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One-Pot Synthesis of Linearly Fused N-Heterocyles from Their Angular Analogues and Studies of Their Redox and Electrochromic Properties

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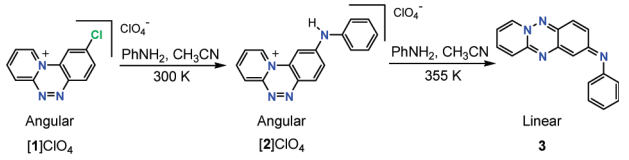

In an unusual chemical transformation, the angular heterocyclic compound [**1**]ClO_4, upon reaction with a primary aromatic amine, is transformed to a linear heterocyclic compound **3** via the angular intermediate [**2**]ClO_4 in one pot. Characterization of the compounds was primarily achieved by ^1H and ^{13}C NMR and mass spectral data. Analyses of single-crystal X-ray structures of the representative compounds confirmed their identities. These compounds exhibit notable spectral and redox properties. Their redox behavior is followed by spectral characterization of the electro-generated radicals. Electrochromic properties of the reference compounds are also explored.

Nitrogen-containing heterocyles exhibit[1] a diverse array of favorable biological and pharmacological properties. Also these are useful materials[2−4] as fluorescent dyes, DNA probes, NLO materials, ionic liquids, etc. Therefore, there is an obvious need to obtain this class of new materials preferably using easy synthesis in the laboratory.

During our work on azo-based ligands in coordination chemistry, we recently discovered[5] an unusual chemical transformation on proton-catalyzed one-pot synthesis of planar triazinium heterocycles from *trans*-2-(arylazo)pyridines. The transformation involves *trans* → *cis* isomerization and cyclization via a new C−N bond formation[6] reaction. The flat triazinium heterocyclic cations are found to be interesting in the context of their easy reducible properties, luminescent properties, and most importantly, their strong DNA binding and photonuclease activities.[5] Moreover, the 6-Cl-substituted triazinium compound, [**1**]ClO_4, is of further interest because it undergoes a variety of novel chemical transformations associated with C−Cl bond activation generating scope of synthesis of new heteroaromatic systems. For example, we recently have reported[6a] a redox-driven dimerization reaction leading to the synthesis of a new aromatic azo dye with versatile redox properties. Herein we report yet another unusual chemical transformation that resulted in the isolation of a linearly fused nitrogen-containing heterocycle **3** from the direct reaction of the planar and angular triazinium salt [**1**]ClO_4 with primary aromatic amines. As far as we are aware, similar chemical transformation of angularly fused polyheterocycles directly to linearly fused polyheterocyles under a mild laboratory condition is not available in the literature. For comparison, flash vacuum pyrolysis up to 525 °C led[7] to valence bond isomerization of the angularly fused starting compound to the corresponding linearly fused derivatives [1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine. The chemical transformations concerning us here are depicted in Scheme 1. Literature survey has revealed that linearly fused tricyclic triazinium salts are usually prepared[8] from α-diaminoisoquinolinium salts and α-dioxo compounds.

The C−Cl bond in the chloro-substituted triazinium compound [**1**]ClO_4 is activated[6a] and susceptible to nucleophilic substitution reactions. Accordingly, the reaction of $ArNH_2$ (Scheme 1, R = H, CH_3, OCH_3) with [**1**]ClO_4 in CH_3CN at reflux for 1 h produced the amine-substituted compound [**2**]ClO_4 ([**2a**]ClO_4 − [**2c**]ClO_4) as the major product[9] (yield, ca. 70%) along with the molecular compound, **3** (**3a**−**c**) as the minor product (yield, ca. 10%). However, the reaction of [**1**]ClO_4 with $ArNH_2$ at room temperature produced the compound [**2**]ClO_4 as the only product (yield, >70%). It may be relevant to note here that the reference transformations in [**1**]ClO_4 were not possible with ammonia or with an

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(9) The reaction of [**1**]ClO_4 with an primary aromatic amine containing an electrowithdrawing group like 4-nitroanline is sluggish. The compound, [**2**]ClO_4 (with R = $-NO_2$, Scheme 1), was isolated in <15% yield even after 4 h reflux.

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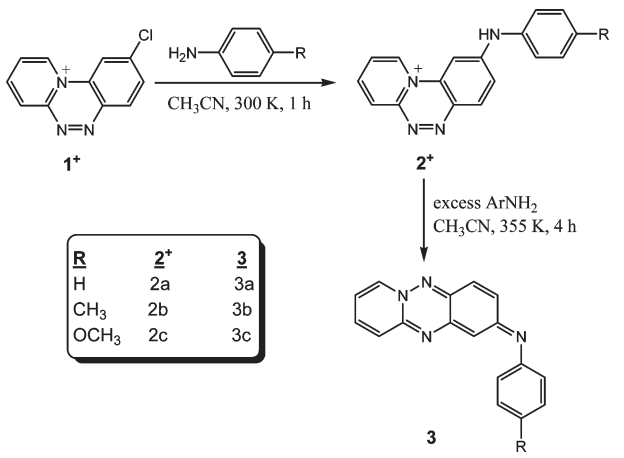
SCHEME 1. Synthetic Reactions



alkylamine like benzylamine. In these cases, a mixture of large number of unidentified products (overlapping bands of different colors on TLC plate) was observed after prolonged reflux.

Interestingly, the preformed compound [**2**]ClO_4, in turn, reacts freely with $ArNH_2$ in acetonitrile at reflux to produce **3** in >80% yield in 4 h. The above results together indicate that the compound [**2**]ClO_4 is an intermediate for the transformation, [**1**]ClO_4 → **3**. Most importantly, the product of the conversion, [**2**]ClO_4 → **3** does not depend on the nature of $ArNH_2$ indicating that the amine acts just as an initiator in the above angular to linear heterocyclic conversion. For example, [**2a**]ClO_4 → **3a** conversion occurs with similar efficiency by both aniline as well as *p*-toluidine. Moreover, the compound [**2b**]ClO_4 is converted to **3b** in acetonitrile upon boiling in the presence of aniline. Furthermore, we wish to note here that the afore-mentioned transformation ceases in the presence of a radical scavenger like TEMPO (2,2,6,6-tetramethylpiperidinoxyl radical) or BHT (2,6-di-*tert*-butyl-4-methylphenol) when a 1.25 equiv quantity is used.

Microanalytical, positive-ion ESI-mass spectra, together with NMR spectral data (Figures S1−S8, Supporting Information) of the compounds, convincingly support the formulation of the compounds as shown in the Scheme 1. For example, the compounds [**2b**]ClO_4 and **3b** both showed an intense peak at *m*/*z* 287 amu due to [**2b**]$^+$ and [H**3b**]$^+$. Finally, structure determination by X-ray diffraction of the representative compounds [**2a**]ClO_4 and **3a** confirms their identities as well as the geometries. Molecular views of the compounds [**2a**]ClO_4 and **3a** are shown in Figures 1 and 2. Their ORTEPs are available as Figures S9−S11 (Supporting Information), and crystallographic data are collected in Table S1 (Supporting Information). Comparison of the bond lengths of [**2a**]ClO_4 with those of **3a** clearly reveals that electronic structures of the tricyclo ring in the above two compounds are different. The carbon−nitrogen bonds connecting the amine nitrogen and the tricyclo ring in these two compounds are different. For example, the C8−N4 length (1.307(4) Å) in **3a** is noticeably shorter[10] than the

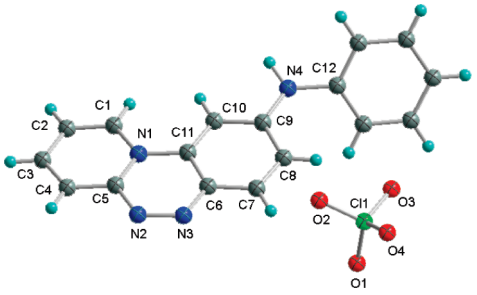


FIGURE 1. Molecular view of [**2a**]ClO_4. Selected bond lengths: C5−N2, 1.361(6); N2−N3, 1.310(5); C6−N3, 1.355(6); C6−C7, 1.403(6); C7−C8, 1.353(6); C8−C9, 1.420(6); C9−N4, 1.362(5); C12−N4, 1.420(6).

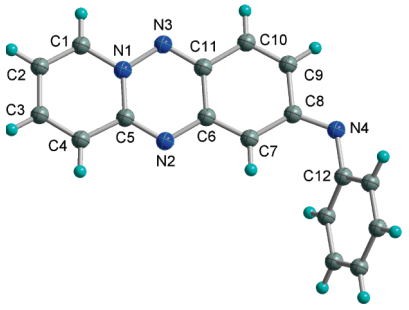


FIGURE 2. Molecular view of **3a**. Selected bond lengths: N1−N2, 1.385(3); C11−N3, 1.301(4); C10−C11, 1.450(4); C9−C10, 1.330(4); C8−C9, 1.473(4); C8−N4, 1.307(4); C12−N4, 1.411(4).

corresponding length C9−N4 (1.362(5) Å) in [**2a**]ClO_4. The observed C−N bond contraction in [**2a**]ClO_4 is attributed to delocalization[6a] of the nonbonding electron on the amine nitrogen to the cationic tricyclo ring. Moreover, *d*(N−N) in the above two compounds are different. The bond is elongated (1.385(3) Å) in **3a**, indicating[6a] that it is a single bond. The linearly fused molecule **3a** has a definite $\pi-\pi$ interaction (Figure S12, Supporting Information) with an intercentroid distance of 3.526 Å. The solutions of the compounds [**2a**]ClO_4−[**2c**]ClO_4 in acetonitrile are 1:1 electrolytic [$\Lambda_{eqiv}(CH_3CN)$, 105−110 Ω^{-1} mol^{-1} cm^2], while those of **3a**−**c** are nonelectrolytic.

The suggested mechanistic path for the formation of compounds **3** from [**2**]ClO_4 is outlined in Scheme 2. The formation of **3** from [**2**]ClO_4 is initiated by aromatic amines under refluxing conditions. We envision that aromatic amine radical ($ArNH^•$), produced by one electron oxidation and proton loss, attacks the carbon center adjacent to the pyridinium nitrogen leading to the formation of an intermediate **A**. Upon subsequent C−N bond cleavage, **A** is transformed into **B**, which is resonance stabilized. Out of the several possible resonating structures of **B**, the form **C** seems to be the most stable one. Radical attack at the terminal double bond through this resonating structure leads to the monoradical species **D** that on removal of $ArNH^•$ and a proton loss produces the final product **3**. To have further support, a similar reaction of [**2**]ClO_4 was carried out using thiophenol in place of an aromatic amine. The reaction did occur producing the compound **3** in nearly 70% yield (for experimental details, see the Supporting Information).

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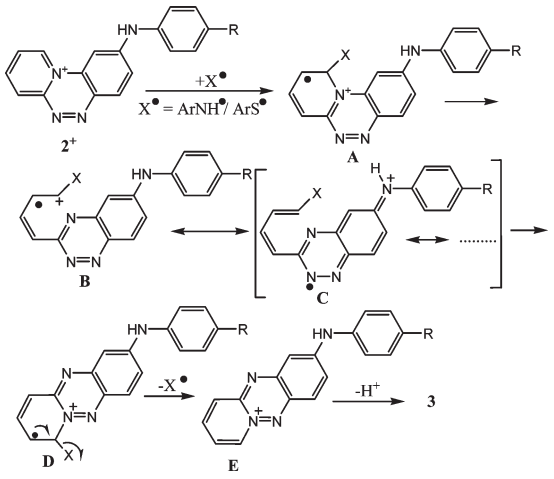
SCHEME 2. Plausible Mechanism of [2]ClO_4 → 3 Conversion



Absorption and emission spectra of the compounds [**2**]ClO_4 and **3** are submitted as Supporting Information (Figures S13 and S14 and Table S2). The compound [**2**]ClO_4 in CH_3CN exhibited emission at 580 nm associated with a shoulder at 550 nm at room temperature (300 K) upon excitation at 490 nm (quantum yield 0.025). The emission is attributed to the intramolecular charge transfer between the electron-rich anilino moiety and the electron-deficient pyridinium ring.[11] The lifetime of a representative [**2a**]ClO_4 at 300 K was found to be 3.92 ns. In comparison, the linearly fused heterocycle **3** showed emission in CH_3CN at 428 nm when excited at 270 nm (quantum yield 0.008), and the lifetime of a representative **3a** at 300 K was found to be 6.62 ns. A decrease in temperature resulted in considerable increment in the fluorescence quantum yields (quantum yields 0.136 and 0.032 for the compounds [**2**]ClO_4 and **3**, respectively, at ethanol−methanol glass) because nonradiative processes related to thermal agitation are less efficient at a glassy state.

The compounds [**2**]ClO_4 and **3** showed a reversible reduction wave near −0.4 and −0.3 V versus the Ag−AgCl, respectively (Table S3, Supporting Information). Cyclic voltammograms of the two compounds [**2a**]ClO_4 and **3a** are displayed in Figure 3. The electrolytically reduced compounds, **2a**$^{\bullet}$ and **3a**$^{\bullet-}$ showed a single line sharp EPR spectrum at *g*, 2.001 and 2.003, respectively (Figure S15, Supporting Information), characterizing the formation of the free radical in each case. Interestingly, the colors of the solutions of the electrogenerated reduced compounds are totally different[12] than those of the parent compounds. For example, the red color of the compound [**2a**]ClO_4 became pale yellow upon reduction (Figure 4). The original compounds are generated quantitatively by the oxidation of the reduced complexes, suggesting that the redox processes are reversible.

Notably, these compounds can also be reduced chemically by an aqueous solution of sodium dithionite. The lowest energy transition in the original compounds, [**2a**]ClO_4 and **3a**, disappeared completely upon addition of excess (10 times)

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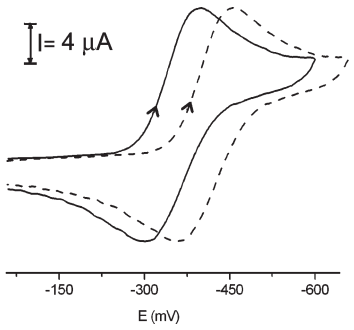

FIGURE 3. Cyclic voltammograms of [**2a**]ClO_4 (---) and **3a**(—).

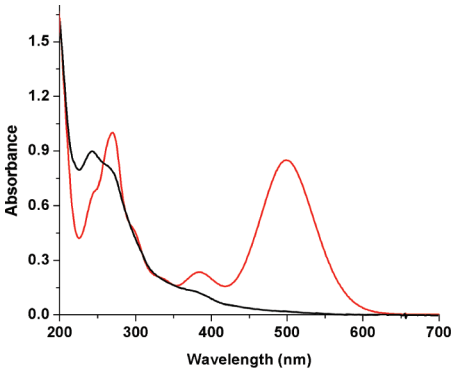

FIGURE 4. UV−vis spectra of [**2a**]ClO_4 (red) and **2a**$^{\bullet}$ (black).

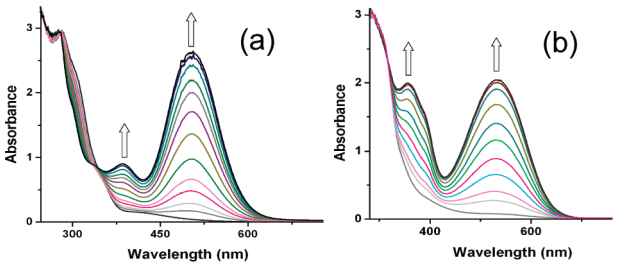

FIGURE 5. Change in absorbance for regeneration of the compounds (a) [**2a**$^{\bullet}$] → [**2a**]ClO_4 and (b) [**3a**$^{\bullet-}$] → **3a** as a function of time. The complexes, [**2a**$^{\bullet}$] and [**3a**$^{\bullet-}$] were generated in situ by mixing excess of aqueous sodium dithionite solution to the aqueous−methanolic (1:1) solutions of [**2a**]ClO_4 and **3a**, respectively.

of sodium dithionite solution. The most notable observation of these experiments is the regeneration of the original compounds (>95% regeneration in 0.5 h) with time (Figure 5; for details of the experiment, see the Supporting Information, Figure S16) generating the scope of using these as catalysts in the radical-induced redox transformations.

In summary, we have introduced one-pot synthesis of linear pyridinyl-1,2,4-triazine from its angular analogue. Primary aromatic amines mediate this transformation, and such a facile but useful chemical transformation is not available in the literature. The end product **3** as well as the cationic intermediate [**2**]ClO_4 undergo reduction at low cathodic potentials producing stable polycyclic radical species. The compounds show potential prospect of using them as catalysts in radical induced chemical reactions. It may be relevant to add here that the electrochromic property

in the linearly fused heterocyclic compound **3** resembles to that of a closely related biomolecule, riboflavin.[13]

Experimental Section

Synthesis of the Compounds [2a]ClO_4 and 3a. Aniline (0.14 mL, 1.5 mmol) was added to a 10 mL acetonitrile solution of [**1**]ClO_4 (0.317 g, 1 mmol), and the mixture was stirred at 300 K for 1 h. The initial yellowish brown solution became red during this period. The crude mass obtained by evaporation of the solution was purified on a preparative alumina TLC plate using the solvent mixture chloroform/acetonitrile (4:1) to afford the compound [**2a**]ClO_4 (0.268 g, 72%): mp 216−217 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 9.24 (d, 1H, J = 6.51 Hz), 8.98 (s, 1H), 8.73 (d, 1H, J = 8.67 Hz), 8.63 (t, 1H, J = 7.53 Hz), 8.54 (d, 1H, J = 9.09 Hz), 8.10 (t, 1H, J = 6.47 Hz), 7.75−7.71 (m, 2H), 7.54 (t, 2H, J = 7.83 Hz), 7.45 (d, 2H, J = 7.50 Hz), 7.38 (t, 1H, J = 7.35 Hz); ^{13}C NMR (125 MHz, CD_3CN) δ 155.5 (C), 143.5 (C), 142.8 (C−H), 140.2 (C), 137.6 (C), 134.8 (C−H), 130.6 (C−H), 130.3 (C−H), 128.9 (C−H), 127.5 (C), 127.1 (C−H), 125.9 (C−H), 123.5 (C−H), 123.4 (C−H), 93.5(C−H); IR (KBr) 1618, 1315, 1085 cm^{-1}; ESI-MS m/z 273 [M]$^+$. Anal. Calcd for $C_{17}H_{13}N_4ClO_4$: C, 54.78; H, 3.52; N, 15.03. Found: C, 54.76; H, 3.49; N, 15.06.

Conversion of [**2a**]ClO_4 into **3a** was achieved from the preformed compound [**2a**]ClO_4 (0.373 g, 1 mmol) by reacting it with aniline (1.4 mL, 15 mmol) in 10 mL of acetonitrile under refluxing conditions for 4 h. The color of the solution changed from red to brownish pink during this period. Purification of the reaction mixture on a preparative alumina TLC plate using chloroform as eluent yielded **3a** (0.23 g, 85%): mp 207−208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 7.20 Hz), 7.35−7.25 (m, 3H), 7.05−7.01 (m, 2H), 6.93 (d, 2H, J = 7.35 Hz), 6.85 (d, 2H, J = 9.04 Hz), 6.48 (t, 1H, J = 6.30 Hz), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160 (C), 149.4 (C), 147.4 (C), 147.1 (C), 142.3 (C−H), 140.4 (C), 136.4 (C−H), 136.3 (C−H), 129.2 (C−H), 126.9 (C−H), 124.3(C−H), 124.2 (C−H), 121.1 (C−H), 112.1 (C−H), 101.1(C−H); IR (KBr) 1643, 1502 cm^{-1}; ESI-MS m/z 273 [HM]$^+$. Anal. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.58. Found: C, 74.95; H, 4.43; N, 20.60.

The substituted compounds [**2b**]ClO_4, [**2c**]ClO_4, and **3b**, **3c** were synthesized using the appropriate $ArNH_2$ according to the methods as noted for the synthesis of [**2a**]ClO_4 and **3a**. Their yields and characterization data are as follows.

[**2b**]ClO_4: yield (0.29 g, 75%); mp 215−217 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 9.24 (d, 1H, J = 6.69 Hz), 9.05 (s, 1H), 8.73 (d, 1H, J = 8.54 Hz), 8.63 (t, 1H, J = 7.47 Hz), 8.53 (d, 1H, J = 9 Hz), 8.09 (t, 1H, J = 6.60 Hz), 7.76−7.72 (m, 2H), 7.54 (t, 2H, J = 7.77 Hz), 7.44 (d, 1H, J = 7.53 Hz), 7.38 (t, 1H, J = 7.26 Hz), 2.19 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 155.6 (C), 143.6 (C), 142.8 (C−H), 140.1 (C), 137.4 (C), 134.8 (C−H), 134.7 (C), 130.7 (C−H), 130.6 (C−H), 128.9 (C−H), 127.6 (C), 125.8 (C−H), 123.5 (C−H), 123.2 (C−H), 93.3 (C−H), 20.3 (CH_3); IR (KBr) 1620, 1313, 1087 cm^{-1}; ESI-MS m/z 287 [M]$^+$. Anal. Calcd for $C_{18}H_{15}N_4ClO_4$: C, 55.89; H, 3.91; N, 14.49. Found: C, 55.84; H, 3.92; N, 14.50.

[**2c**]ClO_4: yield (0.286 g, 71%); mp 218−219 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 9.19 (d, 1H, J = 6.90 Hz), 8.95 (s, 1H), 8.66 (d, 1H, J = 8.55 Hz), 8.58 (t, 1H, J = 8.46 Hz), 8.45 (d, 1H, J = 9.27 Hz), 8.07 (t, 1H, J = 6.97 Hz), 7.65 (d, 1H, J = 9.20 Hz), 7.56 (s, 1H), 7.34 (d, 2H, J = 8.94 Hz), 7.04 (d, 2H, J = 8.92 Hz), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 158.9 (C), 156.3 (C), 143.6 (C), 142.6 (C−H), 140.3 (C), 134.8 (C−H), 130.5 (C−H), 130.1 (C), 128.8 (C−H), 127.7 (C), 125.7 (C−H), 125.6 (C−H), 123.3 (C−H), 115.4 (C−H), 92.8 (C−H), 55.4 (CH_3); IR (KBr) 1620, 1310, 1085 cm^{-1}; ESI-MS m/z 303 [M]$^+$. Anal. Calcd for $C_{18}H_{15}N_4ClO_5$: C, 53.67; H, 3.75; N, 13.91. Found: C, 53.69; H, 3.74; N, 13.89.

3b: yield (0.24 g, 84%); mp 208−209 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 1H, J = 6.84 Hz), 7.41−7.31 (m, 2H), 7.14 (d, 2H, J = 8.04 Hz), 7.08 (d, 1H, J = 9.63 Hz), 6.94−6.89 (m, 3H), 6.56 (t, 1H, J = 6.69 Hz), 6.29 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 160.5 (C), 148.1 (C), 147.7 (C), 143.5 (C−H), 139.5(C), 136.4 (C−H), 136.1 (C−H), 133.3 (C), 129.7 (C−H), 126.4 (C−H), 124.1 (C−H), 120.9 (C), 120.7 (C−H), 111.0 (C−H), 101.8 (C−H), 21 (CH_3); IR (KBr) 1640, 1505 cm^{-1}; ESI-MS m/z 287 [HM]$^+$. Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.5; H, 4.93; N, 19.57. Found: C, 75.51; H, 4.94; N, 19.55.

3c: yield (0.247 g, 81%); mp 207−208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 1H, J = 6.60 Hz), 7.28−7.21 (m, 2H), 6.99−6.89 (m, 3H), 6.84−6.80 (m, 3H), 6.45 (t, 1H, J = 6.84 Hz), 6.25 (s, 1H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.3 (C), 156.7 (C), 148.1 (C), 147.8 (C), 143.3 (C−H), 139.9 (C), 136.5 (C−H), 136.3 (C−H), 126.5 (C−H), 124.2 (C−H), 122.4 (C−H), 114.5 (C−H), 111.4 (C−H), 101.6 (C−H), 55.7 (CH_3), (one carbon in the aromatic region is unresolved); IR (KBr) 1642, 1502 cm^{-1}; ESI-MS m/z 303 [HM]$^+$. Anal. Calcd for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.48; H, 4.66; N, 18.55.

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Supporting Information Available: X-ray crystallographic table of [**2a**]ClO_4, **3a**, and **3b** and relevant figures for characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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