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Aryl-substituted dimethylbenzimidazolines as effective reductants of photoinduced electron transfer reactions

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ABSTRACT

Photoinduced electron transfer (PET) reactions promoted by 2-aryl substituted 1,3-dimethylbenzimidazolines (Ar-DMBIH) were investigated. Excited states of Ar-DMBIH, formed by irradiation using light above 360 nm, initiate PET reductions of various organic substrates, including transformations of epoxy ketones to aldols, free radical rearrangements such as the Dowd-Beckwith ring-expansion and 5-*exo* hexenyl cyclization, deprotection of *N*-sulfonyl-indols, and allylation of acyl formates. In these processes, Ar-DMBIH possessing 1-naphthyl, 2-naphthyl, 1-pyrenyl and 9-anthryl substituents formally act as two electron and one proton donors while the hydroxynaphthyl substituted derivative serves as a two electron and two proton donor. On the basis of the results of absorption spectroscopy studies, cyclic voltammetry and DFT calculation, a mechanistic sequence for these reduction reactions is proposed that involves initial photoexcitation of the aryl chromophore of the Ar-DMBIH followed by single electron transfer (SET) to the organic substrate to generate the radical cation of benzimidazoline and the radical anion of the substrate.

1. Introduction

The single electron transfer (SET) reduction and oxidation (redox) abilities of electronic excited states of organic substances exceed those of their ground states. As a result, photoinduced electron transfer (PET) is a useful method to generate radical ions of organic molecules.[1] A simple way to initiate these processes is by direct photoexcitation of the organic substrate in the presence of an electron donor or acceptor co-reactant. Another approach involves the use of photosensitizers (photocatalysts), which can be designed to absorb longer wavelengths of light and whose electronic excited states can serve as electron donors or acceptors. The latter protocol has advantageous features, which include the avoidance of undesired reactions of the excited state of the substrate and secondary photoreactions of the initially formed product. In the past several years, PET reactions catalyzed by visible light absorbing transition metal complexes, such as those of ruthenium and iridium, have received great attention in the area of synthetic organic chemistry.[2] More recently, metal-free protocols using organo-photocatalysts have gained interest in light of their potential application to green and sustainable synthetic transformations.[3]

Because amines possess relatively strong electron donating abilities compared to those of other organic substances, they have been employed often in the SET promoted reactions,[4] and especially those initiated by PET.[5] 2-Aryl-1,3-dimethylbenzimidazolines (Ar-DMBIH) are a family of *N*-heterocyclic aromatic amines that promote various reduction reactions by serving as hydride, hydrogen atom or electron donors (Scheme 1).[6] Owing to their multidonor character, Ar-DMBIH have been employed for reduction reactions of various organic substances, exemplified by their participation as hydride donors to carbocations as well as cationic salts (Scheme 1, *path 1*).[7] Moreover, certain Ar-DMBIH derivatives react to produce hydrogen gas upon treatment with Brønsted–Lowry acids (*path 1*).[8] Ar-DMBIH also behave as radical chain promoters through a pathway involving hydrogen atom donation followed by ET reactions (*path 2* and *path 4*).[9] In addition, PET reactions of various organic substances using Ar-DMBIH have been described by us and others (*path 3*–*path 5*–*path 4, or path 3*–*path 6*).[10,11] Finally,

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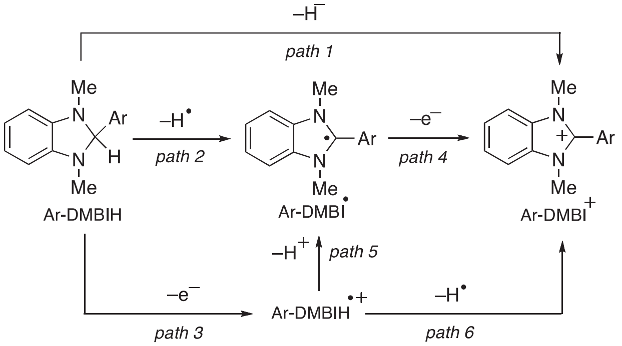
the utility of Ar-DMBIH as electron donors has been expanded by their application in artificial photosynthesis systems[12] as well as organic semiconductor devices[13] (*path 3*).



Scheme 1. Oxidation pathways of 2-aryl-1,3-dimethylbenzimidazoline (Ar-DMBIH).

In investigations of PET promoted reduction reactions using Ar-DMBIH,[10] we have employed approaches that involve both direct excitation of substrates[10a–e,g,j,k] as well as photosensitization using electron donating pyrenes[10d,f,h,i] or transition metal complexes.[10h,l] As a consequence of the fact that visible light promoted organic transformations are highly attractive,[2,3] we focused our attention on the development of Ar-DMBIH, which possess chromophores that absorb at long wavelengths so that desired PET reactions could be promoted without using expensive photocatalysts such transition metal complexes. The concept utilized to design Ar-DMBIH of this type is outlined in Fig. 1. In previous investigations, we demonstrated that phenyl-substituted DMBIH, **1a**, behaves as a two electron and one proton donor in reduction reactions of organic substrates while its phenol counterpart, **1g**, serves as a two electron and two proton donor. Based on this observation and the well-known effects of extended conjugation on the wavelength maximum for light absorption, we anticipated that Ar-DMBIH **1b**–**1f** (Fig. 1), in which various polycyclic aryl moieties are connected to the methylene carbon of the benzimidazoline skeleton, would be suitable long wavelength absorbing PET promoters. In related studies, it has been shown that Hantzsch esters possessing aryl-substiuents also are potential SET photoreductants[14] although the use of these substances to promote reductive transformations has not been explored. In the study described below, we prepared the Ar-DMBIH **1b**–**1f** and demonstrated their utility in promoting PET transformations of the wide variety of organic substrates to form products listed in Fig. 2.

2. Results and discussion

Analysis of the absorption spectra of Ar-DMBIH **1a**–**1g** displayed in Fig. 3 and Fig. 4, shows that these substances at 0.1 M concentrations absorb light at wavelengths >360 nm, which are attained by irradiation using Glass Filter L-39.[15] Absorption spectroscopic data for **1** are accumulated in Table 1. Because 1,2-diaminobenzene has an absorption maximum around 300 nm,[16] the longer wavelength absorption bands at 313 nm for **1a** and 305 nm for **1g** are a consequence of the presence of the benzimidazoline chromophore. In the absorption spectra of **1b**, **1c** and **1f**, the maxima present in the 307–314 nm range are attributed to both the naphthalene and benzimidazoline chromophores.[16] On the other hand, characteristic absorption bands associated with the pyrene[17] and anthracene rings are present in the spectra of **1d** and **1e**, respectively.[16] Under the >360 nm irradiation conditions used in the PET reactions explored (see below), the pyrene moiety of **1d**, anthracene moiety of **1e**, and benzimidazoline moieties of **1a** and **1g** absorb the incident light. On the other hand, competitive absorption by naphthalene and benzimidazoline chromophores is possible for **1b**, **1c** and **1f**.

Based on the results of previous studies, we concluded that reductive ring opening reactions of epoxy ketones **2** (Fig. 2) and radical rearrangement reactions of halo-alkyl substituted cyclic ketones **4** and **8** would serve as model processes to evaluate the Ar-DMBIH based PET protocol described above.[10a–f,h–j,l] In PET promoted reductive ring opening reactions of epoxy ketones **2** that form the corresponding hydroxyl ketones **3**, two hydrogen atoms are formally transferred to the substrates (Scheme 2).[10a,c,d,f,h,i] Because **1a**–**1e** are expected to serve as a two electron and one proton donors, PET reactions of epoxy ketones promoted by these substances require the participation of another proton donor.

To test these proposals, photoreactions of chalcone epoxide **2a** with **1** under the various conditions were explored (Table 2). Ar–DMBIH **1b**–**1e** were found to serve as photoreductants for reactions of epoxy ketone **2a** in THF containing AcOH that are induced by irradiation with light of wavelengths >360 nm (Xe lamp). The yields of these reactions, which are ca. 90% based on the conversion of **2a**, are much higher than those in which the phenyl-substituted benzimidazoline **1a** was employed as the promoter (compare entries 2, 11, 12 and 14 to entry 1). Detailed studies using **1b** as the photoreductant unveiled several characteristic features of the epoxide ring opening reaction. For example, $PhCO_2H$ as well as PhOH serves as proton donors for the reductive ring opening process (entries 3 and 4, also see entries 13 and 15). Moreover, reactions of **2a** in CH_2Cl_2 and DMF proceeded smoothly to generate **3a** in good to excellent yields (entries 5 and 8). Extending the irradiation time does not cause decomposition of **3a** (compare entry 6 to entry 5). Furthermore, decomposition products such as chalcone, acetophenone and benzaldehyde and not **3a** are produced when the photoreactions are conducted in solvents that do not contain proton donors (entry 7). In addition, reactions of **2a** promoted by **1b** using $PhCO_2H$ (entry 9) or PhOH (entry 10) under solvent free conditions formed **3a** with low to moderate efficiencies. Finally, good yields of **3a** are associated with reductive ring opening reactions of **2a** in THF, CH_2Cl_2 or $PhCH_3$ solutions not containing proton donating additives, which are promoted by **1f** and **1g** that contain respective naphthol and phenol proton donor moieties (entries 16–22). It should be noted that these two electron and two proton-donors **1f** and **1g** have some advantage compared to the

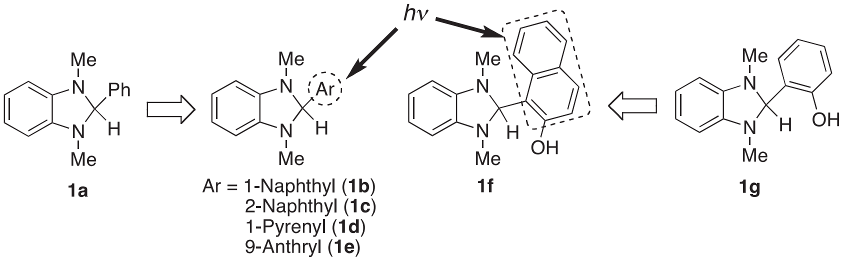


Fig. 1. 2-Aryl substituted 1,3-dimethylbenzimidazolines (Ar-DMBIH) (**1**).

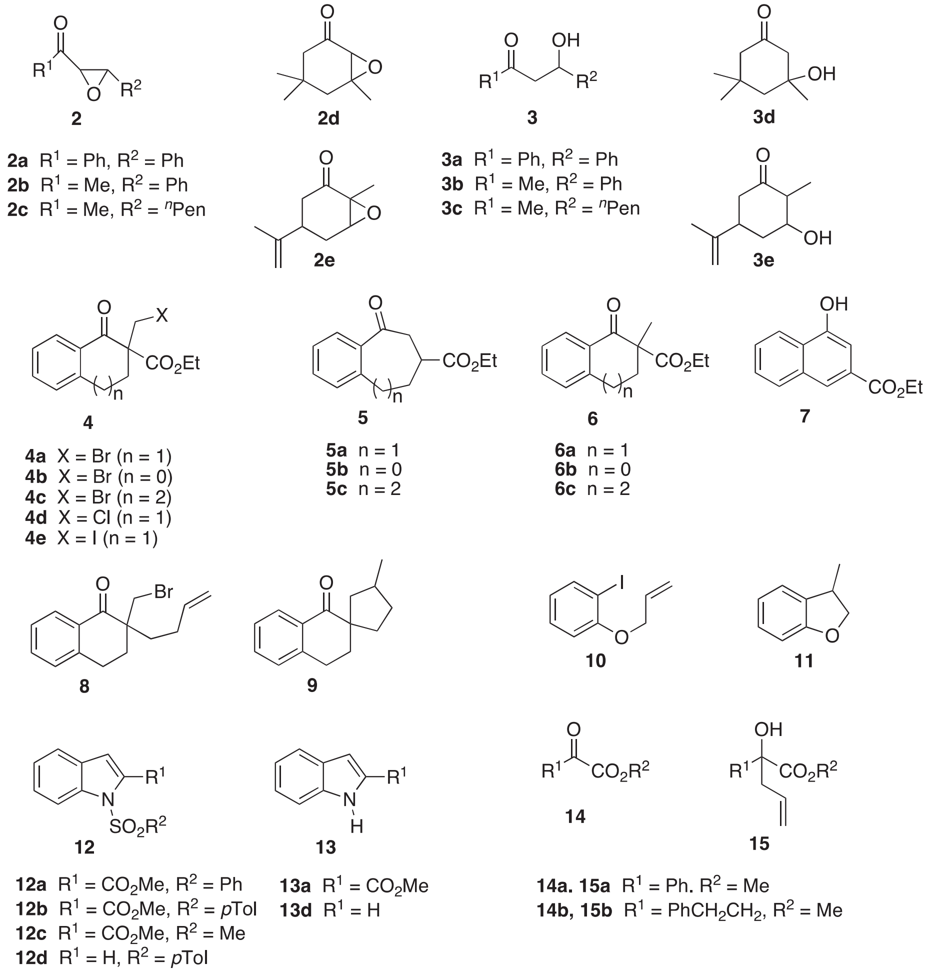


Fig. 2. Substrates **2**, **4**, **8**, **10**, **12**, **14** and products **3**, **5**, **6**, **7**, **9**, **11**, **13**, **15** of photoreduction reactions promoted by Ar-DMBIH (**1**).

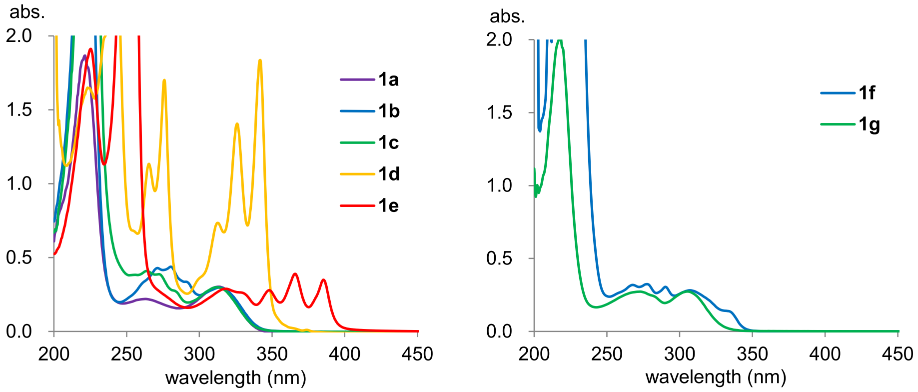


Fig. 3. Absorption spectra of **1** in MeCN at 4.0×10^{-5} M (left for **1a**–**1e**, right for **1f** and **1g**).

two electron and one proton donors such as **1a**–**1e** since it is necessary for latter donors to find a suitable proton donor and to optimize their quantities to improve the yields of **3**.[10a,d,f,18]

Photoreactions promoted by Ar-DMBIH were also explored using benzalacetone epoxide **2b**, which is a weaker electron acceptor ($E^{red}_{1/2}$, no peak less negative than −2.0 V vs SCE) than its phenyl ketone counterpart **2a** ($E^{red}_{1/2}$=−1.68 V). As can be seen by viewing the results given in Table 3, reactions of **2b** promoted by **1b** and **1d** (AcOH in THF, 12 h irradiation) produced hydroxyl ketone **3b** in modestly good yields (entries 2 and 11). On the other hand, only trace quantities of **3b** were generated when **1a** and **1e** are employed as photoreductants although consumption of the starting epoxide was observed to occur (entries 1 and 12). Furthermore, both **1b** and **1c** are equally effective in promoting reactions of **2b** in CH_2Cl_2 (4 h irradiation) (entries 3 and 10) and prolonged irradiation (12 h) of a mixture of **1b** and **2b** did not lead to higher conversions (compare entry 3 to entry 4). Reactions in highly polar solvents such as DMF and MeCN were found to be less efficient than those in solvents with medium polarity such as THF, CH_2Cl_2, $PhCH_3$ and $PhCF_3$ (entries 2, 4–8).[18] On the contrary, the hydroxy-aryl substituted photoreductants **1f** and **1g** promote reaction to give **3b** in excellent yields upon irradiation for only 1 h and with **1f** being more effective

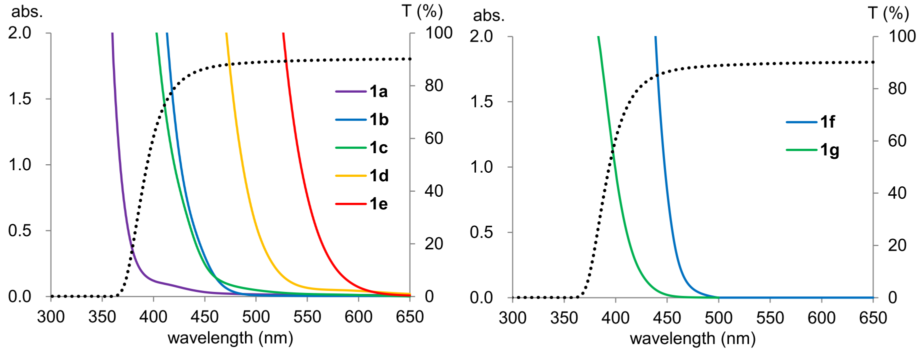
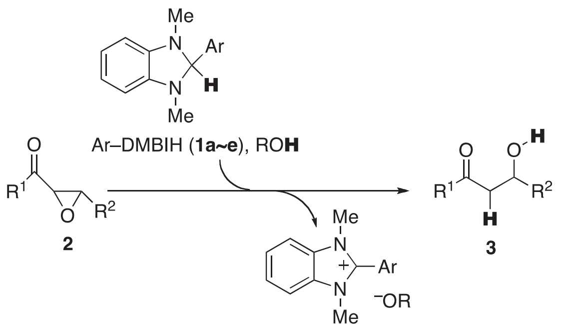


Fig. 4. Absorption spectra of **1** in THF at 0.1 M (left for **1a**–**1e**, right for **1f** and **1g**) and transmittance spectrum of the glass filter L-39 (dotted line).

Table 1
Absorption spectroscopic data of **1a**–**1g**

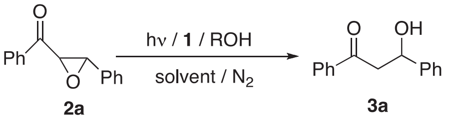
1	λ_{max} (log ε)[a] (nm)	λ_{end}[b] (nm)
1a	263 (3.74), 313 (3.88)	368
1b	271 (4.03), 281 (4.04), 291 (3.92), 314 (3.87)	427
1c	264 (4.01), 273 (3.99), 312 (3.87)	420
1d	267 (4.44), 276 (4.63), 313 (4.26), 326 (4.55), 342 (4.66)	487
1e	318 (3.86), 348 (3.84), 366 (3.99), 386 (3.94)	544
1f	268 (3.90), 278 (3.91), 290 (3.88), 307 (3.94)	447
1g	273 (3.83), 305 (3.83)	399

[a] Measured in MeCN (4.0×10^{-5} M, Fig. 3). λ_{max}: absorption maximum (log ε: log of molar attenuation coefficient).
[b] Measured in THF (0.1 M, Fig. 4). λ_{end}: end-absorption (absorbance ca. 1.0).



Scheme 2. Transformation of epoxy ketones **2** to hydroxyl ketones **3** promoted by **1a**–**1e**.

Table 2
Photoreactions of chalcone epoxide **2a** promoted by **1a**–**1g**[a]



Entry	1	Solvent	ROH (equiv)	Irrad time (h)	Conv of **2a** (%)	Yield of **3a** (%)[b]
1	**1a**	THF	AcOH (2.2)	1	86[c]	55
2	**1b**	THF	AcOH (2.2)	1	100	88
3	**1b**	THF	$PhCO_2H$ (2.2)	1	99[c]	96
4	**1b**	THF	PhOH (3.3)	1	100	93
5	**1b**	CH_2Cl_2	AcOH (2.2)	1	100	95
6	**1b**	CH_2Cl_2	AcOH (2.2)	4	100	92
7	**1b**	CH_2Cl_2	—	4	100	0[e]
8	**1b**	DMF	AcOH (2.2)	1	100	86
9	**1b**	—[d]	$PhCO_2H$ (1.2)	1	90[c]	67
10	**1b**	—[d]	PhOH (3.3)	1	97[c]	28
11	**1c**	THF	AcOH (2.2)	1	93	88
12	**1d**	THF	AcOH (2.2)	1	52[f]	46[f]
13	**1d**	THF	$PhCO_2H$ (2.2)	1	51	40[c]
14	**1e**	THF	AcOH (2.2)	1	63	61
15	**1e**	THF	$PhCO_2H$ (2.2)	1	56[f]	56[f]
16	**1f**	THF	—	1	78	54
17	**1f**	THF	—	4	100	75
18	**1f**	CH_2Cl_2	—	1	90	67
19	**1f**	CH_2Cl_2	—	4	100[f]	82[f]
20	**1f**	$PhCH_3$	—	4	100	72
21	**1f**	DMF	—	4	100	57
22	**1g**	CH_2Cl_2	—	4	61	41

[a] **2a** (0.40 mmol, 0.20 mmol for entries 9 and 10), **1** (1.2 equiv vs **2a**), solvent (4.0 mL), $\lambda>360$ nm.
[b] Isolated yield.
[c] Determined by ^1H NMR.
[d] For details see Experimental section.
[e] Chalcone (35%), acetophenone (9%), and benzaldehyde (4%) were observed.
[f] Average of two independent experiments.

than **1g** (entries 13 and 16). Also, prolonged irradiation in these cases did not cause decomposition of product **3b** (entries 14 and 17). Finally, it should be noted that the reaction promoted by **1f** to afford **3b** occurred in moderate yield under the solvent free conditions (entry 15) while **1b** with $PhCO_2H$ did not promote reaction of **2b** although **1b** was completely oxidized (entry 9).

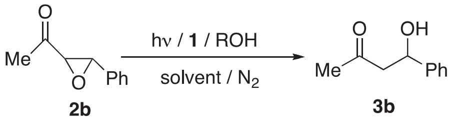
As described above, **1b**–**1e**, in solvent systems containing appropriate proton donors, and **1f** and **1g** in the absence of proton donating additives are effective promoters of the reductive epoxide ring opening reaction of **2a**. Moreover, reactions of **2b** promoted by **1f** and **1g** take place in higher yields than those induced by **1b**–**1e**. Based on these findings, **1f** and **1g** were used to promote reduction reactions of other aliphatic epoxy ketones including **2c**–**2e** (Table 4). In each process, the corresponding hydroxyl ketone **3c**–**3e** was generated in excellent yield (entries 1, 2, 3 and 6). In the reaction of **2d**, DMF was found to be less tolerable solvent than CH_2Cl_2 (entries 4 and 5).[18]

PET promoted reduction reactions of α-halomethyl benzocyclic 1-alkanones such as **4** and **8** are known to take place via pathways involving the intermediacy of primary alkyl radicals formed by carbon-halogen bond cleavage.[10b,e,h–j,l] These radical intermediates undergo rearrangement reactions, such as Dowd-Beckwith (DB) ring-expansion[19,20] and 5-*exo* hexenyl cyclization,[21] to form the corresponding products.

The use of Ar-DMBIH to promote ring expansion reactions of α-halomethyl benzocyclic 1-alkanones **4** was investigated (Table 5). The results show that while **1a**–**1e** all promote reaction of **4a** in CH_2Cl_2, the ratio of ring expansion (**5a**) to reduction (**6a**) products differs depending on the photoreductant used (entries 1, 2, 6, 9 and 13). Moreover, irradiation of a mixture of **1b** and **4a** in different solvents produced mixtures containing varying ratios of **5a** and **6a** (entries 2–4). In the reaction of **4a** promoted by **1c** in CH_2Cl_2, a white solid appeared within 30 min during irradiation (entry 6), a phenomenon, which was not observed in the reaction promoted by **1b** (entry 2).[22] The reaction promoted by **1d** took place smoothly (entry 9) and, in this case, irradiation with shorter wavelength light was similarly effective (entry 11) although some solid precipitate formed after 1 h irradiation. Unexpectedly, the progress of the

Table 3

Photoreactions of benzalacetone epoxide **2b** promoted by **1a**–**1g**[a]



Entry	1	Solvent	ROH (equiv)	Irrad time (h)	Conv of **2b** (%)	Yield of **3b** (%)[b]
1	**1a**	THF	AcOH (6.6)	12	40	0
2	**1b**	THF	AcOH (6.6)	12	79	55
3	**1b**	CH_2Cl_2	AcOH (6.6)	4	68	48
4	**1b**	CH_2Cl_2	AcOH (6.6)	12	68	52
5	**1b**	$PhCH_3$	AcOH (6.6)	12	91[c]	60
6	**1b**	$PhCF_3$	AcOH (6.6)	12	60[c]	30
7	**1b**	DMF	AcOH (6.6)	12	59	13[c]
8	**1b**	MeCN	AcOH (6.6)	12	32	9[c]
9	**1b**	—[d]	$PhCO_2H$ (1.2)	6	—[e]	0
10	**1c**	CH_2Cl_2	AcOH (6.6)	4	75	52
11	**1d**	THF	AcOH (6.6)	12	76[c]	50
12	**1e**	THF	AcOH (6.6)	12	6	Trace
13	**1f**	CH_2Cl_2	—	1	100	94
14	**1f**	CH_2Cl_2	—	4	100	90
15	**1f**	—[d]	—	4	66	34
16	**1g**	CH_2Cl_2	—	1	91	80
17	**1g**	CH_2Cl_2	—	4	100	88

[a] **2b** (0.40 mmol, 0.05 mmol for entry 9 and 0.20 mmol for entry 15), **1** (1.2 equiv vs **2b**), solvent (4.0 mL), λ >360 nm.

[b] Isolated yield.

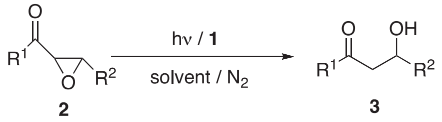
[c] Determined by using ^1H NMR.

[d] For details see Experimental section.

[e] Negligible ^1H NMR peaks other than those for **1b**, oxidized **1b** and **2b**.

Table 4

Photoreactions of aliphatic epoxy ketones **2c**–**2e** promoted by **1f** and **1g**[a]



Entry	2	1	Solvent	Irrad time (h)	Conv of **2** (%)	Yield of **3** (%)[b]
1	**2c**	**1f**	CH_2Cl_2	2	100	92
2	**2d**	**1f**	CH_2Cl_2	1	100	94
3	**2d**	**1g**	CH_2Cl_2	1	100	95
4	**2d**	**1f**	DMF	1	82[c]	39[c]
5	**2d**	**1g**	DMF	1	52[c]	19[c]
6	**2e**	**1f**	CH_2Cl_2	1	100	94

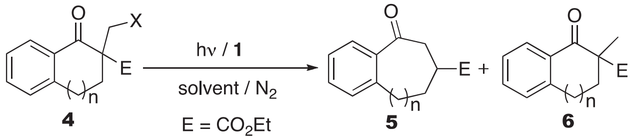
[a] **2** (0.40 mmol for CH_2Cl_2, 0.10 mmol for DMF), **1f** (1.2 equiv vs **2**), solvent (4.0 mL for CH_2Cl_2, 1.0 mL for DMF), λ >360 nm.

[b] Isolated yield.

[c] Determined by ^1H NMR.

Table 5

Photoreactions of haloalkyl substituted cyclic keto esters **4** promoted by **1a**–**1e**[a]



Entry	4	1	Solvent	Irrad time (h)	Conv of **4** (%)[b]	Yields (%)		Ratio
						5[c]	**6**[b]	**5:6**
1	**4a**	**1a**	CH_2Cl_2	2	33	9	9	50:50
2	**4a**	**1b**	CH_2Cl_2	2	44	16	12	57:43
3	**4a**	**1b**	THF	2	41	9	17	36:64
4	**4a**	**1b**	DMSO	2	54	27	12	69:31
5	**4a**	**1b**	—[d]	2	80	33	27	55:45
6	**4a**	**1c**	CH_2Cl_2	2	50[e]	21[e]	16[e]	57:43[e]
7	**4a**	**1d**	CH_2Cl_2	0.5	50	27	18	60:40
8	**4a**	**1d**	CH_2Cl_2	1	68	42	16	73:27
9	**4a**	**1d**	CH_2Cl_2	2	91	67	18	79:21
10	**4a**	**1d**	CH_2Cl_2	6	100	65	20	76:24
11[f]	**4a**	**1d**	CH_2Cl_2	2	90	61	14	81:19
12	**4a**	**1d**	—[d]	2	95	42	38	53:47
13	**4a**	**1e**	CH_2Cl_2	2	20	13	Trace	<100:>0
14	**4b**	**1d**	CH_2Cl_2	2	73	49[b,g]	10	83:17
15	**4c**	**1d**	CH_2Cl_2	2	34	17[b]	Trace	<100:>0
16	**4d**	**1b**	CH_2Cl_2	2	17	4	Trace	<100:>0
17	**4d**	**1d**	CH_2Cl_2	2	12	5	4	56:44
18	**4e**	**1b**	CH_2Cl_2	2	67	22	18	55:45
19	**4e**	**1d**	CH_2Cl_2	2	49	14	11	56:44

[a] **4** (0.40 mmol, 0.20 mmol for entries 5 and 12), **1** (1.2 equiv vs **4**), solvent (4.0 mL), λ >360 nm.

[b] Determined by ^1H NMR.

[c] Isolated yield.

[d] For details see Experimental section.

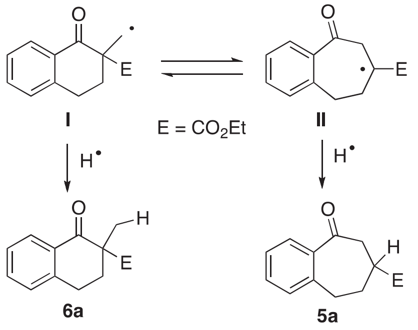
[e] Average of two independent experiments.

[f] Pyrex-filtered irradiation (λ >280 nm).

[g] Naphthol **7** (3%) was included.

reaction of **4a** was significantly slowed when **1e** is used as the photoreductant although **1e** can absorb the incident light (entry 13 and Fig. 4).

The mechanistic pathway for conversion of **4a** to **5a** and **6a** involves the intermediacy of radical **I** (Scheme 3), which is initially formed via PET process with **1** and undergoes competitive hydrogen atom abstraction to produce **6a** or a ring-expansion process to form **II**, which serves as the precursor of **5a**. Consequently, the use of lower concentrations of the hydrogen atom donors such as **1** should enhance formation of **5a**. As expected, the ratio of **5a** to **6a** was observed to increase as the progress of photoreaction of **4a** promoted by **1d** increases and **1d** is consumed (see entries 7–10). In addition, reaction of **4a** in THF, which also is a hydrogen atom donor, takes place to give increased amounts of **6a** (compare entry 3 to entry 2). Solvent free reactions of **4a** using **1b** and **1d** as promoters were found to proceed (entries 5 and 12). Although the conversion of **4a** in the reaction with **1b** is significantly higher than that attending the solution phase reaction, the ratios of **6a** are equivalent each other (compare entry 5 to entry 2). On the other hand, the ratio of **6a** in the solvent free reaction of **4a** with **1d** is greater than that in the solution phase reaction (compare entry 12 to entry 9). Although the reaction mechanism in the solvent free condition is unclear, it is possible that the larger amounts of **6a** produced in reactions taking place under solvent-free conditions are a consequence of close contact between **I** and **1**, which favors hydrogen atom transfer.

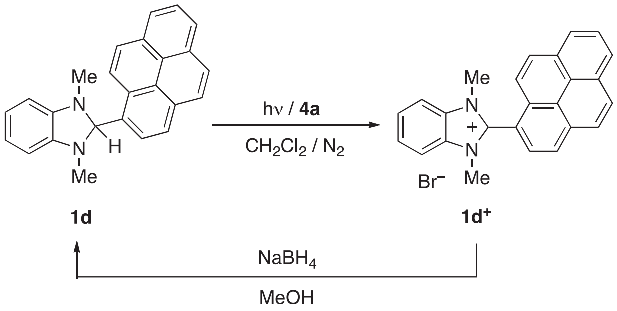


Scheme 3. Mechanism involving competitive hydrogen atom abstraction and ring-expansion in PET reactions of **4a** promoted by **1**.

Reactions of other α-halomethyl benzocyclic 1-alkanones **4b**–**4e** promoted by **1d** were also examined. While reaction of the indanone derivative **4b** occurred smoothly to give **5b** and **6b** along with a small amount of naphthol **7** (entry 14), its larger ring counterpart **4c** was less reactive and the yields of expected products were low (entry 15). Notably, the carbon–chlorine bond of **4d** is cleaved in photoreduction reactions promoted by **1b** and **1d** although the progress of these processes was slow (entries 16 and 17). On the other hand, the corresponding iodide **4e** reacts rapidly to produce the expected products **5e** and **6e** (entries 18 and 19).

Interestingly, over equal irradiation time periods the conversion of **4a** is lower than that of **4e** using **1b** as the promoter (compare entry 2 to 18). In contrast the conversion of bromide **4a** is significantly higher than that of **4e** when **1d** was employed as the photoreductant (compare entry 9 to 19). At this moment, it seems difficult to rationalize these characteristic effects of **1b** and **1d** on the reaction progress of **4a** and **4e**.

In these photoreduction reactions, Ar-DMBIH should be oxidized to form the corresponding imidazolium ion. The fact that this oxidation process takes place is confirmed by the observation that imidazolium **1d**$^+$ formed in the reaction of **4a** promoted by **1d** (Scheme 4). Accordingly, following 6 h irradiation of a mixture of **1d** and **4a** (entry 10 in Table 5), the pale yellow solid formed was isolated and identified to be the imidazolium salt **1d**$^+$**Br**$^-$ by using ^{1}H NMR spectroscopy. Treatment of **1d**$^+$**Br**$^-$ with $NaBH_4$ in MeOH afforded **1d** (94%).

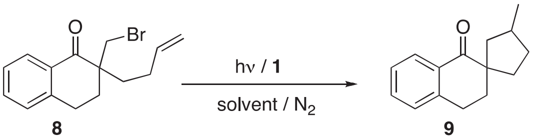


Scheme 4. Isolation and hydride reduction of **1d**$^+$Br$^-$.

We next determined the feasibility of PET reactions of the butenyl side chain containing α-bromomethyl tetralone **8** promoted by **1b**, **1c** and **1d** (Table 6). These processes are expected to generate radical intermediate that undergoes 5-*exo* cyclization. Reactions of **8** in CH_2Cl_2 and DMSO promoted by using **1b** produced the expected spirocyclic product **9** (>90%, based on the conversion of **8**) although the reaction in DMSO is relatively slow (entries 1 and 2). When **1c** was used for reaction of **8** in CH_2Cl_2, the conversion was slightly lower than that using **1b** although the process took place in a similarly high yield (compare entry 3 to entry 1). In a manner similar to that of **4a** (see entry 6 of Table 5), a white solid appeared during irradiation of **1c** with **8**. However, this occurrence did not significantly interfere with the reaction. The conversion of **8** in the reaction promoted by **1c** in DMSO is also lower than that using **1b** (compare entry 4 to entry 2), in which no solid precipitation was observed. In the reaction promoted by **1d**, the conversion of **8** was significantly low although the mass balance remains high (entry 5). It should be mentioned that the yields of **9** (>90% based on the conversion of **8**) in the above reactions are greater than those (40–80%) associated with previously reported PET reactions with Ar-DMBIH.[10e,h,i,l]

Table 6

Photoreaction of bromoalkyl and alkene substituted cyclic ketone **8** promoted by **1b**–**1d**[a]



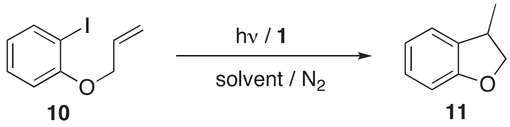
Entry	1	Solvent	Conv of **8** (%)[b]	Yield of **9** (%)[b]
1	**1b**	CH_2Cl_2	97[c]	91[c]
2	**1b**	DMSO	35	33
3	**1c**	CH_2Cl_2	85	80
4	**1c**	DMSO	29	26
5	**1d**	CH_2Cl_2	25	22

[a] **8** (0.20 mmol), **1** (1.2 equiv vs **8**), solvent (2.0 mL), λ>360 nm, 2 h.
[b] Determined by ^{1}H NMR.
[c] Average of two independent experiments.

Ar–DMBIH were applied to promote the 5-*exo* radical cyclization reaction of 2-allyloxy iodobenzene **10** (Table 7). The results show that irradiation of solutions containing **1b** or **1c** and **10** led to formation of the expected cyclization product **11** with yields that are dependent on the solvent. The reactions in DMSO proceeded in only modest yield (entries 2 and 4) and at a significantly higher rate than that in CH_2Cl_2 (entries 1 and 3), which is the reverse of the observation made for the reaction of **8** (see Table 6).

Table 7

Photoreaction of 2-allyloxy iodobenzene **10** promoted by **1b** and **1c**[a]



Entry	1	Solvent	Conv of **10** (%)[b]	Yield of **11** (%)[b]
1	**1b**	CH_2Cl_2	4	Trace
2	**1b**	DMSO	52	30
3	**1c**	CH_2Cl_2	14	9
4	**1c**	DMSO	63	43

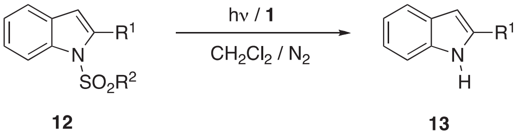
[a] **10** (0.20 mmol), **1** (1.2 equiv vs **10**), solvent (2.0 mL), λ>360 nm, 5 h.
[b] Determined by ^{1}H NMR.

Interesting observations made in the study described above include (1) reaction of **8** with **1b** or **1c** proceeds more smoothly than that using **1d** while **1d** is the most effective photoreductant for DB ring-expansion of **4a** and (2) DMSO is more suitable than CH_2Cl_2 as a solvent for reaction of **10** but not for that of **8** while such a significant difference in the conversion of **4a** between CH_2Cl_2 and DMSO was not observed.

The applicability of this PET protocol using Ar-DMBIH to N–S bond cleavage reactions was determined by investigating desulfonylation reactions of *N*-sulfonylated indoles **12** (Table 8).[10i,23] Photoreaction of **12a** promoted by **1b** in the presence of AcOH took place smoothly to form the deprotected indole **13** (entry 1). On the other hand, by the use of lower quantities of **1f** and without addition of AcOH, the process was highly efficient (entry 2). This protocol was applied to photo-detosylation of **12b** as well as demesylation of **12c**, both of which took place to give **13** in excellent yields (entries 3 and 4). The results of studies with **12d** show that an electron withdrawing substituent such as CO_2Me at the C_2 position of the indole ring is not necessary for the occurrence of the photo-desulfonylation process. However, a greater quantity of **1f** and longer irradiation times are required when this C_2-substituent is absent (entry 5). In these reactions, naphthol moiety of **1f**

Table 8

Photo-desulfonylation reactions of *N*-sulfonylated indoles **12** promoted by **1b** and **1f**[a]



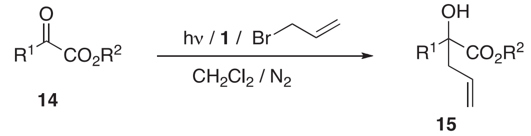
Entry	12	1	AcOH (equiv)	Irrad time (h)	Conv of **12** (%)	Yield of **13** (%)[b]
1	**12a**	**1b**	2.2	2	100	91
2	**12a**	**1f**	—	0.5	100	95
3	**12b**	**1f**	—	1	100	98
4	**12c**	**1f**	—	0.5	100	100
5	**12d**	**1f**	—	2	100	99[c]

[a] **12** (0.40 mmol), **1** (1.8 equiv of **1b** and 1.2 equiv of **1f** vs **12a**–**12c**, 1.5 equiv of **1f** vs **12d**), CH_2Cl_2 (4.0 mL), λ>360 nm.
[b] Isolated yield.
[c] Determined by ^{1}H NMR.

presumably acts as an internal proton donor, similar to the role it plays in the reactions of epoxy ketones **2**.

In the final chemical phase of this effort, Ar-DMBIH were applied to promote carbon–carbon bond forming reactions between α-keto esters **14** and allyl bromide. PET processes of this type were uncovered earlier in a study using other DMBIH.[10k] The results show that irradiation of **1a** in the presence of **14a** and allyl bromide (Table 9) led to formation of the expected allylation product **15a** in modest yield (entry 1). Visible light irradiation of **1d** with **14a** also promotes the reaction although a longer reaction time is required (entry 2). Non-conjugated ester substrates such as **14b** also underwent the allylation reaction to give **15b** although in rather low yield (entry 3).

Table 9
Photo-allylation reactions of α-keto esters **14** promoted by **1b** and **1d**[a]



Entry	14	1	λ (nm)	Irrad time (h)	Conv of **14** (%)	Yield of **15** (%)[b]
1	**14a**	**1b**	>360	4	92	63
2	**14a**	**1d**	>390	8	80	38
3	**14b**	**1b**	>360	12	88	36

[a] **14** (0.40 mmol), **1** (1.2 equiv vs **14**), allyl bromide (3.0 equiv), CH_2Cl_2 (4.0 mL).
[b] Isolated yield.

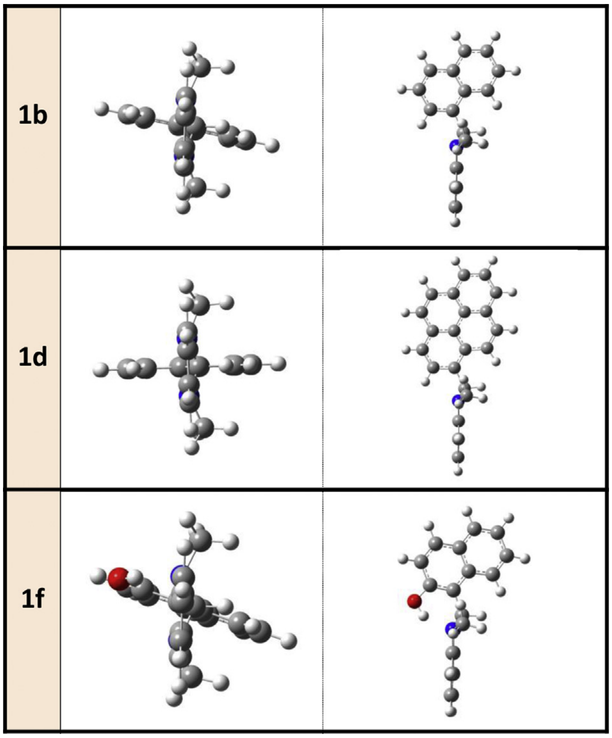


Fig. 5. Energy minimized structures of **1b**, **1d**, and **1f** obtained from DFT calculation (B3LYP/6-31G(d)).

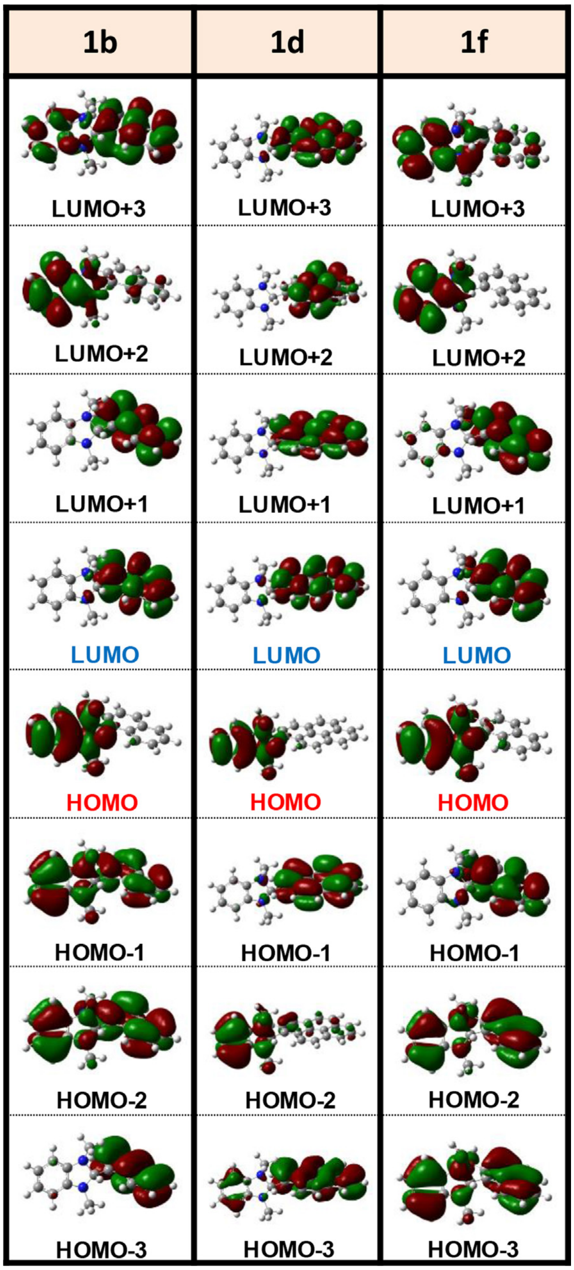


Fig. 6. Molecular orbital coefficients of **1b**, **1d**, and **1f** obtained by using DFT calculations (B3LYP/6-31G(d)).

Discussion on the mechanistic pathways followed in the photoinduced reduction reactions described above is described below. DFT calculations were performed in order to gain insight into the structural and electronic properties of the Ar-DMBIH. As described above, photoexcited Ar-DMBIH, and in particular **1b**, **1d**, and **1f**, effectively promote reduction reactions of various substrates. Therefore, calculations were first performed on these Ar-DMBIH (Figs. 5 and 6, data for other **1** are reported in Supplementary data). As seen by viewing the results displayed in Fig. 5, the benzimidazoline and aryl rings are nearly perpendicular to each other in energy minimized structures of **1b**, **1d**, and **1f** and, in the case of **1f**, hydrogen bonding exists between naphthol hydroxyl group and ring nitrogen.

Inspection of the calculated frontier orbital coefficients of **1b**, **1d**, and **1f**, depicted in Fig. 6, suggests that the highest energy occupied molecular orbitals (HOMO) of **1** are located on the benzimidazoline moiety, an observation that is fully consistent with the fact that these substances have nearly the same oxidation potentials regardless of the aryl substituent at C_2 position of the benzimidazoline (Table 10). On the other hand, the coefficients of the lowest energy unoccupied molecular orbitals (LUMO) are more highly populated on the aryl rings. Therefore, electronic interactions between the frontier orbitals could be less efficient because of the minimal overlap that exists between orbitals on the

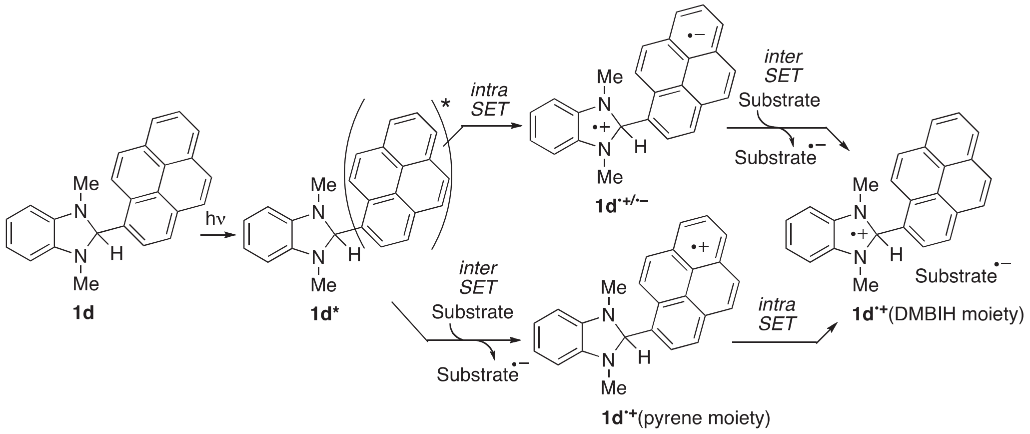
Table 10
Oxidation potential data of **1a**–**1g**[a]

1	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
$E^{ox}{}_{1/2}$ (V vs SCE)	+0.34	+0.36	+0.35	+0.35	+0.35	+0.34	+0.33

[a] Measured in MeCN.

benzimidazoline and aryl moieties (Fig. 5). On the other hand, the HOMO-1 of these compounds have some electronic distributions in the aryl rings. If aryl moieties are selectively irradiated, electronic excitation from the HOMO-1 to the LUMO could occur.

On the basis of the results described above, a plausible sequence for electronic transitions in the Ar-DMBIH, exemplified by pyrene substituted DMBIH **1d**, can be proposed (Scheme 5). Because the absorption band of **1d** in the long wavelength region (Fig. 3) is the same as that for pyrene, a light irradiation of **1d** initially produces a pyrene localized excited state **1d***, corresponding to an electronic transition from HOMO-1 to the LUMO of **1d**. Intramolecular SET from ground state benzimidazoline moiety to the excited pyrene gives the charge separated, zwitterionic biradical **1d**$^{\bullet+/\bullet-}$, corresponding to relaxation of an electron in the doubly occupied HOMO into the singly occupied HOMO-1. The pyrene radical anion then donates an electron to the substrate producing its radical anions along with benzimidazoline radical cation (**1d**$^{\bullet+}$). Alternatively, **1d*** directly donates an electron to the substrate to give the pyrene radical cation of **1d** and the radical anion of the substrate. Then, intramolecular SET from benzimidazoline moiety to pyrene radical cation moiety produces the same **1d**$^{\bullet+}$ formed via the former route. Intermolecular versions of this SET sequence have been proposed previously to describe reactions in which certain electron-donating substituent possessing pyrenes are used as photosensitizers along with DMBIH.[10h,i] On the basis of the redox potentials of **1d** ($E^{ox}{}_{1/2}$=+0.35 V), pyrene ($E^{ox}{}_{1/2}$=+1.16 V and $E^{red}{}_{1/2}$=−2.09 V for pyrene; E^{ex}=+3.34 eV for singlet excitation energy, $E^{ox}{}_{*}$=−2.18 V, $E^{red}{}_{*}$=+1.25 V for the redox potentials of the excited singlet),[24] and the substrates, (e.g., $E^{red}{}_{1/2}$=−1.68 V for **2a**, −1.64 for **4a**,[10l] −1.82 V for **8**,[10l] −1.78 V for **12a**), both of the above pathways should be energetically feasible.



Scheme 5. Plausible pathways of **1d** promoting the reduction reactions.

In an attempt to obtain the information about the nature of species formed by irradiation of **1d**, a laser-flash photolysis study was performed. However, **1d** was found to be labile under the experimental conditions.[25] Thus, 1,2,3-trimethyl-2-pyrenyl benzimidazoline (**1d-Me**, $E^{ox}{}_{1/2}$=+0.32 V) was employed in these experiments, in which transient absorption measurements were made in the 10^{-7}–10^{-4} s time regime following pulsing at 355 nm. Inspection of the time dependent transient absorption spectra displayed in Fig. 7 show that a broad band with a maximum at 430 nm grows until 500 ns, after, which it decays exponentially with no change of spectral shape. The 430 nm band was assigned to the triplet state of pyrene rather than the pyrene radical anion.[26,27] Generation of the triplet pyrene from **1d-Me**$^{\bullet+/\bullet-}$ is energetically possible because the triplet energy of pyrene (2.1 eV)[28] is lower than that of **1d-Me**$^{\bullet+/\bullet-}$ (2.41 eV). The lifetime of triplet pyrene was estimated to be 12 μs from fitting the decay profile at 430 nm (see the Supplementary data). A plausible route to produce triplet pyrene involves charge recombination of the initially formed, zwitterionic biradical **1d**$^{\bullet+/\bullet-}$ like, charge-separated state. Therefore, the proposed mechanism involving the formation of **1d**$^{\bullet+/\bullet-}$ shown in Scheme 5 is plausible for electronic processes that take place earlier than 100 ns after excitation.[29]

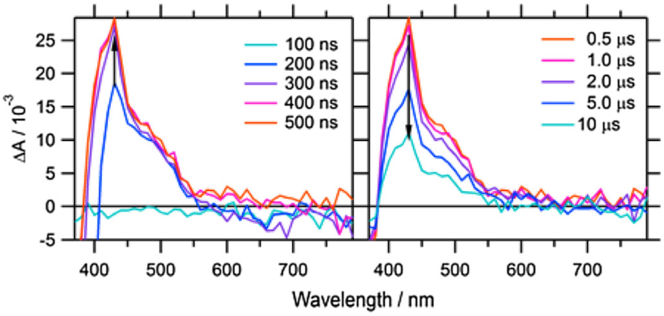


Fig. 7. Transient absorption spectra for **1d-Me** in CH_2Cl_2 (4×10^{-5} M) detected after nanosecond laser flash at 355 nm. Numbers in the figures indicates delay time after flash.

3. Conclusion

In the study described above, we demonstrated that 2-aryl-1,3-dimethylbenzimidazolines (Ar-DMBIH), in which aryl chromophores and benzimidazoline moiety are connected by a methylene carbon, act as effective reductants under the photoirradiation conditions (λ>360 nm). Although the electron donating properties of all Ar-DMBIH, as estimated by their oxidation potentials, are essentially same, the electron donating activities of their photoexcited states are different and vary according to the nature of the aryl substituents at C_2 of the DMBIH moiety. In addition, Ar-DMBIH behave differently depending on the substrates and reactions that they promote, and in some cases solvents have a profound effect on the efficiencies of the photoreactions. Both the naphthyl or pyrenyl substituted DMBIH are effective in promoting carbon-halogen bond cleavage, which initiates Dowd-Beckwith ring-expansion and 5-*exo* hexenyl cyclization processes and allylation reactions of acyl formates. On the other hand, hydroxynaphthyl substituted DMBIH, which acts as a formal two-electron and two-proton-donor, is effective in promoting transformations of epoxy ketones to aldols and deproptection reactions of *N*-sulphonyl indoles. Notably, we demonstrated that the imidazolium salt product can be recovered after the reaction and transformed to the starting Ar-DMBIH by hydride reduction. Unfortunately, the species generated by the photoexcitation of Ar-DMBIH and that responsible for the initial single electron reduction of the substrates could not be identified by using time resolved laser spectroscopy. However, it is believed that in the case of the pyene substituted DMBIH, photoexcitation of aryl chromophore followed by intramolecular SET generates a zwitterionic biradical that could serve as the electron donor in the PET process. Since some of Ar-DMBIH designed and prepared in this study have absorption spectra that extend into the visible region, their application in visible light promoted transformations are possible. We are pursuing this proposal in our current investigations.

4. Experimental section

4.1. General

NMR spectra were recorded using $CDCl_3$ or DMSO-d_6 solutions with tetramethylsilane (Me_4Si) as an internal standard at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on a double focusing mass spectrometer by using electrospray ionization (ESI). Uncorrected melting points are reported. Oxidation and reduction potentials in MeCN were measured using cyclic voltammetry and the previously described procedure.[10h] Calibration of the potential values were performed using the formal potentials of ferrocene/ferrocenium couple, $E°=0.069–0.072$ V and 0.434–0.446 V versus Ag/$AgNO_3$ and SCE, respectively. Photoreactions were conducted using solutions in Pyrex test tubes (1.4 cm diameter) immersed in a water bath at room temperature and irradiated using a 500 W Xe lamp. Column chromatography was performed using silica gel. Preparative thin-layer chromatography (TLC) was performed on 20×20 cm plates coated with silica gel. Anhydrous solvents for photoreactions and preparations of some substrates were obtained as follows. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under N_2. 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 *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), $PhCF_3$, and MeOH were purchased and used without distillation. Other reagents and solvents were purchased and used without purification. Substrates **2a**–**2e**,[10c] **4a**,[19f] **4b**,[10j] **4c**,[19f] **4d**,[10l] **4e**,[10l] **8**,[10h] **10**,[10c] and **12a**,[23] **12b**,[30] **12c**,[31] **12d**,[32] which are known compounds, were prepared by using reported procedures. Compounds **14a** and **14b** are commercially available.

4.2. Preparations of 2-aryl-1,3-dimethylbenziimidazoline (DMBIH) (1)

DMBIH **1a**,[7a] **1b**,[8b], and **1g**,[8c] are known compounds. **1c, 1d, 1e,** and **1f** were prepared by using modified literature procedures.[6a,8b,c,10g] A typical procedure for preparation of **1b** is described below. To a CH_2Cl_2 (10 mL) containing *N*,*N*′-dimethyl-*o*-phenylenediamine (DMPDA) (1.38 g, 10.1 mmol) with molecular sieves 4A (ca. 10g) under N_2 seated in ice-water bath was slowly added 1-naphthoaldehyde (1.42 mL, 10.5 mmol) in CH_2Cl_2 (20 mL). After addition of acetic acid (0.23 mL, 4.0 mmol), the resulting mixture was stirred for 6 h in an ice-water bath and then molecular sieves were removed by filtration. The residue obtained after concentration of the filtrate in vacuo was subjected to column chromatography (benzene with 1% triethylamine) to give **1b** (1.85 g, 6.8 mmol, 67%). In a similar fashion, **1c** (1.61 g, 5.9 mmol, 71%) from DMPDA (1.12 g, 8.2 mmol) and **1e** (1.30 g, 4.0 mmol, 50%) from DMPDA (1.09 g, 8.0 mmol) were prepared. **1d** (1.74 g, 5.0 mmol, 61%) from DMPDA (1.12 g, 8.2 mmol) was rinsed with MeOH after column separation. While **1b**, **1c**, and **1e** were crystallized from dimethoxyethane and EtOH, **1d** was crystallized from CH_2Cl_2 and MeOH before using for the photoreactions. **1f** (595 mg, 2.1 mmol, 49%) from DMPDA (584 mg, 4.3 mmol) was obtained by rinsing the solid with EtOH after column chromatography (EtOAc/benzene=1/6 with 1% triethylamine), and then used for the photoreaction.

*4.2.1. 1,3-Dimethyl-2-(1-naphthyl)benzimidazoline (**1b**).* Pale yellow solid; mp 123.5–124.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (br s, 1H), 7.89 (t, J=8.6 Hz, 2H), 7.59 (br s, 1H), 7.49–7.39 (m, 3H), 6.79–6.75 (m, 2H), 6.51–6.47 (m, 2H), 5.41 (br s, 1H), 2.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 134.4, 133.3, 132.2, 130.3, 129.0, 128.5, 125.7, 124.7, 119.2, 105.8, 33.3; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{17}N_2$ $[M-H]^+$ 273.1386, found 273.1378.

*4.2.2. 1,3-Dimethyl-2-(2-naphthyl)benzimidazoline (**1c**).* Pale yellow solid; mp 124.5–126.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.82 (m, 5H), 7.55–7.51 (m, 2H), 6.77–6.72 (m, 2H), 6.49–6.45 (m, 2H), 5.06 (s, 1H), 2.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 136.4, 134.2, 128.9, 128.6, 128.1, 127.9, 126.5, 126.3, 125.6, 119.4, 105.8, 94.3, 33.2; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{17}N_2$ $[M-H]^+$ 273.1386, found 273.1383.

*4.2.3. 1,3-Dimethyl-2-(1-pyrenyl)benzimidazoline (**1d**).* Yellow solid; mp 161.0–161.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (br s, 1H), 8.22–8.20 (m, 3H), 8.14–8.00 (m, 4H), 6.84–6.79 (m, 2H), 6.56–6.52 (m, 2H), 5.84 (br s, 1H), 2.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 132.1, 130.8, 130.6, 128.3, 128.0, 127.3, 126.0, 125.4, 125.3, 124.7, 124.5, 119.4, 105.9, 33.4; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{19}N_2$ $[M-H]^+$ 347.1543, found 347.1543.

*4.2.4. 2-(9-Anthryl)-1,3-dimethylbenzimidazoline (**1e**).* Orange solid; mp 177.0–178.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, J=9.2 Hz, 1H), 8.56–8.54 (m, 2H), 8.07–8.00 (m, 2H), 7.55–7.45 (m, 3H), 7.39–7.35 (m, 1H), 6.85–6.81 (m, 2H), 6.65 (s, 1H), 6.57–6.53 (m, 2H), 2.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 132.1, 130.8, 130.0, 129.7, 128.7, 127.2, 126.7, 126.6, 125.2, 125.0, 124.6, 121.5, 119.6, 106.3, 87.8, 33.5; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{19}N_2$ $[M-H]^+$ 323.1543, found 323.1533.

*4.2.5. 1,3-Dimethyl-2-(2-hydroxy-1-naphthyl)benzimidazoline (**1f**).* Pale yellow solid; mp 123.5–124.0 °C; ^1H 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 142.2, 134.5, 131.6, 129.2, 128.5, 127.0, 122.8, 121.0, 120.1, 109.0, 108.6, 87.8, 33.9; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{17}N_2O$ $[M-H]^+$ 289.1335, found 289.1325.

4.3. Preparation of 1,2,3-trimethyl-2-pyrenylbenziimidazoline (1d-Me)

To a benzene solution (8 mL) containing *N*,*N*′-dimethyl-*o*-phenylenediamine (400 mg, 2.9 mmol) with molecular sieves 4A (ca. 6.5g) was slowly added 1-acetylpyrene[33] (2.13 g, 8.7 mmol) in benzene (13 mL) under N_2. After addition of trifluoroacetic acid (0.23 mL, 3.0 mmol), the resulting mixture was stirred at reflux for 24 h and filtered. To the residue obtained after concentration of the filtrate in vacuo was added water. Extraction with CH_2Cl_2 gave an extract that was washed with water, sat $NaHCO_3$, brine, and dried over anhydrous $MgSO_4$. Solid obtained by concentration in vacuo was rinsed with Et_2O to give **1d-Me** (633 mg, 1.8 mmol, 60%), which was then crystallized from CH_2Cl_2 and EtOH.

*4.3.1. 1,2,3-Trimethyl-2-(1-pyrenyl)benzimidazoline (**1d-Me**).*- Yellow solid; mp 249.5–250.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J=9.6 Hz, 1H), 8.15–8.19 (m, 4H), 8.06–8.11 (m, 2H), 7.99 (t, J=7.6 Hz, 1H), 7.73 (d, J=9.6 Hz, 1H), 6.72–6.76 (m, 2H), 6.33–6.37 (m, 2H), 2.50 (s, 6H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 133.9, 132.1, 131.2, 131.1, 130.5, 128.1, 127.2, 126.9, 126.8, 126.0, 125.9, 125.6, 125.5, 125.1, 123.4, 118.2, 103.6, 91.3, 28.3, 16.3; HRMS (ESI) m/z calcd for $C_{26}H_{22}N_2$ $[M]^+$ 362.1778, found 362.1774.

4.4. Photoreactions of 2-aryl-1,3-dimethylbenziimidazoline 1 with various substrates

*4.4.1. Photoreactions of **1** with epoxy ketone **2**, sulfonyl indole **12**, or acyl formate **14**.* Independent solutions of **2**, **12** or **14** (0.40 mmol) and **1** (0.48 mmol) in a solvent (4 mL) with or without AcOH, $PhCO_2H$, or PhOH for **2** and **12**, allyl bromide for **14**, were purged with N_2 for 5 min prior to irradiation. The solutions were irradiated (λ>360 nm, except for entry 2 of Table 9 using the light above 390 nm) for appropriate time periods When an acid was present, water was added to the photolysate, and the mixture was extracted Et_2O. The extract was washed with water, sat $NaHCO_3$ for AcOH and $PhCO_2H$ or 20% NaOH for PhOH, brine, and dried over anhydrous $MgSO_4$. When allyl bromide or no additive was present, the precipitate formed by addition of Et_2O to the photolysate was separated by filtration. The residue obtained by the concentration of the extract or the filtrate was subjected to column chromatography (CH_2Cl_2, and then CH_2Cl_2/EtOAc=5/1 for **2** and **14**, CH_2Cl_2 for **12**) to give starting materials and products **3**, **13**, or **15**. When isolation of the products by chromatography could not be achieved, yields were determined by using ^{1}H NMR with appropriate internal references such as triphenylmethane and 1,3,5-trimethoxybenzene. Known products **3a**–**3e**,[10c] **13a**,[23] and **15a**[10k] were characterized by comparing their ^{1}H NMR data with those reported earlier. **13d** is commercially available. Spectral data of unknown **15b** is given below.

*4.4.2. Ethyl 2-hydroxy-2-phenethyl-4-pentenate (**15b**).* Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.20–7.14 (m, 3H), 5.84–5.73 (m, 1H), 5.13 (s, 1H), 5.11–5.08 (m, 1H), 4.26–4.13 (m, 2H), 3.34 (br s, 1H), 2.86–2.78 (m, 1H), 2.52–2.39 (m, 3H), 2.12–1.95 (m, 2H), 1.30 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 141.6, 132.2, 128.4, 128.3, 125.9, 119.0, 76.8, 61.9, 44.1, 40.5, 30.3, 14.3; HRMS (ESI) m/z calcd for $C_{15}H_{20}O_3$ $[M+Na]^+$ 271.1305, found 271.1303.

*4.4.3. Photoreaction of **1** with haloalkyl keto ester **4**, alkene tethered bromoalkyl ketone **8**, or allyloxy iodobenzene **10**.* A solution of a substrate **4**, **8** or **10** (0.40 or 0.20 mmol) and **1** (0.48 mmol or 0.24 mmol) in a solvent (4 mL or 2 mL) was purged with N_2 for 5 min prior to irradiation. Each solution was irradiated. When DMSO was used as a solvent, the photolysate was diluted with water and extracted with Et_2O. Each extract was washed with water, sat $NaHCO_3$, brine, and dried over anhydrous $MgSO_4$. When THF or CH_2Cl_2 was used, the precipitate formed by addition of Et_2O to the photolysate was separated by filtration. The residue obtained by the concentration of the extract or filtrate was subjected to column chromatography (n-hexane/EtOAc=3/1) to give recovered **4** and products **5** and **6**. Since separation of **4** and **6** by chromatography could not be achieved, yields were determined by using ^{1}H NMR. The conversion of **8** and **10** as well as the yields of **9** and **11** were determined by using ^{1}H NMR and appropriate internal references such as triphenylmethane and 1,3,5-trimethoxybenzene. Known products **5a**–**5c**,[19f] **6a**–**6c**,[19f] **7**,[10j] **9**,[10h] and **11**,[10c] were characterized by comparing their ^{1}H NMR data with those reported earlier.

*4.4.4. Solvent free photoreaction of **1** with **2** or **4**.* A CH_2Cl_2 solution of **2** or **4** (0.05–0.20 mmol) and **1** (0.06–0.24 mmol) with an appropriate quantity of $PhCO_2H$ or PhOH for **2** was prepared in a round-bottomed flask and then concentrated in vacuo. The thin-layered residue was flashed with N_2 and irradiated (see Supplementary data). The same work-up, separation and product identification procedures as those used for the photoreactions in solutions were performed.

4.5. Recovery and subsequent transformation of an imidazolium salt ($1d^+$) (entry 10 of Table 5)

A solution of **4a** (124.5 mg, 0.40 mmol) and **1d** (167.2 mg, 0.48 mmol) in CH_2Cl_2 (4 mL) was purged with N_2 for 5 min prior to irradiation. This solution was irradiated for 6 h. The precipitate formed by addition of Et_2O to the photolysate was separated by filtration. To a solution of the precipitate in MeOH (8 mL) was added $NaBH_4$ (62.3 mg, 1.65 mmol) under N_2 in an ice-bath. The resulting mixture was stirred for 1 h, diluted with water and extracted with EtOAc. The extract was washed with sat $Na_2S_2O_3$, brine and dried over $MgSO_4$ and concentrated in vacuo giving a residue that was analyzed by using ^{1}H NMR and identified as **1d** (157.7 mg, 0.45 mmol, 94%).

*4.5.1. 1,3-Dimethyl-2-(1-pyrenyl)benzimidazolium bromide (**$1d^+Br^-$**).* Pale yellow solid; mp 258.0–260.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (d, J=8.0 Hz, 1H), 8.55–8.50 (m, 4H), 8.44–8.40 (m, 2H), 8.27–8.21 (m, 3H), 7.91 (d, J=9.2 Hz, 1H), 7.88–7.82 (m, 2H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.0, 134.2, 132.5, 130.9, 130.7, 130.6, 130.4, 130.2, 129.0, 127.6, 127.5, 127.4, 127.2, 127.0, 125.4, 123.8, 123.32, 123.25, 114.2, 113.9, 33.1; HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2$ $[M-Br]^+$ 347.1543, found 347.1536.

4.6. Density functional theory (DFT) calculations

Calculations were carried out using the Gaussian 03 program package.[34] Geometry optimizations were performed on ground states at the B3LYP/6-31G(d) level. In addition, frequency calculations were performed on all optimized structures to confirm that no imaginary frequencies were obtained. The molecular orbitals (MOs) were visualized with Gauss View 3.09 software.

4.7. Laser flash photolysis

Transient absorption measurements were performed using an in-house-built spectrometer equipped with a nanosecond YAG laser that irradiates the third harmonic of λ=355 nm as a pump light and a continuous wave Xe lamp probe light, of which the spectrum is appropriately shaped with high and low cut-filters. The probe light passing through the sample solution was dispersed by a monochromator and then detected with a photomultiplier tube. The output signal from the photomultiplier tube was recorded with a digital oscilloscope. Dead time of this measurement system is 100 ns.

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Supplementary data

Supplementary data (These data include a experimental set-up of solvent free photoreaction, cyclic voltammograms of **1a**–**1g** and **1d-Me**, selected substrates, absorption spectra of selected substrates, DFT calculation data of **1**, decay profile of transient absorption spectrum for **1d-Me**, ^{1}H NMR and ^{13}C NMR of **1b**–**1f**, **1d-Me**, and **15b**.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.06.071.

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15. A reviewer suggested the possibility of the intermolecular charge transfer (CT) interaction of **1** at the high concentration. We measured the spectrum of the mixture of **1a** and naphthalene expecting their CT interaction, and also measured the absorption spectra of **1a** and **1b** at different concentrations. However, no clear CT absorption bands were observed in both cases.
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18. A reviewer questioned why 1.2 equiv of **1f** and **1g** are enough to be effective even though they have only one hydroxyl group while excess (2.2–6.6 equiv) of proton donors are used for the reaction with **1a**–**e** in solutions. Transformation of **2** to **3** promoted by **1** is considered to proceed within PET generated radical ion pairs, not after dissociation to become free radical ions. Therefore, less polar solvents are more suitable for the reaction than highly polar ones (see Tables 2–4). In the cases of **1f** and **1g**, two electron and two proton transfers to **2**, which are required for the formation of **3**, would smoothly take place within their radical ion pairs.
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