Supporting Information

Selective demethylation of *O*-aryl glycosides by iridium-catalyzed hydrosilylation

Caleb A. H. Jones and Nathan D. Schley*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235 United States

I. General Information

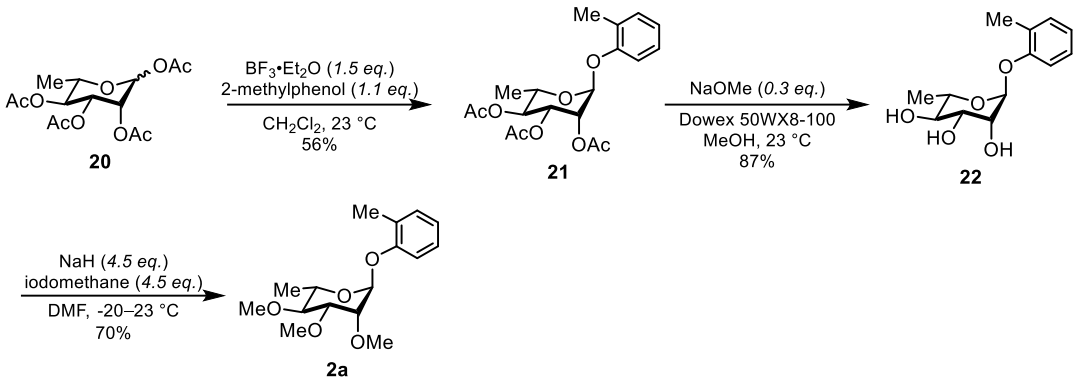
General Considerations. Syntheses and manipulations were conducted in air unless otherwise specified. Tetrahydrofuran, toluene, dichloromethane, pentane, and diethyl ether were degassed with argon and dried over activated alumina using a solvent purification system. All reagents and building blocks for which procedures are not given below were procured from commercial vendors. $[(COD)Ir(PPh_3)_2]BAr^{F}{}_4$,[1] and $[CPh_3]BAr^{F}{}_4$[2,3] were prepared using reported procedures.

Spectroscopy. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker NMR spectrometers at ambient temperature unless otherwise noted. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are referenced to residual solvent signals; $^{31}P\{^{1}H\}$ chemical shifts are referenced to an external H_3PO_4 standard.

Mass Spectrometry. High resolution mass spectrometry was conducted by the Mass Spectrometry Research Center (MSRC) at Vanderbilt University. Solutions of purified products were diluted into an acid-free carrier solvent and analyzed in positive mode by ESI using an Orbitrap mass analyzer.

II. Synthesis and Characterization

Substrate Synthesis

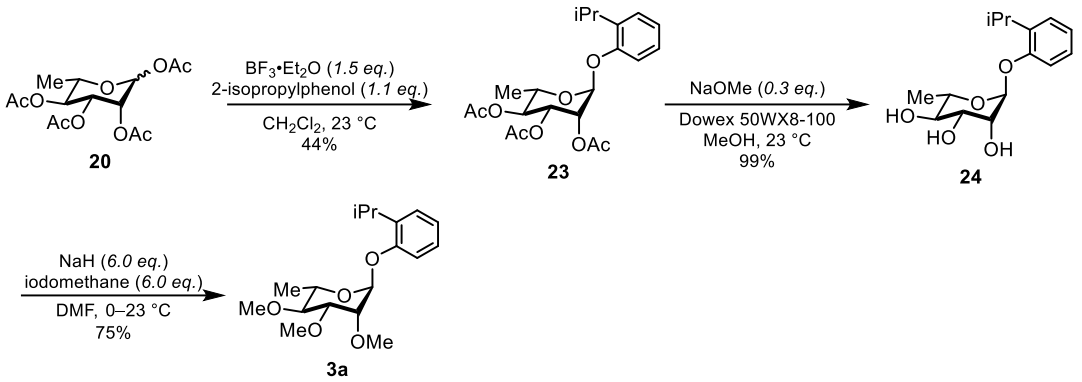


(2-methylphenyl)-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (2a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (90%, 0.301 g, 12.5 mmol, 4.5 equiv.) and fitted with a rubber septum. The vessel was then brought out of the box and attached to a nitrogen manifold. DMF (3 mL) was added followed by a solution of **22** (0.909 g, 2.8 mmol, 1.0 equiv.) in DMF (3 mL). The resulting mixture was stirred at room temperature for 30 minutes then cooled to -20 °C. At this point iodomethane (0.8 mL, 12.5 mmol, 4.5 equiv.) was added dropwise. The reaction mixture was then warmed to room temperature, diluted with a 4 mL aliquot of DMF, and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic phases were then washed twice with water and brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give the product as a colorless solid. Yield: 0.715 g (70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.17 (m, 3H), 6.91-6.94 (td, 6.9, 2.1 Hz, 1H), 5.56 (d, 1.9 Hz, 1H), 3.77-3.79 (dd, 3.3, 2.0 Hz, 1H), 3.68-3.71 (dd, 9.5, 3.2 Hz, 1H), 3.63-3.67 (m, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 3.56 (s, 3H), 3.20-3.24 (t, 9.5 Hz, 1H), 2.22 (s, 3H), 1.26-1.28 (d, 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.5, 130.7, 126.9, 126.9, 121.8, 113.7, 94.8, 82.0, 81.2, 77.4, 68.6, 60.9, 59.1, 57.8, 17.8, 16.1.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_5^+$: 319.1521, found: 319.1525

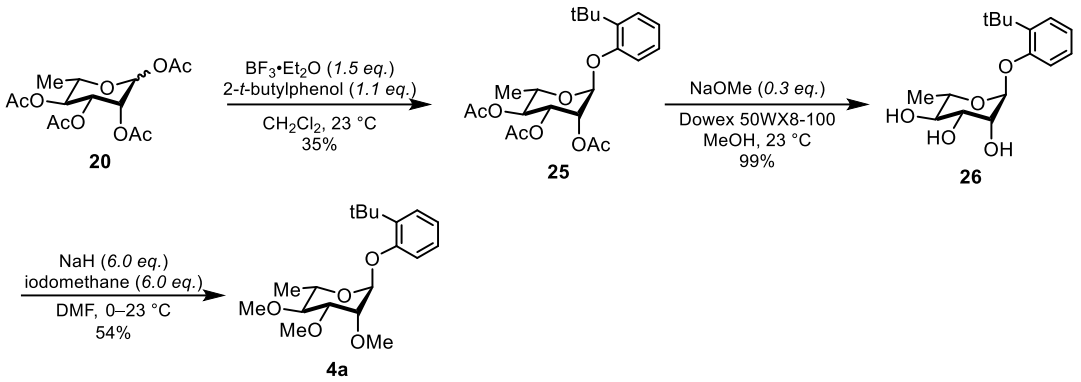


(2-isopropylphenyl)-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (3a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 1.29 g, 32.15 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box and attached to a nitrogen manifold. DMF (3.6 mL) was added followed by a solution of **24** (1.513 g, 5.4 mmol, 1.0 equiv.) in DMF (54 mL). The resulting mixture was stirred at room temperature for 30 minutes after which the solution was cooled to 0 °C and iodomethane (2.0 mL, 32.2 mmol, 6.0 equiv.) was added over the course of an hour in four portions. The reaction mixture was then allowed to warm to room temperature with stirring overnight at which point the reaction was quenched with 50 mL water and extracted with three 50 mL portions of ethyl acetate. The combined organic extracts were washed sequentially with three 50 mL portions of water and then brine, dried over Na_2SO_4, filtered and concentrated under vacuum giving a pale-yellow oil. The residue was then purified using silica gel chromatography (10% to 25% EtOAc/hexanes) to give the product as a colorless solid. Yield: 1.31 g (75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.23 (m, 1H) 7.14-7.19 (m, 2H), 7.00 (td, J = 7.4 Hz, J = 0.9 Hz, 1H), 5.56 (d, J = 1.8 Hz, 1H), 3.77-3.78 (m, 1H), 3.66-3.71 (m, 2H) 3.58 (s, 3H), 3.58 (s, 3H), 3.56 (s, 3H), 3.22-3.26 (m, 2H), 1.29 (d, J = 6.3 Hz, 3H), 1.24 (dd, J = 7.2 Hz, J = 3.2 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.9, 137.1, 126.8, 126.3, 122.2, 114.0, 95.2, 82.1, 81.4, 77.5, 68.8, 61.0, 59.2, 57.9, 27.4, 22.8, 22.6, 17.9.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{18}H_{28}NaO_5^+$: 347.1834, found: 347.1838

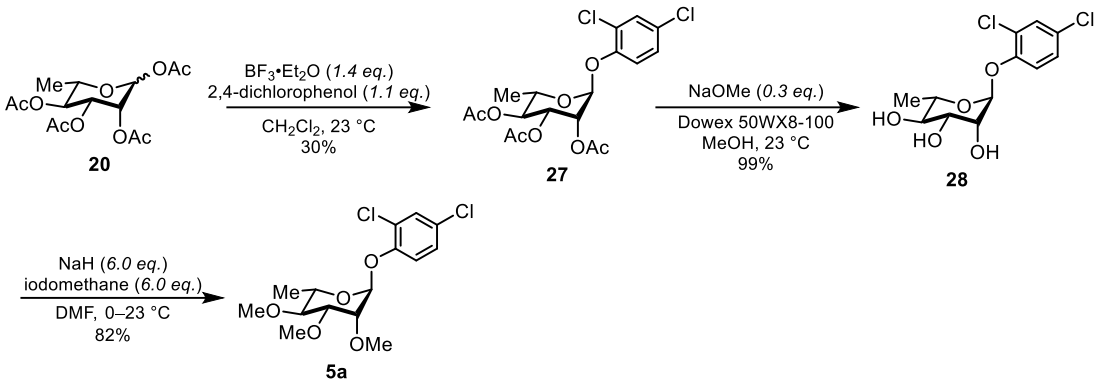


(2-*t*-butylphenyl)-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (4a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (90%, 0.982 g, 40.9 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box and attached to a nitrogen manifold. DMF (27 mL) was added followed by a solution of **26** (2.0 g, 6.8 mmol, 1.0 equiv.) in DMF (68 mL). The resulting mixture was stirred at room temperature for 30 minutes after which the solution was cooled to 0 °C and iodomethane (2.5 mL, 40.9 mmol, 6.0 equiv.) was added dropwise. The reaction mixture was then allowed to warm to room temperature with stirring overnight at which point the reaction was quenched with 100 mL water and extracted with three 50 mL portions of ethyl acetate. The combined organic extracts were washed with 100 mL of water and 100 mL of brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was then purified using silica gel chromatography (6% to 60% EtOAc/hexanes) to give the product as a white solid. Yield: 1.25 g (54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.31 (dd, J = 7.8, 1.6 Hz, 1H), 7.28 (d, 0.90 Hz, 1H), 7.17-7.19 (td, 7.4, 1.6 Hz, 1H), 6.96-6.98 (td, 7.6, 1.1 Hz, 1H), 5.58 (d, 1.7 Hz, 1H), 3.80-3.81 (dd, 3.3, 2.0 Hz, 1H), 3.73-3.75 (dd, 9.5, 3.2 Hz, 1H), 3.66-3.71 (m, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 3.56 (s, 3H), 3.23-3.26 (t, 9.5 Hz, 1H), 1.40 (s, 9H), 1.30-1.31 (d, 6.22 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.8, 137.9, 127.4, 126.8, 121.8, 114.4, 95.5, 82.0, 81.4, 77.4, 68.9, 61.0, 59.3, 57.9, 34.7, 30.1, 17.9.

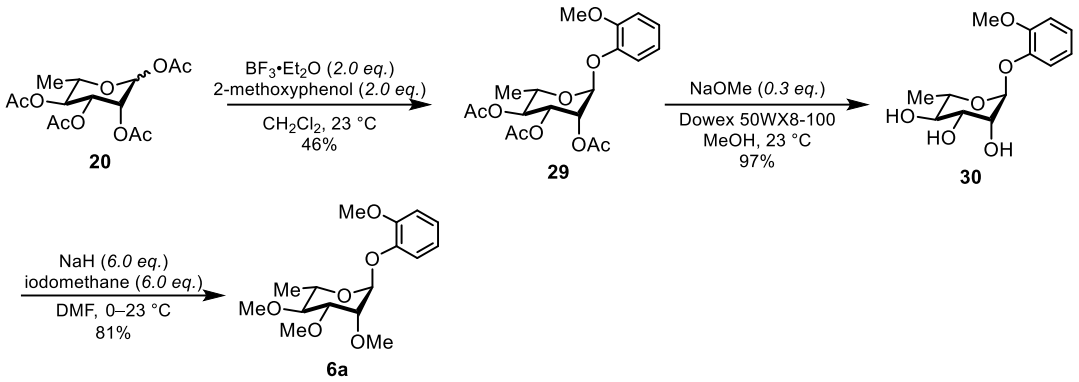
HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{19}H_{30}NaO_5^+$: 361.1991, found: 361.2001



(2,4-dichlorophenyl)-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (5a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (90%, 0.466 g, 19.4 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box and attached to a nitrogen manifold. 13 mL DMF was added followed by a solution of **28** (1.0 g, 3.2 mmol, 1.0 equiv.) in 31 mL DMF. The resulting mixture was stirred at room temperature for 30 minutes after which the solution was cooled to 0 °C and iodomethane (1.2 mL, 19.4 mmol, 6.0 equiv.) was added over the course of an hour in four portions. The reaction mixture was then allowed to warm to room temperature with stirring overnight at which point the reaction was quenched with 50 mL water and extracted with three 50 mL portions of ethyl acetate. The combined organic extracts were washed sequentially with three 50 mL portions of water and then brine, dried over Na_2SO_4, filtered and concentrated under vacuum giving the product as pale-yellow oil. Yield: 0.930 g (82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 2.6 Hz, 1H), 7.17-7.19 (m, 1H), 7.13-7.14 (m, 1H), 5.50 (d, J =1.9 Hz, 1H), 3.84-3.85 (dd, J = 3.4, 2.1 Hz, 1H), 3.70-3.72 (dd, 9.5, 3.3 Hz, 1H), 3.62-3.67 (m, 1H), 3.57 (s, 6H), 3.56 (s, 3H), 3.19-3.23 (t, 9.5 Hz, 1H), 1.25-1.27 (d, 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.7, 130.0, 127.8, 127.6, 124.7, 117.6, 96.4, 81.8, 80.9, 77.1, 69.2, 60.9, 59.4, 58.0, 17.8.

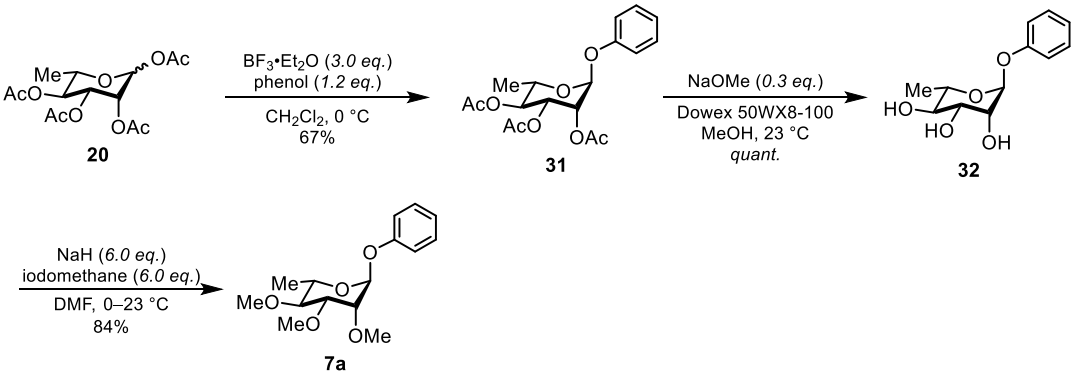


(2-methoxyphenyl)-2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (6a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 1.63 g, 40.8 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box and attached to a nitrogen manifold. 27 mL DMF was added followed by a solution of **30** (1.96 g, 6.80 mmol, 1.0 equiv.) in 68 mL DMF. The resulting mixture was stirred at room temperature for 30 minutes after which the solution was cooled to 0 °C and iodomethane (2.5 mL, 40.8 mmol, 6.0 equiv.) was added over the course of an hour in four portions. The reaction mixture was then allowed to warm to room temperature with stirring overnight at which point the reaction was quenched with 50 mL water and extracted with three 50 mL portions of ethyl acetate. The combined organic extracts were washed with 50 mL of water and 50 mL of brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give the product as a waxy colorless solid. Yield: 1.82 g (81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 7.02 (td, J = 7.7 Hz, 1.4 Hz, 1H), 6.88-6.92 (m, 2H), 5.50 (d, J = 1.7 Hz, 1H), 3.88 (dd, J = 3.3 Hz, J = 2.0 Hz, 1H), 3.82-3.85 (m, 4H), 3.74 (dd, J = 9.5 Hz, J = 3.4 Hz, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 3.55 (s, 3H), 3.20 (t, J = 9.4 Hz, 1H), 1.27 (d, J = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.5, 145.5, 123.5, 121.0, 118.9, 112.4, 96.7, 82.1, 80.8, 77.4, 68.7, 60.9, 59.1, 57.9, 55.8, 17.7.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_6^+$: 335.1471 found: 335.1475

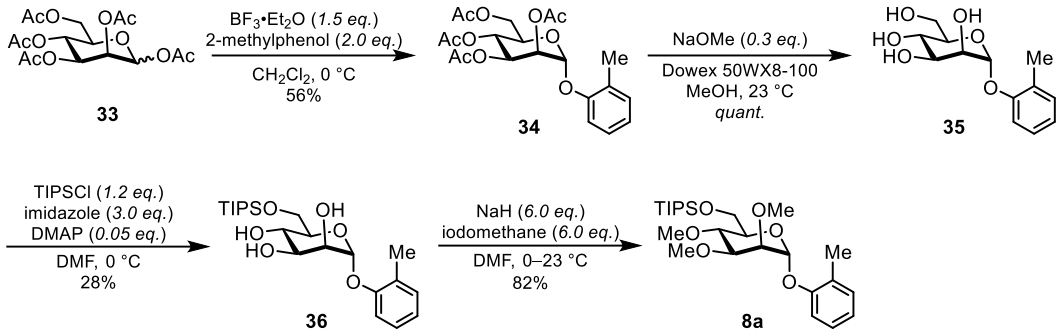


phenyl-2,3,4-tri-*O*-methyl-*α*-L-rhamnopyranoside (7a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60%, 0.998 g, 25.0 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought out of the box and attached to a nitrogen manifold. DMF (12.5 mL) was added followed by a solution of **32** (1.0 g, 4.2 mmol, 1.0 equiv.) in DMF (21 mL). The resulting mixture was stirred at room temperature for 30 minutes then cooled to 0 °C. At this point iodomethane (1.6 mL, 25.0 mmol, 6.0 equiv.) was added in four equal portions over the course of 2 hours. The reaction mixture was then warmed to room temperature, diluted with a 4 mL aliquot of DMF, and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic phases were then washed twice with water and brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was then purified using silica gel chromatography (10% to 25% EtOAc/Hex) to give the product as a colorless oil. Yield: 0.991 g (84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.31 (m, 2H), 7.06-7.07 (m, 2H), 7.01-7.03 (m, 1H), 5.55 (d, J = 1.8 Hz, 1H), 3.76 (dd, J = 3.4 Hz, J = 2.0 Hz, 1H), 3.65-3.70 (m, 2H), 3.57 (s, 6H), 3.55 (s, 3H), 3.20 (t, J = 9.0, 1H), 1.26 (d, J= 6.3 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 156.5, 129.6, 122.3, 116.4, 95.2, 82.2, 81.0, 77.5, 68.7, 61.1, 59.4, 58.0, 17.9

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{15}H_{22}NaO_5^+$: 305.1365 found: 305.1371

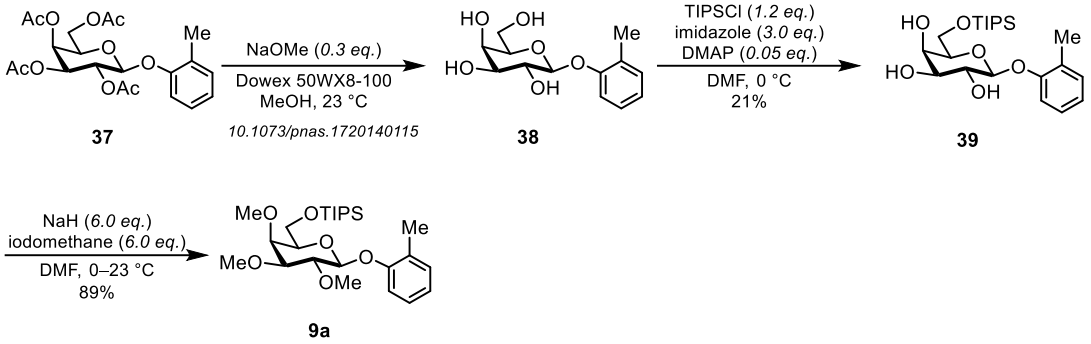


(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-*α*-D-mannopyranoside (8a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 0.452 g, 11.30 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box and attached to a nitrogen manifold and cooled to 0 °C. 19 mL DMF was added followed by a solution of **36** (0.800 g, 1.88 mmol, 1.0 equiv.) in 7.5 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (0.7 mL, 11.30 mmol, 6.0 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organics were then washed twice with water, once with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting residue was then purified by silica gel column chromatography (5% to 15% EtOAc/hexanes) to give the product as a colorless solid. Yield: 0.725 g (82%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.19 (m, 3H), 6.92 (t, J = 7.2 Hz, 1H), 5.60 (d, J = 1.5 Hz, 1H), 3.86-3.89 (m, 2H), 3.78-3.79 (m, 1H), 3.76 (dd, J = 9.3 Hz, J = 3.1 Hz, 1H), 3.67 (t, J = 9.3 Hz, 1H), 3.58 (m, 7H), 3.51 (s, 3H), 2.23 (s, 3H), 0.99-1.12 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.7, 130.6, 127.0, 126.9, 121.8, 114.3, 94.8, 81.2, 77.0, 75.9, 73.7, 62.6, 60.6, 58.3, 57.8, 17.9, 17.8, 16.2, 12.0.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_6Si^+$: 491.2805 found: 491.2814

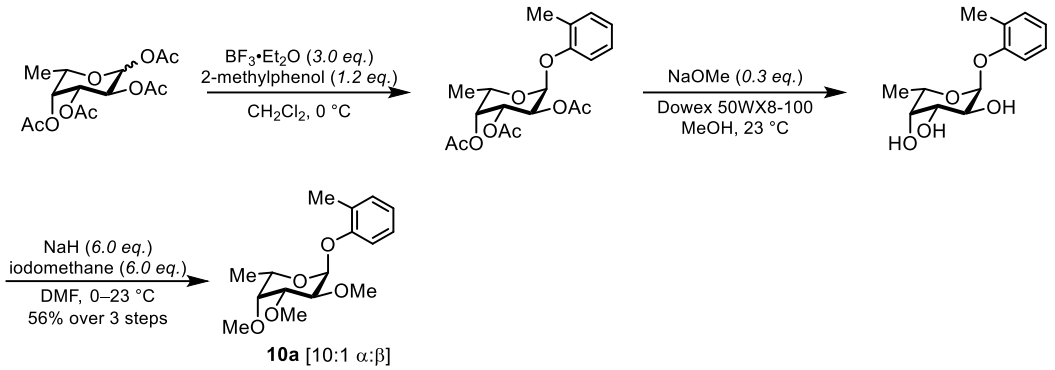


(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-β-D-galactopyranoside (9a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 0.368 g, 9.20 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. DMF (6.0 mL) was added followed by a solution of **39** (0.651 g, 1.53 mmol, 1.0 equiv.) in 15 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (0.6 mL, 9.20 mmol, 6.0 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organics were then washed twice with water, once with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was then purified by silica gel column chromatography (10% to 25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.623 g (89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.13 (m, 2H), 7.00 (d, J = 7.9 Hz, 1H), 6.90-6.92 (m, 1H), 4.84 (d, J = 8.0 Hz, 1H), 3.91-3.94 (m, 1H), 3.82-3.85 (m, 2H), 3.68 (s, 3H), 3.65-3.67 (m, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 3.52-3.54 (m, 1H), 3.27 (dd, J = 9.8 Hz, J = 2.9 Hz, 1H), 2.28 (s, 3H), 0.97-1.15 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.7, 130.7, 127.6, 126.7, 122.0, 114.6, 101.4, 84.2, 80.8, 75.1, 74.3, 61.5, 61.3, 61.1, 58.5, 18.0, 18.0, 16.5, 11.9.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_6Si^+$: 491.2805 found: 491.2817



(2-methylphenyl)-2,3,4-tri-*O*-methyl-L-fucopyranoside (10a):

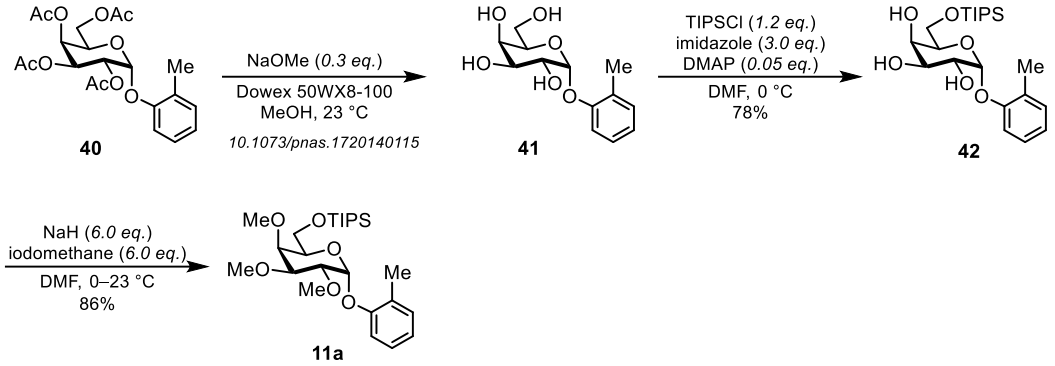
A round bottom flask was charged with tetraacetyl-L-fucose, (4.34 g, 13.07 mmol, 1.0 equiv.) 65 mL dichloromethane, and 2-methylphenol (1.70 g, 15.78 mmol, 1.2 equiv.). The reaction was then cooled to 0 °C and $BF_3 \bullet OEt_2$ (4.8 mL, 39.20 mmol, 3.0 equiv.) was added dropwise and the warmed to room temperature and stirred overnight at room temperature. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. Excess 2-methylphenol was then removed via silica gel column chromatography to give the crude tri-*O*-acetyl-1-aryloxyfucose as an oil. This material was taken up in 10.7 mL MeOH followed by the addition of NaOMe (0.174 g, 3.21 mmol, 30 mol %) and was allowed to stir for two hours. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the crude 1-aryloxyfucose as a colorless solid (2.79 g).

In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with the crude 1-aryloxyfucose as a solution in 100 mL DMF and NaH (60% in mineral oil, 2.77 g, 64.28 mmol, 6.0 equiv.). The flask was fitted with a rubber septum as was brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. Iodomethane (4.1 mL, 64.28 mmol, 6.0 equiv.) was added over the course of an hour in four portions. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed twice with water and twice with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give a pale-yellow oil. The residue was then purified using silica gel chromatography (10% to 25% EtOAc/hexanes) to give the product as a mixture of anomers (10:1 α/β) as a colorless oil. Yield 2.17 g, (56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.14 (m, 3H), 6.91-6.93 (m, 1H), 5.60 (d, J = 3.0 Hz, 1H), 4.03 (q, J = 6.4 Hz, 1H), 3.76-3.80 (m, 2H), 3.64 (s, 3H), 3.58 (s, 3H), 3.53-3.53 (m, 1H), 3.47 (s, 3H), 2.28 (s, 3H), 1.25 (d, J = 6.6 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 155.6, 130.7, 127.9, 126.9, 121.9, 114.8, 95.9, 80.4, 79.0, 77.4, 67.1, 61.8, 58.4, 58.0, 16.5, 16.2.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_5^+$: 319.1521 found: 319.1525

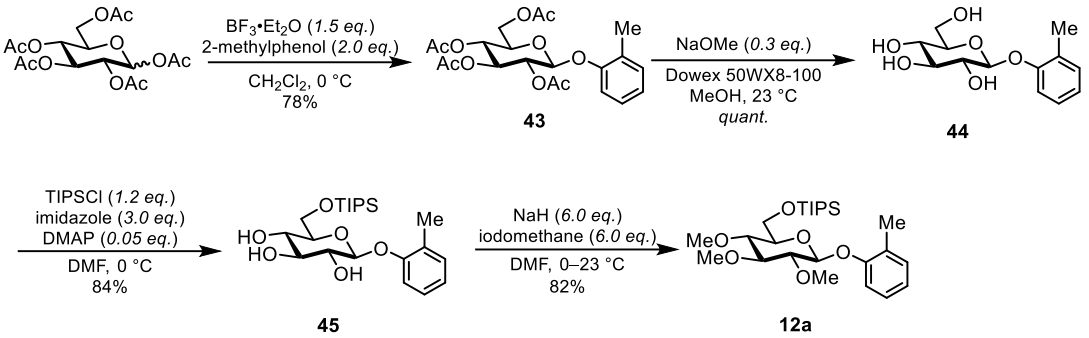


(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-α-D-galactopyranoside (11a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 0.751 mg, 18.80 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. 12.5 mL DMF was then added followed by a solution of **42** (1.330 g, 3.13 mmol, 1.0 equiv.) in 31 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (1.2 mL, 18.80 mmol, 6.0 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organics were then washed twice with water, once with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (10% to 25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 1.256 g (86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.14 (m, 3H), 6.901-6.94 (m, 1H), 5.60 (d, J = 3.0 Hz, 1H), 3.93-3.95 (m, 2H), 3.86-3.89 (t, J = 8.6 Hz, 1H), 3.78-3.83 (m, 2H), 3.70-3.72 (m, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 3.50 (s, 3H), 2.29 (s, 3H), 1.02-1.10 (m, 21H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 155.6, 130.7, 128.2, 126.9, 122.2, 115.5, 96.4, 80.4, 77.9, 74.9, 71.6, 61.3, 61.3, 58.5, 58.0, 18.0, 18.0 16.2, 11.8.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_6Si^+$: 491.2805 found: 491.2818

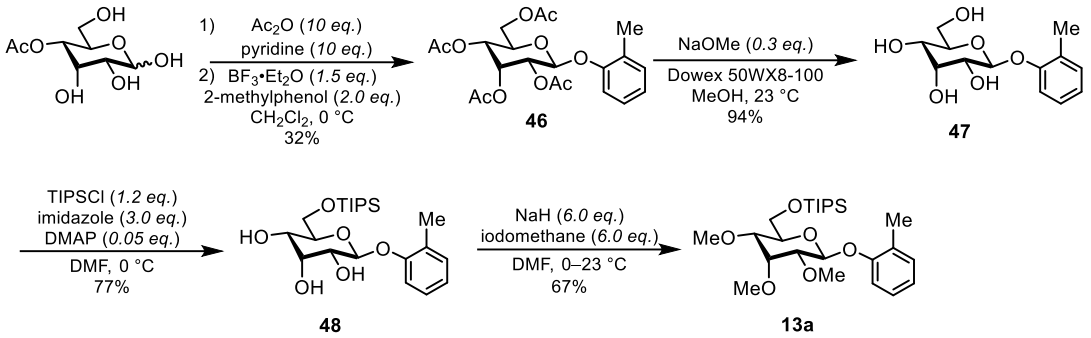


(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-β-D-glucopyranoside (12a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 2.063 g, 51.57 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. 34 mL DMF was added followed by a solution of **45** (3.65 g, 8.60 mmol, 1.0 equiv.) in 86 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (3.2 mL, 51.57 mmol, 6.0 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organics were then washed twice with water, once with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was then purified by silica gel column chromatography (5% to 25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 3.285 g (82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, J = 7.6 Hz, 1H), 7.07-7.10 (m, 2H), 6.91-6.94 (m, 1H), 4.80 (d, J = 7.2 Hz, 1H), 3.97 (dd, J = 11.0 Hz, J = 1.8 Hz, 1H), 3.86 (dd, J = 11.0, J = 5.1, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 3.23-3.33 (m, 4H), 2.28 (s, 3H), 1.03-1.12 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.8, 130.6, 127.7, 126.8, 122.3, 115.7, 101.5, 86.8, 83.9, 79.2, 76.4, 62.6, 61.0, 60.8, 60.4, 18.0, 17.9, 16.5, 11.9.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_6Si^+$: 491.2805 found: 491.2812

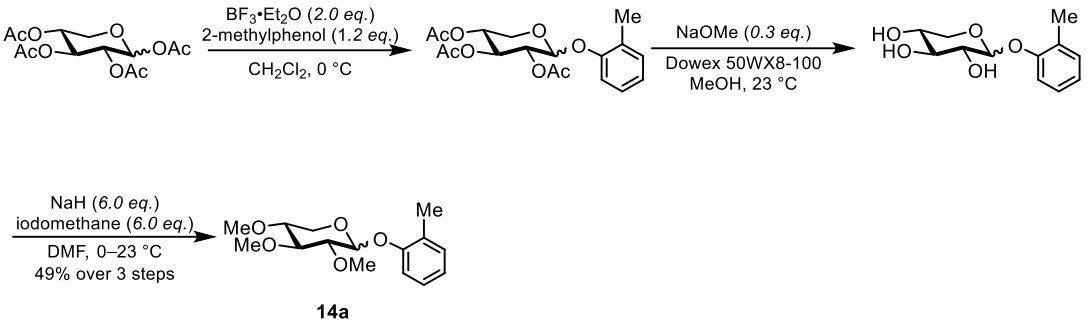


(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-β-D-allopyranoside (13a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 0.266 g, 6.64 mmol, 6.0 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. 4.4 mL DMF was added followed by a solution of **48** (0.470 g, 1.11 mmol, 1.0 equiv.) in 11 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (0.4 mL, 6.64 mmol, 6.0 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were then washed twice with water, once with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (10% to 25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.346 g (67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07-7.14 (m, 3H), 6.89-6.91 (m, 1H), 5.28 (d, J = 7.8 Hz, 1H), 4.08 (t, J = 2.5, 1H), 3.96-3.96 (m, 1H), 3.84-3.88 (m, 2H), 3.64 (s, 3H), 3.63 (s, 3H), 3.46 (s, 3H), 3.34 (dd, J = 9.6 Hz, J = 2.6 Hz, 1H), 3.28 (dd, J = 7.8 Hz, J = 2.6 Hz, 1H), 2.27 (s, 3H), 1.01-1.11 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 156.0, 130.4, 127.7, 126.7, 122.0, 115.8, 99.3, 81.2, 77.3, 76.0, 73.8, 62.8, 61.3, 59.4, 57.4, 18.0, 18.0, 16.5, 12.0.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_6Si^+$: 491.2805 found: 491.2817



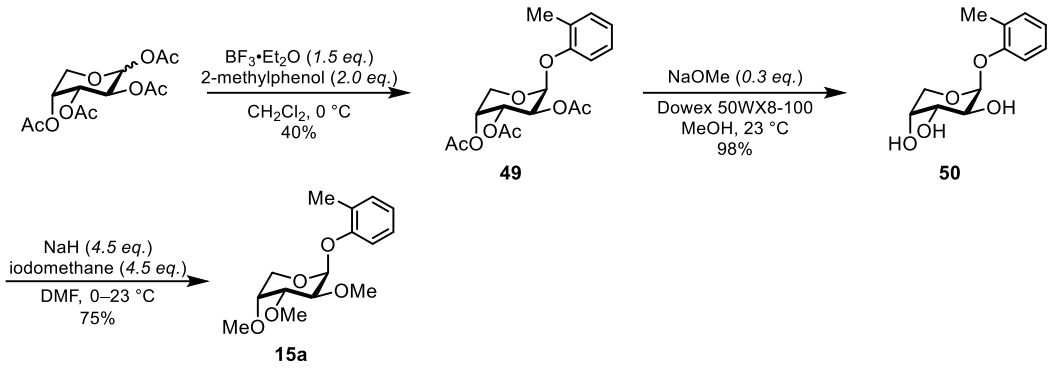
14a

(2-methylphenyl)-2,3,4-tri-*O*-methyl-D-xylopyranoside (14a): A round bottom flask was charged with tetraacetyl xylose, (5.00g, 15.72 mmol, 1.0 equiv.) 79 mL dichloromethane, and 2-methylphenol (2.04 g, 18.86 mmol, 1.2 equiv.). The mixture was then cooled to 0 °C and $BF_3 \bullet OEt_2$ (3.9 mL, 31.43 mmol, 2.0 equiv.) was added dropwise, after which the flask was allowed to warm to room temperature with stirring overnight. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. Excess 2-methylphenol was then removed via silica gel column chromatography to give the crude tri-*O*-acetyl-1-aryloxyxylose as an oil. This material was then dissolved in 16 mL MeOH followed by the addition of NaOMe (0.249 g, 4.70 mmol, 30 mol %) and was allowed to stir for two hours. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the crude 1-aryloxyxylose as a colorless solid (2.29 g). In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with the crude 1-aryloxyxylose as a solution in 100 mL DMF and NaH (60% in mineral oil, 2.28 g, 56.99 mmol, 6.0 equiv.). The flask was fitted with a rubber septum as was brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. Iodomethane (3.5 mL, 56.99 mmol, 6.0 equiv.) was then added over the course of an hour in four portions. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were then washed twice with water and twice with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give a pale-yellow oil. The residue was then purified using silica gel chromatography (10% to 25% EtOAc/hexanes) to give the product as a mixture of anomers (1:2 α/β) as a yellow oil. Yield 2.198 g, (49%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.16 (m, 6H), 7.06-7.08 (m, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.92-7.00 (m, 3H), 5.57 (d, J = 3.4 Hz, 1H), 4.88 (d, J = 7.2 Hz, 2H), 4.05 (dd, J = 11.7 Hz, J = 5.0 Hz, 2H) 3.76-3.78 (m, 2H), 3.69 (s, 3H), 3.65-3.67 (m, 12H), 3.56-3.58 (m, 2H), 3.47-3.52 (m, 15 H), 3.22-3.38 (m, 11H), 2.31 (s, 3H), 2.29 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 155.3, 155.0, 130.9, 130.9, 127.7, 126.9, 126.8, 122.4, 122.1, 114.9, 114.4, 101.6, 95.1, 85.1, 83.1, 82.5, 81.5, 79.7, 79.3, 63.2, 60.9, 60.7, 60.7, 60.2, 58.9, 58.8, 58.7, 16.4.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{15}H_{22}NaO_5^+$: 305.1365 found: 305.1370



(2-methylphenyl)-2,3,4-tri-*O*-methyl-α-L-arabinopyranoside (15a): In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with NaH (60% in mineral oil, 0.830 g, 9.40 mmol, 4.5 equiv.) and fitted with a rubber septum. The vessel was then brought outside of the box, attached to a nitrogen manifold, and cooled to 0 °C. 13 mL DMF was added followed by a solution of **50** (1.11 g, 4.62 mmol, 1.0 equiv.) in 46 mL DMF. The resulting mixture was stirred for one hour after which iodomethane (1.3 mL, 4.62 mmol, 4.5 equiv.) was added in four portions over two hours. The reaction mixture was then warmed to room temperature and stirred overnight at which point the reaction was quenched with water and extracted three times with ethyl acetate. The combined organics were then washed twice with water, once with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude material was purified via flash chromatography with 10-40% EtOAc/hexanes to give the product as a colorless solid. Yield: 0.980g (75%).

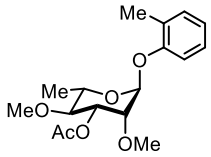
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.01 (m, 3H), 6.86 (dt, J = 7.4 Hz, J = 1.2 Hz, 1H), 5.62 (d, J = 3.0 Hz, 1H), 3.89 (dd, J = 12.6 Hz, J = 2.2, 1H), 3.78-3.83 (m, 2H), 3.76 (dd, J = 12.6 Hz, J = 0.6 Hz, 1H), 3.72-3.73 (m, 1H), 3.56 (s, 3H), 3.51 (s, 3H), 3.50 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 130.8, 127.9, 126.9, 122.1, 114.6, 96.2, 78.4, 77.6, 75.5, 59.5, 59.0, 57.6, 57.5, 16.2.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{15}H_{22}NaO_8^+$: 305.1365 found: 305.1370

Catalytic Products and Procedures

General procedure for iridium-catalyzed 3-demethylation/acetylation: In air, a 20 mL scintillation vial was charged with the phenol-glycoside (0.426 mmol, 1.0 equiv.) and $[(COD)Ir(PPh_3)_2]BAr^F{}_{24}$ (**1**) (0.029 g, 0.0170 mmol, 4 mol %). The vial was then fitted with a screw cap septum and a vent needle. 1.4 mL dichloromethane was added through the septum followed by triethylsilane (0.2 mL, 1.278 mmol, 3 equiv.). The reaction was then stirred at room temperature for 1 hour at which point 2 mL of methanol was added and the mixture was allowed to stir for an additional hour. The crude mixture was then concentrated under vacuum and 2 mL pyridine and 2 mL acetic anhydride was added and the solution stirred overnight. Upon completion the reaction mixture was concentrated under vacuum, and the resulting residue was purified according to the procedures for each product below.



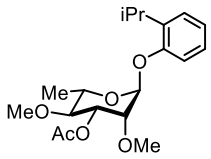
2c

(2-methylphenyl)-3-*O*-acetyl-2,4-di-*O*-methyl-α-L-rhamnopyranoside (2c): This product was prepared according to the general procedure for demethylation/acetylation above using **2a** (0.126 g, 0.426 mmol). After completion the reaction was purified by column chromatography (5%-50% EtOAc/hexanes) to give the product as a colorless oil. Yield 0.097 g (70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.16 (m, 3H), 6.93 (td, J = 7.1 Hz, J = 1.5 Hz, 1H), 5.51 (d, J = 1.9 Hz, 1H), 5.35 (dd, J = 9.7 Hz, J = 3.3 Hz 1H), 3.89 (dd, J = 3.6, J = 2.1 1H), 3.76-3.79 (m, 1H), 3.51-3.51 (m, 6H), 3.41 (t, J = 9.5 Hz, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.4, 154.5, 130.9, 127.4, 126.9, 122.0, 113.8, 95.2, 80.3, 78.7, 73.7, 68.6, 60.6, 59.4, 21.2, 17.9, 16.2.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{17}H_{24}NaO_6^+$: 347.1471 found: 347.1476



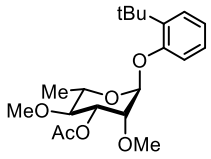
3c

(2-isopropylphenyl)-3-*O*-acetyl-2,4-di-*O*-methyl-*α*-L-rhamnopyranoside (3c): This product was prepared according to the general procedure for demethylation/acetylation above using **3a** (0.138 g, 0.426 mmol). After completion the reaction was purified by column chromatography (10%-50% EtOAc/hexanes) to give the product as a colorless solid. Yield 0.108 g (72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 7.2 Hz, 1H), 7.13-7.16 (m, 2H), 6.99-7.01 (m, 1H), 5.50 (d, J = 1.9 Hz, 1H), 5.34 (dd, J = 9.6 Hz, J = 3.5 Hz, 1H), 3.86 (dd, J = 3.4 Hz, J = 2.1 Hz, 1H), 3.76-3.81 (m, 1H), 3.52 (s, 3H), 3.51 (s, 3H), 3.35 (t, J = 9.6 Hz, 1H), 3.29 (pent, J = 7.0 Hz, 1H), 2.19 (s, 3H), 1.31 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.4, 153.8, 137.5, 126.7,126.4, 122.3, 113.8, 95.3, 80.3, 78.7, 73.7, 68.7, 60.6, 59.4, 27.5, 22.8, 22.6, 21.3, 17.9.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{19}H_{28}NaO_6^+$: 375.1784 found: 375.1788



4c

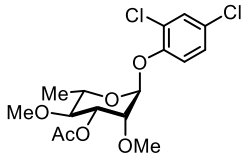
(2-*t*-butylphenyl)-3-*O*-acetyl-6-2,4-di-*O*-methyl-*α*-L-rhamnopyranoside (4c):

This product was prepared according to a minor modification of the general procedure for demethylation/acetylation above using **4a** (0.144 g, 0.426 mmol). For this substrate, 2 hours was allowed to elapse prior to the addition of methanol. After completion the reaction was purified by column chromatography (6%-25% EtOAc/hexanes) to give the product as a colorless oil. Yield 0.124 g (83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.17 (dd, J = 8.3 Hz, J = 1.1 Hz, 1H), 7.10 (td, J = 8.2 Hz, J = 1.7 Hz, 1H), 6.89 (td, J = 7.7 Hz, J = 1.2 Hz, 1H), 5.46 (d, J = 1.8 Hz, 1H), 5.30 (dd, J = 9.9 Hz, J = 3.4 Hz 1H), 3.83 (dd, J = 3.3, J = 2.1 1H), 3.68-3.73 (m, 1H), 3.45 (s, 3H), 3.43 (s, 3H), 3.31 (t, J = 9.6 Hz, 1H), 2.11 (s, 3H), 1.35 (s, 9H), 1.26 (d, J = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 155.6, 138.4, 127.2, 126.9, 121.8, 114.2, 95.3, 80.1, 78.5, 73.9, 68.8, 60.7, 59.5, 34.7, 30.1, 21.2, 17.9.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{20}H_{30}NaO_6^+$: 389.1940 found: 389.1947



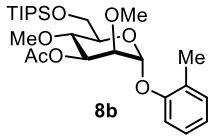
5c

(2,4-dichlorophenyl)-3-*O*-acetyl-2,4-di-*O*-methyl-α-L-rhamnopyranoside (5c): This product was prepared according to the general procedure for demethylation/acetylation above using **5a** (0.126 g, 0.426 mmol). After completion the reaction was purified by column chromatography (25%-50% EtOAc/hexanes) followed by a recrystallization from pentane at -20 °C to give the product as a colorless solid. Yield 0.105 g (65%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, J = 2.5 Hz, 1H), 7.17 (dd, J = 8.8 Hz, J = 2.5 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H), 5.45 (d, J = 2.1 Hz, 1H), 5.35 (dd, J = 9.5 Hz, J = 3.3 Hz, 1H), 3.93 (t, J = 3.1 Hz, 1H), 3.76-3.80 (m, 1H), 3.52 (s, 3H), 3.51 (s, 3H), 3.32 (t, J = 10.0 Hz, 1H), 2.18 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.3, 150.7, 130.1, 127.8, 127.7, 125.1 117.8, 96.7, 80.3, 78.2, 73.1, 69.1, 60.5, 59.6, 21.2, 17.9.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{16}H_{20}Cl_2NaO_6^+$: 401.0535 found: 401.0540



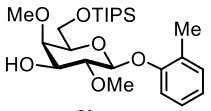
8b

(2-methylphenyl)-3-*O*-acetyl-6-*O*-triisopropylsilyl-2,4-di-*O*-methyl-α-D-mannopyranoside (8b): This product was prepared according to a minor modification of the general procedure for demethylation/acetylation above using **8a** (0.194 g, 0.415 mmol). For this substrate, 2 hours was allowed to elapse prior to the addition of methanol. After completion the reaction was purified by column chromatography (5%-40% EtOAc/hexanes) to give the product as a colorless oil. Yield 0.130 g (63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10-7.16 (m, 3H), 6.92 (td, J = 7.3 Hz, J = 1.0 Hz, 1H), 5.54 (d, J = 2.1 Hz, 1H), 5.40 (dd, J = 9.44 Hz, J = 3.3 Hz 1H), 3.85-3.91 (m, 3H), 3.80 (t, J = 9.5 Hz, 1H), 3.66 (ddd, J = 9.7 Hz, J = 4.3 Hz, J = 1.6 Hz, 1H), 3.52 (s, 3H), 3.43 (s, 3H), 3.46 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 1.06-1.11 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 155.6, 130.8, 127.2, 126.9, 121.8, 114.2, 95.3, 78.3, 74.2, 73.7, 73.6, 62.5, 60.3, 58.6, 21.3, 17.9, 17.9, 16.2, 12.0.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{26}H_{44}NaO_7Si^+$: 519.2754 found: 519.2765
Elemental analysis for $C_{26}H_{44}O_7Si$: C, 62.87; H, 8.93. Found: C 62.56, H, 8.89



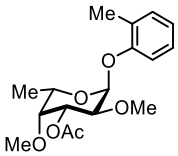
9b

(2-methylphenyl)-6-*O*-triisopropylsilyl-2,4-di-*O*-methyl-β-D-galactopyranoside (9b): This product was prepared according to a minor modification of the general procedure for demethylation/acetylation above using **9a** (0.194 g, 0.415 mmol). For this substrate, 2 hours was allowed to elapse prior to the addition of methanol. The product was isolated as the 3-hydroxy derivative by omission of the acylation step. After completion the reaction was purified by column chromatography (5%-40% EtOAc/hexanes) to give the product as a colorless solid. Yield 0.140 g (75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10-7.14 (m, 2H), 6.97 (d, J = 8.1 Hz, 1H), 6.92 (td, J = 7.4 Hz, J = 0.6 Hz, 1H), 4.87 (d, J = 7.7 Hz, 1H), 3.91-3.94 (m, 1H), 3.84-3.86 (m, 1H) 3.77 (d, J = 3.1 Hz, 1H), 3.72 (s, 3H), 3.68-3.71 (m, 1H), 3.67 (s, 3H), 3.59-3.61 (m, 1H), 3.54-3.57 (m, 1H), 2.28 (s, 3H), 1.00-1.14 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.4, 130.8, 127.4, 126.8, 122.1, 114.3, 101.0, 81.6, 77.2, 75.4, 74.2, 61.7, 61.4, 61.3, 18.0, 18.0, 17.9, 16.6, 11.9.

HRMS (ESI/Q-TOF) m/z $[M+H]^+$ calcd for $C_{24}H_{43}O_6Si^+$: 455.2823 found: 455.2843



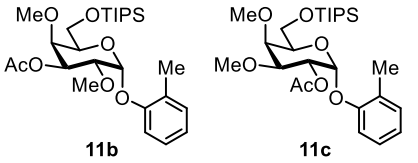
10b

(2-methylphenyl)-3-*O*-acetyl-2,4-tri-*O*-methyl-*α*-L-fucopyranoside (10b): This product was prepared according to the general procedure for demethylation/acetylation above using **10a** (0.126 g, 0.426 mmol). After completion the reaction was purified by column chromatography (5%-40% EtOAc/hexanes) to give the product as a colorless oil. Yield 0.092 g (67%).

^{1}H NMR (600 MHz, $CDCl_3$) 7.11-7.15 (m, 3H), 6.91-6.94 (m, 1H), 5.63 (d, J = 3.7 Hz, 1H), 5.36 (dd, J = 10.9 Hz, J = 3.1 Hz, 1H), 4.12 (q, J = 6.3 Hz, 1H), 3.88 (dd, J = 10.6, J = 3.3 Hz, 1H), 3.59 (d, J = 2.6 Hz, 1H), 3.55 (s, 3H), 3.44 (s, 3H), 2.28 (s, 3H), 2.17 (s, 3H), 1.23 (d, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 155.3, 130.7, 127.9, 126.8, 121.9, 114.3, 95.6, 80.1, 75.4, 73.2, 66.6, 61.8, 58.5, 21.1, 16.1, 16.0.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{17}H_{24}NaO_6^+$: 347.1471 found: 347.1476



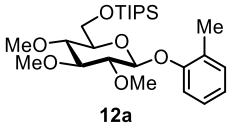
11b **11c**

(2-methylphenyl)-6-*O*-triisopropylsilyl-2,4-di-*O*-methyl-β-D-galactopyranoside (11b & 11c): This product was prepared according to the general procedure for demethylation/acetylation above using **11a** (0.194 g, 0.415 mmol). After completion the reaction was purified by column chromatography (6%-50% EtOAc/hexanes) to give a 5:1 mixture of **11b**:**11c** as a colorless oil. Yield 0.165 g (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.14 (m, 3H), 6.91-6.95 (m, 1H), 5.62 (d, J = 3.4 Hz, 1H), 5.42 (dd, J = 10.5 Hz, J = 3.0 Hz, 1H), 4.02-4.05 (m, 1H), 3.93 (m, 1H), 3.83-3.91 (m, 2H), 3.70-3.73 (m, 1H), 3.57 (s, 3H), 3.46 (s, 3H), 2.29 (s, 3H), 2.18 (s, 3H), 0.98-1.10 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 155.4, 130.7, 126.8, 122.2, 115.2, 96.1, 76.6, 76.0, 72.9, 71.1, 61.4, 61.1, 58.6, 21.2, 17.9, 16.1, 11.8, 11.8.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{26}H_{44}NaO_7Si^+$: 519.2754 found: 519.2764
Elemental analysis for $C_{26}H_{44}O_7Si$: C, 62.87; H, 8.93. Found: C 62.52, H, 9.07



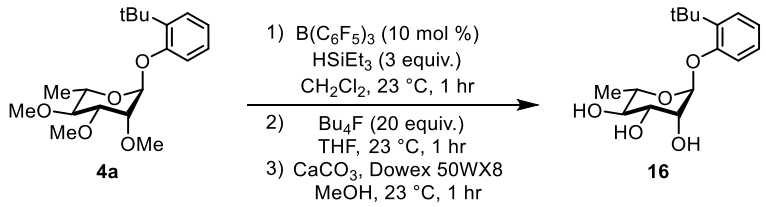
12a

(2-methylphenyl)-6-*O*-triisopropylsilyl-2,3,4-tri-*O*-methyl-β-D-glucopyranoside (12a): The attempted reduction of **12a** (0.194 g, 0.415 mmol) was conducted according to the general procedure for demethylation/acetylation above. After completion the unconverted starting material was separated by column chromatography (5%-25% EtOAc/hexanes). Recovery: 0.074 g (38%) **12a**. No products of 3-demethylation are observed.

General procedure for iridium-catalyzed 3-demethylation/acetylation (NMR-Scale):

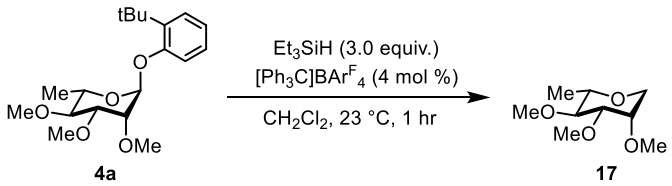
A 4 mL vial was charged with the 1-aryloxy-glycoside (0.030 mmol, 1.0 equiv.), 0.1 mL of a 0.020 g/mL stock solution of $[(COD)Ir(PPh_3)_2]BAr^{F}{}_{24}$ in dichloromethane (0.0012 mmol, 0.04 equiv.) followed by triethylsilane (14 μL, 0.10 mmol, 3 equiv.). The reaction was then allowed to stand at room temperature for 1 hour at which point 0.3 mL of methanol was added and the mixture was stirred for an additional hour. Upon completion the solution was concentrated under vacuum and taken up in $CDCl_3$ for analysis by ^{1}H NMR. 5 μL of tetrachloroethane as an internal standard.

Procedures for Experiments in Equations 2-5



Global demethylation with B(C_6F_5) as the catalyst (16) (eqn. 2): A dry 20 mL scintillation vial equipped with a stir bar in the glove box was charged with **4a** (0.154 g, 0.43 mmol, 1.0 equiv.) and tris(pentafluorophenyl)borane (0.022 g, 0.043 mmol, 10 mol %). 1.4 mL dichloromethane was then added followed by triethylsilane (0.7 mL, 4.26 mmol, 10.0 equiv.). The reaction was fitted with a cap and stirred for one hour. Upon completion the reaction mixture was quenched with 3 mL of methanol and stirred for an additional hour. The crude mixture was then concentrated under vacuum, and the resulting residue was taken up in 3.0 mL THF and treated with solid tetrabutylammonium fluoride hydrate (2.6 g, 9.94 mmol, 20 equiv.). After one hour the reaction mixture was diluted with 6.0 mL methanol and 1.0 g of calcium carbonate and 2.0 g of Dowex® 50WX8-100 were added. The resulting suspension was stirred for an additional hour. Upon completion the mixture was filtered through a pad of Celite which was washed with methanol. The filtrate was then concentrated under vacuum to give the crude triol as a colorless solid. An unidentified tetrabutylammonium salt could not be separated from the product, however the material was assessed to be 85% **16** by mass using ^{1}H NMR against an internal standard. Yield: 0.113 g (71% yield of **16**).

Spectral details match the independently prepared compound (**26**, given below).



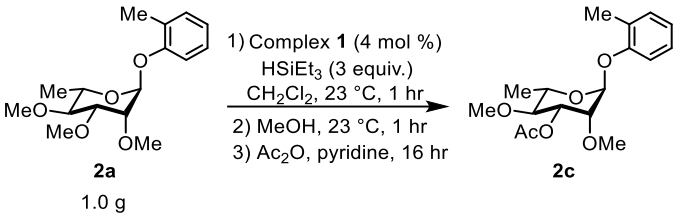
Anomeric reduction of 4a by [triphenylcarbenium][BAr^F_4] (eqn. 3): A one dram vial was charged with **4a** (0.030 mmol, 1.0 equiv.), 0.1 mL of a freshly-prepared 0.013 g/mL stock solution of [Ph_3C]BAr^F_4 in dichloromethane (0.0012 mmol, 0.04 equiv.) followed by triethylsilane (14 μL, 0.10 mmol, 3 equiv.). The vial was fitted with a screw cap and the reaction was stirred at room temperature for 1 hour at which point 0.3 mL of methanol was added and the mixture was allowed to stir for an additional hour. Upon completion, the solution was concentrated under vacuum and taken up in $CDCl_3$ for

analysis by ^{1}H NMR. 5 μL of tetrachloroethane was added as an internal standard. NMR yield of **17**: 65±8%, average of 4 runs.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.09 (dd, J = 12.9 Hz, J = 2.2 Hz, 1H), 3.59 (t, J = 2.4 Hz, 1H), 3.55 (s, 3H), 3.48 (s, 3H), 3.45 (s, 3H), 3.25 (dd, J = 12.9 Hz, J = 0.8 Hz, 1H), 3.13-3.20 (m, 2H), 3.08-3.11 (m, 1H), 1.30 (d, J = 6.0 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 84.4, 82.3, 76.4, 75.6, 65.8, 61.2, 57.5, 57.3, 18.2

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_9H_{18}NaO_4^+$: 213.1103 found: 213.1134



C_3 demethylation using a gram of substrate. In air, a 100 mL round bottom flask was charged with **2a** (1.0 g, 3.37 mmol, 1.0 equiv.) and $[(COD)Ir(PPh_3)_2]BAr^{F}{}_{24}$ (0.226 g, 0.13 mmol, 4 mol %). The round bottom flask was then fitted with a sleeve stopper and a bubbler. 11 mL of anhydrous dichloromethane was added through the stopper, the solution was then cooled to 0 °C followed by the dropwise addition of triethylsilane (1.6 mL, 10.12 mmol, 3 equiv.). The reaction was then stirred at room temperature for 1 hour at which point 20 mL of anhydrous methanol was slowly added and the mixture was allowed to stir for an additional hour. The crude mixture was then concentrated under vacuum and 10 mL pyridine and 10 mL acetic anhydride was added and the solution stirred overnight. After completion the reaction was purified by silica gel column chromatography (5%-50% EtOAc/hexanes) to give the product as a white solid. Yield 0.591 g (59%).

Spectral details match independently prepared **2c** (given above).

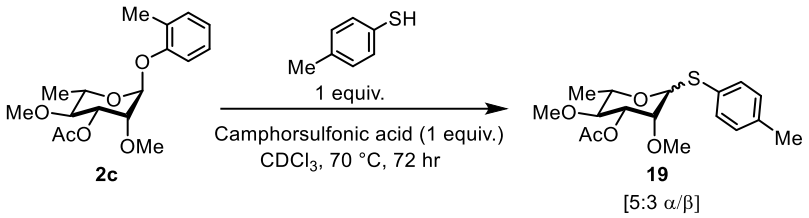
Displacement of 2-methylphenol group to give 18 (eqn. 4): A 20 mL scintillation vial was charged with 1.5 mL methanol followed by the addition of acetyl chloride (22 μL, 0.31 mmol, 1.0 equiv.) and **2c** (0.100 g, 0.31 mmol, 1.0 equiv.). The vial was fitted with a screw cap and the solution was then heated to 70 °C and stirred overnight. The next day the reaction mixture was cooled to room temperature and purified by silica gel

column chromatography (25% to 100% EtOac/hexanes) to give the product as a colorless oil. Yield 0.060 g (95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.69 (d, J = 1.26 Hz, 1H), 3.77 (d, J = 6.42 Hz, 1H), 3.55 (s, 3H), 3.51-3.55 (m, 1H), 3.47 (s, 3H), 3.43 (dd, J = 3.84 Hz, J = 1.56 Hz, 1H), 3.33 (s, 3H), 2.94 (t, J = 9.42 Hz, 1H), 2.44 (bs, 1H), 1.28 (d, J = 6.30 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 97.3, 83.9, 80.7, 71.4, 67.1, 61.0, 59.0, 54.9, 18.0

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_9H_{18}NaO_5^+$: 229.1052 found: 229.1081



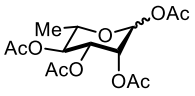
Displacement of 2-methylphenol group with p-thiocresol to give 19 (eqn. 5): A 4 ml scintillation vial was charged with **2c** (0.050 g, 0.15 mmol, 1.0 equiv.), p-thiocresol (0.077 g, 0.62 mmol, 4.0 equiv.) and (1*S*)-(+)-10-camphorsulfonic acid (0.36 g, 0.15 mmol, 1.0 equiv.) and 0.8 mL of deuterated chloroform was added. The vial was sealed and heated to 70 °C for 72 hours. The resulting solution was then purified by silica gel chromatography (6%-50% EtOAc/hexanes) to give the product as a colorless oil containing a mixture of anomers (5:3 α/β). Yield: 0.048 g (92%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.41 (m, 3H), 7.10-7.12 (m, 3H), 5.43 (d, J = 1.7 Hz, 1H), 5.09 (dd, J = 9.5 Hz, J = 3.3 Hz, 1H), 4.80 (dd, J = 9.7 Hz, J = 3,2 Hz, 1H), 4.69 (d, J = 0.8 Hz, 1H) 4.12-4.16 (m, 1H), 3.29 (dd, J = 3.5 Hz, J = 0.5 Hz ,1H), 3.86 (dd, J = 3.2 Hz, J = 2.0 Hz, 1H), 3.61 (s, 2H), 3.50 (s, 3H), 3.49 (s, 2H), 3.41 (s, 3H), 3.31-3.33 (m, 1H), 3.26-3.29 (m, 1H), 2.32 (two singlets, 5H), 2.15 (two singlets, 5H), 1.37 (d, J = 6 Hz, 2H), 1.33 (d, J = 6.2 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 170.4, 137.8, 137.7, 132.2, 132.0, 131.0, 130.8, 129.9, 129.8, 87.7, 84.9, 80.8, 80.7, 80.1, 80.0, 77.3, 76.1, 73.8, 68.9, 62.3, 61.0, 60.7, 58.5 21.3, 21.2, 21.2, 18.1, 17.9

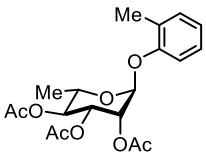
HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{17}H_{24}NaO_5S^+$: 363.1242 found: 363.1234

Substrate Intermediates



20

tetraacetyl-L-rhamnopyranoside (20): This compound was prepared according to a reported procedure.[4]



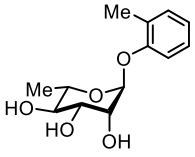
21

(2-methylphenyl)-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (21): A round bottom flask was charged with tetraacetyl-L-rhamnose, (2.0 g, 5.71 mmol, 1.0 equiv.) dichloromethane (19 mL) and $BF_3 \bullet OEt_2$ (1.1 mL, 8.57 mmol, 1.5 equiv.) followed by dropwise addition of 2-methylphenol (0.679 g, 6.28 mmol, 1.1 equiv.). The reaction was then stirred at room temperature overnight at which point the mixture was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was recrystallized from ethyl acetate/hexane to give the product as an off-white solid. Yield: 1.46 g (56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.17 (m, 2H), 7.06-7.07 (m, 1H), 6.95 (td, 7.4, 0.8 Hz, 1H), 5.51-5.54 (m, 1H), 5.45 (m, 2H), 5.17 (t, J = 10.0 Hz, 1H), 3.98-4.02 (m, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.22 (d, J =6.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 170.1, 170.0, 154.2, 131.0, 127.4, 126.9, 122.5, 114.0, 95.7, 70.9, 69.9, 69.1, 67.2, 20.9, 20.8, 20.7, 17.5, 16.2.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{19}H_{24}NaO_8^+$: 403.1369, found: 403.1372



22

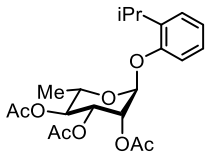
(2-methylphenyl)-α-L-rhamnopyranoside (22): Compound **21** (1.46 g, 3.2 mmol, 1.0 equiv.) was suspended in MeOH (3.2 mL) followed by the addition of NaOMe (0.052 g, 0.97 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate

was concentrated under vacuum to give the product as a colorless solid. Yield: 0.909 g (87%).

^{1}H NMR (600 MHz, DMSO) δ 7.11-7.15 (m, 2H), 7.03-7.04 (m, 1H), 6.87 (td, J = 7.4 Hz, J = 0.5 Hz, 1H), 5.36 (d, 1.4 Hz, 1H), 5.04 (bs, 1H), 4.87 (bs, 2H), 3.85 (q, J = 1.2 Hz, 1H), 3.67 (dd, J = 9.3 Hz, J = 3.4 Hz, 1H), 3.41-3.46 (m, 1H), 3.28 (t, J = 9.4 Hz, 1H), 2.15 (s, 3H), 1.09 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 154.5, 131.1, 127.3, 126.9, 121.9, 114.5, 98.5, 72.3, 71.1, 70.9, 70.0, 18.4, 16.3.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{13}H_{18}NaO_5^{+}$: 277.1052, found: 277.1054



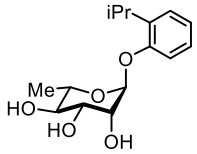
23

(2-isopropylphenyl)-2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranoside (23): A round bottom flask was charged with tetraacetyl-L-rhamnose, (5.0 g, 14.3 mmol, 1.0 equiv.) dichloromethane (48 mL) and BF_3•OEt_2 (2.6 mL, 21.4 mmol, 1.5 equiv.) followed by the slow addition of 2-isopropylphenol (2.6 mL, 15.7 mmol, 1.1 equiv.). The reaction was then stirred at room temperature overnight at which point the mixture was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified using silica gel chromatography (10% to 25% EtOAc/hexanes) to give the product as a colorless solid. Yield: 2.57 g (44%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.25 (m, 1H), 7.09-7.15 (m, 2H), 7.02 (td, J = 7.5 Hz, J = 1.1 Hz, 1H), 5.52 (dd, J = 10.2 Hz, J = 3.0 Hz, 1H), 5.44-5.45 (m, 2H), 5.19 (t, J = 10.0 Hz, 1H), 3.98-4.03 (m, 1H), 3.32 (septet, J = 6.7 Hz, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.27 (t, J = 6.7 Hz, 6H), 1.23 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 170.1, 170.0, 153.4, 137.5, 126.8, 126.5, 122.8, 114.0, 95.9, 70.8, 70.0, 69.2, 67.4, 27.4, 22.8, 22.7, 20.9, 20.8, 20.8, 17.5.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{21}H_{28}NaO_8^{+}$: 431.1682, found: 431.1690

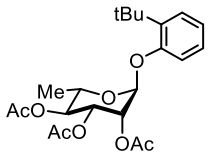


24

(2-isopropylphenyl)-*α*-L-rhamnopyranoside (24): Compound **23** (2.57 g, 5.35 mmol, 1.0 equiv.) was suspended in MeOH (5.4 mL) followed by the addition of NaOMe (0.087 g, 3.2 mmol, 30 mol %) and was stirred overnight. The reaction mixture was neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the product as a colorless solid. Yield: 1.513 g (99%).

^{1}H NMR (600 MHz, DMSO) δ 7.20 (dd, J = 7.7 Hz, J = 1.5 Hz, 1H), 7.11-7.14 (m, 1H), 7.06-7.07 (m, 1H), 6.94 (td, J = 7.4 Hz, J = 0.9 Hz, 1H), 5.35 (d, J = 1.5 Hz, 1H), 5.01 (bs, 3H), 3.85-3.86 (m, 1H), 3.67 (dd, J = 9.6 Hz, J = 3.3 Hz, 1H), 3.44-3.48 (m, 1H), 3.31 (t, J = 9.2 Hz, 1H), 3.20 (septet, J = 6.9 Hz, 1H), 1.17 (d, J = 7.4 Hz, 6H), 1.12 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 153.79, 137.0, 127.2, 126.6, 122.1, 114.4, 98.7, 72.3, 71.1, 70.9, 70.1, 27.3, 23.2, 23.0, 18.4.



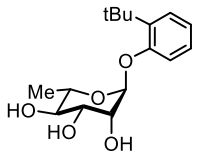
25

(2-*t*-butylphenyl)-2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranoside (25): A round bottom flask was charged with tetraacetyl-L-rhamnose, (5.0 g, 14.3 mmol, 1.0 equiv.) dichloromethane, (48 mL) and BF_3•OEt_2 (2.6 mL, 21.4 mmol, 1.5 equiv.) followed by dropwise addition of 2-*t*-butylphenol (2.4 mL, 15.7 mmol, 1.1 equiv.). The reaction was stirred at room temperature overnight at which point the reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (25% EtOAc/hexanes) and then recrystallized from ethanol to give the product as a colorless solid. Yield: 2.216 g (35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.9, 1.2 Hz, 1H), 7.15-7.19 (m, 2H), 6.97-7.00 (m, 1H), 5.54 (dd, J = 10.2, 3.1 Hz, 1H), 5.49-5.50 (m, 2H), 5.21 (t, J = 10.2 Hz, 1H), 3.96-4.01 (m, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.45 (s, 9H), 1.24 (d, J = 6.2 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.2, 170.2, 170.2, 155.3, 138.5, 127.4, 127.1, 122.4, 114.4, 95.9, 70.8, 69.8, 69.4, 67.7, 34.9, 30.3, 21.0, 21.0, 20.8, 17.7.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{22}H_{30}NaO_8^+$: 445.1838, found: 445.1845

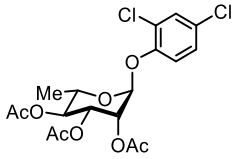


26

(2-*t*-butylphenyl)-α-L-rhamnopyranoside (26): A suspension of compound **25** (3.06 g, 6.92 mmol, 1.0 equiv.) in 7 mL MeOH was treated with NaOMe (0.110 g, 2.04 mmol, 30 mol %) and was stirred for one hour. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was concentrated under vacuum to give the product as a colorless solid. Yield: 2.39 g (99%).

^{1}H NMR (600 MHz, DMSO) δ 7.22-7.24 (m, 1H), 7.13-7.15 (m, 2H), 6.88-6.91 (m, 1H), 5.37 (s, 1H), 5.11 (bs, 3H), 3.90 (m, 1H), 3,72 (dd, J = 9.5 Hz, J = 3.3 Hz, 1H), 3.47-3.49 (m, 1H), 3.34 (t, J = 9.3 Hz, 1H), 1.33 (s, 9H), 1.15 (d, J = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 155.7, 137.5, 127.7, 126.9, 121.5, 114.3, 99.0, 72.3, 71.2, 70.9, 70.2, 34.8, 30.3, 18.5.



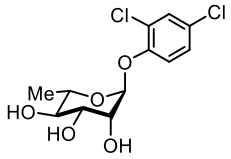
27

(2,4-dichlorophenyl)-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (27): A round bottom flask was charged with tetraacetyl-L-rhamnose, (10.6 g, 31.9 mmol, 1.0) 102 mL dichloromethane, and BF_3•OEt_2 (5.5 mL, 44.6 mmol, 1.4 equiv.) followed by the slow addition of 2,4-dichlorophenol (5.38 g, 33.0 mmol, 1.1 equiv.). The reaction was then stirred at room temperature overnight at which point the reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was recrystallized with ethyl acetate and hexane to give an off-white solid. Yield: 4.18 g (30%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 2.0 Hz, 1H), 7.17 (dd, J = 9.0, 1.9 Hz, 1H), 7.07 (d, J = 8.7 Hz, 1H), 5.53 (dd, J = 9.8, 3.5 Hz, 1H), 5.49 (s, 1H), 5.44 (s, 1H), 5.16 (t, J = 10.2 Hz, 1H), 3.98-4.03 (m, 1H), 2.18 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.20 (d, J = 6.3 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 170.1, 170.0, 150.3, 130.4, 128.4, 127.9, 125.2, 117.6, 96.7, 70.8, 69.6, 68.8, 68.0, 21.0, 20.9, 20.8, 17.5.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{18}H_{20}Cl_2NaO_8^+$: 457.0433 found: 457.0441

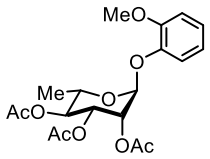


28

(2,4-dichlorophenyl)-*α*-L-rhamnopyranoside (28): A suspension of **27** (4.18 g, 9.6 mmol, 1.0 equiv.) in 8 mL MeOH was treated with NaOMe (0.175 g, 3.2 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was concentrated under vacuum to give the product as a colorless solid. Yield: 2.94 (99%).

^{1}H NMR (600 MHz, DMSO) δ 7.59 (d, J = 2.6 Hz, 1H), 7.35-7.37 (m, 1H), 7.29-7.30 (m, 1H), 5.49 (d, 1.3 Hz, 1H), 5.15 (bs, 1H), 4.96 (bs, 1H), 3.87-3.88 (dd, 3.5, 1.8 Hz, 1H), 3.67-3.69 (dd, 9.4, 3.3 Hz, 1H), 3.40-3.45 (m, 1H), 3.34 (bs, 1H), 3.29-3.32 (t, 9.4 Hz, 1H), 1.08-1.09 (d, 6.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 150.8, 129.9, 128.6, 126.3, 124.0, 118.6, 99.4, 72.0, 70.8, 70.6, 70.4, 18.3.



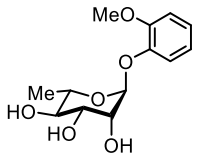
29

(2-methoxyphenyl)-2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranoside (29): A round bottom flask was charged with tetraacetyl-L-rhamnose, (5.44 g, 15.5 mmol, 1.0 equiv.) 31 mL dichloromethane, and BF_3•OEt_2 (3.8 mL, 31.1 mmol, 2.0 equiv.) followed by the slow addition of 2-methoxyphenol (3.5 mL, 31.1 mmol, 2.0 equiv.). The reaction was then stirred at room temperature overnight after which the reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was then purified using silica gel chromatography (25% to 50% EtOAc/hexanes) to give the product as a white solid. Yield: 2.99 g (46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02-7.098 (m, 2H), 6.86-6.91 (m, 2H), 5.57 (dd, J = 10.1 Hz, J = 3.4 Hz, 1H), 5.53 (dd, J = 3.7 Hz, J = 1.8 Hz, 1H) 5.37 (d, J = 1.5 Hz, 1H), 5.14 (t, J = 10.1 Hz, 1H), 4.18-4.23 (m, 1H), 3.84 (s, 3H), 2.17 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.21 (d, J = 6.5 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 170.0, 169.9, 150.8, 145.1, 124.2, 120.9, 119.2, 112.7, 97.6, 71.1, 69.8, 69.0, 67.3, 55.9, 20.9, 20.8, 20.8, 17.4.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{19}H_{24}NaO_9^+$: 419.1318 found: 419.1323

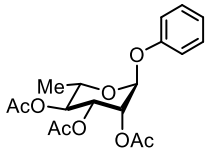


30

(2-methoxyphenyl)-*α*-L-rhamnopyranoside (30): A suspension of **29** (2.94 g, 7.10 mmol, 1.0 equiv.) in 7.1 mL MeOH was treated with NaOMe (0.115 g, 2.13 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the product as a colorless solid. Yield: 1.99 g (97%).

^{1}H NMR (600 MHz, DMSO) δ 7.06 (dd, J = 7.9, 1.1 Hz, 1H), 6.97-7.01 (m, 2H), 6.85-6.88 (m, 1H), 5.24 (d, J = 1.5 Hz, 1H), 3.85 (dd, J = 3.5, 1.8 Hz, 1H), 3.76 (s, 3H), 3.65 (dd, J = 9.5, 3.3 Hz, 1H), 3.58-3.61 (m, 1H), 3.41 (bs, 3H), 3.27 (t, J = 9.4 Hz, 1H), 1.09 (d, J = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 150.7, 145.7, 123.4, 121.2, 118.5, 113.3, 100.1, 72.2, 70.9, 70.8, 70.0, 56.1, 18.3.



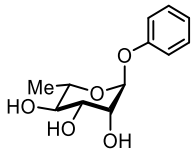
31

phenyl-2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranoside (31): A round bottom flask was charged with tetraacetyl-L-rhamnose, (9.7 g, 27.4 mmol, 1.0 equiv.) dichloromethane (137 mL) and phenol (3.10 g, 32.9 mmol, 1.2 equiv.). The reaction vessel was cooled to 0 °C and BF_3•OEt_2 (10.2 mL, 82.3 mmol, 3.0 equiv.) was added dropwise. The reaction was then warmed to room temperature and stirred overnight at which point the mixture was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was then washed with pentane to give a white solid which was then filtered and then collected to give the product. Yield: 6.69 g (67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.31 (m, 2H), 7.03-7.08 (m, 3H), 5.52 (dd, J = 10.2 Hz, J = 3.5 Hz, 1H), 5.45 (d, J = 1.8, 1H), 5.43 (dd, J = 3.7 Hz, J = 1.9 Hz, 1H), 5.15 (t, J = 9.9 Hz, 1H), 2.19, (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.2, 170.2, 170.1, 156.0, 129.7, 122.8, 116.5, 95.8, 71.1, 69.9, 69.0, 67.2, 21.0, 20.9, 20.9, 17.6

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{18}H_{22}NaO_8^+$: 389.1212 found: 389.1218



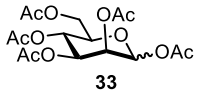
32

phenyl-*α*-L-rhamnopyranoside (32): Compound **31** (5.0 g, 13.6 mmol, 1.0 equiv.) was suspended in MeOH (13.6 mL) followed by the addition of NaOMe (0.221 g, 4.1 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was concentrated under vacuum to give the product as a colorless solid. Yield: 3.37 g (*quant.*).

^{1}H NMR (600 MHz, DMSO) δ 7.30 (t, J = 7.4 Hz, 2H), 7.03 (d, J = 7.7 Hz, 2H), 6.99, (t, J = 7.4 Hz, 1H), 5.37 (d, J = 1.2 Hz, 1H), 4.99 (bs, 3H), 3.84 (dd, J = 3.1 Hz, J = 1.8 Hz, 1H), 3.67 (dd, J = 9.4 Hz, J = 3.3 Hz, 1H), 3.46-3.51 (m, 1H0, 3.30 (t, J = 9.8 Hz, 1H), 1.11 (d, J = 6.5 Hz, 3H)

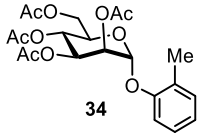
^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 156.2, 129.5, 121.8, 116.5, 98.4, 71.9, 70.5, 70.3, 69.5, 17.9

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{12}H_{16}NaO_5^+$: 263.0895 found: 263.0909



33

Pentaacetyl-*α*-D-mannopyranoside (33): This compound was prepared according to a reported procedure.[5]



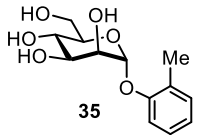
34

(2-methylphenyl)-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside (34): A round bottom flask was charged with pentaacetyl-D-mannopyranoside, (5.0 g, 12.81 mmol, 1.0 equiv.) 26 mL dichloromethane, and 2-methylphenol (2.77 g, 25.62 mmol, 2.0 equiv.). The mixture was then cooled to 0 °C and BF_3•OEt_2 (2.4 mL, 19.21 mmol, 1.5 equiv.) was added dropwise. After addition the flask was allowed to warm to room temperature with stirring overnight. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by column chromatography (25% to 50% EtOAc/hexanes) followed by recrystallization from ethyl acetate/hexanes to give the product as a colorless solid. Yield: 3.122 g (56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, J = 7.4 Hz, 1H), 7.11-7.14 (m, 1H), 7.07-7.09 (m, 1H), 6.96 (td, J = 7.4, 1.1 Hz, 1H), 5.57 (dd, J = 10.0, 3.5 Hz, 1H), 5.51 (d, J = 1.6 Hz, 1H), 5.46 (dd, J = 3.6, 1.9 Hz, 1H), 5.38 (t, J = 10.2 Hz, 1H), 4.27-4.30 (m, 1H), 4.07-4.12 (m, 2H), 2.29 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 2.03 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 170.0, 169.9, 169.7, 153.9, 131.1, 127.5, 126.9, 122.8, 114.2, 95.9, 69.6, 69.2, 69.0, 65.9, 62.2, 20.9, 20.7, 20.7, 16.2.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{21}H_{28}NaO_{10}^{+}$: 461.1424 found: 461.1431



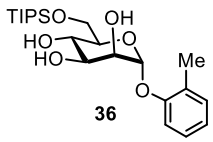
35

(2-methylphenyl)-*α*-D-mannopyranoside (35): A suspension of **34** (3.092 g, 7.05 mmol, 1.0 equiv.) in 7.1 mL MeOH was treated with NaOMe (0.114 g, 2.11 mmol, 30 mol %) and was allowed to stir for three hours. The reaction mixture was then neutralized with Dowex® and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the product as a colorless solid. Yield: 1.914 g (quant.).

^{1}H NMR (600 MHz, DMSO) δ 7.10-7.15 (m, 3H), 6.89 (td, J = 7.1, 1.6 Hz, 1H), 5.36 (d, J = 1.6 Hz, 1H), 5.01 (bs, 1H), 4.88 (bs, 1H), 4.45 (bs, 1H), 3.86 (dd, J = 3.4, 1.9 Hz, 1H), 3.71 (dd, J = 9.5, 3.3 Hz 1H), 3.59 (dd, J = 11.7, 2.0 Hz, 1H), 3.51 (t, J = 9.4 Hz, 1H), 3.45-3.48 (m, 1H), 3.38-3.41 (m, 1H), 3,35 (bs, 1H), 2.16 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 154.9, 131.0, 127.4, 127.1, 122.0, 115.2, 99.0, 75.4, 71.3, 70.7, 67.2, 61.5, 16.4.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{13}H_{18}NaO_6^{+}$: 293.1001 found: 293.1009



36

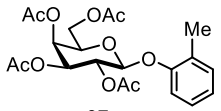
(2-methylphenyl)-6-*O*-triisopropylsilyl-*α*-D-mannopyranoside (36): A solution of **35** (1.884 g, 6.97 mmol, 1.0 equiv.) in 35 mL DMF was treated with imidazole (1.423 g, 20.91 mmol, 3.0 equiv.) and 4-(dimethylamino)pyridine (0.043 g, 0.35 mmol, 5 mol %), and was stirred at room temperature for 10 minutes. The mixture was then cooled to 0 °C and triisopropylchlorosilane (1.8 mL, 8.36 mmol, 1.2 equiv.) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. Upon completion the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with 1M HCl, water, then brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was

purified by silica gel column chromatography (50% to 100% EtOAc/hexanes) to give the product as a colorless solid. Yield: 0.826 g (28%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.14 (m, 3H), 6.92 (td, J = 7.0 Hz, J = 1.3 Hz, 1H), 5.55 (d, J = 1.5 Hz, 1H), 4.17 (bs, 1H), 4.10-4.13 (m, 1H), 3.90-3.99 (m, 3H), 3.87 (s, 1H). 3.73-3.76 (m, 1H), 3.55 (d, J = 3.8 Hz, 1H), 3.18 (d, J = 3.1 Hz, 1H), 2.22 (s, 3H), 0.99-1.11 (m, 21H).

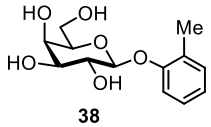
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.3, 130.9, 127.2, 126.9, 122.1, 114.1, 97.5, 71.6, 71.5, 70.5, 70.3, 65.8, 17.8, 17.8, 16.2, 11.7.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{22}H_{38}NaO_6Si^+$: 449.2335 found: 449.2349



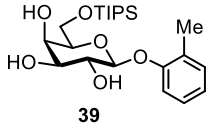
37

(2-methylphenyl)-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (37): This compound was prepared according to a reported procedure.[6]



38

(2-methylphenyl)-β-D-galactopyranoside (38): This compound was prepared according to a reported procedure.[6]



39

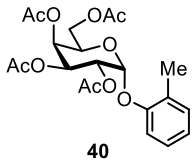
(2-methylphenyl)-6-*O*-triisopropylsilyl-β-D-galactopyranoside (39): A solution of **38** (1.698 g, 7.34 mmol, 1.0 equiv.) in 37 mL DMF was treated with imidazole (1.500 g, 22.03 mmol, 3.0 equiv.) and 4-(dimethylamino)pyridine (0.045 g, 0.36 mmol, 5 mol %), and was stirred at room temperature for 10 minutes. The reaction mixture was then cooled to 0 °C and triisopropylchlorosilane (1.9 mL, 8.81 mmol, 1.2 equiv.) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. Upon completion the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with 1M HCl, water, then brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (25% to 100%

EtOAc/hexanes) followed by recrystallization from EtOAc/hexanes at -20 °C to give the product as a colorless solid. Yield: 0.651 g (21%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10-7.15 (m, 2H), 7.07-7.08 (m, 1H), 6.95 (td, J = 7.3 Hz, J = 1.1 Hz, 1H), 4.82 (d, J = 7.8 Hz, 1H), 4.13 (d, J = 3.0 Hz, 1H), 3.96-4.03 (m, 3H), 3.69 (dd, J = 9.7 Hz, J = 3.5 Hz, 1H), 3.61 (td, J = 5.4 Hz, J = 0.6 Hz, 1H), 3.14 (bs, 2H), 2.85 (bs, 1H) 2.26 (s, 3H), 1.04-1.12 (m, 21H).

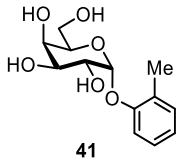
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.4, 130.8, 128.0, 126.8, 122.7, 115.7, 101.8, 74.8, 73.7, 72.0, 69.0, 63.1, 17.9, 17.9, 16.4, 11.8.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{22}H_{38}NaO_6Si^+$: 449.2335 found: 449.2348



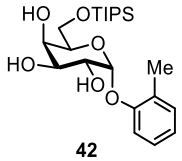
40

(2-methylphenyl)-2,3,4,6-tetra-*O*-acetyl-*α*-D-galactopyranoside (40): This compound was prepared according to a reported procedure.[6]



41

(2-methylphenyl)-*α*-D-galactopyranoside (41): This compound was prepared according to a reported procedure.[6]



42

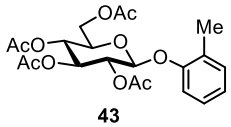
(2-methylphenyl)-6-*O*-triisopropylsilyl-*α*-D-galactopyranoside (42): A solution of **41** (1.081 g, 4.00 mmol, 1.0 equiv.) in 20 mL DMF was treated with imidazole (0.817 g, 12.00 mmol, 3.0 equiv.) and 4-(dimethylamino)pyridine (0.024 g, 0.20 mmol, 5 mol %), and was stirred at room temperature for 10 minutes. The reaction mixture was then cooled to 0 °C and triisopropylchlorosilane (1.0 mL, 4.80 mmol, 1.2 equiv.) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. Upon completion the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with 1M HCl, water, then

brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (50% to 100% EtOAc/hexanes) to give the product as a colorless solid. Yield: 1.33 g (78%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.16 (m, 3H), 6.94 (td, J = 7.1 Hz, J = 1.6 Hz, 1H), 5.60 (d, J = 3.9 Hz, 1H), 4.24 (s, 1H), 4.10 (td, J = 9.8 Hz, J= 3.8 Hz, 1H), 3.97-4.02 (m, 2H), 3.90-3.93 (m, 2H), 3.68 (s, 1H), 3.30 (d, J = 6.3 Hz, 1H), 2.55 (d, J = 9.7 Hz, 1H), 2.25 (s, 3H), 1.03-1.11 (m, 21H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.8, 130.8, 127.3, 127.1, 122.3, 114.8, 97.6, 71.5, 70.5, 70.1, 69.7, 64.0, 17.9, 17.8, 16.4, 11.8.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{22}H_{38}NaO_6Si^+$: 449.2335 found: 449.2347



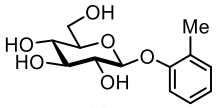
43

(2-methylphenyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (43): A round bottom flask was charged with pentaacetyl-β-D-glucopyranoside, (5.0 g, 12.81 mmol, 1.0 equiv.) 26 mL dichloromethane, and 2-methylphenol. (2.77 g, 25.62 mmol, 2.0 equiv.) The mixture was then cooled to 0 °C and BF_3•OEt_2 (2.4 mL, 19.21 mmol, 1.5 equiv.) was added dropwise after which the mixture was allowed to warm to room temperature with stirring overnight. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was then recrystallized from ethyl acetate/hexanes to give the product as a colorless solid. Yield: 4.353 g (78%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12-7.15 (m, 2H), 6.97-6.99 (m, 2H), 5.28-5.35 (m, 2H), 5.17 (t, J = 9.7 Hz 1H), 5.03 (d, J = 7.8 Hz, 1H), 4.28-4.31 (m, 1H), 4.17-4.19 (m, 1H), 3.84-3.87 (m, 1H), 2.17 (s, 3H), 2.04-2.08 (m, 12H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 170.3, 169.4, 169.2, 155.2, 131.0, 128.1, 126.9, 123.2, 115.1, 99.4, 72.7, 71.9, 71.1, 68.4, 62.0, 20.7, 20.7, 20.6, 20.6, 16.0.

HRMS (ESI/Q-TOF) m/z [M+Na]$^+$ calcd for $C_{21}H_{28}NaO_{10}^+$: 461.1424 found: 461.1431



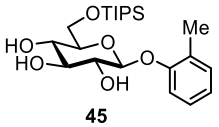
44

(2-methylphenyl)-β- D-glucopyranoside (44): A suspension of **43** (4.35 g, 9.93 mmol, 1.0 equiv.) in 10 mL MeOH was treated with NaOMe (0.161 g, 2.98 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the product as a colorless solid. Yield: 2.753 (*quant.*).

^{1}H NMR (600 MHz, DMSO) δ 7.11-7.14 (m, 2H), 7.05-7.06 (m, 1H), 6.89 (td, J = 7.4, 0.8 Hz, 1H), 5.27 (bs, 3H), 4.78-4.79 (m, 1H), 4.60 (bs, 1H), 3.69 (dd, J = 11.8, 1,9 Hz, 1H), 3.47 (dd, J = 11.9, 5.7 Hz, 1H), 3.25-3.31 (m, 3H), 3.16-3.19 (m, 1H), 2.20 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 156.1, 130.8, 127.3, 127.2, 122.0, 115.1, 101.4, 77.5, 77.1, 73.8, 70.2, 61.2, 16.5.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{13}H_{18}NaO_6^{+}$: 293.1001 found: 293.1008



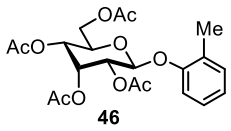
45

(2-methylphenyl)-6-*O*-triisopropylsilyl-β-D-glucopyranoside (45): A solution of **44** (2.753 g, 10.19 mmol, 1.0 equiv.) in 51 mL DMF was treated with imidazole (2.08 g, 30.56 mmol, 3.0 equiv.) and 4-(dimethylamino)pyridine (0.062 g, 0.51 mmol, 5 mol %) and was stirred at room temperature for 10 minutes. The flask was then cooled to 0 °C and triisopropylchlorosilane (2.6 mL, 12.22 mmol, 1.2 equiv.) was added dropwise. The crude mixture was then warmed to room temperature and stirred overnight. Upon completion the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with 1M HCl, water, then brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (50% to 100% EtOAc/hexanes) to give the product as a colorless solid. Yield: 3.65 g (84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 -713 (m, 2H), 7.03-7.04 (m, 1H), 6.94 (t, J = 7.3 Hz, 1H), 4.85 (d, J = 7.3 Hz, 1H), 3.96 (d, J = 5.4 Hz, 2H), 3.90 (bs, 1H), 3.67-3.72 (m, 2H), 3.62-3.65 (m, 1H), 2.24 (s, 3H), 1.08-1.14 (m, 3H), 1.05-1.06 (m, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.5, 130.9, 128.1, 127.0, 122.9, 115.7, 101.4, 76.5, 74.7, 73.5, 73.0, 65.2, 18.0, 16.5, 11.9.

HRMS (ESI/Q-TOF) m/z [M+Na]$^{+}$ calcd for $C_{22}H_{38}NaO_6Si^{+}$: 449.2335 found: 449.2342



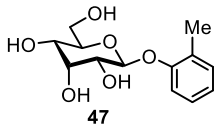
46

(2-methylphenyl)-2,3,4,6-tetra-*O*-acetyl-β-D-allopyranoside (46): To a 40 mL scintillation vial was added D-allose (1.000 g, 5.55 mmol, 1.0 equiv.), acetic anhydride (5.2 mL, 55.51 mmol, 10.0 equiv.), and pyridine (4.5 mL, 55.51 mmol, 10.0 equiv.). The mixture was then stirred overnight at room temperature. The following day the mixture was concentrated under vacuum and the resulting oil dissolved in 11 mL dichloromethane and treated with 2-methylphenol (1.200 g, 11.10 mmol, 2.0 equiv.). The mixture was then cooled to 0 °C and $BF_3 \bullet OEt_2$ (1.0 mL, 8.33 mmol, 1.5 equiv.) was added dropwise, at which point the reaction was allowed to warm to room temperature with stirring overnight. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by column chromatography (25% to 50% EtOAc/hexanes) followed by recrystallization from diethyl ether/pentane to give the product as a colorless solid. Yield: 0.776 g (32%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14-7.17 (m, 2H), 7.07 (d, J = 8.1 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H) 5.74 (t, J = 3.0 Hz, 1H), 5.32 (d, J = 8.1 Hz, 1H), 5.23 (dd, J = 8.3, 3.0 Hz, 1H), 5.06 (dd, J = 9.2, 2.7 Hz, 1H), 4.23-4.29 (m, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.8, 169.1, 169.0, 155.5, 131.0, 128.1, 126.9, 123.1, 115.2, 97.9, 70.4, 68.8, 68.6, 66.3, 62.4, 20.7, 20.7, 20.6, 20.6, 16.0.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{21}H_{28}NaO_{10}^+$: 461.1424 found: 461.1434



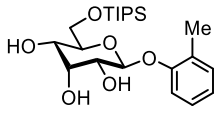
47

(2-methylphenyl)-β-D-allopyranoside (47): A suspension of **46** (0.746 g, 1.70 mmol, 1.0 equiv.) in 1.7 mL MeOH was treated with NaOMe (0.028 g, 0.51 mmol, 30 mol %) and was allowed to stir for three hours. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was concentrated under vacuum to give the product as a colorless solid. Yield: 0.433 g (94%).

^{1}H NMR (600 MHz, DMSO) δ 7.11-7.14 (m, 2H), 7.04 (d, J = 8.1 Hz, 1H), 6.88 (t, J = 7.2 Hz, 1H), 5.06 (d, J = 7.9 Hz, 1H), 5.00 (d, J = 6.9 Hz, 1H), 4.92 (d, J = 3.6 Hz, 1H), 4.64 (d, J = 7.4 Hz, 1H), 4.49 (t, J = 5.5 Hz, 1H), 3.39 (m, 1H), 3.65-3.69 (m, 2H), 3.39-3.47 (m, 3H) 2.19 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO) δ 156.4, 130.8, 127.3, 127.2, 121.9, 115.0, 99.5, 75.1, 72.0, 70.8, 67.8, 61.5, 16.5.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{13}H_{18}NaO_6^+$: 293.1001 found: 293.1005



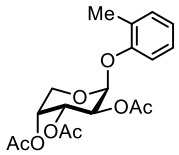
48

(2-methylphenyl)-6-*O*-triisopropylsilyl-β-D-allopyranoside (48): A solution of **47** (0.403 g, 1.49 mmol, 1.0 equiv.) in 7.5 mL DMF was treated with imidazole (0.304 g, 4.47 mmol, 3.0 equiv.) and 4-(dimethylamino)pyridine (0.009 g, 0.075 mmol, 5 mol %), and was stirred at room temperature for 10 minutes. The mixture was then cooled to 0 °C and triisopropylchlorosilane (0.38 mL, 1.79 mmol, 1.2 equiv.) was added dropwise. The solution was then warmed to room temperature and stirred overnight. Upon completion, the reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with 1M HCl, water, then brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (50% to 100% EtOAc/hexanes) to give the product as a clear, viscous oil. Yield: 0.490 g (77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.14 (m, 2H), 7.05 (d, J = 8.1 Hz, 1H), 6.94 (td, J = 7.5 Hz, J = 0.7 Hz, 1H), 5.26 (d, J = 7.8 Hz, 1H), 4.33 (s, 1H), 3.99-4.02 (m, 1H), 3.90-3.94 (m, 2H), 3.76-3.78 (m, 3H), 2.98 (s, 1H), 2.72 (d, J = 6.8 Hz, 1H), 2.27 (s, 3H), 1.04-1.15 (m, 21H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 154.5, 129.8, 126.8, 125.8, 121.5, 114.1, 98.1, 71.1, 70.2, 69.8, 69.3, 64.7, 16.8, 15.3, 10.7.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{22}H_{38}NaO_6Si^+$: 449.2335 found: 449.2347



49

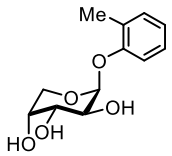
(2-methylphenyl)-2,3,4-tri-*O*-acetyl-*α*-L-arabinopyranoside (49): A round bottom flask was charged with tetraacetyl-L-arabinopyranoside, (5.50 g, 17.28 mmol, 1.0 equiv.) 70 mL dichloromethane, and 2-methylphenol (3.74 g, 34.56 mmol, 2.0 equiv.). The mixture was then cooled to 0 °C and $BF_3 \bullet OEt_2$ (3.2 mL, 25.92 mmol, 1.5 equiv.) was added dropwise, after which the flask was allowed to come to room temperature with stirring overnight. The reaction was neutralized with saturated $NaHCO_3$ and extracted twice with dichloromethane. The combined organic extracts were then washed with brine,

dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by column chromatography (50% EtOAc/hexanes) to give the product as a colorless solid. Yield: 2.49 g (40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.05 (m, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 5.64 (d, J = 3.5 Hz, 1H), 5.50 (dd, J = 10.8 Hz, J = 3.5 Hz, 1H), 5.37 (m, 1H), 5.28 (dd, J = 10.7 Hz, J = 3.4 Hz, 1H), 4.02 (d, J = 13.2 Hz, 1H), 3.71 (dd, J = 13.4 Hz, J = 2.0 Hz, 1H), 2.21 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 170.3, 170.1, 154.9, 130.9, 127.7, 127.0, 122.6, 114.5, 95.6, 68.9, 68.1, 67.3, 61.1, 30.0, 20.8, 20.7, 16.2.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{18}H_{22}NaO_8^+$: 389.1212 found: 389.1216



50

(2-methylphenyl)-*α*-L-arabinopyranoside (50): A suspension of **49** (1.72 g, 4.69 mmol, 1.0 equiv.) in 5 mL MeOH (5 mL) was treated with NaOMe (0.076 g, 1.41 mmol, 30 mol %) and was stirred overnight. The reaction mixture was then neutralized with Dowex® 50WX8-100 and filtered through a pad of Celite. The filtrate was then concentrated under vacuum to give the product as a colorless solid. Yield: 1.11 g (98%).

^{1}H NMR (600 MHz, DMSO) δ 7.16-7.09 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H) 6.88 (t, J = 7.4 Hz, 1H), 5.46 (d, J = 2.5 Hz, 1H), 4.99 (bs, 3H), 3.88-3.77 (m, 3H), 3.69 (d, J = 12.0 Hz, 1H), 3.51 (d, 12.0 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 131.0, 127.5, 127.2, 121.7, 114.7, 98.3, 69.3, 68.9, 68.7, 64.5, 16.4.

HRMS (ESI/Q-TOF) m/z $[M+Na]^+$ calcd for $C_{12}H_{16}NaO_5^+$: 263.0895 found: 263.0899

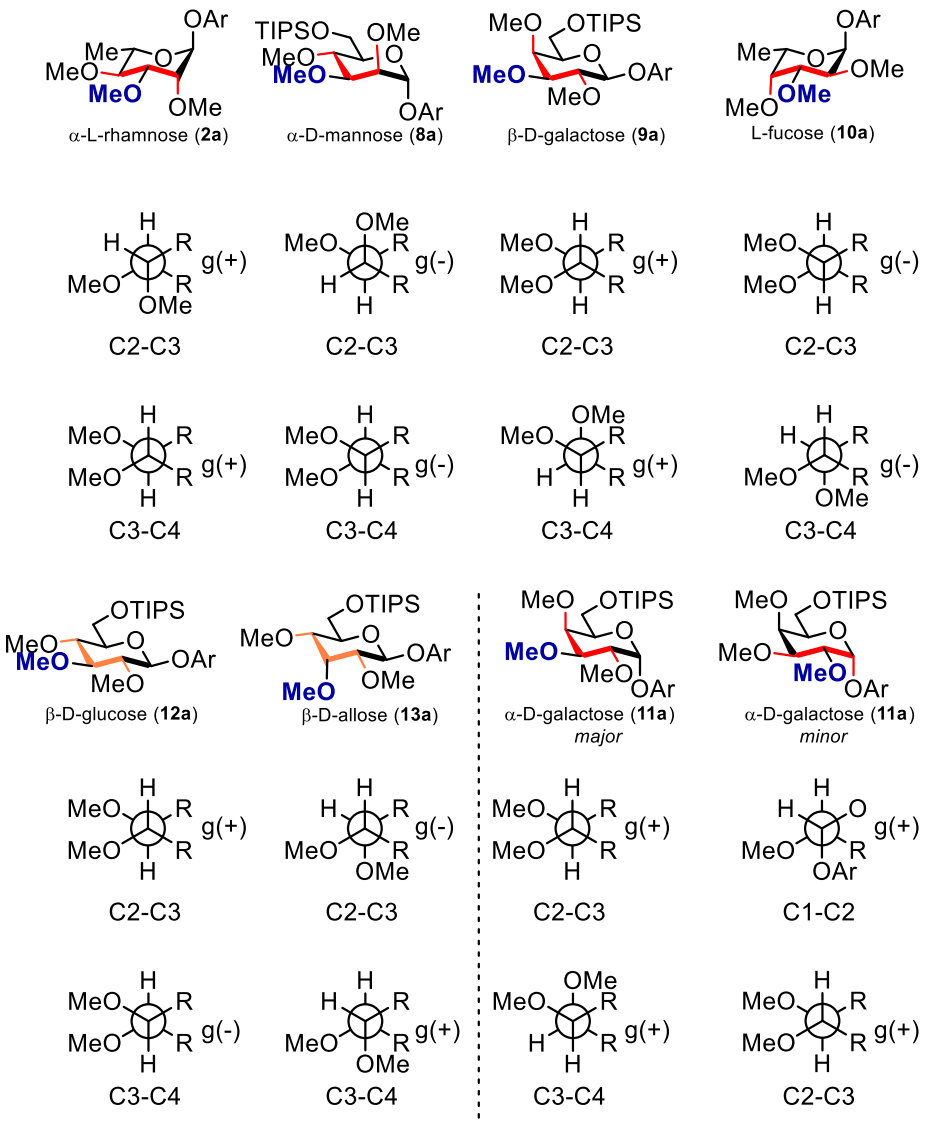


Figure S1. Fischer projections showing local conformation of successful and unsuccessful substrates.

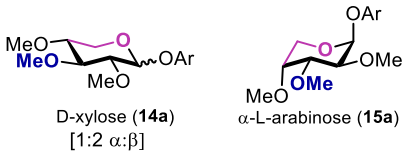


Figure S2. Unsuccessful pentose derivatives.

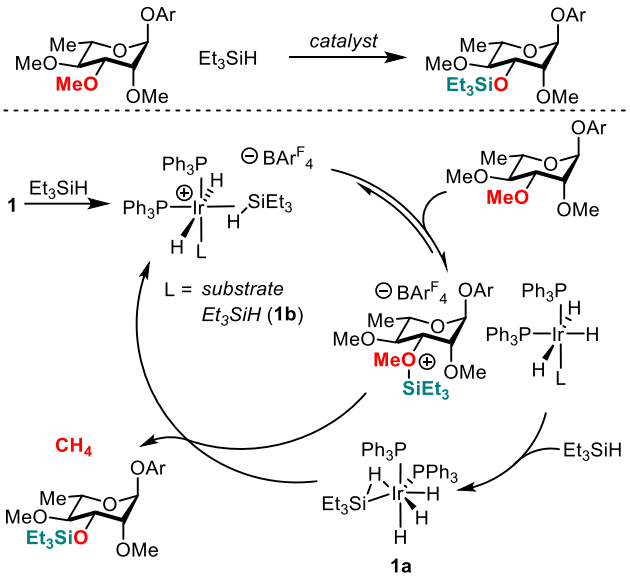
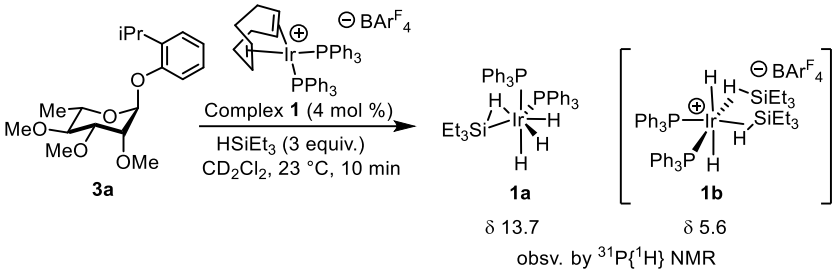
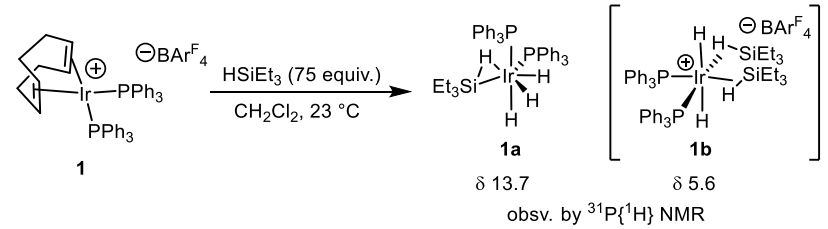


Figure S3. Proposed mechanism for demethylation of rhamnose derivatives.



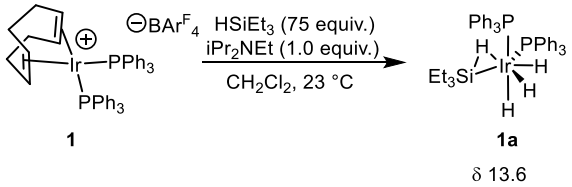
Observation of ^{31}P-containing species during catalysis (A): A septum-capped NMR tube was charged with **3a** (0.055 g, 0.15 mmol, 1.0 equiv.), and [(COD)Ir(PPh$_3$)$_2$]BAr$^F_{24}$ (0.010 g, 0.0060 mmol, 4 mol %) followed by 0.5 mL of CD_2Cl_2. Triethylsilane (70 μL, 0.45 mmol, 3 equiv.) was then added through the septum and the reaction was monitored by ^{31}P{^{1}H} NMR. After 10 minutes two species are observed by ^{31}P{^{1}H} NMR with relative intensity **1a**[7]/**1b**[8] 1 : 2.27. See Figure S4.

^{31}P{^{1}H} (162 MHz, CD_2Cl_2) δ 13.7 (s, **1a**), 5.6 (s, **1b**)



Observation of ^{31}P-containing species in the absence of substrate (B): A septum-capped NMR tube was charged with [(COD)Ir(PPh$_3$)$_2$]BAr$^F_{24}$ (0.010 g, 0.0060 mmol, 1.0 equiv.) in 0.5 mL of CD_2Cl_2. Triethylsilane (70 μL, 0.45 mmol, 75 equiv.) was then added through the septum and the reaction was monitored by ^{31}P{^{1}H} NMR. After 10 minutes two species are observed by ^{31}P{^{1}H} NMR with relative intensity **1a**[7]/**1b**[8] 1 : 15.8. See Figure S4.

^{31}P{^{1}H} (162 MHz, CD_2Cl_2) δ 13.7 (s, 1P, **1a**), 5.6 (s, 16P, **1b**)



Observation of ^{31}P-containing species with iPr$_2$NEt instead of substrate (C): A septum-capped NMR tube was charged with [(COD)Ir(PPh$_3$)$_2$]BAr$^F_{24}$ (0.010 g, 0.0060 mmol, 1.0 equiv.) in 0.5 mL of CD_2Cl_2. Triethylsilane (70 μL, 0.45 mmol, 75 equiv.) and diisopropyl(ethyl)amine (1.0 μL, 0.0060 mmol, 1.0 equiv.) were then added through the

septum and the reaction was monitored by $^{31}P\{^{1}H\}$ NMR. After 10 minutes a single species is observed corresponding to **1a**.[7] See Figure S4.

$^{31}P\{^{1}H\}$ (162 MHz, CD_2Cl_2) δ 13.6.

Summary of ^{31}P-NMR experiments A-C: Both species **1a**[7] and **1b**[8] have been previously reported, though **1b** has only been characterized as the corresponding hexafluoroantimonate salt at low temperature.[8] Formation of **1a** from **1b** likely occurs via transfer of an equivalent of triethylsilylium ion to substrate or another Lewis base. In the absence of substrate, the **1a**/**1b** ratio substantially favors **1b**, while the addition of a strong Lewis base (iPr_2NEt) drives the ratio to favor **1a** exclusively. In previous cases we have examined[7] **1b** is not observed which may point to the reduced Lewis basicity of **3a** relative to simple dialkyl ethers.

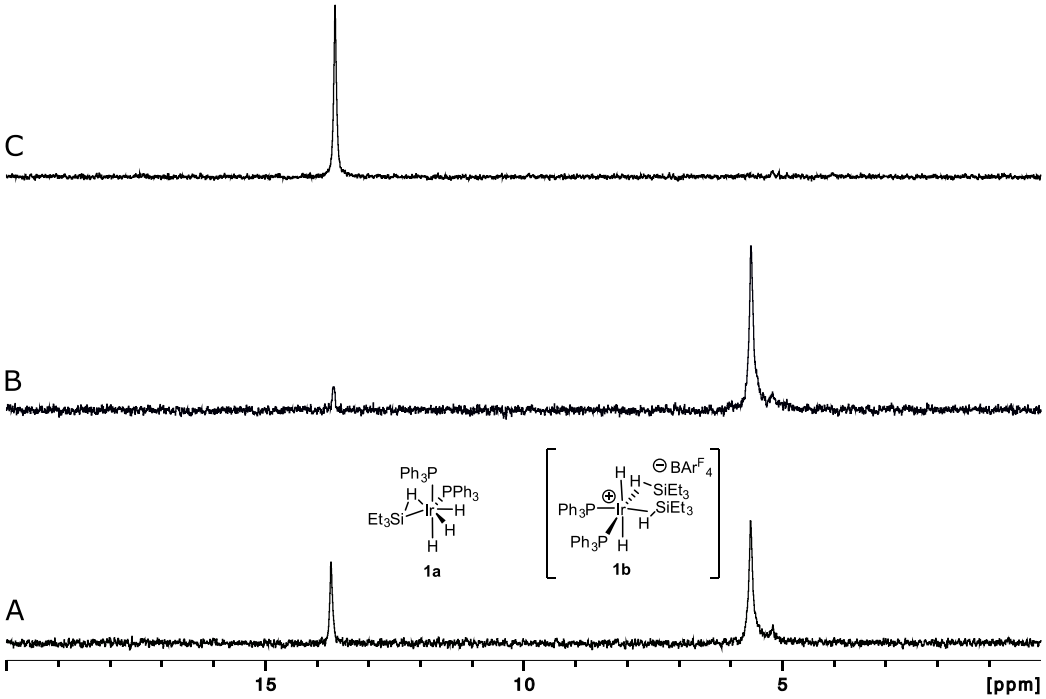


Figure S4. $^{31}P\{^{1}H\}$ spectra of **1a** and **1b** corresponding to experiments **A**-**C** above.

III. Computational Methods

General Methods. Density functional theory (DFT) calculations were performed using Gaussian 09.[9]

Computational treatment of 2a-silyloxonium isomers. Initial atomic coordinates for silyloxonium ions were generated using Avogadro 1.2.0.[10] A minimization was performed for each conformation using molecular mechanics methods. In cases where two plausible rotational isomers (by rotation of the C-$O_{(oxonium)}$-Si-C dihedral angle) were found, both were examined by DFT. The MM-calculated structures were used as the initial coordinates for a DFT optimization and frequency calculation. The free energy of each conformer was then tabulated. In total 17 structures were calculated for O1-O5 silyloxonium ions in two different chair conformations.

Keyword. # opt freq b3lyp/6-31g* geom=connectivity empiricaldispersion=gd3

Computational treatment of the *axial* 1-silyloxonium ion.† No optimized energy minimum could be found for the chair conformation with the 1-aryloxysilyloxonium ion in the axial position. Instead these inputs always optimized to the corresponding oxocarbenium ion with scission of the C-O bond. Scans of the C-O bond length coordinate in both the forward and reverse directions from various starting positions failed to find a stable silyloxonium ion structure for this isomer.

The supplemental file "calc_coords.xyz" contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

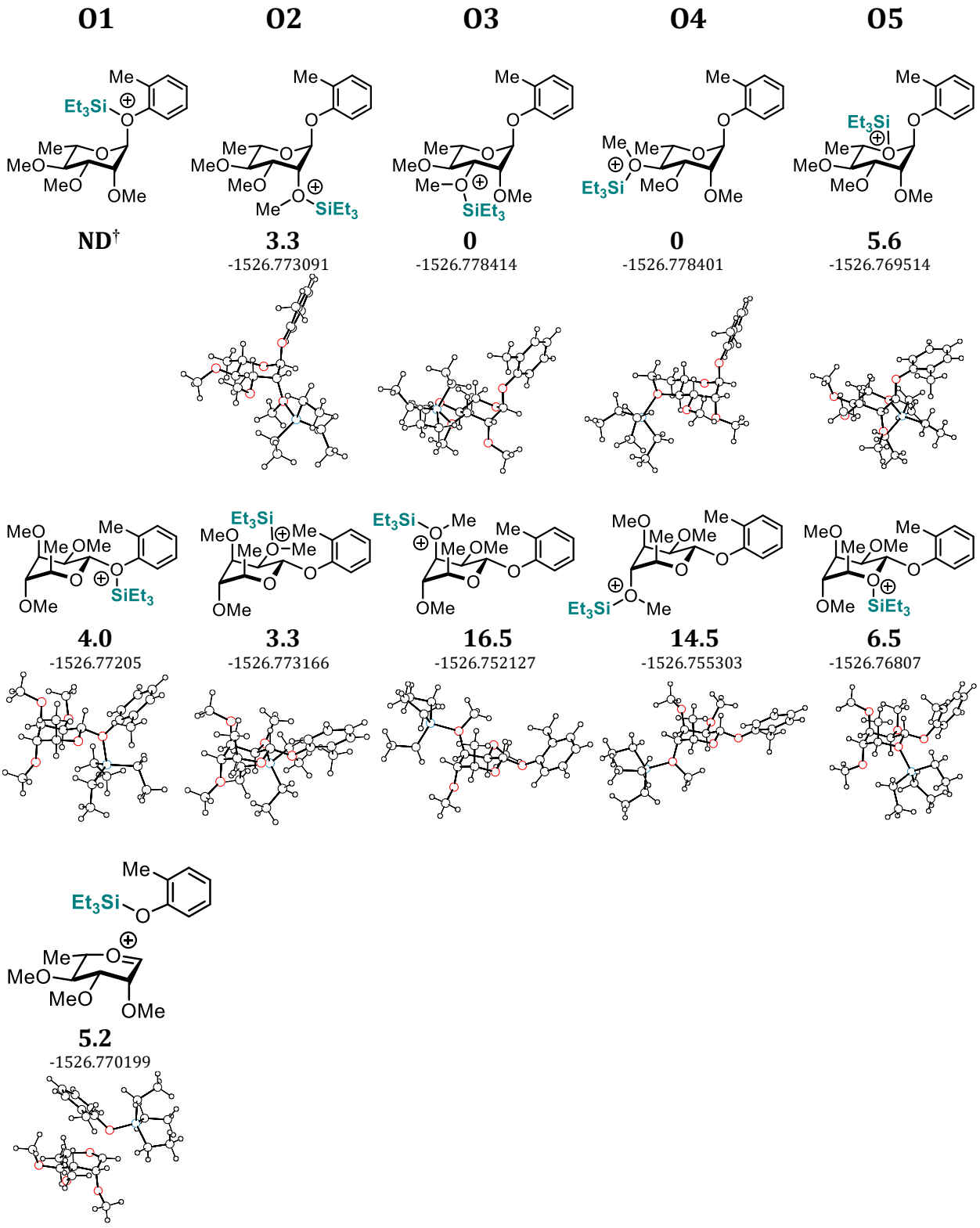


Figure S5. Computed relative free energies of **2a**-silyloxonium isomers (kcal·mol^{-1}). Absolute energies given in hartrees.

IV. NMR Spectra

Substrates

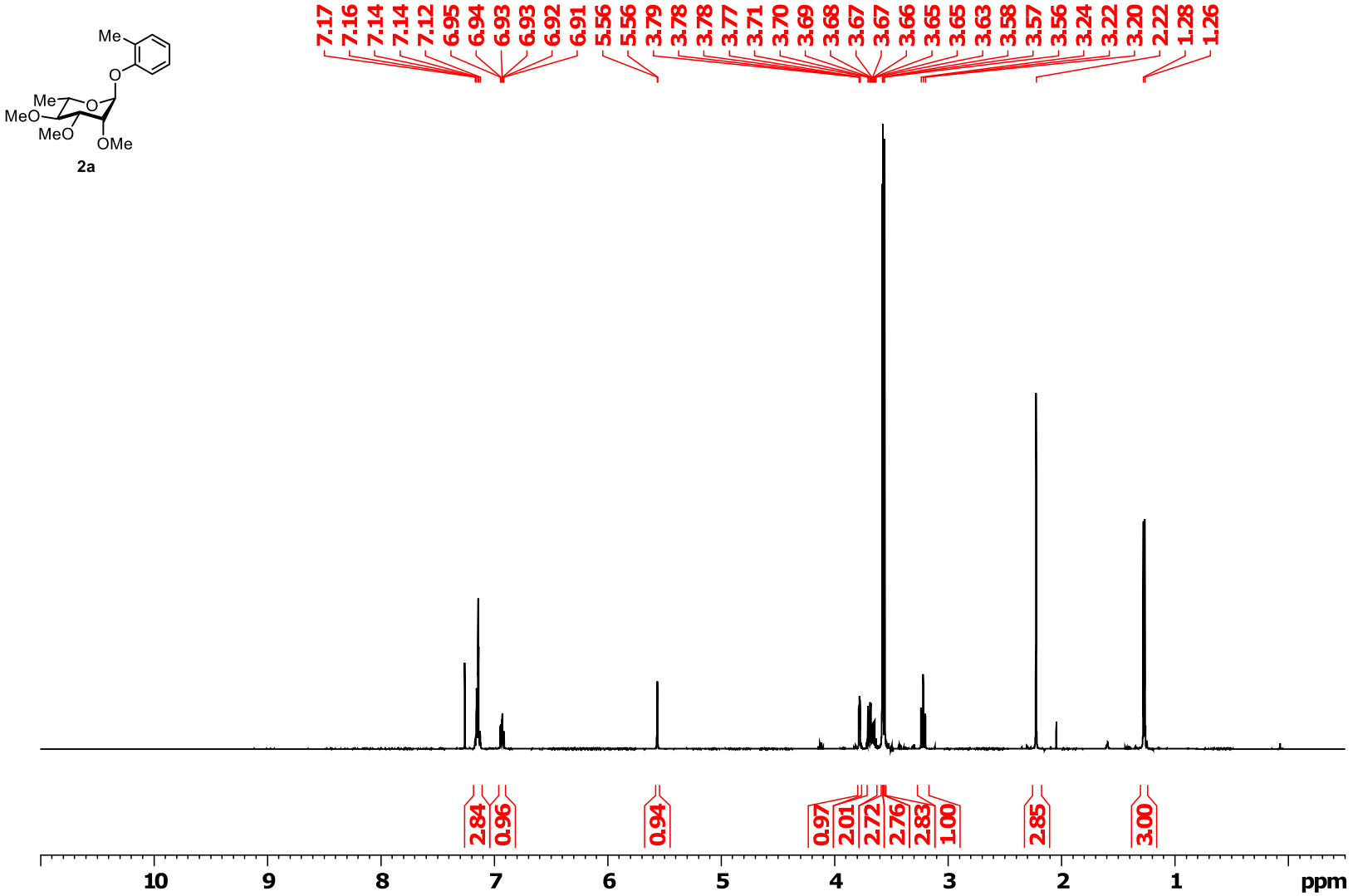


Figure S6. ^{1}H NMR spectrum of **2a**.

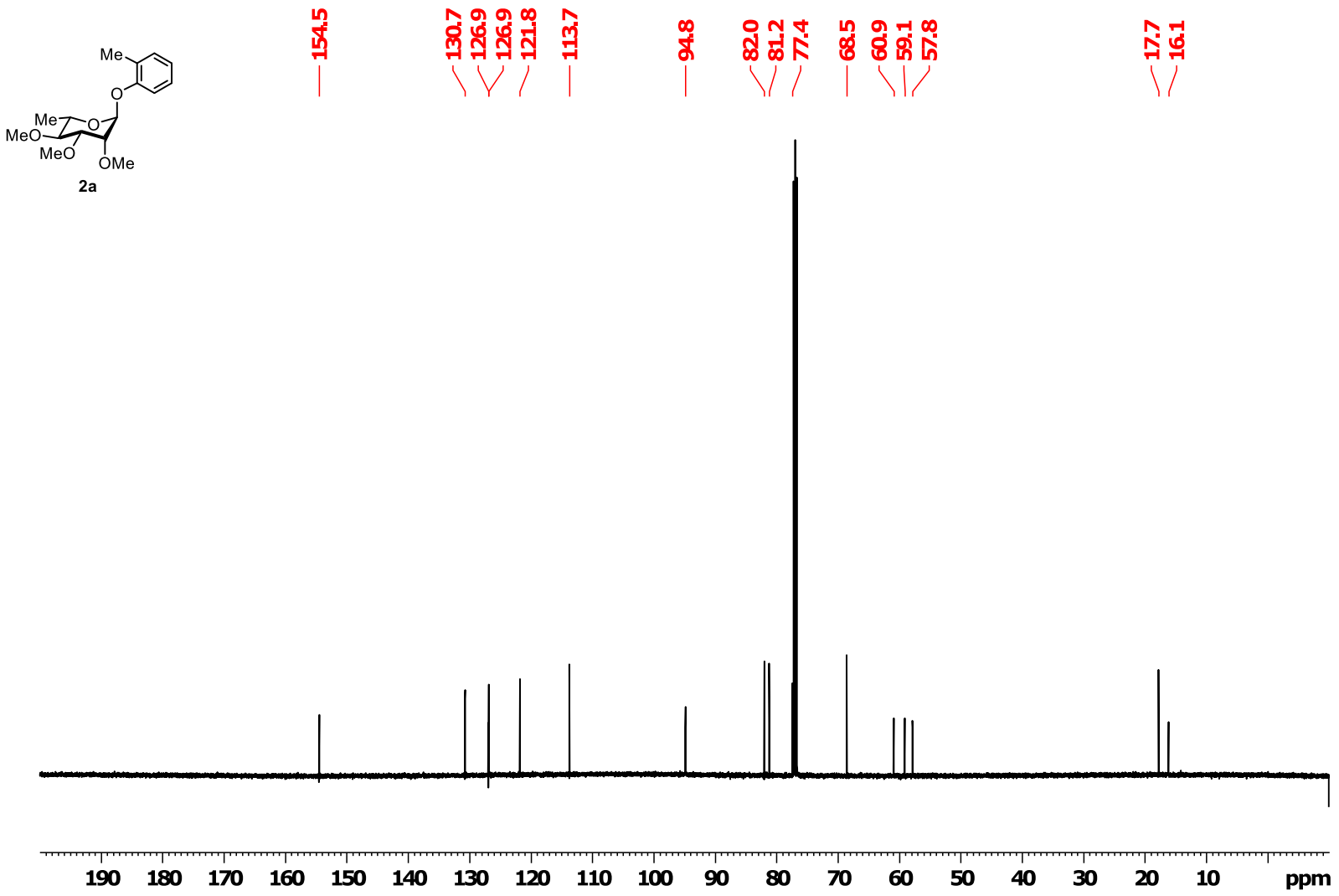


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2a**.

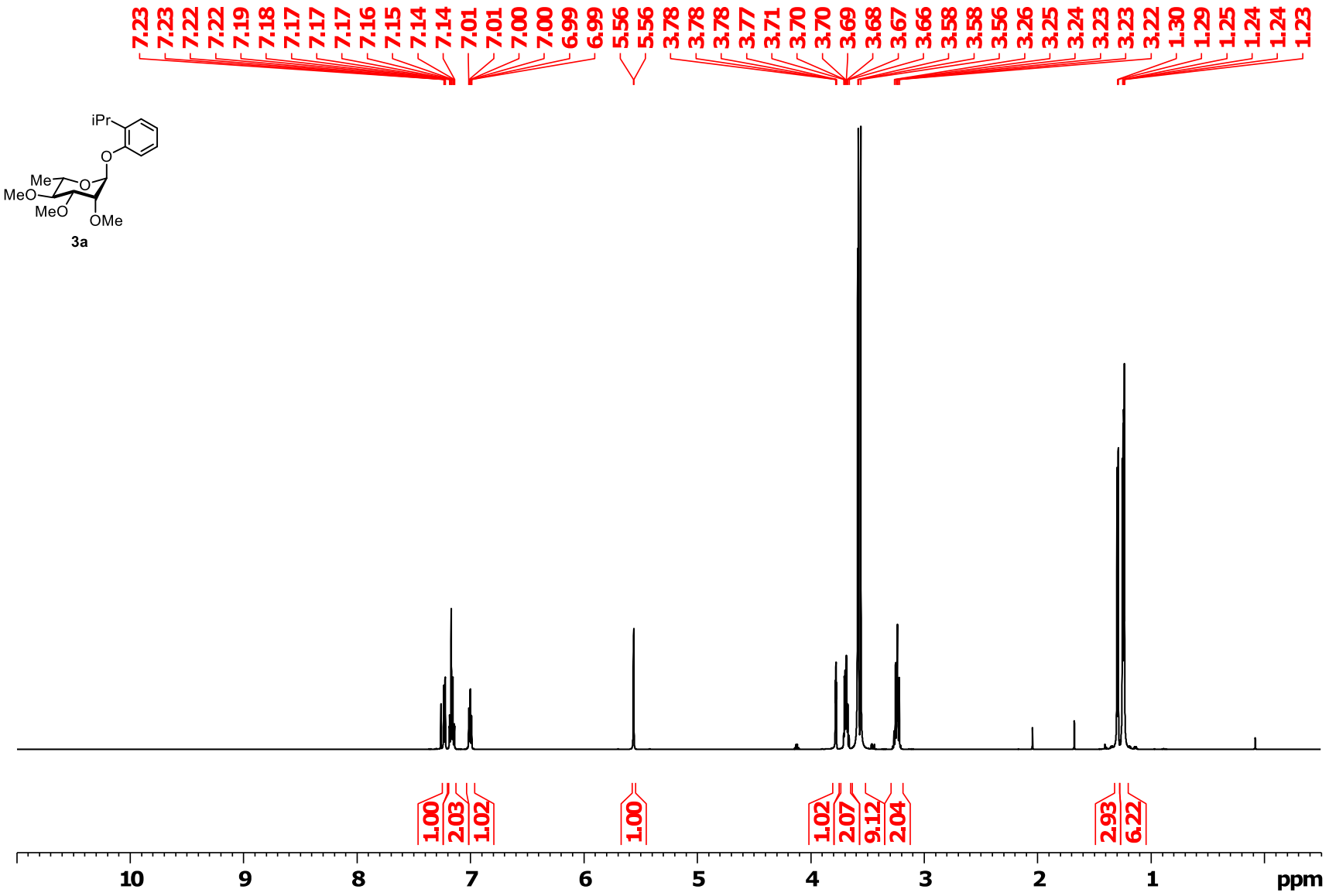


Figure S8. ^{1}H NMR spectrum of **3a**.

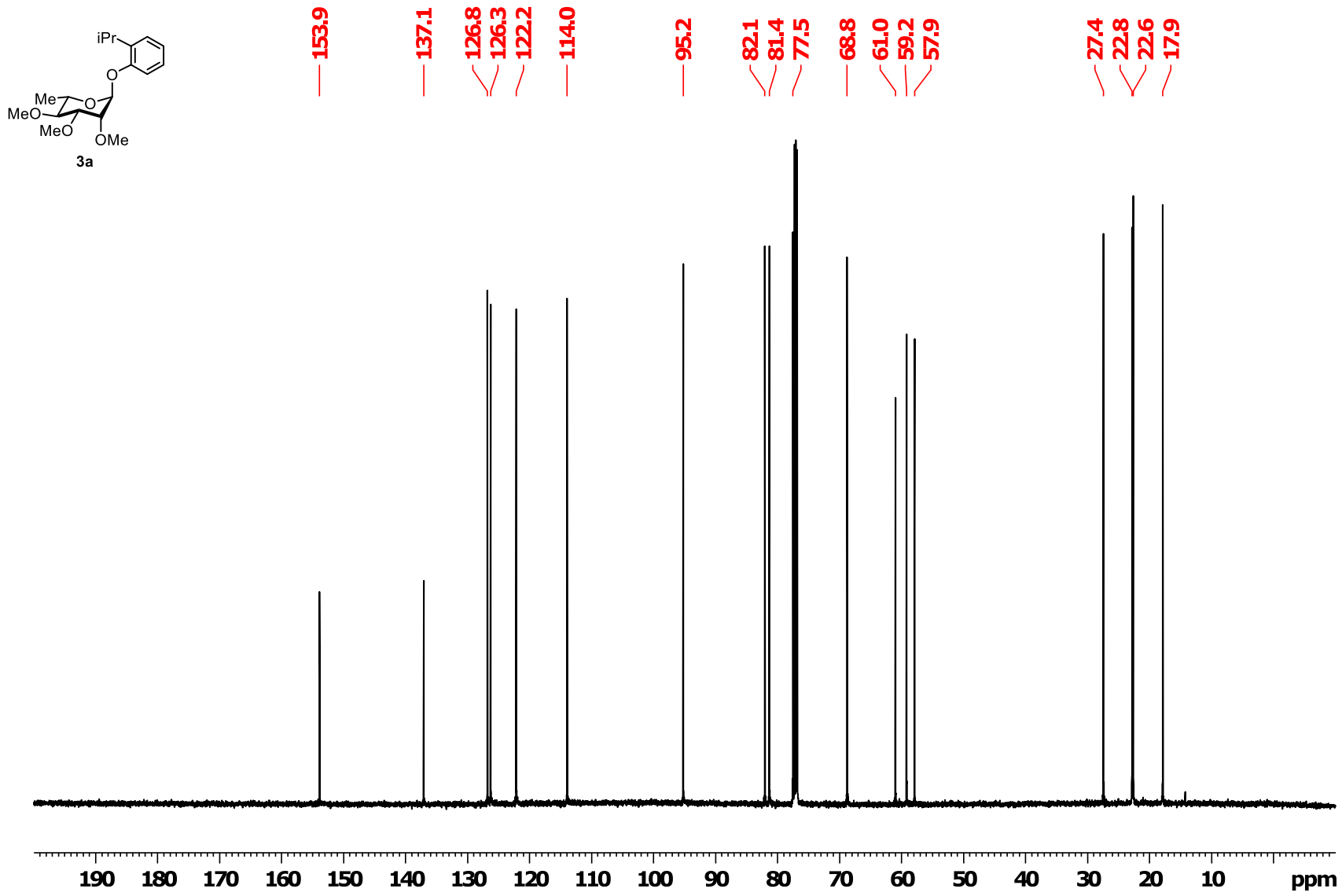


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **3a**.

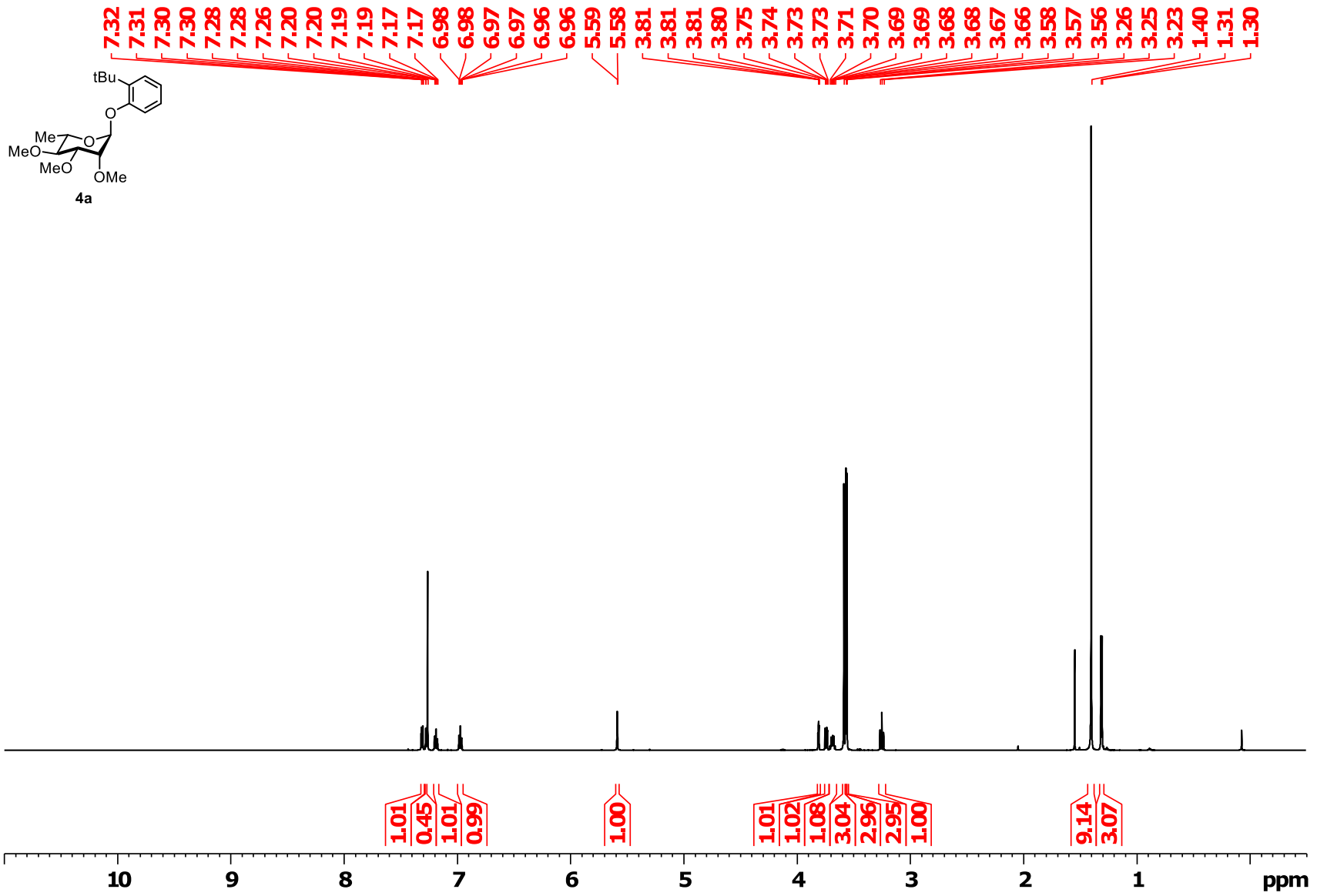


Figure S10. ^{1}H NMR spectrum of **4a**.

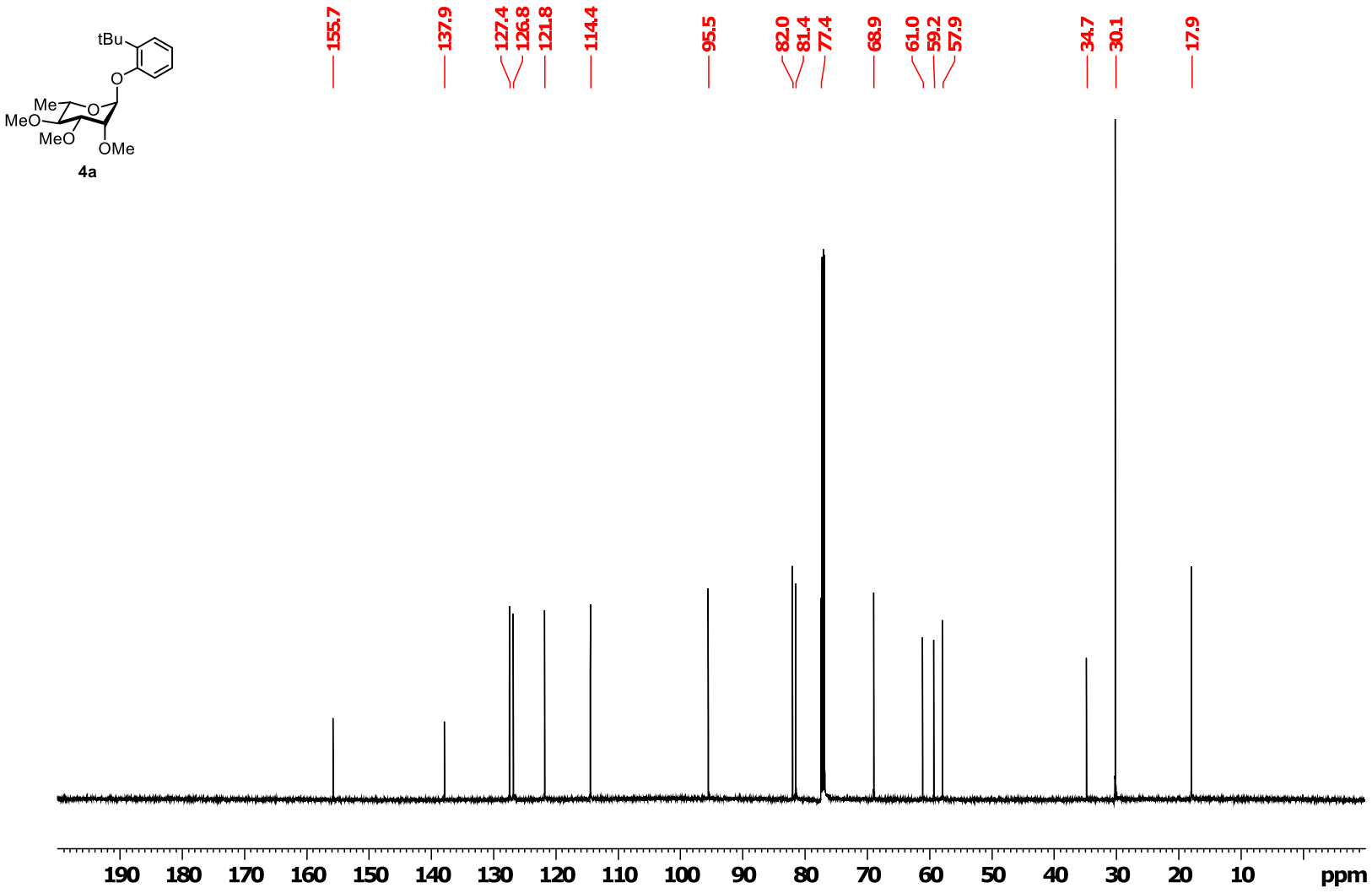


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **4a**.

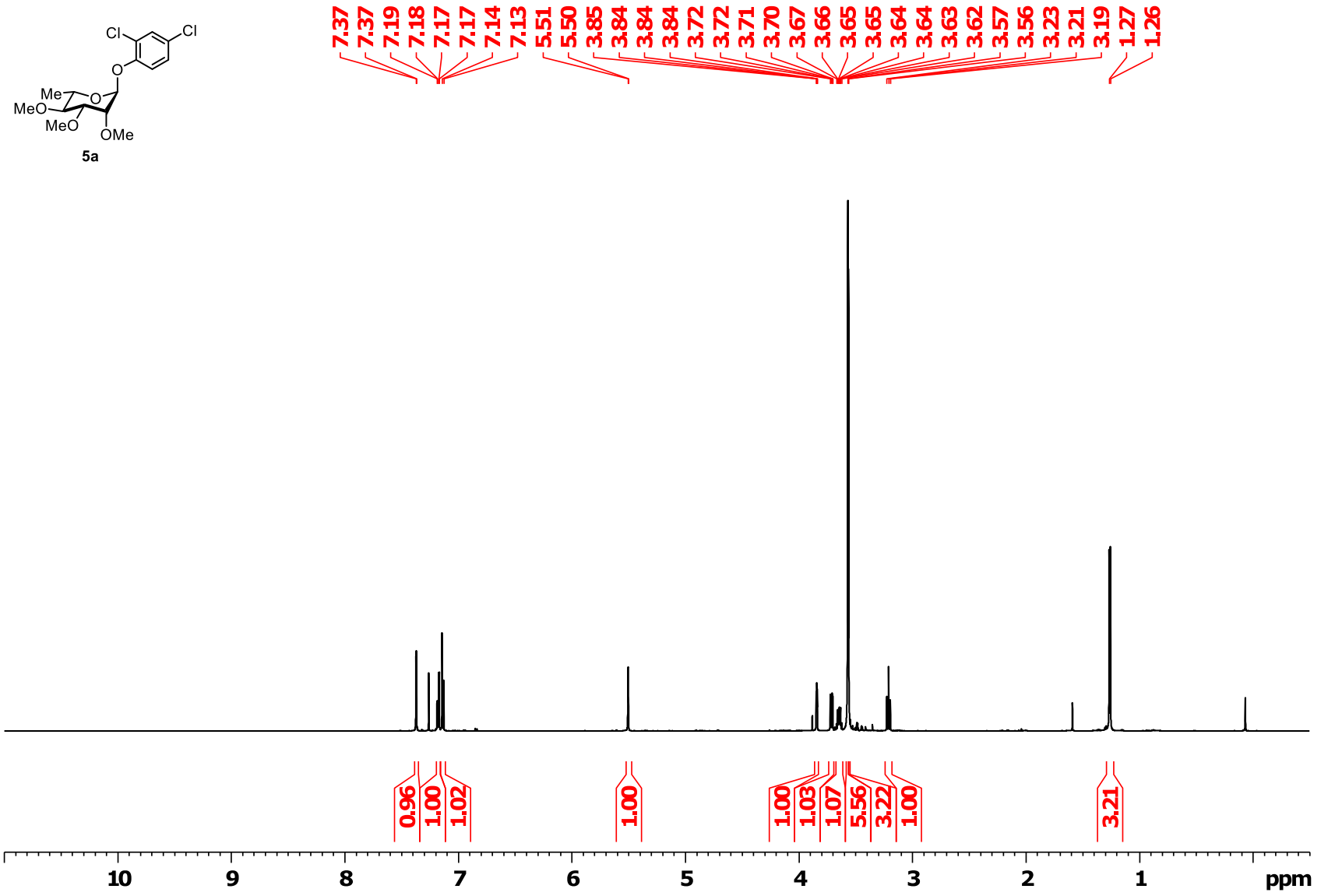


Figure S12. ^{1}H NMR spectrum of **5a**.

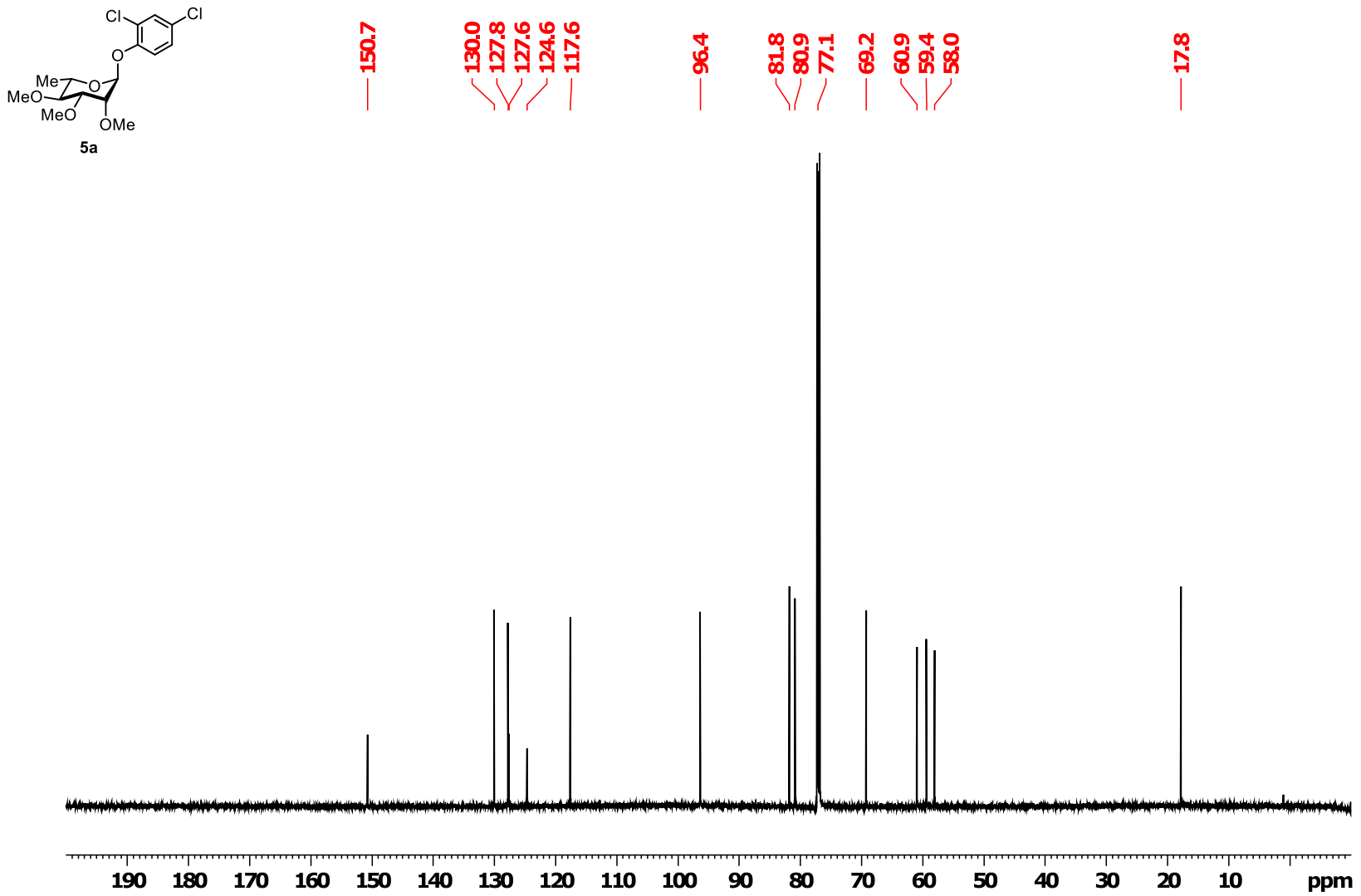


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **5a**.

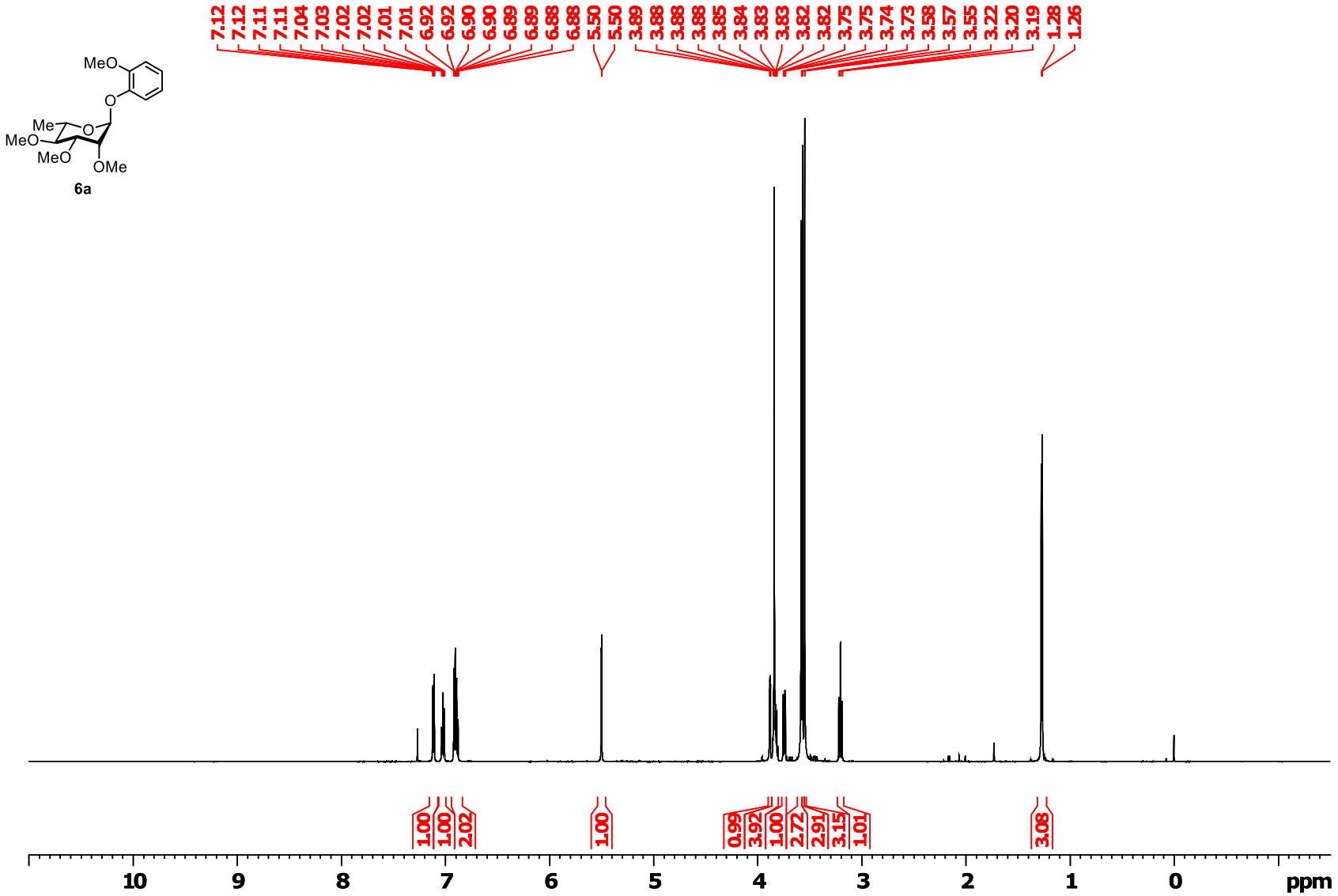


Figure S14. ^{1}H NMR spectrum of **6a**.

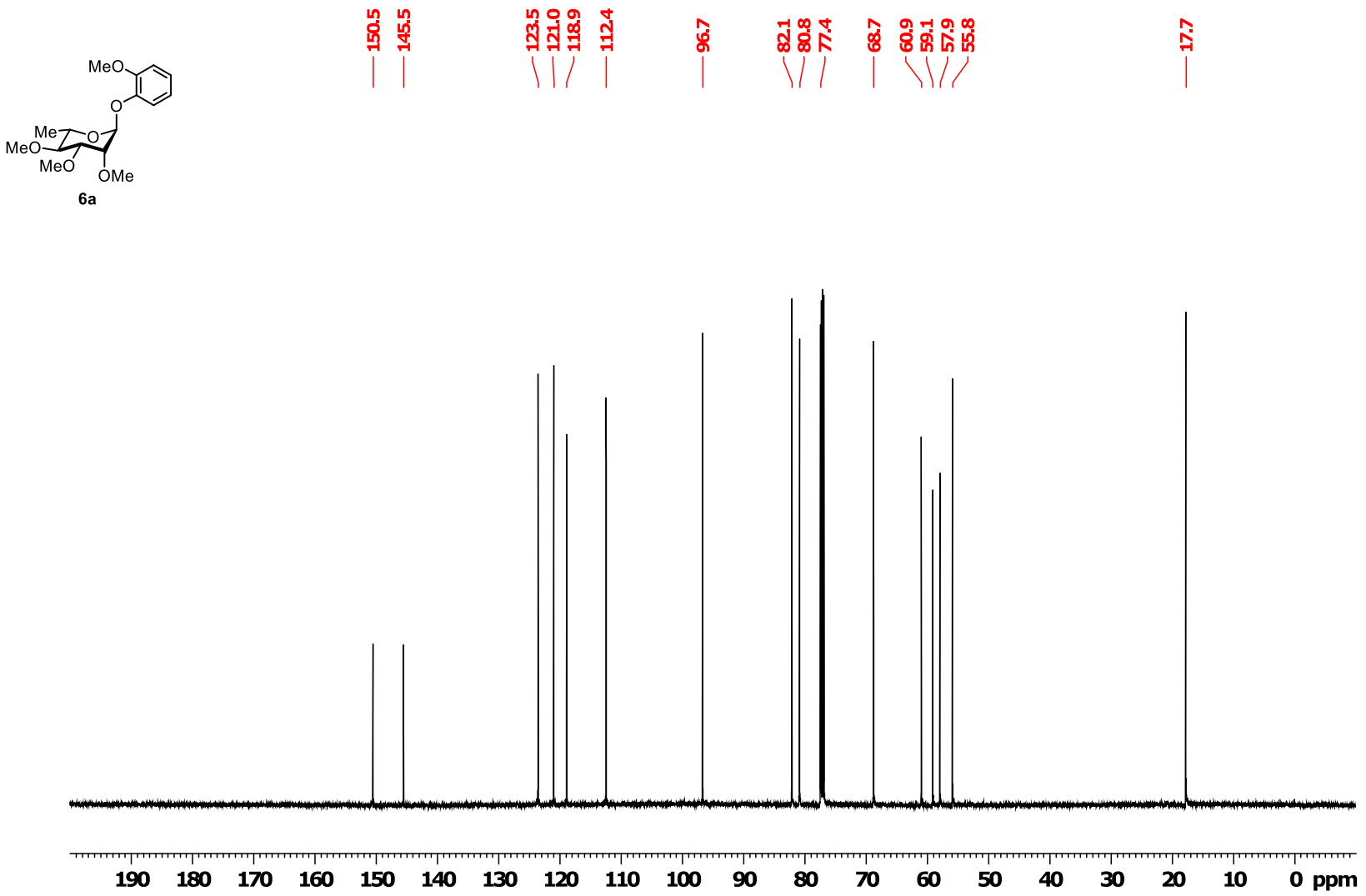


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **6a**.

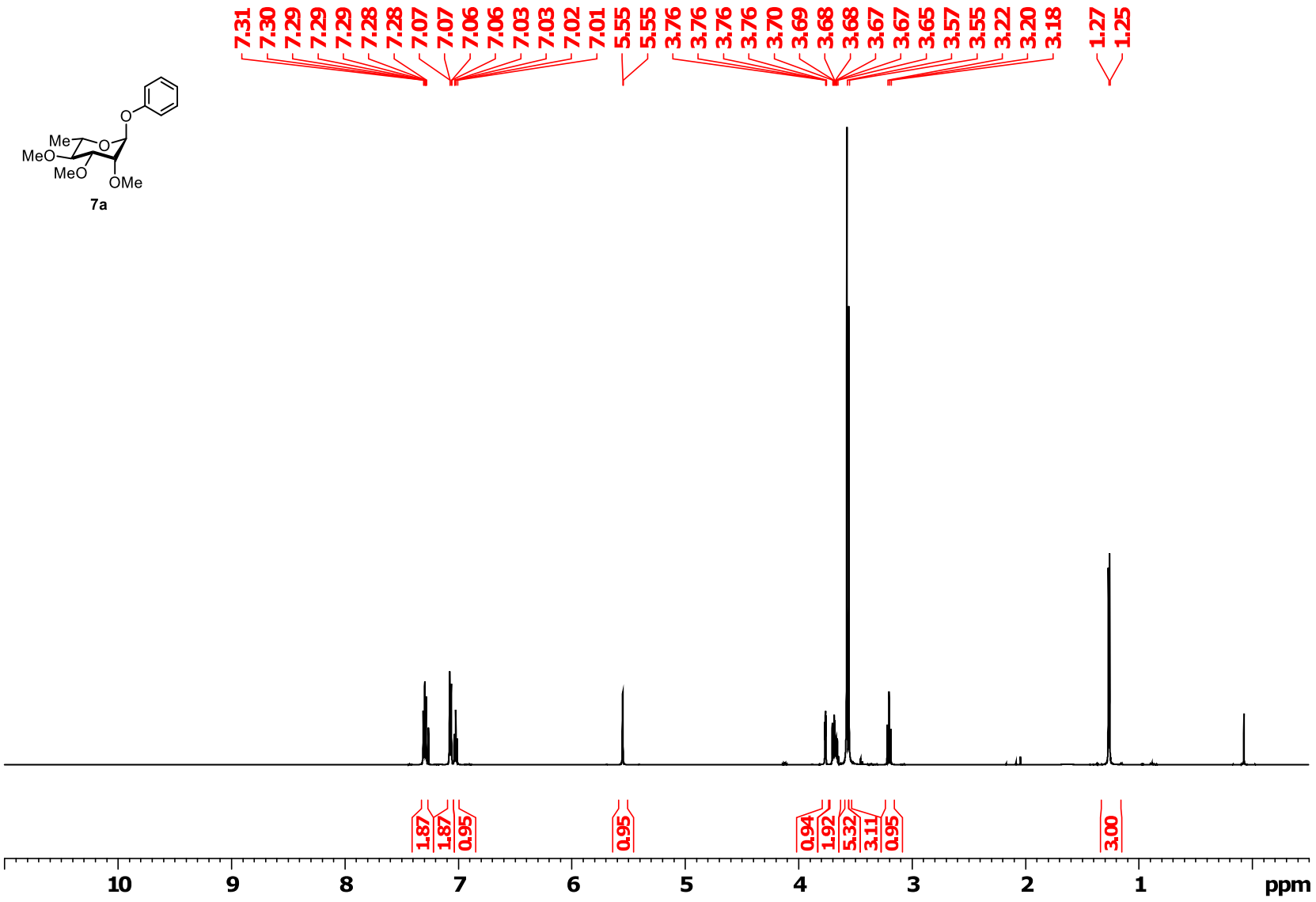


Figure S16. ^{1}H NMR spectrum of **7a**

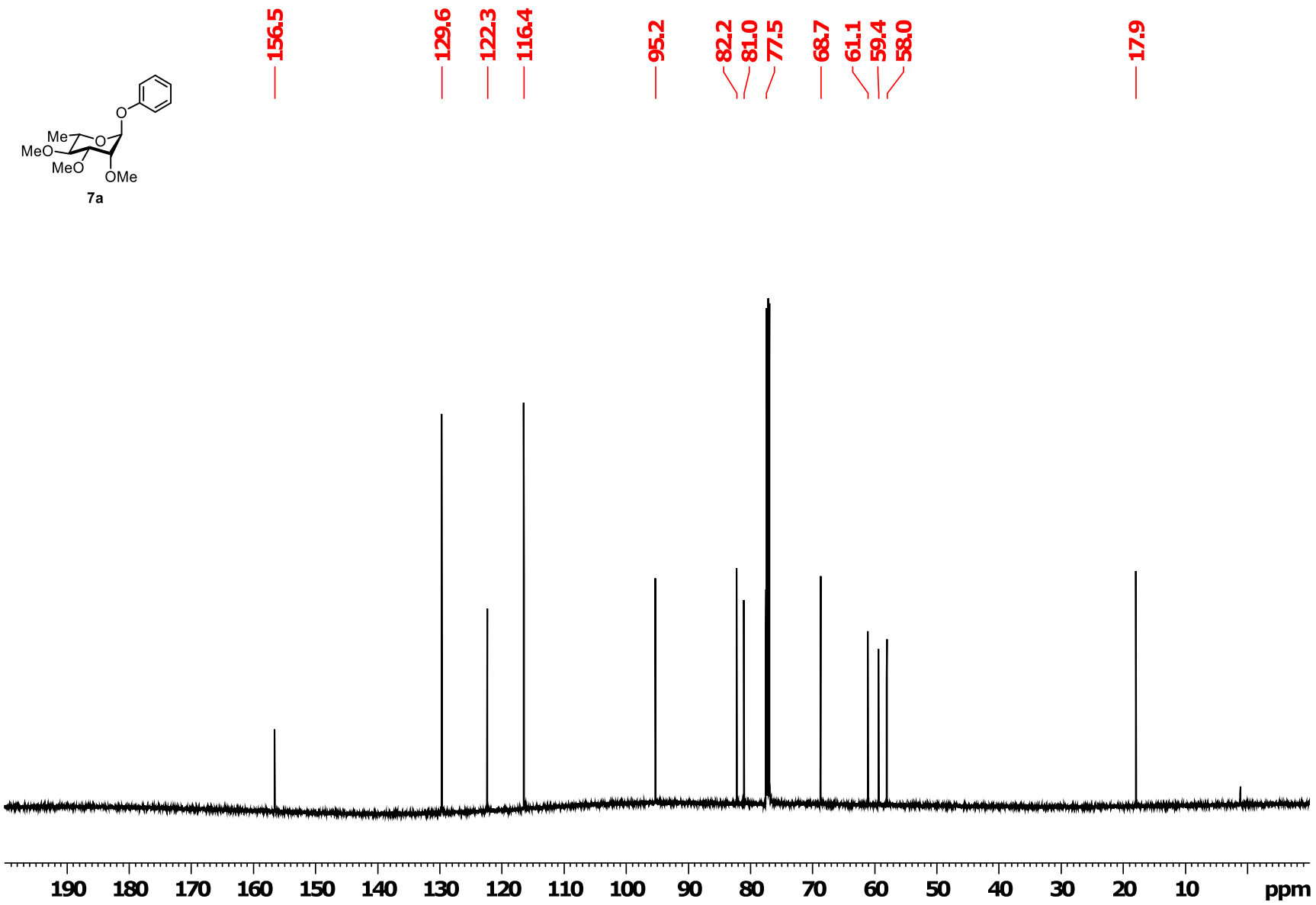


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **7a**

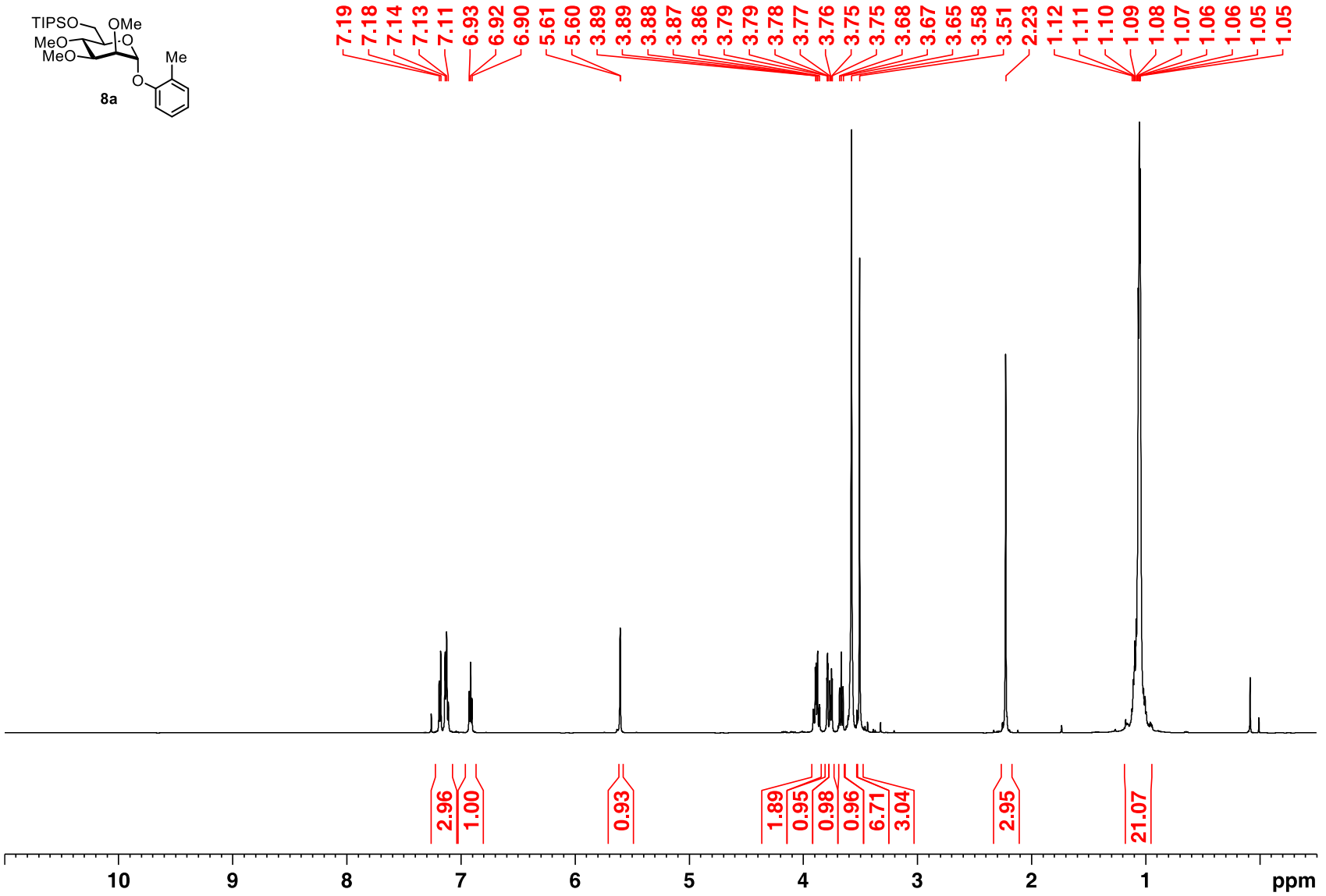


Figure S18. ^{1}H NMR spectrum of **8a**.

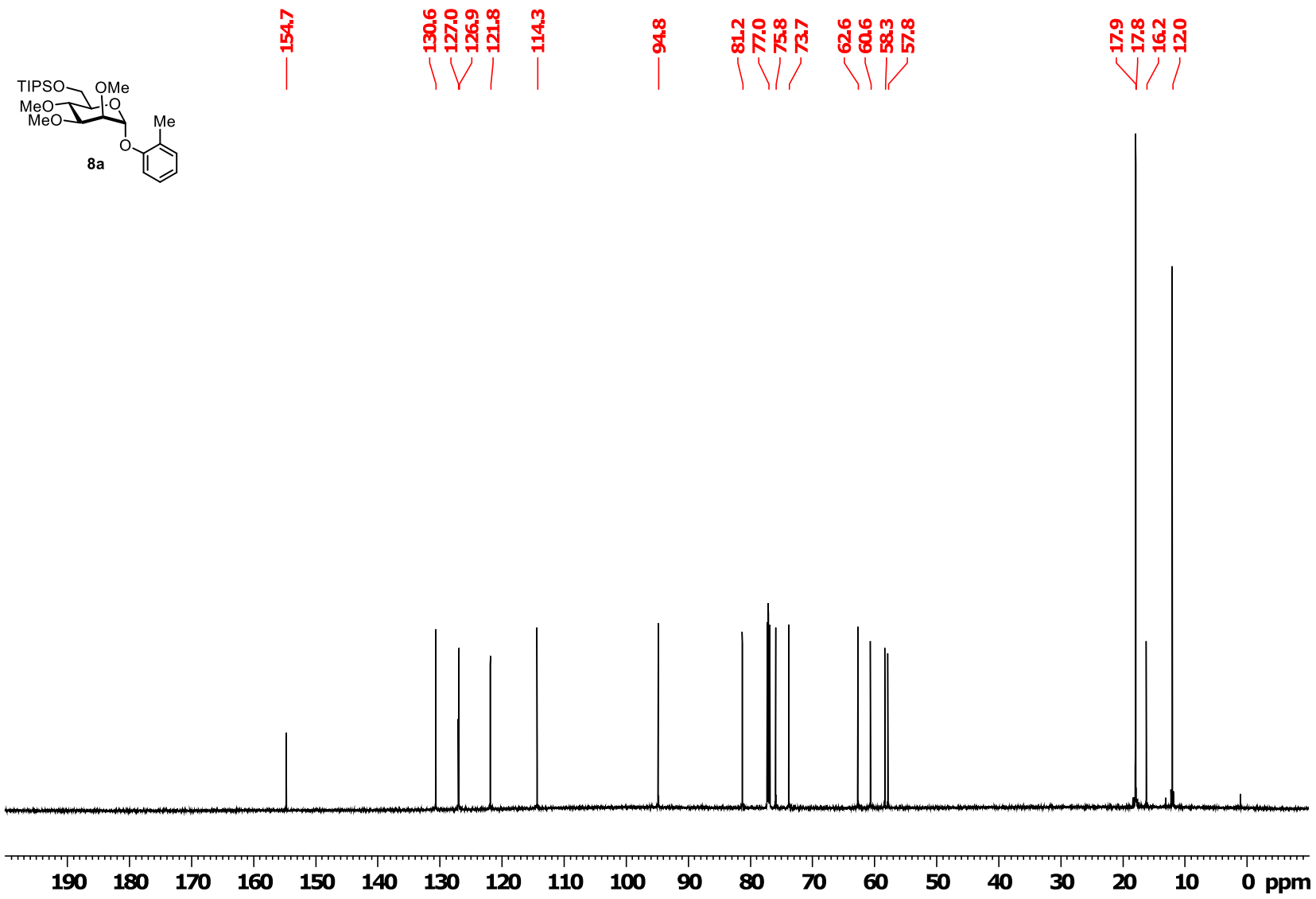


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **8a**.

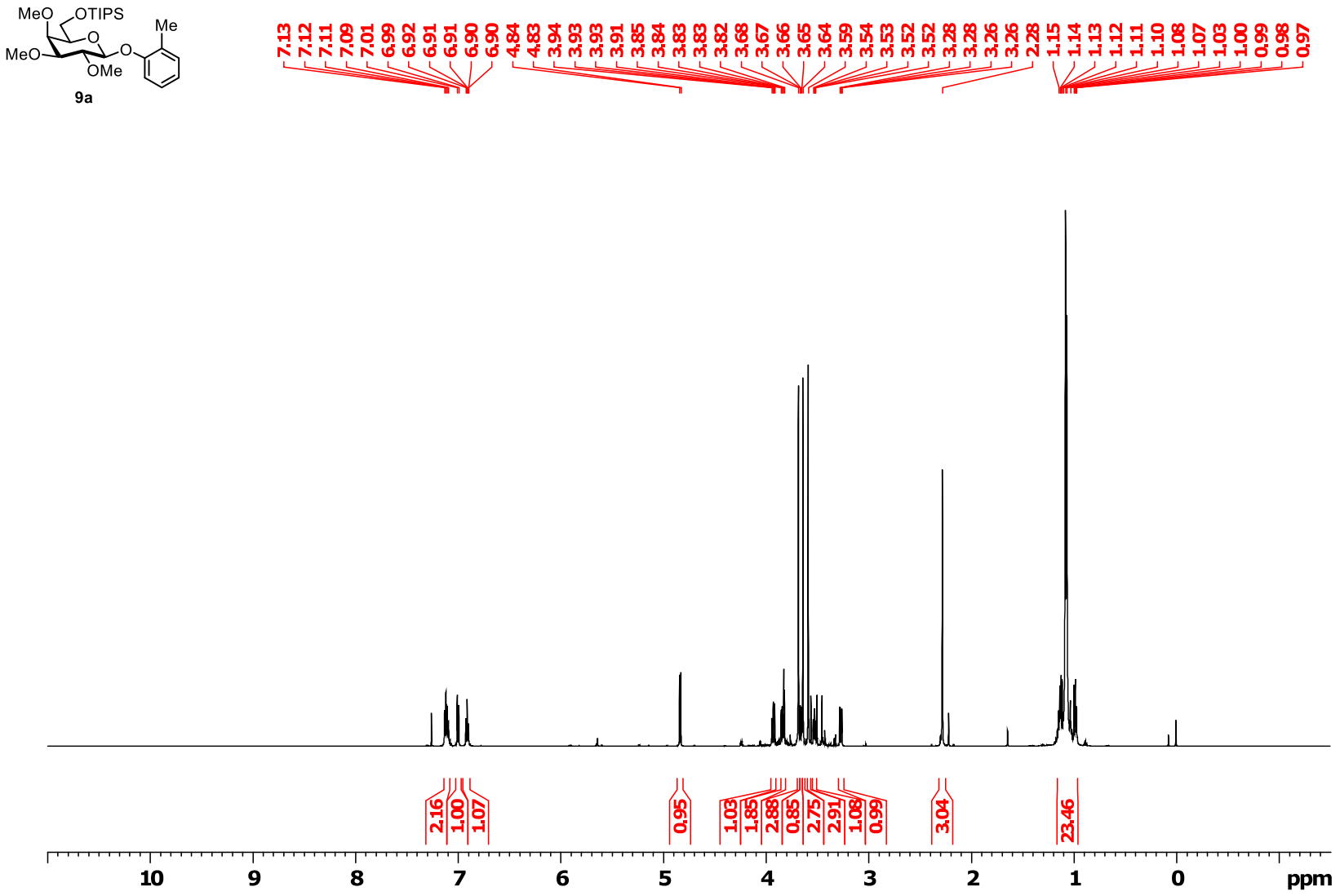


Figure S20. ^{1}H NMR spectrum of **9a**.

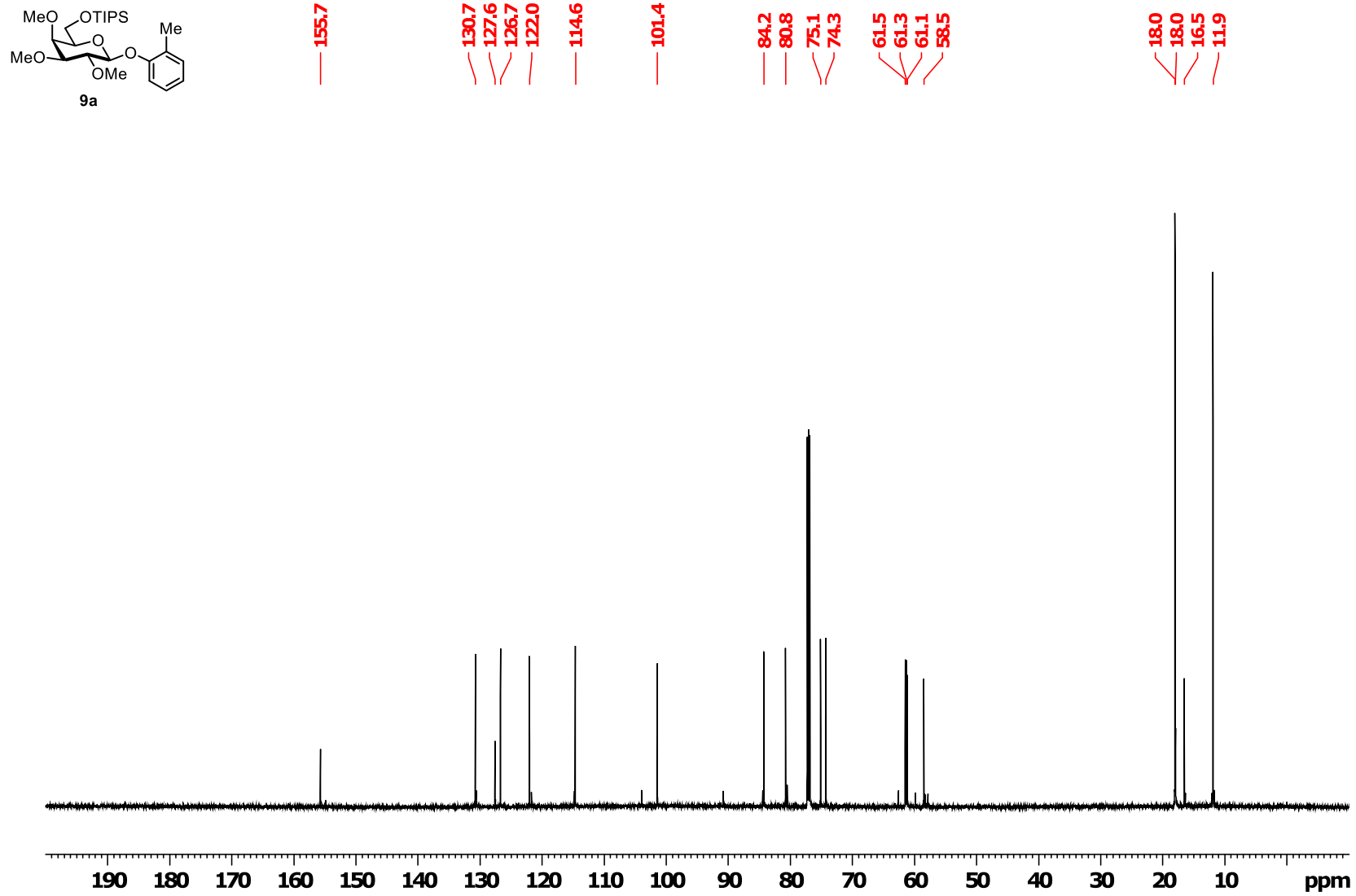


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **9a**.

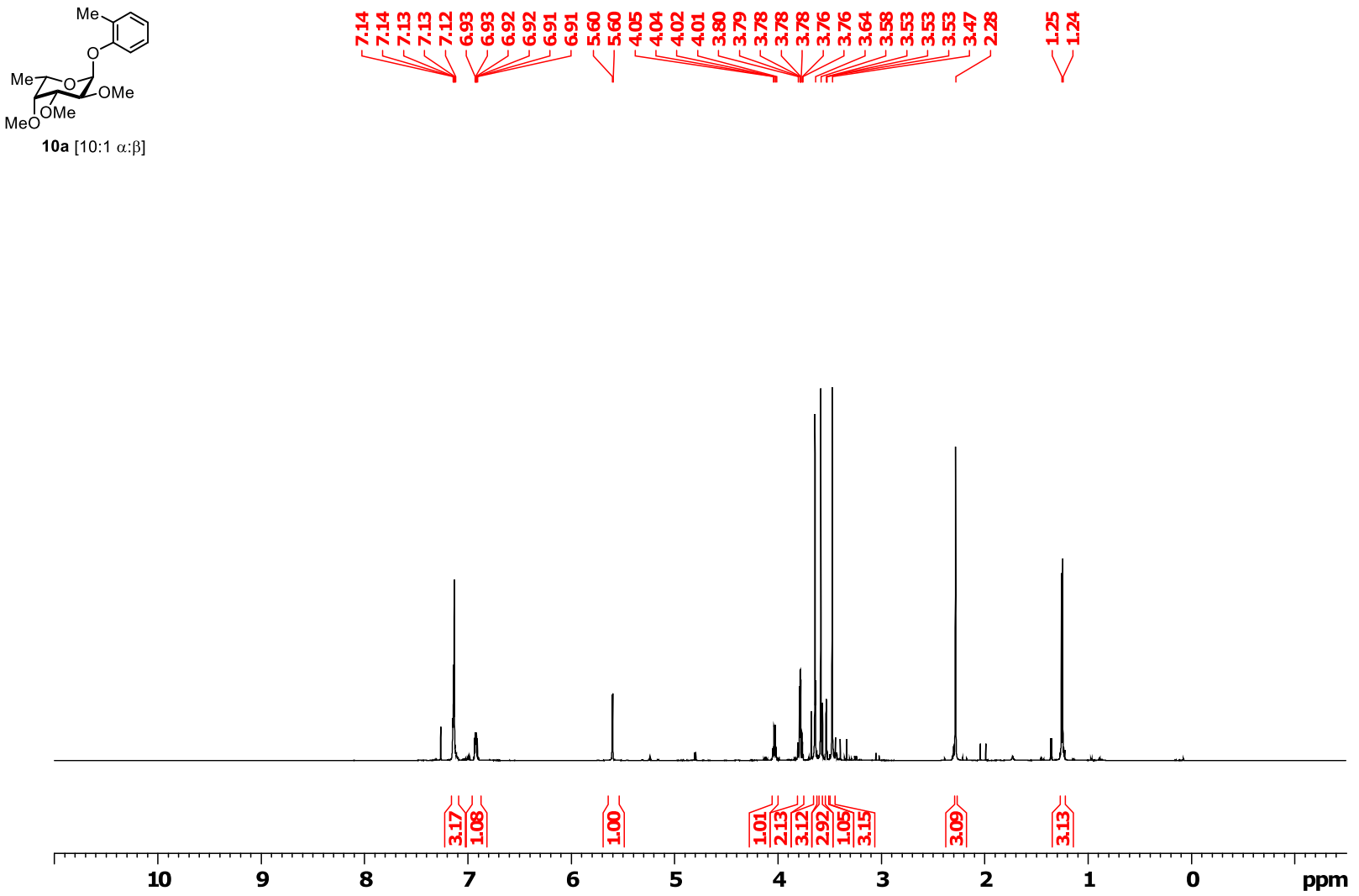


Figure S22. ^{1}H NMR spectrum of **10a**.

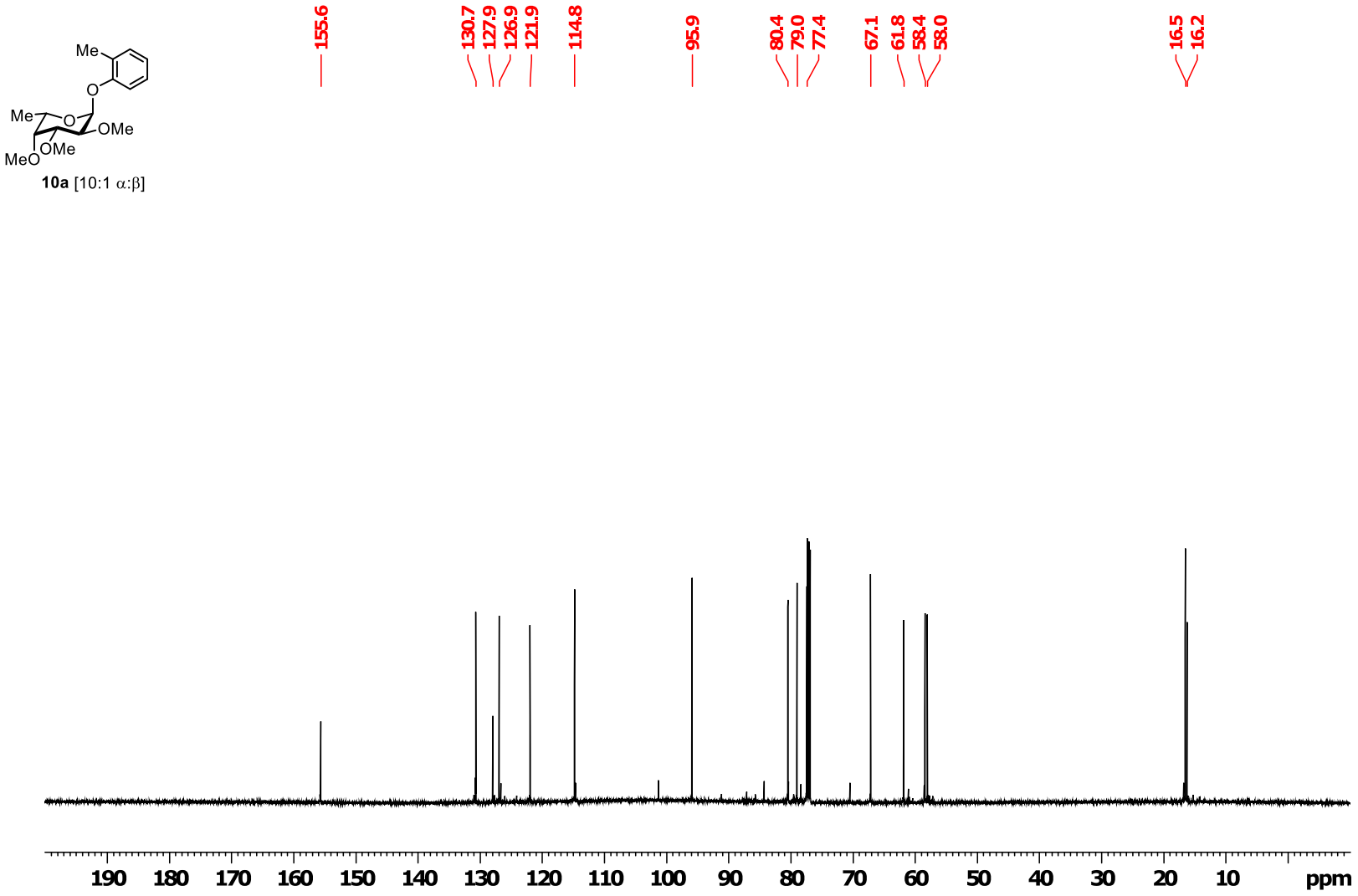


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **10a**.

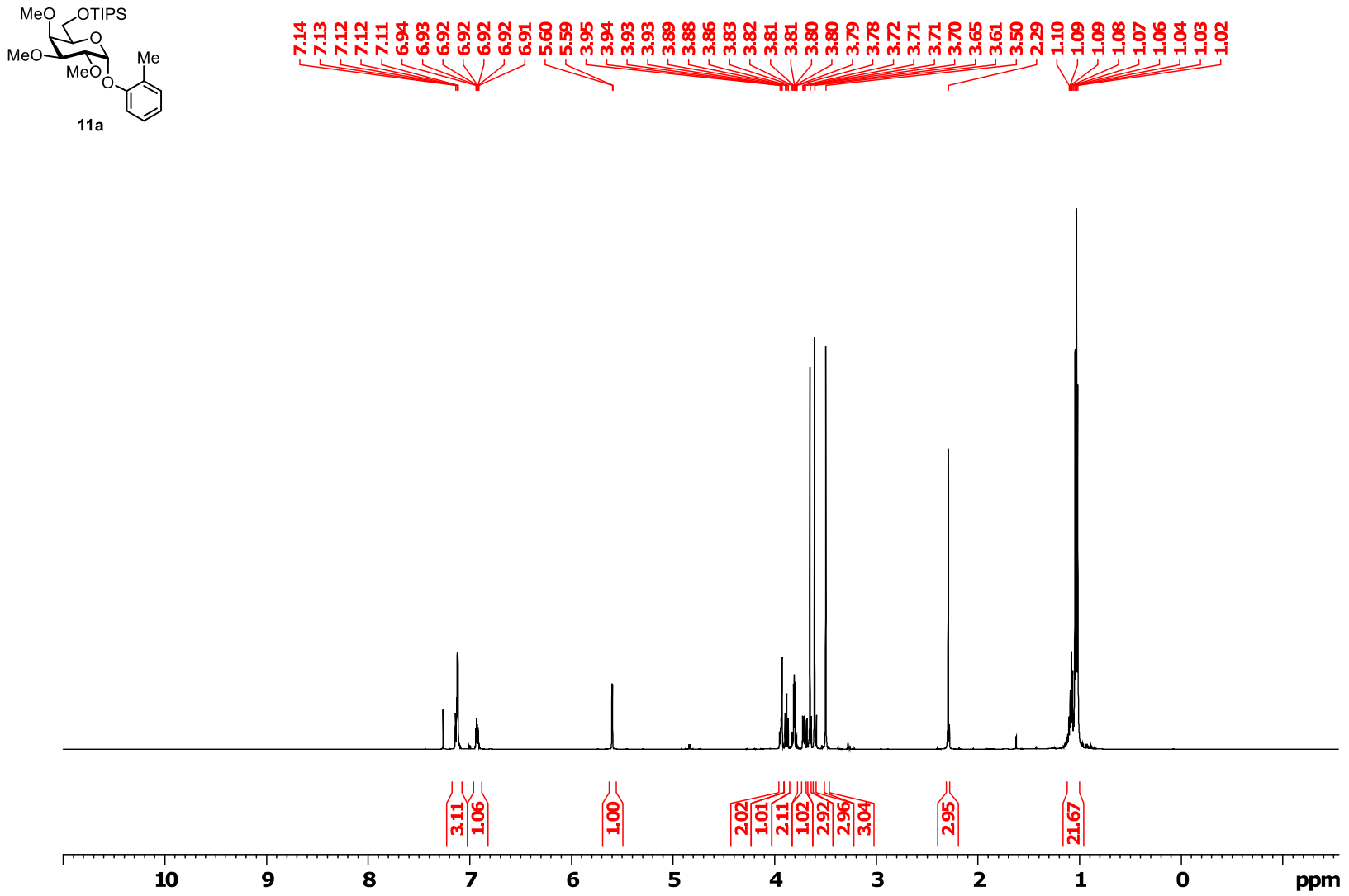


Figure S24. ^{1}H NMR spectrum of **11a**.

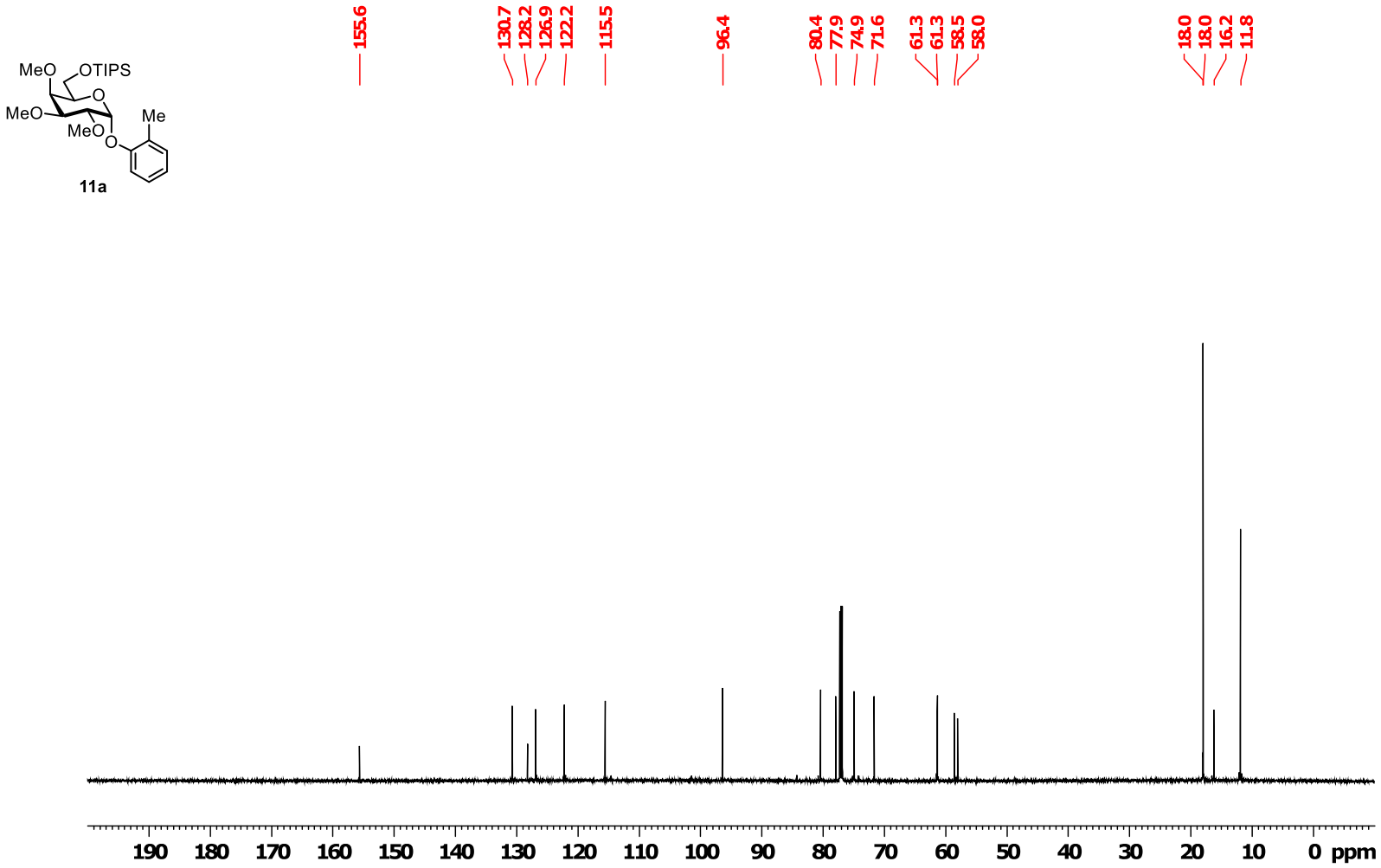


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **11a**.

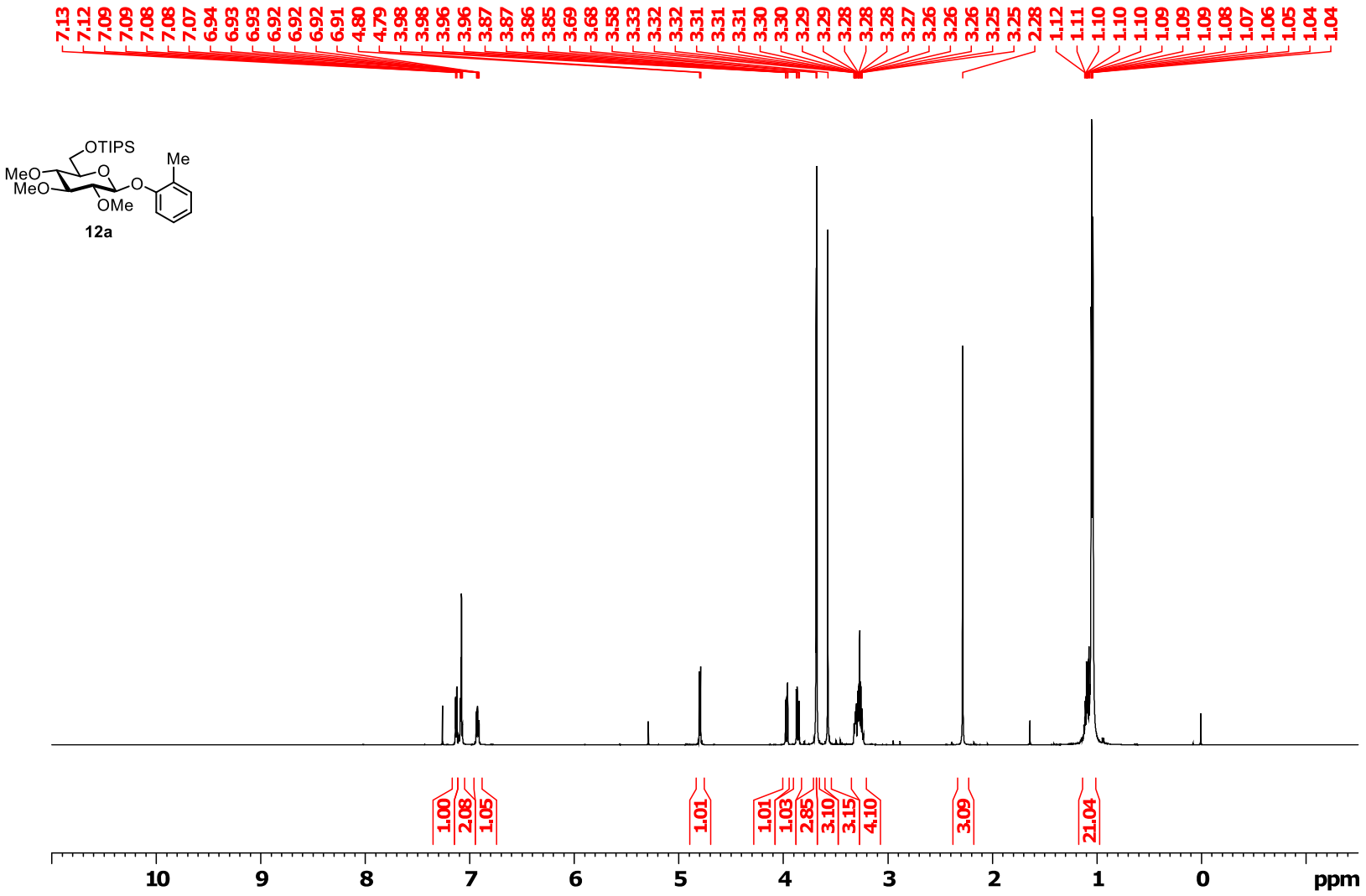


Figure S26. ^{1}H NMR spectrum of **12a**.

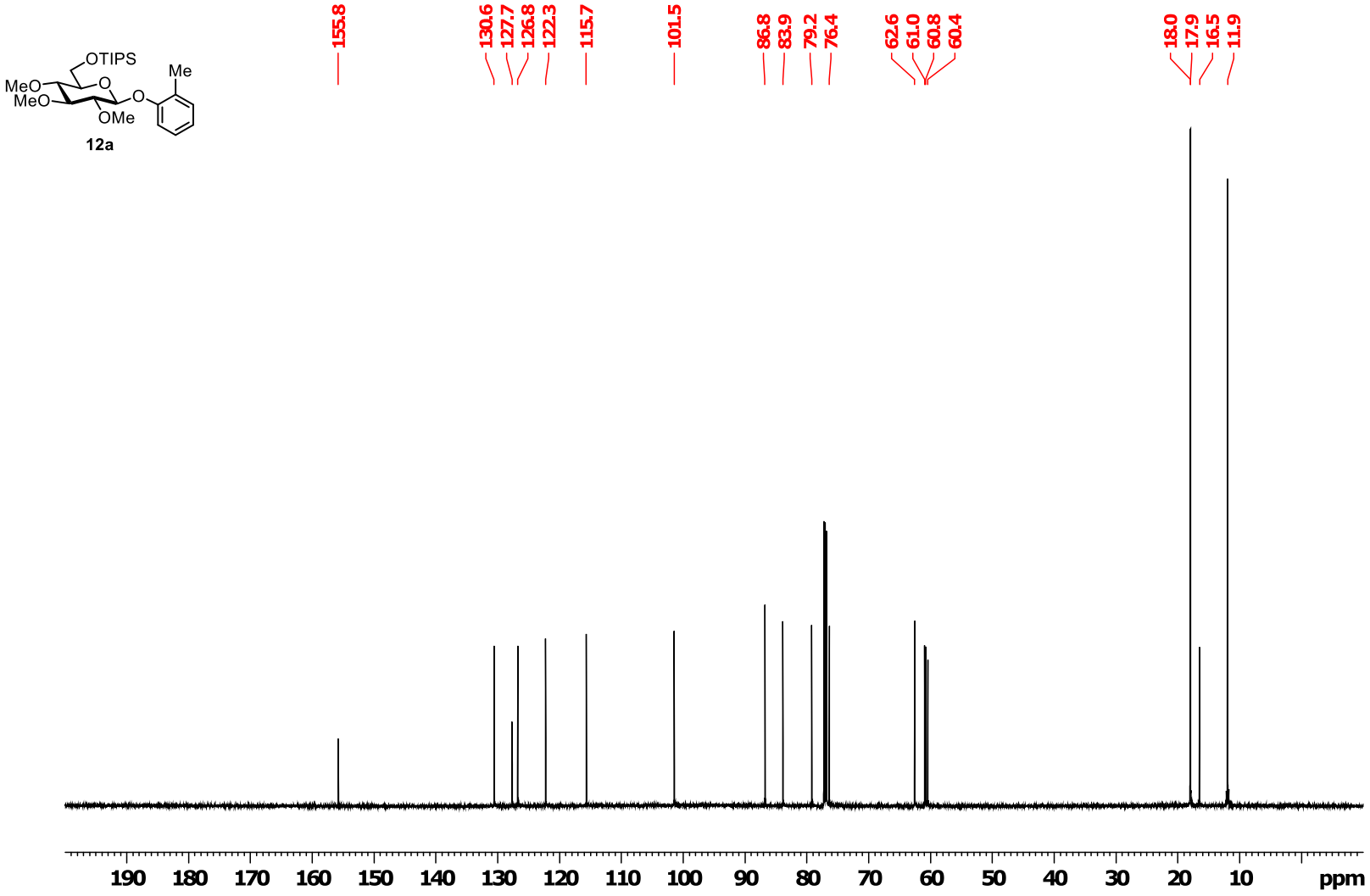


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **12a**.

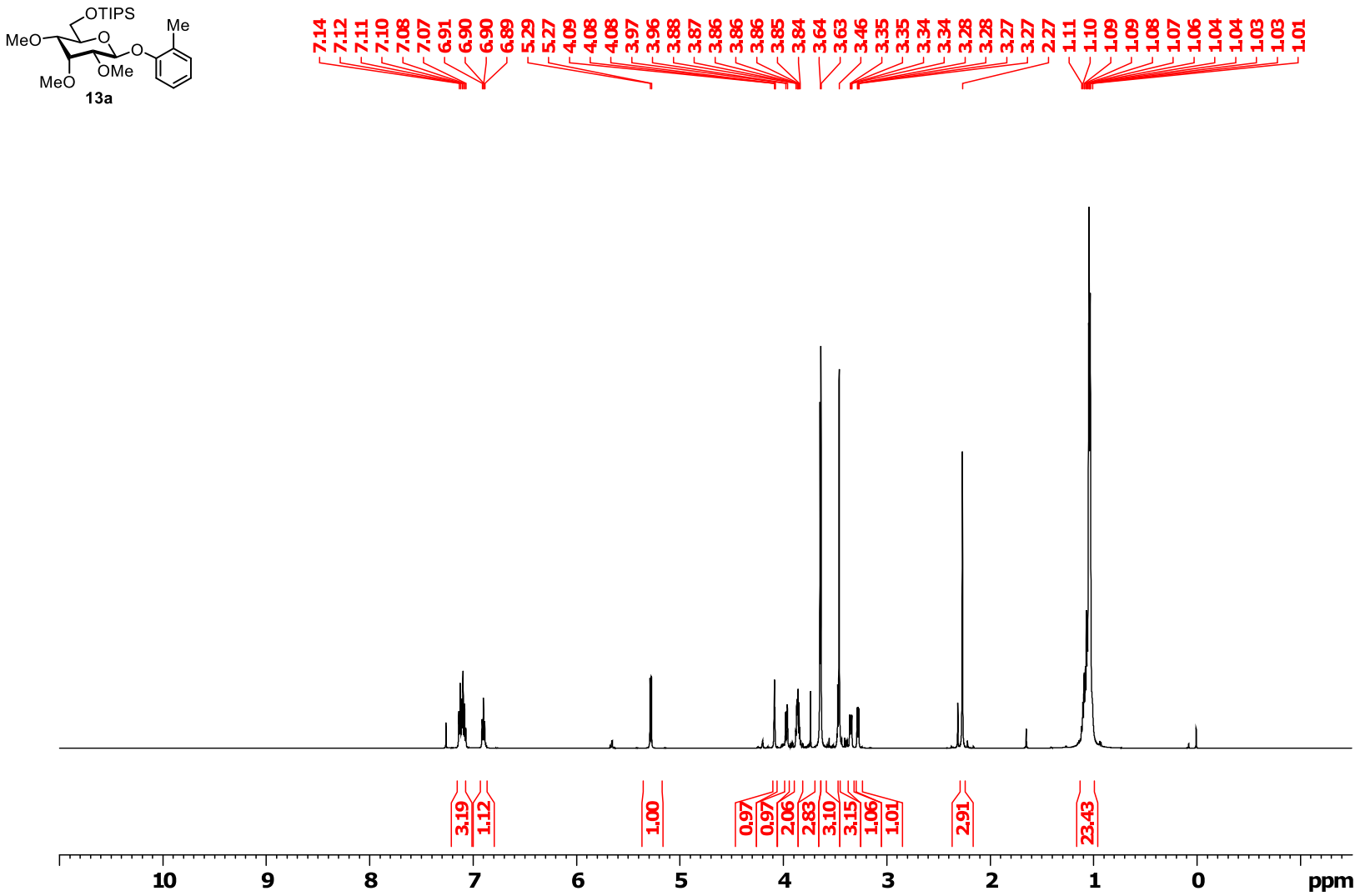


Figure S28. ^{1}H NMR spectrum of **13a**.

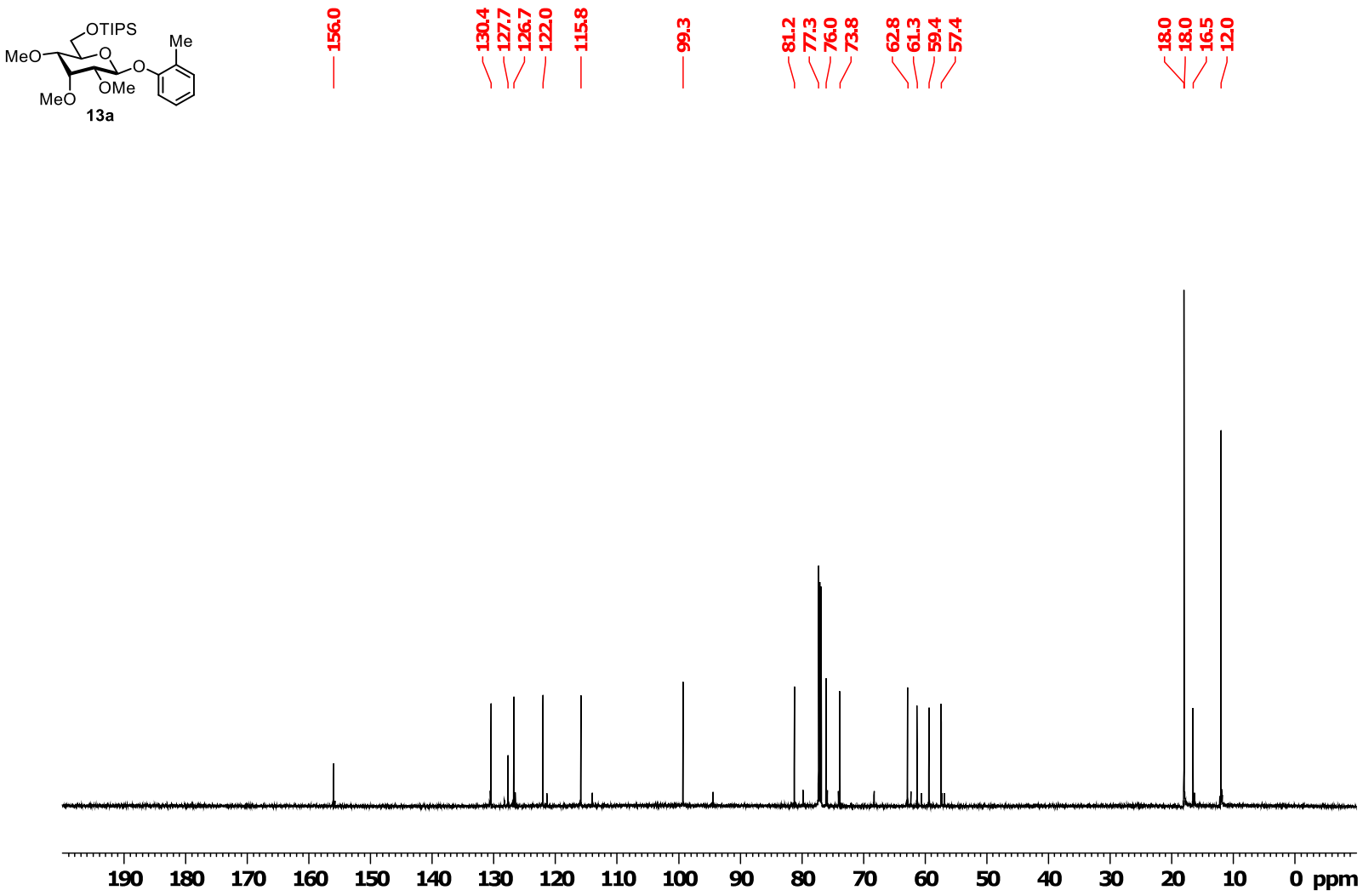


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **13a**.

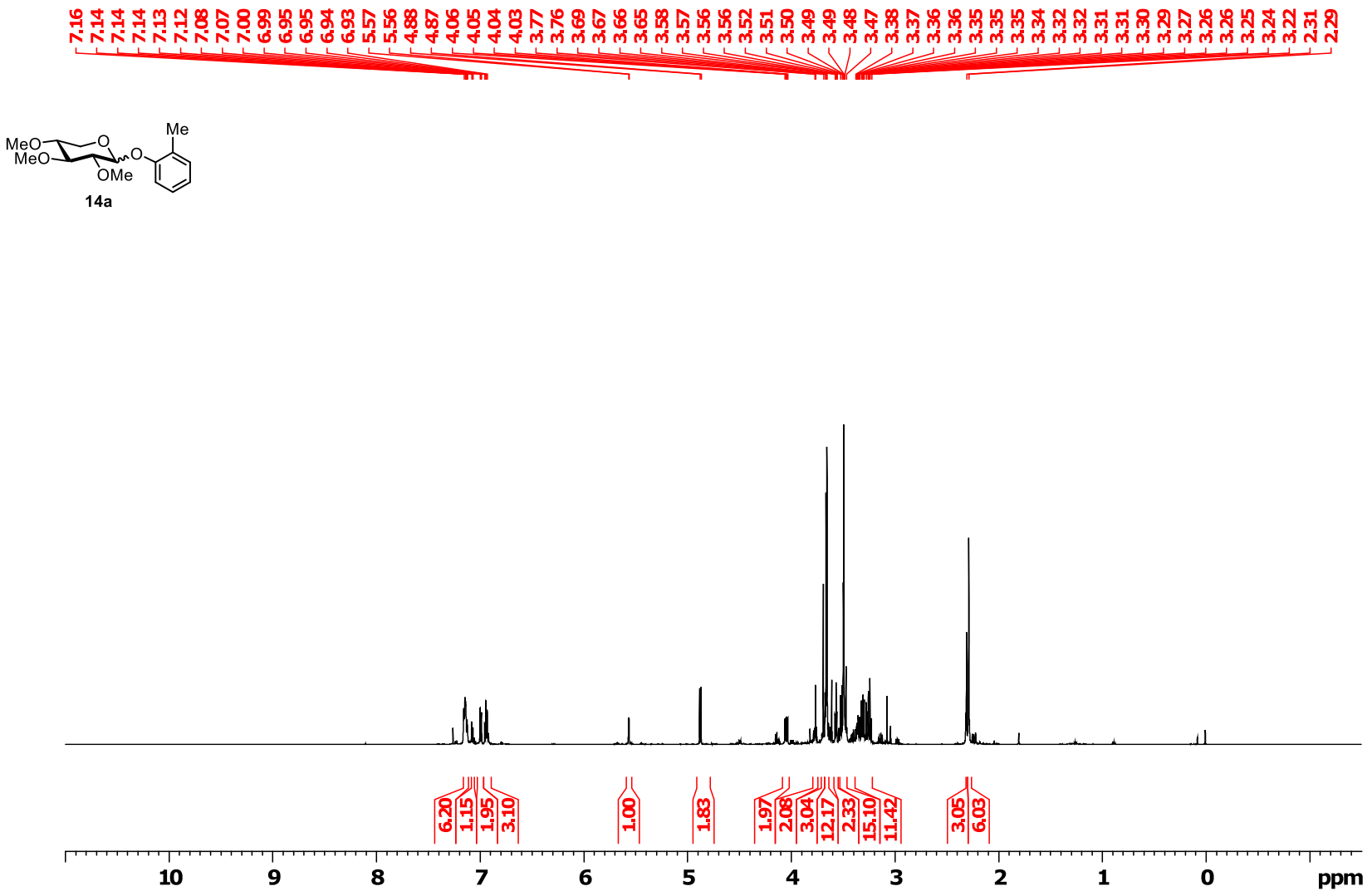


Figure S30. ^{1}H NMR spectrum of **14a** (mixture of anomers).

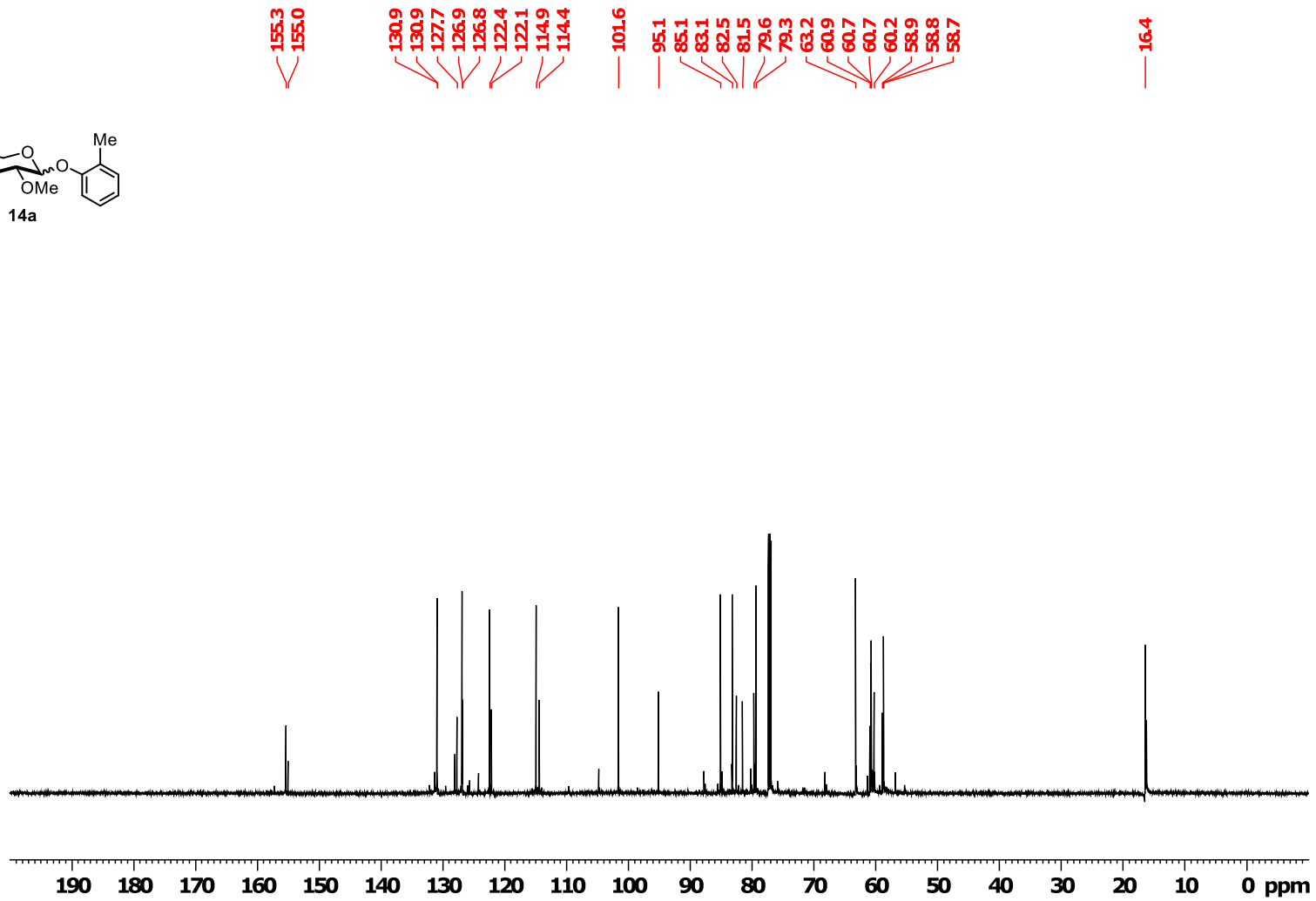


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **14a** (mixture of anomers).

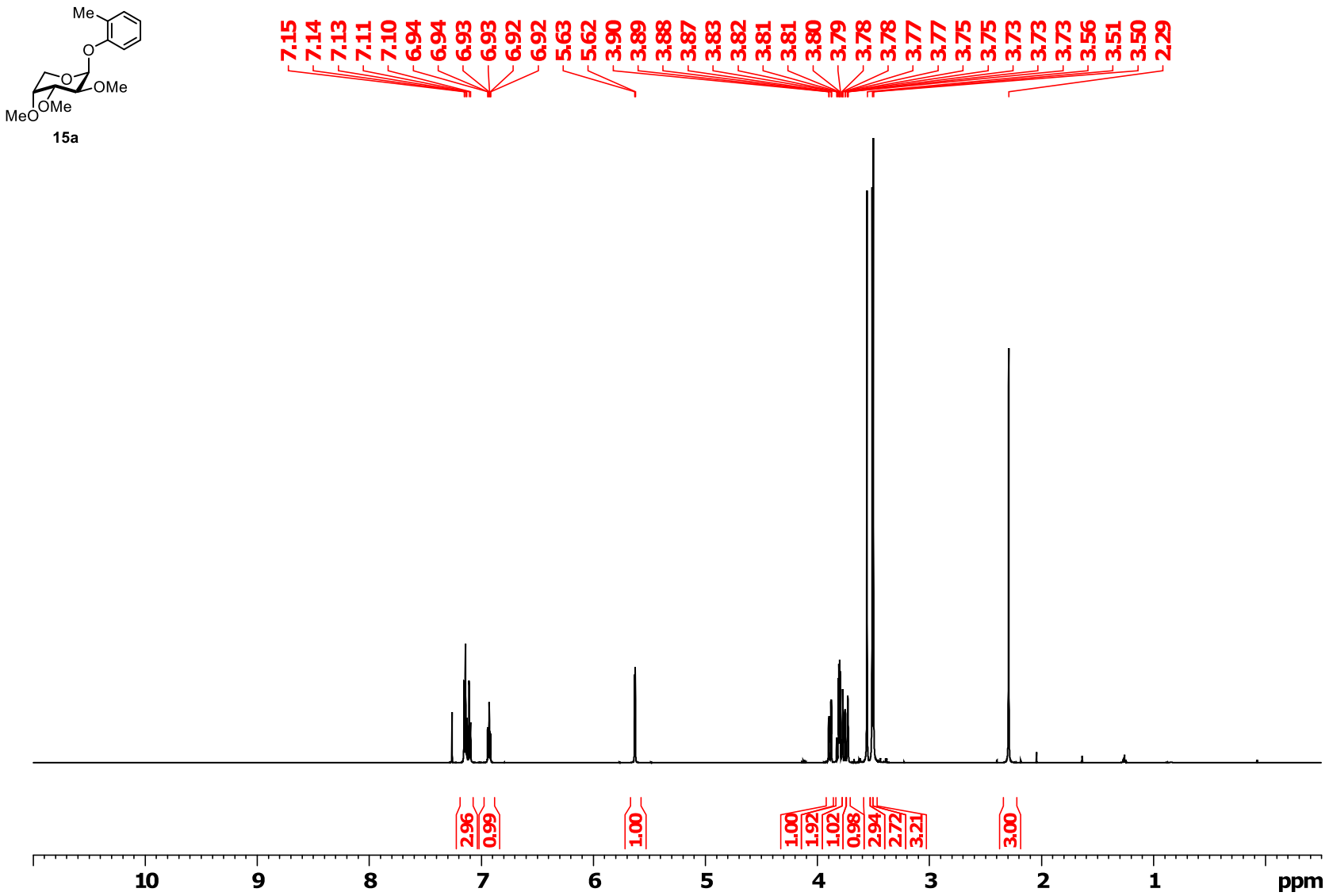


Figure S32. ^{1}H NMR spectrum of **15a**.

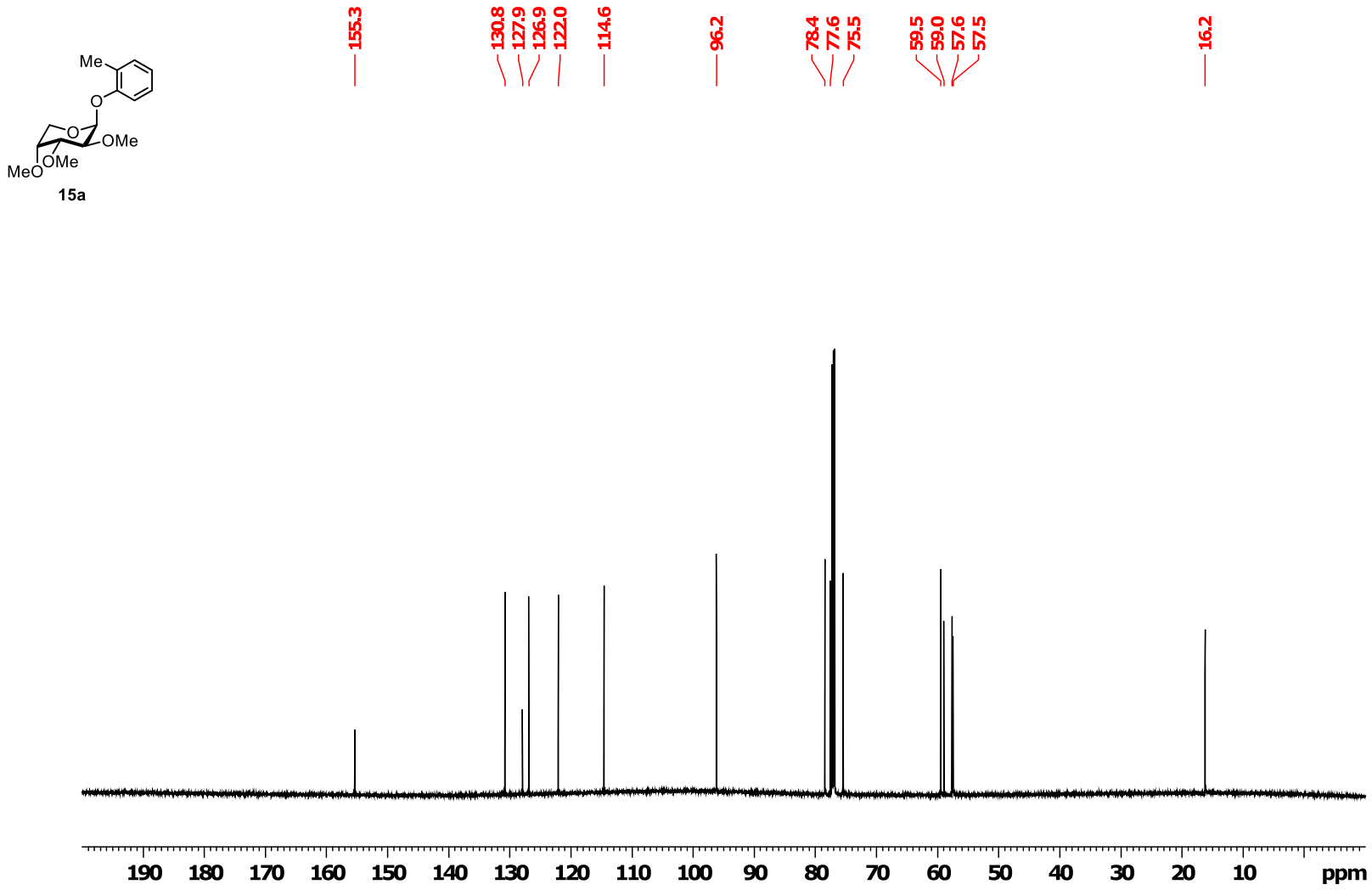


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **15a**.

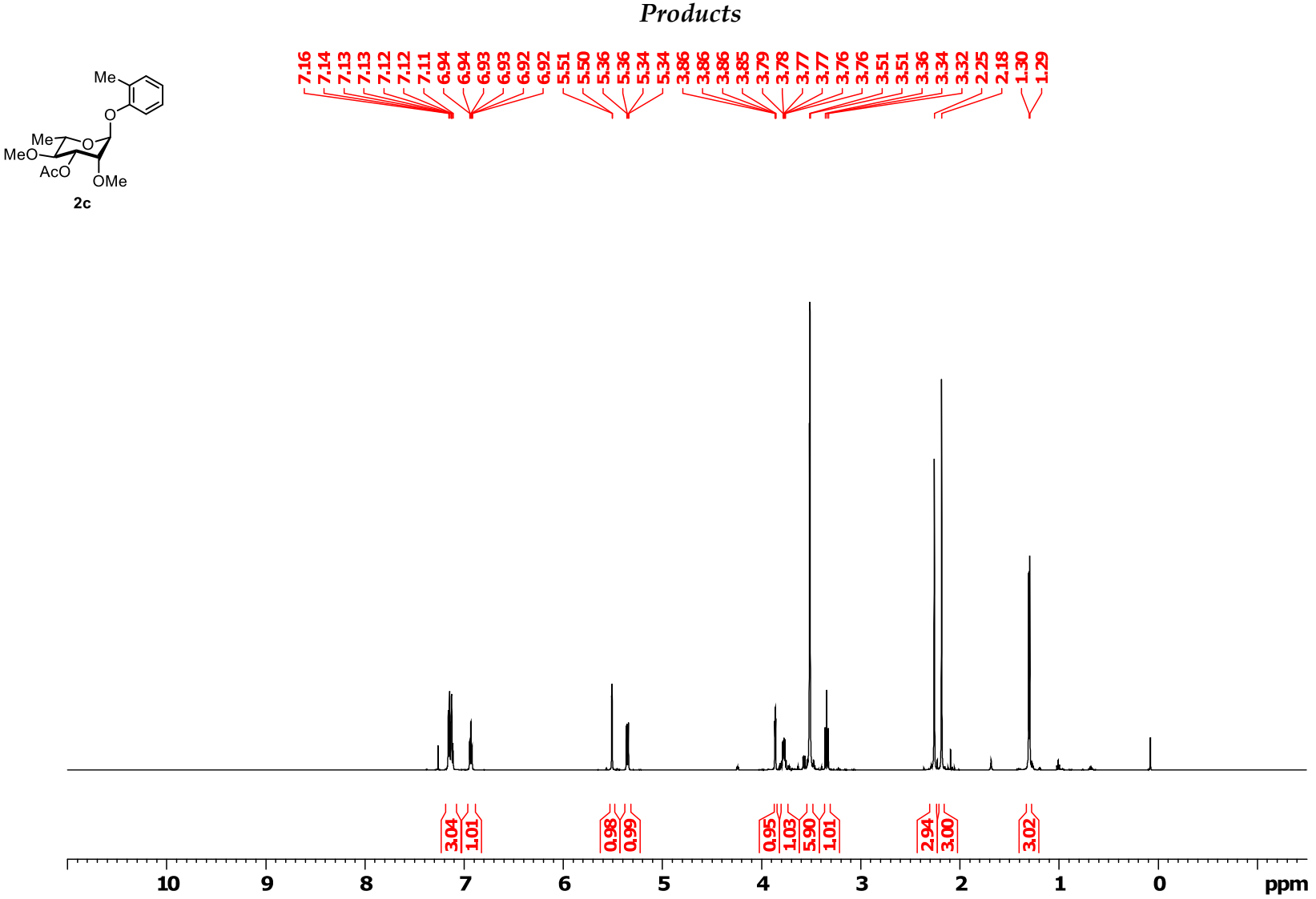


Figure S34. ^{1}H NMR spectrum of **2c**.

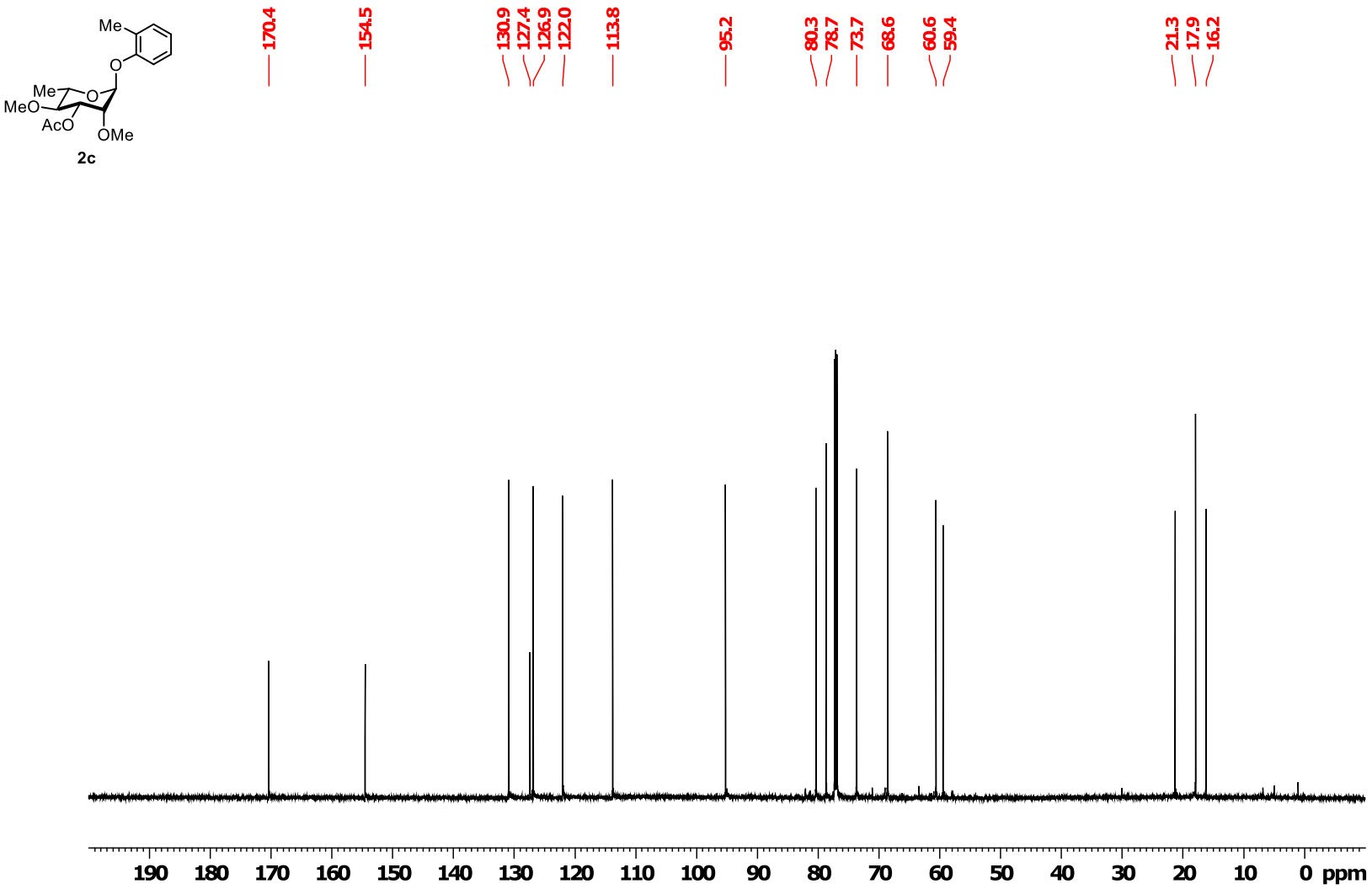


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **2c**.

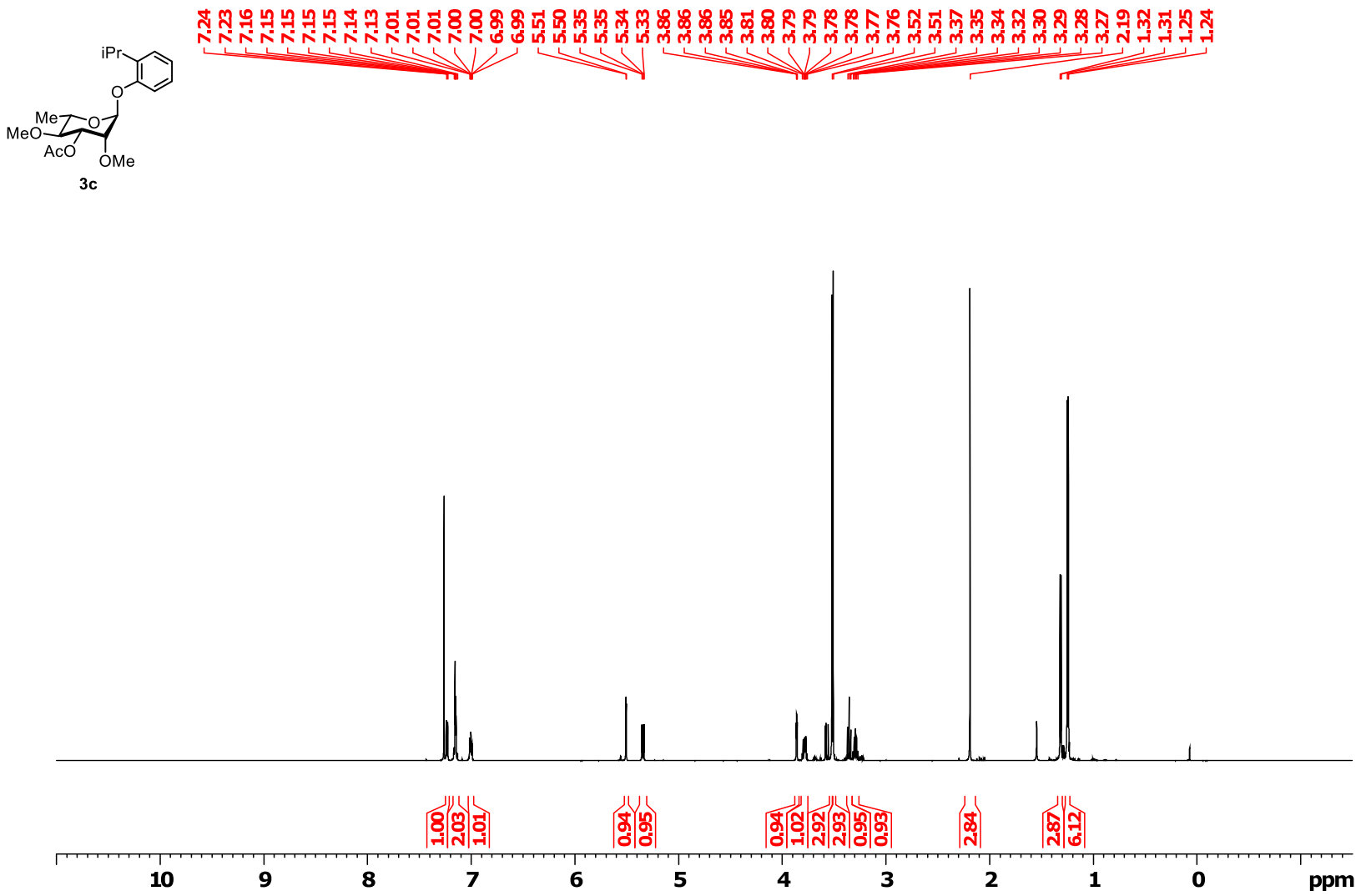


Figure S36. ^{1}H NMR spectrum of **3c**.

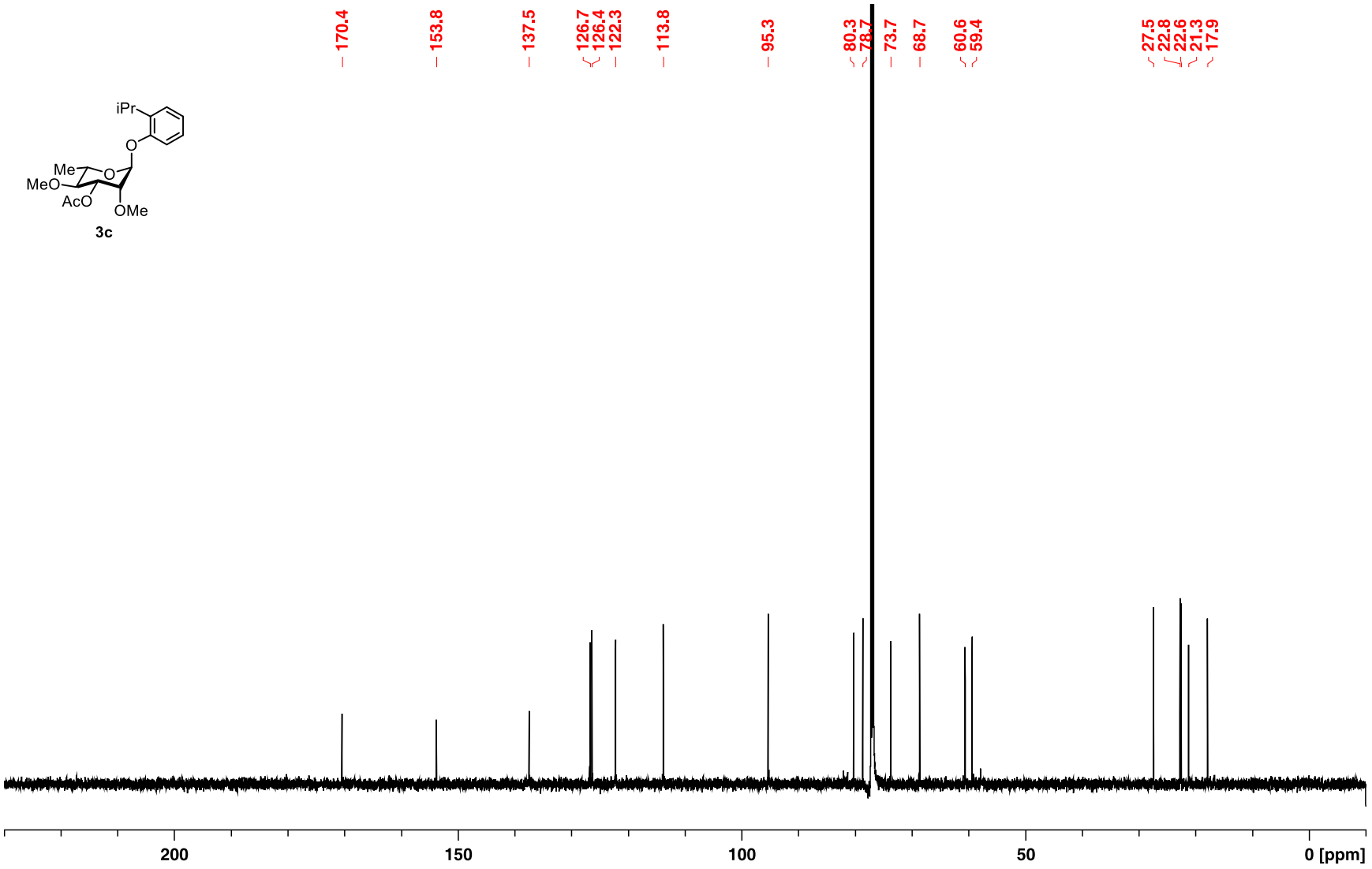


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **3c**.

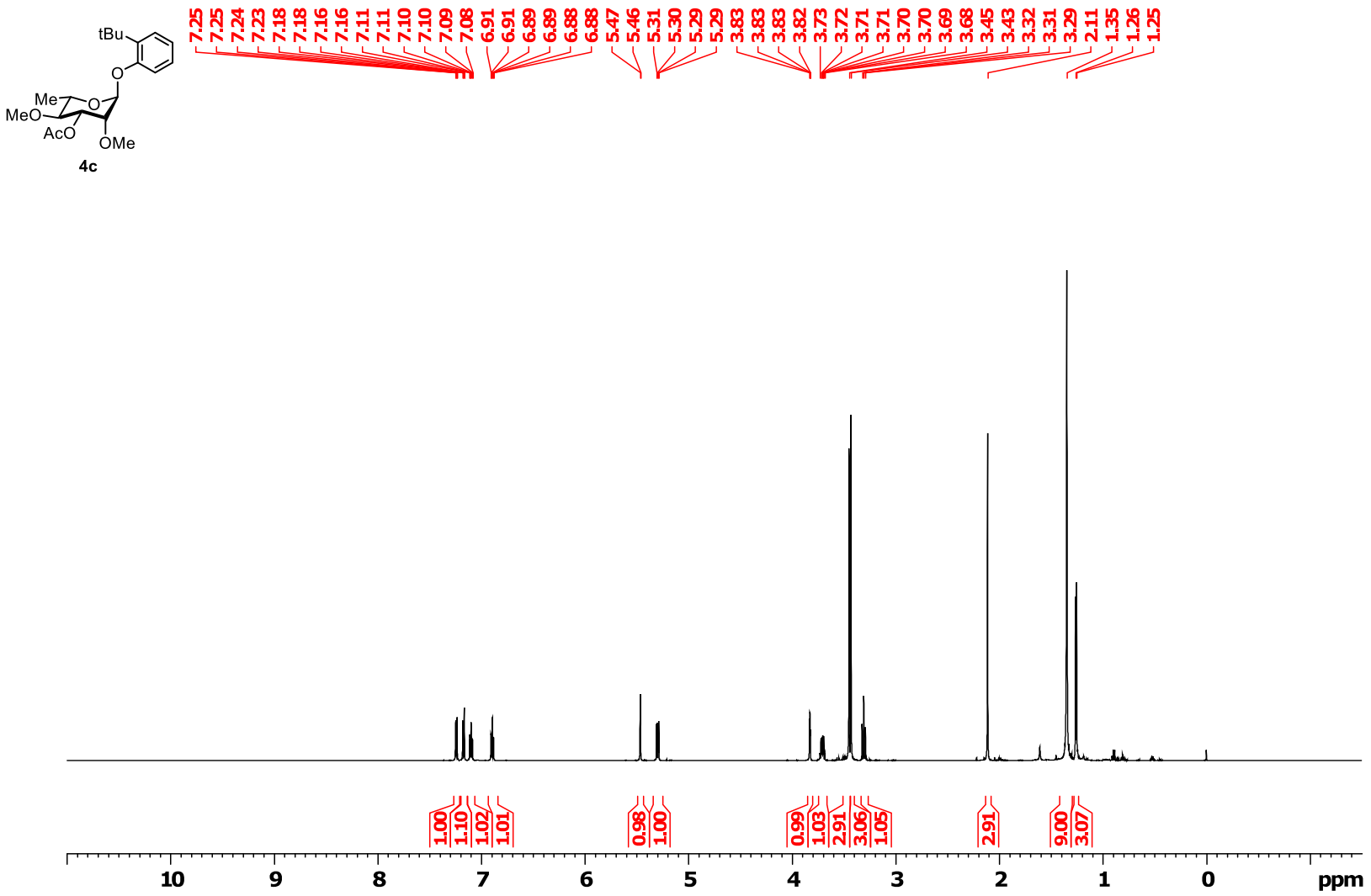


Figure S38. ^{1}H NMR spectrum of **4c**.

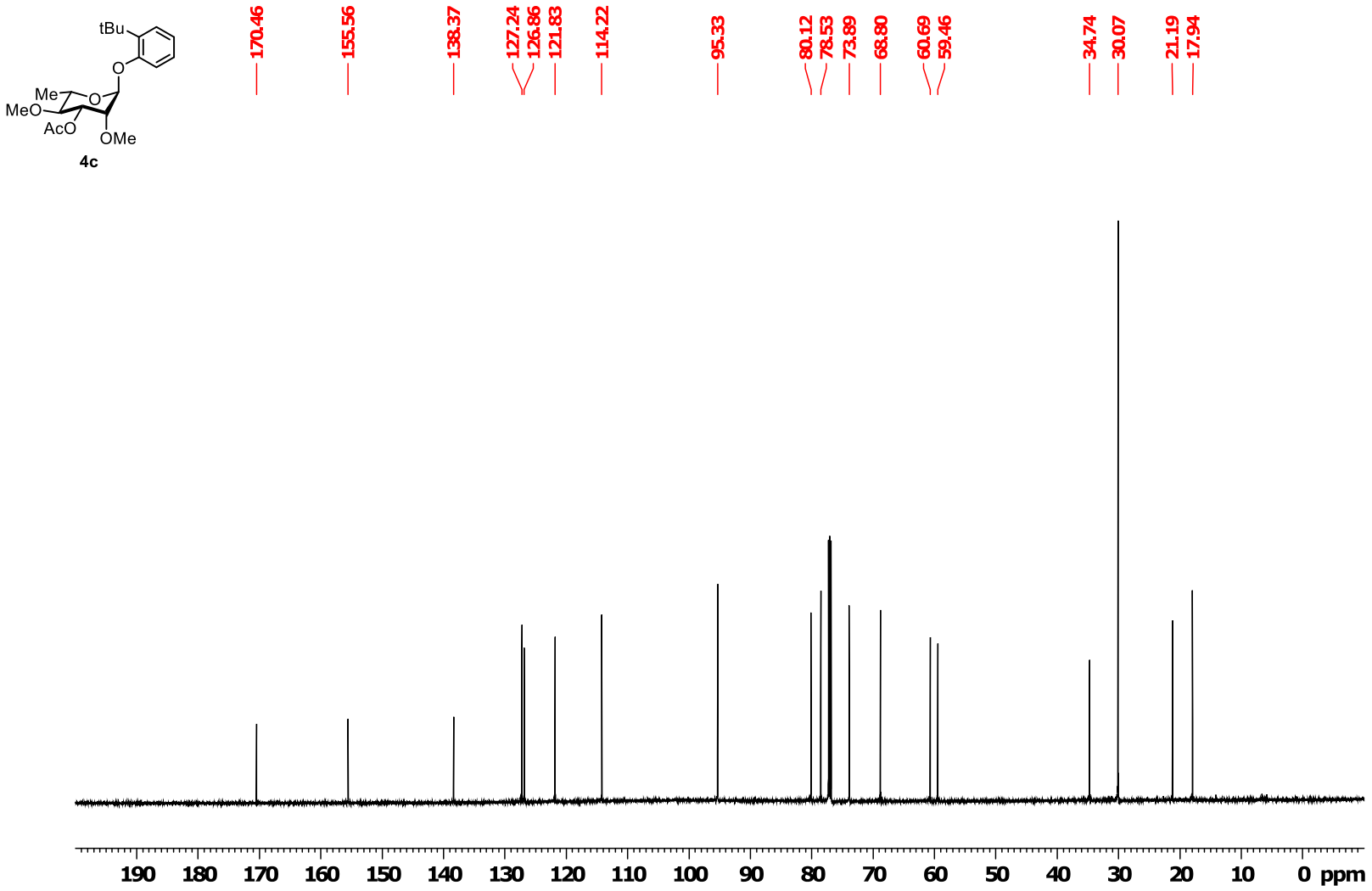


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **4c**.

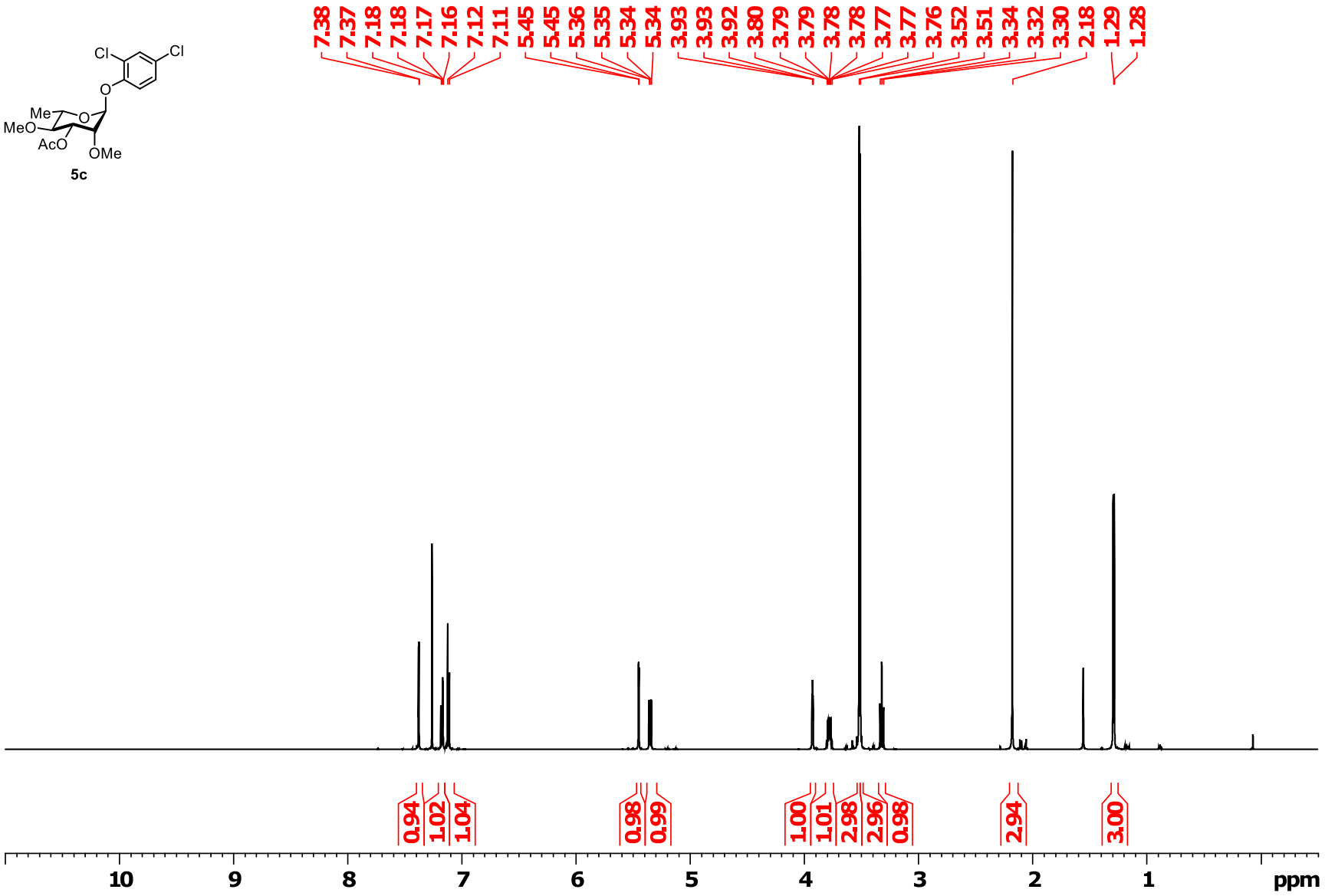


Figure S40. ^{1}H NMR spectrum of **5c**.

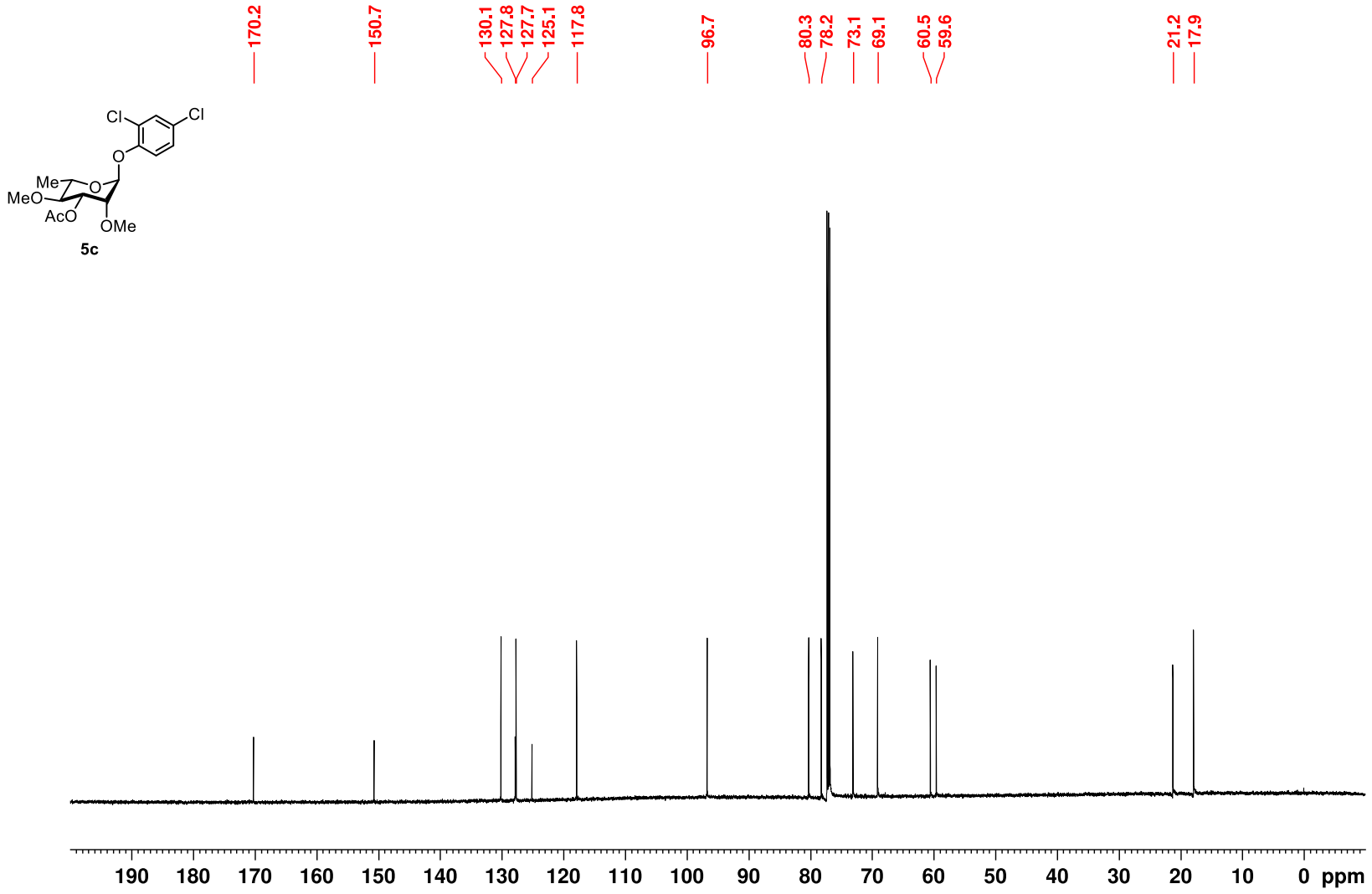


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **5c**.

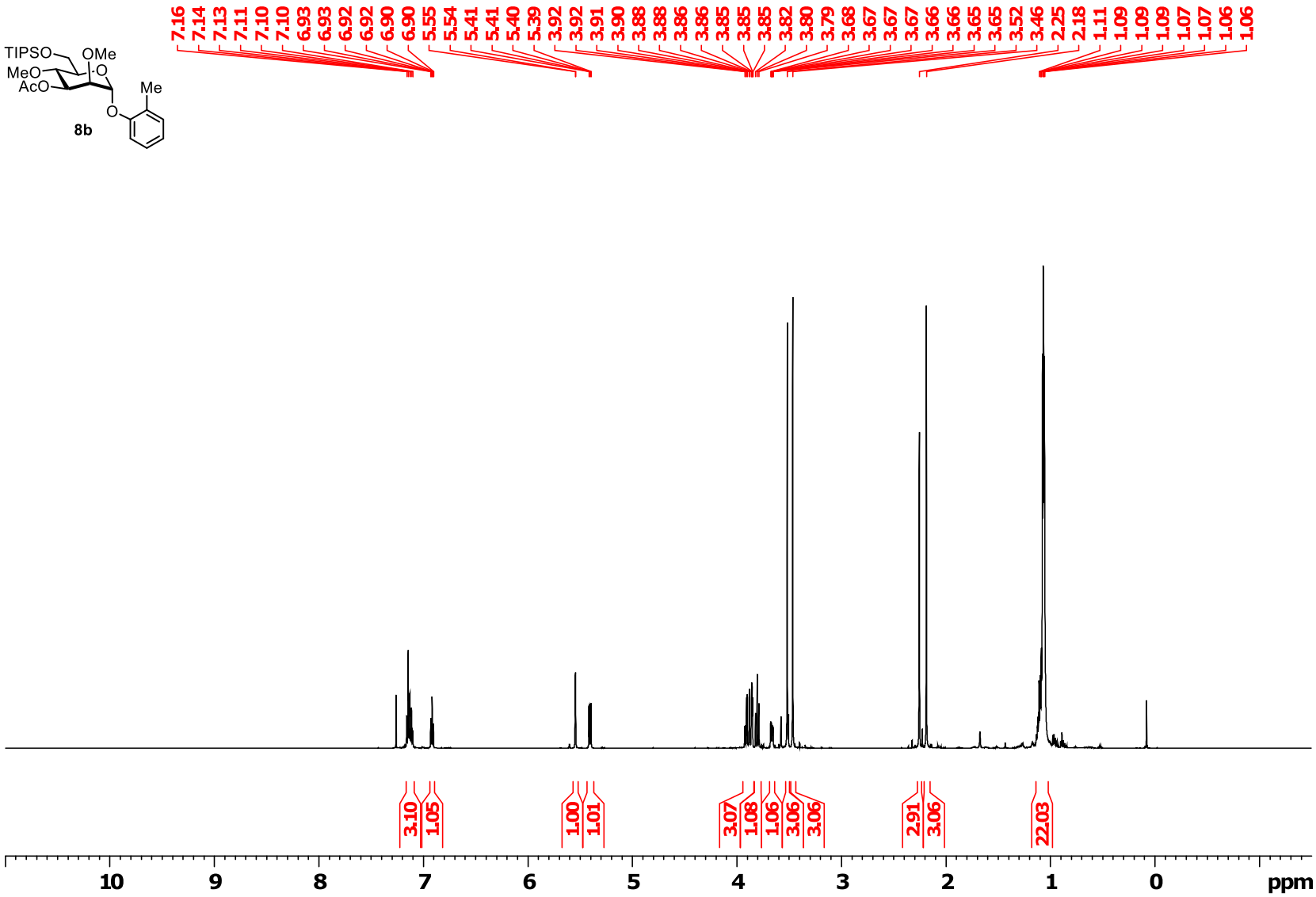


Figure S42. ^{1}H NMR spectrum of **8b**.

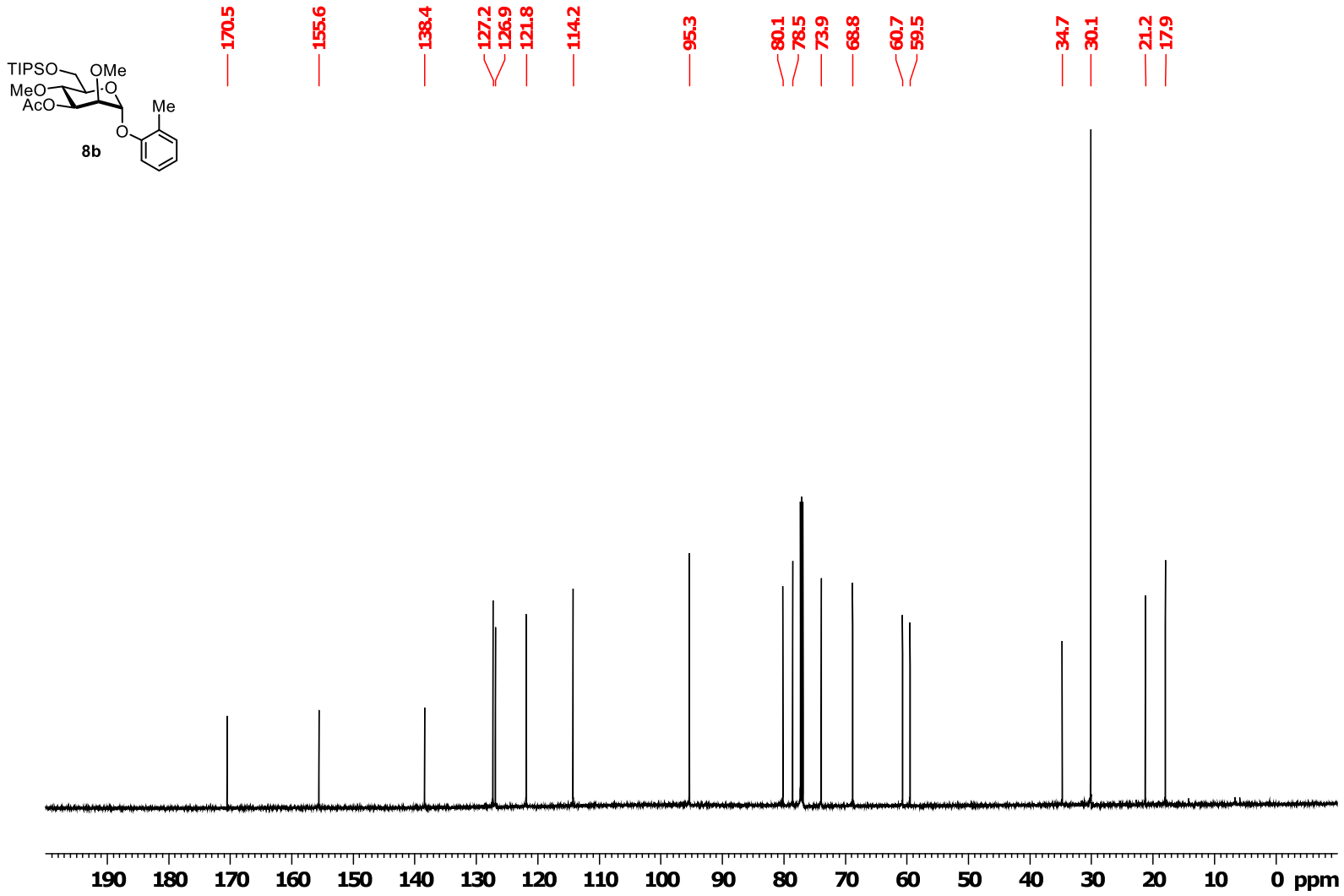


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **8b**.

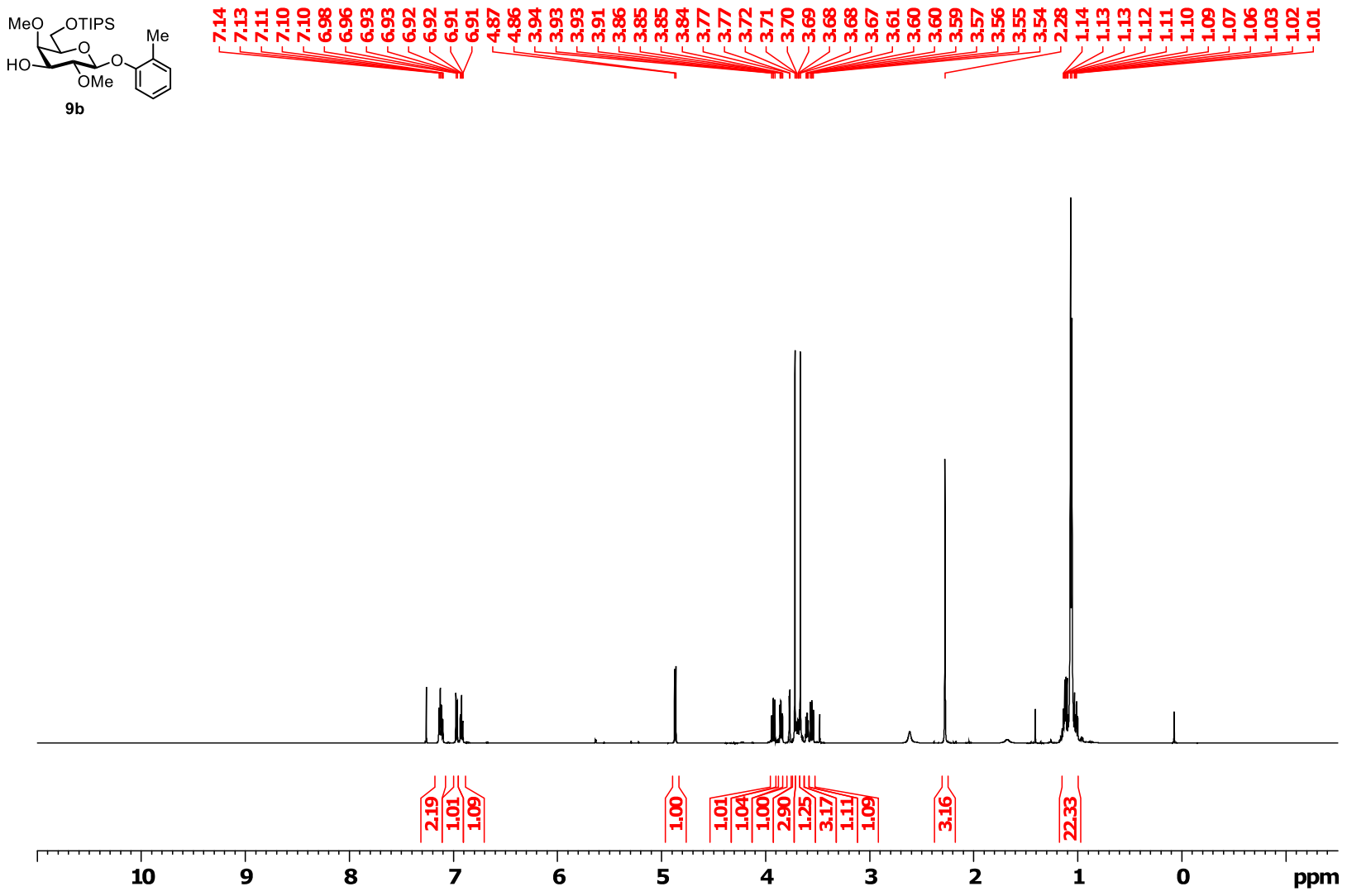


Figure S44. ^{1}H NMR spectrum of **9b**.

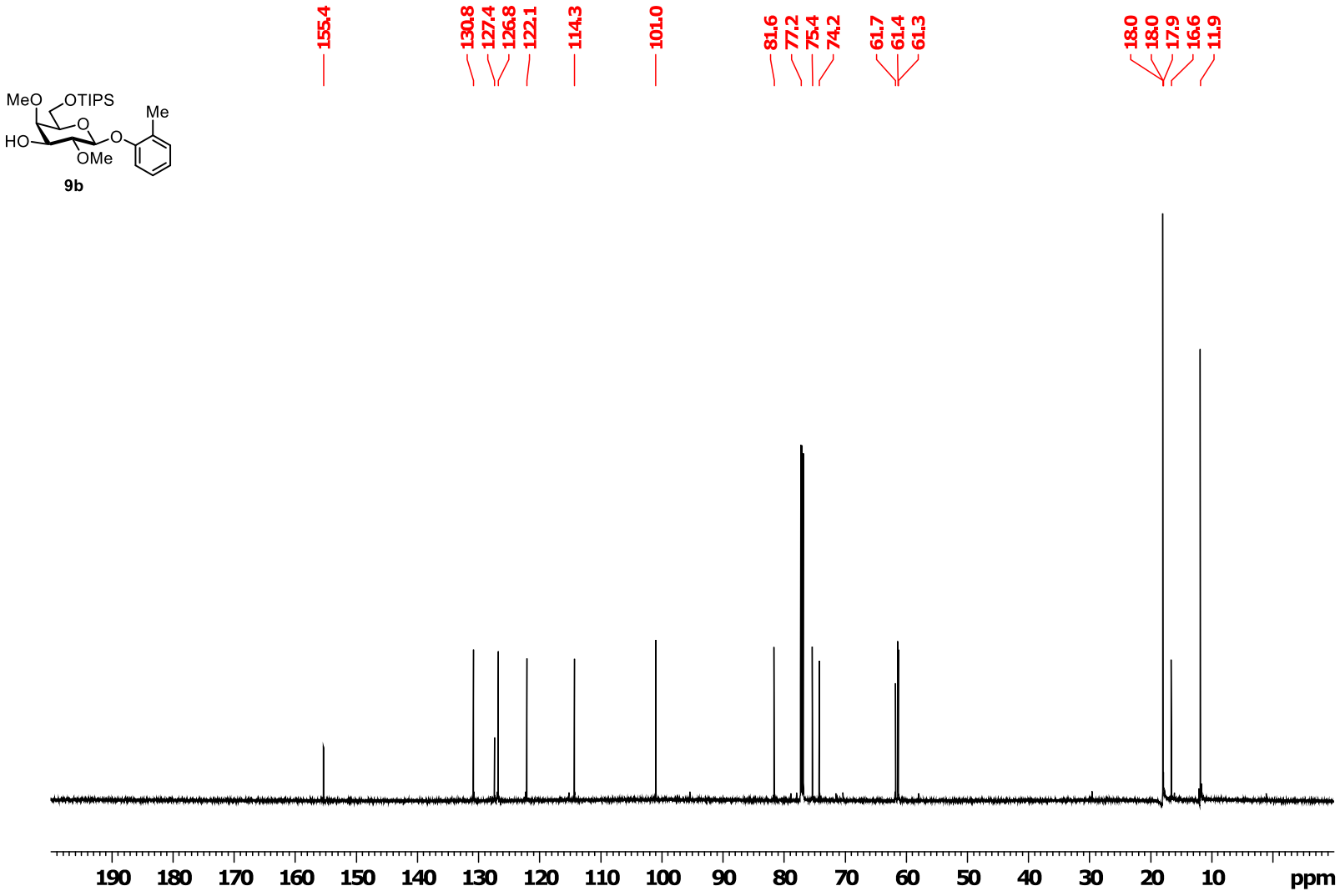


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **9b**.

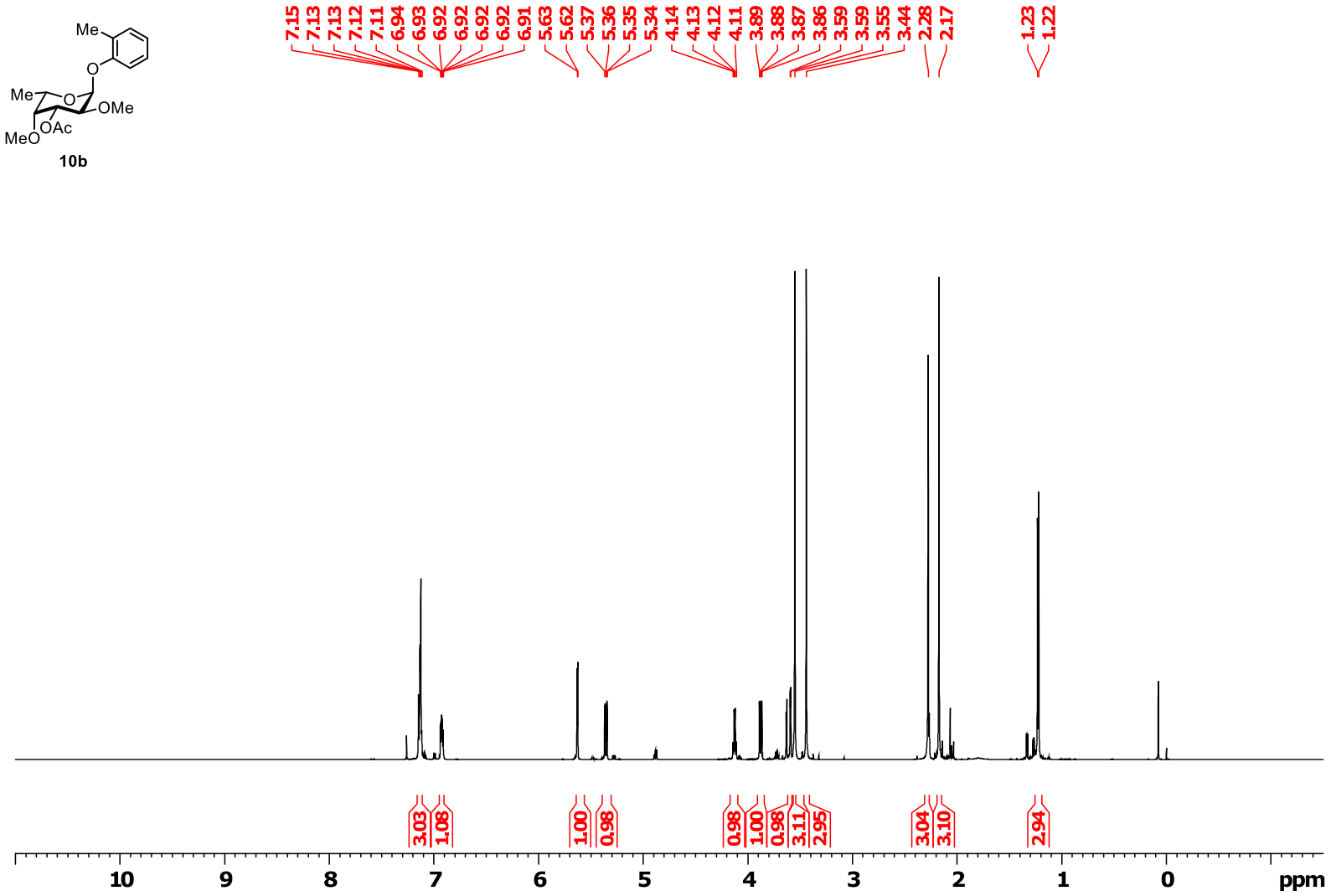


Figure S46. ^{1}H NMR spectrum of **10b**.

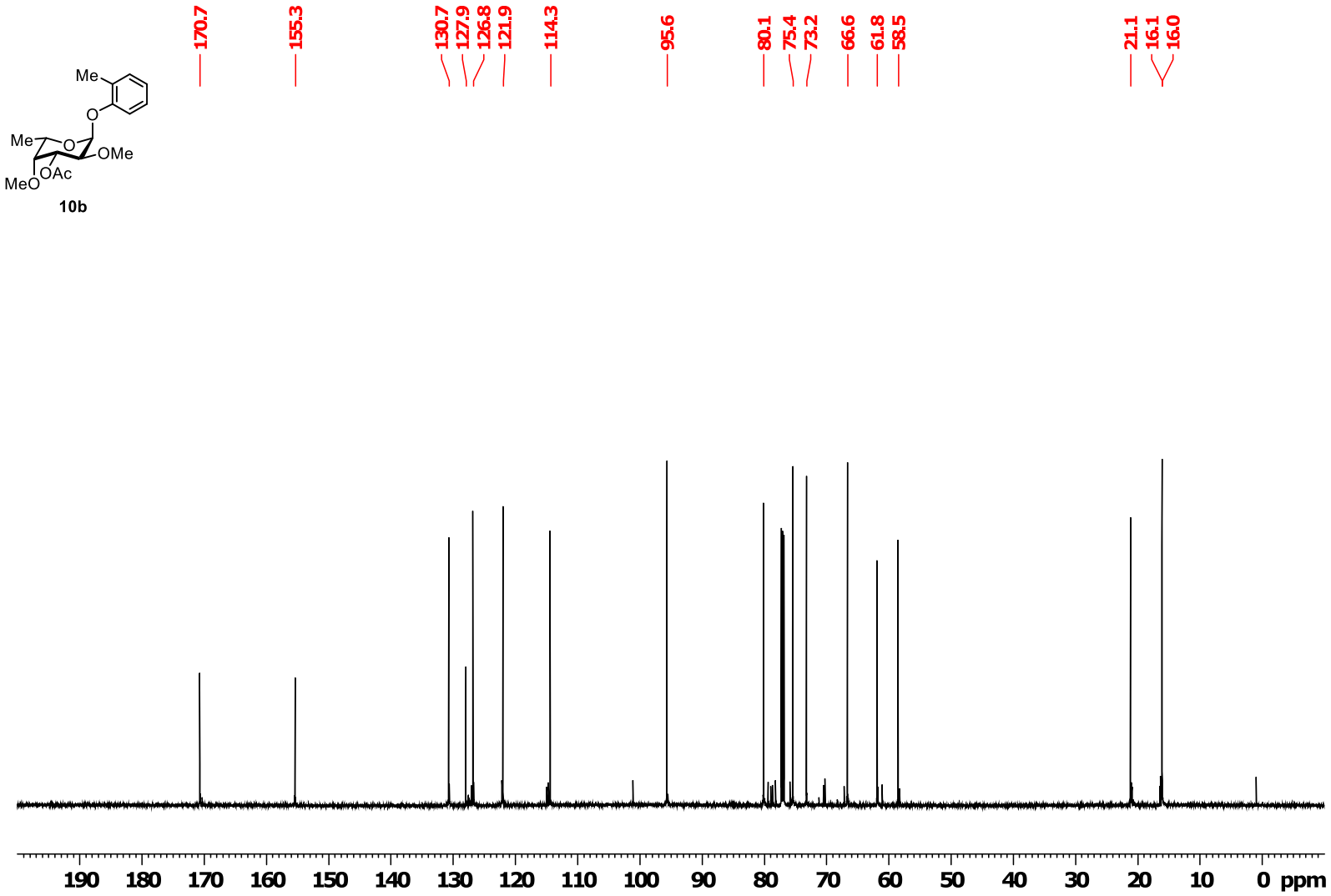


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **10b**.

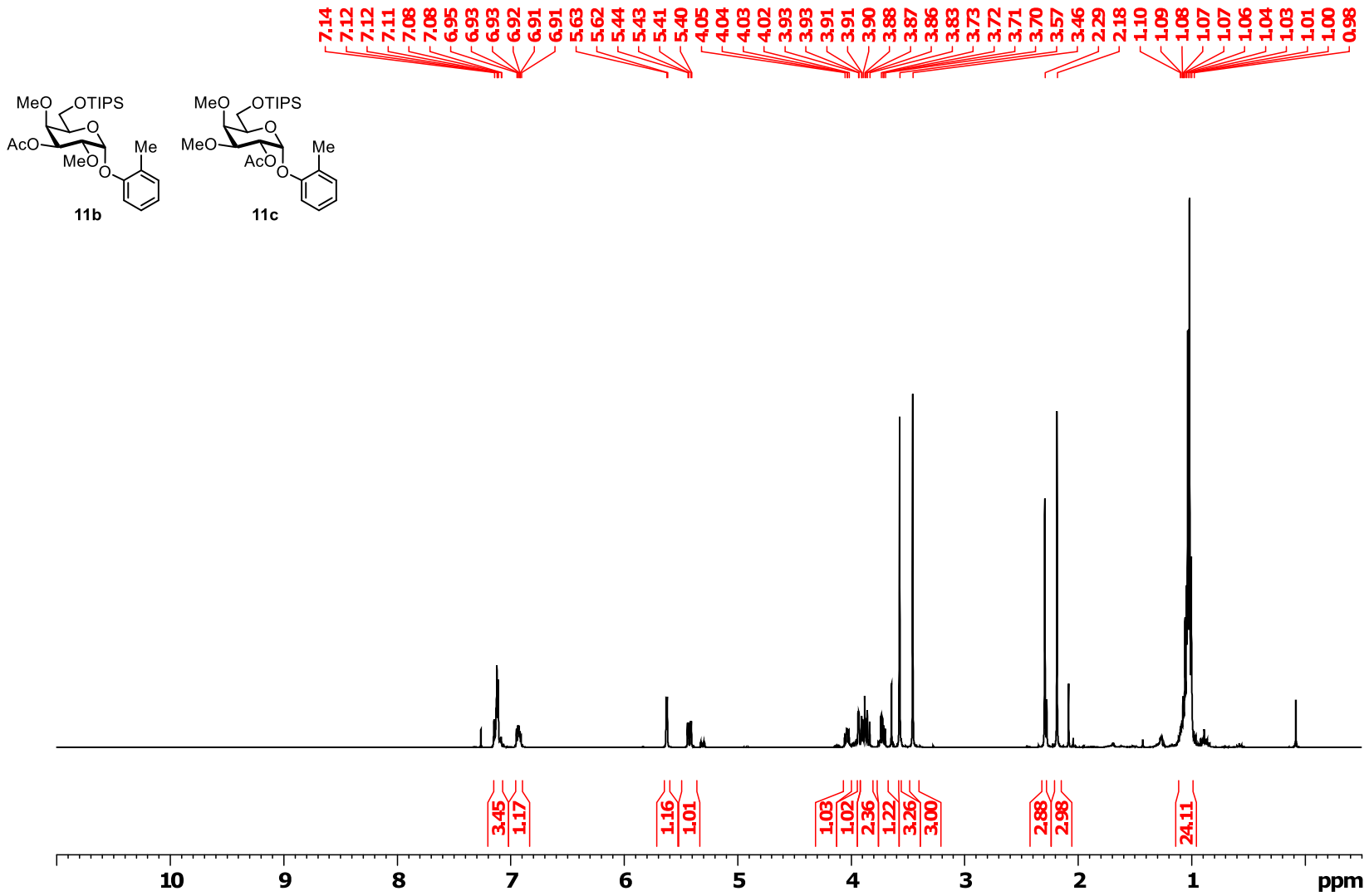


Figure S48. ^{1}H NMR spectrum of **11b**/**11c**.

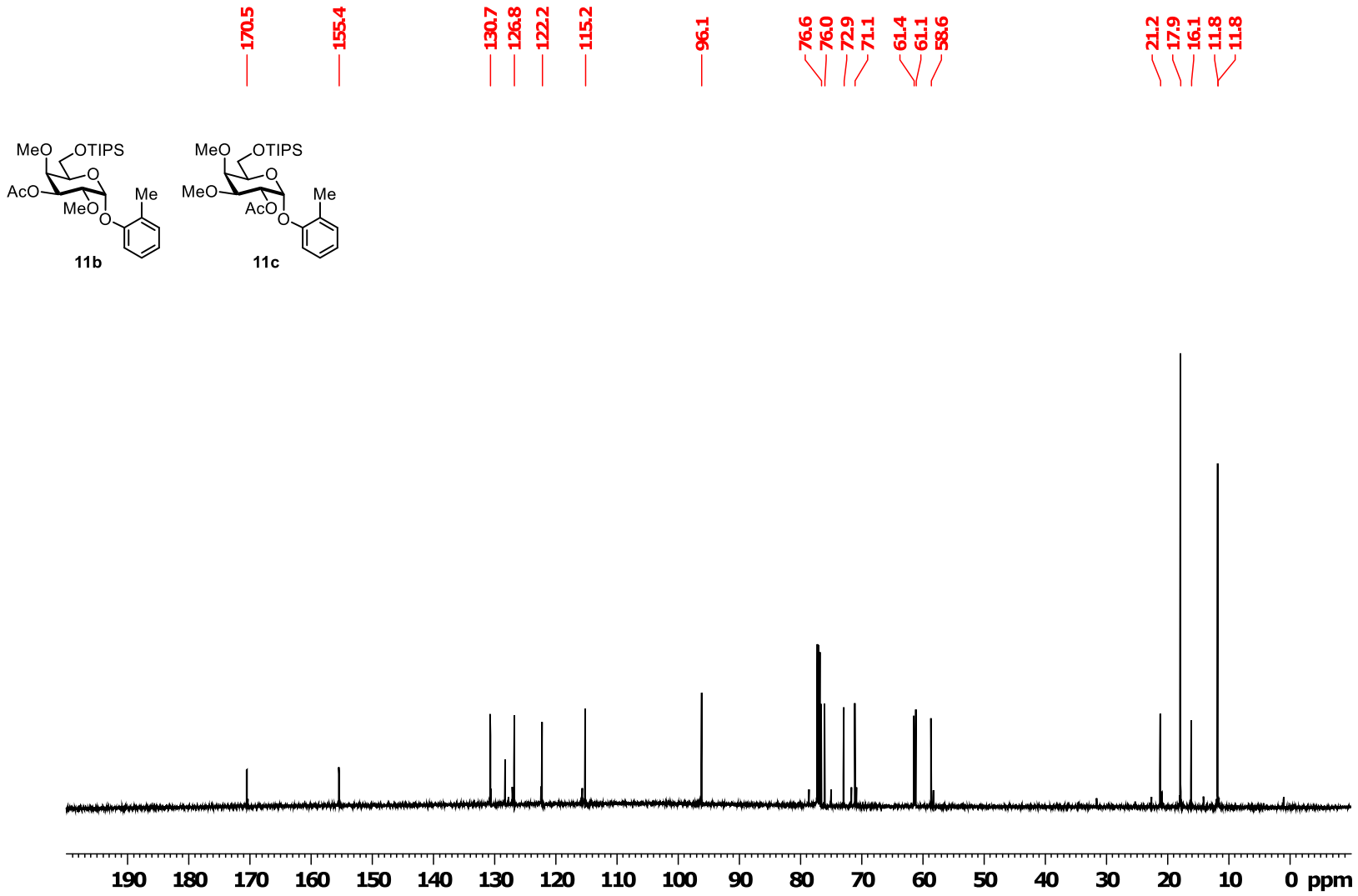


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **11b/11c**.

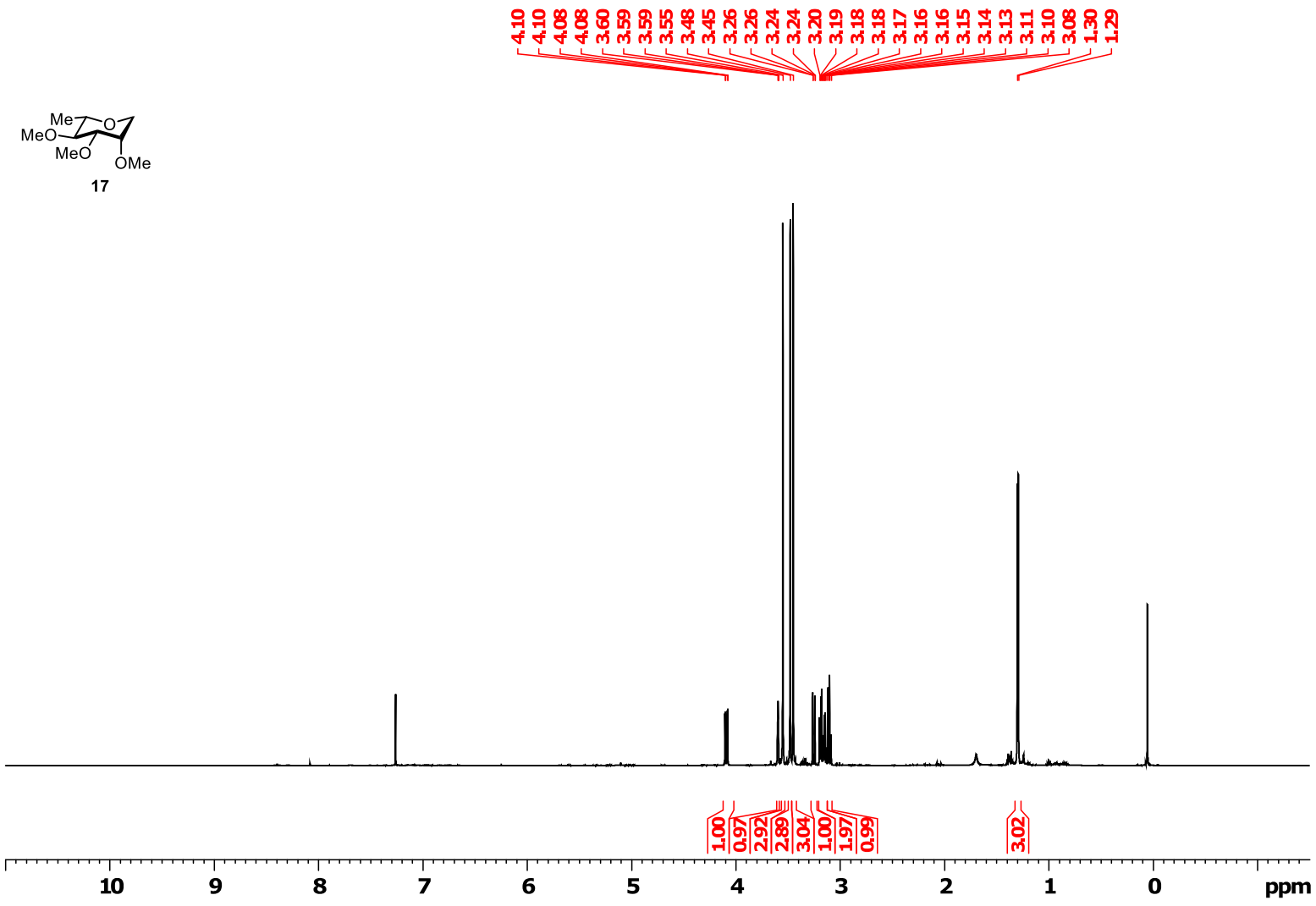


Figure S50. ^{1}H NMR spectrum of **17**.

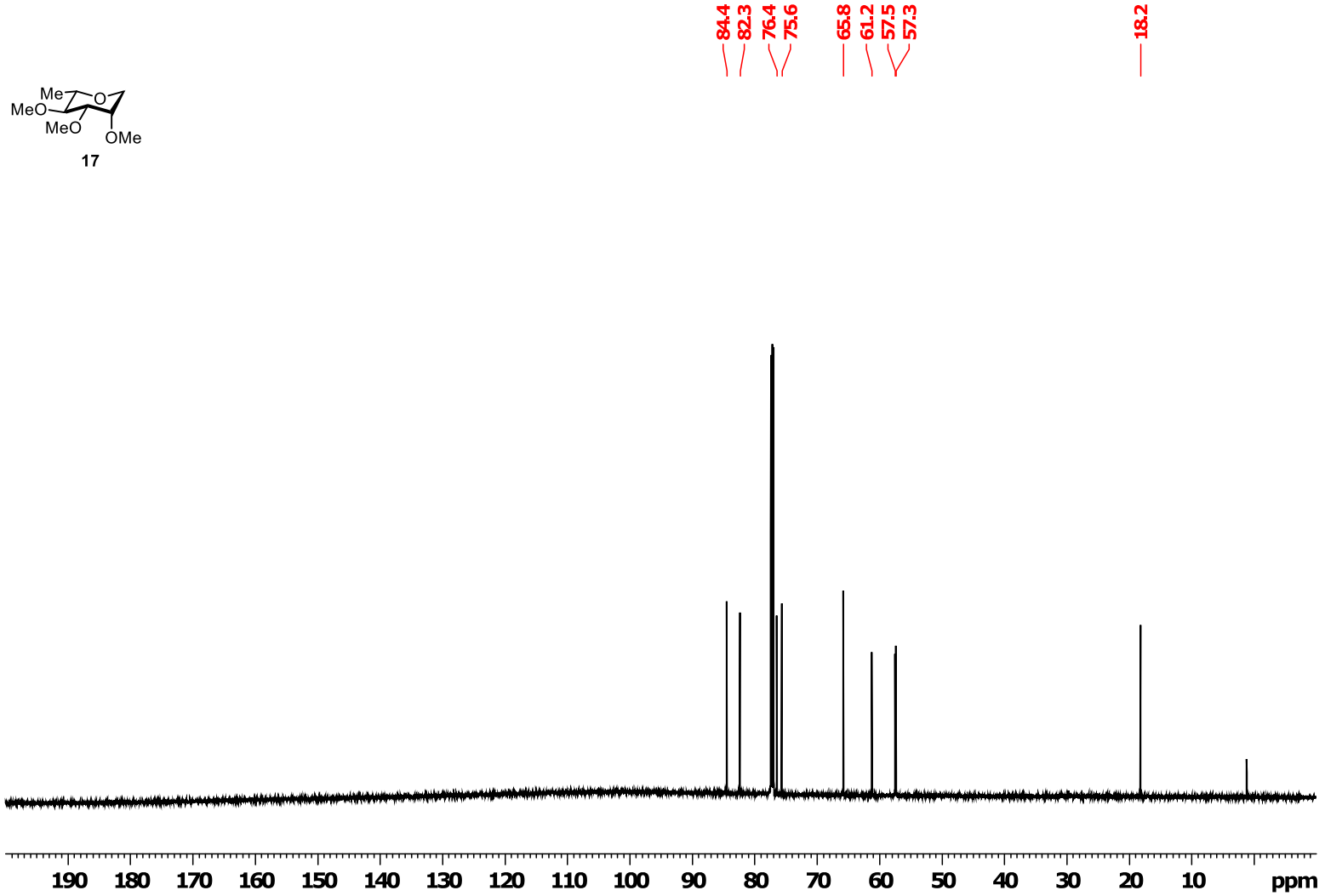


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of **17**.

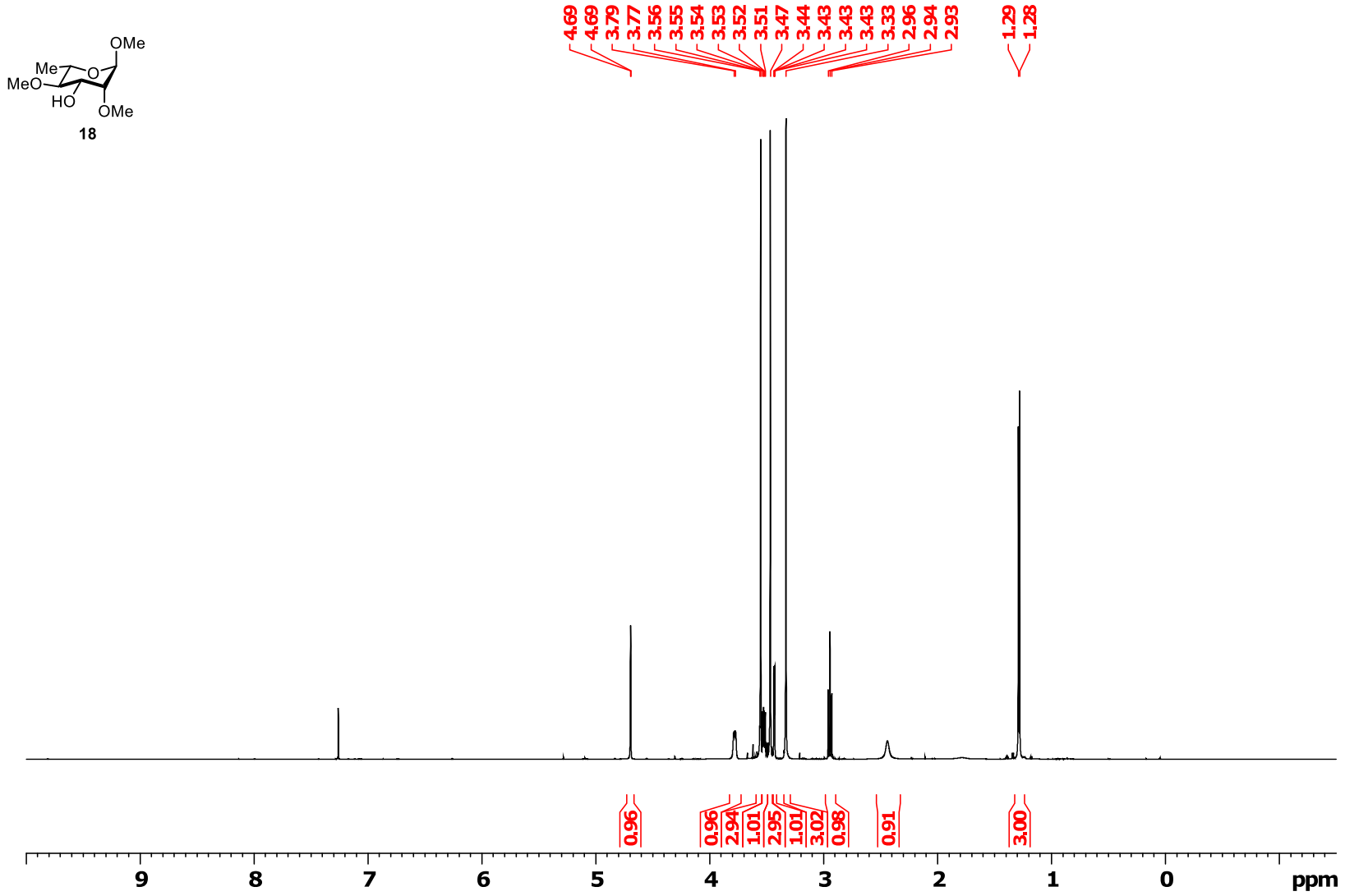


Figure S52. ^{1}H NMR spectrum of **18**.

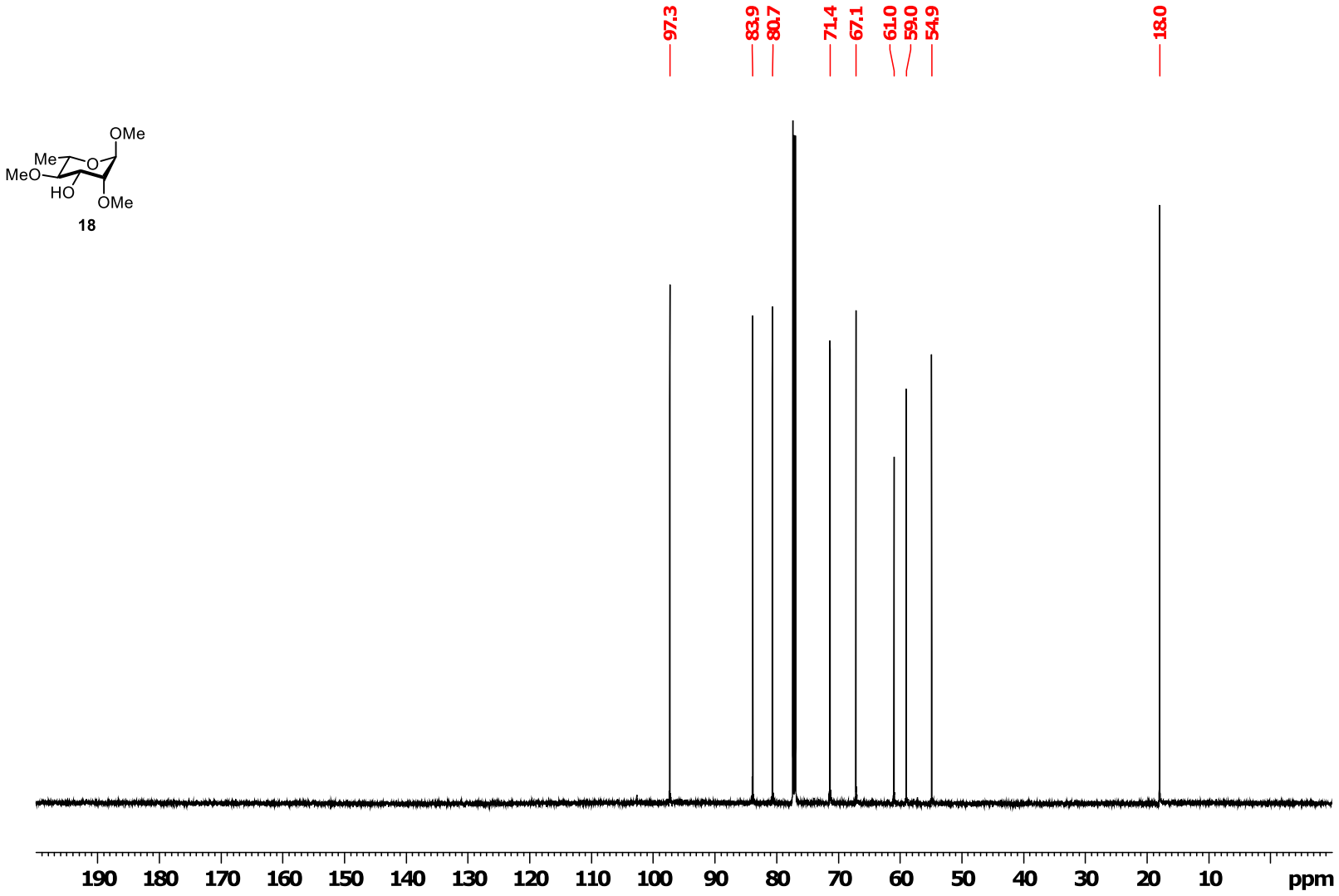


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **18**

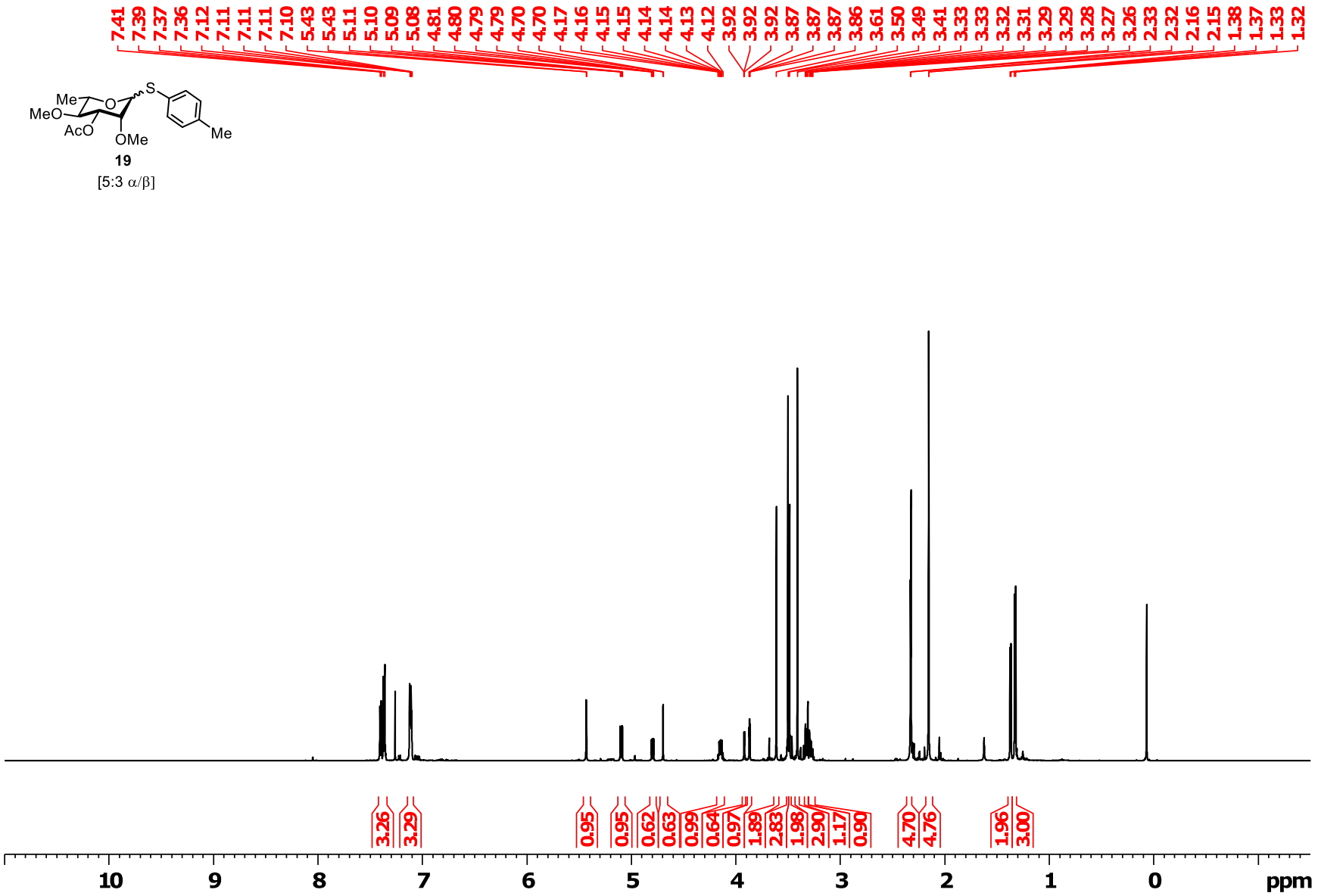


Figure S54. ^{1}H NMR spectrum of **19**.

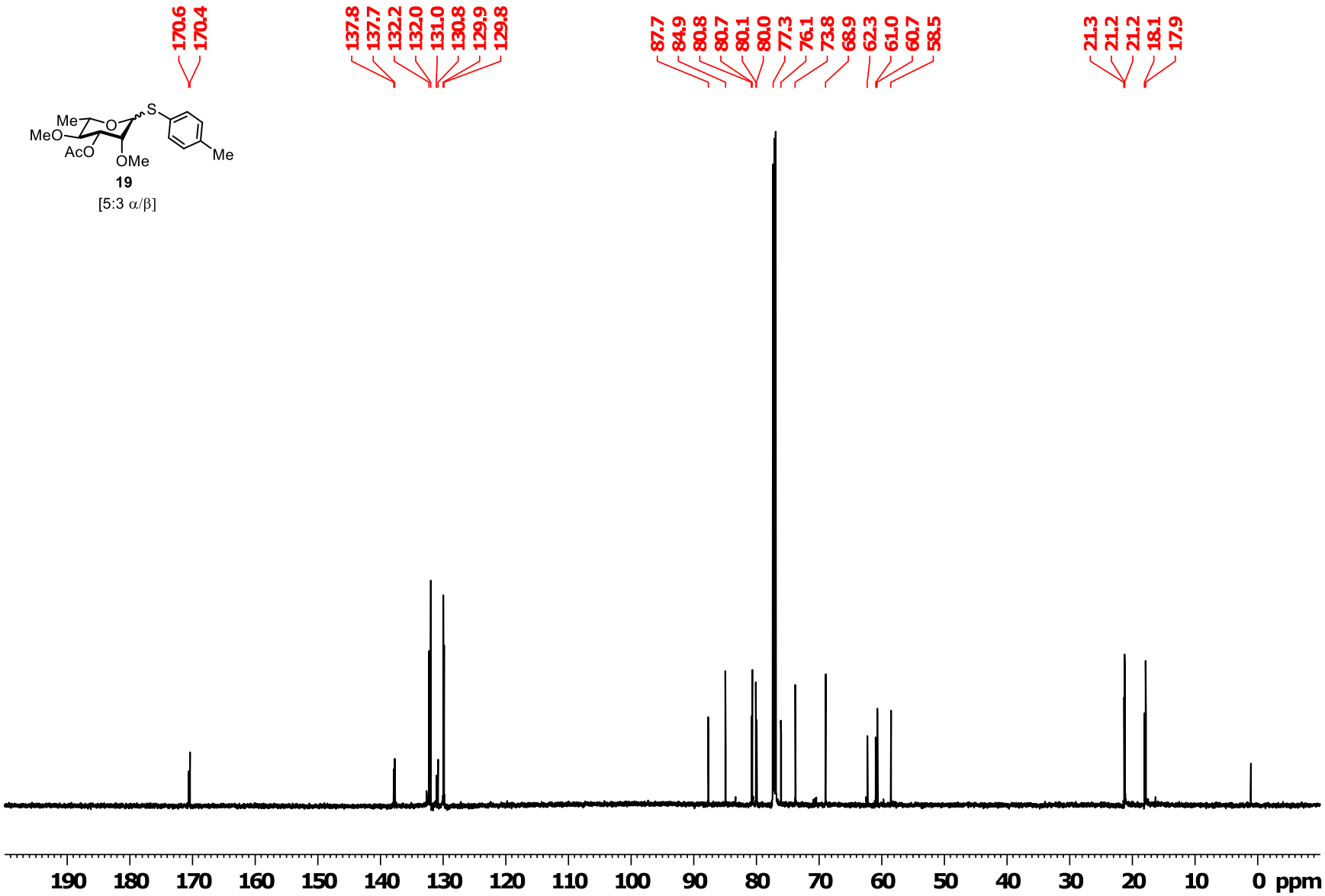


Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of **19.**

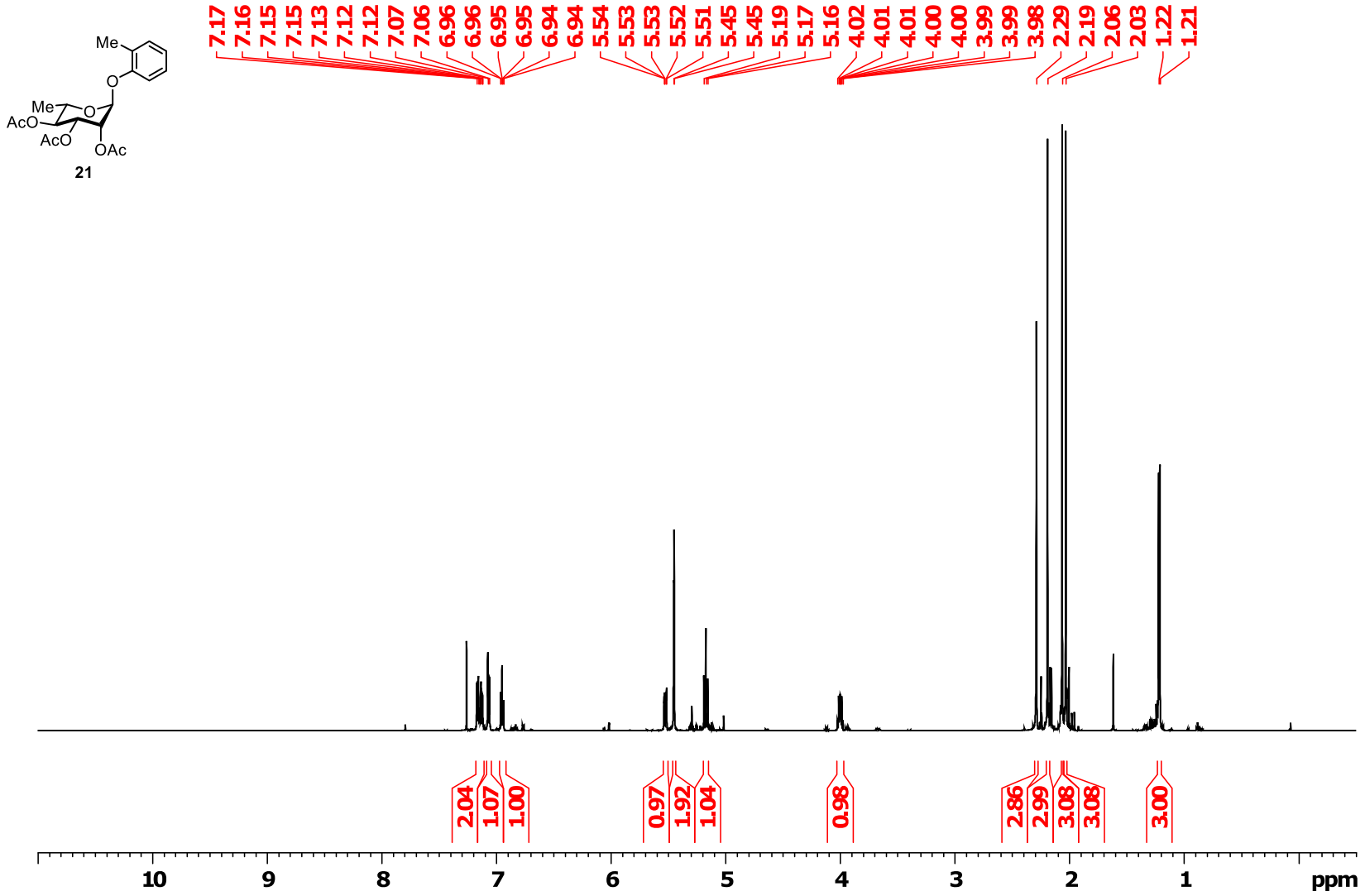


Figure S56. ^{1}H NMR spectrum of **21**.

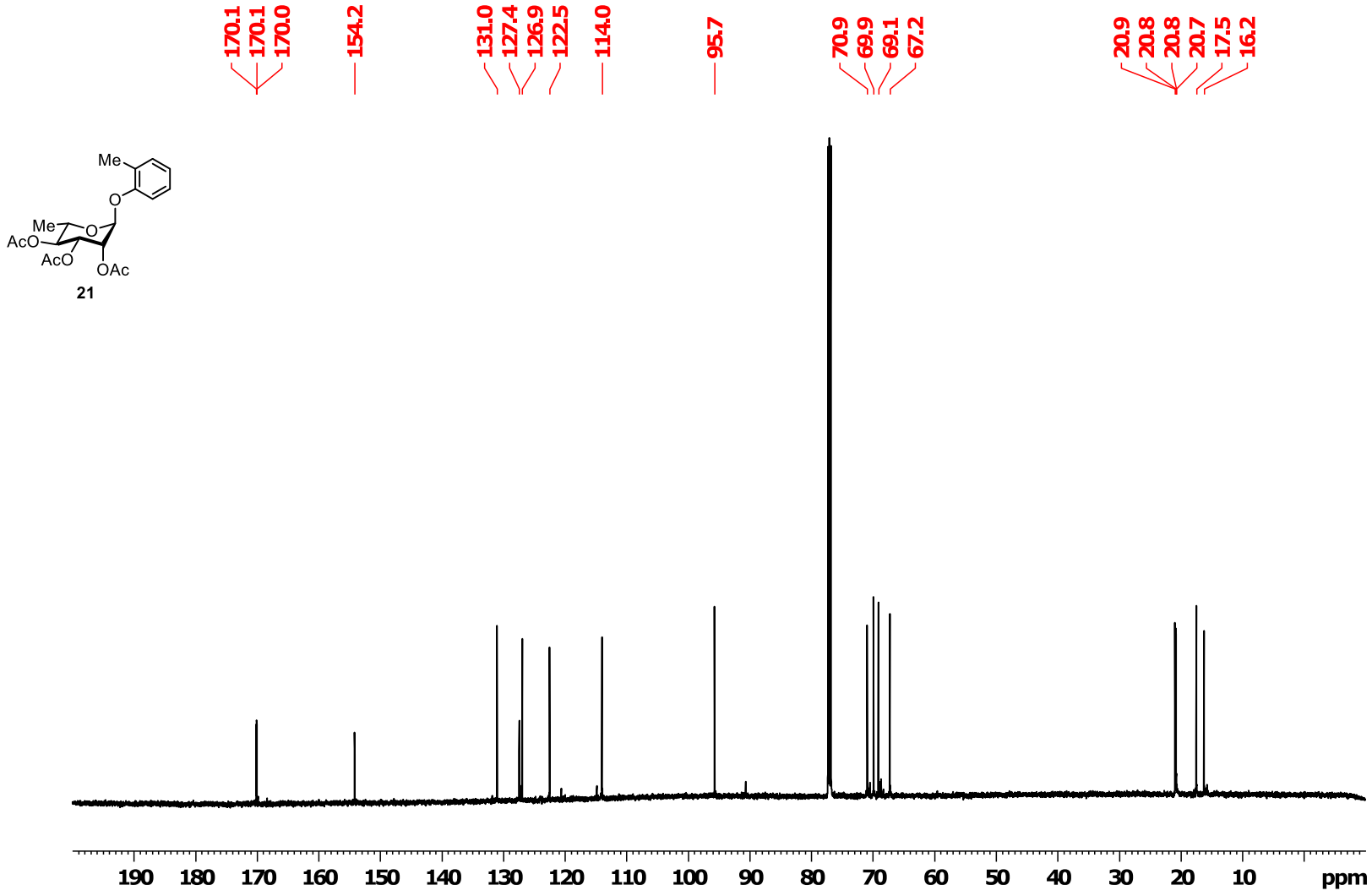


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of **21**.

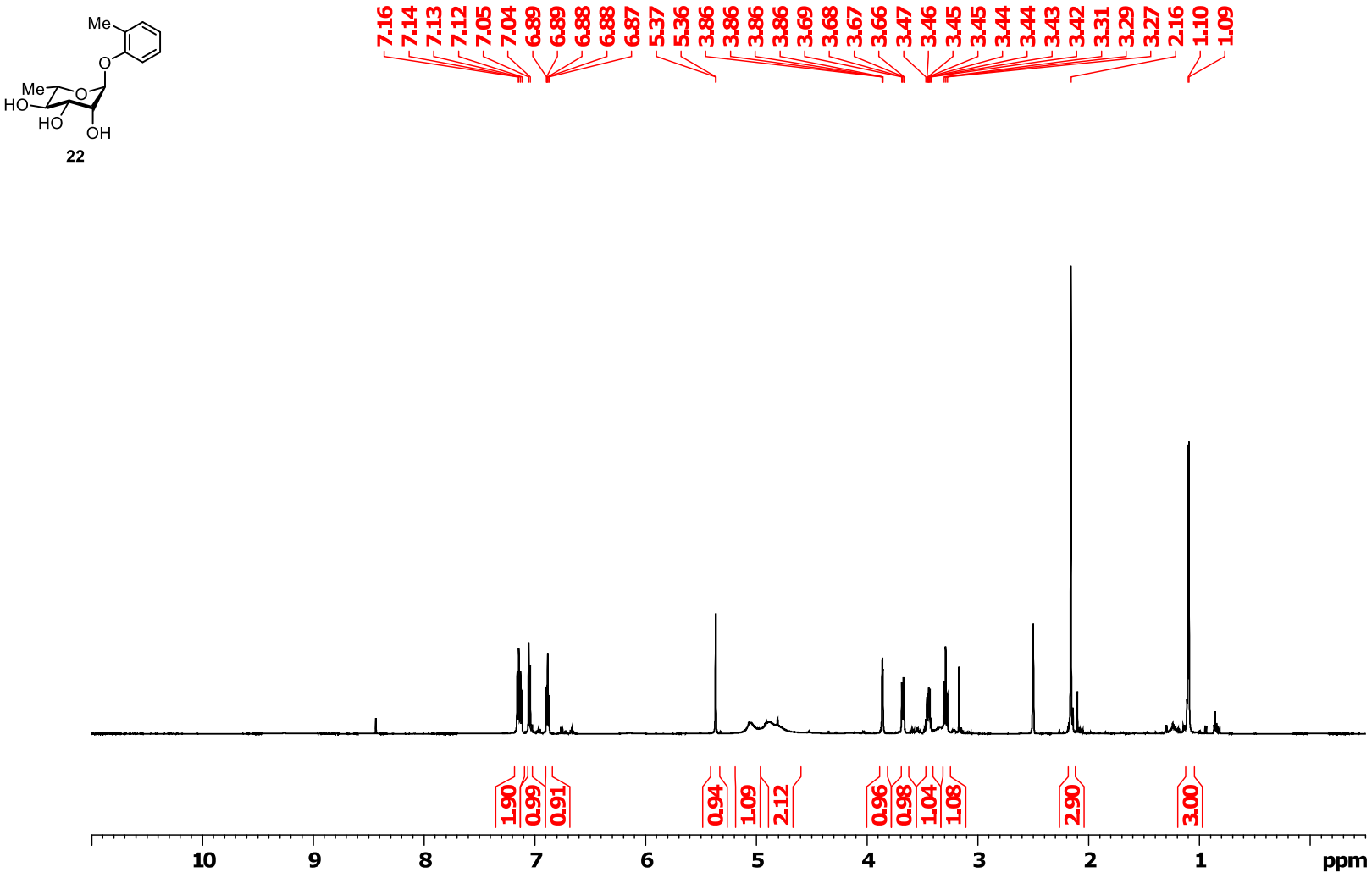


Figure S58. ^{1}H NMR spectrum of **22**.

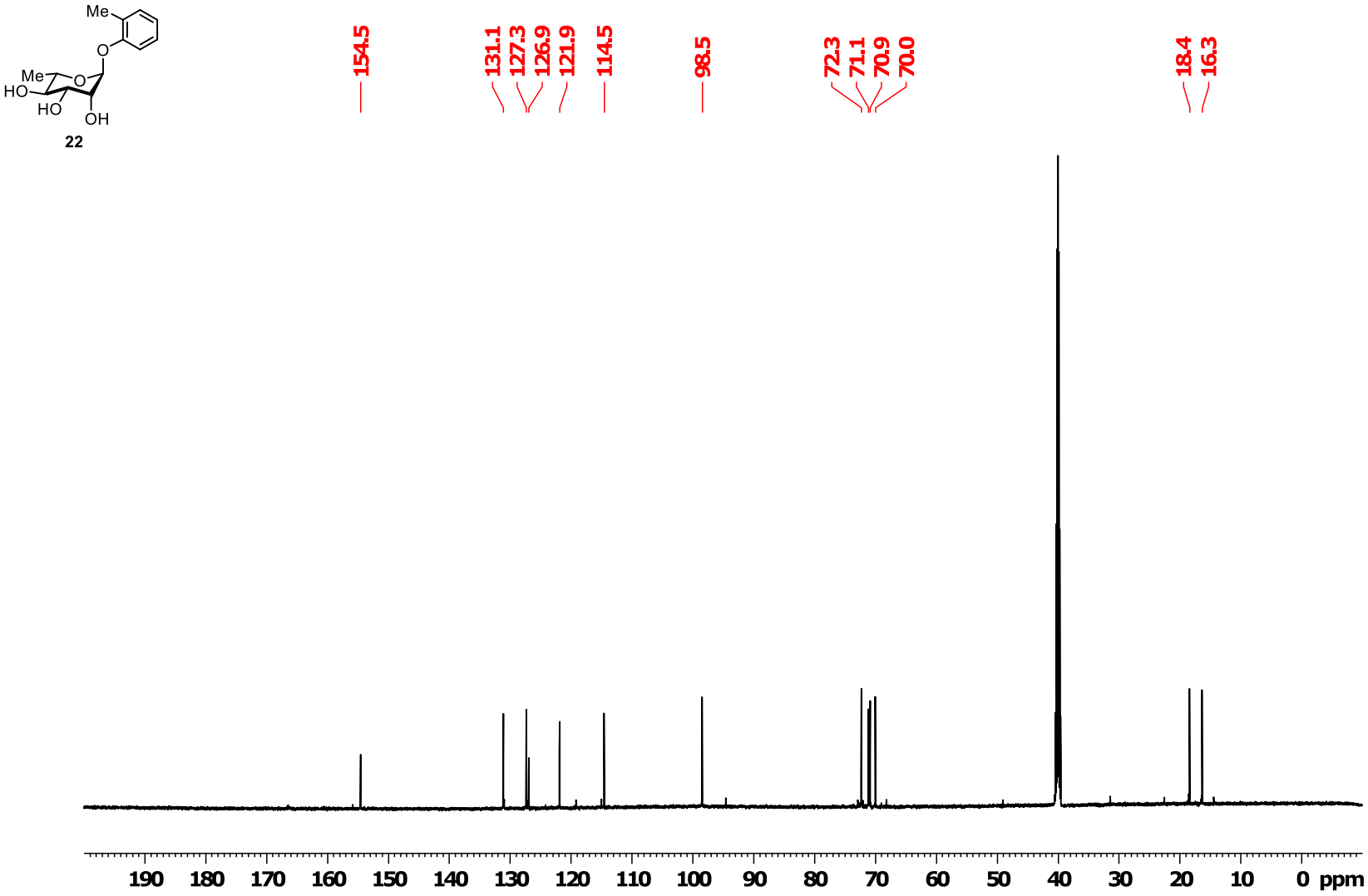


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **22**.

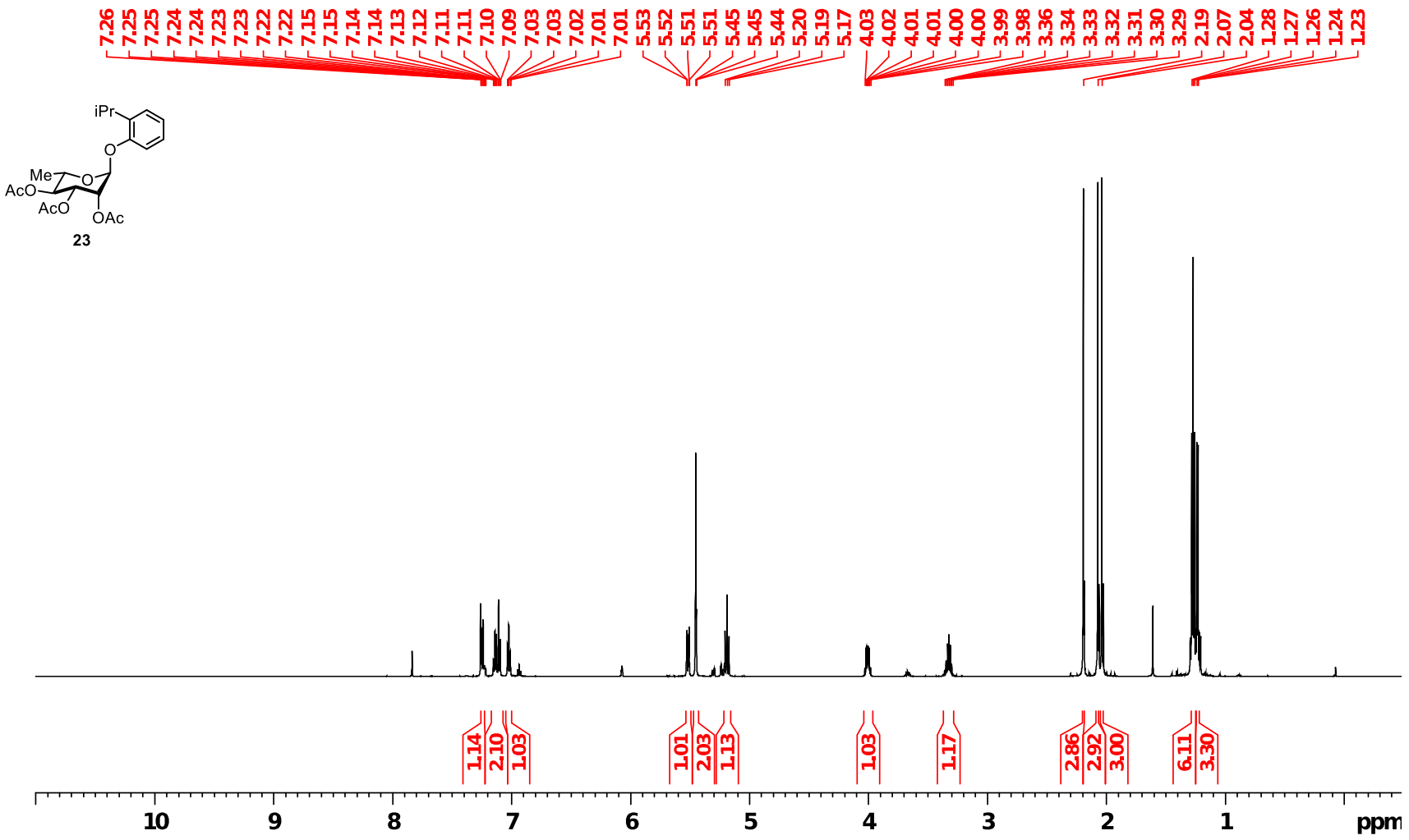


Figure S60. ^{1}H NMR spectrum of **23**.

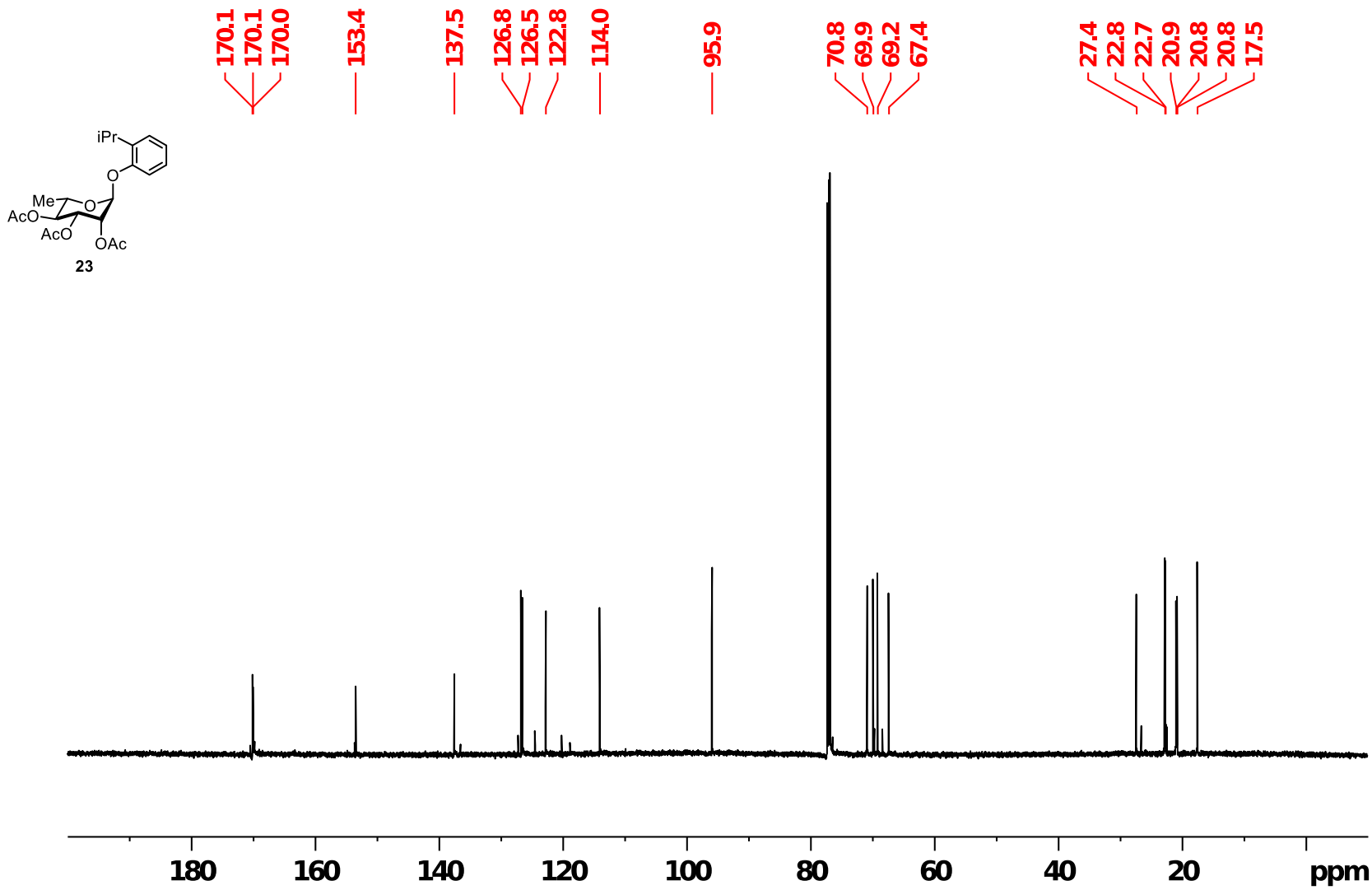


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of **23**.

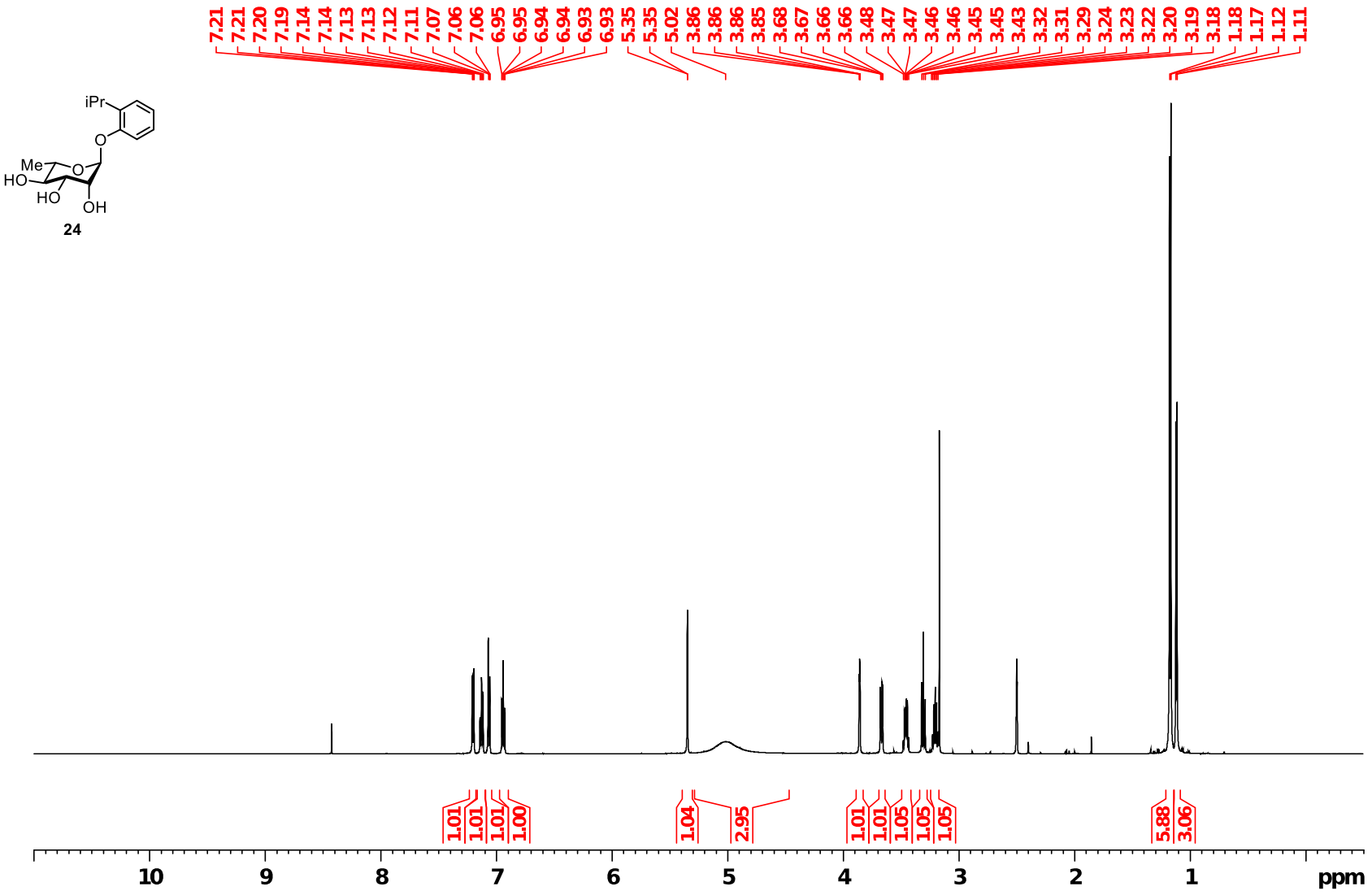


Figure S62. ^{1}H NMR spectrum of **24**.

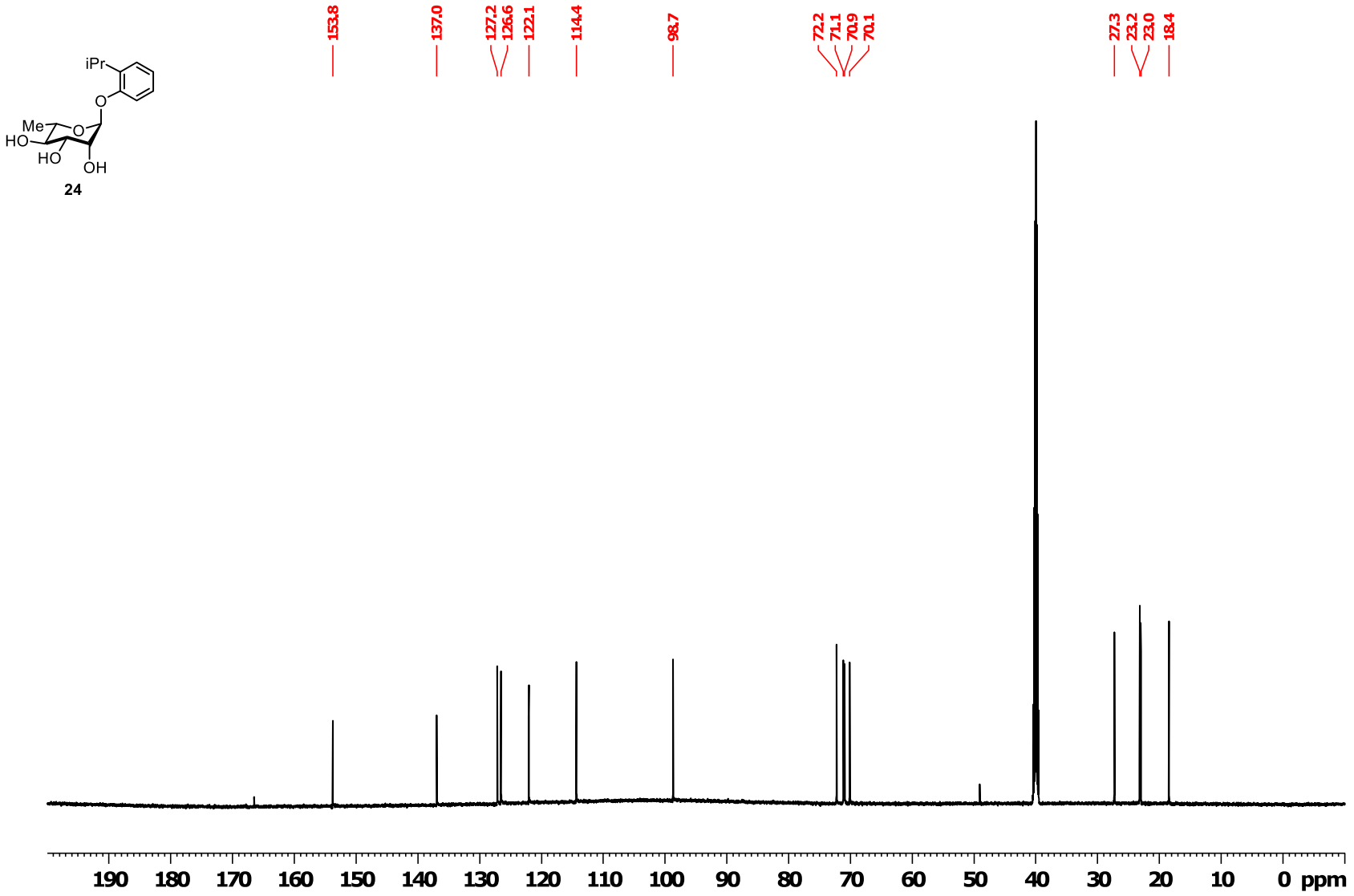


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of **24**.

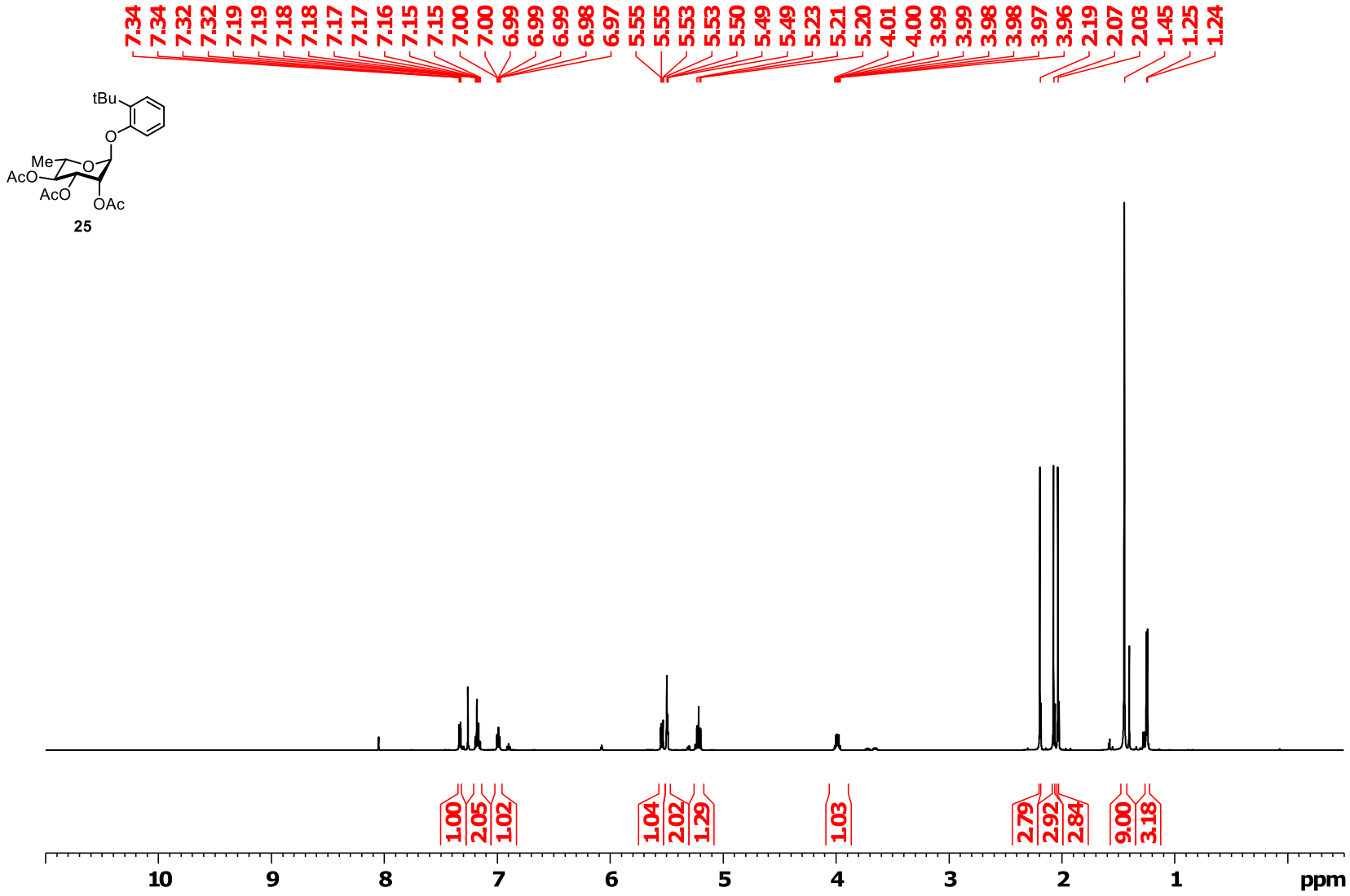


Figure S64. ^{1}H NMR spectrum of **25**.

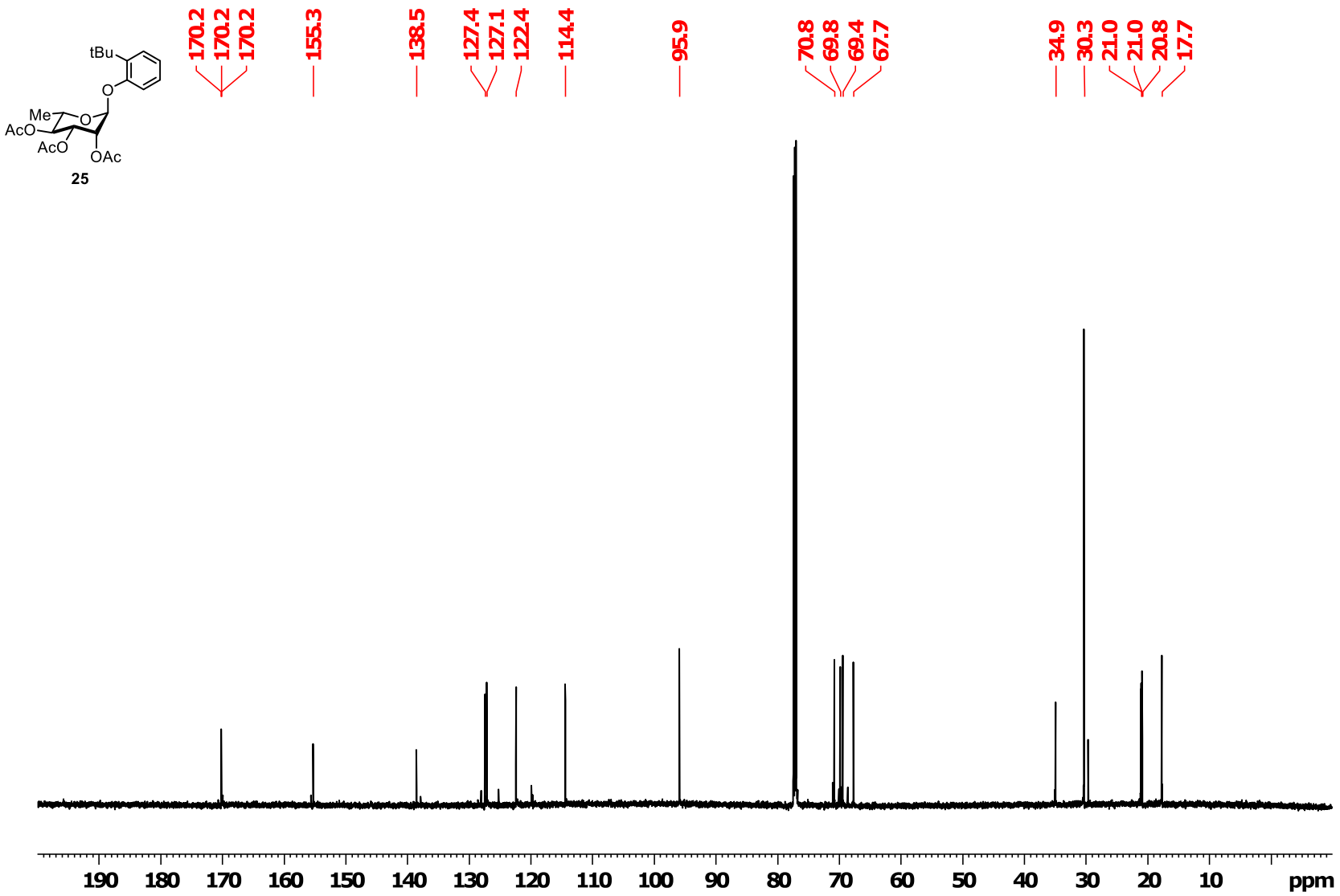


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **25**.

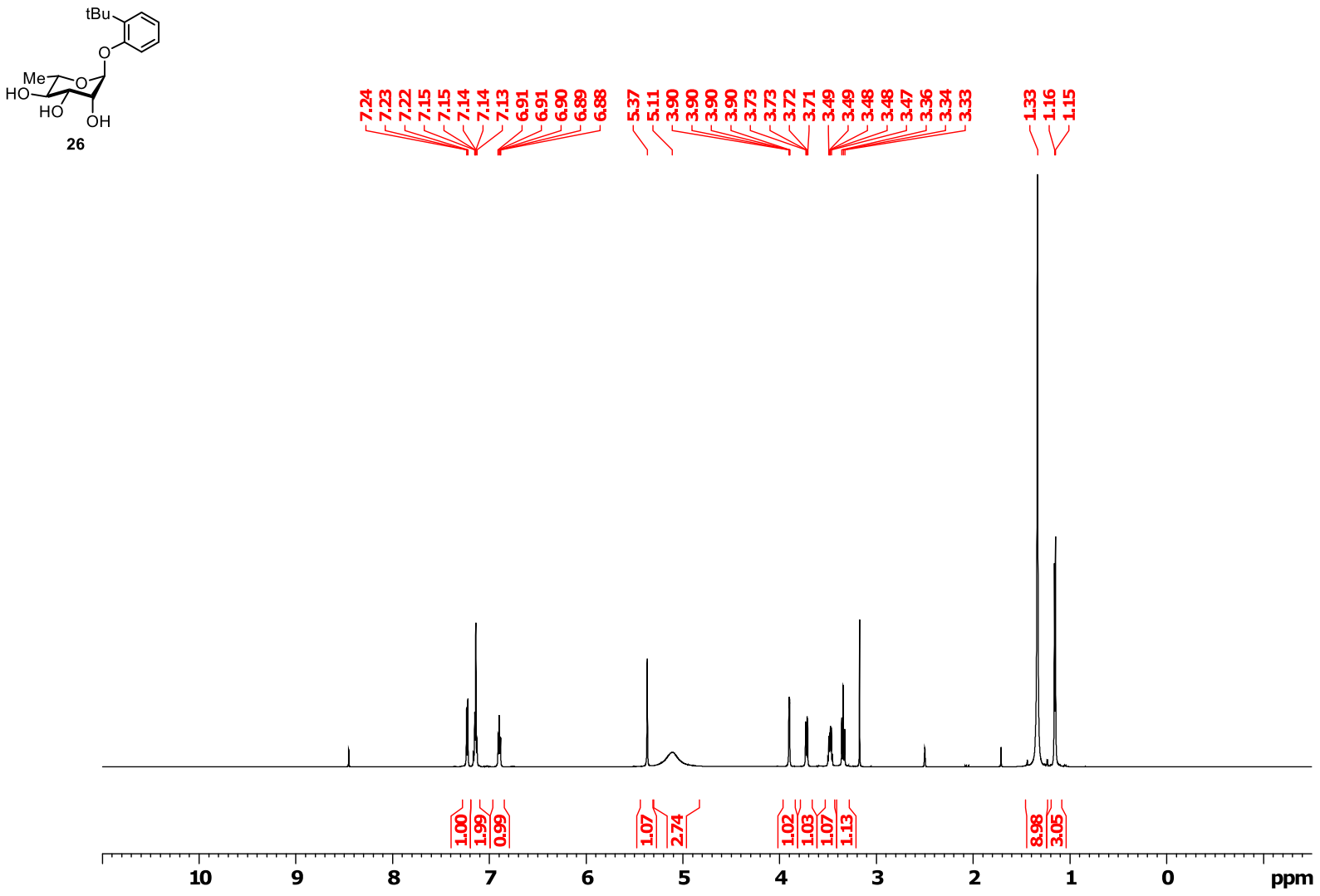


Figure S66. ^{1}H NMR spectrum of **26**.

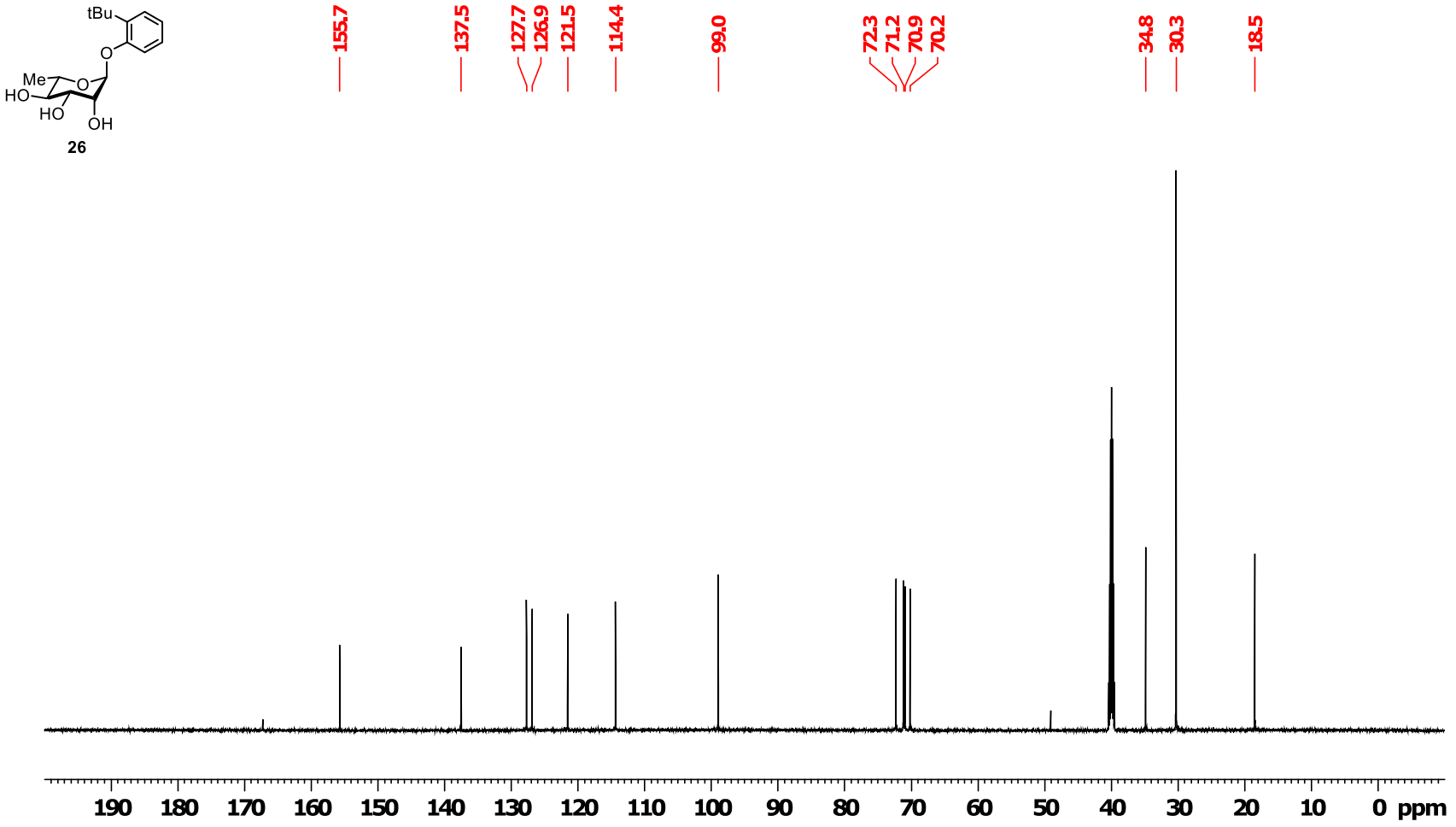


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of **26**.

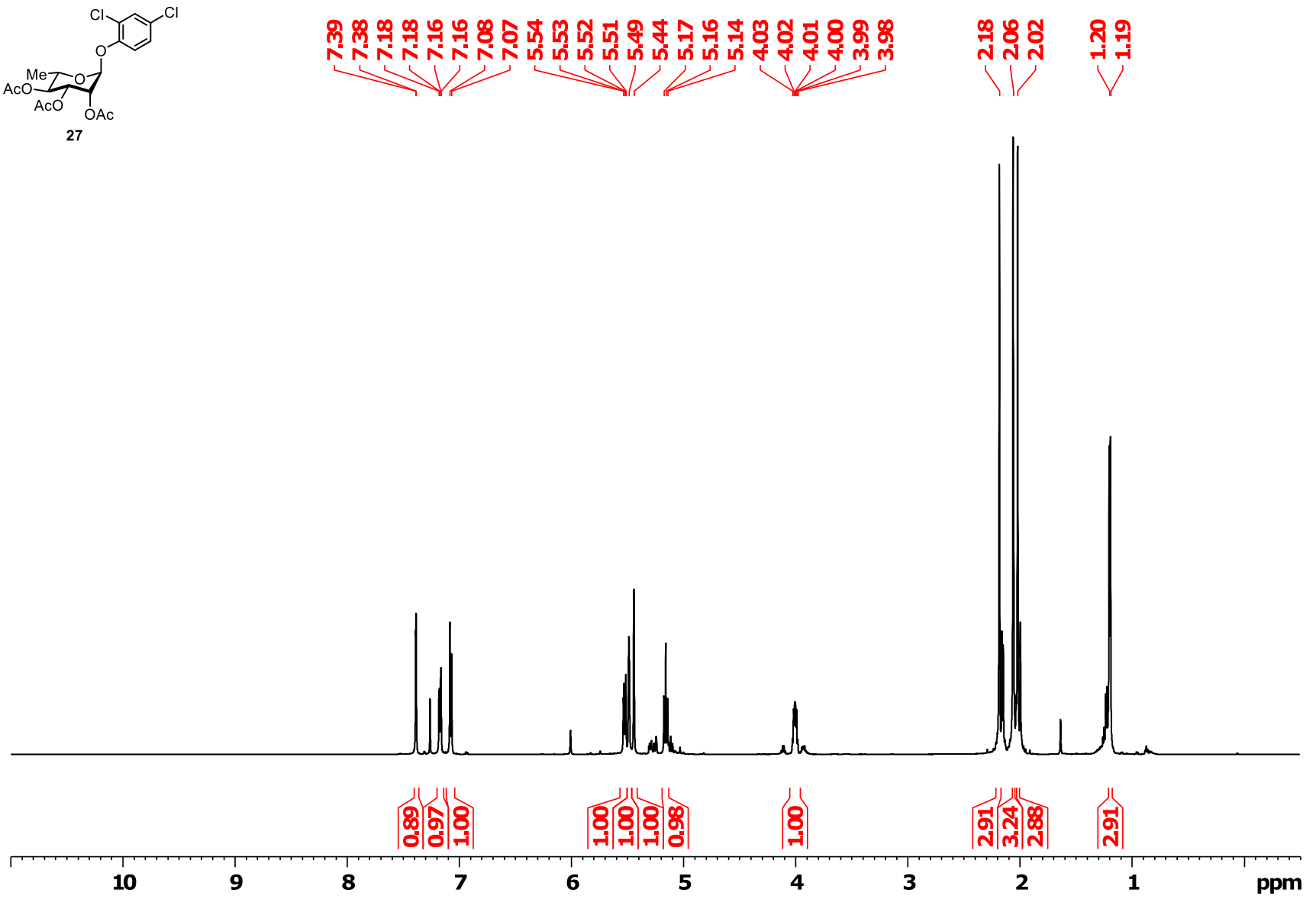


Figure S68. ^{1}H NMR spectrum of **27**.

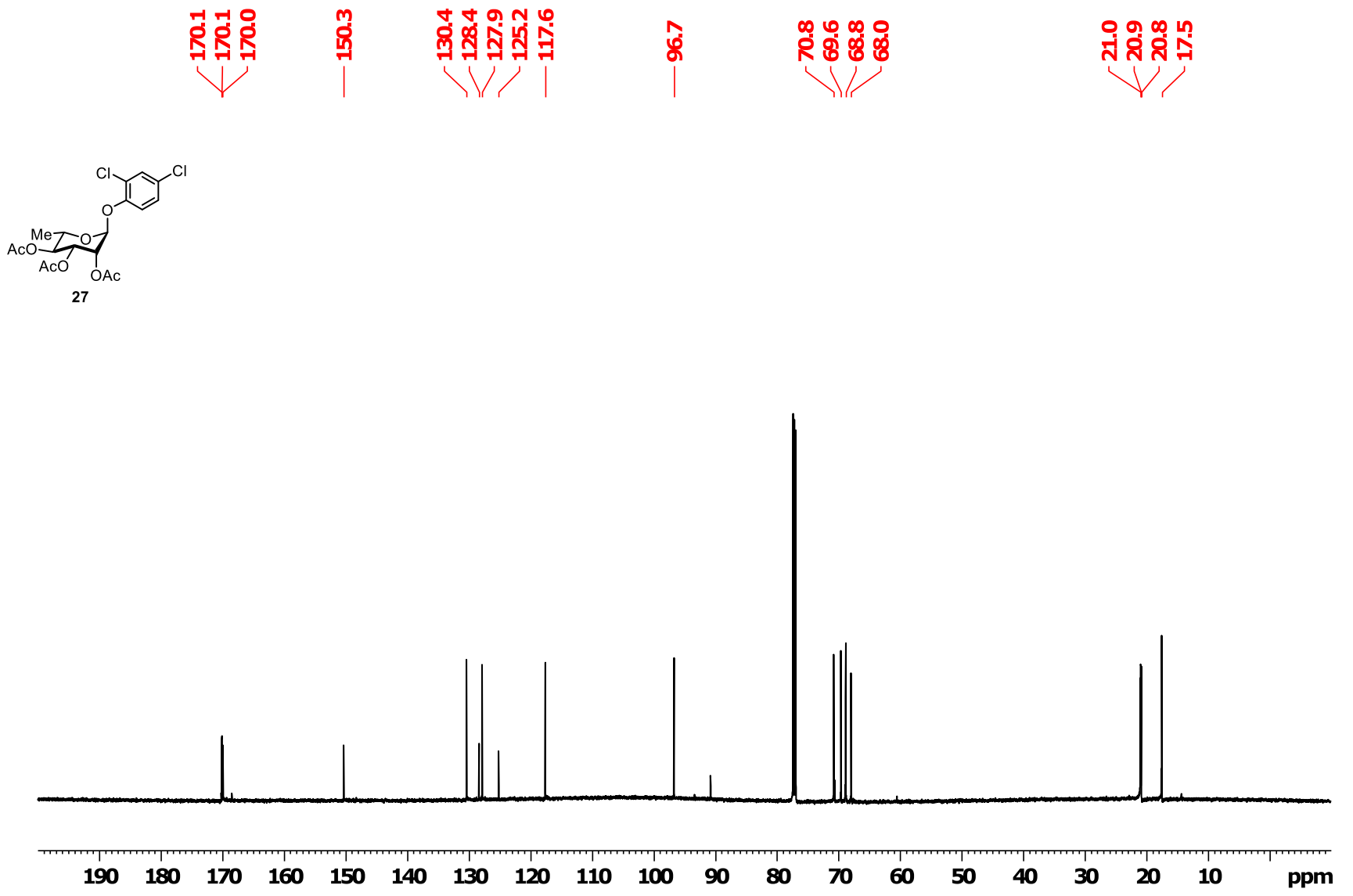


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of **27**.

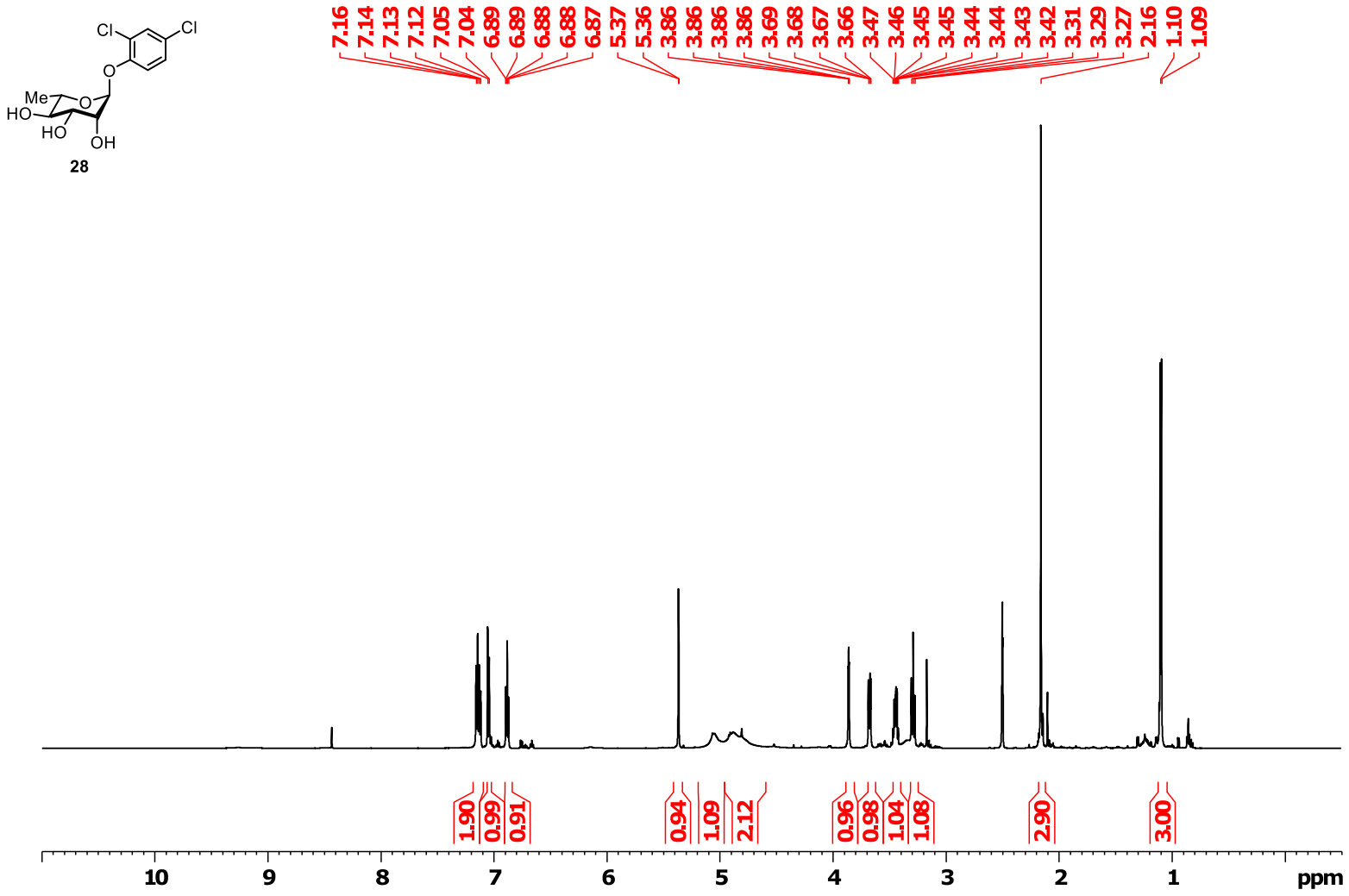


Figure S70. ^{1}H NMR spectrum of **28**.

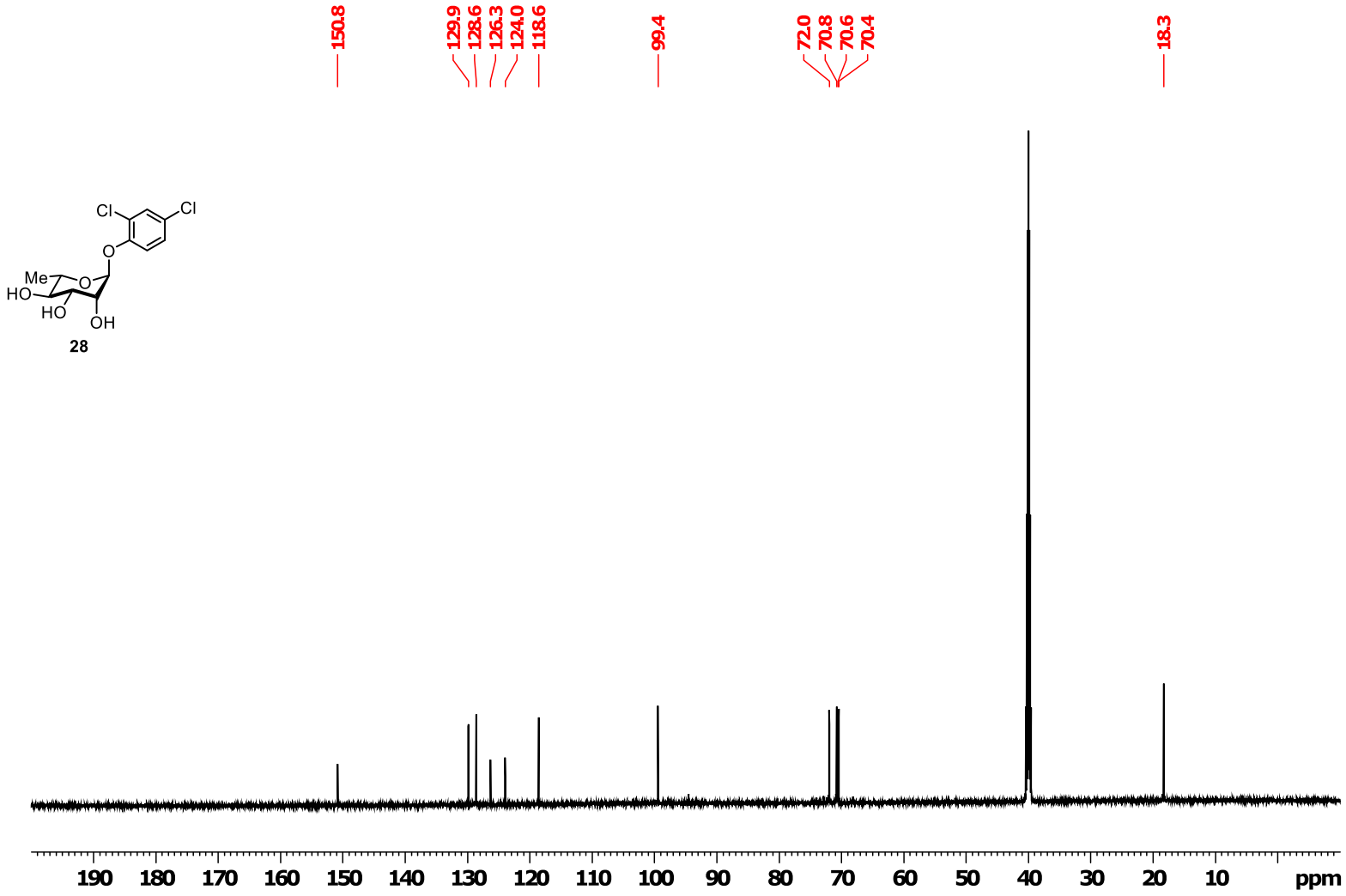


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of **28**.

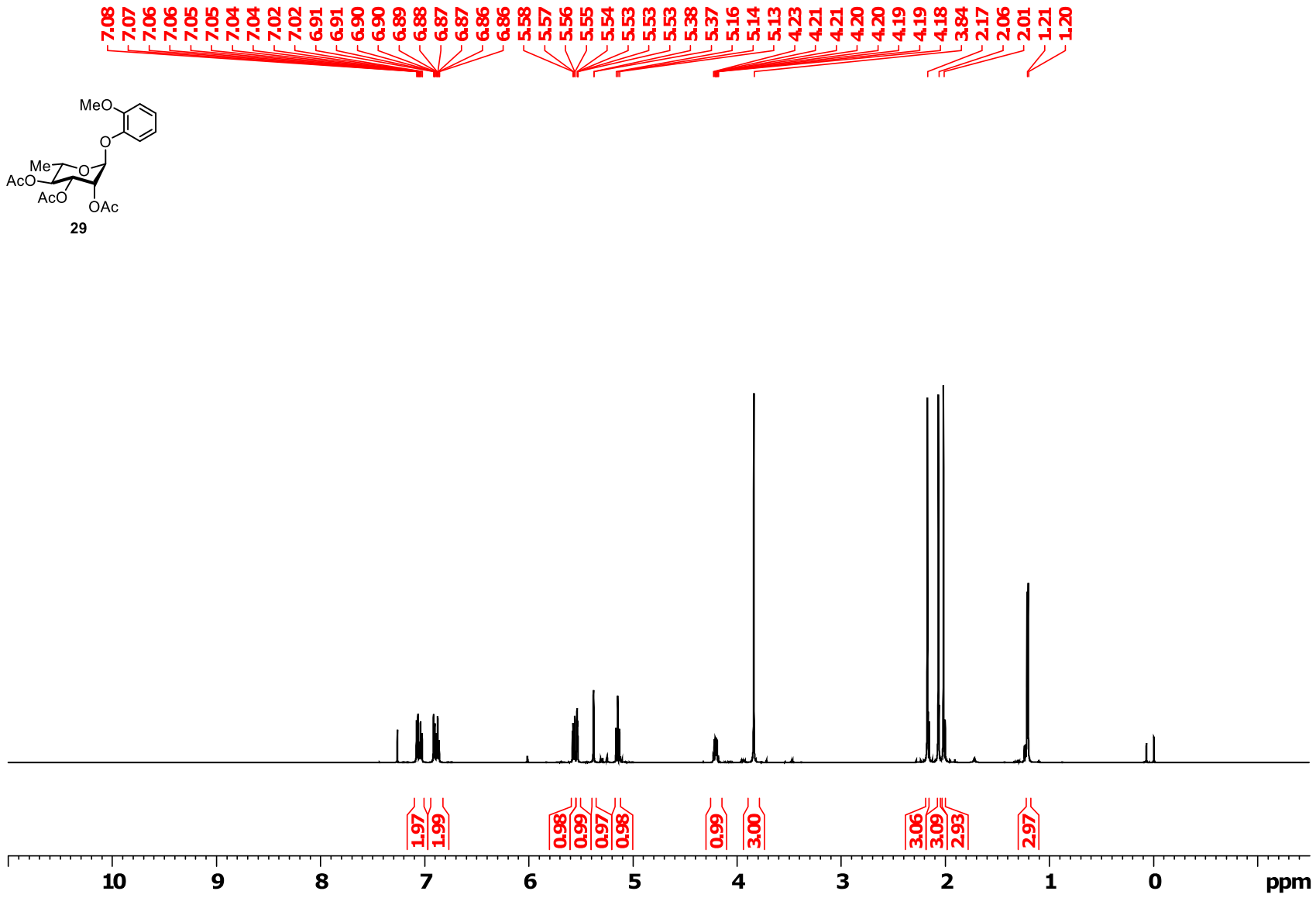


Figure S72. ^{1}H NMR spectrum of **29**.

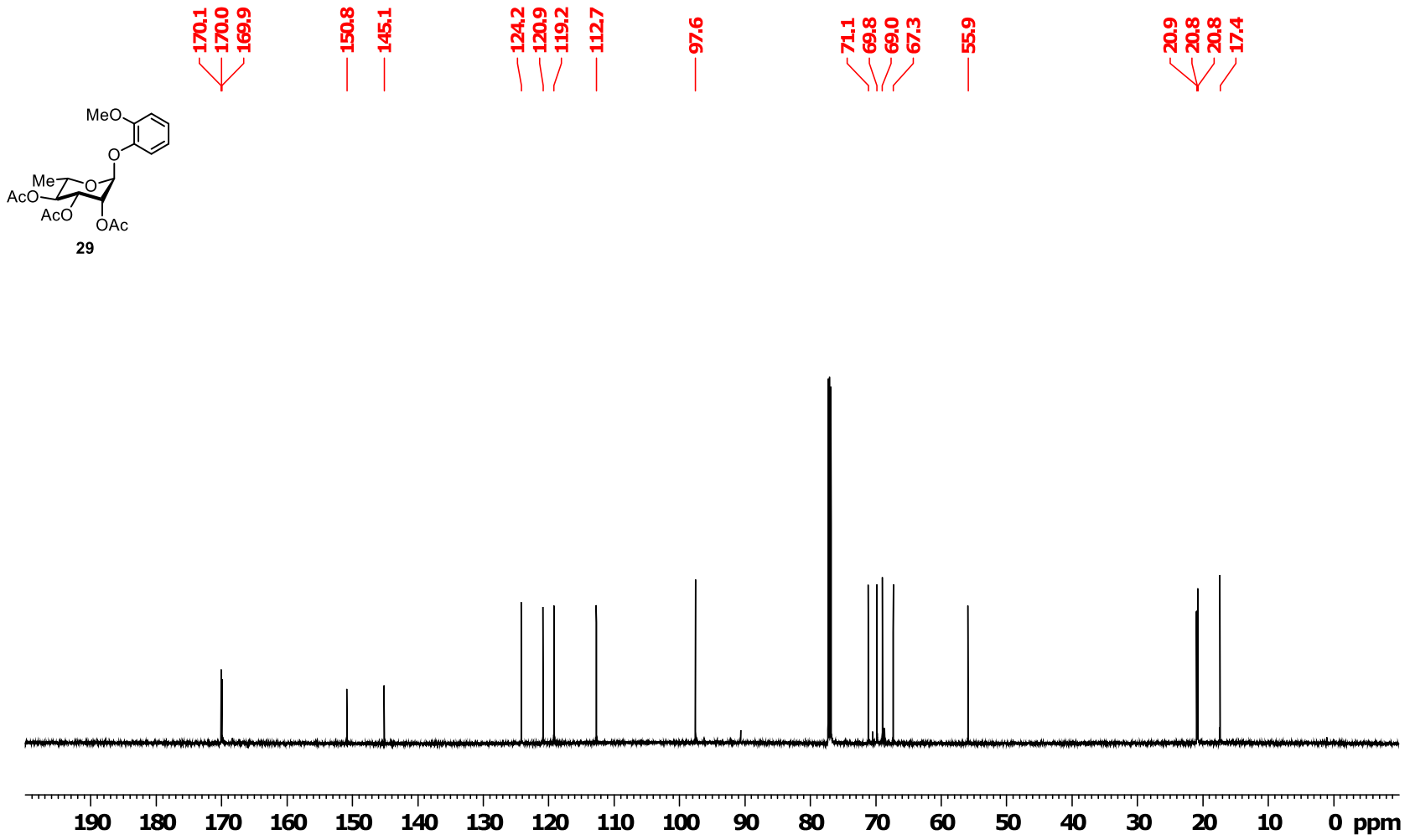


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of **29**.

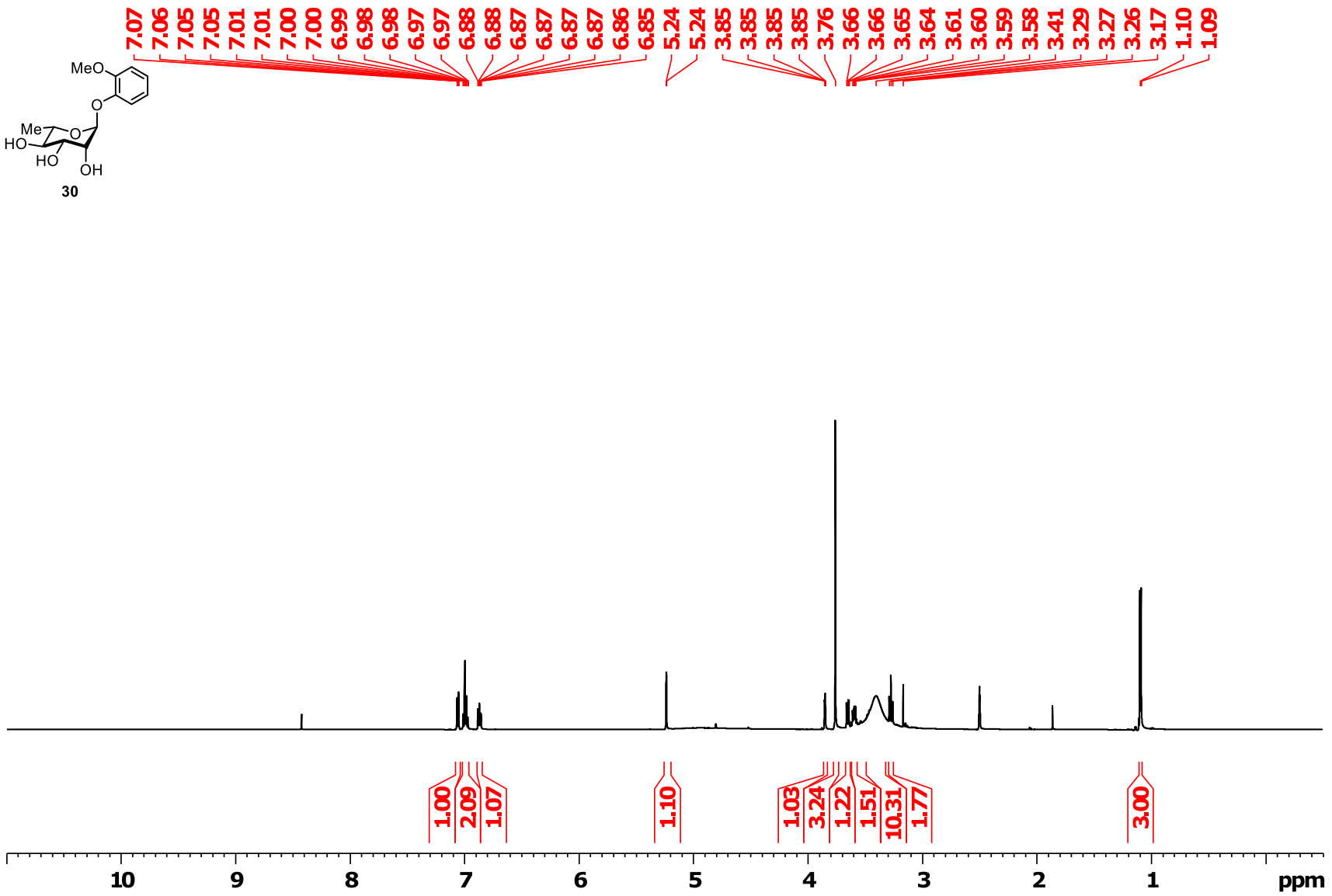


Figure S74. ^{1}H NMR spectrum of **30**.

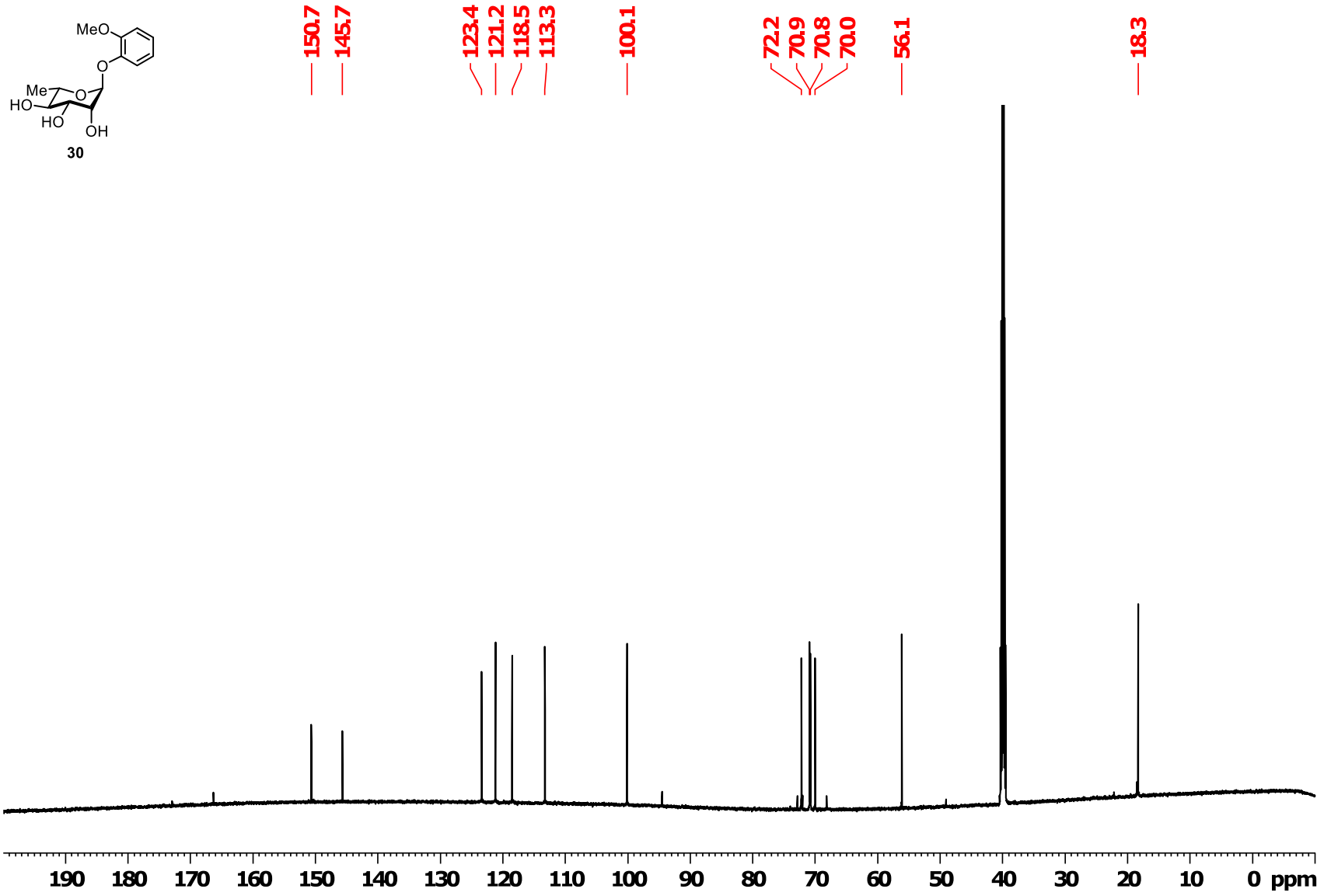


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of **30**.

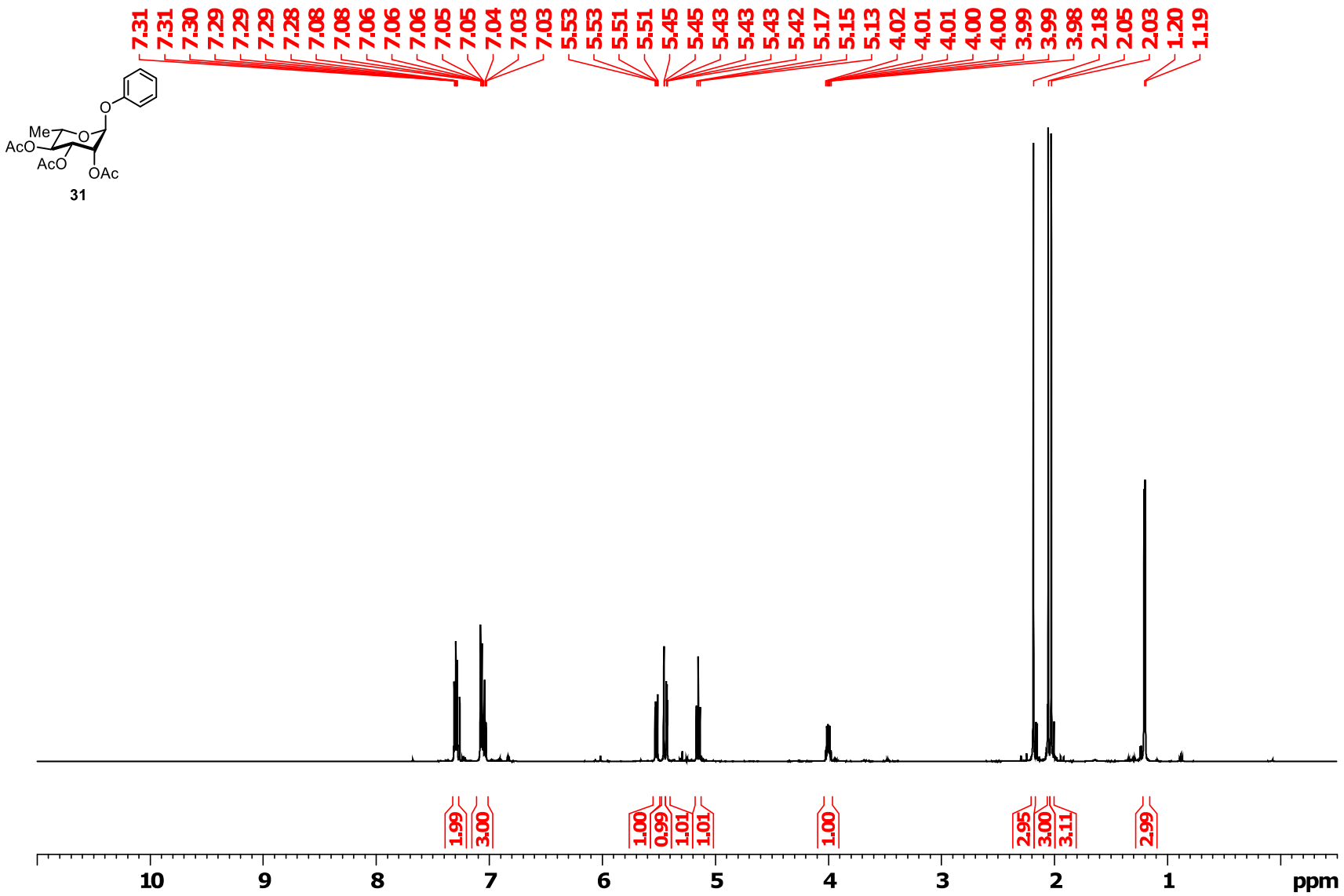


Figure S76. ^{1}H NMR spectrum of **31**

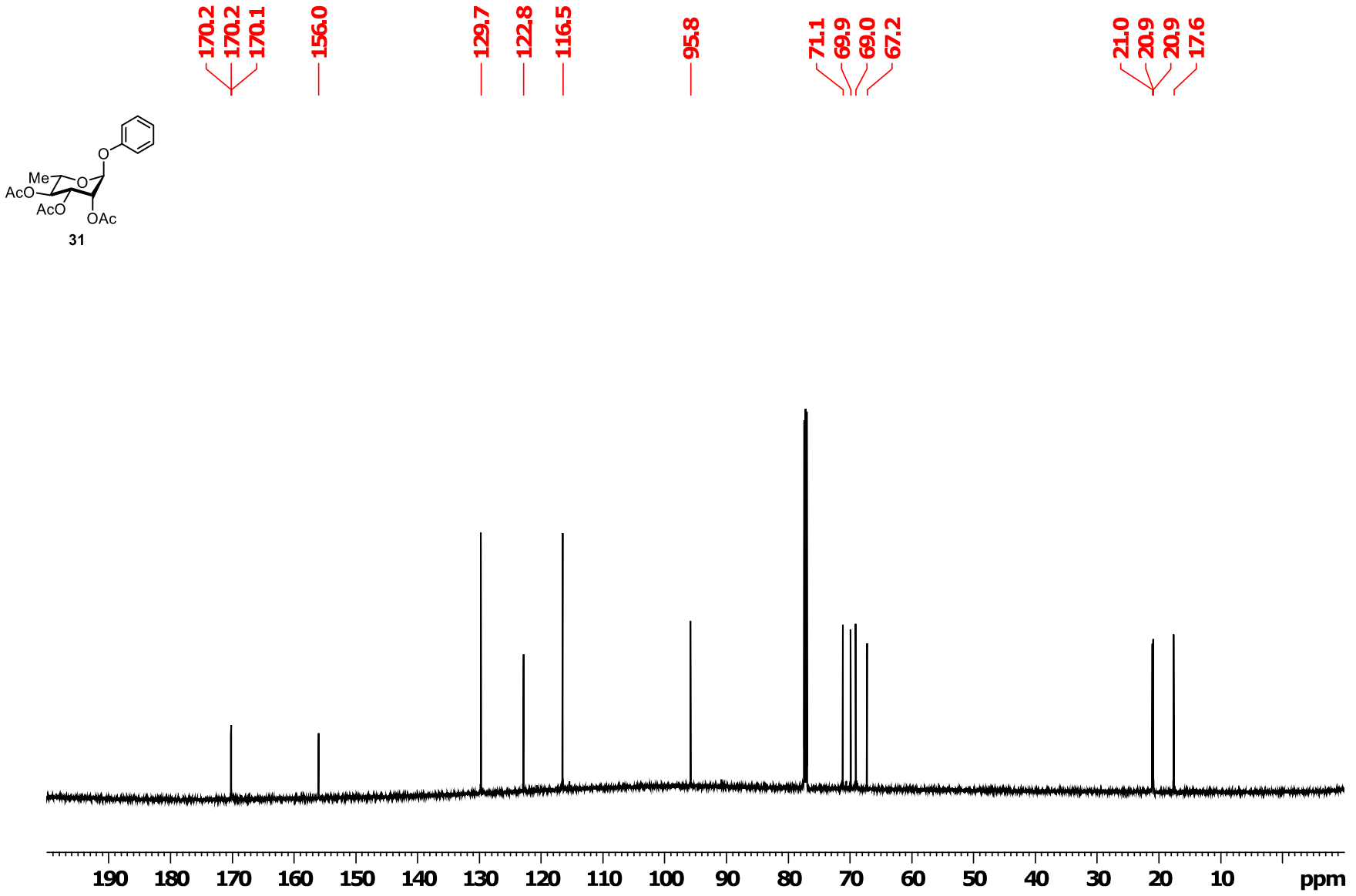


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of **31**

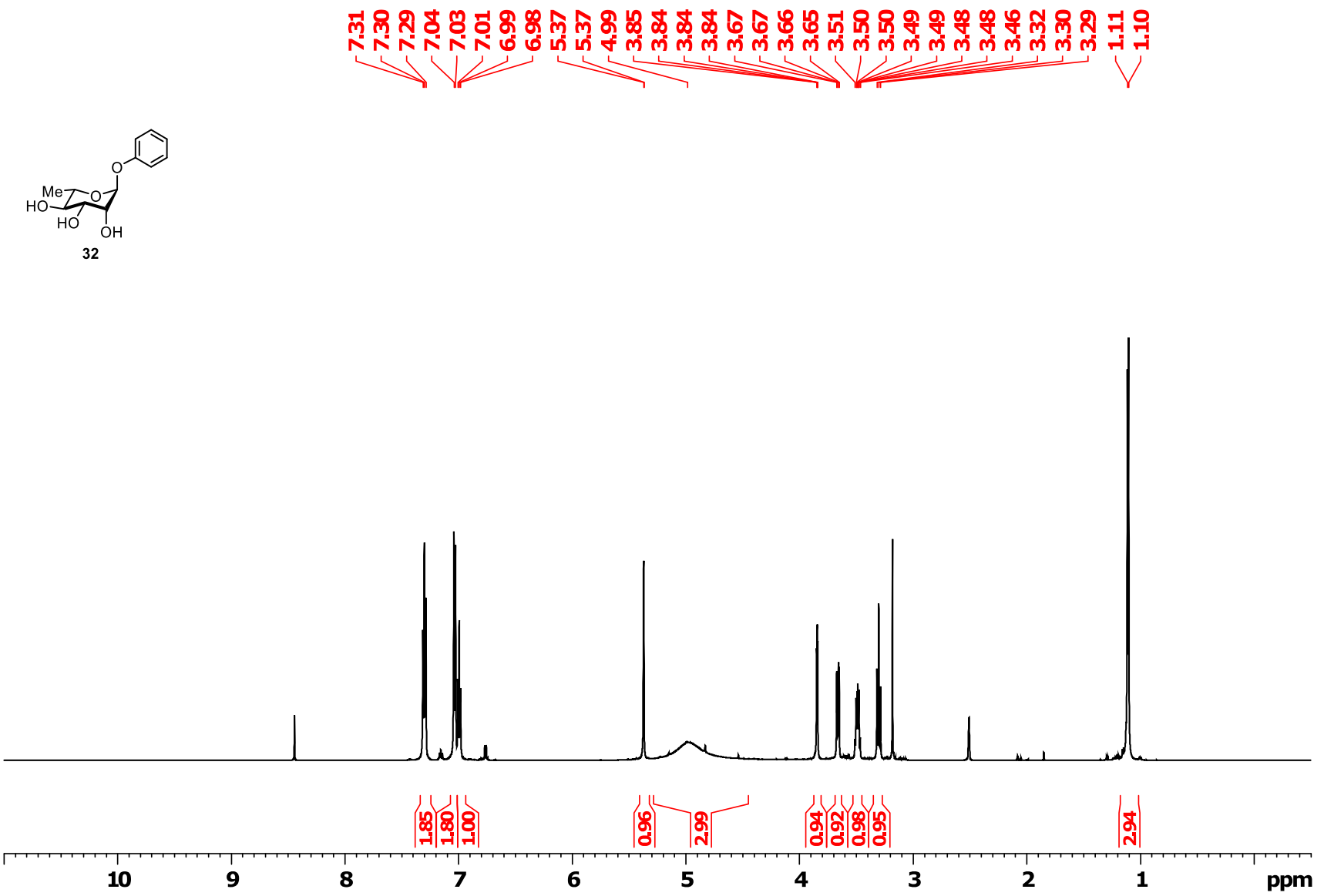


Figure S78. ^{1}H NMR spectrum of **32**

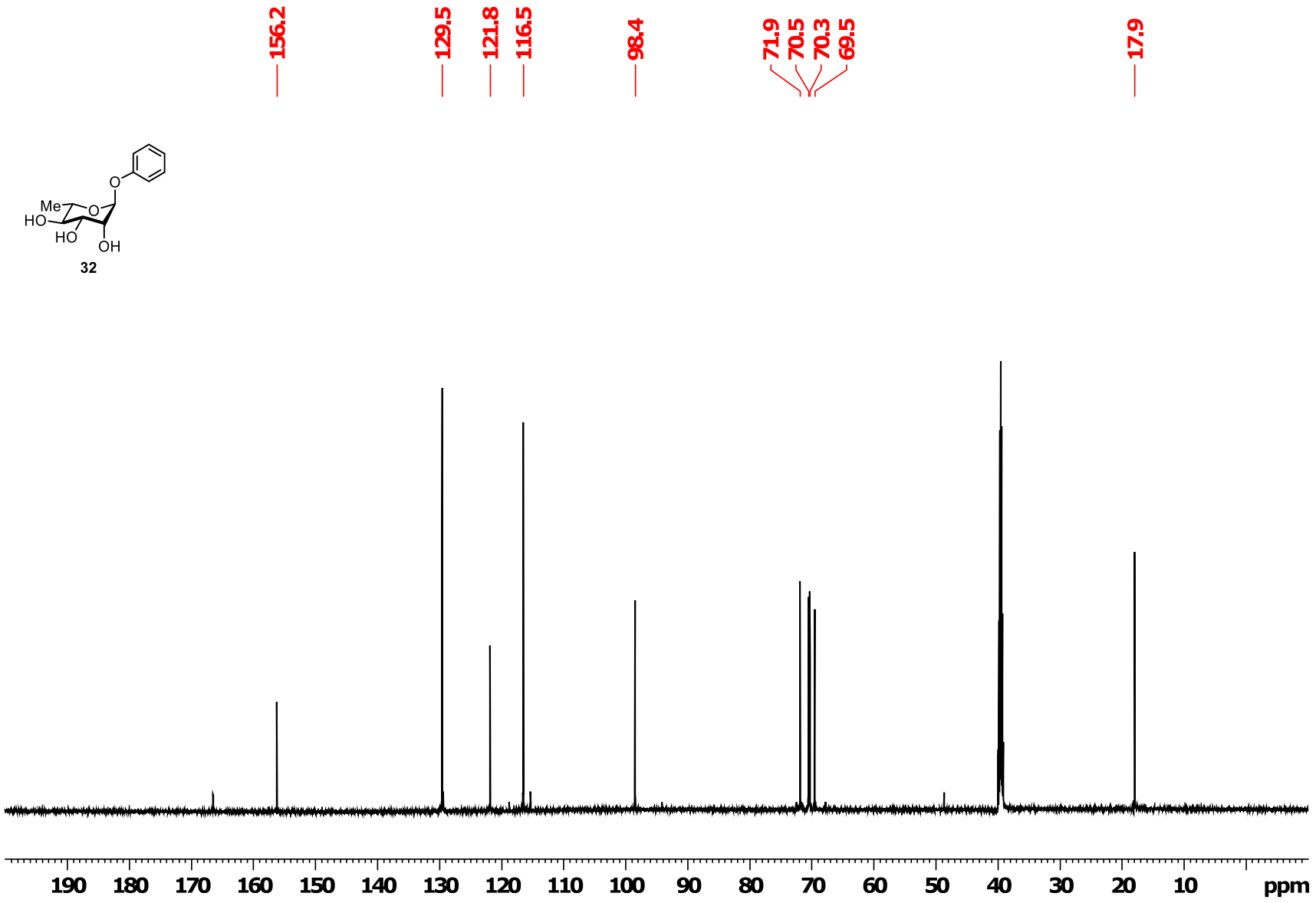


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of **32**

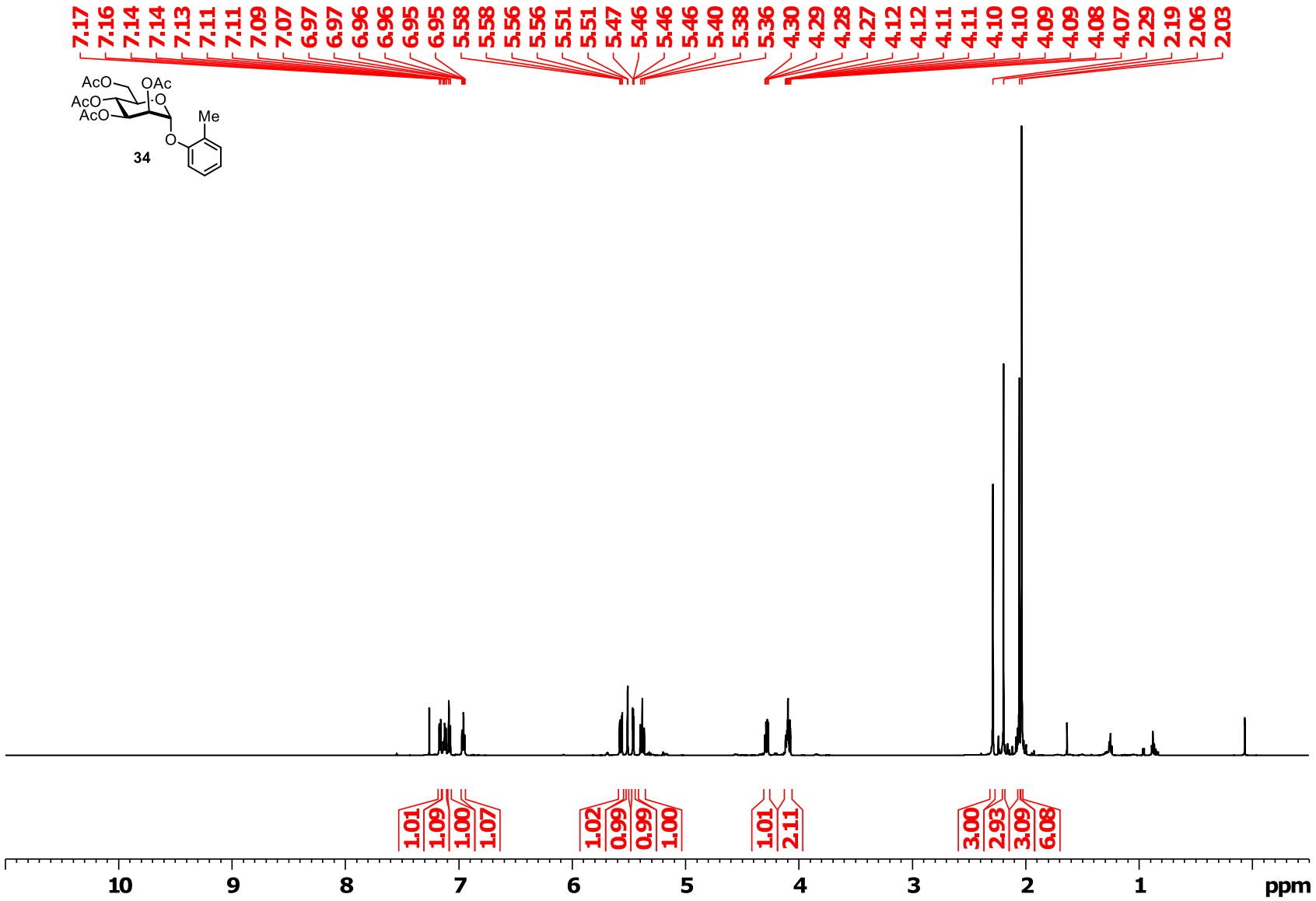


Figure S80. ^{1}H NMR spectrum of **34**.

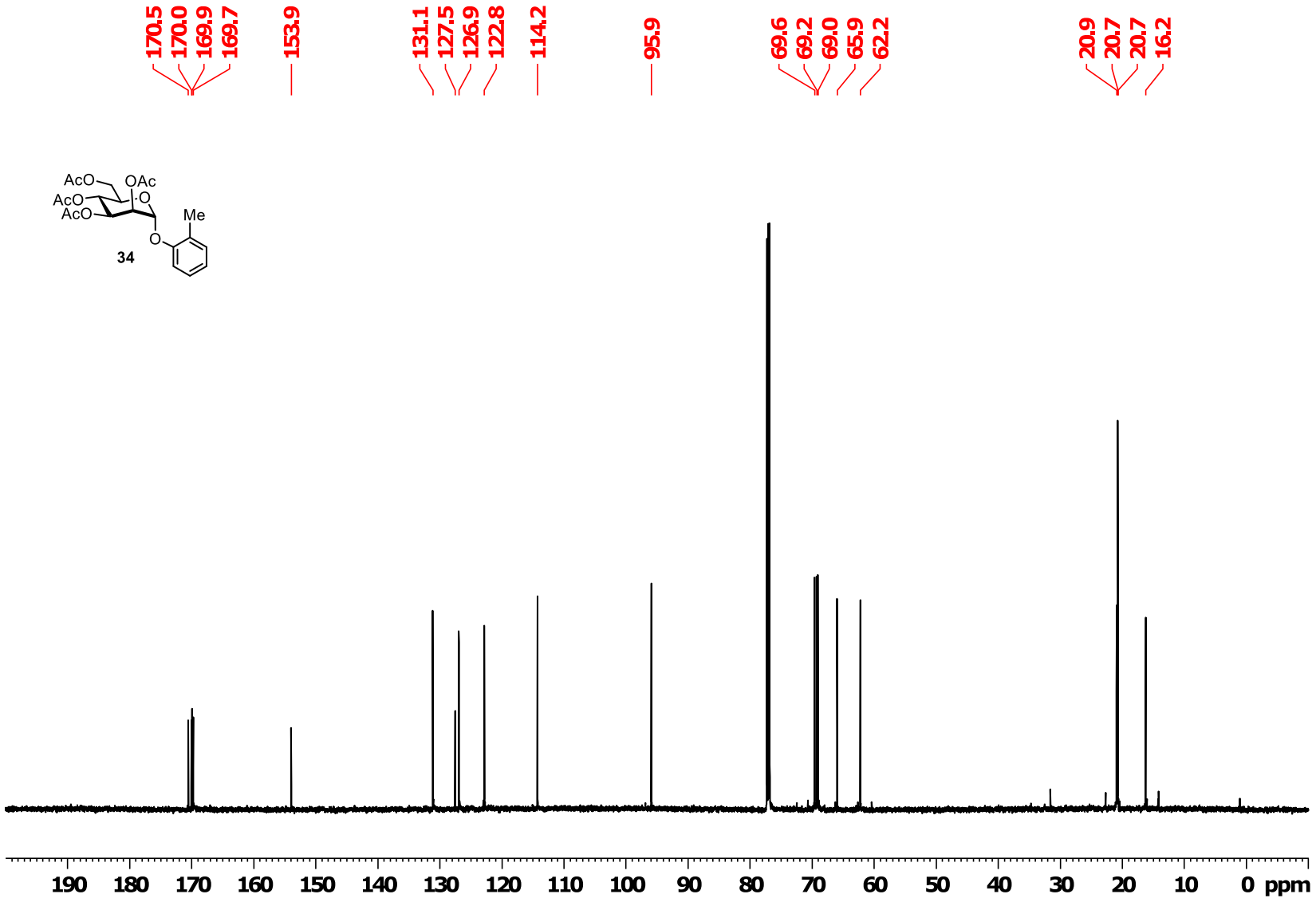


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of **34**.

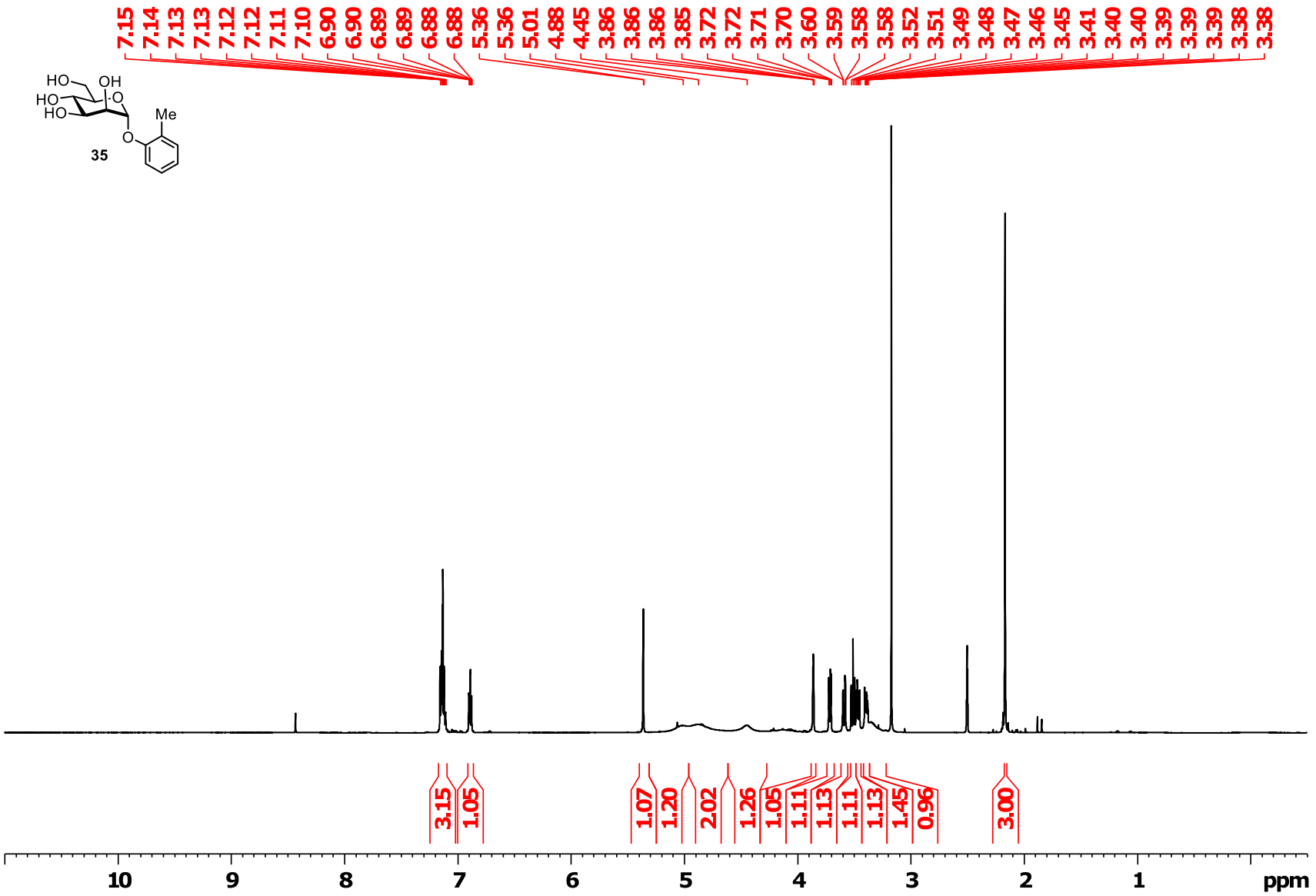


Figure S82. ^{1}H NMR spectrum of **35.**

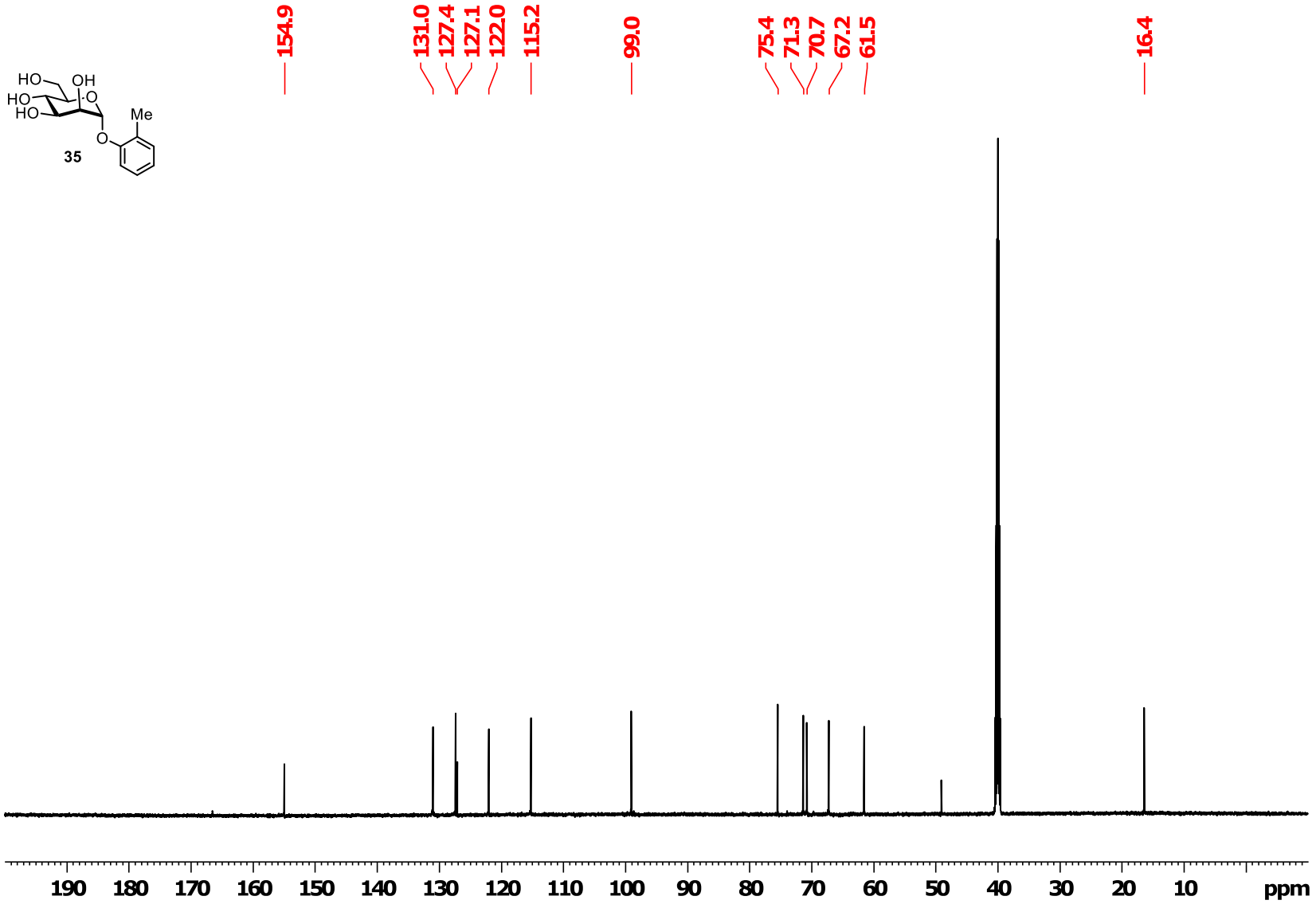


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of **35.**

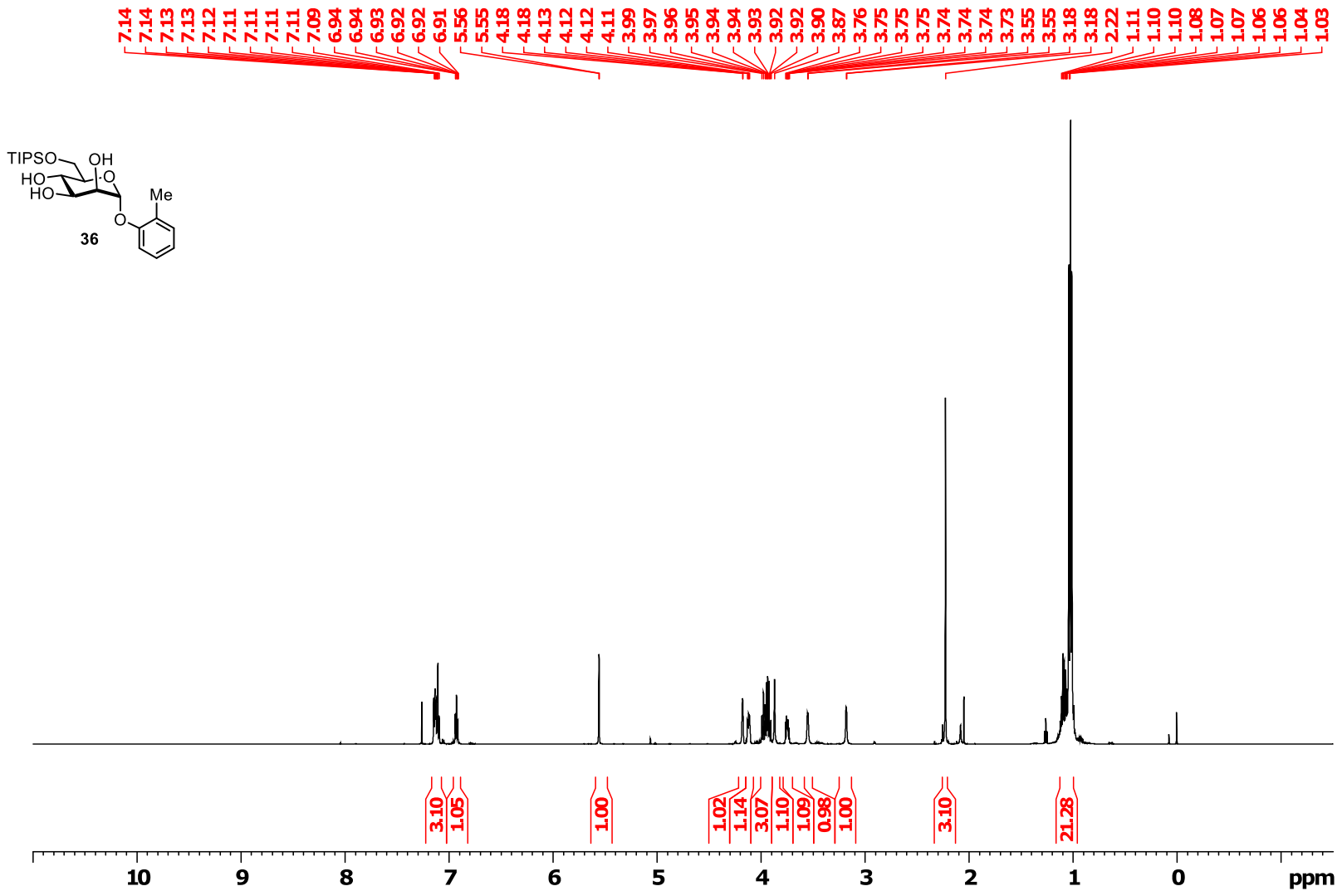


Figure S84. ^{1}H NMR spectrum of **36**.

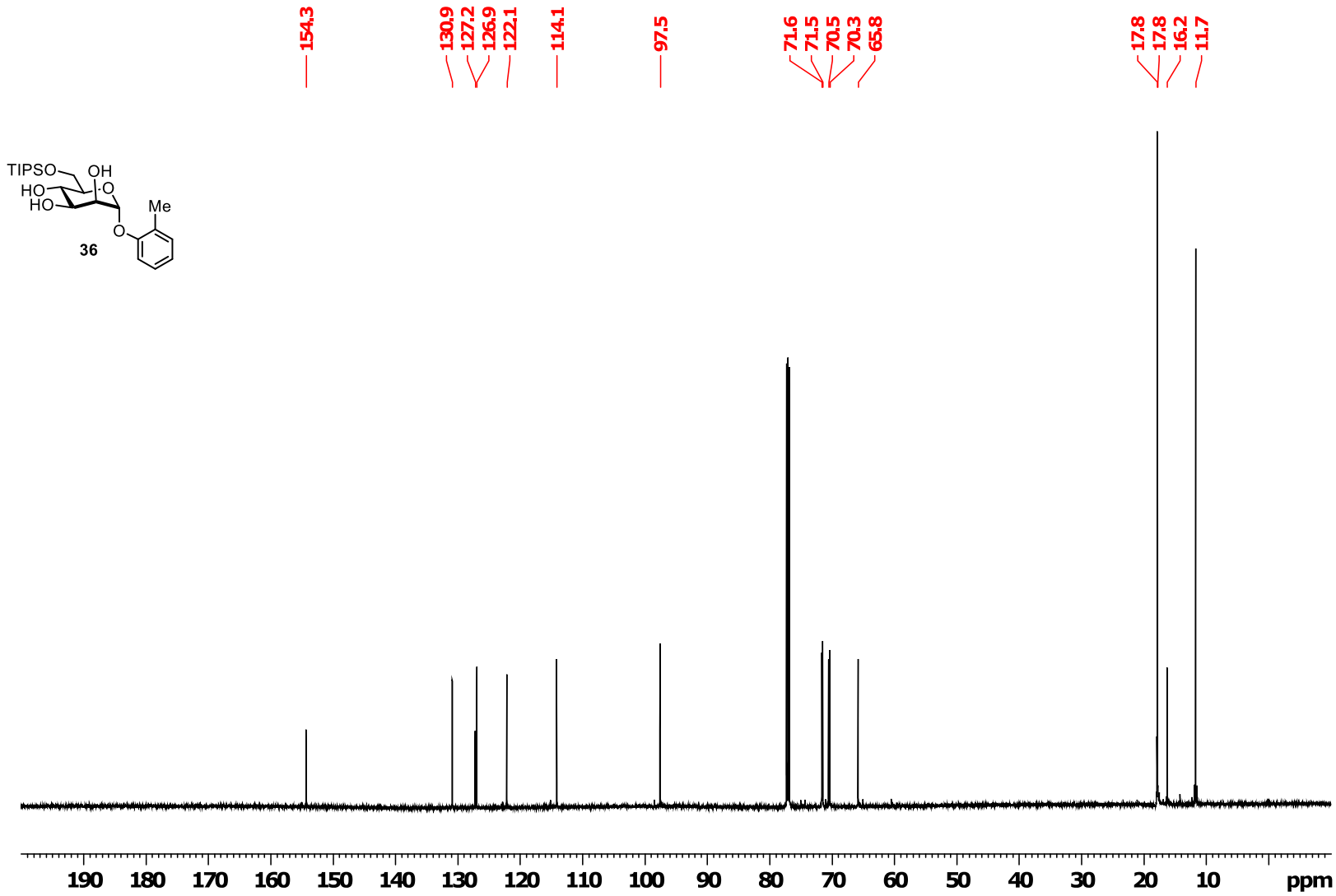


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **36**.

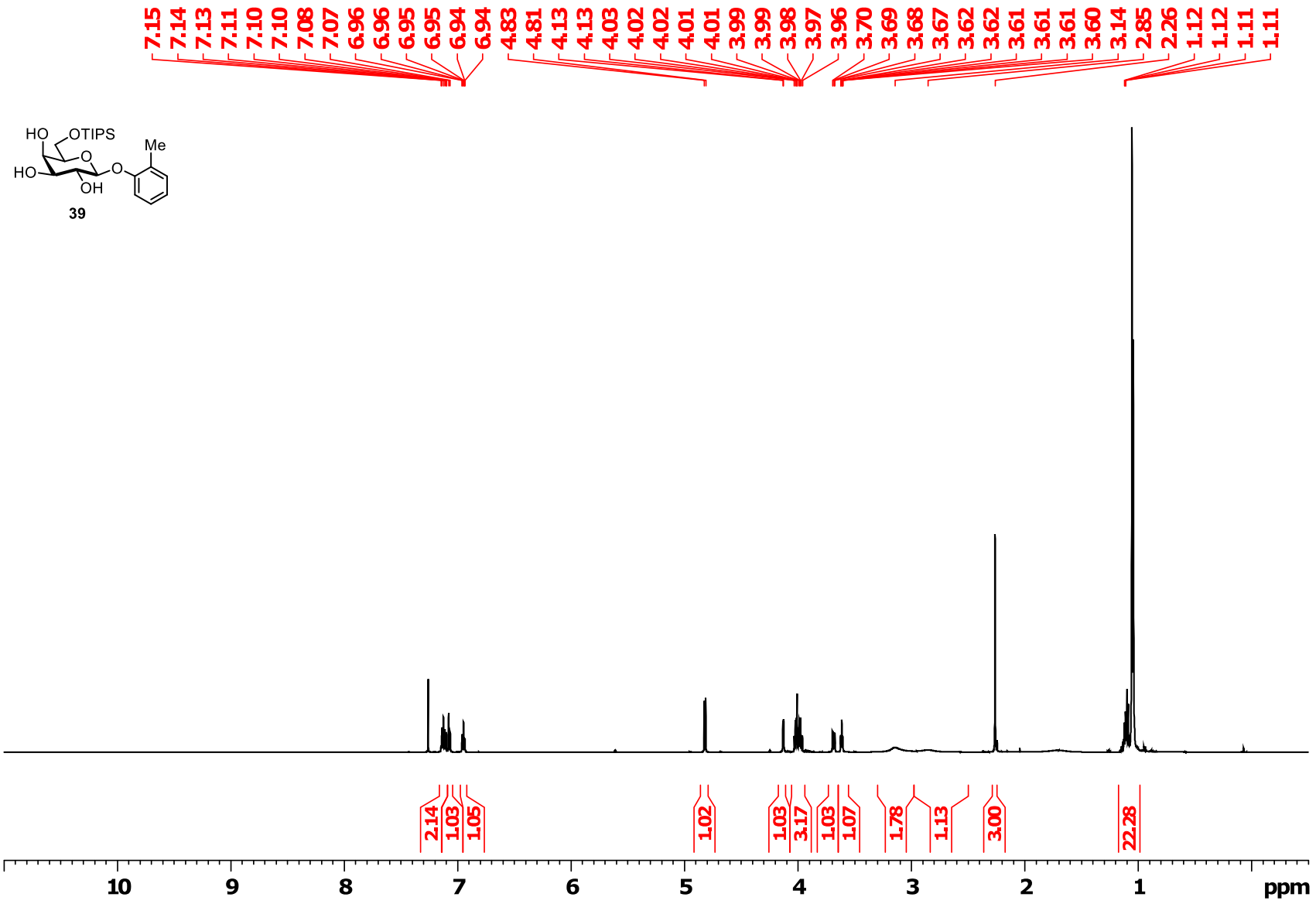


Figure S86. ^{1}H NMR spectrum of **39**.

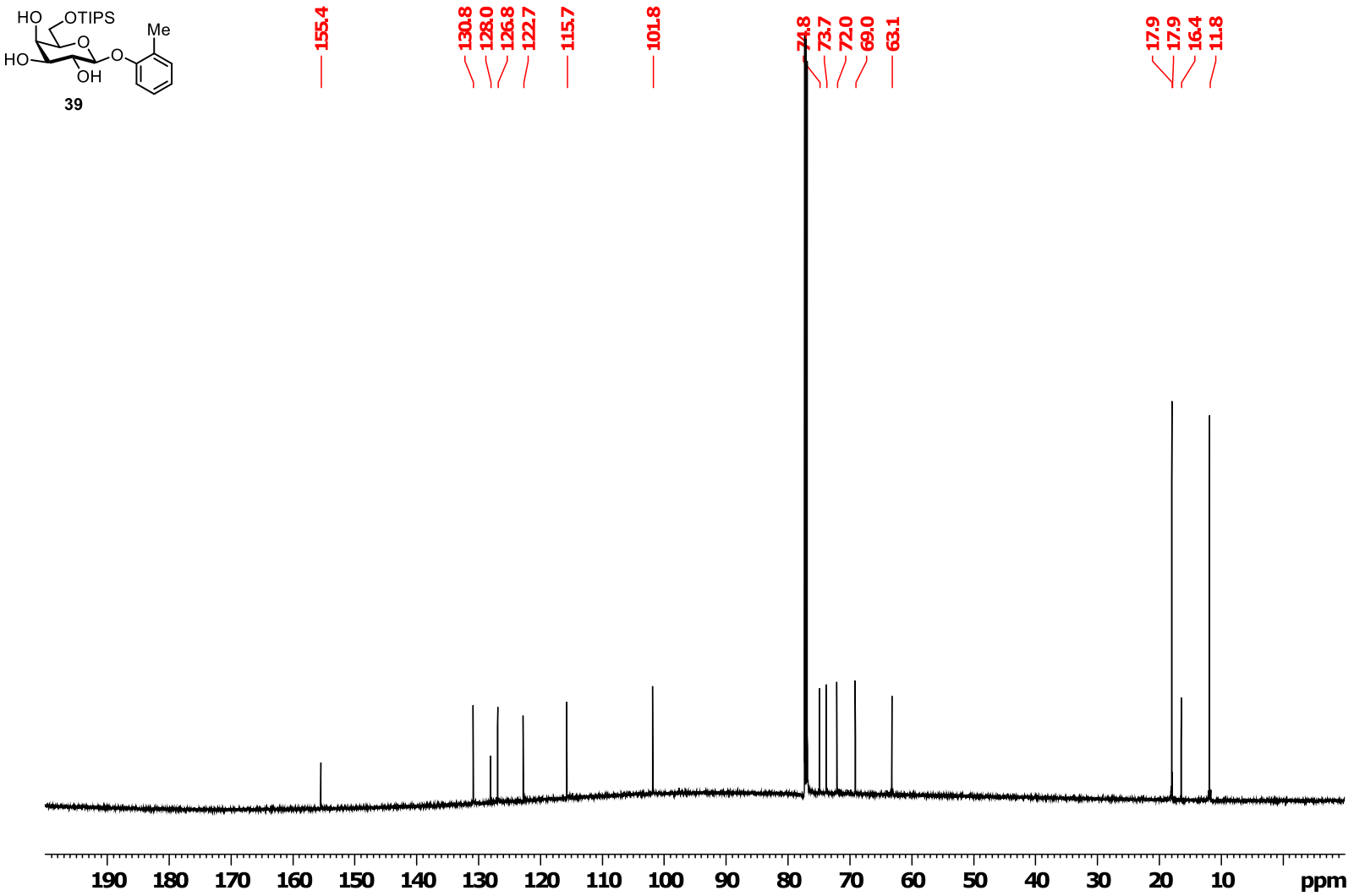


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of **39**.

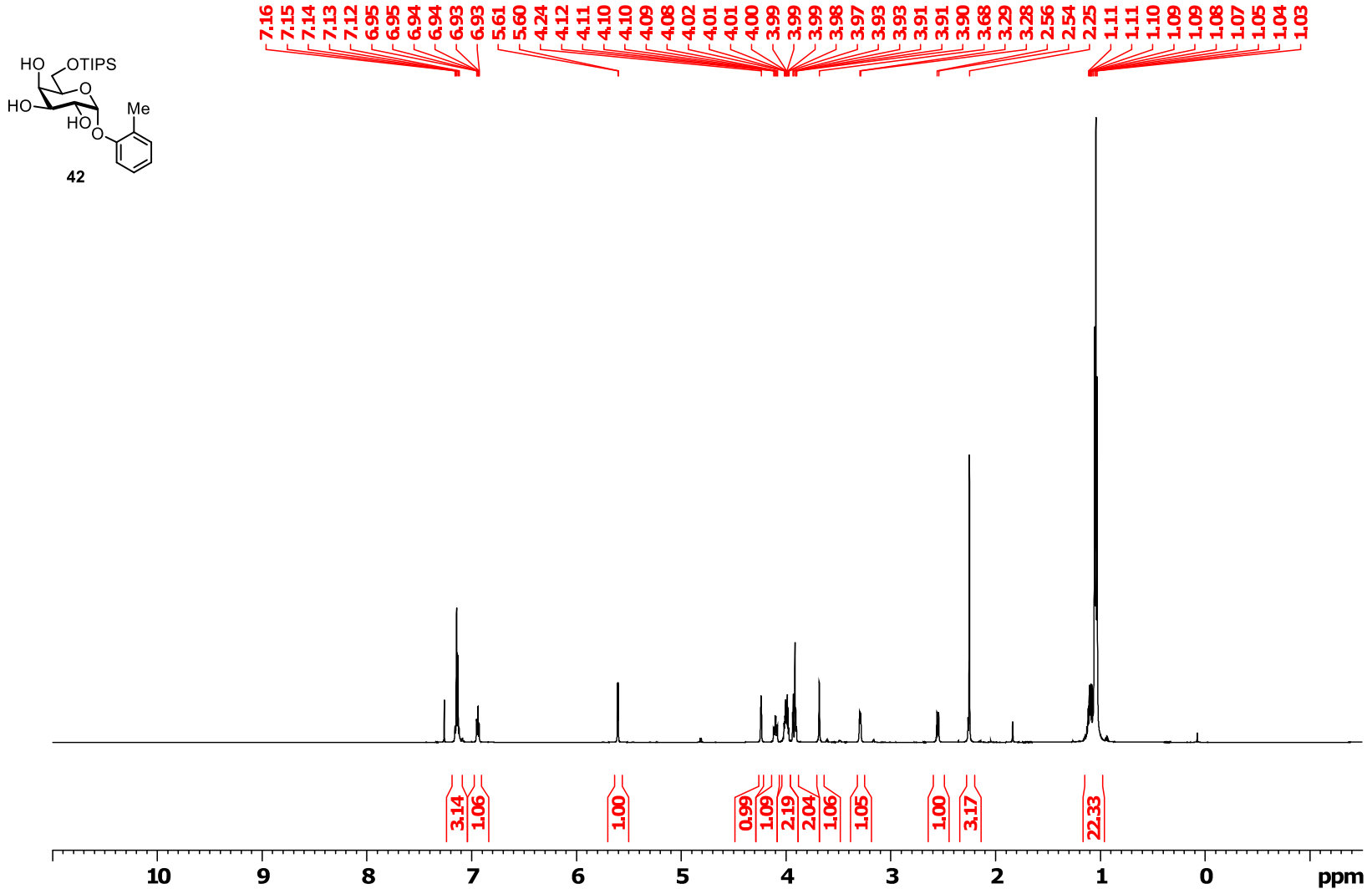


Figure S88. ^{1}H NMR spectrum of **42**.

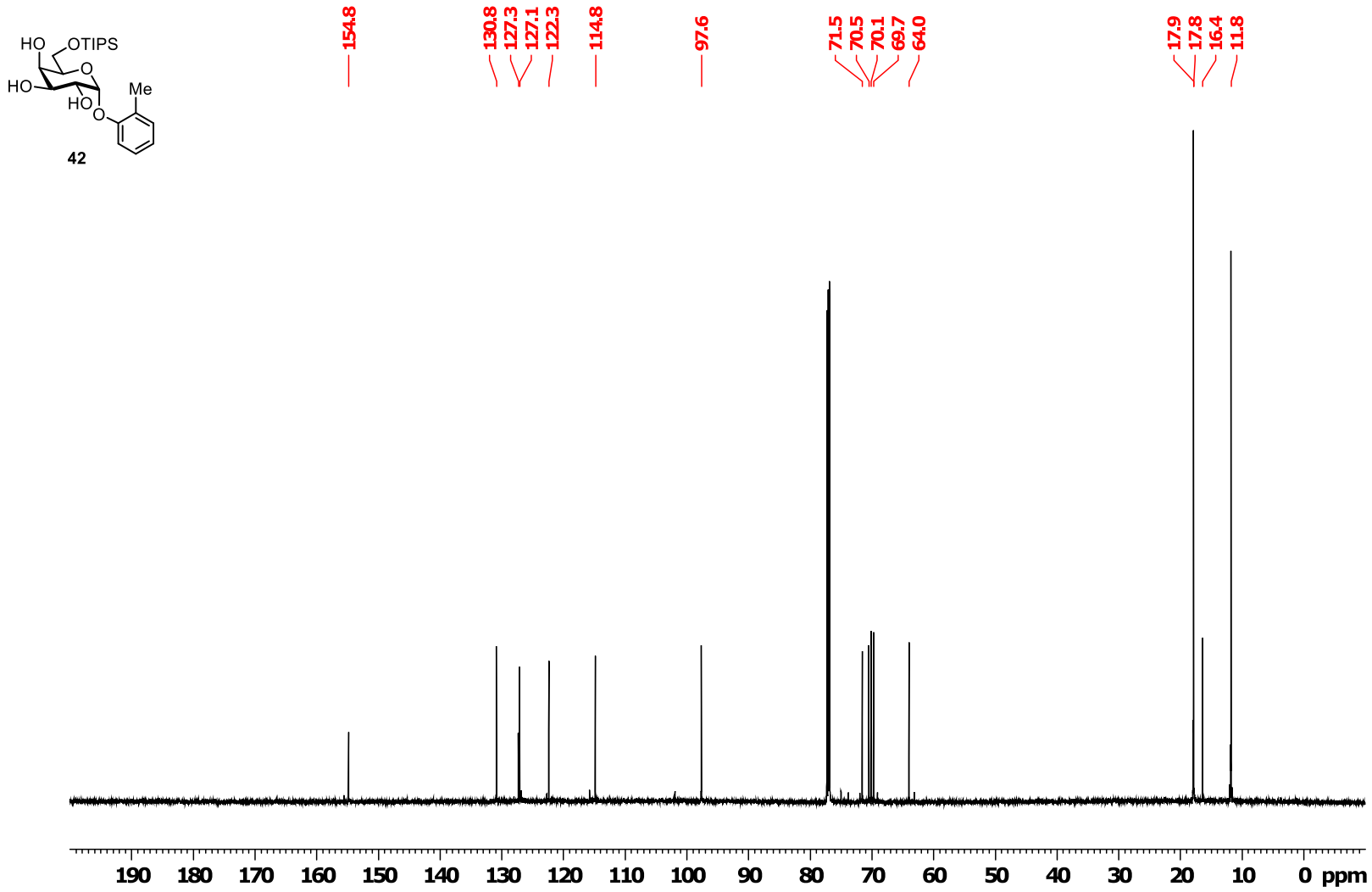


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of **42**.

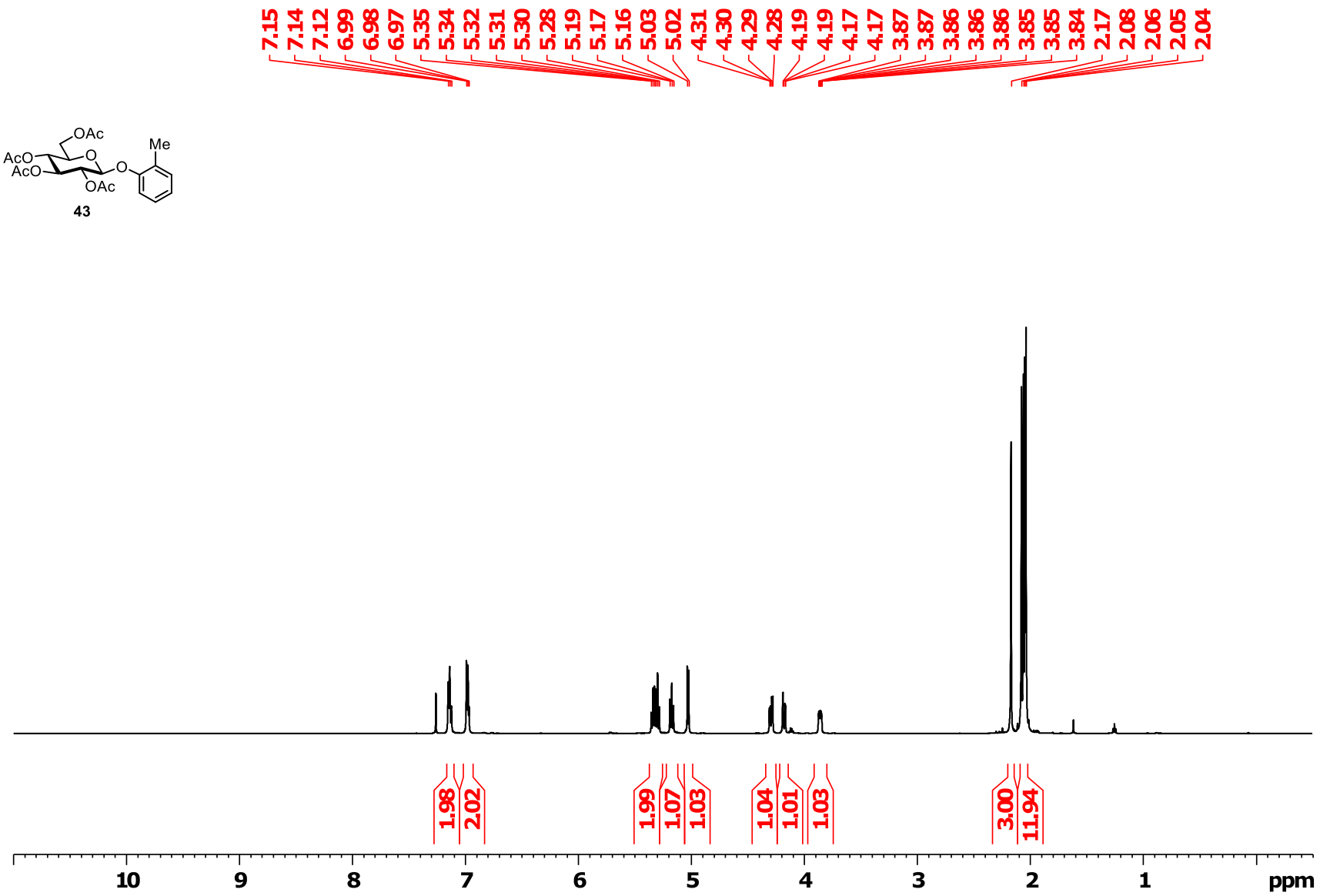


Figure S90. ^{1}H NMR spectrum of **43**.

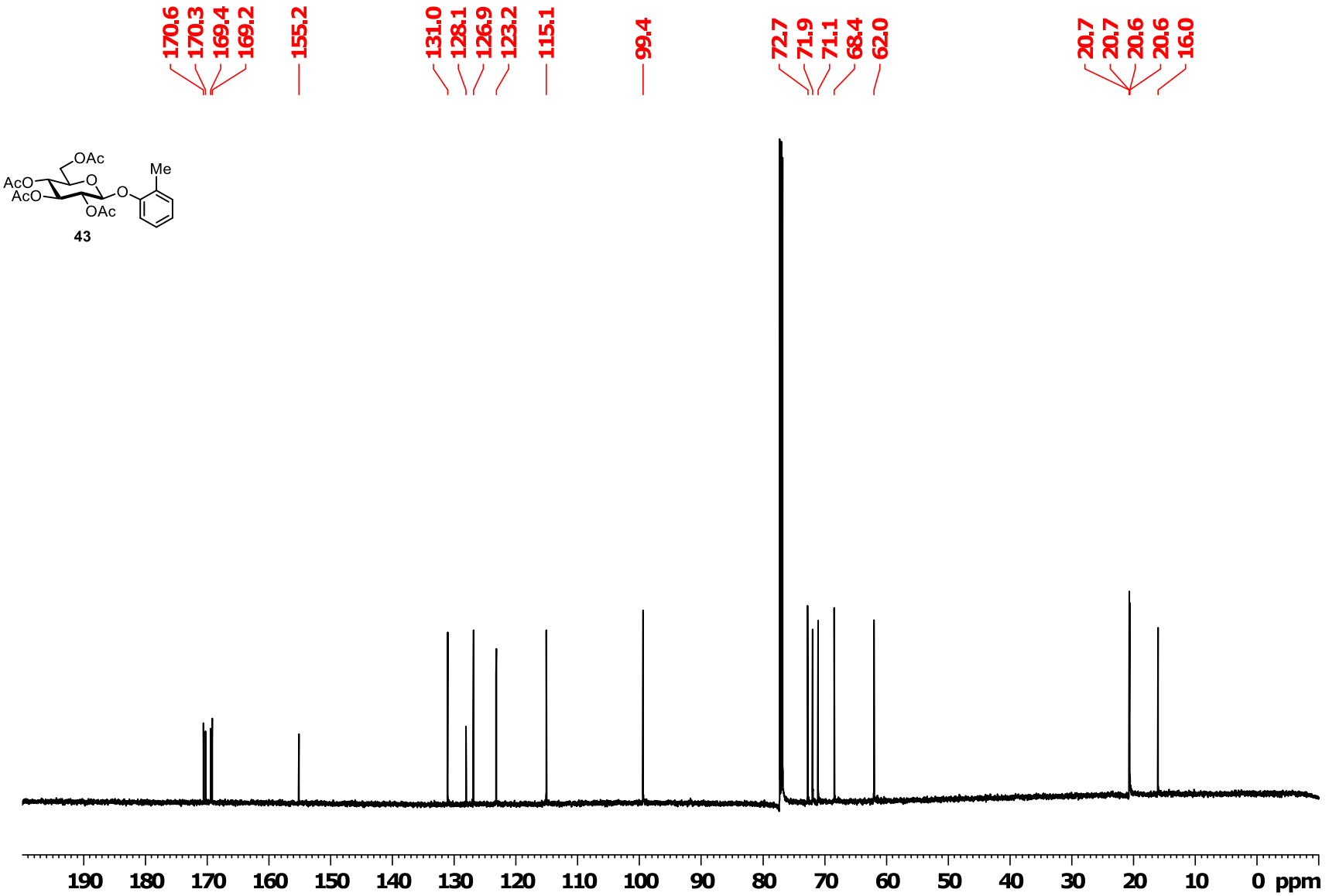


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **43**.

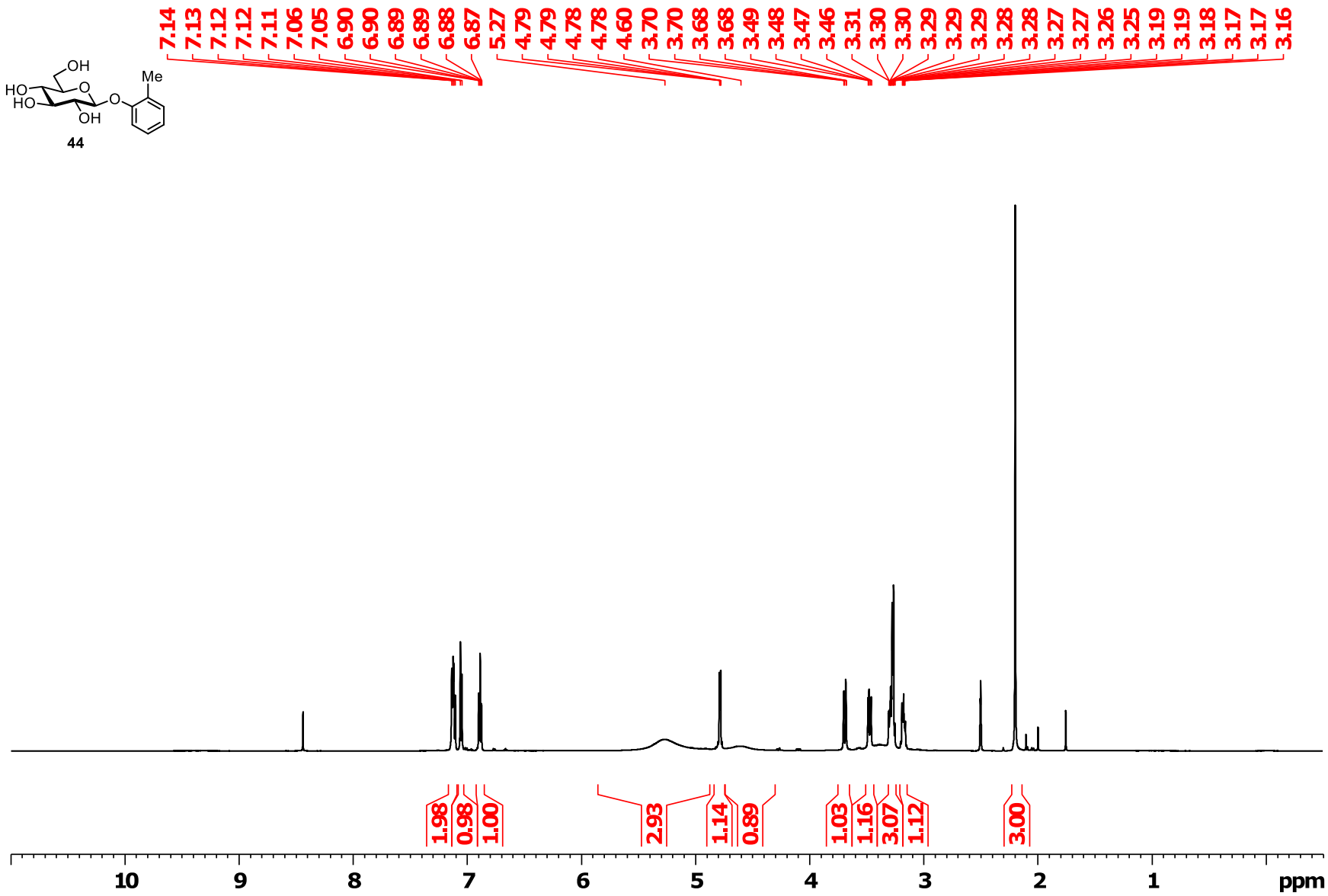


Figure S92. ^{1}H NMR spectrum of **44**.

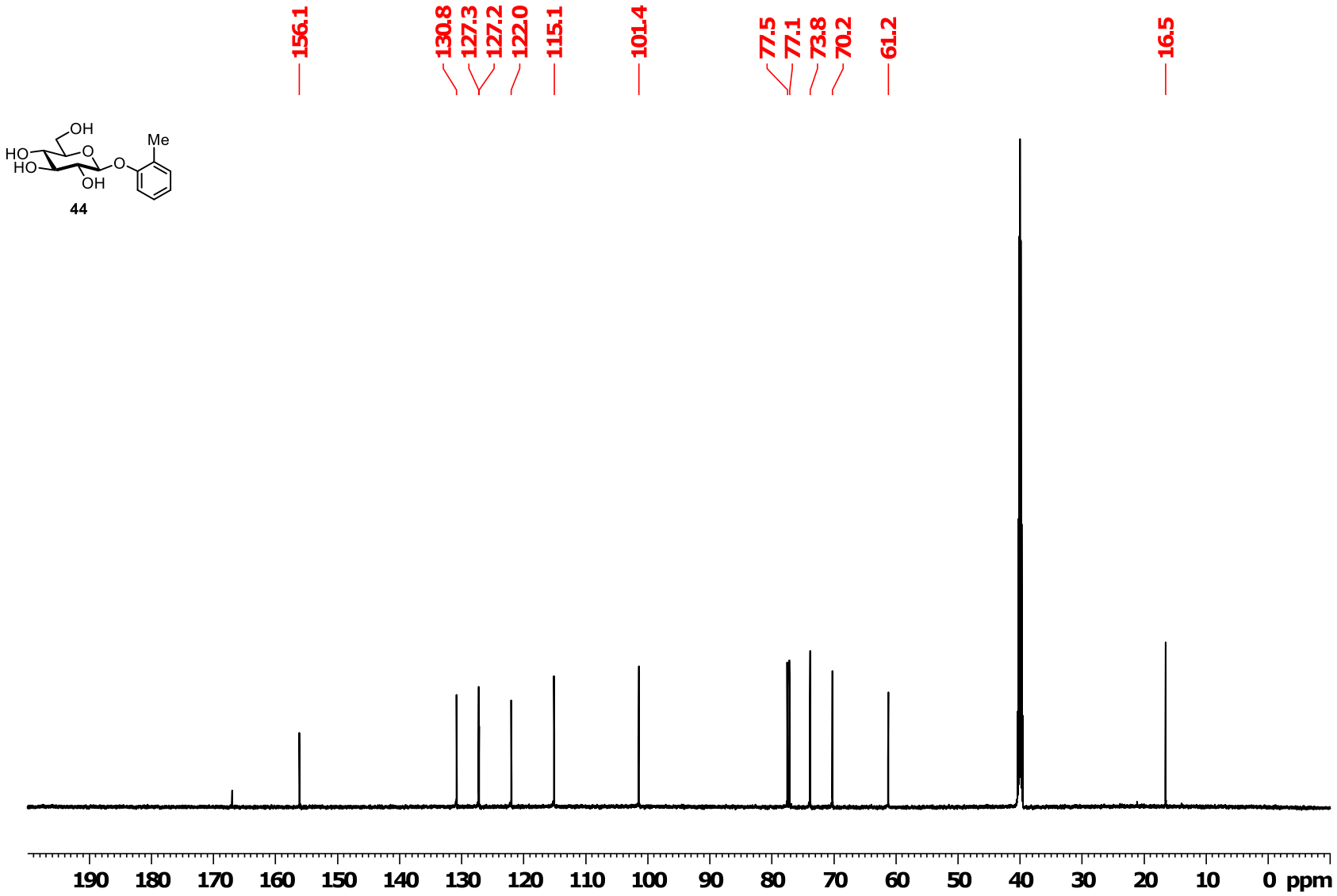


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **44**.

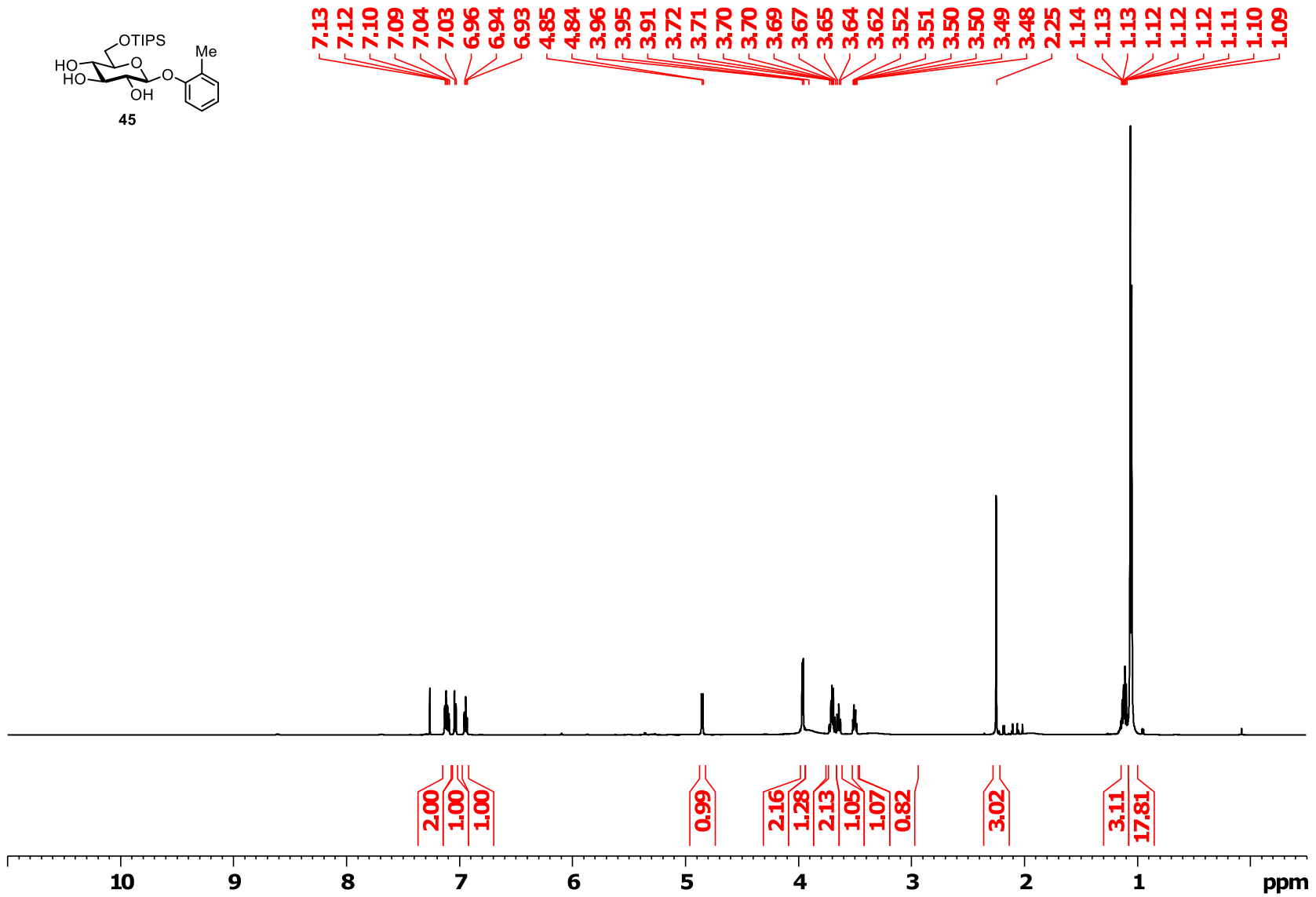


Figure S94. ^{1}H NMR spectrum of **45**.

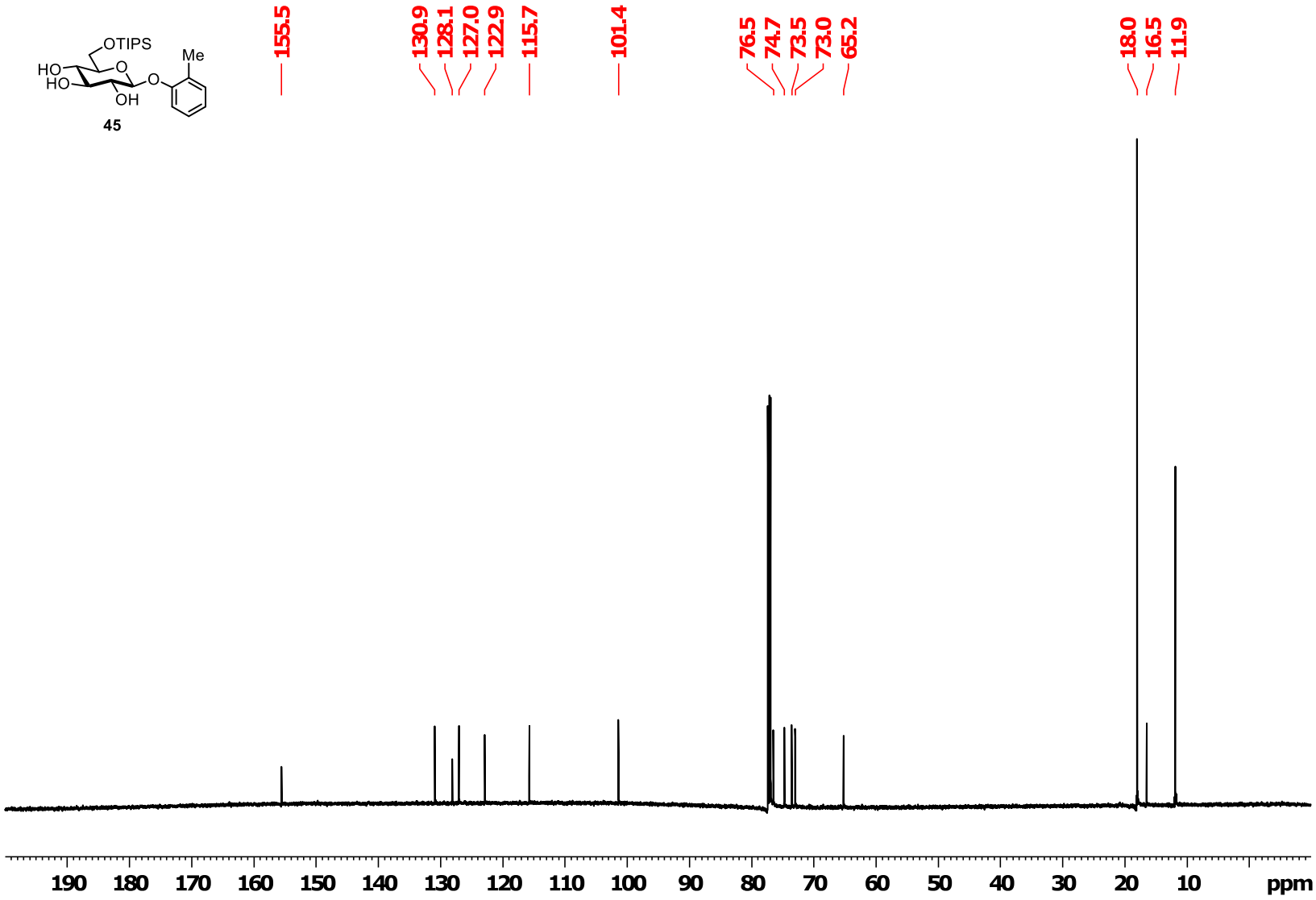


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of **45**.

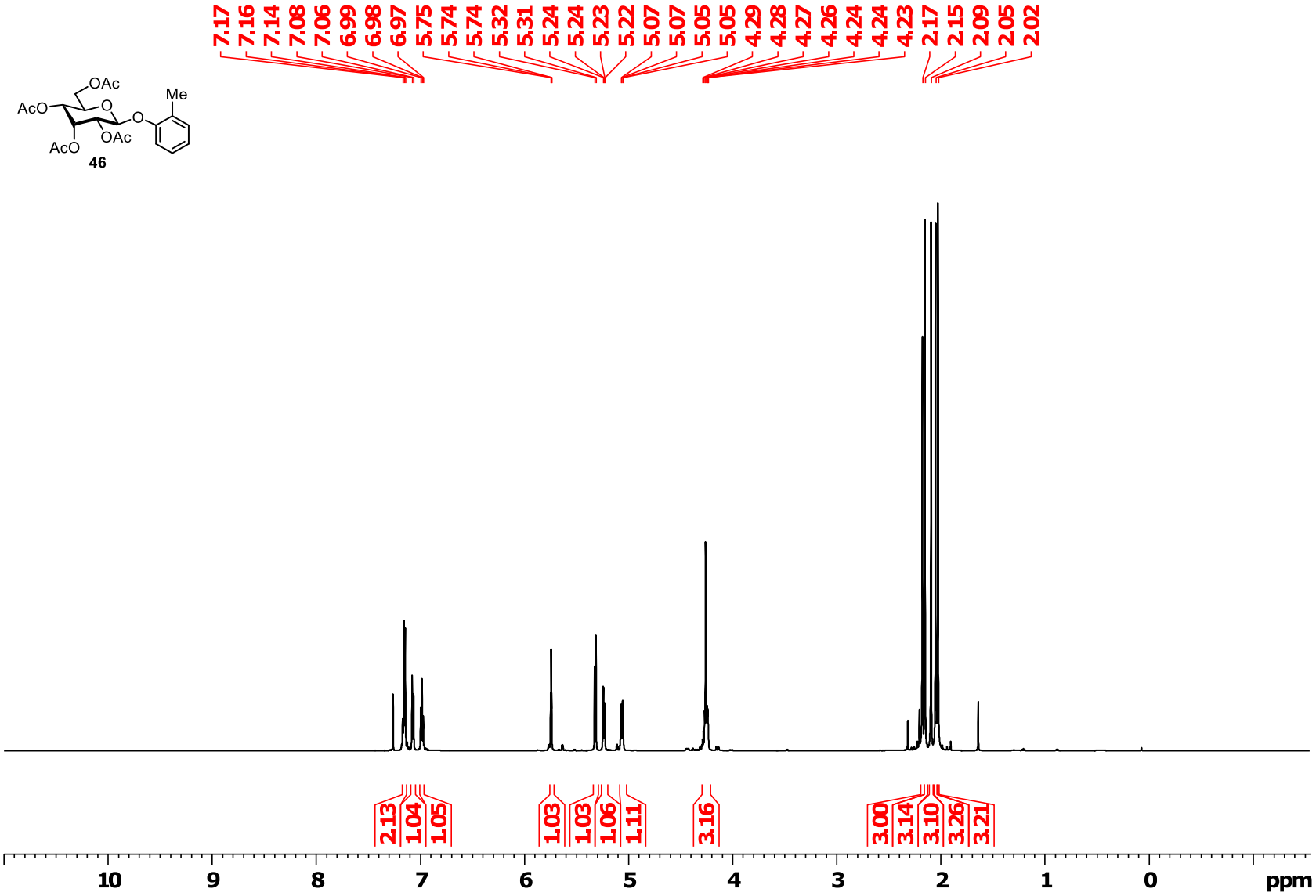


Figure S96. ^{1}H NMR spectrum of **46**.

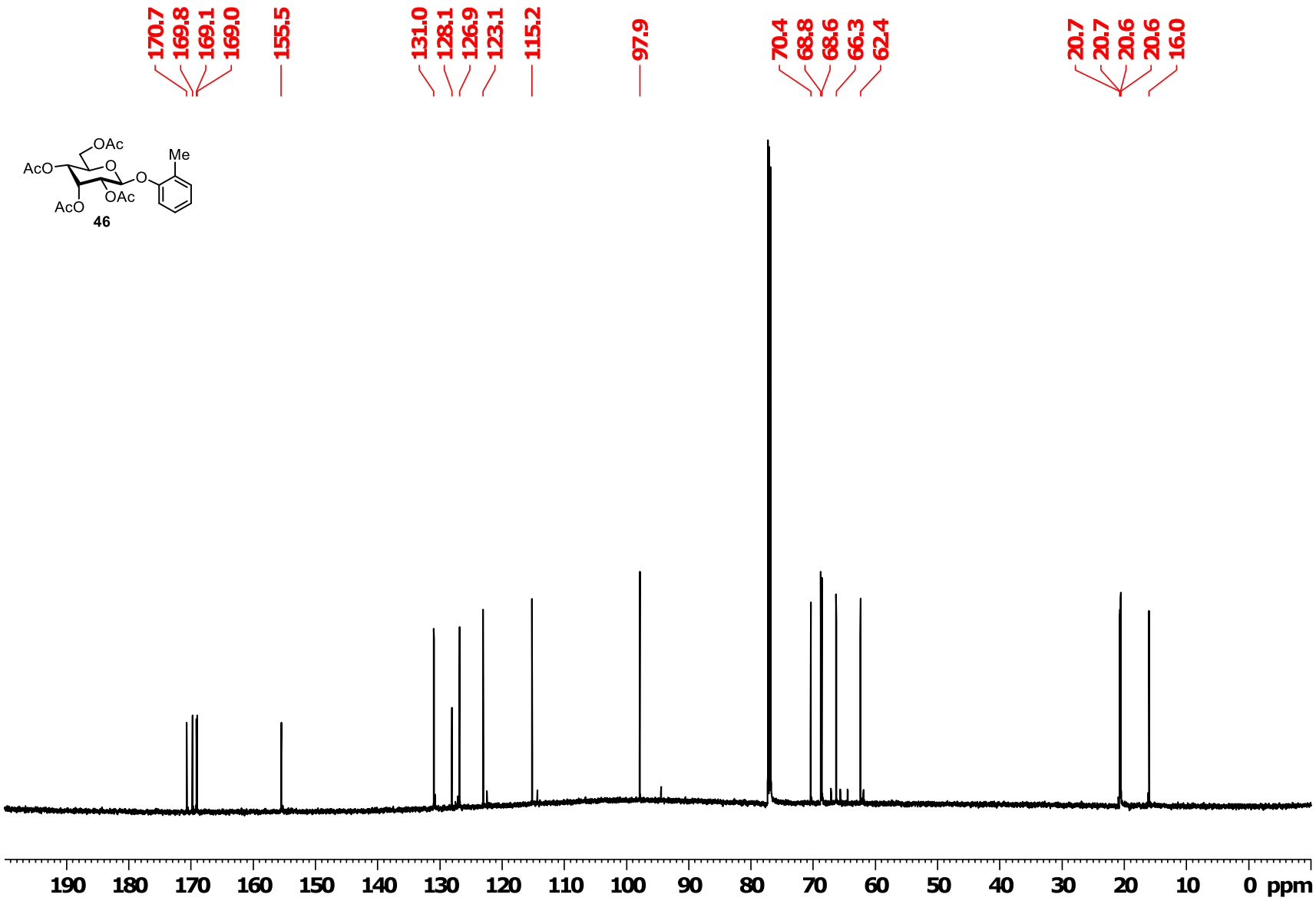


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of **46**.

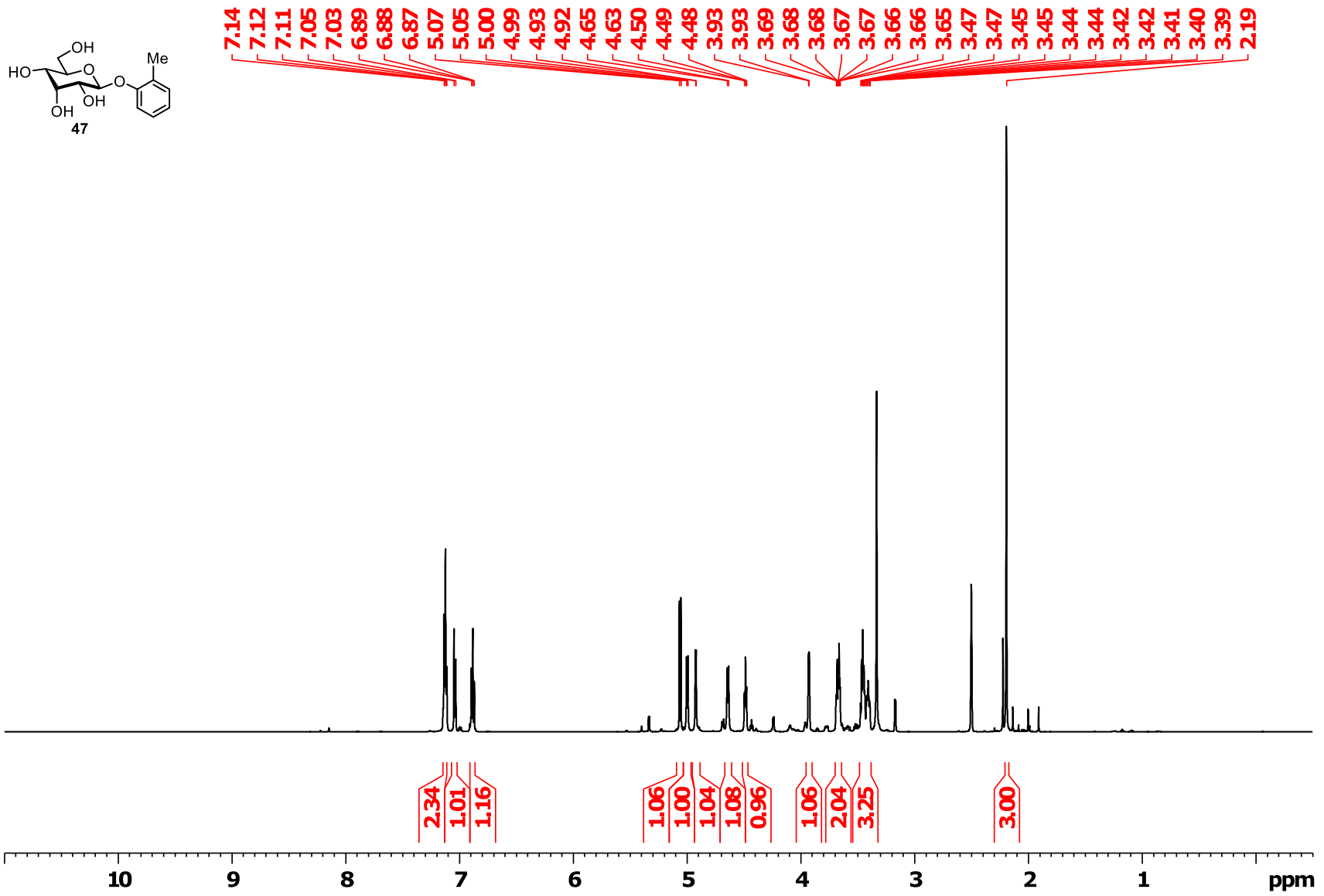


Figure S98. ^{1}H NMR spectrum of **47**.

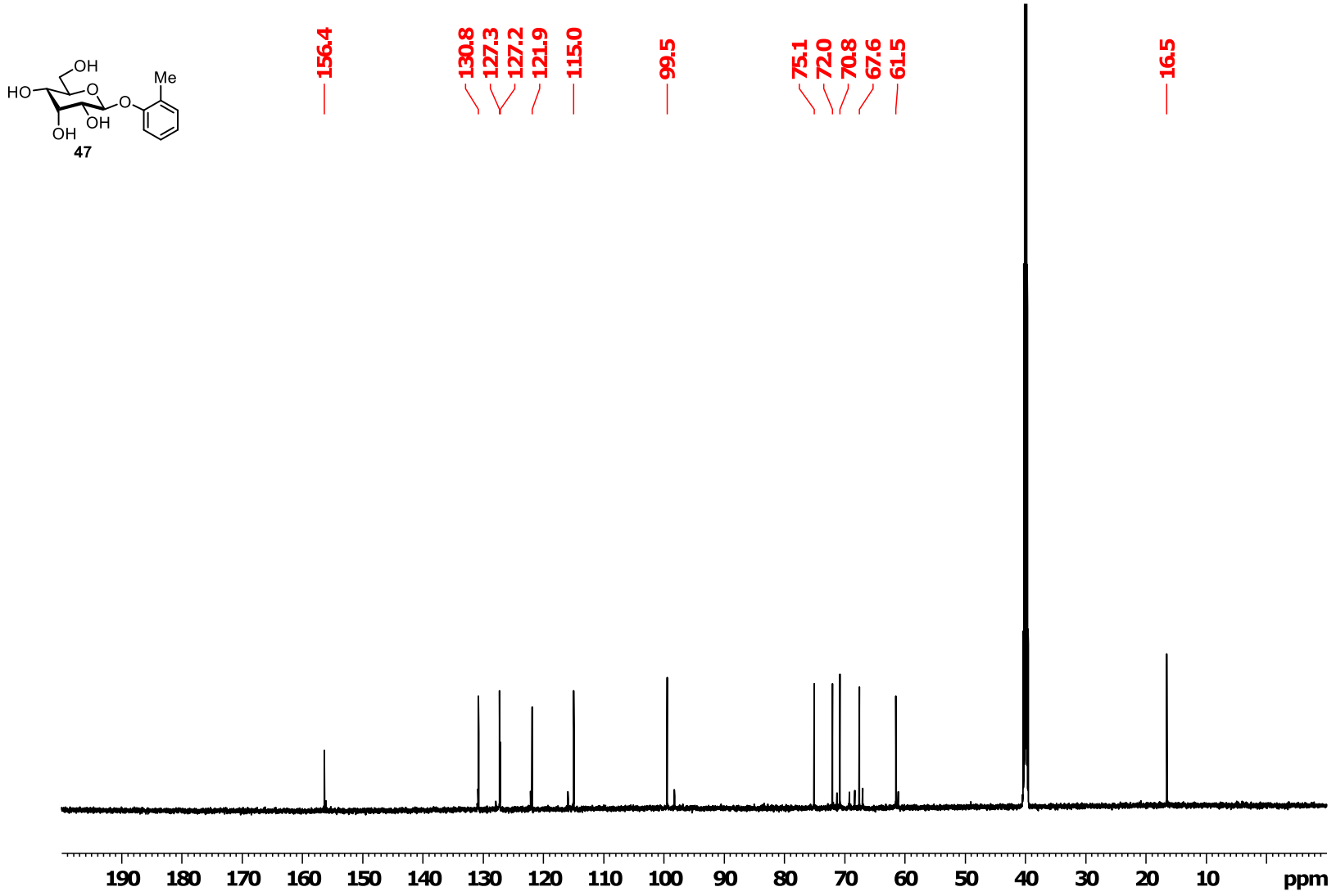


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum of **47**.

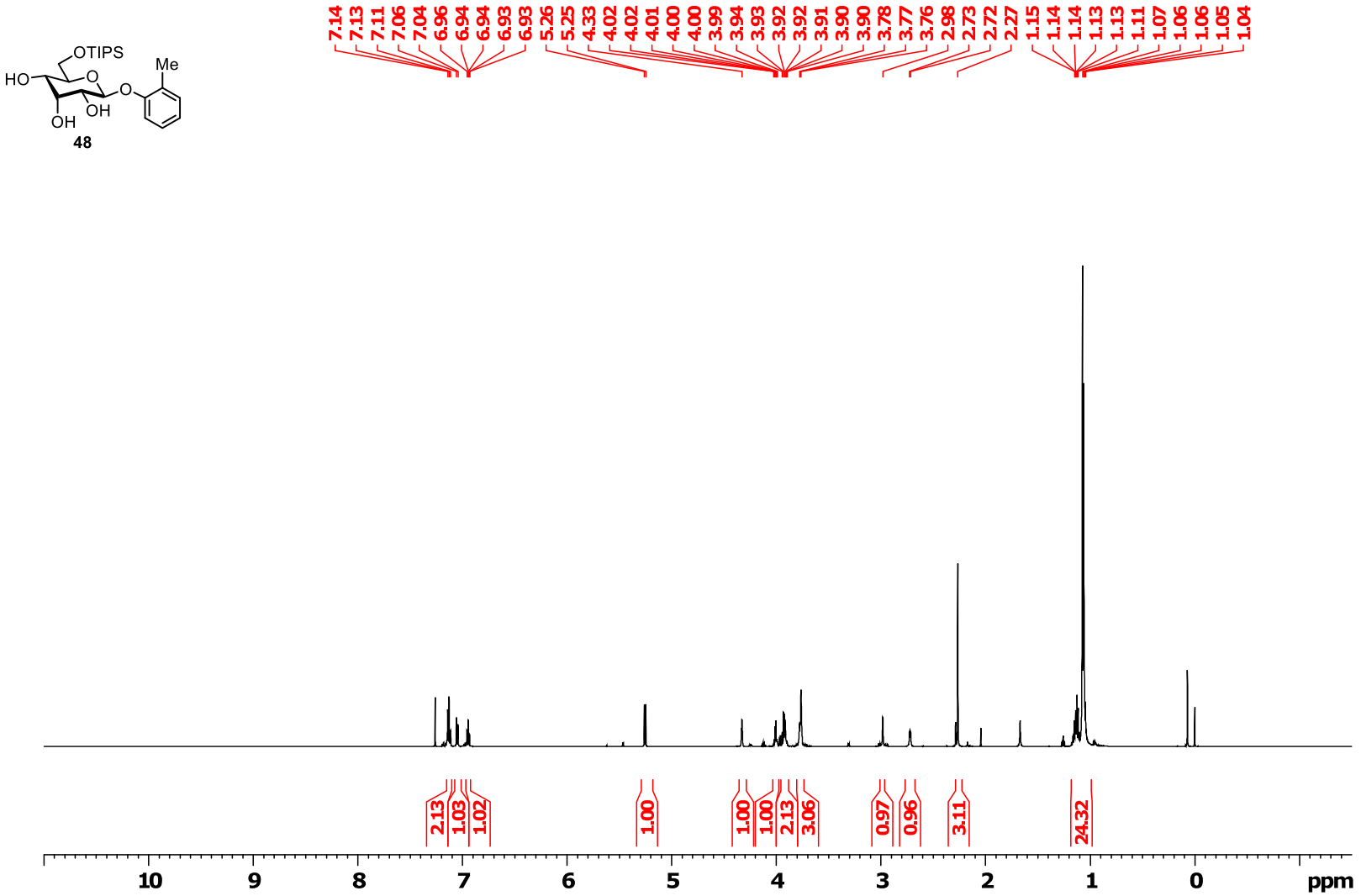


Figure S100. ^{1}H NMR spectrum of **48**.

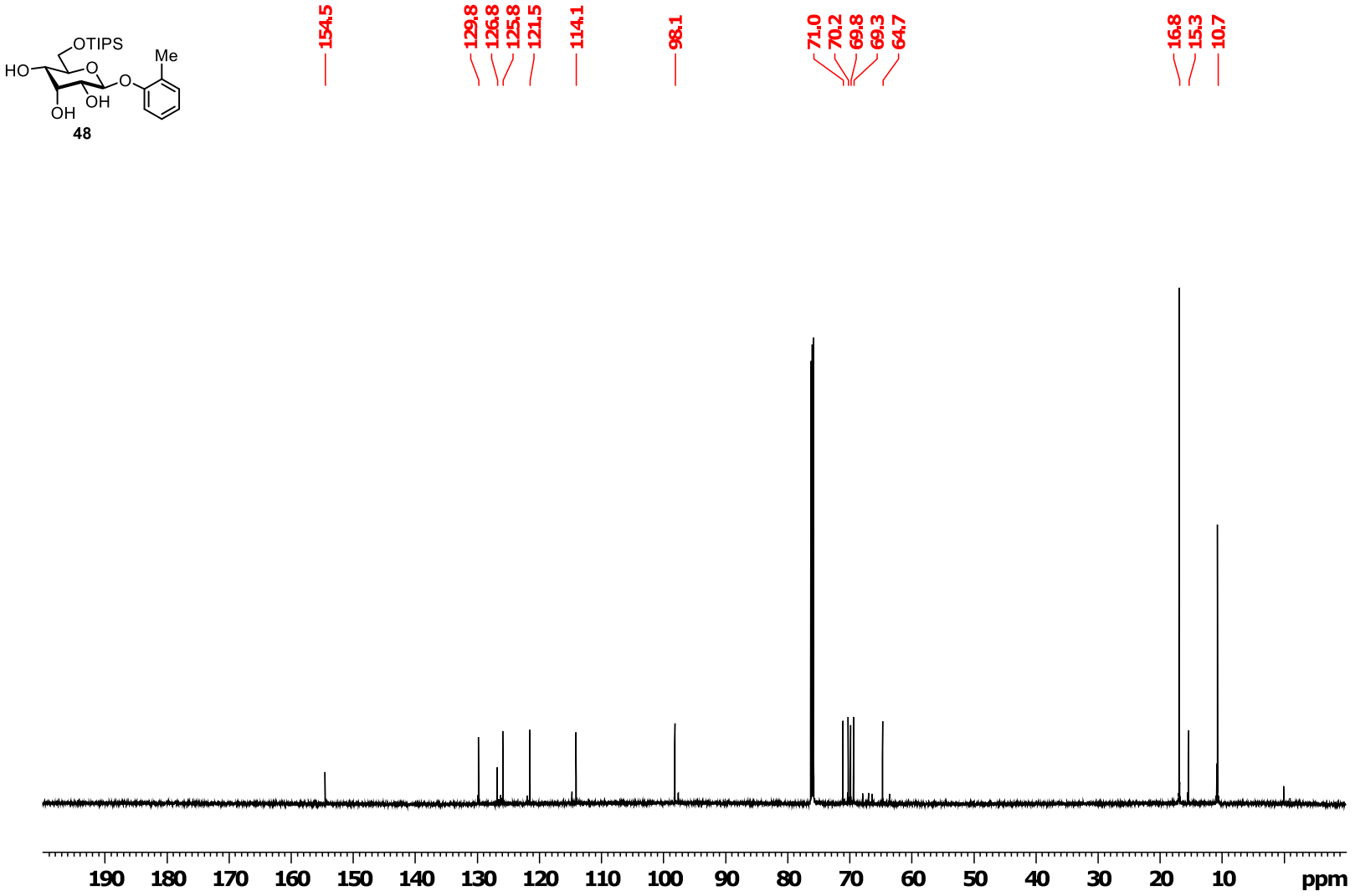


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of **48**.

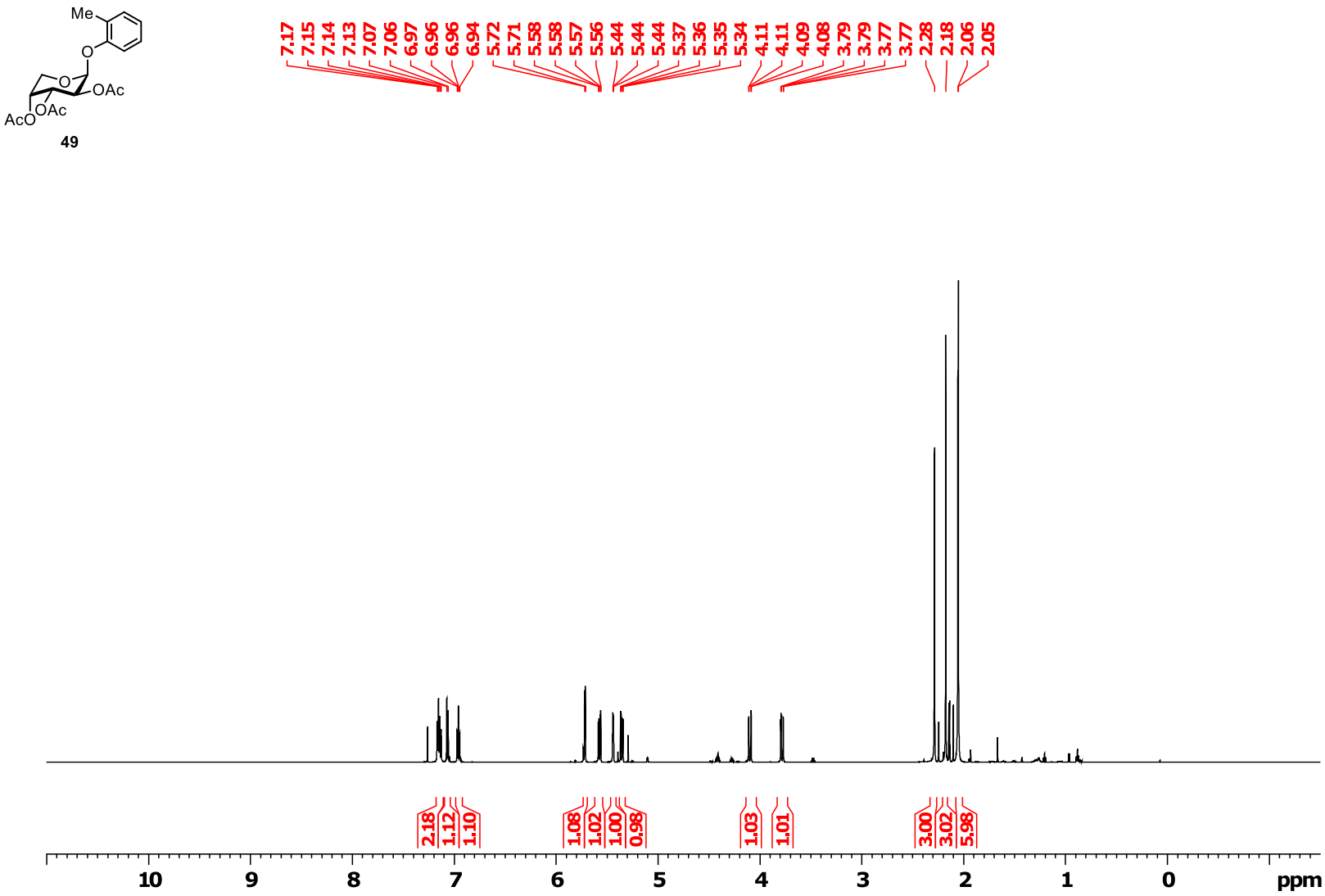


Figure S102. ^{1}H NMR spectrum of **49**.

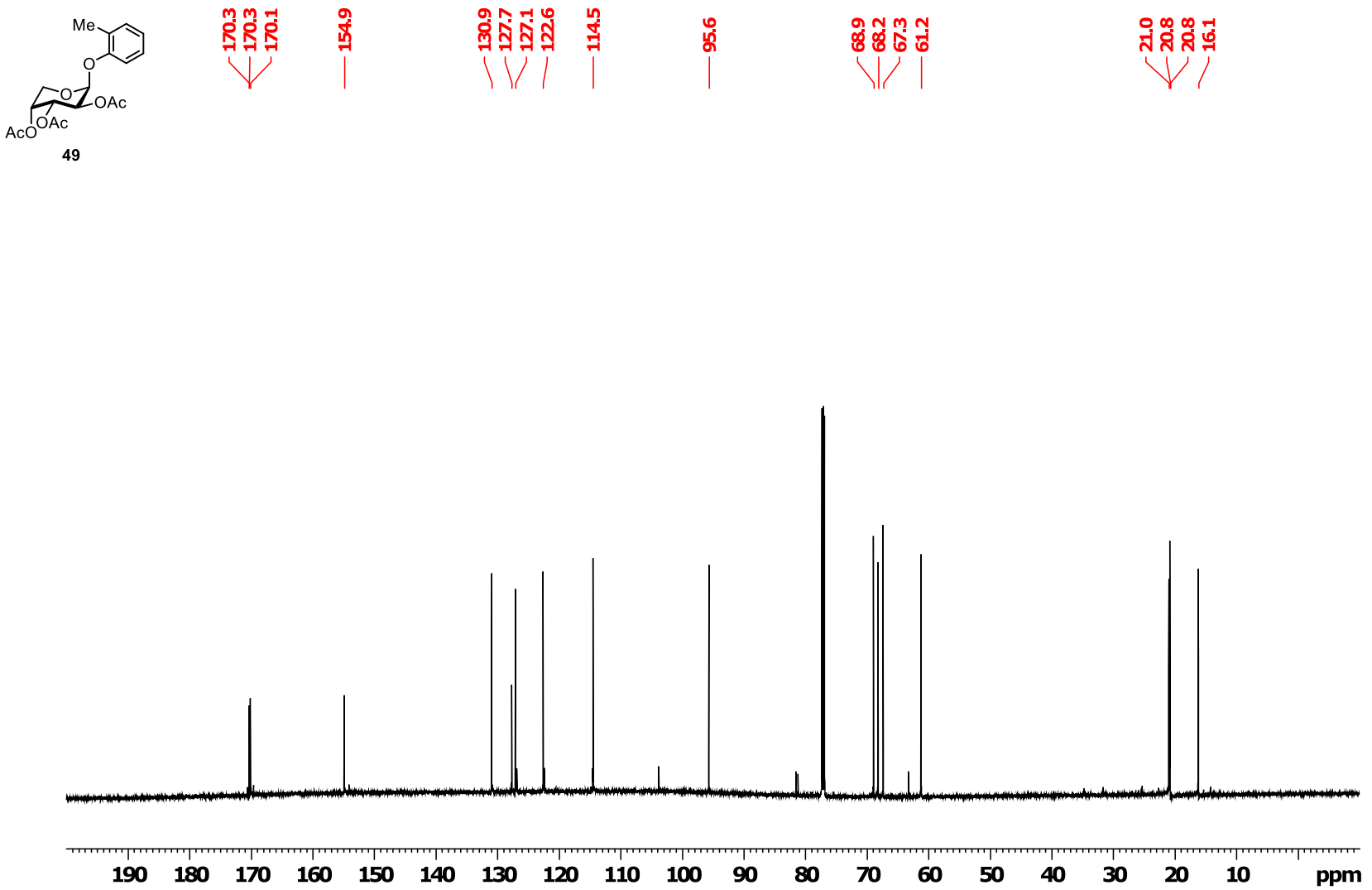


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of **49**.

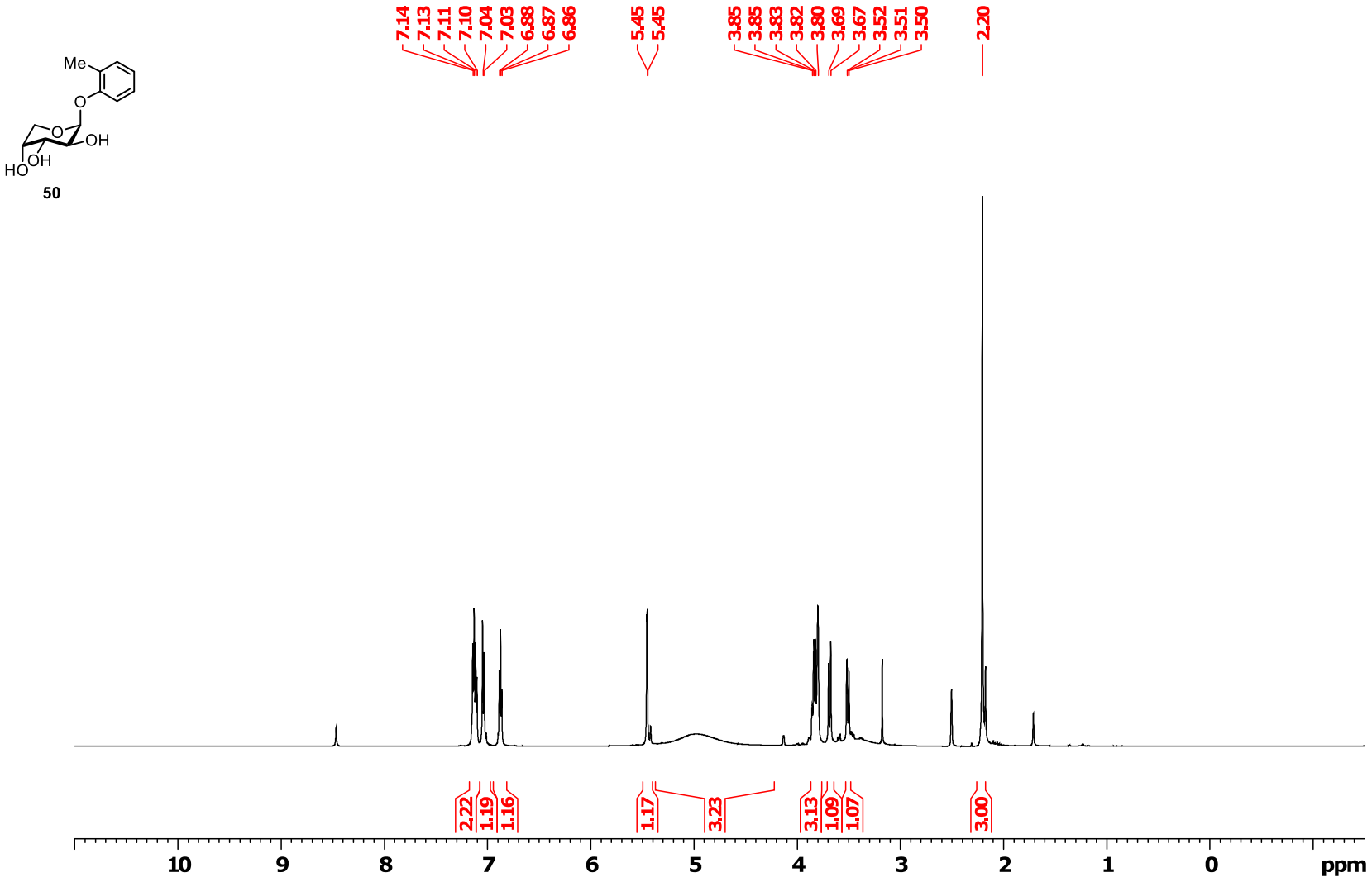


Figure S104. ^{1}H NMR spectrum of **50**.

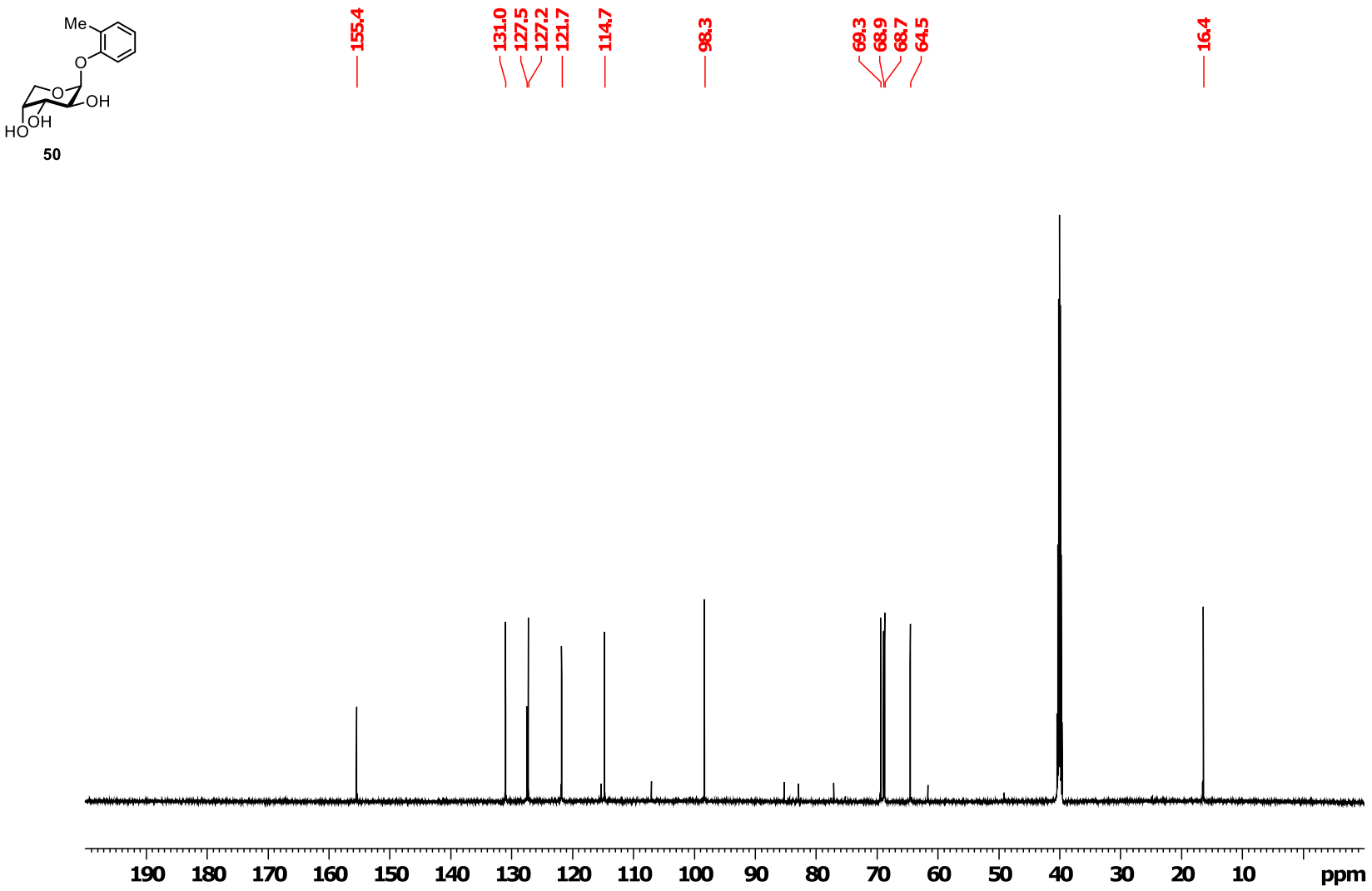


Figure S105. $^{13}C\{^{1}H\}$ NMR spectrum of **50**.

V. X-ray Crystallographic Data

Details of crystallographic refinement

General Methods. A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. Crystal samples were handled under immersion oil and quickly transferred to a cold nitrogen stream. All measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[11] the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package[12] using Least Squares minimization.

Compounds **2a**, **4a**, **5a**, **3c**, and **8a**

These compounds were refined without restraint.

Compound **3a**

Two-site disorder in the isopropyl group (54:46) was modeled with a similarity restraint placed on the thermal parameters of the partially occupied atoms.

Table S1. Crystal data and structure refinement for **2a**.

Empirical formula	$C_{16}H_{24}O_5$	
Formula weight	296.35	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.89131(5) Å	α = 90°
	b = 11.97867(7) Å	β = 90°
	c = 16.99670(9) Å	γ = 90°
Volume	1606.654(16) $Å^3$	
Z	4	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	0.740 mm^{-1}	
F(000)	640	
Crystal size	0.409 x 0.204 x 0.151 mm^3	
Theta range for data collection	4.516 to 73.235°.	
Index ranges	-8<=h<=9, -13<=k<=14, -21<=l<=21	
Reflections collected	15620	
Independent reflections	3209 [R(int) = 0.0213]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3209 / 0 / 195	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0249, wR2 = 0.0647	
R indices (all data)	R1 = 0.0253, wR2 = 0.0651	
Absolute structure parameter	0.00(4)	
Largest diff. peak and hole	0.175 and -0.184 $e/Å^{-3}$	

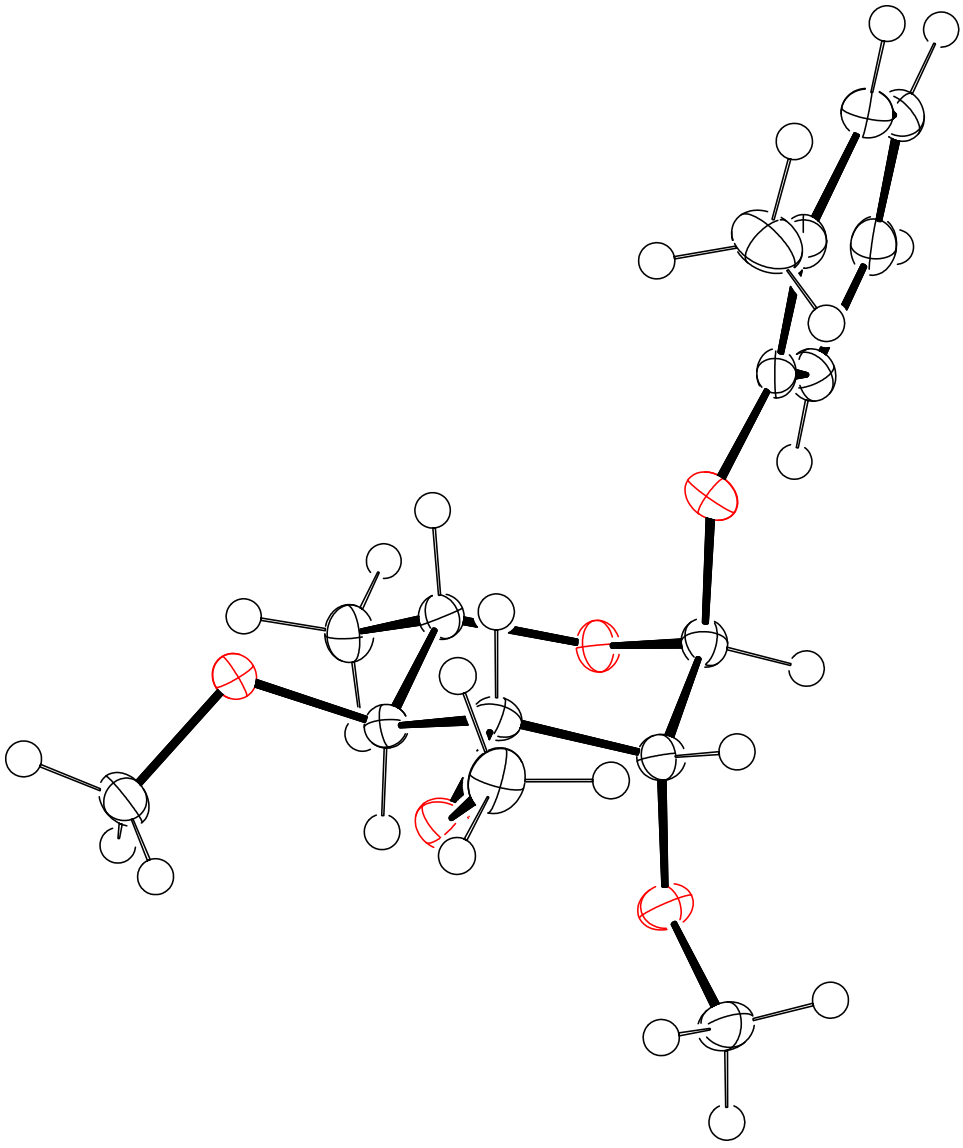


Figure S106. ORTEP of **2a** with ellipsoids shown at 50%.

Table S2. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{18}H_{28}O_5$	
Formula weight	324.40	
Temperature	100(1) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.72846(11) Å	α = 90°
	b = 13.3986(2) Å	β = 90°
	c = 17.3987(3) Å	γ = 90°
Volume	1801.64(5) $Å^3$	
Z	4	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	0.701 mm^{-1}	
F(000)	704	
Crystal size	0.298 x 0.197 x 0.116 mm^3	
Theta range for data collection	4.165 to 73.340°.	
Index ranges	-9<=h<=9, -12<=k<=16, -21<=l<=21	
Reflections collected	13995	
Independent reflections	3583 [R(int) = 0.0259]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3583 / 6 / 225	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1013	
R indices (all data)	R1 = 0.0422, wR2 = 0.1025	
Absolute structure parameter	0.10(6)	
Largest diff. peak and hole	0.345 and -0.215 $e/Å^{-3}$	

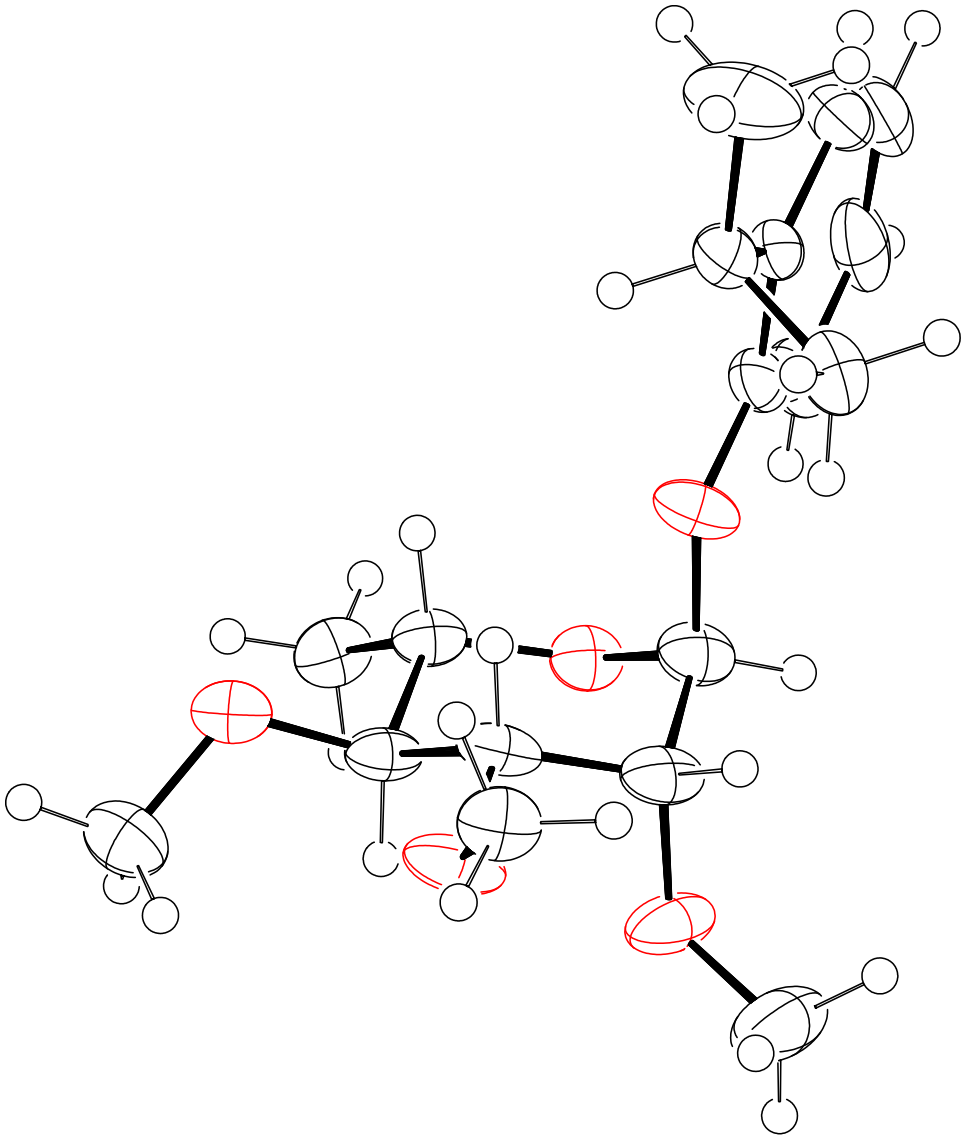


Figure S107. ORTEP of **3a** with ellipsoids shown at 50%. Disorder in the iPr group is omitted for clarity.

Table S3. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{19}H_{30}O_5$	
Formula weight	338.43	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.71828(6) Å	α = 90°
	b = 13.89043(10) Å	β = 90°
	c = 17.59797(13) Å	γ = 90°
Volume	1886.68(2) $Å^3$	
Z	4	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	0.689 mm^{-1}	
F(000)	736	
Crystal size	0.156 x 0.094 x 0.083 mm^3	
Theta range for data collection	4.055 to 73.444°.	
Index ranges	-9<=h<=9, -17<=k<=16, -21<=l<=14	
Reflections collected	18243	
Independent reflections	3759 [R(int) = 0.0280]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.837	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3759 / 0 / 224	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0701	
R indices (all data)	R1 = 0.0290, wR2 = 0.0708	
Absolute structure parameter	-0.04(6)	
Largest diff. peak and hole	0.194 and -0.155 $e/Å^{-3}$	

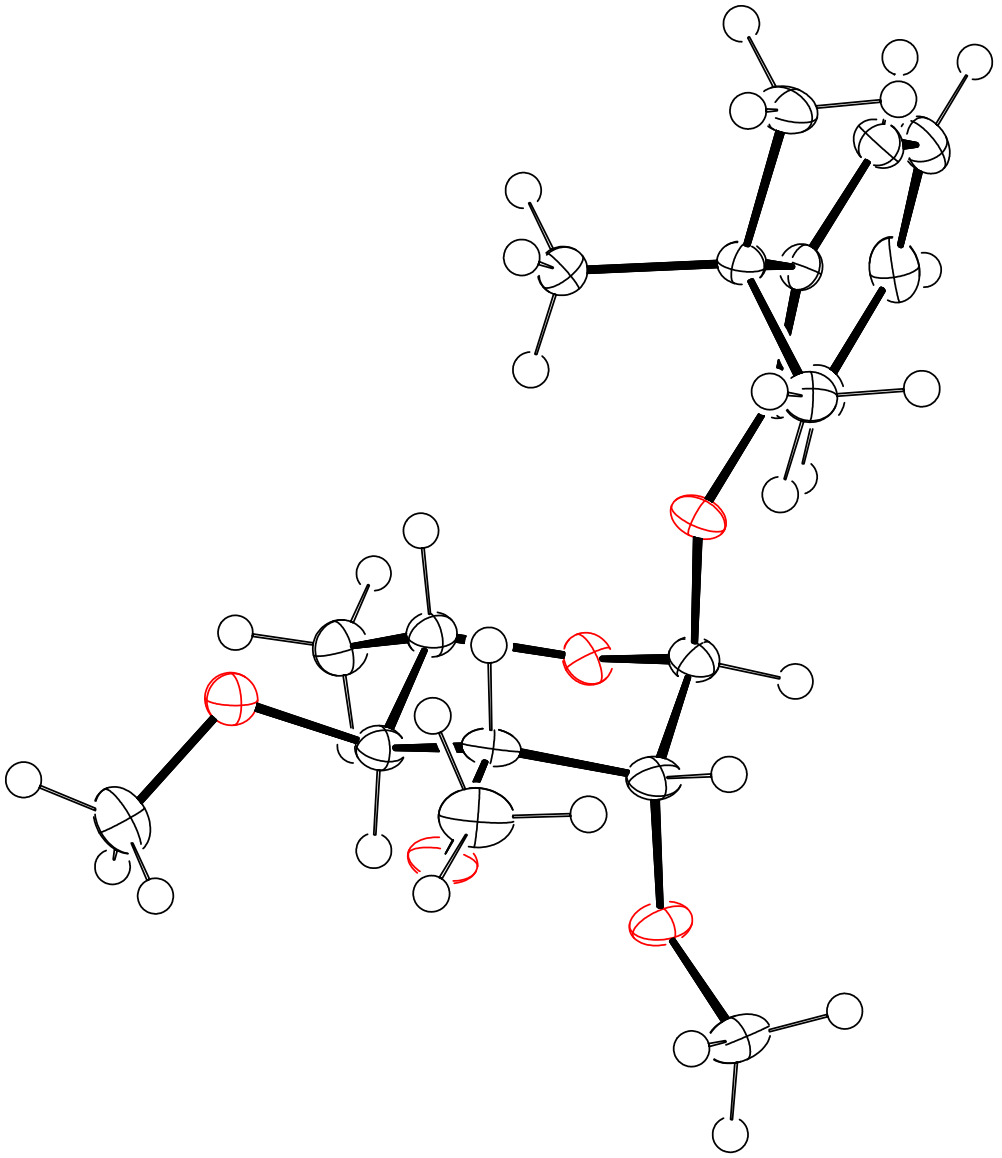


Figure S108. ORTEP of **4a** with ellipsoids shown at 50%.

Table S4. Crystal data and structure refinement for **5a**.

Empirical formula	$C_{15}H_{20}Cl_2O_5$	
Formula weight	351.21	
Temperature	99.97(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.2374(2) Å	α = 64.328(2)°
	b = 12.4665(2) Å	β = 88.439(2)°
	c = 13.7074(3) Å	γ = 86.714(2)°
Volume	1266.59(5) $Å^3$	
Z	3	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	3.638 mm^{-1}	
F(000)	552	
Crystal size	0.327 x 0.209 x 0.1 mm^3	
Theta range for data collection	3.578 to 71.758°.	
Index ranges	-9<=h<=7, -15<=k<=15, -16<=l<=16	
Reflections collected	24899	
Independent reflections	8630 [R(int) = 0.0192]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.415	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8630 / 3 / 607	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0218, wR2 = 0.0573	
R indices (all data)	R1 = 0.0220, wR2 = 0.0574	
Absolute structure parameter	0.003(4)	
Largest diff. peak and hole	0.237 and -0.194 $e/Å^{-3}$	

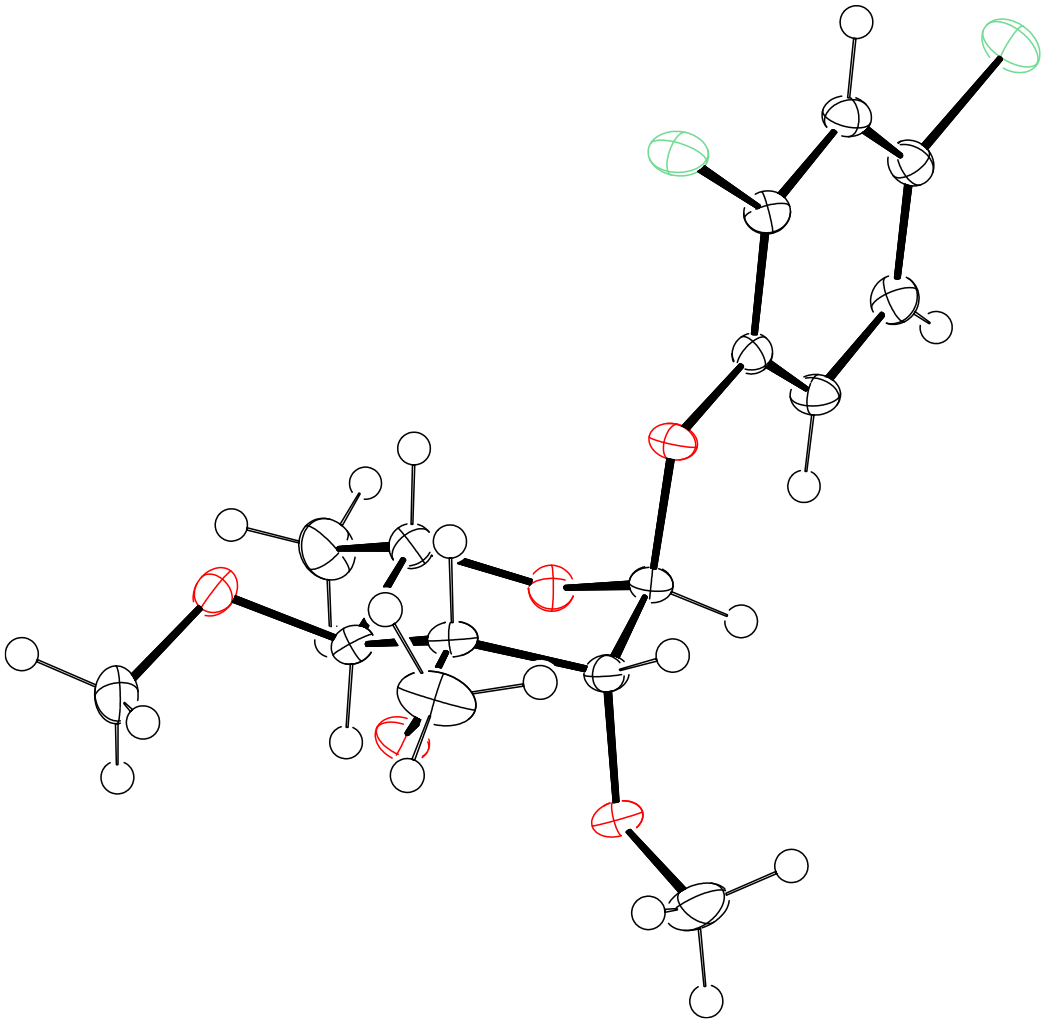


Figure S109. ORTEP of **5a** with ellipsoids shown at 50%.

Table S5. Crystal data and structure refinement for **3c**.

Empirical formula	$C_{19}H_{28}O_6$	
Formula weight	352.41	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.18301(10) Å	α = 90°
	b = 13.55501(11) Å	β = 90°
	c = 13.69931(14) Å	γ = 90°
Volume	1890.93(3) $Å^3$	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	0.751 mm^{-1}	
F(000)	760	
Crystal size	0.196 x 0.153 x 0.112 mm^3	
Theta range for data collection	4.589 to 71.822°.	
Index ranges	-12<=h<=11, -16<=k<=16, -16<=l<=15	
Reflections collected	12760	
Independent reflections	3659 [R(int) = 0.0294]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.740	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3659 / 0 / 232	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0666	
R indices (all data)	R1 = 0.0284, wR2 = 0.0679	
Absolute structure parameter	0.10(8)	
Largest diff. peak and hole	0.176 and -0.183 $e/Å^{-3}$	

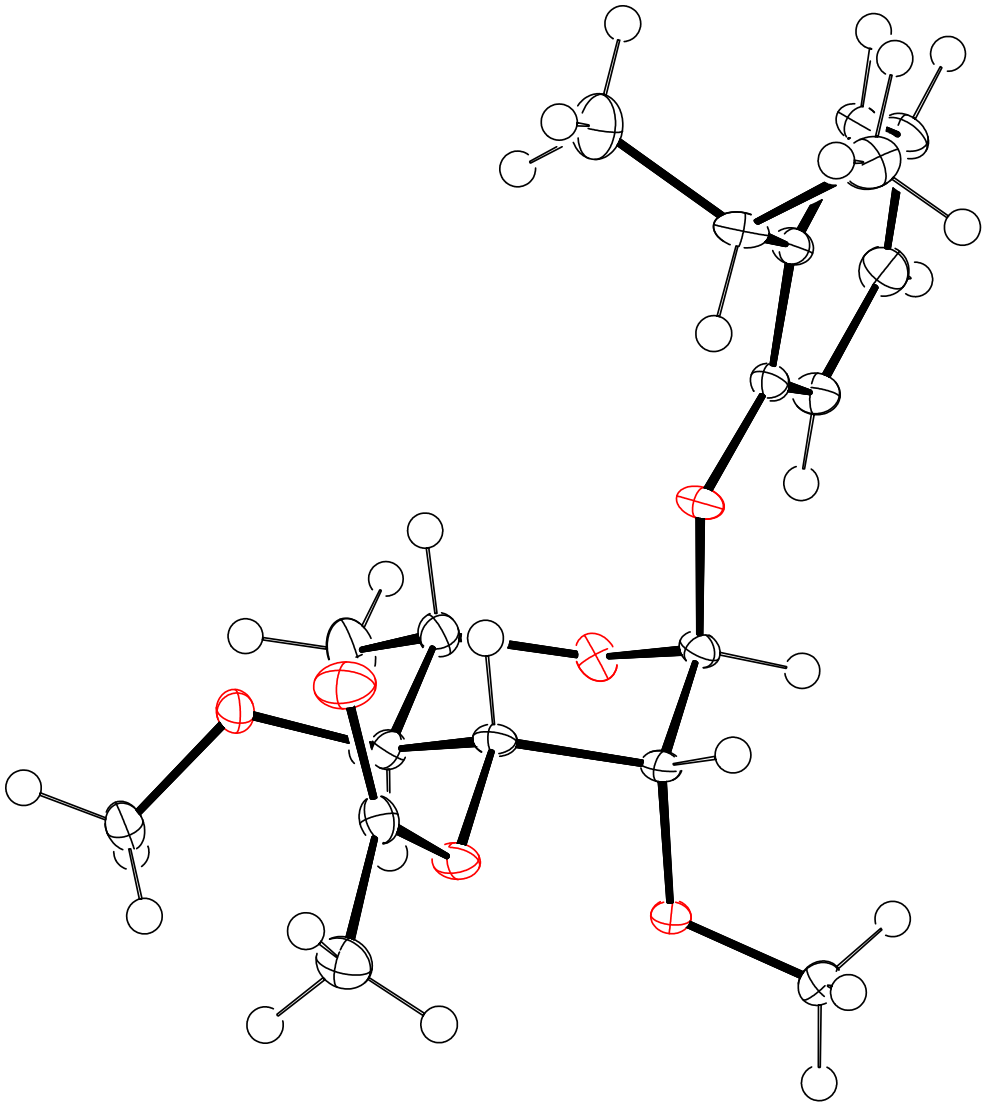


Figure S110. ORTEP of **3c** with ellipsoids shown at 50%.

Table S6. Crystal data and structure refinement for **8a**.

Empirical formula	$C_{25}H_{44}O_6Si$	
Formula weight	468.69	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.7564(2) Å	α = 90°
	b = 13.7188(4) Å	β = 97.463(3)°
	c = 25.4041(8) Å	γ = 90°
Volume	2680.33(14) $Å^3$	
Z	4	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	1.055 mm^{-1}	
F(000)	1024	
Crystal size	0.282 x 0.228 x 0.223 mm^3	
Theta range for data collection	3.509 to 73.545°.	
Index ranges	-9<=h<=9, -17<=k<=16, -31<=l<=31	
Reflections collected	25888	
Independent reflections	9802 [R(int) = 0.0245]	
Completeness to theta = 67.684°	95.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.97891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9802 / 1 / 597	
Goodness-of-fit on F^2	1.126	
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1505	
R indices (all data)	R1 = 0.0555, wR2 = 0.1523	
Absolute structure parameter	0.020(14)	
Largest diff. peak and hole	1.092 and -0.521 $e/Å^{-3}$	

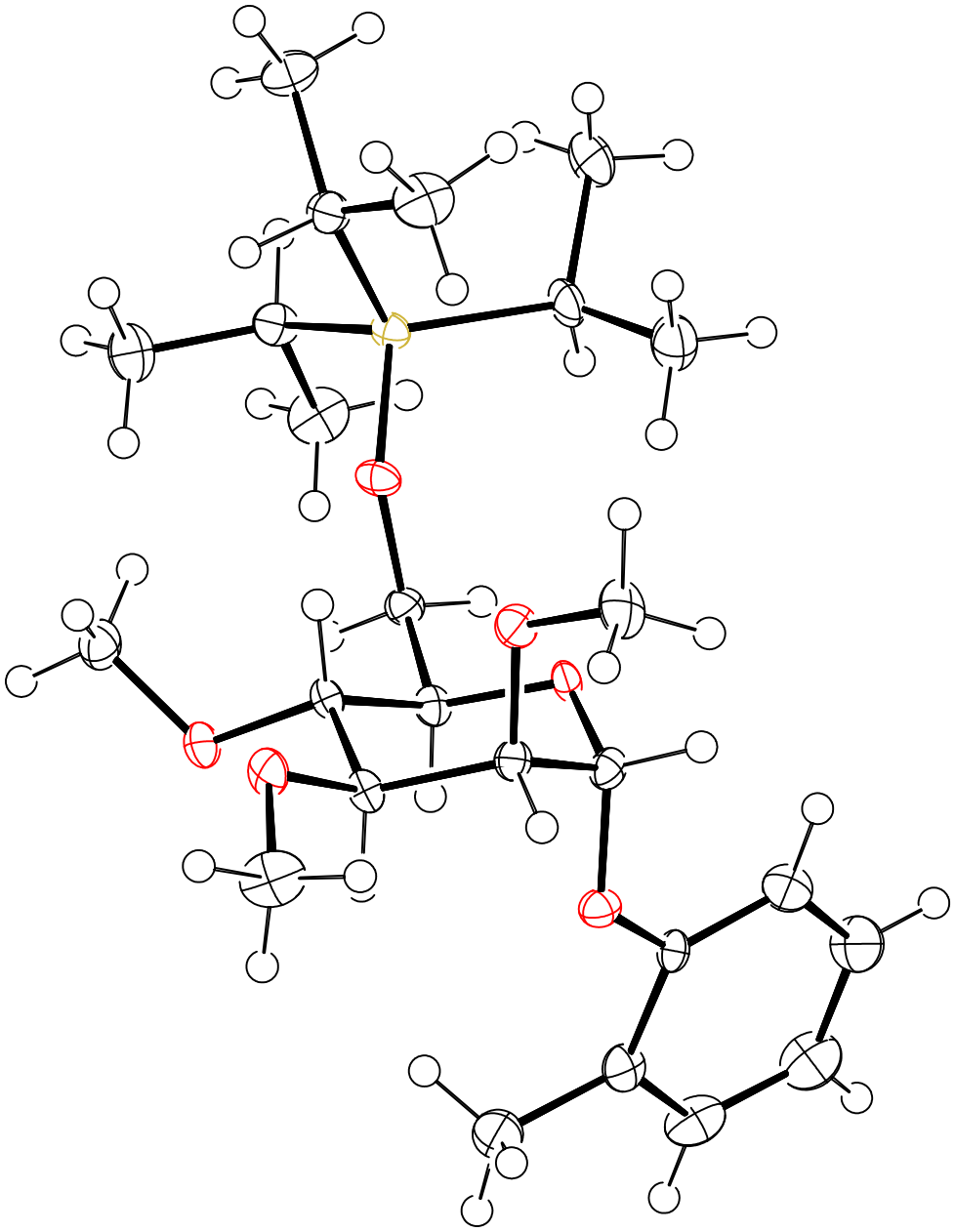


Figure S111. ORTEP of **8a** with ellipsoids shown at 50%.

VI. References

(1) Zhang, Y.; Mueller, B. R. J.; Schley, N. D., Formation of a Delocalized Iridium Benzylidene with Azaquinone Methide Character via Alkoxycarbene Cleavage. Organometallics 2018, 37 (12), 1825-1828.
(2) Bahr, S. R.; Boudjouk, P., Stable silylnitrilium ions. *J. Am. Chem. Soc.* **1993**, 115 (11), 4514-4519.
(3) Straus, D. A.; Zhang, C.; Tilley, T. D., Trityl tetraphenylborate as a reagent in organometallic chemistry. *Journal of Organometallic Chemistry* **1989,** *369* (2), C13-C17.
(4) Xu, Y.; Zhang, Q.; Xiao, Y.; Wu, P.; Chen, W.; Song, Z.; Xiao, X.; Meng, L.; Zeng, J.; Wan, Q., Practical synthesis of latent disarmed S-2-(2-propylthio)benzyl glycosides for interrupted Pummerer reaction mediated glycosylation. *Tet. Lett.* **2017**, 58 (24). 2381-2384.
(5) Šardzik, R.; Noble, G. T.; Weissenborn, M. J.; Martin, A.; Webb, S. J.; Flitsch, S. L., Preparation of aminoethyl glycosides for glycoconjugation. *J. Org. Chem.* **2010**, 6, 699-703
(6) Kalas, V.; Hibbing, M. E.; Maddirala, A. R.; Chugani, R.; Pinkner, J. S.; Mydock-McGrane, L. K.; Conover, M. S.; Janetka, J. W.; Hultgren, S. J., Structure-based discovery of glycomimetic FmlH ligands as inhibitors of bacterial adhesion during urinary tract infection. *Proceedings of the National Academy of Sciences* **2018**, *115*, E2819-E2828.
(7) Fast, C. D.; Jones, C. A. H.; Schley, N. D., Selectivity and Mechanism of Iridium-Catalyzed Cyclohexyl Methyl Ether Cleavage. *ACS Catalysis* **2020**, *10*, 6450-6456.
(8) Luo, X. L.; Crabtree, R. H., Homogeneous catalysis of silane alcoholysis via nucleophilic attack by the alcohol on an Ir(η^2-HSiR$_3$) intermediate catalyzed by [IrH$_2$S$_2$(PPh$_3$)$_2$]SbF$_6$ (S = solvent). *J. Am. Chem. Soc.* **1989**, *111*, 2527-2535.
(9) Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L.

Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(10) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R., Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics* **2012**, *4*, 17.

(11) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

(12) Sheldrick, G., A short history of SHELX. *Acta Crystallographica Section A* **2008**, *64*, 112-122.