Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 215 (2004) 49–53
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Indium triflate: a reusable catalyst for expeditious chemoselective conversion of aldehydes to acylals

Rina Ghosh*, Swarupananda Maiti, Arijit Chakraborty, Rajkumar Halder

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

Received 3 October 2003; accepted 19 January 2004

Abstract

A mild, efficient and expeditious method has been developed for the chemoselective conversion of aldehydes to the corresponding acylals in excellent yields, using acetic anhydride in the presence of catalytic amount (0.01–0.1 mol%) of $In(OTf)_3$. Ketones remain unaffected under the reaction condition. $In(OTf)_3$ can be recovered and reused without any loss of its catalytic activity.

Keywords: Indium triflate; Catalysed; Chemoselective; Acylal

1. Introduction

Because of their stability towards aqueous acids [1] and bases [2], acylals, the *gem*-diacetates of aldehydes have been considered to be important protecting groups, alternative to acetals [3] for protection of aldehydes, in organic synthesis. They are also used as substrates for nucleophilic substitution reactions [4]. Acylals of α,β-unsaturated aldehydes are important precursors for acetoxy dienes [5] and dihalo vinyl acetates [6]. Their utility in the cotton [7] and other industries [8] is also well established.

Generally, acylals can be prepared from aldehydes by treatment with acetic anhydride and a Brønsted [2,9] or Lewis acid [1,10–12]. Solid acidic materials [13] in heterogeneous media have also been used as catalysts for their formation. Recently, NBS [14], iodine [15], CAN [16], etc. catalysed acylal syntheses have also been reported. Many of the reported methods, however, involve strongly acidic or oxidising conditions, corrosive reagents, high temperature, high catalyst loading, longer reaction time and cumbersome procedures. Moreover, some of these are not chemoselective in terms of aldehydes and keto carbonyl functional groups. In view of these, the search for finding a cost effective, mild and simple chemoselective protocol for synthesis of acylals from aldehydes is still relevant.

In recent years, $In(OTf)_3$ has been used as a potential Lewis acid for many organic transformations [17]. In continuation of our research programme on In(III) mediated organic reactions [18], we herein report the results of $In(OTf)_3$ catalysed expedient, simple and cost effective[1] chemoselective conversion of aldehydes to acylals using a catalyst load as low as 0.01–0.1 mol% (Scheme 1, Table 1).

2. Experimental

2.1. Materials and methods

Infrared (IR) spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded on Bruker DPX-300 (300 MHz) spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. All melting points are uncorrected. All known compounds were characterised by comparing their physical data with those in the literature. Solvents used for experiments were dried and distilled according to literature procedures. Indium triflate (Catalog. No. 44,215-1; Batch No. 10716BI) was purchased from Aldrich Chemical Company.

* Corresponding author.
E-mail address: ghoshrina@yahoo.com (R. Ghosh).

[1] Considering very low catalyst load and recyclability of the catalyst.

1381-1169/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2004.01.018

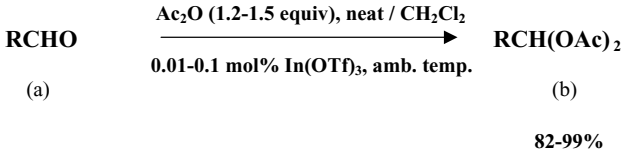
Table 1
$In(OTf)_3$ catalysed conversion of aldehydes to acylals

Entry	RCHO (**a**)	Catalyst load (mol%)	Time (min)	%Yields[a] of $RCH(OAc)_2$ (**b**)
a	Ph-(**1**)	0.1	5	95
b	Ph-(**1**)	0.1	5	93
c	Ph-(**1**)	0.1	5	96 (94)[b]
d	Ph-(**1**)	0.01	0.5	95[c]
e	Ph-(**1**)	0.001	1	94[d]
f	*o*-OMe–C_6H_4-(**2**)	0.1	5	92
g	*m*-OMe–C_6H_4-(**3**)	0.1	12	98
h	*p*-OMe–C_6H_4-(**4**)	0.1	20	88
i	*p*-OMe–C_6H_4-(**4**)	0.01	7	98[c]
j	Piperonal (**5**)	0.1	60	91
k	*m*-OAc–C_6H_4-(**6**)	0.1	40	98
l	*m*-OMe, *p*-OAc–C_6H_3-(**7**)	0.1	30	98
m	*o*-NO_2–C_6H_4-(**8**)	0.1	12	97
n	*m*-NO_2–C_6H_4-(**9**)	0.1	15	98
o	*m*-NO_2–C_6H_4-(**9**)	0.01	0.5	97[c]
p	*p*-NO_2–C_6H_4-(**10**)	0.1	15	99
q	Cinnamaldehyde (**11**)	0.1	15	93
r	Furfural[e] (**12**)	0.1	5	82
s	*p*-*N*,*N*-Dimethylamino benzaldehyde (**13**)	0.1	2 days	No reaction
t	Decanal (**14**)	0.1	30	86
u	*m*-OH–C_6H_4-(**15**)	0.1	40	**6b**, 96
v	Vaniline (**16**)	0.1	2 h	**7b**, 99

[a] Isolated yields.
[b] Value in parenthesis: yield in the tenth experiment using recovered $In(OTf)_3$.
[c] Neat, using 0.01 mol% $In(OTf)_3$.
[d] Neat (50 fold)-PhCHO: Ac_2O 1:1.2, using 0.001 mol% catalyst.
[e] Reaction temperature: 0–20 °C.

2.2. General experimental procedure

(a) In solvent: A mixture of aldehydes (1 equiv.), freshly distilled acetic anhydride (1.2–1.5 equiv.) and $In(OTf)_3$ (0.1 mol%) in dry dichloromethane (3 ml) was stirred at ambient temperature. After completion of the reaction (Table 1) the mixture was diluted with dichloromethane (3 ml) and washed with water (2 ml × 6 ml). The organic layer was dried over anhydrous sodium sulphate and concentrated in vacuum to give pure acylal or chromatographed on silica gel (pet. ether, 60–80 °C ethyl acetate) where necessary. Recovery of $In(OTf)_3$ from the reaction mixture and it reuse: After completion of the reaction, it was quenched with water and the organic layer was washed with water (7 ml × 3 ml). The pooled aqueous layer was evaporated to dryness by repeated codistillation with toluene and finally dried under vacuum at 95–100 °C. Successive recovery of the catalyst with its concomitant use in 10 consecutive experiments (following method a) furnished the acylal in reproducible yield (94%, entry c, Table 1).



Scheme 1. $In(OTf)_3$ catalysed conversion of aldehydes to acylals.

(b) In neat condition: To a mixture of aldehydes (1.0 equiv.) and $In(OTf)_3$ (0.01 mol%) at 5–10 °C was added acetic anhydride (2.0 equiv.) and the reaction mixture was stirred. After completion of the reaction the products were isolated as described in (a).

Physical data of the products:

1b [10b,10c,12,13a,13d]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 44 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 6H), 7.40–7.42 (m, 3H), 7.51–7.54 (m, 2H), 7.68 (s, 1H). IR (KBr): ν_{max} 700, 760, 945, 1010, 1060, 1210, 1240, 1370, 1425, 1500, 1750, 2900–3120 cm^{-1}.

2b [11b]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 73–74 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.12 (s, 6H), 3.85 (s, 3H), 6.92 (bd, *J* 8.3 Hz, 1H), 6.99 (bt, *J* 7.5 Hz, 1H), 7.37 (bt, *J* 7.8 Hz, 1H), 7.49 (bd, *J* 7.6 Hz, 1H), 8.02 (s, 1H). IR (KBr): ν_{max} 760, 950, 995, 1050, 1200, 1245, 1370, 1465, 1495, 1605, 1760, 2980, 3020 cm^{-1}.

3b [11b,16]: Oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 6H), 3.83 (s, 3H), 6.94 (dd, *J* 1.9 and 8.2 Hz, 1H), 7.05–7.12 (m, 2H), 7.32 (t, *J* 7.9 Hz, 1H), 7.65 (s, 1H). IR (neat): ν_{max} 695, 790, 1010, 1040, 1200, 1235, 1365, 1435, 1460, 1490, 1590, 1680, 1755, 2840, 2940, 3000 cm^{-1}.

4b [10b,16]: Oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.11 (s, 6H), 3.82 (s, 3H), 6.92 (d, *J* 8.7 Hz, 2H), 7.46 (d, *J* 8.7 Hz, 2H), 7.62 (s, 1H). IR (neat): ν_{max} 830, 930, 970, 1000, 1055, 1110, 1165, 1200, 1240, 1310, 1360, 1440, 1520, 1590, 1615, 1750, 2840, 2960, 3030 cm^{-1}.

5b [12,13d]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 77–78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.11 (s, 6H), 5.99 (s, 2H), 6.80–6.82 (m, 1H), 7.00–7.02 (m, 2H), 7.57 (s, 1H). IR (KBr): ν_{max} 790, 810, 870, 925, 945, 970, 1000, 1030, 1100, 1130, 1195, 1230, 1360, 1440, 1490, 1605, 1760, 2910 cm^{-1}.

6b [13f]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 76–77 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 6H), 2.31 (s, 3H), 7.13–7.16 (m, 1H), 7.40–7.45 (m, 3H), 7.67 (s, 1H). IR (KBr): ν_{max} 695, 770, 800, 1105, 1200, 1240, 1370, 1450, 1590, 1760, 3060 cm^{-1}.

7b [13d,16]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 90–91 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 6H), 2.32 (s, 3H), 3.87 (s, 3H), 7.04–7.07 (m, 1H), 7.12–7.15 (m, 2H), 7.65 (s, 1H). IR (KBr): ν_{max} 780, 895, 950, 990, 1070, 1120, 1160, 1205, 1250, 1380, 1425, 1465, 1520, 1610, 1750, 1770, 2950 cm^{-1}.

8b [13d]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 85–86 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 6H), 7.56–7.62 (m, 1H), 7.68–7.74 (m, 2H), 8.06 (bd, J 8 Hz, 1H), 8.21 (s, 1H). IR (KBr): ν_{max} 690, 715, 750, 1010, 1095, 1200, 1230, 1360, 1525, 1740, 1765, 3050, 3100 cm^{-1}.

9b [13d]: Off white crystals, (EtOAc-pet. ether, 60–80 °C) mp 64–66 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.17 (s, 6H), 7.61 (t, J 7.9 Hz, 1H), 7.74 (s, 1H), 7.84 (d, J 7.7 Hz, 1H), 8.28 (dd, J 1.1 and 8.2 Hz, 1H), 8.40 (s, 1H). IR (KBr): ν_{max} 670, 680, 695, 740, 815, 1010, 1200, 1235, 1350, 1530, 1760, 3010, 3090 cm^{-1}.

10b [13d]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16, (s, 6H), 7.69–7.73 (m, 3H), 8.26–8.29 (m, 2H). IR (KBr): ν_{max} 695, 750, 825, 855, 940, 970, 1010, 1055, 1200, 1230, 1345, 1370, 1525, 1605, 1760, 2860, 2930, 3010, 3120 cm^{-1}.

11b [10b,10c,12]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 84–85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 6H), 6.21 (dd, J 6.5 and 16.0 Hz, 1H), 6.87 (d, J 16.0 Hz, 1H), 7.27–7.37 (m, 4H), 7.41–7.43 (m, 2H). IR (KBr): ν_{max} 690, 750, 940, 1060, 1135, 1195, 1240, 1370, 1740, 1760, 2920–3080 cm^{-1}.

12b [12,16]: White crystals, (EtOAc-pet. ether, 60–80 °C) mp 52–53 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.14 (s, 6H), 6.39–6.4 (m, 1H), 6.54 (d, J 3.2 Hz, 1H), 7.46 (s, 1H), 7.72 (s, 1H). IR (KBr): ν_{max} 750, 790, 830, 930, 960, 1010, 1060, 1145, 1220, 1370, 1500, 1605, 1750, 3120, 3160 cm^{-1}.

14b [13f]: Oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J 6.9 Hz, 3H), 1.26–1.32 (m, 14H), 1.72–1.76 (m, 2H), 2.08 (s, 6H), 6.77 (t, J 5.6 Hz, 1H). IR (neat): ν_{max} 1005, 1200, 1240, 1370, 1760, 2860, 2920 cm^{-1}.

3. Results and discussion

A variety of aliphatic and aromatic aldehydes reacted in the presence of 0.1 mol% $In(OTf)_3$ with acetic anhydride in dichloromethane at ambient temperature furnishing the corresponding acylals in very good to excellent yields (82–99%) in a very short reaction time (5 min to 1 h). Aromatic aldehydes containing both electron donating (entries f–h, j, Table 1) and electron withdrawing (entries k–n, p, Table 1) groups, irrespective of their positions in the ring, could be converted very efficiently to the respective acylals in excellent yields. The reaction of substrates like furfuraldehyde and cinnamaldehyde proceeded smoothly in high yields without the formation of side products. *p*-*N*,*N*-Dimethylaminobenzaldehyde, however, due to deactivation of the carbonyl group, remained unaffected [13d] under the condition of reaction and the starting material could be recovered even after 2 days. Unlike some of the reported methods (for example with *p*-methoxybenzaldehyde yield 45% [11a]; with *p*-nitrobenzaldehyde, 4% and cinnamaldehyde, 30% [10b], etc.), the present protocol furnished consistently excellent yields with a variety of

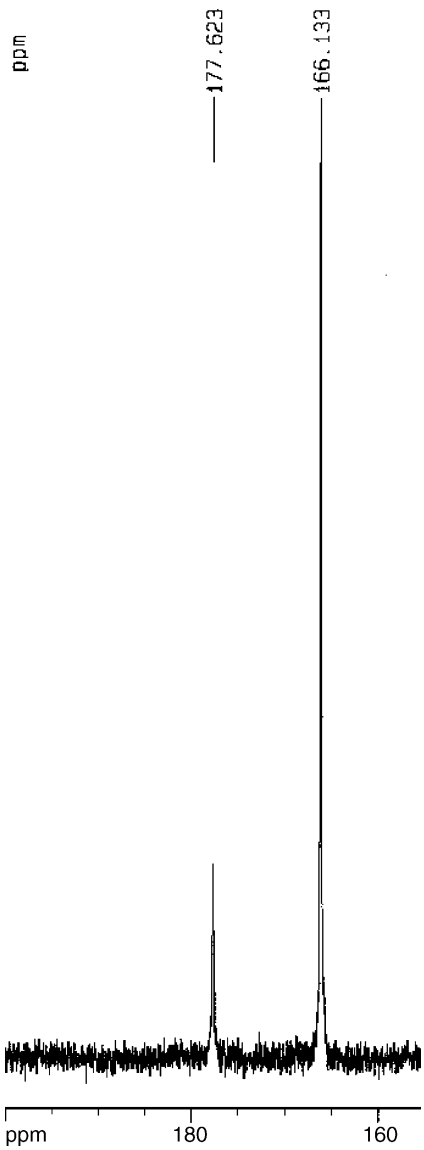


Fig. 1. ^{13}C NMR of the mixture of $In(OTf)_3$ and Ac_2O (*ca* 1:50) in $CDCl_3$.

aromatic and aliphatic aldehydes without any cleavage of acylals during the aqueous work-up. It may also be noted that, as expected [17b], *m*-hydroxy benzaldehyde and vaniline were converted to their corresponding acetylated acylals in respective yields of 96 and 99% with concomitant acetylation of the phenolic –OH groups (entries u and v).

The preparative efficiency of the present method was further established, for example by scaling up of benzaldehyde to approximately 25 fold, resulting in the respective acylal in nearly quantitative yield under the similar reaction condition (entry b, Table 1). After the reaction $In(OTf)_3$ could be recovered and reused without any loss of its activity (entry c, Table 1). The recyclable efficacy of this catalyst was tested by repetition of the experiment several times with the regenerated $In(OTf)_3$ in successive experiments. The yield after the tenth experiment was comparable (94%, Table 1) with that obtained in the presence of fresh $In(OTf)_3$.

Interestingly, the catalytic efficacy of $In(OTf)_3$ was enormously increased (catalyst load approximately 0.01 mol%) in the acylal formation of benzaldehyde and its derivatives incorporating both electron donating and withdrawing groups, under solvent free condition (entries d, i and o, Table 1). In the solvent free condition the reaction could be successfully carried out with 50 fold increase of benzaldehyde even in the presence of 0.001 mol% of the catalyst with almost quantitative conversion to acylal (entry e).

The ^{13}C NMR spectra (Figs. 1 and 2) of the mixture of $In(OTf)_3$ and Ac_2O in $CDCl_3$ in various proportions indicated that discrete AcOTf is formed as evidenced by its ^{13}C NMR peak at δ 177.6, as also reported earlier (δ 177.7) in the $Cu(OTf)_2$ catalysed acetylation reaction of aldehydes [11b]. However, in the high catalyst concentration [$In(OTf)_3$:Ac_2O::1:6], an intense peak of AcOTf appears at δ 180.3; the shift in δ value is possibly due to coordination

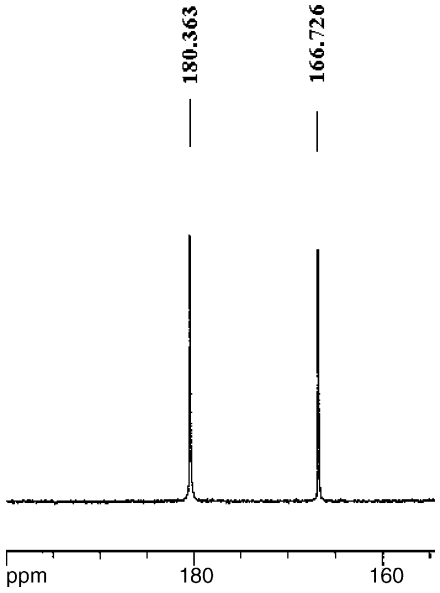
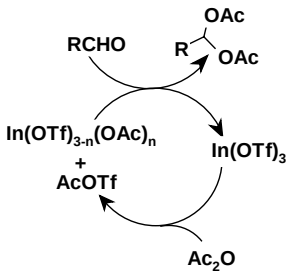


Fig. 2. ^{13}C NMR of the mixture of $In(OTf)_3$ and Ac_2O (*ca* 1:6) in $CDCl_3$.



Scheme 2. Probable catalytic cycle.

of the carbonyl group with the metal. A probable catalytic cycle for the regeneration of $In(OTf)_3$ may be proposed as shown in Scheme 2. The acetylation, thus, involves the initial formation of AcOTf along with $In(OTf)_{3-n}(OAc)_n$ which in turn react with the aldehyde and Ac_2O producing the acylal; $In(OT)_3$ is regenerated in the process. Ketones (acetophenone and cyclohexanone) remained unchanged (even after 24 h) under the similar reaction condition. From a mixture of benzaldehyde and acetophenone in the presence of $In(OTf)_3$ and acetic anhydride in dichloromethane, acetophenone could be recovered unchanged (96%) with concomitant conversion of benzaldehyde to its acylal in 94% yield.

4. Conclusion

In spite of the cost of $In(OTf)_3$ this method, thus, represents a very efficient, expeditious chemoselective transformation of aldehydes to acylals as it involves the use of only 0.01–0.1 mol% catalyst which again is recoverable and reusable.

Acknowledgements

Financial assistance from CSIR, New Delhi to RG (Scheme No. 01/1672/00/EMR-II) and SM (J.R.F.) is gratefully acknowledged. AC is thankful to UGC, New Delhi for financial support in the form of Senior Research Fellowship.

References

[1] K.S. Kochhar, B.S. Bal, R.P. Deshpande, S.N. Rajadhyaksha, H.W. Pinnick, J. Org. Chem. 48 (1983) 1765.
[2] M.J. Gregory, J. Chem. Soc. B (1970) 1201.
[3] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, third ed., Wiley, New York, 1999.
[4] (a) A. Ghribi, A. Alexakis, J.F. Normat, Tetrahedron Lett. 25 (1984) 3079;
(b) L.K. Sydnes, M. Sandberg, Tetrahedron 53 (1997) 12679;
(c) M. Sandberg, L.K. Sydnes, Tetrahedron Lett. 39 (1998) 6361;
(d) J.S. Yadav, B.V. Subba Reddy, G.S.K.K. Reddy, Tetrahedron Lett. 41 (2000) 2695;
(e) B.M. Trost, C.B. Lee, J.M. Weiss, J. Am. Chem. Soc. 117 (1995) 7247.

[5] R.E. Banks, J.A. Miller, M.J. Nunn, P. Stanley, T.R. Weakley, J. Ullah, J. Chem. Soc., Perkin Trans. I (1981) 1096.
[6] B.B. Srider, S.G. Amim, Synth. Commun. 8 (1978) 117.
[7] J.G. Frick, R.J. Harper, J. Appl. Polym. Sci. 29 (1984) 1433.
[8] W.R. Eanderson, Eur. Pat. Appl. FP. 125, 781;
W.R. Eanderson, Chem. Abstr. 102 (1985) 64010K.
[9] F. Freeman, E.M. Karchevski, J. Chem. Eng. Data 22 (1979) 355.
[10] (a) I. Scriabine, Bull. Soc. Chim. Fr. (1961) 1194;
(b) J.K. Michie, J.A. Miller, Synthesis (1981) 824;
(c) G.A. Olah, A.K. Mehrotra, Synthesis (1982) 962
[11] (a) V.K. Aggarwal, S. Fonquerna, G.P. Vennal, Synlett (1998) 849;
(b) K.L. Chandra, P. Saravanan, V.K. Singh, Synlett (2000) 359
[12] J.S. Yadav, B.V.S. Reddy, Ch. Srinivas, Synth. Commun. 32 (2002) 1175.
[13] (a) C. Pereira, B. Gigante, M.J. Marcelo-Curto, H. Carreyre, G. Perot, M. Guisnet, Synthesis (1995) 1077;
(b) P. Kumar, V.R. Hedge, T.P. Kumar, Tetrahedron Lett. 36 (1995) 601;
(c) T.-S. Jin, Y.-R. Ma, Z.-H. Zhang, T.-S. Li, Synth. Commun. 27 (1997) 3379;
(d) T.-S. Li, Z.-H. Zhang, Y.-J. Gao, Synth. Commun. 28 (1998) 4665;
(e) M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, M. Nocchetti, Tetrahedron Lett. 43 (2002) 2709;
(f) G.P. Romanelli, H.J. Thomas, G.T. Baronetti, J.C. Autino, Tetrahedron Lett. 44 (2003) 1301.
[14] B. Karimi, H. Seradj, G.R. Ebrahimian, Synlett (2000) 623.
[15] N. Deka, D.S. Kalita, R. Borah, J.C. Sarma, J. Org. Chem. 62 (1997) 1563.
[16] S.C. Roy, B. Banerjee, Synlett (2002) 1677.
[17] (a) T. Ali, K.K. Chauhan, C.G. Frost, Tetrahedron Lett. 40 (1999) 5621;
(b) K.K. Chauhan, C.G. Frost, I. Love, D. Waite, Synlett (1999) 1743;
(c) S. Gadhwal, J.S. Sandhu, J. Chem. Soc., Perkin Trans. I (2000) 2827;
(d) K.K. Chauhan, C.G. Frost, J. Chem. Soc., Perkin Trans. I (2000) 3015;
(e) D. Prajapati, D.D. Laskar, J.S. Sandhu, Tetrahedron Lett. 41 (2000) 8639;
(f) T.-P. Loh, Q.-Y. Hu, L.T. Ma, J. Am. Chem. Soc. 123 (2001) 2450;
(g) T.-P. Loh, K.-T. Tan, Q.-Y. Hu, Angew. Chem. Int. Ed. Engl. 40 (2001) 2921;
(h) J.S. Yadav, B. Subba Reddy, V.R. Srinivasa Rao, G. Veerendhar, K. Nagaiah, Tetrahedron Lett. 42 (2001) 8067;
(i) T.-P. Loh, Q.-Y. Hu, K.-T. Tan, H.-S. Cheng, Org. Lett. 3 (2001) 2669;
(j) G.K. Friestad, H. Ding, Angew. Chem. Int. Ed. Engl. 40 (2001) 4491;
(k) T.-P. Loh, L.-C. Feng, J.-Y. Yang, Synthesis (2002) 937;
(l) J.S. Yadav, B.V.S. Reddy, K. Sadashiv, K. Harikishan, Tetrahedron Lett. 43 (2002) 2099;
(m) K. Kazahaya, N. Hamada, S. Ito, T. Sato, Synlett (2002) 1535;
(n) S. Muthusamy, S.A. Babu, C. Gunanathan, Tetrahedron Lett. 43 (2002) 3133;
(o) C.G. Frost, J.P. Hartley, D. Griffin, Tetrahedron Lett. 43 (2002) 4789.
[18] (a) R. Ghosh, D. De, B. Shown, S.B. Maiti, Carbohydr. Res. 321 (1999) 1;
(b) R. Ghosh, A. Chakraborty, D. De, S.B. Maiti, Indian J. Chem. 41B (2002) 1299;
(c) R. Ghosh, A. Chakraborty, D.K. Maiti, S.B. Maiti, Indian J. Chem. 41B (2002) 583;
(d) R. Ghosh, A. Chakraborty, D.K. Maiti, Synth. Commun. 33 (2003) 1623;
(e) R. Ghosh, A. Chakraborty, D.K. Maiti, Indian J. Chem. 42B (2003) 602;
(f) R. Ghosh, S. Maiti, A. Chakraborty, D.K. Maiti, J. Mol. Catal. A: Chem. 210 (2004) 53.