Trimethylsilylnitrate: a useful reagent for direct synthesis of 2-deoxy-\(O\)-glycosides from glycals$^5$

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This paper is respectfully dedicated to Prof. P.T. Narasimhan
on the occasion of his 75th birthday
(received 03 Mar 04; accepted 19 May 04; published on the web 22 May 04)

Abstract: Trimethylsilylnitrate acts as a useful reagent for the addition of alcohols to glycals forming 2-deoxy-\(O\)-glycosides in good to excellent yields.

Keywords: 2-Deoxy-\(O\)-glycosides, trimethylsilylnitrate, glycals, ClSiMe\(_3\), AgNO\(_3\)

Introduction

2-Deoxy-\(O\)-glycosides are integral parts of many prominent biologically active natural products$^2$ such as aureolic acids,$^3$ cardiac glycosides$^4$ and antitumor agents such as calicheamycin.$^5$ In view of this, many synthetic methods have been developed for the stereoselective synthesis of \(\alpha\) or \(\beta\)-2-deoxy-\(O\)-glycosides. Although, synthesis of 2-deoxy-\(O\)-glycosides from 2-deoxysugars bearing a leaving group at the anomeric centre is well known, control of the stereochemistry of the \(O\)-glycosidic bond is somewhat difficult because of the lack of a stereodirecting substituent at C-2. The leaving groups at the anomeric centre include halides,$^{6a,b}$ thioglycosides,$^{6c}$ n-pentenyl glycosides,$^{6d}$ trichloroacetimidates,$^{6e}$ sulfoxides,$^{6f}$ phosphites,$^{6g}$ and phosphoramidites.$^{6h}$ These methods, however, need prior preparation of 2-deoxysugars with a desired leaving group at the anomeric centre. Additionally, iodoglycosylation of glycals using iodonium dicollidine perchlorate (IDCP)$^{7a,b}$ or ceric ammonium nitrate (CAN)-NaI$^{7c,d}$ are other methods reported in literature but they require reductive de-iodination in the next step to obtain 2-deoxy-\(O\)-glycosides. Apart from this, direct addition of alcohols to glycals catalyzed by a protic acid (MeOH-HCl,$^{8a}$ cation-exchange resin AG 50 WX$_2$,\(^{8b}\) Ph$_3$P- HBr$^{8c}$) or a Lewis acid (BBr$_3$ or BCl$_3$\(^{9a}$ and CeCl$_3$\(\cdot\)7H$_2$O-NaI\(^{9b}$) has also been reported for this purpose. One of the problems, however, in these direct glycosylations is the possibility of the Ferrier reaction and hence not all

$^5$ Part 9 in the series, ‘Transformations in Carbohydrate Chemistry’ For part 8, see ref. 1.
* Corresponding author.
the protic or Lewis acids are suitable for this purpose. Nevertheless this one pot procedure is useful and hence more recently a polymer-bound Lewis acid\textsuperscript{10} has also been employed for the synthesis of 2-deoxy-\textit{O}-glycosides.

**Results and Discussion**

Recently we have reported a CAN catalyzed transformation of glycals to 2-deoxy-\textit{O}-glycosides under mild conditions.\textsuperscript{11} As part of our ongoing programme\textsuperscript{1,12} to develop newer methods in functionalizing glycals towards obtaining useful carbohydrate intermediates, we have now found that trimethylsilylnitrate (TMSONO\textsubscript{2}), readily made from ClSiMe\textsubscript{3} and AgNO\textsubscript{3}, works as a useful reagent for the synthesis of 2-deoxy-\textit{O}--glycosides. TMSONO\textsubscript{2} has been used\textsuperscript{13} in conjunction with BF\textsubscript{3}·Et\textsubscript{2}O as a source of NO\textsubscript{2}\textsuperscript{+} for nitration of aromatics.

![Scheme 1](image)

**Scheme 1**

We have reported\textsuperscript{14} its use along with CrO\textsubscript{3} to convert olefins into \textit{α}-nitroketones and in converting cyclic ethers into lactones. More recently, we have found\textsuperscript{1} that TMSONO\textsubscript{2} along with Me\textsubscript{3}SiN\textsubscript{3} converts glycals into the corresponding 2-deoxy-\textit{1}-glycosyl azides which, in turn, can be converted into 2-deoxy-\textit{β}-1-\textit{N}--glycopeptides. In an effort to explore the potential of TMSONO\textsubscript{2}, we report in this paper that TMSONO\textsubscript{2} permits addition of alcohols to glycals forming 2-deoxy-\textit{O}--glycosides in good to excellent yields at room temperature in 2-5 h. A wide variety of alcohols were added on to glycals in the presence of 1 eq. of TMSONO\textsubscript{2}. Initial experiments were performed using catalytic amount of TMSONO\textsubscript{2}, however, the glycals were found to be largely unreacted. Our results are summarized in Table-1. In all the cases, \textit{α}-isomer was found to be the major product and in some cases, with a galactal derivative 1 (Scheme 1), it was the exclusive product(entries 1, 2, 11). A disaccharide (entry 14) was also made using this method with galactal 1, although the yield was moderate. When we used compound 2 (a glucal derivative) under the same reaction conditions, we observed formation of a trace amount of the Ferrier product along with 2-deoxy-\textit{O}--glycosides (entries 16, 17).
## Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Glycal</th>
<th>Acceptor</th>
<th>Product</th>
<th>Yield %</th>
<th>Time (h)</th>
<th>α:β</th>
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<tr>
<td>1</td>
<td>1</td>
<td>Methanol</td>
<td>a&lt;sup&gt;11&lt;/sup&gt;</td>
<td>85</td>
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<tr>
<td>2</td>
<td>1</td>
<td>t-Butanol</td>
<td>b&lt;sup&gt;11&lt;/sup&gt;</td>
<td>52</td>
<td>5</td>
<td>α only</td>
</tr>
<tr>
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<td>1</td>
<td>Isopropyl Alcohol</td>
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<td>83</td>
<td>3</td>
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<tr>
<td>4</td>
<td>1</td>
<td>Propargyl Alcohol</td>
<td>d</td>
<td>95</td>
<td>3</td>
<td>91:9</td>
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<tr>
<td>5</td>
<td>1</td>
<td>Cinnamyl Alcohol</td>
<td>e</td>
<td>89</td>
<td>3</td>
<td>90:10</td>
</tr>
<tr>
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<td>1</td>
<td>Benzyl alcohol</td>
<td>f&lt;sup&gt;11&lt;/sup&gt;</td>
<td>85</td>
<td>3</td>
<td>80:20</td>
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<tr>
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<td>1</td>
<td>Homo propargyl Alcohol</td>
<td>g</td>
<td>90</td>
<td>3</td>
<td>90:10</td>
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<td>8</td>
<td>1</td>
<td>3-Bromo-1-propanol</td>
<td>h</td>
<td>92</td>
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<td>1</td>
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<td>j&lt;sup&gt;11&lt;/sup&gt;</td>
<td>80</td>
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<td>Allyl alcohol</td>
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<td></td>
<td>n&lt;sup&gt;6h,11&lt;/sup&gt;</td>
<td>38</td>
<td>4</td>
<td>92:8</td>
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<tr>
<td>15</td>
<td>1</td>
<td>3-Methyl-but-3-en-1-ol</td>
<td>o</td>
<td>92</td>
<td>3</td>
<td>80:20</td>
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<tr>
<td>16</td>
<td>2</td>
<td>Methanol</td>
<td>p&lt;sup&gt;6i,11&lt;/sup&gt;</td>
<td>80</td>
<td>2</td>
<td>(70:30)&lt;sup&gt;a&lt;/sup&gt;,55:45&lt;sup&gt;b&lt;/sup&gt;,90:10&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>t-Butanol</td>
<td>q&lt;sup&gt;6i,11&lt;/sup&gt;</td>
<td>50</td>
<td>4.5</td>
<td>(71:29)&lt;sup&gt;a&lt;/sup&gt;,74:26&lt;sup&gt;b&lt;/sup&gt;,65:35&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio of 2-deoxy-<i>O</i>-glycoside and the Ferrier product. <sup>b</sup> α:β ratio of 2-deoxy–<i>O</i>-glycoside. <sup>c</sup> α:β ratio of the Ferrier product.

With regards to the mechanism of this reaction, we suggest that 2-deoxy-<i>O</i>-glycosides are formed via the corresponding nitrate esters 4 (Scheme 2) by the nucleophilic displacement by alcohols under acidic reaction conditions. Evidence to this effect was gathered from the following observations. Exposure of a solution of 3,4,6-tri-<i>O</i>-benzyl-D-glucal 2 in acetonitrile to
Me₃SiONO₂ (1:1 molar equiv) only, followed by analysis of the reaction mixture by thin-layer chromatography showed a polar spot compared to the starting material. Evaporation of solvent under vacuum gave a product which showed in its IR spectrum a strong peak at 1680 cm⁻¹, whereas its ¹H NMR spectrum showed peaks of no specific splitting patterns NMR spectrum. Mass spectral analysis using electrospray technique (+ ion) suggested the presence of 1-hydroxy sugar derivative 5, however, the –ve ion detection indicated the presence of a peak at m/z 479 corresponding to the nitrate ester 4.

Scheme 2

Further, if the reaction was worked up before the addition of alcohols then the only product that could be isolated was 2-deoxy-3,4,6-tri-O-benzyl-D-glucose 5. It is, therefore, likely that the product of the reaction between a glycal and TMSONO₂ is a nitrate ester of type 4 which is relatively unstable and gets hydrolyzed to compound 5. This is not unexpected, since it is known that anomeric nitrates are susceptible towards hydrolysis on column chromatography. Thus, it is fair to assume that the nitrate esters 4 are formed as intermediates in these reactions and then they are subsequently converted to the corresponding 2-deoxy-O-glycosides 3 by treatment with glycosyl acceptors viz. the alcohols. Further, we presume that the nitrate esters 4 are first converted to the corresponding oxocarbocation 6, under the slightly acidic experimental conditions, before reacting with the glycosyl acceptors. This is in view of the fact that the O-glycosides formed are predominantly α in nature, resulting from the dominant anomeric effect.

In conclusion, we have found that TMSONO₂ is a new reagent for the synthesis of 2-deoxy-O-glycosides in a high stereoselective manner from glycals, and we hope that this methodology will be useful in organic synthesis.
Experimental Section

General Procedures. To a stirred solution of a glycal (0.240 mmol) in CH$_3$CN (2 mL) at room temperature, were added an alcohol (0.268 mmol) and trimethylsilylnitrate $^{13}$ (0.240 mmol). The reaction mixture was stirred for the time indicated in Table-1. After completion of reaction it was extracted with ethyl acetate (2 x 10 mL) and the usual work-up gave a crude product which was purified by column chromatography to give a pure product which was characterized by spectroscopic and analytical means.

Selected data: propargyl 3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$/-$\beta$-D-lyxo-hexopyranoside (3d). Yield: 95%, liquid. [$\alpha$]$^D_{25}$ = + 59.5 (c 2.15, CH$_2$Cl$_2$). IR (CH$_2$Cl$_2$) $\nu$ max: 3300, 2119, 1162, 1065 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.0-2.05 (dd, $J$ = 13.0, 4.4 Hz, 1H, H-2), 2.22-2.29 (dt, $J$ = 12.6, 3.8 Hz, 1H, H-2'), 2.36 (t, $J$ = 2.4 Hz, 1H, -C≡C-H), 3.53-3.58 (m, 2H, H-6, H-6'), 3.87-3.93 (m, 3H, H-3, H-4, H-5), 4.16 (t, $J$ = 2.4 Hz, 2H, -OCH$_2$-C=C), 4.40-4.49 (q, $J$ = 11.7 Hz, 2H, -OCH$_2$Ph), 4.59 (br. s, 2H, -OCH$_2$Ph), 4.63 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph), 4.93 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph), 5.14 (br. d, $J$ = 3.1 Hz, 1H, H-1), 7.23-7.35 (m, 15H, aromatic). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 30.7, 54.0, 69.2, 70.2, 70.3, 72.7, 73.3, 74.2, 74.4, 79.3, 96.5, 127.1-138.7 (m, aromatic). MSES$: 490 [M + NH$_4$]$^+$.

Cinnamyl 3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$/-$\beta$-D-lyxo-hexopyranoside (3e). Yield: 89%, liquid. [$\alpha$]$^D_{25}$ = + 16.0 (c 2.5, CH$_2$Cl$_2$). IR (CH$_2$Cl$_2$) $\nu$ max: 1495, 1097, 1060 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.02-2.06 (br. dd, $J$ = 12.6, 3.4 Hz, 1H, H-2), 2.22-2.29 (dt, $J$ = 12.4, 3.68 Hz, 1H, H-2'), 3.54-3.65 (m, 2H, H-6, H-6'), 3.93-3.98 (m, 3H, H-3, H-4, H-5), 4.09-4.14 (dd, $J$ = 12.8, 6.7 Hz, 1H, -OCH-CH=CH-Ph), 4.26-4.30 (dd, $J$ = 12.8, 5.7 Hz, 1H, -OCH'-CH=CH-Ph), 4.40-4.52 (q, $J$ = 11.7 Hz, 2H, -OCH$_2$Ph), 4.60 (br. s, 2H, -OCH$_2$Ph), 4.62 (d, $J$ = 11.5 Hz, 1H, -OCH$_2$Ph), 4.93 (d, $J$ = 11.5 Hz, 1H, -OCH$_2$Ph), 5.10 (br. d, $J$ = 3.1 Hz, 1H, H-1), 6.24-6.31 (m, 1H, -OCH$_2$-CH=CHPh), 6.57 (br. d, $J$ = 15.8 Hz, 1H, -OCH$_2$-CH=CHPh), 7.21-7.37 (m, 20H, aromatic). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 31.1, 67.6, 69.6, 69.9, 70.4, 72.7, 73.3, 74.2, 74.4, 79.4, 97.1, 125.5, 126.4-128.5 (m, aromatic), 132.6, 136.4, 138.0, 138.4, 138.8. MSES$: 568.2 [M + NH$_4$]$^+$.

Homo propargyl 3,4,6-tri-$O$-benzyl-2-deoxy-$\alpha$/-$\beta$-D-lyxo-hexopyranoside (3g). Yield: 90%, liquid. [$\alpha$]$^D_{25}$ = + 40.0 (c 1.3, CH$_2$Cl$_2$). IR (CH$_2$Cl$_2$) $\nu$ max: 3293, 2118, 1162, 1096 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.94 (t, $J$ = 2.6 Hz, 1H, -C≡C-H), 1.99-2.03 (m, 1H, H-2), 2.19-2.26 (dt, $J$ = 12.6, 3.6 Hz, 1H, H-2'), 2.42-2.47 (dt, $J$ = 7.0, 2.6 Hz, 2H, -OCH$_2$-CH$_2$), 3.53-3.63 (m, 3H, H-6, H-6' and -OCH-CH$_2$), 3.69-3.75 (m, 1H, -OCH'CH$_2$), 3.89-3.96 (m, 3H, H-3, H-4, and H-5), 4.40-4.51 (q, $J$ = 11.9 Hz, 2H, -OCH$_2$Ph), 4.59 (br. s, 2H, -OCH$_2$Ph), 4.62 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph), 4.93 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph), 5.01 (br. d, $J$ = 2.9 Hz, 1H, H-1), 7.22-7.34
(m, 15H, aromatic). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 19.7, 31.0, 65.4, 69.2, 69.4, 69.9, 70.4, 72.8, 73.4, 74.2, 74.7, 81.3, 97.9, 127.2-128.3 (m, aromatic), 138.1, 138.4, 138.8. MSES$^+$: 504 [M + NH$_4$]$^+$. Anal. Caled for C$_{11}$H$_{14}$O$_5$ (486.59): C, 76.52; H, 7.04. Found: C, 76.55; H, 7.10. Characteristic signals for $b$-anomer: $^1$H NMR: $\delta$ 2.06-2.10 (m, 2H, H-2, H-2'), 4.56-4.59 (dd, $J$ = 10.0, 2.2 Hz, 1H, H-1), 4.91 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph). $^{13}$C NMR: $\delta$ 20.0, 32.6, 66.9, 70.1, 71.5, 73.4, 74.0, 100.3, 138.0, 138.3, 138.7.

3-Bromo-n-propyl 3,4,6-tri-O-benzyl-2-deoxy-$\alpha$/$\beta$-D-lyxo-hexopyranoside (3h). Yield: 92%, liquid. $[\alpha]_D^{25}$ = + 24.4 (c 2.05, CH$_2$Cl$_2$). IR (CH$_2$Cl$_2$) $v$$_{\text{max}}$: 1162, 1096 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.95-1.99 (dd, $J$ = 12.9, 4.1 Hz, 1H, H-2), 2.03-2.14 (m, 2H, Ha-2), 2.25-2.26 (dt, $J$ = 12.7, 3.9 Hz, 1H, H-2'), 3.43-3.62 (m, 6H, H-5, H-6, H-6', Ha-3 and Ha-1), 3.73-3.78 (m, 1H, Ha-1'), 3.87-3.92 (m, 2H, H-3, H-4), 4.41-4.94 (m, 6H, 3 x -OCH$_2$Ph), 4.96 (br. d, $J$ = 3.1 Hz, 1H, H-1), 7.23-7.36 (m, 15H, aromatic). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 20.0, 32.6, 66.9, 70.1, 71.5, 73.4, 74.0, 100.3, 138.0, 138.3, 138.7. MSES$^+$: 574 [M + NH$_4$]$^+$. Anal. Caled for C$_{30}$H$_{35}$BrO$_5$ (555.40): C, 64.90; H, 6.41. Characteristic signals for $b$-anomer: $^1$H NMR: $\delta$ 2.03-2.10 (m, 2H, H-2, H-2'), 4.56-4.59 (dd, $J$ = 10.0, 2.2 Hz, 1H, H-1), 4.91 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph). $^{13}$C NMR: $\delta$ 20.0, 32.6, 66.9, 70.1, 71.5, 73.4, 74.0, 100.3, 138.0, 138.3, 138.7.

3-Methyl-3-butenyl 3,4,6-tri-O-benzyl-2-deoxy-$\alpha$/$\beta$-D-lyxo-hexopyranoside (3o). Yield: 92%, liquid. $[\alpha]_D^{25}$ = + 24.4 (c 2.05, CH$_2$Cl$_2$). IR (CH$_2$Cl$_2$) $v$$_{\text{max}}$: 1162, 1096 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.95-1.99 (dd, $J$ = 12.9, 4.1 Hz, 1H, H-2), 2.03-2.14 (m, 2H, H$_a$-2, 2.25-2.26 (dt, $J$ = 12.7, 3.9 Hz, 1H, H-2'), 3.43-3.62 (m, 6H, H-5, H-6, H-6', H$_a$-3 and H$_a$-1), 3.73-3.78 (m, 1H, H$_a$-1'), 3.87-3.92 (m, 2H, H-3, H-4), 4.41-4.94 (m, 6H, 3 x -OCH$_2$Ph), 4.96 (br. d, $J$ = 3.1 Hz, 1H, H-1), 7.23-7.36 (m, 15H, aromatic). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 20.0, 32.6, 66.9, 70.1, 71.5, 73.4, 74.0, 100.3, 138.0, 138.3, 138.7. MSES$^+$: 574 [M + NH$_4$]$^+$. Anal. Caled for C$_{30}$H$_{35}$BrO$_5$ (555.40): C, 64.90; H, 6.41. Characteristic signals for $b$-anomer: $^1$H NMR: $\delta$ 2.03-2.10 (m, 2H, H-2, H-2'), 4.56-4.59 (dd, $J$ = 10.0, 2.2 Hz, 1H, H-1), 4.91 (d, $J$ = 11.7 Hz, 1H, -OCH$_2$Ph). $^{13}$C NMR: $\delta$ 20.0, 32.6, 66.9, 70.1, 71.5, 73.4, 74.0, 100.3, 138.0, 138.3, 138.7.
Octyl 3,4,6-tri-O-benzyl-2-deoxy-α/β-D-lyxo-hexopyranoside (3m). Yield: 88%, liquid. \( [\alpha]_D^{25} = +27.5 \) (c 1.7, CH\(_2\)Cl\(_2\)). IR (CH\(_2\)Cl\(_2\)) \( \nu_{\text{max}}: 1163, 1095 \) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)):\( \delta \) 0.83-1.2 (m, 13H, octyl), 1.5-1.54 (m, 2H, -OCH\(_2\)C\(_6\)H\(_5\)-), 1.96-2.00 (dd, \( J = 12.4, 3.6 \) Hz, 1H, H-2), 2.18-2.25 (dt, \( J = 13.0, 3.6 \) Hz, 1H, H-2'), 3.32-3.38 (m, 1H, -OC\(_6\)H\(_5\)-CH\(_2\)-), 3.54-3.66 (m, 3H, H-6, H-6' and –OC\(_6\)H\(_5\)-CH\(_2\)-), 3.89-3.95 (m, 3H, H-3, H-4, H-5), 4.40-4.52 (q, \( J = 11.9 \) Hz, 2H, -OC\(_6\)H\(_2\)Ph), 4.60 (br. s, 2H, -OC\(_6\)H\(_2\)Ph), 4.62 (d, \( J = 11.5 \) Hz, 1H, -OC\(_6\)H\(_2\)Ph), 4.93 (d, \( J = 11.5 \) Hz, 1H, -OC\(_6\)H\(_2\)Ph), 4.96 (br. d, \( J = 3.1 \) Hz, 1H, H-1), 7.23-7.34 (m, 15H, aromatic). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)):\( \delta \) 22.6, 26.2, 29.2, 29.3, 29.5, 29.6, 31.2, 31.8, 60.4, 69.5, 69.7, 70.4, 73.0, 73.4, 74.2, 74.9, 97.6, 127-128 (m, aromatic), 138.3, 138.5, 138.9. MSES\(^+\): 546 [M + NH\(_4\)]\(^+\). Anal. Calcd. for C\(_{36}\)H\(_{50}\)O\(_5\) (562.78): C, 76.83; H, 8.96. Found: C, 76.88; H, 8.99.

Acknowledgements

We thank the Department of Science and Technology, New Delhi for financial support through a project (SP/S1/G-21/2001).

References and Notes


15. The pH of the reaction mixture was found to be 2.5.