Bis-Triazologlycolipid mimetics - Low molecular weight organogelator

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General procedure for \textit{bis}-propargylated derivatives and its corresponding NMR data are provided in ESI.

\textsuperscript{1}H NMR, \textsuperscript{13}C NMR, DEPT-135, 2D NMR and Mass spectrum are available in the ESI.

Figure 6: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 3.

Figure 7: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 3.

Figure 8: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 5a.

Figure 9: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 5a.

Figure 10: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 7a.

Figure 11: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 7a.

Figure 12: DEPT-135 spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 7a.

Figure 13: \textsuperscript{1}H-\textsuperscript{13}C correlation spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 7a.

Figure 14: Mass spectrum of compound, 7a.

Figure 15: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 4.

Figure 16: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 4.

Figure 17: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 6b.

Figure 18: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 6b.

Figure 19: \textsuperscript{1}H NMR spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 8b.

Figure 20: \textsuperscript{13}C NMR spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 8b.

Figure 21: DEPT-135 spectrum (75 MHz, CDCl\textsubscript{3}) of compound, 8b.

Figure 22 Mass spectrum of compound, 8b.

Figure 23 \textsuperscript{1}H NMR expansion spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 5a.

Figure 24 \textsuperscript{1}H NMR expansion spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 6b.

Figure 25 \textsuperscript{1}H NMR expansion spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 7a.

Figure 26 \textsuperscript{1}H NMR expansion spectrum (300 MHz, CDCl\textsubscript{3}) of compound, 8b.
### Table: 1 Optimisation of solvents

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tertiary butanol</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Acetonitrile</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Tetrahydrofuran</td>
<td>89</td>
</tr>
</tbody>
</table>

While assigning the spectral data, several abbreviations were used and these include ‘Ar’ for aromatic, ‘Sac’ for saccharide ‘Alk’ for alkene and “trz” for triazole respectively.

![Chemical structures and equations](image)

Synthesis of bis-propargylated aldehydes (3) and (4).

1. **General procedure for the synthesis of bis alkylated aldehyde, 3 & 4:**

   To a solution of dihydroxy benzaldehyde, (1 mmol) in dry DMF (15 ml) were added potassium carbonate (5 equiv.) and after stirring the solution for 5 minutes vigorously, propargyl bromide (2.2 equiv.) was added and the reaction mixture kept for stirring for 24 hrs. After careful work up, the product was further purified by column chromatography.

   Spectroscopic data for compounds 3 and 4 are as follows.
1.1 Physicochemical and spectrochemical data of 3,4-bis(prop-2-ynyloxy)benzaldehyde (3):

Colourless crystal, Yield: 89 % (0.19 g), mp 96-98 ºC, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.82 (s, 1H, -CHO), 7.51-7.45 (m, 2H, Ar-H), 7.11 (d, J = 8.1 Hz, 1H, Ar-H), 4.79 (d, J = 2.4 Hz, 2H, -CH$_2$), 4.76 (d, J = 2.4 Hz, 2H, -CH$_2$), 2.50 (m, 2H, -C≡H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 190.7, 152.7, 147.8, 130.8, 126.7, 113.2, 112.6, 77.7, 77.5, 76.7, 76.5, 56.8, 56.7. Elemental Analysis: C, 72.89; H, 4.71, Found: C, 72.82; H, 4.69.

1.2 Physicochemical and spectrochemical data of 2,4-bis(prop-2-ynyloxy)benzaldehyde (4):

Colourless crystal, Yield: 77 % (0.72 g), mp 104-106 ºC, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.32 (s, 1H, -CHO), 7.85 (d, J = 9 Hz, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 6.67 (d, J = 1.8 Hz, 1H, Ar-H), 4.81 (d, J = 2.4 Hz, 2H, -CH$_2$), 4.77 (d, J = 2.4 Hz, 2H, -CH$_2$), 2.60 (s, 2H, -C≡H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 188.1, 163.6, 161.4, 130.6, 120.1, 107.5, 100.4, 77.5, 77.0, 76.7, 76.5, 56.5, 56.1. Elemental Analysis: C, 72.89; H, 4.71, Found: C, 72.85; H, 4.67.

2. General procedure for the synthesis of $\alpha, \beta$-unsaturated $\beta$-C-glycosidic ketones, 5a, 5b, 6a, 6b:

To a solution of $\beta$-C-glycosidic ketone, 1, 2 (1 mmol) in dry DCM (5 ml) were added pyrrolidine (30% mol) and bis-propargylated-benzaldehyde 3, 4 (1.2 mmol). After stirring at room temperature for given period of time, the reaction mixture was evaporated under reduced pressure and extracted by EtOAc-water. The ethylacetate layer was dried over anhyd. Na$_2$SO$_4$ and concentrated to dryness. The product was
further purified by column chromatography.

Spectroscopic data for compounds 5a, 5b, 6a and 6b are as follows.

2.1 Physicochemical and spectral data for (E)-1-(4,6-O-butyldiene-β-D-glucopyranosyl)-4-(3,4-bis prop-1’-oxy-2’-yne phenyl)-but-3-ene-2-one (5a)

White solid, Yield: 91 % (0.43 g), mp 156-158 ºC. ¹H NMR (300 MHz, CDCl₃): δ 7.55 (d, J = 15.9 Hz, 1H, Alk-H), 7.28 (s, 1H, Ar-H), 7.22 (d, J = 8.4 Hz, 1H, Ar-H), 7.08 (d, J = 8.1 Hz, 1H, Ar-H), 6.68 (d, J = 16.2 Hz, 1H, Alk-H), 4.82 (s, 4H, -CH₂), 4.55 (t, J = 5Hz, 1H, Sac-H), 4.15 (dd, J = 3.9 Hz, J = 9.6 Hz, 1H, Sac-H), 3.98-3.92 (m, 1H, Sac-H), 3.47-3.35 (m, 3H, Sac-H), 3.26 (t, J = 9.0 Hz, 1H, Sac-H), 3.17-3.11 (m, 2H, Sac-H, -CH₂), 2.97 (dd, J = 6.9 Hz, J = 16.1 Hz, -CH₂), 1.66-1.62 (m, 2H, -CH₂), 1.44 (q, J = 7.5 Hz, 2H, -CH₂), 0.94 (t, J = 7.2 Hz, 3H, Sac-H), ¹³C NMR (75 MHz, CDCl₃) : δ:198.0, 149.9, 147.6, 143.5, 128.3, 125.1, 123.8, 114.2, 113.9, 102.5, 80.5,78.0, 77.9, 76.4, 76.4, 76.2, 75.4, 74.5, 70.6, 68.3, 57.0, 56.7, 43.4, 36.2, 30.9, 17.5, 13.9, Elemental Analysis: C, 66.37; H, 6.43, Found: C, 66.35; H, 6.41.

2.2 Physicochemical and spectral data for (E)-1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-4-(3,4-bis prop-1’-oxy-2’-yne phenyl)-but-3-ene-2-one (5b)

Syrupy liquid, Yield: 89 % (0.52 g), ¹H NMR (300 MHz, CDCl₃): δ 7.50 (d, J = 16.2 Hz, 1H, Alk-H), 7.28 (m, 2H, Ar-H), 7.27 (d, J = 8.4 Hz, Ar-H), 7.07 (d, J = 8.4 Hz, 1H, Ar-H), 6.63 (d, J = 16.2 Hz, 1H, Alk-H), 5.24 (t, J = 9.3 Hz, 1H, Sac-H), 5.08 (t, J = 9.8 Hz, 1H, Sac-H), 4.99 (t, J = 9.6 Hz, 1H, Sac-H), 4.81 (d, J = 2.4 Hz, 4H, -CH₂), 4.26 (dd, J = 4.8 Hz, J = 12.6 Hz, 1H, Sac-H), 4.15-4.12 (m, 1H, Sac-H), 4.03 (dd, J = 2.1 Hz, J = 12.3 Hz, 1H, Sac-H), 3.74-3.70 (m, 1H, Sac-H), 3.02 (dd, J = 8.4 Hz, J = 16.2 Hz, 1H, -CH₂), 2.67 (dd, J = 3.2 Hz, J = 16.2 Hz, 1H, -CH₂), 2.58-2.55 (m, 2H, -C≡C), 2.02 (t, J = 2.9 Hz, 12H, -OCOCH₃), ¹³C NMR (75 MHz, CDCl₃) : δ 196.0, 170.6,170.2, 170.0, 169.6,
2.3 Physicochemical and spectral data for (E)-1-(4,6-O-butyridene-β-D-glucopyranosyl)-4-(2,4-bis prop-1’-oxo-2’-yne phenyl)-but-3-ene-2-one (6a)

Syrupy liquid, Yield: 79 % (0.89 g), \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.87 (d, \(J = 16.2\) Hz, 1H, Alk-H), 7.52 (d, \(J = 8.7\) Hz, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.72-6.62 (m, 2H, Ar-H, Alk-H), 4.77 (d, \(J = 2.4\) Hz, 2H, -CH\(_2\)), 4.74 (d, \(J = 2.4\) Hz, 2H, -CH\(_2\)), 4.53 (t, \(J = 5.1\) Hz, 1H, Ace-H), 4.16-4.11 (m, 2H, Sac-H), 3.96-3.89 (m, 1H, Sac-H), 3.73 (t, \(J = 8.7\) Hz, 1H, Sac-H), 3.43 (t, \(J = 8.9\) Hz, 2H, Sac-H), 3.25 (t, \(J = 9.0\) Hz, 1H, Sac-H), 3.11 (dd, \(J = 4.3\) Hz, \(J = 16.2\) Hz, 1H, -CH\(_2\)), 2.99 (dd, \(J = 6.9\) Hz, \(J = 16.1\) Hz, 1H, -CH\(_2\)), 2.57 (t, 2.1 Hz, 2H, -C≡CH), 1.65-1.60 (m, 2H, -CH\(_2\)), 1.42 (q, \(J = 7.8\) Hz, 2H, -CH\(_2\)), 0.92 (t, \(J = 7.4\) Hz, 3H, -CH\(_3\)), \(^13\)C NMR (75 MHz, CDCl\(_3\)) : \(\delta\) 198.6, 160.7, 157.8, 138.7, 130.0, 125.3, 117.7, 107.4, 102.5, 100.8, 80.4, 77.9, 75.4, 74.8, 70.6, 68.4, 56.3, 56.0, 43.3, 36.2, 17.5, 13.9, Elemental Analysis: C, 66.37; H, 6.43, Found: C, 66.33; H, 6.38.

2.4 Physicochemical and spectral data for (E)-1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-4-(2,4-bis prop-1’-oxo-2’-yne phenyl)-but-3-ene-2-one (6b)

Syrupy liquid, Yield: 79 % (0.89 g), \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, \(J = 16.2\) Hz, 1H, Alk-H), 7.52 (d, \(J = 8.7\) Hz, 1H, Ar-H), 6.75-6.63 (m, 3H, Alk-H, Ar-H), 5.23 (t, \(J = 9.3\) Hz, 1H, Sac-H), 5.08 (t, \(J = 9.8\) Hz, 1H, Sac-H), 4.99 (t, \(J = 9.8\) Hz, 1H, Sac-H), 4.79 (s, 2H, -CH\(_2\)), 4.74 (s, 2H, -CH\(_2\)), 4.27 (dd, \(J = 4.8\) Hz, \(J = 12.3\) Hz, 1H, Sac-H), 4.16-4.00 (m, 4H, Sac-H), 3.72 (dd, \(J = 3\) Hz, \(J = 9.8\) Hz, 1H, Sac-H), 3.02 (dd, \(J = 8.4\) Hz, \(J = 16.2\) Hz, 1H, Sac-H), 2.67 (dd, \(J = 3\) Hz, \(J = 16.2\) Hz, 1H, Sac-H), 2.59 (d, \(J = 2.1\) Hz,
2H, -C≡H), 2.05-2.01 (m, 12H, -COCH), $^{13}$C NMR (75 MHz, CDCl$_3$) : δ 196.5, 170.7, 170.3, 170.0, 169.6, 160.7, 157.8, 138.5, 130.1, 125.2, 117.6, 107.4, 100.8, 77.9, 77.8, 76.5, 76.2, 75.7, 74.3 (2C), 71.8, 68.6, 62.1, 60.4, 56.3, 56.0, 42.3, 30.9, 21.0, 20.7 (2C), 20.6 (2C), 14.2, Elemental Analysis: C, 61.64; H, 5.52, Found: C, 61.61 ; H, 5.47.

**Synthesis of Gels:**

The gelation ability of the bis-triazologlycolipids was determined by the “inversion tube method.” All the synthesized triazologlycolipids was tested for gelation by the method where 1 mg of the compound was dissolved in 1 mL of the solvent in a close capped vial to result in 1% CGC. The mixture was heated till all the solid gets dissolved and the vial was cooled to 25 °C and left for 12h at this temperature and then turned upside down. When the gelator formed is immobilized at this stage, it is said to be a Gel and it is denoted by “G”. Some of them forms partial gel is denoted as “PG”. Some of them which are insoluble is represented as “I” and those which got precipitated is denoted as “P”.
Figure 6 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 3.
Figure 5A.14 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 226.

Figure 7 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 3.

Figure 7 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 3.
Figure 8 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 5a.
Figure 9 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 5a.
Figure 10 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 7a.
Figure 11. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 7a.
Figure 12 DEPT-135 spectrum (75 MHz, CDCl₃) of compound, 7a.
Figure 13 $^1$H-$^{13}$C correlation spectrum (300 MHz, 75 MHz, CDCl$_3$) of compound, 7a.
Figure 14 Mass spectrum of compound, 7a.

Calc. exact mass, 892.60
m/z found, 893.61 [M+H]^+
Figure 15 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 4.
Figure 16 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 4.
Figure 17 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 6b.
Figure 18 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 6b.
Figure 19 $^1$H NMR spectrum (300 MHz, CDCl$_3$) of compound, 8b.
Figure 20 $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of compound, 8b.
Figure 21 DEPT-135 spectrum (75 MHz, CDCl₃) of compound, 8b.
Figure 22 Mass spectrum of compound, 8b.
Figure 23 $^1$H NMR spectrum (300 MHz, CDCl$_3$) expansion of compound, 5a.
Figure 24. $^1$H NMR spectrum (300 MHz, CDCl$_3$) expansion of compound, 6b.
Figure 25 $^1$H NMR spectrum (300 MHz, CDCl$_3$) expansion of compound, 6b.
Figure 26 $^1$H NMR spectrum (300 MHz, CDCl$_3$) expansion of compound, 8b.