

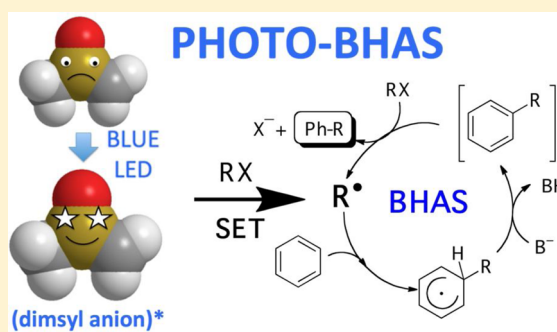
# Initiation in Photoredox C–H Functionalization Reactions. Is Dimsyl Anion a Key Ingredient?

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**S** Supporting Information

**ABSTRACT:** Previous studies have reported the arylation of unactivated arenes with ArX, base (KO<sup>t</sup>Bu or NaO<sup>t</sup>Bu), and an organic additive at high temperatures. Recently, we showed that this reaction proceeds in the absence of additives at rt but employs UV–vis light. However, details of mechanisms that can use a photoinduced base-promoted homolytic aromatic substitution reaction (photo-BHAS) have remained elusive until now. This work examines different mechanistic routes of the essential electron-transfer step (ET) of this reaction in order to identify a possible path for the formation of 1-adamantyl radicals from 1-haloadamantanes (initiation step). On the basis of photochemical and photophysical experiments and computational studies, we propose an unprecedented initiation step that could also be applied to other ET reactions performed in DMSO. For the first time, it is reported that dimsyl anion, formed from a strong base and DMSO (solvent), is responsible for inducing the initiation by a photo-BHAS process on alkyl halides.

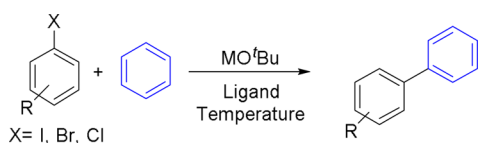


## INTRODUCTION

Direct functionalization of C–H bonds is an attractive strategy in organic synthesis and provides several advantages in relation to new demands for practical and sustainable transformations. In particular, aryl C–H functionalization is the ideal arylation approach, and this has been well developed using transition-metal catalysis<sup>1</sup> as well as metal-free radical strategies.<sup>2,3</sup>

In recent years, there has been a boom in research related to transition-metal-free couplings of haloarenes (ArX) to arenes to form biaryls (Scheme 1). Most of these reactions are induced

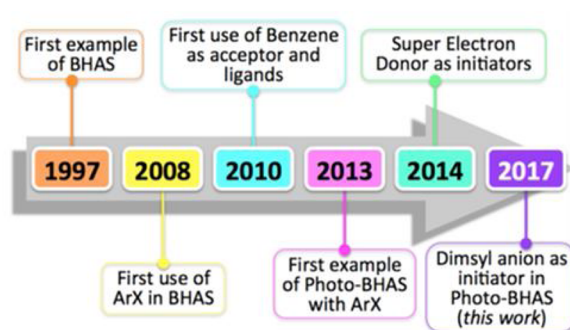
### Scheme 1. Synthesis of biaryls via Base Promoted Homolytic Aromatic Substitution (BHAS)



by alkali metal *tert*-butoxides in the presence of various additives via base-promoted homolytic aromatic substitution (BHAS).<sup>3–7</sup> In this way, the use of equivalent amounts of toxic R<sub>3</sub>SnH or expensive R<sub>3</sub>SiH reagents is avoided and the need for classical radical initiators is eliminated, such as unstable AIBN or peroxides. Russell and co-workers showed that RHgX could be used as precursors of alkyl radicals that coupled with arenes, where DABCO (base) is essential in these reactions. However, because of the use of toxic organomercury precursors, this methodology has not found wide application.<sup>8</sup> In 2008, Itami showed that KO<sup>t</sup>Bu could induce the addition of ArX (X = I,

Br) to electron-poor arenes (activated) under elevated temperatures or microwave (MW) irradiation.<sup>9</sup> Later, different research groups have reported the synthesis of biaryl compounds starting from unactivated arenes by direct C–H activation using NaO<sup>t</sup>Bu or KO<sup>t</sup>Bu in the presence of different organic additives such as ligands and super electron donors (SED) (Figure 1).<sup>10–46</sup> This success in C–H aromatic substitution was followed by C–H functionalization of styrenes with ArX through a similar base-promoted mechanism.<sup>47–50</sup>

In this context, the proposed BHAS reaction involves several important key steps: (A) an initiation process with the generation of an aryl radical from ArX via ET; (B) addition



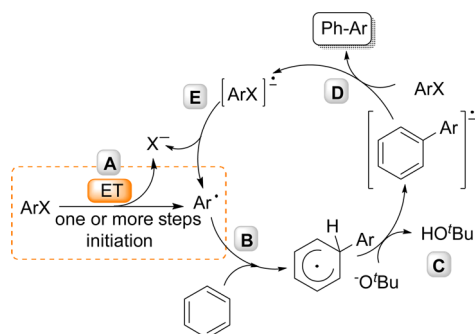
**Figure 1.** Time line in transition-metal-free C–H functionalization reactions.

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of aryl radical to an arene to give a radical  $\sigma$ -complex (cyclohexadienyl-type radical); (C) proton transfer to give a powerful reducing radical anion intermediate; (D) ET to afford a coupling product and the radical anion of aryl halide, and (E) fragmentation of this radical anion to a halide anion and the key intermediate aryl radical, thereby turning over the chain reaction (Scheme 2).<sup>7</sup>

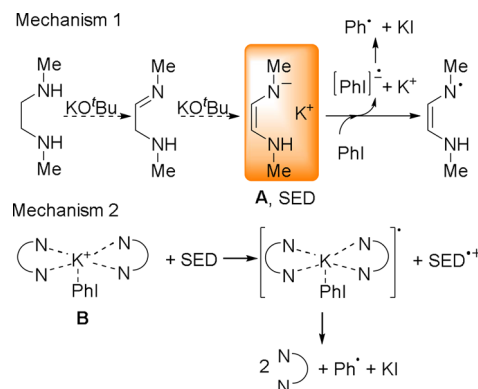
Scheme 2. Mechanism of BHAS



Propagation steps of the BHAS mechanism (B–E in Scheme 2) are widely accepted in the scientific community, with a general agreement about the key participation of radicals, radical anions, and bases. However, the ET initiation mechanism (A in Scheme 2) is still the focus of an intense debate, as some aspects remain unclear in both thermal and photoinitiated systems. Moreover, the photo-BHAS reaction has been poorly explored,<sup>51–53</sup> and the details of its initiation mechanism were recently analyzed mainly in the context of other ET reactions.<sup>54,55</sup>

Initially, the undeniable importance and usefulness of KO<sup>t</sup>Bu promoted the idea that it was irreplaceable, and its direct participation in the key initial ET event of several reactions was assumed despite a lack of clear evidence. Later, comprehensive studies started to reveal the real situation in thermal reactions. Some authors have suggested that ET, from a complex between NaO<sup>t</sup>Bu or KO<sup>t</sup>Bu with an additive to PhI, is the initiation step and produces the radical cation of these complexes and the radical anion of PhI.<sup>10,11,29,49</sup> Nevertheless, Murphy et al. showed, by DFT methods, that the thermodynamics of the ET reaction between the phenanthroline–MO<sup>t</sup>Bu complexes and PhI is highly endergonic for both NaO<sup>t</sup>Bu ( $\Delta G = 63.9$  kcal.mol<sup>-1</sup>) and KO<sup>t</sup>Bu ( $\Delta G = 59.5$  kcal.mol<sup>-1</sup>).<sup>56</sup> Therefore, they proposed that the reactivity of some of these systems (using phenanthrolines, *N*-heterocyclic carbenes, amino acids, 1,2-diols, DMEDA, etc., as additives) could be explained by the in situ formation of a super electron donor (or organic electron donors).<sup>56,57</sup> For DMEDA, they proposed that an electron-rich intermediate (A) could be formed under the reaction conditions (Scheme 3, mechanism 1), after which an ET takes place from this donor to PhI, thereby starting the BHAS process.<sup>57</sup> The formation of intermediate A is based on previous reports where amides are obtained under strong basic conditions.<sup>58,59</sup> Recently, Patil proposed a new alternative concerning the mode of generation of the phenyl radical and the role of additives in these reactions using computational calculations.<sup>60</sup> The suggested mechanism involves ET between the super electron donor and the additive K<sup>+</sup>–PhI complex (B) to form a radical complex, which dissociates to produce a phenyl radical, KI, and the additive in the final step (Scheme 3, mechanism 2). More recently, Jiao et al. proposed an

Scheme 3. Possible Initiation Mechanisms Using Super Electron Donors in BHAS

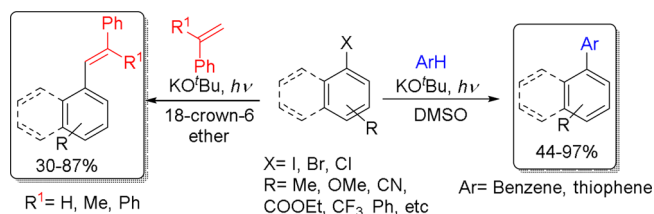


unconventional radical initiation mechanistic network rather than a single initiation pathway.<sup>61</sup>

In the absence of additives, just KO<sup>t</sup>Bu can promote this reaction at high temperature (100–160 °C).<sup>39,40,62</sup> Also, Liu et al. showed that a mixture of alkoxy bases (KOEt/KO<sup>t</sup>Bu) can efficiently promote BHAS at a lower temperature (80 °C).<sup>63</sup> In these systems, it is proposed that benzyne plays an important role in the initiation step.<sup>56,57</sup>

Although the most extensively used initiation method involves the use of additives, there are also a few examples of photoinduced BHAS. Taking into account that KO<sup>t</sup>Bu can initiate photosubstitution reaction with ArX,<sup>55</sup> we were able to show the application of UV–vis light ( $\lambda \geq 350$  nm) for direct arylation of benzene<sup>52</sup> using KO<sup>t</sup>Bu and DMSO at rt in the absence of any additive. The same methodology was applied to the photoarylation of alkenes using only KO<sup>t</sup>Bu and 18-crown-6-ether without any solvent for 15 min<sup>64</sup> (Scheme 4). Later,

Scheme 4. Photoinduced Arylation of Arenes and Alkenes at Room Temperature



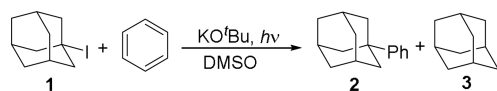
Ir(ppy)<sub>3</sub> was used as an effective photoredox catalyst for the arylation under visible light irradiation.<sup>53</sup> Another activation mode, where the photosensitive complex of KO<sup>t</sup>Bu and phenanthroline were excited by visible light ( $\lambda \geq 420$  nm), was employed to initiate biaryl synthesis.<sup>51</sup>

Despite the vast knowledge related to the mechanism of BHAS reactions, there is no information available related to the initiation step in the free additives photo-BHAS. In the present work, we unraveled the mechanism of photoinduced BHAS through a detailed study of the arylation of alkyl halides and proposed a new alternative for inducing these photoreactions that involves dimethyl anion as a key component. Based on experimental and computational studies, we propose an unprecedented initiation step that replaces KO<sup>t</sup>Bu as the key ingredient and which could also be applied to other ET reactions performed in DMSO.

## RESULTS AND DISCUSSION

As a model system, we selected the reaction of 1-iodoadamantane (**1**) with benzene for studying the initiation step in photoinduced BHAS reactions (Scheme 5). We chose this

Scheme 5. Synthesis of 1-Phenyladamantane by BHAS



system because elimination mechanisms can be ruled out. In addition, the reactivity of **1** is known in ET processes, such as the  $S_{RN}1$  mechanism.<sup>65</sup> When **1** was irradiated ( $\lambda \geq 350$  nm) in the presence of benzene (20 equiv) and KO<sup>t</sup>Bu (3 equiv) in DMSO, 1-phenyladamantane (**2**) was obtained in 95% yield (Table 1, entry 1). A reduced product (adamantane, **3**) or incomplete conversion was observed when the amount of benzene or KO<sup>t</sup>Bu was lowered and when shorter reaction times were employed (entries 2–5, Table 1).

No reaction was found in dark conditions or without KO<sup>t</sup>Bu (entries 6 and 7). Furthermore, the formation of radicals and

Table 1. Photoinduced Arylation Reaction of 1-Iodoadamantane (**1**) with Benzene in DMSO<sup>a</sup>



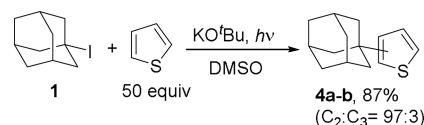
entry	benzene (equiv)	base (equiv)	time (h)	conv <sup>b</sup>	product yields <sup>c</sup> (%)
1	20	KO <sup>t</sup> Bu (3)	3	100	2 (95)
2	10	KO <sup>t</sup> Bu (3)	3	100	2 (91), 3 (6)
3	5	KO <sup>t</sup> Bu (3)	3	100	2 (85), 3 (10)
4	5	KO <sup>t</sup> Bu (3)	2	79	2 (70), 3 (8)
5	5	KO <sup>t</sup> Bu (1)	2	78	2 (42), 3 (13)
6	50	KO <sup>t</sup> Bu (3)	3 (dark)	4	2 (–)
7	50		3	0	2 (–)
8 <sup>d</sup>	5	KO <sup>t</sup> Bu (3)	3	39	2 (–)
9 <sup>e</sup>	5	KO <sup>t</sup> Bu (3)	3	0	2 (–)
10 <sup>f</sup>	10	KO <sup>t</sup> Bu (3)	3	60	2 (35), 3 (4)
11	10	NaH (3) <sup>g</sup>	3	100	2 (76), 3 (5)
12	20	KO <sup>t</sup> Bu (3)	2	100	2 (85), 3 (nd)
13	10	Na <sup>+</sup> CH <sub>2</sub> S(O)Me (0.3)	2	39	2 (35), 3 (4)
14	10	Na <sup>+</sup> CH <sub>2</sub> S(O)Me (0.6)	2	67	2 (67), 3 (7)
15	10	Na <sup>+</sup> CH <sub>2</sub> S(O)Me (1)	2	98	2 (91), 3 (7)
16	10	Li <sup>+</sup> CH <sub>2</sub> S(O)Me (0.5)	2	52	2 (42), 3 (8)
17	10	Li <sup>+</sup> CH <sub>2</sub> S(O)Me (1)	2	88	2 (76), 3 (13)

<sup>a</sup>The photostimulated reaction was carried out under N<sub>2</sub> atmosphere using **1** (1 equiv, 0.2 mmol), KO<sup>t</sup>Bu (3 equiv), DMSO ([**1**] = 0.1 M), and benzene according to method A (entries 1–10), method B (entries 11 and 12), or method C (entries 13–17). In Method A, HPI-T 400W lamps were used, and in Methods B and C irradiation was carried out with blue-LED (3 W). <sup>b</sup>The conversion (conv) was determined by quantification of the recovered substrate. <sup>c</sup>Yields were determined by GC (internal standard method). <sup>d</sup>The reaction was performed in the presence of 30 mol % of TEMPO. <sup>e</sup>The reaction was carried out in the presence of 30 mol % of *m*-DNB. <sup>f</sup>1 equiv of 1-bromoadamantane (**5**) was employed. <sup>g</sup>NaH was used as received from the supplier.

ET events was sustained by experiments adding a radical scavenger (TEMPO) and a good electron acceptor such as *m*-dinitrobenzene (*m*-DNB), which inhibited the ET reactions (Table 1, entries 8 and 9). In comparison, 1-bromoadamantane (**5**) was less reactive than **1** for C–H arylation with benzene as acceptor, giving only a 35% yield of **2** after 3 h of irradiation (entry 10, Table 1). Moreover, when 1-chloroadamantane was evaluated, no arylation product was found (Table S1, entry 21).

The arylation reaction was also effective, replacing benzene by thiophene, giving the products **4a,b** in 87% yield (Scheme 6). The C–H coupling at the C<sub>2</sub> of the thiophene ring was

Scheme 6. Synthesis of 2- and 3-(1-Adamantyl)thiophene by BHAS

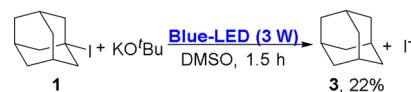


avored, affording a ratio C<sub>2</sub>/C<sub>3</sub> of 97:3. Moreover, the 1-adamantyl radical was previously used in HAS reactions with several benzene derivatives giving Ad-Ar (in 20–50% yields according to the nature of the substituent in the arene)<sup>66</sup> and with 2-substituted benzothiazoles giving 2-adamantylbenzothiazoles (in 50–80% yields depending the nature of the leaving group).<sup>67</sup>

The presence of color in the reaction mixture prompted us to test if only visible light was able to drive the arylation reactions. When the arylation reaction of **1** was photostimulated using blue-LED (3 W, 465 nm), product **2** was obtained in 85% yield after 2 h of irradiation (entry 12). Participation of any vestigial UV light was discarded by performing the reaction with an optical filter (Table S1, entry 19; a transmittance spectrum can be observed in Figures S4 and S5).

Furthermore, reactions in the absence of benzene revealed some conversion, obtaining adamantane (**3**) as the product (Scheme 7 and Table 2) and discarding a key role of benzene in the initiation step.

Scheme 7. Photoinduced Reaction of **1**



All previous results have supported a photoinduced BHAS reaction in the formation of product **2** as depicted in Scheme 2

Table 2. Photoinduced Reduction of **1** with Blue-LED (3 W)<sup>a</sup>

entry	base (equiv)	time (h)	yields <sup>b,c</sup> (%)
1	KO <sup>t</sup> Bu (3)	1.5	3 (22)
2	KO <sup>t</sup> Bu (3)	24	3 (73)
3	Na <sup>+</sup> CH <sub>2</sub> S(O)Me (0.7)	2	3 (13)

<sup>a</sup>The photostimulated reaction was carried out under N<sub>2</sub> atmosphere using **1** (1 equiv, 0.1 mmol) and base in DMSO ([**1**] = 0.1 M) according to method B (entries 1 and 2) or method C (entry 3). <sup>b</sup>Yields were determined by GC (internal standard method). <sup>c</sup>The conversion was not complete.

but replacing the aryl radical ( $\text{Ar}^\bullet$ ) by the 1-adamantyl radical (1-Ad $^\bullet$ ). Related to the initiation event, it is also clear that alkyl halide, base, and light are necessary for the initial ET but benzene is not required (Figure 2). However, questions still

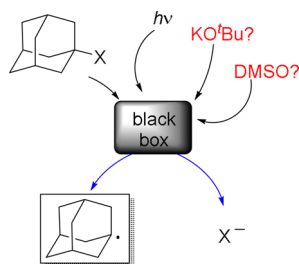


Figure 2. Formation of 1-adamantyl radical by photoinduced BHAS.

remain about the PET initiation step to obtain the initial 1-Ad $^\bullet$ : Is KOtBu the key ingredient or is it something else? And which species is taking the photon?

A screening of different combinations of solvents (DMSO, THF, DMF, MeCN, and DME) and bases (KOtBu, NaOtBu,<sup>68</sup> K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, NaH, DABCO, NEt<sub>3</sub>) (entries 22–41, Table S1, and entries 11–14, Table S2) allowed us to identify two key ingredients in the reaction: DMSO and a strong base (KOtBu, NaH), instead of just KOtBu alone. It was also proved that this method was able to generate radicals in the absence of any chain reaction (Table 2). These experiments and the presence of color in the reaction mixture led us to propose that dimsyl anion or its derivatives, rather than <sup>−</sup>OtBu or <sup>−</sup>H anion, may be responsible for starting the arylation reactions by photostimulated BHAS. Moreover, an analysis of the equilibrium of the anions in the reaction conditions supports the presence of the dimsyl anion at an appreciable concentration.<sup>69</sup> It must be noted that it has been proposed, but not proved, that the dimsyl anion is capable of donating an electron to initiate the transition-metal free reaction.<sup>70–72</sup>

To prove this, dimsyl anion solution was prepared (using NaH or *n*-BuLi in DMSO), and the actual concentration of the dimsyl anion was assayed by titration with carbazole using triphenylmethane as the indicator (see the SI for details).<sup>69</sup> Different equivalents of dimsyl anion were added to a solution containing only **1** and benzene, and after irradiation **2** was obtained in proportional yields (Table 1, entries 13–17). Moreover, the reaction in the absence of benzene gave adamantane **3** in 13% yields (entry 3, Table 2). Finally, the participation of KOtBu as the electron donor was discarded because no product was found when the reaction was assayed in solvents other than DMSO (entries 22–41, Table S1), which was also confirmed in the trapping experiment with norbornene (see below).

Even though the presence of dimsyl anion is clearly essential for the initial PET to take place, a question remains concerning the detailed mechanism. Since the reaction with blue-LED gave the desired product, the species taking the photon should absorb light at  $\lambda > 400$  nm (see emission of blue-LED, Figure S1), and consequently this situation makes it possible to discard the solvent, substrates (**1** and **5**), and benzene as the photoactive species due to the lack of absorption of these compounds above 400 nm (Figure S3). On the other hand, solutions of strong bases in DMSO showed absorption above 400 nm (Figure 3 and Figures S4 and S5).

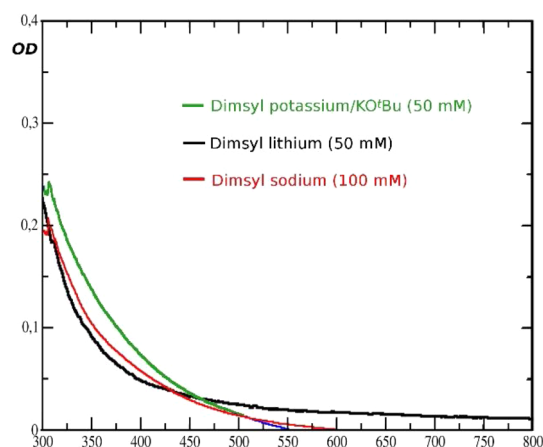


Figure 3. UV-vis spectra of strong bases in DMSO.

These results enabled us to propose three possibilities for the PET involving the dimsyl anion (Scheme 8): photoexcitation of a charge-transfer complex (CTC) formed between the dimsyl anion and substrate **1** followed by ET (path A); ET from an excited dimsyl anion to 1-haloadamantane (path B); or photoejection of an electron from an excited dimsyl anion (path C).

Although a CTC between dimsyl and dithianes was recently proposed in the photoinitiated reductive fragmentation of dithianes,<sup>54</sup> no CTC formation could be found by the UV-vis absorption spectrum between the dimsyl anion and **1** or **5** (see section 5.3 in the SI). Consequently, we studied the photophysical properties of the dimsyl anion to try to understand the nature of the photoinduced initiation step. As expected, the dimsyl anion presented very weak fluorescence, with a small band having a maximum at 477 nm (Figure S9). Fluorescence quenching studies carried out with **1** to support path B in Scheme 8 were not conclusive, and differences were observed with solutions of dimsyl anion prepared by different methodologies.

At this stage, the reported thermal decomposition of DMSO and the dimsyl anion was taken into account as being the possible source of photoactive species which may have participated in the PET. However, the spectroscopic and computational analysis showed that they had no influence in the initiation step.<sup>73</sup>

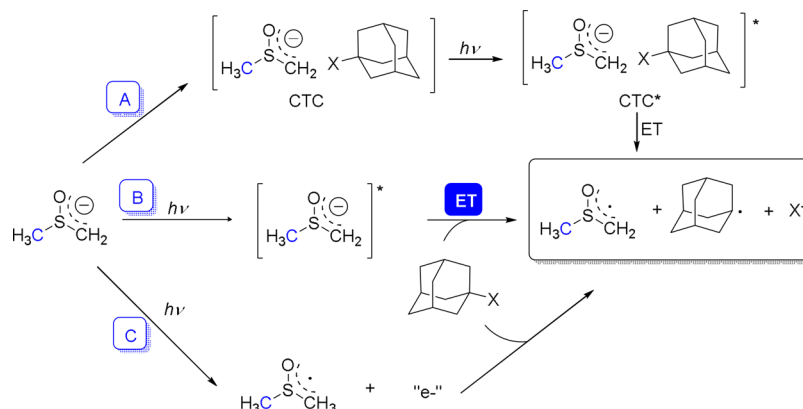
In addition to experimental studies about the initiation step, we employed the Marcus–Hush theory<sup>74</sup> to calculate the activation free energy ( $\Delta G_{\text{ET}}^\ddagger$ ) involved in an outer-sphere ET (eq 1)

$$\Delta G_{\text{ET}}^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{\Delta G_{\text{rel}}}{\lambda} \right) \quad (1)$$

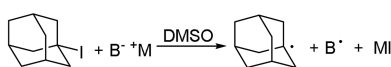
where  $\Delta G_{\text{rel}}$  represents the relative free energy difference between the reactants and products and  $\lambda$  is the reorganization energy. We evaluated the reaction of 1-haloadamantanes with the bases present within the experimental conditions ( $\text{M}^+\text{CH}_2\text{S}(\text{O})\text{CH}_3$  and KOtBu), and the results are summarized in Scheme 9.

In all cases, it was found that the ET process is endergonic from the ground state. However, both  $\text{M}^+\text{CH}_2\text{S}(\text{O})\text{CH}_3$  and KOtBu gave exergonic processes when ET takes place from an excited state, indicating that, when excited, both anions would be able to initiate the arylation reactions. It is clear that dimsyl solution in DMSO absorbs light above 400 nm, but it is not

Scheme 8. Proposed Mechanisms for PET Initiation Step

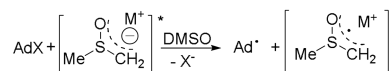
Scheme 9. Calculations of Activation Free Energy ( $\Delta G_{ET}^{\ddagger}$ ) for ET Reactions from Ground State ( $S^0$ ) and Excited State ( $S^1$ ) Using Marcus–Hush Theory

From ground state

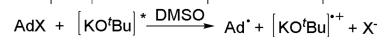


B <sup>+</sup> M	$\Delta G_{rel}$ (kcal.mol <sup>-1</sup> )	$\Delta G_{ET}^{\ddagger}$ (kcal.mol <sup>-1</sup> )
K <sup>+</sup> O <sup>-</sup> Bu	24.8	35.3
Na <sup>+</sup> CH <sub>2</sub> S(O)Me	13.9	29.4
Li <sup>+</sup> CH <sub>2</sub> S(O)Me	15.1	29.4

From excited state



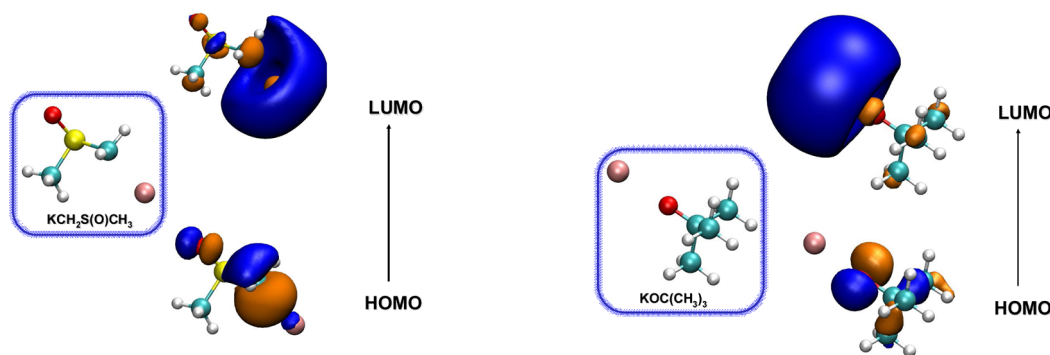
M <sup>+</sup>	X <sup>-</sup>	$\Delta G_{rel}$ (kcal.mol <sup>-1</sup> )	$\Delta G_{ET}^{\ddagger}$ (kcal.mol <sup>-1</sup> )	Conv
Li	I	-71.8	0.49	88
Na	I	-76.1	0.32	98
K	I	-73.0	0.27	100
K	Br	-55.8	4.20	60
K	Cl	-42.5	8.90	0



X	$\Delta G_{rel}$ (kcal.mol <sup>-1</sup> )	$\Delta G_{ET}^{\ddagger}$ (kcal.mol <sup>-1</sup> )
I	-76.6	0.18
Br	-59.3	3.79
Cl	-46.1	8.24

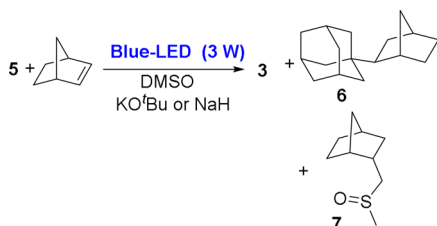
possible experimentally to obtain a solution of pure <sup>-</sup>O<sup>t</sup>Bu in DMSO since there will always be the dimslyl anion present. Hence, an experimental UV–vis spectrum of <sup>-</sup>O<sup>t</sup>Bu in DMF was recorded (Figure S5), discarding any absorption taking place at about 400 nm, and therefore, it is not possible to initiate this reaction if visible light is used. In addition, the absorption (UV–vis) and emission fluorescence spectra were simulated from TD-DFT calculations. In this way, simulated UV–vis spectra revealed a maximum at around ~286 nm for K<sup>+</sup>CH<sub>2</sub>S(O)CH<sub>3</sub> and at ~270 nm for KO<sup>t</sup>Bu (see molecular orbitals HOMO and LUMO in Figure 4 and Figure S12).<sup>75</sup> Meanwhile, for the emission spectra, the maximums were recorded at ~441 nm and ~309 nm, respectively, in agreement with those obtained from the experimental fluorescence spectra (see Figures S9 and S12).

All previous analyses indicated the dimslyl anion as the only base responsible for the initiation step, but it is unclear if path B or C of Scheme 8 is the operating mechanism. In fact, mechanism C cannot be ruled out because photoejection of an electron has been proposed in the photostimulated reaction of **1** with arene thiolate anions.<sup>76</sup> Nevertheless, whatever the case, any ET from the dimslyl anion will generate a dimslyl radical that can be trapped. In order to test an ET from an excited dimslyl anion, radical-trap experiments were performed in the presence of norbornene. In this reaction, we detected the products of the addition of the 1-adamantyl radical and the dimslyl radical to the double bond of norbornene (**6** and **7**, respectively). This finding demonstrated the occurrence of the dimslyl radical and the 1-adamantyl radical from **5** under these working conditions (Scheme 10).<sup>77</sup> Moreover, no products of methylation of

Figure 4. Representations of HOMO–LUMO orbitals of dimslylpotassium and KO<sup>t</sup>Bu. Natural transition orbitals with an isovalue of 0.5 for the HOMO and 0.22 for the LUMO.

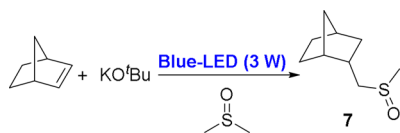
norbornene were detected, which would have been the case if  $^-O^tBu$  had been participating in a ET event (see Schemes S5 and S8).

### Scheme 10. Radical-Trap Experiment



Furthermore, compound 7 was observed even in the absence of substrates 1 or 5, supporting a photoejection mechanism for the initial PET (Scheme 11, path C in Scheme 8).<sup>78</sup> The absence of any product in a dark reaction of Scheme 8 discards the presence of any polar mechanism in the formation of the products.

### Scheme 11. Trapping Dimethyl Radical in the Absence of 5



It may be claimed that the dimethyl radical could be generated via hydrogen atom abstraction by the 1-adamantyl radical from neutral DMSO. However, compound 7 was also detected in the photostimulated reaction of substrate 5, norbornene, and dimethyl anion in THF (a condition in which hydrogen atom abstraction from DMSO is highly unlikely). This result suggests that dimethyl radicals are produced by a PET event, since hydrogen abstraction from the solvent will produce a different radical.

After it was shown that the species responsible for the initiation is clearly independent of the substrate, the present initiation mechanism could be extended to explain other photoinduced related reactions that take place in DMSO in the presence of a strong base, such as BHAS and the S<sub>RN</sub>1 reactions. Initiation by the present mechanism of a BHAS reaction with ArX is supported by the photostimulated reaction of iodobenzene, 4-iodotoluene, 1- and 2-bromonaphthalene, 1-iodonaphthalene, 4-iodobiphenyl, and 9-bromophenanthrene, which gave the reduced expected product (entries 1–7, Table 3). These results indicate that this mechanism is also present in the synthesis of biaryls by photoinduced BHAS, where the reaction does not take place in the absence of DMSO.<sup>52</sup> The commonly observed increase in yield at higher concentrations of the base (KO<sup>t</sup>Bu) in the S<sub>RN</sub>1 reaction also supports the generality of the present initiation.<sup>79–82</sup>

## CONCLUSIONS

In summary, a complete mechanistic picture of the photoinduced ET for C–H functionalization reaction has been presented with a comparative and detailed study carried out at the initiation level allowing us to conclude that the reaction with KO<sup>t</sup>Bu or NaH with DMSO leads to the dimethyl anion, which acts as an electron donor after excitation.

**Table 3. Photoinduced Reduction of ArX with Blue-LED (3 W)<sup>a</sup>**

ArX + KO <sup>t</sup> Bu 3 equiv		Blue-LED (3 W) DMSO, 3 h	ArH + X <sup>−</sup>		
Entry	Substrate	Yields % <sup>b,c</sup>	Entry	Substrate	Yields % <sup>b,c</sup>
1		 37%	5		 61%
2		 58%	6		 32%
3		 38%	7		 34%
4		 41%			

<sup>a</sup>The photostimulated reaction was carried out under N<sub>2</sub> atmosphere using ArX (1 equiv, 0.1 mmol) and KO<sup>t</sup>Bu (3 equiv) in DMSO ([ArX] = 0.1 M) according to method B. <sup>b</sup>Yields were determined by GC (internal standard method). <sup>c</sup>The conversion was not complete.

A direct ET from an excited state or a photoejection of an electron from the dimethyl anion are proposed as being the key step in this photoinduced BHAS, as computational studies supported ET from the excited state but not from the ground state, according with the experimental results. Moreover, the addition of dimethyl radical to the norbornene is a strong proof that the dimethyl radical is present in this mechanism. The presented initiation constitutes a general PET mechanism that could be operating in other photoinduced BHAS or S<sub>RN</sub>1 reactions, and last, but not least, it shows that the energy of visible light is enough to drive this important and sometimes challenging transformation.

## EXPERIMENTAL SECTION

**General Methods and Equipment.** Gas chromatographic analyses were performed using a gas chromatograph with a flame ionization detector and equipped with the following columns: 30 m × 0.25 mm × 0.25 μm column and VF-1 ms 15 m × 0.25 mm × 0.25 μm column. Chromatographic/mass spectrometer analyses were carried out on a GC/MS QP 5050 spectrometer equipped with VF-5 ms, 30 m × 0.25 mm × 0.25 μm column. <sup>1</sup>H NMR (400.16 MHz), <sup>13</sup>C NMR (100.63 MHz) spectra were obtained in CDCl<sub>3</sub> as solvent. Coupling constants are given in hertz, and chemical shifts are reported in δ values in ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. Photoinduced reactions were conducted in a reactor equipped with two Philips HPI-T 400-W lamps (cooled with water) or with blue-LEDs (λ = 465 nm ± 20 nm), 3.5 V, 700 mA emission spectra in Figure S1). Apparatus and irradiation setup is shown in Figure S2.

**Materials.** 1-Iodoadamantane, 1-bromoadamantane, 1-chloroadamantane, iodobenzene, 1-bromonaphthalene, 2-bromonaphthalene, 9-bromophenanthrene, 4-iodotoluene, thiophene, KO<sup>t</sup>Bu, NaH (60% in mineral oil), KOH, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>S·xH<sub>2</sub>O, MeSNa, dimethyl sulfone, 1,4-diazabicyclo[2.2.2]octane (DABCO), triethylamine, 1,4-dinitrobenzene, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), *n*-BuLi (1.6 M in hexane), 18-crown-6-ether, adamantane, benzene, toluene, naphthalene, phenanthrene, carbazole, and triphenylmethane were commercially available and used as received from the supplier otherwise indicated. DMSO, DMF, THF, and 1,2-dimethoxyethane (DME) were dried under molecular sieves (3 Å) according to a reported procedure.<sup>83</sup> Analytical-grade benzene and petroleum ether, stored under Na, were used.

**Typical Procedures for Photoinduced Arylation. Method A.** In a 20 mL flame-dried Schlenk tube, equipped with a N<sub>2</sub> inlet and magnetic stirrer, was added DMSO (5 mL) and the mixture deoxygenated at rt. Then 1-iodoadamantane (0.5 mmol, 131 mg) 1, KO<sup>t</sup>Bu (3 equiv, 177 mg), and benzene were added, and the reaction mixture was irradiated with two Philips HPI-T 400-W lamps (cooled with water) for the time indicated. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with ethyl acetate (3 × 20 mL), and the organic extract was washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under vacuum to leave the crude product.

**Method B.** In a 5 mL snap vial with a magnetic stirring bar were dissolved 1-iodoadamantane (0.1 mmol) and KO<sup>t</sup>Bu in dry DMSO (total volume of the solution 1 mL), and the resulting mixture was degassed by syringe needle. Then benzene (0.40 mmol, 8 equiv) was added under N<sub>2</sub>, and the reaction mixture was irradiated through the plane bottom side of the snap vial using a 465 nm LED. The reaction progress was monitored by GC analysis taking samples with a 50 μL syringe. After the irradiation time, the reaction was transferred into a separating funnel, and 10 mL of water was added. The resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuum.

**Method C.** Reactions with a previously prepared solution of the dimsyl anion: In a 5 mL snap vial with a magnetic stirring bar, 1-iodoadamantane and DMSO (if necessary) were added, and the resulting mixture was degassed by syringe needle. Then a previously prepared solution of dimsyl anion of known concentration (see methods F and G) was introduced under N<sub>2</sub>. Finally, benzene was added (if necessary), and the reaction mixture was irradiated through the plane bottom side of the snap vial using a 465 nm LED. The resulting mixture was extracted with ethyl acetate (3 × 10 mL), transferred into a separating funnel, and 10 mL of water was added. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuum.

**Dark Reactions.** Dark reactions were carried out by covering the vessel with aluminum foil before degasification.

#### Typical Procedure for Gas Chromatographic Quantification.

Two experimental procedures were carried out to quantify substrates and products by the GC (methods D and E). In all cases, the quantification was done by the internal standard method.

**Method D.** Following methods A–C, an internal standard was added to the reaction mixture before workup. After the extraction, the organic layer was injected in the GC without further manipulation.

**Method E.** Reduction reactions were monitored at different reaction times. In a 5 mL snap vial with magnetic stirring bar KO<sup>t</sup>Bu and 0.5 mL of DMSO were added, and the resulting mixture was degassed by syringe needle. Then, 0.5 mL of a degassed solution of the substrate (0.2 M in DMSO) and 10 μL of dodecane (standard) were added via syringe, and the reaction mixture was irradiated through the plane bottom side of the snap vial using a 465 nm LED. Quantification at different reaction times: 50 μL of the crude reaction were taken with a syringe under N<sub>2</sub> and added to a Khan tube with 0.5 mL of ethyl acetate and 0.5 mL of water. After mixing, the organic phase was tacked to another Khan tube, dried with a small portion of Na<sub>2</sub>SO<sub>4</sub>, and injected in the GC.

**Preparation of Dimsyl Solutions in DMSO. Method F.** Dimsyllithium: In a 20 mL flame-dried Schlenk tube equipped with a N<sub>2</sub> inlet and magnetic stirrer was added DMSO (10 mL), and the mixture was degassed. Then *n*-BuLi solution in hexane was added slowly in portions (<0.5 mL each) without stirring to avoid mixing with DMSO. After addition of each portion, hexane was evaporated with vacuum (without stirring) until the upper phase disappeared, and then the mixture was stirred for 1 min. Titration was performed by transferring a 1 mL portion under N<sub>2</sub> (with syringe) to a 5 mL snap vial containing a magnetic stirring bar and triphenylmethane as indicator. The resulting red solution (due to the presence triphenylmethanide anion) was titrated with a degassed solution of carbazole (0.1 M in DMSO) until discoloration of the solution. Titration was performed in triplicate.

**Method G.** Dimsylsodium: In a 20 mL flame-dried Schlenk tube, equipped with a N<sub>2</sub> inlet and a magnetic stirrer, was added NaH 60% in mineral oil (120 mg) and the mixture washed under N<sub>2</sub> with dried petroleum ether (3 × 1 mL). After the last portion of supernatant was taken, vacuum was applied for 5–10 min to eliminate all remaining solvent. Then deoxygenated DMSO (5 mL) was added at rt, and the reaction was stirred at 50 °C during 1 h under N<sub>2</sub>. After this time, the reaction was allowed to reach at rt, and 0.5 mL was taken for titration as previously described for dimsyllithium.

**Characterization Data of Synthesized Compounds.** Adamantane (3), benzene, toluene, naphthalene, and phenanthrene were identified by GC and GC–MS with authentic samples.

**1-Phenyladamantane (2).**<sup>66</sup> The product was purified by radial thin-layer chromatography on silica gel, eluting with petroleum ether, and was isolated as a white solid (113.1 mg, 99% yield from method A): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36–7.29 (4H, m), 7.22–7.16 (1H, m), 2.09 (3H, s), 1.92 (6H, s), 1.80–1.50 (6H, m); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 151.3, 128.1, 125.5, 124.9, 43.2, 36.9, 36.2, 29.0; GC–MS (*m/z*) 212 (M<sup>+</sup>, 53), 169 (13), 156 (19), 155 (100), 115 (14), 94 (14), 91 (22), 79 (11), 77 (13).

**2-(1-Adamantyl)thiophene (4a).**<sup>84</sup> The product was obtained using method A but employing 50 equiv of thiophene instead of benzene in 4 mL of DMSO. The product 4a was purified by column chromatography on silica gel, eluting with pentane/ethyl acetate gradient (100:0 → 80:20), and was isolated as a yellow solid (92.5 mg, 85%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (1H, dd, *J* = 1.2), 6.94 (1H, dd, *J* = 1.6), 6.82 (1H, dd, *J* = 2.4), 2.07 (3H, s br), 1.97 (6H, m), 1.76 (6H, m); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 158.3, 126.3, 121.9, 120.1, 45.0, 36.6, 36.1, 28.9; GC–MS (*m/z*) 219 (M + 1, 10), 218 (M<sup>+</sup>, 62), 162 (15), 161 (100), 128 (13), 124 (24), 97(13), 79 (10).

**3-(1-Adamantyl)thiophene (4b).** Detected by GC–MS and quantified using the same response as 4a: GC–MS (*m/z*) 219 (M + 1, 8), 218 (M<sup>+</sup>, 77), 162 (13), 161 (100), 128 (22), 124 (20), 97(19), 79 (12).

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00822.

Extra experimental details, UV–vis spectra, steady-state fluorescence spectra, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the products, theoretical section (*xyz* of stationary points), Figures S1–S12, and Tables S1–S8 (PDF)

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### Notes

The authors declare no competing financial interest.

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