Copper(I)-catalyzed intramolecular C-N coupling reactions to form 1-cyanobenzimidazoles

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Abstract
Employing a CuI/2,2'-biimidazole catalyst system, the intramolecular C-N coupling reactions of various substituted aryl guanidines could be successfully carried out under mild conditions. A variety of 1-cyanobenzimidazoles were synthesized in good to excellent yields.

Keywords: Copper, intramolecular, C-N coupling, 1-cyanobenzimidazoles

Introduction
Since nitrogen heterocycles are among the most important classes of pharmacologically active compounds, a significant number of methods to synthesize nitrogen containing heterocyclic targets have been developed. Classical copper-mediated Ullmann-type couplings are important in approaches to heterocyclic compounds. Over the past few years, great attention has been paid to the improvement of Ullmann-type couplings, and significant progress has been made. Recently, many ligands have been introduced to promote copper-catalyzed C-N coupling efficiently, including diamines, 1,10-phenanthroline, amino acids, N,N-diethylsalicylamide, ethylene glycol, 8-hydroxyquinoline, an aminoarenethiol, 1,1,1-tris(hydroxymethyl)ethane, 2-aminopyrimidine-4,6-diol, 1,1'-binaphthyl-2,2'-diol, ethyl 2-oxocyclohexanecarboxylate, and so on. These Cu/ligand catalyzed reactions are significantly superior to the conventional Pd-mediated reactions with low cost, mild reaction conditions and good compatibility with functional groups. As a result, a variety of efficient protocols have been reported for the arylation of anilines, amides, hydrazides, alkylamines, amino acids and nitrogen heterocycles.
Since the benzimidazole scaffold is one of the privileged building blocks in medicinal chemistry, there has been much interest in the synthesis and biological evaluation of benzimidazole derivatives over the past few years. Recently, we reported an CuI-catalyzed system using 2,2'-biimidazole as the ligand, for efficient intermolecular N-arylation over a broad spectrum of nitrogen nucleophiles and aryl halides. The reactions were carried out in relatively mild conditions with good to excellent yields (Scheme 1). After demonstrating the utility of the system for intermolecular aminations, our attention was focused on the intramolecular process. Herein, we here describe the use of a catalyst system with a combination of CuI and 2,2'-biimidazole in intramolecular aryl guanidinylation leading to 1-cyanobenzimidazoles.

Scheme 1. CuI-catalyzed intermolecular C-N coupling reactions.

Results and Discussion

The requisite aryl guanidine substrates are readily synthesized from commercially available dimethyl N-cyanodithioiminocarbonate 1 (Scheme 2). Condensation of compound 1 with an o-haloaniline in the presence of Cs2CO3 in DMF at 100 °C for 8 h gave adducts 2. Compounds 2 reacted with the secondary amines in refluxing ethanol to afford the corresponding aryl guanidines 3.

Reagents and conditions: (a) Cs2CO3, DMF, 100 °C; 38-41%. (b) EtOH, reflux; 46-73%

Scheme 2. The synthetic routes to the aryl guanidines 3.

Initial trials using guanidine 3a1 as a model substrate for intramolecular amination using the general conditions established for the intermolecular reaction (0.1 equiv of CuI and 0.2 equiv of 2,2'-biimidazole in DMF) resulted in the generation of the desired product 4a in an excellent
yield (Table 1, entry 1). During the course of our investigation, we found when ligand 2,2'-biimidazole was omitted, the products were obtained in low yield (Table 1, entry 2) and if no CuI was present, no cyclized products were found (Table 1, entry 3). Our investigation of K₂CO₃ and Cs₂CO₃ as the bases showed that Cs₂CO₃ was optimal (Table 1, entries 1 and 4). It was also found that the loadings of catalyst could be decreased to 5 mol% almost without affecting the yield of the desired 1-cyanobenzimidazole (Table 1, entry 5). However, the yield was dramatically reduced when the loadings of catalyst were decreased to 1 mol% (Table 1, entry 6). Thus, the combination of 5 mol% of CuI with 10 mol% of 2,2'-biimidazole in the presence of Cs₂CO₃ was the optimal reaction conditions.

**Table 1. Optimization of CuI-catalyzed intramolecular cyclization**

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuI (mol%)</th>
<th>Ligand (mol%)</th>
<th>Base</th>
<th>Yield (%)b</th>
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<tr>
<td>1</td>
<td>10</td>
<td>2,2'-biimidazole (20)</td>
<td>Cs₂CO₃</td>
<td>94</td>
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<tr>
<td>2</td>
<td>10</td>
<td>No ligand</td>
<td>Cs₂CO₃</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
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<td>Cs₂CO₃</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
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<td>K₂CO₃</td>
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<tr>
<td>5</td>
<td>5</td>
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<td>Cs₂CO₃</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2,2'-biimidazole (2)</td>
<td>Cs₂CO₃</td>
<td>57</td>
</tr>
</tbody>
</table>

*aReaction conditions: 3a1 (1.0 equiv), CuI, 2,2'-biimidazole, bases (2 equiv), under N₂ atmosphere at 80 °C for 10 h. bIsolated yield.*

To extend the generality of the reaction, the intramolecular C-N coupling reactions were carried out under the optimized conditions using a wide range of substrates. As shown in Table 2, the cyclization reaction proceeded well with almost all of these substrates and gave good to excellent yields. Comparison of the results of aryl bromides and aryl iodides showed that aryl iodides were in general superior to aryl bromides (entries 1, 2 and 3, 4). When a range of simple cyclic secondary amines such as piperidine, pyrrolidine, morpholine and N-methylpiperazine were introduced to R¹R²NH substitutions, the corresponding cyclization products were obtained in excellent yields (entries 1-6). The substrates bearing open-chain secondary amino groups were also found to undergo the conversion with good yields (entries 7 and 9), except for the dibenzylamino group, due to possible sterical encumbrance (entry 8).
Table 2. Synthesis of 1-cyanobenzimidazoles 4 via CuI-catalyzed intramolecular cyclizations

<table>
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<th>Product</th>
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<td>2</td>
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<td>I</td>
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Table 2. Continued

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<td>3g</td>
<td>I</td>
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<td>77</td>
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aIsolated yield.

Conclusions

In conclusion, we have developed a CuI/2,2'-biimidazole catalyst system that effectively catalyzes intramolecular C-N coupling reactions of aryl guanidines under mild conditions to produce 1-cyanobenzimidazole derivatives in good to excellent yields. Extensive biological activity investigations of the 1-cyanobenzimidazoles are being undertaken and will be reported in due course.

Experimental Section

General. Unless otherwise indicated, all reactions were carried out under a dry nitrogen atmosphere. DMF was freshly distilled from calcium hydride. The other reagents were used directly without further purification. Melting points (mp) were obtained on a B-540 Büchi melting-point apparatus and are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) data were recorded on a DPX-400 instrument with CDCl$_3$ or DMSO-d$_6$ as solvents and tetramethylsilane (TMS) as the internal standard. Chemical shifts are given in ppm and spin-spin coupling constants, $J$, are given in Hz. IR spectra were recorded on a Perkin Elmer 100 FT-IR spectrometer using KBr pellets. Mass spectra (MS) were recorded on a HP5989A mass spectrometer. Elemental analyses were carried out on a PE EA2400 CHN analyzer.

$N$-(2-Halophenyl)-$N'$-cyano-$S$-methylisothioureas (2a1,a2). Dimethyl cyanodithioimidocarbonate (1.46 g, 10 mmol) was dissolved in DMF (20 mL). To the stirred solution were added o-haloaniline (10 mmol) and Cs$_2$CO$_3$ (4.89 g, 15 mmol). The solution was kept at 100 °C for 8 h and then poured into ice water. Precipitates formed immediately and were collected by filtration. The crude products were purified by chromatography on silica gel with petroleum ether/ethyl acetate to afford the title compounds.

$N$-(2-Iodophenyl)-$N'$-cyano-$S$-methylisothiourea (2a1). Yellow solid, mp 178-180 °C, yield 41%; $^1$H NMR (DMSO-d$_6$) $\delta$: 2.63 (s, 3H), 7.12-7.14 (m, 1H), 7.36-7.48 (m, 2H), 7.92-7.94 (m,
N'-(2-Bromophenyl)-N'-cyano-S-methylisothiourea (2a2). Gray solid, mp 143-145 °C, yield 38%. 1H NMR (DMSO-d6) δ: 2.61 (s, 3H), 7.18-7.21 (m, 1H), 7.33-7.40 (m, 2H), 7.67-7.69 (m, 1H), 9.03 (s, 1H). 13C NMR (DMSO-d6) δ: 13.1, 107.4, 114.5, 123.2, 127.9, 131.0, 133.5, 155.4, 159.8. ESI-MS: [M+1]+ m/z 271.

Aryl guanidines (3a-g). A mixture of 2 (10 mmol) and a secondary amine (12 mmol) in ethanol (30 mL) was heated at reflux for 24 h, then the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to provide the desired aryl guanidines 3a-g.

N'-(2-Iodophenyl)-N'-cyanopiperidine-1-carboximidamide (3a1). Pale yellow solid, mp 88-89 °C, yield 67%. 1H NMR (DMSO-d6) δ: 1.57-1.59 (m, 6H), 3.51-3.53 (m, 4H), 6.96-7.00 (m, 1H), 7.20-7.22 (m, 1H), 7.35-7.39 (m, 1H), 7.84-7.86 (m, 1H), 9.07 (s, 1H). 13C NMR (DMSO-d6) δ: 24.4, 25.6 (2C), 49.5 (2C), 83.8, 115.7, 123.9, 128.8, 130.2, 138.8, 158.2, 159.7. ESI-MS: [M+1]+ m/z 355.

N'-(2-Bromophenyl)-N'-cyanopiperidine-1-carboximidamide (3a2). Grey solid, mp 59-61 °C, yield 58%. 1H NMR (DMSO-d6) δ: 1.56-1.58 (m, 6H), 3.48-3.51 (m, 4H), 7.09-7.11 (m, 1H), 7.24-7.26 (m, 1H), 7.31-7.33 (m, 1H), 7.61-7.64 (m, 1H), 8.45 (s, 1H). 13C NMR (DMSO-d6) δ: 24.5, 25.4 (2C), 49.8 (2C), 106.1, 114.4, 123.1, 128.2, 130.4, 133.7, 155.6, 158.4. ESI-MS: [M+1]+ m/z 308.

N'-(2-Iodophenyl)-N'-cyanopyrrolidine-1-carboximidamide (3b1). Pale yellow solid, mp 82-84 °C, yield 63%. 1H NMR (CDCl3, 400 MHz) δ: 1.93 (t, 4H), 3.44 (t, 4H), 6.91-6.94 (m, 1H), 7.34-7.36 (m, 2H), 7.82-7.84 (m, 1H), 9.12 (s, 1H). 13C NMR (CDCl3, 100 MHz) δ: 25.2 (2C), 49.3 (2C), 83.5, 116.4, 123.6, 128.7, 131.4, 139.5, 159.3, 162.6. ESI-MS: [M+1]+ m/z 341.

N'-(2-Bromophenyl)-N'-cyanopyrrolidine-1-carboximidamide (3b2). Gray solid, mp 55-58 °C, yield 55%. 1H NMR (CDCl3, 400 MHz) δ: 1.96 (t, 4H), 3.43 (t, 4H), 7.02-7.04 (m, 1H), 7.32-7.35 (m, 2H), 7.60-7.63 (m, 1H), 8.53 (s, 1H). 13C NMR (CDCl3, 100 MHz) δ: 25.5 (2C), 49.1 (2C), 108.1, 115.3, 122.1, 128.0, 131.9, 134.8, 156.5, 162.3. ESI-MS: [M+1]+ m/z 294.

N'-(2-Iodophenyl)-N'-cyanomorpholine-4-carboximidamide (3c). Pale yellow solid, mp 163-165 °C, yield 61%. 1H NMR (CDCl3, 400 MHz) δ: 3.54 (t, 4H), 3.66 (t, 4H), 6.98-7.01 (m, 1H), 7.24-7.26 (m, 1H), 7.36-7.39 (m, 1H), 7.84-7.87 (m, 1H), 9.26 (s, 1H). 13C NMR (CDCl3, 100 MHz) δ: 43.7 (2C), 63.9 (2C), 83.1, 116.0, 123.3, 128.3, 130.7, 139.0, 158.6, 160.1. ESI-MS: [M+1]+ m/z 357.

N'-(2-Iodophenyl)-N'-cyano-4-methylpiperazine-1-carboximidamide (3d). Pale yellow solid, mp 113-116 °C, yield 73%. 1H NMR (CDCl3, 400 MHz) δ: 2.20 (s, 3H), 2.35 (t, 4H), 3.57 (t, 4H), 6.96-6.99 (m, 1H), 7.21-7.23 (m, 1H), 7.35-7.37 (m, 1H), 7.83-7.85 (m, 1H), 9.10 (s, 1H). 13C NMR (CDCl3, 100 MHz) δ: 43.6, 45.7 (2C), 54.3 (2C), 83.7, 116.4, 123.1, 128.7, 131.2, 139.3, 158.5, 161.6. ESI-MS: [M+1]+ m/z 370.
1,1-Diethyl-2-(2-iodophenyl)-3-cyanoguanidine (3e). Pale yellow solid, mp 76-79 °C, yield 64%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 1.34 (t, 6H), 3.32 (q, 4H), 6.97-7.00 (m, 1H), 7.22-7.25 (m, 1H), 7.33-7.36 (m, 1H), 7.84-7.86 (m, 1H), 9.16 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 13.4 (2C), 43.0 (2C), 83.2, 116.3, 123.4, 128.8, 131.0, 139.2, 159.1, 162.3. ESI-MS: [M+1]$^+$ m/z 343.

1,1-Dibenzyl-2-(2-iodophenyl)-3-cyanoguanidine (3f). Pale yellow solid, mp 103-105 °C, yield 46%; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 4.18 (s, 4H), 6.97-7.00 (m, 1H), 7.22-7.27 (m, 5H), 7.31-7.38 (m, 7H), 7.84-7.86 (m, 1H), 9.19 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 50.5 (2C), 83.4, 116.2, 123.3, 126.9 (2C), 128.3 (4C), 128.6, 128.8 (4C), 131.1, 138.4 (2C), 139.3, 158.9, 161.7. ESI-MS: [M+1]$^+$ m/z 467.

1,1-Diphenyl-2-(2-iodophenyl)-3-cyanoguanidine (3g). Pale yellow solid, mp 121-123 °C, yield 48%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 6.97-7.00 (m, 1H), 7.03-7.07 (m, 2H), 7.15-7.26 (m, 5H), 7.31-7.39 (m, 5H), 7.82-7.85 (m, 1H), 9.22 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 83.2, 116.5, 119.2 (2C), 120.2 (4C), 123.7, 128.3, 130.0 (4C), 131.0, 139.6, 144.6 (2C), 159.2, 161.4. ESI-MS: [M+1]$^+$ m/z 439.

General procedure for copper-catalyzed intramolecular coupling reactions
A mixture of guanidine (0.5 mmol), CuI (0.025 mmol), 2,2'-biimidazole (0.05 mmol), Cs$_2$CO$_3$ (1.0 mmol) and DMF (5 mL) was heated at 80 °C for 10 h under a nitrogen atmosphere. The resulting suspension was cooled to room temperature, diluted with EtOAc, filtered through a pad of silica gel, and was heated at nitrogen atmosphere with cyclohexane/ethyl acetate to provide the desired product.

2-(Piperidin-1-yl)-1H-benzo[d]imidazole-1-carbonitrile (4a). White solid; mp 68-69 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 1.61-1.67 (m, 6H), 3.53-3.59 (m, 4H), 7.16-7.20 (m, 1H), 7.25-7.28 (m, 1H), 7.40-7.44 (m, 2H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 23.9, 25.1 (2C), 49.8 (2C), 105.6, 109.8, 117.9, 122.4, 125.9, 132.6, 141.4, 154.8. IR (KBr): 3120, 2939, 2262, 1465 cm$^{-1}$. ESI-MS: [M+1]$^+$ m/z 277. Anal. calcd. for C$_{13}$H$_{14}$N$_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 68.87; H, 6.17; N, 24.92.

2-(Pyrrolidin-1-yl)-1H-benzo[d]imidazole-1-carbonitrile (4b). White solid; mp 59-60 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 2.00 (t, 4H), 3.75 (t, 4H), 7.03-7.07 (m, 1H), 7.16-7.22 (m, 1H), 7.26-7.32 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 25.6 (2C), 49.0 (2C), 105.7, 109.4, 117.0, 121.2, 125.4, 132.4, 142.2, 151.5. IR (KBr): 3117, 2962, 2266, 1468 cm$^{-1}$. ESI-MS: [M+1]$^+$ m/z 213. Anal. calcd. for C$_{12}$H$_{12}$N$_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.76; H, 5.63; N, 26.56.

2-Morpholino-1H-benzo[d]imidazole-1-carbonitrile (4c). White solid; mp 83-85 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 3.75 (t, 4H), 3.91 (t, 4H), 7.01-7.05 (m, 1H), 7.13-7.18, (m, 1H), 7.27-7.31 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 44.3 (2C), 65.6 (2C), 105.2, 108.6, 117.1, 121.4, 125.8, 132.9, 143.1, 152.3. IR (KBr): 3123, 2965, 2261, 1463 cm$^{-1}$. ESI-MS: [M+1]$^+$ m/z 229. Anal. calcd. for C$_{12}$H$_{12}$N$_4$O: C, 63.15; H, 5.30; N, 24.55. Found: C, 62.96; H, 5.37; N, 24.72.

2-(4-Methylpiperazin-1-yl)-1H-benzo[d]imidazole-1-carbonitrile (4d). White solid; mp 78-81 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 2.23 (s, 3H), 2.47 (t, 4H), 3.92 (t, 4H), 7.00-7.06 (m, 1H), 7.05-7.13 (m, 2H), 7.22-7.27 (m, 2H), 7.33-7.36 (m, 1H), 7.83-7.86 (m, 1H), 8.91 (s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 23.3 (2C), 43.1 (2C), 83.2, 116.2, 123.4, 128.8, 131.0, 139.2, 141.3, 159.1, 162.3. ESI-MS: [M+1]$^+$ m/z 343.
7.15-7.20 (m, 1H), 7.28-7.34 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 42.3, 45.9 (2C), 54.1 (2C), 105.4, 108.9, 117.2, 121.5, 126.0, 133.2, 143.3, 152.6. IR (KBr): 3119, 2941, 2263, 1461 cm\(^{-1}\). ESI-MS: [M+1] \(^+\) \(m/z\) 242. Anal. calcd. for \(\mathrm{C}_{13}\mathrm{H}_{15}\mathrm{NS}\): C, 64.71; H, 6.27; N, 29.02. Found: C, 64.90; H, 6.23; N, 28.85.

2-(Diethylamino)-1H-benzo[d]imidazole-1-carbonitrile (4e). White solid; mp 72-74 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 1.32 (t, 6H), 3.76 (q, 4H), 7.03-7.06 (m, 1H), 7.19-7.25 (m, 1H), 7.27-7.34 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 13.7 (2C), 43.3 (2C), 105.6, 109.2, 117.2, 121.3, 125.8, 132.8, 143.0, 151.9. IR (KBr): 3121, 2970, 2265, 1464 cm\(^{-1}\). ESI-MS: [M+1] \(^+\) \(m/z\) 215. Anal. calcd. for \(\mathrm{C}_{13}\mathrm{H}_{14}\mathrm{N}_{5}\): C, 67.26; H, 6.59; N, 26.15. Found: C, 67.35; H, 6.64; N, 26.01.

2-(Dibenzylamino)-1H-benzo[d]imidazole-1-carbonitrile (4f). White solid; mp 113-115 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 4.64 (s, 4H), 7.05-7.08 (m, 1H), 7.14-7.19 (m, 1H), 7.23-7.32 (m, 4H), 7.34-7.37 (m, 8H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 50.5 (2C), 105.2, 108.7, 117.0, 121.1, 125.6, 126.6 (2C), 128.1 (4C), 128.5 (4C), 132.7, 138.1 (2C), 142.5, 151.7. IR (KBr): 3031, 2941, 2267, 1502, 1462 cm\(^{-1}\). ESI-MS: [M+1] \(^+\) \(m/z\) 339. Anal. calcd. for \(\mathrm{C}_{22}\mathrm{H}_{18}\mathrm{N}_{4}\): C, 78.08; H, 5.36; N, 16.56. Found: C, 78.37; H, 5.26; N, 16.33.

2-(Diphenylamino)-1H-benzo[d]imidazole-1-carbonitrile (4g). White solid; mp 156-159 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.00-7.06 (m, 3H), 7.13-7.23 (m, 5H), 7.29-7.38 (m, 6H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 105.7, 109.4, 117.0, 117.6 (2C), 119.3 (4C), 121.2, 125.4, 130.5 (4C), 132.4, 142.2, 146.1 (2C), 151.5. IR (KBr): 3125, 3023, 2262, 1499, 1465 cm\(^{-1}\). ESI-MS: [M+1] \(^+\) \(m/z\) 311. Anal. calcd. for \(\mathrm{C}_{20}\mathrm{H}_{14}\mathrm{N}_{4}\): C, 77.40; H, 4.55; N, 18.05. Found: C, 77.60; H, 4.62; N, 17.76.

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References