Rhodium-catalyzed Coupling Reaction of 2-Vinylpyridines with Allyl Ethers

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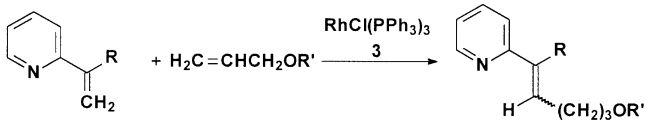
Transition metal catalyzed C-C bond formation *via* C-H bond activation is currently one of the most interesting fields.[1] The efficient catalytic coupling reactions with alkenes through C(sp^2)-H bond activation have been reported.[2-4] The rhodium-catalyzed coupling reactions of α-substituted vinylpyridines, vinylquinolines and phenylpyridines with alkenes have been reported by us.[4]

The application of allyl ethers in transition metal catalytic reactions is still rare.[5] Moreover, the coupling reaction of 2-vinylpyridines with allyl alcohol did not occur. In order to obtain the coupled product having the hydroxyl group, we chose allyl ethers instead of allyl alcohol; protection of the hydroxyl group of allyl alcohol to allyl ether and after this coupling reaction deprotection to alcohol. We have already shown the feasibility from results of the coupling reaction of 2-vinylpyridine with allyl phenyl ether.[4e] So we decided the study about the coupling reaction of 2-vinylpyridines with allyl ethers.

We now wish to report the coupling reaction of 2-vinylpyridines with various allyl ethers and the synthesis of 2-(hydroxyalkenyl)pyridines through removal of the trimethylsilyl group with ^{n}Bu$_4$NF.

The coupling reaction of 2-vinylpyridines with allyl ethers gave exclusively the anti-Markovnikov addition product in high isolated yield. The Markovnikov addition product, branched isomer was not detected in the reaction mixture.

Substrate **1a** reacted with **2a** (R' = ^{n}Pr, 3 equiv.) in the presence of the Wilkinson complex **3** (10 mol%) in toluene (3 mL) at 135 °C for 20 h to give a mixture of *E* and *Z* isomers (*E* : *Z* = 95 : 5) of **4a** in 75% isolated yield after column chromatography. In this reaction, small amounts of **1a** were remained. In order to achieve full conversion, four equivalents of **2a** were used under the same reaction conditions. After the reaction was proceeded fully, the desired product **4a** was obtained in 84% isolated yield (*E* : *Z* = 92 : 8) (run 2). As the results were satisfied, allyl ethers were used 4 equiv. to **1** under the same reaction conditions in all cases.



1a R=CH_3
1b R=H
1c R=cyclohexyl
1d R=Ph

2a R'=^{n}Pr
2b R'=^{n}Bu
2c R'=$Si(CH_3)_3$
2d R'=Et
2e R'=Ph

4a R=CH_3, R'=^{n}Pr
4b R=CH_3, R'=^{n}Bu
4c R=CH_3, R'=$Si(CH_3)_3$
4d R=CH_3, R'=Et
4e R=CH_3, R'=Ph
4f R=H, R'=$Si(CH_3)_3$
4h R=Ph, R'=$Si(CH_3)_3$

Scheme 1

Table 1. the results of the coupling reaction of 2-vinylpyridines with allyl ethers[a]

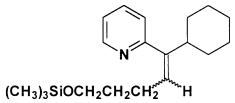
Entry	Substrate	**2** (Equiv)	Yield[b] (%)	*E* : *Z*[c]
1	**1a**	**2a** (3)	**4a**, 74	95 : 5
2	**1a**	**2a** (4)	**4a**, 84	92 : 8
3	**1a**	**2b** (4)	**4b**, 84	93 : 7
4	**1a**	**2c** (4)	**4c**, 94	90 : 10
5	**1a**	**2d** (4)	**4d**, 86	94 : 6
6	**1a**	**2e** (4)	**4e**, 83	88 : 12
7	**1b**	**2c** (4)	**4f**, 26	80 : 20
8	**1c**	**2c** (4)	**4g**, 74	14 : 86
9	**1d**	**2c** (4)	**4h**, 74	84 : 16

[a]10 mol% of Wilkinson catalyst was used. Solvent : toluene, 3 mL. [b]Isolated yield. [c]The ratio of isomers was determined by ^{1}H NMR and GC-MS.

The results of the coupling reaction of 2-vinylpyridines with allyl ethers are listed in Table 1.

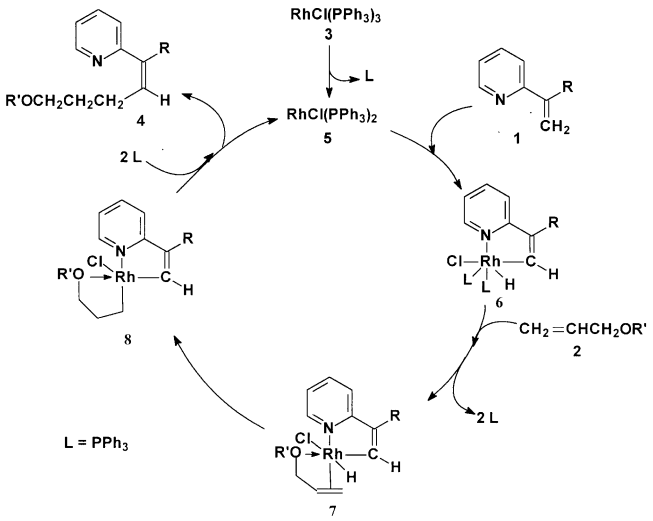
The coupling reaction of **1a** with **2b** (R = ^{n}Bu, 4 equiv.) under the same reaction conditions gave a mixture of *E* and *Z* isomers (*E* : *Z* = 93 : 7) of **4b** in 84% isolated yield (run 3). Allyloxytrimethylsilane **2c** worked well and gave a mixture of *E* and *Z* isomers (*E* : *Z* = 90 : 10) of **4c** in 94% isolated yield (run 4). Other allyl ethers **2d** and **2e** were also good partners and gave a mixture of *E* and *Z* isomers (*E* : *Z* = 94 : 6) of **4d** (86% yield) and a mixture of *E* and *Z* isomers (*E* : *Z* = 88 : 12) of **4e** (83%), respectively (runs 5 and 6).

Other substrates **1b**, **1c** and **1d** were applied to this coupling reaction with **2c**. 2-Vinylpyridine **1b** reacted with **2c** in the presence of the Wilkinson complex (10 mol%) in toluene (3 mL) at 135 °C for 20 h to give a mixture of *E* and *Z* isomers (*E* : *Z* = 80 : 20) of **4f** in 26% isolated yield (run 7). Substrate **1c** reacted with **2c** under the same reaction conditions to give a mixture of *E* and *Z* isomers (*E* : *Z* = 14 : 86) of **4g** in 74% isolated yield (run 8). Product **4g** has a different structure from other products. Since the cyclohexyl group is larger than the pyridyl group, **4g** formed by reductive elimination has a thermodynamically stable form directly. Substrate **1d** also proceeded well with **2c** to give a mixture of *E* and *Z* isomers (*E* : *Z* = 84 : 16) of **4h** in 73% isolated yield (run 9).



4g

The same reaction of an aromatic substrate such as 3-



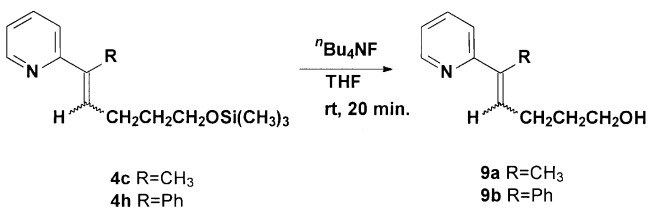
Scheme 2

methyl-2-phenylpyridine with **2c** did not give any product by the action of $[(C_8H_{14})_2RhCl]_2/Cy_3P$ which is known as an efficient catalyst system for the alkylation of 2-phenylpyridines with terminal alkenes.[4d]

A possible mechanism for the reaction may be postulated as shown in Scheme 2. The reaction appears to be initiated by formation of the highly reactive rhodium complex **5** by liberation of one ligand which reacts with **1** to form the rhodium(III) hydride complex **6** by cleavage of a vinyl C-H bond. The insertion of a hydride from the vinyl hydride rhodium(III) complex **7**, stabilized by oxygens directing effect,[6] into the coordinated allyl ether should form the hydrometallated complex intermediate **8** according to the anti-Markovnikov rule. This intermediate **8** then gives **4** and **5** for the catalytic cycle by external ligand. The *Z* isomer forms first and then isomerizes to the *E* isomer, except **4g**.

To obtain the 2-(hydroxyalkenyl)pyridines, deprotection of trimethylsilylethers was carried out. It is well known that the trimethylsilyl group in ether is easily deprotected by treatment with $^nBu_4NF$.[7] Trimethylsilylethers **4c** and **4h** were treated with $^nBu_4NF$ (1 equiv.) in tetrahydrofuran (THF) at room temperature for 20 min and the deprotected product **9a** and **9b** were obtained in 97% isolated yield and 93% isolated yield, respectively (Scheme 3).

In summary, we have found that the coupling reaction of 2-vinylpyridines with allyl ethers gave the coupled product **4** in high yields and the 2-(hydroxyalkenyl)pyridines were also obtained from **4c** and **4h** easily by deprotection of the trimethylsilyl group.



Scheme 3

Experimental Section

^{1}H NMR spectra were recorded on Bruker AC-300F (300 MHz) instrument. The chemical shifts are reported in ppm relative to internal tetramethylsilane in $CDCl_3$. ^{13}C NMR spectra were recorded on Bruker AC-300F (75 MHz) machine. Mass spectra were measured with a HP-5971A mass spectrometer which was equipped with a Hewlett-Packard 5890 series II gas chromatograph using the electron impact method (70 eV). The silica gel used in column chromatograhpy was from Aldrich (Merck, 70-230 mesh). Toluene and THF were refluxed and then distilled over calcium hydride. Substrates **1a**, **1c** and **1d** were synthesized as described in the literature.[8] 2-Vinylpyridine **1b**, tetrabutylammonium fluoride (1.0 mol solution in THF) and $RhCl(PPh_3)_3$ were purchased from Aldrich. All allyl ethers **2a-e** were purchased from Aldrich and used without further purification.

General procedure for the coupling reaction of 2-vinylpyridines with **2**.

A screw-capped vial (5 mL) was charged with **1**a (50 mg, 0.42 mmol), **2** (1.68 mmol, 4 equiv.) and **3** (38.8 mg, 0.42 mmol, 10 mol%) in toluene (3 mL). The stirred reaction mixture was heated at 135 °C for 20 h and then concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc-hexane, 1 : 5).

4a (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, 1H, J = 4.5 Hz, 6-H in py), 7.61 (dt, 1H, J = 7.8, 1.9 Hz, 4-H in py), 7.39 (d, 1H, J = 8.0 Hz, 3-H in py), 7.07-7.12 (m, 1H, 5-H in py), 6.39 (dt, 1H, J = 7.4, 1.3Hz, =C-***H***), 3.46 (t, 2H, J = 6.4Hz, C***H₂***O), 3.38 (t, 2H, J = 6.7 Hz, OC***H₂***), 2.35 (quartet, 2H, J = 7.4 Hz, =CHC***H₂***), 2.10 (s, 3H, =C-C***H₃***), 1.78 (quintet, 2H, J = 7.0 Hz, =CHCH$_2$C***H₂***), 1.60 (sextet, 2H, J = 7.3 Hz, C***H₂***CH$_3$), 0.93 (t, 3H, J = 7.4 Hz, C***H₃***); ^{13}C NMR (75 MHz) δ 159.82, 148.59, 136.10, 134.76, 131.08, 121.20, 119.49, 72.48, 70.01, 29.27, 25.34, 22.84, 14.10, 10.52; MS (EI) m/z 51 (10), 78 (16), 93 (10), 106 (13), 117 (55), 120 (68), 131 (58), 144 (51), 146 (100), 158 (13), 176 (16), 190 (3), 219 (13, M$^+$).

4b (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54-8.56 (m, 1H, 6-H in py), 7.61 (dt, 1H, J = 7.9, 1.8 Hz, 4-H in py), 7.39 (d, 1H, J = 8.0 Hz, 3-H in py), 7.08-7.13 (m, 1H, 5-H in py), 6.38 (dt, 1H, J = 7.4, 1.3 Hz, =C-***H***), 3.39-3.48 (4H, C***H₂***O), 2.35 (quartet, 2H, J = 7.3 Hz, =CHC***H₂***), 2.10 (s, 3H, =C-C***H₃***), 1.77 (quintet, 2H, J = 7.1 Hz, =CHCH$_2$C***H₂***), 1.51-1.77 (2H, C***H₂***), 1.33-1.42 (2H, C***H₂***), 0.92 (t, 3H, J = 7.2 Hz, C***H₃***); ^{13}C NMR (75 MHz) δ 159.86, 148.62, 136.12, 134.76, 131.11, 121.21, 119.51, 70.61, 70.09, 31.77, 29.28, 25.37, 19.29, 14.12, 13.86; MS (EI) m/z 51 (8), 78 (14), 93 (10), 106 (14), 117 (55), 120 (73), 131 (58), 144 (53), 146 (100), 158 (13), 176 (19), 190 (3), 233 (11, M$^+$).

4c (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53-8.55 (m, 1H, 6-H in py), 7.59 (dt, 1H, J = 7.9, 1.7 Hz, 4-H in py), 7.37 (d, 1H, J = 8.0 Hz, 3-H in py), 7.06-7.11 (m, 1H, 5-H in py), 6.37 (dt, 1H, J = 7.2, 1.2Hz, =C-***H***), 3.64 (t, 2H, J = 6.4 Hz, C***H₂***O), 2.32 (quartet, 2H, J = 7.5 Hz, =CHC***H₂***), 2.10 (s, 3H, =C-C***H₃***), 1.72 (quintet, 2H, J = 7.0 Hz,

=CHCH$_2$C***H$_2$***), 0.12 [s, 9H, Si(C***H$_3$***)$_3$]; ^{13}C NMR (75 MHz) δ 159.85, 148.60, 136.09, 134.70, 131.12, 121.19, 119.46, 62.02, 32.18, 25.12, 14.16 (CH_3), –0.56 (Cs of $SiMe_3$); MS (EI) m/z 51 (12), 73 (35), 78 (12), 117 (52), 120 (66), 131 (58), 144 (58), 146 (100), 158 (18), 181 (29), 218 (9), 234 (10), 249 (11, M^+).

4d (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53-8.56 (m, 1H, 6-H in py), 7.61 (dt, 1H, *J* = 7.7, 1.7 Hz, 4-H in py), 7.39 (d, 1H, *J* = 8.0 Hz, 3-H in py), 7.07-7.12 (m, 1H, 5-H in py), 6.38 (dt, 1H, *J* = 7.4, 1.3 Hz, =C-***H***), 3.48 (q, 4H, *J* = 7.1 Hz, C***H$_2$***O), 2.35 (quartet, 2H, *J* = 7.4 Hz, =CHC***H$_2$***), 2.11 (s, 3H, =C-C***H$_3$***), 1.78 (quintet, 2H, *J* = 7.4 Hz, =CHCH$_2$C***H$_2$***), 1.21 (t, 3H, *J* = 7.0 Hz, C***H$_3$***); ^{13}C NMR (75 MHz) δ 159.79, 148.57, 136.10, 134.77, 131.00, 121.19, 119.48, 69.86, 66.01, 29.26, 25.32, 15.12, 14.08; MS (EI) m/z 59 (3), 78 (18), 93 (10), 104 (13), 117 (70), 130 (57), 146 (100), 160 (12), 176 (28), 190 (2), 205 (37, M^+)

4e (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52-8.55 (m, 1H, 6-H in py), 7.61 (t, 1H, *J* = 7.5 Hz, 4-H in py), 7.37 (d, 1H, *J* = 7.9 Hz, 3-H in py), 6.81-7.29 (6H, 5-H in py and Hs in Ph), 6.40 (t, 1H, *J* = 7.4 Hz, =C-***H***), 3.98 (t, 2H, *J* = 6.3 Hz, C***H$_2$***O), 2.45 (quartet, 2H, *J* = 7.3 Hz, =CHC***H$_2$***), 2.10 (s, 3H, C***H$_3$***) 1.95 (quintet, 2H, *J* = 6.9 Hz, =CHCH$_2$C***H$_2$***); ^{13}C NMR (75 MHz) δ 159.76, 158.88, 148.47, 136.42, 135.05, 130.85, 129.30, 121.45, 120.44, 119.80, 114.40, 66.89, 28.79, 25.17, 14.27;

4f (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, 1H, 6-H in py), 7.59 (dt, 1H, *J* = 7.7, 1.7 Hz, 4-H in py), 7.23 (d, 1H, *J* = 7.9 Hz, 3-H in py), 7.08 (dd, 1H, 5.0, 2.3 Hz, 5-H in py), 6.74 (dt, 1H, *J* = 15.8, 6.9 Hz, =C-***H***), 6.50 (d, 1H, *J* = 15.7 Hz, =C-***H***), 3.64 (t, 2H, *J* = 6.4 Hz, C***H$_2$***O), 2.33 (quartet, 2H, *J* =6.8 Hz, =CHC***H$_2$***), 1.75 (quintet, 2H, *J* = 6.9 Hz, =CHCH$_2$C***H$_2$***), 0.12 [s, 9H, Si(C***H$_3$***)$_3$]; ^{13}C NMR (75 MHz) δ 159.90, 149.31, 136.34, 135.16, 130.08, 121.53, 120.93, 61.92, 31.79, 29.11, -0.51 (Cs of $SiMe_3$); MS (EI) m/z 59 (19), 73 (59), 78 (21), 93 (23), 106 (81), 117 (99), 132 (100), 144 (67), 181 (49), 190 (27), 204 (49), 220 (67), 235 (72, M^+)

4g (*Z* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60-8.62 (m, 1H, 6-H in py), 7.61 (dt, 1H, *J* = 7.7, 1.8 Hz, 4-H in py), 7.09-7.15 (2H, 3,5-Hs in py), 5.48 (dt, 1H, *J* = 7.4, 1.2 Hz, =C-***H***), 3.50 (t, 2H, *J* = 6.6 Hz, C***H$_2$***O), 2.38-2.51 (m, 1H, C***H*** in cyclohexyl), 1.96 (quartet, 2H, *J* = 7.5 Hz, =CHC***H$_2$***), 1.04-1.80 (12H, Hs of cyclohexyl and β-C***H***$_2$ to OSi), 0.06 [s, 9H, Si(C***H$_3$***)$_3$]; ^{13}C NMR (75 MHz) δ 160.12, 149.21, 135.38, 125.55, 124.31, 121.13, 62.02, 43.80, 32.90, 32.23, 31.58, 26.88, 26.60, 26.30, 25.05, –0.58 (Cs of $SiMe_3$); MS (EI) m/z 59 (6), 73 (14), 78 (6), 93 (7), 104 (8), 117 (28), 130 (30), 143 (40), 156 (31), 170 (24), 181 (45), 186 (38), 200 (38), 214 (100), 226 (9), 234 (4), 274 (9), 302 (43), 317 (51, M^+)

4h: (a mixture of *E* and *Z* isomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65-8.69 (m, 0.2H, 6-H in py, *Z* isomer), 8.56-8.59 (m, 0.8H, 6-H in py, *E* isomer), 7.67 (dt, 0.2H, *J* = 7.5, 1.9Hz, 4-H in py, *Z* isomer), 7.48 (dt, 0.8H, *J* = 7.5, 1.9 Hz, 4-H in py, *E* isomer), 6.85-7.42 (7.8H, 3,5-Hs in py, ph and =C-***H***), 6.19 (t, 0.2H, *J* = 7.5 Hz, =C-***H***), 3.57 (t, 2H, *J* = 6.6 Hz, C***H$_2$***O), 2.12-2.25 (2H, =CHC***H$_2$***), 1.71 (quintent, 2H, *J* = 6.9 Hz, C***H***$_2$), 0.07 [s, 9H, Si(C***H$_3$***)$_3$].

General procedure for deprotection of the coupled products.

A screw-capped vial (5 mL) was charged with **4c** (50 mg, 0.2 mmol), 0.2 ml of ^{n}Bu$_4$NF solution (1 M in THF, 0.2 mmol, 1 equiv.) in THF (1 mL). The stirred reaction mixture was at room temperature for 20 min and then concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc-hexane, 1 : 1).

9a (*E* isomer)**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52-8.55 (m, 1H, 6-H in py), 7.62 (dt, 1H, *J* = 8.0, 1.8 Hz, 4-H in py), 7.38 (d, 1H, *J* = 8.9 Hz, 3-H in py), 7.08-7.13 (m, 1H, 5-H in py), 6.36 (dt, 1H, *J* = 6.0, 1.3 Hz, =C-***H***), 3.70 (t, 2H, *J* = 6.4 Hz, C***H$_2$***O), 2.96 (bs, 1H, O***H***), 2.35 (quartet, 2H, *J* = 7.4 Hz, =CHC***H$_2$***), 2.10 (s, 3H, =C-C***H$_3$***), 1.76 (quintet, 2H, *J* = 7.0 Hz, =CHCH$_2$C***H$_2$***); ^{13}C NMR (75 MHz) δ 159.80, 148.57, 136.32, 134.74, 131.12, 121.35, 119.68, 62.20, 32.16, 25.11, 14.25(CH_3); MS (EI) m/z 51 (12), 65 (6), 78 (23), 93 (17), 109 (22), 117 (79), 132 (73), 146 (100), 177 (25, M^+)

9b: (a mixture of *E* and *Z* isomers) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55-8.58 (m, 1H, 6-H in py), 7.66 (dt, 0.26H, *J* = 8.0, 1.9 Hz, 4-H in py, *Z* isomer), 7.49 (dt, 0.74H, *J* = 7.5, 1.9 Hz, 4-H in py, *E* isomer), 6.84-7.40 (7.74H, 3,5-Hs in py, ph and =C-***H*** in *E* isomer), 6.05 (t, 0.26H, *J* = 7.5 Hz, =C-***H*** in *Z* isomer), 3.70 (t, 0.52H, *J* = 7.0 Hz, C***H$_2$***O in *Z* isomer), 3.60 (t, 1.48H, *J* = 6.6 Hz, C***H$_2$***O in *E* isomer), 2.59 (bs, 1H, O***H***), 2.38-2.46 (0.52H, =CHC***H$_2$*** in *Z* isomer), 2.19 (q, 1.48H, =CHC***H$_2$*** in *E* isomer), 1.73 (quintent, 2H, *J* = 7.0 Hz, C***H***$_2$).

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