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# Ferrier Rearrangement of tri-*O*-acetyl-D-glycals in the Presence of 3, 5-Dinitrobenozic acid

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***Abstract:*** *A novel procedure for Ferrier rearrangement of tri-O-acetyl-D-glycals in the presence of 3,5-dinitrobenozic acid has been developed. 3,5-Dinitrobenzoic acid is an effective, very cheap and viable catalyst in above synthetic transformations with various alcohols and thiophenols.*
***Keywords:*** *Organocatalyst, 3,5-Dinitrobenzoic acid, Ferrier rearrangement, Alcohols, Thiophenols.*

## I. Introduction

The importance of 2,3-unsaturated glycopyranosides as useful chiral intermediates[1,2] in the synthesis of biologically active compounds such as glycopeptide building blocks,[3] oligosaccharides,[4] modified carbohydrates,[5] several reports have been appeared in the literature. The synthesis of 2,3-unsaturated glycopyranosides are generally achieved by treatment of corresponding glycal with an alcohol or thiol in presence of either Lewis acid or Brønsted acid as a catalyst. This reaction was discovered by Ferrier in 1969 by using $BF_3.Et_2O$ as a Lewis acid catalyst and is popularly known as the Ferrier 1 reaction.[2a] Apart from $BF_3Et_2O$ several other Lewis acid catalysts, oxidants or protic acids such as $ZnCl_2$,[6] $H_3PO_4$,[7] $InCl_3$,[8] $SnCl_4$,[9] $Yb(OTf)_3$,[10] $FeCl_3$,[11] montmorillionite K-10,[12] $Dy(OTf)_3$,[13] DDQ,[14] $I_2$,[15] $I(Coll)_2ClO_4$,[16] CAN,[17] $CeCl_3.7H_2O$,[18] $HClO_4/SiO_2$,[19] MeOH.HCl[20] and N-iodosuccinamide[21] have been reported to affect this rearrangement. Owing to the importance of the Ferrier rearrangement products, the introduction of new and efficient catalysts for this transformation is still in demand.

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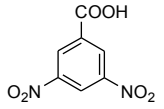
## II. Results and Discussions

In our preliminary experiments, we allowed to stir a mixture of benzyl alcohol (1 mmol) and glucal (**3**, 1 mmol) in the presence of 3,5-DNBA (20 mol%) in $CH_2Cl_2$ at room temperature for 24 h. However, the reaction did not proceed. Then we carried out the reaction in $CH_3CN$ at 80 $^oC$ the reaction underwent smoothly to give 2,3-unsaturated-O-glucopyranoside (Table 2, **5e**) in 81% yield.




3,5-Dinitrobenzoic acid
(3,5-DNBA)

In a typical experiment, a solution of tri-O-acetyl-D-glycal and alcohol or thiol in acetonitrile was stirred with 20 mol% 3,5-DNBA at 80 $^oC$. The reaction was completed within 2 to 3 h to produce exclusively the corresponding a 2,3-unsaturated glycopyranosides in high yield (Scheme 1, Table 2). We obtained predominately the α-anomer, as confirmed by spectroscopic data. The predominant formation of this α–anomer may arise from a thermodynamic anomeric effect.

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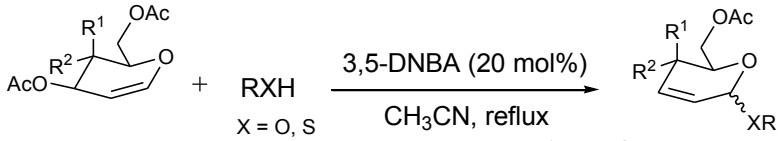
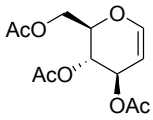
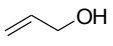
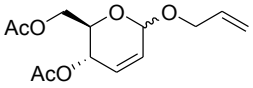
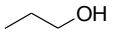
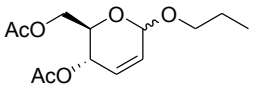
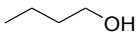
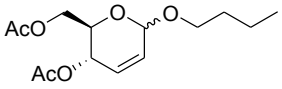
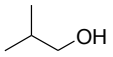
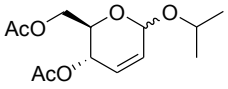
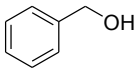
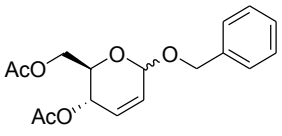
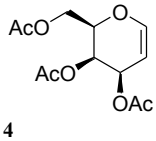
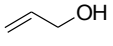
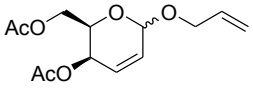
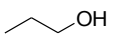
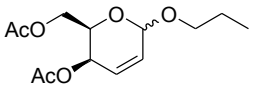
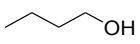
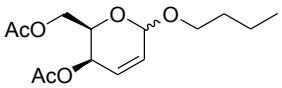
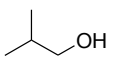
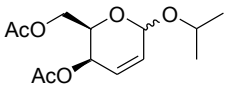
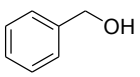
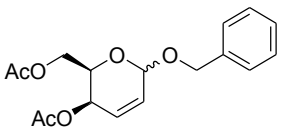
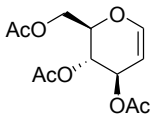
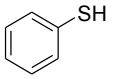
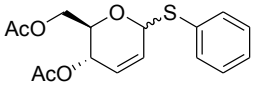
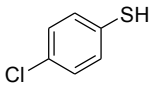
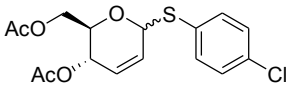
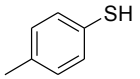
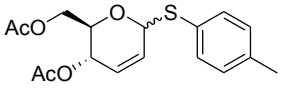
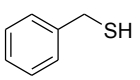
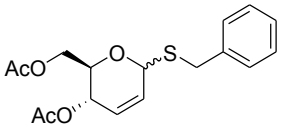
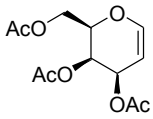
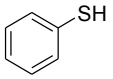
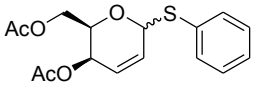



**3**: $R^1$ = H, $R^2$ = OAc
**4**: $R^1$ = OAc, $R^2$ = H

**5**: $R^1$ = H, $R^2$ = OAc, X = O
**6**: $R^1$ = OAc, $R^2$ = H, X = O
**7**: $R^1$ = H, $R^2$ = OAc, X = S
**8**: $R^1$ = OAc, $R^2$ = H, X = S

**Table 1**. Ferrier rearrangement of 2,3-tri-O-acetyl-D-glycals with alcohols and thiols in the presence of the 2,3-DNBA.[a]

| Entry | Substrate | Alcohol/Thiol | Time (h) | Product | | Yield [a](%) | α/β[b] |
|---|---|---|---|---|---|---|---|
| 1 |  **3** |  | 2 |  | **5a** | 86 | 5:1 |
| 2 | **3** |  | 2 |  | **5b** | 84 | 6:1 |
| 3 | **3** |  | 2.5 |  | **5c** | 86 | 4:1 |
| 4 | **3** |  | 2.5 |  | **5d** | 82 | 8:1 |
| 5 | **3** |  | 2 |  | **5e** | 81 | 10:1 |
| 6 |  **4** |  | 2 |  | **6a** | 89 | 6:1 |
| 7 | **4** |  | 2 |  | **6b** | 82 | 9:1 |
| 8 | **4** |  | 2.5 |  | **6c** | 86 | 14:1 |
| 9 | **4** |  | 2.5 |  | **6d** | 80 | 12:1 |
| 10 | **4** |  | 2 |  | **6e** | 87 | 22:1 |
| 11 |  **3** |  | 1.5 |  | **7a** | 91 | 6:1 |
| 12 | **3** |  | 2 |  | **7b** | 86 | 7:1 |
| 13 | **3** |  | 1.5 |  | **7c** | 89 | 13:1 |
| 14 | **3** |  | 1 |  | **7d** | 95 | 17:1 |
| 15 |  **4** |  | 1.5 |  | **8a** | 85 | 4:1 |

| | | | | | | | |
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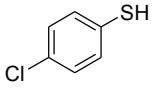
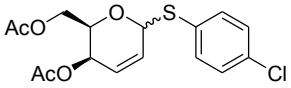
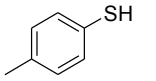
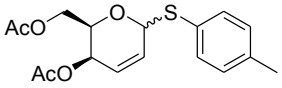
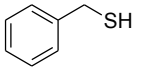
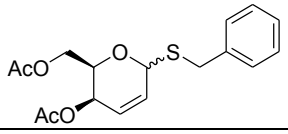
| 16 | **4** |  | 2 |  | **8b** | 81 | 7:1 |
| 17 | **4** |  | 1.5 |  | **8c** | 85 | 12.5:1 |
| 18 | **4** |  | 1 |  | **8d** | 87 | 20:1 |

[a]Yields are of pure isolated products. [b]The α/β ratio was determined by the anomeric proton ratio from the $^1$H NMR (500 MHz) spectra.

## III. Conclusion

In conclusion, we have developed a simple and convenient method for Ferrier rearrangement of of tri-O-acetyl-D-glycals in the presence of 3,5-dinitrobenozic acid has been developed. 3,5-dinitrobenzoic acid is an effective, very cheap and viable catalyst in above synthetic transformations with various alcohols, thiols. We believe that this methodology is valuable addition to modern synthetic methodologies.

## IV. Experimental

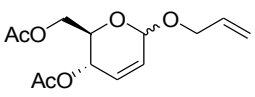
**General methods**

All reactions were carried out under dry conditions and at room temperature with dry solvents. Methylene chloride and acetonitrile was distilled over $P_2O_5$. Reagents were purchased at the highest commercially quality and used without further purification. Yields refer to chromatographically homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and/or ethanolic solution of p-anisaldehyde and heat as developing agent. Silica gel (particle size 100- 200 mesh) was used for column chromatography. NMR spectra were recorded on Brüker AMX-500 instrument. The signals from solvent $CDCl_3$, 7.25 and 77.0 ppm, are set as the reference peaks in $^1$H NMR and $^{13}$C NMR spectra, respectively. Mass spectra were recorded by GC-MS (Perkin-Elmer Clarus 500, EI, 70 eV). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

**General procedure for preparation of 2,3-unsaturated glycosides:**

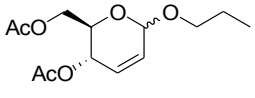
To a mixture of 2,4,6-tri-O-acetyl-D-glycal (135 mg, 0.5 mmol) and alcohol or thiol (1 equiv) in acetonitrile (5 mL) was added 3,5-dinitrobenzoic acid (0.1 mmol, 20 mol%) at room temperature. The mixture was stirred at 80 $^o$C for a specified period of time (Table 1), and the progress of reaction was monitored by TLC analysis. Evaporation of the solvent under reduced pressure, followed by purification of the residue by silica gel column chromatography (ethyl acetate/hexanes, 1/4, as the eluent) gave the desired 2,3-unsaturated glycoside.

**Prop-2-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5a)**



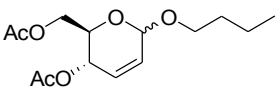
IR (neat) $\nu_{max}$ 3062, 2948, 1756, 1465, 952 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 5.94-5.85 (m, 1H), 5.28-5.23 (m, 1H), 5.17 (d, J = 10.5 Hz, 1H), 5.13-5.08 (m, 3H), 5.02 (bs, 1H), 3.97-4.25 (m, 5H), 2.05 (s, 3H), 2.02 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.6, 170. 3, 134.5, 129.2, 127.5, 117.3, 93.7, 69.2, 67.0, 65.5, 63.2, 21.2, 20.9 ppm. MS: m/z = 270 [M ]$^+$.

**Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5b)**



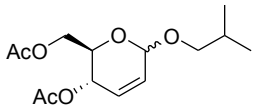
IR (neat) $\nu_{max}$ 3052, 2952, 1752, 1591, 861 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 5.84-5.98 (m, 2H), 5.34 (dd, J = 1.2, 9.6 Hz, 1H), 5.07 (s, 1H), 4.12-4.31 (m, 3H), 3.48-3.45 (m, 1H), 3.35-3.30 (m, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 1.41-1.38 (m, 2H), 1.25 (t, J = 7.25 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.7, 170.3, 129.0, 128.0, 94.5, 66.8, 65.3, 64.3, 63.0, 20.9, 20.7, 19.2, 15.3 ppm. MS: m/z = 272 [M ]$^+$.

**Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5c)**



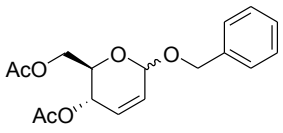
IR (neat) $\nu_{max}$ 3058, 2854, 1748, 1620, 923, cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 5.81 (bs, 2H), 5.30-5.25 (dd, J = 9.2, 1.1 Hz, 1H), 5.02 (bs, 1H), 4.20- 4.15 (m, 2H), 4.11-4.0 (m, 1H), 3.81-3.66 (m, 1H), 3.53-3.49 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 1.51-1.40 (m, 2H), 1.33-1.24 (m, 2H,), 0.99-0.90 (t, J = 4.9 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.5, 129.1, 128.6, 94.3, 67.1, 65.5, 65.0, 63.1, 30.2, 21.1, 21.0, 19.4, 14.6 ppm. MS: m/z = 286 [M ]$^+$.

**isoButyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5d)**



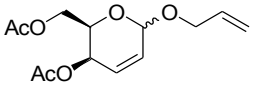
IR (neat) $\nu_{max}$ 3065, 2998, 1751, 1245, 883 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.87 (m, 2H), 5.23 (dd, J = 1.5, 9.6 Hz, 1H), 5.06 (bs, 1H), 4.01-4.19 (m, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 3.89 (dt, J = 7.5, 12.0 Hz, 1H), 3.82 (dt, J = 7.5, 12.0 Hz, 1H), 1.52-1.43 (m, 2H), 1.34-1.30 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.8, 170.3, 128.8, 92.9, 70.8, 66.8, 65.4, 63.2, 23.5, 22.0, 15.6 ppm. MS: m/z = 286 $[M]^+$.

**Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5e)**



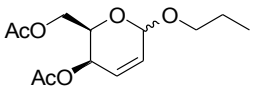
IR (neat) $\nu_{max}$ 3050, 2925, 1746, 1530, 862 $cm^{-1}$; $^1H$ NMR (500 MHz): δ 7.27-7.30 (m, 5H), 5.79-5.85 (m, 2H), 5.27 (d, J = 1.2, 9.6 Hz, 1H), 5.06 (bs, 1H), 4.74 (d, J = 12 Hz, 1H), 4.53 (d, J = 12 Hz, 1H), 4.00-4.24 (m, 3H), 2.03 (s, 3H), 2.01 (s, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.9, 170.3, 138.2, 129.4, 128.5, 128.0, 127.9, 127.8, 93.6, 67.3, 67.1, 65.3, 62.9, 21.0, 20.9 ppm. MS: m/z = 320 $[M]^+$.

**Prop-2-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (6a)**



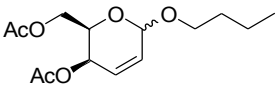
IR (neat) $\nu_{max}$ 3060, 2941, 1740, 1221, 923 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.96-5.83 (m, 1H), 5.29-5.25 (m, 1H), 5.16 (d, J = 10.5 Hz, 1H), 5.1-5.27 (m, 3H), 5.01 (bs, 1H), 3.97-4.25 (m, 5H), 2.03 (s, 3H), 2.01 (s, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.8, 170.3, 134.1, 129.3, 127.8, 117.6, 93.7, 69.3, 67.0, 65.3, 63.0, 21.0, 20.8 ppm. MS: m/z = 270 $[M]^+$.

**Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (6b)**



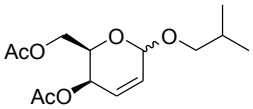
IR (neat) $\nu_{max}$ 3055, 2932, 1753, 1135, 1025 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.82-5.98 (m, 2H), 5.36 (dd, J = 1.2, 9.6 Hz, 1H), 5.06 (s, 1H), 4.31-4.15 (m, 3H), 3.48-3.45 (m, 1H), 3.32-3.30 (m, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 1.41-1.39 (m, 2H), 1.26 (t, J = 7.25 Hz, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.6, 170.8, 129.2, 128.1, 94.2, 66.6, 65.4, 64.5, 63.0, 20.5, 20.7, 19.5, 15.8 ppm. MS: m/z = 272 $[M]^+$.

**Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (6c)**



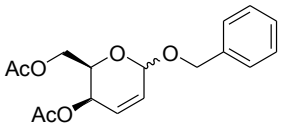
IR (neat) $\nu_{max}$ 3042, 2935, 1743, 1530, 1221, 866 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.84 (bs, 2H), 5.30-5.24 (dd, J = 9.2, 1.1 Hz, 1H), 5.03 (bs, 1H), 4.22- 4.18 (m, 2H), 4.11-4.08 (m, 1H), 3.82-3.68 (m, 1H), 3.55-3.49 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 1.50-1.45 (m, 2H), 1.34-1.23 (m, 2H,), 0.99 (t, J = 4.9 Hz, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.8, 170.3, 129.5, 128.7, 94.3, 67.3, 65.5, 65.2, 63.1, 30.5, 21.5, 21.0, 19.6, 14.5 ppm. MS: m/z = 286 $[M]^+$.

**isoButyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (6d)**



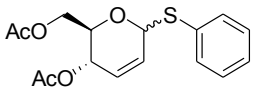
IR (neat) $\nu_{max}$ 3058, 2954, 1756, 1530, 1025 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.85 (m, 2H), 5.27 (dd, J = 1.5, 9.6 Hz, 1H), 5.04 (bs, 1H), 4.19-4.08 (m, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 3.87 (dt, J = 7.5, 12.0 Hz, 1H), 3.82 (dt, J = 7.5, 12.0 Hz, 1H), 1.52-1.43 (m, 2H), 1.34-1.32 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.5, 170.0, 128.7, 92.6, 70.5, 66.6, 65.2, 63.2, 23.3, 22.0, 15.2 ppm. MS: m/z = 286 $[M]^+$.

**Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (6e)**



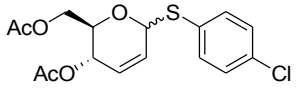
IR (neat) $\nu_{max}$ 3056, 2845, 1743, 1561, 951 $cm^{-1}$; $^1H$ NMR (500 MHz): δ 7.30-7.25 (m, 5H), 5.85-5.79 (m, 2H), 5.27 (d, J = 1.2, 9.6 Hz, 1H), 5.03 (bs, 1H), 4.75 (d, J = 12 Hz, 1H), 4.59 (d, J = 12 Hz, 1H), 4.22-4.19 (m, 3H), 2.04 (s, 3H), 2.01 (s, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.9, 170.5, 138.0, 129.2, 128.1, 128.0, 127.5, 127.0, 93.1, 67.2, 67.0, 65.1, 62.2, 21.1, 20.2 ppm. MS: m/z = 320 $[M]^+$.

**Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (7a)**



IR (neat) $\nu_{max}$ 3052, 2952, 1752, 1620, 1591, 866 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.47-7.37 (m, 5H), 6.15 (dd, J = 3.5, 10.0 Hz, 1H), 6.04 (dd, J = 1.5, 5.0 Hz, 1H), 5.77 (s, 1H), 5.06 (dd, J = 2.5, 6.5 Hz, 1H), 4.64-4.62 (m, 1H), 4.19-4.03 (m, 2H), 2.00 (s, 3H), 1.96 (s, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 171.6, 171.1, 157.0, 129.3, 121.5, 116.4,126.4, 123.8, 82.4, 66.4, 63.0, 62.3, 20.2, 19.5 ppm. MS: m/z = 322 $[M]^+$.

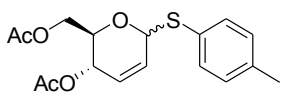
**p-Chlorophenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (7b)**



IR (neat) $\nu_{max}$ 3065, 2921, 1739, 1622, 1565, 1025, 952 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.13 (dd, J = 3.5, 10.0, Hz, 1H), 6.05 (dd, J = 5.0, 10.0, Hz, 1H), 5.73 (d, J = 1.0 Hz, 1H),

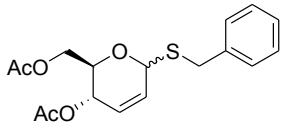
5.06 (dd, J = 2.5, 5.0 Hz, 1H), 4.62-4.59 (m, 1H), 4.22-4.17 (m, 2H), 2.04 (s, 3H), 1.99 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.6, 133.5,132.2, 130.8, 130.1, 128.5, 124.6, 83.9, 67.6, 63.6, 62.2, 20.8, 20.5 ppm. MS: m/z = 356 $[M]^+$.

**p-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (7c)**



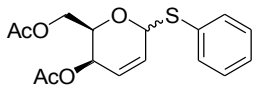
IR (neat) $\nu_{max}$ 3065, 2891, 1752, 1631, 1530, 861 $cm^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.15 (dd, J = 3.5, 5.0 Hz, 1H), 6.08 (dd, J = 2.0 5.5 Hz, 1H), 5.65 (dd, J = 2.0, 3.0 Hz, 1H), 5.05 (dd, J = 2.5, 5.5 Hz, 1H), 4.67 (dd, J = 2.5, 6.0 Hz, 1H), 4.19-4.10 (m, 2H), 2.25 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 172.2, 171.1, 155.2, 131.5, 129.2, 126.4, 125.3, 117.6, 82.5, 66.5, 64.4, 61.6, 30.1, 20.9, 20.3 ppm. MS: m/z = 336 $[M]^+$.

**Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (7d)**



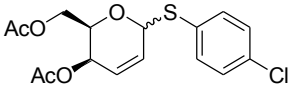
IR (neat) $\nu_{max}$ 3052, 2952, 1752, 1620, 1591, 923 $cm^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.35-7.15 (m, 5H), 5.95-5.92 (m, 2H), 5.38 (dd, J = 2.0, 6.5 Hz, 1H), 5.02 (dd, J = 2.5, 5.0 Hz, 1H), 4.53-4.50 (m, 1H), 4.23-4.12 (m, 2H), 3.85-3.80 (m, 1H), 3.69 (d, J = 12.5 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.9, 171.3, 140.1, 129.0, 128.1, 127.6, 127.0, 124.3, 84.0, 68.1, 64.3, 62.9, 62.1, 21.9, 20.5 ppm. MS: m/z = 336 $[M]^+$.

**Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-1-thio-hex-2-enopyranoside (8a)**



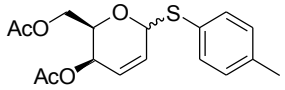
IR (neat) $\nu_{max}$ 3062, 2865, 1601, 1587, 1223, 1024 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.46-7.22 (m, 5H), 6.15 (dd, J = 3.5, 10.0 Hz, 1H), 6.03 (dd, J = 1.5, 5.0 Hz, 1H), 5.73 (s, 1H), 5.10 (dd, J = 2.5, 6.5 Hz, 1H), 4.64-4.61 (m, 1H), 4.19-4.03 (m, 2H), 2.00 (s, 3H), 1.98 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.5, 171.0, 157.6, 129.8, 121.4, 116.4,126.6, 123.2, 82.2, 67.1, 63.5, 62.6, 20.9, 19.6 ppm. MS: m/z = 322 $[M]^+$.

**p-Chlorophenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-1-thio-hex-2-enopyranoside (8b)**



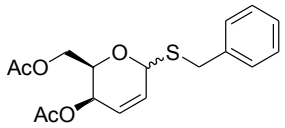
IR (neat) $\nu_{max}$ 3056, 2854, 1752, 1645, 1587, 1004 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.12 (dd, J = 10.0, 3.5 Hz, 1H), 6.04 (dd, J = 10.0, 3.5 Hz, 1H), 5.73 (bs, 1H), 5.06-5.05 (m, 1H), 4.61-4.59 (m, 1H), 4.21-4.18 (m, 2H), 2.01 (s, 3H), 1.97 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.4, 170.1, 133.1,132.4, 130.9, 129.2, 128.9, 124.7, 83.4, 67.2, 63.1, 62.6, 20.7, 20.6 ppm. MS: m/z = 356 $[M]^+$.

**p-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-1-thio-hex-2-enopyranoside (8c)**



IR (neat) $\nu_{max}$ 3048, 2934, 1752, 1620, 1591, 1241, 861 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.15 (dd, J = 3.5, 5.0 Hz, 1H), 6.03 (dd, J = 2.0 5.5 Hz, 1H), 5.69 (dd, J = 2.0, 3.0 Hz, 1H), 5.05 (dd, J = 2.5, 5.5 Hz, 1H), 4.65 (dd, J = 2.5, 6.0 Hz, 1H), 4.21-4.19 (m, 2H), 2.25 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 172.5, 171.8, 155.8, 131.7, 129.2, 117.5, 126.4, 125.3, 82.6, 66.3, 64.1, 61.6, 30.8, 20.9, 20.2 ppm. MS: m/z = 336 $[M]^+$.

**Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-threo-1-thio-hex-2-enopyranoside (8d)**



IR (neat) $\nu_{max}$ 3053, 2886, 1749, 1632, 1595, 923, $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.26-7.23 (m, 5H), 5.97-5.93 (m, 2H), 5.38 (dd, J = 2.0, 6.5 Hz, 1H), 5.03 (dd, J = 2.5, 5.0 Hz, 1H), 4.53-4.51 (m, 1H), 4.21-4.16 (m, 2H), 3.82-3.81 (m, 1H), 3.67 (d, J = 12.5 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.5, 171.0, 139.3, 128.5, 127.7, 127.3, 126.4, 124.6, 83.5, 67.5, 64.2, 62.6, 61.7, 21.0, 20.6 ppm. MS: m/z = 336 $[M]^+$.

## References


[1]. (a)Ferrier, R. J. Adv. Carbohydr. Chem. Biochem. 1969, 24, 199–266; (b) Schmidt, R. R.; Angerbauer, R. Carbohydr. Res. 1979, 72, 272–275; (c) Fraser, R. B. Acc. Chem. Res. 1985, 18, 347–354; (d) Toshima, K.; Tatsuta, K. Chem. Rev. 1993, 93, 1503–1531; (e) Dorgan, B. J.; Jackson, R. F. W. Synlett 1996, 859–861; (f) Danishefsky, S. J.; Bilodeau, M. T. Angew. Chem., Int. Ed. Engl. 1996, 35, 1380–1419; (g) Liu, Z. J.; Zhou, M.; Min, J. M.; Zhang, L. H. Tetrahedron: Asymmetry 1999, 10, 2119–2127; (h) Nicolaou, K. C.;Mitchell, H. J. Angew. Chem., Int. Ed. 2001, 40, 1576–1624.

[2]. Bussolo, V. D.; Kim, Y. J.; Gin, D. Y. J. Am. Chem. Soc. 1998, 120, 13515–13516.

[3]. (a)Schmidt, R. R.; Angerbauer, R. Carbohydr. Res. 1981, 89, 159–162; (b) Angerbauer, R.; Schmidt, R. R. Carbohydr. Res. 1981, 89, 193–201.

[4]. Tolstikov, A. G.; Tolstikov, G. A. Russ. Chem. Rev. 1993, 62, 579–601.

[5]. Bettadaiah, B. K.; Srinivas, P. Tetrahedron Lett. 2003, 44, 7257–7259.

[6]. Gorityala, B. K.; Cai, S.; Lorpitthaya, R.; Ma, J.; Pasunooti, K. K.; Liu, X. W. Tetrahedron Lett. 2009, 50, 676–679.

[7]. Babu, B. S.; Balasubramanian, K. K. Tetrahedron Lett. 2000, 41, 1271–1274.
[8]. (a)Grynkiewicz, G.; Priebe,W.; Zamojski, A. Carbohydr. Res. 1979, 68, 33–41; (b) Bhate, P.; Horton, D.; Priebe, W. Carbohydr. Res. 1985, 144, 331–337.
[9]. Takhi, M.; Rahman, A.; Adel, A. H.; Schmidt, R. R. Tetrahedron Lett. 2001, 42, 4053–4056.
[10]. Masson, C.; Soto, J.; Bessodes, M. Synlett 2000, 1281–1282.
[11]. (a)Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M. Synlett 1995, 306–308; (b) Shanmugasundaram, B.; Bose, A. K.; Balasubramanian, K. K. Tetrahedron Lett. 2002, 43, 6795–6798; (c) Oliviera, R. N.; Freitas, J. R. F.; Srivastava, R. M. Tetrahedron Lett. 2002, 43, 2141–2143.
[12]. Yadav, J. S.; Reddy, B. V. S.; Reddy, J. S. S. J. Chem. Soc., Perkin Trans. 1 2002, 2390–2394.
[13]. Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M.; Kinoshita, M. J. Chem. Soc., Chem. Commun. 1993, 704–706.
[14]. Koreeda, M.; Houston, T. A.; Shull, B. K.; Klemke, E.; Tuinman, R. J. Synlett 1994, 90–92.
[15]. Lopez, J. C.; Fraser, R. B. J. Chem. Soc., Chem. Commun. 1992, 94–96.
[16]. Yadav, J. S.; Reddy, B. V. S.; Pandey, S. K. New J. Chem. 2001, 25, 538–540.
[17]. Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Satyanarayana, M. Tetrahedron Lett. 2002, 43, 7009–7012.
[18]. (a)Misra, A. K.; Tiwari, P.; Agnihotri, G. Synthesis 2005, 260–266; (b) Agarwal, A.; Rani, S.; Vankar, Y. D. J. Org. Chem. 2004, 69, 6137–6140.
[19]. Hadfield, A. F.; Sartoli, A. C. Carbohydr. Res. 1982, 101, 197–208.
[20]. Lopez, J. C.; Gomez, A. M.; Valverde, S.; Fraser, R. B. J. Org. Chem. 1995, 60, 3851–3858.