Synthesis and structural, spectroscopic, and electrochemical characterization of benzo[c]quinolizinium and its 5-aza-, 6-aza, and 5,6-diaza analogues

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1. Introduction

The benzo[c]quinolizinium (1a) and several of its derivatives have been known for over four decades. The cation has been intensely investigated as a possible pharmacophore for the treatment of cystic fibrosis and diseases related to smooth muscle cell constriction, such as arterial hypertension and asthma. It has also been used as a structural element of highly solvatochromic dyes and columnar liquid crystals. Recently, a diaza analogue of 1a, triazinium 1b, and an amino derivative of the mono-aza analogue 1c were described in the literature. It was demonstrated that 1b is highly cytotoxic to cisplatin-resistant tumor cell lines, and undergoes a reversible 1e reduction process. For these reasons cations, such as 1a and 1b are attractive for development of pharmacologically active compounds and molecular materials with multi-redox properties, tunable electronic absorption spectra, and self-organization. Therefore, we focused on a series of cations 1a–d, in which the CH groups in the bridging 5,6 positions of 1a are systematically replaced with nitrogen atoms, and investigated the effect of the bridge modification on the molecular and electronic properties of the cations.

The preparation of cation 1a involves high temperature intramolecular cyclization of chlorostilbazole 2a formally by intramolecular nucleophilic substitution reaction. In contrast, the preparation of 1b and 1c involves 6π-electrocyclization as the key step followed by oxidative rearomatization. Thus, the quinolizinium cation 1b was obtained at ambient temperature in Au(III)-catalyzed light-induced electrocyclization of phenylazopyridine. Later, the Lewis acid was replaced with a Brønsted acid in preparation of 1b and several of its derivatives. The proposed mechanism involves sunlight trans-to-cis isomerization, acid-induced tautomerization, electrocyclization, and oxidative rearomatization. The reaction requires concentrated mineral acid and long exposures to light, which limits its practicality. The formation of 9-amino derivative of 1c is a Cu(II)-mediated process in which
a radical cation formed by intramolecular one-electron transfer to the coordinated metal undergoes electrocyclization. Cation 1c was not formed under Brønsted acid conditions described for 1b.9

We previously demonstrated that the azo group activates halogen toward nucleophilic aromatic substitution.10 Particularly reactive was fluoride, which undergoes substitution with the thiolate at ambient temperature. Therefore, we considered fluorophenylazopyridine 3b as a suitable substrate for a facile intramolecular cyclization to cation 1b in which the fluoride is replaced by pyridine. Such a reaction could offer practical access to functionalized derivatives of 1b under mild and pH neutral conditions, and could be extended to the preparation of remaining three cations 1a, 1c, and 1d.

Here we describe the preparation of cations 1a–d by Ca2+-assisted intramolecular cyclization of fluorides 3. The mechanism of this transformation is investigated with DFT computational methods. The effect of substitution of N for a CH in the cations on their molecular and electronic structures is probed using XRD, spectroscopic and electrochemical methods, and the experimental work is augmented with DFT and MP2 level calculations.

2. Results and discussion

2.1. Synthesis

Benzyl[c]-quinolinium (1a) was prepared according to a modified literature procedure11 by thermally induced cyclization of chloro derivative 2a in benzonitrile at 160 °C in the presence of catalytic amounts of I2, which permitted trans–cis equilibration. The product was obtained in 54% yield as the perchlorate salt 1a[ClO4] (Scheme 1).

![Scheme 1](image)

Similar thermal reaction of chloro diazene 2b or fluoro diazene 3b in benzonitrile in the absence of I2, or in warm MeCN using sunlight or strong Pyrex-filtered halogen lamp light to effect trans–cis isomerization did not lead to the formation of the triazinium ion 1b. No reaction of 2b was observed either in refluxing MeCN nor in hot PhCN. Similar reactions of fluoro derivative 3b were equally fruitless even though the fluoride usually is a significantly more mobile leaving group than chloride.

To activate the halogen toward displacement and intramolecular cyclization, we used an equimolar amount of AgOTs as an auxiliary role of Ca2+-assisted cyclization proved to be successful also for the preparation of salts 1c and 1d from appropriate fluorides. Thus, thermal cyclization of 3c and 3d in hot PhCN in the presence of solid Ca(OTs)2 gave complete conversion of the fluorides and formation of the cations as the main identifiable products. The reaction mixture contained substantial amounts of intractable products presumably formed by decomposition of the azomethine group labile under the reaction conditions. Cations 1c and 1d were isolated as perchlorates in 12% and 18% yield, respectively. The attempted cyclization of 3d in (i) hot PhCN in the absence of Ca(OTs)2, or (ii) in MeCN with Ca(OTs)2 and irradiated with a halogen lamp gave only the starting material.

The auxiliary role of Ca2+ in the successful preparation of cations 1b–d prompted us to investigate cyclization reactions of fluorostilbazole 3a in the presence of Ca(OTs)2. Under reaction conditions developed for the preparation of 1b (MeCN, Ca(OTs)2), halogen lamp, 10% water) fluoride 3a showed the formation of cation 1a as the sole product. The reaction time for the complete transformation of 3a was longer than that for cyclization of 3b, presumably due to lower absorption in the visible range of the spectrum. The same reaction of fluoride 3a in the absence of Ca(OTs)2 showed no product formation.

Preparation of stilbazoles 2a1 and 3a11 followed literature procedures and involved acetic anhydride-assisted condensation of appropriate halobenzaldehyde and 2-picoline (Scheme 2). Halodiazenes 2b and 3b were prepared by condensation of 2-chloronitrosobenzene12 (4) and 2-fluoronitrosobenzene13 (5), respectively, with 2-aminopyridine under basic conditions, as described for the chloro derivative 2b.12 Schiff bases 3c and 3d were prepared using standard acid-catalyzed condensation of appropriate aldehyde and amine (Scheme 2).

![Scheme 2](image)

2.2. Molecular and crystal structures

Crystals of 1a[ClO4] and 1d[ClO4] were grown by slow evaporation of MeCN solutions. Solid–state structures for both compounds (Fig. 1) were determined by X-ray diffraction14 and their selected bond lengths are shown in Table 1.

The two structures are essentially planar. The C(1)–N(11)–C(10a)–C(10) angle in cation 1a is 2.1(2)° in molecule A and 5.6(2)° in molecule B. In the structure 1d, the deviation from planarity is similar [2.4(3)°]. The cations are characterized by a short C(10a)–N(11) distance of 1.425(2) Å in both structures. This distance is comparable to that reported for 9-amino derivative of 1c (1.424 (3) Å),9 longer than that observed in 1b (1.401(5) Å),8 and significantly shorter than the analogous Ph–N distance in N-phenylpyridinium15 (1.45 Å). The short N–Ph distance is a consequence of the decreasing distance between the bridging atoms X(6)–Y(5) from 1.342(3) Å in 1a through 1.297(3) Å in 1d to the shortest, 1.275 (6) Å in 1b. With the falling X–Y distance, the C(1)···C(10) bay in the cations opens up by about 0.06 Å in 1b in comparison to 1a (Table 1). These results are well reproduced by computational methods (vide infra).
Fig. 1. Thermal ellipsoid diagram for 1a(ClO₄) (molecule A) and 1d(ClO₄) drawn at 50% probability. For clarity the anion is omitted. Interatomic distances are listed in Table 1. Atom numbering scheme according to the chemical structure.

Table 1

<table>
<thead>
<tr>
<th>Distances/A</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
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<tbody>
<tr>
<td>C(4)–C(4a)</td>
<td>1.402(2)</td>
<td>1.408</td>
<td>1.379(6)</td>
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<tr>
<td>C(4a)–Y(5)</td>
<td>1.426(2)</td>
<td>1.418</td>
<td>1.387(5)</td>
<td>1.432</td>
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<tr>
<td>Y(5)–X(6)</td>
<td>1.342(3)</td>
<td>1.353</td>
<td>1.275(6)</td>
<td>1.273</td>
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<tr>
<td>X(6)–C(6a)</td>
<td>1.429(2)</td>
<td>1.423</td>
<td>1.387(3)</td>
<td>1.377</td>
</tr>
<tr>
<td>C(10a)–C(6a)</td>
<td>1.408(2)</td>
<td>1.415</td>
<td>1.401(5)</td>
<td>1.411</td>
</tr>
<tr>
<td>C(10a)–N(11)</td>
<td>1.425(2)</td>
<td>1.426</td>
<td>1.401(5)</td>
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<td>C(1)–N(11)</td>
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<td>C(4a)–N(11)</td>
<td>1.384(2)</td>
<td>1.385</td>
<td>1.385(4)</td>
<td>1.377</td>
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<tr>
<td>C(1)–C(10)</td>
<td>2.863</td>
<td>2.874</td>
<td>2.91</td>
<td>2.936</td>
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</table>

a Distances for molecule A. See Ref. 14.

b B3LYP/6-311G(2d,p) geometry optimization at C₃ point group symmetry. Numbering system according to the chemical structure.

c CF₃SO₃⁺ salt, Ref. 8.

d X–Y=–CH.

e X–Y=–N.

The unit cell of 1a(ClO₄) contains two distinct cations and two anions per asymmetric unit. These cations and anions are arranged about an approximate non-crystallographic local center at approximately (0.22, 0.73, 0.30). This serves only to increase the contents of the asymmetric unit to Z=2. Both cations are disordered leading to exchange of the C(10a) and N(11) positions, each in different ratios: 0.95:0.05 in cation 1a and C(4a)–N(5) in 1d. With these two results excluded from analysis the error decreases to 0.002:0.004 A (absolute mean 0.003:0.002 A). The same analysis for cation 1b gave higher mean error 0.005:0.010 A (absolute mean 0.010:0.005 A) for all bonds, which is consistent with significant experimental uncertainty of ±0.006 A (Table 1).

On the basis of geometry optimization results, the B3LYP/6-311G (2d,p) method was used in subsequent mechanistic studies (Table 2), assignment of NMR chemical shifts (Table 3), analysis of electronic absorption spectra (Table 4), and investigation of reduction for cations 1 (Table 5).

Table 2

<table>
<thead>
<tr>
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<tr>
<td>a</td>
<td>8.3</td>
<td>&gt;45</td>
<td>&gt;35</td>
<td>31.4</td>
<td>&gt;-23.7</td>
</tr>
<tr>
<td>b</td>
<td>10.6</td>
<td>&gt;45</td>
<td>&gt;35</td>
<td>24.9</td>
<td>16.3</td>
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<tr>
<td>c</td>
<td>15.8</td>
<td>40.2</td>
<td>24.5</td>
<td>29.9</td>
<td>17.8</td>
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<td>d</td>
<td>17.2</td>
<td>35.3</td>
<td>17.7</td>
<td>22.4</td>
<td>5.7</td>
</tr>
<tr>
<td>e</td>
<td>6.2</td>
<td>20.0</td>
<td>13.7</td>
<td>35.0</td>
<td>&gt;-15.5</td>
</tr>
<tr>
<td>f</td>
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<td>19.9</td>
<td>11.6</td>
<td>27.3</td>
<td>17.7</td>
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<td>g</td>
<td>10.2</td>
<td>23.6</td>
<td>13.4</td>
<td>32.0</td>
<td>&gt;-20.6</td>
</tr>
<tr>
<td>h</td>
<td>11.0</td>
<td>18.8</td>
<td>7.8</td>
<td>24.2</td>
<td>12.8</td>
</tr>
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</table>

a B3LYP/6-311G-Cl(2d,p)//B3LYP/6-311G(2d,p) level calculations in MeCN di-electric medium.
b ΔG°₂₉₈ = G°₂₉₈(Z)–G°₂₉₈(E) for the two global minima conformers Z and E.
c ΔG°₂₉₈ for conversion of the global minimum conformer of E to Z.
d ΔG°₂₉₈ for conversion of the global minimum conformer of Z to E.

e Upper line ΔG°₂₉₈ = G°₂₉₈(Z)–G°₂₉₈(1-Cl). Cl⁻ coordinated to 1. Lower line, ΔG°₂₉₈ = G°₂₉₈(Z)–G°₂₉₈(6).

2.4. Mechanistic analysis

The mechanism for the formation of cations 1 from halo pyridine derivatives 2 and 3 involves E to Z isomerization and subsequent intramolecular attack of the pyridine N atom on the C(Hal) atom of the halophenyl ring. In principle, the cation 1 can be formed directly from the cis isomer or through non- aromatic cyclic product 6 (Scheme 3), which undergoes rearrangement upon departure of the halide. The success of the reaction depends on (i) the access to the Z isomer, and (ii) relative height of the barriers to cyclization versus back isomerization to the E isomer. To assess these factors, transformations of chloro and fluoro pyridine derivatives 2 and 3 to the cations 1 were investigated at the B3LYP/6-311G-Cl(2d,p)//B3LYP/6-311G(2d,p) level of theory in MeCN dielectric medium without participation of metal ions.

For a better understanding of properties of cations 1, we conducted quantum-mechanical calculations. To select a suitable computational protocol, equilibrium geometries of 1 were obtained with B3LYP and MP2(fc) methods and several bases sets, and results were compared to experimental solid-state structures of 1a, 1b, and 1d.

In general, all four cations converged to planar structures using the DFT method with four basis sets: 6-31G(d,p), 6-311G(2d,p), 6-311+G(2d,p), and cc-pVDZ, and the MP2 level of theory with 6-31G(d,p), 6-311G(2d,p), and cc-pVDZ basis sets. The only exception is cation 1a, which is predicted by the MP2/6-31G(d,p) method to be twisted with the C(1)–N(11)–C(10a)–C(10) torsional angle of 6.7°.

Detailed comparison of theoretical and experimental bond lengths demonstrated that the DFT method performed better than the MP2 method in geometry optimization of cations 1. In both methods the cc-pVDZ basis set performed least satisfactory giving the largest mean error. Results closest to the experimental interatomic distances were obtained with the B3LYP/6-311G(2d,p) method, and selected data are shown in Table 1. For cations 1a and 1d the mean difference was 0.001±0.005 Å (absolute mean 0.004±0.005 Å), which is close to the typical experimental uncertainty of ±0.003 Å. The largest difference between the calculated and experimental distances was found for the C(5)–C(6) bond in 1a and C(4a)–N(5) in 1d. With these two results excluded from analysis the error decreases to 0.002:0.004 Å (absolute mean 0.003:0.002 Å). The same analysis for cation 1b gave higher mean error 0.005:0.010 Å (absolute mean 0.010:0.005 Å) for all bonds, which is consistent with significant experimental uncertainty of ±0.006 Å (Table 1).
Assignment of experimental and calculated $^{13}$C and $^1$H NMR chemical shifts for 1

Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental a</th>
<th>Theoretical b</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Absorption $\lambda_{max}$/nm</td>
<td>Emission $\lambda_{max}$(nm)</td>
</tr>
<tr>
<td>1a(ClO$_4$)</td>
<td>363, 257 d</td>
<td>394 (347) e</td>
</tr>
<tr>
<td>1b(ClO$_4$)</td>
<td>359, 259 f</td>
<td>340 (0.23), 268 (0.51)</td>
</tr>
<tr>
<td>1c(ClO$_4$)</td>
<td>363, 242 g</td>
<td>347 (0.18), 286 (0.13), 268 (0.34)</td>
</tr>
<tr>
<td>1d(ClO$_4$)</td>
<td>349, 250 h</td>
<td>320 (0.15), 273 (0.19), 261 (0.45)</td>
</tr>
</tbody>
</table>

Initial computational effort concentrated on identifying global conformational minima for trans and cis isomers of 2 and 3 by comparison of SCF energies obtained in MeCN medium. Results for 2-E and 3-E showed that the most stable conformation for a, and d in MeCN is of type E-IV, while conformer E-III is the most stable form of 2c-E and 3c-E (Fig. 2). For the cis isomer the most stable conformers in MeCN are of type Z-II (2c and 3c), Z-III (2a, 2b, 3a), Z-IV (2b, 3b), and E-IV (2c, 3c).

Table 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental a</th>
<th>Calculated b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{1/2}^{\text{red}}$ ($+/−$/V)</td>
<td>$E_{1/2}^{\text{red}}$ ($+/−$/V)</td>
</tr>
<tr>
<td>1a</td>
<td>$d$</td>
<td>$−0.91$</td>
</tr>
<tr>
<td>1b</td>
<td>$−0.21$ c</td>
<td>$−0.24$</td>
</tr>
<tr>
<td>1c</td>
<td>$d$</td>
<td>$−0.66$</td>
</tr>
<tr>
<td>1d</td>
<td>$d$</td>
<td>$−0.67$</td>
</tr>
</tbody>
</table>

a Recorded in MeCN.

b Obtained with TD B3LYP/6-311+G(2d,p)/B3LYP/6-311G(2d,p) method in MeCN dielectric medium.

c Second cathodic wave at $E_{2}^{\text{red}}$ $= −0.89$ V.

d Similar spectral characteristic reported in Ref. 8.

e Second cathodic wave at $E_{2}^{\text{red}}$ $= −0.26$ V and $E_{2}^{\text{red}}$ $= −1.10$ V (0.1 M [Et$_4$N]$^+$ [ClO$_4$]$^−$ in MeCN versus SCE) Ref. 8.

f Not reported.

g Cathodic peak potential.

h Irreversible process.
transformation of different in gas phase. Selected optimized structures involved in the interactions (free energy of activation calculated for the global minima of each isomer. For simplicity, the Z
and 3b.

and Z-IV (2d, 3d). This preference for conformational minimum is different in gas phase. Selected optimized structures involved in the transformation of 2b and 3b to 1b are shown in Fig. 3.

![Scheme 3.](image)

Results shown in Table 2 demonstrate that cis and trans forms interconvert thermally only for azomethine derivatives c and d. The barrier $\Delta G_{298}^a$ calculated for 3c and 3d is about 19 kcal/mol for the $E \rightarrow Z$ isomerization and is less than 12 kcal/mol for the reverse process. The analogous barriers to isomerization for the chloro derivatives 2c and 2d are higher by up to 5.6 kcal/mol calculated for 2d-Z $\rightarrow$ 2d-E. For all four compounds the concentration of the cis isomers at the equilibrium is small, less than 0.1%. The calculated low activation energy for $Z \rightarrow E$ conversion is consistent with that experimentally established for isomerization of benzylideneaniline ($E_a=17.3$ kcal/mol in MeCN$^{21}$) and pyridyl phenyl azomethine ($E_a=13.1-14.3$ kcal/mol) $^{22}$ which are the closest experimental models of c and d.

![Fig. 2. Conformers of E and Z isomers.](image)

![Fig. 3. B3LYP/6-311G(2d,p) optimized geometries for selected structures involved in cyclization 3b to 6b and 1-Cl formed from 2-Z-I.](image)

All four conformers of 3a-E, and also 2a-E-I, 2b-E-III, 2d-E-IV, and 3b-E-III converged to planar structures as confirmed by frequency calculations for $C_s$-constrained molecules. Surprisingly, fully optimized structure of one conformer of cis stilbazole, 3a-Z-IV, also has the $C_s$ symmetry, apparently due to favorable C-H⋯N interactions ($d=2.102$ Å).

The energy difference between the cis and trans forms was calculated for the global minima of each isomer. For simplicity, the free energy of activation $\Delta G_{298}^a$ for the cis $\rightarrow$ trans isomerization was calculated for 2-Z and 3-Z global minimum conformers in MeCN (Table 2). The transition state structure for isomerization of stilbazoles 2a and 3a could not be located using standard methods, but it was estimated at >40 kcal/mol. Analysis of the TS structures demonstrates that the cis $\rightarrow$ trans isomerization for the nitrogen-containing derivatives 2b-d and 3b-d proceeds through inversion at the N atom, which is consistent with previous computational results for phenylazopyridine$^{17}$ and N-benzylideneaniline.$^{18-20}$

Results for azenes b indicate that the cis isomers 2b-Z and 3b-Z cannot be thermally populated due to high $E \rightarrow Z$ isomerization barrier of $\Delta G_{298}^a >35$ kcal/mol, but both cis forms can thermally isomerize to the more stable trans isomers 2b-E and 3b-E. The calculated height of the barrier of $\Delta G_{298}^a=24.5$ kcal/mol (Table 2) in MeCN for the $2b-Z \rightarrow 2b-E$ process is in good agreement with the experimental activation energy for phenylazopyridine ($\Delta G_{298}^a=25.5$ kcal/mol, $\Delta S^f=-14.5$ cal/mol).$^{23}$ The same barrier for the fluoro analogue is lower by nearly 7 kcal/mol. Finally, high barriers to isomerization estimated for stilbazoles 2a and 3a and established experimentally for Z-stilbene ($E_a=42.8$ kcal/mol)$^{24}$ prevent thermal isomerization of either a-Z or a-E.
The intramolecular cyclization of halophenyl derivatives occurs form the 2-Z-1 and 3-Z-1 conformers and proceeds by an apparent 6π-electrocyclic process. The former yields nearly planar conjugated with the chloride anion weakly coordinated to the C1 position (d(Cl/C1) = 2.3 Å – 2.5 Å) in 1-Cl, while the cyclization of the later, fluorophenyl derivatives 3-Z-1, leads to non-aromatic product 6. The free energy of activation ΔG°298 required for the cyclization of chlorophenyls 2-Z-1 is in a range of about 30 kcal/mol (2b-Z) – 35 kcal/mol (2e-Z) and the reaction is exergonic by 18–24 kcal/mol. In contrast, cyclization of fluorophenyl 2-Z-1 to the non-aromatic 6 has lower activation barrier by 6–8 kcal/mol than that for the chloro analogues, but the process is significantly endergonic by 6–18 kcal/mol and thermally reversible. The least unfavorable cyclization is calculated for 3b-Z (ΔG°298 = 5.7 kcal/mol), while the formation of 6a and 6c is most endergonic and requires additional 10.6 and 12 kcal/mol, respectively. This order of energies is consistent with that of the C–F distance in 6; the shortest is found in 6b (d(CF) = 1.446 Å) and the longest in 6a (d(CF) = 1.471 Å).

The difference in behavior of the two halides presumably results from much better solvation of the chloride in organic media than that of F–. As a consequence, the progress of the reaction of Z-1 is ‘frozen’ at the stage of 6, while reaction of chlorophenyl derivatives 2 progresses to the formation of chlorides 1.

Computational data are consistent with experimental results, which demonstrate that only 1a-Cl can be obtained thermally from 2a in a metal-ion-free process. The cyclization reaction is exothermic and is faster than isomerization of 2a-Z to 2a-E. The later is also true for 3a-Z but the reaction is significantly endothermic and the product is not formed. For the remaining chlorophenyl and fluorophenyl derivatives, the cis-to-trans isomerization reaction is faster than cyclization and no product formation is observed. In addition, cyclization reactions of fluorophenyl derivatives 2 are endothermic.

Experimental results of successful formation of cations 1 upon addition of Ag+ to chlorides 2 and Ca2+ to fluorides 3 suggest that the ions coordinate to the halogens and significantly alter the potential energy surface for the cyclization and presumably for isomerization processes. The activation energy for cyclization of the coordinated halide becomes lower than that for isomerization, and consequently formation of 1 is faster for halides 2 and 3.

The formation of the requisite cis isomers of the Schiff bases, 3c-Z and 3d-Z, is accomplished thermally, which, in accordance with the computational results, shows that the two isomers are in thermal equilibrium. The generation of 2b-Z and 3b-Z isomers in concentrations sufficient for efficient formation cyclization requires intense light, since both thermally convert to 2b-E and 3b-E and neither can be transformed thermally back to the cis forms. Finally, the preparation of 1a requires Li2 catalysis at high temperature to equilibrate the a-E and a-Z forms. Without the catalyst the requisite 2a-Z and 3a-Z isomers are thermally inaccessible from the trans forms. However, both can be obtained photochemically.

### 2.5. NMR chemical shift assignment

Structural assignment of 1H and 13C signals in cations 1 was accomplished by taking advantage of peak multiplicity, by analysis of 2-D (1H-1H-1H) and DEPT-90 NMR spectra recorded in DMSO-d6 solutions, and by using DFT-calculated 13C chemical shifts in the solvent's dielectric medium. In all four cations the assignment started from the highly deshielded proton appearing as a doublet at the C(1) carbon atom adjacent to the pyridinium nitrogen atom. Assignment for the benzene ring was helped by DFT results showing that the C(10) carbon atom is the most shielded in the molecule and appears at about 115 ppm in the spectrum. The quaternary carbon atoms, C(4a), C(5a), and C(10a), were identified by DEPT-90 technique and assigned according to the DFT results. Computational results also helped with the assignment of the resonance to the C(5) and C(6) nuclei in 1a. Assigned experimental and calculated chemical shifts are shown in Table 3.

A comparison of the computed chemical shifts with experimental values in Table 3 demonstrates a close agreement for the 13C nuclei. The mean difference between experimental and theoretical values is −0.6 ± 2.0 ppm (absolute 1.7 ± 1.1 ppm). The largest differences Δδ between experiment and theory are observed for the C(1) carbon in all cations (Δδ > 3 ppm), and for C(7) in 1b (Δδ = 4.1 ppm). 1H NMR chemical shifts are less accurately predicted and larger differences Δδ are observed especially for the C(1)–H nuclei for which Δδ values are in a range of 0.59–0.74 ppm. The mean deviation for all 1H NMR datapoints is 0.23 ± 0.21 ppm (absolute 0.25 ± 0.19 ppm), while without the C(1)–H nuclei it improves to 0.18 ± 0.16 ppm (absolute 0.20 ± 0.13 ppm).

### 2.6. Electronic spectra

Experimental absorption and emission spectra for salts 1a [ClO4]- - 1d [ClO4] were recorded in MeCN and selected data are presented in Fig. 4 and Table 4.

All four cations exhibit moderate absorption in the region of about 340 nm and significantly stronger absorption at about 260 nm. The low energy absorption exhibits vibronic structure with the splitting of about 1330 cm⁻¹ for 1a and 1d and about 950 cm⁻¹ for 1b. Table 4 lists the (0,0) transitions for the cations. Two of the four cations fluoresce at ambient temperature. Thus, solutions of 1a [ClO4] and 1c [ClO4] in MeCN exhibit a moderate fluorescence with a maximum at 394 nm (λex = 347 nm). Despite efforts, fluorescence that was reported for 1b at 535 nm was not observed even for a wide range of excitation wavelengths.

To shed more light on the nature and origin of the observed transitions, we conducted TD DFT calculation in MeCN dielectric medium. Calculations demonstrated that there are three main π-π* excitations of moderate intensity in a range of about 340 nm, 270 nm, and 250 nm. This is consistent with experimental spectra assuming that the two high energy excitations are merged into a broad absorption band observed e.g., at 257 nm for 1a (Fig. 1). The lowest energy excitation involves transition mainly from the HOMO to the LUMO, both orbitals delocalized over the entire molecule as shown for 1d in Fig. 5. The higher energy excitation involves HOMO+1-LUMO+1 and HOMO+2-LUMO as the main transitions in 1a and 1d. The excitation in 1b at 286 nm involves HOMO-2-LUMO, since HOMO-2 is A1 symmetry orbital and contains the lone pairs. In cation 1c, this medium energy excitation is apparently split into two bands: one at 329 nm involving the HOMO-1→LUMO transition, and the second at 286 nm originating from the HOMO-→LUMO+1 transition. The next highest π-π* excitation at about
250 nm involves the HOMO-1→LUMO+1 transition for 1a, 1c, and 1d, and HOMO-2→LUMO+1 transition for 1b.

The non-bonding electrons of the nitrogen atoms constitute the HOMO-1 in 1b and HOMO-2 in 1c and 1d (Fig. 5). The forbidden n−π* excitation for 1b is predicted at 429 nm and 310 nm, which is consistent with the observed low intensity absorption band tailing to about 450 nm. The n−π* excitations in 1c and 1d are calculated at 311 nm and 288 nm, respectively, and presumably are obscured by the more intense π−π* bands.

2.7. Reduction of cations 1

One electron reduction of cations 1 leads to π-delocalized heteroaromatic radicals 1* (Scheme 4), which are analogues of pyridyl radicals obtained from pyridinium salts.26 Further reduction of the radicals results in anions 1− (Scheme 4). The formation and stability of these species was studied electrochemically and computationally.

A comparison of computational results for the two isomeric species c and d demonstrates that cation 1d is more thermodynamically stable than 1c by 2.9 kcal/mol, while radical 1c is more stable than 1d by 3.4 kcal/mol in MeCN dielectric medium. The former reflects better stabilization of the positive charge by the C(6) carbon atom delocalized from the pyridinium, while the unpaired electron in 1* is better accommodated by the nitrogen atom in the same position (Scheme 4).

3. Conclusions

Results demonstrate that cations 1a–d are accessible from fluoro derivatives 3 by Ca2+-promoted cyclization. The process involves trans-to-cis isomerization of 3 followed by Ca2+-assisted electrocyclization to cation 1. In the absence of Ca2+ ions cyclization of 3-Z leads to an endothermic intermediate 6 through a barrier higher (for b–d) than that for isomerization to 3-E, according to DFT calculations. The reaction conditions, such as the use of heat or light to populate the less thermodynamically stable cis isomer 3-Z necessary for the cyclization, are consistent with the calculated barriers for isomerization.

A comparison of the experimental and theoretical molecular structures for three of the four cations demonstrated that the B3LYP method with the 6-311G(2d,p) basis set particularly well reproduces the experimental geometry and provides a tool for assessing formation and properties of this class of organic cations. The DFT method was used successfully to assign NMR chemical shifts, analysis of electronic absorption spectra, and study of reduction of cations 1 to radicals 1*. In general, experimental results were well reproduced by DFT calculations.

Spectroscopic analysis demonstrated that all four cations exhibit two main regions of absorption at about 350 nm and 260 nm related to π−π* excitation. Among the cations only 1a and 1c exhibit fluorescence with a maximum at about 394 nm. Fluorescence reported for 1b was not confirmed.

Electrochemical analysis revealed that only 1b exhibits irreversible (+/−) reduction with half potential of −0.21 V, while the remaining three cations undergo irreversible reduction at more...
cathodic potentials. Substitution at high spin density site C(3) with an electron-withdrawing group may lead to stabilization of the radicals and reversible reduction of the cations.

The sequential introduction of the nitrogen atoms to the X(6)–Y (5) bridge of 1a has a significant effect on electrochemical behavior of the cation, but much less on their photophysical properties. Interestingly, the position of the nitrogen atom in the bridge has an effect on photoluminescence properties, relative stability, and the energy profile for the formation of the two isomeric cations from 3c and 3d. Overall, the results demonstrate a potentially general method for the preparation of heterocyclic cations, analogues of 1a–d, and derivatives that are suitable for incorporation into more complex molecular architectures. The developed computational protocol permits the design of new cations and evaluation of their formation and properties.

4. Computational details

Quantum-mechanical calculations were carried out with the B3LYP27,28 and MP2/6-31G(d,p) methods with 6-311G(d,p), 6-311G(2d,p), 6-31+G(2d,p), and cc-pVDZ basis set using the Gaussian 03 and Gaussian 09 packages.30,31 Geometry optimizations were undertaken using appropriate symmetry constraints and tight convergence limits. Vibrational frequencies were used to characterize the nature of the stationary points achieved with the DFT method, and to obtain thermodynamic parameters. Zero-point energy (ZPE) corrections were scaled by 0.9806.32 Geometry optimizations at the MP2 level were initially performed without symmetry constraints, and the resulting planar structures were reoptimized with the imposed C3 symmetry.

Electronic excitation energies for cations 1 were obtained at the B3LYP/6-311+G(2d,p)/B3LYP/6-311G(2d,p) level using the time-dependent DFT calculations33 supplied in the Gaussian package. Solvent effect on electronic excitations was included using the PCM model34 [keywords: SCRF(PC solvent=CH3CN)].

NMR shielding tensors for 1 were obtained at the B3LYP/6-311+G(2d,p)/B3LYP/6-311G(2d,p) level using the GIAO method35 and solvent effects were included using keywords: SCRF(PC solvent=DMso). The computed isotropic shielding parameters for 1 were referenced using chemical shift of benzene calculated at the same level of theory and experimentally observed36 in DMSO-d6 (7.37 ppm for 'H and 128.3 ppm for 13C).

Reduction potentials E°1 were based on energies calculated for cations 1, radicals 1, and anions 1– at the B3LYP/6-311+G(2d,p)/B3LYP/6-311G(2d,p) level of theory with tight convergence criteria in MeCN dielectric medium using the IPCM model37 [keywords: SCRF=IPCM and epsilon value of 36.64]. The free energies calculated with thermodynamic corrections derived from B3LYP/6-311G (2d,p) calculations were converted to volts using the expression AG(sol) = -FΔG° where F is the Faraday constant, and correcting by 4.189 V for the difference between the absolute potential for standard hydrogen electrode (SHE, 4.43 V)18 and SCE electrode relative to SHE (0.241 V).

Mechanistic studies were conducted at the B3LYP/6-311G(2d,p) level of theory with tight convergence criteria. Global conformational minima for each trans and cis isomers, 3-E and 3-Z, were established by comparison of SCF energies for four conformers at fully optimized geometries without symmetry constraints. Transition state structures for cis–trans isomerization and formation of 6 were located using the STQN method39 requested with the QST2 keyword and default convergence criteria. Final energies for each optimized structure were calculated with the B3LYP/6-311+G (2d,p)/B3LYP/6-311G(2d,p) method and inclusion of solvation effects requested with the SCRF=IPCM keyword (epsilon=36.64).

5. Experimental section

5.1. General remarks

Melting points are uncorrected. NMR spectra were recorded at 400 or 500 MHz (1H), and 75 or 100 MHz (13C), respectively, in CDCl3 (7.26 and 77.0 ppm), CD2CN (1.95 ppm), anhydrous DMSO-d6 (2.49 and 39.5 ppm) as specified. DMSO-d6 was taken from freshly opened ampule. Chemical shifts were referenced to TMS (1H) or solvent (13C). UV spectra were recorded in spectrophotometric-grade CH2CN. Molar extinction coefficients were obtained by fitting maximum absorbance against concentration in agreement with Beer’s law.

5.2. Photocyclization

Solutions of halide 2 or 3 were placed in a Pyrex NMR tube or flask and irradiated without filter with a Husky work light (WLS500/SPC-H) setup equipped with a 500 W (125–130 V) clear halogen double ended lamp (T3 base) at a distance of about 50 cm. The reaction mixtures were spontaneously heated up by the lamp.

5.3. Cyclic voltammetry

Electrochemical analysis of 1[ClO4] was conducted under dry argon in MeCN (distilled over CaH2) containing freshly dried [Bu4N][ClO4] (50 °C, P2O5, vacuum, overnight) as the supporting electrolyte (0.1 M) and Pt microdisk working electrode with Ag/AgCl pseudoelectrode as reference. The concentration of 1[ClO4] was about 1 mM and the scanning rate was 0.1 V/s. Peak potentials were referenced to the Fe/Fe+ couple by adding small amounts of ferrocene to the solution, which was assumed to be +0.462 V versus SCE [MeCN, 0.1 M [Bu4N][ClO4]]40.

5.3.1. Benzoc-[quinolinium perchlorate (1a[ClO4])]. A mixture of 2a (250 mg, 1.1 mmol) and catalytic amounts of I2 was refluxed in dry benzonitrile (5 mL) for 36 h. The solvent was removed in vacuum, the residue was dissolved in water, insoluble brown solid was filtered, and 70% aqueous HClO4 was added to the filtrate. The resulting pale yellow solid was filtered, washed with water and Et2O, and recrystallized (EtOH) to afford 150 mg (54% yield) of 1a [ClO4] as yellowish crystals: mp 195–197 °C (lit. mp 187–189 °C); 1H NMR (400.1 MHz, CDCl3) δ 8.06 (td, J = 7.6 Hz, J = 0.7 Hz, 1H), 8.15–8.22 (m, 2H), 8.18 (d, J = 9.0 Hz, 1H), 8.32 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 8.49–8.57 (m, 2H), 8.58 (d, J = 9.2 Hz, 1H), 8.83 (d, J = 9.0 Hz, 1H), 9.96 (d, J = 7.0 Hz, 1H); 13C NMR (500 MHz, DMSO-d6) δ 80.8 (t, J = 7.5 Hz, 1H), 8.21 (td, J = 8.0 Hz, J = 1.6 Hz, 1H), 8.28 (td, J = 7.0 Hz, J = 1.8 Hz, 1H), 8.39 (d, J = 9.0 Hz, 1H), 8.40 (dd, J = 7.9 Hz, J = 1.5 Hz, 1H), 8.66 (td, J = 7.7 Hz, J = 0.9 Hz, 1H), 8.71 (dd, J = 8.3 Hz, J = 1.6 Hz, 1H), 8.74 (d, J = 9.0 Hz, 1H), 9.16 (d, J = 8.9 Hz, 1H), 10.39 (d, J = 7.0 Hz, 1H); 13C NMR (75.5 MHz, DMSO-d6, DEPT 90) δ 118.0, 122.9, 124.3, 126.8 (q), 128.4, 130.4, 130.5, 132.8, 134.2 (q), 134.6, 136.6, 140.5, 143.3 (q); UV (CH3CN), λmax (log ε 22) 423 (4.47), 227 (4.83), 253 (4.47), 277 (3.99), 299 (3.62), 332 (3.72), 347 (4.07), 363 (4.18) nm (lit.3 E0H λmax (log ε 228) 228 (3.85), 255 (4.07), 348 (3.68), 363 (3.80) nm). Anal. Calcd for C13H10ClNO4: C, 55.83; H, 3.56; N, 4.83; Found: C, 55.83; H, 3.37; N, 4.99.

5.3.2. Pyrido[2,1-c][1,2,4]benzotriazin-11-ium p-toluenosulfonate (1b[OTs]). 2-[(2-Fluorophenyl)pyridine (3b, 201 mg, 1.0 mmol) and calcium p-toluenosulfonate (190 mg, 1.0 mmol) were dissolved in a MeCN/H2O mixture (9:1, 30 mL). The resulted solution was irradiated with a halogen lamp and refluxed during 1–1.5 h (until TLC control showed reaction was completed). Then, solvents were evaporated. Residue was dried in a desiccator over P2O5 (12 h). The solid was suspended in CH2Cl2 and filtered. Subsequently, it was...
dissolved in hot MeCN, solution filtered, and the solvent was evaporated to give a yellow-green solid. The product was recrystallized (toluene/MeCN) to give 250 mg (85% yield) of 1b (OTs) as green-black crystals: mp 244–246 °C. 1H NMR (CD3CN) δ 2.31 (s, 3H), 7.12 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 8.37 (t, J = 8.0 Hz, 1H), 8.51 (t, J = 8.6 Hz, 1H), 8.59 (t, J = 7.0 Hz, 1H), 8.92 (d, J = 8.7 Hz, 1H), 9.08–9.03 (m, 2H), 9.27 (d, J = 8.4 Hz, 1H), 10.08 (d, J = 6.6 Hz, 1H); 13C NMR (75.5 MHz, DMSO-d6, DEPT 90) δ 20.8 (CH3), 116.9, 123.2 (q), 125.4, 128.0, 129.2, 130.4, 132.2, 137.6 (q), 138.8, 141.4 (q), 142.4 (q), 145.6 (q), 146.0. Anal. Calc. for C12H9ClN2O4: C, 51.35; H, 3.23; N, 9.98. Found: C, 51.44; H, 3.34; N, 9.98.

5.3.6. trans-2-[(Chlorophenyl)vinyl]pyridine (2a)11. A mixture of 2-picoline (3.0 g, 32.30 mmol) and 2-chlorobenzaldehyde (4.74 g, 33.70 mmol) was refluxed in acetic anhydride (6 mL) for 20 h under Ar atmosphere. Acetic anhydride was removed under vacuum, a mixture of cyclohexane and EtOAc (1:1, 20 mL) was added, the resulting solution was washed with satd NaHCO3, dried (Na2SO4), and the solvents were evaporated. The crude product was purified using a silica gel plug (CH2Cl2) and subsequent recrystallization from hexane to give 4.73 g (68% yield) of 2a as pale yellow crystals: mp 78–79 °C (lit.11 mp 75–76.6 °C). 1H NMR (400 MHz, CDCl3) δ 7.17 (d, J = 16.1 Hz, 1H), 7.15–7.20 (m, 1H), 7.23 (dd, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.29 (td, J = 7.4 Hz, J = 1.4 Hz, 1H), 7.41 (dd, J = 7.8 Hz, J = 1.4 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.68 (td, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.73 (dd, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.98 (d, J = 16.2 Hz, 1H), 8.63 (dd, J = 4.8 Hz, J = 0.8 Hz, 1H), 8.73 (d, J = 7.1 Hz, J = 1.8 Hz, 1H), 8.74 (d, J = 7.1 Hz, J = 1.8 Hz, 1H), 8.76 (dd, J = 9.3 Hz, J = 2.1 Hz, 1H), 10.50 (d, J = 6.6 Hz, 1H); 13C NMR (75.5 MHz, DMSO-d6, DEPT 90) δ 116.8, 113.1 (q), 129.2, 130.5, 132.3, 133.0, 133.3, 133.9, 141.4 (q), 142.4 (q), 146.0; UV (CH3CN), ϵmax (log ε) 259 (4.32), 347 (3.87), 359 (3.88) [lit.11 CH3CN], ϵmax (log ε) 258 (4.37), 348 (3.90), 359 (3.91), 375 sh (3.73). Anal. Calc. for C12H9ClN2O4: C, 46.91; H, 2.86; N, 14.92. Found: C, 47.04; H, 2.78; N, 14.70.

5.3.7. 2-(2-Chlorophenyl)pyrazolo[3,4-d]pyridine (2b)11. To the solution of 2-aminopyridine, (67 mg, 0.77 mmol) in toluene (0.1 mL), a solution of NaOH (50% in water, 0.7 mL) followed by 2-chlorotrosobenzene (102 mg, 0.7 mmol) was added. The mixture was vigorously stirred with mechanistic stirrer for 25 min at 50 °C. After cooling, water was added and mixture was extracted with CH2Cl2, combined extracts were dried (Na2SO4), and the solvents were evaporated. The residue was purified using a silica gel plug (hexane/CHCl3, 5:1) followed by recrystallization from hexane to give 69 mg (61% yield) of 2b as red crystals: mp 52–54 °C; (lit.11 mp 54–55 °C). 1H NMR (CDCl3) δ 8.77 (m, 1H), 7.94–7.84 (m, 3H), 7.58 (d, J = 8.0 Hz, 1H), 7.49–7.42 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H).

5.3.8. 2-(2-Fluorophenyl)vinylpyridine (3a)11. Prepared similarly to 2a, 3a was obtained in 34% yield as brown-yellow crystals: mp 74–76 °C (lit.11 mp 71–72 °C). 1H NMR (400 MHz, CDCl3) δ 7.09 (ddd, J = 10.8 Hz, J = 8.2 Hz, J = 1.1 Hz, 1H), 7.16 (br d, J = 7.5 Hz, 1H), 7.15–7.19 (m, 1H), 7.23–7.28 (m, 1H), 7.36 (d, J = 16.4 Hz, 1H), 7.43 (br d, J = 7.9 Hz, 1H), 7.64 (td, J = 7.7 Hz, J = 1.7 Hz, 1H), 7.67 (td, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.76 (d, J = 16.3 Hz, 1H), 8.62 (dd, J = 4.8 Hz, J = 0.8 Hz, 1H); 13C NMR (500 MHz, CDCl3) δ 7.17 (dd, J = 10.8 Hz, J = 8.6 Hz, 1H), 7.21–7.26 (m, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.32–7.38 (m, 1H), 7.34 (d, J = 16.2 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.75 (dd, J = 7.7 Hz, J = 1.7 Hz, 1H), 7.78 (dd, J = 7.7 Hz, J = 1.5 Hz, 1H), 8.73 (d, J = 16.2 Hz, 1H), 8.60 (d, J = 4.4 Hz, 1H).

5.3.9. 2-(2-Fluorophenyl)pyrazolo[3,4-d]pyridine (3b). Prepared similarly to that for 2b, 3b was obtained in 71% yield as brown-red crystals: mp 52–54 °C. 1H NMR (CDCl3) δ 8.76 (dm, J = 5.1 Hz, 1H), 7.94–7.83 (m, 3H), 7.56–7.49 (m, 1H), 7.43 (t, J = 6.2 Hz, 1H), 7.33–7.22 (m, 2H); 13C NMR (75.5 MHz, CDCl3, DEPT 90) δ 114.2, 117.1 (d, J = 20 Hz), 117.8, 124.3 (d, J = 12.5 Hz), 125.3, 133.3 (d, J = 9–13 Hz), 136.8, 140.2 (q), 149.5, 160.7 (q, J = 260 Hz), 163.0 (q). Anal. Calc. for C11H9FN2; C, 65.67; H, 4.01; N, 20.88. Found: C, 65.88; H, 4.07; N, 20.62.

5.3.10. 2-Fluoro-N-(pyridin-2-ylmethylene)aniline (3c). Using analogous procedure described for 3d, imine 3c was prepared in 55% yield as pale yellow crystals: mp 50–51 °C. 1H NMR (400 MHz, CDCl3) δ 7.13–7.25 (m, 4H), 7.39 (ddd, J = 7.7 Hz, J = 4.8 Hz, J = 1.2 Hz, 1H), 7.83 (td, J = 7.7 Hz, J = 1.5 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.67 (s,
1H), 8.72 (dq, J = 8.0 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.45–7.52 (m, 2H), 7.76 (dd, J = 7.1 Hz, J = 2.1 Hz, 1H), 8.25 (dd, J = 7.5 Hz, J = 1.7 Hz, 1H), 8.51 (dd, J = 4.8 Hz, J = 1.1 Hz, 1H), 9.45 (s, 1H).

13C NMR (75.5 MHz, CDCl3, DEPT-90) δ 115.9 (d, J = 21 Hz), 118.7, 122.0, 123.6 (d, J = 4 Hz), 124.3 (d, J = 4 Hz), 128.1 (d, J = 2 Hz), 133.5 (d, J = 9 Hz), 138.0, 148.9, 156.2 (d, J = 5 Hz), 161.0(q), 163.3 (d, J = 255 Hz). Anal. Calcld for C14H15NO2: C, 79.22; H, 6.32; N, 9.14. Found: C, 79.08; H, 6.33; N, 9.09.

13.2. 2-Chloronitrosobenzene (4).12 Prepared similarly to 5, 4 was obtained in 60% yield as yellow crystals: mp 64.5–65.5 °C (lit. mp 65–66 °C); 1H NMR (300 MHz, CDCl3) δ 7.36 (t, J = 7.9 Hz, 1H), 7.49–7.42 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.94–7.84 (m, 3H), 8.77 (dd, J1 = 16 Hz, J2 = 4.8 Hz, 1H). Anal. Calcld for C6H4ClNO: C, 48.89; H, 2.85; N, 9.89. Found: C, 49.03; H, 2.78; N, 9.89.

13.2. 2-Fluoronitrosobenzene (5).13 To a solution of 2-fluorooxime (0.90 mL, 9.30 mmol) in CH2Cl2 (20 mL), a water (80 mL) solution of Oxone® (110 g, 179 mmol) was added, and the reaction stirred at rt under N2 atmosphere, with exclusion of light, for 24 h. The organic layer was separated and the aqueous layer was extracted with CH2Cl2. The combined organic layers were washed with 5% of HCl followed by satd NaHCO3 and then water, dried (NaSO4), and the solvents were evaporated. The residue was passed through a silica gel plug (hexane/CH2Cl2, 9:1) and crystallized (MeOH/H2O) to give 460 mg (41% yield) of 5 as pale yellow crystals: mp 68–70 °C (lit. mp 66–68 °C); 1H NMR (300 MHz, CDCl3) δ 6.49 (dd, J1 = 10.5 Hz, J2 = 2.8 Hz, 1H, J = 1.8 Hz, 1H), 7.14 (t, J = 7.0 Hz, 1H), 7.51 (dd, J1 = 8.0 Hz, J2 = 7.0 Hz, J3 = 1.1 Hz, 1H), 7.76–7.68 (m, 18H). Anal. Calcld for C9H6FNO: C, 65.71; H, 3.22; N, 10.94. Found: C, 66.1; H, 3.34; N, 10.94.

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Supplementary data

These data include 2-D NMR spectra for [1][ClO4]−, tabularized theoretical interatomic distances for 1, distribution of spin density for 1, crystal data for [1][ClO4]− and [1][ClO4]−, archive of calculated equilibrium geometries for 1 and 1; 1 - 2, 2, 3, 4, 5, 6, and 6-7.

CCDC 792984 and 792983 contains the supplementary crystallographic data for [1][ClO4]− and [1][ClO4]−. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.03.023.

References and notes