

A Novel Route to Imidoylbenzotriazoles and Their Application for the Synthesis of Enaminones

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1. General methods.

Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were obtained in CDCl_3 with TMS as the internal standard for ^1H (300 MHz) or the solvent as the internal standard for ^{13}C (75 MHz). THF and diethyl ether were dried over sodium / benzophenone and were used freshly distilled. Column chromatography was conducted on silica gel 200–425 mesh.

Materials. 1-Chloro-1*H*-benzotriazole [Hughes, T. V.; Hammond, S. D.; Cava, M. P. *J. Org. Chem.* **1998**, *63*, 401.] and *N*-phenyl-morpholine-4-carboxamide (**2i**) [Beaver, D. J.; Roman, D. P.; Stoffel, P. *J. J. Am. Chem. Soc.* **1957**, *79*, 1236.] were prepared according to the previously published procedures.

2. Characterization data for imidoylbenzotriazoles **3c,d,f,h,i**.

***N*-[Benzotriazol-1-yl(phenyl)methylidene]-4-chloroaniline (3c).** Yellow crystals from ethyl acetate / hexanes (80%), mp 139–141 °C; ^1H NMR δ 8.49 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.68–7.63 (m, 1H), 7.55–7.50 (m, 1H), 7.36–7.22 (m, 6H), 7.09–7.04 (m, 1H), 6.83 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ 115.3, 120.0, 121.3, 124.4, 125.7, 128.6, 129.0, 129.4, 131.5, 131.9, 136.5, 146.4, 146.6, 152.6. Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{ClN}_4$: C, 68.57; H, 3.94; N, 16.84. Found: C, 68.47; H, 4.32; N, 16.53.

***N*-[Benzotriazol-1-yl(phenyl)methylidene]-5-chloro-2-methylaniline (3d).** White microcrystals from ethyl acetate / hexanes (80%), mp 121–123 °C; ^1H NMR δ 8.56 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.68–7.62 (m, 1H), 7.55–7.50 (m, 1H), 7.44–7.34 (m, 5H), 7.20 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.57 (s, 1H), 2.18 (s, 3H); ^{13}C NMR δ 20.9, 115.5, 120.0, 122.2, 122.4, 125.7, 125.8, 128.1, 129.4, 129.5, 129.6, 130.6, 132.2, 137.2, 144.4, 146.5, 155.1. Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_4$: C, 69.26; H, 4.36; N, 16.15. Found: C, 68.95; H, 4.68; N, 16.08.

N-[1-(Benzotriazol-1-yl)ethylidene]ethylamine (3f). Red microcrystals from ethyl acetate / hexanes (40%), mp 79–80 °C (lit.⁹ 80–81 °C); ¹H NMR δ 8.48 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.57–7.52 (m, 1H), 7.45–7.40 (m, 1H), 3.66 (q, *J* = 7.2 Hz, 2H), 2.75 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H); ¹³C NMR δ 14.1, 16.1, 44.6, 115.7, 119.5, 124.9, 128.7, 131.4, 146.6, 153.4.

N-[1-(Benzotriazol-1-yl)ethylidene]-4-methoxyaniline (3h). White microcrystals from hexanes / ethyl acetate (81%), mp 128–129 °C; ¹H NMR δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.61–7.56 (m, 1H), 7.49–7.44 (m, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 2.77 (s, 3H); ¹³C NMR δ 16.2, 55.5, 114.5, 115.8, 119.7, 121.6, 125.3, 129.1, 131.3, 140.4, 146.6, 154.1, 156.7. Anal. Calcd for C₁₅H₁₄N₄O: C, 67.65; H, 5.30; N, 21.04. Found: C, 67.43; H, 5.43; N, 20.61.

N-[Benzotriazol-1-yl(morpholin-4-yl)methylidene]aniline (3i). White microcrystals from hexanes / ethyl acetate (82%), mp 91–92 °C; ¹H NMR δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.38–7.28 (m, 3H), 6.96–6.91 (m, 2H), 6.77–6.72 (m, 1H), 6.56 (d, *J* = 7.4 Hz, 2H), 3.85 (br s, 4H), 3.42 (br s, 4H); ¹³C NMR δ 46.8, 66.3, 110.4, 119.9, 121.2, 123.2, 124.7, 128.6, 128.7, 132.0, 142.2, 144.7, 146.6. Anal. Calcd for C₁₇H₁₇N₅O: C, 66.43; H, 5.57; N, 22.79. Found: C, 66.06; H, 5.57; N, 22.62.