Synthesis of 1,3-diaryl-3-aminopropynes *via* the dethiolation of thioamides promoted by the samarium/samarium diiodide mixed reagent

Weimin Zhu[a], Weixing Qian[a] and Yongmin Zhang[a,b]*

[a]*Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou, Zhejiang, 310028, P.R. China*

[b]*State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, P. R. China*

Promoted by the samarium/samarium diiodide mixed reagent, the C–H insertion of phenyl acetylene via the dethiolation of N,N-disubstituted aromatic thioamides was successfully performed to afford 1,3-diaryl-3-aminopropynes in good yields.

Keywords: samarium, C–H insertion, dethiolation, thioamides, 1,3-diaryl-3-aminopropynes

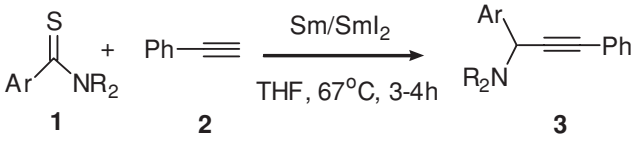
Samarium diiodide (SmI_2) has been recognised as a versatile reagent in synthetic organic chemistry since its introduction by Kagan's group and the reactivities of samarium reagents have been exploited in a variety of ways.[1] Our group has recently found that the samarium/samarium diiodide mixed reagent can promote the intermolecular reductive cyclisation of ketones and chalcones to afford dihydrofurans,[2] and the cross-coupling of arylamides and diarylketones to provide enamines.[3]

These results inspired us to investigate the application of the Sm/SmI_2 mixed reagent to other functional groups. We have recently investigated the reactivities of thioamides with samarium reagents. Here we report our results, *i.e.*, the synthesis of 1,3-diaryl-3-aminopropynes *via* the dethiolation of *N,N*-disubstituted aromatic thioamides promoted by Sm/SmI_2.

1,3-Disubstituted-3-aminopropynes can also be produced from terminal acetylenes by other methods.[4] During these methods, however, terminal acetylenes must usually be transferred to their metal reagents, *e.g.*, the alkynyl lithium or the alkynyl magnesium halides, which then add to the C=N double bond. Obviously, these methods usually suffer from severe or complex operations.

Ogawa also gave one example of 1,3-disubstituted-3-aminopropyne (1,3-diphenyl-3-piperidinopropyne) *via* the deoxygenation of aromatic amides promoted by the Sm/SmI_2 mixed reagent.[5] Aromatic amides, however, are usually prepared from aromatic carboxylic acids in complex steps. Compared with amides, thioamides can be readily synthesised directly from aldehaydes, sulfur and amines.[6]

In our experiment, by contrast, promoted by the samarium/samarium diiodide mixed reagent, utilising easy available aromatic thioamides **1** and phenyl acetylene **2**, 1,3-diaryl-3-aminopropynes **3** can be easily synthesised in good yields (Scheme 1).

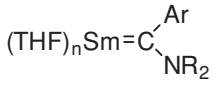


Scheme 1

Table 1 summarises our experimental results. A variety of *N,N*-disubstituted aromatic thioamides **1** was subjected to the reaction which proceeds smoothly and efficiently. Besides phenyl acetylene, we also tried other aliphatic terminal acetylenes such as 1-hexyne, but no desired products were obtained.

The detailed mechanism of the above reaction has not been clarified enough. On the deoxygenative coupling of amides promoted by the Sm/SmI_2 mixed reagent, Ogawa thought that an α-aminocarbene species might be involved.[7] However, according to other documents,[8-11] we think that the more reasonable intermediate may be a Sm α-aminocarbenoid **4**, which is generated *via* the dethiolation of thioamides promoted by Sm/SmI_2 and then inserts the terminal C–H bond of phenyl acetylene.

In summary, an efficient method to synthesise 1,3-diaryl-3-aminopropynes has been developed *via* the dethiolation of aromatic thioamides promoted by Sm/SmI_2. The remarkable features of this procedure are easy available starting materials,



4

Table 1 Synthesis of 1,3-diaryl-3-aminopropynes *via* the dethiolation of *N,N*-disubstituted aromatic thioamides promoted by Sm/SmI_2[a, b]

Entry	Ar,	NR_2 in thioamides **1**	Yield of **3**/%[c]
1	4-$MeOC_6H_4$,	morpholino (**1a**)	83 (**3a**)
2	C_6H_5,	morpholino (**1b**)	80 (**3b**)
3	4-$MeOC_6H_4$,	piperidino (**1c**)	85 (**3c**)
4	4-MeC_6H_4,	morpholino (**1d**)	78 (**3d**)
5	4-$MeOC_6H_4$	pyrrolidinyl (**1e**)	87 (**3e**)
6	4-ClC_6H_4,	morpholino (**1f**)	73 (**3f**)
7	Benzo[1,3]dioxol-5-yl,	piperidino (**1g**)	90 (**3g**)
8	Benzo[1,3]dioxol-5-yl,	pyrrolidinyl (**1h**)	90 (**3h**)
9	Benzo[1,3]dioxol-5-yl,	morpholino (**1i**)	82 (**3i**)
10	4-MeC_6H_4,	piperidino (**1j**)	85 (**3j**)
11	Benzo[1,3]dioxol-5-yl,	NEt_2 (**1k**)	95 (**3k**)
12	4-$MeOC_6H_4$	NEt_2 (**1l**)	92 (**3l**)

[a]Thioamide (1mmol), phenyl acetylene (9.1mmol, 1ml), Sm (1.1mmol), SmI_2 (2.2mmol), THF (5ml), 67°C, 3–4h. [b]All products were identified with IR, ^1H NMR, ^{13}C NMR, MS, and EA. [c]Isolated yield in terms of the thioamide.

* Correspondent. E-mail: yongminzhang@zju.edu.cn

mild conditions, simple operations and high yields. All these data indicate that it may be a competitive way to prepare 1, 3-diaryl-3-aminopropynes.

Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Metallic samarium (99.9%) and all the other solvents were purchased from commercial sources, without further purification before use. The thioamides were synthesised by the literature method.[6] IR spectra were determined on a Bruker Vector-22 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 spectrometer as $CDCl_3$ solutions using TMS as the internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. Mass spectra were recorded on a HP 5989B MS spectrometer (EI) or Bruker esquire 3000 plus (ESI). Elemental analyses were performed on a Carlo Erba EA-1110 instrument.

Typical procedure for the synthesis of 1,3-diaryl-3-aminopropynes promoted by Sm/SmI$_2$: Under a nitrogen atmosphere, a solution of thioamide **1** (1mmol) and phenyl acetylene **2** (9.1mmol, 1ml) was added to a solution of SmI_2 (2.2mmol) and Sm (1mmol) in THF (5ml) at room temperature. The mixture was stirred at 67°C for 3–4h (The reaction was monitored by TLC analysis). After the reaction was complete, saturated $NaHCO_3$ (30ml) was added to the reaction mixture, and the products were extracted with diethyl ether (30ml × 3). The combined extract was dried over anhydrous Na_2SO_4, and the solvent was removed in a vacuum. Using cyclohexane/EtOAc (4:1) as an eluent, the residue was purified by column chromatography to afford the desired product.

1-Phenyl-3-(4-methoxyphenyl)-3-morpholinopropyne (**3a**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2956, 2853, 1609, 1510, 1450, 1321, 1303, 1281, 1249, 1173, 1115, 1071, 1034, 1001, 971, 926, 849, 757, 692. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.53 (d, 2H, *J* = 8.4Hz, Ar–H), 7.51–7.49 (m, 2H, Ar–H), 7.33–7.31 (m, 3H, Ar–H), 6.89 (dd, 2H, *J* = 1.6, 8.4Hz, Ar–H), 4.72 (s, 1H, –CH_2–), 3.80 (s, 3H, CH_3–O–), 3.72 (dd, 4H, *J* = 4.8, 11.6Hz, –CH_2–O–CH_2–), 2.61 (dd, 4H, *J* = 4.8, 11.6Hz, –CH_2–N–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 159.3, 131.8, 129.9, 129.7, 128.3, 128.2, 123.1, 113.6, 88.3, 85.5, 67.2, 61.5, 55.3, 49.9. MS (EI), *m/z* (%): 307 (M$^+$, 6.03), 221 (100.00). Anal. calcd. for $C_{20}H_{21}NO_2$: C 78.2, H 6.9, N 4.6. Found: C 78.4, H 6.7, N 4.6%.

1,3-Diphenyl-3-morpholinopropyne (**3b**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 3060, 3029, 2957, 2853, 2822, 1683, 1598, 1491, 1450, 1392, 1322, 1286, 1247, 1207, 1177, 1157, 1116, 1072, 1029, 1003, 970, 936, 916, 866, 833, 799, 757, 726, 697 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.63 (d, 2H, *J* = 7.6Hz, Ar–H), 7.52–7.50 (m, 2H, Ar–H), 7.38–7.29 (m, 6H, Ar–H), 4.78 (s, 1H, –CH–), 3.72 (dd, 4H, *J* = 4.8, 11.2Hz, –CH_2–O–CH_2–), 2.63 (brs, 4H, –CH_2–N–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 137.9, 131.8, 128.6, 128.3, 128.2, 127.8, 123.0, 88.5, 85.1, 67.2, 62.1, 49.9. MS (EI), *m/z* (%): 277 (M$^+$, 12.06), 191 (100.00). Anal. calcd. for $C_{19}H_{19}NO$: C 82.3, H 6.9, N 5.1. Found: C 82.4, H 6.9, N 5.3%.

1-Phenyl-3-(4-methoxyphenyl)-3-piperidinopropyne (**3c**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 3059,3028,2932, 2853, 1678, 1605, 1510, 1492, 1447, 1301, 1249, 1174, 1114, 1034, 993, 914, 832, 756, 695 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.53 (d, 2H, *J* = 8.4Hz, Ar–H), 7.51–7.49 (m, 2H, Ar–H), 7.34–7.30 (m, 3H, Ar–H), 6.89 (d, 2H, *J* = 8.4Hz, Ar–H), 4.75 (s, 1H, –CH–), 3.80 (s, 3H, CH_3–O–), 2.55 (brs, 4H, –CH_2–N–CH_2–), 1.61–1.56 (m, 4H, –CH_2–), 1.45–1.42 (m, 2H, –CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 159.0, 131.8, 130.6, 129.7, 128.2, 128.0, 123.4, 113.4, 87.7, 86.4, 61.8, 55.3, 50.6, 26.2, 24.5. MS (ESI), *m/z*: 327.8 (M$^+$ + Na). Anal. calcd. for $C_{21}H_{23}NO$: C 82.6, H 7.6, N 4.6. Found: C 82.8, H 7.5, N 4.8%.

1-Phenyl-3-(4-methylphenyl)-3-morpholinopropyne (**3d**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 3026, 2955, 2922, 2854, 1679, 1603, 1511, 1491, 1449, 1320, 1286, 1178, 1116, 1071, 1027, 1002, 928, 867, 821, 757, 694 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.51–7.49 (m, 4H, Ar–H), 7.32–7.31 (m, 3H, Ar–H), 7.17 (d, 2H, *J* = 8.0Hz, Ar–H), 4.74 (s, 1H, –CH–), 3.71 (dd, 4H, *J* = 4.8, 11.6Hz, –CH_2–O–CH_2–), 2.62 (dd, 4H, *J* = 4.8, 11.6Hz, –CH_2–N–CH_2–), 2.35 (s, 3H, Ar–CH_3). ^{13}C NMR (100MHz, $CDCl_3$) δ: 137.5, 134.8, 131.8, 128.9, 128.5, 128.3, 128.2, 123.1, 88.3, 85.4, 67.2, 61.8, 49.9, 21.1. MS (ESI), *m/z*: 313.9 (M$^+$ + Na). Anal. calcd. for $C_{20}H_{21}NO$: C 82.4, H 7.3, N 4.8. Found: C 82.6, H 7.1, N 5.0%.

1-Phenyl-3-(4-methoxyphenyl)-3-pyrrolidinylpropyne (**3e**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2962, 2835, 1609, 1510, 1490, 1460, 1442, 1302, 1249, 1172, 1109, 1070, 1034, 834, 757, 692 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.52 (d, 2H, *J* = 8.8Hz, Ar–H), 7.49–7.46 (m, 2H, Ar–H), 7.30–7.29 (m, 3H, Ar–H), 6.88 (d, 2H, *J* = 8.8Hz, Ar–H), 4.85 (s, 1H, –CH–), 3.79 (s, 3H, CH_3–O–), 2.70 (brs, 4H, –CH_2–N–CH_2–), 1.81–1.78 (m, 4H, –CH_2–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 159.1, 131.8, 131.6, 129.4, 128.3, 128.1, 123.3, 113.6, 86.9, 86.8, 58.5, 55.3, 50.2, 23.5. MS (ESI), *m/z*: 313.9 (M$^+$ + Na). Anal. calcd. for $C_{20}H_{21}NO$: C 82.4, H 7.3, N 4.8. Found: C 82.5, H 7.4, N 5.0%.

1-Phenyl-3-(4-chlorophenyl)-3-morpholinopropyne (**3f**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 3058, 2957, 2922, 2854, 2824, 1683, 1596, 1489, 1450, 1401, 1319, 1285, 1116, 1093, 1004, 972, 912, 850, 783, 757, 733, 692 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.58 (d, 2H, *J* = 8.4Hz, Ar–H), 7.51–7.50 (m, 2H, Ar–H), 7.35–7.33 (m, 5H, Ar–H), 4.76 (s, 1H, –CH–), 3.72 (dd, 4H, *J* = 4.4, 11.2Hz, –CH_2–O–CH_2–), 2.61 (dd, 4H, *J* = 4.4, 11.2Hz, –CH_2–N–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 136.6, 133.7, 131.9, 130.0, 128.5,128.4, 122.8, 89.0, 84.5, 67.2, 61.5, 49.9. MS (ESI), *m/z*: 333.8 (M$^+$ + Na). Anal. calcd. for $C_{19}H_{18}ClNO$: C 73.2, H 5.8, N 4.5. Found: C 73.4, H 5.8, N 4.7%.

1-Phenyl-3-(4-benzo[1,3]dioxol-5-yl)-3-piperidinopropyne (**3g**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2933, 2853, 2803, 1601, 1487, 1441, 1361, 1317, 1247, 1155, 1093, 1040, 991, 936, 908, 869, 814, 756, 732, 692 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.51–7.49 (m, 2H, Ar–H), 7.32–7.31 (m, 3H, Ar–H), 7.14 (s, 1H, Ar–H), 7.11 (d, 1H, *J* = 8.0Hz, Ar–H), 6.78 (d, 1H, *J* = 8.0Hz, Ar–H), 5.95 (s, 2H, –O–CH_2–O–), 4.69 (s, 1H, –CH–), 2.56–2.53 (m, 4H, –CH_2–N–CH_2–), 1.61–1.57 (m, 4H, –CH_2–), 1.45–1.42 (m, 2H, –CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 147.6, 147.0, 132.8, 131.9, 128.4, 128.2, 123.4, 121.9, 109.1, 107.7, 101.1, 87.9, 86.2, 62.2, 50.7, 26.3, 24.6. MS (ESI), *m/z*: 341.9 (M$^+$ + Na). Anal. calcd. for $C_{21}H_{21}NO_2$: C 79.0, H 6.6, N 4.4. Found: C 79.2, H 6.5, N 4.6%.

1-Phenyl-3-(4-benzo[1,3]dioxol-5-yl)-3-pyrrolidinylpropyne (**3h**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2964, 2809, 1601, 1487, 1441, 1350, 1248, 1105, 1039, 937, 871, 814, 786, 757, 692 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.49–7.46 (m, 2H, Ar–H), 7.31–7.30 (m, 3H, Ar–H), 7.13 (s, 1H, Ar–H), 7.06 (d, 1H, *J* = 8.0Hz, Ar–H), 6.78 (d, 1H, *J* = 8.0Hz, Ar–H), 5.95 (s, 2H, –O–CH_2–O–), 4.77 (s, 1H, –CH–), 2.67 (brs, 4H, –CH_2–N–CH_2–), 1.79 (brs, 4H, –CH_2–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 147.7, 147.1, 133.6, 131.9, 128.4, 128.2, 123.3, 121.6, 108.9, 107.9, 101.1, 87.0, 86.8, 58.9, 50.3, 23.6. MS (ESI), *m/z*: 327.9 (M$^+$ + Na). Anal. calcd. for $C_{20}H_{19}NO_2$: C 78.7, H 6.3, N 4.6. Found: C 78.7, H 6.2, N 4.7%.

1-Phenyl-3-(4-benzo[1,3]dioxol-5-yl)-3-morpholinopropyne (**3i**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2916, 2854, 1687, 1601, 1487, 1442, 1359, 1319, 1283, 1249, 1116, 1071, 1039, 1002, 935, 912, 868, 815, 782, 757, 733, 692 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.50–7.49 (m, 2H, Ar–H), 7.33–7.32 (m, 3H, Ar–H), 7.14 (s, 1H, Ar–H), 7.11 (d, 1H, *J* = 8.4Hz, Ar–H), 6.79 (d, 1H, *J* = 8.4Hz, Ar–H), 5.96 (s, 2H, –O–CH_2–O–), 4.68 (s, 1H, –CH–), 3.76–3.65 (m, 4H, –CH_2–O–CH_2–), 2.65–2.54 (m, 4H, –CH_2–N–CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 147.8, 147.3, 132.0, 131.9, 128.4, 123.0, 122.0, 109.0, 107.8, 101.2, 88.5, 85.2, 67.3, 61.9, 49.9. MS (ESI), *m/z*: 343.9 (M$^+$ + Na). Anal. calcd. for $C_{20}H_{19}NO_3$: C 74.5, H 6.0, N 4.4. Found: C 74.9, H 5.8, N 4.5%.

1-Phenyl-3-(4-methylphenyl)-3-piperidinopropyne (**3j**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 3026, 2929, 2854, 2804, 2749, 1599, 1510, 1490, 1447, 1380, 1319, 1271, 1203, 1175, 1154, 1092, 1030, 990, 968, 914, 847, 821, 756, 691 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.51–7.49 (m, 4H, Ar–H), 7.32–7.31 (m, 3H, Ar–H), 7.16 (d, 2H, *J* = 8.0Hz, Ar–H), 4.75 (s, 1H, –CH–), 2.56–2.54 (m, 4H, –CH_2–N–CH_2–), 2.35 (s, 3H, Ar–CH_3), 1.62–1.55 (m, 4H, –CH_2–), 1.45–1.42 (m, 2H, –CH_2–). ^{13}C NMR (100MHz, $CDCl_3$) δ: 137.2, 135.7, 131.9, 128.8, 128.6, 128.3, 128.1, 123.6, 87.7, 86.5, 62.3, 50.8, 26.3, 24.6, 21.2. MS (ESI), *m/z*: 311.8 (M$^+$ + Na). Anal. calcd. for $C_{21}H_{23}N$: C 87.2, H 8.0, N 4.8. Found: C 87.3, H 7.9, N 5.0%.

1-Phenyl-3-(4-benzo[1,3]dioxol-5-yl)-3-(N,N-diethylamino) propyne (**3k**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2969, 2930, 2821, 1692, 1600, 1487, 1440, 1382, 1237, 1194, 1119, 1094, 1041, 988, 937, 869, 810, 758, 693 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ_H: 7.49–7.48 (m, 2H, Ar–H), 7.32–7.31 (m, 3H, Ar–H), 7.18–7.16 (m, 2H, Ar–H), 6.78 (d, 1H, *J* = 8.0Hz, Ar–H), 5.95 (s, 2H, –O–CH_2–O–), 4.94 (s, 1H, –CH–), 2.68–2.59 (m, 2H, –CH_2–N–), 2.57–2.48 (m, 2H, –CH_2–N–), 1.07 (t, 6H, *J* = 7.2Hz, CH_3-). ^{13}C NMR (100MHz, $CDCl_3$) δ: 147.6, 146.8, 134.1, 131.9, 128.4, 128.1, 123.5, 121.6, 109.0, 107.7, 101.1, 87.5, 86.3, 56.9, 44.6, 13.7. MS (ESI), *m/z*: 329.9 (M$^+$ + Na). Anal. calcd. for $C_{20}H_{21}NO_2$: C 78.2, H 6.9, N 4.6. Found: C 78.4, H 6.7, N 4.7%.

1-Phenyl-3-(4-methoxyphenyl)-3-(N,N-diethylamino)propyne (**3l**): Yellow oil. IR ν_{max}(KBr)/cm^{-1}: 2968, 2932, 2833, 1609, 1510, 1463, 1381, 1300, 1248, 1173, 1113, 1037, 967, 833, 803, 757,

692 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ_H: 7.58 (d, 2H, J = 8.4Hz, Ar–H), 7.51–7.49 (m, 2H, Ar–H), 7.32–7.31 (m, 3H, Ar–H), 6.89 (d, 2H, J = 8.4Hz, Ar–H), 4.99 (s, 1H, –CH–), 3.81 (s, 3H, CH_3–O–), 2.68–2.59 (m, 2H, –CH_2–N–), 2.57–2.49 (m, 2H, –CH_2–N–), 1.07 (t, 6H, J = 7.2Hz, CH_3-). ^{13}C NMR (100MHz, $CDCl_3$) δ: 159.0, 132.0, 131.9, 129.6, 128.4, 128.1, 123.6, 113.5, 87.4, 86.6, 56.6, 55.4, 44.6, 13.7. MS (ESI), *m/z*: 315.9 (M^+ + Na). Anal. calcd. for $C_{20}H_{23}NO$: C 81.9, H 7.9, N 4.8. Found: C 81.9, H 7.9, N 4.6.

We are grateful to the National Natural Science Foundation of China (Project No. 20072033) and Specialised Research Fund for the Doctoral Program of Higher Education of China.

Received 12 January 2005; accepted 20 March 2005
Paper 05/3002

References

1 For reviews of samarium diiodide, see: (a) D.P. Curran, C.P. Jasperse and M.J. Totleben, *Synlett*, 1992, 943; (b) G.A. Molander, *Chem. Rev*., 1992, **92**, 29; (c) G.A. Molander and C.R. Harris, *Chem. Rev*., 1996, **96**, 29; (d) G.A Molander and C.R. Harris, *Tetrahedron*, 1998, **54**, 3321; (e) G.A. Molander, *Acc. Chem. Res*., 1998, **31**, 603; (f) A. Krief and A.M. Laval, *Chem. Rev*., 1999, **99**, 745; (g) H.B. Kagan, *Tetrahedron*, 2003, **59**, 10351.
2 Y.M. Ma, Y.M. Zhang and J. Chen, *Synthesis,* 2001, 1004.
3 X.L. Xu and Y.M. Zhang, *Tetrahedron*, 2002, **58**, 503.
4 K.B. Aubrecht, M.D. Winemiller and D.B. Collum, *J. Am. Chem. Soc.,* 2000,**122**, 11084.
5 A. Ogawa, N. Takami, T. Nanke, S. Ohya and T. Hirao, *Tetrahedron*, 1997, **53**, 12895.
6 J.H. Poupaert, K. Bouinidane, M. Renard, D.M. Lambert and M. Isa, *Organic Preparat. Proced. Int*., 2001, **33**, 335.
7 (a) A. Ogawa, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe and N.Sonoda, *J. Am. Chem. Chem. Soc*., 1992, **114**, 8729; (b) A. Ogawa, T. Nanke, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe and N. Sonoda, *Appl. Organomet. Chem*., 1995, **9**, 461.
8 E.O. Fischer, *Angew. Chem*., 1974, **86**, 651.
9 O.S. Mills and A.D. Redhouse, *J. Chem. Soc. A*., 1968, 642.
10 T.E. Taylor and M.B. Hall, *J. Am. Chem. Soc*., 1984, **106**, 1576.
11 H.M.L. Davies, P.R. Bruzinski, D.H. Lake, N. Kong and M.J. Fall, *J. Am. Chem. Soc*., 1996, **118**, 6897.