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Note

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Palladium-Catalyzed Alkenylation via sp^2 C–H Bond Activation Using Phenolic Hydroxyl as the Directing Group

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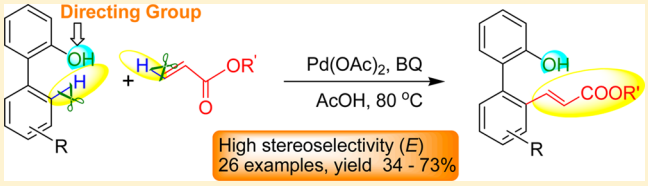
Supporting Information

ABSTRACT: This note describes the efficient and highly regioselective synthesis of 2-(2′-alkenylphenyl)phenol derivatives via palladium-catalyzed 2′-alkenylation of 2-arylphenols directed by the phenolic hydroxyl group using benzoquinone as the oxidant in an atmosphere of air. This reaction can tolerate a series of functional groups and provides the alkenylation products regio- and stereoselectively in moderate to good yields.



Transition-metal-catalyzed C–H bond activation/functionalization has constituted an expedient carbon–carbon and carbon–heteroatom bond formation protocol with features of step economy and green chemistry primarily,[1] and therefore, laborious arene prefunctionalization like that required for traditional palladium(0)-catalyzed cross-coupling reactions such as the Mizoroki–Heck reaction would be or is now no longer required in many cases. In general, the selectivity of C–H functionalization is controlled by the coordinating functional groups. Using substrates with weakly coordinating directing groups is a powerful approach for developing synthetically versatile reactions because of the higher reactivity of the cyclometalated intermediates in the functionalization step.[2] Therefore, the use of some weakly coordinating groups (e.g., carboxyl,[3] carbonyl,[4] and cyano[5]) as directing groups in transition-metal-catalyzed C–H functionalizations has aroused much attention in recent years. Hydroxyl is a very important functional group in organic chemistry, and also, it exhibits weak coordination to transition metals.[2] This characteristic enables it to play an important role in several transition-metal-catalyzed transformations, for example, tertiary alcoholic or phenolic hydroxyl-directed Pd- or Ru-catalyzed *ortho*-C–H cleavage and subsequent CO insertion into the Pd–C bond;[6] Pd-, Cu-, or Ru-catalyzed tertiary alcoholic or phenolic hydroxyl-directed C–O cyclization;[7] Ir-catalyzed *ortho* alkylation of phenol with norbornene;[8] Rh-catalyzed *ortho* arylation of phenols;[9] Pd-catalyzed tertiary alcoholic or silanolic hydroxyl-directed alkenylation;[10] and Rh-catalyzed dehydrogenative Heck reaction.[11] However, to the best of our knowledge, the C–H alkenylation reaction using the phenolic hydroxyl group as a directing group to form $C(sp^2)$–$C(sp^2)$ bonds has never been approached. In the past decade, metal-catalyzed direct C–H olefination [the Fujiwara–Moritani reaction, also called the dehydrogenative Heck reaction (DHR)] has emerged as a powerful method for the introduction of alkenyl motifs into aromatic compounds because of its chemical versatility and its environmental advantages.[12] In continuation of our longstanding interest in directed C–H functionalization, herein we describe a Pd-catalyzed, phenolic hydroxyl-directed alkenylation of the $C(sp^2)$–H bond at the 2′-position of 2-arylphenols to form 2-(2′-alkenylphenyl)phenol derivatives selectively.

We initiated our studies with the direct C–H alkenylation of 2-phenylphenol (**1a**) (1 mmol) with methyl acrylate (**2a**) (2 mmol) using $Pd(OAc)_2$ (10 mol %) as the catalyst and benzoquinone (BQ) (1 equiv) as the oxidant. The results are presented in Table 1. The reaction could take place in an atmosphere of air. In AcOH at 80 °C, the reaction resulted in the 2′-alkenylation product **3aa** in 72% yield after 12 h (entry 1). It was found that AcOH was a suitable solvent for this coupling. In PivOH, however, a lower yield of 58% was obtained (entry 2). Disappointingly, when other commonly used solvents such as DCE, dioxane, DMSO, DMF, toluene, and CH_3CN were employed, either no or a little amount of product formed (entries 3–8). Using mixed solvents also reduced the yield (entries 9 and 10). In the absence of oxidant, the reaction gave the product in a poor yield of 32% (entry 18). Among the oxidants we tested, BQ was shown to be the most effective one, while other oxidants such as $Na_2S_2O_8$, O_2, $PhI(OAc)_2$ (entries 12–14) as well as the transition metal salts Ag_2CO_3, Ag_2O, and $Cu(OAc)_2$ (entries 15–17) proved to be less effective. In the presence of 1 equiv of BQ, the reaction gave a yield of 72% (entry 1), and increasing the amount of oxidant to 2 equiv did not result in an obvious rise in the yield (entry 11). The appropriate reaction temperature was 80 °C. Raising the temperature to 100 °C did not increase the yield evidently, but reducing it to 60 °C led to a significant decrease in the reaction activity (entry 1). Additionally, we also explored other Pd(II) catalysts such as

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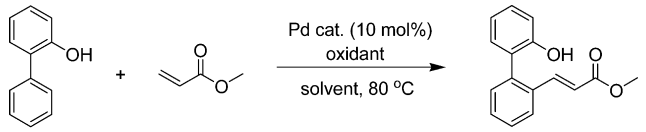
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	catalyst	oxidant (equiv)	solvent	yield (%)[b]
1	$Pd(OAc)_2$	BQ (1)	AcOH	72 (31, 73)[c]
2	$Pd(OAc)_2$	BQ (1)	PivOH	58
3	$Pd(OAc)_2$	BQ (2)	DCE	25
4	$Pd(OAc)_2$	BQ (2)	dioxane	0
5	$Pd(OAc)_2$	BQ (2)	DMSO	30
6	$Pd(OAc)_2$	BQ (2)	DMF	trace
7	$Pd(OAc)_2$	BQ (2)	toluene	0
8	$Pd(OAc)_2$	BQ (2)	CH_3CN	21
9	$Pd(OAc)_2$	BQ (1)	DCE/AcOH (1:1)	46
10	$Pd(OAc)_2$	BQ (1)	CH_3CN/AcOH (1:1)	33
11	$Pd(OAc)_2$	BQ (2)	AcOH	75
12	$Pd(OAc)_2$	$Na_2S_2O_8$ (2)	AcOH	33
13	$Pd(OAc)_2$	O_2 (1 atm)	AcOH	45
14	$Pd(OAc)_2$	$PhI(OAc)_2$ (2)	AcOH	<10
15	$Pd(OAc)_2$	Ag_2CO_3 (2)	AcOH	35
16	$Pd(OAc)_2$	Ag_2O (2)	AcOH	24
17	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	AcOH	<10
18	$Pd(OAc)_2$	none	AcOH	32
19	$Pd(OAc)_2$	BQ (1)	AcOH	76[d]
20	$Pd(OAc)_2$	BQ (1)	AcOH	57[e]
21	none	BQ (1)	AcOH	0
22	$PdCl_2$	BQ (1)	AcOH	trace
23	$PdCl_2(CH_3CN)_2$	BQ (1)	AcOH	trace

[a]Unless otherwise specified, the reaction was carried out in a sealed tube in the presence of **1a** (1 mmol), **2a** (2 mmol), solvent (2 mL), catalyst (10 mol %), and oxidant at 80 °C under an atmosphere of air for 12 h. [b]Isolated yields. [c]Values in the parentheses are yields at 60 and 100 °C, respectively. [d]**2a** (4 mmol) was used. [e]$Pd(OAc)_2$ (5 mol %) was used.

$PdCl_2$ and $PdCl_2(CH_3CN)_2$ and found them to be substantially less effective in the reaction under the certain reaction conditions (entries 22 and 23).

With the optimal conditions in hand, we next assessed the scope of the developed methodology. We achieved the Pd-catalyzed 2′-alkenylation of differently substituted 2-phenylphenols with terminal olefinic compounds selectively (Table 2). For most of the reactants we used, the reaction gave the corresponding coupling products in moderate to good yields, and all of the products obtained were proved to be *E* isomers by ^{1}H NMR spectroscopy. For the 2′-alkenylation reactions of **1a** with coupling partners such as ethyl acrylate, butyl acrylate, and *tert*-butyl acrylate, yields of 73%, 70%, and 66%, respectively, were obtained, indicating that larger alkyl groups might decrease the yield slightly (**3ab**−**3ad**). Unfortunately, when an electron-rich olefin such as styrene or 1-hexene was used, almost no desired product (**3ae** or **3af**, respectively) was detected under our present reaction conditions.

After several alkenes were screened, a series of 2-phenylphenol derivatives were employed with this protocol. The C−H bond alkenylation at the 2′-position proceeded smoothly with various substituted 2-arylphenols, and no bisolefinated product was found under the present reaction conditions. The substrates with a methyl group at the *meta* or *para* position of the phenyl group reacted with the different acrylates to give yields of 61−71% (**3ba**−**3cc**), and 4′-ethyl- or phenyl-substituted substrates showed similar reactivity (**3fa**, **3fb**, **3ja**). From the reactants with electron-donating methoxy or acyloxy groups at the *meta* or *para* position, the 2′-alkenylation products were also obtained (**3da**−**3ec** and **3ka**). It is worth mentioning that when a substituent group was at the *meta* position of the phenyl, the alkenylation took place selectively at the less hindered C−H bond. In the presence of electron-withdrawing Cl and F groups, the corresponding coupling products were also obtained, although the yields were somewhat decreased (**3ga**−**3ia**). However, with the chloro substituent at the *ortho* position of the phenyl, the reaction almost could not take place (**3la**). In addition, the presence of a strongly electron-withdrawing nitro group also led to the failure of the reaction (**3ma**).

On the basis of the experiment results and the related transition-metal-catalyzed C−H activation reactions, a proposed mechanism for the formation of product **3** is given in Scheme 1. We envisioned that the reaction would start by hydroxyl-assisted insertion of Pd(II) into the C−H bond of **1** to form cyclopalladated intermediate **A**.[7a,b] Next, the coordination of olefin **2** to **A** would take place to generate intermediate **B**, which would be followed by insertion of the C═C bond into the C−Pd bond to form intermediate **C**. It is noteworthy that acetic acid as a ligand would play an important role in this process to stabilize the reaction intermediates. Subsequent reductive elimination may occur to release the final product **3** and liberate Pd(0). The Pd(0) species would then be oxidized by BQ and air to regenerate Pd(II), which would continue the catalytic cycle. The high regioselectivity could also provide strong evidence to support this mechanism.

In summary, we have developed a new Pd-based catalytic system that successfully effects C−H alkenylation of 2-arylphenols to produce 2-(2′-alkenylphenyl)phenols selectively in moderate to good yields. The reaction proceeds in an atmosphere of air under relatively mild reaction conditions, making the method highly applicable.

EXPERIMENTAL SECTION

General. All of the reactions were run in a sealed tube with a Teflon-lined cap under and atmosphere of air. Chemicals were commercially available and were used without purification. 2-Phenylphenols were purchased or prepared according to the literature procedures.[6d] ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using $(CH_3)_4Si$ (for ^{1}H, δ 0.00; for ^{13}C, δ 77.00) as an internal standard. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points are uncorrected. HRMS data were obtained by ESI on a TOF mass analyzer.

General Experimental Procedure and Characterizations. 2-Phenylphenol derivative (1 mmol), acrylate (2 mmol), $Pd(OAc)_2$ (0.1 mmol), BQ (1 mmol), and AcOH (2 mL) were added to a 25 mL sealed tube with a Teflon-lined cap. The mixture was heated at 80 °C (oil bath temperature) for 12 h and then cooled to room temperature. The volatiles were removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel using hexane/ethyl acetate as the eluent to give the corresponding product.

*(E)-Methyl 3-(2′-Hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3aa**).* Yield: 72% (183 mg). Light-yellow solid, mp 108−110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.59 (d, J = 16.0 Hz, 1H), 7.51−7.43 (m, 2H), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.33−7.28 (m, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.04−6.96 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 5.31 (s, 1H), 3.73 (s, 3H). ^{13}C NMR

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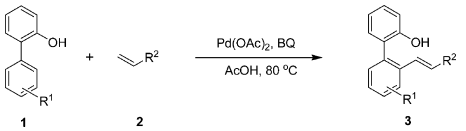
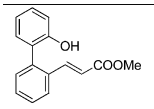
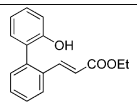
Table 2. Palladium-Catalyzed 2′-Alkenylation of 2-Arylphenols[a]





3aa 72%



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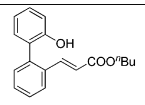

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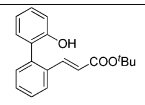

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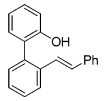

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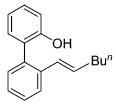

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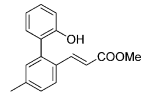

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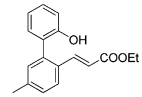

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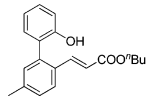

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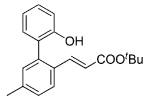

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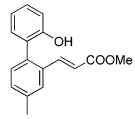

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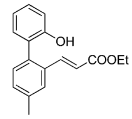

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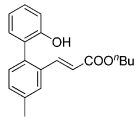

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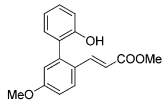

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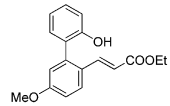

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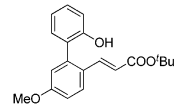

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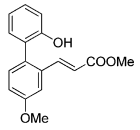

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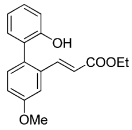

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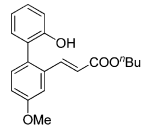

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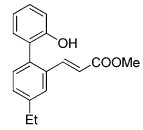

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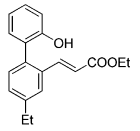

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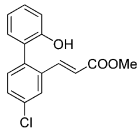

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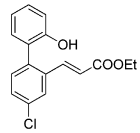

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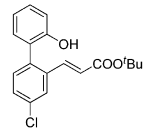

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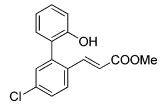

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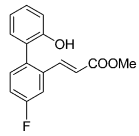

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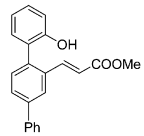

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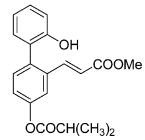

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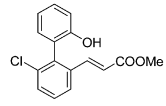

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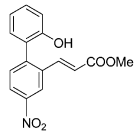

3ma trace

[a]Unless otherwise specified, the reaction was carried out with 2-phenylphenol derivative **1** (1 mmol), acrylate **2** (2 mmol), AcOH (2 mL), $Pd(OAc)_2$ (10 mol %), and BQ (1 mmol) under an atmosphere of air at 80 °C for 12 h. Isolated yields are listed. [b]At 100 °C for 20 h.

($CDCl_3$, 100 MHz): δ 167.4, 152.7, 143.0, 137.9, 133.7, 131.3, 131.1, 130.4, 129.8, 128.5, 126.9, 126.1, 120.7, 119.1, 115.9, 51.7. HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_3$ $[M + H]^+$ 255.1016, found 255.1016.

*(E)-Ethyl 3-(2′-Hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3ab**).* Yield: 73% (196 mg). Light-yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.52−7.46 (m, 2H), 7.38 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.34−7.30 (m, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.04−6.98 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 4.96 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 152.6, 142.5, 137.6, 133.8, 131.2,

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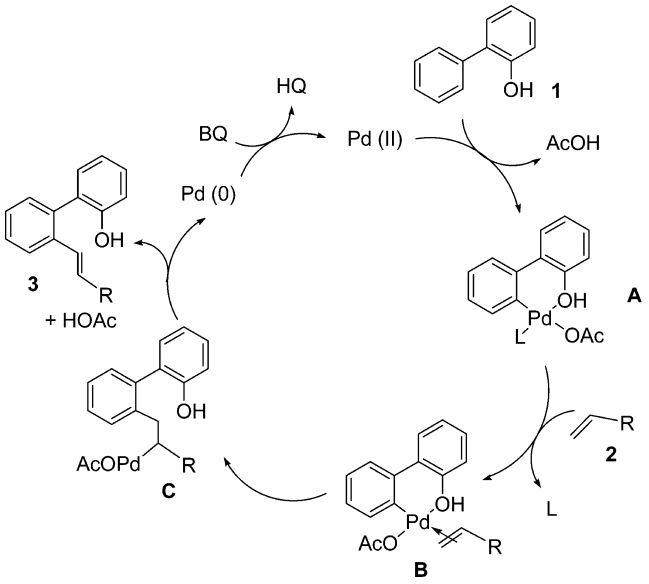
Scheme 1. Plausible Reaction Mechanism



131.0, 130.4, 129.8, 128.6, 126.9, 126.0, 120.7, 119.7, 115.9, 60.5, 14.2. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1172, found 269.1174.

(E)-Butyl 3-(2′-Hydroxy-[1,1′-biphenyl]-2-yl)acrylate (***3ac***). Yield: 70% (207 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.59 (d, J = 16.0 Hz, 1H), 7.51−7.43 (m, 2H), 7.38 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.33−7.29 (m, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.96 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 5.21 (s, 1H), 4.14 (t, J = 6.8 Hz, 2H), 1.66−1.59 (m, 2H), 1.42−1.33 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 152.7, 142.7, 137.8, 133.7, 131.2, 131.1, 130.4, 129.7, 128.5, 126.8, 126.0, 120.6, 119.5, 115.9, 64.4, 30.6, 19.1, 13.7. HRMS-ESI (m/z): calcd for $C_{19}H_{21}O_3$ $[M + H]^+$ 297.1485, found 297.1475.

(E)-tert-Butyl 3-(2′-Hydroxy-[1,1′-biphenyl]-2-yl)acrylate (***3ad***). Yield: 66% (195 mg). Light-yellow solid, mp 101−103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.49−7.41 (m, 2H), 7.36 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.31−7.27 (m, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.95 (m, 2H), 6.36 (d, J = 16.0 Hz, 1H), 5.28 (s, 1H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 152.7, 141.6, 137.8, 133.8, 131.2, 131.1, 130.2, 129.7, 128.5, 126.6, 126.1, 121.2, 120.6, 115.9, 80.5, 28.1. HRMS-ESI (m/z): calcd for $C_{19}H_{21}O_3$ $[M + H]^+$ 297.1485, found 297.1487.

(E)-Methyl 3-(2′-Hydroxy-5-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3ba***). Yield: 71% (190 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 16.0 Hz, 1H), 7.32−7.24 (m, 2H), 7.19 (s, 1H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.96 (m, 2H), 6.36 (d, J = 16.0 Hz, 1H), 5.44 (s, 1H), 3.72 (s, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.6, 152.8, 143.0, 140.9, 138.0, 131.9, 131.0, 130.8, 129.7, 129.4, 126.8, 126.2, 120.6, 118.0, 115.9, 51.7, 21.4. HRMS-ESI (m/z): calcd for $C_{17}H_{16}O_3Na$ $[M + Na]^+$ 291.0992, found 291.0975.

(E)-Ethyl 3-(2′-Hydroxy-5-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3bb***). Yield: 68% (192 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 15.6 Hz, 1H), 7.33−7.26 (m, 2H), 7.19 (s, 1H), 7.11 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.97 (m, 2H), 6.37 (d, J = 16.0 Hz, 1H), 5.07 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 152.7, 142.5, 140.9, 137.6, 131.8, 131.0, 129.7, 129.5, 126.9, 126.1, 120.6, 118.6, 115.8, 60.4, 21.4, 14.2. HRMS-ESI (m/z): calcd for $C_{18}H_{18}O_3Na$ $[M + Na]^+$ 305.1148, found 305.1125.

(E)-Butyl 3-(2′-Hydroxy-5-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3bc***). Yield: 71% (220 mg). Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 16.0 Hz, 1H), 7.32−7.25 (m, 2H), 7.20 (s, 1H), 7.11 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.97 (m, 2H), 6.37 (d, J = 16.0 Hz, 1H), 5.14 (s, 1H), 4.13 (t, J = 6.8 Hz, 2H), 2.43 (s, 3H), 1.66−1.59 (m, 2H), 1.40−1.34 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1, 152.7, 142.5, 140.9, 137.7, 131.8, 131.0, 130.9, 129.7, 129.5, 126.8, 126.0, 120.6, 118.5, 115.8, 64.3, 30.7, 21.4, 19.2, 13.7. HRMS-ESI (m/z): calcd for $C_{20}H_{22}O_3Na$ $[M + Na]^+$ 333.1461, found 333.1449.

(E)-tert-Butyl 3-(2′-Hydroxy-5-methyl-[1,1′-biphenyl]-2-yl)-acrylate (***3bd***). Yield: 62% (192 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 16.0 Hz, 1H), 7.30−7.23 (m, 2H), 7.18 (s, 1H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.01−6.95 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 5.29 (s, 1H), 2.42 (s, 3H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 152.7, 141.5, 140.6, 137.7, 131.8, 131.0, 129.6, 129.4, 126.6, 126.2, 120.5, 120.2, 115.8, 80.4, 28.1, 21.3. HRMS-ESI (m/z): calcd for $C_{20}H_{22}O_3Na$ $[M + Na]^+$ 333.1461, found 333.1437.

(E)-Methyl 3-(2′-Hydroxy-4-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3ca***). Yield: 65% (174 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (s, 1H), 7.57 (d, J = 16.0 Hz, 1H), 7.32−7.26 (m, 3H), 7.10 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.96 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.27 (s, 1H), 3.73 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 152.8, 143.1, 138.4, 135.0, 133.4, 131.4, 131.2, 129.6, 127.4, 126.0, 120.6, 118.8, 115.8, 51.7, 21.2. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1172, found 269.1168.

(E)-Ethyl 3-(2′-Hydroxy-4-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3cb***). Yield: 61% (172 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (s, 1H), 7.57 (d, J = 16.0 Hz, 1H), 7.31−7.26 (m, 3H), 7.10 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.01−6.95 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 5.39 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 152.9, 143.0, 138.3, 135.1, 133.5, 131.3, 131.2, 131.1, 129.6, 127.4, 126.0, 120.5, 119.2, 115.8, 60.5, 21.2, 14.2. HRMS-ESI (m/z): calcd for $C_{18}H_{18}O_3Na$ $[M + Na]^+$ 305.1148, found 305.1140.

(E)-Butyl 3-(2′-Hydroxy-4-methyl-[1,1′-biphenyl]-2-yl)acrylate (***3cc***). Yield: 67% (208 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (s, 1H), 7.56 (d, J = 16.0 Hz, 1H), 7.32−7.26 (m, 3H), 7.10 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.96 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 5.22 (s, 1H), 4.13 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 1.66−1.59 (m, 2H), 1.42−1.33 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 152.8, 142.8, 138.3, 134.9, 133.5, 131.3, 131.2, 131.1, 129.6, 127.3, 125.9, 120.6, 119.2, 115.8, 64.4, 30.7, 21.2, 19.2, 13.7. HRMS-ESI (m/z): calcd for $C_{20}H_{22}O_3Na$ $[M + Na]^+$ 333.1461, found 333.1442.

(E)-Methyl 3-(2′-Hydroxy-5-methoxy-[1,1′-biphenyl]-2-yl)acrylate (***3da***). Yield: 63% (179 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.34−7.29 (m, 1H), 7.13 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.04−6.97 (m, 3H), 6.87 (d, J = 2.8 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H), 5.28 (s, 1H), 3.86 (s, 3H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 161.2, 152.7, 142.5, 139.6, 130.9, 129.9, 128.5, 126.1, 126.0, 120.7, 116.7, 116.0, 115.8, 115.0, 55.5, 51.6. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1112.

(E)-Ethyl 3-(2′-Hydroxy-5-methoxy-[1,1′-biphenyl]-2-yl)acrylate (***3db***). Yield: 68% (203 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 16.0 Hz, 1H), 7.34−7.30 (m, 1H), 7.13 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.04−6.98 (m, 3H), 6.87 (d, J = 2.8 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 5.08 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 161.2, 152.6, 142.1, 139.4, 130.8, 129.9, 128.5, 126.3, 125.9, 120.7, 117.2, 115.9, 115.7, 115.1, 60.3, 55.5, 14.2. HRMS-ESI (m/z): calcd for $C_{18}H_{18}O_4Na$ $[M + Na]^+$ 321.1097, found 321.1098.

(E)-tert-Butyl 3-(2′-Hydroxy-5-methoxy-[1,1′-biphenyl]-2-yl)-acrylate (***3dd***). Yield: 45% (147 mg). Light-yellow solid, mp 119−121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 15.6 Hz, 1H), 7.32−7.27 (m, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.02−6.96 (m, 3H), 6.86 (d, J = 2.8 Hz, 1H), 6.24 (d, J = 15.6 Hz, 1H), 5.31 (s, 1H), 3.85 (s, 3H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 161.0, 152.7, 141.1, 139.5, 130.9, 129.8, 128.2, 126.3, 126.0, 120.6, 118.8, 115.9, 115.6, 115.0, 80.2, 55.5, 28.2. HRMS-ESI (m/z): calcd for $C_{20}H_{21}O_4$ $[M - H]^+$ 325.1445, found 325.1445.

(E)-Methyl 3-(2′-Hydroxy-4-methoxy-[1,1′-biphenyl]-2-yl)acrylate (***3ea***). Yield: 64% (182 mg). Light-yellow solid, mp 101−102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 16.0 Hz, 1H), 7.32−7.27 (m,

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3H), 7.11−7.07 (m, 2H), 7.05−6.99 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.85 (s, 1H), 3.91 (s, 3H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 159.6, 152.9, 142.8, 134.8, 132.4, 131.3, 130.1, 129.6, 125.7, 120.6, 119.4, 116.7, 115.8, 111.5, 55.5, 51.7. HRMS-ESI (m/z): calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1127.

*(E)-Ethyl 3-(2′-Hydroxy-4-methoxy-[1,1′-biphenyl]-2-yl)acrylate (**3eb**).* Yield: 56% (167 mg). Light-yellow solid, mp 61−63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 16.0 Hz, 1H), 7.32−7.28 (m, 3H), 7.11−7.04 (m, 2H), 7.02−6.98 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.97 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 159.7, 152.9, 142.5, 135.0, 132.4, 131.3, 129.9, 129.6, 125.6, 120.6, 119.8, 116.7, 115.7, 111.5, 60.5, 55.5, 14.2. HRMS-ESI (m/z): calcd for $C_{18}H_{18}O_4Na$ $[M + Na]^+$ 321.1097, found 321.1070.

*(E)-Butyl 3-(2′-Hydroxy-4-methoxy-[1,1′-biphenyl]-2-yl)acrylate (**3ec**).* Yield: 59% (192 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 16.0 Hz, 1H), 7.32−7.28 (m, 3H), 7.10−7.04 (m, 2H), 7.01−6.97 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.04 (s, 1H), 4.14 (t, J = 6.8 Hz, 2H), 3.90 (s, 3H), 1.66−1.59 (m, 2H), 1.42−1.33 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 159.6, 152.9, 142.5, 134.9, 132.4, 131.3, 130.0, 129.6, 125.6, 120.6, 119.7, 116.7, 115.7, 111.3, 64.4, 55.5, 30.6, 19.1, 13.7. HRMS-ESI (m/z): calcd for $C_{20}H_{21}O_4$ $[M - H]^+$ 325.1445, found 325.1443.

*(E)-Methyl 3-(4-Ethyl-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3fa**).* Yield: 63% (178 mg). Light-yellow solid, mp 103−105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, J = 1.2 Hz, 1H), 7.56 (d, J = 16.0 Hz, 1H), 7.36−7.28 (m, 3H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.98 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 4.99 (s, 1H), 3.74 (s, 3H), 2.75 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 152.8, 144.7, 142.9, 134.9, 133.6, 131.2, 131.1, 130.3, 129.7, 126.4, 125.9, 120.7, 119.0, 115.8, 51.7, 28.6, 15.4. HRMS-ESI (m/z): calcd for $C_{18}H_{18}O_3Na$ $[M + Na]^+$ 305.1148, found 305.1125.

*(E)-Ethyl 3-(4-Ethyl-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3fb**).* Yield: 57% (169 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, J = 1.2 Hz, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.35−7.28 (m, 3H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.02−6.97 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 5.14 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 152.8, 144.6, 142.8, 135.0, 133.6, 131.2, 131.1, 130.2, 129.6, 126.3, 126.0, 120.6, 119.3, 115.8, 60.4, 28.6, 15.4, 14.2. HRMS-ESI (m/z): calcd for $C_{19}H_{20}O_3K$ $[M + K]^+$ 335.1044, found 335.1023.

*(E)-Methyl 3-(4-Chloro-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3ga**).* Yield: 53% (153 mg). Light-yellow solid, mp 104−106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 16.0 Hz, 1H), 7.44 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 7.33−7.28 (m, 2H), 7.09 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.29 (s, 1H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1, 152.7, 141.9, 136.5, 135.3, 134.5, 132.6, 131.1, 130.2, 130.1, 126.6, 125.1, 120.9, 120.1, 116.1, 51.8. HRMS-ESI (m/z): calcd for $C_{16}H_{13}ClO_3K$ $[M + K]^+$ 327.0185, found 327.0181.

*(E)-Ethyl 3-(4-Chloro-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3gb**).* Yield: 47% (142 mg). Light-yellow solid, mp 95−97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.44 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.32−7.27 (m, 2H), 7.09 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.99 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.43 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 152.7, 141.8, 136.6, 135.3, 134.4, 132.6, 131.2, 130.1, 130.0, 126.5, 125.1, 120.8, 120.4, 116.1, 60.7, 14.2. HRMS-ESI (m/z): calcd for $C_{17}H_{16}ClO_3$ $[M + H]^+$ 303.0782, found 303.0755.

*(E)-tert-Butyl 3-(4-Chloro-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3gd**).* Yield: 42% (139 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, J = 2.4 Hz, 1H), 7.42 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.32−7.28 (m, 2H), 7.09 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.99 (m, 1H), 6.95 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 5.09 (s, 1H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 152.6, 140.3, 136.6, 136.2, 135.5, 134.5, 132.5, 131.1, 130.0, 126.5, 125.1, 122.4, 120.8, 116.0, 80.8, 28.1. HRMS-ESI (m/z): calcd for $C_{19}H_{19}ClO_3Na$ $[M + Na]^+$ 353.0915, found 353.0917.

*(E)-Methyl 3-(5-Chloro-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3ha**).* Yield: 43% (124 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.35−7.31 (m, 1H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.05−7.00 (m, 1H), 6.97 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 5.09 (s, 1H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 152.5, 141.9, 139.6, 136.1, 132.1, 131.2, 131.0, 130.2, 128.7, 128.0, 125.0, 121.0, 119.4, 116.1, 51.8. HRMS-ESI (m/z): calcd for $C_{16}H_{13}ClO_3K$ $[M + K]^+$ 327.0185, found 327.0183.

*(E)-Methyl 3-(4-Fluoro-2′-hydroxy-[1,1′-biphenyl]-2-yl)acrylate (**3ia**).* Yield: 45% (122 mg). Light-yellow solid, mp 117−119 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 15.6 Hz, 1H), 7.44 (dd, J_1 = 9.6 Hz, J_2 = 2.8 Hz, 1H), 7.37−7.29 (m, 2H), 7.22−7.17 (m, 1H), 7.09 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.95 (m, 2H), 6.38 (d, J = 15.6 Hz, 1H), 5.29 (s, 1H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1, 152.8, 142.1 (d, J_{C-F} = 2.4 Hz), 134.0 (d, J_{C-F} = 3.2 Hz), 133.1 (d, J_{C-F} = 8.1 Hz), 131.9, 131.3, 130.0, 125.2, 120.8, 120.1, 117.5 (d, J_{C-F} = 21.6 Hz), 116.8 (d, J_{C-F} = 14.4 Hz), 116.0, 113.2 (d, J_{C-F} = 22.0 Hz), 51.9. HRMS-ESI (m/z): calcd for $C_{16}H_{13}FO_3Na$ $[M + Na]^+$ 295.0741, found 295.0750.

*(E)-Methyl 3-(2-Hydroxy-[1,1′:4′,1″-terphenyl]-2′-yl)acrylate (**3ja**).* Yield: 69% (227 mg). Light-yellow solid, mp 82−84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 1.6 Hz, 1H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 16.0 Hz, 1H), 7.54−7.45 (m, 2H), 7.44−7.41 (m, 2H), 7.36−7.32 (m, 1H), 7.17 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.07−7.00 (m, 2H), 6.49 (d, J = 16.0 Hz, 1H), 5.25 (s, 1H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 152.8, 143.0, 141.6, 140.1, 136.7, 134.0, 131.8, 131.2, 129.9, 129.2, 129.0, 127.9, 127.2, 125.7, 125.6, 120.8, 119.4, 116.0, 51.8. HRMS-ESI (m/z): calcd for $C_{22}H_{18}O_3Na$ $[M + Na]^+$ 353.1148, found 353.1160.

*(E)-Methyl 3-(2′-Hydroxy-4-(isobutyryloxy)-[1,1′-biphenyl]-2-yl)-acrylate (**3ka**).* Yield: 34% (116 mg). Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 16.0 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.35−7.30 (m, 1H), 7.21 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.10 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.03−6.97 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.04 (s, 1H), 3.74 (s, 3H), 2.87 (m, 1H), 1.37 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.6, 167.0, 152.7, 150.9, 142.0, 135.2, 135.1, 132.4, 131.2, 130.0, 125.2, 123.7, 120.8, 120.1, 119.7, 116.0, 51.8, 34.2, 18.9. HRMS-ESI (m/z): calcd for $C_{20}H_{20}O_5Na$ $[M + Na]^+$ 363.1203, found 363.1210.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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