Supporting Information

Synthesis of Aryl Ethers of Carbohydrates via Reaction with Arynes: Selective *O*-Arylation of Trans Vicinal Dihydroxyl Groups in Carbohydrates

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1. General Information:

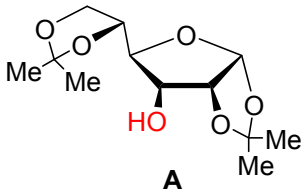
All reagents were purchased from commercial sources and used without treatment. Silica gel coated aluminum plates were used for TLC. The products were purified by column chromatography on silica gel (100-200 mesh) using hexane-ethyl acetate as the eluent. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$, using $CDCl_3$ (for 1 H, $\delta = 7.26$) as the internal standard. ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ using $CDCl_3$ (for ^{13}C, $\delta = 77.0$) as internal standard. Chemical shifts are expressed in parts per million (δ ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, m = multiplet, s br = singlet broad. Exact mass of all products was analysed by using HRMS having QTOF analyser.

2. General experimental procedures for the synthesis of *O*-arylated sugars

To a solution of sugar partner (1 equiv) in 3 mL of MeCN in an oven dried round bottom flask under N_2 atmosphere. Aryne source (1.2 equiv), KF (5 equiv) and 18-crown-6 (2.5 equiv) were also added and the resulting reaction mixture was stirred at rt under N_2 atmosphere until complete consumption of starting material was observed by TLC analysis. After completion the reaction mixture was diluted with 25 mL of ethyl acetate and washed with 20 mL of brine. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography on silica gel (60-120 mesh) and pet ether/ ethyl acetate (95/5) as eluent to obtained desired *O*-arylated product as colorless oil in moderate yield.

3. Preparation of carbohydrates substrate:

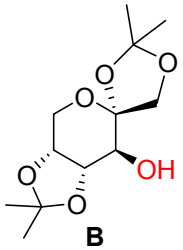
3.1 Synthesis of 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (A)



A

Compound **A** was commercially available obtained from Sigma Aldrich.

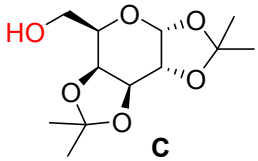
3.2 Synthesis of 1,2:4,5-Di-*O*-isopropylidene-β-D-fructopyranose (B)



B

Compound **B** was prepared via literature protocol.[1]

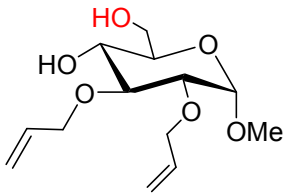
3.3 Synthesis of 1,2:3,4-Di-O-isopropylidene-D-galactopyranose (C)



C

Compound **C** was commercially available obtained from Sigma Aldrich.

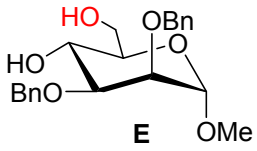
3.4 Synthesis of 4,5-bis(allyloxy)-2-(hydroxymethyl)-6-methoxytetrahydro-2H-pyran-3-ol (D)



D

Compound **D** was prepared via literature protocol.[2]

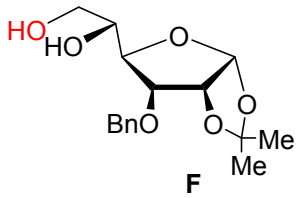
3.5 Synthesis of 4,5-bis(benzyloxy)-2-(hydroxymethyl)-6-methoxytetrahydro-2H-pyran-3-ol (E)



E

Compound **E** was prepared via literature protocol.[3]

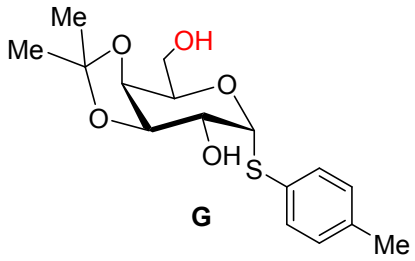
3.6 Synthesis of 6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (F)



F

Compound **F** was prepared via literature protocol.[4]

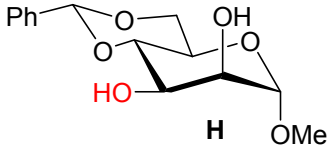
3.7 Synthesis of 4-(hydroxymethyl)-2,2-dimethyl-6-(p-tolylthio)tetrahydro-4H-[1,3]dioxolo[4,5-c]pyran-7-ol (G)



G

Compound **G** was prepared via literature protocol.[5]

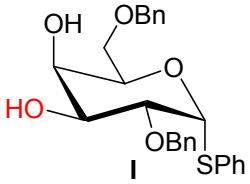
3.8 Synthesis of 6-methoxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol (H)



H

Compound **H** was prepared via literature protocol.[6]

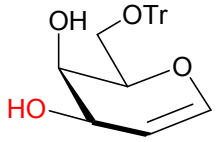
3.9 Synthesis of 5-(benzyloxy)-2-((benzyloxy)methyl)-6- (phenylthio)tetrahydro-2H-pyran-3,4-diol (I)



I

Compound **I** was prepared via literature protocol.[5]

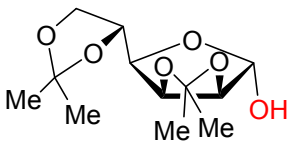
3.10 Synthesis of 2-((trityloxy)methyl)-3,4-dihydro-2H-pyran-3,4-diol (J)



J

Compound **J** was prepared via literature protocol.[7]

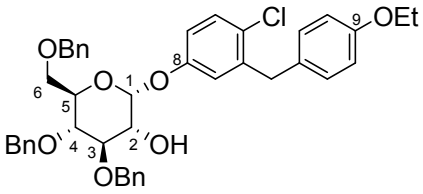
3.11 Synthesis of 2,3:5,6-Di-O-isopropylidene-α-D-mannofuranose (K)



K

Compound **K** was prepared via literature protocol.[8]

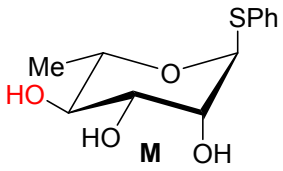
3.12 Synthesis of 4, 5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(4-chloro-3-(4-ethoxybenzyl)phenoxy)tetrahydro-2H-pyran-3-ol (L)



In an oven dried double neck round bottom flask charged with magnetic bead and flashed three times with N_2, 4-chloro-3-(4-ethoxybenzyl)phenylboronic acid[11] (200 mg, 0.69

mmol) in 3 mL of moist toluene was added and allowed to stir at room temperature. In this solution diethylzinc solution 1.0 M in hexanes (2 mL, 2 mmol) was added and continued stirring at r.t for 15 min then the reaction mixture was taken to stir at 60 °C for 1 hr. The same reaction mixture was allowed to cool to room temperature then glucal epoxide[12] (298 mg, 0.69 mmol) was added and continued to stirring at 60 °C until complete consumption of starting material was observed by TLC analysis. After completion the reaction mixture was diluted with ethyl acetate and washed with saturated solution of ammonium chloride. The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography on silica gel (60-120 mesh) and pet ether as eluent. The desired product **L** was obtained as white solid (240 mg, 50 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.28 (m, 9H), 7.25 – 7.20 (m, 5H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.02 – 6.93 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.56 (d, *J* = 3.5 Hz, 1H), 4.99 (q, *J* = 11.2 Hz, 2H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.78 – 4.55 (m, 4H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.10 – 3.97 (m, 5H), 3.90 (d, *J* = 9.7 Hz, 2H), 3.86 – 3.76 (m, 3H), 3.60 (d, *J* = 10.9 Hz, 1H), 2.30 (s, 1H), 1.45 (t, *J* = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, CDCl3)** δ 157.6 (C-9), 155.1 (C-8), 140.6, 138.6, 138.1, 137.9, 130.3, 130.0, 128.5, 128.4, 127.9, 127.8, 119.5, 115.8, 114.6, 97.4 (C-1), 83.1 (C-3), 75.5 (C-4), 75.1, 73.5, 72.7 (C-2), 71.4 (C-5), 68.3 (C-6), 63.4, 38.5, 31.9, 29.8, 29.4, 22.7, 14.9. HRMS (ESI+): m/z calcd. For $C_{42}H_{44}ClO_7$ (M+H)+: 695.2776; found 695.2768.

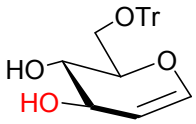
3.13 Synthesis of 2-methyl-6-(phenylthio)tetrahydro-2H-pyran-3,4,5-triol (M)



M

Compound **M** was prepared via literature protocol.[9]

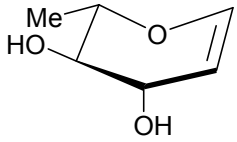
3.14 Synthesis of 2-((trityloxy)methyl)-3,4-dihydro-2H-pyran-3,4-diol (N)



N

Compound **N** was prepared via literature protocol.[7]

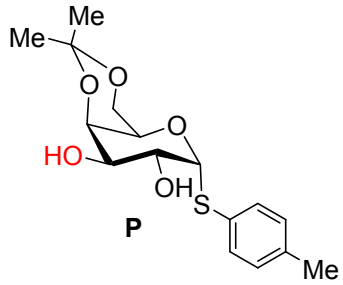
3.15 Synthesis of 2-methyl-3,4-dihydro-2H-pyran-3,4-diol (O)



O

Compound **O** was prepared via literature protocol.[10]

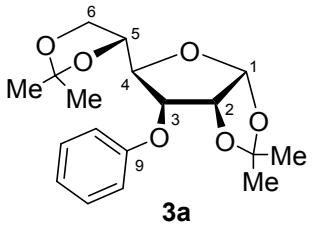
3.16 Synthesis of 2,2-dimethyl-6-(p-tolylthio)hexahydropyrano[3,2-d][1,3] dioxine-7,8-diol (P)



P

Compound **P** was prepared via literature protocol.[6]

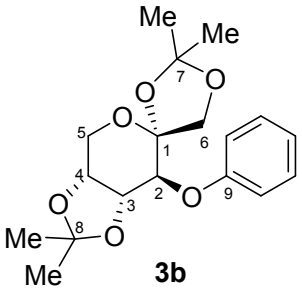
4. Characterization Data of *O*-arylated Products:



3a

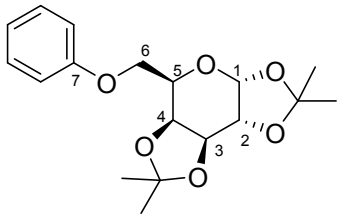
Prepared according to the general procedure 2 from diacetonide-D-glucal (A) (100 mg, 0.38 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (113 µl, 0.45 mmol), KF (110 mg, 1.19 mmol) and 18-crown-6 (256 mg, 0.95 mmol). The desired product **3a** was obtained as colorless oil (97 mg, 76 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.27 (m, 2H), 7.03 (dd, *J* = 11.6, 7.7 Hz, 3H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.76 (d, *J* = 3.1 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.51 (dd, *J* = 13.1, 5.9 Hz, 1H), 4.37 (dd, *J* = 7.4, 3.1 Hz, 1H), 4.16 (qd, *J* = 8.6, 5.9 Hz, 2H), 1.58 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9 (C-9), 129.7, 121.8, 115.5, 112.1 (CMe_2), 109.2 (CMe_2), 105.3 (C-1), 82.2 (C-3), 80.5

(C-4), 79.8 (C-2), 72.4 (C-5), 67.0 (C-6), 26.8 (CH_3), 26.7 (CH_3), 26.3 (CH_3), 25.1 (CH_3). HRMS (ESI+): m/z calcd. For $C_{18}H_{25}O_6$ (M+H)+: 337.1651; found 337.1634.



3b

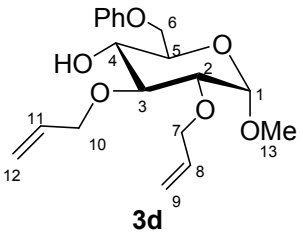
Prepared according to the general procedure 2 from diacetonide-D-fructose (B) (100 mg, 0.38 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (113 µl, 0.45 mmol), KF (110 mg, 1.9 mmol) and 18-crown-6 (256 mg, 0.95 mmol). The desired product **3b** was obtained as colorless oil (88 mg, 69 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (dd, *J* = 8.3, 7.2 Hz, 2H), 6.93 (dd, *J* = 14.5, 7.6 Hz, 3H), 4.62 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.54 (d, *J* = 2.6 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.14 (d, *J* = 10.1 Hz, 1H), 4.02 (d, *J* = 10.1 Hz, 1H), 3.96 (dd, *J* = 13.0, 1.8 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 1.47 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6 (C-9), 129.5, 121.1, 114.7, 109.1 (CMe_2), 108.9 (CMe_2), 102.1 (C-1), 71.0 (C-2), 70.27 (C-3), 70.1(C-2), 68.8 (C-6), 61.2 (C-5), 26.6 (CH_3), 25.9 (CH_3), 25.4 (CH_3), 24.1(CH_3). HRMS (ESI+): m/z calcd. For $C_{18}H_{24}NaO_6$ (M+Na)+: 359.1471; found 359.1476.



3c

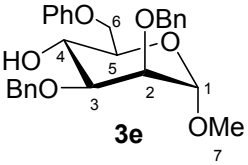
Prepared according to the general procedure 2 from diacetonide–D-galactal (C) (100 mg, 0.38 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (112.6 µl, 0.45 mmol), KF (110 mg, 1.14 mmol) and 18-crown-6 (256 mg, 0.95 mmol). The desired product **3c** was obtained as colorless oil (106 mg, 83 %). **^{1}H NMR (400 MHz, CDCl3)** δ 7.34 – 7.26 (m, 2H), 6.97 (dd, *J* = 8.4, 7.7 Hz, 3H), 5.61 (d, *J* = 5.0 Hz, 1H), 4.68 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.45 – 4.36 (m, 2H), 4.28 – 4.12 (m, 3H), 1.54 (s, 3H), 1.50 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 158.6 (C-7), 129.4, 120.9, 114.9, 109.4 (CMe_2), 108.7 (CMe_2), 96.4 (C-1), 71.0 (C-4), 70.7(C-2), 66.5 (C-5), 66.5 C-3), 66.2(C-6), 26.1 (CH_3), 26.0 (CH_3), 24.9

(CH_3), 24.5 (CH_3). HRMS (ESI+): m/z calcd. For $C_{18}H_{24}NaO_6$ (M+Na)+: 359.1471; found 359.1477.



3d

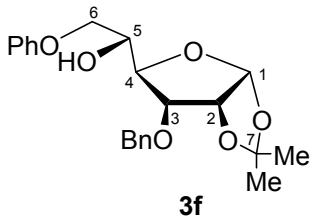
Prepared according to the general procedure 2 from compound D (100 mg, 0.36 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (107 µl, 0.43 mmol), KF (104 mg, 1.8 mmol) and 18-crown-6 (239 mg, 0.90 mmol). The desired product **3d** was obtained as colorless oil (92 mg, 73 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (dd, *J* = 9.7, 6.1 Hz, 2H), 7.01 – 6.90 (m, 3H), 6.05 – 5.89 (m, 2H), 5.35 – 5.26 (m, 2H), 5.20 (dd, *J* = 10.2, 4.3 Hz, 2H), 4.84 (d, *J* = 3.4 Hz, 1H), 4.46 (dd, *J* = 12.6, 5.4 Hz, 1H), 4.31 – 4.12 (m, 5H), 3.95 – 3.87 (m, 1H), 3.68 (dd, *J* = 7.1, 2.4 Hz, 2H), 3.45 (s, 3H), 2.59 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.7 (*O*-Ar), 135.0, 134.6, 129.4, 121.0, 117.9, 117.3, 114.7, 98.3 (C-1), 81.1, 79.5, 74.2, 72.3, 69.9, 69.5, 67.0, 55.2 (CH_3). HRMS (ESI+): m/z calcd. For $C_{19}H_{26}NaO_6$ (M+Na)+: 373.1627; found 473.1620.



3e

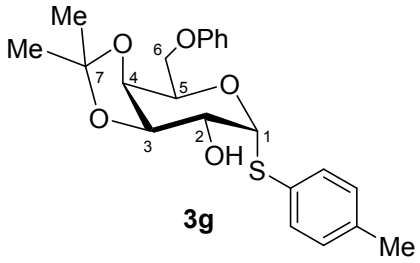
Prepared according to the general procedure 2 from compound E (100 mg, 0.27 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (80 µl, 0.32 mmol), KF (78 mg, 1.35 mmol) and 18-crown-6 (178 mg, 0.67 mmol). The desired product **3e** was obtained as colorless oil (93 mg, 77%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.26 (m, 12H), 7.09 – 6.93 (m, 3H), 4.88 (d, *J* = 1.1 Hz, 1H), 4.78 – 4.61 (m, 3H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.39 (dd, *J* = 10.5, 2.2 Hz, 1H), 4.25 (dd, *J* = 10.4, 6.3 Hz, 1H), 4.14 (t, *J* = 9.6 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.86 (dd, *J* = 2.9, 1.7 Hz, 1H), 3.78 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5 (*O*-Ar), 129.7, 128.4, 128.3, 128.2, 127.9, 127.6, 121.9, 121.4, 116.61, 116.4, 100.4(C-1), 79.5 (C-3), 75.0(C-2), 73.8 (C-5), 73.6 (OBn CH_2), 71.2 (C-4), 68.9 (C-6),

54.9 (CH_3), 30.9, 29.7, 22.7. HRMS (ESI+): m/z calcd. For $C_{27}H_{30}NaO_6$ (M+Na)+: 473.1940; found 473.1947.



3f

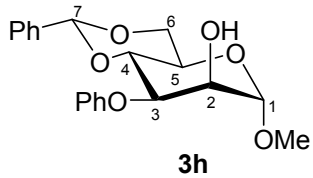
Prepared according to the general procedure 2 from compound F (100 mg, 0.32 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (95 µl, 0.38 mmol), KF (93 mg, 1.6 mmol) and 18-crown-6 (211 mg, 0.8 mmol). The desired product **3f** was obtained as colorless oil (98 mg, 79 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.29 (m, 7H), 6.98 (dd, *J* = 17.8, 7.6 Hz, 3H), 6.00 (d, *J* = 3.7 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.70 – 4.64 (m, 2H), 4.44 – 4.36 (m, 1H), 4.33 – 4.21 (m, 3H), 4.10 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.77 (s, 1H), 1.53 (s, 3H), 1.37 (s, 3H**). ^{13}C NMR (126 MHz, CDCl3)** δ 158.6 (*O*-Ar), 137.2, 129.5, 128.72, 128.2, 127.9, 121.1, 114.7, 111.9, 105.2 (C-1), 82.2 (C-2), 81.9 (C-3), 79.6 (C-4), 72.4 (OBn-CH_2), 69.9 (C-5), 67.9 (C-6), 26.8 (CH_3), 26.3 (CH_3). HRMS (ESI+): m/z calcd. For $C_{22}H_{27}O_6$ (M+H)+: 387.1808; found 387.1812.



3g

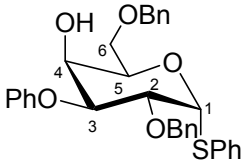
Prepared according to the general procedure 2 from compound G (100 mg, 0.31 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (92 µl, 0.37 mmol), KF (90 mg, 1.55 mmol) and 18-crown-6 (205 mg, 0.77 mmol). The desired product **3g** was obtained as colorless oil (92 mg, 74 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 15.0, 7.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 14.5, 7.6 Hz, 3H), 4.47 (d, *J* = 10.2 Hz, 1H), 4.31 (qd, *J* = 9.9, 6.1 Hz, 3H), 4.19 – 4.10 (m, 2H), 3.67 – 3.57 (m, 1H), 2.52 (s, 1H), 2.37 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6 (*O*-Ar), 138.4, 133.12, 133.0, 129.8, 129.8, 129.6, 129.5, 128.3, 121.1, 114.8, 114.7, 110.4(C-7), 89.0, 88.5

(C-1), 79.0 (C-5), 75.1 (C-4), 73.6 (C-3), 71.6 (C-2), 67.1 (C-6), 28.1 (CH_3), 26.4 (CH_3), 21.2 (CH_3). HRMS (ESI+): m/z calcd. For $C_{22}H_{27}O_5S$ (M+H)+: 403.1579; found 403.1583.



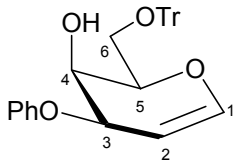
3h

Prepared according to the general procedure 2 from compound H (100 mg, 0.35 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (104 µl, 0.42 mmol), KF (102 mg, 1.75 mmol) and 18-crown-6 (231 mg, 0.87 mmol). The desired product **3h** was obtained as colorless oil (95 mg, 76 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.45 – 7.27 (m, 5H), 7.11 – 7.03 (m, 3H), 5.67 (s, 1H), 4.87 (s, 1H), 4.65 (dd, *J* = 3.6, 1.0 Hz, 1H), 4.37 – 4.28 (m, 2H), 4.12 (dd, *J* = 12.5, 6.3 Hz, 1H), 3.97 – 3.83 (m, 2H), 3.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1 (*O*-Ar), 137.4, 129.7, 129.2, 128.3, 126.3, 122.4, 116.8, 102.2 (C-7), 98.9 (C-1), 79.3 (C-3), 77.8 (C-4), 68.8 (C-2), 68.3 (C-6), 63.6 (C-5), 55.1 (CH_3). HRMS (ESI+): m/z calcd. For $C_{20}H_{23}O_6$ (M+H)+: 359.1495; found 359.1498.



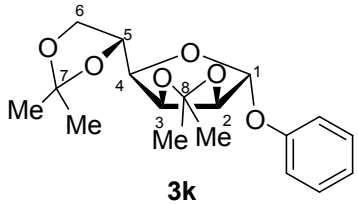
3i

Prepared according to the general procedure 2 from compound I (100 mg, 0.22 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (65 µl, 0.26 mmol), KF (64 mg, 1.1 mmol) and 18-crown-6 (660.2 mg, 2.5 mmol). The desired product **3i** was obtained as colorless oil (85 mg, 73%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (t, *J* = 5.3 Hz, 2H), 7.48 – 7.28 (m, 14H), 7.19 – 7.02 (m, 4H), 4.87 – 4.70 (m, 3H), 4.62 (s, 1H), 4.43 – 4.35 (m, 1H), 4.28 (dd, *J* = 15.2, 7.0 Hz, 1H), 4.01 (t, *J* = 9.3 Hz, 1H), 3.94 – 3.81 (m, 2H), 3.78 – 3.67 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.1, 157.6 (*O*-Ar), 138.0, 137.8, 137.6, 133.9, 133.73, 132.1, 131.6, 129.8, 129.6, 129.0, 129.0, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 127.9, 127.9, 127.9, 127.9, 127.8, 127.5, 127.4, 122.3, 121.8, 117.2, 116.5, 87.8 (C-1), 87.7, 82.8 (C-3), 78.6, 76.5 (C-5), 75.8, 75.8 (C-2), 75.6, 75.0, 73.8 (C-4), 73.6, 69.5 (C-6). HRMS (ESI+): m/z calcd. For $C_{32}H_{32}NaO_5S$ (M+Na)+: 551.1868; found 551.1866.



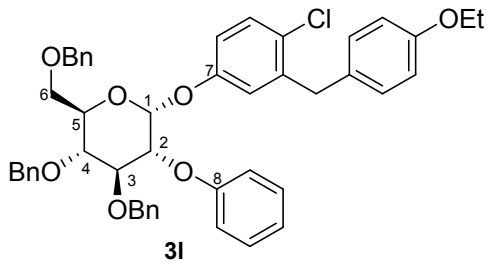
3j

Prepared according to the general procedure 2 from compound J (100 mg, 0.26 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (77 µl, 0.31 mmol), KF (75 mg, 1.3 mmol) and 18-crown-6 (172 mg, 0.65 mmol). The desired product **3j** was obtained as colorless oil (63 mg, 52%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 7.4 Hz, 6H), 7.34 – 7.21 (m, 12H), 7.02 – 6.89 (m, 1H), 6.47 (d, *J* = 5.5 Hz, 1H), 4.97 (s, 1H), 4.79 (d, *J* = 6.3 Hz, 1H), 4.26 (s, 1H), 4.08 (t, *J* = 5.9 Hz, 1H), 3.51 (d, *J* = 5.2 Hz, 2H), 2.61 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.8 (*O*-Ar), 145.7, 143.8, 129.7, 128.7, 127.9, 127.1, 121.8, 116.1, 98.1(C-1), 87.1 (C-2), 75.8 (C-5), 70.4 (C-3), 64.0 (C-4), 62.89 (C-6). HRMS (ESI+): m/z calcd. For $C_{31}H_{29}O_4$ (M+H)+: 465.2066; found 465.2073.



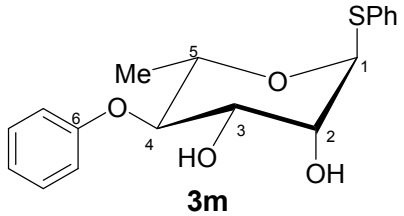
3k

Prepared according to the general procedure 2 from diacetonide mannose (K) (100 mg, 0.38 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (113 µl, 0.45 mmol), KF (110 mg, 1.9 mmol) and 18-crown-6 (251 mg, 0.95 mmol). The desired product **3k** was obtained as colorless oil (47 mg, 37 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 2H), 7.04 (t, *J* = 8.2 Hz, 3H), 5.66 (s, 1H), 4.95 (dd, *J* = 5.8, 3.5 Hz, 1H), 4.90 (d, *J* = 5.9 Hz, 1H), 4.50 – 4.44 (m, 1H), 4.12 (dt, *J* = 8.3, 4.2 Hz, 2H), 4.01 (dd, *J* = 8.8, 4.3 Hz, 1H), 1.54 (s, 1H), 1.46 (s, 1H), 1.40 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.3 (*O*-Ar), 129.5, 122.3, 116.7, 113.0 (C-8), 109.4 (C-7), 104.9 (C-1), 85.5 (C-2), 81.2 (C-4), 79.6 (C-3), 73.0 (C-5), 66.9 (C-6), 26.9 (CH_3), 25.9 (CH_3), 25.2 (CH_3), 24.6 (CH_3). HRMS (ESI+): m/z calcd. For $C_{18}H_{25}O_6$ (M+H)+: 337.1651; found 337.1630.



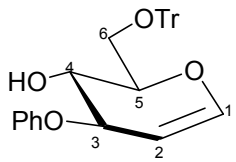
3l

Prepared according to the general procedure 2 from *O*-glycosides of benzylated Dapagliflozin (L) (50 mg, 0.07 mmol) in 3 mL of MeCN in an oven dried round bottom flask under N_2 atmosphere. 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (21 µl, 0.08 mmol), KF (20 mg, 0.35 mmol) and 18-crown-6 (46 mg, 0.17 mmol). The desired product **3l** was obtained as colorless oil (22 mg, 41%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.23 (m, 11H), 7.20 – 7.16 (m, 1H), 7.12 – 7.00 (m, 3H), 6.94 – 6.90 (m, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 5.59 (d, J = 3.4 Hz, 1H), 4.99 (d, *J* = 10.6 Hz, 1H), 4.87 (dd, *J* = 25.1, 10.7 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.56 – 4.42 (m, 2H), 4.38 – 4.31 (m, 1H), 4.06 – 3.96 (m, 2H), 3.89 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.77 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.57 (d, *J* = 10.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4 (C-8 *O*-Ar), 158.9, 156.8 (C-7), 141.8, 139.6, 139.3, 131.3, 131.1, 129.8, 129.7, 129.6, 129.2, 129.1, 123.5, 121.2, 118.2, 117.5, 115.9, 97.1 (C-1), 82.7 (C-4), 80.5 (C-2), 77.1 (C-3), 76.6, 74.9, 72.6 (C-5), 69.7 (C-6), 64.8, 39.9, 16.3 (CH_3). HRMS (ESI+): m/z calcd. For $C_{48}H_{48}ClO_7$ (M+H)+: 771.3089; found 771.3092.



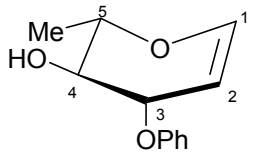
3m

Prepared according to the general procedure 2 from thioprotected *L*-rhamnose (M) (100 mg, 0.39 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (115 µl, 0.46 mmol), KF (113 mg, 1.95 mmol) and 18-crown-6 (257 mg, 0.98 mmol). The desired product **3m** was obtained as colorless oil (73 mg, 59%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.45 (m, 2H), 7.37 – 7.24 (m, 5H), 7.09 – 6.95 (m, 3H), 5.54 (t, *J* = 4.0 Hz, 1H), 4.53 – 4.25 (m, 3H), 4.17 – 3.87 (m, 1H), 1.26 (dd, *J* = 9.4, 5.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.4 (C-6, *O*-Ar), 133.9, 131.5, 131.4, 129.9, 129.7, 129.2, 129.1, 127.6, 127.5, 122.5, 121.8, 116.5, 116.3, 87.5 (C-1) 87.3, 80.4 (C-4), 79.1, 72.5 (C-3), 71.6, 69.7 (C-2), 69.4, 68.5 (C-5), 17.8(CH_3). HRMS (ESI+): m/z calcd. For $C_{18}H_{20}NaO_4S$ (M+Na)+: 355.0980; found 335.0969.



4a

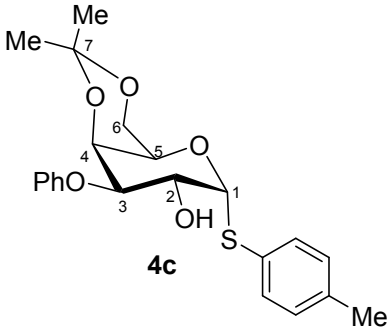
Prepared according to the general procedure 2 from compound N (100 mg, 0.26 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (77µl, 0.31 mmol), KF (75 mg, 1.3 mmol) and 18-crown-6 (172 mg, 0.65 mmol). The desired product **4a** was obtained as colorless oil (69 mg, 57 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.6 Hz, 6H), 7.38 – 7.21 (m, 12H), 6.95 (dd, *J* = 19.3, 7.7 Hz, 2H), 6.47 (d, *J* = 6.1 Hz, 1H), 4.88 (dd, *J* = 6.1, 2.0 Hz, 1H), 4.81 (d, *J* = 6.5 Hz, 1H), 4.26 (dd, *J* = 10.8, 4.7 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.55 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.48 (dd, *J* = 10.4, 4.5 Hz, 1H), 2.38 (d, *J* = 3.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5 (*O*-Ar), 145.5, 143.7, 129.6, 128.7, 127.9, 127.2, 121.3, 116.0, 98.7 (C-1), 86.9 (C-2), 74.7 (C-3), 68.4 (C-4), 62.6 (C-6). HRMS (ESI+): m/z calcd. For $C_{31}H_{29}O_4$ (M+H)+: 465.2066; found 465.2071.



4b

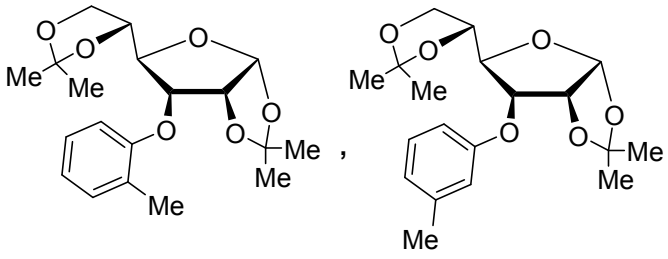
Prepared according to the general procedure 2 from L-Rhamnal (O) (50 mg, 0.38 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (135 µl, 0.45 mmol), KF (110 mg, 1.9 mmol) and 18-crown-6 (251 mg, 0.95 mmol). The desired product **4b** was obtained as colorless oil in 53 % yield 41 mg.

^{1}H NMR (400 MHz, CDCl3) δ 7.42 – 7.27 (m, 2H), 7.10 – 6.93 (m, 3H), 6.43 (dd, J = 6.1, 1.0 Hz, 1H), 4.90 (dd, J = 6.1, 2.1 Hz, 1H), 4.86 – 4.81 (m, 1H), 4.16 – 4.05 (m, 1H), 3.86 (dd, J = 8.9, 7.0 Hz, 1H), 2.68 (s, 1H), 1.49 (d, J = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 157.4 (*O*-Ar), 145.5, 129.7, 121.4, 115.9 (C-1), 98.5 (C-2), 75.3 (C-3), 74.4 (C-5), 72.4 (C-4), 17.1 (CH_3). HRMS (ESI+): m/z calcd. For $C_{12}H_{15}O_3$ (M+H)+: 207.1021; found 207.1034



4c

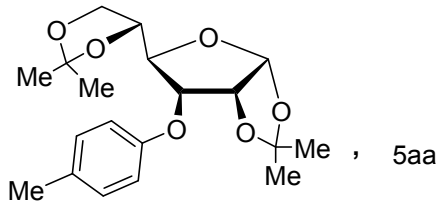
Prepared according to the general procedure 2 from compound P (100 mg, 0.31 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (92 µl, 0.37 mmol), KF (90 mg, 1.55 mmol) and 18-crown-6 (205 mg, 0.77 mmol). The desired product **4c** was obtained as colorless oil (80 mg, 64 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 9.3, 8.0 Hz, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 3H), 4.54 (d, *J* = 9.4 Hz, 1H), 4.23 (d, *J* = 2.8 Hz, 1H), 4.17 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.07 – 4.00 (m, 3H), 3.42 (s, 1H), 2.37 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.3 (*O*-Ar), 138.6, 133.40, 129.9, 129.8, 127.8, 122.7, 117.4, 88.8 (C-1), 82.1 (C-3), 78.2 (C-2), 68.1 (C-4), 67.5 (C-5), 62.7 (C-6), 29.7 (CH_3), 22.7 (CH_3), 21.2 (CH_3). HRMS (ESI+): m/z calcd. For $C_{22}H_{27}O_5S$ (M+H)+: 403.1579; found 403.1581.



5a:5aa (1:1.2)

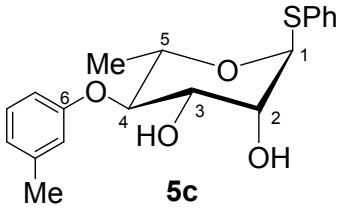
Prepared according to the general procedure 2 from diacetonide-D-glucal (A) (100 mg, 0.38 mmol), 2-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (119 µl, 0.45 mmol), KF (110 mg, 1.9 mmol) and 18-crown-6 (251 mg, 0.95 mmol). The product was obtained as inseparable mixture of **5a:5aa** as colorless oil (97 mg, 73 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.17 (m, 2H), 7.03 – 6.91 (m, 1H), 6.84 (t, *J* = 9.9 Hz, 1H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.77 (dd, *J* = 12.6, 3.1 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.59 – 4.48 (m, 1H), 4.37 (dt, *J* = 7.0, 3.5 Hz, 1H), 4.24 – 4.12 (m, 2H), 2.37 (s, 1H), 2.25 (s, 1H), 1.59 (d, *J* = 2.4 Hz, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 156.9 (*O*-Ar), 154.9 (*O*-Ar), 139.9, 131.2, 129.4, 127.5, 126.9, 122.6, 121.3, 116.4, 112.3, 112.1,

112.0, 109.2, 109.1, 105.4 (Anomeric), 105.3, 82.3, 80.8, 80.6, 79.8, 79.8, 72.4, 72.4, 67.3, 67.0, 31.9, 29.7, 29.4, 26.8, 26.8, 26.3, 25.3, 25.2, 22.7, 21.5. HRMS (ESI+): m/z calcd. For $C_{19}H_{27}O_6$ (M+H)+: 351.1808; found 351.1799.



5b:5aa (1.5:1)

Prepared according to the general procedure 2 from diacetonide-D-glucal (A) (100 mg, 0.38 mmol), 4-methyl-2-(trimethylsilyl)phenyltrifluoromethanesulfonate (119 µl, 0.45 mmol), KF (110 mg, 1.9 mmol) and 18-crown-6 (251 mg, 0.95 mmol). The product was obtained as inseparable mixture of **5b:5aa** as colorless oil (98 mg, 74 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.10 (m, 2H), 6.93 – 6.80 (m, 2H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.73 (dd, *J* = 13.7, 3.1 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.54 – 4.47 (m, 1H), 4.39 – 4.34 (m, 1H), 4.21 – 4.12 (m, 2H), 2.37 (s, 2H), 2.33 (s, 1H), 1.58 (d, J = 2.4 Hz, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.34 (d, *J* = 3.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9 (*O*-Ar), 139.9, 131.1, 130.13, 129.4, 122.6, 116.4, 115.4, 112.3, 112.1, 112.0, 109.1, 105.3 (Anomeric), 82.2, 80.5, 79.7, 77.4, 77.0, 76.7, 72.4, 67.0, 26.8, 26.8, 26.3, 25.3, 21.5. HRMS (ESI+): m/z calcd. For $C_{19}H_{27}O_6$ (M+H)+: 351.1808; found 351.1825.



5c

Prepared according to the general procedure 2 from thioprotected *L*-rhamnose (M) (100 mg, 0.39 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (122 µl, 0.47 mmol), KF (113 mg, 1.95 mmol) and 18-crown-6 (257 mg, 0.97 mmol). The desired product **5c** was obtained as colorless oil (74 mg, 55 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.41 – 7.27 (m, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.87 (dd, *J* = 21.8, 8.3 Hz, 1H), 5.57 (d, *J* = 1.3 Hz, 1H), 4.42 – 4.36 (m, 1H), 4.31 (s, 1H), 4.13 (d, *J* = 4.2 Hz, 1H), 3.22 (s, 1H), 2.96 (s, 1H), 2.37 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.9 (*O*-Ar), 141.2, 135.4, 132.9, 132.8, 130.8, 130.6, 130.5, 128.9, 124.1, 118.6, 114.6, 88.8 (C-1), 81.7 (C-4), 73.9 (C-3),

73.0 (C-2), 69.9 (C-4), 22.9 (CH_3), 19.2 (CH_3). HRMS (ESI+): m/z calcd. For $C_{19}H_{22}NaO_4S$ (M+Na)+: 369.1136; found 369.1142.

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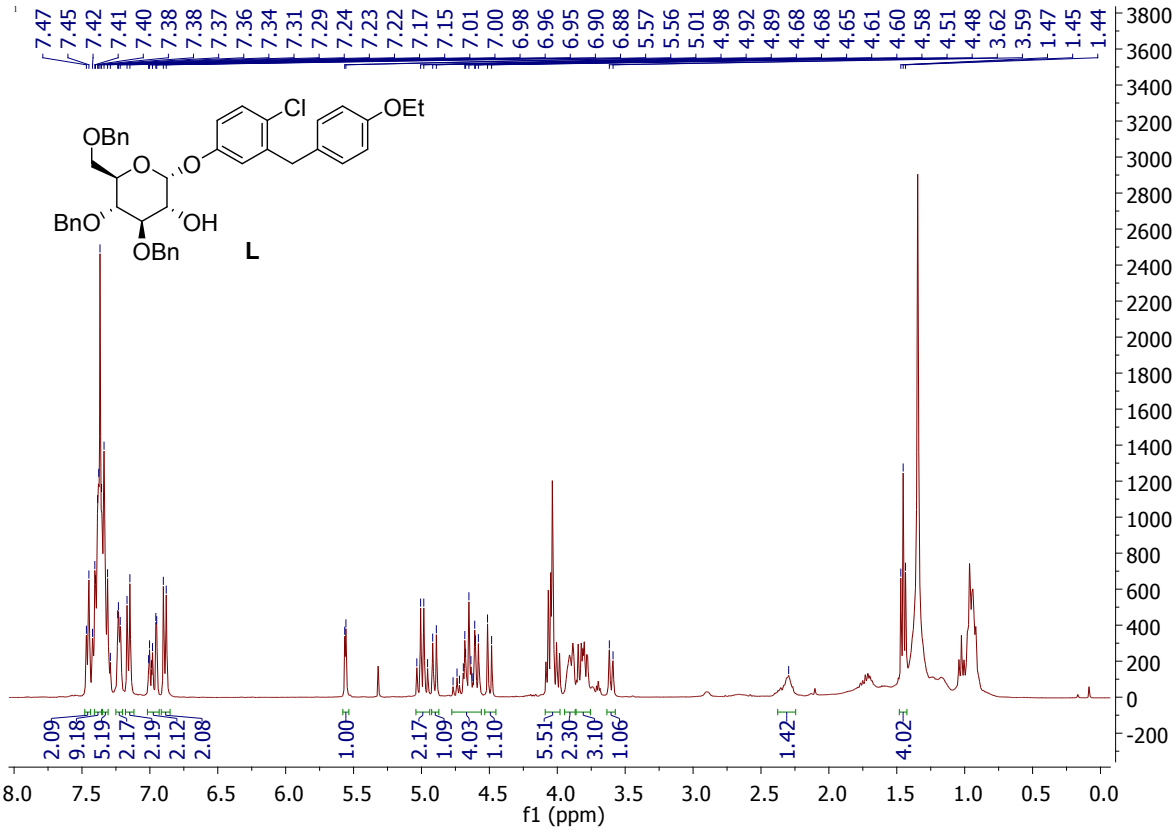
NMR Spectra: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O
BnO
OH
OBn
L
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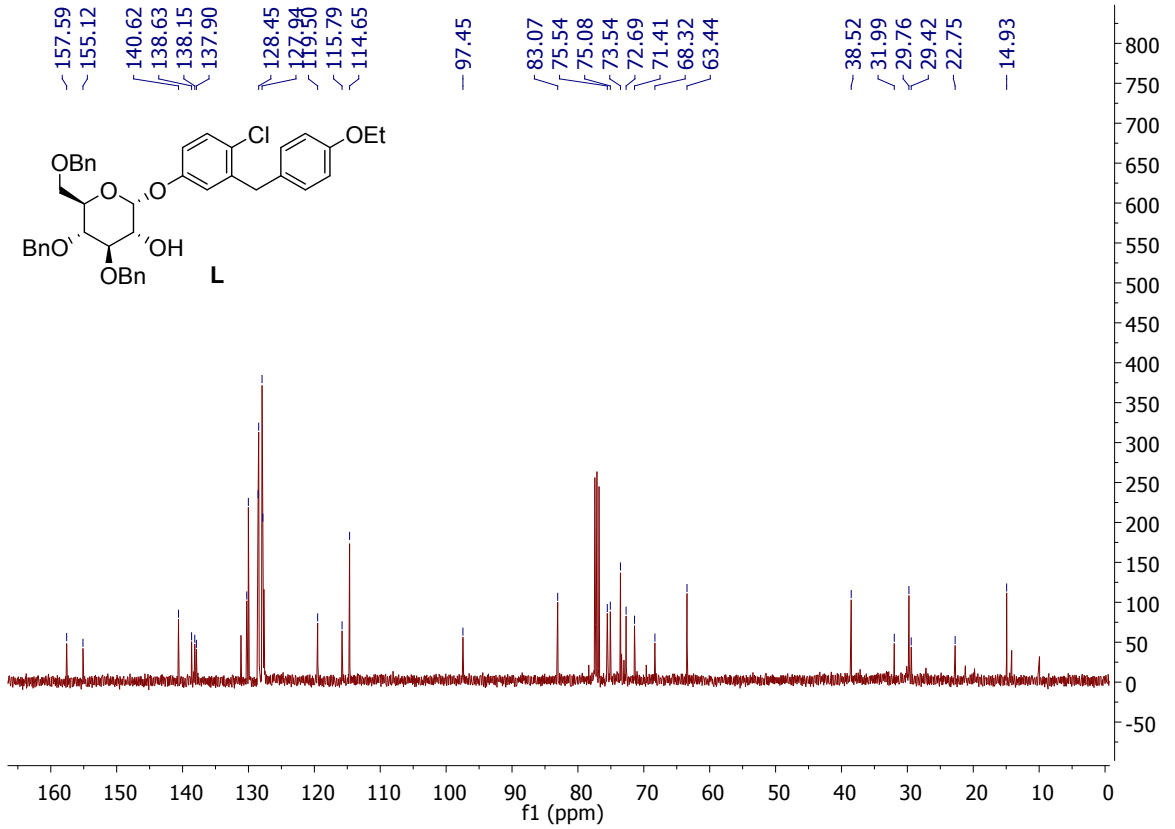
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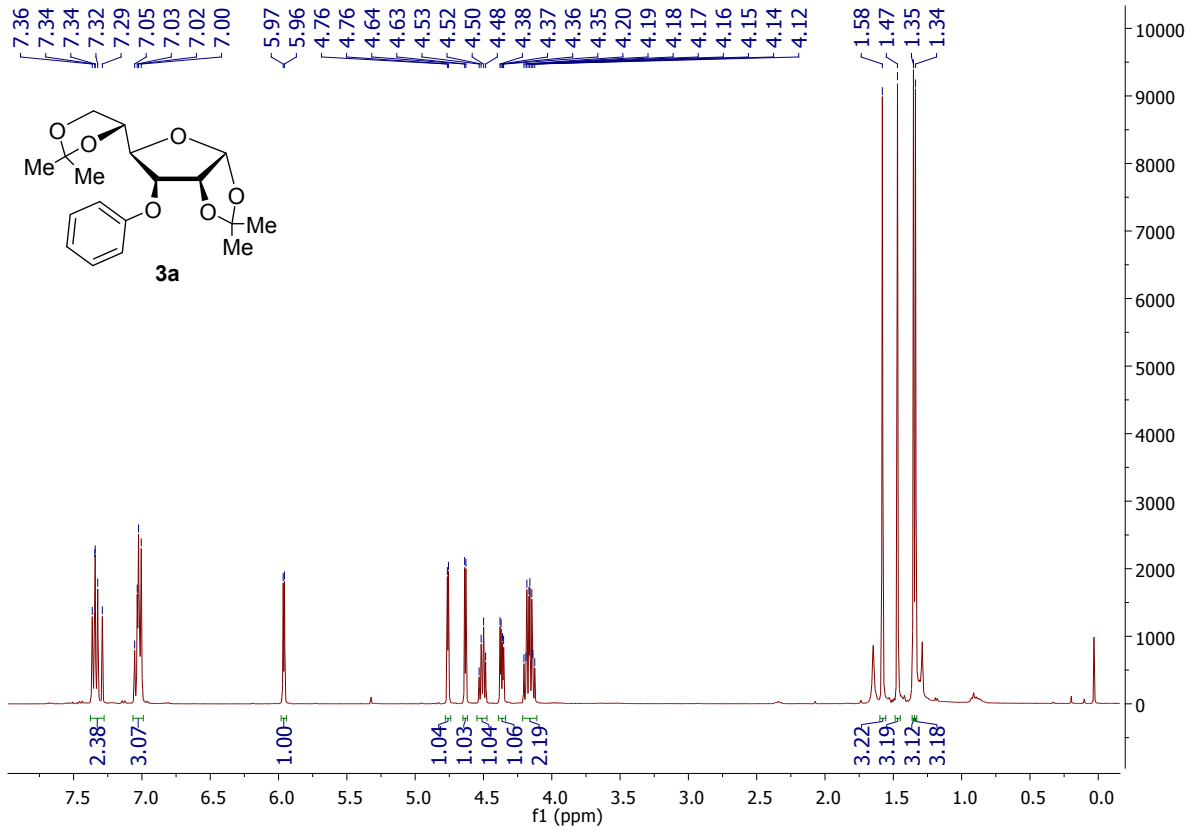
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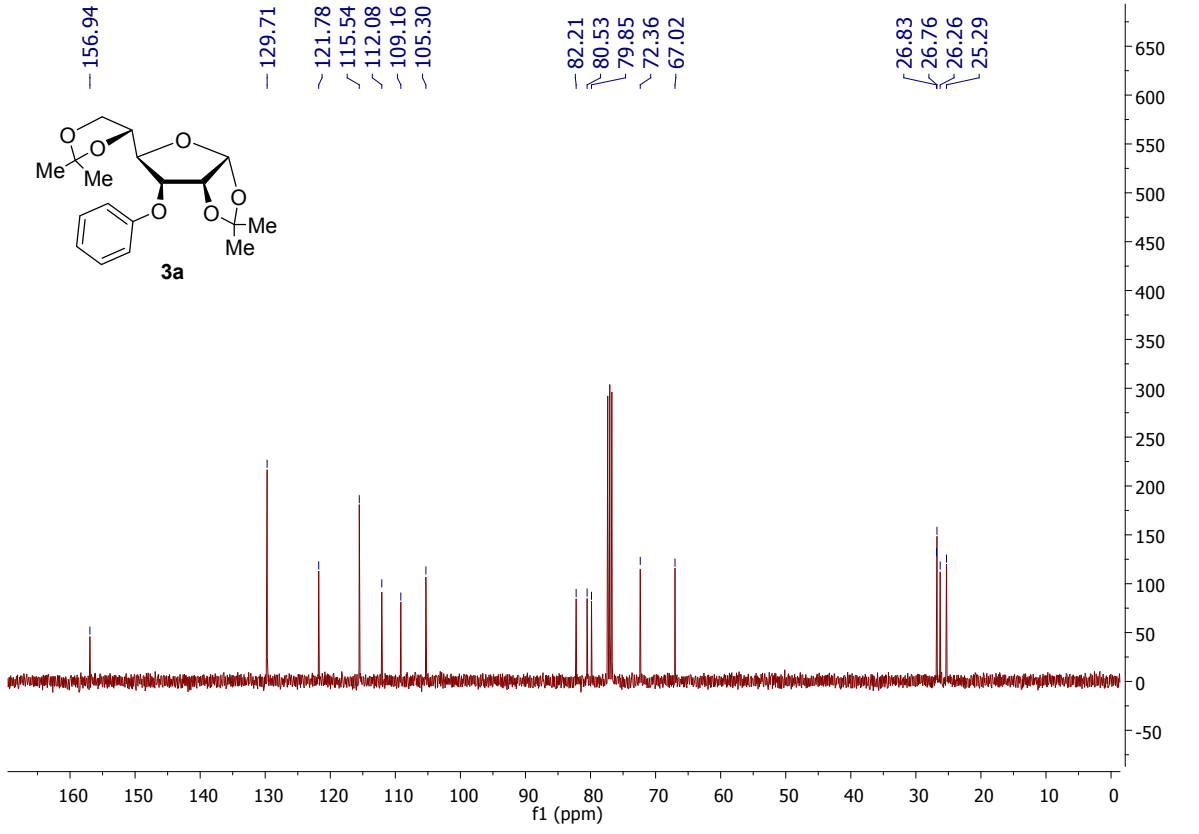
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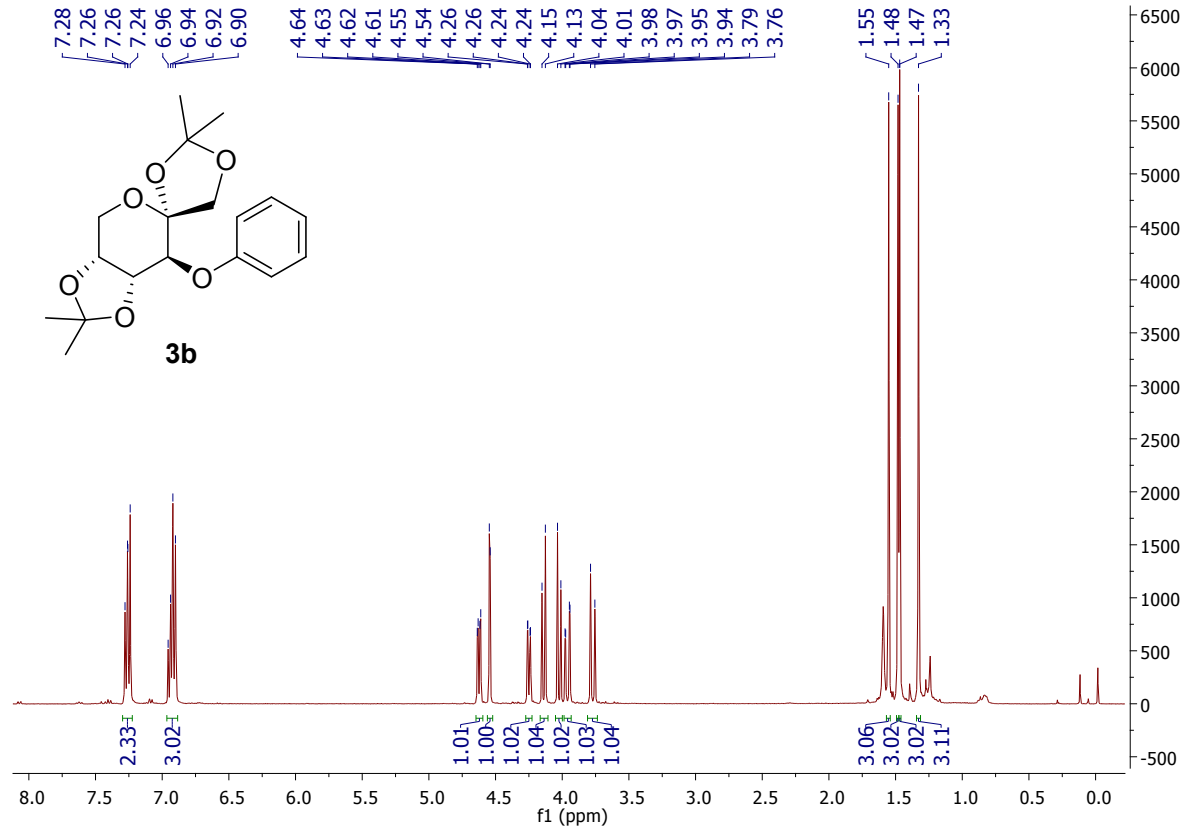
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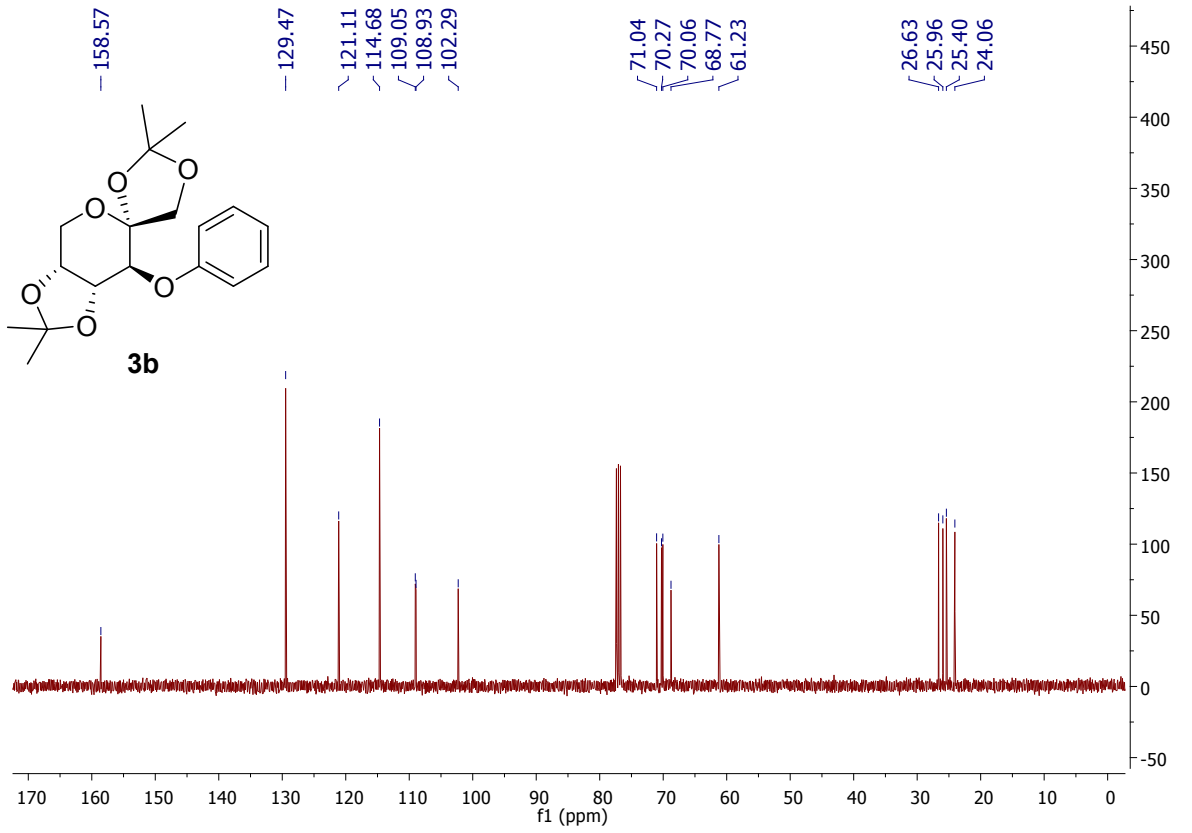
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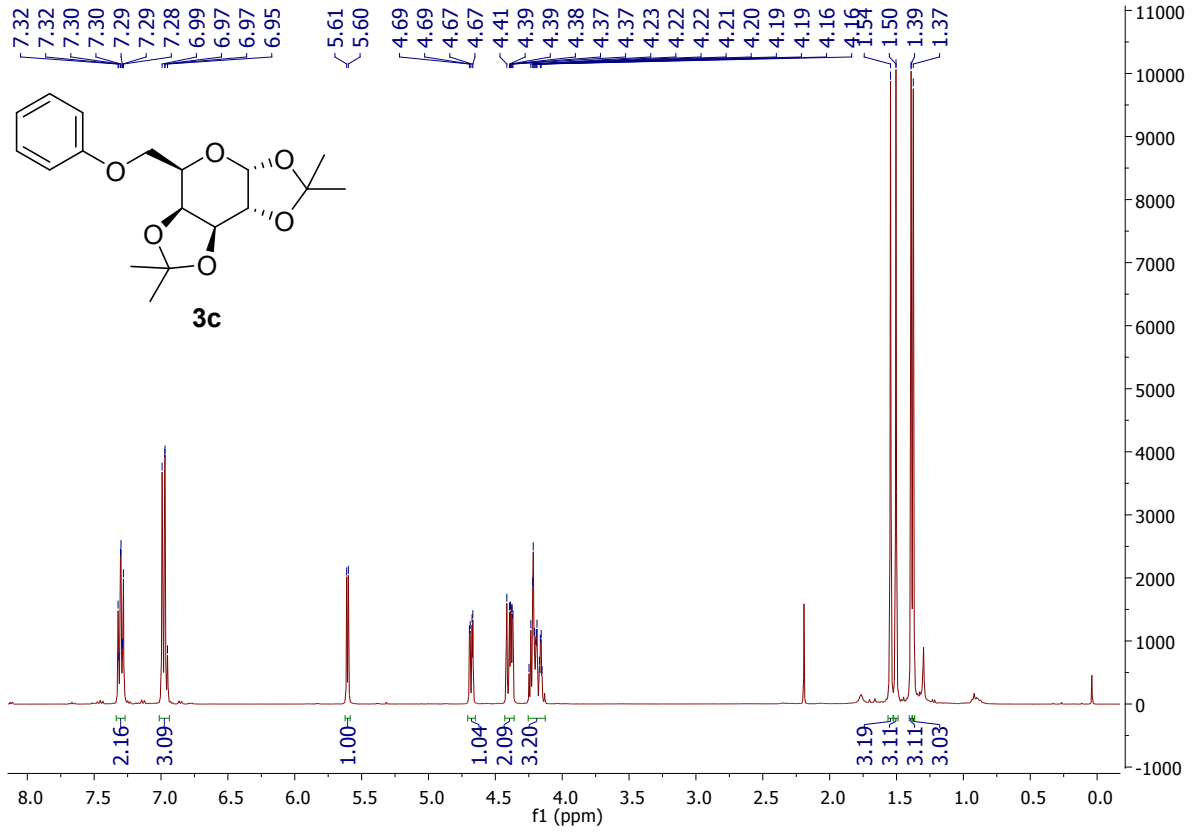
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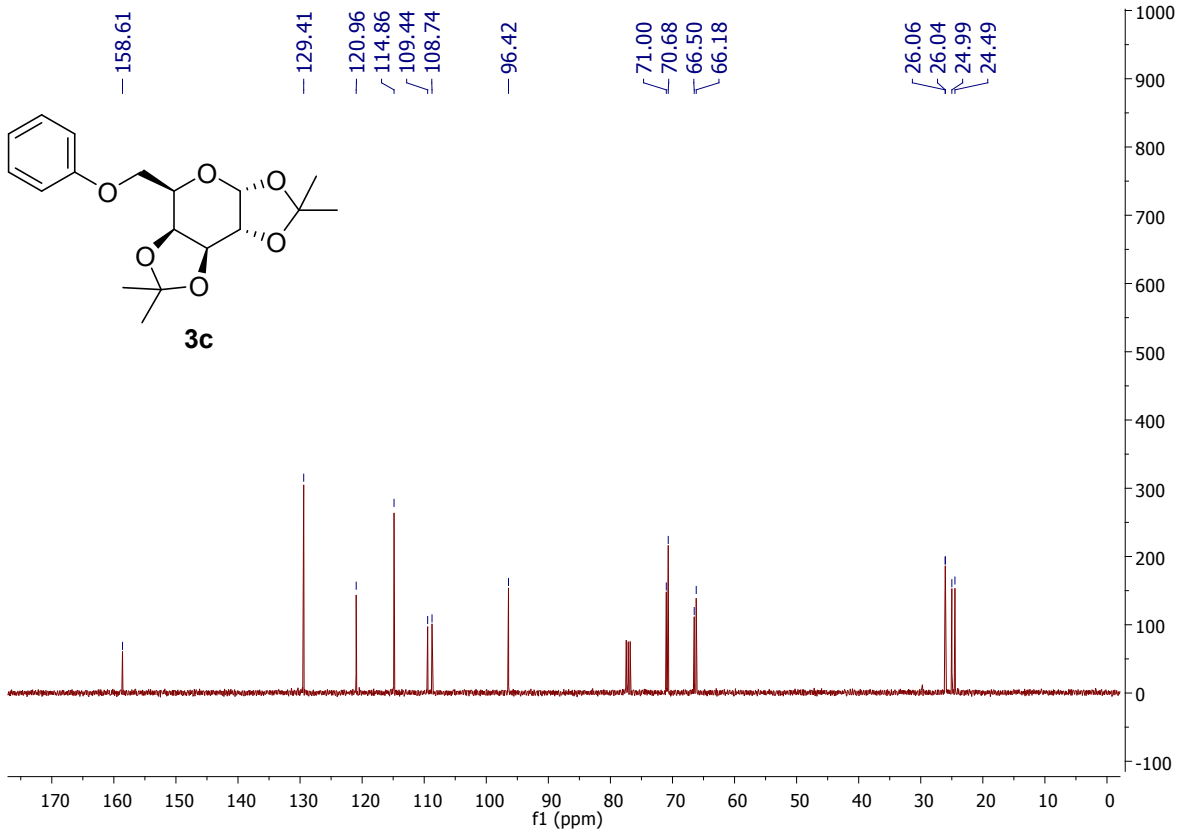
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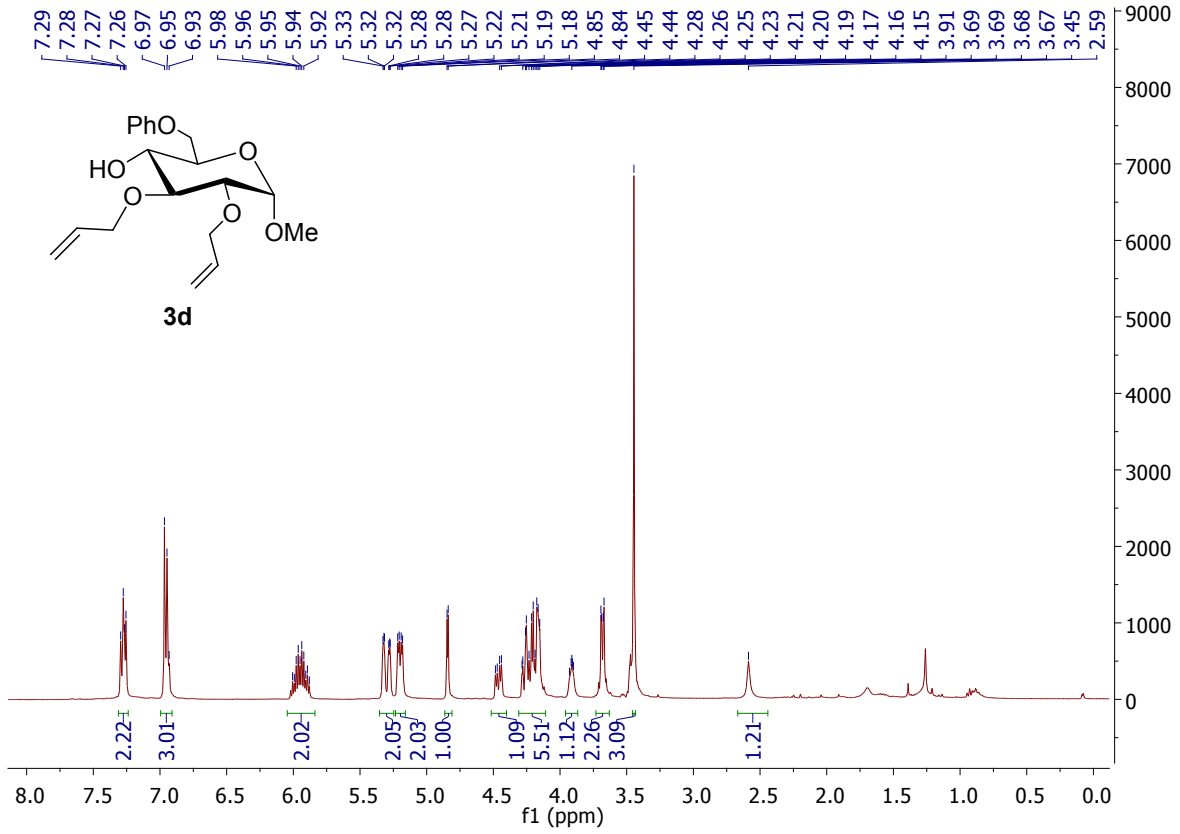
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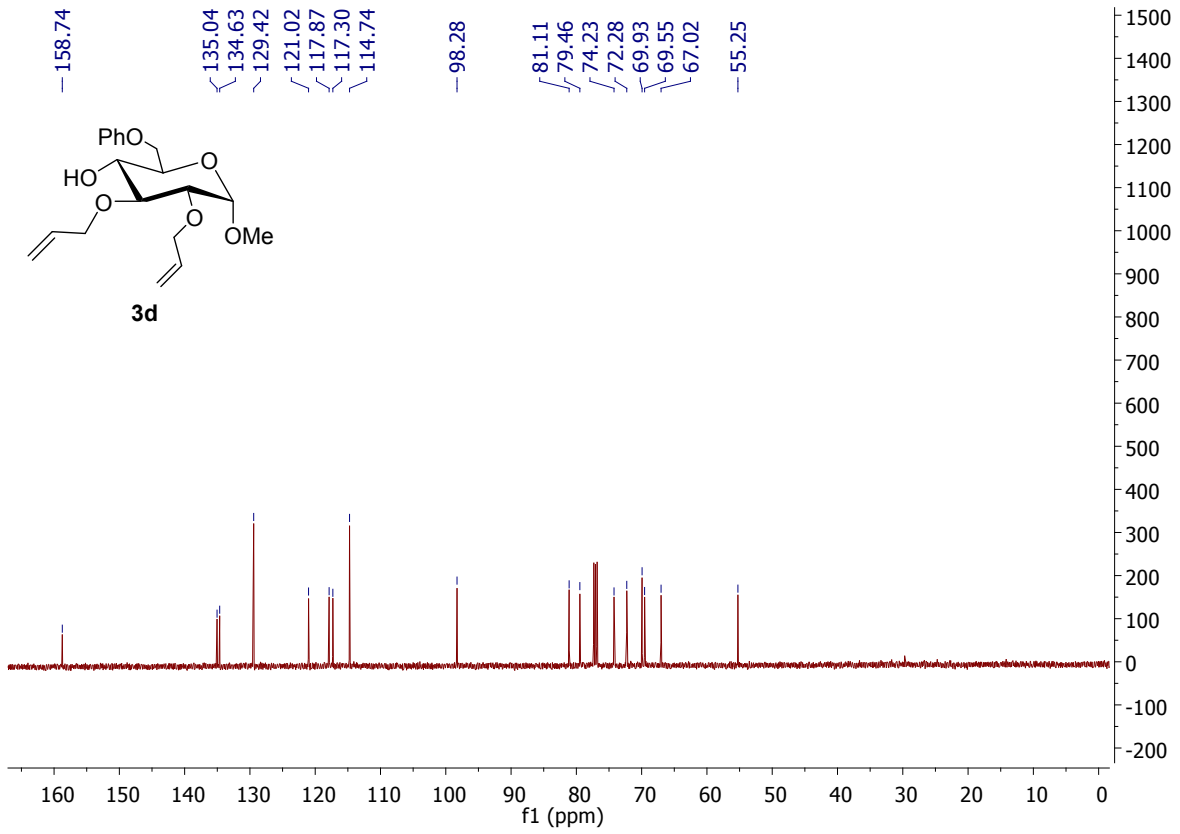
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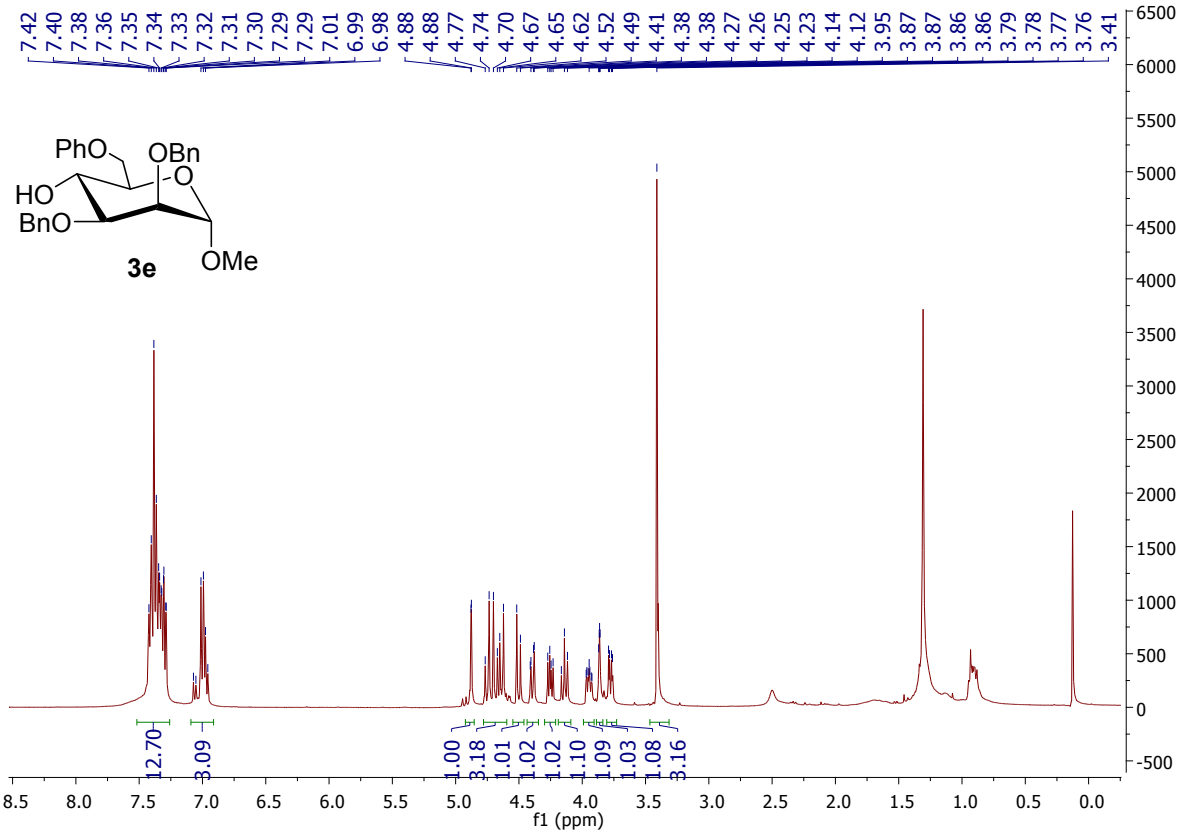
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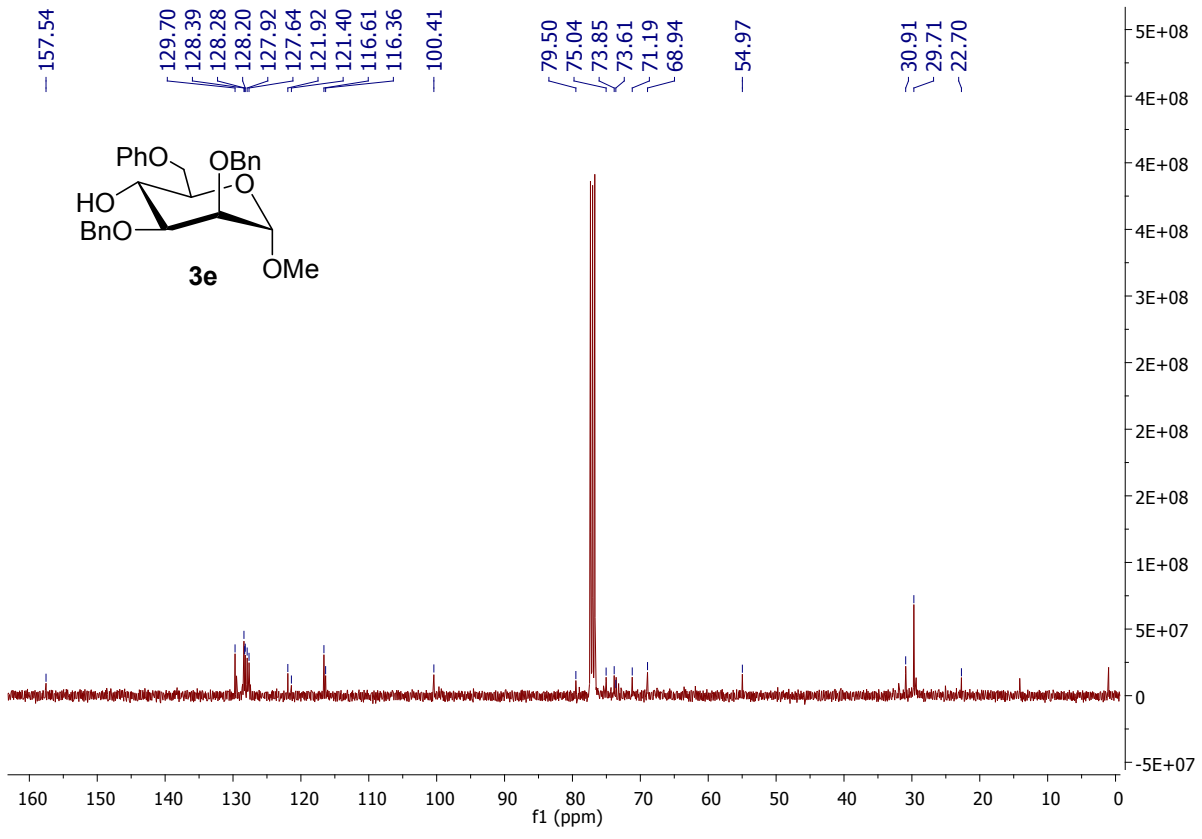
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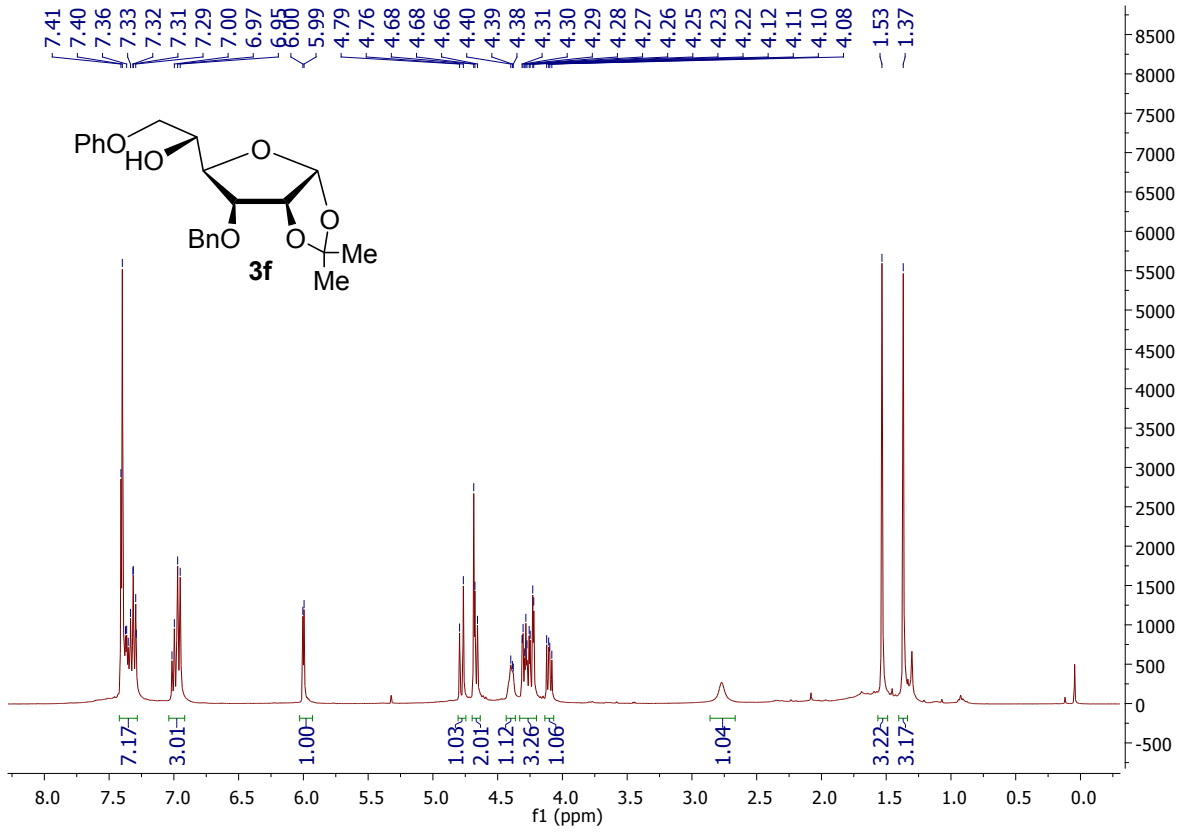
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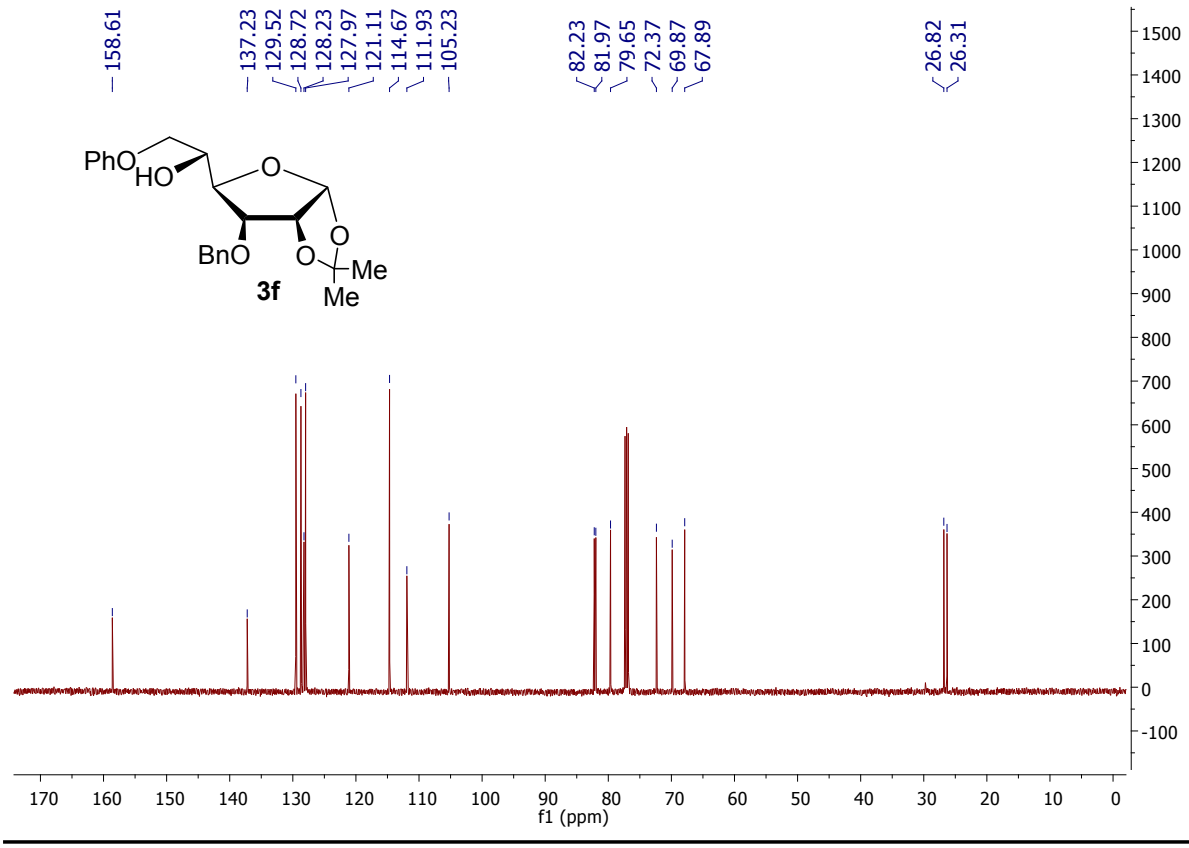
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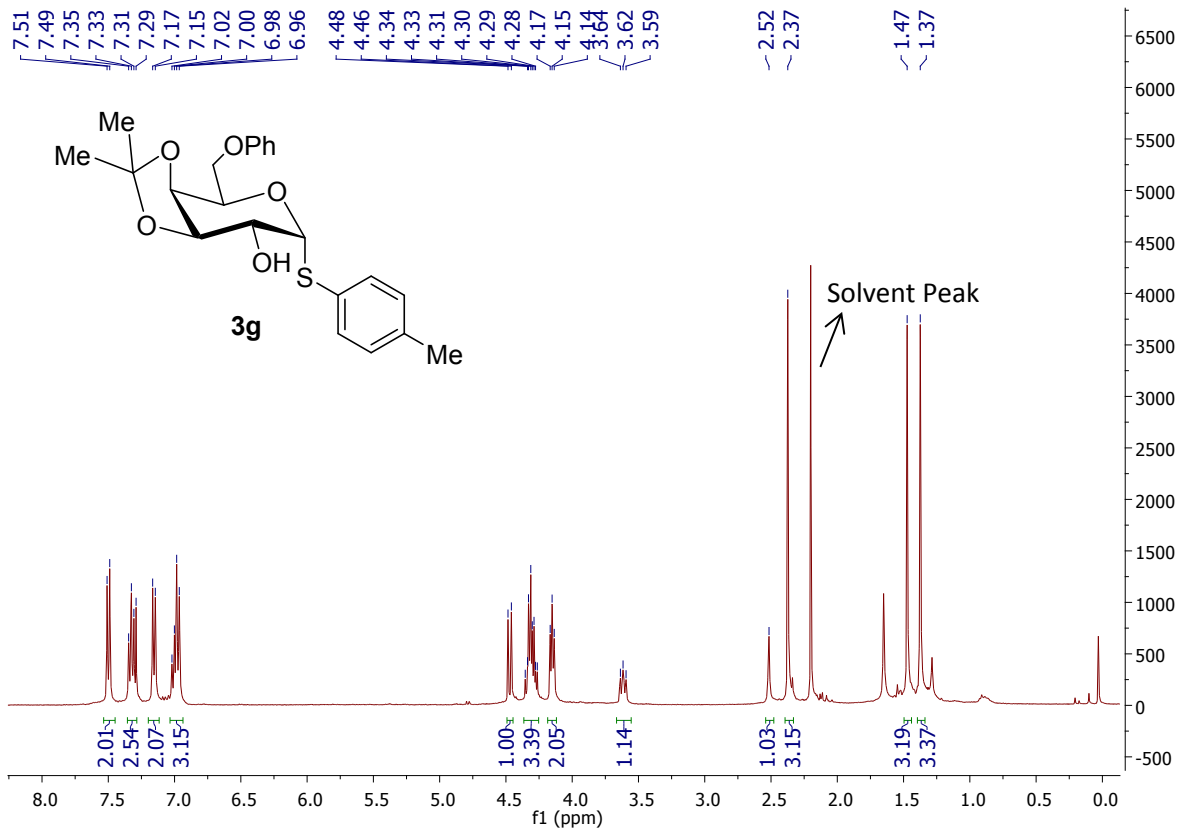
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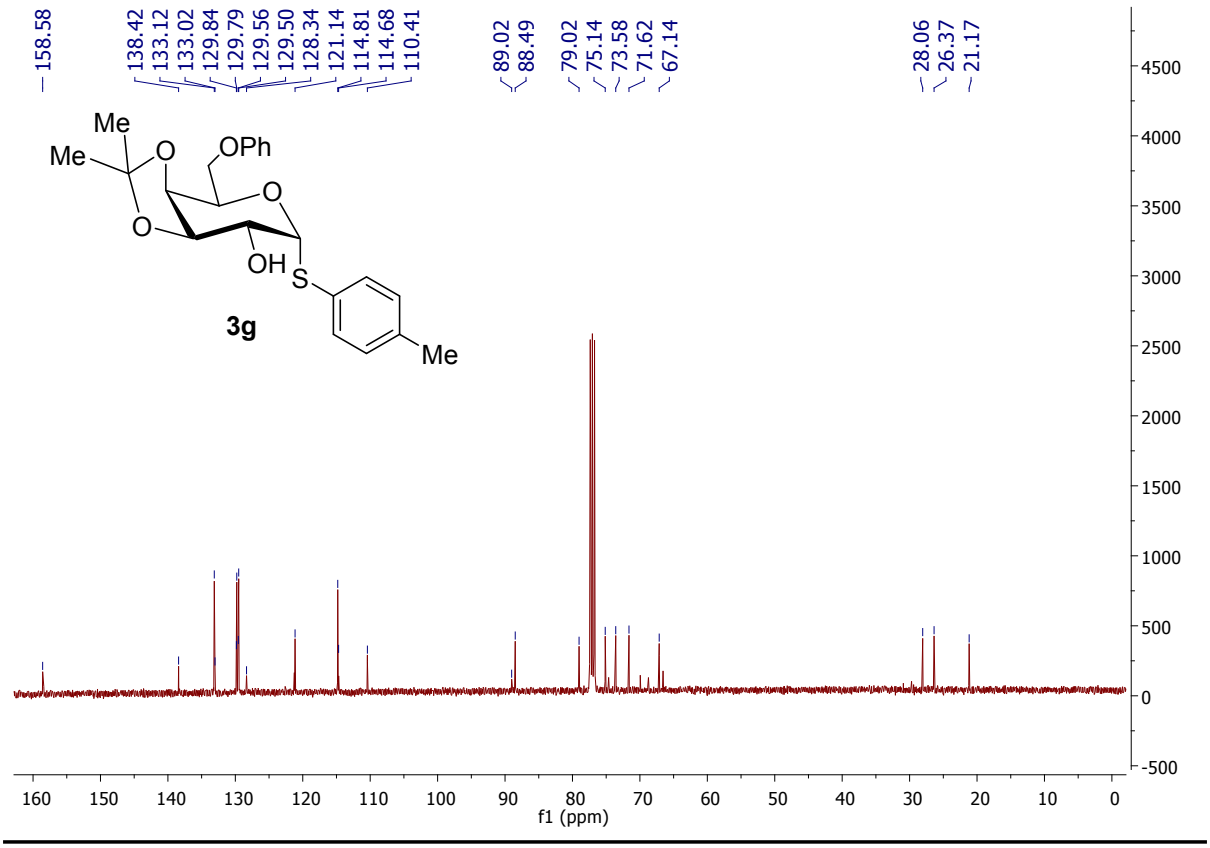
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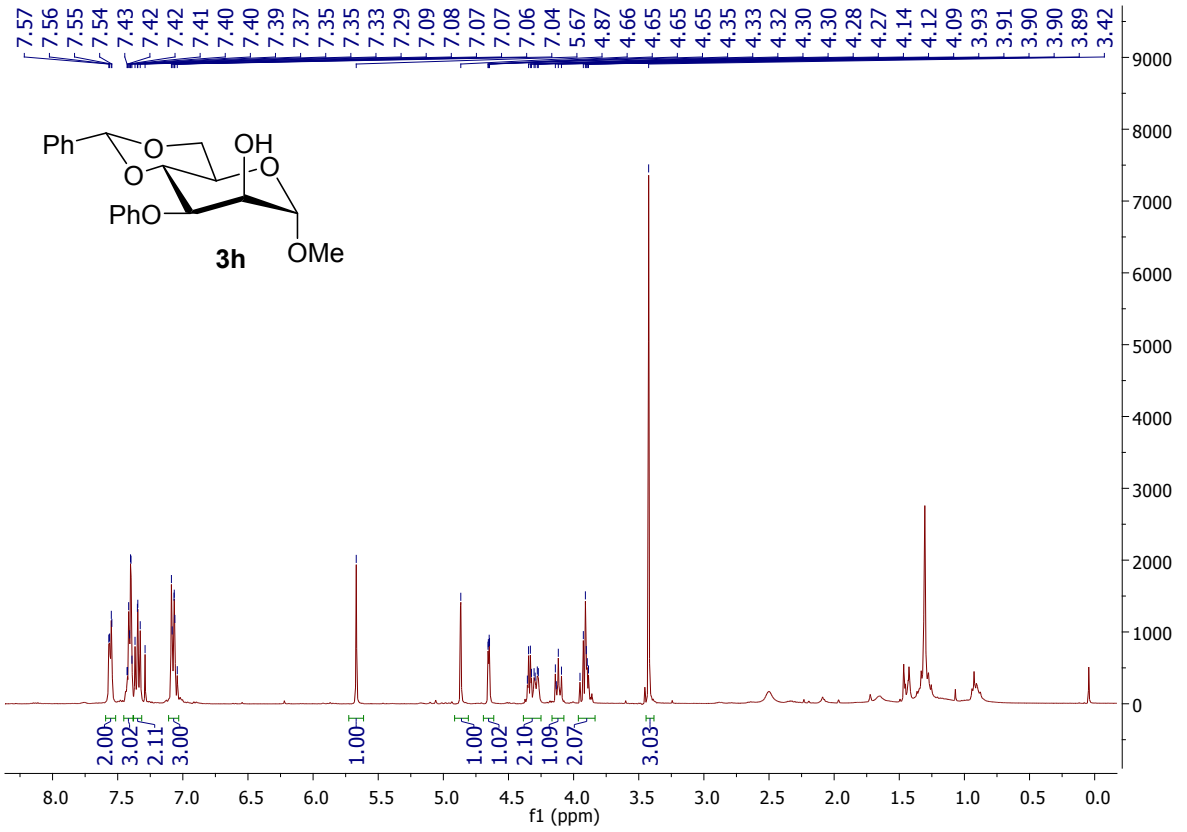
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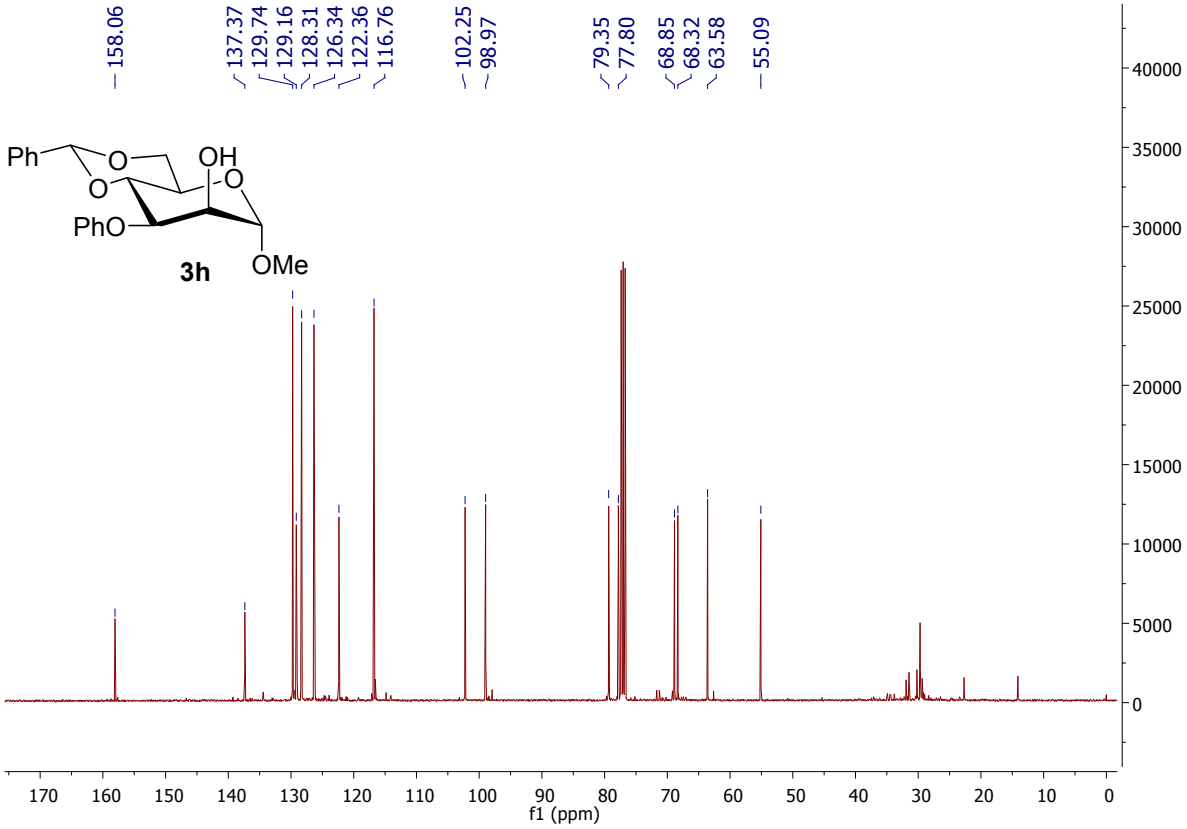
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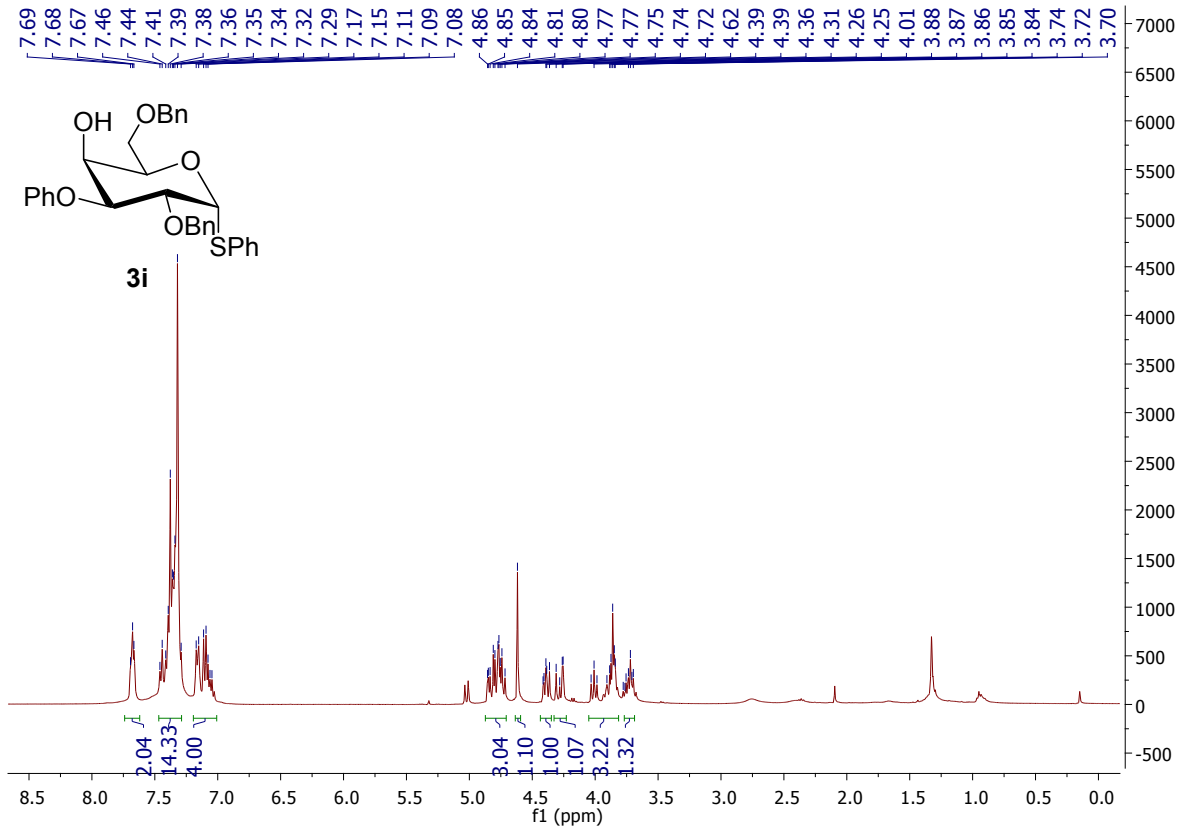
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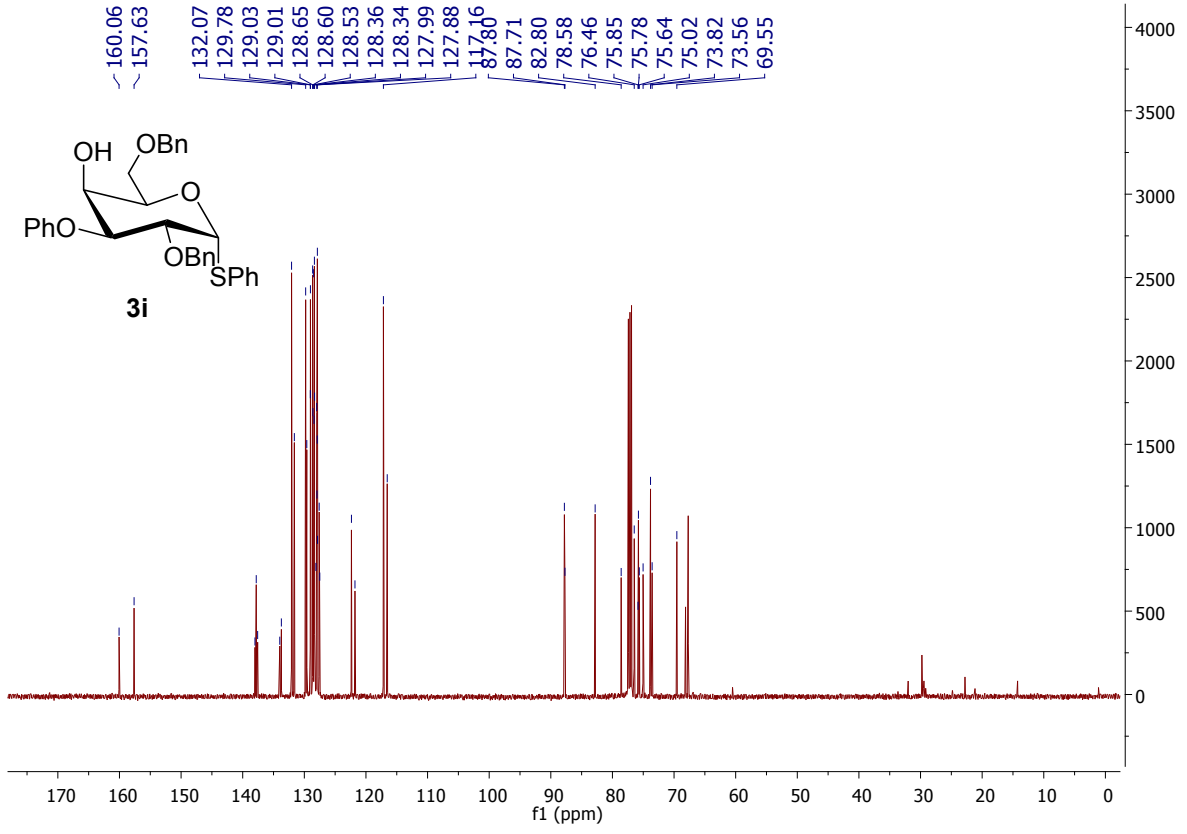
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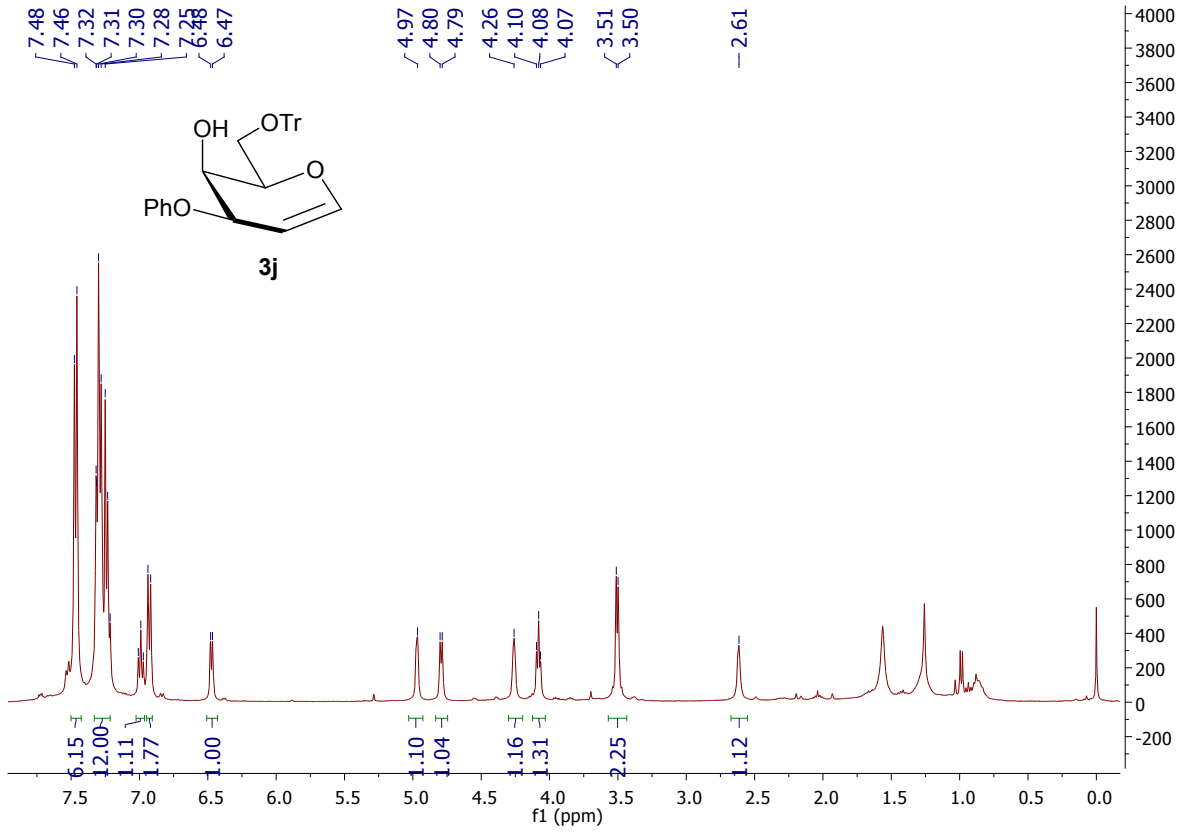
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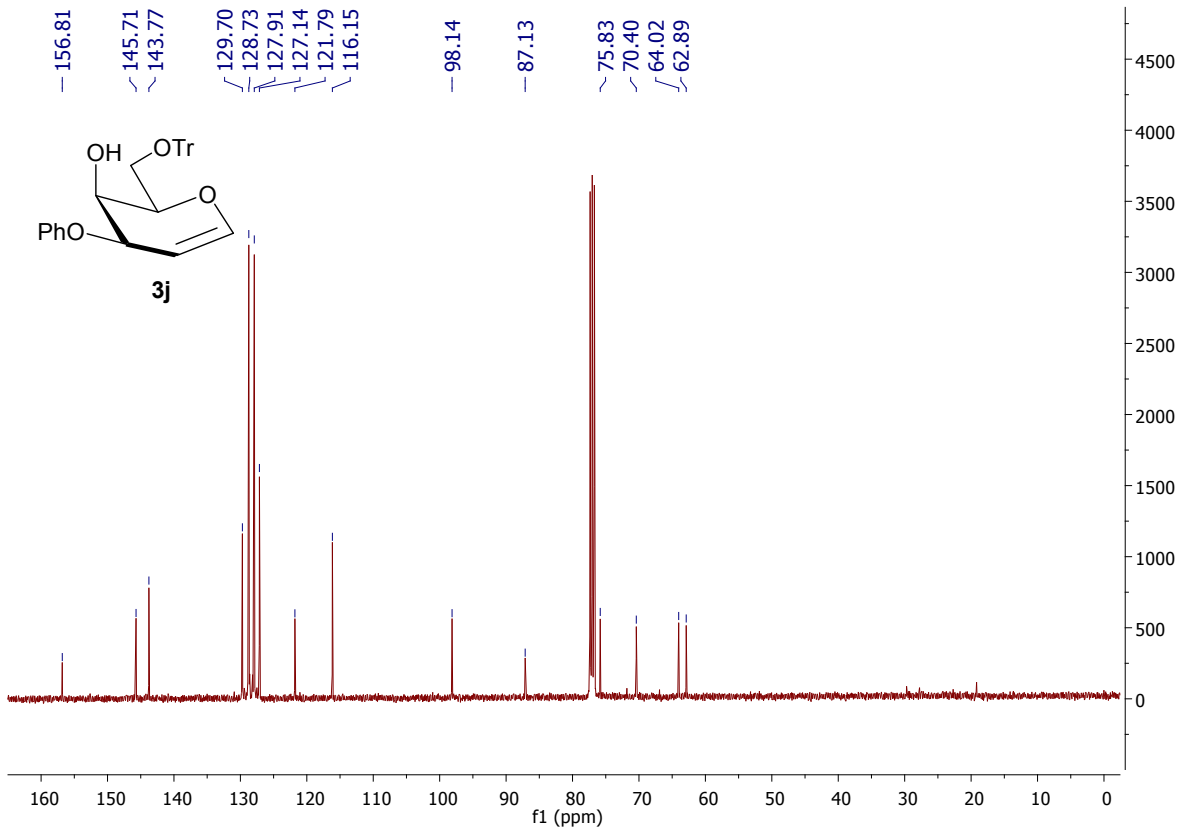
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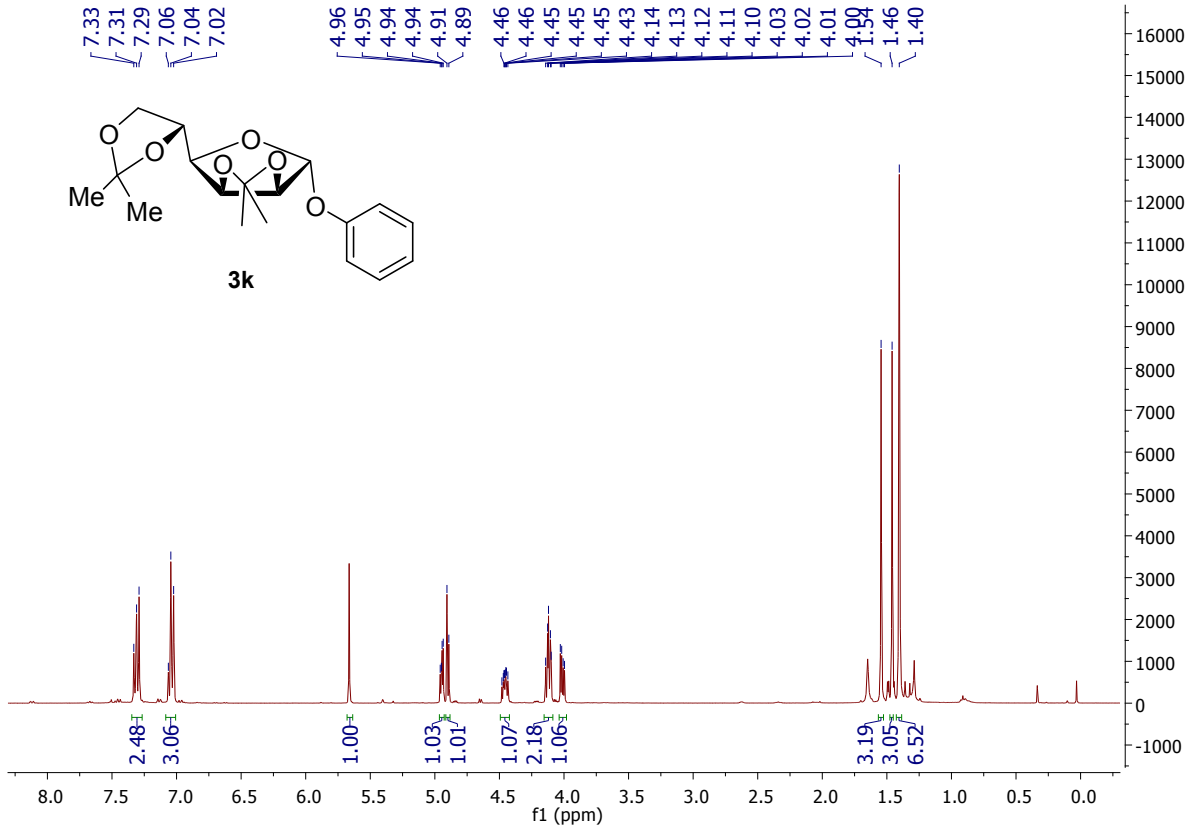
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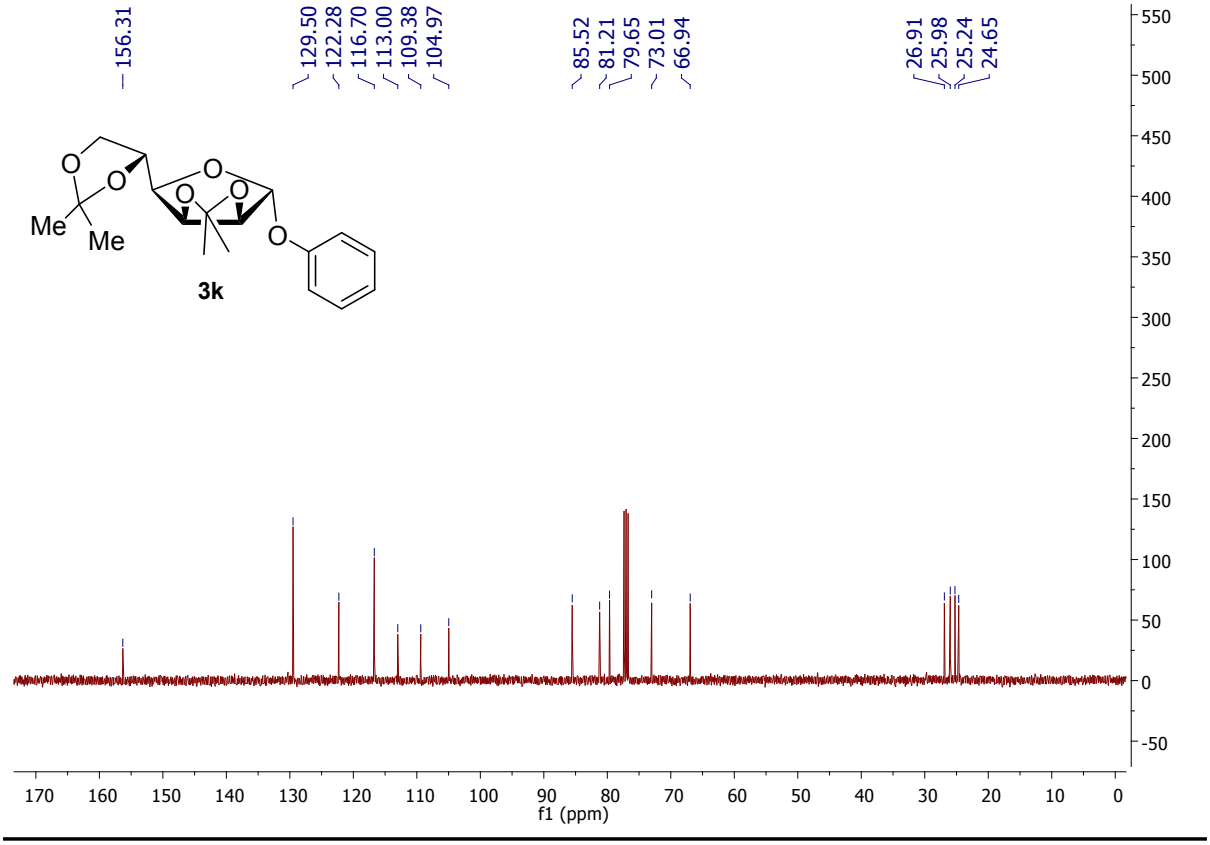
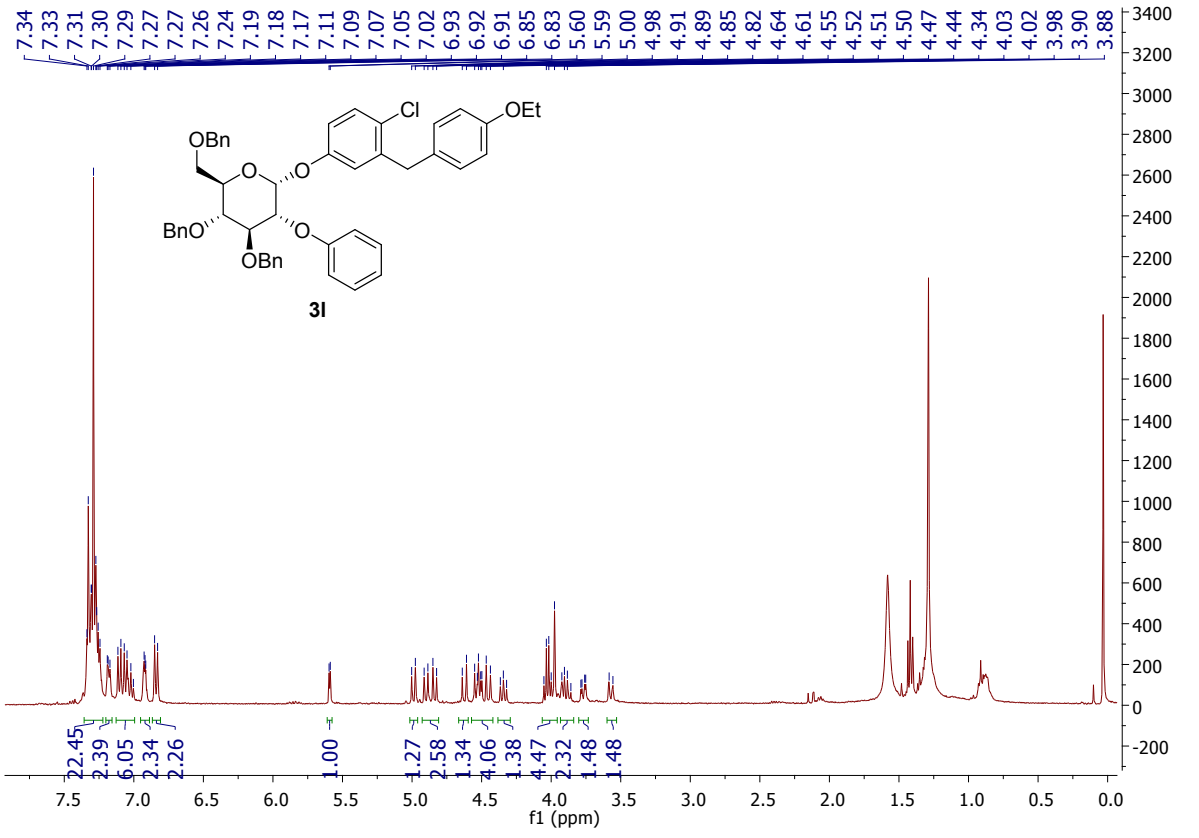
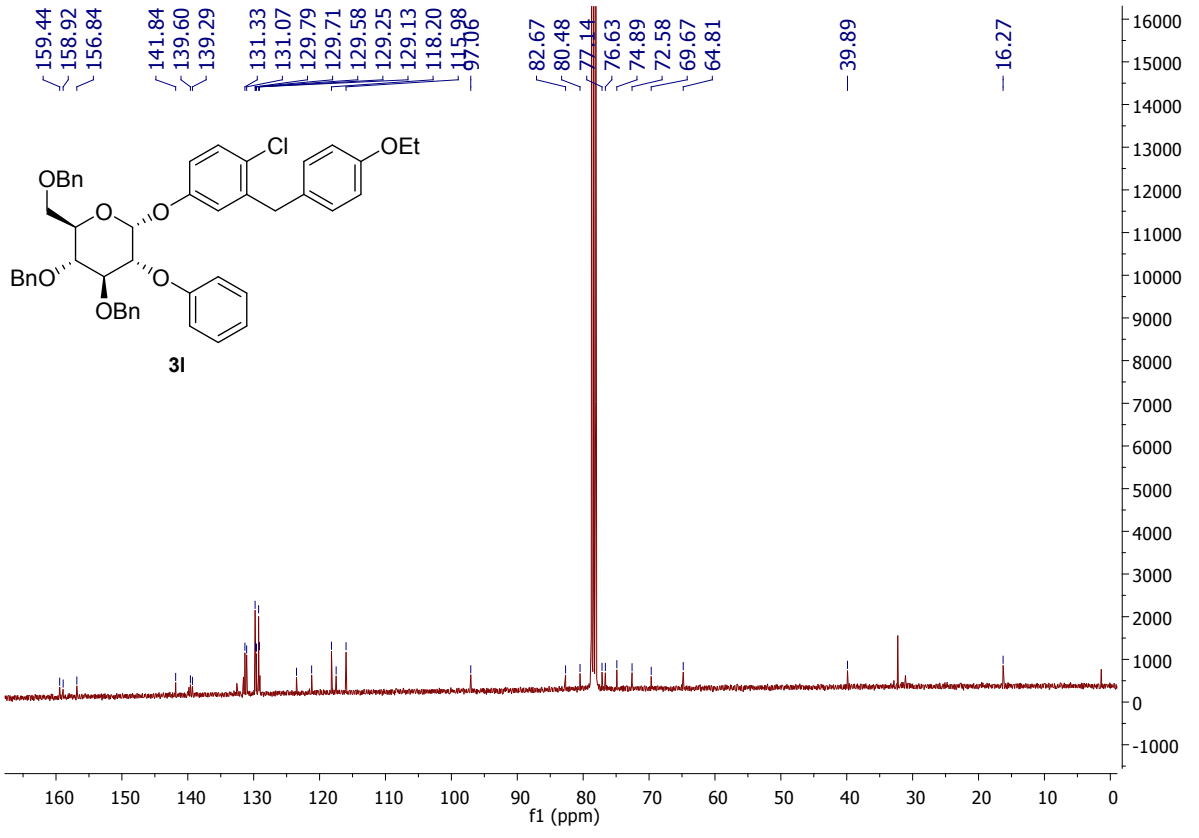
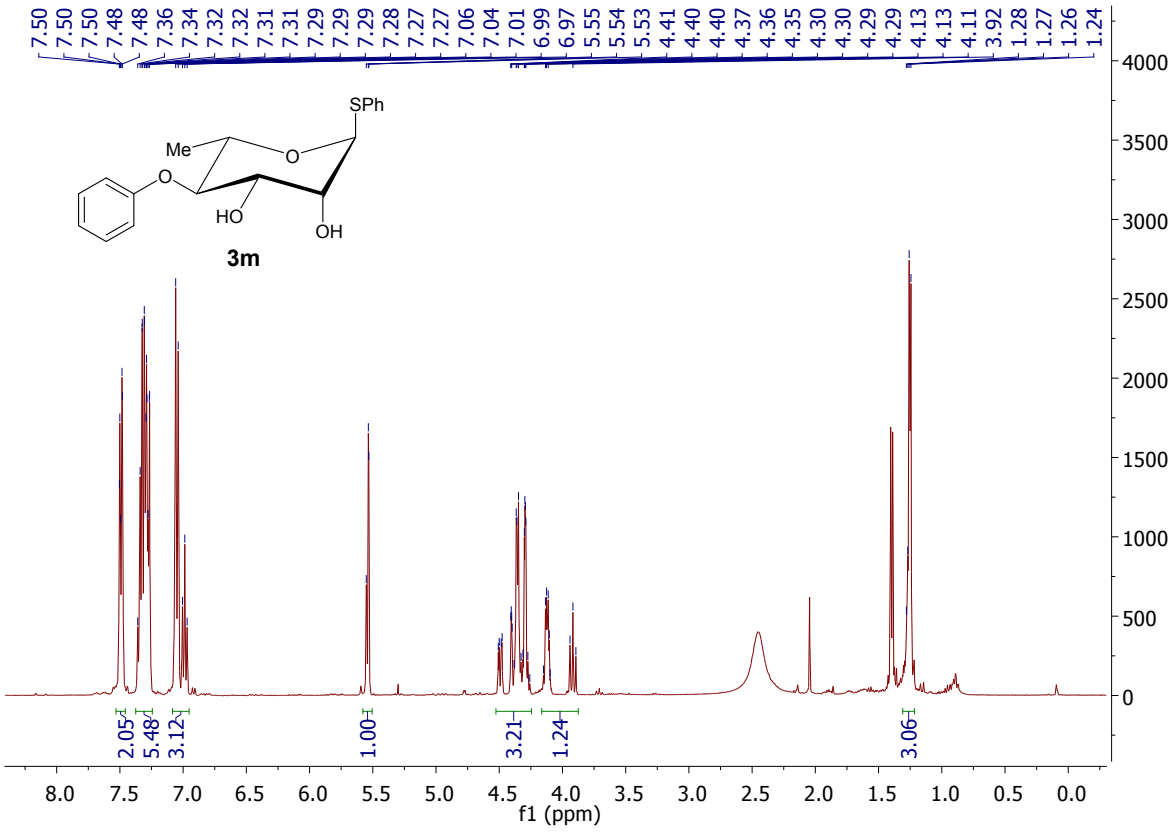
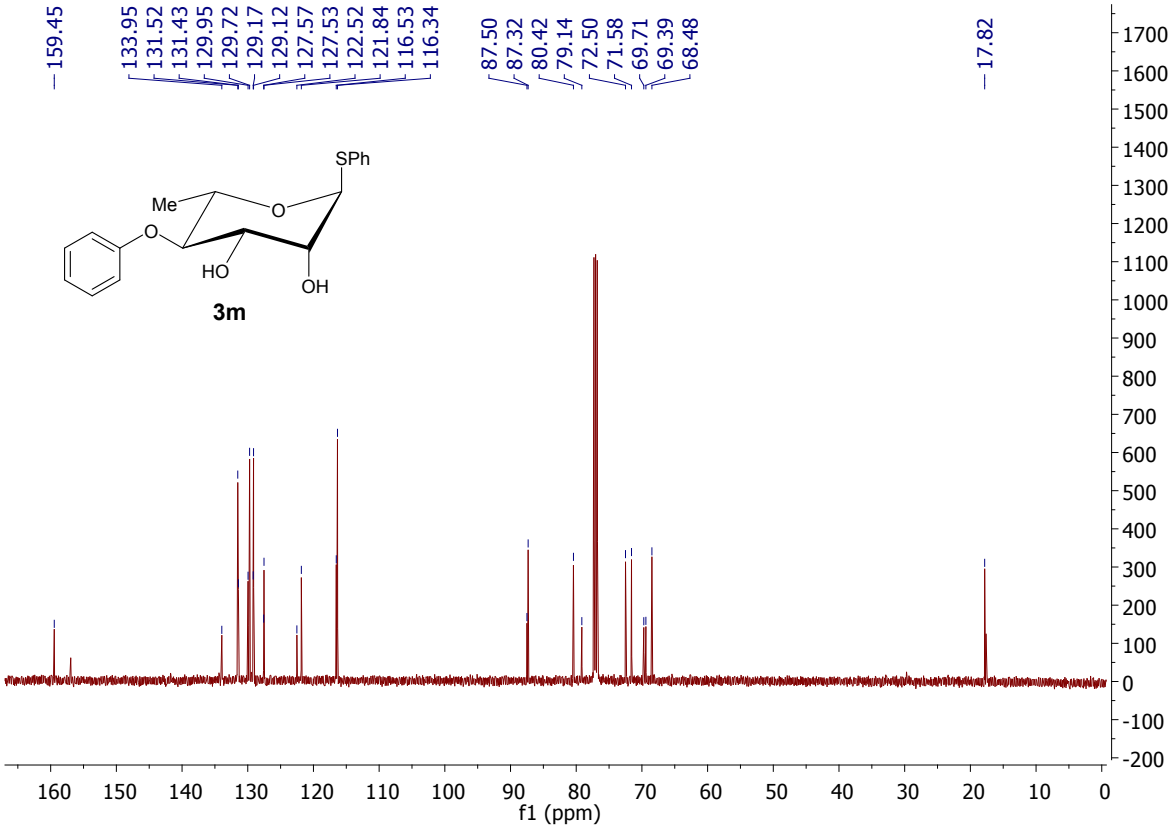
Me
3k
2.48
3.06
1.00
1.03
1.01
1.07
2.18
1.06
3.19
3.05
6.52
f1 (ppm)

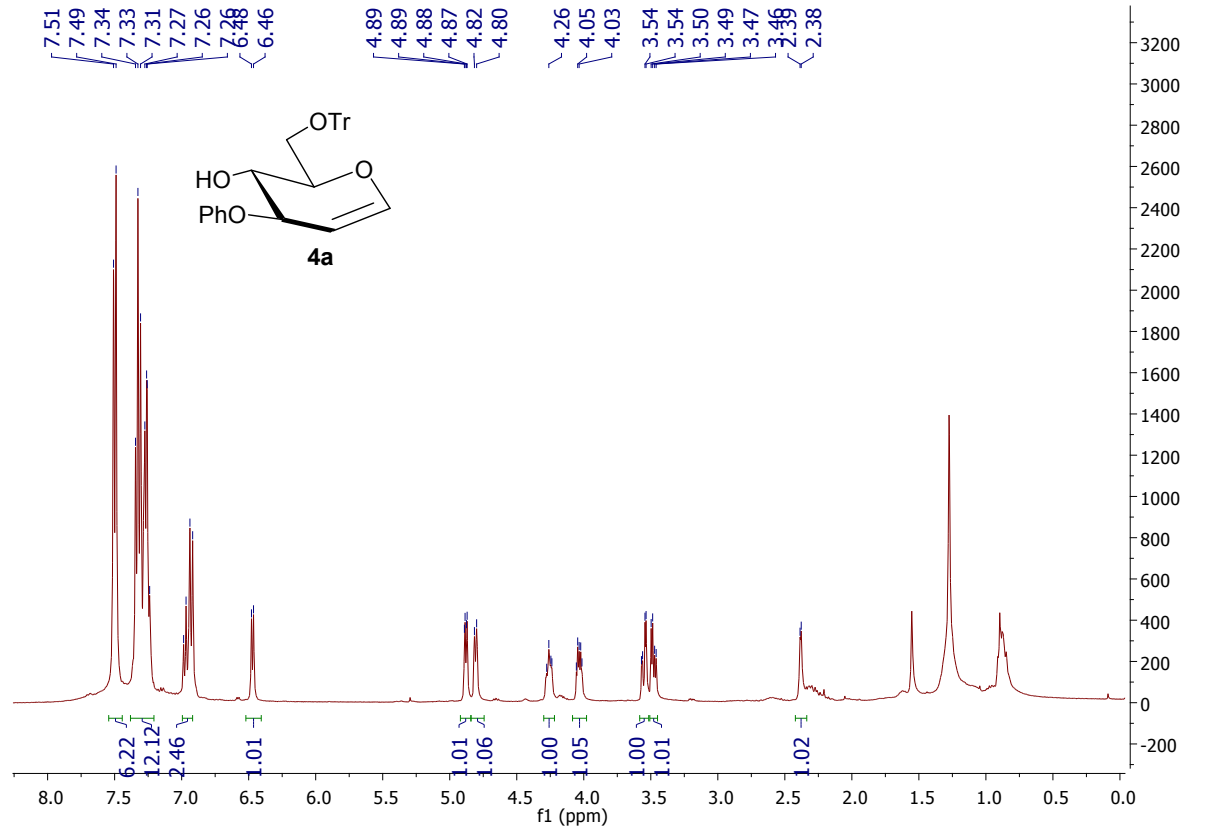

156.31
129.50
122.28
116.70
113.00
109.38
104.97
85.52
81.21
79.65
73.01
66.94
26.91
25.98
25.24
24.65
Me
Me
3k
f1 (ppm)

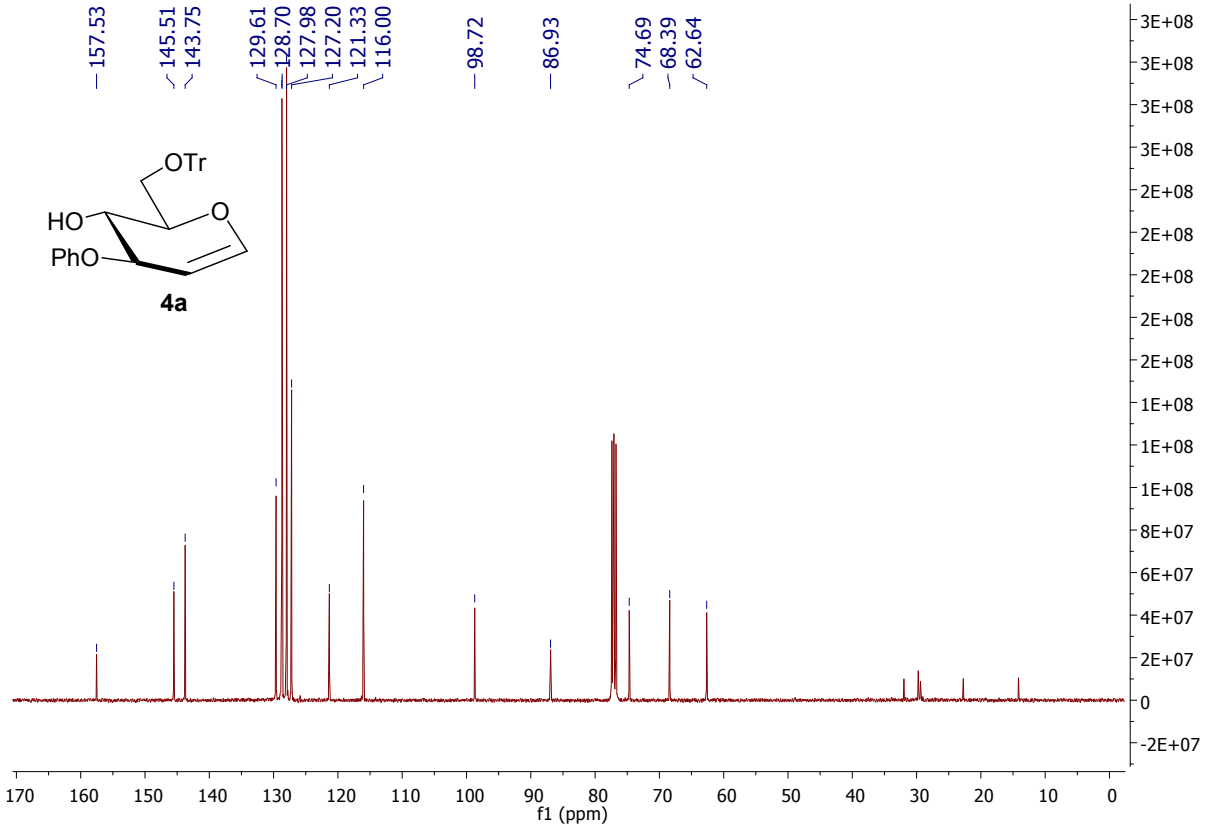

7.34 7.33 7.31 7.30 7.29 7.27 7.27 7.26 7.24 7.19 7.18 7.17 7.11 7.09 7.07 7.05 7.02 6.93 6.92 6.91 6.85 6.83 5.60 5.59 5.00 4.98 4.91 4.89 4.85 4.82 4.64 4.61 4.55 4.52 4.51 4.50 4.47 4.44 4.34 4.03 4.02 3.98 3.90 3.88
Cl
OEt
OBn
O
O
BnO
O
OBn
3l
22.45 2.39 6.05 2.34 2.26 1.00 1.27 2.58 1.34 4.06 1.38 4.47 2.32 1.48 1.48
f1 (ppm)


159.44 158.92 156.84 141.84 139.60 139.29 131.33 131.07 129.79 129.71 129.58 129.25 129.13 118.20 115.98 97.06 82.67 80.48 77.14 76.63 74.89 72.58 69.67 64.81 39.89 16.27
Cl
OEt
OBn
O
O
BnO
O
OBn
3l
f1 (ppm)

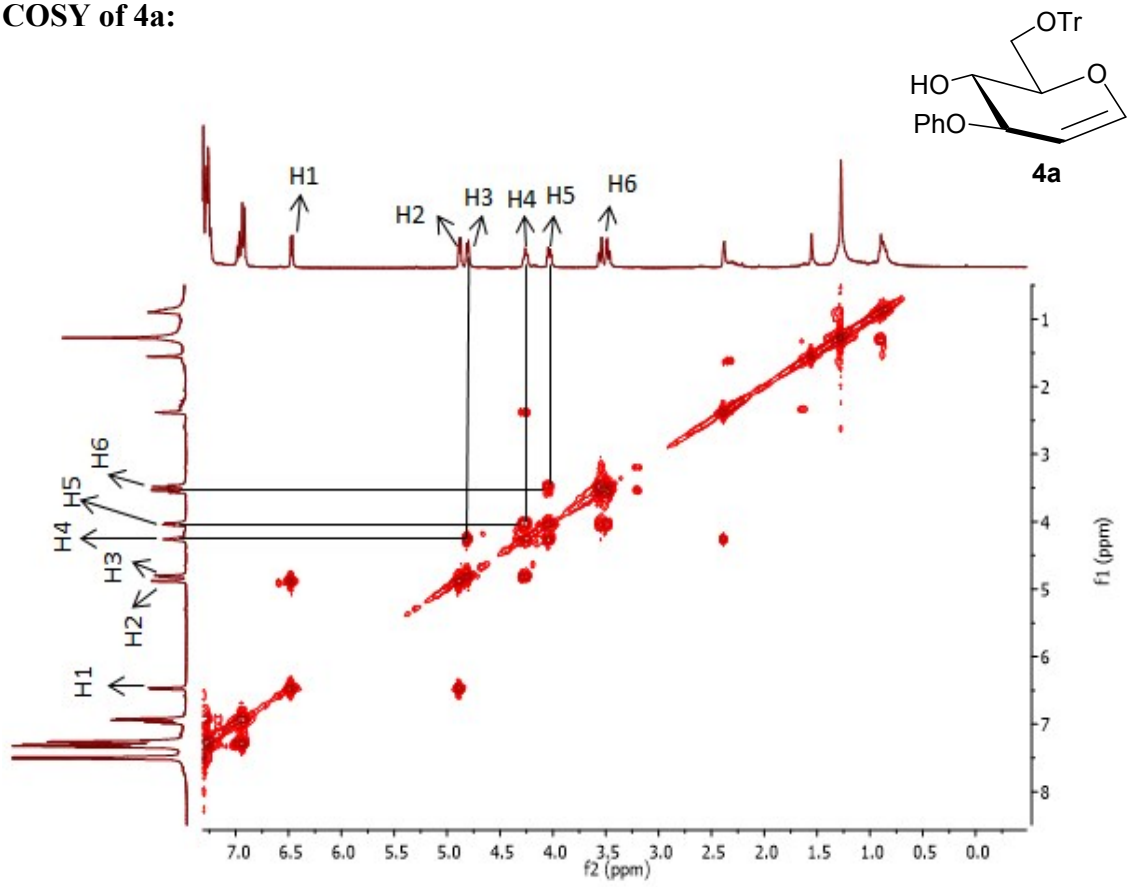

7.50 7.50 7.48 7.48 7.36 7.34 7.32 7.32 7.31 7.31 7.29 7.29 7.29 7.28 7.27 7.27 7.06 7.04 7.01 6.99 6.97 5.55 5.54 5.53 4.41 4.40 4.40 4.37 4.36 4.35 4.30 4.30 4.29 4.29 4.13 4.13 4.11 3.92 1.28 1.27 1.26 1.24
SPh
Me
O
O
HO
OH
3m
2.05
5.48
3.12
1.00
3.21
1.24
3.06
f1 (ppm)


159.45
133.95 131.52 131.43 129.95 129.72 129.17 129.12 127.57 127.53 122.52 121.84 116.53 116.34
87.50 87.32 80.42 79.14 72.50 71.58 69.71 69.39 68.48
17.82
SPh
Me
O
O
HO
OH
3m
f1 (ppm)


7.51
7.49
7.34
7.33
7.31
7.27
7.26
6.48
6.46
4.89
4.89
4.88
4.87
4.82
4.80
4.26
4.05
4.03
3.54
3.54
3.50
3.49
3.47
2.39
2.38
OTr
HO
PhO
O
4a
6.22
12.12
2.46
1.01
1.01
1.06
1.00
1.05
1.00
1.01
1.02
f1 (ppm)

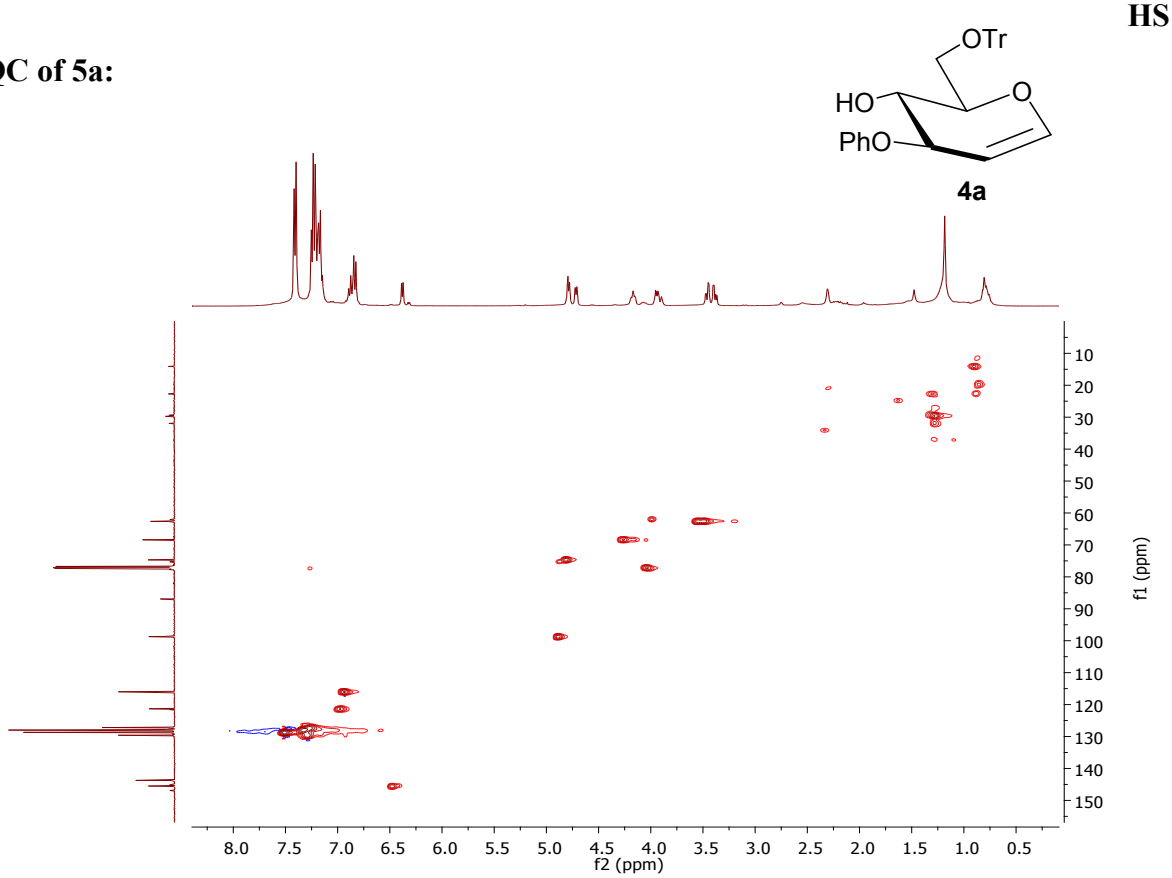

157.53
145.51
143.75
129.61
128.70
127.98
127.20
121.33
116.00
98.72
86.93
74.69
68.39
62.64
OTr
HO
PhO
O
4a
f1 (ppm)

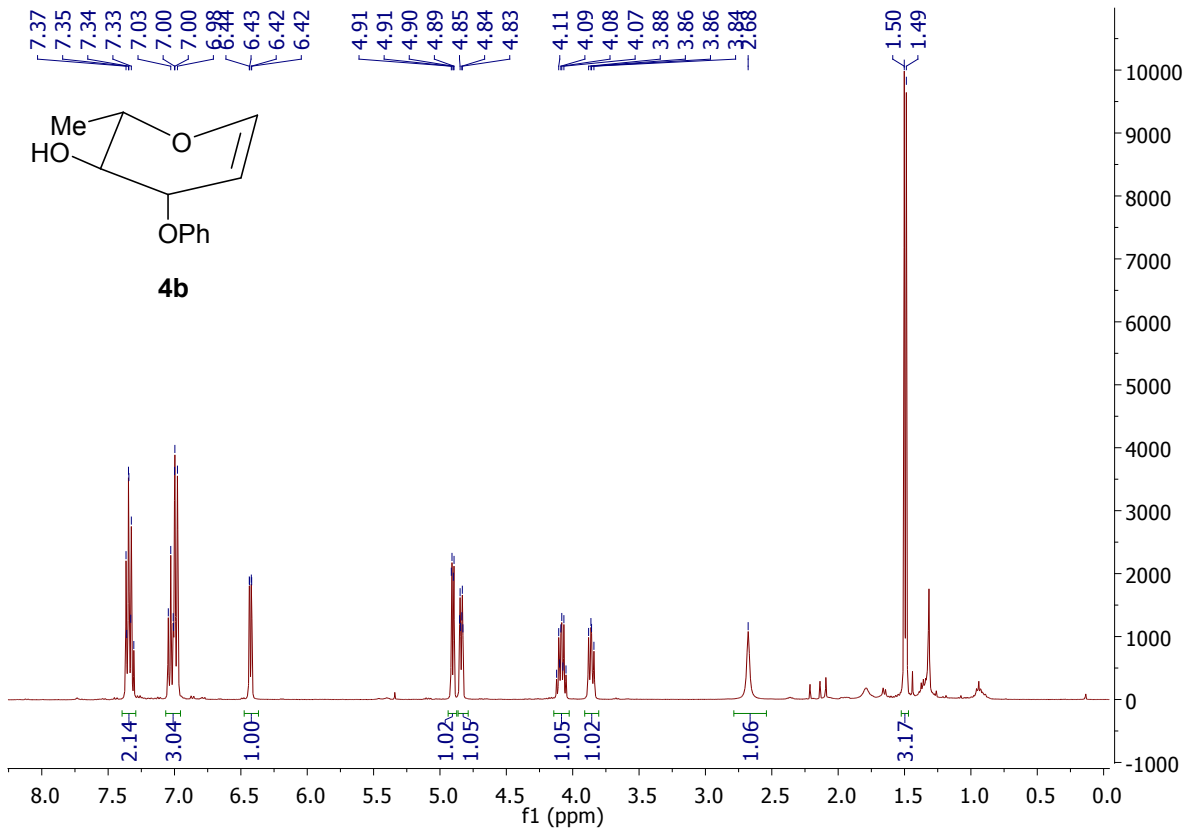
COSY of 4a:

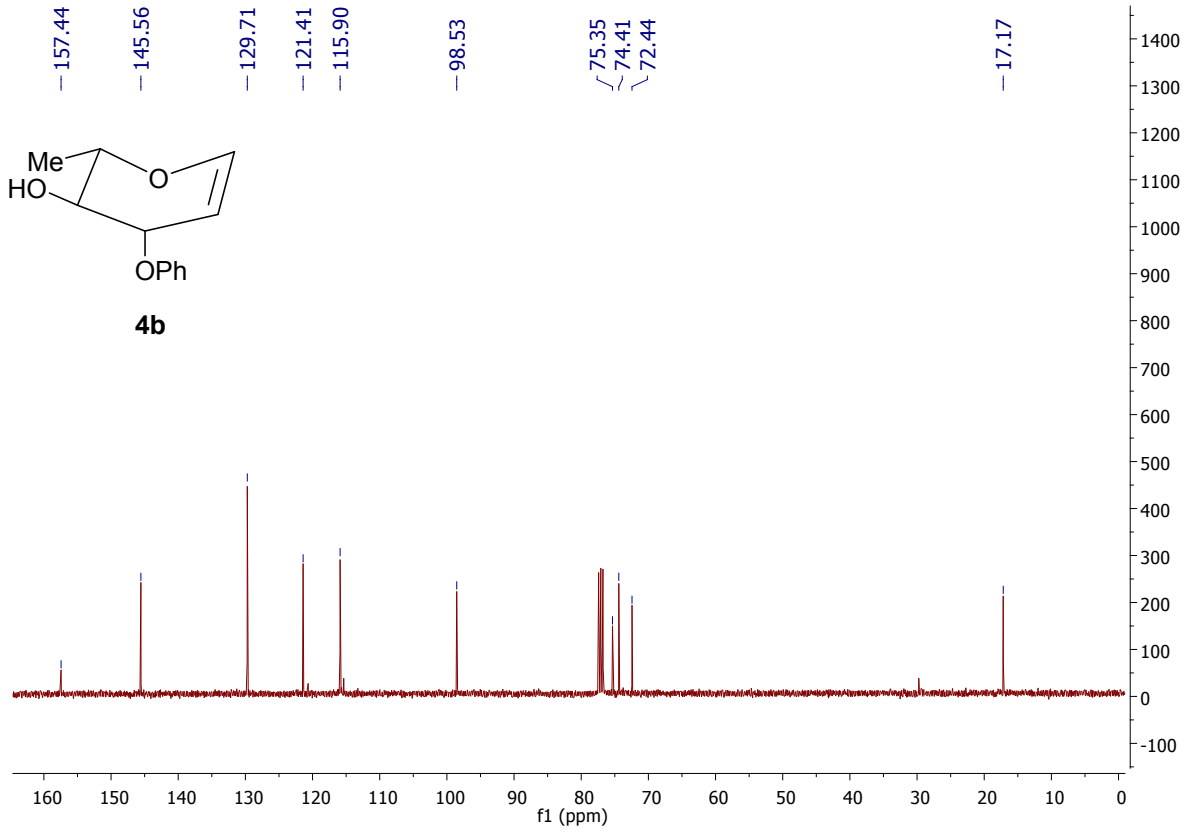


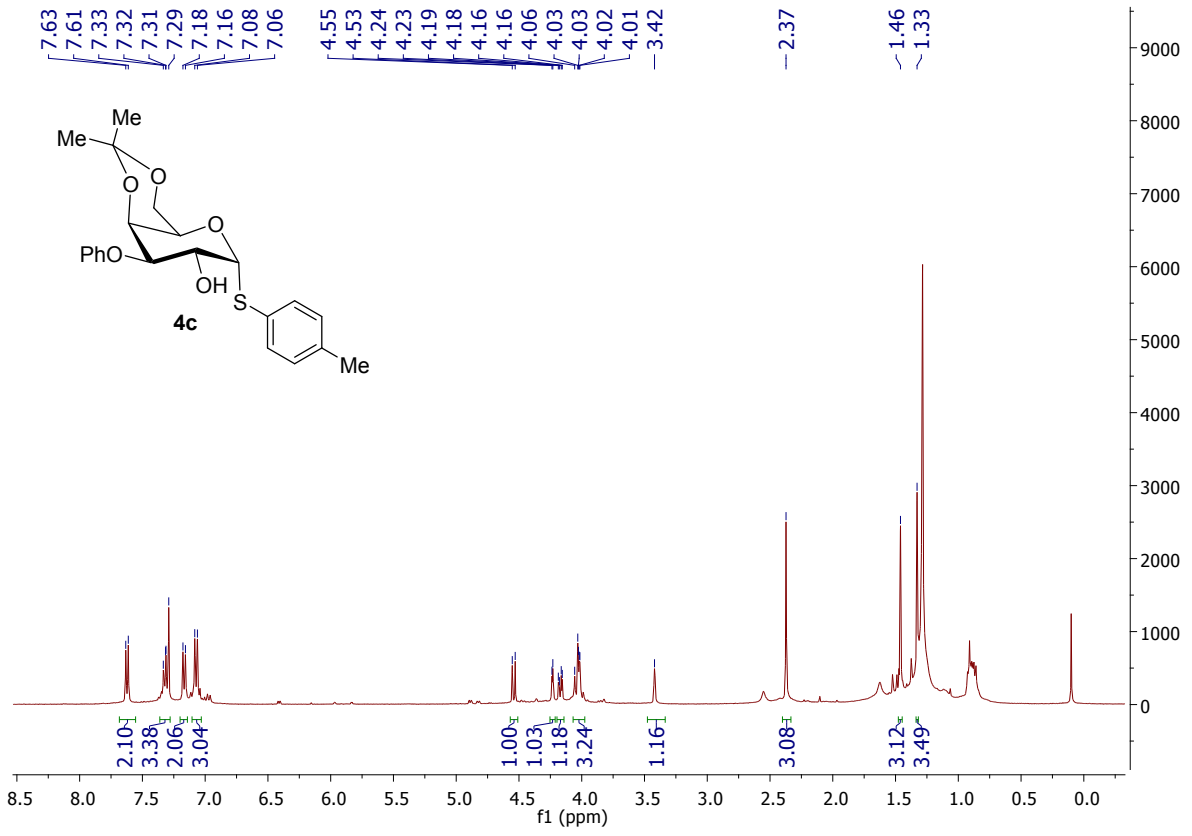
HS

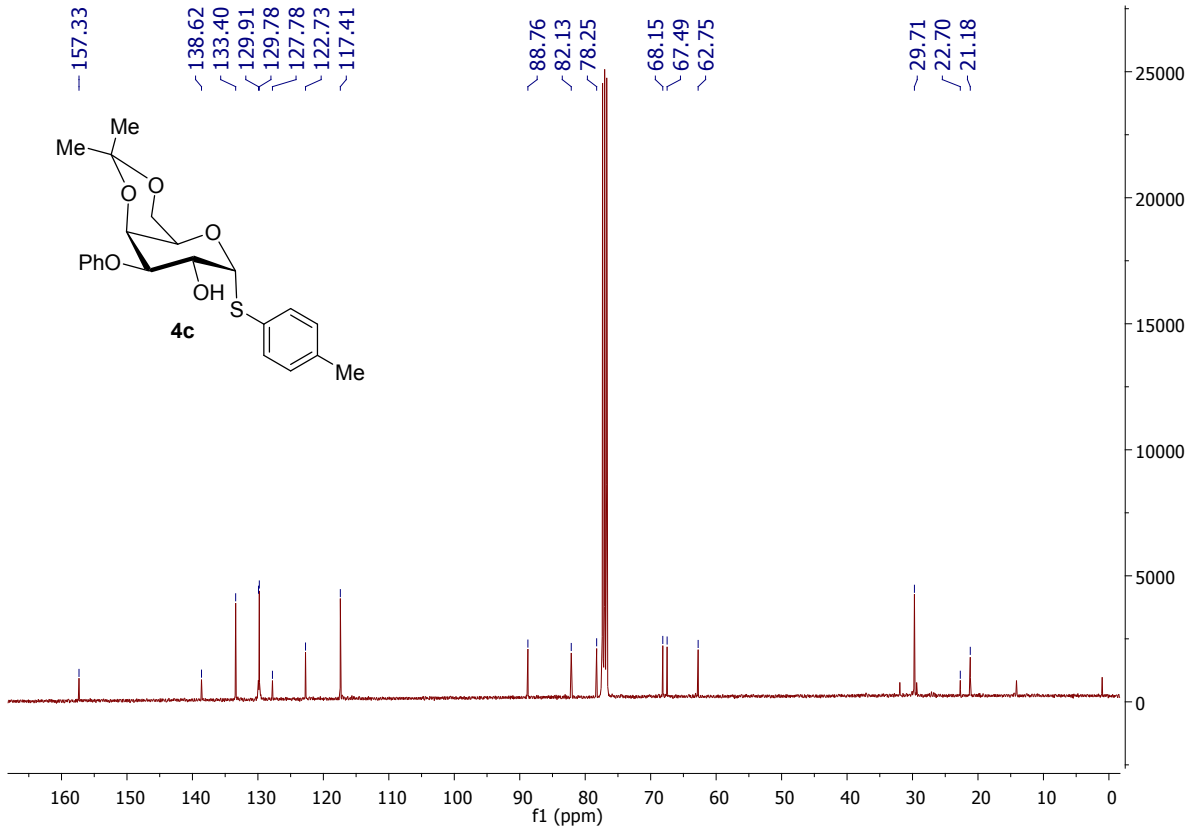
QC of 5a:

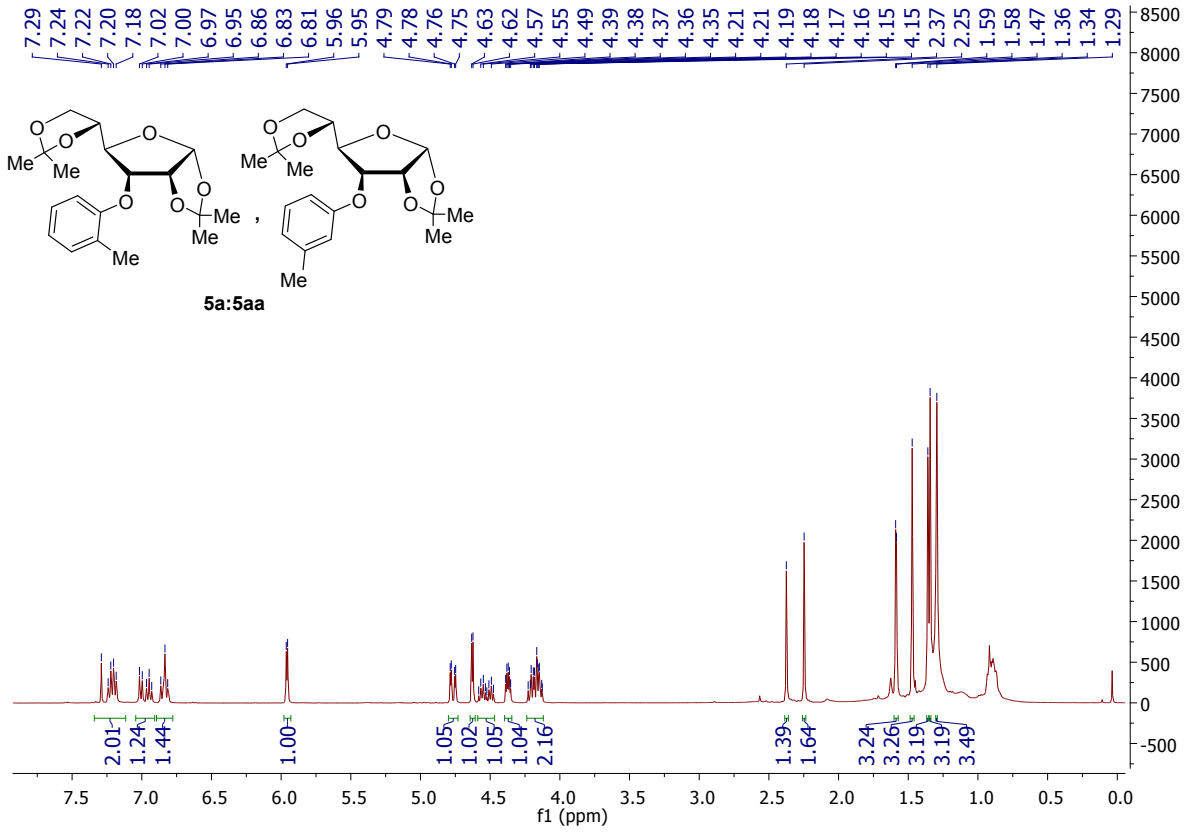


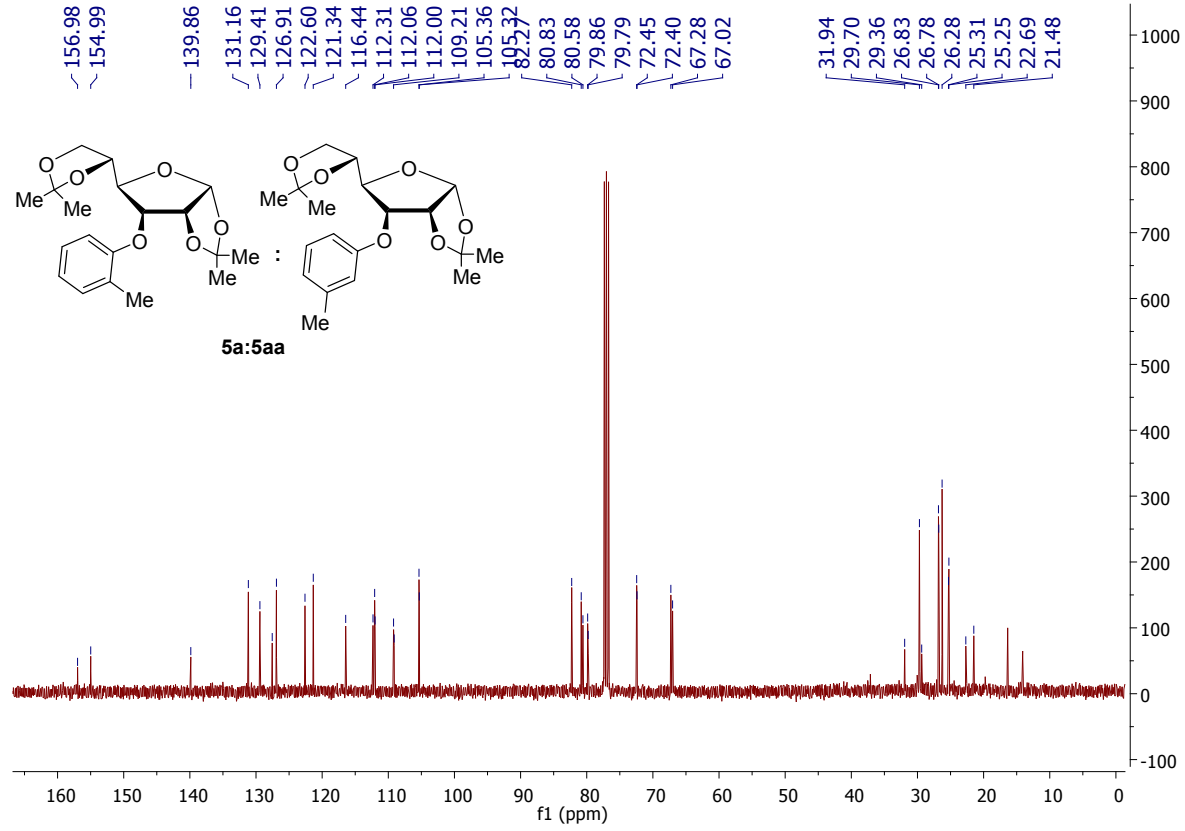

Me
HO
O
OPh
4b
f1 (ppm)

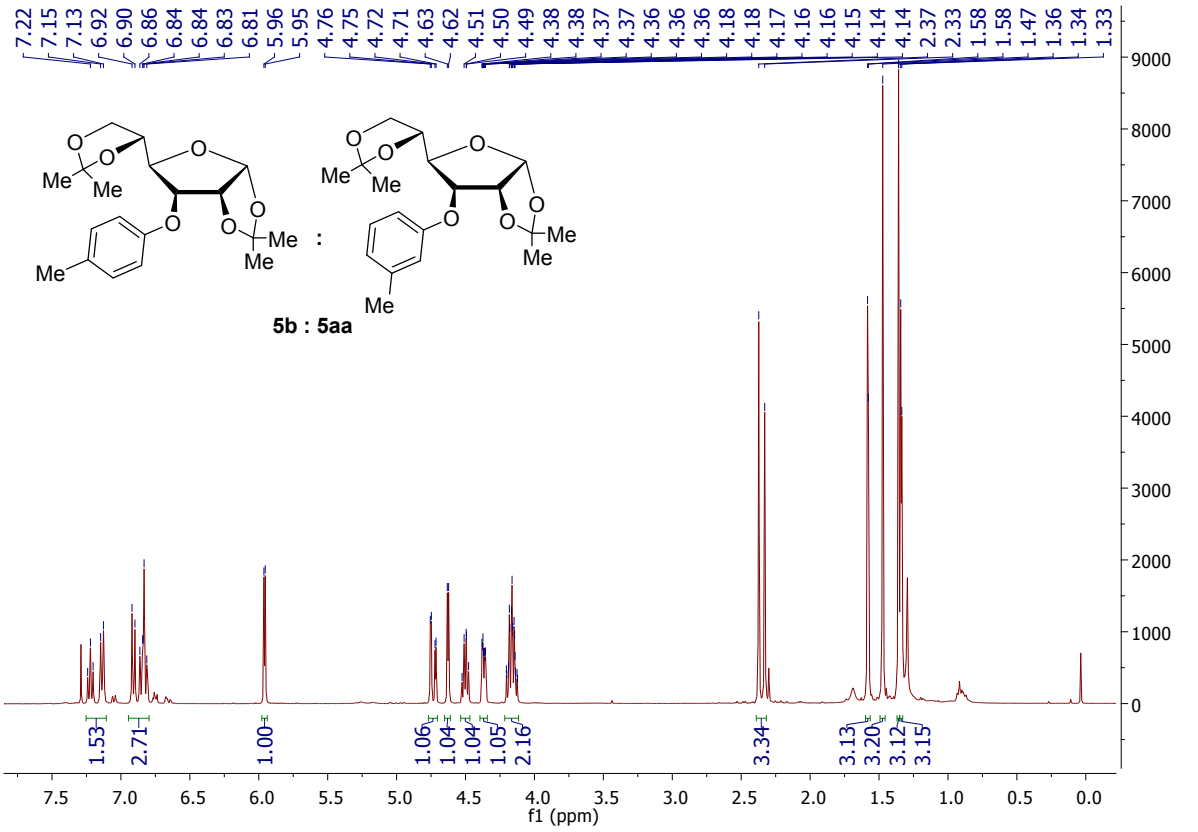

157.44
145.56
129.71
121.41
115.90
98.53
75.35
74.41
72.44
17.17
Me
HO
O
OPh
4b
f1 (ppm)

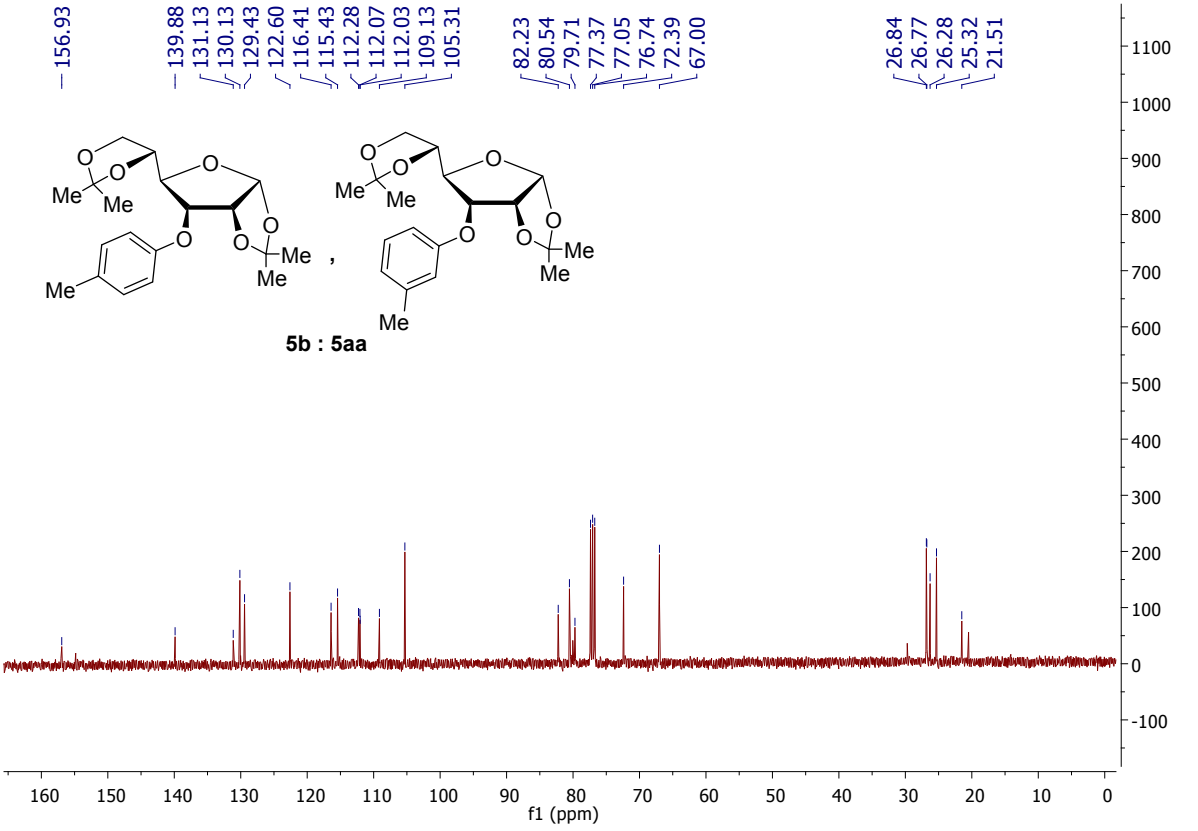

7.63
7.61
7.33
7.32
7.31
7.29
7.18
7.16
7.08
7.06
4.55
4.53
4.24
4.23
4.19
4.18
4.16
4.16
4.06
4.03
4.03
4.02
4.01
3.42
2.37
1.46
1.33
Me
Me
O
O
O
PhO
OH
S
Me
4c
2.10
3.38
2.06
3.04
1.00
1.03
1.18
3.24
1.16
3.08
3.12
3.49
f1 (ppm)

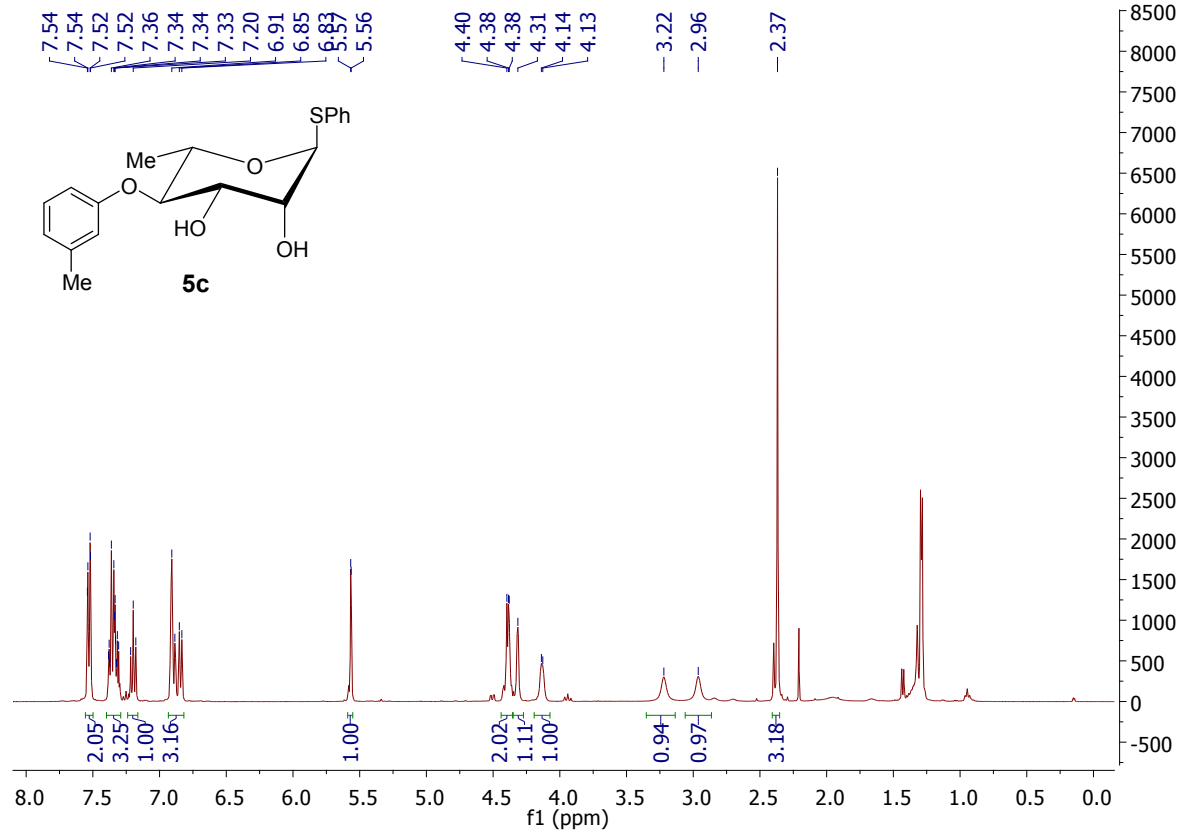

157.33
138.62
133.40
129.91
129.78
127.78
122.73
117.41
88.76
82.13
78.25
68.15
67.49
62.75
29.71
22.70
21.18
Me
Me
O
O
O
PhO
OH
S
Me
4c
25000
20000
15000
10000
5000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

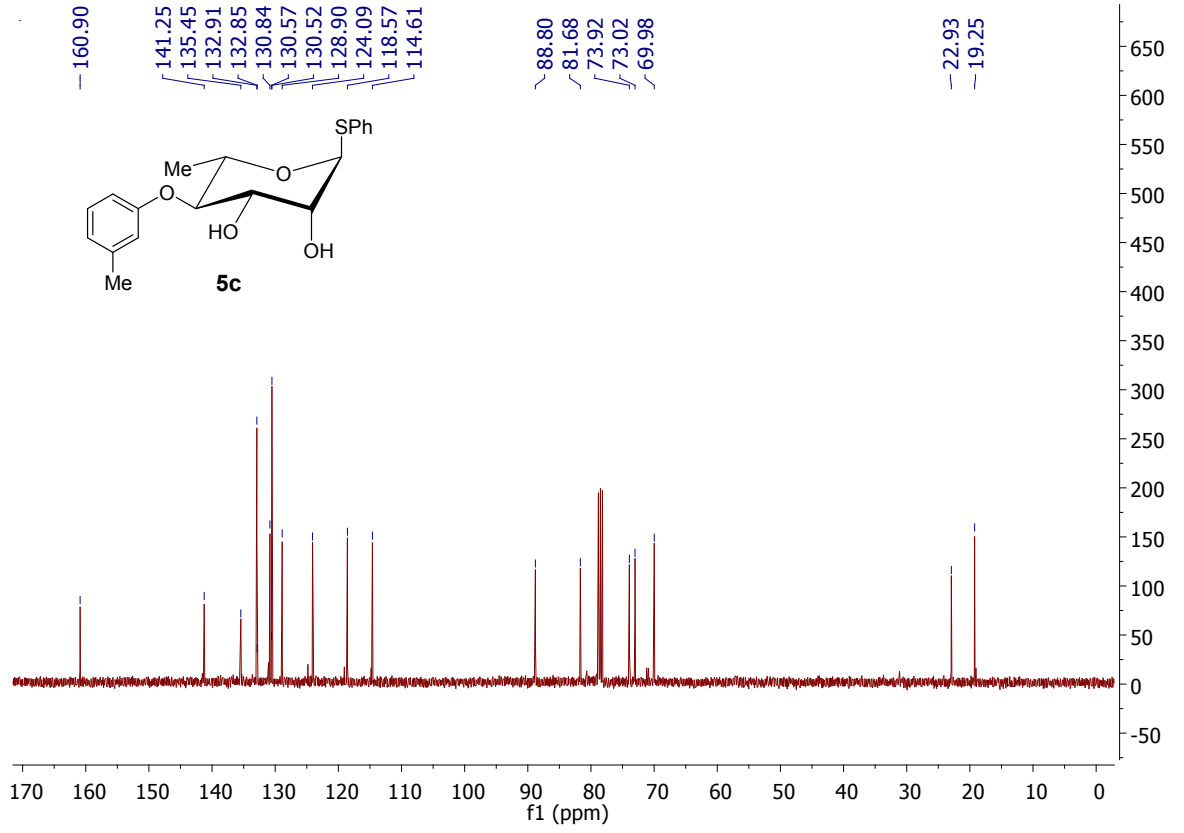

7.29 7.24 7.22 7.20 7.18 7.02 7.00 6.97 6.95 6.86 6.83 6.81 5.96 5.95 4.79 4.78 4.76 4.75 4.63 4.62 4.57 4.55 4.49 4.39 4.38 4.37 4.36 4.35 4.21 4.21 4.19 4.18 4.17 4.16 4.15 4.15 2.37 2.25 1.59 1.58 1.47 1.36 1.34 1.29
5a:5aa
2.01 1.24 1.44 1.00 1.05 1.02 1.05 1.04 2.16 1.39 1.64 3.24 3.26 3.19 3.19 3.49
f1 (ppm)


156.98 154.99 139.86 131.16 129.41 126.91 122.60 121.34 116.44 112.31 112.06 112.00 109.21 105.36 105.32 82.27 80.83 80.58 79.86 79.79 72.45 72.40 67.28 67.02 31.94 29.70 29.36 26.83 26.78 26.28 25.31 25.25 22.69 21.48
5a:5aa
f1 (ppm)


7.22 7.15 7.13 6.92 6.90 6.86 6.84 6.84 6.83 6.81 5.96 5.95 4.76 4.75 4.72 4.71 4.63 4.62 4.51 4.50 4.49 4.38 4.38 4.37 4.37 4.36 4.36 4.36 4.18 4.18 4.17 4.16 4.16 4.15 4.14 4.14 2.37 2.33 1.58 1.58 1.47 1.36 1.34 1.33
Me Me Me Me Me
:
Me Me Me Me Me
5b : 5aa
1.53 2.71 1.00 1.06 1.04 1.04 1.05 2.16 3.34 3.13 3.20 3.12 3.15
f1 (ppm)


156.93 139.88 131.13 130.13 129.43 122.60 116.41 115.43 112.28 112.07 112.03 109.13 105.31 82.23 80.54 79.71 77.37 77.05 76.74 72.39 67.00 26.84 26.77 26.28 25.32 21.51
Me Me Me Me Me
,
Me Me Me Me Me
5b : 5aa
f1 (ppm)


7.54
7.54
7.52
7.52
7.36
7.34
7.34
7.33
7.20
6.91
6.85
6.83
5.57
5.56
4.40
4.38
4.38
4.31
4.14
4.13
3.22
2.96
2.37
SPh
Me
O
O
HO
OH
Me
5c
2.05
3.25
1.00
3.16
1.00
2.02
1.11
1.00
0.94
0.97
3.18
f1 (ppm)


160.90
141.25
135.45
132.91
132.85
130.84
130.57
130.52
128.90
124.09
118.57
114.61
88.80
81.68
73.92
73.02
69.98
22.93
19.25
SPh
Me
O
O
HO
OH
Me
5c
f1 (ppm)