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A novel highly regio- and diastereoselective haloamination of alkenes catalyzed by divalent palladium

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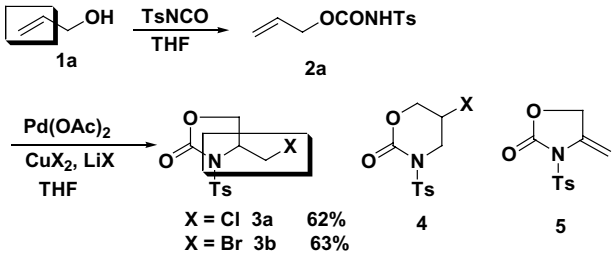
Abstract—From the readily available allylic alcohols or allylic amines, a novel Pd(II)–$CuCl_2$-catalyzed haloamination reaction of alkenes with high chemo-, regio-, and diastereo-selectivity was developed. The reaction proceeds through *trans*-aminopalladation of alkenes, followed by oxidative cleavage of the carbon–palladium bond with retention of configuration.

In Pd(II)-catalyzed reaction, the key step is quenching the carbon–palladium bond to regenerate the Pd(II) species making the reaction catalytically possible. In a series of our works initiated with nucleopalladation, we have successfully used β-heteroatom elimination,[1] oxidative cleavage,[2] and protonolysis reaction[3] to quench the carbon–palladium bonds. Herein, we wish to report our recent results of a novel haloamination reaction of alkenes initiated by aminopalladation followed by oxidative cleavage of the carbon–palladium bond with $CuCl_2$ as a novel entry in the field of oxidative multifunctionalization of alkenes.[4]



Scheme 1.

The reaction of *O*-allylic carbamate **2a** (1 mmol), which was formed from the reaction of allylic alcohol and *p*-toluenesulfonyl isocyanate (TsNCO) in THF (5 mL), in the presence of a catalytic amount of $Pd(OAc)_2$, $CuCl_2$ (5 mmol), and LiCl (2 mmol) at room temperature afforded the chloroamination product, oxazolidinone **3a**, in 62% yield. Under the similar condition, using $CuBr_2$/LiBr instead of $CuCl_2$/LiCl, the bromoamination product **3b** was obtained in 63% yield (Scheme 1). The regioisomeric product **4** formed by the attack of the nitrogen nucleophile to the terminal carbon atom of alkene was not observed (Scheme 1).[5] In addition, no β-hydride elimination product **5** was formed, which may be due to the presence of excess halide ions.[3e]

Allylic amines can also be used as substrates to afford corresponding imidazolidinones easily under similar condition. As compared with allylic primary amine **1g** (Table 1, entries 5 and 6), the reactions of the *N*-benzyl allylic amine **1i** gave almost quantitative yields indicating that the substituents attached on the nitrogen atom are important in the cyclization (Table 1, entries 7 and 8).

It is noteworthy that the reaction can be carried out in a one-pot manner via the in situ generation of the *N*-tosyl-carbamates or ureas from the corresponding allylic alcohols or allylic amines and TsNCO,[6] followed by the Pd(II)-catalyzed reaction. Substituted allylic alcohols **1** were examined under the similar conditions (Table 1), and they all gave exclusively the haloamination products.[7] Using the substrates, which contain a

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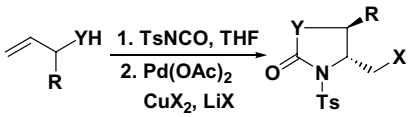
Table 1. Haloamination of alkenes catalyzed by divalent palladium complex[a]



1 *trans-3*

Entry	Substrates					Products
	1	R	Y	X	**3**	Yield[b] (%)
1	**1c**	Me	O	Cl	**3c**[c]	66
2	**1c**	Me	O	Br	**3d**	65
3	**1e**	n-C_5H_{11}	O	Cl	**3e**	64
4	**1e**	n-C_5H_{11}	O	Br	**3f**	70
5	**1g**	H	NH	Cl	**3g**	86
6	**1g**	H	NH	Br	**3h**	78
7	**1i**	H	NBn	Cl	**3i**	97
8	**1i**	H	NBn	Br	**3j**	93

[a] Substrate (1 mmol) reacted with TsNCO (1.1 mmol) in THF at rt for 10 min under Ar. Then cupric halide (5 mmol), lithium halide (2 mmol), and $Pd(OAc)_2$ (0.05 mmol) were added, the reaction was monitored by TLC.
[b] Isolated yield.
[c] The *trans*/*cis* ratio was determined by the ^1H NMR spectra.

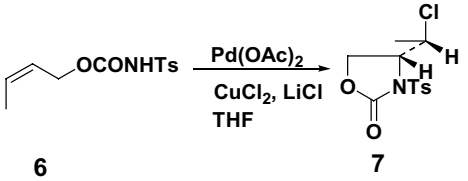
substituent at the allylic position, the *trans*-disubstituted products were unambiguously obtained as determined by ^1H NOESY spectra of **3c** and X-ray diffraction study of **3d**.[8]

When the 3-substituted allyl alcohol **6** was used as the substrate, only single diastereoisomeric product **7** was obtained in 50% yield. The X-ray diffraction result of **7** showed that the oxidative cleavage of carbon–palladium bond occurred with retention of configuration of the carbon atom if the *trans*-aminopalladation happened in the first step (Scheme 2),[9,10] which is consistent with our previous report.[2d]

Using this method, oxazindinones **9** were obtained as the corresponding haloamination products of alkenes in excellent yield when the homoallylic alcohol **8** was used as the substrates (Scheme 3).

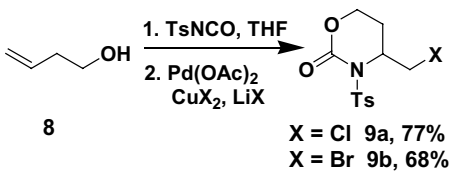
When the readily available homochiral allylic alcohol (*R*)-**1e** was used as the substrate, (4*S*,5*R*)-**3e** (>97% ee) was easily obtained (Scheme 4).

A speculated mechanism is shown in Scheme 5: Firstly, a carbon–palladium bond was formed from the intramolecular *trans*-nucleopalladation to alkenes[10] activated by



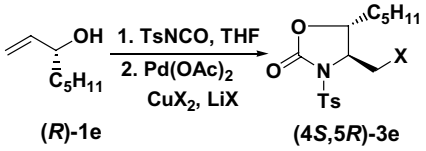
6 7

Scheme 2.



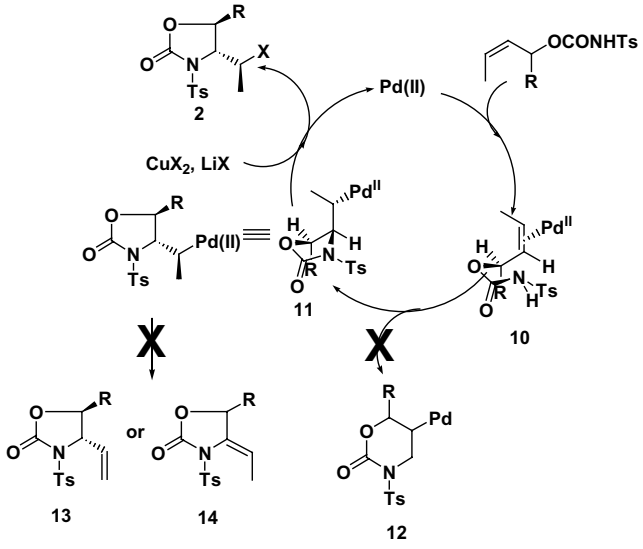
8

Scheme 3.



(*R*)-1e (4*S*,5*R*)-3e

Scheme 4.



Scheme 5.

the divalent palladium species; then followed by the oxidative cleavage of the carbon–palladium bond in the presence of cupric halide and lithium halide (Scheme 5).[2,11] During our observation, only five-membered cyclic intermediate **11** was formed.[5] When the substrates contain a substituent at allylic position, the addition of the nucleophile to the carbon–carbon double bond from the opposite side of the substituent occurred (intermediate **10**), which determined the *trans*-selectivity of the reaction.[12] The reaction is highly selective for the oxidative cleavage reaction of the carbon–palladium bond, no β-hydride elimination products (**13** and **14**) were found. The presence of excess halide ions in the reaction may inhibit the β-hydride elimination of the carbon–palladium bond making the reaction highly chemoselective.[3e]

In summary, we developed an oxidative multifunctionalization of alkenes via the palladium(II)-catalyzed reaction from readily available allylic alcohols or allylic

amines, from which oxazolidinones and imidazolidinones are easily obtained from corresponding substrates. Moreover, utilizing the readily available homochiral allylic alcohol as the starting material, the highly optically active oxazolidinones, which are the precursor of amino alcohols, are easily obtained implying the synthetic utility of this reaction.

Acknowledgements

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(d) Zhu, G.; Ma, S.; Lu, X.; Huang, Q. *J. Chem. Soc., Chem. Commun.* **1995**, 271–273; (e) Zhu, G.; Lu, X. *J. Organomet. Chem.* **1996**, *508*, 83–90.
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5. In the absence of cupric halide, the six-membered cyclic intermediate **9** was reported to be the possible intermediate: Lei, A.; Lu, X. *Org. Lett.* **2000**, *2*, 2357–2360.
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7. Typical procedure for the reaction: Compound **1c** (1.0 mmol) was reacted with TsNCO (1.1 mmol) in THF (5 mL) for 10 min at rt under N_2; then, $Pd(OAc)_2$ (0.05 mmol), LiBr (2.0 mmol), and $CuCl_2$ (5.0 mmol) were added and the reaction was stirred at rt. After the reaction was complete as monitored by TLC, the solvent was removed and the residue was purified by column chromatography on silica gel to give product **3c** with 66% yield.
3a: mp 159–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 4.72–4.63 (m, 1H), 4.38 (dd, $J = 9.0$, 8.6 Hz, 1H), 4.25 (dd, $J = 3.9$, 9.1 Hz, 1H), 3.84 (dd, $J = 6.0$, 11.7 Hz, 1H), 3.79 (dd, $J = 3.1$, 11.7 Hz, 1H), 2.39 (s, 3H); IR (neat) 3039, 2973, 1769, 1595, 1441, 1389, 1359, 1329, 1209, 1172, 1132, 1089, 820, 757, 672, 607, 573, 543 cm^{-1}; MS *m/e* 292 (^{37}M$^+$+1), 290 (^{35}M$^+$+1), 225, 176, 155, 139, 91, 65; Anal. Calcd for $C_{11}H_{12}ClNO_4S$: C, 45.60; H, 4.17; N, 4.83. Found: C, 45.54; H, 4.03; N, 4.84.
3b: mp 147–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 4.70–4.62 (m, 1H), 4.44–4.35 (m, 1H), 4.24–4.15 (m, 1H), 3.73–3.54 (m, 2H), 2.34 (s, 3H); IR (neat) 3039, 2973, 1768, 1596, 1496, 1471, 1435, 1390, 1361, 1336, 1325, 1207, 1173, 1123, 1091, 1069, 821, 754, 670, 618, 582, 573, 541 cm^{-1}; MS *m/e* 336 (^{81}M$^+$+1), 334 (^{79}M$^+$+1), 271, 269, 254, 176, 155, 139, 91, 65; Anal. Calcd for $C_{11}H_{12}BrNO_4S$: C, 39.54; H, 3.62; N, 4.19. Found: C, 39.54; H, 3.39; N, 4.19.
3c: mp 105–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 4.52 (dq, $J = 3.4$, 6.4 Hz, 1H), 4.14 (ddd, $J = 3.4$, 3.2, 7.2 Hz, 1H), 3.84 (dd, $J = 3.2$, 11.7 Hz, 1H), 3.75 (dd, $J = 7.2$, 11.7 Hz, 1H), 2.40 (s, 3H), 1.32 (d, $J = 6.4$ Hz, 3H); IR (neat) 1789, 1596, 1450, 1360, 1329, 1209, 1170, 1145, 1087, 1047, 816, 755, 735, 665, 578, 542 cm^{-1}; MS *m/e* 306 (^{37}M$^+$+1), 304 (^{35}M$^+$+1), 239, 190, 155, 146, 91, 65; Anal. Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61. Found: C, 47.51; H, 4.68; N, 4.40.
3d: mp 126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 4.55 (ddq, $J = 0.7$, 3.2, 5.8 Hz, 1H), 4.22 (ddd, $J = 0.6$, 3.0, 8.1 Hz, 1H), 3.78 (ddd, $J = 0.6$, 2.8, 6.7 Hz, 1H), 3.2 (ddq, $J = 0.7$, 8.1, 10.6 Hz, 1H), 2.37 (s, 3H), 1.39 (d, $J = 5.8$ Hz, 3H); IR (neat) 3046, 2988, 1786, 1595, 1358, 1204, 1167, 1137, 1085, 104, 816, 753, 672, 660, 574, 541 cm^{-1}; MS *m/e* 350 (^{81}M+1), 348 (^{79}M+1), 285, 283, 190, 155, 91, 65; Anal. Calcd for $C_{12}H_{14}BrNO_4S$: C, 41.39; H, 4.05; N, 4.02. Found: C, 41.56; H, 4.01; N, 3.88.
3e: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 4.70–4.57 (m, 1H), 4.43 (dt, $J = 3.4$, 6.4 Hz, 1H), 4.30–4.23 (m, 1H), 3.86–3.84 (m, 1H), 2.45 (s, 3H), 1.63–1.56 (m, 2H), 1.34–1.26 (m, 6H); 0.89 (t, $J = 6.4$ Hz, 3H); IR (neat) 2956, 2930, 1781, 1596, 1368, 1174, 1138, 1091, 665 cm^{-1}; MS *m/e* 362 (^{37}M$^+$+1), 360 (^{35}M$^+$+1), 310, 246, 155, 108, 91, 65; Anal. Calcd for $C_{16}H_{22}ClNO_4S$: C, 53.40; H, 6.16; N, 3.89. Found: C, 53.80; H, 6.48; N, 3.91.
3f: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 4.33 (dt, $J = 3.0$, 6.3 Hz, 1H), 4.18 (dt, $J = 2.9$, 7.9 Hz, 1H), 3.68 (dd, $J = 2.8$, 10.6 Hz, 1H), 3.56 (dd, $J = 7.9$, 10.6 Hz, 1H), 2.38 (s, 3H), 1.54–1.49 (m, 2H); 1.28–1.19 (m, 6H), 0.80 (t, $J = 6.7$ Hz, 3H); IR (neat) 2950, 2927, 2859, 1782, 1596, 1461, 1371, 1134, 1090, 1044, 814, 752, 704, 668, 575, 545 cm^{-1}; MS *m/e* 406 (^{81}M+1), 404 (^{79}M+1), 310, 260, 246, 155, 108, 91, 65; HRMS calcd for $C_{16}H_{22}BrNO_4S$: 403.0453, found: 403.0468.
3g: mp 167.5–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 5.89 (br, 1H), 4.54–4.46 (m, 1H), 3.84 (dd, $J = 3.1$, 11.2 Hz, 1H), 3.73 (dd, $J = 7.6$, 11.2 Hz, 1H), 3.53 (t, $J = 9.4$ Hz, 1H), 3.36 (ddd, $J = 1.0$, 4.0, 9.5 Hz, 1H), 2.37 (s, 3H); IR (neat) 3250, 1743, 1363, 1163, 1090, 664, 577, 541 cm^{-1}; MS *m/e* 291 (^{37}M$^+$+1), 289 (^{35}M$^+$+1), 239, 224, 175, 155, 139, 91, 65; Anal. Calcd for $C_{11}H_{13}ClN_2O_3S$: C, 45.76; H, 4.54; N, 9.70. Found: C, 45.54; H, 4.41; N, 9.65.
3h: mp 199–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.22 (br, 1H), 4.57–4.49 (m, 1H), 3.76 (dd, $J = 3.0$, 10.4 Hz, 1H), 3.62–3.52 (m, 2H), 3.34 (ddd, $J = 1.1$, 8.1, 9.6 Hz, 1H), 2.37 (s, 3H); IR (neat) 3250, 3138, 1741, 1364, 1171, 1070, 671, 574 cm^{-1} ; MS *m/e* 335 (^{81}M$^+$+1), 333 (^{79}M$^+$+1), 310, 268, 239, 175, 155, 139, 91, 65; Anal. Calcd for $C_{11}H_{13}BrN_2O_3S$: C, 39.65; H, 3.93; N, 8.41. Found: C, 39.50; H, 3.78; N, 8.41.

3i: mp 179–179.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.23–7.19 (m, 3H), 7.28–7.03 (m, 2H), 4.43–4.40 (m, 1H), 4.27 (d, $J = 14.9$ Hz, 1H), 4.22 (d, $J = 14.9$ Hz, 1H), 3.81–3.68 (m, 2H), 3.33 (t, $J = 9.5$ Hz, 1H), 3.12 (dd, $J = 4.1$, 9.5 Hz, 1H), 2.38 (s, 3H); IR (neat) 3054, 3024, 2922, 1744, 1721, 1440, 1362, 1170, 1105, 588, 546 cm^{-1}; MS m/e 381 (^{37}M$^+$+1), 379 (^{35}M$^+$+1), 329, 314, 265, 263, 91, 65; Anal. Calcd for $C_{18}H_{19}ClN_2O_3S$: C, 57.06; H, 5.05; N, 7.39. Found: C, 57.21; H, 5.03; N, 7.31.

3j: mp 203–203.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.32–7.27 (m, 3H), 7.15–7.1203 (m, 2H), 4.52–4.45 (m, 1H), 4.37 (d, $J = 14.9$ Hz, 1H), 4.29 (d, $J = 14.9$ Hz, 1H), 3.76 (dd, $J = 2.9$, 10.4 Hz, 1H), 3.61 (d, $J = 7.7$, 10.4 Hz, 1H), 3.42 (t, $J = 9.5$ Hz, 1H), 3.16 (dd, $J = 4.3$, 9.6 Hz, 1H), 2.47 (s, 3H); IR (neat) 3054, 3024, 2922, 1743, 1594, 1493, 1486, 1447, 1439, 1360, 1175, 1332, 1265, 1188, 764, 702, 663, 586, 546 cm^{-1}; MS m/e 425 (^{81}M$^+$+1), 423 (^{79}M$^+$+1), 358, 267, 265, 155, 91, 65; Anal. Calcd for $C_{18}H_{19}BrN_2O_3S$: C, 51.07; H, 4.52; N, 6.62. Found: C, 51.23; H, 4.50; N, 6.54.

7: mp 155–155.5 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 4.71 (ddd, $J = 3.6$, 3.7, 8.7 Hz, 1H), 4.65 (dq, $J = 3.9$, 6.7 Hz, 1H), 4.45 (dd, $J = 3.3$, 9.7 Hz, 1H), 4.35 (d, $J = 8.6$, 9.7 Hz, 1H), 2.46 (s, 3H), 1.41 (d, $J = 6.7$ Hz, 3H); IR (neat) 3054, 3024, 2922, 1773, 1377, 1178 cm^{-1}; MS m/e 306 (^{37}M$^+$+1), 304 (^{35}M$^+$+1), 240, 176, 155, 91, 65; Anal. Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61. Found: C, 47.58; H, 4.61; N, 4.45.

9a: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 4.82–4.79 (m, 1H), 4.39 (dt, $J = 3.4$, 11.5 Hz, 1H), 4.33–4.29 (m, 1H), 4.00 (ddd, $J = 0.7$, 3.6, 11.3 Hz, 1H), 3.68 (dd, $J = 9.8$, 11.2 Hz, 1H), 2.51–2.43 (m, 4H), 2.22–2.14 (m, 1H); IR (neat) 2924, 1738, 1657, 1596, 1400, 1358, 1280, 1170, 1087, 814, 667, 613, 539 cm^{-1} ; MS m/e 306 (^{37}M$^+$+1), 304 (^{35}M$^+$+1), 268, 239, 203, 190, 155, 146, 91, 65; Anal. Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61. Found: C, 47.76; H, 4.91; N, 4.58.

9b: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 4.84–4.79 (m, 1H), 4.37–4.30 (m, 2H), 3.88 (dd, $J = 3.6$, 0.5 Hz, 1H), 3.50 (t, $J = 10.4$ Hz, 1H), 2.57–2.49 (m, 1H), 2.44 (s, 3H) 2.34–2.15 (m, 1H); IR (neat) 2968, 2925, 1734, 1596, 1409, 1351, 1270, 1172, 1087, 814, 667 cm^{-1}; MS m/e 350 (^{81}M$^+$+1), 348 (^{79}M$^+$+1), 285, 283, 190, 155, 146, 118, 91, 65; Anal. Calcd for $C_{12}H_{14}BrNO_4S$: C, 41.39; H, 4.05; N, 4.02. Found: C, 41.58; H, 4.15; N, 3.65.

8. There is strong NOE between 4-H and 5-CH_3, 4-CH_2Cl and 5-H in the NOESY spectra of compound **3c**. In addition, there is no NOE between 4-H and 5-H. The direct evidence for the stereo-configuration is the X-ray crystallography of **3d** in which 4-CH_2Br and 5-CH_3 are in *trans*-configuration.
9. Deposit number of **3d** from Crystallographic Data Centre: CCDC 212346. Deposit number of **7** from Crystallographic Data Centre: CCDC 212345. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.
10. *N*-Tosyl carbamates could be used as the efficient nucleophiles in the *trans*-aminopalladation reaction of alkenes or alkynes (a) Trost, B. M.; Vranken, D. L.-V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 228–230; (b) Tamaru, Y.; Kimura, M. *Synlett* **1997**, 749–757.
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