Synergistic enhancement of catalytic activity of $InCl_3$ - Me_3SiCl combination towards carbon Ferrier rearrangement in glycal derivatives

Rina Ghosh,* Arijit Chakraborty, and Swarupananda Maiti

Department of Chemistry, Jadavpur University, Kolkata 700 032, India
E-mail: ghoshrina@yahoo.com

Dedicated to Professor (Mrs.) A. Chatterjee on her 85th anniversary

(received 21 Jan 04; accepted 23 Apr 04; published on the web 30 Apr 04)

Abstract

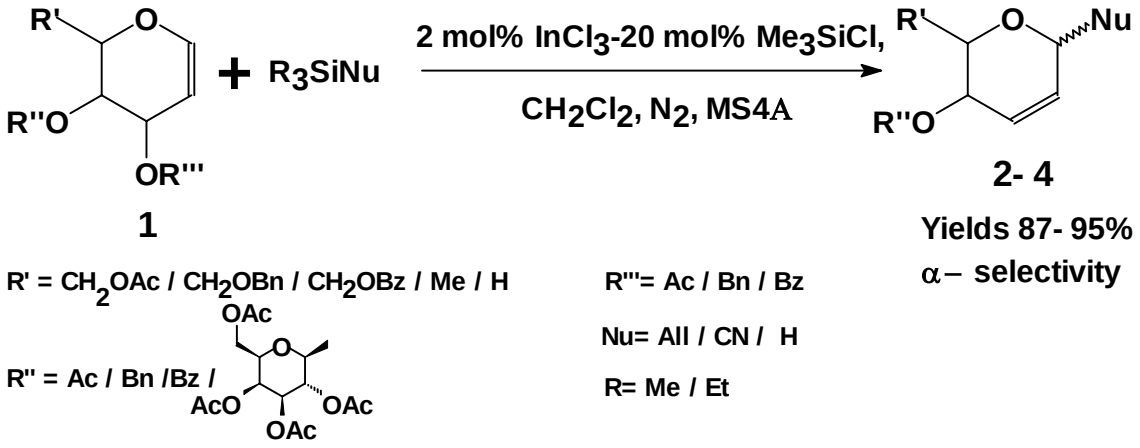
$InCl_3$ (2 mol%) in combination with Me_3SiCl (20 mol%) efficiently catalyze Ferrier rearrangement in a variety of glycal derivatives with different silyl nucleophiles to afford the corresponding C-pseudoglycals or unsaturated pyrans in nearly quantitative yields. The stereoselectivities of the C-glycosides are good to excellent in favor of the α-anomers. A stoichiometric amount of $InCl_3$ is necessary for similar transformations in the absence of Me_3SiCl. The $InCl_3$ can be recovered and reused without any loss of its activity.

Keywords: $InCl_3$, Me_3SiCl, combination catalyst, glycals, C-glycosylation, carbon Ferrier rearrangement

Introduction

Because of numerous applications, the synthesis of C-glycosides has attracted considerable attention during the last two decades. These are potential chiral building blocks for the synthesis of a number of biologically important macromolecules like palytoxin, spongistatin, halichondrin *etc*.[1] The pharmacological importance of naturally occurring C-nucleosides and inhibitory role of C-glycosides towards carbohydrate processing enzymes add more impetus in this direction.[2] Because of the presence of the double bond or cyano group, which can be readily functionalized, allyl C-pseudoglycals,[3] glycosyl cyanides or pyrans are attractive chiral synthetic intermediates.[4] Since its first report[5] the Ferrier rearrangement has been extensively exploited for the C-glycosylation reactions of glycals. A variety of Lewis acids[6] and other reagents[7] have been utilized towards this end. However, many of the reported procedures have their own limitations in terms of yields, stereoselectivity, amount and reusability of the catalyst, besides the stringent experimental conditions in some cases. In an earlier report[6f] we demonstrated that a

stoichiometric amount of $InCl_3$ promotes carbon Ferrier rearrangement in glycal derivatives in excellent yields and stereoselectivities. While we were exploring the possibility of a catalytic version of $InCl_3$ mediated C-glycosylation, Baba *et. al.*[8] reported that a number of organic transformations can be efficiently carried out based on the combination catalyst incorporating $InCl_3$ and $R^1R^2R^3SiCl$ due to remarkable enhancement of Lewis acidity of such systems. We were delighted to observe that a combination of $InCl_3$ and Me_3SiCl generates a highly efficient catalyst system in C-glycosylation of glycals. We present, herein, our results on Ferrier rearrangement in glycal derivatives using this combination catalyst (Schemes 1 and 2, Tables 1 and 2).



Scheme 1

Results and Discussion

By varying the proportions of the $InCl_3$-Me_3SiCl combination (Table 1), the minimum catalyst load was established in the reaction of per-O-acetyl-D-glucal (**1a**) with allyltrimethylsilane in dichloromethane at room temperature in the presence of 4Å molecular sieves. Thus, a combination of 2 mol% $InCl_3$ and 20 mol% Me_3SiCl was found to be the optimum condition for maximum yield and stereoselectivity (entry 6, Table 1). It may be mentioned that C-glycosylation in glucal, **1a** can also be effected using ca 50 mol% Me_3SiCl in excellent yield but with reduced stereoselectivity (entry 3, Table 1), whereas a stoichiometric amount of $InCl_3$ is necessary for the generation of allyl C-pseudoglycal (**2a**) from **1a** in almost quantitative yield with very good stereoselectivity (entry 1, Table 1). Thus the enhancement of the catalytic activity and high stereoselectivity of the $InCl_3$-Me_3SiCl combination may involve a synergistic process.

Table 1. Effect of combined catalyst ($InCl_3$-Me_3SiCl) on Ferrier rearrangement in per-O-acetyl-D-glucal

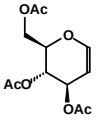
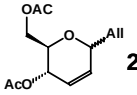
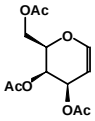
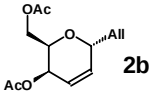
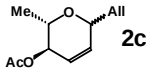
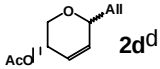
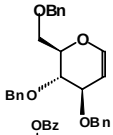
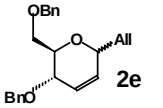
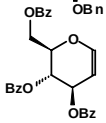
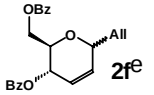
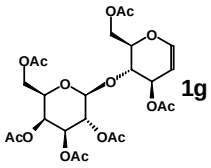
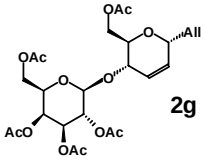
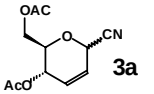
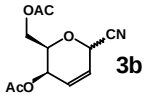
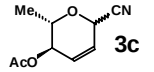
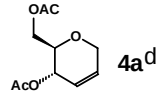
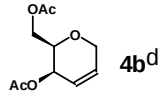
Entry	Catalyst load (mol%)	Time (h)	% Yield[a]	α/β [b]
1	$InCl_3$ (100) + Me_3SiCl (0)	1	95	9:1
2	$InCl_3$ (50) + Me_3SiCl (0)	24	incomplete	
3	$InCl_3$ (0) + Me_3SiCl (50)	3.5	95	4:1
4	$InCl_3$ (0) + Me_3SiCl (30)	24	65	
5	$InCl_3$ (5) + Me_3SiCl (30)	1	88	7:1
6	$InCl_3$ (2) + Me_3SiCl (20)	1	90	9:1
7	$InCl_3$ (2) + Me_3SiCl (10)	24	17	
8	$InCl_3.3H_2O$ (2) + Me_3SiCl (20)	1	86	8.7:1

[a] Isolated chromatographed yields. [b] by ^{1}H-NMR.

Accordingly, per-O-acetyl-D-glucal (**1a**) reacted with allyltrimethylsilane in the presence of 2 mol% $InCl_3$ and 20 mol% Me_3SiCl at room temperature, in dichloromethane in the presence of molecular sieves within 1 hour affording the corresponding allyl C-glucoside in 90 % yield and 9:1 α-anomeric selectivity (entry 1, Table 2).

Similarly, per-O-acetyl-D-galactal (**1b**), -L-rhamnal (**1c**) and –D-arabinal (**1d**) also were converted efficiently to their respective C-pseudoglycals in excellent yields with nearly exclusive α-anomeric selectivities (entries 5-7, Table 2). The mild reaction condition was amicable towards benzyl and benzoyl protections also. Thus, the yields and α-anomeric selectivities of both allyl per-O-benzyl- and per-O-benzoyl-C-pseudoglucals (**2e** and **2f**) were equally excellent under similar reaction conditions (entries 8 and 9, Table 2). Per-O-benzoyl-D-glucal (**1f**), however, needed the presence of 5 mol% $InCl_3$ and 20 mol% Me_3SiCl for efficient conversion to the product. The efficacy of the combination catalyst system was further extended in the effective transformation of per-O-acetyl-D-lactal (**1g**) to its corresponding allyl C-pseudo lactal (**2g**) in nearly quantitative yield and exclusive α-selectivity (entry 10, Table 2). Other silyl nucleophiles, such as, trimethylsilyl cyanide and triethylsilane were also employed in such reactions in the presence of this catalyst system with the generation of the corresponding C-glycosyl cyanides (entries 11-13, Table 2) and unsaturated pyran derivatives (entries 14 and 15, Table 2) with equal efficacy. However, the anomeric selectivities of glycosyl cyanides were lower than those of the allyl C-pseudoglycals.

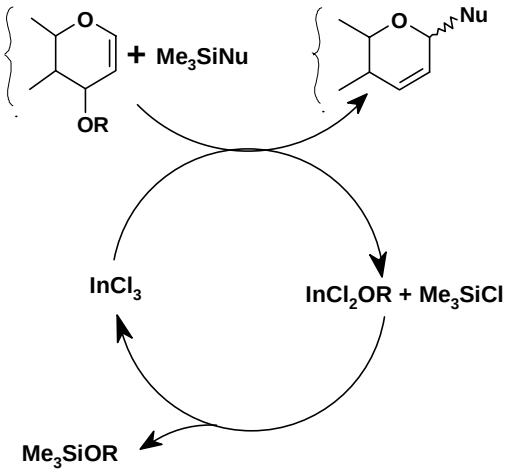
Table 2. 2 mol% $InCl_3$ and 20 mol% Me_3SiCl catalysed Ferrier rearrangement of glycal derivatives with silyl nucleophiles

Entry	Substrate	Nucleophile/Time	Product	% Yield[f] / α/β[g]	Ref
1	 **1a**	Me_3SiAll / 1h (1.2 equiv.)	 **2a**	90 / 9:1	6d
2	**1a**	"/ 5min	**2a**[a]	95 / 9:1	
3	**1a**	" /1h	**2a**[b]	92 / 9:1	
4	**1a**	" /1h	**2a**[c]	92 / 9:1	
5	 **1b**	" / 3h	 **2b**	91 / α only	6f,i
6	 **1c**	"/ 2h	 **2c**	93 / 12:1	6f
7	 **1d**	" / 1h	 **2d**[d]	87 / 12:1	6f
8	 **1e**	" / 3h	 **2e**	89 / 13:2	6i
9	 **1f**	" / 3.5h	 **2f**[e]	94 / 7:1	6i,7b
10	 **1g**	" / 1h	 **2g**	93 / α only	6j
11	**1a**	Me_3SiCN / 1h (1.5 equiv.)	 **3a**	90 / 11:5[h]	6i,j
12	**1b**	" / 3h	 **3b**	90 / 10:3[h]	6i,j
13	**1c**	" / 1h	 **3c**	94 / 7:5[h]	6j
14	**1a**	Et_3SiH / 4h (1.2 equiv.)	 **4a**[d]	90	6k
15	**1b**	" / 4h	 **4b**[d]	95	6k

[a] neat. [b] with recovered $InCl_3$. [c] scale up with 0.6g **1a**. [d] reaction mixture was stirred at 20-25°. [e] in the presence of 5 mol% $InCl_3$- 20 mol% Me_3SiCl. [f] isolated chromatographed yields. [g] anomeric ratios were determined by ^{1}H-NMR. [h] based on the isolated yields of anomers.

The present catalyst system is equally effective in solvent free condition. Thus, **1a** reacted in neat with allyltrimethylsilane in the presence of 2 mol% $InCl_3$ and 20 mol% Me_3SiCl forming **2a** within 5 minutes with equal efficacy (entry 2, Table 2). $InCl_3$ can be recovered and reused without any loss of its activity after the reaction (entry 3, Table 2). A similar efficiency of the catalyst system was observed in a scaled up experiment (6 fold) of **1a** that also produced **2a** in 92% yield and 9:1 α selectivity (entry 4, Table 2).

A plausible catalytic cycle of the reaction for regeneration of $InCl_3$ may be depicted as shown in Scheme 2. In this combination catalyst system, Me_3SiCl probably assists in the regeneration of $InCl_3$ from the $InCl_2OR$ intermediates.



Scheme 2. Plausible catalytic cycle for regeneration of $InCl_3$.

In conclusion, we have demonstrated that $InCl_3$ in combination with Me_3SiCl acts as an efficient catalyst system for stereoselective C-glycosylation of glycal derivatives. The advantages of the present method are: its operational simplicity, low catalyst load, excellent yields, excellent stereoselectivities with allyl C-pseudoglycals and the reusability of the recovered $InCl_3$ retaining its complete activity. The present methodology, thus constitutes an important addition and may gainfully substitute some of the existing procedures.

Experimental Section

General Procedures. All melting points are uncorrected. All known compounds were characterized by IR, NMR and by comparing their physical data with those in the literature. IR spectra were recorded on Perkin Elmer 297 spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker DPX-300 (300 MHz) spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. Optical rotations were measured on Perkin Elmer electronic polarimeter 241 or on Jasco digital polarimeter model P-1020.

General experimental conditions for preparation of C-pseudoglycals: (a) In solvent

To a solution of glycal derivative (1 equiv.) in dry CH_2Cl_2 (3 ml) were added R_3SiNu (1.2-1.5 equiv.) and activated molecular sieves 4Å (~300 mg) under nitrogen. Finally Me_3SiCl (20 mol%) and $InCl_3$ (2 mol%) were added to the reaction mixture at 0°C and it was stirred at room temperature (30-32°C) till completion (checked by TLC, EtOAc-pet. ether). Then the mixture was filtered through celite bed, the bed was washed well with CH_2Cl_2 and the combine filtrate and washings (20 ml) were washed subsequently with $NaHCO_3$ (20 ml) and H_2O (2 x 15 ml). The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the crude residue was purified on silica-gel (60-120 mesh) column with EtOAc-pet. ether (60-80º).

(b) Typical procedure in solvent free condition. To a mixture of per-O-acetyl-D-glucal (100 mg, 0.37 m mol) and Me_3SiAll (0.07 ml, 0.44 m mol) was added Me_3SiCl (0.01 ml, 20 mol%) and $InCl_3$ (1.6 mg, 2 mol%) at 0°C and the mixture was stirred for 5 minutes at room temperature. After completion the mixture was diluted with CH_2Cl_2 and washed subsequently with $NaHCO_3$ (20 ml) and water (2 x 15 ml). The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and finally purified by column chromatography on silica gel (5% EtOAc-pet. ether) affording pure **2a** as syrup (88.6 mg, 95%, α/β 9:1).

Physical and spectroscopic data of products

2a. Elution of the product with 5% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_D^{26}$ +66.2 (c 1, $CHCl_3$); IR (neat) ν_{max} 3080, 2940, 1745, 1640, 1430, 1360, 1230, 1035, 905, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 6H), 2.28-2.37 (m, 1H), 2.42-2.50 (m, 1H), 3.94-3.99 (dt, *J* 6.5 and 3.5 Hz, 1H), 4.13-4.18 (dd, *J* 11.8 and 3.5 Hz, 1H), 4.21-4.32 (m, 2H), 5.10-5.18 (m, 3H), 5.77-5.96 (m, 3H).

2b. Elution of the product with 5% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_D^{26}$ –267 (c 1.2, $CHCl_3$); IR (neat) ν_{max} 3080, 2940, 1740, 1640, 1435, 1370, 1230, 1050, 920, 840, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H), 2.08 (s, 3H), 2.27-2.34 (m, 1H), 2.39-2.49 (m, 1H), 4.11-4.16 (m, 1H), 4.18-4.22 (m, 2H), 4.34-4.38 (m, 1H), 5.07-5.09 (dd, *J* 2.4 and 4.8 Hz, 1H), 5.11 (bs, 1H), 5.13-5.18 (m, 1H), 5.78-5.92 (m, 1H), 5.96-6.01 (ddd, *J* 1.8, 4.8 and 10.3 Hz, 1H), 6.04-6.08 (dd, *J* 2.8 and 10.3 Hz, 1H).

2c. Elution of the product with 2% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_D^{26}$ –92.03 (c 1.5, $CHCl_3$); IR (neat) ν_{max} 3070, 3040, 2980, 2940, 1740, 1640, 1440, 1370, 1230, 1190, 1130, 1095, 1030, 910, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.23-1.25 (d, *J* 6.5 Hz, 3H), 2.09 (s, 3H), 2.29-2.36 (m, 1H), 2.40-2.45 (m, 1H), 3.89-3.97 (m, 1H), 4.17-4.24 (m, 1H), 4.87-4.90 (m, 1H), 5.09-5.17 (m, 2H), 5.72-5.96 (m, 3H).

2d. Elution of the product with 2% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_{578}^{25}$ +152.3 (c 0.24, $CHCl_3$); IR (neat) ν_{max} 3080, 3040, 2980, 2940, 2860, 1735, 1640, 1430, 1370, 1230, 1095, 1030, 915, 820, 775, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H), 2.24-2.40 (m, 2H), 3.51-3.57 (dd, *J* 6.9 and 11.4 Hz, 1H), 4.10-4.15 (dd, J 5.0 and 11.4 Hz, 1H), 4.16-4.22 (m, 1H), 5.09-5.16 (m, 2H), 5.23-5.28 (m, 1H), 5.76-5.94 (m, 3H).

2e. Elution of the product with 4% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_D^{26}$+38.6 (c 0.9, $CHCl_3$); IR (neat) ν_{max} 3060, 3030, 1640, 1495, 1450, 1390, 1365, 1305, 1205, 1090, 915, 735, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.26-2.35 (m, 1H), 2.44-2.51 (m, 1H), 3.66-3.68 (m, 2H), 3.80-3.85 (m, 1H), 3.98-4.00 (m, 1H), 4.22-4.27 (m, 1H), 4.43-4.66 (m, 4H), 5.06-5.13 (m, 2H), 5.79-5.95 (m, 3H), 7.26-7.35 (m, 10H).

2f. Elution of the product with 3% EtOAc-pet. ether; α-anomer: white crystals, mp. 78-79°C (EtOAc : pet. ether 60-80); $[\alpha]_D^{26}$+90.8 (c 0.65, $CHCl_3$); IR (KBr) ν_{max} 3070, 2950, 2880, 1750, 1640, 1600, 1580, 1490, 1450, 1375, 1330, 1310, 1265, 1170, 1100, 1065, 1045, 1025, 990, 810, 710 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 2.35-2.44 (m, 1H), 2.49-2.59 (m, 1H), 4.28-4.33 (m, 1H), 4.36-4.41 (m, 1H), 4.49-4.52 (m, 2H), 5.06-5.10 (m, 1H), 5.11-5.17 (dd, J 1.59 and 17.1 Hz, 1H), 5.47-5.49 (m, 1H), 5.97-6.00 (m, 3H), 7.38-7.46 (m, 4H), 7.52-7.57 (m, 2H), 8.02-8.07 (m, 4H).

2g. Elution of the product with 25% EtOAc-pet. ether; α-anomer: syrup, $[\alpha]_{578}^{25}$+24.1 (c 0.65, $CHCl_3$); IR (neat) ν_{max} 3080, 2980, 2940, 2890, 1750, 1640, 1430, 1365, 1250-1220, 1165, 1080-1040, 915, 740 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 1.98 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 2.24-2.33 (m, 1H), 2.41- 2.51 (m, 1H), 3.80-3.85 (m, 1H), 3.91-3.95 (t, *J* 6.6 Hz, 1H), 4.02-4.06 (dd, *J* 1.4 and 8 Hz, 1H), 4.09-4.25 (m, 5H), 4.58-4.60 (d, *J* 8 Hz, 1H), 4.99-5.04 (dd, *J* 3.4 and 10.4 Hz, 1H), 5.09-5.14 (m, 2H), 5.20-5.30 (m, 1H), 5.39-5.40 (d, *J* 3.2 Hz, 1H), 5.76-5.90 (m, 2H), 5.95-5.99 (d, *J* 10.5, 1H).

3a. Elution of the product with 15% EtOAc-pet. ether; α-anomer: white needles, mp. 88-89°C (EtOAc : pet. ether, 60-80); $[\alpha]_D^{28.2}$ –11.94 (c 0.82, $CHCl_3$); IR (KBr) ν_{max} 3010, 2970, 2940, 2900, 1745, 1440, 1415, 1375, 1215, 1140, 1095, 1045, 980, 905, 830, 720, 670, 650, 610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 2.12 (s, 3H), 4.01-4.07 (m, 1H), 4.26-4.27 (d, *J* 3.9 Hz, 2H), 5.06-5.09 (m, 1H), 5.32-5.37 (m, 1H), 5.87-5.92 (m, 1H), 6.01-6.06 (m, 1H).

3b. Elution of the product with 17% EtOAc-pet. ether; α-anomer: white needles, mp. 120°C (EtOAc : pet. ether 60-80); $[\alpha]_{578}^{24}$ –385.9 (c 0.44, $CHCl_3$); IR (KBr) ν_{max} 2940, 1735, 1380, 1365, 1240, 1090, 1050-1020, 910, 840 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$, $CDCl_3$): δ 2.09 (s, 3H), 2.10 (s, 3H), 4.22-4.25 (m, 3H), 5.14-5.18 (m, 2H), 6.05-6.09 (dd, J 3.7 and 9.9 Hz, 1H), 6.25-6.30 (ddd, J 1.9, 5.5 and 9.9 Hz, 1H).

3c. Elution of the product with 3% EtOAc- pet. ether; α-anomer: white needles, mp. 65 °C (Et_2O-pet.ether, 40-60^0); $[\alpha]_D^{26}$ –306.8 (c 0.34, $CHCl_3$); IR (neat) ν_{max} 2980, 2930, 1735, 1440, 1370, 1230, 1195, 1130, 1100, 1030, 920, 800 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 1.34 (d, J 6.3 Hz, 3H), 2.09 (s, 3H), 3.74 (q, J 6.5 Hz, 1H), 5.08 (bs, 1H), 5.90 (d, J 10.3 Hz, 1H), 6.01 (d, J 10.1 Hz, 1H);

4a. Elution of the product with 8% EtOAc-pet. ether; syrup, $[\alpha]_{578}^{24}$ +89.7 (c 0.78, $CHCl_3$); IR (neat) ν_{max} 3040, 2940, 2815, 1740, 1445, 1445, 1370, 1230, 1030-1050, 965, 905, 815, 750 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.11 (s, 3H), 3.71-3.76 (m, 1H), 4.15-4.26 (m, 4H), 5.24-5.29 (m, 1H), 5.74-5.80 (m, 1H), 5.92-5.98 (m, 1H).

4b. Elution of the product with 10% EtOAc-pet. ether; syrup, $[\alpha]_{578}^{24}$ –321.36 (c 0.76, $CHCl_3$); IR (neat) ν_{max} 3040, 2840, 2720, 1735, 1440, 1365, 1220-1245, 1185, 1090, 1045, 1015, 950, 905, 830, 810, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 6H), 3.86-3.91(m, 1H), 4.15-4.19 (m, 1H), 4.22-4.27 (m, 2H), 4.31-4.38 (m, 1H), 5.09-5.13 (m, 1H), 5.98-6.04 (m, 1H), 6.08-6.13 (m, 1H).

Acknowledgements

Financial assistances from CSIR, New Delhi (Scheme No. 01/1672/00/EMR-II) to RG and SM (JRF) and from UGC, New Delhi to AC (SRF) are gratefully acknowledged. Thanks are also extended to Professor A. Patra, University of Calcutta, India for his generous help in recording optical rotations.

References

1. (a) Lewis, M. D.; Cha, J. K.; Kishi, Y, *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Paterson, L.; Keown, L. E. *Tetrahedron Lett.* **1997**, *38,* 5727.
2. (a) Weatherman, R. V.; Mortell, K. H.; Chervenak, M.; Kiessling, L. L.; Tonne, E. J. *Biochemistry* **1996**, *35*, 3619. (b) Sutherlin, D. P.; Stark, T. M.; Hughes, R.; Armstrong, R. W. *J. Org. Chem*. **1996**, *61*, 8350.
3. Takhi, M.; Abdel Rahman, A. –H.; Schmidt, R. R. *Tetrahedron Lett*. **2001**, *42*, 4053.
4. (a) Hanessian, S. *Total Synthesis of Natural Products: The Chiron Approach*; Pergamon Press: Oxford, 1984. (b) Nicolaou, K. C.; Dugan, M. E.; Hwang, C. K.; Somers, P. K.; *J. Chem. Soc., Chem. Comm*. **1985**, 1359. (c) Wincott, F. E.; Danishefsky, S. J.; Schutte, G. *Tetrahedron Lett*. **1987**, *28*, 4951.
5. Ferrier, R. J.; Prasad, N. *J. Chem. Soc.* C **1969**, 570.
6. (a) Danishefsky, S. J.; Keerwin, J. F. *J. Org. Chem*. **1982**, *47*, 3803. (b) Grynkiewicz, G.; BeMiller, J. N. *J. Carbohydr. Chem.* **1982**, *1*, 121. (c) Dawe, R. D.; Fraser-Reid, B. *J. Chem. Soc., Chem. Comm*. **1981**, 1180. (d) Marco-Contelles, J. L.; Fernandez, C.; Gomez, A.; Martin-Leon, N.; *Tetrahedron Lett.* **1990**, *31*, 1467. (e) Toshima, K.; Miyamito, N.; Matsuo, G.; Nakata, M.; Matsumura, S. *J. Chem. Soc., Chem. Comm.* **1996**, 1379. (f) Ghosh, R.; De, D.; Shown, B.; Maiti, S. B. *Carbohydr. Res*. **1999**, *321*, 1. (g) Yadav, J. S.; Subba Reddy, B. V.; Chandraiah, L.; Reddy, K. S.; *Carbohydr. Res*. **2001**, *332*, 221. (h) Yadav, J. S.; Subba Reddy, B. V.; Chand, P. K. *Tetrahedron Lett*. **2001**, *42*, 4057. (i) Yadav, J. S.; Reddy, B. V. S. *Synthesis* **2002**, 511. (j) Ghosh, R.; Chakraborty, A.; Maiti, D. K. *Synth. Comm*. **2003**, *33*, 1623. (k) Das, S. K.; Reddy, K. A.; Abbineni, C.; Roy, J.; Rao, K. V. L. N.; Sachwani, R. H.; Iqbal, J. *Tetrahedron Lett*. **2003**, *44*, 4507.

7. (a) Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M. *Chem. Lett*. **1993**, 2013. (b) Yadav, J. S.; Subba Reddy, B. V.; Rao, C. V.; Chand, P. K.; Prasad, A. R. *Synlett* **2001**, 1638.
8. Onishi, Y.; Ito, T.; Yasuda, M.; Baba, A. *Tetrahedron* **2002**, *58*, 8227.

