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# Palladium-Catalyzed Multicomponent Synthesis of 2-Aryl-2-imidazolines from Aryl Halides and Diamines

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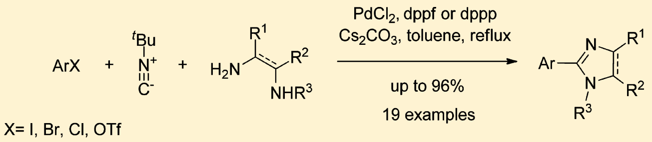
*Supporting Information*

**ABSTRACT:** An efficient palladium-catalyzed three-component reaction that combines aryl halides, isocyanides, and diamines provides access to 2-aryl-2-imidazolines in yields up to 96%. Through variation of the diamine component, the reaction can be extended to the synthesis of 2-aryl-1*H*-benzimidazoles and 2-aryl-1,4,5,6-tetrahydropyrimidines.

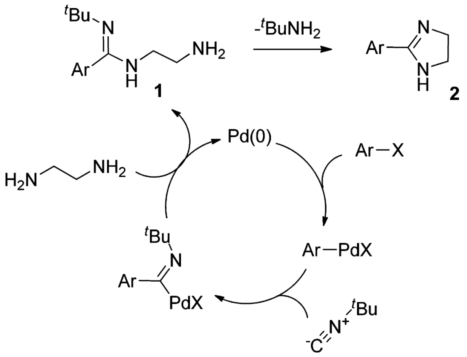


2-Imidazolines are an important class of heterocyclic compound which target numerous pharmaceutically relevant binding sites and receptors and which act as ligands in homogeneous catalysis.[1] Of these, 2-aryl-2-imidazolines have demonstrated anticancer[2] and appetite stimulant activity[3] and have been used as ligands in polymer[4] and asymmetric synthesis.[5] A range of methods have been developed for the preparation of 2-aryl-2-imidazolines, but most commonly they have been made by reacting a 1,2-diamine with a carboxylic acid or its equivalent (usually an imidate or orthoester) or with an aldehyde in the presence of an oxidant.[1]

In the search for a general, catalytic route to 2-aryl-2-imidazolines, we were attracted to the report by Whitby et al. concerning the preparation of amidines by palladium-catalyzed coupling of an aryl halide, isocyanide, and amine.[6] Since this initial report,[6] palladium-catalyzed isocyanide insertion has been utilized in the preparation of various nitrogen heterocycles including cyclic amidines and imidates,[7] oxazolines and benzoxazoles,[8] quinazoline[3,2-*a*]quinazolines,[9] 4-aminoquinazolines,[10] quinazolin-4(3*H*)-imines,[11] 4-aminophthalazin-1(2*H*)-ones,[12] 2-substituted 1*H*-indole-3-carboxamides,[13] 6-aminoindolo[3,2-*c*]quinolines,[14] 4-amine-benzo[*b*][1,4]-oxazepines,[15] 4-imino-3,4-dihydroquinazolin-2-ylphosphonates,[16] and guanidine-containing heterocycles.[17]

By replacement of the amine component with a diamine, we imagined that this chemistry could provide a simple and general entry into imidazolines such as **2** through initial formation of amidine **1** and subsequent cyclization with loss of *tert*-butylamine (Scheme 1).

**Scheme 1. Proposed Catalytic Cycle for the Preparation of 2-Aryl-2-imidazolines**



Reaction of iodobenzene, *tert*-butyl isocyanide and ethylenediamine in toluene using $PdCl_2{\cdot}dppf{\cdot}CH_2Cl_2$ as catalyst provided 2-phenyl-2-imidazoline (**3**) in a very encouraging 79% yield (Table 1, entry 1). Additional catalyst and ligand combinations were screened (entries 2−9), and $PdCl_2$ in combination with the dppp ligand led to further improvement to 94% yield (Table 1, entry 7). The reaction proceeds in excellent yield using 5 equiv of ethylenediamine, but lower yields are seen when the stoichiometry is reduced (Table 1, entries 10 and 11). The reaction proceeds well in toluene, 1,4-dioxane, and THF (entries 7, 12, and 13), but the yield is reduced when acetonitrile is used as the solvent (entry 14). Commercially available *tert*-butyl isocyanide proved to be the most convenient isocyanide source for this reaction. Alternative isocyanide sources (BnNC, 4-$MeOC_6H_4NC$, CyNC, $PhMe_2CNC$, and $Ph_3CNC$) all proved inferior. For example, when cumyl isocyanide ($PhMe_2CNC$) was used, 2-phenyl-2-imidazoline (**3**) was produced in just 43% yield under the conditions employed in Table 1, entry 7. When studying amidine synthesis, Whitby made similar observations.[6] When the experiment detailed in entry 7 was performed without dppp, or separately without cesium carbonate, the yield of **3** reduced to 26% and 71%, respectively. These results indicate the importance of both the phosphine ligand and the inorganic base to achieving high yields.

Having optimized the reaction conditions, we then explored variation in the aryl halide component. A broad range of aryl halides and heteroaromatic halides, and an aryl triflate, were screened with our best two catalyst/ligand combinations (Table 2). Most substrates were found to give the desired imidazolines in good yield, with eight examples furnishing the product in greater than 90% yield (entries 1, 3, 6−7, 9, and 11−13). Initial

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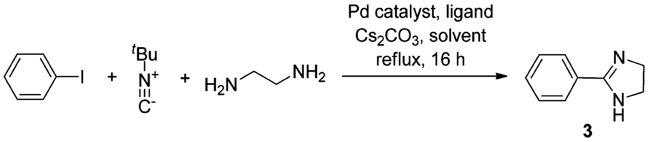
**Table 1. Optimization of Multicomponent Synthesis of 2-Phenyl-2-imidazoline (3)[a]**



| entry | catalyst | ligand | solvent | yield[b] (%) |
|---|---|---|---|---|
| 1 | $PdCl_2 \cdot dppf \cdot CH_2Cl_2$ | | toluene | 79 |
| 2 | $Pd(OAc)_2$ | dppf[a] | toluene | 76 |
| 3 | $Pd_2(dba)_3$ | dppf[a] | toluene | 74 |
| 4 | $Pd(OAc)_2$ | $PCy_3$[b] | toluene | 45 |
| 5 | $Pd(OAc)_2$ | XantPhos[a] | toluene | 35 |
| 6 | $PdCl_2$ | dppe[a] | toluene | 77 |
| 7 | $PdCl_2$ | dppp[a] | toluene | 94 |
| 8 | $Pd(PPh_3)_4$ | | toluene | 59 |
| 9 | $Pd(P^tBu_3)_2$ | | toluene | 36 |
| 10 | $PdCl_2 \cdot dppf \cdot CH_2Cl_2$ | | toluene | 52[c] |
| 11 | $PdCl_2 \cdot dppf \cdot CH_2Cl_2$ | | toluene | 8[d] |
| 12 | $PdCl_2$ | dppp[a] | 1,4-dioxane | 90 |
| 13 | $PdCl_2$ | dppp[a] | THF | 91 |
| 14 | $PdCl_2$ | dppp[a] | MeCN | 48 |

[a]Reaction conditions: *tert*-butyl isocyanide (1.5 equiv), Pd catalyst (5 mol %), ligand ((a) 10 mol % or (b) 20 mol %), ethylenediamine (5 equiv except (c) 3 equiv and (d) 1 equiv), $Cs_2CO_3$ (1.3 equiv), reflux. [b]Yield of isolated product after column chromatography.

attempts to extend the reaction to nonaromatic halides have not been fruitful.[18]

$PdCl_2$ in combination with dppp was found to give better yields with most aryl halides (Table 2, entries 1–4, 6, and 11–14), while $PdCl_2 \cdot dppf \cdot CH_2Cl_2$ was the superior catalyst with electron-rich aryl bromides and triflates (entries 7–9). Both ligands gave a low yield of **6** (entry 5) which may be attributed to the sterically hindered nature of 2-iodotoluene. Satisfyingly, 2,6-dibromopyridine was found to give bis-imidazoline **11** in an excellent yield of 94% via a 5-component reaction. The structure of this bis-imidazoline was unambiguously established by X-ray crystallography (see the Supporting Information). While no imidazoline formation was observed using chlorobenzene, 4-chloroanisole, and 3-chloropyridine, a 96% yield of **10** was achieved from 2-chloropyridine (entry 12). To our knowledge, this is the first example of a high-yielding, palladium-catalyzed iminocarbonylative cross-coupling of an aryl chloride. It is not clear why **10** is formed from 2-bromo- or 2-chloropyridine in much higher yield with dppp than dppf (entries 11 and 12), while 3-bromopyridine, which is not activated toward oxidative addition, gives **9** in a higher yield with dppf (entry 10).

To extend the usefulness of this reaction we then investigated the reaction of alternative diamines (Table 3). 1,3-Diaminopropane was found to give tetrahydropyrimidine **13** in 95% yield (entry 1), and *N*-alkylated ethylenediamines were also found to react successfully (entries 2 and 3). Simultaneous substitution of both carbons of the ethylenediamine unit was well tolerated (entries 4 and 5), and 1,2-diaminobenzenes were found to give benzimidazoles, albeit in lower yields (entries 6 and 7).

The successful formation of **11** (Table 2, entry 13) and **17** (Table 3, entry 5) encouraged us to attempt the one-pot synthesis of the chiral pybim ligand **20**, which has found applications in ruthenium-catalyzed asymmetric transfer hydrogenation[5a] and epoxidation reactions[5b,c] (Scheme 2). This 5-component reaction successfully yielded **20** in 51% yield (after purification by recrystallization) via the formation of 2 × C−C and 4 × C−N bonds. The relatively modest yield reflects difficulties associated with product purification rather than low chemical conversion (see the Experimental Section).

In conclusion, a structurally diverse range of 2-aryl-2-imidazolines, 2-aryl-1*H*-benzimidazoles, and a 2-aryl-1,4,5,6-tetrahydropyrimidine have been prepared from aryl halides in one step in up to 96% yield by a novel palladium-catalyzed 3-component reaction. Good variation in the aryl halide and the diamine components has been demonstrated, which will enable the rapid preparation of libraries of compounds with potential as pharmaceuticals, agrochemicals, or ligands in homogeneous catalysis.

## ■ EXPERIMENTAL SECTION

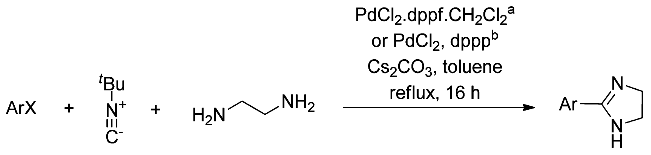
HRMS analyses were performed on a time-of-flight mass spectrometer equipped with an ESI source.

**Synthesis of 3−20: General Procedure.** Cesium carbonate (1.3 mmol, 1.3 equiv), anhydrous toluene (5 mL), aryl halide (1.0 mmol), isocyanide (1.5 mmol, 1.5 equiv), diamine (5.0 mmol, 5 equiv), palladium catalyst, and ligand (5 mol % $PdCl_2 \cdot dppf \cdot CH_2Cl_2$, or 5 mol % $PdCl_2$ and 10 mol % 1,3-bis(diphenylphosphino)propane, dppp) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography to provide the nitrogen heterocycle.

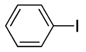
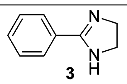
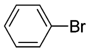
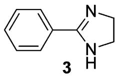
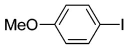
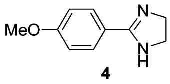
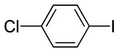
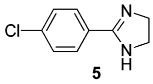
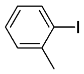
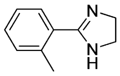
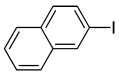
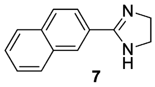
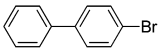
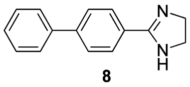
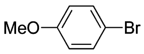
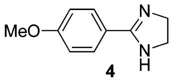
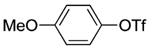
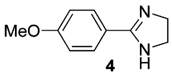
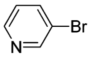
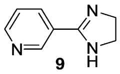
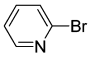
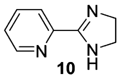
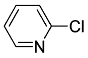
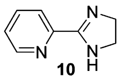
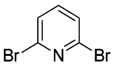
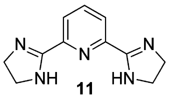
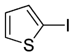
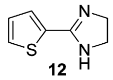
*2-Phenyl-4,5-dihydro-1H-imidazole (**3**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography ($SiO_2$, 60:5:1, dichloromethane/methanol/triethylamine) to provide **3** as a beige solid (137 mg, 94%):[19] $R_f$ (60:5:1, dichloromethane/methanol/triethylamine) 0.27; mp 100–102 °C (lit.[19] mp 99–101 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3193, 2927, 2866, 1610, 1598, 1573, 1508, 1269, 981, 778, 693; $\delta_H$ (400 MHz, $CDCl_3$) 7.78 (2H, d, $J$ = 7.9 Hz), 7.49–7.37 (3H, m), 4.70–4.40 (1H, br s), 3.79 (4H, br s); $\delta_C$ (100 MHz, $CDCl_3$) 164.8 (C), 130.7 (CH), 130.3 (C), 128.5 (CH), 127.0 (CH), 50.2 ($CH_2$); $m/z$ ($ES^+$) 147 ($MH^+$), found $(MH)^+$ 147.0919, $C_9H_{10}N_2$ requires $(MH)^+$, 147.0917.

*2-(4-Methoxyphenyl)-4,5-dihydro-1H-imidazole (**4**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 4-iodoanisole (234 mg, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography ($SiO_2$, 30:5:1, dichloromethane/methanol/triethylamine) to provide **4** as a beige solid (170 mg, 96%):[19] $R_f$ (30:5:1, dichloromethane/methanol/triethylamine) 0.35; mp 136–138 °C (lit.[19] mp 136–138 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3183, 2923, 2835, 1603, 1570, 1512, 1251, 1174, 1025, 833; $\delta_H$ (400 MHz, $CDCl_3$) 7.77 (2H, d, $J$ = 8.8 Hz), 6.91 (2H, d, $J$ = 8.8 Hz), 4.95–4.70 (1H, br s), 3.83 (3H, s), 3.75 (4H, s); $\delta_C$ (100 MHz, $CDCl_3$) 164.5 (C), 161.8 (C), 128.8 (CH), 122.1 (C), 113.8 (CH), 55.4 ($CH_3$), 49.7 ($CH_2$); $m/z$ ($ES^+$) 177 ($MH^+$), found $(MH)^+$ 177.1026, $C_{10}H_{12}N_2O$ requires $(MH)^+$, 177.1022.

Table 2. Preparation of 2-Aryl-2-imidazolines (2)[a]

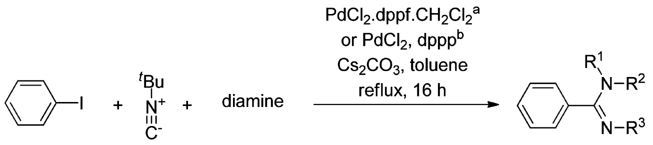


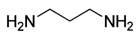
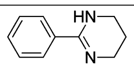
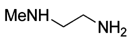
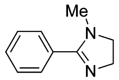
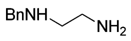
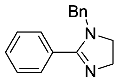
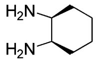
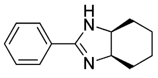
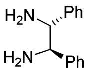
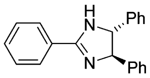
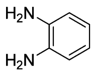
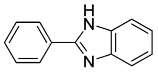
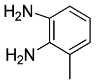
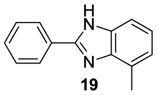
**2**

| entry | ArX | imidazoline | yield (%)[a] | yield (%)[b] |
|---|---|---|---|---|
| 1 |  |  **3** | 79 | 94 |
| 2 |  |  **3** | 21 | 51 |
| 3 |  |  **4** | 88 | 96 |
| 4 |  |  **5** | 69 | 77 |
| 5 |  |  **6** | 32 | 29 |
| 6 |  |  **7** | 86 | 95 |
| 7 |  |  **8** | 94 | 62 |
| 8 |  |  **4** | 74 | 31 |
| 9 |  |  **4** | 93 | 75 |
| 10 |  |  **9** | 51 | 8 |
| 11 |  |  **10** | 44 | 96 |
| 12 |  |  **10** | 18 | 96 |
| 13 |  |  **11** | 74 | 94 |
| 14 |  |  **12** | 51 | 81 |

[a]Reaction conditions: *tert*-butyl isocyanide (1.5 or 3 equiv for **11**), ethylenediamine (5 or 10 equiv for **11**), $Cs_2CO_3$ (1.3 equiv), (a) $PdCl_2{\cdot}dppf{\cdot}CH_2Cl_2$ (5 mol %), (b) $PdCl_2$ (5 mol %) and dppp (10 mol %), toluene, reflux.

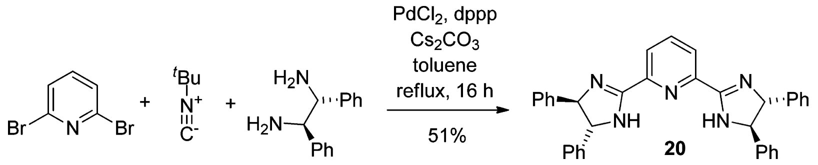
Table 3. Reaction of Other Diamines[a]



| entry | diamine | product | yield (%)[b] |
|---|---|---|---|
| 1 |  |  **13** | 95[a] |
| 2 |  |  **14** | 82[a] |
| 3 |  |  **15** | 60[a] |
| 4 |  |  **16** | 82[b] |
| 5 |  |  **17** | 50[b] |
| 6 |  |  **18** | 58[b] |
| 7 |  |  **19** | 39[a] |

[a]Reaction conditions: *tert*-butyl isocyanide (1.5 equiv), ethylenediamine (5 equiv), $Cs_2CO_3$ (1.3 equiv), (a) $PdCl_2·dppf·CH_2Cl_2$ (5 mol %), (b) $PdCl_2$ (5 mol %) and dppp (10 mol %), toluene, reflux. [b]Yield of isolated product after column chromatography. Highest yielding conditions are reported.

Scheme 2. One-Pot Preparation of Chiral Pybim Ligand (20)[a]



[a]Reaction conditions: *tert*-butyl isocyanide (3 equiv), (1*R*,2*R*)-(+)1,2-diphenyl ethylenediamine (10 equiv), $Cs_2CO_3$ (1.3 equiv), $PdCl_2$ (5 mol %), dppp (10 mol %), toluene, reflux.

*2-(4-Chlorophenyl)-4,5-dihydro-1H-imidazole* (**5**). Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 1-chloro-4-iodobenzene (238 mg, 1.0 mmol), *tert*-butyl isocyanide (170 μL, 1.5 mmol), ethylenediamine (334 μL, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography ($SiO_2$, 60:3:1, dichloromethane/methanol/triethylamine) to provide **5** as a cream solid (139 mg, 77%):[19] $R_f$ (60:3:1, dichloromethane/methanol/triethylamine) 0.63; mp 186–188 °C (lit.[19] mp 188 °C); $\nu_{max}$ (film)/$cm^{-1}$ 3105, 2969, 2920, 2862, 1605, 1593, 1559, 1515, 1467, 1270, 1090, 987, 837, 724; $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, $J$ = 8.6 Hz), 7.38 (2H, d, $J$ = 8.6 Hz), 3.79 (4H, s); $\delta_C$ (100 MHz, $CDCl_3$) 163.8 (C), 136.8 (C), 128.8 (C), 128.7 (CH), 128.4 (CH), 50.3 ($CH_2$); $m/z$ ($ES^+$) 181 ($MH^+$), found $(MH)^+$ 181.0534, $C_9H_9{}^{35}ClN_2$ requires $(MH)^+$, 181.0527.

*4,5-Dihydro-2-(2-methylphenyl)-1H-imidazole* (**6**). Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2-iodotoluene (127 μL, 1.0 mmol), *tert*-butyl isocyanide (170 μL, 1.5 mmol), ethylenediamine (334 μL, 5.0 mmol), and $PdCl_2·dppf·CH_2Cl_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography ($SiO_2$, 60:3:1, dichloromethane/methanol/triethylamine) to provide **6** as a beige solid (51 mg, 32%):[20] $R_f$ (60:3:1, dichloromethane/methanol/triethylamine) 0.45; mp 83−85 °C (lit.[20] mp 88 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3149, 2922, 1611, 1588, 1498, 1262, 980, 767, 730; $\delta_H$ (400 MHz, CDCl$_3$) 7.44 (1H, d, $J$ = 7.5 Hz), 7.28 (1H, t, $J$ = 7.5 Hz), 7.22−7.14 (2H, m), 4.82−4.63 (1H, br s), 3.72 (4H, s), 2.46 (3H, s); $\delta_C$ (100 MHz, CDCl$_3$) 165.7 (C), 136.9 (C), 131.0 (C), 130.9 (CH), 129.6 (CH), 128.4 (CH), 125.6 (CH), 50.2 (CH$_2$), 20.5 (CH$_3$); $m/z$ (ES$^+$) 161 (MH$^+$), found (MH)$^+$ 161.1070, $C_{10}H_{12}N_2$ requires (MH)$^+$, 161.1073.

*4,5-Dihydro-2-(2-naphthalenyl)-1H-imidazole (**7**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2-iodonaphthalene (254 mg, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:3:1, dichloromethane/methanol/triethylamine) to provide **7** as a beige solid (186 mg, 95%):[21] $R_f$ (60:3:1, dichloromethane/methanol/triethylamine) 0.55; mp 116−118 °C (lit.[21] mp 118 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3168, 3054, 2929, 2857, 1632, 1609, 1588, 1567, 1514, 1489, 1273, 984, 859, 820, 745; $\delta_H$ (400 MHz, CDCl$_3$) 8.21 (1H, s), 7.93 (1H, d, $J$ = 8.6 Hz), 7.85−7.82 (3H, m), 7.53−7.47 (2H, m), 4.90−4.68 (1H, br s), 3.81 (4H, s); $\delta_C$ (100 MHz, CDCl$_3$) 164.9 (C), 134.4 (C), 132.7 (C), 128.7 (CH), 128.2 (CH), 127.8 (CH), 127.6 (C), 127.2 (CH), 126.9 (CH), 126.6 (CH), 124.3 (CH), 50.3 (CH$_2$); $m/z$ (ES$^+$) 197 (MH$^+$), found (MH)$^+$ 197.1072, $C_{13}H_{12}N_2$ requires (MH)$^+$, 197.1073.

*2-(1,1′-Biphenyl)-4-yl-4,5-dihydro-1H-imidazole (**8**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 4-bromobiphenyl (233 mg, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, was cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:3:1, dichloromethane/methanol/triethylamine) to provide **8** as a cream solid (209 mg, 94%):[22] $R_f$ (60:3:1, dichloromethane/methanol/triethylamine) 0.55; mp 195−196 °C (lit.[22] mp 200−201 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3207, 3057, 2921, 2838, 1614, 1600, 1578, 1526, 1491, 1476, 1267, 1114, 979, 845, 766, 728, 688; $\delta_H$ (400 MHz, CDCl$_3$) 7.89 (2H, d, $J$ = 8.3 Hz), 7.64 (2H, d, $J$ = 8.3 Hz), 7.61 (2H, d, $J$ = 7.2 Hz), 7.45 (2H, t, $J$ = 7.2 Hz), 7.37 (1H, t, $J$ = 7.2 Hz), 4.30−3.90 (1H, br s), 3.80 (4H, s); $\delta_C$ (125 MHz, CDCl$_3$) 164.5 (C), 143.7 (C), 140.1 (C), 128.7 (CH), 128.4 (C), 127.9 (CH), 127.7 (CH), 127.2 (CH), 127.1 (CH), 49.9 (CH$_2$); $m/z$ (ES$^+$) 223 (MH$^+$), found (MH)$^+$ 223.1231, $C_{15}H_{14}N_2$ requires (MH)$^+$, 223.1230.

*4,5-Dihydro-2-(pyridin-3-yl)-1H-imidazole (**9**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 3-bromopyridine (96.3 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:5:1, dichloromethane/methanol/triethylamine) to provide **9** as a cream solid (74 mg, 51%):[23] $R_f$ (60:5:1, dichloromethane/methanol/triethylamine) 0.24; mp 106−108 °C (lit.[23] mp 110−111 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3153, 2926, 2853, 1607, 1587, 1561, 1512, 1467, 1410, 1277, 1029, 983, 823, 703; $\delta_H$ (400 MHz, CDCl$_3$) 8.98 (1H, d, $J$ = 2.0 Hz), 8.67 (1H, dd, $J$ = 4.8, 2.0 Hz), 8.13 (1H, dt, $J$ = 8.0, 2.0 Hz), 7.34 (1H, dd, $J$ = 8.0, 4.8 Hz), 4.80 (1H, br s), 3.82 (4H, s); $\delta_C$ (100 MHz, CDCl$_3$) 162.5 (C), 151.6 (CH), 148.1 (CH), 134.7 (CH), 126.3 (C), 123.4 (CH), 50.3 (CH$_2$); $m/z$ (ES$^+$) 148 (MH$^+$), found (MH)$^+$ 148.0871, $C_8H_9N_3$ requires (MH)$^+$, 148.0869.

*4,5-Dihydro-2-(pyridin-2-yl)-1H-imidazole (**10**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2-bromopyridine (95.4 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, was cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:3:1, dichloromethane/methanol/triethylamine) to provide **10** as a cream solid (142 mg, 96%):[20] $R_f$ (60:3:1, dichloromethane/methanol/triethylamine) 0.33; mp 100−102 °C (lit.[20] mp 94 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3246, 3050, 2854, 1593, 1560, 1500, 1457, 1423, 1278, 976, 802, 752; $\delta_H$ (400 MHz, CDCl$_3$) 8.57 (1H, dd, $J$ = 4.8, 1.7 Hz), 8.18 (1H, dd, $J$ = 7.8, 1.7 Hz), 7.77 (1H, td, $J$ = 7.8, 1.7 Hz), 7.38−7.33 (1H, m), 6.20−5.80 (1H, br s), 4.30−3.77 (2H, br s), 3.90−3.40 (2H, br s); $\delta_C$ (100 MHz, CDCl$_3$) 164.3 (C), 148.6 (CH), 148.2 (C), 136.6 (CH), 125.2 (CH), 122.4 (CH), 50.2 (CH$_2$); $m/z$ (ES$^+$) 148 (MH$^+$), found (MH)$^+$ 148.0869, $C_8H_9N_3$ requires (MH)$^+$, 148.0869.

*2,6-Bis(4,5-dihydro-1H-imidazol-2-yl)pyridine (**11**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2,6-dibromopyridine (237 mg, 1.0 mmol), *tert*-butyl isocyanide (340 $\mu$L, 3.0 mmol), ethylenediamine (668 $\mu$L, 10.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 30:5:1, dichloromethane/methanol/triethylamine) to provide **11** as a white solid (203 mg, 96%): $R_f$ (30:5:1, dichloromethane/methanol/triethylamine) 0.30; mp 219−220 °C; $\nu_{max}$ (film)/cm$^{-1}$ 3229, 2927, 2868, 1599, 1567, 1495, 1484, 1449, 1278, 832, 749; $\delta_H$ (500 MHz, DMSO-$d_6$) 8.06 (2H, d, $J$ = 7.7 Hz), 7.96 (1H, t, $J$ = 7.7 Hz), 3.70 (8H, br s); $\delta_C$ (125 MHz, DMSO-$d_6$) 162.9 (C), 147.4 (C), 137.5 (CH), 122.8 (CH), 50.2 (CH$_2$); $m/z$ (ES$^+$) 216 (MH$^+$), found (MH)$^+$ 216.1242, $C_{11}H_{13}N_5$ requires (MH)$^+$, 216.1244.

*4,5-Dihydro-2-(2-thienyl)-1H-imidazole (**12**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2-iodothiophene (110 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), ethylenediamine (334 $\mu$L, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:5:1, dichloromethane/methanol/triethylamine) to provide **12** as a pale orange solid (124 mg, 81%):[24] $R_f$ (60:5:1, dichloromethane/methanol/triethylamine) 0.30; mp 174−176 °C (lit.[24] mp 175 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3140, 2930, 2855, 1676, 1595, 1529, 1494, 1268, 1246, 1100, 1081, 984, 846, 707; $\delta_H$ (400 MHz, CDCl$_3$) 7.41 (1H, d, $J$ = 5.0 Hz), 7.38 (1H, d, $J$ = 3.8 Hz), 7.06 (1H, dd, $J$ = 5.0, 3.8 Hz), 4.90−3.80 (1H, br), 3.78 (4H, s); $\delta_C$ (125 MHz, CDCl$_3$) 159.7 (C), 133.4 (C), 128.9 (CH), 127.7 (CH), 127.5 (CH), 50.2 (CH$_2$); $m/z$ (ES$^+$) 153 (MH$^+$), found (MH)$^+$ 153.0482, $C_7H_8N_2S$ requires (MH)$^+$, 153.0481.

*1,4,5,6-Tetrahydro-2-phenylpyrimidine (**13**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), 1,3-diaminopropane (417 $\mu$L, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (basic alumina, 6:3:1, hexane/dichloromethane/methanol) to provide **13** as a beige solid (152 mg, 95%):[25] mp 84−86 °C (lit.[26] mp 84−86 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3184, 2930, 2845, 1615, 1602, 1573, 1531, 1363, 1303, 1185, 779, 694; $\delta_H$ (400 MHz, CDCl$_3$) 7.62 (2H, d, $J$ = 6.7 Hz), 7.38−

7.29 (3H, m), 5.26−5.15 (1H, br s), 3.44 (4H, t, $J$ = 5.7 Hz), 1.79 (2H, quintet, $J$ = 5.7 Hz); $\delta_C$ (100 MHz, CDCl$_3$) 154.7 (C), 137.3 (C), 129.5 (CH), 128.2 (CH), 126.0 (CH), 42.2 (CH$_2$), 20.7 (CH$_2$); $m/z$ (ES$^+$) 161 (MH$^+$), found (MH)$^+$ 161.1073, $C_{10}H_{12}N_2$ requires (MH)$^+$, 161.1073.

*4,5-Dihydro-1-methyl-2-phenyl-1H-imidazole (**14**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), *N*-methylethylenediamine (436 $\mu$L, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:5:1, dichloromethane/methanol/triethylamine) to provide **14** as a pale yellow oil (131 mg, 82%):[27] $R_f$ (60:5:1, dichloromethane/methanol/triethylamine) 0.14; $\nu_{max}$ (film)/cm$^{-1}$ 3281, 3058, 2933, 1636, 1602, 1577, 1535, 1487, 1293, 693; $\delta_H$ (300 MHz, CDCl$_3$) 7.56−7.51 (2H, m), 7.42−7.36 (3H, m), 3.85 (2H, t, $J$ = 9.8 Hz), 3.43 (2H, t, $J$ = 9.8 Hz), 2.78 (3H, s); $\delta_C$ (75 MHz, CDCl$_3$) 167.4 (C), 130.5 (C), 129.1 (CH), 127.6 (CH), 127.5 (CH), 53.4 (CH$_2$), 52.3 (CH$_2$), 35.8 (CH$_3$); $m/z$ (ES$^+$) 161 (MH$^+$), found (MH)$^+$ 161.1074, $C_{10}H_{12}N_2$ requires (MH)$^+$, 161.1073.

*4,5-Dihydro-2-phenyl-1-(phenylmethyl)-1H-imidazole (**15**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), *N*-benzylethylenediamine (751 $\mu$L, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 10:1, ethyl acetate/triethylamine) to provide **15** as a pale yellow gum (142 mg, 60%):[20] $R_f$ (10:1, ethyl acetate/triethylamine) 0.38; $\nu_{max}$ (film)/cm$^{-1}$ 3308, 3060, 2924, 1629, 1601, 1576, 1534, 739, 694; $\delta_H$ (400 MHz, CDCl$_3$) 7.77 (2H, d, $J$ = 7.4 Hz), 7.46 (1H, t, $J$ = 7.4 Hz), 7.38 (2H, t, $J$ = 7.4 Hz), 7.32−7.21 (4H, m), 7.06 (1H, m), 3.78 (2H, s), 3.50 (2H, t, $J$ = 6.0 Hz), 2.84 (2H, t, $J$ = 6.0 Hz); $\delta_C$ (100 MHz, CDCl$_3$) 167.7 (C), 139.8 (C), 134.6 (C), 131.3 (CH), 128.5 (CH), 128.2 (CH), 127.2 (CH), 127.0 (CH), 126.7 (CH), 53.4 (CH$_2$), 47.8 (CH$_2$), 39.4 (CH$_2$); $m/z$ (ES$^+$) 237 (MH$^+$), found (MH)$^+$ 237.1387, $C_{16}H_{16}N_2$ requires (MH)$^+$, 237.1386.

*(3aR*,7aS*)-3a,4,5,6,7,7a-Hexahydro-2-phenyl-1H-benzimidazole (**16**).* Cesium carbonate (212 mg, 0.65 mmol), anhydrous toluene (2.5 mL), iodobenzene (56 $\mu$L, 0.5 mmol), *tert*-butyl isocyanide (85 $\mu$L, 0.75 mmol), *cis*-1,2-diaminocyclohexane (300 $\mu$L, 2.5 mmol), palladium(II) chloride (4.5 mg, 0.025 mmol), and dppp (20.6 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, was cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 60:3:1, dichloromethane/methanol/triethylamine) then (SiO$_2$, 98:2, ethyl acetate/triethylamine) to provide **16** as a beige solid (82 mg, 82%): $R_f$ (98:2, ethyl acetate/triethylamine) 0.22; mp 139−141 °C; $\nu_{max}$ (film)/cm$^{-1}$ 3105, 2930, 2849, 1610, 1594, 1563, 1506, 1471, 1353, 1000, 774; $\delta_H$ (400 MHz, CDCl$_3$) 7.81 (2H, d, $J$ = 6.8 Hz), 7.43−7.33 (3H, m), 5.82−5.60 (1H, br s), 3.88−3.81 (1H, m), 1.80−1.70 (2H, m), 1.69−1.60 (2H, m), 1.58−1.46 (2H, m), 1.38−1.24 (2H, m); $\delta_C$ (100 MHz, CDCl$_3$) 164.2 (C), 130.6 (CH), 128.4 (CH), 126.9 (CH), 60.3 (CH), 28.5 (CH$_2$), 21.0 (CH$_2$); $m/z$ (ES$^+$) 201 (MH$^+$), found (MH)$^+$ 201.1391, $C_{13}H_{16}N_2$ requires (MH)$^+$, 201.1386.

*(4R,5R)-4,5-Dihydro-2,4,5-triphenyl-1H-imidazole (**17**).* Cesium carbonate (85 mg, 0.26 mmol), anhydrous toluene (1 mL), iodobenzene (22.4 $\mu$L, 0.2 mmol), *tert*-butyl isocyanide (34 $\mu$L, 0.3 mmol), (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (212 mg, 1.0 mmol), palladium(II) chloride (1.8 mg, 0.01 mmol), and dppp (8.2 mg, 0.02 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 1:1, hexane/ethyl acetate) to provide **17** as a cream solid (30 mg, 50%):[28] $R_f$ (1:1, hexane/ethyl acetate) 0.22; mp 174−176 °C (lit.[28] mp 175−178 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3144, 3025, 1597, 1574, 1500, 1451, 1014, 761, 692; $\delta_H$ (400 MHz, CDCl$_3$) 7.92 (2H, d, $J$ = 7.4 Hz), 7.49 (1H, t, $J$ = 7.4 Hz), 7.42 (2H, t, $J$ = 7.4 Hz), 7.36−7.24 (10H, m), 5.83−5.67 (1H, br s), 4.88 (2H, s); $\delta_C$ (100 MHz, CDCl$_3$) 163.3 (C), 143.2 (C), 131.3 (CH), 129.6 (C), 128.8 (CH), 128.6 (CH), 127.6 (CH), 127.6 (CH), 126.6 (CH), 74.8 (CH); $m/z$ (ES$^+$) 299 (MH$^+$), found (MH)$^+$ 299.1540, $C_{21}H_{18}N_2$ requires (MH)$^+$, 299.1543]; $[\alpha]_D$ (25 °C) = +47.5 ($c$ 0.2, EtOH).

*2-Phenyl-1H-benzimidazole (**18**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), *o*-phenylenediamine (541 mg, 5.0 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 1:1, hexane/ethyl acetate) to provide **18** as a beige solid (113 mg, 58%):[29] $R_f$ (1:1, hexane/ethyl acetate) 0.67; mp 290−292 °C (lit.[30] mp 290−292 °C); $\nu_{max}$ (film)/cm$^{-1}$ 2627, 1621, 1590, 1541, 1443, 1409, 1275, 969, 737; $\delta_H$ (300 MHz, CDCl$_3$) 8.05 (2H, d, $J$ = 8.3 Hz), 7.70−7.55 (2H, br s), 7.52−7.40 (3H, m), 7.30−7.20 (3H, m); $\delta_C$ (176 MHz, CDCl$_3$) 151.5 (C), 130.3 (CH), 129.8 (C), 129.1 (CH), 126.5 (CH), 123.0 (CH); $m/z$ (ES$^+$) 195 (MH$^+$), found (MH)$^+$ 195.0916, $C_{13}H_{10}N_2$ requires (MH)$^+$, 195.0917.

*7-Methyl-2-phenyl-1H-benzimidazole (**19**).* Cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), iodobenzene (112 $\mu$L, 1.0 mmol), *tert*-butyl isocyanide (170 $\mu$L, 1.5 mmol), 3-methyl-*o*-phenylenediamine (611 mg, 5.0 mmol), and PdCl$_2$·dppf·CH$_2$Cl$_2$ (40.8 mg, 0.05 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 1:1, hexane/ethyl acetate) to provide **19** as an orange solid (81 mg, 39%):[31] $R_f$ (1:1, hexane/ethyl acetate) 0.73; mp 246−248 °C (lit.[31] mp 246−247 °C); $\nu_{max}$ (film)/cm$^{-1}$ 2715, 1619, 1597, 1537, 1458, 1449, 779, 746, 702; $\delta_H$ (400 MHz, DMSO-$d_6$)[32] 12.8 (0.55H, br s), 12.6 (0.45H, br s), 8.25 (0.9H, d, $J$ = 7.2 Hz), 8.19 (1.1H, d, $J$ = 7.2 Hz), 7.60−7.45 (3.45H, m), 7.35 (0.55H, d, $J$ = 7.9 Hz), 7.11 (0.45H, t, $J$ = 7.6 Hz), 7.09 (0.55H, t, $J$ = 7.6 Hz), 7.03−6.98 (1H, m), 2.60 (1.65H, s), 2.56 (1.35H, s); $\delta_C$ (100 MHz, DMSO-$d_6$) 151.1 (C), 150.3 (C), 143.5 (C), 143.2 (C), 134.6 (C), 134.5 (C), 130.3 (C), 129.7 (CH), 129.6 (CH), 128.9 (CH), 128.8 (CH), 128.3 (C), 126.7 (CH), 126.4 (CH), 123.1 (CH), 122.4 (CH), 121.8 (CH), 121.7 (CH), 121.3 (C), 116.3 (CH), 108.7 (CH), 17.1 (CH$_3$), 16.7 (CH$_3$); $m/z$ (ES$^+$) 209 (MH$^+$), found (MH)$^+$ 209.1069, $C_{14}H_{12}N_2$ requires (MH)$^+$, 209.1073.

*2,6-Bis[(4R,5R)-4,5-Dihydro-4,5-diphenyl-1H-imidazol-2-yl]pyridine (**20**).* Cesium carbonate (85 mg, 0.26 mmol), anhydrous toluene (1 mL), 2,6-dibromopyridine (47.4 mg, 0.2 mmol), *tert*-butyl isocyanide (68 $\mu$L, 0.6 mmol), (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (425 mg, 2.0 mmol), palladium(II) chloride (1.8 mg, 0.01 mmol), and dppp (8.2 mg, 0.02 mmol) were added to an oven-dried, three-necked flask under nitrogen. The mixture was heated to reflux for 16 h, cooled to room temperature, and filtered through a pad of Celite which was washed well with ethyl acetate. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (SiO$_2$, 99:1, ethyl acetate/triethylamine) to provide **20** as a yellow solid (103 mg, >80% purity). Recrystallization from cyclohexane gave **20** as a cream solid (53 mg, 51%):[5b] $R_f$ (99:1, ethyl acetate/triethylamine) 0.19; mp 122−124 °C (lit.[5b] 123−126 °C); $\nu_{max}$ (film)/cm$^{-1}$ 3287, 3026, 1602, 1564, 1450, 1266, 1008, 830, 750, 697; $\delta_H$ (400 MHz, CDCl$_3$)[31] 8.46 (2H, d, $J$ = 7.8 Hz), 7.96 (1H, t, $J$ = 7.8 Hz), 7.36−7.25 (20H, m), 6.47 (2H, br s), 5.17 (2H, d, $J$ = 8.7 Hz), 4.75 (2H, d, $J$ = 8.7 Hz); $\delta_C$ (100 MHz, CDCl$_3$) 161.8 (C), 147.6

(C), 143.2 (C), 142.8 (C), 137.6 (CH), 128.8 (CH), 128.7 (CH), 127.9 (CH), 127.5 (CH), 127.0 (CH), 126.5 (CH), 124.6 (CH), 81.2 (CH), 70.0 (CH); *m*/*z* (ES$^+$) 520 (MH$^+$), found (MH)$^+$ 520.2491, $C_{35}H_{29}N_5$ requires (MH)$^+$, 520.2496]; $[\alpha]_D$ (25 °C) = +82.5 (*c* = 0.2, $CHCl_3$).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Copies of $^1$H and $^{13}$C NMR spectra for compounds **3−20** and the X-ray crystal structure of compound **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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