Copper-Catalyzed Regioselective Allylic Cyanation of Allylic Compounds with Trimethylsilyl Cyanide

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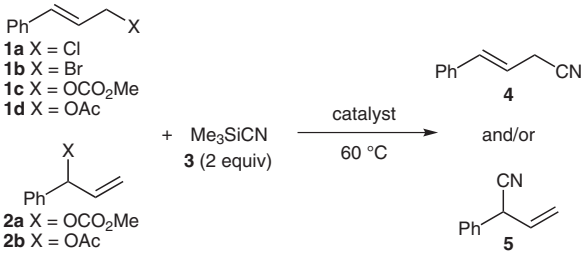
Abstract: The copper-catalyzed regioselective allylic cyanation of allylic compounds with trimethylsilyl cyanide (TMSCN) is described. Copper(I) iodide (CuI), copper(I) cyanide (CuCN) and copper(II) chloride ($CuCl_2$) are shown to effectively catalyze the cyanation of various allylic substrates to afford the corresponding allylic cyanides in good yields and high regioselectivities. The reaction in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) reveals that the cyanation proceeds via a radical pathway.

Key words: copper, catalysis, regioselectivity, radical reaction, nitriles

The transition-metal-catalyzed allylic substitution of allylic compounds represents a very useful procedure for the construction of allylic substituted compounds, and several different nucleophiles have been employed in this type of reaction.[1] On the other hand, compounds containing a cyano group are synthetically useful because the cyano substituent can easily be converted into other functionalities; metal cyanides, such as potassium cyanide (KCN) and sodium cyanide (NaCN) were mainly used as the source of the cyano group. As an alternative cyanating reagent, trimethylsilyl cyanide (TMSCN), which is easy to handle and even reacts with several secondary or cyclic compounds, including allylic substrates, in common organic solvents, is also widely used.[2,3] To the best of our knowledge, however, there is only a single example of the metal-catalyzed allylic substitution of allylic compounds with trimethylsilyl cyanide as the cyanating reagent.[3] In 1993, Tsuji described the palladium-catalyzed allylic cyanation of allylic esters with trimethylsilyl cyanide.[3] Based on this background, we initiated a study to realize the allylic cyanation of allylic compounds with trimethylsilyl cyanide using alternative transition metal catalysts, and we report herein the copper-catalyzed allylic cyanation of allyl chlorides and allyl esters with trimethylsilyl cyanide.

We initially examined the reaction of cinnamyl chloride (**1a**) with trimethylsilyl cyanide (**3**) in acetonitrile without a catalyst, but did not obtain any products (Table 1, entry 1). Subsequent screening with the aim of finding an effective copper catalyst[4,5] for the allylic cyanation reaction was performed using various copper salts. In the event, several copper(I) salts were found to catalyze the desired

Table 1 Copper-Catalyzed Cyanation of Allylic Compounds



Entry	Substrate	[Cu] (mol%)	Solvent	Yield (%)[a]	Ratio of **4**:**5**[b]
1	**1a**	–	MeCN	0	–
2	**1a**	CuCl (5)	MeCN	9	>98:2
3	**1a**	CuBr (5)	MeCN	67	>98:2
4	**1a**	CuI (5)	MeCN	87	>98:2
5	**1a**	CuOTf (5)	MeCN	0	–
6	**1a**	CuI (5)	DMF	53	>98:2
7	**1a**	CuI (5)	DMSO	32	>98:2
8	**1a**	CuI (5)	DME	0	>98:2
9	**1a**	CuI (5)	THF	<5	>98:2
10	**1a**	CuI (5)	toluene	0	–
11	**1b**	CuI (5)	MeCN	29	>98:2
12	**1b**	CuI (25)	MeCN	50	>98:2
13	**1c**	CuI (25)	MeCN	<5	>98:2
14[c]	**1c**	CuI (25)	MeCN	77	>98:2
15[c]	**1d**	CuI (25)	MeCN	23	>98:2
16[c]	**2a**	CuI (5)	MeCN	76	>98:2
17	**2b**	CuI (25)	MeCN	80	>98:2

[a] Yield of isolated product **4**.
[b] Ratio was determined by ^{1}H NMR spectroscopy of the crude products.
[c] Reaction was conducted at 80 °C.

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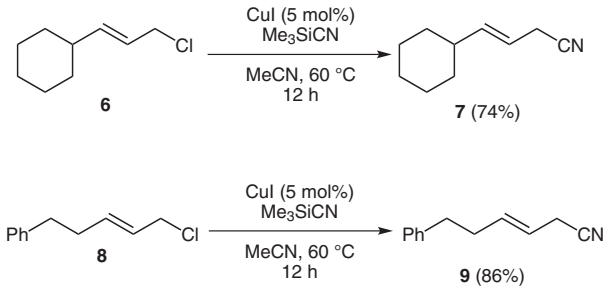
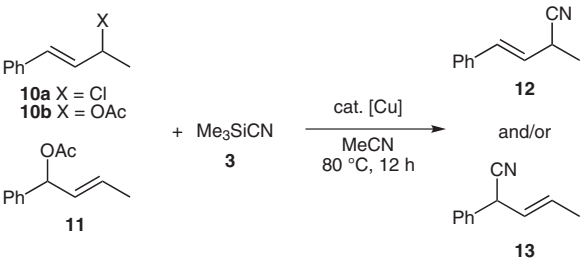
reaction to give cyanide **4** (Table 1, entries 2–5). Copper(I) iodide (CuI) exhibited the highest catalyst activity providing an 87% yield of isolated product **4** (Table 1, entry 4). We also confirmed that the reaction proceeded with high regioselectivity and linear allylic cyanide **4** was obtained as a single regioisomer. Next, we examined the influence of the solvent on the cyanation reaction; solvents including *N*,*N*-dimethylformamide, dimethyl sulfoxide, 1,2-dimethoxyethane (DME), tetrahydrofuran and toluene all proved inferior in comparison with acetonitrile (Table 1, entries 6–10). We next investigated the reaction of other cinnamyl-based compounds **1b**–**d** using the copper(I) iodide catalyst. The reaction of cinnamyl bromide (**1b**) gave a low yield (29%), and the yield could only be increased to 50% when using 25 mol% of copper(I) iodide (Table 1, entries 11 and 12). Decreased reactivity was also observed for the allylic carbonate **1c**, but we succeeded in obtaining an improved 77% yield of product **4** by increasing the reaction temperature from 60 °C to 80 °C (Table 1, entries 13 and 14). Unfortunately, the reaction of cinnamyl acetate (**1d**) resulted in only a 23% yield of cyanide **4** (Table 1, entry 15). Furthermore, we examined the reaction of branched allylic esters **2a** and **2b** and obtained the desired product **4** in yields of 76% (5 mol% of CuI) and 80% (25 mol% of CuI, at 60 °C), respectively (Table 1, entries 16 and 17). These results indicate that the reactivity of branched allylic esters **2** is higher than that of cinnamyl allylic esters **1** in the copper(I) iodide catalyzed allylic cyanation with trimethylsilyl cyanide. We also found that the allyl chlorides **6** and **8** possessing an alkyl group provided allylic cyanides **7** and **9** in good yields under our optimized conditions (Scheme 1).



Scheme 1 Allylic cyanation of allylic chlorides **6** and **8** possessing an alkyl group

We next examined the copper-catalyzed allylic cyanation of 1,3-disubstituted allylic substrates. As shown in Table 2, the reaction of allylic chloride **10a** proceeded smoothly to give the allylic cyanide **12** as a single regioisomer (Table 2, entry 1); in contrast, allyl acetate **10b** exhibited lower reactivity and gave the desired product in a very low yield (Table 2, entry 2).[6] Therefore, we reinvestigated the effect of different copper catalysts for the cyanation of **10b** and found that copper(I) cyanide (CuCN) catalyzed the formation of product **12** in an acceptable 68% yield, albeit a longer reaction time (36 h) was required (Table 2, entries 6 and 7). Although the reaction of allylic acetate **11**, which is a regioisomer of **10b**, resulted in a low yield (35%), the regioselectivity was the same as that obtained in the reaction of **10b** (Table 2, entry 8).

Table 2 Cyanation of Disubstituted Allylic Substrates



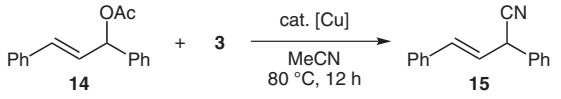
Entry	Substrate	[Cu] (mol%)	Yield (%)[a]	Ratio of **12**:**13**[b]
1[c]	**10a**	CuI (25)	67	>98:2
2	**10b**	CuI (25)	<5	>98:2
3	**10b**	CuBr (25)	33	>98:2
4	**10b**	CuCl (25)	26	>98:2
5	**10b**	CuOTf (25)	0	–
6	**10b**	CuCN (25)	38	>98:2
7[d]	**10b**	CuCN (25)	68	>98:2
8	**11**	CuCN (25)	35	>98:2

[a] Yield of isolated product **12**.
[b] Ratio was determined by ^{1}H NMR spectroscopy of the crude products.
[c] Reaction was conducted at 60 °C.
[d] The reaction time was 36 h.

Despite succeeding in realizing the allylic cyanation of 1,3-disubstituted allylic compounds **10a** and **10b**, we found that copper(I) cyanide did not catalyze the cyanation reaction of 1,3-diphenylallyl acetate (**14**) (Table 3, entry 1). Once again, we screened several copper catalysts and found that copper(I) iodide and copper(I) bromide (CuBr) provided the desired cyanated product **15** (Table 3, entries 2 and 3). Although copper(I) cyanide and copper(I) bromide exhibited similar catalytic activity with **10b** (Table 2, entries 3 and 6), these catalysts showed different activity in the cyanation of allylic acetate **14** (Table 3, entries 1 and 3). The reason for such a difference is not clear, but the steric interaction between the methyl or phenyl group of the allylic substrate and the cyanide or bromine ligand on the copper salt might be responsible for the observed results. Furthermore, we found that some copper(II) salts also catalyzed the desired cyanation reaction (Table 3, entries 4–6). In particular, copper(II) chloride ($CuCl_2$) demonstrated acceptable catalytic activity for the cyanation of **14**, and provided allylic cyanide **15** in 79% yield (Table 3, entry 6).

We further conducted two reactions to gain an insight into the reaction mechanism. The reaction of enantiomerically enriched allyl acetate (*S*)-**10b** (99% ee) gave racemic

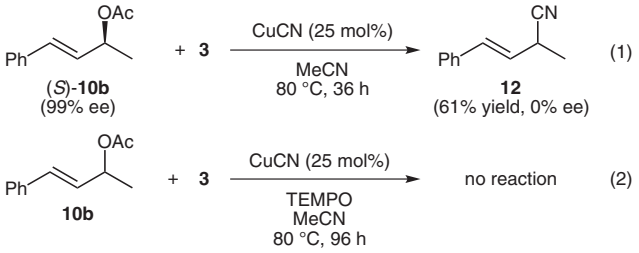
Table 3 Cyanation of 1,3-Diphenylallyl Acetate



Entry	[Cu] (mol%)	Yield (%)[a]
1	CuCN (25)	0
2	CuI (25)	59
3	CuBr (25)	70
4	$Cu(OAc)_2$ (25)	50
5	$CuBr_2$ (25)	63
6	$CuCl_2$ (25)	79

[a] Yield of isolated product.

product **12** in 61% yield under the optimized conditions (Scheme 2, eq 1). The formation of racemic product **12** suggests that the reaction proceeded through a radical pathway. To clarify this hypothesis, we ran the copper(I) cyanide catalyzed reaction of **10b** with trimethylsilyl cyanide (**3**) in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) (1 equiv with respect to **10b**), and found that the allylic cyanation did not occur (Scheme 2, eq 2). From these results, we concluded that the copper-catalyzed allylic cyanation of allylic compounds with trimethylsilyl cyanide proceeds through a radical pathway.[7]



Scheme 2 Mechanistic investigations

In summary, we have demonstrated the copper-catalyzed allylic cyanation of allylic compounds with trimethylsilyl cyanide and found that the reactions provide allylic cyanides with high regioselectivity. Although the selection of appropriate copper catalyst depends on the type of allylic substrate employed, we succeeded in realizing the cyanation of mono- and 1,3-disubstituted allylic compounds with trimethylsilyl cyanide. We further discovered that the reaction proceeds via a radical pathway.

All reactions were carried out under a nitrogen atmosphere. Allylic compounds **1c**,[8] **2**,[9] **6**,[10] **8**,[10] **10**[10] and **11**[10] were prepared according to the literature. All other allylic compounds (**1a**, **1b**, **1d** and **14**) and other chemicals/reagents, including the copper salts, were purchased from commercial sources and used without further purification. Column chromatography was performed on Kanto silica gel 60N (spherical, neutral, 63–210 μm). Melting points were recorded using a Yanaco MP-500P apparatus. IR spectra were measured on a Jasco FT/IR-4100 spectrophotometer. NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL EX-250 spectrometer (270 MHz for ^{1}H, 67 MHz for ^{13}C), a JEOL JNM ECP-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a Bruker Biospin AVANCE II 600 (600 MHz for ^{1}H and 150 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm and are referenced to an internal standard ($SiMe_4$) for ^{1}H NMR, and residual chloroform (δ 77.0) as an internal reference for ^{13}C NMR. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP instrument.

(*E*)-4-Phenylbut-3-enenitrile (4);[8b] Typical Procedure

A solution of CuI (2.7 mg, 0.014 mmol), cinnamyl chloride (**1a**) (43 mg, 0.28 mmol) and TMSCN (**3**) (56 mg, 0.56 mmol) in anhydrous MeCN (1.0 mL) was stirred at 60 °C for 12 h. The mixture was quenched with H_2O and extracted with EtOAc (3 × 2 mL). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–EtOAc, 4:1) to give allylic cyanide **4**.

Yield: 35 mg (87%); brownish solid; mp 54–55 °C.

IR (neat): 3025, 2923, 2254, 1412, 968, 737, 692 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 5 H), 6.74 (dt, *J* = 15.8, 1.8 Hz, 1 H), 6.06 (dt, *J* = 15.8, 5.6 Hz, 1 H), 3.30 (dd, *J* = 5.6, 1.8 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 135.7, 134.6, 128.8, 128.3, 126.5, 117.4, 116.8, 20.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{10}N$: 144.0813; found: 144.0820.

(*E*)-4-Cyclohexylbut-3-enenitrile (7)

Yield: 31 mg (74%); pale yellow oil.

IR (KBr): 2925, 2249, 1449, 970 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.76 (dd, *J* = 15.8, 6.9 Hz, 1 H), 5.32–5.27 (m, 1 H), 3.05 (d, *J* = 5.5 Hz, 2 H), 2.03–1.98 (m, 1 H), 1.74–1.64 (m, 4 H), 1.31–1.22 (m, 3 H), 1.19–1.06 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8, 117.8, 114.7, 40.3, 32.4, 25.9, 25.7, 20.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{16}N$: 150.1283; found: 150.1277.

(*E*)-6-Phenylhex-3-enenitrile (9)

Yield: 42 mg (86%); pale yellow oil.

IR (KBr): 3026, 2927, 2249, 1496, 1454, 969, 748 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 7.4 Hz, 2 H), 7.16 (dd, *J* = 16.6, 7.4 Hz, 3 H), 5.85–5.79 (m, 1 H), 5.34–5.28 (m, 1 H), 2.96 (d, *J* = 5.7 Hz, 2 H), 2.67 (t, *J* = 7.6 Hz, 2 H), 2.35 (q, *J* = 7.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.0, 134.9, 128.24, 128.18, 125.8, 117.8, 117.5, 35.0, 33.7, 20.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}N$: 172.1126; found: 172.1106.

(*E*)-2-Methyl-4-phenylbut-3-enenitrile (12)[2g]

A solution of CuCN (5.9 mg, 0.066 mmol), (*E*)-4-phenylbut-3-en-2-yl acetate (**10b**) (50 mg, 0.26 mmol) and TMSCN (**3**) (52 mg, 0.52 mmol) in anhydrous MeCN (1.0 mL) was stirred at 80 °C for 36 h. The mixture was quenched with H_2O and extracted with EtOAc (3 × 2 mL). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–EtOAc, 4:1) to give allylic cyanide **12**.

Yield: 28 mg (68%); colorless oil.

IR (neat): 3029, 2986, 2242, 1450, 966, 748, 694, 505 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 5 H), 6.71 (dd, *J* = 15.8, 6.1 Hz, 1 H), 6.06 (dd, *J* = 15.8, 6.1 Hz, 1 H), 3.50 (m, 1 H), 1.50 (d, *J* = 7.3 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 135.7, 132.5, 128.8, 128.3, 126.6, 124.3, 120.9, 28.4, 19.1.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{12}N$: 158.0970; found: 158.0959.

(*E*)-2,4-Diphenylbut-3-enenitrile (15)[2g]

A solution of $CuCl_2$ (6.7 mg, 0.050 mmol), (*E*)-1,3-diphenylallyl acetate (**14**) (50 mg, 0.20 mmol) and TMSCN (**3**) (39 mg, 0.40 mmol) in anhydrous MeCN (1.0 mL) was stirred at 80 °C for 12 h. The mixture was quenched with H_2O and extracted with EtOAc (3 × 2 mL). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–EtOAc, 4:1) to give allylic cyanide **15**.

Yield: 34 mg (79%); white solid; mp 70–71 °C.

IR (KBr): 3061, 3027, 2907, 2240, 1494, 1449, 972, 747, 691 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.39–7.22 (m, 10 H), 6.80 (d, *J* = 15.8 Hz, 1 H), 6.18 (dd, *J* = 15.8, 6.3 Hz, 1 H), 4.67 (dd, *J* = 6.3, 1.0 Hz, 1 H).

^{13}C NMR (67 MHz, $CDCl_3$): δ = 135.4, 134.5, 133.3, 129.2, 128.7, 128.4, 127.5, 126.7, 123.3, 118.7, 40.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{14}N$: 220.1126; found: 220.1133.

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Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000084.

References

(1) (a) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, **2010**, 967–1014. (b) Tsuji, J. *Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis*; John Wiley & Sons: Chichester, **2000**, 109–168. (c) Lu, Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258.

(2) (a) Reetz, M. T.; Chatziiosifidis, I.; Künzer, H.; Müller-Starke, H. *Tetrahedron* **1983**, *39*, 961. (b) Miyake, H.; Yamamura, K. *Tetrahedron Lett.* **1986**, *27*, 3025. (c) Murakami, M.; Kato, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1167. (d) Hayashi, Y.; Mukaiyama, T. *Chem. Lett.* **1987**, 1811. (e) Tsuji, Y.; Taniguchi, M.; Yasuda, T.; Kawamura, T.; Obora, Y. *Org. Lett.* **2000**, *2*, 2635. (f) Singh, V.; Pathak, R.; Batra, S. *Catal. Commun.* **2007**, *8*, 2048. (g) Chen, G.; Wang, Z.; Wu, J.; Ding, K. *Org. Lett.* **2008**, *10*, 4573. (h) Wang, J.; Masui, Y.; Onaka, M. *ACS Catal.* **2011**, *1*, 446. (i) He, Y.-T.; Li, L.-H.; Yang, Y.-F.; Zhou, Z.-Z.; Hus, H.-L.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2014**, *16*, 270.

(3) (a) Tsuji, Y.; Yamada, N.; Tanaka, S. *J. Org. Chem.* **1993**, *58*, 16. (b) Tsuji, Y.; Kusui, T.; Kojima, T.; Sugiura, Y.; Yamada, N.; Tanaka, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 4835.

(4) (a) Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796. (b) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. *Chem. Rev.* **2008**, *108*, 2824. (c) Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 4435. (d) Wen, Q.; Jin, J.; Zhang, L.; Luo, Y.; Lu, P.; Wang, Y. *Tetrahedron Lett.* **2014**, *55*, 1271.

(5) (a) Karlström, A. S. E.; Bäckvall, J.-E. *Chem. Eur. J.* **2001**, *7*, 1981. (b) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034. (c) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856. (d) Bartholomew, E. R.; Bertz, S. H.; Cope, S.; Murphy, M.; Ogle, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 11244. (e) Yoshikai, N.; Zhang, S.-L.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 12862. (f) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *Pure Appl. Chem.* **2008**, *80*, 1039. (g) Ohmiya, H.; Yokokawa, N.; Sawamura, M. *Org. Lett.* **2010**, *12*, 2438. (h) Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 8656. (i) Li, D.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 5672. (j) Miyake, Y.; Ota, S.-i.; Nishibayashi, Y. *Chem. Eur. J.* **2012**, *18*, 13255. (k) Li, H.; Alexakis, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 1055. (l) Nagao, K.; Yokobori, U.; Makida, Y.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 8982. (m) Shido, Y.; Yoshida, M.; Tanabe, M.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 18573. (n) Makida, Y.; Ohmiya, H.; Sawamura, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 4122. (o) Li, D.; Ohmiya, H.; Sawamura, M. *Synthesis* **2012**, *44*, 1304. (p) Makida, Y.; Takayama, Y.; Ohmiya, H.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 5350. (q) Hornillos, V.; Pérez, M.; Fañanás-Mastral, M.; Feringa, B. L. *Chem. Eur. J.* **2013**, *19*, 5432. (r) Sheng, W.; Wang, M.; Lein, M.; Jiang, L.; Wei, W.; Wang, J. *Chem. Eur. J.* **2013**, *19*, 14126.

(6) We also found that the reactions of substrates **10a** and **10b** with NaCN resulted in no reaction at 80 °C in MeCN.

(7) (a) Nishikata, T.; Noda, Y.; Fujimoto, R.; Sakashita, T. *J. Am. Chem. Soc.* **2013**, *135*, 16372. (b) Presset, M.; Oehlrich, D.; Rombouts, F.; Molander, G. A. *J. Org. Chem.* **2013**, *78*, 12837. (c) Chu, L.; Qing, F.-L. *Org. Lett.* **2012**, *14*, 2106. (d) Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410. (e) Parsons, A. T.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 9120. (f) Jakubowski, W.; Tsarevsky, N. V.; Higashihara, T.; Faust, R.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 2318. (g) Celio, H.; Scheer, K. C.; White, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 2990.

(8) (a) Lehmann, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, *51*, 8863. (b) Hoveyda, H. R.; Vézina, M. *Org. Lett.* **2005**, *7*, 2113.

(9) (a) Kawatsura, M.; Uchida, K.; Terasaki, S.; Tsuji, H.; Minakawa, M.; Itoh, T. *Org. Lett.* **2014**, *16*, 1470. (b) Kawatsura, M.; Tsuji, H.; Uchida, K.; Itoh, T. *Tetrahedron* **2011**, *67*, 7686. (c) Kawatsura, M.; Ata, F.; Hayase, S.; Itoh, T. *Chem. Commun.* **2007**, 4283.

(10) (a) Kawatsura, M.; Sato, M.; Tsuji, H.; Ata, F.; Itoh, T. *J. Org. Chem.* **2011**, *76*, 5485. (b) Kawatsura, M.; Ikeda, D.; Komatsu, Y.; Mitani, K.; Tanaka, T.; Uenishi, J. *Tetrahedron* **2007**, *63*, 8815. (c) Fuchter, M. J.; Levy, J.-N. *Org. Lett.* **2008**, *10*, 4919.

