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Copper-Mediated Synthesis of Substituted 2-Aryl-*N*-benzylbenzimidazoles and 2-Arylbenzoxazoles via C−H Functionalization/C−N/C−O Bond Formation

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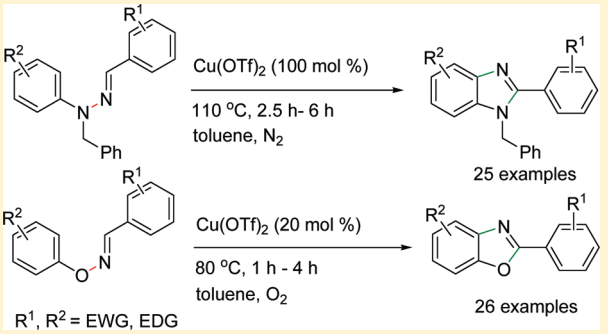
Supporting Information

ABSTRACT: An efficient method for the transformation of *N*-benzyl bisarylhydrazones and bisaryloxime ethers to functionalized 2-aryl-*N*-benzylbenzimidazoles and 2-arylbenzoxazoles is described. The protocol involves a copper(II)-mediated cascade C−H functionalization/C−N/C−O bond formation under neutral conditions. Substrates having either electron-donating or -withdrawing substituents undergo the cyclization to afford the target heterocycles at moderate temperature.



INTRODUCTION

Benzimidazoles[1] and benzoxazoles[2] are privileged structural units that are encountered in a wide range of biologically active and medicinally significant compounds (Figure 1). Recent medicinal chemistry applications of benzimidazole and benzoxazole derivatives include the factor Xa (FXa) inhibitors,[3a] poly(ADP-ribose)polymerase (PARP) inhibitors,[3b] human cytomegalovirus (HCMV) inhibitors,[3c] HIV reverse transcriptase inhibitor L-697,661,[3d] estrogen receptor-b agonist ERB-041,[3e] anticancer agent NSC-693638,[3f] and 5-HT$_3$ receptor agonist.[3g] In addition, benzimidazoles and benzoxazoles are recognized as important scaffolds in fluorescent probes.[4] Development of effective methods for the construction of the benzimidazole and benzoxazole structural framework has thus been important in organic synthesis.

The common methods used for the construction of the benzimidazole and benzoxazole framework involve the condensation of 2-aminoaniline[5] and 2-aminophenol[6] with either carboxylic acid or aldehyde followed by intramolecular cyclization (Figure 2a). These reactions are, however, often limited because of nonavailability of suitably substituted starting precursors and, sometimes, the requirement of harsh reaction conditions such as involvement of strong acids in combination with high temperature (Figure 2a). Some of these drawbacks have been overcome by the recent development in metal-catalyzed cross-coupling reactions that allow the construction of the target heterocyclic frameworks under relatively milder conditions. For example, the synthesis of benzimidzoles[7] and benzoxazoles[8] have been accomplished by copper-catalyzed domino C−N/C−O cross-coupling of 1,2-dihaloarenes with amidines and primary amides, respectively

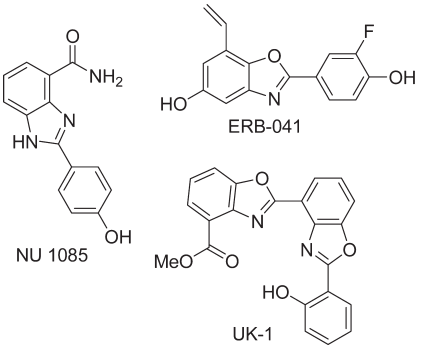


Figure 1. Examples of some biologically active compounds.

(Figure 2b). Palladium-,[9] copper-,[10] and cobalt-catalyzed[11] intramolecular C−N cross-coupling of 2-haloarylamidines has been successfully explored for the synthesis of functionalized benzimidazoles. The synthesis of substituted benzoxazoles has been achieved from 2-haloanilides by intramolecular C−O cross-coupling using copper-,[10,12] cobalt-,[11] and iron-based[13] catalytic systems at moderate temperature (Figure 2c).

In recent years, carbon−carbon[14] and carbon−heteroatom[15−17] bond formation through C−H functionalization using transition metal complexes has gained importance because it obviates the need for prior activation steps. Intramolecular version of these processes has been successfully explored for the synthesis of benz-fuzed

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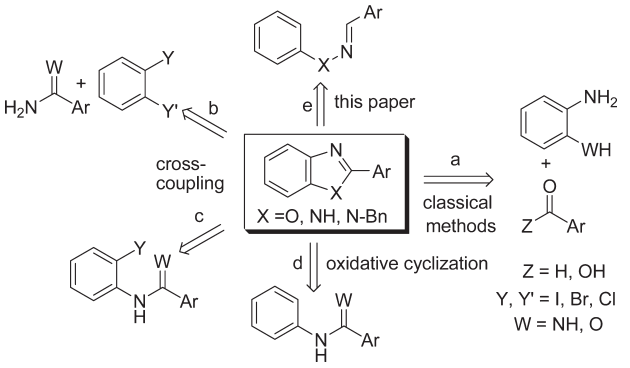


Figure 2. Benzimidazoles and benzoxazoles synthesis: (a) classical methods with 2-aminoanilines and 2-aminophenols, (b) domino C−N/C−O cross-coupling, (c) intramolecular C−N/C−O cross-coupling, and (d, e) C−H Functionalization/C−N/C−O bond formation.

heterocycles from simple precursors. For example, the synthesis of carbazoles[15b] has been accomplished using palladium-catalyzed C−H activation followed by intramolecular C−N bond formation. Subsequently, the scope of the palladium-catalyzed C−H activation and carbon−heteroatom bond formation has been explored for the access to other classes of benz-fuzed heterocycles such as benzothiazoles,[17] indazoles,[18] indolines,[19] oxindoles,[20] benzothiophenes,[21] and benzotriazoles.[22] In addition, copper(II)-catalyzed oxidative cyclization has been explored for the synthesis of benzimidazoles[15a] and benzoxazoles[16a] via C−H functionalization followed by carbon−heteroatom bond formation (Figure 2d). In a recent report, we showed a copper(II)-catalyzed cascade synthesis of benzoxazoles via C−H functionalization/C−N/C−O bond formation from bisaryloxime ethers (Figure 2e).[23] In this contribution, we report a detailed study of the scope of the synthesis of 2-aryl-*N*-benzylbenzimidazoles and 2-arylbenzoxazoles from *N*-benzyl bisarylhydrazones and bisaryloxime ethers, respectively, by intramolecular C−H functionalization/C−N/C−O bond formation. A series of substrates have been cyclized to afford the target heterocycles in short time at moderate temperature.

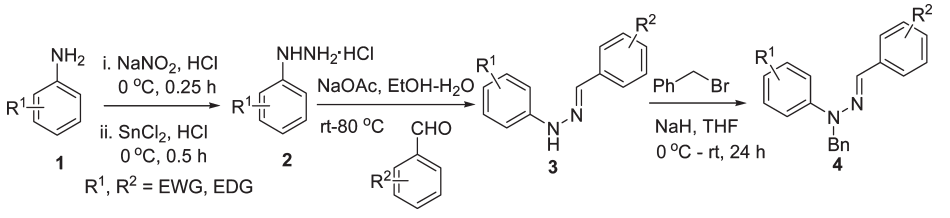
RESULTS AND DISCUSSION

Synthesis of *N*-Benzyl Bisarylhydrazones and Bisaryloxime Ethers. The reaction of anilines **1** with $NaNO_2$/HCl gave the corresponding aryl diazonium salts that could be readily converted into aryl hydrazines **2** in the presence of $SnCl_2 \cdot 2H_2O$ and HCl at 0 °C under air.[24] Condensation of **2** with aryl aldehydes provided arylhydrazones[25] **3**, which could be alkylated with benzyl bromide in the presence of NaH to afford the desired *N*-benzyl bisarylhydrazones **4** in high yield (Scheme 1).

The synthesis of bisaryloxime ethers **8** is shown in Scheme 2.[25] The copper-mediated C−O cross-coupling of *N*-hydroxyphthalimide **5** and arylboronic acid provided *N*-aryloxyphthalimide **6** that could be treated with hydrazine to give aryloxyamine **7**. The target bisaryloxime ether **8** could be obtained by the condensation of **7** with aldehydes in the presence of a catalytic amount of AcOH under ambient conditions.

Optimization of Reaction Conditions. The cyclizations of *N*-benzyl bisarylhydrazone **9a** and bisaryloxime ether **11a** were investigated as model substrates (Table 1). The reaction of bisarylhydrazone **9a** was found to be effective at 110 °C to afford the desired 2-aryl-*N*-benzylbenzimidazole **10a** in 64% yield along with ~5% of benzaldehyde[26] as byproduct in the presence of 100 mol % of $Cu(OTf)_2$ under nitrogen atmosphere. Either lowering of the reaction temperature (100 °C) or decrease in the amount of $Cu(OTf)_2$ (20 mol %) led to the formation of **10a** in <40% yield. The reaction was moderately effective under oxygen atmosphere, affording **10a** in 50% yield along with 10% of benzaldehyde[26] as byproduct. The benzylation of N−H of the bisarylhydrazone **3** was essential, as its absence caused the substrate **3** to undergo C=N cleavage to give benzaldehyde in 80% yield,[26] whereas the cyclization of bisaryloxime ether **11a** could be carried out using 20 mol % of $Cu(OTf)_2$ at 80 °C under oxygen atmosphere to afford the target 2-arylbenzoxazole **12a** in 80% yield along with a trace (~3%) of 1:1 mixture of phenol and benzonitrile as byproducts.[23] The reactions were found to be effective in toluene and xylene, and the former gave the best results. In contrast, polar solvents such as DMSO and

Scheme 1. Synthesis of *N*-Benzyl Bisarylhydrazones



Scheme 2. Synthesis of Bisaryloxime Ethers

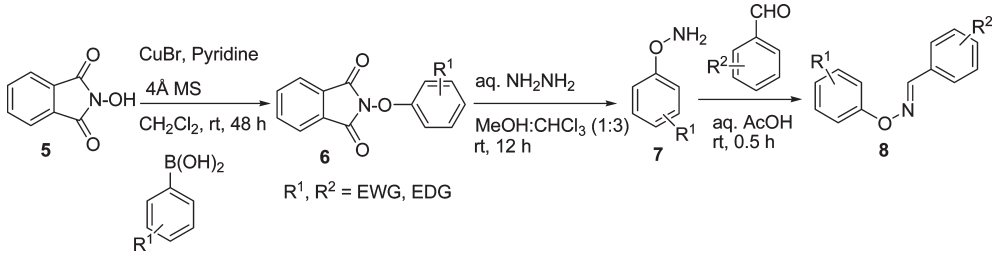


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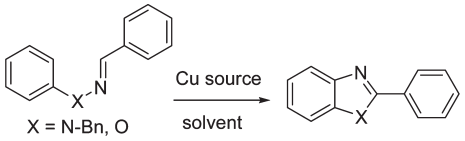
Table 1. Optimization of Reaction Conditions



entry	substrate	[Cu] (mol %)	temp. (°C)	solvent	time (h)	N_2/O_2/air	product	yield (%)[a]
1[b]		$Cu(OTf)_2$(20)	110	toluene	4	O_2		9
2[c]		$Cu(OTf)_2$(20)	110	toluene	4	N_2		14
3[d]		$Cu(OTf)_2$(20)	110	toluene	4	Air		10
4[c]		$Cu(OTf)_2$(100)	110	toluene	4	N_2		64
5[b]		$Cu(OTf)_2$(100)	110	toluene	4	O_2		50
6[e]		$Cu(OTf)_2$(100)	110	1,4-dioxane	7	N_2		21
7		$Cu(OTf)_2$(100)	110	DMSO	7	N_2		n.d.
8[b]	**9a**	$Cu(OTf)_2$(100)	110	xylene	5	N_2	**10a**	55
9		CuCl/CuI(100)	110	toluene	7	N_2		n.d.
10		$Cu(OAc)_2$(100)	110	toluene	7	N_2		n.d.
11[f]		$CuCl_2$(100)	110	toluene	8	N_2		5
12		$CuSO_4 \cdot 5H_2O$(100)	110	toluene	8	N_2		n.d.
13[b]		$Cu(OTf)_2$(100)	100	toluene	4	N_2		40
14[b]		-	110	toluene	4	N_2		n.d.
15[g]		$Cu(OTf)_2$(20)	80	toluene	3	O_2		80
16[g]		$Cu(OTf)_2$(20)	80	xylene	4	O_2		78
17[h]		$Cu(OTf)_2$(20)	80	1,4-dioxane	12	O_2		25
18[h]		$Cu(OTf)_2$(20)	80	DMSO	0.5	O_2		27
19[i]		$Cu(OAc)_2$(20)	80	toluene	24	O_2		20
20[i]		$CuSO_4 \cdot 5H_2O$(20)	80	toluene	24	O_2		30
21	**11a**	$Cu(OTf)_2$(10)	80	toluene	8	O_2	**12a**	70
22		$Cu(OTf)_2$(20)	70	toluene	4	O_2		45
23[j]		$Cu(OTf)_2$(10)	80	toluene	3	Air		66
24[k]		$Cu(OTf)_2$(20)	80	toluene	3	N_2		53
25		-	80	toluene	3	O_2		n.d.

[a] Reaction conditions: substrate (0.5 mmol) and copper source (20−100 mol %) were stirred in appropriate solvent (2 mL). n.d. = not detected. [b] 10% benzaldehyde was obtained. [c] 5% benzaldehyde was obtained. [d] 8% benzaldehyde was obtained. [e] 50% benzaldehyde was obtained. [f] 20% benzaldehyde was obtained. [g] A 1:1 mixture of phenol and benzonitrile (3%) was obtained. [h] A 1:1 mixture of phenol and benzonitrile (45%) was obtained. [i] A 1:1 mixture of phenol and benzonitrile (15%) was obtained. [j] A 1:1 mixture of phenol and benzonitrile (20%) was obtained. [k] A 1:1 mixture of phenol and benzonitrile (35%) was obtained.

1,4-dioxane afforded inferior results.[23] Control experiments without $Cu(OTf)_2$ showed no cyclized target molecules, providing benzaldehyde (10%, in case of **9a**) and a 1:1 mixture of phenol and benzonitrile (~3%, in case of **11a**) as products due to cleavage of C═N and O−N bonds.

Synthesis of Benzimidazoles. With the optimized conditions in hand, the scope of the protocol was further explored for the reactions of a variety of substituted *N*-benzyl bisarylhydrazones (Table 2). The reactions of the substrates having substituents in both as well as one of the aryl rings were studied. For example, *N*-benzyl bisarylhydrazone **9b** having 4-CO_2Me substituent underwent cyclization to give the desired 2-aryl-*N*-benzylbenzimidazole **10b** in 3.0 h with 54% yield. Similarly, the substrates **9c**−**l** bearing 2-OMe, 4-Br, 4-Cl, 4-F, 4-OMe, and 4-Me substituents in the aryl ring could be transformed to the corresponding 2-aryl-*N*-benzylbenzimidazoles **10c**−**k** in <5.0 h with 60−75% yield. Recrystallization of **10i** in CH_3CN gave single crystals whose structure was confirmed by X-ray analysis (see Supporting Information). Furthermore, *N*-benzyl bisarylhydrazones **9 m**−**s** having 4-Me, 4-Cl, 4-OMe, 3,4-diOMe, 3,5-diMe, and 3,4,5-triOMe substituents on one or both the rings proceeded the cyclization to afford benzimidazoles **10l**−**r** in <6 h with 31−67% yield. In addition, *N*-benzyl aryl furanylhydrazone **9t**, *N*-benzyl aryl thiophenylhydrazone **9u** and *N*-benzyl aryl naphthylhydrazones **9w**−**x** were cyclized to give the benzimidazoles **10s**−**v** in <6.0 h with 36−78% yield. Under

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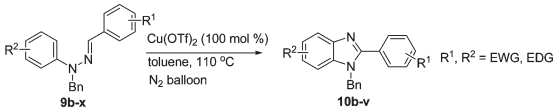
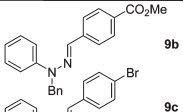
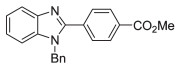
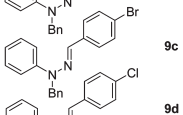
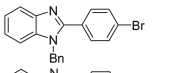
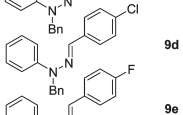
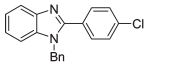
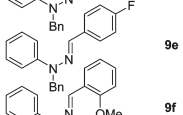
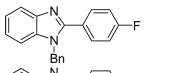
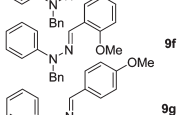
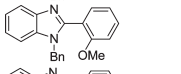
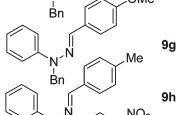
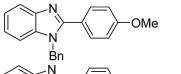
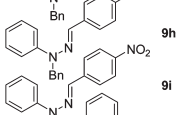
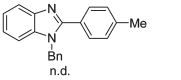
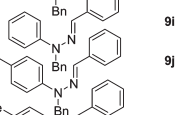
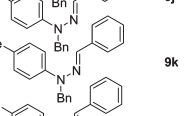
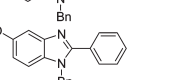
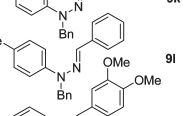
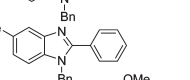
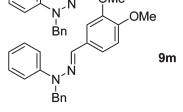
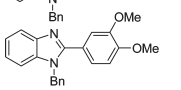
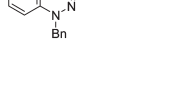
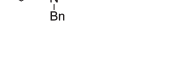
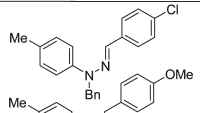
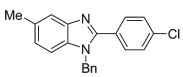
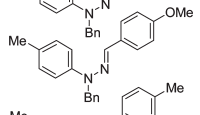
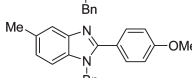
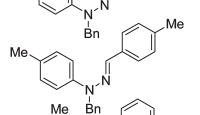
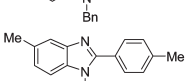
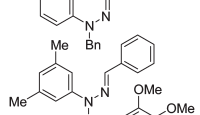
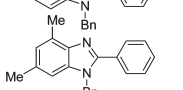
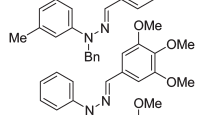
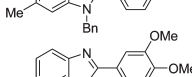
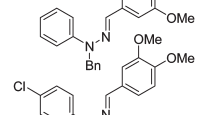
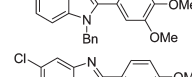
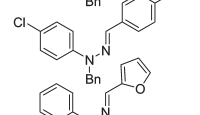
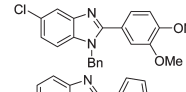
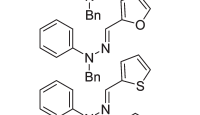
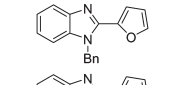
Table 2. Scope of Copper-Mediated Cyclization of *N*-Benzyl Bisarylhyrazones



Entry	Substrate	Time (h)	Product	Yield (%)[a,b]
1	 **9b**	3.0	 **10b**	54
2	 **9c**	3.5	 **10c**	72
3	 **9d**	4.0	 **10d**	70
4	 **9e**	2.5	 **10e**	75
5	 **9f**	4.0	 **10f**	62
6	 **9g**	4.0	 **10g**	60
7	 **9h**	3.5	 **10h**	65
8	 **9i**	4.0	n.d.	- -
9	 **9j**	5.0	 **10i**	68
10	 **9k**	5.0	 **10j**	70
11	 **9l**	4.0	 **10k**	64
12	 **9m**	3.0	 **10l**	65
13	 **9n**	4.5	 **10m**	41
14	 **9o**	5.5	 **10n**	48
15	 **9p**	5.0	 **10o**	52
16	 **9q**	5.0	 **10p**	67
17	 **9r**	3.0	 **10q**	63
18	 **9s**	6.0	 **10r**	31
19	 **9t**	4.0	 **10s**	78
20	 **9u**	3.5	 **10t**	70
21	**9v**	4.0	n.d.	- -
22	**9w**	4.5	**10u**	70
23	**9x**	6.0	**10v**	36

[a] Reaction conditions: substrate **9a**−**x** (0.5 mmol) and $Cu(OTf)_2$ (100 mol %) were stirred in toluene (2 mL) at 110 °C under N_2 balloon. [b] Aldehyde (~5%) was obtained as byproduct. n.d. = not detected.

Scheme 3. Reaction of *meta*-Substituted *N*-Benzyl Bisarylhydrazone

these conditions, *N*-benzyl bisarylhydrazone having 4-NO_2 group **9i** and *N*-benzyl aryl pyridylhydrazone **9v** exhibited no desired cyclization undergoing C═N cleavage to give the corresponding aldehydes in quantitative yield. In the case of *N*-benzyl bisarylhydrazone **9y** containing 3-Me substituent, the cyclization proceeded to give a 1:2 mixture of the regioisomers **10w** and **10x** in 37% yield (Scheme 3).

Synthesis of Benzoxazoles. The cyclization of bisaryloxime ethers was next explored (Table 3).[23] Monosubstituted bisaryloxime ethers **11b**−**i** having 2-Br, 2-OMe, 3-Br, 4-Br, 4-Cl, 4-F, 4-OMe, and 4-Me groups on the aryl ring underwent cyclization to give the corresponding 2-arylbenzoxazoles **12b**−**i** in 57−90% yield. Likewise, the cyclization of the disubstituted bisaryloxime ethers **11k**−**r** with 4−Br, 4-Cl, 4-OMe, 4-Me, and 4-vinyl groups on the aryl rings could be accomplished to provide the desired substituted 2-arylbenzoxazoles **12j**−**q** in 38−88% yield. Furthermore, 2,4,5-trimethoxy substituted bisaryloxime ether **11s** underwent the desired transformation to give the corresponding benzoxazole **12r** in 2 h with 80% yield. In addition, aryl furanyloxime ethers **11t**−**u**, aryl thiophenyloxime ether **11v**, aryl naphthyloxime ethers **11w**−**x**, aryl 8-methoxyquinolinyloxime ether **11y** and aryl pyrenyloxime ether **11z** proceeded reaction to give the substituted benzoxazoles **12s**−**y** in <4.0 h with 41−85% yield. In contrast, bisaryloxime ether **11j** having 4-NO_2

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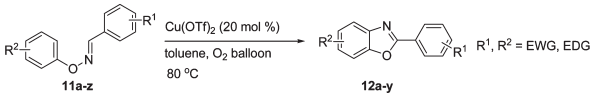
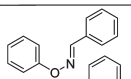
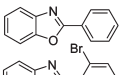
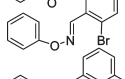
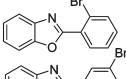
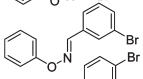
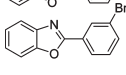
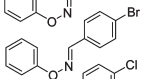
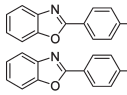
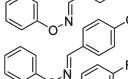
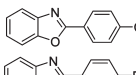
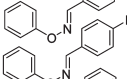
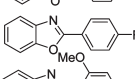
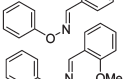
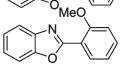
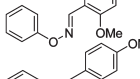
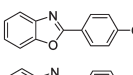
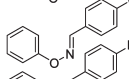
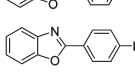
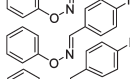
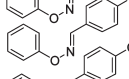
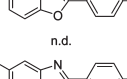
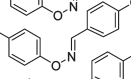
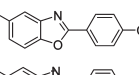
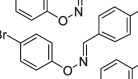
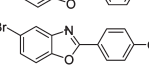
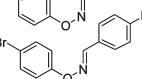
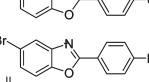
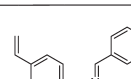
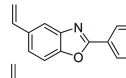
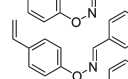
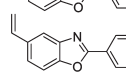
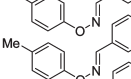
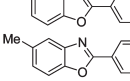
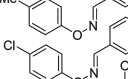
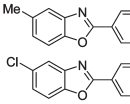
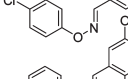
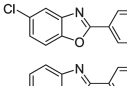
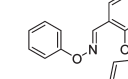
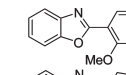
Table 3. Scope of Copper-Mediated Cyclization of Bisaryloxime Ethers



Entry	Substrate		Time (h)	Product		Yield(%)[a,b]
1		**11a**	3.0		**12a**	80
2		**11b**	1.0		**12b**	60
3		**11c**	3.0		**12c**	83
4		**11d**	3.0		**12d**	81
5		**11e**	3.5		**12e**	82
6		**11f**	1.0		**12f**	57
7		**11g**	1.0		**12g**	67
8		**11h**	3.5		**12h**	85
9		**11i**	3.0		**12i**	90
10		**11j**	2.5	n.d.		-
11		**11k**	1.5		**12j**	51
12		**11l**	1.5		**12k**	38
13		**11m**	2.0		**12l**	50
14		**11n**	3.0		**12m**	80

Entry	Substrate		Time (h)	Product		Yield(%)[a,b]
15		**11o**	3.0		**12n**	62
16		**11p**	3.0		**12o**	56
17		**11q**	3.0		**12p**	88
18		**11r**	1.5		**12q**	84
19		**11s**	2.0		**12r**	80
20		**11t**	3.5		**12s**	62
21		**11u**	3.0		**12t**	41
22		**11v**	4.0		**12u**	80
23		**11w**	2.5		**12v**	80
24		**11x**	2.5		**12w**	81
25		**11y**	1.5		**12x**	85
26		**11z**	2.0		**12y**	74

[a] Reaction conditions: substrate **11a**−**z** (0.5 mmol) and $Cu(OTf)_2$ (20 mol %) were stirred in toluene (2 mL) at 80 °C under O_2 balloon. [b] A mixture phenol and nitrile (3−5%) was obtained as byproduct. n.d. = not detected.

Scheme 4. Reaction of Alkyl phenyloxime and Allyl phenyloxime Ethers

Scheme 5. Reaction of Bisphenyloxime Thioether

group showed no desired cyclization giving a 1:1 mixture of 4-nitrophenol and benzonitrile in quantitative yield due to cleavage of N−O bond. Similar results were obtained with alkyl aryloxime ether **13** and allyl aryloxime ether **14** affording a 1:1 mixture of the respective phenol and nitrile in quantitative yield (Scheme 4).

Using these conditions, the reaction of bisphenyloxime thioether **15** was also investigated (Scheme 5). However, the substrate **15** exhibited no desired cyclization proceeding N−S cleavage to afford a mixture of benzonitrile and diphenyldisulfide in quantitative yield (Scheme 5).

Mechanism. Bisaryloxime ether **16** having an α-methyl group showed no reaction, and the starting material was recovered intact, which suggests that the imine C−H is crucial for the cyclization process. Crossover experiment with the substrates **11i** and **11x** afforded **12i** and **12w**, respectively, as the only cyclized products (Scheme 6). This result reveals that the reaction involves an intramolecular process. Kinetic isotope studies with **11i** and **11i (D)** showed k_H/k_D= 0.96 (see Supporting Information), which suggests that the imine C−H bond cleavage is not involved in the rate determining step (Scheme 7). In addition, the substrates having electron-withdrawing substituents showed greater reactivity compared to those bearing

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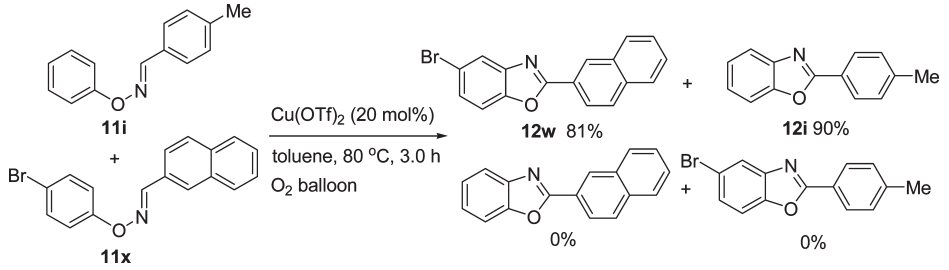
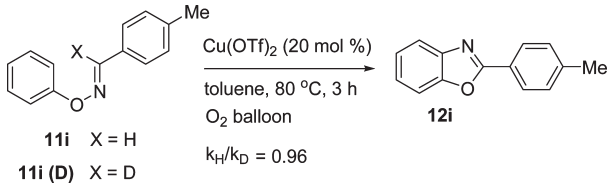
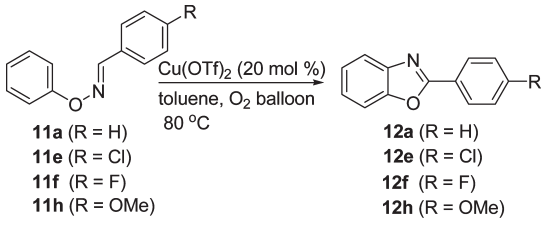
Scheme 6. Crossover Experiments for Intramolecular Cyclization



Scheme 7. Kinetic Isotope Effect





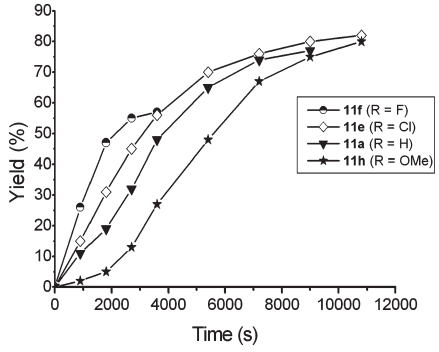
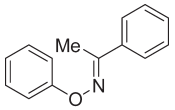


Figure 3. Study of relative rates of bisaryloxime ethers **11a**, **11e**, **11f**, and **11h**.

electron-donating group. For example, bisaryloxime ethers **11e** and **11f** having 4-Cl and 4-F groups, respectively, showed enhanced reactivity compared to unsubstituted bisaryloxime ether **11a**, while the substrate **11h** having 4-OMe group exhibited less reactivity (Figure 3). These results suggest that the reaction of bisaryloxime ether bearing an electron-withdrawing group in the imine aryl ring is facilitated compared to that having an electron-donating group. Thus, the reaction involve a Lewis acid assisted C−H functionalization followed by C−N/C−O bond formation (Scheme 8). Copper(II) triflate may undergo coordination with the imine nitrogen of the substrates **9** and **11** to give the intermediate **a**. The activated intermediate **a** may then lead to the formation of **b** by electrophilic aromatic substitution at the Cu Center. The formation of the six-membered metallocycle **c** and the subsequent reductive elimination could give the target heterocycles and copper(0) species.[27,16a] The copper(0) species may undergo reaction with trifluoromethanesulfonic acid to regenerate the catalyst.[28] The substrate **9** gave the best results under nitrogen atmosphere,[29] whereas the reaction of bisaryloxime ether **11** was found to be superior under oxygen atmosphere.[16a]



CONCLUSIONS

Copper(II)-mediated conversion of *N*-benzyl bisarylhydrazones and bisaryloxime ethers into *N*-benzyl 2-arylbenzimidazoles and 2-arylbenzoxazole has been developed via a cascade C−H functionalization/C−N/C−O bond formation. The observed experimental results suggest that the reactions involve an intramolecular process. The substrates having electron-withdrawing groups have exhibited greater reactivity in comparison to those bearing electron-donating groups.

EXPERIMENTAL SECTION

General Experimental Methods. Aldehydes, anilines, benzyl bromide (98%), NaH (60%), phenylboronic acid (95%), *N*-hydroxyphthalimide (97%), CuCl (97%), $SnCl_2 \cdot 2H_2O$ (97%), and $Cu(OTf)_2$ (98%) were purchased from Aldrich and used as received. Toluene and THF were freshly distilled from sodium under nitrogen prior to use. HPLC grade CH_3CN and 2-propanol were purchased from Merck. Purification of the reaction products was carried out by column chromatography using Rankem silica gel (230−400 mesh). Analytical TLC was performed on Merck silica gel G/GF 254 plate. NMR spectra were recorded on 400 MHz spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Chemical shifts (δ) are reported in ppm, and spin−spin coupling constants (J) are given in hertz. Melting points were determined using melting point apparatus and are uncorrected. IR spectra were recorded using FT-IR spectrometer. Elemental analyses were recorded using CHNS analyzer. Mass spectra were recorded on a Q-Tof mass spectrometer. HPLC analysis was carried out using Waters C_{18} column with 2% 2-propanol in CH_3CN as eluent. Single crystal X-ray data were recorded using Mo Kα radiation equipped with a CCD area detector. The structures were solved by direct method using SHELLX-97 (Göttingen, Germany). Bisaryhydrazones and bisaryloxime ethers were prepared according to reported procedure.[25]

General Procedure for Preparation of Arylhydrazine Hydrochlorides 2[24]. To a stirred solution of anilines **1** (6 mmol) in conc

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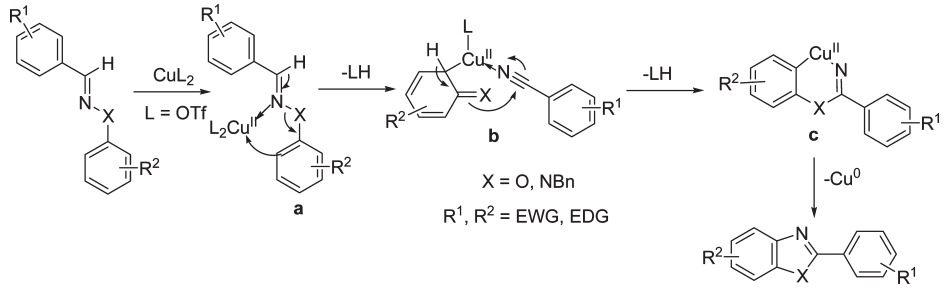
Scheme 8. Proposed Catalytic Cycle



HCl (10.4 mL) at 0 °C was added dropwise an ice-cooled solution of $NaNO_2$ (6.38 mmol) in distilled water (2.5 mL) for 0.25 h (Scheme 1). A solution of $SnCl_2 \cdot 2H_2O$ (13.3 mmol) in conc HCl (3.0 mL) was then added dropwise for 0.1 h, and the stirring was continued for an additional 0.5 h. The precipitate was filtered and dried under vacuum to give the titled hydrazine hydrochlorides **2** that were used without further purification for the condensation with aldehydes.

General Procedure for *N*-Benzylation of Bisarylhydrazones 3. To a stirred suspension NaH (5 mmol) in THF (2 mL) at 0 °C were added bisarylhydrazones **3** (5 mmol) in THF (3 mL) dropwise under nitrogen atmosphere (Scheme 1). After 2 h, the solution was treated with benzyl bromide (5 mmol) in THF (2 mL) dropwise, and the resultant mixture was allowed to stir for 24 h at ambient temperature. Evaporation of the solvent gave a residue that was extracted using ethyl acetate (30 mL). The organic layer was washed with water (2 × 15 mL), dried (Na_2SO_4), and evaporated under reduced pressure to give a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford the titled compounds **9a**−**y** that were used for the cyclization reactions.

1-Benzyl-2-benzylidene-1-phenylhydrazine 9a. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.40; colorless solid; yield 88%; mp 111−112 °C (lit.[30a] mp 112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.2 Hz, 2H), 7.42−7.23 (m, 13H), 6.97 (t, J = 7.2 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 136.6, 135.8, 132.6, 129.3, 129.1, 128.6, 128.0, 127.4, 126.3, 126.1, 120.9, 114.9, 50.4; FT-IR (KBr) 3085, 3060, 3024, 3003, 2949, 2922, 1950, 1599, 1589, 1561, 1491, 1462, 1453, 1442, 1393, 1352, 1331, 1312, 1296, 1285, 1248, 1223, 1191, 1157, 1148, 1070, 1046, 1027 cm^{-1}; (ESI-MS) m/z 287.17 $[M + H]^+$. Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.95; H, 6.31; N, 9.74.

2-(4-Carbomethoxybenzylidene)-1-benzyl-1-phenylhydrazine 9b. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; light yellow solid; yield 85%; mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.41−7.39 (m, 2H), 7.34−7.26 (m, 6H), 7.20 (d, J = 7.2 Hz, 2H), 6.99−6.96 (m, 1H), 5.14 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 147.7, 141.0, 135.3, 131.1, 130.0, 129.4, 129.2, 128.9, 127.6, 126.1, 125.9, 121.6, 115.3, 52.1, 50.7; FT-IR (KBr) 3032, 2948, 2868, 1717, 1596, 1586, 1555, 1495, 1454, 1431, 1410, 1393, 1353, 1331, 1314, 1275, 1242, 1160, 1149, 1110 cm^{-1}; (ESI-MS) m/z 345.16 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.79 H, 5.87; N, 8.07.

2-(4-Bromobenzylidene)-1-benzyl-1-phenylhydrazine 9c. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 92%; mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.24 (m, 14H), 6.98 (t, J = 7.2 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 135.7, 135.5, 131.7, 131.2, 129.4, 129.2, 127.7, 127.5, 126.1, 121.6, 121.2, 115.1, 50.7; FT-IR (KBr) 3082, 3059, 3022, 2868, 1590, 1576, 1552, 1496, 1453, 1398, 1352, 1333, 1302, 1245, 1227, 1150, 1099, 1069, 1041, 1028, 1005 cm^{-1}; (ESI-MS) m/z 365.08, 367.08 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}BrN_2$: C, 65.76; H, 4.69; N, 7.67. Found: C, 65.84; H, 4.66; N, 7.61.

2-(4-Chlorobenzylidene)-1-benzyl-1-phenylhydrazine 9d. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 90%; mp 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2H), 7.40−7.21 (m, 12H), 6.98 (t, J = 7.2 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 135.6, 135.3, 133.5, 131.3, 129.4, 129.2, 128.9, 127.6, 127.5, 126.2, 121.2, 115.1, 50.7; FT-IR (KBr) 3086, 3061, 3023, 1593, 1577, 1555, 1497, 1454, 1401, 1392, 1353, 1331, 1302, 1292, 1245, 1229, 1219, 1192, 1149, 1100, 1086, 1041, 1029, 1008 cm^{-1}; (ESI-MS) m/z 321.13 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}ClN_2$: C, 74.88; H, 5.34; N, 8.73. Found: C, 74.95; H, 5.32; N, 8.79.

2-(4-Fluorobenzylidene)-1-benzyl-1-phenylhydrazine 9e. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.45; colorless solid; yield 88%; mp 93−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (m, 2H), 7.40−7.22 (m, 10H), 7.03−6.94 (m, 3H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5, 147.9, 135.7, 132.9, 131.5, 129.3, 129.2, 127.9, 127.8, 127.5, 126.2, 121.0, 115.7, 115.5, 115.0, 50.7; FT-IR (KBr) 3060, 3024, 2923, 2851, 1654, 1599, 1566, 1489, 1451, 1407, 1394, 1352, 1331, 1290, 1227, 1212, 1192, 1148, 1092, 1075, 1047, 1028 cm^{-1}; (ESI-MS) m/z 305.15 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}FN_2$: C, 78.92; H, 5.63; N, 9.20. Found: C, 78.84; H, 5.60; N, 9.28.

2-(2-Methoxybenzylidene)-1-benzyl-1-phenylhydrazine 9f. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 80%; mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.81 (s, 1H), 7.41 (d, J = 7.6 Hz, 2H), 7.34−7.18 (m, 8H), 6.99−6.90 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 5.17 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 148.1, 136.0, 129.3, 129.0, 128.8, 128.6, 127.3, 126.4, 125.6, 125.3, 121.0, 120.6, 114.8, 111.3, 55.6, 50.2; FT-IR (KBr) 3014, 2967, 2939, 2835, 1597, 1561, 1485, 1462, 1428, 1391, 1350, 1329, 1283, 1239, 1199, 1145, 1105, 1072, 1047, 1025 cm^{-1}; (ESI-MS) m/z 317.17 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.78; H, 6.34; N, 8.79.

2-(4-Methoxybenzylidene)-1-benzyl-1-phenylhydrazine 9g. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; light yellow solid; yield 90%; mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 3H), 7.37−7.24 (m, 9H), 6.92−6.86 (m, 3H), 5.15 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 148.1, 136.1, 132.6, 129.5, 129.3, 129.1, 127.6, 127.4, 126.2, 120.5, 114.6, 114.1, 55.4, 50.4; FT-IR (KBr) 3023, 2965, 2926, 2840, 1647, 1604, 1590, 1563, 1496, 1453, 1444, 1415, 1394, 1354, 1331, 1295, 1247, 1220, 1193, 1179, 1160, 1152, 1106, 1075, 1046, 1027, cm^{-1}; (ESI-MS) m/z 317.18 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.79; H, 6.39; N, 8.81.

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2-(4-Methylbenzylidene)-1-benzyl-1-phenylhydrazine 9h. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.45; colorless solid; yield 81%; mp 136−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.42−7.12 (m, 12H), 6.95−6.93 (m, 1H), 5.17 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 138.0, 136.0, 134.0, 132.8, 129.3, 129.2, 127.4, 126.3, 126.2, 120.7, 114.9, 50.6, 21.5; FT-IR (KBr) 3054, 3024, 2916, 1589, 1578, 1558, 1497, 1453, 1393, 1353, 1331, 1301, 1246, 1190, 1158, 1148, 1109, 1078, 1045, 1027 cm^{-1}; (ESI-MS) m/z 301.17 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.88; H, 6.73; N, 9.39.

2-(4-Nitrobenzylidene)-1-benzyl-1-phenylhydrazine 9i. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; orange solid; yield 83%; mp 119−121 °C (lit.[30a] mp 121−124 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.16 (m, 2H), 7.73−7.71 (m, 2H), 7.45−7.42 (m, 2H), 7.39−7.35 (m, 5H), 7.32 (d, J = 7.6 Hz, 1H), 7.26−7.22 (m, 2H), 7.07−7.05 (m, 1H), 5.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 146.5, 142.9, 134.7, 129.5, 129.4, 129.2, 127.7, 126.2, 126.0, 124.0, 122.2, 115.6, 50.9; FT-IR (KBr) 3057, 3029, 2921, 2852, 1596, 1557, 1508, 1495, 1450, 1411, 1397, 1338, 1247, 1181, 1161, 1152, 1108, 1024 cm^{-1}; (ESI-MS) m/z 332.15 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.55; H, 5.15; N, 12.75.

1-Benzyl-2-benzylidene-1-(4-chlorophenyl)hydrazine 9j. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.80; light yellow solid; yield 85%; mp 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.39−7.19 (m, 13H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 136.2, 135.2, 133.2, 129.2, 129.1, 128.6, 128.2, 127.5, 126.4, 126.0, 125.6, 115.9, 50.1; FT-IR (KBr) 3063, 3033, 2971, 2916, 2868, 1953, 1589, 1558, 1493, 1454, 1441, 1410, 1394, 1356, 1329, 1312, 1303, 1241, 1221, 1193, 1182, 1148, 1094, 1071, 1026, 1001 cm^{-1}; (ESI-MS) m/z 321.12 $[M + H]^+$. Anal. Calcd for $C_{20}H_{17}ClN_2$: C, 74.88; H, 5.34; N, 8.73. Found: C, 74.82; H, 5.31; N, 8.80.

1-Benzyl-2-benzylidene-1-(4-methoxyphenyl)hydrazine 9k. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.30; light yellow solid; yield 91%; mp 112−113 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.34−7.18 (m, 11H), 6.88−6.86 (m, 2H), 5.12 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 142.3, 136.9, 136.2, 131.8, 129.1, 128.6, 127.7, 127.4, 126.3, 126.1, 116.8, 114.7, 55.8, 51.7; FT-IR (KBr) 3029, 2961, 2935, 2853, 1590, 1557, 1509, 1453, 1441, 1423, 1394, 1356, 1326, 1295, 1248, 1177, 1157, 1072, 1044, 1026 cm^{-1}; (ESI-MS) m/z 317.18 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.66; H, 6.35; N, 8.91.

1-Benzyl-2-benzylidene-1-*p*-tolylhydrazine 9l. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; yellow solid; yield 88%; mp 137−138 °C (lit.[30b] mp 138 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.59 (m, 2H), 7.34−7.22 (m, 11H), 7.13−7.11 (m, 2H), 5.15 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 136.8, 136.0, 132.0, 130.2, 129.8, 129.1, 128.6, 127.8, 127.4, 126.2, 115.1, 50.7, 20.7; FT-IR (KBr) 3061, 3026, 2917, 2857, 1611, 1590, 1558, 1510, 1495, 1453, 1442, 1392, 1355, 1329, 1316, 1282, 1245, 1224, 1191, 1151, 1072, 1028 cm^{-1}; (ESI-MS) m/z 301.18 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.90; H, 6.68; N, 9.42.

2-(3,4-Dimethoxybenzylidene)-1-benzyl-1-phenylhydrazine 9m. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 92%; mp 117−118 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.23 (m, 11H), 7.01−6.94 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 3.95 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.8, 135.8, 132.5, 129.7, 129.1, 128.9, 127.2, 126.0, 120.4, 120.0, 114.5, 110.8, 107.8, 55.8, 50.3; FT-IR (KBr) 3023, 2998, 2966, 2936, 2838, 1594, 1566, 1516, 1497, 1454, 1412, 1394, 1337, 1299, 1266, 1241, 1203, 1191, 1167, 1148, 1138, 1128, 1080, 1023 cm^{-1}; (ESI-MS) m/z 347.19 $[M + H]^+$. Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.35; H, 6.37; N, 8.14.

1-(4-Chlorobenzylidene)-2-benzyl-2-*p*-tolylhydrazine 9n. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.40; light yellow solid; yield 80%; mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2H), 7.36−7.21 (m, 10H), 7.14 (d, J = 8.4 Hz, 2H), 5.15 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 135.8, 135.4, 133.3, 130.7, 129.9, 129.2, 128.8, 127.5, 127.3, 126.2, 115.2, 51.0, 20.7; FT-IR (KBr) 3027, 3000, 2917, 1604, 1594, 1553, 1510, 1489, 1455, 1401, 1355, 1329, 1247, 1168, 1152, 1085, 1011 cm^{-1}; (ESI-MS) m/z 335.14 $[M + H]^+$. Anal. Calcd for $C_{21}H_{19}ClN_2$: C, 75.33; H, 5.72; N, 8.37. Found: C, 75.41; H, 5.75; N, 8.30.

1-(4-Methoxybenzylidene)-2-benzyl-2-*p*-tolylhydrazine 9o. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; light brown solid; yield 81%; mp 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2H), 7.32−7.22 (m, 8H), 7.12 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.12 (s, 2H), 3.80 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.0, 136.2, 132.0, 129.8, 129.1, 127.5, 127.3, 126.2, 114.8, 114.1, 55.4, 50.6, 20.7; FT-IR (KBr) 3060, 3024, 3002, 2934, 2916, 2838, 1608, 1561, 1507, 1453, 1415, 1393, 1345, 1332, 1316, 1256, 1182, 1149, 1104, 1076, 1031 cm^{-1}; (ESI-MS) m/z 331.18 $[M + H]^+$. Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 80.05; H, 6.74; N, 8.42.

1-(4-Methylbenzylidene)-2-benzyl-2-*p*-tolylhydrazine 9p. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.60; light yellow solid; yield 80%; mp 188−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.32−7.22 (m, 9H), 7.13−7.10 (m, 3H), 5.14 (s, 2H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 137.8, 136.2, 134.1, 132.3, 130.1, 129.8, 129.4, 129.1, 127.4, 126.3, 126.2, 115.0, 50.8, 21.5, 20.7; FT-IR (KBr) 3063, 3023, 2994, 2916, 1611, 1589, 1556, 1508, 1454, 1391, 1355, 1329, 1315, 1301, 1245, 1223, 1193, 1186, 1153, 1108, 1075, 1028 cm^{-1}; (ESI-MS) m/z 315.20 $[M + H]^+$. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.11; H, 7.03; N, 8.86.

1-Benzyl-2-benzylidene-1-(3,5-dimethylphenyl)hydrazine 9q. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 89%; mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.34−7.21 (m, 9H), 7.04 (s, 2H), 6.62 (s, 1H), 5.16 (s, 2H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 138.9, 136.8, 136.0, 132.4, 129.1, 128.6, 127.9, 127.4, 127.3, 126.3, 126.25, 126.20, 123.0, 112.9, 50.8, 21.9; FT-IR (KBr) 3060, 3025, 2969, 2915, 2851, 1598, 1585, 1558, 1494, 1474, 1453, 1440, 1396, 1378, 1355, 1330, 1305, 1294, 1282, 1227, 1207, 1167, 1148, 1072, 1028 cm^{-1}; (ESI-MS) m/z 315.20 $[M + H]^+$. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.09; H, 7.02; N, 8.89.

2-(3,4,5-Trimethoxybenzylidene)-1-benzyl-1-phenylhydrazine 9r. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.40; light yellow solid; yield 81%; mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.23 (m, 10H), 6.98 (t, J = 7.2 Hz, 1H), 6.87 (s, 2H), 5.18 (s, 2H), 3.89 (s, 6H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 147.8, 138.2, 135.6, 132.3, 132.2, 129.2, 129.1, 127.3, 126.0, 120.8, 114.8, 103.2, 60.9, 56.1, 50.4; FT-IR (KBr) 3088, 3064, 3026, 2998, 2987, 2958, 2926, 2825, 1595, 1565, 1495, 1455, 1430, 1413, 1394, 1351, 1325, 1277, 1238, 1181, 1163, 1130, 1079, 1051, 1040, 1026, 1003 cm^{-1}; (ESI-MS) m/z 377.19 $[M + H]^+$. Anal. Calcd for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.28; H, 6.45; N, 7.37.

1-(3,4-Dimethoxybenzylidene)-2-benzyl-2-(4-chlorophenyl)hydrazine 9s. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; light brown solid; yield 83%; mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.20 (m, 11H), 7.02−7.00 (m, 1H), 6.83 (d, J = 8.4 Hz, 1H), 5.14 (s, 2H), 3.95 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 149.3, 146.4, 135.4, 133.3, 129.3, 129.1, 129.0, 127.4, 125.9, 125.2, 120.2, 115.6, 110.9, 107.9, 55.9, 55.8,

50.2; FT-IR (KBr) 3077, 3061, 3021, 3002, 2961, 2936, 2839, 1593, 1563, 1514, 1492, 1455, 1417, 1395, 1340, 1320, 1303, 1240, 1200, 1187, 1165, 1146, 1135, 1119, 1105, 1094, 1073, 1022, 1001 cm^{-1}; (ESI-MS) m/z 381.15 $[M + H]^+$. Anal. Calcd for $C_{22}H_{21}ClN_2O_2$: C, 69.38; H, 5.56; N, 7.36. Found: C, 69.31; H, 5.58; N, 7.32.

1-Benzyl-2-((furan-2-yl)methylene)-1-phenylhydrazine 9t. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 90%; mp 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.22 (m, 11H), 6.97−6.94 (m, 1H), 6.46−6.40 (m, 2H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 147.6, 142.4, 135.4, 129.3, 129.1, 127.5, 126.1, 123.4, 121.1, 115.1, 111.6, 108.1, 50.6; FT-IR (KBr) 3131, 3109, 3086, 3062, 3029, 3007, 1956, 1867, 1676, 1593, 1544, 1496, 1483, 1452, 1391, 1377, 1357, 1329, 1315, 1301, 1246, 1217, 1191, 1162, 1153, 1142, 1082, 1030, 1013 cm^{-1}; (ESI-MS) m/z 277.14 $[M + H]^+$. Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.29; H, 5.82; N, 10.08.

1-Benzyl-1-phenyl-2-((thiophen-2-yl)methylene)hydrazine 9u. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 88%; mp 130−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.36−7.17 (m, 11H), 6.94 (d, J = 3.2 Hz, 2H), 5.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 142.4, 135.4, 129.2, 129.1, 127.6, 127.4, 127.2, 126.0, 125.9, 125.1, 120.8, 114.7, 50.5; FT-IR (KBr) 3097, 3081, 3062, 3030, 2985, 2923, 2857, 1953, 1650, 1593, 1567, 1520, 1495, 1453, 1436, 1381, 1359, 1346, 1327, 1311, 1299, 1246, 1219, 1194, 1182, 1079, 1041, 1028 cm^{-1}; (ESI-MS) m/z 293.12 $[M + H]^+$. Anal. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58; S, 10.97. Found: C, 73.87; H, 5.50; N, 9.61; S, 11.02.

1-Benzyl-1-phenyl-2-((pyridine-2-yl)methylene)hydrazine 9v. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; brown solid; yield 90%; mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46−8.44 (m, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.68−7.63 (m, 1H), 7.50 (s, 1H), 7.45−7.42 (m, 2H), 7.37−7.21 (m, 7H), 7.12−7.09 (m, 1H), 7.02−6.98 (m, 1H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 149.0, 147.5, 136.2, 134.9, 133.2, 129.3, 129.0, 127.4, 126.0, 122.1, 121.5, 119.3, 115.2, 50.7; FT-IR (KBr) 3054, 3027, 3000, 1950, 1681, 1593, 1567, 1495, 1473, 1454, 1431, 1388, 1352, 1329, 1283, 1192, 1168, 1154, 1089, 1048, 1029 cm^{-1}; (ESI-MS) m/z 288.16 $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41 H, 5.96; N, 14.62. Found: C, 79.36; H, 5.94; N, 14.70.

1-Benzyl-2-((naphthalen-2-yl)methylene)-1-phenylhydrazine 9w. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.70; colorless solid; yield 90%; mp 190−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.81−7.74 (m, 4H), 7.55 (s, 2H), 7.47−7.25 (m, 10H), 6.99 (t, J = 6.4 Hz,1H) 5.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 135.9, 134.5, 133.7, 133.5, 132.9, 129.4, 129.2, 128.4, 128.1, 128.0, 127.5, 126.7, 126.4, 126.2, 126.1, 123.3, 121.0, 115.1, 50.7; FT-IR (KBr) 3060, 3032, 2981, 1933, 1625, 1595, 1577, 1560, 1496, 1454, 1431, 1400, 1377, 1356, 1327, 1313, 1299, 1272, 1241, 1187, 1180, 1161, 1145, 1076, 1045, 1028 cm^{-1}; (ESI-MS) m/z 337.18 $[M + H]^+$. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.76; H, 5.96; N, 8.28.

2-Benzyl-1-((naphthalen-2-yl)methylene)-2-*p*-tolylhydrazine 9x. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.45; colorless solid; yield 87%; mp 296−298 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 1H), 7.80−7.73 (m, 4H), 7.51−7.14 (m, 12H), 5.21 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 135.3, 134.0, 133.0, 132.7, 131.5, 129.7, 129.3, 128.6, 127.7, 127.4, 127.3, 126.9, 125.9, 125.8, 125.7, 125.4, 122.6, 114.5, 50.1, 20.1; FT-IR (KBr) 3032, 2928, 2857, 1614, 1560, 1511, 1455, 1430, 1403, 1377, 1357, 1321, 1306, 1242, 1188, 1153, 1028 cm^{-1}; (ESI-MS) m/z 351.20 $[M + H]^+$. Anal. Calcd for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.78; H, 6.29; N, 7.93.

2-Benzyl-1-benzylidene-2-m-tolylhydrazine 9y. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.55; colorless solid; yield 92%; mp 146−147 °C (lit.[30b] mp 145 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.2 Hz, 2H), 7.35−7.19 (m, 12H), 6.79−6.77 (m, 1H), 5.16 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 139.1, 136.7, 135.9, 132.5, 129.2, 128.7, 128.0, 127.4, 126.3, 126.2, 121.9, 115.7, 112.2, 50.7, 22.1; FT-IR (KBr) 3054, 3030, 2925, 1637, 1606, 1585, 1560, 1494, 1452, 1442, 1395, 1351, 1329, 1312, 1254, 1225, 1200, 1167, 1148, 1074, 1028 cm^{-1}; (ESI-MS) m/z 301.19 $[M + H]^+$. Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.90; H, 6.73; N, 9.37.

General Procedure for the Cyclization of *N*-Benzyl Bisarylhydrazones 9a−y. Substrates **9a−y** (0.5 mmol) and $Cu(OTf)_2$ (0.5 mmol) were stirred at 110 °C in toluene (2 mL) under a nitrogen balloon (Table 2). Progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and poured into 30% aqueous NH_4OH (5 mL). The solution was extracted with EtOAc (3 × 15 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford the desired *N*-benzyl 2-arylbenzimidazoles **10a−x** in analytically pure form.

1-Benzyl-2-phenyl-1*H*-benzo[*d*]imidazole 10a[30c]. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.20; colorless solid; yield 64%; mp 123−124 °C (lit.[30c] mp 132−133 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 7.2 Hz, 3H), 7.36−7.30 (m, 4H), 7.26−7.21 (m, 2H), 7.12 (d, J = 6.8 Hz, 2H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.0, 136.5, 136.1, 132.7, 130.2, 129.5, 129.2, 128.9, 128.0, 126.1, 123.3, 123.0, 120.1, 110.7, 48.5; FT-IR (KBr) 3060, 3029, 2962, 2928, 1706, 1600, 1508, 1492, 1469, 1449, 1441, 1392, 1361, 1330, 1314, 1261, 1177, 1163, 1097, 1028, 1002 cm^{-1}; (ESI-MS) m/z 285.14 $[M + H]^+$. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.60; H, 5.65; N, 9.75.

Methyl 4-(1-Benzyl-1*H*-benzo[*d*]imidazol-2-yl)benzoate 10b. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.20; light yellow solid; yield 54%; mp 179−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.11 (m, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.79−7.77 (m, 2H), 7.36−7.26 (m, 6H), 7.11−7.09 (m, 2H), 5.47 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 153.0, 143.2, 136.4, 136.2, 134.4, 131.4, 130.1, 129.4, 129.3, 128.1, 126.0, 123.7, 123.1, 120.3, 110.7, 52.4, 48.5; FT-IR (KBr) 3060, 2950, 2925, 2851, 1713, 1610, 1593, 1518, 1428, 1410, 1310, 1277, 1237, 1157, 1108, 1029, 1015 cm^{-1}; (ESI-MS) m/z 343.15 $[M + H]^+$. Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.11; H, 5.29; N, 8.23.

1-Benzyl-2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole 10c. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 72%; mp 130−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 1H), 7.60−7.54 (m, 4H), 7.35−7.26 (m, 6H), 7.10 (d, J = 6.4 Hz, 2H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 143.0, 136.3, 132.2, 130.9, 129.3, 129.0, 128.4, 128.1, 126.0, 124.8, 123.6, 123.2, 120.2, 110.7, 48.5; FT-IR (KBr) 3058, 2963, 2917, 2855, 1611, 1459, 1446, 1409, 1360, 1328, 1303, 1261, 1162, 1096, 1025 cm^{-1}; (ESI-MS) m/z 363.05, 365.05 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}BrN_2$: C, 66.13; H, 4.16; N, 7.71. Found: C, 66.19; H, 4.14; N, 7.66.

1-Benzyl-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole 10d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.20; colorless solid; yield 70%; mp 137−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.63−7.61 (m, 2H), 7.44−7.42 (m, 2H), 7.34−7.31 (m, 4H), 7.26−7.24 (m, 2H), 7.10 (d, J = 6.8 Hz, 2H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 142.7, 136.5, 136.2, 136.1, 130.7, 129.3, 129.2, 128.3, 128.1, 126.0, 123.6, 123.2, 120.1, 110.7, 48.5; FT-IR (KBr) 3083, 3059, 3032, 2963, 2855, 1638, 1612, 1601, 1570, 1495, 1459, 1447, 1412, 1390, 1360, 1329, 1303, 1286, 1261, 1180, 1163, 1093, 1027 cm^{-1}; (ESI-MS) m/z 319.11 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}ClN_2$: C, 75.35; H, 4.74; N, 8.79. Found: C, 75.42; H, 4.72; N, 8.85.

1-Benzyl-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole 10e. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.20; colorless solid; yield 75%; mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.86 (m, 1H), 7.68−7.65 (m, 2H), 7.34−7.31 (m, 3H), 7.26−7.23 (m, 3H), 7.17−7.09 (m, 4H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.7, 153.3, 142.9, 136.3, 136.1, 131.6, 131.5, 129.3, 128.1, 126.1, 123.5, 123.1, 120.1, 116.2, 116.0, 110.7, 48.5; FT-IR (KBr) 3033, 2926, 2854, 1717, 1607, 1534, 1462, 1450, 1418, 1391, 1361, 1329, 1279, 1258, 1231, 1162, 1102, 1027 cm^{-1}; (ESI-MS) m/z 303.14 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}FN_2$: C, 79.45; H, 5.00; N, 9.27. Found: C, 79.52; H, 4.97; N, 9.23.

1-Benzyl-2-(2-methoxyphenyl)-1*H*-benzo[*d*]imidazole 10f. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.20; colorless liquid; yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 6.0 Hz, 2H), 7.50−7.45 (m, 1H), 7.27−7.15 (m, 5H), 7.08−7.03 (m, 2H), 6.98 (d, J = 8.4 Hz, 2H), 5.23 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 152.3, 143.2, 136.5, 135.3, 132.7, 131.9, 128.7, 127.6, 126.8, 122.9, 122.4, 121.2, 120.0, 119.4, 111.1, 110.8, 55.4, 48.6; FT-IR (KBr) 2962, 2931, 2857, 1608, 1519, 1462, 1455, 1394, 1331, 1287, 1258, 1181, 1162, 1076, 1023 cm^{-1}; (ESI-MS) m/z 315.15 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.17; H, 5.79; N, 8.96.

1-Benzyl-2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole 10g. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.20; colorless liquid; yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.34−7.20 (m, 6H), 7.12 (d, J = 6.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.44 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 154.3, 143.2, 136.7, 136.2, 130.9, 130.3, 129.3, 127.9, 126.1, 123.0, 122.8, 119.9, 114.4, 110.6, 55.5, 48.6; FT-IR (KBr) 3031, 2997, 2961, 2927, 2854, 1718, 1610, 1575, 1509, 1495, 1453, 1442, 1420, 1389, 1362, 1329, 1302, 1260, 1179, 1163, 1097, 1033 cm^{-1}; (ESI-MS) m/z 315.16 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.28; H, 5.79; N, 8.86.

1-Benzyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole 10h. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 65%; mp 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.31−7.21 (m, 8H), 7.12 (d, J = 6.4 Hz, 2H), 5.45 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.1, 140.3, 136.6, 136.1, 129.6, 129.3, 129.2, 127.9, 127.1, 126.1, 123.1, 122.8, 120.0, 110.6, 48.5, 21.6; FT-IR (KBr) 3032, 2939, 2925, 2855, 1611, 1448, 1416, 1392, 1362, 1331, 1279, 1251, 1190, 1163, 1115, 1027 cm^{-1}; (ESI-MS) m/z 299.16 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.59; H, 6.06; N, 9.35.

1-Benzyl-5-chloro-2-phenyl-1*H*-benzo[*d*]imidazole 10i. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 68%; mp 145−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 1.6 Hz, 1H), 7.66−7.64 (m, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.32−7.29 (m, 2H), 7.19−7.16 (m, 2H), 7.10−7.05 (m, 4H), 5.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 144.2, 136.1, 134.8, 130.4, 129.8, 129.4, 129.3, 129.0, 128.5, 128.2, 126.1, 123.6, 119.9, 111.5, 48.7; FT-IR (KBr) 3046, 2957, 2928, 1608, 1496, 1470, 1453, 1426, 1390, 1362, 1321, 1312, 1258, 1179, 1162, 1076, 1057, 1027 cm^{-1}; (ESI-MS) m/z 319.11 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}ClN_2$: C, 75.35; H, 4.74; N, 8.79. Found: C, 75.28; H, 4.76; N, 8.74.

1-Benzyl-5-methoxy-2-phenyl-1*H*-benzo[*d*]imidazole 10j. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.20; colorless liquid; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.64 (m, 2H), 7.44 (d, J = 6.4 Hz, 3H) 7.33−7.27 (m, 4H), 7.09−7.04 (m, 3H), 6.87 (dd, J = 8.8 Hz, 2.4 Hz, 1H) 5.41 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 154.5, 144.1, 136.6, 130.9, 130.4, 130.0, 129.4, 129.2, 128.9, 128.0, 126.2, 113.3, 111.1, 102.3, 56.0, 48.7; FT-IR (KBr) 3063, 2933, 2834, 1621, 1514, 1488, 1472, 1453, 1435, 1392, 1342, 1277, 1199, 1154, 1116, 1075, 1028 cm^{-1}; (ESI-MS) m/z 315.16 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.30; H, 5.75; N, 8.87.

1-Benzyl-5-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 10k[30d]. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 64%; mp 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.64 (m, 3H), 7.44 (d, J = 6.8 Hz, 3H), 7.31−7.27 (m, 3H), 7.09−7.05 (m, 4H), 5.41 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.3, 136.6, 134.2, 132.6, 130.1, 130.0, 129.4, 129.1, 128.8, 127.9, 126.1, 124.7, 119.8, 110.2, 48.5, 21.7; FT-IR (KBr) 3029, 2963, 1699, 1603, 1493, 1471, 1449, 1421, 1392, 1364, 1326, 1312, 1261, 1172, 1096, 1027 cm^{-1}; (ESI-MS) m/z 299.17 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.46; H, 6.10; N, 9.44.

1-Benzyl-2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole 10l. Analytical TLC on silica gel, 2:3 ethyl acetate/hexane R_f = 0.20; colorless liquid; yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 1H), 7.45 (s, 1H) 7.35−7.22 (m, 7H), 7.15−7.09 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 5.47 (s, 2H), 3.91 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.8, 149.3, 142.7, 136.8, 136.2, 129.6, 129.3, 128.0, 126.0, 123.3, 123.1, 122.1, 119.8, 112.6, 111.3, 110.5, 56.1, 55.9, 48.6; FT-IR (KBr) 2961, 2935, 2034, 1707, 1638, 1605, 1495, 1456, 1439, 1355, 1325, 1266, 1225, 1178, 1140, 1024 cm^{-1}; (ESI-MS) m/z 345.17 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.78 H, 5.87; N, 8.08.

1-Benzyl-2-(4-chlorophenyl)-5-methyl-1*H*-benzo[*d*]imidazole 10m. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 41%; mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.58 (m, 3H), 7.41 (d, J = 8.4 Hz, 2H), 7.32−7.28 (m, 4H), 7.08−7.06 (m, 3H), 5.39 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 152.9, 143.5, 136.4, 136.2, 132.7, 130.6, 130.0, 129.2, 129.1, 128.7, 128.0, 126.0, 124.9, 119.9, 110.1, 48.4, 21.7; FT-IR (KBr) 3028, 2922, 2854, 1624, 1599, 1569, 1496, 1489, 1468, 1452, 1430, 1408, 1386, 1359, 1325, 1298, 1279, 1259, 1171, 1143, 1092, 1028, 1012 cm^{-1}; (ESI-MS) m/z 333.12 $[M + H]^+$. Anal. Calcd for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.42. Found: C, 75.70; H, 5.18; N, 8.47.

1-Benzyl-2-(4-methoxyphenyl)-5-methyl-1*H*-benzo[*d*]imidazole 10n. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.20; colorless solid; yield 48%; mp 73−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.58 (m, 3H), 7.31−7.27 (m, 3H), 7.10−7.03 (m, 4H), 6.94 (d, J = 8.8 Hz, 2H), 5.39 (s, 2H), 3.82 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.1, 143.4, 136.7, 134.2, 132.3, 130.7, 129.1, 127.7, 126.0, 124.3, 122.4, 119.5, 114.2, 110.0, 55.4, 48.4, 21.6; FT-IR (KBr) 3028, 2924, 2855, 1610, 1578, 1536, 1479, 1465, 1450, 1417, 1391, 1353, 1324, 1295, 1254, 1175, 1113, 1025 cm^{-1}; (ESI-MS) m/z 329.17 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.54; H, 6.12; N, 8.48.

1-Benzyl-5-methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole 10o. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; colorless solid; yield 52%; mp 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.32−7.23 (m, 5H), 7.10−7.04 (m, 4H), 5.41 (s, 2H), 2.49 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.5, 140.0, 136.7, 134.3, 132.3, 129.5, 129.2, 129.1, 127.7, 127.3, 126.0, 124.4, 119.7, 110.1, 48.4, 21.7, 21.5; FT-IR (KBr) 3028, 2956, 2923, 2854, 1606, 1503, 1467, 1452, 1416, 1386, 1364, 1323, 1280, 1259, 1171, 1141, 1104, 1027 cm^{-1}; (ESI-MS) m/z 313.18 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.51; H, 6.47; N, 9.02.

1-Benzyl-4,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole 10p. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless liquid; yield 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 6.8, 1.6 Hz, 2H), 7.41 (d, J = 6.4 Hz, 3H), 7.34−7.26 (m, 3H), 7.07 (d, J = 7.2 Hz, 2H), 6.93 (s, 1H), 6.81 (s, 1H), 5.35 (s, 2H), 2.68 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 140.8, 136.9, 136.1, 133.1, 130.6, 129.8, 129.5, 129.1, 128.8, 127.8, 126.1, 124.9, 120.2, 120.0,

107.9, 48.3, 21.9, 16.9; FT-IR (KBr) 2919, 2856, 1627, 1495, 1452, 1392, 1359, 1332, 1262, 1230, 1174, 1075, 1027 cm^{-1}; (ESI-MS) m/z 313.17 $[M + H]^+$. Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.66; H, 6.42; N, 8.92.

1-Benzyl-2-(3,4,5-trimethoxyphenyl)-1*H*-benzo[*d*]imidazole 10q. Analytical TLC on silica gel, 2:3 ethyl acetate/hexane R_f = 0.25; colorless liquid; yield 63%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 5.2 Hz, 1H), 7.34−7.26 (m, 4H), 7.14 (d, J = 7.2 Hz, 2H), 6.85 (s, 2H), 5.46 (s, 2H), 3.85 (s, 3H), 3.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.5, 142.7, 139.7, 136.9, 136.4, 131.2, 129.4, 128.0, 125.8, 124.9, 123.5, 123.2, 120.0, 110.4, 106.6, 104.0, 61.1, 56.5, 56.1, 48.6; FT-IR (KBr) 2967, 2933, 2151, 1957, 1635, 1588, 1455, 1416, 1328, 1238, 1177, 1125, 1012 cm^{-1}; (ESI-MS) m/z 375.18 $[M + H]^+$. Anal. Calcd for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C, 73.86; H, 5.95; N, 7.44.

1-Benzyl-5-chloro-2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole 10r. Analytical TLC on silica gel, 1:1 ethyl acetate/hexane R_f = 0.50; colorless liquid; yield 31%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.6 Hz, 1H), 7.35−7.29 (m, 3H), 7.20−7.17 (m, 3H), 7.11−7.08 (m, 3H), 6.90 (d, J = 8.0 Hz, 1H), 5.43 (s, 2H), 3.89 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 150.8, 149.2, 143.9, 136.3, 135.0, 129.3, 128.3, 128.0, 125.8, 123.4, 122.0, 119.5, 112.2, 111.1, 56.0, 55.8, 48.6; FT-IR (KBr) 2928, 1639, 1491, 1464, 1314, 1265, 1219, 1175, 1136, 1051, 1024 cm^{-1}; (ESI-MS) m/z 379.13 $[M + H]^+$. Anal. Calcd for $C_{22}H_{19}ClN_2O_2$: C, 69.75; H, 5.05; N, 7.39. Found: C, 69.69; H, 5.08; N, 7.45.

1-Benzyl-2-(furan-2-yl)-1*H*-benzo[*d*]imidazole 10s. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.30; light yellow solid; yield 78%; mp 126−127 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.32−7.23 (m, 6H), 7.15 (d, J = 6.4 Hz, 2H), 7.09 (d, J = 2.8 Hz, 1H), 6.56 (dd, J = 3.6, 1.6 Hz, 1H), 5.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.6, 144.3, 143.2, 136.6, 135.9, 129.1, 127.9, 126.5, 123.5, 123.2, 120.1, 113.1, 112.2, 110.2, 48.5; FT-IR (KBr) 3146, 3127, 3030, 2963, 2926, 2854, 1618, 1604, 1514, 1495, 1450, 1424, 1354, 1328, 1283, 1261, 1226, 1173, 1150, 1091, 1071, 1026 cm^{-1}; (ESI-MS) m/z 275.12 $[M + H]^+$. Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.87; H, 5.16; N, 10.15.

1-Benzyl-2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole 10t. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.35; light yellow solid; yield 70%; mp 136−137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 5.2 Hz, 1H), 7.35−7.25 (m, 7H), 7.14 (d, J = 6.8 Hz, 2H), 7.09−7.07 (m, 1H), 5.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 143.2, 136.5, 136.3, 132.2, 131.1, 129.3, 129.0, 128.1, 126.1, 123.5, 123.2, 120.1, 110.2, 48.4; FT-IR (KBr) 2963, 2927, 2855, 2215, 1726, 1638, 1494, 1453, 1421, 1388, 1355, 1324, 1261, 1225, 1095, 1023 cm^{-1}; (ESI-MS) m/z 291.10 $[M + H]^+$. Anal. Calcd for $C_{18}H_{14}N_2S$: C, 74.45; H, 4.86; N, 9.65; S, 11.04. Found: C, 74.38; H, 4.84; N, 9.69; S, 11.09.

1-Benzyl-2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole 10u. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 70%; mp 131−132 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92−7.85 (m, 3H), 7.81−7.75 (m, 2H), 7.53−7.49 (m, 2H), 7.35−7.29 (m, 4H), 7.26−7.25 (m, 2H), 7.15 (d, J = 6.8 Hz, 2H), 5.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.1, 136.6, 136.3, 133.9, 133.1, 129.5, 129.3, 128.7, 128.0, 127.9, 127.4, 127.2, 126.9, 126.3, 126.2, 123.4, 123.0, 120.1, 110.7, 48.7; FT-IR (KBr) 3056, 2963, 2927, 2853, 1693, 1599, 1525, 1494, 1459, 1451, 1436, 1399, 1354, 1328, 1285, 1260, 1229, 1095, 1019 cm^{-1}; (ESI-MS) m/z 335.16 $[M + H]^+$. Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.28; H, 5.40; N, 8.32.

1-Benzyl-5-methyl-2-(naphthalen-3-yl)-1*H*-benzo[*d*]imidazole 10v. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless solid; yield 36%; mp 169−170 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.90−7.75 (m, 5H), 7.68 (s, 1H), 7.53−7.49 (m, 2H), 7.34−7.30 (m, 3H), 7.14−7.07 (m, 3H), 5.47 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.7, 136.7, 134.5, 133.8, 133.0, 132.6, 129.4, 129.2, 129.1, 128.6, 128.3, 127.9, 127.5, 127.3, 126.8, 126.3, 126.1, 124.8, 119.9, 110.1, 48.6, 21.7; FT-IR (KBr) 3019, 2921, 2853, 1601, 1525, 1496, 1487, 1445, 1423, 1390, 1357, 1341, 1321, 1254, 1228, 1196, 1160, 1137, 1075, 1030 cm^{-1}; (ESI-MS) m/z 349.18 $[M + H]^+$. Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 86.24; H, 5.77; N, 7.99.

1-Benzyl-4-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 10w. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; gummy liquid; yield 12%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67−7.64 (m, 2H), 7.45−7.43 (m, 3H), 7.33−7.27 (m, 3H), 7.13−7.03 (m, 5H), 5.40 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 142.7, 136.7, 135.8, 130.5, 130.3, 130.0, 129.6, 129.2, 128.9, 127.9, 126.2, 123.2, 123.1, 108.2, 48.5, 17.0; FT-IR (KBr) 3059, 3029, 2950, 2923, 2854, 1610, 1496, 1470, 1452, 1423, 1384, 1353, 1333, 1264, 1246, 1206, 1153, 1112, 1075, 1029 cm^{-1}; (ESI-MS) m/z 299.17 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.59; H, 6.06; N, 9.35.

1-Benzyl-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 10x[30e]. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.45; colorless solid; yield 25%; mp 196−197 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 1H), 7.65−7.63 (m, 2H), 7.44−7.41 (m, 3H), 7.34−7.29 (m, 3H), 7.13−7.08 (m, 3H), 6.98 (s, 1H), 5.41 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 141.4, 136.7, 136.5, 133.3, 130.3, 129.9, 129.4, 129.2, 128.9, 127.9, 126.1, 124.5, 119.6, 110.5, 48.4, 22.0; FT-IR (KBr) 3057, 3029, 2924, 2854, 1615, 1603, 1493, 1470, 1450, 1394, 1367, 1330, 1313, 1276, 1204, 1179, 1142, 1123, 1068, 1029 cm^{-1}; (ESI-MS) m/z 299.17 $[M + H]^+$. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.48; H, 6.10; N, 9.42.

General Procedure for the Cyclization of Bisaryloxime Ethers 11a−z. Substrates **11a−z** (0.5 mmol) and $Cu(OTf)_2$ (20 mol %) were stirred at 80 °C in toluene (2 mL) under an oxygen balloon (Table 3). Progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and passed through a short pad of silica gel using hexane followed by a mixture of ethyl acetate and hexane as eluent to afford the titled compounds **12a−y** in analytically pure form.

Characterization data of **12a**, **12c−e**, **12 h−i**, **12m**, **12p−r**, and **12u−x** were identical with those reported in the preliminary communication.[23]

2-(2-Bromophenyl)benzo[*d*]oxazole 12b. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.35; colorless solid; yield 60%; mp 54−55 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 1H), 7.85−7.83 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62−7.60 (m, 1H), 7.47−7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 150.7, 141.7, 134.8, 132.3, 132.1, 127.7, 127.6, 125.7, 124.8, 122.0, 120.6, 110.9; FT-IR (KBr) 2925, 1606, 1565, 1530, 1469, 1450, 1427, 1307, 1262, 1251, 1235, 1081, 1016 cm^{-1}; (ESI-MS) m/z 273.99, 275.99 $[M + H]^+$. Anal. Calcd for $C_{13}H_8BrNO$: C, 56.96; H, 2.94; N, 5.11. Found: C, 56.91; H, 2.96; N, 5.14.

2-(4-Fluorophenyl)benzo[*d*]oxazole 12f[31]. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 57%; mp 95−96 °C (lit.[31] mp 94−96 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.26−8.22 (m, 2H), 7.76−7.73 (m, 1H), 7.57−7.54 (m, 1H), 7.36−7.33 (m, 2H), 7.22−7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3 (d, J = 252 Hz), 162.4, 151.0, 142.3, 130.1 (d, J = 9 Hz), 125.3, 124.9, 123.7, 120.2, 116.5 (d, J = 22 Hz), 110.8; FT-IR (KBr) 2927, 1622, 1498, 1470, 1454, 1414, 1243, 1231, 1156, 1092, 1055 cm^{-1}; (ESI-MS) m/z 214.08 $[M + H]^+$. Anal. Calcd for $C_{13}H_8FNO$: C, 73.23; H, 3.78; N, 6.57. Found: C, 73.28; H, 3.80; N, 6.53.

2-(2-Methoxyphenyl)benzo[*d*]oxazole 12g[12b]. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; orange solid; yield 67%; mp 53−54 °C (lit.[12b] mp 53−55 °C); ^1H NMR

(400 MHz, $CDCl_3$) δ 8.14−8.11 (m, 1H), 7.82−7.79 (m, 1H), 7.59−7.56 (m, 1H), 7.51−7.47 (m, 1H), 7.34−7.32 (m, 2H), 7.11−7.07 (m, 2H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 158.7, 150.5, 142.3, 133.0, 131.5, 125.2, 124.5, 120.9, 120.4, 116.3, 112.3, 110.6, 56.3; FT-IR (KBr) 2925, 2853, 1616, 1583, 1548, 1496, 1456, 1432, 1282, 1264, 1243, 1197, 1165, 1055, 1029, 1017 cm^{-1}; (ESI-MS) m/z 226.09 $[M + H]^+$. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.71; H, 4.89; N, 6.27.

5-Bromo-2-(4-chlorophenyl)benzo[*d*]oxazole 12j. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 51%; mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.88 (s, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.46−7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 149.6, 143.5, 133.3, 129.3, 128.9, 128.2, 125.0, 122.9, 117.3, 111.8; FT-IR (KBr) 2862, 1648, 1547, 1480, 1447, 1401, 1273, 1260, 1092, 1080, 1025 cm^{-1}; (ESI-MS) m/z 307.95, 309.95 $[M + H]^+$. Anal. Calcd for $C_{13}H_7BrClNO$: C, 50.60; H, 2.29; N, 4.54. Found: C, 50.67; H, 2.31; N, 4.49.

5-Bromo-2-(4-methoxyphenyl)benzo[*d*]oxazole 12k. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.35; colorless solid; yield 38%; mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H), 7.40 (s, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.9, 149.9, 144.1, 129.8, 129.0, 127.7, 122.8, 117.3, 114.6, 111.8, 55.7; FT-IR (KBr) 2961, 2927, 1639, 1614, 1601, 1553, 1497, 1464, 1449, 1419, 1305, 1292, 1256, 1199, 1169, 1059, 1042, 1028 cm^{-1}; (ESI-MS) m/z 304.01, 306.01 $[M + H]^+$. Anal. Calcd for $C_{14}H_{10}BrNO_2$: C, 55.29; H, 3.31; N, 4.61. Found: C, 55.23; H, 3.34; N, 4.65.

5-Bromo-2-*p*-tolylbenzo[*d*]oxazole 12l. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 50%; mp 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.86 (s, 1H), 7.42 (s, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 149.9, 144.0, 142.8, 129.9, 128.0, 127.9, 124.1, 123.0, 117.4, 111.9, 21.9; FT-IR (KBr) 2923, 1620, 1556, 1497, 1447, 1408, 1278, 1259, 1178, 1116, 1059, 1036, 1012 cm^{-1}; (ESI-MS) m/z 288.01, 290.01 $[M + H]^+$. Anal. Calcd for $C_{14}H_{10}BrNO$: C, 58.36; H, 3.50; N, 4.86. Found: C, 58.43; H, 3.53; N, 4.82.

2-(4-Chlorophenyl)-5-vinylbenzo[*d*]oxazole 12n. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 62%; mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.15 (m, 2H), 7.77 (s, 1H), 7.51−7.48 (m, 3H), 7.43 (dd, J = 8.4, 1.6 Hz, 1H), 6.85 (dd, J = 17.6, 10.8 Hz, 1H), 5.79 (dd, J = 18.4, 0.8 Hz, 1H), 5.29 (d, J = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.7, 142.7, 136.7, 132.7, 131.1, 129.5, 129.0, 125.8, 124.1, 117.6, 114.1, 110.6; FT-IR (KBr) 2962, 2930, 1600, 1580, 1473, 1402, 1381, 1261, 1202, 1089, 1073, 1052, 1022 cm^{-1}; (ESI-MS) m/z 256.07 $[M + H]^+$. Anal. Calcd for $C_{15}H_{10}ClNO$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.40; H, 3.96; N, 5.54.

2-*p*-Tolyl-5-vinylbenzo[*d*]oxazole 12o. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 56%; mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.76 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.85 (dd, J = 17.6, 10.8 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 150.7, 142.8, 136.8, 134.9, 129.9, 127.8, 125.2, 124.5, 123.7, 117.4, 113.8, 110.5, 21.9; FT-IR (KBr) 2963, 2922, 1618, 1553, 1499, 1474, 1435, 1407, 1260, 1201, 1177, 1095, 1053, 1018 cm^{-1}; (ESI-MS) m/z 236.11 $[M + H]^+$. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.75; H, 5.55; N, 5.89.

2-(Furan-2-yl)benzo[*d*]oxazole 12s[32a]. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless solid; yield 62%; mp 85−86 °C (lit.[32b] mp 83−85 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.73 (m, 1H), 7.66−7.65 (m, 1H), 7.56−7.54 (m, 1H), 7.35−7.33 (m, 2H), 7.27−7.26 (m, 1H), 6.61−6.60 (dd, J = 3.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.3, 146.0, 142.8, 141.8, 125.5, 125.1, 120.3, 114.6, 112.5, 110.8; FT-IR (KBr) 2961, 2925, 2854, 1645, 1637, 1591, 1540, 1527, 1451, 1394, 1343, 1299, 1261, 1246, 1157, 1081, 1059, 1019 cm^{-1}; (ESI-MS) m/z 186.06 $[M + H]^+$. Anal. Calcd for $C_{11}H_7NO_2$: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.29; H, 3.83; N, 7.51.

5-Bromo-2-(furan-2-yl)benzo[*d*]oxazole 12t. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; yield 41%; mp 91−92 °C (lit.[32b] mp 92−93 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 1.6 Hz, 1H), 7.67−7.66 (m, 1H), 7.44−7.42 (m, 2H), 7.29−7.28 (m, 1H), 6.62 (dd, J = 3.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 149.3, 146.4, 143.4, 142.2, 128.5, 123.2, 120.0, 115.3, 112.6, 111.9; FT-IR (KBr) 3095, 2962, 2926, 1642, 1627, 1580, 1531, 1482, 1456, 1442, 1421, 1325, 1293, 1260, 1236, 1156, 1090, 1068, 1039, 1017 cm^{-1}; (ESI-MS) m/z 263.97, 265.97 $[M + H]^+$. Anal. Calcd for $C_{11}H_6BrNO_2$: C, 50.03; H, 2.29; N, 5.30. Found: C, 50.09; H, 2.27; N, 5.25.

2-(Pyren-1-yl)benzo[*d*]oxazole 12y. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane R_f = 0.50; yellow solid; yield 74%; mp 188−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, J = 9.2 Hz, 1H), 8.88 (d, J = 8.0 Hz, 1H), 8.32−8.04 (m, 7H), 7.94−7.91 (m, 1H), 7.70−7.68 (m, 1H), 7.43−7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.6, 142.8, 133.7, 131.4, 130.8, 130.1, 129.7, 129.5, 127.8, 127.4, 126.5, 126.4, 126.3, 125.5, 125.4, 125.2, 124.8, 124.7, 124.5, 120.4, 110.7; FT-IR (KBr) 2962, 2926, 2855, 1595, 1548, 1531, 1455, 1261, 1209, 1095, 1016 cm^{-1}; (ESI-MS) m/z 320.12 $[M + H]^+$. Anal. Calcd for $C_{23}H_{13}NO$: C, 86.50; H, 4.10; N, 4.39. Found: C, 86.62; H, 4.08; N, 4.33.

Reaction Rate Experiments of the Cyclization of Bisaryloxime Ethers 11a, 11e, 11f, and 11h (Figure 3). Bisaryloxime ethers **11a**, **11e**, **11f**, **11h** (0.5 mmol), and Cu(OTf)2 (20 mol %) were stirred at 80 °C in toluene (2 mL) under an oxygen balloon. Progress of the reactions was monitored at 0.25 h interval by taking a portion of the reaction mixture and passing it through a short pad of silica gel using ethyl acetate and hexane as eluent to remove toluene and copper salt. The eluent having the product and starting material was evaporated to dryness. The product yield (%) was determined by HPLC with C_{18} column using 2% 2-propanol in CH_3CN as eluent by comparing the product/substrate ratio [λ = 254 nm, flow rate 0.5 mL/min for all substrates].

Kinetic Isotope Effect Experiments of 11i and 11i (D) (Scheme 7). Bisaryloxime ether **11i** (0.48 mmol, 102 mg) and $Cu(OTf)_2$ (20 mol %, 35.7 mg) were stirred at 80 °C in toluene (2 mL) under an oxygen balloon. The product formation was measured at 0.5 h intervals by removing 40 μL of the reaction mixture and passing through a short pad of silica gel using hexane followed by hexane/ethyl acetate as eluent. The solvent was evaporated under reduced pressure, the residue containing the starting material **11i** and the product **12i** was dissolved in 3.5 mL of CH_3CN, and 20 μL was injected for HPLC analysis (see the Supporting Information).

The reaction of bisaryloxime ether **11i** (**D**) (0.47 mmol, 100 mg) to **12i** was performed as described for the conversion of **11i** to **12i**.

■ ASSOCIATED CONTENT

Supporting Information. Data of kinetic isotope studies of **11i** and **11i** (**D**), NMR spectra of *N*-benzyl bisarylhydrazones (^{1}H and ^{13}C) **9a**−**y** and benz-fuzed azoles **10a**−**x** and **12a**−**y**, and the crystal structure (including data) of **10i** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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