# Stereoselective Preparation of β-C-Aryl/Vinyl Glucosides via Nickel-Catalyzed Reductive Couplings

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# I. Experimental Section

## Part 1. General Information

### 1. Chemicals and Reagents

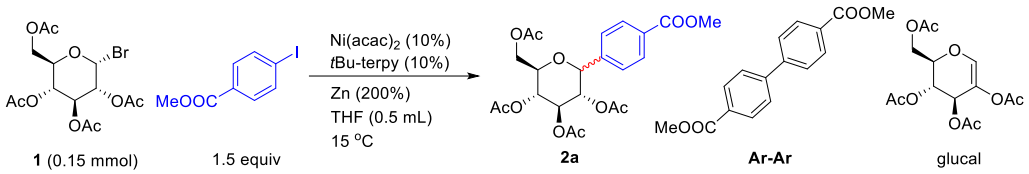
All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glovebox techniques. THF was distilled from Na/benzophenone ketyl prior to use under $N_2$. Deuterated solvents were used as received. $Ni(acac)_2$ (Alfa Aesar), $Ni(COD)_2$ (Strem), $Ni(ClO_4)_2$ (Alfa Aesar) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Anhydrous $MgCl_2$ (Alfa Aesar) was purchased and used directly. Acetobromo-α-D-glucose (1% $CaCO_3$) and acetobromo-α-D-galactose (1% $CaCO_3$) were purified by passing through a silica column prior to use. The glycosyl bromide and chlorides were synthesized according to the literature procdures.[1,2] 3,4,6-Tri-Oacetyl-2-deoxy-2-phthalimido-D-glucopyranosyl bromide was prepared from D-(+)-glucosamine hydrochloride.[3] 3,4,6-Tri-O-acetyl-2-O-allyl-α-D-glucopyranosyl bromide was prepared according to the reported procedures.[4] Vinyl bromide was prepared according to the reported procedures.[5-10] Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

### 2. Physical method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz or 600 MHz spectrometer. $^1H$ NMR and $^{13}C$ NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in $^1H$ NMR and $^{13}C$ NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

## Part 2. Control Experiments and Optimization

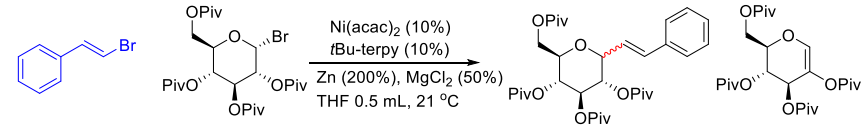
**Table S1**. Variations from the standard conditions A (method A) for the formation of **2a**.[a,b]




| Entry | Variation from the standard method A | Yield for **2a**[a] | Glucal[a] | Ar-Ar[a] |
|---|---|---|---|---|
| 1 | none | 85% (1:12)[b] | 13% | trace |
| 2 | $Ni(ClO_4)\cdot 6H_2O$ | 32% (1:11) | 40% | 10% |
| 3 | $MgCl_2$ (100%) | 80% (1:3) | 16% | 20% |
| 4 | DMA | trace | 90% | 80% |
| 5 | w/o $Ni(acac)_2$, w/o *t*Bu-Terpy | N.D. | 80% | N.D. |
| 6 | dtbBpy | trace | trace | trace |
| 7 | 0 °C | N.D. | trace | trace |
| 8 | 25 °C | 66% (1:12) | 26% | 10% |
| 9 | 21 °C | 74% (1:12) | 23% | trace |
| 10 [c] | $Ni(cod)_2$, w/o $MgCl_2$ | 55% (1:17) | 50% | N.A. |

[a] Yield determined by $^1$H NMR spectroscopy using 2,5-dimethylfuran as the internal reference. [b] Isolated yields. [c] 1-iodo-4-methoxybenzene instead, and 100 mol % aryl iodides, 150 mol % **1** and 15 mol % $MgCl_2$ were used for electron-rich aryl halides.

**Table S2**. Variations from the standard conditions B (method B) for the formation of **9a**.[a,b]




| Entry | Variation from the standard method B | Yield for **9a**[a] | Glucal[a] |
|---|---|---|---|
| 1 | none | 65% (1:8)[b] | 50% |
| 2 | **7** (100%), *E*-**8** (200%) | 38% (1:8) | 40% |
| 3 | w/o $MgCl_2$ | N.D. | trace |
| 4 | $MgCl_2$ (30%) | 62% (1:9) | 50% |
| 5 | $MgCl_2$ (100%) | 50% (1:5) | 60% |
| 6 | 0 °C | 35% (1:10) | 20% |
| 7 | **1** instead of **7** | 78% (1:3)[b] | 50% |

[a] Yield determined by $^1$H NMR spectroscopy using 2,5-dimethylfuran as the internal reference. [b] Isolated yields.

## Part 3. Mechanistic Considerations

(1) Details of the reactions of **1** with the Ni(II) complexes **15**.

Stoichiometric reaction of **15** with **1** was examined. No appreciable **2a** was obtained for the reaction of **15** and **1**, regardless of the presence of $MgCl_2$. With Zn, **2a** was obtained in 55% yield with high β-selectivity.

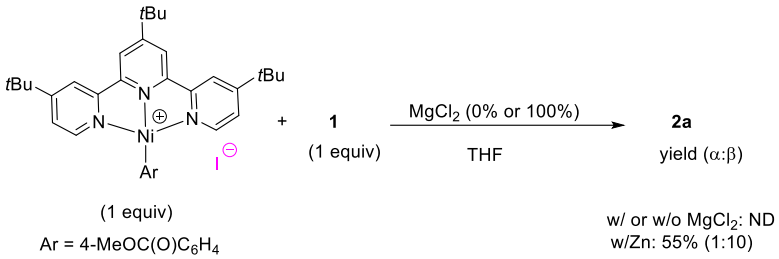
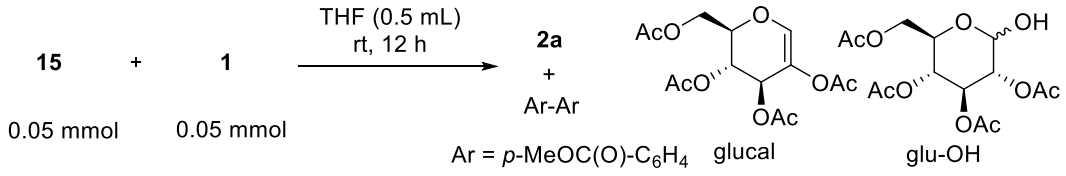
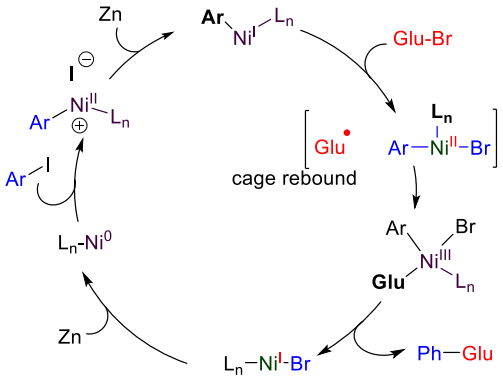



**Table S3**. Equimolar reaction of **15** with **1**.




| Entry | Variation | Yield for **2a** | Glucal | **1** | Glu-OH |
|---|---|---|---|---|---|
| 1 | none | not detected | NA | 55% | 35% |
| 2 | Zn (2 equiv) | 55% (1/10) | 40% | NA | NA |
| 3 | $MgCl_2$ (1equiv) | trace | not detected | 60% | 30% |

(2) Proposed Catalytic Cycles



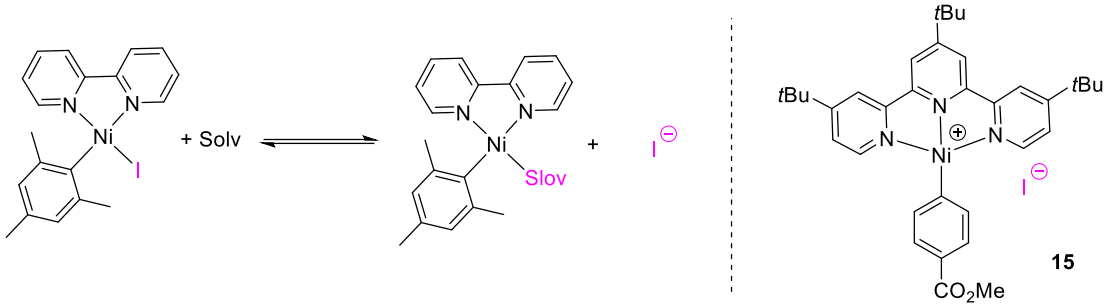

Proposed Catalytic Cycle via double oxidative addtion mechanism

**Scheme S1**. Proposed reaction pathways: double oxidative addition.

(3) Synthesis of complex **15**.

The dissociation rate for an [(bpy)Ni(Mes)I] in $CH_3CN$ was determined to be 0.176 $M^{-1}S^{-1}$, but its chloride analog undergoes very slow dissociative solvolysis ($k$ = 5.18 *$10^{-5}$ $M^{-1}S^{-1}$) (see: *Inorg.*

*Chem*. **2008**, *47*, 11324). Based on the $^1$H NMR analysis, it is reasonable to conclude that complex **15** exists as cationic form in the polar solvents such as THF.




**Scheme S2**. Proposed deionization of a Ni-I complex.

Procedure for the synthesis of complex **15**: In a glove box, a suspension of Ni(cod)$_2$ (330.4 mg, 1.20 mmol, 100 mol %) in 8 mL of dry THF was stirred for 1 minute in a 50 mL of a flame-dried Schlenk tube, at which point a solution of *t*Bu-Terpy (481.2 mg, 1.20 mmol, 100 mol %) in 8 mL of dry THF was added dropwise. The resulting mixture stir for 2 hours at ambient temperature. A solution of methyl 4-iodobenzoate (314.4 mg, 1.20 mmol, 100 mol %) in 4 mL of dry THF was added via syringe. The resultant mixture was allowed to stir for 2 hours. The solvent was removed under vacuum, and the residue was filtrated with a fritted funnel, and washed with pentane (6×3 mL). The title compound was obtained in 68% yield (589.1 mg, 0.81 mmol) as a green solid, which was stored in the glove box at -30 °C.

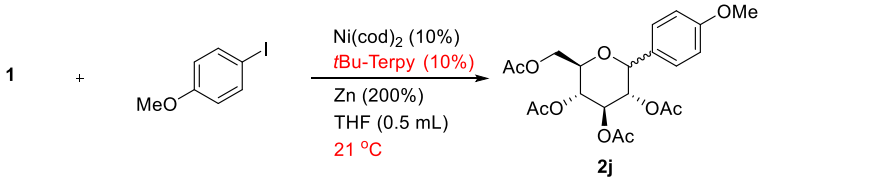
**$^1$H NMR** (500 MHz, Acetone) δ = 8.86 (s, 1H), 8.83 (s, 1H), 8.19 (d, *J* = 6.3 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 4.6 Hz, 1H), 7.46 (d, *J* = 5.9 Hz, 1H), 3.93 (s, 2H), 1.60 (s, 4H), 1.46 (s, 9H).

**$^{13}$C NMR** (126 MHz, Acetone) δ = 169.50, 168.99, 167.80, 158.55, 154.92, 153.51, 138.01, 128.50, 128.01, 126.22, 123.10, 121.91, 52.72, 38.58, 37.46, 31.71, 31.14.

**HRMS** (ESI) ([$C_{35}H_{42}IN_3NiO_2$– $I^-$]$^+$): m/z 594.2625; found: 594.2635.

(4) Role of $MgCl_2$: Control experiments for the reactions without $MgCl_2$

In the catalytic reaction of **1** with methyl 4-bromobenzoate, a mixture of Ni(acac)$_2$/$MgCl_2$ generated identical results to Ni(COD)$_2$ without $MgCl_2$. **2j** was obtained in 55% yield with a high β-selectivity when *t*Bu-Terpy was used as the ligand. Addition of 15% of $MgCl_2$ only boosted the yield by 10% at 21 °C.

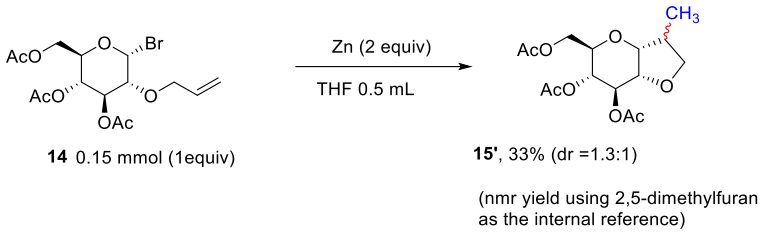



w/o $MgCl_2$: 55% (1:17)
Ni(acac)$_2$ w/ $MgCl_2$ (15%): 66% (1:20)
Ni(acac)$_2$ w/ $MgCl_2$ (15%), 15 °C: 78% (1:22)

**Scheme S3**. Coupling of **1** with Ar-X using Ni(cod)$_2$.

(5) Zn reduction of **14**:

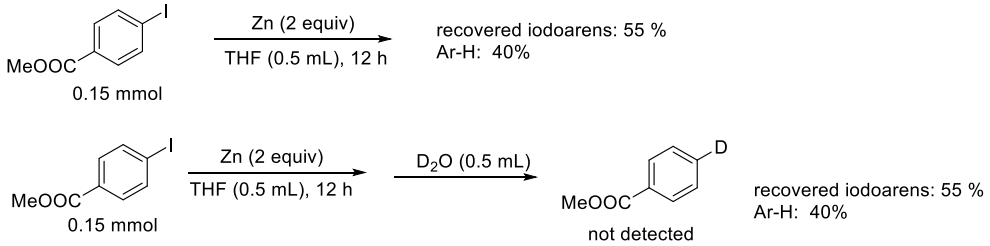
Reaction of **14** in the presence of Zn produced **15**' in 33% yield (NMR yield), indicating Zn alone can induce glucosyl radical formation, although low efficiency was observed.




**Scheme S4**. Reduction of **14** with Zn.

(6) Exclusion of organozinc mechanisms

To identify whether an in situ organozinc/Negishi mechanism is involved in the coupling using *t*Bu-Terpy as the ligand, 4-methyl iodobenzoate was treated with Zn in THF at room temperature. After 12 hours, 55% of the iodo substrate was recovered along with ~40% of its conversion into deiodo hydroarene. A parallel experiment by quenching with $D_2O$ did not produce detectable deuterated arene. These results indicated that formation of organozinc in situ is less likely. We reason that an aryl radical may form under the reduction conditions, which abstract H from the solvent to afford Ar-H.




**Scheme S5**. Verification of organozinc mechanisms.

## Part 4. Reductive coupling of vinyl bromide or aryl halides and glycosyl Halides

*1. General procedure*

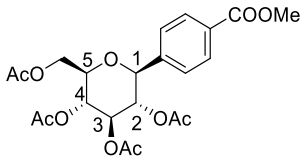
(1) Method A: To a flame-dried Schlenk tube was charged aryl iodide (0.225 mmol, 150 mol %, if solid), glycosyl bromide (0.15 mmol, 100 mol %), Zn (20 mg, 0.30 mmol, 200 mol %), $Ni(acac)_2$ (3.8 mg, 0.015 mmol, 10 mol %), 4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine (6.0 mg, 0.12 mmol, 10 mol %). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, aryl iodide (0.225 mmol, 150 mol %, if liquid) was added via a syringe followed by addition of THF (0.5 mL) via a syringe. The reaction mixture was allowed to stir for 12 h under a $N_2$ atmosphere at 15 $^oC$, and was directly loaded onto a silica column without work-up. The residue was rinsed with small amount of DCM or the eluent prior to column chromatography, with which the product was isolated.

(2) Method B: To a flame-dried Schlenk tube was charged vinyl bromide (0.15 mmol, 100 mol %, if solid), glycosyl bromide (0.195 mmol, 130 mol %), Zn (20 mg, 0.30 mmol, 200 mol %), $Ni(acac)_2$ (3.8 mg, 0.015 mmol, 10 mol %), 4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine (6.0 mg, 0.12 mmol, 10 mol %), $MgCl_2$ (7.2 mg, 0.075 mmol, 50 mol %). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, vinyl bromide (0.15 mmol, 100 mol %, if liquid) was added via a syringe followed by addition of THF (0.5 mL) via a syringe. The reaction mixture was allowed to stir for 12 h under a $N_2$ atmosphere at 21 $^oC$, and was directly loaded onto a silica column without work-up. The residue was rinsed with small amount of DCM or the eluent prior to column chromatography, with which the product was isolated.

*Note: Throughout the paper, a crude reaction mixture was subjected to quick flash silica column chromatography to afford a new mixture containing both α and β anomers and many other impurities. The α/β ratios were determined by analysis of the $^1H$ NMR spectra of the new mixture, based on the ratios of the characteristic peaks of the two anomers.*

*2. <u>Details of the characterization data for new compounds</u>*

**(*2R,3R,4R,5S,6S*)-2-(Acetoxymethyl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3, 4,5-triyl triacetate (2a).**[11]




**2a**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), methyl 4-iodobenzoate (59.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:12 α to β anomers based on NMR) as a white solid (59.4 mg, 0.127 mmol, 85% yield). Spectroscopic data matches a previously reported synthesis.

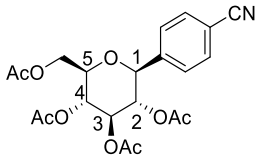
**<u>$^1$H NMR</u>** (600 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 5.30 (t, J = 9.5 Hz, 1H, *H*$_3$), 5.20 (t, J = 9.7 Hz, 1H, *H*$_4$), 5.05 (t, J = 9.7 Hz, 1H, *H*$_2$), 4.43 (d, J = 9.8 Hz, 1H, *H*$_1$), 4.26 (dd, J = 12.4, 4.8 Hz, 1H), 4.13 (dd, J = 12.4, 2.1 Hz, 1H), 3.86 (s, 3H), 3.82 (ddd, J = 10.0, 4.7, 2.1 Hz, 1H, *H*$_5$), 2.05 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.77 (s, 3H).

**<u>$^{13}$C NMR</u>** (151 MHz, $CDCl_3$) δ = 170.73, 170.36, 169.53, 168.78, 166.61, 141.25, 130.60, 129.71, 127.09, 79.62, 76.20, 74.06, 72.56, 68.46, 62.26, 52.21, 20.79, 20.65, 20.38.

**<u>M.p</u>**. 124-126 ºC.

**<u>[α]$_D^{20}$</u>** = -9.1 (*c* = 0.48, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-(4-cyanophenyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2b).**[11]




**2b**

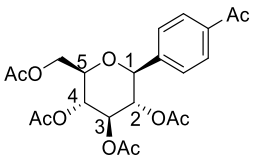
This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), 4-iodobenzonitrile (51.5 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:10 α to β anomers based on NMR) as a white solid (48.7 mg, 0.112 mmol, 75% yield). Spectroscopic data matches a previously reported synthesis.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.62 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.31 (t, J = 9.5 Hz, 1H), 5.20 (t, J = 9.7 Hz, 1H), 5.03 (t, J = 9.7 Hz, 1H), 4.44 (d, J = 9.9 Hz, 1H), 4.27 (dd, J = 12.5, 4.9 Hz, 1H), 4.14 (dd, J = 12.4, 2.0 Hz, 1H), 3.83 (ddd, J = 10.0, 4.8, 2.1 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.68, 170.31, 169.50, 168.76, 141.55, 132.29, 127.82, 118.41, 112.84, 79.25, 76.30, 73.91, 72.47, 68.35, 62.19, 20.80, 20.66, 20.40.

**$[\alpha]_D^{20}$** = -20.2 (*c* = 1.58, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-(4-acetylphenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2c).**



**2c**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), 1-(4-iodophenyl)ethan-1-one (55.3 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:10 α to β anomers based on NMR) as a white solid (54.7 mg, 0.121 mmol, 81% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.91 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 5.33 (t, J = 9.4 Hz, 1H, $H_3$), 5.22 (t, J = 9.7 Hz, 1H, $H_4$), 5.09 (t, J = 9.7 Hz, 1H, $H_2$), 4.45 (d, J = 9.8 Hz, 1H, $H_1$), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 2.1 Hz, 1H), 3.84 (ddd, J = 10.0, 4.8, 2.2 Hz, 1H, $H_5$), 2.57 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H).

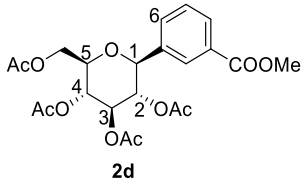
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 197.66, 170.77, 170.40, 169.58, 168.88, 141.46, 137.46, 128.52, 127.37, 79.64, 76.28, 74.12, 72.58, 68.52, 62.32, 26.74, 20.85, 20.71, 20.46.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{26}NaO_{10}^+$): m/z 473.1418; found: 473.1409.

**M.p**. 96-98 ºC.

**$[\alpha]_D^{20}$** = -19.4 (*c* = 0.58, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-(3-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3, 4,5-triyl triacetate (2d).**[11]



**2d**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), methyl 3-iodobenzoate (59.2 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a white solid (35.6 mg, 0.076 mmol, 51% yield). Spectroscopic data matches a previously reported synthesis.

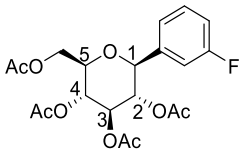
**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.98 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 5.33 (t, J = 9.4 Hz, 1H, *H*$_3$), 5.23 (t, J = 9.7 Hz, 1H, *H*$_4$), 5.10 (t, J = 9.6 Hz, 1H, *H*$_2$), 4.45 (d, J = 9.8 Hz, 1H, *H*$_1$), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.16 (dd, J = 12.5, 2.0 Hz, 1H), 3.90 (s, 3H), 3.84 (ddd, J = 10.0, 4.8, 2.2 Hz, 1H, *H*$_5$), 2.08 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H)

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.84, 170.45, 169.60, 168.98, 166.69, 136.90, 131.40, 130.36, 130.14, 128.81, 128.57, 79.72, 76.30, 74.17, 72.68, 68.59, 62.38, 52.33, 20.89, 20.75, 20.48.

**HRMS** (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_{11}^+$): m/z 489.1367; found: 489.1359.

**M.p**. 126-128 ºC.

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-(3-fluorophenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2e).**



**2e**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide ((62.0 mg, 0.15 mmol, 100 mol %), 1-fluoro-3-iodobenzene (50.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a white solid (44.7 mg, 0.105 mmol, 70% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.30 (td, J = 7.9, 5.9 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.06 (d, J = 9.4 Hz, 1H), 7.00 (td, J = 8.4, 2.0 Hz, 1H), 5.32 (t, J = 9.4 Hz, 1H, *H*$_3$), 5.22 (t, J = 9.7 Hz, 1H, *H*$_4$), 5.07 (t, J = 9.7 Hz, 1H, *H*$_2$), 4.39 (d, J = 9.8 Hz, 1H, *H*$_1$), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.16

(dd, J = 12.4, 2.1 Hz, 1H), 3.83 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H, $H_5$), 2.08 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.83 (s, 3H).

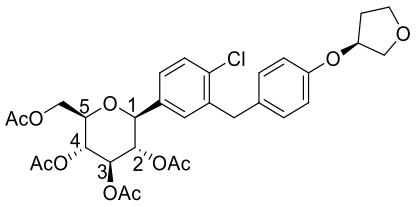
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.86, 170.49, 169.61, 168.94, 162.75 (d, J = 246.7 Hz), 138.90 (d, J = 7.4 Hz), 130.11 (d, J = 8.1 Hz), 122.77 (d, J = 2.8 Hz), 115.97 (d, J = 21.1 Hz), 114.24 (d, J = 22.4 Hz), 79.54, 76.26, 74.18, 72.69, 68.54, 62.34, 20.89, 20.76, 20.75, 20.50.

**$^{19}$F NMR** (565 MHz, CDCl3) δ = -112.37 – -112.47 (m).

**M.p**. 113-115 ºC.

**[α]$_D^{20}$** = -13.6 (*c* = 0.68, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-(4-chloro-3-(4-(((S)-tetrahydrofuran-3-yl)oxy)benzyl) phenyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2f).**



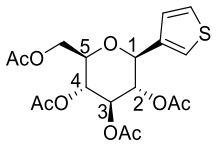
**2f**

This compound was prepared according to the *Method **A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*S*)-3-(4-(2-chloro-5-iodobenzyl)phenoxy)tetrahydrofuran (93.1 mg, 0.25 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a white solid (60.3 mg, 0.097 mmol, 65% yield).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ = 7.34 (d, J = 8.3 Hz, 1H), 7.18 (dd, J = 8.2, 1.6 Hz, 1H), 7.08 (d, J = 1.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 5.28 (t, J = 9.4 Hz, 1H), 5.19 (t, J = 9.7 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.88 (dd, J = 5.6, 4.5 Hz, 1H), 4.31 (d, J = 9.8 Hz, 1H), 4.25 (dd, J = 12.4, 4.7 Hz, 1H), 4.13 (dd, J = 12.3, 1.7 Hz, 1H), 4.04 (d, J = 15.5 Hz, 1H), 3.99 – 3.93 (m, 4H), 3.88 (td, J = 8.3, 4.3 Hz, 1H), 3.79 (ddd, J = 9.8, 4.4, 1.9 Hz, 1H), 2.20 – 2.10 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.70 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.82, 170.46, 169.61, 168.86, 156.03, 139.01, 135.25, 134.71, 131.65, 130.02, 129.94, 129.88, 126.21, 115.47, 79.56, 77.34, 76.21, 74.18, 73.22, 72.62, 68.55, 67.29, 62.37, 38.35, 33.09, 20.88, 20.75, 20.41.

***(2R,3R,4R,5S,6S)*-2-(acetoxymethyl)-6-(thiophen-3-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2g).**[11]



**2g**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 3-iodothiophene (31.5 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:35 α to β based on $^1H$ NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.59 ppm for α and 3.81 ppm for β) as a white solid (32.9 mg, 0.079 mmol, 53% yield). Spectroscopic data matches a previously reported synthesis.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.31 – 7.27 (m, 2H), 7.08 (dd, J = 4.9, 1.2 Hz, 1H), 5.30 (t, J = 9.4 Hz, 1H, $H_3$), 5.21 (t, J = 9.7 Hz, 1H, $H_4$), 5.16 (t, J = 9.7 Hz, 1H, $H_2$), 4.54 (d, J = 9.9 Hz, 1H, $H_1$), 4.27 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 2.2 Hz, 1H), 3.81 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H, $H_5$), 2.08 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H)

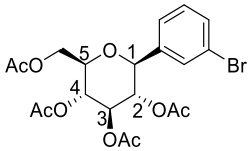
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.88, 170.52, 169.63, 169.14, 137.34, 126.47, 126.12, 123.76, 76.27, 76.19, 74.32, 72.34, 68.63, 62.41, 20.91, 20.79, 20.77, 20.59.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{23}O_9S^+$): m/z 415.1057; found: 415.1096.

**M.p**. 147-148 °C.

**$[\alpha]_D^{20}$** = -8.4 (*c* = 0.31, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-(3-bromophenyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2h).**[11]



**2h**

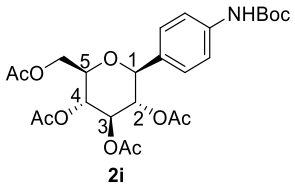
This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 1-bromo-3-iodobenzene (42.3 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:21 α to β anomers based on NMR) as a white solid (60.6 mg, 0.124 mmol, 83% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.45 (s, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 5.29 (t, J = 9.5 Hz, 1H), 5.18 (t, J = 9.7 Hz, 1H), 5.03 (t, J = 9.6 Hz, 1H), 4.34 (d, J = 9.8 Hz, 1H), 4.25 (dd, J = 12.5, 4.8 Hz, 1H), 4.13 (dd, J = 12.4, 2.1 Hz, 1H), 3.80 (ddd, J = 10.2, 5.0, 2.0 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.82 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.81, 170.43, 169.56, 168.91, 138.62, 132.03, 130.31, 130.15, 125.56, 122.44, 79.37, 76.25, 74.08, 72.63, 68.47, 62.31, 20.88, 20.73, 20.72, 20.50.

**$[\alpha]_D^{20}$** = -16.7 (*c* = 1.76, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-(4-((tert-butoxycarbonyl)amino)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2i).**



**2i**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), *tert*-butyl (4-iodophenyl) carbamate (71.7 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:17 α to β anomers based on NMR) as a white solid (56.4 mg, 0.108 mmol, 72% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.33 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.65 (s, 1H), 5.30 (t, J = 9.4 Hz, 1H, $H_3$), 5.20 (t, J = 9.7 Hz, 1H, $H_4$), 5.11 (t, J = 9.7 Hz, 1H, $H_2$), 4.33 (d, J = 9.8 Hz, 1H, $H_1$), 4.26 (dd, J = 12.4, 4.8 Hz, 1H), 4.13 (dd, J = 12.4, 2.0 Hz, 1H), 3.81 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H, $H_5$) , 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H), 1.49 (s, 9H).

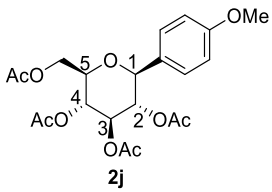
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.88, 170.50, 169.65, 169.09, 152.65, 139.10, 130.57, 128.02, 118.16, 79.97, 76.14, 74.37, 72.60, 68.69, 62.46, 28.40, 20.87, 20.76, 20.74, 20.54.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{25}H_{34}NO_{11}^+$): m/z 524.2126; found: 524.2109.

**M.p**. 151-153 ºC.

**$[\alpha]_D^{20}$** = -12.9 (*c* = 0.52, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-(4-methoxyphenyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2j).**[11]



**2j**

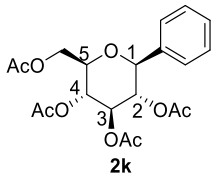
This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 1-iodo-4-methoxybenzene (35.1 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:22 α to β anomers based on NMR) as a white solid (51.2 mg, 0.117 mmol, 78% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.25 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.30 (t, J = 9.4 Hz, 1H), 5.21 (t, J = 9.7 Hz, 1H), 5.13 (t, J = 9.7 Hz, 1H), 4.34 (d, J = 9.8 Hz, 1H), 4.26 (dd, J = 12.4, 4.7 Hz, 1H), 4.13 (dd, J = 12.3, 2.0 Hz, 1H), 3.81 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H), 3.77 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.79 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.86, 170.50, 169.63, 169.04, 160.03, 128.62, 128.33, 113.94, 80.05, 76.14, 74.40, 72.61, 68.70, 62.47, 55.30, 20.88, 20.78, 20.75, 20.52.

**$[\alpha]_D^{20}$** = -8.9 (*c* = 0.74, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-phenyltetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2k).**[11]



**2k**

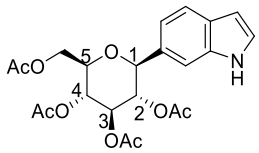
This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), iodobenzene (45.9 mg, 0.225 mmol, 150 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a white solid (39.8 mg, 0.097 mmol, 65% yield). Spectroscopic data matches a previously reported synthesis.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.36 – 7.30 (m, 5H), 5.33 (t, J = 9.4 Hz, 1H, $H_3$), 5.23 (t, J = 9.7 Hz, 1H, $H_4$), 5.14 (t, J = 9.7 Hz, 1H, $H_2$), 4.39 (d, J = 9.8 Hz, 1H, $H_1$), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.16 (dd, J = 12.4, 2.1 Hz, 1H), 3.84 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H, $H_5$), 2.08 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.79 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.90, 170.55, 169.67, 169.01, 136.33, 129.06, 128.58, 127.27, 80.38, 76.25, 74.37, 72.76, 68.71, 62.47, 20.91, 20.80, 20.78, 20.51.

**M.p**. 153-155 ºC.

***(2R,3R,4R,5S,6S)*-2-(acetoxymethyl)-6-(1*H*-indol-6-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2l).**



**2l**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 6-iodo-*1H*-indole (36.5 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:17 α to β based on $^1$H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.69 ppm for α and 3.86 ppm for β) as a brown solid (43.5 mg, 0.097 mmol, 65% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.41 (s, 1H), 7.20 (t, J = 2.6 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 5.37 (t, J = 9.4 Hz, 1H, *$H_3$*), 5.30 – 5.24 (m, 2H, *$H_4$*, *$H_2$*), 4.52 (d, J = 9.8 Hz, 1H, *$H_1$*), 4.31 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 1.6 Hz, 1H), 3.86 (ddd, J = 9.9, 4.6, 1.8 Hz, 1H, *$H_5$*), 2.07 (s, 6H), 2.01 (s, 3H), 1.75 (s, 3H).

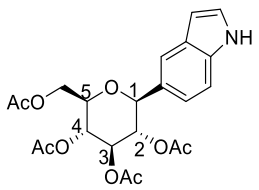
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.97, 170.61, 169.76, 169.18, 135.79, 129.91, 128.56, 125.29, 120.64, 119.60, 109.86, 102.54, 81.07, 76.20, 74.64, 72.89, 68.84, 62.63, 20.91, 20.81, 20.79, 20.57.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{26}NO_9^+$): m/z 448.1602; found: 448.1599.

**M.p**. 121-123 ºC.

**[α]$_D^{20}$** = -12.9 (*c* = 0.52, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(acetoxymethyl)-6-(*1H*-indol-5-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (2m).**



**2m**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 5-iodo-*1H*-indole (36.5 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography

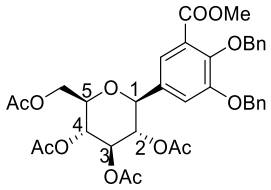
($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:17 α to β based on $^1$H NMR spectra) as a brown solid (40.1 mg, 0.09 mmol, 60% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 7.59 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.20 – 7.17 (m, 2H), 6.52 (s, 1H), 5.37 (t, J = 9.4 Hz, 1H, *H*$_3$), 5.27 (td, J = 9.6, 3.8 Hz, 2H, *H*$_{4,}$ *H*$_2$), 4.49 (d, J = 9.8 Hz, 1H, *H*$_1$), 4.30 (dd, J = 12.4, 4.7 Hz, 1H), 4.16 (dd, J = 12.4, 2.0 Hz, 1H), 3.87 (ddd, J = 9.9, 4.7, 2.2 Hz, 1H, *H*$_5$), 2.07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.74 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 171.02, 170.63, 169.76, 169.21, 136.15, 127.74, 127.53, 124.95, 121.06, 120.23, 111.36, 102.87, 81.31, 76.15, 74.65, 72.92, 68.88, 62.64, 20.93, 20.84, 20.81, 20.58.

**$[\alpha]_D^{20}$** = -4.7 (*c* = 0.42, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(acetoxymethyl)-6-(3,4-bis(benzyloxy)-5-(methoxycarbonyl)phenyl)tetra hydro-*2H*-pyran-3,4,5-triyl triacetate (2n).**[11]



**2n**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), methyl 2,3-bis(benzyloxy)-5-iodobenzoate (71.1 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:15 α to β anomers based on NMR) as a white solid (69.1 mg, 0.102 mmol, 68% yield). Spectroscopic data matches a previously reported synthesis.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.49 – 7.19 (m, 12H), 5.33 (t, J = 9.4 Hz, 1H, *H*$_3$), 5.23 (t, J = 9.7 Hz, 1H, *H*$_4$), 5.17 – 5.04 (m, 5H, *H*$_2$), 4.38 (d, J = 9.8 Hz, 1H, *H*$_1$), 4.29 (dd, J = 12.5, 4.9 Hz, 1H), 4.17 (dd, J = 12.4, 2.0 Hz, 1H), 3.87 – 3.83 (m, 1H, *H*$_5$), 3.83 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.82 (s, 3H).

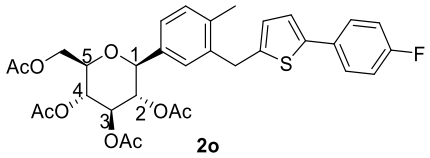
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.78, 170.40, 169.61, 169.03, 166.34, 153.19, 148.61, 137.22, 136.36, 132.09, 128.67, 128.33, 128.26, 128.06, 127.75, 126.30, 122.23, 115.79, 79.55, 76.29, 75.65, 74.15, 72.33, 71.39, 68.58, 62.43, 52.29, 20.90, 20.73, 20.72, 20.48.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{36}H_{39}O_{13}^{+)}$: m/z 679.2385; found: 679.2352.

**M.p**. 127-129 ºC.

**[α]$_D^{20}$** = +62.2 (*c* = 1.03, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-(Acetoxymethyl)-6-(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (2o).**[4]



**2o**

This compound was prepared according to the *Method **A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 2-(4-fluorophenyl)-5-(5-iodo-2-methylbenzyl)thiophene (33.3 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a white solid (44.7 mg, 0.105 mmol, 70% yield). Spectroscopic data matches a previously reported synthesis.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.47 (dd, J = 8.8, 5.2 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.07 – 6.99 (m, 3H), 6.61 (d, J = 3.6 Hz, 1H), 5.31 (t, J = 9.5 Hz, 1H, *H$_3$*), 5.23 (t, J = 9.7 Hz, 1H, *H$_4$*), 5.13 (t, J = 9.6 Hz, 1H, *H$_2$*), 4.36 (d, J = 9.8 Hz, 1H, *H$_1$*), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.3, 2.1 Hz, 1H), 4.14 – 4.05 (m, 2H), 3.82 (ddd, J = 9.9, 4.7, 2.2 Hz, 1H, *H$_5$*), 2.30 (s, 3H), 2.08 (d, J = 13.0 Hz, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.76 (s, 3H).

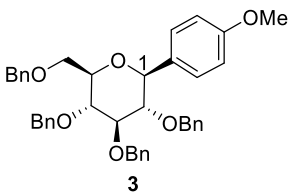
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.92, 170.56, 169.68, 169.01, 162.21 (d, J = 246.7 Hz), 143.20, 141.70, 138.20, 137.29, 134.33, 130.92, 128.64, 127.20 (d, J = 7.9 Hz), 126.09, 125.64, 122.79, 115.86 (d, J = 21.8 Hz), 80.14, 76.20, 74.45, 72.77, 68.74, 62.52, 34.12, 20.92, 20.81, 20.79, 20.56, 19.43.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{32}H_{34}FO_9S^+$): m/z 613.1902; found: 613.2017.

**M.p**. 158-160 ºC.

**[α]$_D^{20}$** = -8.8 (*c* = 0.42, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(4-methoxyphenyl)tetrahydro-*2H*-pyran (3).**[14]



**3**

This compound was prepared according to the *Method **A*** for electron-rich aryl halides using

(*2R,3R,4S,5R,6R*)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-chlorotetrahydro-*2H*-pyran (125.7 mg, 0.225 mmol, 150 mol %), 1-iodo-4-methoxybenzene (35.1 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 10% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:5 α to β anomers based on NMR) as a white solid (56.7 mg, 0.09 mmol, 60% yield);

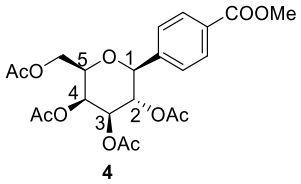
**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.43 – 7.27 (m, 15H), 7.24 – 7.18 (m, 5H), 7.00 – 6.95 (m, 2H), 6.93 (d, J = 8.7 Hz, 2 H), 4.99 – 4.87 (m, 3H), 4.68 (d, J = 4.0 Hz, 1H), 4.66 (d, J = 2.4 Hz, 1H), 4.58 (d, J = 12.2 Hz, 1H), 4.39 (d, J = 10.2 Hz, 1H), 4.23 (d, J = 9.5 Hz, 1H, $H_1$), 3.87 – 3.76 (m, 8H), 3.63 – 3.57 (m, 1H), 3.56 – 3.47 (m, 1H).

**$^{13}$C NMR** (125MHz, $CDCl_3$) δ = 159.70, 138.87, 138.51, 138.37, 137.88, 131.64, 128.97, 128.54, 128.47, 128.39, 128.35, 128.13, 127.86, 127.84, 127.78, 127.71, 127.65, 113.86, 86.83, 84.56, 81.47, 79.43, 78.50, 75.78, 75.24, 74.99, 73.59, 69.29, 55.44.

**M.p**. 84-86 ºC.

**[α]$_D^{20}$** =1.6 (*c* = 0.56, $CH_2Cl_2$).

***(2R,3S,4R,5S,6S)*-2-(acetoxymethyl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (4).**[13]



**4**

This compound was prepared according to the *Method* ***A*** using 2,3,4,6-tetra-O-acetyl-alpha-D-galactopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), methyl 4-iodobenzoate (58.9 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:20 α to β anomers based on NMR) as a colorless gummy liquid (41.9 mg, 0.09 mmol, 60% yield);

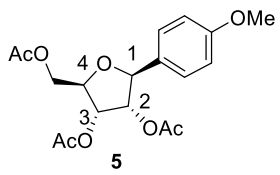
**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 5.52 (d, J = 3.1 Hz, 1H, $H_4$), 5.29 (t, J = 9.9 Hz, 1H, $H_2$), 5.18 (dd, J = 10.2, 3.3 Hz, 1H, $H_3$), 4.41 (d, J = 9.7 Hz, 1H, $H_1$), 4.22 – 4.13 (m, 2H), 4.07 (t, J = 6.5 Hz, 1H, $H_5$), 3.90 (s, 3H), 2.20 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.60, 170.41, 170.32, 168.97, 166.75, 141.63, 130.65, 129.75, 127.35, 80.34, 74.82, 72.10, 69.94, 67.84, 61.83, 52.30, 20.87, 20.83, 20.74, 20.58.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{27}O_{11}^+$): m/z 467.1548; found: 467.1537.

**[α]$_D^{20}$** = +5.5 (*c* = 0.75, $CH_2Cl_2$).

**(*2R,3R,4S,5S*)-2-(acetoxymethyl)-5-(4-methoxyphenyl)tetrahydrofuran-3,4-diyl diacetate (5).**



**5**

This compound was prepared according to the *Method* ***A*** using (*2R,3R,4R,5S*)-2-(acetoxymethyl)-5-chlorotetrahydrofuran-3,4-diyl diacetate (66.1 mg, 0.225 mmol, 150 mol %), 1-iodo-4-methoxybenzene (35.1 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave product as a colorless gummy liquid (23.0 mg, 0.063 mmol, 42% yield);

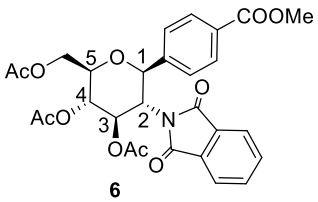
**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.31 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.28 (brs, 1H, *H$_3$*), 5.07 (brs, 1H, *H$_2$*), 4.95 (d, J = 6.7 Hz, 1H, *H$_1$*), 4.43 (dd, J = 11.3, 2.4 Hz, 1H), 4.33 – 4.25 (m, 2H), 3.80 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.79, 169.95, 169.88, 159.82, 129.98, 127.54, 114.10, 81.99, 79.83, 76.54, 71.73, 63.83, 55.40, 20.99, 20.80, 20.73.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{23}O_8^+$): m/z 367.1387; found: 367.1392.

**[α]$_D^{20}$** = -93.0 (*c* = 1.7, $CH_2Cl_2$).

**(*2R,3S,4R,5S,6S*)-2-(acetoxymethyl)-5-(1,3-dioxoisoindolin-2-yl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4-diyl diacetate (6).**



**6**

This compound was also prepared according to the standard *Method* ***A*** for electron-deficient aryl iodides using (*2R,3S,4R,5R*)-2-(acetoxymethyl)-6-bromo-5-(1,3-dioxoisoindolin-2-yl)tetrahydro-*2H*-pyran-3,4-diyl diacetate (74.7 mg, 0.15 mmol, 100 mol %), methyl 4-iodobenzoate (58.9 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:19 α to β anomers based on NMR) as a white solid (55.5 mg, 0.100 mmol, 67% yield);

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.88 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 7.3 Hz, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.37 (d, J = 8.3 Hz, 2H), 5.92 (dd, J = 10.2, 9.3 Hz, 1H, *H$_3$*), 5.41 (d,

J = 10.4 Hz, 1H, $H_1$), 5.32 (t, J = 9.6 Hz, 1H, $H_4$), 4.48 (t, J = 10.4 Hz, 1H, $H_2$), 4.34 (dd, J = 12.4, 4.6 Hz, 1H), 4.18 (dd, J = 12.3, 1.9 Hz, 1H), 4.02 (ddd, J = 10.1, 4.5, 2.0 Hz, 1H, $H_5$), 3.82 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.83 (s, 3H).

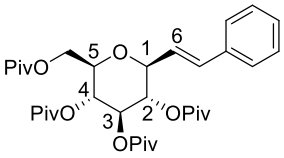
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.88, 170.26, 169.69, 168.23, 166.73, 166.60, 141.37, 134.57, 134.41, 131.26, 130.73, 130.68, 129.98, 127.07, 123.74, 123.70, 77.26, 76.40, 71.66, 69.14, 62.42, 55.93, 52.25, 20.92, 20.78, 20.55.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{28}H_{28}NO_{11}^+$): m/z 554.1657; found: 554.1642.

**M.p**. 75-77 ºC.

**[α]$_D^{20}$** = -19.3 (*c* = 0.29, $CH_2Cl_2$).

***(2R,3R,4R,5S,6S)*-2-((pivaloyloxy)methyl)-6-((*E*)-styryl)tetrahydro-*2H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate*)* (9a).**



**9a**

This compound was prepared according to the *Method* ***B*** using (*2R,3R,4S,5R,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %), (*E*)-(2-bromovinyl)benzene (27.5 mg, 0.15 mmol, 100 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:8 α to β based on $^1$H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 6.20 ppm for α and 6.02 ppm for β) as a white solid (58.5 mg, 0.097 mmol, 65% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.34 – 7.28 (m, 4H), 7.25 (t, J = 6.8 Hz, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.02 (dd, J = 15.8, 7.9 Hz, 1H), 5.38 (t, J = 9.5 Hz, 1H, $H_3$), 5.21 (t, J = 9.7 Hz, 1H, $H_4$), 5.06 (t, J = 9.6 Hz, 1H, $H_2$), 4.20 (dd, J = 12.4, 1.6 Hz, 1H), 4.12 (dd, J = 12.4, 4.7 Hz, 1H), 4.00 (dd, J = 9.2, 8.2 Hz, $H_1$), 3.78 (ddd, J = 10.0, 4.5, 1.7 Hz, 1H, $H_5$), 1.22 (s, 9H), 1.16 (s, 9H), 1.12 (s, 9H), 1.03 (s, 9H).

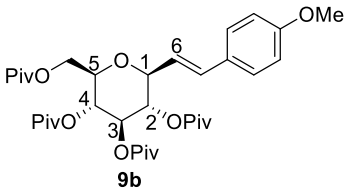
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.30, 177.41, 176.82, 176.53, 135.89, 135.55, 128.71, 128.41, 126.86, 124.36, 80.31, 76.21, 73.34, 71.21, 68.05, 62.11, 39.01, 38.88, 38.86, 38.78, 27.32, 27.25, 27.19, 27.16.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{34}H_{51}O_9^+$): m/z 603.3528; found: 603.3511.

**M.p**. 160-162 ºC.

**$[\alpha]_D^{20}$** = -10.6 (*c* = 0.17, $CH_2Cl_2$).

**(*2S,3S,4R,5R,6R*)-2-((E)-4-methoxystyryl)-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (9b).**



**9b**

This compound was prepared according to the *Method **B*** using *(E)*-1-(2-bromovinyl)-4-methoxybenzene (32.0 mg, 0.15 mmol, 100 mol %), (*2R,3R,4S,5R,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:7 α to β based on $^1$H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 6.28 ppm for α and 5.88 ppm for β) as a white solid (55.9 mg, 0.088 mmol, 59% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.25 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 15.8 Hz, 1H), 5.88 (dd, J = 15.8, 8.1 Hz, 1H), 5.36 (t, J = 9.5 Hz, 1H, $H_3$), 5.20 (t, J = 9.7 Hz, 1H, $H_4$), 5.05 (t, J = 9.6 Hz, 1H, $H_2$), 4.19 (d, J = 11.3 Hz, 1H), 4.11 (dd, J = 12.5, 4.5 Hz, 1H), 4.00 (t, J = 8.9 Hz, 1H, $H_1$), 3.79 (s, 3H), 3.78 – 3.74 (m, 1H, $H_5$), 1.22 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H), 1.02 (s, 9H).

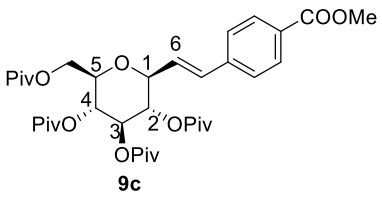
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.29, 177.41, 176.83, 176.52, 159.82, 135.23, 128.68, 128.15, 122.10, 114.09, 80.61, 76.20, 73.38, 71.29, 68.10, 62.15, 55.36, 39.01, 38.87, 38.86, 38.78, 27.32, 27.25, 27.20, 27.16.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{35}H_{53}O_{10}^+$): m/z 633.3633; found: 633.3607.

**M.p**. 127-128 ºC.

**$[\alpha]_D^{20}$** = -25.2 (*c* = 0.52, $CH_2Cl_2$).

***(2S,3S,4R,5R,6R)*-2-((*E*)-4-(methoxycarbonyl)styryl)-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (9c).**



**9c**

This compound was prepared according to the *Method* ***B*** using methyl (*E*)-4-(2-bromovinyl)benzoate (36.1 mg, 0.15 mmol, 100 mol %), (*2R,3R,4S,5R,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:9 α to β based on $^1$H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 6.52 ppm for α and 6.13 ppm for β) as a white solid (74.0 mg, 0.112 mmol, 75% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 7.8 Hz, 1H), 5.38 (t, J = 9.5 Hz, 1H, $H_3$), 5.20 (t, J = 9.7 Hz, 1H, $H_4$), 5.05 (t, J = 9.6 Hz, 1H, $H_2$), 4.20 (dd, J = 12.5, 1.6 Hz, 1H), 4.11 (dd, J = 12.5, 4.6 Hz, 1H), 4.05 (dd, J = 9.3, 8.1 Hz, 1H, $H_1$), 3.89 (s, 3H), 3.78 (ddd, J = 10.1, 4.5, 1.7 Hz, 1H, $H_5$), 1.22 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H), 1.02 (s, 9H).

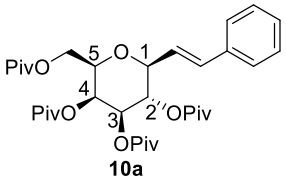
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.26, 177.39, 176.82, 176.51, 166.85, 140.29, 134.19, 130.10, 129.87, 127.04, 126.74, 79.95, 76.32, 73.25, 71.20, 68.01, 62.05, 52.26, 39.02, 38.88, 38.87, 38.80, 27.31, 27.25, 27.19, 27.15.

**HRMS** (ESI) exact mass calculated for [M+$Na^+$] ($C_{36}H_{52}NaO_{11}^+$): m/z 683.3402; found: 683.3386.

**M.p**. 142-143 ºC.

**$[\alpha]_D^{20}$** = -38.3 (*c* = 1.57, $CH_2Cl_2$).

***(2R,3S,4R,5S,6S)*-2-((pivaloyloxy)methyl)-6-((*E*)-styryl)tetrahydro-*2H*-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (10a).**



**10a**

This compound was prepared according to the *Method* ***B*** using (*E*)-(2-bromovinyl)benzene (27.5 mg, 0.15 mmol, 100 mol %), (*2R,3R,4S,5S,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture

of diastereomers (1:10 α to β anomers based on NMR) as a white solid (50.5 mg, 0.084 mmol, 56% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.34 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 15.8 Hz, 1H), 6.08 (dd, J = 15.8, 7.9 Hz, 1H), 5.49 (d, J = 3.0 Hz, 1H, $H_4$), 5.28 (t, J = 9.9 Hz, 1H, $H_2$), 5.20 (dd, J = 10.2, 3.2 Hz, 1H, $H_3$), 4.18 (dd, J = 9.8, 5.2 Hz, 1H), 4.05 (t, J = 8.7 Hz, $H_1$), 4.05 – 3.98 (m, 2H, $H_5$), 1.29 (s, 9H), 1.18 (s, 9H), 1.12 (s, 9H), 1.04 (s, 9H).

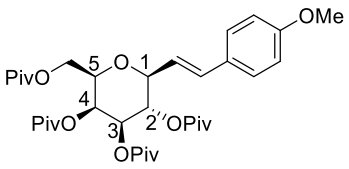
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.06, 177.51, 177.03, 176.97, 135.96, 135.59, 128.70, 128.39, 126.89, 124.54, 80.58, 74.41, 71.99, 68.61, 67.45, 61.37, 39.23, 38.91, 38.85, 38.83, 27.34, 27.26, 27.21, 27.17.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{34}H_{51}O_9^+$): m/z 603.3528; found: 603.3515.

**M.p**. 171-173 ºC.

**[α]$_D^{20}$** = -14.2 (*c* = 0.50, $CH_2Cl_2$).

***(2S,3S,4R,5S,6R)*-2-((*E*)-4-methoxystyryl)-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (10b).**



**10b**

This compound was prepared according to the *Method* ***B*** using *(E)*-1-(2-bromovinyl)-4-methoxybenzene (32.0 mg, 0.15 mmol, 100 mol %), (*2R,3R,4S,5S,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %),. Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:6 α to β anomers based on NMR) as a white solid (44.5 mg, 0.070 mmol, 47% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.28 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 15.8 Hz, 1H), 5.94 (dd, J = 15.8, 8.1 Hz, 1H), 5.48 (d, J = 3.2 Hz, 1H, $H_4$), 5.27 (t, J = 9.8 Hz, 1H, $H_2$), 5.20 (dd, J = 10.2, 3.2 Hz, 1H, $H_3$), 4.18 (dd, J = 8.4, 3.7 Hz, 1H), 4.06 – 3.97 (m, 3H, $H_1$, $H_5$), 3.80 (s, 3H), 1.29 (s, 9H), 1.18 (s, 9H), 1.12 (s, 9H), 1.03 (s, 9H).

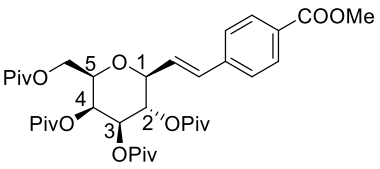
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.05, 177.50, 177.02, 176.99, 159.81, 135.31, 128.71, 128.17, 122.22, 114.07, 80.88, 74.34, 71.98, 68.65, 67.45, 61.36, 55.36, 39.22, 38.90, 38.84, 38.81, 27.33, 27.25, 27.21, 27.16.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{35}H_{53}O_{10}^+$): m/z 633.3633; found: 633.3609.

**M.p**. 137-139 ºC.

**[α]$_D^{20}$** = -4.4 (*c* = 0.54, $CH_2Cl_2$).

***(2S,3S,4R,5S,6R)*-2-((*E*)-4-(methoxycarbonyl)styryl)-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (10c).**



**10c**

This compound was prepared according to the *Method* ***B*** using methyl (*E*)-4-(2-bromovinyl)benzoate (36.1 mg, 0.15 mmol, 100 mol %), (*2R,3R,4S,5S,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:14 α to β anomers based on NMR) as a white solid (59.4 mg, 0.090 mmol, 60% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 6.66 (d, J = 15.8 Hz, 1H), 6.19 (dd, J = 15.8, 7.8 Hz, 1H), 5.48 (d, J = 2.9 Hz, 1H, $H_4$), 5.27 (t, J = 9.8 Hz, 1H, $H_2$), 5.21 (dd, J = 10.2, 3.1 Hz, 1H, $H_3$), 4.17 (dd, J = 10.4, 5.8 Hz, 1H), 4.07 (t, J = 8.7 Hz, $H_1$), 4.05 – 3.97 (m, 2H, $H_5$), 3.89 (s, 3H), 1.28 (s, 9H), 1.17 (s, 9H), 1.11 (s, 9H), 1.03 (s, 9H).

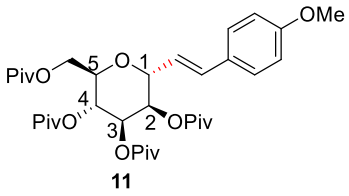
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.04, 177.46, 176.97, 176.97, 166.85, 140.31, 134.27, 130.07, 129.81, 127.17, 126.75, 80.23, 74.45, 71.84, 68.50, 67.35, 61.29, 52.25, 39.21, 38.89, 38.83, 38.82, 27.31, 27.22, 27.19, 27.13.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{36}H_{53}O_{11}^+$): m/z 661.3582; found: 661.3550.

**M.p**. 131-133 ºC.

**[α]$_D^{20}$** = -24.9 (*c* = 0.77, $CH_2Cl_2$).

**(*2R,3R,4R,5R,6R*)-2-((*E*)-4-methoxystyryl)-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (11).**



**11**

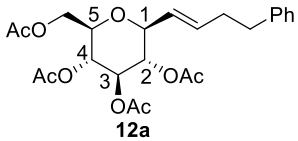
This compound was prepared according to the *Method* ***B*** using (*E*)-1-(2-bromovinyl)-4-methoxybenzene (31.9 mg, 0.15 mmol, 100 mol %), (*2R,3S,4S,5R,6R*)-2-bromo-6-((pivaloyloxy)methyl)tetrahydro-*2H*-pyran-3,4,5-triyltris(2,2-dimethylpropanoate) (113.0 mg, 0.195 mmol, 130 mol %). Flash column chromatography ($SiO_2$: 5% ethyl acetate in petroleum ether) gave a α products as a colorless gummy liquid (56.8 mg, 0.09 mmol, 60% yield).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.74 (dd, J = 16.3, 1.5 Hz, 1H), 6.08 (dd, J = 16.3, 4.7 Hz, 1H), 5.55 – 5.45 (m, 2H, $H_4$, $H_2$), 5.26 (dd, J = 9.7, 3.0 Hz, 1H, $H_3$), 4.68 – 4.60 (m, 1H, $H_1$), 4.27 (dd, J = 12.3, 4.8 Hz, 1H), 4.14 (dd, J = 12.3, 1.7 Hz, 1H), 4.03 (ddd, J = 9.2, 4.8 Hz, 1.7H, $H_5$), 3.81 (s, 3H), 1.27 (s, 9H), 1.25 (s, 9H), 1.15 (s, 9H), 1.15 (s, 9H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 178.28, 177.69, 177.50, 176.82, 160.02, 134.52, 128.60, 128.10, 120.48, 114.23, 75.99, 71.31, 70.70, 70.07, 65.91, 62.33, 55.45, 39.05, 39.03, 38.92, 27.30, 27.28, 27.22, 27.18.

**$[\alpha]_D^{20}$** = -38.3 (*c* = 1.57, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-((*E*)-4-phenylbut-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12a).**



**12a**

This compound was prepared according to the *Method* ***B*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (124.0 mg, 0.3 mmol, 200 mol %), (*E*)-(4-bromobut-3-en-1-yl) benzene (31.6 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %), 25 °C. Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:6 α to β based on $^1$H NMR spectra) as a white solid (34.6 mg, 0.075 mmol, 50% yield).

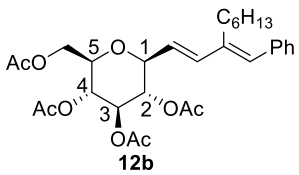
**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ = 7.26 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 5.82 (dt, J = 15.1, 6.7 Hz, 1H), 5.43 (dd, J = 15.4, 7.8 Hz, 1H), 5.19 (t, J = 9.5 Hz, 1H, *H*$_3$), 5.07 (t, J = 9.7 Hz, 1H, *H*$_4$), 4.91 (t, J = 9.6 Hz, 1H, *H*$_2$), 4.23(dd, J = 12.4, 4.7 Hz, 1H), 4.09 (dd, J = 12.4, 2.1 Hz, 1H), 3.80 (dd, J = 9.4, 8.1 Hz, 1H, *H*$_1$), 3.67 (ddd, J = 10.0, 4.6, 2.2 Hz, 1H, *H*$_5$), 2.69 – 2.57 (m, 2H), 2.38 – 2.29 (m, 2H), 2.07 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.92 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.80, 170.40, 169.53, 169.47, 141.30, 136.78, 128.44, 128.33, 126.03, 125.75, 79.52, 75.52, 73.94, 71.33, 68.49, 62.29, 35.22, 33.94, 20.84, 20.75, 20.72, 20.67.

**M.p**. 114-116 °C.

**$[\alpha]_D^{20}$** = +5.5 (*c* = 0.58, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-((*E*)-3-((*E*)-benzylidene)non-1-en-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12b).**



**12b**

This compound was prepared according to the *Method* ***B*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (124.0 mg, 0.3 mmol, 200 mol %), ((*E*)-2-((*E*)-2-bromovinyl)oct-1-en-1-yl)benzene (44.0 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %), 25 °C. Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:5.5 α to β based on $^{1}$H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.69 ppm for α and 3.74 ppm for β) as a white solid (51.3 mg, 0.095 mmol, 63% yield).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ = 7.34 (t, J = 7.6 Hz, 2H), 7.30 – 7.15 (m, 3H), 6.49 (s, 1H), 6.35 (d, J = 15.7 Hz, 1H), 5.62 (dd, J = 15.7, 7.7 Hz, 1H), 5.26 (t, J = 9.5 Hz, 1H, *H*$_3$), 5.12 (t, J = 9.7 Hz, 1H, *H*$_4$), 5.01 (t, J = 9.6 Hz, 1H, *H*$_2$), 4.29 (dd, J = 12.4, 4.6 Hz, 1H), 4.14 (dd, J = 12.4, 1.5 Hz, 1H), 3.96 (t, J = 8.7 Hz, 1H, *H*$_1$), 3.74 (ddd, J = 9.7, 4.5, 2.1 Hz, 1H, *H*$_5$), 2.47 – 2.31 (m, 2H), 2.10 (s, 1H), 2.04 (s, 1H), 2.02 (s, 1H), 1.98 (s, 1H), 1.53 – 1.41 (m, 2H), 1.37 – 1.27 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H).

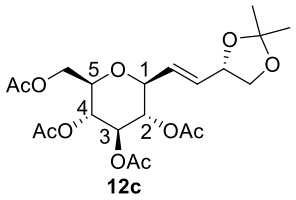
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.90, 170.50, 169.63, 169.51, 139.81, 139.71, 137.37, 132.89, 128.89, 128.41, 127.09, 122.93, 80.16, 75.82, 74.02, 71.60, 68.72, 62.44, 31.63, 29.71, 28.89, 27.48, 22.77, 20.93, 20.81, 20.77, 20.75, 14.19.

**M.p**. 117-119 ºC.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{35}H_{53}O_{10}^+$): m/z 633.3633; found: 633.3620.

**[α]$_D^{20}$** = -26.1 (*c* = 0.36, $CH_2Cl_2$).

**(*2R,3R,4R,5S,6S*)-2-(acetoxymethyl)-6-((*E*)-2-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (12c).**



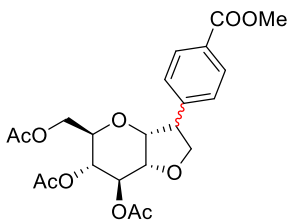
**12c**

This compound was prepared according to the *Method* ***B*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (124.0 mg, 0.3 mmol, 200 mol %), (*E*)-4-(2-bromovinyl)-2,2-dimethyl-1,3-dioxolane (31.0 mg, 0.15 mmol, 100 mol %), $MgCl_2$ (2.1 mg, 0.0225 mmol, 15 mol %), 25 ºC. Flash column chromatography ($SiO_2$: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1:9 α to β based on $^1$H NMR spectra) as a colorless gummy liquid (31.6 mg, 0.069 mmol, 46% yield).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ = 5.74 (dd, J = 15.6, 6.9 Hz, 1H), 5.63 (dd, J = 15.7, 6.8 Hz, 1H), 5.17 (t, J = 9.5 Hz, 1H, *H$_3$*), 5.02 (t, J = 9.7 Hz, 1H, *H$_4$*), 4.84 (t, J = 9.7 Hz, 1H, *H$_2$*), 4.45 (q, J = 6.8 Hz, 1H), 4.18 (dd, J = 12.4, 4.9 Hz, 1H), 4.06 (dd, J = 12.4, 1.8 Hz, 1H), 4.02 (dd, J = 8.0, 6.4 Hz, 1H), 3.85 (dd, J = 9.7, 7.0 Hz, 1H, *H$_1$*), 3.65 (ddd, J = 10.0, 4.8, 2.0 Hz, 1H, *H$_5$*), 3.46 (t, J = 7.7 Hz, 1H), 2.03 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ = 170.73, 170.34, 169.50, 169.34, 133.16, 128.21, 109.68, 78.29, 75.93, 75.67, 73.88, 71.32, 69.17, 68.51, 62.30, 26.64, 25.81, 20.80, 20.71, 20.68, 20.63.

**(*3aR,5R,6R,7R,7aS*)-5-(acetoxymethyl)-3-(4-(methoxycarbonyl)phenyl)hexahydro-*2H*-furo[3,2-*b*]pyran-6,7-diyl diacetate(15)**



dr = 1.4:1

This compound was prepared according to the *Method* ***A*** using (*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-5-(allyloxy)-6-bromotetrahydro-*2H*-pyran-3,4-diyl diacetate (61.3 mg, 0.15 mmol, 100 mol %), methyl

methyl 4-iodobenzoate (58.9 mg, 0.225 mmol, 150 mol %). Flash column chromatography ($SiO_2$: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1.4:1 based on NMR) as a colorless gummy liquid (43.2 mg, 0.096 mmol, 64% yield).

NMR data for mixture of diastereomers:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2.8H), 7.29 (d, *J* = 8.3 Hz, 2.8H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.25 – 5.19 (m, 2.4H), 4.92 – 4.83 (m, 2.4H), 4.32 – 4.25 (m, 3.4H), 4.19 (t, *J* = 4.2 Hz, 1.4H), 4.13 – 3.90 (m, 9.8H), 3.90 – 3.87 (m, 7.4H), 3.74 (dd, *J* = 11.0, 8.0 Hz, 1.4H), 3.53 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.95 (dd, *J* = 13.5, 9.1 Hz, 1.4H), 2.88 (dd, *J* = 10.0, 7.4 Hz, 1H), 2.74 – 2.67 (m, 3.4H), 2.57 – 2.46 (m, 1.5H), 2.05 (d, *J* = 3.5 Hz, 7.4H), 2.04 (d, *J* = 3.0 Hz, 7.4H), 2.02 (d, *J* = 2.2 Hz, 7.4H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ = 170.58, 170.54, 169.99, 169.86, 169.55, 145.69, 144.49, 129.96, 129.82, 128.77, 128.72, 128.56, 128.31, 80.54, 79.25, 78.27, 73.40, 72.32, 72.15, 71.96, 71.20, 71.08, 70.97, 67.65, 67.03, 62.27, 62.22, 52.10, 52.08, 46.83, 44.22, 37.08, 30.99, 20.87, 20.79, 20.74, 20.70.

**HRMS** (ESI) exact mass calculated for [M+H$^+$] ($C_{34}H_{43}O_{19}^+$): m/z 755.2393; found: 755.2346.

## II. Reference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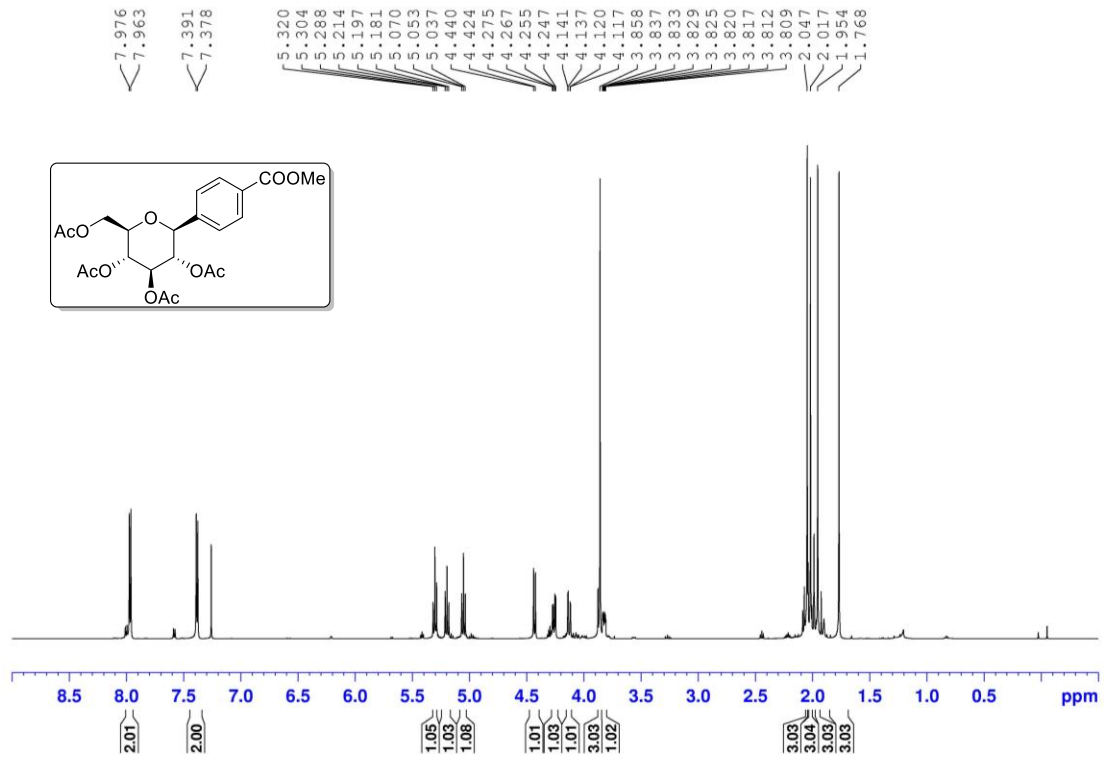
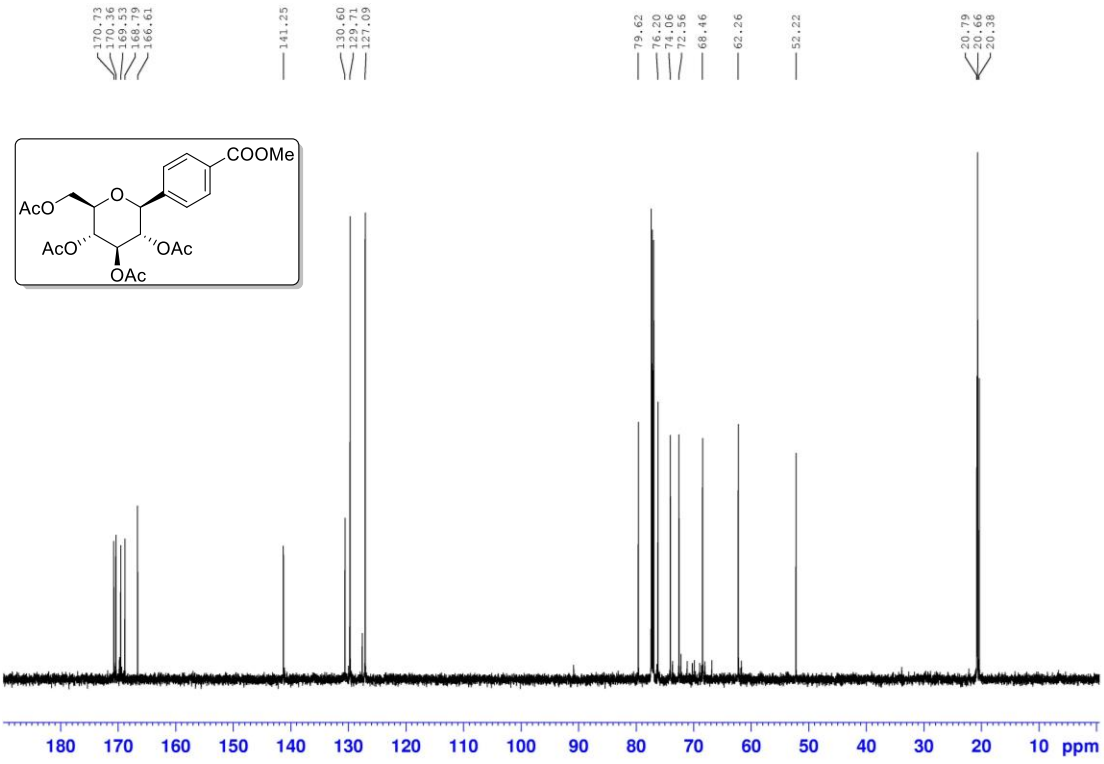
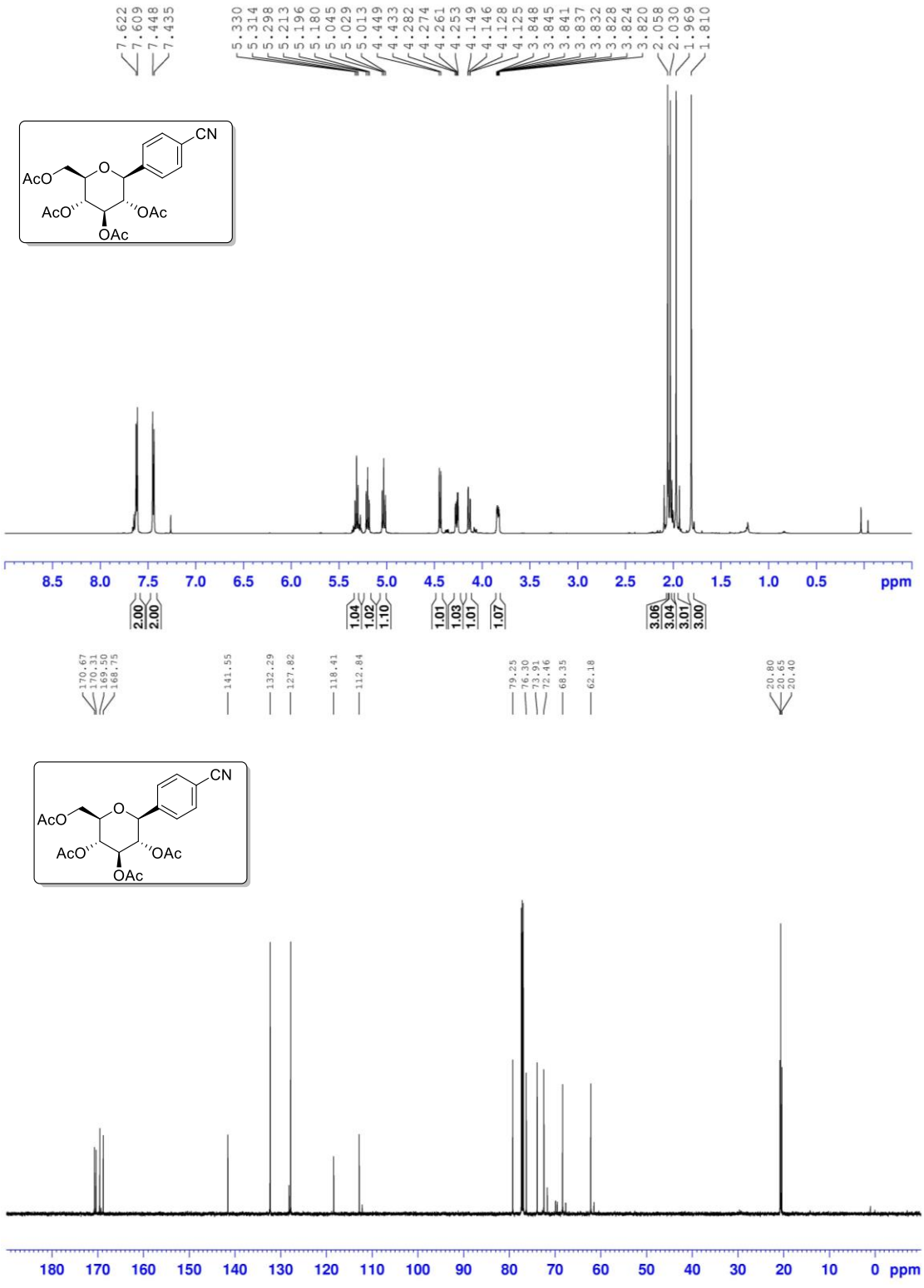
## III. NMR Data for New Compounds

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2.00
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1.02
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1.01
1.03
1.01
1.07
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3.01
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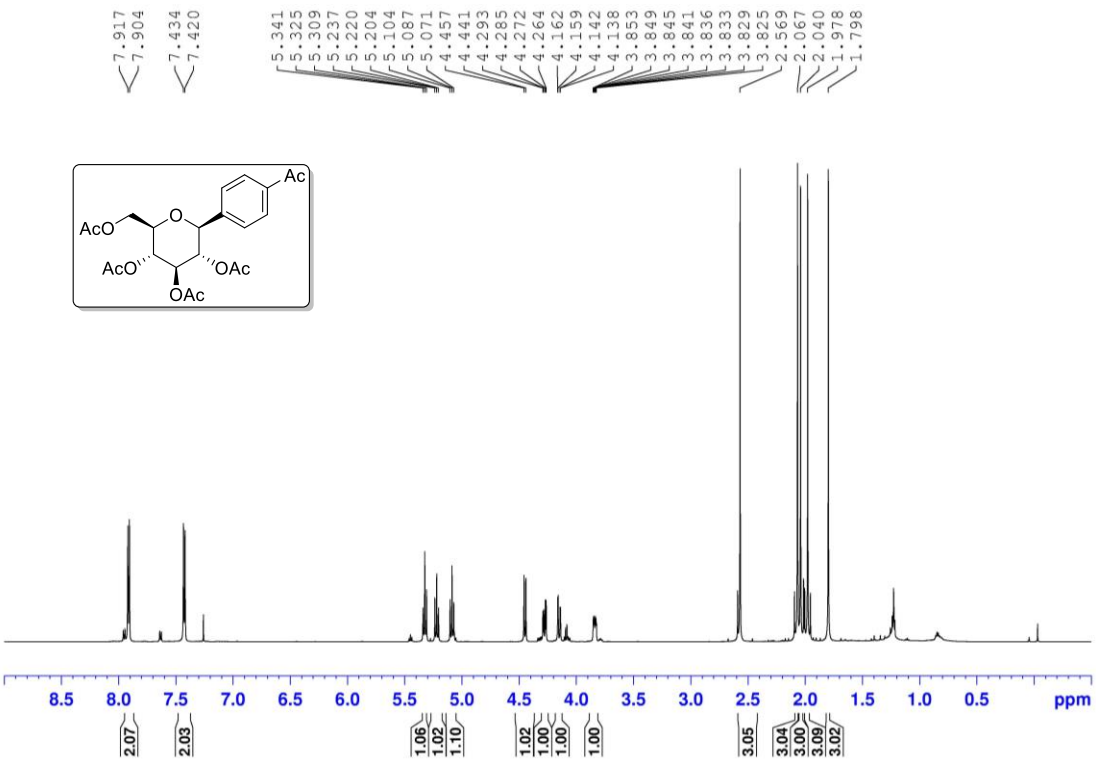
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4.264
4.162
4.159
4.142
4.138
3.853
3.849
3.845
3.841
3.836
3.833
3.829
3.825
2.569
2.067
2.040
1.978
1.798
Ac
AcO
O
AcO
OAc
OAc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.07
2.03
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1.10
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1.00
1.00
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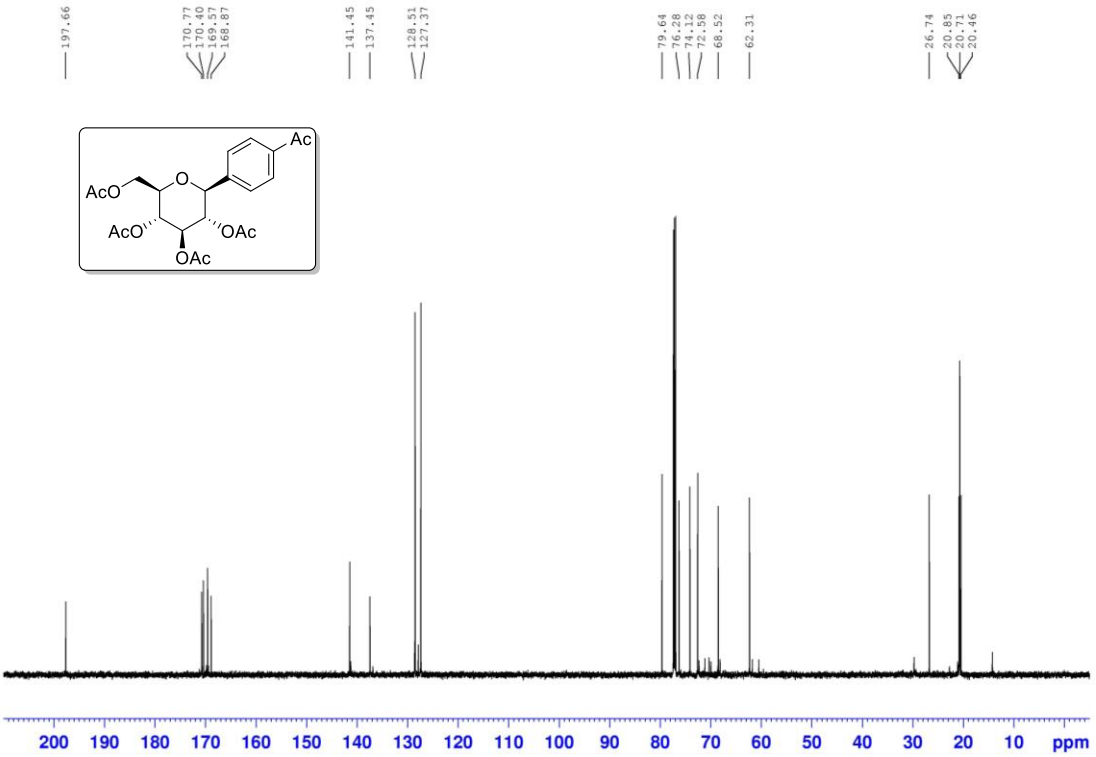
3.04
3.00
3.09
3.02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72.58
68.52
62.31
26.74
20.85
20.71
20.46
Ac
AcO
O
AcO
OAc
OAc
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70
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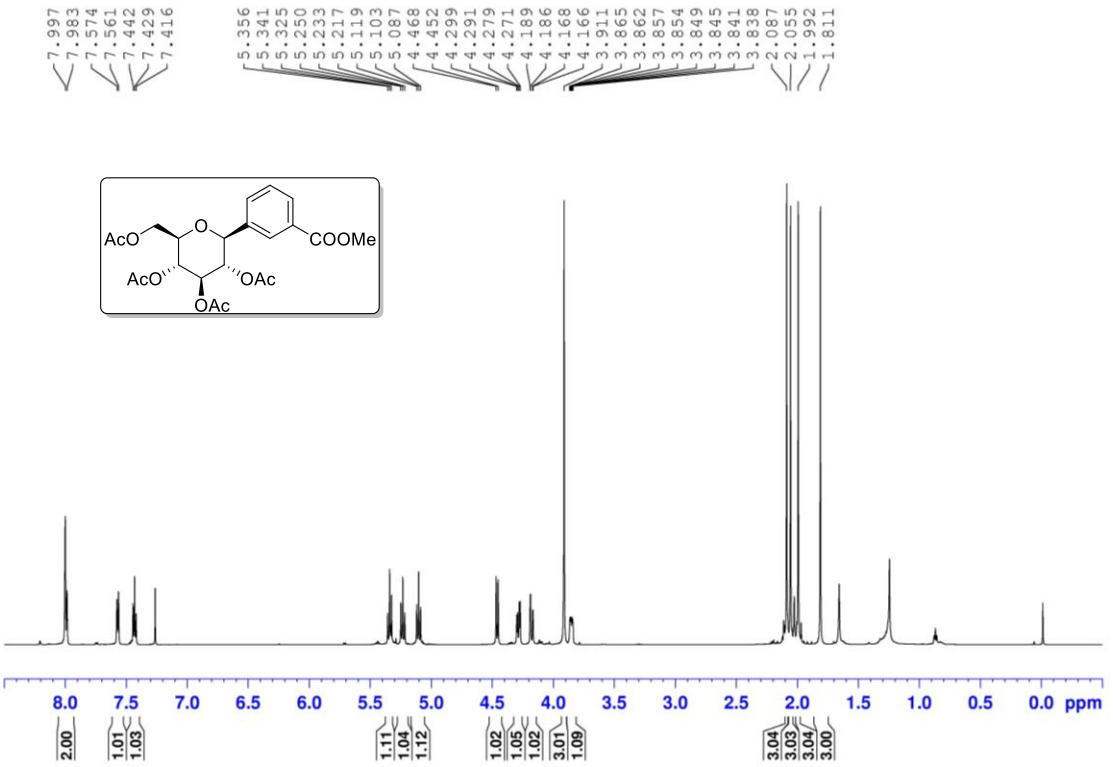
30
20
10
ppm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5.233
5.217
5.119
5.103
5.087
4.468
4.452
4.299
4.291
4.279
4.271
4.189
4.186
4.168
4.166
3.911
3.865
3.862
3.857
3.854
3.849
3.845
3.841
3.838
2.087
2.055
1.992
1.811
AcO
O
COOMe
AcO
OAc
OAc
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.01
1.03
1.11
1.04
1.12
1.02
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1.02
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1.09
3.04
3.03
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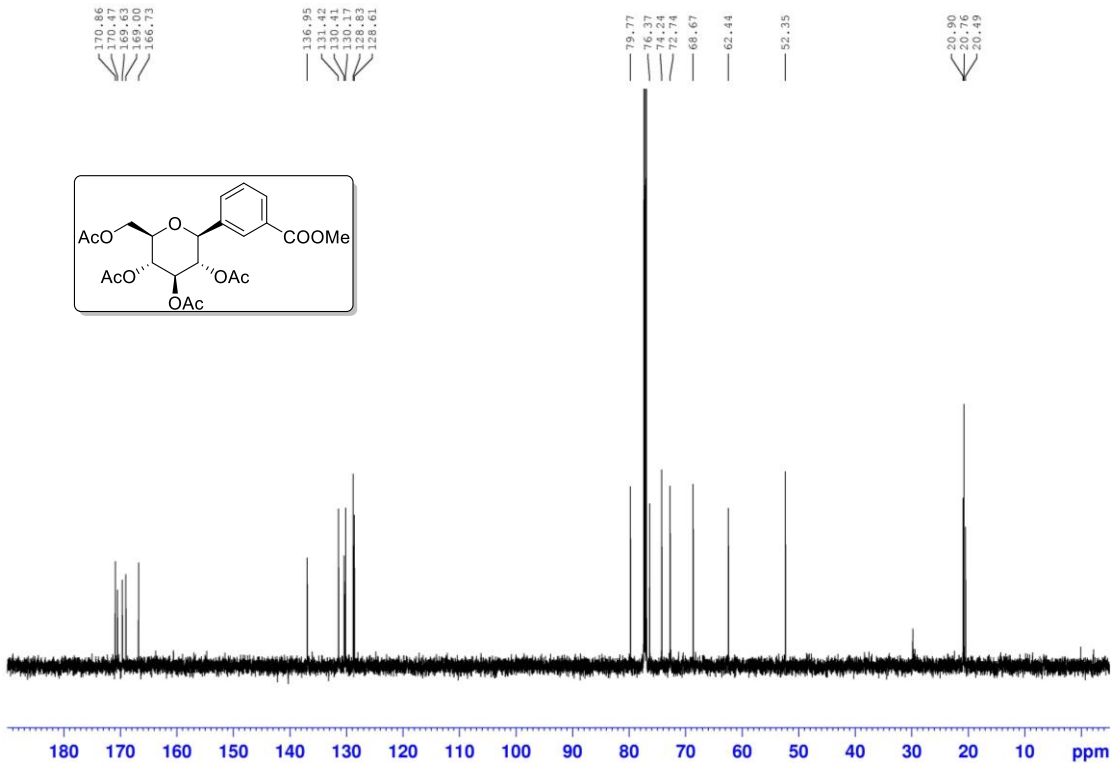
3.00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130.41
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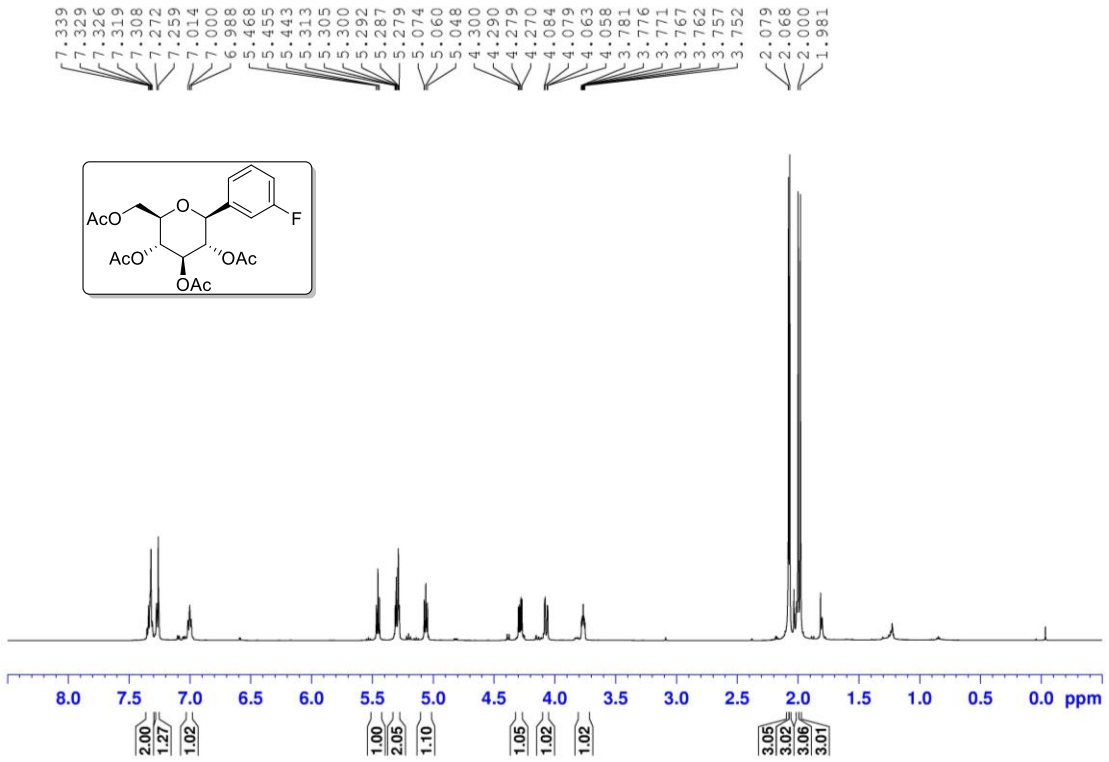
128.61
79.77
76.37
74.24
72.74
68.67
62.44
52.35
20.90
20.76
20.49
AcO
O
COOMe
AcO
OAc
OAc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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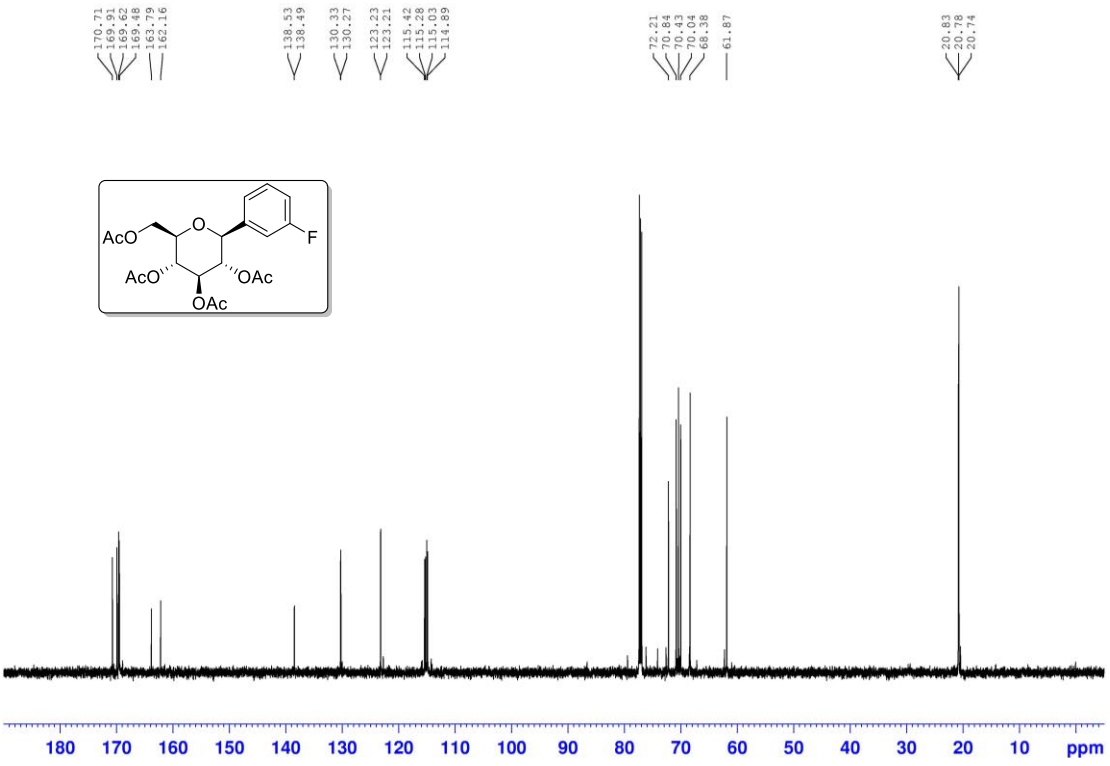
7.014
7.000
6.988
5.468
5.455
5.443
5.313
5.305
5.300
5.292
5.287
5.279
5.074
5.060
5.048
4.300
4.290
4.279
4.270
4.084
4.079
4.063
4.058
3.781
3.776
3.771
3.767
3.762
3.757
3.752
2.079
2.068
2.000
1.981
AcO
O
F
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.27
1.02
1.00
2.05
1.10
1.05
1.02
1.02
3.05
3.02
3.06
3.01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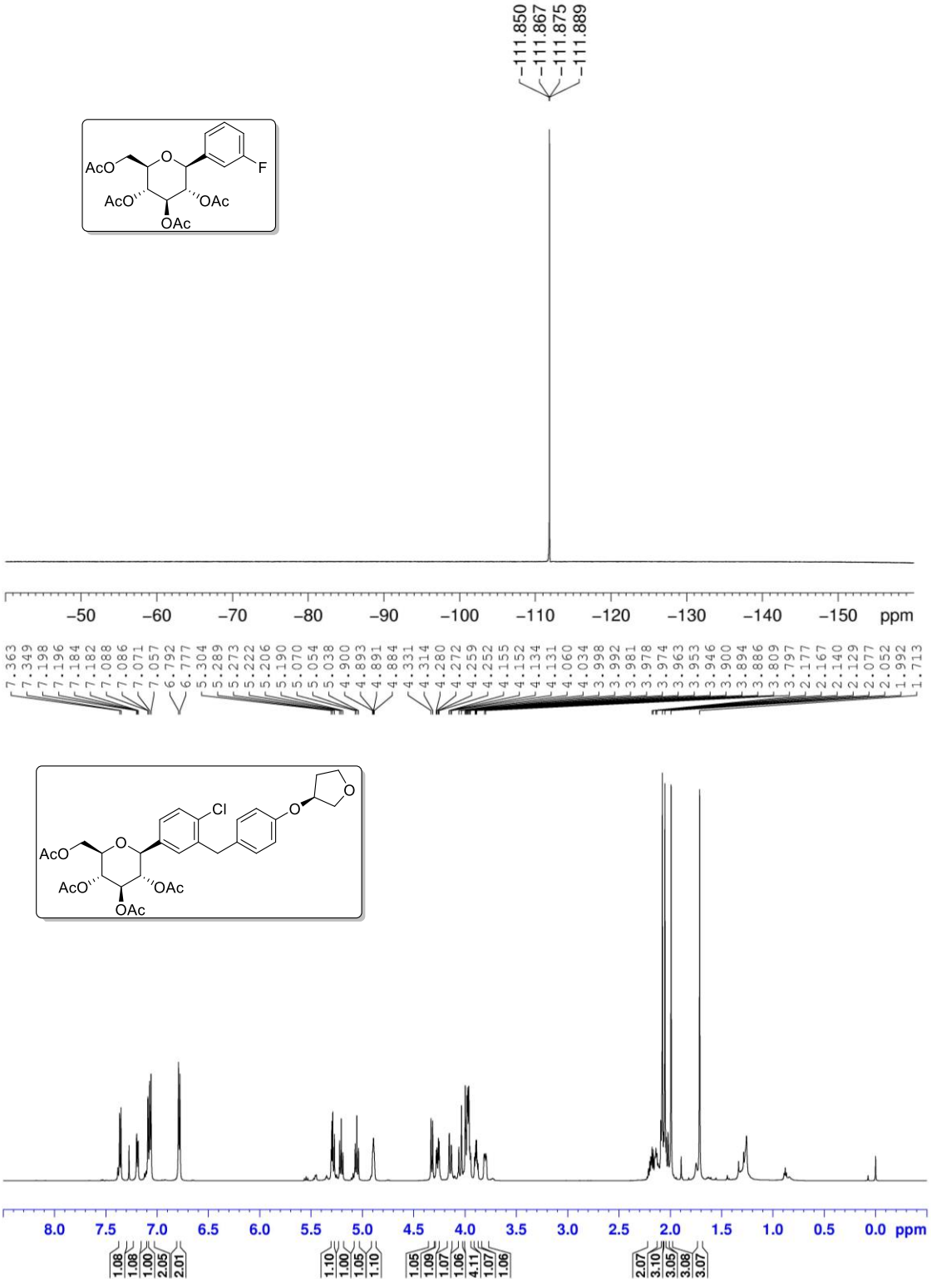
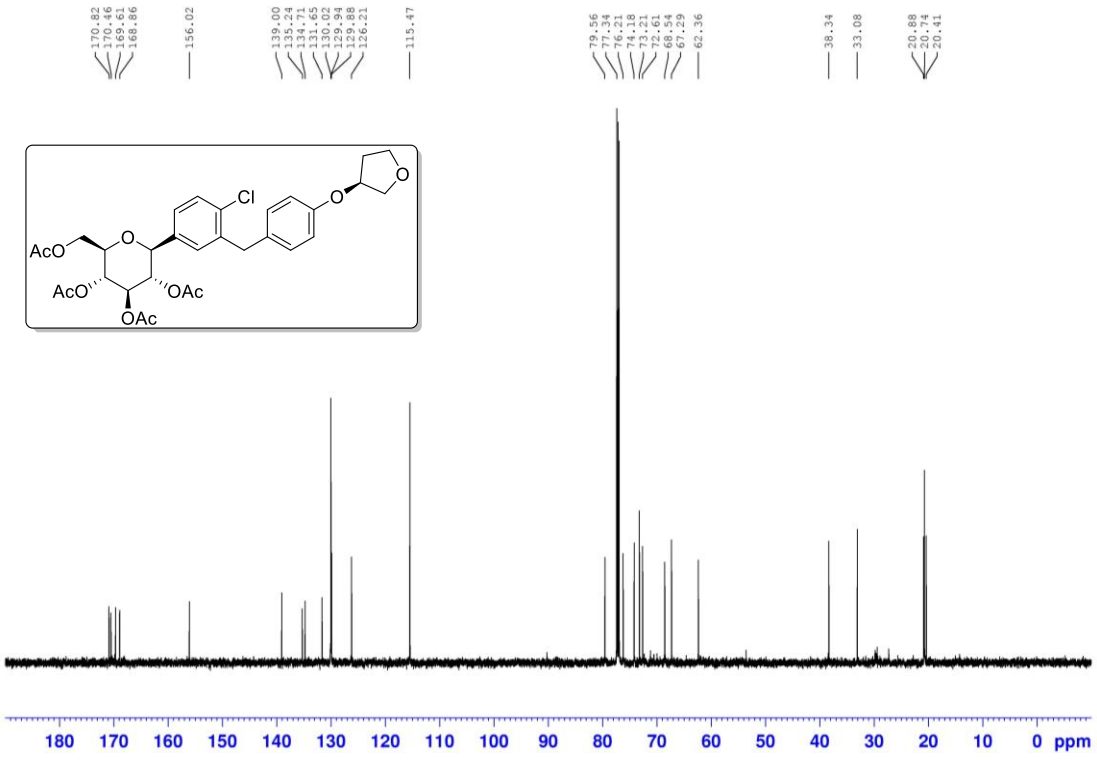
163.79
162.16
138.53
138.49
130.33
130.27
123.23
123.21
115.42
115.28
115.03
114.89
72.21
70.84
70.43
70.04
68.38
61.87
20.83
20.78
20.74
AcO
O
F
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


−111.850
−111.867
−111.875
−111.889
AcO
O
F
AcO
OAc
OAc
−50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 ppm
7.363 7.349 7.198 7.196 7.184 7.182 7.088 7.086 7.071 7.057 6.792 6.777 5.304 5.289 5.273 5.222 5.206 5.190 5.070 5.054 5.038 4.900 4.893 4.891 4.884 4.331 4.314 4.280 4.272 4.259 4.252 4.155 4.152 4.134 4.131 4.060 4.034 3.998 3.992 3.981 3.978 3.974 3.963 3.953 3.946 3.900 3.894 3.886 3.809 3.797 2.177 2.167 2.140 2.129 2.077 2.052 1.992 1.713
Cl
O
O
AcO
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.08 1.08 1.00 2.05 2.01
1.10 1.00 1.05 1.10
1.05 1.09 1.07 1.06 4.11 1.07 1.06
2.07 3.10 3.05 3.08 3.07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169.61
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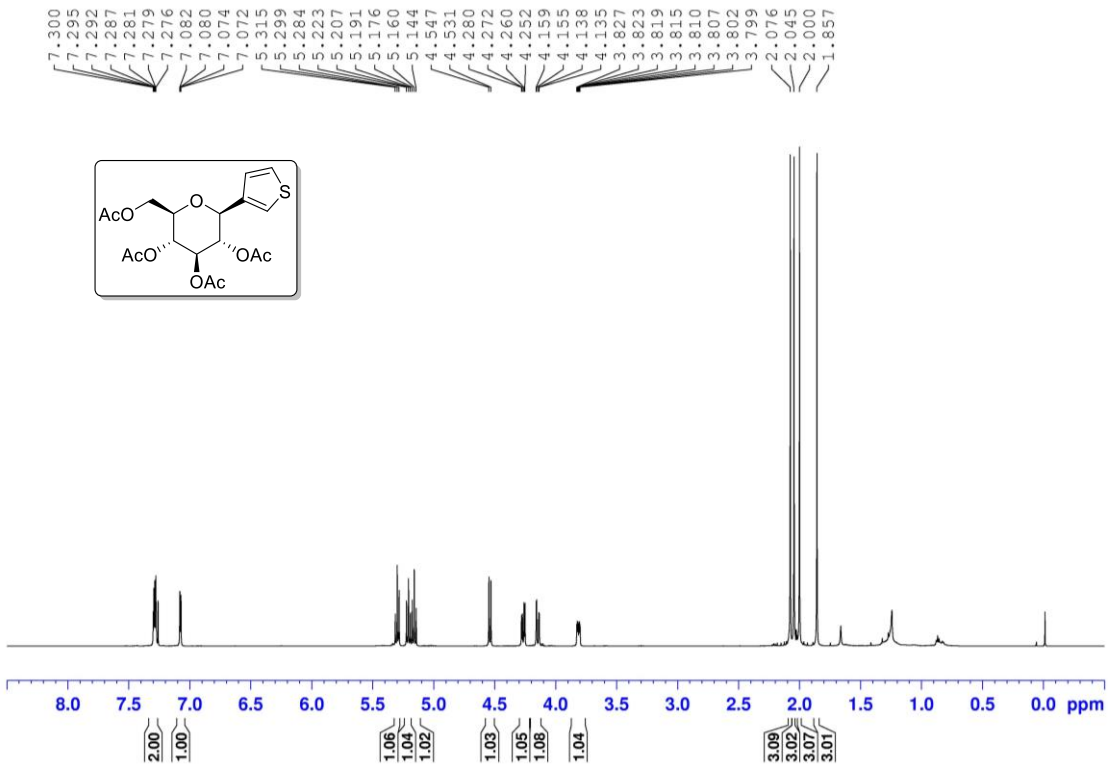
135.24
134.71
131.65
130.02
129.94
129.88
126.21
115.47
79.56
77.34
76.21
74.18
73.21
72.61
68.54
67.29
62.36
38.34
33.08
20.88
20.74
20.41
Cl
O
AcO
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.279
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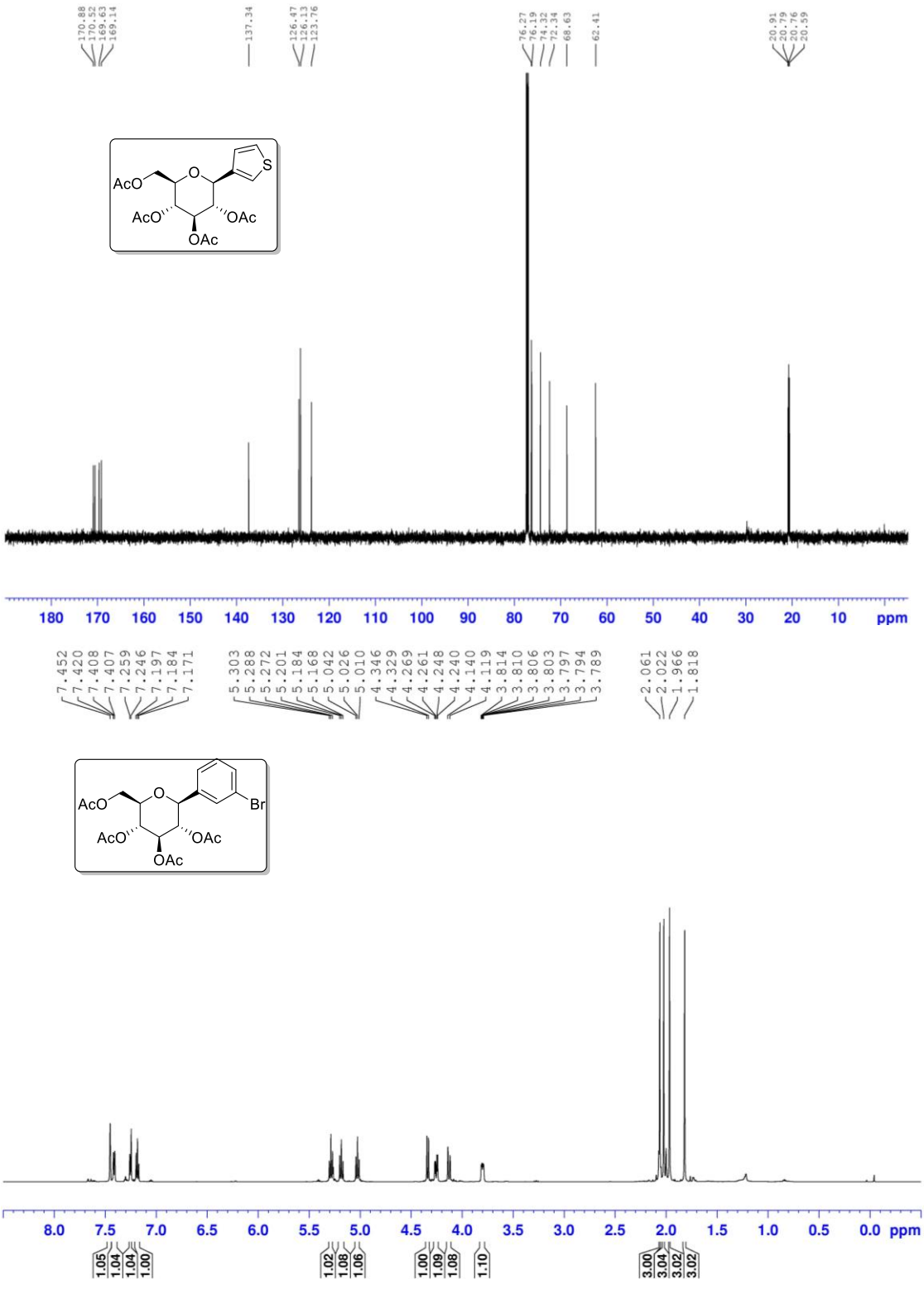
7.082
7.080
7.074
7.072
5.315
5.299
5.284
5.223
5.207
5.191
5.176
5.160
5.144
4.547
4.531
4.280
4.272
4.260
4.252
4.159
4.155
4.138
4.135
3.827
3.823
3.819
3.815
3.810
3.807
3.802
3.799
2.076
2.045
2.000
1.857
S
AcO
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.00
1.06
1.04
1.02
1.03
1.05
1.08
1.04
3.09
3.02
3.07
3.01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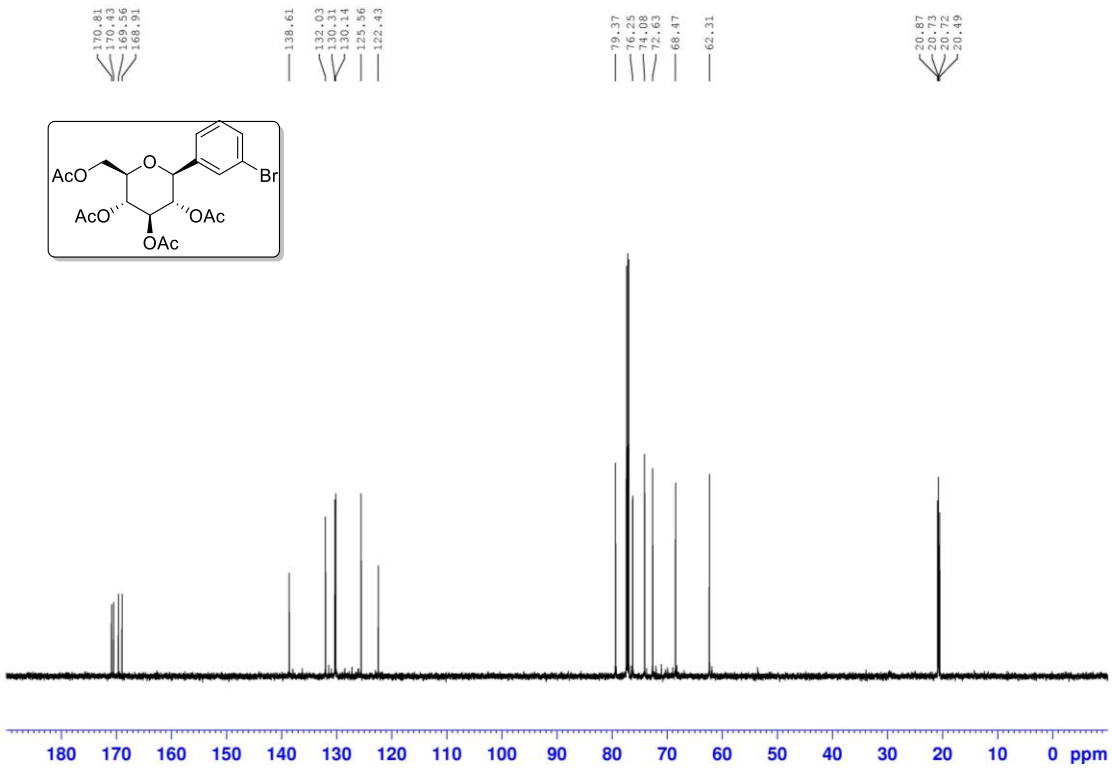
169.14
137.34
126.47
126.13
123.76
76.27
76.19
74.32
72.34
68.63
62.41
20.91
20.79
20.76
20.59
AcO
AcO
OAc
OAc
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.452
7.420
7.408
7.407
7.259
7.246
7.197
7.184
7.171
5.303
5.288
5.272
5.201
5.184
5.168
5.042
5.026
5.010
4.346
4.329
4.269
4.261
4.248
4.240
4.140
4.119
3.814
3.810
3.806
3.803
3.797
3.794
3.789
2.061
2.022
1.966
1.818
AcO
AcO
OAc
OAc
Br
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05
1.04
1.04
1.00
1.02
1.08
1.06
1.00
1.09
1.08
1.10
3.00
3.04
3.02
3.02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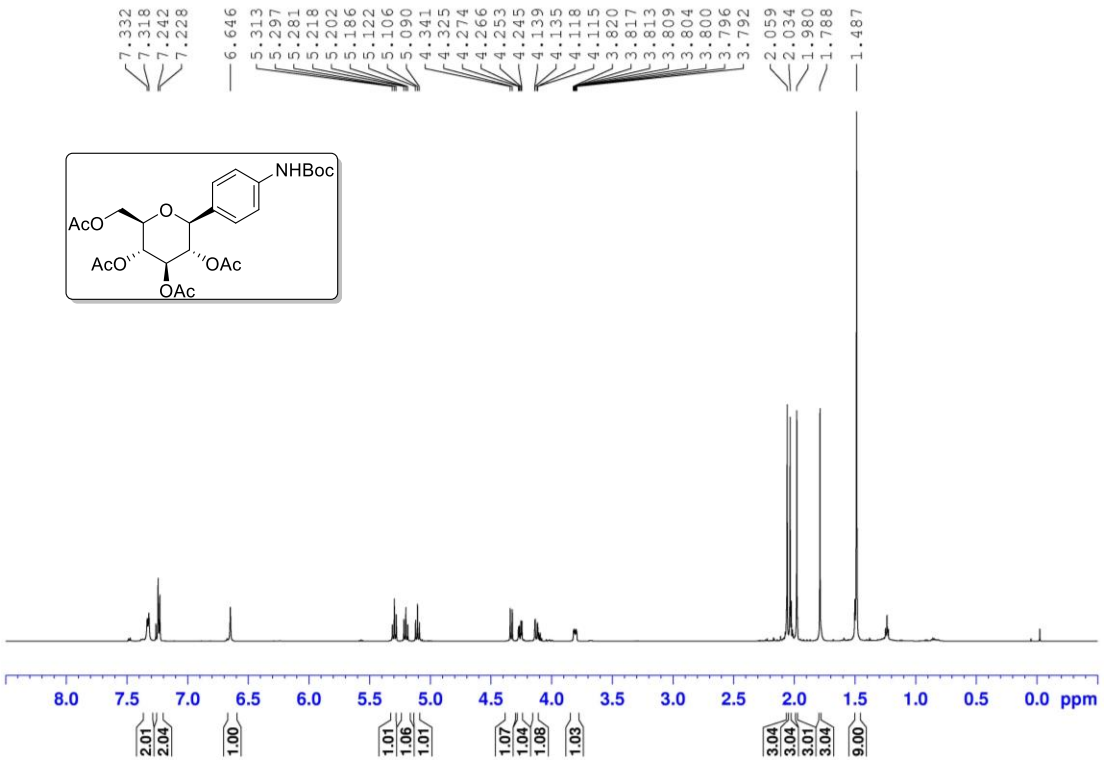
132.03
130.31
130.14
125.56
122.43
79.37
76.25
74.08
72.63
68.47
62.31
20.87
20.73
20.72
20.49
AcO
O
Br
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.228
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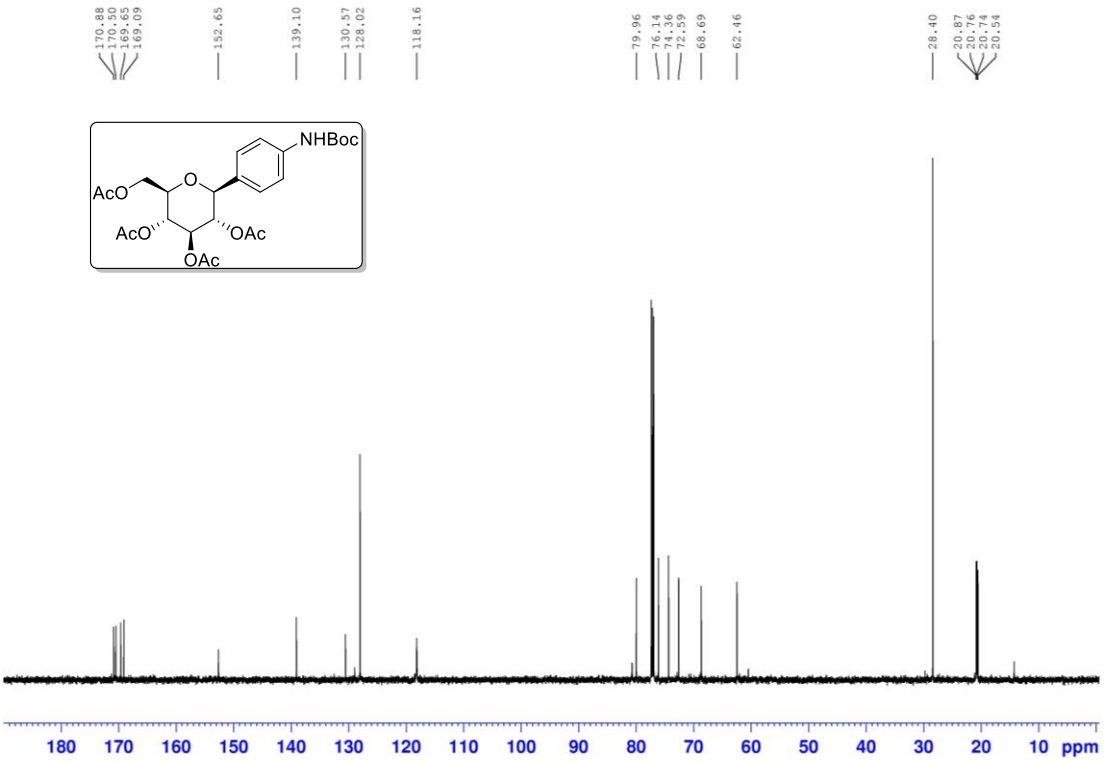
5.281
5.218
5.202
5.186
5.122
5.106
5.090
4.341
4.325
4.274
4.266
4.253
4.245
4.139
4.135
4.118
4.115
3.820
3.817
3.813
3.809
3.804
3.800
3.796
3.792
2.059
2.034
1.980
1.788
1.487
NHBoc
AcO
O
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
2.04
1.00
1.01
1.06
1.01
1.07
1.04
1.08
1.03
3.04
3.04
3.01
3.04
9.00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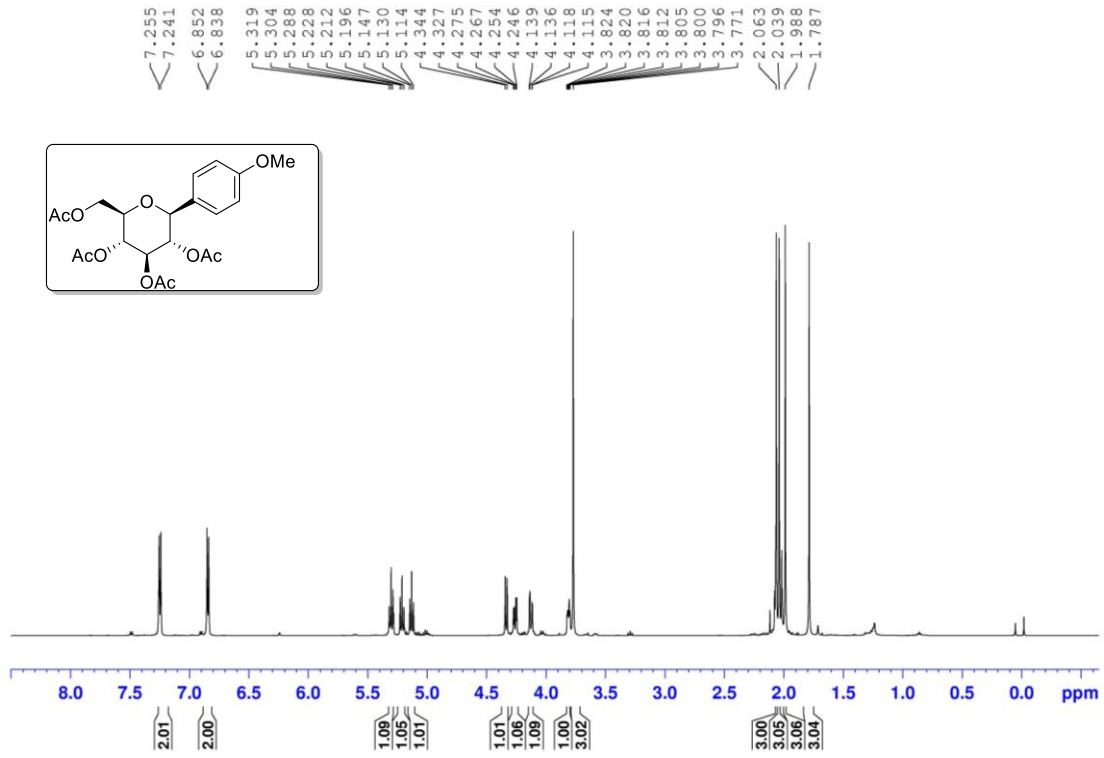
128.02
118.16
79.96
76.14
74.36
72.59
68.69
62.46
28.40
20.87
20.76
20.74
20.54
NHBoc
AcO
AcO
OAc
OAc
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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5.228
5.212
5.196
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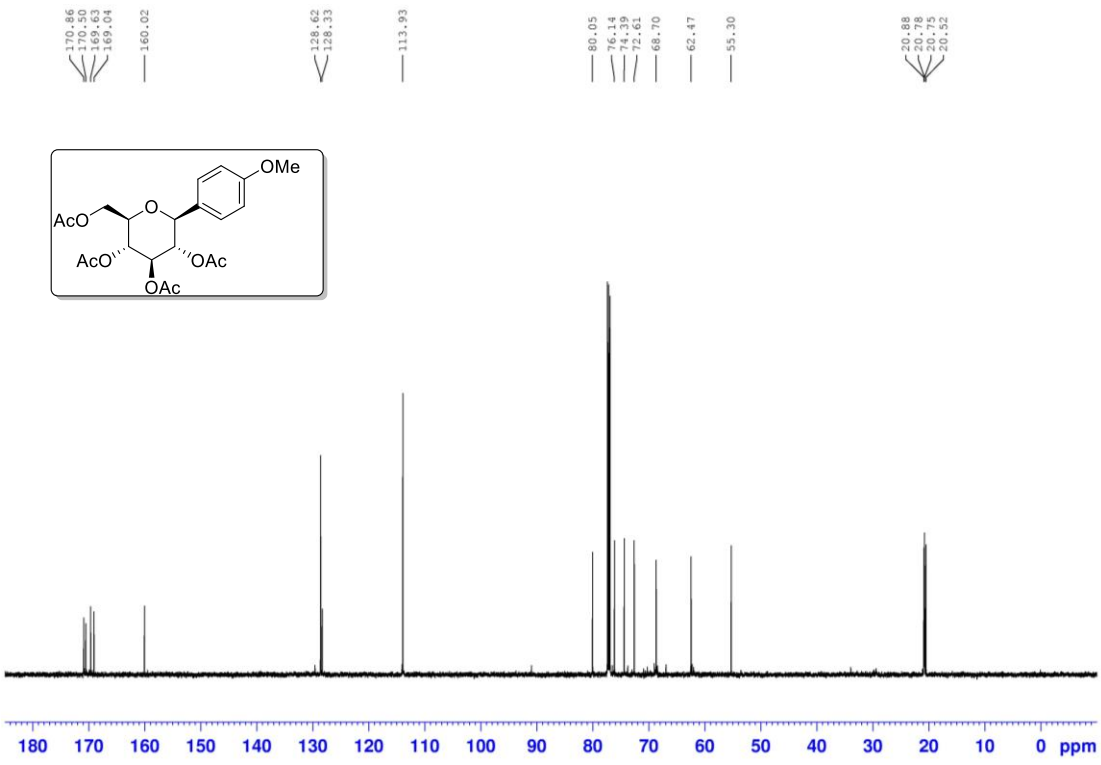
5.114
4.344
4.327
4.275
4.267
4.254
4.246
4.139
4.136
4.118
4.115
3.824
3.820
3.816
3.812
3.805
3.800
3.796
3.771
2.063
2.039
1.988
1.787
OMe
AcO
AcO
OAc
OAc
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
2.00
1.09
1.05
1.01
1.01
1.06
1.09
1.00
3.02
3.00
3.05
3.06
3.04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169.04
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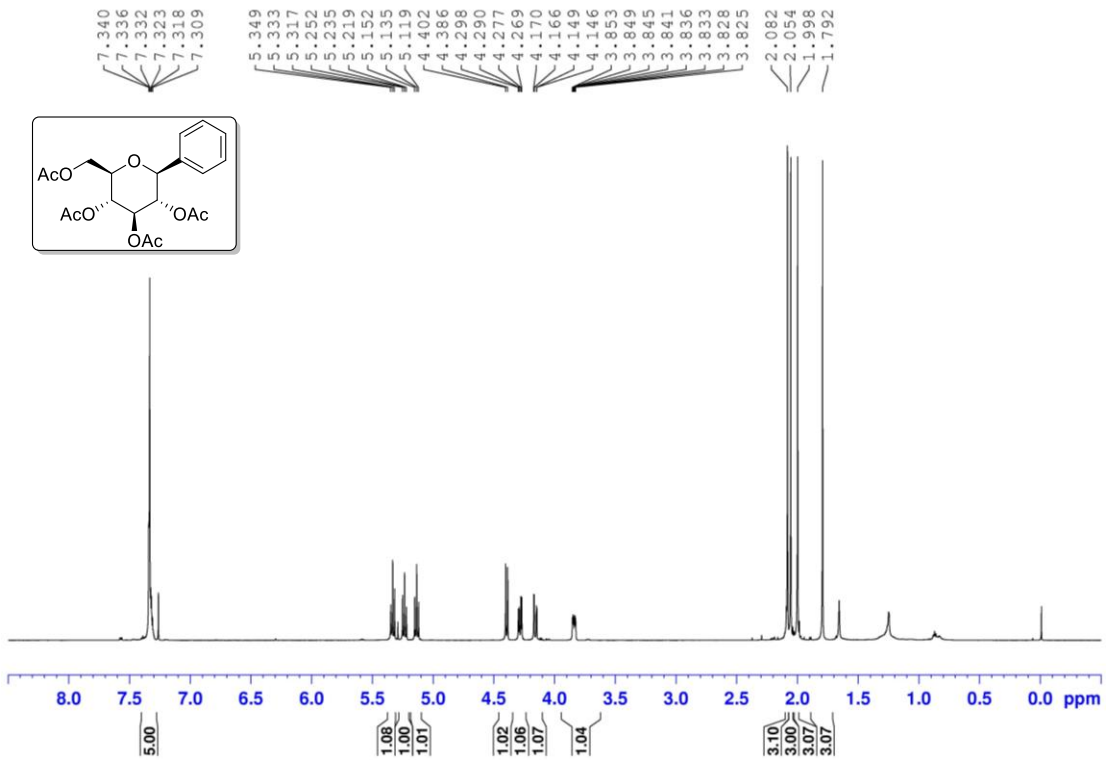
128.33
113.93
80.05
76.14
74.39
72.61
68.70
62.47
55.30
20.88
20.78
20.75
20.52
OMe
AcO
O
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.323
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5.333
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5.252
5.235
5.219
5.152
5.135
5.119
4.402
4.386
4.298
4.290
4.277
4.269
4.170
4.166
4.149
4.146
3.853
3.849
3.845
3.841
3.836
3.833
3.828
3.825
2.082
2.054
1.998
1.792
AcO
O
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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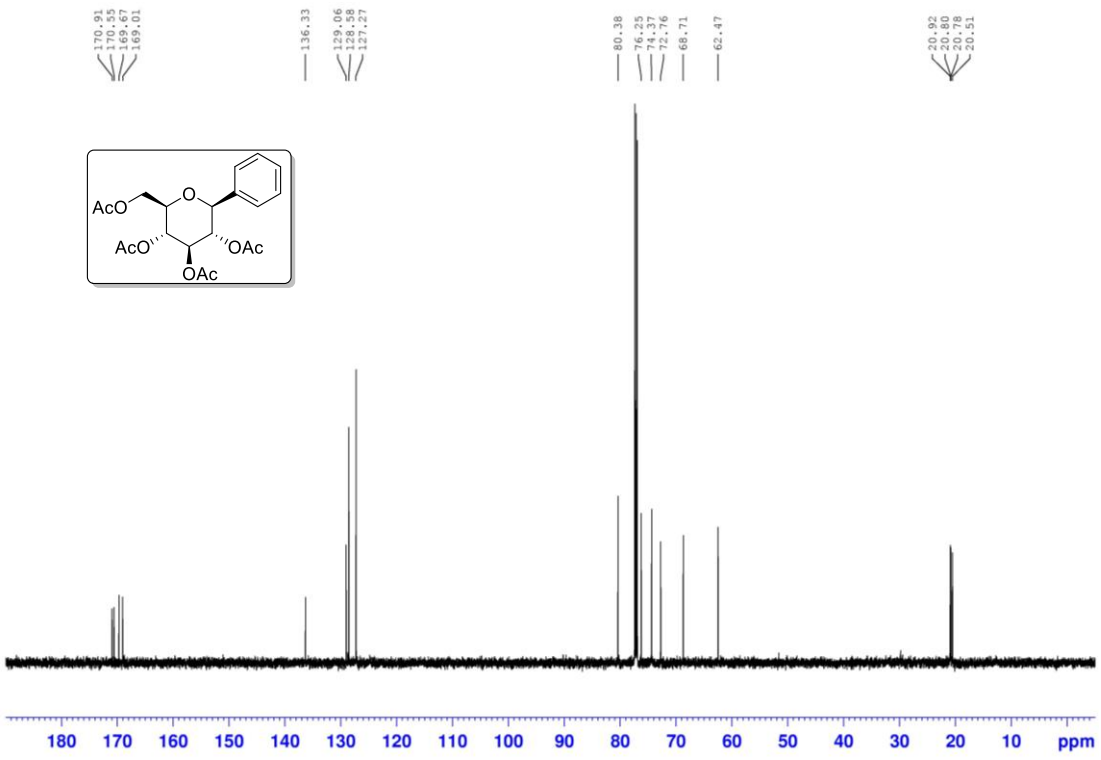
1.08
1.00
1.01
1.02
1.06
1.07
1.04
3.10
3.00
3.07
3.07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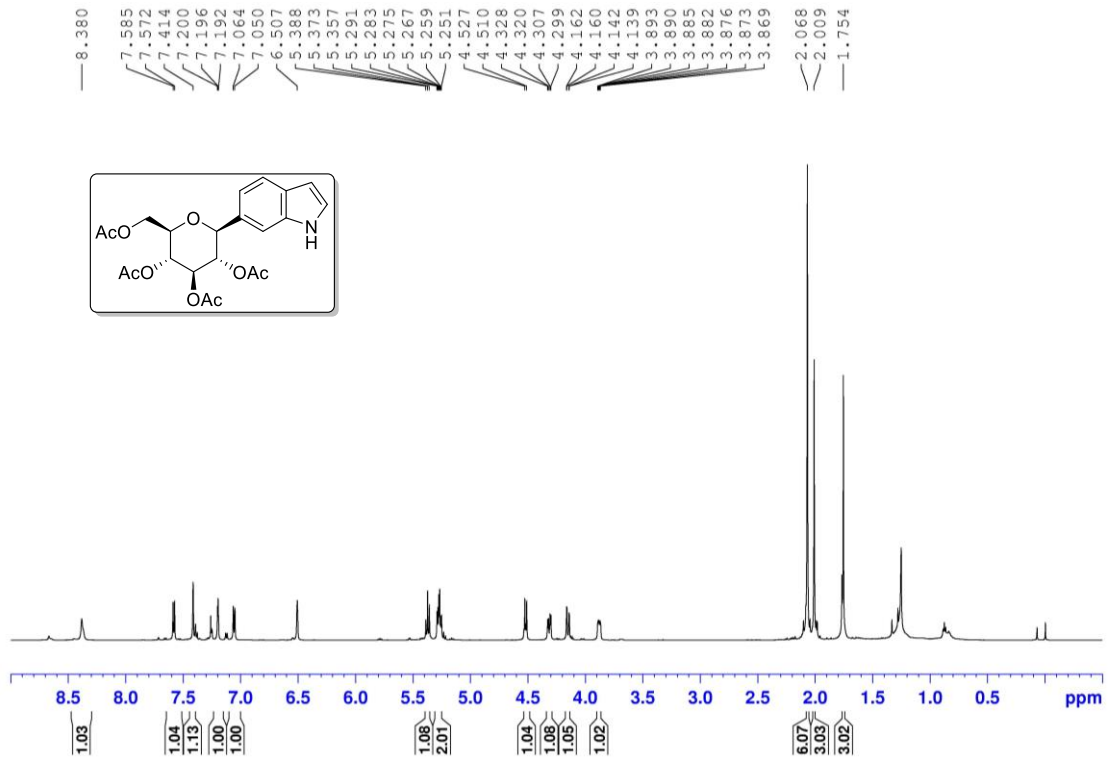
127.27
80.38
76.25
74.37
72.76
68.71
62.47
20.92
20.80
20.78
20.51
AcO
AcO
OAc
OAc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.388
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5.357
5.291
5.283
5.275
5.267
5.259
5.251
4.527
4.510
4.328
4.320
4.307
4.299
4.162
4.160
4.142
4.139
3.893
3.890
3.885
3.882
3.876
3.873
3.869
2.068
2.009
1.754
AcO
AcO
OAc
OAc
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
1.04
1.13
1.00
1.00
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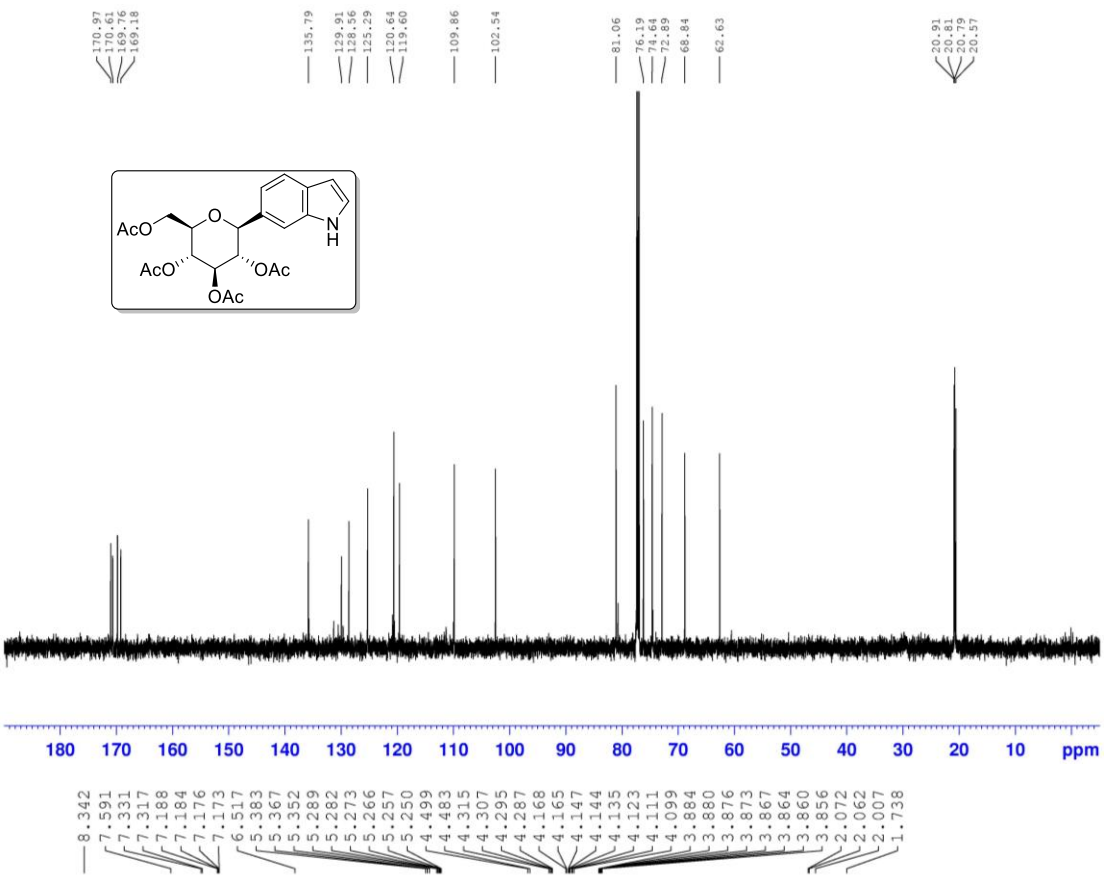
1.04
1.08
1.05
1.02
6.07
3.03
3.02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119.60
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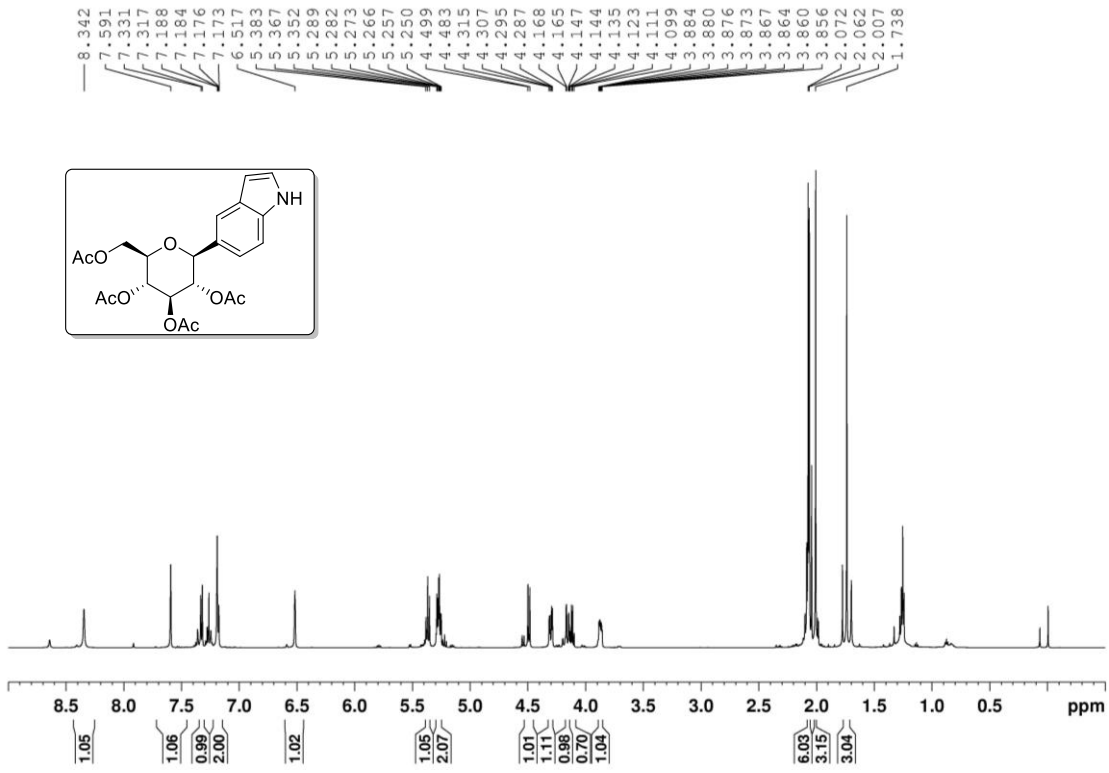
102.54
81.06
76.19
74.64
72.89
68.84
62.63
20.91
20.81
20.79
20.57
AcO
AcO
OAc
OAc
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.289
5.282
5.273
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5.257
5.250
4.499
4.483
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4.307
4.295
4.287
4.168
4.165
4.147
4.144
4.135
4.123
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4.099
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3.873
3.867
3.864
3.860
3.856
2.072
2.062
2.007
1.738
NH
AcO
AcO
OAc
OAc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.05
1.06
0.99
2.00
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2.07
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1.11
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0.70
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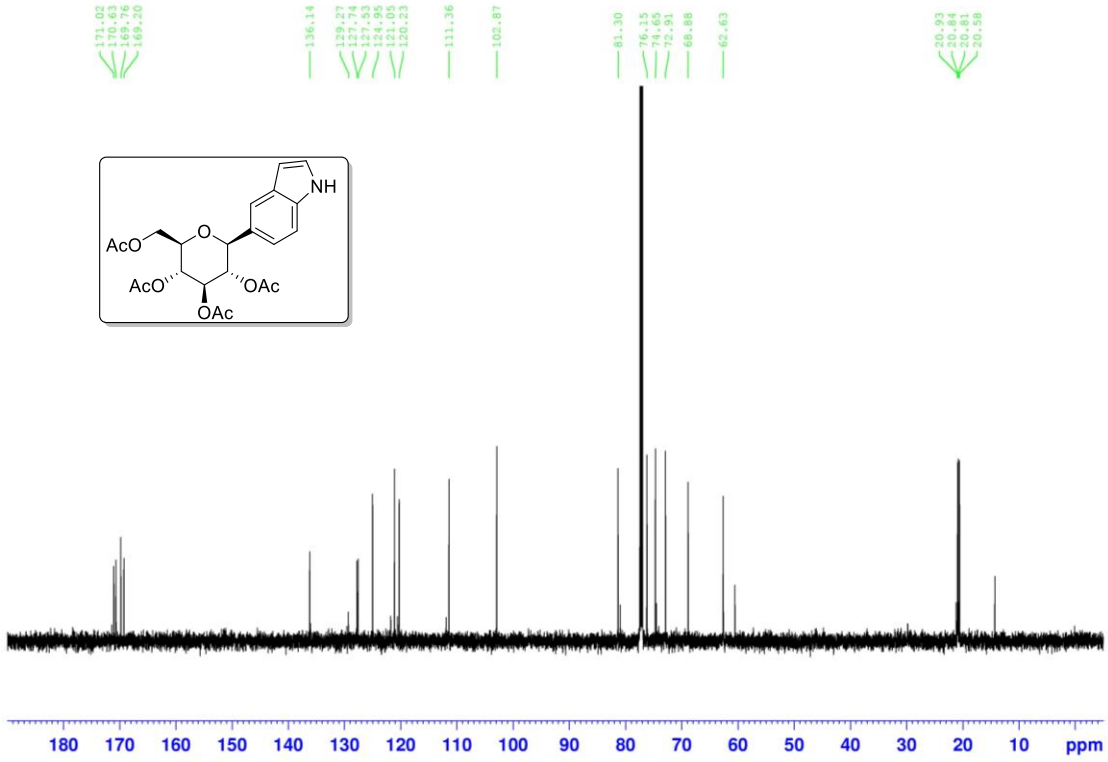
6.03
3.15
3.04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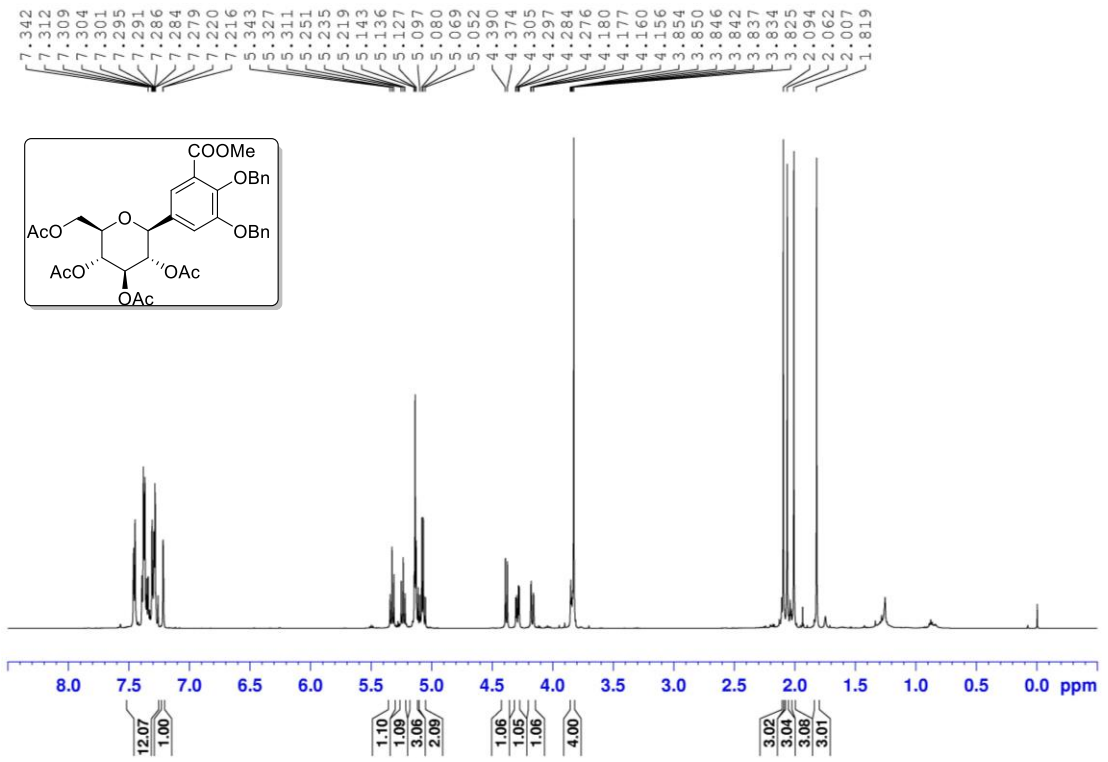
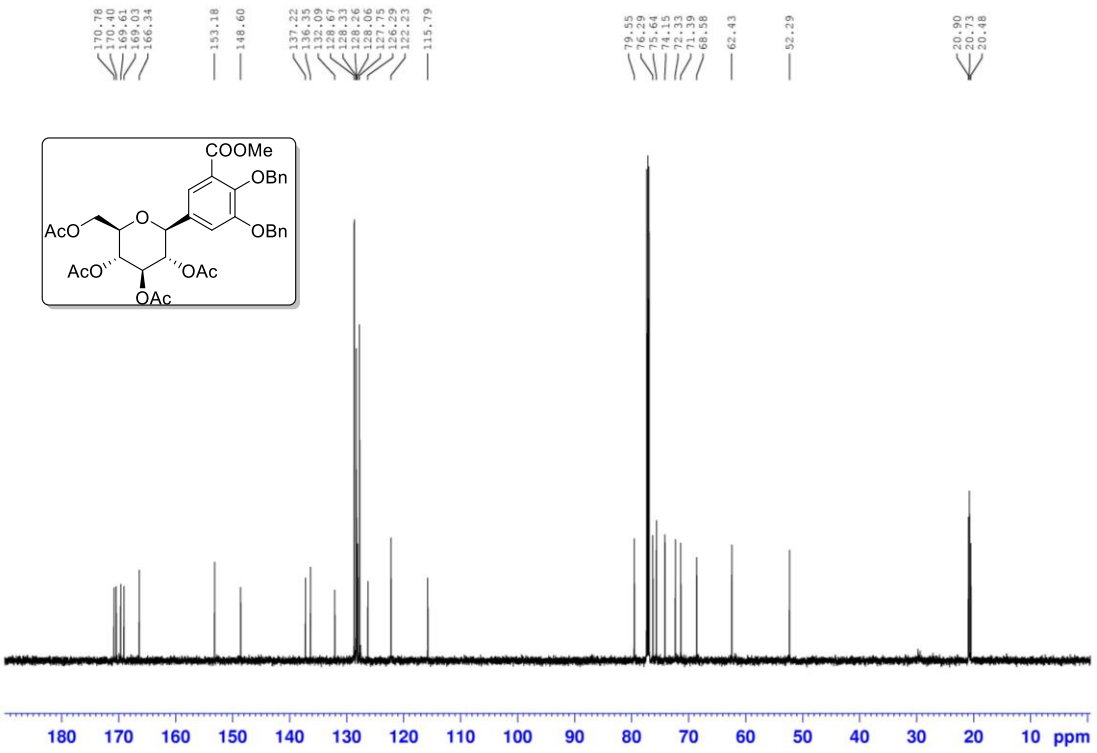
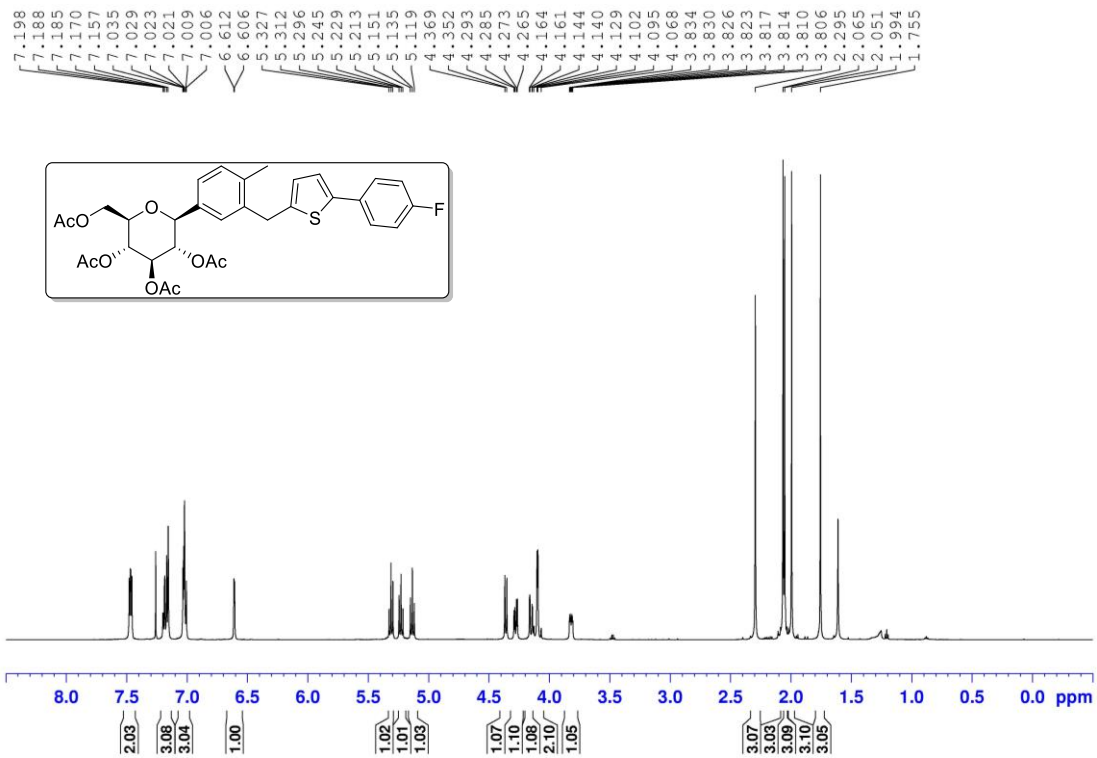
169.20
136.14
129.27
127.74
127.53
124.95
121.85
120.23
111.36
102.87
81.30
76.15
74.65
72.91
68.88
62.63
20.93
20.84
20.81
20.58
NH
AcO
O
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.342
7.312
7.309
7.304
7.301
7.295
7.291
7.286
7.284
7.279
7.220
7.216
5.343
5.327
5.311
5.251
5.235
5.219
5.143
5.136
5.127
5.097
5.080
5.069
5.052
4.390
4.374
4.305
4.297
4.284
4.276
4.180
4.177
4.160
4.156
3.854
3.850
3.846
3.842
3.837
3.834
3.825
2.094
2.062
2.007
1.819
COOMe
OBn
OBn
AcO
O
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
12.07
1.00
1.10
1.09
3.06
2.09
1.06
1.05
1.06
4.00
3.02
3.04
3.08
3.01


170.78
170.40
169.61
169.03
166.34
153.18
148.60
137.22
136.35
128.69
128.67
128.33
128.26
128.06
127.75
126.29
122.23
115.79
79.55
76.29
75.64
74.15
72.33
71.39
68.58
62.43
52.29
20.90
20.73
20.48
COOMe
OBn
OBn
AcO
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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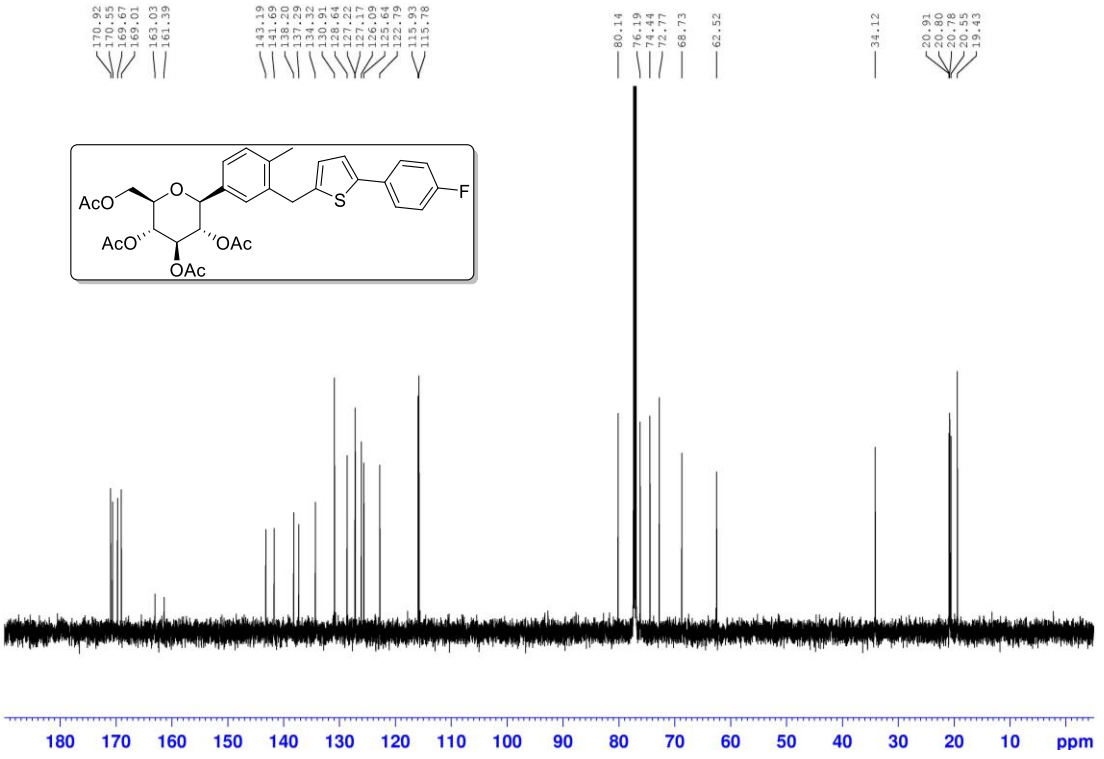
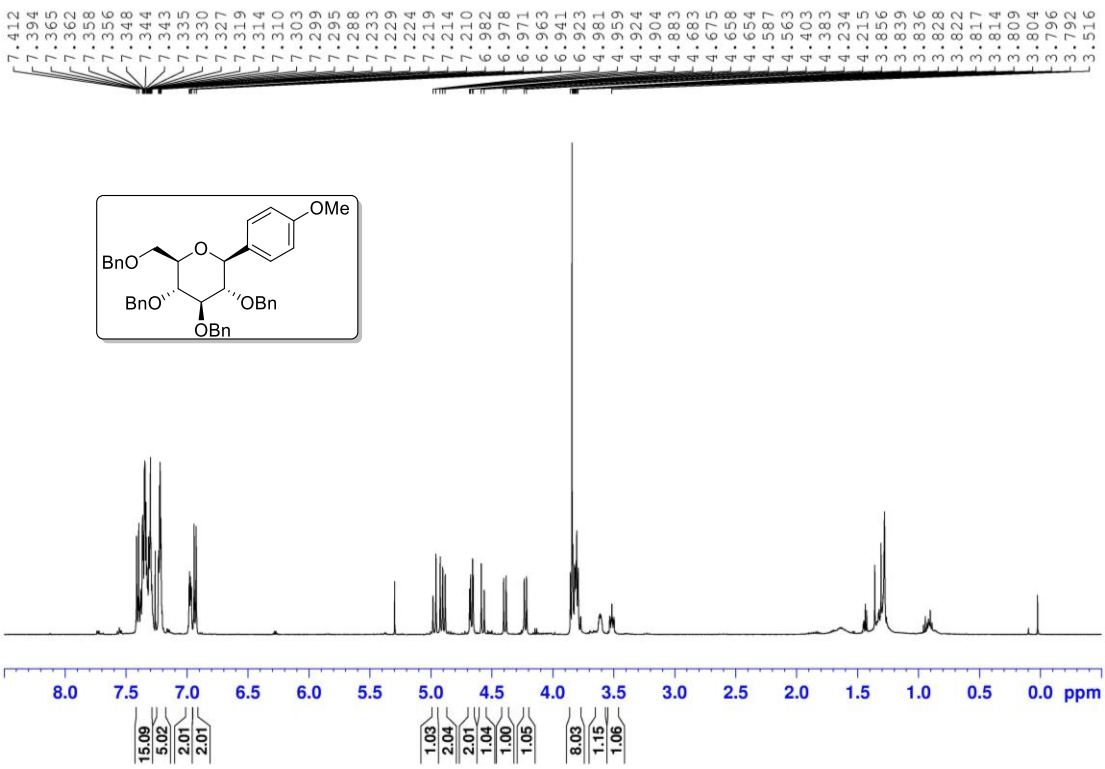
7.188
7.185
7.170
7.157
7.035
7.029
7.023
7.021
7.009
7.006
6.612
6.606
5.327
5.312
5.296
5.245
5.229
5.213
5.151
5.135
5.119
4.369
4.352
4.293
4.285
4.273
4.265
4.164
4.161
4.144
4.140
4.129
4.102
4.095
4.068
3.834
3.830
3.826
3.823
3.817
3.814
3.810
3.806
2.295
2.065
2.051
1.994
1.755
AcO
AcO
OAc
OAc
S
F
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03
3.08
3.04
1.00
1.02
1.01
1.03
1.07
1.10
1.08
2.10
1.05
3.07
3.03
3.09
3.10
3.05


170.92
170.55
169.67
169.01
163.03
161.39
143.19
141.69
138.20
137.29
134.32
130.91
129.64
129.22
127.17
126.09
125.64
122.79
115.93
115.78
80.14
76.19
74.44
72.77
68.73
62.52
34.12
20.91
20.80
20.78
20.55
19.43
AcO
AcO
OAc
OAc
O
S
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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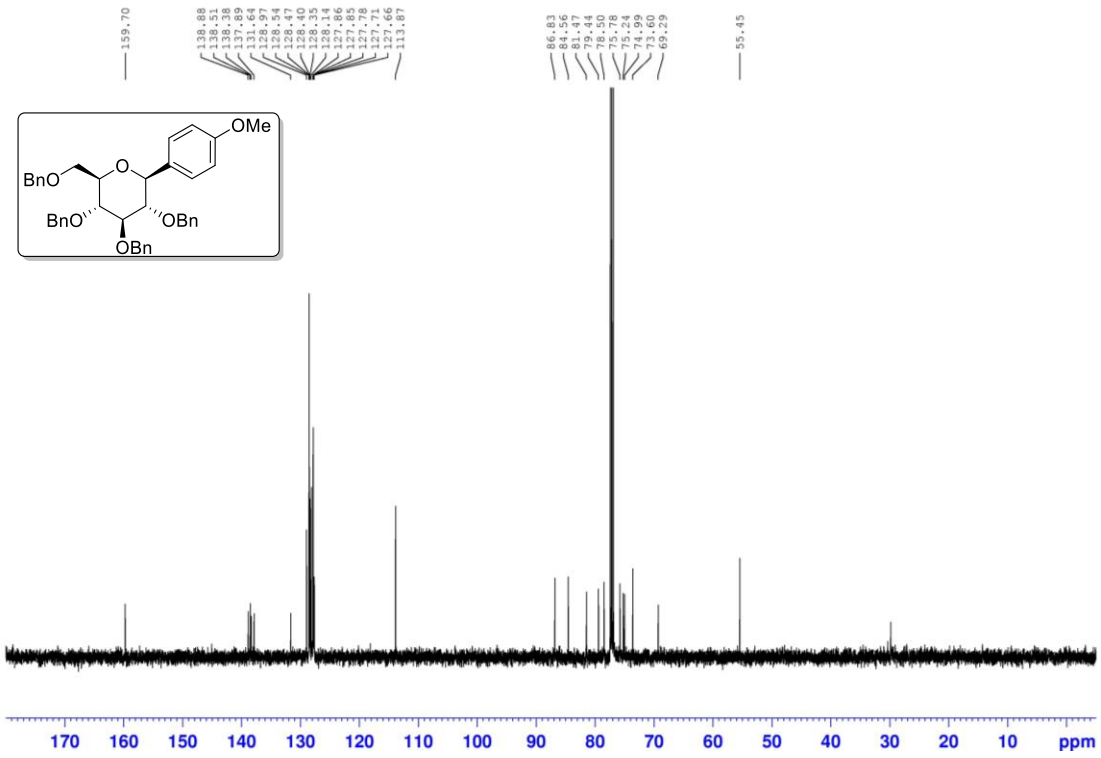
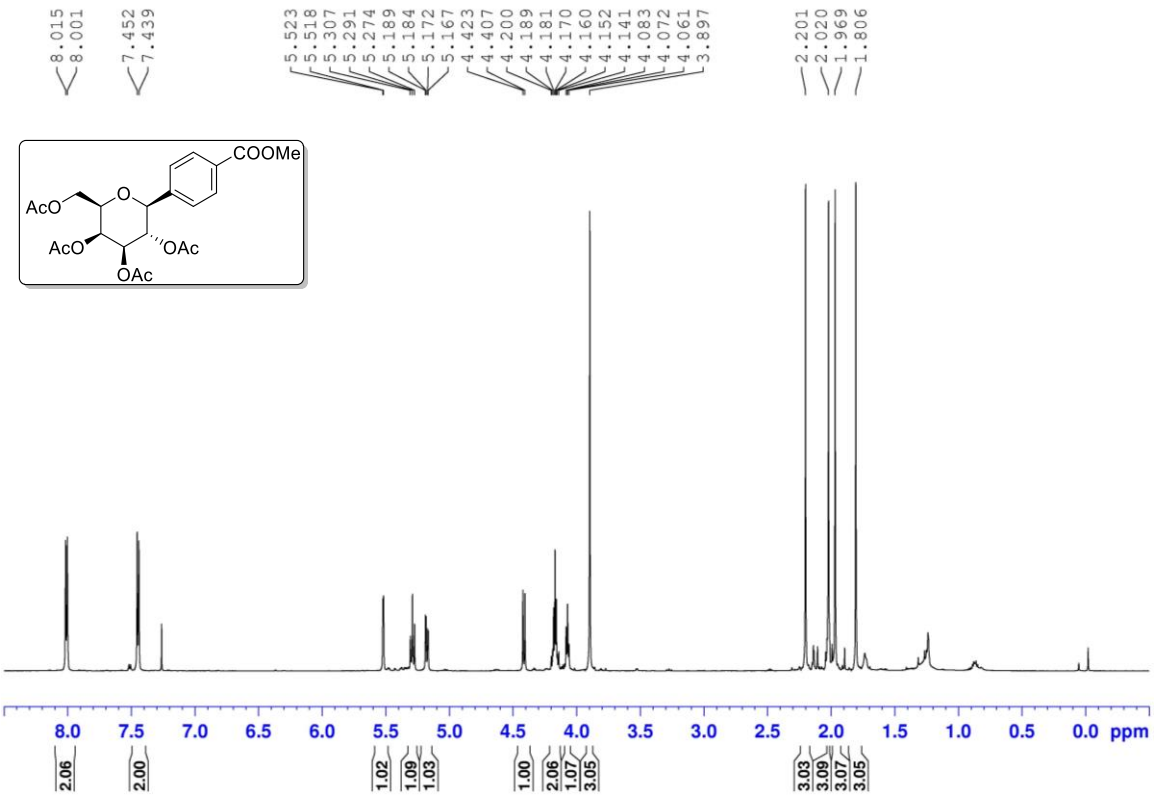
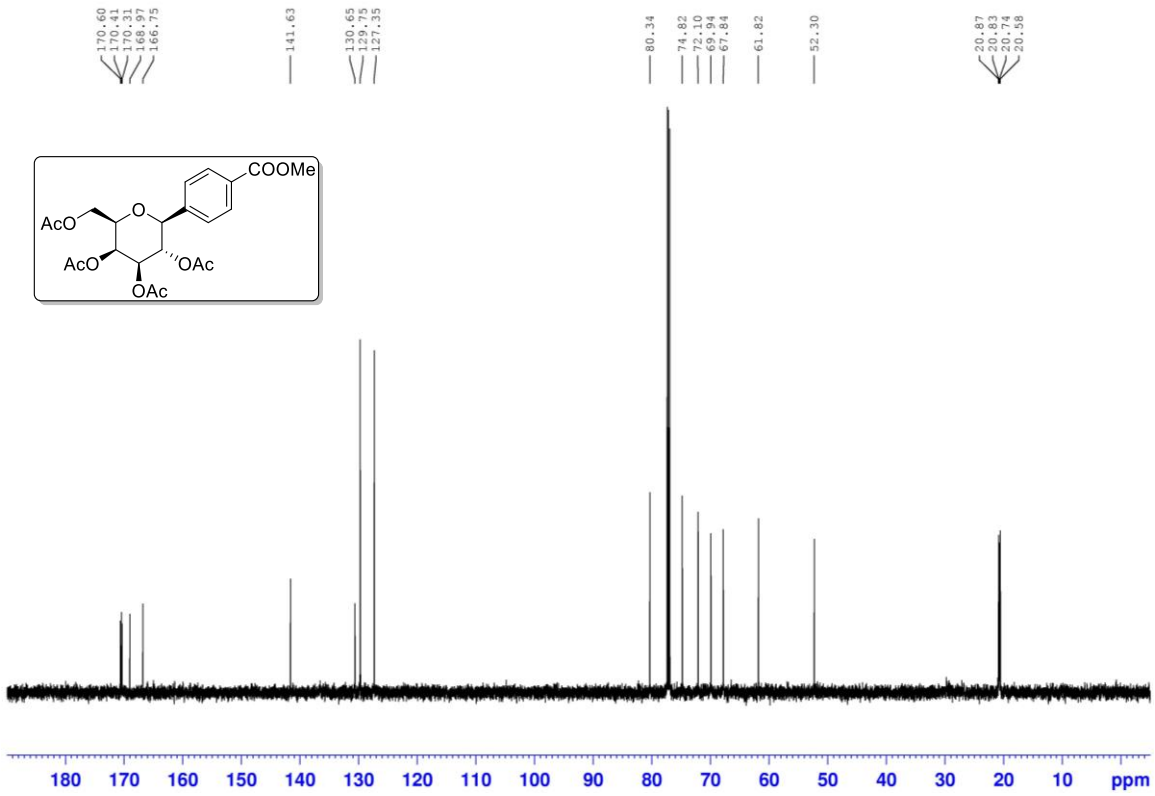
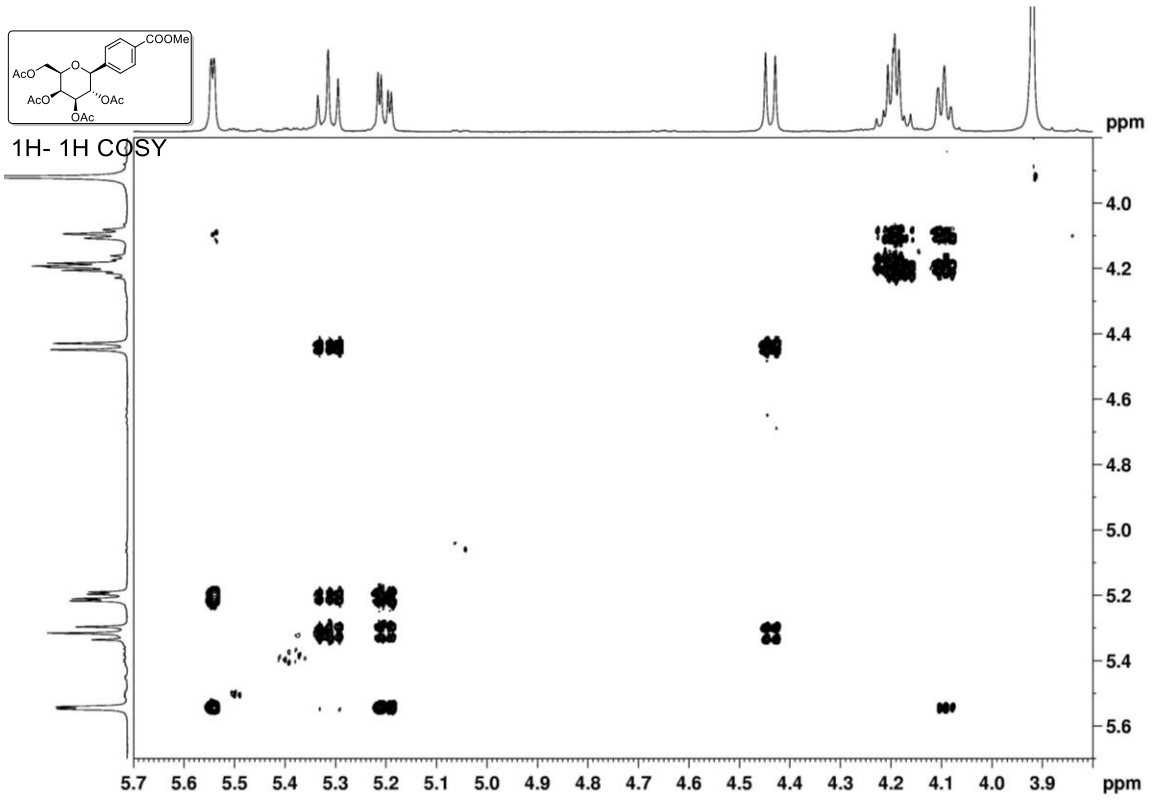
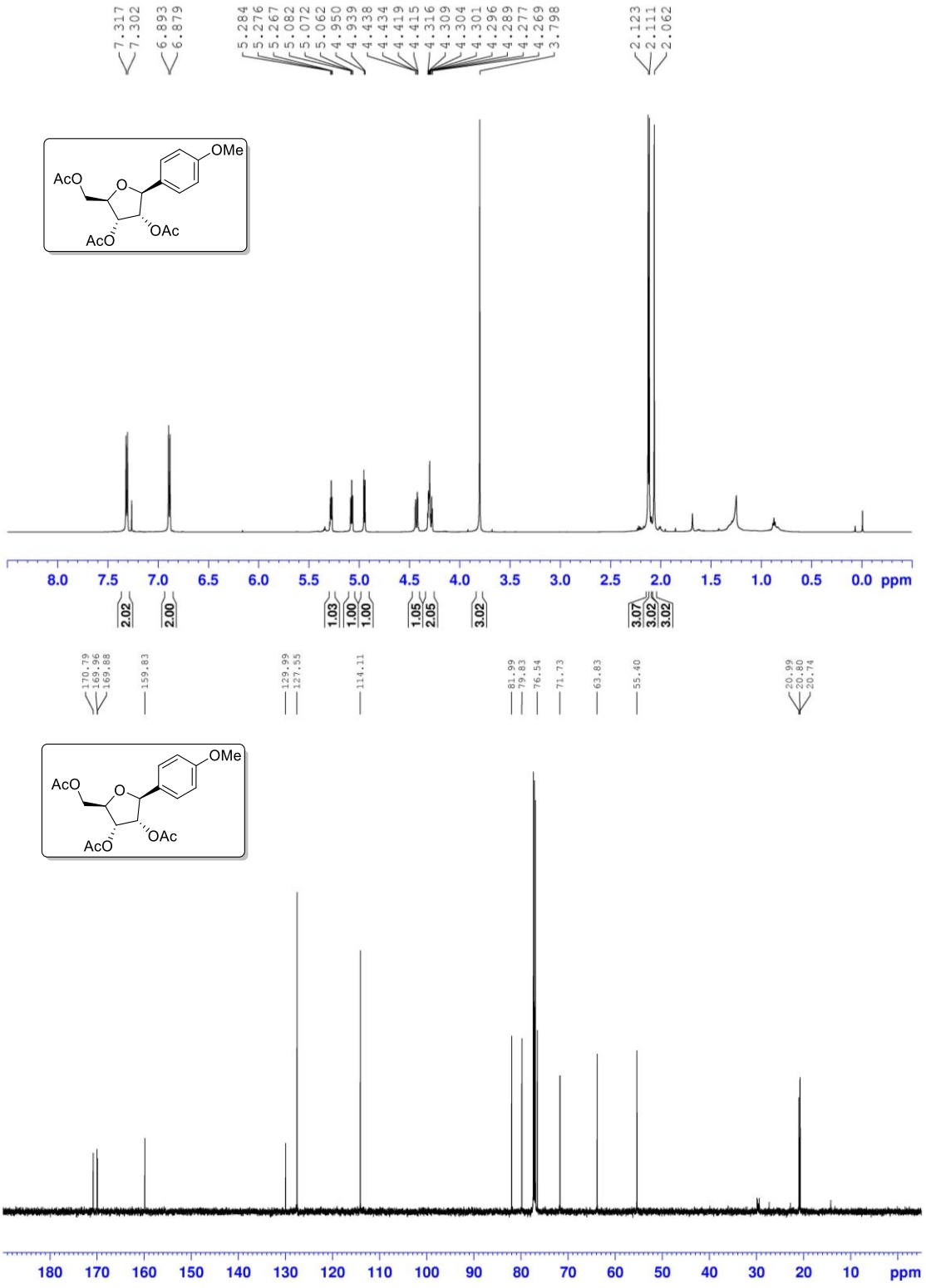
7.394
7.365
7.362
7.358
7.356
7.348
7.344
7.343
7.335
7.330
7.327
7.319
7.314
7.310
7.303
7.299
7.295
7.288
7.233
7.229
7.224
7.219
7.214
7.210
6.982
6.978
6.971
6.963
6.941
6.923
4.981
4.959
4.924
4.904
4.883
4.683
4.675
4.658
4.654
4.587
4.563
4.403
4.383
4.234
4.215
3.856
3.839
3.836
3.828
3.822
3.817
3.814
3.809
3.804
3.796
3.792
3.516
OMe
BnO
BnO
OBn
OBn
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
15.09
5.02
2.01
2.01
1.03
2.04
2.01
1.04
1.00
1.05
8.03
1.15
1.06

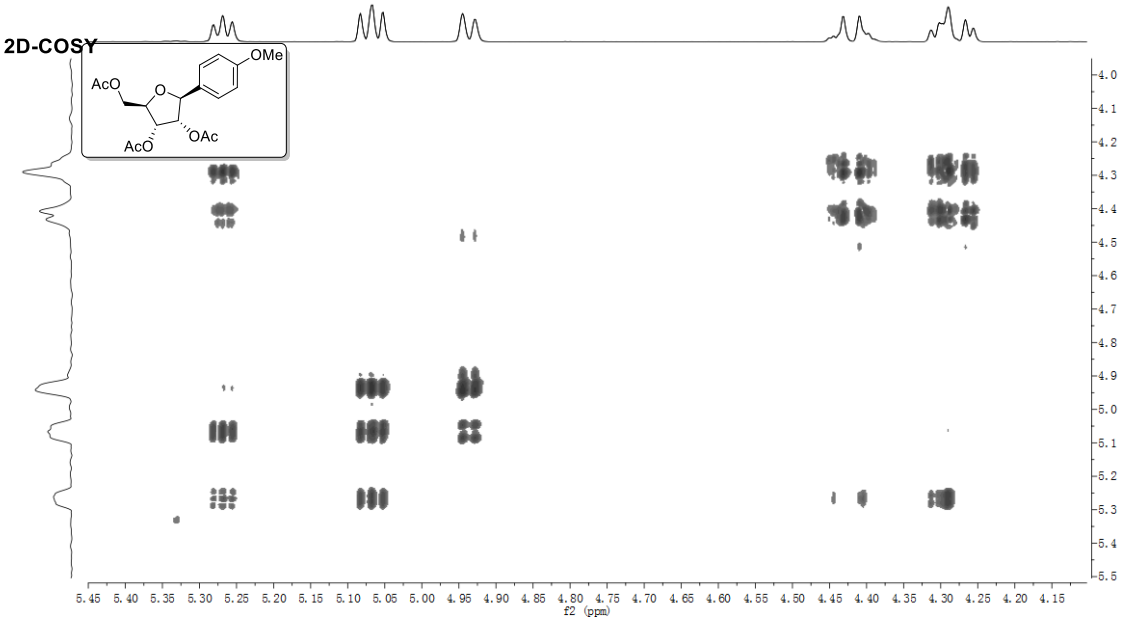

159.70
138.88
138.51
138.38
137.89
131.64
128.97
128.54
128.47
128.40
128.35
128.14
127.86
127.85
127.78
127.71
127.66
113.87
86.83
84.56
81.47
79.44
78.50
75.78
75.34
74.99
73.60
69.29
55.45
OMe
BnO
O
BnO
OBn
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

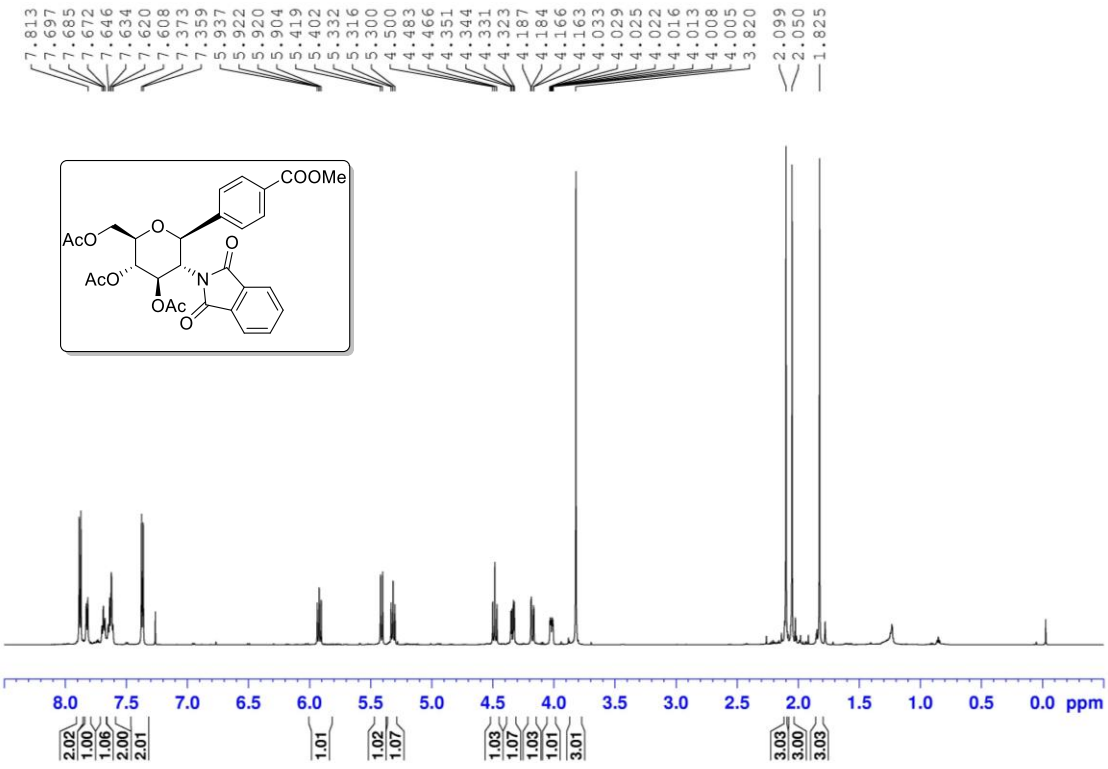

8.015
8.001
7.452
7.439
5.523
5.518
5.307
5.291
5.274
5.189
5.184
5.172
5.167
4.423
4.407
4.200
4.189
4.181
4.170
4.160
4.152
4.141
4.083
4.072
4.061
3.897
2.201
2.020
1.969
1.806
COOMe
AcO
O
AcO
OAc
OAc
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.06
2.00
1.02
1.09
1.03
1.00
2.06
1.07
3.05
3.03
3.09
3.07
3.05

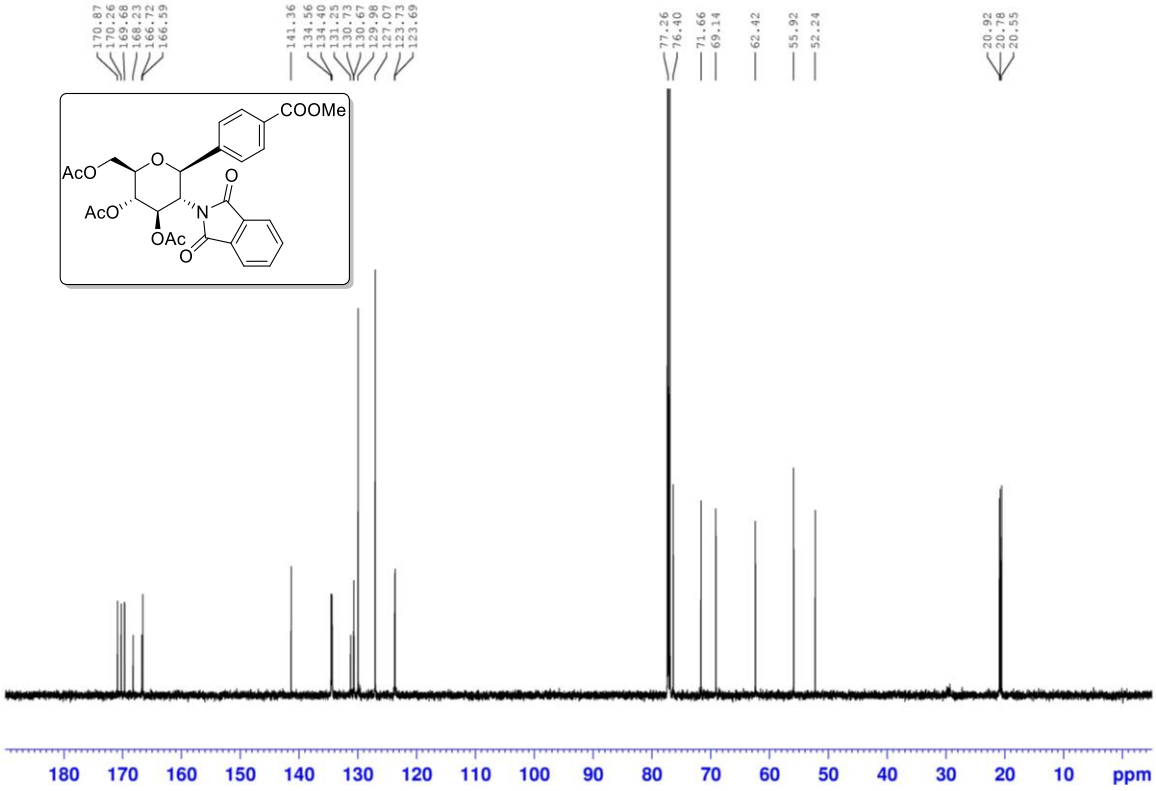

170.60
170.41
170.31
168.97
166.75
141.63
130.65
129.75
127.35
80.34
74.82
72.10
69.94
67.84
61.82
52.30
20.87
20.83
20.74
20.58
COOMe
AcO
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

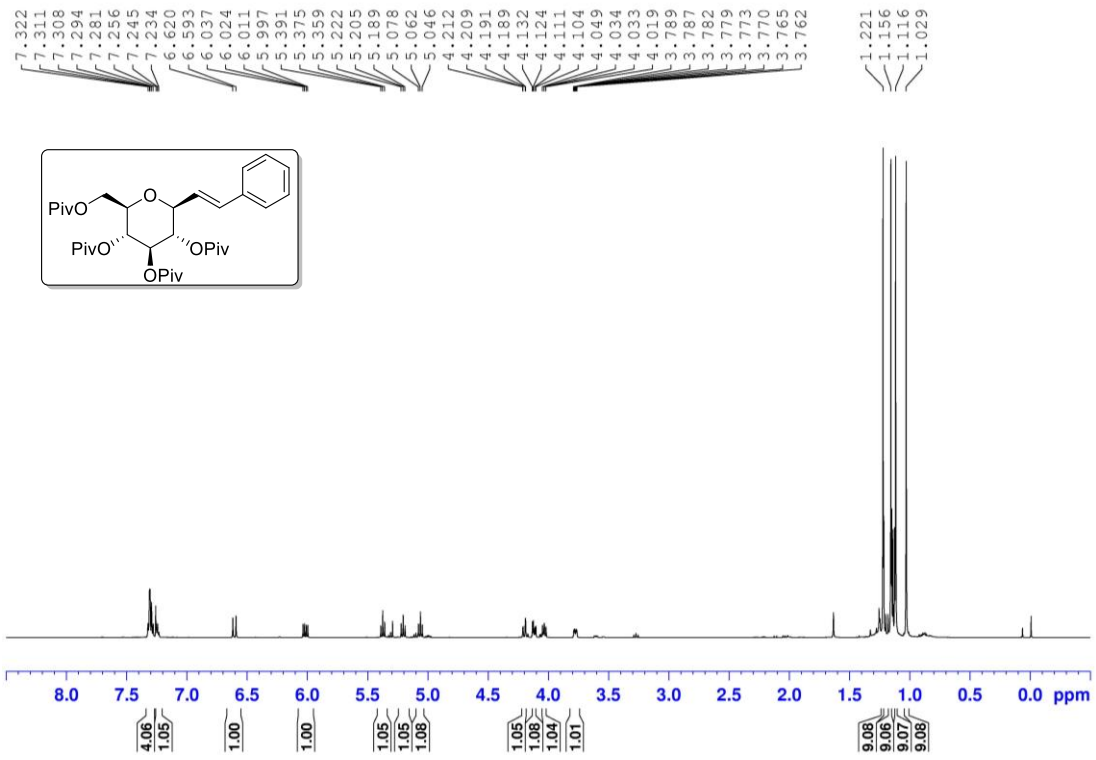

COOMe
AcO
AcO
OAc
OAc
1H- 1H COSY
ppm
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 ppm

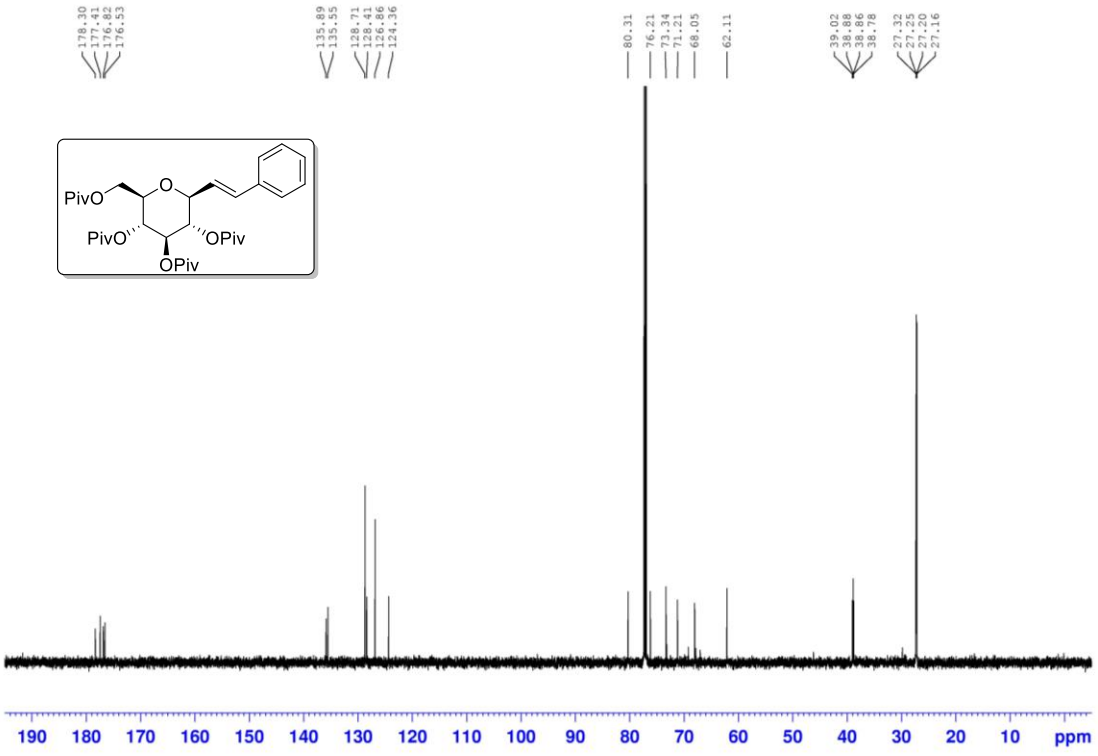

7.317
7.302
6.893
6.879
5.284
5.276
5.267
5.082
5.072
5.062
4.950
4.939
4.438
4.434
4.419
4.415
4.316
4.309
4.304
4.301
4.296
4.289
4.277
4.269
3.798
2.123
2.111
2.062
OMe
AcO
O
OAc
AcO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
2.00
1.03
1.00
1.00
1.05
2.05
3.02
3.07
3.02
3.02
170.79
169.96
169.88
159.83
129.99
127.55
114.11
81.99
79.83
76.54
71.73
63.83
55.40
20.99
20.80
20.74
OMe
AcO
O
OAc
AcO
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

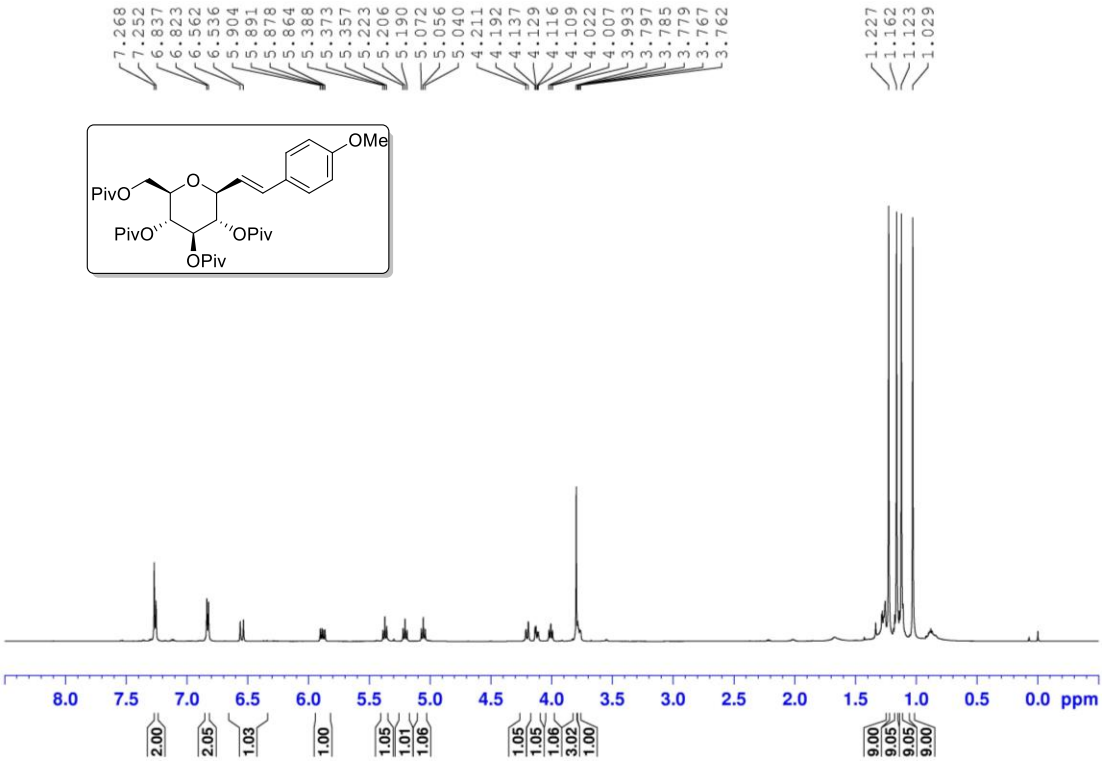

2D-COSY
OMe
AcO
AcO
OAc
f2 (ppm)

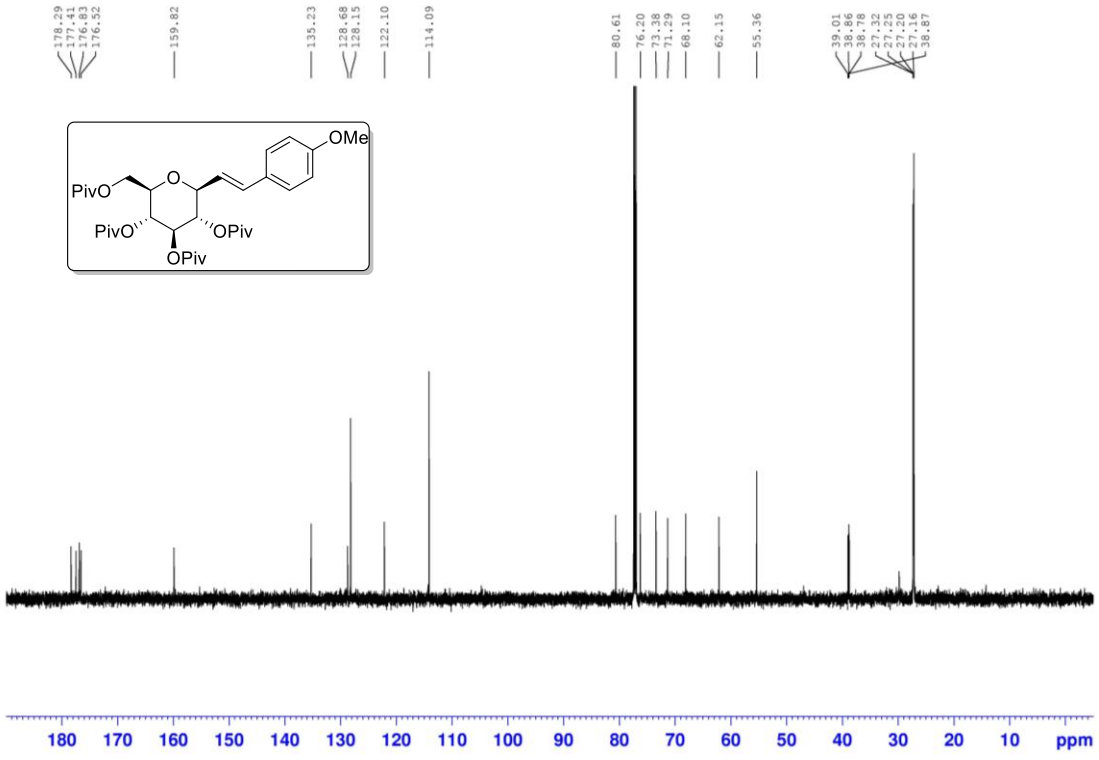

7.813
7.697
7.685
7.672
7.646
7.634
7.620
7.608
7.373
7.359
5.937
5.922
5.920
5.904
5.419
5.402
5.332
5.316
5.300
4.500
4.483
4.466
4.351
4.344
4.331
4.323
4.187
4.184
4.166
4.163
4.033
4.029
4.025
4.022
4.016
4.013
4.008
4.005
3.820
2.099
2.050
1.825
COOMe
AcO
AcO
OAc
O
N
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.02
1.00
1.06
2.00
2.01
1.01
1.02
1.07
1.03
1.07
1.03
1.01
3.01
3.03
3.00
3.03

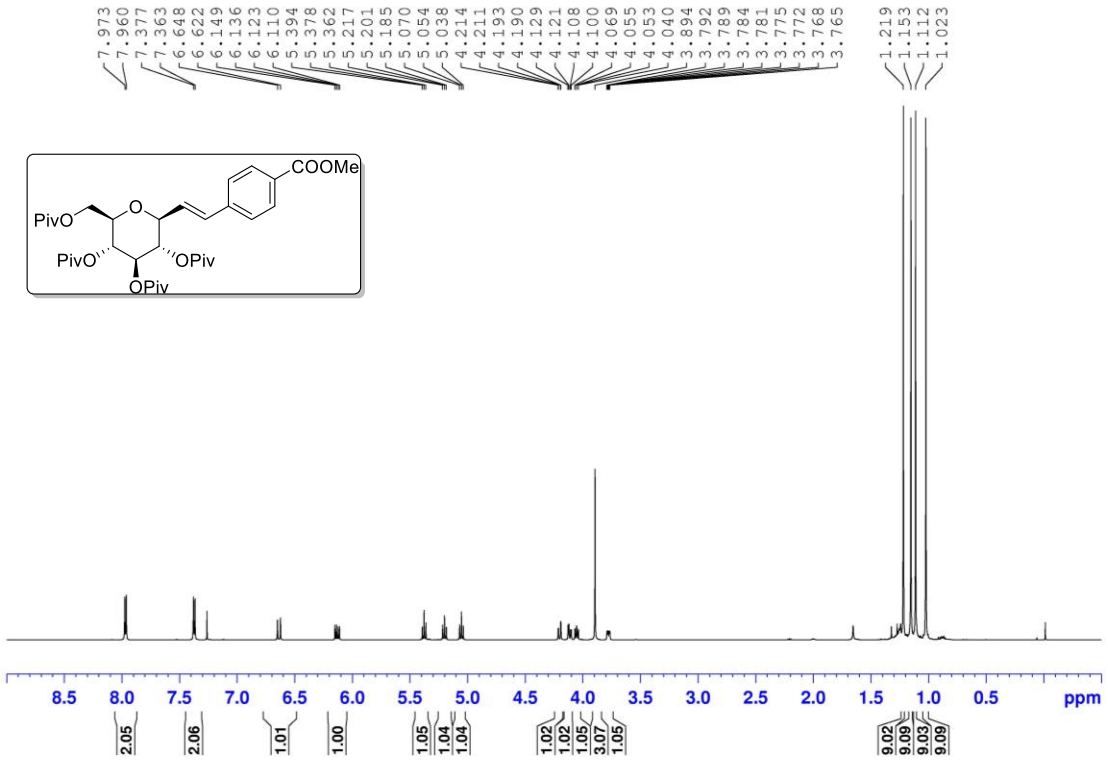

170.87
170.26
169.68
168.23
166.72
166.59
141.36
134.56
134.40
131.25
130.73
130.67
129.98
127.07
123.73
123.69
77.26
76.40
71.66
69.14
62.42
55.92
52.24
20.92
20.78
20.55
COOMe
AcO
AcO
OAc
O
N
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

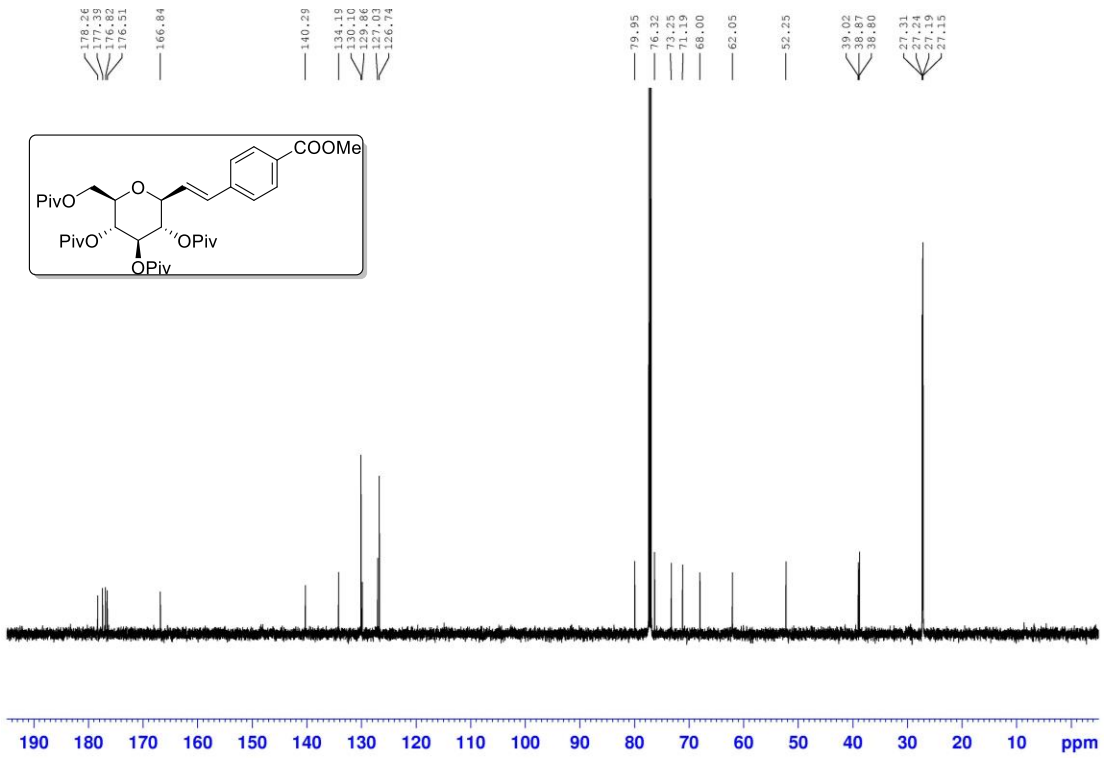

7.322
7.311
7.308
7.294
7.281
7.256
7.245
7.234
6.620
6.593
6.037
6.024
6.011
5.997
5.391
5.375
5.359
5.222
5.205
5.189
5.078
5.062
5.046
4.212
4.209
4.191
4.189
4.132
4.124
4.111
4.104
4.049
4.034
4.033
4.019
3.789
3.787
3.782
3.779
3.773
3.770
3.765
3.762
1.221
1.156
1.116
1.029
PivO
PivO
OPiv
OPiv
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.06
1.05
1.00
1.00
1.05
1.05
1.08
1.05
1.08
1.04
1.01
9.08
9.06
9.07
9.08

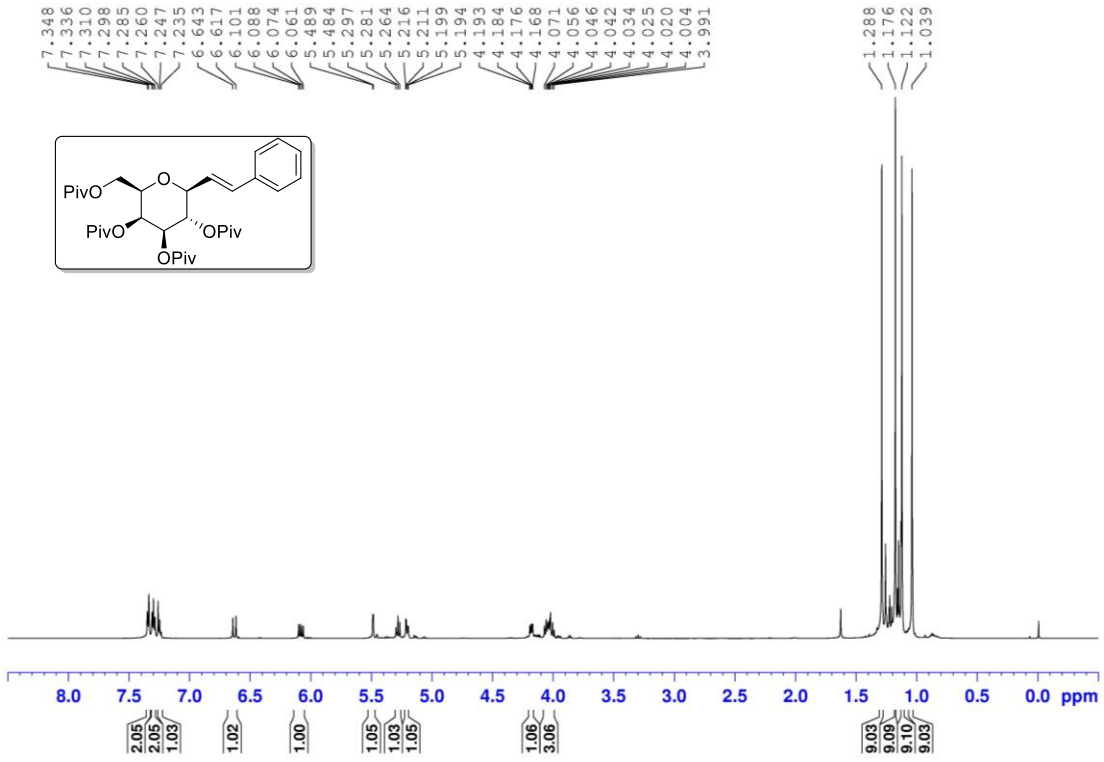

178.30
177.41
176.82
176.53
135.89
135.55
128.71
128.41
126.86
124.36
80.31
76.21
73.34
71.21
68.05
62.11
39.02
38.88
38.86
38.78
27.32
27.25
27.20
27.16
PivO
PivO
OPiv
OPiv
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.268
7.252
6.837
6.823
6.562
6.536
5.904
5.891
5.878
5.864
5.388
5.373
5.357
5.223
5.206
5.190
5.072
5.056
5.040
4.211
4.192
4.137
4.129
4.116
4.109
4.022
4.007
3.993
3.797
3.785
3.779
3.767
3.762
1.227
1.162
1.123
1.029
OMe
PivO
PivO
OPiv
OPiv
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
2.05
1.03
1.00
1.05
1.01
1.06
1.05
1.05
1.06
3.02
1.00
9.00
9.05
9.05
9.00


178.29
177.41
176.83
176.52
159.82
135.23
128.68
128.15
122.10
114.09
80.61
76.20
73.38
71.29
68.10
62.15
55.36
39.01
38.86
38.78
27.32
27.25
27.20
27.16
38.87
OMe
PivO
PivO
OPiv
OPiv
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.973
7.960
7.377
7.363
6.648
6.622
6.149
6.136
6.123
6.110
5.394
5.378
5.362
5.217
5.201
5.185
5.070
5.054
5.038
4.214
4.211
4.193
4.190
4.129
4.121
4.108
4.100
4.069
4.055
4.053
4.040
3.894
3.792
3.789
3.784
3.781
3.775
3.772
3.768
3.765
1.219
1.153
1.112
1.023
COOMe
PivO
PivO
OPiv
OPiv
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05
2.06
1.01
1.00
1.05
1.04
1.04
1.02
1.02
1.05
3.07
1.05
9.02
9.09
9.03
9.09


178.26
177.33
176.82
176.51
166.84
140.29
134.19
130.10
129.86
127.03
126.74
79.95
76.32
73.25
71.19
68.00
62.05
52.25
39.02
38.87
38.80
27.31
27.24
27.19
27.15
COOMe
PivO
O
PivO
OPiv
OPiv
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.348
7.336
7.310
7.298
7.285
7.260
7.247
7.235
6.643
6.617
6.101
6.088
6.074
6.061
5.489
5.484
5.297
5.281
5.264
5.216
5.211
5.199
5.194
4.193
4.184
4.176
4.168
4.071
4.056
4.046
4.042
4.034
4.025
4.020
4.004
3.991
1.288
1.176
1.122
1.039
PivO
O
PivO
OPiv
OPiv
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
2.05
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1.05
1.03
1.05
1.06
3.06
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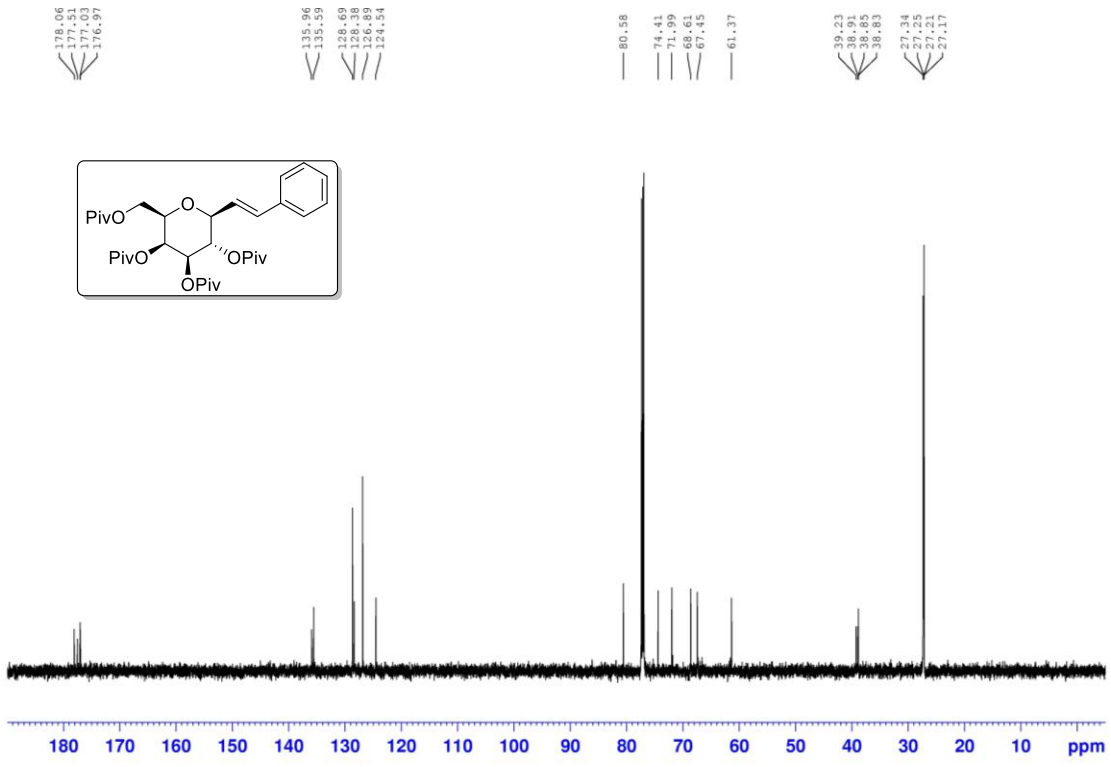
9.10
9.03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67.45
61.37
39.23
38.91
38.85
38.83
27.34
27.25
27.21
27.17
PivO
PivO
OPiv
OPiv
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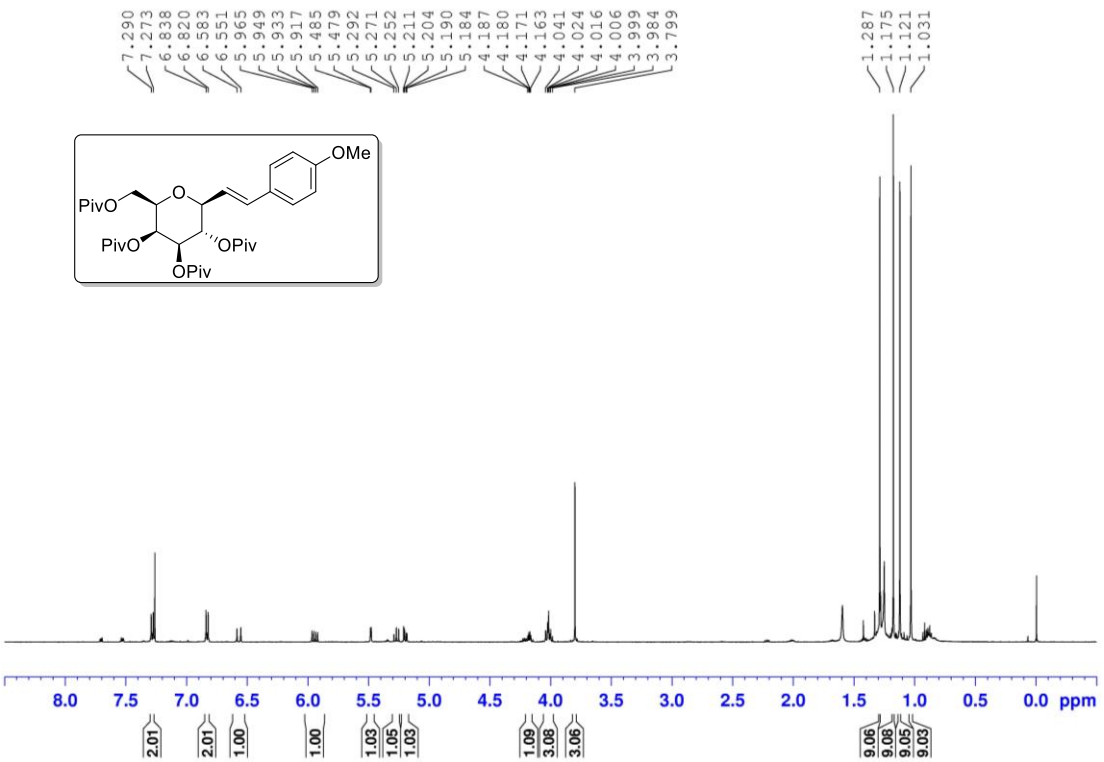
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5.479
5.292
5.271
5.252
5.211
5.204
5.190
5.184
4.187
4.180
4.171
4.163
4.041
4.024
4.016
4.006
3.999
3.984
3.799
1.287
1.175
1.121
1.031
OMe
PivO
PivO
OPiv
OPiv
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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2.01
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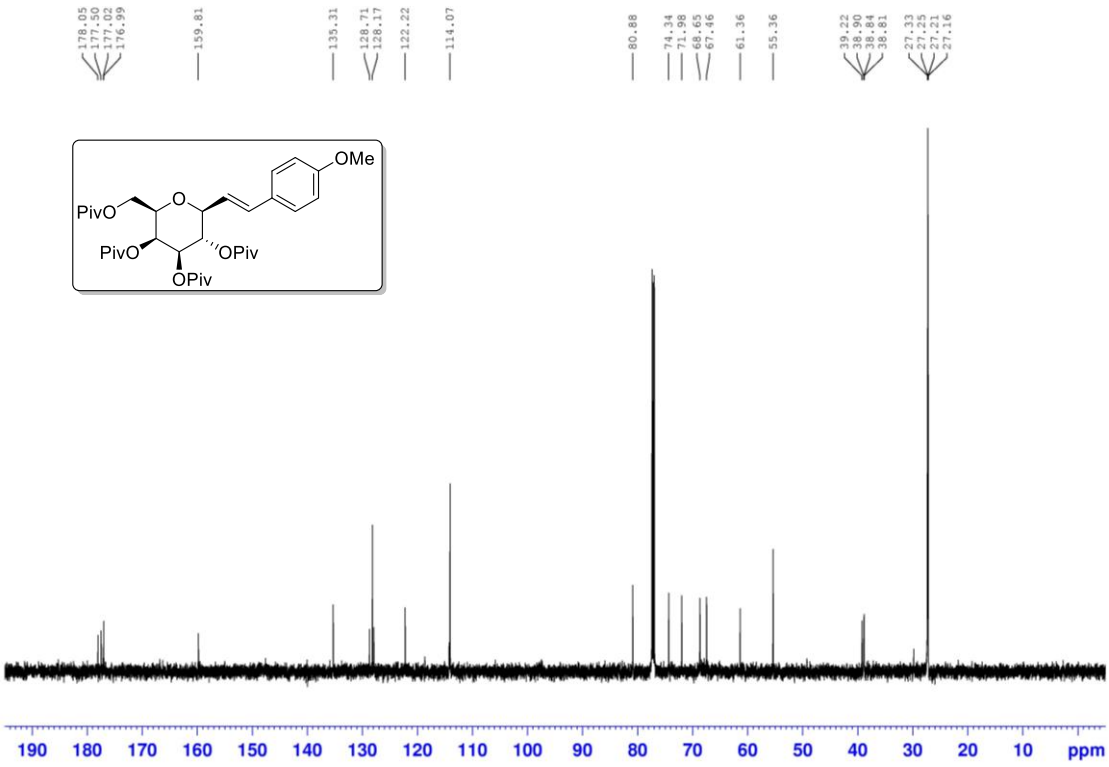
9.03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68.65
67.46
61.36
55.36
39.22
38.90
38.84
38.61
27.33
27.25
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27.16
OMe
PivO
O
PivO
OPiv
OPiv
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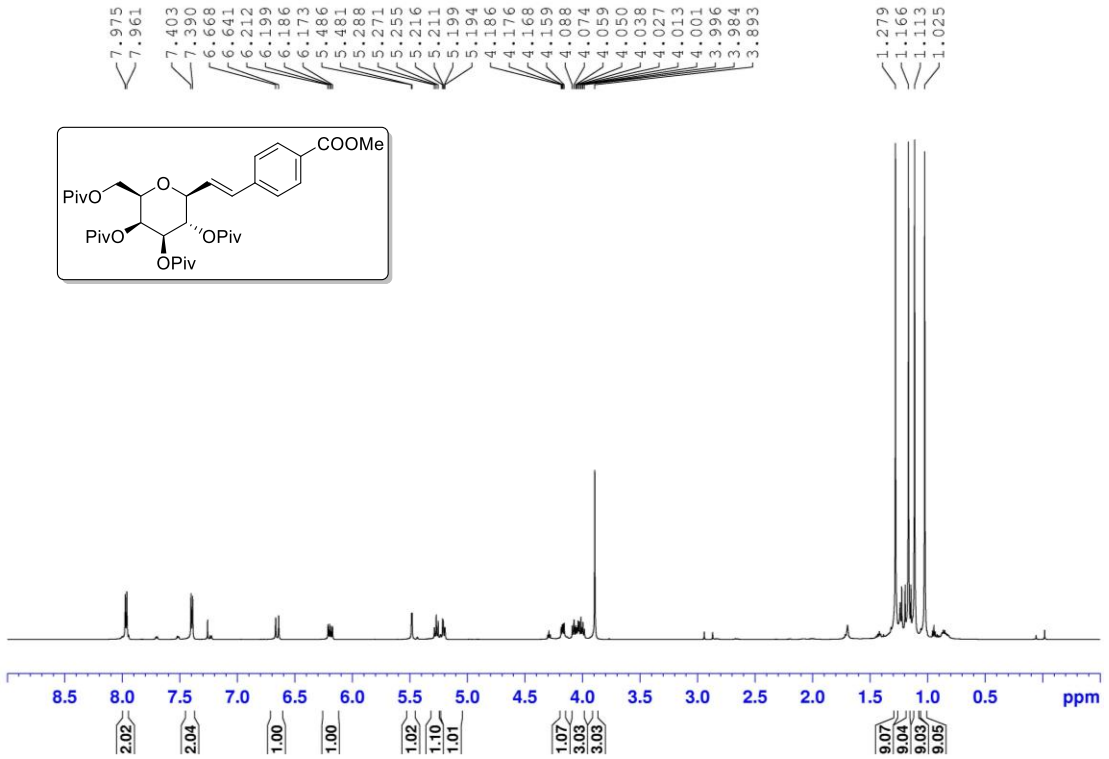
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5.271
5.255
5.216
5.211
5.199
5.194
4.186
4.176
4.168
4.159
4.088
4.074
4.059
4.050
4.038
4.027
4.013
4.001
3.996
3.984
3.893
1.279
1.166
1.113
1.025
COOMe
PivO
O
PivO
OPiv
OPiv
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
2.04
1.00
1.00
1.02
1.10
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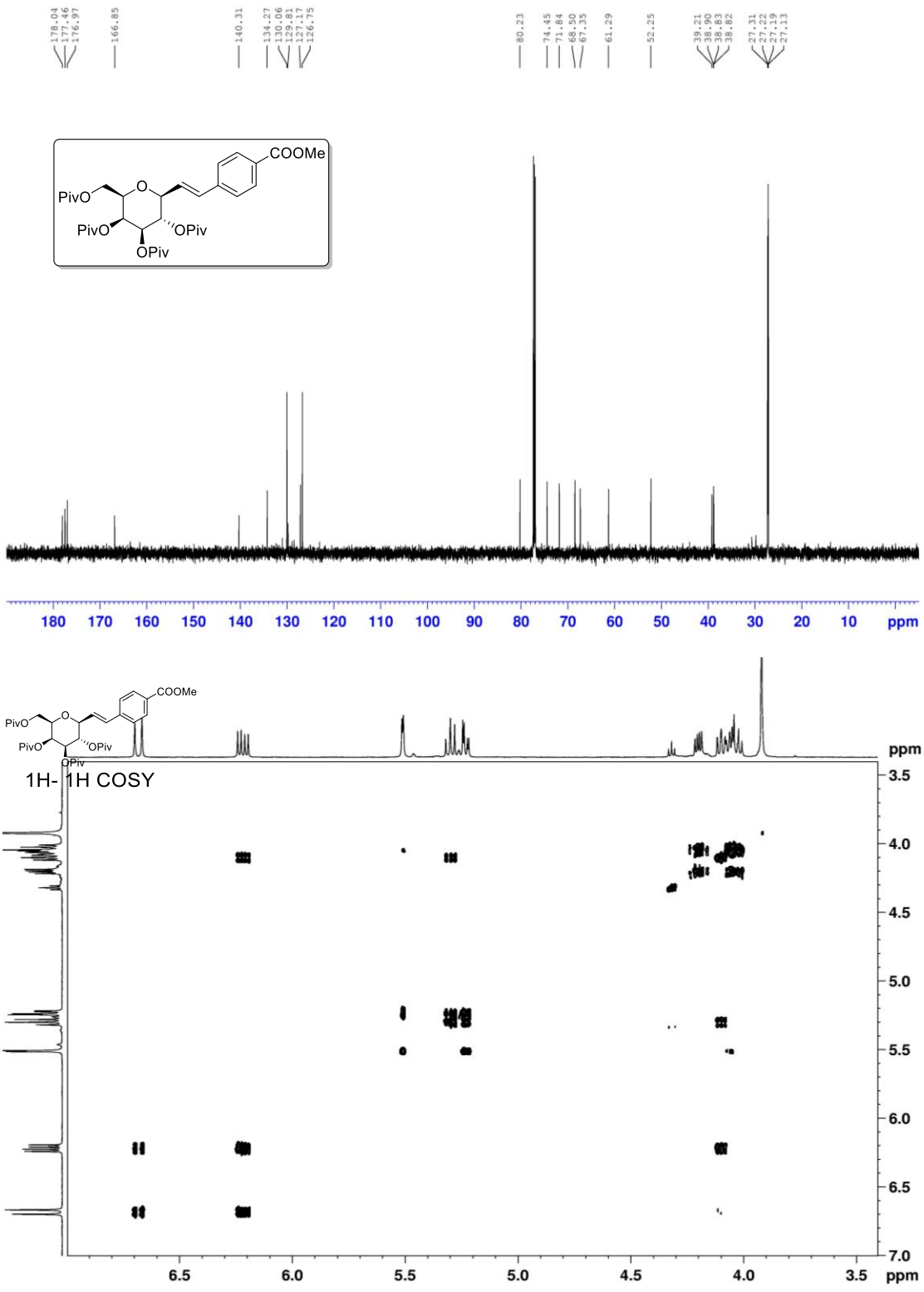
1.07
3.03
3.03
9.07
9.04
9.03
9.05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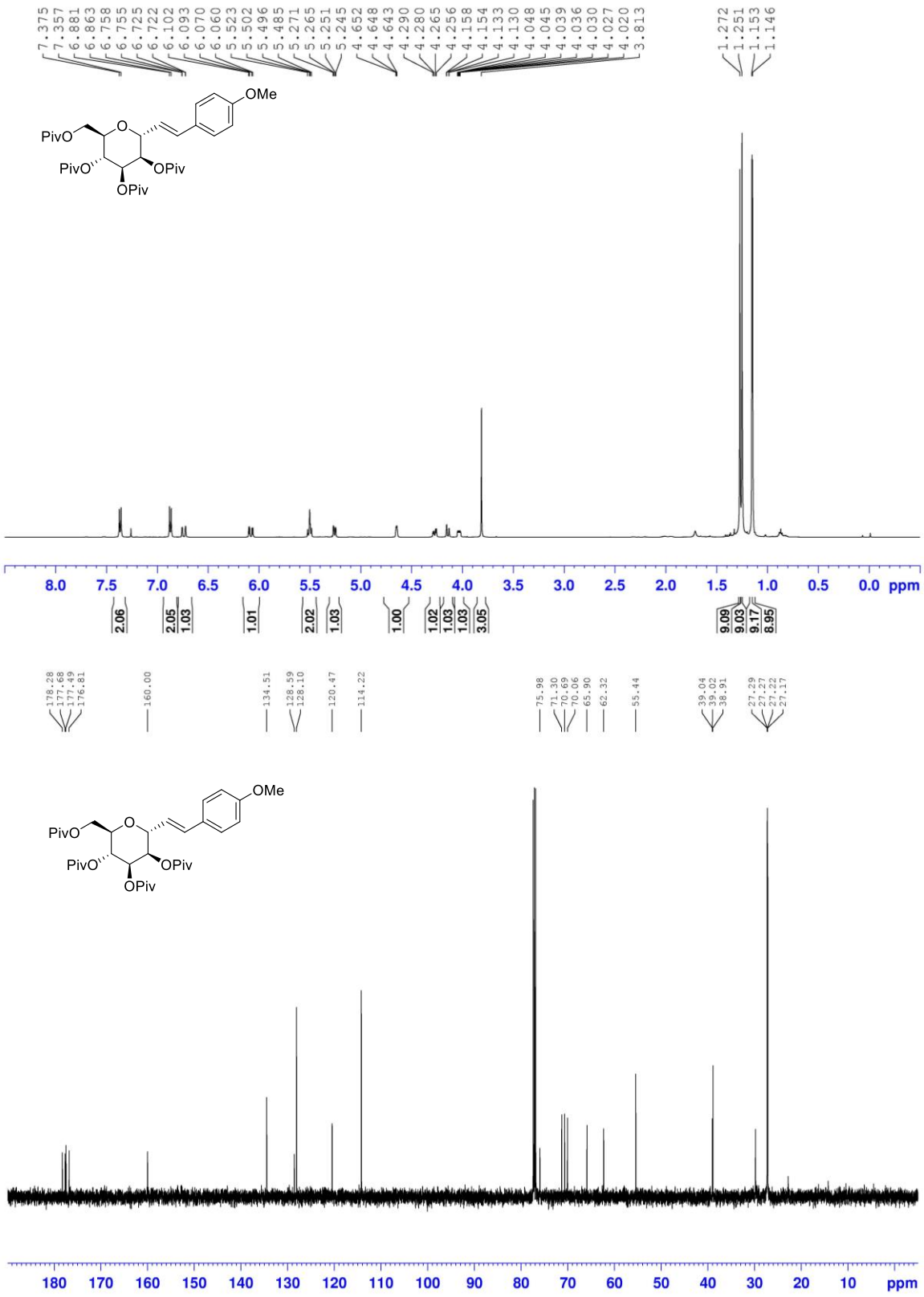
67.35
61.29
52.25
39.21
38.90
38.83
38.82
27.31
27.22
27.19
27.13
COOMe
PivO
PivO
OPiv
OPiv
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
1H- 1H COSY
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm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6.722
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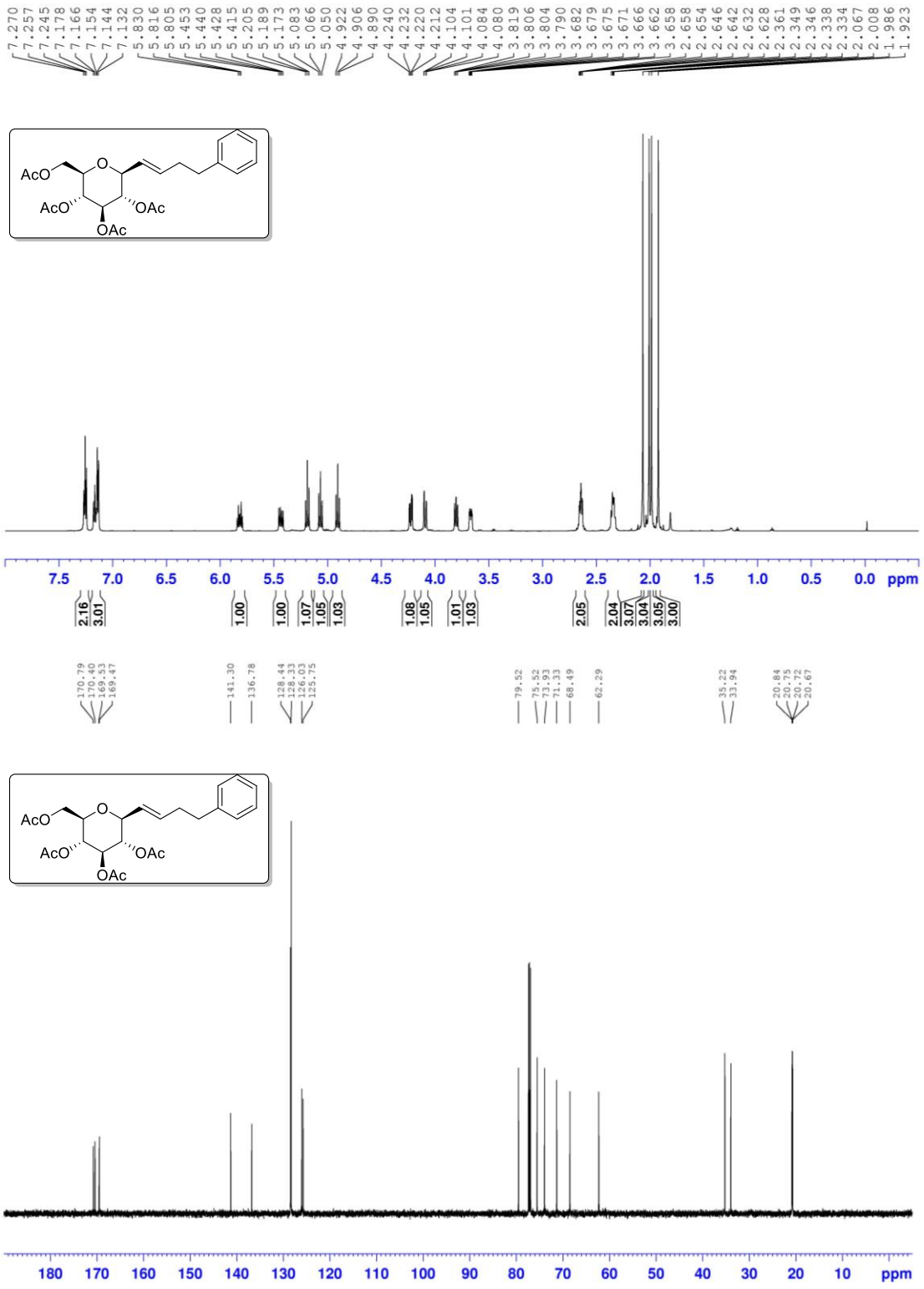
6.093
6.070
6.060
5.523
5.502
5.496
5.485
5.271
5.265
5.251
5.245
4.652
4.648
4.643
4.290
4.280
4.265
4.256
4.158
4.154
4.133
4.130
4.048
4.045
4.039
4.036
4.030
4.027
4.020
3.813
1.272
1.251
1.153
1.146
OMe
PivO
PivO
OPiv
OPiv
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.06
2.05
1.03
1.01
2.02
1.03
1.00
1.02
1.03
1.03
3.05
9.09
9.03
9.17
8.95
178.28
177.68
177.49
176.81
160.00
134.51
128.59
128.10
120.47
114.22
75.98
71.30
70.69
70.06
65.90
62.32
55.44
39.04
39.02
38.91
27.29
27.27
27.22
27.17
OMe
PivO
PivO
OPiv
OPiv
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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5.428
5.415
5.205
5.189
5.173
5.083
5.066
5.050
4.922
4.906
4.890
4.240
4.232
4.220
4.212
4.104
4.101
4.084
4.080
3.819
3.806
3.804
3.790
3.682
3.679
3.675
3.671
3.666
3.662
3.658
2.658
2.654
2.646
2.642
2.632
2.628
2.361
2.349
2.346
2.338
2.334
2.067
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1.923
AcO
O
AcO
OAc
OAc
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.16
3.01
1.00
1.00
1.07
1.05
1.03
1.08
1.05
1.01
1.03
2.05
2.04
3.07
3.04
3.05
3.00
170.79
170.40
169.53
169.47
141.30
136.78
128.44
128.33
126.03
125.75
79.52
75.52
73.93
71.33
68.49
62.29
35.22
33.94
20.84
20.75
20.72
20.67
AcO
O
AcO
OAc
OAc
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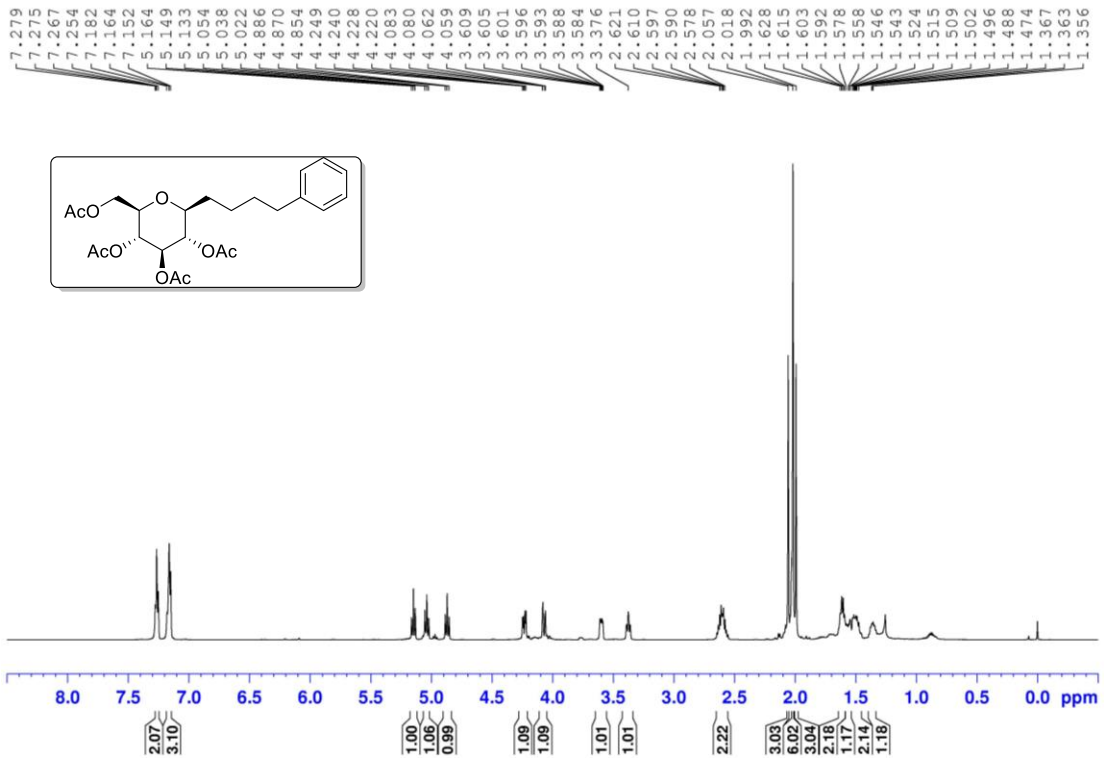
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.022
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4.854
4.249
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4.228
4.220
4.083
4.080
4.062
4.059
3.609
3.605
3.601
3.596
3.593
3.588
3.584
3.376
2.621
2.610
2.597
2.590
2.578
2.057
2.018
1.992
1.628
1.615
1.603
1.592
1.578
1.558
1.546
1.543
1.524
1.515
1.509
1.502
1.496
1.488
1.474
1.367
1.363
1.356
AcO
AcO
OAc
OAc
O
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
3.10
1.00
1.06
0.99
1.09
1.09
1.01
1.01
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3.03
6.02
3.04
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1.17
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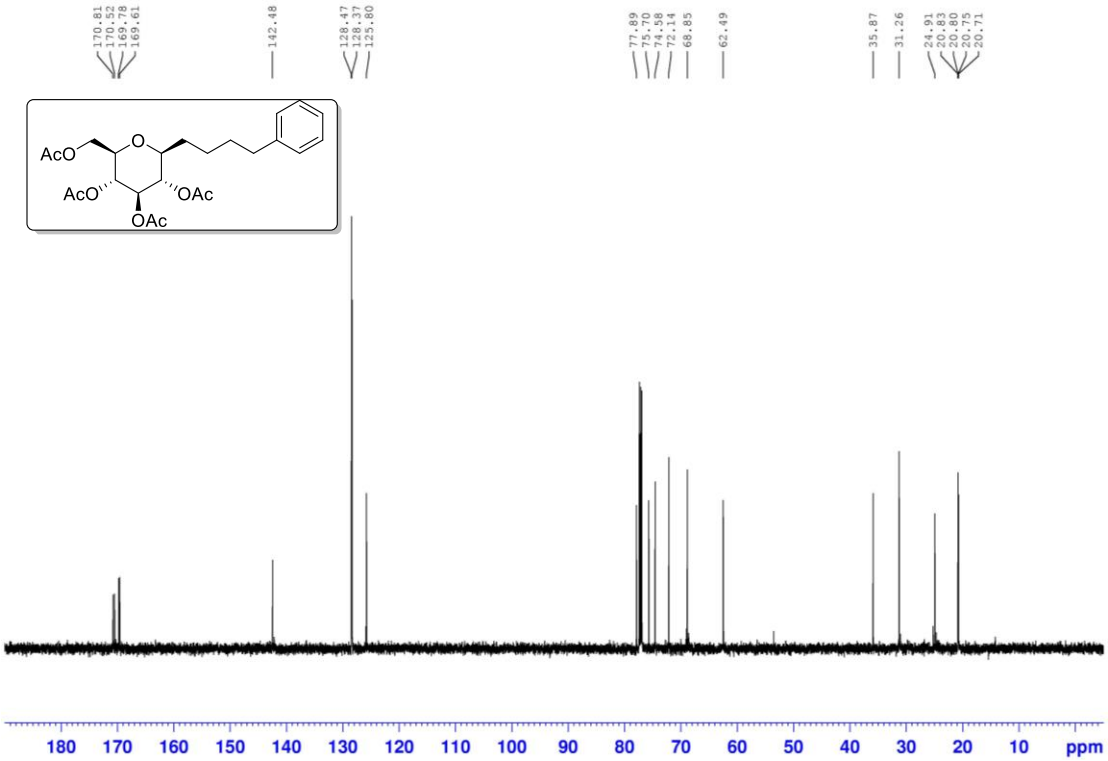
1.18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75.70
74.58
72.14
68.85
62.49
35.87
31.26
24.91
20.83
20.80
20.75
20.71
AcO
AcO
OAc
OAc
O
180
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150
140
130
120
110
100
90
80
70
60
50
40
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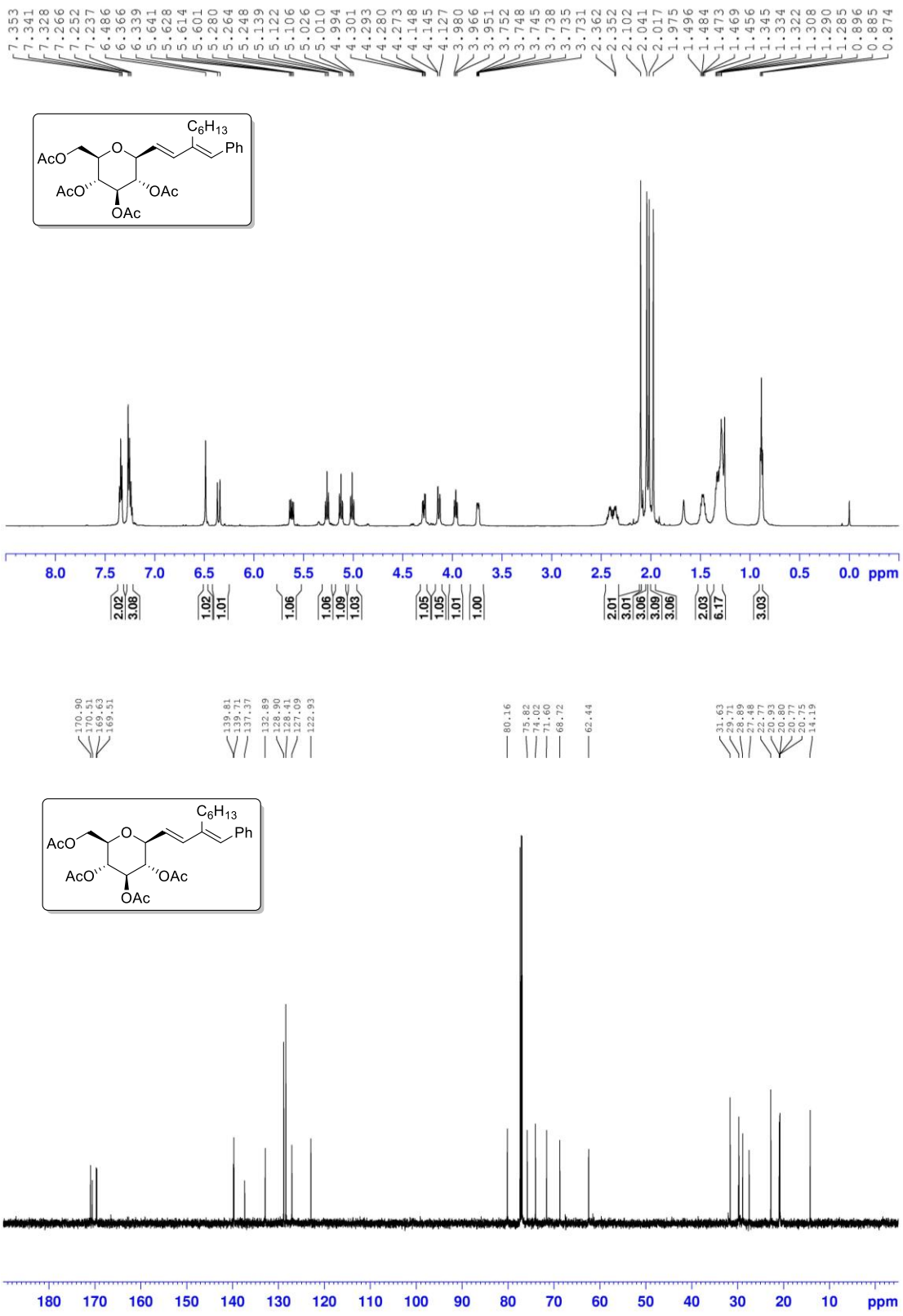
20
10
ppm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5.280
5.264
5.248
5.139
5.122
5.106
5.026
5.010
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4.301
4.293
4.280
4.273
4.148
4.145
4.127
3.980
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3.951
3.752
3.748
3.745
3.738
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3.731
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1.473
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1.334
1.322
1.308
1.290
1.285
0.896
0.885
0.874
C6H13
Ph
AcO
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02 3.08 1.02 1.01 1.06 1.06 1.09 1.03 1.05 1.05 1.01 1.00 2.01 3.01 3.06 3.09 3.06 2.03 6.17 3.03
170.90
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169.63
169.51
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139.71
137.37
132.89
128.90
128.41
127.09
122.93
80.16
75.82
74.02
71.60
68.72
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31.63
29.71
28.89
27.48
22.77
20.93
20.80
20.77
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C6H13
Ph
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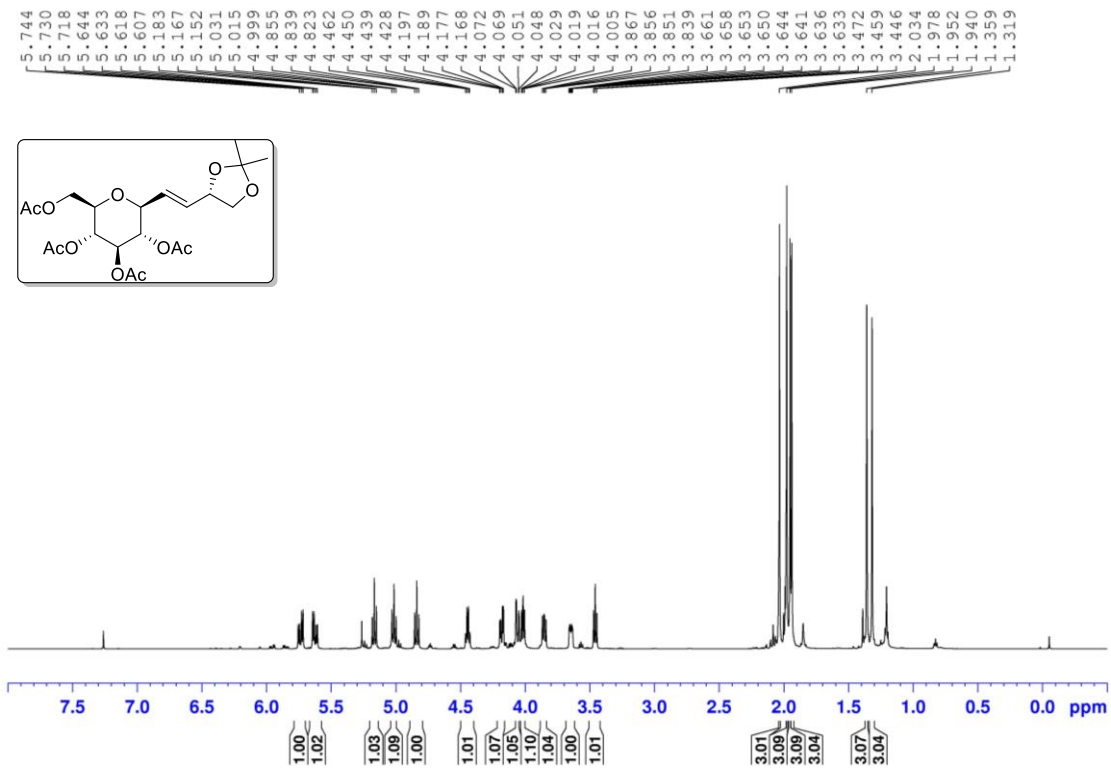
AcO
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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4.823
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4.072
4.069
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4.019
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4.005
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1.319
AcO
AcO
OAc
OAc
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.02
1.03
1.09
1.00
1.01
1.07
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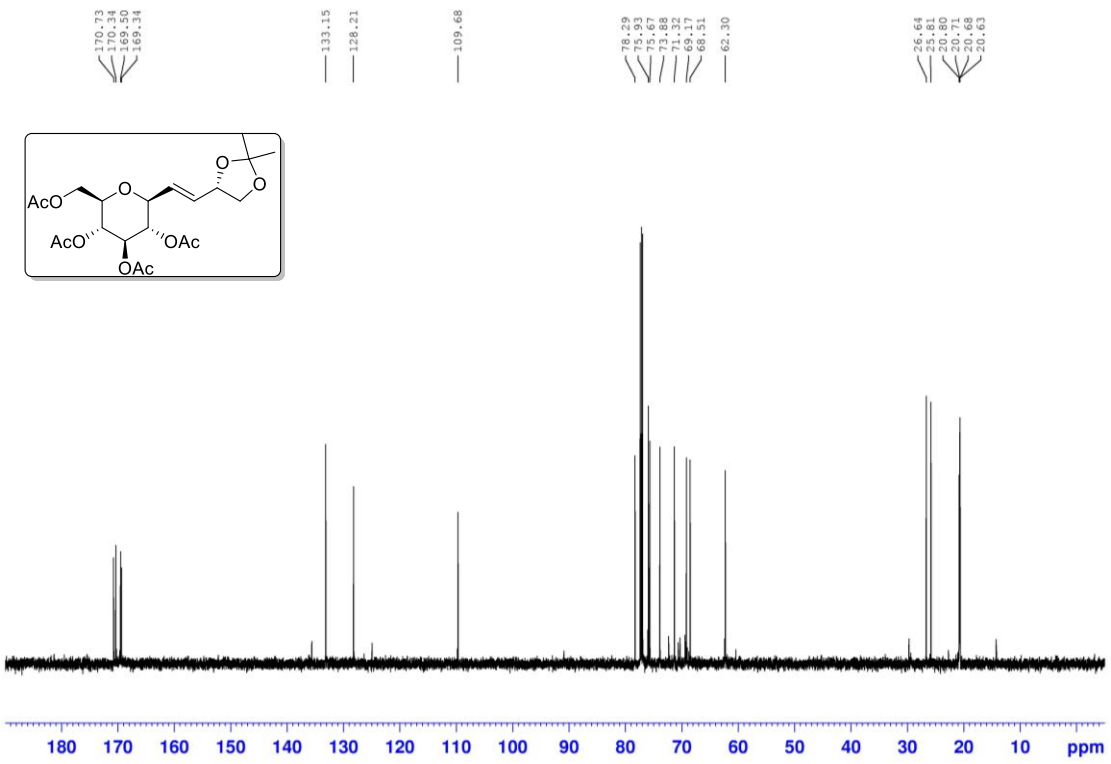
1.04
1.00
1.01
3.01
3.09
3.09
3.04
3.07
3.04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69.17
68.51
62.30
26.64
25.81
20.80
20.71
20.68
20.63
AcO
AcO
OAc
OAc
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150
140
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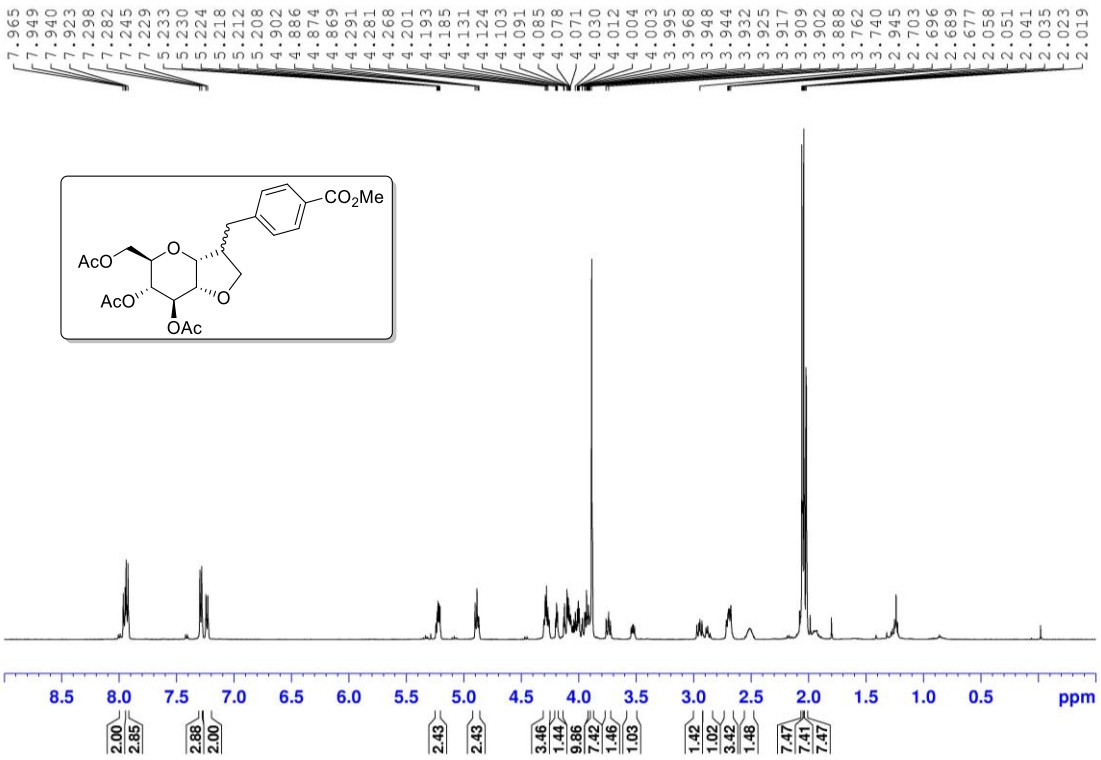
10
ppm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5.212
5.208
4.902
4.886
4.874
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4.291
4.281
4.268
4.201
4.193
4.185
4.131
4.124
4.103
4.091
4.085
4.078
4.071
4.030
4.012
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4.003
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3.948
3.944
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3.909
3.902
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3.740
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2.703
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2.051
2.041
2.035
2.023
2.019
CO2Me
AcO
AcO
OAc
O
O
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
0.5
ppm
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2.00
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3.46
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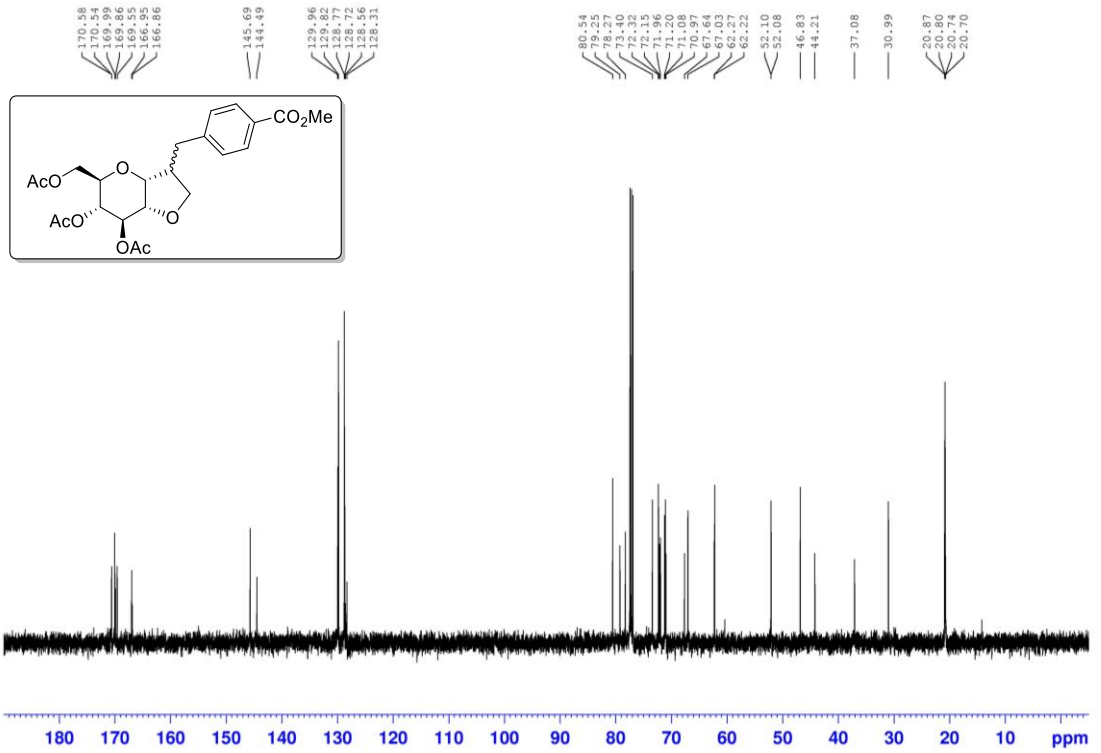
7.47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129.82
128.77
128.72
128.56
128.31
80.54
79.25
78.27
73.40
72.32
72.15
71.96
71.20
71.08
70.97
67.64
67.03
62.27
62.22
52.10
52.08
46.83
44.21
37.08
30.99
20.87
20.80
20.74
20.70
CO2Me
AcO
AcO
OAc
O
O
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150
140
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100
90
80
70
60
50
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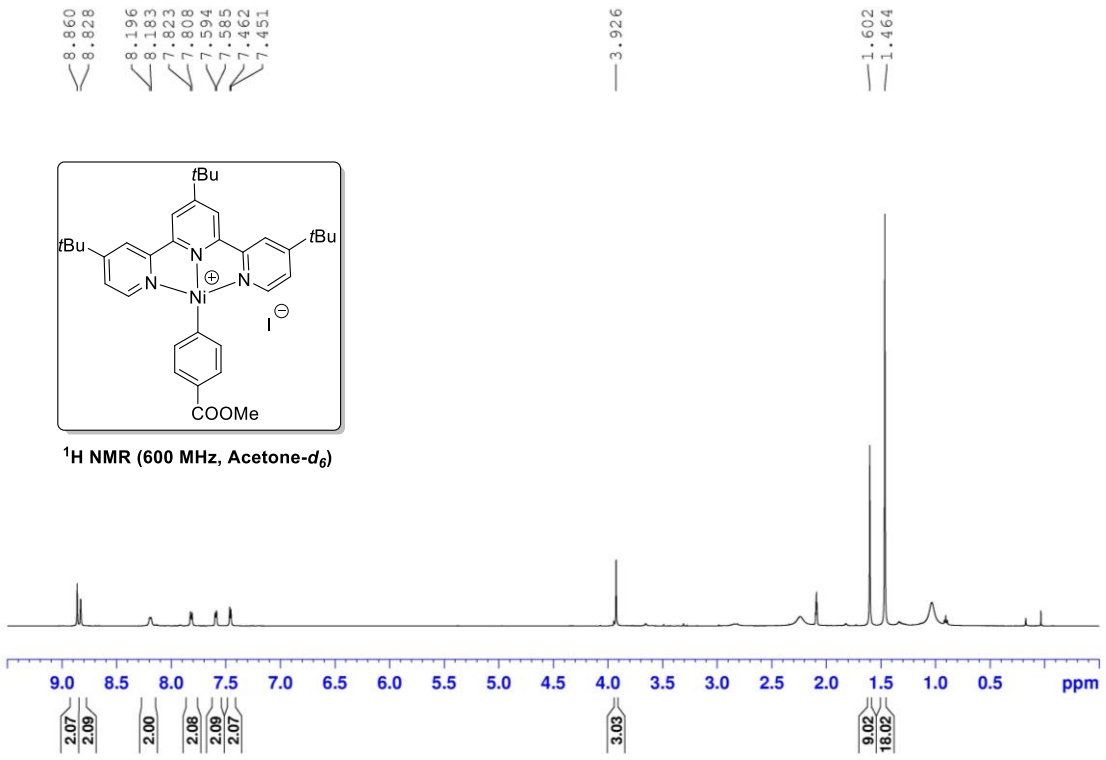
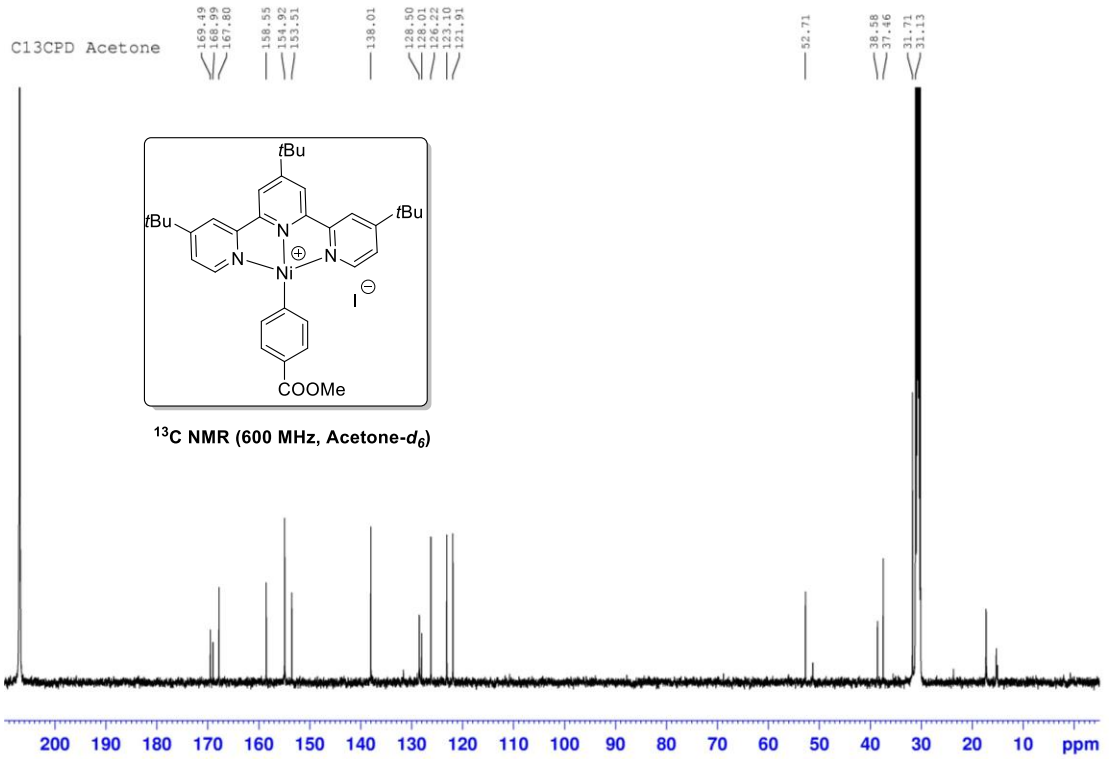
10
ppm




$^{1}$H NMR (600 MHz, Acetone-$d_6$)




$^{13}$C NMR (600 MHz, Acetone-$d_6$)