

Cyanosilylation of Carbonyl Compounds Catalyzed by Potassium L-Aspartate

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Received September 28, 2007

Potassium L-aspartate has been used as a catalyst for the cyanosilylation of carbonyl compounds producing corresponding cyanohydrin trimethylsilyl ethers in excellent yield of up to 98%. Although the catalyst is chiral, the enantioselectivities observed are generally poor except for one case, α -naphthaldehyde, 89% ee.

Key Words : Cyanohydrins, Aldehydes, Ketones, Potassium L-aspartate

Introduction

Cyanosilylation of carbonyl compounds is an acceptable strategy in organic synthesis for the effective intermediary method for the preparation of α -hydroxy acids, α -hydroxy aldehydes, 1, 2 diols, α -amino alcohols.¹⁻¹⁰ Tremendous progress has been made in the development of catalytic systems for the synthesis of cyanohydrins cyanosilyl ether for the past few decades.¹¹⁻²³ We have also reported several chiral²⁴⁻²⁸ and achiral²⁹⁻³⁵ catalytic systems for the developments of cyanohydrins during the last few years.

There are very few reports available in the literature regarding the use of amino acids for organic reactions. L-proline has been used as an organocatalyst in several reactions.³⁶⁻³⁸ Recently Feng and co-workers reported that sodium salt of L-phenyl glycine is an effective catalyst for the enantioselective cyanosilylation of ketones.³⁹ We have found sodium salt of L-histidine is a good catalyst for the cyanosilylation of aldehydes.³⁵ In this work we have explored the catalytic potential of potassium L-aspartate for the cyanosilylation of carbonyl compounds.

Results and Discussion

Benzaldehyde was selected as substrate for the optimization studies. The reaction was conducted at rt in mixture of THF and CH₂Cl₂. As shown in Table 1, potassium L-aspartate exhibits excellent catalytic activity at rt. The reaction with 20 mol % of the catalyst produced trimethylsilyl ether with 98% yield. In order to study the effect of temperature on the reactions, we have reduced the temperature from rt to -40 °C (entries 2 to 6 Table 1). At rt the reaction took 90 minutes for completion of the reaction whereas 46 hours was required for the same reaction at -40 °C. However there is no improvement in ee by reducing the temperature. We have further increased the catalyst amount up to 30 mol % and observed sizable reduction in the reaction time (entry 7). But there is again no improvement in ee. Among these studies the product with 98% yield (entry 7) is taken as the optimal. Accordingly we have proceeded further studies with 30 mol% of the potassium L-aspartate.

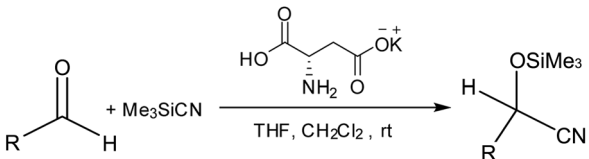
A series of carbonyl compounds were reacted with TMSCN in presence of potassium L-aspartate at rt so as to give the cyanation products in good to excellent isolated yield as shown in Table 2. However ee is very poor in most of the cases. The aromatic aldehydes are converted into the corresponding trimethylsilyl ether in excellent yield at rt. The experimental results indicate that the substituents on aromatic ring do not exhibit consistent electronic effects. *p*-Methoxybenzaldehyde took longer reaction time compared to other benzaldehydes (except for *m*-methylbenzaldehyde) with yield of 90% and ee of 52% despite the strong electron releasing power. *p*-*t*-Butylbenzaldehyde consumes 90 minutes for yield of 84%. *m*-Methylbenzaldehyde took (5 h, 83%) longer reaction time than *p*-methylbenzaldehyde (40 min, 94%). *m*-Phenoxybenzaldehyde costs 50 minutes to obtain 91% yield. The effects of *o*, *m*, and *p*-chloro substituents on the cyanosilylation of benzaldehydes were examined (entries 7, 8, and 9). *o*-Chlorobenzaldehyde took longest reaction time (2 h, 30 min) with less yield compared to *m*- and *p*-counterparts. This can be due to the steric effect of chloro group on the cyanosilylation. *m*-Chloro benzaldehyde

Table 1. Cyanosilylation of Benzaldehyde under Various Conditions

Entry	Catalyst ^b (mol %)	Time (h)	Temp	Yield ^c (%)	ee ^d
1	20	90 min	rt	98	0
2	20	4 h 30 min	0	90	3
3	20	7 h	-10 °C	92	1
4	20	10 h	-20 °C	94	1
5	20	24 h	-30 °C	94	1
6	20	46 h	-40 °C	93	1
7	30	50 min	rt	98	1
8 ^e	30	70 min	rt	98	-

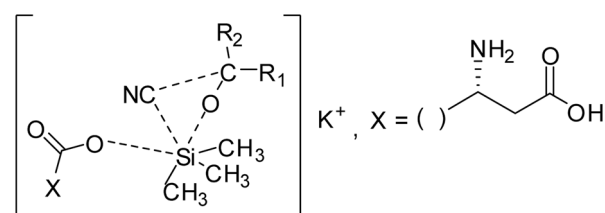
^a0.5 mL of THF and CH₂Cl₂ was used to make total 1 mL of solvent. ^bWe found that at lower concentration of the catalyst loading, the reaction does not take place. ^cisolated yield. ^dee determined from by Chiracel AS column. ^eReaction conducted in presence of 2,6, di-*tert*-butyl pyridine.⁴⁴

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Table 2. Cyanosilylation of Various Aldehydes and Ketones with Potassium L-Aspartate^a


Entry	Substrate	Time (min)	Yield (%) ^b	ee (%) ^c R or S
1		50	98	–
2		40	94	–
3		5 h	83	–
4 ^d		5 h	90	52, R ^f
5		90	84	–
6		5-	85	–
7		2 h 30 min	77	–
8		30 min	89	–
9		2 h	93	–
10		30	89	87, R ^f
11	CH ₃ CH=CHCHO	2 h	70	–
12	(CH ₃) ₂ CHCHO	60	65	–
13		30	94	–
14		120 h	50	–
15 ^e		168 h	75	–

^a1 mmol of the benzaldehyde, 2 equivalent of TMSCN and 0.5 mL of solvent are added to 30 mol% of the catalyst. ^bIsolated yield and 100% conversion by ¹H NMR analysis. ^cee determined from by Chiralcel AS column. ^d20 mol% of the catalyst is used. ^e40 mol % of the catalyst is used. ^fAbsolute configuration was determined by optical rotation.^{24,25,40-42}



R₁ = H and R₂ = Phenyl with aldehydes and R₁ = alkyl and R₂ = alkyl or cyclohexyl with ketones.

Figure 1. Transition State Involved in the Cyanosilylation of Carbonyl Compounds by Potassium L-Aspartate.

hyde has undergone the reaction within 30 minutes with 89% yield whereas *p*-chlorobenzaldehyde needs 2 h for the reaction with 93% yield. But the ee of all chloro substituted benzaldehydes is negligibly small. The cyanosilylation of 1-naphthaldehyde was completed within 30 minutes with 89% yield and 87% ee, the highest enantioselectivity observed for the reactions. Crotonaldehyde was predominately converted into 1, 2 adducts leaving the olefinic function intact and conjugate addition product was not observed. Higher yields was observed in the cyanosilylation of cyclohexane carboxaldehyde compared to other aliphatic aldehydes (entries 11, 12 and 13). Trimethylsilyl ether was produced within 30 minutes with 94% yield. We have examined the catalytic activity of potassium L-aspartate for ketones (entries 14 and 15). Ketones are found to be less susceptible to cyanosilylation reaction in presence of potassium L-aspartate. 2-Cyclohexene-1-one took 120 h to produce the cyanohydrin with yield of 50%. 2-Octanone needs 168 h for 75% yield. The reactions with the aldehydes are much more facile than with ketones probably due to the steric effects.

The mechanism of cyanosilylation of carbonyl compounds with potassium L-aspartate may be proposed as follows. A hypervalent silicon intermediate is formed by the interaction between the carboxylate anion of potassium L-aspartate and TMSCN. It is an active cyanation intermediate since the nucleophilicity of the cyano group is enhanced by the electron donation from the hypervalent silicon. The silicon intermediate readily reacts with carbonyl compound followed by the immediate silylation to give the corresponding product. The transition state formed in the reaction is shown in Figure 1. There is less possibility of reaction with HCN formed by the interaction between TMSCN and moisture, because reaction is smoothly carried out even in presence of 2,6-di-*tert*-butyl pyridine.⁴⁴ Otherwise HCN would react with 2,6-di-*tert*-butyl pyridine which might prevent formation of cyanosilylation product. Further there is no characteristic peak of HCN in the ¹³C NMR spectra of the mixture of TMSCN and potassium L-aspartate (Refer to Experimental for detail). On the other hand there is a slight shift in the TMSCN peak from $\delta = 1.98$ to $\delta = 2.03$ in the spectra of mixture of TMSCN and potassium L-aspartate. This may support the view of the formation of hypervalent silicon intermediate. In order to understand the role of amino group of potassium L-aspartate on cyanosilylation reaction we have

conducted the reaction with BOC protected L-potassium aspartate. We could not notice any significant change in the yield or ee of the cyanohydrin formed by using BOC protected L-potassium aspartate.

Conclusion

Potassium L-aspartate is an active, inexpensive and simple catalyst for the cyanosilylation of carbonyl compounds especially aldehydes. The important features of our method are: mild reaction conditions, simple work up and wide substrate scope. The reaction condition of asymmetric cyanosilylation of ketone by sodium salt of L-phenyl glycine is quite drastic in terms of reaction time (1-2 days) and temperature ($-45\text{ }^{\circ}\text{C}$) compared to those of cyanosilylation by sodium L-aspartate and sodium L-histidine (reaction time: 10 min-5 h, temperature: rt).

Experimental

Materials and instruments. In all cases the ^1H NMR (200 MHz) spectra were recorded with Varian Gemini 2000 spectrophotometer. Chemical shifts are reported in ppm in CDCl_3 with tetramethylsilane as internal standard. ^{13}C NMR data were collected on a Varian Unity Inova 400 (400 MHz) spectrophotometer at a field of 9.34T. Enantiomeric excess was determined by HPLC analysis on Chiralcel OD and AS column in comparisons with authentic racemates. HRMS analysis was carried on a Hewlett-Packard 5890A Gas chromatograph/Jeol JMS-DX303 Mass Spectrometer by chemical ionization method with methane as the flow gas. Analytical high performance liquid chromatography (HPLC) was performed on Shimadzu HPLC (LC 10-AD-VP) using the indicated chiral column. All data was in accordance with literature values. The absolute configurations were determined by optical rotation.^{24,25,40-42} L-Potassium aspartic acid (98% purity) is supplied by Sigma Aldrich. All aldehydes, ketones and TMSCN were purchased from Aldrich.

Preparation of cyanohydrin trimethylsilylether. To 30 mol% of the potassium L-aspartate, TMSCN (1.5 equiv) and THF (0.5 mL) and CH_2Cl_2 (0.5 mL) were added and stirred at room temperature in a 10 mL round bottom flask. To this mixture aldehyde or ketone (1 mmol) was added dropwise using a syringe pump. The reaction mixture was stirred continuously under the conditions mentioned in Table 1 and progress of the reaction was followed by TLC. The reaction mixture was purified by silica gel flash chromatography by using EtOAc-hexane (1:9) mixture as eluent. The silylethers thus obtained were identified by ^1H , ^{13}C NMR and HRMS data, which are consistent with the structure. HPLC grade of THF (water by KF, coluometric 0.003%) and CH_2Cl_2 (water by KF, coluometric 0.002%) were used as solvent for the reactions and were supplied by J.T Baker U.S.A. Caution: TMSCN must be used in a well ventilated hood due to its high toxicity and moisture sensitive nature.

2-Phenyl-2-(trimethylsilyloxy)acetonitrile. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.257$ (s, 9H), 5.52 (s, 1H), 7.42-

7.47 (m, 5H).

^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.32$, 63.59, 119.12, 126.29, 128.87, 129.27, 136.18.

HPLC (DAICEL CHIRALCEL AS, $^i\text{PrOH}$ /hexane = 0.25/99.75, flow = 0.25 mL/min) 9.48 and 10.81 min. HRMS (EI)⁴³: m/z calcd. for $\text{C}_{11}\text{H}_{15}\text{NOSi}$ (M^+): 205.0923; found: 205.0912.

2-(4-Methylphenyl)-2-(trimethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.142$ (s, 9H), 2.29 (s, 3H), 5.49 (s, 1H), 7.18 (d, 2H) 7.25 (d, 2H), ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.28$, 55.78, 63.87, 114.66, 119.47, 127.58, 128.78, 160.23. HPLC (DAICEL CHIRALCEL AS, $^i\text{PrOH}$ /hexane = 0.5/99.5, flow = 0.75 mL/min) 15.82 and 16.51 min. HRMS (EI)⁴³: m/z calcd for $\text{C}_{12}\text{H}_{17}\text{NOSi}$ (M^+): 219.1079; found: 219.1069.

m-Tolyl-2-(trimethylsilyloxy)acetonitrile. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.232$ (s, 9H), 5.45 (s, 1H), 2.38 (m, 3H) 7.26-7.28 (m, 4H) ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = 0.123$, 21.46, 63.72, 119.21, 123.41, 126.93, 128.74, 130.02, 136.07, 138.74, HRMS (EI): m/z calcd. for $\text{C}_{12}\text{H}_{17}\text{NOSi}$ (M^+): 219.1077; found : 219.1087.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.38$ (s, 9H), 3.83 (s, 3H), 5.44 (s, 1H), 6.96 (d, 2H), 7.42 (d, 2H), ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.26$, 55.34, 63.34, 114.25, 119.32, 127.93, 128.46, 160.33. HRMS (EI)⁴³: m/z calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{Si}$ (M^+): 235.1029; found: 235.1032, R enantiomer in 57% ee. HPLC (DAICEL CHIRALCEL AS, $^i\text{PrOH}$ /hexane = 0.5/99.5, flow = 0.75 mL/min) 12.54 and 12.84 min.

2-(4-tert-Butylphenyl)-2-(trimethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.23$ (s, 9H), 1.32 (s, 9H), 5.38 (s, 1H), 7.09-7.21 (m, 5H). ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.39$, 31.12, 34.52, 63.33, 119.28, 125.73, 126.04, 133.19, 152.47. HRMS (EI)⁴³: m/z calcd. for $\text{C}_{15}\text{H}_{23}\text{NOSi}$ (M^+): 261.1549; found: 261.1552.

2-(3-Phenoxyphenyl)-2-(trimethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.218$ (s, 9H), 5.42 (s, 1H), 7.01-7.20 (m, 5H), 7.34-7.38 (m, 4H). ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = 0.16$, 63.28, 116.37, 118.85, 119.17, 119.30, 120.64, 123.75, 129.81, 130.22, 138.08, 156.39, 157.88.

2-(2-Chlorophenyl)-2-(timethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.252$ (s, 9H), 5.81(s, 1H) 7.32-7.4 (m, 3H), 7.72 (d, 1H) ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.206$, 60.75, 127.46, 128.26, 129.64, 130.51. HPLC (DAICEL CHIRALCEL AS, $^i\text{PrOH}$ /hexane = 1/99, flow = 0.25 mL/min) 14.79 and 15.82 min.

2-(3-Chlorophenyl)-2-(timethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.25$ (s, 9H), 5.42 (s, 1H) 7.35-7.37 (m, 3H), 7.47 (s, 1H) ^{13}C NMR (CDCl_3 , 400 MHz): $\delta = -0.176$, 62.93,124.256, 126.39, 129.45, 130.14.

HPLC (DAICEL CHIRALCEL OD, $^i\text{PrOH}$ /hexane = 1/99, flow = 0.3 mL/min) 20.05 and 20.80 min.

2-(4-Chlorophenyl)-2-(timethylsilyloxy)acetonitrile.

^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.25$ (s, 9H), 5.48(s, 1H) 7.38-7.42 (m, 4H).

^{13}C NMR (CDCl_3 , 400 MHz): $\delta = 0.161$, 63.01, 118.71, 127.05, 127.59, 129.09, 134.74.

HPLC (DAICEL CHIRALCEL OD, ⁱPrOH/hexane = 1/99, flow = 0.3 mL/min) 18.97 and 20.47 min.

2-(Naphthalen-1-yl)-2-(trimethylsilyloxy)acetonitrile. ¹H NMR (200 MHz, CDCl₃): δ = 0.226 (s, 9H), 6.05 (s, 1H), 7.45-7.7 (m, 3H), 7.85-7.95 (m, 3H), 8.23 (d, 1H), ¹³C NMR (CDCl₃, 400 MHz): δ = -0.285, 63.4, 118.45, 122.37, 125.62, 125.01, 126.3, 128.3, 131.01, 133.45, 136.12. R enantiomer in 87% ee. HPLC (DAICEL CHIRALCEL AS, ⁱPrOH/hexane = 0.5/99.5, flow = 0.75 mL/min) 9.33 and 10.95 min.

2-(Trimethylsilyloxy) pent-3-enenitrile. ¹H NMR (CDCl₃, 200 MHz): δ = 0.24 (s, 9H), 1.74 (d, 3H), 4.90 (d, 1H), 5.51-5.62 (m, 1H), 5.93-6.04 (m, 1H). ¹³C NMR (CDCl₃, 400 MHz): δ = -0.40, 17.17, 61.92, 118.45, 126.06, 130.88.

3-Methyl-2-trimethylsilyloxybutanenitrile. ¹H NMR (200 MHz, CDCl₃): δ = 0.2 (s, 9H), 0.88-1.05 (m, 6H), 1.94-1.96 (m, 1H), 4.16 (d, 1H). ¹³C NMR (CDCl₃, 400 MHz): δ = -0.335, 17.68, 33.921, 67.28, 119.94.

Cyclohexyl (trimethylsilyloxy)acetonitrile. ¹H NMR (CDCl₃, 200 MHz): δ = 0.26 (s, 9H), 1.18-1.29 (m, 5H), 1.68-1.88 (m, 6H), 4.15 (d, 1H). ¹³C NMR (CDCl₃, 400 MHz): δ = -0.335, 25.47, 26.09, 28.15, 28.21, 42.98, 66.55, 119.39.

1-(Trimethylsilyloxy)-2-cyclohexenecarbonitrile. ¹H NMR (CDCl₃, 200 MHz): δ = 0.24 (s, 9H), 1.74-1.86 (m, 2H), 1.91-1.98 (m, 2H), 2.04-2.18 (m, 2H) 5.72-5.8 (m, 1H) 5.97-5.99 (d, 1H). ¹³C NMR (CDCl₃, 400 MHz): δ = 1.62, 18.45, 24.39, 37.00, 66.50, 121.80, 127.5, and 132.5. HRMS (EI): m/z calcd. for C₁₀H₁₇NOSi (M⁺): 195.1079; found: 195.1083.

2-(Trimethylsilyloxy)-2-methyloctanenitrile. ¹H NMR (CDCl₃, 200 MHz): δ = 0.22 (s, 9H), 0.87-0.91 (t, 3H) 1.29-1.32 (m, 8H), 1.56 (s, 3H) 1.68-1.71 (m, 2H) ¹³C NMR (CDCl₃, 400 MHz): δ = 1.42, 14.12, 22.62, 24.32, 28.98, 29.05, 31.69, 43.44, 69.70, and 122.16. HRMS (EI): m/z calcd. for C₁₂H₂₅NOSi (M⁺): 227.1705; found: 227.1710.

Trimethyl silanecarbonitrile (TMSCN). ¹³C NMR (CDCl₃, 400 MHz): δ = 1.98, 126.97.

A Mixture of trimethyl silanecarbonitrile and potassium L-aspartate. (TMSCN + Potassium aspartic acid). ¹³C NMR (CDCl₃, 400 MHz): 2.038, 40.49, 52.18, 127, 172, 174. ¹³C NMR (CDCl₃): The absence of HCN peak around 115-120.

Acknowledgments. We warmly thank the Centre for Biological Modulators for the financial support. Korea Research Foundation should be mentioned for BK21.

References

- North, M. *Synlett* **1993**, 807.
- Effenberger, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1555.
- Gregory, R. J. H. *Chem. Rev.* **1999**, *99*, 3649.
- Shibasaki, M.; Kanai, M.; Funabashi, K. *Chem. Commun.* **2002**, 1989.
- North, M. *Tetrahedron: Asymmetry* **2003**, *14*, 147.
- Brunel, J. M.; Holmes, I. P. *Angew. Chem. Int. Ed.* **2004**, *43*, 2752.
- Special Symposium for the Synthesis of Nonracemic Cyanohydrins, see: *Tetrahedron* **2004**, *60*, 10371.
- Chen, F.-X.; Feng, X. *Synlett* **2005**, 892.
- Kanai, M.; Kato, N.; Ichikawa, E.; Shibasaki, M. *Synlett* **2005**, 1491.
- Achard, T. R. J.; Clutterbuck, L. A.; North, M. *Synlett* **2005**, *12*, 1828.
- Holmes, I. P.; Kagan, H. B. *Tetrahedron Lett.* **2000**, *41*, 7457.
- Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A. *Tetrahedron Lett.* **2001**, *42*, 3041.
- Bandini, M.; Cozzi, P. G.; Garelli, A.; Melchiorre, P.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2002**, 3243.
- Cordoba, R.; Plumet, J. *Tetrahedron Lett.* **2003**, *44*, 6157.
- Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *Tetrahedron Lett.* **2003**, *44*, 6813.
- Lundgren, S.; Lutsenko, S.; Jonsson, C.; Moberg, C. *Org. Lett.* **2003**, *5*, 3663.
- Li, Y.; He, B.; Qin, B.; Feng, X.; Zhang, G. *J. Org. Chem.* **2004**, *69*, 7910.
- Shen, Y.; Feng, X.; Li, Y.; Zhang, G.; Jiang, Y. *Tetrahedron* **2003**, *59*, 5667.
- Chen, F.-X.; Liu, X.; Qin, B.; Zhou, H.; Feng, X.; Zhang, G. *Synthesis* **2004**, 2266.
- Aspinall, H. C.; Bickley, J. F.; Greeves, N.; Kelly, R. V.; Smith, P. M. *Organometallics* **2005**, *24*, 3458.
- Chen, F.-X.; Feng, X. *Synlett* **2005**, 892.
- Liu, Y.; Liu, X.; Xin, J.; Feng, X. *Synlett* **2006**, 1085.
- Qin, B.; Liu, X.; Shi, J.; Zheng, K.; Zhao, H.; Feng, X. *J. Org. Chem.* **2007**, *72*, 2374.
- Kim, S. S.; Song, D. H. *Eur. J. Org. Chem.* **2005**, 1777.
- Kim, S. S.; Lee, S. H. *Synthetic Commun.* **2005**, *35*, 751.
- Kim, S. S.; Kwak, J. M. *Tetrahedron* **2006**, *63*, 49.
- Kim, S. S.; Lee, S. H.; Kwak, J. M. *Tetrahedron: Asymmetry* **2006**, *17*, 1165.
- Kim, S. S.; Kwak, J. M.; George, S. C. *Appl. Organomet. Chem.* **2007**, *21*, 809.
- Kim, S. S.; Rajagopal, G.; Song, D. H. *J. Organomet. Chem.* **2004**, *689*, 1734.
- Kim, S. S.; Kim, D. W.; Rajagopal, G. *Synthesis* **2004**, 213.
- Kim, S. S.; Rajagopal, G.; Kim, D. W.; Song, D. H. *Synth. Commun.* **2004**, *34*, 2973.
- Kim, S. S.; Rajagopal, G. *Synthesis* **2007**, 215.
- Rajagopal, G.; Kim, S. S.; George, S. C. *Appl. Organomet. Chem.* **2007**, *21*, 198.
- Kim, S. S.; Rajagopal, G.; George, S. C. *Appl. Organomet. Chem.* **2007**, *21*, 368.
- George, S. C.; Kim, S. S.; Rajagopal, G. *Appl. Organomet. Chem.* **2007**, *21*, 798.
- List, B. *Tetrahedron* **2002**, *58*, 5573.
- Yamaguchi, M.; Shiraishi, T.; Hiram, M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1176.
- Yamaguchi, M.; Shiraishi, T.; Hiram, M. *J. Org. Chem.* **1996**, *61*, 3520.
- Liu, X.; Qin, B.; Zhou, X.; He, B.; Feng, X. *J. Am. Chem. Soc.* **2005**, *127*, 12224.
- Hwang, C.-D.; Hwang, D.-R.; Uang, B.-J. *J. Org. Chem.* **1998**, *63*, 7662.
- Yang, W.-B.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 1356.
- Belokon, Y. N.; Caveda, C. S.; Green, B.; Ikonnikov, N. S.; Khrustalev, V. N.; Larichev, V. S.; Moscalenko, M. A.; North, M.; Orizu, C.; Tarrov, V. I.; Tasinazzo, M.; Timofeeva, I. G.; Yashkina, L. V. *J. Am. Chem. Soc.* **1999**, *121*, 3968.
- Kim, S. S.; Lee, J. T.; Song, D. H.; Lee, I.-M.; Park, S. Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 265.
- Wabnit, T. C.; Yu, J.-Q.; Spencer, J. B. *Chem. Eur. J.* **2004**, *10*, 484.