Electronic Supporting Information

Microwave-Assisted Protocols Applied on the Available Methods for the Synthesis of 1',2,3,3',4,4'-Hexa-*O*- Benzylsucrose

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6,6'-Di-*O*-triphenylmethylosucose (2)

m.p. 98-100 °C; Lit.^[1] m.p. 99-102°C.

$[\alpha]_D^{20} +36.8$ (c 1.1, CH₃OH); Lit.^[1] $[\alpha]_D +38.7$ (c 1.09, CH₃OH).

$R_f = 0.65$ (Hex-AcOEt, 1:2)

IR: $\nu_{\max}$ (KBr): 3422 (O-H), 3056 (C-H, stretch, unsaturated), 2925 (C-H, stretch, saturated), 1700, 1654, 1596 (Ar), 1490, 1448 (C-C, stretch), 1221 (C-C-O), 1073 (C-O-C, C-O-H, stretch), 747, 701, 632 (Ar) cm⁻¹.

¹H NMR (400 MHz, CDCl₃) δ : 7.54-7.41 (m, 20H, Ar-H), 7.35-7.17 (m, 35H, Ar-H), 5.81 (d, $J_{1,2} = 3.7$ Hz, 1H, H-1), 4.32 (t, $J_{3',4'} = J_{4',5'} = 8.2$ Hz, 1H, H-4'), 4.18-4.08 (m, 1H, H-3'), 3.92-3.82 (m, 2H, H-5, H-5'), 3.56-3.41 (m, 4H, H-6', H-1'), 3.35-3.18 (m, 4H, H-3, H-4, 2H-6), 3.13-3.05 (m, 1H, H-2).

¹³C NMR (100 MHz, CDCl₃) δ : 143.7, 143.6 (quat. C_{Ar(Tr)}), 136.1, 128.8, 128.0, 127.5, 127.2, 123.8 (C_{Ar}), 104.8 (C-2'), 90.9 (C-1), 87.4, 87.1 (2 x C_{Ph3}), 79.2, 77.3, 74.7, 74.3, 71.6, 71.2, 70.9 (C-2,3,3',4,4',5,5'), 66.1, 64.4, 62.8 (C-1',6,6').

Figure 2.1. IR (KBr) of 2

Figure 2.2. ^1H NMR (CDCl_3 , 400 MHz) of **2**

Figure 2.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **2**

1',2,3,3',4,4'-Hexa-*O*-benzyl-6,6'-di-*O*-triphenylmethylsucrose (3)

m.p. 97-100 °C; no report in lit.

$[\alpha]_D^{20} +17.6$ (c 0.8, CHCl_3); Lit.^[1] $[\alpha]_D +20.6$ (c 1.0, CHCl_3).

$R_f = 0.59$ (Hex-AcOEt, 5:1)

IR: ν_{max} (KBr): 3029 (C-H, stretch, unsaturated), 2914 (C-H, stretch, saturated), 1604, 1596 (Ar); 1490, 1448 (C-C, stretch), 1362 (C-H, assym.), 1088, 1026 (C-O-C, C-O-H, stretch), 746, 697 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.50 (dd, $J_1 = 15.3$, $J_2 = 7.6$ Hz, 14H, Ar-H), 7.41 (d, $J = 7.8$ Hz, 7H, Ar-H), 7.37-7.11 (m, 48H, Ar-H), 7.10-7.02 (m, 7H, Ar-H), 6.91 (d, $J = 7.5$ Hz, 2H, Ar-H), 6.76 (d, $J = 6.7$ Hz, 2H, Ar-H), 6.40 (d, $J_{1,2} = 3.4$ Hz, 1H, H-1), 4.87 (t, $J_{3,4'} = J_{4',5'} = 9.0$ Hz, 1H, H-4'), 4.78-4.56 (m, 7H, H-5', H-6, Ar- CH_2), 4.38-4.31 (m, 2H, H-6, Ar- CH_2), 4.25-4.02 (m, 6H, H-3', H-5, H-6', H-4, Ar- CH_2), 3.93 (d, $J = 10.1$ Hz, 1H, Ar- CH_2), 3.79 (t, $J_{2,3} = J_{3,4} = 9.3$ Hz, 1H, H-3), 3.73-3.63 (m, 2H, H-1'), 3.58-3.51 (m, 2H, H-2, Ar- CH_2), 3.28 (d, $J = 10.1$ Hz, 1H, Ar- CH_2), 3.06 (d, $J = 9.9$ Hz, 1H, Ar- CH_2), 2.79 (d, $J = 9.1$ Hz, 1H, Ar- CH_2).

^{13}C NMR (100 MHz, CDCl_3) δ : 143.7, 143.6 (Cq trityl), 139.0, 138.7, 138.5, 137.6 (Cq benzyl), 128.9, 128.8, 128.3, 128.2, 128.1, 127.9, 127.7, 127.4, 127.2, 127.0, 126.7 (C_{Ar}), 104.2 (C-2'), 88.1 (C-1), 87.1, 86.7 (2 x CPh_3), 85.9, 84.6, 82.0, 80.5, 79.3, 78.3, 77.6, 75.9, 74.7, 73.1, 72.4, 71.9, 70.8 (C-2,3,3',4,4',5,5', 6 x OCH_2Ph), 67.1, 62.0, 61.7 (C-1',6,6').

Anal. Calcd for $\text{C}_{92}\text{H}_{86}\text{O}_{11}$: C, 80.79; H, 6.34. Found: C, 80.81; H 6.28.

Figure 3.1. IR (KBr) of 3

Figure 3.2. ^1H NMR (CDCl_3 , 400 MHz) of 3

Figure 3.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **3**

Figure 3.4. COSY of 3

Figure 3.5. HMQC of 3

Figure 3.6. Elemental analysis of 3

AMOSTRA

Identificação TL23-3
(até cinco caracteres)

☒ Sólido ☐ Goma ☐ Líquido
☐ Líquido viscoso

FÓRMULA MOLECULAR: C₉₂H₈₆O₁₁

ESTRUTURA / TIPO DE COMPOSTO:

PROPRIEDADES:

Sensível a:

☐ Humidade ☐ Explosivo
☐ Ar ☐ Tóxico
☐ Luz ☐ Outras duplicado
☐ Calor

ANÁLISE	☒ C	☐ N	☒ H	☐ S	☐ Halogénio ()	☐ Outras ()
Calculado	80,79		6,34			
Determinado	80,81		6,28

Group No : 3	Element %			
Sample Name	Nitrogen%	Carbon%	Hydrogen%	Sulphur%
TL23-3	0.00	80.69	6.19	0.00
TL23-3	0.00	80.93	6.37	0.00

2 Sample(s) in Group No : 3				
Component Name	Average	Std. Dev.	% Rel. S. D.	Variance
Nitrogen%	0.00	0	0.0000	0.0000
Carbon%	80.81	.1697041	0.2100	0.0288
Hydrogen%	6.28	.1272791	2.0267	0.0162
Sulphur%	0.00	0	0.0000	0.0000

1',2,3,3',4,4'-Hexa-*O*-benzylsucrose (4)

$[\alpha]_D^{20} +37.6$ (c 0.9, CHCl_3); Lit.^[2] $[\alpha]_D +40.8$ (c 1.0, CHCl_3)

$R_f = 0.49$ (Hex-AcOEt, 1:2)

IR: ν_{max} (NaCl): 3380 (O-H), 3028 (C-H, stretch, unsaturated), 2916 (C-H, stretch, saturated), 1654, 1604 (Ar), 1496, 1453 (C-C, stretch), 1362 (C-H, assym.), 1065 (C-O-C, C-O-H, stretch), 732, 696 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.23 (m, 30H, Ar-H), 5.18 (s, 1H, H-1), 4.99-4.58 (m, 12H, H-4', H-6, H-5', Ar-CH₂), 4.22-4.14 (m, 1H, H-3'), 4.02-3.75 (m, 5H, H-3', 5, 6, 3), 3.75-3.62 (m, 3H, H-1', Ar-CH₂), 3.60-3.49 (m, 3H, Ar-CH₂), 3.45-3.28 (m, 3H, H-2, H-4, Ar-CH₂).

^{13}C NMR (100 MHz, CDCl_3) δ : 138.6, 138.3, 138.1, 138.0, 137.7 (C_q), 128.4, 127.9, 127.8, 127.7, 127.6 (C_{Ar}), 103.9 (C-2'), 90.7 (C-1), 83.5, 81.7, 81.0, 79.9, 79.5, 77.6 and 71.3 (C-2,3,3',4,4',5,5'), 75.6, 75.0, 73.4, 73.1, 73.0, 72.5 (C-1', 6 x OCH_2Ph), 61.9, 61.0 (C-6,6').

Figure 4.1. IR (NaCl) of 4

Figure 4.2. ^1H NMR (CDCl_3 , 400 MHz) of **4**

Figure 4.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **4**

6,6'-Di-*O-tert*-butyldiphenylsilylsucrose (**5**)

m.p. = 178-181 °C; Lit.^[3] m.p. 175-180 °C.

$[\alpha]_D^{20} +28.9$ (*c* 1.0, CH₃OH); Lit.^[3] $[\alpha]_D^{20} +27.2$ (*c* 1.0, CH₃OH).

*R*_f = 0.55 (AcOEt-Acetone-H₂O, 10:10:1)

IR: $\nu_{\max}$ (KBr): 3384 (O-H), 2928 (C-H, stretch, insaturated), 2855 (C-H, stretch, saturated), 1471 (C-C, stretch), 1427, 1389, 1361 (C-H, assym.), 1266 (Si-C), 1112, 1011 (C-O-C, C-O-H, stretch), 823 (Ar) cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.66-7.55 (m, 8H, Ar-*H*), 7.45-7.26 (m, 12H, Ar-*H*), 5.32 (d, *J*_{1,2} = 3.2 Hz, 1H, H-1), 5.17 (d, *J* = 7.5 Hz, 1H, OH), 5.08 (d, *J* = 7.5 Hz, 1H, OH), 4.91-4.81 (m, 3H, H-3', H-4', H-6a), 4.53 (d, *J* = 8.0 Hz, 1H, OH), 3.96 (t, *J*_{2,3}=*J*_{3,4}=9.3 Hz, 1H, H-3), 3.85-3.77 (m, 3H, H-5', H-6b, H-6'a), 3.77-3.72 (m, 1H, H-5), 3.66 (d, *J* = 9.5 Hz, 1H, H-6'b), 3.53 (d, *J* = 8.3 Hz, 2H, H-1'), 3.50-3.45 (m, 1H, H-2), 3.21-3.15 (m, 1H, H-4), 0.94 (s, 9H, CH₃), 0.92 (s, 9H, CH₃).

¹³C NMR (100 MHz, DMSO-*d*₆) δ : 135.0, 133.3, 133.1, 130.0, 127.7 (C_{Ar}), 104.8 (C-2'), 92.0 (C-1), 82.1, 76.9, 74.9, 73.0, 72.5, 71.7, 69.4 (C-2,3,3',4,4',5,5'), 65.6 (C-1'), 63.1, 61.8 (C-6,6'), 26.6 (CH₃), 18.8 (Si-C(CH₃)₃).

Figure 5.1. IR (KBr) of **5**

Figure 5.2. ^1H NMR (DMSO- d_6 , 400 MHz) of 5

Figure 5.3. ^{13}C NMR (DMSO- d_6 , 100 MHz) of **5**

1',2,3,3',4,4'-Hexa-*O*-benzyl-6,6'-di-*O*-*tert*-butyldiphenylsilylsucrose (6)

$[\alpha]_D + 29.7$ (c 1.0, CHCl_3); Lit.^[3] $[\alpha]_D + 30.1$ (c 1.0, CHCl_3).

$R_f = 0.75$ (Hex-AcOEt, 5:1)

IR: ν_{max} (KBr): 3029 (C-H, stretch, unsaturated), 2858 (C-H, stretch, saturated), 1496, 1454 (C-C, stretch), 1427, 1361 (C-H, assym.), 1090, 1028 (C-O-C, C-O-H, stretch), 736, 697 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.78-7.55 (m, 10H, Ar-*H*), 7.41-7.05 (m, 50H, Ar-*H*), 5.95 (d, $J_{1-2} = 3.0$ Hz, 1H, H-1), 4.91 (d, $J = 10.8$ Hz, 1H, $\text{CH}_2\text{-Ph}$), 4.84 (d, $J = 10.5$ Hz, 1H, $\text{CH}_2\text{-Ph}$), 4.80-4.64 (m, 4H, H-3', $\text{CH}_2\text{-Ph}$), 4.63-4.56 (m, 3H, H-4', $\text{CH}_2\text{-Ph}$), 4.53-4.41 (m, 5H, H-6,6', $\text{CH}_2\text{-Ph}$), 4.40-4.28 (m, 3H, H-5, $\text{CH}_2\text{-Ph}$), 4.05-3.97 (m, 2H, $\text{CH}_2\text{-Ph}$), 3.96-3.87 (m, 3H, H-5', $\text{CH}_2\text{-Ph}$), 3.87-3.81 (m, 1H, H-3), 3.74 (d, $J = 10.8$ Hz, 1H, $\text{CH}_2\text{-Ph}$), 3.59-3.49 (m, 3H, H-1',4, $\text{CH}_2\text{-Ph}$), 1.06 (s, 9H, CH_3), 1.01 (s, 9H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ : 138.9, 138.6, 138.3, 138.0 (C_q benzyl groups), 135.8, 135.6, 134.8, 133.3, 129.6, 128.2, 128.0, 127.7, 127.6, 127.4 (C_{Ar}), 104.4 (C-2'), 89.5 (C-1), 84.2, 82.2, 82.0, 80.6, 80.5, 75.8, 74.7, 73.5, 73.2, 72.6, 71.9, 71.8, 71.5 (C-2,3,3',4,4',5,5', 6 x OCH_2Ph and C-1'), 64.5, 62.3 (C-6,6'), 27.0 (CH_3), 19.3 ($\text{Si-C}(\text{CH}_3)_3$).

Figure 6.1. IR (KBr) of 6

Figure 6.2. ^1H NMR (CDCl_3 , 400 MHz) of **6**

Figure 6.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **6**

1',2,3,3',4,4'-Hexa-*O*-benzyl-6,6'-dichloro-6,6'-dideoxysucrose (10)

$[\alpha]_D^{20} +31.5$ (c 0.9, CHCl_3); Lit.^[1] $[\alpha]_D +32.0$ (c 1.0, CHCl_3).

R_f 0.40 (Hex-AcOEt, 5:1)

IR: ν_{max} (NaCl): 3430 (O-H), 3029 (C-H, stretch, insaturated), 2920 (C-H, stretch, saturated), 1604 (Ar), 1496, 1453 (C-C, stretch), 1359 (C-H, assym.), 1272 (C-C-O, C-Cl), 1209 (C-C-O), 1094 (C-O-C, C-O-H, stretch), 732, 696 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.14 (m, 30H, Ar-H), 5.73 (d, $J_{1,2} = 3.1$ Hz, 1H, H-1), 4.93 (d, $J = 11.2$ Hz, 1H, Ar- CH_2), 4.70-4.37 (m, 12H, H-3',4',5,6a,6b, 7x Ar- CH_2), 4.20-4.02 (m, 4H, H-3,5',6'a, Ar- CH_2), 3.72-3.64 (m, 3H, H-1', Ar- CH_2), 3.62-3.45 (m, 5H, H-4, 6'b, 3xAr- CH_2), 3.34 (dd, $J_{1,2} = 3.3$ Hz, $J_{2,3} = 9.5$ Hz).

^{13}C NMR (100 MHz, CDCl_3) δ : 138.6, 138.3, 138.0, 137.9 (C_q), 128.4, 127.9, 127.8, 127.6 (C_{Ar}), 105.2 (C-2'), 90.3 (C-1), 84.0, 83.4, 81.5, 80.6, 79.7, 78.1, 75.5, 75.1, 73.5, 73.1, 72.5, 72.4, 70.7, 70.2 (C-1',2,3,3',4,4',5,5'+6 OCH_2Ph), 45.0, 44.9 (C-6,6').

Figure 10.1. IR (NaCl) of 10

Figure 10.2. ^1H NMR (CDCl_3 , 400 MHz) of 10

Figure 10.3. ^{13}C NMR (CDCl_3 , 100 MHz) of 10

6,6'-Di-*O*-acetyl-1',2,3,3',4,4'-hexa-*O*-benzylsucrose (11)

$[\alpha]_D^{20} +49.2$ (c 1.0, CHCl_3); Lit.^[1] $[\alpha]_D +50.6$ (c 1.0, CHCl_3).

R_f 0.40 (Hex-AcOEt, 3:1)

IR: ν_{max} (NaCl): 3443 (H_2O), 3030 (C-H, stretch, unsaturated), 2916 (C-H, stretch, saturated), 1725 (C=O), 1602 (Ar), 1495, 1453 (C-C, stretch), 1363, 1269 (C-H, assym.), 1207 (C-C-O), 1090 (C-O-H, stretch), 1027, 997 (O-C-C, st as, ester, C-O-C, st sym, ether), 737, 698 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.41-7.21 (m, 30H, Ar-*H*), 6.32 (d, $J = 3.1$ Hz, 1H, H-1), 5.62 (d, $J = 8.2$ Hz, 1H, Ar- CH_2), 4.99 (d, $J = 10.8$ Hz, 1H, Ar- CH_2), 4.94-4.46 (m, 11H, Ar- CH_2 , H-3', 4', 6), 4.32-3.90 (m, 8H, Ar- CH_2 , H-1', 5, 6'), 3.85-3.81 (m, 1H, H-5'), 3.75 (t, $J_{2-3} = J_{3-4} = 8.8$ Hz, 1H, H-3), 3.71-3.62 (m, 2H, H-2, Ar- CH_2), 3.61-3.53 (m, 2H, H-4, Ar- CH_2), 2.15 (s, 3H, OAc), 2.05 (s, 3H, OAc).

^{13}C NMR (100 MHz, CDCl_3) δ : 170.6, 170.2 (CO), 138.4, 138.2, 138.0, 137.5 (C_q benzyl groups), 128.5, 128.1, 127.8 (C_{Ar}), 107.3 (C-2'), 89.6 (C-1), 86.6, 84.8, 83.3, 81.6, 81.0, 80.0, 78.9, 75.7, 75.3, 75.0, 73.7, 73.2, 72.3, 71.1 (C-2,3,3',4,4',5,5', C-1', 6 x OCH_2Ph), 64.0, 62.7 (C-6,6'), 21.0, 20.8 (2 x $\text{OC}(\text{O})\text{CH}_3$).

Figure 11.1. IR (NaCl) of 11

Figure 11.2. ^1H NMR (CDCl_3 , 400 MHz) of **11**

Figure 11.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **11**

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