JOC The Journal of Organic Chemistry

Article

Ruthenium-Catalyzed Regioselective C2 Alkenylation of Indoles and Pyrroles via C-H Bond Functionalization

Bin Li, Jianfeng Ma, Weijia Xie, Haibin Song, Shansheng Xu, and Baiquan Wang

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo401579m • Publication Date (Web): 28 Aug 2013

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

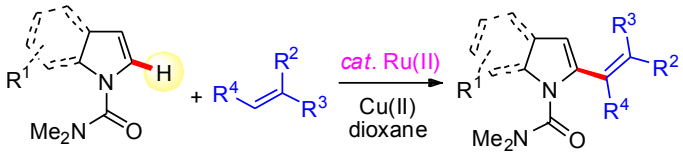
Ruthenium-Catalyzed Regioselective C2 Alkenylation of Indoles and Pyrroles via C-H Bond Functionalization

Bin Li,*[,†] Jianfeng Ma,[†,§] Weijia Xie,[†,§] Haibin Song,[†] Shansheng Xu,[†] and Baiquan Wang*[,†,‡]

[†]State Key Laboratory of Element-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071

[‡]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

Email: nklibin@nankai.edu.cn, bqwang@nankai.edu.cn



· **Highly regio- and stereoselective · broad substrate scope**
· **readily available and easily removable directing group**

ABSTRACT: An efficient ruthenium-catalyzed oxidative coupling of indoles and pyrroles with various alkenes at the C2-position assisted by employing the *N*,*N*-dimethylcarbamoyl moiety as a directing group is reported. The catalytic reaction proceeds in an excellent regio- and stereoselective manner.

INTRODUCTION

The catalytic functionalization of C-H bonds[1] has become an increasingly efficient and reliable approach for new carbon-carbon[2] and carbon-heteroatom[3] bond formations. The Fujiwara-Moritani reaction[4]—a process of oxidative alkenylation of normally unreactive aryl C-H bonds—has become an important and attractive alternative to the traditional Mizorki-Heck reaction.[5] For the past decades, various catalytic systems, mainly employing palladium[6] and rhodium[7] complexes as catalysts, have been developed for oxidative Heck transformations. In these studies, a neighbouring directing group[8] was often used to obtain a regioselective C-H activation, and an easily installed and readily removed directing group is more favoured.

Undoubtedly, indole derivatives represent one of the most important classes of heterocyclic compounds, because of their extensive existence in biologically active natural products and pharmaceutical products.[9] As a result, the efficient functionalization of indole derivatives has attracted much attention. However, direct C2-alkenylation of indole via transition-metal-catalyzed C-H bond activation is still a challenge due to the electrophilic nature of the reaction as well as the higher C-H nucleophilic reactivity of the C3-position than that of the C2-position. Up to now, four palladium-catalyzed protocols for intermolecular C2-alkenylation of indole were developed.[10] Gaunt et al. demonstrated a selective Pd(II)-catalyzed C2- and C3- oxidative alkenylation of free (NH) indoles by varying the nature of the solvent and additives.[10d] Assisted by *N*-2-pyridylmethyl or *N*-(2-pyridyl)sulfonyl as the directing group, the groups of Ricci,[10e] Carretero and Arrayás[10a,b] independently reported the functionalization of indole at the C2-position with excess of alkenes in the presence of a Pd(II) catalyst. Miura, Satoh and co-workers described an exclusive C2-alkenylation method of indoles through Pd(II)-catalyzed C–H olefination of indole-3-carboxylic acids, in which decarboxylation of the carboxyl group occurred during the reaction process.[10c] In

these cases, high catalyst loading (often 10 mol %) was required, and a limited substrate scope of alkenes (mostly restricted to acrylates) was observed. Thus, the development of a new catalytic system for this transformation is highly desired.

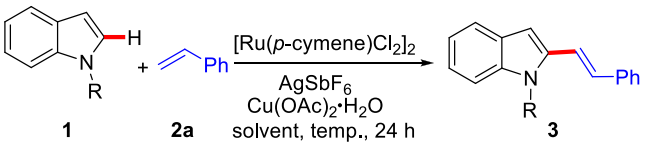
On the other hand, the less-expensive ruthenium(II) complex has emerged into the field of chelation-assisted oxidative olefination of arenes as a useful catalyst. In this regard, the research groups of Satoh and Miura,[11] Ackermann,[12] Bruneau and Dixneuf,[13] Jeganmohan,[14] Lam,[15] Ramana,[16] and ours[17] have shown that use of the [{RuL_2(*p*-cymene)}$_2$] (L = Cl or OAc) catalyst allows the oxidative coupling between aromatic acids, aryl ketones, *N*-arylpyrazoles, anilides, amides, aromatic aldehydes, aromatic esters, and aryl carbamates with olefins by using copper acetate as oxidant. Moreover, we have reported the dehydrogenative alkenylation of *N*-methoxybenzamides with styrene and acrylates in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] as catalyst using CONH(OMe) as an oxidizing directing group.[18] Very recently, Prabhu *et al*. reported the first *N*-benzoyl directed Ru-catalyzed regioselective C2-alkenylation of indoles. However, only acrylates were used as coupling partners in this method.[19] Based on these findings, we envisioned that using a proper directing group, [{$RuCl_2$(*p*-cymene)}$_2$] could be a suitable catalyst for the oxidative C2-olefination of indoles and pyrroles with broader alkene substrates scope. Herein, we disclose our development of a ruthenium-catalyzed regioselective coupling of indoles and pyrroles with alkenes at the C2-position via C-H activation with the use of easily removed *N*,*N*-dimethylcarbamoyl as the directing group.[20]

RESULTS AND DISCUSSION

We started our study with the oxidative coupling reaction of various *N*-substituted indoles (**1**)

and styrene (**2a**). The choice of the protecting group on indole was found to be crucial, with *N*,*N*-dimethylcarbamoyl being optimal (Table 1, entries 1-7). Treatment of *N*,*N*-dimethyl-1H-indole-1-carboxamide (**1a**) (1.0 equiv) with **2a** (2.0 equiv) in the presence of 5.0 mol % of [{$RuCl_2$(*p*-cymene)}$_2$], 20.0 mol% of $AgSbF_6$, and 2.0 equiv of $Cu(OAc)_2 \cdot H_2O$ in dioxane at 100 °C for 24 h gave the desired alkenylation product **3aa** in 87% yield (entry 1). To our delight, the reaction proceeded in excellent regio- and stereoselectivity with the formation of exclusive C2 *E*-alkenylation product. Screening of the solvent indicated that THF was also suitable for the reaction, giving **3aa** in comparable yield (entry 10). But a change of solvent to *t*-AmOH (*t*-Am = *tert*-amyl) and DME led to a low yield (entries 8 and 9). Later, it was found that reducing the catalyst loading to 2.5 mol % and the amount of copper acetate to 1.0 equiv resulted in no loss in yield of **3aa** (88%, entry 14), and lowering the reaction temperature to 80 °C decreased the yield from 88% to 67% (entry 17). The stoichiometric amount of Cu salt is used as an oxidant to regenerate the catalyst. Note that the use of 4 equiv of $AgSbF_6$ per molecule of [{$RuCl_2$(*p*-cymene)}$_2$] is crucial (entry 18), which is used to remove all the chlorides to generate cationic Ru catalyst. Moreover, no desired product was obtained in the absence of a ruthenium catalyst (entry 19).

Table 1 Optimization of the Reaction Conditions[a]



1 2a 3

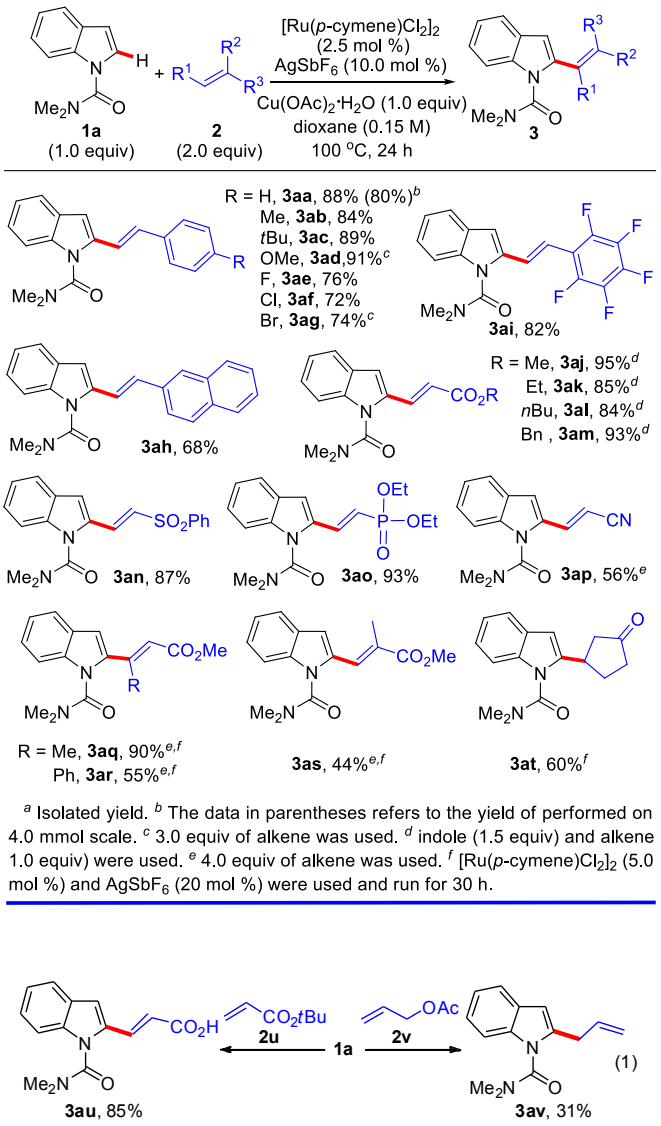
entry	R =	cat. (x mol %)	solvent	isolated yield (%)
1	$CONMe_2$ (**1a**)	5.0	Dioxane	87
2	H	5.0	Dioxane	NR
3	Me	5.0	Dioxane	NR
4	Ph	5.0	Dioxane	NR
5	Bn	5.0	Dioxane	NR
6	Ac	5.0	Dioxane	trace
7	(2-pyridyl)CH_2-	5.0	Dioxane	NR
8	$CONMe_2$	5.0	*t*-AmylOH	36
9	$CONMe_2$	5.0	DME	63
10	$CONMe_2$	5.0	THF	85
11	$CONMe_2$	4.0	Dioxane	87
12	$CONMe_2$	2.5	Dioxane	88
13	$CONMe_2$	1.0	Dioxane	78
14[b]	$CONMe_2$	2.5	Dioxane	88
15[b]	$CONMe_2$	2.5	THF	66
16[c]	$CONMe_2$	2.5	Dioxane	46
17[d]	$CONMe_2$	2.5	Dioxane	67
18[e]	$CONMe_2$	2.5	Dioxane	NR
19	$CONMe_2$	none	Dioxane	NR

[a] Reaction condition: Indole **1** (0.30 mmol), styrene **2a.** (0.60 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ / $AgSbF_6$ = 1 / 4, and $Cu(OAc)_2$ H_2O (2.0 equiv) with solvent (2.0 mL), 100 °C, 24 h, under Ar. [b] $Cu(OAc)_2$·H_2O (1.0 equiv) was used. [c] $Cu(OAc)_2$·H_2O (0.5 equiv) was used. [d] 80 °C. [e] No $AgSbF_6$.

We then explored the alkene scope of the ruthenium-catalyzed oxidative olefination transformation of **1a** under the optimized reaction conditions (Scheme 1). The styrene derivatives reacted with indole **1a** smoothly, and styrenes with electron-donating group (**3ab-3ad**) gave higher yields than those with electron-withdrawing groups (**3ae-3ag**, **3ai**). The molecular structure of **3af** was confirmed by X-ray diffraction analysis.[21] The electrophilic alkenes were then tested for our reaction. Various acrylates, such as methyl acrylate, ethyl acrylate, *n*-butyl acrylate, and benzyl acrylate performed well to afford the desired products in up to 95% yield (**3aj-3am**),[22] whereas in the reaction of **1a** with *tert*-butyl acrylate, it furnished the product **3au** in which the acrylic ester hydrolyzed into acrylic acid under the reaction conditions (eq 1). Other alkenes bearing electron-withdrawing groups were also tested: products **3an** and **3ao** could be generated from (phenylsulfonyl)ethene and diethyl vinylphosphonate in high yields (87% and 93%, respectively);

while acrylonitrile showed a lower reactivity with the formation of **3ap** in a moderate yield. Employment of the allyl acetate as the coupling partner resulted in the formation of nonconjugated terminal alkene product **3av** (eq 1). The formation of related terminal olefins starting from allyl acetate has been reported.[7e,23] Nevertheless, the coupling with 3,3-dimethyl-1-butene, α-methylstyrene, norbornylene and 2,5-norbornadiene failed using our current method.

Scheme 1. Olefin Scope of Ruthenium-Catalyzed C2 Alkenylation of **1a**.[a]



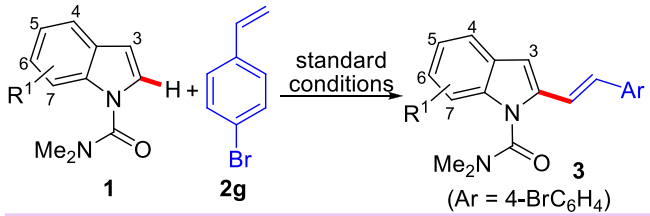
[a] Isolated yield. [b] The data in parentheses refers to the yield of performed on 4.0 mmol scale. [c] 3.0 equiv of alkene was used. [d] indole (1.5 equiv) and alkene 1.0 equiv) were used. [e] 4.0 equiv of alkene was used. [f] $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol %) and $AgSbF_6$ (20 mol %) were used and run for 30 h.

This protocol can also be applied to higher substituted alkenes: (*E*)-methyl crotonate, (*E*)-methyl cinnamate, and methyl methacrylate were successfully coupled with **1a** to provide the corresponding trisubstituted alkene products **3aq**, **3ar**, and **3as** in 90%, 55% and 44% yields,

respectively.[24] The *E* configuration of the double bond in these compounds was confirmed by NOESY.[21] Interestingly, the coupling of cyclic Michael acceptor cyclopent-2-enone with indole **1a** resulted in the addition product **3at** in good yield.[25] The molecular structure of **3at** was determined by single crystal X-ray diffraction.[21]

The scope of the reaction with respect to indole reactant was explored with *p*-bromostyene (**2g**) as the model olefin (Table 2). This coupling reaction turned out to be a versatile reaction, as the alkenylation could tolerate various functional groups, such as OMe (entry 6), F (entry 3), Cl (entries 2, 4 and 8), Br (entry 5), and NO_2 (entry 7), under the reaction conditions. The indole counterpart with the 7-methyl group gave the desired product in low yield. This might be due to the steric hindrance between the C7 methyl and the *N*,*N*-dimethylcarbamoyl directing group, which greatly increased the difficulty of the carbamoyl group directed C-H bond activation at C2-position (Scheme 2).

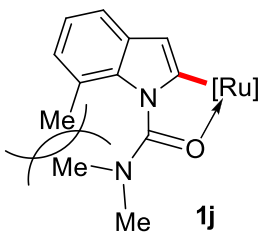
Table 2. C2 Oxidative Alkenylation of Various Indole Substrates[a]



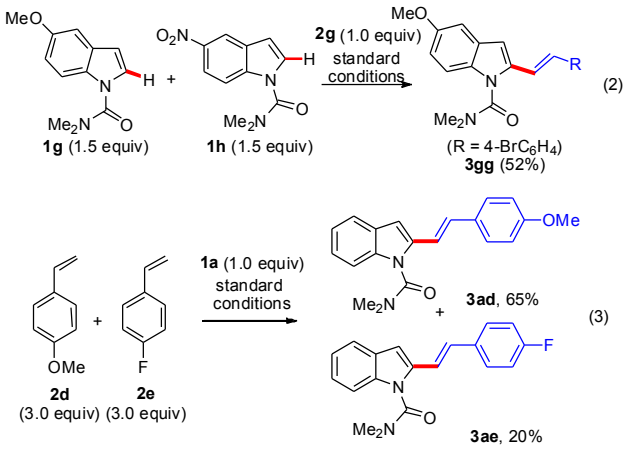
entry	R^1 =	product	isolated yield (%)	entry	R^1 =	product	isolated yield (%)
1	3-Me	**3bg**	60[b]	6	5-OMe	**3gg**	60
2	4-Cl	**3cg**	93	7	5-NO_2	**3hg**	45[b]
3	5-F	**3dg**	72	8	6-Cl	**3ig**	92
4	5-Cl	**3eg**	83	9	7-Me	**3jg**	9[b]
5	5-Br	**3fg**	90				

[a] Isolated yield. [b] [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol %), $AgSbF_6$ (20 mol %) and **2g** (3.0 equiv) were used and run for 30 h.

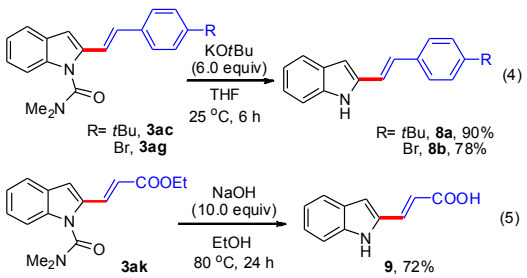
Scheme 2



We tried several times for the isolation of the Ru(II) cyclometallation organometallic species but did not get anything. We next conducted experiments to probe the working mode of the reaction. First, intermolecular competition experiments between indoles **1g** and **1h** with a single equivalent of alkene **2g** under the standard conditions revealed that electron-rich indole **1g** was transformed preferentially (eq 2), suggesting an S_EAr-type mechanism of the cyclometalated step. Then, intermolecular competition experiments between substituted styrenes **2d** and **2e** with a single equivalent of indole **1a** indicated that the electron rich styrene was more reactive under this catalytic system (eq 3), which can be rationalized in terms that the electron-rich olefins are more favorable for the coordination to Ru after the cyclometalated step.

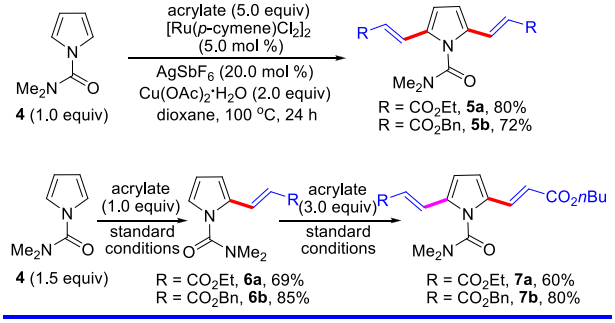


The reactions performed well on large scale (4.0 mmol, 80% for **3aa**, Scheme 1). Moreover, the dimethylcarbamoyl group can be easily removed under mild reaction conditions (eqs 4 and 5). Both of these results highlight the potential synthetic utility of this method.



Finally, we were pleased to find that the current catalytic system could be successfully applied to pyrrole substrates (Scheme 3). By changing the ratio of reactants, pyrrole **4** successfully coupled with acrylates to yield C2,C5-double alkenylated products **5** or C2-monoalkenylated products **6**. Furthermore, unsymmetrical C2,C5-dialkenylated products **7** could be efficiently achieved by subsequent C5-alkenylation of **6** with a different olefin with employing our method.

Scheme 3. Regioselective Alkenylation of Pyrrole Carbamate.



CONCLUSIONS

In summary, we have developed a Ru(II)-catalyzed oxidative C2-alkenylation of indoles and pyrroles assisted by an easily removed directing group with a broad substrate scope. The catalytic reaction proceeded with excellent regio- and stereoselectivity. Further studies to explore the ruthenium-catalyzed oxidative C-H bond transformation and the detailed mechanistic investigation are in progress in our laboratory.

Experimental Section

General Procedures. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 MHz) and ^{13}C NMR (100MHz) were recorded with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical

shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). HRMS were done on Varian 7.0 T FTICR-mass spectrometers. [{$RuCl_2$(*p*-cymene)}$_2$] was prepared from $RuCl_3 \cdot xH_2O$ following a literature procedure.[26]

General Procedure for installation of *N,N*-dimethylcarbamoyl moiety. A solution of indole (10.0 mmol, 1.0 equiv) in DMF (6.0 mL) was slowly added to a suspension of NaH (20.0 mmol) in DMF (3.0 mL) at 0 ^oC. The resulting solution was then stirred at 75 ^oC for 2-3 hours. To which dimethylcarbamic chloride (15.0 mmol, in 5 mL DMF) was added dropwise at 0 ^oC. The reaction was then stirred at 75 ^oC over night. After that, the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography.

The structure of indole substrate **1a**, **1e**, **1g**, and **1h**, which were confirmed by ^1H and ^{13}C NMR spectroscopy, are consistent with those reported previously.[20a]

N,N,3-trimethyl-1H-indole-1-carboxamide (1b). This compound was obtained as a colorless solid (1.76 g, 87% yield). M.p.: 115-117 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.31-7.25 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 3.09 (br s, 6H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3, 135.8, 130.2, 123.5, 123.4, 121.3, 118.9, 114.9, 113.5, 38.4, 9.6; IR (cm^{-1}): ν 3108, 2962, 2917, 1673, 1491, 1454, 1391, 1377, 1203, 1051, 751, 547; HRMS (ESI): Calcd for $C_{12}H_{14}N_2ONa$ $[M+Na]^+$ 225.0998, Found: 225.1002.

4-chloro-N,N-dimethyl-1H-indole-1-carboxamide (1c). This compound was obtained as light yellow oil (2.08 g, 94% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.21 (d, *J* = 2.6 Hz, 1H), 7.20 (s, 1H), 6.72 (d, *J* = 3.5 Hz, 1H), 3.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 136.2, 128.1, 126.6, 126.1, 124.1, 121.5, 112.0, 103.9, 38.4; IR

(cm^{-1}): ν 3140, 1684, 1489, 1457, 1426, 1395, 1263, 1177, 1158, 891, 750; HRMS (ESI): Calcd for $C_{11}H_{11}ClN_2ONa$ $[M+Na]^+$ 245.0452, Found: 245.0455.

5-fluoro-N,N-dimethyl-1H-indole-1-carboxamide (1d). This compound was obtained as a light yellow solid (1.96 g, 95% yield). M.p.: 86-88 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61 (dd, J = 9.0, 4.5 Hz, 1H), 7.34 (d, J = 3.5 Hz, 1H), 7.24 (dd, J = 9.1, 2.6 Hz, 1H), 7.02 (td, J = 9.1, 2.5 Hz, 1H), 6.56 (dd, J = 3.5, 0.4 Hz, 1H), 3.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7 (d, J_{C-F} = 237.6 Hz), 154.8, 132.0, 130.0 (d, J_{C-F} = 10.0 Hz), 127.6, 114.4 (d, J_{C-F} = 9.5 Hz), 111.6 (d, J_{C-F} = 25.6 Hz), 106.0 (d, J_{C-F} = 23.8 Hz), 105.5 (d, J_{C-F} = 4.2 Hz), 38.4; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -122.2 (s); IR (cm^{-1}): ν 3309, 3138, 2972, 1683, 1676, 1653, 1471, 1475, 1398, 1027, 848, 624; HRMS (ESI): Calcd for $C_{11}H_{11}FN_2ONa$ $[M+Na]^+$ 229.0748, Found: 229.0743.

5-bromo-N,N-dimethyl-1H-indole-1-carboxamide (1f). This compound was obtained as a colorless solid (2.45 g, 92% yield). M.p.: 139-141 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 1.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.37 (dd, J = 8.8, 1.9 Hz, 1H), 7.31 (d, J = 3.5 Hz, 1H), 6.54 (dd, J = 3.5, 0.4 Hz, 1H), 3.09 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.6, 134.2, 131.0, 127.2, 126.4, 123.5, 115.0, 114.9, 105.0, 38.4; IR (cm^{-1}): ν 3142, 2957, 2918, 1676, 1500, 1489, 1456, 1397, 1313, 1023, 861, 731; HRMS (ESI): Calcd for $C_{11}H_{11}BrN_2ONa$ $[M+Na]^+$ 288.9947, Found: 288.9951.

6-chloro-N,N-dimethyl-1H-indole-1-carboxamide (1i). This compound was obtained as a colorless solid (1.98 g, 89% yield). M.p.: 107-109 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 3.5 Hz, 1H), 7.17 (dd, J = 8.4, 1.8 Hz, 1H), 6.57 (d, J = 3.5 Hz, 1H), 3.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.6, 135.9, 129.5, 127.8, 126.7, 122.4, 121.7, 113.6, 105.5, 38.4; IR (cm^{-1}): ν 3126, 3105, 1675, 1491, 1454, 1439, 1395, 1203, 1160, 1121, 891, 679; HRMS (ESI): Calcd for $C_{11}H_{11}ClN_2ONa$ $[M+Na]^+$ 245.0452, Found: 245.0450.

N,N,7-trimethyl-1H-indole-1-carboxamide (1j). This compound was obtained as light red solid (1.66 g, 82% yield). M.p.: 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.1 Hz, 1H), 6.61 (d, J = 3.4 Hz, 1H), 3.04 (s, 6H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.0, 134.8, 129.5, 126.0, 125.5, 122.5, 121.7, 118.8, 105.4, 37.5 (br s), 18.6; IR (cm^{-1}): ν 3100, 1683, 1653, 1490, 1456, 1391, 1300, 1194, 1020, 787, 758; HRMS (ESI): Calcd for $C_{12}H_{14}N_2ONa$ $[M+Na]^+$ 225.0998, Found: 225.1003.

N,N-dimethyl-1H-pyrrole-1-carboxamide (4). This compound was obtained as a gray solid (1.36 g, 99% yield). A. M.p.: 70-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (t, J = 2.2 Hz, 2H), 6. 23 (t, J = 2.2 Hz, 2H), 3.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.6, 120.4, 110.3, 38.5; IR (cm^{-1}): ν 3122, 3101, 2956, 2933, 1682, 1490, 1453, 1405, 1392, 1297, 1091, 1077, 963, 745, 690, 621; HRMS (ESI): Calcd for $C_7H_{10}N_2ONa$ $[M+Na]^+$ 161.0685, Found: 161.0687.

General preparation for the product 3, **5**, **6**, **and 7**. A mixture of indole or pyrrole substrate (**1** or **4**) (0.30 mmol, 1.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (4.59 mg, 0.0075 mmol, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (60.0 mg, 0.30 mmol, 1.0 equiv.) and alkene (**2**) (0.60 mmol, 2.0 equiv) was combined in a Schlenk tube followed by addition of Dioxane (2.0 mL) under Ar atmosphere. Then the reaction mixture was heated to 100 ^{o}C with stirring for 24 hours. Afterwards, the vial was cooled to room temperature. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

(E)-N,N-dimethyl-2-styryl-1H-indole-1-carboxamide (3aa). This compound was obtained as a light yellow oil (77 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 7.51 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 8.2 Hz, 1H), 7.20-7.15 (m, 2H), 7.10 (d, J = 7.7 Hz, 1H), 7.07-7.06 (m, 2H), 6.79 (s, 1H), 2.94 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 137.0, 136.7, 136.1, 130.6, 128.6, 128.4, 127.9, 126.5 123.3, 121.6, 120.6, 117.3, 111.1,

102.9, 37.6 (br s); IR (cm^{-1}): ν 3055, 2929, 1686, 1494, 1450, 1392, 1348, 1307, 1179, 1066, 751, 693; HRMS (MALDI): Calcd for $C_{19}H_{19}N_2O$ $[M+H]^+$ 291.1492, Found: 291.1500.

(E)-N,N-dimethyl-2-(4-methylstyryl)-1H-indole-1-carboxamide (3ab). This compound was obtained as a light yellow oil (77 mg, 84% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.25 (td, *J* = 8.2, 1.2 Hz, 1H), 7.19-7.15 (m, 3H), 7.11 (br s, 2H), 6.84 (s, 1H), 3.02 (br s, 6H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 138.0, 137.3, 136.1, 134.0, 130.7, 129.4, 128.5, 126.5, 123.2, 121.5, 120.6, 116.4, 111.1, 102.6, 37.6 (br s), 21.3; IR (cm-1): ν 3045, 2963, 2922, 1686, 1508, 1489, 1450, 1390, 1306, 1179, 805; HRMS (ESI): Calcd for $C_{20}H_{21}N_2O$ $[M+H]^+$ 305.1648, Found: 305.1653.

(E)-2-(4-tert-butylstyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3ac). This compound was obtained as a light yellow solid (92 mg, 89% yield). M.p.: 91-93 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.24 (td, *J* = 8.2, 0.8 Hz, 1H), 7.16 (td, *J* = 7.9, 0.8 Hz, 1H), 7.11 (br s, 2H), 6.84 (s, 1H), 3.00 (br s, 6H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 151.2, 137.2, 136.1, 134.0, 130.6, 128.5, 126.3, 125.6, 123.2, 121.5, 120.5, 116.6, 111.1, 102.7, 37.7 (br s), 34.6, 31.2; IR (cm^{-1}): ν 3051, 2961, 2867, 1686, 1450, 1391, 1307, 1263, 1180, 1065, 818, 800; HRMS (MALDI): Calcd for $C_{23}H_{26}N_2ONa$ $[M+Na]^+$ 369.1937, Found: 369.1942.

(E)-2-(4-methoxystyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3ad). This compound was obtained as a light yellow solid (87 mg, 91% yield) by following the general procedure except 3.0 equiv of styrene was used. M.p.: 153-154 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.45-7.43 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 (td, *J* = 8.2, 1.1 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 7.00 (d, *J* = 16.3 Hz, 1H), 6.91-6.89 (m, 2H), 6.81 (s, 1H), 3.84 (s, 3H), 3.02 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 154.1, 137.5, 136.1, 130.4, 129.7,

128.6, 127.9, 123.1, 121.5, 120.5, 115.3, 114.2, 111.1, 102.2, 55.3, 37.8 (br s), 37.5 (br s); IR (cm^{-1}): ν 3034, 2964, 1683, 1601, 1508, 1450, 1391, 1175, 816, 650; HRMS (ESI): Calcd for $C_{20}H_{20}N_2O_2Na$ $[M+Na]^+$ 343.1417, Found: 343.1412.

(E)-2-(4-fluorostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3ae). This compound was obtained as a light yellow solid (70 mg, 76% yield). M.p.: 136-138 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 7.8 Hz, 1H), 7.50-7.43 (m, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.24 (td, J = 8.2, 1.2 Hz, 1H), 7.19-7.14 (td, J = 7.4, 1.1 Hz, 1H), 7.08-7.02 (m, 4H), 6.85 (s, 1H), 3.02 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, J_{C-F} = 247.9 Hz), 154.0, 137.0, 136.1, 133.0 (d, J_{C-F} = 3.1 Hz), 129.5, 128.4, 128.1 (d, J_{C-F} = 8.0 Hz), 123.4, 121.6, 120.7, 117.2 (d, J_{C-F} = 2.4 Hz), 115.7 (d, J_{C-F} = 21.8 Hz), 111.2, 102.9, 37.5 (br s); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -113.4 (s); IR (cm^{-1}): ν 3062, 2935, 1684, 1652, 1506, 1489, 1450, 1395, 1180, 822; HRMS (MALDI): Calcd for $C_{19}H_{18}FN_2O$ $[M+H]^+$ 309.1398, Found: 309.1404.

(E)-2-(4-chlorostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3af). This compound was obtained as a colorless solid (70 mg, 72% yield). M.p.: 221-223 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 7.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.34-7.29 (m, 3H), 7.24 (td, J = 8.2, 1.2 Hz, 1H), 7.18 (td, J = 7.8, 1.2 Hz, 1H), 7.13 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 16.1 Hz, 1H), 6.87 (s, 1H), 3.03 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 136.9, 136.2, 135.4, 133.5, 129.3, 128.9, 128.4, 127.7, 123.5, 121.7, 120.8, 118.0, 111.2, 103.3, 38.0 (br s); IR (cm^{-1}): ν 3076, 2932, 2360, 1683, 1487, 1448, 1393, 1345, 1175, 1089, 940, 751; HRMS (ESI): Calcd for $C_{19}H_{17}ClN_2ONa$ $[M+Na]^+$ 347.0922, Found: 347.0919.

(E)-2-(4-bromostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3ag). This compound was obtained as a light yellow solid (82 mg, 74% yield) by following the general procedure except 3.0 equiv of styrene was used. M.p.: 134-136 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 7.8 Hz,

1H), 7.49-7.46 (m, 2H), 7.37-7.35 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.24 (td, *J* = 8.2, 1.2 Hz, 1H), 7.17 (td, *J* = 7.9, 1.2 Hz, 1H), 7.15 (d, *J* = 16.4 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.87 (s, 1H), 3.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 136.8, 136.1, 135.8, 131.8, 129.3, 128.4, 128.0, 123.6, 121.7, 120.8, 118.1, 111.2, 103.4, 37.7 (br s), 37.6 (br s) (one signal missing due to overlap); IR (cm^{-1}): ν 3024, 2926, 1695, 1684, 1653, 1558, 1473, 1392, 1066, 952; HRMS (ESI): Calcd for $C_{19}H_{17}BrN_2ONa$ $[M+Na]^+$ 391.0417, Found: 391.0416.

(E)-N,N-dimethyl-2-(2-(naphthalen-2-yl)vinyl)-1H-indole-1-carboxamide (3ah). This compound was obtained as light brown solid (69 mg, 68% yield). M.p.: 176-178 ^oC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.83 (m, 4H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.52-7.46 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31-7.26 (m, 3H), 7.23-7.20 (m, 1H), 6.93 (s, 1H), 3.05 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 137.2, 136.2, 134.3, 133.6, 133.1, 130.8, 128.5, 128.3, 128.0, 127.6, 126.8, 126.4, 126.1, 123.4, 123.3, 121.6, 120.7, 117.6, 111.2, 103.1, 37.7 (br s), 37.5 (br s); IR (cm^{-1}): ν 2961, 1700, 1684, 1675, 1653, 1559, 1541, 1507, 1394, 1304, 821, 745; HRMS (ESI): Calcd for $C_{23}H_{20}N_2ONa$ $[M+Na]^+$ 363.1468, Found: 363.1465.

(E)-N,N-dimethyl-2-(perfluorostyryl)-1H-indole-1-carboxamide (3ai). This compound was obtained as a colorless solid (93 mg, 82% yield). M.p.: 180-182 ^oC; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 16.8 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 (td, *J* = 7.1, 0.7 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 16.7 Hz, 1H), 6.97 (s, 1H), 3.06 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.6, 144.7 (dm, J_{C-F} = 250.8 Hz), 139.8 (dm, J_{C-F} = 254.9 Hz), 137.7 (dm, J_{C-F} = 251.5 Hz), 136.6, 136.1, 128.2, 125.8 (td, J_{C-F} = 8.9, 2.0 Hz), 124.3, 121.9, 121.1, 113.8, 112.1 (td, J_{C-F} = 13.7, 4.2 Hz), 111.4, 105.0, 37.62, 37.58; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -142.6 (dd, *J* = 21.5, 7.7 Hz, 2F), -155.9 (td, *J* = 20.8, 3.9 Hz, 1F), -162.7 (td, *J* = 20.6, 7.6 Hz, 2F); IR (cm^{-1}): ν 2935, 1685, 1518, 1497, 1387, 1349, 1304, 1180, 1002, 962, 754; HRMS (ESI): Calcd for

$C_{19}H_{13}F_5N_2ONa$ $[M+Na]^+$ 403.0840, Found: 403.0844.

(E)-methyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3aj). This compound was obtained as a light yellow oil (78 mg, 95% yield) by following the general procedure except using 0.45 mmol of **1a** (1.5 equiv) and 0.30 mmol of alkene (**2j**) (1.0 equiv). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.31-7.30 (m, 2H), 7.06-7.20 (m, 1H), 7.00 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.01 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ166.9, 153.1, 136.9, 133.7, 133.07, 127.6, 125.1, 121.9, 121.5, 117.9, 111.3, 108.3, 51.6, 37.4(br s); IR (cm^{-1}): ν 2949, 1689, 1631, 1447, 1391, 1346, 1305, 1273, 1173, 749; HRMS (ESI): Calcd for $C_{15}H_{16}N_2O_3$ $[M+Na]^+$ 295.1053, Found: 295.1055.

(E)-ethyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3ak). This compound was obtained as a light red oil (73 mg, 85% yield) by following the general procedure except using 0.45 mmol of **1a** (1.5 equiv) and 0.30 mmol of alkene (**2k**) (1.0 equiv). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.32-7.27 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.02 (br s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 153.2, 137.0, 133.8, 132.8, 127.8, 125.1, 121.9, 121.5, 118.5, 111.4, 108.3, 60.5, 37.5 (br s), 14.2; IR (cm^{-1}): ν 2980, 2932, 1699, 1633, 1447, 1392, 1345, 1304, 1183, 1036, 973, 747; HRMS (MALDI): Calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$ 309.1210, Found: 309.1209.

(E)-butyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3al). This compound was obtained as a light yellow oil (79 mg, 84% yield) by following the general procedure except using 0.45 mmol of **1a** (1.5 equiv) and 0.30 mmol of alkene (**2l**) (1.0 equiv). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.33-7.27 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.98 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.02 (br s, 6H), 1.72-1.65 (m, 2H),

1.47-1.38 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 153.2, 137.0, 133.8, 132.8, 127.8, 125.1, 121.9, 121.5, 118.5, 111.4, 108.2, 64.4, 37.6 (br s), 30.6, 19.1, 13.7; IR (cm^{-1}): ν 2959, 2873, 1695, 1632, 1499, 1448, 1391, 1345, 1306, 1272, 1181, 1146, 744; HRMS (MALDI): Calcd for $C_{18}H_{22}N_2O_3Na$ $[M+Na]^+$ 337.1523, Found: 337.1524.

(E)-benzyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3am). This compound was obtained as a light yellow oil (97 mg, 93% yield) by following the general procedure except using 0.45 mmol of **1a** (1.5 equiv) and 0.30 mmol of alkene (**2m**) (1.0 equiv). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.44-7.35 (m, 5H), 7.32-7.31 (m, 2H), 7.21-7.17 (m, 1H), 7.00 (s, 1H), 6.41 (d, J = 16.0 Hz, 1H), 5.25 (s, 2H), 3.01 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 153.2, 137.1, 135.9, 133.8, 133.5, 128.5, 128.3, 128.2, 127.8, 125.2, 122.0, 121.7, 118.0, 111.5, 108.6, 66.4, 37.6 (br s); IR (cm^{-1}): ν 3553, 3413, 1690, 1630, 1447, 1390, 1345, 1303, 1271, 1181, 1163, 1145, 745, 693; HRMS (ESI): Calcd for $C_{21}H_{20}N_2O_3$ $[M+Na]^+$ 371.1366, Found: 371.1370.

(E)-N,N-dimethyl-2-(2-(phenylsulfonyl)vinyl)-1H-indole-1-carboxamide (3an). This compound was obtained as a light red oil (93 mg, 87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, J = 7.4 Hz, 2H), 7.73 (d, J = 15.4 Hz, 1H), 7.60 (dd, J = 7.7, 2.8 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.36-7.31 (m, 2H), 7.21-7.17 (m, 1H), 6.99 (s, 1H), 6.77 (d, J = 15.4 Hz, 1H), 2.98 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.9, 140.4, 137.3, 133.4, 131.4, 131.1, 129.3, 127.5, 127.4, 126.7, 125.8, 122.2, 121.9, 111.6, 110.4, 37.6 (br s), 37.5 (br, s); IR (cm^{-1}): ν 3057, 2963, 1684, 1607, 1446, 1394, 1308, 1261, 1145, 1084, 842; HRMS (MALDI): Calcd for $C_{19}H_{18}N_2O_3SNa$ $[M+Na]^+$ 377.0930, Found: 377.0931.

(E)-diethyl 2-(1-(dimethylcarbamoyl)-1H-indol-2-yl)vinylphosphonate (3ao). This compound was obtained as a light red oil (98 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 7.9

Hz, 1H), 7.48 (dd, *J* = 22.9, 17.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.93 (s, 1H), 6.14 (t, *J* = 17.3 Hz, 1H), 4.15-4.08 (m, 4H), 2.99 (br s, 6H), 1.33 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2, 137.0, 136.9 (d, J_{C-P} = 5.1 Hz), 134.3 (d, J_{C-P} = 27.7 Hz), 127.6, 125.1, 122.0, 121.6, 115.4, 113.5, 111.4, 107.9, 62.0, 61.9, 37.8 (br s), 37.5 (br s), 16.34, 16.30; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 18.7 (s); IR (cm^{-1}): ν 2982, 2931, 1684, 1616, 1447, 1392, 1341, 1247, 1179, 1024, 964, 852, 750; HRMS (ESI): Calcd for $C_{17}H_{23}N_2O_4PNa$ $[M+Na]^+$ 373.1288, Found: 373.1285.

(E)-2-(2-cyanovinyl)-N,N-dimethyl-1H-indole-1-carboxamide (3ap). This compound was obtained as a light red oil (40 mg, 56% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 20.0 mol % of $AgSbF_6$ and 4.0 equiv of alkene (**2p**) for 30 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 16.6 Hz, 1H), 7.37-7.33 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23-7.19 (m, 1H), 7.01 (s, 1H), 5.83 (d, *J* = 16.6 Hz, 1H), 3.04 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.0, 138.8, 137.1, 133.0, 127.5, 125.9, 122.4, 122.0, 118.0, 111.6, 108.6, 96.1, 38.0 (br s), 37.7 (br s); IR (cm^{-1}): ν 3060, 2930, 2213, 1684, 1489, 1445, 1393, 1345, 1307, 1181, 1065, 800; HRMS (ESI): Calcd for $C_{14}H_{13}N_3ONa$ $[M+Na]^+$ 262.0951, Found: 262.0955.

(E)-methyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)but-2-enoate (3aq). This compound was obtained as a light red oil (77 mg, 90% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 20.0 mol % of $AgSbF_6$ and 4.0 equiv of alkene (**2q**) for 30 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30 (td, *J* = 7.6, 1.1 Hz, 1H), 7.18 (td, *J* = 7.4, 1.0 Hz, 1H), 6.83 (s, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 3.74 (s, 3H), 3.16 (s, 3H), 2.85 (s, 3H), 2.58 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 154.0, 145.8, 140.3, 137.4, 127.8, 124.8, 121.9, 121.4, 116.6, 111.3, 108.2, 51.2, 37.8 (br s), 37.0 (br s), 17.7; IR (cm^{-1}): ν 2949, 1693, 1623, 1450, 1392, 1206, 1163, 1050, 810, 744; HRMS (MALDI): Calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$ 309.1210, Found: 309.1214.

(E)-methyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)-3-phenylacrylate (3ar). This compound was obtained as a light yellow solid (57 mg, 55% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 20.0 mol % of $AgSbF_6$ and 4.0 equiv of alkene (**2r**) for 30 h. M.p.: 111-113 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 7.9 Hz, 1H), 7.38-7.35 (m, 3H), 7.31-7.26 (m, 3H), 7.22-7.16 (m, 2H), 6.76 (s, 1H), 6.38 (s, 1H), 3.63 (s, 3H), 2.79 (br s, 3H), 2.62 (br s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 153.1, 148.1, 140.2, 137.4, 136.9, 129.5, 128.8, 127.8, 127.5, 124.8, 121.9, 121.6, 117.3, 111.3, 110.1, 51.4, 38.4, 36.4; IR (cm^{-1}): ν 2949, 1719, 1683, 1558, 1474, 1449, 1388, 1206, 1166, 1130, 763, 699; HRMS (MALDI): Calcd for $C_{21}H_{20}N_2O_3Na$ $[M+Na]^+$ 371.1366, Found: 371.1375.

(E)-methyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)-2-methylacrylate (3as). This compound was obtained as light brown oil (38 mg, 44% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 20.0 mol % of $AgSbF_6$ and 4.0 equiv of alkene (**2s**) for 30 h. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.62 (m, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 6.90 (s, 1H), 3.82 (s, 3H), 3.01 (br s, 6H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 153.4, 135.7, 133.9, 128.9, 128.3, 126.9, 124.7, 121.8, 121.4, 111.5, 109.3, 52.2, 37.8 (br), 14.9; IR (cm^{-1}): ν 3054, 2951, 1699, 1627, 1490, 1449, 1391, 1309, 1262, 1218, 1113, 802, 751; HRMS (ESI): Calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$ 309.1210, Found: 309.1210.

N,N-dimethyl-2-(3-oxocyclopentyl)-1H-indole-1-carboxamide (3at). This compound was obtained as a light yellow solid (49 mg, 60% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$ and 20.0 mol % of $AgSbF_6$ for 30 h. M.p.: 174-176 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 7.8 Hz, 1H), 7.25-7.21 (m, 1H), 7.18-7.13 (m, 2H), 6.40 (s, 1H), 3.88-3.84 (m, 1H), 3.09 (br s, 6H), 2.73-2.70 (m, 1H), 2.47-2.09 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 217.5, 154.2, 142.3, 135.5, 128.0, 122.9, 121.3, 120.6, 110.8, 101.9, 44.5, 38.0, 34.2, 29.0

(br s) (one carbon signal missing due to overlap); IR (cm^{-1}): ν 2918, 1742, 1685, 1637, 1617, 1456, 1392, 1300, 1187, 1060, 749, 621; HRMS (ESI): Calcd for $C_{16}H_{18}N_2O_2$ $[M+Na]^+$ 293.1261, Found: 293.1263.

(E)-3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylic acid (3au). This compound was obtained as a gray white solid (66 mg, 85% yield). M.p.: 172-174 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 15.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 2H), 7.23-7.18 (m, 1H), 7.07 (s, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.07 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 153.3, 137.2, 135.0, 133.5, 127.7, 125.5, 122.1, 121.8, 117.4, 111.5, 109.2, 37.6 (br s); IR (cm^{-1}): ν 2928, 1684, 1629, 1489, 1448, 1394, 1183, 748; HRMS (ESI): Calcd for $C_{14}H_{14}N_2O_3$ $[M-H]^-$ 257.0932, Found: 257.0935.

2-allyl-N,N-dimethyl-1H-indole-1-carboxamide (3av). This compound was obtained as light yellow oil (21 mg, 31% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 20.0 mol % of $AgSbF_6$ and 4.0 equiv of alkene (**2v**). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J* = 7.7 Hz, 1H),7.19 (d, *J* = 3.7 Hz, 2H), 7.16-7.11 (m,1H), 6.38 (s, 1H), 6.00-5.90 (m, 1H), 5.18-5.10 (m, 2H), 3.63 (d, *J* = 6.4 Hz, 2H), 3.01 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.2, 138.5, 135.6, 134.7, 128.4, 122.4, 121.0, 120.3, 116.8, 110.8, 104.0, 37.6 (br s), 37.4 (br s), 31.7; IR (cm^{-1}): ν 3054, 2961, 2926, 1684, 1489, 1455, 1391, 1302, 1063, 797; HRMS (ESI): Calcd for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$ 251.1155, Found: 251.1156.

(E)-2-(4-bromostyryl)-N,N,3-trimethyl-1H-indole-1-carboxamide (3bg). This compound was obtained as a slight yellow oil (69 mg, 60% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$ and 0.90 mmol of 4-Bromostyrene (3.0 equiv) for 30 h. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.30-7.26 (m, 1H), 7.23-7.17 (m, 2H), 6.76 (d, *J* = 16.5 Hz, 1H), 3.00 (br s,

6H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 136.2, 135.8, 132.1, 131.7, 129.4, 129.0, 127.7, 124.1, 121.4, 121.1, 119.1, 117.7, 114.8, 110.9, 37.5 (br s), 9.8; IR (cm^{-1}): ν 3049, 2926, 1684, 1630, 1487, 1454, 1392, 1108, 1008, 807; HRMS (ESI): Calcd for $C_{20}H_{19}BrN_2ONa$ $[M+Na]^+$ 405.0573, Found: 405.0570.

(E)-2-(4-bromostyryl)-4-chloro-N,N-dimethyl-1H-indole-1-carboxamide (3cg). This compound was obtained as a slight yellow oil (112 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.20 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.18-7.14 (m, 2H), 7.13-7.11 (m, 2H), 6.97 (s, 1H), 3.14 (br s, 3H), 2.91 (br s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2, 137.3, 136.4, 135.4, 131.7, 130.4, 128.0, 127.2, 125.8, 123.9, 121.9, 121.3, 117.3, 109.7, 101.1, 37.5 (br s); IR (cm^{-1}): ν 3056, 2962, 2927, 1690, 1487, 1426, 1397, 1261, 1168, 1071, 1008, 808; HRMS (MALDI): Calcd for $C_{19}H_{16}BrClN_2ONa$ $[M+Na]^+$ 425.0027, Found: 425.0026.

(E)-2-(4-bromostyryl)-5-fluoro-N,N-dimethyl-1H-indole-1-carboxamide (3dg). This compound was obtained as a slight yellow solid (83 mg, 72% yield). M.p.: 182-184 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.21-7.25 (m, 2H), 7.11 (d, *J* = 16.4 Hz, 1H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.98 (td, *J* = 9.1, 2.5 Hz, 1H), 6.82 (s, 1H), 3.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.8 (d, J_{C-F} = 237.5 Hz), 153.7, 138.4, 135.6, 132.6, 131.9, 130.1, 129.0 (d, J_{C-F} = 10.6 Hz), 128.1, 122.0, 117.8, 112.0 (d, J_{C-F} = 9.7 Hz), 111.7 (d, J_{C-F} = 26.2 Hz), 105.7 (d, J_{C-F} = 23.8 Hz), 103.0 (d, J_{C-F} = 4.5 Hz), 37.7 (br s); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -112.1 (s); IR (cm^{-1}): ν 3064, 2931, 1683, 1615, 1581, 1486, 1444, 1068, 941, 807; HRMS (ESI): Calcd for $C_{19}H_{16}BrFN_2ONa$ $[M+Na]^+$ 409.0322, Found: 409.0325.

(E)-2-(4-bromostyryl)-5-chloro-N,N-dimethyl-1H-indole-1-carboxamide (3eg). This compound was obtained as a slight yellow solid (100 mg, 83% yield). M.p.: 174-176 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H),

7.22 (d, *J* = 8.7 Hz, 1H), 7.18 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.79 (s, 1H), 3.00 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.4, 138.1, 135.4, 134.4, 131.8, 130.2, 129.4, 128.0, 127.2, 123.6, 122.0, 120.1, 117.5, 112.2, 102.4, 37.7 (br s), 37.6 (br s); IR (cm^{-1}): ν 3028, 2933, 1684, 1653, 1488, 1437, 1392, 1175, 1059, 963, 813; HRMS (MALDI): Calcd for $C_{19}H_{17}BrClN_2O$ $[M+H]^+$ 403.0207, Found: 403.0209.

(E)-2-(4-bromostyryl)-5-bromo-N,N-dimethyl-1H-indole-1-carboxamide (3fg). This compound was obtained as a slight yellow solid (121 mg, 90% yield). M.p.: 145-147 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.80 (s, 1H), 3.01 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.4, 138.0, 135.5, 134.7, 131.9, 130.4, 130.1, 128.1, 126.3, 123.2, 122.0, 117.5, 114.9, 112.6, 102.3, 37.74 (br s), 37.68 (br s); IR (cm^{-1}): ν 3025, 2932, 1686, 1487, 1436, 1390, 1307, 1175, 1050, 812; HRMS (ESI): Calcd for $C_{19}H_{16}Br_2N_2ONa$ $[M+Na]^+$ 468.9522, Found: 468.9514.

(E)-2-(4-bromostyryl)-5-methoxy-N,N-dimethyl-1H-indole-1-carboxamide (3gg). This compound was obtained as a slight red solid (72 mg, 60% yield). M.p.: 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.13 (d, *J* = 16.3 Hz, 1H), 7.02(dd, *J* = 9.4, 6.9 Hz, 2H), 6.89 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.80 (s, 1H), 3.86 (s, 3H), 3.02 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.4, 154.0, 137.5, 135.4, 131.8, 131.3, 129.14, 129.06, 128.0, 121.7, 118.2, 113.5, 112.1, 103.2, 102.3, 55.7, 37,9 (br s), 37.7 (br s); IR (cm^{-1}): ν 2962, 1674, 1653, 1487, 1471, 1262, 1100, 1068, 1031, 802; HRMS (MALDI): Calcd for $C_{20}H_{20}BrN_2O_2$ $[M+H]^+$ 399.0703, Found: 399.0706.

(E)-2-(4-bromostyryl)-N,N-dimethyl-5-nitro-1H-indole-1-carboxamide (3hg). This compound was obtained as a light yellow solid (56 mg, 45% yield) by following the general

procedure except using 5.0 mol % of [Ru(*p*-cymene)Cl_2]$_2$ and 0.90 mmol of 4-Bromostyrene (3.0 equiv) for 30 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, *J* = 1.9 Hz, 1H), 8.13 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 3H), 7.14 (d, *J* = 16.3 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.98 (s, 1H), 3.26 (s, 3H), 2.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.6, 143.2, 139.9, 138.7, 135.1, 132.0, 131.8, 128.2, 127.8, 122.6, 118.8, 117.4, 116.7, 111.1, 103.8, 37.6 (br s), 37.2 (br s); IR (cm^{-1}): ν 2936, 1698, 1507, 1488, 1395, 1338, 1303, 1178, 1073, 810, 745, 669; HRMS (ESI): Calcd for $C_{19}H_{16}BrN_3O_3Na$ $[M+Na]^+$ 436.0267, Found: 436.0268.

(E)-2-(4-bromostyryl)-6-chloro-N,N-dimethyl-1H-indole-1-carboxamide (3ig). This compound was obtained as a light yellow solid (111 mg, 92% yield). M.p.: 144-146 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 8.3 Hz, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 (br s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.82 (s, 1H), 3.03 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.3, 137.5, 136.4, 135.5, 131.8, 129.8, 129.3, 128.0, 126.9, 122.4, 121.9, 121.5, 117.6, 111.2, 103.1, 37.9 (br s), 37.6 (br s); IR (cm^{-1}): ν 2962, 1683, 1486, 1389, 1302, 1261, 1100, 1070, 1053, 1008, 805; HRMS (ESI): Calcd for $C_{19}H_{16}BrClN_2ONa$ $[M+Na]^+$ 425.0027, Found: 425.0032.

(E)-2-(4-bromostyryl)-N,N,7-trimethyl-1H-indole-1-carboxamide (3jg). This compound was obtained as a light yellow oil (10 mg, 9% yield) by following the general procedure except using 5.0 mmol % of [Ru(*p*-cymene)Cl_2]$_2$ and 0.90 mmol of 4-Bromostyrene (3.0 equiv) for 30 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.12-7.05 (m, 2H), 7.01-6.96 (m, 2H), 6.85 (s, 1H), 3.25 (s, 3H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.9, 135.73, 135.72, 135.0, 131.8, 129.5, 128.6, 128.0, 125.5, 121.7, 121.5, 121.0, 118.7, 117.2, 102.3, 37.7, 36.6, 17.4; IR (cm^{-1}): ν 3047, 2958, 2925, 1689, 1486, 1394, 1311, 1263, 1072, 1008, 809, 741; HRMS (ESI): Calcd for $C_{20}H_{19}BrN_2ONa$ $[M+Na]^+$ 405.0573,

Found: 405.0574.

(2E,2'E)-diethyl 3,3'-(1-(dimethylcarbamoyl)-1H-pyrrole-2,5-diyl)diacrylate (5a). This compound was obtained as a light green oil (80 mg, 80% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 5.0 equiv of acrylic acid ester and 2.0 equiv of $Cu(OAc)_2 \cdot H_2O$. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, J = 15.9 Hz, 1H), 6.68 (s, 2H), 6.20 (d, J = 15.9 Hz, 2H), 4.22 (qd, J = 7.1, 1.7 Hz, 4H), 3.23 (s, 3H), 2.61 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 152.0, 131.4, 130.8, 116.7, 114.0, 60.5, 37.7, 37.0, 14.3; IR (cm^{-1}): ν 2981, 2935, 1704, 1620, 1410, 1393, 1332, 1166, 1039, 970, 794; HRMS (MALDI): Calcd for $C_{17}H_{22}N_2O_5Na$ $[M+Na]^+$ 357.1421, Found: 357.1428.

(2E,2'E)-benzyl 3,3'-(1-(dimethylcarbamoyl)-1H-pyrrole-2,5-diyl)diacrylate (5b). This compound was obtained as a light red oil (98 mg, 72% yield) by following the general procedure except using 5.0 mol % of $[Ru(p\text{-cymene})Cl_2]_2$, 5.0 equiv of acrylic acid ester and 2.0 equiv of $Cu(OAc)_2 \cdot H_2O$. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 15.9 Hz, 2H), 7.39-7.38 (m, 6H), 6.69 (s, 2H), 6.25 (d, J = 15.9 Hz, 2H), 5.22 (s, 4H), 3.21 (s, 3H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 151.7, 135.9, 131.4, 131.3, 128.5, 128.1, 116.3, 114.1, 66.3, 37.6, 36.9 (one signal missing due to overlap); IR (cm^{-1}): ν 3065, 3033, 2949, 1704, 1620, 1497, 1409, 1391, 1263, 1159, 969, 785; HRMS (MALDI): Calcd for $C_{27}H_{26}N_2O_5Na$ $[M+Na]^+$ 481.1734, Found: 481.1731.

(E)-ethyl 3-(1-(dimethylcarbamoyl)-1H-pyrrol-2-yl)acrylate (6a). This compound was obtained as a light brown solid (49 mg, 69% yield) by following the general procedure except using 1.5 equiv of pyrrole substrate and 1.0 equiv of acrylic acid ester. M.p.: 68-70 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, J = 15.9 Hz, 1H), 6.94-6.93 (m, 1H), 6.67-6.66 (m, 1H), 6.26 (t, J = 2.9 Hz, 1H), 6.11 (d, J = 15.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.96 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 153.5, 132.5, 129.1, 123.8, 114.7, 113.6, 111.1, 60.2, 37.8 (br s),

14.3; IR (cm^{-1}): ν 3146, 3128, 3070, 2964, 1700, 1684, 1653, 1625, 1437, 1387, 1262, 1100, 1058, 1028, 880, 800, 727; HRMS (MALDI): Calcd for $C_{12}H_{16}N_2O_3Na$ $[M+Na]^+$ 259.1053, Found: 259.1060.

(E)-benzyl 3-(1-(dimethylcarbamoyl)-1H-pyrrol-2-yl)acrylate (6b). This compound was obtained as a colorless solid (76 mg, 85% yield) by following the general procedure except using 1.5 equiv of pyrrole and 1.0 equiv of acrylic acid ester. M.p.: 70 - 72 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.41-7.32 (m, 5H), 6.96 (dd, *J* = 2.9, 1.5 Hz, 1H), 6.69 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.28 (t, *J* = 3.3 Hz, 1H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.22 (s, 2H), 2.96 (br s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 153.4, 136.1, 133.0, 129.0, 128.4, 128.09, 128.06, 124.0, 114.2, 113.8, 111.2, 66.0, 37.8 (br s); IR (cm^{-1}): ν 3123, 3066, 3039, 2932, 1670, 1684, 1653, 1623, 1558, 1489, 1456, 1275, 1157, 741; HRMS (MALDI): Calcd for $C_{17}H_{18}N_2O_3Na$ $[M+Na]^+$ 321.1210, Found: 321.1216.

(E)-butyl 3-(1-(dimethylcarbamoyl)-5-((E)-3-ethoxy-3-oxoprop-1-enyl)-1H-pyrrol-2-yl)acrylate (7a). This compound was obtained as a slight red oil (65 mg, 60% yield) by following the general procedure except using 3.0 equiv of acrylic acid ester. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, *J* = 15.9 Hz, 1H), 7.37 (d, *J* = 15.9 Hz, 1H), 6.68 (s, 2H), 6.189 (d, *J* = 15.9 Hz, 1H), 6.185 (d, *J* = 15.9 Hz, 1H), 4.24-4.14 (m, 4H), 3.22 (s, 3H), 2.60 (s, 3H), 1.68-1.61 (m, 2H), 1.44-1.35 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.85, 166.80, 152.0, 131.4, 130.8, 116.7, 114.0, 113.9, 64.4, 60.5, 37.7, 37.0, 30.7, 19.1, 14.3, 13.7; IR (cm^{-1}): ν 3524, 3446, 3306, 2960, 1704, 1626, 1558, 1457, 1393, 1304, 1265, 1168, 1038; HRMS (ESI): Calcd for $C_{19}H_{26}N_2O_5$ $[M+Na]^+$ 385.17341, Found: 385.1739.

(E)-benzyl 3-(5-((E)-3-butoxy-3-oxoprop-1-enyl)-1-(dimethylcarbamoyl)-1H-pyrrol-2-yl)acrylate (7b). This compound was obtained as a slight red oil (102 mg, 80% yield) by following the general

procedure except using 3.0 equiv of acrylic acid ester. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 15.9 Hz, 1H), 7.40-7.33 (m, 6H), 6.69 (s, 2H), 6.25 (d, J = 16.5 Hz, 1H), 6.21 (d, J = 16.1 Hz, 1H), 5.22 (s, 2H), 4.17 (td, J = 6.7, 1.0 Hz, 2H), 3.22 (s, 3H), 2.61 (s, 3H), 1.69-1.62 (m, 2H), 1.45-1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 166.4, 151.6, 135.8, 131.5, 131.3, 131.2, 130.6, 128.4, 128.1, 116.8, 116.1, 114.0, 113.8, 66.2, 64.3, 37.6, 36.9, 30.5, 19.0, 13.6; IR (cm^{-1}): ν 2923, 1704, 1558, 1539, 1456, 1393, 1265, 1161, 970, 749, 699; HRMS (ESI): Calcd for $C_{24}H_{28}N_2O_5$ $[M+Na]^+$ 447.1890, Found: 447.1893.

Competition experiments with indoles 1g and 1h (eq 2). A mixture of indole substrates **1g** (0.45 mmol, 1.5 equiv), **1h** (0.45 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (4.59 mg, 0.0075 mmol, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (60.0 mg, 0.30 mmol, 1.0 equiv.), and 4-bromostyrene (**2g**) (0.30 mmol, 1.0 equiv) was combined in a Schlenk tube followed by addition of Dioxane (2.0 mL) under Ar atmosphere. Then the reaction mixture was heated to 100 ^{o}C with stirring for 24 hours. Afterwards, the vial was cooled to room temperature. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel. Only the product **3gg** (62 mg, 52% yield) was isolated.

Competition Experiments with Alkenes 2d and 2e (eq 3). A mixture of indole substrate (**1a**) (0.30 mmol, 1.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (4.59 mg, 0.0075 mmol, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (60.0 mg, 0.30 mmol, 1.0 equiv.), 4-vinylanisole (**2d**) (0.90 mmol, 3.0 equiv) and 4-fluorostyrene (**2e**) (0.90 mmol, 3.0 equiv) was combined in a Schlenk tube followed by addition of dioxane (2.0 mL) under Ar atmosphere. Then the reaction mixture was heated to 100 ^{o}C with stirring for 24 hours. Afterwards, the vial was cooled to room temperature. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford products **3ad** (62 mg, 65% yield) and **3ae** (18 mg, 20%

yield).

Procedure for removal of dimethylcarbamoyl moiety (eq 4). *N*,*N*-dimethyl-2-styryl-1*H*-indole-1-carboxamide (0.15 mmol) was charged in a 50 mml round bottom flask, then 6.0 equiv KO*t*Bu (0.90 mmol, 101 mg) and THF (2.5 mL) was added. The reaction mixture was stirred at 25 ^{o}C for about 16h. The solution was then diluted with NH_4Cl solution, the aqueous phase was extacted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Then the crude product can be purified by column chromatography on silica gel.

(*E*)-2-(4-*tert*-butylstyryl)-1*H*-indole (8a). This compound was obtained as a grey solid (37 mg, 90% yield). M.p.: 127-129 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.11-7.07 (m, 2H), 6.90 (d, J = 16.5 Hz, 1H), 6.60 (s, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.0, 136.9, 136.5, 134.0, 129.0, 127.0, 126.0, 125.7, 122.7, 120.5, 120.1, 118.2, 110.5, 103.5, 34.6, 31.3. IR (cm^{-1}): ν 3450, 2962, 2865, 1457, 1410, 1362, 1262, 1103, 1024, 819, 800, 737. HRMS (ESI): Calcd for $C_{20}H_{20}N$ $[M-H]^-$ 274.1601, Found: 274.1603.

(*E*)-2-(4-bromostyryl)-1*H*-indole (8b). This compound was obtained as a light yellow solid (35 mg, 78% yield). M.p.: 229-231 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.40 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52-7.49 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 16.5 Hz, 1H), 7.17-7.09 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 137.4, 136.5, 136.3, 131.7, 128.3, 128.1, 125.7, 122.3, 120.5, 120.3, 120.2, 119.3, 111.0, 103.5. IR (cm^{-1}): ν 3393, 1684, 1653, 1635, 1558, 1486, 1031, 998, 966, 810, 752, 655. HRMS (ESI): Calcd for $C_{16}H_{11}BrN$ $[M-H]^-$ 296.0080, Found: 296.0082.

Procedure for removal of dimethylcarbamoyl moiety (eq 5). (*E*)-ethyl

3-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)acrylate (1.0 mmol) was charged in a 50 mml round bottom flask, then NaOH solid (10.0 mmol) and Ethanol (10 mL) was added. The mixture was stirred at 80 ^{o}C for 24 hours. After the reaction completed, EtOH was evaperated under reduced pressure, the residue was diluted with Et_2O (25 mL). The pH of the solution was adjusted to 2-3 at 0 ^{o}C using a solution of 3M HCl. The aqueous solution was extacted with Et_2O (3 × 20 mL) and the combined the organic layers was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (eluent: CH_3OH/CH_2Cl_2 = 1 : 40, v/v) to give the (*E*)-3-(1*H*-indol-2-yl)acrylic acid (**9**)[27] as a sligtly yellow solid (135 mg, 72% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.34 (s, 1H), 11.55 (s, 1H), 7.56 (d, *J* = 16.1 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 6.45 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.8, 138.1, 134.5, 134.0, 128.0, 123.8, 121.1, 119.8, 116.9, 111.5, 108.0.

X-ray crystallography studies: Data collection was performed by using graphite-monochromated MoKα radiation (ω-2θ scans). Semiempirical absorption corrections were applied for all complexes.[28] The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system.[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. The crystal data and summary of the X-ray data collection are presented in Table S1 in the Supporting Information.

ASSOCIATED CONTENT

Supporting information

Full spectroscopic data for all new compounds, and CIF files giving X-ray structural

information for **3af** and **3at**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Email: nklibin@nankai.edu.cn, bqwang@nankai.edu.cn

Author Contributions

[§]J. Ma and W. Xie contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are grateful to NSFC (Nos. 21072097, 21072101, 21121002, and 21372121) and SRFDP (No. 20110031110009) for financial support.

REFERENCE

(1) For selected recent reviews about C-H bond functionalizations, see: (a) Ackermann, L. *Acc. Chem. Res.* **2013**, DOI: 10.1021/ar3002798. (b) Kozhushkov, S. I.; Ackermann, L. *Chem. Sci*. **2013**, *4*, 886. (c) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (e) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (f) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (g) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (h) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31. (i) Engle, K. M.; Mei, T. S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (j) Colby, D.

A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (k) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev*. **2012**, *41*, 5588.

(2) (a) Bugaut, X.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 7479. (b) Ackermann, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3842. (c) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (d) Ashenhurst, J. A. *Chem. Soc. Rev.* **2010**, *39*, 540.

(3) (a) Hartwig, J. F. *Chem. Soc. Rev.* **2011**, *40*, 1992. (b) Enthaler, S.; Company, A. *Chem. Soc. Rev.* **2011**, *40*, 4912. (c) Stokes, B. J.; Driver, T. G. *Eur. J. Org. Chem.* **2011**, 4071. (d) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(4) For first report, see: (a) Moritani, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, *8*, 1119. For reviews, see: (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (c) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev*. **2007**, *107*, 5318.

(5) For recent reviews, see: (a) *The Mizoroki-Heck Reaction*; Oestreich, M., Ed.; Wiley: Chichester, 2009. (b) Bräse, S.; de Meijere, A. In *Metal-Catalyzed Cross-Coupling Reaction*s; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: New York, 2004; Chapter 5.

(6) For selected examples, see: (a) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *Chem. Commun.* **2011**, *47*, 12789. (b) Lu, Y.; Leow, D.; Wang, X.; Engel, K. M.; Yu, J.-Q. *Chem. Sci.* **2011**, *2*, 967. (c) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010**, *327*, 315. (d) Shi,B. -F.; Zhang, Y.-H.; Lam, J. K.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 460. (e) Lu, Y. Wang, D.-H.; Engle, K.-M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 5916. (f) Wasa, M.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 3680. (g) Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 1972 and references cited therein.

(7) For selected examples, see: (a) Zhu, C.; Flack, J. R. *Chem. Commun.* **2012**, *48*, 1674. (b) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (c) Patureau,

F. W.; Besset, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1064. (d) Besset, T.; Kuhl, N.; Patureau, F. W.; Glorius, F. *Chem. Eur. J.* **2011**, *17*, 7167. (e) Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**, *13*, 540. (f) Park, S.; Kim, J. Y.; Chang, S. *Org. Lett.* **2011**, *13*, 2372. (g) Feng, C.; Loh, T.-P. *Chem. Commun.* **2011**, 47, 10458. (h) Gong, T.-J.; Xiao, B.; Liu, Z.-J.; Wan, J.; Xu, J.; Luo, D.-F.; Fu, Y.; Liu, L. *Org. Lett.* **2011**, *13*, 3235. (i) Mochida, S.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2011**, *76*, 3024. (j) Wang, F.; Song, G.; Du, Z.; Li, X. *J. Org. Chem.* **2011**, *76*, 2926. (k) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982.

(8) Selected reviews for C-H functionalization employing directing groups, see: (a) Lyons, T. W.; Sanford, M. S. *Chem. Rev*. **2010**, 110, 1147. (b) Alberico,D.; Scott, M. E.; Lautens, M. *Chem*. *Rev*. **2007**, 107, 174.

(9) (a) Sundberg, R. J. *The Chemistry of Indoles*, Academic Press, New York, 1970. (b) Thomson, R. H. *The Chemistry of Natural Products*, Blackie and Son, Glasgow, 1985. (c) Gribble, G. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1045. (d) Garg, N. K.; Sarpong, R.; Stoltz, B. M. *J. Am. Chem. Soc.* **2002**, *124*, 13179. (e) Tois, J.; Franzén, R.; Koskinen, A. *Tetrahedron* **2003**, *59*, 5395. (f) Chen, F.-E.; Huang, J. *Chem. Rev*. **2005**, *105*, 4671.

(10) (a) García-Rubia, A.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 6515. (b) García-Rubia, A.; Arrayás, R. G.; Carretero, J. C. *Chem. Eur. J.* **2010***, 16,* 9676. (c) Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett*. **2008**, *10*, 1159. (d) Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem. Int. Ed*. **2005**, *44*, 3125. (e) Capito, E.; Brown, J. M.; Ricci, A. *Chem*. *Commun*. **2005**, 1854.

(11) a) Ueyama, T.; Mochida, S.; Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2011**, *13*, 706. (b) Hashimoto, Y.; Ortloff, T.; Hirano, K.; Satoh, T.; Bolm, C.; Miura, M. *Chem. Lett.* **2012**, *41*, 151.

(12) (a) Ackermann, L.; Pospech, J. *Org. Lett.* **2011**, *13*, 4153. (b) Ackermann, L.; Wang, L.; Wolfram, R.; Lygin, A. V. *Org. Lett.* **2012**, *14*, 728. (c) Graczyk, K.; Ma, W.; Ackermann, L. *Org. Lett.* **2012**, *14*, 4110. (d) Li, J.; Kornhaaß, C.; Ackermann, L. *Chem. Commun.*, **2012**, *48*, 11343.

(13) (a) Arockiam, P. B.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *Green Chem.*, **2011**, *13*, 3075. (b) Singh, K. S.; Dixneuf, P. H. *Organometallics* **2012**, *31*, 7320.

(14) (a) Padala, K.; Jeganmohan, M. *Org. Lett.* **2011**, *13*, 6144. (b) Padala, K.; Jeganmohan, M. *Org. Lett.* **2012**, *14*, 1134.

(15) Chidipudi, S. R.; Wieczysty, M. D.; Khan, I.; Lam, H. W. *Org. Lett.* **2013**, *15*, 570.

(16) Goriya Y.; Ramana C. V. *Chem.-Eur. J.* **2012**, *18*, 13288.

(17) Li, B.; Ma, J.; Liang, Y.; Wang, N.; Xu, S.; Song, H.; Wang, B. *Eur. J. Org. Chem*. **2013**, 1950.

(18) (a) Li, B.; Ma, J.; Wang, N.; Feng, H.; Xu, S.; Wang, B. *Org. Lett*. **2012**, *14*, 736. (b) Li, B.; Feng, H.; Xu, S.; Wang B. *Chem.-Eur. J.* **2011**, *17*, 12573.

(19) (a) Lanke, V.; Prabhu, K. *Org. Lett*. **2013**, *15*, 2818. In addition, for Rh-catalyzed C2 oxidative olefination of indole, see ref 7k and (b) Li, B.; Ma, J.; Xie, W.; Song, H.; Xu, S.; Wang B. *Chem.-Eur. J.* **2013**, *19*, 11863..

(20) Using carbamoyl group as a directing group for Rh-catalyzed indole C-H activation at C2-position, see: (a) Schipper, D. J.; Hutchinson, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6910. (b) Zhou, B.; Yang, Y.; Li, Y. *Chem*. *Commun*., **2012**, *48*, 5163 and also see ref 19b.

(21) See Supporting Information for details.

(22) Excess of acrylates afforded a mixture of C2-monoalkenylated and C2,C7-dialkenylated products.

(23) (a) Wang, H.; Schröder, N.; Glorius, F. *Angew. Chem., Int. Ed*. **2013**, *52*, 5386. (b) Li, X.; Gong, X.; Zhao, M.; Song, G.; Deng, J.; Li, X. *Org. Lett*. **2011**, *13*, 5808 and references cited therein. (c) The possibility that the allyl substrate affords product by a different mechanism, see: Zaitsev, A. B.; Gruber, S.; Plüss, P. A.; Pregosin, P. S.; Veiros, L. F.; Wörle M. *J. Am. Chem. Soc.* **2008**, *130*, 11604.

(24) For an excellent report on the Pd(II)-catalyzed diastereoselective C-2 alkenylation of indoles, see: Kandukuri, S. R.; Schiffner, J. A.; Oestreich M. *Angew. Chem. Int. Ed*. **2012**, *51*, 1265.

(25) At present, we do not know the exact reason why cyclopent-2-enone gave the addition product. Lee *et al*. recently reported that more polar solvents promote the oxidative Heck reaction over conjugate addition on cyclic Michael acceptor substrates, see: Walker, S. E.; Boehnke, J.; Glen, P. E.; Levey, S.; Patrick, L.; Jordan-Hore, J. A.; Lee, A.-L. *Org. Lett*. **2013**, *15*, 1886.

(26) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.*, **1974**, 233.

(27) Hibino, S.; Sugino, E.; Kuwada, T.; Ogura, N.; Sato, K.; Choshi, T. *J. Org. Chem.* **1992**, *57*, 5917.

(28) Sheldrick, G. M. Program for Empirical Absorption Correction of Area Detector data; University of Göttingen, Göttingen, Germany, 1996.

(29) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Germany, 1997.