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Palladium (II)-catalyzed mono- and bis-alkenylation of *N*-acetyl-2-aminobiaryls through regioselective C–H bond activation

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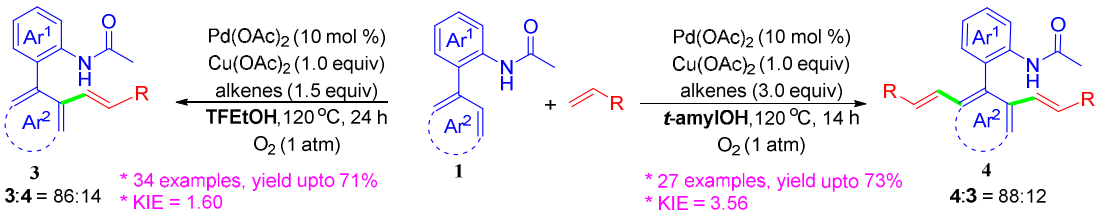


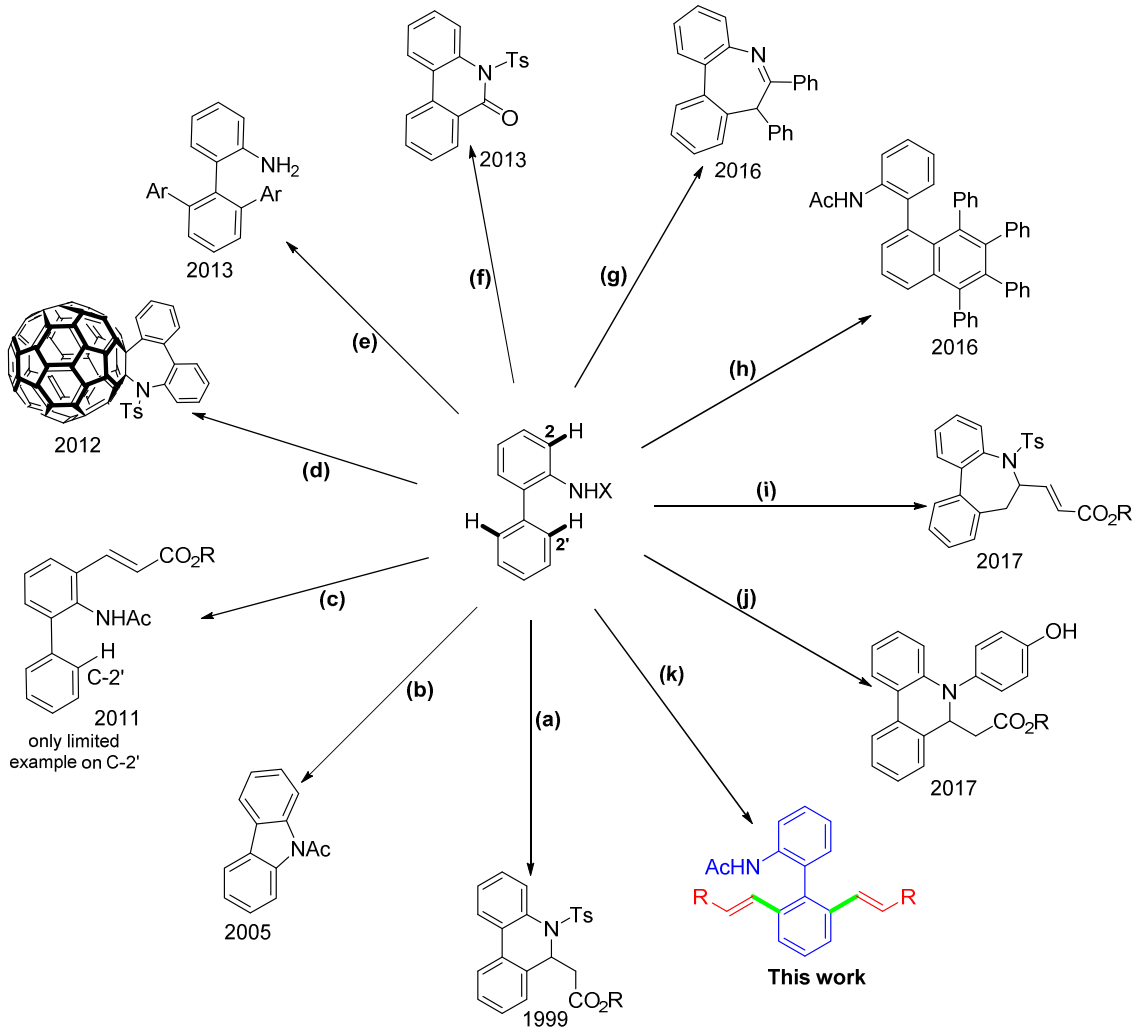
ABSTRACT: We developed palladium-catalyzed oxidative coupling of olefins with *N*-acyl 2-aminobiaryls through a sequence of *ortho* C–H bond activation/alkene insertion/reductive elimination. Furthermore, we controlled the selectivity of mono- and bis-alkenylation products with the solvent effect. The developed protocol was promising for a broad substrate scope ranging from activated olefins with a wide variety of functional groups to unactivated olefins.

INTRODUCTION

In recent decades, direct C–H bond activation has attracted considerable attention because of its wide range of applications compared with the conventional coupling reaction.[1] It has created a synthetic platform to construct a wide range of C–C, C–N, and other heteroatom bond formations based on the molecules of interest,[2] including viable chemoselective, regioselective, and stereoselective chemical processes.[3] Generally, regioselectivity, chemoselectivity, and stereoselctivity can be achieved through directing group-assisted, chelation-assisted, template-controlled, and transient mediator strategies.[4] The most common directing groups used are ketones, amines, imines, amides, sulfoximine, sulfonamides, phosphonates, and sulfonates.[4b, 4f, 5] In recent years, direct C–H functionalization was used for site-selective functionalization that further led to the synthesis of natural products, pharmaceuticals, and organic materials.[3a, 6] In 1967, Fujiwara and Moritani first reported the intermolecular oxidative coupling of nonfunctionalized arenes directly with olefins.[7] Later, the Fujiwara–Moritani strategy coupled with directing group or chelation-assisted methods was extended for various applications ranging from bioactive molecules to materials.[8]

The Pd-catalyzed direct *ortho* or *meta* C–H functionalization of *N*-free and *N*-protected biarylamines have received sustained interests. Miura reported the first synthesis of dihydrophenanthridines from the reaction of *N*-tosyl-2-arylanilines with activated olefins catalyzed by Pd,[9a] and Youn and co-workers followed this method (Scheme 1a-c). Gaunt, Miura, and Buchwald developed a method to synthesize carbazoles from *N*-substituted 2-aminobiphenyls through Pd(II)- and Cu(II)-catalyzed intramolecular coupling, respectively (Scheme 1b).[9] Youn reported the C-2 alkenylation of *N*-acyl biraylamine, but had limited examples of selective

C-2' alkenylation (Scheme 1c).[10] We achieved Pd-catalyzed C2′–H activation of *N*-substituted 2-aminobiaryls followed by the insertion of [60]fullerene, carbon monoxide (CO), and diphenylacetylene to yield fullerobenzoazepines, phenanthridinones, and highly substituted naphthalenes, respectively (Scheme 1d, 1f, 1h).[5a, 11] We further demonstrated a Pd-catalyzed C–H bond activation reaction through a redox-neutral pathway for the preparation of dihydrophenanthridine, phenanthridine, and carbazole derivatives from biaryl 2-iminoquinones (Scheme 1j).[12] It was believed that C2–H activation will be favored under more acidic solvents such as trifluoroacetic acid, and C2′–H activation will be favored under less acidic solvents such as trifluoroethanol, *t*-amyl alcohol, dimethylformamide, dimethyl sulfoxide and acetonitrile. Reactions carried out under more acidic solvents will make palladium center more cationic and thereby favoring carbonyl oxygen coordination to the palladium and enabling C2–H activation, while that under less acidic solvents will make nitrogen from NHAc moiety more coordinating and thus activating C2′–H bond. When studying the reactivity of 2-aminobiaryls toward versatile reactions, Zhang reported direct C–H bis-arylation of biaryl amines (Scheme 1e),[13] and Luan reported the formation of azepines through the assembly of biarylamines with diphenylacetylene (Scheme 1g).[14] In 2017, Luan demonstrated diastereoselective azepine synthesis through Pd-catalyzed [5+2] annulation of conjugated dienes with *o*-arylanilines (Scheme 1i).[15] The dehydrogenative coupling has been demonstrated as an efficient tool for the preparation of useful molecules. For example, Murakami achieved optically active clavicipitic acid and Yu reported an elegant approach to lithospermic acid and other drug diversification synthesis. These syntheses were achieved using dehydrogenative coupling as the key step.[16] However, the selective mono and bis-alkenylation in the biarylamine system have not yet been reported. Based on the above synthetic application of dehydrogenative coupling and other studies on functionalization of biaryl 2-amines through C – H activation, we report a simple and ligand-free catalytic system using *N*-acyl-2-amine as a directing group for chelation-assisted *ortho* dehydrogenative coupling with controlled regioselectivity ranging from activated olefins to unactivated aliphatic olefins.



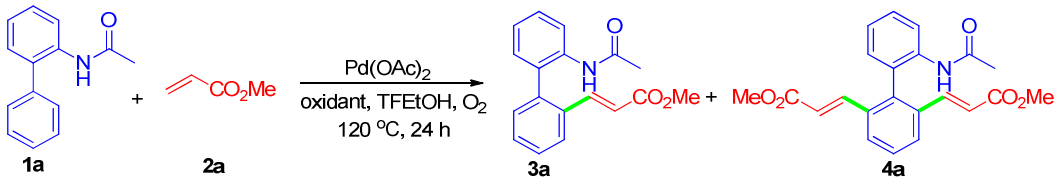
Scheme 1. Representative studies of directing-group-assisted *N*-free and substituted biarylamines for functionalization through C-H activation. (a) Pd (II), X = Ts, acrylates (b) Pd (II), X = Ac (c) Pd (II), X = Ac, acrylates (d) Pd (II), X = Ts, C_{60} (e) Pd (II), X = H, aryl iodides (f) Pd (II), X = Ts, CO (g) Pd (II), X = H, diphenyl acetylene (h) Pd (II), X = Ac, diphenyl acetylene (i) Pd (II), X = Ts, dienes (j) Pd (II), X = iminoquinone, acrylates (k) Pd (II), X = Ac, sunstituted olefins.

RESULTS AND DISCUSSION

We initiated an experiment with 0.3 mmol of *N*-acyl 2-aminobiphenyl (**1a**), 0.9 mmol of methyl acrylate (**2a**), 10 mol % of $Pd(OAc)_2$ (0.03 mmol), 50 mol % of NaOAc, and 1 equivalent of $Cu(OAc)_2$ under 1 atm O_2 atmosphere in trifluoroethanol (TFEtOH) at 120 °C for 14 h. Under these conditions, the experiment yielded 53% of (*E*)-methyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (**3a**) and (2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (**4a**) as the *ortho* dehydrogenative coupled products with a molar ratio of **3a** to **4a** of 92:8 (Table 1, entry 1). We confirmed the structures of **3a** and **4a** through single-crystal X-ray diffraction analysis.[17] Next, we extended the reaction time to 18 and 24 h, which provided comparable yields of 58% and 48%, respectively (entries 2 and 3). Notably, the reactions became low-yielding, 7% and 14%, respectively, when the $Cu(OAc)_2$ or the $Cu(OAc)_2$ oxidant and NaOAc were absent from the reaction (entries 4 and 5). The reaction produced 81% of **3a** and **4a** in a 3:1 ratio when the reaction was conducted without NaOAc as an additive for 18 h (Table 1, entry 6). The studied reac-

tions gave 0%, 50%, and 10% yields in the absence of a catalyst, in an AcOH solvent, or in toluene, respectively (entries 7 – 9). We further investigated the effects of the oxidants and noted that $Cu(OAc)_2$ was the most favorable choice compared with AgOAc and $AgNO_3$ in this dehydrogenative coupling reaction (entries 10–13). It was noteworthy that the ratio of **3a**/**4a** at reaction time of 24 h was superior to that at time of 16 h under the same condition, although their yields are identical. This was presumably due to the faster reaction rate for the first alkenylation compared to the rate of second alkenylation (entries 6 and 13). Under a different equivalence of methyl acrylate, we discovered that the addition of 0.45 mmol of **2a** gave a yield of 83% with a high selectivity in a 87:13 molar ratio (entries 14–17). We attempted using lower loads of catalyst, but the reaction produced only 62% and 68% yield with 5 mol % of $Pd(OAc)_2$ (entries 18 and 19). Further attempts at using air as a co-oxidant or reducing the amount of $Cu(OAc)_2$ to 0.5 and 0.25 equivalents did not produce significant results (entries 20–22). In brief, the most favorable condition was the use of **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (10 mol %), and $Cu(OAc)_2$ (1 equiv) in 2 mL of TFEtOH at 120 °C for 24 h under 1 atm O_2 (entry 15).

Table 1. Optimization of the mono-alkenylation reaction conditions[a]



entry	**2a** (mmol)	oxidants (equiv)	time (h)	yield[b] (%)	ratio **3a**:**4a**[b]
1[c]	0.9	$Cu(OAc)_2$ (1)	14	53	92:8
2[c]	0.9	$Cu(OAc)_2$ (1)	18	58	91:9
3[c]	0.9	$Cu(OAc)_2$ (1)	24	48	90:10
4[c]	0.9	-	24	7	>99:1
5	0.9	-	24	14	>99:1
6	0.9	$Cu(OAc)_2$ (1)	18	81	76:24
7[d]	0.9	$Cu(OAc)_2$ (1)	18	0	–
8[e]	0.9	$Cu(OAc)_2$ (1)	18	50	46:54
9[f]	0.9	$Cu(OAc)_2$ (1)	18	10	>99:1
10	0.9	AgOAc (1)	18	39	87:13
11	0.9	$AgNO_3$ (1)	24	38	79:21
12	0.9	$AgNO_3$ (2)	24	37	76:24
13	0.9	$Cu(OAc)_2$ (1)	24	81	83:17
14	0.6	$Cu(OAc)_2$ (1)	24	78	87:13

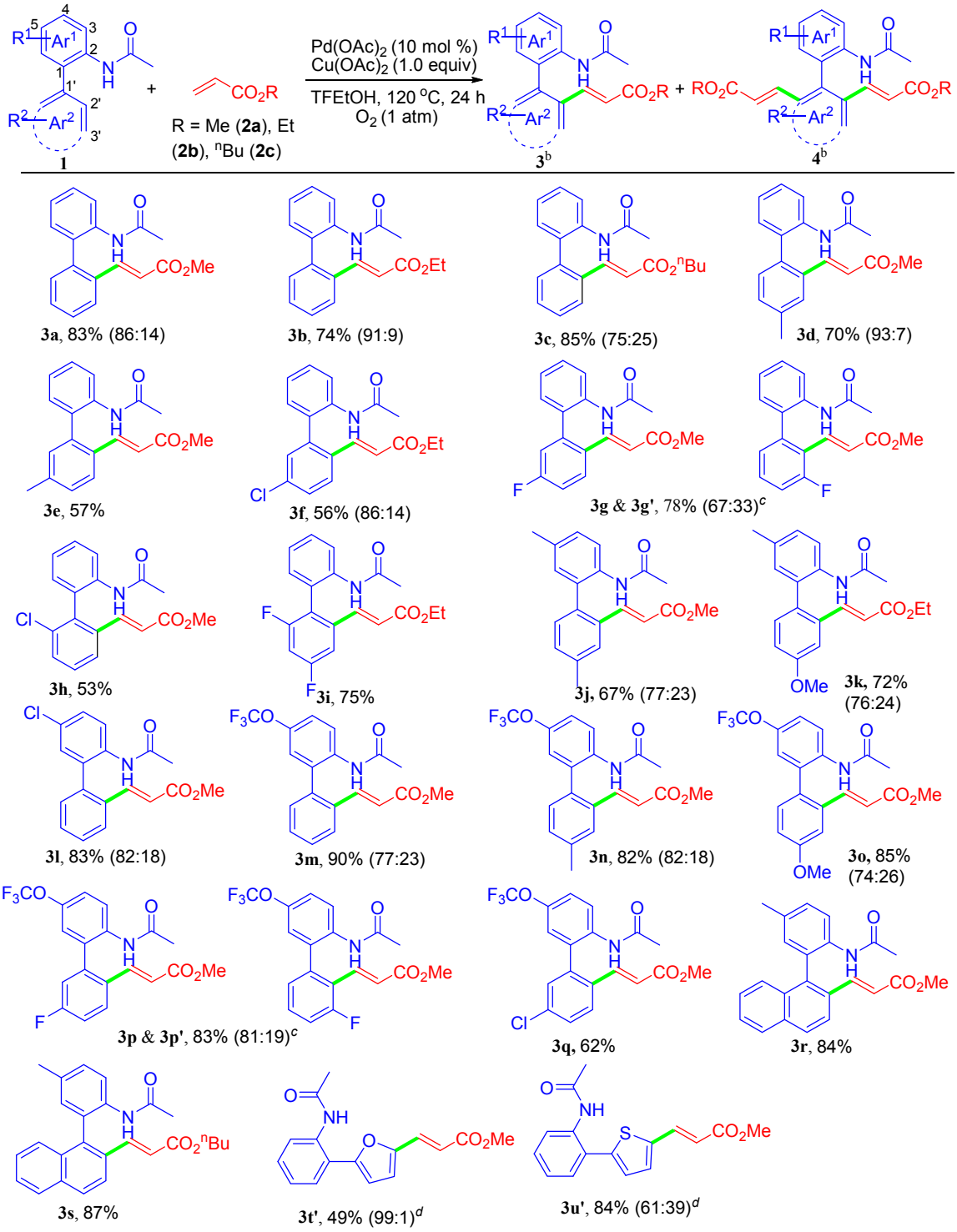
15	0.45	$Cu(OAc)_2$ (1)	24	83	87:13
16	0.53	$Cu(OAc)_2$ (1)	24	82	87:13
17	0.36	$Cu(OAc)_2$ (1)	24	78	84:16
18[h]	0.36	$Cu(OAc)_2$ (1)	24	62	90:10
19[h]	0.45	$Cu(OAc)_2$ (1)	24	68	86:14
20[g,h]	0.36	$Cu(OAc)_2$ (1)	24	56	93:7
21	0.45	$Cu(OAc)_2$ (0.5)	24	42	91:9
22	0.45	$Cu(OAc)_2$ (0.25)	24	27	>99:1

[a]All reactions were performed with 0.3 mmol of **1a**, 0.9 mmol of **2a**, 10 mol % of $Pd(OAc)_2$, and the oxidant in the listed solvent at 120 °C under O_2 (1 atm) unless otherwise noted. [b]Yields and selectivities were determined using ^1H NMR spectroscopy with mesitylene as an internal standard. [c]50 mol % of additive NaOAC was added. [d]The reaction was conducted without $Pd(OAc)_2$. [e]The reaction was conducted in 2 mL of AcOH. [f]The reaction was conducted in 2 mL of toluene and 0.1 mL of TFEtOH. [g]The reactions were conducted under air. [h]The reaction was conducted with 5 mol % of $Pd(OAc)_2$.

By using these optimized conditions, we surveyed the reactivity of different substituted 2-aminobiaryls, equipped with electron-withdrawing groups (EWGs) and electron-donating groups (EDGs) in the upper and bottom ring of the *N*-acyl 2-aminobiaryls, toward *ortho* dehydrogenative alkenylation (Table 2). We first studied this alkenylation with different alkyl acrylates (**2a-c**) and found that they produced a 74% – 85% yield of **3a-c** with a selectivity of up to 91:9 (**3**:**4**). We next found that the electronic effect of the bottom ring greatly influenced the chemical yields and the selectively. The reaction with 4'-methyl substituted *N*-acyl 2-aminobiphenyl produced 70% of **3d** with a maximum selectivity of 92:8. However, the reaction with the 3'-methyl substitute produced only 57% yield of the *para*-selective *ortho*-alkenylation product **3e**. In a similar fashion, the reaction with the 3'-chloro substituted substrate provided 56% of the *para*-selective *ortho*-alkenylation product **3f**. Because of the smaller size of the fluorine substituent compared with the chlorine one, the reaction with the 3'-fluoro substituted substrate provided a mixture of isomeric products **3g** and **3g'** in a 78% yield, with a moderate mono to bis product selectivity (**3**/**4**) of 67:33. The mixture contained products from *para* and *ortho* C – H alkenylation of the fluorine substituent in a ratio of 55:45 (**3g**/**3g'**). Although fluorine is considered electron-pulling moiety, its influence on the reactivity toward C – H activation did not seem to be large and could be compromised by resonance effect—therefore only minor effect on the reaction yield was observed. When a substrate had *ortho* chlorine substitution, it produced a C-2' alkenylation product **3h** with only a moderate yield. Notably, a favorable yield of C-2' alkenylation product **3i** was obtained using a 2',4'-difluorine substituted substrate. Moreover, the reaction had a yield of nearly 80% for the C-2' alkenylation products when the upper ring was substituted with EWG functionality but a relatively lower yield with EDG functionality. For example, products **3j** and **3k** were produced at 67% and 70%, respectively, with a regioselectivity of up to 77:23 when the upper aryl ring had a 5-methyl moiety. An obvious increase in the alkenylation yields can be observed from substrates with upper rings with EWG moieties. For example, with 5-chloro and 5-trifluoromethyl substitution, products **3l**, **3m**, **3n**, **3o**, and **3p** and **3p'** were produced with chemical yields of 83%, 90%, 82%, 85%, and 83%, respectively, with a maximum selectivity of up to 82:18.

However, when the bottom ring was substituted with a chlorine moiety, the reaction produced **3q** with a 62% yield. Other bottom aryl substitutions also produced alkenylation with favorable yields. For instance, 1-naphthyl-substituted substrates produced **3r** and **3s** with 84% and 87% yields, respectively. Notably, substrates with 2-furyl and 2-thienyl substitution produced the corresponding alkenylation products **3t'** and **3u'** with substantially different yields of 49% and 84%, respectively, with a selectivity of up to 61:39. This alkenylation did not occur in the *ortho* C-H moiety, but at the C-4' position.

Table 2. Substrate scope study for mono-alkenylation[a]

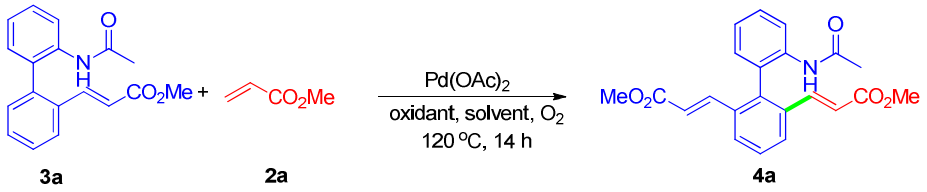


[a]All reactions were conducted with substrate **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (10 mol %), and $Cu(OAc)_2$ (1 equiv) in 2 mL of TFEtOH at 120 °C for 24 h under O_2 (1 atm) unless otherwise noted. [b]Yields and selectivities were measured using ^1H NMR spectroscopy with mesitylene as an internal standard. The ratios in the parenthesis are mono to bis product selectivity **3**/**4**. [c]Isomeric ratio **3g**:**3g'** (55:45), **3p**:**3p'** (55:45). [d]The reactions used AgOAc (3 equiv) instead of $Cu(OAc)_2$ under N_2.

In the above alkenylation study, mono-alkenylation product **3** was formed with some bis-alkenylation product **4**. However, bis-alkenylation can proceed all the way if an excess amount of methyl acrylate were added under the optimized conditions. Therefore, we tuned the second alkenylation on C-6' position that enabled bis-alkenylation by changing the solvent and the equivalence

of methyl acrylate. We started by using 0.1 mmol of (*E*)-methyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (**3a**), 0.3 mmol of methyl acrylate (**2a**) in the presence of 10 mol % of $Pd(OAc)_2$, 50 mol % of NaOAc, and 1 equivalent of $Cu(OAc)_2$ under O_2 atmosphere in AcOH at 120 °C for 14 h. The reaction produced 36% of (2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (**4a**) or 55% based on converted **3a** (Table 3, entry 1). The bis-alkenylation yield did not improve with the addition of more **2a** or when the reaction time was extended (entries 2 and 3). However, changing the solvent significantly increased the yield. The reaction performed in pivalic acid produced a 26% yield; however, a yield of 58% was obtained in *t*-butanol (entries 4 and 5). Because of this promising improvement, we could screen the effects of oxidant and temperature on improving the chemical yields (entries 6 – 14). However, none of the tested conditions provided favorable results. Further screening with other solvents, such as *n*-BuOH, isoamyl alcohol, and *t*-amyl alcohol, yielded promising results (entries 15-17). The second alkenylation could be achieved with up to 75% chemical yield (88% based on converted **3a**, entry 17). Further tuning of the reaction time (14 h) and the amount of **2a** produced comparable yields (entries 18-21). In the presence of air as the co-oxidant, the reaction became less efficient (59%, entry 22). Notably, the second alkenylation nearly produced a 60% yield for a reaction time of 3 and 9 h (entries 23 and 24). Based on the above systematic screening, the optimal results were obtained with **3a** (0.1 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), and $Cu(OAc)_2$ (1 equiv) in 2 mL of *tert*-amyl alcohol (*t*-amylOH) at 120 °C for 14 h under 1 atm of O_2 (entry 18) (Condition A).

Table 3. Optimization of the reaction conditions for the second alkenylation from a mono-alkenylated substrate[a]



3a **2a** **4a**

entry	**2a** (mmol)	Oxidants (equiv)	Solvent	temp (°C)	time (h)	yield (%)[b]
1	0.3	$Cu(OAc)_2$ (1)	AcOH	120	18	36(55)
2	0.4	$Cu(OAc)_2$ (1)	AcOH	120	18	39(56)
3	0.4	$Cu(OAc)_2$ (1)	AcOH	120	24	32(57)
4	0.4	$Cu(OAc)_2$ (1)	PivOH	120	18	26(47)
5	0.4	$Cu(OAc)_2$ (1)	*t*-BuOH	120	18	58
6	0.4	AgOAc (1)	*t*-BuOH	120	18	12
7	0.4	$K_2S_2O_8$ (1)	*t*-BuOH	120	18	trace
8[c]	0.4	BQ (1)	*t*-BuOH	120	18	5(83)
9[c]	0.4	$Cu(OAc)_2$ (1)	*t*-BuOH	120	18	46

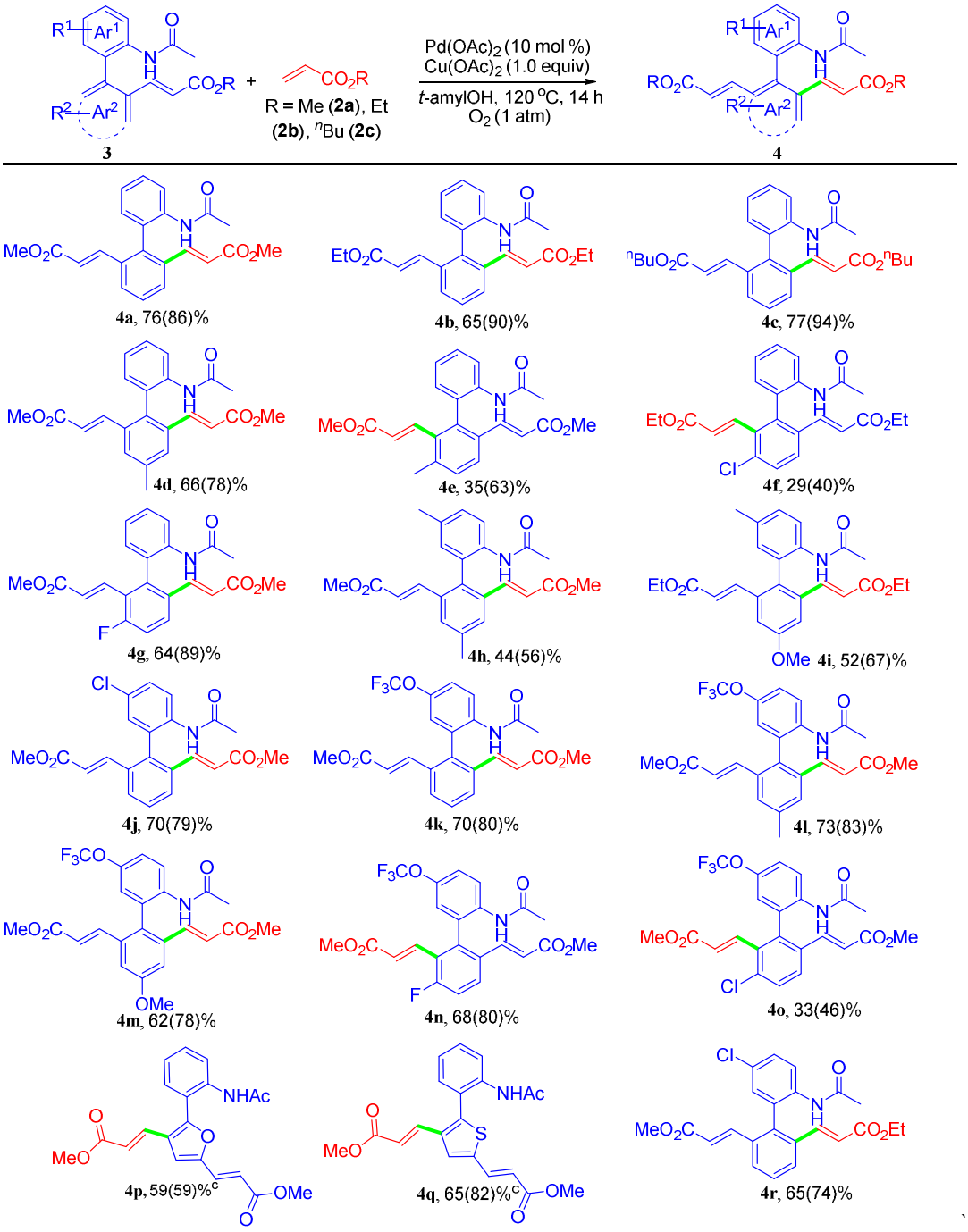
10[d]	0.4	–	*t*-BuOH	120	18	trace
11	0.4	$Cu(OAc)_2$ (1)	*t*-BuOH	80	18	22
12	0.4	$Cu(OAc)_2$ (1)	*t*-BuOH	90	18	34
13	0.4	$Cu(OAc)_2$ (1)	*t*-BuOH	110	18	40
14	0.4	$Cu(OAc)_2$ (2)	*t*-BuOH	120	18	46
15	0.4	$Cu(OAc)_2$ (1)	*n*-BuOH	120	18	63
16	0.4	$Cu(OAc)_2$ (1)	*iso*-amylOH	120	18	31(48)
17	0.4	$Cu(OAc)_2$ (1)	*t*-amylOH	120	18	75(88)
18	0.4	$Cu(OAc)_2$ (1)	*t*-amylOH	120	14	74(88)
19	0.5	$Cu(OAc)_2$ (1)	*t*-amylOH	120	14	72(91)
20	0.3	$Cu(OAc)_2$ (1)	*t*-amylOH	120	14	76(86)
21	0.2	$Cu(OAc)_2$ (1)	*t*-amylOH	120	14	67(88)
22[c]	0.3	$Cu(OAc)_2$ (1)	*t*-amylOH	120	14	59(69)
23	0.3	$Cu(OAc)_2$ (1)	*t*-amylOH	120	9	63(77)
24	0.3	$Cu(OAc)_2$ (1)	*t*-amylOH	120	3	60(90)

[a]All reactions were performed with 0.1 mmol of **3a**, **2a**, 10 mol % of $Pd(OAc)_2$ and the oxidant in the listed solvent (1 mL) under O_2 (1 atm) unless otherwise noted. [b]Yields were determined using ^1H NMR spectroscopy with mesitylene as an internal standard. Values in parentheses were based on converted **3a**. [c]Reactions were conducted under air. [d]The reaction was conducted without oxidants.

Under the aforementioned optimized conditions, we studied the substrate scope toward the second alkenylation with different alkyl acrylates and different EWGs and EDGs on both aryl rings of the *N*-acyl 2-aminobiaryls. It provided chemical yields from 65% to 77% for the second alkenylation, or 86% to 94% based on converted **3a–c** when the reaction was conducted with methyl, ethyl, and *n*-butyl acrylates (Table 4, **4a–c**). When the bottom aryl ring was functionalized, the alkenylation was hindered by steric effects. For instance, a 66% yield of **4d** was obtained when C-4' was subsitituted with a methyl group, but only a 35% yield (63% based on the converted substrate) of **4e** was obtained when the methyl moiety was susbtituted at the C-5' position. A larger chlorine substitution at the C-5' position further hindered the second alkenylation, producing **4f** only with a 29% yield. However, a fluorine substitution at the C-5' position produced **4g** with a yield of 64% (89% based on the converted substrate). For substrates with a methyl substitution at the upper ring C-5 position and a methyl or methoxy moiety at the C-4' position, the second alkenylation produced **4h** and **4i** with 44% and 52% yields, respectively. Notably, substrates with EWG substitutions in the upper ring produced high alkenylation yields. Compounds **4j–n** were produced with a 62%–73% yield (78%–83% based on the converted substrate) when C-5 was substituted with a chlorine or trifluoromethoxy moiety. However, a substrate with a chlorine substitution at C-5' again produced a lower yield (33%) of **4o** when the upper ring had a trifluoromethoxy moiety at C-5. Two representative examples of 2'-heteroaryl aminobiaryls were demonstrated with 2-furyl and 2-thienyl substitution. The bis-alkenylation products **4p** and **4q** were isolated with yields of 59% and 65%, respectively (59% and 82% based on the converted substrates). C-4' alkenylation occurred prior to the C-2'

alkenylation because C-4' alkenylation was the only isolated product in the first alkenylation experiment. Finally, a bis-alkenylation product **4r** with methyl and ethyl acrylates was isolated with a 65% yield when substrate **3a** was used to react with ethyl acrylate.

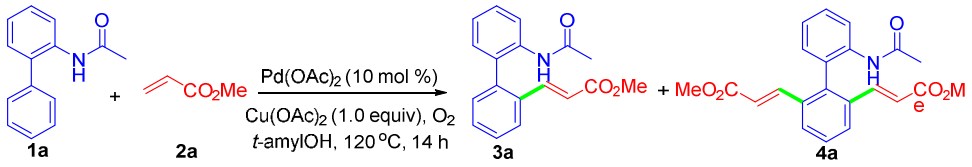
Table 4. Substrate scope study for the second alkenylation from mono-alkenylated substrates[a]



[a]All reactions were conducted with substrate **3** (0.1 mmol), **2** (0.3 mmol), $Pd(OAc)_2$ (10 mol-%), and $Cu(OAc)_2$ (0.1 mmol) in 1 mL of *t*-amylOH at 120 °C for 14 h under O_2 (1 atm) unless otherwise noted. [b]Values in parentheses were based on converted **3**. [c]The reactions were conducted under N_2 (1 atm).

After our success on the first and second alkenylation of *N*-Ac 2-aminobiaryls, we focused on one-pot sequential double alkenylation. Based on the knowledge gained using TFEtOH as a solvent for mono-alkenylation and using *t*-amylOH for the second alkenylation, we believe that bis-alkenylation is solvent-controlled. To ensure high yields and high regioselectivity, alcoholic or polar protic solvents were selected for bis-alkenylation. This avoided Micheal-type additions that formed dihydrophenanthridines. Therefore, we tuned the double alkenylation by increasing the equivalence of methyl acrylate (Table 5). The double alkenylation obviously reached saturation with two equivalents of methyl acrylate (entries 1–5), providing nearly a yield of 80% with a selectivity of mono- to bis-alkenylation of 21:79. Further increasing the amount of **2a** or $Pd(OAc)_2$ to 15 mol % produced 92% and 71% yields with a selectivity of 33:67 and 19:81, respectively. We concluded that the double alkenylation in one-pot could be achieved using 3 equiv of methyl acrylate in *t*-amylOH (Entry 4, Condition B).

Table 5. Optimization of reaction conditions for solvent-controlled bis-alkenylation[a]



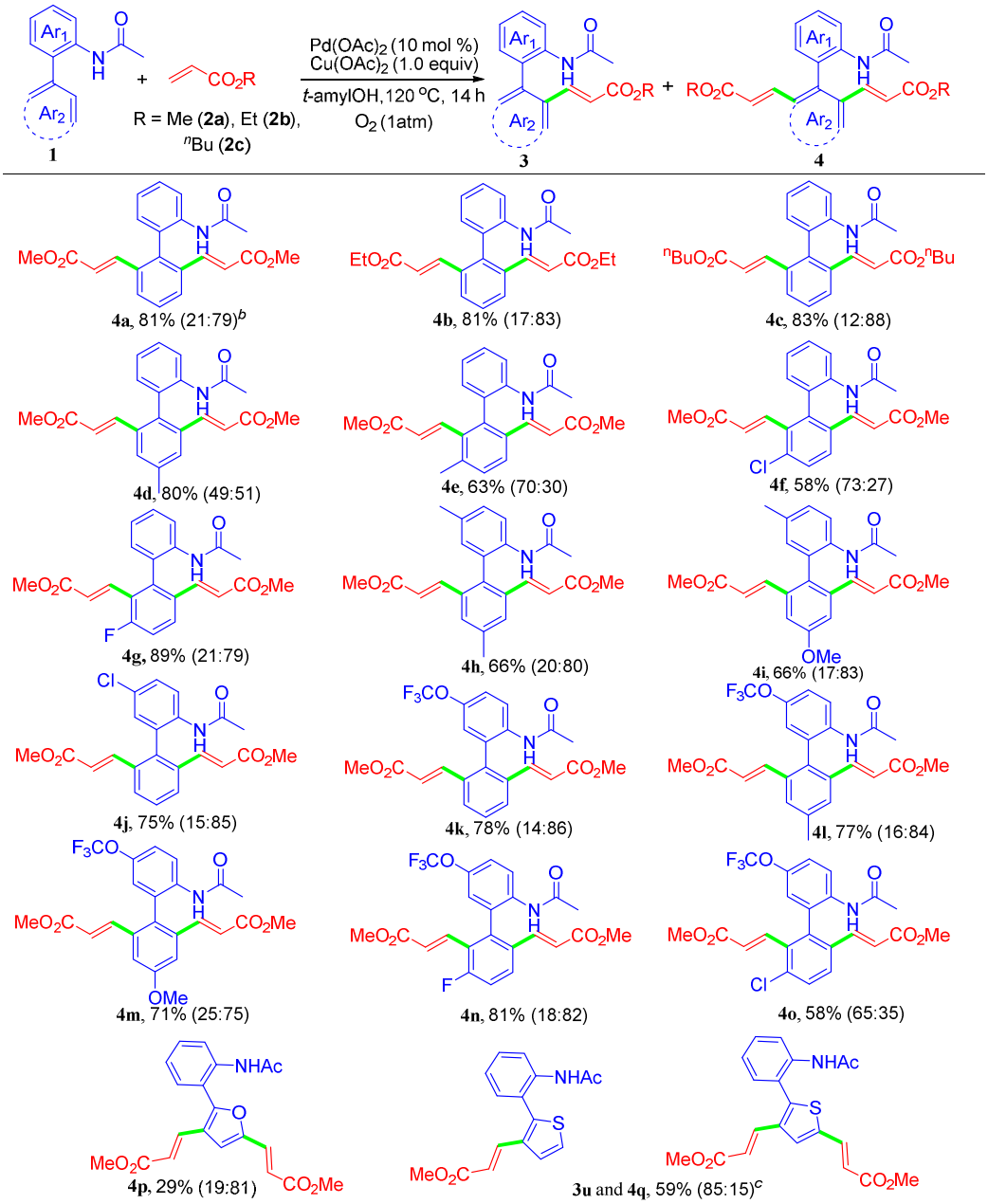
entry	**2a** (mmol)	$Pd(OAc)_2$ (mol %)	Yield (%)[b]	**3a**:**4a**[b]
1	0.1	10	57	18:82
2	0.15	10	75	31:69
3	0.2	10	78	21:79
4	0.3	10	81	21:79
5	0.4	10	79	22:78
6	0.5	10	92	33:67
7	0.5	15	71	19:81

[a]All reactions were performed with **1a** (0.1 mmol), **2a** (0.3 mmol), 10 mol % of $Pd(OAc)_2$, and $Cu(OAc)_2$ (1 equiv) in 1 mL of *t*-amylOH at 120 °C for 14 h under O_2 (1 atm). [b] Selectivity was determined using ^1H NMR spectroscopy with mesitylene as an internal standard.

The scope for bis-alkenylation was studied with different alkyl acrylates and biarylamines **1** with different EWG and EDG present on the top and bottom ring of the *N*-acyl 2-aminobiaryls in a solvent-controlled one-pot strategy, with directing group-assisted sequential alkenylation. The reactions with methyl, ethyl, and butyl acrylates were well tolerated and exhibited a favorable bis-alkenylation selectivity with yields of 81%–83% and mono- to bis-alkenylation ratios of up to 12:88 (Table 6, **4a**–**4c**). The reactions with *N*-acyl 2-aminobiaryls containing an EDG, methyl substitution, on the C-4', produced mono- and bis-alkenylation products

with a yield of 80% at a 1:1 molar ratio (**4d**). However, methyl substitution on C-3' provided mono- and bis-alkenylation products with only a 63% yield and a 7:3 molar ratio due to steric effects (**4e**). Substrates with halo-substitution on the C-3' were also effective in this strategy and had moderate to high yields of 58%–89% (**4f**–**4g**). Due to steric effects, chlorine-substituted substrates generated more mono-alkenylation products. Reactions with substrates containing an EDG on both the top and bottom rings at C-5 and C-4' and substrates containing Cl and OCF_3 on the top ring at C-5 provided moderate to high yields of 66%–78% with mono- to bis-alkenylation ratios of up to 14:86 (**4h**–**4k**). The examples with an EWG at C-5 on the top ring and an EDG on the bottom ring at the C-4' position also formed the desired products with high yields of 58%–77% and mono- to bis-alkenylation ratios of up to 16:84 (**4l**–**4o**). Furthermore, heterocyclic substrates with a 2-furyl moiety underwent bis-alkenylation in a regioselective manner with a poor yield of 29%. In this example, dehydrogenative coupling occurred at C-4' followed by directing-group-assisted *ortho* C – H activation and alkenylation (**4p**). However, the substrate with a 2-thienyl moiety gave only C-2' mono-alkenylation major compound **3u** and minor usual bis alkenylation **4q** with 85:15 ratio and moderate yield of 59% in the present optimized conditions.

Table 6. Substrate scope study for solvent-controlled bis-alkenylation[a]

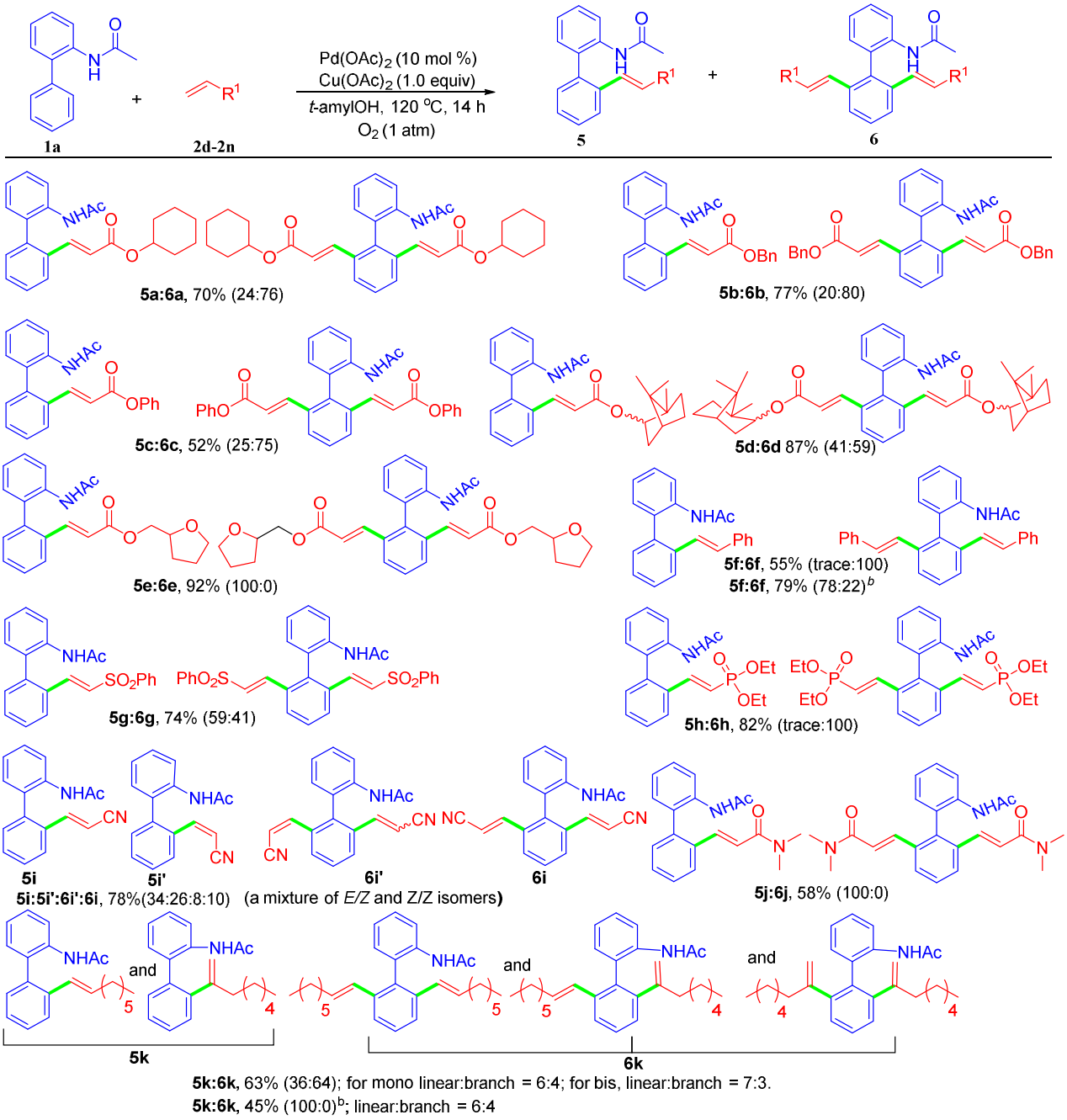


[a] All reactions were conducted with substrate **1** (0.1 mmol), **2** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), and $Cu(OAc)_2$ (0.1 mmol) in 1 mL of *t*-amylOH at 120 °C for 14 h under O_2 (1 atm) unless otherwise noted. [b] Yields and selectivities were measured using ^1H NMR spectroscopy with mesitylene as an internal standard; molar ratio and combined yields of **3**:**4**. [c] The reaction was conducted under N_2 (1 atm). [d] Compound **3u** represented mono *ortho* C-2' alkenylation product.

Furthermore, we examined the reactivity with different substituted olefins (**2d–2n**) and found that almost all the studied functional groups were tolerated (Table 7). The reactions with activated olefins with different functional groups, cyclohexyl (**2d**), benzyl (**2e**) and phenyl acrylates (**2f**), formed the corresponding products with a high selectivity, yielding 52%–77% of mono- and bis-alkenylated products with a ratio of up to 20:80 (**5a**/**6a**, **5b**/**6b**, **5c**/**6c**). Other activated olefins, such as isobornyl acrylate **2g**, also underwent efficient conversion to yield 87% of mono- and bis-alkenylated products in a nearly equal ratio of 41:59 (**5d/6d**). In the reaction with 2-tetrahydrofurfuryl acrylate (**2h**), the mono-alkenylated product **5e** was selectively formed with a 92% yield probably because of its electronic coordination through the 2-tetrahydrofurfuryl moiety. Notably, aryl-substituted olefins, such as styrene

2i, also underwent dehydrogenative coupling with the same presented strategy with moderate product conversion. The solvent-controlled mono- and bis-alkenylated selectivity was 78:22 in TFEtOH (**5f/6f**) and trace:100 in *t*-AmOH (**5f/6f**), respectively. Moreover, the reaction with more EWGs such as phenyl vinyl sulfone (**2j**) yielded 74% of **5g/6g** in a 59:41 ratio. The reaction with diethyl vinyl phosphonate (**2k**) formed 82% of **5h/6h** (trace:100), favoring the formation of the bis-alkenylated product due to its electronic factor. With acrylonitrile (**2l**), the selectivity was poor because of the formation of multiple products. Four compounds were isolated with a 78% yield in this alkenylation reaction: **5i** through the usual C-2' *ortho* C–H bond-activated mono-alkenylation product in *trans* form and **5i'** through C-2' *ortho* C–H bond-activated mono-alkenylation product in *cis* form. Furthermore, **6i'** obtained through bis-alkenylation at the C-2' and C-6' positions was a mixture of *E*/*Z* and *Z*/*Z* isomers and **6i** as the usual bis C-2' and C-6' *ortho* C–H bond-activated products. Reactions with *N*,*N*-dimethyl acryl amide (**2m**) formed an alkenylation product (**5j**) with sole mono-selectivity at a 58% yield (100:0). We also investigated aliphatic olefins, such as 1-octene (**2n**)**,** as a model coupling partner for *N*-acyl 2-aminobiarylamine. It underwent dehydrogenative oxidative coupling and formed **5k/6k** with a 63% yield (36:64). The ratios for linear to branch alkenylations were 6:4 and 7:3 in the mono- and bis-alkenylated products, respectively. When 2 mL of TFEtOH was used as a solvent, 45% of **5k** was produced with a linear to branch ratio of 6:4.

Table 7. Substrate scope study for the alkenylation of activated and unactivated olefins[a]

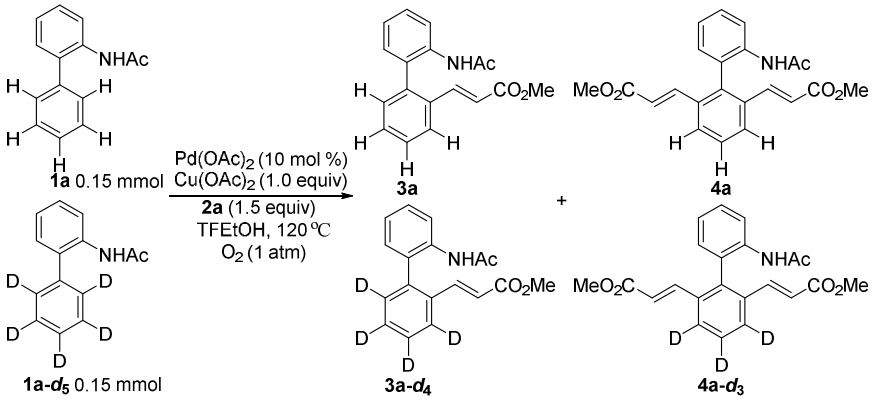


[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), and $Cu(OAc)_2$ (1 equiv) in 1 mL of *t*-amylOH at 120 °C for 14 h under O_2 (1 atm), [b] Reaction conducted using 2 mL of TFEtOH as a solvent for 24 h.

The mechanisms of directing-group-assisted mono-, mono- to bis-, and sequential bis-alkenylation were systematically studied using deuterium-labeling experiments. A kinetic isotope effect (KIE) study revealed a k_H/k_D value of 1.60 in the initial 5 min of the reaction. Further controlled experiments with durations of 20, 60, and 120 min revealed that mono-alkenylation was with primary KIE (Table 8). Similarly, mono- to bis-alkenylation was more likely for the primary KIE due to its k_H/k_D value of 1.71 and 1.98 for durations of 10 and 20 min, respectively (Table 9). Relatively large KIE values were observed in the one-pot bis-alkenylation experiments (Table 10). For a reaction time of 5 min, a k_H/k_D value of 1.78 was observed due to the primary KIE. For this duration,

bis-alkenylation has not yet been observed. However, for a reaction time of 10 min, a k_H/k_D value of 1.44 was observed for mono-alkenylation, but the k_H/k_D value for bis-alkenylation was 3.56. This indicated that the second step of alkenylation might be slower than the first step. Further extension of the reaction time to 20 min resulted in a k_H/k_D value of 1.08 for mono-alkenylation and 2.64 for bis-alkenylation. This confirmed that the second step of alkenylation was slower than the first step.

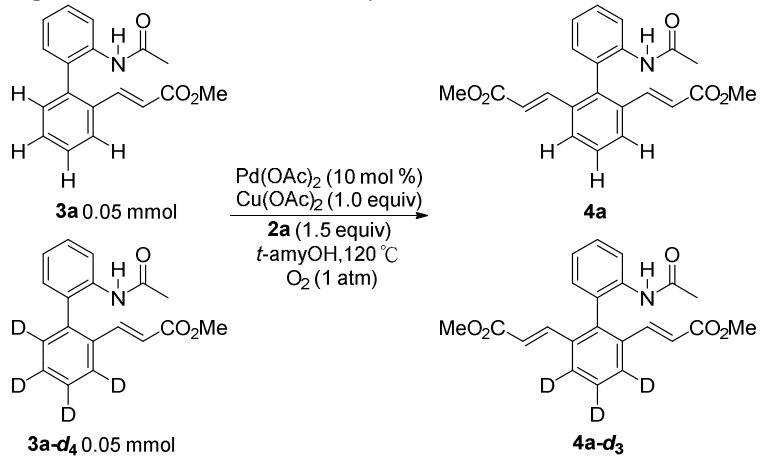
Table 8. Deuterium labeling experiments for mono-alkenylation[a].



Entry	Time (min)	Yield (%)	mono:bis	**1a**/**1a**-d_5	**3a**/**3a**-d_4	**4a**/**4a**-d_3
1[a]	5	26	100:trace	0.89	1.60	-
2	20	45	93:7	0.44	1.75	3.91
3	60	53	85:15	0.48	1.51	3.08
4	120	57	86:14	0.46	1.70	3.74

[a] The reaction was conducted with substrate **1a** (0.075 mmol), **1a**–d_5 (0.075 mmol), and $Pd(OAc)_2$ (5 mol %) under standard conditions.

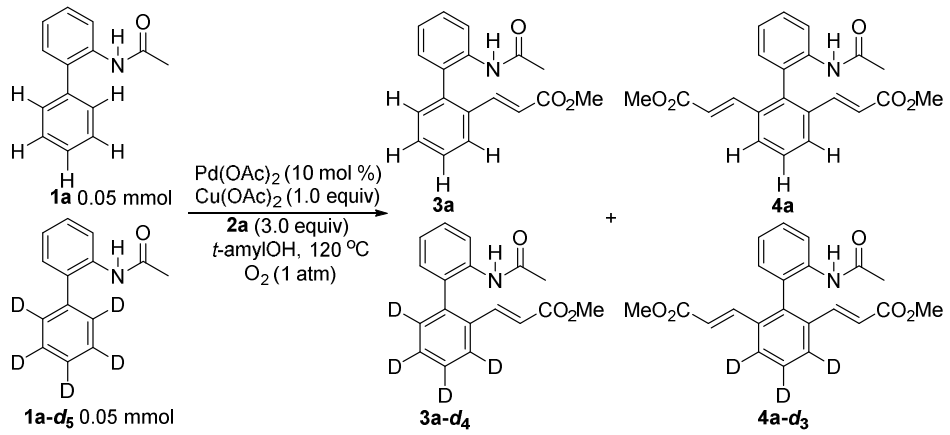
Table 9. Deuterium labeling experiments for mono- to bis-alkenylation[a]



Entry	Time (min)	Yield (%)	**3a**/**3a**-d_4	**4a**/**4a**-d_3
1[a]	10	17	0.86	1.71
2	20	21	0.93	1.98

[a] The reaction was conducted with 5 mol % of $Pd(OAc)_2$.

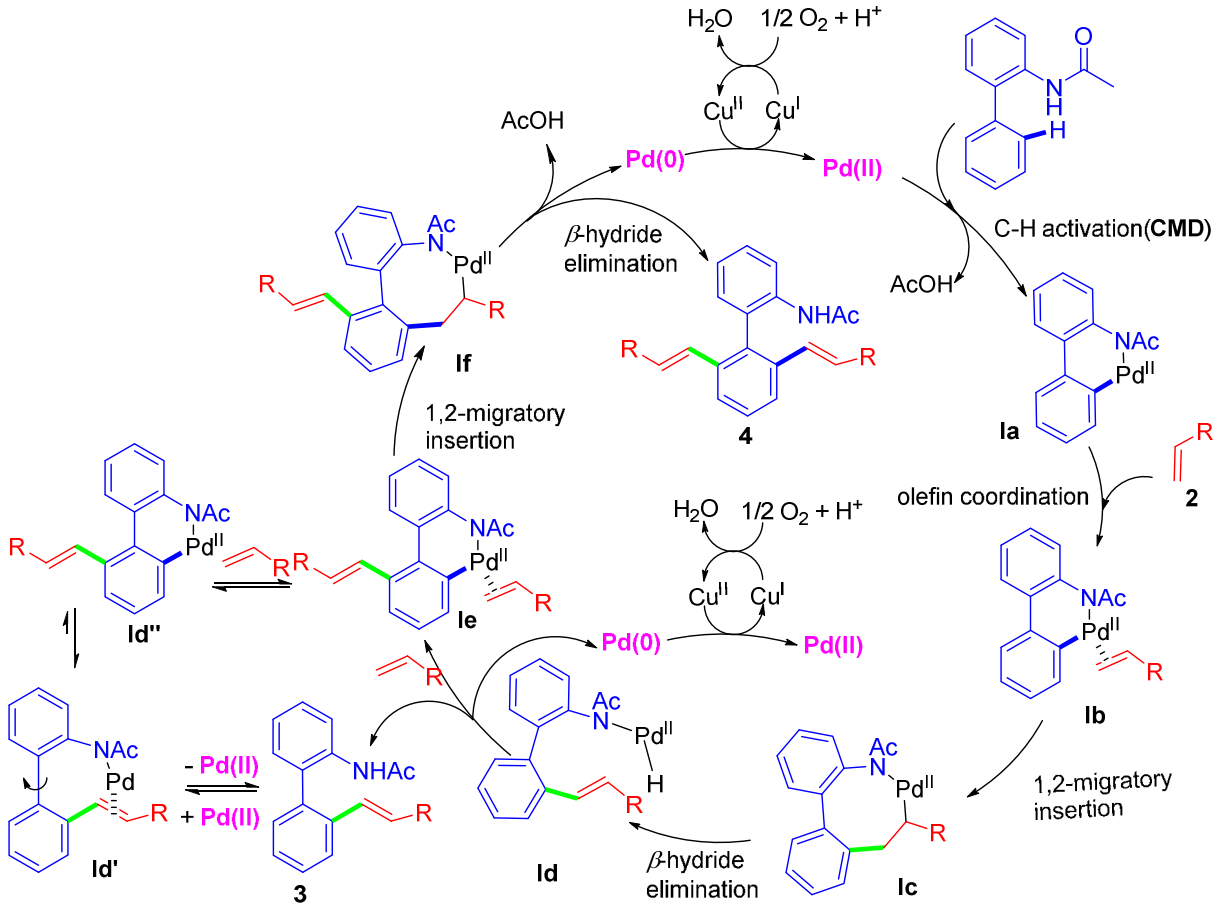
Table 10. Deuterium labeling experiments for one-pot bis-alkenylation[a]



entry	time (min)	yield (%)	mono : di	**1a**/**1a**-d_5	**3a**/**3a**-d_4 (KIE_1)	**4a**/**4a**-d_3 (KIE_2)
1[a]	5	7	100:trace	0.96	1.78	-
2	10	41	90:10	0.55	1.44	3.56
3	20	66	82:18	0.49	1.08	2.64

[a] The reaction was conducted with 5 mol% of $Pd(OAc)_2$.

A tentative yet plausible mechanism involving two sequential *ortho* C–H bond activations and alkene insertions is presented in Scheme 2. Initially, the *ortho* C–H on the bottom ring at the C-2' position was activated to yield intermediate **Ib** after coordination of substrate **1** with Pd(II). Coordination and insertion of alkenes **2** to intermediate **Ia** produced a seven-membered palladacycle intermediate **Id**. β-Hydride elimination and dissociation of the Pd(II)-N bond led to the formation of mono-alkenylated product **3**. Then, the regenerated Pd(II) was used for the next *ortho* C–H activation, insertion of olefins, and reductive elimination sequence to yield the bis-alkenylated product **4**. Because *t*-amylOH is stronger coordinating than TFEOH, it breaks down a coordination complex **Id'** to facilitate carbon-carbon bond rotation. Thereby, it forms a complex **Id″** after second *ortho* C-H activation and proceeds toward second alkenylation. However, a reaction with TFEOH as a solvent will primarily proceed up to intermediate **Id'**, thus limiting its progress toward second alkenylation.



Scheme 2. Proposed catalytic cycle for alkenylation.

CONCLUSION

In conclusion, directing-group-assisted sequential mono- and bis-alkenylation was achieved through a synthetically important direct dehydrogenative coupling strategy with *N*-acyl 2-aminobiaryl as a substrate with activated and unactivated olefins. We controlled the selectivity of mono- and bis-alkenylation products through the solvent. The developed protocol is promising for a wide substrate scope under a simple and efficient catalytic system.

EXPERIMENTAL SECTION

General. Infrared analysis was recorded on a FT-IR spectrophotometer. ^{1}H NMR data was recorded on a 300 or 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported with reference to either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CHCl_3$ (δH = 7.26 ppm). ^{13}C NMR data was recorded on a 75 or 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δC = 77.00 ppm]. High-resolution mass values (HR-MS) were measured on Q-TOF electron spray ionization (ESI) mode. All chemicals were used as purchased unless otherwise mentioned. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use.

General procedure for the synthesis of 2-aminobiaryls. Arylboronic acid (3.20 mmol), K_2CO_3 (10.8 mmol), and $PdCl_2(PPh_3)_2$ (10 mol %) were added to DMF/H_2O (13 mL/3 mL) in a flame-dried round-bottom flask containing 2-bromoaniline (2.70 mmol) . The resulting mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere. After completion of the reaction, the reaction mixture was allowed to cool down to room temperature and was extracted several times with CH_2Cl_2. The combined organic layer was washed twice with saturated NaCl and dried over anhydrous Na_2SO_4. The organic layer was then concentrated under vacuum, and

the crude residue was purified using flash silica gel column chromatography (hexanes/EtOAc) to produce the coupling product 2-aminobiaryl.

General procedure for the synthesis of *N*-acetyl-2-aminobiaryls (1a−1r). Pyridine (0.88 mL, 11 mmol) and acetyl chloride (0.78 mL, 11 mmol) were added to a solution of 2-aminobiaryls (1.691 g, 10 mmol) in CH_2Cl_2 (50 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was heated to room temperature and stirred until the completion of the reaction. The solvent was removed *in vacuo*. The residue was diluted with H_2O (15 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine (40 mL), dried over anhydrous sodium sulfate, and concentrated. The residue was purified using column chromatography on silica gel with ethyl acetate and hexanes as eluents to form *N*-acetyl-2-aminobiaryls.

General procedure for mono-alkenylation of *N*-acetyl-2-aminobiaryl 1 with alkene 2. Compound **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), $Cu(OAc)_2$ (0.3 mmol, 54.5 mg), and a stir bar were added to 1.5 mL of TFEtOH in a sealed tube containing N-acetyl-2-aminobiaryls. The tube was closed with a septum and O_2 (1 atm) gas was purged for 1 min. Then, alkene **2** (0.45 mmol) in 0.5 mL TFEtOH was injected into the tube with a syringe. Then, the septum was removed and the tube was sealed with a Teflon cap. The mixture was heated for 24 h at 120 °C. Upon completion of the reaction, the mixture was cooled down to room temperature and diluted with ethyl acetate before filtration through a thin pad of celite. The filtrate was concentrated by vacuum and the crude residue was purified by silica gel column chromatography (hexanes/EtOAc) to yield product **3**.

Spectroscopic and physical data of 3 (*E*)-methyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (3a). Yield 72% (64 mg); white solid; m.p. 138−140 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, *J* = 6.8 Hz, 1H), 7.73−7.71 (m, 1H), 7.43−7.36 (m, 4H), 7.26−7.25 (m, 1H), 7.15−7.10 (m, 2H), 6.74 (br, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.66 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.8, 142.1, 138.3, 135.3, 133.4, 131.0, 130.5, 130.4, 129.7, 129.0, 128.7, 126.9, 124.3, 121.8, 119.6, 51.7, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{18}H_{17}NO_3$ (M^+) 295.1208, found 295.1207.

(*E*)-methyl 3-(2'-acetamido-3',4',5',6'-*d*$_4$-[1,1'-biphenyl]-2-yl)acrylate (3a-*d*$_4$). Isolated yield 48% (42 mg); white solid; m.p. 134−136 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.44−7.42 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 6.71 (br, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 1.92 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.8, 142.0, 138.2, 135.3, 133.3, 130.5, 129.9 (t, *J* = 24.6 Hz), 129.6, 129.1, 128.3 (t, *J* = 24.7 Hz), 126.6 (t, *J* = 22.4 Hz), 124.3, 121.7, 119.7, 51.7, 24.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{18}H_{14}D_4NO_3^+$ $[M+H]^+$ 300.1532, found 300.1532.

(*E*)-ethyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (3b).
Yield 67% (62 mg); white solid; m.p. 116−118 °C; R_f = 0.46 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.78−7.75 (m, 1H), 7.50−7.39 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.72 (br, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.92 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.4, 141.9, 138.3, 135.3, 133.5, 131.1, 131.0, 130.4, 130.0, 129.1, 128.8, 126.9, 124.2, 121.7, 120.1, 60.5, 24.6, 14.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1698, 1639 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{19}NO_3$ (M^+) 309.1365, found 309.1364.

(*E*)-butyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (3c).
Yield 64% (65 mg); white solid; m.p. 96−98 °C; R_f = 0.28 (hexanes/EA = 5 : 2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.78−7.76 (m, 1H), 7.46−7.30 (m, 5H), 7.18−7.13 (m, 2H), 6.85 (br, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.91 (s, 3H), 1.62−1.57 (m, 2H), 1.37−1.30 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.0, 166.4, 141.8, 138.3, 135.3, 133.3, 130.9, 130.5, 130.3, 129.6, 128.9, 128.7, 126.7, 124.1, 121.7, 119.9, 64.3, 30.5, 24.4, 19.0, 13.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1707, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{21}H_{23}NO_3$ (M^+) 337.1678, found 337.1677.

(*E*)-methyl 3-(2'-acetamido-4-methyl-[1,1'-biphenyl]-2-yl)acrylate (3d). Yield 65% (60 mg); white solid; m.p. 164−166 °C; R_f = 0.36 (hexanes/EA = 3 : 1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.56 (s, 1H), 7.41−7.36 (m, 2H), 7.30 (d, *J* = 7.2, 1H), 7.18−7.10 (m, 3H), 6.79 (br, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.69 (s, 3H), 2.44 (s, 3H), 1.91 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.0, 166.8, 142.2, 138.5, 135.4, 133.1, 131.3, 130.9, 130.6, 129.5, 128.9, 127.4, 124.1, 121.5, 119.3, 51.6, 24.5, 21.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1703, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{19}NO_3$ (M^+) 309.1365, found 309.1367.

(*E*)-methyl 3-(2'-acetamido-5-methyl-[1,1'-biphenyl]-2-yl)acrylate (3e). Yield 57% (53 mg); white solid; m.p. 180−182 °C; R_f = 0.38 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.41−7.34 (m, 2H), 7.26−7.24 (m, 1H), 7.18−7.08 (m, 3H), 6.71 (br, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H), 2.39 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 167.0, 142.0, 141.0, 138.3, 135.3, 131.7, 130.5, 130.4, 129.7, 129.0, 126.9, 124.2, 121.5, 118.7, 51.7, 24.6, 21.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{19}NO_3$ (M^+) 309.1365, found 309.1367.

(*E*)-ethyl 3-(2'-acetamido-5-chloro-[1,1'-biphenyl]-2-yl)acrylate (3f). Yield 56% (58 mg); white solid; m.p. 134−136 °C; R_f = 0.33 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.40−7.38 (m, 2H), 7.32−7.24 (m, 2H), 7.17−7.16 (m, 1H), 7.09 (d, *J* = 6.8 Hz, 1H), 6.73 (br, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.13 (q, *J* = 6.9 Hz, 2H), 1.91 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.1, 140.7, 140.0, 136.1, 135.1, 131.9, 131.0, 130.3, 129.4, 128.9, 128.8, 128.1, 124.5, 122.4, 120.4, 60.6, 24.4, 14.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1713, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{18}ClNO_3$ (M^+) 343.0975, found 343.0977.

(*E*)-methyl 3-(2'-acetamido-5-fluoro-[1,1'-biphenyl]-2-yl)acrylate (3g) + *(E)*-methyl 3-(2'-acetamido-3-fluoro-[1,1'-biphenyl]-2-yl)acrylate (3g'). Yield 52% (48 mg); white solid; m.p. 96−98 °C; R_f = 0.31 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (s, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.41−7.38 (m, 4H), 7.32 (d, *J* = 16.0 Hz, 1H), 7.30−7.07 (m, 6H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.83 (br, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.672 (s, 3H), 3.665 (s, 3H), 1.91 (s, 6H) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1719, 1637 cm^{-1}; HRMS (ESI^+), calcd for $C_{18}H_{16}FNO_3$ (M^+) 313.1114, found 313.1114.

(*E*)-methyl 3-(2'-acetamido-6-chloro-[1,1'-biphenyl]-2-yl)acrylate (3h). Yield 53% (52 mg); white solid; m.p. 126−128 °C; R_f = 0.31 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.24−7.17 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.84 (br, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 1.88 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 166.3, 141.5, 136.5, 136.2, 135.5, 135.1, 130.9, 130.3, 129.6, 129.4, 127.0, 125.2, 124.4, 122.2, 120.6, 51.6, 24.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1637 cm^{-1}; HRMS (ESI^+), calcd for $C_{18}H_{16}ClNO_3$ (M^+) 329.0819, found 329.0820.

(*E*)-ethyl 3-(2'-acetamido-3,5-difluoro-[1,1'-biphenyl]-2-yl)acrylate (3i). Yield 75% (78 mg); white solid; m.p. 110−112 °C; R_f = 0.39 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.30−7.21 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.00−6.96 (m, 1H), 6.71 (br, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 165.8, 162.6 (dd, $^1J_{FC}$ = 249.1 Hz, $^3J_{FC}$ = 13.1 Hz), 160.4 (dd, $^1J_{FC}$ = 264.7 Hz, $^3J_{FC}$ = 13.7 Hz), 139.8, 137.4, 136.0, 131.4, 129.9, 124.8, 122.9, 122.4, 122.0 (d, $^2J_{FC}$ = 17.1 Hz), 109.5 (dd, $^2J_{FC}$ = 22.2 Hz, $^4J_{FC}$ = 3.3 Hz), 105.2 (dd, $^2J_{FC}$= 24.5 Hz, $^2J_{FC}$ = 22.8 Hz), 60.8, 24.3, 14.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1712, 1617 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{17}F_2NO_3$ (M^+) 345.1178, found 345.1175.

(*E*)-methyl 3-(2'-acetamido-4,5'-dimethyl-[1,1'-biphenyl]-2-yl)acrylate (3j). Yield 52% (50 mg); white solid; m.p. 194−196 °C; R_f = 0.39 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.55 (s, 1H), 7.40 (d, *J* = 16.2 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 7.21−7.15 (m, 2H), 6.91 (s, 1H), 6.38 (br, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 3.70 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.9, 142.4, 138.4, 135.8, 133.8, 133.0, 132.9, 131.3, 131.0, 129.8, 129.5, 127.3, 121.8, 119.2, 51.6, 24.4, 21.2, 20.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1638 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{21}NaNO_3^+$ $[M+Na]^+$ 346.1414, found 346.1414.

(*E*)-ethyl 3-(2'-acetamido-4-methoxy-5'-methyl-[1,1'-biphenyl]-2-yl)acrylate (3k). Yield 55% (59 mg); white solid; m.p. 122−124 °C; R_f = 0.47 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 16.0 Hz, 1H), 7.23−7.18 (m, 3H), 7.03−7.00 (m, 1H), 6.91 (s, 1H), 6.68 (br, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.33 (s, 3H), 1.90 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.4, 159.5, 142.1, 134.4, 133.8, 133.1, 132.2, 131.3, 131.0, 129.5, 129.4, 121.7, 120.0, 116.6, 111.2, 60.5, 55.4, 24.5, 20.8, 14.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1708, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{21}H_{23}NO_4$ (M^+) 353.1627, found 353.1626.

(*E*)-methyl 3-(2'-acetamido-5'-chloro-[1,1'-biphenyl]-2-yl)acrylate (3l). Yield 67% (66 mg); white solid; m.p. 180−182 °C; R_f = 0.32 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, *J* = 8.8 Hz, 1H), 7.75−7.73 (m, 1H), 7.50−7.47 (m, 2H), 7.38−7.33 (m, 2H), 7.26−7.24 (m, 1H), 7.12 (s, 1H), 6.65 (br, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 1.89 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.6, 141.4, 136.9, 134.1, 133.3, 131.2, 131.0, 130.6, 130.0, 129.3, 129.2, 129.1, 127.0, 122.8, 120.2, 51.8, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1710, 1631 cm^{-1}; HRMS (ESI^+), calcd for $C_{18}H_{16}ClNO_3$ (M^+) 329.0819, found 329.0820.

(*E*)-methyl 3-(2'-acetamido-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)acrylate (3m). Yield 69% (79 mg); white solid; m.p. 126−128 °C; R_f = 0.38 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 8.8 Hz, 1H), 7.79−7.77 (m, 1H), 7.53−7.50 (m, 2H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.31−7.28 (m, 2H), 7.03 (s, 1H), 6.70 (br, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 1.94 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.6, 144.9, 141.3, 136.6, 134.1, 133.4, 131.0, 130.9, 130.6, 129.4, 127.2, 123.1, 123.0, 121.7, 120.5 (q, $^1J_{FC}$ = 256.0 Hz), 120.4, 51.8, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{16}F_3NO_4$ (M^+) 379.1031, found 379.1031.

(*E*)-methyl 3-(2'-acetamido-4-methyl-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl) acrylate (3n). Yield 68% (80 mg); white solid; m.p. 134−136 °C; R_f = 0.39 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 8.8 Hz, 1H), 7.53 (s, 1H), 7.32−7.20 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.80 (br, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.65 (s, 3H), 2.40 (s, 3H), 1.88 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 166.6, 144.8, 141.5, 139.3, 134.2, 133.8, 133.1, 131.5, 131.0, 130.7, 127.6, 123.2, 122.8, 121.4, 120.4 (q, $^1J_{FC}$ = 255.9 Hz), 119.9, 51.7, 24.4, 21.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1698, 1639 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{18}F_3NO_4$ (M^+) 393.1188, found 393.1190.

(*E*)-methyl 3-(2'-acetamido-4-methoxy-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl) acrylate (3o). Yield 63% (77 mg); white solid; m.p. 70−72 °C; R_f = 0.31 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, *J* = 8.8 Hz, 1H), 7.30−7.14 (m, 4H), 7.02−7.00 (m, 1H), 6.94 (s, 1H), 6.88 (br, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.66 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 166.5, 160.0, 144.8, 141.5, 134.5, 134.4, 132.0, 130.8, 129.0, 123.4, 122.9, 121.7, 120.4 (q, $^1J_{FC}$ = 256.3 Hz), 120.2, 116.6, 111.7, 55.4, 51.7, 24.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1697, 1638 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{18}F_3NO_5$ (M^+) 409.1137, found 409.1137.

(*E*)-methyl 3-(2'-acetamido-5-fluoro-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)acrylate (3p) + (*E*)-methyl 3-(2'-acetamido-3-fluoro-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl) acrylate (3p'). Yield 67% (80 mg); white solid; m.p. 122−124 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28−8.26 (m, 2H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.30−7.19 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03−7.01(m, 2H), 6.79 (br, 2H), 6.48 (d, *J* = 16.4 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 1.94 (s, 6H) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1722, 1638 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{15}F_4NO_4$ (M^+) 397.0937, found 397.0937.

(*E*)-methyl 3-(2'-acetamido-5-chloro-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl) acrylate (3q). Yield 62% (77 mg); white solid; m.p. 164−166 °C; R_f = 0.33 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.47−7.45 (m, 3H), 7.30 (s, 1H), 7.00 (s, 1H), 6.77 (br, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 1.94 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 166.4, 145.1, 140.2, 138.3, 136.5, 133.9, 131.8, 130.8, 130.1, 129.6, 128.4, 123.7, 122.9, 122.0, 120.7,

120.4 (q, $^1J_{FC}$ = 256.3 Hz), 51.9, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1727, 1639 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{15}ClF_3NO_4$ (M^+) 413.0642, found 413.0640.

(*E*)-methyl3-(1-(2-acetamido-5-methylphenyl)naphthalen-2-yl)acrylate (3r). Yield 84% (91 mg); white solid; m.p. 168−170 °C; R_f = 0.13 (hexanes/EA = 3 : 1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.94−7.88 (m, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.56−7.47 (m, 2H), 7.44−7.40 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 6.94 (br, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.47 (m, 1H), 3.71 (s, 3H), 2.36 (s, 3H), 1.69 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 167.0, 142.2, 136.5, 134.2, 133.9, 133.8, 132.4, 131.5, 130.9, 130.0, 129.1, 128.1, 127.5, 127.4, 126.83, 126.75, 122.9, 121.6, 119.7, 51.7, 24.4, 20.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1630 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{21}NO_3$ (M^+) 359.1521, found 359.1522.

(*E*)-butyl 3-(1-(2-acetamido-5-methylphenyl)naphthalen-2-yl)acrylate (3s). Yield 87% (105 mg); white solid; m.p. 142−144 °C; R_f = 0.23 (hexanes/EA = 3 : 1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.93−7.82 (m, 3H), 7.55−7.47 (m, 2H), 7.42−7.40 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 6.94 (br, 1H), 6.51−6.45 (m, 2H), 4.12−4.08 (m, 2H), 2.36 (s, 3H), 1.65 (s, 3H), 1.62−1.55 (m, 2H), 1.40−1.28 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.0, 166.54, 142.0, 136.5, 134.1, 133.8, 133.7, 132.3, 131.5, 131.0, 129.9, 129.1, 128.1, 127.4, 127.3, 126.8, 126.7, 122.8, 121.5, 120.0, 64.3, 30.6, 24.3, 20.8, 19.1, 13.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1710, 1630 cm^{-1}; HRMS (ESI^+), calcd for $C_{26}H_{27}NO_3$ (M^+) 401.1991, found 401.1989.

(*E*)-methyl 3-(5-(2-acetamidophenyl)furan-2-yl)acrylate (3t'). Yield 49% (42 mg); light brown solid; m.p. 128−130 °C; R_f = 0.21 (hexanes/EA = 2 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38−8.22 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 15.6 Hz, 1H), 7.36−7.32 (m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.74−6.69 (m, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 167.1, 154.6, 150.4, 134.4, 130.5, 129.7, 127.7, 124.6, 123.0, 119.8, 117.0, 115.1, 110.7, 51.8, 25.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 1636 cm^{-1}; HRMS (ESI^+), calcd for $C_{16}H_{15}NO_4$ (M^+) 285.1001, found 285.1002.

(*E*)-methyl 3-(5-(2-acetamidophenyl)thiophen-2-yl)acrylate (3u'). Yield 51% (46 mg); yellow solid; m.p. 118−120 °C; R_f = 0.25 (hexanes/EA = 2 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.55 (br, 1H), 7.43−7.33 (m, 2H), 7.24−7.23 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08−7.07 (m, 1H), 6.21 (d, 15.6 Hz, 1H), 3.77 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.5, 167.0, 142.5, 140.3, 136.7, 134.7, 131.5, 130.4, 130.2, 129.5, 127.6, 124.9, 123.2, 116.9, 51.7, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1715, 1621 cm^{-1}; HRMS (ESI^+), calcd for $C_{16}H_{15}NO_3S$ (M^+) 301.0773, found 301.0774.

General procedure for mono-alkenylation of 3 with alkenes 2 under condition A. To a sealed tube containing **3** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), $Cu(OAc)_2$ (0.1 mmol, 18.2 mg) and a stir bar was added 0.5 mL of *t*-amylOH. The tube was closed with septum and purged O_2 (1atm) gas for 1 min. Then alkenes **2** (0.3 mmol) in 0.5 mL *t*-amylOH was injected into the tube with a syringe. Further, septum was removed and sealed with a Teflon cap. The mixture was heated for 14 h at 120 °C. Upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated by vacuum and crude residue was purified by silica gel column chromatography (hexanes/EtOAc) to afford products **4**.

General procedure for bis-alkenylation of *N*-acetyl-2-aminobiaryls 1 with alkenes 2 under condition B. To a sealed tube containing *N*-acetyl-2-aminobiaryls **1** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), $Cu(OAc)_2$ (0.1 mmol, 18.2 mg) and a stir bar was added 0.5 mL of *t*-amylOH. The tube was closed with septum and purged O_2 (1atm) gas for 1 min. Then alkenes **2** (0.3 mmol) in 0.5 mL *t*-amylOH was injected into the tube with a syringe. Further, septum was removed and sealed with a Teflon cap. The mixture was heated for 14 h at 120 °C. Upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated by vacuum and crude residue was purified by silica gel column chromatography (hexanes / EtOAc) to afford products **4**.

Spectroscopic and physical data of 3

(*E*)-methyl 3-(2-(2-acetamidophenyl)thiophen-3-yl)acrylate (3u). Yield: condition B 50% (15 mg); white solid; m.p. 164−166 °C; R_f = 0.25 (hexanes/EA = 2 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.45−7.41 (m, 2H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.29 (d, *J* = 16.0 Hz, 1H), 7.26−7.23 (m, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.08 (br, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 1.98 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 167.1, 140.5, 136.3, 136.2, 134.9, 131.7, 130.2, 127.1, 125.6, 124.2, 122.1, 121.9, 118.9, 51.7, 24.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1701, 1630 cm^{-1}; HRMS (ESI^+), calcd for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0845.

Spectroscopic and physical data of 4

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (4a). Yield: Condition A 76% (29 mg), condition B 64% (24 mg); white solid; m.p. 160−162 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, *J* = 6.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.51−7.44 (m, 2H), 7.27−7.20 (m, 3H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.56 (br, 1H), 6.31 (d, *J* = 16.0 Hz, 2H), 3.67 (s, 6H), 1.84 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.5, 141.7, 138.1, 135.8, 134.9, 130.7, 129.8, 129.1, 128.3, 126.4, 124.5, 121.9, 120.5, 51.7, 24.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1633 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{21}NO_5$ (M^+) 379.1420, found 379.1420.

(2*E*,2'*E*)-diethyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (4b). Yield: Condition A 65% (26 mg), condition B 67% (27 mg); white solid; m.p. 118−120 °C; R_f = 0.39 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.52−7.44 (m, 2H), 7.27 (d, *J* = 16.0 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 6.8 Hz, 1H), 6.50 (br, 1H), 6.32 (d, *J* = 16.0 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 1.86 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 166.11, 141.5, 138.0, 135.8, 135.0, 130.7, 129.8, 129.1, 128.1, 126.2, 124.3, 121.7, 120.9, 60.6, 24.6, 14.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1712, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{26}NO_5$ $[M+H]^+$ 408.1806, found 408.1805.

(2*E*,2'*E*)-dibutyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (4c). Yield: Condition A 77% (36 mg), condition B 73% (34 mg); red oil; R_f = 0.55 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.53−7.44 (m, 2H), 7.30−7.19 (m, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.45 (br, 1H), 6.33 (d, *J* = 16.0 Hz, 2H), 4.09 (t, *J* = 6.6 Hz, 4H),

1.86 (s, 3H), 1.61−1.54 (m, 4H), 1.36−1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 166.2, 141.4, 138.1, 135.9, 135.0, 130.6, 129.7, 129.1, 128.1, 126.1, 124.3, 121.5, 120.9, 64.5, 30.5, 24.6, 19.1, 13.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1711, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{28}H_{34}NO_5$ $[M+H]^+$ 464.2432, found 464.2431.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (4d). Yield: Condition A 77% (36 mg), condition B 73% (34 mg); white solid; m.p. 168−170 °C; R_f = 0.22 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.29 (d, J = 7.6 Hz, 1H), 7.55 (s, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.24−7.17 (m, 3H), 6.97 (d, J = 6.4 Hz, 1H), 6.50 (br, 1H), 6.28 (d, J = 16.0 Hz, 2H), 3.66 (s, 6H), 2.44 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.6, 141.8, 138.9, 135.9, 135.3, 134.7, 130.8, 129.7, 129.1, 126.2, 124.4, 121.6, 120.3, 51.7, 24.6, 21.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{24}NO_5$ $[M+H]^+$ 394.1649, found 394.1651.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-3-methyl-[1,1'-biphenyl]-2,6-diyl)diacrylate (4e). Yield: Condition A 35% (14 mg), condition B 19% (7 mg); white solid, m.p. 156−158 °C; R_f = 0.26 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.29 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.44−7.35 (m, 3H), 7.23 (d, J = 16.0 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 6.8 Hz, 1H), 6.49 (s, 1H), 6.29 (d, J = 16.0 Hz, 1H), 5.69 (d, J = 16.4 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 2.37 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 166.8, 166.4, 141.8, 141.4, 139.7, 137.3, 135.5, 134.9, 132.3, 131.5, 130.5, 129.6, 127.3, 126.9, 124.4, 121.5, 119.5, 51.72, 51.70, 24.7, 21.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{24}NO_5$ $[M+H]^+$ 394.1649, found 394.1649.

(2*E*,2'*E*)-diethyl 3,3'-(2'-acetamido-3-chloro-[1,1'-biphenyl]-2,6-diyl)diacrylate (4f). Yield: Condition A 29% (12 mg), condition B 27% (16 mg); yellow oil; R_f = 0.22 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, J = 6.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.46−7.36 (m, 2H), 7.18 (d, J = 15.6 Hz, 2H), 6.98 (s, 1H), 6.58 (br, 1H), 6.29 (d, J = 16.0 Hz, 1H), 5.88 (d, J = 16.4 Hz, 1H), 4.15−4.08 (m, 4H), 1.90 (s, 3H), 1.24−1.19 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 165.9, 165.8, 140.8, 139.2, 138.6, 135.9, 135.4, 133.7, 133.6, 130.7, 130.6, 129.9, 127.7, 126.7, 126.1, 124.6, 122.3, 121.0, 60.7, 60.6, 24.5, 14.09, 14.07 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{25}ClNO_5$ $[M+H]^+$ 442.1416, found 442.1416.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-3-fluoro-[1,1'-biphenyl]-2,6-diyl)diacrylate (4g). Yield: Condition A 64% (25 mg), condition B 70% (28 mg); white solid; m.p. 180−182 °C; R_f = 0.21 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, J = 7.6 Hz, 1H), 7.72−7.70 (m, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.23−7.19 (m, 2H), 7.19 (s, 1H), 7.37 (d, J = 16.4 Hz, 1H), 6.99 (d, J = 6.4 Hz, 1H), 6.64 (br, 1H), 6.42 (d, J = 16.4 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 3.66 (s, 6H), 1.86 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.8, 166.5, 162.4 (d, $^1J_{FC}$ = 258.8 Hz), 140.9, 140.7, 135.6, 131.0, 130.6, 130.1, 129.2 (d, $^3J_{FC}$ = 10.3 Hz), 126.2, 124.7 (d, $^3J_{FC}$ = 14.0 Hz) , 122.7 (d, $^3J_{FC}$ = 11.4 Hz), 122.4, 120.1, 116.9 (d, $^2J_{FC}$ = 23.6 Hz), 51.8, 51.7, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1631 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{20}FNO_5$ (M^+) 397.1326, found 397.1327.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-4,5'-dimethyl-[1,1'-biphenyl]-2,6-diyl) diacrylate (4h). Yield: Condition A 44% (18 mg), condition B 53% (22 mg); white solid; m.p. 186−188 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.0 Hz, 1H), 7.57 (s, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.28−7.24 (m, 3H), 6.79 (s, 1H), 6.44 (br, 1H), 6.31 (d, J = 16.0 Hz, 2H), 3.69 (s, 6H), 2.46 (s, 3H), 2.33 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 166.7, 142.0, 138.7, 135.6, 134.7, 134.0, 133.5, 131.1, 130.3, 129.0, 126.4, 121.7, 120.1, 51.7, 24.5, 21.3, 20.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1631 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{26}NO_5$ $[M+H]^+$ 408.1806, found 408.1806.

(2*E*,2'*E*)-diethyl 3,3'-(2'-acetamido-4-methoxy-5'-methyl-[1,1'-biphenyl]-2,6-diyl)diacrylate (4i). Yield: Condition A 52% (24 mg), condition B 55% (25 mg); yellow oil; R_f = 0.41 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, J = 7.9 Hz, 1H), 7.28−7.23 (m, 5H), 6.80 (s, 1H), 6.54 (br, 1H), 6.31 (d, J = 16.0 Hz, 2H), 4.15 (q, J = 7.0 Hz, 4H), 3.92 (s, 3H), 2.33 (s, 3H), 1.85 (s, 3H), 1.24 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 166.1, 159.4, 141.7, 136.1, 133.8, 133.7, 131.4, 131.1, 130.2, 126.0, 121.6, 120.7, 113.3, 60.5, 55.5, 24.4, 20.8, 14.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1709, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{26}H_{30}NO_6$ $[M+H]^+$ 452.2068, found 452.2068.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-5'-chloro-[1,1'-biphenyl]-2,6-diyl)diacrylate (4j). Yield: Condition A 70% (30 mg), condition B 64% (26 mg); white solid; m.p. 224−226 °C; R_f = 0.23 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 16.0 Hz, 2H), 7.01 (s, 1H), 6.51 (br, 1H), 6.32 (d, J = 16.0 Hz, 2H), 3.70 (s, 6H), 1.86 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.4, 141.0, 136.4, 134.9, 134.6, 130.2, 129.8, 129.6, 129.4, 128.4, 127.8, 122.9, 121.1, 51.8, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1695, 1633 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{21}ClNO_5$ $[M+H]^+$ 414.1103, found 414.1109.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2,6-diyl)diacrylate (4k).
Yield: Condition A 70% (33 mg), condition B 67% (31 mg); white solid; m.p. 180−182 °C; R_f = 0.26 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 16.0 Hz, 2H), 6.91 (s, 1H), 6.62 (br, 1H), 6.32 (d, J = 16.0 Hz, 2H), 3.68 (s, 6H), 1.86 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.3, 144.9, 141.0, 136.1, 134.9, 134.6, 129.7, 128.4, 127.8, 123.5, 123.2, 122.3, 121.2, 120.4 (q, $^1J_{FC}$ = 256.1 Hz), 51.8, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1698, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{21}F_3NO_6$ $[M+H]^+$ 464.1316, found 464.1318.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-4-methyl-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2,6-diyl)diacrylate (4l).
Yield: Condition A 73% (35 mg), condition B 65% (31 mg); white solid; m.p. 164−166 °C; R_f = 0.18 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, J = 8.8 Hz, 1H), 7.54 (s, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 16.0 Hz, 2H), 6.84 (s, 1H), 6.71 (br, 1H), 6.27 (d, J = 16.0 Hz, 2H), 3.64 (s, 6H), 2.43 (s, 3H), 1.83 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.3,

144.8, 141.2, 139.5, 134.8, 134.7, 133.5, 129.1, 127.7, 123.6, 123.0, 122.2, 120.8, 120.4 (q, $^1J_{FC}$ = 256.0 Hz), 51.7, 24.4, 21.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1719, 1633 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{23}F_3NO_6$ $[M+H]^+$ 478.1472, found 478.1472.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-4-methoxy-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2,6-diyl)diacrylate (4m). Yield: Condition A 62% (31 mg), condition B 53% (26 mg); white solid; m.p. 144−146 °C; R_f = 0.18 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 6.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 2H), 7.15 (d, *J* = 15.6 Hz, 2H), 6.86 (s, 1H), 6.78 (br, 1H), 6.28 (d, *J* = 16.0 Hz, 2H), 3.89 (s, 3H), 3.65 (s, 6H), 1.85 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 166.2, 159.9, 144.7, 141.1, 136.1, 135.1, 128.8, 127.6, 123.9, 123.0, 122.1, 121.0, 120.4 (q, $^1J_{FC}$ = 256.0 Hz), 113.6, 55.5, 51.7, 24.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1710, 1635 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{23}F_3NO_7$ $[M+H]^+$ 494.1421, found 494.1421.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-3-fluoro-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2,6-diyl)diacrylate (4n). Yield: Condition A 68% (27 mg), condition B 66% (32 mg); white solid; m.p. 152−154 °C; R_f = 0.26 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.75−7.72 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31−7.26 (m, 1H), 7.15 (d, *J* = 16.0 Hz, 1H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.91 (s, 1H), 6.58 (br, 1H), 6.46 (d, *J* = 16.4 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.69 (s, 6H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.5, 166.2, 162.4 (d, $^1J_{FC}$ = 259.2 Hz), 145.1, 140.2, 138.5, 134.8, 134.4, 131.0, 129.4 (d, $^3J_{FC}$ = 10.3 Hz), 127.5, 125.4 (d, $^3J_{FC}$ = 13.7 Hz), 123.7, 123.4, 122.9, 122.8, 120.9, 120.4 (q, $^1J_{FC}$ = 256.5 Hz), 117.6 (d, $^2J_{FC}$ = 23.5 Hz), 51.87, 51.86, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1718, 1631 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{19}F_4NO_6$ (M^+) 481.1149, found 481.1149.

(2*E*,2'*E*)-dimethyl 3,3'-(2'-acetamido-3-chloro-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2,6-diyl)diacrylate (4o). Yield: Condition A 33% (14 mg), condition B 20% (8 mg); white solid; m.p. 138−140 °C; R_f = 0.21 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.36−7.29 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 6.86 (s, 1H), 6.83 (br, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 5.85 (d, *J* = 16.4 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 1.89 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 166.2, 165.9, 145.0, 140.4, 138.5, 137.3, 136.1, 134.2, 133.8, 133.4, 131.1, 128.3, 127.9, 126.1, 124.0, 123.5, 122.5, 121.2, 120.4 (q, $^1J_{FC}$ = 256.3 Hz), 51.84, 51.3, 24.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1670, 1638 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{20}ClF_3NO_6$ $[M+H]^+$ 498.0926, found 498.0926.

(2*E*,2'*E*)-dimethyl 3,3'-(5-(2-acetamidophenyl)furan-2,4-diyl)diacrylate (4p). Yield: Condition A 59% (22 mg), condition B 24% (9 mg); white solid; m.p. 180−178 °C; R_f = 0.16 (hexanes/EA = 2 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, *J* = 7.2 Hz, 1H), 7.82 (s, 1H), 7.47−7.42 (m, 3H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.26−7.23 (m, 1H), 6.89 (s, 1H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 166.83, 166.79, 153.9, 151.0, 136.0, 133.9, 131.1, 130.8, 130.1, 124.6, 123.1, 121.9, 119.8, 119.1, 117.3, 113.2, 51.9, 51.8, 24.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 1637 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{20}NO_6$ $[M+H]^+$ 370.1285, found 370.1285.

(2*E*,2'*E*)-dimethyl 3,3'-(5-(2-acetamidophenyl)thiophene-2,4-diyl)diacrylate (4q). Yield: Condition A 65% (25 mg), condition B 9% (3 mg); white solid; m.p. 178−180 °C; R_f = 0.16 (hexanes/EA = 2 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.49−7.44 (m, 2H), 7.26−7.18 (m, 3H), 7.06 (br, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 15.6 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.01 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 166.9, 166.7, 142.7, 140.3, 136.1, 135.6, 135.5, 131.5, 130.7, 128.7, 124.5, 122.6, 121.9, 119.7, 118.6, 51.9, 51.8, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1717, 1626 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{19}NO_5S$ (M^+) 385.0984, found 385.0986.

(*E*)-ethyl 3-(2'-acetamido-5'-chloro-6-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)acrylate (4r). Yield: Condition A 65% (28 mg); white solid, m.p. 168−170 °C; R_f = 0.28 (hexanes/EA = 1 : 1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.78−7.76 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45−7.42 (m, 1H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.22 (d, *J* = 16.0 Hz, 1H), 7.02 (s, 1H), 6.48 (br, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 1.86 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 166.4, 165.9, 141.1, 140.8, 136.4, 135.0, 134.9, 134.6, 130.2, 129.8, 129.6, 129.4, 128.3, 127.7, 122.8, 121.5, 121.1, 60.7, 51.8, 24.5, 14.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1705, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{23}ClNO_5$ $[M+H]^+$ 428.1259, found 428.1259.

General procedure for thebis-alkenylation of *N*-acetyl-2-aminobiaryl 1 with different alkenes 2 . To a sealed tube containing *N*-acetyl-2-aminobiaryl **1** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), $Cu(OAc)_2$ (0.1 mmol, 18.2 mg) and a stir bar was added 0.5 mL of *t*-amylOH. The tube was closed with septum and purged O_2 (1atm) gas for 1 min. Then alkenes **2** (0.3 mmol) in 0.5 mL *t*-amylOH was injected into the tube with a syringe. Further, septum was removed and sealed with a Teflon cap. The mixture was heated for 14 h at 120 °C. Upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate followed by filtration through a thin pad of celite. The filtrate was concentrated by vacuum and crude residue was purified by silica gel column chromatography (hexanes / EtOAc) to afford products **5/6**.

(*E*)-cyclohexyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (5a). Yield 17% (6.1 mg); white solid; m.p. 102−104 °C; R_f = 0.33 (hexanes/EA/DCM = 1:5:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.37−7.45 (m, 4H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.11−7.19 (m, 2H), 6.76 (m, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.76−4.80 (m, 1H), 1.90 (s, 3H), 1.77-1.80 (m, 2H), 1.63−1.64 (m, 2H), 1.23−1.50 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 165.8, 141.6, 138.3, 135.4, 133.4, 130.9, 130.5, 130.2, 129.7, 128.9, 128.7, 126.7, 124.1, 121.7, 120.5, 72.6, 31.4, 25.3, 24.5, 23.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1707, 1634cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{26}NO_3$ $[M+H]^+$ 364.1913, found 364.1919 .

(2*E*,2'*E*)-dicyclohexyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (6a). Yield 53% (27.3 mg); white solid; m.p. 134−136 °C; R_f = 0.22 (hexanes/EA/DCM = 1:5:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, *J* = 6.8 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.39−7.46 (m, 2H), 7.16−7.22 (m, 3H), 6.98−6.99 (m, 2H), 6.62 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.70−4.73 (m, 2H), 1.86 (s, 3H), 1.73−1.81 (m, 4H), 1.57−1.58 (m, 4H), 1.22-1.45 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 165.5, 141.3, 138.1, 136.0, 134.9, 130.7, 129.5, 129.0, 127.9, 126.2, 124.1, 121.6, 121.2, 72.5, 31.5, 25.3, 24.5, 23.3, ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1708, 1633 cm^{-1}; HRMS (ESI^+), calcd for $C_{32}H_{38}NO_5$ $[M+H]^+$ 516.2750, found 516.2759.

(*E*)-benzyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (5b). Yield 15% (5.6 mg); pale yellow solid; m.p. 102−105 °C; R_f = 0.32 hexanes/EA/DCM = 1:3 :1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.41−7.50 (m, 4H), 7.29−7.36 (m, 6H), 7.12−7.20 (m, 2H), 6.72 (s, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.15 (s, 2H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.0, 142.4, 138.4, 135.8, 135.3, 133.2, 130.9, 130.5, 130.4, 129.5 ,129.0, 128.7, 128.4, 128.0, 127.9, 126.8, 124.2, 121.7, 119.5, 66.2, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1712, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{22}NO_3$ $[M+H]^+$ 372.1598, found 372.1604.

(2*E*,2'*E*)-dibenzyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (6b). Yield 62% (33 mg); light yellow solid; m.p. 50−55 °C; R_f = 0.2 (hexanes/EA =1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.48−7.51 (m, 2H), 7.21−7.37 (m, 13H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.47 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 2H), 5.14 (s, 4H), 1.85 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 165.8, 142.0, 138.2, 135.9, 135.8, 134.8, 130.7, 129.7, 129.1, 128.5, 128.2, 128.1, 127.9, 126.2, 124.4, 121.7, 120.5, 66.2, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1712, 1632 cm^{-1}; HRMS (ESI^+), calcd for $C_{34}H_{29}NO_5Na$ $[M+Na]^+$ 554.1943, found 554.1939.

(*E*)-phenyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (5c). Yield 13% (4.6 mg); white solid; m.p. 54−56 °C; R_f = 0.45 (hexanes/EA = 3:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.42-7.51 (m, 2H), 7.26−7.41 (m, 4H), 7.15−7.22 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 1.93 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 164.8, 150.6, 143.9, 138.7, 135.3, 133.2, 131.1, 130.8, 130.6, 129.8, 129.3, 129.2, 128.8, 127.1, 125.7, 124.4, 122.2, 121.5, 119.1, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1727, 1695 cm^{-1}; HRMS (ESI^+), calcd for $C_{23}H_{20}NO_3$ $[M+H]^+$ 358.1443, found 358.1437.

(2*E*,2'*E*)-diphenyl 3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (6c). Yield 39% (19.6 mg); white solid; m.p. 124−126 °C; R_f = 0.40 (hexanes/EA = 3:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, *J* = 6.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.44−7.60 (m, 4H), 7.34−7.38 (m, 4H), 7.19−7.23 (m, 3H), 7.08–7.10 (m, 5H), 6.56–6.58 (m, 2H), 6.52 (s, 1H), 1.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 164.5, 150.5, 143.5, 138.7, 135.8, 134.8, 130.8, 130.0, 129.4, 129.3, 128.7, 126.4, 125.8, 124.7, 122.5, 121.5, 120.0, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1727, 1693 cm^{-1}; HRMS (ESI^+), calcd for $C_{32}H_{25}NO_5$ Na $[M+Na]^+$ 526.1630, found 526.1632.

(*E*)-(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (5d). Yield 36% (15 mg); colorless sticky liquid; R_f = 0.45 (hexanes/EA = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.29 (*t*, *J* = 9.4 Hz, 1H), 7.78 (d, *J* = 6.4 Hz, 1H), 7.30-7.76 (m, 5H), 7.10−7.18 (m, 2H), 6.70 (m, 1H), 6.35 (dd, *J* = 16.0, 1H), 4.64−4.68 (m, 1H), 1.90 (s, 3H), 1.62−1.79 (m, 4H), 1.48−1.54 (m, 1H), 0.98−1.14 (m, 2H), 0.71−0.79 (m, 9H), ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 165.8, 141.2, 141.1, 138.3, 135.4, 135.3, 133.4, 133.39, 130.9, 130.4, 130.37, 130.3, 129.4, 129.04, 129.0, 128.8, 126.6, 126.5, 124.15, 124.1, 121.5, 121.3, 120.6, 120.5, 81.1, 81.0, 48.79, 48.76, 46.84, 46.82, 44.96, 44.95, 38.7, 38.6, 33.6, 26.9, 24.5, 20.0, 19.7, 11.34, 11.32 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1706, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{27}H_{32}NO_3$ $[M+H]^+$ 418.2382, found 418.2376.
[Note: The ^{1}H and ^{13}C NMR show a mixture of diastereomers]

(2*E*,2'*E*)-bis((1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)3,3'-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)diacrylate (6d). Yield 51% (32 mg); white solid; m.p. 138−140 °C; R_f = 0.40 (hexanes/EA = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.38−7.48 (m, 2H), 7.14−7.21 (m, 3H), 6.97 (*d*, *J* = 6.4 Hz, 1H), 6.53 (m, 1H), 6.27 (dd, *J* = 16.0, 2H), 4.59−4.61 (m, 2H), 1.81 (s, 3H), 1.59−1.75 (m, 8H), 1.44−1.50 (m, 2H), 1.00−1.10 (m, 4H), 0.65−0.75 (m, 18H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 165.5, 140.9, 140.8, 138.1, 135.96, 135.90, 134.8, 130.4, 129.6, 129.09, 127.88, 127.83, 126.1, 124.2, 121.7, 121.5, 121.3, 121.2, 81.2, 81.1, 48.73, 48.71, 46.81, 46.78, 44.92, 44.89, 38.7, 38.6, 33.6, 33.5, 26.9, 24.5, 20.0, 19.7, 11.32, 11.31 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) cm^{-1} 1708, 1635 HRMS (ESI^+), calcd for $C_{40}H_{50}NO_5$ $[M+H]^+$ 624.3689, found 624.3684.
[Note: The ^{1}H and ^{13}C NMR show a mixture of diastereomers]

(*E*)-(tetrahydrofuran-2-yl)methyl 3-(2'-acetamido-[1,1'-biphenyl]-2-yl)acrylate (5e). Yield 92% (33.6 mg); white solid; m.p. 102−104 °C; R_f= 0.33 (hexanes/EA/DCM = 1:5:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* = 3.6 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.48−7.36 (m, 4H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.11−7.18 (m, 2H), 6.76 (m, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.19−4.01 (m, 3H), 3.80−3.72 (m, 2H), 1.89 (s, 3H), 1.98−1.79 (m, 3H), 1.60−1.53 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 166.1, 142.2, 138.3, 135.2, 133.2, 130.9, 130.4, 130.3, 129.6, 128.9, 128.7, 126.7, 126.6, 124.1, 121.7, 119.4, 68.3, 66.3, 27.6, 25.6, 24.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1712, 1634 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{23}NO_4Na$ $[M+Na]^+$ 388.1525, found 388.1522.

(*E*)-*N*-(2'-styryl-[1,1'-biphenyl]-2-yl)acetamide (5f). Yield (trace); white solid; m.p. 82−84 °C; R_f= 0.51 (hexanes/EA/DCM = 1: 6:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.42−7.48 (m, 3H), 7.37−7.40 (m, 5H), 7.28-7.31 (m, 3H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.92 (s, 1H), 6.84 (d, *J* = 16.4 Hz, 1H), 1.87 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 136.9, 136.5, 136.0, 135.4, 131.0, 130.6, 130.5, 128.7 (3C), 128.1, 127.9, 126.6 (2C), 125.9, 125.4, 124.2, 121.5, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1682, 1582 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{20}NO$ $[M+H]^+$ 314.1545, found 314.1567.

***N*-(2',6'-di((*E*)-styryl)-[1,1'-biphenyl]-2-yl)acetamide (6f).** Yield 55% (22.8 mg); white solid; m.p. 192−194 °C; R_f = 0.43 (hexanes/EA/DCM = 1:6:2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.42−7.47 (m, 2H), 7.12−7.253 (m, 13H), 7.04 (d, *J* = 16.0 Hz, 2H), 6.82 (s, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 1.79 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 136.9, 136.7, 135.8, 134.5, 131.0, 130.4, 128.8, 128.6, 128.4, 127.8, 127.7, 126.4, 125.9, 124.5, 123.9, 121.1, 24.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683, 1598 cm^{-1}; HRMS (ESI^+), calcd for $C_{30}H_{26}NO$ $[M+H]^+$ 416.2014, found 416.2009.

(*E*)-*N*-(2'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl)acetamide (5g). Yield 44% (17 mg); colorless oil; R_f = 0.28 (hexanes/EA = 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.56−7.61 (m, 2H), 7.45−7.51 (m, 3H), 7.25−7.42 (m, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 6.74 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 140.1, 140.0, 138.6, 135.1, 133.3, 131.3, 131.1, 131.0, 130.3, 129.4, 129.2,

129.2 (2C), 128.7, 127.5 (2C), 124.3, 121.9, 24.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1677, 1443, 1304 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{20}NO_3S$ $[M+H]^+$ 378.1164, found 378.1163.

***N*-(2',6'-bis((*E*)-2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-yl)acetamide (6g).** Yield 30% (16 mg); white solid; m.p. 122−124 °C; R_f = 0.11 (hexanes/EA = 1:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 4H), 7.58−7.65 (m, 4H), 7.42−7.52 (m, 6H), 7.18−7.26 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 15.6 Hz, 2H), 6.50 (s, 1H), 1.86 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 139.8, 139.6, 138.7, 135.8, 133.6, 133.2, 130.7, 130.4, 129.5, 129.4, 129.3, 129.1, 127.7, 126.0, 124.7, 122.3, 21.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1690, 1447, 1305 cm^{-1}; HRMS (ESI^+), calcd for $C_{30}H_{26}NO_5S_2$ $[M+H]^+$ 544.1252, found 544.1242.

(*E*)-diethyl (2-(2'-acetamido-[1,1'-biphenyl]-2-yl)vinyl)phosphonate (5h). Yield (trace); colorless oil; R_f = 0.38 (hexanes/EA = 1:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.40−7.65 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 (br, 1H), 7.03−7.13 (m, 3H), 6.89 (s, 1H), 6.15 (t, *J* = 18.2 Hz, 1H), 3.90−3.97 (m, 4H), 1.85 (s, 3H), 1.15−1.19 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 145.1 (d, J_{PC} = 6.9 Hz), 137.7, 135.2, 133.6 (d, J_{PC} = 22.8 Hz), 130.8, 130.2, 130.1, 129.7, 128.7 (d, J_{PC} = 19.3 Hz), 126.4, 124.0, 121.6, 117.2, 115.2, 61.8 (d, J_{PC} = 5.7 Hz), 24.2, 16.0 (d, J_{PC} = 6.4 Hz) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1689, 1246 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{25}NO_4P$ $[M+H]^+$ 374.1521, found 374.1548.

Tetraethyl ((1*E*,1'*E*)-(2'-acetamido-[1,1'-biphenyl]-2,6-diyl)bis(ethene-2,1-diyl))bis(phosphonate) (6h). Yield 82% (44 mg); colorless oil; R_f = 0.28 (hexanes/EA = 1:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 6.0 Hz, 2H), 7.36−7.47 (m, 2H), 7.14 (t, *J* = 6.8 Hz, 1H), 6.90−7.00 (m, 3H), 6.69 (s, 1H), 6.13 (t, *J* = 18.0 Hz, 2H), 3.93−3.98 (m, 8H), 1.82 (s, 3H), 1.14-1.17 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 144.5 (d, J_{PC} = 6.9 Hz), 137.0, 135.8, 135.1 (d, J_{PC} = 23.2 Hz), 130.6, 129.2 (d, J_{PC} = 39.9 Hz), 127.8, 126.5, 124.2, 121.6, 118.3, 116.4, 61.9 (d, J_{PC} = 5.7 Hz), 24.3, 16.0 (d, J_{PC} = 6.4 Hz) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1688, 1243 cm^{-1}; HRMS (ESI^+), calcd for $C_{26}H_{36}NO_7P_2$ $[M+H]^+$ 536.1967, found 536.1947.

(*E*)-*N*-(2'-(2-cyanovinyl)-[1,1'-biphenyl]-2-yl)acetamide (5i). Yield 34% (8.9 mg); off-white solid; m.p. 118−122 °C; R_f = 0.175 (hexanes/EA/DCM = 1:3:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 6.8 Hz, 1H), 7.43−7.55 (m, 3H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.08−7.21 (m, 3H), 6.68 (s, 1H), 5.82 (d, *J* = 16.8 Hz, 1H), 1.94 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 148.0, 138.2, 135.1, 132.4, 131.3, 131.1, 130.4, 129.4, 129.2, 128.9, 126.1, 124.5, 122.3, 117.7, 97.8, 24.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2217, 1669 cm^{-1}; HRMS (ESI^+), calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1184, found 263.1183.

(*Z*)-*N*-(2'-(2-cyanovinyl)-[1,1'-biphenyl]-2-yl)acetamide (5i'). Yield 26% (6.83 mg); yellow solid; m.p. 138−140 °C; R_f = 0.275 (hexanes/EA/DCM = 1:3:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.53−7.55 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.32−7.34 (m, 1H), 7.13−7.21 (m, 2H), 6.90 (d, *J* = 12.0 Hz, 1H), 6.74 (s, 1H), 5.38 (d, *J* = 12.4 Hz, 1H), 1.96 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.3, 147.5, 138.2, 135.4, 132.7, 131.0, 130.7, 130.1, 129.9, 129.1, 128.8, 128.0, 124.5, 122.4, 116.9, 97.0, 24.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2216, 1670 cm^{-1}; HRMS (ESI^+), calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1184, found 263.1177.

***N*-(2'-((*Z*)-2-cyanovinyl)-6'-(2-cyanovinyl)-[1,1'-biphenyl]-2-yl)acetamide (6i').** Yield 8% (2.51 mg); yellow solid; m.p. 65−70 °C; R_f = 0.15 (hexanes/EA/DCM = 1:3:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, *J* = 6.4 Hz, 1H), 7.76 (s, 1H), 7.50−7.60 (m, 2H), 7.27 (s, 1H), 7.02−7.08 (m, 3H), 6.82 (d, *J* = 10.8 Hz, 1H), 6.52 (s, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 5.41 (d, *J* = 11.2 Hz, 1H), 1.94 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4, 147.6, 147.5, 147.3, 147.0, 137.8, 135.8, 134.5, 134.0, 133.5, 130.8, 130.6, 130.5, 130.3, 130.1, 129.5, 128.2, 127.7, 127.0, 125.3, 123.6, 117.4, 117.3, 116.6, 116.5, 99.4, 99.0, 98.9, 98.6, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2221, 1704 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{16}N_3O$ $[M+H]^+$ 314.1293, found 314.1288.

[Note:The ^{13}C NMR shows a mixture of *E/Z* and *Z/Z* isomers]

***N*-(2',6'-bis((*E*)-2-cyanovinyl)-[1,1'-biphenyl]-2-yl)acetamide (6i).** Yield 10% (3.14 mg); yellow solid; m.p. 105−110 °C; R_f = 0.05 (hexanes/EA/DCM = 1:3:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 6.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.01−7.05 (m, 3H), 6.54 (s, 1H), 5.81 (d, *J* = 16.4 Hz, 2H), 1.88 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 147.5, 138.0, 135.5, 134.0, 130.7, 130.4, 129.3, 128.0, 127.1, 125.6, 123.5, 117.3, 99.1, 24.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2220, 1694 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{15}N_3O$ $[M+Na]^+$ 336.1113, found 336.1109.

(*E*)-3-(2'-acetamido-[1,1'-biphenyl]-2-yl)-*N*,*N*-dimethylacrylamide (5j). Yield 58% (17.8 mg); white solid; m.p. 180−182 °C; R_f = 0.28 (EA/MeOH = 9.5:0.5); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 4.8 Hz, 1H), 7.36−7.44 (m, 5H), 7.15−7.18 (m, 2H), 6.83 (s, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 2.95 (s, 3H), 2.92 (s, 3H), 1.91 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4, 167.1, 139.6, 137.7, 135.1, 134.1, 131.2, 131.0, 130.3, 129.6, 128.8, 128.6, 128.4, 124.6, 122.2, 120.3, 37.8, 35.8, 24.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1679, 1648 cm^{-1}; HRMS (ESI^+), calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$ 309.1603, found 309.1601.

(*E*)-*N*-(2'-(oct-1-en-1-yl)-[1,1'-biphenyl]-2-yl)acetamide (5k). Yield 23% (7.4 mg), l:b (6:4); colorless liquid; R_f = 0.36 (Hex /EA = 8.5:1.5); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.5 (s, 1H), 7.28−7.36 (m, 7H), 7.13−7.25 (m, 5H), 6.85 (s, 1H), 6.77 (s, 1H), 6.18−6.25 (m, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 5.32−5.37 (m, 1H), 5.18−5.27 (m, 1H), 3.0 (s, 1H), 2.05−2.07 (m, 4H), 1.96−2.0 (m, 1H), 1.91 (s, 6H), 1.23−1.34 (m, 14H), 0.84−0.86 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 167.9, 139.8, 136.6, 135.5, 135.4, 133.5, 132.4, 131.3, 130.8, 130.7, 130.3, 130.2, 129.9, 128.9, 128.8, 128.6, 128.5, 128.3, 127.7, 127.3, 127.2, 126.6, 126.4, 125.5, 123.9, 123.7, 121.1, 120.6, 120.5, 36.2, 33.7, 33.0, 32.4, 32.1, 31.6, 31.3, 29.3, 28.8, 24.6, 22.5, 22.4, 14.06, 14.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1703, 1584 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{28}NO$ $[M+H]^+$ 322.2171, found 322.2166.

[Note: linear and branched structural isomers are not separable].

***N*-(2',6'-di((*E*)-oct-1-en-1-yl)-[1,1'-biphenyl]-2-yl)acetamide (6k).** Yield 40% (17.2 mg), l:b (7:3); colorless liquid; R_f = 0.30 (Hex /EA = 8.5:1.5); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.35 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45−7.50 (m, 3H), 7.25−7.38 (m, 6H), 7.18−7.22 (m, 2H), 7.12−7.13 (m, 2H), 7.03−7.04 (m, 3H), 6.79 (s, 1H), 6.69 (s, 1H), 6.63 (d, *J* = 7.2 Hz, 1H), 6.06−6.16 (m, 3H),

5.90−5.94 (m, 3H), 5.11−5.34 (m, 4H), 2.96−2.97 (m, 2H), 1.99−2.04 (m, 9H), 1.87 (s, 12H), 1.21−1.30 (m, 36H), 0.84−0.87 (m, 14H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 167.9, 150.8, 144.0, 141.5, 140.2, 137.49, 137.43, 137.31, 135.81, 135.75, 134.0, 133.3, 133.1, 133.1, 133.0, 132.7, 132.14, 132.11, 131.1, 131.09, 130.8, 130.7, 130.5, 130.1, 129.9, 129.4, 128.8, 128.7, 128.5, 128.4, 128.37, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.47, 127.4, 127.2, 124.4, 124.0, 123.6, 123.5, 123.2, 123.1, 123.0, 120.5, 120.4, 120.3, 120.1, 119.7, 116.1, 114.4, 113.9, 36.68, 36.64, 36.3, 34.5, 33.6, 33.5, 32.9, 32.3, 32.0, 31.8, 31.6, 31.5, 31.4, 31.3, 31.2, 29.59, 29.51, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.4, 27.7, 24.5, 22.49, 22.43, 22.4, 22.0, 13.97, 13.94, 13.88, 13.81, 13.52 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1702, 1583 cm^{-1}; HRMS (ESI^+), calcd for $C_{30}H_{42}NO$ $[M+H]^+$ 432.3264, found 432.3257. [Note: linear/branched structural isomers were observed].

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Copies of ^{1}H and ^{13}C-NMR spectra of **3a-3u**, **4a-4r**, **5a-5k** and **6a-6k**; crystallographic data for compound **3a** and **4a**.

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Notes

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