Electronic Supplementary Information

for

$HClO_4$·SiO_2 catalysed synthesis of alkyl 3-deoxy-hex-2-enopyranosides from 2-hydroxy-glucal ester: Application in the synthesis of a *cis*-fused bicyclic ether and a 4-amino-*C*-glucoside

Preeti Gupta, Nitee Kumari, Aditi Agarwal and Yashwant D. Vankar*
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India
E-mail: vankar@iitk.ac.in; Fax: 0091-512-259 7492

CONTENTS

Octanyl 2,4,6-tri-O-acetyl-3-deoxy-α/β–D-erythro-hex-2-enopyranoside (9).

Yield: 85% (10:1 mixture of α:β anomer). Found: C, 60.12; H, 7.88. Calc. for $C_{20}H_{32}O_8$ C, 59.98; H, 8.05%; R_f 0.6 (hexane : ethyl acetate, 7 : 3); IR (neat) ν_{max}/cm^{-1} 2928, 1746; δ_H (400 MHz, $CDCl_3$) (α-anomer) 0.88 (3H, t, *J* = 6.8 Hz, C*H*$_3$), 1.28 (10H, m, 5 x (C*H*$_2$)), 1.59-1.61 (2H, m, OCH_2-C*H*$_2$), 2.08 (3H, s, COC*H*$_3$), 2.10 (3H, s, COC*H*$_3$), 2.17 (3H, s, COC*H*$_3$), 3.45-3.53 (1H, m, -OC*H*$_2$), 3.74-3.87 (1H, m, -OC*H*$_2$), 4.11-4.29 (3H, m, H-5, H-6, H-6'), 5.05 (1H, s, H-1), 5.45 (1H, br d, *J* = 9.5 Hz, H-4), 5.72 (1H, d, *J* = 2.2 Hz, H-3); (β-anomer) 5.27 (1H, s, H-1), 5.76 (1H, d, *J* = 4.6 Hz, H-3); δ_C (100 MHz, $CDCl_3$) (α-anomer) 14.0, 20.7, 20.9, 22.6, 26.0, 29.2, 29.5, 31.7, 62.5, 65.3, 67.0, 69.3, 72.5, 93.8, 112.0, 115.0, 146.6, 168.1, 170.0, 170.6; $MSES^+$: 418 $[M + Na]^+$.

Cyclohexyl 2,4,6-tri-*O*-acetyl-3-deoxy-α/β-D-erythro-hex-2-enopyranoside (10).

Yield: 92% (8:1 mixture of α:β anomer). Found: C, 58.29; H, 7.11. Calc. for $C_{18}H_{26}O_8$ C, 58.37; H, 7.08%; R_f 0.6 (hexane : ethyl acetate, 7 : 3); IR (neat) ν_{max}/cm^{-1} 2933, 1745; δ_H (400 MHz, $CDCl_3$) (α-anomer) 1.19-1.93 (10H, m, *cyclohexyl* protons), 2.07 (3H, s, COC*H*$_3$), 2.09 (3H, s, COC*H*$_3$), 2.16 (3H, s, COC*H*$_3$), 3.60 (1H, m, H-1'), 4.21-4.28 (3H, m, H-5, H-6, H-6'), 5.21 (1H, s, H-1), 5.43 (1H, dd, *J* = 2.4, 9.3 Hz, H-4), 5.71 (1H, d, *J* = 2.0 Hz, H-3); (β-anomer) 5.39 (1H, s, H-1), 5.75 (1H, d, *J* = 4.9 Hz, H-3); δ_C (100 MHz, $CDCl_3$) (α-anomer) 20.7, 20.8, 20.9, 23.8, 24.0, 25.4, 31.9, 33.5, 62.7, 65.4, 67.0, 72.4, 92.4, 114.9, 146.8, 168.1, 170.1, 170.6; $MSES^+$: 393 $[M + Na]^+$.

Benzyloxy-but-2-enyl 2,4,6-tri-*O*-acetyl-3-deoxy-α/β-D-erythro-hex-2-enopyrano-side (13).

Yield: 80% (3:1 mixture of α:β anomer). Found: C, 61.56; H, 6.35. Calc. for $C_{23}H_{28}O_9$ C, 61.60; H, 6.29%; R_f 0.5 (hexane : ethyl acetate, 7 : 3); IR (neat) ν_{max}/cm^{-1} 2926, 1746; δ_H (400 MHz, $CDCl_3$) (α–anomer) 2.04 (3H, s, COC*H*$_3$), 2.05 (3H, s, COC*H*$_3$), 2.12 (3H, s, COC*H*$_3$), 4.06-4.27 (7H, m, H-1', H-1'', H-4', H-4'', H-5, H-6, H-6'), 4.48, 4.49 (2H, 2s, OC*H*$_2$$C_6H_5$), 5.05 (1H, s, H-1), 5.42 (1H, d, *J* = 2.9, 9.5 Hz, H-4), 5.69-5.81 (3H, m, H-3, H-2', H-3'), 7.27 (5H, m, OCH_2C_6*H*$_5$); (β-anomer) 5.24 (1H, s, H-1); δ_C(100 MHz, $CDCl_3$) (α-anomer) 20.7, 20.8, 20.9, 29.6, 58.7, 62.5, 64.1, 64.2, 65.2, 65.6, 67.1, 72.3, 93.1, 115.3, 127.7, 128.4, 130.3, 132.2, 137.9, 146.2, 168.1, 170.0, 170.6; $MSES^+$: 466 $[M + NH_4]^+$.

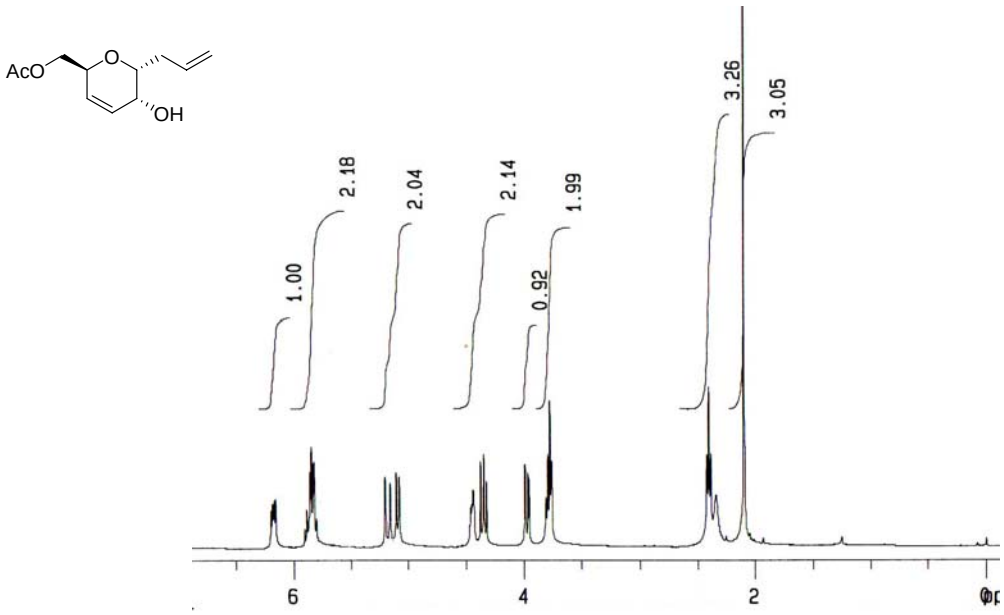
Phenyl 2,4,6-tri-*O*-acetyl-3-deoxy-α/β-D-erythro-hex-2-enopyranoside (14).

Yield: 84% (8:1 mixture of α:β anomer). Found: C, 59.31; H, 5.53. Calc. for $C_{18}H_{20}O_8$ C, 59.34; H, 5.53%; R_f 0.5 (hexane : ethyl acetate, 7 : 3); IR (neat) ν_{max}/cm^{-1} 2923, 1743; δ_H (400 MHz, $CDCl_3$) (α-anomer) 1.99 (3H, s, COC*H*$_3$), 2.11 (3H, s, COC*H*$_3$), 2.18 (3H, s, COC*H*$_3$), 4.16-4.17 (3H, m, H-5, H-6, H-7), 5.53 (1H, br d, J = 8.5 Hz, H-4), 5.68 (1H, s, H-1), 5.88 (1H, d, J = 2.2 Hz, H-3), 7.04-7.10 (3H, m, C_6H_5), 7.29-7.33 (2H, m, C_6H_5); (β-anomer) 5.85 (1H, s, H-1), 5.97 (d, 1H, J = 5.6 Hz, H-3); δ_C(100 MHz, $CDCl_3$) (α-anomer) 20.6, 20.9, 21.0, 29.6, 62.2, 63.0, 65.1, 67.9, 92.6, 116.1, 116.3, 117.1, 122.8, 129.5, 145.5, 168.1, 170.1, 170.6; MSES$^+$: 387 $[M + Na]^+$.

***p*-Methylthiophenyl 2,4,6-tri-*O*-acetyl-3-deoxy-α/β-D-erythro-hex-2-enopyrano-side (18)**.

Yield: 82% (5:1 mixture of α:β anomer). Found: C, 57.79; H, 5.64; S, 8.18. Calc. for $C_{19}H_{22}O_7S$ C, 57.86; H, 5.62; S, 8.13%; R_f 0.6 (hexane : ethyl acetate, 7 : 3); IR (neat) ν_{max}/cm^{-1} 2924, 1744; δ_H(400 MHz, $CDCl_3$) (α-anomer) 2.02 (3H, s, COC*H*$_3$), 2.03 (3H, s, COC*H*$_3$), 2.14 (3H, s, COC*H*$_3$), 2.27 (3H, s, *p*C*H*$_3$-C_6H_4), 4.16-4.23 (2H, m, H-6, H-6'), 4.42-4.46 (1H, m, H-5), 5.39 (1H, dd, J = 1.4, 9.5 Hz, H-4), 5.60 (1H, s, H-1), 5.64 (1H, d, J = 1.4 Hz, H-3), 7.03-7.07 (2H, d, J = 8.1 Hz, C_6H_4), 7.35 (2H, d, J = 8.1 Hz, C_6H_4); (β-anomer) 5.68 (1H, d, H-3), 5.81 (1H, s, H-1); δ_C (100 MHz, $CDCl_3$) (α-anomer) 20.7, 20.9, 21.0, 21.1, 62.7, 64.9, 67.5, 83.9, 115.1, 129.5, 129.7, 132.7, 132.7, 134.1, 138.2, 146.6, 168.0, 170.1, 170.7; MSES$^+$: 412 $[M + NH_4]^+$.

^{1}H NMR for compound 21



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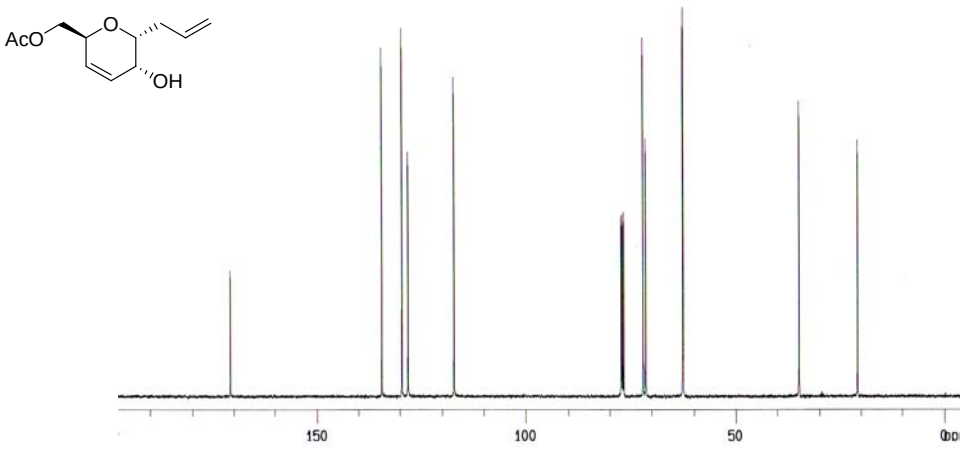

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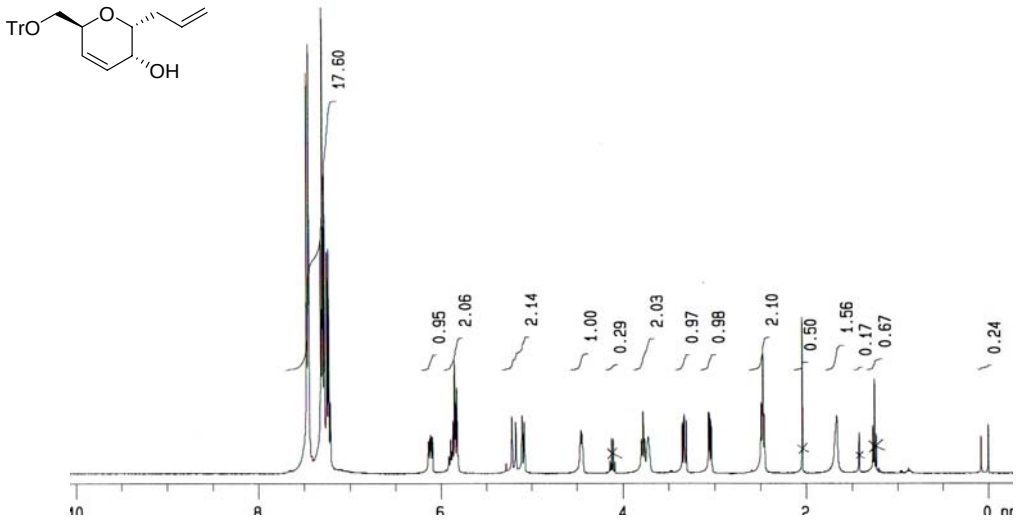

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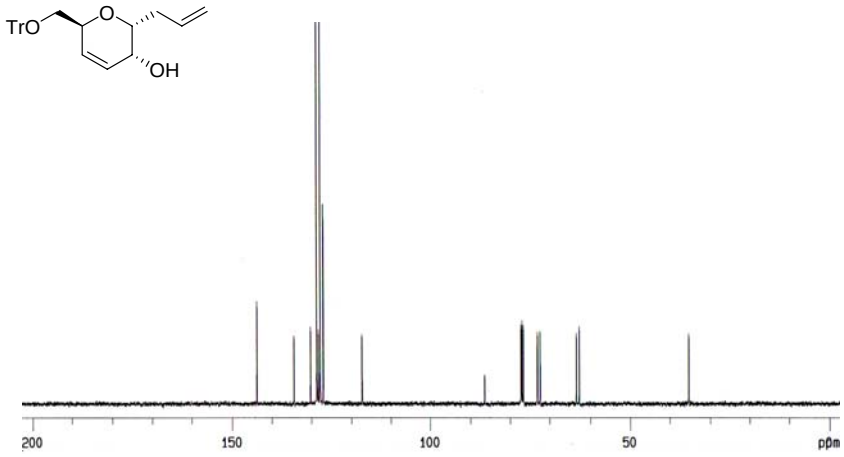

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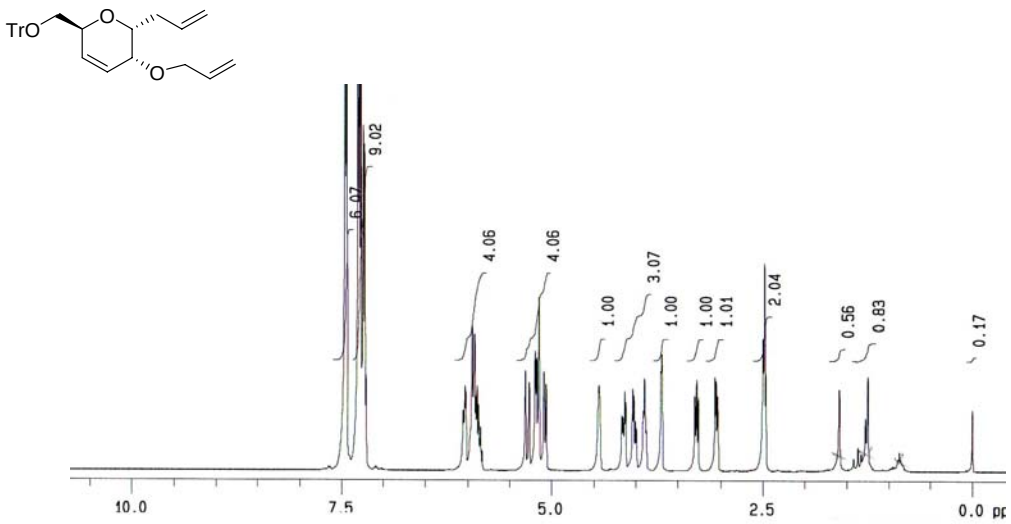

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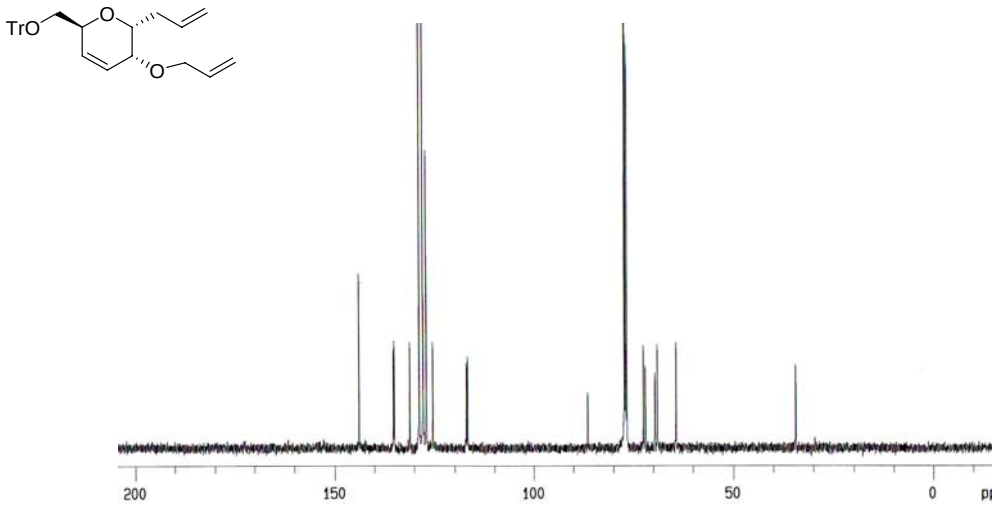
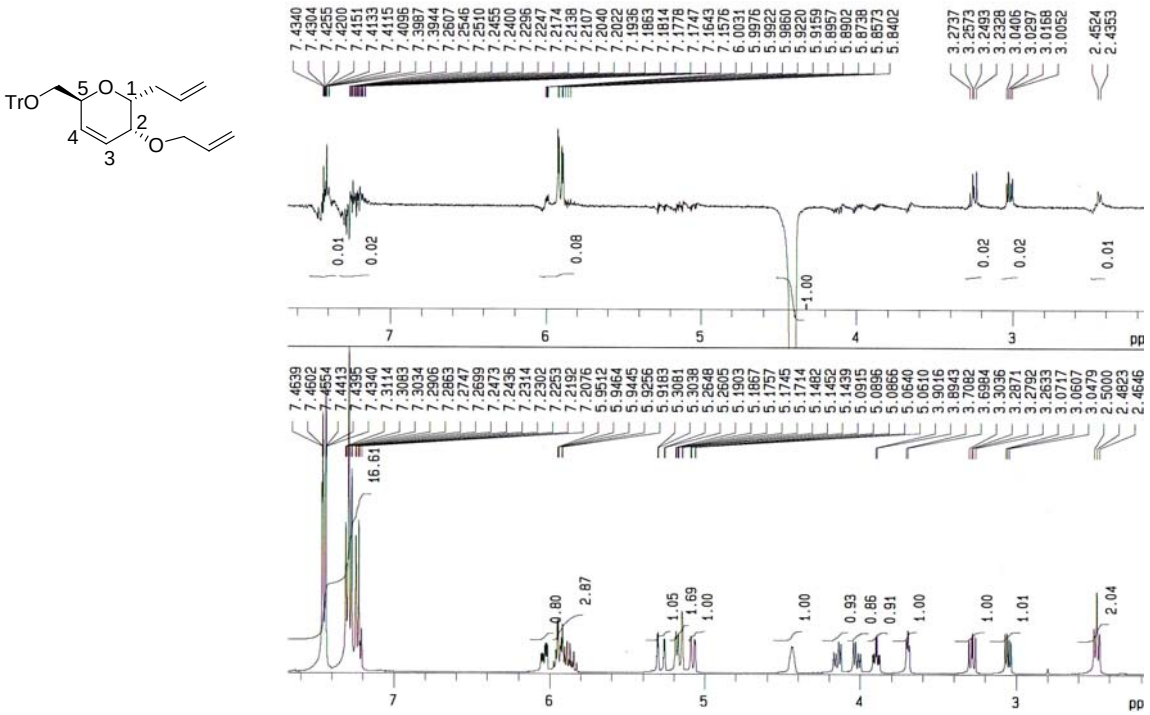


COSY spectrum for compound 23

nOe for compound 23 (Irradiation of H-5)



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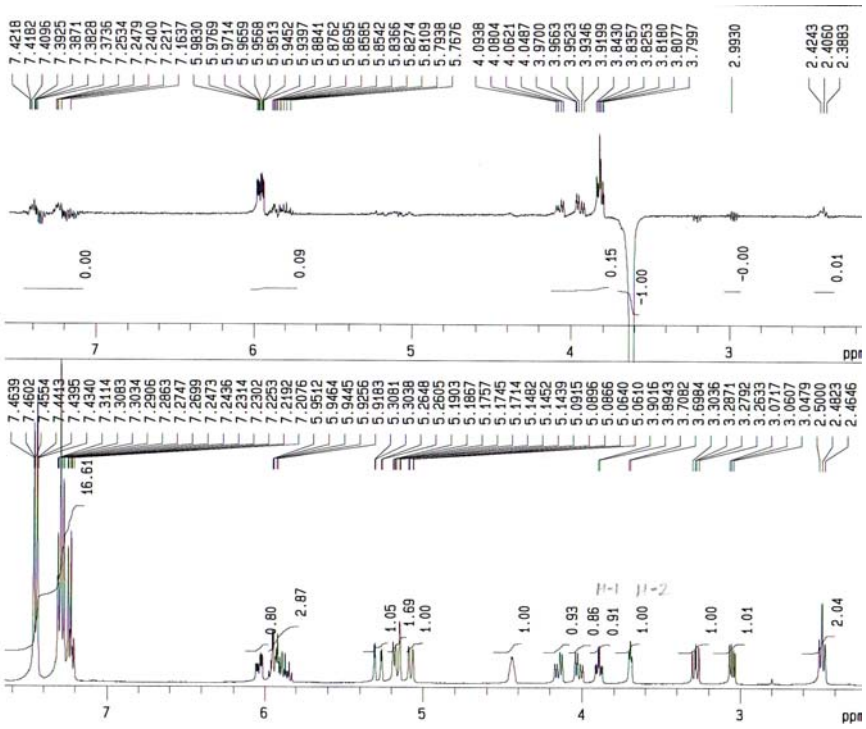

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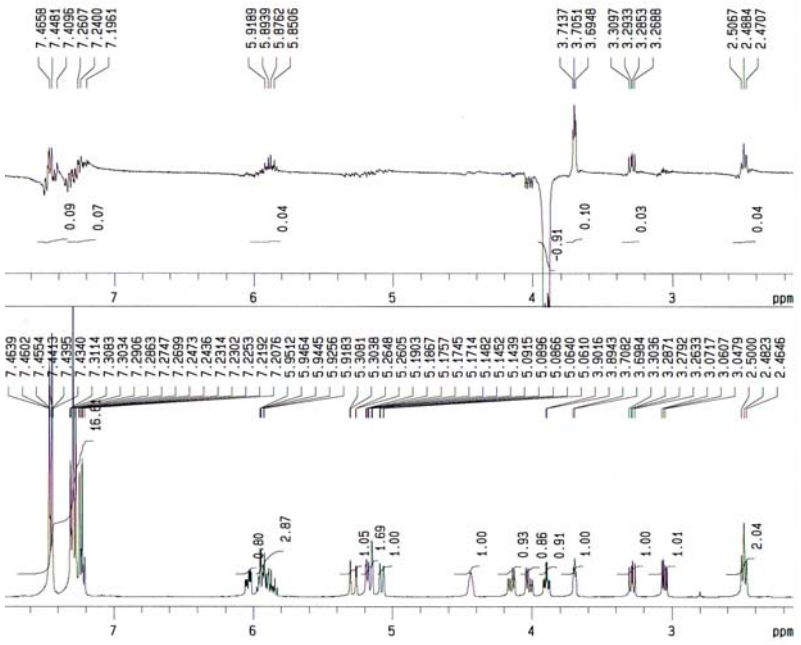
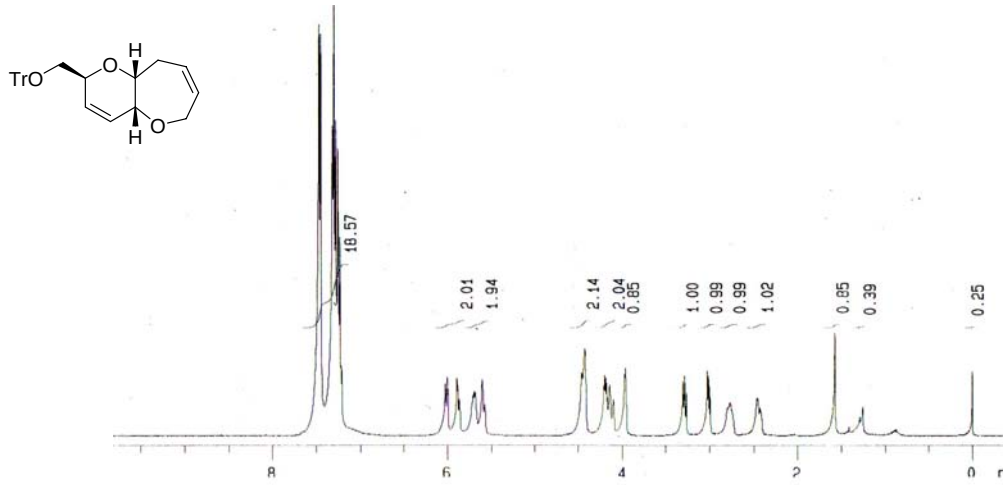
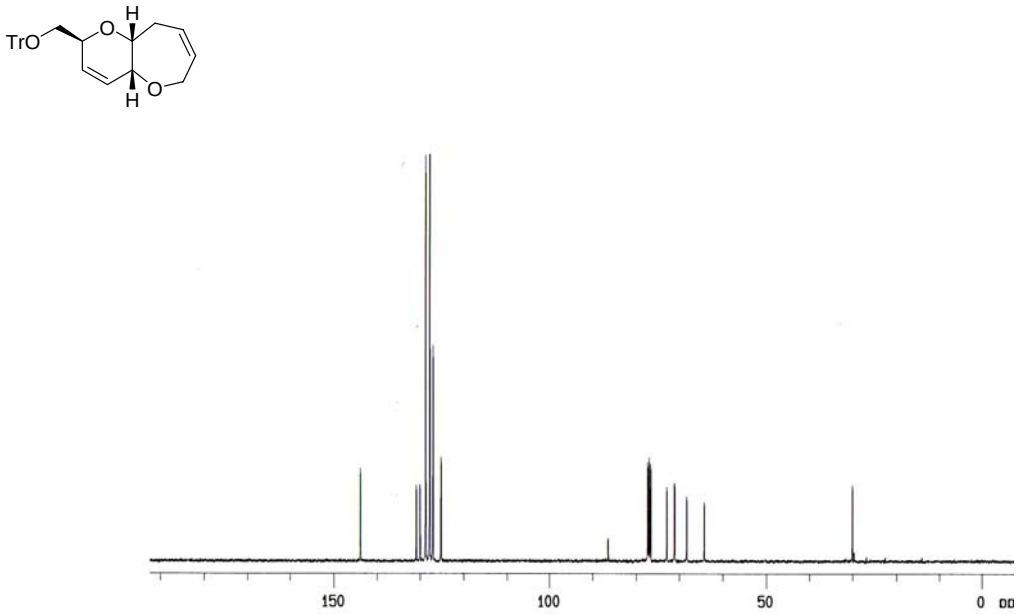


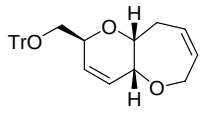
^{1}H NMR for compound 24

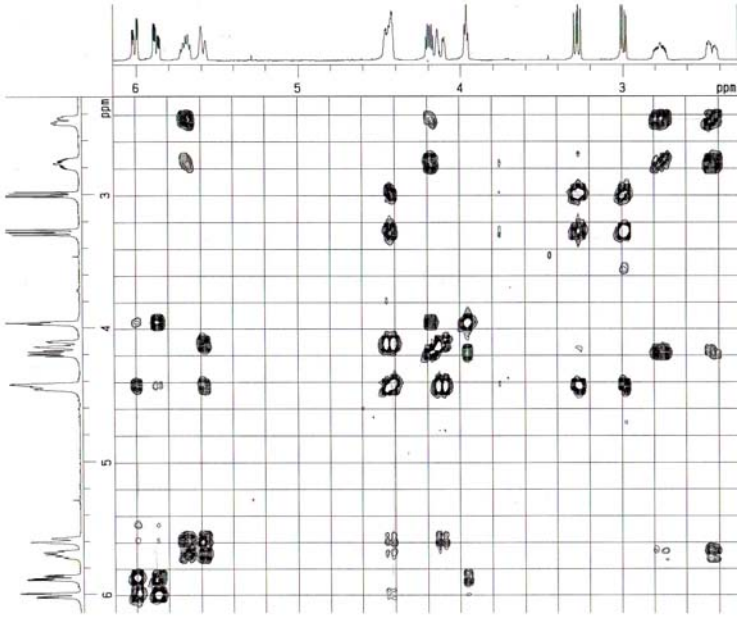


^{13}C NMR for compound 24

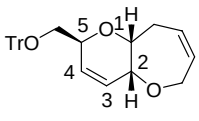


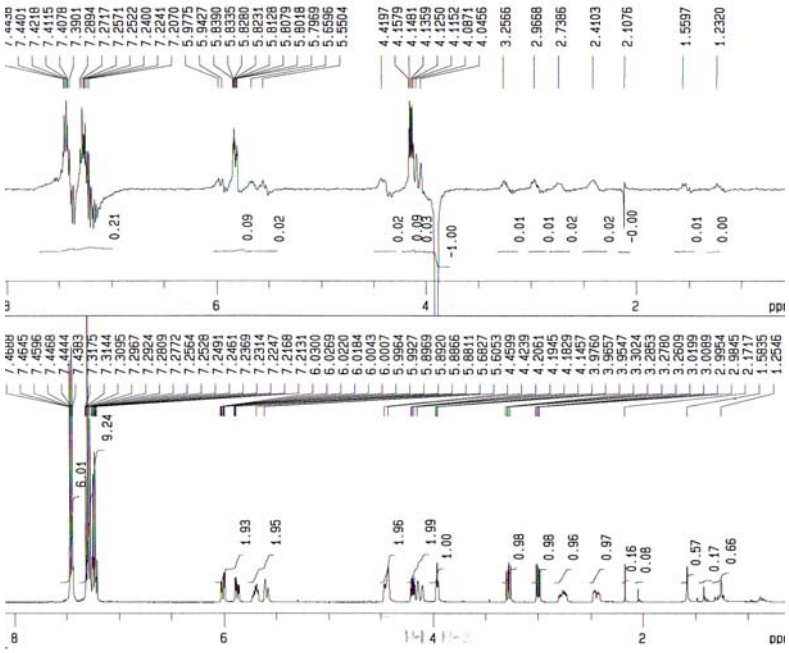
COSY spectrum for compound 24



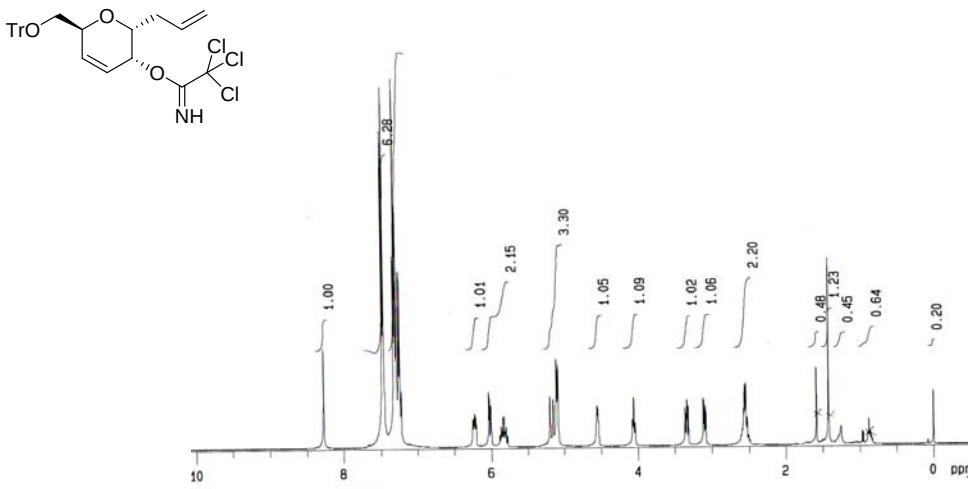


nOe for compound 24 (Irradiation of H-2)

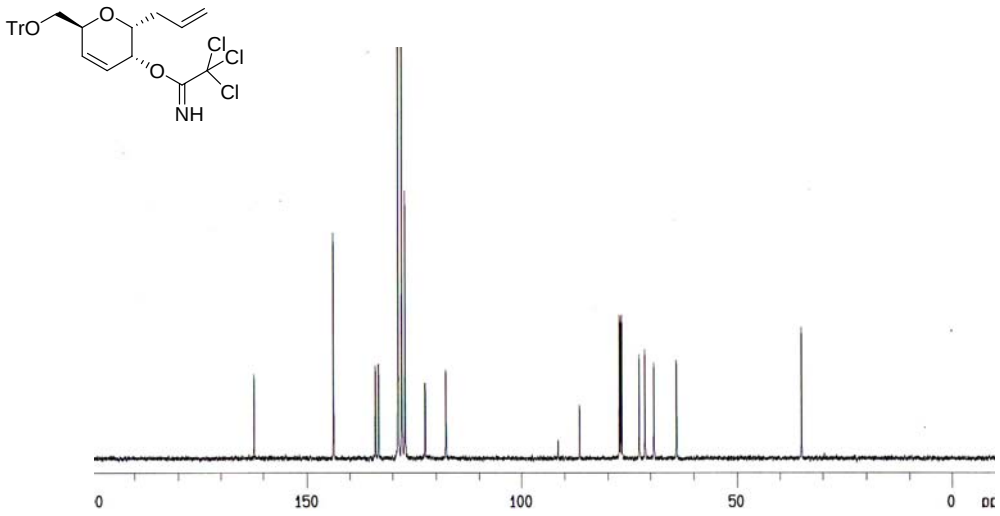




^{1}H NMR for compound 25



^{13}C NMR for compound 25



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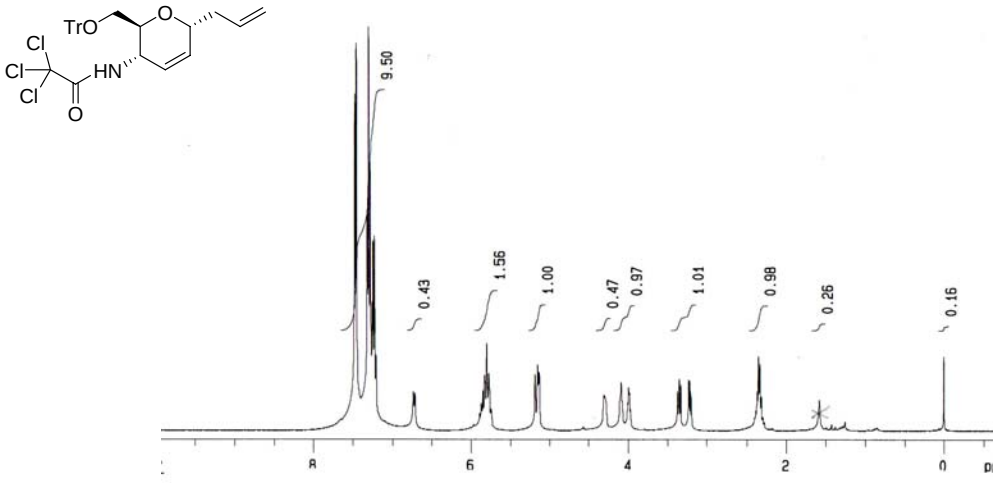

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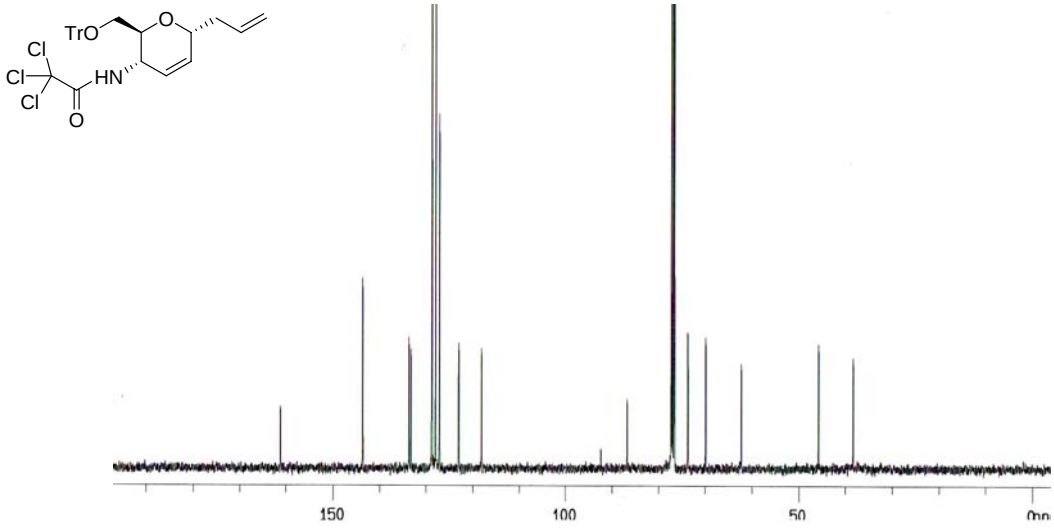

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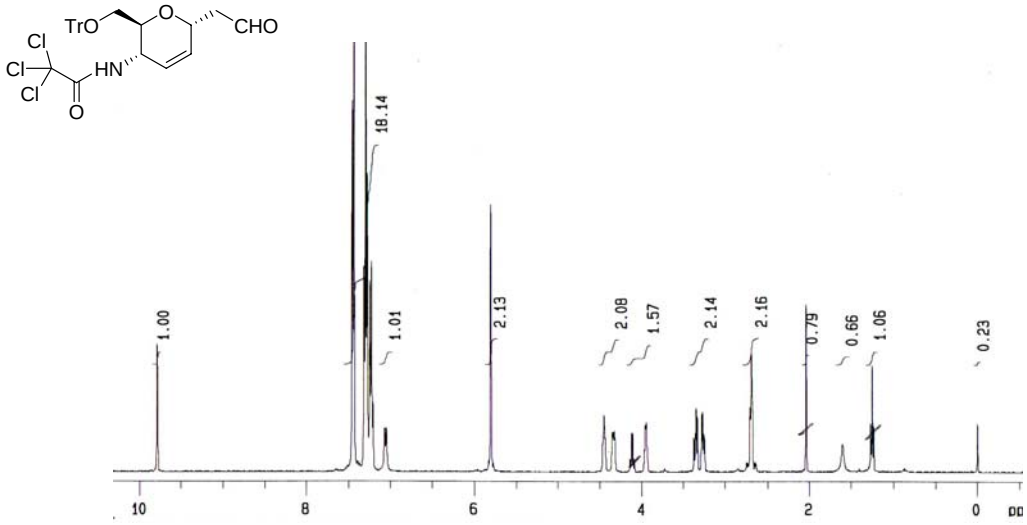

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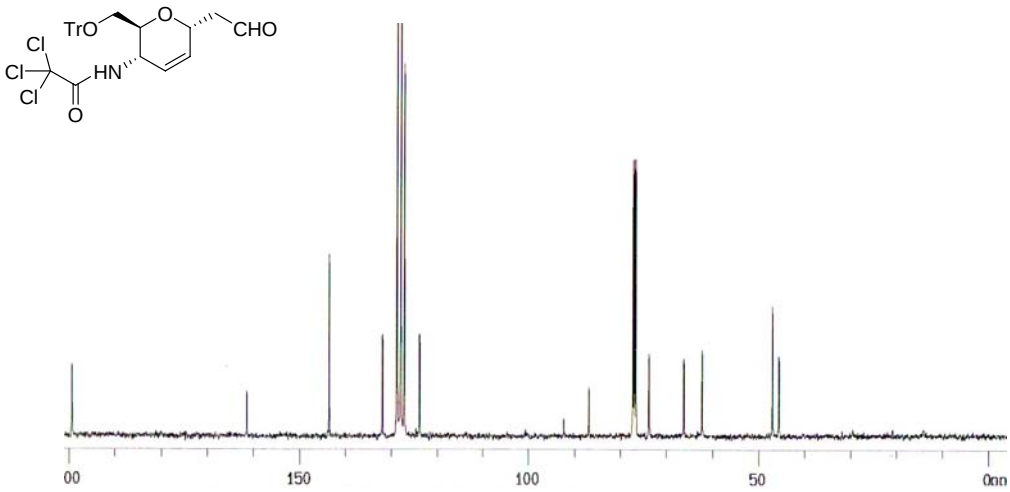
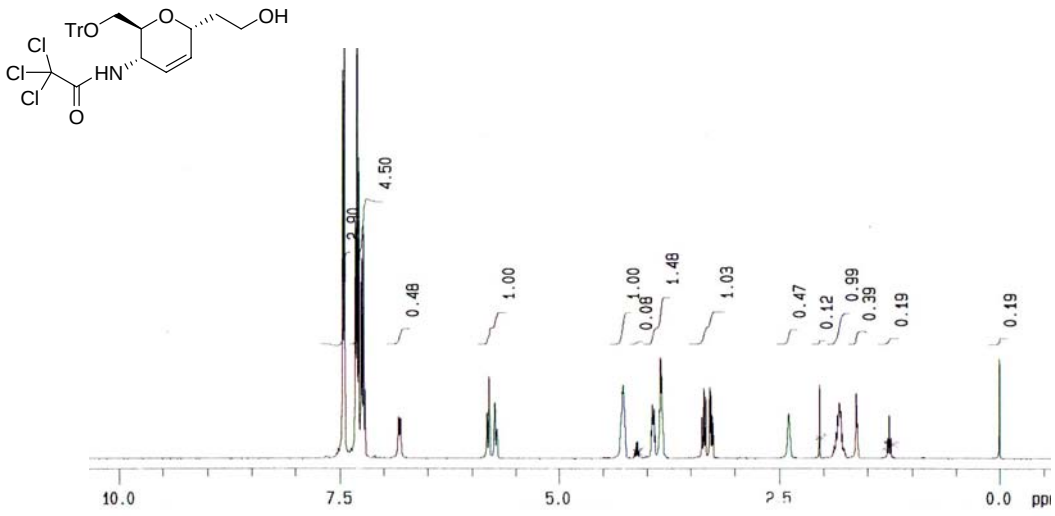


^{1}H NMR for compound 28



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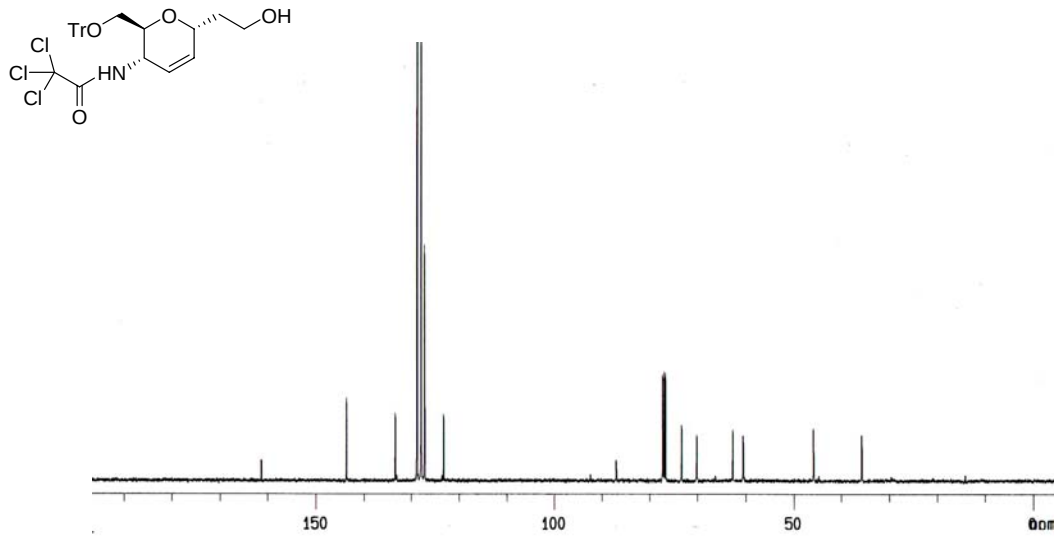

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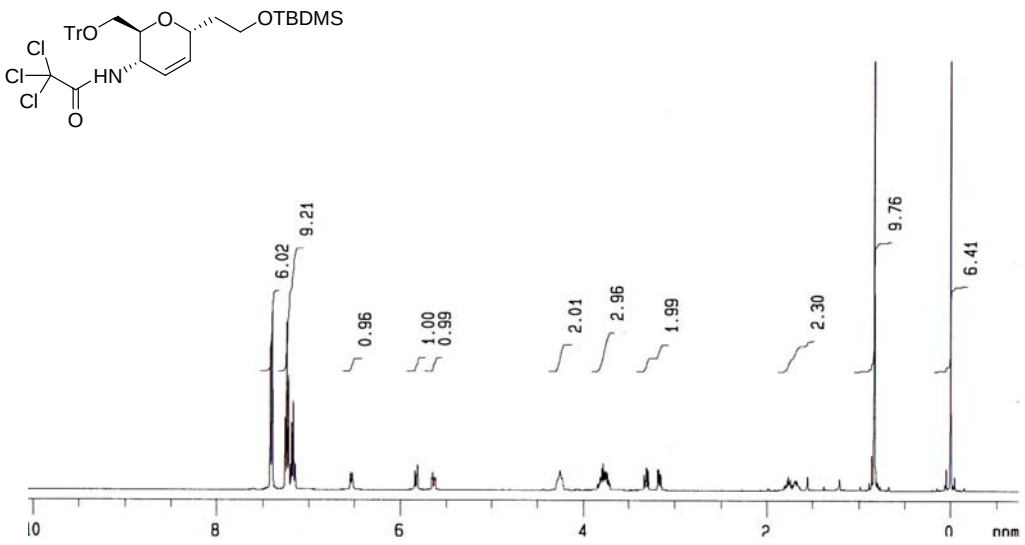

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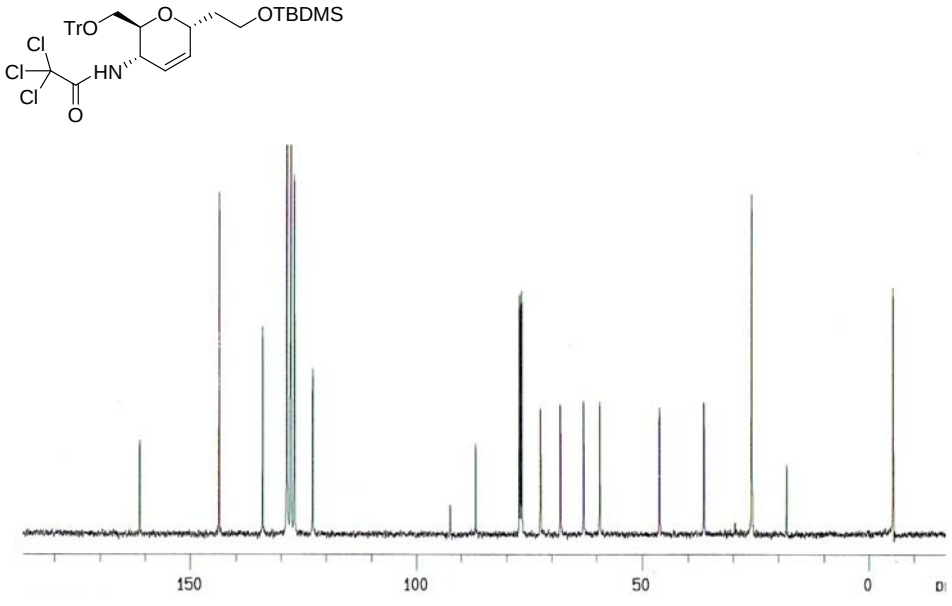

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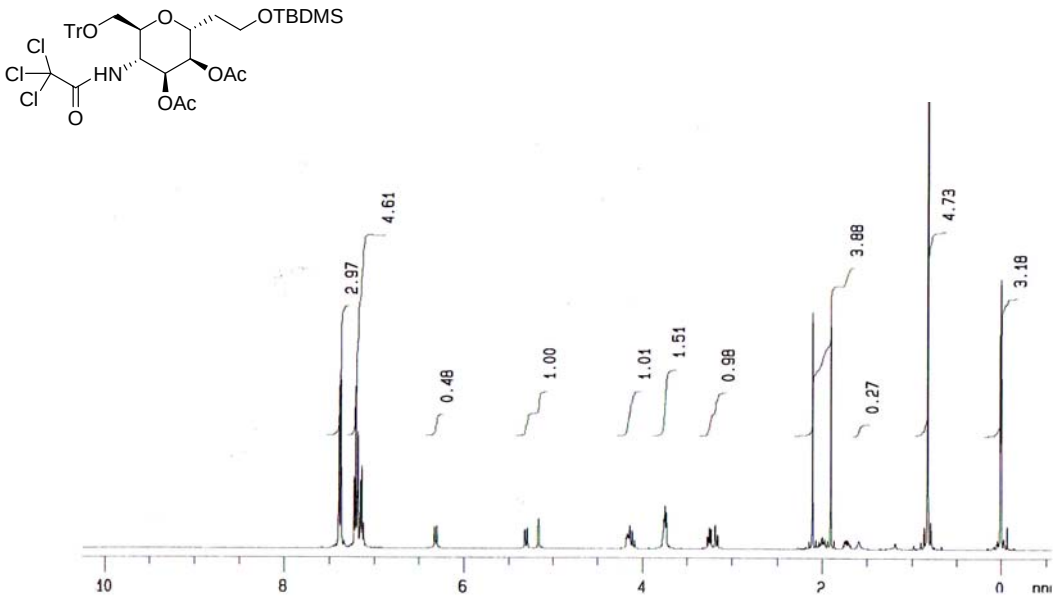

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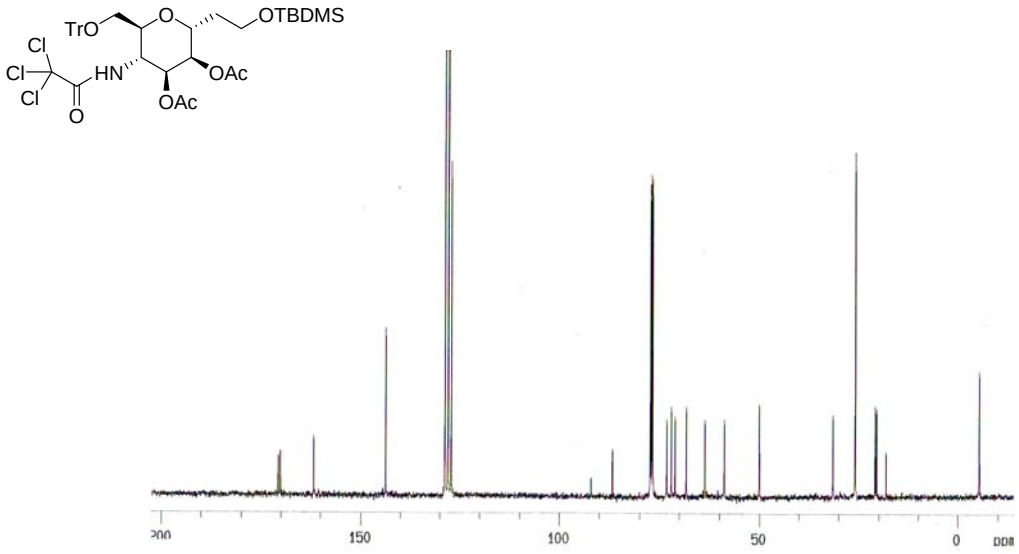

COSY spectrum for compound 30