aryl bromides and chlorides to the corresponding aryl radicals. These results mandate reconsideration of mechanistic proposals involving 2-azaallyl intermediates in nucleophilic cross couplings reported over the past century.[7e, 11]

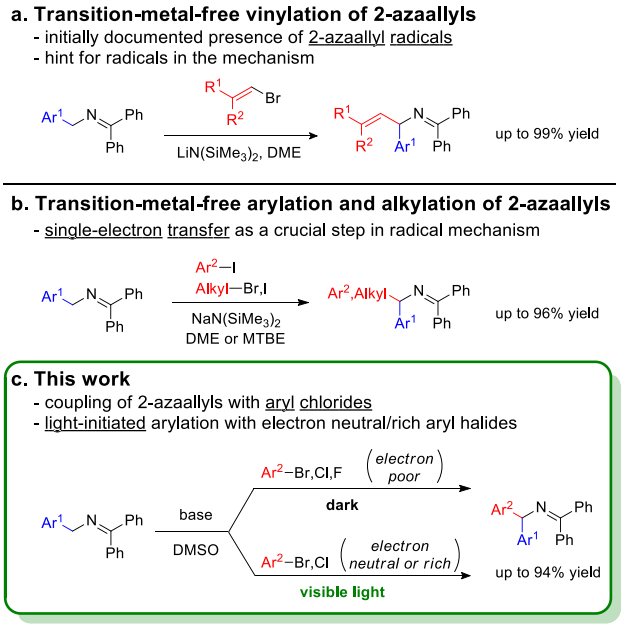

Figure 1. Previous research on 2-azaallyl radicals, their reactivity, and scope of this work.[7h-8]

Results and discussion

Non-irradiated reactions

Previous attempts to couple 2-azaallyl anions with various aryl bromides and chlorides required the use of either a palladium or nickel catalyst to achieve acceptable yields.[7f-7j, 12] Under these reaction conditions, electron-rich aryl halides tend to outperform their electron-deficient counterparts. In considering a radical pathway for the coupling without added transition-metals,[11] however, the redox potential of the aryl halide is paramount and should favor electron-deficient substrates. Accordingly, we focused on *p*-chloroacetophenone (**2a**) as a plausible substrate. Examination of the palladium-free coupling between the lithiated anion of **1a** and electron-poor aryl chloride **2a** in THF showed no reaction. Since it is known that solvent polarity can have a drastic effect on the reactivity of radical reactions,[13] we screened several solvents and found that switching to DMSO resulted in the formation of **3aa** (13%, see *Supporting Information* for complete optimization studies). Further optimization of the reaction conditions showed that use of NaH (1.5 equiv) as base and a 3:1 ratio of ketimine **1a** to aryl chloride **2a** in the absence of exogenous light provided the highest isolated yield of **3aa** (82%). With these conditions in hand, we tested the substrate scope with a collection of electron-poor aryl bromides, chlorides, and fluorides (**2a–d**, **2b'–c'**, **2b"–d"**, Figure 2) and obtained yields for the corresponding arylated products **3** ranging from 34% to 89%. The optimal base for the coupling reaction proved to be substrate specific. For example, using $LiN(SiMe_3)_2$ (2.5 equiv) as base afforded a near doubling in the resulting yields for aryl chlorides **2d** (34% → 61%) and **2c** (46% → 91%), as well as aryl bromide **2c"** (56% → 94%). Importantly, the new C-C bond formed exclusively at the formerly halogenated positions on the aromatic substrates despite the presence of potentially competitive electrophilic functional groups such as ketones (**2a**), aldehydes (**2b**, **2b'**, and **2b"**), nitriles (**2c**, **2c'**, and **2c"**), and esters (**2d**, **2d"**).

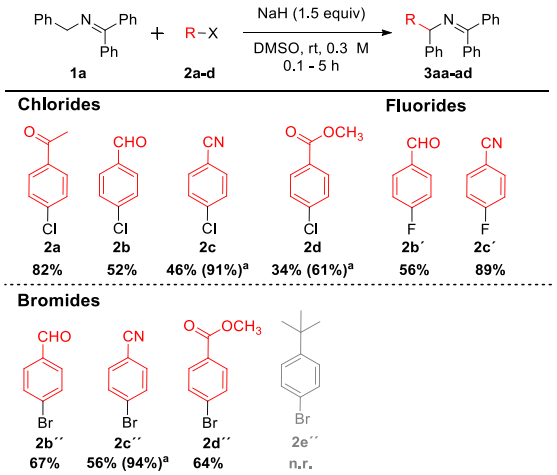

Figure 2. Substrate scope for the arylation of the 2-azaallyl anion from **1a** with electron-poor aryl halides **in the dark** (0.3 mmol ketimine, 0.1 mmol aryl halide, 1 mL DMSO, 0.15 mmol NaH). [a] 0.25 mmol $LiN(SiMe_3)_2$ used as a base instead of 0.15 mmol NaH.

Irradiated reactions

As shown in Figure 2, attempts to use these reaction conditions to couple **1a** with the relatively electron-rich 4-(*tert*-butyl)bromobenzene **2e''** failed to afford product **3ae**. Given our previous success in coupling 2-azaallyl anions with aryl iodides, this lack of reactivity may indicate that the reducing power of the anion of **1a** is not sufficient to undergo SET with aryl bromide **2e"**. Accordingly, increasing the reducing power of the 2-azaallyl anion SED should allow for coupling with less reactive aryl halides. Given that the 2-azaallyl anion generated by deprotonation of **1a** is deeply colored (reddish-purple), we reasoned that photoexcitation of this anionic intermediate with visible light should result in a more reactive excited state species. Indeed when **1a** was deprotonated with

$LiN(SiMe_3)_2$ in the presence of **2e''** and irradiated with blue LEDs for 4 h, 18% of the arylated product **3ae** was observed (see *Supporting Information*). Further optimization of these photo-irradiated reaction conditions revealed that using ketimine **1a** as the limiting reagent (with up to 10 equiv of the aryl halide) and *n*-butyl lithium (*n*-BuLi, 2 equiv; deprotonation likely takes place via the anion of DMSO) as base resulted in both the highest yield and shortest reaction time (see *Supporting Information* for complete optimization studies). If necessary, the amount of aryl halide can be scaled down to 2 equiv. resulting in only a 10% decrease in yield (see *Supporting Information*, Figure S5). Moreover, irradiation with lower-energy green LEDs resulted in similar yields but was preferred for its milder character. In contrast to the non-irradiated couplings with activated aryl halides (Figure 2), photo irradiated coupling between **1a** and 4-(*tert*-butyl)bromobenzene (**2e"**) produced a small amount of the regioisomeric product **4ae** in addition to diarylmethylimine **3ae** (**3ae**:**4ae,** 4:1, Figure 3).[10] These conditions were successfully applied to an array of aryl bromides (**2e''–k''**) and aryl chlorides (**2f,g,i**) to afford the resulting arylated products, as a mixture of regioisomers (Figure 3). This mixture can be separated by column chromatography. Combined yields tended to be modest and decreased as the electron density of the aryl halides increased. For example, electron-neutral substrates bromobenzene (**2f"**) and chlorobenzene (**2f**) coupled with the anion of **1a** upon irradiation with green light to afford a 4:1 mixture of **3af** and **4af** in 58% or 52% combined yield, respectively.

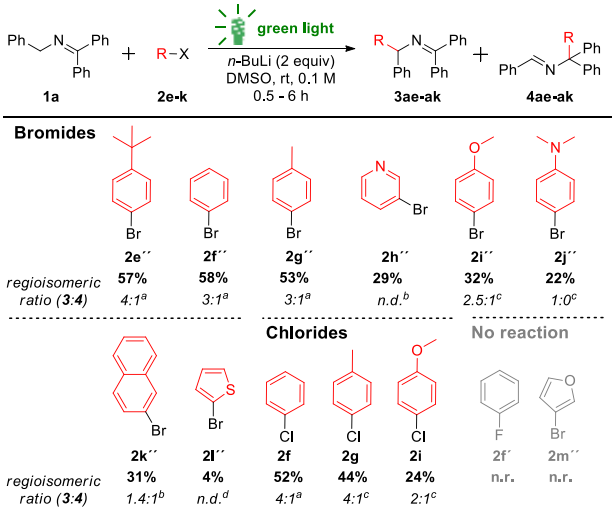

Figure 3. Substrate scope for the transition-metal-free arylation of the 2-azaallyl anion from **1a** with aryl halides **in the presence of green light** (0.2 mmol **1a**, 2 mmol aryl halide, 2 mL DMSO, 0.4 mmol *n*-BuLi).[a] Determined via ^{1}H NMR analysis, [b] Isolated yield refers to **3ah** only; **4ah** decomposed during purification, [c] Determined after isolation via column chromatography, [d] Isolated yield refers to **3al** only; **4al** was not isolated.

Coupling with the electron-rich *p*-haloanisoles **2i"** and **2i**, on the other hand, produced a roughly 2:1 mixture of **3ai** and **4ai** in 32% or 24% combined yield. 2-Bromoaniline **2j"** was unreactive. In all cases, the aryl bromides afforded higher yields of the coupled products in comparison to the analogous aryl chlorides. *S*-Heterocycle 2-bromothiophene **2l''** exhibited reactivity (quick discoloration of the reaction mixture when irradiated), but afforded only very low amounts of product **3al** (4%). Under both of our reaction conditions (dark or irradiated), neither bromofurane **2m"** nor fluorobenzene **2f'** coupled with **1a**. Nevertheless, access to such a broad substrate scope of electron-poor aryl halides under non-irradiated conditions (**2a-d**, **2b',c'**, **2b"-d"**, Figure 2) and electron-neutral/rich aryl bromides and chlorides under irradiated conditions (**2f,g,i**, **2e''-k''**, Figure 3) is of great importance and unprecedented for transition-metal-free radical-mediated C-C cross couplings.

Different 2-azaallyls

In order to further explore the scope of this method, we prepared three aldimines, which upon deprotonation generated similarly colored 2-azaallyls (Figure 4). We selected these substrates for their variable electron density, from the electron-donating methoxy group in **1b** to the electron-withdrawing cyano substituent in **1d**. It is possible that electron density could have an effect on the reducing power of the 2-azaallyl anion. Moreover, in order to test the robustness of the method and provide a strategy for the introduction of heterocycles, the thiophene derivative **1c** was also prepared. So as to focus our attention on electronic factors, we only examined 1,1,3-tris-arylated 2-azaallyl anions with relatively similar pK_a values and steric constraints. Alkyl aldimines are not appropriate for this strategy as they preferentially form 1-azaallyl anions (enaminates) under our reaction conditions.[14]

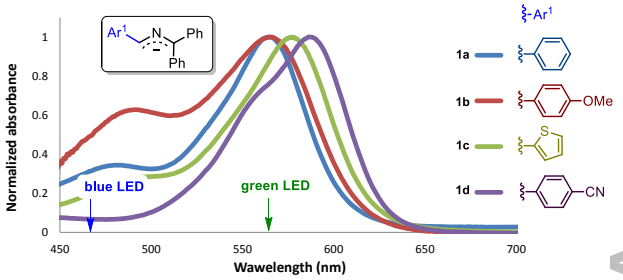

Figure 4. Normalized UV-Vis spectra of 2-azaallyl anions.

In coupling these three aldimines (**1b**–**d**), individually, with 4-chlorobenzonitrile **2c** in the absence of light, we observed very similar reactivity (albeit with lower isolated yields, 29–65%, Figure 5) to that which we observed with the 2-azaallyl anion generated from ketimine **1a** (91%). Arylation of these 2-azaallyl anions with bromobenzene (**2f''**) took place *only in*

10.1002/adsc.201800396

the presence of visible light. This approach proved to be much better for the preparation of heterocycle-containing derivatives like **3al**. In the case of *p*-cyanobenzaldimine **1d**, only a trace amount of product **3df** was observed (<7%) under green light irradiation, but a 2:1 mixture of regioisomers **3df** and **4df** was obtained in 63% combined yield upon using blue light. Very similar reactivity was recorded between the anion of **1d** with chlorobenzene (**2f´**). The similar reactivity patterns make evident that slight electronic modifications to the 2-azaallyl anion framework do not afford significant differences in the resulting redox potential. The only noticeable difference is that the electron poor cyano derivative **1d** required the use of higher energy blue light to couple with halobenzenes **2f"** and **2f**.

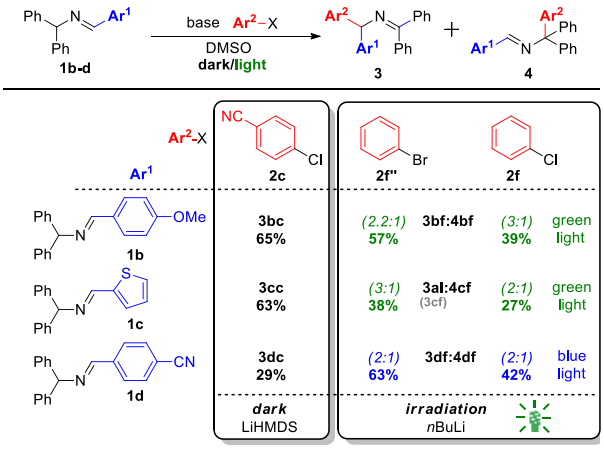

Figure 5. Isolated yields and regioselectivities for the arylation of 2-azaallyl anions generated from aldimines **1b-d**.

Application

To explore the overall utility, we first applied the coupling of 2-azaallyl anions with activated aryl halides to the modification of fenofibrate, a drug used to manage high cholesterol levels. All four 2-azaallyl anions generated from imines **1a–d** successfully coupled with fenofibrate in the absence of light to afford the modified compounds (**5**, **6**, **7**, and **8**, respectively) in moderate to good yields (38%-64%, Figure 6). Moreover, the benzophenone imine moiety in derivative **5** was successfully hydrolyzed to obtain free amine **9** in 85% isolated yield. The method was also successfully used to modify the important bromonaphthaleneimide chromophore **10**[15] in high yield (>80%) at both microgram and a gram scale. Hydrolysis of the resulting imine **11** proceeded smoothly to obtain amine **12** (59% yield), allowing for further derivatization or linkage of the chromophore to other scaffolds.

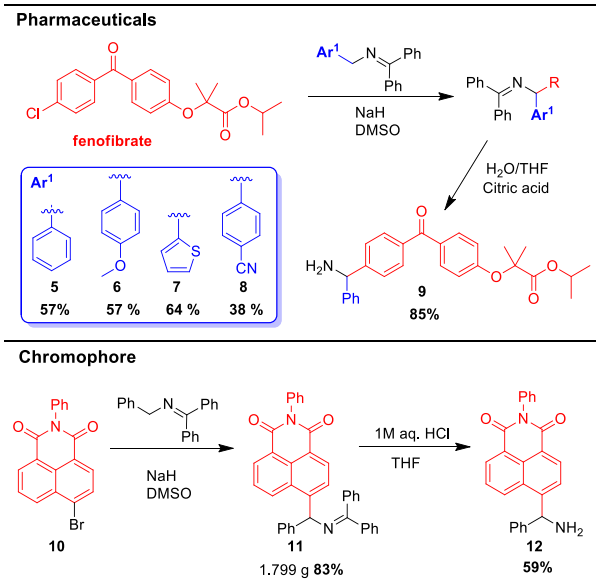

Figure 6. Modification of the marketed drug fenofibrate and chromophore **10** under non-irradiated conditions.

Mechanistic studies

In our previous studies with electron-neutral/rich aryl iodides, we proposed that the 2-azaallyl anion intermediates act as SEDs to perform SET with the organohalides.[8] In those studies, we noted that mixtures of regioisomers, e.g **3** and **4**, were formed unless steric factors, such as substituents *ortho* to the iodide leaving group, dictated otherwise. Under the photo-irradiated reaction conditions for the coupling of excited-state 2-azaallyls with electron-rich aryl bromides and chlorides reported herein, we observed essentially identical regioselectivities (**3**:**4**) as observed for the non-irradiated couplings with the corresponding aryl iodides. Accordingly, we propose a similar reaction mechanism for these transformations. Namely, direct coupling between the aryl radical generated after ejection of the halide and the relatively persistent 2-azaallyl radical formed in the initial SET event (Figure 7, top). It should be emphasized that the observed regioselectivities using electron neutral/rich aryl halides are dependent on only the nature of the 2-azaallyl framework and not the particular halide employed.

The non-irradiated couplings between 2-azaallyls and electron-deficient aryl halides are unique in that arylation only occurs at the less substituted carbon of the 2-azaallyl framework, leading to the exclusive formation of regioisomer **3**. This dramatic difference in observed regioselectivity may indicate, but does not necessitate, that the transformations proceed via a different reaction mechanism (Figure 7, bottom). SET between the 2-azaallyl anion SED and activated aryl halide still would form a 2-azaallyl radical and, after ejection of the halide, an aryl radical. In this circumstance, however, the electron-withdrawing group (EWG) on the aromatic ring could stabilize the aryl radical intermediate. Such increased stability

10.1002/adsc.201800396

could lead to better regioselectivity in the direct coupling with the 2-azaallyl radical. Alternatively, as depicted in Figure 7 (bottom), the relatively persistent aryl radical could couple with the more abundant 2-azaallyl anion species via an $S_{RN}1$ pathway. Reduction of the resultant radical anion either by SET with another equivalent of aryl halide (*shown*) or the 2-azaallyl radical (*not shown*) would afford the observed product **3**. Prior mechanistic studies using Bunnett and Crearys' 1,4-dihalobenzenes[7, 15] did not support a $S_{RN}1$ mechanism, but such a pathway cannot be ruled out at this time for the coupling of 2-azaallyls with electron-deficient aryl halides.

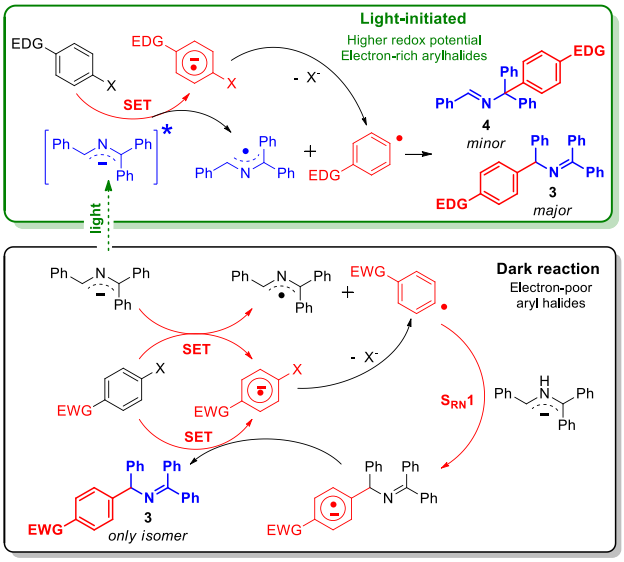

Figure 7. Potential mechanisms for the arylation of 2-azaallyl anions using either electron-rich aryl halides with visible light (top) or electron-deficient aryl halides in the dark (bottom).

To further explore the reaction mechanisms, we performed several experiments. Ketimine **1a** successfully coupled with 2,6-dimethylbromobenzene (**2n**) upon irradiation of the reaction mixture with green light to afford the product **3an** in 32% yield, thus excluding benzyne intermediates (Figure 8a). Additionally, the coupling between the 2-azaallyl anions and aryl halides in the light or in the dark occurred exclusively at the aromatic carbon where the halogen atom was originally located. In a separate experiment, we carefully analyzed the coupling between **1a** and 4-*tert*-butylbromobenzene (**2a**) by GC-MS and detected the presence of several byproducts that most likely arise by radical-radical coupling (dimer **13**) or hydrogen atom transfer (HAT, *tert*-butylbenzene, Figure 8b). It should be noted that dimer **13** was typically the major side product (up to 50% as a 1.5:1 mixture of *meso* and *rac* diastereomers) in all of the coupling reactions involving ketimine **1a** throughout both these and our previous studies.[8] Another potential mechanism for the arylation of 2-azaallyl anions with electron-poor aryl halides in the absence of added transition-metals is S_NAr. To test this possibility, we synthesized two radical-clock probes, aryl chloride **14** and fluoride **15** (Figure 8c). SET to generate an aryl radical will result in rapid cyclization with the pendant allyl moiety prior to any intermolecular couplings. In the case of chloride **14** with ketimine **1a**, use of either NaH or $LiN(SiMe_3)_2$ as base resulted in a diastereomeric mixture (dr = 1.1:1, see *Supporting Information*) of cyclized products (**16**) in 68% yield. This result provides concrete evidence that electron-poor aryl chlorides (and most likely aryl bromides) couple with 2-azaallyl anions via a radical mechanism.[8] Such a result is remarkable and would not have been predicted prior to our identification of 2-azaallyl anions as SEDs. The reaction between the fluorinated derivative **15** and the 2-azaallyl anion derived from **1a** afforded the non-cyclized S_NAr product **17** in 63% yield. This result was not surprising given the difficulty in reducing unactivated aryl fluorides,[16] which also explains the lack of reactivity for fluorobenzene (**2d"**, Figure 3). Compounds **3an** and **16** also serve as evidence that this arylation strategy can be used for more substituted aryl halides.

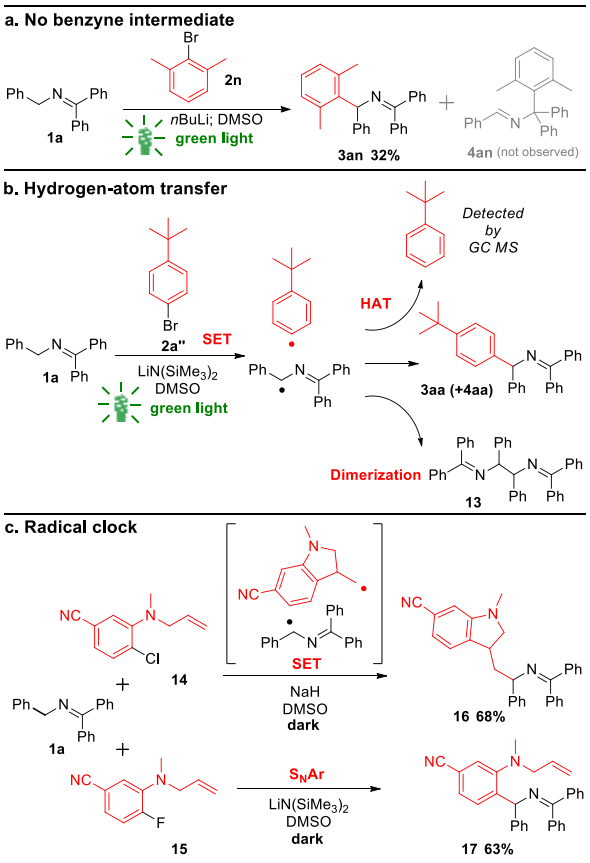

Figure 8. Selection of mechanistic studies that support a radical pathway for aryl chlorides and bromides with and without light.

Redox potential estimates

Given that the first step in the proposed mechanism for the reaction of the ground state and excited state

2-azaallyl anions with the aryl halide is SET, estimation of the redox potentials of these species is of paramount importance. Our previous efforts to measure the redox potential of this anion by cyclic voltammetry failed due to the rapid dimerization of the 2-azaallyl radical upon formation. A rough estimate for the reducing power of the 2-azaallyl anion derived from **1a** can be made by comparison with the known redox potentials of the aryl halide substrates (Figure 9). The resulting estimated values are illustrative of the remarkable potentials as single-electron reducing agents. As seen in Figure 9, there is a clear difference in reducing ability between the ground-state anion and its photo-excited counterpart. Based on reactivity studies, the ground state 2-azaallyl anion can be estimated at –2.1 V; most aryl halide substrates with redox potentials below this value will not couple to the 2-azaallyl anion from **1a** in the dark. It is worth mentioning that the reported redox potentials of compounds like chlorobenzene (**2f**, –2.61 V) and 4-chloroanisole (**2i**, –2.77 V) are significant and out-of-reach for a majority of other reported organic or organometallic photocatalysts, hence forming radicals from them is a very challenging task.[17] Such unprecedented reactivity demonstrates that the visible light photo-excited states of 2-azaallyl anions indeed have exceptionally strong reducing capabilities, with redox potentials around –2.8 V! As seen for modified 2-azaallyls prepared from compounds **1b-d**, the reactivity is similar to **1a** and none of the compounds require light to react with 4-chlorocyanobenzonitrile **2c**. Moreover, none of these 2-azaallyl anions can reduce bromobenzene **2f''** in the dark. Overall, this shows that electronic variations in the parent 2-azaallyl anion framework do not drastically impact the resulting redox potentials.

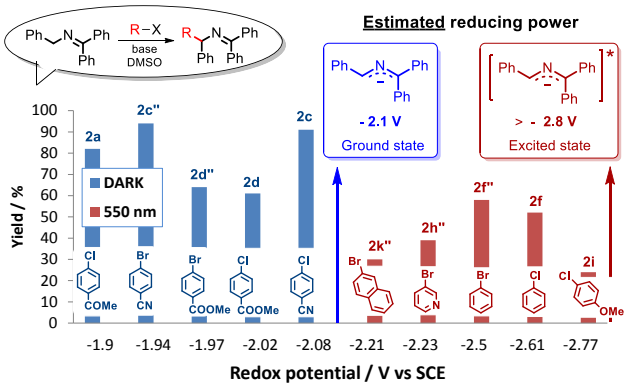

Figure 9. Reducing power of a 2-azaallyl anion (from **1a**) in ground (**blue**) and excited states (**red**) as estimated from a correlation of its yields depending on the redox potentials (*vs* SCE) of the aryl halide substrates.[18]

Conclusions

In conclusion, we present a new feature of 2-azaallyl anions, namely that they are light-tunable SEDs with remarkable reducing potentials capable of forming aryl radicals from even electron-rich aryl chlorides when irradiated with visible light. To the best of our knowledge, this is the first example of a photochemical transformation of 2-azaallyl anions using visible light. Even in the dark, however, the radical-mediated coupling between (ground state) 2-azaallyl anions and electron-poor aryl halides offers a robust and high-yielding method for the construction of pharmaceutically-relevant diarylmethylamine derivatives. We hope that these findings provide not only a valuable synthetic to1bol but, more importantly, a possible template for designing other SEDs and organic dyes with high redox potentials. Investigations in these directions are currently underway.

Experimental Section

Preparation of ketimine 1a and aldimines 1b–d

N-(Diphenylmethylene)-1-phenylmethanamine ***(1a)***

Prepared by a modification of published procedures.[19] A flame-dried round-bottom flask equipped with a stir bar was charged with benzophenone imine (5.2 mL, 31 mmol), dichloromethane (12.5 mL), and benzylamine (3.4 mL, 31 mmol) and the resulting reaction mixture was stirred at 25°C for 16 h. The solvent was evaporated under reduced pressure. The resulting residue was then crystalized from EtOAc/hexanes to provide ketimine **1a** as a white solid (6.308 g, 75%). The NMR spectra matched previously published data.[20]

N-(4-Methoxybenzylidene)-1,1-diphenylmethanamine ***(1b)***

A flame-dried round-bottom flask equipped with a stir bar was charged with *p*-methoxybenzaldehyde (688 mg, 5 mmol), followed by addition of diphenylmethanamine (1 mL, 5.5 mmol) via syringe. The resulting mixture was then stirred at 65 ºC for 4 h under vacuum and the produced solid was recrystallized from EtOAc/hexanes to afford aldimine **1b** as a white solid (1.145 g, 76%). The NMR spectra matched previously published data.[21]

1,1-Diphenyl-N-(thiophen-2-ylmethylene)methanamine ***(1c)***

A flame-dried round-bottom flask equipped with a stir bar was charged with 2-thiophenaldehyde (1 mL, 10.7 mmol), followed by addition of diphenylmethanamine (2 mL, 11.8 mmol) via syringe. The resulting mixture was then stirred at 65 ºC for 5 h under vacuum and the produced solid was recrystallized from EtOAc/hexanes to afford **1c** as a white solid (2.553 g, 86%). The NMR spectra matched the previously published data.[22]

4-((Benzhydrylimino)methyl)benzonitrile ***(1d)***

A flame-dried round-bottom flask equipped with a stir bar was charged with 4-cyanobenzaldehyde (2.360 g, 18 mmol), followed by addition of diphenylmethanamine (3.4 mL, 19.8 mmol) via syringe. The resulting mixture was then stirred at 65 °C for 4 h under vacuum and the produced solid was recrystallized from EtOAc/hexane to provide aldimine **1d** as a white solid (4.268 g, 80%). The NMR spectra matched the previously published data.[23]

General procedures for arylation

Procedure A: Arylation using electron-poor aryl halides (dark reaction conditions)

A flame-dried vial charged with a stir bar and ketimine/aldimine **1** (0.3 mmol) was left under reduced pressure for 30 min, then, after refilling the vial with argon, aryl halide (0.1 mmol) was introduced. The vial was then further degassed with three consecutive vacuum/argon-fill cycles, after which NaH (6 mg, 60% dispersion in mineral oil, 0.15 mmol) was added in a glove-box. Dry DMSO (1 mL) then was added under argon via syringe through the rubber septum (the reaction mixture slowly turned dark purple/blue). The reaction mixture was stirred at room temperature (20-25 °C) in the dark (covered with a thick cardboard box). Progress was monitored by TLC until reaction completion. The vial was then opened to air, poured into a half-saturated aqueous solution of NH_4Cl (8 mL), extracted with EtOAc (4 × 2 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography using the indicated eluent.

Procedure A': Arylation using electron-poor aryl halides (dark reaction conditions)

A flame-dried vial charged with a stir bar and ketimine/aldimine **1** (0.3 mmol) was left under reduced pressure for 30 min, then, after refilling the vial with argon, aryl halide (0.1 mmol) was introduced. The vial was then further degassed with three consecutive vacuum/argon-fill cycles. Dry DMSO (1 mL) was added under argon via syringe through the rubber septum followed by a solution of $LiN(SiMe_3)_2$ in THF (0.25 mL, 1M, 0.25 mmol); the reaction quickly turned dark purple/blue. The reaction mixture was stirred at room temperature (20-25 °C) in the dark (covered with a thick cardboard box). Progress was monitored by TLC until reaction completion. The vial was then opened to air, poured into a half-saturated aqueous solution of NH_4Cl (8 mL), extracted with EtOAc (4 × 2 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography using the indicated eluent.

Procedure B: Arylation using electron-rich aryl halides (photochemical conditions)

A flame-dried vial charged with a stir bar and ketimine/aldimine **1** (0.2 mmol) was left under reduced pressure for 30 min, then, after refilling the vial with argon, aryl halide (2 mmol) was introduced. Dry DMSO (2 mL) then was added under argon via syringe through the rubber septum. The reaction mixture was degassed with three consecutive vacuum/argon-fill cycles, followed by addition of a solution of *n*-BuLi (1.6 M, 0.25 mL, 0.4 mmol). The resulting dark purple/blue solution was irradiated with green LED light while stirring at room temperature (20-25 °C). Reaction completion was determined to occur when the dark color disappeared and the reaction turned yellow/green. The vial was then opened to air, poured into a half-saturated aqueous solution of NH_4Cl (8 mL), extracted with EtOAc (4 × 2 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using the indicated eluent.

Arylations in dark

*1-(4-(((Diphenylmethylene)amino)(phenyl)methyl)phenyl)ethanone (**3aa**)*

The reaction was performed following general procedure A using ketimine **1a** (81 mg, 0.3 mmol) and 4-chloroacetophenone **2a** (13 µl, 15 mg, 0.1 mmol) with a reaction time of 6 h. The crude material was purified by column chromatography (eluent: 1% Et_3N in 2% EtOAc/petroleum ether) to afford **3aa** (32 mg, 82%) as a colorless thick oil. An analytical sample for characterization was further purified using normal-phase HPLC (10% 2-propanol/hexane). R_f = 0.19 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.78 – 7.70 (m, 2H), 7.48 – 7.16 (m, 13H), 7.08 – 7.01 (m, 2H), 5.59 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 167.7, 150.4, 144.1, 139.6, 136.5, 135.7, 130.4, 128.8, 128.7, 128.6, 128.6, 128.1, 127.7, 127.7, 127.6, 127.1, 69.7, 26.6; IR (thin film): ν_{max} 3058.6, 1681.4, 1614.3; HRMS (ESI+) m/z 390.1835. [$(M+H)^+$; calculated mass for $C_{28}H_{24}NO^+$: 390.1852].

*4-(((Diphenylmethylene)amino)(phenyl)methyl)benzaldehyde (**3ab**)*

From fluoride: The reaction was performed following general procedure A using ketimine **1a** (81 mg, 0.3 mmol) and 4-fluorobenzaldehyde **2b'** (11 µL, 12 mg, 0.1 mmol) with a reaction time of 10 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ab** (21 mg, 56%) as a colorless thick oil.

From chloride: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and 4-chlorobenzaldehyde **2b** (14 mg, 0.1 mmol) with a reaction time of 10 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether)

to give the product **3ab** (20 mg, 52%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and 4-bromobenzaldehyde **2b''** (19 mg, 0.1 mmol) with a reaction time of 6 min. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ab** (25 mg, 67%) as a colorless thick oil.

An analytical sample for characterization was further purified using HPLC (1.3% 2-propanol/hexane). R_f = 0.41 (10% EtOAc /petroleum ether + 1% Et_3N); ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.85 – 7.70 (m, 4H), 7.55 – 7.17 (m, 13H), 7.09 – 6.99 (m, 2H), 5.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 167.9, 151.9, 143.9, 139.5, 136.5, 135.1, 130.4, 130.0 128.8, 128.7, 128.6, 128.6, 128.2, 128.1, 127.6, 127.6, 127.1, 69.8; IR (thin film): ν_{max} 2923.8, 1699.4, 1605.9, 1579.1 ; HRMS (ESI+) m/z 376.1681. [$(M+H)^+$; calculated mass for $C_{27}H_{22}NO^+$: 376.1696].

*4-(((Diphenylmethylene)amino)(phenyl)methyl)benzonitrile (**3ac**)*

From fluoride: The reaction was performed following general procedure A with ketimine **1a** (81 mg, 0.3mmol) and 4-florobenzonitrile **2c'** (12 mg, 0.1 mmol) with a reaction time of 10 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ac** (33 mg, 89%) as colorless thick oil.

From chloride: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol), 4-chlorobenonitrile 2c (14 mg, 0.1 mmol) with a reaction time of 7 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ac** (17 mg, 46%) as a colorless thick oil.

The reaction was also performed following general procedure A' with ketimine **1a** (82 mg, 0.3 mmol) and 4-chlorobenonitrile **2c** (14 mg, 0.1 mmol) with a reaction time of 1 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ac** (34 mg, 91%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and 4-bromobenonitrile **2c''** (18 mg, 0.1 mmol) with a reaction time of 7 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ac** (21 mg, 56%) as a colorless thick oil.

The reaction was also performed following general procedure A' with ketimine **1a** (82 mg, 0.3 mmol), 4-bromobenzonitrile **2c''** (18 mg, 0.1 mmol) with a reaction time of 15 min. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ac** (35 mg, 94%) as a colorless thick oil.

In all cases, the NMR spectra matched the previously published data.[7f]

*Methyl 4-(((diphenylmethylene)amino)(phenyl)methyl)benzoate (**3ad**)*

From chloride: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and methyl 4-chlorobenzoate **2d** (17 mg, 0.1mmol) with a reaction time of 1 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3ad** (14 mg, 34%) as a thick colorless oil.

The reaction was also performed following general procedure A' with ketimine **1a** (82 mg, 0.3mmol) and methyl 4-chlorobenzoate **2d** (17 mg, 0.1mmol) with a reaction time of 4 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc /petroleum ether) to give the product **3ad** (25 mg, 61%) as a thick colorless oil.

From bromide: The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and methyl 4-bromobenzoate **2d''** (22 mg, 0.1 mmol) with a reaction time of 1 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc /petroleum ether) to give the product **3ad** (26 mg, 64%) as a colorless thick oil.

R_f = 0.28 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.47 – 7.17 (m, 13H), 7.07 – 7.02 (m, 2H), 5.59 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 167.1, 150.1, 144.2, 139.6, 136.6, 130.3, 129.8, 128.8, 128.7, 128.6, 128.52, 128.5, 128.1, 127.7, 127.6, 127.5, 127.0, 69.7, 52.0; IR (thin film): ν_{max} 1721.4, 1608.6; HRMS (ESI+) m/z 406.1785. [$(M+H)^+$; calculated mass for $C_{28}H_{24}NO_2^+$: 406.1802].

Arylations under irradiation

*1-(4-(tert-Butyl)phenyl)-N-(diphenylmethylene)-1-phenylmethanamine (**3ae**) + N-Benzylidene-1-(4-(tert-butyl)phenyl)-1,1-diphenylmethanamine (**4ae**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 4-bromo-4-*tert*-butylbenzene **2e''** (0.28 mL, 2 mmol), with a reaction time of 2.5 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3ae** and **4ae** (4:1, 46 mg, 57%) as a colorless thick oil. The NMR spectra matched the previously published data.[7f-8]

*N-(Diphenylmethylene)-1,1-diphenylmethanamine (**3af**) + N-Benzylidene-1-phenyl-1,1-diphenylmethanamine (**4af**)*

From chloride: The reaction was performed following general procedure B with ketimine **1a** (54

mg, 0.2 mmol) and chlorobenzene **2f** (0.2 mL, 2 mmol) with a reaction time of 4 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3af** and **4af** (4:1, 36 mg, 52%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2 mmol) and bromobenzene **2f''** (0.2 mL, 2 mmol) with a reaction time of 3 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3af** and **4af** (3:1, 40 mg, 58%) as a colorless thick oil.

The NMR spectra matched the previously published data.[7f-24]

*N-(Diphenylmethylene)-1-(4-methylphenyl)-1-phenylmethanamine (**3ag**) + N-Benzylidene-1-(4-methyl-phenyl)-1,1-diphenylmethanamine (**4ag**)*

From chloride: The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2 mmol) and 4-chlorotoluene **2g** (0.236 mL, 2 mmol) with a reaction time of 3.5 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3ag** and **4ag** (4:1, 32 mg, 44%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 4-bromotoluene **2g''** (0.240 mL, 2 mmol) with a reaction time of 3.5 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3ag** and **4ag** (3:1, 38 mg, 53%) as a colorless thick oil.

3ag: The NMR spectra matched the previously published data.[7f]

4ae: R_f = 0.73 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 3H), 7.44 – 7.40 (m, 3H), 7.33 – 7.21 (m, 10H), 7.16 – 7.08 (m, 4H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 146.1, 142.7, 136.8, 136.4, 130.7, 129.8, 128.6, 128.6, 128.5, 127.7, 126.7, 78.1, 21.0; IR (thin film): ν_{max} 2924.4, 1642.1; HRMS (ESI+) m/z 362.1907. [$(M+H)^+$; calculated mass for $C_{27}H_{24}N^+$: 362.1903].

*N-(Diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine (**3ah**) + N-Benzylidene-1-(pyridin-3-yl)-1,1-diphenylmethanamine (**4ah**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2 mmol) and 3-bromopyridine **2h''** (0.193 mL, 2 mmol) with a reaction time of 2 h. The crude material was purified by column chromatography on silica gel (eluted with 10% → 25% Et_2O/petroleum ether) to give the **3ah** (20 mg, 29%) as a colorless thick oil. Product **4ah** was most likely present and isolated in the reaction mixture with R_f = 0.81 (100% EtOAc), but proper characterization failed due to decomposition and/or hydrolysis of the compound upon chromatography.

3ah: The NMR spectra matched the previously published data.[7f]

*N-(Diphenylmethylene)-1-(4-methylphenyl)-1-phenylmethanamine (**3ai**) + N-Benzylidene-1-(4-methoxy-phenyl)-1,1-diphenylmethanamine (**4ai**)*

From chloride: The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2 mmol) and 4-chloroanisole **2i** (0.246 mL, 2 mmol) with a reaction time of 6 h. The crude material was purified by column chromatography on silica gel (eluted with 2% Et_2O/petroleum ether) to obtain the **3ai** (12 mg, 16%) and **4ai** (6 mg, 8%) as a colorless thick oils.

From bromide: The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2 mmol) and 4-bromoanisole **2i''** (0.251 mL, 2 mmol) with a reaction time of 1 h. The crude material was purified by column chromatography on silica gel (eluted with 2% Et_2O/petroleum ether) to obtain the **3ai** (17 mg, 21%) and **4ai** (7 mg, 11%) as a colorless thick oils.

The NMR spectra matched the previously published data.[7f-8]

*4-(((Diphenylmethylene)amino)(phenyl)methyl)-N,N-dimethylaniline (**3aj**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 4-bromo-*N*,*N*-dimethylaniline **2j''** (400 mg, 2 mmol) with a reaction time of 2 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 10% Et_2O/petroleum ether) to obtain **3aj** (17 mg, 22%) as a colorless thick oil. The NMR spectra matched the previously published data.[7f]

*N-(Diphenylmethylene)-1-(naphthalen-2-yl)-1-phenylmethanamine (**3ak**) + N-Benzylidene-1-(naphthalen-2-yl)-1,1-diphenylmethanamine (**4ak**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 2-bromonaphthalene **2k''** (414 mg, 2 mmol) with a reaction time of 0.5 h. The crude material was purified by column chromatography on silica gel (eluted with 2% Et_2O/petroleum ether) to give **3ak** (14 mg, 13%) and **4ak** (10 mg, 18%) as a colorless thick oils. The NMR spectra matched the previously published data.[8]

*N-(Diphenylmethylene)-1-phenyl-1-(thiophen-2-yl)methanamine (**3al**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 2-bromothiophene **2l''** (0.194 mL, 2 mmol) with a reaction time of 0.5 h. The crude material was purified by column chromatography on silica gel

(eluted with 1% Et_2O/petroleum ether) to obtain **3al** (2.6 mg, 4%) as a colorless thick oil. R_f = 0.5 (5% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.48 – 7.16 (m, 12H), 7.11 (dd, *J* = 6.4, 3.0 Hz, 2H), 6.90 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.75 (d, *J* = 3.4 Hz, 1H), 5.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 149.1, 144.2, 139.6, 136.3, 130.3, 128.9, 128.7, 128.5, 128.4, 128.1, 127.8, 127.4, 127.1, 126.4, 124.4, 123.3, 66.0; IR (thin film): ν_{max} 3059.0, 1622.2, 1599.0, 1489.9; HRMS (E+) m/z 354.1274 [$(M+H)^+$; calculated mass for $C_{24}H_{20}NS^+$: 354.1311.

*1-(2,6-Dimethylphenyl)-N-(diphenylmethylene)-1-phenylmethanamine (**3an**)*

The reaction was performed following general procedure B with ketimine **1a** (54 mg, 0.2mmol) and 2-bromo-m-xylene **2l** (0.266 mL, 2 mmol) with a reaction time of 4 h. The crude material was purified by column chromatography on silica gel (eluted with 2% Et_2O/petroleum ether) to obtain **3an** (24 mg, 32%) as a colorless thick oil. The NMR spectra matched the previously published data.[8]

Arylation of selected aldimines

*4-(((Diphenylmethylene)amino)(4-methoxyphenyl)methyl)benzonitrile (**3bc**)*

The reaction was performed following general procedure A' with aldimine **1b** (90 mg, 0.3mmol) and 4-chlorobenzonitrile **2c** (14 mg, 0.1 mmol) with a reaction time of 20 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% → 5% EtOAc/petroleum ether) to give the product **3bc** (26 mg, 65%) as a colorless thick oil. R_f = 0.36 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.31 (m, 8H), 7.20 – 7.15 (m, 2H), 7.06 – 7.00 (m, 2H),, 6.85 – 6.79 (m, 2H), 5.52 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 158.7, 150.6, 139.4, 136.4, 135.9, 132.3, 130.4, 128.8, 128.6, 128.1, 127.6, 119.1, 114.0, 110.4, 68.9, 55.3; IR (thin film): ν_{max} 3061.5, 2225.9, 1610.9, 1505.3; HRMS (E+) m/z 403.1797 [$(M+H)^+$; calculated mass for $C_{28}H_{23}N_2O^+$: 403.1805.

*4-(((Diphenylmethylene)amino)(thiophen-2-yl)methyl)benzonitrile (**3cc**)*

The reaction was performed following general procedure A with aldimine **1c** (83 mg, 0.3mmol) and 4-chlorobenzonitrile **2c** (14 mg, 0.1 mmol) with a reaction time of 1 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% EtOAc/petroleum ether) to give the product **3cc** (24 mg, 63%) as a thick colorless oil. R_f = 0.3 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.31 (m, 8H), 7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.91 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 149.4, 147.5, 139.1, 135.9, 132.4, 130.7, 129.0, 128.9, 128.7, 128.2, 128.1, 127.5, 126.6, 125.1, 123.7, 119.0, 110.9, 65.5; IR (thin film): ν_{max} 3064.3, 2923.2, 2356.2, 2227.2, 1614.1; HRMS (ESI+) m/z 379.1247. [$(M+H)^+$; calculated mass for $C_{25}H_{19}N_2S^+$: 379.1263].

*4,4'-(((Diphenylmethylene)amino)methylene)dibenzonitrile (**3dc**)*

The reaction was performed following general procedure A' with aldimine **1d** (89 mg, 0.3mmol) and 4-chlorobenonitrile **2c** (14 mg, 0.1 mmol) with a reaction time of 3 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 5% → 10% EtOAc/petroleum ether) to give the product **3dc** (12 mg, 29%) as a colorless thick oil. R_f = 0.15 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.51 – 7.33 (m, 10H), 7.00 (dd, *J* = 7.7, 1.5 Hz, 2H), 5.60 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 148.8, 138.9, 136.0, 132.5, 130.9, 129.1, 128.8, 128.8, 128.3, 128.2, 127.3, 118.7, 111.2, 69.0; IR (thin film): ν_{max} 3062.9, 2924.9, 2373.6, 2228.7, 1613.4; HRMS (ESI+) m/z 398.1652. [$(M+H)^+$; calculated mass for $C_{28}H_{20}N_3^+$: 398.1652].

*N-(Diphenylmethylene)-1-(4-methylphenyl)-1-phenylmethanamine (**3bf**) + N-Benzylidene-1-(4-methoxy-phenyl)-1,1-diphenylmethanamine (**4bf**)*

From chloride: The reaction was performed following general procedure B with aldimine **1b** (60 mg, 0.2 mmol), chlorobenzene **2f** (0.2 mL, 2 mmol) with a reaction time of 1 h. The crude material was purified by a column chromatography (eluted with 1% Et_3N in 3% Et_2O/petroleum ether) to give the mixture of **3bf** and **4bf** (4:1, 29 mg, 39%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure B with aldimine **1b** (60 mg, 0.2 mmol) and bromobenzene **2f'** (0.2 mL, 2 mmol) with a reaction time of 40 min. The crude material was purified by a column chromatography (eluted with 1% Et_3N in 3% Et_2O/petroleum ether) to obtain the **3bf** (30 mg, 39%) and **4bf** (14 mg, 18%) as a colorless thick oils.

The NMR spectra matched the previously published data.[7f-8-21]

*N-(Diphenylmethylene)-1-phenyl-1-(thiophen-2-yl)methanamine (**3al**) + N-benzylidene-1,1-diphenyl-1-(thiophen-2-yl)methanamine (**4cf**)*

From chloride: The reaction was performed following general procedure B with aldimine **1c** (56 mg, 0.2 mmol) and chlorobenzene **2f** (0.2 mL, 2 mmol) with a reaction time of 3 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3al** and **4cf** (2:1, 19 mg, 27%) as a

colorless thick oil. Sample of **4cf** for characterization was isolated using HPLC (50% 2-propanol/hexane).

From bromide: The reaction was performed following general procedure B with aldimine **1c** (56 mg, 0.2 mmol) and bromobenzene **2f''** (0.210 mL, 2 mmol) with a reaction time of 2 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 2% Et_2O/petroleum ether) to give the mixture of **3al** and **4cf** (3:1, 26.7 mg, 38%) as a colorless thick oil. Sample of **4cf** for characterization was isolated using HPLC (50% 2-propanol/hexane).

4cf: Thick colorless oil. R_f = 0.56(5% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.43 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.33 – 7.22 (m, 15H), 7.20 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 145.7, 143.9, 130.7, 129.7, 129.2, 127.8, 127.4, 126.8, 78.0; IR (thin film): ν_{max} 3059.6, 2923.2, 1629.7, 1489.0; HRMS (E+) m/z 354.1314 [$(M+H)^+$; calculated mass for $C_{24}H_{20}NS^+$: 354.1311].

*4-(((Diphenylmethylene)amino)(phenyl)methyl)benzonitrile (3df) + 4-((tritylimino)methyl)benzonitrile (**4df**)*

From chloride: The reaction was performed following general procedure B with aldimine **1d** (59 mg, 0.2 mmol) and chlorobenzene **2f** (0.200 mL, 2 mmol), reaction irradiated with blue LED for 3 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 5% Et_2O/petroleum ether) to give the mixture of **3df** and **4df** (2:1, 31 mg, 42%) as a colorless thick oil.

From bromide: The reaction was performed following general procedure B with aldimine **1d** (59 mg, 0.2 mmol) and bromobenzene **2f''** (0.200 mL, 2 mmol), reaction irradiated with blue LED for 4.5 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 5% Et_2O/petroleum ether) to give the mixture of **3df** and **4df** (2:1, 48 mg, 63%) as a colorless thick oil. Sample of **4df** for characterization was isolated using HPLC (1.1% 2-propanol/hexane).

The reaction was also performed following general procedure B with aldimine **1d** (59.3 mg, 0.2mmol), bromobenzene **2f''** (0.200 mL, 2 mmol), reaction irradiated with green LED for 5 h to give the minute amount of product **3df** (less than 7%, estimated from crude ^1H NMR using 1,4-dimethoxybenzene as an internal standard).

3df: The NMR spectra matched the previously published data.[7f]

4df: R_f = 0.36 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.85 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.21 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 145.2, 140.4, 132.4, 129.7, 129.0, 127.9, 127.1, 118.6, 114.0, 78.8; IR (thin film): ν_{max} 2925.1, 2230.8, 1633.9, 1484.3, 1447.7 ;HRMS (ESI+) m/z 373.1755. [$(M+H)^+$; calculated mass for $C_{27}H_{21}N_2^+$: 373.1699].

Other derivatives

*Isopropyl 2-(4-(4-(((diphenylmethylene)amino)(phenyl)methyl)-benzoyl)phenoxy)-2-methylpropanoate (**5**)*

The reaction was performed following general procedure A' with ketimine **1a** (82 mg, 0.3 mmol) and fenofibrate (36 mg, 0.1 mmol) with a reaction time of 30 min. The crude material was purified by a column chromatography (eluted with 1% Et_3N in 5% EtOAc/petro-leum ether) to give the product **5** (34 mg, 57%) as a colorless oil. R_f = 0.22 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.18 (m, 13H), 7.10 – 7.04 (m, 2H), 6.86 – 6.81 (m, 2H), 5.61 (s, 1H), 5.07 (hept, *J* = 6.3 Hz, 1H), 1.65 (d, *J* = 5.6 Hz, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 173.2, 167.6, 159.5, 149.2, 144.2, 139.7, 136.6, 132.0, 130.8, 130.3, 130.0, 128.8, 128.7, 128.5, 128.5, 128.3, 128.1, 127.7, 127.6, 127.4, 127.0, 117.1, 79.4, 69.7, 69.3, 25.4, 21.5; IR (thin film): ν_{max} 2981.7, 1729.3, 1653.6, 1598.6; HRMS (ESI+) m/z 596.2799 [$(M+H)^+$; calculated mass for $C_{40}H_{38}NO_4^+$: 596.2795].

*Isopropyl 2-(4-(4-(((diphenylmethylene)amino)(4-methoxy-phenyl)-methyl)benzoyl)phenoxy)-2-methylpropanoate (**6**)*

The reaction was performed following general procedure A with aldimine **1b** (91 mg, 0.3 mmol) and fenofibrate (36 mg, 0.1 mmol) with a reaction time of 20 min. The crude material was purified by column chromatography (eluted with 1% Et_3N in 5% EtOAc/petro-leum ether) to give the product **6** (36 mg, 57%) as a thick colorless oil. R_f = 0.48 (20% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 4H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.28 (m, 8H), 7.27 – 7.21 (m, 2H), 7.11 – 7.0 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 5.57 (s, 1H), 5.13 – 5.02 (m, 1H), 3.78 (s, 3H), 1.65 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 173.2, 167.3, 159.5, 158.6, 149.5, 139.7, 136.6, 136.5, 136.5, 132.0, 130.8, 130.2, 130.0, 128.8, 128.7, 128.7, 128.1, 127.7, 127.2, 117.1, 113.9, 79.4, 69.3, 69.1, 55.3, 25.4, 21.5; IR (thin film): ν_{max} 2927.1, 1732.0, 1653.0, 1601.6; HRMS (E+) m/z 626.2912 [$(M+H)^+$; calculated mass for $C_{41}H_{40}NO_5^+$: 626.2901].

*Isopropyl 2-(4-(4-(((diphenylmethylene)amino)(thiophen-2-yl)-methyl)benzoyl)phenoxy)-2-methylpropanoate (**7**)*

The reaction was performed following general procedure A with aldimine **1c** (83 mg, 0.3mmol) and fenofibrate (36 mg, 0.1 mmol) with a reaction time of 20 min .The crude material was purified by a column chromatography (eluted with 1% Et_3N in 5% EtOAc/petroleum ether) to give the product **7** (39 mg, 64%) as a thick colorless oil. R_f = 0.56 (20% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 4H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.43 (m, 5H), 7.42 – 7.33 (m, 3H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 – 6.82 (m, 2H), 6.80 – 6.77 (m, 1H), 5.85 (s, 1H), 5.09 (hept, *J* = 6.3 Hz, 1H), 1.65 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 195.2, 173.2, 168.2, 159.5, 148.3, 148.3, 139.4, 136.9, 136.1, 132.0, 130.7, 130.5, 130.1, 128.9, 128.8, 128.6, 128.1, 127.7, 127.2, 126.6, 124.7, 123.5, 117.2, 79.4, 69.3, 65.8, 25.4, 21.5; IR (thin film): ν_{max} 2983.9, 2934.9, 1730.5, 1653.7, 1601.3; HRMS (ESI+) m/z 602.2349 [$(M+H)^+$; calculated mass for $C_{38}H_{36}NO_4S^+$: 602.2360].

*Isopropyl 2-(4-(4-((4-cyanophenyl)((diphenylmethylene)amino)-methyl)benzoyl)phenoxy)-2-methylpropanoate (**8**)*

The reaction was performed following general procedure A with aldimine **1d** (89 mg, 0.3 mmol) and fenofibrate (36 mg, 0.1 mmol) with a reaction time of 6 h. The crude material was purified by a column chromatography (eluted with 1% Et_3N in 5% → 10% EtOAc/petroleum ether) to give the product **8** (24 mg, 38%) as a thick colorless oil. R_f = 0.54 (20% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 4H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.46 (m, 5H), 7.41 – 7.36 (m, 5H), 7.04 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.63 (s, 1H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.65 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1 173.2, 168.9, 159.6, 149.5, 147.6, 139.2, 137.1, 136.2, 132.4, 132.0, 130.7, 130.5, 130.2, 129.0, 128.8, 128.7, 128.3, 128.2, 127.5, 127.3, 118.9, 117.1, 110.9, 79.4, 69.3, 69.3, 25.4, 21.5; IR (thin film): ν_{max} 2985.0, 2930.6, 2226.9, 1733.9, 1654.2, 1604.9; HRMS (E+) m/z 621.2765[$(M+H)^+$; calculated mass for $C_{41}H_{37}N_2O_4^+$: 621.2748.

*Isopropyl 2-(4-(4-(amino(phenyl)methyl)benzoyl)phenoxy)-2-methyl-propanoate (**9**)*

A vial equipped with a stir bar was charged with compound **5** (34 mg, 0.06 mmol), which was dissolved in THF (0.6 mL). Then aq. citric acid (1M, 0.6 mL, 0.6 mmol) was added at once. The reaction mixture was stirred at room temperature for 6 h and progress monitored by TLC. Upon completion the reaction mixture was made basic with sat. $NaHCO_3$ and the mixture was extracted with EtOAc (4 × 2 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by a column chromatography (eluted with 1% Et_3N/EtOAc) to give the product **9** (21 mg, 85%) as a thick colorless oil. R_f = 0.27 (100% EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 6.87 – 6.82 (m, 2H), 5.28 (s, 1H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.65 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 173.2, 159.5, 149.7, 145.0, 136.8, 132.0, 130.7, 130.1, 128.7, 127.3, 126.9, 126.7, 117.2, 79.4, 69.3, 59.7, 25.4, 21.5; IR (thin film): ν_{max} 2980.0, 2929.9, 1729.3, 1652.1, 1598.9; HRMS (ESI+) m/z 432.2170 [$(M+H)^+$; calculated mass for $C_{27}H_{30}NO_4^+$: 432.2169].

*6-(((Diphenylmethylene)amino)(phenyl)methyl)-2-phenyl-1H-phenalene-1,3(2H)-dione (**11**)*

The reaction was performed following general procedure A with ketimine **1a** (82 mg, 0.3 mmol) and 6-bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**10**, 35 mg, 0.1 mmol) with a reaction time of 15 min. The crude material was purified by a column chromatography (eluted with 10% EtOAc/petroleum ether + 1% Et_3N) to give the product **11** (48 mg, 88%) as a thick oil which solidified on a pump.

Gram sacle: The reaction was performed following general procedure A with ketimine **1a** (3.257 g, 12 mmol), 6-bromo-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**10**, 1.404 g, 4 mmol) with a reaction time of 30 min. The crude material was purified by a column chromatography (eluted with 1% Et_3N in 10% EtOAc /petroleum ether) to give the product **11** (1.799 g, 83%) as a thick oil which solidified under vacuum: mp 138 – 140 °C, R_f = 0.32 (15% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.61 (m, 1H), 8.57 (dd, *J* = 7.3, 1.0 Hz, 1H), 8.44 (dd, *J* = 8.6, 0.9 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.63 – 7.17 (m, 17H), 7.07 (d, *J* = 6.7 Hz, 2H), 6.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 164.5, 164.3, 147.9, 143.3, 139.3, 136.3, 135.5, 132.0, 131.6, 131.2, 130.6, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 128.7, 128.2, 127.6, 127.4, 127.2, 127.2, 126.5, 123.2, 122.0, 67.6; IR (thin film): ν_{max} 1712.2, 1667.6, 1591.9 ;HRMS (ESI+) m/z 543.2070 [$(M+H)^+$, calculated mass for $C_{38}H_{27}N_2O_2^+$: 543.2067].

*6-(Amino(phenyl)methyl)-2-phenyl-1H-phenalene-1,3(2H)-dione (**12**)*

A vial equipped with a stir bar was charged with compound **11** (55 mg, 0.1 mmol). THF (1 mL) was added and the reaction was cooled at 0 °C. Then aq. HCl (1M, 1 mL) was added to the reaction and during stirring solution was warmed to room temperature and progress was monitored by TLC until complete consumption of **11** (reaction completed in 1 h). The reaction mixture was made basic with 1M NaOH until the pH reached 14, then the solution was extracted with EtOAc (5 × 2mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N/EtOAc) to give the amine **12** (23 mg, 59%) as a yellow solid: mp 235 – 237 °C, R_f = 0.26 (100% EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 6.7 Hz, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.57 – 7.43 (m, 3H), 7.39 – 7.23 (m, 7H), 6.05 (s, 1H), 2.03 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 164.2, 148.5, 144.2, 135.4, 131.6, 131.2, 130.6, 129.6, 129.4, 129.1, 129.0, 128.7, 128.7, 127.7, 127.2, 126.9, 125.2, 123.4, 122.0, 56.5; IR (thin film): ν_{max} 1707.6, 1665.1, 1589.8; HRMS (ESI+) m/z 379.1429 [$(M+H)^+$; calculated mass for $C_{25}H_{19}N_2O_2^+$: 378.1441].

3-(Allylamino)-4-chlorobenzonitrile

In a dried flask under Ar were dispersed 3-amino-4-chlorobenzonitrile (740 mg, 4.85 mmol) and potassium carbonate (6692 mg, 48.5 mmol) in dry DMF (15 mL) at room temperature. Under stirring, allyl bromide (588 mg, 4.85 mmol, 0.421 mL) was added dropwise and the temperature was increased to 100 °C; the reaction mixture was stirred for 6 h. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluted with 20% EtOAc/petroleum ether) to give the product (367 mg, 39%) as a colorless oil. R_f = 0.13 (8% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.82 (d, *J* = 1.8 Hz, 1H), 5.98 – 5.86 (m, 1H), 5.34 – 5.21 (m, 2H), 4.71 (bs, 1H), 3.89 – 3.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 133.4, 129.8, 123.7, 120.6, 118.9, 117.2, 113.9, 111.5, 45.7; IR (thin film): ν_{max} 3414.0, 2231.2, 1590.3, 1511.6; HRMS (ESI-) m/z 191.0390 [$(M-H)^-$; calculated mass for $C_{10}H_8ClN_2^-$: 191.0381].

*3-(Allyl(methyl)amino)-4-chlorobenzonitrile (**14**)*

In a dried flask under Ar was dissolved 3-(allylamino)-4-chlorobenzonitrile (285 mg, 1.48 mmol) in dry THF (15 mL) and the solution was cooled to 0 °C. Under stirring, *n*-BuLi (1.110 mL, 1.6 M in hexanes, 1.78 mmol) was added dropwise followed by dropwise addition of methyl iodide (0.12 mL, 1.92 mmol). The reaction mixture allowed to warm to room temperature and stirred for additional 5 h. The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 5% EtOAc/petroleum ether) to give the product **14** (295 mg, 96%) as a colorless oil. R_f = 0.56 (10% EtOAc/petrol-eum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.94 – 5.82 (m, 1H), 5.31 – 5.20 (m, 2H), 3.67 (d, *J* = 6.1 Hz, 2H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 133.9 133.3, 131.7, 125.9, 124.2, 118.4, 111.2, 58.3, 39.5; IR (thin film): ν_{max} 2231.5, 1585.8; HRMS (ESI+) m/z 207.0659 [$(M+H)^+$; calculated mass for $C_{11}H_{12}ClN_2^+$: 207.0684].

3-(Allylamino)-4-fluorobenzonitrile

In a dried flask under Ar was dispersed 3-amino-4-fluorobenzonitrile (435 mg, 3.195 mmol) and potassium carbonate (2.207 g, 15.975 mmol) in dry DMF (5 mL) at room temperature. Under stirring, allyl bromide (425 mg, 3.519 mmol, 0.304 mL) was added dropwise and the temperature was increased to 100 °C; the resulting reaction mixture was stirred for 6 h. After cooling to room temperature, the reaction mixture was poured into water (30 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 10% Et_2O/petroleum ether) to give the product (238 mg, 42%) as a colorless oil. R_f = 0.33 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 11.1, 8.3 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.88 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.98 – 5.85 (m, 1H), 5.35 – 5.20 (m, 2H), 4.33 (s, 1H), 3.85 – 3.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5 (d, *J* = 248.3 Hz), 137.3 (d, *J* = 12.4 Hz), 133.6 (s), 121.2 (d, *J* = 8.0 Hz), 119.0 (s), 117.1 (s), 115.2 (d, *J* = 20.3 Hz), 1155.0 (d, *J* = 5.1 Hz), 108.7 (d, *J* = 3.7 Hz), 45.6 (s); IR (thin film): ν_{max} 3417.9, 2229.1, 1612.2, 1522.5; HRMS (ESI-) m/z 175.0703. [$(M-H)^-$; calculated mass for $C_{10}H_8FN_2^-$: 175.0677].

*3-(Allyl(methyl)amino)-4-fluorobenzonitrile (**15**)*

In a dried flask under Ar was dissolved 3-(allylamino)-4-fluorobenzonitrile (186 mg, 1.056 mmol) in dry THF (10 mL) and the solution was cooled to 0 °C. Under stirring, *n*-BuLi (0.50 mL, 2.5M in hexanes, 1.267 mmol) was added dropwise followed by dropwise addition of methyl iodide (0.10 mL, 1.584 mmol). The reaction mixture was allowed to warm to room temperature and stirred for additional 4 h. The reaction was quenched with sat. aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 10% Et_2O/petroleum ether) to give the product **15** (167 mg, 83%) as a colorless oil. R_f = 0.44 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.00 (m, 3H), 5.92 – 5.77 (m, 1H), 5.26 – 5.16 (m, 2H), 3.79 (d, *J* = 5.9 Hz, 2H), 2.86 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.72 (d, *J* = 254.1 Hz), 140.47 (d, *J* = 9.2 Hz), 133.43 (s), 124.37 (d, *J* = 8.9 Hz), 121.85 (d, *J* = 5.4 Hz), 118.79 (s), 117.86 (s), 117.29 (d, *J* = 23.2 Hz), 108.51 (d, *J* = 3.6 Hz), 57.34 (d, *J* = 6.3 Hz), 38.92 (d, *J* = 2.7 Hz); IR (thin film): ν_{max} 2228.9, 1600.6, 1508.1, ; HRMS (ESI+) m/z 191.0987. [$(M+H)^+$; calculated mass for $C_{11}H_{12}FN_2^+$: 191.0979].

*3-(((Diphenylmethylene)amino)(phenyl)methyl)-1-methylindol-ine-6-carbonitrile (**16**)*

The reaction was performed following general procedure A' using ketimine **1a** (109.3 mg, 0.4 mmol), 3-(allyl(methyl)amino)-4-chlorobenzonitrile (28 mg, 0.13 mmol) and $NaN(SiMe_3)_2$ (0.4 mL, 1M, 0.4 mmol) with a reaction time of 1 h. The crude material was purified by column chromatography on silica gel (eluted with 1% Et_3N in 5% EtOAc/petroleum ether) to give the product **16** as a mixture of diastereomers (1.1:1, 39 mg, 68%) in the form of

thick colorless oil. R_f = 0.29 (10% EtOAc/petroleum ether). HRMS (ESI+) m/z 442.2269. [$(M+H)^+$; calculated mass for $C_{31}H_{28}N_3^+$: 442.2278]. Diastereomeric ratio was determined based on indoline methyl group (3H, ~ 2.7 ppm) and aliphatic H (1H, ~ 2.0 ppm), see ^1H spectra for determination of diastereomeric ratio.

*3-(Allyl(methyl)amino)-4-(((diphenylmethylene)amino)(phenyl)-methyl)benzonitrile (**17**)*

The reaction was also performed following general procedure A' with ketimine **1a** (92 mg, 0.33 mmol), 3-(allyl(methyl)amino)-4-fluorobenzonitrile (22 mg, 0.11 mmol) and $LiN(SiMe_3)_2$ (0.283 mL, 1M, 0.283 mmol) with a reaction time of 12 h. The crude material was purified by column chromatography (eluted with 1% Et_3N in 10% Et_2O/petroleum ether) to give the product **17** (28 mg, 63%) as a white solid: mp 150 – 153 °C, R_f = 0.44 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.48 – 7.13 (m, 13H), 7.07 – 6.98 (m, 2H), 6.17 (s, 1H), 5.30 – 5.17 (m, 1H), 4.99 – 4.89 (m, 2H), 3.06 (d, *J* = 6.2 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 151.7, 146.5, 144.0, 139.6, 136.9, 134.6, 130.6, 130.2, 128.8, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 126.8, 125.8, 119.1, 117.6, 110.9, 64.0, 60.5, 41.3; IR (thin film): ν_{max} 2919.9, 2850.2, 2226.9, 1489.6 ;HRMS (E+) m/z 442.2270 [$(M+H)^+$; calculated mass for $C_{31}H_{28}N_3^+$: 442.2278].

Acknowledgements

J.J.C. thanks the National Natural Science Foundation of China (NSFC-21372159) and P.J.W. thanks the National Science Foundation (CHE-1464744) for financial support. M.P. and J.J.C. kindly appreciate Profs. Da-Gang Yu and Cheng Yang (Sichuan University) for use of their GC-MS and preparatory HPLC equipment, respectively.

References

[1] C.-L. Sun, Z.-J. Shi, *Chem. Rev.* **2014**, *114*, 9219-9280.

[2] M. Yan, J. C. Lo, J. T. Edwards, P. S. Baran, *J. Am. Chem. Soc.* **2016**, *138*, 12692-12714.

[3] a) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075-10166; b) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898-6926; c) J. K. Matsui, S. B. Lang, D. R. Heitz, G. A. Molander, *ACS Catalysis* **2017**, *7*, 2563-2575.

[4] a) I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725-728; b) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035-10074; c) X. Lang, J. Zhao, X. Chen, *Chem. Soc. Rev.* **2016**, *45*, 3026-3038.

[5] a) E. Doni, J. A. Murphy, *Chem. Commun.* **2014**, *50*, 6073-6087; b) J. A. Murphy, *J. Org. Chem.* **2014**, *79*, 3731-3746; c) H. S. Farwaha, G. Bucher, J. A. Murphy, *Org. Biomol. Chem.* **2013**, *11*, 8073-8081; d) J. Broggi, T. Terme, P. Vanelle, *Angew. Chem. Int. Ed.* **2014**, *53*, 384-413; e) B. Eberle, E. Kaifer, H.-J. Himmel, *Angew. Chem. Int. Ed.* **2017**, *56*, 3360-3363.

[6] a) B. Liu, C.-H. Lim, G. M. Miyake, *J. Am. Chem. Soc.* **2017**, *139*, 13616-13619; b) C. G. S. Lima, T. de M. Lima, M. Duarte, I. D. Jurberg, M. W. Paixão, *ACS Catalysis* **2016**, *6*, 1389-1407; c) M. A. Fox, J. Younathan, G. E. Fryxell, *J. Org. Chem.* **1983**, *48*, 3109-3112; d) S. Hoz, J. F. Bunnett, *J. Am. Chem. Soc.* **1977**, *99*, 4690-4699.

[7] a) A. A. Yeagley, J. J. Chruma, *Org. Lett.* **2007**, *9*, 2879-2882; b) W. H. Fields, A. K. Khan, M. Sabat, J. J. Chruma, *Org. Lett.* **2008**, *10*, 5131-5134; c) X. Qian, P. Ji, C. He, J.-O. Zirimwabagabo, M. M. Archibald, A. A. Yeagley, J. J. Chruma, *Org. Lett.* **2014**, *16*, 5228-5231; d) W. H. Fields, J. J. Chruma, *Org. Lett.* **2010**, *12*, 316-319; e) S. Tang, J. Y. Park, A. A. Yeagley, M. Sabat, J. J. Chruma, *Org. Lett.* **2015**, *17*, 2042-2045; f) M. Li, B. Yucel, J. Adrio, A. Bellomo, P. J. Walsh, *Chem. Sci.* **2014**, *5*, 2383-2391; g) X. Cao, S.-C. Sha, M. Li, B.-S. Kim, C. Morgan, R. Huang, X. Yang, P. J. Walsh, *Chem. Sci.* **2016**, *7*, 611-618; h) M. Li, O. Gutierrez, S. Berritt, A. Pascual-Escudero, A. Yeşilçimen, X. Yang, J. Adrio, G. Huang, E. Nakamaru-Ogiso, M. C. Kozlowski, P. J. Walsh, *Nat Chem* **2017**, *9*, 997-1004; i) M. Li, M. González-Esguevillas, S. Berritt, X. Yang, A. Bellomo, P. J. Walsh, *Angew. Chem. Int. Ed.* **2016**, *55*, 2825-2829; j) M. Li, S. Berritt, P. J. Walsh, *Org. Lett.* **2014**, *16*, 4312-4315.

[8] M. Li, S. Berritt, L. Matuszewski, G. Deng, A. Pascual-Escudero, G. B. Panetti, M. Poznik, X. Yang, J. J. Chruma, P. J. Walsh, *J. Am. Chem. Soc.* **2017**, *139*, 16327-16333.

[9]a) J. A. Grant, J.-M. Riethuisen, B. Moulaert, C. DeVos, *Ann. of Allergy, Asthma & Immunol.* **2002**, *88*, 190-197; b) B. Zhou, Z.-F. Liu, G.-G. Deng, W. Chen, M.-Y. Li, L.-J. Yang, Y. Li, X.-D. Yang, H.-B. Zhang, *Org. Biomol. Chem.* **2016**, *14*, 9423-9430; c) N. Plobeck, D. Delorme, Z.-Y. Wei, H. Yang, F. Zhou, P. Schwarz, L. Gawell, H. Gagnon, B. Pelcman, R. Schmidt, S. Y. Yue, C. Walpole, W. Brown, E. Zhou, M. Labarre, K. Payza, S. St-Onge, A. Kamassah, P.-E. Morin, D. Projean, J. Ducharme, E. Roberts, *J. Med. Chem.* **2000**, *43*, 3878-3894; d) Y. Zhou, K. Duan, L. Zhu, Z. Liu, C. Zhang, L. Yang, M. Li, H. Zhang, X. Yang, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 460-465. e) X. Yang, B.-S. Kim, M. Li, P. J. Walsh, *Org. Lett.* **2016**, *18*, 2371-2374.

[10] A. Studer, *Chem. Eur. J.* **2001**, *7*, 1159-1164.

[11] a) T. Kauffmann, A. Busch, K. Habersaat, E. Käppelmonn, *Angew. Chem. Int. Ed.* **1973**, *12*, 569-570; b) T. Kauffmann, R. Eidenschink, *Chem. Ber.* **1977**, *110*, 651-655; c) T. Kauffmann, H. Berg, E. Kiippelmann, D. Kuhlmann, *Chem. Ber.* **1977**, *110*, 2659-2664; d) T. Kauffmann, D. Berger, B. Scheerer, A. Woltermann, *Chem. Ber.* **1977**, *110*, 3034-3039; e)

E. Erlenmeyer, J. Kunlin, *Justus Liebigs Ann. Chem.* **1899**, *307*, 163-170.

[12] J. A. Fernandez-Salas, E. Marelli, S. P. Nolan, *Chem. Sci.* **2015**, *6*, 4973-4977.

[13] H. Mohapatra, S. Umapathy, *J. Phys. Chem. A* **2009**, *113*, 6904-6909.

[14] a)A. Claesson, C. Sahlberg, *Tetrahedron* **1982**, *38*, 363-368; b)R. R. Fraser, M. Bresse, N. Chuaqui-Offermanns, K. N. Houk, N. G. Rondan, *Can. J. Chem.* **1983**, *61*, 2729-2734.

[15] a) J. Pancholi, D. J. Hodson, K. Jobe, G. A. Rutter, S. M. Goldup, M. Watkinson, *Chem. Sci.* **2014**, *5*, 3528-3535; b) T. D. Ashton, K. A. Jolliffe, F. M. Pfeffer, *Chem. Soc. Rev.* **2015**, *44*, 4547-4595; c) G. Tu, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, F. Wang, *Synth. Met.* **2005**, *152*, 233-236.

[16] E. Kariv-Miller, Z. Vajtner, *J. Org. Chem.* **1985**, *50*, 1394-1399.

[17] a) S. R. Park, N. J. Findlay, J. Garnier, S. Zhou, M. D. Spicer, J. A. Murphy, *Tetrahedron* **2009**, *65*, 10756-10761; b) I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566-1577; c) Y. Qu, H. Tateno, Y. Matsumura, T. Kashiwagi, M. Atobe, *Molecules* **2017**, *22*, 413; d) M. Brasholz, *Angew. Chem. Int. Ed.* **2017**, *56*, 10280-10281; e) H. Yin, Y. Jin, J. E. Hertzog, K. C. Mullane, P. J. Carroll, B. C. Manor, J. M. Anna, E. J. Schelter, *J. Am. Chem. Soc.* **2016**, *138*, 16266-16273; f) H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714-723.

[18] a) C. Costentin, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **2004**, *126*, 16051-16057; b) L. Pause, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **1999**, *121*, 7158-7159; c) M. Kimura, H. Miyahara, N. Moritani, Y. Sawaki, *J. Org. Chem.* **1990**, *55*, 3897-3902.

[19] K. Li, A. E. Weber, L. Tseng, S. J. Malcolmson, *Org. Lett.* **2017**, *19*, 4239-4242.

[20] Y. Koyama, P. G. Gudeangadi, *Chem. Commun.* **2017**, *53*, 3846-3849.

[21] Y. Goriya, H. Y. Kim, K. Oh, *Org. Lett.* **2016**, *18*, 5174-5177.

[22] C.-X. Guo, W.-Z. Zhang, H. Zhou, N. Zhang, X.-B. Lu, *Chem. Eur. J.* **2016**, *22*, 17156-17159.

[23] D. Green, G. Patel, S. Elgendy, J. A. Baban, G. Claeson, V. V. Kakkar, J. Deadman, *Tetrahedron* **1994**, *50*, 5099-5108.

[24] A. E. Wendlandt, S. S. Stahl, *Org. Lett.* **2012**, *14*, 2850-2853.

10.1002/adsc.201800396

FULL PAPER

2-Azaallyl anions as light-tunable super-electron-donors: coupling with aryl fluorides, chlorides, and bromides

Adv. Synth. Catal. **2018**, *Volume*, Page – Page

Qianmei Wang, Michal Poznik*, Minyan Li, Patrick J. Walsh, Jason J. Chruma*