Regular Article

Clean Synthesis of *N*-Pyrrolyl Azoles by Metal-Free Oxidative Cross-Coupling Using Recyclable Hypervalent Iodine Reagent

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The facile and clean oxidative coupling reaction of pyrroles with azoles has been achieved using the recyclable hypervalent iodine(III) reagents having adamantane structures. These iodine(III) reagents could be recovered from the reaction mixtures by a simple solid–liquid separation, *i.e.*, filtration, for reuse.

Key words oxidative coupling; hypervalent iodine reagent; recycle; pyrrole; azole; C–N bond formation

The *N*-pyrrolyl azoles are important fragments in the molecules of biological systems or in many pharmaceuticals, insecticides, and functional materials, especially, fluorescent dyes.[1–4] In spite of this interest, the preparations of *N*-aryl azoles are severely restricted because the nitrogen heteroaromatics are sometimes not a good substrate to use in the traditional arylation methods such as the Ullmann coupling,[5–11] since the pyrrole-based metal and halide compounds are sometimes unstable. Katritzky *et al*. reported the synthesis of pyrrolyl-benzotriazoles by the Mannich condensation of *o*-phthalaldehyde and 2,5-dimethoxy-2,5-dihydrofuran with primary amines,[12] but this method was not effective for pyrroles, and the desired products were produced only in less than 10% yields. As a new approach, the oxidative C–H bond functionalization strategies of pyrroles[13–22] might be expected to be an attractive methodology for enabling rapid access to these molecules. Recently, we have developed a new hypervalent iodine-induced oxidative coupling of pyrroles at the N^1-positions of the azoles.[23] In 2014, Chen and colleagues reported the oxidative coupling method of 1,2,3-triazoles with pyrroles using *N*-iodosuccinimide (NIS) as an oxidant, in which the reactions preferentially occurred at the N^2-position of the 1,2,3-triazoles.[24] However, these methods produced stoichiometric quantities of iodoarene or succinimide as a waste product after the reaction (Chart 1).

Hypervalent iodine reagents have received much attention due to their mild oxidation abilities and low toxicity, easy handling, as alternatives to toxic heavy metal reagents.[25–32] For developing a new coupling for heteroaromatic compounds, we have been engaged in the study of the oxidative C–H bond arylations using hypervalent iodine reagents that utilize the new reactivities of the heteroaromatic iodonium intermediates.[33–37] As mentioned, we developed a hypervalent iodine-induced oxidative coupling of pyrroles at the N^1-positions of the azoles.[23] This new method is versatile in allowing the reactions under metal-free and mild conditions, and tolerates a diverse series of functionalities of the pyrroles and azole coupling partners. We envisioned that a recycling version of this oxidative coupling should become feasible and provide an eco-friendly synthetic method (Chart 2) because a number of recent studies have demonstrated the utility of the recyclable hypervalent iodine reagents.[38–40]

Results and Discussion

The use of recyclable hypervalent iodine reagents in reactions should be a further promising and ecological approach for enhancing the practicability of the methods and for reducing the coproduction of stoichiometric amounts of iodoarenes as a result of the easy removal of the reagents from the reaction mixtures and their reuse.[41–59] Therefore, various types of recyclable hypervalent iodine reagents have been reported. First, the polymer-supported hypervalent iodine reagents, such as poly(diacetoxyiodo)styrene (PDAIS) and poly[bis(trifluoroacetoxyiodo)]styrene (PBTIS), incorporating phenyliodine(III) diacetate (PIDA) and phenyliodine(III) bis(trifluoroacetate) (PIFA) in their polymer backbones were developed.[41–48] Inspired by this study, other chemists have also reported new recyclable hypervalent iodine compounds having fluorous tags[49–52] and ionic supports.[53–55]

We have previously developed a structurally new recyclable hypervalent iodine reagent **1a**, namely, 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane (Fig. 1), having a very similar reactivity to that of PIDA, which was easily recovered by precipitation utilizing the insolubility of the tetraiodide **2**, stoichiometrically produced from **1a** after the reactions, in common polar solvents.[56–59] Our recyclable hypervalent iodine(III) reagents **1** having an adamantane core have several advantages over the conventional polymer-supported reagents in reactivity and recyclability; they typically show higher reactivities compared to the polymer-supported reagents and no degradation of their backbones after repeated use, which are derived from the well-defined tetrahedral structures. Considering the background of the recyclable iodine reagent, we improved our coupling reaction conditions by using the recyclable iodine reagent and avoided the generation of a stoichiometric amount of iodobenzene waste from our initial conditions.

Based on our initial studies, we thus attempted the cross-coupling reaction of *N*-benzylpyrrole **3a** with triazole **4a** using the recyclable reagent **1a** based on the standard reaction conditions in $Cl(CH_2)_2Cl$ (DCE) in combination with bromotrimethylsilane (TMSBr) at 70°C, yielding the cross-product **5aa** in 74% yield (Chart 3, Eq. 1). Other adamantane-based

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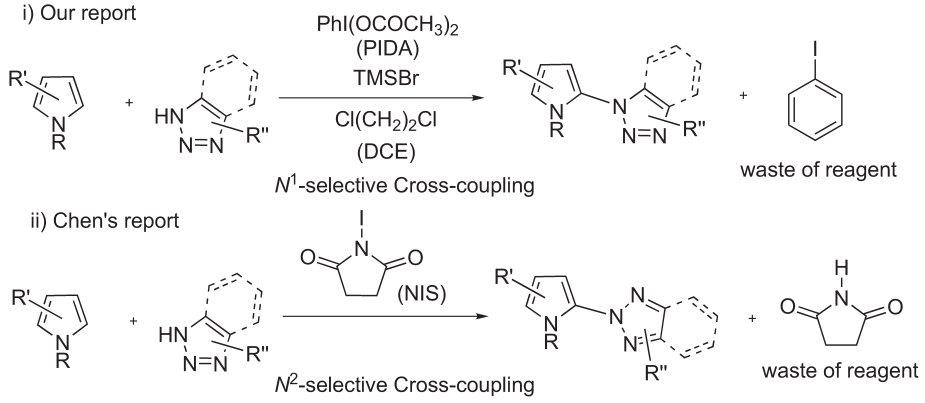


Chart 1. Reported Metal-Free Oxidative Cross-Coupling Reactions of Pyrroles with Azoles

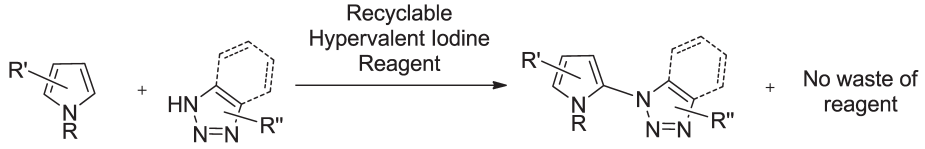


Chart 2. C–N Coupling Reaction of Triazoles with Pyrroles Using Recyclable Hypervalent Iodine Reagent

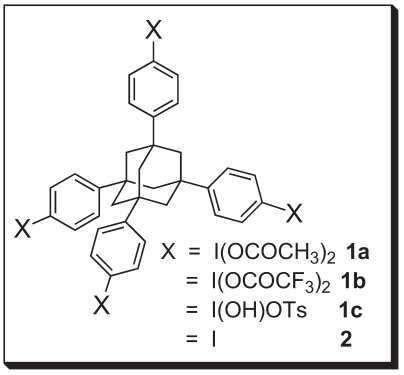


Fig. 1. Recyclable Hypervalent Iodine(III) Reagents Having Adamantane Cores

recyclable iodine(III) reagents **1b** and **c** (Fig. 1) were less effective for the coupling reaction of *N*-benzylpyrrole **3a** with triazole **4a** than the recyclable reagent **1a**. In addition, the less reactive polymer-supported reagent, the commercially available PDAIS, gave no coupling product **5aa** under the given condition. As a result, the recyclable iodine(III) reagent **1a** and TMSBr in DCE at 70°C gave the best result. The use of a highly polar, but low nucleophilic solvent, such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, $(CF_3)_2CHOH$), trifluoroethanol (TFE), or other Lewis acids, such as $BF_3 \cdot Et_2O$ and trimethylsilyl trifluoromethane sulfonate (TMSOTf) in DCE, resulted in no production of the desired coupling product.

The oxidants **1a** could be easily separated from the reaction mixtures as the corresponding reduced forms, *i.e.*, the tetraiodide **2** by a simple solid–liquid separation. The procedure to recover the tetraiodide started with the removal of the solvent under reduced pressure by a rotary evaporator. Methanol was then added to the resulting oily residues to precipitate the tetraiodide **2**. As the tetraiodides are hardly soluble in methanol, they were simultaneously precipitated as a white powder by adding methanol and were collected by filtration to recover the tetraiodide **2**. A series of recycling processes was finally completed by reoxidation of the recovered tetraiodide **2** to the initial reagents **1a** using *m*-chloroperbenzoic acid (*m*CPBA). In this way, the reagents could be reproduced with almost the same purity and have been repeatedly used without any loss of activities.[58,59] Indeed, the reuse of the reagent **1a** in the same reaction showed a comparable result in terms of the product yield and recovery of the tetraiodide **2**.

With the reagent **1a** (1×1/4 eq, 100 mol% of iodine(III) atom relative to the substrates), the reactions of the pyrroles **3** with azoles **4** smoothly proceeded under the homogeneous conditions in the presence of TMSBr in DCE (Chart 4). This method revealed a tolerance toward the *N*-protecting groups (see substrates **3b**, **c** and **d**), and in most cases, good yields were obtained. In the case of the *N*-free pyrrole **3e**, the coupling reaction efficiently proceeded and the corresponding coupling product **5ea** was obtained in 62% yield. 2-Ethyl pyrrole **3f** gave the desired coupling product **5fa** in a significant yield. When we attempted the coupling reaction of the poly-substituted pyrroles, **3g**, **h** and **i**, the coupling products, **5ga**, **ha** and **ia**, were obtained in moderate yield, respectively. When the reaction was performed using 3-methylindole **3j**, the reaction proceeded and gave the coupling product **5ja** in 70% yield.

Encouraged by these results, we applied this reaction to other azoles to synthesize various 2-(azol-1-yl)pyrrole and indole derivatives (Chart 5). The reactions of pyrroles **3a** and **e** with different azoles **4b**–**e** smoothly proceeded and the coupling products **5ab**–**ee** were produced in good to excellent yields. The 4-butyl-1,2,3-triazole **4b** also afforded the desired coupling adduct **5ab** in 76% yield (Eq. 1). The reaction of *N*-benzylpyrrole **3a** with pyrazole **4c** and imidazole **4d** smoothly proceeded to give **5ac** and **ad** in good yields (Eq. 2). The *N*-free pyrrole **3e** coupled with benzotriazole **4e** afforded the coupling product **5ee** in 69% yield (Eq. 3).

Conclusion

We have demonstrated the facile and clean method for the

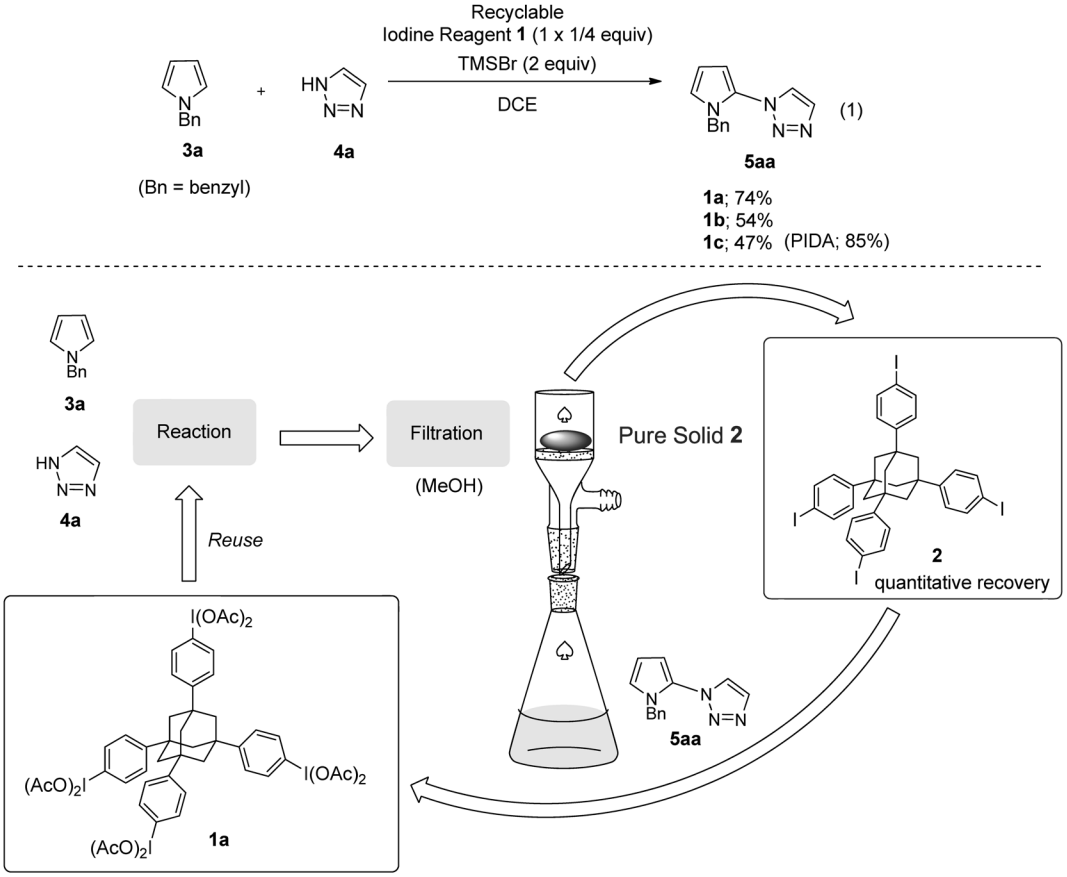
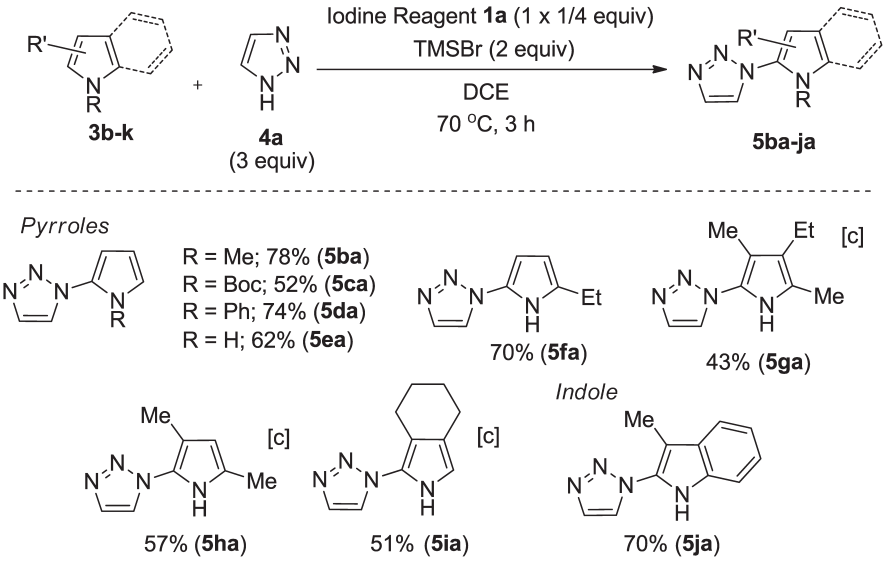


Chart 3. Oxidative Cross-Coupling Reaction of Pyrrole **3a** with Triazole **4a** Using Recyclable Hypervalent Iodine(III) Reagents **1**



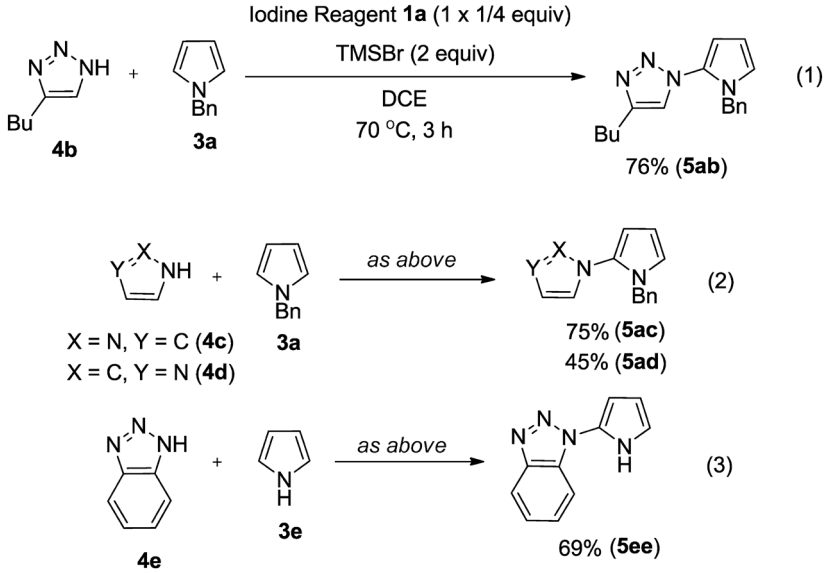
Reaction conditions: (a) Pyrroles **3** (0.4 mmol), 1,2,3-triazole **4a** (1.2 mmol), TMSBr (0.8 mmol), and iodine reagent **1a** (0.4×1/4 mmol) in DCE (4 mL) at 70°C for 3 h. (b) Yields are those for the isolated N^1-selective coupling products. (c) Reaction performed at room temperature. Boc=*tert*-butoxycarbonyl.

Chart 4. Scope of Reactions[a, b]

oxidative C–N cross-coupling reaction of pyrroles and azoles using recyclable hypervalent iodine reagents. The present protocol provided easy and less waste access to *N*-functionalized azoles. The advantageous features of this coupling method are a metal-free procedure and mild reaction conditions. Further studies are underway to extend this coupling to other types of substrates.

Experimental

General Remarks The ^{1}H- and ^{13}C-NMR spectra were recorded by a JEOL JMN-400 spectrometer operating at 400 MHz in chloroform-d_3 ($CDCl_3$) at 25°C with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, brs=broad sin-



Reaction conditions: Pyrroles **3** (0.4 mmol), azoles **4** (1.2 mmol), TMSBr (0.8 mmol), and iodine reagent **1a** (0.4×1/4 mmol) in DCE (4 mL) at 70°C for 3 h.

Chart 5. Cross-Coupling Reaction of Different Azoles with Pyrrole

glet, m=multiplet), coupling constant (Hz). The infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer, absorptions are reported in reciprocal centimeters. The mass spectra were obtained using a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. The high resolution mass spectra were performed by the Elemental Analysis Section of Osaka University. Column chromatography and TLC were carried out on Merck Silica gel 60 (230–400 mesh) and Merck Silica gel F254 plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254, 365 nm).

Preparation of a Recyclable Hypervalent Iodine Reagent 1a To a stirred solution of 1,3,5,7-tetrakis(4-iodophenyl)-adamantane **2** (1.42 g, 1.5 mmol) in dichloromethane (150 mL)–acetic acid (150 mL) was added *m*CPBA (*ca.* 69% purity, 3.12 g, 18 mmol) at room temperature. The mixture was stirred for 12 h under the same reaction conditions during which the cloudy solution became clear. The resultant mixture was filtered, and dichloromethane was removed using a rotary evaporator. Hexane was added to the residue to precipitate the 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane **1a**. After filtration, the almost pure product was obtained in nearly quantitative yield.

General Procedure for the Oxidative C–N Coupling Reaction of Azoles with Pyrroles Using a Recyclable Iodine Reagent 1a (Charts 3–5) To a stirred solution of *N*-benzylpyrrole **3a** (46 mg, 0.30 mmol) in DCE (3 mL) was added recyclable reagent **1a** (106.2 mg, 0.30×1/4 mmol). TMSBr (92 mg, 0.6 mmol) and 1,2,3-triazole **4a** (51 mg, 0.9 mmol) were then added at room temperature. The reaction mixture was stirred at 70°C for 3 h, then dichloromethane and saturated sodium hydrogen carbonate aqueous were successively added with stirring. The organic layer was then separated and evaporated to dryness. Methanol was added to the reaction mixture, and it was filtered to give the tetraiodide **2** (confirmed by ^{1}H-NMR analysis and TLC), which was washed several times with small portion of methanol (MeOH) for purification. The filtrate was evaporated and subjected to column chromatography (SiO_2, hexane) to give 1-(1-benzyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole **5aa** (57 mg, 74%).

1-(1-Benzyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5aa) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.01 (2H, s), 6.27 (1H, t, J=4.0 Hz), 6.32–6.34 (1H, m), 6.80 (1H, t, J=4.0 Hz), 6.93–6.95 (2H, m), 7.23–7.27 (3H, m), 7.46 (1H, s), 7.70 (1H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 50.4, 105.7, 107.5, 121.9, 124.8, 126.8, 126.9, 127.7, 128.6, 133.1, 136.6 ppm; IR (KBr) ν 3126, 2927, 1709, 1573, 1497, 1323, 1068, 1013, 783, 719, 616 cm^{-1}; MS matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) Calcd for $C_{13}H_{13}N_4$ m/z 225.11 $[M+H]^+$, Found 224.2 (39), 225.2 (100).

1-(1-Methyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5ba) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.49 (3H, s), 6.18 (1H, t, J=3.4 Hz), 6.24–6.26 (1H, m), 6.67 (1H, t, J=3.4 Hz), 7.73 (1H, s), 7.80 (1H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.5, 104.8, 107.1, 122.1, 125.1, 126.5, 133.2 ppm; IR (KBr) ν 3125, 2950, 1574, 1503, 1321, 1270, 1230, 1091, 1035, 1034, 787, 722, 611 cm^{-1}; MS (MALDI-TOF) Calcd for $C_7H_9N_4$ m/z 149.08 $[M+H]^+$, Found: 148.1 (24), 149.2 (100).

***tert*-Butyl 2-(1*H*-1,2,3-Triazol-1-yl)-1*H*-pyrrole-1-carboxylate (5ca)** ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (9H, s), 6.26 (1H, t, J=3.4 Hz), 6.41–6.42 (1H, m), 7.36 (1H, t, J=3.4 Hz), 7.74 (1H, s), 7.76 (1H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 27.3, 84.9, 109.2, 112.4, 121.8, 124.0, 127.4, 132.5, 147.1 ppm; IR (KBr) ν 3127, 2982, 1749, 1597, 1433, 1317, 1149, 957, 843, 736 cm^{-1}; MS (MALDI-TOF) Calcd for $C_{11}H_{14}N_4O_2$ m/z 234.11 $[M]^+$, Found 234.3 (100), 235.3 (14).

1-(1-Phenyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5da) A brown solid; mp 105–107°C; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ: 6.40 (1H, t J=3.4 Hz), 6.52–6.54 (1H, m), 7.00–7.01 (1H, m), 7.06–7.08 (2H, m), 7.29–7.32 (3H, m), 7.57 (1H, d, J=1.0 Hz), 7.64 (1H, d, J=1.0 Hz) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 107.8, 108.4, 122.3, 124.6, 126.9, 127.8, 129.4, 133.3, 137.4 ppm; IR (KBr) ν 3125, 1596, 1477, 1457, 1354, 1260, 1237, 1038, 935, 765 cm^{-1}; high resolution (HR)-MS (FAB) Calcd for $C_{12}H_{11}N_4$ m/z 211.0984 $[M+H]^+$, Found 211.0978.

1-(1*H*-Pyrrol-2-yl)-1*H*-1,2,3-triazole (5ea) ^{1}H-NMR

(400 MHz, $CDCl_3$) δ: 6.24–6.25 (2H, m), 6.77–6.78 (1H, m), 7.78 (1H, s), 7.86 (1H, s), 9.26 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 98.1, 108.8, 116.9, 121.9, 126.0, 133.9 ppm; IR (KBr) ν 3151, 1589, 1499, 1299, 1050, 1028, 912, 743 cm^{-1}; MS (MALDI-TOF) Calcd for $C_6H_7N_4$ m/z 135.07; $[M+H]^+$, Found: 133.9 (84), 134.9 (100).

1-(5-Ethyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5fa) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.25 (3H, t, J=7.2 Hz), 2.65 (2H, q, J=7.2 Hz), 5.91 (1H, s), 6.12 (1H, t, J=3.0 Hz), 7.73 (1H, s), 7.81 (1H, s), 9.30 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.4, 20.7, 98.0, 104.6, 121.6, 124.4, 133.5, 133.7 ppm; IR (KBr) ν 3152, 2969, 1601, 1597, 1223, 1050, 1018, 776 cm^{-1}; MS (MALDI-TOF) Calcd for $C_8H_{11}N_4$ m/z 163.10 $[M+H]^+$, Found 162.18 (92), 163.19 (100).

1-(4-Ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5ga) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.07 (3H, t J=7.6 Hz), 2.01 (3H, s), 2.19 (3H, s), 2.41 (2H, q, J=1.7 Hz), 7.75–7.77 (2H, m), 8.37 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 8.7, 10.8, 15.5, 17.5, 109.4, 119.7, 121.2, 122.0, 123.7, 133.4 ppm; IR (KBr) ν 3195, 2961, 1619, 1542, 1450, 1384, 1284, 1035, 913, 782 cm^{-1}; MS (MALDI-TOF) Calcd for $C_{10}H_{15}N_4$ m/z 191.13 $[M+H]^+$, Found 190.15 (64), 191.16 (100).

1-(3,5-Dimethyl-1*H*-pyrrol-2-yl)-1*H*-1,2,3-triazole (5ha) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.06 (3H, s), 2.25 (3H, s), 5.77 (1H, d, J=2.9 Hz), 7.765 (1H, s), 7.77 (1H, s), 8.56 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 10.5, 12.8, 108.42, 108.44, 110.3, 123.6, 126.4, 133.4 ppm; IR (KBr) ν 3148, 2925, 1618, 1538, 1326, 1224, 1094, 953, 793 cm^{-1}; MS (MALDI-TOF) Calcd for $C_8H_{11}N_4$ m/z 163.10 $[M+H]^+$, Found 162.13 (56), 163.14 (100).

1-(1*H*-1,2,3-Triazole-1-yl)-4,5,6,7-tetrahydro-2*H*-isoindole (5ia) A white solid; mp 127–129°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.70–1.81 (4H, m), 2.58–2.61 (4H, m), 6.47 (1H, d, J=2.5 Hz), 7.77 (1H, s), 7.81 (1H, s), 8.86 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 21.5, 22.0, 23.3, 23.4, 109.6, 111.6, 120.6, 121.8, 133.7 ppm; IR (KBr) ν 3148, 2925, 1714, 1533, 1325, 1230, 1034, 767, 592 cm^{-1}; MS (MALDI-TOF) Calcd for $C_{10}H_{13}N_4$ m/z 189.11 $[M+H]^+$, Found 188.05 (40), 189.06 (100).

3-Methyl-2-[1,2,3]triazol-1-yl-1*H*-indole (5ja)[59] ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.34 (3H, s), 7.14 (1H, dd, J=8.0, 1.0 Hz), 7.25 (1H, dd, J=8.0, 1.0 Hz), 7.37 (1H, d, J=8.0 Hz), 7.56 (1H, d, J=8.0 Hz), 7.83 (1H, s), 7.97 (1H, s), 9.44 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 8.4, 101.9, 111.4, 119.3, 120.3, 123.6, 123.7, 127.4, 127.8, 133.5, 133.9 ppm.

1-(1-Benzyl-1*H*-pyrrol-2-yl)-4-butyl-1*H*-1,2,3-triazole (5ab) A brown solid; mp 73–77°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.6 Hz), 1.31–1.41 (2H, m), 1.59–1.67 (2H, m), 2.71 (2H, t, J=7.8 Hz), 5.01 (2H, s), 6.25 (1H, t, J=3.7 Hz), 6.29–6.31 (1H, m), 6.78–6.79 (1H, m), 6.94–6.97 (2H, m), 7.15 (1H, s), 7.24–7.29 (3H, m) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.8, 22.1, 25.0, 31.3, 50.4, 105.4, 107.3, 121.6, 123.9, 125.3, 126.9, 127.7, 128.6, 136.8, 147.6 ppm; IR (KBr) ν 3111, 2956, 2859, 1950, 1576, 1496, 1453, 1274, 1230, 1274, 1070, 1007, 913, 722 cm^{-1}; MS (MALDI-TOF) Calcd for $C_{17}H_{21}N_4$ m/z 281.18 $[M+H]^+$, Found 281.13 (100), 282.13 (20).

1-(1-Benzyl-1*H*-pyrrol-2-yl)-1*H*-pyrazole (5ac) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.96 (2H, s), 6.16 (1H, t, J=3.4 Hz), 6.19–6.21 (1H, m), 6.28 (1H, s), 6.64 (1H, s), 6.95 (2H, d, J=8.3 Hz), 7.18–7.23 (3H, m), 7.36 (1H, d, J=2.4 Hz), 7.69 (1H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 50.0, 104.4, 106.1, 107.0, 120.4, 127.0, 127.5, 128.5, 129.0, 132.7, 137.5, 141.1 ppm; IR (KBr) ν 3107, 3063, 2930, 1577, 1496, 1487, 1455, 1281, 1251, 1112, 1068, 996, 756, 714 cm^{-1}; HR-MS (FAB) Calcd for $C_{14}H_{14}N_3$ m/z 224.1188 $[M+H]^+$, Found 224.1182.

1-(1-Benzyl-1*H*-pyrrol-2-yl)-1*H*-imidazole (5ad) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.79 (2H, s), 6.19–6.20 (2H, m), 6.71 (1H, t, J=2.4 Hz), 6.82 (1H, s), 6.87–6.90 (2H, m), 7.06 (1H, s), 7.20–7.29 (3H, m), 7.37 (1H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 49.5, 105.7, 107.3, 120.8, 121.7, 125.2, 126.3, 127.8, 128.7, 129.2, 137.0, 139.1 ppm; IR (KBr) ν 3110, 2924, 1708, 1574, 1490, 1348, 1311, 1235, 1060, 819, 720, 660 cm^{-1}; HR-MS (FAB) Calcd for $C_{14}H_{14}N_3$ m/z 224.1188 $[M+H]^+$, Found 224.1182.

1-(1*H*-Pyrrol-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (5ee) A white solid; mp 110–113°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.36–6.38 (1H, m), 6.44–6.48 (1H, m), 6.86–6.88 (1H, m), 7.42 (1H, t, J=8.0 Hz), 7.56 (1H, t, J=8.0 Hz), 7.73 (1H, d, J=8.3 Hz), 8.09 (1H, d, J=8.3 Hz), 9.17 (1H, brs) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 99.4, 109.0, 110.5, 116.8, 120.0, 124.6, 124.9, 128.5, 131.9, 145.6 ppm; IR (KBr) ν 3202, 2571, 1714, 1583, 1442, 1216, 1085, 1027, 938, 744, 658 cm^{-1}; HR-MS (FAB) Calcd for $C_{10}H_9N_4$ m/z 185.0826 $[M+H]^+$, Found 185.0822.

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