Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Supporting Information

## Syntheses of 2-*O*-(indole-3-acetyl)-*myo*-inositol IAInos

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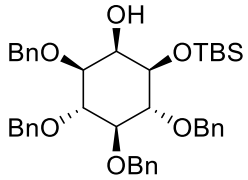
**Contents:**

**General**

All chemicals used were of reagent grade. All solvents were dried by established methods.[1] Flash chromatography was performed on Kieselgel 60, particle size 0.032–0.063 mm. Preparative TLC: silica gel Merck 60 $GF_{254}$. Analytical TLC: Aluminium-backed silica gel Merck 60 $F_{254}$. Infrared (FTIR) spectra were obtained using commercial ATR-FT-R spectrophotometer and are in cm−1. Melting points were determined with a capillary apparatus and are uncorrected. HRMS was recorded on a commercial apparatus (ESI Source). NMR spectra were obtained on a commercial instrument 400 MHz ($^1$H NMR), 101 MHz ($^{13}$C NMR) using $CDCl_3$, $D_2O$ or $(CD_3)_2SO$ as solvent. Chemical shifts are reported in ppm relative to TMS. The peak assignments of all compounds were made on the basis of observed crosspeaks in 2D NMR experiments as COSY, HMQC and HMBC.

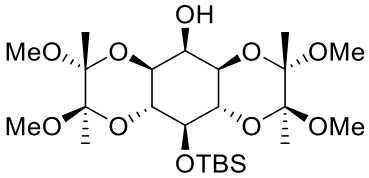
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 5**




To a solution of (±)-3,4,5,6-tetrakis-*O*-benzyl-*myo*-inositol **3**[2] (1.1 g, 2.0 mmol) in dry dichloromethane (10 mL) was added diisopropylethylamine (1.2 eq, 430 µL) and *tert*-butyldimethylsilyl triflate (1.2 eq, 560 µL) at 0 °C. After 15 min of stirring at the same temperature, the reaction mixture was quenched with a sodium bicarbonate saturated aqueous solution (20 mL) and extracted with dichloromethane (3x20 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (9:1), afforded the title compound (1.2 g, 90%) as a white solid.

White solid. M.p.=89-90 °C. $^1$H NMR $CDCl_3$ δ: 7.39-7.19 (20H, m, Ar), 4.93 (1H, d, $^2J$=10.7, $CH_2$ Bn), 4.87-4.77 (6H, m, $CH_2$ Bn), 4.71 (1H, d, $^2J$=11.9, $CH_2$ Bn), 4.02 (1H, t, $J_{6,5}$=$J_{6,1}$=9.6, H-6), 3.93 (1H, t, $J_{2,1}$=$J_{2,3}$=2.5, H-2), 3.79 (1H, t, $J_{4,3}$=$J_{4,2}$=9.4, H-4), 3.52 (1H, dd, $J_{3,4}$=9.3, $J_{3,2}$=2.7, H-3), 3.45-3.38 (2H, m, H-5, H-1), 2.45 (1H, s, OH); 0.89 (9H, s, $^t$Bu TBS), 0.032 (3H, s, Me TBS), 0.028 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 138.8, 138.7, 138.1 (4xCquat Ar), 128.5, 128.4, 128.3, 128.2, 128.01, 128.00, 127.9, 127.8, 127.54, 127.47, 127.4, 127.3 (Ar), 83.3 (C5), 81.7 (C4), 81.3 (C6), 79.5 (C1), 75.90, 75.85, 75.7, 72.9 (4x$CH_2$ Bn), 73.6 (C3), 71.1 (C2), 25.9 (3x$CH_3$ $^t$Bu TBS), 18.1 (Cquat $^t$Bu TBS), -4.5 (Me TBS), -4.8 (Me TBS). FTIR(neat): 1062 (C-O-C st., C-O st., Si-O-C st.); 834 (Si-O-C bend); 723, 695 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{50}NaO_6Si$ 677.3269; Found 677.3265.

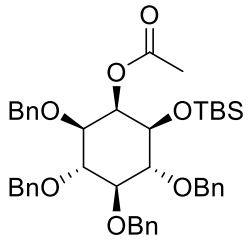
**1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 6**




To a solution of 1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-*myo*-inositol **4**[3] (0.5 g, 1.2 mmol) in dry dichloromethane (4 mL) was added diisopropylethylamine (1.5 eq, 310 µL) and tert-butyldimethylsilyl triflate (1.1 eq, 310 µL) at 0 °C. After 2 hours of stirring at room temperature, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane (3x10 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (2:1), afforded the title compound (504 mg, 79%) as a white solid.

White solid. M.p.>250 °C. $^{1}$H NMR $CDCl_3$ δ: 4.00 (1H, t, $J_{2,1}$=$J_{2,3}$=2.5, H-2), 3.90 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.58 (1H, t, $J_{5,4}$= $J_{5,6}$=9.2, H-5), 3.51 (2H, dd, $J_{1,6}$=10.2, $J_{1,2}$=2.6, H-1, H-3), 3.26 (6H, s, 2xOMe), 3.24 (6H, s, 2xOMe), 2.34 (1H, s, OH), 1.32 (6H, s, 2xMe), 1.25 (6H, s, 2xMe), 0.90 (9H, s, $^{t}$Bu TBS), 0.12 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 99.9, 99.1 (C1', C2'), 71.4 (C5), 69.3 (C4, C6), 69.1 (C2), 68.6 (C1, C3), 47.94, 47.93 (OMe), 25.9 (3x$CH_3$ $^{t}$Bu TBS), 18.3 (Cquat $^{t}$Bu TBS), 17.7, 17.5 (Me), -4.3 (2xMe TBS). FTIR(neat): 1135, 1108, 1035 (C-O-C st., C-O st., Si-O-C st.). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{46}NaO_{10}Si$ 545.2752; Found 545.2750.

**(±)-2-*O*-Acetyl-3,4,5,6-tetrakis-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 9**

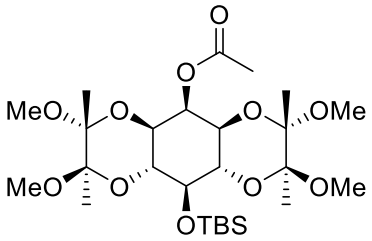



To a solution of **5** (100 mg, 0.15 mmol) in dry dichloromethane (1 mL) at room temperature was added triethylamine (2.5 eq, 50 µL), acetic anhydride (2.0 eq, 30 µL) and DMAP (cat.). After 20 hours of stirring at the same temperature, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane (3x10 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by TLC, eluted with hexane/ethyl acetate (8:2), afforded the title compound (107 mg, quant.) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 7.35-7.19 (20H, m, Ar), 5.54 (1H, t, $J_{2,1}$=$J_{2,3}$=2.6, H-2), 4.90 (1H, d, $^{2}J$=10.7, $CH_2$ Bn), 4.88-4.78 (5H, m, $CH_2$ Bn), 4.74 (1H, d, $^{2}J$=11.3, $CH_2$ Bn), 4.53 (1H, d, $^{2}J$=11.2, $CH_2$ Bn), 3.86 (1H, t, $J_{6,5}$=$J_{6,1}$=9.6, H-6), 3.77 (1H, t, $J_{4,3}$=$J_{4,2}$=9.4, H-4), 3.61 (1H, dd, $J_{3,4}$=9.5, $J_{3,2}$=2.8, H-3), 3.50-3.45 (2H, m, H-5, H-1), 2.14 (3H, s, $CH_3$ Ac), 0.87 (9H, s, $^{t}$Bu TBS), 0.09 (3H, s, Me TBS), 0.02 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 170.1 (C=O Ac), 138.84, 138.79, 138.5, 137.7 (4xCquat Ar), 128.40, 128.36, 128.33, 128.2, 128.0, 127.9, 127.8, 127.60, 127.55, 127.33, 127.28 (Ar), 83.1 (C5), 82.2 (C4), 81.6 (C6), 78.2 (C1), 76.1, 75.8, 75.7, 72.2 (4x$CH_2$ Bn), 71.6 (C3), 70.7 (C2), 25.7 (3x$CH_3$ $^{t}$Bu TBS), 21.1 (Cquat $^{t}$Bu TBS), 17.9 ($CH_3$ Ac), -4.79 (Me TBS), -4.81 (Me TBS). FTIR(neat):

1746 (C=O st.); 1231 (C-O-C st. ester); 1088, 1071 (C-O-C st., Si-O-C st.); 837 (Si-O-C bend); 734, 696 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{52}NaO_7Si$ 719.3375; Found 719.3370.

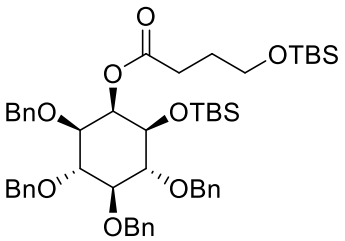
**2-*O*-Acetyl-1,6:3,4-bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 10**




To a solution of **6** (170 mg, 0.33 mmol) in dry dichloromethane (1 mL) at room temperature was added diisopropylethylamine (1.5 eq, 90 µL), acetic anhydride (1.3 eq, 40 µL) and DMAP (cat.). After 18 hours of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (8:2), afforded the title compound (135 mg, 74%) as a white solid.

White solid. M.p.=191 °C. $^1$H NMR $CDCl_3$ δ: 5.38 (1H, t, $J_{2,1}$=$J_{2,3}$=2.7, H-2), 3.78 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.61-3.57 (3H, m, H-1, H-3, H-5), 3.26 (6H, s, 2xOMe), 3.21 (6H, s, 2xOMe), 2.14 (3H, s, $CH_3$ Ac), 1.23 (6H, s, 2xMe), 1.22 (6H, s, 2xMe), 0.92 (9H, s, $^t$Bu TBS), 0.13 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 170.6 (C=O Ac), 99.7, 99.1 (C1', C2'), 71.4 (C5), 69.8 (C4, C6), 69.5 (C2), 67.1 (C1, C3), 48.0 (OMe), 25.9 (3x$CH_3$ $^t$Bu TBS), 21.3 ($CH_3$ Ac), 18.3 (Cquat $^t$Bu TBS), 17.49, 17.45 (Me), -4.3 (2xMe TBS). FTIR(neat): 1755 (C=O st.); 1112, 1040 (C-O-C st., Si-O-C st.); 836 (Si-O-C bend.). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{48}NaO_{11}Si$ 587.2858; Found 587.2832.

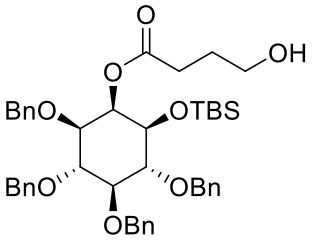
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-2-*O*-[4-[(*tert*-butyldimethylsilyl)oxy]butanoyl]-*myo*-inositol 11**




To a solution of **5** (280 mg, 0.43 mmol) and 4-[(*tert*-butyldimethylsilyl)oxy]-butanoic acid[4] (1.5 eq, 141 mg) in dry dichloromethane (2 mL) at room temperature was added EDC (1.5 eq, 126 mg) and DMAP (1 eq, 53 mg). After 4 days of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (95:5), afforded the title compound (203 mg, 56%) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 7.34-7.19 (20H, m, Ar), 5.56 (1H, t, $J_{2,1}$=$J_{2,3}$=2.5, H-2), 4.91-4.72 (7H, m, $CH_2$ Bn), 4.52 (1H, d, $^{2}J$=11.3, $CH_2$ Bn), 3.84 (1H, t, $J_{6,5}$=$J_{6,1}$=9.6, H-6), 3.76 (1H, t, $J_{4,3}$=$J_{4,2}$=9.4, H-4), 3.66 (2H, t, $J_{4',3'}$=6.2, H-4'), 3.61 (1H, dd, $J_{3,4}$=9.5, $J_{3,2}$=2.7, H-3), 3.49-3.44 (2H, m, H-5, H-1), 2.48 (2H, t, $J_{2',3'}$=7.6, H-2'), 1.87 (2H, p, $J_{3',2'}$= $J_{3',4'}$=6.9, H-3'), 0.89 (9H, s, $^{t}$Bu TBS), 0.86 (9H, s, $^{t}$Bu TBS), 0.09 (3H, s, Me TBS), 0.05 (6H, s, 2xMe TBS), 0.02 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 172.8 (C1'), 138.9, 138.8, 138.5, 137.7 (4xCquat Ar), 128.36, 128.35, 128.32, 128.29, 128.2, 127.98, 127.95, 127.8, 127.6, 127.5, 127.33, 127.27 (Ar), 83.1 (C5), 82.2 (C4), 81.6 (C6), 78.2 (C1), 76.1, 75.8, 75.7, 72.1 (4x$CH_2$ Bn), 71.7 (C3), 70.5 (C2), 62.0 (C4'), 30.8 (C2'), 28.3 (C3'), 26.0 (3x$CH_3$ $^{t}$Bu TBS), 25.8 (3x$CH_3$ $^{t}$Bu TBS), 18.3, 17.9 (2xCquat $^{t}$Bu TBS), -4.79, -4.83, -5.3 (4xMe TBS). FTIR(neat): 1742 (C=O st.); 1088, 1072 (C-O-C st., Si-O-C st.); 835 (Si-O-C bend); 696 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{70}NaO_8Si_2$ 877.4501; Found 877.4504.

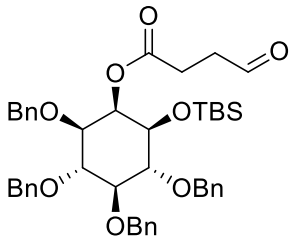
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-hydroxybutanoyl)-*myo*-inositol 12**




To a solution of **11** (195 mg, 0.23 mmol) in dry tetrahydrofuran (1 mL) at room temperature was added triethylamine trihydrofluoride (5 eq, 190 µL). After 7 hours of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by TLC, eluted with hexane/ethyl acetate (2:1), afforded the title compound (137 mg, 81%) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 7.34-7.19 (20H, m, Ar), 5.56 (1H, t, $J_{2,1}$=$J_{2,3}$=2.8, H-2), 4.89 (1H, d$^{2}J$=10.8, $CH_2$ Bn), 4.87-4.78 (5H, m, $CH_2$ Bn), 4.72 (1H, d$^{2}J$=11.2, $CH_2$ Bn), 4.54 (1H, d, $^{2}J$=11.2, $CH_2$ Bn), 3.83 (1H, t, $J_{6,5}$=$J_{6,1}$=9.6, H-6), 3.75 (1H, t, $J_{4,3}$=$J_{4,2}$=9.4, H-4), 3.67 (2H, q, $J_{4',3'}$= $J_{4',OH}$=5.7, H-4'), 3.62 (1H, dd, $J_{3,4}$=9.5, $J_{3,2}$=2.8, H-3), 3.49-3.45 (2H, m, H-5, H-1), 2.53 (2H, t, $J_{2',3'}$=7.4, H-2'), 1.90 (2H, p, $J_{3',2'}$= $J_{3',4'}$=6.8, H-3'), 1.69 (1H, $J_{OH,4'}$=5.3, OH), 0.86 (9H, s, $^{t}$Bu TBS), 0.09 (3H, s, Me TBS), 0.03 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 172.9 (C1'), 138.8, 138.7, 138.5, 137.6 (4xCquat Ar), 128.39, 128.36, 128.35, 128.33, 128.2, 127.97, 127.95, 127.87, 127.61, 127.57, 127.33, 127.29 (Ar), 83.1 (C5), 82.1 (C4), 81.5 (C6), 78.1 (C1), 76.2, 75.8, 75.7, 72.2 (4x$CH_2$ Bn), 71.6 (C3), 70.8 (C2), 61.9 (C4'), 31.2 (C2'), 27.9 (C3'), 25.7 (3x$CH_3$ $^{t}$Bu TBS), 17.9 (2xCquat $^{t}$Bu TBS), -4.78, -4.83 (2xMe TBS). FTIR(neat): 1741 (C=O st.); 1088, 1071 (C-O-C st., C-O st., Si-O-C st.); 837 (Si-O-C bend); 735, 697 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{56}NaO_8Si$ 763.3637; Found 763.3636.

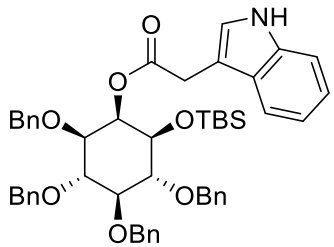
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-1-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-oxobutanoyl)-*myo*-inositol 13**



To a solution of oxalyl chloride (1.5 eq, 22 µL) in dry dichloromethane (0.5 mL) at -78 °C was added dry dimethylsulfoxide (3 eq, 36 µL). After 5 minutes of stirring at the same temperature, a solution of **12** (127 mg, 0.17 mmol) in dry dichloromethane was added and, after further 15 min, triethylamine (5 eq, 120 µL) was also added. After 30 min of stirring at -78 °C, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by TLC, eluted with hexane/ethyl acetate (8:2), afforded the title compound (121 mg, 96%) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 9.80 (1H, s, H-4'), 7.32-7.19 (20H, m, Ar), 5.55 (1H, t, $J_{2,1}$=$J_{2,3}$=2.8, H-2), 4.89 (1H, d$^{2}J$=10.7, $CH_2$ Bn), 4.87-4.78 (5H, m, $CH_2$ Bn), 4.70 (1H, d, $^{2}J$=11.2, $CH_2$ Bn), 4.52 (1H, d, $^{2}J$=11.2, $CH_2$ Bn), 3.82 (1H, t, $J_{6,5}$=$J_{6,1}$=9.6, H-6), 3.74 (1H, t, $J_{4,3}$=$J_{4,2}$=9.4, H-4), 3.62 (1H, dd, $J_{3,4}$=9.5, $J_{3,2}$=2.8, H-3), 3.49-3.45 (2H, m, H-5, H-1), 2.77 (4H, s, H-2', H-3'), 0.86 (9H, s, $^{t}$Bu TBS), 0.08 (3H, s, Me TBS), 0.02 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 199.8 (C4'), 171.5 (C1'), 138.8, 138.7, 138.5, 137.6 (4xCquat Ar), 128.41, 128.38, 128.35, 128.30, 128.24, 127.99, 127.96, 127.86, 127.62, 127.60, 127.36, 127.32, (Ar), 83.1 (C5), 82.1 (C4), 81.6 (C6), 78.1 (C1), 76.1, 75.9, 75.7, 72.2 (4x$CH_2$ Bn), 71.5 (C3), 71.3 (C2), 38.6, 26.8 (C2', C3'), 25.8 (3x$CH_3$ $^{t}$Bu TBS), 17.9 (2xCquat $^{t}$Bu TBS), -4.77, -4.81 (2xMe TBS). FTIR(neat): 1742 (C=O st.); 1088, 1071 (C-O-C st., Si-O-C st.); 837 (Si-O-C bend); 735, 697 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{54}NaO_8Si$ 761.3480; Found 761.3480.

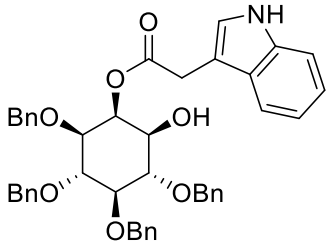
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-2-*O*-[2-(1*H*-indol-3-yl)acetyl]-1-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 14**



To a solution of **13** (114 mg, 0.15 mmol) in dry toluene (1 mL) at room temperature was added phenylhydrazine (1.2 eq, 18 µL). After 30 min of stirring at the same temperature, zinc chloride (3 eq, 63 mg) was added. After 5 hours of stirring at 105 °C, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by TLC, eluted with dichloromethane, afforded the title compound (111 mg, 89%) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 7.93 (1H, s, NH), 7.64 (1H, d, $J_{4'',5''}$=7.9, H-4''), 7.32 (1H, d, $J_{7'',6''}$=8.1, H-7''), 7.28-7.20 (20H, Ar Bn), 7.17 (1H, t, $J_{6'',5''}$= $J_{6'',7''}$=7.5, H-6''), 7.14 (1H, d, $J_{2'',NH}$=2.3, H-2''), 7.09 (1H, t, $J_{5'',6''}$= $J_{5'',4''}$=7.5, H-5''), 5.57 (1H, t, $J_{2,3}$= $J_{2,1}$=2.2, H-2), 4.82 (1H, d, $^{2}J$=10.7, $CH_2$ Bn), 4.78-4.70 (5H, m, $CH_2$ Bn), 4.65 (1H, d, $^{2}J$=10.9, $CH_2$ Bn), 4.49 (2H, d, $^{2}J$=11.2, $CH_2$ Bn), 3.87 (2H, s, H-2'), 3.70 (1H, t, $J_{6,1}$=$J_{6,5}$=9.5, H-6), 3.62 (1H, t, $J_{4,3}$=$J_{4,5}$=9.2, H-4), 3.58 (1H, dd, $J_{3,4}$=9.5, $J_{3,2}$=2.3, H-3), 3.44 (1H, dd, $J_{1,6}$=9.5, $J_{1,2}$=2.6, H-1), 3.41 (1H, t, $J_{5,4}$=$J_{5,6}$=8.8, H-5), 0.81 (9H, s, $^{t}$Bu TBS), 0.06 (3H, s, Me TBS), 0.02 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 171.0 (C1'), 138.9, 138.84, 138.76, 137.8 (4xCquat Ar Bn), 136.1 (C7a''), 128.31, 128.30, 128.28, 128.2, 128.0, 127.8, 127.7, 127.51, 127.45, 127.40, 127.3 (Ar Bn), 127.43 (C3a''), 123.1 (C2'), 122.2 (C6''), 119.8 (C5''), 119.1 (C4''), 111.0 (C7''), 108.7 (C3''), 83.0 (C5), 82.0 (C4), 81.4 (C6), 78.2 (C3), 75.8, 75.7, 75.6, 72.1 (4x$CH_2$ Bn), 71.6 (C1), 71.0 (C2), 31.4 (C2'), 25.7 (3x$CH_3$ $^{t}$Bu TBS), 17.8 (2xCquat $^{t}$Bu TBS), -4.8, -4.9 (2xMe TBS). FTIR(neat): 1733 (C=O st.); 1067 (C-O-C st., Si-O-C st.); 734, 696 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{50}H_{57}NNaO_7Si$ 834.3797; Found 834.3792.

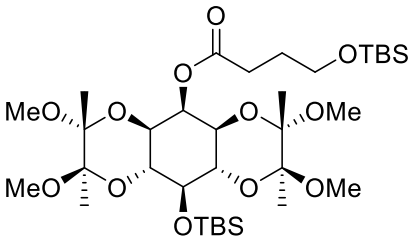
**(±)-3,4,5,6-Tetrakis-*O*-benzyl-2-*O*-[2-(1*H*-indol-3-yl)acetyl]-*myo*-inositol 15**




To a solution of **14** (50 mg, 0.23 mmol) in dry tetrahydrofuran (1 mL) at room temperature was added triethylamine trihydrofluoride (20 eq, 200 µL). After 7 days of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by TLC, eluted with hexane/ethyl acetate (1:1), afforded the title compound (32 mg, 74%) as a colorless oil.

Colorless oil. $^{1}$H NMR $CDCl_3$ δ: 7.94 (1H, s, NH), 7.61 (1H, d, $J_{4'',5''}$=7.8, H-4''), 7.34-7.24 (21H, Ar Bn, H-7''), 7.17 (1H, t, $J_{6'',5''}$= $J_{6'',7''}$=7.5, H-6''), 7.12-7.08 (2H, m, H-2'', H-5''), 5.71 (1H, s, H-2), 4.88 (1H, d, $^{2}J$=10.9, $CH_2$ Bn), 4.79 (1H, d, $^{2}J$=11.1, $CH_2$ Bn), 4.77 (1H, d, $^{2}J$=10.8, $CH_2$ Bn), 4.72 (2H, d, $^{2}J$=11.2, $CH_2$ Bn), 4.62 (1H, d, $^{2}J$=10.7, $CH_2$ Bn), 4.50 (1H, d, $^{2}J$=11.2, $CH_2$ Bn), 4.45 (1H, d, $^{2}J$=11.1, $CH_2$ Bn), 3.87 (2H, s, H-2'), 3.67 (1H, t, $J_{6,1}$=$J_{6,5}$=9.4, H-6), 3.55-3.53 (2H, m, H-3, H-4), 3.49-3.41 (2H, m, H-5, H-1), 2.10 (1H, s, OH). $^{13}$C NMR $CDCl_3$ δ: 171.5 (C1'), 138.64, 138.55, 138.4, 137.7 (4xCquat Ar Bn), 136.09 (C7a''), 128.6, 128.4, 128.34, 128.33, 128.2, 128.01, 127.96, 127.92, 127.8, 127.7, 127.64, 127.60 (Ar Bn), 127.3 (C3a''), 123.2 (C2''), 122.2 (C6''), 119.9 (C5''), 119.0 (C4''), 111.2 (C7''), 108.61 (C3''), 83.0 (C5), 81.7, 81.5 (C4, C6), 78.5 (C1), 75.8, 75.6, 75.5, 72.1 (4x$CH_2$ Bn), 70.3 (C3), 69.7 (C2), 31.5 (C2'). FTIR(neat): 1733 (C=O st.); 1068 (C-O-C st., C-O st.); 735, 696 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{43}NNaO_7$ 720.2932; Found 720.2935.

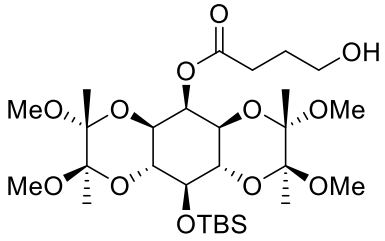
**1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-5-*O*-(*tert*-butyldimethylsilyl)-2-*O*-[4-[(*tert*-butyldimethylsilyl)oxy]butanoyl]-*myo*-inositol 16**




To a solution of **6** (480 mg, 0.92 mmol) and 4-[(*tert*-butyldimethylsilyl)oxy]-butanoic acid[4] (1.5 eq, 300 mg) in dry dichloromethane (4mL) at room temperature was added EDC (1.5 eq, 263 mg) and DMAP (1 eq, 112 mg). After 4 days of stirring at the same temperature, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane (3x10 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (9:1), afforded the title compound (356 mg, 54%) as a white solid.

White solid. M.p.=168-169 °C. $^{1}$H NMR $CDCl_3$ δ: 5.39 (1H, t, $J_{2,1}$=$J_{2,3}$=2.7, H-2), 3.77 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.77 (2H, t, $J_{4',3'}$=6.2, H-4'), 3.61-3.56 (3H, m, H-1, H-3, H-5), 3.24 (6H, s, 2xOMe), 3.21 (6H, s, 2xOMe), 2.47 (2H, t, $J_{2',3'}$=7.5, H-2'), 1.90 (2H, p, $J_{3',2'}$= $J_{3',4'}$=6.8, H-3'), 1.23 (6H, s, 2xMe), 1.21 (6H, s, 2xMe), 0.91 (9H, s, $^{t}$Bu TBS), 0.90 (9H, s, $^{t}$Bu TBS), 0.13 (6H, s, 2xMe TBS), 0.06 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 173.0 (C1'), 99.7, 99.1 (CMeOMe), 71.4 (C5), 69.8 (C4, C6), 69.2 (C2), 67.1 (C1, C3), 62.2 (C4'), 48.0, 47.9 (OMe), 31.4 (C2'), 28.5 (C3'), 25.94, 25.93 (3x$CH_3$ $^{t}$Bu TBS), 18.31, 18.29 (Cquat $^{t}$Bu TBS), 17.5, 17.4 (Me), -4.3, -5.3 (2xMe TBS). FTIR(neat): 1750 (C=O st.); 1139, 1114, 1044 (C-O-C st., Si-O-C st.); 837 (Si-O-C bend.). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{66}NaO_{12}Si_2$ 745.3985; Found 745.3988.

**2-*O*-(4-Hydroxybutanoyl)-1,6:3,4-bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-5-*O*-(*tert*-butyldimethylsilyl)-myo-inositol 17**

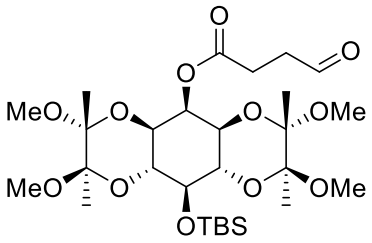



To a solution of **16** (340 mg, 0.47 mmol) in dry tetrahydrofuran (2 mL) at room temperature was added triethylamine trihydrofluoride (5 eq, 380 µL). After 7 hours of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (2:1), afforded the title compound (246 mg, 86%) as a white solid.

White solid. M.p.=165 °C. $^{1}$H NMR $CDCl_3$ δ: 5.42 (1H, t, $J_{2,1}$=$J_{2,3}$=2.7, H-2), 3.78 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.69 (2H, t, $J_{4',3'}$=6.2, H-4'), 3.64-3.58 (3H, m, H-1, H-3, H-5), 3.27 (6H, s, 2xOMe), 3.23 (6H, s, 2xOMe), 2.77 (1H, t, $J_{OH,4'}$=5.6, OH), 2.55 (2H, t, $J_{2',3'}$=6.6, H-2'), 1.92 (2H, p, $J_{3',2'}$=$J_{3',4'}$=6.3, H-3'), 1.24 (12H, s, 4xMe), 0.91 (9H, s, $^{t}$Bu TBS), 0.13 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 172.8

(C1'), 99.7, 99.3 (CMeOMe), 71.3 (C5), 69.9 (C4, C6), 69.0 (C2), 67.1 (C1, C3), 60.6 (C4'), 48.1, 48.0 (OMe), 31.4 (C2'), 28.2 (C3'), 25.9 (3x$CH_3$ $^t$Bu TBS), 18.3 (Cquat $^t$Bu TBS), 17.45, 17.44 (Me), -4.3 (2xMe TBS). FTIR(neat): 1728 (C=O st.); 1137, 1112, 1035 (C-O-C st., C-O st., Si-O-C st.); 838 (Si-O-C bend.). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{52}NaO_{12}Si$ 631.3120; Found 631.3123.

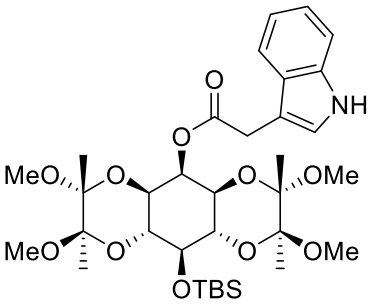
**1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-2-*O*-(4-oxobutanoyl)-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 18**




To a solution of oxalyl chloride (1.5 eq, 48 µL) in dry dichloromethane (0.5 mL) at -78 °C was added dry dimethylsulfoxide (3 eq, 80 µL). After 5 min of stirring at the same temperature, a solution of **17** (228 mg, 0.37 mmol) in dry dichloromethane (1 mL) was added and, after further 15 min, triethylamine (5 eq, 260 µL) was also added. After 30 min of stirring at -78 °C, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (8:2), afforded the title compound (214 mg, 94%) as a white solid.

White solid. M.p.=139 °C. $^1$H NMR $CDCl_3$ δ: 9.82 (1H, s, H-4'), 5.38 (1H, t, $J_{2,1}$=$J_{2,3}$=2.4, H-2), 3.74 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.61-3.57 (3H, m, H-1, H-3, H-5), 3.26 (6H, s, 2xOMe), 3.21 (6H, s, 2xOMe), 2.82 (2H, t, $J_{3',2'}$=6.5, H-3'), 2.76 (2H, t, $J_{2',3'}$= $J_{2',3'}$=6.3, H-3'), 1.23 (6H, s, 2xMe), 1.22 (6H, s, 4xMe), 0.92 (9H, s, $^t$Bu TBS), 0.13 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 200.4 (C4'), 171.7 (C1''), 99.7, 99.2 (CMeOMe), 71.2 (C5), 70.0 (C2), 69.8 (C4, C6), 67.0 (C1, C3), 48.03, 47.97 (OMe), 39.1 (C3'), 27.6 (C2'), 25.9 (3x$CH_3$ $^t$Bu TBS), 18.3 (Cquat $^t$Bu TBS), 17.5, 17.4 (Me), -4.3 (2xMe TBS). FTIR(neat): 1749, 1726 (C=O st.); 1134, 1111, 1038 (C-O-C st., Si-O-C st.); 836 (Si-O-C bend.). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{51}O_{12}Si$ 607.3144; Found 607.3141.

**1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-2-*O*-[2-(1*H*-indol-3-yl)acetyl]-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 19**

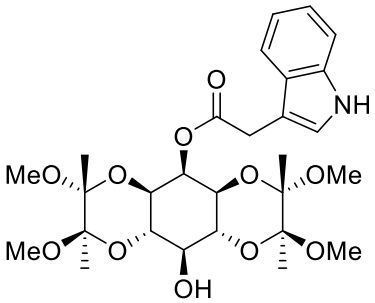



To a solution of **18** (196 mg, 0.32 mmol) in dry toluene (1,5 mL) at room temperature was added phenylhydrazine (1.2 eq, 40 µL). After 30 min of stirring at the same temperature, zinc chloride (3 eq, 132 mg) was added. After 5 hours of stirring at 105 °C, the reaction mixture

was quenched with water (5 mL) and extracted with dichloromethane (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with dichloromethane, afforded the title compound (207 mg, 94%) as a white solid.

White solid. M.p.=223 °C. $^{1}$H NMR $CDCl_3$ δ: 8.03 (1H, s, NH), 7.62 (1H, d, $J_{4'',5''}$=7.7, H-4''), 7.47 (1H, s, H-2''), 7.35 (1H, d, $J_{7'',6''}$= 8.0, H-7''), 7.18 (1H, t, $J_{6'',5''}$=$J_{6'',7''}$=7.5, H-6''), 7.13 (1H, t, $J_{5'',4''}$=$J_{5'',6''}$=7.4, H-5''), 5.51 (1H, t, $J_{2,1}$=$J_{2,3}$=2.6, H-2), 3.87 (2H, s, H-2'), 3.81 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.66-3.58 (3H, m, H-1, H-3, H-5), 3.24 (6H, s, 2xOMe), 3.22 (6H, s, 2xOMe), 1.25 (6H, s, 2xMe), 1.24 (6H, s, 4xMe), 0.90 (9H, s, $^{t}$Bu TBS), 0.12 (6H, s, 2xMe TBS). $^{13}$C NMR $CDCl_3$ δ: 171.1 (C1'), 136.0 (C7a''), 127.5 (C3a''), 123.2(C2'), 122.0 (C6''), 119.6 (C5''), 118.7 (C4''), 110.9 (C7''), 108.7 (C3''), 99.8, 99.2 (CMeOMe), 71.2 (C5), 69.9 (C4, C6), 69.6 (C2), 67.2 (C1, C3), 48.03, 47.99 (OMe), 31.8 (C2'), 25.9 (3x$CH_3$ $^{t}$Bu TBS), 18.3 (Cquat $^{t}$Bu TBS), 17.6, 17.5 (Me), -4.3 (2xMe TBS). FTIR(neat): 1727 (C=O st.); 1135, 1113, 1036 (C-O-C st., Si-O-C st.); 838 (Si-O-C bend.); 731 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{53}NNaO_{11}Si$ 702.3280; Found 702.3268.

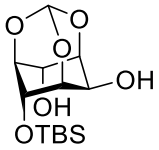
**1,6:3,4-Bis-[*O*-(2,3-dimethoxybutane-2,3-diyl)]-2-*O*-[2-(1*H*-indol-3-yl)acetyl]-*myo*-inositol 20**




To a solution of **19** (130 mg, 0.19 mmol) in dry tetrahydrofuran (1mL) at room temperature was added a commercial tetrabutylammonium fluoride solution (1 M in THF, 3 eq, 600 µL). After 48 hours of stirring at the same temperature, the reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3x5 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (from 2:1 to 0:1), afforded the title compound (69 mg, 64%) as a white solid and **15** (28 mg, 22%) was recovered.

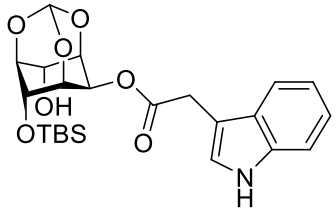
White solid. M.p.>250 °C. $^{1}$H NMR $(CD_3)_2SO$ δ: 10.92 (1H, d, $J_{NH,2''}$=1.3, NH), 7.53 (1H, d, $J_{4'',5''}$=7.9, H-4''), 7.37 (1H, d, $J_{2'',NH}$=2.2, H-2''), 7.35 (1H, d, $J_{7'',6''}$= 8.1, H-7''), 7.07 (1H, t, $J_{6'',5''}$=$J_{6'',7''}$=7.6, H-6''), 6.96 (1H, t, $J_{5'',4''}$=$J_{5'',6''}$=7.5, H-5''), 5.33 (1H, s, H-2), 5.23 (1H, d, $J_{OH,5}$=5.7, OH), 3.76-3.69 (6H, m, H-1, H-3, H-4, H-6, H-2'), 3.41-3.35 (1H, m, H-5), 3.20 (6H, s, 2xOMe), 3.15 (6H, s, 2xOMe), 1.21 (6H, s, 2xMe), 1.17 (6H, s, 4xMe). $^{13}$C NMR $(CD_3)_2SO$ δ: 170.9 (C1'), 136.6 (C7a''), 127.6 (C3a''), 124.4 (C2'), 121.5 (C6''), 118.9 (C5'', C4''), 111.7 (C7''), 107.3 (C3''), 99.6, 99.1 (CMeOMe), 70.1 (C4, C6), 70.0 (C2), 69.0 (C5), 67.2 (C1, C3), 48.2, 47.8 (OMe), 31.6 (C2'), 18.0, 17.9 (Me). FTIR(neat): 1743 (C=O st.); 1139, 1114, 1031 (C-O-C st., C-O st.). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{39}NNaO_{11}$ 588.2415; Found 588.2414.

**(±)-1,3,5-*O*-Methylidyne-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 22[5]**




To a solution of 1,3,5-*O*-methylidyne-*myo*-inositol[6] (1.17g, 6.15mmol) in dry dimethylformamide (25 mL) at 0 °C was added sodium hydride (1.2 eq., 177 mg). After 30 min of stirring at the same temperature, *tert*-butyldimethylsilyl chloride (1.2 eq, 1.1 g) was added. After 12 hours of stirring at room temperature, the reaction mixture was quenched with water (50 mL) and extracted with dichloromethane (3x30 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (8:2), afforded the title compound (1.215 g, 65%) as a colorless oil.

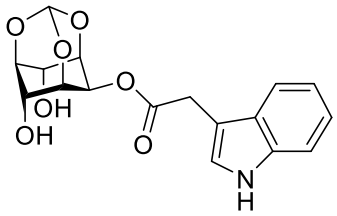
**(±)-2-*O*-[2-(1*H*-Indol-3-yl)acetyl]-1,3,5-*O*-methylidyne-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol 23**




To a solution of **22** (1.2 g, 3.9 mmol) and 3-indoleacetic acid (1 eq, 683 mg) in dry dichloromethane (15 mL) at room temperature was added EDC (1 eq, 748 mg) and DMAP (cat.). After 19 hours of stirring at the same temperature, the reaction mixture was quenched with water (50 mL) and extracted with dichloromethane (3x30 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with dichloromethane/ethyl acetate (95:5), afforded the title compound (1.505 g, 83%) as white solid.

White solid. M.p.=48-49 °C. $^{1}$H NMR $CDCl_3$ δ: 8.12 (1H, s, NH), 7.66 (1H, d, $J_{4'',5''}$=7.8, H-4''), 7.36 (1H, d, $J_{7'',6''}$= 8.0, H-7''), 7.23-7.18 (2H, m, H-2'',H-6''), 7.14 (1H, td, $J_{5'',4''}$=$J_{5'',6''}$=7.4, $J_{5'',7''}$=0.9 H-5''), 5.55 (1H, d, $J_{CHO3,2}$=1.0, $CHO_3$), 5.34 (1H, q, $J_{2,1}$=$J_{2,3}$=$J_{2,CHO3}$=1.4, H-2), 4.61 (1H, td, $J_{4,3}$=$J_{4,5}$=4.1, $J_{4,6}$=2.0, H-4), 4.49 (1H, dtd, $J_{6,OH}$=10.0, $J_{6,5}$= $J_{6,1}$=3.9, $J_{6,4}$=2.1, H-6), 4.33 (1H, dq, $J_{1,6}$=3.9, $J_{1,2}$=$J_{1,3}$=$J_{1,5}$=1.9, H-1), 4.28 (1H, dq, $J_{3,4}$=4.0, $J_{3,1}$=$J_{3,2}$=$J_{3,5}$=1.9, H-3), 4.22 (1H, tt, $J_{5,4}$=$J_{5,6}$=3.5, $J_{5,1}$=$J_{5,3}$=1.8, H-5), 3.97 (1H, d, $J_{OH,6}$=10.2, OH), 3.94 (2H, s, H-2'), 0.90 (9H, s, $^{t}$Bu TBS), 0.164 (3H, s, Me TBS), 0.158 (3H, s, Me TBS). $^{13}$C NMR $CDCl_3$ δ: 171.4 (C1'), 136.1 (C7a''), 127.7 (C3a''), 123.2(C2'), 122.3 (C6''), 119.7 (C5''), 118.9 (C4''), 111.2 (C7''), 108.0 (C3''), 102.4 ($CHO_3$), 72.6 (C1), 71.5 (C3), 69.1 (C4), 68.9 (C5), 68.2 (C6), 63.2 (C2), 31.3 (C2'), 25.6 (3x$CH_3$ $^{t}$Bu TBS), 17.8 (Cquat $^{t}$Bu TBS), -5.0, -5.4 (2xMe TBS). FTIR(neat): 3414 (O-H st.); 1735 (C=O st.); 1161 (C-O-C st., C-O st., Si-O-C st.); 836 (Si-O-C bend.); 739 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{31}NNaO_7Si$ 484.1762; Found 484.1760.

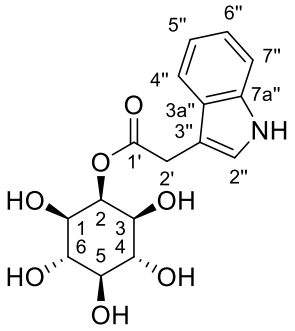
**2-*O*-[2-(1*H*-Indol-3-yl)acetyl]-1,3,5-*O*-methylidyne-*myo*-inositol 24**



To a solution of **23** (1.4 g, 3.0 mmol) in dry tetrahydrofuran (12 mL) at room temperature was added a commercial tetrabutylammonium fluoride solution (1 M in THF, 1.8 eq, 5.4 mL). After 30 min of stirring at the same temperature, the reaction mixture was quenched with water (50 mL) and extracted with ethyl acetate (3x25 mL). The combined organic phases were dried with magnesium sulfate and evaporated to dryness. Purification by flash column chromatography, eluted with hexane/ethyl acetate (from 1:1), afforded the title compound (1.036 g, 98%) as a white solid.

White solid. M.p.=100-104 °C. $^{1}$H NMR $CDCl_3$ δ: 8.10 (1H, s, NH), 7.64 (1H, d, $J_{4'',5''}$=7.9, H-4''), 7.36 (1H, d, $J_{7'',6''}$= 8.1, H-7''), 7.22 (1H, td, $J_{6'',5''}$=$J_{6'',7''}$=7.6, $J_{6'',4''}$=1.0 H-6''), 7.18 (1H, d, $J_{2'',NH}$=2.3, H-2''), 7.15 (1H, td, $J_{5'',4''}$=$J_{5'',6''}$=7.5, $J_{5'',7''}$=1.0 H-5''), 5.52 (1H, d, $J_{CHO3,2}$=1.2, $CHO_3$), 5.28 (1H, q, $J_{2,1}$=$J_{2,3}$=$J_{2,CHO3}$=0.8, H-2), 4.43 (2H, br s, H-4, H-6), 4.26 (2H, dq, $J_{1,6}$=2.7, $J_{1,2}$=$J_{1,3}$=$J_{1,5}$=1.7, H-1, H-3), 4.20 (1H, tt, $J_{5,4}$=$J_{5,6}$=3.5, $J_{5,1}$=$J_{5,3}$=1.7, H-5), 3.93 (2H, s, H-2'), 3.67 (2H, br s, 2xOH). $^{13}$C NMR $CDCl_3$ δ: 172.6 (C1'), 136.1 (C7a''), 127.1 (C3a''), 123.4(C2'), 122.5 (C6''), 119.9 (C5''), 118.8 (C4''), 111.3 (C7''), 107.7 (C3''), 102.4 ($CHO_3$), 71.8 (C1, C3), 68.4 (C5), 67.9 (C4, C6), 63.7 (C2), 31.3 (C2'). FTIR(neat): 3404 (O-H st.); 1723 (C=O st.); 1157(C-O-C st., C-O st.); 943; 742 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_7$ 348.1078; Found 348.1081.

**2-*O*-[2-(1*H*-Indol-3-yl)acetyl]-*myo*-inositol 1**



**Method 1**

A mixture of **20** (15 mg, 0.027 mmol), dichloromethane (1 mL) and trifluoroacetic acid (0.189 mmol, 15 µL) was stirred for 3.5 hours in a closed tube at 40 °C. The solvent was evaporated to dryness, the product dissolved in water (10 mL) and washed with ethyl acetate (10 mL). Evaporation of the aqueous phase afforded the title compound (9 mg, quant.) as a white solid.

**Method 2**

A mixture of **24** (200 mg, 0.58 mmol), ethanol (1 mL), water (1 mL) and trifluoroacetic acid (4.06 mmol, 310 µL) was stirred for 1 hour at 60 °C in a closed tube. The solvent was evaporated to dryness, the product dissolved in water (10 mL) and washed with ethyl acetate (10 mL). After

evaporation of the aqueous phase, the obtained crude (containing *myo*-inositol) was recrystallized from water affording the title compound (150 mg, 73%) as a white solid.

White solid. M.p.=184-187 °C. $^{1}$H NMR $(CD_3)_2SO$ δ: 10.88 (1H, s, NH), 7.51 (1H, d, $J_{4'',5''}$=7.8, H-4''), 7.34 (1H, d, $J_{7'',6''}$= 8.1, H-7''), 7.28 (1H, d, $J_{2'',NH}$=1.8, H-2''), 7.07 (1H, t, $J_{6'',5''}$=$J_{6'',7''}$=7.5, H-6''), 6.96 (1H, t, $J_{5'',4''}$=$J_{5'',6''}$=7.4, H-5''), 5.26 (1H, s, H-2), 4.81 (2H, d, *J*=4.2, OH), 4.72 (3H, d, *J*=3.8, OH), 3.73 (2H, s, H-2'), 3.39-3.33 (5H, m, H-1, H-3, H-4, H-5, H-6), 3.02-2.96 (1H, m, OH). $^{13}$C NMR $(CD_3)_2SO$ δ: 171.4 (C1'), 136.5 (C7a''), 127.7 (C3a''), 124.4 (C2'), 121.4 (C6''), 119.1 (C4''), 118.8 (C5''), 111.7 (C7''), 107.8 (C3''), 75.5, 75.4 (C2, C5), 73.5, 70.3 (C1, C3, C4, C6), 31.2 (C2'). FTIR(neat): 3432, 3349, 3284 (O-H st.); 1736 (C=O st.); 1046 (C-O st.); 753, 724 (Ar C-H o.o.p. bend). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{19}NNaO_7$ 360.1054; Found 360.1055.

$^{1}$H NMR $D_2O$ δ: 7.59 (1H, d, $J_{4'',5''}$=8.6, H-4''), 7.45 (1H, d, $J_{7'',6''}$= 8.4, H-7''), 7.27 (1H, s, H-2''), 7.19 (1H, t, $J_{6'',5''}$=$J_{6'',7''}$=7.2, H-6''), 7.11 (1H, t, $J_{5'',4''}$=$J_{5'',6''}$=7.6, H-5''), 5.37 (1H, t, $J_{2,1}$=$J_{2,3}$=2.8, H-2), 3.93 (2H, s, H-2'), 3.62 (2H, dd, $J_{1,6}$=9.9, $J_{1,2}$=2.9, H-1, H-3), 3.45 (2H, t, $J_{4,3}$=$J_{4,5}$=9.7, H-4, H-6), 3.21 (1H, t, $J_{5,4}$=$J_{5,6}$=9.5, H-5).

**References**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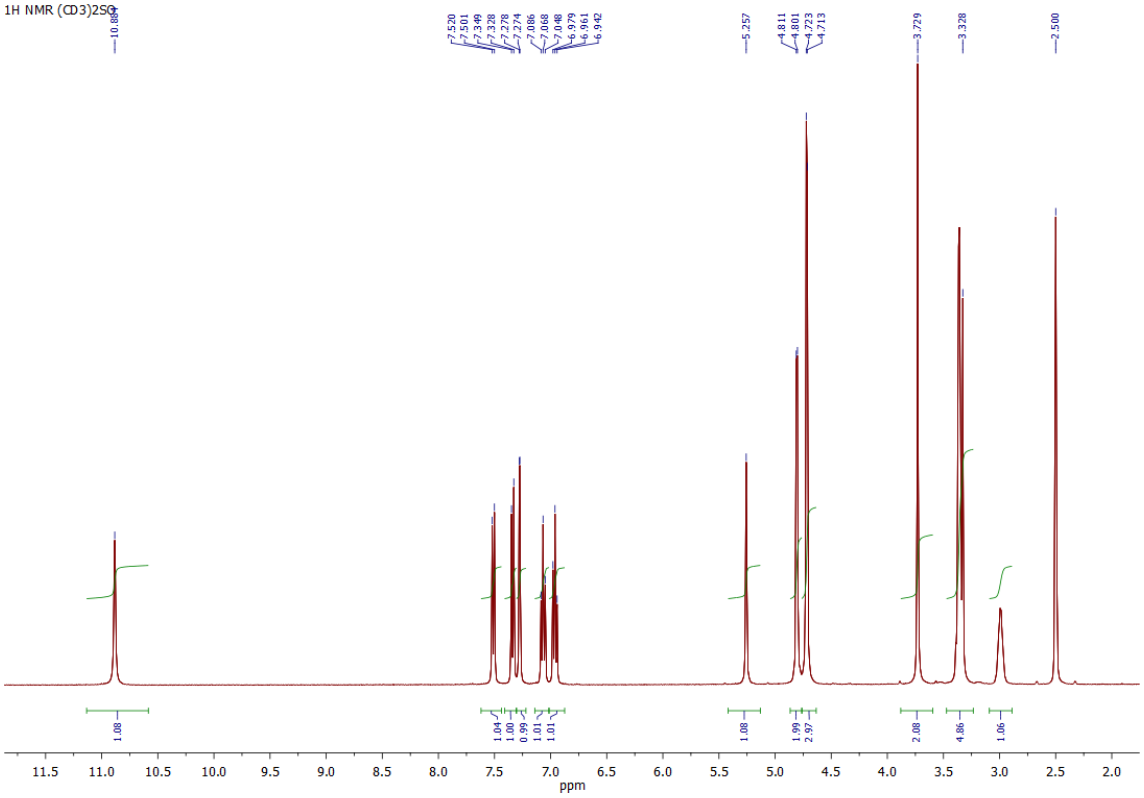
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6.942
5.257
4.811
4.801
4.723
4.713
3.729
3.328
2.500
1.08
1.04
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1.01
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2.08
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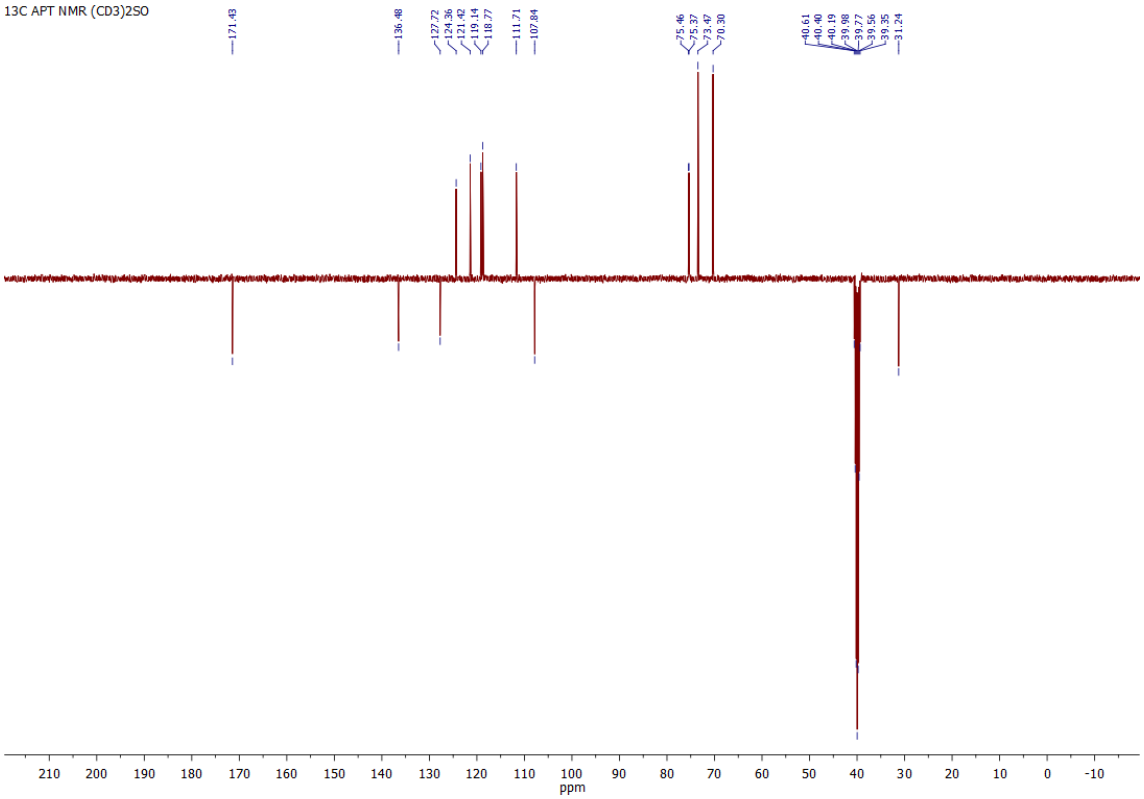
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39.98
39.77
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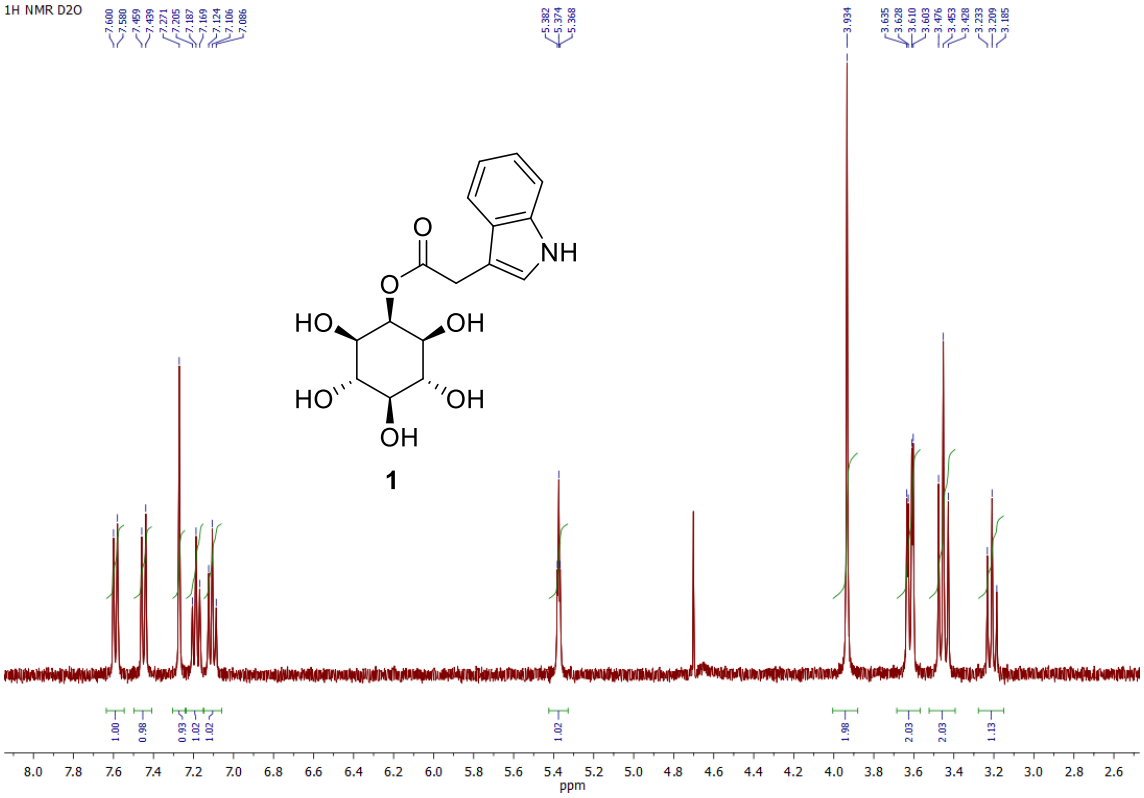
39.35
31.24
ppm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7.459
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3.635
3.628
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3.605
3.476
3.453
3.428
3.233
3.209
3.185
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O
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OH
HO
OH
OH
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1.98
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2.03
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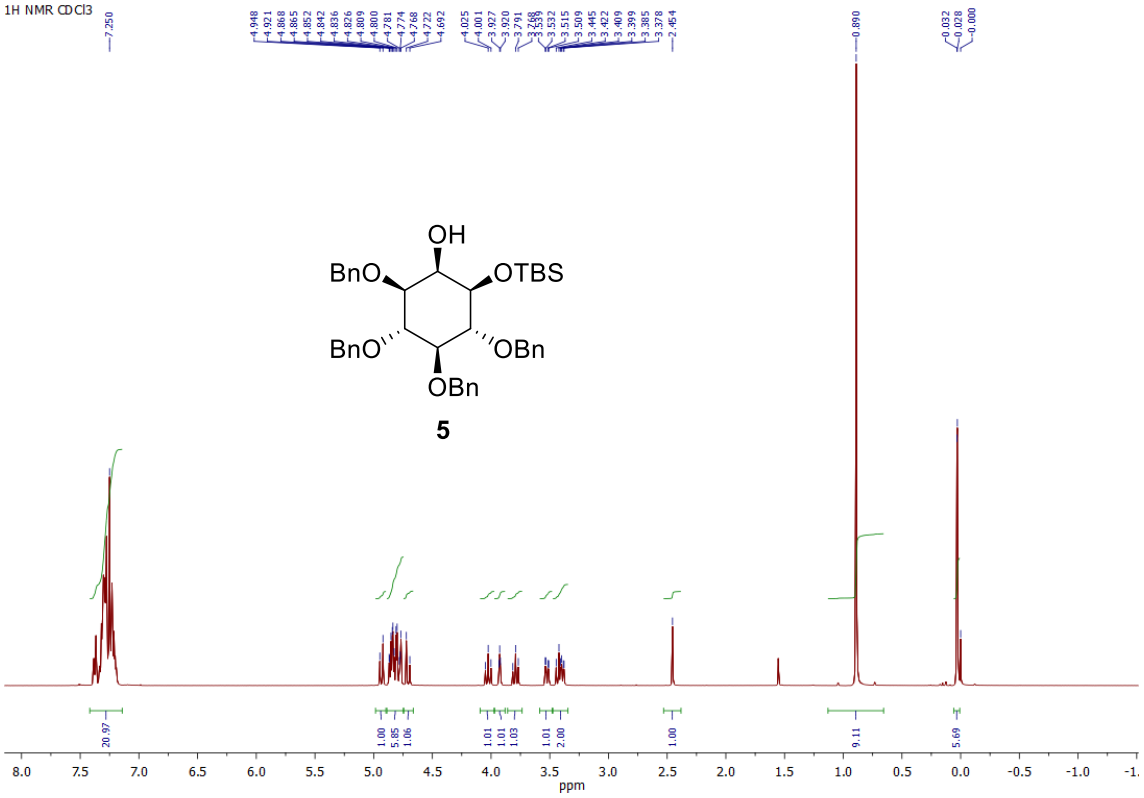
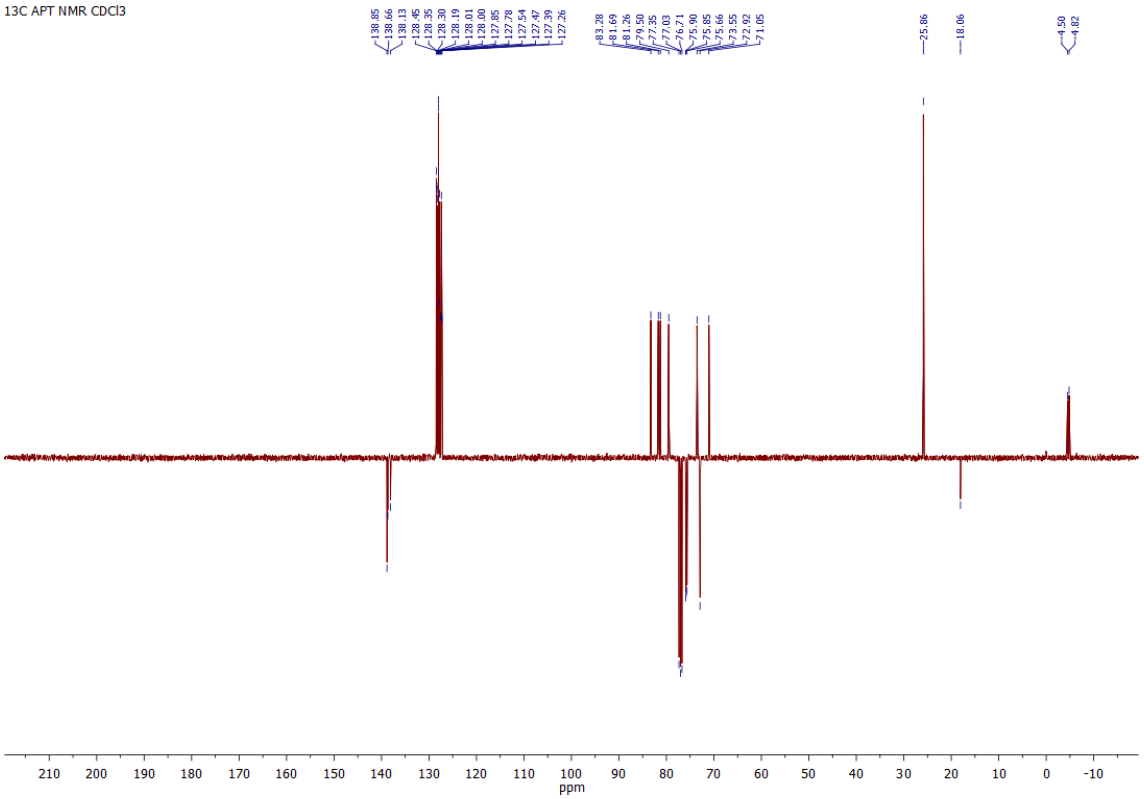



**5**



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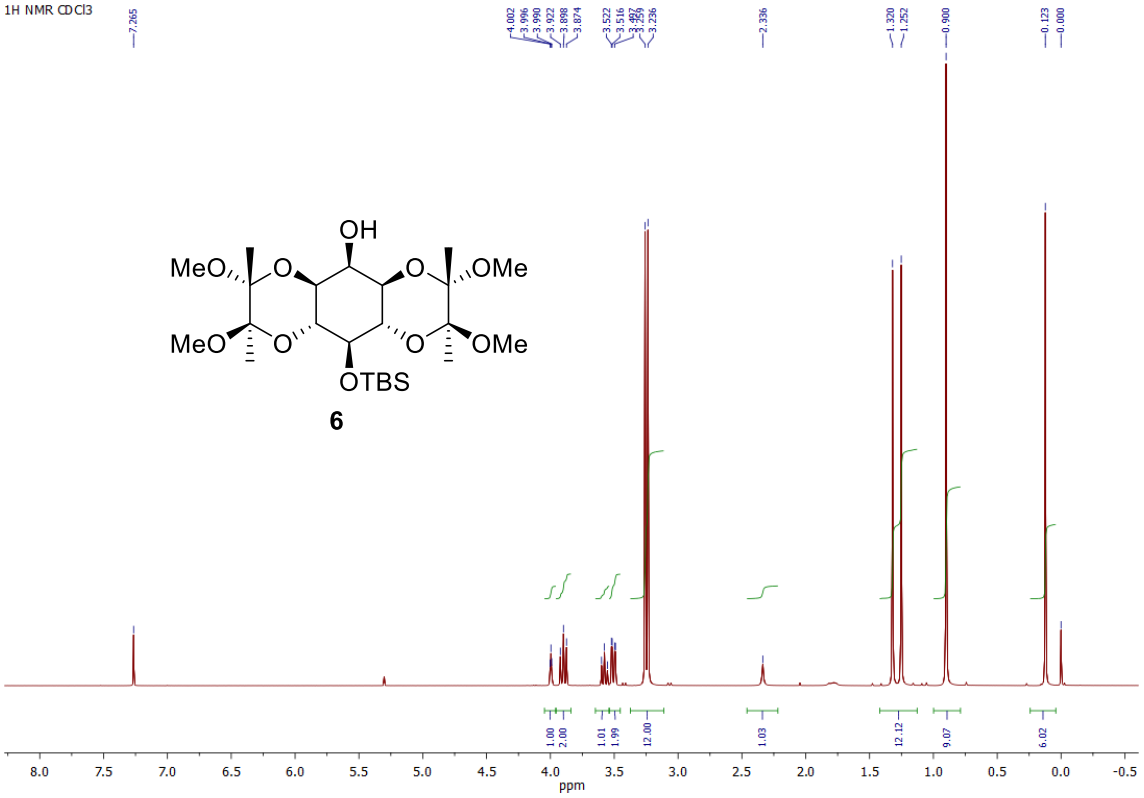





**6**

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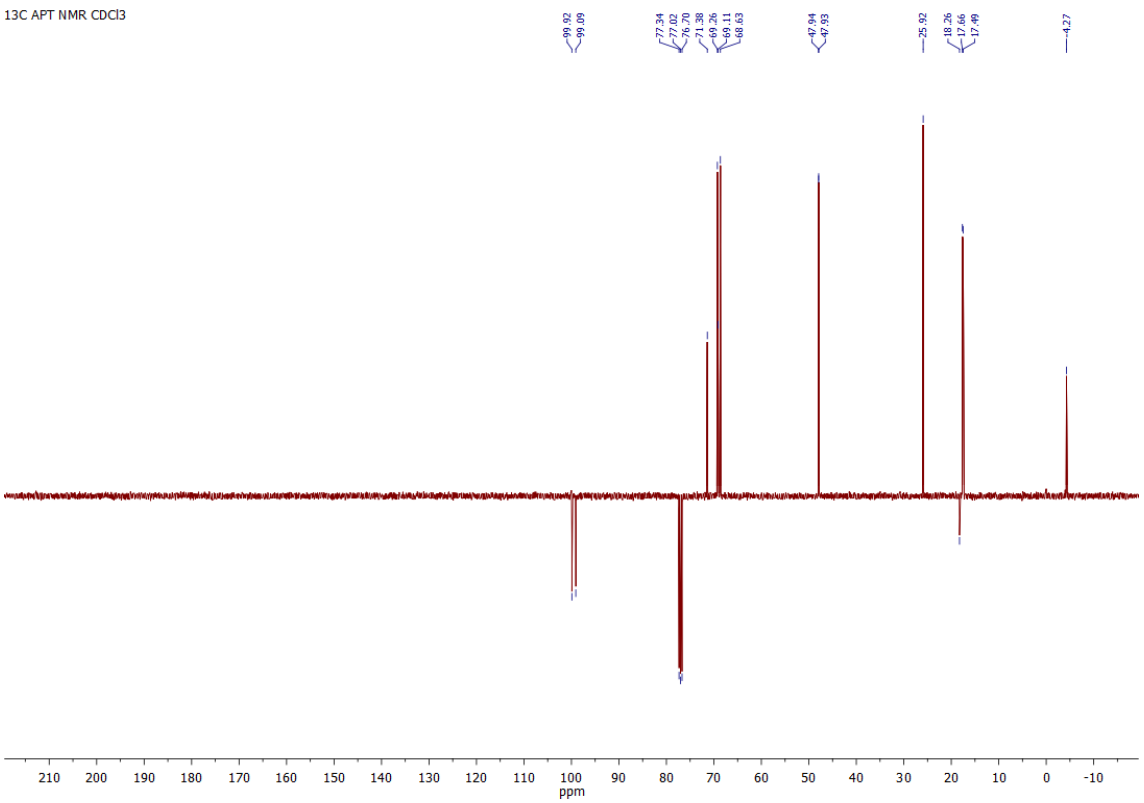

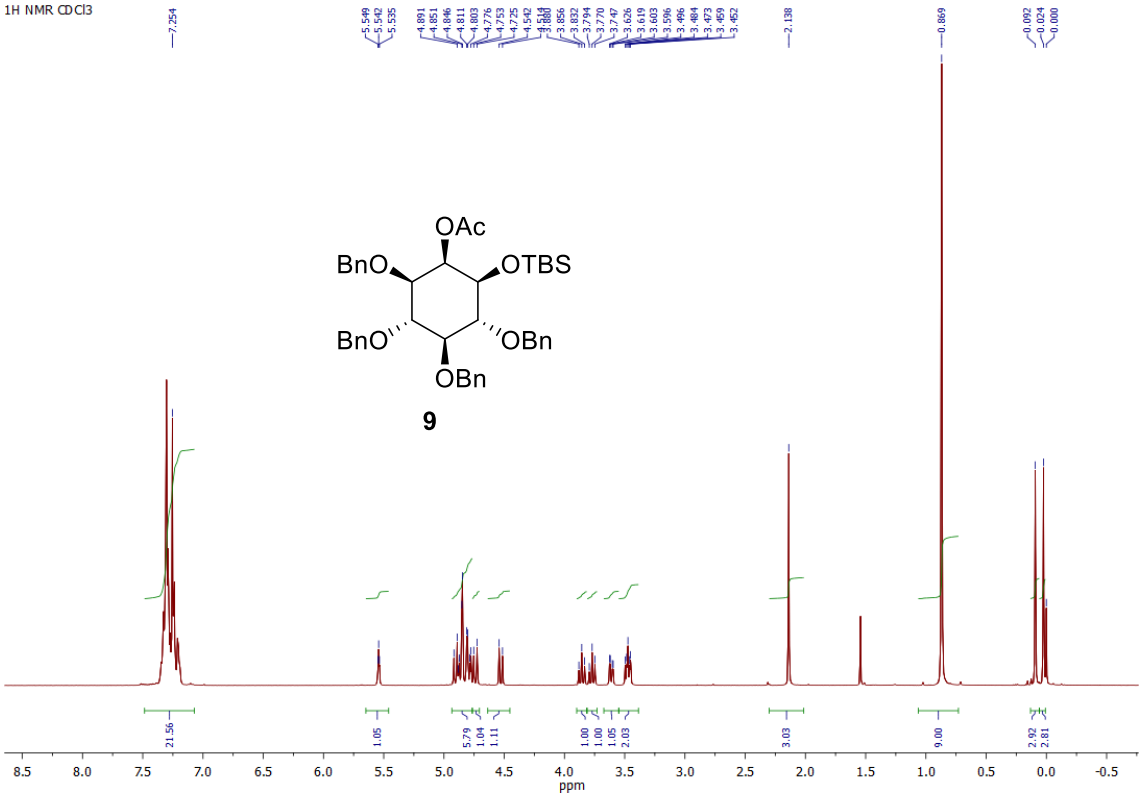
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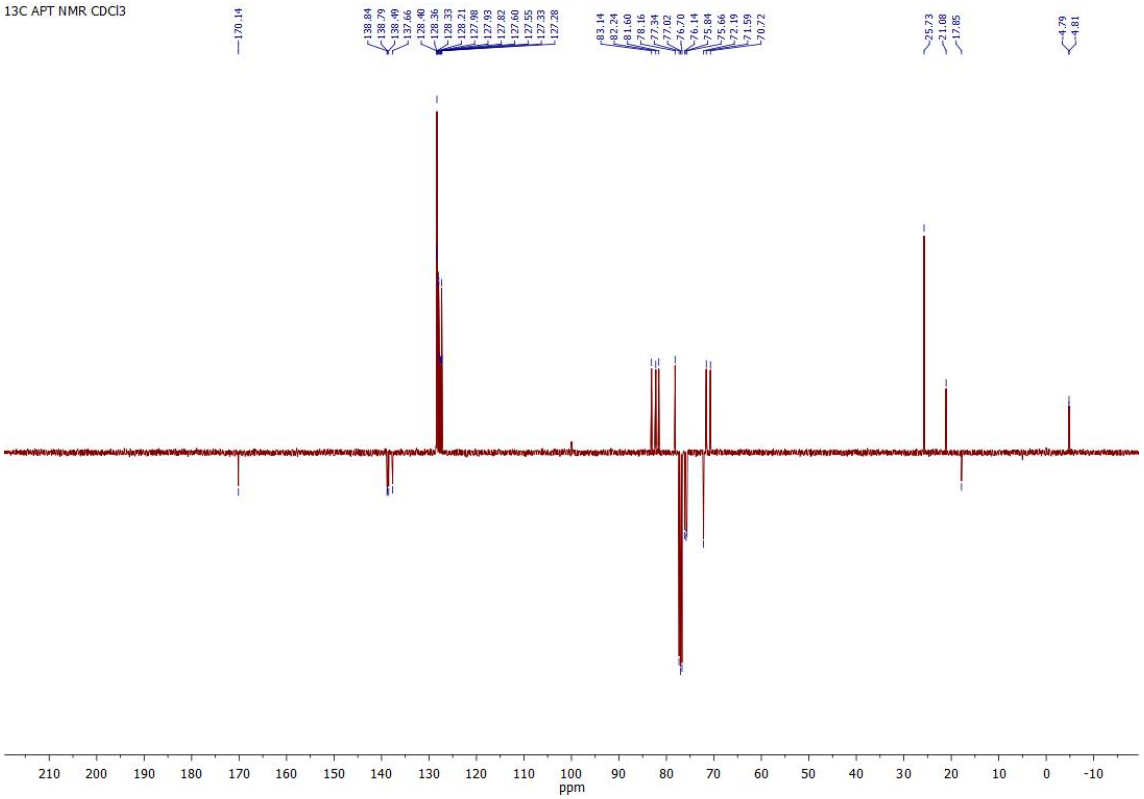
OBn
OBn
9
ppm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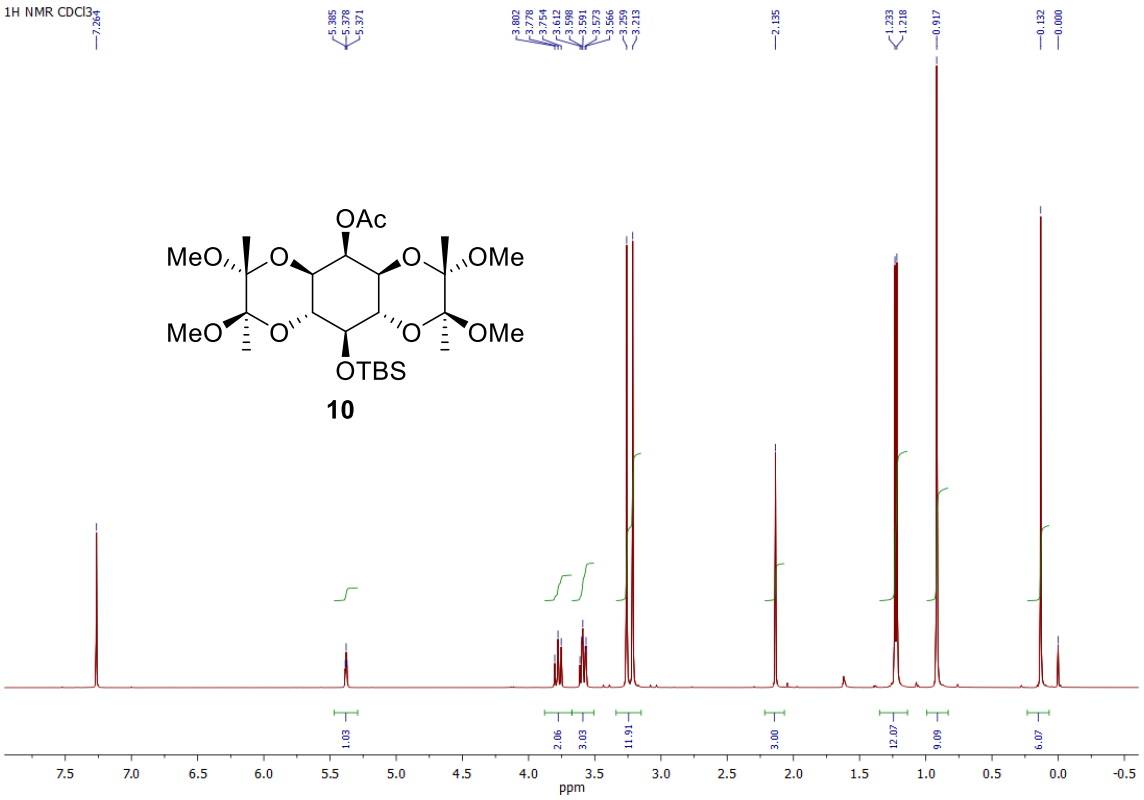
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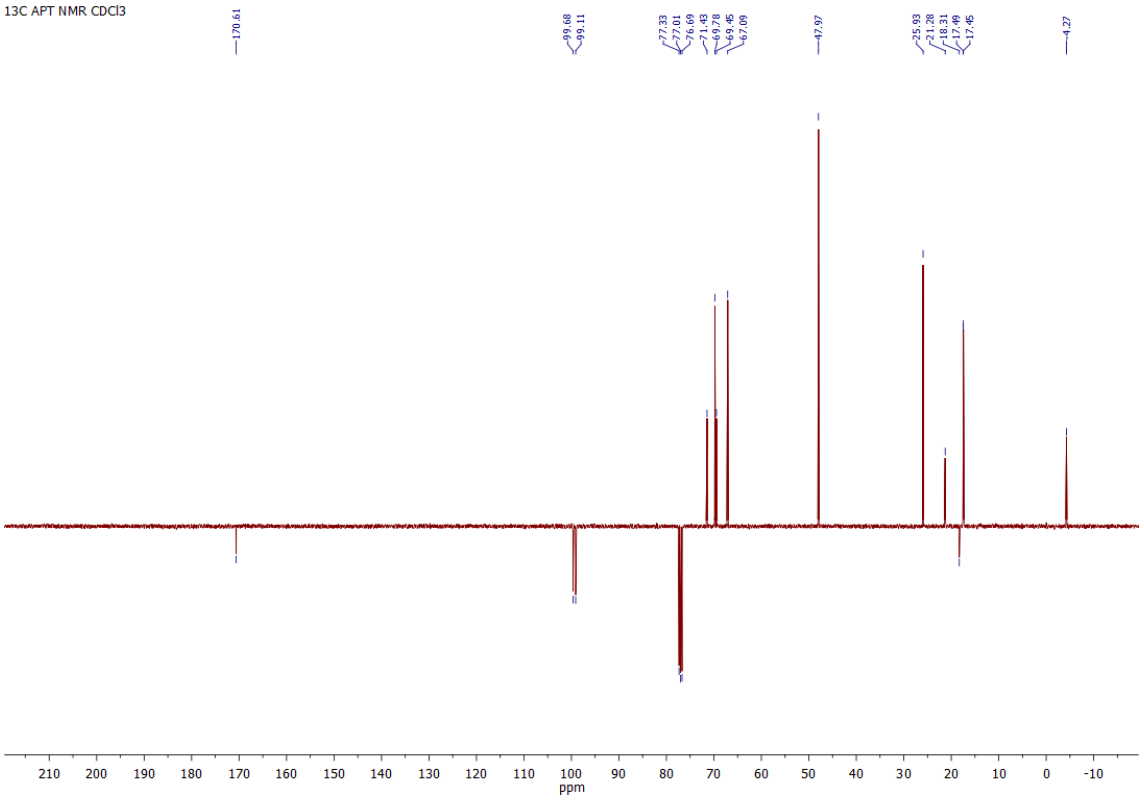
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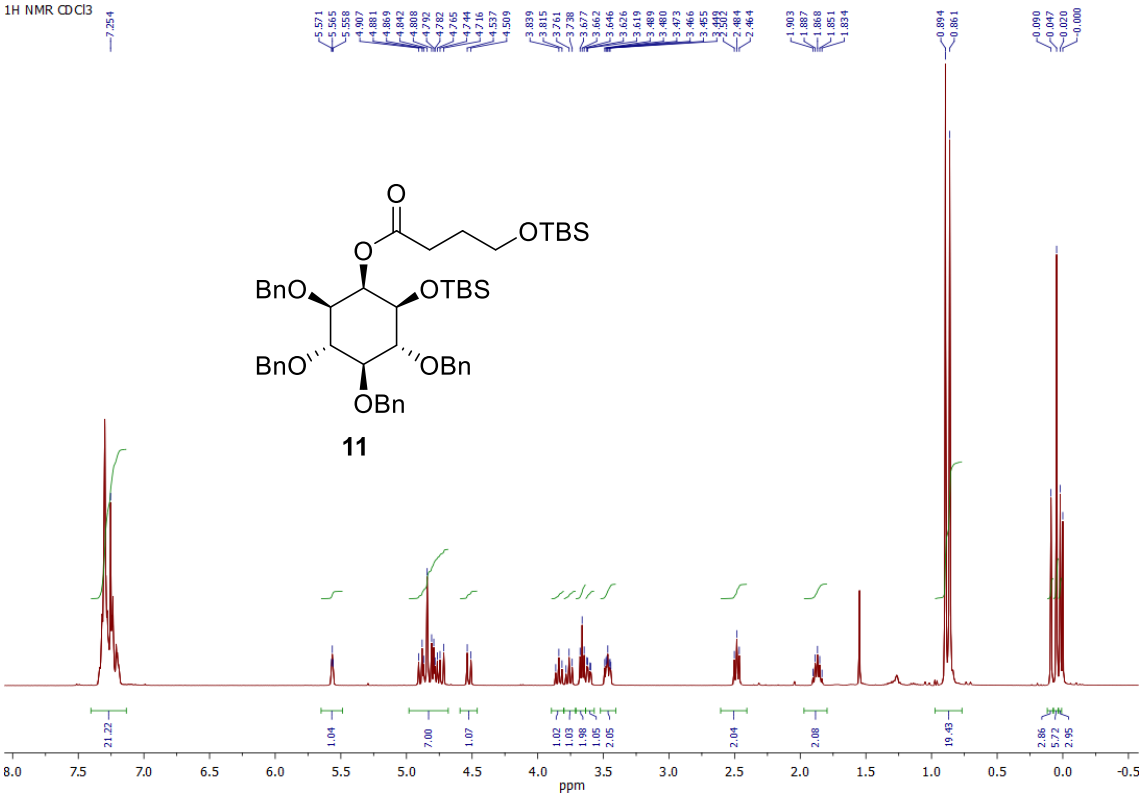
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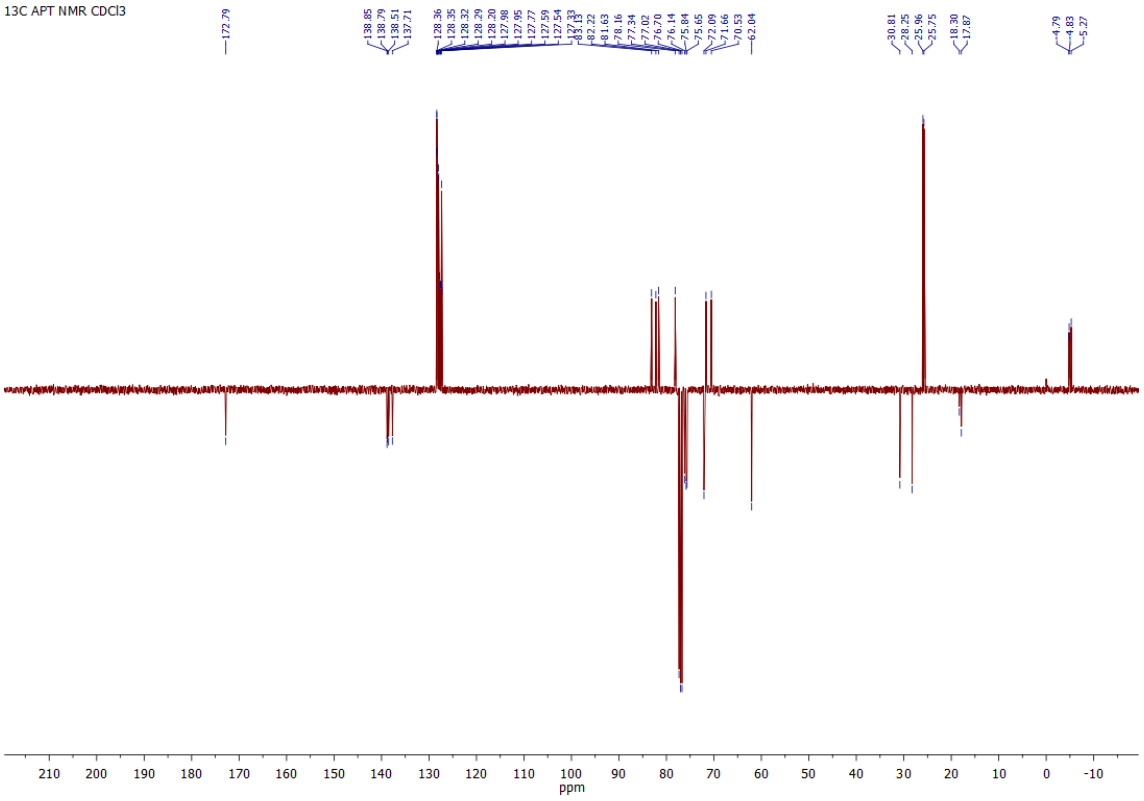
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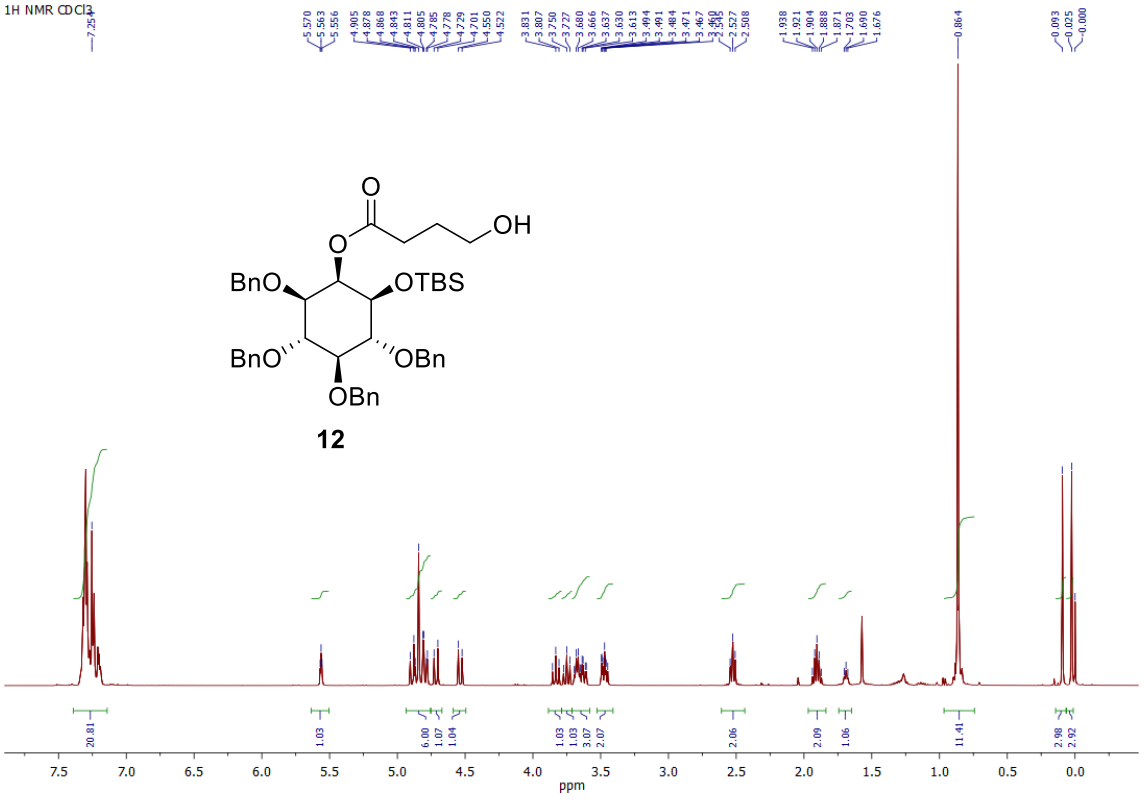
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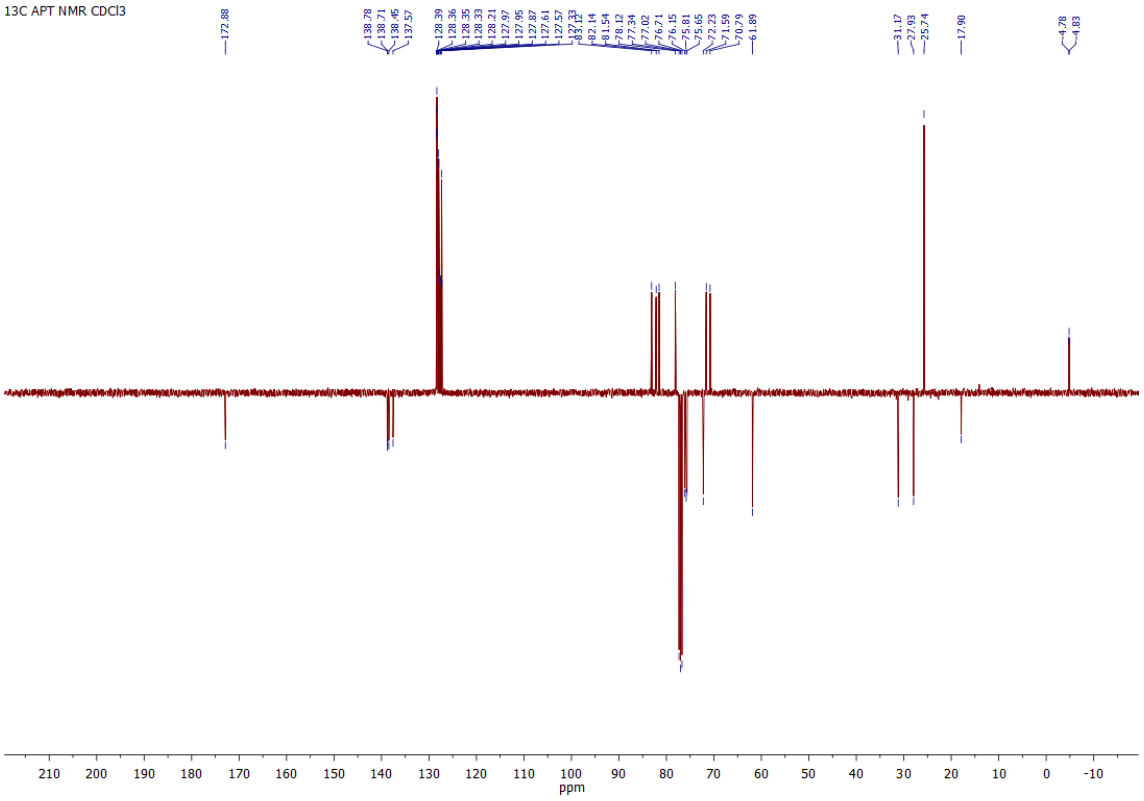
OBn
ppm

**12**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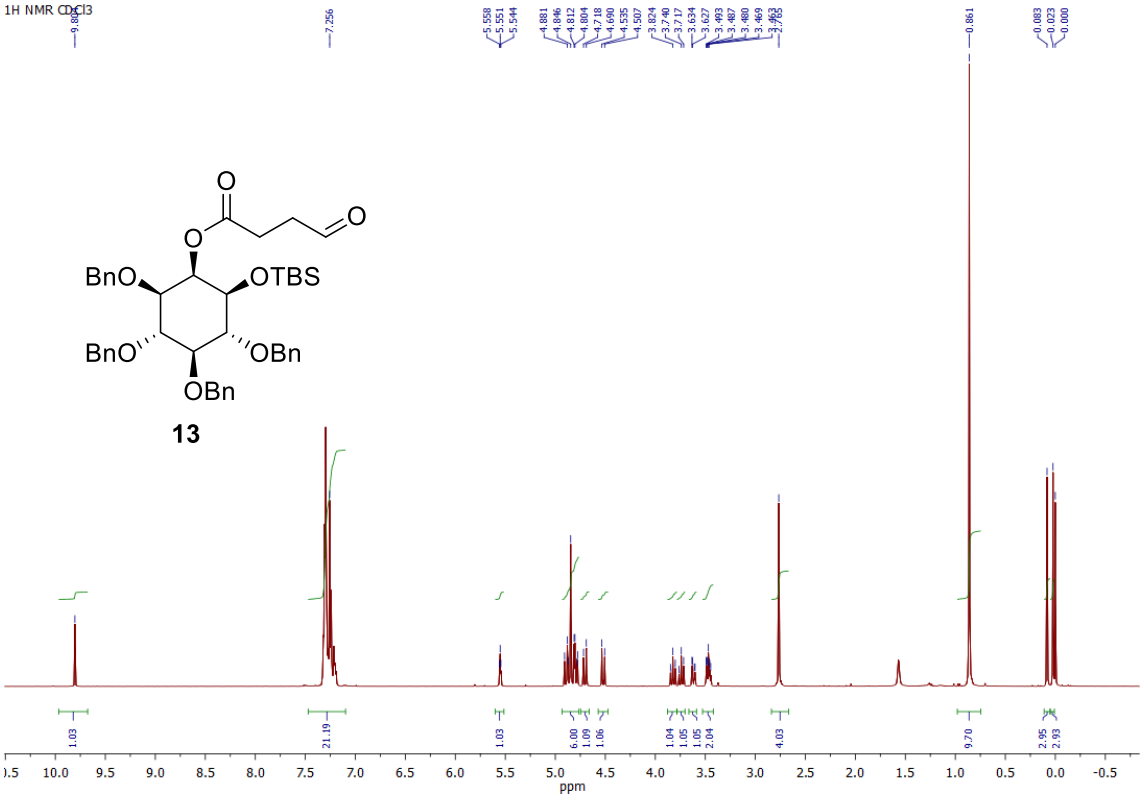
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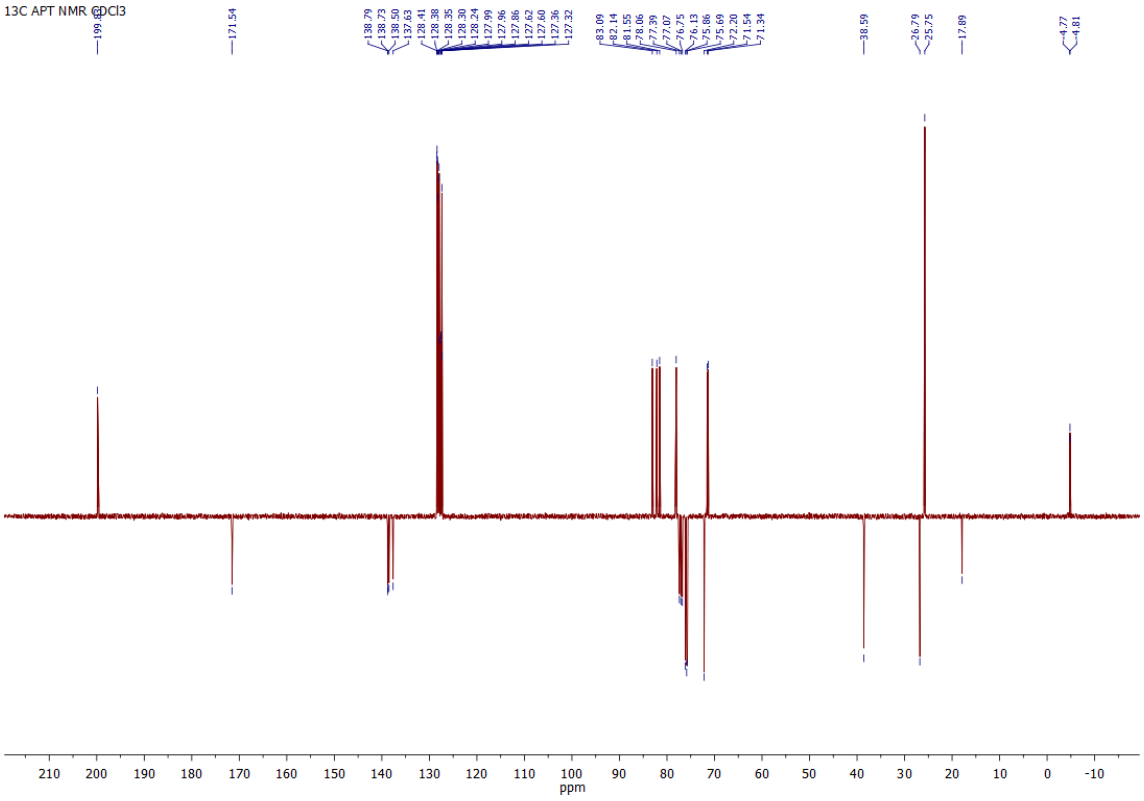
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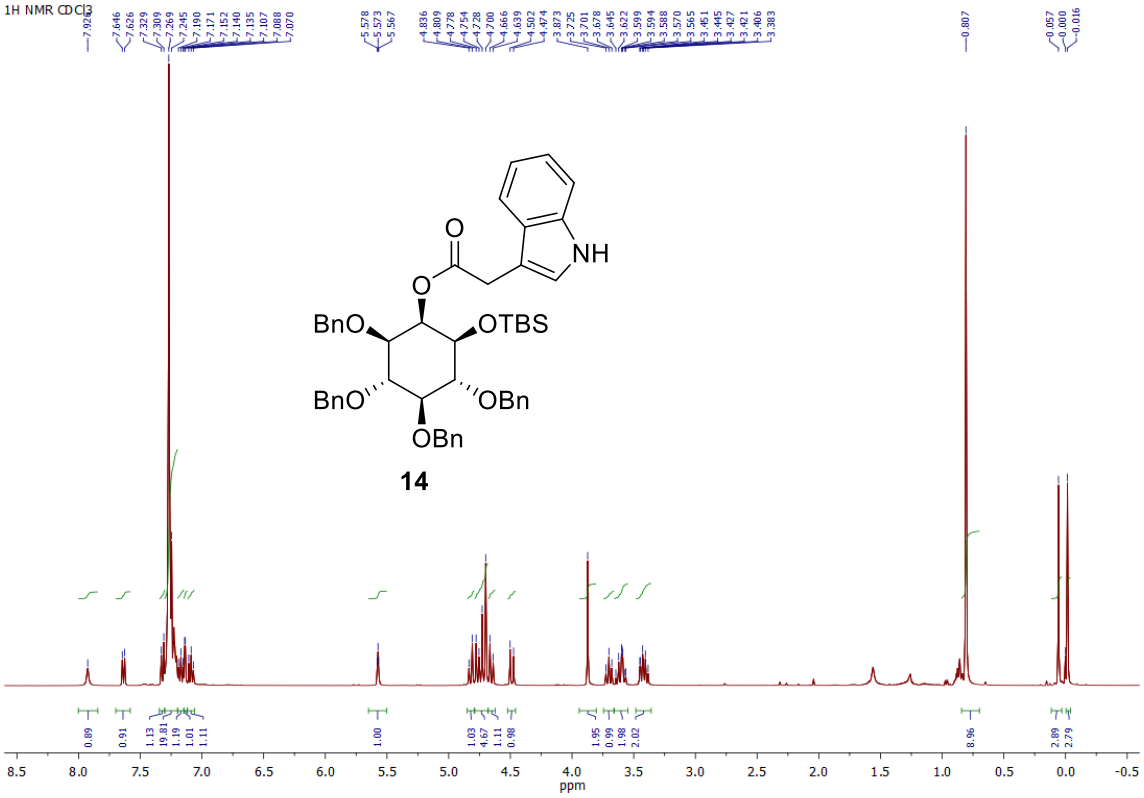
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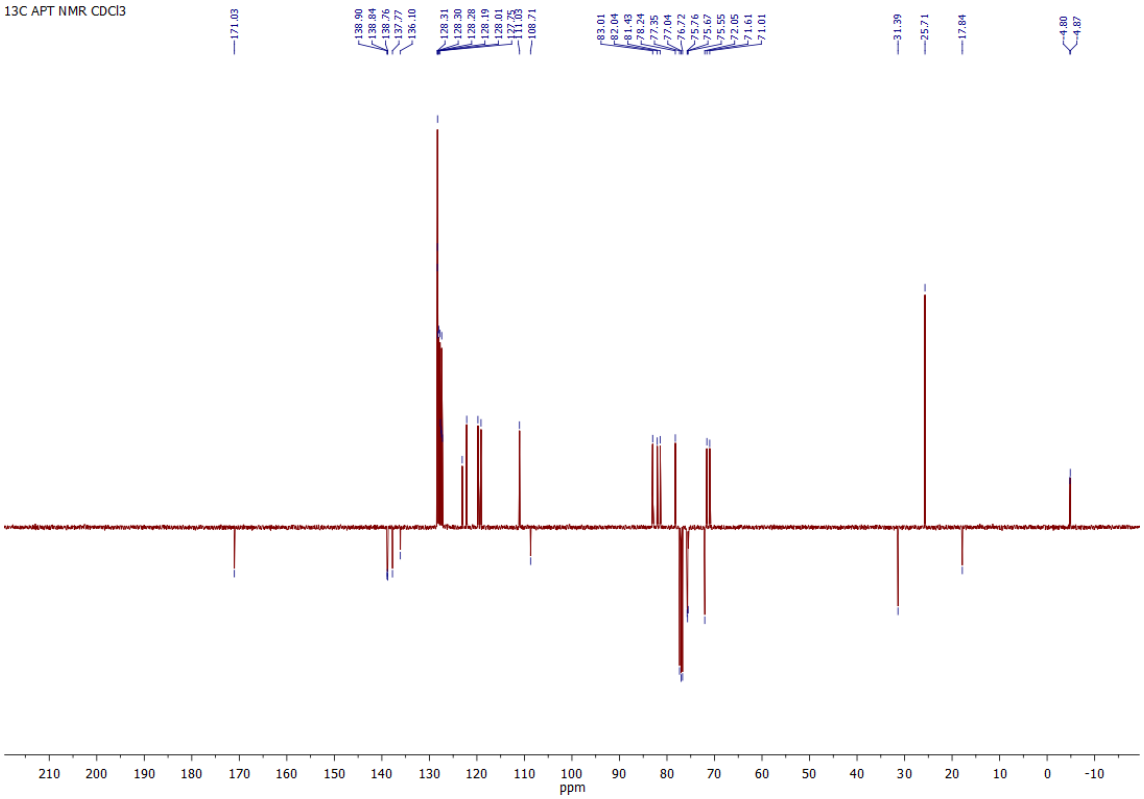
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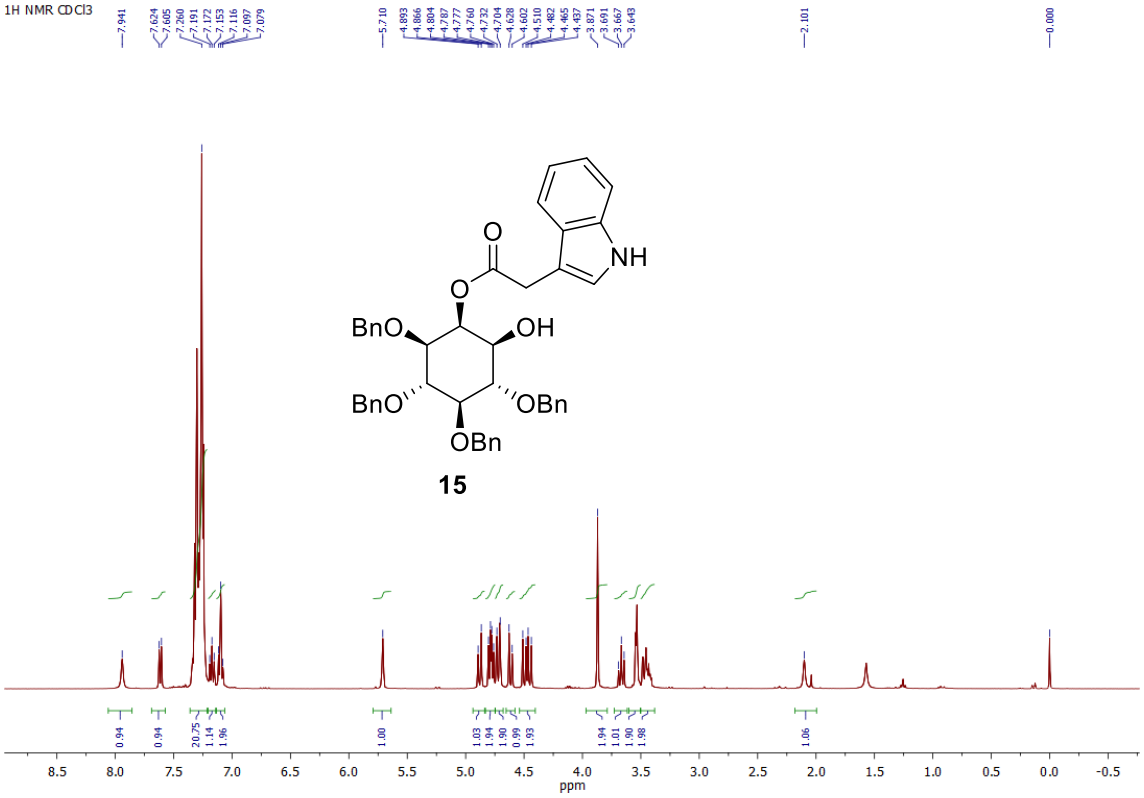





**15**

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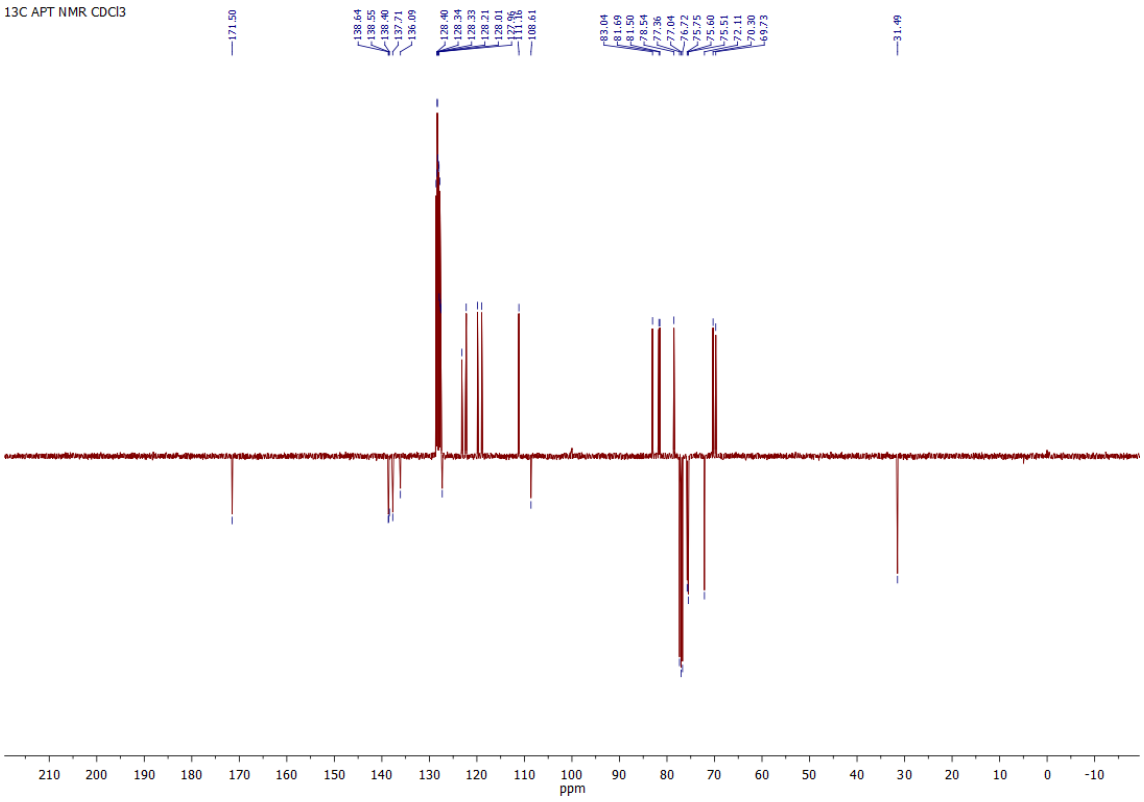

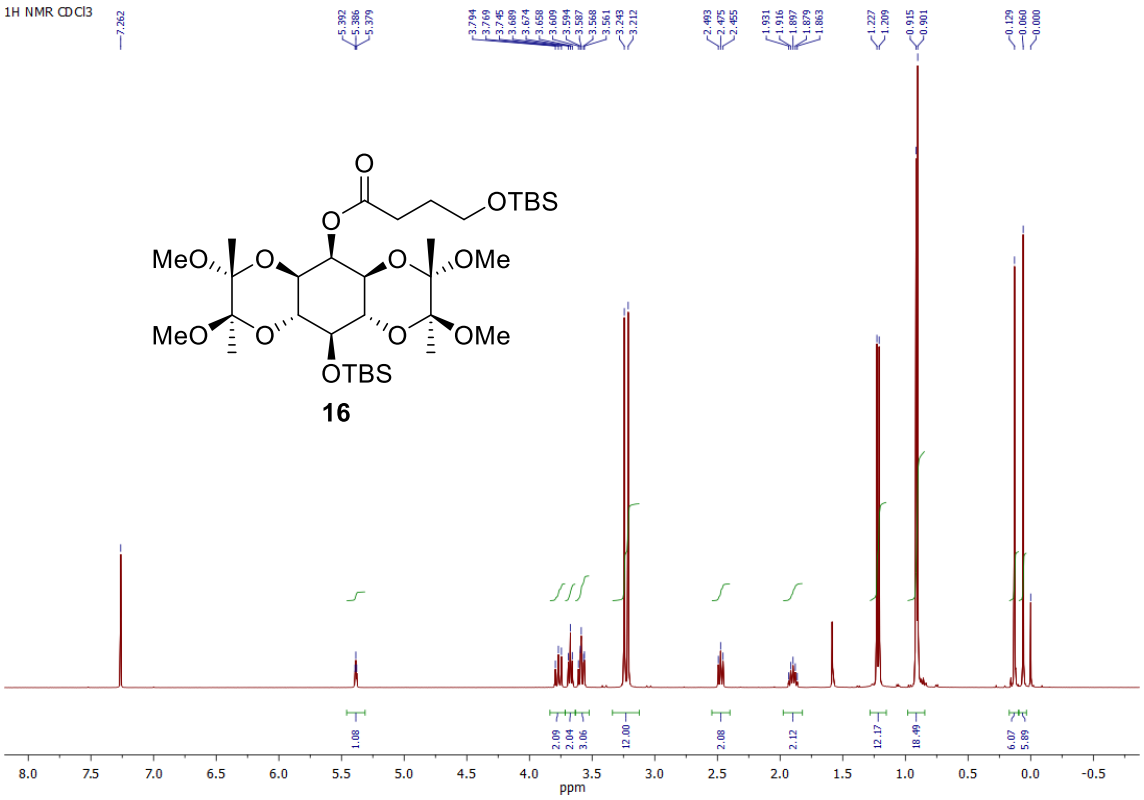
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OMe
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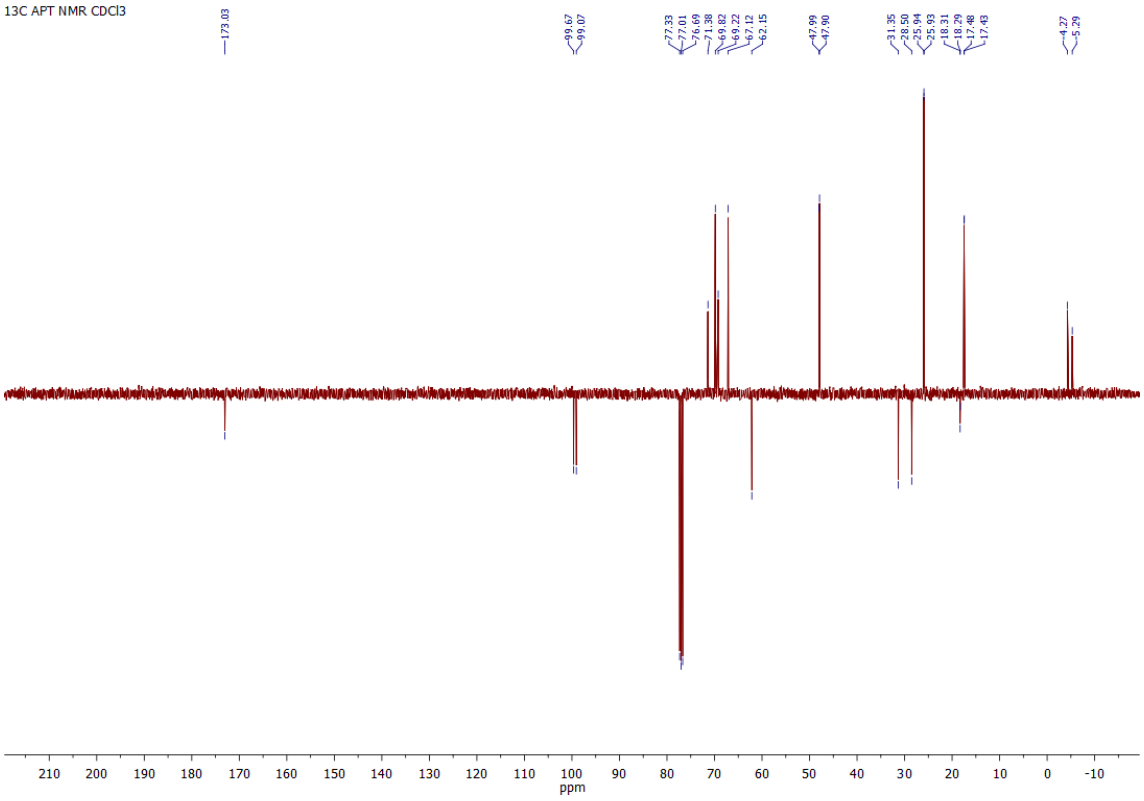
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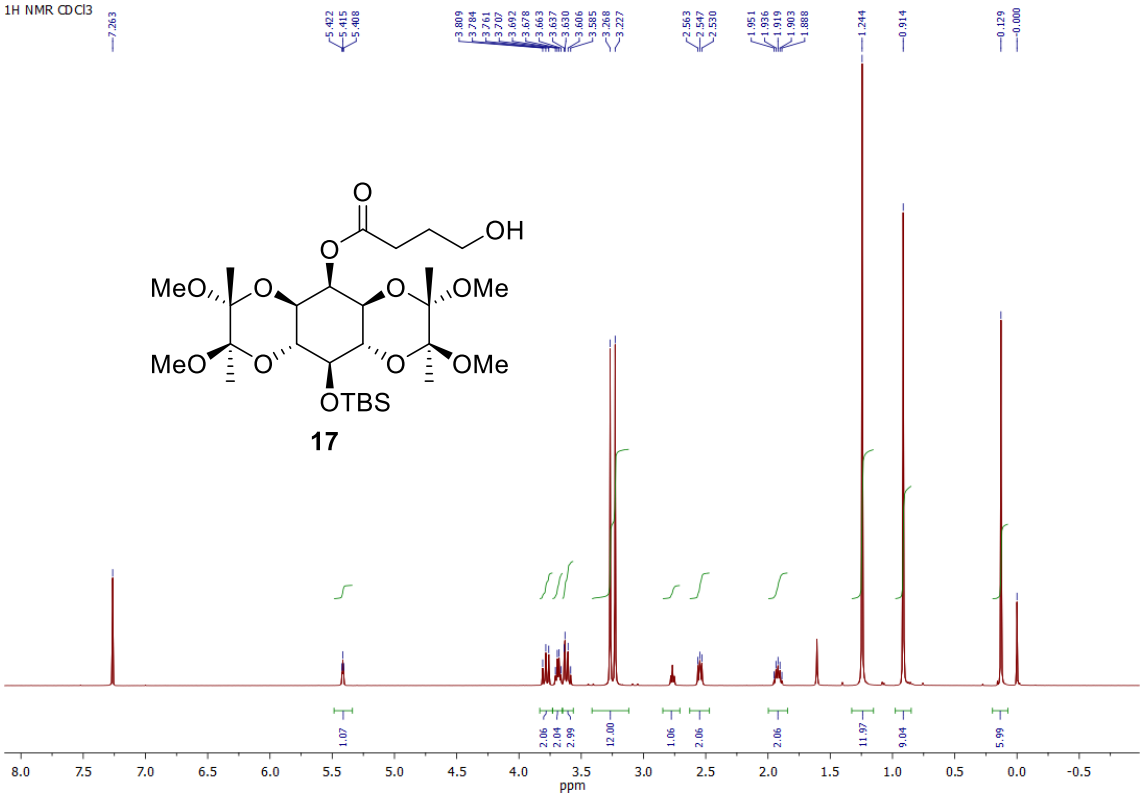
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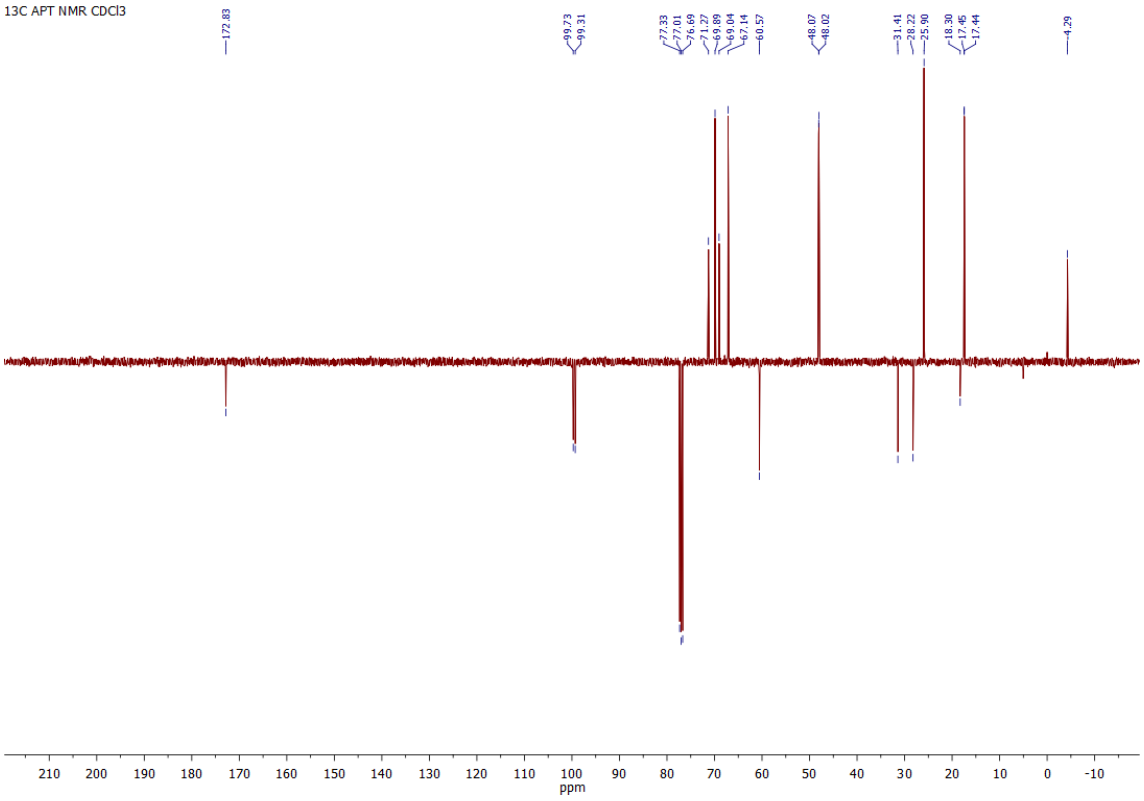
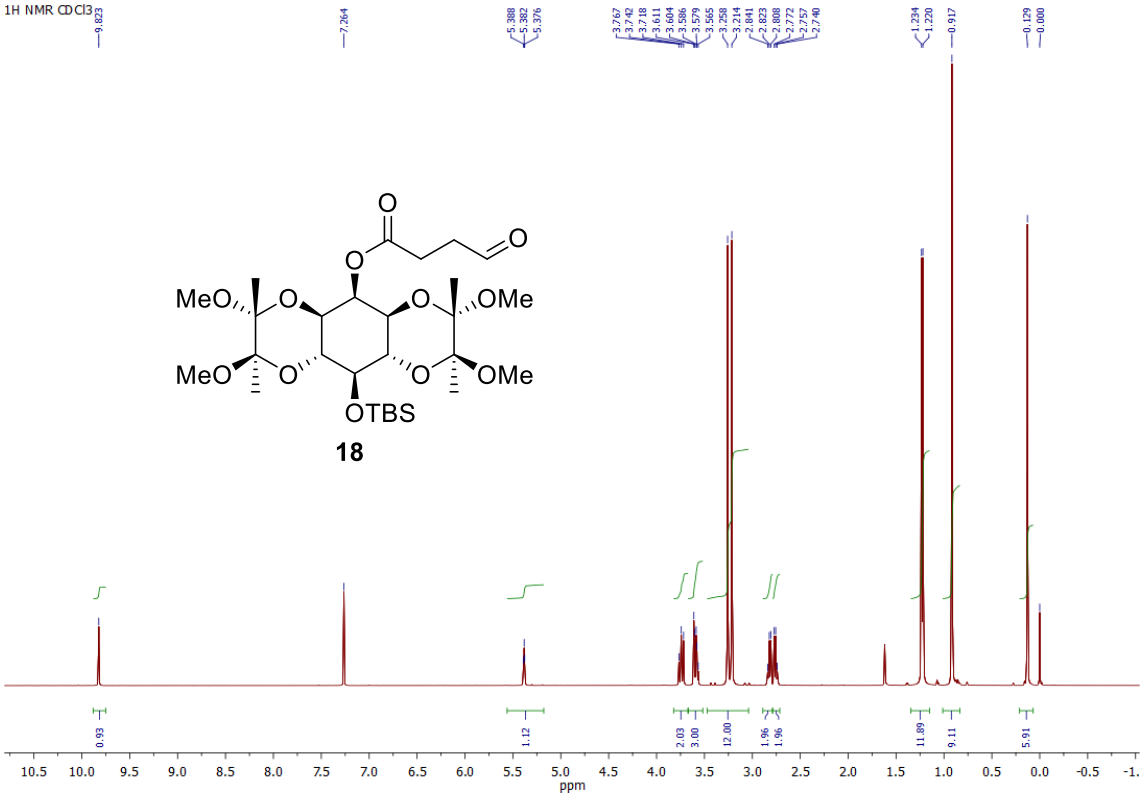
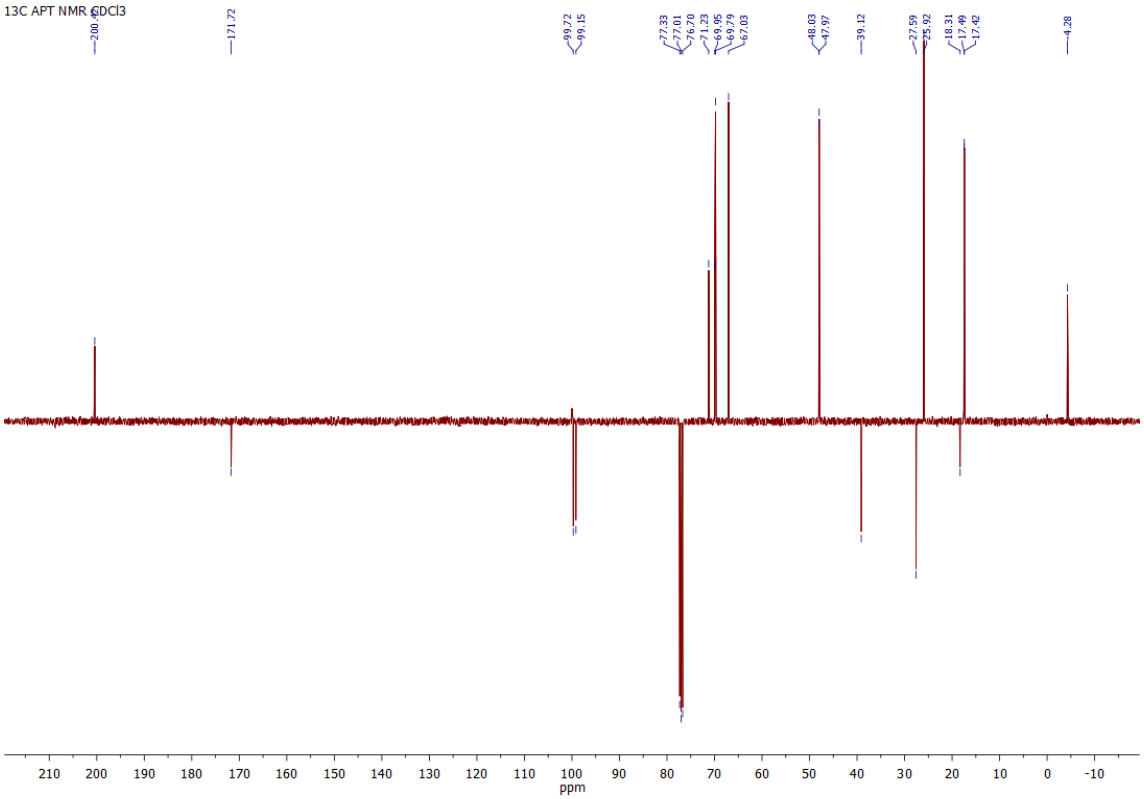
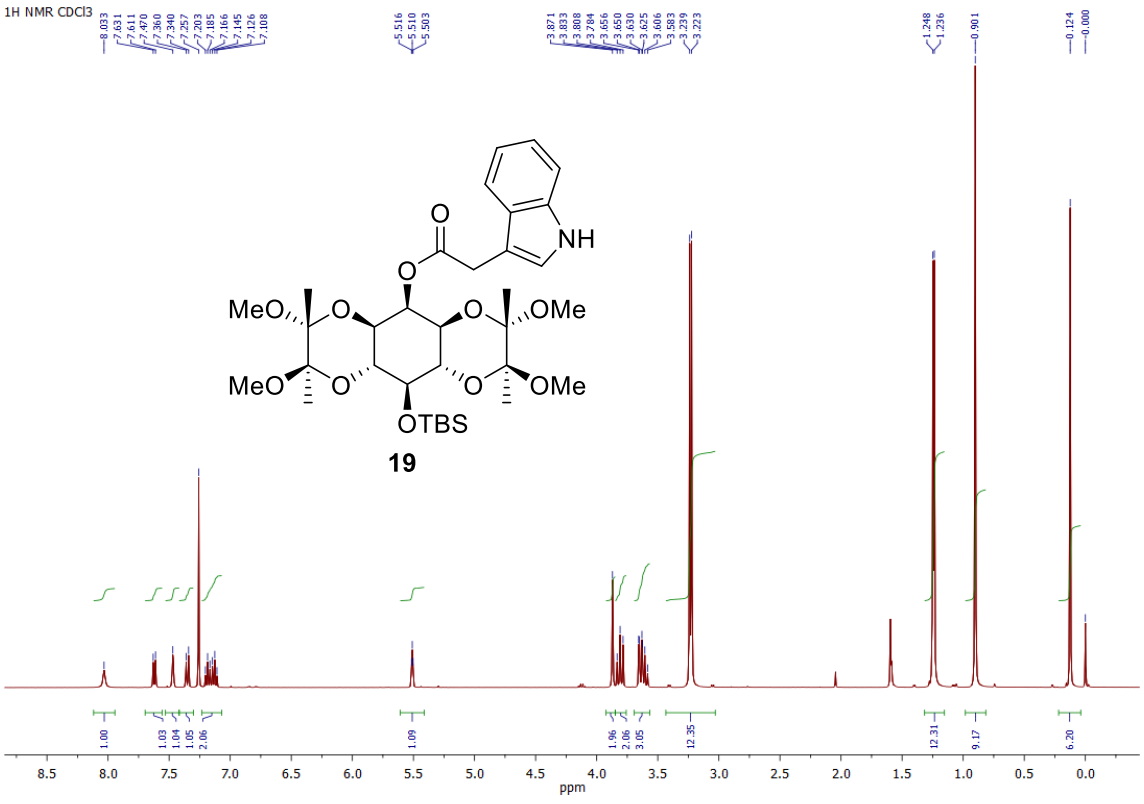
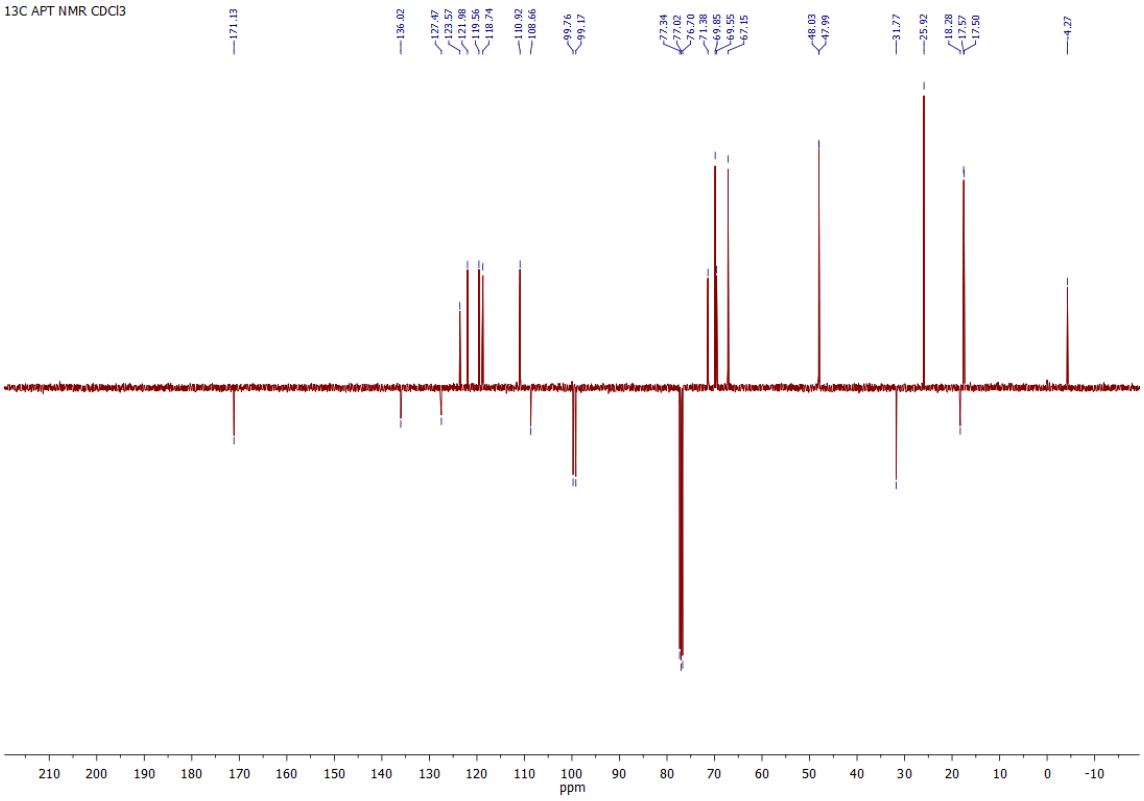

13C APT NMR CDCl3
ppm

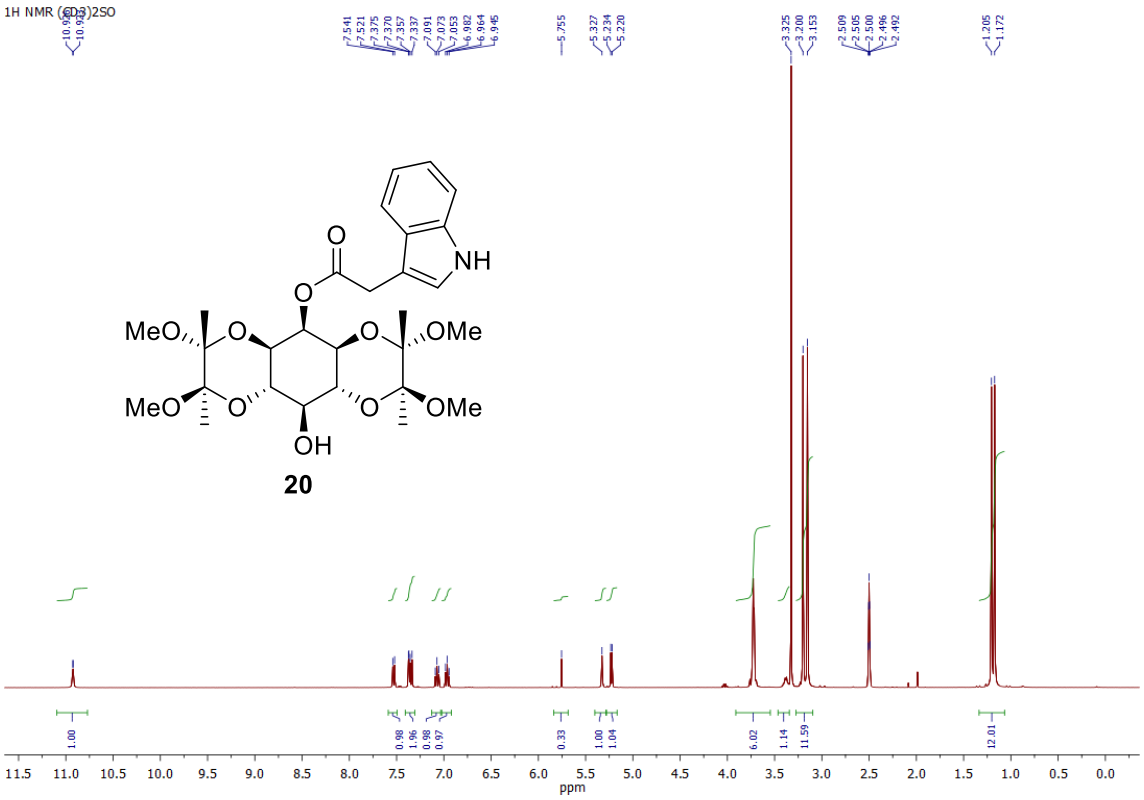


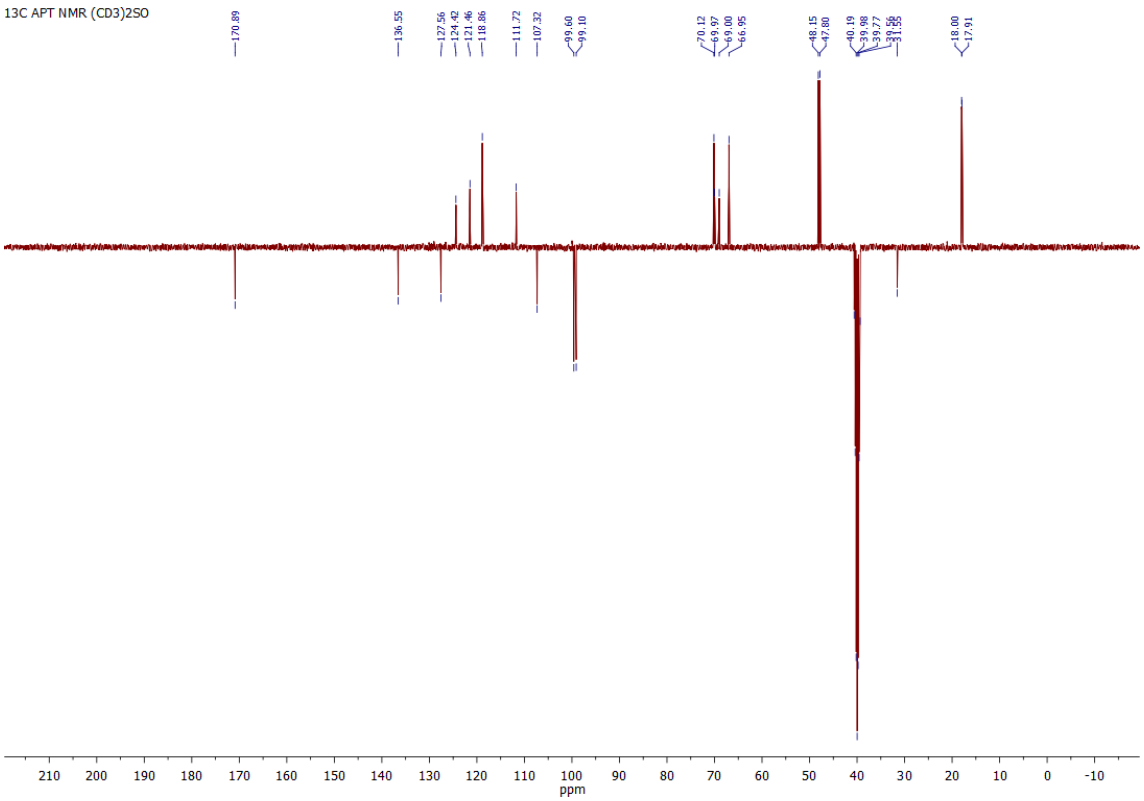

**18**



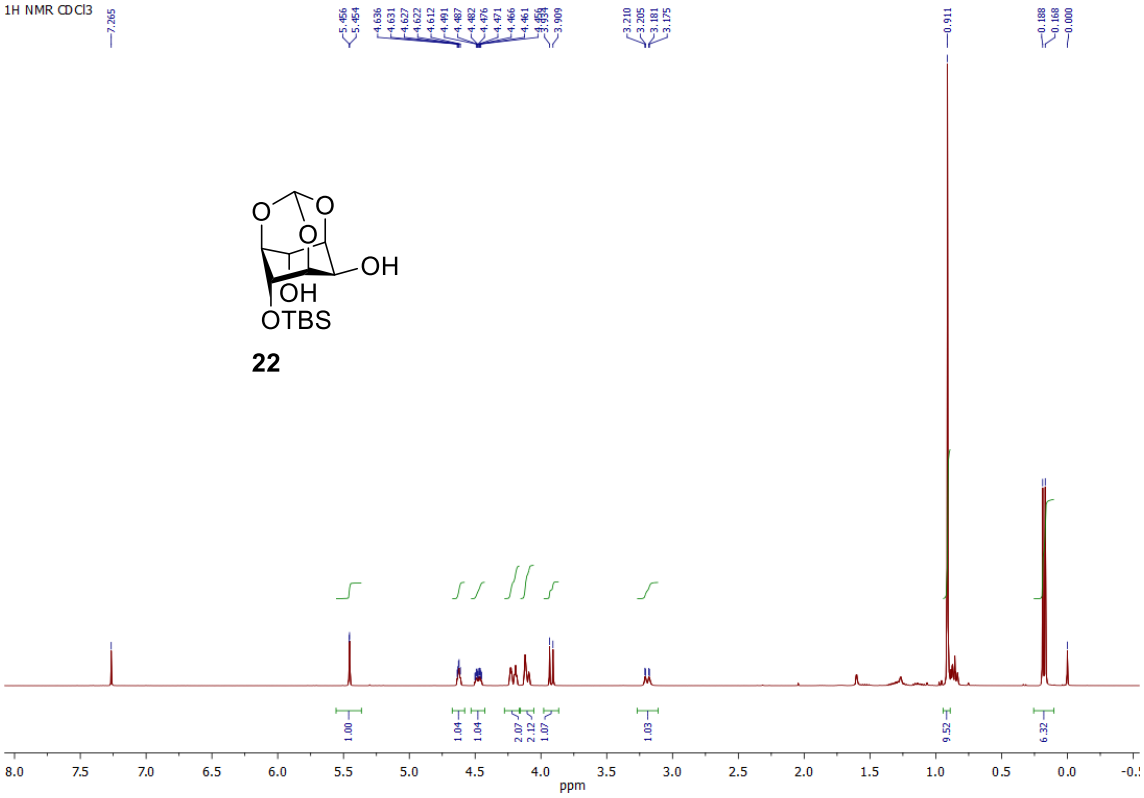

1H NMR CDCl3
MeO
MeO
OMe
OMe
OTBS
NH
O
19
ppm


13C APT NMR CDCl3
ppm


1H NMR (CD3)2SO
MeO
MeO
OMe
OMe
OH
NH
O
20
ppm


13C APT NMR (CD3)2SO
ppm

1H NMR CDCl3

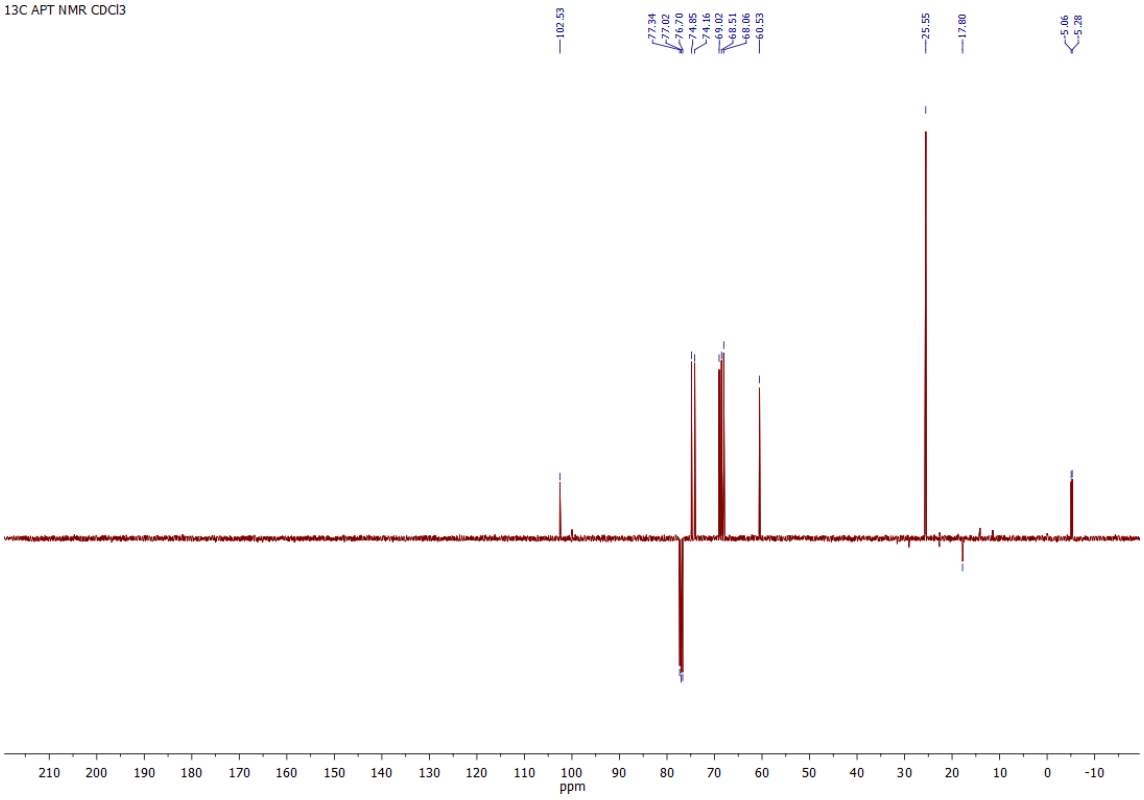




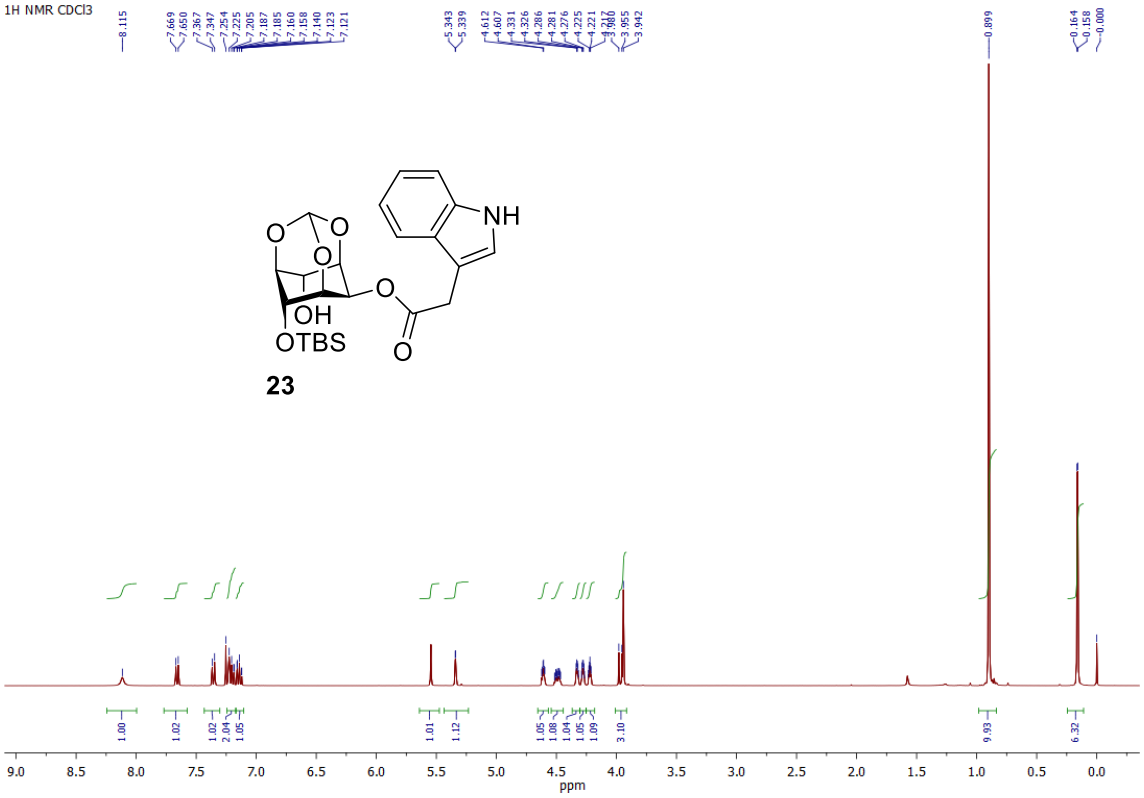


**22**

13C APT NMR CDCl3

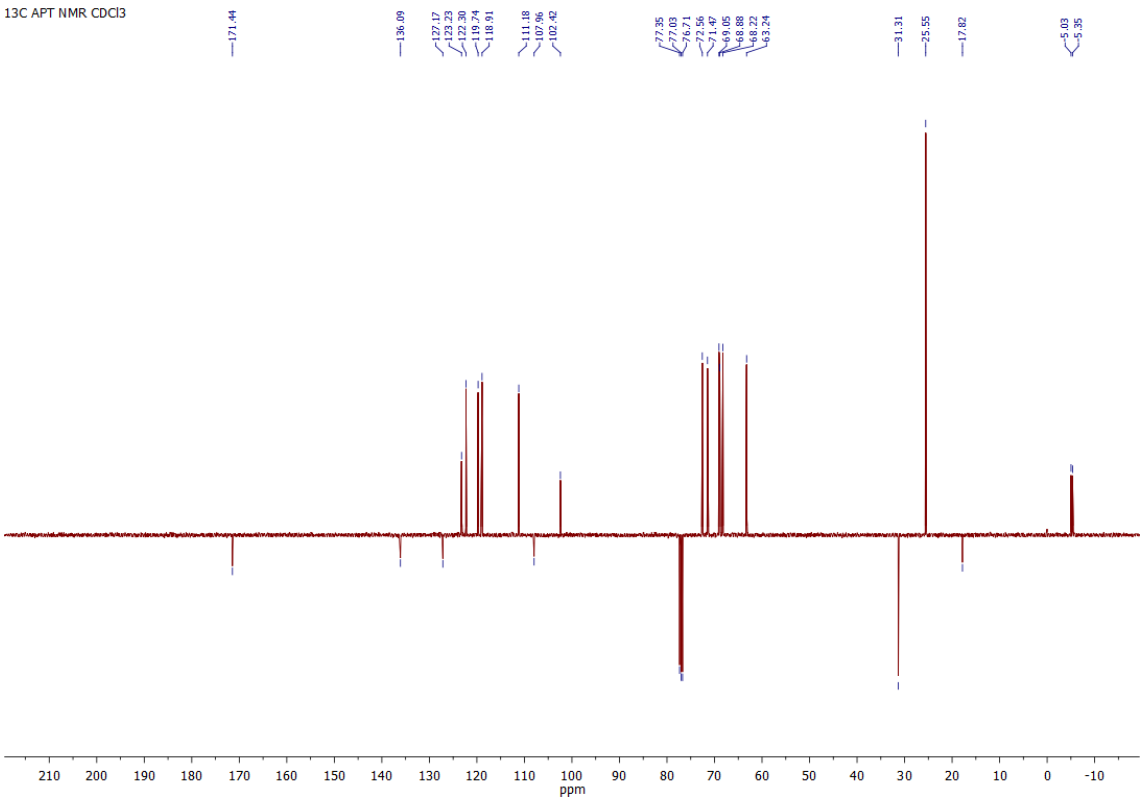


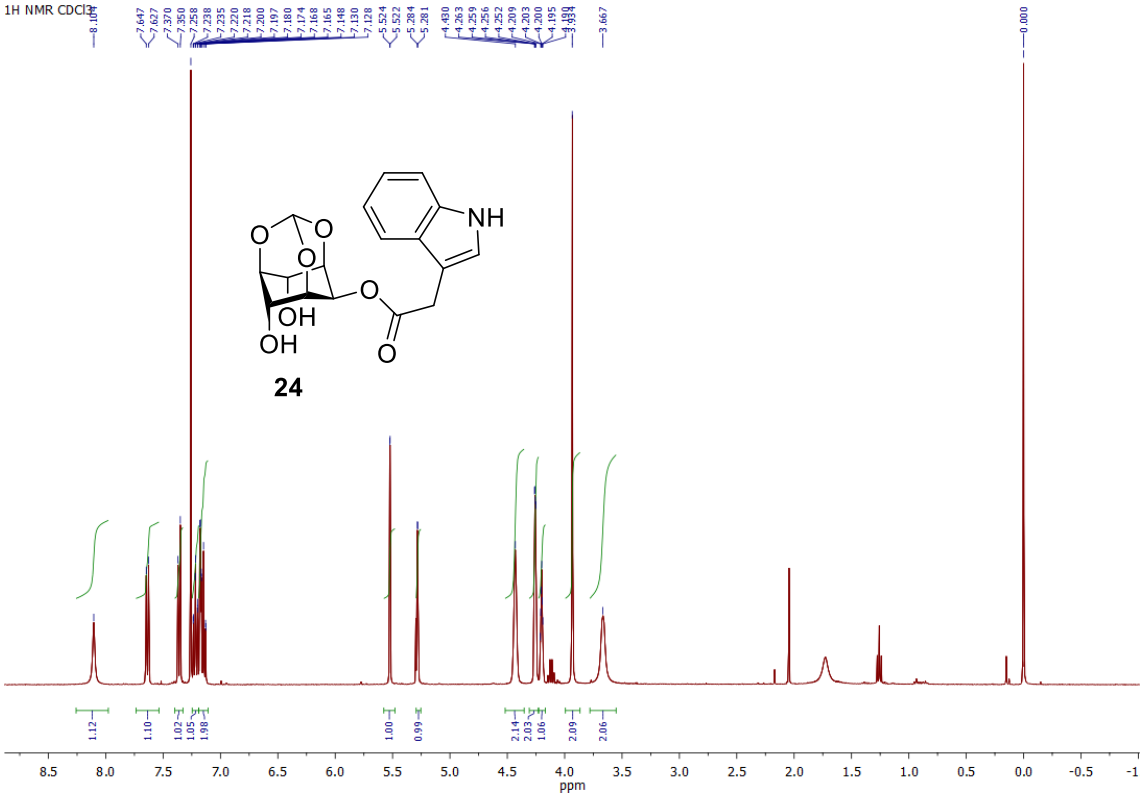
1H NMR CDCl3

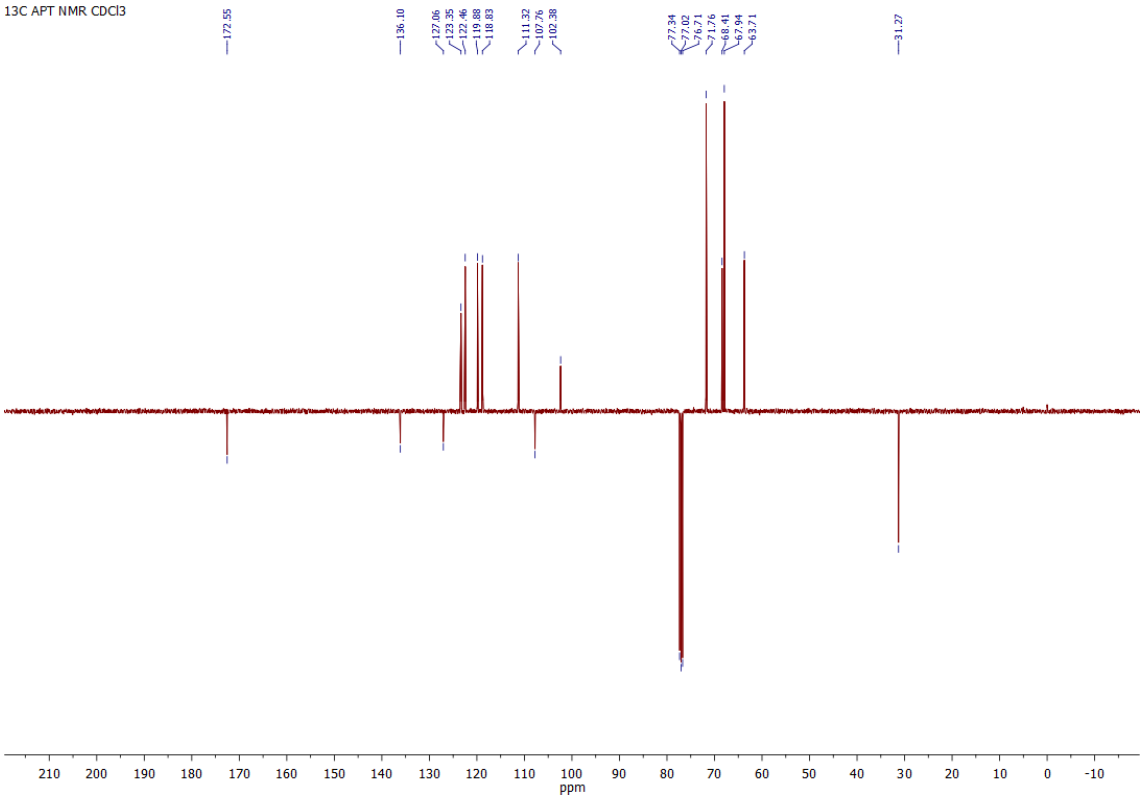



**23**

13C APT NMR CDCl3




1H NMR CDCl3
NH
O
O
O
O
OH
OH
O
24
ppm


13C APT NMR CDCl3
ppm