Stereoselective Synthesis of 2,6-Disubstituted-4-Aryltetrahydropyrans Using Sakurai–Hosomi–Prins–Friedel–Crafts Reaction

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Keywords: Multicomponent reactions / Diastereoselectivity / Cyclization / Oxygen heterocycles

The reaction of aldehydes with allyltrimethylsilane in arene solvents gives symmetrical 2,6-disubstituted-4-aryltetrahydropyrans in good yields. The reaction is highly stereoselective. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

Introduction

Multicomponent reactions are important in organic synthesis because of their ability to construct multiple bonds in a single step, which is crucial for pharmaceutically active and natural product synthesis.^[1] The synthesis of the tetrahydropyran unit is important because of its presence in many natural products.^[2] The all-*cis* 2,6-disubstituted-4-aryltetrahydropyrans have olfactory properties.^[3] and shows nonredox 5-lipoxygenase inhibiting properties.^[4] These tetrahydropyrans are prepared by hetero-Diels–Alder methods,^[5] manipulation of carbohydrates,^[6] Prins cyclization,^[7] and intramolecular Michael reactions.^[8] Although the synthesis of 4-halo-,^[9] 4-thio-,^[10] 4-azido-,^[11] 4-amino-,^[12] and 4-hydroxytetrahydropyrans^[7e,7f,9d,13] have been reported in the literature, the synthesis of 2,6-disubstituted-4-aryltetrahydropyrans is limited.^[14,2h]

We have shown in our previous investigation that 2,6disubstituted-4-amidotetrahydropyrans can be synthesized in high yields with excellent stereoselectivity through BF₃·Et₂O-mediated cyclization of aldehydes and allyltrimethylsilane in acetonitrile. In this protocol, a Sakurai– Hosomi–Prins–Ritter reaction sequence was used.^[12e]

We disclose here a stereoselective one-pot, three-component synthesis of 2,6-disubstituted-4-aryltetrahydropyrans from aldehydes, allyltrimethylsilane, and arenes by using a Sakurai–Hosomi–Prins–Friedel–Crafts reaction.

Results and Discussion

To start, benzaldehyde (1.0 mmol) was treated with allyltrimethylsilane (0.6 mmol) in benzene (5.0 mL) in the presence of $BF_3 \cdot Et_2O(1.2 \text{ mmol})$ at 0 °C, and the reaction was warmed to room temperature. 2,4,6-Triphenyltetrahydropyran was obtained in 74% yield. To prove the general applicability of this reaction, a variety of alkyl and aryl aldehydes were investigated as shown in Scheme 1. The results are summarized in Table 1.



Scheme 1. Synthesis of symmetrical 2,6-disubstituted-4-aryltetrahydropyran (R = alkyl, aryl).

In all the cases studied, 4-aryltetrahydropyrans 1b–16b (Table 1) could be obtained in high purity without any side products. Both aliphatic and aromatic aldehydes gave good yields with high diastereoselectivity, as determined from the ¹H and ¹³C NMR spectra of the crude products. The substituents on the aromatic ring play an important role in this reaction: electron-withdrawing substituents and simple aldehydes gave better yields than those obtained when electron-donating groups were on the ring. Aliphatic aldehydes were found to be better substrates for this reaction. The substituents at the 2-, 4-, and 6-positions of the tetrahydropyran ring are in a *cis* relationship and are equatorial. This is revealed from the coupling constants of the 2,6-H (J = 11.2 and 2.0 Hz) and the 4-H (J = 11.2 and 2.0 Hz)hydrogen atoms of compound 2b (Figure 1). This was also confirmed by an NOE experiment and single-crystal X-ray analysis.^[15]

To explore further utility of the method, other arenes were also studied as nucleophiles as shown in Table 2. Thus, the reaction of *m*-nitrobenzaldehyde (**3a**) in toluene gave product **17** as an inseparable mixture of two regioisomers with a ratio of 4.7:1 and 97% overall yield. *o*-Xylene gave



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Table 1. Synthesis of 2,6-disubstituted-4-phenyltetrahydropyran.

[a] Yields refer to isolated products. Compounds were characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy.



Figure 1. Coupling constants and NOE of compound 2b.

product 18 as an inseparable mixture of two regioisomers with a ratio of 4:1 and 100% overall yield. In contrast, p-xylene gave single product 19 with 100% yield.

Table 2. Reaction of *m*-nitrobenzaldehyde with other aromatic nucleophiles.



[a] Yields refer to isolated products. Compounds were characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy. [b] Inseparable mixture of regioisomers. Ratio was determined by ¹H NMR spectroscopy. [c] o/p-Isomers were separated and their ratio was 2:1. [d] Reaction with 5.0 equiv. of anisole in CH₂Cl₂.

Similarly, *m*-xylene gave product **20** as an inseparable mixture of two regioisomers with a ratio of 1:2 and 100% overall yield. Anisole is a good nucleophile, as it gave **21** with 95% yield within 30 min. (**21**p/**21**o, 1:2). Even at a low concentration of anisole in dichloromethane a good yield was obtained (90%, Table 2). Electron-deficient aromatic compounds such as halobenzenes and nitrobenzene do not act as nucleophiles in the Friedel–Crafts reaction. Aromatic compounds having electron-donating groups, such as



methyl and methoxy groups, behave as strong nucleophiles in comparison to benzene, which is evident from their reaction times and yields (Tables 1 and 2). Other aromatic compounds like naphthalene, 2-methoxynaphthalene, and other fused-ring aromatic compounds were inactive under these reaction conditions. This might be due to steric hindrance.

The reaction was also carried out with two different aldehydes. The reaction was performed by allowing aldehyde A to react with allyltrimethylsilane for 1 h, followed by the addition of aldehyde **B**. The reaction was not selective and gave three different products: symmetric products C and D and cross product E (Table 3). The yield of the cross product was always less than that of the symmetric products. Allowing the first aldehyde to react with allyltrimethylsilane for a longer time period resulted in lower amounts of cross products. This indicates that the rate of formation of homoallylic alcohol (Sakurai-Hosomi reaction) is slower than the Prins cyclization reaction. That is, all the molecules of aldehyde A do not form the homoallylic alcohol intermediate so that aldehyde B can take part in Prins cyclization to give only the cross product. The possibility of allyl transfer from the initially formed homoallyloxy intermediate (species 2, Scheme 2) to the second aldehyde cannot be ruled out.

Table 3. Reaction with mixed aldehydes.



[a] Yields refer to isolated products. Compounds were characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy.



Scheme 2. Mechanism of the reaction.

The mechanism of the reaction can be explained as follows: In the presence of Lewis acid allyltrimethylsilane (1) reacts with the aldehyde to afford intermediate 2 (Scheme 2). Intermediate 2 reacts with another molecule of the aldehyde to give tetrahydropyranyl cation 3, which in the presence of an aryl nucleophile, gives intermediate 4. Species 4 after deprotonation gives 2,6-disubstituted-4-aryltetrahydropyran 5.

Conclusions

In summary, an efficient, highly diastereoselective, onepot method for the synthesis of 2,6-disubstituted-4-aryltetrahydropyrans in good yields has been developed. The scope and synthetic applications of this novel reaction is under investigation in our laboratory.

Experimental Section

General Procedure for the Synthesis of 2,6-Disubstituted-4-aryltetrahydropyrans: To a mixture of aldehyde (1.0 mmol), $BF_3 \cdot Et_2O$ (1.2 mmol), and aryl compound (3.0 mL) was added a mixture of allyltrimethylsilane (0.6 mmol) and aryl compound (2.0 mL) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by shortcolumn chromatography over silica gel to give the title compounds.

2.4.6-Triphenvltetrahvdropyran (1b): To a mixture of benzaldehyde (1a: 0.10 mL, 1.0 mmol), benzene (3.0 mL), and BF₃·Et₂O (0.15 mL, 1.2 mmol) was added allyltrimethylsilane (0.10 mL, 0.6 mmol.) in benzene (2.0 mL) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for 14 h. The progress of the reaction was monitored by TLC (EtOAc/hexane, 1:9). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short-column chromatography over silica gel to give 1b (116 mg, 74%) as a gum. ¹H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.76–1.85 (m, 2 H, 3ax,5ax-CH), 2.16–2.20 (m, 2 H, 3eq,5eq-CH), 3.17 [tt, $J_{4ax,(3,5)ax} = 12.0$ Hz, $J_{4ax,(3,5)eq} = 3.6$ Hz, 1 H, 4ax-CH], 4.75 (dd, $J_{2ax,3ax} = 11.2$ Hz, $J_{2ax,3eq} = 2.0$ Hz, 2 H, 2ax,6ax-CH), 7.19-7.37 (m, 12 H, ArH), 7.47-7.49 (m, 3 H, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 41.4, 42.6, 80.0, 126.0, 126.6, 126.9, 127.5, 128.5, 128.7, 143.1, 145.3 ppm. IR: $\tilde{v} = 3063$, 2915, 2874, 1598, 1573, 1476, 1443, 1208, 1133, 1079, 1051, 1035, 753 cm⁻¹. C₂₃H₂₂O (314.42): calcd. C 87.86, H 7.05; found C 87.68, H 7.21.

4-(4-Methoxyphenyl)-2,6-bis(3-nitrophenyl)tetrahydro-2*H*-pyran (21*p*) and 4-(2-Methoxyphenyl)-2,6-bis(3-nitrophenyl)tetrahydro-2*H*-pyran (21*o*): To a solution of 3a (302 mg, 2.0 mmol) and BF₃·Et₂O (0.30 mL, 2.4 mmol) in dichloromethane (2.0 mL) was added a solution of allyltrimethylsilane (0.22 mL, 1.4 mmol.) and anisole (1.10 mL, 10.0 mmol) drop by drop at 0 °C; the temperature was slowly increased to room temperature over 1 h. The reaction mixture was stirred at room temperature for 24 h. The progress of the

reaction was monitored by TLC (EtOAc/hexane; 1:9). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na_2SO_4) and evaporated to leave the crude product, which was purified by thin-layer chromatography over silica gel to give 210 and 21p in a 2:1 ratio (390 mg, 90% of overall yield) as a solid. Data for 21p: Solid. M.p. 164–168 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.74–1.84 (m, 2 H, 3ax,5ax-CH), 2.21–2.25 (m, 2 H, 3eq,5eq-CH), 3.20 [tt, $J_{4ax,(3,5)ax} = 12.4$ Hz, $J_{4ax,(3,5)eq} = 3.6$ Hz, 1 H, 4ax-CH], 3.78 (s, 3 H, -OCH₃), 4.88 (dd, $J_{2ax,3ax} = J_{6ax,5ax} =$ 10 Hz, $J_{2ax,3eq} = J_{6a,5eq} = 1.2$ Hz, 2 H, 2ax,6ax-CH), 6.86 (d, J =8.4 Hz, 2 H, ArH, 7.18 (d, J = 8.4 Hz, 2 H, ArH, 7.56 (m, 2 H, 1000 H)ArH), 7.83 (d, J = 7.6 Hz, 2 H, ArH), 8.15 (d, J = 8.0 Hz, 2 H, ArH), 8.34 (s, 2 H, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 41.2, 41.4, 55.5, 79.2, 114.3, 121.1, 122.8, 127.8, 129.7, 132.1, 136.3, 144.5, 148.5, 158.6 ppm. IR: $\tilde{v} = 2933$, 2853, 1528, 1350, 1250, 1103, 1072, 810, 737 cm⁻¹. C₂₄H₂₂N₂O₆ (434.45): calcd. C 66.35, H 5.10, N 6.45; found C 66.50, H 5.27, N 6.57. Data for 21o: Solid. M.p. 124–128 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.73–1.85 (m, 2 H, 3ax,5ax-CH), 2.20-2.24 (m, 2 H, 3ex,5ex-CH), 3.69 [tt, $J_{4ax,(3,5)ax} = 12.4 \text{ Hz}, J_{4ax,(3,5)eq} = 3.6 \text{ Hz}, 1 \text{ H}, 4ax-CH], 3.90 (s, 3)$ H, -OCH₃), 4.92 (dd, $J_{2ax,3ax} = J_{6ax,5ax} = 10$ Hz, $J_{2ax,3eq} = J_{6a,5eq} =$ 1.2 Hz, 2 H, 2ax,6ax-CH), 6.88-6.95 (m, 2 H, ArH), 7.16-7.24 (m, 2 H, ArH), 7.56 (m, 2 H, ArH), 7.84 (d, J = 7.6 Hz, 2 H, ArH), 8.14-8.17 (m, 2 H, ArH), 8.33 (s, 2 H, ArH) ppm. ¹³C NMR

(100 MHz, CDCl₃): δ = 35.1, 39.6, 55.6, 79.4, 110.7, 121.0, 121.1, 122.7, 126.6, 127.8, 129.6, 132.2 (2 C), 144.7, 148.5, 156.9 ppm. IR: \tilde{v} = 2920, 2850, 1528, 1348, 1241, 1102, 1070, 810, 736 cm⁻¹. C₂₄H₂₂N₂O₆ (434.44): calcd. C 66.35, H 5.10, N 6.45; found C 66.52, H 5.23, N 6.49.

General Procedure for Crossed 2,6-Disubstituted-4-phenyltetrahydropyrans: To a mixture of aldehyde (1.0 mmol) and $BF_3 \cdot Et_2O$ (1.2 mmol) in benzene (2.0 mL) was added allyltrimethylsilane (0.6 mmol) in benzene (1.0 mL) drop by drop at 0 °C. The reaction mixture was stirred for 1 h at the same temperature, and the other aldehyde (1.2 mmol) and $BF_3 \cdot Et_2O$ (1.4 mmol) in benzene (2 mL) was added drop by drop at same temperature. The temperature was then slowly brought to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short-column chromatography over silica gel to give the title compounds.

6-(4-Nitrophenyl)-2,4-diphenyltetrahydropyran (1E): To a mixture of benzaldehyde (106 mg, 1.0 mmol) and BF3·Et2O (0.20 mL, 1.2 mmol) in benzene (2.0 mL) was added allyltrimethylsilane (0.10 mL, 0.6 mmol) in benzene (1.0 mL) drop by drop at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and then *p*-nitrobenzaldehyde (181 mg, 1.2 mmol) and BF₃·Et₂O (1.8 mg, 1.4 mmol) in benzene (2 mL) were added drop by drop at the same temperature. The temperature was slowly brought to room temperature over 1 h. The reaction mixture was stirred at room temperature for the specified time. The progress of the reaction was monitored by TLC (ethyl acetate/hexane). After completion of the reaction, the product was extracted with ethyl acetate and washed with brine and water. The organic layer was dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by short-column chromatography over silica gel to give compounds 1b (100 mg, 32%), 2b (129 mg, 32%), and 1E (68 mg, 19%). Data for 1E: Solid. M.p. 101-103 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.70 (q, J = 12.4 Hz, 1 H), 1.80 (q, J = 12.8 Hz,

1 H), 2.15–2.18 (m, 2 H), 3.17 (tt, J = 12.0, 3.6 Hz, 1 H), 4.73 (dd, J = 11.2, 2.0 Hz, 1 H), 4.80 (dd, J = 11.2, 2.0 Hz, 1 H), 7.18–7.39 (m, 8 H), 7.46 (d, J = 8.8 Hz, 2 H), 7.59 (d, J = 8.4 Hz, 2 H), 8.16 (d, J = 8.8 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 41.0$, 41.2, 42.3, 78.9, 80.1, 123.7, 125.9, 126.3, 126.6, 126.9, 127.7, 128.6, 128.8, 142.5, 144.6, 147.2, 150.3 ppm. IR: $\tilde{v} = 3062$, 3029, 2941, 2849, 1602, 1516, 1495, 1345, 1287, 1102, 1078, 1030, 987, 851, 748 cm⁻¹. C₂₃H₂₁NO₃ (359.42): calcd. C 76.86, H 5.89, N 3.90; found C 76.92, H 5.78, N 3.88.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra of **1b–8b**, **11b–16b**, and **17–21**; ¹H, ¹³C, and ¹⁹F NMR spectra of compounds **9b** and **10b**; crude ¹H NMR spectra of compound **11b**; NOESY spectrum of **2b**; X-ray structure and crystal parameters of compound **8b**.

Acknowledgments

A. K. S. and U. C. R. are grateful to the Council of Scientific & Industrial Research (CSIR), New Delhi for financial support [Grant No. 01(1809)/02/EMR II] and a fellowship, respectively. The authors gratefully acknowledge the X-ray facility provided by the department of Science and Technology (DST) under the FIST program.

- a) L. F. Tietze, U. Beifuss, Angew. Chem. Int. Ed. Engl. 1993, 32, 131–163; b) L. F. Tietze, Chem. Rev. 1996, 96, 115–136; c) A. T. Khan, L. H. Choudhury, T. Parvin, M. A. Ali, Tetrahedron Lett. 2006, 47, 8137–8141; d) C. Hulme, V. Gore, Curr. Med. Chem. 2003, 10, 51–80.
- [2] a) K. C. Nicolaou, E. J. Sorensen, Classics in Total Synthesis VCH, Weinheim, 1996; b) F. Perron, K. F. Albizati, J. Org. Chem. 1987, 52, 4130–4133; c) Y. J. Class, P. DeShong, Chem. Rev. 1995, 95, 1843–1857; d) D. J. Kopecky, S. D. Rychnovsky, J. Am. Chem. Soc. 2001, 123, 8420–8421; e) Y. Wang, J. Janjic, S. A. Kozmin, J. Am. Chem. Soc. 2002, 124, 13670–13671; f) D. L. Aubele, S. Wan, P. E. Floreancig, Angew. Chem. Int. Ed. 2005, 44, 3485–3488; g) K. B. Bahnck, S. D. Rychnovsky, Chem. Commun. 2006, 2388–2390; h) X. T. Tian, J. J. Jaber, S. D. Rychnovsky, J. Org. Chem. 2006, 71, 3176–3183; i) A. B. Smith III, R. J. Fox, T. M. Razler, Acc. Chem. Res. 2008, 41, 675–678.
- [3] T. S. Balaban, A. Buettner, C. Roussel, N. Vanthuyne, P. Schieberle, *State-of-the-Art in Flavour Chemistry and Biology*, Proceedings of the Wartburg Symposium on Flavour Chemistry and Biology, 7th, Eisenach, Germany, Apr. 21–23, 2004, pp. 31–36.
- [4] a) D. Delorme, Y. Ducharme, C. Brideau, C.-C. Chan, N. Chauret, S. Desmarais, D. Dubé, J.-P. Falgueyret, R. Fortin, J. Guay, P. Hamel, T. R. Jones, C. Lépine, C. Li, M. Malia McAuliffe, C. S. McFarlane, D. A. Nicoll-Griffith, D. Riendeau, J. A. Yergey, Y. Girard, *J. Med. Chem.* 1996, *39*, 3951–3970; b) R. N. Young, L. A. Trimble, J. W. Gillard, J. Scheigetz, Y. Girard, Y. Ducharme, J. A. Yergey, D. A. Nicoll-Griffith, J. H. Hutchinson (Merck Frosst Canada Inc., Canada), Eur. Pat. Appl. EP 501579, A1 19920902, 1992.
- [5] a) D. L. Boger, S. M. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic, San Diego, **1987**; b) K. Gademann, D. E. Chavez, E. N. Jacobson, *Angew. Chem. Int. Ed.* **2002**, *41*, 3059–3061; c) V. Gouverneur, M. Reiter, *Chem. Eur. J.* **2005**, *11*, 5806–5815.
- [6] a) S. Hanessian, *Total Synthesis of Natural products: The "Chiron Approach"* (Ed.: J. E. Baldwin), Pergamon, Oxford, **1983**;
 b) J. C. Esteveza, A. J. Fairbanks, G. W. J. Fleet, *Tetrahedron* **1998**, *54*, 13591–13620.
- [7] a) S. R. Crosby, J. R. Harding, C. D. King, G. D. Parker, C. L. Willis, Org. Lett. 2002, 4, 577–580; b) K.-P. Chan, A.-H. Seow,



T.-P. Loh, *Tetrahedron Lett.* 2007, 48, 37–41; c) E. Arundale, L. A. Mikeska, *Chem. Rev.* 1952, 51, 505–555; d) D. R. Adams, S. P. Bhatnagar, *Synthesis* 1977, 661–672; e) C.-J. Li, W.-C. Zhang, *Tetrahedron* 2000, 56, 2403–2411; f) W.-C. Zhang, G. S. Viswanathan, C.-J. Li, *Chem. Commun.* 1999, 291–292; g) J. S. Yadav, B. V. S. Reddy, G. M. Kumar, C. V. S. R. Murthy, *Tetrahedron Lett.* 2001, 42, 89–91.

- [8] a) P. A. Clarke, S. Santos, *Eur. J. Org. Chem.* 2006, 2045–2053 and references cited therein; b) R. D. Little, M. R. Masjedizadeh, O. Wallquist, J. I. McLoughlin, *Org. React.* 1995, 47, 661.
- [9] a) L. Coppi, A. Ricci, M. Taddei, *Tetrahedron Lett.* 1987, 28, 973–976; b) S. D. Rychnovsky, Y. Hu, B. Ellsworth, *Tetrahedron Lett.* 1998, 39, 7271–7274; c) J. Yang, G. S. Viswanathan, C.-J. Li, *Tetrahedron Lett.* 1999, 40, 1627–1630; d) E. H. Al-Mutairi, S. R. Crosby, J. Darzi, J. R. Harding, R. A. Hughes, C. D. King, T. J. Simpson, R. W. Smith, C. L. Willis, *Chem. Commun.* 2001, 835–836.
- [10] J. S. Yadav, B. V. S. Reddy, T. Maity, G. G. K. S. N. Kumar, *Tetrahedron Lett.* 2007, 48, 8874–8877.
- [11] J. S. Yadav, B. V. S. Reddy, T. Maity, G. G. K. S. N. Kumar, *Tetrahedron Lett.* 2007, 48, 7155–7159.
- [12] a) N. Chandrasekara, K. Ramalingam, M. D. Herd, K. D. Berlin, J. Org. Chem. 1980, 45, 4352–4358; b) N. Chandrasekara, K. Ramalingam, N. Satyamurthy, K. D. Berlin, J. Org.

Chem. **1983**, *48*, 1591–1597; c) O. L. Epstein, T. Rovis, *J. Am. Chem. Soc.* **2006**, *128*, 16480–16481; d) J. S. Yadav, B. V. S. Reddy, G. G. K. S. N. Kumar, G. M. Reddy, *Tetrahedron Lett.* **2007**, *48*, 4903–4906; e) U. C. Reddy, B. R. Raju, E. K. P. Kumar, A. K. Saikia, *J. Org. Chem.* **2008**, *73*, 1628–1630.

- [13] a) M. Markert, I. Buchen, H. Kruger, R. Mahrwald, *Tetrahedron* 2004, 60, 993–999; b) H. M. S. Kumar, N. A. Qazi, S. Shafi, V. N. Kumar, A. D. Krishna, J. S. Yadav, *Tetrahedron Lett.* 2005, 46, 7205–7207; c) J. S. Yadav, B. V. S. Reddy, M. S. Reddy, N. Niranjan, *J. Mol. Catal. A* 2004, 210, 99–103; d) C. S. Barry, N. Bushby, J. R. Harding, R. A. Hughes, G. D. Parker, R. Roe, C. L. Willis, *Chem. Commun.* 2005, 3727–3729; e) W.-C. Zhang, C.-J. Li, *Tetrahedron* 2000, 56, 2403–2411.
- [14] a) X.-F. Yang, M. Wang, Y. Zhang, C.-J. Li, *Synlett* 2005, 1912–1916; b) Y. Hu, D. J. Skalitzky, S. D. Rychnovsky, *Tetrahedron Lett.* 1996, 37, 8679–8682; c) I. Shiina, M. Suzuki, K. Yokoyama, *Tetrahedron Lett.* 2002, 43, 6395–6398.
- [15] CCDC-692425 (for 8b) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: January 5, 2008 Published Online: February 18, 2009