TTMPP: An efficient organocatalyst in the ring-opening of aziridines with silylated nucleophiles†

Satoru Matsukawa* and Kumiko Tsukamoto

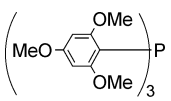
Received 27th April 2009, Accepted 27th May 2009
First published as an Advance Article on the web 16th July 2009
DOI: 10.1039/b908322g

The ring-opening of *N*-tosylaziridines with silylated nucleophiles catalyzed by tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) afforded the corresponding β-functionalized sulfonamides in excellent yield under mild reaction conditions.

Introduction

Aziridines are very useful intermediates for the synthesis of numerous nitrogen-containing, biologically active compounds.[1] Therefore, nucleophilic ring-opening of aziridines has been widely examined and developed.[2] Among these approaches, the ring-opening reaction using silylated nucleophiles, such as silyl cyanide, azide or halides, is an important approach to produce highly functionalized compounds. Therefore, the catalytic ring-opening reaction with silylated nucleophiles using Lewis acids[3] and fluoride ion[4] has been developed to realize high yields and selectivities. However, when compared to other silylated nucleophiles, examples of catalytic ring-opening of aziridines with silyl cyanide remain scarce, although the resulting β-amino nitriles are easily converted to 1,3-diamines and β-amino acids.[5] Recently, Lewis base-catalyzed reactions have also been reported. Komatsu reported that *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) acts as a Lewis base catalyst in this ring-opening reaction with various silylated nucleophiles.[6] However, in the reaction with silylcyanide, the presence of toxic KCN was required for high yields. Furthermore, catalyst loading is high and reactions usually needed a long time for completion. Although DMF,[7a] *N*-heterocyclic carbenes[7b] and DMSO[7c] also act as good promoters or catalysts, examples of them are limited in reactions with reactive silylated nucleophiles. In search of a broadly applicable reaction, we planned to use a highly basic phosphine, tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP),[8] as a Lewis base catalyst.

Tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) is known to be a highly basic phosphine owing to its methoxy substitutents. Based on this property, some unique catalytic reactions have been reported.[9] We have also reported that TTMPP acts as a good Lewis base catalyst in the reaction with silylated nucleophiles *via* O–Si and C–Si bond activation.[10] In an effort to apply this phosphine to other useful reactions, we examined the ring-opening of aziridines with trimethylsilyl cyanide[11] and other silylated nucleophiles.

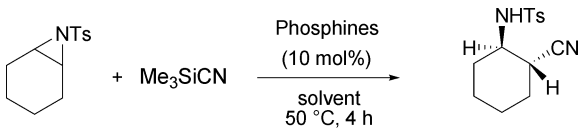


TTMPP

Department of Science Education, Faculty of Education, Ibaraki University, Ibaraki, 310-8512, Japan. E-mail: smatsuka@mx.ibaraki.ac.jp; Fax: +81 29 228 8234

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/b908322g

Table 1 Optimization of the reaction conditions



1a 2a

Entry	Phosphine	Solvent	Yield (%)
1	TTMPP	DMF	98
2[a]	TTMPP	DMF	86
3[b]	TTMPP	DMF	50
4	TTMPP	THF	77
5[c]	TTMPP	Toluene	34
6[c]	TTMPP	MeCN	51
7	TMPP[d]	DMF	35
8	Ph_3P	DMF	30
9	$^{n}Bu_3P$	DMF	50
10	None	DMF	trace

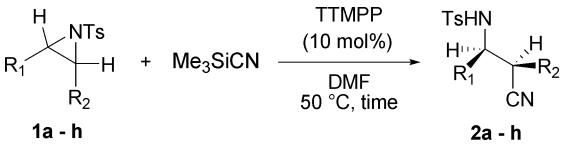
[a] 2 mol% of TTMPP was used. [b] The reaction was carried out at room temperature. [c] The reaction was carried out for 24 h. [d] Tris(4-methoxyphenyl)phosphine.

Results and discussion

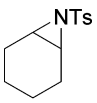
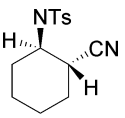
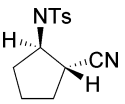
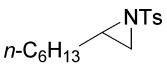
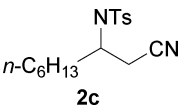
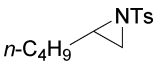
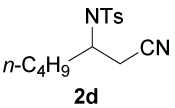
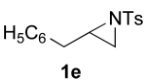
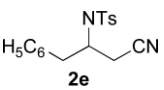
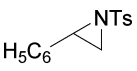
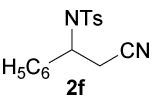
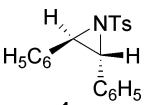
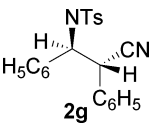
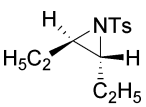
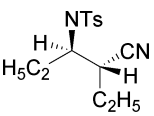
Initially, the ring-opening reaction of *N*-tosylaziridine **1a** with trimethylsilyl cyanide was examined in the presence of 10 mol% of TTMPP in DMF at 50 °C. The reaction proceeded smoothly and the desired product was obtained at 98% yield in 4 h (Table 1, entry 1). This reaction also proceeded smoothly when 2 mol% of TTMPP was used. The product was obtained in moderate to low yield when other phosphines, such as triphenylphosphine, tributylphosphine[12] and TMPP, were used instead of TTMPP (Table 1, entries 1 *vs.* 7–9). Without catalyst, only trace amounts of the products were obtained. The reactions performed in MeCN, THF and toluene were inferior to the reaction in DMF.

In order to clarify the scope of this reaction, several *N*-tosylaziridines were examined in the presence of 10 mol% TTMPP. Good results were obtained for both 2-substituted aziridines and 2,3-disubstituted aziridines. High yields of the corresponding product were obtained using bicyclic aziridine and alkyl-substituted aziridines (Table 2, entries 1–7). In the case of 2-substituted *N*-tosylaziridines, reaction also proceeded smoothly when 2 mol% TTMPP was used (Table 2, entries 5 and 7). Furthermore, complete regioselectivity with nucleophilic attack on the less substituted carbon was observed (Table 2, entries 3–8).

Table 2 TTMPP-catalyzed ring-opening of various aziridines with Me_3SiCN



1a - h **2a - h**

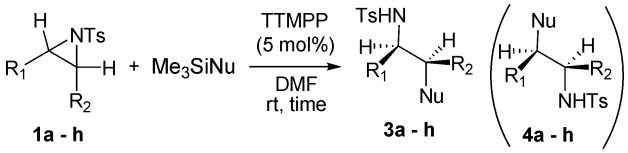
Entry	Aziridine	Product	Time	Yield (%)[a]
1	 **1a**	 **2a**	4 h	98
2	 **1b**	 **2b**	9 h	99
3	 **1c**	 **2c**	3 h	88
4	 **1d**	 **2d**	3 h 6 h	91 82
6 7[b]	 **1e**	 **2e**	1 h 4 h	92 88
8	 **1f**	 **2f**	3 h	50
9	 **1g**	 **2g**	24 h	Trace
10[c]	 **1h**	 **2h**	24 h	68

[a] Isolated yield. [b] 2 mol% of TTMPP was used. [c] The reaction was carried out at 100 °C.

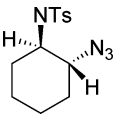
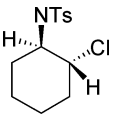
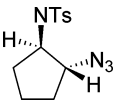
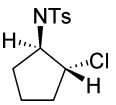
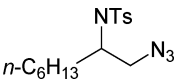
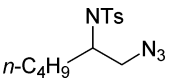
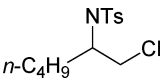
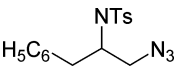
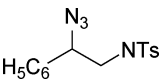
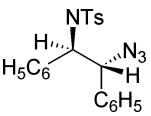
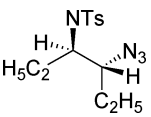
Unfortunately, in the case of phenyl-substituted aziridine **1f**, the yield was unsatisfactory owing to the occurrence of elimination of the *N*-tosyl group from the product. Moderate to low yields of the product were obtained using 2,3-diphenylaziridine, possibly due to steric inhibition.

This TTMPP-catalyzed reaction is also applicable to other silylated nucleophiles, trimethylsilyl azides and halides (Table 3). Although the reaction can proceed without catalyst at high temperatures in some cases, this TTMPP-catalyzed reaction proceeded smoothly at room temperature in shorter times with higher yields. High yields of the corresponding product were obtained using

Table 3 TTMPP-catalyzed ring-opening of aziridines with other silylated nucleophiles



1a - h **3a - h** **4a - h**

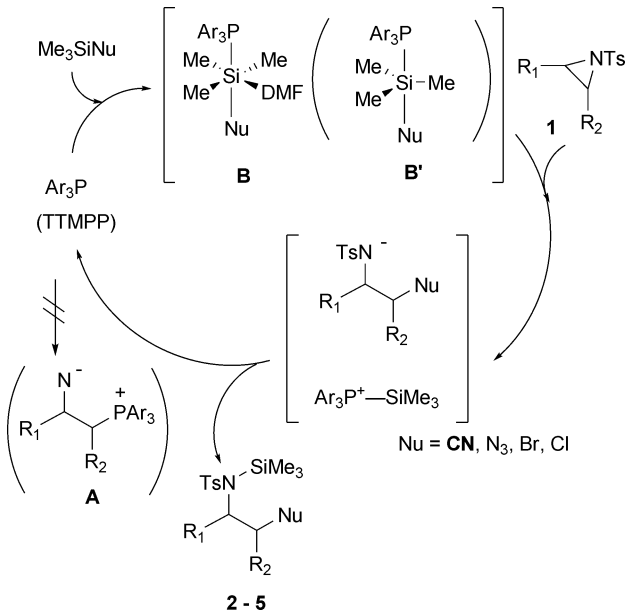
Entry	Aziridine	Nu	Product	Time	Yield (%)[a,b]
1	**1a**	N_3		3 h	98 (**3a**)
2	**1a**	Cl		3 h	88 (**3a′**)
3	**1b**	N_3		6 h	95 (**3b**)
4	**1b**	Cl		4 h	83 (**3b′**)
5	**1c**	N_3		5 h	95 (**3c**)
6	**1d**	N_3		3 h	98 (**3d**)
7	**1d**	Cl		1.5 h	96 (**3d′**)
8	**1e**	N_3		1 h	89 (**3e**)
9	**1f**	N_3		2 h	93 (**3f**, **4f**)[c]
10	**1g**	N_3		12 h	95 (**3g**)
11[d]	**1g**	N_3		12 h	Trace
12	**1h**	N_3		12 h	77 (**3h**)
13[d]	**1h**	N_3		12 h	Trace

[a] Isolated yield. [b] The product was **3a–h** unless otherwise noted. [c] Regioisomer ratio **3f** : **4f** = 21 : 79. [d] The reaction was carried out without catalyst.

both 2-substituted aziridines and 2,3-disubstituted aziridines. 2,3-Diphenylaziridine also gave good results. Almost complete regioselectivity was observed when using alkyl-substituted aziridines

as substrates. However, for phenyl-substituted aziridine **1f**, the regioselectivity was not satisfactory due to electronic effects.

A possible mechanism is illustrated in Scheme 1. Hou proposed phosphonium intermediate **A** (produced from phosphine and aziridine) as an active species in the tributylphosphine-catalyzed ring-opening reaction of aziridines with phenols, thiols and amines.[12a] However, this species could not confirmed by ^{1}H NMR analysis with the 1:1 mixture of TTMPP and aziridine **1a** in DMF-d_7. We thus propose the following alternative mechanism. First, TTMPP coordinates the silicon atom of the silylated nucleophile to form activated hexa-coordinated silicon species **B** (mainly in DMF) or penta-coordinated silicon species **B′**, with the C–Si bond being activated. The nucleophilicity of the silylated nucleophile is thus enhanced, and it readily reacts with an electrophile to produce an amino ion and silylphosphonium salt. Finally, immediate silylation occurs to give the silylated adduct with regeneration of TTMPP.



Scheme 1 Proposed mechanism.

Conclusions

In conclusion, we have demonstrated that TTMPP catalyzes ring-opening of aziridines with silylated nucleophiles. A broad range of silyl nucleophiles, including silyl cyanide, azide and halides, can be applied under mild conditions using 2–10 mol% TTMPP. This reaction provides a simple route to the synthesis of highly functionalized β-amino acids, 1,2-diamines and 1,3-diamines.

Experimental

All reactions were performed under an argon atmosphere using oven-dried glassware. Flash column chromatography was performed using silica gel Wakogel C-200. Preparative thin-layer chromatography was carried out on silica gel Wakogel B-5F. Dehydrate DMF, THF, toluene and CH_3CN were purchased from Wako Chemicals. Other commercially available reagents was used as received without further purification. The aziridines were prepared according to a literature procedure.[13]

General procedure

To a solution of TTMPP (0.05 mmol) in DMF (1 mL) was added aziridine (0.5 mmol) and silylated nucleophile (0.75 mmol) at room temperature or 50 °C. After the reaction was complete (checked by TLC), the resultant mixture was quenched with water (2 mL). The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by preparative TLC to afford the corresponding product.

***N*-(2-Cyanocyclohexyl)-4-methylbenzenesulfonamide[4] (2a).** IR (KBr, cm^{-1}) 3250, 2250, 1620; ^{1}H NMR (400 Hz, $CDCl_3$) δ 1.28 (m, 3H), 1.58 (m, 3H), 1.84 (m, 1H), 2.04 (m, 1H), 2.43 (s, 3H), 2.66 (m, 1H), 3.37 (m, 1H), 5.73 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.6, 23.2, 27.8, 30.9, 34.4, 52.5, 120.4, 127.2, 129.3, 137.0, 144.0; Anal. Found: C, 60.56; H 6.67; N 9.96. Calc. for $C_{14}H_{18}N_2O_2S$: C, 60.41; H 6.52; N 10.06%.

***N*-(2-Cyanocyclopentyl)-4-methylbenzenesulfonamide[4] (2b).** IR (KBr, cm^{-1}) 3260, 2250, 1600; ^{1}H NMR (400 Hz, $CDCl_3$) δ 1.48 (m, 1H), 1.72 (m, 2H), 1.88 (m, 1H), 1.99 (m, 1H), 2.08 (m, 1H), 2.45 (s, 3H), 2.83 (dt, J = 6.0, 8.8 Hz, 1H), 3.76 (m, 1H), 5.03 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.6, 28.8, 31.9, 35.4, 58.5, 121.0, 126.9, 129.6, 137.4, 143.9; Anal. Found: C, 58.82; H 6.07; N 10.49. Calc. for $C_{13}H_{16}N_2O_2S$: C, 59.07; H 6.10; N 10.60%.

***N*-(2-Cyanooctyl)-4-methylbenzenesulfonamide[4] (2c).** IR (neat, cm^{-1}) 3310, 2250, 1600; ^{1}H NMR (400 Hz, $CDCl_3$) δ 0.83 (t, J = 6.8 Hz, 3H), 1.07–1.30 (m, 8H), 1.52 (m, 2H), 2.44 (s, 3H), 2.54 (dd, J = 4.1, 17.2 Hz, 1H), 2.64 (dd, J = 6.4, 17.2 Hz, 1H), 3.42 (m, 1H), 4.95 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 22.6, 25.0, 25.2, 28.8, 31.4, 33.4, 50.5, 116.6, 127.0, 129.5, 137.5, 144.0; Anal. Found: C, 61.92; H 7.93; N 8.90. Calc. for $C_{16}H_{24}N_2O_2S$: C, 62.30; H 7.84; N 9.08%.

***N*-(2-Cyanobutyl)-4-methylbenzenesulfonamide[4] (2d).** IR (neat, cm^{-1}) 3270, 2240, 1600; ^{1}H NMR (400 Hz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.08–1.31 (m, 4H), 1.51 (m, 2H), 2.44 (s, 3H), 2.55 (dd, J = 4.0, 17.2 Hz, 1H), 2.65 (dd, J = 6.0, 17.2 Hz, 1H), 3.42 (m, 1H), 4.93 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 25.1, 28.8, 31.4, 33.4, 50.5, 116.6, 127.2, 129.8, 137.5, 143.9; Anal. Found: C, 60.16; H 7.28; N 9.90. Calc. for $C_{14}H_{20}N_2O_2S$: C, 59.97; H 7.19; N 9.99%.

***N*-(2-Cyano-1-benzylethyl)-4-methylbenzenesulfonamide[6] (2e).** IR (neat, cm^{-1}) 3270, 2250, 1600; ^{1}H NMR (400 Hz, $CDCl_3$) δ 2.42 (s, 3H), 2.56 (dd, J = 4.0, 16.4 Hz, 1H), 2.66 (dd, J = 6.0, 16.4 Hz, 1H), 2.77 (dd, J = 7.6, 14.0 Hz, 1H), 2.90 (dd, J = 6.8, 14.0 Hz, 1H), 3.64 (m, 1H), 4.82 (m, 1H), 6.98 (d, J = 7.6 Hz, 2H), 7.20 (m, 5H), 7.55 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 24.1, 39.8, 51.0, 116.6, 126.8, 127.2, 128.4, 128.6, 129.7, 134.2, 136.2, 143.5; Anal. Found: C, 64.68; H 5.74; N 8.80. Calc. for $C_{17}H_{18}N_2O_2S$: C, 64.94; H 5.77; N 8.91%.

***N*-(2-Cyano-1-phenylethyl)-4-methylbenzenesulfonamide[4] (2f).** IR (KBr, cm^{-1}) 3280, 2250, 1590; ^1H NMR (400 Hz, $CDCl_3$) δ 2.43 (s, 3H), 2.87 (dd, $J = 7.6$, 17.2 Hz, 1H), 2.93 (dd, $J = 6.0$, 17.2 Hz, 1H), 4.57 (m, 1H), 5.40 (br, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.28 (m, 5H), 7.65 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 26.3, 54.1, 116.6, 126.0, 127.2, 128.6, 128.9, 129.7, 136.2, 136.9, 143.5; Anal. Found: C, 64.22; H 5.45; N 9.48. Calc. for $C_{16}H_{16}N_2O_2S$: C, 63.98; H 5.37; N 9.33%.

***N*-(2-Cyano-2-ethylbutyl)-4-methylbenzenesulfonamide (2h).** Obtained as a colorless viscous oil after preparative TLC (Rf = 0.26 in Hex/AcOEt = 1/1); IR (neat, cm^{-1}) 3270, 2250, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 0.72 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 6.8$ Hz, 3H), 1.47 (m, 2H), 1.59 (m, 2H), 2.43 (s, 3H), 2.75 (td, $J = 4.8$, 6.0 Hz, 1H), 3.21 (td, $J = 4.8$, 5.2 Hz, 1H), 4.65 (br, 1H), 7.32 (d, $J = 7.2$ Hz, 2H), 7.75 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 12.1, 21.6, 23.0, 23.8, 40.9, 55.8, 119.6, 126.9, 129.8, 137.4, 143.8; Anal. Found: C, 60.08; H 7.08; N 10.06. Calc. for $C_{14}H_{20}N_2O_2S$: C, 59.97; H 7.19; N 9.99%.

***N*-(2-Azidocyclohexyl)-4-methylbenzenesulfonamide[4] (3a).** IR (KBr, cm^{-1}) 3300, 2940, 2090, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 1.20–1.30 (m, 4H), 1.60–1.70 (m, 2H), 2.02 (m, 2H), 2.43 (s, 3H), 2.93 (m, 1H), 3.09 (m, 1H), 5.09 (m, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 23.6, 23.8, 30.2, 32.4, 59.0, 63.5, 127.0, 129.5, 137.5, 143.2.

***N*-(2-Chlorocyclohexyl)-4-methylbenzenesulfonamide[4] (3a′).** IR (KBr, cm^{-1}) 3270, 2860, 1920, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 1.28 (m, 3H), 1.62 (m, 3H), 1.84 (m, 1H), 2.04 (m, 1H), 2.41 (s, 3H), 3.15 (m, 1H), 3.66 (m, 1H), 4.85 (br, 1H), 7.32 (d, $J =$ 8.0 Hz, 2H), 7.78 (d, $J = 8.0$ Hz, 2H); Anal. Found: C, 54.04; H 6.11; N 5.00. Calc. for $C_{13}H_{18}ClNO_2S$: C, 54.25; H 6.30; N 4.87%.

***N*-(2-Azidocyclopentyl)-4-methylbenzenesulfonamide[4] (3b).** IR (KBr, cm^{-1}) 3260, 2960, 2100, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 1.40 (m, 1H), 1.62 (m, 3H), 1.92 (m, 2H), 2.43 (s, 3H), 3.38 (dt, $J = 5.2$, 5.6 Hz, 1H), 3.71 (m, 1H), 5.45 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 26.9, 29.0, 30.8, 59.7, 66.9, 126.7, 129.6, 137.0, 143.5.

***N*-(2-Chlorocyclopentyl)-4-methylbenzenesulfonamide[4] (3b′).** IR (KBr, cm^{-1}) 3260, 2890, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 1.41 (m, 1H), 1.60 (m, 3H), 1.92 (m, 2H), 2.41 (s, 3H), 3.55 (m, 1H), 4.10 (m, 1H), 4.80 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H); Anal. Found: C, 52.80; H 6.05; N 5.12. Calc. for $C_{12}H_{16}ClNO_2S$: C, 52.64; H 5.89; N 5.12%.

***N*-(2-Azidooctyl)-4-methylbenzenesulfonamide[4] (3c).** IR (neat, cm^{-1}) 3280, 2940, 2100, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 0.85 (t, $J = 7.2$ Hz, 3H), 1.10–1.55 (m, 10H), 2.43 (s, 3H), 3.30 (m, 3H), 4.86 (m, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 22.5, 25.4, 28.8, 31.6, 32.6, 53.2, 55.0, 127.0, 129.6, 137.0, 143.5.

***N*-(2-Azidobutyl)-4-methylbenzenesulfonamide[4] (3d).** IR (neat, cm^{-1}) 3280, 2100, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 0.74 (t, $J = 7.0$ Hz, 3H), 1.14–1.55 (m, 6H), 2.42 (s, 3H), 3.28 (m, 3H), 5.00 (m, 1H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 21.5, 22.1, 27.5, 32.2, 53.2, 54.8, 126.9, 129.6, 137.6, 143.4.

***N*-(2-Chlorobutyl)-4-methylbenzenesulfonamide[7a] (3d′).** IR (neat, cm^{-1}) 3270, 2850, 1610; ^1H NMR (400 Hz, $CDCl_3$) δ 0.76 (t, $J = 7.2$ Hz, 3H), 1.10–1.50 (m, 6H), 2.42 (s, 3H), 3.33 (m, 3H), 5.10 (br, 1H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 2H); Anal. Found: C, 54.02; H 6.65; N 5.12. Calc. for $C_{12}H_{16}ClNO_2S$: C, 53.87; H 6.96; N 4.83%.

***N*-(2-Azido-1-benzylethyl)-4-methylbenzenesulfonamide[6] (3e).** IR (neat, cm^{-1}) 3270, 2090, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 2.42 (s, 3H), 2.72 (dd, $J = 7.0$, 11.2 Hz, 2H), 3.32 (dd, $J = 4.4$, 12.4 Hz, 1H), 3.54 (m, 1H), 5.00 (br, 1H), 6.98 (d, $J = 8.0$ Hz, 2H), 7.20 (m, 5H), 7.58 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 38.8, 53.7, 54.4, 126.8, 127.2, 128.4, 128.6, 129.0, 129.5, 136.0, 136.7, 143.3.

***N*-(2-Azido-1-phenylethyl)-4-methylbenzenesulfonamide[4] (3f).** IR (KBr, cm^{-1}) 3280, 2100, 1590; ^1H NMR (400 Hz, $CDCl_3$) δ 2.37 (s, 3H), 3.56 (d, $J = 6.0$ Hz, 1H), 4.45 (m, 1H), 5.40 (br, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.20 (m, 5H), 7.61 (d, $J = 8.4$ Hz, 2H).

***N*-(2-Azido-2-phenylethyl)-4-methylbenzenesulfonamide[4] (4f).** IR (KBr, cm^{-1}) 3280, 2100, 1590; ^1H NMR (400 Hz, $CDCl_3$) δ 2.43 (s, 3H), 3.07 (ddd, $J = 4.4$, 4.8, 9.2 Hz, 1H), 3.20 (ddd, $J =$ 2.8, 4.4, 9.2 Hz, 1H), 4.59 (dd, $J = 5.6$, 8.8 Hz, 1H), 4.95 (br, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.20 (m, 5H), 7.73 (d, $J = 8.4$ Hz, 2H).

***N*-(2-Azido-1,2-diphenylethyl)-4-methylbenzenesulfonamide[14] (3g).** IR (KBr, cm^{-1}) 3270, 2960, 2100, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 2.40 (s, 3H), 4.61 (t, $J = 6.8$ Hz, 1H), 4.80 (d, $J = 6.0$ Hz, 1H), 5.69 (d, $J = 6.8$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.19 (m, 5H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 62.3, 70.1, 126.8, 127.3, 127.4, 127.7, 128.0,128.4, 129.1, 135.4, 136.9, 137.0, 142.9; HRMS: for $C_{21}H_{20}NO_2S$ $(M - N_3)^+$ calcd 350.1215, found 350.1212.

***N*-(2-Azido-2-ethylbutyl)-4-methylbenzenesulfonamide (3h).** Obtained as a white solid after preparative TLC (Rf = 0.67 in Hex/AcOEt = 1/1); mp 78–79 °C; IR (KBr, cm^{-1}) 3240, 2090, 1600; ^1H NMR (400 Hz, $CDCl_3$) δ 0.73 (t $J = 7.6$ Hz, 3H), 0.92 (t $J = 7.4$ Hz, 3H), 1.30(m, 2H), 1.53 (m, 2H), 2.43 (s, 3H), 3.17–3.27 (m, 2H), 4.83 (d, $J = 8.8$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.2, 11.0, 21.5, 21.8, 24.4, 58.1, 67.8, 126.9, 129.3, 137.9, 143.4; HRMS: for $C_{13}H_{20}NO_2S$ $(M - N_3)^+$ calcd 254.1215, found 254.1220.

References

1 (*a*) J. B. Sweeny, *Chem. Soc. Rev.*, 2002, **31**, 247; (*b*) A. Padwa, W. H. Pearson, B. N. Lian, S. C. Bergmeier, in *Comprehensive Heterocyclic Chemistry II*, ed. A. R. Katritzky, C. W. Rees and E. F. V. Scriven, Pergamon, New York, 1996, vol. 1a; (*c*) D. Tanner, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 599; (*d*) A. Padwa, A. D. Woolhouse, in *Comprehensive Heterocyclic Chemistry*, ed. W. Lwowski, Pergamon, Oxford, 1984, vol. 7.

2 For recent reviews, see: (*a*) X. E. Hu, *Tetrahedron*, 2004, **60**, 2701; (*b*) I. D. G. Watson, L. Yu and A. K. Yudin, *Acc. Chem. Res.*, 2006, **39**, 194; (*c*) *Aziridines and Epoxides in Organic Synthesis*, ed. A. K. Yudin, Wiley-VCH, Weinheim, 2006; (*d*) G. S. Singh, M. D'hooghe and N. D. Kimpe, *Chem. Rev.*, 2007, **107**, 2080.

3 (*a*) S. Matsubara, T. Kodama and K. Utimoto, *Tetrahedron Lett.*, 1990, **31**, 6379; (*b*) H. M. I. Osborn and J. B. Sweeney, *Synlett*, 1994, 145; (*c*) W.-H. Leung, M. T. Yu, M. C. Wu and L.-L. Yeung, *Tetrahedron Lett.*, 1996, **37**, 891; (*d*) D. Ferraris, W. J. Drury, III, C. Cox and J. Lectka, *J. Org. Chem.*, 1998, **63**, 4568; (*e*) Z. Li, M. Fernandez and E. N.

Jacobsen, *Org. Lett.*, 1999, **1**, 1611; (*f*) M. Chandrasekhar, G. Sekar and V. K. Singh, *Tetrahedron Lett.*, 2000, **41**, 4677; (*g*) S.-H. Shin, E. Y. Han, C. S. Park, W. K. Lee and H.-J. Ha, *Tetrahedron: Asymmetry*, 2000, **11**, 3293; (*h*) M. A. Reddy, L. R. Reddy, N. Bhanumathi and K. R. Rao, *Chem. Lett.*, 2001, 246; (*i*) M. Chandrasekhar, G. Sekar and V. K. Singh, *Tetrahedron Lett.*, 2000, **41**, 10079; (*j*) J. S. Yadav, B. V. S. Reddy, G. M. Kumar; and V. S. R. Murhty, *Synth. Commun.*, 2002, **32**, 1797; (*k*) T. Mita, I. Fujimori, R. Wada, J. Wen, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2005, **127**, 11252; (*l*) Y. Fukuta, T. Mita, N. Fukuda, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2006, **128**, 6312; (*m*) I. Fujimori, T. Mita, K. Maki, M. Shiro, A. Sato, S. Furusho, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2006, **128**, 16438; (*n*) E. B. Rowland, G. B. Rowland, E. Rivera-Otero and J. C. Antilla, *J. Am. Chem. Soc.*, 2007, **129**, 12084; (*o*) R. Yu, Y. Yamashita and S. Kobayashi, *Adv. Synth. Catal.*, 2009, **351**, 147; (*p*) B. Wu, J. C. Gallucci, J. R. Parquette and T. V. RajanBabu, *Angew. Chem., Int. Ed.*, 2009, **48**, 1126.

4 J. Wu, X.-L. Hou and L.-X. Dai, *J. Org. Chem.*, 2000, **65**, 1344.

5 (*a*) Cyanomethylation of imines is an alternative route to synthesize β-amino nitriles, see: P. Sun and Y. Zhang, *Synth. Commun.*, 1997, **27**, 3175; (*b*) N. Kumagai, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2004, **126**, 13632; (*c*) Y. Kawano, H. Fujisawa and T. Mukaiyama, *Chem. Lett.*, 2005, **34**, 1134; (*d*) N. Kumagai, S. Matsunaga and M. Shibasaki, *Tetrahedron*, 2007, **63**, 8598; (*e*) T. Mukaiyama and M. Michida, *Chem. Lett.*, 2007, 1245.

6 S. Minakata, Y. Okada, Y. Oderaotoshi and M. Komatsu, *Org. Lett.*, 2005, **7**, 3509.

7 (*a*) J. Wu, X. Sun and H.-G. Xia, *Eur. J. Org. Chem.*, 2005, 4769; (*b*) J. Wu, X. Sun, Y. Shengqing and W. Sun, *Tetrahedron Lett.*, 2006, **47**, 4813; (*c*) J. Wu, X. Sun and W. Sun, *Org. Biomol. Chem.*, 2006, **4**, 4231.

8 M. Wada and S. Higashizaki, *J. Chem. Soc., Chem. Commun.*, 1984, 482.

9 (*a*) S. M. Maddock and M. G. Finn, *Organometallics*, 2000, **19**, 2684; (*b*) K. Yoshimoto, H. Kawabata, N. Nakamichi and M. Hayashi, *Chem. Lett.*, 2001, 934; (*c*) H. Kawabata and M. Hayashi, *Tetrahedron Lett.*, 2002, **43**, 5645; (*d*) S. Röper, R. Wartchow and M. R. Hoffmann, *Org. Lett.*, 2002, **4**, 3179; (*e*) S. Chuprakov, D. A. Malyshev, A. Trofimov and V. Gevorgyan, *J. Am. Chem. Soc.*, 2007, **129**, 14868; (*f*) J. A. Weeden and J. D. Chisholm, *Tetrahedron Lett.*, 2006, **47**, 9313; (*g*) A. Trofimov, A. and V. Gevorgyan, *Org. Lett.*, 2009, **11**, 253.

10 (*a*) S. Matsukawa, N. Okano and T. Imamoto, *Tetrahedron Lett.*, 2000, **41**, 103; (*b*) S. Matsukawa and K. Obu, *Chem. Lett.*, 2004, **33**, 1626; (*c*) S. Matsukawa and E. Kitazaki, *Tetrahedron Lett.*, 2008, **49**, 2982; (*d*) S. Matsukawa and M. Saijo, *Tetrahedron Lett.*, 2008, **49**, 4655.

11 For examples of phosphine- or phosphonium salt-catalyzed silylcyanation of carbonyl compounds with TMSCN, see: (*a*) S. Kobayashi, Y. Tsuchiya and T. Mukaiyama, *Chem. Lett.*, 1991, 537; (*b*) R. Cordoba and J. Plumet, *Tetrahedron Lett.*, 2003, **44**, 6157; (*c*) X. Wang and S.-K. Tian, *Tetrahedron Lett.*, 2007, **48**, 6010.

12 For examples of tributylphosphine-catalyzed ring-opening reaction of aziridines, see: (*a*) X.-L. Hou, R.-H. Fan and L.-X. Dai, *J. Org. Chem.*, 2002, **67**, 5295; (*b*) R.-H. Fan and X.-L. Hou, *J. Org. Chem.*, 2003, **68**, 726.

13 V. V. Thakur and A. Sudalai, *Tetrahedron Lett.*, 2003, **44**, 989.

14 A. Hayes, G. Clarkson and M. Wills, *Tetrahedron: Asymmetry*, 2004, **15**, 2079.

