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Synthesis of *N*-Cycloalkenylazoles

Alan R. Katritzky,*,‡ Rexiat Maimait,‡ Yong-Jiang Xu,‡ and Young Soo Gyoung§

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Department of Chemistry, Kangnung National University, Kangnung, Kangwondo 210-702, Korea

katritzky@chem.ufl.edu

Received May 15, 2002

N-(1-Cycloalkenyl)pyrroles **3a**,**b**, -pyrazoles **6a**,**b**, and -imidazoles **9a**,**b** were synthesized via elimination of benzotriazole or 5-phenyltetrazole from the corresponding 1-[1-(heterocycyl)cycloalkyl]-benzotriazoles **2**, **5**, and **8** or 1-[1-(heterocycyl)cyclohexyl]-5-phenyltetrazole (**12** and **14**). Intermediates **2**, **5**, **8**, **12** and **14** were obtained by cyclizations of dihaloalkanes with *N*-(benzotriazol-1-ylmethyl)heterocycles, 1-imidazol-1-ylmethyl-5-phenyltetrazole (**11**), or 1-pyrazol-1-ylmethyl-5-phenyltetrazole (**13**) in the presence of *n*-BuLi.

Introduction

Molecules containing *N*-(1-cycloalkenyl)heterocycles have potential biological activity; thus, 1-[2-(methylsulfanyl)-1-cyclopentenyl]imidazole (**I**) and 1-[2-(2-thienyl)-1-cyclopentenyl]imidazole (**II**) have been reported as neuronal injury inhibitors[1] (Figure 1); however, few synthetic approaches to compounds of this type have been reported. No literature was found for *N*-(1-cycloalkenyl)-pyrroles **3a**,**b**. A single paper reported *N*-(1-cyclopent-1-enyl)pyrazole (**6a**) and *N*-(1-cyclohex-1-enyl)pyrazole (**6b**), which were prepared in 73% and 78% yields, respectively, from the corresponding 1,1-bispyrazolylcycloalkanes[2] (Scheme 1, i). *N*-(1-Cyclohex-1-enyl)imidazole (**9b**) was formed (9% yield) as a byproduct in the preparation of 1,1-bis(imidazol-1-yl)cyclohexane[3] (Scheme 1, ii). Compound **II** was obtained (64%) using 1-(2-bromocyclopenten-1-yl)imidazole, $(Ph_3P)_4Pd$, and 2-thienylboronic acid with $NaHCO_3$ in DME/H_2O in a German patent[1] (Scheme 1, iii), which also describes the synthesis of **I**.

N-Vinylpyrroles are extensively studied synthetic intermediates:[4] General routes include (Scheme 2); (i) cyclization of ketoximes and acetylenes in a strong base−DMSO system;[4] (ii) vinylation of pyrrole in superbase media;[5] (iii) reactions[6,7] of potassium pyrrole with epoxides in dry DMF. 1-Vinylimidazoles were also made from the potassium imidazole and corresponding epoxides.[7,8] A recent paper reported the synthesis of

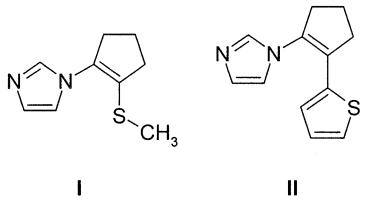
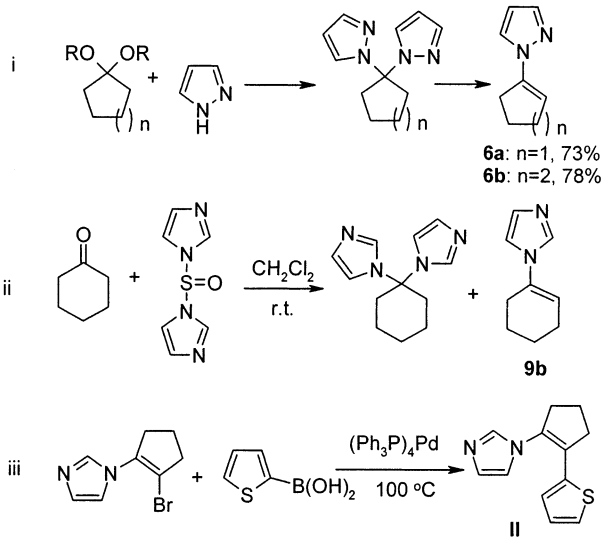


FIGURE 1.

SCHEME 1



N-vinyl derivatives of nucleobases via direct vinyl exchange of the acetyl group of vinyl acetate with pyrimidine and purine bases using TMSOTf as acid catalyst[9] (Scheme 2, iv). Palladium−phosphine complexes catalyzed vinylation of various azoles with vinyl bromides to

‡ University of Florida.
§ Kangnung National University.

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(5) Trofimov, B. A.; Tarasova, O. A.; Mikhaleva, A. I.; Kalinina, N. A.; Sinegovskaya, L. M.; Henkelmann, J. *Synthesis* **2000**, 1585.
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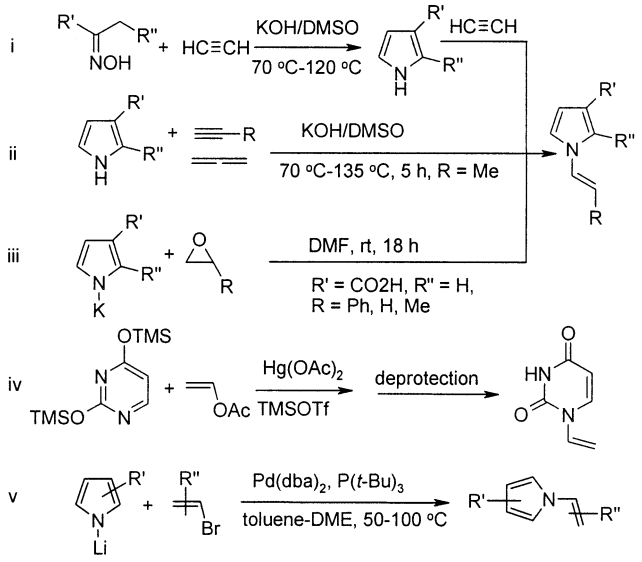
10.1021/jo020336m CCC: $22.00
Published on Web 10/10/2002

SCHEME 2



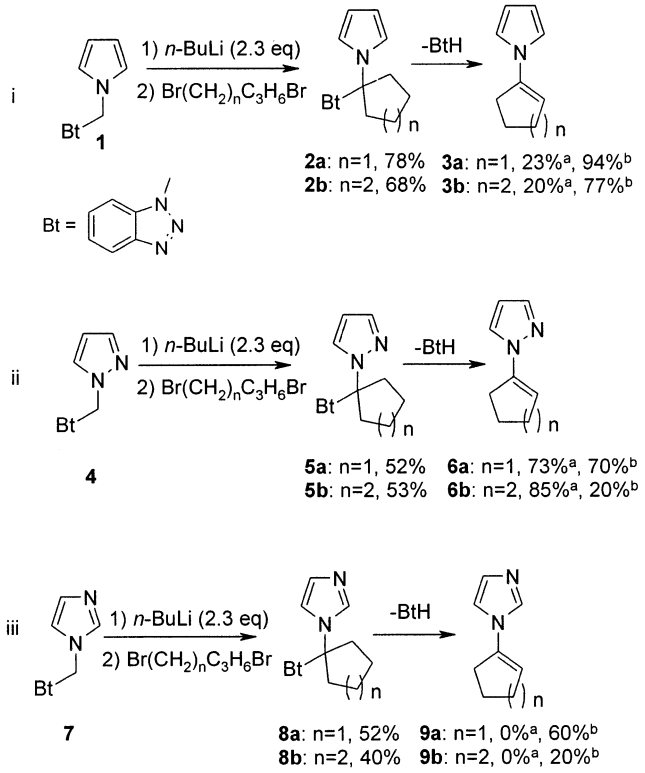
give *N*-vinylazoles in 30−99% yields (Scheme 2, v).[10] These routes, however, are not directly applicable for the synthesis of *N*-(1-cycloalkenyl)pyrroles or -imidazoles. We now report a new approach to *N*-(1-cycloalkenyl)heteroaromatics using benzotriazole methodology.

Results and Discussion

Synthesis of Cyclic Compounds 2, 5, 8, 12 and 14. *N*-(Benzotriazol-1-ylmethyl)heterocycles were previously synthesized in our group.[11] 1-(Imidazol-1-yl)methyl-5-phenyltetrazole (**11**) was synthesized by the reaction of imidazole with 1-chloromethyl-5-phenyltetrazole in the presence of sodium hydroxide in 77% yield, and compound **13** was similarly made from pyrazole and 1-chloromethyl-5-phenyltetrazole in 64% yield. Precursor molecule **1, 4**, **7**, **11**, or **13** was treated with 2.3 equiv of *n*-BuLi in THF at −78 °C for 1 h followed by the addition of 1,4-dibromobutane or 1,5-dibromopentane to yield the desired 5- or 6-membered cyclic ring systems in moderate to good yields (Schemes 3 and 4). The structures of products **2**, **5**, **8**, **12**, and **14** are clearly characterized by ^{1}H and ^{13}C NMR and microanalysis. The ^{1}H NMR spectra of the cyclization products showed the absence of any singlet peak around 6.5 ppm that was ascribed to BtCH_2N in the precursor molecules. The expected four separate groups of peaks (for a 6-membered ring) or three groups of peaks (for a 5-membered ring) appear in the aliphatic region.

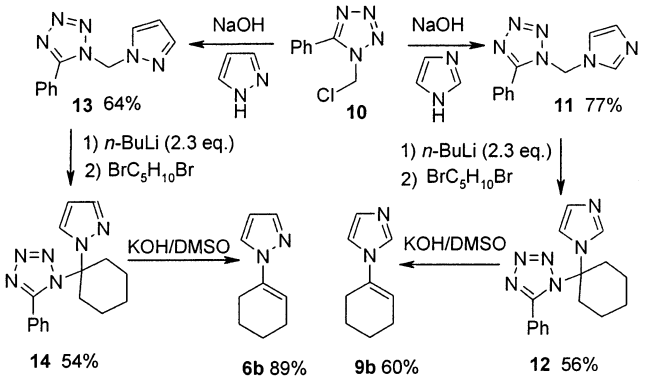
Synthesis of *N*-(1-Cycloalkenyl)pyrroles, -pyrazoles, and -imidazoles. Two methods have been used in the present work for the removal of benzotriazole to form the *N*-(1-cycloalkenyl)heterocycles: (i) Lewis acid promoted removal of the benzotriazolyl group (method A);[12] (ii) base/DMSO effected removal of the benzotriazole or tetrazole group based on their low pK_a value (method

SCHEME 3[a]



[a] Key: (a): yields obtained using method A; (b) yields obtained using method B.

SCHEME 4



B). Using the first approach, **6a** and **b** were obtained in 73% and 85% yields by heating of compounds **5a** and **5b**, respectively, with $ZnBr_2$ in toluene at 80 °C for 30 min (Scheme 3, ii). However, compounds **3a** and **3b** were obtained in only 23% and 20% yields using the same reaction system starting from compounds **2a** and **2b** (Scheme 3, i). Moreover, no desired *N*-(1-cycloalkenyl)-imidazoles were detected in $ZnBr_2$/toluene, $ZnBr_2$/THF, or $ZnBr_2/CH_2Cl_2$ reaction systems after exploring various reaction conditions (varying time and temperature) starting from compound **8** or from **12** in which the tetrazole group was anticipated to be removed more easily than benzotriazole.

Fortunately, the desired compounds **9a**,**b** were obtained in good yields by the reaction of **8a** (Scheme 3, iii) and **12** (Scheme 4) with KOH/DMSO mixture at 130 °C for 3 h. The expected pyrrole products **3a**,**b** were

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obtained in 94% and 77% yields, respectively, as shown in Scheme 3, i, in this KOH/DMSO mixture. The pyrazole products **6a**,**b** were also formed under this reaction mixture, but the yields were lower than that obtained in the $ZnBr_2$/toluene system (Scheme 3, ii). However, **6b** was obtained in 89% yield from **14** in KOH/DMSO mixture (Scheme 4). The reasons for these variations in yields are unknown.

The structures of products were fully supported by their ^{1}H and ^{13}C NMR and microanalysis data. In the proton NMR spectrum of **3a**, a multiplet at 5.48−5.50 ppm was ascribed to the vinylic proton in the 5-membered ring. For **6a** and **9a**, a multiplet at 5.85−5.89 ppm and 5.65−5.68 ppm also confirmed the formation of the *N*-(1-cyclopentenyl)heterocycles. Similarly, a multiplet at 5.71−5.74 ppm in the ^{1}H NMR of **3b** was due to the vinylic proton in the 6-membered ring. For **6b** and **9b**, a multiplet at 6.10−6.13 ppm and 5.82−5.85 ppm also characterized the structures of *N*-(1-cyclohexenyl)heterocycles.

In summary, 1-[1-(heterocycyl)cycloalkyl]benzotriazoles and 1-[1-(heterocycyl)cyclohexyl]-5-phenyltetrazoles were easily obtained via cyclization of the corresponding starting materials in good yields. The benzotriazolyl or 5-phenyltetrazolyl groups in these compounds can be eliminated to give *N*-(1-cycloalkenyl)azoles, a compound class previously rarely reported.

Experimental Section

General Comments. Tetrahydrofuran was distilled under nitrogen from sodium-benzophenone immediately before use. All reactions with moisture-sensitive compounds were carried out under a dry argon atmosphere.

General Procedure for the Synthesis of Compounds 2, 5, 8, 12, and 14. The corresponding starting material (10.0 mmol) was dissolved in THF (180 mL) at −78 °C, and *n*-BuLi (23.0 mmol, 14.4 mL, 1.6 M in hexane) was added dropwise. The resulting solution was stirred for 45−60 min. An appropriate dibromoalkane (1.2 equiv, 12.0 mmol) was then added dropwise. The mixture was stirred overnight and allowed to come to 20 °C. The reaction was quenched with 20 mL of water, and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was dried over $MgSO_4$ and concentrated to give a brown oil. The product was purified by column chromatography on silica gel.

1-[1-(1*H*-Pyrrol-1-yl)cyclopentyl]-1*H*-1,2,3-benzotriazole (2a): white prisms (78%) (from ethyl acetate/hexanes); mp 120−123 °C; ^{1}H NMR δ 1.93−1.98 (m, 4H), 2.73−2.82 (m, 2H), 3.11−3.20 (m, 2H), 6.20 (t, J = 2.1 Hz, 2H), 6.87 (t, J = 2.1 Hz, 2H), 6.90 (d, J = 5.4 Hz, 1H), 7.26−7.33 (m, 2H), 8.00−8.04 (m, 1H); ^{13}C NMR δ 22.2, 38.6, 85.3, 109.6, 110.8, 119.0, 119.9, 124.0, 127.5, 131.7, 146.8. Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.20. Found: C, 71.12; H, 6.82; N, 22.23.

1-[1-(1*H*-Pyrrol-1-yl)cyclohexyl]-1*H*-1,2,3-benzotriazole (2b): white crystals (68%) (from ethyl acetate/hexanes); mp 120−122 °C; ^{1}H NMR δ 1.56−174 (m, 4H), 1.78−1.90 (m, 2H), 2.60−2.75 (m, 2H), 2.98−3.06 (m, 2H), 6.28 (br s, 2H), 6.32 (d, J = 8.1 Hz, 1H), 6.95 (br s, 2H), 7.18−7.29 (m. 2H), 8.00 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 22.4, 24.6, 37.4, 78.5, 109.8, 111.0, 118.8, 119.7, 123.8, 127.5, 131.6, 146.2. Anal. Calcd for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04. Found: C, 71.77; H, 6.81; N, 20.77.

1-[1-(1*H*-Pyrazol-1-yl)cyclopentyl]-1*H*-1,2,3-benzotriazole (5a): white prisms (52%) (from ethyl acetate/hexanes); mp 119−121 °C; ^{1}H NMR δ 1.92−1.97 (m, 4H), 3.12−3.28 (m, 4H), 6.27 (t, J = 2.1 Hz, 1H), 7.30−7.38 (m, 2H), 7.40−7.48 (m, 2H), 7.52−7.58 (m, 1H), 7.98−8.03 (m, 1H); ^{13}C NMR δ 22.2, 37.8, 86.9, 107.6, 111.6, 119.9, 124.1, 127.5, 127.7, 131.8, 139.1, 146.8. Anal. Calcd for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65. Found: C, 66.32; H, 6.10; N, 27.66.

1-[1-(1*H*-Pyrazol-1-yl)cyclohexyl]-1*H*-1,2,3-benzotriazole (5b): white prisms (53%) (from ethyl acetate/hexanes); mp 149−151 °C; ^{1}H NMR δ 1.55−1.82 (m, 6H), 2.97−3.11 (m, 4H), 6.33 (t, J = 1.8 Hz, 1H), 7.07−7.11 (m, 1H), 7.26−7.31 (m, 2H), 7.51 (d, J = 2.4 Hz, 1H), 7.63 (br s, 1H), 7.98−8.03 (m, 1H); ^{13}C NMR δ 22.2, 24.6, 36.2, 80.3, 107.5, 111.6, 119.9, 123.9, 127.4, 127.5, 131.6, 139.3, 146.5. Anal. Calcd for $C_{15}H_{17}N_5$: C, 67.39; H, 6.41; N, 26.20. Found: C, 67.43; H, 6.30; N, 26.43.

1-[1-(1*H*-Imidazol-1-yl)cyclopentyl]-1*H*-1,2,3-benzotriazole (8a): white prisms (52%) (from chloroform); mp 144−148 °C; ^{1}H NMR δ 1.94−2.04 (m, 4H), 2.78−2.90 (m, 2H), 3.19−3.28 (m, 2H), 7.00 (s, 1H), 7.04−7.14 (m, 2H), 7.32−7.40 (m, 2H), 7.81 (s, 1H), 8.02−8.10 (m, 1H); ^{13}C NMR δ 22.0, 38.4, 83.9, 110.3, 117.4, 120.4, 124.4, 128.1, 130.5, 131.3, 135.1, 147.0. Anal. Calcd for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65. Found: C, 66.34; H, 6.35; N, 27.50.

1-[1-(1*H*-Imidazol-1-yl)cyclohexyl]-1*H*-1,2,3-benzotriazole (8b): white prisms (40%) (from chloroform); mp 165−167 °C; ^{1}H NMR δ 1.60−1.90 (m, 6H), 2.62−2.74 (m, 2H), 3.12−3.24 (m, 2H), 6.76−6.84 (m, 1H), 7.00 (s, 1H), 7.10 (s, 1H), 7.29−7.36 (m, 2H), 7.86 (s, 1H), 8.02−8.10 (m, 1H); ^{13}C NMR δ 22.2, 24.4, 37.0, 77.6, 110.5, 116.8, 120.4, 124.3, 128.0, 130.4, 131.2, 134.9, 146.6. Anal. Calcd for $C_{15}H_{17}N_5$: C, 67.39; H, 6.41; N, 26.20. Found: C, 67.67; H, 6.59; N, 26.52.

1-[1-(1*H*-Imidazol-1-yl)cyclohexyl]-5-phenyl-1*H*-1,2,3,4-tetrazole (12): white needles (56%) (from chloroform); mp 105−106 °C; ^{1}H NMR δ 1.40−1.90 (m, 6H), 2.62−2.76 (m, 2H), 3.20−3.54 (m, 2H), 7.04 (s, 1H), 7.19 (s, 1H), 7.44−7.54 (m, 3H), 7.88 (s, 1H), 8.08−8.18 (m, 2H); ^{13}C NMR δ 21.9, 24.1, 35.6, 78.1, 116.0, 126.9, 127.0, 128.9, 130.0, 130.6, 134.4, 165.1. Anal. Calcd for $C_{16}H_{18}N_6$: C, 65.29; H, 6.16; N, 28.55. Found: C, 65.14; H, 6.38; N, 28.43.

1-[1-(1*H*-Pyrazol-1-yl)cyclohexyl]-5-phenyl-1*H*-1,2,3,4-tetrazole (14): white prisms (54%) (ethyl acetate/hexanes); mp 111−113 °C; ^{1}H NMR δ 1.50−1.80 (m, 6H), 2.90−3.20 (m, 4H), 6.31 (br s, 1H), 7.40−7.48 (m, 3H), 7.56 (br s, 1H), 7.74 (d, J = 2.4 Hz, 1H), 8.10−8.18 (m, 2H); ^{13}C NMR δ 22.0, 24.3, 35.1, 81.3, 106.9, 127.0, 127.2, 127.3, 128.8, 130.3, 140.2, 164.7. Anal. Calcd for $C_{16}H_{18}N_6$: C, 65.29; H, 6.16; N, 28.55. Found: C, 65.67; H, 6.03; N, 28.71.

Typical Procedure for the Synthesis of *N*-Cycloalkenylazoles. Method A. Compound **2a** (0.25 g, 1 mmol) and $ZnBr_2$ (0.45 g, 2 mmol) were placed in a dry flask under argon, 5 mL of toluene was added, and the mixture was heated at 80 °C for 45 min. The reaction mixture was then cooled to room temperature, extracted with ethyl ether, dried ($MgSO_4$), and concentrated to give a white solid that was purified by column chromatography with hexane as eluent to give 30 mg of white powder.

Method B. Compound **2a** (0.10 g, 0.4 mmol) was dissolved in 5 mL of dry DMSO, and KOH powder (0.10 g, 1.6 mmol, 86%) was added. The resulting mixture was heated at 110 °C for 3 h under nitrogen atmosphere with stirring. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2, the organic layer was washed with water (5 × 5 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure in an ice−water bath. The product was purified by column chromatography on silica gel using 5% ethyl ether in pentane.

***N*-(1-Cyclopenten-1-yl)-1*H*-pyrrole (3a):** white solid (from pentane); mp 32−34 °C; ^{1}H NMR δ 1.99−2.10 (m, 2H), 2.46−2.51 (m, 2H), 2.73−2.79 (m, 2H), 5.48−5.50 (m, 1H), 6.21 (t, J = 2.1 Hz, 2H), 6.91 (t, J = 2.1 Hz, 2H); ^{13}C NMR δ 22.0, 30.5, 31.8, 109.2, 109.3, 118.7, 140.1. Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.98; H, 8.63; N, 10.39.

***N*-(1-Cyclohexen-1-yl)-1*H*-pyrrole (3b):** colorless oil; ^{1}H NMR δ 1.61−1.69 (m, 2H), 1.77−1.85 (m, 2H), 2.14−2.21 (m, 2H), 2.42−2.47 (m, 2H), 5.71−5.74 (m, 1H), 6.18−6.20 (m, 2H), 6.88−6.90 (m, 2H); ^{13}C NMR δ 22.0, 22.6, 24.2, 27.1, 108.6,

112.8, 117.9, 136.2; HRMS calcd for $C_{13}H_{13}N$ (M) 147.1048, found 147.1087.

***N*-(1-Cyclopenten-1-yl)-1*H*-pyrazole (6a):**[2] colorless oil; ^{1}H NMR δ 2.04−2.14 (m, 2H), 2.50−2.58 (m, 2H), 2.83−2.91 (m, 2H), 5.85−5.89 (m, 1H), 6.32−6.33 (m, 1H), 7.59 (br d, J = 2.7 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 22.1, 30.7, 31.4, 106.3, 112.3, 127.2, 140.3, 140.4.

***N*-(1-Cyclohexen-1-yl)-1*H*-pyrazole (6b):**[2] colorless oil; ^{1}H NMR δ 1.63−1.71 (m, 2H), 1.80−1.88 (m, 2H), 2.19−2.26 (m, 2H), 2.55−2.61 (m, 2H), 6.10−6.13 (m, 1H), 6.30−6.31 (m, 1H), 7.58 (br d, J = 1.8 Hz, 1H), 7.61 (dd, J = 2.4, 0.6 Hz, 1H); ^{13}C NMR δ 21.9, 22.4, 24.0, 26.0, 105.8, 113.9, 125.8, 136.5, 139.6.

***N*-(1-Cyclopenten-1-yl)-1*H*-imidazole (9a):** off-white prisms (ethyl acetate/hexanes); mp 40−42 °C; ^{1}H NMR δ 2.04−2.14 (m, 2H), 2.48−2.55 (m, 2H), 2.74−2.81 (m, 2H), 5.65−5.68 (m, 1H), 7.08 (br s, 1H), 7.14−7.16 (m, 1H), 7.67 (br s, 1H); ^{13}C NMR δ 21.8, 30.4, 31.7, 113.3, 116.9, 129.7, 135.1, 136.9; HRMS calcd for $C_8H_{10}N_2$ (M) 134.0844, found 134.0856.

***N*-(1-Cyclohexen-1-yl)-1*H*-imidazole (9b):**[3] brown oil; ^{1}H NMR δ 1.65−1.71 (m, 2H), 1.78−1.86 (m, 2H), 2.18−2.22 (m, 2H), 2.40−2.44 (m, 2H), 5.82−5.85 (m, 1H), 7.08 (s, 1H), 7.09 (s, 1H), 7.67 (s, 1H); ^{13}C NMR δ 21.4, 22.1, 23.8, 27.1, 116.2, 116.4, 129.0, 133.5, 134.2.

General Procedure for the Synthesis of Compounds 11 and 13.[11] Imidazole or pyrazole (20 mmol) and NaOH powder (1.6 g, 40 mmol) were dissolved in DMSO (20 mL, dried over molecular sieves) and heated at 60 °C for 30 min. Then, 1-chloromethyl-5-phenyltetrazole (3.8 g, 20 mmol) was added in one portion and the mixture heated at 60 °C for 1 h. The reaction mixture was cooled to room temperature and poured over 100 g of ice in a beaker with rapid stirring. After 10 min, the precipitate was filtered off and washed with cold water (100 mL). The product was purified via recrystallization.

1-(1*H*-Imidazol-1-ylmethyl)-5-phenyl-1*H*-1,2,3,4-tetrazole (11): brown prisms (ethyl acetate/hexanes); mp 123−126 °C; ^{1}H NMR δ 6.65 (s, 2H), 7.11 (s, 1H), 7.24 (s, 1H), 7.45−7.54 (m, 3H), 7.87 (s, 1H), 8.12−8.18 (m, 2H); ^{13}C NMR δ 60.3, 118.9, 126.4, 127.0, 128.9, 130.9, 131.0, 137.4, 166.2. Anal. Calcd for $C_{11}H_{10}N_6$: C, 58.40; H, 4.46; N, 37.15. Found: C, 58.69; H, 4.66; N, 37.03.

1-(1*H*-Pyrazol-1-ylmethyl)-5-phenyl-1*H*-1,2,3,4-tetrazole (13): white needles (ethyl acetate/hexanes); mp 115−116 °C; ^{1}H NMR δ 6.37 (t, J = 2.1 1H), 6.82 (s, 2H), 7.46−7.48 (m, 3H), 7.62 (d, J = 1.5 Hz, 1H), 7.80 (d, J = 2.4 Hz, 1H), 8.15−8.18 (m, 2H); ^{13}C NMR δ 64.9, 108.0, 126.6, 126.9, 128,8, 130.3, 130.6, 141.8, 165.8. Anal. Calcd for $C_{11}H_{10}N_6$: C, 58.40; H, 4.46; N, 37.15. Found: C, 58.60; H, 4.40; N, 37.02.

JO020336M