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# A Practical Synthesis of Tris(pyrazolyl)methylaryls

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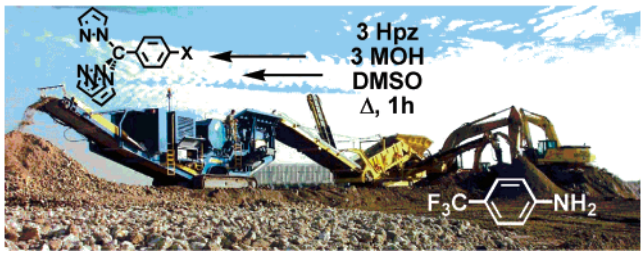


The preparation of three tris(pyrazolyl)toluidines from trifluoromethylaniline reagents is described that likely takes advantage of (quinoidal) resonance-stabilized activation of the C−F bonds. Subsequent transformations lead to two additional (for a total of five new) tris(pyrazolyl)methylaryls. This simple reaction is remarkable because only one other tris(pyrazolyl)methylaryl has been reported previously, because it is usually very difficult to activate fluoroalkane C−F bonds, and because of the potential scope of the reaction.

Since the seminal reports on the preparation and coordination chemistry of tris(pyrazolyl)borates and tris(pyrazolyl)methanes,[1] variations on these so-called scorpionate ligands have permeated all aspects of inorganic chemistry. Substantial research effort first went into developing multiple generations of tris(pyrazolyl)-borates, such as developing bulky derivatives to stabilize unusual coordination complexes.[2] On the other hand, the chemistry of the parent tris(pyrazolyl)methane, $HC(pz)_3$ (pz = pyrazolyl), and its derivatives was relegated to near obscurity until an efficient high-yield synthetic route reported by the Reger group incited vigorous research on these derivatives (nearly 30 years after the initial report).[3] Currently, there exists a disparity in the chemistry of certain "third-generation" scorpionates (ligands functionalized at the "back" boron or methine position). That is, the synthetic methodology and coordination chemistry of aryltris(pyrazolyl)borates (Figure 1, left) have been well-developed,[4] which has permitted significant advances in iron(II) spin-crossover chemistry.[5] On the other hand, the chemistry of analogous tris(pyrazolyl)methane derivatives (Figure 1, right) are almost unknown because synthetic difficulties render these derivatives nearly inaccessible by standard routes. The lone reported example of a tris(pyrazolyl)methyl bound directly to an arene is $PhC(pz^{2py})_3$, prepared in a mere 8% yield from trichlorotoluene and the sodium pyrazolide.[6] To make matters more grim, similar reactions with other pyrazolyls fail to give usable quantities of desired products.[7] It occurred to us during the course of our investigations into developing new fluorescent turn-on sensors based on modified aniline derivatives[8] that it may be possible to take advantage of the quinoidal resonance forms of electron donors such as commercially available trifluoromethylaniline to provide access to tris(pyrazolyl)-toluidines via an elimination−addition mechanism, as depicted in Scheme 1. Derivatives such as $H_2NC_6H_4C(pz)_3$ would also be appealing since they would contain a built-in entry point for further functionalization (including the possibility of serving as monomers for new polyanilines). We now communicate the successful implementation of this strategy for the preparation of three new electroactive tris(pyrazolyl)toluidines, *p*- and *o*-$H_2NC_6H_4C(pz)_3$ and *p*-$EtNHC_6H_4C(pz)_3$. Subsequent conversion of the former to *p*-$BrC_6H_4C(pz)_3$ or to *p*-$Et_2NHC_6H_4C(pz)_3$ is also described. Future reports will elaborate on the organic and coordination chemistry of these derivatives.

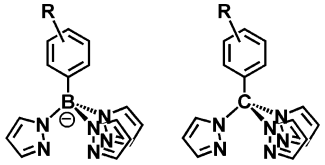


**FIGURE 1.** Third generation scorpionates based on tris(pyrazolyl)-borates (left) and tris(pyrazolyl)methanes (right).

The optimized one-pot preparative route to tris(pyrazolyl)-toluidines is found in Scheme 2. A summary of synthetic variants is presented in Table 1. Several details are worth noting

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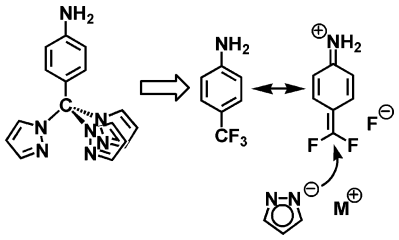
**SCHEME 1. Retrosynthetic Approach to Tris(pyrazolyl)toluidines**



**SCHEME 2. Preparative Route to Tris(pyrazolyl)toluidines**

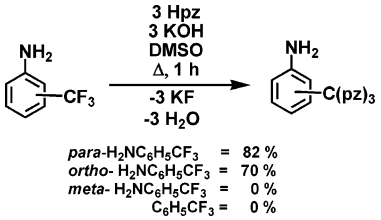
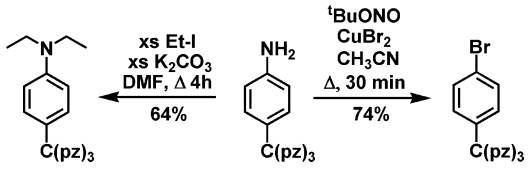



**TABLE 1. Attempted Preparations of Tris(pyrazolyl)methylaryls**

| reagent | base | solvent | time (h) | yield[a] (%) |
|---|---|---|---|---|
| *p*-$H_2NC_6H_4CF_3$ | NaOH | DMSO | 1 | 80 |
| | KOH | DMSO | 1 | 82 |
| | $NEt_4(OH)$ | DMSO | 2 | 22 |
| | $Cs_2CO_3$ | DMSO | 0.5 | 41 |
| | $K_2CO_3$ | DMSO | 1 | 46 |
| | $K_2CO_3$ | $Ph_2O$ | 2 | 22 |
| | $Na_2CO_3$ | DMSO | 12 | 16 |
| *p*-$EtNHC_6H_4CF_3$ | KOH | DMSO | 1 | 46 |
| *p*-$Et_2NC_6H_4CF_3$ | KOH | DMSO | 5 | 0 |
| *o*-$H_2NC_6H_4CF_3$ | KOH | DMSO | 1 | 70 |
| | $K_2CO_3$ | DMSO | 5 | 5 |
| *m*-$H_2NC_6H_4CF_3$ | KOH | DMSO | 3 | 0 |
| $C_6H_5CF_3$ | KOH | DMSO | 3 | 0 |

[a] Isolated scorpionate of the type $ArylC(pz)_3$.

**SCHEME 3. Preparative Route to Tris(pyrazolyl)methylaryls**




First, only *p*- and *o*-trifluoromethylaniline derivatives gave the desired scorpionate in good yields. The yield of the deriviative from *o*-$H_2NC_6H_4CF_3$ was slightly lower than that from *p*-$H_2NC_6H_4CF_3$, presumably due to steric hindrance between the *o*-$NH_2$ group and pyrazolyls.

Both *m*-$H_2NC_6H_4CF_3$ and $C_6H_5CF_3$ remained unchanged under the reaction conditions. Such observations diminish the possibility of an $S_N2$-type mechanistic pathway but might be expected if the ionic resonance form in Scheme 1 were operative. Here, the electron-donating amino group plays a vital role since it is usually very difficult to activate C−F fluoroalkane bonds.[9] Interestingly, *p*-$EtNHC_6H_4CF_3$ gave the desired scorpionate but *p*-$Et_2NC_6H_4CF_3$ did not undergo any reaction (the desired *p*-$Et_2NC_6H_4C(pz)_3$ had to be prepared indirectly, vide infra). Given that *p*-$Et_2NC_6H_4CF_3$ is the strongest electron donor of the three para-substituted anilines, hydrogen bonding involving the NH-group may play a significant role in facilitating the reaction. Other solvent systems ($Ph_2O$, xylenes, toluene, xylene/$H_2O$ with phase transfer catalyst) and Bronsted base combinations were also explored (some, but not all, are found in Table 1); however, low solubility of the base typically led to significantly lower yields, longer reaction times, and in the case of $Ph_2O$, also to extensive decomposition due to this solvent's high boiling point. Noteworthy is that the reaction employing $(NEt_4)(OH)$ in DMSO was more sluggish and gave lower yields than that with either NaOH or KOH, indicating an important role for the metal cation (presumably facilitating fluoride abstraction).

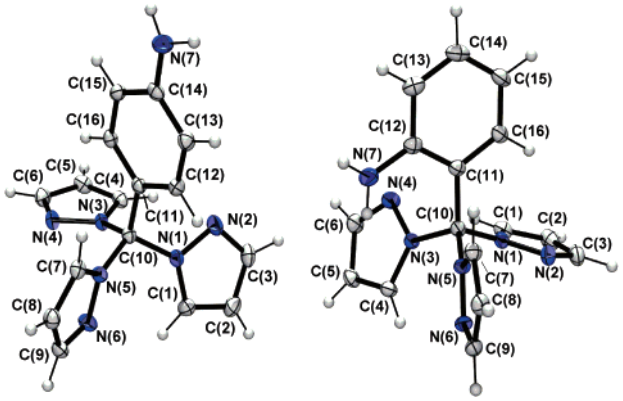



**FIGURE 2.** ORTEP drawing (50% ellipsoids) with atom labeling of *p*- (left) and *o*-$H_2NC_6H_4C(pz)_3$ (right).

Scheme 3 summarizes the initial demonstrations of using tris(pyrazolyl)toluidines as synthetically viable reagents. First, *p*-$Et_2NC_6H_4C(pz)_3$, a derivative that could not be prepared directly from *p*-$Et_2NC_6H_4CF_3$, was obtained in modest yield from $H_2NC_6H_4C(pz)_3$ and ethyl iodide. Also, *p*-$H_2NC_6H_4C(pz)_3$ was converted to *p*-$BrC_6H_4C(pz)_3$ in good yield (74%) by adapting a literature method.[10]

The new scorpionates have been characterized by multiple methods including by single-crystal X-ray diffraction studies of each *p*- and *o*-$H_2NC_6H_4C(pz)_3$, Figures 2 and 3, respectively. In both, the molecules are associated into polymeric chains via intermolecular hydrogen bonding interactions involving the amino group hydrogens and pyrazolyl nitrogens of neighboring molecules (Figure 3). There are two independent molecules in the unit cell of the para derivative. One molecule serves as a hydrogen donor to two neighboring molecules while the other only donates to one other molecule, forming the polymeric tape as in Figure 3a. The ortho derivative has one accessible N−H hydrogen for intermolecular hydrogen bonding (to the pyrazolyl nitrogen of a neighboring molecule) and therefore forms a single-stranded polymer chain as in Figure 3b. The thermal properties of the *o*-$H_2NC_6H_4C(pz)_3$ are quite interesting as this compound forms a clear yellow glass upon heating past ca. 185 °C and retains its appearance on cooling. Subsequent reheating to 80 °C causes recrystallization then "remelting" upon reaching 185 °C; all other derivatives simply form a glass but do not exhibit this unusual recrystallization behavior. Finally, since it is established that aniline derivatives undergo one-

(9) See for instance: (a) Haeffner, F.; Marquez, M.; Gonzalez, C. *J. Phys. Chem. A* **2007**, *111*, 268. (b) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

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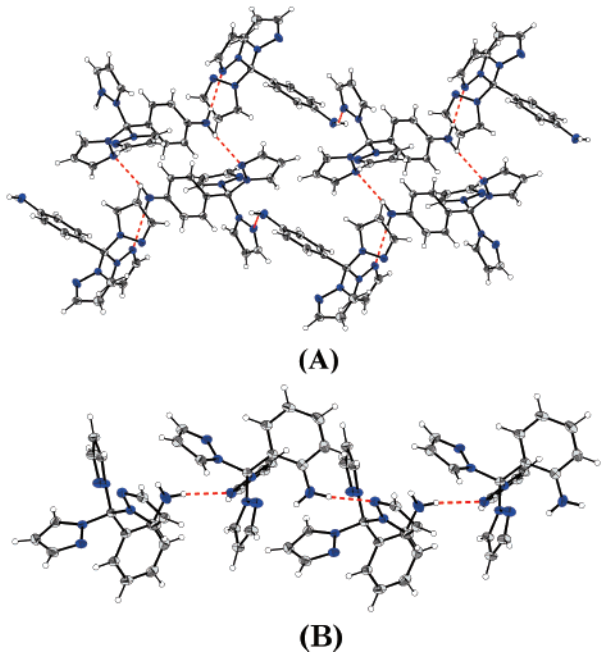


**FIGURE 3.** Views of hydrogen bonding interactions (red dashed lines) resulting in (A) a polymeric tape of *p*-$H_2NC_6H_4C(pz)_3$ and (B) a polymeric chain of *o*-$H_2NC_6H_4C(pz)_3$.

**TABLE 2. Oxidation Potentials (V vs Ag/AgCl) of Aniline Derivatives**[a]

| compd | $E_{pa}$ | $E_{pc}$ |
|---|---|---|
| *p*-$H_2NC_6H_4CF_3$ | 1.31 | |
| *p*-$EtNHC_6H_4CF_3$ | 1.22 | |
| *p*-$Et_2NC_6H_4CF_3$ | 1.15 | 0.99 |
| *o*-$H_2NC_6H_4CF_3$ | 1.43 | |
| *p*-$H_2NC_6H_4C(pz)_3$ | 1.15 | |
| *p*-$EtNHC_6H_4C(pz)_3$ | 1.08 | |
| *p*-$Et_2NC_6H_4C(pz)_3$ | 1.01 | 0.84 |
| *o*-$H_2NC_6H_4C(pz)_3$ | 1.25 | |

[a] $CH_3CN$, $NBu_4(PF_6)$ supporting electrolyte, scan rate 0.1 V/s.

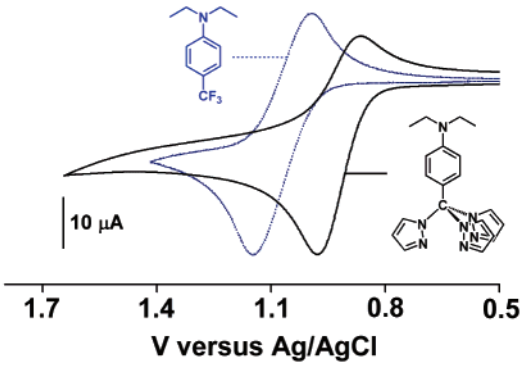


**FIGURE 4.** Cyclic voltammograms of $CH_3CN$ solutions of *p*-$Et_2NC_6H_4CF_3$ (blue) and of *p*-$Et_2NC_6H_4C(pz)_3$ (black) acquired at a scan rate of 0.1 V/s with $NBu_4(PF_6)$ as the supporting electrolyte.

electron oxidation,[11] the electrochemistry of the starting materials and new derivatives was investigated and the results are summarized in Table 2 and Figure 4. The *N*,*N*-diethyl derivatives were unique in that they exhibit (quasi)reversible oxidation (Figure 4); all other aniline derivatives are irreversibly oxidized and display only anodic waves in their cyclic voltammograms (Supporting Information); *p*-$BrC_6H_4C(pz)_3$ is electrochemically silent in the solvent potential window. As anticipated from inductive effects, the tris(pyrazolyl)toluidines are easier to oxidize than the trifluoromethylanilines and oxidation also becomes more favorable with increasing *N*-ethyl substitution. The greater electron donating effect of para versus ortho substitution is also demonstrated by comparing the oxidation potentials of the two $H_2NC_6H_4C(F \text{ or } pz)_3$ isomers.

In conclusion, a simple, high-yielding route to tris(pyrazolyl)-toluidines ("third-generation" scorpionates with an aniline groups bound to the "back" methine position) has been discovered that is likely facilitated by ionic quinoidal intermediates derived from trifluoromethylaniline starting materials. The electron donating amino group is vital since it is usually very difficult to otherwise activate fluoroalkane C−F bonds. Both resonance and steric effects are operatives as only para and ortho isomers of $H_2NC_6H_4CF_3$ afforded the desired tris(pyrazolyl)-methylanilines (with the yield of the para being higher than that of the ortho); neither *m*-$H_2NC_6H_4CF_3$ nor $C_6H_5CF_3$ gives any desired products under comparable or more forcing conditions. Hydrogen bonding may play a role in arbitrating the reaction pathway since yields decrease on substituting one N−H with an *N*-ethyl as in $EtNHC_6H_4CF_3$ and vanish for the di-*N*-ethyl derivative. The feasibility of using *p*-$H_2NC_6H_4C(pz)_3$ as a reagent was also demonstrated in the preparation of two other scorpionates *p*-$XC_6H_4C(pz)_3$ (X = $Et_2N$, Br). For the latter, further derivatization via Pd-catalyzed coupling reactions can be envisioned. Future reports will elaborate on the organic transformations and coordination chemistry of these and related derivatives and will address the scope of this resonance-assisted elimination/addition reaction involving trifluoromethylanilines.

## Experimental Section

**Preparation of *p*-$H_2NC_6H_4C(pz)_3$.** A mixture of 1.61 g (9.99 mmol) of *p*-$H_2NC_6H_4CF_3$, 1.68 g (29.9 mmol) of KOH, and 2.04 g (30.0 mmol) of pyrazole in 10 mL of DMSO was heated at reflux for 1 h. After cooling to room temperature, 50 mL each of water and $CH_2Cl_2$ was added. The organic and aqueous layers were separated, the aqueous layer was extracted twice with 50 mL of $CH_2Cl_2$, and the combined organics were dried over $MgSO_4$. Purification of the organic fraction by flash chromatography on $SiO_2$ with $Et_2O$ yields unreacted aniline in the band near the solvent front then the desired product in the following pale yellow band ($R_f$ 0.4). After removing solvent, the resulting waxy solid was triturated with $Et_2O$ to afford 2.50 g (82%) of pure *p*-$H_2NC_6H_4C(pz)_3$ as a very pale yellow solid after collecting by filtration and drying under vacuum. Mp 127−129 °C dec to yellow glass. Anal. Calcd (found) for $C_{16}H_{15}N_7$: C, 62.94 (63.32); H, 4.95 (4.87); N, 32.11 (32.48). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta_H$ 7.71 (d, $J$ = 1 Hz, 3H), 7.53 (d, $J$ = 2 Hz, 3H), 6.86 (part of AA′BB′, 2H), 6.63 (part of AA′BB′, 2H), 6.34 (dd, $J$ = 2, 1 Hz, 3H), 3.88 (br s, 2H). $^{13}C$ NMR (75.5 MHz, $CDCl_3$) $\delta_C$ 148.3, 141.1, 132.2, 129.8, 126.4, 114.1, 106.2, 93.3. HRMS-direct probe (*m*/*z*): calcd (found) for $C_{16}H_{15}N_7$ 305.1389 (305.1386). Crystals suitable for X-ray diffraction were grown by layering a benzene solution with hexanes and allowing solvents to slowly diffuse overnight.

The following two derivatives were prepared analogously with the same amount of solvent, millimoles of (appropriate) reagents, and identical heating time. Therefore only the purification procedure, yield, and characterization data are provided.

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***o*-$H_2NC_6H_4C(pz)_3$.** Column chromatography with $Et_2O$ ($R_f$ 0.7) afforded 2.14 g (70%) of pure *p*-$H_2NC_6H_4C(pz)_3$ as a colorless solid after trituration with $Et_2O$, filtration, and drying as above. Mp 185−187 °C dec to yellow glass. Anal. Calcd (found) for $C_{16}H_{15}N_7$: C, 62.94 (62.57); H, 4.95 (5.18); N, 32.11 (31.88). $^1$H NMR (300 MHz, $CDCl_3$) $\delta_H$ 7.74 (d, $J$ = 2 Hz, 3H), 7.73 (d, $J$ = 1 Hz, 3H), 7.30 (m, 2H), 6.77−6.70 (br m, 4H), 6.40 (dd, $J$ = 2, 1 Hz, 3H), 5.93 (part of AA′BB′, 2H), 3.57 (br s, 2H). $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta_C$ 145.44, 145.39, 141.5, 132.8, 131.9, 128.2, 122.5, 118.80, 118.76, 117.6, 107.1, 93.1. HRMS-direct probe (*m*/*z*): calcd (found) for $C_{16}H_{15}N_7$ 305.1389 (305.1393). Crystals suitable for X-ray diffraction were grown by layering a benzene solution with hexanes and allowing solvents to slowly diffuse overnight.

***p*-$EtNHC_6H_4C(pz)_3$.** Column chromatography of the organic fraction from workup with $Et_2O$ ($R_f$ 0.8) as an eluent afforded 2.14 g (46%) of pure *p*-$H_2NC_6H_4C(pz)_3$ as a colorless solid after trituration with $Et_2O$, filtration, and drying as above. Crystals are obtained either by cooling hot concentrated hexanes solution or layering a benzene solution with hexanes. Mp 134−135 °C dec to yellow glass. Anal. Calcd (found) for $C_{18}H_{19}N_7$: C, 64.85 (65.13); H, 5.74 (6.02); N, 29.41 (29.18). $^1$H NMR (300 MHz, $CDCl_3$) $\delta_H$ 7.72 (d, $J$ = 1 Hz, 3H), 7.55 (d, $J$ = 2 Hz, 3H), 6.86 (part of AA′BB′, 2H), 6.54 (part of AA′BB′, 2H), 6.34 (dd, $J$ = 2, 1 Hz, 3H), 3.88 (br s, 1H), 3.16 (q, $J$ = 7.3 Hz, 2H), 1.25 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta_C$ 149.8, 141.2, 134.2, 129.9, 125.1, 111.6, 106.2, 93.5, 38.2, 14.9. HRMS-direct probe (*m*/*z*): calcd (found) for $C_{18}H_{19}N_7$ 333.1702 (333.1696).

***p*-$Et_2NC_6H_4C(pz)_3$.** A mixture of 1.00 g (3.38 mmol) of *p*-$H_2NC_6H_4C(pz)_3$, 1.60 mL (19.9 mmol) of ethyl iodide, and 2.68 g (19.4 mmol) of $K_2CO_3$ in 10 mL of DMF was heated at reflux 4 h. After cooling to room temperature, 25 mL each of $H_2O$ and $CH_2Cl_2$ were added. The organic and aqueous layers were separated, the aqueous layer was extracted twice with 50 mL of $CH_2Cl_2$, the combined organics were dried over $MgSO_4$ and filtered onto 5 g of silica gel, and solvent was removed by rotary evaporation to adsorb the product mixture. The adsorbed mixture was added to a short column of fresh silica and the desired compound was eluted in the first band ($R_f$ ca. 0.5) with 2:1 hexanes:ethyl acetate. After triturating with $Et_2O$, crude *p*-$Et_2NC_6H_4C(pz)_3$ was collected by filtration. Colorless crystals (0.758 g, 64%) of pure *p*-$Et_2NC_6H_4C(pz)_3$ were grown by allowing a boiling supersaturated hexane solution to slowly cool to room temperature over the course of a few hours. Mp 115−117 °C dec to yellow glass. Anal. Calcd (found) for $C_{20}H_{23}N_7$: C, 66.46 (66.55); H, 6.41 (6.80); N, 27.13 (26.82). $^1$H NMR (300 MHz, $CDCl_3$) $\delta_H$ 7.72 (d, $J$ = 1 Hz, 3H), 7.57 (d, $J$ = 2 Hz, 3H), 6.87 (part of AA′BB′, 2H), 6.60 (part of AA′BB′, 2H), 6.34 (dd, $J$ = 2, 1 Hz, 3H), 3.36 (q, $J$ = 7.3 Hz, 4H), 1.16 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta_C$ 149.0, 141.2, 132.4, 129.9, 123.1, 110.4, 106.2, 93.7, 44.4, 12.7. HRMS-direct probe (*m*/*z*): calcd (found) for $C_{20}H_{23}N_7$ 361.2015 (361.2008).

***p*-$BrC_6H_4C(pz)_3$.** A 0.813 g (2.66 mmol) sample of solid *p*-$H_2NC_6H_4C(pz)_3$ was added to a nitrogen-purged solution of 0.595 g (2.66 mmol) of $CuBr_2$ and 0.65 mL (5.46 mmol) of $^t$BuONO in 20 mL of anhydrous $CH_3CN$. Gas evolution concomitant with a solution color change from deep green to purple occurred immediately on mixing. The reaction mixture was heated at reflux for 30 min until gas evolution was no longer detected via an attached oil bubbler. Aqueous workup followed by separation by column chromatography on silica gel with $Et_2O$ as an eluent ($R_f$ 0.8) afforded 0.731 g (74%) of pure *p*-$BrC_6H_4C(pz)_3$ as a colorless solid. Colorless crystals can be grown by cooling a nearly saturated $Et_2O$ solution in a −30 °C freezer overnight. Mp 120−121 °C. Anal. Calcd (found) for $C_{16}H_{13}BrN_6$: C, 52.05 (51.86); H, 3.55 (3.69); N, 22.76 (22.95). $^1$H NMR (300 MHz, $CDCl_3$) $\delta_H$ 7.74 (d, $J$ = 1 Hz, 3H), 7.55 (part of AA′BB′, 2H), 7.43 (d, $J$ = 2 Hz, 3H), 7.08 (part of AA′BB′, 2H), 6.38 (dd, $J$ = 2, 1 Hz, 3H). $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta_C$ 141.7, 136.6, 132.3, 131.5, 130.7, 125.2, 106.9, 92.9. HRMS-direct probe (*m*/*z*): calcd (found) for $C_{16}H_{13}BrN_6$ 368.0385 (368.0373).

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**Supporting Information Available:** NMR spectra, voltammograms, and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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