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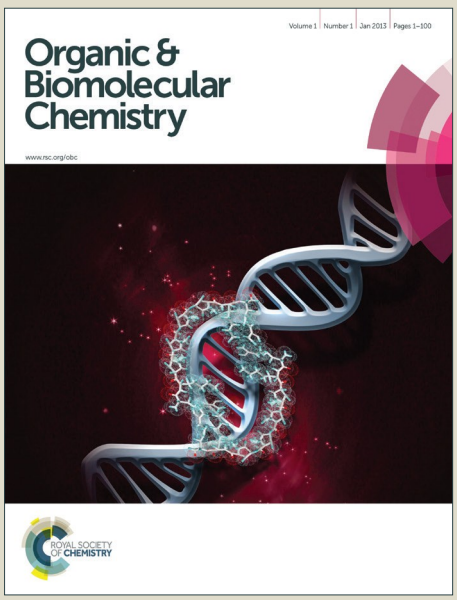

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ARTICLE

Aminoquinoline-Assisted Vinylic C–H Arylation of Unsubstituted Acrylamide for the Selective Synthesis of *Z* Olefins

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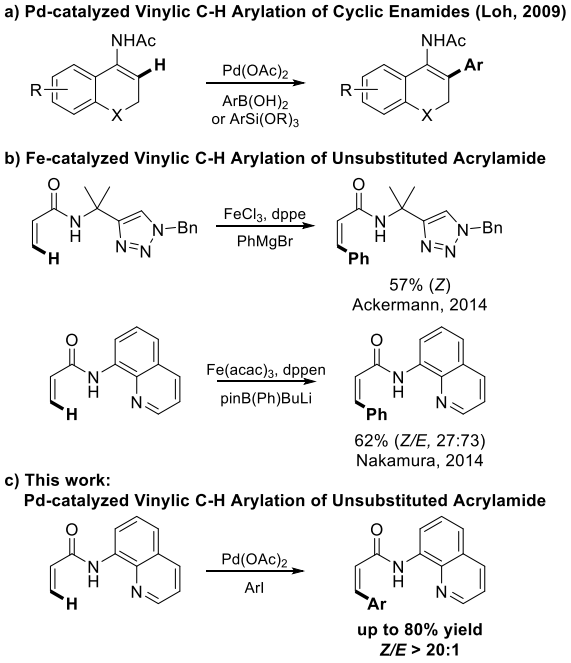
A method for Pd-catalyzed, aminoquinoline-directed arylation of vinylic C–H bonds with aryl iodides has been developed. This reaction represents a rare example of Pd-catalyzed vinylic C–H functionalization of unsubstituted acrylamide, allowing for the highly regio- and stereoselective preparation of *Z*-olefins. High tolerance to functional groups is observed with good yields and excellent selectivity. It offers a complementary synthetic method to traditional pathways for *Z*-olefins.

Alkenes are important functional groups in a large number of natural and industrial products, as well as fundamental building blocks for many chemical transformations. The stereochemistry of alkenes (the *E*- or *Z*- isomers) determines the property of the molecules and also alters the stereochemical outcome of their reactions. While *Z*-alkenes are of great use in synthesis and are commonly found in natural products,[1] current methods for direct access to the thermodynamically less-stable *Z*-alkenes are far less common. Common ways to access *Z*-alkenes include semihydrogenation of alkynes,[2] Wittig reaction[3] or modified Horner-Wadsworth-Emmons reaction,[4] cross-coupling of *Z*-vinyl halides or organometallic reagents,[5] more recently *Z*-selective olefin metathesis[6] and selective alkene isomerization.[7]

Over the past decade, metal-catalyzed, directing-group-mediated selective C–H functionalization has emerged as a powerful strategy for C–C bond formations.[8] Most achievements in the field of C(sp^2)–H functionalization to form new C–C bonds have been extensively focused on arenes. In comparison, synthetically useful protocols for metal-catalyzed direct C–H functionalization of olefins are considerably less studied.[9] Direct activation of non-aromatic vinylic C–H bonds is more challenging, because of the increased reactivity and lability of olefins. It is well known that bidentate directing groups[10-12] promote activation of C–H bonds *via* formation of a stoichiometric amount of stable metallacycles. We envisioned that directed C–H activation of vinylic C–H bonds will happen in a *syn*-fashion that would allow the formation of *Z*-alkene product regio- and stereoselectively, which is different from the exclusive generation of *E*-alkenes in oxidative olefination reactions.[13]



Scheme 1 Transition-Metal Catalyzed Vinylic C–H Arylation.

In the past decade several reports regarding chelation-assisted direct functionalization of olefins using Ru,[14] Rh,[15] Pd,[16] Cu,[17] Fe,[18] Co[19] or Ni[20] catalysts have been published. Indeed, in both Loh[14a] and Chatani's[20a] seminal work on vinylic C–H functionalization of acrylamides, the presence of a substitution at the α-position of alkene was crucial to facilitate direct vinylic C–H functionalization in terms of the reactivity and selectivity of the substrate. Usually, substitution (alkyl or aryl group) was required at α- or β-position of alkenes containing directing group.[14-20] For direct vinylic C–H arylation reaction, only two examples of Pd-catalyzed arylation of cyclic

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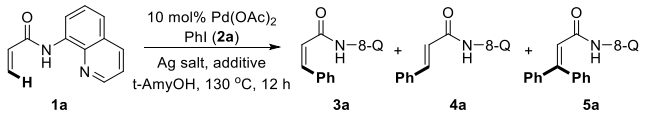
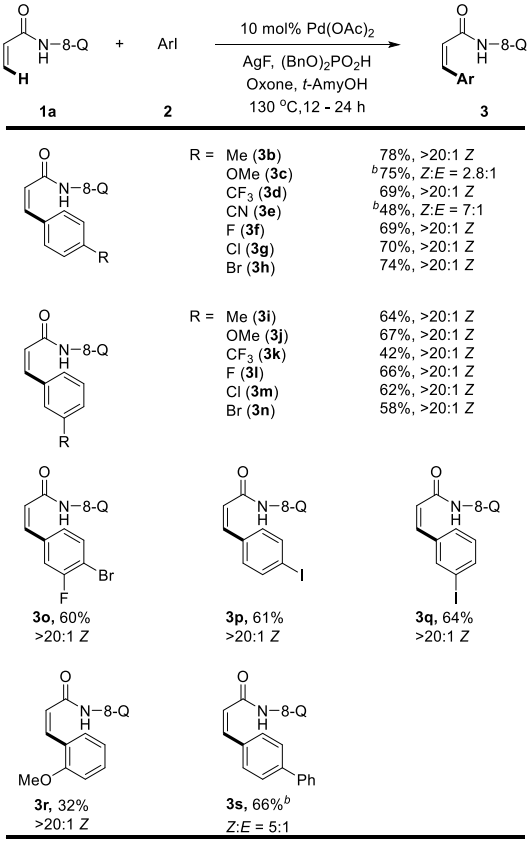
Table 1 Optimization of Vinylic C−H Arylation of Acrylamide[a]



entry	Ag salt (equiv)	additive/oxidant (equiv)	ratio[b] 3a/4a/5a	yield[b] of 3a
1	Ag_2CO_3(1.5)	--	0.9/1/0.08	30
2	Ag_2CO_3(1.5)	CH_3COOH(0.5)	2.2/1/0.52	57
3	AgOAc(1.5)	CH_3COOH(0.5)	4.2/1/0.54	73
4	AgF(1.5)	CH_3COOH(0.5)	4.8/1/0.19	80
5	AgF(1.5)	PivOH(0.5)	3.3/1/0.07	54
6	AgF(1.5)	$(BnO)_2PO_2H$(0.5)	5.9/1/0	86
7	AgF(1.5)	$(BnO)_2PO_2H$(1.0)	4.8/1/0	80
8	AgF(1.5)	$(BnO)_2PO_2H$(0.3)	5.1/1/0	80
9	AgF(0.8)	$(BnO)_2PO_2H$(0.5)	7.1/1/0	76
10	AgF(3.0)	$(BnO)_2PO_2H$(0.5)	1.3/1/0	25(56[c])
11	AgF(1.5)	$(BnO)_2PO_2H$(0.5), BQ(1)	20.0/1/0	90
12[d]	AgF(1.5)	$(BnO)_2PO_2H$(0.5), BQ(1)	5.6/1/0	81
13	AgF(1.5)	$(BnO)_2PO_2H$(0.5), BQ(2)	11.1/1/0	89
14	AgF(1.5)	$(BnO)_2PO_2H$(0.5), $K_2S_2O_8$(1)	14.3/1/0	93
15	**AgF**(1.5)	**$(BnO)_2PO_2H$(0.5), oxone(1)**	**>20/1/0**	**93(80[e])**

[a] Conditions: the reaction was carried on a 0.1 mmol scale, 12 h, 130 °C, BQ = benzoquinone. [b] The ratio and yields were determined by ^{1}H NMR spectroscopy. [c] The amount of starting material recovered. [d] The reaction time for 24 h. [e] Reaction was carried out at 0.2 mmol. Isolated yields are given in parentheses.

Table 2 Vinylic C−H Arylation of Acrylamide with Various Aryl Iodides[a]



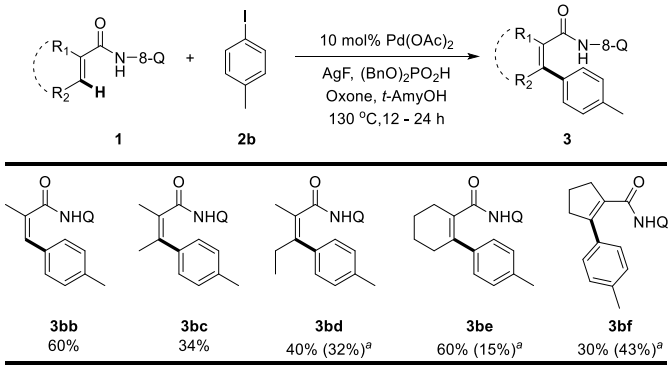
[a] Conditions: substrate **1a** (0.2 mmol), ArI (3 equiv), $Pd(OAc)_2$ (10 mmol%), AgF (1.5 equiv.), $(BnO)_2PO_2H$ (0.5 equiv.), oxone (1 equiv.), t-AmyOH (1 mL), 130 °C, 12 - 24 h. [b] Total yields were given.

enamides with aryl boronic acids and organosilane reagents were reported by Loh and co-workers in 2009 (Scheme 1, a).[16a,b] In 2012, Glorius and co-workers developed the Rh-catalyzed dehydrogenative alkene-arene coupling reaction of mono- or disubstituted acrylamides utilizing directed vinylic C–H activation strategy, which affords *Z*-arylated olefins.[15a] In 2014, Shi et al. reported a Rh-catalyzed pyridinyl-group-assisted C–H functionalization of cyclic enamines employing simple caboxylic acids as coupling partners.[15b] Recently, both Ackerman and Nakamura reported several examples of iron catalyzed C−H arylation of unsubstituted acrylamide, which either gave moderate yield or poor selectivity (Scheme 1, b).[18a,b] Here we report our study of Pd-catalyzed vinylic C−H arylation of unsubstituted acrylamide (Scheme 1, c). This reaction is a rare example of Pd-catalyzed direct vinylic C−H arylation of unsubstituted acrylamide for the efficient and *Z*-selective synthesis of arene-substituted olefins.[21]

We began our investigation by studying vinylic C−H arylation of *N*-(quinolin-8-yl) acrylamide **1a** with phenyl iodide **2a** in the presence of $Pd(OAc)_2$ as catalyst under various reaction conditions (Table 1). With Ag_2CO_3 as the I^- scavenger and oxidant at 130 °C, both *Z*-product (**3a**) and *E*-product (**4a**) were detected with a poor selectivity along with a small amount of diarylated product **5a** (entry 1). When acetic acid was added to the reaction, which are known to play the key role in the concerted palladation-deprotonation C−H activation step,[22] both the yield and selectivity were slightly improved (entry 2). Further screening with different silver salts and acid additives led to the combination of AgF and $(BnO)_2PO_2H$ (entries 3-6) which gave a good yield and stereoselectivity without the formation of **5a**. $(BnO)_2PO_2H$ was suspected as solid-to-solution phase-transfer catalyst (PTC) for silver salts and a ligand (L) for palladium during the OA and RE steps.[10k, 11b] Varying the amount of AgF and $(BnO)_2PO_2H$ didn't give further improvements (entries 7-10) (for more condition screenings, see ESI†). At this point, we speculated the formation of the *E* product **4a** might result from the Heck pathway. Accordingly, we tested different additional oxidants for palladium catalysis in order to circumvent the formation of Pd(0) completely. To our delight, the addition of oxidants to the reaction greatly improved the stereoselectivity and provided *Z* alkene as the major product (entries 11-14). The best conditions of using 10 mol% $Pd(OAc)_2$, 1.5 equivalent of AgF, 0.5 equivalent of $(BnO)_2PO_2H$ and 1.0 equivalent of oxone at 130 °C for 12 hs led to 80% isolated yield and >20:1 *Z*/*E* selectivity of **3a** (entry 15).

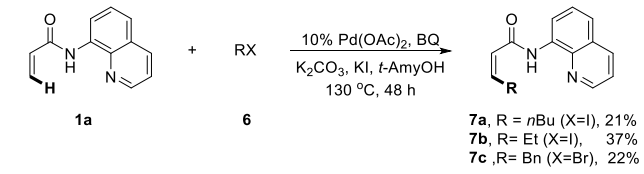
Subsequently, the scope of aryl iodides with diverse functional groups was examined in the *syn*-selective vinylic C−H arylation of acrylamide under the optimized conditions (Table 2). In most cases, full conversion of acrylamide could be obtained. The desired products were isolated in moderate to good yields. Most substrates showed excellent stereoselectivity with only *Z* isomer being detected by NMR spectroscopy except three substrates noted in the Table. As

Table 3 Vinylic C–H Arylation of Various α,β-Unsaturated Amides

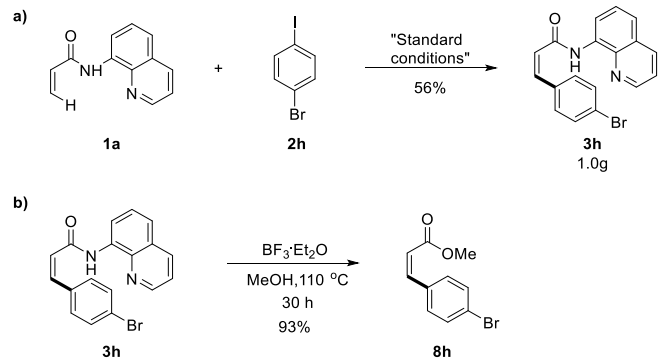


[a] The yields in the parentheses are recovered starting material **1**.

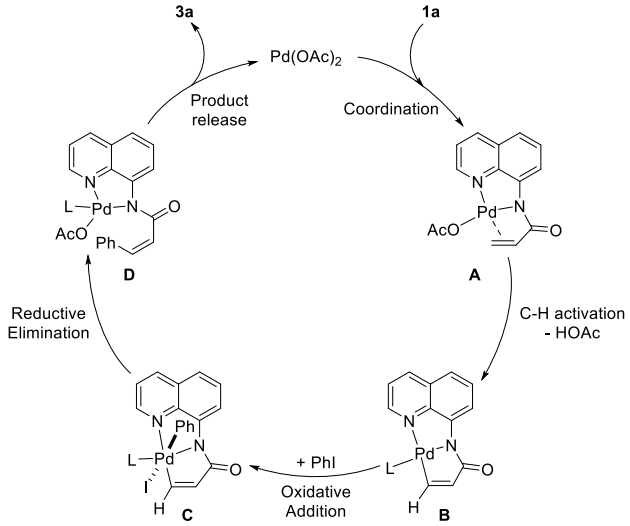
shown in Table 2, aryl iodides bearing electron-donating *para*- or *meta*-methyl (**3b** and **3i**), *meta*-methoxy (**3j**), electron-withdrawing *para*- or *meta*-trifluoromethyl (**3d** and **3k**) groups gave good yields with excellent *Z*/*E* selectivity. Aryl iodides with electron-withdrawing groups tended to give lower yields than the ones with electron-donating groups. However, aryl iodides with *para*-methoxy (**3c**) and *para*-cyano (**3e**) groups gave the products with poor to moderate *Z*/*E* selectivity. Control experiment indicated *Z*-isomer **3c** converted to its *E*-isomer **4c** under the reaction conditions (see ESI†). Aryl iodides bearing halogen groups (F, Cl, Br) at either *para*- or *meta*-positions (**3f**-**3h** and **3l**-**3o**) all gave good yields with excellent *Z*/*E* selectivity. Strikingly, for diiodobenzenes (**3p** and **3q**), the reaction gave mono-iodo substituted product in good yield and



Scheme 2 Vinylic C–H Alkylation of Acrylamide with Alkyl Halides



Scheme 3 (a) Gram-Scale Synthesis; (b) Directing Group Cleavage



Scheme 4 Plausible reaction mechanism.

excellent *Z*/*E* selectivity. Aryl iodide with an *ortho*-methoxy group (**3r**) gave poor yield of product probably due to the sterics, but the *Z*/*E* selectivity remained great. Finally, aryl iodide with a *para*-phenyl group (**3s**) delivered the product in good yield, but the *Z*/*E* selectivity was moderate.

Moreover, this newly developed catalytic protocol is not limited to unsubstituted acrylamides but is also applicable to substituted acrylamide derivatives (Table 3), in which case the arylated products were accompanied in a highly stereo-controlled manner under the optimal reaction conditions. Acrylamides **1b** and **1e** reacted with aryl iodide **2b** affording the desired products **3bb** and **3be** in good yields. However, acrylamides **1c**, **1d** and **1f** gave poor yields of the desired products **3bc**, **3bd** and **3bf** along with certain amount of recovered starting materials.

Attempts to expand this chemistry to alkyl iodides allowing the vinylic C–H alkylation reactions proved unviable (Scheme 2).[23] With extensive optimization of the conditions, the alkylation reactions were less efficient (low conversion), affording decreased yields of products even with extended reaction time.

Next, we carried out the arylation reaction on a gram scale with 1-bromo-4-iodobenzene (**2h**). Product **3h** could be successfully obtained with a slightly decreased yield (Scheme 3, a). Finally, we attempted the removal of the 8-aminoquinoline directing group.[10] Upon treatment of **3h** with $BF_3{\cdot}Et_2O$ in methanol,[10l] the removal of directing group took prolonged reaction time to reach full conversion. Gratifyingly, the crude NMR spectrum showed a Z/E product ratio of 100:3 (see ESI†). Methyl (*Z*)-3-(4-bromophenyl)acrylate (**8h**) was isolated in 93% yield (Scheme 3, b).

Based on the above results, the known reports on palladium-catalyzed C–H activation through bidentate directing groups[24] and high-valent palladium catalysis,[25] and the cyclic vinylpalladium complex as the intermediate during the palladium-catalyzed olefination reaction of enamides,[16c] a

plausible mechanism involving a Pd(II)/Pd(IV) catalytic cycle was proposed (Scheme 4). The coordination of acrylamide with palladium acetate forms complex **A**, which further undergoes a rapid cyclometalation of vinyl group resulting in the formation of **B**. Oxidative addition of aryl iodide to **B** produces Pd(IV) complex **C**. Reductive elimination to **D** followed by ligand exchange releases product **3a** and regenerates the Pd(II) catalyst to fulfill the catalytic cycle. Intermolecular competition experiments between differently substituted aryl iodides **2** revealed electronic properties of the aryl iodides has little effect on the catalytic reaction (see ESI†).

Experimental

General remarks

All reagents and metal catalysts were obtained from commercial sources without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. IR spectra were recorded on a Nicolet IS-10 Fourier transform infrared spectrometer. High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with an EI source. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-300 spectrometer operating at 300 MHz/500 MHz and 75 MHz/125 MHz respectively, with chemical shift values being reported in ppm relative to chloroform (δ=7.26 ppm) for ^{1}H NMR, and chloroform (δ=77.16 ppm) for ^{13}C NMR.

General Procedures for Vinylic C–H Arylation of Acrylamide

To a 15 mL Schlenk tube, substrate **1a** (39.6 mg, 0.2 mmol), aryl iodide (0.6 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), AgF (38.0 mg, 0.3 mmol), $(BnO)_2PO_2H$ (27.8 mg, 0.1 mmol), oxone(122.0 mg, 0.2mmol) and *t*-AmyOH (1 mL) were combine added under air, sealed with a Teflon cap. The tube was heated at 130 °C in an oil bath and stirring for 12-24 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (15 mL) and washed with H_2O (10 mL), aqueous layer was extracted by DCM (3 X 5 mL). Combined organic layers were dried over Na_2SO_4. To remove the solvent by evaporation after filtration, the residue was purified by flash chromatography to give the target products.

(*Z*)-3-phenyl-*N*-(quinolin-8-yl)acrylamide(3a):This amide was obtained as a colorless oil liquid. Purified by column chromatography (DCM) (43.9 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.84 (d, *J* = 7.1 Hz, 1H), 8.62 (d, *J* = 5.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.55 (m, 4H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 3H), 6.99 (d, *J* = 12.5 Hz, 1H), 6.29 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.55, 147.57, 138.61, 137.96, 135.83, 134.56, 134.05, 129.04, 128.33, 127.95, 127.48, 126.99, 124.31, 121.25, 121.14, 116.22. IR (neat) 3345, 2926, 1676, 1524, 1485, 1424, 1383, 1325, 1162, 825, 791, 694. HRMS (EI) calcd. for $C_{18}H_{14}N_2O$: 274.1106. Found: 274.1103.

(*Z*)-*N*-(quinolin-8-yl)-3-(p-tolyl)acrylamide(3b):This amide was obtained as a white oil liquid. Purified by column chromatography (DCM) as a white solid (44.8 mg, 78%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.85 (d, *J* = 7.0 Hz, 1H), 8.73-8.47 (m, 1H), 8.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.63-7.46 (m, 4H), 7.39 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 12.4 Hz, 1H), 6.22 (d, *J* = 12.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.75, 147.53, 138.85, 138.46, 138.01, 135.81, 134.14, 131.73, 129.15, 128.64, 127.50, 126.99, 123.33, 121.19, 116.23, 20.97. IR (neat) 3342 , 2911 , 1669 , 1518 , 1481 , 1422 , 1381 , 1322 , 1182 , 1160 , 823 , 789 , 755. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1255.

(Z)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3c):This amide was obtained as a white solid. Purified by column chromatography (DCM) and prepare TLC (46.5 mg, 75%, Z/E=2.8/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.86 (dd, *J* = 7.3, 1.4 Hz, 1H), 8.66 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72-7.63 (m, 2H), 7.60-7.45 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.99-6.75 (m, 3H), 6.16 (d, *J* = 12.5 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.79, 159.80, 147.56, 138.88, 138.00, 135.88, 134.21, 131.16, 127.54, 127.18, 127.02, 121.92, 121.13, 116.24, 112.96, 54.85. IR (neat) 3345, 2923, 1665, 1602, 1524, 1507, 1484, 1423, 1383, 1323, 1251, 1174, 1159, 1028, 824, 790. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1219.

(*Z*)-*N*-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)acrylamide (3d):This amide was obtained as a pale yellow oil liquid. Purified by column chromatography (DCM) (46.9 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 6.6, 2.3 Hz, 1H), 8.61 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63-7.48 (m, 4H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.99 (d, *J* = 12.4 Hz, 1H), 6.38 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.68, 147.68, 138.17, 137.93, 137.27, 135.89, 133.76, 130.00, 129.23, 127.78, 127.51, 126.93, 126.15, 125.44, 124.83, 121.83, 121.57, 121.24, 116.33. IR (neat) 3336, 2928, 1668, 1520, 1484, 1318, 1161, 1110, 1065, 1017, 824, 789. HRMS (EI) calcd. for $C_{19}H_{13}F_3N_2O$: 342.0980. Found: 342.0988.

(*Z*)-3-(4-cyanophenyl)-*N*-(quinolin-8-yl)acrylamide(3e):This amide was obtained as a yellow solid. Purified by column chromatography (DCM) (28.8 mg, 48%, Z/E=7/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81-8.74 (m, 1H), 8.67 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.55-7.52 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.96 (d, *J* = 12.4 Hz, 1H), 6.42 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.32, 147.74, 139.26, 137.89, 137.05, 136.04, 133.64, 132.24, 131.57, 129.60, 127.99, 127.55, 126.96, 126.69, 121.74, 121.36, 116.43. IR (neat) 3336, 2920, 2225, 1674, 1522, 1484, 1424, 1383, 1324, 1164, 825, 791. HRMS (EI) calcd. for $C_{19}H_{13}N_3O$: 299.1059. Found: 299.1063.

(*Z*)-3-(4-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide(3f):This amide was obtained as a white solid. Purified by column chromatography (DCM) (40.4 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.83 (dd, *J* = 6.9, 1.6 Hz, 1H), 8.72-8.55 (m, 1H), 8.14 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.52 (q, *J* = 6.7 Hz, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.10-6.84 (m, 3H), 6.26 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ

164.25, 158.91(d, *J* = 304.1 Hz), 147.64, 137.95, 135.97, 133.95, 131.32, 131.21, 130.66, 127.53, 127.01, 123.89, 121.40, 121.26, 116.29, 115.07, 114.78. IR (neat) 3339, 2923, 1671, 1520, 1507, 1483, 1423, 1381, 1323, 1228, 1158, 824, 789. HRMS (EI) calcd. for $C_{18}H_{13}FN_2O$: 292.1012. Found: 292.1020.

(*Z*)-3-(4-chlorophenyl)-*N*-(quinolin-8-yl)acrylamide(3g):This amide was obtained as a white solid. Purified by column chromatography (DCM) (43.0 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.82 (dd, *J* = 6.9, 1.9 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63-7.46 (m, 4H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 12.5 Hz, 1H), 6.29 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.05, 147.67, 137.93, 137.66, 135.89, 134.29, 133.90, 133.02, 130.51, 128.13, 127.51, 126.96, 124.68, 121.43, 121.24, 116.28. IR (neat) 3339 , 2923 , 1674 , 1519 , 1482 , 1422 , 1381 , 1323 , 1161 , 1089 , 1014 , 822 , 788 , 756. HRMS (EI) calcd. for $C_{18}H_{13}ClN_2O$: 308.0716. Found: 308.0712.

(*Z*)-3-(4-bromophenyl)-*N*-(quinolin-8-yl)acrylamide(3h):This amide was obtained as a pale yellow solid. Purified by column chromatography (DCM) (52.1 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81 (dd, *J* = 6.6, 2.0 Hz, 1H), 8.66 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.64-7.32 (m, 7H), 6.90 (d, *J* = 12.5 Hz, 1H), 6.30 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.05, 147.71, 137.93, 137.71, 135.91, 133.88, 133.46, 131.72, 131.10, 130.74, 127.51, 126.97, 124.81, 122.63, 121.46, 121.27, 116.28. IR (neat) 3339 , 2928 , 1667 , 1518 , 1482 , 1422 , 1381 , 1323 , 1161 , 1070 , 1009 , 823 , 788 , 755. HRMS (EI) calcd. for $C_{18}H_{13}BrN_2O$: 352.0211. Found: 352.0215.

(*Z*)-*N*-(quinolin-8-yl)-3-(m-tolyl)acrylamide(3i):This amide was obtained as a white oil liquid. Purified by column chromatography (DCM) (36.9 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.85 (d, *J* = 7.2 Hz, 1H), 8.58 (dd, *J* = 4.0, 1.1 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.60-7.46 (m, 2H), 7.40 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 12.5 Hz, 1H), 6.25 (d, *J* = 12.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.69, 147.52, 138.62, 137.96, 137.52, 135.79, 134.49, 134.09, 129.64, 129.08, 127.90, 127.47, 126.98, 126.01, 124.29, 121.21, 121.12, 116.19, 20.95. IR (neat) 3342, 2917, 1668, 1517, 1482, 1423, 1381, 1323, 1162, 824, 789, 689. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1259.

(*Z*)-3-(3-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3j):This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (40.9 mg, 67%).This amide was obtained as a pale yellow oil liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.84 (dd, *J* = 7.1, 1.4 Hz, 1H), 8.60 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.62-7.45 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.26-7.08 (m, 3H), 6.96 (d, *J* = 12.5 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.28 (d, *J* = 12.5 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.63, 159.08, 147.59, 138.12, 137.94, 135.83, 134.03, 129.03, 127.47, 126.97, 124.74, 121.52, 121.29, 121.17, 116.19, 114.68, 113.56, 54.78. IR (neat) 3339, 2921, 1670, 1518, 1482, 1423, 1381, 1323, 1258, 1239, 1161, 1041, 824, 788, 685. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1216.

(*Z*)-3-(pyridin-3-yl)-*N*-(quinolin-8-yl)acrylamide(3k):This amide was obtained as white solid. Purified by column chromatography (DCM) as (28.8 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.82 (dd, *J* = 6.8, 1.9 Hz, 1H), 8.70-8.56 (m, 1H), 8.16 (d, *J* = 7.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.59-7.49 (m, 3H), 7.42 (m, 2H), 7.00 (d, *J* = 12.5 Hz, 1H), 6.40 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.73, 147.53, 140.17, 140.03, 137.77, 137.30, 136.42, 136.08, 135.34, 133.69, 132.26, 128.34, 127.52, 127.02, 125.84, 124.86, 123.96, 121.52, 121.19, 116.50. IR (neat) 3342, 2923, 1678, 1524, 1486, 1383, 1328, 1162, 1124, 1075, 825, 791, 688. HRMS (EI) calcd. for $C_{19}H_{13}F_3N_2O$: 342.0980. Found: 342.0983.

(*Z*)-3-(3-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide(3l):This amide was obtained as a white solid. Purified by column chromatography (DCM) (38.6 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.83 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.53 (dd, *J* = 12.5, 5.2 Hz, 2H), 7.46-7.32 (m, 3H), 7.27 (dd, *J* = 8.1, 5.7 Hz, 1H), 7.09-6.88 (m, 2H), 6.32 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.95, 163.24, 160.62, 147.64, 137.97, 137.31, 136.76, 136.65, 135.88, 133.90, 129.47, 129.36, 127.50, 126.98, 125.36, 124.90, 121.42, 121.20, 116.32, 115.84, 115.20. IR (neat) 3336, 2920, 1672, 1578, 1519, 1483, 1423, 1381, 1324, 1163, 1131, 824, 788, 680. HRMS (EI) calcd. for $C_{18}H_{13}FN_2O$: 292.1012. Found: 292.1017.

(*Z*)-3-(3-chlorophenyl)-*N*-(quinolin-8-yl)acrylamide(3m): This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (38.2 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.82 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 (s, 1H), 7.58-7.45 (m, 3H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28-7.17 (m, 2H), 6.91 (d, *J* = 12.5 Hz, 1H), 6.32 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.86, 147.66, 137.93, 137.20, 136.38, 135.88, 133.84, 129.18, 128.98, 128.27, 127.49, 127.14, 126.97, 125.57, 121.43, 121.20, 116.31. IR (neat) 3345, 2923, 1674, 1522, 1484, 1424, 1382, 1325, 1163, 825, 790, 680. HRMS (EI) calcd. for $C_{18}H_{13}ClN_2O$: 308.0716. Found: 308.0719.

(*Z*)-3-(3-bromophenyl)-*N*-(quinolin-8-yl)acrylamide(3n):This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (40.9 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.81 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.74 (s, 1H), 7.61-7.47 (m, 3H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 12.5 Hz, 1H), 6.31 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.84, 147.68, 137.94, 137.09, 136.68, 135.88, 133.85, 131.86, 131.18, 129.45, 127.57, 126.97, 125.63, 121.94, 121.44, 121.21, 116.31. IR (neat) 3336, 2917, 1673, 1520, 1483, 1423, 1382, 1324, 1162, 824, 789, 681. HRMS (EI) calcd. for $C_{18}H_{13}BrN_2O$: 352.0211. Found: 352.0217.

(*Z*)-3-(4-bromo-3-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide (3o):This amide was obtained as a white solid. Purified by column chromatography (DCM) (44.7 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.81 (dd, *J* = 6.4, 2.4 Hz, 1H), 8.68 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.61-7.34 (m, 5H), 7.31-7.22 (m, 1H), 6.85 (d, *J* = 12.5 Hz, 1H), 6.34 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.55, 147.74, 137.92, 136.72, 135.98, 133.75, 132.88, 127.54, 126.98, 126.14,

125.67, 121.60, 121.28, 117.19, 116.87, 116.41, 109.22, 108.94. IR (neat) 3336, 2917, 1674, 1521, 1483, 1422, 1382, 1324, 1164, 1039, 824, 789. HRMS (EI) calcd. for $C_{18}H_{12}BrFN_2O$: 370.0117. Found: 370.0121.

(*Z*)-3-(4-iodophenyl)-*N*-(quinolin-8-yl)acrylamide(3p):This amide was obtained as a white solid. Purified by column chromatography (DCM) (48.8 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.82 (d, *J* = 7.0 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.3 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.52 (dd, *J* = 8.9, 6.9 Hz, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 12.5 Hz, 1H), 6.31 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.20, 147.90, 144.84, 138.54, 138.02, 137.38, 137.06, 136.40, 134.05, 129.87, 128.45, 127.83, 127.35, 125.83, 122.73, 121.77, 121.49, 116.84, 109.80, 93.93. IR (neat) 3334, 2923, 2845, 1674, 1521, 1482, 1423, 1382, 1323, 1161, 1005, 823, 789. HRMS (EI) calcd. for $C_{18}H_{13}IN_2O$: 400.0073. Found: 400.0070.

(*Z*)-3-(3-iodophenyl)-*N*-(quinolin-8-yl)acrylamide(3q):This amide was obtained as a white solid. Purified by column chromatography (DCM) (51.2 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.73 (d, *J* = 7.2 Hz, 1H), 8.63-8.55 (m, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.45 (dt, *J* = 8.2, 7.6 Hz, 2H), 7.35 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 12.5 Hz, 1H), 6.22 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.34, 147.86, 138.20, 137.97, 137.34, 136.50, 134.21, 131.14, 129.49, 127.87, 127.36, 125.16, 121.80, 121.53, 116.89, 94.84. IR (neat) 3336, 2914, 2842, 1672, 1519, 1482, 1422, 1381, 1324, 1160, 824, 787, 755, 683, 656. HRMS (EI) calcd. for $C_{18}H_{13}IN_2O$: 400.0073. Found: 400.0071.

(*Z*)-3-(2-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3r):This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (19.5 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81 (dd, *J* = 7.2, 1.4 Hz, 1H), 8.56 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.62-7.43 (m, 3H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.31-7.22 (m, 1H), 7.16 (d, *J* = 12.4 Hz, 1H), 6.86 (dd, *J* = 16.3, 8.2 Hz, 2H), 6.29 (d, *J* = 12.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.71, 156.83, 147.44, 137.98, 135.72, 134.51, 134.18, 130.25, 129.79, 127.43, 126.98, 124.74, 123.59, 121.03, 120.08, 116.06, 110.11, 55.13. IR (neat) 3339, 2917, 1667, 1519, 1483, 1461, 1424, 1381, 1323, 1248, 1159, 1109, 1025, 825, 790, 751. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1221.

(*Z*)-3-([1,1'-biphenyl]-4-yl)-*N*-(quinolin-8-yl)acrylamide(3s): This amide was obtained as a white solid. Purified by column chromatography (DCM) (46.0 mg, 66%, Z/E=5/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.88 (d, *J* = 7.3 Hz, 1H), 8.59 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.45 (m, 12H), 7.01 (d, *J* = 12.5 Hz, 1H), 6.30 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.81, 147.78, 142.30, 141.28, 139.89, 138.08, 136.11, 134.27, 133.40, 129.69, 129.01, 128.51, 128.18, 127.62, 127.39, 127.15, 126.67, 121.30, 121.01, 118.62, 116.53. IR (neat) 3350, 3187, 2919, 1646, 1624, 1523, 1485, 1423, 1385, 1260, 1161, 1076, 826, 791, 767, 679. HRMS (EI) calcd. for $C_{24}H_{18}N_2O$: 350.1419. Found: 350.1426.

(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)acrylamide(3bb):This amide was obtained as a colorless solid. Purified by column chromatography (DCM/PE=50/50) (36.3 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.82 (d, *J* = 7.3 Hz, 1H), 8.51 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.51 (dt, *J* = 8.2, 7.5 Hz, 3H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.71 (s, 1H), 2.25 (d, *J* = 1.2 Hz, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.77, 147.39, 137.01, 135.68, 134.11, 133.68, 132.50, 130.55, 129.19, 128.60, 127.84, 127.42, 126.92, 121.17, 120.96, 116.17, 21.56, 20.69. HRMS (EI) calcd. for $C_{20}H_{18}N_2O$: 302.1419. Found: 302.1421.

(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)but-2-enamide(3bc): This amide was obtained as a colorless solid. Purified by column chromatography (DCM/PE=50/50) as a white solid (21.5 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.68 (d, *J* = 7.4 Hz, 1H), 8.53 (d, *J* = 2.9 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 2.18 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.38, 147.20, 139.55, 138.49, 137.99, 136.82, 136.26, 134.42, 130.43, 128.74, 127.63, 127.48, 127.31, 121.07, 116.97, 116.43, 29.61, 21.25, 20.85, 17.08. IR (neat)3339, 2922, 2851, 1666, 1520, 1483, 1424, 1384, 1326, 823, 791. HRMS (EI) calcd. for $C_{21}H_{20}N_2O$: 316.1576. Found: 316.1580.

(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)pent-2-enamide (3bd): This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (26.4 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.66 (d, *J* = 7.4 Hz, 1H), 8.56 (d, *J* = 3.9 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.40-7.29 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.19 (s, 3H), 2.04 (s, 4H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.36, 147.32, 144.46, 138.10, 136.73, 135.94, 134.53, 129.95, 128.73, 127.97, 127.57, 127.20, 121.08, 120.94, 27.93, 20.85, 16.25, 11.93. IR (neat) 3337, 2969, 2926, 1633, 1519, 1483, 1459, 1423, 1384, 1326, 824, 791. HRMS (EI) calcd. for $C_{22}H_{22}N_2O$: 330.1732. Found: 330.1735.

4'-methyl-*N*-(quinolin-8-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide(3be): This amide was obtained as a white solid. Purified by column chromatography (DCM) (41.0 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.69 (d, *J* = 7.4 Hz, 1H), 8.53 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.40 (ddd, *J* = 16.1, 11.9, 6.3 Hz, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 2.61 (s, 2H), 2.49 (s, 2H), 2.08 (s, 3H), 1.82 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.79, 147.24, 140.58, 138.82, 136.95, 136.05, 134.54, 132.56, 128.83, 127.61, 127.43, 127.25, 121.07, 120.98, 116.30, 31.91, 27.13, 22.70, 22.11, 20.90. IR (neat) 3342, 2927, 2854, 1662, 1521, 1483, 1423, 1384, 1325, 825, 791. HRMS (EI) calcd. for $C_{23}H_{22}N_2O$: 342.1732. Found: 342.1736.

***N*-(quinolin-8-yl)-2-(p-tolyl)cyclopent-1-ene-1-carboxamide (3bf):**This amide was obtained as a white solid. Purified by column chromatography (DCM) (19.7 mg, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.70 (d, *J* = 7.5 Hz, 1H), 8.52 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 2.61 (s, 2H), 2.48 (s, 2H), 2.07 (s, 3H), 1.87-1.79 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.79, 147.24, 140.58, 138.82, 136.95, 136.05, 134.54, 132.56, 128.83, 127.61, 127.43, 127.25, 121.07, 120.98, 116.30, 31.91,

27.13, 22.70, 22.11, 20.90. IR (neat) 3310, 2917, 2845, 1660, 1521, 1484, 1423, 1384, 1324, 824, 790. HRMS (EI) calcd. for $C_{22}H_{20}N_2O$: 328.1576. Found: 328.1573.

(*Z*)-*N*-(quinolin-8-yl)hept-2-enamide(7a): This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (10.7 mg, 21%).^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.85 (dd, *J* = 7.1, 1.7 Hz, 1H), 8.84-8.70 (m, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63-7.36 (m, 3H), 6.20 (dt, *J* = 11.5, 7.2 Hz, 1H), 6.14-6.01 (m, 1H), 2.81 (dt, *J* = 8.3, 4.1 Hz, 2H), 1.55-1.34 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 164.63, 147.68, 147.29, 138.03, 136.00, 135.48, 134.30, 127.59, 127.07, 122.58, 121.19, 121.03, 116.01, 31.14, 28.30, 22.07, 13.57. IR (neat) 3351, 2955, 2923, 2860, 1679, 1522, 1485, 1426, 1382, 1325, 1164, 825, 791. HRMS (EI) calcd. for $C_{16}H_{18}N_2O$: 254.1419. Found: 254.1422.

(*Z*)-*N*-(quinolin-8-yl)pent-2-enamide(7b): This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (16.7 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.93 -8.71 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.65-7.36 (m, 3H), 6.19 (dt, *J* = 11.4, 7.3 Hz, 1H), 6.07 (t, *J* = 6.3 Hz, 1H), 2.82 (pd, *J* = 7.5, 1.3 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.58, 148.60, 147.69, 138.03, 136.00, 134.28, 127.57, 127.05, 122.14, 121.19, 121.05, 115.99, 21.96, 13.40. IR (neat) 3345, 2969, 2929, 2857, 1679, 1523, 1486, 1425, 1382, 1325, 1162, 825, 791, 670. HRMS (EI) calcd. for $C_{14}H_{14}N_2O$: 226.1106. Found: 226.1103.

(*Z*)-4-phenyl-*N*-(quinolin-8-yl)but-2-enamide(7c): This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (12.7 mg, 22%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.90 (dd, *J* = 7.1, 1.5 Hz, 1H), 8.81 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.62-7.51 (m, 2H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.32 (d, *J* = 4.3 Hz, 3H), 7.26-7.10 (m, 2H), 6.36 (dt, *J* = 11.3, 7.4 Hz, 1H), 6.20 (d, *J* = 11.3 Hz, 1H), 4.22 (dd, *J* = 7.4, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.34, 147.74, 145.17, 139.57, 138.02, 136.08, 134.18, 128.34, 128.22, 127.61, 127.08, 125.86, 122.68, 121.25, 116.19, 34.63. IR (neat) 3342, 2969, 2923, 2871, 1678, 1636, 1522, 1483, 1459, 1426, 1383, 1325, 1186, 1165, 825, 790,757. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1267.

Conclusions

In conclusion, we have developed a palladium-catalyzed direct cross-coupling method for arylation of unsubstituted acrylamide with aryl iodides by vinylic C−H activation to produce a wide variety of *cis*-cinnamic acid derivatives. The aminoquinoline directing group can be easily converted to an ester for further transformations. Further understanding of the reaction mechanism and application of this approach to other synthetically useful substrates will be communicated in due course in our laboratory.

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