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BF_3·Et_2O-Promoted Cleavage of the C_{sp}−C_{sp2} Bond of 2-Propynolphenols/Anilines: Route to C2-Alkenylated Benzoxazoles and Benzimidazoles

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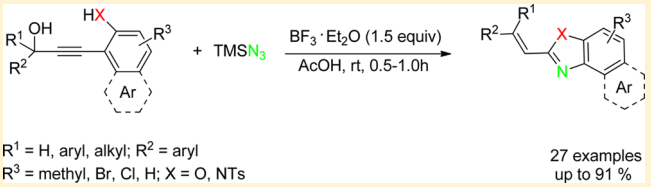
Supporting Information

ABSTRACT: A novel BF_3·Et_2O-promoted tandem reaction of easily prepared 2-propynolphenols/anilines and trimethylsilyl azide is developed to give C2-alkenylated benzoxazoles and benzimidazoles in moderate to good yields. Most reactions could be accomplished in 30 min at room temperature. This tandem process involves a C_{sp}−C_{sp2} bond cleavage and a C−N bond formation. Moreover, both tertiary and secondary propargylic alcohols with diverse functional groups were tolerated under the mild conditions.

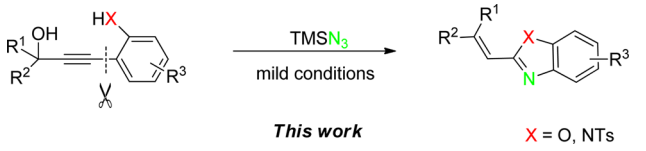


INTRODUCTION

Nitrogen-containing five-member heterocyclic rings, such as benzoxazoles and benzimidazoles, are important scaffolds present in natural products as well as biologically and pharmaceutically active compounds.[1] These compounds have been extensively studied for their biological and therapeutic activities. Such compounds have been used as cathepsin S inhibitors,[2] HIV reverse transcriptase inhibitors,[3] topoisomerase II inhibitors,[4] estrogen receptor β agonists,[5] melatonin receptor agonists,[6] and anticancer agents.[7] Moreover, benz-fused azoles are also widely used in materials science, especially in the field of fluorescent materials.[8] Over the past few decades, some general methods for the synthesis of functionalized benz-fused azoles have been developed. These methods include: (a) the reactions of 2-aminophenol and 2-aminoanlines with either aldehyde[9] or carboxylic acid derivatives,[10] (b) the reactions of 2-aminophenols and 2-aminoanlines with ketone derivatives,[11] (c) the reactions of *o*-hydroxy nitroso aryls with alkyl halides and benzyl halides,[12] (d) the transition metal-catalyzed cyclization of 2-haloanilides/analogues or 2-aminophenols, and others.[13] Despite these pioneering methodologies for the synthesis of benzoxazoles and benzimidazoles, some of them suffered one or more shortcomings, such as complicated catalyst, transition metal catalyst, use of oxidant, and/or harsh conditions (high temperature, microwave radiation). Therefore, the development of novel and more effective synthetic strategies is undoubtedly attractive and desirable.

The tandem reaction strategy has attracted considerable attention for the construction of highly functionalized compounds. Such processes have been regarded as atom-/step-economic, as they enable more than one bond formations in one single operation, avoiding tedious purification procedures. Recently, our group has developed a tandem process to synthesize useful nitrogen-containing compounds by using propargylic alcohols as a versatile allenyl cation synthon, such as tetrazoles[14] and enamides.[15] To the best of our knowledge, the direct transformation of 2-propynolphenols/anilines to C2-alkenylated benzoxazoles and benzimidazoles, which commonly are constructed by metal-catalyzed C−H alkenylation of benz-fused azoles,[16] has not yet been disclosed. On the other hand, 2-alkenylated benzoxazoles and benzimidazoles have also shown a great variety of fluorescent and biological activities.[17] Herein, we report a novel and efficient Lewis acid mediated implanting nitrogen into 2-propynolphenols/anilines to construct C2-alkenylated benzoxazoles and benzimidazoles through the C_{sp}−C_{sp2} bond cleavage and C−N bond formation under mild reaction conditions (Scheme 1).

Scheme 1. Our Strategy for the Construction of C2-Alkenylated Benzoxazoles and Benzimidazoles via C_{sp}−C_{sp2} Bond Cleavage and C−N Bond Formation



RESULTS AND DISCUSSION

The desired reaction was investigated by using 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl) phenol (**1a**) as the model substrate with $TMSN_3$, and the results are shown in Table 1. The initial reactions were run in the presence of *p*-TsOH (1.5 equiv) in acetic acid at room temperature for 0.5 h (entry 1). The desired

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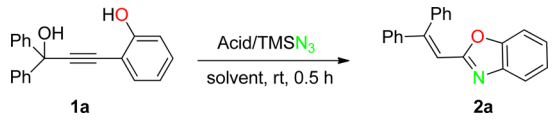
Table 1. Optimization of the Reaction Conditions[a]



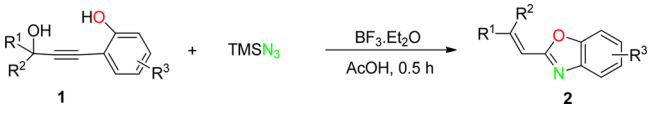
entry	acid (equiv)	$TMSN_3$(equiv)	solvent	yield
1	*p*-TsOH (1.5)	3.5	HOAc	78
2	TMSCl (1.5)	3.5	HOAc	trace
3	TFA (1.5)	3.5	HOAc	30
4	TfOH (1.5)	3.5	HOAc	37
5	$BF_3{\cdot}Et_2O$ (1.5)	3.5	HOAc	85
6	$BF_3{\cdot}Et_2O$ (1.5)	3.5	CH_3NO_2	35
7	$BF_3{\cdot}Et_2O$ (1.5)	3.5	CH_3CN	45
8	$BF_3{\cdot}Et_2O$ (1.5)	3.5	Toluene	17
9	$BF_3{\cdot}Et_2O$ (1.5)	3.5	CH_2Cl_2	21
10	$BF_3{\cdot}Et_2O$ (1.5)	3.5	MeOH	trace
11	$BF_3{\cdot}Et_2O$ (1.5)	3.5	EtOH	trace
12	$BF_3{\cdot}Et_2O$ (1.0)	3.5	HOAc	65
13	$BF_3{\cdot}Et_2O$ (2.0)	3.5	HOAc	75
14	$BF_3{\cdot}Et_2O$ (1.5)	3.0	HOAc	70
15	$BF_3{\cdot}Et_2O$ (1.5)	4.0	HOAc	82
16	$BF_3{\cdot}Et_2O$ (1.5)	3.5	HOAc	75[b]
17	$BF_3{\cdot}Et_2O$ (1.5)	3.5	HOAc	60[c]
18[d]	$BF_3{\cdot}Et_2O$ (1.5)	3.5	HOAc	<10
19[e]	$BF_3{\cdot}Et_2O$ (1.5)	3.5	HOAc	<5
20		3.5	HOAc	0

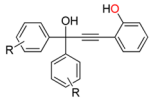
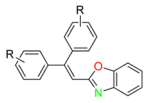
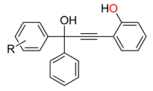
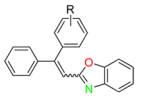
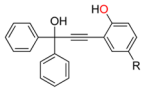
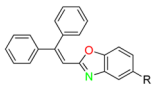
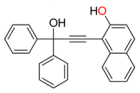
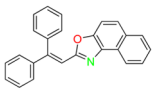
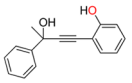
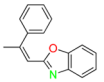
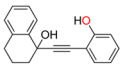
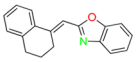
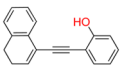
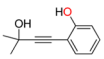
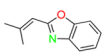
[a]Unless otherwise noted, all reactions were performed with 0.1 mmol of **1a** with $TMSN_3$, in solvent (1.0 mL) at room temperature. [b]At 10 °C. [c]At 50 °C. [d]NaN_3 was used instead of $TMSN_3$. [e]DPPA was used instead of $TMSN_3$, DPPA = diphenylphosphory azide. TMS = trimethylsilyl, TFA = trifluoroacetic acid, *p*-TsOH = *p*-toluenesulfonic acid.

product 2-(2,2-diphenylvinyl)benzo[*d*]oxazole **2a** was obtained in 78% yield along with 8% yield of Meyer-Schuster rearrangement product 1-(2-hydroxyphenyl)-3,3-diphenyl-prop-2-en-1-one (**7**)[18] as the byproduct. Then a series of representative acids were screened, among which $BF_3{\cdot}Et_2O$ was found to be the most efficient, and the desired product **2a** was isolated in 85% yield (entries 2−5). After testing other solvents, such as CH_3NO_2, CH_3CN, toluene, DCM, MeOH, and EtOH, HOAc was considered to be the best (entries 6−11). Further exploration of the amount of $BF_3{\cdot}Et_2O$ revealed that 1.5 equiv was optimal for this reaction (entries 12−13). Moreover, when changing the load of $TMSN_3$ to 3.0 or 4.0 equiv, no superior results were obtained (entries 14−15). When the temperature was increased to 50 °C, **2a** was obtained in a lower yield (entry 17). We considered that the high temperature prompted the side reaction. Furthermore, other nitrogen sources such as sodium azide and diphenylphosphoryl azide were found less efficient than $TMSN_3$ (entries 18−19). No reaction was observed without an acid promoter (entry 20). Therefore, we decided to perform the subsequent reactions of 2-propynol-phenols/anilines and $TMSN_3$ in the presence of $BF_3{\cdot}Et_2O$ as the Lewis acid promoter at room temperature in acetic acid for 0.5 h.

With the optimized reaction conditions in hand, the substrate scope of this reaction was investigated (Table 2). Notably, a variety of tertiary propargylic alcohols were smoothly transformed into the corresponding C2-alkenylated benzoxazoles in moderate to excellent yields (up to 91%). These results with high chemoselectivity indicated the aryl groups migrate

Table 2. Transformation of Tertiary Propargylic Alcohols into C2-Alkenylated Benzoxazoles[a]



substrate		product	yield (%)
	R = H (**1a**)		85 (**2a**)
	R = *p*-Me (**1b**)		81 (**2b**)
	R = *m*-Me (**1c**)		67 (**2c**)
	R = *o*-OMe (**1d**)		70 (**2d**)
	R = *m*-Cl (**1e**)		65 (**2e**)[b]
	R = *p*-Cl (**1f**)		81 (**2f**)
	R = *p*-F (**1g**)		78 (**2g**)
	R = *p*-Me (**1h**)		73 (**2h**)[c]
	R = *m*-Cl (**1i**)		76 (**2i**)[c]
	R = Me (**1j**)		88 (**2j**)
	R = Cl (**1k**)		80 (**2k**)
	R = Br (**1l**)		76 (**2l**)
	**1m**		91 (**2m**)
	**1n**		30 (**2n**)
	**1o**		trace (**2o**)[d]
			50 (**2o'**)
	**1p**		trace (**2p**)

[a]Unless otherwise noted, all reactions were performed with 0.1 mmol of **1**, 0.35 mmol of $TMSN_3$, 1.5 equiv of $BF_3{\cdot}Et_2O$ in CH_3COOH (1.0 mL) at room temperature. [b]For 1.0 h. [c]The olefin isomer ratios of **2h** and **2i** are 1.0:1.0 and 1.3:1.0, respectively. [d]1,3-Enyne compound **2o'** was obtained in 50% yield.

preferentially over the alkenyl groups during the Schmidt-type rearrangement.[19] First, various substituted tertiary propargylic alcohols **1** were reacted with $TMSN_3$ to examine the substituents' effects. In general, propargylic alcohols bearing electron-donating (Me and OMe) and electron-withdrawing substituents (F and Cl) on either of the two aryl groups (R^1 = R^2) were compatible in this transformation and offered the desired products in good-to-excellent yields (**2a−2g**). Moreover, the position of the substituents on the two aryl groups (para-, meta-, and ortho-position) did not affect the transformation reactivity (**2b−2d**). It is noteworthy that the reaction of chloro-substituted substrates (**1e−1f**) proceeded smoothly to furnish the corresponding benzoxazoles (**2e−2f**), which offered an opportunity for the further transformations through the cross-coupling reactions. The structure of **2f** was confirmed by an X-ray diffraction (see the Supporting Information). When the substrates with two different aryl groups ($R^1 \neq R^2$) were employed under the reaction conditions, the corresponding regioisomers were obtained in good yields (**2h−2i**). Furthermore, when another aryl group attached on alkyne bearing electron-donating or electron-withdrawing substituents (R^3), the reaction also proceeded well and gave the desired products in good-to-excellent yields (**2j−2m**). The 1-methyl-1-phenyl-substituted tertiary propargylic alcohol **1n** was also suitable for

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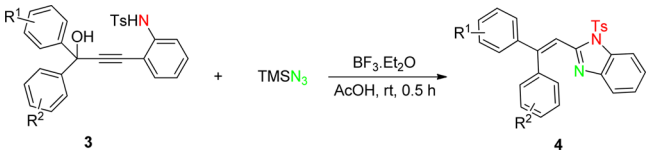
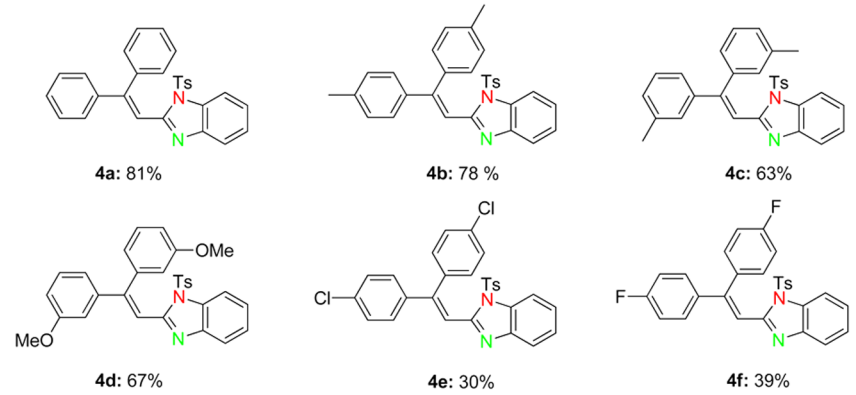
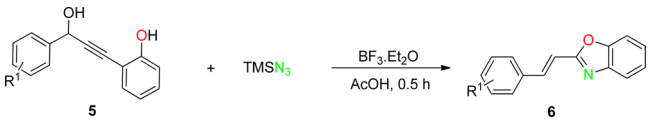
Table 3. Transformation of Tertiary Propargylic Alcohols into C2-Alkenylated Benzimidazoles[a]

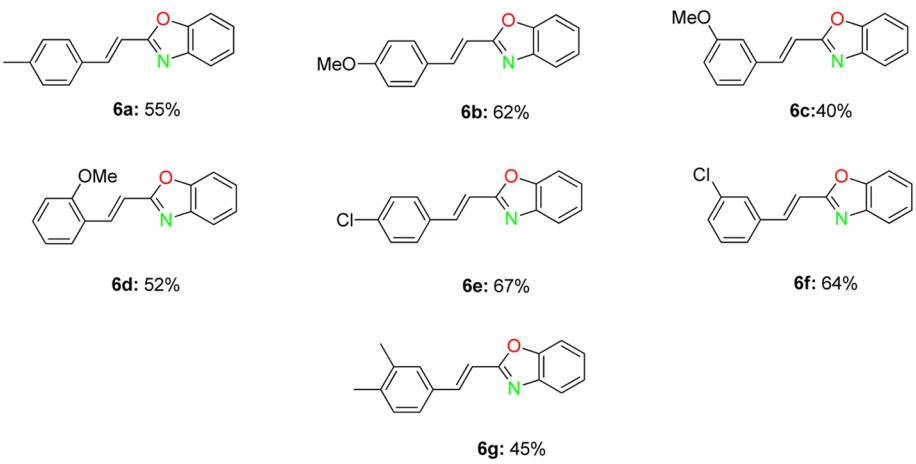




[a]Unless otherwise noted, all reactions were performed with 0.1 mmol of **3**, 0.35 mmol of $TMSN_3$, and 1.5 equiv of $BF_3{\cdot}Et_2O$ in CH_3COOH (1.0 mL) at room temperature.

Table 4. Transformation of Secondary Propargylic Alcohols into Enbenzoxazoles[a]





[a]Unless otherwise noted, all reactions were performed with 0.2 mmol of **5**, 0.7 mmol of $TMSN_3$, 1.5 equiv of $BF_3{\cdot}Et_2O$ in CH_3COOH (2.0 mL) at room temperature.

the reaction and gave the desired product **2n** in moderate yield with high stereoselectivity. However, when tensional propargylic alcohol **1o** was subjected to the reaction conditions, the corresponding product **2o** was not obtained, which indicated that tensile force played an important role in influencing the formation of allene cation in this reaction. No desired product was detected when alkyl-substituted propargylic alcohol **1p** ($R^1 = R^2 = Me$) was employed in this reaction.

Having successfully achieved the direct synthesis of C2-alkenylated benzoxazoles, the catalytic system was further expanded to the direct synthesis of C2-alkenylated benzimidazole by using 2-propynolanilines as starting materials under the optimized reaction conditions (Table 3). Various representative substrates **3a**−**3f** smoothly transformed into the corresponding C2-alkenylated benzimidazoles in moderate-to-good yields (**4a**−**4f**). Notably, the electronic properties of the substituent (R^1 and R^2) on the aryl groups attached to the hydroxyl affected the reaction. Substrates with electron-donating aryl groups showed better results than those with electron-withdrawing aryl groups in this tandem reaction (**3b**−**3d** vs **3e**−**3f**).

In addition, a variety of secondary 2-propynolphenols/aniline could also be successfully converted into the expected C2-alkenylated benzoxazoles in moderate-to-good yields under the

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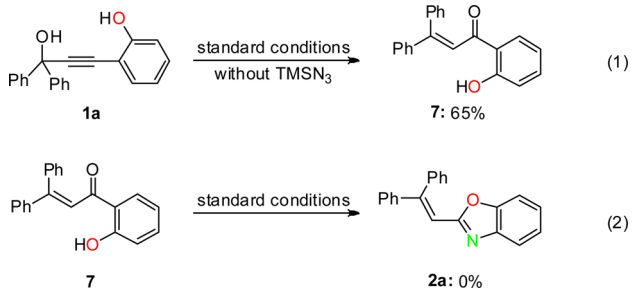
optimized reaction conditions (Table 4). It should be noted that a single isomer was obtained in all cases.

To gain insight into the mechanistic studies of this transformation, a possible intermediate was examined. 2-Propynolphenol **1a** can easily rearrange to the corresponding α,β-unsaturated carbonyl compounds through Meyer-Schuster rearrangement under the standard conditions without $TMSN_3$ [Scheme 2, eq (1)]. We assumed that one possible pathway is a

Scheme 2. Control Experiments



cascade process involves Lewis acid promoted Meyer-Schuster rearrangement of propargylic alcohols to the α,β-unsaturated ketones, and then the Schmidt reaction occurred to form benzoxazoles.[19] However, when α,β-unsaturated ketone **7** was performed under the standard conditions, the desired product **2a** was not observed [Scheme 2, eq (2)]. Therefore, the α,β-unsaturated ketone **7** was excluded as the intermediate in this transformation.

On the basis of the above experimental results and previous reports,[14,15,20] a plausible mechanism is proposed as shown in Scheme 3. First, propargylic alcohol **1a** is converted to the propargylic cation **A** in the presence of $BF_3{\cdot}Et_2O$,[21] which would then undergo mesomerism to produce the allenic cation **B**. Then the allenic substitution occurs by the attack of the azide anion, resulting in the allenylazide **C**. The allenylazide **C** could then be protonated to give allyl azide cation **D**. Subsequently, the mesomerism of intermediate **D** would lead to intermediate **E**,[22] which could release nitrogen gas through the Schmidt-type rearrangement process involving the highly chemoselective aryl migration from the carbon to the nitrogen atom to produce the intermediate **F**. The intramolecular nucleophilic addition of intermediate **F** would form adduct **G**, followed by deprotonation to give product **2a**.

CONCLUSION

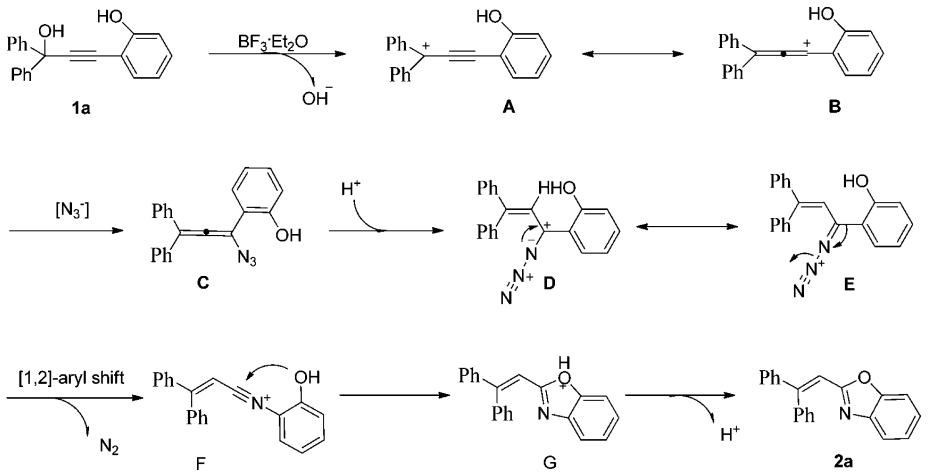
In conclusion, we have developed a novel $BF_3{\cdot}Et_2O$ promoted transformation of easily prepared materials into the corresponding 2-alkenylated benzoxazoles and benzimidazoles through $C_{sp}-C_{sp2}$ bond cleavage. Such processes could be performed at room temperature in the absence of oxidant and metal catalysts, giving the target compounds in good yields and broad substrate scope. Notably, this protocol not only offers a new synthetic strategy for the synthesis of biologically and pharmaceutically important benzoxazoles and benzimidazoles, but it also provides an opportunity to extend the application of propargylic alcohols synthons in organic synthesis. Further investigations on related reactions for the preparation of other useful heterocycles are still underway in our laboratory.

EXPERIMENTAL SECTION

General Remarks. Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in $CDCl_3$ or acetone, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ or *d*-acetone. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet), or m (multiplet). IR spectra were recorded on a FT-IR spectrometer, and only major peaks are reported in cm^{-1}. HR-MS was obtained using a Q-TOF instrument equipped with ESI source. Copies of their ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Commercially available reagents were used without further purification. All solvents were dried under standard method.

General Procedure for the Preparation of 2-Propynolphenols. *Step 1: Synthesis of S1.* To a dried Schlenk flask was added $Pd(PPh_3)_2Cl_2$ (0.1 mmol), CuI (0.2 mmol), iodobenzene (6.0 mmol), alkynols (5.0 mmol), and freshly distilled Et_3N (20 mL) under argon. The resulting mixture was stirred for 16 h at r.t. After the reaction was completed as determined by TLC, the reaction mixture was quenched with saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in

Scheme 3. Proposed Mechanism



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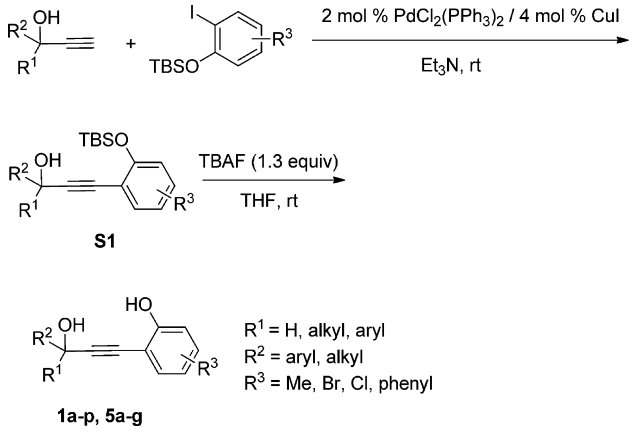
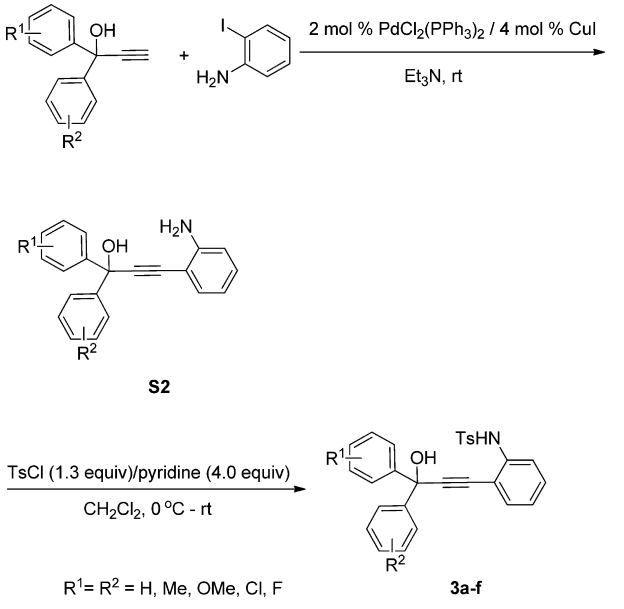


vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **S1**.

*Step 2: Synthesis of 2-Propynolphenols **1a−1p, 5a−5g**.* To a stirring solution of **S1** (5 mmol) in THF (1.0 M) was added tetrabutylammonium fluoride (1.3 equiv) at room temperature for 15 min. After the reaction was completed as determined by TLC, the reaction mixture was quenched by addition of water (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel to obtain the pure product **1a−1p, 5a−5g.**

General Procedure for the Preparation of 2-Propynolanilines. *Step 1: Synthesis of **S2**.* To a dried Schlenk flask was



added $Pd(PPh_3)_2Cl_2$ (0.1 mmol), CuI (0.2 mmol), 2-iodoanline (6.0 mmol), alkynols (5.0 mmol), and freshly distilled Et_3N (20 mL) under argon. The resulting mixture was stirred for 16 h at r.t. After the reaction was completed as determined by TLC, the reaction mixture was quenched with saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **S2**.

*Step 2: Synthesis of 2-Propynolanilines **3a−3f**.* **S2** (5 mmol) was dissolved in dry CH_2Cl_2 (20 mL), dry pydine (4.0 equiv), and cooled to 0 °C. TsCl (1.3 equiv) was added portion-wise, and the mixture was warmed to r.t, stirring until complete consumption of the starting material. The mixture was concentrated in vacuo, and the residue was diluted with ethyl acetate and wash successively with water, 5% HCl (aq), water, and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **3a−3f**.

General Procedure for the Preparation of Product C2-Alkenylated Benzoxazoles and Benzimidazoles. The reaction of 2-propynolphenols (**1a**) (30.0 mg, 0.1 mmol), azidotrimethylsilane (50 μL, 0.35 mmol), in AcOH (1.0 mL) at room temperature under air atmosphere. After 0.5 h, as monitored by TLC, the appropriate amounts of water and ethyl acetate were added to the mixture. Then the organic phase was washed with saturated aqueous Na_2CO_3. The combined organic layers were washed with brine and dried over Na_2SO_4. The resultant product was then concentrated and purified by flash chromatography on silica gel to afford 25.5 mg of **2a**.

*2-(2,2-Diphenylvinyl)benzo[d]oxazole (**2a**).*[16g] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2a** as a white solid (25.5 mg, yield 85%); mp: 64−66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ*. 7.03 (s, 1 H), 7.16−7.20 (m, 1 H), 7.21−7.26 (m, 2 H), 7.27−7.31 (m, 2 H), 7.35−7.44 (m, 8 H), 7.63−7.65 (m, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 110.3, 113.1, 119.8, 124.3, 125.0, 128.0, 128.2, 128.3, 128.4, 129.2, 129.9, 139.1, 141.3, 141.7, 150.1, 152.4, 162.3. HRMS (ESI, *m*/*z*): calcd for $C_{21}H_{16}NO$, $[M + H]^+$ = 298.1226; found, 298.1219. IR (neat, cm^{-1}): 3298, 3057, 2925, 2373, 1721, 1625, 1544, 1449, 1348, 1246, 1031, 937, 844, 767, 745, 697, 578, 537, 436.

*2-(2,2-Di-p-tolylvinyl)benzo[d]oxazole (**2b**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2b** as a white solid (26.3 mg, yield 81%); mp: 190−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ*. 2.37 (s, 3 H), 2.44 (s, 3 H), 6.95 (s, 1 H), 7.15−7.29 (m, 11 H), 7.63 (d, *J* = 7.2 Hz, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 21.2, 21.4, 110.3, 112.0, 119.7, 124.2, 124.8, 128.3, 128.7, 129.1, 129.9, 136.2, 138.1, 138.9, 139.3, 141.8, 150.1, 152.6, 162.7. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{20}NO$, $[M + H]^+$ = 326.1539; found, 326.1530. IR (neat, cm^{-1}): 3338, 2920, 1655, 1628, 1594, 1513, 1449, 1346, 1300, 1244, 1209, 1043, 937, 823, 743, 621, 519, 441.

*2-(2,2-Di-m-tolylvinyl)benzo[d]oxazole (**2c**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2c** as a colorless liquid (21.8 mg, yield 67%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ*. 2.35 (s, 6 H), 6.98 (s, 1 H), 7.10 (d, *J* = 2.0 Hz, 2 H), 7.16−7.31 (m, 9 H), 7.63−7.65 (m, 1 H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* 21.4, 110.3, 112.9, 119.7, 124.2, 124.9, 125.6, 127.0, 127.8, 128.3, 128.9, 129.0, 129.9, 130.4, 137.5, 138.0, 139.0, 141.6, 141.8, 150.1, 152.8, 162.5. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{20}NO$, $[M + H]^+$ = 326.1539; found, 326.1532. IR (neat, cm^{-1}): 3370, 3041, 2922, 2858, 1727, 1627, 1600, 1454, 1454, 1346, 1246, 1001, 938, 853, 786, 745, 701, 507.

*2-(2,2-Bis(2-methoxyphenyl)vinyl)benzo[d]oxazole (**2d**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2d** as a colorless liquid (25.0 mg, yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ*. 3.55 (s, 3 H), 3.75 (s, 3 H), 6.88−6.96 (m, 4 H), 7.11−7.30 (m, 7 H), 7.33−7.37 (m, 1 H),

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7.62−7.64 (m, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 55.6, 55.7, 110.1, 110.9, 111.7, 117.5, 119.7, 120.2, 120.5, 124.0, 124.6, 129.1, 129.6, 129.7, 130.5, 130.8, 131.0, 141.8, 145.5, 150.2, 157.2, 157.5, 162.9. HRMS (ESI, m/z): calcd for $C_{23}H_{20}NO_3$, $[M + H]^+$ = 358.1438; found, 358.1429. IR (neat, cm^{-1}): 3368, 3068, 2929, 2835, 1629, 1596, 1489, 1453, 1433, 1247, 1026, 936, 846, 749, 633, 524.

*2-(2,2-Bis(3-chlorophenyl)vinyl)benzo[d]oxazole (**2e**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2e** as a white solid (23.8 mg, yield 65%); mp: 80−82 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 7.03 (s, 1 H), 7.18 (d, J = 7.6 Hz, 1 H), 7.22−7.31 (m, 6 H), 7.33−7.39 (m, 3 H), 7.43−7.46 (m, 1 H), 7.65−7.67 (m, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.4, 114.9, 120.1, 124.6, 125.5, 126.2, 128.0, 128.1, 128.7, 129.3, 129.5, 129.7, 129.8, 134.2, 134.7, 140.1, 141.6, 142.5, 149.0, 150.1, 161.3. HRMS (ESI, m/z): calcd for $C_{21}H_{14}Cl_2NO$, $[M + H]^+$ = 366.0447; found, 366.0439. IR (neat, cm^{-1}): 3367, 2922, 2374, 1629, 1589, 1491, 1448, 1347, 1244, 1091, 1014, 822, 745, 496.

*2-(2,2-Bis(4-chlorophenyl)vinyl)benzo[d]oxazole (**2f**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2f** as a white solid (29.7 mg, yield 81%); mp: 166−168 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 6.99 (s, 1 H), 7.22−7.30 (m, 7 H), 7.33−7.35 (m, 2 H), 7.39−7.41 (m, 2 H), 7.65 (dd, J = 2.4, 6.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.4, 113.9, 120.0, 124.5, 125.4, 128.5, 128.8, 129.4, 131.3, 134.6, 135.5, 137.0, 139.4, 141.6, 149.6, 150.1, 161.6. HRMS (ESI, m/z): calcd for $C_{21}H_{14}Cl_2NO$, $[M + H]^+$ = 366.0447; found, 366.0441. IR (neat, cm^{-1}): 3372, 2924, 2376, 1722, 1627, 1592, 1563, 1450, 1421, 1343, 1245, 1042, 788, 745, 706, 623.

*2-(2,2-Bis(4-fluorophenyl)vinyl)benzo[d]oxazole (**2g**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2g** as a white solid (26.0 mg, yield 78%); mp: 80−82 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 6.96 (s, 1 H), 7.04−7.13 (m, 4 H), 7.21−7.30 (m, 5 H), 7.33−7.37 (m, 2 H), 7.63−7.65 (m, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.3, 113.3, 115.2 (d, J = 22.0 Hz), 115.6 (d, J = 21.0 Hz), 119.9, 124.4, 125.2, 130.0 (d, J = 8.0 Hz), 131.7 (d, J = 8.0 Hz), 134.7 (d, J = 4.0 Hz), 137.4 (d, J = 4.0 Hz), 141.6, 150.0 (d, J = 6.0 Hz), 162.9 (d, J = 246.0 Hz), 161.9, 163.5 (d, J = 249.0 Hz). HRMS (ESI, m/z): calcd for $C_{21}H_{14}F_2NO$, $[M + H]^+$ = 334.1038; found, 334.1028. IR (neat, cm^{-1}): 3342, 2925, 2376, 1894, 1599, 1510, 1451, 1347, 1231, 1159, 935, 835, 746, 589, 522, 405.

*2-(2-Phenyl-2-(p-tolyl)vinyl)benzo[d]oxazole (**2h**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2h** as a white solid (22.7 mg, yield 73%); mp: 94−96 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 2.37 (s, 3 H), 2.43 (s, 3 H), 6.97 (s, 1 H), 7.01 (s, 1 H), 7.14−7.30 (m, 16 H), 7.33−7.42 (m, 8 H), 7.62−7.65 (m, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 21.2, 21.4, 110.2, 110.3, 112.2, 112.8, 119.7, 119.7, 124.2, 124.9, 124.9, 128.0, 128.1, 128.2, 128.4, 128.7, 129.1, 129.2, 129.8, 129.9, 136.0, 138.2, 138.5, 139.2, 139.4, 141.7, 141.8, 150.1, 152.4, 152.6, 162.4, 162.5. HRMS (ESI, m/z): calcd for $C_{22}H_{18}NO$, $[M + H]^+$ = 312.1383; found, 312.1379. IR (neat, cm^{-1}): 3371, 3055, 2921, 1724, 1625, 1517, 1450, 1348, 1246, 1185, 1136, 1002, 935, 818, 745, 698, 491, 435.

*2-(2-(3-Chlorophenyl)-2-phenylvinyl)benzo[d]oxazole (**2i**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2i** as a colorless liquid (25.2 mg, yield 76%). ^1H NMR (400 MHz, $CDCl_3$): δ. 7.01 (s, 1 H), 7.06 (s, 1 H), 7.17−7.45 (m, 24 H), 7.64−7.65 (m, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.3, 113.8, 114.2, 119.9, 124.4, 124.4, 125.2, 125.3, 126.3, 128.1, 128.1, 128.2, 128.2, 128.4, 128.6, 128.6, 129.1, 129.3, 129.4, 129.6, 129.8, 134.0, 134.5, 138.3, 140.6, 140.8, 141.6, 143.2, 150.1, 150.1, 150.5, 150.8, 161.8, 161.8. HRMS (ESI, m/z): calcd for $C_{21}H_{15}ClNO$, $[M + H]^+$ = 332.0837; found, 332.0831. IR (neat, cm^{-1}): 3059, 2925, 1944, 1724, 1627, 1564, 1450, 1420, 1347, 1246, 1146, 936, 871, 766, 745, 699, 580, 434.

*2-(2,2-Diphenylvinyl)-5-methylbenzo[d]oxazole (**2j**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2j** as a white solid (27.4 mg, yield 88%); mp: 92−94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 2.41 (s, 3 H), 7.01−7.06 (m, 3 H), 7.29 (dd. J = 1.6, 7.6 Hz, 2 H), 7.33−7.42 (m, 9 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 24.3, 109.7, 113.3, 119.7, 126.2, 128.0, 128.3, 128.5, 129.1, 129.9, 134.1, 139.2, 141.4, 142.0, 148.4, 152.1, 162.5. HRMS (ESI, m/z): calcd for $C_{22}H_{18}NO$, $[M + H]^+$ = 312.1383; found, 312.1375. IR (neat, cm^{-1}): 3366, 3055, 2923, 2374, 1721, 1625, 1599, 1512, 1443, 1340, 1263, 1190, 1075, 1030, 940, 799, 738, 698, 599, 570, 402.

*5-Chloro-2-(2,2-diphenylvinyl)benzo[d]oxazole (**2k**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2k** as a faint yellow solid (26.5 mg, yield 80%); mp: 114−116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 7.00 (s, 1 H), 7.10 (d, J = 7.6 Hz, 1 H), 7.19 (dd, J = 2.0, 7.6 Hz, 1 H), 7.25−7.29 (m, 2 H), 7.34−7.44 (m, 8 H), 7.61 (d, J = 1.6 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 111.0, 112.7, 119.7, 125.3, 128.1, 128.3, 128.4, 128.5, 129.4, 129.8, 138.9, 141.1, 142.9, 148.7, 153.5, 163.6. HRMS (ESI, m/z): calcd for $C_{21}H_{15}ClNO$, $[M + H]^+$ = 332.0837; found, 332.0829. IR (neat, cm^{-1}): 3344, 3047, 2924, 2373, 2116, 1624, 1590, 1446, 1258, 1191, 1116, 1053, 922, 860, 769, 739, 698, 637, 595, 513.

*5-Bromo-2-(2,2-diphenylvinyl)benzo[d]oxazole (**2l**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2l** as a faint yellow solid (28.5 mg, yield 76%); mp: 118−120 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 7.00 (s, 1 H), 7.05 (d, J = 8.8 Hz, 1 H), 7.26−7.29 (m, 2 H), 7.31−7.34 (m, 1 H), 7.36−7.44 (m, 8 H), 7.76 (d, J = 1.6 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 111.5, 112.6, 117.1, 122.7, 128.0, 128.1, 128.3, 128.5, 128.5, 129.4, 129.8, 138.9, 141.1, 143.4, 149.1, 153.5, 163.5. HRMS (ESI, m/z): calcd for $C_{21}H_{15}BrNO$, $[M + H]^+$ = 376.0332; found, 376.0324. IR (neat, cm^{-1}): 3303, 3057, 2924, 2854, 2113, 1953, 1725, 1626, 1596, 1443, 1336, 1259, 1189, 1041, 911, 864, 800, 770, 697, 637, 587, 432.

*2-(2,2-Diphenylvinyl)naphtho[1,2-d]oxazole (**2m**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2m** as a yellow liquid (31.6 mg, yield 91%). ^1H NMR (400 MHz, $CDCl_3$): δ. 7.17 (s, 1 H), 7.31−7.38 (m, 6 H), 7.40−7.44 (m, 5 H), 7.46−7.51 (m, 1 H), 7.59−7.61 (m, 1 H), 7.63−7.67 (m, 1 H), 7.89 (d, J = 8.0 Hz, 1 H), 8.41 (d, J = 8.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.6, 113.2, 122.1, 125.3, 126.0, 126.3, 126.9, 128.1, 128.2, 128.2,

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128.4, 128.5, 129.0, 129.9, 131.1, 137.2, 139.2, 141.4, 147.4, 151.2, 161.7. HRMS (ESI, *m*/*z*): calcd for $C_{25}H_{18}NO$, $[M + H]^+$ = 348.1383; found, 348.1377. IR (neat, cm^{-1}): 3298, 3056, 2924, 2375, 1620, 1599, 1510, 1443, 1373, 1237, 1076, 1029, 1006, 941, 803, 762, 697, 613, 560, 521, 465.

*(Z)-2-(2-Phenylprop-1-en-1-yl)benzo[d]oxazole (**2n**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2n** as a colorless liquid (7.1 mg, yield 30%). ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.34 (d, *J* = 1.6 Hz, 3 H), 6.54 (d, *J* = 1.6 Hz, 1 H), 7.18−7.25 (m, 3 H), 7.28−7.30 (m, 2 H), 7.35−7.37 (m, 3 H), 7.61 (dd, *J* = 1.2, 6.8 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 27.6, 110.2, 113.4, 119.7, 124.1, 124.7, 127.5, 128.0, 128.0, 140.7, 141.5, 150.0, 151.0, 161.9. HRMS (ESI, *m*/*z*): calcd for $C_{16}H_{14}NO$, $[M + H]^+$ = 236.1070; found, 236.1064. IR (neat, cm^{-1}): 3298, 3051, 2925, 2853, 2104, 1724, 1648, 1601, 1524, 1452, 1349, 1245, 1153, 1074, 1028, 857, 747, 698, 512, 433.

*2-((3,4-Dihydronaphthalen-1-yl)ethynyl)phenol (**2o′**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **2o′** as a colorless liquid (12.3 mg, yield 50%). ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.42−2.48 (m, 2 H), 2.84 (t, *J* = 8.0 Hz, 2 H), 5.84 (s, 1 H), 6.59 (t, *J* = 4.8 Hz, 1 H), 6.88−6.92 (m, 1 H), 6.98 (dd, *J* = 0.8, 8.4 Hz, 1 H), 7.14−7.15 (m, 1 H), 7.19−7.28 (m, 3 H), 7.42 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 23.73, 27.1, 83.8, 94.3, 109.8, 114.7, 120.4, 121.3, 124.9, 126.8, 127.6, 127.9, 130.3, 131.8, 132.2, 135.0, 136.6, 156.5. HRMS (ESI, *m*/*z*): calcd for $C_{18}H_{15}O$, $[M + H]^+$ = 247.1117; found, 247.1115. IR (neat, cm^{-1}): 3506, 3060, 2931, 2368, 1801, 1602, 1575, 1485, 1450, 1338, 1289, 1239, 1211, 1189, 1153, 1125, 1034, 909, 829, 753, 609, 581, 4476, 447.

*2-(2,2-Diphenylvinyl)-1-tosyl-1H-benzo[d]imidazole (**4a**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4a** as a faint yellow liquid (36.5 mg, yield 81%). ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.38 (s, 3 H), 6.71−6.73 (m, 2 H), 7.08 (t, *J* = 7.6 Hz, 2 H), 7.16−7.20 (m, 1 H), 7.22−7.26 (m, 3 H), 7.31−7.35 (m, 2 H), 7.39 (s, 5 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 8.11 (d, *J* = 8.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.6, 113.6, 114.9, 120.5, 124.6, 125.1, 127.2, 127.7, 127.8, 128.4, 128.5, 128.9, 129.8, 130.0, 132.6, 135.7, 139.0, 142.1, 142.5, 145.9, 149.8, 152.4. HRMS (ESI, *m*/*z*): calcd for $C_{28}H_{23}N_2O_2S$, $[M + H]^+$ = 451.1475; found, 451.1461. IR (neat, cm^{-1}): 3316, 3055, 2924, 1951, 1597, 1525, 1446, 1375, 1254, 1170, 1089, 1046, 959, 812, 766, 741, 699, 672, 573, 543.

*2-(2,2-Di-p-tolylvinyl)-1-tosyl-1H-benzo[d]imidazole (**4b**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4b** as a faint yellow liquid (37.3 mg, yield 78%). ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.25 (s, 3 H), 2.38 (s, 3 H), 2.41 (s, 3 H), 6.57 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 7.6 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.24−7.29 (m, 6 H), 7.31−7.35 (m, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 8.12 (d, *J* = 8.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.2, 21.3, 21.6, 113.6, 113.7, 120.4, 124.6, 124.9, 127.3, 128.4, 128.5, 129.1, 129.8, 130.0, 132.7, 135.7, 136.1, 137.6, 139.0, 139.6, 142.5, 145.8, 150.2, 152.5. HRMS (ESI, *m*/*z*): calcd for $C_{30}H_{27}N_2O_2S$, $[M + H]^+$ = 479.1788; found, 479.1774. IR (neat, cm^{-1}): 3338, 2924, 2856, 2374, 1597, 1448, 1377, 1262, 1170, 1044, 813, 741, 671, 579, 543, 480.

*2-(2,2-Di-m-tolylvinyl)-1-tosyl-1H-benzo[d]imidazole (**4c**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4c** as a colorless liquid (30.0 mg, yield 63%). ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.07 (s, 3 H), 2.39 (s, 6 H), 6.44−6.47 (m, 2 H), 6.92−6.99 (m, 2 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.21−7.24 (m, 2 H), 7.25−7.27 (m, 5 H), 7.31−7.36 (m, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 2 H), 8.12 (d, *J* = 8.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.2, 21.5, 21.7, 113.6, 114.7, 120.5, 124.6, 125.0, 125.8, 127.0, 127.2, 127.5, 128.2, 128.6, 129.1, 129.7, 130.0, 130.4, 132.6, 135.7, 137.1, 138.0, 138.9, 142.2, 142.5, 145.9, 150.0, 152.9. HRMS (ESI, *m*/*z*): calcd for $C_{30}H_{27}N_2O_2S$, $[M + H]^+$ = 479.1788; found, 479.1776. IR (neat, cm^{-1}): 3338, 3049, 2923, 1597, 1447, 1376, 1260, 1168, 1089, 1045, 933, 740, 672, 574, 544, 495.

*2-(2,2-Bis(2-methoxyphenyl)vinyl)-1-tosyl-1H-benzo[d]-imidazole (**4d**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4d** as a white solid (34.2 mg, yield 67%); mp: 140−142 °C. ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.39 (s, 3 H), 3.04 (s, 3 H), 3.74 (s, 3 H), 6.67−6.77 (m, 3 H), 6.93−6.96 (m, 2 H), 7.13−7.19 (m, 1 H), 7.21−7.23 (m, 1 H), 7.24−7.33 (m, 5 H), 7.38 (d, *J* = 7.2 Hz, 1 H), 7.63 (s, 1 H), 7.93 (d, *J* = 8.4 Hz, 2 H), 8.05 (d, *J* = 8.0 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.6, 55.1, 55.8, 110.8, 112.0, 113.3, 118.2, 120.0, 120.3, 120.5, 124.3, 124.6, 127.6, 128.5, 129.3, 129.7, 129.8, 130.5, 131.0, 132.1, 132.3, 135.8, 142.8, 145.5, 145.5, 150.3, 156.8, 157.5. HRMS (ESI, *m*/*z*): calcd for $C_{30}H_{27}N_2O_4S$, $[M + H]^+$ = 511.1686; found, 511.1674. IR (neat, cm^{-1}): 3335, 3059, 2927, 1596, 1490, 1450, 1373, 1250, 1168, 1088, 1046, 810, 750, 672, 577, 544.

*2-(2,2-Bis(4-chlorophenyl)vinyl)-1-tosyl-1H-benzo[d]-imidazole (**4e**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4e** as a white solid (15.6 mg, yield 30%); mp: 138−140 °C. ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.40 (s, 3 H), 6.68 (dd, *J* = 1.6, 6.4 Hz, 2 H), 7.09 (dd, *J* = 1.6, 6.4 Hz, 2 H), 7.24−7.30 (m, 6 H), 7.31−7.38 (m, 3 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 8.10 (d, *J* = 8.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.7, 113.6, 115.7, 120.6, 124.9, 125.4, 127.1, 128.2, 128.8, 129.6, 130.1, 131.2, 132.6, 134.1, 135.3, 135.6, 137.0, 140.1, 142.4, 146.1, 149.2, 149.7. HRMS (ESI, *m*/*z*): calcd for $C_{28}H_{21}Cl_2N_2O_2S$, $[M + H]^+$ = 519.0695; found, 519.0681. IR (neat, cm^{-1}): 3320, 3057, 2924, 2854, 1904, 1735, 1594, 1521, 1490, 1447, 1375, 1255, 1169, 1089, 1045, 960, 826, 763, 743, 667, 577, 543, 488, 452.

*2-(2,2-Bis(4-fluorophenyl)vinyl)-1-tosyl-1H-benzo[d]-imidazole (**4f**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 40:1−15:1, v/v) to afford **4f** as a white solid (19.0 mg, yield 39%); mp: 150−152 °C. ^1H NMR (400 MHz, $CDCl_3$): *δ*. 2.39 (s, 3 H), 6.70−6.75 (m, 2 H), 6.78−6.82 (m, 2 H), 7.09 (t, *J* = 8.4 Hz, 2 H), 7.25−7.29 (m, 4 H), 7.33−7.37 (m, 3 H), 7.45−7.47 (m, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 8.10 (d, *J* = 8.0 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* 21.7, 113.6, 114.9 (d, *J* = 21.0 Hz), 115.5 (d, *J* = 22.0 Hz), 120.5, 124.8, 125.3, 127.1, 130.1, 130.2 (d, *J* = 8.0 Hz), 131.6 (d, *J* = 9.0 Hz), 132.6, 134.7 (d, *J* = 3.0 Hz), 135.7, 138.0 (d, *J* = 3.0 Hz), 142.4, 146.0, 149.5, 150.1, 162.5 (d, *J* = 246.0 Hz), 163.3 (d, *J* = 248.0 Hz). HRMS (ESI, *m*/*z*): calcd for $C_{28}H_{21}F_2N_2O_2S$, $[M + H]^+$ = 487.1286;

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found, 487.1276. IR (neat, cm^{-1}): 3339, 3054, 2924, 2856, 2377, 1896, 1598, 1509, 1447, 1376, 1225, 1088, 1044, 961, 836, 740, 703, 670, 578, 542, 502.

*(E)-2-(4-Methylstyryl)benzo[d]oxazole (**6a**).*[13g] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6a** as a white solid (25.8 mg, yield 55%). ^1H NMR (400 MHz, $CDCl_3$): δ. 2.39 (s, 3 H), 7.03 (d, J = 16.0 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.30−7.34 (m, 2 H), 7.48−7.53 (m, 3 H), 7.69−7.73 (m, 1 H), 7.77 (d, J = 16.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 21.4, 110.3, 112.9, 119.8, 124.4, 125.1, 127.5, 129.7, 132.4, 139.5, 140.1, 142.2, 150.4, 163.0.

*(E)-2-(4-Methoxystyryl)benzo[d]oxazole (**6b**).*[16g] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6b** as a white solid (31.1 mg, yield 62%); mp: 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 3.82 (s, 3 H), 6.90−6.94 (m, 3 H), 7.27−7.32 (m, 2 H), 7.47−7.53 (m, 3 H), 7.67−7.70 (m, 1 H), 7.73 (d, J = 16.0 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 55.3, 110.1, 111.5, 114.4, 119.6, 124.3, 124.8, 127.9, 129.0, 139.1, 142.2, 150.3, 160.9, 163.2. HRMS (ESI, m/z): calcd for $C_{16}H_{14}NO_2$, $[M + H]^+$ = 252.1019; found, 252.1011. IR (neat, cm^{-1}): 3343, 3049, 2926, 2101, 1641, 1600, 1536, 1454, 1301, 1254, 1172, 1029, 960, 932, 822, 739, 572, 518.

*(E)-2-(3-methoxystyryl)benzo[d]oxazole (**6c**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6c** as a colorless liquid (20.0 mg, yield 40%). ^1H NMR (400 MHz, $CDCl_3$): δ. 3.85 (s, 3 H), 6.91−6.94 (m, 1 H), 7.06 (d, J = 16.4 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 7.19 (d, J = 7.6 Hz, 1 H), 7.31−7.35 (m, 3 H), 7.50−7.54 (m, 1 H), 7.69−7.73 (m, 1 H), 7.75 (d, J = 16.0 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 55.3, 110.3, 112.5, 114.2, 115.5, 119.9, 120.2, 124.5, 125.2, 129.9, 136.5, 139.3, 142.2, 150.4, 160.0, 162.7. HRMS (ESI, m/z): calcd for $C_{16}H_{14}NO_2$, $[M + H]^+$ = 252.1019; found, 252.1013. IR (neat, cm^{-1}): 3341, 3058, 2926, 2836, 2121, 1736, 1690, 1642, 1597, 1580, 1536, 1452, 1288, 1271, 1245, 1158, 1046, 968, 930, 855, 780, 745, 681, 572, 434.

*(E)-2-(2-Methoxystyryl)benzo[d]oxazole (**6d**).*[23] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6d** as a white solid (26.1 mg, yield 52%); mp: 64−66 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 3.90 (s, 3 H), 6.91 (d, J = 8.4 Hz, 1 H), 6.98 (t, J = 7.6 Hz, 1 H), 7.20 (d, J = 16.4 Hz, 1 H), 7.25−7.34 (m, 3 H), 7.48−7.52 (m, 1 H), 7.56−7.58 (m, 1 H), 7.68−7.72 (m, 1 H), 8.08 (d, J = 16.4 Hz, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 55.4, 110.2, 111.1, 114.5, 119.7, 120.7, 124.0, 124.3, 124.9, 128.3, 130.8, 134.9, 142.2, 150.4, 158.0, 163.4. HRMS (ESI, m/z): calcd for $C_{16}H_{14}NO_2$, $[M + H]^+$ = 252.1019; found, 252.1011. IR (neat, cm^{-1}): 3346, 3066, 3003, 2960, 2937, 2837, 2106, 1637, 1597, 1535, 1484, 1453, 1302, 1248, 1026, 974, 936, 845, 748, 624, 604, 574, 507, 475, 433.

*(E)-2-(4-Chlorostyryl)benzo[d]oxazole (**6e**).*[13g] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6e** as a white solid (34.2 mg, yield 67%). ^1H NMR (400 MHz, $CDCl_3$): δ. 7.04 (d, J = 16.4, 1 H), 7.33−7.41 (m, 4 H), 7.50−7.53 (m, 3 H), 7.71−7.75 (m, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.3, 114.5, 119.9, 124.6, 125.4, 128.7, 129.2, 133.6, 135.6, 137.9, 142.1, 150.4, 162.4.

*(E)-2-(3-Chlorostyryl)benzo[d]oxazole (**6f**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6f** as a white solid (32.7 mg, yield 64%); mp: 100−102 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 7.07 (d, J = 16.4, 1 H), 7.32−7.37 (m, 4 H), 7.45−7.48 (m, 1 H), 7.52−7.55 (m, 1 H), 7.57 (s, 1 H), 7.70−7.74 (m, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 110.4, 115.4, 120.0, 124.6, 125.5, 125.6, 127.4, 129.6, 130.2, 135.0, 137.0, 137.8, 142.1, 150.4, 162.2. HRMS (ESI, m/z): calcd for $C_{15}H_{11}ClNO$, $[M + H]^+$ = 256.0524; found, 256.0518. IR (neat, cm^{-1}): 3338, 2922, 2375, 1721, 1641, 1596, 1566, 1530, 1450, 1348, 1300, 1223, 1116, 1043, 963, 908, 843, 780, 741, 707, 670, 626.

*(E)-2-(3,4-Dimethylstyryl)benzo[d]oxazole (**6g**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1−20:1, v/v) to afford **6g** as a white solid (22.4 mg, yield 45%); mp: 98−100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ. 2.30 (s, 3 H), 2.31 (s, 3 H), 7.02 (d, J = 16.4, 1 H), 7.18 (d, J = 8.0 Hz, 1 H), 7.31−7.37 (m, 4 H), 7.51−7.53 (m, 1 H), 7.69−7.77 (m, 2 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 19.8, 19.8, 110.2, 112.7, 119.7, 124.4, 125.0, 125.2, 128.8, 130.2, 132.9, 137.2, 138.9, 139.7, 142.3, 150.4, 163.1. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO$, $[M + H]^+$ = 250.1226; found, 250.1220. IR (neat, cm^{-1}): 3342, 3059, 2924, 2371, 1888, 1727, 1640, 1604, 1531, 1450, 1347, 1283, 1242, 1176, 1123, 1073, 1043, 973, 926, 853, 812, 744, 623, 558, 429.

*1-(2-Hydroxyphenyl)-3,3-diphenylprop-2-en-1-one (**7**).*[24] The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1, v/v) to afford **7** as a yellow liquid (19.5 mg, yield 65%). ^1H NMR (400 MHz, $CDCl_3$): δ. 6.82−6.86 (m, 1 H), 6.95 (d, J = 8.0 Hz, 1 H), 7.16−7.22 (m, 3 H), 7.30−7.45 (m, 9 H), 7.84 (dd, J = 1.2, 8.0 Hz, 1 H), 12.20 (s, 1 H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 118.3, 118.7, 120.6, 122.6, 128.2, 128.5, 128.6, 128.7, 129.6, 130.8, 136.2, 138.9, 141.2, 155.6, 162.9, 197.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General remarks, crystal preparation and x-ray diffraction analysis, ^1H and ^{13}C NMR spectra of the products, and a CIF file. 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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