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Visible light and hydroxynaphthylbenzimidazoline promoted transition-metal-catalyst-free desulfonylation of *N*-sulfonylamides and *N*-sulfonylamines

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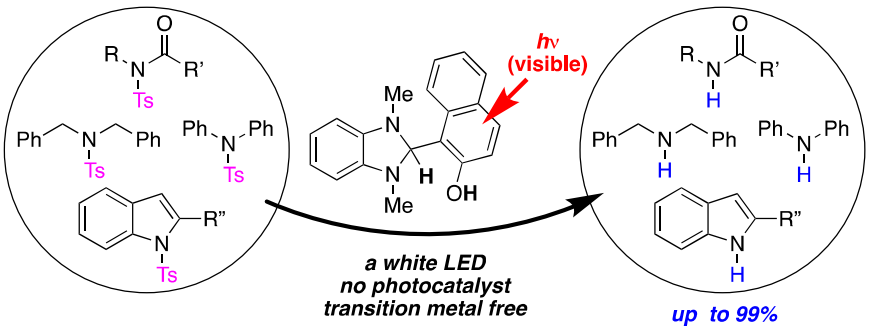


ABSTRACT: A visible light promoted process for desulfonylation of *N*-sulfonylamides and -amines has been developed, in which 1,3-dimethyl-2-hydroxynaphthylbenzimidazoline (HONap-BIH) serves as a light absorbing, electron and hydrogen atom donor, and a household white light-emitting diode serves as a light source. The process transforms various *N*-sulfonylamide and -amine substrates to desulfonylated products in modest to excellent yields. The observation that the fluorescence of 1-methyl-2-naphthoxy anion is efficiently quenched by the substrates suggests that the mechanism for the photoinduced desulfonylation reaction begins with photoexcitation of the naphthoxide chromophore in HONap-BIH, which generates an excited species via intramolecular proton transfer between the HONap and BIH moieties. This process triggers single electron transfer to the substrate, which promotes loss of the sulfonyl group to form the free amide or amine. Results of studies employing radical probe substrates as well as DFT calculations suggest that selective nitrogen-sulfur bond cleavage of the substrate radical anion generates either a pair of an amide or amine anion and sulfonyl radical or that of an amidyl or aminyl radical and sulfinate anion, depending on the nature of the *N*-substituent on the substrate. An intermolecular version of this protocol, in which 1-methyl-2-naphthol and 1,3-dimethyl-2-phenylbenzimidazoline are used concomitantly, was also examined.

INTRODUCTION

Single electron transfer (SET) to LUMOs or from HOMOs of neutral organic molecules generates radical ions, in which one or more covalent bonds are weakened. As a result, various types of bond cleavage reactions of organic radical ions are promoted by SET.[1] Some of these processes, which produce free radical and ionic intermediates, take place efficiently and selectively. As a result, they are valuable for the design of synthetically useful reactions.[2] Because the sulfonyl group is useful for protecting nitrogen containing compounds such as amines and amides, the development of efficient, selective and mild deprotection (desulfonylation) protocols is an important goal in synthetic organic chemistry.[3] Consequently, various methods to promote desulfonylation reactions of *N*-sulfonylamines and -amides, which follow SET induced routes, have been described.[4] The most common approaches of this type include reduction reactions promoted by magnesium and alkaline metals,[5] samarium diiodide,[6] low valent titanium,[7] transition metal salts,[8] organic electron donors,[9] and electrochemistry.[10] Photoinduced electron transfer (PET) is another process that can be employed to initiate reductive *N*-desulfonylation reactions.[11] In seminal studies about three decades ago, Yonemitsu et al uncovered a PET process for desulfonylation of sulfonylamines, which utilizes organic electron donating photocatalysts such as methoxyarenes along with hydride donors such as $NaBH_4$.[11a] Padwa et al later described a direct UV irradiation protocol, in which NEt_3 serves as both an electron and proton donor, and nBu$_3$SnH as a hydrogen atom donor.[11b] Recently, Xiao et al

demonstrated that a process, utilizing an iridium complex as a visible light absorbing catalyst and Hantzsch ester as both an electron and hydrogen atom donor, promotes desufonylation reactions of *N*-sulfonylbenzamides.[11c]

2-Aryl-1,3-dimethylbenzimidazolines (Ar-BIHs) are analogues of the reduced form (NADH) of nicotinamide adenine dinucleotide (NAD^+). As such, these substances serve as effective hydride, hydrogen atom and electron donors.[12] Chikashita et al first recognized that 1,3-dimethyl-2-phenylbenzimidazoline (Ph-BIH) donates a hydride ion to cationic intermediates, generated by complexation of organic substrates with Lewis acids.[13] Subsequently, Tanner et al demonstrated that Ph-BIH also participates in reactions as a sequential hydrogen atom and electron donor.[14] Based on this foundation, about two decades ago we initiated an investigation of reactions, using PET and Ph-BIH, that lead to reductive transformations of organic substances.[15] Ensuing studies by us and others demonstrated that Ph-BIH and related substances do indeed act as effective electron donating reductants in PET promoted reduction reactions.[16,17] Moreover, the redox activity of Ar-BIHs has been used advantageously in investigations related to hydrogen gas evolution,[18] artificial photosynthesis,[19] solar cells,[20] organic semiconductors,[21] and SO_2 activation.[22]

Visible light promoted redox-catalyzed reactions have received recent attention in the area of synthetic organic chemistry.[23] Complexes of transition metals, such as ruthenium and iridium, have been frequently used to promote these types of transformations. However, more economical as well

as sustainable PET procedures, which do not use expensive transition metals, are also highly attractive. Because of these features, our studies have focused on the design of visible light promoted redox reactions that are analogous to those in which Ar–BIH serves as a reductant. In this context, we developed a desulfonylation reaction of *N*-sulfonylindoles, which utilizes substituted pyrenes as organic photocatalysts and Ar-BIHs as reductants.[16b] In recent investigations, we designed Ar–BIH analogues, which contain arene or hydroxyarene chromophores connected to the BIH framework to extend their light absorption profile into the visible light region.[24] Thus, investigations of PET promoted desulfonylation reactions of *N*-tosylbenzamides independently conducted by Yu[17a] and Xiao[11c] (Figure 1), particularly motivated us to apply the protocol utilizing a visible light absorbing HOAr-BIH to the desulfonyltaion reactions of their substrates and others. In the study described below, we discovered that one substance of this type, 1,3-dimethy-2-(2-hydroxynaphthyl)bennzimidazoline (HONap-BIH, **1a**), serves as an effective visible light absorbing reducing agent in desulfonylation reactions of *N*-tosylbenzamides **2**, dibenzyl tosylamine **4,** diphenyl tosylamine **6**, *N*-sulfonyl indols **8** to produce respective desulfonylated compounds **3**, **5**, **7**, and **9** by using a household 7.3 W white light-emitting diode (LED). The new protocol has the highly advantageous feature of not requiring a visible light absorbing transition metal catalyst because HONap-BIH absorbs light in the visible region, and

HONap-BIH serves as a formal two hydrogen atom donor in a manner that is similar to that of Hantzsch ester.[24a,24b]

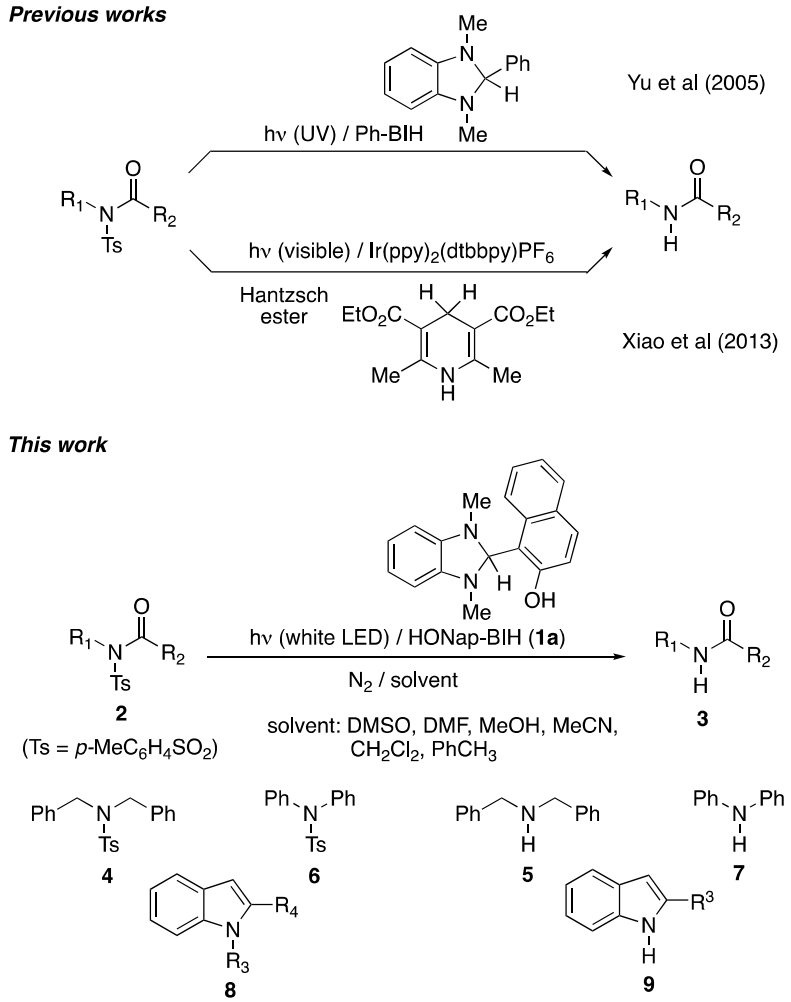


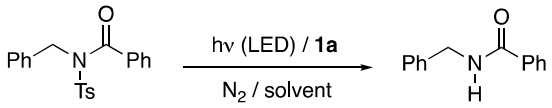
Figure 1. PET promoted desufonylation reactions of sulfonamides.

RESULTS AND DISCUSSION

In the initial phase of this study, we assessed the viability of desulfonylation reactions of *N*-sulfonylamides promoted by hydroxynaphthylbennzimidazoline **1a**. For this purpose,

photoreactions of *N*-benzyl-*N*-tosylbenzamide (**2a**) (0.1 M) in various solvents were carried out in the presence of **1a** with irradiation using a white LED for 1 h (Table 1, and also see Figure S1). Under these conditions, the expected desulfonylation product, *N*-benzylbenzamide (**3a**) is formed in excellent yields when DMSO, DMF and $PhCH_3$ are used as solvents (entries 1, 2, 3 and 9). Although reactions in MeOH, MeCN and CH_2Cl_2 do not proceed to completion, the yields of **3a** based on the conversion of **2a** are high (entries 6, 7, and 8). While the yields of **3a** decrease as the quantity of **1a** is reduced for reactions of **2a** in DMF, an excellent mass-balance is maintained (entries 4 and 5).[25]

Table 1. Photodesulfonylation of *N*-benzyl-*N*-tosylbenzamide (2a) in various solvents[a]



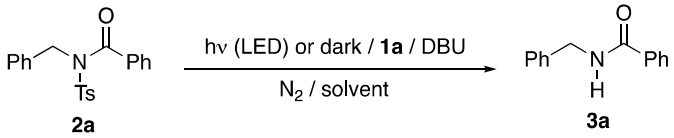
2a **3a**

entry	**1a** (equiv)	solvent	conv of **2a** (%)[b]	yield of **3a** (%)[b,c]
1	1.5	DMSO	100	97 [99][d]
2	1.5	DMF	100	99
3	1.2	DMF	100	97
4	1.0	DMF	87	81 (93)
5	0.5	DMF	49	49 (100)
6	1.5	MeOH	34	30 (88)
7	1.5	MeCN	87	83 (95)
8	1.5	CH_2Cl_2	94	93 (99)
9	1.5	$PhCH_3$	100	98

[a]**2a** (0.10 mmol), **1a** (0.5~1.5 equiv vs **2a**), solvent (1.0 mL); 7.3 W white LED, 1 h. [b]Determined by using ^{1}H NMR. [c]The yields in the parenthesis are based on conversion of **2a**. [d]Yield of **3a** isolated by column separation.

While conducting experiments described above, we found that reaction of **2a** in the presence of **1a** proceeds to some extent in the absence of LED irradiation. To obtain information about this phenomenon, the irradiation time was shortened from 1 h to 20 min, at which time 2-bromoacetophenone was added to prevent further reaction of **2a** caused by the remained **1a** with a ambient light during work up.[26] Also, the effect of base on the process was examined by including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the reaction mixture.[24b,24c,27] As can be seen by viewing the results in Table 2, the extent of the reaction promoted by 20 min LED irradiation (LED-ON) of a mixture of **1a** and **2a** is significantly greater than that occurring without irradiation (LED-off) in all solvents employed.[28] Moreover, the presence of DBU enhances the progress of the reaction conducted using either dark or irradiation conditions (compare entries 6 and 8 to 5 and 7 respectively).

Table 2. The effect of LED irradiation on photodesulfonylation of 2a in the presence or absence of DBU in various solvents[a]



2a **3a**

entry	LED	DBU	solvent	conv of **2a** (%)[b]	yield of **3a** (%)[b,c]
1	ON	-	DMSO	83	80 (96)
2	off	-	DMSO	9	8 (89)
3	ON	-	DMF	100	94
4	off	-	DMF	12	9 (75)

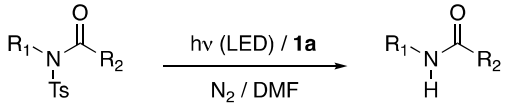
5	ON	-	CH_2Cl_2	42	41 (98)
6	ON	added	CH_2Cl_2	91	84 (92)
7	off	-	CH_2Cl_2	12	11 (92)
8	off	added	CH_2Cl_2	29	27 (93)
9	ON	-	$PhCH_3$	100	99
10	off	-	$PhCH_3$	13	11 (85)

[a]**2a** (0.10 mmol), **1a** (1.5 equiv vs **2a**), DBU (1.5 equiv vs **2a**), solvent (1.0 mL); 7.3 W white LED or in the dark, 20 min. [b]Determined by ^{1}H NMR. [c]Yields in the parenthesis are based on the conversion of **2a**.

Next, this protocol was applied to desulfonylation of sufonamides **2**, which contain various *N*- and carbonyl substituents with differing electron accepting and donating abilities (Table 3). The results show that the extents of substrate conversion and yields of these reactions directly correlate with the electron accepting abilities of the R_2 group in the carbonyl moiety (except for the *p*-nitrophenyl substituted amide **2c**, entry 3), which are estimated using reduction potentials ($E^{red}_{1/2}$, see Figure S4 and Table S2) of the corresponding *N*-tosylamides (see entries 1, 2, 4, 6, 8, 10). Although substrates possessing *p*-methoxyphenyl (**2d**) as well as alkyl (**2f**) or nonconjugated alkenyl (**2g**) carbonyl substituents require longer irradiation times for completion, all substrates except for **2c** react to form the corresponding desulfonylated amides in >90% yields. The behavior of **2c** is interesting in that, although it is consumed, it does not produce the expected desulfonylated product **3c** under the conditions used to smoothly desulfonylate other *N*-tosylamides (entry 3). Analysis of the reversible cyclic voltammogram (CV) of **2c** (Figure 2) suggests that its radical anion

formed by SET is more stable than those of related amides **2** and, thus, this intermediate might be less prone to N-S bond cleavage (see below).[29] Also it should be noted that alkene tethered substrates **2f** and **2g**, which are designed to undergo intramolecular amidyl radical trap via fast 5-exo cyclization,[30] did not produce the expected cyclized products (Figure 3). This observation suggests that the amidyl radicals would not be produced by fragmentation of the radical anions of **2f** and **2g** (see below).

Table 3. Photodesulfonylation of various *N*-tosylamides 2 in DMF[a]



2 **3**

entry	**2**	R^1	R^2	$E^{red}_{1/2}$ (V *vs* SCE)	time (h)	conv of **2** (%)[b]	yield of **3** (%)[b,c]
1[d]	**2a**	$PhCH_2$	Ph	-1.58	1	100	97
2	**2b**	$PhCH_2$	*p*-ClC_6H_4	-1.52	1	100	91
3	**2c**	$PhCH_2$	*p*-$NO_2C_6H_4$	-0.87. -1.16	1	23	0
4	**2d**	$PhCH_2$	*p*-$MeOC_6H_4$	-1.69	1	32	31 (97)
5					4	100	98
6	**2e**	$CH_3(CH_2)_3$	Ph	-1.64	1	54	40 (74)
7					3	100	95
8	**2f**	CH_2=$CH(CH_2)_3$	Ph	-1.66	1	70	65 (93)
9					2	100	97
10	**2g**	$PhCH_2$	CH_2=$CH(CH_2)_2$	-1.94	1	17	12 (71)
11					4	32	30 (94)
12					24	100	90

[a]**2** (0.10 mmol), **1a** (1.2 equiv vs **2**, 1.5 equiv and 2.0 equiv for entries 11 and 12), DMF (1.0 mL); 7.3 W white LED. [b]Determined by ^{1}H NMR. [c]Yields in the parenthesis are based on the conversion of **2a**. [d]Same as entry 3 of Table 1.

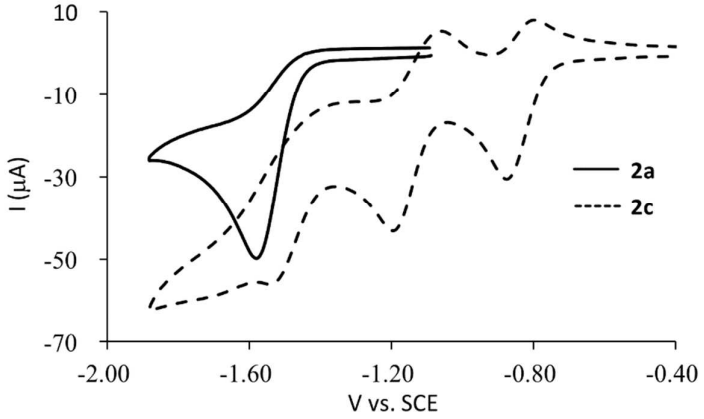


Figure 2. Cyclic voltammograms of **2a** and **2c** in MeCN.

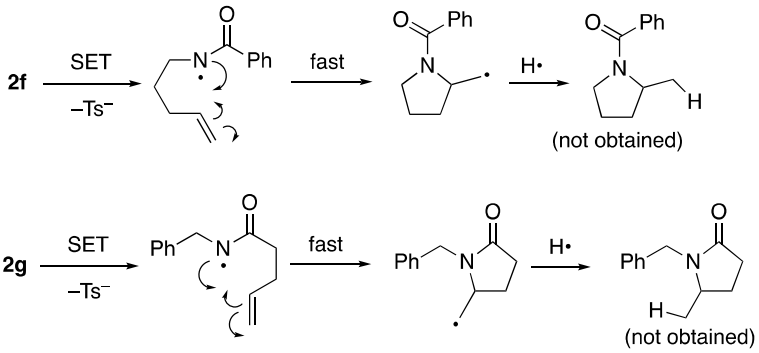


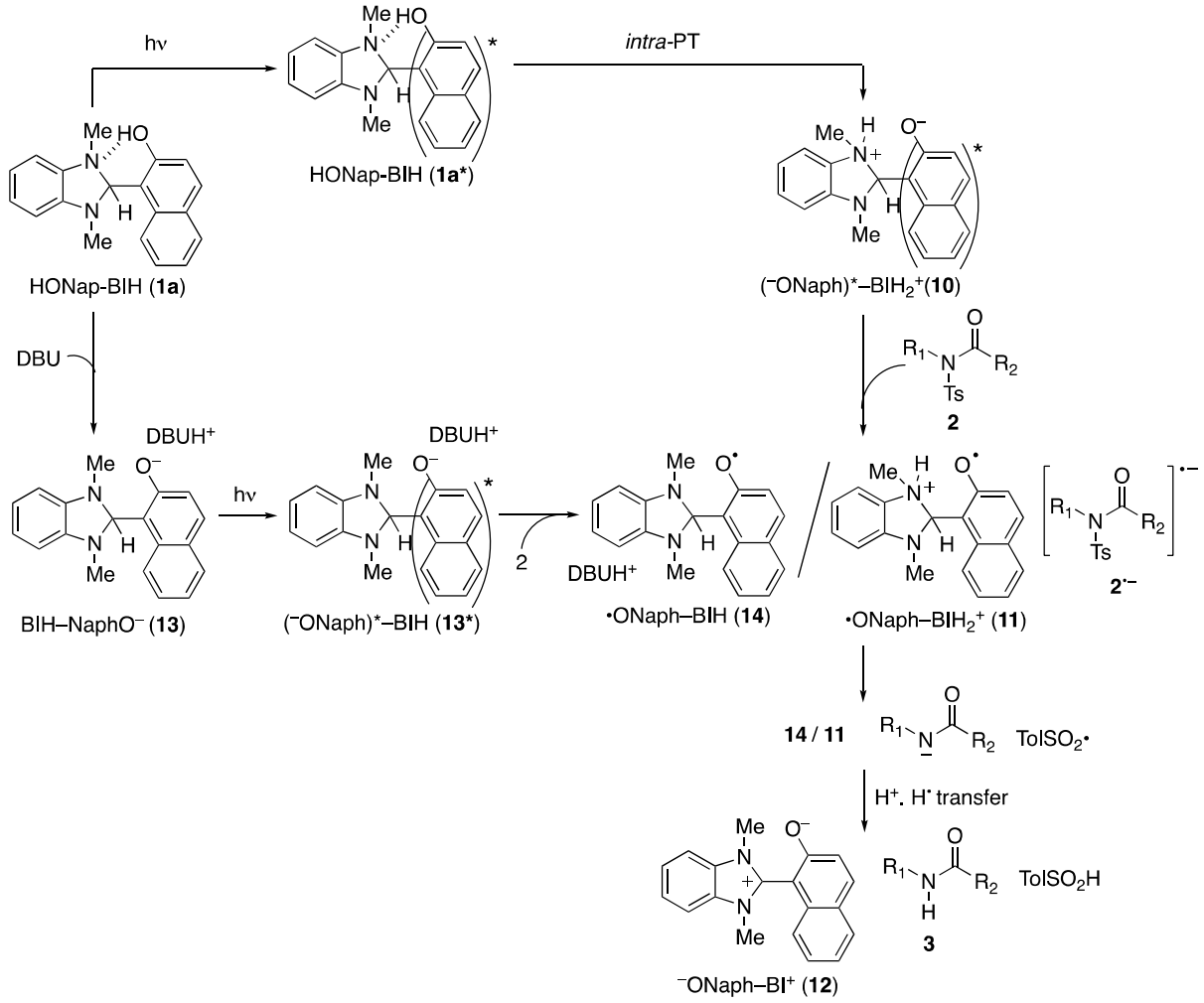
Figure 3. Expected radical cyclization of *N*-centered radicals derived from **2f** and **2g**.

A plausible mechanism for the photoinduced desulfonylation reaction, which is consistent with the observations described above, is shown in Scheme 1. It is known that photoexcitation of naphthols enhances their acidities and that deprotonation of their excited states produces excited states of naphthoxides.[31] In addition, the observation that the ^{1}H NMR spectra of **1a** in $CDCl_3$,[24a]

CD_3CN and DMSO-d_6 contain respective peaks at 10.43, 10.54, and 9.95 ppm (see Experimental Section), suggests the existence of an intramolecular hydrogen bond between the hydroxyl substituent of the naphthol group and nitrogen of the benzimidazoline moiety.[32] As a result, a suitable conformation appears to exist in the ground state of **1a** for intramolecular proton transfer (*intra*-PT) between hydroxynaphthyl and benzimidazoline moieties. Because the photoexcited 2-naphthol is sufficiently acidic to donate proton to an aromatic amine,[31b] it is plausible to suggest that photoexcited **1a** (**1a***) undergoes rapid intramolecular proton transfer to give the excited state species **10** containing a protonated benzimidazoline group and naphthoxide moiety. Subsequent SET from **10** to the tosylbenzamide **2** produces the corresponding naphthoxy radical **11** and radical anion $\mathbf{2}^{\bullet-}$.[33] Nitrogen-sulfur (N-S) bond cleavage in $\mathbf{2}^{\bullet-}$ then occurs to form a benzamide anion and sulfonyl radical. This proposal is also consistent with the observation that substrates **2f** and **2g** did not produce the expected amidyl radical cyclization products (see above and below). Finally proton transfer and hydrogen atom from **11** to the respective benzamide anion and sulfonyl radical fragments produce amide **3** and *p*-toluenesulphenic acid along with benzimidazolium naphthoxide **12**.[34] When present in the reaction medium, DBU deprotonates **1a** generating bennzimidazoline nahthoxide **13**, which serves as the light absorbing species.[24b,24c] In this case, photoexcitation of **13** forms **13***, which donates an electron to **2** giving bennzimidazoline nahthoxyl radical **14** and $\mathbf{2}^{\bullet-}$,

which follow a reaction pathway that is similar to that of the **11** and $\mathbf{2}^{\bullet-}$ pair to ultimately produce **3** and *p*-toluenesulphenic acid along with benzimidazolium naphthoxide **12**.[33]

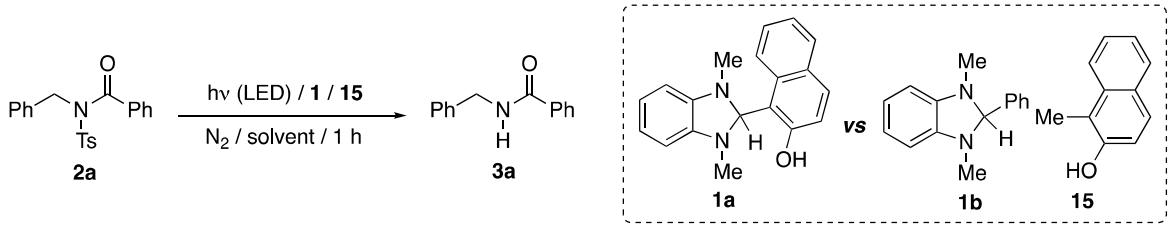
Scheme 1. Plausible mechanism for the photodesulfonylation reaction of 2 promoted by photoexcitation of 1a



As described above, photoexcitation of naphthoxy moiety of **1a** is the initial step in the mechanistic route for the desufonylation reaction. Moreover, we have previously developed the

photosensitization system in which organic sensitizers such as substituted pyrenes and anthracenes cooperate with 1,3-dimethyl-2-phenylbenzimidazoline (**1b**) and its derivatives.[16b,16c] Above discussion and our previous effort lead to the question of whether or not a combination of 1-methyl-2-naphthol (**15**) and **1b**, an intermolecular photo-reductant (inter-PR) analog of **1a**, would promote photoinduced desulfonylation reaction of **2** upon visible light irradiation (see Figure S2). The results of experiments designed to answer this question (Table 4) show that the inter-PR system comprised of **15** and **1b** effectively promotes desulfonylation of **2a** in DMF to form **3a** in excellent yields that are comparable to those for the reaction using **1a** (see entries 1 and 2). Moreover, the inter-PR-system promotes desulfonylation reaction of **2a** in nonpolar solvent such as $PhCH_3$, albeit less efficiently than that induced by **1a** (compare entry 6 to 5). Notably, reaction of **2a** does occur using **15** in the absence of **1b** while **1b** alone does promote the reaction inefficiently in DMF but not in $PhCH_3$ (entries 3 and 7).

Table 4. Comparison of photodesulfonylation of 2a promoted by 1a with that induced by the intermolecular photo-reductant (inter-PR) comprised of Ph-BIH (1b) and MeNaphOH (15)[a]



entry	**1**	**15**	solvent	conv of **2a** (%)[b]	yield of **3a** (%)[b,c]
1[d]	**1a**	-	DMF	100	97

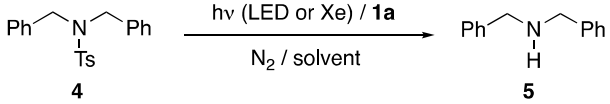
2	**1b**	added	DMF	100	98
3	**1b**	-	DMF	37	35 (95)
4	-	added	DMF	3	0
5[e]	**1a**	-	$PhCH_3$	100	98
6	**1b**	added	$PhCH_3$	34	26 (76)
7	**1b**	-	$PhCH_3$	2	0

[a]**2a** (0.10 mmol), **1** (1.2 equiv vs **2a**, 1.5 equiv of **1a** for entry 5), **15** (1.2 equiv vs **2a**), solvent (1.0 mL); 7.3 W white LED, 1 h. [b]Determined by using ^{1}H NMR. [c]Yields in the parenthesis are based on the conversion of **2a**. [d]Same as entry 3 of Table 1. [e]Same as entry 9 of Table 3.

A possibility exists that the high reactivity of *N*-tosylamides **2** in photoinduced desulfonylation reaction could be a consequence of the presence of an electron withdrawing aroyl substituents. To investigate this issue, we explored the applicability of the protocol to desulfonylation reactions of *N*-tosyl-*N,N*-dibenzylamine (**4**) which is a much weaker electron acceptor than the amide analog **2a** as demonstrated by its large reduction potential ($E^{red}_{1/2}$ = -2.39 V vs SCE). Photoreactions were carried on mixtures of **1a** and **4** in various solvents by utilizing not only LED but also Xe-lamp irradiation. LED irradiation of a mixture of **1a** and **4** in DMSO for 24 h does not lead to formation of *N,N*-dibenzylamine (**5**) (Table 5, entry 1). In contrast, irradiation of a mixture that also contains *t*-BuOK to activate **1a**,[24c] leads to desulfonylation of **4** to give **5** although only in a modest yield (entry 2). Irradiation using a Xe lamp for a shorter 6 h time period also promotes reaction of **4** to give **5** in slightly higher yield (entry 7). Interestingly, the results of a solvent optimization study (entries 5, 6 and 11–14) show that photoreaction in a 1:1 mixture of DMSO and $PhCH_3$ occurs with

the highest conversion of **4** and yield of **5**. Another notable observation is that the presence of 1,4-cyclohexadiene, while decelerating the process, leads to a significant enhancement in the yield of **5** (compare entries 3 and 9 to 1 and 8 respectively). On the other hand, styrene does not greatly influence the conversion of **4** as well as the yield of **5** (entries 4 and 10). Finally, the inter-PR-system comprised of **1b** and **15** does not promote desulfonylation of **4** (results not shown in Table 5).

Table 5. Photodesulfonylation of *N,N*-dibenzyl-*N*-tosylamine (4)[a]

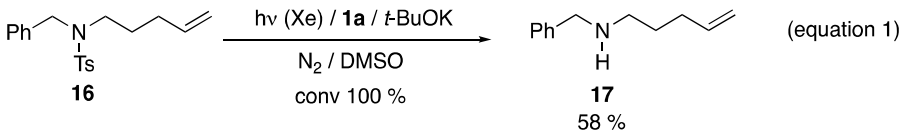


4 **5**

entry	*t*-BuOK (equiv)	Additive (equiv)	solvent	lamp	time (h)	conv of **4** (%)[b]	yield of **5** (%)[b,c]
1	-	-	DMSO	LED	24	11	0
2	1.5	-	DMSO	LED	24	84	47 (56)
3	1.5	CHD (5.3)	DMSO	LED	24	56	53 (95)
4	1.5	styrene (3.0)	DMSO	LED	24	89	53 (60)
5	1.5	-	DMSO/$PhCH_3$ (1/1)	LED	24	100	73
6	1.5	-	$PhCH_3$	LED	24	56	45 (80)
7	1.5	-	DMSO	Xe	6	75	58 (77)
8	1.5		DMSO/$PhCH_3$ (1/1)	Xe	6	100	56
9	1.5	CHD (5.3)	DMSO/$PhCH_3$ (1/1)	Xe	6	66	59 (89)
10	1.5	styrene (1.0)	DMSO/$PhCH_3$ (1/1)	Xe	6	85	69 (81)
11	1.5		DMSO/$PhCH_3$ (1/4)	Xe	6	64	62 (97)
12	2.0		DMSO/$PhCH_3$ (1/4)	Xe	6	100	81
13	2.0		DMSO/$PhCH_3$ (1/9)	Xe	6	45	44 (98)
14	1.5		$PhCH_3$	Xe	6	26	10 (38)

[a]**4** (0.10 mmol), **1a** (1.5 equiv vs **4**), *t*-BuOK (1.5–2.0 equiv vs **4**), additive: 1,4-cyclohexadiene (CHD) and styrene, solvent (1.0 mL); 7.3 W white LED and and 500 W Xe-lamp ($\lambda > 390$ nm). [b]Determined by using ^{1}H NMR. [c]Yields in the parenthesis are based on the conversion of **4**.

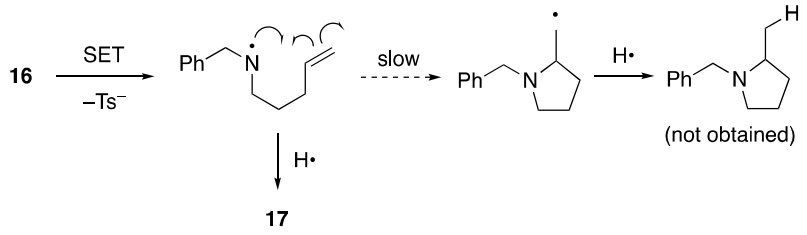
Although it is difficult to explain some of these observations, the fact that the presence of hydrogen atom donors such as CHD and $PhCH_3$ lead to increased yields of **5** does suggest that radical intermediates are involved in the process. Then, in order to gain the information of the expected radical intermediate, we examined the reaction of alkene tethered substrate **16**. However, the expected radical cyclization product was not formed while the deprotected amine **17** was obtained in modest yield as a major product (equation 1).



(equation 1)

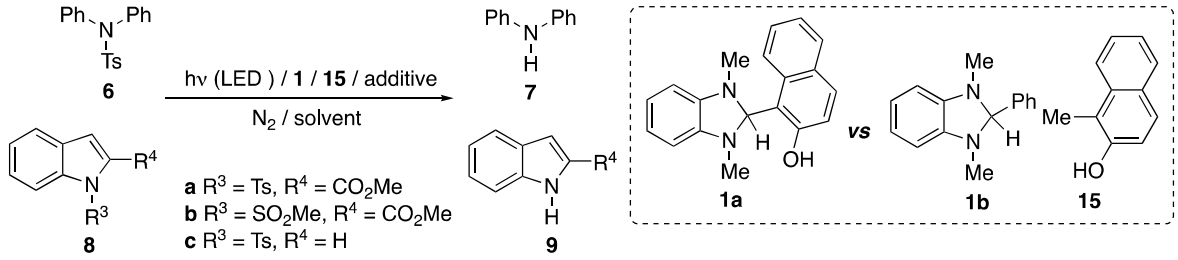
Since 5-exo cyclization of aminyl radical is much slower process than that of amidyl radical,[35] the aminyl radical derived from **16**, even if it is formed, would undergo a competitive hydrogen atom abstraction from a appropriate donor, for example **14** in Scheme 1 (Scheme 2).

Scheme 2. Competitive radical pathways of aminyl radical derived from 16



The visible light promoted process, using **1a** or the inter-PR-system analog comprised of **15** and **1b**, is applicable to the desulfonylation reaction of *N,N*-diphenylsulfonylamine **6** ($E^{red}_{1/2}$ = -2.07 V vs SCE) and the *N*-sulfonylindoles **8a**–**8c** ($E^{red}_{1/2}$ = -1.67 V, -1.74 V, and -1.92 V vs SCE for **8a**, **8b**, and **8c**, respectively). The results (Table 6) demonstrate that 24 h irradiation of DMSO solution of **6** containing **1a** produces the secondary amine **7** in a good yield and that presence of DBU in the reaction mixture enhances the efficiency of the process enabling **7** to be formed in high yield after only a 2 h irradiation period (entries 2-6). Likewise, photodesulfonylation of **8** using **1a** produces the corresponding deprotected indoles **9** in good to excellent yields (entries 7, 8, and 9). The inter-PR-system of **1b** and **15** was found to promote formation of **9** from **8** in modest to good yields (entries 10- 14).

Table 6. Photodesulfonylation reactions of 6 and 8 by using 1a and the inter-PR system comprised of 1b and 15



entry	substrate	1	15	DBU	solvent	time (h)	conv (%)	product	yield (%)
1	**6**	**1a**	-	-	DMSO	2	38	**7**	32 (84)
2	**6**	**1a**	-	added	DMSO	2	73	**7**	66 (90)
3	**6**	**1a**	-		DMSO	24	84	**7**	79 (94)
4	**6**	**1b**	-	-	DMSO	2	29	**7**	28 (97)
5	**6**	**1b**	-	added	DMSO	2	44	**7**	32 (73)
6	**6**	**1b**	added		DMSO	24	100	**7**	79
7	**8a**	**1a**	-	-	DMF	3	100	**9a**	97 [99][d]
8	**8b**	**1a**	-	-	DMF	3	100	**9a**	98
9	**8c**	**1a**	-	-	DMF	3	100	**9c**	83
10	**8a**	**1b**	added	-	DMF	3	100	**9a**	90
11	**8a**	**1b**	-	-	DMF	3	15	**9a**	0
12	**8a**	**-**	added		DMF	3	5	**9a**	0
13	**8b**	**1b**	added	-	DMF	3	100	**9a**	76
14	**8c**	**1b**	added	-	DMF	3	79	**9c**	55 (70)

[a]**6** or **8** (0.10 mmol), **1** (1.2 equiv vs substrate), **15** (1.2 equiv vs substrate), DBU (1.2 equiv vs **6**), solvent (1.0 mL); 7.3 W white LED. [b]Determined by using ^{1}H NMR. [c]Yields in the parenthesis are based on the conversion of **6** or **8**. [d]Yield of **9a** isolated by column separation.

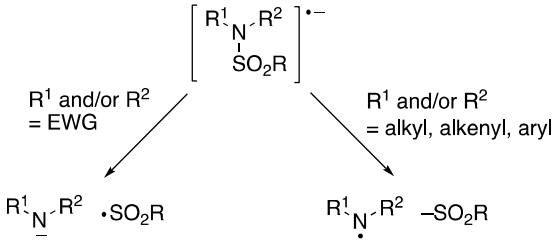
A key step in the proposed mechanism for the visible light promoted desulfonylation reaction of *N*-sulfonlyamides and -amines involves SET. The observation of quenching of emission (fluorescence) from a photoexcited substance is a general method employed to determine if and when it interacts with a substrate through SET. In the proposed mechanistic route (Scheme 1),

photoexcitation of **1a** or its corresponding anion **13** produces the excited naphthoxide species, which donates and electron to the sulfonamide substrate. Unfortunately, the use of emission spectroscopy to gain evidence for the occurrence of this SET process is blocked by the fact that the excited state of **1a** is non-emissive. However, we observed that 1-methyl-2-naphthoxy anion, derived from the corresponding naphthol **15**, emits.[36] Specifically, a solution of DBU and **15** in DMSO emits light with a wavelength maximum at 469 nm when excited at 400 nm, a wavelength at which **15** does not absorb light (Figure S2 and Figure S6). As a result, fluorescence quenching experiments were carried out using the DBU and **15** system and the representative sulfonylamides and -amines **2a**, **4**, **6**, and **8a** as quenchers (Figure S7). As expected based on the reduction potentials of the quenchers (see above), fluorescence quenching occurs with efficiencies (k_q) that are directly dependent on the electron accepting abilities of *N*-sulfonylamides and -amine ($10^9 k_q$ $(M^{-1}s^{-1})$ = 24.9 for **2a**, 12.8 for **8a**, 4.34 for **6**, 3.28 for **4**).[37] The results suggest that the excited napthoxide species formed from **1a** participates in SET to the substrates in the photoreactions.

Radical anions derived from *N*-sulfonylamides and -amines are proposed to be intermediates in the visible light promoted desulfonylation process. N–S bond cleavage in these radical anions can generate either *N*-centered anions or -radicals in a manner that should be dependent on the nature of the *N*-substituent.[6b,9b,10a,10c,11,16b,17a] Accordingly, radical anions derived from substrates with electron withdrawing (EWG) *N*-substituents (eg., **2**) should prefer fragmentation to give amide

anions ($R_1R_2N^-$ in Scheme 3) and sulfonyl radicals ($RSO_2^{\bullet}$), while those containing electron donating alkyl substituents (eg., **4** and **6**) should produce aminyl radicals ($R_1R_2N^{\bullet}$) and sulfinate anions (RSO_2^-). On the other hand, radical anions of **8** are expected to react by either route depending on the nature of the C_2 substituent.

Scheme 3. Hypothetical N–S bond cleavage reactions of *N*-sulfoyl-amide and -amine radical anions.



In order to gain additional information about the electronic structures as well as the nature of N-S bond cleavage in the *N*-sulfonylamide and -amine radical anions, DFT calculations using B3LYP/6-31+G(d) were conducted on neutral forms as well as radical anions of representative substrates.[38a] The LUMO electron distributions of **2a**, **2c**, **4**, **6**, **8a**, and **8c** are shown in Figure 4. While LUMO coefficients exist only on nitrobenzoyl moiety of **2c**, those of **2a**, **4**, **6**, **8a** and **8c** are located on the tosyl moieties and N–S bonds. Although several conformers with close energies exist for all *N*-sulfonylamides and -amines (see the cases of **2a** and **2c** in Table S5 and Table S7,

respectively), the LUMO distributions of these species are nearly identical for all conformers. The geometry optimized radical anions, calculated starting with the initial geometries of the corresponding neutral molecules, have structures containing elongated N–S bonds (see the case of **2a** in Table S6), which suggests that these bonds are significantly weakened. Another local energy minimum conformer of the radical anion of **2a** contains a normal N–S bond (ca. 1.7 Å) , but the barrier for its N–S cleavage was calculated to be small (< 2.82 kcal mol^{-1}, see Table S9 and Figure S8). This finding suggests that rapid dissociation to form two fragments takes place prior to a conformational change in all cases except the radical anion of **2c** (see below).

The optimized global minimum energy structures of the radical anions are given in Figure 5 (also see Table S10). The N–S atomic distances of radical anions of **2a** (2.722 Å) and **4** (4.665 Å) are significantly longer than those of their neutral forms, **2a** (1.730 Å) and **4** (1.675 Å). The global minimum structure of the radical anion of **2c** has an elongated N–S bond (Figure 5) However, careful optimization, using its neutral form (1.736 Å, conformer A in Table S7) as the initial geometry, affords a structure having a slightly shortened N–S bond (1.699 Å, conformer A in Table S8) and an activation energy of N–S cleavage (5.32–9.24 kcal mol^{-1}), which is much greater than that of **2a** (see Table S9 and Figure S8). The results are consistent with the observations that **2c** is less reactive compared to other *N*-sulfonylamides and -amines (see Table 3) and its CV displays quasi-reversible redox behavior (Figure 2).

Finally, the results of atomic charge and spin by natural population analysis [38b] reveal that the radical anion of **2a** should undergo preferential fragmentation to give benzamide anion- ($BzBnN^-$, fragment charge –0.62) and *N*-tosyl radical ($TS^•$, fragment spin 0.61) species while the aminyl radical- ($Bn_2N^•$, fragment spin 0.97) and tosyl anion (TS^-, fragment charge –0.92) are generated preferentially from the radical anion of **4** (details see Table S10 and Table S11). Also, the results suggest that cleavage of the radical anion of the sulfonylindole, which lacks a methoxycarbonyl substitutent, slightly favors formation of the aminyl radical (compare **8c** to **8a**).

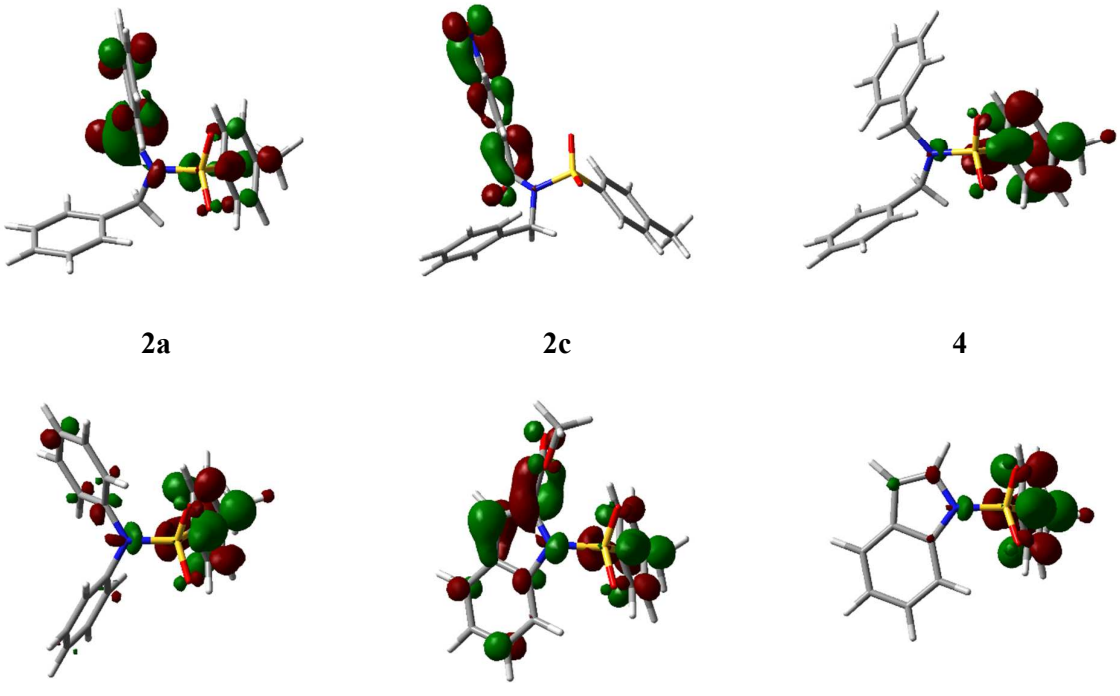


Figure 4. LUMO distributions of **2a**, **2c**, **4, 6, 8a,** and **8c**.

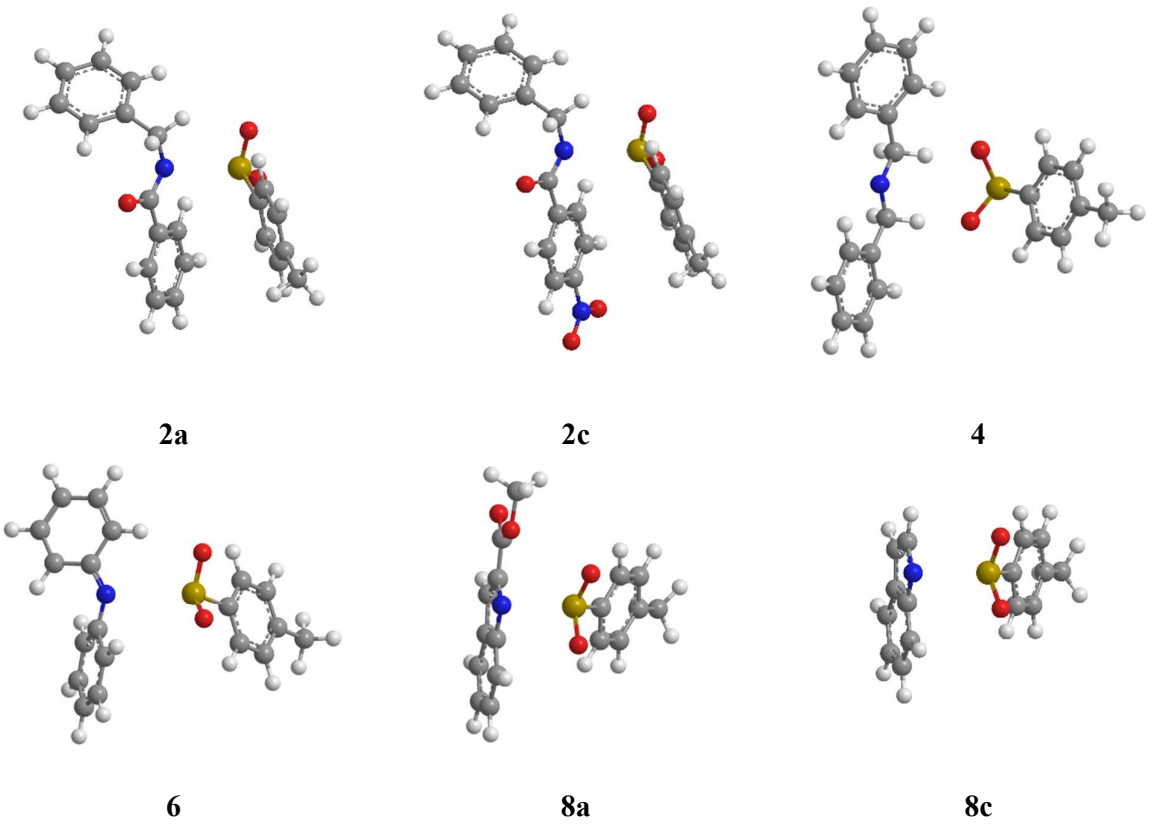


Figure 5. Optimized global minimum structures of radical anions of **2a**, **2c**, **4, 6, 8a,** and **8c**.

DFT calculation of the radical probe substrates **2f**, **2g** and **16** show that they have LUMO distributions that are similar to those of **2a** and **4** respectively (Figure 6)**.** As a result, **2f** and **2g** should undergo fragmentation in a similar manner to form amide anions and *N*-tosyl radicals (Figure 7, also see Table S10 and Table S11). This prediction is consistent with the reaction of **2f** and **2g** because the amide anion derived from the radical anions is not expected to undergo cyclization. Moreover, the calculation suggest that cyclization of the corresponding amidyl radical ($H_2C{=}CH(CH_2)_3BzN^{\bullet}$) would be energetically feasible (ΔG = –6.75 kcal/mol, $\Delta G^{\ddagger}$ = 9.70 kcal.mol)

(see Table S12). On the other hand, aminyl radical (H_2C=CH(CH_2)$_3$BnN$^{\bullet}$) generated from radical anion of **16** is less likely to cyclize because this process is slightly endergonic (ΔG = 2.68 kcal/mol) and has a high activation energy ($\Delta G^{\ddagger}$ = 16.32 kcal/mol) (see Table S12).

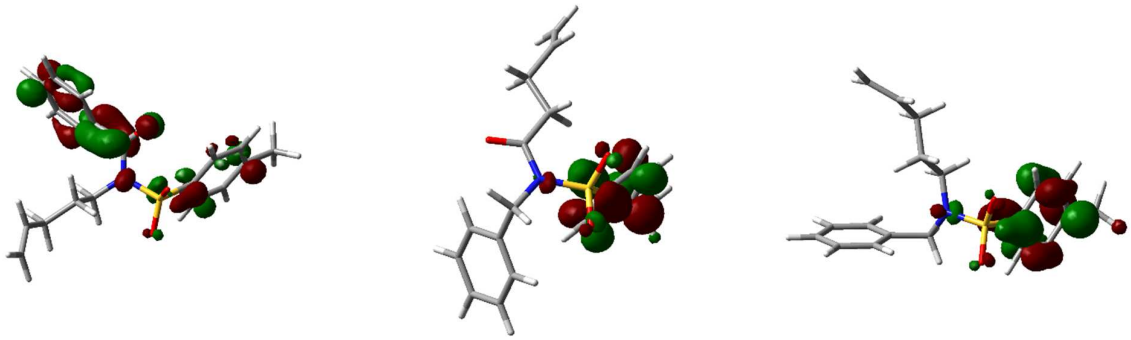


Figure 6. LUMO distributions of **2f**, **2g**, and **16.**

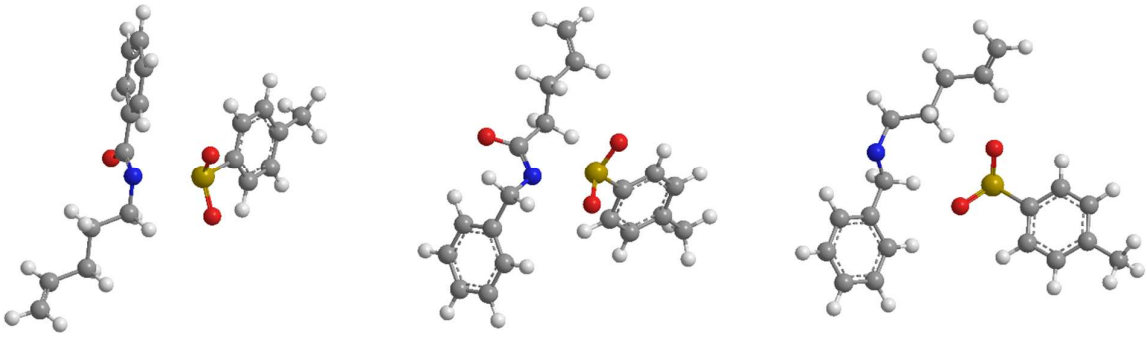


Figure 7. Optimized structures of radical anions of **2f**, **2g**, and **16.**

CONCLUSION

In the effort described above, we developed a visible light promoted desulfonylation process utilizing 1,3-dimethyl-2-hydroxynaphthylbenzimidazoline (**1a**), which is applicable to a variety of

N-sulfonylamides and -amines. Although only briefly explored, a combination of 1-methyl-2-naphthol (**15**) and 1,3-dimethyl-2-phenylbenzimidazoline (**1b**) was also found to promote the photo-desulfonylation reaction. In the initial step in the mechanism proposed for the process promoted by **1a**, photo-excited **1a** donates an electron to the substrates. Support for this proposal came from the observation that the fluorescence of 2-methyl-1-naphthoxy anion derived from **15** was efficiently quenched by representative sulfonylamide and -amine substrates. These observations suggest that an excited naphthoxide species generated from **1a** acts as an electron donor in the reaction. This proposal is supported by the well-known photoinduced deprotonation reactions of 2-naphthol derivatives.[31] DFT calculations provided information about the selectivity of N-S bond cleavage in the radical anions of the substrates for this reaction, which is consistent with the results obtained from studies of desulfonylation reactions of radical probe substrates. Although several desulfonylation reactions that take place via PET induced pathways have been previously developed, they often require expensive transition metal photocatalysts,[11c] harmful UV irradiation,[17a] toxic hydrogen atom donors[11b] and/or extremely strong electron donors.[9b] Therefore, the new visible light promoted, transition metal free protocol has several attractive features, including that a preparation of **1a** requires only short sequence, **1a** is easily handled under air at ambient temperature, and the process is activated by using a household white LED. Further

investigations aimed at expanding the substrate tolerance and more fully understanding the reaction mechanism are underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on $CDCl_3$ with tetramethylsilane (Me_4Si) as an internal standard, and DMSO-d_6 and CD_3CN at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Proton-decoupled carbon data of ^{13}C NMR are reported. High resolution mass spectra (HRMS) were recorded on a double-focusing mass spectrometer by using Atmospheric Pressure Chemical Ionization (APCI). Oxidation and reduction potentials in MeCN were measured using cyclic voltammetry and a previously described procedure.[16b] Calibration of the potentials were performed using the formal potentials of ferrocene/ferrocenium couple, which are 0.067 V and 0.442 V versus $Ag/AgNO_3$ and SCE, respectively. Half-wave potentials ($E_{1/2}$) reported in the manuscript were obtained from the peak potentials by subtracting or adding 0.029 V. Light sources for photoreactions were a 500 W Xe lamp with glass filter L-42 ($\lambda > 390$ nm) and a 7.3 W white LED. Column chromatography was performed with silica gel. Anhydrous solvents for photoreactions were obtained as follows. CH_2Cl_2 and $PhCH_3$ were purified in a same manner by the treatment with H_2SO_4, water, 5% NaOH, water, and $CaCl_2$ and then distilled over CaH_2. MeCN was distilled over P_2O_5 and subsequently distilled with K_2CO_3. Anhydrous DMF, DMSO, and MeOH

were purchased and used without distillation. Other reagents and solvents were used without further purification.

Substrates **2a,**[11c] **2e,**[11c] **2f**,[11c] **4**,[39] **6**,[24c,40] **8a**,[24a,41] **8b**,[24a,42] **8c**,[24a,43] and **16**,[44] which are known compounds, were prepared by using reported procedures. Preparation procedure and spectroscopic data of substrates **2b-2d, 2g** are described below. 1-Methyl-2-hydroxy naphthalene **15** is also known,[45] and was prepared from 2-naphthol**.**

Preparation of benzimidazolines. 1,3-Dimethylbenzimidazoline (BIH) derivatives **1a**,[24a] **1b**,[16a] 2-(2-hydroxyphenyl)-BIH[16a] and 2-(4-hydroxyphenyl)-BIH[16a] were prepared using previously reported procedures. While all of these substances were already characterized, chemical shifts of ^{1}H-NMR for **1a** in $CDCl_3$,[24a] CD_3CN and DMSO-d_6 are described below for the discussion in the text. *2-(2-hydroxynaphthyl)-1,3-dimethybennzimidazoline (**1a**).* ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.43 (br s, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.85–7.80 (m, 2H), 7.51–7.45 (m, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 9.2 Hz, 1H), 6.90–6.84 (m, 2H), 6.68–6.63 (m, 2H), 5.84 (s, 1H), 2.68 (s, 6H); ^{1}H-NMR (400 MHz,CD_3CN) δ 10.54 (br s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.90–7.85 (m, 2H), 7.52–7.48 (m, 1H), 7.38-7.34 (m, 1H), 7.14 (d, J = 8.8 Hz, 1H), 6.83 (s, 2H), 6.70 (s, 2H), 5.91 (s, 1H), 2.62 (s, 6H). ^{1}H-NMR (400 MHz,DMSO-d_6) δ 9.95 (br s, 1H), 8.53-8.51 (m, 1H), 7.80–7.76 (m, 2H), 7.25-7.19 (m, 3H), 6.65–6.63 (m, 2H), 6.49-6.47 (m, 2H), 6.01 (s, 1H), 2.46(s, 6H).

Preparation of *N*-Benzyl-*N*-tosylbezamides 2b, 2c, 2d, and 2g. *Synthesis of N-Benzyl-N-tosylamine.* To benzylamine (2.2 ml, 20 mmol) and *p*-toluenesulfonyl chloride (4.577 g, 23.9 mmol) was added pyridine (20 mL) with cooling in ice-water bath. The resulting mixture was purged with N_2 for 10 min and subsequently heated at 50 ºC for 20 h. Then, after addition of water (50 mL), extraction with Et_2O (50 mL × 3) was performed. The extract was washed with 2M HCl (50 mL), 2M NaOH (50 mL), and brine (50 mL), and then dried over anhydrous $MgSO_4$. Addition of EtOH to the residue obtained after concentration gave *N*-benzyl-*N*-tosylamine as a colorless solid (4.185 g, 16.0 mmol, 80%).

*Synthesis of N-Benzyl-N-tosyl-4-chlorobenzamide (**2b**).* To *N*-benzyl-*N*-tosylamine (785 mg, 3.0 mmol) in DMF(11 ml) were added NaH (~60%, 204 mg, 5.1 mmol) and *p*-chlorobenzoyl chloride (0.42 mL, 3.3 mmol) with cooling in ice-water bath. This mixture was stired at room temp for 6 h and then extracted with Et_2O (40 mL × 2) after addition of water (40 mL). The extract was washed with water (40 mL x 2) and brine (40 ml), and then dried over anhydrous $MgSO_4$. The residue obtained by concentration was subjected to column chromatography using EtOAc and *n*-C_6H_{14} (1/4). The obtained solid was crystalized from EtOH to give **2b** (720 mg, 1.8 mmol, 60%). Colorless solid; mp 99.5–100.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27–7.20 (m, 7H), 4.93 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 145.0, 138.2, 136.1, 153.7, 133.6, 129.9, 129.7, 128.7, 128.6, 128.5,

128.1, 128.0, 51.2, 21.8.; HRMS (ESI) m/z calcd for $C_{21}H_{19}ClNO_3S$ $[M+H]^+$ 400.0769, found 400.0776.

*Synthesis of N-Benzyl-N-tosyl-4-nitrobenzamide (**2c**).* A procedure similar to that used for the synthsis of **2b** was performed except for the reaction time and column separation (not performed). *N*-benzyl-*N*-tosylamine (784 mg, 3.0 mmol), NaH (~60%, 191 mg, 4.8 mmol), *p*-nitrobenzoyl chloride (557 mg, 3.0 mmol), 7 h, **2c** (895 mg, 2.0 mmol, 66%). Colorless solid; mp 147.0–148.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.8 Hz, 2H), 7.55–7.51 (m, 4H), 7.31–7.25 (m, 7H), 4.96 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 149.2, 145.6, 141.1, 135.8, 135.5, 129.9, 129.1, 128.9, 128.3, 128.2, 128.2, 123.3, 50.8, 21.8.; HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2O_5S$ $[M+H]^+$ 411.1009, found 411.1012.

*Synthesis of N-Benzyl-N-tosyl-4-methoxybenzamide(**2d**).* A procedure similar to that used for the synthsis of **2b** was performed except for the reaction time and column separation solvents. *N*-benzyl-*N*-tosylamine (784 mg, 3.0 mmol), NaH (~60%, 193 mg, 4.8 mmol), *p*-methoxybenzoyl chloride (0.41 mL, 3.0 mmol), 15 h, column chromatography using EtOAc and C_6H_6 (1/20), **2d** (743 mg, 1.9 mmol, 63%). Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.26–7.18 (m, 7H), 6.85 (d, J = 8.4 Hz, 2H), 4.89 (s, 2H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 162.9, 144.5, 136.1, 158.8, 131.3, 129.5, 128.5,

128.4, 128.1, 127.7, 127.1, 113.5, 55.5, 51.4, 21.6.; HRMS (ESI) m/z calcd for $C_{22}H_{22}NO_4S$ $[M+H]^+$ 396.1264, found 396.1271.

*Synthesis of N-Benzyl-N-tosyl-4-pentenamide (**2g**).* A procedure similar to that used for the synthsis of **2b** was performed except for the reaction time and column separation solvents. *N*-benzyl-*N*-tosylamine (1.307 g, 5.0 mmol), NaH (~60%, 324 mg, 8.0 mmol), 4-pentenoyl chloride (0.66 mL, 6.0 mmol), 3 h, column chromatography using EtOAc and n-C_6H_{14} (1/4), **2g** (1.508 g, 4.4 mmol, 88%). Colorless solid; mp 58.0–59.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.38–7.27 (m, 5H), 7.26 (d, J = 8.0 Hz, 2H), 5.71–5.60 (m, 1H), 5.10 (s, 2H), 4.91–4.85 (m, 2H), 2.65 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.30–2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 145.0, 136.9, 136.6, 129.9, 128.8, 128.00, 127.95, 127.9, 115.7, 49.6, 35.7, 28.5, 21.8.; HRMS (ESI) m/z calcd for $C_{19}H_{22}NO_3S$ $[M+H]^+$ 344.1315, found 344.1318.

Photoreaction Procedure. Solutions containing substrates **2**, **4**, **6**, or **8**, and **1a** with or without base in Pyrex test tubes (1.4 cm diameter) were irradiated with a 7.3 W white LED or using a Xe lamp at room temperature. The tubes were immersed in a water bath in Xe-lamp irradiation reactions. A typical procedure is described below. An appropriate solvent (1.0 mL) containing **1a** (43.6 mg, 0.15 mmol) and **2a** (36.5 mg, 0.10 mmol) was purged with N_2 for 10 min and then irradiated with LED. The photolysate was diluted with water (30 mL) and extracted with Et_2O (20 mL × 3). The combined extracts were washed with water (30 mL × 2), brine (30 mL), dried over

anhydrous $MgSO_4$ and concentrated in vacuo to give a residue. The conversion of **2a** and the yield of **3a** were determined by using ^{1}H NMR analysis of the residue with triphenylmethane as an internal reference. Photo-products **3a**,[11c] **3b**,[46] **3c**,[46] **3d**,[46] **3e**,[11c] **3f**,[11c] **3g**,[47] **9a**,[24a,48] **17**[49] are known compounds while **5**, **7** and **9c** are commercial materials. The conversions of **2b**–**2g**, **4**, **6**, **8a**–**8c** and **16**, and the yields of the corresponding photo-products were determined by ^{1}H-NMR in a similar manner to that for **2a** and **3a**. ^{1}H-NMR charts of the reaction mixtures of selected experiments are presented in the Supporting Information. Preparative photoreactions of **2a** and **8a** with **1a** were performed (see below), and ^{1}H-NMR charts of **3a** and **9a** obtained by column separation are shown in the Supporting Information. Since **3c** was not obtained in the reaction of **2c** (see entry 3 in Table 3), we needed to synthesize **3c** for an authentic sample as described below.

*Preparative photoreaction of **2a** with **1a**.* Irradiation of **1a** (43.6 mg, 0.15 mmol) and **2a** (36.5 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 1 of Table 1. The reaction mixture obtained after same work-up procedure described above was subjected to column separation using EtOAc and *n*-C_6H_{14} (1/4) to give **3a** (21.0 mg, 0.099 mol, 99%). Colorless solid; mp 97.0–99.5 °C (98–100 °C);[50] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81–7.78 (m, 2H), 7.52–7.48 (m, 1H), 7.45–7.41 (m, 2H), 7.36 (d, J = 4.4 Hz, 4H), 7.34–7.29 (m, 1H), 6.42 (br s, 1H), 4.65 (d, J = 5.6 Hz, 2H).

*Preparative photoreaction of **8a** with **1a**.* Irradiation of **1a** (69.7 mg, 0.24 mmol) and **8a** (65.9 mg, 0.20 mol) in DMF (2.0 mL) was carried out under the same condition as that for entry 7 of Table 6. The reaction mixture obtained after same work-up procedure described above was subjected to column separation using EtOAc and *n*-C_6H_{14} (1/7) to give **9a** (34.7 mg, 0.198 mol, 99%). Colorless solid; mp 147.0–149.5 °C (152.5–153.0 °C);[48] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.87 (br s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.4, 0.8 Hz, 1H), 7.33 (td, J = 7.2, 1.2 Hz, 1H), 7.23–7.22 (m, 1H), 7.16 (td, J = 7.6, 0.8 Hz, 1H), 3.95 (s, 3H).

*Synthesis of N-Benzyl-4-nitrobenzamide (**3c**).* To benzylamine (0.55 ml, 5 mmol) and NEt3 (1.04 mL, 7.5 mmol) in MeCN (13.4 mL) was added *p*-nitrobenzoyl chloride (1.114 g, 6.0 mmol) with cooling in ice-water bath. The resulting mixture was stired at room temp for 17 h and then concentrated. The residue was subjected to column chromatography using EtOAc and *n*-C_6H_{14} (1/2) to give **3c** as white sold (881 mg, 3.5 mmol, 69%).

Fluorescence Quenching Experiments. Fluorescence quenching of 1-methyl-2-naphthoxy anion was conducted at room temperature by dissolving **15** (1.50×10^{-4} M) in aerated DMSO containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.15 M). Fluorescence intensities at 469 nm by excitation at 400 nm were measured at three or four different concentrations of a quencher (**1a**, **4**, **6**, or **8a**). Slopes ($k_q\tau$, M^{-1}) of Stern-Volmer plots were determined by using a linear approximation treatment. The intrinsic lifetime (τ) of fluorescence for 1-methyl-2-naphthoxy anion was measured

with time-correlated single photon counting and determined to be 17.5 ns under air in DMSO, while the longer lifetime was obtained as 20.5 ns under argon. The quenching rate constants (k_q, $M^{-1}s^{-1}$) were calculated using 17.5 ns as τ value.

Density Functional Theory Calculations. Calculations were carried out using the Gaussian 16 program package.[38a] The structures of neutral forms of *N*-sulfonylamides and -amines were optimized at the restricted B3LYP/6-31+G(d) level, while the structures of open shell species were optimized using the unrestricted theory at the same level. The transition states for N–S cleavage and for radical cyclization were optimized using Berny algorithm. Frequency analysis was performed for each optimized structure to confirm that no or one imaginary frequency were obtained for the energy-minimum or the transition-state structures, respectively. To estimate charge and spin distribution natural population analysis built in the Gaussian was performed.[38b] The optimized structure and molecular orbitals (MOs) were visualized with GaussView 6.0 software.[38c] In MO figures the isosurface value was set to 0.05.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Data of absorption spectra, cyclic voltammograms, additional photoreactions, fluorescence quenching, DFT calculations, ^{1}H NMR charts of selected photoreaction products, and ^{1}H and ^{13}C NMR spectra of new **2** (PDF).

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(25) While both 2-(2-hydroxyphenyl)- and 2-(4-hydroxyphenyl)-1,3-dimethybennzimidazolines were also effective photo-reductants, irradiation of Hantzsch ester did not promote the reaction at all (see Table S3).

(26) We previously found that 2-bromoacetphenone smoothly reacts with Ar-BIHs without irradiation.[24a] Thus, **1a** is converted to its oxidized form $^{-}$ONap-BI^{+} by the treatment with 2-bromoacetphenone.

(27) Since addition of bases such as DBU and *t*-BuOK were found to cause decomposition of **2a** in DMF, we chose less polar solvent such as CH_2Cl_2 as more suitable solvent.

(28) The reaction was monitored by ^{1}H NMR every 10 minutes in DMSO-d_6. After 20 minutes, 92 % formation of **3a** was observed at 94 % conversion of **2a**. As methyl peak of Ts-substituent at 2.40 ppm of **2a** decreased, the new peak at 2.27 ppm, which is assigned to methyl of $CH_3C_6H_4SO_2H$ (2.35 ppm, Reichardt, C.; Erfurt, H. P.; Harms, K.; Schäfer G. Syntheses, Absolute Configurations, and UV/Vis Spectroscopic Properties of New Chiral Tri- and Pentamethinium Streptocyanine Dyes with 4- Aminophenyl 4- Methylphenyl Sulfoxide Endgroups. *Eur. J. Org. Chem.* **2002**, 439–452), increased (see Figure S5 and Table S4).

(29) The peaks observed in CV of **2c** would be due to the reduction of *p*-nitrobenzoyl moiety since CV of **3c**, which is independently synthesized, gave the reduction peaks around similar region (see Figure S4 and Table S2).

(30) Rate constant of 5-exo cyclization of amidyl radical is reported to be 2 x 10^9 s^{-1}. Horner, J, H.; Musa, O. M.; Bouvier, A.; Newcomb, M. Absolute Kinetics of Amidyl Radical Reactions. *J. Am. Chem. Soc.* **1998**, *120*, 7738–7748.

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(32) We previously reported that DFT calculation of **1a** also suggests the energy minimized structure in which hydroxy on naphthol moiety is located close to nitrogen of benzimidazoline moiety.[24a]

(33) The oxidation potential of the excited naphthoxide moiety for **10** and **13*** (E^{ox}*) is estimated to be about –2.77 V by using the end-absorption wavelength (λ = 447 nm, absorbance = 0.02 at 4.0 x 10^{-5} M) to determine excited state energy (E^{ex} = 2.77 eV) and oxidation potential ($E^{ox}_{1/2}$ = –0.01~+0.02 V)[24c] of the deprotonated **1** (see Figures S1, Figure S3 and Table S1).

(34) We recently discovered that **12** acts as an effective photocatalyst cooperating with Ph-BIH to promote the transformation of **2a** to **3a** (Hasegawa, E.; Izumiya, N.; Miura, T.; Ikoma, T.; Iwamoto, H.; Takizawa, S.; Murata, S. Benzimidazolium Naphthoxide Betaine Is a Visible Light Promoted Organic Photoredox Catalyst. *J. Org. Chem.* **2018**, *83*, 3921–3927). Therefore, this type of photocatalytic mechanism involving **12** and **1a** may also operate at the later stage of the reaction.

(35) Rate constant of 5-exo cyclization of aminyl radical is reported to be 2 x 10^4 s^{-1}. Musa, O. M.; Horner, J, H.; Shahin, H.; Newcomb, M. A Kinetic Scale for Dialkylaminyl Radical Reactions. *J. Am. Chem. Soc.* **1996**, *118*, 3862–3868.

(36) PET processes of naphthoxy anions with electron acceptors. (a) Soumillion, J. P.; Vandereecken, P.; Van Der Auweraer, M.; De Schryver, F. C.; Schanck, A. Photophysical

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(37) Since it turned out that absorption spectrum of **15** with DBU in DMSO gradually changed upon addition of **2a**, $k_q\tau$ value obtained would have some ambiguity compared to those for **4**, **6** and **8a**. This might be due to the reaction of **2a** with **15** in the presence of DBU in DMSO which is similar behavior of **2a** toward **1a** and DBU in DMF.[27]

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