Twisted Push−Pull Alkenes Bearing Geminal Cyclicdiamino and Difluoroaryl Substituents

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ABSTRACT: The systematic combination of N-heterocyclic olefins (NHOs) with fluoroarenes resulted in twisted push−pull alkenes. These alkenes carry electron-donating cyclicdiamino substituents and two electron-withdrawing fluoroaryl substituents in the geminal positions. The synthetic method can be extended to a variety of substituted push−pull alkenes by varying the NHO as well as the fluoroarenes. Solid-state molecular structures of these molecules reveal a notable elongation of the central C−C bond and a twisted geometry in the alkene motif. Absorption properties were investigated with UV−vis spectroscopy. The redox properties of the twisted push−pull alkenes were probed with electrochemistry as well as UV−vis/NIR and EPR spectroelectrochemistry, while the electronic structures were computationally evaluated and validated.
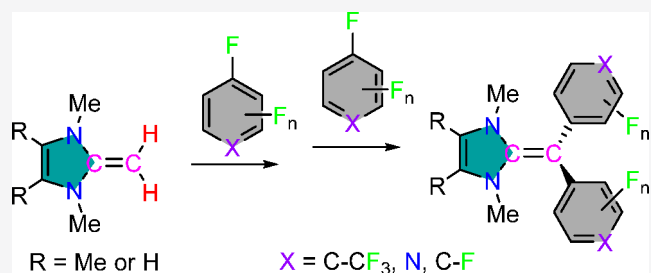
INTRODUCTION

Alkenes, in ideal cases, considering the hybridization and bonding overlap of the frontier orbitals, have a planar geometry with a nonpolarized C−C double bond **I** (Scheme 1). However, the C−C double bond of an alkene motif within a restricted environment and/or in the presence of sterically bulky substituents and/or bearing electronically distinctly polarized substituents can have an altered geometry: from merely twisted **II**[1] to (syn-/anti-)pyramidized **IIIa/IIIb**.[2] The normally nonpolarized electronic nature of the olefin can be modulated similarly: polarized (charge separated/push−pull—planar or perpendicular) **IVa/IVb**[3] and singlet state to triplet state **V**.[4] Geometrically and electronically modified classes of alkenes are known for various applications ranging from high-performance nonlinear optical,[5] to photoswitchable,[6] and to low bandgap materials.[7] These unusual alkenes have also spurred interest in respective theoretical analyses of their bonding and electronic characteristics.[8] Among them, in particular, 9,9′-bifluorenylidene **VI**,[9] octahydro-4,4′-biphenan-thrylidene **VII**,[10] and ketene N,N′-acetal **VIII**[11] derivatives have attracted substantial attention in recent years due to their utilization as solar cell materials,[12] in molecular machines,[13] and in organocatalysis,[14] respectively.

In the case of twisted push−pull alkenes, to induce the polarization in the alkenyl C−C bond, electron-donating and electron-withdrawing substituents are needed in the vicinal arrangement. At the same time, to induce twisting, sterically hindered bulky substituents are required. In most of the reported planar and twisted push−pull alkenes, amino (−NR₂)

or mercapto (−SR) substituents were used as the electron-donating groups while carbonyl, amide, or triflyl substituents were employed as electron-withdrawing groups.[15]

To the best of our knowledge, there is to date no report of any kind of push−pull alkenes with twisted or nontwisted geometry that comprise two geminal perfluoroaryl groups as electron-withdrawing groups in any combination with electron-donating groups on the adjacent carbon. Accordingly, we were interested in the chemistry of twisted push−pull alkenes bearing two geminal perfluoroaryl groups as electron-with-drawing groups along with cyclicdiamino substituents on the adjacent carbon. Herein, we report the systematic synthesis, characterization, solid-state molecular structures, absorption properties, and quantum chemical calculations of several such twisted push−pull alkenes **IX** (Scheme 1). We further address the redox chemistry of the newly synthesized twisted push−pull alkenes and the formation of radical cations. Previously, radical cations from planar and twisted alkenes were reported.[16]

Scheme 1. Chemical Structures of I–IX

RESULTS AND DISCUSSION

We recently reported N-heterocyclic olefin 1,3,4,5-tetramethyl-2-methyleneimidazoline (NHO^{Me_4})-derived monofluoroaryl substituted alkenes such as **1** and **2** (Scheme 2).[17] Now **1** and **2** were employed as synthons for the synthesis of twisted push–pull alkenes bearing two geminal perfluoroaryl groups. The reactions of **1** and **2** with octafluorotoluene and pentafluoropyridine, respectively, in the presence of Et$_3$N led to the formation of **3** and **4** (Scheme 2).[18] In addition, a different N-heterocyclic olefin 1,3,-dimethyl-2-methyleneimidazoline NHO^{Me_2} **5**[19] was used as building block (Scheme 2). The reactions of the *in situ* generated **5** with different fluoroarenes: hexafluorobenzene, pentafluorobenzene, and 1,2,3,4–tetrafluorobenzene lead to regioselective NHO^{Me_2}-derived monofluoroaryl substituted alkenes **6**, **7**, and **8** (Scheme 2).[18] In the case of pentafluoropyridine, we were not able to isolate [**9**], as the synthesis directly leads to **13**. Apparently, the NHO^{Me_2}-derived monofluoroaryl substituted alkene [**9**] is more reactive than the corresponding NHO^{Me_4}-derived monofluoroaryl substituted alkene **2**. We have investigated the reaction of **5** and pentafluorobenzene in more detail, and the formation of the 1,2,3-trimethylimidazolium cation and HF$_2^-$ counteranion was confirmed by solution-state NMR spectroscopy. Subsequently, the reactions of *in situ*

generated **6**, **7**, and **8** with pentafluoropyridine led to the formation of **10**, **11**, and **12** (Scheme 2).[18]

Compounds **3**, **4**, **6**–**8**, and **10**–**13** were characterized spectroscopically. Solution-state ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were all consistent with the expected chemical structures. It was also possible to grow single crystals of all these compounds suitable for single crystal X-ray diffraction studies. Analyses of the single crystal X-ray diffraction data (Figure 1 and Figure S75) reveal a significantly elongated C–C bond of the central alkene moiety of the bis-fluoroaryl substituted alkenes (**3**: 1.445(3) Å, **4**: 1.447(4) Å, **10**: 1.436(3) Å, **11**: 1.407(11) Å, **12**:1.433(6) Å, and **13**: 1.444(2) Å) in comparison to normal C–C double bonds which are also longer than those of the corresponding monofluoroaryl substituted alkenes (**1**: 1413(2) Å, **2**: 1.417(2) Å, **6**: 1.370(3) Å, **7**: 1.384(2) Å, and **8**: 1.373(2) Å) (Table 1). The geometry of the central alkene moiety is substantially twisted (47.12(4)–57.55(8)°) from planarity. The extent of twisting is also elevated in case of bis-fluoroaryl substituted alkenes compared to the corresponding mono-fluoroaryl substituted species (Table 1). The twist angles of these fluoroaryl substituted alkenes surpass that found in 9,9′-bifluorenylidene **VI** (32.09–33.02°).[9b]

Frontier molecular orbital analyses of **3**, **4**, **10**, and **13** suggest that the HOMOs are delocalized over most of the molecule, with a large contribution from the C-center attached to the two fluoroaryl groups, while the LUMOs are mostly centered on the fluorinated aryl groups (Figure 2, top for the HOMO, LUMO, and LUMO+1 of compound **3** and Figure S92 for the remaining).[18]

UV–vis studies show that compounds **3** and **4** exhibit longest wavelength absorption at $\lambda_{max}(\varepsilon)$ = 418 (41000) and 391 (42100) nm (L mol^{-1}cm^{-1}), respectively (Figures S42–S45). On the other hand bis-fluoroaryl substituted N-heterocyclic olefins **10** and **12** exhibit the longest wavelength absorptions at $\lambda_{max}(\varepsilon)$ = 374 (63400) and 377 (39700) nm (L mol^{-1}cm^{-1}), respectively (Table S1). This indicates that in the twisted push–pull alkenes with greater electron-donating cyclic-diamino and greater electron-withdrawing difluoroaryl substituents, the absorption spectra are red-shifted (**3**/**4** vs **10**/**12**). TD-DFT calculations of **3** and **4** allow the assignment of these bands to direct HOMO–LUMO transitions (Table S16 and Figures S93 and S94).[18] As a result, bis-fluoroaryl substituted N-heterocyclic olefins **3**, **4**, and **10**–**13** are yellow in color, whereas ketene N,N′-acetals **VIII** with amide electron-withdrawing groups are colorless/white in nature.[11a,b] On the other hand, 1,1′,3,3′,6,6′,8,8′-octachloro-9,9′-bifluorenylidene (twist angle: 55° and longest wavelength absorption at $\lambda_{max}(\varepsilon)$ = 536 (22900) nm (L mol^{-1}cm^{-1})) and perchloro-9,9′-bifluorenylidene (twist angle: 66° and longest wavelength

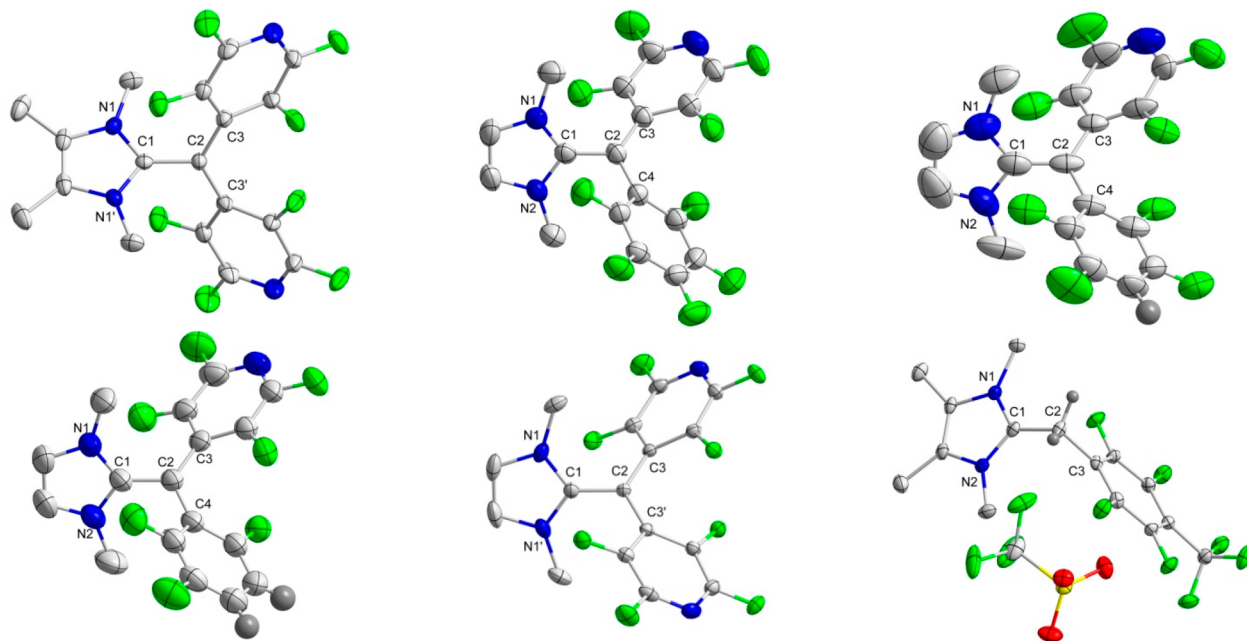## Scheme 2. Synthesis of 3, 4, 6–8, and 10–13

Figure 1. Solid-state molecular structures of **4** (top-left), **10** (top-center), **11** (top-right), **12** (bottom-left), **13** (bottom-middle), and **15** (bottom-right) with thermal ellipsoids at 50% probability level; H atoms are omitted for clarity except at C2 for **15**.

absorption at $\lambda_{max}(\varepsilon)$ = 591 (16800) nm (L mol^{-1}cm^{-1})),[20] belonging to the 9,9′-bifluorenylidene **VI** class of twisted alkenes, are red-shifted in comparison to **3**, **4**, **10**, and **12**.

The density difference isosurfaces between the LUMO/LUMO+1 and HOMO (Figure 2, bottom-left and bottom-center for compound **3** and Figures S94−S98 for the remaining) show that the main absorptions in all studied molecules correspond to charge-transfer transitions from the cyclic diaminocarbene fragment to the fluoroaryl moieties, nicely emphasizing the push−pull effect. The extinction coefficients (>40000 L mol^{-1}cm^{-1}) of these compounds are remarkably high for such small and structurally simple organic compounds and, in fact, lie in the range of values typical for porphyrinoid systems.[21] Moreover, the extinction coefficients of our synthesized bis-fluoroaryl substituted N-heterocyclic olefins are greater than those of recently reported highly polarized (strongly ylidic) mesoionic N-heterocyclic olefins.[11d] These large values also underscore the unique nature of these novel twisted push−pull alkenes.

The push−pull effect can also be seen in the electron density differences between the entire molecule and their corresponding cyclic diaminocarbene scaffold after computationally splitting the molecules at their central olefinic C1−C2 bonds (Figure 2, bottom-right for compound **3** and Figures S86−S91 for the remaining). These calculations suggest that the electron density, donated mainly by the cyclic diaminocarbene fragment, is redistributed to the fluorinated aryl fragment carbons. Comparison of these results with calculations performed on nonfluorinated analogs suggests that the push effect of the cyclic diaminocarbene is prevalent over the pull effect of the two fluoroaryl groups.

The calculated vibrational frequencies (Table S15) for the central alkene C−C bond stretching fall in the 1500−1650 cm^{-1} range and clearly lie in the double-bond region. However, the HOMO isosurfaces show a much larger contribution from the C2 atom in support of the polarization of this double bond.

In order to address the redox properties of twisted push−pull alkenes, we have considered compounds **1**−**4** as prototype examples. Cyclic voltammograms of **1** and **2** in THF (0.1 M Bu$_4$NPF$_6$, GC working electrode) reveal irreversible oxidation waves at $E_{1/2}$ = 0.43 and 0.61 V, respectively (Figures S63 and S64). In contrast, **3** and **4** show reversible oxidation waves at $E_{1/2}$ = 0.18 and 0.32 V, respectively (Figure 3, left, Figures S65 and S66). EPR spectra obtained upon *in situ* spectroelectrochemical oxidation of **1** and **3** (Figures S70 and S71) revealed featureless singlet signals.

The chemical oxidation of **1** with 1 equiv of AgOTf in THF leads to **15** (Scheme 3).[18] We assume its formation follows the initial formation of [**14**], which was detected by SEC-EPR spectroscopy followed by H-abstraction. Solution-state NMR spectroscopy and solid-state molecular structure determination confirm the identity of compound **15** (Figure 1, bottom-right). Upon one electron oxidation, both **3** and **4** exhibit a decrease of the bands at 418 and 391 nm, respectively, and the appearance of strong absorption bands around 610 nm indicates the formation of corresponding radical cations (Figure 3, middle and Figure S68). The spectra show clear isosbestic points in agreement with their reversible redox transitions in the cyclic voltammetry experiments, thus showcasing the ability of these molecules to display electrochromic behavior.

Chemical oxidation of **3** with AgOTf in THF results in the partial formation of anticipated radical cation **16** (mixed with compound **3** as confirmed by UV−vis spectroscopy) as a dark green colored solid, which shows a similar featureless EPR signal (g = 2.004; Figure S71) as obtained by *in situ* spectroelectrochemical oxidation of **3**.[18] However, the reaction of **3** with NOSbF$_6$ leads to its complete oxidation, and we have isolated compound **16** as a dark blue solid (Scheme 3). The EPR obtained from the isolated compound **16** also shows a similar featureless EPR signal both at 278 and 93 K (g = 2.004; Figures S72 and S73). The spin density plot of **16** shows that the radical character is delocalized into the whole molecule

Table 1. Selected Bond Lengths (Å) and Twist Angles (°) of 1–4, 6–8, 10–13, and 15

compd	1	3	2	4	6	10	7	11	8	12	13	15
C1–C2	1.413(2)	1.445(3)	1.417(2)	1.447(4)	1.370(3)	1.436(3)	1.384(2)	1.407(11)	1.373(2)	1.433(6)	1.444(2)	1.496(3)
∠N1–C1–N2/C3–C2–C3′/C4/H	35.83(12)	47.39(6)	45.77(8)	57.55(8)	18.96(19)	49.88(18)	19.27(13)	49.32(37)	20.06(10)	50.85(32)	47.12(4)	–

(Figure 3, right), although it has a relatively higher weight at the carbon center which is attached to the two fluoroaryl groups. Therefore, the electron spin experiences hyperfine couplings to most of the F, both N, and several H nuclei, which could be the reason for the radical not exhibiting resolved hyperfine splitting. Also, calculations of EPR hyperfine constants and simulation of the spectrum show that the featureless EPR spectrum is a result of a large number of hyperfine couplings combined with a not very optimal line width (Figure S74 and Table S2). To address the reversible electron transfer between **3** and **16**, we performed the reduction of **16**. The 1:1 reaction of **16** and KC_8 in THF leads to the formation of **3** (Scheme 3). It is to be noted that the formation of **16** was observed through and confirmed with electrochemistry, UV−vis spectroelectrochemistry, EPR spectroelectrochemistry, UV−vis spectroscopy, EPR spectroscopy, and follow-up reactivity. Further efforts toward its isolation as a crystalline material are underway.

Moreover, the absorption spectrum (Figure S58) of the chemically oxidized species exhibits a similar signature with λ_{max} = 611 nm, as we obtained from UV−vis/NIR spectroelectrochemistry. TD-DFT calculations of **16** allow the assignment of this band to the HOMO-β to LUMO-β transition (Table S16 and Figure S101).[18] Notably, the simulated UV−vis spectra of **3** and **16** based on TD-DFT calculations are in good agreement with the corresponding experimental spectra (Figure S102). The absorbance of **16** is red-shifted in comparison with electron-rich alkene-derived radical cations.[22]

In conclusion, we report the systematic synthesis of twisted push−pull alkenes based on geminal cyclicdiamino and difluoroaryl motifs. We addressed their physical properties by a combination of electrochemical, spectroscopic, and computational studies. Moreover, the redox properties of these newly synthesized twisted push−pull alkenes were investigated by (electro)chemical means. The results presented here show that these twisted push−pull alkenes display remarkably large extinction coefficients for the bands in the visible region in their optical spectra. Additionally, the completely substituted push−pull alkenes display a completely reversible redox behavior. Given the modular synthetic methodology established in this study, these results pave the way for several applications of such twisted push−pull alkenes as redox-active materials with unique optical properties.

■ EXPERIMENTAL SECTION

General Considerations. All experiments were carried out under an argon atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox. Hexane, diethyl ether, THF, and toluene were dried with a PS-MD-5 Innovative Technology solvent purification system. Compounds **1**,[17] **2**,[17] and **5**[19] were prepared according to literature procedures. Benzene-d_6 was dried and distilled over potassium under argon. Chloroform-d_1 and acetonitrile-d_3 were dried and distilled over CaH_2 under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself ($^{13}C\{^1H\}$). $^{19}F\{^1H\}$ and ^{19}F NMR spectra were referenced to external tol-CF_3. It was not possible to assign the aryl-C resonances in the $^{13}C\{^1H\}$ NMR spectra due to not well-resolved signals. In the reactions between **5** and fluoroarenes, HF was eliminated. Compound **5** acts as HF scavenger under the formation of the corresponding imidazolium cation along with different possible counteranions such as F^- and HF_2^-. ^1H, ^{19}F, and $^{19}F\{^1H\}$ NMR studies of the crude
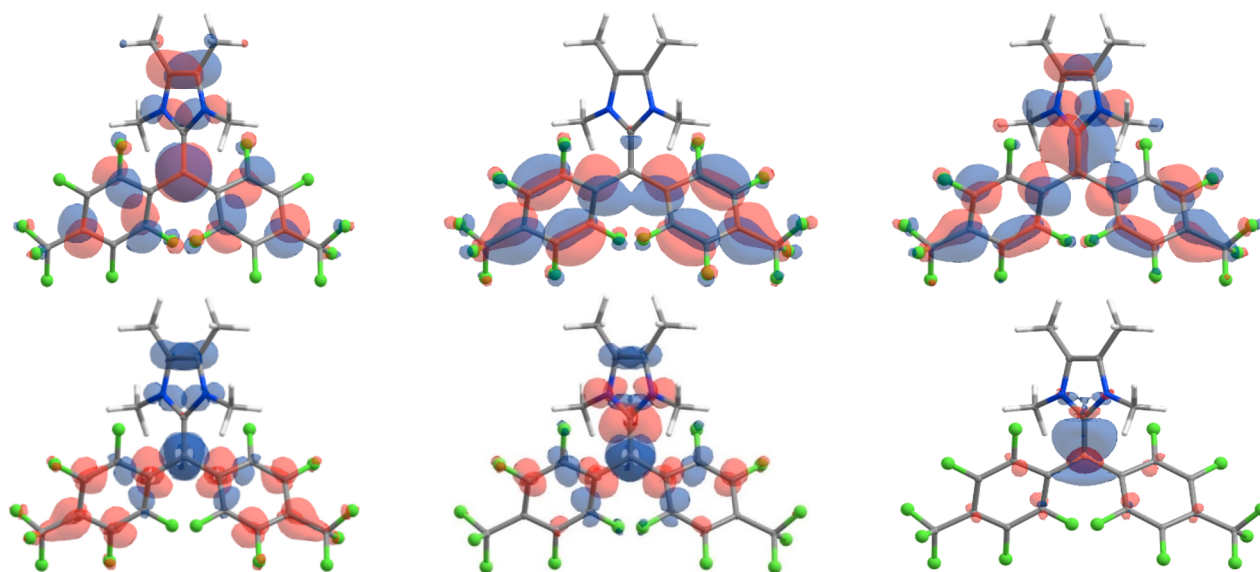
Figure 2. HOMO (top-left), LUMO (top-center), and LUMO+1 (top-right), density difference isosurface plot $\rho(\text{LUMO})-\rho(\text{HOMO})$ (bottom-left) and $\rho(\text{LUMO+1})-\rho(\text{HOMO})$ (bottom-center), and electron density difference between whole molecule and carbene fragments (bottom-right) of **3** (red = positive, blue = negative).
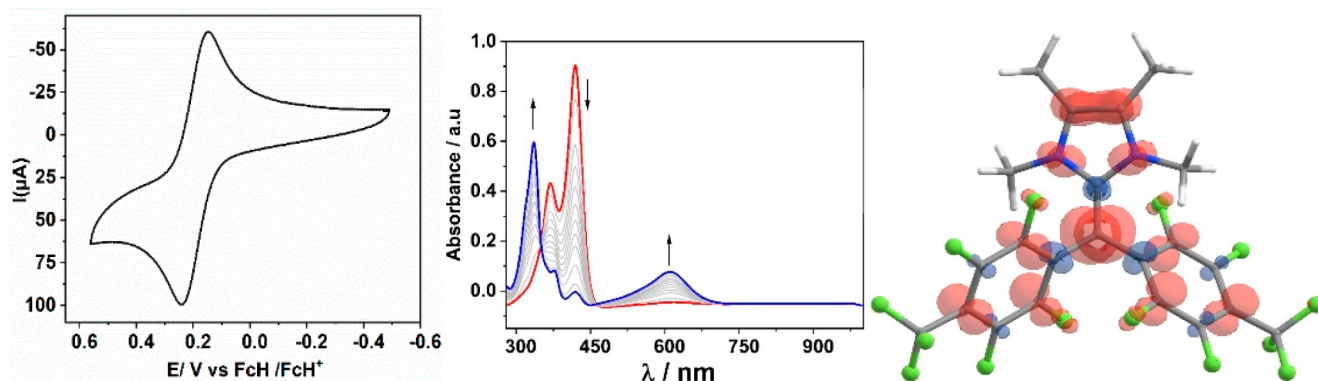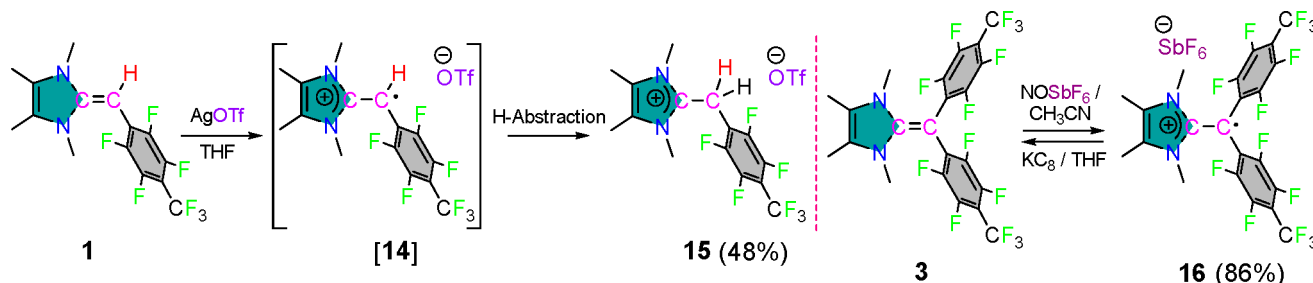

Figure 3. Cyclic voltammogram (left), changes in the UV−vis-NIR spectrum (middle) during spectroelectrochemistry of **3** in THF/0.1 M Bu$_4$NPF$_6$, and spin density plot of radical cation **16** (right) at the PBE/def2-SVP/SMD(THF) level of theory (isovalue of 0.003).

Scheme 3. Chemical Oxidation of 1 and 3

reaction mixture of **5** and C$_6$F$_5$H revealed the formation of 1,2,3-trimethylimidazolium cation with HF$_2$ as counteranion **5H·HF$_2$**. Therefore, we have considered **5H·HF$_2$** as a HF scavenger product in the reaction schemes. However, we cannot rule out the possibility of the formation of 1,2,3-trimethylimidazolium cations with different counteranions. Melting points were determined in closed NMR tubes under an argon atmosphere and are uncorrected. UV−vis spectra were acquired using a Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. Elemental analyses were performed on a PerkinElmer Analyzer 240. A Bruker Daltonics micrOTOF-Q instrument was used for electron spray mass spectrometry. All ESI-

MS data were recorded in a positive operating mode. UV−vis/NIR spectroelectrochemical measurements were recorded on a J&M TIDAS spectrometer instrument by using an optically transparent thin-layer electrochemical (OTTLE) cell.[23] Cyclic voltammetry was carried out in 0.1 M NBu$_4$PF$_6$/CH$_3$CN solutions using a three-electrode configuration (glassy carbon working, Pt wire counter, and Ag reference electrodes) and were performed using a Metrohm Autolab potentiostat. The ferrocene/ferrocenium (FcH/FcH$^+$) couple served as internal reference. EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 benchtop EPR spectrometer equipped with a rectangular TE 102 cavity. The

measurements were carried out in synthetic quarz glass tubes. For EPR spectroelectrochemistry, a three-electrode setup was employed using two Teflon-coated platinum wires (0.005" bare, 0.008" coated) (or a Teflon-coated gold wire: 0.003" bare, 0.0055" coated) as working electrode and counter electrode and a Teflon-coated silver wire (0.005" bare, 0.007" coated) as pseudoreference electrode.

Synthesis of 3. Octafluorotoluene (2.66 g, 11.26 mmol) was added to a toluene solution mixture of **1** (1.0 g, 2.822 mmol, 40 mL toluene) and Et$_3$N (40 mL, 282.98 mmol) at room temperature, and the resulting mixture was heated at 80 °C for 4 days in an oil bath. Upon cooling the reaction mixture, a yellow colored precipitate was observed. Then the reaction mixture was filtered, and the residue was extracted with dry DCM (20 mL). Upon evaporation of the DCM extract, a bright yellow colored solid was obtained as desired product **3**. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **3** at room temperature for 2 days. Yield: 0.810 g, 1.420 mmol (50% with respect to **1**). Mp: >200 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 2.31 (s, 6H, NCH_3), 1.10 (s, 6H, NCCH_3), ppm. ^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$, 298 K): δ = 148.5 (NCN), 122.3 (2C, CCH$_3$), 31.0 (2C, NCH$_3$), 7.9 (2C, CCH$_3$), ppm. ^{19}F{^{1}H} NMR (282.4 MHz, C$_6$D$_6$, 298 K): δ = −54.3 (t, 6F, CF$_3$), −145.0 (m, 4F, *meta*-Ar-F), −146.9 (br, 4F, *ortho*-Ar-F), ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 418 (41000) nm (L mol^{-1}cm^{-1}). Anal. calcd for C$_{22}$H$_{12}$F$_{14}$N$_2$ (570.3296): C, 46.33; H, 2.12; N, 4.91; found C, 46.45; H, 2.19; N, 4.88. ESI-MS: Calcd (*m/z*) ([M + H]$^+$) 571.0855; found 571.0715.

Synthesis of 4. Pentafluoropyridine (3.238 g, 19.15 mmol) was added to a toluene solution of **2** (1.30 g, 4.789 mmol, 80 mL of toluene) and Et$_3$N (26.70 mL, 191.56 mmol) at room temperature, and the resulting mixture was heated at 80 °C for 6 h in an oil bath. Upon cooling the reaction mixture, a yellow colored precipitate was observed. Then the reaction mixture was filtered, and the residue was extracted with dry DCM (20 mL). Upon evaporation of the DCM extract, a bright yellow colored solid was obtained as the desired product **4**. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **4** at room temperature for 2 days. Yield: 1.37 g, 3.139 mmol (65% with respect to **2**). Mp: >200 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 3.27 (s, 6H, NCH_3), 2.24 (s, 6H, NCCH_3), ppm. ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 298 K): δ = 9.2 (2C, CCH$_3$), 32.1 (2C, NCH$_3$), 123.5 (2C, CCH$_3$), 145.7 (NCN) ppm. ^{19}F{^{1}H} NMR (282.4 MHz, CDCl$_3$, 298 K): δ = −96.8 (m, 4F, *ortho*-Ar-F) −150.5 (br, 4F, *meta*-Ar-F), ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 391 (42100) nm (L mol^{-1}cm^{-1}). Anal. calcd for C$_{18}$H$_{13}$F$_8$N$_4$ (436.3092): C, 49.55; H, 2.77; N, 12.84; found C, 49.44; H, 2.79; N, 12.85. ESI-MS: Calcd (*m/z*) ([M + H]$^+$) 437.1012; found 437.1256.

Synthesis of 5H·I. MeI (8.51 g, 60 mmol) was added to a solution of 1,2-dimethylimidazole (3.84 g, 40 mmol) in Et$_2$O (50 mL), and the reaction mixture was stirred at ambient temperature overnight. The white precipitate of **5·HI** was obtained, filtered off, washed with Et$_2$O, and dried *in vacuo*. Yield: 3.6 g, 0.015 mol (38%). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ = 7.61 (s, 2H, C = C), 3.76 (s, 6H, NCH_3), 2.57 (s, 3H, CCH_3) ppm.[19]

Synthesis of 5. KH (168 mg, 4.200 mmol) was added to a solution of **5H·I** (500 mg, 2.100 mmol) in diethyl ether at room temperature. The reaction mixture was stirred for 2 days at room temperature under the protection from light by covering the reaction Schlenk flask with aluminum foil. Then the resulting reaction mixture was filtered, and after evaporating the filtrate, **2** was obtained as a white crystalline solid. Yield: 95 mg, 0.862 mmol (41%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 5.44 (s, 2H, C=C), 2.75 (s, 2H, CCH_2), 2.53 (s, 6H, NCH_3) ppm.[19]

In Situ Preparation of 5. *n*BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.100 mmol) in THF at −78 °C. Then the reaction mixture was slowly warmed to room temperature and stirred for 12 h under the protection from light by covering the reaction Schlenk flask with aluminum foil. During the reaction, the color of the reaction mixture changed to light yellow. After that a ^{1}H NMR spectrum was recorded of the crude reaction mixture showing the formation of compound **5** which was used

immediately for the following reaction, assuming its quantitative formation.

Synthesis of 6. "BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.10 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was again cooled to −78 °C, and C$_6$F$_6$ (195 mg, 1.05 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 24 h. Then THF was evaporated, and the crude product was extracted with toluene to obtain **6** as light-yellow colored solid. Yield: 140 mg (0.507 mmol, 48% with respect to C$_6$F$_6$). Mp: 141−143 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 5.39 (s, 2H, CH=CH), 3.61 (s, 1H, NCCH), 2.33 (s, 6H, NCH_3) ppm. ^{13}C{^{1}H} NMR (75.43 MHz, C$_6$D$_6$, 298 K): δ = 150.4 (NCN), 143.1(1C, Ar-C), 140.1 (1C, Ar-C), 136.9 (1C, Ar-C), 135.3 (1C, Ar-C), 132.1 (1C, Ar-C), 118.5 (1C, Ar-C), 115.6 (CH = CH), 46.1 (NCCH), 33.7 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C$_6$D$_6$, 298 K): δ = −147.8 (m, 2F, *ortho*-Ar-F), −166.7 (m, 2F, *meta*-Ar-F), −174.4 (m, 1F, *para*-Ar-F) ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 369 (39000) nm (L mol^{-1}cm^{-1}). ESI-MS: Calcd (*m/z*) ([M + H]$^+$) 277.0764; found 277.0767.

Synthesis of 7. "BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of (500 mg, 2.100 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and C$_6$F$_5$H (176.5 mg, 1.05 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 24 h. Then THF was evaporated, and the crude product was extracted with toluene to obtain **7** as light-yellow colored solid. Yield: 123 mg (0.476 mmol, 45% with respect to C$_6$F$_5$H). Mp: 135−137 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 6.17−6.05 (m, 1H, C$_6$F$_4$$H$), 5.46 (s, 2H, C$H$=C$H$), 3.83 (s, 1H, NCC$H$), 2.42 (s, 6H, NC$H_3$) ppm. ^{13}C{^{1}H} NMR (75.43 MHz, C$_6$D$_6$, 298 K): δ = 150.6 (NCN), 148.6(Ar-C), 145.4 (Ar-C), 142.8 (Ar-C), 139.7 (Ar-C), 124.2 (Ar-C), 115.9 (CH = CH), 91.7 (t, $^2J_{CF}$ = 24.1 Hz, Ar-C), 48.9 (t, $^3J_{CF}$ = 3.8 Hz, NCCH), 33.7 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C$_6$D$_6$, 298 K): δ = −143.4 (m, 2F, Ar-F), −148.0 (m, 2F, Ar-F) ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 378 (35200) nm (L mol^{-1}cm^{-1}). ESI-MS: Calcd (*m/z*) ([M + H]$^+$) 259.08583; found 259.0843.

Synthesis of 8. "BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.100 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and C$_6$F$_4$H$_2$ (157.5 mg, 1.050 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow and stirring was continued at room temperature for 24 h. Then THF was evaporated, and the crude product was extracted with toluene to obtain **8** as light-yellow colored solid. Yield: 134.7 mg, 0.561 mmol (53% with respect to C$_6$F$_4$H$_2$). Mp: 140−143 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ = 6.55−6.47 (br m, 1H, Ar-H), 6.28−6.18 (m, 1H, Ar-H), 5.51 (s, 2H, CH=CH), 3.87 (s, 1H, NCCH), 2.48 (s, 6H, NCH_3) ppm. ^{13}C{^{1}H} NMR (75.43 MHz, C$_6$D$_6$, 298 K): δ = 155.7 (ddd, $^1J_{CF}$ = 236.1 Hz, $^2J_{CF}$ = 7.5 Hz, $^3J_{CF}$ = 1.5 Hz, *ortho*-Ar-F), 148.5 (ddd, $^1J_{CF}$ = 231.6 Hz, $^2J_{CF}$ = 13.6 Hz, $^3J_{CF}$ = 2.3 Hz, *meta*-Ar-F), 145.4 (td, $^1J_{CF}$ = 238.3 Hz, $^2J_{CF}$ = 10.6 Hz, *para*-Ar-F), 122.8 (dd, $^2J_{CF}$ = 23.4 Hz, $^3J_{CF}$ = 14.3 Hz, *ipso*-Ar-F), 115.7 (CH = CH), 109.3 (ddd, $^2J_{CF}$ = 24.9 Hz, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$ = 3.0 Hz, Ar-C), 103.2 (dd, $^3J_{CF}$ = 20.4 Hz, $^3J_{CF}$ = 20.4 Hz, Ar-C), 48.7 (dd, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$= 3.8 Hz, NCCH), 33.8 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C$_6$D$_6$, 298 K): δ = −121.1 (dd, J_{FF} = 10.2 Hz, J_{FF} = 5.1 Hz, 1F, Ar-F), −140.7 (dd, J_{FF} = 13.5 Hz, J_{FF} = 6.8 Hz, 1F, Ar-F), −144.9 (dd, J_{FF} = 15.2 Hz, J_{FF} = 6.8 Hz, 1F, Ar-F) ppm. UV−vis (THF): λ_{max} = 377 nm. ESI-MS: Calcd (*m/z*) ([M + H]$^+$) 241.0952; found 241.0497.

Synthesis of 10. "BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.100 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and C$_6$F$_6$ (195 mg, 1.05 mmol) was added. After warming up

to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 12 h. After 12 h, the reaction mixture was cooled again to −78 °C, and C_5F_5N (320 mg, 1.89 mmol) was added. Then THF was evaporated, and the crude product was extracted with toluene to obtain **10** as yellow colored solid. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **10** at room temperature for 2 days. Yield: 119.5 mg, 0.281 mmol (27% with respect to C_6F_6). Mp: 150−153 °C. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 5.45 (s, 2H, C*H*=C*H*), 2.19 (s, 6H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, 25 °C): δ = 149.9 (NCN), 118.3 (CH = CH), 34.2 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C_6D_6, 298 K): δ = −97.7 (br, 2F, *ortho*-Ar-*F* of C_5F_4N), −145.1 (m, 2F, *meta*-Ar-*F* of C_6F_5), −150.4 (br, 1F, *meta*-Ar-*F* of C_5F_4N), −156.3 (br, 1F, *meta*-Ar-*F* of C_5F_4N), −163.9 (m, 1F, *para*-Ar-*F* of C_6F_5), −164.6 (m, 2F, *ortho*-Ar-*F* of C_6F_5) ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 374 (63400) nm (L mol^{-1}cm^{-1}). Anal. calcd for $C_{17}H_8F_9N_3$(425.2576): C, 48.01; H, 1.90; N, 9.88; found C, 48.29; H, 2.09; N, 9.94. ESI-MS: Calcd (m/z) ([M + H]$^+$) 426.0652; found 426.0683.

Synthesis of 11. ^{n}BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.10 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and C_6F_5H (176 mg, 1.05 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 12 h. After 12 h, the reaction mixture was cooled again to −78 °C, and C_5F_5N (320 mg, 1.89 mmol) was added. Then THF was evaporated, and the crude product was extracted with toluene to obtain **11** as yellow colored solid. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **11** at room temperature for 3 days. Yield: 180 mg, 0.441 mmol (42%with respect to C_6F_5H). Mp: 147−149 °C. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 6.31−6.19 (m, 1H, Ar-*H*), 5.68 (s, 2H, C*H*=C*H*), 2.36 (s, 6H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, 298 K): δ = 149.8 (NCN), 147.9 (Ar-*C*), 145.7 (Ar-*C*), 144.6 (Ar-*C*), 142.6 (Ar-*C*), 133.6 (Ar-*C*), 121.6 (Ar-*C*), 118.7 (CH = CH), 98.8 (t, $^2J_{CF}$ = 23.4 Hz, Ar-*C*), 49.6 (C$_6$F$_4$N-*C*-C$_6$F$_4$H), 34.2 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C_6D_6, 298 K): δ = −98.6 (br, 2F, *ortho*-Ar-*F* of C_5F_4N), −141.5 (m, 2F, *ortho*-Ar-*F* of C_6F_4H), −145.1 (m, 2F, *meta*-Ar-*F* of C_6F_4H),−150.4 (br, 1F, *meta*-Ar-*F* of C_5F_4N), −156.3 (br, 1F, *meta*-Ar-*F* of C_5F_4N) ppm. UV−vis (THF): λ_{max} = 377 nm. Anal. calcd for $C_{17}H_9F_8N_3$ (407.27): C, 50.14; H, 2.23; N, 10.32; found 50.19; H, 2.27; N, 10.34. ESI-MS: Calcd (m/z) ([M + H]$^+$) 408.0746; found 408.0746.

Synthesis of 12. ^{n}BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of **5H·I** (500 mg, 2.10 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and 1,2,3,4-$C_6F_4H_2$ (157 mg, 1.05 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 12 h. After 12 h, the reaction mixture was cooled again to −78 °C, and C_5F_5N (320 mg, 1.89 mmol) was added. Then THF was evaporated, and the crude product was extracted with toluene to obtain **12** as yellow colored solid. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **12** at room temperature for 2 days. Yield: 154 mg, 0.395 mmol (38% with respect to $C_6F_4H_2$). Mp: 142−145 °C. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 6.40−6.35 (m, 2H, Ar-*H*), 5.72 (s, 2H, C*H*=C*H*), 2.42 (s, 6H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, 298 K): δ = 158.0 (d, $^2J_{CF}$ = 7.5 Hz, Ar-*C*), 154.8 (d, $^2J_{CF}$ = 4.5 Hz, Ar-*C*), 150.2 (NCN), 149.9 (dd, $^2J_{CF}$ = 14.3 Hz, $^2J_{CF}$ = 13.5 Hz, Ar-*C*),149.5 (dd, $^2J_{CF}$ = 12.8 Hz, $^2J_{CF}$ = 14.3 Hz, Ar-*C*), 146.8 (dd, $^2J_{CF}$ = 8.2 Hz, $^2J_{CF}$ = 8.3 Hz, Ar-*C*), 146.2 (dd, $^2J_{CF}$ = 14.3 Hz, $^2J_{CF}$ = 14.3 Hz, Ar-*C*), 143.8Ar-*C*), 133.8 Ar-*C*), 120.3(dd, $^2J_{CF}$ = 20.4 Hz, $^2J_{CF}$ = 13.6 Hz, Ar-*C*), 118.6 (CH = CH), 110.7−109.4 (m, *ipso*-Ar-*C*), 50.0 (C$_5$F$_5$N-*C*-C$_6$F$_3$H$_2$), 34.3 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C_6D_6, 298 K): δ = −97.5 (br, 2F, *ortho*-Ar-*F* of C_5F_4N), −145.01 (dd, J_{FF} = 13.5 Hz, J_{FF} = 13.5 Hz, 1F, *para*-Ar-*F* of $C_6F_3H_2$), −150.6 (br s, 1F, *meta* Ar-*F*

of C_5F_4N), −156.1 (br s, 1F, *meta* Ar-*F* of C_5F_4N), −163.9 (m, 2F, Ar-*F* of $C_6F_3H_2$), −164.7 (m, 2F, Ar-*F* of $C_6F_3H_2$) ppm. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 377(39700) nm (L mol^{-1}cm^{-1}). Anal. calcd for $C_{17}H_{10}F_7N_3$ (389.08): C, 52.45; H, 2.59; N, 10.79; found C, 52.49; H, 2.60, N, 10.83. ESI-MS: Calcd (m/z) ([M + H]$^+$) 390.0841; found 390.0836.

Synthesis of 13. ^{n}BuLi (1.3 mL, 1.6 M in hexane, 2.10 mmol) was added to a solution of 1,2,3-trimethylimidazolium iodide (500 mg, 2.100 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. After 12 h, the reaction mixture was cooled again to −78 °C, and C_5F_5N (320 mg, 1.890 mmol) was added. After warming up to room temperature, the reaction mixture color changed to yellow, and stirring was continued at room temperature for 24 h. Then THF was evaporated, and the crude product was extracted with toluene to obtain **13** as light-yellow colored solid. Crystals suitable for single crystal XRD measurement were obtained by keeping the concentrated benzene solution of **13** at room temperature for 3 days. Yield: 237 mg, 0.580 mmol (31% with respect to C_6F_5N). Mp: 145−147 °C. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 5.45 (s, 2H, C*H*=C*H*), 2.15 (s, 6H, NC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, 298 K): δ = 149.5 (NCN), 146.3 (Ar-*C*), 144.3 (Ar-*C*), 143.1 (Ar-*C*), 141.2 (Ar-*C*), 125.7 (Ar-*C*), 118.5 (CH = CH), 47.8 (C$_5$F$_4$N-*C*- C$_5$F$_4$N), 34.1 (NCH$_3$) ppm. ^{19}F NMR (282.4 MHz, C_6D_6, 298 K): δ = −54.4 (t, J_{FF} = 11.8 Hz, 2F, *ortho* Ar-*F*), −144.7 (br t, 2F, *meta* Ar-*F*) ppm. ESI-MS: Calcd (m/z) ([M + H]$^+$) 409.0699; found 409.0701.

Synthesis of 15. Thirty mL THF was added into the toluene solution of **1** (354 mg, 1 mmol) and AgOTf (257 mg, 1 mmol) at −78 °C, and the mixture was stirred for 1 h. Initially, the color of the reaction mixture was green, and after a few minutes, it changed to colorless. After warming up to room temperature, the reaction mixture was stirred for another hour. Then the reaction mixture was filtered, and upon evaporation of the filtrate, a colorless solid of **15** was obtained. The product crystallized from a concentrated THF solution of it at −30 °C after 4 days. Yield: 242 mg, 0.48 mmol (48%). Mp: 128−130 °C. ^1H NMR (300 MHz, CD$_3$CN, 298 K): δ = 4.49 (s, 2H, NCC*H*$_2$), 3.59 (s, 6H, NC*H*$_3$), 2.21 (s, 6H, NCC*H*$_3$), ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD$_3$CN, 298 K): δ = 139.8 (NCN), 128.1 (2C, NCCH$_3$), 33.0 (2C, NCH$_3$), 19.4 (2C, NCCH$_2$), 8.8 (2C, CCH$_3$), ppm. $^{19}F\{^1H\}$ NMR (282.4 MHz, CD$_3$CN, 298 K): δ = −57.3 (t, 3F, C*F*$_3$), −79.4 (t, 3F, CF$_3$SO$_3^-$), −141.3 (m, 2F, Ar-*F*), −142.1 (m, 2F, Ar-*F*), ppm. Anal. calcd for $C_{16}H_{14}F_{10}N_2O_3S$ (504.34): C, 38.10; H, 2.80; N, 5.55; found C, 38.29; H, 2.83; N, 5.48. ESI-MS: Calcd (m/z) 504.0565; found ([M]$^+$) 504.0528.

Reaction of 3 with AgOTf. Thirty mL THF was added into the toluene solution of **3** (285 mg, 0.5 mmol) and excess AgOTf (386 mg, 1.5 mmol) at −78 °C, and the mixture was stirred for 1 h. The color of the reaction mixture changed to green. The reaction mixture was warmed to room temperature slowly and stirred at room temperature overnight. Then the reaction mixture was filtered, and the formation of **16** as a dark-green colored solid was confirmed by UV−vis/NIR spectroscopy of the filtrate solution. Also, the EPR measurement of the crude reaction mixture indicated the partial formation of **16**.

Synthesis of 16. About 15 mL of CH$_3$CN was added into the Schlenk flask containing **3** (285 mg, 0.5 mmol) and NOSbF$_6$ (133 mg, 0.5 mmol) at 0 °C, and the mixture was stirred for 1 h. The color of the reaction mixture turned dark blue immediately. After warming up to room temperature, the reaction mixture was stirred for another 30 min. Subsequently, all volatiles were removed under vacuum, and **16** was obtained as dark blue solid. Yield: 342 mg, 0.43 mmol (86%). Mp: 170−172 °C. UV−vis (THF): $\lambda_{max}(\varepsilon)$ = 336(4800), 604(700) nm (L mol^{-1}cm^{-1}).

Reduction of 16 with KC$_8$. About 15 mL of THF was added into the Schlenk flask containing freshly prepared **16** (obtained by the reaction of **3** (143 mg, 0.25 mmol) and NOSbF$_6$ (67 mg, 0.25 mmol)) and KC$_8$ (34 mg, 0.25 mmol) at −78 °C. The dark-blue color of the reaction solution turned to yellow, and the reaction mixture was warmed to room temperature slowly. Subsequently, all the volatiles were removed under vacuum, and the resulting residue was extracted using 15 mL DCM. Evaporation of all volatiles yields compound **3**.

The product was confirmed by ^{1}H, ^{19}F{^{1}H} NMR as well as UV−vis spectroscopy. Yield: 113 mg, 0.2 mmol (79%).

NMR-Scale Reaction of 5 and C_6F_5H. Compound **5** (5.7 mg, 0.052 mmol) in C_6D_6 was mixed with pentafluoro benzene (4.34 mg, 0.026 mmol) in C_6D_6 and transferred to a NMR tube inside a glovebox. The reaction mixture color changed to yellowish-orange immediately after mixing, and a white precipitate was observed at the bottom of the NMR tube. After measuring the NMR spectrum, C_6D_6 was evaporated from the NMR tube, and DMSO-d_6, in which the white precipitate also dissolves, was added to the same NMR tube to check the NMR again.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01201.

> Experimental Section, plots of NMR spectra for new compounds, and complete details of computational calculations (PDF)

> FAIR data, including the primary NMR FID files, for compounds **3**, **4**, **6−8**, **10−13**, and **15** (ZIP)

Accession Codes

CCDC 2062687−2062691, 2062693−2062694, and 2062696−2062698 contain 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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Notes

The authors declare no competing financial interest.

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