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Synthesis of Oxazoles by Tandem Cycloisomerization/Allylic Alkylation of Propargyl Amides with Allylic Alcohols: $Zn(OTf)_2$ as π Acid and σ Acid Catalyst

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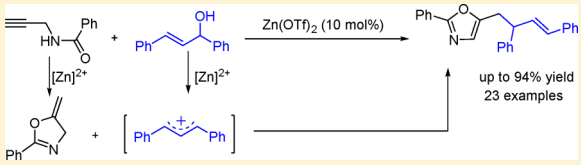
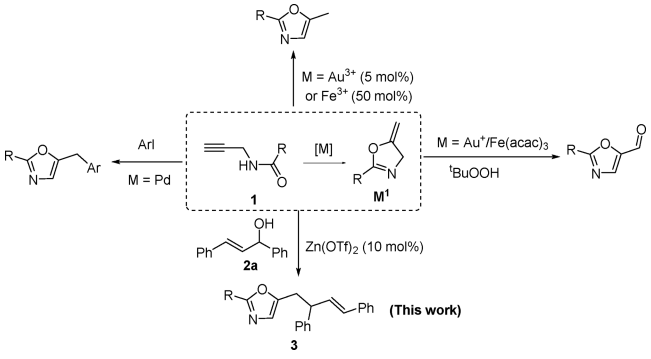
Supporting Information

ABSTRACT: A $Zn(OTf)_2$-catalyzed tandem cycloisomerization/allylic alkylation of *N*-(propargyl)arylamides and allylic alcohols to produce oxazole derivatives has been successfully developed. The zinc catalyst served as π acid and also σ acid in this reaction. The target allylic oxazoles have been transformed into multisubstituted diene structures, which are potential aggregation-induced emission active optical materials.



Oxazole derivatives are privileged five-membered heterocycles widely presented in a variety of natural products and pharmaceuticals with significant biological activities.[1] Oxazoles are useful synthetic intermediates in organic synthesis and also important ligands for transition-metal catalysis.[2] Thus, the development of a practical and useful method to access this heterocycle is of great importance. Recently, propargylic amides have been well studied as versatile building blocks to prepare oxazoles.[3] Various transition-metal catalysts could catalyze these transformations, and significant progress has been made in this area (Scheme 1). For example, a

Scheme 1. Transition-Metal-Catalyzed Cyclization/Functionalization of Propargylic Amides To Synthesize Oxazoles



Pd(0)-catalyzed coupling/cyclization of propargylic amide **1** with ArI has been developed to synthesize disubstituted oxazoles in 2001.[4] Later in 2010, Hashmi and co-workers developed a gold(III)-catalyzed cyclization of propargylic amide **1** to access methyl oxzaoles.[5] Very recently, Shi and Jiao developed a synergistic gold(I)/Fe(III) dual catalysis from propargylic amide to oxazole aldehyde.[6] We report here a cheap metal $Zn(OTf)_2$-catalyzed cyclization/allylic alkylation cascade reaction of propargylic amides with allylic alcohol **2** to prepare oxazole derivatives. In this transformation, elimination of one molecule of water is the only byproduct. More importantly, $Zn(OTf)_2$ acted as a π acid to catalyze the cyclization of propargylic amide, but also served as a σ acid to activate the allylic alcohol, which is the most important feature of this work.

Previously we combined Au as the π acid and another early transition metal as the σ acid and developed a series of bimetallic relay catalysis to access various biologically important fused or spiro aminals.[7] Following this chemistry, π acids such as gold(I) catalysts or Zn(II) catalysts could catalyze the cyclization of **1a** to form an exocyclic double bond intermediate $\mathbf{M^1}$, which could act as a nucleophile to participate in another asymmetric allylic alkylation[8] in the presence of a palladium catalyst and chiral phosphine ligands to build chiral oxazole derivatives (Scheme 2). To our great surprise, whatever chiral ligands such as Trost's ligand or SEGPHOS were used, the coupled products **3a** were all racemic (eq 1). These results indicated that the chiral palladium catalyst might not participate in this reaction. Then the chiral palladium catalysts were removed from the reaction system, and the product **3a** was isolated in similar yield (eq 2). Herein the zinc catalyst not only served as π acid to catalyze the cyclization of propargylic amide but also acted as σ acid to activate the allylic carbonate

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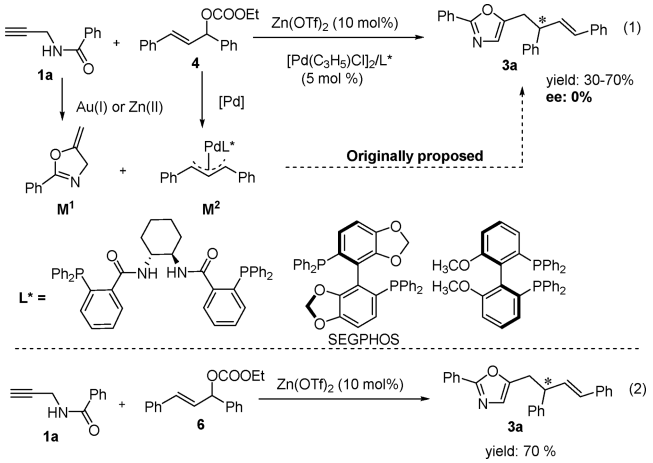
Scheme 2. Unexpected $Zn(OTf)_2$-catalyzed cycloisomerization/allylic alkylation cascade to synthesize oxazoles

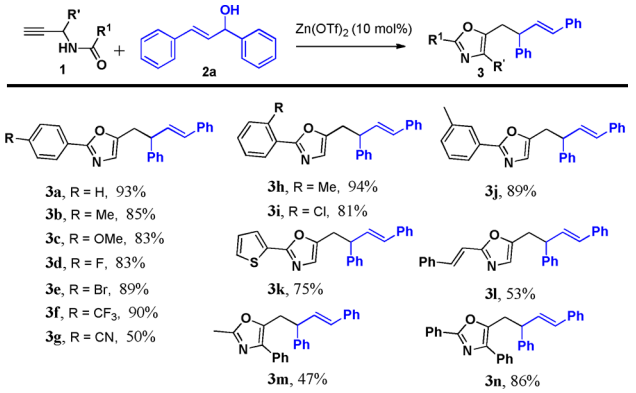


Allylic alkylation was usually catalyzed by precious metal catalysts such as Pd and Ir, but in comparison zinc salts[9] are cheap and readily available; we thereby decided to study this reaction in detail. Compared with allylic carbonates or acetates, such reactions of allylic alcohols[10] are more atom-economic considering water as the only byproduct, and the whole synthetic process is shorter because allylic carbonates are synthesized from the corresponding alcohols.[11] However, because the hydroxyl group is not a good leaving group, moreover, the in situ formed intermediate $\mathbf{M^1}$ is very easy to isomerize into methyl oxazole **5a** in the presence of Brønsted acid or Lewis acid, such a reaction is very challenging.

To test this hypothesis, propargylic amide **1a** and allylic alcohol **2a** were subjected to this reaction in the presence of zinc triflate. To our delight, the target product **3a** could be isolated in 76% yield (entry 1, Table 1). Inspired by the observed results, we continued to optimize the reaction conditions. It turned out that other Lewis acids such as $In(OTf)_3$ and $Ph_3PAuNTf_2$ could also generate product **3a** in less than 60% yields (entries 2–5). The reaction of $FeCl_3$ could not produce the coupled product **3a**, but only the isomerized methyl oxazole **5a**. Solvent screening showed that DCE is the optimal solvent (entries 8–11). The desired product could be isolated in 93% yield by raising the temperature to 70 °C (entry 12). In addition, the use of protic acid HOTf instead of $Zn(OTf)_2$ could not afford any product.

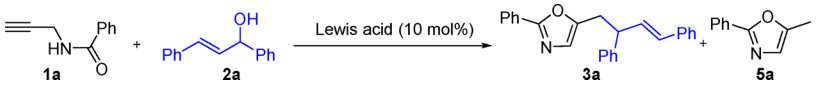
With the optimized conditions established, the scope of various propargylic amides was examined at first. As summarized in Table 2, a large variety of disubstituted or trisubstituted oxazole derivatives were synthesized in good to excellent yields with very wide scope. For the para-substituted substrates, the reaction afforded the desired products in good yields (**3b–g**), independent of electron-withdrawing or electron-donating groups. A series of functional groups such as fluoro, bromo, methoxyl, trifluoromethyl, and cyano were well tolerated under this reaction condition. Substituents at the *meta* or *ortho* position did not affect this reaction, giving the corresponding

Table 2. Substrate Scope of the Propargylic Amides[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), $Zn(OTf)_2$ (10 mol %), 4 Å molecular sieves (65 mg), C_{2a} = 0.1 M, 70 °C, 13 h, isolated yields were reported.

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	1a:2a	solvent	T/°C	yield %[b]
1	$Zn(OTf)_2$	2:1	DCE	60	76
2	$In(OTf)_3$	2:1	DCE	60	56
3	$Cu(OTf)_2$	2:1	DCE	60	23
4[c]	$Ph_3PAuNTf_2$	2:1	DCE	60	58
5	$FeCl_3$	2:1	DCE	60	<10
6	ZnI_2	2:1	DCE	60	<10
7	$ZnCl_2$	2:1	DCE	60	21
8	$Zn(OTf)_2$	1.5:1	Toluene	60	24
9	$Zn(OTf)_2$	1.5:1	CH_3CN	60	<5
10	$Zn(OTf)_2$	1.5:1	THF	60	<5
11	$Zn(OTf)_2$	1.5:1	DCE	50	59
12	$Zn(OTf)_2$	1.5:1	DCE	70	93
13[d]	$Zn(OTf)_2$	1.5:1	DCE	70	93
14[e]	$Zn(OTf)_2$	1.5:1	DCE	70	85
15	HOTf	1.5:1	DCE	70	0

[a]Reaction conditions: **2a** (0.1 mmol), Lewis acid (10 mol %), 4 Å molecular sieves (50 mg), C_{2a} = 0.05 M, 13 h. [b]Isolated yield. [c]5 mol % of catalyst. [d]C_{2a} = 0.1 M. [e]5 mol % of catalyst, C_{2a} = 0.1 M.

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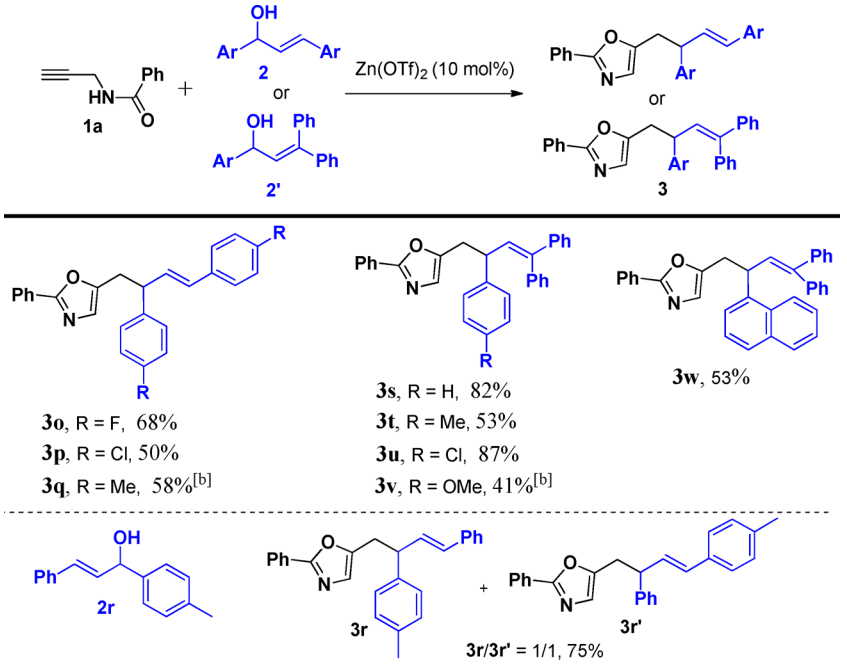
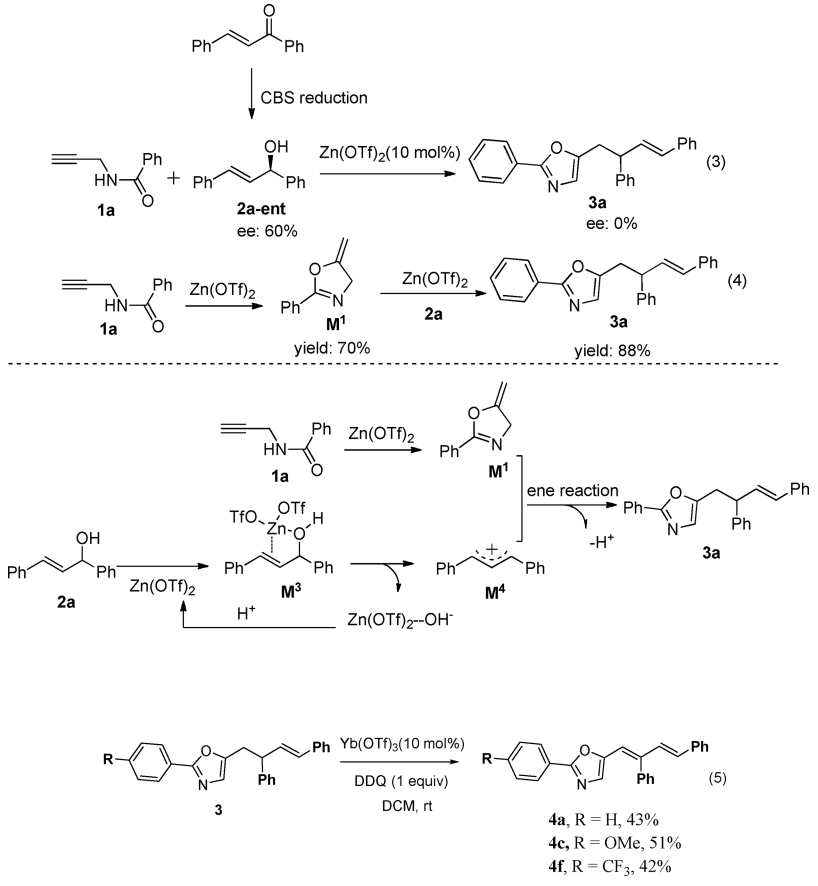
Table 3. Substrate Scope of Allylic Alcohols[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), $Zn(OTf)_2$ (10 mol %), 4 Å molecular sieves (65 mg), C_{2a} = 0.1 M, 70 °C, 13 h, isolated yields were reported. [b]At 60 °C.

Scheme 3. Control Experiments and Proposed Reaction Mechanism



oxazoles in very good yields (**3h**–**j**). Substrates bearing a thienyl or styryl group were all suitable substrates for this transformation and gave the corresponding oxazoles in 75% and 53% yields (**3k**, **3l**). In addition, adding one more substitutent at the propargylic position could generate fully substituted oxazole derivatives smoothly (**3m**, **3n**).

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Next, the scope of allylic alcohols was investigated (Table 3). Various symmetric diaryl allylic alcohols were suitable substrates for this transformation, giving the corresponding products in 50−68% yields (**3o**−**3q**). *gem*-Diphenyl alcohols **2′** also reacted smoothly and gave the corresponding functionalized oxazoles in moderate to good yields (**3s**−**3w**). When asymmetric allylic alcohol **2r** was used in this reaction, equal amounts of two regioisomers were obtained (**3r**/**3r′** = 1/1), which in principle suggested that both S_N2 and S_N2' mechanisms were involved in this reaction. Unfortunately, other alcohols such as cinnamyl alcohol and diphenylcarbinol did not react in this transformation. These results may help to understand the reaction mechanism.

To better understand the reaction process, control experiments were conducted. A nonracemic allylic alcohol **2a-ent** (60% ee) was prepared by CBS reduction of chalcone. When this chiral alcohol **2a-ent** was subjected to the standard reaction, racemic product **3a** was obtained (eq 3, Scheme 3), which suggested a possible allylcarbenium ion mechanism. The reaction of **1a** in the presence of $Zn(OTf)_2$ could form oxazoline $\mathbf{M^1}$ in 70% yield. The isolated $\mathbf{M^1}$ was subjected to standard reaction with alcohol **2a**, and the product **3a** was isolated in 88% yield (eq 4, Scheme 3).

A plausible mechanism was proposed in Scheme 3. First, $Zn(OTf)_2$ acted as π acid to activate the triple bond of **1a** and subsequent intramolecular 5-*exo*-*dig* cyclization forming the oxazoline intermediate $\mathbf{M^1}$. At the same time, the zinc catalyst coordinated with the hydroxyl group and double bond of alcohol **2a** to form a relatively stable allylcarbenium ion intermediate $\mathbf{M^4}$.[12] The intermolecular ene type reaction between nucelophilic $\mathbf{M^1}$ and electrophilic $\mathbf{M^4}$ produced the aromatic oxazole derivatives. At the same time, the released proton and $[Zn(OTf)_2OH]^-$ reacted together to regenerate the zinc catalyst. Thus, the S_N1 type reaction mechanism led to the racemic product when chiral **2a** was used.

The obtained allylic oxazoles belong to a unique type of structure, which is difficult to access by other methods. These compounds could be oxidized to conjugated dienes **4** in the presence of catalytic amounts of $Yb(OTf)_3$ and 1 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature (eq 5, Scheme 3).[13] Both an electron-donating group and an electron-withdrawing group were tolerated and gave functionalized dienes in respectable yields (**4c**, **4f**). The structure of **4f** was unambiguously characterized by single X-ray crystallography (for details, see Supporting Information).[14] These products all are large conjugated functionalized molecules and might have peculiar photophysical characteristics. The UV/vis absorption and emission spectra of the dienes **4a**, **4c**, and **4f** in solution were characterized and are shown in Figure 1 (left). They displayed maximum absorption peak around 370 nm, and exhibited blue emission around 450 nm.

Tetrasubstituted or trisubstituted olefins may have an extraordinary photophysical phenomenon of aggregation-induced emission (AIE) that is nonemissive or low-emissive in solution, but induced to emit efficiently by aggregate formation in the solid state.[15] It is very interesting that the obtained dienes are also AIE active molecules. As illustrated in Figure 1 (right), when the water fraction increased to 90%, the fluorescence intensity greatly increased relative to its pure THF solution. As water was a poor solvent for **4a**, increasing the vol % of water in the mix solvent of THF/H_2O induced aggregation of **4a**. These functionalized molecules are very promising as blue emissive materials such as organic light-emitting diodes (OLED).

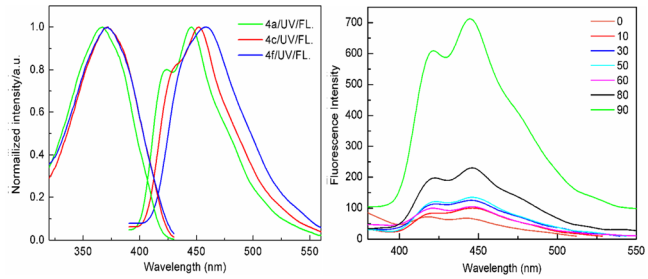

Figure 1. UV/vis absorption and fluorescence spectra of **4a**, **4c**, and **4f** in dilute dichloromethane solution (left). Emission spectra of **4a** in THF/H_2O solvent mixtures with different volume percents of H_2O (right). Concentration of 10^{-5} M.

In conclusion, we have developed a zinc-catalyzed cyclization/allylic alkylation cascade reaction as a convenient synthetic method toward functionalized oxazoles. The zinc catalyst acted as a π acid to activate *N*-(propargyl)arylamides, but also served as σ acid to facilitate C−O bond cleavage of allylic alcohols to form an allylcarbenium ion, which is the most important feature of this reaction. The allylic oxazoles were easily transformed into large π-conjugated dienes, which proved to be good AIE luminogens and will potentially have more applications as the AIE active materials.

EXPERIMENTAL SECTION

General Details. All NMR spectras were recorded on a 400 MHz spectrometer. High-resolution mass spectrometry (HRMS) was measured in positive-ion mode on a Q-TOF instrument with an ESI ion source. Routine monitoring of the reaction was performed by TLC using precoated silica gel plates. All the reagents and solvents used in this reaction such as DCE were purchased from a local company and used directly. Allylic alcohols **2s**−**2w** were prepared by a reported procedure.[16]

General Procedure for the Synthesis of Compounds 3. **2** (0.2 mmol, 0.1 mol/L), **1** (0.30 mmol), $Zn(OTf)_2$ (10 mol %), and 4 Å molecular sieves were mixed in 2 mL of DCE. The mixture was kept stirring at 70 °C for 13 h. After the reaction was completed (monitored by TLC), the solution was filtered on Celite and then evaporated under reduced pressure. Purification by flash column chromatography afforded the desired product **3**.

*(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-phenyloxazole (**3a**):* yellow oil (65.3 mg, 93%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.90 (m, 2H), 7.45−7.15 (m, 13H), 6.75 (s, 1H), 6.42 (d, J = 3.1 Hz, 2H), 3.91 (ddd, J = 10.4, 7.2, 2.9 Hz, 1H), 3.30−3.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.7, 142.8, 137.1, 132.2, 130.7, 130.0, 128.8, 128.7, 128.6, 127.7, 127.6, 127.4, 126.9, 126.309, 126.1, 125.2, 47.7, 32.5; IR (neat) ν (cm^{-1}) 3057, 3025, 1594, 1548, 1489, 1448, 1353, 1264, 1120, 1064, 1025, 962, 826, 773, 734, 709, 688, 547, 525, 491; HRMS exact mass calcd for ($C_{25}H_{21}NO$ + H) requires m/z 352.1701, found m/z 352.1696.

*(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(p-tolyl)oxazole (**3b**):* yellow oil (62.4 mg, 85%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.36−7.13 (m, 12H), 6.72 (s, 1H), 6.41 (d, J = 2.9 Hz, 2H), 3.94−3.83 (m, 1H), 3.27−3.13 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.4, 142.9, 140.2, 137.2, 132.3, 130.7, 129.5, 128.8, 128.6, 127.7, 127.4, 126.9, 126.3, 126.1, 125.12, 125.09, 47.7, 32.5, 21.5; IR (neat) ν (cm^{-1}) 3057, 3023, 2918, 1723, 1679, 1599, 1553, 1497, 1451, 1256, 1178, 1113, 1067, 965, 824, 729, 695, 505; HRMS exact mass calcd for ($C_{26}H_{23}NO$ + H) requires m/z 366.1858, found m/z 366.1864.

*(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(4-methoxyphenyl)oxazole (**3c**):* yellow oil (63.6 mg, 83%, petroleum ether/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.38−7.13 (m, 10H), 6.92 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 6.45−6.37 (m, 2H), 3.89 (dd, J = 6.8, 3.3 Hz, 1H), 3.81 (s, 3H), 3.28−3.13 (m, 2H);

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^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 160.9, 150.1, 142.9, 137.1, 132.3, 130.6, 128.7, 128.6, 127.69, 127.66, 127.4, 126.8, 126.3, 125.0, 120.7, 114.2, 55.4, 47.7, 32.5; IR (neat) ν (cm^{-1}) 3059, 3023, 2836, 1611, 1494, 1451, 1358, 1302, 1249, 1169, 1120, 1103, 1025, 962, 833, 739, 692, 610, 522; HRMS exact mass calcd for ($C_{26}H_{23}NO_2$ + H) requires m/z 382.1807, found m/z 382.1807.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(4-fluorophenyl)oxazole (**3d**): yellow oil (61.4 mg, 83%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.78 (m, 2H), 7.37−7.13 (m, 10H), 7.11−7.01 (m, 2H), 6.73 (s, 1H), 6.42 (d, J = 3.2 Hz, 2H), 3.96−3.79 (m, 1H), 3.32−3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, $^1J_{C-F}$ = 248.0 Hz), 160.0, 150.8, 142.8, 137.1, 132.2, 130.7, 128.8, 128.6, 128.1 (d, $^3J_{C-F}$ = 9.0 Hz), 127.6, 127.5, 126.9, 126.3, 125.2, 124.1 (d, $^4J_{C-F}$ = 3.0 Hz), 115.9 (d, $^2J_{C-F}$ = 22.0 Hz), 47.8, 32.4; IR (neat) ν (cm^{-1}) 3059, 3025, 2916, 1730, 1604, 1558, 1494, 1451, 1412, 1232, 1152, 1123, 1091, 962, 838, 736, 692, 605, 518; HRMS exact mass calcd for ($C_{25}H_{20}FNO$ + H) requires m/z 370.1607, found m/z 370.1607.

(E)-2-(4-Bromophenyl)-5-(2,4-diphenylbut-3-en-1-yl)oxazole (**3e**): yellow oil (77.0 mg, 89%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.39−7.13 (m, 10H), 6.75 (s, 1H), 6.41 (d, J = 2.6 Hz, 2H), 3.88 (dd, J = 6.7, 3.5 Hz, 1H), 3.29−3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 151.1, 142.7, 137.1, 132.1, 132.0, 130.7, 128.8, 128.6, 127.6, 127.53, 127.51, 126.9, 126.6, 126.3, 125.4, 124.4, 47.7, 32.5; IR (neat) ν (cm^{-1}) 3057, 3023, 2917, 1724, 1679, 1590, 1553, 1497, 1451, 1256, 1178, 1113, 1067, 965, 827, 729, 695; HRMS exact mass calcd for ($C_{25}H_{20}BrNO$ + H) requires m/z 430.0807, found m/z 430.0801.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(4-(trifluoromethyl)phenyl)-oxazole (**3f**): yellow oil (75.7 mg, 90%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.40−7.15 (m, 10H), 6.80 (s, 1H), 6.45−6.39 (m, 2H), 3.91 (ddd, J = 10.6, 7.2, 3.4 Hz, 1H), 3.32−3.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 151.7, 142.6, 137.0, 132.0, 131.7, 131.4, 130.8, 129.7, 128.8, 128.6, 127.6, 127.5, 127.0, 126.3, 126.2, 126.0, 125.8, 125.8, 125.7, 125.3, 122.6, 47.8, 32.4; IR (neat) ν (cm^{-1}) 3059, 3029, 2921, 1732, 1605, 1558, 1494, 1451, 1418, 1153, 1123, 1091, 972, 838, 737, 692, 609; HRMS exact mass calcd for ($C_{26}H_{20}F_3NO$ + H) requires m/z 420.1575, found m/z 420.1578.

(E)-4-(5-(2,4-Diphenylbut-3-en-1-yl)oxazol-2-yl)benzonitrile (**3g**): yellow solid (37.5 mg, 50%, petroleum ether/EtOAc = 10/1); mp 104−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.41−7.15 (m, 10H), 6.83 (s, 1H), 6.45−6.38 (m, 2H), 3.90 (ddd, J = 9.5, 7.2, 3.0 Hz, 1H), 3.32−3.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.2, 142.5, 136.9, 132.6, 131.9, 131.4, 130.8, 128.8, 128.6, 127.6, 127.0, 126.4, 126.28, 126.27, 126.0, 118.5, 113.2, 47.8, 32.4; IR (neat) ν (cm^{-1}) 3059, 3025, 2923, 2221, 1594, 1489, 1448, 984, 972, 836, 756, 741, 690, 651, 549, 486; HRMS exact mass calcd for ($C_{26}H_{20}N_2O$ + H) requires m/z 377.1654, found m/z 377.1652.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(o-tolyl)oxazole (**3h**): yellow oil (68.6 mg, 94%, petroleum ether/EtOAc = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.35−7.15 (m, 13H), 6.80 (s, 1H), 6.44−6.39 (m, 2H), 3.90 (ddd, J = 10.4, 7.1, 3.0 Hz, 1H), 3.30−3.17 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 150.2, 142.9, 137.2, 137.1, 132.3, 131.6, 130.7, 129.6, 128.8, 128.7, 128.6, 127.6, 127.4, 126.9, 126.8, 126.3, 125.9, 125.0, 47.9, 32.4, 22.0; IR (neat) ν (cm^{-1}) 3059, 3025, 2923, 1679, 1599, 1492, 1451, 1242, 1108, 962, 729, 695, 525; HRMS exact mass calcd for ($C_{26}H_{23}NO$ + H) requires m/z 366.1858, found m/z 366.1857.

(E)-2-(2-Chlorophenyl)-5-(2,4-diphenylbut-3-en-1-yl)oxazole (**3i**): yellow oil (62.5 mg, 81%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.3, 2.2 Hz, 1H), 7.48−7.41 (m, 1H), 7.36−7.14 (m, 12H), 6.84 (s, 1H), 6.42 (d, J = 3.1 Hz, 2H), 3.97−3.86 (m, 1H), 3.31−3.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.2, 142.7, 137.1, 132.3, 132.1, 131.2, 130.73, 130.72, 130.67, 128.8, 128.6, 127.6, 127.5, 126.9, 126.8, 126.5, 126.3, 125.3, 47.9, 32.4; IR (neat) ν (cm^{-1}) 3057, 3025, 2920, 1599, 1570, 1492, 1451, 1431, 1239, 1130, 1038, 962, 826, 763, 731, 692, 654, 525; HRMS exact mass calcd for ($C_{25}H_{20}ClNO$ + H) requires m/z 386.1312, found m/z 386.1313.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(m-tolyl)oxazole (**3j**): yellow oil (65.2 mg, 89% petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 9.2 Hz, 2H), 7.40−6.93 (m, 12H), 6.74 (s, 1H), 6.50−6.12 (m, 2H), 3.91 (dd, J = 6.8, 3.2 Hz, 1H), 3.42−2.88 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 150.6, 142.8, 138.5, 137.1, 132.2, 130.8, 130.7, 128.74, 128.65, 128.55, 127.6, 127.4, 126.9, 126.7, 126.3, 125.2, 123.2, 47.8, 32.5, 21.4; IR (neat) ν (cm^{-1}) 3057, 3025, 2918, 1599, 1548, 1492, 1451, 1264, 1195, 1118, 1069, 962, 792, 724, 690, 525; HRMS exact mass calcd for ($C_{26}H_{23}NO$ + H) requires m/z 366.1858, found m/z 366.1860.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-(thiophen-2-yl)oxazole (**3k**): yellow oil (53.6 mg, 75%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.51 (m, 1H), 7.40−7.15 (m, 11H), 7.06 (dd, J = 4.8, 3.8 Hz, 1H), 6.69 (s, 1H), 6.44−6.37 (m, 2H), 3.93−3.84 (m, 1H), 3.27−3.13 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 150.2, 142.7, 137.1, 132.1, 130.7, 130.4, 128.8, 128.6, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 126.3, 125.1, 47.6, 32.4; IR (neat) ν (cm^{-1}) 3059, 3023, 2906, 1596, 1492, 1448, 1424, 1113, 962, 850, 719, 692, 542, 488; HRMS exact mass calcd for ($C_{23}H_{19}NOS$ + H) requires m/z 358.1266, found m/z 358.1269.

5-((E)-2,4-Diphenylbut-3-en-1-yl)-2-((E)-styryl)oxazole (**3l**): yellow oil (40.0 mg, 53%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.41−7.16 (m, 14H), 6.87 (d, J = 16.4 Hz, 1H), 6.71 (s, 1H), 6.42 (d, J = 3.1 Hz, 2H), 3.90 (ddd, J = 10.4, 7.2, 3.0 Hz, 1H), 3.28−3.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 150.4, 142.8, 137.1, 135.7, 135.1, 132.2, 130.7, 129.0, 128.9, 128.8, 128.6, 127.6, 127.5, 127.1, 126.9, 126.3, 125.4, 114.2, 47.7, 32.5; IR (neat) ν (cm^{-1}) 3058, 3026, 2921, 1596, 1524, 1494, 1447, 1201, 1111, 1072, 1025, 960, 745, 689, 486; HRMS exact mass calcd for ($C_{27}H_{23}NO$ + H) requires m/z 378.1858, found m/z 378.1857.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2-methyl-4-phenyloxazole (**3m**): yellow oil (34.3 mg, 47%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.45 (m, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.32−7.14 (m, 11H), 6.41−6.29 (m, 2H), 3.96 (dd, J = 14.3, 7.1 Hz, 1H), 3.32 (ddd, J = 22.0, 14.9, 7.7 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.2, 142.9, 137.2, 135.9, 132.3, 132.0, 130.5, 128.7, 128.6, 128.5, 127.6, 127.4, 127.3, 126.9, 126.8, 126.3, 47.7, 32.7, 13.9; IR (neat) ν (cm^{-1}) 3056, 3026, 2924, 1669, 1596, 1492, 1447, 1262, 1072, 962, 745, 693, 530; HRMS exact mass calcd for ($C_{26}H_{23}NO$ + H) requires m/z 366.1858, found m/z 366.1852.

(E)-5-(2,4-Diphenylbut-3-en-1-yl)-2,4-diphenyloxazole (**3n**): yellow oil (60.0 mg, 86%, petroleum ether/EtOAc = 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 6.6, 3.0 Hz, 2H), 7.58 (d, J = 7.3 Hz, 2H), 7.47−7.35 (m, 5H), 7.35−7.12 (m, 11H), 6.49−6.33 (m, 2H), 4.05 (q, J = 7.3 Hz, 1H), 3.44 (ddd, J = 34.1, 14.9, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.7, 142.8, 137.5, 137.1, 132.3, 132.0, 130.6, 130.1, 128.7, 128.6, 128.5, 127.7, 127.62, 127.61, 127.4, 127.25, 127.24, 126.9, 126.28, 126.25, 47.9, 32.9; IR (neat) ν (cm^{-1}) 3058, 3024, 2921, 1667, 1596, 1555, 1491, 1445, 1069, 1006, 962, 774, 742, 715, 689, 484; HRMS exact mass calcd for ($C_{31}H_{25}NO$ + H) requires m/z 428.2014, found m/z 428.2018.

(E)-5-(2,4-Bis(4-fluorophenyl)but-3-en-1-yl)-2-phenyloxazole (**3o**): yellow oil (52.1 mg, 68%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 6.5, 3.0 Hz, 2H), 7.47−7.36 (m, 3H), 7.32−7.15 (m, 4H), 7.06−6.90 (m, 4H), 6.75 (s, 1H), 6.31 (dt, J = 15.9, 11.3 Hz, 2H), 3.89 (q, J = 7.3 Hz, 1H), 3.20 (qd, J = 15.2, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C-F}$ = 245.0 Hz), 161.7 (d, $^1J_{C-F}$ = 243.0 Hz), 160.9, 150.3, 138.3 (d, $^4J_{C-F}$ = 3.0 Hz), 133.1 (d, $^4J_{C-F}$ = 3.0 Hz), 131.70,131.68, 130.1, 129.6, 129.1 (d, $^3J_{C-F}$ = 8.0 Hz), 128.8, 127.8 (d, $^3J_{C-F}$ = 8.0 Hz), 127.6, 126.0, 125.3, 115.6 (d, $^2J_{C-F}$ = 21.0 Hz), 115.5 (d, $^2J_{C-F}$ = 22.0 Hz), 46.9, 32.5; IR (neat) ν (cm^{-1}) 3041, 2921, 1726, 1599, 1547, 1506, 1447, 1221, 1157, 1120, 1096, 967, 833, 774, 708, 691, 515; HRMS exact mass calcd for ($C_{25}H_{19}F_2NO$ + H) requires m/z 388.1513, found m/z 388.1514.

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*(E)-5-(2,4-Bis(4-chlorophenyl)but-3-en-1-yl)-2-phenyloxazole (**3p**):* yellow oil (41.9 mg, 50%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 6.6, 3.0 Hz, 2H), 7.46−7.38 (m, 3H), 7.30 (d, J = 8.4 Hz, 2H), 7.24−7.26 (m, 4H), 7.18 (d, J = 8.4 Hz, 2H), 6.75 (s, 1H), 6.35 (d, J = 2.9 Hz, 2H), 3.88 (dt, J = 10.3, 3.6 Hz, 1H), 3.20 (qd, J = 15.2, 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 150.1, 140.9, 135.3, 133.2, 132.7, 132.3, 130.1, 129.9, 129.0, 128.9, 128.8, 128.7, 127.6, 127.5, 126.0, 125.3, 47.1, 32.3; IR (neat) ν (cm^{-1}) 3026, 2921, 1682, 1594, 1547, 1489, 1447, 1406, 1282, 1120, 1089, 1013, 964, 828, 808, 774, 708, 689, 501; HRMS exact mass calcd for ($C_{25}H_{19}Cl_2NO$ + H) requires m/z 420.0922, found m/z 420.0919.

*(E)-5-(2,4-Di-p-tolylbut-3-en-1-yl)-2-phenyloxazole (**3q**):* yellow oil (43.9 mg, 58%, petroleum ether/EtOAc = 25/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 2H), 7.44−7.38 (m, 3H), 7.25−7.18 (m, 2H), 7.17−7.10 (m, 4H), 7.09−7.04 (m, 2H), 6.74 (s, 1H), 6.36 (d, J = 5.5 Hz, 2H), 3.86 (dd, J = 13.0, 7.4 Hz, 1H), 3.27−3.14 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 150.9, 139.9, 137.1, 136.3, 134.4, 131.4, 130.3, 129.9, 129.4, 129.2, 128.7, 127.8, 127.5, 126.2, 126.0, 125.2, 47.2, 32.6, 21.2, 21.0; IR (neat) ν (cm^{-1}) 3019, 2921, 2855, 1594, 1547, 1514, 1484, 1450, 1262, 1118, 1064, 1020, 964, 798, 772, 711, 689, 503; HRMS exact mass calcd for ($C_{27}H_{25}NO$ + H) requires m/z 380.2014, found m/z 380.2010.

*(E)-2-Phenyl-5-(4-phenyl-2-(p-tolyl)but-3-en-1-yl)oxazole and (E)-2-phenyl-5-(2-phenyl-4-(p-tolyl)but-3-en-1-yl)oxazole (**3r**/**3r′**):* yellow oil (54.9 mg, 75%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 2H), 7.45−7.37 (m, 3H), 7.35−7.05 (m, 9H), 6.75 (s, 1H), 6.39 (dd, J = 13.6, 4.2 Hz, 2H), 3.93−3.84 (m, 1H), 3.29−3.15 (m, 2H), 2.32 (s, 1.77H), 2.31 (s, 1.22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.8, 142.9, 139.7, 137.2, 136.4, 134.3, 132.4, 131.2, 130.5, 130.4, 129.9, 129.4, 129.2, 128.7, 128.5, 127.8, 127.6, 127.5, 127.4, 126.8, 126.3, 126.2, 126.0, 125.2, 47.7, 47.3, 32.5, 21.2, 21.1; IR (neat) ν (cm^{-1}) 3024, 2921, 1682, 1596, 1547, 1513, 1484, 1447, 1250, 1120, 1064, 1023, 962, 813, 745, 708, 686, 501; HRMS exact mass calcd for ($C_{26}H_{23}NO$ + H) requires m/z 366.1858, found m/z 366.1854.

*2-Phenyl-5-(2,4,4-triphenylbut-3-en-1-yl)oxazole (**3s**):* yellow oil (70.0 mg, 82%, petroleum ether/EtOAc = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 6.6, 2.9 Hz, 2H), 7.44−7.36 (m, 3H), 7.32 (t, J = 7.5 Hz, 2H), 7.27−7.11 (m, 11H), 6.96−6.87 (m, 2H), 6.78 (s, 1H), 6.27 (d, J = 10.5 Hz, 1H), 3.88 (dt, J = 10.4, 7.4 Hz, 1H), 3.11 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.7, 143.8, 142.9, 142.1, 139.6, 130.6, 130.0, 129.6, 128.8, 128.7, 128.3, 128.1, 127.7, 127.4, 127.32, 127.26, 127.19, 126.7, 126.2, 125.2, 44.4, 33.6; IR (neat) ν (cm^{-1}) 3053, 3014, 2919, 1596, 1547, 1489, 1445, 1355, 1262, 1120, 1069, 1023, 977, 830, 759, 688, 630, 574, 532, 464; HRMS exact mass calcd for ($C_{31}H_{25}NO$ + H) requires m/z 428.2014, found m/z 428.2015.

*5-(4,4-Diphenyl-2-(p-tolyl)but-3-en-1-yl)-2-phenyloxazole (**3t**):* yellow oil (46.9 mg, 53%, petroleum ether/EtOAc = 18/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 6.4, 3.0 Hz, 2H), 7.44−7.37 (m, 3H), 7.28−7.10 (m, 12H), 6.95−6.88 (m, 2H), 6.78 (s, 1H), 6.25 (d, J = 10.5 Hz, 1H), 3.85 (dt, J = 10.5, 7.4 Hz, 1H), 3.09 (d, J = 7.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.8, 142.6, 142.1, 140.8, 139.6, 136.2, 130.8, 129.9, 129.6, 129.5, 128.6, 128.2, 128.1, 127.7, 127.4, 127.2, 127.11, 127.09, 126.1, 125.1, 43.9, 33.7, 21.1; IR (neat) ν (cm^{-1}) 3055, 3021, 2921, 1596, 1545, 1513, 1486, 1443, 1355, 1120, 1072, 1025, 979, 815, 759, 691, 623, 593, 528; HRMS exact mass calcd for ($C_{32}H_{27}NO$ + H) requires m/z 442.2171, found m/z 442.2158.

*5-(2-(4-Chlorophenyl)-4,4-diphenylbut-3-en-1-yl)-2-phenyloxazole (**3u**):* yellow oil (80.4 mg, 87%, petroleum ether/EtOAc = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 6.6, 2.9 Hz, 2H), 7.44−7.35 (m, 3H), 7.32−7.10 (m, 12H), 6.94−6.86 (m, 2H), 6.78 (s, 1H), 6.22 (d, J = 10.4 Hz, 1H), 3.85 (dt, J = 10.2, 7.4 Hz, 1H), 3.08 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 150.3, 143.4, 142.3, 141.9, 139.5, 132.4, 130.0, 129.9, 129.5, 128.9, 128.7, 128.6, 128.3, 128.2, 127.6, 127.5, 127.33, 127.31, 126.1, 125.3, 43.8, 33.6; IR (neat) ν (cm^{-1}) 3055, 3021, 2921, 1594, 1547, 1489, 1445, 1357, 1262, 1118, 1089, 1011, 979, 825, 759, 691, 585, 532; HRMS exact mass calcd for ($C_{31}H_{24}ClNO$ + H) requires m/z 462.1625, found m/z 462.1632.

*5-(2-(4-Methoxyphenyl)-4,4-diphenylbut-3-en-1-yl)-2-phenyloxazole (**3v**):* yellow oil (37.2 mg, 41%, petroleum ether/EtOAc = 12/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.85 (m, 2H), 7.44−7.37 (m, 3H), 7.27−7.13 (m, 10H), 6.92 (dd, J = 7.6, 1.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.78 (s, 1H), 6.24 (d, J = 10.5 Hz, 1H), 3.84 (dt, J = 10.6, 7.5 Hz, 1H), 3.79 (s, 3H), 3.09 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 158.3, 150.8, 142.5, 142.1, 139.6, 135.9, 130.9, 129.9, 129.6, 128.6, 128.22, 128.16, 128.10, 127.7, 127.34, 127.25, 127.1, 126.1, 125.1, 114.2, 55.3, 43.5, 33.7; IR (neat) ν (cm^{-1}) 3055, 3021, 2924, 2833, 1595, 1547, 1508, 1486, 1443, 1357, 1245, 1174, 1120, 1072, 1030, 977, 828, 762, 691, 625, 593, 542; HRMS exact mass calcd for ($C_{32}H_{27}NO_2$ + H) requires m/z 458.2120, found m/z 458.2119.

*5-(2-(Naphthalen-1-yl)-4,4-diphenylbut-3-en-1-yl)-2-phenyloxazole (**3w**):* yellow solid (50.8 mg, 53%, petroleum ether/EtOAc = 15/1); mp 67−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 11.5, 5.6 Hz, 3H), 7.74 (dd, J = 15.2, 8.3 Hz, 2H), 7.58 (d, J = 7.1 Hz, 1H), 7.51−7.34 (m, 6H), 7.29−7.10 (m, 8H), 6.87 (d, J = 7.2 Hz, 2H), 6.81 (s, 1H), 6.51 (d, J = 10.2 Hz, 1H), 4.75 (td, J = 9.6, 5.0 Hz, 1H), 3.22 (ddd, J = 24.5, 15.3, 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.8, 143.2, 142.3, 140.3, 139.5, 134.2, 130.8, 130.6, 130.0, 129.7, 129.1, 128.7, 128.22, 128.15, 127.7, 127.6, 127.4, 127.31, 127.26, 126.14, 126.08, 125.7, 125.6, 125.2, 124.3, 123.0, 39.2, 34.0; IR (neat) ν (cm^{-1}) 3048, 2953, 2924, 2853, 1596, 1545, 1482, 1445, 1264, 1118, 1069, 1023, 977, 876, 825, 796, 767, 737, 701, 686, 642, 564; HRMS exact mass calcd for ($C_{35}H_{27}NO$ + H) requires m/z 478.2171, found m/z 478.2174.

General Procedure for the Synthesis of Compounds 4. To a solution of $Yb(OTf)_3$ (0.02 mmol) and **3** (0.2 mmol) in CH_2Cl_2 (1.5 mL) was slowly added a solution of DDQ (0.2 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). After removal of the solvent under reduced pressure, the residue was purified through column chromatography.

*5-((1Z,3E)-2,4-Diphenylbuta-1,3-dien-1-yl)-2-phenyloxazole (**4a**):* pale yellow solid (30.0 mg, 43%, petroleum ether/EtOAc = 40/1); mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.3, 2.0 Hz, 2H), 7.95 (d, J = 16.1 Hz, 1H), 7.56−7.28 (m, 14H), 6.63 (d, J = 16.1 Hz, 1H), 6.38 (s, 1H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 161.2, 150.4, 141.2, 141.0, 137.3, 135.4, 130.5, 129.2, 128.93, 128.88, 128.82, 128.4, 128.2, 128.0, 127.4, 126.9, 126.8, 126.4, 114.5; IR (neat) ν (cm^{-1}) 3060, 3021, 2955, 2921, 2850, 1726, 1682, 1472, 1447, 1257, 1130, 1069, 1023, 979, 967, 862, 772, 745, 686, 523,490; HRMS exact mass calcd for ($C_{25}H_{19}NO$ + H) requires m/z 350.1545, found m/z 350.1564.

*5-((1Z,3E)-2,4-Diphenylbuta-1,3-dien-1-yl)-2-(4-methoxyphenyl)-oxazole (**4c**):* pale yellow solid (38.1 mg, 51%, petroleum ether/EtOAc = 20/1); mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 16.1 Hz, 1H), 7.54−7.24 (m, 11H), 7.00 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 16.1 Hz, 1H), 6.37 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.4, 149.9, 141.1, 140.6, 137.4, 135.1, 129.2, 128.83, 128.80, 128.4, 128.11, 128.10, 127.9, 126.9, 120.2, 116.4, 114.7, 114.4, 55.4.; IR (neat) ν (cm^{-1}) 3077,2953, 2921, 2850, 1606, 1513, 1482, 1369, 1299, 1248, 1167, 1140, 1106, 1020, 972, 874, 833, 750, 701, 689, 613, 586, 520, 484; HRMS exact mass calcd for ($C_{26}H_{21}NO_2$ + H) requires m/z 380.1651, found m/z 380.1648.

*5-((1Z,3E)-2,4-Diphenylbuta-1,3-dien-1-yl)-2-(4-(trifluoromethyl)-phenyl)oxazole (**4f**):* pale yellow solid (35.1 mg, 42%, petroleum ether/EtOAc = 30/1); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 16.1 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.53−7.26 (m, 11H), 6.66 (d, J = 16.1 Hz, 1H), 6.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 151.2, 142.3, 140.8, 137.1, 136.1, 130.5, 129.13, 129.11, 128.97, 128.87, 128.85, 128.42, 128.40,128.2, 126.9, 126.5, 125.96, 125.92, 114.1; IR (neat) ν (cm^{-1}) 2960, 2921, 2853, 1689, 1494, 1457, 1374, 1321, 1257, 1164, 1059,

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1016, 795, 750, 691,669, 589, 523, 476; HRMS exact mass calcd for ($C_{26}H_{18}F_3NO$ + H) requires m/z 418.1419, found m/z 418.1407.

*3,3-Diphenyl-1-(p-tolyl)prop-2-en-1-ol (**2t**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.31 (m, 3H), 7.30−7.19 (m, 9H), 7.15 (d, J = 7.8 Hz, 2H), 6.29 (d, J = 9.4 Hz, 1H), 5.22 (d, J = 9.4 Hz, 1H), 2.34 (s, 3H), 1.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.7, 140.6, 139.2, 137.4, 130.3, 129.9, 129.4, 128.4, 128.2, 127.73, 127.68, 127.65, 126.3, 71.6, 21.2; HRMS exact mass calcd for ($C_{22}H_{20}O$−OH) requires m/z 283.1481, found m/z 283.1495.

*1-(4-Methoxyphenyl)-3,3-diphenylprop-2-en-1-ol (**2v**):* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.12 (m, 12H), 6.88 (d, J = 8.6 Hz, 2H), 6.30 (d, J = 9.3 Hz, 1H), 5.21 (d, J = 9.3 Hz, 1H), 3.79 (s, 3H), 1.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.0, 141.7, 139.3, 133.9, 129.9, 128.4, 128.11, 128.05, 127.97, 127.6, 127.5, 113.9, 113.7, 74.8, 55.3; HRMS exact mass calcd for ($C_{22}H_{20}O_2$−OH) requires m/z 299.1430, found m/z 299.1447.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02382.

Synthesis, HPLC and X-ray crystal data, luminescence images, and ^{1}H and ^{13}C NMR and HRMS spectra (PDF)
X-ray crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389. (b) Jin, Z. *Nat. Prod. Rep.* **2003**, *20*, 584. (c) Jin, Z. *Nat. Prod. Rep.* **2009**, *26*, 382. (d) Dalvie, D. K.; Kalgutkar, A. S.; Khojasteh-Bakht, S. C.; Obach, R. S.; O'Donnell, J. P. *Chem. Res. Toxicol.* **2002**, *15*, 269. (e) Mulder, R. J.; Shafer, C. M.; Molinski, T. F. *J. Org. Chem.* **1999**, *64*, 4995. (f) Pettit, G. R.; Hogan, F.; Xu, J. P.; Tan, R.; Nogawa, T.; Cichacz, Z.; Pettit, R. K.; Du, J.; Ye, Q. H.; Cragg, G. M.; Herald, C. L.; Hoard, M. S.; Goswami, A.; Searcy, J.; Tackett, L.; Doubek, D. L.; Williams, L.; Hooper, J. N. A.; Schmidt, J. M.; Chapuis, J. C.; Tackett, D. N.; Craciunescu, F. *J. Nat. Prod.* **2008**, *71*, 438.

(2) For example: Gissibl, A.; Finn, M. G.; Reiser, O. *Org. Lett.* **2005**, *7*, 2325.

(3) (a) Hu, Y.; Xin, X.; Wan, B. *Tetrahedron Lett.* **2015**, *56*, 32. (b) Hu, Y.; Yi, R.; Wang, C.; Xin, X.; Wu, F.; Wan, B. *J. Org. Chem.* **2014**, *79*, 3052. (c) Yu, X.; Xin, X.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 4895. (d) Hashmi, A. S. K.; Blanco Jaimes, M. C.; Schuster, A. M.; Rominger, F. *J. Org. Chem.* **2012**, *77*, 6394. (e) Senadi, G. C.; Hu, W. P.; Hsiao, J. S.; Vandavasi, J. K.; Chen, C. Y.; Wang, J. J. *Org. Lett.* **2012**, *14*, 4478. (f) Egorova, O. A.; Seo, H.; Kim, Y.; Moon, D.; Rhee, Y. M.; Ahn, K. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 11446. (g) Saito, A.; Iimura, K.; Hanzawa, Y. *Tetrahedron Lett.* **2010**, *51*, 1471. (h) Hashmi, A. S. K.; Schuster, A. M.; Schmuck, M.; Rominger, F. *Eur. J. Org. Chem.* **2011**, *2011*, 4595.

(4) Arcadi, A.; Cacchi, S.; Cascia, L.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2001**, *3*, 2501.

(5) Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W. *Chem. - Eur. J.* **2010**, *16*, 956.

(6) Peng, H.; Akhmedov, N. G.; Liang, Y.; Jiao, N.; Shi, X. *J. Am. Chem. Soc.* **2015**, *137*, 8912.

(7) (a) Wang, X.; Dong, S.; Yao, Z.; Feng, L.; Daka, P.; Wang, H.; Xu, Z. *Org. Lett.* **2014**, *16*, 22. (b) Wang, X.; Yao, Z.; Dong, S.; Wei, F.; Wang, H.; Xu, Z. *Org. Lett.* **2013**, *15*, 2234. (c) Zhang, S.; Xu, Z.; Jia, J.; Tung, C.-H.; Xu, Z. *Chem. Commun.* **2014**, *50*, 12084. (d) Zhang, S.; Chen, Y.; Wang, J.; Pan, Y.; Xu, Z.; Tung, C.-H. *Org. Chem. Front.* **2015**, *2*, 578.

(8) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163. (c) Braun, M.; Meier, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 6952. (d) Zheng, C.; Zhuo, C. X.; You, S.-L. *J. Am. Chem. Soc.* **2014**, *136*, 16251. (e) Chen, W. Y.; Chen, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 15825. (f) Qu, J.; Roßberg, L.; Helmchen, G. *J. Am. Chem. Soc.* **2014**, *136*, 1272. (g) Hamilton, J. Y.; Hauser, N.; Sarlah, D.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2014**, *53*, 10759. (h) Lei, B. L.; Ding, C. H.; Yang, X. F.; Wan, X. L.; Hou, X.-L. *J. Am. Chem. Soc.* **2009**, *131*, 18250.

(9) For a review, see: (a) Sarkar, A.; Santra, S.; Kundu, S. K.; Ghosal, N. C.; Hajra, A.; Majee, A. *Synthesis* **2015**, *47*, 1379. For recent examples, see: (b) Jadhav, A. M.; Pagar, V. V.; Huple, D. B.; Liu, R. S. *Angew. Chem., Int. Ed.* **2015**, *54*, 3812. (c) Li, L.; Zhou, B.; Wang, Y.; Shu, C.; Pan, Y.-F.; Lu, X.; Ye, L.-W. *Angew. Chem., Int. Ed.* **2015**, *54*, 8245. (d) González, M. J.; González, J.; López, L. A.; Vicente, R. *Angew. Chem., Int. Ed.*, 2015, *54*, DOI: 10.1002/anie.201505954;. (e) Cheng, C.; Liu, S.; Zhu, G. *Org. Lett.* **2015**, *17*, 1581. (f) González, M. J.; López, L. A.; Vicente, R. *Org. Lett.* **2014**, *16*, 5780. (g) Song, B.; Li, L.-H.; Song, X.-R.; Qiu, Y.-F.; Zhong, M.-J.; Zhou, P.-X.; Liang, Y.-M. *Chem. - Eur. J.* **2014**, *20*, 5910.

(10) (a) Bandini, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 994. (b) Lumbroso, A.; Cooke, M. L.; Breit, B. *Angew. Chem., Int. Ed.* **2013**, *52*, 1890. (c) Sundararaju, B.; Achard, M.; Bruneau, C. *Chem. Soc. Rev.* **2012**, *41*, 4467. (d) Krautwald, S.; Schafroth, M. A.; Sarlah, D.; Carreira, E. M. *J. Am. Chem. Soc.* **2014**, *136*, 3020. (e) Krautwald, S.; Sarlah, D.; Schafroth, M. A.; Carreira, E. M. *Science* **2013**, *340*, 1065. (f) Zhang, X.; Yang, Z.-P.; Liu, C.; You, S.-L. *Chem. Sci.* **2013**, *4*, 3239.

(11) For a review on dehydrative coupling reactions, see: Kumar, R.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2013**, *42*, 1121.

(12) (a) Stopka, T.; Niggemann, M. *Org. Lett.* **2015**, *17*, 1437. (b) Tan, W.; Du, B.; Li, X.; Zhu, X.; Shi, F.; Tu, S.-J. *J. Org. Chem.* **2014**, *79*, 4635. (c) Zhang, T.; Qiao, Z.; Wang, Y.; Zhong, N.; Liu, L.; Wang, D.; Chen, Y.-J. *Chem. Commun.* **2013**, *49*, 1636. (d) Xiao, J. *Org. Lett.* **2012**, *14*, 1716. (e) Guo, C.; Song, J.; Huang, J.; Chen, P.; Luo, S.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 1046. (f) Capdevila, M. G.; Benfatti, F.; Zoli, L.; Stenta, M.; Cozzi, P. G. *Chem. - Eur. J.* **2010**, *16*, 11237. (g) Cozzi, P. G.; Benfatti, F.; Zoli, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 1313.

(13) Guo, C.; Song, J.; Luo, S.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 5558.

(14) CCDC 1421020 (**4f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(15) For reviews on AIE effect, see: (a) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332. (b) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361. For the applications of AIE active materials, see: (c) Wang, H.; Liu, J.; Han, A.; Xiao, N.; Xue, Z.; Wang, G.; Long, J.; Kong, D.; Liu, B.; Yang, Z.; Ding, D. *ACS Nano* **2014**, *8*, 1475. (d) Gao, M.; Sim, C. K.; Leung, C. W. T.; Hu, Q.; Feng, G.; Xu, F.; Tang, B. Z.; Liu, B. *Chem. Commun.* **2014**, *50*, 8312. (e) Song, C.; Sun, Y.; Wang, J.; Chen, H.; Yao, J.; Tung, C.-H.; Xu, Z. *Org. Chem. Front.* **2015**, *2*, 1366.

(16) (a) Xu, C.; Xu, M.; Yang, L.; Li, C. *J. Org. Chem.* **2012**, *77*, 3010. (b) Teral, Y.; Roubaud, G.; Aubert, C.; Faure, R.; Campredon, M. *Aust. J. Chem.* **2005**, *58*, 517.

DOI: 10.1021/acs.joc.5b02382
J. Org. Chem. 2015, 80, 12718−12724