

Novel Synthesis, Properties, and NAD⁺-NADH Type Redox Ability of 1,3-Dimethylcyclohepta[4,5]pyrrolo[2,3-d]pyrimidine-2,4(1,3H)-dionylium Ions Annulated with Additional Pyrrolo[2,3-d]pyrimidine-1,3(2,4H)-dione and Furan Analogue, and Their Hydride Adducts

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A convenient preparation of novel cations $11a_{,b}^{+}\cdot BF_{4}^{-}$ and $12a_{,b}^{+}\cdot BF_{4}^{-}$, which are derived from annulation of the 1,3-dimethylcyclohepta[4,5]pyrrolo[2,3-d]pyrimidine-2,4(1,3H)-dionylium ion with additional pyrrolo[2,3-d] pyrimidine-1,3(2,4H)-dione and a furan analogue, was accomplished by a novel oxidative cyclization of 1,7-dihydro-7-[1',3'-dimethyl-2',4'(1',3'H)-dioxo-6'-(phenylamino)pyrimidin-5'-yl]-1,3-dimethyl-10-phenylcyclohepta[4,5]pyrrolo[2,3-d]pyrimidine-2,4(1,3H)-dione 9 and its furan-analogue by using DDQ or photoirradiation under aerobic conditions. Structural characteristics of 11a,b⁺ and 12a,b⁺ were clarified on inspection of the UV-vis and NMR spectral data as well as X-ray crystal analyses. The stability of cations 11a,b⁺ and 12a,b⁺ is expressed by the p $K_{\rm R+}$ values that were determined spectrophotometrically to be 10.7–12.6. The electrochemical reduction of $11a, b^+ \cdot BF_4^-$ and $12a, b^+ \cdot BF_4^-$ exhibited reduction potential at -0.93 to -1.00 (V vs Ag/AgNO₃). The first reduction potential of $11a^+$ was reversible due to steric hindrance of two phenyl groups. The photoinduced oxidation reaction of $11a,b^+BF_4^-$ and $12a,b^+BF_4^-$ toward some amines under aerobic conditions was carried out to give the corresponding imines (isolated by converting to the corresponding 2.4-dinitrophenvlhydrazones) with the recycling numbers of 0.6-30.3. Furthermore, as an example of the NAD⁺-NADH models, the reduction of a pyruvate analogue and some carbonyl compounds with the hydride-adduct of $11a^+ \cdot BF_4^-$ was accomplished for the first time to give the corresponding alcohol derivatives.

Introduction

Coenzyme NADH, a cofactor of L-lactate dehydrogenase, functions as an enantioselective agent that reduces pyruvate to L-lactate during anaerobic glycolysis. During several decades, efforts have been made to create model compounds mimicking the activity of the NAD⁺-NADH redox couple.^{1–11} The introduction of an optically active *N*-substituent in the amide of 1-alkylated 1,4-dihydronicotinamides, e.g., **1**, can induce a modest to moderate chirality transfer toward carbonyl compounds (Figure 1).^{12,13} Furthermore, Ohno and co-workers have improved considerably a chirality transfer by the additional introduction of methyl groups at the C2 and C4 in the NADH model, e.g., compound **2**.¹⁴ The new chiral center at the

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FIGURE 1.

C4 controls the mode of hydride transfer. Moreover, the reduction of carbonyl compounds by using 1,5-dihydro-5-deazaflavin 3 has been reported.¹⁵ As reported, most of the NADH models are alternant aromatic compounds consisting of six-membered rings. In contrast, however, it has not been reported that nonalternant heteroaromatic compounds such as heteroazulenes have been used for the NADH model reduction. In this context, we have reported the synthesis, properties, and reactivity of 1,3dimethylcyclohepta[4,5]furo[2,3-d]pyrimidine-2,4(1,3H)dionylium ion $4a^+ \cdot BF_4^{-16}$ and its thiophene and pyrrole analogues $4b^+ \cdot BF_4^{-17}$ and $4c^+ \cdot BF_4^{-18}$ as well as their

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novel photoinduced autorecycling oxidizing reactions toward some alcohols and amines.¹⁹ In these studies, it was clarified that the pyrrole analogue $4c^+ \cdot BF_4^-$ has higher stability ($pK_{R+} = 10.9$, vide infra) when compared with $4\mathbf{a},\mathbf{b}^+\cdot\mathbf{BF_4}^-$ ($4\mathbf{a}^+\cdot\mathbf{BF_4}^-$ p $K_{\mathrm{R}+}$ = ca. 6.0; $4\mathbf{b}^+\cdot\mathbf{BF_4}^$ $pK_{R+} = 5.1$). The π -conjugation mode in polycyclic conjugated π -systems containing more than one (4n + 2)conjugation loop is an important subject from both theoretical and experimental viewpoints. Combination of more than one π -system can endow the original π -system with new properties. From this viewpoint, we have recently reported the synthesis, properties, and oxidizing ability of $\mathbf{5}^+ \cdot \mathbf{BF_4}^{-20}$ and $\mathbf{6a, b}^+ \cdot \mathbf{BF_4}^{-.21}$ The properties and reactivity of compound $5^+ \cdot \mathbf{BF_4}^-$ indicated that much perturbation occurs by the benzo-annulation onto $4a^+$. $\mathbf{BF_4}^-$, and the p $K_{\mathbb{R}^+}$ value of $\mathbf{5^+} \cdot \mathbf{BF_4}^-$ is reduced to 4.7 as compared with the parent cation $4\mathbf{a}^+ \cdot \mathbf{BF_4}^-$ (p $K_{R+} = ca$. 6.0). The properties and reactivity of compounds 6a,b⁺. \mathbf{BF}_{4}^{-} were also much perturbed by the annulation of the furopyrimidine ring onto $4\mathbf{a}^+ \cdot \mathbf{BF_4}^-$; however, the p $K_{\mathbf{R}^+}$ values of $6a,b^+ \cdot BF_4^-$ were larger to be 8.8 and 8.6, respectively. The higher stability of $6a_{,b}^{+} \cdot BF_{4}^{-}$ demonstrates the stabilizing effect of additional annulation of the furopyrimidine ring onto $4a^+ \cdot BF_4^-$. Furthermore, the cation $6a,b^+ \cdot BF_4^-$ was converted to the C12-hydride adducts, which were used for the attempted reduction of carbonyl compounds. However, the reduction did not proceed and the starting materials were recovered. Since the stability of cations $6a, b^+ \cdot BF_4^-$ was not so high, their hydride adducts do not have enough lability toward carbonyl compounds. The pyrrole analogues of $6a, b^+ \cdot BF_4^$ are expected to have higher stability as compared with $4\mathbf{a}-\mathbf{c}^+\cdot\mathbf{BF_4}^-$ and $6\mathbf{a},\mathbf{b}^+\cdot\mathbf{BF_4}^-$. Thus, the studies of the pyrrole analogues of $6a,b^+ \cdot BF_4^-$, such as $11a,b^+ \cdot BF_4^$ and $12a,b^+ \cdot BF_4^-$ (Scheme 2), seemed to be a very interesting project from the viewpoint of exploration of novel functions. In this study, we report the synthesis, properties, and structural details of novel cations 11a, $b^+ \cdot BF_4^-$ and 12a, $b^+ \cdot BF_4^-$, which are derived from annulation of $4c^+$ with additional pyrrolo[2,3-d]pyrimidine-1.3(2.4H)-dione and a furan analogue. The photoinduced oxidizing reaction of $11a, b^+ \cdot BF_4^-$ and $12a, b^+ \cdot$ \mathbf{BF}_4^- toward some amines was studied as well. Furthermore, as an example of NAD⁺-NADH models, the reduction of a pyruvate analogue and some carbonyl compounds with hydride-adduct 23a of $11a^+ \cdot BF_4^-$ was investigated for the first time to give the corresponding alcohol derivatives. We report here the results in detail.

Results and Discussion

Synthesis. A strategy for the synthesis of $11a_{,b}^{+} \cdot BF_{4}^{-}$ and $12a_{,b}^{+} \cdot BF_{4}^{-}$ consists of the oxidative cyclization of **9** and **10** and subsequent anion exchange. The reaction of 2-chlorotropone 7 with 2 molar equiv amounts of 6-phenylamino-1,3-dimethyluracil 8 in EtOH in the presence of $Bu^t NH_2$ at room temperature for 48 h gave 9 as pale yellow solids in 75% yield (Scheme 1). Similarly to the synthesis of $4a, b^+ \cdot BF_4^-$, ^{16,17} the reaction would proceed as follows: the reaction of **7** with **8** affords $4c^+$, which undergoes a reaction with the second 8 to give 9.

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 a Reagents and conditions: (i) Bu'NH2, EtOH, rt, 48 h; (ii) NaH, CH3CN, rt, 48 h.

Furthermore, the reaction of $4a^+ \cdot BF_4^{-16}$ with 6-phenylamino-1,3-dimethyluracil 8 in CH₃CN in the presence of NaH at room temperature for 48 h gave 10 as pale yellow solids in 89% yield. Compounds 9 and 10 were sensitive to acidic conditions, and the reactions of 9 and 10 with 42% aqueous HBF₄ in Ac₂O gave $4a^+ \cdot BF_4^-$ and $4c^+ \cdot BF_4^-$ in quantitative yields, respectively.

The oxidative cyclization of 9 and 10 was carried out to give $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$, respectively (Scheme 2, Table 1). The reaction of 9 with 2.2 molar equiv of DDQ in PhH at room temperature for 24 h and subsequent anion exchange reaction by using aqueous HBF₄ in Ac₂O afforded a mixture of $11a^+ \cdot BF_4^-$ and $11b^+{\boldsymbol{\cdot}}BF_4{}^-$ in a good combined yield (93%, run 1). The ratio of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ was determined to be 2:1 from the ¹H NMR spectrum of the mixture. Separation of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ was accomplished by fractional recrystallization from CH₃CN/AcOEt to give pure samples of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$. The reaction of 9 by using PhH proceeded slowly, and thus a similar reaction at room temperature for 1 h gave a mixture of $11a^+ \cdot BF_4^-$, $11b^+ \cdot BF_4^-$, and tropylium cation $13^+ \cdot BF_4^-$ (run 2). Under elevated temperature, the reaction was completed in 2 h to give a mixture of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ in a ratio of 2.5:1 (run 3); however, the reaction of 9 with 1 molar equiv of DDQ in Ac_2O at -16°C for 1 h and the following anion exchange reaction afforded cation $13^+ \cdot BF_4^-$ in a quantitative yield. Thus, the oxidative cyclization of 9 would proceed via a pathway as outlined in Scheme 2. The oxidation of 9 gives cation 13^+ , which undergoes deprotonation to give intermediate 15. The intermediate 15 undergoes cyclization reactions to give two kinds of intermediates, 17a and 17b, the hydrogen abstraction of which by another DDQ gives cations, $11a^+$ and $11b^+$, respectively. Subsequent anion exchange reaction with aqueous HBF₄ solution results in the formation of $11a^{+} \cdot BF_{4}^{-}$ and $11b^{+} \cdot BF_{4}^{-}$. The reaction of 9 in CH₂Cl₂, on the other hand, proceeded more quickly and afforded a mixture of $11a^+ \cdot BF_4^-$ and 11b⁺•BF₄⁻ in good combined yield (89%) in a ratio of 4:1 (run 4). In a similar reaction of 9 in DMF, a mixture of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ was obtained in a ratio of 15:1 (run 5). The facts show that selectivity of cyclization of 9 would correlate with the polarity of the solvent as in the order DMF > CH_2Cl_2 > PhH. Thus, decrease of the solvent polarity would cause a lowering of selectivity. The intermediate 13^+ is less stabilized by the solvent having smaller polarity, and thus the cyclization reaction of 13^+

giving 17a,b via 15 in the less polar solvent would proceed more quickly. Consequently, the selectivity of the cyclization would depend on the stability of the intermediate 13^+ .

Molecular-orbital (MO) calculation of 15 was carried out using the AM1 method (MOPAC97),²² and the coefficients of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of 15 at the C6 and the C8 are depicted in Figure 2. Regarding the coefficients of both HOMO and LUMO for 15, the value is larger for C8 than for C6, suggesting that the reaction of the former position giving 17a occurs preferentially over that of the latter position giving 17b. Furthermore, by X-ray crystal analysis of $11a^+ \cdot BF_4^-$ (vide infra), the interaction between the contained solvent (Et_2O) and four phenyl groups of two closely located molecules of $11a^+$ was observed in the solid state. Thus, there may be possibility that the formation of $11a^+ \cdot BF_4^$ as the major product would be attributable partially to the solvent-mediated interaction between two phenyl groups.

On the other hand, the reactions of **10** with DDQ in both CH₂Cl₂ and DMF, respectively, afforded mixtures of $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$ in a ratio of 1:1 in good combined yields (runs 7 and 8). Although the MO calculation of 16 showed a tendency similar to that of 15 (Figure 2), the cyclization of 14^+ in both polar and less polar solvents would proceed unselectively. The feature seems to be attributable to the instability of 14^+ (cf. $4a^+$ $pK_{R+} = ca. 6.0; 4c^+ pK_{R+} = 10.9$). The reaction of 10 with an equivalent amount of DDQ in Ac_2O at -16 °C for 1 h and subsequent anion exchange reaction did not afford cation $14^+ \cdot BF_4^-$, and a mixture of $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$ was obtained in addition to $4a^+ \cdot BF_4^-$, which was generated by the reaction of unreacted **10** with HBF₄. The feature suggests the instability of 14^+ , which cyclizes immediately after generation. Separation of $12a^+ \cdot BF_4^$ and $12b^+ \cdot BF_4^-$ was also accomplished by fractional recrystallization from CH₃CN/AcOEt to give pure samples of $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$.

Furthermore, the photoinduced oxidative cyclization of **9** and **10** in the presence of NH_4BF_4 in CH_3CN gave mixtures of $11a, b^+ \cdot BF_4^-$ and $12a, b^+ \cdot BF_4^-$, respectively (runs 6 and 9). The oxidative cyclization of 9 and 10 would proceed via a pathway similar to the reaction by using DDQ as outlined in Scheme 2. On the other hand, photoirradiation of $13^+ \cdot BF_4^-$ under aerobic conditions was monitored by NMR spectroscopy in CD₃CN. After irradiation for 16 h, $13^+ \cdot BF_4^-$ was completely converted to $11a^+ \cdot BF_4^-$ as a single product. In addition, the photoirraditation of the isolated cation $13^+ \cdot BF_4^-$ in the presence of 42% aqueous HBF₄ (0.2 mL) in CH₃CN for 96 h afforded $11a^+ \cdot BF_4^-$ in quantitative yield. Thus, the selective preparation of cation $11a^+ \cdot BF_4^-$, which is useful for the NAD⁺-NADH model reduction (vide infra), was achieved.

Properties. Compounds 9, 10, $11a,b^+ \cdot BF_4^-$, $12a,b^+ \cdot BF_4^-$, and $13^+ \cdot BF_4^-$ were fully characterized on the basis of ¹H NMR, ¹³C NMR, IR, UV–vis, and mass spectral data, as well as elemental analyses and X-ray analyses.

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TABLE 1. Results for Preparation of Cations 11a,b⁺·BF₄⁻ and 12a,b⁺·BF₄⁻

run	compd	oxidant	solvent	time/h ^a	product (yield/%)	ration of $11a^+{:}11b^+$ and $12a^+{:}12b^+$
1	9	DDQ	PhH	24	$11a^+ \cdot BF_4^-$ (62), $11b^+ \cdot BF_4^-$ (31)	2:1
2	9	DDQ	PhH	1	$11a^+ \cdot BF_4^-$ (39), $11b^+ \cdot BF_4^-$ (22), $13^+ \cdot BF_4^-$ (31)	1.8:1
3	9	DDQ	PhH	2^b	$11a^+ \cdot BF_4^-$ (71), $11b^+ \cdot BF_4^-$ (29)	2.5:1
4	9	DDQ	CH_2Cl_2	1	$11a^+ \cdot BF_4^-$ (71), $11b^+ \cdot BF_4^-$ (18)	4:1
5	9	DDQ	\mathbf{DMF}	1	$11a^+ \cdot BF_4^- (93), 11b^+ \cdot BF_4^- (6)$	15:1
6	9	air, hv ^c	CH_3CN	3	$11a^+ \cdot BF_4^- (70), 11b^+ \cdot BF_4^- (30)$	2.3:1
7	10	DDQ	CH_2Cl_2	1	$12a^+ \cdot BF_4^-$ (45), $12b^+ \cdot BF_4^-$ (45)	1:1
8	10	DDQ	\mathbf{DMF}	1	$12a^+ \cdot BF_4^- (49), 12b^+ \cdot BF_4^- (49)$	1:1
9	10	air, $h\nu^c$	CH_3CN	3	$12a^+ \cdot BF_4^-$ (47), $12b^+ \cdot BF_4^-$ (52)	0.9:1

^{*a*} Unless otherwise specified, reaction was carried out at room temperature. ^{*b*} Reaction was carried out under reflux. ^{*c*} In the presence of NH₄BF₄.

SCHEME 2^a



^a Reagents and conditions: (i) (a) DDQ, conditions listed in Table 1 or $h\nu$, aerobic, NH₄BF₄, CH₃CN, rt, 3 h; (b) 42% aq HBF₄, Ac₂O, 0 °C, 1 h; (ii) (a) DDQ, Ac₂O, -16 °C, 1 h; (b) 42% aq HBF₄, Ac₂O, -16 °C, 1 h; (iii) (a) $h\nu$, aerobic, 42% aq HBF₄, CH₃CN, rt, 96 h; (b) 42% aq HBF₄, Ac₂O, 0 °C, 1 h.

The analytical data of $13^+ \cdot BF_4^-$ is not satisfactory because of its instability under recrystallization; however, correct HRMS was obtained. Mass spectra of $11a,b^+ \cdot BF_4^$ and $12a,b^+ \cdot BF_4^-$ exhibited the correct $M^+ - BF_4^-$ ion peak, which is indicative of the cationic nature of the compound. The characteristic absorption band for the counterion BF_4^- was observed at 1084 cm⁻¹ in the IR spectra. UV-vis spectra of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$





FIGURE 2.



FIGURE 3. UV–vis spectra of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ in CH₃CN.

in acetonitrile are shown in Figure 3. The spectra of **11a,b**⁺·**BF**₄⁻ and **12a,b**⁺·**BF**₄⁻ are similar and the longest wavelengths absorption maxima (λ_{max}) show similar values (**11a**⁺ 461 nm; **11b**⁺ 462 nm; **12a**⁺ 465 nm; **12b**⁺ 467 nm). The λ_{max} of **11a,b**⁺ and **12a,b**⁺ appear at longer wavelength than that of **4c**⁺ (414 nm),¹⁸ suggesting that cations **11a,b**⁺ and **12a,b**⁺ have a more enlongated conjugation as compared with that of **4c**⁺. In addition, cations **12a,b**⁺ having a furopyrimidine ring show the peaks at ca. 390 nm. The fact seems to show that cations **12a,b**⁺ retain a partial structural feature similar to cation **4a**⁺.

Single crystals of $11a,b^+ \cdot BF_4^-$ were obtained by recrystallization from CH₃CN/Et₂O. Thus, X-ray crystal analyses of $11a,b^+ \cdot BF_4^-$ were performed, and the ORTEP drawings are shown in Figure 4.²³ The counteranion (BF₄⁻) in $11a,b^+ \cdot BF_4^-$ and the solvent molecule (1/2 Et₂O) contained in $11a^+ \cdot BF_4^-$ are omitted for clarity. It was interesting that the Et₂O molecule contained in the



FIGURE 4. ORTEP drawings of **11a**, **b**⁺ · **BF**₄⁻ with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) of **11a**⁺ · **BF**₄⁻: N1-C2 1.402(4), N1-C9 1.372(5), N4-C7 1.401(5), N4-C11 1.368(5), C1-C2 1.389(5), C2-C3 1.433(5), C3-C4 1.404(5), C4-C5 1.372(5), C5-C6 1.414(5), C6-C7 1.429(5), C1-C7 1.374(5), C3-C8 1.409(5), C8-C9 1.383(5), C6-C10 1.413(5), C10-C11 1.375(3). Selected bond lengths (Å) of **11b**⁺ · **BF**₄⁻: N1-C2 1.405(3), N1-C9 1.366(3), N4-C7 1.401(3), N4-C11 1.382(3), C1-C2 1.371(3), C2-C3 1.441(3), C3-C4 1.401(3), C4-C5 1.383(3), C5-C7 1.386(3), C6-C7 1.430(3), C1-C6 1.395(3), C3-C8 1.416(3), C8-C9 1.383(3), C6-C10 1.414(3), C10-C11 1.375(3).

single crystal is surrounded by four phenyl groups of two closely located molecules of $11a^+ \cdot BF_4^-$. The π -system of **11a,b**⁺**·BF**₄⁻ has a nearly planar structure. The planes of the phenyl groups are twisted 72.6-87.8° against the plane of the π -system. In both compounds **11a**,**b**⁺•**BF**₄⁻, the bond lengths of N1-C9 and N4-C11 are shorter than those of N1–C2 and N4–C7, suggesting that the former bonds have a larger bond order. Furthermore, in compound $11a^+ \cdot BF_4^-$, the bond length of C4–C5 is shorter than those of C3-C4 and C5-C6. In compound 11b+. $\mathbf{BF_4}^-$, the bond length of C1–C2 is shorter than that of C1-C6. These facts suggest the existence of bond alternation as shown in the canonical structures of 11a,b⁺-B and **11a,b⁺-C** (Figure 5). Concerning the two canonical structures, 11b⁺-B and 11b⁺-C, the contribution of the former structure would be larger than that of the latter structure due to the stability of the closed pyrrole ring. The difference between the contributions of 11b⁺-B and **11b⁺-C** seems to cause the slight deformation of **11b⁺** from planarity. MO calculation of **11a,b**⁺ was carried out by using the $6-31G^*$ basis set of the MP2 level²⁴ and demonstrated that the bond length alternations obtained by the MO calculations are very similar to those obtained by the X-ray analysis in the solid state.

The affinity of the carbocation toward hydroxide ions expressed by the pK_{R+} value is the most common criterion of carbocation stability.²⁵ The pK_{R+} values of cations **11a,b**⁺ and **12a,b**⁺ were determined spectrophotometri-



FIGURE 5.

cally in buffer solutions prepared in 50% aqueous CH₃-CN and are summarized in Table 2, along with those of the reference compounds **4a,c**^{+,16,18} As expected, the pK_{R+} values of **11a**⁺ ($pK_{R+} = 12.6$) and **11b**⁺ ($pK_{R+} = 12.6$) are larger than that of **4c**⁺ ($pK_{R+} = 10.9$).¹⁸ Similarly, the pK_{R+} values of **12a**⁺ ($pK_{R+} = 10.9$) and **12b**⁺ ($pK_{R+} = 10.7$) are also larger than that of **4a**⁺ ($pK_{R+} = ca. 6.0$).¹⁶ Thus, the additional annulation of the pyrrolopyrimidine ring onto the cations **4a,c**⁺ stabilizes the cations quite effectively. The pK_{R+} values are similar for **11a**⁺ and **11b**⁺ as well as for **12a**⁺ and **12b**⁺; the difference in perturbation originating from the annulating position of the pyrrolopyrimidine ring is small.^{20,21,26,27}

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TABLE 2. λ_{max} , pK_{R+} Values, and Reduction Potentials^{*a*} of Cations 11a,b⁺ and 12a,b⁺,^{*b*} and Reference Compounds 4a,c⁺

compd	$\lambda_{ m max}$	$\mathrm{p}K_{\mathrm{R}+}$	reduction potential $(E1_{red})$
$11a^+$	461	12.6	$-0.95 (-0.93)^{e}$
$11b^+$	462	12.6	-1.00
$12a^+$	465	10.9	-0.77
$12b^+$	467	10.7	-0.84
$4a^{+ c}$	397	${\sim}6.0$	-0.58
$\mathbf{4c}^{+ \ d}$	414	10.9	-0.84

^{*a*} V vs Ag/AgNO₃; cathodic peak potential. ^{*b*} Salts **11a,b**⁺•**BF**₄⁻ and **12a,b**⁺•**BF**₄⁻ were used for the measurement. ^{*c*} Reference 16. ^{*d*} Reference 18. ^{*e*} Reversible process.

The reduction potentials of $11a,b^+$ and $12a,b^+$ were determined by cyclic voltammentry (CV) in CH₃CN. Except that of $E1_{red}$ of $11a^+$, the reduction waves were irreversible under the conditions of the CV measurements; thus, the peak potentials are summarized in Table 1, together with those of the reference compounds $4a,c^+$.^{16,18} Both $E1_{red}$ values of $11a,b^+$ and $12a,b^+$ are more negative than those of $4c^+$ and $4a^+$, respectively. The feature is similar to the nature of their pK_{R+} values. The p $K_{\rm R+}$ values of **11a,b** are similar; however, the $E1_{\rm red}$ of $11a^+$ is less negative than that of $11b^+$. Similarly, the $E1_{\rm red}$ of $12a^+$ is less negative than that of $12b^+$. The irreversible nature is probably due to the formation of a radical species and its dimerization, as reported to be a typical property of uracil-annulated heteroazulenvlium ions such as $4a - c^+$.¹⁶⁻¹⁸ Cation $11a^+$ shows the reversible reduction wave for the first time in the series of uracilannulated heteroazulenylium ions. The feature would be due to the phenyl groups, which inhibit dimerization of the radical species sterically.

Autorecycling Oxidation of Amines. We have previously reported that compounds $4\mathbf{a} - \mathbf{c}^+ \cdot \mathbf{BF_4}^-$ undergo autorecycling oxidation toward some alcohols and amines under photoirradiation.^{16–19} In this context, we found that compounds 11a,b⁺·BF₄⁻ and 12a,b⁺·BF₄⁻ have oxidizing ability toward benzylamine, 1-phenylethylamine, hexylamine, and cyclohexylamine to give the corresponding imines under aerobic and photoirradiation conditions (Scheme 3). Imine $R^1R^2C=NH$ is produced at first; however, it reacts with another amine to result in the formation of R¹R²C=N-CHR¹R². Then the reaction mixture was diluted with ether and filtered, and the filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound. The results are summarized in Table 3. Direct irradiation of the amines in the absence of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ (named "blank") gives the corresponding carbonyl compounds in low to modest yields. Thus, the yields are calculated by subtraction of the "blank" yield from the yield of the carbonyl compound in the presence of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$. The recycling numbers are more than 1 (Table 3) and thus autorecycling oxidation clearly proceeds; however, hexylamine and 1-phenylethylamine were not oxidized effectively by $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$, respectively (Table 3, runs 11 and 14).

SCHEME 3^a



^{*a*} Reagents and conditions: (i) $h\nu$, aerobic, CH₃CN, rt, 16 h.

TABLE 3. Autorecycling Oxidation of Some Amines by $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ under Photoirradiation^{*a*}

run	compd	amine	yield/µmol ^{b,c}	recycling no. ^d
1	$11a^+ \cdot BF_4^-$	$PhCH_2NH_2$	138.1	27.6
2	$11a^+ \cdot BF_4^-$	PhCH(Me)NH ₂	151.4	30.3
3	$11a^+ \cdot BF_4^-$	hexylamine	17.5	3.5
4	$11a^+ \cdot BF_4^-$	cyclohexylamine	24.5	4.9
5	$11b^+ \cdot BF_4^-$	$PhCH_2NH_2$	96.9	19.4
6	$11b^+ \cdot BF_4^-$	PhCH(Me)NH ₂	87.7	17.5
7	$11b^+ \cdot BF_4^-$	hexylamine	25.7	5.1
8	$11b^+ \cdot BF_4^-$	cyclohexylamine	32.8	6.6
9	$12a^+ \cdot BF_4^-$	$PhCH_2NH_2$	140.2	28.0
10	$12a^+ \cdot BF_4^-$	PhCH(Me)NH ₂	129.4	25.9
11	$12a^+ \cdot BF_4^-$	hexylamine	2.9	0.6
12	$12a^+ \cdot BF_4^-$	cyclohexylamine	37.8	7.6
13	$12b^+ \cdot BF_4^-$	$PhCH_2NH_2$	79.4	15.9
14	$12b^+ \cdot BF_4^-$	PhCH(Me)NH ₂	0^e	0.0
15	$12b^+ \cdot BF_4^-$	hexylamine	6.8	1.4
16	$12b^+ \cdot BF_4^-$	cyclohexylamine	26.6	5.3

^{*a*} A CH₃CN (16 mL) solution of compound **11a,b**⁺•**BF**₄⁻ or **12a,b**⁺•**BF**₄⁻ (5 μ mol) and amines (2.5 mmol, 500 equiv) was irradiated by RPR-100, 350 nm lamps under aerobic conditions for 16 h. ^{*b*} Isolated by converting to the corresponding 2,4dinitrophenylhydrazone. ^{*c*} The yield is calculated by subtraction of the blank yield from the total yield. ^{*d*} Recycling number of **11a,b**⁺•**BF**₄⁻ and **12a,b**⁺•**BF**₄⁻. ^{*e*} The blank yield was higher than the yield in the presence of **12b**⁺•**BF**₄⁻.

We propose that the present autorecycling oxidation proceeds via electron transfer from amine to the excited state of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ as shown in Scheme $3.^{19,28}$ The electron transfer from amine to the excited state of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ would occur to produce radicals $11a,b^+$ and $12a,b^+$ and a cation radical 19. On the other hand, there is an alternative possibility that the photoinduced homolysis of the amine adducts, which are generated by the reaction of $11a,b^+$. BF_4^- and $12a,b^+ \cdot BF_4^-$ with amines, would afford radicals $11a,b^+$ and $12a,b^+$ and cation radical 19 directly. An electron transfer from radical species $11a,b^-$ and $12a,b^+$ to molecular oxygen would give the superoxide anion radical, $11a,b^+$, and $12a,b^+$; tropyl radical derivatives are

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SCHEME 4^a



 a Reagents and conditions: (i) NaBH4, CH3CN, rt, 1 h; (ii) (a) DDQ, CH2Cl2, rt, 1 h; (b) 42% aq HBF4, Ac2O, 0 °C, 1 h.

known to be oxidized readily by molecular oxygen.²⁹ Then, a proton transfer from cation radical **19** to the superoxide anion radical would occur, followed by formation of the products **21** and H_2O_2 . Compound **21** reacts with excess amine to give imine **22**.

Reducing Ability toward Some Carbonyl Compounds. The hydride adduct 23a, obtained by reduction of $11a^+ \cdot BF_4^-$ with NaBH₄, achieved reduction of a pyruvate analogue and some carbonyl compounds to produce the corresponding alcohols in the presence of Mg- $(ClO_4)_2$. Whereas the reduction of $4\mathbf{a}-\mathbf{c}^+\cdot\mathbf{BF_4}^-$ with NaBH₄ proceeded at the C5, C7, and C9 to give mixtures of three regioisomers,^{16–18} the reduction of $11a,b^+ \cdot BF_4^$ and $12a, b^+ \cdot BF_4^-$ occurred at the C12 to give single products containing two closed pyrrolopyrimidine rings or pyrrolopyrimidine and furopyrimidine ring, 23a,b and 24a,b in good yields, respectively (Scheme 4). Upon hydride abstraction with DDQ and subsequent anion exchange reaction, compounds 23a,b and 24a,b regenerated $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ in 82–100% yields, respectively. Thus, to investigate the reducing ability of 23a,b and 24a,b, reduction of the pyruvate analogue, methyl benzoylformate, and some carbonyl compounds was carried out in the presence of $Mg(ClO_4)_2$ (Scheme 5). Although the reduction of methyl benzoylformate 25 by using 23b and 24a,b did not proceed at even 60 °C (Table 4, runs 2–4), the reduction of 25 with 23a in CH_2Cl_2 -CH₃CN (2/1) at room temperature for 20 h afforded methyl mandelate 29 in quantitative yield (run 1). In addition, generated cation $11a^+$ was recovered in 82% yield by converting to 23a on treatment with NaBH₄. Thus, the NADH model reduction by using nonalternant heteroaromatic compounds was accomplished for the first time. The low reactivity of 24a,b would be attributable to the lower stability of the corresponding cations **12a**, $\mathbf{b}^+ \cdot \mathbf{BF}_4^-$. The stability of cation $\mathbf{11b}^+ \cdot \mathbf{BF}_4^-$ is similar to that of $11a^+ \cdot BF_4^-$ (vide supra); however, only 23a could reduce 25. The difference of the reactivity of 23a and 24b is unclear at this stage. Furthermore, we found that 23a has reducing ability toward benzaldehyde 26, 4-phenyl-2-butanone 27, and acetophenone 28 (runs 5-12). Yields are calculated by the ratios of alcohols and carbonyl compounds obtained by the ¹H NMR data of the mixtures. The reduction of aromatic aldehyde 26 by using 23a at 60 °C afforded benzyl alcohol 30 in good yield (89%, run 5). At elevated temperature (100 °C), the





 a Reagents and conditions: (i) Mg(ClO_4)_2, conditions listed in Table 4.

reduction of 26 was almost completed to give 30 in 96% yield (run 6). Furthermore, the reduction of dialkylated ketone 27 by using 24a at 60 °C afforded 4-phenyl-2butanol 31 in modest yield (42%, run 7). At elevated temperature (140 °C), the reduction of 27 proceeded smoothly to give 31 in 81% yield (run 8). In addition, compound 23a reduced an aromatic ketone 28 at 60 °C to give 1-phenylethanol **32** in modest yield (38%, run 9); however, the yields were not improved by the raising temperature (runs 10 and 11). By using 3 molar equiv of 23a, reduction of 28 was almost completed to give 32 in good yield (92%, run 12). Thus, spontaneous hydride elimination seems to occur at elevated temperature. In all reactions, cation **11a⁺** was recovered by converting to 23a in good yield (76–91%). These facts show that 23a could reduce activated ketone, aromatic aldehyde, aromatic ketone as well as aliphatic ketone. This is the first example of the reduction of carbonyl compounds by nonalternant heteroaromatic compounds (heteroazulenes), which provides promising possibility for the exploration of novel reduction systems.

Conclusion

A convenient preparation of novel cations $11a,b^+ \cdot BF_4^$ and $12a,b^+ \cdot BF_4^-$, which are derived from annulation of $4c^+$ with additional pyrrolo[2,3-*d*]pyrimidine-1,3(2,4*H*)dione and a furan analogue, was accomplished by the novel oxidative cyclization of **9** and **10** by using DDQ or photoirradiation under aerobic conditions. Structural characteristics of **11a,b**⁺ and **12a,b**⁺ were clarified on inspection of the UV-vis and NMR spectral data as well as X-ray crystal analyses. The stability of cations **11a,b**⁺ and **12a,b**⁺ is expressed by the pK_{R+} values, which were determined spectrophotometrically to be 10.7-12.6. The electrochemical reduction of **11a,b**⁺ $\cdot BF_4^-$ and **12a,b**⁺ $\cdot BF_4^-$

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run	hydride adduct	carbonyl compd	temp/°C	time	product (yield)	recovery of cations/% ^e
1	23a	25	rt^a	20 h	29 (100%)	82
2	23b	25	60^b	67 h	25 (81%)	87
3	24a	25	60^b	96 h	25 (88%)	75
4	24b	25	60^b	96 h	25 (100%)	64
5	23a	26	60^b	7 d	30 (89%), 26 (11%) ^d	85
6	23a	26	100^{c}	7 d	30 (96%), 26 $(4\%)^d$	78
7	23a	27	60^b	7 d	31 (42%), 27 (58%) ^{d}	82
8	23a	27	140^{c}	7 d	31 (81%), 27 (19%) ^{d}	91
9	23a	28	60^b	7 d	32 (38%), 28 (62%) ^{d}	80
10	23a	28	100^c	7 d	32 (42%), 28 (58%) ^{d}	87
11	23a	28	140^{c}	7 d	32 (44%), 28 (56%) ^{d}	89
12	$\mathbf{23a}^{f}$	28	60^b	7 d	32 (92%), 28 (8%) ^{d}	76
^a CH ₂ C	l ₂ –CH ₃ CN was used. ^b	CHCl ₃ -CH ₃ CN was us	ed. c (CH ₂ Cl) ₂ -	CH ₃ CN was	s used. ^d The vield was deter	rmined by ¹ H NMR spectrum

of the mixture. e Isolated by converting to **23a,b** and **24a,b** by treatment with NaBH₄. f 3 molar equiv was used.

exhibited reduction potential at -0.93 to -1.00 (V vs Ag/AgNO₃). The photoinduced oxidation reaction of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ toward some amines under aerobic conditions was carried out to give the corresponding imines with the recycling number of 0.6–30.3. By using 23a, which is the hydride adduct of $11a^+ \cdot BF_4^-$, the reduction of some carbonyl compounds including a pyruvate analogue was accomplished; thus, a novel NADH model system is designed. Further studies including the mechanistic aspects and enantioselective reduction of carbonyl compounds will be reported in due course.

Experimental Section

Preparation of 9. A solution of 2-chlorotropone **7** (70 mg, 0.5 mmol), 1,3-dimethyl-6-phenylaminopyrimidine-2,4(1,3*H*)-dione **8** (231 mg, 1 mmol), and Bu^tNH₂ (91 mg, 1.3 mmol) in EtOH (10 mL) was stirred at room temperature for 48 h. The precipitate was collected by filtration and washed with EtOH to give **9** (205 mg, 75%).

Preparation of 10. A solution of $4a^+ \cdot BF_4^-$ (660 mg, 2 mmol) and 8 (462 mg, 2 mmol) in CH₃CN (25 mL) in the presence of NaH (48 mg, 2 mmol) was stirred at room temperature for 48 h. The precipitate was collected by filtration and washed with EtOH to give 10 (839 mg, 89%).

Reaction of 9 and 10 with HBF₄. To a stirred solution of **9** or **10** (1 mmol) in Ac₂O (10 mL) was added 42% aqueous HBF₄ (2 mL) at 0 °C and the mixture was stirred for 1 h until the reaction completed. To the mixture was added Et₂O (200 mL) and the precipitate was collected by filtration and washed with Et₂O to give $4c^+ \cdot BF_4^-$ (397 mg, 98%) or $4a^+ \cdot BF_4^-$ (330 mg, 100%).

Synthesis of $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ by Using DDQ. To a stirred solution of 9 or 10 (1 mmol) in a solvent (20 mL) was added DDQ (515 mg, 2.2 mmol) and the mixture was stirred under conditions described in Table 1. After evaporation of the solvent, the residue was dissolved in a mixture of Ac₂O (10 mL) and 42% aqueous HBF₄ (2 mL) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et₂O (200 mL) and the precipitate was collected by filtration and washed with Et₂O to give a mixture of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ or a mixture of $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$ (Table 1).

Synthesis of 11a,b⁺·BF₄⁻ and 12a,b⁺·BF₄⁻ by Photoirradiation. A solution of 9 or 10 (0.1 mmol) and NH₄BF₄ (0.1 mmol) in CH₃CN (30 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions for 3 h until the reaction was completed. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of acetic anhydride (10 mL) and 42% aqueous HBF₄ (2 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added Et₂O (100 mL) and the precipitate was collected by filtration to give a mixture of $11a^+ \cdot BF_4^-$ and $11b^+ \cdot BF_4^-$ or a mixture of $12a^+ \cdot BF_4^-$ and $12b^+ \cdot BF_4^-$ (Table 1).

Synthesis of 13⁺·BF₄⁻. To a stirred solution of 9 (54.8 mg, 0.1 mmol) in Ac₂O (2 mL) at -16 °C was added DDQ (35 mg, 0.15 mmol) and the mixture was stirred at -16 °C for 1 h. To the mixture was added 42% aqueous HBF₄ (0.4 mL) at -16 °C and the mixture was stirred for 1 h. To the mixture was added Et₂O (50 mL) and the precipitate was collected by filtration and washed with Et₂O to give 13^+ ·BF₄⁻ (63 mg, 100%).

¹H NMR Monitoring of the Photoirradiation of 13⁺· **BF**₄⁻. A solution of compound 13⁺·**BF**₄⁻ (6.3 mg, 0.01 mmol) in CD₃CN (0.5 mL) was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature in an NMR tube. After 16 h, the NMR measurement confirmed the exclusive formation of $11a^+ \cdot BF_4^-$.

Photoinduced Oxidative Cyclization of $13^+ \cdot BF_4^-$. A CH₃CN (15 mL) solution of compound $13^+ \cdot BF_4^-$ (31.7 mg, 0.05 mmol) in the presence of 42% aqueous HBF₄ (0.2 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions for 96 h. After evaporation of CH₃CN, the residue was dissolved in a mixture of Ac₂O (1 mL) and 42% aqueous HBF₄ (0.2 mL) at 0 °C, and the mixture was stirred for another 1 h. To the mixture was added Et₂O (50 mL) and the precipitate was collected by filtration to give $11a^+ \cdot BF_4^-$ (31.6 mg, 100%).

Determination of pK_{R^+} Values of 11a,b⁺ and 12a,b⁺. Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of Na₂B₄O₇ (0.025 M) and HCl (0.1 M) (for pH 8.2–9.0), $Na_2B_4O_7$ (0.025 M) and NaOH (0.1 M) (for 9.2-10.8), Na₂HPO₄ (0.05 M), and NaOH (0.1 M) (for pH 11.0-12.0) and KCl (0.2M) and NaOH (0.1 M) (for pH 12.0–14.0) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 6 mg of compound $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^$ in CH₃CN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and CH₃CN (1 mL). The UV–vis spectrum was recorded for each cation $11a,b^+ \cdot BF_4^-$ and $12a,b^+ \cdot BF_4^-$ in 20 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelength (456 nm for $11a^+ \cdot BF_4^-$; 458 nm for $11b^+ \cdot BF_4^-$; 460 nm for $12a^+ \cdot BF_4^-$; 462 nm for $12b^+ \cdot BF_4^-$) of each cation $11a, b^+ \cdot BF_4^-$ and $12a, b^+ \cdot BF_4^$ was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

Cyclic Voltammetry of Cations 11a,b⁺ and 12a,b⁺. The reduction potential of 11a,b⁺ and 12a,b⁺ was determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference Ag/AgNO₃ electrode. Nitrogen was bubbled through a CH₃CN solution (4 mL) of each cation 11a,b⁺·BF₄⁻ and 12a,b⁺·BF₄⁻ (0.5 mmol dm⁻³) and Bu₄NClO₄ (0.1 mol dm⁻³) to deaerate it. The measurements were made

at a scan rate of 0.1 V s⁻¹ and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X-Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) $(E_{1/2} = +0.083)$ was added as the internal standard, and the observed peak potential was corrected with reference to this standard. The cations **11a**,**b**⁺·**BF**₄⁻ and **12a**,**b**⁺·**BF**₄⁻ exhibited reduction waves, and they are summarized in Table 2.

General Procedure for Autorecycling Oxidation of Amines in the Presence of 11a,b⁺·BF₄⁻ and 12a,b⁺·BF₄⁻. A CH₃CN (16 mL) solution of compound 11a,b⁺·BF₄⁻ (3.16 mg, 5 μ mol) or 12a,b⁺·BF₄⁻ (2.79 mg, 5 μ mol) and amines (2.5 mmol, 500 equiv) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and diluted with Et₂O and filtered. The ¹H NMR spectra of the filtrates revealed the formation of the corresponding imines. The filtrate was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compounds. The results are summarized in Table 3.

Reaction of 11a,b⁺•**BF**₄⁻ and 12a,b⁺•**BF**₄⁻ with NaBH₄. A solution of 11a,b⁺•**BF**₄⁻ and 12a,b⁺•**BF**₄⁻ (0.1 mmol) and NaBH₄ (8 mg, 0.2 mmol) in CH₃CN (15 mL) was stirred at room temperature for 1 h. To the mixture was added saturated aqueous NH₄Cl solution, and the mixture was extracted with CH₂Cl₂. The extract was dried over Na₂SO₄ and concentrated in vacuo to give **23a,b** and **24a,b** (**23a** 53 mg, 97%; **23b** 53 mg, 97%; **24a** 37 mg, 64%; **24b** 46 mg, 88%).

Oxidation of 23a,b and 24a,b. To a stirred solution of **23a,b** and **22a4b** (0.05 mmol) in CH₂Cl₂ (5 mL) was added DDQ (25 mg, 0.11 mmol), and the mixture was stirred at room temperature for 0.5 h. After evaporation of CH₂Cl₂, the residue was dissolved in a mixture of Ac₂O (1 mL) and 42% aqueous HBF₄ (0.2 mL) at 0 °C, and the mixture was stirred for another 1 h. To the mixture was added Et₂O (20 mL) and the precipitate was collected by filtration to give **11a,b⁺·BF₄**⁻ and **12a,b⁺·BF₄**⁻ (**11a⁺·BF₄**⁻ 31 mg, 98%; **11b⁺·BF₄**⁻ 32 mg, 100%; **12a⁺·BF₄**⁻ 23 mg, 82%; **12b⁺·BF₄**⁻ 27 mg, 96%).

Reduction of Some Carbonyl Compound by Using 23a,b and 24a,b. To a solution of 23a,b and 24a,b (0.1 mmol) and Mg(ClO₄)₂ (22 mg, 0.1 mmol) in CH₃CN (5 mL) and CH₂-Cl₂ (5 mL) or CHCl₃ (5 mL) or (CH₂Cl)₂ (5 mL) was added **25**-28 (0.1 mmol), and the mixture was stirred under the conditions indicated in Table 4. To the resulting mixture was added AcOH (6 mg, 0.1 mmol), and concentrated in vacuo. The resulting residue was dissolved in Et₂O and the precipitated solids were collected by filtration. The filtrate was concentrated in vacuo to give a reduced alcohol derivative or a mixture of carbonyl compound and alcohol derivative as summarized in Table 4. On the other hand, the collected crystals containing $11a,b^+ \cdot ClO_4^-$ and $12a,b^+ \cdot ClO_4^-$ were dissolved in CH₃CN and reacted with NaBH₄ (8 mg, 0.2 mmol), and stirred at room temperature for 1 h. To the mixture was added saturated aqueous NH₄Cl solution, and the mixture was extracted with CH₂Cl₂. The extract was dried over Na₂SO₄ and concentrated in vacuo to recover 23a,b and 24a,b as summarized in Table 4.

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Supporting Information Available: Physical, analytical, and spectroscopic data of 9, 10, 11a,b⁺·BF₄⁻, 12a,b⁺·BF₄⁻, 13⁺·BF₄⁻, 23a,b, and 24a,b. ¹H and ¹³C NMR spectra of 9, 10, 11a,b⁺·BF₄⁻, 12a,b⁺·BF₄⁻, 13⁺·BF₄⁻, 23a,b, and 24a,b. Cyclic voltammogram of 11a,b⁺·BF₄⁻. CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. JO0514523