An Efficient Method for the Chemoselective Preparation of Benzyolated 1,2-Diols from Epoxides

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Dedicated to Professor Habib Firouzabadi on the occasion of his 60th birthday.

Abstract: A very efficient and highly regioselective ring-opening reaction of epoxides with benzoic acid and its derivatives in the presence of cat. amount of tetrabutylammonium bromide (TBAB) in anhydrous acetonitrile has been developed. This effective method is useful for the preparation of selectively protected diols as precursor for many organic syntheses such as those of acyclic nucleosides and other synthetic purposes. The advantages of this method are efficiency, selectivity, low cost, and the applicability in large-scale synthesis of β-benzoyloxyalkanols.

Key words: benzyolated 1,2-diol, benzoic acid, epoxides, acetonitrile, TBAB

Selective protection of hydroxyl groups in polyols is very important in organic synthesis.1-4 There are miscellaneous methods and reagents elaborated for the direct protection of hydroxyl groups in a molecule.2-4 One way for the indirect preparation of the titled compounds is the regioselective ring opening of epoxides with removable oxygen containing nucleophiles. They are usually exemplified for acid or base catalyzed alcoholysis of epoxides5 or ring opening reaction of epoxides with carboxylic acids. Epoxides are well-known and fully established carbon electrophiles capable of reacting with various nucleophiles. Their ability to undergo regioselective ring opening reactions contributes largely to their synthetic value.6 Carboxylic acids are interesting because of low cost and ease of handling and because their reaction with epoxides provides a direct and appealing route to 1,2-diol mono-esters.5,6,7 The reactions of epoxides with carboxylic acids are generally limited to the reaction of HOAc catalyzed by different Lewis acids.7 The use of NaOAc/HOAc5 and benzoic acid/Co(salen)/i-Pr3NH8 were also reported. β-Hydroxy esters were prepared by esterification of carboxylic acid with vicinal epoxides by the use of FeCl3 as catalyst in the presence of Et3N or N-methylmorpholine.9 Tetrabutylammonium chloride (TBAC) mediated ring opening of 1-phenylthio-2,3-epoxypropane with benzoic acid in anhydrous toluene was reported as the only example for the synthesis of functionalized substituted α,β-un-saturated carbonyl compounds in low yield (18%).10 β-Carboxyalkanols were obtained by the ring opening of epoxides with carboxylates in micellar media catalyzed by Ce(OTf)3.11 Benzoic acid and its derivatives were found to be the very useful carboxylic acids in ring opening reaction of epoxides and are superior with respect to other carboxylic acids. This is due to the fact that mono-benzoate of 1,2-diols shows little tendency to isomerize as compared to other mono-esters of 1,2-diols, especially mono-acetate of 1,2-diols.12 Related to our interest in the synthesis of some novel acyclic nucleosides,13 we wish to report the synthesis of β-benzoyloxyalkanols as useful intermediates for organic synthesis. Herein we describe a very efficient and highly chemoselective synthesis of benzyolated 1,2-diols using epoxides in the presence of tetrabutylammonium bromide (TBAB) in anhydrous MeCN.

Benzoic acid and its derivatives were allowed to react with a set of terminal epoxides and the reaction afforded the corresponding β-benzoyloxy alkanols 1-19 (Tables 1 and 2) by using cat. amount of TBAB in anhydrous MeCN (Scheme 1). In most epoxide ring opening reactions, it is well demonstrated that both protic or Lewis acids act as promoter for nucleophilic ring opening of epoxides. We have conducted some experiments to find out the role of phase transfer catalysts (PTC) and solvents. The absence of TBAB in the reaction media gave no yields after refluxing for 24 hours. This confirms the critical role of TBAB for this reaction.

Scheme 1

We also examined the effect of other halides analogs of TBAB including TBAF, TBAC and TBAI to understand the generality of these PTC’s role in our reaction. For this purpose, we selected the reaction of benzoic acid and epichlorohydrin (Table 1, entry 1) as a model reaction, which was treated with cat. amount of tetrabutylammonium halides (TBAX). Good yield (70%) was obtained by using TBAC instead of TBAB. In the case of TBAF, we expected higher yield due to the more basic properties of F- ion. On the contrary, lower yield (43%) was ob-
Table 1  Reaction of Epoxides with Benzoic acid and Catalytic Amount of TBAB in Anhydrous MeCN

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxides</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Yield(^b)(%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cl</td>
<td><img src="image" alt="Cl Product" /></td>
<td>5</td>
<td>97</td>
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<td>2</td>
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<td>86</td>
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<td>3</td>
<td>CH(_3)</td>
<td><img src="image" alt="CH(_3) Product" /></td>
<td>4</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>OPh</td>
<td><img src="image" alt="OPh Product" /></td>
<td>6</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>C(_5)H(_12)</td>
<td><img src="image" alt="C(_5)H(_12) Product" /></td>
<td>5</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>CH(_3)CH(_3)</td>
<td><img src="image" alt="CH(_3)CH(_3) Product" /></td>
<td>5</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>CH(_2)CH(_2)CH(_2)</td>
<td><img src="image" alt="CH(_2)CH(_2)CH(_2) Product" /></td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>Ph</td>
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<td>5</td>
<td>ca. 100(^c)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>4</td>
<td>98</td>
</tr>
</tbody>
</table>

\(^a\) Products were characterized by \(^1\)H NMR, \(^13\)C NMR, IR spectroscopy.

\(^b\) Yields of pure isolated products based on the starting epoxides.

\(^c\) This compound gave two isomer products in ratio of (75:25).
served. Use of TBAI has limitations because of the nucleophilic attack of I ions at the epoxide ring. The formation of an iodohydrin as a side product is inevitable in this case; however, good yield was obtained (61%).

Several reactions were also carried out to understand the effect of other solvents beside MeCN on the efficiency and regioselectivity for product formation. A set of anhydrous aprotic solvents was used for the previously described model reaction of benzoic acid, TBAB and epichlorohydrin. The results are depicted in Table 2.

**Table 2** Effect of Various Solvents on the Reaction of Epichlorohydrin with Benzoic Acid in the Presence of TBAB

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>7</td>
<td>42</td>
</tr>
<tr>
<td>DMSO</td>
<td>7</td>
<td>34</td>
</tr>
<tr>
<td>HMPA</td>
<td>9</td>
<td>31</td>
</tr>
<tr>
<td>THF</td>
<td>7</td>
<td>65</td>
</tr>
<tr>
<td>Acetone</td>
<td>10</td>
<td>32</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td>MeCN</td>
<td>5</td>
<td>97</td>
</tr>
<tr>
<td>PhMe</td>
<td>7</td>
<td>24</td>
</tr>
</tbody>
</table>

*a* Yield of pure isolated products based on the starting epoxides.

As Table 2 shows, there is no meaningful correlation between the efficiency of reaction and the dielectric constant of the solvent since solvents with higher dielectric constant compared to MeCN such as DMSO and DMF show little selectivity in the ring opening reaction of epichlorohydrin. In contrast, solvent such as THF with lower dielectric constant can be taken into account as the next eligible solvent for the above-mentioned reaction. We also studied the reaction trend of other benzoic acid derivatives to realize the effect of both electron-donating and electron-accepting substituents on the regioselectivity and yield of reaction. The ability of these derivatives was investigated by using 2-(phenoxymethyl)oxirane as selected model epoxide in the presence of TBAB in anhydrous MeCN. The results are shown in Table 3.

In addition, as shown in Table 3, satisfactory yields were observed for benzoic acid derivatives with both electron-accepting and electron-donating groups.

An interesting example on the selectivity of this method is shown by the hydroxy benzoic acid derivatives (Table 3, entries 14–16). In basic media, these benzoic acid derivatives are known to isomerize, and such isomerization is very fast in acidic or alkaline media. This becomes a serious drawback for chemoselective preparation of mono-esters of 1,2-diols. Under these conditions use of quenching agent is essential for inhibition of isomerization. A remarkable advantage of our method in comparison with direct acylation of 1,2-diols is that neither base nor acid was used to catalyze the reaction; therefore isomerization is blocked during the course of reaction. In conclusion, we have developed an efficient method for preparation of chemoselective benzoylated 1,2-diols from epoxides. The reaction proceeds with various epoxides.
benzoic acid or its derivatives in the presence of a catalytic amount of TBAB in anhydrous MeCN within 4–7 hours. Furthermore, this method is highly regioselective.

The chemicals were obtained from Fluka or Merck. Purification and dehydration of solvents were done using the reported methods and the anhydrous solvents were stored over molecular sieves. With TLC using silica gel SILG/UV 254 plates the progress of the reaction was followed. IR spectra were run on a Shimadzu FTIR-8300.

### Table 3  Reaction of Benzoic Acid Derivatives with 2-(Phenoxymethyl)oxirane Catalyzed by TBAB in Anhydrous MeCN

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid</th>
<th>Product</th>
<th>Reaction Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td></td>
<td><img src="image1.png" alt="Image" /></td>
<td>5</td>
<td>62</td>
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<tr>
<td>12</td>
<td></td>
<td><img src="image2.png" alt="Image" /></td>
<td>6</td>
<td>73</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td><img src="image3.png" alt="Image" /></td>
<td>5</td>
<td>84</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td><img src="image4.png" alt="Image" /></td>
<td>4</td>
<td>92</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td><img src="image5.png" alt="Image" /></td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td><img src="image6.png" alt="Image" /></td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td><img src="image7.png" alt="Image" /></td>
<td>5</td>
<td>91</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td><img src="image8.png" alt="Image" /></td>
<td>4</td>
<td>98</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td><img src="image9.png" alt="Image" /></td>
<td>5</td>
<td>90</td>
</tr>
</tbody>
</table>

*Products were characterized by $^1$H NMR, $^{13}$C NMR, IR

$^a$ Yields of pure isolated products based on the starting epoxides.
spectrophotometer. The 1H NMR and 13C NMR spectra were recorded on a Bruker Advanced DXP-250, FT-NMR spectrometer (δ in ppm). Melting points were determined on a Büchi 510 in open capillary tubes and are uncorrected. All yields refer to the isolated products.

Preparation of β-Benzoyloxy Alkoanol: General Procedure

To a solution of epoxides (0.01 mol) in anhyd MeCN (40 mL) were added benzoic acid (1.5 g, 0.012 mol) and cat. amount of TBAB (0.1 g, 0.31 mmol), and the solution was refluxed for 4–7 h (Tables 1 and 2). When TLC indicated disappearance of the starting epoxides, the solvent was evaporated and the crude mixture was suspended in 5% K2CO3 solution (50 mL) to remove unreacted benzoic acid. The organic layer was extracted with CHCl3 (2 × 100 mL) and dried over Na2SO4 (20 g). Filtration and evaporation of the solvent gave the crude product, which was purified with appropriate methods described below.

3-Chloro-2-hydroxypropyl Benzoate (1)

Column chromatography purification on silica gel with n-hexane–EtOAc (5:3) gave a colorless foam (2.22 g, 86%); Rf 0.79 (50% EtOAc (7:2) gave a colorless oil (1.64 g, 92%); Rf 0.54 (50% EtOAc (5:3) gave a colorless oil (2.00 g, 97%); Rf 0.75 (50% EtOAc (5:2) gave a colorless oil (2.21 g, 94%); Rf 0.60 (50% EtOAc (5:3) gave a colorless foam (2.00 g, 97%); Rf 0.75 (50% EtOAc (5:2) gave a colorless foam (2.22 g, 97%); Rf 0.75 (50% EtOAc (7:2) gave a white crystals (2.40 g, 96%); mp 48–50 °C; Rf 0.81 (50% n-hexane–EtOAc).

IR (KBr): 3600–3200 (br), 3150, 2980, 1734 (s), 1275 cm−1.

1H NMR (250 MHz, CDCl3): δ = 8.41–7.36 (m, 5 H, Ph), 6.21 (s, 1 H, =CCH2H), 5.63 (s, 1 H, =CCH2), 4.64–4.50 (m, 2 H, PhCO2CH2), 4.49–4.43 (m, 3 H, CH2CH2C(C(Me)2CO2CH3)), 3.33–3.01 (1 H, br, OH, exchangeable with D2O), 2.05 (3 H, s, CH3).

13C NMR (62.5 MHz, CDCl3): δ = 167.21, 166.32, 132.62, 131.05, 130.06, 128.51, 125.22, 69.90, 65.22, 65.09, 65.00, 20.31.

3-((Allyloxy)-2-hydroxypropyl Benzoate (7)11

Column chromatography purification on silica gel with n-hexane–EtOAc (5:3) gave a colorless oil (2.21 g, 94%); Rf 0.60 (50% n-hexane–EtOAc).

IR (liquid film): 3600–3150 (br), 3050, 2980, 1735 (2 bands), 1250, 1230 cm−1.

1H NMR (250 MHz, CDCl3): δ = 8.41–7.42 (m, 5 H, Ph), 6.00–5.72 (m, 1 H, =CCH2H), 5.23–4.89 (dd, J = 10.4, 7.7 Hz, 2 H, =CCH2), 4.42–4.17 (dd, J = 4.4 Hz, 2 H, PhCO2CH2), 4.11–4.00 (m, 1 H, HCOH), 3.50–3.38 (1 H, br, OH, exchangeable with D2O), 2.76 (s, 1 H, OH, exchangeable with D2O).

13C NMR (62.5 MHz, CDCl3): δ = 167.22, 163.28, 135.01, 130.24, 132.62, 117.31, 117.28, 74.41, 71.22, 69.32, 65.13.

2-Hydroxy-3-iso-propoxypropyl Benzoate (8)12

Column chromatography purification on silica gel with n-hexane–EtOAc (5:2) gave a colorless oil (2.10 g, 92%); Rf 0.83 (50% n-hexane–EtOAc).

IR (liquid film): 3600–3100 (br), 3050, 2980, 1735, 1265 cm−1.

1H NMR (250 MHz, CDCl3): δ = 8.28–7.32 (m, 5 H, Ph), 4.53–4.22 (m, 3 H, CH2OHCH2), 2.34–1.85 (br, 1 H, OH), 3.43–1.22 (d, J = 5.9 Hz, 3 H, CH3).

13C NMR (62.5 MHz, CDCl3): δ = 163.71, 134.32, 131.36, 131.02, 127.64, 74.81, 70.33, 70.02, 66.32, 22.23.

2-Hydroxy-2-phenylethyl Benzoate (9)17,19

Column chromatography purification on silica gel elution with n-hexane–EtOAc (7:3) gave pale yellow crystals (1.80 g, 75%); mp 65–67 °C; Rf 0.75 (50% n-hexane–EtOAc).

IR (KBr): 3600–3200 (br), 3050, 2980, 1735 (2 bands), 1265 cm−1.

1H NMR (250 MHz, CDCl3): δ = 8.28–7.32 (m, 10 H, Ph2), 5.43–5.26 (dd, J = 3.5, 7.9 Hz, 1 H, PhCHOH), 4.74–4.51 (dd, J = 3.5, 7.9 Hz, 1 H, PhCHO).

13C NMR (62.5 MHz, CDCl3): δ = 167.21, 135.01, 129.91, 127.63, 70.21, 70.01, 66.92, 63.24.

2-Hydroxyoctylcyclohexyl Benzoate (5)17

Column chromatography purification on silica gel with n-hexane–EtOAc (7:2) gave white crystals (2.49 g, 96%); mp 48–50 °C; Rf 0.81 (50% n-hexane–EtOAc).

IR (KBr): 3600–3160 (br), 3100, 2980, 1730 (s), 1250 cm−1.

1H NMR (250 MHz, CDCl3): δ = 8.24–7.72 (m, 5 H, Ph), 4.43–4.10 (m, 2 H, PhCO2CH2), 4.10–3.90 (quint, J = 4.4 Hz, 2 H, CH2OH), 3.50–3.26 (dd, J = 2.6, 5.2 Hz, 2 H, PhCO2CH2), 2.76–2.20 (br, 2 H, CH2OH).

13C NMR (62.5 MHz, CDCl3): δ = 167.21, 166.32, 132.62, 131.02, 130.24, 132.62, 117.31, 117.28, 74.41, 71.22, 69.32, 65.13.
11.5 Hz, 1 H, PhCO_2CH=CH_2), 4.51–4.32 (dd, J = 11.5, 8.0 Hz, 1 H, PhCO_2CH=CH_2), 3.01–2.54 (br, 1 H, OH, exchangeable with D_2O).

^1^C NMR (62.5 MHz, CDCl_3): δ = 167.34, 140.33, 134.99, 131.61, 130.03, 129.64, 129.53, 128.96, 127.36, 74.77, 70.29.

2-Hydroxy-1-phenylethyl Benzoate (9b)^19 Column chromatography purification on silica gel with n-hexane–EtOAc (7:3) gave a pale yellow oil (0.60 g, 25%); R_f 0.68 (50% n-hexane–EtOAc).

IR (liquid film): 3600–3100 (br), 3100, 2985, 1734 (s), 1250 cm ^{-1} .

^1^H NMR (250 MHz, CDCl_3): δ = 8.33–7.03 (m, 10 H, Ph), 6.34–6.02 (dd, J = 3.6, 7.1 Hz, 1 H, PhCO_2CH=CH_2), 4.34–3.85 (m, 2 H, CH=OH), 2.31–2.00 (br s, 1 H, OH, exchangeable with D_2O).

^1^C NMR (62.5 MHz, CDCl_3): δ = 164.22, 138.22, 135.01, 131.24, 131.06, 129.64, 129.39, 128.83, 126.52, 79.61, 67.33.

2-Hydroxy-cyclohexyl Benzoate (10)^11 Column chromatography purification on silica gel with n-hexane–EtOAc (5:2) gave white crystals (2.13 g, 98%); mp 104–105 ºC; R_f 0.73 (50% n-hexane–EtOAc).

IR (KBr): 3600–3100 (br), 3050, 2980, 1735 (s), 1265 cm ^{-1} .

^1^H NMR (250 MHz, CDCl_3): δ = 8.00–7.20 (m, 5 H, Ph), 4.80–4.76 (m, 1 H, PhCO_2CH=CH_2), 3.68–3.64 (m, 1 H, HOCH), 2.26 (s, 1 H, OH, exchangeable with D_2O), 2.10–1.26 (m, 8 H, CH(CH_2)_3).

^1^C NMR (62.5 MHz, CDCl_3): δ = 165.84, 135.59, 132.80, 130.21, 128.96, 72.68, 68.73, 31.42, 29.82, 21.48, 21.39.

2-Hydroxy-3-phenoxypropyl-4-nitro Benzoate (11) Column chromatography purification on silica gel with n-hexane–EtOAc (5:2) gave pale yellow crystals (2.19 g, 62%); mp 85–87 ºC; R_f 0.80 (50% n-hexane–EtOAc).

IR (liquid film): 3600–3100 (br), 3100, 2985, 1730(s), 1250 cm ^{-1} .

^1^H NMR (250 MHz, CDCl_3): δ = 7.86–6.93 (m, 9 H, m-HOPh, Ph), 4.63–4.50 (dd, J = 2.2, 4.9 Hz, 2 H, m-HOPhCO_2CH_2), 4.50–4.32 (quint, J = 4.9 Hz, 1 H, HOCH), 4.29–4.00 (dd, J = 3.1, 4.9 Hz, 2 H, CH=OH), 4.00–3.00 (br s, 1 H, HOCH, exchangeable with D_2O), 2.50–2.00 (br s, 1 H, OH, exchangeable with D_2O).

^1^C NMR (62.5 MHz, CDCl_3): δ = 167.33, 159.23, 156.31, 131.32, 130.29, 130.02, 132.62, 132.02, 132.07, 116.24, 115.00, 69.68, 69.41, 66.32.

2-Hydroxy-3-phenoxypropyl salcylate (16) Column chromatography purification on silica gel with n-hexane–EtOAc (5:2) gave a colorless oil (2.40 g, 90%); mp 63–65 ºC; R_f 0.53 (50% n-hexane–EtOAc).

IR (KBr): 3600–3140 (br), 3100, 2980, 1730(s), 1250 cm ^{-1} .

^1^H NMR (250 MHz, CDCl_3): δ = 7.91–7.83 (m, 9 H, m-HOPh, Ph), 4.63–4.50 (dd, J = 2.2, 4.9 Hz, 2 H, m-HOPhCO_2CH_2), 4.50–4.32 (quint, J = 4.9 Hz, 1 H, HOCH), 4.29–4.00 (dd, J = 2.0, 4.9 Hz, 2 H, CH=OH), 4.00–3.00 (br s, 1 H, HOCH, exchangeable with D_2O), 2.50–2.00 (br s, 1 H, OH, exchangeable with D_2O).

^1^C NMR (62.5 MHz, CDCl_3): δ = 167.54, 160.16, 156.34, 136.24, 131.42, 130.24, 130.02, 122.31, 120.00, 117.62, 115.00, 70.51, 70.32, 66.50.

2-Hydroxy-3-phenoxypropyl-4-methyl Benzoate (17) Column chromatography purification on silica gel with n-hexane–EtOAc (7:3) gave white crystals (2.60 g, 91%); mp 68–70 ºC; R_f 0.93 (50% n-hexane–EtOAc).

IR (KBr): 3600–3150 (br), 3100, 2985, 1728(s), 1250 cm ^{-1} .
2-Hydroxy-3-phenoxypentyl-4-methoxy Benzoate (18)
Column chromatography purification on silica gel with n-hexane–
EtOAc (5:2) gave white crystals (2.94 g, 98%); mp 82–84 ºC;
1H NMR (250 MHz, CDCl3): δ = 8.21–7.90 (d, J = 8.8 Hz, 2 H, p-
MeOPh); 7.49–7.41 (d, J = 8.8 Hz, 2 H, p-MeOPh); 6.70–6.62 (m, 5 H, Ph); 4.73–4.51 (dd, J = 1.9, 5.1 Hz, 2 H, p-MeOPhCO2CH2),
4.50–4.41 (quint, J = 5.1 Hz, 1 H, HCOCH), 4.39–4.21 (dd, J = 2.0,
5.1 Hz, 2 H, CH2OPh), 3.90 (s, 3 H, OMe), 3.00 (s, 1 H, OH).
13C NMR (62.5 MHz, CDCl3): δ = 172.8, 170.2, 167.4, 165.0,
160.0, 133.6, 131.0, 127.0, 124.5, 122.1, 115.0, 70.6, 70.2, 67.4.
IR (KBr): 3600–3150 (br), 3100, 2985, 1735 (s), 1250 cm –1 .

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spectra.

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