**General Methods.** Melting points were determined with a capillary melting point apparatus equipped with a digital thermometer. $^1H$ and $^{13}C$ NMR spectra were collected on a 300 MHz NMR spectrometer (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Column chromatography was conducted with silica gel grade 230–400 mesh for the *N*-aryl substituted imidoylbenzotriazoles or with basic alumina for the *N*-alkyl substituted imidoylbenzotriazoles with hexanes and ethyl acetate gradients. Solvents were distilled before use.

**General Procedure for the Preparation of Compounds 5.** The corresponding oxime **2** (1 mmol), BtTs (1 mmol), *t*-BuOK (1 mmol) and crown ether 18C6 (0.1 mmol) were stirred and heated in the adequate solvent (10 mL) (see Table 1). After completion of the reaction (TLC), the mixture was allowed to reach room temperature, and hydrolyzed by $H_2O$ (10 mL). After extraction, the organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was subjected to purification (method A: extraction with hot hexanes, method B: flash column chromatography).

**1-(3,4,5,6-Tetyrahydro-2*H*-azepin-7-yl)-1*H*-1,2,3-benzotriazole (5a):** method A; 55% yield; yellow solid, mp 101.0 °C; $^1H$ NMR δ 1.71-1.81 (m, 4H), 1.90-2.00 (m, 2H), 3.50-3.54 (m, 2H), 3.88-3.91 (m, 2H), 7.42 (dd, $J$ = 7.3 Hz, $J$ = 7.7 Hz, 1H), 7.54 (dd, $J$ = 7.2 Hz, $J$ = 7.9 Hz, 1H), 8.07 (d, $J$ = 8.2 Hz, 1H), 8.44 (d, $J$ = 8.4 Hz, 1H); $^{13}C$ NMR δ 23.2, 26.4, 29.5, 31.1, 50.4, 115.7, 119.4, 124.9, 128.6, 131.3, 146.8, 162.0. Anal. Calcd for $C_{12}H_{14}N_4$: C, 67.27; H, 6.59; N, 26.15. Found: C, 66.90; H, 6.84; N, 25.77.

**1-(3,4,5,6-Tetyrahydro-2-pyridinyl)-1*H*-1,2,3-benzotriazole (5b):** method A; 50% yield; yellow solid, mp 74.0 °C; $^1H$ NMR δ 1.75-1.86 (m, 2H), 1.91-2.06 (m, 2H), 3.13-

3.26 (m, 2H), 3.87-3.99 (m, 2H), 7.41 (dd, $J$ = 7.4 Hz, $J$ = 7.9 Hz, 1H), 7.53 (dd, $J$ = 7.2 Hz, $J$ = 7.9 Hz, 1H), 8.07 (d, $J$ = 8.1 Hz, 1H), 8.43 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR δ 19.5, 21.9, 26.1, 48.0, 115.3, 119.5, 124.9, 128.6, 131.1, 146.3, 155.9. Anal. Calcd for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 66.21; H, 6.30.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl)ethylidene]aniline (5c)**: method B; 60% yield; yellow solid, mp 106.0 °C (lit.[95H231-15] mp 108.0 °C); $^1$H NMR δ 2.76 (s, 3H), 6.95 (d, $J$ = 7.6 Hz, 2H), 7.19 (dd, $J$ = 7.2 Hz, $J$ = 7.3 Hz, 1H), 7.40-7.51 (m, 3H), 7.60 (dd, $J$ = 7.3 Hz, $J$ = 7.7 Hz, 1H), 8.13 (d, $J$ = 8.1 Hz, 1H), 8.54 (d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR δ 16.2, 115.7, 119.7, 120.2, 124.3, 125.3, 129.2, 131.3, 146.6, 147.3, 154.0.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methylidene]aniline (5d):** method B; 70% yield; yellow solid, mp 129.0 °C (lit.[95H231-15] mp 130.0-132.0 °C); $^1$H NMR δ 6.85 (d, $J$ = 7.9 Hz, 2H), 7.03-7.06 (m, 1H), 7.21 (d, $J$ = 7.4 Hz, 2H), 7.35-7.47 (m, 5H), 7.51 (dd, $J$ = 7.4 Hz, $J$ = 7.7 Hz, 1H), 7.64 (dd, $J$ = 7.2 Hz, $J$ = 7.9 Hz, 1H), 8.16 (d, $J$ = 8.1 Hz, 1H), 8.49 (d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR δ 115.3, 120.0, 120.5, 121.4, 124.2, 125.5, 128.2, 128.8, 129.2, 130.1, 130.3, 132.0, 146.4, 146.4, 146.9, 153.7.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl)ethylidene]methanamine (5e):** method A; 84% yield; yellow solid, mp 52.0-53.0 °C; $^1$H NMR δ 2.76 (s, 3H), 3.44 (s, 3H), 7.42 (dd, $J$ = 7.3 Hz, $J$ = 7.9 Hz, 1H), 7.54 (dd, $J$ = 7.3 Hz, $J$ = 7.9 Hz, 1H), 8.07 (d, $J$ = 8.2 Hz, 1H), 8.43(d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR δ 13.9, 37.2, 115.5, 119.5, 124.9, 128.7, 129.5, 146.5, 155.4. HRMS(EI) Calcd for $C_9H_{12}N_4$(M+2): 176.0984. Found: 176.1062.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methylidene]pyridin-2-amine (5f):** method B; 50% yield; beige solid, mp 125.0 °C; $^1$H NMR δ 6.73 (d, $J$ = 8.2 Hz, 1H), 6.94 (dd, $J$ = 5.5 Hz, $J$ = 7.5 Hz, 1H), 7.32 (d, $J$ = 7.5 Hz, 2H), 7.38-7.39 (dd, $J$ = 1.3 Hz, $J$ =

8.8 Hz, 3H), 7.51 (td, $J$ = 7.7 Hz, $J$ = 7.9 Hz, 2H), 7.62 (t, $J$ = 7.9 Hz, 1H), 8.14 (d, $J$ = 8.2 Hz, 1H), 8.34 (d, $J$ = 4.9 Hz, 1H), 8.53(d, $J$ = 8.5 Hz, 1H); $^{13}$C NMR δ 115.5, 116.0, 119.4, 119.9, 125.7, 128.0, 129.4, 130.0, 130.4, 130.5, 131.9, 137.6, 146.4, 148.7, 155.9, 159.8. Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.22; H, 4.38; N, 23.40. Found: C, 72.30; H, 4.50; N, 23.26.

**1-(2-Methyl-3,4,5,6-tetyrahydro-2*H*-azepin-7-yl)-1*H*-1,2,3-benzotriazole (5g):** method B; 87% yield; beige solid, mp 106.0-107.0 °C; $^1$H NMR δ 1.38-1.59 (m, 5H), 1.72-1.90 (m, 2H), 1.90-2.11 (m, 2H), 2.89 (t, $J$ = 13 Hz, 1H), 3.80-3.90 (m, 1H), 4.09-4.19 (m, 1H), 7.42 (dd, $J$ = 7.5 Hz, $J$ = 7.6 Hz, 1H), 7.54 (dd, $J$ = 7.3 Hz, $J$ = 8.0 Hz, 1H), 8.07 (d, $J$ = 8.3 Hz, 1H), 8.47 (d, $J$ = 8.3 Hz, 1H); $^{13}$C NMR δ 22.8, 25.5, 29.5, 30.1, 34.0, 56.0, 115.9, 119.4, 124.9, 128.6, 131.4, 146.9, 159.4. Anal. Calcd for $C_{13}H_{16}N_4$: C, 68.39; H, 7.06; N, 24.54. Found: C, 68.18; H, 7.45; N, 24.40.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-2,2-dimethylpropylidene]methanamine (5h):** method B; 60% yield; colorless oil; $^1$H NMR δ 1.50 (s, 9H), 2.85 (s, 3H), 7.40 (dd, $J$ = 7.4 Hz, $J$ = 7.7 Hz, 1H), 7.52 (dd, $J$ = 7.1 Hz, $J$ = 7.9 Hz, 1H), 8.06 (d, $J$ = 8.3 Hz, 1H), 8.44 (d, $J$ = 8.3 Hz, 1H); $^{13}$C NMR δ 18.2, 30.6, 54.6, 116.0, 119.5, 124.7, 128.4, 131.4, 146.6, 150.5. Anal. Calcd for $C_{12}H_{16}N_4$: C, 66.64; H, 7.46; N, 25.90. Found: C, 66.70; H, 7.73; N, 26.26.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl)ethylidene]-*N*-ethylamine (5i):** method B; 45% yield; white solid, mp 80.0-81.0 °C; $^1$H NMR δ 1.40 (t, $J$ = 7.2 Hz, 3H), 2.75 (s, 3H), 3.66 (q, $J$ = 7.2 Hz, 2H), 7.42 (dd, $J$ = 7.3 Hz, $J$ = 7.9 Hz, 1H), 7.54 (dd, $J$ = 7.4 Hz, $J$ = 7.4 Hz, 1H), 8.07 (d, $J$ = 8.3 Hz, 1H), 8.48 (d, $J$ = 8.3 Hz, 1H); $^{13}$C NMR δ 14.1, 16.1,

44.6, 115.7, 119.4, 124.9, 128.6, 131.3, 146.5, 153.4. Anal. Calcd for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43; N, 29.77. Found: C, 63.84; H, 6.59.

***N*-[(E)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-phenylethylidene](phenyl)methanamine (5j):** method B; 20% yield; yellow oil; $^1$H NMR δ 4.79 (s, 2H), 4.97 (s, 2H), 7.20-7.35 (m, 6H), 7.35-7.45 (m, 5H), 7.54 (dd, *J* = 7.2 Hz, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H); $^{13}$C NMR δ 34.0, 53.9, 115.7, 119.6, 125.1, 126.9, 127.0, 127.5, 128.5, 128.6, 128.9, 129.0, 131.5, 134.5, 139.3, 146.7, 155.5. Anal. Calcd for $C_{21}H_{18}N_4$: C, 77.28; H, 5.56; N, 17.17. Found: C, 77.21; H, 5.61.

***N*-[(E,Z)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-methylpropylidene]propan-2-amine (5k):** method B; 35% yield; yellow oil; $^1$H NMR δ 1.10 (d, *J* = 6.2 Hz, 6H), 1.17 (d, *J* = 7.1 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.53 (d, *J* = 6.9 Hz, 6H), 3.10 (h, *J* = 6.0 Hz, 2H), 3.80 (h, *J* = 7.0 Hz, 1H), 4.13 (h, *J* = 6.0 Hz, 1H), 7.34-7.42 (m, 3H), 7.49-7.54 (m, 2H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H); $^{13}$C NMR δ. [19.4] 19.7, [23.7] 24.3, 29.0 [36.8], 49.6 [51.2], [109.4] 115.4, 119.2 [120.1], [124.2] 124.5, 128.2, 132.1 [132.6], [144.6] 145.5, [151.4] 158.0. Anal. Calcd for $C_{13}H_{18}N_4$: C, 67.79; H, 7.88; N, 24.33. Found: N, 24.46.

***N*-[(E,Z)-1-(1*H*-1,2,3-Benzotriazol-1-yl(cyclopropyl)methylidene]cyclopropanamine (5l):** method B; 64% yield; white solid, mp 59.0 °C; $^1$H NMR δ 0.77-0.80 (m, 1H), 0.90-1.17 (m, 12H), 1.21-1.27 (m, 3H), 1.92-2.00 (m, 1H), 2.22-2.31 (m, 1H), 2.50-2.55 (m, 1H), 3.58-3.64 (m, 1H), 7.35-7.66 (m, 5H), 8.04-8.16 (m, 3H); $^{13}$C NMR δ 7.8 [8.6], [9.6] 9.7, 10.9 [17.1], 32.2 [33.4], [110.7] 114.9, 119.5 [120.1], [124.4] 124.6, 128.3, 131.7, 145.9, 154.8. Anal. Calcd for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 68.84; H, 6.02.