Palladium-Mediated Olefination of 2-(*tert*-Butyldimethylsilyl)pyridine by sp^3 C–H Activation

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Abstract: An unprecedented direct alkenylation of 2-(*tert*-butyldimethylsilyl)pyridine with acrylates through palladium-mediated C-H activation on a nonacidic sp^3 carbon is reported. This method provides an efficient approach to allylsilanes.

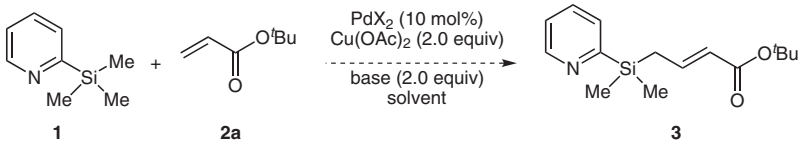
Key words: palladium, olefination, pyridine

Transition metal-catalyzed cross coupling reactions to form carbon–carbon or carbon–heteroatom bonds are among the most important reactions for the construction of organic molecules.[1] Among these, direct cross coupling of (hetero)arenes through palladium-catalyzed C–H functionalization,[2] has received considerable attention over the past decade, and significant achievements has been made in recent years.[3] In comparison, palladium-catalyzed or palladium-mediated C–H activation of nonacidic sp^3 carbons is still a challenge because of the strength of the C–H bond. Some recent progress has been made in this area.[4] However, most of the processes developed apply only to benzylic C–H bonds or to substrates with a *tert*-butyl fragment. In our continuing efforts to develop oxidative cross coupling reactions on novel substrates, we report a direct alkenylation of 2-(*tert*-butyldimethylsilyl)pyridine with acrylates by palladium-mediated C–H activation of an sp^3 carbon.

This work was triggered by an earlier report on the cyclopalladation of 2-(trimethylsilyl)pyridine (**1**) with palladium(II) acetate in benzene under mild conditions.[5] Our investigation therefore began with attempts to couple 2-(trimethylsilyl)pyridine (**1**) with *tert*-butyl acrylate (**2a**) in the presence of 10 mol% of palladium(II) acetate or chloride and two equivalents of copper(II) acetate as an oxidant (Scheme 1). Decomposition of the pyridine **1** occurred during the reaction and none of the desired product **3** was obtained. Faced with this problem, we decided to replace the substrate with more-stable 2-(*tert*-butyldimethylsilyl)pyridine (**4**) and we obtained the desired product **5a**, albeit in poor yield, when tetrahydrofuran, toluene, or 1,2-dichloroethane was used as the solvent (Table 1, entries 1–3). We noted that a source of palladium(II) is required for this coupling reaction (entry 4). Further screening of various palladium(II) sources, oxidants, bases, reaction temperatures, and times (entries 5–19) unfortunately resulted in no improvement in the coupling yield. Therefore, the coupling reaction was carried out with a stoichiometric amount of benzonitrile(dichloro)palladium(II) [$Pd(PhCN)_2Cl_2$] in the absence of copper(II) acetate. Surprisingly, the yield was only slightly improved (entry 20). Presumably, the product acts as a bidentate ligand to coordinate palladium(II), and thus consumes this metal species. To solve this problem, we used an oxidant to oxidize the palladium(0) generated in the reaction system back to palladium(II), and we obtained a reasonable yield (entry 21). Further studies showed that optimal results were obtained with a stoichiometric amount of palladium(II) chloride in the presence of an excess of copper(II) actetate (entry 23).

Next, by using the optimized reaction conditions described above, we examined the scope for the selection of the alkene (Table 2). As expected, monosubstituted terminal acrylates **2a**–**e** gave the corresponding products **5a**–**e** in good yields (52–82%; entries 1–5). The sterically hindered acrylate **2f** was also compatible, although the product **5f** was obtained in a low yield (entry 6). Furthermore, terminal alkene products (**5g** and **5h**) were isolated in good yield from the coupling of **4** with alkenes **2g** and **2h** in 75 and 73% yield, respectively (entries 7 and 8); this is presumably the result of a steric effect during the β-hydride elimination step in the Heck cycle.

In conclusion, we have developed a novel procedure for the direct alkenylation of 2-(*tert*-butyldimethylsilyl)pyridine (**4**) with acrylates **2** by palladium-mediated sp^3 C–H activation. Because the pyridylsilyl group is potentially



1 2a 3

Scheme 1

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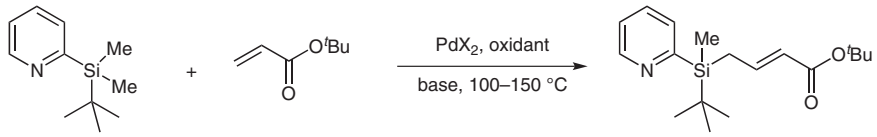
Table 1 Optimization of the Reaction Conditions



4 2a 5a

Entry[a]	PdX_2 (mol%)	Oxidant (2 equiv)	Solvent	Base	Temp (°C)	Time (h)	Yield[b] (%)
1	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	19
2	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	toluene	K_3PO_4	100	12	15
3	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	DCE	K_3PO_4	100	12	18
4	–	$Cu(OAc)_2$	THF	K_3PO_4	100	12	–
5	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	9
6	$Pd(CH_3CN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	13
7	$PdBr_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	10
8	Na_2PdCl_4 (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	13
9	$Pd(PhCN)_2Cl_2$ (10)	AgOAc	THF	K_3PO_4	100	12	11
10	$Pd(PhCN)_2Cl_2$ (10)	$Ce(SO_4)_2$	THF	K_3PO_4	100	12	14
11	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_2HPO_4	100	12	16
12	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_2CO_3	100	12	14
13	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	AgOAc	100	12	14
14	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	Na_2CO_3	100	12	11
15	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	*t*-BuONa	100	12	14
16	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	120	12	21
17	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	150	12	22
18	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	120	24	19
19	$Pd(PhCN)_2Cl_2$ (10)	$Cu(OAc)_2$	THF	K_3PO_4	100	48	21
20	$Pd(PhCN)_2Cl_2$ (100)	–	THF	K_3PO_4	100	12	30
21	$Pd(MeCN)_2Cl_2$ (100)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	65
22	$Pd(OAc)_2$ (100)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	66
23	$PdCl_2$ (100)	$Cu(OAc)_2$	THF	K_3PO_4	100	12	70[c]

[a] Conditions: **4** (0.2 mmol), **2a** (0.4 mmol), PdX_2 (0.02 or 0.2 mmol), oxidant (0.4 mmol), base (0.4 mmol, 2 equiv), solvent (2 mL), 100–150 °C, 12–48 h.
[b] Yields are based on **4** and were determined by ^{1}H NMR of the crude product using CH_2Br_2 as the internal standard.
[c] Isolated yield 64%.

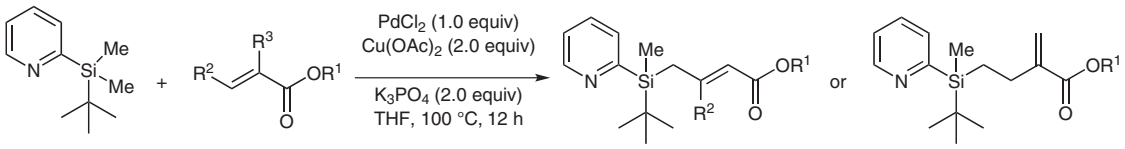
removable or convertible,[6] this method should find a broad range of applications in the preparation of synthetically useful allylsilyl intermediates. Further studies on a catalytic version of this transformation are currently in progress in our laboratory.

All reactions were carried out in oven-dried glassware. The palladium(II) compounds, oxidants, bases, and solvents were purchased from Acros or Sigma-Aldrich and used directly. For TLC analysis, precoated plates (w/h F254, 0.25-mm thick; Dynamic Adsorbents Inc.) were used. Flash silica gel (32–63 μm; Dynamic Adsorbents Inc.) was used for air-flashed column chromatography. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Fourier-transform NMR spectrometer.

2-(*tert*-Butyldimethylsilyl)pyridine (4)

A 2.5 M soln of BuLi in hexanes (20 mL, 50 mmol) was slowly added over 30 min to a stirred soln of 2-bromopyridine (7.9 g, 50 mmol) in anhyd THF (100 mL) at –78 °C, and the resulting mixture was stirred at the –78 °C for 30 min. A soln *t*-BuSi(Cl)Me_2 (7.5 g, 50 mmol) in THF (20 mL) was then added dropwise at –78 °C, and the mixture was allowed to warm to r.t. and stirred overnight. The reac-

Table 2 Scope of Alkenes in the C–H Functionalization



4 2 5a–f 5g,h

Entry[a]	Substrate **2**	Product **5**	Yield (%)[b]
1	**2a**	**5a**	64
2	**2b**	**5b**	52
3	**2c**	**5c**	62
4	**2d**	**5d**	65
5	**2e**	**5e**	82
6	**2f**	**5f**	39
7	**2g**	**5g**	75
8	**2h**	**5h**	73

[a] Reaction conditions: **4** (0.2 mmol), **2a–h** (0.4 mmol), $PdCl_2$ (0.2 mmol), $Cu(OAc)_2$ (0.4 mmol), K_3PO_4 (0.4 mmol), THF (4 mL), 100 °C, 12 h.
[b] Isolated yields based on **4**.

tion was quenched by slow addition of brine (100 mL) at 0 °C. The organic phase was then separated and the aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under vacuum to give the crude product as a dark oil. This was purified by flash chromatography (hexanes–EtOAc, 30:1) and further purified by distillation under reduced pressure to give a colorless liquid; yield: 5.2 g (54%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, 1 H, *J* = 4.5), 7.57 (td, 1 H, *J* = 7.5, 1.5 Hz), 7.49 (d, 1 H, *J* = 7.5 Hz), 7.20–7.15 (m, 1 H), 0.92 (s, 9 H), 0.32 (s, 6 H).

Alkyl *tert*-Butyl (2*E*)-4-[*tert*-butyl(methyl)pyridin-2-ylsilyl]but-2-enoates and Alkyl 2-{2-[*tert*-butyl(methyl)pyridin-2-ylsilyl]ethyl}acrylates (5); General Procedure

An oven-dried pressure tube was charged with silylpyridine **4** (0.2 mmol), acrylate **2** (0.4 mmol), $PdCl_2$ (0.2 mmol), $Cu(OAc)_2$ (0.4 mmol), K_3PO_4 (0.4 mmol), and THF (4 mL). The tube was sealed, stirred at 100 °C for 12 h, and then cooled to r.t. The mixture was diluted with EtOAc, filtered through a pad of Celite, and concentrated under vacuum. The residue was purified by flash chromatography (hexanes–EtOAc, 30:1)

tert-Butyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]but-2-enoate (5a)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 (td, *J* = 4.5, 1.5 Hz, 1 H), 7.57 (td, *J* = 7.5, 2.0 Hz, 1 H),7.45 (d, *J* = 7.5 Hz, 1 H), 7.22–7.15 (m, 1 H), 6.95–6.88 (m, 1 H), 5.60 (d, *J* = 14.5 Hz, 1 H), 2.28–2.20 (m, 1 H), 2.05–1.95 (m, 1 H), 1.42 (s, 9 H), 0.94 (s, 9 H), 0.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 164.1, 150.0, 146.3, 133.7, 130.3, 122.9, 121.5, 79.5, 28.2, 26.7, 18.3, 17.5, –8.6.

Methyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]but-2-enoate (5b)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 4.5 Hz, 1 H), 7.58 (t, *J* = 7.0 Hz, 1 H), 7.45 (d, *J* = 7.0 Hz, 1 H), 7.25–7.19 (m, 1 H), 7.10–7.00 (m, 1 H), 5.69 (d, *J* = 15.5 Hz, 1 H), 3.65 (s, 3 H), 2.34–2.20 (m, 1 H), 2.10–2.03 (m, 1 H), 0.94 (s, 9 H), 0.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 163.9, 150.1, 148.1, 133.7, 130.4, 123.0, 119.3, 51.2, 26.7, 18.7, 17.6, –8.6.

Ethyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]but-2-enoate (5c)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 5.0 Hz, 1 H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.46 (d, *J* = 7.5 Hz, 1 H), 7.23–7.19 (m, 1 H), 7.07–6.95 (m, 1 H), 5.67 (d, *J* = 15.0 Hz, 1 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 2.32–2.27 (m, 1 H), 2.08–2.03 (m, 1 H), 1.23 (t, *J* = 7.0 Hz, 3 H), 0.94 (s, 9 H), 0.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 164.0, 150.1, 147.7, 133.7, 130.4, 123.0, 119.7, 59.8, 26.7, 18.6, 17.5, 14.3, –8.6.

Butyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]but-2-enoate (5d)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 4.5 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.23–7.18 (m, 1 H), 7.07–6.95 (m, 1 H), 5.67 (d, *J* = 15.5 Hz, 1 H), 4.05 (t, *J* = 6.5 Hz, 2 H), 2.33–2.27 (m, 1 H), 2.08–2.03 (m, 1 H), 1.60–1.58 (m, 2 H), 1.34–1.31 (m, 2 H), 0.94 (s, 9 H), 0.91 (t, *J* = 7.5 Hz, 3 H), 0.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 164.0, 150.0, 147.6, 133.7, 130.4, 123.0, 119.7, 63.8, 30.7, 26.7, 19.2, 18.7, 17.6, 13.7, –8.6.

Benzyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]but-2-enoate (5e)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 4.5 Hz, 1 H), 7.57 (td, *J* = 7.5, 2.0 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.40–7.30 (m, 5 H), 7.25–7.20 (m, 1 H), 7.15–7.05 (m, 1 H), 5.73 (d, *J* = 15.5 Hz, 1 H), 5.11 (s, 2 H), 2.35–2.28 (m, 1 H), 2.08–2.03 (m, 1 H), 0.94 (s, 9 H), 0.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 163.9, 150.1, 148.6, 141.8, 136.4, 133.7, 130.4, 128.5, 128.0, 123.0, 119.3, 65.7, 26.7, 18.8, 17.6, –8.5.

Methyl (2*E*)-4-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]-3-methylbut-2-enoate (5f)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 1.0 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.22–7.18 (m, 2 H), 5.50 (s, 1 H), 3.61 (s, 3 H), 2.42 (d, *J* = 12.0 Hz, 1 H), 2.05–1.95 (m, 4 H), 0.94 (s, 9 H), 0.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.2, 164.3, 160.9, 150.0, 133.7, 130.4, 123.0, 113.5, 50.5, 26.7, 26.4, 21.4, 17.6, –8.5.

Methyl 2-{2-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]ethyl}acrylate (5g)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 5.0 Hz, 1 H), 7.57 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.50 (d, *J* = 7.5, 1 H), 7.20–7.15 (m, 1 H), 6.09 (d, *J* = 1.0 Hz, 1 H), 5.56 (d, *J* = 1.0 Hz, 1 H), 3.73 (s, 3 H), 2.30–2.20 (m, 2 H), 1.25–1.13 (m, 1 H), 1.05–1.00 (m, 1 H), 0.93 (s, 9 H), 0.37 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.8, 165.0, 150.1, 143.1, 133.7, 130.3, 123.5, 122.6, 51.3, 26.7, 26.4, 17.2, 9.3, –8.6.

***tert*-Butyl 2-{2-[*tert*-Butyl(methyl)pyridin-2-ylsilyl]ethyl}acrylate (5h)**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 5.0 Hz, 1 H), 7.60–7.55 (m, 1 H), 7.50–7.45 (m, 1 H), 7.23–7.15 (m, 1 H), 6.00 (d, *J* = 1.5 Hz, 1 H), 5.46 (d, *J* = 1.5 Hz, 1 H), 2.43–2.13 (m, 2 H), 1.48 (s, 9 H), 1.22–1.15 (m, 1 H), 1.05–0.95 (m, 1 H), 0.93 (s, 9 H), 0.36 (s, 3 H).

^{13}C NMR (125 MHz, CDCl3): δ =166.7, 165.5, 150.0, 144.8, 133.5, 130.2, 122.8, 122.3, 80.3, 28.1, 26.8, 17.2, 12.2, 9.4, –8.6.

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