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Study on Palladium(II)-Catalyzed Mono-1-alkenylation of 9*H*-Carbazoles

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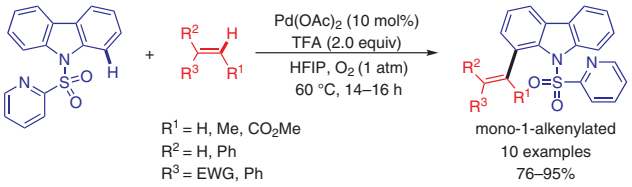

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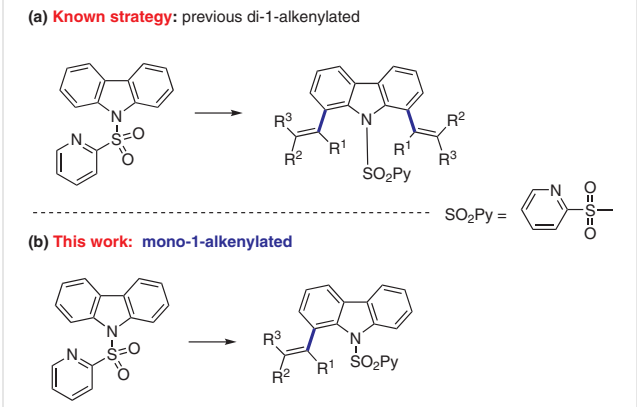
Abstract A general and efficient method is reported for the direct mono-1-alkenylation of 9*H*-carbazole molecules with divalent palladium as a catalyst and an *N*-(2-pyridyl)sulfanyl directing group. This method also provides an efficient synthetic route for the synthesis of cross-di-alkenylated carbazoles.

Key words alkenylation, palladium catalysis, C–H activation, carbazoles

Carbazoles are an important group of nitrogen-containing heterocyclic compounds, as the carbazole ring is a structural unit commonly found in many bioactive substances and pharmaceutical compounds.[1,2] Carbazole derivatives are also of great significance in materials science.[3] The modification of carbazole rings has therefore long been of great interest to organic chemists.[4,5] Although template-assisted methodologies have been widely employed for C–H bond olefinations,[6] further development is required for C–H functionalization of carbazoles compared with that of other heterocyclic compounds.[7–9] Recently, some highly monoselective C–H functionalizations of carbazoles have been reported.[10] Carretero and co-workers proposed a Pd-catalyzed alkenylation of carbazoles directed by an *N*-(2-pyridyl)sulfonyl group, from which dialkenylated carbazoles were the main products (Scheme 1a).[11] The Song group reported a Ru-catalyzed mono-1-alkenylation of carbazoles directed by an *N*-dimethylcarbamoyl group.[10f] However, there are few reports on metal-catalyzed monoalkenylations of carbazoles with high selectivity. We are pleased to report that such a reaction (Scheme 1b) was achieved by the method described below.



Scheme 1 Alkenylation of carbazoles with various alkenes

Initially, palladium(II) acetate [$Pd(OAc)_2$] was selected as the catalyst with trifluoroacetic acid (TFA) as an additive. This combination was chosen on the basis that TFA interacts with $Pd(OAc)_2$ to produce a more active $[Pd(II)O_2CCF_3]^+$ species that then forms a σ-carbazole–Pd complex. Compared with $[Pd(II)OAc]^+$, the complex has a higher activity in electrophilic substitution of C–H bonds,[12–14] which further facilitates the reaction.

Because of the potential directing effect at the C-1 site exerted by the carbazole N-protecting group, we first screened various protecting groups for the reaction between carbazoles **1** and methyl acrylate (**2a**) at 60 °C (Table 1). The catalyst for the reaction was 10 mol% $Pd(OAc)_2$ and the additive was two equivalents of TFA. The reaction was carried out in DCE with dioxygen (1 atm) as the oxidant. With tosyl or acetate as the N-protecting group, only a trace of the corresponding product **3** was obtained (<10%) (Table 1, entry 1). However, with a (2-pyridyl)sulfonyl[15,16] as the

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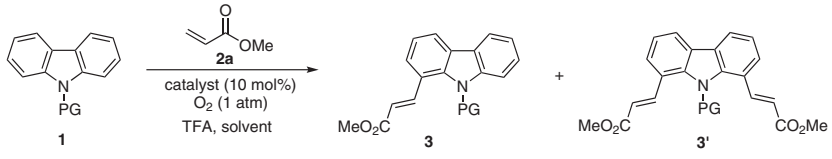
N-protecting group, the yield of the monoalkenylated product **3** significantly increased to 76% (entry 2). We then investigated the effect of the catalyst and found that the reaction did not proceed in the absence of a palladium catalyst (entry 3), whereas both $Pd(OAc)_2$ and $Pd(TFA)_2$ were effective catalysts, giving similar yields (entry 2). However, because of its lower cost, $Pd(OAc)_2$ was chosen as the catalyst for subsequent reactions. By thorough solvent screening for the reaction (entries 4 and 5), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) emerged as the optimal solvent, showing promising results in terms of a high yield and a superior mono- to disubstitution ratio. The use of three or four equivalents of **2a** under otherwise identical conditions gave similar results to that obtained with two equivalents of **2a** (entry 5). Subsequently, the doses of TFA and $Pd(OAc)_2$ were tested. With two equivalents of TFA as the additive, $Pd(OAc)_2$ gave almost identical results to $Pd(TFA)_2$ (entry 6), but a smaller amount of TFA resulted in an incomplete reaction (entry 7). In addition, when the dose of $Pd(OAc)_2$ was reduced to 5%, the conversion rate was significantly reduced (entry 8). We also tried other potential directing groups, such as 2-pyridyl (Py)[10a–d] and 2-pyrimidinyl (Pym),[10e] but only a trace of product was obtained (entry 9). Pleasingly, when we used an *N*-dimethylcarbamoyl (Dmc) group as the directing group under the standard reaction conditions, the monoalkenylation product **3** was isolated 62% yield (entry 10).

Having determined the optimal reaction conditions, we tested various alkenes to examine the tolerance of the method to various substituent groups. First, the effects of electronic and structural variations in the alkene were investigated (Scheme 2). The reaction was found to tolerate a range of alkenes. Monosubstituted alkenes, including both electrophilic alkenes and more challenging nonactivated styrene derivatives, reacted successfully with **1**, producing the corresponding C1-alkenylated products **3a–j** in high yields of 76–95%. Interestingly, the reactions of monosubstituted alkenes gave monoalkenylated products **3a–d** containing *E*-double bonds in yields of 91–95%. The molecular structure of **3b** was confirmed by X-ray crystallography (see Supporting Information).[17] Promisingly, 1,2-disubstituted alkenes successfully coupled to the carbazole at the C(1) site to give the corresponding double-bond isomerization products **3e–g** in high yields.[18] In addition, a 1,1-disubstituted alkene (1,1-diphenylethylene) also gave the corresponding alkenylated carbazole **3h** in 82% yield.

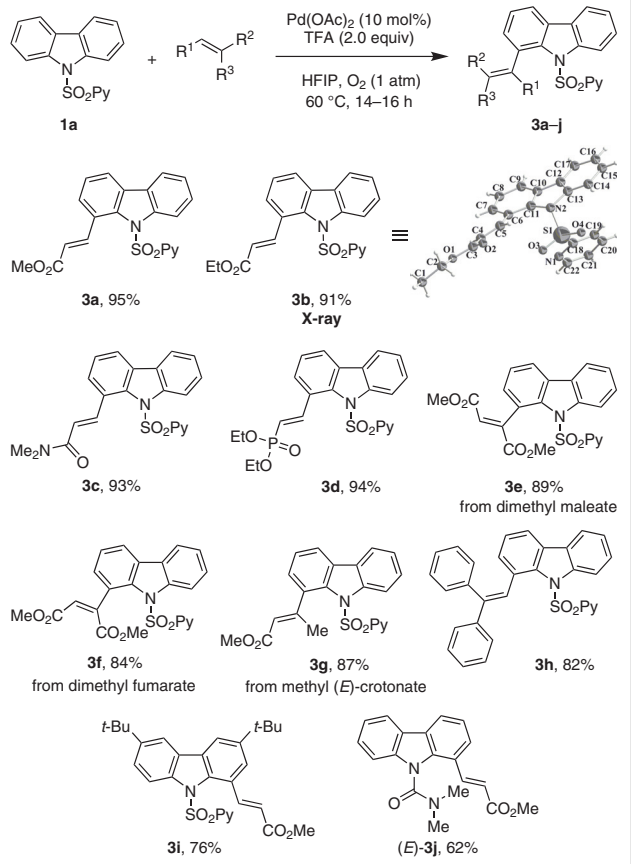
Application of this protocol was also successfully extended to the corresponding 3,6-di-*tert*-butyl-9*H*-carbazole, providing the desired products **3i** in 76% yield. In addition, 9-(dimethylcarbamoyl)-9*H*-carbazole[10f] afforded the corresponding mono-*o*-olefination product **3j** in 62% yield.

Table 1 Optimization of Reaction Conditions[a]



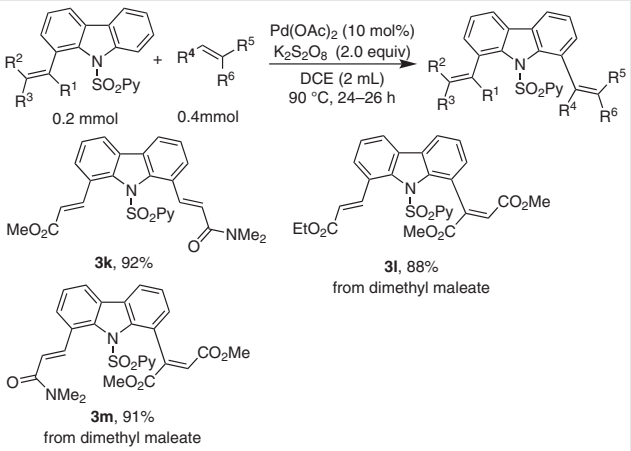
Entry	Catalyst	PG	Solvent	Mono/di	Yield[b] (%) of **3**
1	$Pd(OAc)_2$	Ts or Ac	DCE	–	trace
2	$Pd(OAc)_2$[c]	2-SO_2Py	DCE	<1:20	76
3	–	2-SO_2Py	DCE	–	–
4	$Pd(OAc)_2$	2-SO_2Py	solvent[d]	<1:20	<10
5[e]	$Pd(OAc)_2$	2-SO_2Py	HFIP	>10:1	95
6	$Pd(TFA)_2$	2-SO_2Py	HFIP	>10:1	96
7[f]	$Pd(OAc)_2$	2-SO_2Py	HFIP	>10:1	65
8[g]	$Pd(OAc)_2$	2-SO_2Py	HFIP	>10:1	55
9	$Pd(OAc)_2$	Py or Pym	HFIP	–	trace
10	$Pd(OAc)_2$	Dmc	HFIP	>10:1	62

[a] Reaction conditions: **1** (1.0 mmol), **2a** (2.0 mmol), catalyst, O_2 (1 atm), TFA (2.0 mmol), solvent (10 mL), 60 °C, 16 h.
[b] Isolated yield after purification by flash column chromatography.
[c] With $Pd(TFA)_2$ as the catalyst, the result was almost identical.
[d] Solvent: toluene, AcOH, 1,4-dioxane, DMSO, MeOH, MeCN, THF, DMA, *i*-PrOH, *t*-BuOH, F_3CCH_2OH, or $MeNO_2$.
[e] With three or four equivalents of **2a**, the results were almost identical.
[f] TFA (1.0 mmol).
[g] 5 mol% $Pd(OAc)_2$.

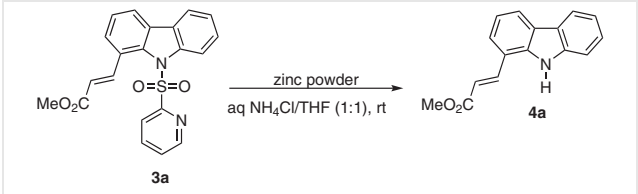


Scheme 2 Mono-C(1)-alkenylation of carbazoles with various alkenes

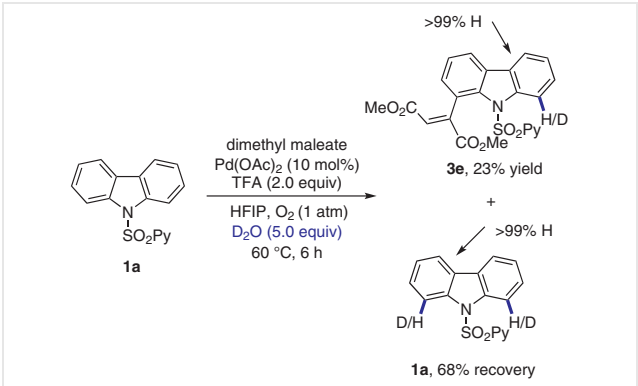
Encouraged by the successful mono-1-olefination of carbazoles, we investigated the synthesis of cross-dialkenylated carbazoles (Scheme 3), Under the optimized reaction conditions, the mono-C(1)-alkenylated carbazoles **3a–c** reacted with a second alkene to produce cross-di-*o*-alkenylated carbazoles **3k–m** in high yields.



Scheme 3 Synthesis of cross-dialkenylated carbazole derivatives



Scheme 4 Deprotection of the *N*-(2-pyridyl)sulfonyl group



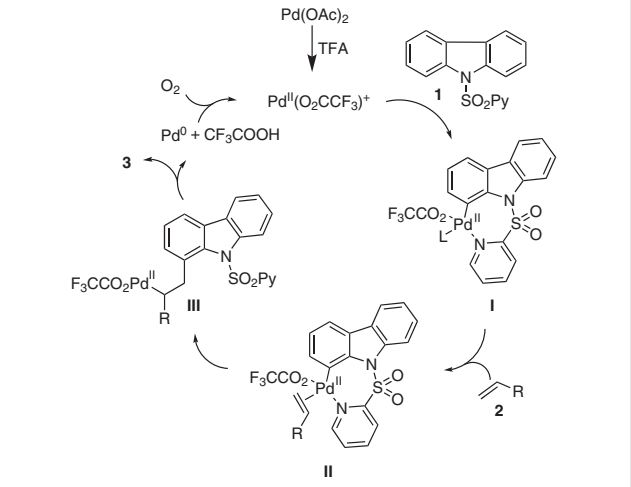
Scheme 5 H/D exchange experiment

The *N*-(2-pyridyl)sulfonyl protecting/directing group of product **3a** was easily removed by treatment with zinc powder in 1:1 THF–aq NH_4Cl at room temperature, without affecting the stereochemistry of the alkene (Scheme 4).

When the reaction of nondeuterated **1a** with dimethyl maleate was carried out under the standard conditions in the presence of D_2O (5.0 equiv) for six hours, product **3e** was isolated in 23% yield together with 68% of the recovered starting material **1a** (Scheme 5). ^1H NMR analysis revealed the presence of traces of -incorporation of deuterium in compounds **1a** and **3e**, suggesting that the C–H activation process is irreversible.[19]

A plausible reaction mechanism is shown in Scheme 6. Treatment of $Pd(OAc)_2$ with TFA produces a more active $Pd(O_2CCF_3)^+$ complex,[20–22] and palladium attacks the substrate to form the seven-membered palladium-containing intermediate **I**.[23–27] Subsequently, coordination of the alkene to form intermediate **II** and insertion into its C=C bond result in the formation of palladium(II) complex **III**. Elimination of the β-hydrogen atom gives the alkenylated carbazole product **3** with release of zero-valent palladium, which is reoxidized to $Pd(O_2CCF_3)^+$ by O_2 in the presence of TFA to complete the catalytic cycle.[28,29]

In conclusion, a simple and efficient palladium(II)-catalyzed *N*-(2-pyridyl)sulfonyl group-directed approach for mono-1-olefination of carbazoles has been developed.[30] The directing group introduced into the reaction system is easily removed after completion of the reaction. This approach has prospects for widespread application in the fields of synthetic and medical chemistry. Further studies



Scheme 6 Plausible mechanism for the transformation

on the detailed mechanism and extensions to similar reactions of other organic molecules are in progress.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1387-5435.

Primary Data

Primary data for this article are available online at https://zenodo.org/record/4633398 and can be cited using the following DOI: 10.5281/zenodo.4633398.

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(30) **1-Alkenyl-9*H*-carbazoles 3a–j; General Procedure**

A sealed tube containing 9-(2-pyridylsulfonyl)-9*H*-carbazole (**1a**; 0.2 mmol) and $Pd(OAc)_2$ (5.0 mg, 10 mol%) was evacuated and filled with O_2 gas by using an O_2-containing balloon. HFIP (2 mL), the appropriate alkene (0.4 mmol), and TFA (0.4 mmol) were sequentially added from a syringe under O_2, and the mixture was heated at 60 °C for 14–16 h until the reaction was complete (TLC). The mixture was then allowed to cool to r.t., concentrated under reduced pressure, diluted with EtOAc (30 mL), and washed with sat. aq $NaHCO_3$ (3 × 2 mL). The combined organic phase was (Na_2SO_4) and concentrated under reduced pressure, and the residue was purified by flash chromatography.

Methyl (2*E*)-3-[9-(Pyridin-2-ylsulfonyl)-9*H*-carbazol-1-yl]acrylate (3a)

Purified by flash column chromatography [silica gel, PE–EtOAc (3:1)] as a white solid; yield: 37.0 mg (95%); mp 171–172 °C. IR (KBr): 3027, 2951, 1702, 1578, 1429, 1406, 1359, 1272, 1182, 1116, 1031, 956, 860, 752, 663, 586 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 15.8 Hz, 1 H), 8.31 (d, *J* = 4.0 Hz, 1 H), 8.22 (d, *J* = 8.3 Hz, 1 H), 7.83–7.78 (m, 2 H), 7.74–7.70 (m, 2 H), 7.64 (d, *J* = 7.8 Hz, 1 H), 7.43–7.37 (m, 2 H), 7.32–7.27 (m, 2 H), 6.46 (d, *J* = 15.8 Hz, 1 H), 3.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 154.5, 149.8, 144.0, 140.6, 139.3, 137.6, 130.1, 127.4, 126.0, 125.4, 125.2, 122.8, 121.1, 119.8, 118.5, 117.1, 51.7. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{16}N_2NaO_4S$: 415.0723; found: 415.0721.

Unsymmetrical Dialkenylated Carbazoles 3k–m; General Procedure

A sealed tube was charged with the appropriate monoalkenylated carbazole **3** (0.2 mmol), $Pd(OAc)_2$ (5.0 mg, 10 mol%), and $K_2S_2O_8$ (108.0 mg, 0.4 mmol). DCE (2 mL) and the appropriate alkene (0.4 mmol) were added, and the mixture was heated to 90 °C for 24–26 h until the reaction was complete (TLC). The mixture was allowed to cool to r.t., diluted with EtOAc (50 mL), and washed with H_2O (3 × 5 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure and purified by flash chromatography.

Methyl (2*E*)-3-[8-[(1*E*)-3-(Dimethylamino)-3-oxoprop-1-en-1-yl]-9-(pyridin-2-ylsulfonyl)-9*H*-carbazol-1-yl]acrylate (3k)

Purified by flash column chromatography [silica gel, PE–EtOAc (3:1)] as an oil; yield: 44.9 mg (92%). IR (KBr): 3394, 3189, 2921, 2850, 1708, 1646, 1465, 1419, 1371, 1263, 1168, 1110, 869, 794, 727, 642, 572 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 16.0 Hz, 1 H), 8.22–8.19 (m, 2 H), 7.66–7.62 (m, 2 H), 7.60–7.49 (m, 3 H), 7.38–7.30 (m, 3 H), 7.25–7.22 (m, 1 H), 7.05 (d, *J* = 15.6 Hz, 1 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 3.88 (s, 3 H), 3.27 (s, 3 H), 3.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 152.6, 149.1, 141.9, 141.4, 138.8, 137.0, 132.0, 131.7, 129.3, 127.9, 127.1, 126.8, 126.5, 125.9, 123.3, 121.0, 120.2, 118.8, 118.1, 51.9, 37.8, 35.9. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{26}H_{23}N_3NaO_5S$: 512.1251; found: 512.1252.

Methyl (2*E*)-3-(9*H*-carbazol-1-yl)acrylate (4a); Typical Procedure

A suspension of **3a** (39 mg, 0.1 mmol) and nonactivated Zn powder (325 mg, 5 mmol) in 1:1 THF–sat. aq NH_4Cl (4 mL) was stirred at 30 °C until the starting material was consumed (TLC). The mixture was then filtered through a pad of Celite to remove the Zn powder, and the filtrate was extracted with EtOAc (15 mL). The extracts were washed with sat. aq NH_4Cl and brine, and the combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography [silica gel, PE–EtOAc (4:1)] to give a light-yellow solid; yield: 24.1 mg (95%); mp 98–99 °C.

IR (KBr): 3355, 2123, 1707, 1325, 1173, 1028, 754, 602 cm^{-1}. ^1H NMR (400 MHz, DMSO): δ = 11.84 (s, 1 H), 8.31 (d, *J* = 16.0 Hz, 1 H), 8.20 (d, *J* = 7.6 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.59 (d, *J* = 8.1 Hz, 1 H), 7.51–7.40 (m, 1 H), 7.19–7.21 (m, 1 H), 6.82 (d, *J* = 16.0 Hz, 1 H), 3.79 (s, 3 H). ^{13}C NMR (100 MHz, DMSO): δ = 167.5, 140.8, 140.6, 139.0, 126.6, 124.8, 124.3, 123.2, 122.6, 120.8, 119.7, 119.4, 117.7, 111.8, 51.9. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{13}NNaO_2$: 274.0838; found: 274.0834.