Sensitizer-free photochemical regeneration of benzimidazoline organohydride

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Abstract

Organohydrides are an important class of organic compounds that can provide hydride anions for chemical and biochemical reactions, as demonstrated by reduced nicotinamide adenine dinucleotide serving as an important natural redox cofactor. The coupling of hydride transfer from the organohydride to the substrate and subsequent regeneration of the organohydride from its oxidized form can realize organohydride-catalyzed reduction reactions. Depending on the structure of the organohydride, its hydridicity and ease of regeneration vary. Benzimidazoline (BIH) is one of the strongest synthetic C–H hydride donors; however, its reductive regeneration requires highly reducing conditions. In this study, we synthesized various oxidized and reduced forms of BIH derivatives with aryl groups at the 2-position and investigated their photophysical and electrochemical properties. 4-(Dimethylamino)phenyl-substituted BIH exhibited salient red-shifted absorption compared to other synthesized BIH derivatives, and visible-light-driven regeneration without using an external photosensitizer was achieved. This knowledge has significant implications for the future development of solar-energy-based catalytic photoreduction technologies that utilize organohydride regeneration strategies.

Transition metal (TM) hydrides are crucial chemical species in organic synthesis and can provide either hydride ions (consisting of two electrons and a proton) or hydrogen atoms (consisting of one electron and a proton) for the reduction of substrates.[1-3] The transient and repeated generation of TM hydrides occurs in a reduction reaction system, and TMs are often utilized as catalysts. However, the scarcity of TMs[4] has led to the development of metal-free hydrides (organohydrides)[5-6] exhibiting reactivities similar to those of TM hydrides. In the H–A bond, the hydrogen atom displays a hydride character when A is more electropositive than hydrogen, as demonstrated by the borohydride species ($[R_3B–H]^-$), which is one of the most commonly used organohydrides. Although the hydrogen atom in a C–H bond is typically partially positively charged and exhibits limited hydride character owing to the higher

electronegativity of carbon compared to that of hydrogen (Pauling electronegativity: C 2.6, H 2.2), certain cyclic compounds can serve as hydride donors by acquiring aromatic stabilization upon release of the hydride from the C–H bond.[5-6] In nature, the concept of hydride transfer via cyclic compounds is utilized by the enzymatic cofactor reduced nicotinamide adenine dinucleotide phosphate (NADPH), which serves as a crucial carrier of electrons in biological systems. Living organisms have a mechanism to reduce $NADP^+$, the oxidized form of NADPH, after a reduction reaction, and utilize NADPH as a catalyst. Researchers have taken inspiration from the functions of NADPH to develop reduction reactions using synthetic NADPH analogs, such as the Hantzsch ester.[7-10] Additionally, the catalytic use of hydride donors has been achieved by in situ regeneration using reductants.[11-14]

Benzimidazoline (BIH) is one of the strongest isolable synthetic C–H hydride donors. Chikashita et al. used a BIH derivative to reduce carbon–halogen bonds at the α-position of carbonyl groups and α,β-unsaturated carbonyl compounds.[15-16] Lim and Musgrave et al. reported the reduction of CO_2 to formate using a BIH molecule.[17] The BIH molecule has also been utilized as a potent electron donor in photochemical reactions[18-19] since its first use by Hasegawa et al.[20] While the BIH molecule was used as a stoichiometric reducing agent in these reactions, its utilization as a catalyst is an attractive research goal. However, the hydridicity of an organohydride is generally inversely proportional to the ease of regeneration from its oxidized form. While BIH has a strong reducing capability, its oxidized form, the benzimidazolium cation (BI^+), has a low reduction potential. Therefore, reductive regeneration of BIH requires highly reducing conditions. Lim and Musgrave et al. demonstrated the electrochemical reduction of **BI^+-Me** to **BIH-Me** in a separate vessel from CO_2 reduction (Figure 1b).[17] Hasegawa et al. reported photochemical hydrodesulfonylation using a catalytic amount of **BI^+-1Nap-O^-** in the presence of stoichiometric $NaBH_4$ (Figure 1c).[21] Recently, Glusac[22] and our group [23-24] independently reported the photochemical regeneration of BIH (Figure 1d,e). Using photochemical regeneration, metal-free CO_2 reduction to formate was achieved (Figure 1e),[24] in which the excited state of the carbazole photosensitizer **PS2** with high reducing capability[25-27] performed the first one-electron transfer in the two-electron reduction process of **BI^+-Me** to **BIH-Me**.

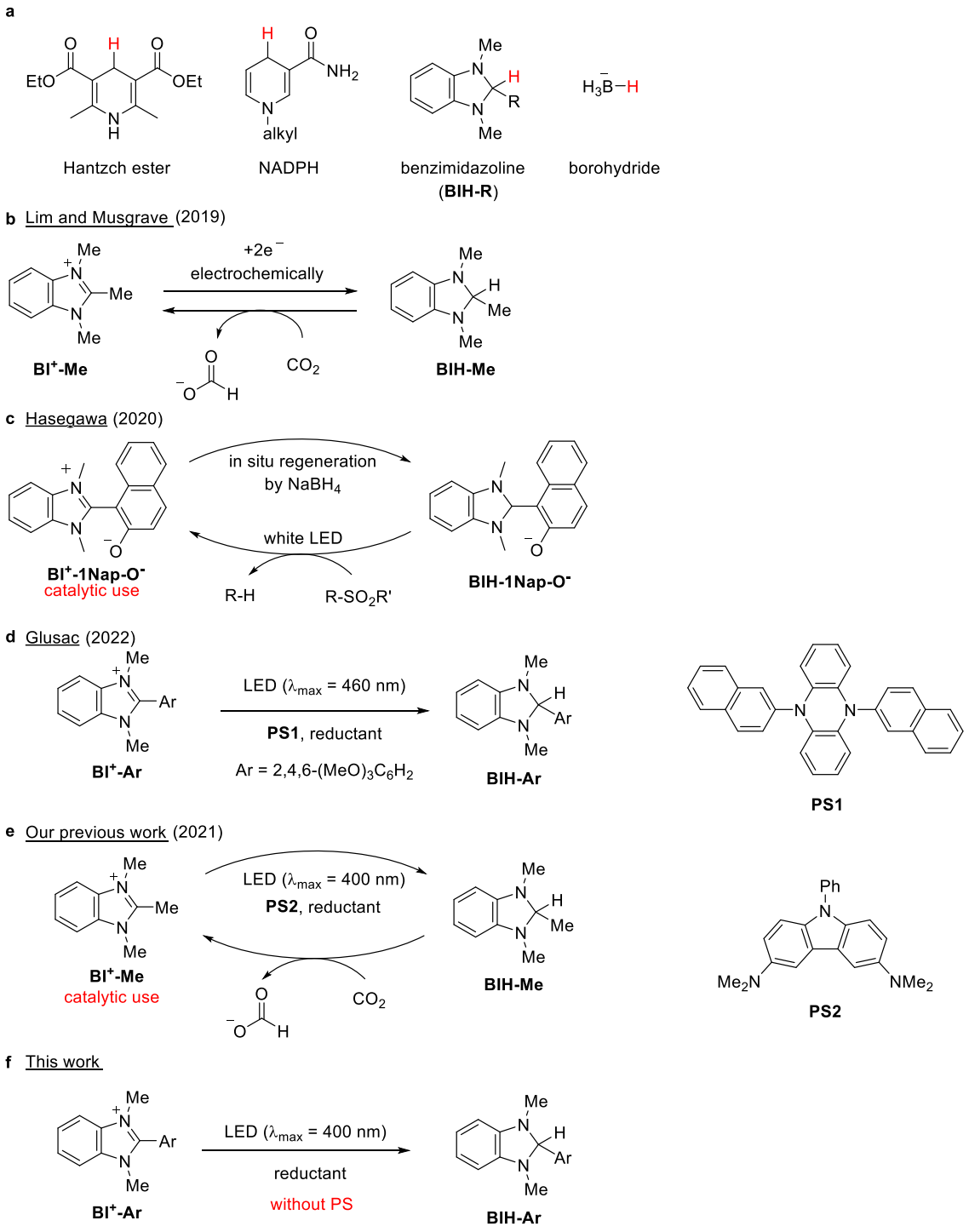


Figure 1. Organohydride regeneration strategy. (a) Examples of organohydrides. (b,c) Electrochemical or chemical regeneration of BIH organohydrides. (d,e) Photochemical regeneration of BIH organohydrides using an external photosensitizer. (f) Photosensitizer (PS)-free photochemical regeneration of BIH organohydrides (this work).

In this study, we aimed to develop a stand-alone hydridic BIH that can be regenerated from BI^+ using visible light without the use of an external photosensitizer. We synthesized various oxidized and reduced forms of BIH derivatives with aryl groups at the 2-position, anticipating that the aryl group could exhibit extended π-electron conjugation with the benzimidazolium moiety, causing a bathochromic shift in absorption. Herein, we report the synthesis, optoelectronic properties, and photochemical behaviors of these BIH molecules.

Results and Discussion

Synthesis of BI^+-Ar and BIH-Ar molecules

All **BI^+-Ar** and **BIH-Ar** molecules were successfully synthesized according to the literature (Figure 2), and the details are described in the experimental section. **BI^+-Ar** molecules, except **BI^+-Ph-CH_2** and **BI^+-1Nap-O^-**, were prepared from the corresponding benzimidazoles **1,** which were readily synthesized from *o*-phenylenediamine (Figure 2a). Depending on the identity of the 2-aryl group, a one-step (method **a**) or two-step (method **b**) procedure was applied. The counter anion of **BI^+-Ar** was iodide in all cases. **BIH-Ar** molecules were synthesized from **BI^+-Ar** by reduction with $NaBH_4$. The six **BIH-Ar** molecules synthesized were sufficiently stable to be characterized under ambient conditions. **BI^+-Ph-CH_2**, in which the benzimidazolium moiety and the 2-aryl group are connected through a fused 6-membered ring, was synthesized from **3** and **4** in two steps (Figure 2b). Although the corresponding reduced form **BIH-Ph-CH_2** was detected by ^1H NMR spectroscopic analysis in the reduction reaction of **BI^+-Ph-CH_2** using $NaBH_4$, the isolation and characterization of **BIH-Ph-CH_2** were difficult because of its instability in air. The reason for the instability of this compound will be discussed later in the study. **BIH-1Nap-OH** and **BI^+-1Nap-O^-** were developed by Hasegawa et al[28] as hydrogen atom and/or electron donors and photosensitizers. They were synthesized according to a previously reported method (Figure 2c).

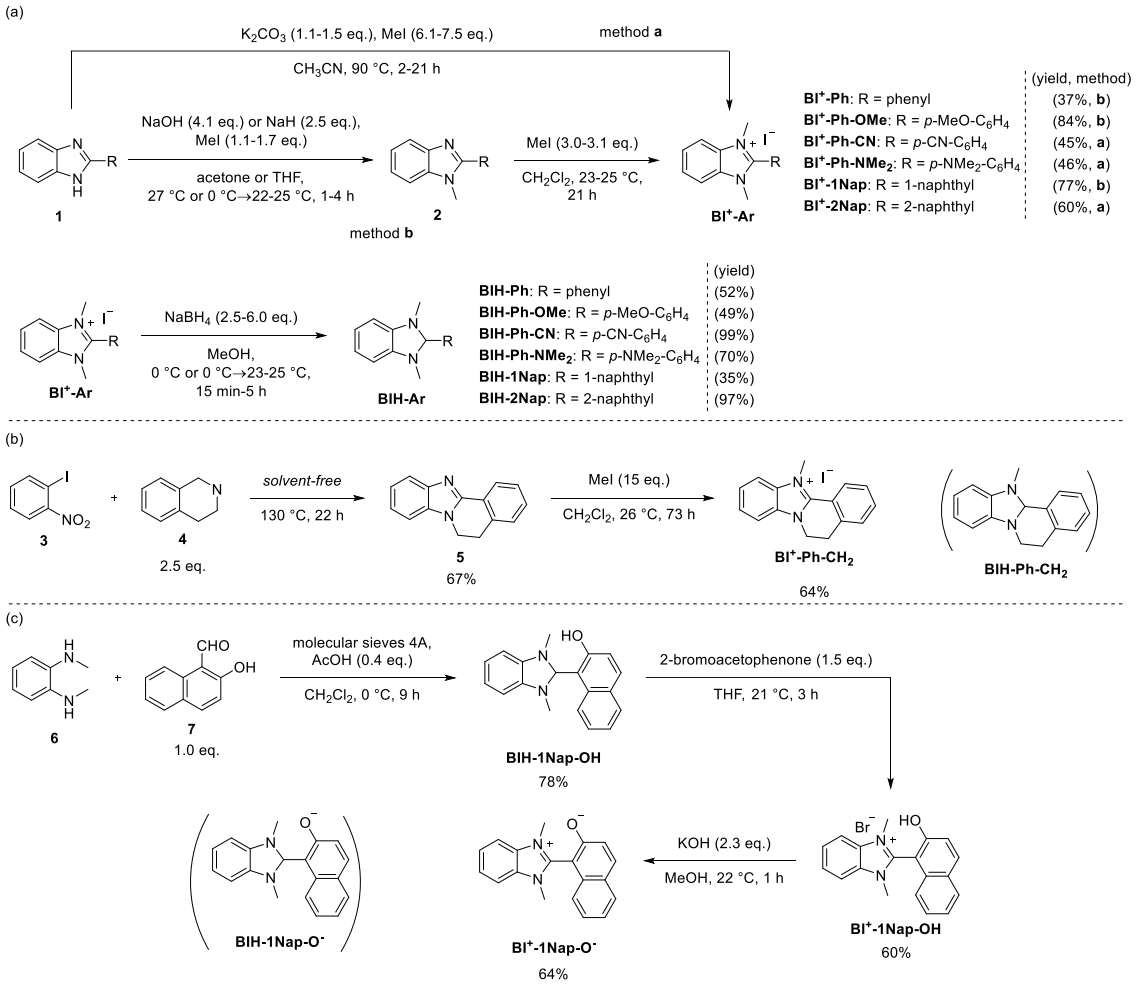


Figure 2. Synthesis of **BI⁺-Ar** and **BIH-Ar** molecules. See the experimental section for details.

Photophysical and electrochemical properties

The absorption spectra of the synthesized **BI⁺-Ar** molecules in dimethylsulfoxide (DMSO) are shown in Figure 3a. **BI⁺-Ph** exhibited the lowest-energy absorption band, with a peak maximum at 280 nm and a peak edge at approximately 320 nm (Figure 3c). The absorption spectra of **BI⁺-Ph-OMe**, **BI⁺-Ph-CN**, **BI⁺-Ph-1Nap**, and **BI⁺-Ph-2Nap** were similar to that of **BI⁺-Ph**, with peak maxima at approximately 280–300 nm and peak edges at approximately 330–350 nm. The slightly red-shifted absorption compared to **BI⁺-Ph** is attributed to the expanded π-conjugation on the 2-aryl substituents.

BI⁺-Ph-CH₂ exhibited further red-shifted and resolved absorption with a maximum peak at 315 nm, which can be attributed to the better π-conjugation of **BI⁺-Ph-CH₂** compared to that of **BI⁺-Ph**, owing to the restricted rotation of the C–C bond between the BI^+ backbone and the 2-phenyl substituent. This assumption does not contradict the density functional theory (DFT)-calculated dihedral angles between the BI^+ and 2-phenyl π-planes of 59° and

20° for **BI⁺-Ph** and **BI⁺-Ph-CH₂**, respectively. However, the absorption of **BI⁺-Ph-CH₂** ceased at 350 nm.

BI⁺-Ph-NMe₂ exhibited a further red-shifted and broad absorption band with a peak maximum at 345 nm and a peak edge at approximately 400 nm, suggesting that **BI⁺-Ph-NMe₂** can absorb visible light (see Figure 3c for comparison with **BI⁺-Ph**). The DFT-optimized (B3LYP/6-31G(d)) ground-state structure and the lowest-energy vertical excitation based on the ground-state structure obtained by time-dependent DFT (TD-DFT) calculations (B3LYP/6-31G++(d,p)) for **BI⁺-Ph** and **BI⁺-Ph-NMe₂** are shown in Figure 4. The calculated values of the longest absorption (274 and 365 nm for **BI⁺-Ph** and **BI⁺-Ph-NMe₂**, respectively) and oscillator strength matched well with the experimental results, giving validity to the following discussion based on this quantum calculation. The dihedral angles between the BI^+ and 2-phenyl π-planes were 59° and 48° for **BI⁺-Ph** and **BI⁺-Ph-NMe₂**, respectively, suggesting that the π-orbitals of the BI^+ and 2-phenyl moieties were partially conjugated for both compounds. Single-crystal X-ray diffraction analysis of **BI⁺-Ph-NMe₂** revealed the dihedral angle between BI^+ and the 2-phenyl π-plane to be 54°, which is close to the value obtained from DFT calculations (48°). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **BI⁺-Ph** extended over the conjugated π-electron region. The observed lowest-energy absorption of **BI⁺-Ph** was ascribed to the π-π* locally excited (LE) transition because the calculated lowest-energy vertical excitation of **BI⁺-Ph** was the HOMO→LUMO transition. In contrast, the HOMO and LUMO of **BI⁺-Ph-NMe₂** were relatively localized over the 2-aryl and BI^+ moieties, respectively. The calculated lowest-energy vertical excitation of **BI⁺-Ph-NMe₂** was the HOMO→LUMO transition; therefore, the observed lowest-energy absorption of **BI⁺-Ph-NMe₂** was ascribed to charge-transferred (CT) transition. The HOMO-LUMO energy gap decreased and the absorption wavelength increased because the strong electron-donating property of the NMe_2 group affected the HOMO more than the LUMO.

BI⁺-1Nap-O⁻ demonstrated significantly red-shifted absorption reaching approximately 460 nm, reproducing the results of Hasegawa.[29] This absorption was ascribed to LE excitation in the 1-naphtholate anion because this long-wavelength absorption was also observed for **BIH-1Nap-O⁻** but not for **BI⁺-1Nap-OH**[21].

In contrast to **BI⁺-Ar**, the **BIH-Ar** series exhibited similar absorption spectra, with the lowest energy peak maximum at approximately 310 nm (Figure 3b). Therefore, with the exception of the redox pairs **BI⁺-Ph-NMe₂**/**BIH-Ph-NMe₂** and **BI⁺-1Nap-O⁻**/**BIH-1Nap-OH**, **BI⁺-Ar** exhibited shorter wavelength absorption than **BIH-Ar** (Figure 3c). This result is counterintuitive because **BI⁺-Ar** exhibited a higher degree of unsaturation and aromatization than **BIH-Ar**. In contrast to **BI⁺-Ph**, **BIH-Ph** demonstrated a perfectly orthogonal relationship

between BIH and 2-aryl planes (Figure 4). The vertical excitation of **BIH-Ph** is a HOMO→LUMO+2 transition. The HOMO is localized on the BIH plane, while the LUMO+2 corresponds to the mixed σ* orbitals of the hydridic C–H bond of BIH and the ortho C–H bond of the 2-phenyl substituent. The electronic transitions involving the lowest-energy excitation are thus distinct between **BI⁺-Ar** and **BIH-Ar**, which causes the counterintuitive absorption spectra.

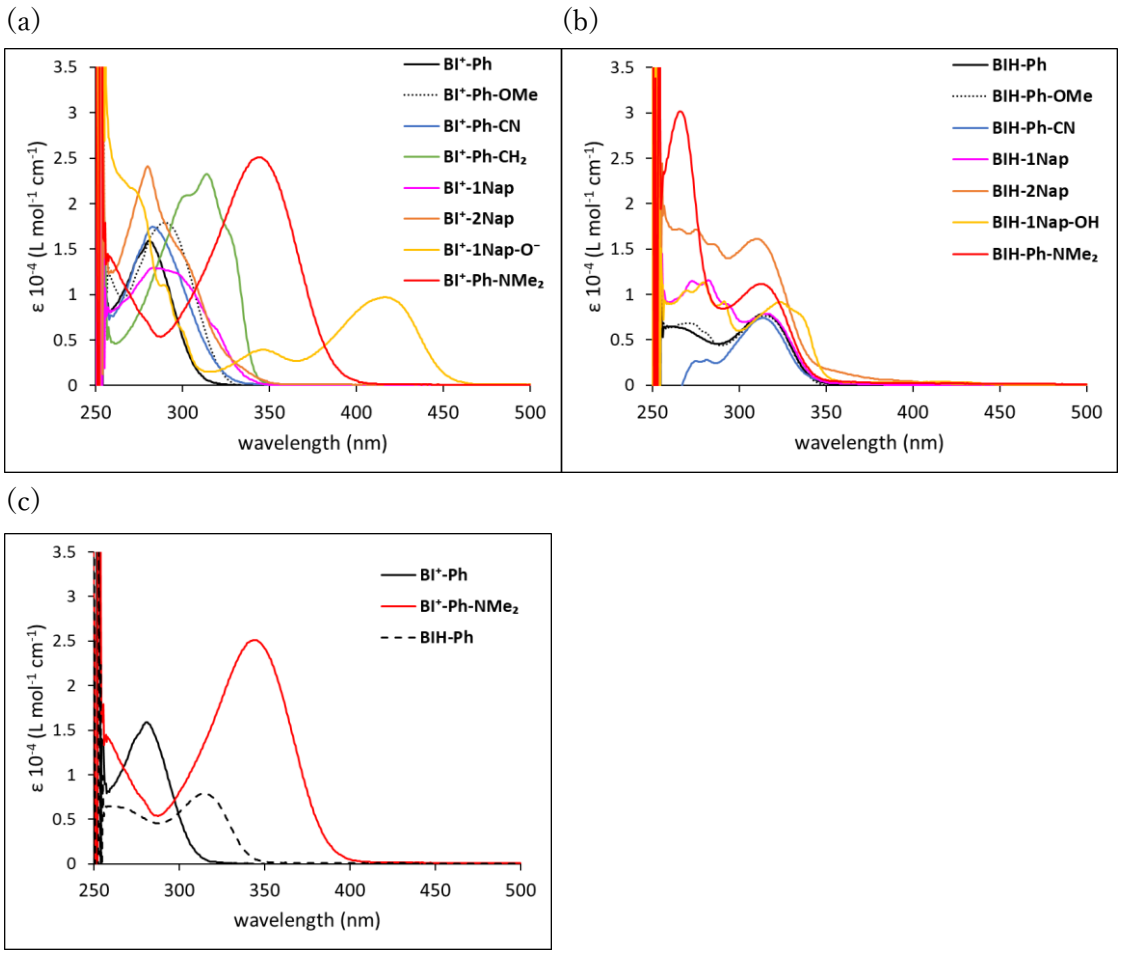


Figure 3. Absorption spectra of **BI⁺-Ar** and **BIH-Ar** molecules. Solvent: DMSO, temperature: 25 °C. (a) **BI⁺-Ar**, (b) **BIH**. (c) Selected absorption spectra (**BI⁺-Ph**, **BI⁺-Ph-NMe₂**, and **BIH-Ph**) for comparison.

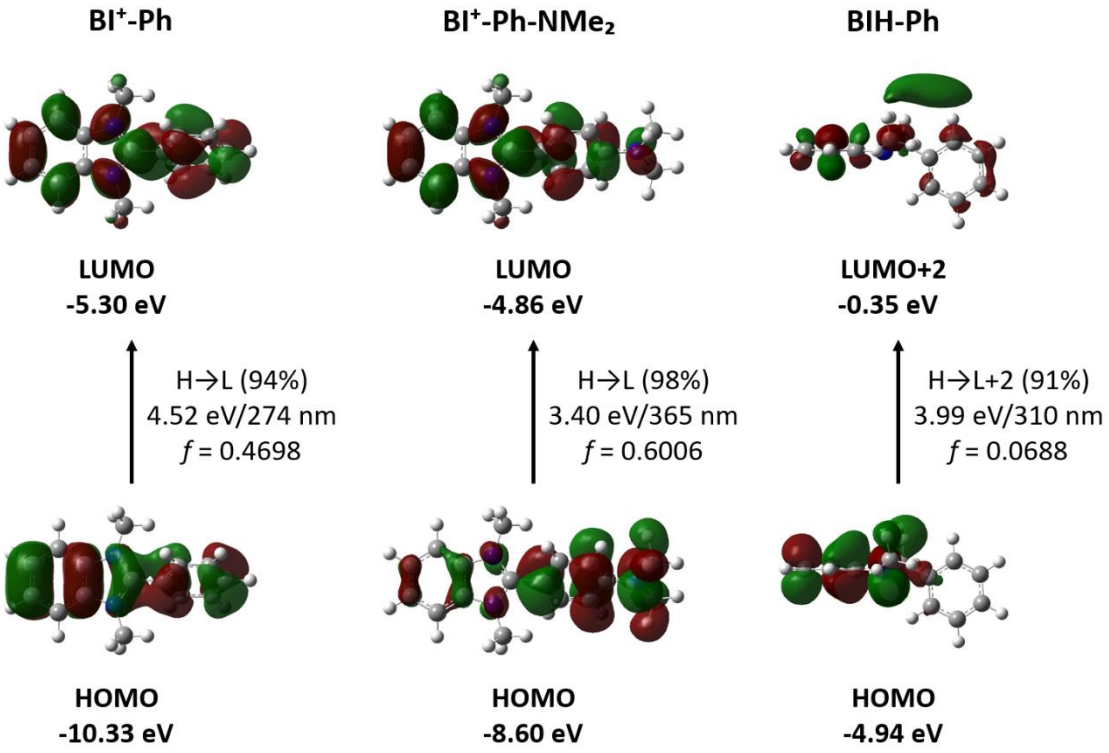


Figure 4. Calculated lowest-energy vertical excitation of **BI⁺-Ph**, **BI⁺-NMe₂**, and **BIH-Ph**. The geometries were optimized by DFT at the B3LYP/6-31G(d) level of theory. The vertical excitations were obtained by TD-DFT at the B3LYP/6-31G++(d,p) level of theory based on the optimized ground-state geometry. The composition (contribution), excitation energy, and oscillator strength (*f*) are presented. The calculated orbital energy levels are presented in units of electron volts.

The partially conjugated geometry between the BI^+ and 2-aryl planes in **BI⁺-Ph** and the orthogonal geometry in **BIH-Ph** (Figure 4) were accounted for by considering the balance between electronic and structural effects. The bulkiness of the 2-phenyl group drives the molecules to adopt an orthogonal geometry to avoid steric repulsion between the 2-phenyl group and the two N–Me groups of the BI^+/BIH backbone. Therefore, **BIH-Ph** had an orthogonal geometry. For **BI⁺-Ph**, as the dihedral angle approaches zero, the complex experiences more electronic stabilization through conjugation between the BI^+ and 2-phenyl π-orbitals, and **BI⁺-Ph** adopts a partially conjugated geometry that balances the electronic and structural effects. **BIH-Ph-CH₂**, a reduced hydride form of **BI⁺-Ph-CH₂**, cannot adopt an orthogonal geometry because of the restricted rotation between BIH and the 2-phenyl rings, making **BIH-Ph-CH₂** unstable and difficult to isolate (vide supra).

Most of the synthesized **BI⁺-Ar** molecules exhibited structureless broad fluorescence (Figure 5). Only **BI⁺-Ph-CH₂**, with a rigid structure owing to restricted bond rotation, showed a resolved shoulder peak. The singlet state energies (^1E_S) of **the BI⁺-Ar** molecules were estimated (Table 1) from the fluorescence wavelengths and ranged from 3.40 to 3.94 eV.

Cyclic voltammetry (CV) measurements were performed to investigate the electrochemical properties of the synthesized **BI⁺-Ar** molecules. The corresponding voltammograms are shown in Figure S2, and the reduction potentials (E_{red}) are listed in Table 1. Using the Rehm-Weller equation,[30] the reduction potential of each molecule in the singlet excited state ($^1E_{red}$*), which represents the capability of the molecule to accept an electron in its singlet excited state, was calculated. The E_{red}* values ranged from 1.37 to 2.29 V vs saturated calomel electrode (SCE).

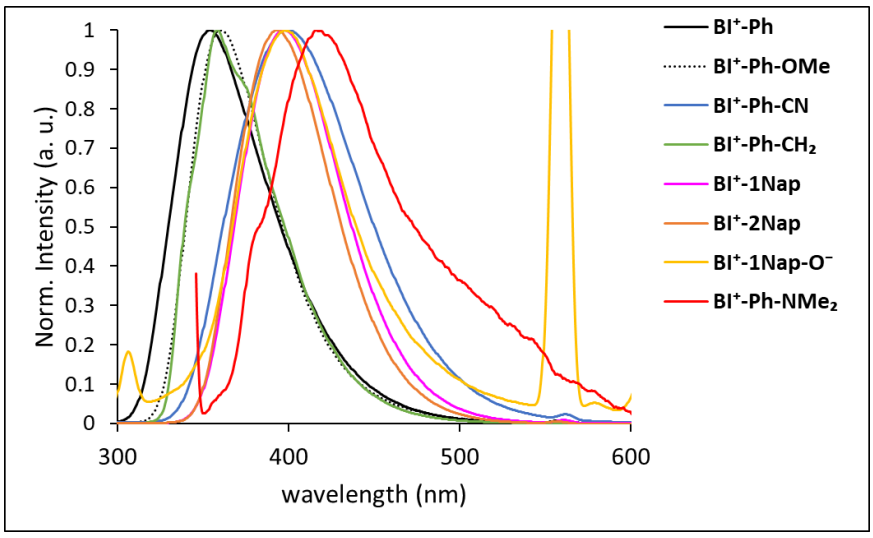


Figure 5. Normalized fluorescence spectra of **BI⁺-Ar**. Concentration: 10–18 μM. Solvent: MeOH. Temperature: 25 °C. Excitation wavelength: 280 nm (**BI⁺-Ph**, **BI⁺-2Nap**, **BI⁺-1Nap-O⁻**), 281 nm (**BI⁺-1Nap**), 282 nm (**BI⁺-Ph-CN**), 289 nm (**BI⁺-Ph-OMe**), 312 nm (**BI⁺-Ph-CH₂**), and 341 nm (**BI⁺-Ph-NMe₂**).

Table 1. Optoelectronic data of **BI⁺-Ar**.

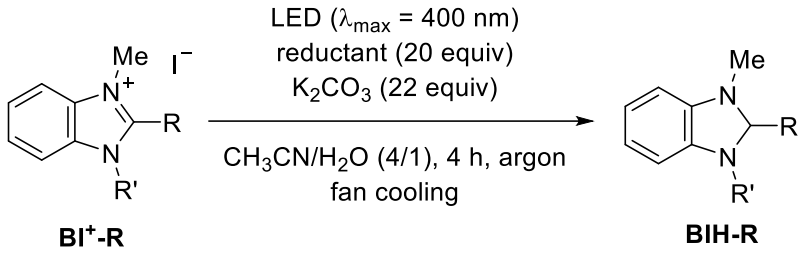
Molecule	^1E_S /eV	E_{red} /V vs SCE	$^1E_{red}$* /V vs SCE
BI⁺-Ph	3.94	–1.65	2.29
BI⁺-Ph-OMe	3.79	–1.76	2.03
BI⁺-Ph-CN	3.63	–1.34	2.29
BI⁺-Ph-CH₂	3.76	–1.51	2.25
BI⁺-1Nap	3.53	–1.64	1.89

BI$^+$-2Nap	3.54	–1.56	1.98
BI$^+$-1Nap-O$^-$	3.67	–2.30	1.37
BI$^+$-Ph-NMe$_2$	3.40	–1.84	1.56

^1E_S: Singlet state energies approximated as the high-energy onset of fluorescence (in MeOH at 298 K), where the emission intensity is 10% that obtained at the maximum emission wavelength.[31-32] E_{red}: Reduction potential of ground–state molecules obtained from CV analysis. $^1E_{red}$*: Reduction potential of molecules in the singlet excited state calculated using the Rehm–Weller equation.[30]

With the knowledge that **BI$^+$-Ar** molecules have sufficient oxidizing ability in their excited state (Table 1) and that some of them absorb visible light (Figure 3a), we next investigated the visible-light-mediated generation of the organohydride **BIH-Ar** from **BI$^+$-Ar** without using an external photosensitizer (Table 2). LED lamps with λ_{max} = 400 nm and a light intensity of 270–360 mW cm^{-1} were employed as light sources. Ascorbic acid was initially used as a terminal reductant, with K_2CO_3 as a base to deprotonate and activate ascorbic acid as a reductant. The reaction mixture was cooled with a fan such that the reaction temperature was below 45 °C. First, various **BI$^+$-Ar** substrates were subjected to photochemical reduction reactions (entries 1–9). **BI$^+$-1Nap-O$^-$** and **BI$^+$-Ph-NMe$_2$**, both of which absorbs visible light (Figure 3), afforded **BIH-1Nap-OH** and **BIH-Ph-NMe$_2$**, respectively, in moderate yields (entries 8 and 9), while the reactions using the other **BI$^+$-Ar** molecules barely proceeded (entries 1–7) due to the poor absorption of visible light. The mass balances (sum of the yields of **BI$^+$-Ar** and recovered **BIH-Ar**) were 67% and 100% for **BIH-1Nap-OH** and **BIH-Ph-NMe$_2$**, respectively, indicating that **BI$^+$-Ph-NMe$_2$**/**BIH-Ph-NMe$_2$** can constitute a robust organohydride-recycling photocatalytic system. As suggested in a previous study,[24] the observed moderate yield (54%) of **BIH-Ph-NMe$_2$** in the photochemical regeneration of organohydrides is not problematic for future application as a catalyst. Control experiments suggested that light irradiation, a base, and ascorbic acid were indispensable for this reaction (entries 10–12). Other reducing agents (Et_3N, triethanolamine, and Na_2SO_3) did not provide **BIH-Ph-NMe$_2$** (entries 13–15), resulting in the complete recovery of **BI$^+$-Ph-NMe$_2$**.

Table 2. Photochemical conversion of **BI$^+$-R** to **BIH-R**.[a]



BI⁺-R **BIH-R**

entry	Substrate	Reductant	Yield /%[b]
1	**BI⁺-Me**	ascorbic acid	1(97)
2	**BI⁺-Ph**	ascorbic acid	3 (97)
3	**BI⁺-Ph-OMe**	ascorbic acid	3 (97)
4	**BI⁺-Ph-CN**	ascorbic acid	0 (100)
5	**BI⁺-Ph-CH₂**	ascorbic acid	0 (94)
6	**BI⁺-1Nap**	ascorbic acid	0 (100)
7	**BI⁺-2Nap**	ascorbic acid	0 (100)
8	**BI⁺-Ph-1Nap-O⁻**	ascorbic acid	43 (24)
9	**BI⁺-Ph-NMe₂**	ascorbic acid	54 (46)
10[c]	**BI⁺-Ph-NMe₂**	ascorbic acid	0 (100)
11[d]	**BI⁺-Ph-NMe₂**	ascorbic acid	0 (84)
12	**BI⁺-Ph-NMe₂**	–	0 (89)
13	**BI⁺-Ph-NMe₂**	Et_3N	0 (100)
14	**BI⁺-Ph-NMe₂**	triethanolamine	0 (100)
15	**BI⁺-Ph-NMe₂**	Na_2SO_3	0 (100)

[a] Reaction procedure: A mixture of **BI⁺-R** (2.5 mM, 1 equiv), reductant (20 equiv), and K_2CO_3 (22 equiv) in CH_3CN/H_2O (4/1) was irradiated using an LED lamp (λ_{max} = 400 nm) under argon with fan cooling for 4 h. [b] Determined by ^1H NMR analysis. The recovered **BI⁺-R** yields are shown in parentheses. [c] In the dark. At 38 °C. [d] No K_2CO_3

Based on the experimental results and knowledge obtained from the literature,[24] a reaction mechanism is proposed (Figure 6). **BI⁺-Ph-NMe₂** is excited with visible light to obtain **BI⁺-Ph-NMe₂***. Ascorbic acid (**H₂A**) is deprotonated, and the stronger electron donor **HA⁻** is generated. According to the redox potentials E(**BI⁺-Ph-NMe₂***/**BI•-Ph-NMe₂**) of 1.56 V (Table 1) and E(**HA•**/**HA⁻**) of 0.47 V,[33] the single electron transfer from **HA⁻** to **BI⁺-Ph-NMe₂*** is sufficiently exergonic and should proceed. According to our previous results,[24] the next step is hydrogen atom transfer from **HA•** or **HA⁻** to **BI•-Ph-NMe₂**. The calculated driving forces are $\Delta G_0 = -14.6$ (from **HA•**) and −14.0 kcal mol^{-1} (from **HA⁻**), and the activation barrier is $\Delta G^{\ddagger}$ =

15.2 kcal mol^{-1} (from **HA$^-$**),[34] suggesting that the proposed hydrogen atom transfer events to generate **BIH-Ph-NMe$_2$** are plausible.

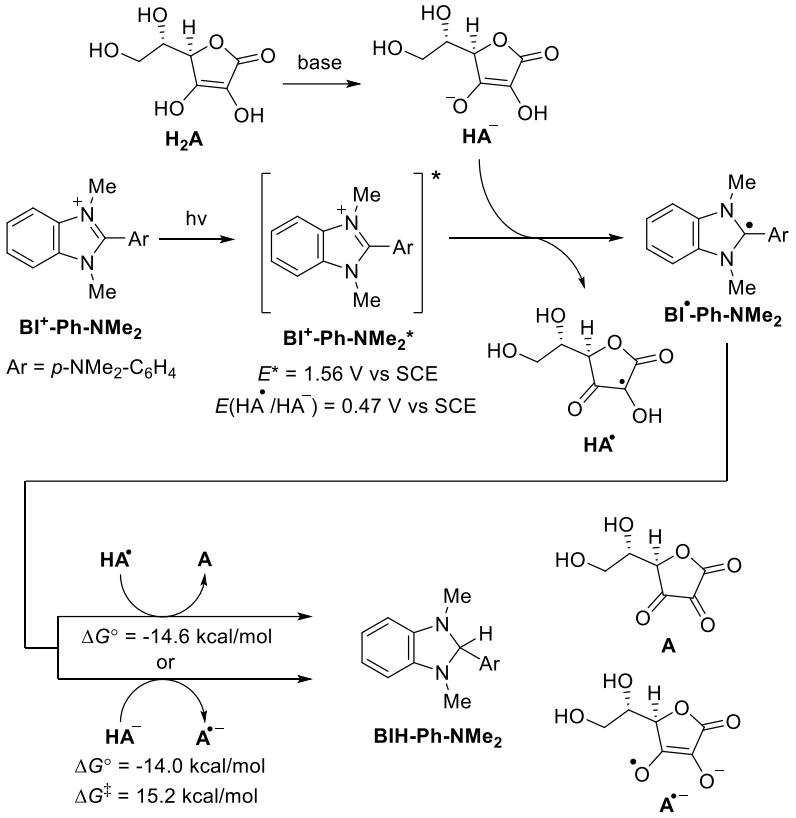


Figure 6. Proposed mechanism for the photochemical reduction of **BI$^+$-Ar**. **BI$^+$-Ph-NMe$_2$** is excited by visible light and generates **BI$^+$-Ph-NMe$_2$***, which undergoes electron transfer from **HA$^-$**, forming **BI$^•$-Ph-NMe$_2$** and **HA$^•$**. **BI$^•$-Ph-NMe$_2$** reacts with **HA$^•$** or **HA$^-$** via the hydrogen atom transfer mechanism, generating product **BIH-Ph-NMe$_2$**. The Gibbs free energy changes of hydrogen atom transfer were calculated by DFT at the B3LYP/6-31G++(d,p)/PCM(acetonitrile) level of theory.

In summary, we investigated the visible light-driven regeneration of BIH, a metal-free and powerful hydride donor, without the addition of an external photosensitizer. **BI$^+$-Ph-NMe$_2$** was found to be suitable for this purpose, displaying CT absorption up to 400 nm owing to the electron donor and acceptor properties of the NMe_2-substituted phenyl and cationic benzimidazolium moieties, respectively, and it was transformed into its reduced form, **BIH-Ph-NMe$_2$**, with visible light. Our results demonstrate that strategic structural design allows for the development of organohydrides that can self-regenerate using visible-light energy without the assistance of external photosensitizers. This knowledge is crucial for the future

development of catalytic photoreduction technologies that utilize solar energy based on organohydride regeneration strategies.

Experimental Section

Unless otherwise noted, all reactions were conducted in well cleaned glasswares with magnetic stirring. All starting materials were purchased from commercial sources. Melting points were measured on a Yanaco MP-500D and are not corrected. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra (400 and 101 MHz, respectively) were recorded on a Bruker Avance III HD 400. Residual solvent peak(s) for ^{1}H NMR analysis ($CDCl_3$ (7.26 ppm), MeOD (3.31 ppm), DMSO-d_6 (2.50 ppm)) and deuterated solvent peak(s) for $^{13}C\{^{1}H\}$ NMR analysis ($CDCl_3$ (77.2 ppm), MeOD (49.0 ppm), DMSO-d_6 (39.5 ppm), Acetone-d_6 (29.8 ppm)) were used as internal references. The following abbreviations are used in connection with NMR; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, br = broad. Mass spectra were measured using LTQ Orbitrap XL (Thermo Fisher Scientific, Brehmen, Germany) with an electrospray ionization (ESI) ion source and an atmospheric pressure chemical ionization (APCI). Preparative column chromatography was performed using Kanto Chemical silica gel 60 N (spherical, neutral). Analytical thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminium sheets. The photocatalytic regenerations of **BIH-Ar** with visible light were performed under self-manufactured LED lamp sets (λ_{max} = 400 nm).

Spectroscopy

Ultra visible near-infrared absorption spectra were recorded at room temperature using dilute (13–23 μM) solutions in spectroscopic grade solvents on a Shimadzu UV-1800 spectrometer with a 1 cm × 1 cm quartz absorption cuvette (light path: 1 cm). Steady-state photoluminescence spectra were recorded at room temperature using dilute (10–18 μM) solutions in spectroscopic grade solvents on a spectrofluorometer (JASCO FP-6500) with a 1 cm × 1 cm quartz absorption cuvette (light path: 1 cm).

Redox property

Cyclic voltammetric measurements were performed at 298 K on an ALS CHI606S electrochemical analyzer, using 1 mM solutions of analytes in MeCN deaerated by argon bubbling for 30–60 min before each measurement. The supporting electrolyte was 0.10 M $TBAClO_4$. A conventional three-electrode cell with a platinum working electrode and platinum wire as the counter electrode was employed. The cyclic voltammograms were

recorded with respect to the $Ag/AgNO_3$ (10 mM) reference electrode at a sweep rate of 50 mV/s. The reduction potentials (E_{red}) were corrected to the SCE scale based on the measurement of the Fc/Fc^+ couple redox potential as the standard (0.38 V vs SCE).[35] For the determination of E_{red} of the ground state of molecules, when reversible cyclic voltammograms were obtained, standard reduction potentials (E^0) were calculated by averaging the forward and reverse peak potentials. When irreversible cyclic voltammograms were obtained, half-peak potentials ($E_{p/2}$), corresponding to the potential at half the maximum current of the cyclic voltammogram, were used as an estimate of E^0.[36] IR compensation has not been conducted since, using the same setup as employed in the measurements of the analytes, the standard Fc/Fc^+ couple current waves appeared with the difference between the anodic and cathodic peak potentials of 70–73 mV, indicating that the effect of the ohmic drop on the conclusion of this study should be marginal.

DFT calculations

All calculations were performed with the Gaussian 09 package.[37] Geometry optimization for the ground and transition states of molecules was performed by the B3LYP/6-31++G(d,p) or B3LYP/6-31G(d) DFT method with or without the polarizable continuum solvation model (PCM, acetonitrile) (the applied method for each compound is indicated in the figure captions). The transition state was optimized with Berny algorithm[38] and verified by the intrinsic reaction coordinate (IRC) calculation.[39] Frequency analyses were also carried out to identify the stationary points (no imaginary frequency for the ground state and one imaginary frequency for the transition state were confirmed) and to estimate thermodynamic properties at 298.15 K and 1 atm and Gibbs free energies. The vertical excitation was calculated by the time-dependent (TD)-DFT method using B3LYP functional with 6-31++G(d,p) basis set based on the ground-state geometries optimized by the DFT method.

X-ray diffraction analysis

Single crystal X-ray diffraction analyses were conducted using Bruker Apex-II diffractometer equipped with a CCD detector using monochromatic Mo-$K\alpha$ radiation (0.71069 Å). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms attached to carbon atoms were treated as riding atoms, using isotropic displacement parameters. Single crystals of **BI$^+$-Ph-NMe$_2$** suitable for X-ray diffraction analysis were obtained by recrystallization from Et_2O/MeOH by vapor diffusion.

Synthesis and characterization

2-Phenyl-1*H*-benzimidazole[40-41] In a flame-dried Schlenk tube under an argon atmosphere, *o*-phenylenediamine (2.0401 g, 18.87 mmol, 1.0 eq.) and benzoic acid (3.3862 g, 27.73 mmol, 1.5 eq.) were added. The reaction was stirred at 175 ℃ for 1.5 h. Then benzoic acid (3.3950 g, 27.80 mmol, 1.5 eq.) and CH_2Cl_2 were added. The reaction was stirred at 175 ℃ for another 1.5 h. The reaction mixture was quenched with sat. $NaHCO_3$ aq. The residue was dissolved in CH_2Cl_2 and MeOH. The solution was concentrated under reduced pressure. After washed with CH_2Cl_2, the resulting solid was dissolved in hot CH_2Cl_2 and filtered. The solution was concentrated under reduced pressure to give brown solid product (1.45 g, 7.46 mmol, 40% yield). ^{1}H NMR (400 MHz, MeOD): δ 8.16 – 8.04 (m, 2H), 7.60 (dd, J = 6.0, 3.2 Hz, 2H), 7.56 – 7.45 (m, 3H), 7.25 (dd, J = 6.1, 3.1 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, MeOD): δ 153.4, 131.3, 131.0, 130.1, 127.8, 123.9 ppm.

1-Methyl-2-phenyl-1*H*-benzimidazole[42] In a flame-dried Schlenk tube under an argon atmosphere, 2-phenyl-1*H*-benzimidazole (1.1587 g, 5.97 mmol, 1.0 eq.), NaOH (0.9782 g, 24.46 mmol, 4.1 eq.) and 10 mL acetone were added. The mixture was stirred at room temperature (27 ℃) for 1 h. After that, iodomethane (0.9681 g, 6.82 mmol, 1.1 eq.) in 20 mL acetone was added. The reaction was stirred at room temperature for 1 h. The reaction mixture was then concentrated under reduced pressure. After quenched with water, the reaction mixture was extracted with CH_2Cl_2 and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 4 : 1→1 : 1) to give pale yellow solid product (648.6 mg, 3.11 mmol, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.81 (m, 1H), 7.80 – 7.72 (m, 2H), 7.60 – 7.47 (m, 3H), 7.44 – 7.37 (m, 1H), 7.37 – 7.28 (m, 2H), 3.87 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.7, 142.9, 136.5, 130.1, 129.7, 129.4, 128.6, 122.7, 122.4, 119.7, 109.6, 31.6 ppm.

BI$^+$-Ph[43] This compound was synthesized according to modified literature procedures.[43] In a flame-dried Schlenk tube under an argon atmosphere, 1-methyl-2-phenyl-1*H*-benzimidazole (257.5 mg, 1.24 mmol, 1.0 eq.), 1.7 mL CH_2Cl_2 and 0.23 mL iodomethane (524.4 mg, 3.69 mmol, 3.0 eq.) were added. The reaction was stirred at room temperature (23 ℃) for 21 h in the dark. The reaction mixture was then concentrated under reduced pressure and washed with Et_2O to give white solid product (310.1 mg, 0.89 mmol, 72% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.15 (dd, J = 6.2, 3.2

Hz, 2H), 7.95 – 7.88 (m, 2H), 7.88 – 7.73 (m, 5H), 3.90 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 150.3, 132.9, 131.7, 130.8, 129.5, 126.6, 121.0, 113.4, 32.9 ppm.

BIH-Ph[44] This compound was synthesized according to modified literature procedures.[45] In a flame-dried Schlenk tube under an argon atmosphere, **BI^{+}-Ph** (252.7 mg, 0.72 mmol, 1.0 eq.) and 9.5 mL MeOH were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then $NaBH_4$ (67.9 mg, 1.79 mmol, 2.5 eq.) was added portionwise over 40 min. The reaction was stirred at room temperature (25 ℃) for 5 h. The reaction mixture was then concentrated under reduced pressure. After quenched with water, the reaction mixture was extracted with Et_2O three times. The solution was washed with water and brine. After dried with anhydrous Na_2SO_4, the mixture was filtered and concentrated under reduced pressure. The crude product was recrystallized from EtOH and water to give white solid product (83.6 mg, 0.37 mmol, 52% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.59 – 7.51 (m, 2H), 7.49 – 7.40 (m, 3H), 6.62 (dd, J = 5.4, 3.2 Hz, 2H), 6.46 (dd, J = 5.4, 3.2 Hz, 2H), 4.86 (s, 1H), 2.47 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 142.0, 138.8, 129.3, 128.7, 128.5, 119.1, 105.8, 93.2, 33.1 ppm.

2-(4-Methoxyphenyl)-1*H*-benzimidazole[46] This compound was synthesized according to modified literature procedures.[47] In a 300 mL round-bottom flask, *o*-phenylenediamine (1.0819 g, 10.00 mmol, 1.0 eq.), 90 mL DMF, 10 mL distilled water, 1.4 mL *p*-methoxybenzaldehyde (1.568 g, 11.52mmol, 1.2 eq.) were added. The reaction was stirred at 80 ℃ for 66 h under air. The reaction mixture was then dissolved in hexane : ethyl acetate = 1 : 1 and washed with water five times to remove DMF. After dried with anhydrous Na_2SO_4, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 3 : 2→1 : 1) to give brown solid product (1.2085 g, 5.39 mmol, 54% yield). ^{1}H NMR (400 MHz, MeOD): δ 8.06 – 7.98 (m, 2H), 7.56 (br s, 2H), 7.22 (dd, J = 6.0, 3.1 Hz, 2H), 7.11 – 7.03 (m, 2H), 3.86 (s, 3H) ppm.

2-(4-Methoxyphenyl)-1-methyl-1*H*-benzimidazole[42] This compound was synthesized according to modified literature procedures.[48] In a flame-dried Schlenk tube under an argon atmosphere, 2-(4-methoxyphenyl)-1*H*-benzimidazole (999.3 mg, 4.46 mmol, 1.0 eq.) and 30 mL THF were added. The mixture was cooled to 0 ℃ in an ice-water bath and NaH (60% dispersion in paraffin liquid, 387.1 mg, 9.68 mmol, 2.2 eq.) was then added. After stirring at 0 ℃ for 15 min, 0.32 mL iodomethane (729.6 mg, 5.14 mmol, 1.2 eq.) was added. The reaction was stirred at room temperature (22 ℃) for 90 min. NaH (60% dispersion in paraffin liquid, 78.0 mg, 1.95 mmol, 0.4 eq.) and 0.16 mL iodomethane (364.8 mg, 2.57 mmol, 0.6 eq.) were added at 0 ℃ following the above procedures. The reaction was stirred at room temperature for another 60 min. The reaction mixture was then quenched with water and concentrated under reduced pressure to remove THF. The mixture was dissolved in ethyl acetate and washed with water and brine. After dried with anhydrous Na_2SO_4, the mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on

SiO_2 (hexane : ethyl acetate = 2 : 1) to give pale yellow solid product (966.7 mg, 4.06 mmol, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.77 (m, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.9, 153.9, 143.1, 136.7, 131.0, 122.7, 122.6, 122.4, 119.7, 114.2, 109.6, 55.5, 31.8 ppm.

BI$^+$-Ph-OMe This compound was synthesized according to modified literature procedures.[43] In a flame-dried Schlenk tube under an argon atmosphere, 2-(4-methoxyphenyl)-1-methyl-1*H*-benzimidazole (500.5 mg, 2.10 mmol, 1.0 eq.), 2.9 mL CH_2Cl_2 and 0.4 mL iodomethane (912 mg, 6.43 mmol, 3.1 eq.) were added. The reaction was stirred at room temperature (25 °C) for 21 h. The reaction mixture was then concentrated under reduced pressure and washed with Et_2O to give pale yellow solid product (735.5 mg, 1.93 mmol, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.75 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 162.5, 150.5, 132.7, 131.7, 126.5, 115.0, 113.3, 112.5, 55.8, 32.8 ppm. IR (neat): 3014, 1603, 1512, 1485, 1471, 1301, 1262, 1176, 1012, 857, 825, 758, 749 cm^{-1}. Mp 231.2 – 231.6 °C. HRMS (ESI) *m*/*z*: $[M - I]^+$ Calcd for $C_{16}H_{17}N_2O^+$ 253.1335; Found 253.1336.

BIH-Ph-OMe[49] This compound was synthesized according to modified literature procedures.[45] In a flame-dried Schlenk tube under an argon atmosphere, **BI$^+$-Ph-OMe** (201.3 mg, 0.53 mmol, 1.0 eq.) and 7.0 mL MeOH were added. The mixture was cooled to 0 °C in an ice-water bath. Then $NaBH_4$ (54.5 mg, 1.44 mmol, 2.7 eq.) was added portionwise over 40 min. The reaction was stirred at room temperature (25 °C) for 3 h. The reaction mixture was then concentrated under reduced pressure. After quenched with water, the reaction mixture was extracted with Et_2O three times. The solution was washed with water and brine. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The crude product was recrystallized from EtOH and water to give white solid product (65.8 mg, 0.26 mmol, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.72 (dd, *J* = 5.5, 3.2 Hz, 2H), 6.44 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.83 (s, 1H), 3.85 (s, 3H), 2.56 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 160.6, 142.2, 131.1, 130.1, 119.4, 113.9, 105.8, 93.7, 55.5, 33.2 ppm.

4-(1*H*-Benzimidazol-2-yl)benzonitrile[50] This compound was synthesized according to modified literature procedures.[47] In a 300 mL round-bottom flask, *o*-phenylenediamine (1.0808 g, 9.99 mmol, 1.0 eq.), 4-formylbenzonitrile (1.4430 g, 11.00 mmol, 1.1 eq.), 90 mL DMF and 10 mL distilled water were added. The reaction was stirred at 80 °C for 40 h under air. The reaction mixture was then dissolved in hexane : ethyl acetate = 1 : 1 and washed with water four times to remove DMF. After washed with brine and dried with anhydrous Na_2SO_4, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 3 : 7) to give pale yellow solid product (1.8904 g, 8.62 mmol, 86%

yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.19 (s, 1H), 8.34 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.71 (br s, 1H), 7.59 (br s, 1H), 7.35 – 7.16 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 149.4, 143.8, 135.1, 134.3, 133.0, 127.0, 123.4, 122.2, 119.3, 118.6, 111.9, 111.7 ppm.

BI^{+}-Ph-CN This compound was synthesized according to modified literature procedures.[45] In a 50 mL round-bottom flask under an argon atmosphere, 4-(1*H*-benzimidazol-2-yl)benzonitrile (1.1741 g, 5.36 mmol, 1.0 eq.), K_2CO_3 (0.7420 g, 5.37 mmol, 1.0 eq.), 6.2 mL CH_3CN and 1.0 mL iodomethane (2.28 g, 16.06 mmol, 3.0 eq.) were added. After stirring at 90 ℃ for 16 h, the reaction mixture became solid. Then 9.3 mL CH_3CN, K_2CO_3 (370.9 mg, 2.68 mmol, 0.5 eq.), 1.5 mL iodomethane (3.42 g, 24.09 mmol, 4.5 eq.) were added. The reaction mixture was stirred at 80 ℃ for another 5 h. The reaction was poured to water. The precipitate was filtered and washed with water to give pale yellow solid product (901.6 mg, 2.40 mmol, 45% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31 (d, J = 8.5 Hz, 2H), 8.17 (dd, J = 6.3, 3.2 Hz, 2H), 8.13 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 6.3, 3.1 Hz, 2H), 3.90 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 148.7, 133.3, 132.0, 131.8, 126.9, 125.5, 117.9, 115.5, 113.6, 32.9 ppm. IR (neat): 3010, 2228, 1515, 1486, 1467, 1412, 1273, 1016, 847, 829, 773, 751, 732, 636, 621, 566 cm^{-1}. Mp 236.8 – 239.4 ℃. HRMS (ESI) m/z: [M – I]$^{+}$ Calcd for $C_{16}H_{14}N_3^{+}$ 248.1182; Found 248.1182.

BIH-Ph-CN[49] This compound was synthesized according to modified literature procedures.[45] In a flame-dried Schlenk tube under an argon atmosphere, **BI^{+}-Ph-CN** (280.9 mg, 0.75 mmol, 1.0 eq.) and 10 mL MeOH were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then $NaBH_4$ (170.4 mg, 4.50 mmol, 6.0 eq.) was added portionwise over 40 min with stirring. The reaction mixture was quenched with water and MeOH was evaporated under reduced pressure. The reaction was extracted with $CHCl_3$ three times. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure to give pale yellow solid product (183.9 mg, 0.74 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.69 (m, 4H), 6.76 (dd, J = 5.5, 3.1 Hz, 2H), 6.47 (dd, J = 5.5, 3.2 Hz, 2H), 4.95 (s, 1H), 2.57 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.8, 141.8, 132.5, 129.7, 119.9, 118.7, 113.4, 106.2, 93.4, 33.5 ppm.

5,6-Dihydrobenzimidazo[2,1-*a*]isoquinoline[51] This compound was synthesized according to modified literature procedures.[51] In a flame-dried Schlenk tube under an argon atmosphere, *o*-iodonitrobenzene (1.0211 g, 4.10 mmol, 1.0 eq.) and 1.3 mL 1,2,3,4-tetrahydroisoquinoline (1.365 g, 10.25 mmol, 2.5 eq.) were added. The reaction mixture was stirred at 130 ℃ for 22 h. The reaction was quenched with 2M NH_3 in MeOH and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 4 : 1→18 : 7) to give pale yellow solid product (601.0 mg, 2.73 mmol, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 – 8.28 (m, 1H), 7.91 – 7.80 (m, 1H), 7.49 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 4.34 (t, J = 6.8 Hz, 2H), 3.30 (t, J = 6.8 Hz, 2H) ppm.

BI^{+}-Ph-CH$_2$ This compound was synthesized according to modified literature procedures.[43] In a

flame-dried Schlenk tube under an argon atmosphere, 5,6-dihydrobenzimidazo[2,1-*a*]isoquinoline (495.7 mg, 2.25 mmol, 1.0 eq.), 3 mL CH_2Cl_2 and 0.7 mL iodomethane (1.596 g, 11.24 mmol, 5.0 eq.) were added. After stirring at room temperature (26 °C) for 18 h, 0.7 mL iodomethane (1.596 g, 11.24 mmol, 5.0 eq.) were added. The reaction mixture was stirred at room temperature for another 24 h. Then 0.7 mL iodomethane (1.596 g, 11.24 mmol, 5.0 eq.) were added. The reaction mixture was stirred at room temperature for another 24 h. The precipitate was filtered and washed with CH_2Cl_2. The crude product was recrystallized from MeOH and Et_2O to give white solid product (521.1 mg, 1.44 mmol, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.32 (d, J = 7.6 Hz, 1H), 8.24 – 8.12 (m, 1H), 8.12 – 8.03 (m, 1H), 7.91 – 7.59 (m, 5H), 4.66 (t, J = 6.9 Hz, 2H), 4.35 (s, 3H), 3.39 (t, J = 6.9 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 145.1, 138.4, 133.7, 132.8, 130.1, 129.3, 128.0, 127.9, 126.5, 126.4, 119.8, 113.2, 112.9, 41.1, 34.3, 27.2 ppm. IR (neat): 3014, 1603, 1517, 1489, 1470, 1451, 1420, 1345, 1297, 1246, 1211, 1138, 1024, 783, 768, 752, 743, 733, 697 cm^{-1}. Mp > 300 °C. HRMS (ESI) *m/z*: $[M - I]^+$ Calcd for $C_{16}H_{15}N_2^+$ 235.1230; Found 235.1230.

2-(1-Naphthyl)-1*H*-benzimidazole[52] This compound was synthesized according to modified literature procedures.[47] In a 300 mL round-bottom flask, *o*-phenylenediamine (1.0838 g, 10.02 mmol, 1.0 eq.), 1-naphthaldehyde (85% purity (w/w), 2.0226 g, 11.01 mmol, 1.1 eq.), 90 mL DMF and 10 mL distilled water were added. The reaction was stirred at 80 °C for 67 h under air. The reaction mixture was then poured to ice. The precipitate was filtered and dissolved in MeOH. After dried with anhydrous Na_2SO_4, the mixture was filtered and concentrated under reduced pressure. The crude product was recrystallized from acetone and water and dried with anhydrous Na_2SO_4 in acetone to give pale brown solid product (1.1948 g, 4.89 mmol, 49% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.93 (s, 1H), 9.15 – 9.03 (m, 1H), 8.10 (d, J = 8.2 Hz, 1H), 8.07 – 7.96 (m, 2H), 7.88 – 7.47 (m, 5H), 7.35 – 7.18 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 151.4, 143.9, 134.5, 133.7, 130.5, 130.2, 128.4, 127.9, 127.5, 127.1, 126.4, 126.4, 125.3, 122.7, 121.7, 119.1, 111.4 ppm.

1-Methyl-2-(1-naphthyl)-1*H*-benzimidazole[42] This compound was synthesized according to modified literature procedures.[48] In a flame-dried Schlenk tube under an argon atmosphere, 2-(1-naphthyl)-1*H*-benzimidazole (1.1008 g, 4.51 mmol, 1.0 eq.) and 30 mL THF were added. The mixture was cooled to 0 °C in an ice-water bath and NaH (60% dispersion in paraffin liquid, 454.3 mg, 11.36 mmol, 2.5 eq.) was then added. After stirring at 0 °C for 15 min, 0.3 mL iodomethane (684 mg, 4.82 mmol, 1.1 eq.) was added. The reaction was stirred at room temperature (25 °C) for 4 h. The reaction mixture was then quenched with water. NaCl and ethyl acetate were added to the mixture. After extraction, the ethyl acetate solution was washed with brine another two times. After dried with anhydrous Na_2SO_4, the mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 2 : 1) to give pale yellow solid product (997.7 mg, 3.86 mmol, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 7.0,

1.3 Hz, 1H), 7.61 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.58 – 7.43 (m, 3H), 7.43 – 7.34 (m, 2H), 3.62 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 153.0, 143.3, 136.0, 133.7, 132.3, 130.4, 129.0, 128.6, 127.9, 127.3, 126.5, 125.6, 125.1, 122.9, 122.5, 120.2, 109.7, 31.2 ppm.

BI$^+$-1Nap This compound was synthesized according to modified literature procedures.[43] In a flame-dried Schlenk tube under an argon atmosphere, 1-methyl-2-(1-naphthyl)-1*H*-benzimidazole (501.2 mg, 1.94 mmol, 1.0 eq.), 2.7 mL CH_2Cl_2 and 0.36 mL iodomethane (820.8 mg, 5.78 mmol, 3.0 eq.) were added. The reaction was stirred at room temperature (25 °C) for 21 h in the dark. The reaction mixture was then concentrated under reduced pressure and washed with Et_2O to give white solid product (694.5 mg, 1.74 mmol, 89% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, *J* = 8.3 Hz, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.19 (dd, *J* = 6.3, 3.1 Hz, 2H), 8.14 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.90 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.82 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.78 – 7.71 (m, 1H), 7.71 – 7.64 (m, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 149.3, 133.5, 133.0, 132.1, 131.3, 130.4, 129.1, 128.9, 127.6, 126.7, 125.7, 124.1, 117.9, 113.7, 32.8 ppm. IR (neat): 3010, 2963, 1540, 1516, 1484, 1474, 1409, 1337, 1138, 1019, 824, 803, 772, 763, 747 cm^{-1}. Mp 265.6 – 266.5 °C. HRMS (ESI) *m*/*z*: $[M - I]^+$ Calcd for $C_{19}H_{17}N_2^+$ 273.1386; Found 273.1386.

BIH-1Nap[53] This compound was synthesized according to modified literature procedures.[45, 53] In a flame-dried Schlenk tube under an argon atmosphere, **BI$^+$-1Nap** (299.9 mg, 0.75 mmol, 1.0 eq.) and 10 mL MeOH were added. The mixture was cooled to 0 °C in an ice-water bath. Then $NaBH_4$ (170.0 mg, 4.49 mmol, 6.0 eq.) was added portionwise over 40 min. The reaction was stirred at room temperature (25 °C) for 15 min. The reaction mixture was quenched with water and MeOH was evaporated under reduced pressure. The reaction was extracted with $CHCl_3$ three times. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The crude product was recrystallized from 1,2-dimethoxyethane and EtOH to give pale yellow solid product (72.9 mg, 0.27 mmol, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (br s, 1H), 7.91 (t, *J* = 8.3 Hz, 2H), 7.79 – 7.34 (m, 4H), 6.79 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.51 (dd, *J* = 5.4, 3.2 Hz, 2H), 5.44 (br s, 1H), 2.57 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 142.3, 134.6, 133.5, 132.4, 130.5, 129.2, 128.7, 125.9, 124.9, 119.4, 106.0, 33.6 ppm.

2-(2-Naphthyl)-1*H*-benzimidazole[54] This compound was synthesized according to modified literature procedures.[47] In a 300 mL round-bottom flask, *o*-phenylenediamine (1.0806 g, 9.99 mmol, 1.0 eq.), 2-naphthaldehyde (1.7196 g, 11.01 mmol, 1.1 eq.), 90 mL DMF and 10 mL distilled water were added. The reaction was stirred at 80 °C for 67 h under air. The reaction mixture was then dissolved in hexane : ethyl acetate = 1 : 1 and washed with water four times to remove DMF. After washed with brine and dried with anhydrous Na_2SO_4, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 3 : 1→1 : 3) to give pale yellow solid product (2.0394 g, 8.35 mmol, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.08 (s, 1H), 8.80 – 8.72 (m, 1H), 8.32 (dd, *J* = 8.6,

1.7 Hz, 1H), 8.13 – 8.02 (m, 2H), 8.02 – 7.95 (m, 1H), 7.70 (br s, 1H), 7.65 – 7.49 (m, 3H), 7.32 – 7.15 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 151.3, 143.9, 135.2, 133.5, 132.8, 128.6, 128.5, 127.8, 127.6, 127.1, 126.9, 125.8, 123.9, 122.7, 121.8, 118.9, 111.4 ppm.

1-Methyl-2-(2-naphthyl)-1*H*-benzimidazole[42] This compound was synthesized according to modified literature procedures.[48] In a flame-dried Schlenk tube under an argon atmosphere, 2-(2-naphthyl)-1*H*-benzimidazole (460.1 mg, 1.88 mmol, 1.0 eq.) and 12 mL THF were added. The mixture was cooled to 0 ℃ in an ice-water bath and NaH (60% dispersion in paraffin liquid, 201.0 mg, 5.03 mmol, 2.7 eq.) was then added. After stirring at 0 ℃ for 20 min, 0.13 mL iodomethane (296.4 mg, 2.09 mmol, 1.1 eq.) was added. The reaction was stirred at room temperature (25 ℃) for 2 h. The reaction mixture was then quenched with water and extracted with ethyl acetate once. After washed with brine twice and dried with anhydrous Na_2SO_4, the mixture was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 4 : 1) to give pale yellow solid product (459.4 mg, 1.78 mmol, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.84 (m, 4H), 7.61 – 7.53 (m, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.31 (m, 2H), 3.95 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 153.8, 143.2, 136.8, 133.7, 133.0, 129.4, 128.6, 128.6, 127.9, 127.6, 127.3, 126.9, 126.4, 122.9, 122.6, 119.9, 109.8, 31.9 ppm.

BI^{+}-2Nap This compound was synthesized according to modified literature procedures.[43, 45]

Procedure 1: In a flame-dried Schlenk tube under an argon atmosphere, 1-methyl-2-(2-naphthyl)-1*H*-benzimidazole (418.2 mg, 1.62 mmol, 1.0 eq.), 2.2 mL CH_2Cl_2 were added. After 40 min stirring, 0.3 mL iodomethane (684 mg, 4.82 mmol, 3.0 eq.) was added. The reaction was stirred at 30 ℃ for 20 h. The reaction mixture was then concentrated under reduced pressure and washed with Et_2O. The crude product was recrystallized from MeOH and Et_2O to give white solid product (122.8 mg, 0.31 mmol, 19% yield).

Procedure 2: In a flame-dried Schlenk tube under an argon atmosphere, 2-(2-naphthyl)-1*H*-benzimidazole (1.2219 g, 5.00 mmol, 1.0 eq.), 8.6 mL CH_3CN, K_2CO_3 (0.7601 g, 5.50 mmol, 1.1 eq.) and 1.9 mL iodomethane (4.332 g, 30.52 mmol, 6.1 eq.) were added. The reaction mixture was stirred at 90 ℃ for 2 h. The reaction was poured to water. The precipitate was filtered and washed with water. The crude product was washed with Et_2O, decolored with activated carbon and recrystallized from MeOH and Et_2O to give off-white solid product (1.2004 g, 3.00 mmol, 60% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.57 (s, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.22 – 8.12 (m, 4H), 7.93 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.84 – 7.72 (m, 4H), 3.97 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ 150.4, 134.3, 132.3, 132.0, 131.8, 129.2, 129.2, 129.0, 128.1, 127.7, 126.7, 125.8, 118.3, 113.4, 33.0 ppm. IR (neat): 3015, 1541, 1515, 1500, 1475, 1400, 1352, 1161, 1129, 1014, 947, 938, 892, 877, 867, 841, 814, 782, 754, 664, 563 cm^{-1}. Mp 287.3– 288.4 ℃. HRMS (ESI) *m*/*z*: $[M - I]^+$ Calcd for $C_{19}H_{17}N_2^+$ 273.1386; Found 273.1387.

BIH-2Nap[53] This compound was synthesized according to modified literature procedures.[45] In a flame-dried Schlenk tube under an argon atmosphere, **BI$^+$-2Nap** (300.3 mg, 0.75 mmol, 1.0 eq.) and 10 mL MeOH were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then $NaBH_4$ (170.4 mg, 4.50 mmol, 6.0 eq.) was added portionwise over 40 min with stirring. The reaction mixture was quenched with water and MeOH was evaporated under reduced pressure. The reaction was extracted with $CHCl_3$ three times. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure to give pale yellow solid product (200.6 mg, 0.73 mmol, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.87 (m, 4H), 7.85 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.54 (dd, *J* = 6.2, 3.3 Hz, 2H), 6.76 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.48 (dd, *J* = 5.4, 3.2 Hz, 2H), 5.07 (s, 1H), 2.60 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.3, 136.6, 134.3, 133.1, 129.0, 128.7, 128.2, 128.0, 126.6, 126.4, 125.7, 119.5, 105.9, 94.4, 33.3 ppm.

***N*, *N'*-Ditosyl-*o*-phenylenediamine**[55] This compound was synthesized according to modified literature procedures.[55] In a 300 mL round-bottom flask under an argon atmosphere, *o*-phenylenediamine (5.0012 g, 46.25 mmol, 1.0 eq.), 125 mL CH_2Cl_2 and 7.4 mL pyridine (7.2742 g, 91.96 mmol, 2.0 eq.) were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then tosyl chloride (17.6388 g, 92.52 mmol, 2.0 eq.) was added portionwise. After stirring at 0 ℃ for 5 min, the reaction was stirred at room temperature (24 ℃) for 40 h. The reaction mixture was then quenched with water and the precipitate was filtered (Crude1). The product remaining in the solution was extracted with CH_2Cl_2. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure (Crude2). The crude product (Crude1 and Crude2) was recrystallized from ethyl acetate and hexane to give pink solid product (17.56 g, 42.16 mmol, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.3 Hz, 4H), 7.22 (d, *J* = 8.1 Hz, 4H), 7.03 (dd, *J* = 6.0, 3.6 Hz, 2H), 6.95 (dd, *J* = 5.9, 3.7 Hz, 2H), 6.89 (s, 2H), 2.39 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 144.9, 136.9, 131.9, 130.4, 128.3, 127.5, 126.0, 21.4 ppm.

***N*,*N'*-Dimethyl-*N*,*N'*-ditosyl-*o*-phenylenediamine**[56]: This compound was synthesized according to modified literature procedures.[56] In a 200 mL round-bottom flask under an argon atmosphere, NaH (60% dispersion in paraffin liquid, 3.6302 g, 90.76 mmol, 3.1 eq.) and 60 mL DMF were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then *N*, *N'*-ditosyl-*o*-phenylenediamine (12.0818 g, 29.01 mmol, 1.0 eq.) was added and 15 mL iodomethane (34.2 g, 240.95 mmol, 8.3 eq.) was added dropwise. The reaction was stirred at room temperature (25 ℃) for 9 h. After quenched with water, the precipitate was filtered. The crude product was dissolved in CH_2Cl_2 and dried with anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure to give off-white solid product (13.1380 g, 29.55 mmol, 102% yield). The product was used for the next step without further purification, although it contains water and paraffin liquid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.59 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.1 Hz, 4H), 7.30 (dd, *J* = 6.0, 3.5 Hz, 2H), 6.79 (dd, *J* = 6.0, 3.6 Hz, 2H), 3.12 (s, 6H), 2.43 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 143.7, 140.5, 134.2, 129.8,

129.2, 128.0, 127.8, 38.6, 21.1 ppm.

***N*,*N'*-Dimethyl-*o*-phenylenediamine**[56] This compound was synthesized according to modified literature procedures.[56] In a 300 mL round-bottom flask under an argon atmosphere, 45 mL 90% H_2SO_4 aq. was added. The solution was cooled to 0 ℃ in an ice-water bath. Then *N*,*N'*-dimethyl-*N*,*N'*-ditosyl-*o*-phenylenediamine (8.8905 g, 20.00 mmol, 1.0 eq.) was added portionwise. The remaining substrate was added by washing with 10 mL 90% H_2SO_4 aq. After stirring at room temperature (25 ℃) for 30 min, the reaction was stirred at 100 ℃ for 14 h. The reaction mixture was poured to ice and made basic with NaOH. The reaction was then extracted with Et_2O three times. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 9 : 1→ethyl acetate only) to give brown oily liquid product (2.0842 g, 15.30 mmol, 77% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.56 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.40 (dd, *J* = 5.7, 3.5 Hz, 2H), 4.53 (q, *J* = 4.9 Hz, 2H), 2.70 (d, *J* = 5.1 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 137.3, 117.1, 108.4, 30.3 ppm.

BIH-1Nap-OH[53] This compound was synthesized according to modified literature procedures.[53] In a 100 mL round-bottom flask under an argon atmosphere, molecular sieves 4A (ca. 10 g), *N*, *N'*-dimethyl-*o*-phenylenediamine (1.3824 g, 10.15 mmol, 1.0 eq.) and 10 mL CH_2Cl_2 were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then 2-hydroxy-1-naphthaldehyde (1.8137 g, 10.53 mmol, 1.0 eq.) in 20 mL CH_2Cl_2 was added dropwise. The reaction mixture was stirred at 0 ℃ for 9 h. The reaction was filtered with celite and concentrated under reduced pressure. The crude product was purified by column chromatography on SiO_2 (hexane : ethyl acetate = 83 : 17 with 1.5% NEt_3) and washing with EtOH to give yellow solid product (2.2929 g, 7.90 mmol, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.54 – 7.45 (m, 1H), 7.40 – 7.31 (m, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 5.5, 3.2 Hz, 2H), 6.67 (dd, *J* = 5.5, 3.2 Hz, 2H), 5.85 (s, 1H), 2.69 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.8, 142.3, 134.7, 131.8, 129.3, 128.6, 127.2, 123.0, 121.1, 120.3, 120.2, 109.2, 108.7, 88.0, 34.0 ppm.

BI$^+$-1Nap-OH(Br$^-$)[29] This compound was synthesized according to modified literature procedures.[29] In a flame-dried Schlenk tube under an argon atmosphere, **BIH-1Nap-OH** (901.8 mg, 3.11 mmol, 1.0 eq.), 2-bromoacetophenone (925.4 mg, 4.65 mmol, 1.5 eq.) and 30 mL THF were added. The reaction mixture was stirred at room temperature (21 ℃) for 3 h. The reaction was poured to Et_2O and the precipitate was filtered. The crude product was recrystallized from MeOH and Et_2O to give white solid product (688.9 mg, 1.87 mmol, 60% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 8.29 (d, *J* = 9.1 Hz, 1H), 8.16 (dd, *J* = 6.3, 3.1 Hz, 2H), 8.07 (d, *J* = 7.4 Hz, 1H), 7.80 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.62 – 7.43 (m, 3H), 7.33 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 156.9, 148.1, 135.6, 132.1, 131.8, 129.1, 129.0, 127.5, 126.7, 124.4, 122.5, 118.1, 113.7, 99.0, 32.5 ppm.

BI$^+$-1Nap-O$^-$[29] This compound was synthesized according to modified literature procedures.[29] In

a flame-dried Schlenk tube under an argon atmosphere, KOH (139.1 mg, 2.48 mmol, 2.3 eq.) and 12.5 mL MeOH were added. Then **BI$^+$-1Nap-OH(Br$^-$)** (399.1 mg, 1.08 mmol, 1.0 eq.) was added to the solution. The reaction mixture was stirred at room temperature (22 ℃) for 1 h. The reaction was then quenched with water and extracted with CH_2Cl_2 eight times. After washed with brine and dried with anhydrous $MgSO_4$, the reaction was filtered and concentrated under reduced pressure. The crude product was recrystallized from CH_2Cl_2 and Et_2O to give yellow solid product (200.7 mg, 0.70 mmol, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (dd, J = 6.2, 3.1 Hz, 2H), 7.69 – 7.61 (m, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.23 – 7.14 (m, 1H), 6.98 – 6.90 (m, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.71 (d, J = 9.2 Hz, 1H), 3.75 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 170.7, 154.6, 134.9, 133.6, 131.9, 128.4, 127.3, 127.1, 125.4, 123.2, 119.3, 118.4, 112.6, 94.7, 32.3 ppm.

4-(1*H*-Benzimidazol-2-yl)-*N*,*N*-dimethylaniline[57] This compound was synthesized according to modified literature procedures.[58-59]

Procedure 1: In a 200 mL round-bottom flask, *o*-phenylenediamine (2.1624 g, 20.00 mmol, 1.0 eq.), *p*-dimethylaminobenzaldehyde (2.9831 g, 20.00 mmol, 1.0 eq.) and 40 mL DMSO were added. The reaction with a condenser was stirred at 150 – 160 ℃ for 22 h. The reaction mixture was then poured to ice and sonicated for 10 min. The precipitate was filtered and washed with water. The precipitate was dissolved MeOH. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The mixture was added to water and extracted with $CHCl_3$ three times. After washed with brine and dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The resulting solid was washed with CH_2Cl_2 to give pale yellow solid product (888.2 mg, 3.74 mmol, 19% yield).

Procedure 2: In a 300 mL round-bottom flask under an argon atmosphere, *o*-phenylenediamine (1.0808 g, 9.99 mmol, 1.0 eq.), *p*-dimethylaminobenzaldehyde (1.4928 g, 10.01 mmol, 1.0 eq.), $Na_2S_2O_5$ (3.8006 g, 19.99 mmol, 2.0 eq.), 90 mL EtOH and 10 mL distilled water were added. The reaction was stirred at 80 ℃ for 4 h. The reaction mixture was then filtered with celite. The solution was concentrated under reduced pressure. The resulting solid was added to water and extracted with $CHCl_3$. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure (Crude 1). The precipitate remaining in water was filtered and washed with water (Crude 2). The crude product (Crude1 and Crude2) was washed with CH_2Cl_2 to give pale yellow solid product (1.8060 g, 7.61 mmol, 76% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (d, J = 9.0 Hz, 2H), 7.53 (dd, J = 6.0, 3.2 Hz, 2H), 7.16 (dd, J = 6.0, 3.2 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 3.00 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 152.0, 151.5, 138.6, 127.7, 121.8, 116.2, 114.2, 111.9, 39.8 ppm.

BI$^+$-Ph-NMe$_2$[58] This compound was synthesized according to modified literature procedures [45, 58].

Procedure 1: In a 100 mL round-bottom flask under an argon atmosphere, 4-(1*H*-benzimidazol-2-yl)-*N*,*N*-dimethylaniline (702.4 mg, 2.96 mmol, 1.0 eq.), 40 mL THF and ^{t}BuOK (363.4 mg, 3.24 mmol, 1.1 eq.) were added. The remaining ^{t}BuOK was added by washing with 3 mL THF. After stirring for

30 min, 0.92 mL iodomethane (2.0976 g, 14.78 mmol, 5.0 eq.) was added. After stirring for another 30 min, the reaction was stirred at 60 ℃ for 89 h. The reaction mixture was then quenched with water and concentrated under reduced pressure to remove THF. The mixture was extracted with CH_2Cl_2 three times. After washed with brine and dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure. The crude product was recrystallized from MeOH and Et_2O to give off-white solid product (697.8 mg, 1.77 mmol, 60% yield).

Procedure 2: In a flame-dried Schlenk tube under an argon atmosphere, 4-(1*H*-benzimidazol-2-yl)-*N*,*N*-dimethylaniline (1.1868 g, 5.00 mmol, 1.0 eq.), 8.6 mL CH_3CN, K_2CO_3 (759.8 mg, 5.50 mmol, 1.1 eq.) and 1.9 mL iodomethane (4.332 g, 30.52 mmol, 6.1 eq.) were added. The reaction was stirred at 90 ℃ for 6 h. The reaction mixture was poured to water and the precipitate was filtered (Crude 1). The product remaining in water was extracted with CH_2Cl_2 three times. After dried with anhydrous Na_2SO_4, the solution was filtered and concentrated under reduced pressure (Crude 2). Crude 1 (almost colorless) was used without further purification. Crude 2 was recrystallized from MeOH and Et_2O to give off-white solid product. The total yield was 46% (903.4 mg, 2.30 mmol). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.06 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.71 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 6H), 3.08 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 152.6, 151.5, 132.0, 131.8, 126.2, 113.0, 111.6, 105.6, 39.6, 32.9 ppm.

BIH-Ph-NMe$_2$[58] This compound was synthesized according to modified literature procedures.[45] In a flame-dried Schlenk tube under an argon atmosphere, **BI$^+$-Ph-NMe$_2$** (295.0 mg, 0.75 mmol, 1.0 eq.) and 10 mL MeOH were added. The mixture was cooled to 0 ℃ in an ice-water bath. Then $NaBH_4$ (170.5 mg, 4.51 mmol, 6.0 eq.) was added portionwise over 40 min with stirring. The reaction mixture was quenched with water. The precipitate was filtered and washed with water to give white solid product (140.7 mg, 0.53 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.71 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.43 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.79 (s, 1H), 3.00 (s, 6H), 2.56 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.4, 142.4, 129.8, 126.2, 119.2, 112.2, 105.7, 94.0, 40.7, 33.2 ppm.

Photochemical reaction[24]

In a flame-dried Schlenk tube under an argon atmosphere, L-ascorbic acid (88.1 mg, 0.50 mmol, 20 eq.), K_2CO_3 (76.1 mg, 0.55 mmol, 22 eq.), **BI$^+$-Ph-NMe$_2$** (9.8 mg, 0.025 mmol, 1.0 eq.), 8 mL CH_3CN and 2 mL distilled water were added. The solution was degassed by three freeze-pump-thaw cycles and backfilled with argon. The Schlenk tube was placed 3 cm away from the lamp. The reaction was stirred under visible-light irradiation (with a maximum wavelength of 400 nm and an intensity of 320 mW/cm^2) and fan cooling for 4 h. After the reaction, 1,3,5-trimethoxybenzene (12.0 mg) as an internal standard and 3 mL distilled water were added under an argon atmosphere. Then 0.6 ml of the solution was transferred to an NMR tube and subjected to ^{1}H NMR spectroscopic analysis using the solvent

suppression technique. The yield of **BIH-Ph-NMe$_2$** and the recovery of **BI$^+$-Ph-NMe$_2$** were 54% and 46%, respectively.

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Photographic image of photoirradiation system; cyclic voltammograms; crystallographic data; copies of ^{1}H and ^{13}C{^{1}H} NMR spectra; and Cartesian coordinates of all optimized and transition state structures

Accession Codes

CCDC 2254352 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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