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Palladium-Catalyzed Intermolecular C-2 Alkenylation of Indoles Using Oxygen as the Oxidant

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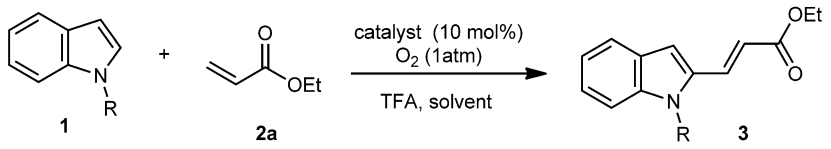
Abstract: A general and efficient palladium-catalyzed intermolecular direct C-2 alkenylation of indoles using oxygen as the oxidant has been developed. The reaction is of complete regio- and stereoselectivity. All products are *E*-isomers at the C-2-position with no *Z*-isomers and 3-substituted products were detected.

Keywords: C-2 alkenylation; C–H activation; indoles; oxygen oxidation; palladium-catalyzed reaction

The indole ring is a widespread structural unit in pharmaceuticals, agrochemicals, and functional materials.[1] The development of efficient strategies for the functionalization of the indole nucleus has been a long-standing topic in organic synthesis.[2] Among them the metal-catalyzed alkenylation reaction is a very appealing approach for the direct functionalization of indoles. Because of the higher nucleophilic character of the C-3 position compared with the C-2 position in indole, the C-3-position of indole is the inherently more reactive site.[3,4] Therefore, the C-2 alkenylation of C-2/C-3-unsubstituted indoles is a challenge. To the best of our knowledge, only a few protocols have been reported so far for the direct C–H alkenylation with alkenes at the C-2 position of indoles, despite the potential utility of such products.[5] In 2005, Gaunt et al. realized a palladium(II)-catalyzed direct and solvent-controlled regioselective C-2 alkenylation of indoles using *tert*-butyl benzoyl peroxide (*t*-BuOOBz, 0.9 equiv.) as the oxidant.[6] However, the yields were low to moderate ($\leq$57%). In the same year, Ricci et al. described a palladium(II)-catalyzed regiocontrolled C-2 alkenylation of indole directed by a non-removable *N*-2-pyridylmethyl group using a stoichiometric amount of $Cu(OAc)_2$ as the oxidant.[7] In 2008, Miura, Satoh et al. reported the palladium(II)-catalyzed C-2 vinylation of indole-3-carboxylic acids using $Cu(OAc)_2 \cdot H_2O$ (2 equiv.) as the oxidant, in which the carboxyl group blocks the C-3 position and acts as a removable directing group.[8] In 2009, Arrayás, Carretero et al. disclosed an elegant palladium(II)-catalyzed regioselective direct C-2 alkenylation of indoles assisted by the removable *N*-(2-pyridyl)sulfonyl directing group using $Cu(OAc)_2 \cdot H_2O$ (1–2 equiv.) as the oxidant; nevertheless the excess of alkenes (2–5 equiv.) was employed.[9] More recently, Prabhu et al. developed a ruthenium(II)-catalyzed C-2 alkenylation of *N*-benzoylindoles using $Cu(OAc)_2 \cdot H_2O$ (1 equiv.) as oxidant and $AgSbF_6$ (20 mol%) as an activator.[10] In spite of these important advances, some challenging issues still remain: for example, (i) a large excess of oxidants was used to regenerate the catalyst;[8,9] (ii) stoichiometric amounts of the reduced external oxidant [such as $Cu(OAc)_2$,[7,9] *t*-BuOOBz[6]] were produced as waste; and (iii) substrate scope was limited and some cases poor yields were obtained.[6] Herein, we describe a general, efficient and structurally versatile palladium(II)-catalyzed intermolecular C-2 alkenylation of indoles employing the easily installed and removed *N*-(2-pyridyl)sulfonyl directing group, characterized by oxygen as oxidizing agent, with complete regio- and stereoselectivity. Compared with $Cu(OAc)_2$ and *t*-BuOOBz, oxygen is an ideal oxidant and offers attractive industrial prospects in terms of green and sustainable chemistry while no reduced waste is produced.[11]

An effective strategy for regioselective C-2 alkenylation of indoles is to utilize the coordination of a directing group in the indole substrate to the metal center of a catalyst, and the approach probably involves a five- or six-membered metal-cyclic intermediate to activate the C-2 position of indole.[4a,7,9b,10] Therefore, our study commenced by examining the

Table 1. Optimization of reaction conditions.[a]



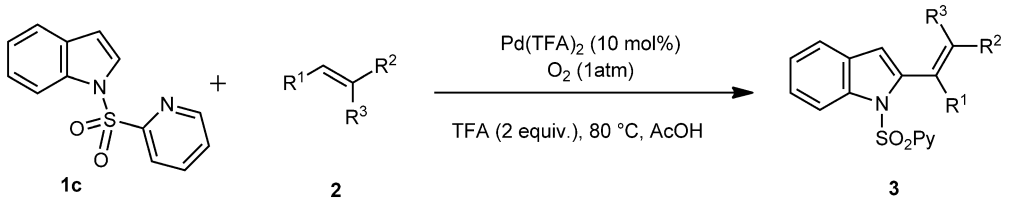
Entry	R	Catalyst	Solvent	Time [h]	Conversion [%][b]
1	Boc- (**1a**)	$Pd(OAc)_2$	DMA	24	–
2	Ts- (**1b**)	$Pd(OAc)_2$	DMA	24	<10
3	(2-pyridyl)SO_2- (**1c**)	$Pd(OAc)_2$	DMA	24	35 (30)
4	Ac- (**1d**)	$Pd(OAc)_2$	DMA	24	<10
5	Bz- (**1e**)	$Pd(OAc)_2$	DMA	24	<10
6	(2-pyridyl)SO_2- (**1c**)	$PdCl_2$	DMA	24	<10
7	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	DMA	24	80 (55)
8	(2-pyridyl)SO_2- (**1c**)	$Pd(OH)_2$	DMA	24	–
9	(2-pyridyl)SO_2- (**1c**)	$Pd(PPh_3)_2Cl_2$	DMA	24	–
10	(2-pyridyl)SO_2- (**1c**)	–	DMA	24	–
11	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	DMF	24	62 (50)
12	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	Anisole	24	92 (65)
13	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	AcOH	24	100 (75)
14	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	solvents[c]	24	<20
15[d]	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	AcOH	4	100 (73)
16[d,e]	(2-pyridyl)SO_2- (**1c**)	$Pd(TFA)_2$	AcOH	4	100 (93)

[a] *Reaction conditions:* **1** (1 mmol), **2a** (1.5 mmol), catalyst (0.1 mmol), O_2 (1 atm) and TFA (8 mmol) in solvent (5 mL) at 60 °C.
[b] The results in parentheses are isolated yields.
[c] Solvents: 1,4-dioxane, toluene, DMSO, MeOH, CH_3CN, THF, pyridine, CH_3NO_2.
[d] At 80 °C.
[e] TFA (2 mmol) was used.

indole *N*-protecting groups which have potential directing feature for the C-2 functionalization of indole instead of the more nucleophilic C-3 position. A set of protecting groups was tested for the reaction of indole derivatives (**1**) and ethyl acrylate (**2a**) with 10 mol% $Pd(OAc)_2$ as the catalyst, oxygen as the oxidant and trifluoroacetic acid (TFA) as additive in *N*,*N*-dimethylacetamide (DMA) (Table 1). The reaction was found to proceed in low conversion (<10%) when the *N*-protecting group was Boc, Ts, Ac or Bz (entries 1, 2, 4, 5). The *N*-(2-pyridyl)sulfonyl group, which can be easily removed by mild reduction conditions,[9a] turned out to be the best protecting group to give 35% conversion (entry 3). To our delight, *N*-(2-pyridyl)sulfonylindole (**1c**) provided complete C-2 regioselectivity and *E* stereoselectivity. Then the palladium source was investigated (entries 6–9), and the conversion improved remarkably to 80% when $Pd(TFA)_2$ was used. In the absence of a palladium catalyst, the reaction would not occur (entry 10). After careful solvent screening, acetic acid (AcOH) proved to be the best solvent to give complete conversion and good yield (entries 11–14). Increasing the temperature could greatly improve the reaction rate; the reaction was done within 4 h at 80 °C with a similar yield, and a higher temperature led to a significant drop in the yield due to decomposition of the starting material and product (entry 15). The amount of TFA dramatically affected the yield, 2 equiv. of TFA were the optimal amount to afford the desired product in 93% yield (entry16, for details see the Supporting Information). Accordingly, the reaction conditions were optimized as follows: $Pd(TFA)_2$ (10% mol), TFA (2 equiv.) under oxygen atmosphere in AcOH at 80 °C.

After identifying the optimized conditions, we moved on to explore the scope of the C-2 alkenylation reaction. First, we studied the effect of electronic and structural variations on the alkene (Table 2). The present reaction tolerated a variety of alkenes. Monosubstituted alkenes, not only electrophilic alkenes but also the more challenging non-activated styrene, reacted with **1c** to give the corresponding C-2 alkenylation products with complete regio- and stereoselectivity in good to excellent yields (65–98%) (entries 1–7). Indole phosphonate **3ch** could also be generated from vinyl phosphonate **2h** in excellent yield (entry 8). Pleasingly, 1,1-disubstituted alkenes successfully coupled with indole at the C-2 position to give the corresponding double-bond isomerized products in high yields (entries 9, 10). Particularly noticeable is the performance of 1,2-disubstituted alkenes in the reaction in view of the small number of precedents and lower reactivity of this kind of olefin in oxidative al-

Table 2. Alkenylation of **1c** with various alkenes.[a]



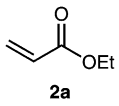
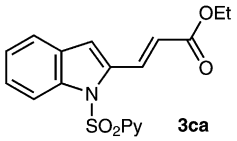
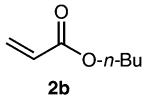
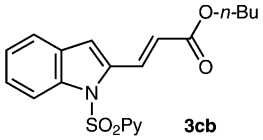
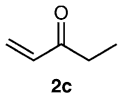
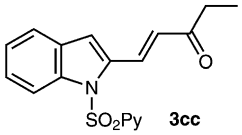
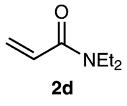
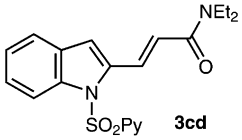
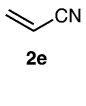
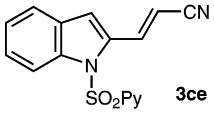
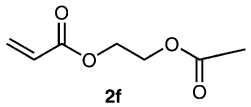
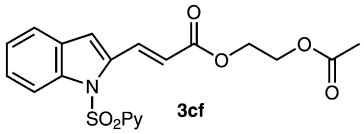
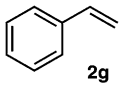
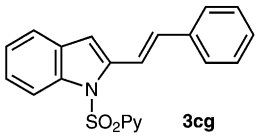
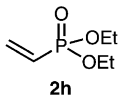
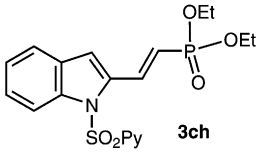
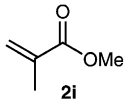
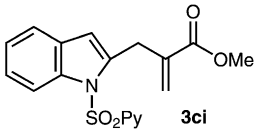
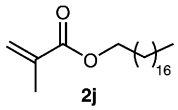
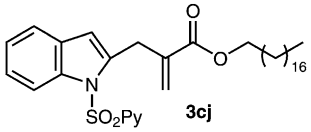
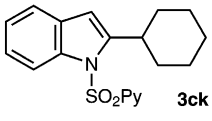
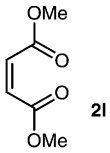
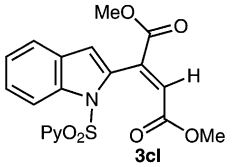
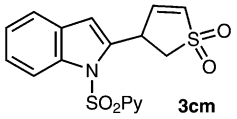
Entry	Alkene	Product	Time [h]	Yield [%][b]
1	 **2a**	 **3ca**	4	93
2	 **2b**	 **3cb**	4	98
3	 **2c**	 **3cc**	24	83
4	 **2d**	 **3cd**	6	95
5	 **2e**	 **3ce**	24	65
6	 **2f**	 **3cf**	8	97
7	 **2g**	 **3cg**	18	90
8	 **2h**	 **3ch**	12	94
9[c]	 **2i**	 **3ci**	2.5	92
10[c]	 **2j**	 **3cj**	4	97
11	 **2k**	 **3ck**	24	63[d]

Table 2. (Continued)

Entry	Alkene	Product	Time [h]	Yield [%][b]
12	 **2l**	 **3cl**	6	97
13[c]	 **2m**	 **3cm**	24	75

[a] *Reaction conditions:* **1c** (1 mmol), **2** (1.5 mmol), $Pd(TFA)_2$ (0.1 mmol), O_2 (1 atm) and TFA (2 mmol) in AcOH (5 mL) at 80 °C.
[b] Isolated yields.
[c] Double bond isomer of the alkenylation product.
[d] After hydrogenation.

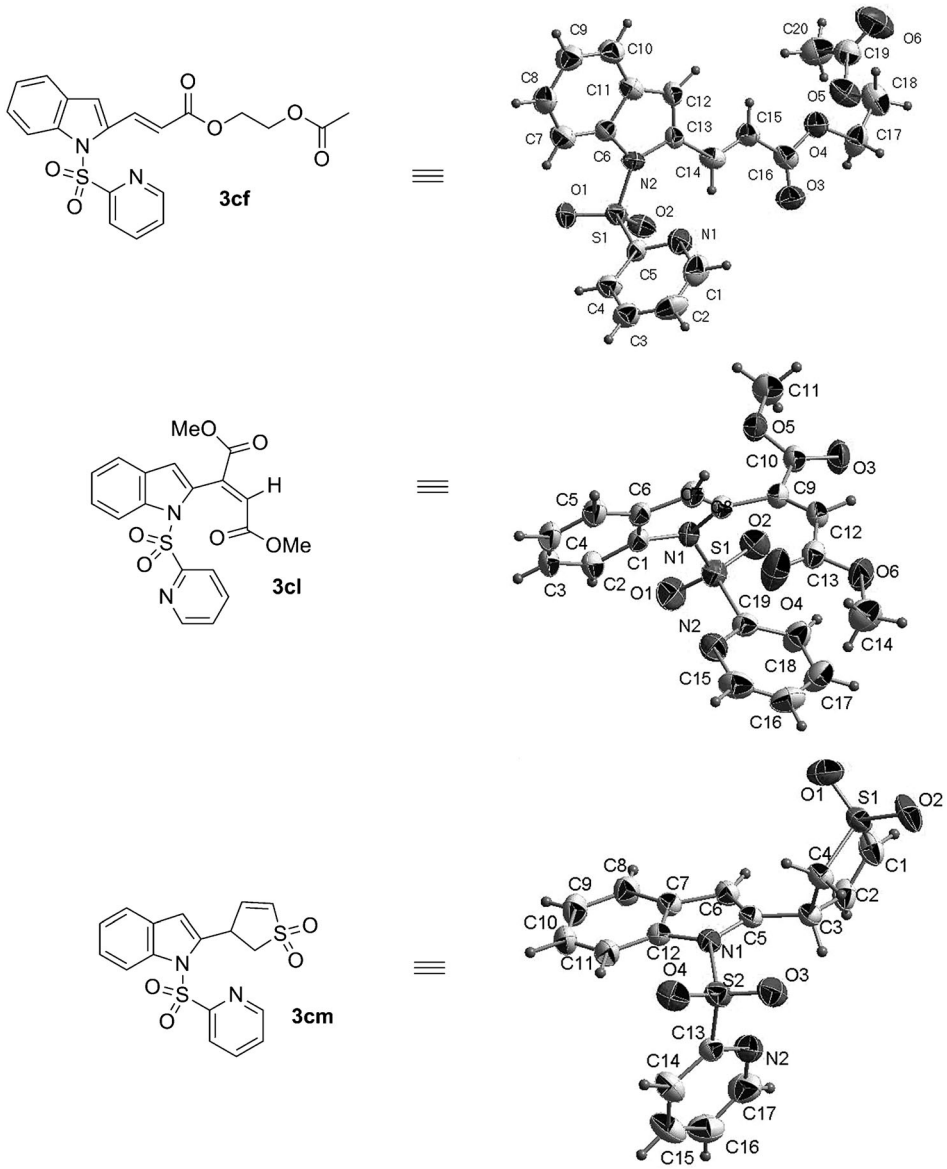
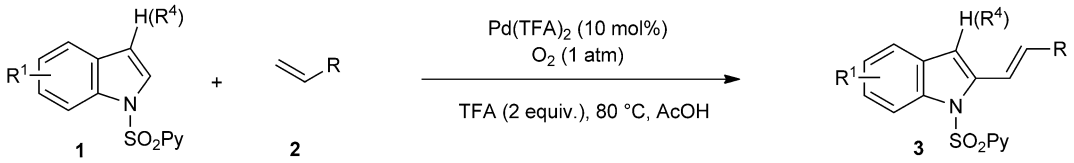


Figure 1. X-ray crystal structures of compounds **3cf**, **3cl** and **3cm**.

Table 3. The C-2 H-alkenylation for structural variation of the indole with ethyl acrylate and styrol.[a]



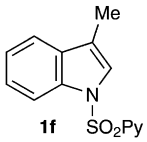
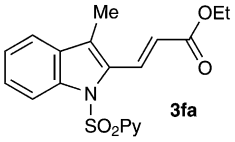
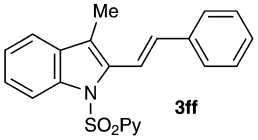
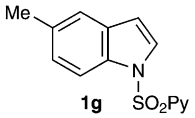
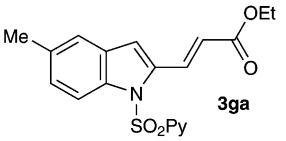
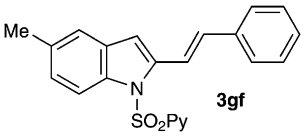
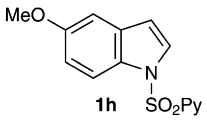
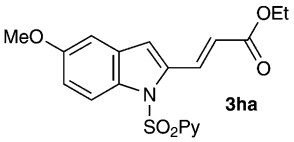
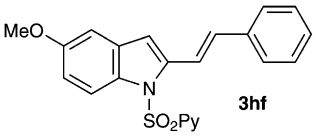
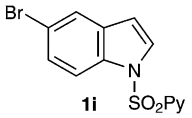
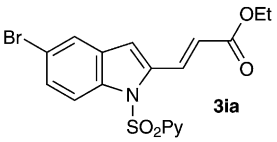
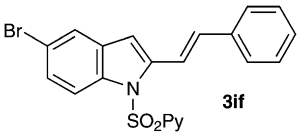
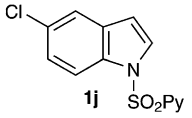
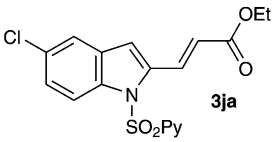
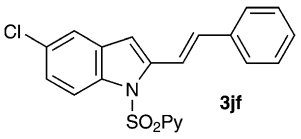
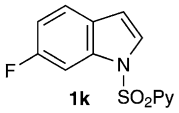
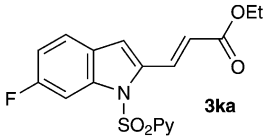
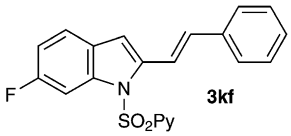
Entry	Alkene	Product	Time [h]	Yield [%][b]
1			4	96
			15	73
2			12	95
			15	91
3			8	87
			8	93
4			24	40 (96%)[c]
			24	56 (93%)[c]
5			18	93
			24	78

Table 3. (Continued)

Entry	Alkene	Product	Time [h]	Yield [%][b]
6	 **1k**	 **3ka**	24	87
		 **3kf**	18	89

[a] *Reaction conditions:* **1c** (1 mmol), **2** (1.5 mmol), $Pd(TFA)_2$ (0.1 mmol), O_2 (1 atm) and TFA (2 mmol) in AcOH (5 mL) at 80 °C.
[b] Isolated yields.
[c] Yield in parentheses are based on recovered indole **1i**.

kenylation (Fujiwara–Moritani) reactions.[12] Under these reaction conditions, cyclohexene underwent a smooth reaction with **1c** to afford the corresponding trisubstituted alkene products **3ck** (63% yield, after hydrogenation) (entry 11). It is interesting that dimethyl maleate which has the *Z*-configration reacted with **1c** to afford a single *E*- configration diastereomer **3cl** (93% yield) (entry 12). Butadiene sulfone, as a solid source of butadiene, was also compatible with the reaction to provide the double-bond isomerized product **3cm** in 75% yield (entry 13). The molecular structures of compound **3cf**, **3cl** and **3cm** were confirmed by X-ray crystallographic analysis (Figure 1).[13]

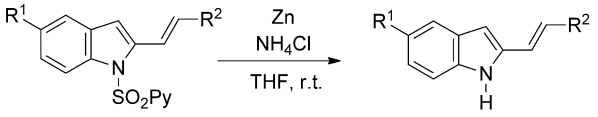
Next, we explored the reaction of various indole derivatives with ethyl acrylate and styrol (Table 3).

Indoles possessing either electron-withdrawing groups or electron-donating groups smoothly reacted and provided C-2 alkenylation products **3** in good to excellent yields (73–96%), albeit 5-bromoindole (**1i**) proved to be less reactive than other substituted indoles (entry 4). Many functional substituents such as F, Cl, Br and MeO were compatible under these conditions, which could be further transformed into other functionalities.

As shown in Scheme 1, blocking the C-2 position of indole resulted in the formation of the C-3 alkenylation product. Compared with C-2 alkenylation of *N*-(2-pyridyl)sulfonyl-3-methylindole (**1f**), C-3 alkenylation of *N*-(2-pyridyl)sulfonyl-2-methylindole (**1l**) was much slower. This case indicated that the *N*-(2-pyridyl)sulfonyl group was not only a readily removable directing group but also an activating group in the C-2 alkenylation reaction of indole.

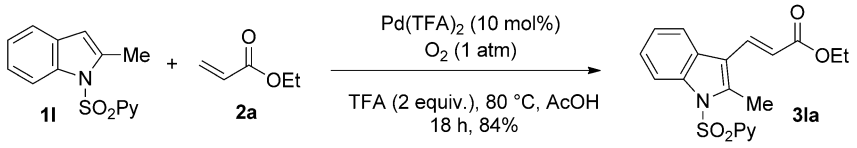
Removal of the 2-pyridysulfonyl group from the alkenylation products was easily achieved by reduction with zinc in NH_4Cl (aq)/THF (1:1) at room temperature, with the stereochemistry of the olefin moiety untouched. For instance, the products **3ca** and **3hf** were converted to their free indole derivatives **4ca** and **4hf** under the conditions in 92% and 85% yields, respectively (Scheme 2).

In summary, we have developed a general, simple and efficient method for the intermolecular direct C-2 alkenylation of indoles using palladium(II) as catalyst and oxygen as the oxidant. The reaction not only can proceed well without Cu(II), but shows complete regio- and stereoselectivity. All products are *E*-isomers at the C-2 position, and no *Z*-isomers and 3-substituted products can be detected on analyzing the reaction mixtures. The method should have many applications in organic and medical chemistry. Detailed



3ca R^1 = H, R^2 = CO_2Et
3hf R^1 = OMe, R^2 = Ph
4ca R^1 = H, R^2 = CO_2Et 92%
4hf R^1 = OMe, R^2 = Ph 85%

Scheme 2. Deprotection of 2-alkenyl-*N*-(2-pyridyl)sulfonylindoles.



Scheme 1. The C-3 alkenylation of 2-substituted indoles.

mechanistic investigations and the development of a more efficient catalytic system are currently underway.

Experimental Section

General Information

All commercial reagents and solvents were used as received without further purification. Flash chromatographies were carried out on silica gel 200–300 mesh. All NMR spectra were obtained at ambient temperature using a Varian INOVA-400 MHz spectrometer. The following abbreviations are used to show the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All new products were further characterized on Bruker EQUINOX55 instrument and AXIMA-CFR™plusMALDI-TOF mass spectrometers. In addition, X-ray crystal structure analyses were measured on a Bruker Smart APEXIICCD instrument using Mo-K_α radiation.

General Procedure for Palladium-Catalyzed Intermolecular C-2 Alkenylation of Indoles Using Oxygen as the Oxidant

A sealed tube containing the *N*-(2-pyridyl)sulfonylindole derivative **1c** (0.39 mmol), $Pd(TFA)_2$ (10 mol%), was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, AcOH (2.0 mL), alkene **2** (0.58 mmol) and trifluoroacetic acid (TFA) (0.78 mmol) were sequentially added to the system *via* syringe under an oxygen atmosphere. The mixture was heated to 80 °C for 8–24 h (as indicated in each case). Then the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL) and washed with saturated aqueous $NaHCO_3$ (3 × 5 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash chromatography afforded the C.2 alkenylated indole derivative **3**.

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[13] CCDC 958552 (**3cf**), CCDC 958553 (**3cl**), and CCDC 958554 (**3cm**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

