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Synthesis of *o*-Alkenylated 2-Arylbenzoxazoles via Rh-Catalyzed Oxidative Olefination of 2-Arylbenzoxazoles: Scope Investigation, Structural Features, and Mechanism Studies

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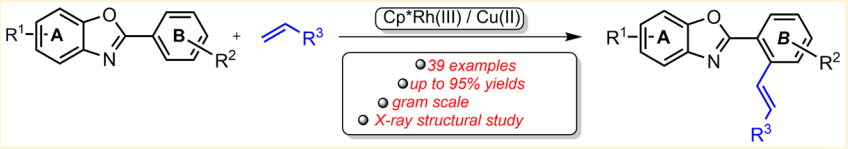
Supporting Information



ABSTRACT: 2-Arylbenzazoles are promising molecules for potential applications in medicine and material areas. Efficient protocols for direct regioselective functionalization of 2-arylbenzoxazoles are in high demand. Herein, we disclose a general method for selective *ortho*-olefination of 2-arylbenzo[*d*]oxazoles with alkenes enabled by versatile Cp*Rh(III) in high yields. This protocol features broad functional group tolerance and high regioselectivity. Intermolecular competition studies and kinetic isotope effect experiments imply that the oxidative olefination process occurs via an electrophilic C−H activation pathway. The molecular structure of the *m*-fluoro-substituted olefination product confirms regioselective C−H activation/olefination at the more hindered site in cases where the *meta* F atom or heteroatom substituent existed. Apparent torsion angles were observed in the structures of mono- and bis-olefination products, which resulted in distinct different chemical shifts of olefinic protons. Additionally, two gram-scale reactions and further transformation experiments demonstrate that this method is practical for synthesis of *ortho*-alkenylated 2-arylbenzoxazole derivatives.

1. INTRODUCTION

Benzazoles, owing to their diversified biological properties, including antibacterial, antifungal, and antiparasitic, are important heterocyclic molecular skeletons for medicinal chemistry.[1] In recent years, 2-arylbenzoxazoles have been applied for the study of Alzheimer's disease[2] and preparation of photoredox catalysts.[3] In addition, the alkenylated 2-arylbenzoxazoles derivatives possess extended π-conjugated systems and could have potential applications in medical[4] and material[5] areas. Most of the known methods for the synthesis of 2-arylbenzoxazole derivatives could be catalogued into two paths: (i) cyclization of 2-aminophenol derivatives with benzoic acid,[6] benzaldehyde,[7] or phenylmethanol[8] using acid, oxidant, or hydrogen-borrowing catalyst, respectively, and (ii) coupling of benzoxazole derivatives with aryl organometallic reagents by a transition-metal catalyst.[9] Despite these advances, no general methods to directly construct diverse arrays of alkenylated 2-arylbenzoxazoles are available. Therefore, developing an effective protocol for the synthesis 2-arylbenzoxazole derivatives and to enrich the chemists' toolbox remains highly desirable.

Initially reported by Moritani, Fujiwara, et al.,[10] the oxidative olefination of aromatic compounds bearing directing groups have been achieved in the presence of Pd(II),[11] Ru(II),[12] or Rh(III)[13] catalysts. Site-selective C−H activation and olefination reaction of arenes have been developed utilizing an array of proximal directing groups with weak coordination ability, for example, esters,[14] ketones,[15] amide,[16] sulfamidate,[17] sulfonamide,[18] and other weak directing groups.[19] With this in mind, we reasoned that the weakly coordinating benzoxazolyl moiety of 2-arylbenzoxazoles may serve as a directing group as well,[15,20] therefore leading to *ortho*-selective C−H activation of the adjacent phenyl ring. Noteworthy, although there are some reports on direct C−H arylation,[21] acylation,[22] hydroxylation,[23] and fluorination[24] of 2-arylbenzoxazoles with limited scope and transformation, *ortho*-selective C−H activation and olefination of 2-arylbenzoxazoles have not been developed yet. Therefore, we focused on olefination of 2-arylbenzoxazoles using benzoxazolyls as weak directing groups and hoped to establish an efficient method for the synthesis of alkenylated 2-arylbenzoxazoles derivatives.

In this context, we herein report a general method with the idea of utilizing benzoxazolyl moieties as weak directing groups for the synthesis *ortho*-alkenylated 2-arylbenzoxazoles via Cp*Rh-catalyzed oxidative olefination. In addition, single-crystal X-ray diffraction studies were also employed to investigate the molecular structures of alkenylated 2-arylbenzoxazoles. Note taht a concise study of the olefination mechanism has also been conducted. Additionally, wide substrate scope and gram-scale reactions have been examined as well.

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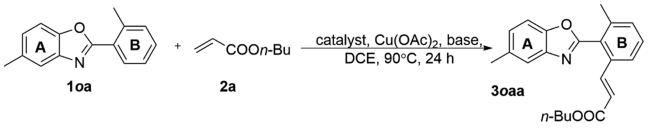
2. RESULTS AND DISCUSSION

Inspired by the oxidative Heck reaction,[25] we first modulated the 5-methyl-2-(*o*-tolyl)benzo[*d*]oxazole (**1*o*a**) olefination reaction with *n*-butyl acrylate (**2a**) in the presence of a catalytic amount of $[(p\text{-cymene})RuCl_2]_2$, 1.0 equiv of anhydrous NaOAc as base, and 1.0 equiv of anhydrous $Cu(OAc)_2$ as external oxidant in DCE at 90 °C (Table 1, entry 1). To our

Table 1. Optimization of Reaction Conditions[a,b]



1oa 2a 3oaa

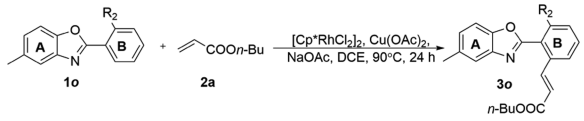
entry	catalyst	$Cu(OAc)_2$ (equiv)	base	yield (%)
1	$[RuCl_2(p\text{-cymene})_2]_2$	1.0	NaOAc	51[c]
2	$[(cod)RhCl]_2$	1.0	NaOAc	NR[c]
3	$[Cp^*IrCl_2]_2$	1.0	NaOAc	46
4	$[Cp^*RhCl_2]_2$	1.0	NaOAc	78
5	$[Cp^*RhCl_2]_2$	2.0	NaOAc	89
6	$[Cp^*RhCl_2]_2$	0.5	NaOAc	40
7	$[Cp^*RhCl_2]_2$	0	NaOAc	trace
8	$[Cp^*RhCl_2]_2$	2.0	K_3PO_4	50
9	$[Cp^*RhCl_2]_2$	2.0	KH_2PO_4	80
10	$[Cp^*RhCl_2]_2$	2.0	K_2CO_3	34
11	$[Cp^*RhCl_2]_2$	2.0	Na_2CO_3	55
12	$[Cp^*RhCl_2]_2$	2.0	KOAc	46
13	$[Cp^*RhCl_2]_2$	2.0	NaOAc	trace[d]
14	$[Cp^*RhCl_2]_2$	2.0	NaOAc	trace[e]
15	$[Cp^*RhCl_2]_2$	2.0	NaOAc	trace[f]
16	$[Cp^*RhCl_2]_2$	2.0	NaOAc	trace[g]

[a]Reaction condition: **1*o*a** (0.2 mmol), **2a** (0.6 mmol), catalyst (2.5 mol %), $Cu(OAc)_2$, base (1.0 equiv), DCE (1,2-dichloroethane) (2 mL), 90 °C, 24 h, N_2. [b]Isolated yields. [c]catalyst (5 mol %). [d]*N*,*N*-dimethylformamide (DMF) instead of DCE. [e]*N*-methyl-2-pyrrolidone (NMP) instead of DCE. [f]THF instead of DCE. [g]1,4-Dioxane instead of DCE.

delight, successful conversion to product was observed albeit in moderate isolated yield (**3*o*aa**, 51%), with exclusive *E*-stereoselectivity and *ortho*-regioselectivity. Afterward, screening of frequently used catalysts, including $[Rh(cod)Cl]_2$, $[Cp^*IrCl_2]_2$, and $[Cp^*RhCl_2]_2$ (entries 2−4), revealed that $[Cp^*RhCl_2]_2$ was the most effective with 78% isolated yield. Further experiments proved that increasing the amount of $Cu(OAc)_2$ to 2.0 equiv was necessary for higher conversion (entries 5−7). Next we screened other bases, including K_3PO_4, KH_2PO_4, K_2CO_3, Na_2CO_3, and KOAc (entries 8−12), and no base gave a better result than NaOAc. Additionally, changing the solvent did not improve the yield of the desired product (entries 13−16). Overall, the best result was achieved when 2.5 mol % of $[Cp^*RhCl_2]_2$, 2.0 equiv of $Cu(OAc)_2$, and 1.0 equiv of NaOAc in 1,2-dichloroethane at 90 °C for 24 h were used, providing **3*o*aa** in 89% yield with excellent regioselectivity. The product **3*o*aa** with *E*-conformation was unambiguously assigned by NMR spectroscopy.

With the optimized reaction conditions in hand, we then commenced exploration of the scope of substrates. Considering that 2-arylbenzoxazoles possessed two aryl rings, the aryl rings of benzoxazolyl and 2-aryl were denoted as ring A and ring B, respectively. Initially, substrates with a single activated available C−H bond that is *ortho* to the benzoxazolyl substitution (Table 2) were employed to investigate two issues: (i) electronic and

Table 2. Scope of 2-Arylbenzoxazoles with *Ortho* Substitution on Ring B[a,b] [a]



1o 2a 3o

Entry	Substrates **1*o***	Product **3*o***	Yield (%) [b]
1	**1*o*a**: R^2=Me	**3*o*aa**	89
2	**1*o*b**: R^2=F	**3*o*b**	80
3	**1*o*c**: R^2=Cl	**3*o*c**	48
4	**1*o*d**: R^2= Br	**3*o*d**	26
5	**1*o*e**: R^2= OMe	**3*o*e**	95
6	**1*o*f** : R^2= *p*-$MeOC_6H_4$	**3*o*f**	92
7	**1*o*g**: R^2= F	**3*o*g**	56
8	**1*o*h**: R^2= OMe	**3*o*h**	91
9	**1*o*i**: R^2= Me	**3*o*i**	80
10	**1*o*j**: R^2= F	**3*o*j**	72
11	**1*o*k**: R^2= O^{t}Bu	**3*o*k**	93
12	**1*o*l**: R^2= Me	**3*o*l**	83
13	**1*o*m**	**3*o*m**	65
14	**1*o*n**: R^2=OMe	**3*o*n**	58
15	**1*o*o**: R^2=F	**3*o*o**	33[c]
16	**1*o*p**: X=O	**3*o*p**	51
17	**1*o*q**: X=S	**3*o*q**	81

[a]Reaction condition: **1*o*** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (2.0 equiv), NaOAc (1.0 equiv), DCE (2 mL), N_2, 90 °C, 24 h. [b]Isolated yields. [c]48 h.

steric effects of different functional groups on the *ortho*-position of ring B and (ii) the electronic effect of different functional groups of ring A. At first, ring A was substituted by a methyl group, while ring B was *ortho*-substituted with different substituents including electron-donating and -withdrawing groups. The substrates with electron-donating groups (methyl and methoxy) and electron-withdrawing groups (fluoro) were well tolerated and proceeded smoothly to the desired product in good to excellent yields (entries 1, 2, and 5). For substrates with a sterically hindered functional group (*p*-MeO-C_6H_4) furnished on *ortho*-position of ring B, a quantitative conversion to olefination product was observed with 92% isolated yield (entry 6). In contrast, bromo and chloro substituted on the *ortho*-position of ring B proceeded sluggishly under the reaction conditions for **3*o*c** and **3*o*d** (entries 3 and 4) in which dehalogenation/olefination products accounted for a large portion. We subsequently examined the effect of substitutions on ring A. When ring A was not substituted or substituted by a weak electron-withdrawing group, moderate to good yields

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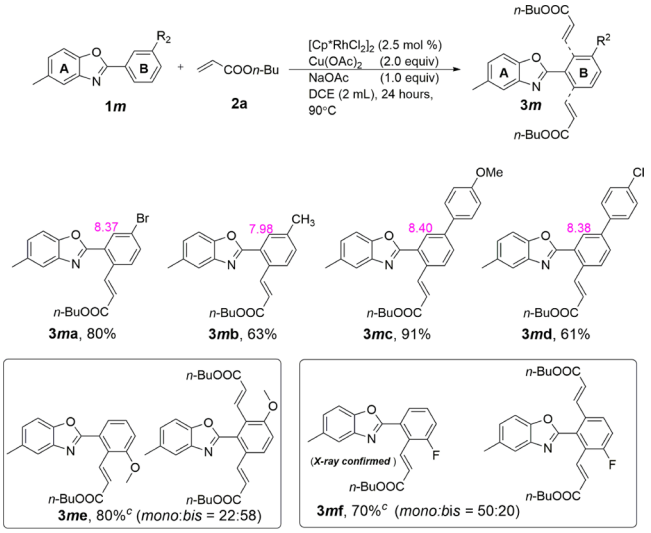
were obtained (entries 7−12). However, strong electron-withdrawing groups, like acetyl and fluoro, substituted on ring A had a significant negative effect on the catalytic efficiency, and no side products were observed (entries 13−15). It is well-known that the acetyl group could serve as an excellent directing group for the ruthenium-catalyzed C−H bond activation reactions.[25a]

The result of entry 13 indicates that the benzoxazolyl fragment chelates with Cp*Rh better than acetyl groups. Finally, the present methodology can be further extended to the 2-heteroaromatic benzoxazoles. Under the optimized conditions, the reactions of **1*o*p** and **1*o*q** with **2a** afforded **3*o*p** and **3*o*q** in 51% and 81% yields (entries 16 and 17), respectively.

Next 2-arylbenzoxazoles with *meta*-substituents on ring B were used to investigate the C−H activation regioselectivity in the case where two nonequivalent *ortho* C−H bonds existed (Scheme 1). It was found that electron-donating, -withdrawing,

Scheme 1. Scope of 2-Arylbenzoxazoles with *Meta*-Substitution on Ring B[a,b]

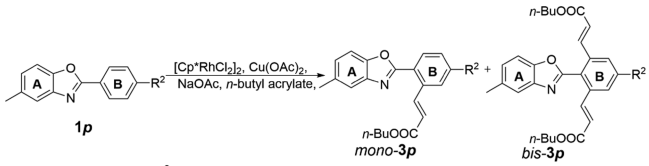


[a]Reaction condition: **1*m*** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (2.0 equiv), NaOAc (1.0 equiv), DCE (2 mL), 90 °C, 24 h, N_2. [b]Isolated yields. [c]Total isolated yields and the ones of mono and bis products were in parentheses.s

and sterically bulky substitutions at the *meta*-position of the ring B were well tolerated, and smoothly reacted with *n*-butyl acrylate to give the corresponding oxidative olefination products **3*m*a−*m*d** in good to excellent yields (61−91%). Selective *ortho* C−H functionalization was observed at the less hindered site for substrates bearing bromo, methyl, *p*-methoxyphenyl, and *p*-chlorophenyl groups, and the regiochemistry was confirmed by the existence of the single peak at 7.98−8.40 ppm in ^{1}H NMR spectra (pink color in Scheme 1); meanwhile no bis-olefinated products were observed. In contrast, mono- and bis-olefination products were isolated in total yields of 80% (**3*m*e**, mono/bis = 22:58) and 70% (**3*m*f**, mono/bis = 50:20) when *meta*-substitution on ring B was a methoxy and fluoro group, respectively. More interesting, the single peak near 8.2 ppm was not observed in the ^{1}H NMR spectra of mono-olefination products mono-**3*m*e** and mono-**3*m*f**, which suggested C−H activation olefination occurred at the sterically hindered *ortho* position.[13b,26] To our delight, the molecular structure of mono-**3*m*f** was confirmed by X-ray single-crystal diffraction (see the SI), and two intermolecular hydrogen bonds were found in this molecule. The distance N···H (C*H*═CH−COO*n*-Bu) is 2.343 Å, and the F···H (CH═C*H*-COO*n*-Bu) is 2.327 Å. The regioselective oxidative olefination at sterically hindered position (mono-**3*m*f** and mono-**3*m*e**) is likely due to the ligating effect of the *meta* F atom or heteroatom with its reduced steric bulk.[26]

Lastly, substrates with a *para*-substituted ring B were tested. Under the optimized conditions, substrates bearing different functional groups at the *para* position of ring B were well tolerated with high conversions (Scheme 2). Mostly, mono-

Scheme 2. Scope of 2-Arylbenzoxazoles with *Para*-Substitution on Ring B[a,b]



1*p*a	R^2 = H	**3*p*a**, 83% (*mono*: *bis* = 21:63)
1*p*b	R^2 = CH_3	**3*p*b**, 66% (*mono*: *bis* = 16:50)
1*p*c	R^2 = ^{t}Bu	**3*p*c**, 91% (*mono*: *bis* = 25:66)
1*p*d	R^2 = OCH_3	**3*p*d**, 80% (*mono*: *bis* = 21:57)
1*p*e	R^2 = OCF_3	**3*p*e**, 62% (*mono*: *bis* = 62:0)
1*p*f	R^2 = F	**3*p*f**, 80% (*mono*: *bis* = 21:57)
1*p*g	R^2 = Cl	**3*p*g**, 75% (*mono*: *bis* = 75:0)[c]
1*p*h	R^2 = Br	**3*p*h**,95% (*mono*: *bis* = 15:80)[c]
1*p*i	R^2 = COOEt	**3*p*i**, 99% (*mono*: *bis* = 40:59)

[a]Reaction conditions: **1*p*** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (2.0 equiv), NaOAc (1.0 equiv), DCE (2 mL), N_2, 90 °C, 24 h. [b]Reaction conditions: **1*p*** (0.2 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (2.0 equiv), NaOAc (1.0 equiv), DCE (2 mL), N_2, 90 °C, 24 h. [c]48 h.

and bis-oxidative olefination products (**3*p*a−*p*d,*p*f,*p*h−*p*i**) were afforded, while substrates with OCF_3 and Cl groups only forged the mono-olefination products (mono-**3*p*e** and mono-**3*p*g**). Furthermore, we have made several attempts to improve the selectivity of mono-olefination. Reducing the equivalence of **2a** did improve mono/bis selectivity, but conversion was obviously decreased. Decreasing the reaction temperature and equivalence of copper(II) acetate does not improve the selectivity of mono-olefination.

It is noteworthy that Chang and co-workers[14c] recently described a rhodium-catalyzed *ortho*-olefination of ethyl benzoate with methyl acrylate and demonstrated that the ester moiety can also serve as an effective chelating/activating group. The product **3*p*i** (mono/bis = 40:59) was quantitatively afforded, which could also indicate that that benzoxazolyl moiety has a stronger chelating ability than the ester group. Additionally, a distinctive difference in the olefinic C−*H* chemical shift was observed between the mono- and bis-olefination products. The C−*H* (−C*H*═CHCOO*n*-Bu) chemical shifts of mono-**3*p*c** and bis-**3*p*c** were 8.86 and 7.77 ppm, respectively, nearly above 1 ppm difference, and other mono/bis olefination products also have such a difference. To clarify the correlation between chemical shifts with structures, the single crystals of a pair of mono/bis olefination products were obtained by slowly evaporating their ethyl acetate solution. The molecular structures of mono-**3*p*c** and bis-**3*p*c** disclosed the different spatial orientation between ring A and ring B planes (Figure 1). For mono-**3*p*c**, benzoxazolyl was almost coplanar with the olefinated ring B, and the torsion

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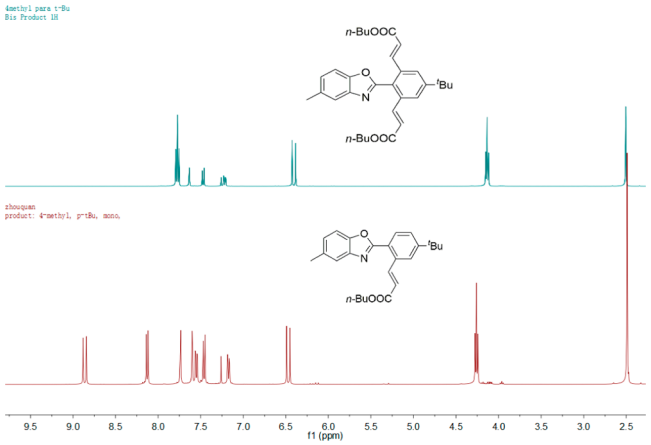
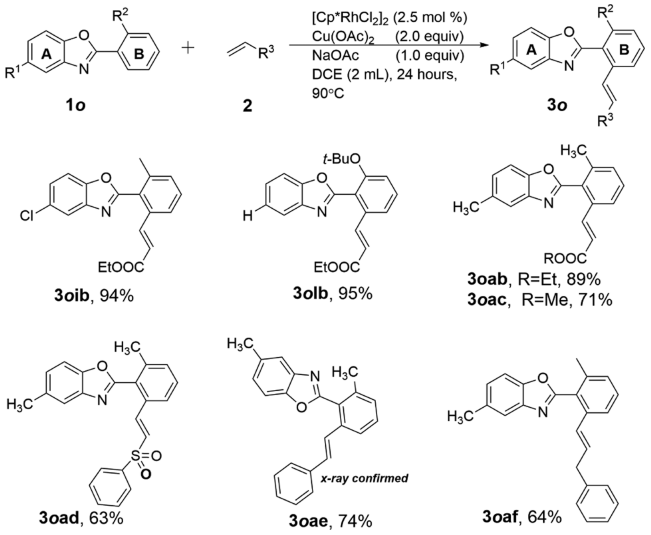


Figure 1. ^{1}H NMR spectra of mono-**3*pc*** and bis-**3*pc***.

angle [O(1)−C(1)−C(8)−C(13)] was 23°. The two relative planes of bis-**3*pc*** were nearly mutually perpendicular with the torsion angle [O(1)−C(1)−C(8)−C(9)] 85°. Additionally, one intramolecular hydrogen bond was observed between olefinic hydrogen and nitrogen atom from the benzoxazolyl group (2.315 Å) (see the SI).

In addition to 2-arylbenzoxazoles, the substrate scope of alkenes was also examined (Scheme 3). Ethyl acrylate (**2b**) and

Scheme 3. Scope with Respect to Alkenes[a,b]



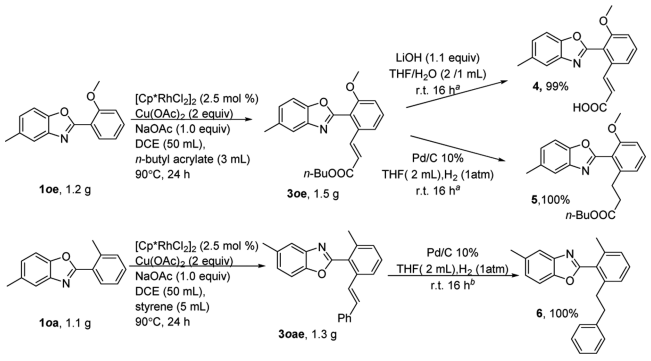
[a]Reaction conditions: **1*o*** (0.2 mmol), **2** (0.6 mmol), [Cp*RhCl$_2$]$_2$ (2.5 mol %), Cu(OAc)$_2$ (2.0 equiv), NaOAc (1.0 equiv), DCE (2 mL), N$_2$, 90 °C, 24 h. [b]Isolated yields.

methyl acrylate (**2c**) as olefins gave olefination products (**3*o*ib**, **3*o*lb**, **3*o*ac**, and **3*o*ab**) in good to quantitative yields. (Vinylsulfonyl)benzene (**2d**) could proceed with 63% yield (**3*o*ad**). Compared to acrylates, olefination could also forge with styrene (**2e**) to yield 74% of **3*o*ae**. The molecular structure of **3*o*ae** shows that the olefinic protons do not form a hydrogen bond with the nitrogen atom of the benzoxazolyl moiety (see the SI). Furthermore, allylbenzene (**2f**) could also afford oxidative olefinated product **3*o*af** in moderate yield.

However, other electron-rich olefins such as acrylonitrile, cinnamaldehyde, allyl 4-methylbenzoate, 4-vinylpyridine, and methyl methacrylate did not give the corresponding olefination products, which indicated that the coupling reactions largely depended on the electronic or steric effects of the olefins.[27]

To further evaluate the reaction efficacy on a preparative scale, two gram-scale reactions were then conducted (Scheme 4). In total, 1.5 g of **3*o*e** and 1.3 g **3*o*ae** were obtained in 83%

Scheme 4. Gram-Scale Reactions and Transformations

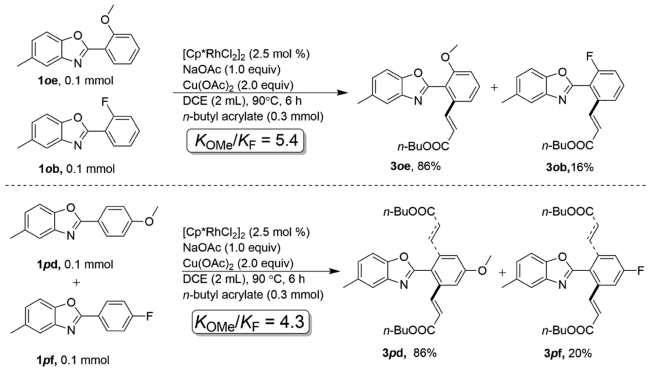


[a]0.2 mmol scale. [b]1.0 mmol scale.

and 81% yield, respectively, with 2.5 mol % of Cp*Rh(III) catalyst when the reactions were run for 24 h, demonstrating that the reaction system is practical. Further transformation of **3*o*e** and **3*o*ae** by Pd/C plus H_2 reduction afforded the hydrogenated products **5** and **6** in quantitative yields, and the treatment of **3*o*e** with LiOH in THF/H_2O led to hydrolysis product **4** with 99% yield.

To gain some insight into the mechanism, the intermolecular competition experiments between electron-deficient and electron-rich 2-arylbenzoxazoles were performed to determine the electronic preference of the reaction (Scheme 5).

Scheme 5. Intermolecular Competition Experiments



When an equimolar mixture of *ortho*-substituted **1*o*e** and **1*o*b** was allowed to compete under the optimal conditions in the coupling with *n*-butyl acrylate for 6 h, the electron-rich **1*o*e** exhibited higher reactivity with conversion ratios of 5.4:1. *Para*-substituted **1*p*d** and **1*p*f** gave the same preference with the ratios being 4.3:1.[28] The result demonstrates that the electron-donating substituent of 2-arylbenzoxazoles is beneficial for the reactivity of the olefination and seems to agree with an electrophilic olefination pathway.[29]

Subsequently, to probe the possible mechanism, isotope-labeling experiments were then performed (Scheme 6). An H/D exchange experiment was conducted between **1*o*a** and acetic acid-d_4 (Scheme 6A). In the presence of 10 equiv of

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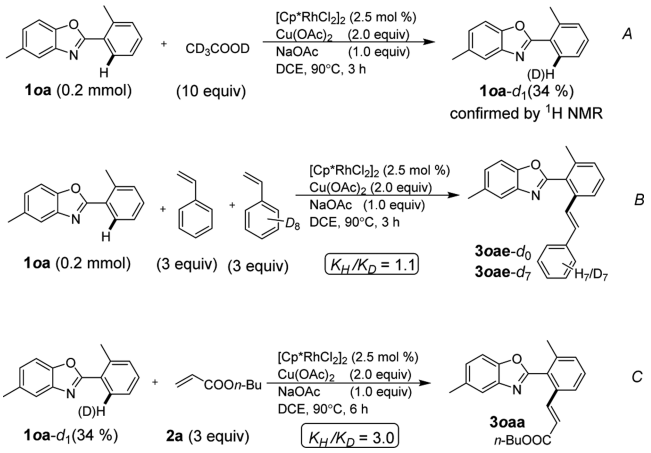
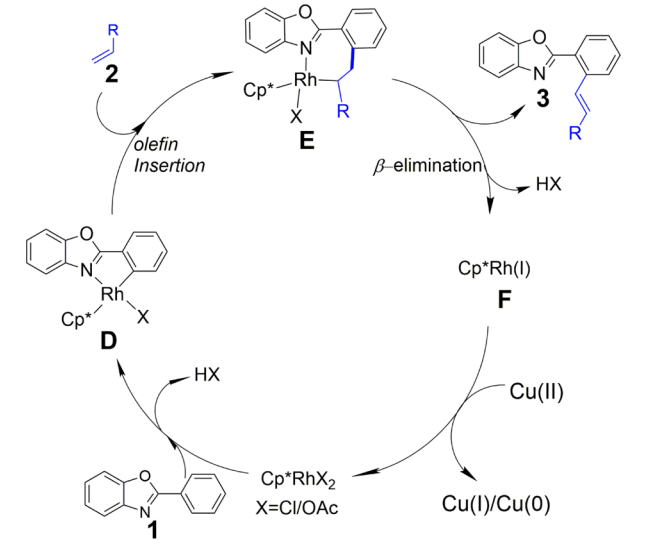
Scheme 6. Mechanism Studies



CD_3COOD, it was found that 34% D was incorporated into the *ortho* position of the 2-aryl ring. Furthermore, an intermolecular competition reaction between styrene and styrene-d_8 with **1*o*a** was performed (Scheme 6B), and the intermolecular kinetic isotope effect (KIE, K_H/K_D = 1.1) shows that the alkene insertion is not the rate-determing step. Additionally, the KIE (K_H/K_D = 3.0) was observed by comparison of the product yields between **1*o*a** and the monodeuterated **1*o*a**-d_1 substrate (66:34), suggesting that *ortho* C−H bond cleavage is likely the rate-determing step (Scheme 6C).[30]

Finally, to account for the observed transformation, a proposed catalytic cycle for this oxidative olefination was given in Scheme 7 on the basis of the above results and

Scheme 7. Proposed Mechanism



literature.[31] First, C−H activation of 2-arylbenzoxazole formed a five-membered rhodacycle species (**D**), followed elimination of HX through chelation-directed C−H activation. The olefin **2** then inserted into the C−Rh bond to give an intermediate (**E**) that is prone to β-H elimination, delivering the desired product **3** and Cp*Rh(I) species (**F**), the later was oxidated via Cu(II) which regenerated the Rh(III) species and fulfilled the catalytic cycle.[27,32]

3. CONCLUSIONS

In summary, we have developed a mild, efficient, and regioselective Rh(III)-catalyzed oxidative olefination protocol for the synthesis of *ortho*-alkenylated 2-arylbenzoxazole derivatives. The scope of this transformation is broad with regard to substrates, especially those bearing highly valuable bromo and chloro substitutents. Selective C−H functionalization at the more hindered site for the substrate bearing a fluoro atom was confirmed by single-crystal X-ray diffraction. This strategy can be applied on a gram scale, and these products could be straightforwardly converted to other useful synthetic intermediates. Moreover, mono- and bis-olefination of *para*-substituted 2-arylbenzoxazoles have shown an interesting angle torsion between the planes of two aromatic rings, which resulted in obviously different chemical shift on olefinic protons. These results might support the development of new strategies for constructing useful olefinated 2-arylbenzoxazole derivatives with biological activity and medicinal value. Additionally, the intermolecular competition studies and the kinetic isotope effect experiments imply that this oxidative olefination process occur via an electrophilic C−H activation pathway. More efforts on functionalization of 2-arylbenzoxazoles and the studies of these olefination products are ongoing in our laboratories.

4. EXPERIMENTAL SECTION

All commercially available compounds were used without purification. Unless otherwise noted, all olefinations were carried out under an atmosphere of nitrogen in dried glasswares. All substrates were synthesized according to relative references (see the SI). Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. 1,2-Dichloroethane, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), 1,4-dioxane, teterhydrofuran (THF), and dichloromethane (DCM) were purified by distillation over CaH_2 and were transferred and stored under nitrogen atomsphere.[33] All starting materials for substrate synthesis were purchased and used as received unless otherwise stated. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on 400 MHz spectrometers and are reported as chemical shifts (δ) in parts per million (ppm), and multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, m = multiplet. Internal standards or residual solvent signals were used as reference. HRMS (m/z) was recorded using ESI (Q-Tof, positive ion) mode. Single-crystal X-ray intensity data were recorded in recorded in a diffractometer with Mo Kα radiation. The CIF files were deposited at CCDC (Nos. 1490965−1490968) and can be obtained at https://summary.ccdc.cam.ac.uk/structure-summary-form.

Substrates (**1*o*a**,[34a] **1*o*b**,[34b] **1*o*c**,[34c] **1*o*d**,[34d] **1*o*e**,[34a] **1*o*g**,[34e] **1*o*h**, **1*o*j**,[34e] **1*o*m**, **1*o*n**, **1*o*o**, **1*o*p**,[34f] **1*o*q**,[8b] **1*m*a**, **1*p*a**,[8b] **1*p*f**,[34h] **1*p*g**,[34g] and **1*p*h**[34g]) were synthesized through 2-aminophenol derivative oxidative cyclization with corresponding aromatic aldehydes according to the relative reference.[7b] Additionally, substrates (**1*o*i**, **1*o*l**,[9a] **1*m*b**,[34h] **1*m*e**,[34i] **1*m*f**,[34e] **1*p*b**,[8b] **1*p*c**,[34j] **1*p*d**,[34k] **1*p*e**, and **1*p*i**) were prepared by palladium-catalyzed benzoxazoles C−H-activated and cross-coupled with aromatic bromides or iodides.[9a] Substrate **1*o*k** was prepared according to the standard conditions in the corresponding reference, and the abnormal product was afforded.[9f] Additionally, **1*o*f**,[34d] **1*m*c**, and **1*m*d** were prepared with the appropriate bromo-substituted 2-arylbenzoxazoles and appropriate aromatic boronic acid following the Suzuki cross-coupling method.[35] Characterization data of newly synthesized 2-arylbenzoxazoles are as follows.

Characterization Data of Newly Synthesized Substrates. *5-Chloro-2-(2-methoxyphenyl)benzo[d]oxazole (**1oh**):* 650 mg, yield 50% (5 mmol scale); brown solid; mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 1.0 Hz, 1H), 7.52−7.45 (m, 2H), 7.28 (dd, J = 8.6, 1.5 Hz, 1H), 7.11−7.03 (m,

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2H), 3.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 158.5, 148.9, 143.2, 133.1, 131.3, 129.7, 125.1, 120.7, 120.0, 115.6, 112.1, 111.1, 56.1; HRMS (ESI) calcd for $C_{14}H_{11}ClNO_2$ (M + H$^+$) 260.0478 (100.0), found 260.0474 (100.0).

*5-Chloro-2-(o-tolyl)benzo[d]oxazole (**1oi**):* 1250 mg, yield 92%, (5 mmol scale); white solid; mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.6 Hz, 1H), 7.76 (s, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.44−7.39 (m, 1H), 7.33 (dd, J = 13.8, 7.5 Hz, 3H), 2.79 (s, 3H); 13C NMR (101 MHz, $CDCl_3$) δ164.6, 148.8, 143.2, 139.1, 131.9, 131.2, 129.9, 129.9, 126.1, 125.6, 125.2, 120.0, 111.1, 22.2; HRMS (ESI) calcd for $C_{14}H_{11}ClNO$ (M + H$^+$) 244.0529 (100.0), found 244.0527 (100.0).

*2-(2-tert-Butoxyphenyl)benzo[d]oxazole (**1ok**):* 668 mg, yield 50% (5 mmol scale); brown solid; mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 7.7, 1.5 Hz, 1H), 7.81 (dd, J = 6.2, 2.9 Hz, 1H), 7.63−7.59 (m, 1H), 7.48−7.42 (m, 1H), 7.38−7.34 (m, 2H), 7.25−7.18 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 155.1, 150.7, 141.7, 133.1, 131.3, 130.5, 124.9, 124.6, 124.3, 123.3, 122.9, 120.0, 110.5, 81.0, 28.8; HRMS (ESI) calcd for $C_{17}H_{18}NO_2$ (M + H$^+$) 268.1338 (100.0), found 268.1332 (100.0).

*1-(2-(2-Methoxyphenyl)benzo[d]oxazol-5-yl)ethan-1-one (**1om**):* 668 mg, yield 50% (5 mmol scale); gray solid; mp 146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.13 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.10 (t, J = 8.0 Hz, 2H), 4.02 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 163.0, 158.6, 153.2, 142.2, 134.1, 133.3, 131.3, 125.6, 121.0, 120.7, 115.4, 112.1, 110.4, 56.1, 26.7; HRMS (ESI) calcd for $C_{16}H_{14}NO_3$ (M + H$^+$) 268.0974 (100.0), found 268.0968 (100.0).

*5, 7-Difluoro-2-(2-methoxyphenyl)benzo[d]oxazole (**1on**):* 240 mg, yield 46% (2 mmol scale); white solid; mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.7, 1.6 Hz, 1H), 7.62−7.50 (m, 1H), 7.38−7.30 (m, 1H), 7.12 (t, J = 8.3 Hz, 2H), 6.91 (td, J = 9.8, 2.3 Hz, 1H), 4.04 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.78 to −115.95 (m), −130.46 to −132.28 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 159.3 (dd, J = 242.4, 9.5 Hz), 158.7, 146.0 (dd, J = 254.4, 14.5 Hz), 145.1 (d, J = 13.2 Hz), 133.5, 131.4, 120.7, 115.1, 112.1, 102.5 (dd, J = 25.7, 4.7 Hz), 101.0 (dd, J = 29.8, 20.5 Hz), 56.2; HRMS (ESI) calcd for $C_{13}H_{17}F_3NO$ [M + H]$^+$ 260.0680, found 260.0675.

*5,7-Difluoro-2-(2-fluorophenyl)benzo[d]oxazole (**1oo**):* 323 mg, yield 65% (2 mmol scale); white solid; mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (t, J = 7.5 Hz, 1H), 7.58 (dd, J = 13.2, 7.2 Hz, 1H), 7.39−7.27 (m, 3H), 6.99−6.86 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.13 (s), −114.28 (d, J = 10.1 Hz, 1F), −130.46 (d, J = 10.9 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, J = 5.1 Hz), 159.6 (dd, J = 243.4, 9.3 Hz), 146.2 (dd, J = 255.3, 14.6 Hz), 144.7 (d, J = 18.0 Hz), 133.9 (d, J = 8.7 Hz), 130.6 (s), 124.6 (d, J = 3.4 Hz), 117.2 (d, J = 21.3 Hz), 114.5 (d, J = 10.4 Hz), 102.7 (dd, J = 25.7, 4.7 Hz), 101.6 (dd, J = 29.8, 20.4 Hz); HRMS (ESI) calcd for $C_{13}H_7F_3NO$ [M + H]$^+$ 250.0480, found 250.0478.

*2-(3-Bromophenyl)-5-methylbenzo[d]oxazole (**1ma**):* 4590 mg, yield 80% (20 mmol scale); white solid; mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (t, J = 1.5 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 149.0, 142.0, 134.6, 134.2, 130.4, 129.2, 126.7, 125.9, 122.9, 120.0, 110.0, 21.5; HRMS (ESI) calcd for $C_{14}H_{11}BrNO$: (M + H$^+$) 288.0024 (100.0), 290.0004 (97.3), found 288.0018 (100.0), 289.9999 (97.3).

*2-(4′-Methoxy[1,1′-biphenyl]-3-yl)-5-methylbenzo[d]oxazole (**1mc**):* 598 mg, yield 95% (2 mmol scale); gray solid; mp 147−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.17 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.60−7.51 (m, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 3.86 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 159.5, 149.0, 142.3, 141.5, 134.4, 132.6, 129.6, 129.3, 128.2, 127.7, 126.3, 125.7, 119.9, 114.3, 109.9, 55.3, 21.5; HRMS (ESI) calcd for $C_{21}H_{18}NO_2$ (M + H$^+$) 316.1338 (100.0), found 316.1332 (100.0).

*2-(4′-Chloro[1,1′-biphenyl]-3-yl)-5-methylbenzo[d]oxazole (**1md**):* 197 mg, yield 31% (2 mmol scale); white solid; mp 126−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 1.4 Hz, 1H), 8.30−8.16 (m, 1H), 7.75−7.67 (m, 1H), 7.61 (dt, J = 15.8, 3.6 Hz, 4H), 7.47 (t, J = 8.1 Hz, 3H), 7.19 (d, J = 8.3 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 149.0, 142.2, 140.7, 138.5, 134.5, 133.9, 129.7, 129.4, 129.0, 128.4, 127.9, 126.5, 126.4, 125.9, 119.9, 109.9, 21.5; HRMS (ESI) calcd for $C_{20}H_{15}ClNO$ (M + H$^+$) 320.0842 (100.0), found 320.0837 (100.0).

*5-Methyl-2-(4-(trifluoromethoxy)phenyl)benzo[d]oxazole (**1pe**):* 234 mg, yield 40% (2 mmol scale); white solid; mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2H), 7.56 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.2 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 151.3, 149.0, 142.16, 134.6, 129.2, 126.5, 125.9, 120.9, 120.4, 120.0, 116.5, 109.9, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.63 (s); HRMS (ESI) calcd for $C_{15}H_{11}F_3NO_2$ (M + H$^+$) 294.0742 (100.0), found 294.0736 (100.0).

*Ethyl 4-(5-methylbenzo[d]oxazol-2-yl)benzoate (**1pi**):* 337 mg, yield 60% (2 mmol scale); white solid; mp146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (t, J = 13.7 Hz, 2H), 8.21−8.07 (m, 2H), 7.52 (d, J = 22.0 Hz, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 162.0, 149.0, 142.1, 134.7, 132.6, 131.0, 130.0, 127.3, 126.8, 120.1, 110.0, 61.3, 21.5, 14.3; HRMS (ESI) calcd for $C_{17}H_{16}NO_3$ (M + H$^+$) 282.3190 (100.0), found 282.3194 (100.0%).

General Protocol for the Olefination of 2-Arybenzoxazoles with Alkenes. *Small (Milligram) Scale.* Into a flame-dried 25 mL Schlenk tube were added 2-arylbenz[*d*]oxazole (1.0 equiv) (normally 0.2 mmol scale), $[Cp^*RhCl_2]_2$ (3 mg, 2.5 mol %), NaOAc (16 mg, 1equiv), and $Cu(OAc)_2$ (64 mg, 2.0 equiv) under nitrogen flow, the tube was sealed with rubber, evacuated, and refilled with nitrogen three times, and then DCE (2 mL) and alkenes were added via syringe. The tube was sealed with a glass stopper, evacuated, and refilled with nitrogen three times and heated at 90 °C for the duration of the reaction. After being cooled to room temperature, the reaction mixture was quenched with 10 mL of saturated ammonium chloride solution and extracted with ethyl acetate (3 × 10 mL), the organic phase was combined, washed with brine (2 × 10 mL), dried under anhydrous magnesium sulfate, and concentrated under reduced pressure, and the residue mixture was purified by flash column chromatography.

Large (Gram) Scale. Into a dried round-bottom flask were layered $[Cp^*RhCl_2]_2$ (77.5 mg, 0.126 mmol, 2.5 mol %), NaOAc (410 mg, 5 mmol, 1.0 equiv), $Cu(OAc)_2$ (1.66 g, 10 mmol, 2.0 equiv), and 5-methyl-2-(*o*-tolyl)benzo[*d*]oxazole (**1oa**) (1.1 g, 5 mmol) dissolved in 50 mL of 1,2-dichloroethane, styrene (**2e**) (1.2 mL, 42.9 mmol, 10 equiv) was added in three portions, and the flask was protected with a nitrogen bag and lowered into a preheated oil bath at 90 °C for 24 h with efficient stirring. After being cooled to room temperature, the reaction mixture was filtered through a short pad of silica gel, the filter cake was washed with ethyl acetate (3 × 10 mL), the collected organic solvent was concentrated under reduced pressure, and the residue was purified through flash chromatography, which afforded the olefinated product **3oae** (1.3 g) as a white solid.

In a dried round-bottom flask were layered $[Cp^*RhCl_2]_2$ (77.5 mg, 0.126 mmol, 2.5 mol %), NaOAc (410 mg, 5 mmol, 1.0 equiv), $Cu(OAc)_2$ (1.66 g, 10 mmol, 2.0 equiv), and 2-(2-methoxyphenyl)-5-methylbenzo[*d*]oxazole (**1oe**) (1.2 g, 5 mmol) dissolved in 50 mL of 1,2-dichloroethane, butyl acrylate (**2a**) (3 mL, 42.9 mmol, 4 equiv) was added, and the flask was protected with a nitrogen bag and lowered into a preheated oil bath at 90 °C for 24 h with efficient stirring. After being cooled to room temperature, the reaction mixture was filtered through a short of silica pad, the filter cake was washed with ethyl acetate (3 × 10 mL), the collected organic solvent was concentrated under reduced pressure, and the residue was purified through flash chromatography, which afforded the olefinated product **3oe** (1.5 g) as a colorless oil.

Characterization Data of Oxidative Olefination Products. *Butyl (E)-3-(3-Methyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-*

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*acrylate (**3oaa**).* Starting from **1oa** with *n*-butyl acrylate, following the general procedure: colorless oil, yield 89% (62 mg) (eluent = PE/EA 100:1−30:1); R_f (PE/EA = 10:1) = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 15.9 Hz, 1H), 7.63 (s, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 4.11 (t, J = 6.5 Hz, 2H), 2.50 (s, 3H), 2.35 (s, 3H), 1.61−1.53 (m, 2H), 1.30 (dt, J = 14.4, 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.3, 149.0, 142.1, 141.6, 139.4, 135.5, 134.4, 131.8, 130.5, 128.3, 126.5, 124.2, 120.8, 120.3, 110.1, 64.3, 30.6, 21.4, 20.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{22}H_{24}NO_3$ $[M + H]^+$ 350.1756, found 350.1751.

*Ethyl (E)-3-(3-Methyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3oab**).* Starting from **1oa** with ethyl acrylate, following the general procedure: yield 89% (57 mg) (eluent = PE/EA 100:1−30:1); colorless oil; R_f (PE/EA = 30:1) = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 16 Hz, 1H), 7.63 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.21 (dd, J = 1.2 and 8.4 Hz, 1H), 6.38 (d, J = 16 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 2.51 (s, 3H), 2.35 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400M) δ 166.4, 161.3, 149.0, 142.2, 141.6, 139.4, 135.5, 134.4, 131.8, 130.5, 128.2, 126.5, 124.3, 120.8, 120.3, 110.1, 60.4, 21.4, 20.4, 14.2; HRMS (ESI) calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.1443, found 322.1438.

*Methyl (E)-3-(3-methyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3oac**):* yield 71% (43 mg) (eluent = PE/EA 100:1−30:1); colorless oil; R_f (PE/EA = 30:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16 Hz, 1H), 7.64 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.21 (dd, J = 0.8 and 8.0 Hz, 1H), 3.70 (s, 3H), 2.51 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 400M) δ 166.9, 161.3, 149.0, 142.4, 141.6, 139.5, 135.4, 134.4, 131.9, 130.6, 128.3, 126.6, 124.3, 120.4, 120.4, 110.2, 51.7, 21.5, 20.4; HRMS (ESI) calcd for $C_{19}H_{18}NO_3$ $[M + H]^+$ 308.1287, found 308.1281.

*Butyl (E)-3-(3-fluoro-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3ob**):* yield 80% (56 mg) (eluent = PE/EA 30:1−10:1); colorless oil; R_f (PE/EA = 10:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 15.9 Hz, 1H), 7.64 (s, 1H), 7.58−7.48 (m, 3H), 7.29−7.21 (m, 2H), 6.45 (d, J = 15.9 Hz, 1H), 4.17 (t, J = 6.5 Hz, 2H), 2.50 (d, J = 6.7 Hz, 3H), 1.67−1.59 (m, 2H), 1.39 (dd, J = 15.0, 7.5 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.69 (dd, J = 9.7, 5.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.4 (d, J = 255.2 Hz), 157.2, 149.2, 141.2 (d, J = 3.1 Hz), 141.2, 137.4, 134.6, 132.2 (d, J = 9.2 Hz), 126.9, 122.8 (d, J = 3.4 Hz), 122.2, 120.4, 117.2 (d, J = 22.1 Hz), 116.3 (d, J = 13.8 Hz), 110.2, 64.5, 30.6, 21.4, 19.1, 13.7; HRMS (ESI) calcd for $C_{21}H_{21}FNO_3$ $[M + H]^+$ 354.1505, found 354.1500.

*Butyl (E)-3-(3-chloro-2-(5-methylbenzo[d]oxazol-2-yl) phenyl)-acrylate (**3oc**):* yield 48% (35 mg) (eluent = PE/EA 25:1−10:1); colorless oil; R_f (PE/EA = 15:1) = 0.25; in addition, mono-**3pa** and bis-**3pa** (R_f (PE/EA = 20:1)) were also isolated 10% and 20% in this reaction; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 1H), 7.64 (s, 1H), 7.54(d, J = 16 Hz, 1H), 7.54−7.49 (m, 3H), 7.24 (d, J = 8.4 Hz, 1H), 4.10 (t, J = 6.4 Hz, 2H), 2.51 (s, 3H), 1.57 (m, 2H), 1.28 (m, J = 7.2 Hz, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13} C NMR ($CDCl_3$, 100M) δ 166.0, 158.8, 149.1, 141.3, 140.5, 137.5, 135.7, 134.6, 131.6, 130.8, 128.1, 126.9, 124.9, 122.3, 120.5, 110.2, 64.5, 30.5, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{21}ClNO_3$ $[M + H]^+$ 370.1210, found 370.1204.

*Butyl (E)-3-(3-bromo-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3od**):* yield 26% (21 mg) (eluent = PE/EA 25:1−10:1); colorless oil; R_f (PE/EA = 20:1) = 0.2; in addition, mono-**3pa** and bis-**3pa** were also isolated 18% and 32% in this reaction; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.8, 1.0 Hz, 1H), 7.65−7.62 (m, 1H), 7.58−7.47 (m, 4H), 7.26−7.22 (m, 1H), 6.39 (d, J = 15.9 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H), 2.52 (s, 3H), 1.62−1.55 (m, 2H), 1.30 (m,, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 158.8, 149.1, 141.3, 140.5, 137.5, 135.7, 134.6, 131.6, 130.8, 128.1, 126.9, 124.9, 122.3, 120.5, 110.3, 64.5, 30.5, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{21}BrNO_3$ $[M + H]^+$ 414.0705 (100.0), 416.0684 (97.3), found 414.0699 (100.0), 416.0680 (97.3).

*Butyl (E)-3-(3-methoxy-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3oe**):* yield 95% (69 mg); (eluent = PE/EA 50:1−10:1); mp 66−69 °C; R_f (PE/EA = 10:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 15.9 Hz, 1H), 7.61 (s, 1H), 7.49 (dd, J = 14.6, 8.1 Hz, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.20 (d, J = 8.3 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H), 3.82 (s, 3H), 2.50 (s, 3H), 1.68−1.44 (m, 2H), 1.30 (dt, J = 14.9, 7.5 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 159.4, 159.1, 149.3, 141.7, 141.4, 136.8, 134.1, 131.9, 126.3, 121.4, 120.3, 118.7, 118.0, 112.3, 110.1, 64.3, 56.1, 30.6, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1705, found 366.1700.

*Butyl (E)-3-(4′-methoxy-2-(5-methylbenzo[d]oxazol-2-yl)[1,1′-biphenyl]-3-yl)acrylate (**3of**):* yield 92% (81 mg); mp 93−95 °C; eluent = PE/EA = 10:1; R_f (PE/EA = 6:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 15.8 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.54 (s, 1H), 7.50 (dd, J = 7.7, 1.0 Hz, 1H), 7.26 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 1.2 Hz, 1H), 6.74 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 15.8 Hz, 1H), 4.12 (t, J = 6.5 Hz, 2H), 3.72 (s, 3H), 2.46 (s, 3H), 1.77−1.50 (m, 2H), 1.32 (dd, J = 15.1, 7.5 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ166.4, 161.1, 158.9, 148.8, 143.6, 141.8, 141.4, 135.9, 134.1, 132.5, 131.6, 130.6, 129.4, 127.3, 126.4, 125.1, 121.3, 120.3, 113.8, 110.0, 64.3, 55.1, 30.6, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{28}H_{28}NO_4$ $[M + H]^+$ 442.2018, found 442.2013.

*(E)-5-Methyl-2-(2-Methyl-6-(2-(phenylsulfonyl)vinyl)phenyl)-benzo[d]oxazole (**3oad**).* Starting substrate **1oa**, following the general procedure, gave white solid **3oad** through preparative thick-layer chromatography in 63% (48 mg) yield: mp 132−133 °C; R_f (PE/EA= 6:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 15.3 Hz, 1H), 7.61 (s, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.54−7.47 (m, 3H), 7.44 (d, J = 10.3 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.28−7.22 (m, 1H), 6.73 (d, J = 15.3 Hz, 1H), 2.54 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ160.9, 149.0, 141.4, 141.3, 140.3, 139.7, 134.6, 133.8, 133.3, 132.7, 130.6, 129.9, 129.2, 128.1, 127.7, 126.8, 125.1, 120.3, 110.1, 21.5, 20.5; HRMS (ESI) calcd for $C_{23}H_{20}NO_3S$ $[M + H]^+$ 390.1164, found 390.1158.

*(E)-5-Methyl-2-(2-methyl-6-styrylphenyl)benzo[d]oxazole (**3oae**):* yield 74% (48 mg) (eluent = PE/EA (100:1)); mp 89−91 °C; R_f (PE/EA = 50:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.1 Hz, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.1 Hz, 2H), 7.27 (m, 5H), 7.11 (s, 2H), 2.57 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 149.0, 141.7, 139.0, 138.3, 137.1, 134.3, 131.3, 130.4, 129.4, 128.6, 127.8, 127.0, 126.7, 126.3, 126.2, 123.2, 120.3, 110.1, 21.5, 20.4; HRMS (ESI) calcd for $C_{23}H_{20}NO$ $[M + H]^+$ 326.1545, found 326.1539

*(E)-5-Methyl-2-(2-methyl-6-(3-phenylprop-1-en-1-yl)phenyl) benzo[d]oxazole (**3oaf**):* yield 64% (43 mg) (eluent = PE/EA = 100:1); colorless oil; R_f (PE/EA = 50:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.27−7.11 (m, 8H), 6.26−6.07 (m, 2H), 3.56 (d, J = 5.8 Hz, 2H), 2.52 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 148.8, 141.6, 140.8, 138.8, 137.2, 134.1, 131.1, 130.4, 128.3, 128.2, 128.2, 128.0, 127.1, 126.9, 126.2, 126.0, 120.1, 110.0, 37.6, 21.4, 20.2; HRMS (ESI) calcd for $C_{24}H_{22}NO$ $[M + H]^+$ 340.1701, found 340.1696.

*Butyl (E)-3-(2-(5-chlorobenzo[d]oxazol-2-yl)-3-methylphenyl)-acrylate (**3oi**):* yield 80% (59 mg); mp 47−49 °C; R_f (PE/ethyl acetate 10:1) = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.64 (d, J = 15.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 8.6, 4.2 Hz, 1H), 7.42 (dd, J = 14.2, 7.2 Hz, 1H), 7.38−7.29 (m, 2H), 6.37 (dd, J = 15.8, 2.5 Hz, 1H), 4.19−3.99 (m, 2H), 2.33 (d, J = 3.6 Hz, 3H), 1.66−1.50 (m, 2H), 1.29 (dt, J = 10.9, 5.8 Hz, 2H), 0.92−0.77 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 162.7, 149.3, 142.4, 141.8, 139.4, 135.5, 131.9, 130.9, 130.1, 127.5, 125.8, 124.3, 121.1, 120.4, 111.5, 64.4, 30.6, 20.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{21}ClNO_3$ $[M + H]^+$ 370.1210, found 370.1204.

*Ethyl (E)-3-(2-(5-chlorobenzo[d]oxazol-2-yl)-3-methylphenyl) acrylate (**3oib**).* Starting substrate **1oi** with ethyl acrylate, following

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the general procedure, gave colorless oil **3oib** in 94% (64 mg) yield: R_f (PE/EA = 20:1) 0.35; mp 82−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.0 Hz, 1H), 7.65 (t, J = 10.7 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.42−7.34 (m, 2H), 6.40 (d, J = 15.8 Hz, 1H), 4.28−4.15 (m, 2H), 2.37 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 162.7, 149.3, 142.4, 141.9, 139.4, 135.5, 131.9, 130.8, 130.1, 127.5, 125.8, 124.4, 121.1, 120.4, 111.5, 60.5, 20.4, 14.1; HRMS (ESI) calcd for $C_{19}H_{17}O_3ClN$ $[M + H]^+$ 342.0897, found 342.0892.

*Butyl (E)-3-(2-(5-chlorobenzo[d]oxazol-2-yl)-3-fluorophenyl)-acrylate (**3og**):* yield 56% (42 mg); mp 63−65 °C; R_f (PE/EA = 10:1) = 0.25;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 15.9 Hz, 1H), 7.84 (d, J = 1.9 Hz, 1H), 7.61−7.51 (m, 3H), 7.39 (dd, J = 8.7, 2.1 Hz, 1H), 7.27 (ddd, J = 7.3, 5.4, 2.8 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 1.64 (dt, J = 14.5, 6.6 Hz, 2H), 1.39 (dd, J = 15.1, 7.5 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.35, −110.37, −110.38, −110.38, −110.39, −110.41; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 161.4 (d, J = 255.7 Hz), 158.6, 149.4, 142.4, 140.9, 137.4, 132.7 (d, J = 9.2 Hz), 130.3, 126.2, 123.0 (d, J = 2.8 Hz), 122.5, 120.5, 117.3 (d, J = 22.0 Hz), 115.6 (d, J = 13.6 Hz).111.6, 64.6, 30.6, 19.1, 13.7; HRMS (ESI) calcd for $C_{20}H_{18}ClFNO_3$ $[M + H]^+$ 374.0959, found 374.0954.

*Butyl (E)-3-(2-(5-chlorobenzo[d]oxazol-2-yl)-3-methoxyphenyl)-acrylate (**3oh**):* yield 80% (61 mg); R_f (PE/EA = 5:1) = 0.6; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 1.7 Hz, 1H), 7.63 (d, J = 15.9 Hz, 1H), 7.58−7.46 (m, 2H), 7.42−7.29 (m, 2H), 7.07 (d, J = 8.3 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 4.13 (t, J = 6.5 Hz, 2H), 3.85 (s, 3H), 1.65−1.52 (m, 2H), 1.37−1.25 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 160.9, 159.1, 149.6, 142.6, 141.1, 136.8, 132.2, 129.9, 125.6, 121.7, 120.3, 118.8, 117.2, 112.3, 111.5, 64.4, 56.2, 30.6, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{21}ClNO_4$ $[M + H]^+$ 386.1159, found 386.1154.

*Butyl (E)-3-(2-(benzo[d]oxazol-2-yl)-3-fluorophenyl)acrylate (**3oj**):* yield 72% (49 mg); colorless oil; R_f (PE/EA = 15:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08(d, J = 16 Hz, 1H), 7.88−7.86 (m, 1H), 7.65−7.62 (m, 1H), 7.58−7.45 (m, 2H), 7.44−7.40 (m, 2H), 7.26 (m, 1H), 6.47 (d, J = 16 Hz, 1H), 4.18 (t, J = 6.4 Hz, 2H), 1.63 (m, 2H), 1.39 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.4 (d, J = 255.3 Hz), 157.2, 150.9, 141.4, 141.1, 137.3, 132.3 (d, J = 9.2 Hz), 125.8, 124.7, 122.9 (d, J = 2.6 Hz), 122.3, 120.6, 117.2 (d, J = 22.1 Hz), 116.1 (d, J = 13.7 Hz), 110.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.57, −110.58, −110.59, −110.61; HRMS (ESI) calcd for $C_{20}H_{19}FNO_3$ $[M + H]^+$ 340.1349, found 340.1340.

*Butyl (E)-3-(2-(benzo[d]oxazol-2-yl)-3-tert-butoxyphenylacrylate (**3ok**):* yield 93% (73 mg); colorless oil; R_f (PE/EA = 15:1) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.79 (m, 1H), 7.73 (t, J = 11.0 Hz, 1H), 7.64−7.57 (m, 1H), 7.48−7.41 (m, 2H), 7.38 (d, J = 5.5 Hz, 2H), 7.23 (dd, J = 6.8, 2.3 Hz, 1H), 6.41 (t, J = 10.6 Hz, 1H), 4.13 (dt, J = 23.3, 6.5 Hz, 2H), 1.63−1.50 (m, 2H), 1.37−1.25 (m, 2H), 1.21 (s, 9H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 160.1, 156.2, 150.8, 141.7, 141.4, 136.6, 131.2, 125.3, 124.3, 123.9, 123.8, 121.2, 121.1, 120.4, 110.6, 81.0, 77.4, 77.0, 76.7, 64.3, 30.6, 28.9, 19.1, 13.6; HRMS (ESI) calcd for $C_{24}H_{28}NO_4$ $[M + H]^+$ 394.2018, found 394.2024.

*Ethyl (E)-3-(2-(benzo[d]oxazol-2-yl)-3-tert-butoxyphenyl)acrylate (**3okb**):* yield 93% (68 mg); colorless oil; R_f (PE/EA = 15:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 1H), 7.76 (d, J = 15.9 Hz, 1H), 7.64−7.58 (m, 1H), 7.47−7.41 (m, 2H), 7.41−7.34 (m, 2H), 7.27−7.19 (m, 1H), 6.42 (t, J = 9.8 Hz, 1H), 4.20−4.12 (m, 2H), 2.01 (d, J = 14.4 Hz, 1H), 1.29−1.20 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.28, 160.08, 156.26, 150.82, 141.74, 141.43, 136.63, 131.14, 125.26, 124.30, 123.77, 121.17, 121.04, 120.36, 110.53, 80.94, 60.40, 28.90, 14.14; HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1705, found 366.1700.

*Butyl (E)-3-(2-(benzo[d]oxazol-2-yl)-3-methylphenyl)acrylate (**3ol**):* yield 83% (55 mg); mp 55−57 °C; R_f (PE/EA = 10:1) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.8, 3.3 Hz, 1H), 7.68 (d, J = 15.8 Hz, 1H), 7.63−7.55 (m, 2H), 7.46−7.37 (m, 3H), 7.34 (d, J = 7.6 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.10 (t, J = 6.5 Hz, 2H), 2.35 (s, 3H), 1.60−1.48 (m, 2H), 1.30 (dd, J = 14.9, 7.4 Hz, 2H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.2, 150.7, 142.0, 141.4, 139.4, 135.5, 131.8, 130.6, 128.1, 125.4, 124.6, 124.2, 120.9, 120.7, 110.7, 64.3, 30.6, 20.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{22}NO_3$ $[M + H]^+$ 336.1600, found 336.1594.

*Butyl (E)-3-(2-(5-acetylbenzo[d]oxazol-2-yl)-3-methoxyphenyl)-acrylate (**3om**):* yield 65% (51 mg); colorless oil; eluent = PE/EA = 10:2; R_f (PE/EA = 10:2) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 1.3 Hz, 1H), 8.10 (dd, J = 8.6, 1.7 Hz, 1H), 7.64 (d, J = 15.8 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 3.84 (s, 3H), 2.70 (s, 3H), 1.58 (dt, J = 14.4, 6.6 Hz, 2H), 1.31 (dd, J = 15.0, 7.5 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 197.1, 166.3, 161.1, 159.1, 141.6, 141.1, 136.8, 134.2, 132.4, 125.9, 121.8, 121.5, 118.9, 112.3, 110.9, 64.4, 56.2, 30.6, 26.8, 19.1, 13.6; HRMS (ESI) calcd for $C_{23}H_{23}NO_5$ $(M + H)^+$ 394.1654, found 394.1649.

*Butyl (E)-3-(2-(5,7-difluorobenzo[d]oxazol-2-yl)-3-methoxy-phenyl)acrylate (**3on**):* yield 58% (45 mg); mp 64−66 °C; eluent = PE/EA = 20:1; R_f (PE/EA = 20:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 15.9 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.34 (dd, J = 11.6, 4.7 Hz, 2H), 7.06 (d, J = 8.3 Hz, 1H), 6.95 (td, J = 9.7, 2.2 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 4.12 (t, J = 6.5 Hz, 2H), 3.84 (s, 3H), 1.64−1.54 (m, 2H), 1.33 (dq, J = 14.6, 7.3 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.91 to −115.96 (m), −130.15 (dd, J = 10.6, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.7, 159.4 (dd, J = 243.0, 9.5 Hz), 159.1, 146.2 (dd, J = 254.9, 14.6 Hz), 144.3 (dd, J = 14.7, 3.0 Hz), 140.9, 136.8, 132.5, 121.9, 118.8, 116.5, 112.3, 102.8 (dd, J = 25.6, 4.8 Hz), 101.5 (dd, J = 29.8, 20.4 Hz), 64.5, 56.2, 30.6, 19.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{20}F_2NO_4$ $[M + H]^+$ 388.1360, found 388.1355.

*Butyl (E)-3-(2-(5,7-difluorobenzo[d]oxazol-2-yl)-3-fluorophenyl)-acrylate (**3oo**):* yield 33% (24 mg); colorless oil; R_f (PE/EA = 40:1) = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 15.9 Hz, 1H), 7.58 (q, J = 3.6 Hz, 2H), 7.37 (ddd, J = 7.9, 2.3, 1.0 Hz, 1H), 7.29 (ddd, J = 9.6, 6.2, 3.5 Hz, 1H), 6.99 (td, J = 9.7, 2.3 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 1.66 (dd, J = 14.5, 7.2 Hz, 2H), 1.40 (d, J = 7.6 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.95 (dd, J = 9.3, 3.4 Hz), −113.72 to −114.31 (m), −129.79 (dd, J = 9.8, 2.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) 166.1, 162.7, 159.6 (dd, J = 243.8, 9.3 Hz), 160.2, 159.4, 146.2 (dd, J = 255.7, 14.4 Hz), 144.2 (dd, J = 14.7, 2.9 Hz), 140.7 (d, J = 3.1 Hz), 137.5, 133.0 (d, J = 9.4 Hz), 123.1 (d, J = 3.3 Hz), 122.8, 117.4 (d, J = 22.0 Hz); 115.0 (d, J = 13.6 Hz); 103.0 (dd, J = 25.7, 5.0 Hz); 102.1 (dd, J = 29.9, 20.3 Hz), 64.7, 30.6, 19.1, 13.7; HRMS (ESI) calcd for $C_{20}H_{17}F_3NO_3$ $[M + H]^+$ 376.1161, found 376.1170.

*Butyl (E)-3-(2-(5-methylbenzo[d]oxazol-2-yl)furan-3-yl)acrylate (**3op**):* yield 51% (33 mg); mp 70−72 °C; R_f (PE/EA= 30:1) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.47 (d, J = 16 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 7.18 (d J = 8.4 Hz, 1H), 6.76 (d, J = 3.6 Hz, 1H), 6.64 (d, J = 16 Hz, 1H), 4.20 (t, J = 6.4 Hz, 2H), 2.48 (s, 3H), 1.68 (m, 2H), 1.43(m, 2H), 0.97(t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 166.6, 154.6, 153.4, 148.4, 143.8, 141.8, 134.9, 129.6, 126.9, 120.1, 119.1, 115.8, 115.8, 110.0, 64.5, 30.7, 21.4, 19.1, 13.7; HRMS (ESI) calcd for $C_{19}H_{20}NO_4$ $(M + H^+)$ 326.1392, found 326.1387.

*Butyl (E)-3-(2-(5-methylbenzo[d]oxazol-2-yl)thiophene-3-yl)-acrylate (**3oq**):* yield 81% (59 mg); mp 65−67 °C; R_f (PE/EA= 10:1) = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 16 Hz, 1H), 7.50 (s, 1H), 7.42 (d, J = 5.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 5.6 Hz,1H), 6.40 (d, J = 16 Hz, 1H), 4.23 (t, J = 6.4 Hz, 2H), 2.47 (s, 3H), 1.73−1.69 (m, 2H), 1.50−1.45 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.0, 158.2, 148.4, 141.9, 138.3, 136.8, 134.7, 129.2, 129.0, 126.6, 126.6, 121.3, 120.0, 109.9, 64.5, 30.7, 21.5, 19.2, 13.8; HRMS (ESI) calcd for $C_{19}H_{20}NO_3S$ $(M + H^+)$ 342.1164, found 342.1158.

*Butyl (E)-3-(4-bromo-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3ma**):* yield 80% (65 mg); mp 83−86 °C; eluent = PE/EA = 100:1−50:1; R_f (PE/EA = 50:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 15.9 Hz, 1H), 8.37 (d, J = 1.9 Hz, 1H), 7.64 (dd, J = 8.5, 1.8 Hz, 1H), 7.60 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.47 (d, J =

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8.3 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 4.24 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.74−1.64 (m, 2H), 1.56−1.41 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 160.4, 148.7, 142.4, 142.1, 134.7, 134.0, 133.7, 132.8, 129.2, 128.0, 127.0, 123.8, 121.5, 120.5, 110.0, 64.5, 30.7, 21.4, 19.2, 13.7; HRMS (ESI) calcd for $C_{21}H_{21}BrNO_3$ $[M + H]^+$ 414.0705 (100.0), 416.0684 (97.3), 417.0718 (22.1), 415.0738 (16.2), found 414.0704 (100.0), 416.0687 (97.3), 417.0712 (22.1), 415.0732 (16.2).

*Butyl (E)-3-(4-methyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3mb**):* yield 63% (44 mg); R_f (PE/EA = 10:1) = 0.3; mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 15.9 Hz, 1H), 7.98 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 162.1, 148.7, 143.3, 142.2, 140.1, 134.4, 132.0, 131.9, 130.63, 127.7, 126.5, 126.4 120.3, 120.1, 109.9, 64.3, 30.8, 21.5, 21.2, 19.3, 13.8; HRMS (ESI) calcd for $C_{22}H_{24}NO_3$ $[M + H]^+$ 350.1756, found 350.1751.

*Butyl (E)-3-(4′-methoxy-3-(5-methylbenzo[d]oxazol-2-yl)[1,1′-biphenyl]-4-yl)acrylate (**3mc**):* yield 91% (80 mg); white solid (mp 91−93 °C); (eluent = EA/PE = 20%); R_f = 0.2 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 15.9 Hz, 1H), 8.38 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.7 Hz, 2H), 7.62 (s, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.50 (d, J = 15.9 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 3.87 (s, 3H), 2.51 (s, 3H), 1.77−1.69 (m, 2H), 1.50 (td, J = 14.8, 7.4 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.0, 159.9, 148.8, 143.0, 142.3, 142.2, 134.5, 132.9, 131.7, 128.9, 128.2, 128.1, 127.0, 126.6, 120.5, 120.4, 114.4, 109.9, 64.4, 55.3, 30.8, 21.5, 19.2, 13.8; HRMS (ESI) calcd for $C_{28}H_{28}NO_4$ $[M + H]^+$ 442.2018, found 442.2013.

*Butyl (E)-3-(4′-chloro-3-(5-methylbenzo[d]oxazol-2-yl)[1,1′-biphenyl]-4-yl)acrylate (**3md**):* yield 61% (54 mg); mp 88−90 °C; (eluent = EA/PE = 10%); R_f = 0.4 (PE/EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 15.9 Hz, 1H), 8.38 (d, J = 1.8 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.70 (dd, J = 8.2, 1.6 Hz, 1H), 7.62 (s, 1H),7.56 (d, J = 8.4 Hz, 3H), 7.49 (d, J = 8.3 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.3 Hz, 1H), 6.50 (d, J = 15.9 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 2.50 (s, 3H), 1.79−1.70 (m, 2H), 1.50 (dd, J = 15.0, 7.5 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.7, 148.8, 142.8, 142.2, 141.3, 137.7, 134.6, 134.4, 133.9, 129.2, 129.2, 128.5, 128.3, 127.1, 126.8, 121.1, 120.4, 110.0, 64.5, 30.8, 21.5, 19.3, 13.8; HRMS (ESI) calcd for $C_{27}H_{25}ClNO_3$ $[M + H]^+$ 446.1523, found 446.1517.

*Dibutyl 3,3′-(4-Methoxy-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3me**) and Butyl (E)-3-(4-Methoxy-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3me**).* Starting from **1me** (0.2 mmol), following the general procedure, bis-**3me** and mono-**3me** were isolated in 58% (57 mg) and 22% (16 mg) yields through preparative thick-layer chromatography: bis-**3me**, colorless oil, R_f (PE/EA = 10:2) = 0.15; mono-**3me** colorless solid, R_f (PE/EA = 10:2) = 0.6. For bis-**3me** (mp 65−67 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.9 Hz, 1H), 7.62 (s, 1H), 7.49 (d, J = 16.2 Hz, 1H), 7.47 (d, J = 15.8 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H), 6.47 (d, J = 16.1 Hz, 1H), 6.28 (d, J = 15.8 Hz, 1H), 4.12−4.05 (m, 2H), 4.03 (t, J = 6.5 Hz, 2H), 3.96 (s, 3H), 2.50 (s, 3H), 1.60−1.51 (m, 2H), 1.51−1.44 (m, 2H), 1.26 (dt, J = 10.6, 5.5 Hz, 2H), 1.25−1.15 (m, 2H), 0.82 (dt, J = 11.8, 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 166.4, 159.8, 159.7, 149.0, 141.3, 140.8, 137.5, 134.6, 130.6, 128.6, 128.1, 126.9, 124.6, 124.4, 120.5, 119.3, 113.4, 110.2, 64.3, 64.2, 56.0, 30.6, 30.5, 21.4, 19.1, 19.0, 13.6, 13.6; HRMS (ESI) calcd for $C_{29}H_{34}NO_6$ $[M + H]^+$ 492.2386, found 492.2381. For mono-**3me** (mp 53−55 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 16.1 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.60 (s, 1H), 7.47−7.40 (m, 2H), 7.18 (d, J = 8.3 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.77 (d, J = 16.1 Hz, 1H), 4.20 (t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 2.49 (s, 3H), 1.70−1.64 (m, 2H), 1.43 (dd, J = 15.1, 7.5 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.3, 159.2, 148.9, 142.1, 138.7, 134.4, 130.0, 129.1, 126.6, 124.3, 123.3, 122.8, 120.4, 113.5, 110.0, 64.2, 55.8, 30.8, 21.5, 19.2, 13.8; HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $[M + H]^+$ 366.1705, found 366.1700.

*Dibutyl 3,3′-(4-Fluoro-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3mf**) and Butyl (E)-3-(2-Fluoro-6-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3mf**).* Starting from **1mf** (0.2 mmol), following the general procedure, bis-**3mf** and mono-**3mf** were isolated in 20% (19 mg) and 50% (35 mg) yields, respectively. (eluent = EA/PE = 20%); bis-**3mf**, R_f (PE/EA = 10:1) = 0.2, mono-**3mf**, R_f (PE/EA = 10:1) = 0.5; For bis-**3mf** (mp 71−73 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.8, 5.0 Hz, 1H), 7.66 (s, 1H), 7.59 (d, J = 15.9 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 16.3 Hz, 1H), 7.40−7.33 (m, 1H), 7.26 (dd, J = 8.5, 1.2 Hz, 1H), 6.54 (dd, J = 16.3, 0.7 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 4.12 (m, 4H), 2.53 (s, 3H), 1.64−1.52 (m, 4H), 1.39−1.21 (m, 4H), 0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.0, 161.7 (d, J = 258.5 Hz), 158.7, 149.1, 141.3, 140.3, 135.0, 134.9, 132.5 (d, J = 3.4 Hz), 130.4, 128.9 (d, J = 9.8 Hz), 127.2, 126.0 (d, J = 13.3 Hz), 124.1 (d, J = 13.0 Hz),121.6, 120.6, 118.9 (d, J = 23.8 Hz), 110.2, 64.5, 30.5, 30.5, 21.4, 19.1, 19.0, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.38 (dd, J = 10.3, 5.0 Hz); HRMS (ESI) calcd for $C_{28}H_{31}FNO_5$ $[M + H]^+$ 480.2186, found 480.2181; For mono-**3mf** (mp 53−56 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 16.3 Hz, 1H), 8.03−7.90 (m, 1H), 7.61 (s, 1H), 7.44 (ddd, J = 10.5, 6.9, 4.0 Hz, 2H), 7.27 (dd, J = 12.1, 7.2 Hz, 1H), 7.20 (d, J = 8.3 Hz, 1H), 6.67 (dd, J = 16.3, 1.8 Hz, 1H), 4.24 (t, J = 6.5 Hz, 2H), 2.48 (s, 3H), 1.76−1.62 (m, 2H), 1.47 (dq, J = 14.6, 7.4 Hz, 2H), 0.95 (d, J = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 161.6 (d, J = 253.5 Hz), 161.00 (d, J = 4.0 Hz), 160.4, 148.7, 142.1, 136.5 (d, J = 1.4 Hz), 134.6, 130.2 (d, J = 9.8 Hz), 128.8 (d, J = 4.0 Hz), 126.9, 126.1 (d, J = 3.4 Hz), 125.4 (d, J = 14.1 Hz), 122.8 (d, J = 13.4 Hz), 120.5, 118.6 (d, J = 23.8 Hz), 110.0, 64.5, 30.7, 21.5, 19.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.67 to −109.79 (m); HRMS (ESI) calcd for $C_{21}H_{21}FNO_3$ $[M + H]^+$ 354.1505, found 354.1493.

*Dibutyl 3,3′-(2-(5-Methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3pa**) and Butyl (E)-3-(2-(5-Methylbenzo[d]-oxazol-2-yl)phenyl)acrylate (Mono-**3pa**).* Starting from **1pa** (0.2 mmol), following the general procedure, bis-**3pa** and mono-**3pa** were isolated in 63% (58 mg) and 21% (14 mg) yields, respectively (eluent = EA/PE = 3−10%); bis-**3pb** R_f = 0.2, mono-**3pb** R_f = 0.5 (PE/EA = 40:1). For bis-**3pa** (mp 60−63 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 15.8 Hz, 2H), 7.65 (s, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.24 (dd, J = 8.4, 1.2 Hz, 1H), 6.41 (d, J = 15.8 Hz, 2H), 4.13 (t, J = 6.5 Hz, 4H), 2.52 (s, 3H), 1.65−1.54 (m, 4H), 1.39−1.27 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 159.7, 149.2, 141.5, 141.4, 136.2, 134.7, 130.9, 128.1, 128.0, 127.0, 121.8, 120.5, 110.2, 64.5, 30.6, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{28}H_{32}NO_5$ $[M + H]^+$ 462.2280, found 462.2275. For mono-**3pa** (mp 43−45 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 15.9 Hz, 1H), 8.20−8.18 (m, 1H), 7.75−7.63(m, 1H), 7.61 (s, 1H), 7.54−7.51 (m, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.19 (dd, J = 8.3, 0.8 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 4.25 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.73−1.67 (m, 2H), 1.49 (m, J = 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.9, 148.8, 143.5, 142.3, 134.9, 134.4, 131.0, 130.1, 129.7, 127.8, 126.6, 126.6, 121.1, 120.4, 109.9, 64.4, 30.8, 21.5, 19.2, 13.8; HRMS (ESI) calcd for $C_{21}H_{22}NO_5$ $[M + H]^+$ 336.1600, found 336.1594.

*Dibutyl 3,3′-(5-methyl-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3pb**) and Butyl (E)-3-(5-Methyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3pb**).* Following the general procedure, starting from **1pb** (0.2 mmol), bis-**3pb** and mono-**3pb** were isolated in 50% (47 mg) and 16% (11 mg) yields, respectively (eluent = EA/PE = 3−10%); bis-**3pb** R_f = 0.2 (PE/EA = 10:1); mono-**3pb** R_f = 0.2 (PE/EA = 40:1). For bis-**3pb** (mp 78−80 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 15.8 Hz, 2H), 7.63 (s, 1H), 7.57 (s, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 6.39 (d, J = 15.8 Hz, 2H), 4.12 (t, J = 6.4 Hz, 4H), 2.50 (s, 3H), 2.47 (s, 3H), 1.57 (m, J = 6.7 Hz, 4H), 1.32 (m, J = 7.4 Hz, 4H), 0.87 (t, J = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 166.3, 160.0, 149.2, 141.7 141.5, 141.1, 136.1 134.6, 128.8, 126.8, 125.5 121.5, 120.4, 110.1, 64.4, 30.6, 21.5, 21.4, 19.1, 13.6; HRMS (ESI) calcd for

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$C_{29}H_{34}NO_5$ $[M + H]^+$ 476.2437, found 476.2431. For mono-**3*p*b** (mp 60−62 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 15.9 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.61−7.57 (m, 1H), 7.54 (s, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.3, 1.4 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 4.25 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 2.44 (s, 3H), 1.75−1.68 (m, 2H), 1.50 (dd, J = 15.1, 7.5 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.1, 148.7, 143.6, 142.3, 141.4, 134.7, 134.3, 130.6, 130.1, 128.4, 126.4, 123.9, 120.8, 120.3, 109.8, 64.4, 30.8, 21.5, 19.2, 13.8; HRMS (ESI) calcd for $C_{22}H_{24}NO_3$ $[M + H]^+$ 350.1756, found 350.1751.

*Dibutyl 3,3′-(5-tert-Butyl-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (bis-**3pc**) and Butyl (E)-3-(5-tert-Butyl-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3pc**).* Starting from **1*p*c** (0.2 mmol), following the general procedure, bis-**3*p*c** and mono-**3*p*c** were isolated in 66% (68 mg) and 25% (19 mg) yields, respectively (eluent = EA/PE = 5−10%); bis-**3*p*c** R_f = 0.3 (PE/EA = 10:1); mono-**3*p*c** R_f = 0.2 (PE/EA = 40:1). For bis-**3*p*c** (mp 122−123 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.8 Hz, 2H), 7.77 (s, 2H), 7.63 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.22 (dd, J = 8.3, 1.1 Hz, 1H), 6.40 (d, J = 15.9 Hz, 2H), 4.13 (t, J = 6.5 Hz, 4H), 2.51 (s, 3H), 1.66−1.51 (m, 4H), 1.41 (s, 9H), 1.34 (dd, J = 7.5 Hz, 4H), 0.88 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 160.0, 154.2, 149.2, 142.2, 141.6, 135.9, 134.6, 126.8, 125.4, 121.4, 120.5, 110.1, 64.4, 35.1, 31.0, 30.6, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{32}H_{40}NO_5$ $[M + H]^+$ 518.2906, found 518.2877. For mono-**3*p*c** (mp 81−83 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 15.9 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 1.8 Hz, 1H), 7.60 (s, 1H), 7.55 (dd, J = 8.3, 1.9 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.17 (dd, J = 8.3, 1.0 Hz, 1H), 6.47 (d, J = 15.9 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.77−1.68 (m, 2H), 1.50 (d, J = 7.6 Hz, 2H), 1.39 (s, 9H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.1, 154.5, 148.7, 144.2, 142.3, 134.5, 134.3, 130.0, 127.1, 126.4, 124.7, 123.8, 120.7, 120.3, 109.9, 64.4, 35.0, 31.0, 30.8, 21.5, 19.3, 13.8; HRMS (ESI) calcd for $C_{25}H_{30}NO_3$ $[M + H]^+$ 392.2226, found 392.2220.

*Dibutyl 3,3′-(5-Methoxy-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3pd**) and Butyl (E)-3-(5-Methoxy-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3pd**).* Starting from substrate **1*p*d**, following the general procedure, bis-**3*p*d** and mono-**3*p*d** were isolated in 57% (55 mg) and 21% (14 mg) yields by flash chromatography (eluent = PE/EA = 20:1); bis-**3*p*d** colorless oil, R_f (PE/EA = 6:1) = 0.15; mono-**3*p*d**, colorless oil, R_f (PE/EA = 6:1) = 0.45. For bis-**3*p*d** (mp 73−75 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 16 Hz, 2H), 7.618(s, 1H, Ph), 7.64 (s, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.25 (s, 2H), 7.21 (dd, J = 1.2 and 8.0 Hz, 1H), 6.39 (d, J = 16 Hz, 2H), 4.13 (t, J = 7.2 Hz, 4H), 3.92 (s, 3H), 2.50 (s, 3H, $-CH_3$), 1.62−1.58 (m, J = 7.2 Hz, 4H), 1.37−1.24 (m, J = 7.2 Hz, 4H), 0.87 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 161.0, 160.0, 149.2, 141.7, 141.6, 137.8, 134.5, 126.7, 121.8, 120.8, 120.4, 113.5, 110.1, 64.5, 55.6, 30.6, 21.4, 19.1, 13.6; HRMS (ESI) calcd for $C_{29}H_{34}NO_6$ $(M + H^+)$ 492.2386, found 492.2391. For mono-**3*p*d** (mp 56−58 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 16 Hz, 2H), 8.13 (d, J = 8.8 Hz, 1H), 7.56 (s, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.03 (dd, J = 2.4, 8.8 Hz), 6.44 (d, J = 16 Hz, 1H), 4.25 (t, J = 6.4 Hz, 2H), 3.89 (s, 3H), 2.47 (s, 3H), 1.73−1.70 (m, 2H), 1.52−1.47 (m, 2H, Bu), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.7, 162.0, 161.5, 148.6, 143.6, 142.4, 136.6, 134.2, 131.8, 126.1, 121.1, 120.1, 119.3, 115.7, 112.5,109.7, 64.5, 55.5, 30.7, 21.4, 19.2, 13.8; HRMS (ESI) calcd for $C_{22}H_{24}NO_4$ $(M + H^+)$ 366.1705, found 366.1692.

*Butyl (E)-3-(2-(5-Methylbenzo[d]oxazol-2-yl)-5-(trifluoromethoxy)phenyl)acrylate (**3pe**):* yield 62% (51 mg); mp 78−79 °C (eluent = EA/PE = 10%); R_f (PE/EA = 10:1) = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 15.9 Hz, 1H), 8.24 (d, J = 8.7 Hz, 1H), 7.60 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.36 (dd, J = 8.7, 1.2 Hz, 1H), 7.20 (dd, J = 8.3, 1.2 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.73 (m, J = 6.6 Hz, 2H), 1.54−1.45 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 160.7, 150.8, 150.8, 148.7, 142.1, 137.1, 134.7, 131.9, 126.9, 124.9, 122.5, 121.5, 120.3 (q, J = 258.9 Hz), 120.5, 119.6, 110.0, 64.6, 30.7, 21.4, 19.2, 13.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −57.58; HRMS (ESI) calcd for $C_{22}H_{21}F_3NO_4$ $[M + H]^+$ 420.1423, found 420.1417.

*Butyl (E)-3-(5-Fluoro-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (Mono-**3pf**) and Dibutyl 3,3′-(5-Fluoro-2-(5-methylbenzo-[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3pf**).* Starting from **1*p*f** (0.2 mmol), following the general procedure, bis-**3*p*f** and mono-**3*p*f** were isolated in 50% (47 mg) and 20% (13 mg) yield through thick-layer chromatography, respectively (eluent = EA/PE = 10%); bis-**3*p*f**, R_f = 0.2, yellow solid; mono-**3*p*f** R_f = 0.4, light yellow solid (PE/EA = 10:1). For bis-**3*p*f** (mp 45−48 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 15.8 Hz, 2H), 7.63 (s, 1H), 7.48 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 8.5 Hz, 1H), 6.40 (d, J = 15.8 Hz, 2H), 4.13 (t, J = 6.5 Hz, 4H), 2.51 (s, 3H), 1.58 (d, J = 7.9 Hz, 4H), 1.32 (d, J = 7.5 Hz, 4H), 0.88 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 164.8, 162.3, 159.0, 149.2, 141.4, 140.4 (d, J = 2.2 Hz), 138.9 (d, J = 8.6 Hz), 127.1, 122.9, 120.5, 114.8 (d, J = 23.1 Hz), 110.2, 64.6, 30.6, 21.4, 19.1, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.94 (t, J = 8.9 Hz); HRMS (ESI) calcd for $C_{28}H_{31}FNO_5$ $[M + H]^+$ 480.2186, found 480.2181. For mono-**3*p*f** (mp 59−61 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 15.9 Hz, 1H), 8.20 (dd, J = 8.7, 5.8 Hz, 1H), 7.60 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.42 (dd, J = 9.7, 2.2 Hz, 1H), 7.25−7.21 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 2.49 (s, 3H), 1.76−1.66 (m, 2H), 1.50 (dq, J = 14.5, 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.00, −108.01, −108.02, −108.03, −108.04, −108.06; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.9 (d, J = 252.9 Hz), 161.1, 148.7, 142.3 (d, J = 1.8 Hz), 142.2, 137.5 (d, J = 8.3 Hz), 134.5, 132.5, 132.4, 126.6, 122.9, 122.2, 120.4, 117.0 (d, J = 22.0 Hz), 114.5 (d, J = 22.9 Hz), 109.9, 64.6, 30.7, 21.5, 19.2, 13.7; HRMS (ESI) calcd for $C_{21}H_{21}FNO_3$ $[M + H]^+$ 354.1505, found 354.1500.

*Butyl (E)-3-(5-Chloro-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)-acrylate (**3pg**):* yield 75% (55 mg); R_f (PE/EA = 50:1) = 0.35); mp 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 15.9 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 15.5 Hz, 1H), 7.54−7.42 (m, 2H), 7.21 (d, J = 8.3 Hz, 1H), 6.47 (d, J = 15.9 Hz, 1H), 4.27 (t, J = 6.5 Hz, 2H), 2.51 (s, 3H), 1.73 (dd, J = 14.8, 6.8 Hz, 3H), 1.51 (dq, J = 14.6, 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.0, 148.7, 142.2, 137.2, 136.5, 134.6, 131.3, 129.7, 127.8, 126.8, 124.8, 122.2, 120.4, 109.9, 64.6, 30.7, 21.4, 19.2, 13.7; HRMS (ESI) calcd for $C_{21}H_{21}ClNO_3$ $(M + H^+)$ 370.1210 (100.0), 372.1180 (32.0), 371.1244 (22.7), found 370.1214 (100.0), 372.1177 (32.0), 371.1238 (22.7).

*Dibutyl 3′-(5-Bromo-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3ph**) and Butyl (E)-3-(5-Bromo-2-(5-methylbenzo[d]oxazol-2-yl)phenyl)acrylate (Mono-**3ph**).* Starting from substrate **1ph**, following the general procedure, bis-**3ph** and mono-**3ph** were isolated in 80% (86 mg) and 15% (12 mg) yields through preparative thick-layer chromatography; bis-**3ph** white solid; mp 68−70 °C;, R_f (PE/EA = 20:1) = 0.15; mono-**3ph** colorless oil, R_f (PE/EA = 20:1) = 0.3. For bis-**3ph**: ^{1}H NMR (100 MHz, $CDCl_3$) 7.88 (s, 2H), 7.67 (d, J = 16 Hz, 1H), 7.63 (s, 1H), 7.48 (dd, J = 0.8 and 8.4 Hz, 1H), 6.40 (d, J = 16 Hz, 1H), 4.13 (t, J = 6.4 Hz, 4H), 2.51 (s, 3H), 1.61−1.57 (m, 4H), 1.35−1.30 (m, 4H), 0.88 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 158.9, 149.2, 141.4, 138.0, 134.9, 130.8, 127.2, 126.7, 125.5, 122.9, 120.6, 110.3, 110.0, 64.6, 30.6, 21.5, 19.1, 13.6; HRMS (ESI) calcd for $C_{28}H_{31}BrNO_5$ $(M + H^+)$ 540.1386 (100.0), 542.1365 (97.3), 541.1419 (30.3), 543.1399 (29.5), found 540.1380 (100.0), 542.1361 (97.3), 541.1414 (30.3), 543.1393 (29.5). For mono-**3ph**: mp 74−77 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 16 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H), 7.65 (dd, J = 2.0 and 8.4 Hz, 1H), 7.61 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 1.2 and 8.4 Hz,), 6.47 (d, J = 16 Hz, 1H), 4.26 (t, J = 6.4 Hz, 2H), 1.73 (m, J = 6.4 Hz, 2H), 1.50 (t, J = 6.4 Hz, 2H), 1.00 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 161.1,148.7, 142.1, 136.6, 134.6, 132.6, 131.4, 130.8, 126.9, 125.6, 125.3, 122.2, 120.5, 109.9, 64.6, 30.7, 21.4, 19.2, 13.7; HRMS (ESI) calcd for $C_{21}H_{21}BrNO_3$ $(M + H^+)$ 414.0705 (100), 416.0684 (97),

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417.0718 (22), 415.0738 (16), found 414.0699 (100), 416.0680 (97), 417.0712 (22), 415.0733 (16).

*Dibutyl 3,3′-(5-(Ethoxycarbonyl)-2-(5-methylbenzo[d]oxazol-2-yl)-1,3-phenylene)-(2E,2′E)-diacrylate (Bis-**3pi**) and Ethyl (E)-3-(3-Butoxy-3-oxoprop-1-en-1-yl)-4-(5-methylbenzo[d]oxazol-2-yl)-benzoate (Mono-**3pi**).* Starting from substrate **1pi** following the general procedure, bis-**3pi** and mono-**3pi** were isolated in 57% (60.5 mg) and 21% (16.9 mg) yields by flash chromatography (eluent = PE/EA = 40:1); bis-**3pi** white solid, R_f (PE/EA = 10:1) = 0.15; mono-**3pi** white solid, R_f (PE/EA = 10:1) = 0.45. For bis-**3pi** (mp 111−113 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s,2H, Ph), 7.73 (d, J = 16 Hz, 2H), 7.64 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 5.51 (d, J = 16 Hz,), 4.45 (q, J = 7.2 Hz, 2H), 4.13 (t, J = 6.8 Hz, 4H), 2.50 (s, 3H), 1.59 (t, J = 4.8 Hz, 4H), 1.44 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.0, 164.9, 158.9, 141.4, 140.7, 136.7, 135.0, 132.8, 131.2, 128.6, 127.3, 122.8, 120.6, 110.3, 64.6, 61.9, 30.6, 21.4, 19.1, 14.3, 13.6; HRMS (ESI) calcd for $C_{31}H_{36}NO_7$ $(M + H)^+$ 534.2492, found 534.2486. For mono-**3pi** (mp 89−90 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 16 Hz, 2H), 8.38 (d, J = 1.2 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.14, (dd, J = 1.6 and 8.4 Hz, 1H), 7.61 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.21(dd, J = 1.2 and 8.4 Hz, 1H), 6.56 (d, J = 16 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.26 (t, J = 6.4 Hz, 2H), 2.49 (s, 3H), 1.72 (m, 2H), 1.49 (m, 2H), 1.44 (t, J = 7.2 Hz), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.6, 165.4, 161.0, 148.8, 142.7, 142.2, 135.0, 134.7, 132.5, 130.2, 130.1, 129.8, 127.2, 122.1, 120.6, 64.5, 61.6, 30.7, 21.5, 19.2, 14.3, 13.7; HRMS (ESI) calcd for $C_{24}H_{26}NO_5$ $(M + H^+)$ 408.1811, found 408.1805.

*Transformation of **3oe** to Hydrolysis Product **4**.* Into a 25 mL round flask was layered **3oe** (73 mg, 0.2 mmol), $LiOH{\cdot}H_2O$ (9 mg, 0.22 mmol), and THF/H_2O (2/1 mL), and the mixture was stirred at room temperature for 12 h and monitored by TLC. After competition, the solvents were diluted with 6 mL of deionized water, the solution was acidified by dropwise addition of 1 N HCl, adjusted to pH ≈ 5, and yellow oil precipitated. The water layer was carefully removed, and the oil was washed with deionized water (3 × 2 mL) and dried under vacuum to afford yellow oil **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 15.9 Hz, 1H), 7.66 (s, 1H), 7.52 (dd, J = 17.6, 8.3 Hz, 2H), 7.40−7.34 (m, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 10.5 Hz, 1H), 6.48−6.33 (m, 1H), 3.92−3.74 (m, 3H), 2.52 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 159.4, 159.1, 149.2, 143.5, 141.5, 136.4, 134.3, 132.0, 126.5, 120.8, 120.3, 119.0, 117.8, 112.6, 110.2, 56.1, 21.5; HRMS (ESI) calcd for $C_{18}H_{16}NO_4$ $[M + H]^+$ 310.1079, found 310.1074.

*Transformations of **3oe** and **3oae** to Hydrogenated Products **5** and **6**.* Into a 25 mL Schlenk tube were layered the corresponding olefinated product **3**, Pd/C (10% w/w), and dissolved in THF, and the reaction tube was evacuated and refilled with hydrogen gas with a hydrogen bag. The mixture was stirred under room temperature for 16 h and monitored by TLC. After completion, the reaction solution was filtered by a Celite pad, and the filtrate was concentrated and dried under vacuum. The purity was good enough for NMR, which afforded a colorless oil **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.41 (t, J = 8.1 Hz, 1H), 7.19 (dd, J = 8.3, 0.9 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.99 (t, J = 6.7 Hz, 2H), 3.78 (s, 3H), 2.96−2.84 (m, 2H), 2.62−2.54 (m, 2H), 2.51 (s, 3H), 1.55−1.45 (m, 2H), 1.31−1.25 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 160.6, 158.9, 149.1, 142.9, 141.8, 133.9, 131.8, 126.0, 121.5, 120.1, 117.4, 110.1, 109.1, 64.3, 55.9, 35.6, 30.5, 28.897, 21.4, 19.0, 13.6; HRMS (ESI) calcd for $C_{22}H_{26}NO_4$ $[M + H]^+$ 368.1862, found 368.1856. Hydrogenated product **6** was synthesized in the similar procedure on 1 mmol scale, which afforded white solid: mp 70−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.21 (tq, J = 16.1, 8.1 Hz, 6H), 7.06 (d, J = 6.9 Hz, 2H), 2.97−2.80 (m, 4H), 2.56 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 148.9, 142.3, 141.7, 141.6, 138.7, 134.2, 130.3, 128.3, 128.2, 128.1, 127.8, 127.1, 126.2, 125.8, 120.1, 110.0; HRMS (ESI) calcd for $C_{23}H_{22}NO$ $[M + H]^+$ 328.1701, found 328.1696.

Mechanistic Experiments. *H−D Exchange Experiment.* The reaction between **1oa** (0.2 mmol) and CD_3COOD (10 equiv) was carried out in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol %), NaOAc (1.0 equiv), and $Cu(OAc)_2$ (2.0 equiv) with 1,2-dichloroethane (2 mL) as a solvent at 90 °C for 3 h. After standard workup and purification, a mixture of **1oa** and **D1-1oa** was obtained. ^{1}H NMR analysis of the mixture showed 34% D was incorporated into the *ortho* positions of the 2-aryl ring (see the SI for details).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01836.

^{1}H, ^{19}F, and ^{13}C NMR spectra for all new compounds; intermolecular competition and mechanism study experiments (PDF)

Single-crystal X-ray diffraction data for compounds mono-**3mf**, mono-**3pc**, bis-**3pf**, and **3oae** (CIF)

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Notes

The authors declare no competing financial interest.

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