Stereoselective Preparation of α-*C*-Vinyl/Aryl Glycosides via Nickel-Catalyzed Reductive Coupling of Glycosyl Halides with Vinyl and Aryl Halides

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I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents

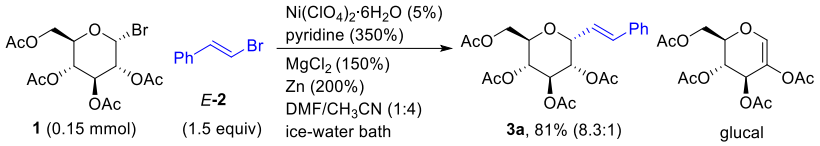
All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glovebox techniques. DMA (*N*,*N*-dimethylacetamide, 99.5%, extra dry, Acros), DMF (*N*,*N*-dimethylforamide, 99.5%, extra dry, Acros), CH_3CN (Acetonitrile, 99.5%, extra dry, Acros) were purchased and used directly. Deuterated solvents were used as received. $NiCl_2$ (Alfa Aesar), $NiBr_2$ (Alfa Aesar), NiI_2 (Alfa Aesar), $Ni(acac)_2$ (Alfa Aesar), $Ni(COD)_2$ (Strem), $Ni(ClO_4)_2$ (Alfa Aesar), $Ni(acac)_2$ (Maclin Co., China) 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 was 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 unless otherwise indicated. ^{1}H 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 ^{1}H 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 (Method A1) for the formation of **3a**.[a,b]



Entry	Variation from the standard Method A1	Yield for **3a**[c]	Glucal[c]
1	none	81% (8.3:1)[d]	trace
2	25 °C instead of 0 °C	76% (6:1)	9%
3	DMF	20% (7.2:1)	5%
4	CH_3CN	trace	trace
5	w/o $MgCl_2$	trace	trace
6	w/o $Ni(ClO_4)\cdot 6H_2O$	N.D.	50%
7	w/o pyridine	20% (2:1)	40%
8	DMAP	trace	30%
9	Bpy (10%)	20% (2.2:1)	65%
10	dtbBpy (10%)	24% (2.8:1)	30%
12	*t*Bu-Terpy (10%)	30% (1.2:1)	65%
13	*i*Pr-Pybox (10%)	20% (1:1)	6%
14	$Ni(acac)_2$	63% (7:1)	51%
15	1 (0.15 mmol), 2 (0.15 mmol)	74% (8.1:1)	trace
16	3 mmol	75% (8.8:1)[d]	-
17	(Z)-1-(2-bromovinyl)-4-methoxybenzene instead of *E*-**2**	73% (8:1) (E: Z = 1:3)	trace

[a] Reaction Conditions: see Table 1, entry 1, 12h. [b] Formation of vinyl-vinyl accounts for the major mass balance for vinyl bromides. [c] Yield determined by ^{1}H NMR spectroscopy using 2,5-dimethylfuran as the internal reference. [d] Isolated yields.

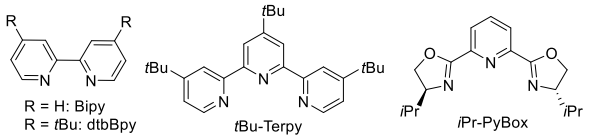
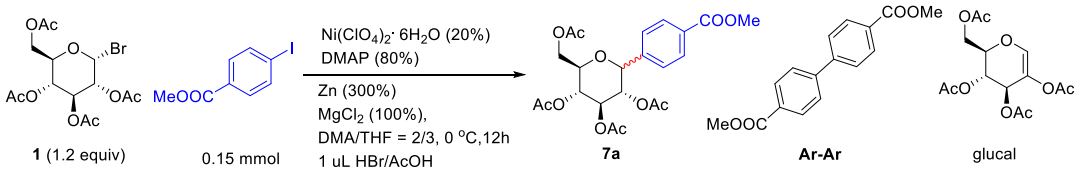


Table S2. Variations from the standard conditions A2 (method A2) for the formation of **7a**.[a,b]



Entry	Variation from the standard method A2	Yield for **7a**[a]	Glucal[a]	Ar-Ar[a]
1	none	85% (6:1)[b]	25%	trace
2	$Ni(cod)_2$, w/o $MgCl_2$	25% (2.4:1)	50%	13%
3	DMA	30% (5:1)	11%	50%
4	THF	trace	80%	10%
5	w/o $MgCl_2$	trace	5%	trace
6	w/o $Ni(ClO_4)\cdot 6H_2O$	N.D.	80%	N.D.
7	w/o DMAP	N.D.	70%	trace
8	pyridine	42% (3.6:1)	52%	20%
9	dtbBpy (10%)	90% (2.5:1)	7%	5%
10	*t*Bu-Terpy (10%)	40% (1:1.1)	50%	60%
11	25 °C instead of 0 °C	46% (4.6:1)	30%	20%

[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 **14** and **15**.

Stoichiometric reactions of **14, 15** with **1** were examined. For complex **14**, $MgCl_2$ is crucial for the formation of 7**a** with high α-selectivity. The reaction of complex **15** with **1** produced 7**a** in 60% or 30% yields with a 2:1 α/β ratio in the presence or absence of $MgCl_2$.

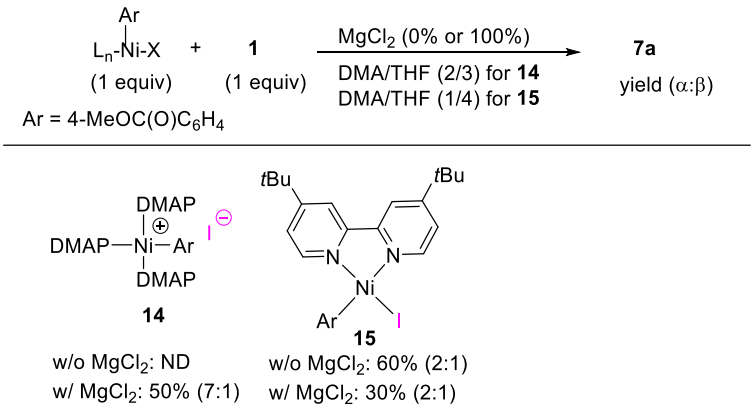
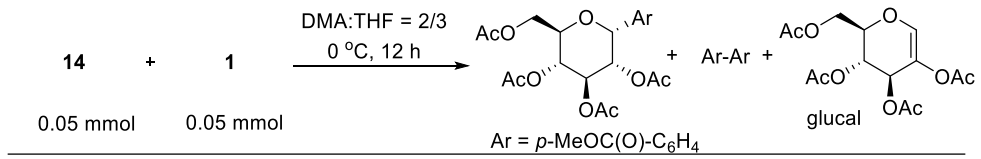
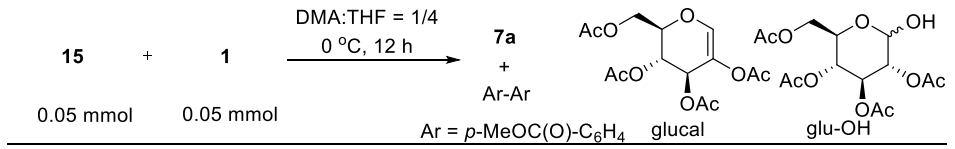


Table S3. Equimolar reaction of **14** with **1**.



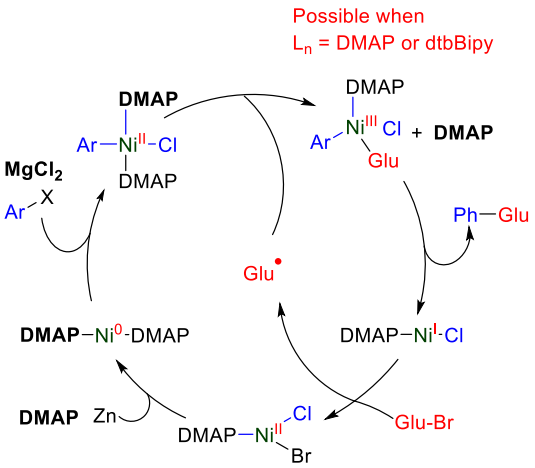
Entry	Variation	Yield	Ar-Ar	glucal
1	none	trace	40%	~100%
2	Zn (2 equiv)	trace	40%	~100%
3	Zn (2 equiv), $MgCl_2$ (1equiv)	80% (7/1)	trace	16%
4	$MgCl_2$ (1equiv)	50% (7/1)	trace	47%

Table S4. Equimolar reaction of **15** with **1**.



Entry	Variation	Yield for **7a**	Ar-Ar	Glucal
1	none	60% (2/1)	25%	16%
2	Zn (2 equiv)	82% (2.3/1)	15%	trace
3	Zn (2 equiv), $MgCl_2$ (1equiv)	85% (2.3/1)	13%	trace
4	$MgCl_2$ (1equiv)	~30% (2.2:1)	43%	trace

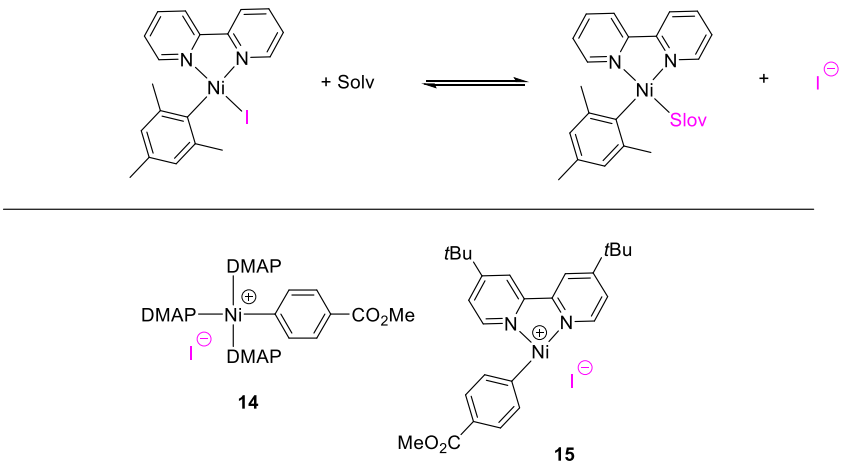
(2) Proposed Catalytic Cycles



Scheme S1. Proposed reaction pathways: radical-chain mechanism.

(3) Synthesis of complexes **14** and **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 ^1H NMR analysis, it is reasonable to conclude that complexes **14-15** exist as cationic form in the polar solvents such as DMA and THF.



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

<u>Procedure for the synthesis of complex **14**</u>: 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 flame-dried Schlenk tube, at which point a solution of DMAP (483.1 mg, 1.20 mmol, 330 mol %) in 8 mL of dry THF was added dropwise. The resulting mixture was allowed to 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. Excess pentane was added, and the residue was filtrated with a fritted funnel, After filtration, and dried in

vacuum, the title compound was obtained in 85% yield (736.4 mg, 1.02 mmol), which was stored in the glove box at -30 °C.

^{1}H NMR (600 MHz, DMSO) δ = 8.41 (d, *J* = 6.2 Hz, 4H), 8.32 – 8.07 (s, br, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.64 – 6.38 (s, br, 2H), 6.47 (d, *J* = 6.6 Hz, 4H), 3.67 (s, 3H), 2.84 (s, 18H).

^{13}C NMR (151 MHz, DMSO) δ 167.73, 154.12, 149.64, 148.33 (br), 135.52, 125.09, 124.07, 108.02, 51.90, 39.10.

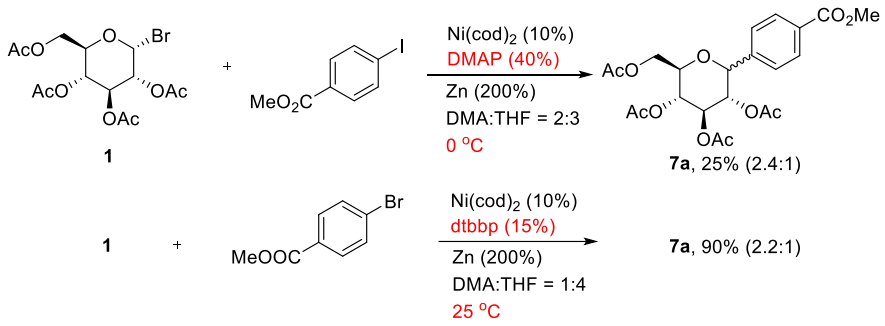
Elementary Analysis: calculated for ($C_{29}H_{37}IN_6NiO_2$) C, 50.68; H, 5.43; N, 12.23, found: C, 50.29; H, 5.52; N, 12.27.

Complexes **15** was prepared according to our previous work.[12]

(4) Role of $MgCl_2$

(a) Control experiments for the reactions without $MgCl_2$

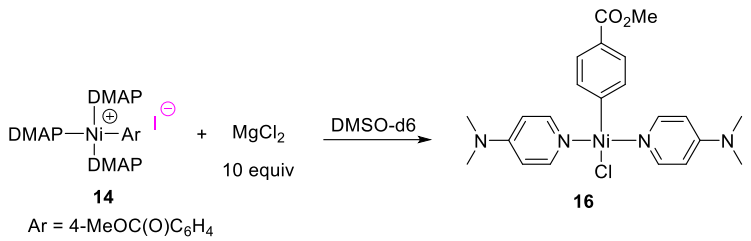
In the catalytic reaction of **1** with methyl 4-bromobenzoate using dtbBpy as the ligand, a mixture of $Ni(acac)_2/MgCl_2$ generated identical results to $Ni(COD)_2$ without $MgCl_2$. No reaction took place if $MgCl_2$ was removed from the $Ni(acac)_2$ case, suggesting activation of Zn with $MgCl_2$ may become crucial for the reduction of Ni^{II} salt to Ni^0. Formation of 7**a** using DMAP as the ligand is much less effective when $Ni(cod)_2$ was used as the precatalyst, which supported that formation of **16** was crucial when pyridine and DMAP were used as the ligands.



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

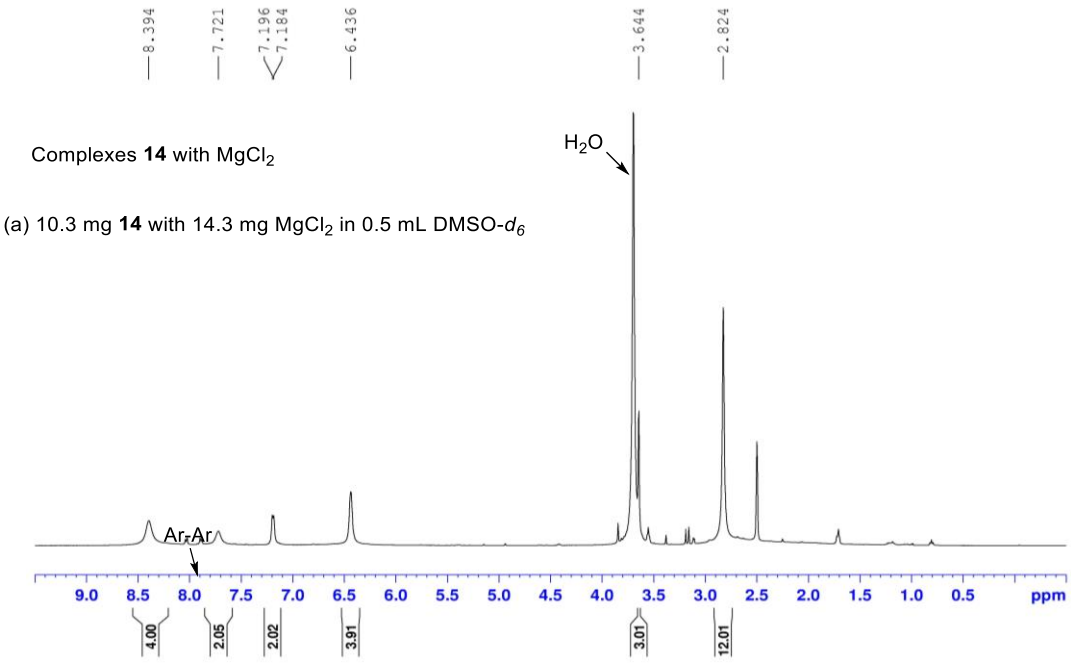
(b) Reaction of $MgCl_2$ with **14**.

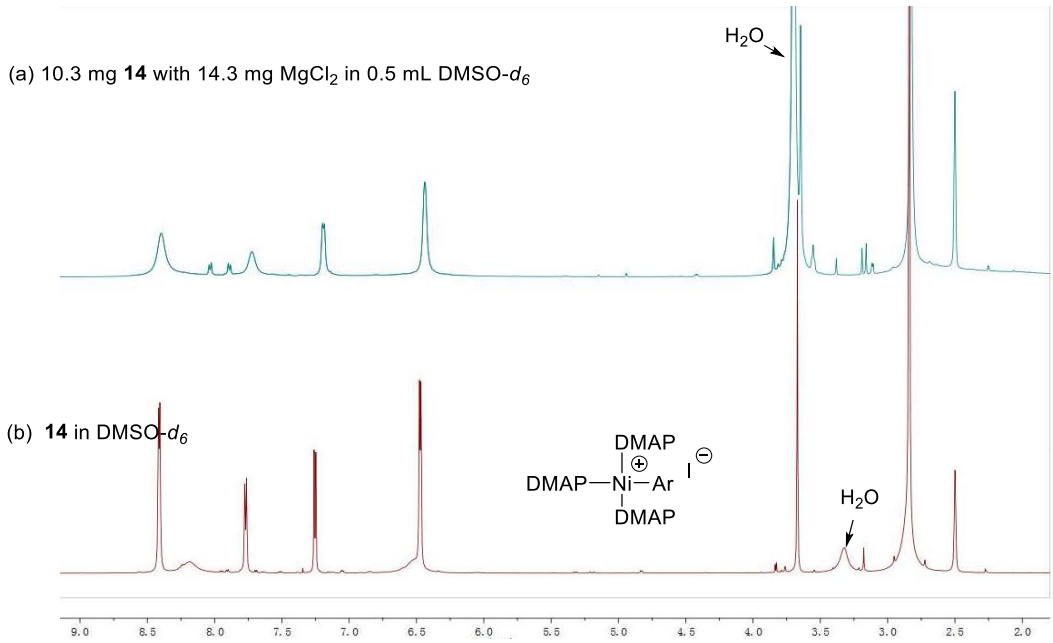
A reaction of **14** with excess $MgCl_2$ (pre-dissolved in DMSO-d_6) yielded a neutral $(DMAP)_2Ni^{II}$–Ar(Cl) species **16** by substitution of a DMAP ligand with Cl^-, which may account for the authentic intermediate for intercepting a glycosyl radical. Note: the ^{1}H NMR was obtained after filtration of the reaction mixture with a micron filter (size: 0.22 μm, Nylon-6). Due to the instability of the complex **16** in polar solvent, ^{13}C NMR of **16** was not available.



Scheme S4. Reaction of $MgCl_2$ with **14**.

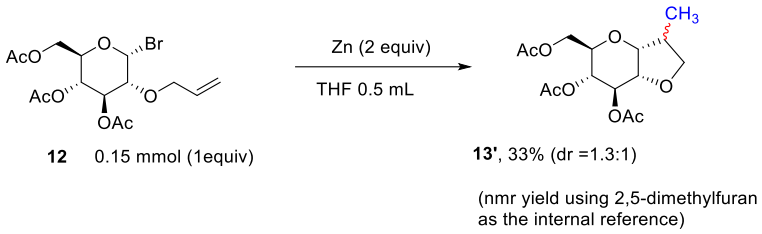
^{1}H NMR of **14** (1 equiv) in the presence of 10 equiv of $MgCl_2$: (500 MHz, DMSO-d_6) δ 8.40 (brs, 4H), 7.72 (brs, 2H), 7.19 (d, J = 6.5 Hz, 2H), 6.44 (brs, 4H), 3.65 (s, 3H), 2.83 (s, 12H).





(5) Zn Reduction of **11**:

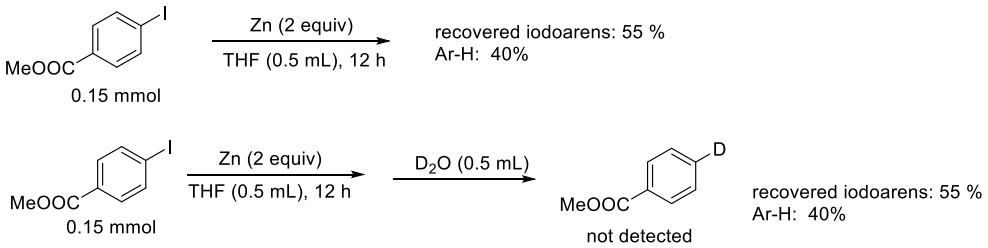
Reaction of **12** in the presence of Zn produced **13**' in 33% yield (NMR yield), indicating Zn alone can induce glucosyl radical formation, although low efficiency was observed.



Scheme S5. Reduction of **11**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 in 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 S6. Elimination of organozinc mechanism.

Part 4. Reductive Coupling of Vinyl Bromide or Aryl Halides and Glycosyl Halides

1. *General procedure*

***Method A1* for α-selective preparation of *C*-vinyl glycosides (pyridine as the ligand/additive):**

To a flame-dried Schlenk tube was charged with vinyl bromide (0.225 mmol, 150 mol %, if solid), glycosyl bromide (0.15 mmol, 100 mol %), Zn (20 mg, 0.30 mmol, 200 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (2.7 mg, 0.008 mmol, 5 mol %), $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, vinyl bromide (0.225 mmol, 150 mol %, if liquid) and pyridine (41.5 mg, 0.525 mmol, 350 mol %) were added via a syringe followed by addition of DMF/CH_3CN (0.2/0.8 mL) via a syringe. The reaction mixture was allowed to stir for 12 h under a N_2 atmosphere at ice-water bath, 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 ^{1}H NMR spectra of the new mixture, based on the ratios of the characteristic peaks of the two anomers.

***Method A2* for α-selective preparation of *C*-aryl glycosides (DMAP as the ligand/additive)**:

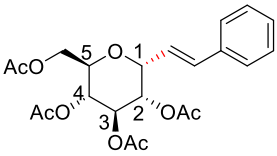
To a flame-dried Schlenk tube was charged with aryl iodide (0.15 mmol, 100 mol %, if solid), glycosyl bromide (0.18 mmol, 120 mol %), Zn (29.6 mg, 0.45 mmol, 300 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (11 mg, 0.03 mmol, 20 mol %), DMAP (14.6 mg, 0.12 mmol, 80 mol %), $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, aryl iodide (0.15 mmol, 100 mol %, if liquid) were added via a syringe. Following this, 1 uL of HBr/AcOH (33 wt. %) dissolved in DMA, and DMA/THF (0.2/0.3 mL) was added via a syringe. The reaction mixture was allowed to stir for 12 h under a N_2 atmosphere at ice-water bath, 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.

Method A3 **for preparation of *C*-aryl glycosides (dtbBpiy as the ligand)**:

To a flame-dried Schlenk tube was charged with aryl iodide (0.15 mmol, 100 mol %, if solid), glycosyl bromide (0.225 mmol, 150 mol %), Zn (20 mg, 0.30 mmol, 200 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), 4,4'-di-tert-butyl-2,2'-bipyridine (6.0 mg, 0.0225 mmol, 15 mol %), $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol %). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, aryl iodide (0.15 mmol, 100 mol %, if liquid) was added via a syringe followed by addition of DMA (1 mL) via a syringe. The reaction mixture was allowed to stir for 12 h under a N_2 atmosphere at ice-water bath, 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. *Details of the Characterization Data for New Compounds*

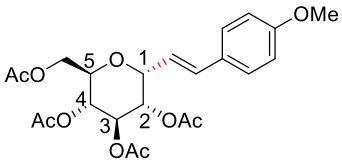


***(2R,3R,4R,5S,6R)*-2-(Acetoxymethyl)-6-((*E*)-styryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3a).**[11]

This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), β-bromostyrene (41.2 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (8.3:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 4.03 ppm for α and 3.75 ppm for β) as a white solid (52.7 mg, 0.121 mmol, 81% yield). Spectroscopic data matches a previously reported synthesis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.77 (dd, J = 16.1, 1.2 Hz, 1H), 6.37 (dd, J = 16.1, 6.2 Hz, 1H), 5.40 (t, J = 9.6 Hz, 1H, H_3), 5.14 (dd, J = 10.1, 6.2 Hz, 1H, H_2), 5.08 (t, J = 9.6 Hz, 1H, H_4), 4.91 (td, J = 6.2, 1.3 Hz, 1H, H_1), 4.24 (dd, J = 12.3, 4.8 Hz, 1H), 4.10 (dd, J = 12.3, 2.4 Hz, 1H), 4.03 (ddd, J = 9.9, 4.7, 2.3 Hz, 1H, H_5), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.80, 170.35, 169.82, 169.64, 137.14, 135.92, 128.83, 128.66, 126.83, 120.75, 73.24, 70.89, 70.65, 69.47, 69.17, 62.46, 20.85, 20.83, 20.80, 20.71.



***(2R,3R,4R,5S,6R)*-2-(Acetoxymethyl)-6-((*E*)-4-methoxystyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3b).**

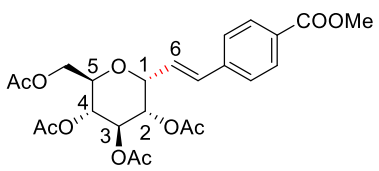
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (48.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (7.5:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 4.02 ppm for α and 3.74 ppm for β) as a white solid (65.4 mg, 0.141 mmol, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 16.0, 6.5 Hz, 1H), 5.40 (t, J = 9.8 Hz, 1H, H_3), 5.12 (dd, J = 10.1, 6.2 Hz, 1H H_2), 5.07 (t, J = 9.6 Hz, 1H, H_4), 4.88 (t, J = 6.3 Hz, 1H, H_1), 4.23 (dd, J = 12.3, 4.7 Hz, 1H), 4.09 (dd, J = 12.3, 2.3 Hz, 1H), 4.02 (ddd, J = 10.0, 4.6, 2.4 Hz, 1H, H_5), 3.81 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.71, 170.30, 169.76, 169.56, 159.98, 136.75, 128.60, 128.06, 118.13, 114.12, 73.38, 70.86, 70.65, 69.24, 69.12, 62.39, 55.35, 20.76, 20.75, 20.72, 20.63.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_{10}^+$): m/z 465.1755; found: 465.1749.

M.p. 86-88 ºC.



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

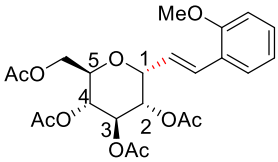
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), methyl (*E*)-4-(2-bromovinyl) benzoate (54.2 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (7.2:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 6.46 ppm for α and 6.15 ppm for β) as a white solid (60.5 mg, 0.123 mmol, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 15.4 Hz, 1H), 6.46 (dd, J = 16.1, 5.8 Hz, 1H), 5.36 (t, J = 9.6 Hz, 1H, H_3), 5.15 (dd, J = 10.0, 6.2 Hz, 1H, H_2), 5.06 (t, J = 9.5 Hz, 1H, H_4), 4.91 (t, J = 5.3 Hz, 1H, H_1), 4.23 (dd, J = 12.3, 4.8 Hz, 1H), 4.09 (dd, J = 12.3, 2.3 Hz, 1H), 4.01 (ddd, J = 9.8, 4.6, 2.3 Hz, 1H, H_5), 3.90 (s, 3H)2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.71, 170.28, 169.73, 169.57, 166.70, 140.19, 135.75, 130.11, 129.99, 126.71, 123.66, 72.99, 70.79, 70.46, 69.69, 69.06, 62.38, 52.24, 20.82, 20.81, 20.76, 20.67.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{24}H_{29}O_{11}^+$): m/z 493.1704; found: 493.1691.

M.p. 130-132 ºC.



***(2R,3R,4R,5S,6R)*-2-(Acetoxymethyl)-6-((*E*)-2-methoxystyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3d).**

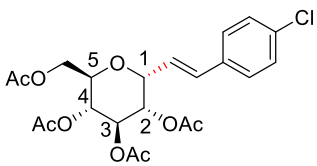
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-2-methoxybenzene (48.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (8.2:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 4.07 ppm for α and 3.75 ppm for β) as a white solid (59.7 mg, 0.129 mmol, 86% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (d, J = 7.0 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 16.1 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.37 (dd, J = 16.2, 6.3 Hz, 1H), 5.40 (t, J = 9.6 Hz, 1H, H_3), 5.14 (dd, J = 10.1, 6.2 Hz, 1H, H_2), 5.07 (t, J = 9.6 Hz, 1H, H_4), 4.91 (t, J = 5.8 Hz, 1H, H_1), 4.24 (dd, J = 12.2, 4.7 Hz, 1H), 4.11 (dd, J = 12.3, 1.9 Hz, 1H), 4.07 (ddd, J = 9.8, 4.6, 2.3 Hz, 1H, H_5), 3.84 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.69, 170.22, 169.74, 169.55, 156.91, 131.97, 129.60, 127.04, 124.98, 120.95, 120.64, 110.97, 73.51, 70.86, 70.65, 69.26, 69.16, 62.38, 55.44, 20.71, 20.61.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{23}H_{28}NaO_{10}^+$): m/z 487.1575; found: 487.1581.

M.p. 135-137 ºC.



***(2R,3R,4R,5S,6R)*-2-(acetoxymethyl)-6-((*E*)-4-chlorostyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3e).**

This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E)*-1-(2-bromovinyl)-4-chlorobenzene (48.8 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (7.7:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5

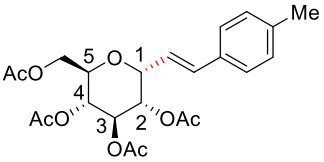
of the two anomers: 4.03 ppm for α and 3.75 ppm for β) as a white solid (49.1 mg, 0.105 mmol, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (q, J = 8.7 Hz, 4H), 6.72 (dd, J = 16.1, 1.4 Hz, 1H), 6.34 (dd, J = 16.1, 6.1 Hz, 1H), 5.37 (t, J = 9.6 Hz, 1H, H_3), 5.14 (dd, J = 10.1, 6.1 Hz, 1H, H_2), 5.07 (t, J = 9.6 Hz, 1H, H_4), 4.89 (td, J = 6.1, 1.5 Hz, 1H, H_1), 4.24 (dd, J = 12.3, 4.7 Hz, 1H), 4.09 (dd, J = 12.3, 2.4 Hz, 1H), 4.00 (ddd, J = 9.9, 4.7, 2.4 Hz, 1H, H_5), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.76, 170.34, 169.77, 169.61, 135.75, 134.40, 134.38, 129.02, 128.05, 121.53, 73.11, 70.83, 70.57, 69.59, 69.13, 62.43, 20.85, 20.83, 20.80, 20.71.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{26}ClO_9^+$): m/z 469.1260; found: 469.1252.

M.p. 122-124 ºC.



***(2R,3R,4R,5S,6R)*-2-(acetoxymethyl)-6-((*E*)-4-methylstyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3f).**

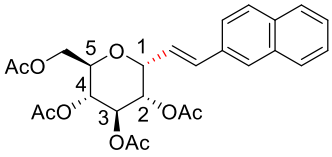
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methylbenzene (44.3 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (7.7:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 4.02 ppm for α and 3.75 ppm for β) as a white solid (58.2 mg, 0.130 mmol, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.74 (d, J = 15.4 Hz, 1H), 6.32 (dd, J = 16.0, 6.4 Hz, 1H), 5.40 (t, J = 9.7 Hz, 1H, H_3), 5.14 (dd, J = 10.1, 6.2 Hz, 1H, H_2), 5.08 (t, J = 9.5 Hz, 1H, H_4), 4.90 (td, J = 6.3, 1.0 Hz, 1H, H_1), 4.24 (dd, J = 12.3, 4.7 Hz, 1H), 4.09 (dd, J = 12.3, 2.3 Hz, 1H), 4.02 (ddd, J = 10.0, 4.6, 2.3 Hz, 1H, H_5), 2.36 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.80, 170.37, 169.84, 169.65, 138.71, 137.20, 133.17, 129.52, 126.78, 119.58, 73.39, 70.95, 70.72, 69.41, 69.22 , 62.48, 21.36, 20.86, 20.84, 20.82, 20.73.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_9^+$): m/z 449.1806; found: 449.1829.

M.p. 128-130 ºC.



***(2R,3R,4R,5S,6R)*-2-(Acetoxymethyl)-6-((*E*)-2-(naphthalen-2-yl) vinyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3g).**

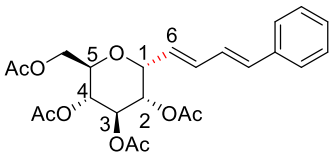
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-2-(2-bromovinyl)naphthalene (52.4 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (6.1:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 4.09 ppm for α and 3.79 ppm for β) as a white solid (51.5 mg, 0.106 mmol, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.80 (m, 3H), 7.78 (s, 1H), 7.64 (dd, J = 8.6, 1.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 6.94 (d, J = 15.9 Hz, 1H), 6.50 (dd, J = 16.0, 6.3 Hz, 1H), 5.46 (t, J = 9.6 Hz, 1H, H_3), 5.19 (dd, J = 10.1, 6.2 Hz, 1H, H_2), 5.12 (t, J = 9.6 Hz, 1H, H_4), 4.98 (t, J = 5.7 Hz, 1H, H_1), 4.28 (dd, J = 12.3, 4.6 Hz, 1H), 4.14 (dd, J = 12.3, 2.2 Hz, 1H), 4.09 (ddd, J = 9.9, 4.5, 2.4 Hz, 1H, H_5), 2.11 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.83, 170.43, 169.88, 169.67, 137.33, 133.56, 133.51, 133.34, 128.56, 128.24, 127.84, 127.30, 126.67, 126.53, 123.51, 121.02, 73.41, 70.99, 70.72, 69.55, 69.21, 62.48, 20.90, 20.85, 20.75.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{26}H_{29}O_9^+$): m/z 485.1806; found: 485.1845.

M.p. 150-152 ºC.



***(2R,3R,4R,5S,6R)*-2-(Acetoxymethyl)-6-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-3h).**

This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), ((1*E*,3*E*)-4-bromobuta-1,3-dien-1-yl) benzene (47.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the

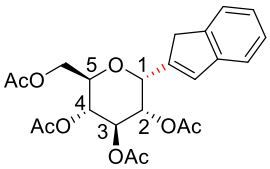
two anomers: 5.97 ppm for α and 5.71 ppm for β) as a white solid (41.4 mg, 0.09 mmol, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (s, 2H), 6.82 (dd, J = 15.5, 10.6 Hz, 1H), 6.64 – 6.50 (m, 2H), 5.97 (dd, J = 15.4, 6.3 Hz, 1H), 5.35 (t, J = 9.7 Hz, 1H, H_3), 5.13 – 5.03 (m, 2H, H_2, H_4), 4.84 (t, J = 6.1 Hz, 1H, H_1), 4.23 (dd, J = 12.3, 4.6 Hz, 1H), 4.08 (dd, J = 12.2, 1.8 Hz, 1H), 3.99 – 3.96 (m, 1H, H_5), 2.10 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.89, 170.45, 169.88, 169.70, 137.31, 136.72, 134.86, 128.86, 128.26, 127.66, 126.71, 124.54, 73.04, 70.89, 70.65, 69.42, 69.10, 62.45, 20.93, 20.90, 20.87, 20.78.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{24}H_{28}NaO_9^+$): m/z 483.1626; found: 483.1614.

M.p. 83-85 ºC.

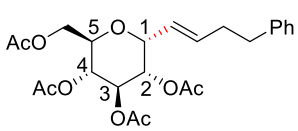


(*2R,3R,4R,5S,6R*)-2-(acetoxymethyl)-6-(1*H*-inden-2-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (α-3i).

This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (124.0 mg, 0.3 mmol, 200 mol %), 2-bromo-1*H*-indene (29.3 mg, 0.15 mmol, 150 mol %). Flash column chromatography (20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5.5:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.71 ppm for α and 3.79 ppm for β) as a colorless gummy liquid (34.1 mg, 0.076 mmol, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.44 (dd, J = 10.0, 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.21 (s, 1H), 5.70 (dd, J = 9.9, 9.3 Hz, 1H), 5.28 (dd, J = 10.2, 6.0 Hz, 1H), 5.23 (d, J = 5.8 Hz, 1H), 5.09 (t, J = 9.5 Hz, 1H), 4.22 (dd, J = 12.3, 5.1 Hz, 1H), 4.03 (dd, J = 12.2, 2.3 Hz, 1H), 3.71 (ddd, J = 10.0, 5.0, 2.3 Hz, 1H), 3.51 (d, J = 22.9 Hz, 1H), 3.37 (d, J = 22.9 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.73, 170.54, 169.88, 169.66, 143.95, 142.82, 141.16, 133.20, 126.82, 125.64, 123.83, 121.75, 71.95, 70.99, 70.70, 69.88, 69.20, 62.40, 40.27, 20.91, 20.87, 20.85, 20.71.



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

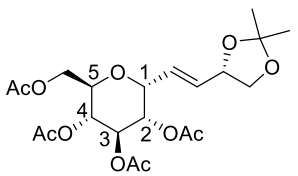
This compound was prepared according to the *Method* ***A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-(4-bromobut-3-en-1-yl) benzene (47.4 mg, 0.225 mmol, 150 mol %), tetrabutylammonium iodide (55.3 mg, 0.15 mmol, 100 mol %), 25 °C. Preparative TLC (1% ethyl acetate in dichloromethane) gave a mixture of diastereomers (4:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.73 ppm for α and 3.67 ppm for β) as a white solid (35.3 mg, 0.076 mmol, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 (t, J = 7.6 Hz, 2H), 7.19 – 7.11 (m, 3H), 5.94 – 5.85 (m, 1H), 5.62 (dd, J = 15.6, 6.3 Hz, 1H), 5.26 (t, J = 9.7 Hz, 1H, H_3), 5.03 – 4.97 (m, 2H, H_2, H_4), 4.66 (t, J = 6.1 Hz, 1H, H_1), 4.16 (dd, J = 12.3, 4.4 Hz, 1H), 3.98 (dd, J = 12.3, 2.3 Hz, 1H), 3.73 (ddd, J = 10.0, 4.4, 2.3 Hz, 1H, H_5), 2.78 – 2.68 (m, 2H), 2.45 (q, J = 7.3 Hz, 2H), 2.06 (s, 3H), 2.01 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.77, 170.32, 169.71, 169.57, 141.16, 138.22, 128.52, 128.48, 126.06, 122.62, 72.88, 70.78, 70.59, 69.06, 68.93, 62.30, 35.24, 34.30, 20.80, 20.77, 20.76, 20.69.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{24}H_{31}O_9^+$): m/z 463.1963; found: 463.19527.

M.p. 70-72 °C.



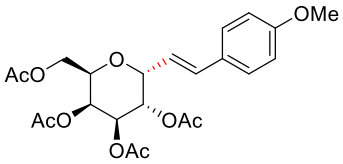
(*2R,3R,4R,5S,6R*)-2-(acetoxymethyl)-6-((*E*)-2-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (α-3k).

This compound was prepared according to the *Method* ***A1*** 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 %),

tetrabutylammonium iodide (55.3 mg, 0.15 mmol, 100 mol %), 25 °C. Flash column chromatography (SiO_2: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (4:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.89 ppm for α and 3.65 ppm for β) as a colorless gummy liquid (48.0 mg, 0.105 mmol, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.97 (dd, J = 15.7, 5.7 Hz, 1H), 5.87 (dd, J = 15.7, 6.6 Hz, 1H), 5.26 (t, J = 9.5 Hz, 1H, H_3), 5.04 (dd, J = 10.0, 6.2 Hz, 1H, H_2), 5.00 (t, J = 9.6 Hz, 1H, H_4), 4.75 (t, J = 5.8 Hz, 1H, H_1), 4.57 (q, J = 6.6 Hz, 1H), 4.18 (dd, J = 12.3, 5.0 Hz, 1H), 4.13 (dd, J = 8.0, 6.5 Hz, 1H), 4.05 (dd, J = 12.4, 2.2 Hz, 1H), 3.89 (ddd, J = 9.7, 4.6, 2.4 Hz, 1H, H_5), 3.59 (t, J = 7.6 Hz, 1H), 2.06 (s, 3H), 2.01 – 1.98 (m, 9H), 1.41 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.74, 170.27, 169.71, 169.59, 135.67, 125.00, 109.85, 76.06, 72.36, 70.68, 70.36, 69.47, 69.36, 69.06, 62.43, 26.70, 25.87, 20.80, 20.77, 20.69.



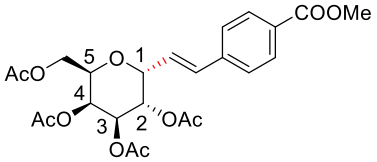
***(2R,3S,4R,5S,6R)*-2-(Acetoxymethyl)-6-((*E*)-4-methoxystyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-4a).**

This compound was prepared according to the *Method* ***A1*** using (*2R,3S,4S,5R,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (48.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (14:1 α to β anomers based on NMR) as a colorless gummy liquid (59.1 mg, 0.127 mmol, 85% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 5.9 Hz, 1H), 5.43 (brs, 1H, H_4), 5.37 (dd, J = 10.5, 5.9 Hz, 1H, H_2), 5.21 (dd, J = 10.5, 2.6 Hz, 1H, H_3), 4.94 (t, J = 5.8 Hz, 1H, H_1), 4.23 (t, J = 6.3 Hz, 1H, H_5), 4.15 – 4.05 (m, 2H), 3.81 (s, 3H), 2.15 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.57, 170.35, 170.25, 170.06, 159.90, 135.86, 128.76, 128.02, 118.14, 114.16, 73.49, 68.51, 68.27, 68.21, 62.04, 55.41, 20.95, 20.83, 20.81, 20.79.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_{10}^+$): m/z 465.1755; found: 465.1742.



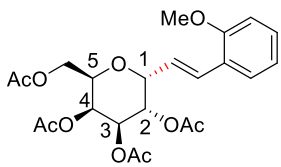
(*2R,3S,4R,5S,6R*)-2-(Acetoxymethyl)-6-((*E*)-4-(methoxycarbonyl)styryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-4b).

This compound was prepared according to the *Method* ***A1*** using (*2R,3S,4S,5R,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (62.0 mg, 0.15 mmol, 100 mol %), methyl (*E*)-4-(2-bromovinyl)benzoate (54.2 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (11:1 α to β anomers based on NMR) as a colorless gummy liquid (45.7 mg, 0.093 mmol, 62% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.02 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 6.80 (dd, J = 16.2, 1.4 Hz, 1H), 6.42 (dd, J = 16.2, 5.3 Hz, 1H), 5.44 (dd, J = 3.1, 1.7 Hz, 1H, H_4), 5.41 (dd, J = 10.5, 5.9 Hz, 1H, H_2), 5.19 (dd, J = 10.4, 3.3 Hz, 1H, H_3), 4.98 (td, J = 5.8, 1.6 Hz, 1H, H_1), 4.24 (ddd, J = 6.5 Hz, 1.8 Hz,1H, H_5), 4.19 (dd, J = 11.3, 6.9 Hz, 1H), 4.11 (dd, J = 11.3, 5.9 Hz, 1H), 3.92 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.62, 170.33, 170.25, 170.03, 166.82, 140.37, 134.90, 130.18, 129.91, 126.67, 123.70, 73.03, 68.71, 68.53, 68.10, 68.08, 61.95, 52.32, 21.00, 20.88, 20.83.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{24}H_{29}O_{11}^+$): m/z 493.1704; found: 493.1687.



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

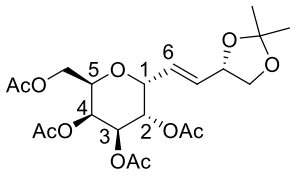
This compound was prepared according to the *Method* ***A1*** using (*2R,3S,4S,5R,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (62.0 mg, 0.15 mmol, 100 mol %), methyl (*E*)-1-(2-bromovinyl)-2-methoxybenzene (48.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (14:1 α to β anomers based on NMR) as a colorless gummy liquid (54.2 mg, 0.117 mmol, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 (t, J = 13.4 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.30 (dd, J = 16.2, 5.6 Hz, 1H),

5.42 (brs, 1H, H_4), 5.37 (dd, J = 10.4, 6.0 Hz, 1H, H_2), 5.20 (d, J = 10.5 Hz, 1H, H_3), 4.95 (t, J = 5.3 Hz, 1H, H_1), 4.26 (t, J = 6.0 Hz, 1H, H_5), 4.15– 4.08 (m, 2H), 3.82 (s, 3H), 2.13 (s, 3H), 2.03 (s, 6H), 1.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.47, 170.27, 170.13, 169.97, 156.89, 131.15, 129.47, 127.08, 125.15, 121.07, 120.66, 110.94, 73.59, 68.53, 68.27, 68.24, 68.18, 62.01, 55.43, 20.84, 20.72, 20.69.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_{10}^+$): m/z 465.1755; found: 465.1745.

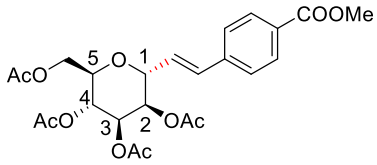


(*2R,3S,4R,5S,6R*)-2-(Acetoxymethyl)-6-((*E*)-2-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4d).

This compound was prepared according to the *Method **A1*** using 2,3,4,6-tetra-O-acetyl-alpha-D-galactopyranosyl 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 %), tetrabutylammonium iodide (55.3 mg, 0.15 mmol, 100 mol %), 25 ^{o}C. Flash column chromatography (SiO_2: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (7.4:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 5.90 ppm for α and 5.74 ppm for β) as a colorless gummy liquid (46.0 mg, 0.100 mmol, 67% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.90 (dd, J = 15.7, 4.8 Hz, 1H), 5.84 (dd, J = 15.8, 6.4 Hz, 1H), 5.35 (d, J = 1.8 Hz, 1H, H_4), 5.26 (dd, J = 10.3, 6.1 Hz, 1H, H_2), 5.06 (dd, J = 10.4, 2.9 Hz, 1H, H_3), 4.79 (t, J = 5.1 Hz, 1H, H_1), 4.54 (q, J = 6.6 Hz, 1H), 4.13 – 4.01 (m, 4H, H_5), 3.57 (t, J = 7.7 Hz, 1H), 2.10 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.74, 170.27, 169.71, 169.59, 135.67, 125.00, 109.85, 76.06, 72.36, 70.68, 70.36, 69.47, 69.36, 69.06, 62.43, 26.70, 25.87, 20.80, 20.77, 20.69.



***(2R,3R,4R,5R,6R)*-2-(Acetoxymethyl)-6-((*E*)-4-(methoxycarbonyl)styryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-5a).**

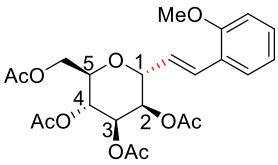
This compound was prepared according to the *Method* ***A1*** using (*2R,3R,4S,5S,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (62.0 mg, 0.15 mmol, 100 mol %), methyl (*E*)-4-(2-bromovinyl)benzoate (54.2 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a α products as a white solid (59.7 mg, 0.121 mmol, 85% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.1 Hz, 2H), 7.98 (t, J = 9.6 Hz, 2H), 7.45 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 16.4 Hz, 1H), 6.30 (dd, J = 16.4, 4.4 Hz, 1H), 5.51 (t, J = 2.8 Hz, 1H, H_2), 5.30 (t, J = 9.2 Hz, 1H, H_4), 5.20 (dd, J = 9.4, 3.0 Hz, 1H, H_3), 4.72 (brs, 1H, H_1), 4.34 (dd, J = 12.2, 5.7 Hz, 1H), 4.12 (dd, J = 12.1, 2.0 Hz, 1H), 3.99 (ddd, J = 2.6, 5.7, 9.2 Hz, 1H), 3.89 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 2.02 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.75, 170.37, 170.24, 169.67, 166.70, 140.00, 133.91, 130.09, 129.95, 126.68, 125.52, 75.28, 71.34, 70.30, 69.44, 66.68, 62.66, 52.23, 21.04, 20.86, 20.77.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{24}H_{29}O_{11}^+$): m/z 493.1704; found: 493.1695.

M.p. 124-126 ºC.



***(2R,3R,4R,5R,6R)*-2-(acetoxymethyl)-6-((*E*)-2-methoxystyryl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (α-5b).**

This compound was prepared according to the *Method* ***A1*** using (*2R,3R,4S,5S,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (62.0 mg, 0.15 mmol, 100 mol %), (*E*)-1-(2-bromovinyl)-2-methoxybenzene (48.0 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a α products as a white solid (43.8 mg, 0.094 mmol, 63% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (d, J = 7.5 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 16.5 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.17 (dd, J = 16.5, 4.5 Hz, 1H),

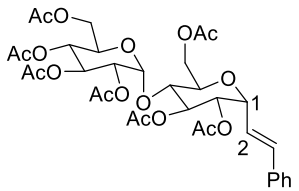
5.46 (t, J = 2.8 Hz, 1H, H_2), 5.25 (t, J = 9.3 Hz, 1H, H_4), 5.20 (dd, J = 9.5, 2.9 Hz, 1H, H_3), 4.66 (brs, 1H, H_1), 4.26 (dd, J = 12.1, 5.7 Hz, 1H), 4.09 (dd, J = 12.0, 1.4 Hz, 1H), 4.01 – 3.96 (m, 1H, H_5), 3.80 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.88, 170.49, 170.18, 169.81, 157.13, 130.27, 129.67, 127.36, 124.81, 122.95, 120.75, 111.07, 76.08, 70.88, 70.85, 69.57, 66.90, 62.85, 55.58, 21.15, 20.90, 20.84, 20.82.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_{10}^+$): m/z 465.1755; found: 465.1745.

M.p. 134-136 ºC.

(*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-6-(((*2R,3R,5S,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((*E*)-styryl)tetrahydro-*2H*-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6).



This compound was prepared according to the *Method* ***A1*** using (*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-6-(((*2R,3R,5R,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (104.8 mg, 0.15 mmol, 100 mol %), (*E*)-(2-bromovinyl)benzene (41.1 mg, 0.225 mmol, 150 mol %). Flash column chromatography (SiO_2: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (32:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H2 of the two anomers: 6.32 ppm for α and 5.98 ppm for β) as a white solid (76.8 mg, 0.106 mmol, 71% yield).

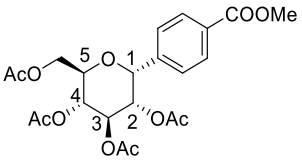
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 15.9 Hz, 1H), 6.32 (dd, J = 16.1, 5.9 Hz, 1H), 5.38 – 5.28 (m, 3H), 5.07 – 4.99 (m, 2H), 4.87 (dd, J = 10.5, 3.9 Hz, 1H, H_1), 4.78 (t, J = 5.2 Hz, 1H), 4.41 (dd, J = 12.1, 2.7 Hz, 1H), 4.23 (ddd, J = 12.6, 8.3, 4.5 Hz, 2H), 4.08 – 3.99 (m, 3H), 3.89 (t, J = 8.0 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.63, 170.58, 170.07, 169.96, 169.95, 169.51, 136.01, 135.99, 128.77, 128.48, 126.85, 121.36, 96.20, 73.98, 72.57, 72.42, 70.68, 70.36, 70.11, 69.47, 68.53, 68.11, 63.17, 61.60, 21.02, 20.93, 20.80, 20.75, 20.67, 20.65, 20.64.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{34}H_{43}O_{17}^+$): m/z 723.2495; found: 723.2457.

M.p. 63-65 ºC.

(*2R,3R,4R,5S*)-2-(Acetoxymethyl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7a).[11]



This compound was prepared according to the *Method* ***A2*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (74.4 mg, 0.17 mmol, 120 mol %), methyl 4-iodobenzoate (39.5 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (6:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.79 ppm for α and 3.82 ppm for β) as a white solid (59.4 mg, 0.127 mmol, 85% yield). Spectroscopic data matches a previously reported synthesis.

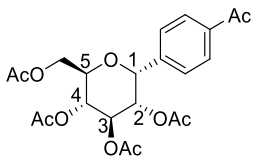
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.02 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 5.44 (t, J = 7.1 Hz, 1H, H_3), 5.34 – 5.29 (m, 2H, H_1, H_2), 5.08 – 5.04 (m, 1H, H_4), 4.31 (dd, J = 12.2, 5.9 Hz, 1H), 4.07 (dd, J = 12.3, 2.9 Hz, 1H), 3.90 (s, 3H), 3.81 – 3.77 (m, 1H, H_5), 2.09 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.67, 169.79, 169.59, 169.41, 166.67, 141.09, 130.07, 129.85, 127.67, 72.31, 71.15, 70.30, 69.97, 68.14, 61.77, 52.30, 20.85, 20.80, 20.76, 20.68.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{27}O11^+$): m/z 467.1548; found: 467.1589.

M.p. 142-144 ºC.

***(2R,3R,4R,5S)*-2-(Acetoxymethyl)-6-(4-acetylphenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7b).**

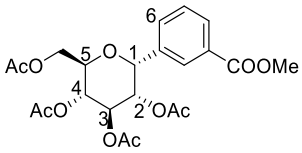


This compound was prepared according to the *Method* ***A2*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (74.4 mg, 0.17 mmol, 120 mol %), 1-(4-iodophenyl)ethan-1-one (37.0 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5:1 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 3.84 ppm for β) as a colorless gummy liquid (47.2 mg, 0.105 mmol, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 5.46 (t, J = 7.1 Hz, 1H, H_3), 5.35 – 5.30 (m, 2H, H_1, H_2), 5.07 (t, J = 7.5 Hz, 1H, H_4), 4.33 (dd, J = 12.2, 5.8 Hz, 1H), 4.07 (dd, J = 12.2, 3.0 Hz, 1H), 3.81 – 3.76 (m, 1H, H_5), 2.60 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 197.70, 170.71, 169.86, 169.61, 169.45, 141.27, 136.90, 128.63, 127.93, 72.34, 71.17, 70.33, 69.97, 68.17, 61.77, 26.77, 20.88, 20.83, 20.78, 20.73.

***(2R,3R,4R,5S)*-2-(Acetoxymethyl)-6-(3-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7c).**[11]



This compound was prepared according to the *Method* ***A2*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (74.4 mg, 0.17 mmol, 120 mol %), methyl 3-iodobenzoate (39.5 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H6 of the two anomers: 7.73 ppm for α and 7.56 ppm for β) as a white solid (42.0 mg, 0.09 mmol, 60% yield). Spectroscopic data matches a previously reported synthesis.

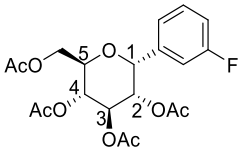
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 5.42 (t, J = 7.0 Hz, 1H, H_3), 5.32 (d, J = 4.5 Hz, 1H, H_1), 5.29 (dd, J = 7.2, 4.5 Hz, 1H, H_2), 5.05 (t, J = 7.5 Hz, 1H, H_4), 4.34 (dd, J = 12.1, 6.2 Hz, 1H), 4.09 (dd, J = 12.1, 3.2 Hz, 1H), 3.90 (s, 3H), 3.85 (ddd, J = 8.0, 6.3, 3.2 Hz, 1H, H_5), 2.10 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.79, 169.79, 169.66, 169.47, 166.77, 136.58, 131.88, 130.73, 129.47, 129.03, 128.73, 72.13, 71.17, 70.36, 69.92, 68.14, 61.80, 52.36, 20.88, 20.80, 20.71.

HRMS (ESI) exact mass calculated for [M+Na^{+}] ($C_{22}H_{26}NaO_{11}^{+}$): m/z 489.1367; found: 489.1354.

M.p. 76-78 ºC.

***(2R,3R,4R,5S)*-2-(Acetoxymethyl)-6-(3-fluorophenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7d).**



This compound was prepared according to the *Method* ***A2*** using 2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (74.4 mg, 0.17 mmol, 120 mol %), 1-fluoro-3-iodobenzene (33.3 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (4.5:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.77 ppm for α and 3.83 ppm for β) as a white solid (42.1 mg, 0.099 mmol, 66% yield).

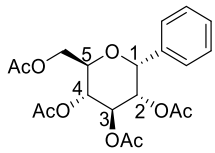
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 – 7.30 (m, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 5.46 (t, J = 7.5 Hz, 1H, H_3), 5.32 – 5.26 (m, H_1, H_2), 5.06 (t, J = 7.8 Hz, 1H, H_4), 4.29 (dd, J = 12.2, 5.7 Hz, 1H), 4.07 (dd, J = 12.2, 2.9 Hz, 1H), 3.77 (ddd, J = 8.5, 5.7, 2.9 Hz, 1H, H_5), 2.08 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.71, 169.91, 169.62, 169.48, 162.97 (d, J = 246.5 Hz), 138.51 (d, J = 7.1 Hz), 130.30 (d, J = 8.1 Hz), 123.22 (d, J = 2.8 Hz), 115.35 (d, J = 21.1 Hz), 114.96 (d, J = 22.8 Hz), 72.21, 70.84, 70.42, 70.03, 68.37, 61.87, 20.83, 20.78, 20.74.

^{19}F NMR (565 MHz, CDCl3) δ = -111.81 – -111.93 (m).

M.p. 72-74 ºC.

***(2R,3R,4R,5S,)*-2-(Acetoxymethyl)-6-phenyltetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7e).**[11]



This compound was prepared according to the *Method* ***A2*** using iodobenzene (30.6 mg, 0.15 mmol, 100 mol %)2,3,4,6-tetra-O-acetyl-alpha-D-glucopyranosyl bromide (74.4 mg, 0.17 mmol, 120 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (6.2:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.72 ppm for α and 3.84 ppm for β) as a

white solid (14.3 mg, 0.03 mmol, 23% yield). Spectroscopic data matches a previously reported synthesis.

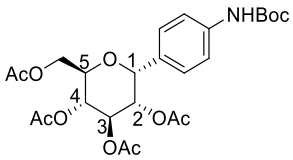
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.56 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 4.8 Hz, 1H), 5.61 – 5.56 (m, 1H, H_3), 5.37 – 5.32 (m, 2H, H_1, H_2), 5.11 (t, J = 8.3 Hz, 1H, H_4), 4.27 (dd, J = 12.2, 5.2 Hz, 1H), 4.05 (dd, J = 12.2, 2.8 Hz, 1H), 3.72 (ddd, J = 8.4, 5.1, 2.9 Hz, 1H, H_5), 2.09 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.77, 170.14, 169.66, 169.62, 135.70, 128.76, 128.39, 128.06, 73.08, 70.80, 70.45, 70.28, 68.69, 62.00, 20.89, 20.84, 20.80, 20.77.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{20}H_{25}O_9^+$): m/z 409.1493; found: 409.1492.

M.p. 76-78 ºC.

***(2R,3R,4R,5S)*-2-(Acetoxymethyl)-6-(4-((tert-butoxycarbonyl)amino)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7f).**



This compound was prepared according to the *Method* ***A3*** for electron-rich aryl halides 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 (47.9 mg, 0.15 mmol, 100 mol %), 25 ºC. Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (2.8:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.65 ppm for α and 3.81 ppm for β) as a white solid (62.7 mg, 0.12 mmol, 80% yield).

NMR data for the α-anomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 1H), 5.57 (t, *J* = 7.9 Hz, 1H, H_3), 5.32 – 5.28 (m, 2H, H_1, H_2), 5.08 (t, *J* = 8.4 Hz, 1H, H_4), 4.23 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.00 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.65 (ddd, *J* =9.0, 5.0, 2.8 Hz,1H, H_5), 2.06 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.77, 170.16, 169.65, 169.63, 152.76, 138.53, 129.76, 128.95, 118.52, 72.85, 70.80, 70.45, 69.86, 68.76, 61.99, 28.37, 20.84, 20.81, 20.79, 20.72.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{25}H_{34}NO_{11}^+$): m/z 524.2126; found: 524.2112.

NMR data for the β-anomer:

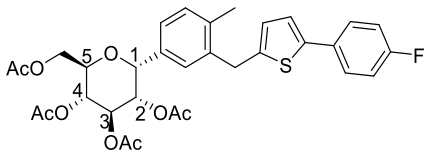
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.65 (s, 1H), 5.30 (t, J = 9.4 Hz, 1H, H_3), 5.20 (t, J = 9.7 Hz, 1H, H_4), 5.11 (t, J = 9.7 Hz, 1H, H_2), 4.33 (d, J = 9.8 Hz, 1H, H_1), 4.26 (dd, J = 12.4, 4.8 Hz, 1H), 4.13 (dd, J = 12.4, 2.0 Hz, 1H), 3.81 (ddd, 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.

***(2R,3R,4R,5S)*-2-(Acetoxymethyl)-6-(3-((5-(4-fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7g).**[4]



This compound was prepared according to the *Method* ***A3*** for electron-rich aryl halides 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 %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (2:1 α to β based on ^{1}H NMR spectra, determined by the ratio of the characteristic peaks of H5 of the two anomers: 3.75 ppm for α and 3.82 ppm for β) as a colorless gummy liquid (57.5 mg, 0.135 mmol, 90% yield). Spectroscopic data matches a previously reported synthesis.

NMR data for the α-anomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.46 (dd, J = 8.6, 5.3 Hz, 2H), 7.43 (s, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.03 (d, J = 3.6 Hz, 1H), 7.01 (t, J = 8.6 Hz, 2H), 6.69 (d, J = 3.5 Hz, 1H), 5.62 – 5.57 (m, 1H, H_3), 5.37 – 5.31 (m, 2H, H_1, H_2), 5.12 – 5.09 (m, 1H, H_4), 4.26 (dd, J = 12.2, 5.2 Hz, 1H), 4.17 – 4.09 (m, 2H), 4.05 (dd, J = 12.2, 2.8 Hz, 1H), 3.77 – 3.73 (ddd, J = 9.0, 5.0, 2.7 Hz, 1H, H_5), 2.33 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.72, 170.06, 169.59, 169.57, 162.13 (d, J = 246.6 Hz), 143.06, 141.68, 138.80, 136.55, 133.49, 130.80 (d, J = 3.4 Hz), 130.76, 129.18, 127.11 (d, J = 7.9

Hz), 126.47, 126.15, 122.77, 115.79 (d, J = 21.7 Hz), 72.89, 70.84, 70.41, 70.09, 68.81, 62.03, 34.18, 20.81, 20.75, 20.71, 20.70, 19.23.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{32}H_{34}FO_9S^+$): m/z 613.1902; found: 613.2016.

NMR data for the β-anomer:

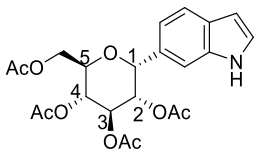
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.47 (dd, J = 8.8, 5.2 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.07 – 6.99 (m, 3H), 6.61 (d, J = 3.6 Hz, 1H), 5.31 (t, J = 9.5 Hz, 1H, H_3), 5.23 (t, J = 9.7 Hz, 1H, H_4), 5.13 (t, J = 9.6 Hz, 1H, H_2), 4.36 (d, J = 9.8 Hz, 1H, H_1), 4.28 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, 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.

***(2R,3R,4R,5S,6R)*-2-(acetoxymethyl)-6-(*1H*-indol-6-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7h).**



This compound was prepared according to the *Method* ***A3*** for electron-rich aryl halides 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 %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (3.2:1 α to β anomers based on NMR) as a brown solid (54.9 mg, 0.123 mmol, 82% yield)

NMR data for the α-anomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.52 (s, 1H), 7.71 (s, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.25 (t, J = 2.5 Hz, 1H), 6.54 (s, 1H), 5.79 (t, J = 8.8 Hz, 1H, H_3), 5.53 (d, J = 5.5 Hz, 1H, H_1), 5.42 (dd, J = 9.4, 5.6 Hz, 1H, H_2), 5.16 (t, J = 8.7 Hz, 1H, H_4), 4.24 (dd, J = 12.2, 4.7 Hz,

1H), 4.02 (dd, J = 12.2, 2.3 Hz, 1H), 3.72 – 3.65 (m, 1H, H_5), 2.10 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.84, 170.49, 169.73, 169.68, 135.53, 128.77, 127.63, 125.40, 121.15, 120.18, 111.28, 102.44, 73.91, 71.21, 70.81, 69.53, 69.00, 62.05, 20.90, 20.85, 20.82, 20.72.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{26}NO_9^+$): m/z 448.1602; found: 448.1592.

M.p. 103-105 ºC.

NMR data for the β-anomer:

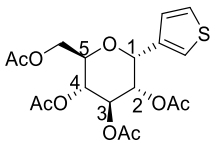
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.41 (s, 1H), 7.20 (t, J = 2.6 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 5.37 (t, J = 9.4 Hz, 1H, H_3), 5.30 – 5.24 (m, 2H, H_4, H_2), 4.52 (d, J = 9.8 Hz, 1H, H_1), 4.31 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 1.6 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.

***(2R,3R,4R,5S)*-2-(acetoxymethyl)-6-(thiophen-3-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (7i).**[11]



This compound was prepared according to the *Method **A3*** for electron-rich aryl halides 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 %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (3:1 α to β anomers based on NMR) as a white solid (27.9 mg, 0.067 mmol, 45% yield)

NMR data for the α-anomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.60 – 7.56 (m, 1H), 7.36 (dd, J = 5.0, 2.9 Hz, 1H), 7.16 (dd, J = 5.0, 1.1 Hz, 1H), 5.61 (dd, J = 10.1, 9.0 Hz, 1H, H_3), 5.40 (d, J = 5.7 Hz, 1H, H_1), 5.31 (dd, J = 10.2, 5.9 Hz, 1H, H_2), 5.09 (dd, J = 9.8, 9.1 Hz, 1H, H_4), 4.20 (dd, J = 12.3, 4.8 Hz, 1H), 4.02 (dd, J = 12.3, 2.4 Hz, 1H), 3.59 (ddd, J = 9.9, 4.8, 2.4 Hz, 1H, H_5), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.74, 170.42, 169.64, 169.59, 136.01, 127.67, 126.60, 124.50, 71.40, 70.98, 70.61, 69.79, 69.06, 62.20, 20.86, 20.82, 20.69.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{23}O_9S^+$): m/z 415.1057; found: 415.1099.

M.p. 112-113 ºC.

NMR data for the β-anomer:

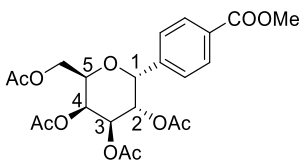
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 – 7.27 (m, 2H), 7.08 (dd, J = 4.9, 1.2 Hz, 1H), 5.30 (t, J = 9.4 Hz, 1H, H_3), 5.21 (t, J = 9.7 Hz, 1H, H_4), 5.16 (t, J = 9.7 Hz, 1H, H_2), 4.54 (d, J = 9.9 Hz, 1H, H_1), 4.27 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (dd, J = 12.4, 2.2 Hz, 1H), 3.81 (ddd, J = 10.0, 4.7, 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 ºC.

***(2R,3S,4R,5S)*-2-(acetoxymethyl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (8a).**[13]



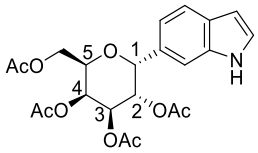
This compound was prepared according to the *Method **A2*** using 2,3,4,6-tetra-O-acetyl-alpha-D-galactopyranosyl bromide (74.0 mg, 0.18 mmol, 120 mol %), methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 100 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), DMAP (7.3 mg, 0.06 mmol, 40 mol %), w/o HBr/AcOH. Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (13:1 α to β anomers based on NMR) as a colorless gummy liquid (51.7 mg, 0.111 mmol, 74% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 5.46 (dd, J = 4.9, 3.2 Hz, 1H, H_4), 5.36 (dd, J = 6.4, 3.1 Hz, 1H, H_3), 5.33 (dd, J = 6.2, 3.1 Hz, 1H, H_2), 5.29 (d, J = 3.1 Hz, 1H, H_1), 4.62 (dd, J = 12.1, 8.7 Hz, 1H), 4.25 – 4.19 (m, 1H, H_5), 4.12 (dd, J = 12.2, 3.9 Hz, 1H), 3.88 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.82, 169.81, 169.42, 169.25, 166.75, 141.26, 129.91, 129.60, 127.15, 71.40, 70.70, 70.01, 67.74, 66.48, 60.06, 52.21, 20.92, 20.81, 20.76, 20.56.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{27}O_{11}^+$): m/z 467.1548; found: 467.1540.

***(2R,3S,4R,5S,6R)*-2-(acetoxymethyl)-6-(*1H*-indol-6-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (8b).**

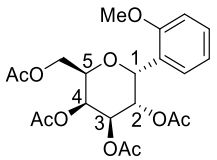


This compound was prepared according to the *Method* ***A3*** using 2,3,4,6-tetra-O-acetyl-alpha-D-galactopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 6-iodo-*1H*-indole (36.5 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (9.6:1 α to β anomers based on NMR) as a brown solid (49.0 mg, 0.101 mmol, 73% yield);

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.40 (s, 1H), 7.80 (s, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.20 (t, J = 2.5 Hz, 1H), 6.53 (s, 1H), 5.58 (dd, J = 7.7, 3.4 Hz, 1H), 5.49 – 5.44 (m, 3H), 4.44 (dd, J = 11.2, 7.8 Hz, 1H), 4.17 – 4.09 (m, 2H), 2.14 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.82, 170.20, 169.90, 169.74, 135.48, 127.72, 126.91, 124.94, 121.87, 120.10, 111.25, 102.95, 72.58, 70.17, 70.01, 68.09, 67.41, 60.83, 20.99, 20.88, 20.87, 20.85.

***(2R,3S,4R,5S,6R)*-2-(acetoxymethyl)-6-(2-methoxyphenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (8c).**



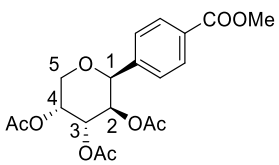
This compound was prepared according to the *Method* ***A3*** using 2,3,4,6-tetra-O-acetyl-alpha-D-galactopyranosyl bromide (93.0 mg, 0.225 mmol, 150 mol %), 1-iodo-2-methoxybenzene (32.2 mg, 0.15 mmol, 100

mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5.3:1 α to β anomers based on NMR) as a yellow oil (26.2 mg, 0.06 mmol, 40% yield);

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.44 (dd, J = 7.5, 1.0 Hz, 1H), 7.23 (td, J = 8.0, 1.8 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 5.52 (dd, J = 6.3, 3.0 Hz, 1H), 5.48 (d, J = 1.3 Hz, 1H), 5.34 – 5.29 (m, 2H), 4.71 (dd, J = 12.4, 9.1 Hz, 1H), 4.45 (ddd, J = 9.2, 6.3, 3.1 Hz, 1H), 4.27 (dd, J = 12.5, 3.1 Hz, 1H), 3.81 (s, 3H), 2.18 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (151MHz, $CDCl_3$) δ = 171.08, 169.74, 169.37, 169.11, 155.78, 128.90, 127.73, 124.46, 120.09, 109.88, 72.18, 69.00, 68.15, 65.95, 64.85, 59.91, 55.49, 21.05, 20.94, 20.83, 20.43.

(*3R,4R,5R*)-2-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (9).



This compound was prepared according to the *Method* ***A2*** using (*2R,3S,4R,5R*)-2-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (61.0 mg, 0.18 mmol, 120 mol %), methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 100 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), DMAP (7.3 mg, 0.06 mmol, 40 mol %), w/o HBr/AcOH. Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1.7:1 α to β anomers based on NMR) as a colorless gummy liquid (29.5 mg, 0.075 mmol, 50% yield);

NMR data for the α-anomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 5.40 (t, J = 3.0 Hz, 1H, H_3), 5.29 (ddd, J = 8.2, 5.2, 3.2 Hz, 1H, H_4), 5.15 (dd, J = 3.8, 1.6 Hz, 1H, H_2), 4.92 (brs, 1H, H_1), 4.04 (dd, J = 10.8, 5.4 Hz, 1H, H_{5a}), 3.89 (s, 3H), 3.83 (t, J = 11.0 Hz, 1H, H_{5b}), 2.21 (s, 3H), 2.02 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 169.88, 169.27, 169.03, 166.87, 141.85, 129.82, 129.52, 126.30, 75.59, 70.53, 66.90, 65.09, 63.95, 52.24, 21.00, 20.86, 20.50.

HRMS (ESI) exact mass calculated for $[M+H^+]$ ($C_{19}H_{23}O_9^+$): m/z 395.1337; found: 395.1335.

NMR data for the β-anomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 5.40 (brs, 1H, H_4), 5.34 (t, J = 9.9 Hz, 1H, H_2), 5.18 (dd, J = 10.1, 3.4 Hz, 1H, H_3), 4.33 (d, J = 9.7 Hz, 1H, H_1),

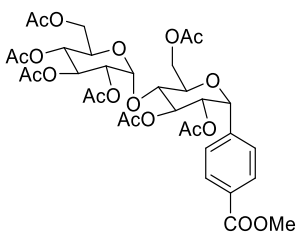
4.16 (d, J = 13.3 Hz, 1H, H_{5a}), 3.90 (s, 3H), 3.82 (d, J = 13.3 Hz, 1H, H_{5b}), 2.22 (s, 3H), 2.00 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.57, 170.37, 169.03, 166.78, 141.93, 130.62, 129.78, 127.32, 80.94, 71.82, 70.17, 68.95, 68.62, 52.30, 21.19, 20.83, 20.60.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{19}H_{23}O_9^+$): m/z 395.1337; found: 395.1340.

M.p. 136-138 ºC.

(*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-6-(((*2R,3R,5S,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(4-(methoxycarbonyl)phenyl)tetrahydro-*2H*-pyran-3-yl)oxy)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (10).



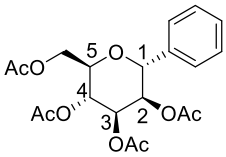
This compound was prepared according to the *Method **A2*** for electron-deficient aryl halides using (*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-6-(((*2R,3R,5R,6R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (125.7 mg, 0.18 mmol, 120 mol %), methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 100 mol %), $Ni(ClO_4)_2{\cdot}6H_2O$ (5.5 mg, 0.015 mmol, 10 mol %), DMAP (7.3 mg, 0.06 mmol, 40 mol %), w/o HBr/AcOH at 25 ºC. Flash column chromatography (SiO_2: 30% ethyl acetate in petroleum ether) gave a mixture of diastereomers (5:1 α to β anomers based on NMR) as a white solid (62.2 mg, 0.082 mmol, 55% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 5.36 (t, J = 9.8 Hz, 1H), 5.33 (d, J = 3.8 Hz, 1H), 5.30 – 5.25 (m, 2H), 5.18 – 5.14 (m, 1H), 5.06 (t, J = 9.8 Hz, 1H), 4.91 (dd, J = 10.3, 3.7 Hz,1H), 4.41 – 4.32 (m, 2H), 4.26 – 4.12 (m, 4H), 3.93 (s, 3H), 3.72 (dd, J = 6.3, 3.3 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.55, 170.48, 170.15, 169.95, 169.81, 169.42, 169.39, 142.14, 129.65, 126.22, 97.01, 77.36, 74.52, 72.59, 71.29, 70.05, 69.76, 69.53, 69.00, 68.46, 68.21, 62.44, 61.80, 52.12, 20.89, 20.75, 20.61, 20.53, 20.52, 20.44, 20.42.

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

(2R,3R,4R,5R,6R)-2-(acetoxymethyl)-6-phenyltetrahydro-2H-pyran-3,4,5-triyl triacetate (11). [11]

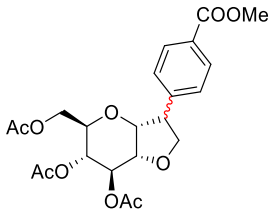


This compound was prepared according to the *Method* ***A3*** for electron-deficient aryl halides using (*2R,3R,4S,5S,6R*)-2-(acetoxymethyl)-6-bromotetrahydro-*2H*-pyran-3,4,5-triyl triacetate (93.0 mg, 0.225 mmol, 150 mol %), iodobenzene (30.6 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave α-anomers as a white solid (51.4 mg, 0.126 mmol, 84% yield);

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (d, J = 7.9 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 5.98 (t, J = 3.1 Hz, 1H, H_2), 5.33 (t, J = 8.9 Hz, 1H, H_4), 5.15 (dd, J = 9.1, 3.2 Hz, 1H, H_3), 5.10 (d, J = 2.5 Hz, 1H, H_1), 4.36 (dd, J = 12.1, 6.1 Hz, 1H), 4.12 (dd, J = 12.1, 2.7 Hz, 1H), 3.75 (ddd, J = 8.7, 6.1, 2.7 Hz, 1H, H_5), 2.14 (s, 3H), 2.11 (s, 1H), 2.04 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.74, 170.36, 170.32, 169.69, 135.36, 129.17, 128.56, 126.56, 75.86, 71.29, 69.77, 69.29, 66.93, 62.50, 21.03, 20.84, 20.80, 20.77.

(*3aR,5R,6R,7R,7aS*)-5-(acetoxymethyl)-3-(4-(methoxycarbonyl)phenyl)hexahydro-*2H*-furo[3,2-*b*]pyran-6,7-diyl diacetate(13)



dr = 1.2:1

This compound was prepared according to the *Method* ***A3*** for electron-deficient aryl halides using (*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-5-(allyloxy)-6-bromotetrahydro-*2H*-pyran-3,4-diyl diacetate (93.0 mg, 0.25 mmol, 150 mol %), methyl methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 100 mol %). Flash column chromatography (SiO_2: 20% ethyl acetate in petroleum ether) gave a mixture of diastereomers (1.2:1 based on NMR) as a colorless gummy liquid (28.3 mg, 0.063 mmol, 42% 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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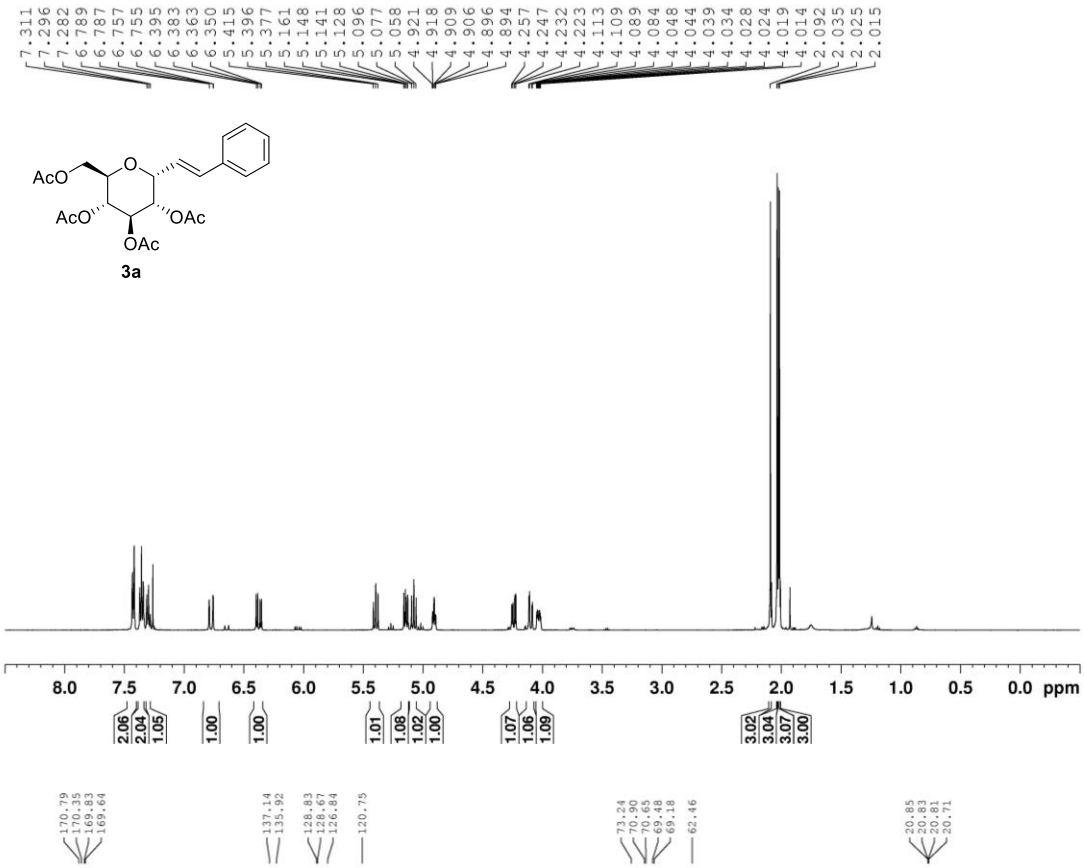
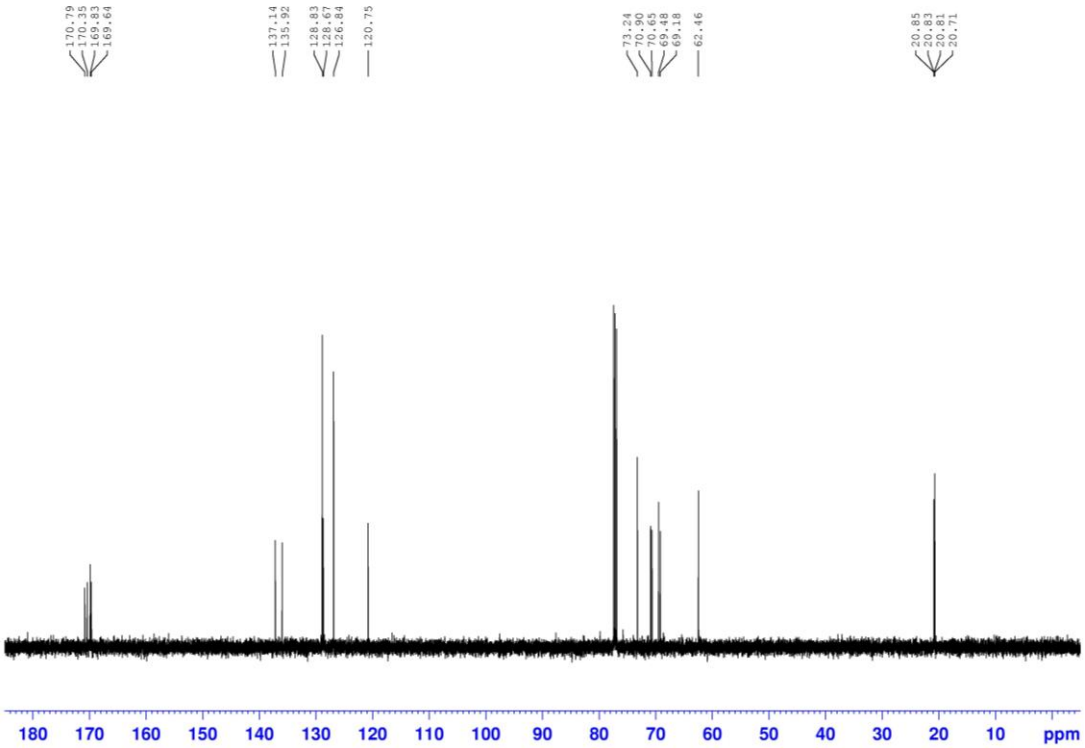
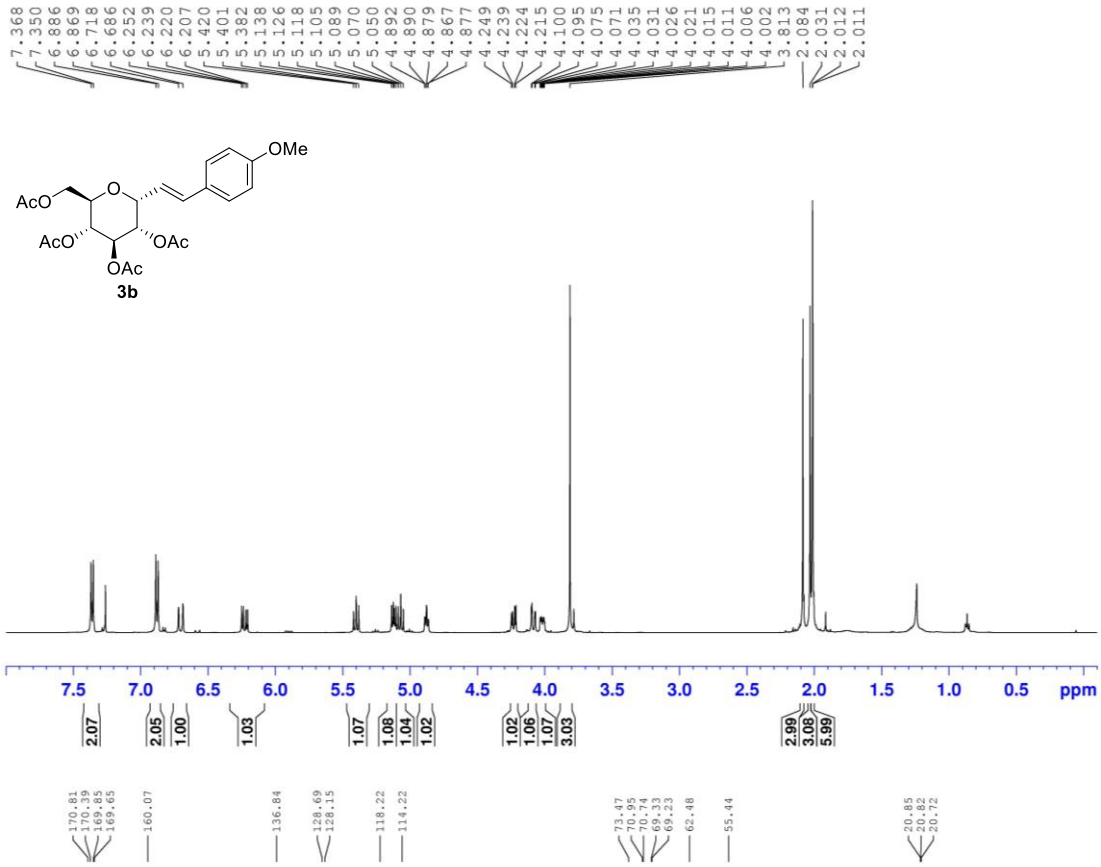
III. NMR Data for New Compounds



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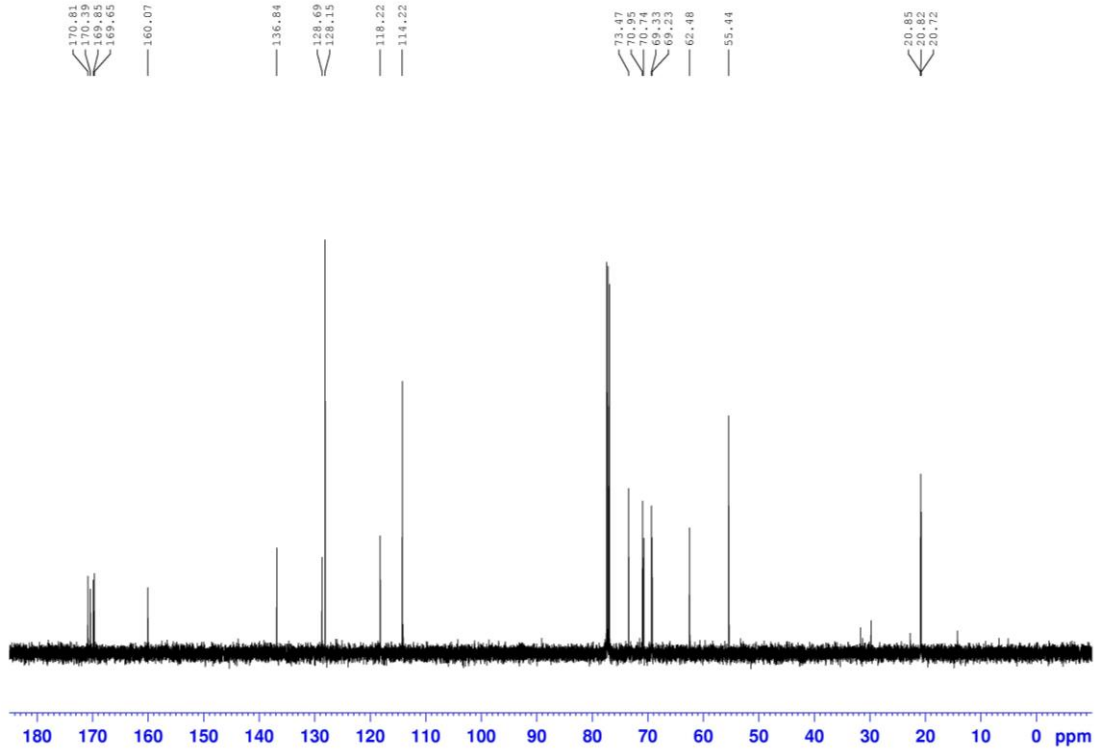
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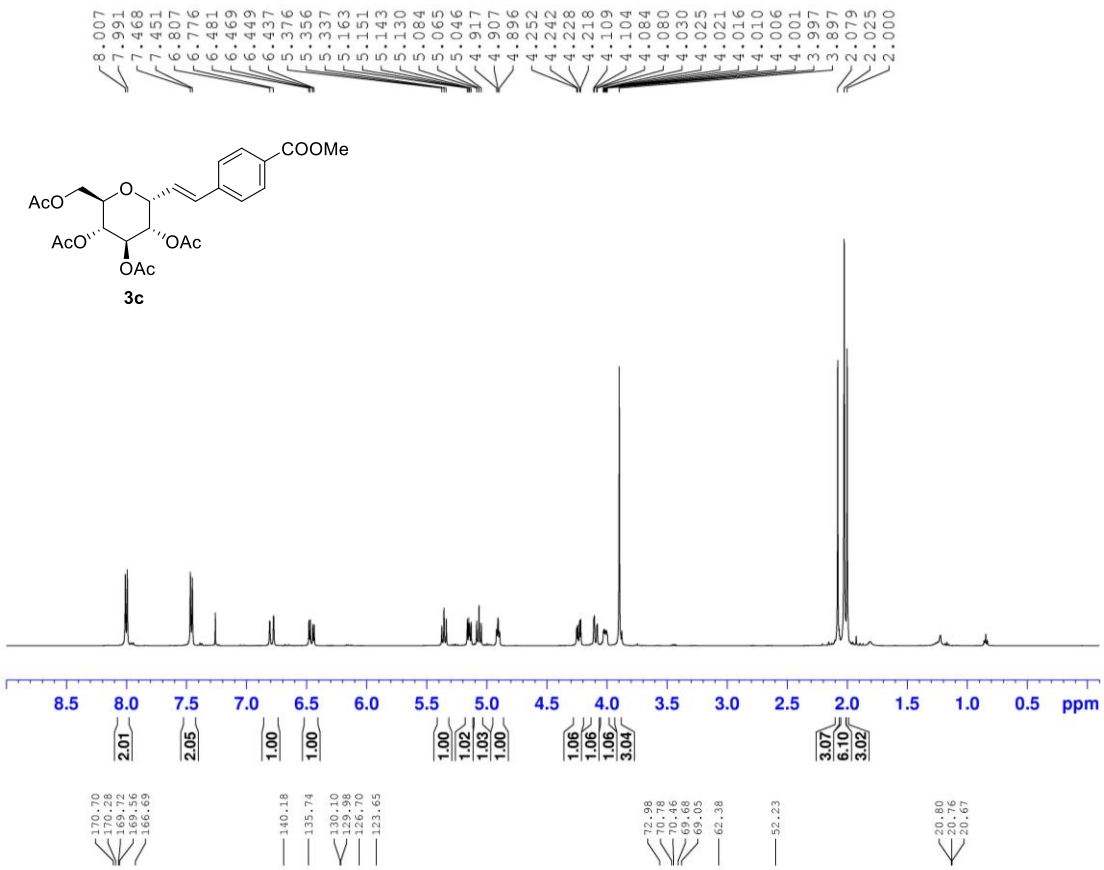
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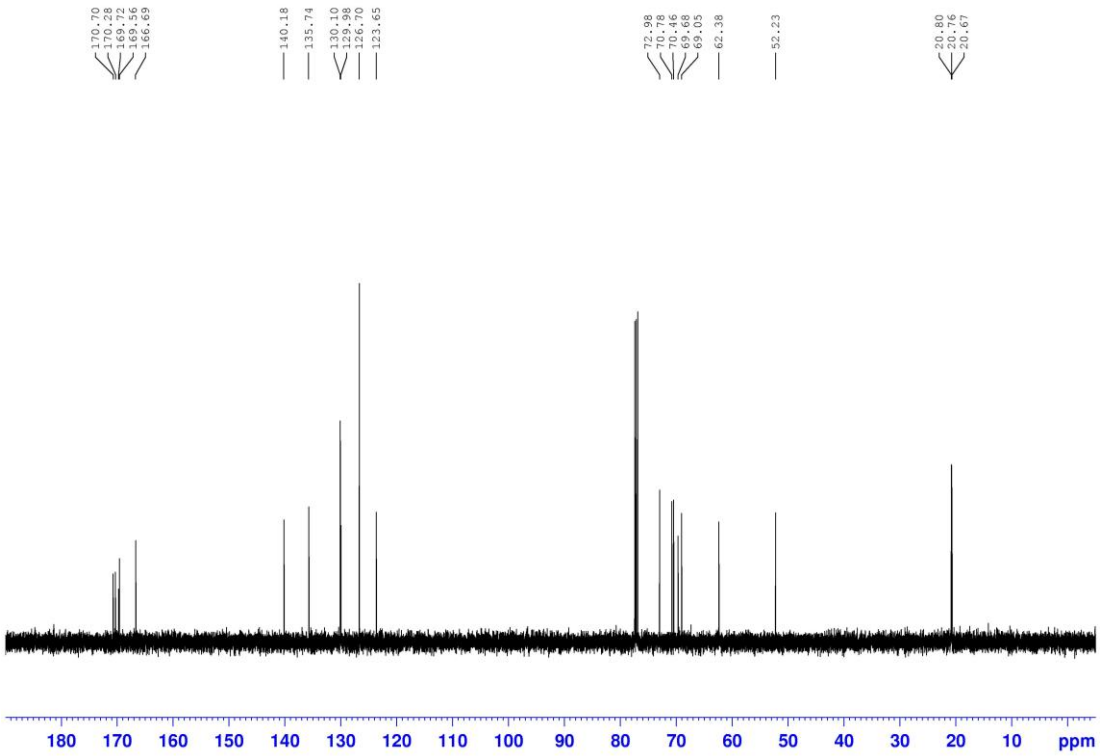
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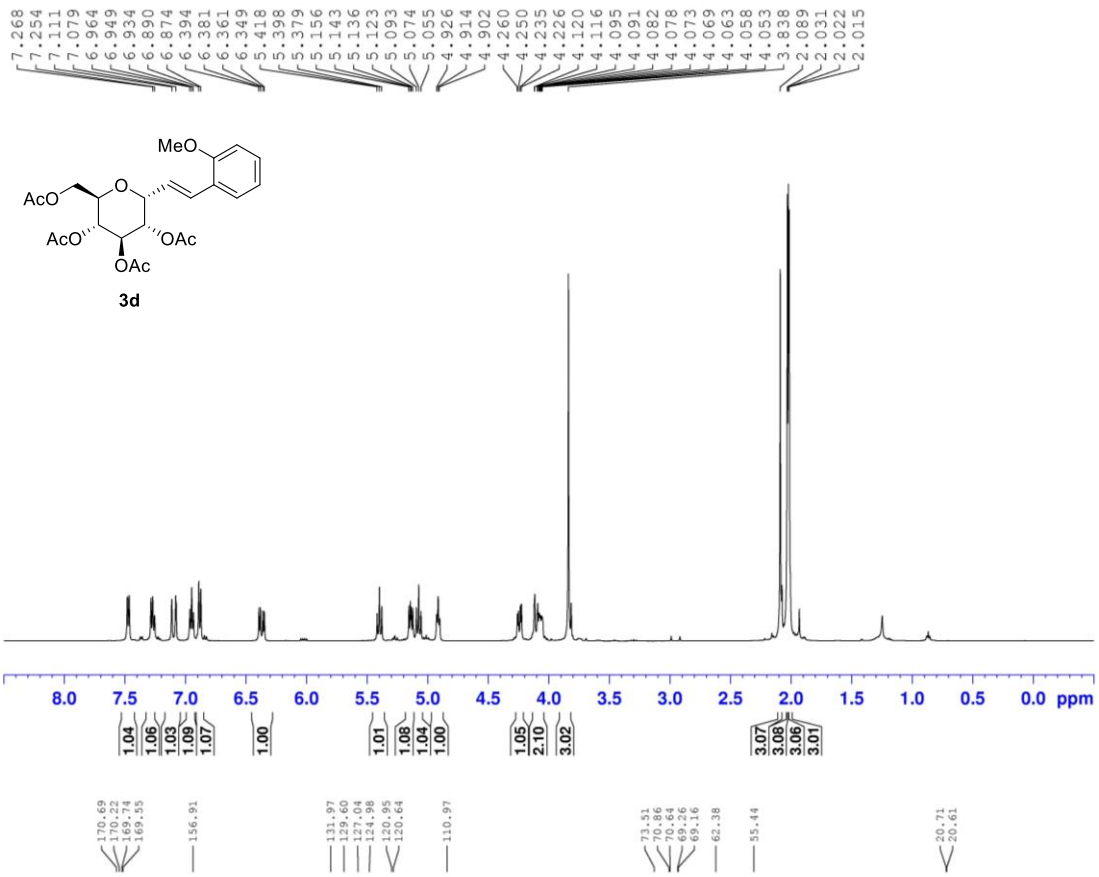
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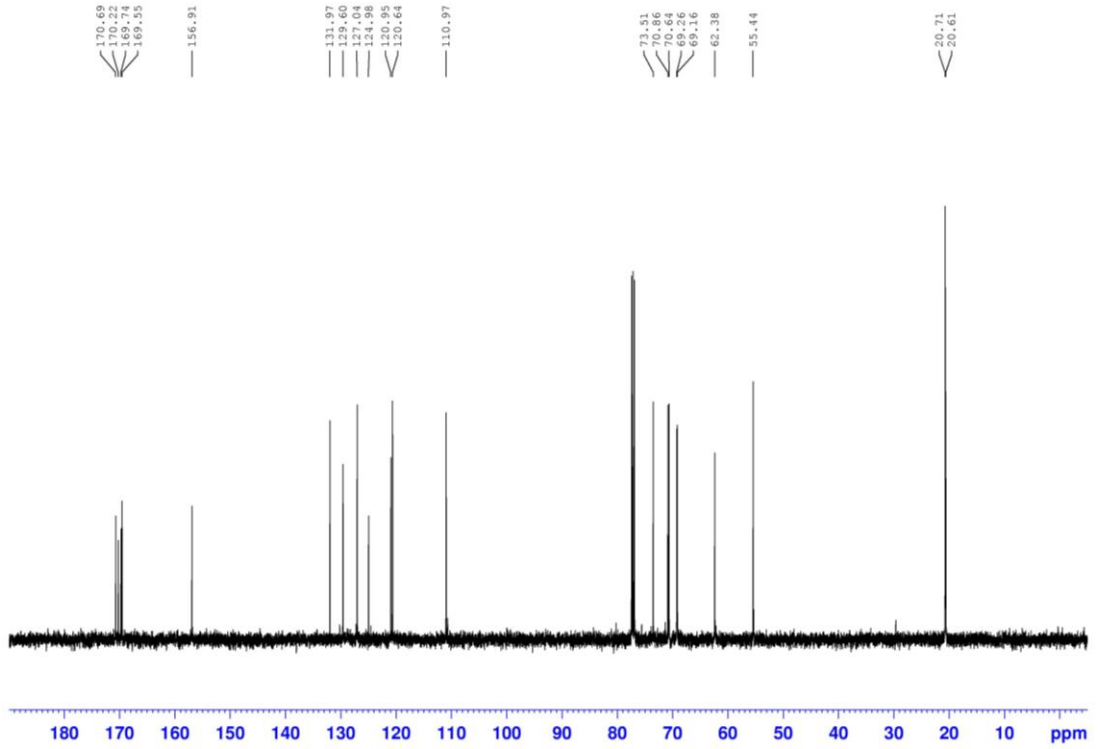
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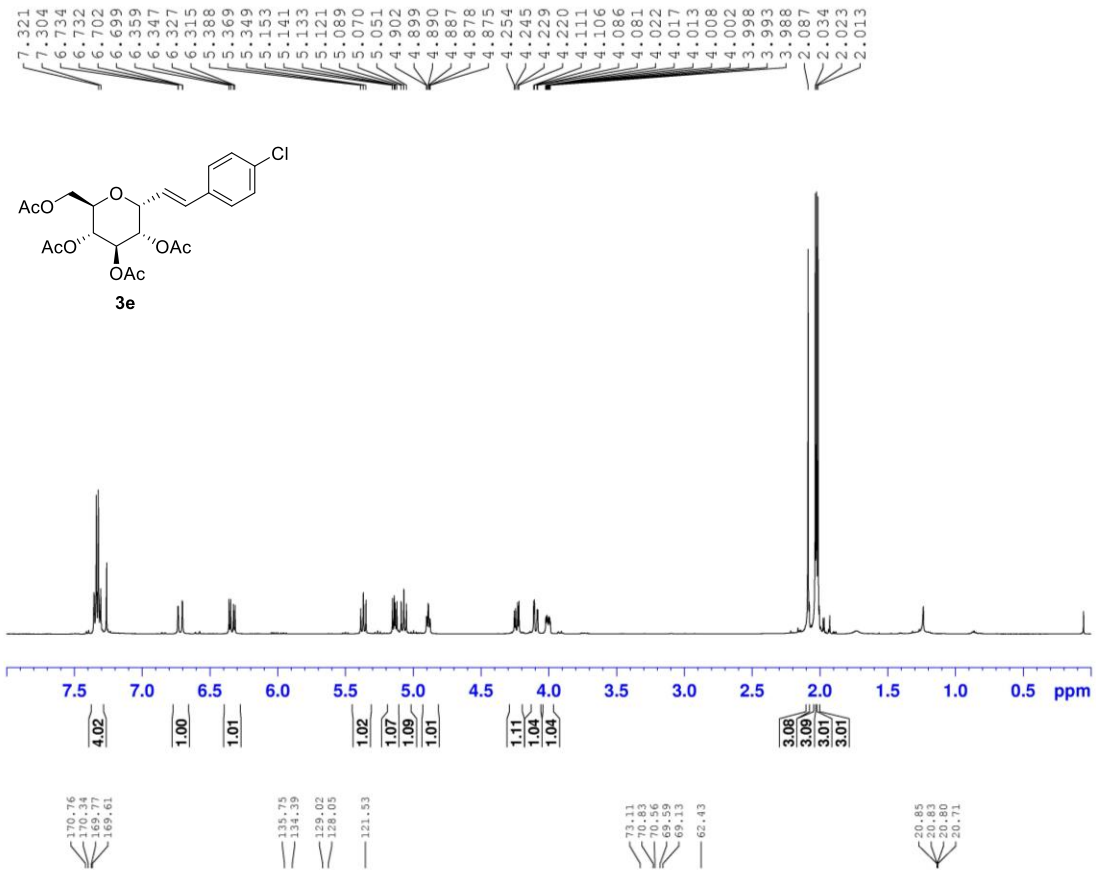
20.71
20.61
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.304
6.734
6.732
6.702
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6.359
6.347
6.327
6.315
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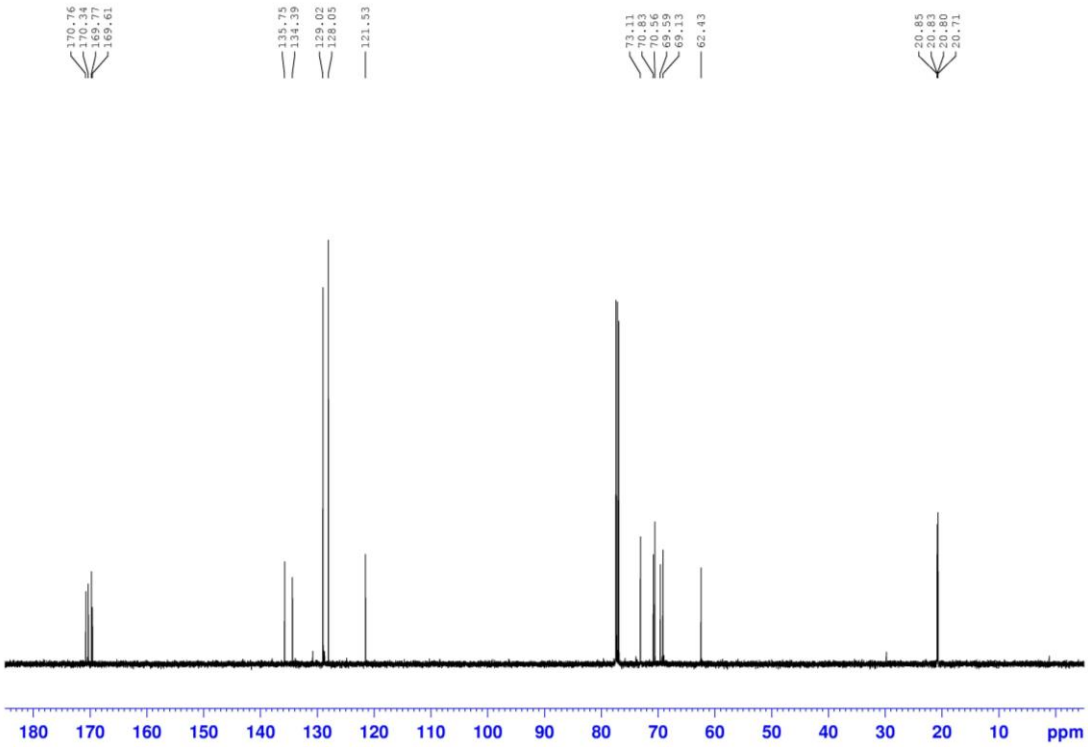
5.369
5.349
5.153
5.141
5.133
5.121
5.089
5.070
5.051
4.902
4.899
4.890
4.887
4.878
4.875
4.254
4.245
4.229
4.220
4.111
4.106
4.086
4.081
4.022
4.017
4.013
4.008
4.002
3.998
3.993
3.988
2.087
2.034
2.023
2.013
Cl
AcO
O
AcO
OAc
OAc
3e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.02
1.00
1.01
1.02
1.07
1.09
1.01
1.11
1.04
1.04
3.08
3.09
3.01
3.01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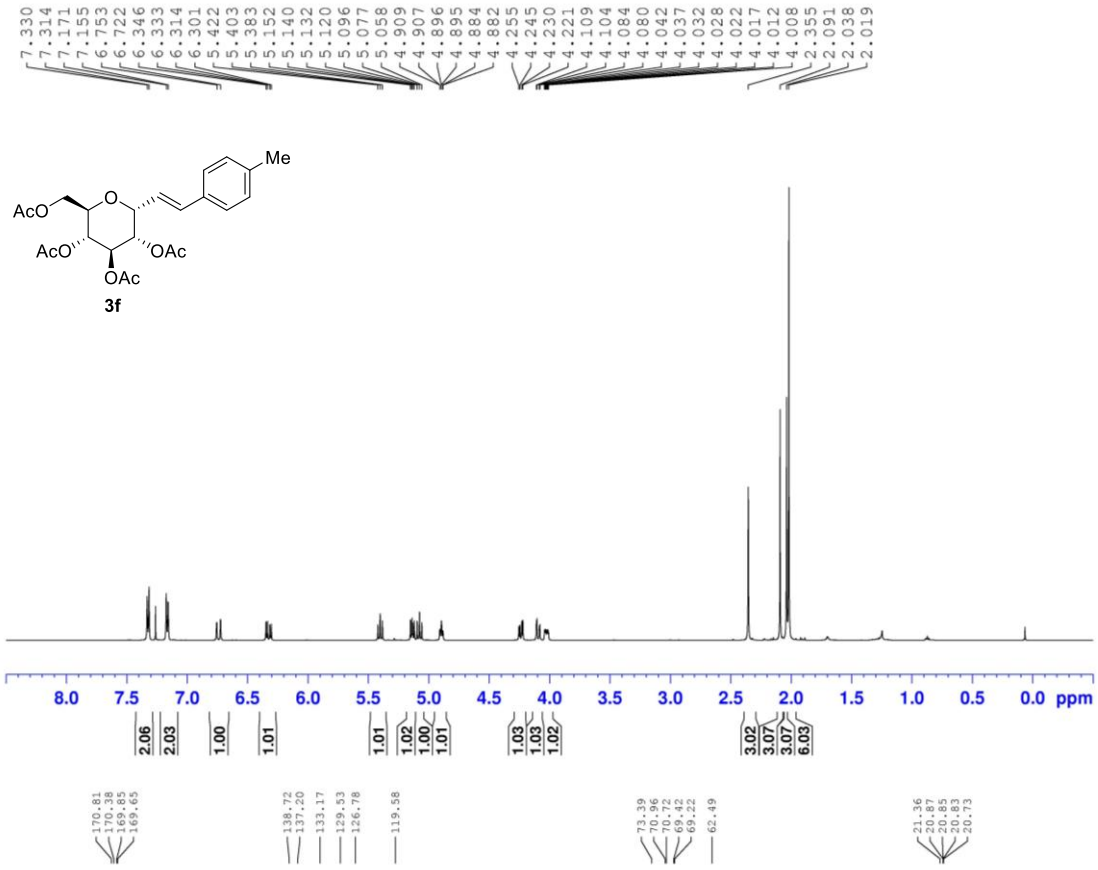
170.34
169.77
169.61
135.75
134.39
129.02
128.05
121.53
73.11
70.83
70.56
69.59
69.13
62.43
20.85
20.83
20.80
20.71
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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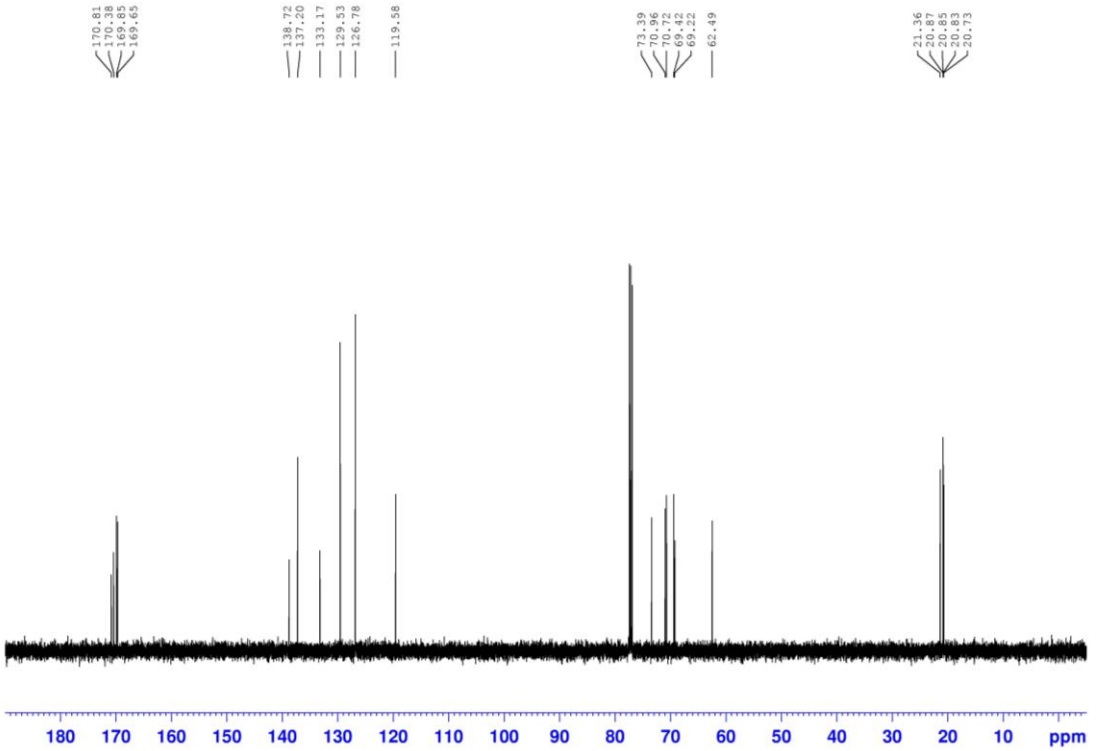
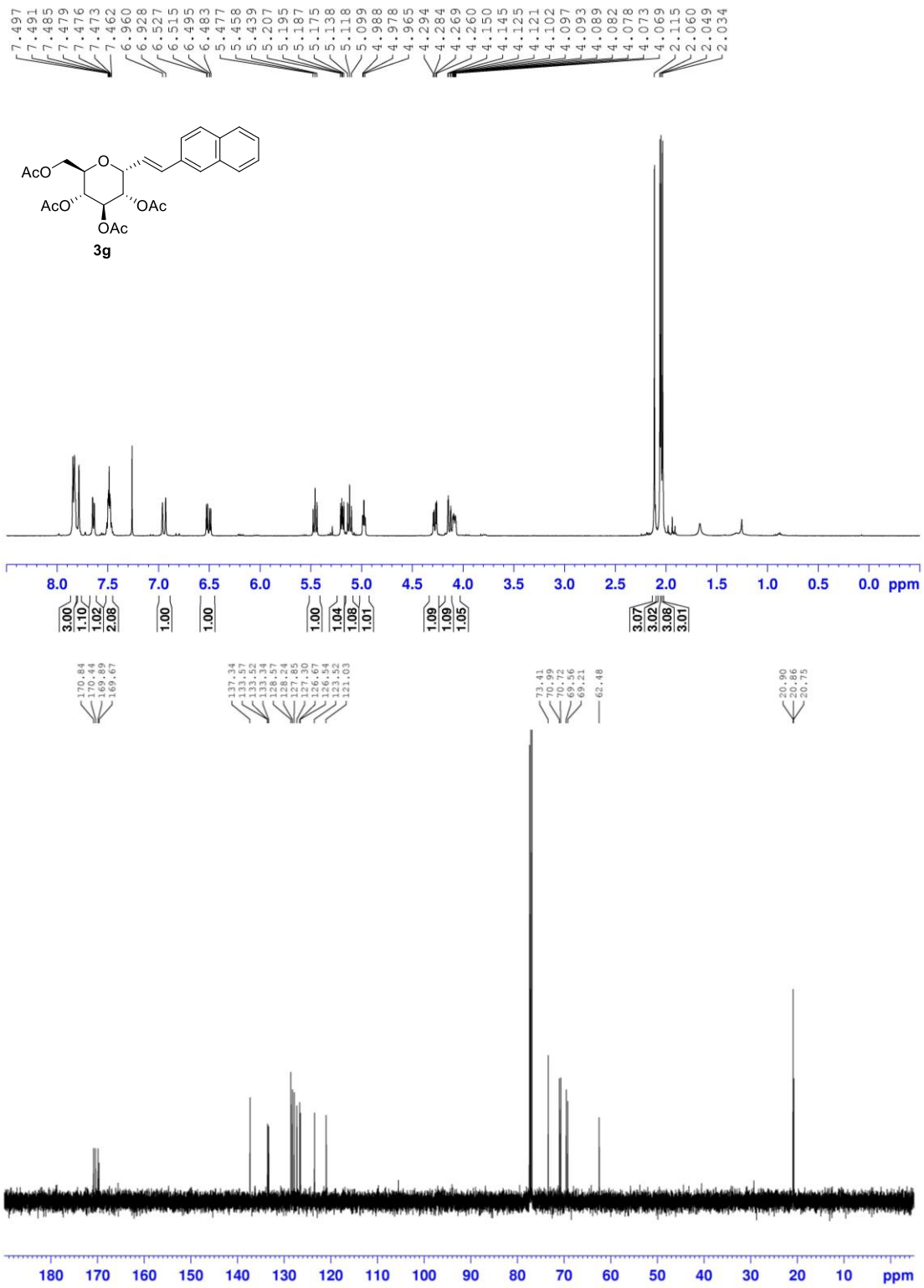
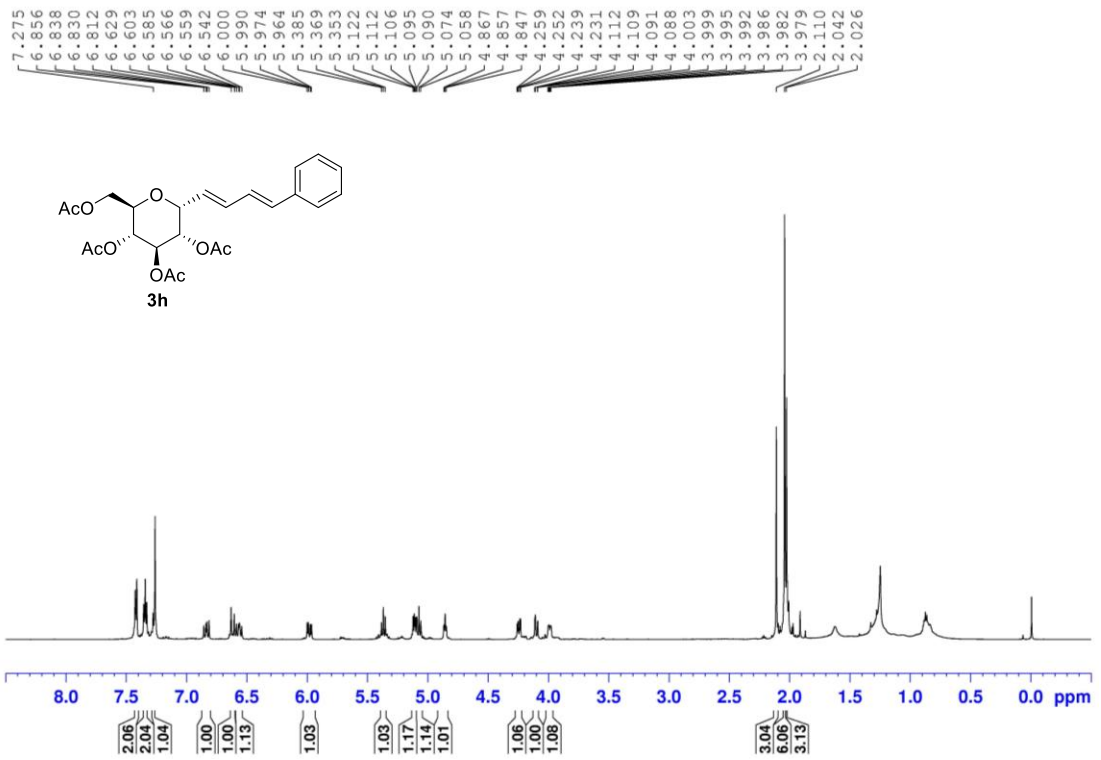
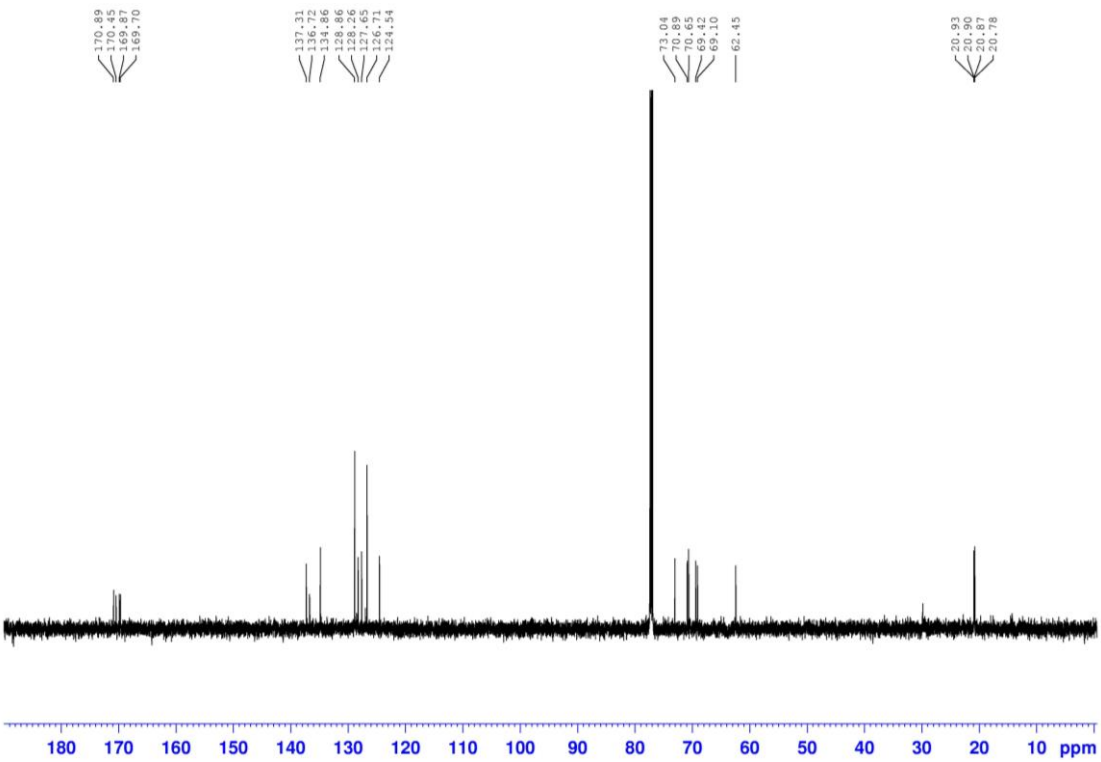
7.314
7.171
7.155
6.753
6.722
6.346
6.333
6.314
6.301
5.422
5.403
5.383
5.152
5.140
5.132
5.120
5.096
5.077
5.058
4.909
4.907
4.896
4.895
4.884
4.882
4.255
4.245
4.230
4.221
4.109
4.104
4.084
4.080
4.042
4.037
4.032
4.028
4.022
4.017
4.012
4.008
2.355
2.091
2.038
2.019
Me
AcO
O
AcO
OAc
OAc
3f
8.0 7.5 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
2.03
1.00
1.01
1.01
1.02
1.00
1.01
1.03
1.03
1.02
3.02
3.07
3.07
6.03


170.81
170.38
169.85
169.65
138.72
137.20
133.17
129.53
126.78
119.58
73.39
70.96
70.72
69.42
69.22
62.49
21.36
20.87
20.85
20.83
20.73
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.497
7.491
7.485
7.479
7.476
7.473
7.462
6.960
6.928
6.527
6.515
6.495
6.483
5.477
5.458
5.439
5.207
5.195
5.187
5.175
5.138
5.118
5.099
4.988
4.978
4.965
4.294
4.284
4.269
4.260
4.150
4.145
4.125
4.121
4.102
4.097
4.093
4.089
4.082
4.078
4.073
4.069
2.115
2.060
2.049
2.034
AcO
O
AcO
OAc
OAc
3g
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
3.00 1.10 1.02 2.08 1.00 1.00 1.00 1.04 1.08 1.01 1.09 1.09 1.05 3.07 3.02 3.08 3.01
170.84
170.44
169.89
169.67
137.34
133.57
133.52
133.34
128.57
128.24
127.85
127.70
127.67
126.54
123.52
121.03
73.41
70.99
70.72
69.56
69.21
62.48
20.90
20.86
20.75
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.275
6.856
6.838
6.830
6.812
6.629
6.603
6.585
6.566
6.559
6.542
6.000
5.990
5.974
5.964
5.385
5.369
5.353
5.122
5.112
5.106
5.095
5.090
5.074
5.058
4.867
4.857
4.847
4.259
4.252
4.239
4.231
4.112
4.109
4.091
4.088
4.003
3.999
3.995
3.992
3.986
3.982
3.979
2.110
2.042
2.026
AcO
O
AcO
OAc
OAc
3h
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
2.04
1.04
1.00
1.00
1.13
1.03
1.03
1.17
1.14
1.01
1.06
1.00
1.08
3.04
6.06
3.13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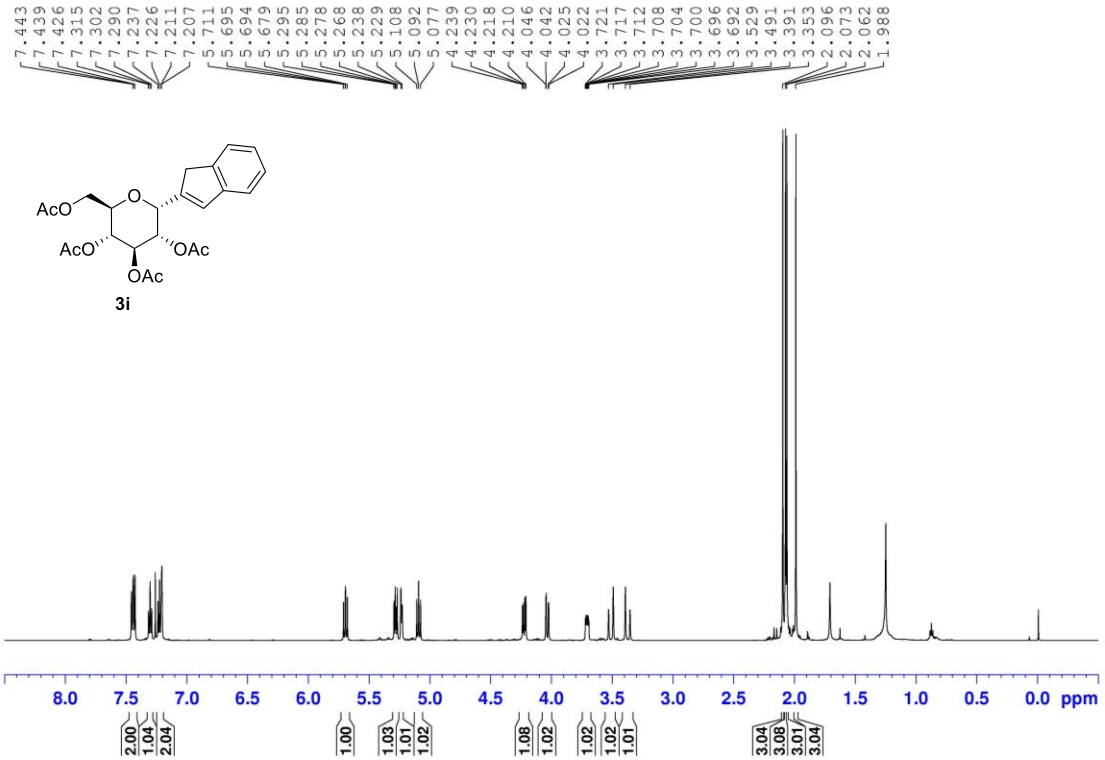
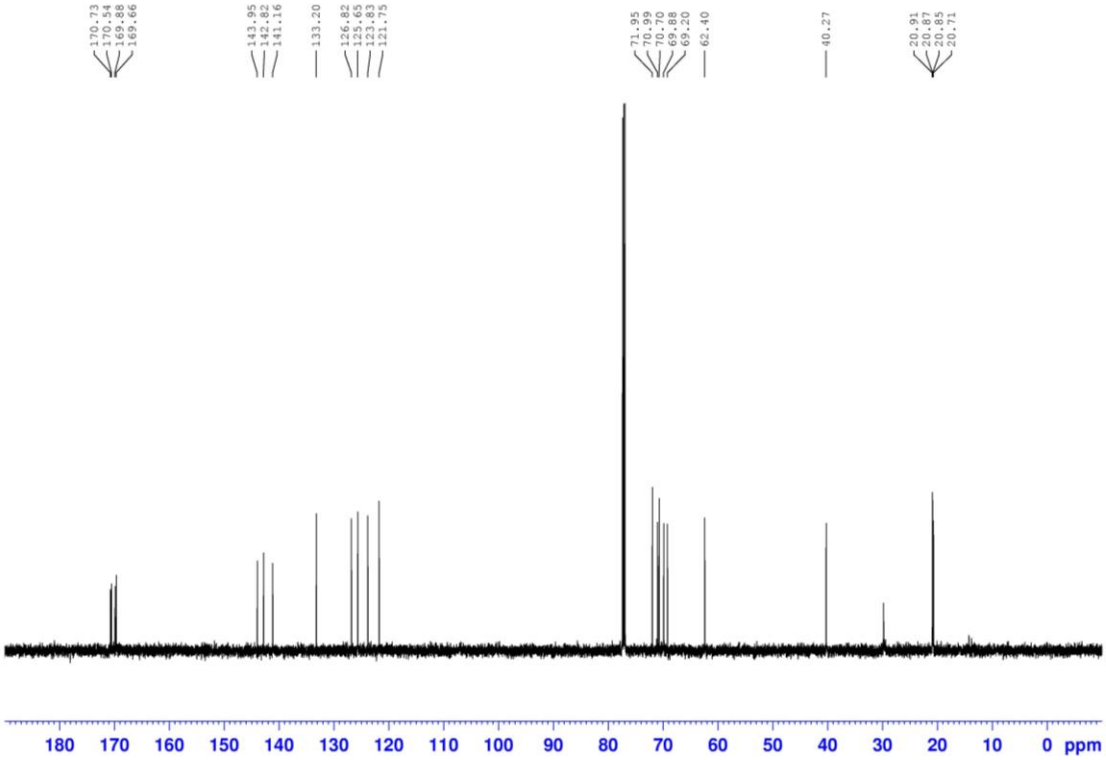
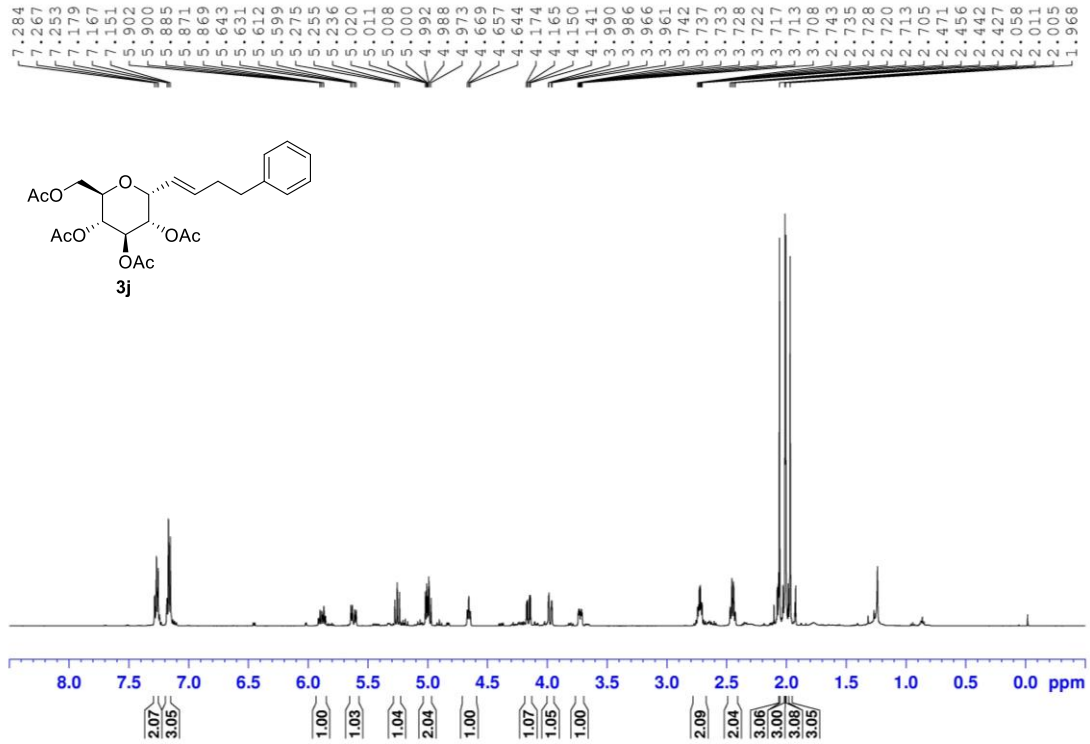
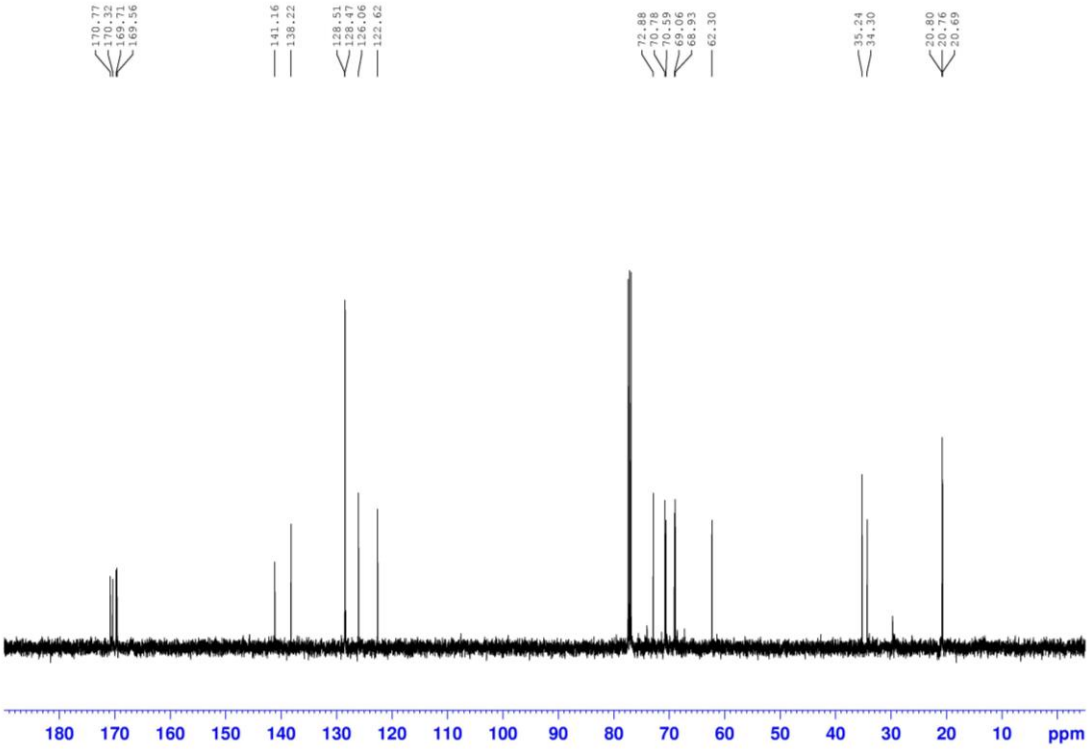
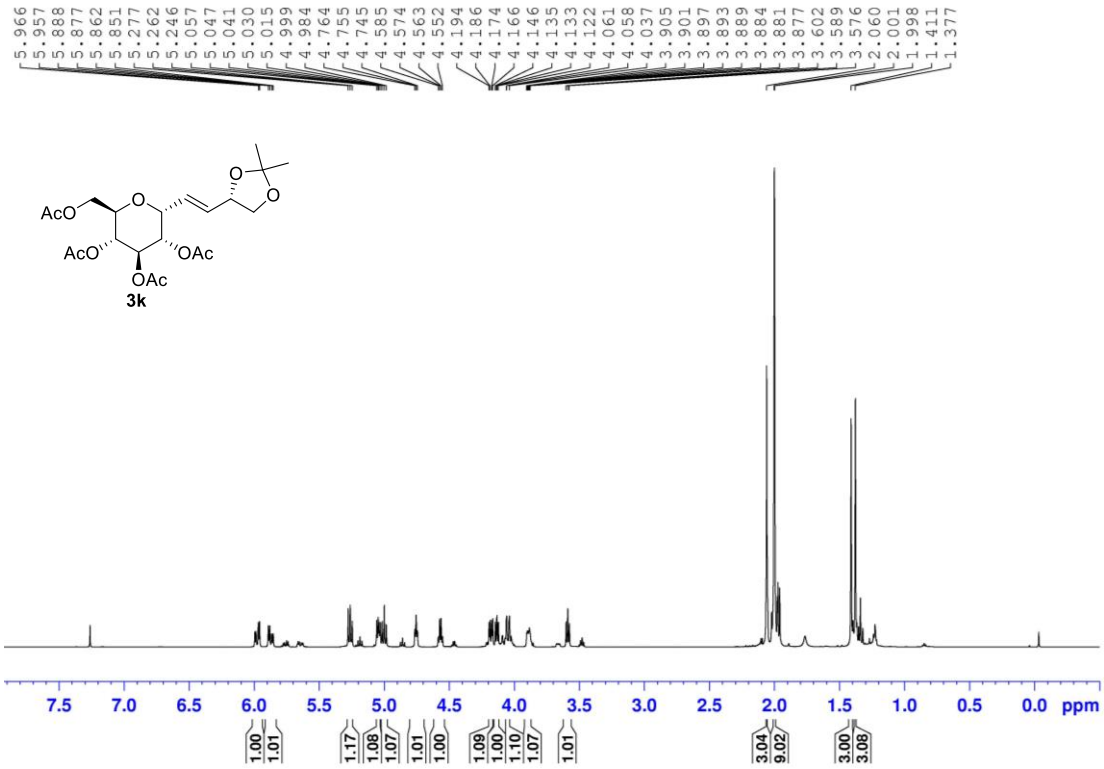
170.45
169.87
169.70
137.31
136.72
134.86
128.86
128.26
127.65
126.71
124.54
73.04
70.89
70.65
69.42
69.10
62.45
20.93
20.90
20.87
20.78
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.443
7.439
7.426
7.315
7.302
7.290
7.237
7.226
7.211
7.207
5.711
5.695
5.694
5.679
5.295
5.285
5.278
5.268
5.238
5.229
5.108
5.092
5.077
4.239
4.230
4.218
4.210
4.046
4.042
4.025
4.022
3.721
3.717
3.712
3.708
3.704
3.700
3.696
3.692
3.529
3.491
3.391
3.353
2.096
2.073
2.062
1.988
AcO
O
AcO
OAc
OAc
3i
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
1.04
2.04
1.00
1.03
1.01
1.02
1.08
1.02
1.02
1.02
1.01
3.04
3.08
3.01
3.04


170.73
170.54
169.88
169.66
143.95
142.82
141.16
133.20
126.82
125.65
123.83
121.75
71.95
70.99
70.70
69.88
69.20
62.40
40.27
20.91
20.87
20.85
20.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.284
7.267
7.253
7.179
7.167
7.151
5.902
5.900
5.885
5.871
5.869
5.643
5.631
5.612
5.599
5.275
5.255
5.236
5.020
5.011
5.008
5.000
4.992
4.988
4.973
4.669
4.657
4.644
4.174
4.165
4.150
4.141
3.990
3.986
3.966
3.961
3.742
3.737
3.733
3.728
3.722
3.717
3.713
3.708
2.743
2.735
2.728
2.720
2.713
2.705
2.471
2.456
2.442
2.427
2.058
2.011
2.005
1.968
AcO
O
AcO
OAc
OAc
3j
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
2.07
3.05
1.00
1.03
1.04
2.04
1.00
1.07
1.05
1.00
2.09
2.04
3.06
3.00
3.08
3.05


170.77
170.32
169.71
169.56
141.16
138.22
128.51
128.47
126.06
122.62
72.88
70.78
70.59
69.06
68.93
62.30
35.24
34.30
20.80
20.76
20.69
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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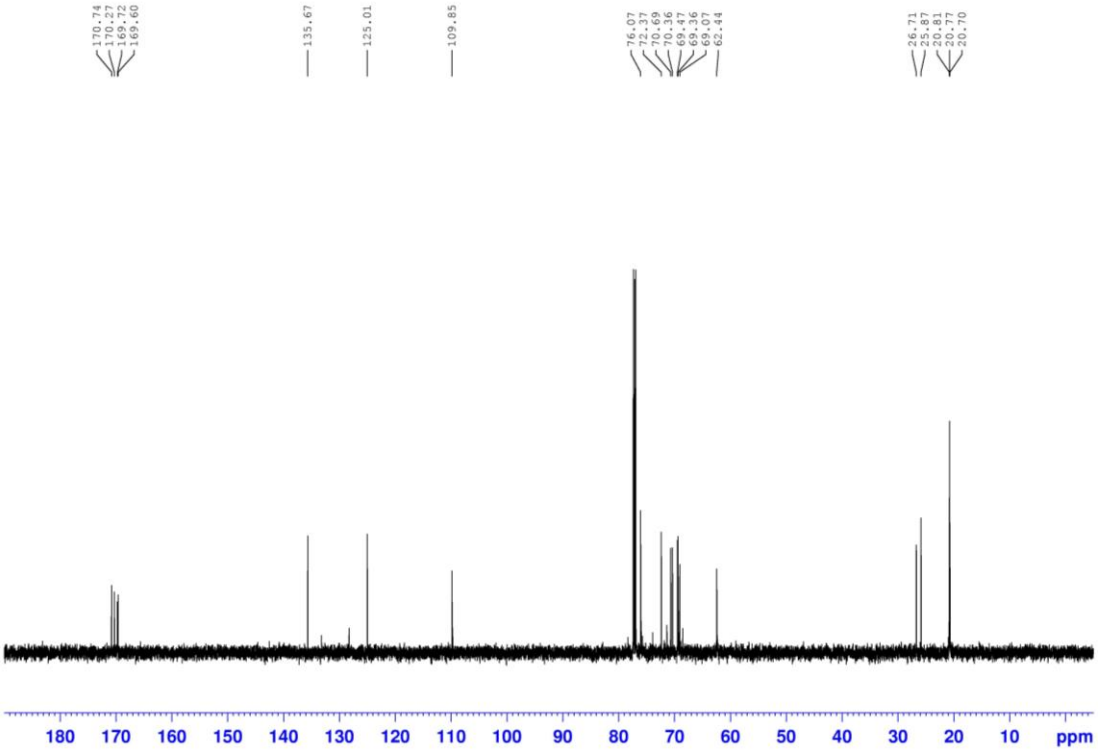
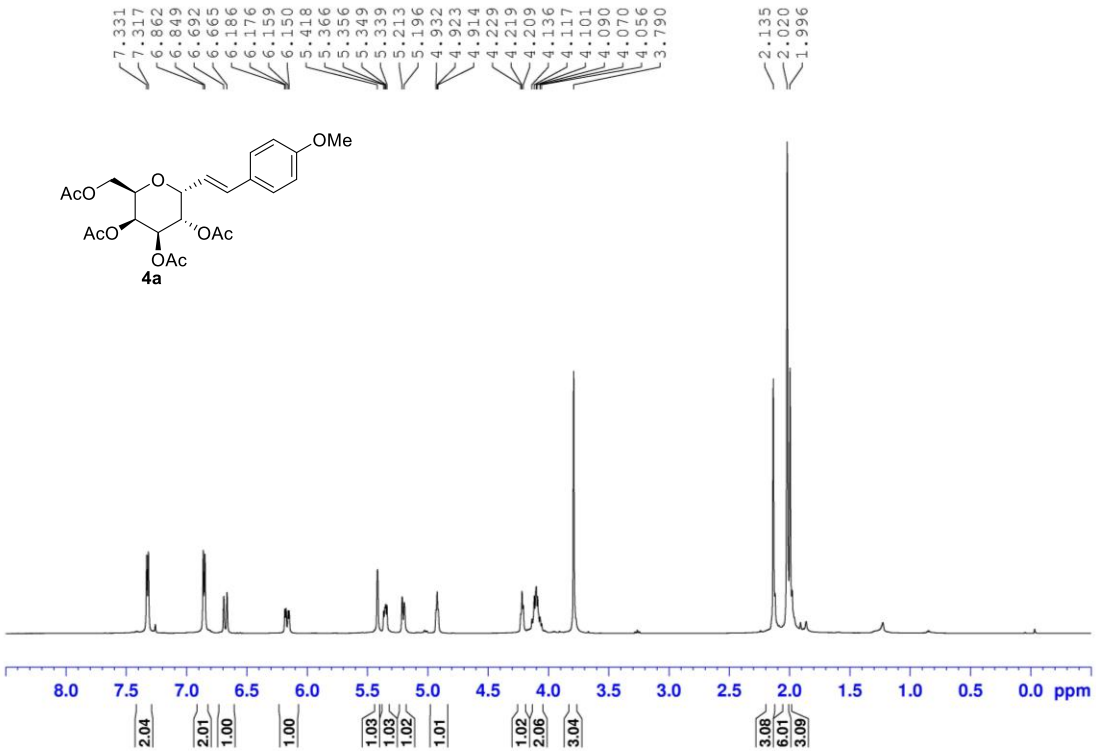
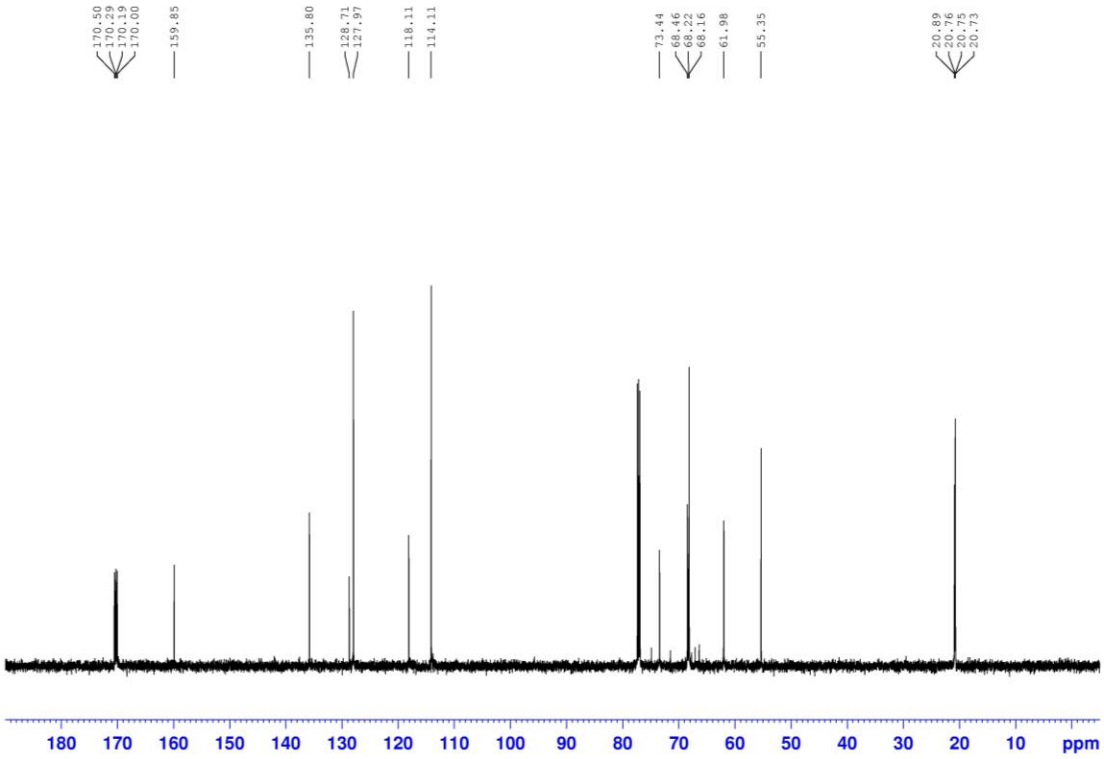
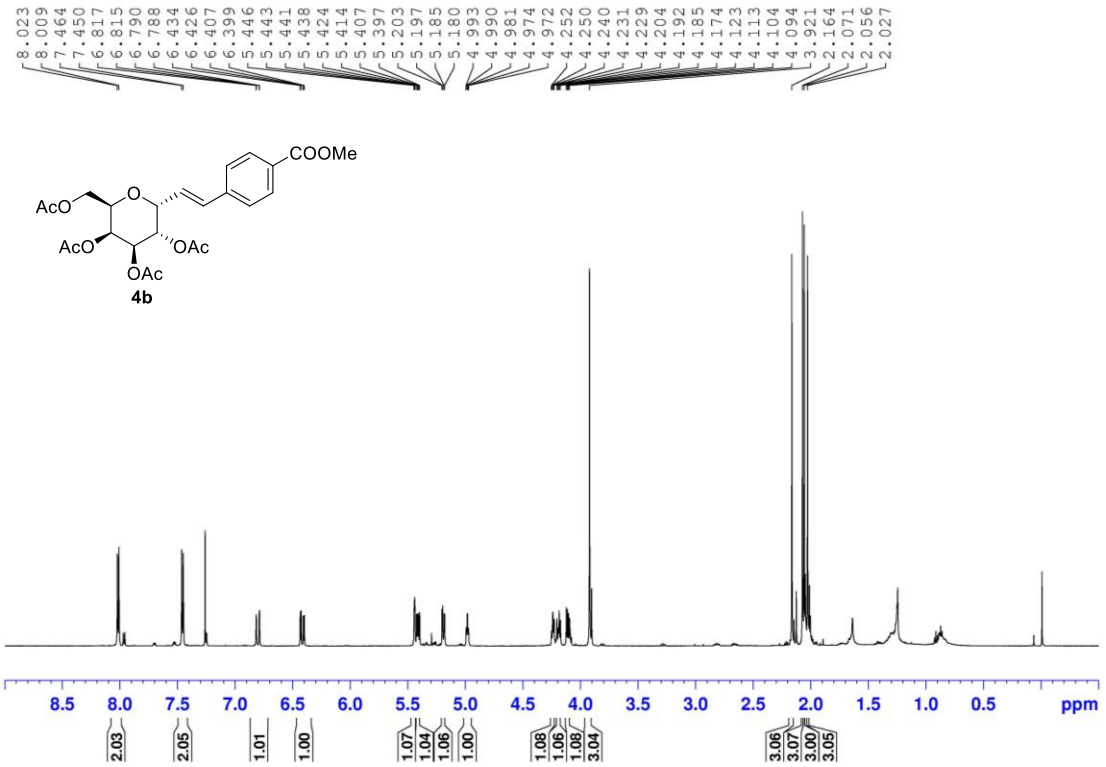
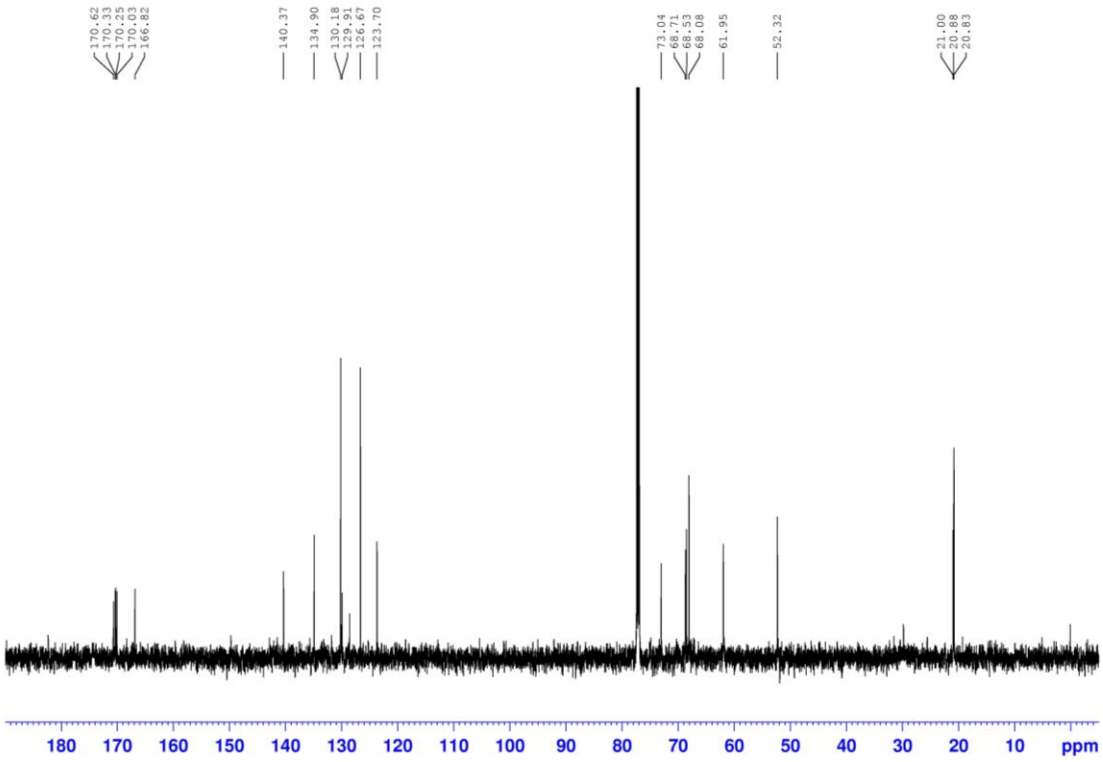
AcO
AcO
OAc
OAc
O
O
O
O
3k
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.01 1.17 1.08 1.07 1.01 1.00 1.09 1.00 1.10 1.07 1.01 3.04 9.02 3.00 3.08

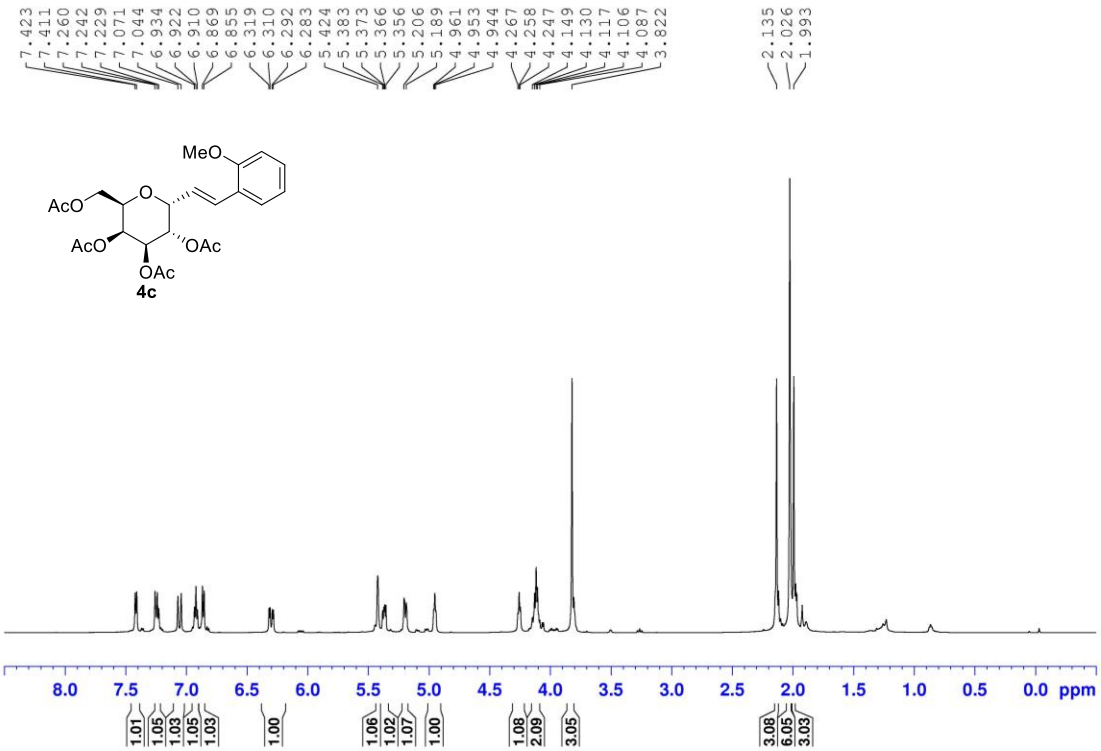

170.74 170.27 169.72 169.60
135.67
125.01
109.85
76.07 72.37 72.69 70.36 69.47 69.36 69.07 62.44
26.71 25.87 20.81 20.77 20.70
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

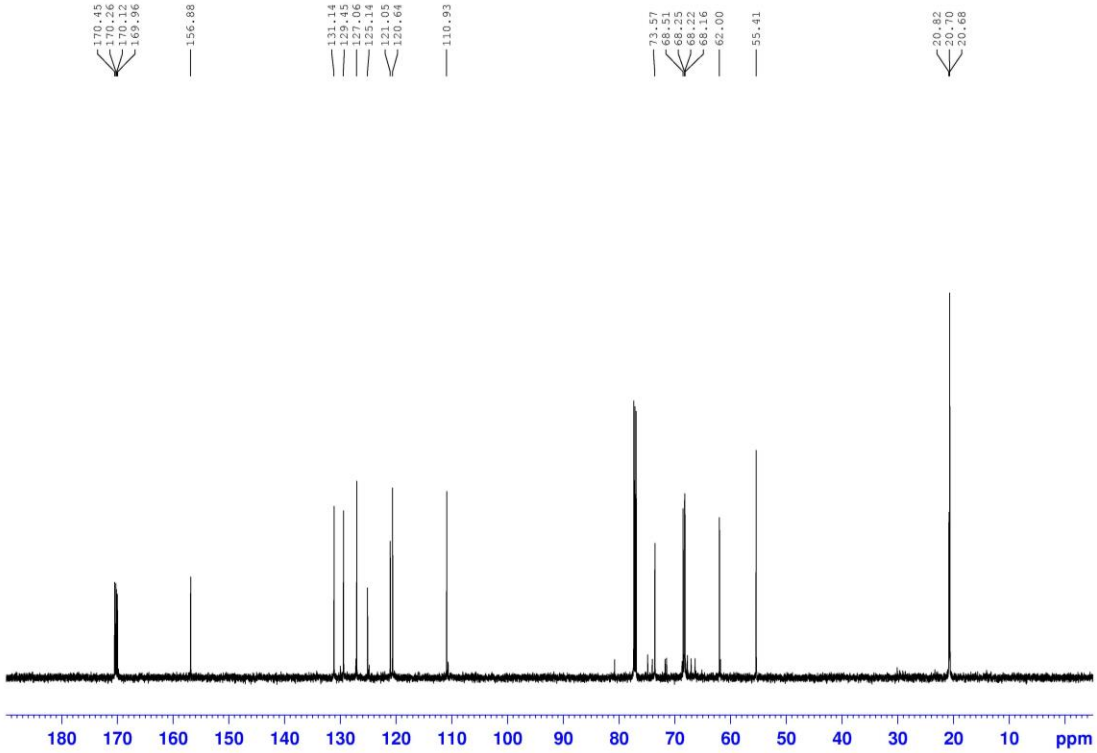

7.331
7.317
6.862
6.849
6.692
6.665
6.186
6.176
6.159
6.150
5.418
5.366
5.356
5.349
5.339
5.213
5.196
4.932
4.923
4.914
4.229
4.219
4.209
4.136
4.117
4.101
4.090
4.070
4.056
3.790
2.135
2.020
1.996
OMe
AcO
AcO
OAc
OAc
4a
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.04
2.01
1.00
1.00
1.03
1.03
1.02
1.01
1.02
2.06
3.04
3.08
6.01
3.09

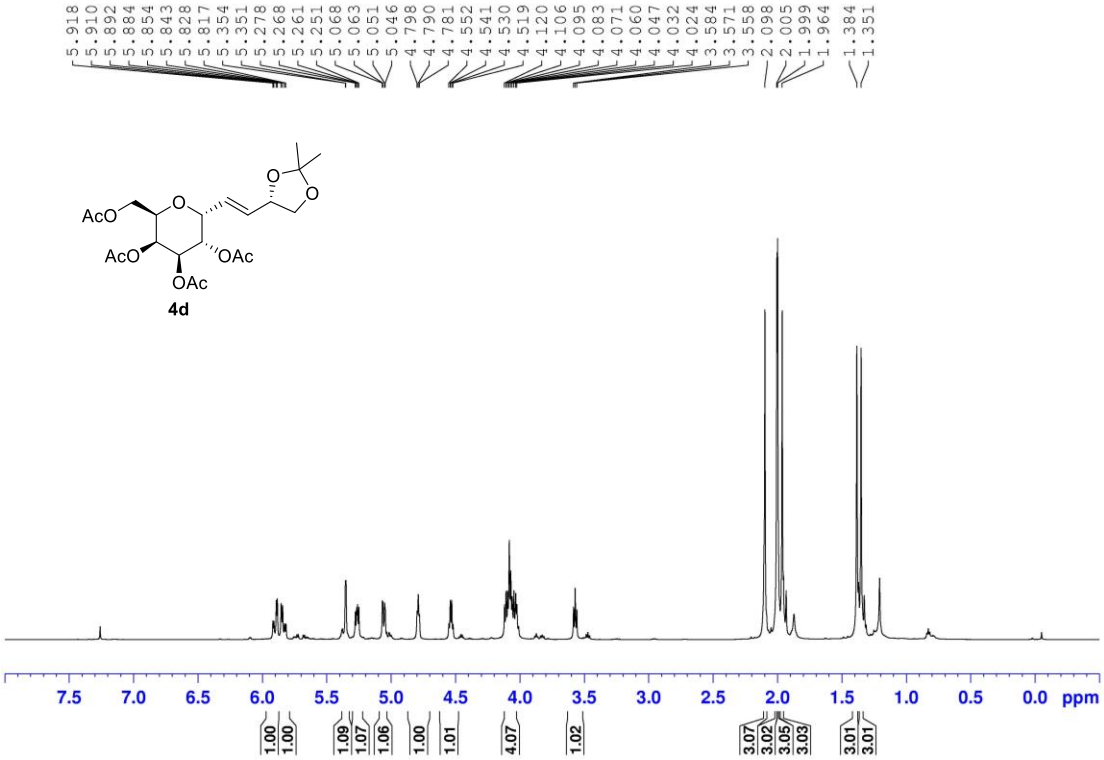

170.50
170.29
170.19
170.00
159.85
135.80
128.71
127.97
118.11
114.11
73.44
68.46
68.22
68.16
61.98
55.35
20.89
20.76
20.75
20.73
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.023
8.009
7.464
7.450
6.817
6.815
6.790
6.788
6.434
6.426
6.407
6.399
5.446
5.443
5.441
5.438
5.424
5.414
5.407
5.397
5.203
5.197
5.185
5.180
4.993
4.990
4.981
4.974
4.972
4.252
4.250
4.240
4.231
4.229
4.204
4.192
4.185
4.174
4.123
4.113
4.104
4.094
3.921
2.164
2.071
2.056
2.027
COOMe
AcO
O
AcO
OAc
OAc
4b
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
2.03
2.05
1.01
1.00
1.07
1.04
1.06
1.00
1.08
1.06
1.08
3.04
3.06
3.07
3.00
3.05


170.62
170.33
170.25
170.03
166.82
140.37
134.90
130.18
129.91
126.67
123.70
73.04
68.71
68.53
68.08
61.95
52.32
21.00
20.88
20.83
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.423
7.411
7.260
7.242
7.229
7.071
7.044
6.934
6.922
6.910
6.869
6.855
6.319
6.310
6.292
6.283
5.424
5.383
5.373
5.366
5.356
5.206
5.189
4.961
4.953
4.944
4.267
4.258
4.247
4.149
4.130
4.117
4.106
4.087
3.822
2.135
2.026
1.993
MeO
AcO
AcO
OAc
OAc
4c
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
1.01
1.05
1.03
1.05
1.03
1.00
1.06
1.02
1.07
1.00
1.08
2.09
3.05
3.08
6.05
3.03


170.45
170.26
170.12
169.96
156.88
131.14
129.45
127.06
125.14
121.05
120.64
110.93
73.57
68.51
68.25
68.22
68.16
62.00
55.41
20.82
20.70
20.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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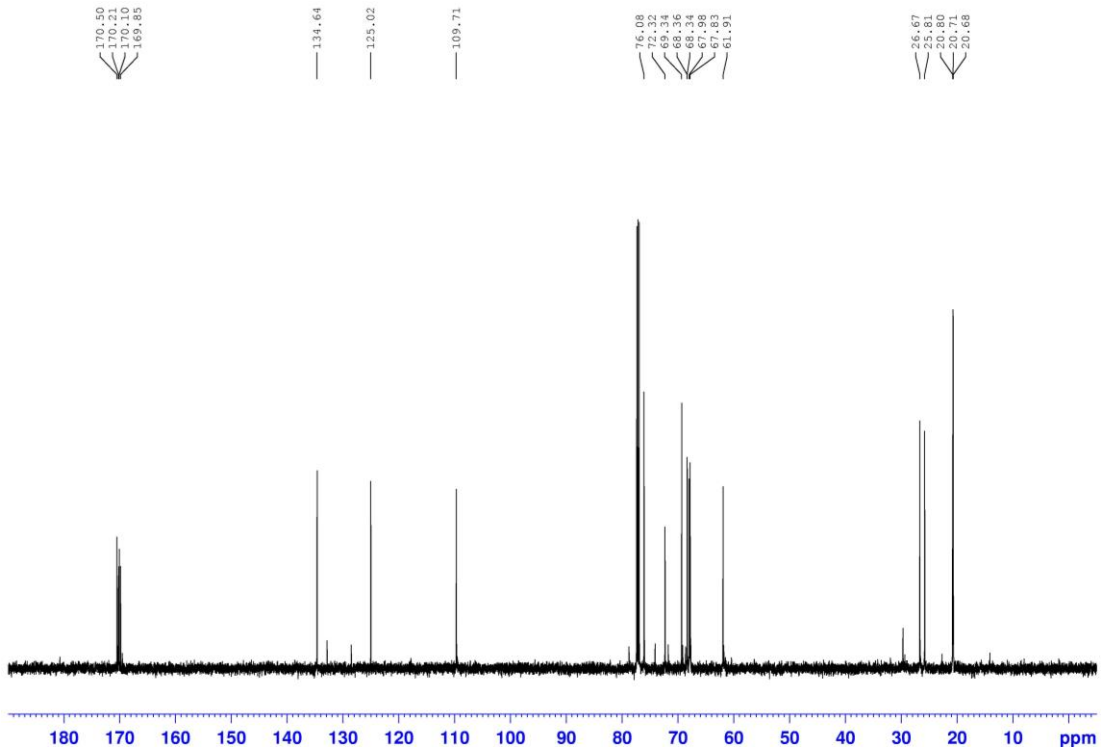
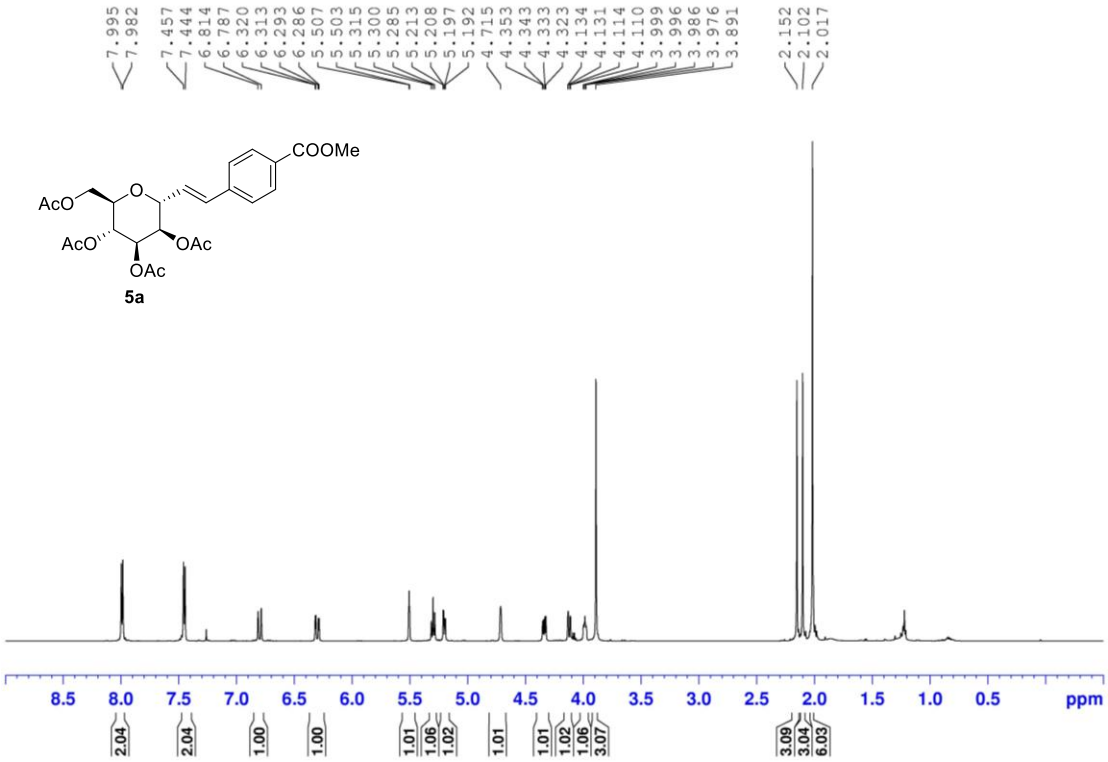
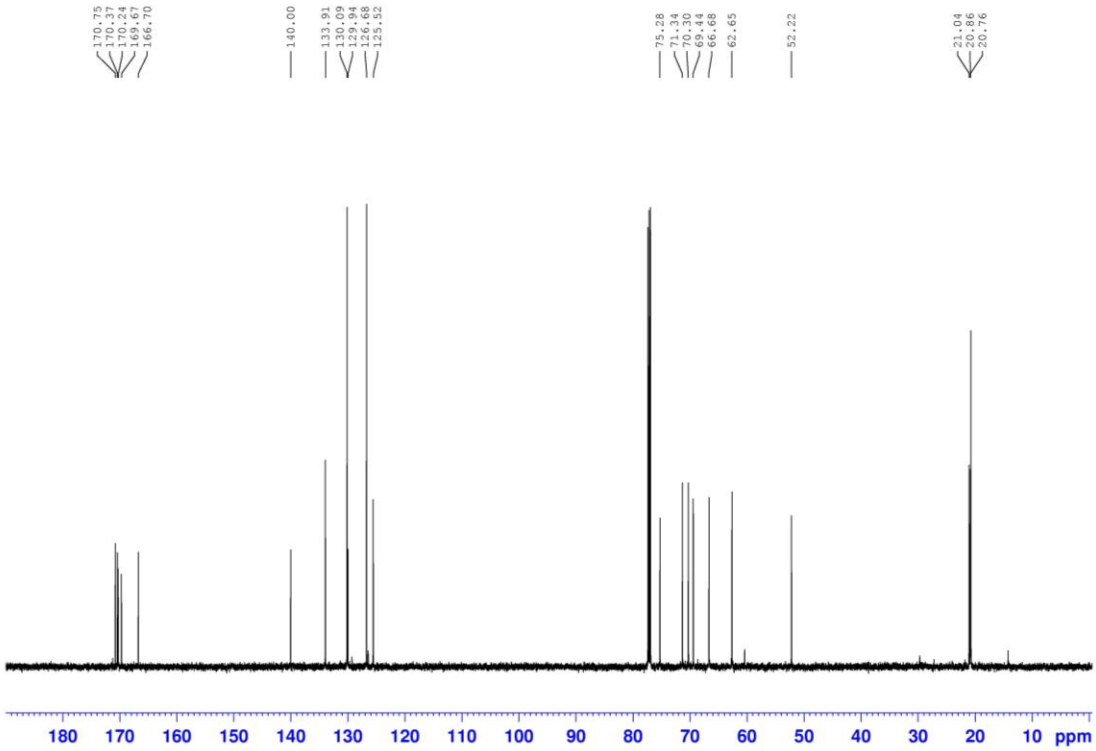
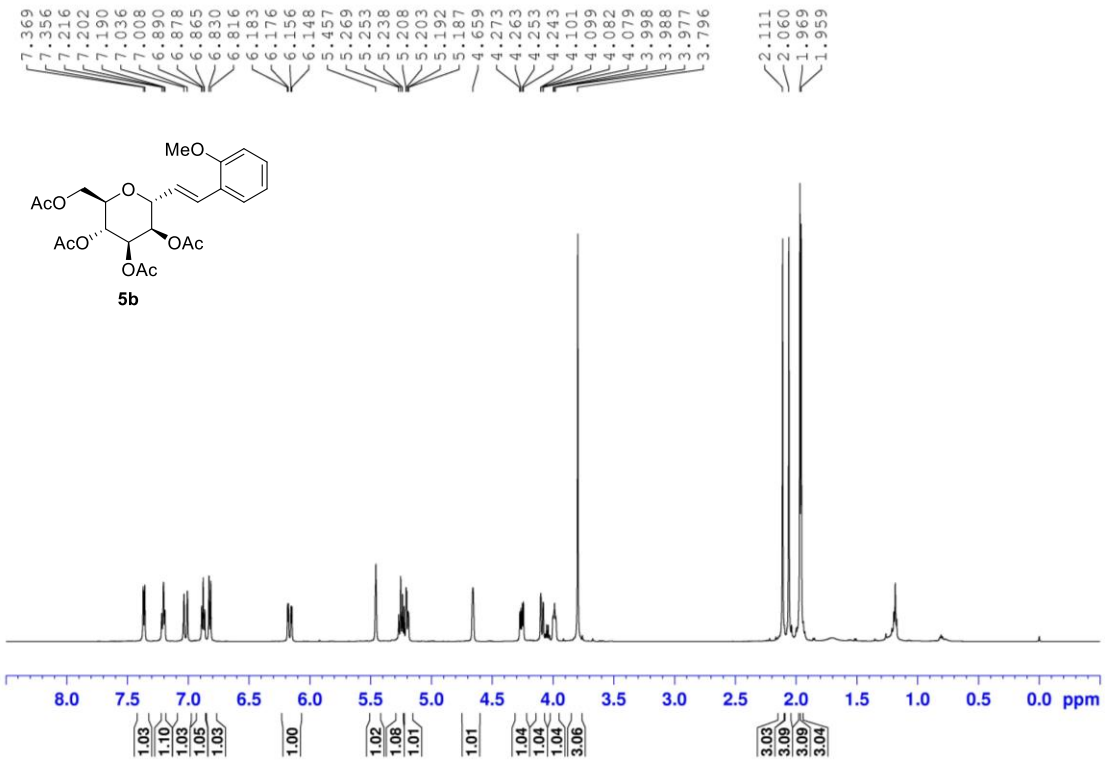
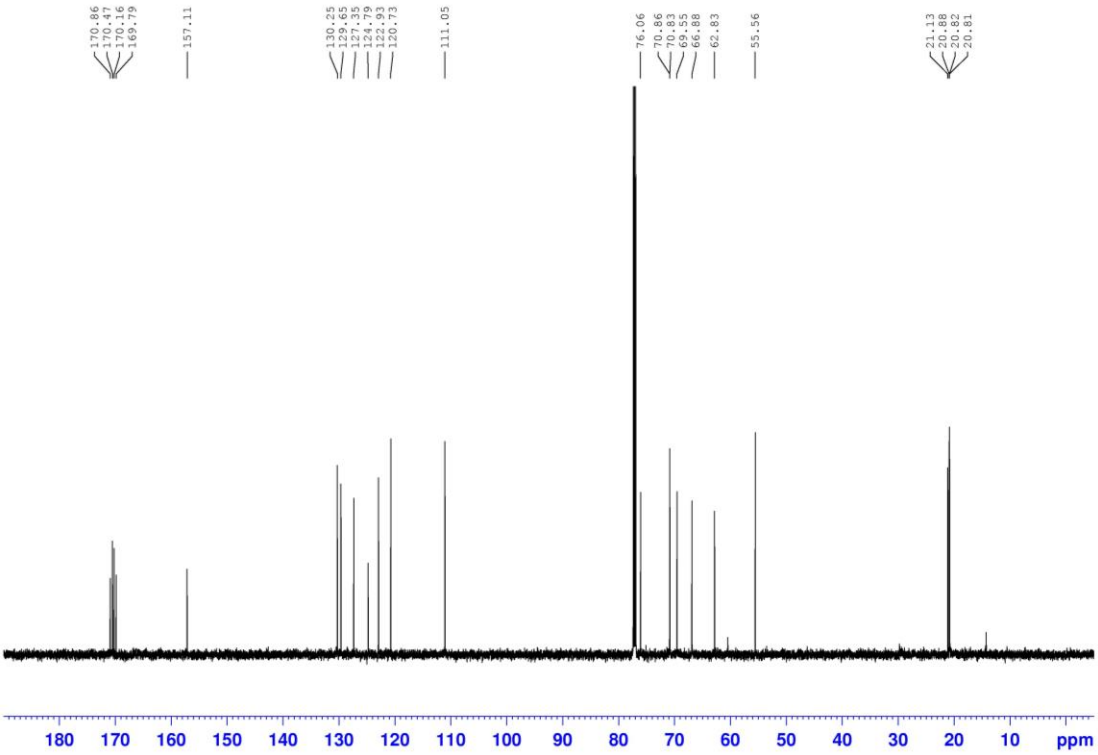
5.910
5.892
5.884
5.854
5.843
5.828
5.817
5.354
5.351
5.278
5.268
5.261
5.251
5.068
5.063
5.051
5.046
4.798
4.790
4.781
4.552
4.541
4.530
4.519
4.120
4.106
4.095
4.083
4.071
4.060
4.047
4.032
4.024
3.584
3.571
3.558
2.098
2.005
1.999
1.964
1.384
1.351
AcO
AcO
OAc
OAc
4d
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.09
1.07
1.06
1.00
1.01
4.07
1.02
3.07
3.02
3.05
3.03
3.01
3.01

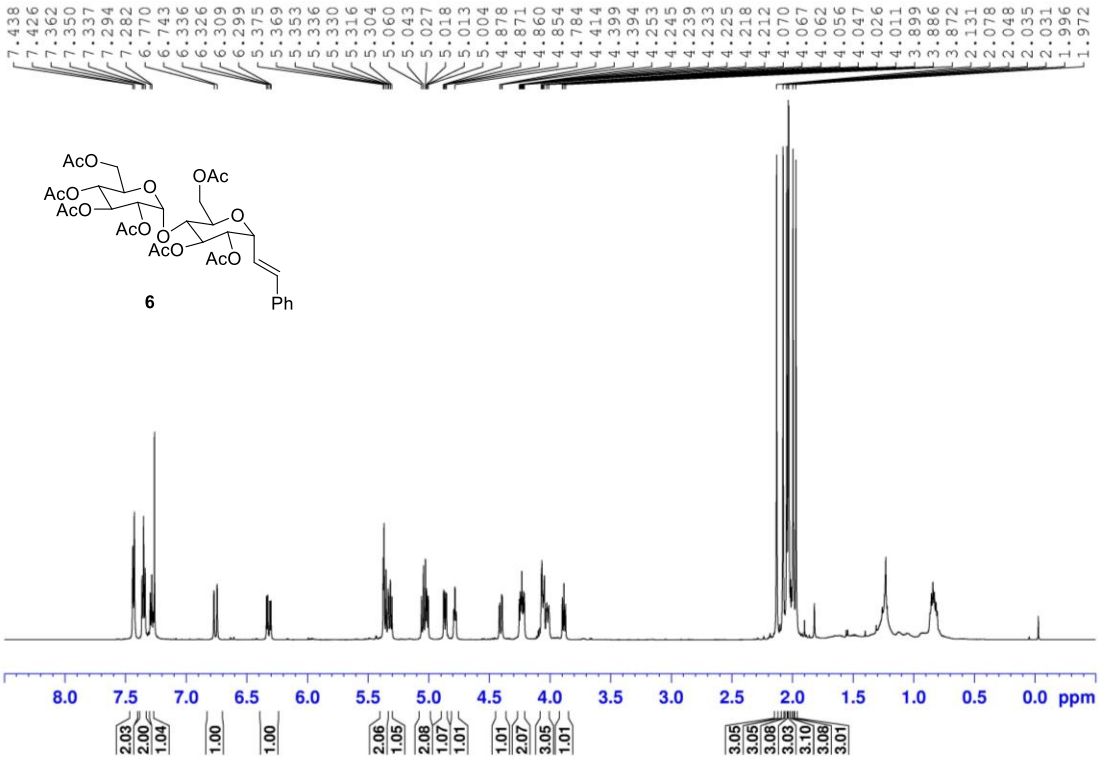

170.50
170.21
170.10
169.85
134.64
125.02
109.71
76.08
72.32
69.34
68.36
68.34
67.98
67.83
61.91
26.67
25.81
20.80
20.71
20.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

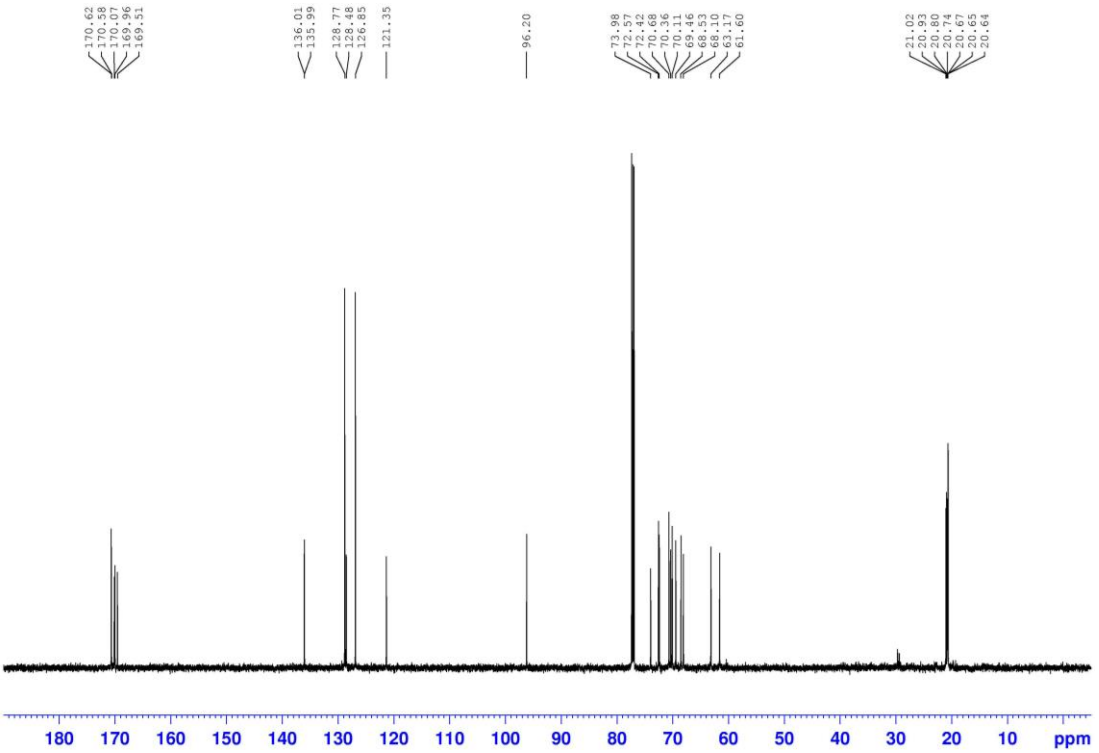

7.995
7.982
7.457
7.444
6.814
6.787
6.320
6.313
6.293
6.286
5.507
5.503
5.315
5.300
5.285
5.213
5.208
5.197
5.192
4.715
4.353
4.343
4.333
4.323
4.134
4.131
4.114
4.110
3.999
3.996
3.986
3.976
3.891
2.152
2.102
2.017
COOMe
AcO
O
AcO
OAc
OAc
5a
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.04
2.04
1.00
1.00
1.01
1.06
1.02
1.01
1.01
1.02
1.06
3.07
3.09
3.04
6.03

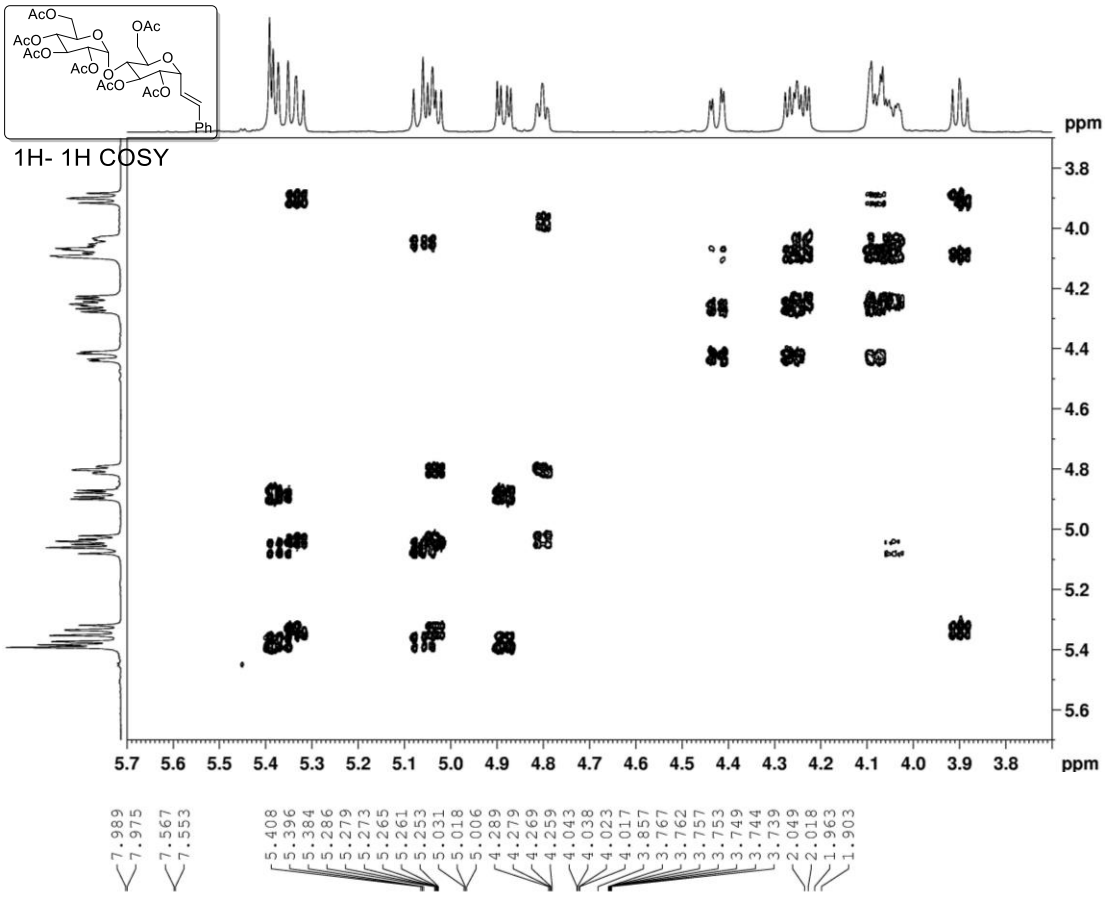

170.75
170.37
170.24
169.67
166.70
140.00
133.91
130.09
129.94
126.68
125.52
75.28
71.34
70.30
69.44
66.68
62.65
52.22
21.04
20.86
20.76
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

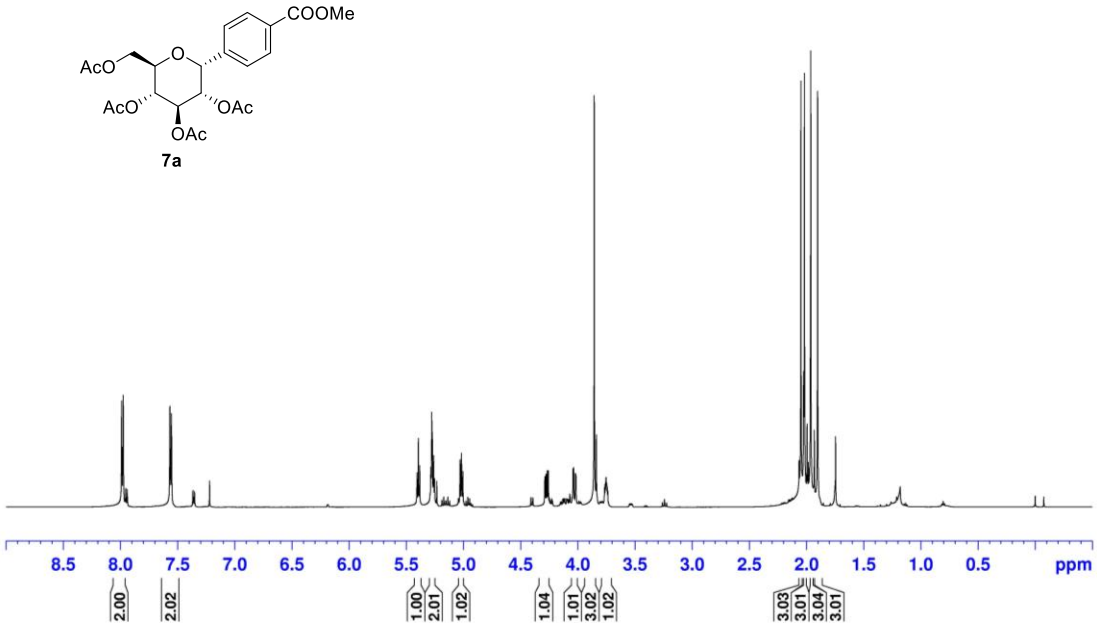

7.369
7.356
7.216
7.202
7.190
7.036
7.008
6.890
6.878
6.865
6.830
6.816
6.183
6.176
6.156
6.148
5.457
5.269
5.253
5.238
5.208
5.203
5.192
5.187
4.659
4.273
4.263
4.253
4.243
4.101
4.099
4.082
4.079
3.998
3.988
3.977
3.796
2.111
2.060
1.969
1.959
MeO
AcO
O
AcO
OAc
OAc
5b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
1.10
1.03
1.05
1.03
1.00
1.02
1.08
1.01
1.01
1.04
1.04
1.04
3.06
3.03
3.09
3.09
3.04

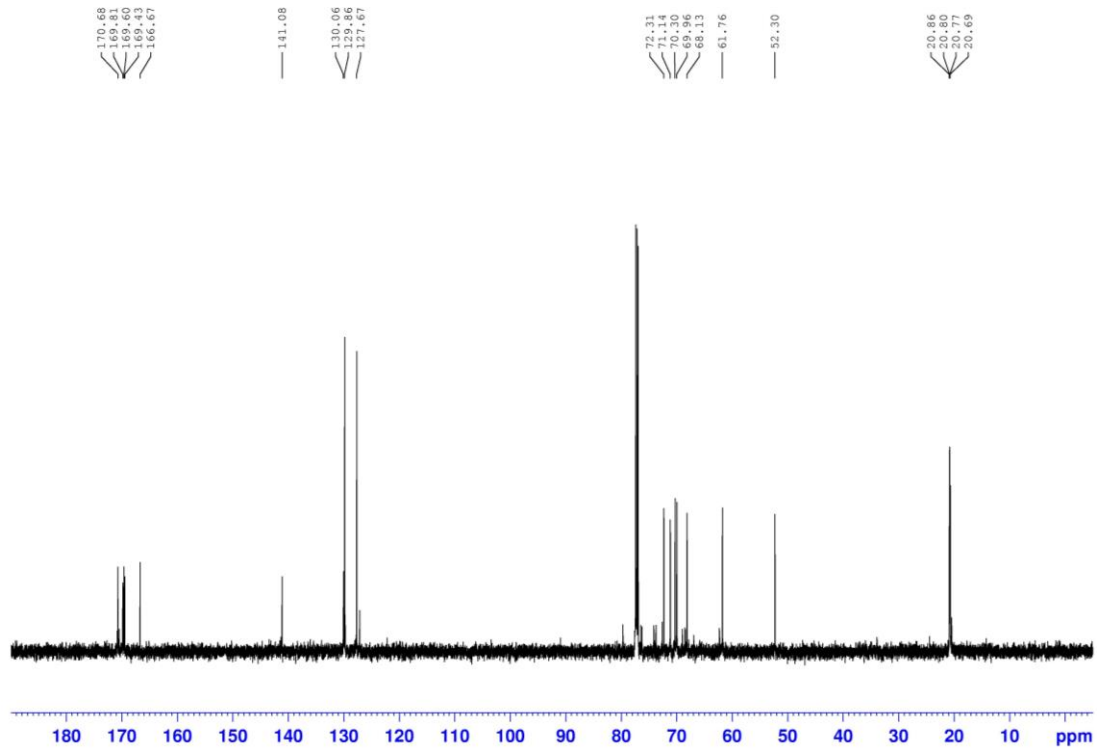

170.86
170.47
170.16
169.79
157.11
130.25
129.65
127.35
124.79
122.93
120.73
111.05
76.06
70.86
70.83
69.55
66.88
62.83
55.56
21.13
20.88
20.82
20.81
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

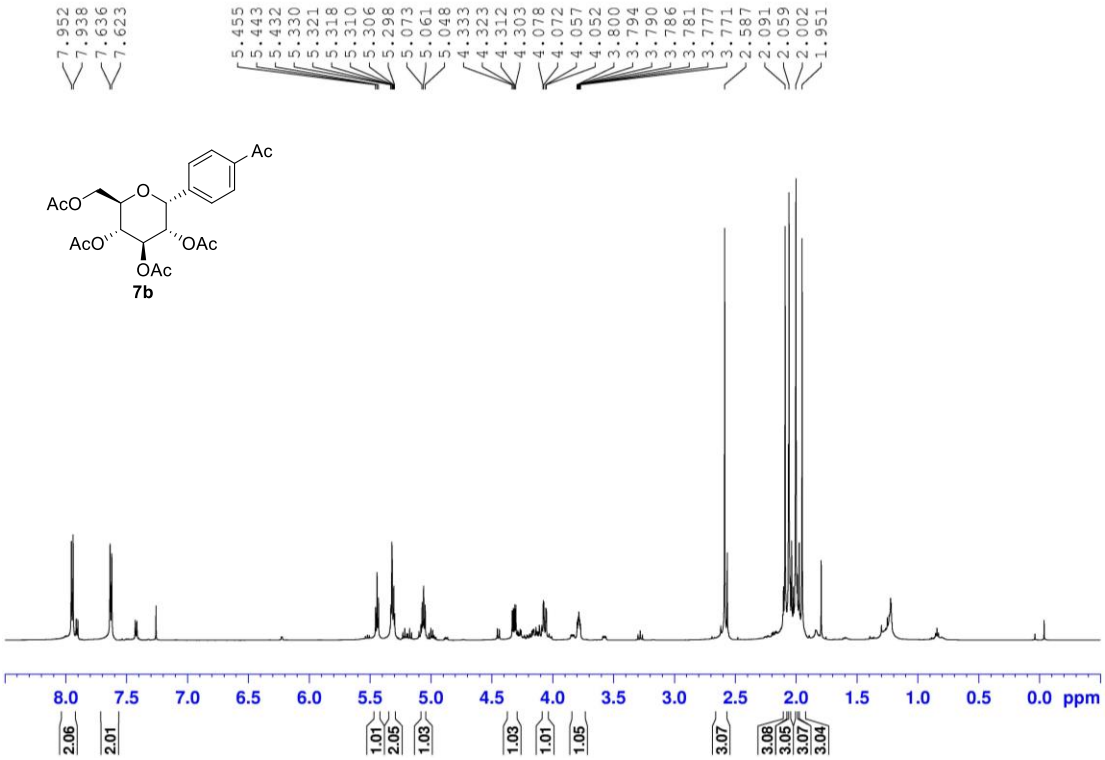

7.438 7.426 7.362 7.350 7.337 7.294 7.282 6.770 6.743 6.336 6.326 6.309 6.299 5.375 5.369 5.353 5.336 5.330 5.316 5.304 5.060 5.043 5.027 5.018 5.013 5.004 4.878 4.871 4.860 4.854 4.784 4.414 4.399 4.394 4.253 4.245 4.239 4.233 4.225 4.218 4.212 4.070 4.067 4.062 4.056 4.047 4.026 4.011 3.899 3.886 3.872 2.131 2.078 2.048 2.035 2.031 1.996 1.972
AcO
AcO
AcO
AcO
AcO
AcO
OAc
O
O
O
6
Ph
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 2.00 1.04 1.00 1.00 2.06 1.05 2.08 1.07 1.01 1.01 2.07 3.05 1.01 3.05 3.05 3.08 3.03 3.10 3.08 3.01

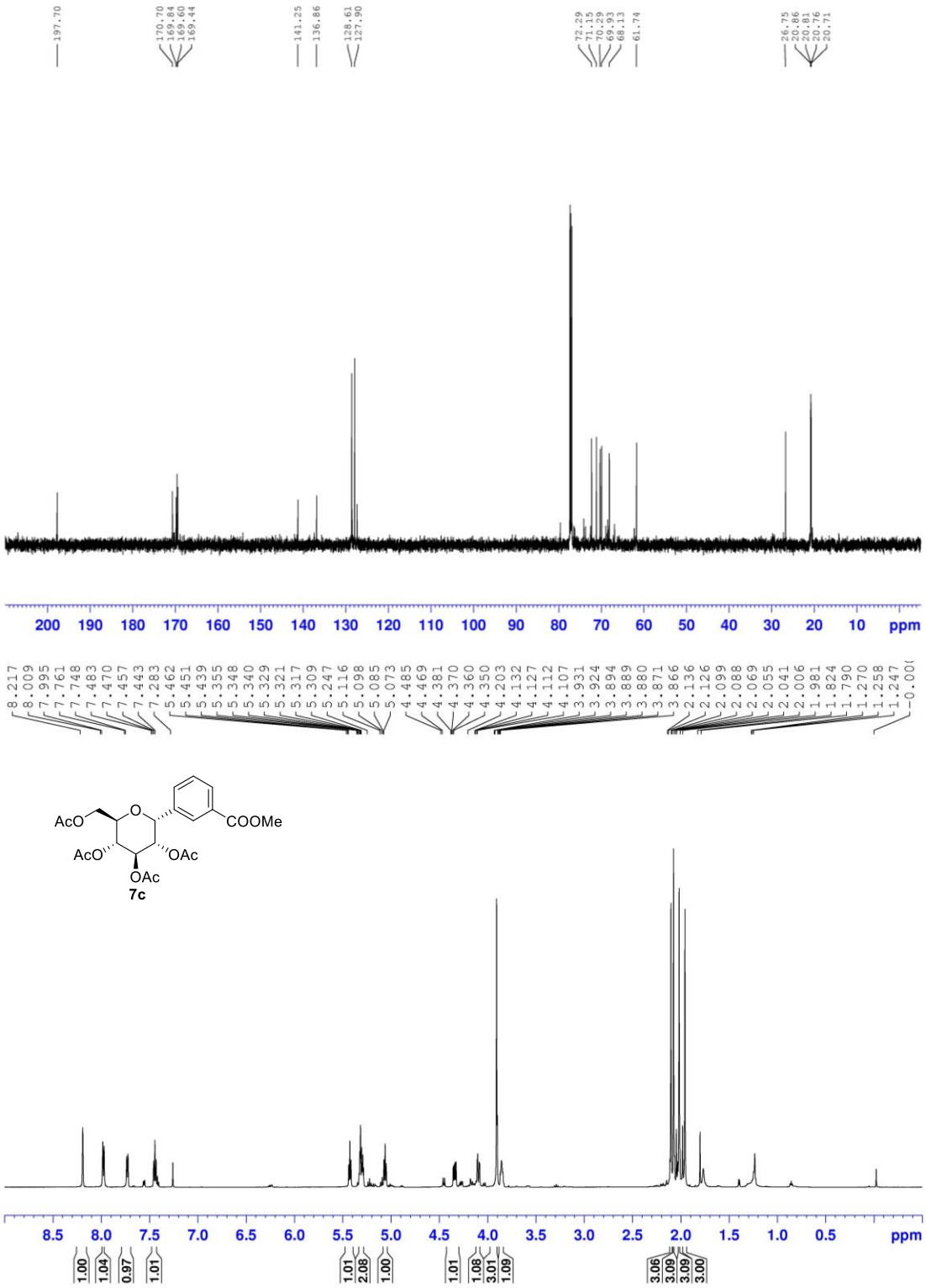

170.62 170.58 170.07 169.96 169.51
136.01 135.99
128.77 128.48 126.85
121.35
96.20
73.98 72.57 72.42 70.68 70.36 70.11 69.46 68.53 68.10 63.17 61.60
21.02 20.93 20.80 20.74 20.67 20.65 20.64
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

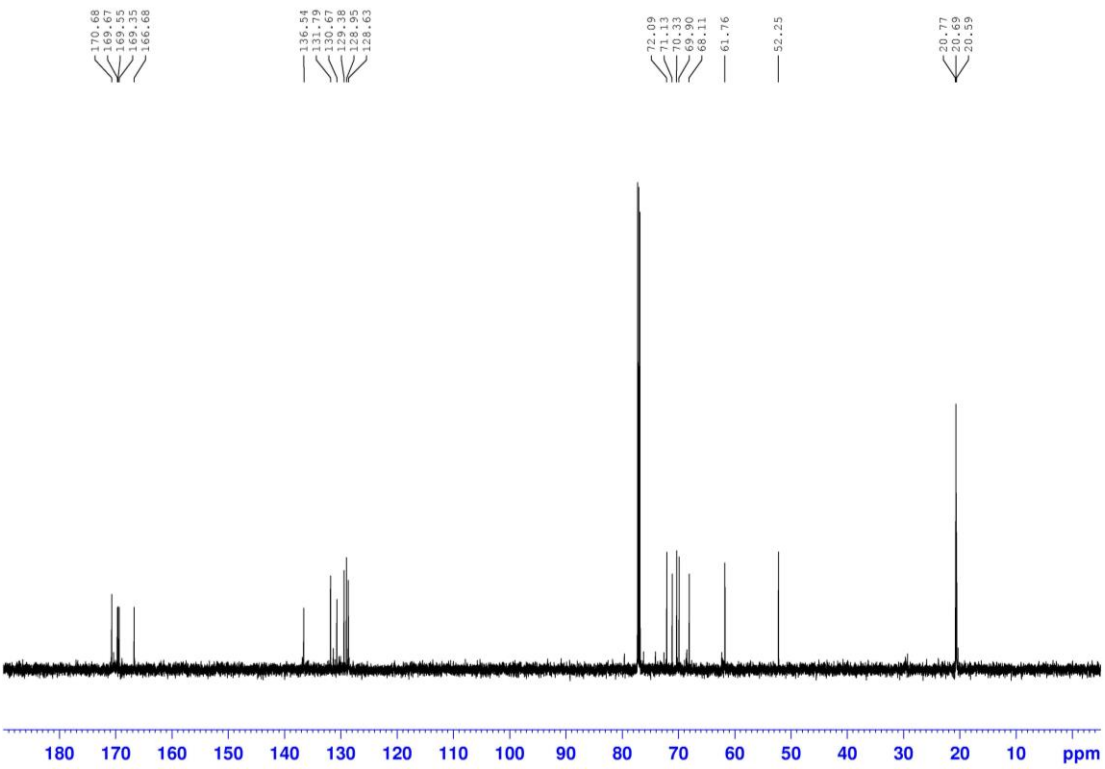

1H- 1H COSY
ppm
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 ppm
7.989 7.975 7.567 7.553 5.408 5.396 5.384 5.286 5.279 5.273 5.265 5.261 5.253 5.031 5.018 5.006 4.289 4.279 4.269 4.259 4.043 4.038 4.023 4.017 3.857 3.767 3.762 3.757 3.753 3.749 3.744 3.739 2.049 2.018 1.963 1.903

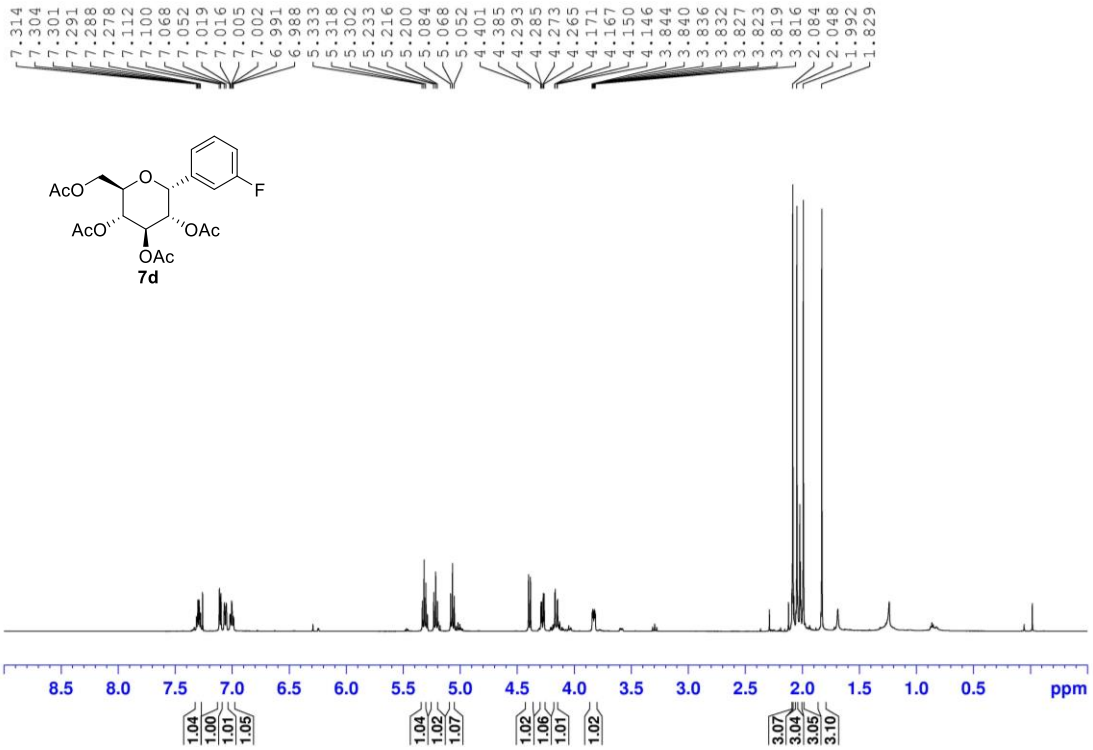

COOMe
AcO
AcO
OAc
OAc
7a
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 2.02 1.00 2.01 1.02 1.04 1.01 3.02 1.02 3.03 3.01 3.04 3.01

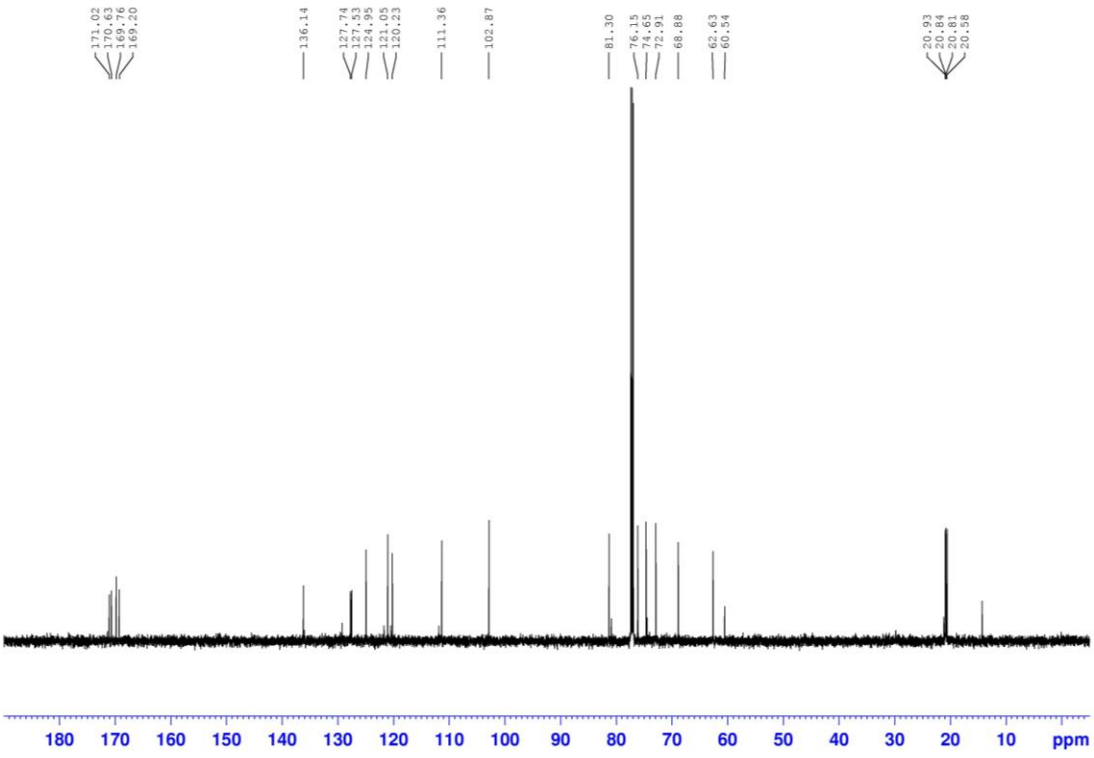

170.68
169.81
169.40
169.23
166.67
141.08
130.06
129.66
127.67
72.31
71.14
70.30
69.96
68.13
61.76
52.30
20.86
20.80
20.77
20.69
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

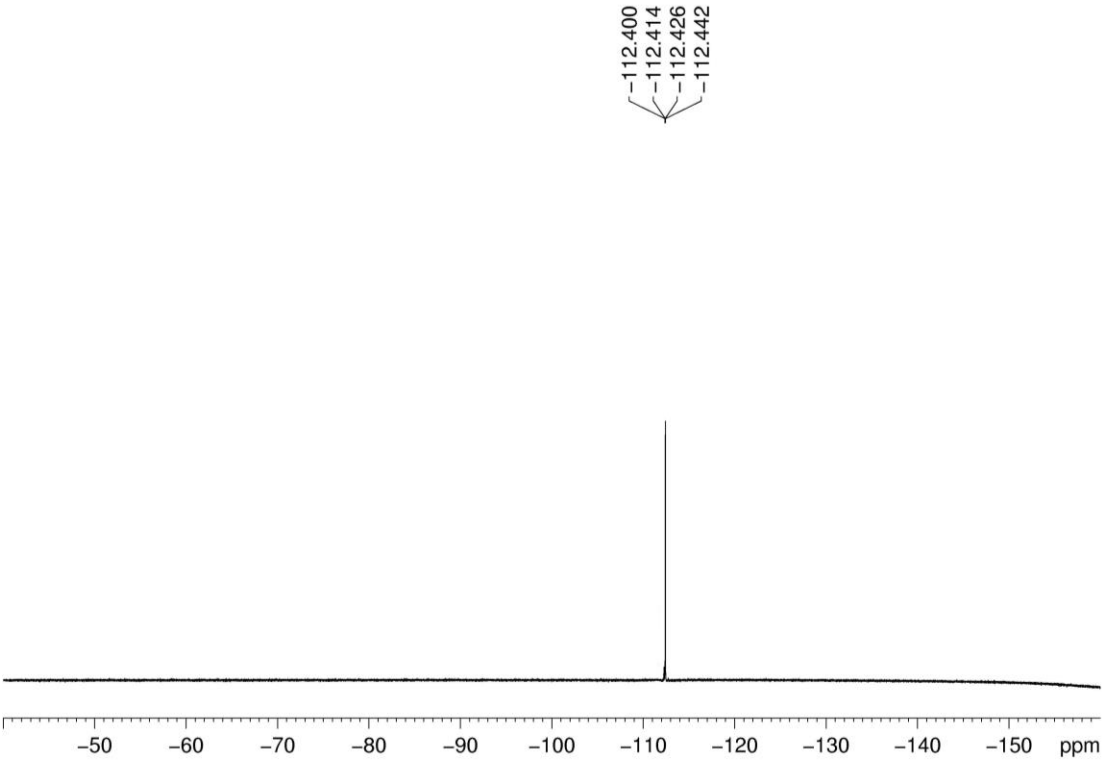

7.952
7.938
7.636
7.623
5.455
5.443
5.432
5.330
5.321
5.318
5.310
5.306
5.298
5.073
5.061
5.048
4.333
4.323
4.312
4.303
4.078
4.072
4.057
4.052
3.800
3.794
3.790
3.786
3.781
3.777
3.771
2.587
2.091
2.059
2.002
1.951
Ac
AcO
O
AcO
OAc
OAc
7b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.06
2.01
1.01
2.05
1.03
1.03
1.01
1.05
3.07
3.08
3.05
3.07
3.04

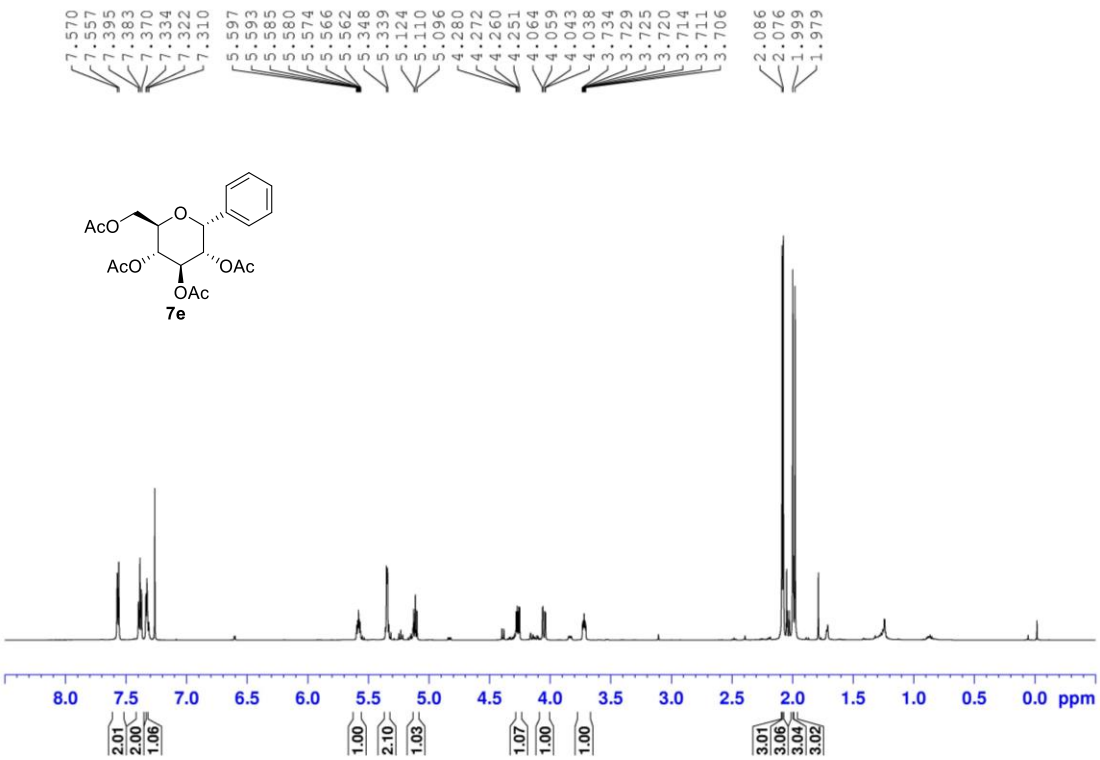

197.70
170.70
169.84
169.60
169.44
141.25
136.86
128.61
127.90
72.29
71.15
70.29
69.93
68.13
61.74
26.75
20.86
20.81
20.76
20.71
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
8.217
8.009
7.995
7.761
7.748
7.483
7.470
7.457
7.443
7.283
5.462
5.451
5.439
5.355
5.348
5.340
5.329
5.321
5.317
5.309
5.247
5.116
5.098
5.085
5.073
4.485
4.469
4.381
4.370
4.360
4.350
4.203
4.132
4.127
4.112
4.107
3.931
3.924
3.894
3.889
3.880
3.871
3.866
2.136
2.126
2.099
2.088
2.069
2.055
2.041
2.006
1.981
1.824
1.790
1.270
1.258
1.247
AcO
O
COOMe
AcO
OAc
OAc
7c
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
1.00
1.04
0.97
1.01
1.01
2.08
1.00
1.01
1.08
3.01
1.09
3.06
3.09
3.09
3.00

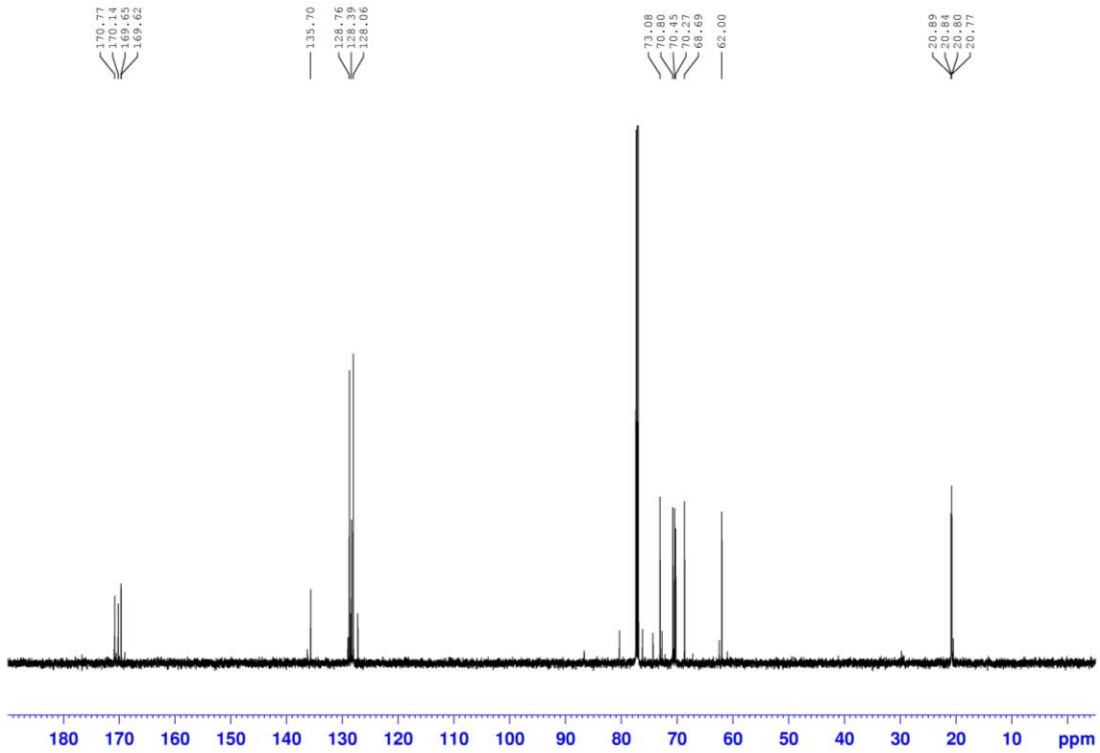

170.68
169.67
169.55
169.35
166.68
136.54
131.79
130.67
129.38
128.95
128.63
72.09
71.13
70.33
69.90
68.11
61.76
52.25
20.77
20.69
20.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

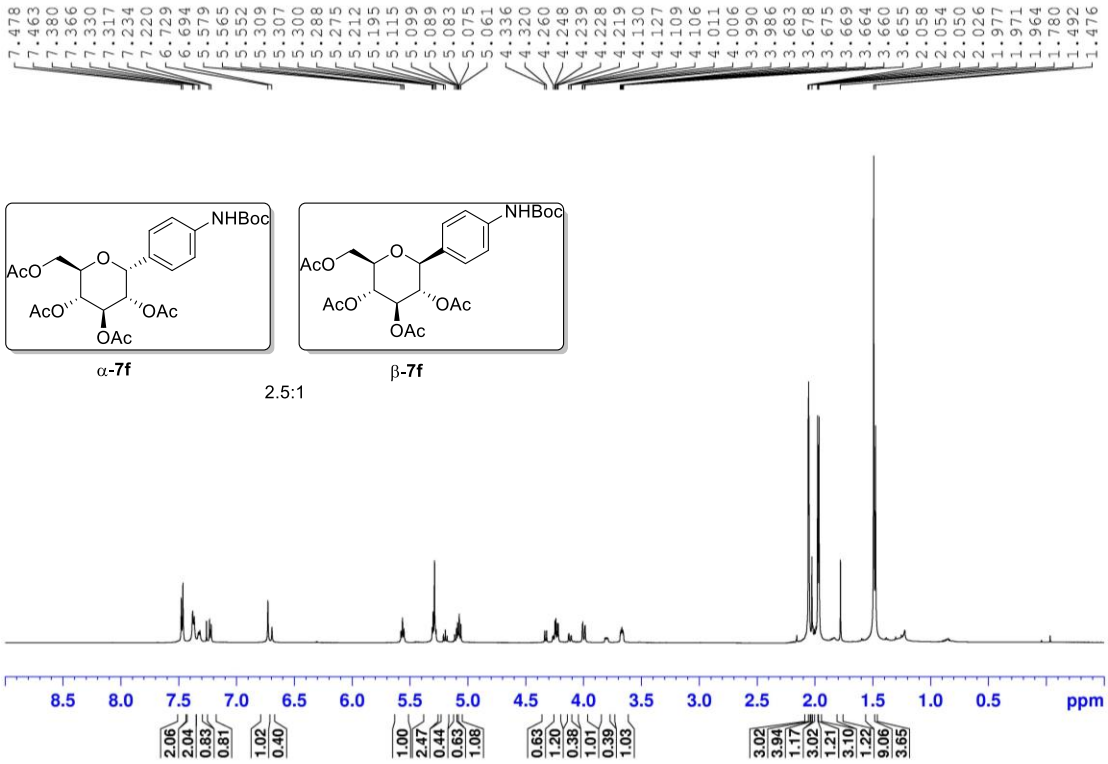

7.314
7.304
7.301
7.291
7.288
7.278
7.112
7.100
7.068
7.052
7.019
7.016
7.005
7.002
6.991
6.988
5.333
5.318
5.302
5.233
5.216
5.200
5.084
5.068
5.052
4.401
4.385
4.293
4.285
4.273
4.265
4.171
4.167
4.150
4.146
3.844
3.840
3.836
3.832
3.827
3.823
3.819
3.816
2.084
2.048
1.992
1.829
AcO
O
F
AcO
OAc
OAc
7d
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
1.04
1.00
1.01
1.05
1.04
1.02
1.07
1.02
1.06
1.01
1.02
3.07
3.04
3.05
3.10

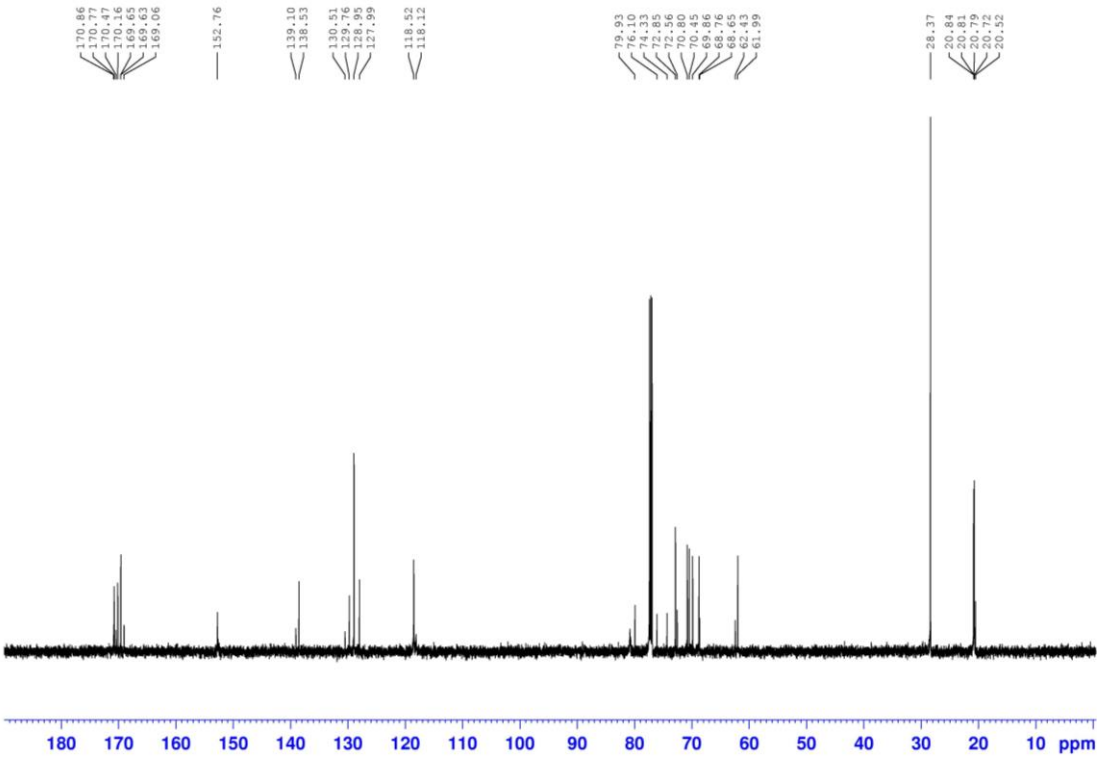

171.02
170.63
169.76
169.20
136.14
127.74
127.53
124.95
121.05
120.23
111.36
102.87
81.30
76.15
74.65
72.91
68.88
62.63
60.54
20.93
20.84
20.81
20.58
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

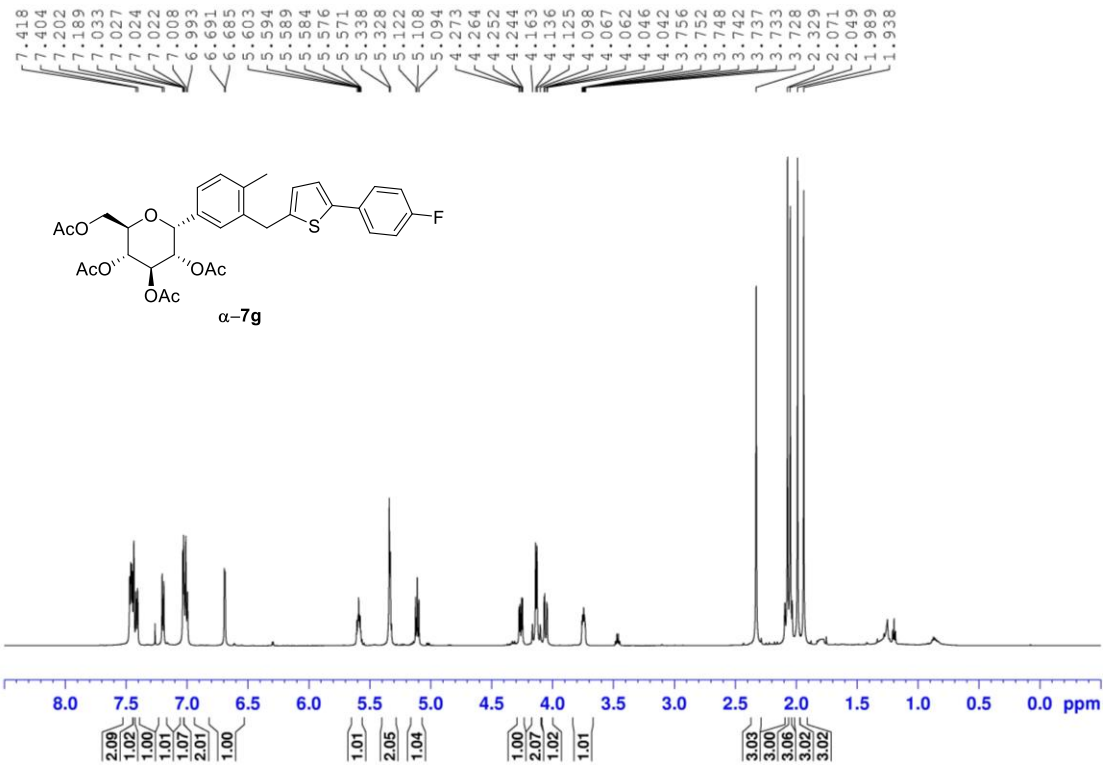

−112.400
−112.414
−112.426
−112.442
−50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 ppm

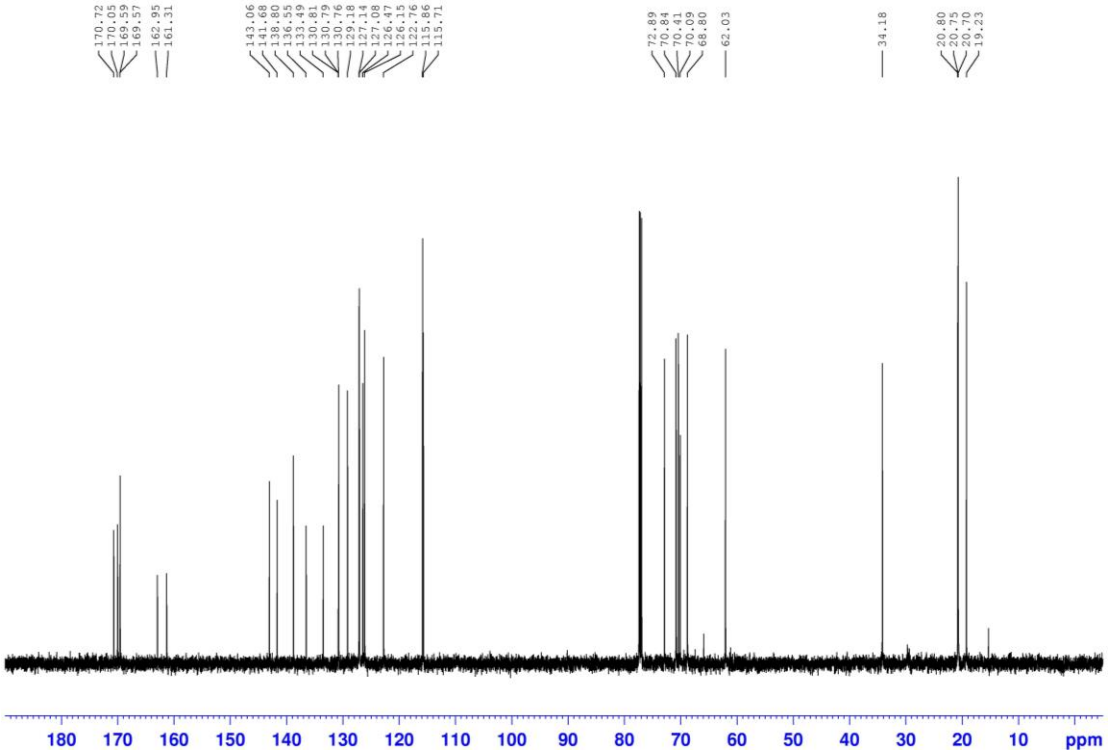

7.570
7.557
7.395
7.383
7.370
7.334
7.322
7.310
5.597
5.593
5.585
5.580
5.574
5.566
5.562
5.348
5.339
5.124
5.110
5.096
4.280
4.272
4.260
4.251
4.064
4.059
4.043
4.038
3.734
3.729
3.725
3.720
3.714
3.711
3.706
2.086
2.076
1.999
1.979
AcO
AcO
OAc
OAc
O
7e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
2.00
1.06
1.00
2.10
1.03
1.07
1.00
1.00
3.01
3.06
3.04
3.02

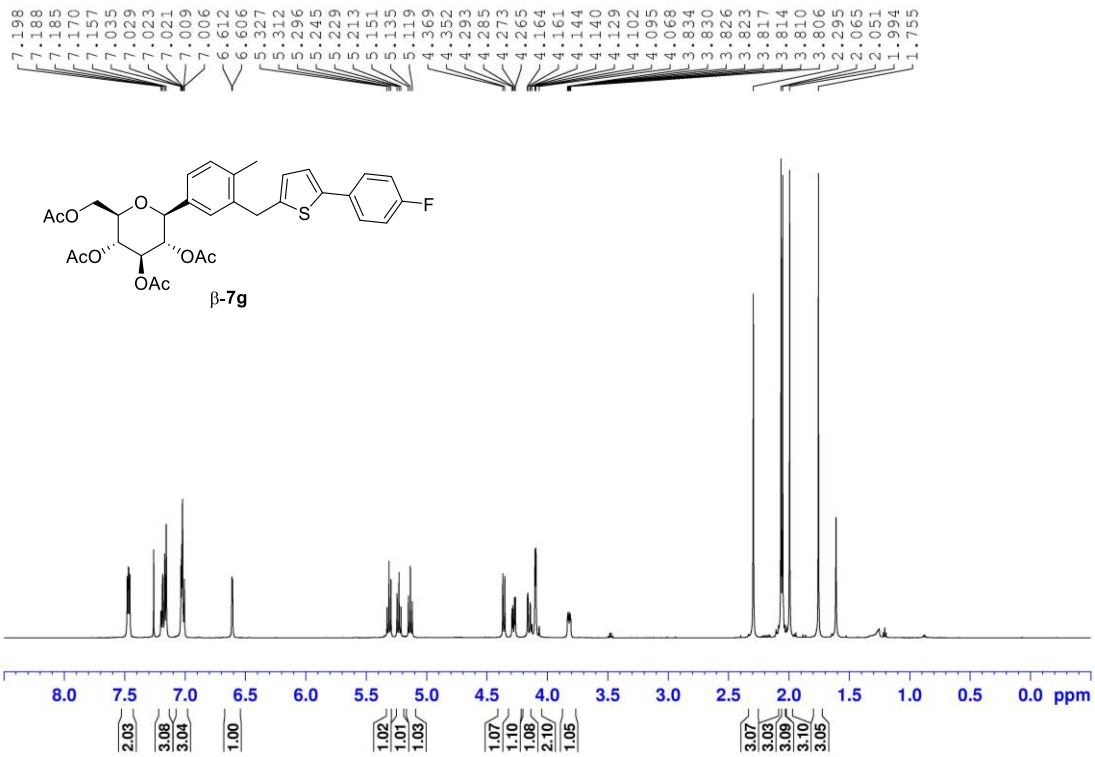

170.77
170.14
169.65
169.62
135.70
128.76
128.39
128.06
73.08
70.80
70.45
70.27
68.69
62.00
20.89
20.84
20.80
20.77
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

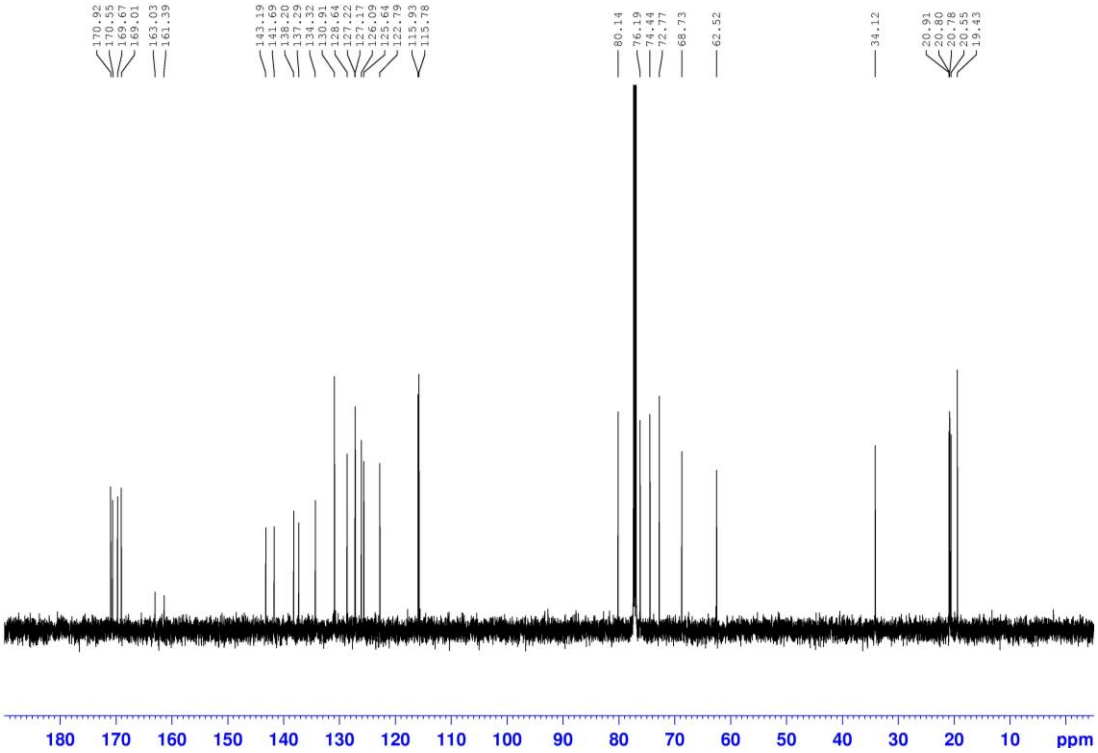

NHBoc
AcO
AcO
OAc
OAc
α-7f
β-7f
2.5:1
ppm

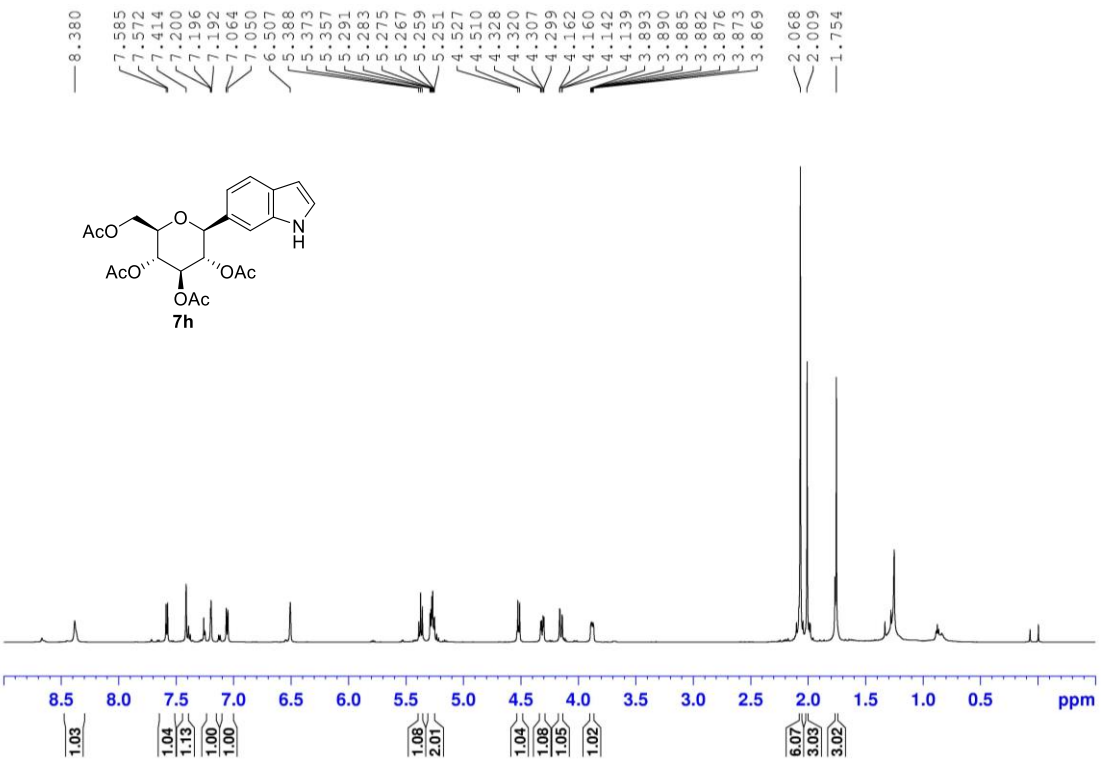

ppm

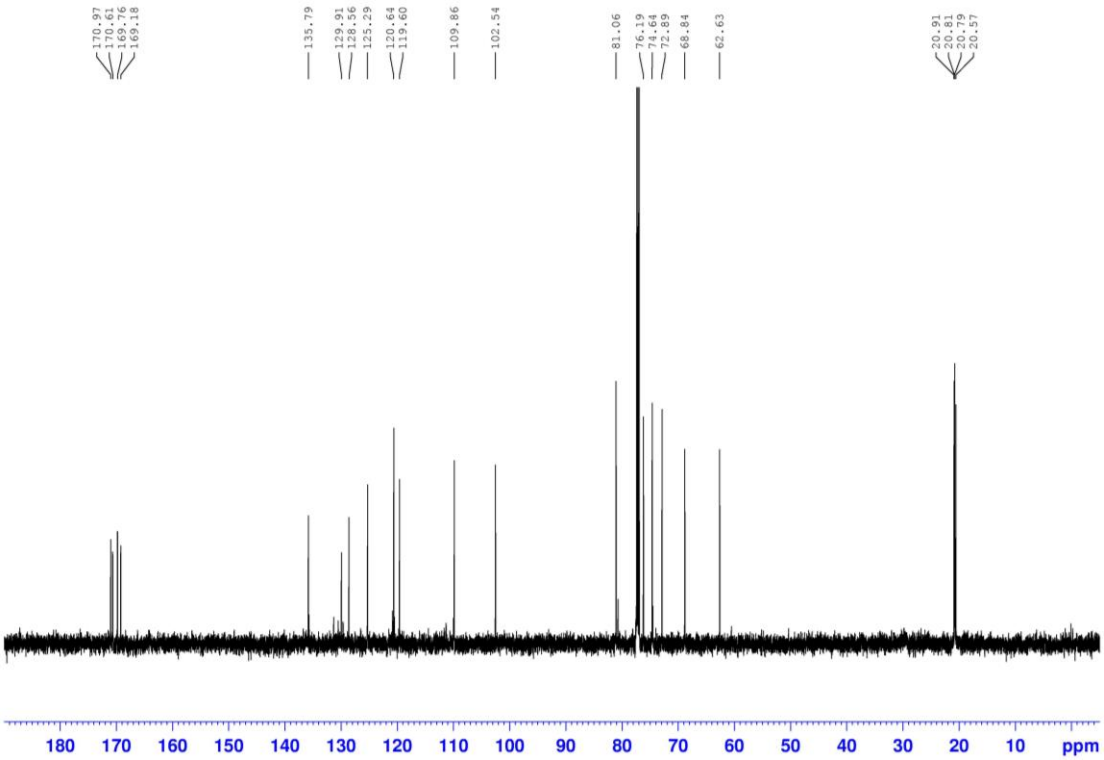

7.418 7.404 7.202 7.189 7.033 7.027 7.024 7.022 7.008 6.993 6.691 6.685 5.603 5.594 5.589 5.584 5.576 5.571 5.338 5.328 5.122 5.108 5.094 4.273 4.264 4.252 4.244 4.163 4.136 4.125 4.098 4.067 4.062 4.046 4.042 3.756 3.752 3.748 3.742 3.737 3.733 3.728 2.329 2.071 2.049 1.989 1.938
AcO
O
S
F
AcO
OAc
OAc
α–7g
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
2.09 1.02 1.00 1.01 1.07 2.01 1.00 1.01 2.05 1.04 1.00 2.07 1.02 1.01 3.03 3.00 3.06 3.02 3.02

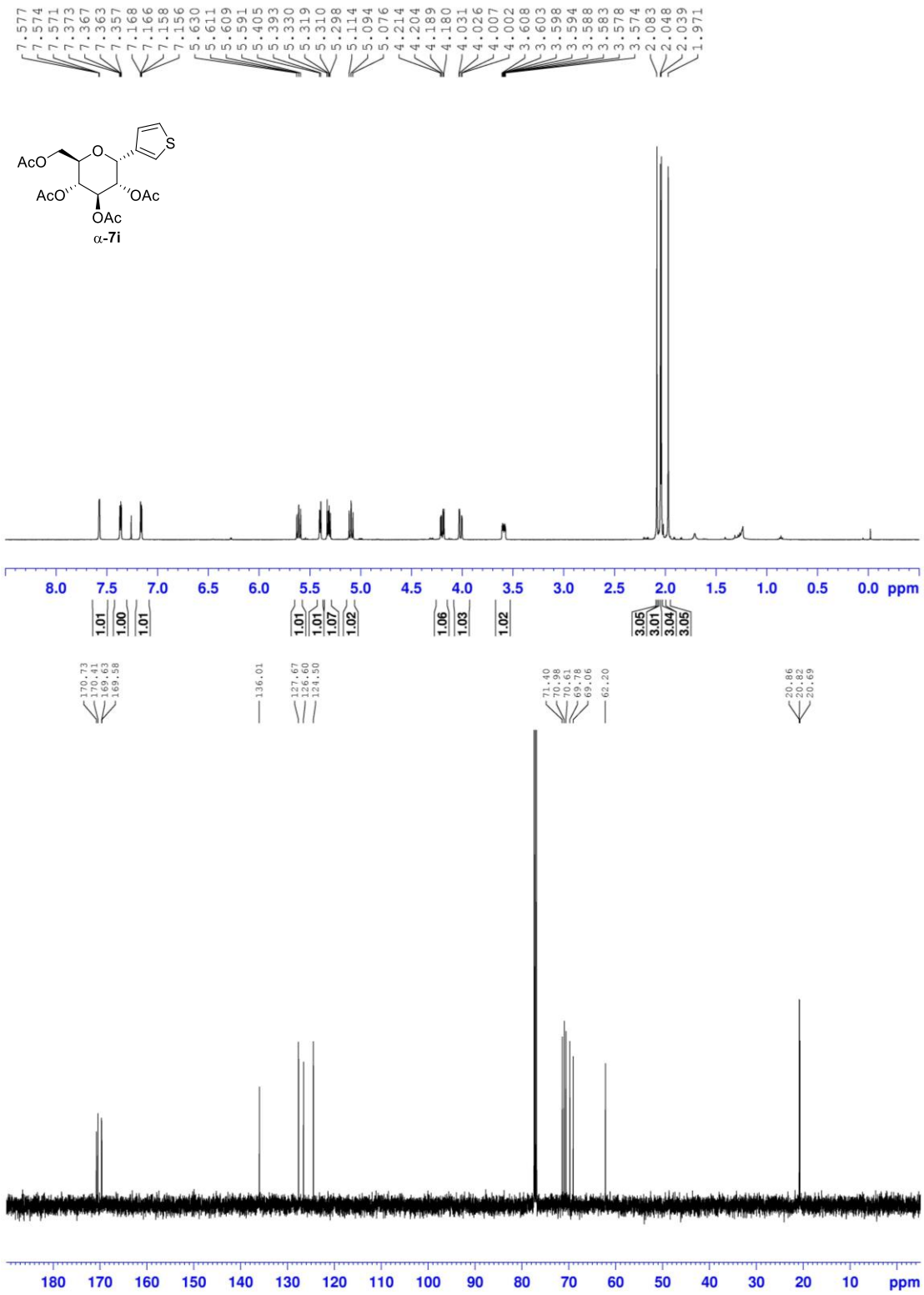

170.72 170.65 169.59 169.57 162.95 161.31 143.06 141.68 138.80 136.55 133.49 130.81 130.79 130.76 129.18 127.14 127.08 126.47 126.15 122.76 115.86 115.71 72.89 70.84 70.41 70.09 68.80 62.03 34.18 20.80 20.75 20.70 19.23
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

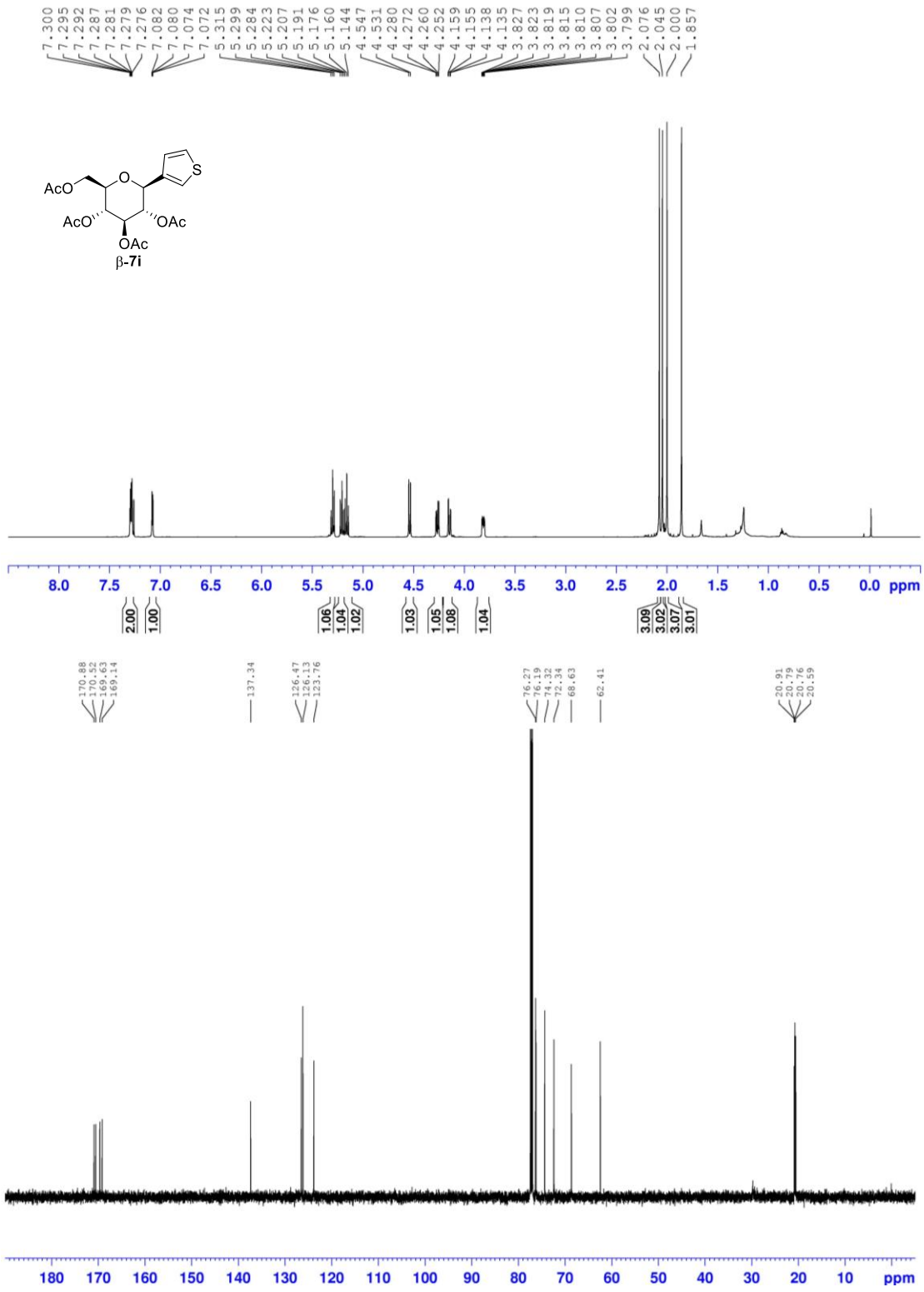

7.198 7.188 7.185 7.170 7.157 7.035 7.029 7.023 7.021 7.009 7.006 6.612 6.606 5.327 5.312 5.296 5.245 5.229 5.213 5.151 5.135 5.119 4.369 4.352 4.293 4.285 4.273 4.265 4.164 4.161 4.144 4.140 4.129 4.102 4.095 4.068 3.834 3.830 3.826 3.823 3.817 3.814 3.810 3.806 2.295 2.065 2.051 1.994 1.755
AcO
O
S
F
AcO
OAc
OAc
β-7g
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

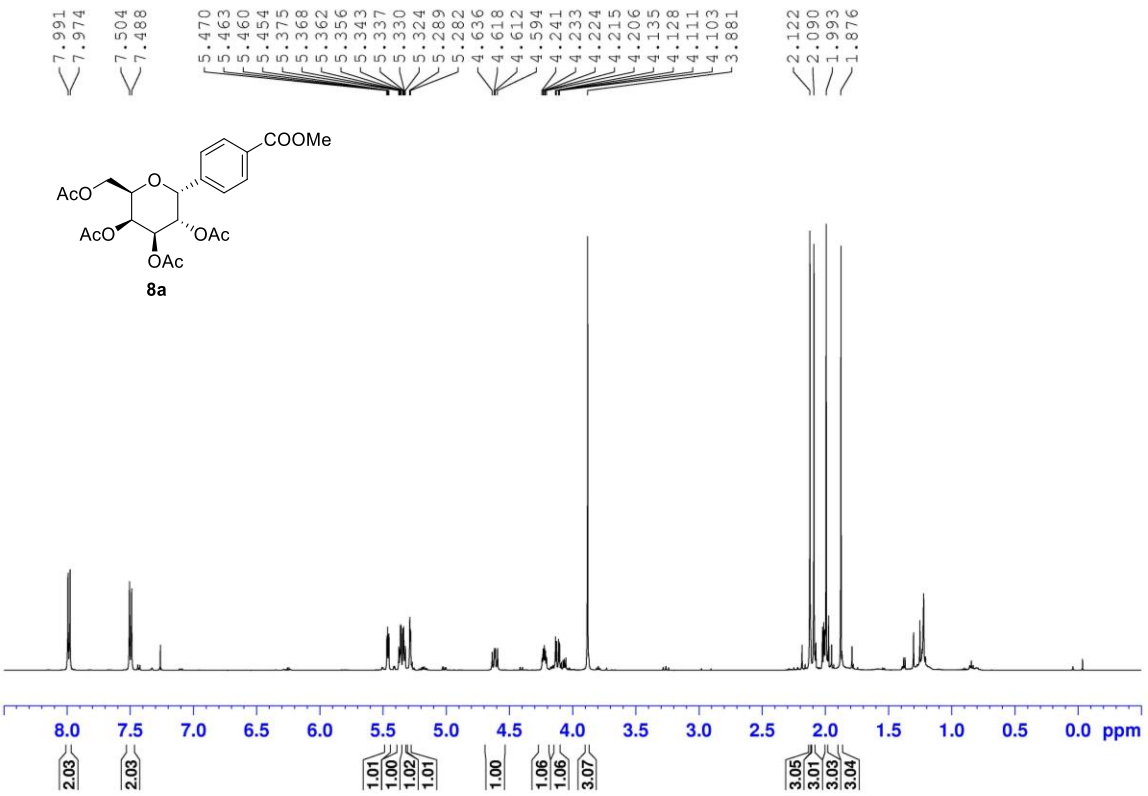

170.92 170.55 169.67 169.01 163.03 161.39 143.19 141.69 138.20 137.29 134.32 130.91 129.64 128.22 127.17 126.09 125.64 122.79 115.93 115.78 80.14 76.19 74.44 72.77 68.73 62.52 34.12 20.91 20.80 20.78 20.75 19.43
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

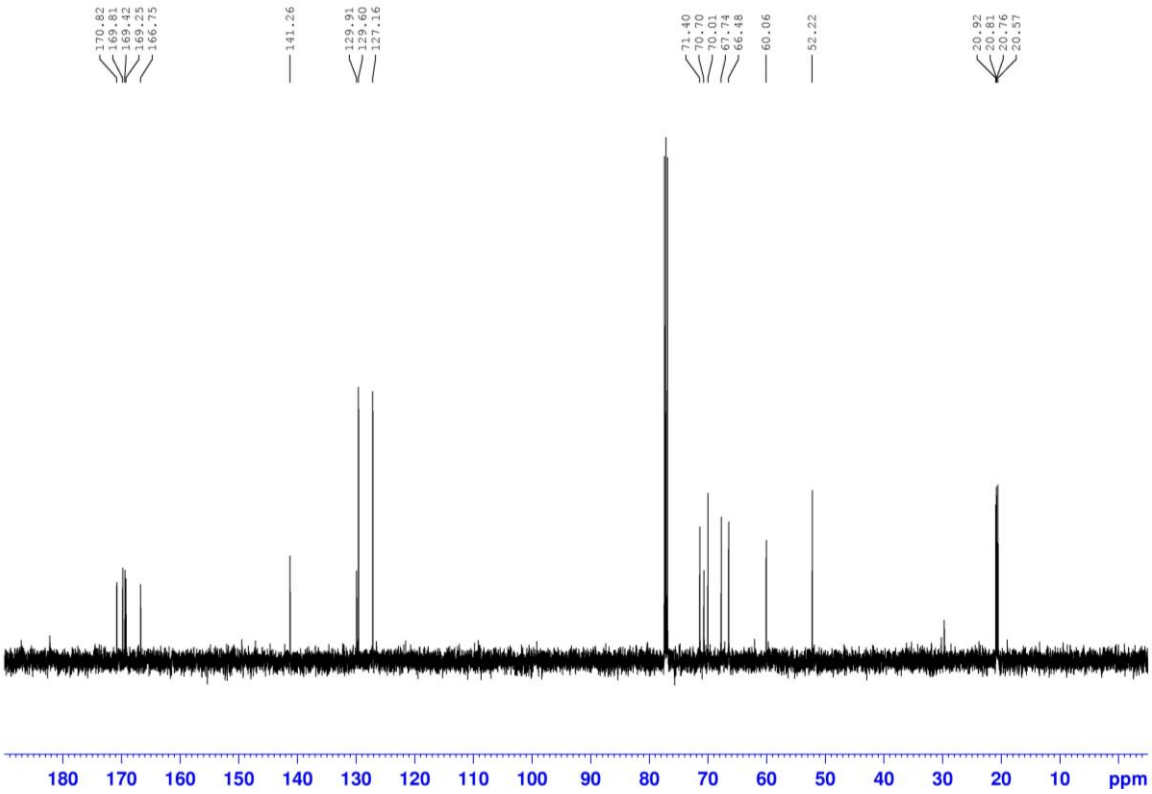

8.380
7.585
7.572
7.414
7.200
7.196
7.192
7.064
7.050
6.507
5.388
5.373
5.357
5.291
5.283
5.275
5.267
5.259
5.251
4.527
4.510
4.328
4.320
4.307
4.299
4.162
4.160
4.142
4.139
3.893
3.890
3.885
3.882
3.876
3.873
3.869
2.068
2.009
1.754
AcO
O
N
H
AcO
OAc
OAc
7h
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
1.04
1.13
1.00
1.00
1.08
2.01
1.04
1.08
1.05
1.02
6.07
3.03
3.02

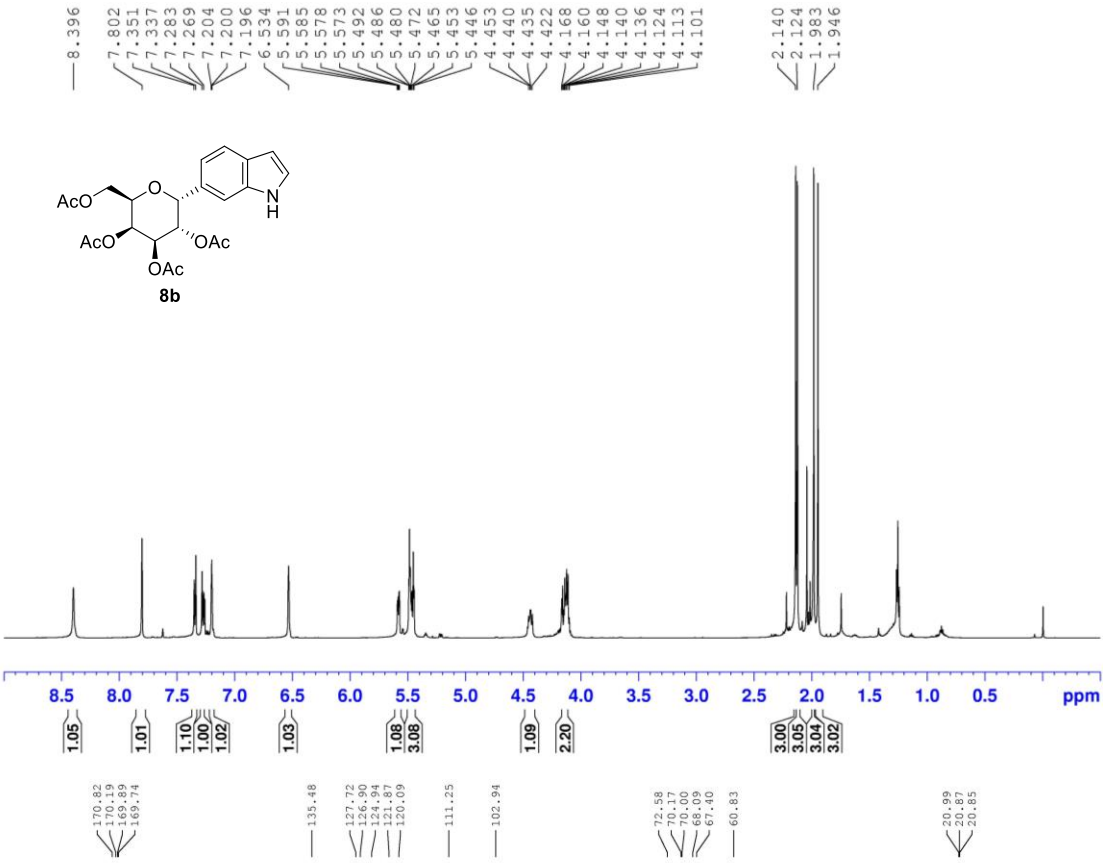

170.97
170.61
169.76
169.18
135.79
129.91
128.56
125.29
120.64
119.60
109.86
102.54
81.06
76.19
74.64
72.89
68.84
62.63
20.91
20.81
20.79
20.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

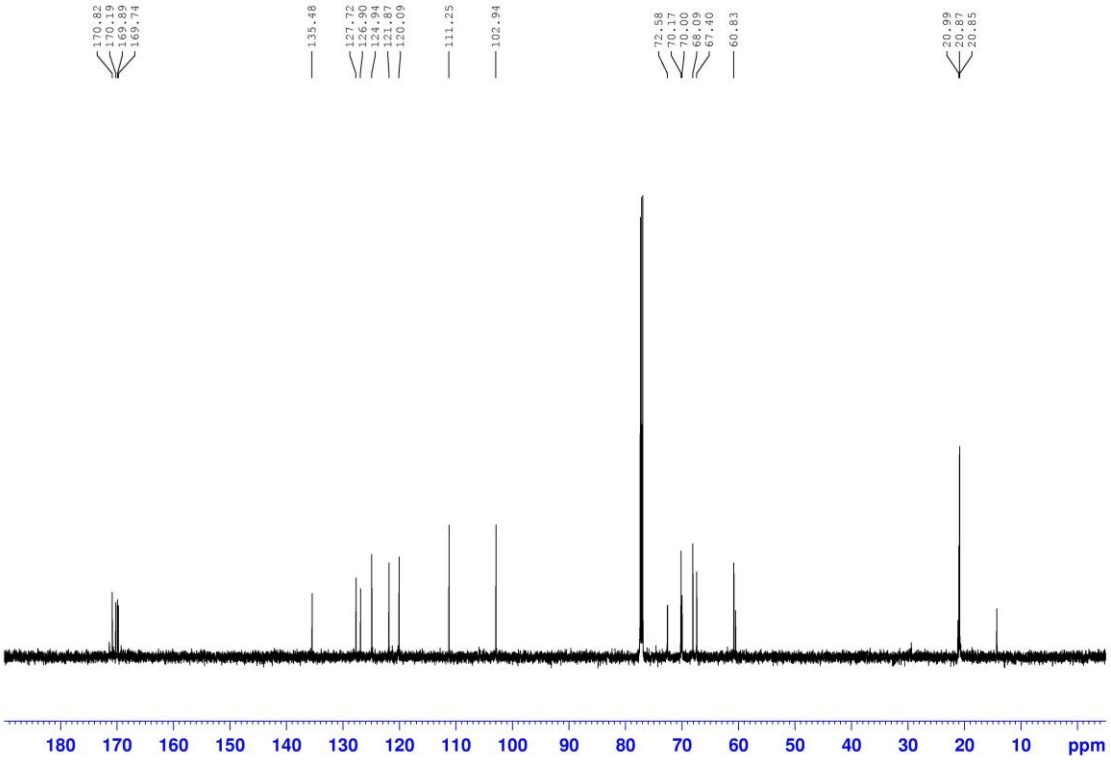

7.577 7.574 7.571 7.373 7.367 7.363 7.357 7.168 7.166 7.158 7.156 5.630 5.611 5.609 5.591 5.405 5.393 5.330 5.319 5.310 5.298 5.114 5.094 5.076 4.214 4.204 4.189 4.180 4.031 4.026 4.007 4.002 3.608 3.603 3.598 3.594 3.588 3.583 3.578 3.574 2.083 2.048 2.039 1.971
AcO
O
S
AcO
OAc
OAc
α-7i
8.0 7.5 7.0 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
1.01 1.00 1.01 1.01 1.01 1.07 1.02 1.06 1.03 1.02 3.05 3.01 3.04 3.05
170.73 170.41 169.63 169.58 136.01 127.67 126.60 124.50 71.40 70.98 70.61 69.78 69.06 62.20 20.86 20.82 20.69
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

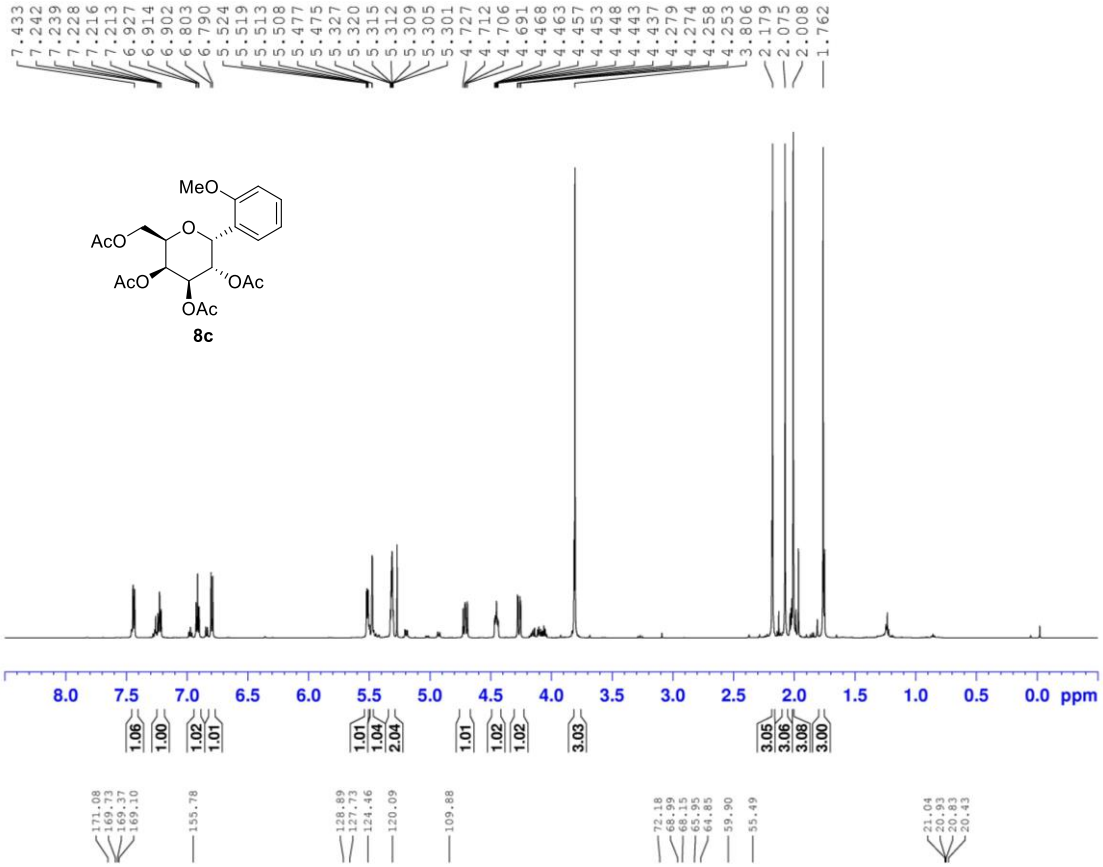

7.300 7.295 7.292 7.287 7.281 7.279 7.276 7.082 7.080 7.074 7.072 5.315 5.299 5.284 5.223 5.207 5.191 5.176 5.160 5.144 4.547 4.531 4.280 4.272 4.260 4.252 4.159 4.155 4.138 4.135 3.827 3.823 3.819 3.815 3.810 3.807 3.802 3.799 2.076 2.045 2.000 1.857
AcO
O
S
AcO
OAc
OAc
β-7i
8.0 7.5 7.0 6.5 6.0 5.5 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
170.88 170.52 169.65 169.14 137.34 126.47 126.13 123.76 76.27 76.19 74.32 72.34 68.63 62.41 20.91 20.79 20.76 20.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

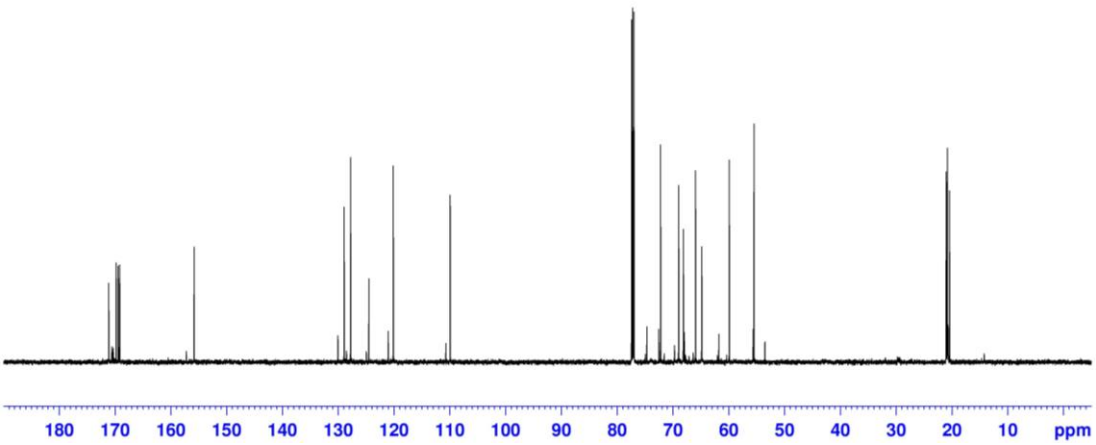

7.991
7.974
7.504
7.488
5.470
5.463
5.460
5.454
5.375
5.368
5.362
5.356
5.343
5.337
5.330
5.324
5.289
5.282
4.636
4.618
4.612
4.594
4.241
4.233
4.224
4.215
4.206
4.135
4.128
4.111
4.103
3.881
2.122
2.090
1.993
1.876
COOMe
AcO
AcO
OAc
OAc
O
8a
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03
2.03
1.01
1.00
1.02
1.01
1.00
1.06
1.06
3.07
3.05
3.01
3.03
3.04

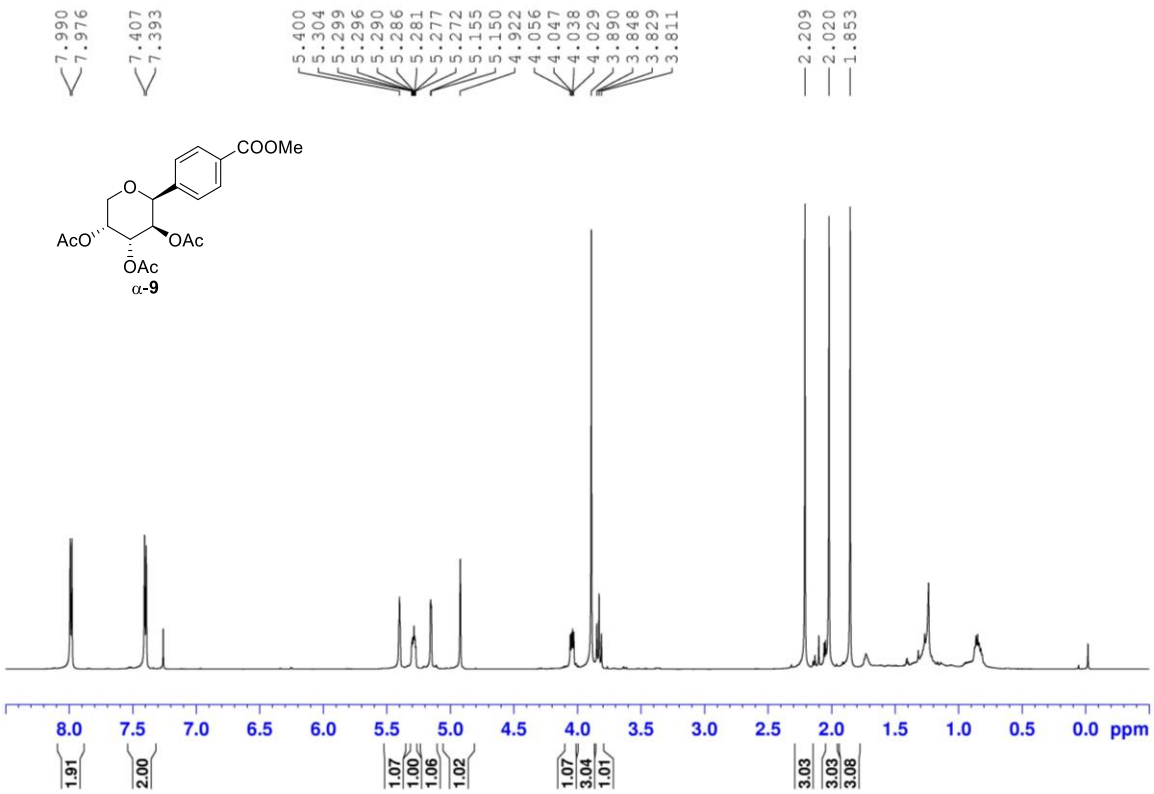

170.82
169.81
169.42
169.25
166.75
141.26
129.91
129.60
127.16
71.40
70.70
70.01
67.74
66.48
60.06
52.22
20.92
20.81
20.76
20.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

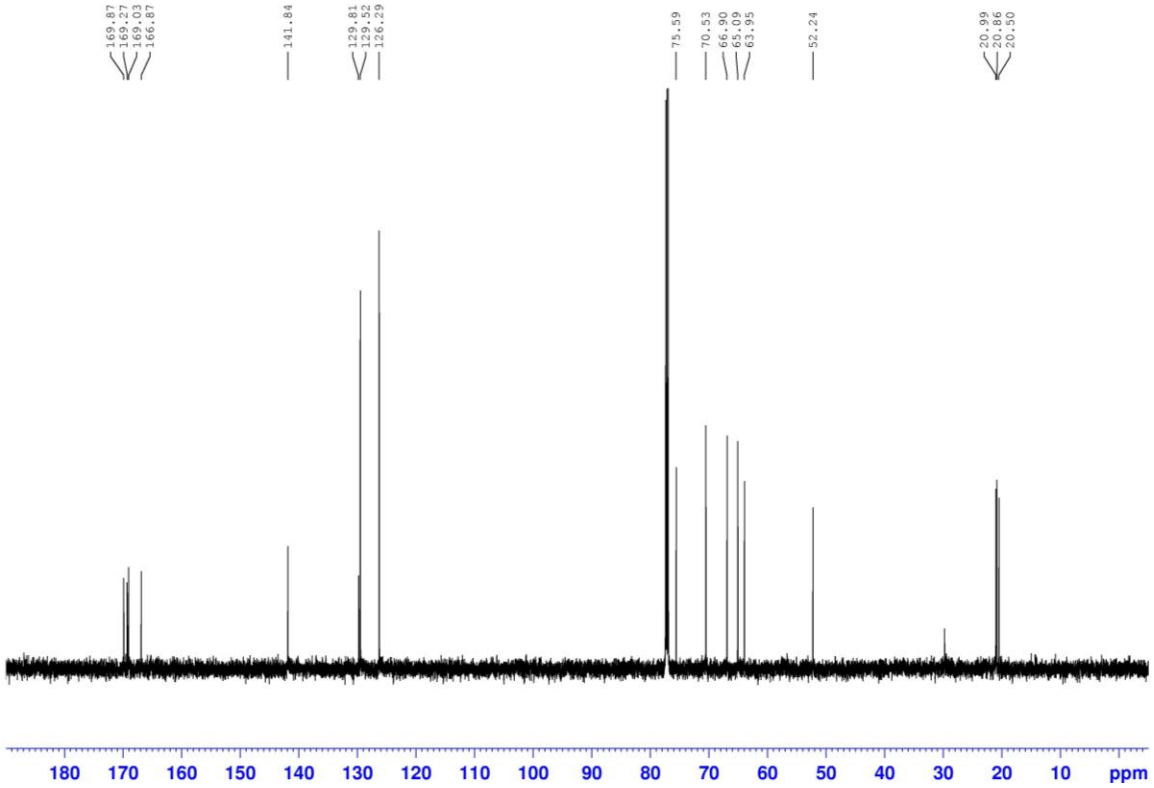

8.396
7.802
7.351
7.337
7.283
7.269
7.204
7.200
7.196
6.534
5.591
5.585
5.578
5.573
5.492
5.486
5.480
5.472
5.465
5.453
5.446
4.453
4.440
4.435
4.422
4.168
4.160
4.148
4.140
4.136
4.124
4.113
4.101
2.140
2.124
1.983
1.946
AcO
O
N
H
AcO
OAc
OAc
8b
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.05
1.01
1.10
1.00
1.02
1.03
1.08
3.08
1.09
2.20
3.00
3.05
3.04
3.02

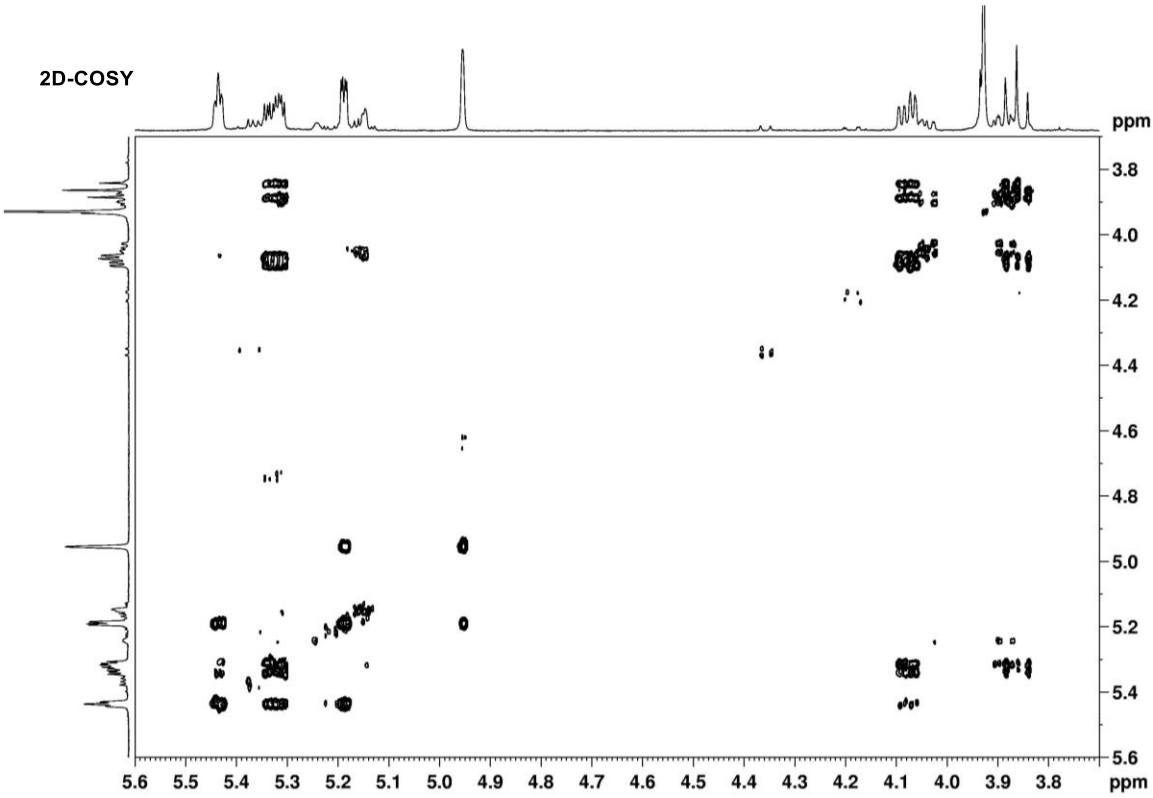

170.82
170.19
169.89
169.74
135.48
127.72
126.90
124.94
121.87
120.09
111.25
102.94
72.58
70.17
70.00
68.09
67.40
60.83
20.99
20.87
20.85
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

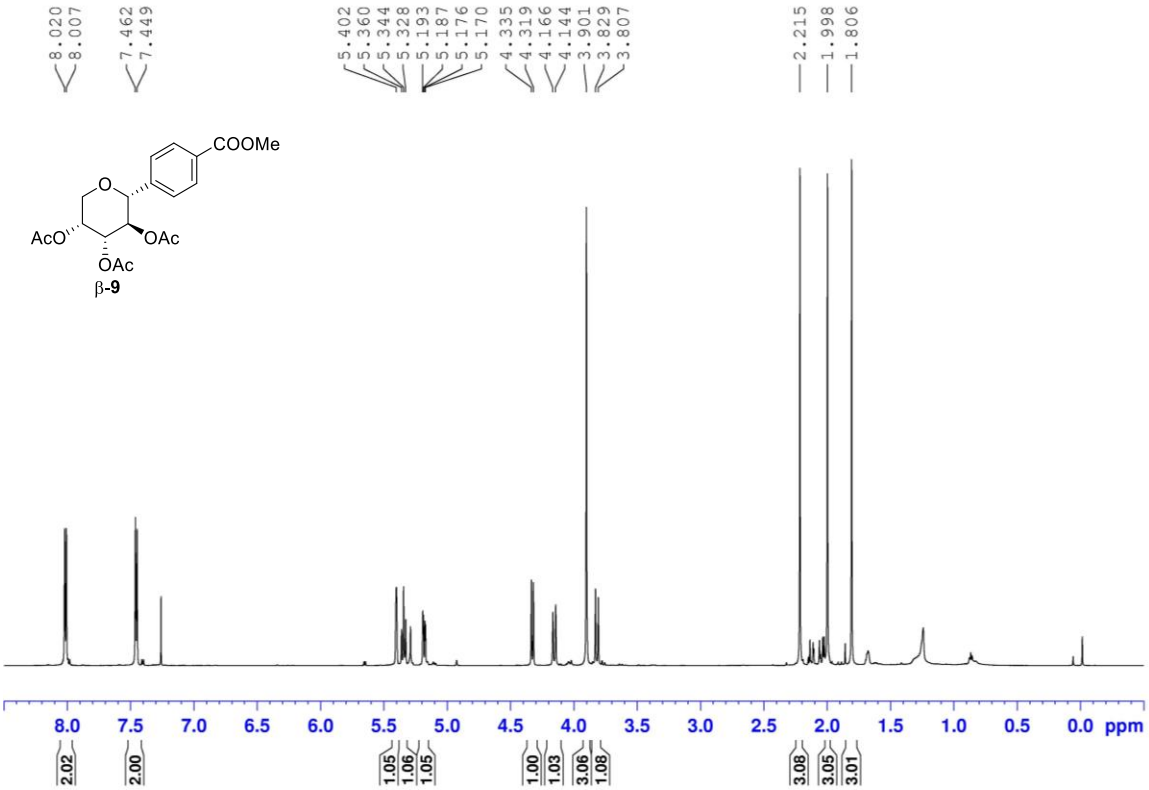

7.433
7.242
7.239
7.228
7.216
7.213
6.927
6.914
6.902
6.803
6.790
5.524
5.519
5.513
5.508
5.477
5.475
5.327
5.320
5.315
5.312
5.309
5.305
5.301
4.727
4.712
4.706
4.691
4.468
4.463
4.457
4.453
4.448
4.443
4.437
4.279
4.274
4.258
4.253
3.806
2.179
2.075
2.008
1.762
MeO
AcO
O
AcO
OAc
OAc
8c
8.0 7.5 7.0 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
1.06
1.00
1.02
1.01
1.01
1.04
2.04
1.01
1.02
1.02
3.03
3.05
3.06
3.08
3.00
171.08
169.73
169.37
169.10
155.78
128.89
127.73
124.46
120.09
109.88
72.18
68.99
68.15
65.95
64.85
59.90
55.49
21.04
20.93
20.83
20.43

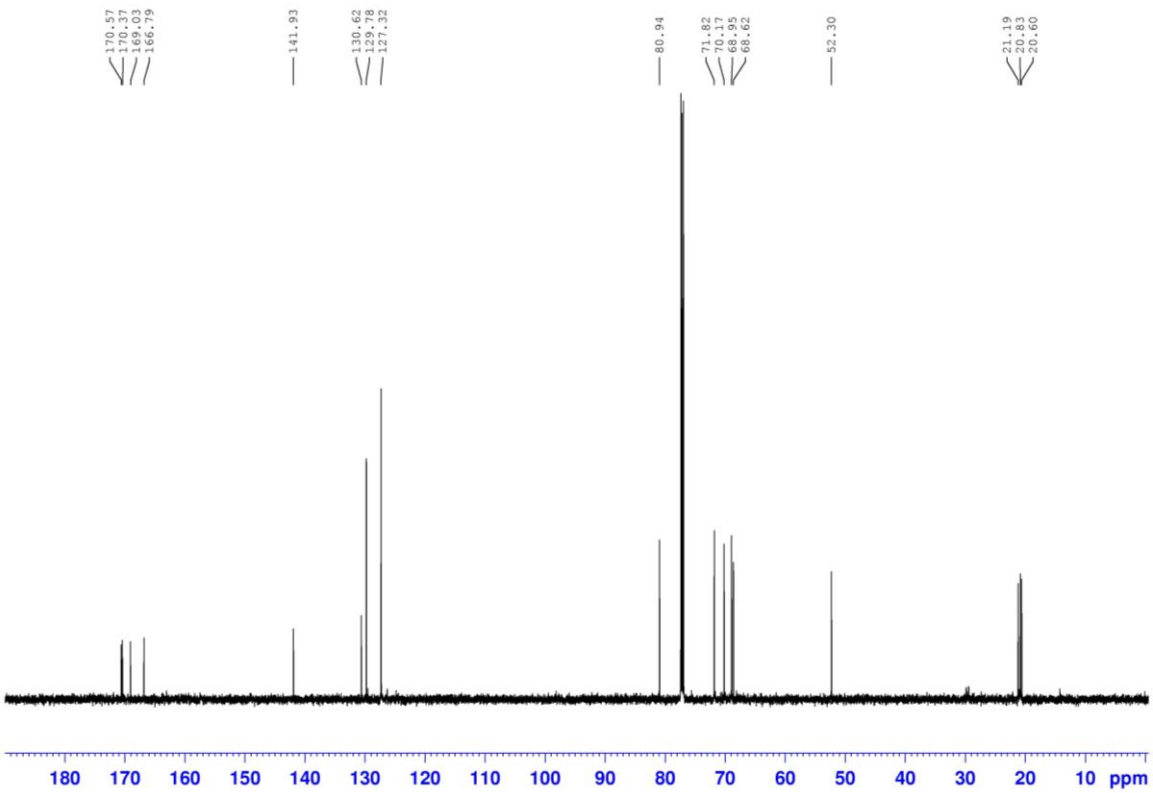

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

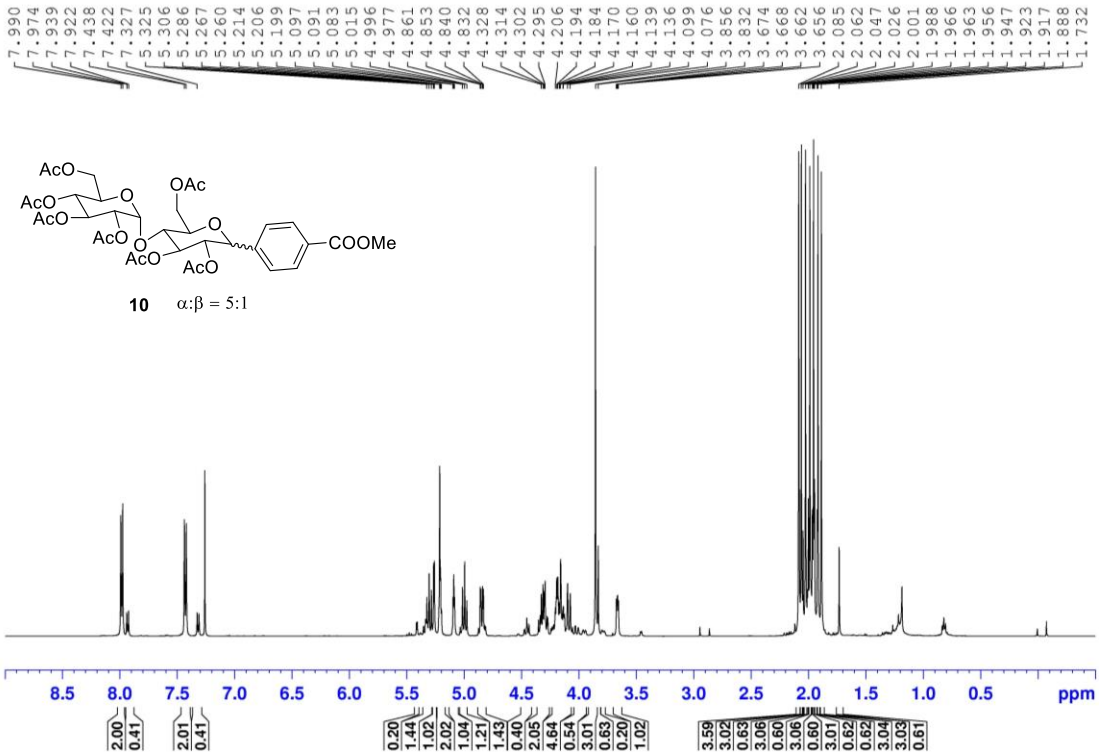

7.990
7.976
7.407
7.393
5.400
5.304
5.299
5.296
5.290
5.286
5.281
5.277
5.272
5.155
5.150
4.922
4.056
4.047
4.038
4.029
3.890
3.848
3.829
3.811
2.209
2.020
1.853
COOMe
O
AcO
OAc
OAc
α-9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.91
2.00
1.07
1.00
1.06
1.02
1.07
3.04
1.01
3.03
3.03
3.08

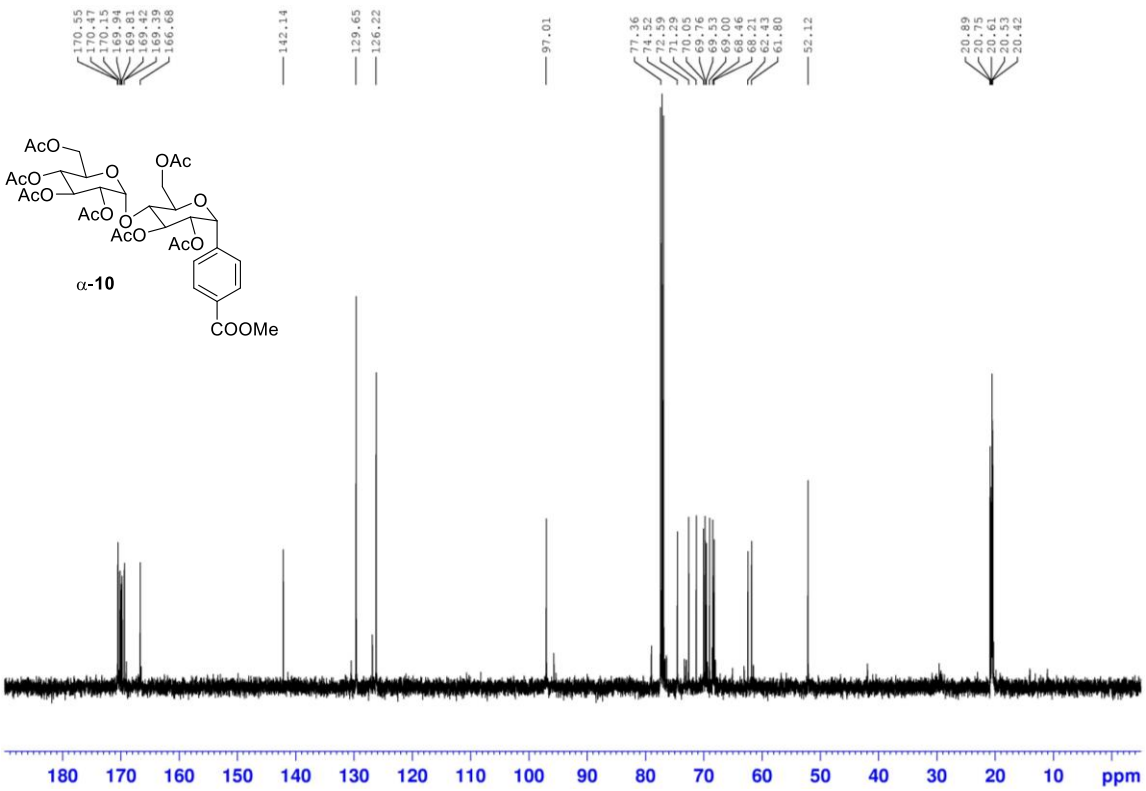

169.87
169.27
169.03
166.87
141.84
129.81
129.52
126.29
75.59
70.53
66.90
65.09
63.95
52.24
20.99
20.86
20.50
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

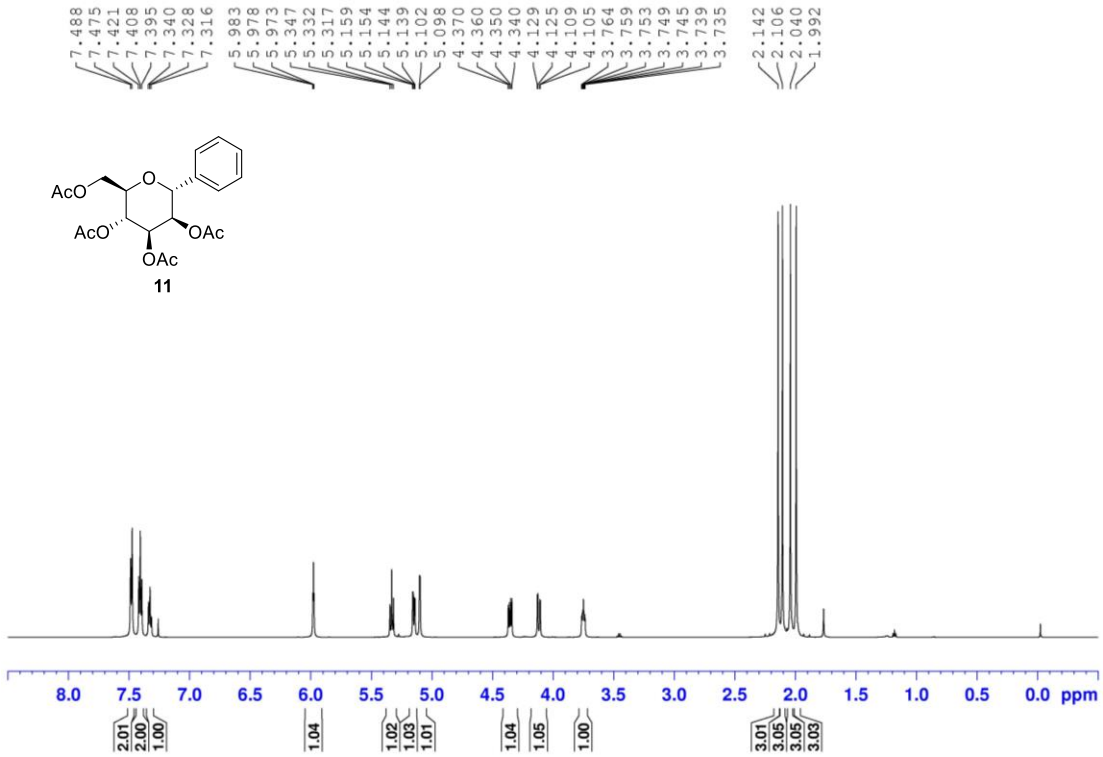

2D-COSY
ppm
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8
ppm

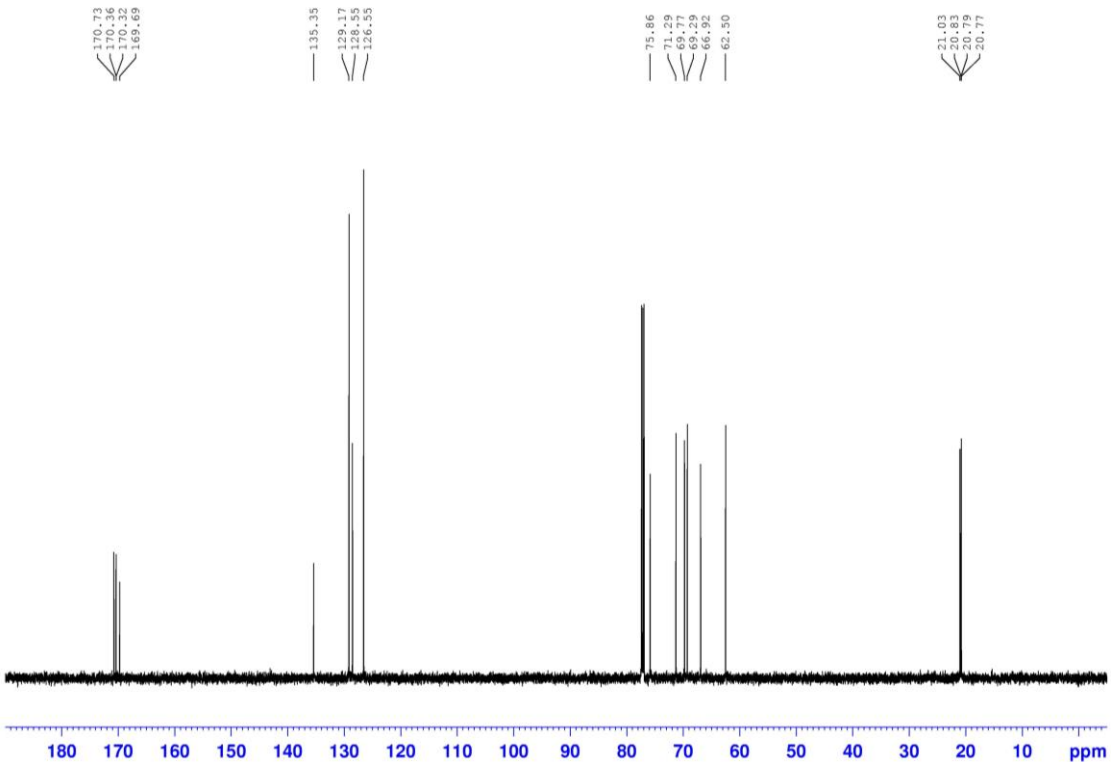

8.020
8.007
7.462
7.449
5.402
5.360
5.344
5.328
5.193
5.187
5.176
5.170
4.335
4.319
4.166
4.144
3.901
3.829
3.807
2.215
1.998
1.806
COOMe
O
AcO
OAc
OAc
β-9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
2.00
1.05
1.06
1.05
1.00
1.03
3.06
1.08
3.08
3.05
3.01

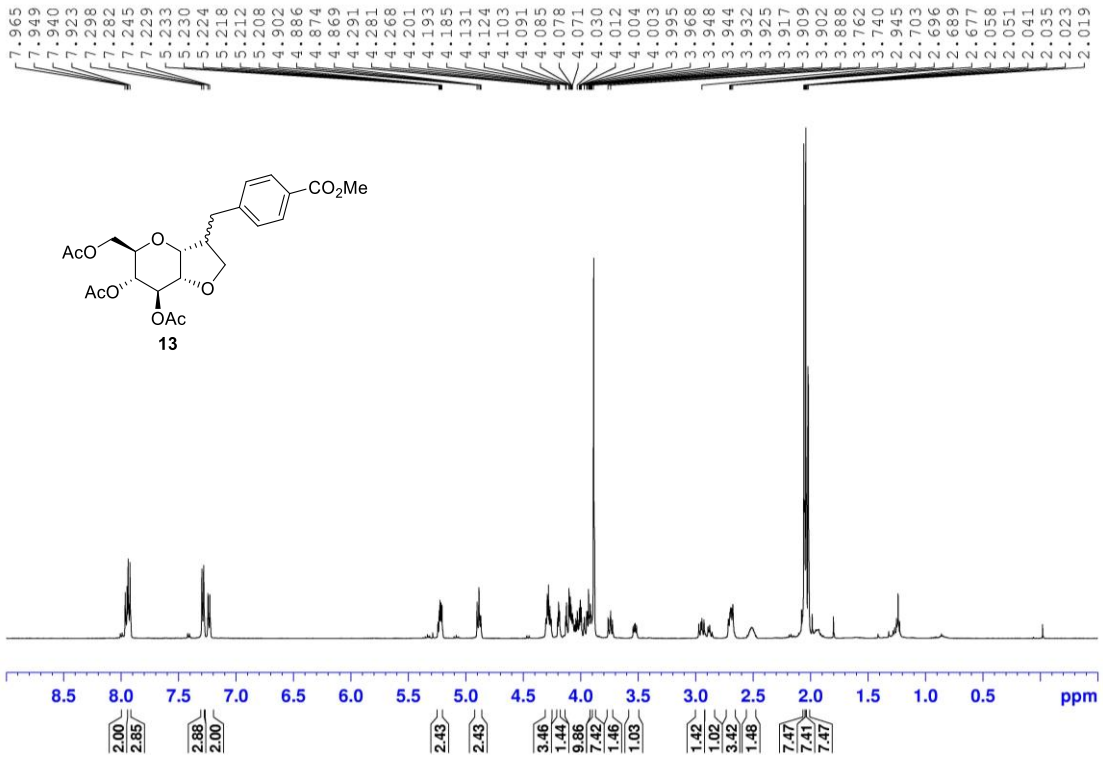

170.57
170.37
169.03
166.79
141.93
130.62
129.78
127.32
80.94
71.82
70.17
68.95
68.62
52.30
21.19
20.83
20.60
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

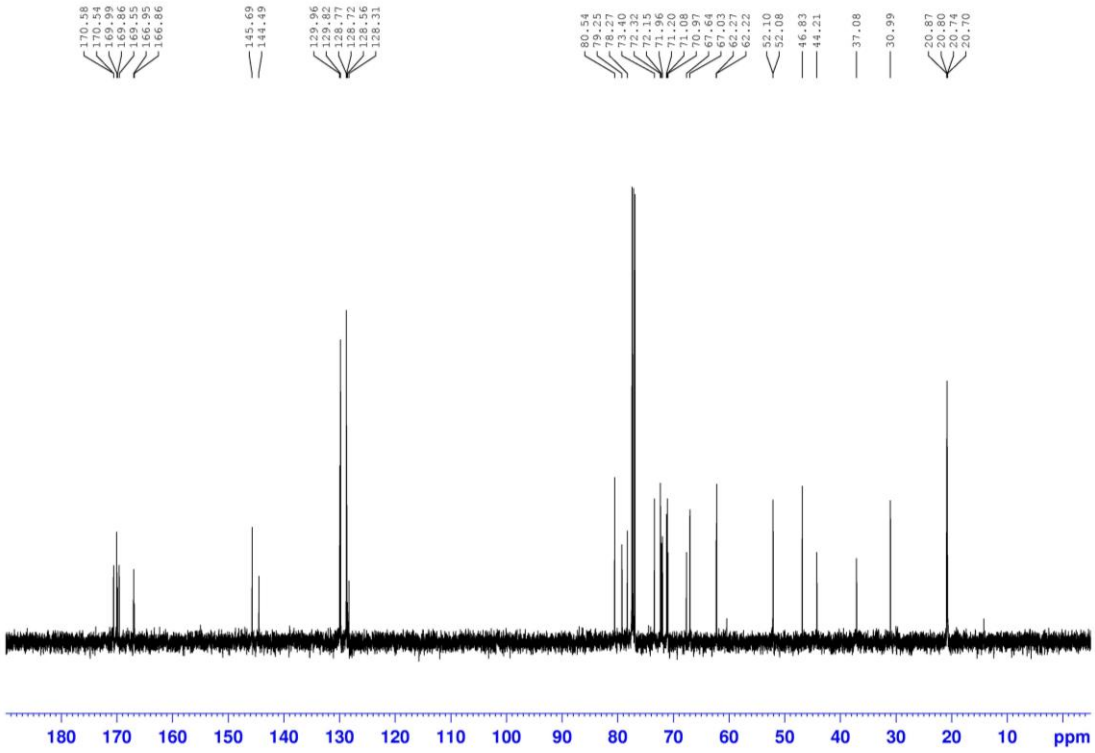

7.990
7.974
7.939
7.922
7.438
7.422
7.327
5.325
5.306
5.286
5.267
5.260
5.214
5.206
5.199
5.097
5.091
5.083
5.015
4.996
4.977
4.861
4.853
4.840
4.832
4.328
4.314
4.302
4.295
4.206
4.194
4.184
4.170
4.160
4.139
4.136
4.099
4.076
3.856
3.832
3.674
3.668
3.662
3.656
2.085
2.062
2.047
2.026
2.001
1.988
1.966
1.963
1.956
1.947
1.923
1.917
1.888
1.732
AcO
AcO
AcO
AcO
AcO
AcO
OAc
O
O
O
O
COOMe
10 α:β = 5:1
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
2.00
0.41
2.01
0.41
0.20
1.44
1.02
2.02
1.04
1.21
1.43
0.40
2.05
4.64
0.54
3.01
0.63
0.20
1.02
3.59
3.02
0.63
3.06
0.60
3.06
0.60
3.01
0.62
0.62
3.04
3.03
0.61

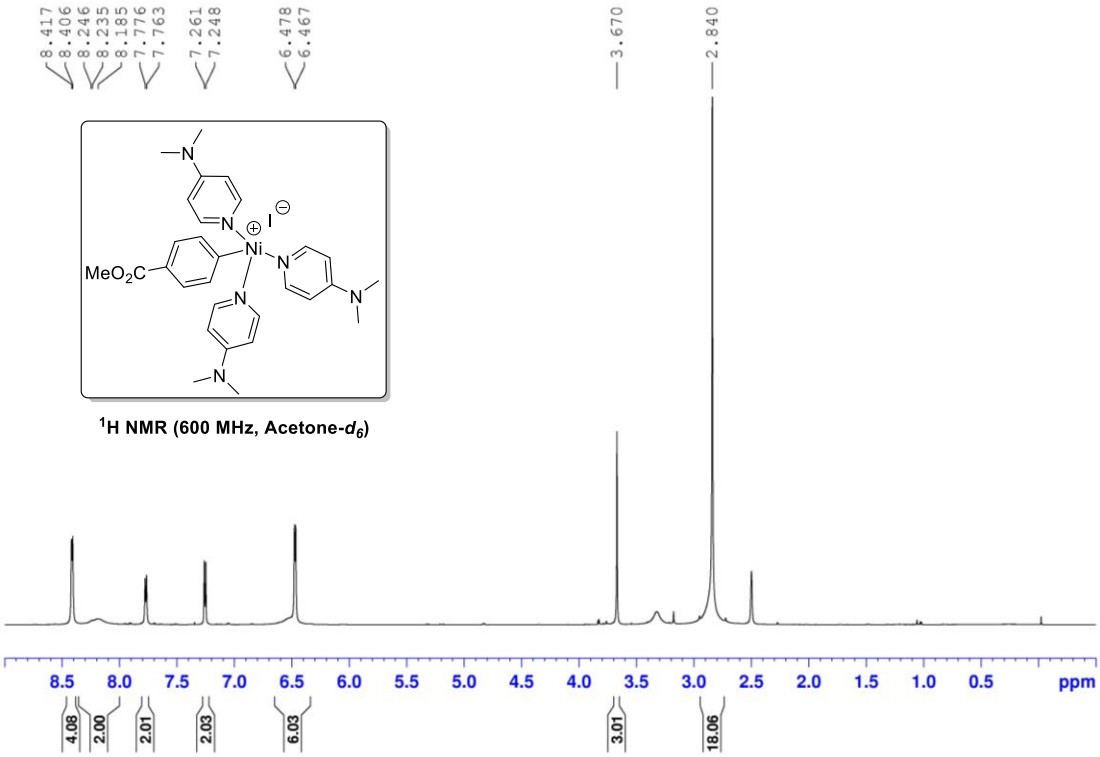

170.55
170.47
170.15
169.94
169.81
169.42
169.39
166.68
142.14
129.65
126.22
97.01
77.36
74.52
72.59
71.29
70.05
69.76
69.53
69.00
68.46
68.21
62.43
61.80
52.12
20.89
20.75
20.61
20.53
20.42
AcO
AcO
AcO
AcO
AcO
AcO
OAc
O
O
O
AcO
α-10
COOMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.488
7.475
7.421
7.408
7.395
7.340
7.328
7.316
5.983
5.978
5.973
5.347
5.332
5.317
5.159
5.154
5.144
5.139
5.102
5.098
4.370
4.360
4.350
4.340
4.129
4.125
4.109
4.105
3.764
3.759
3.753
3.749
3.745
3.739
3.735
2.142
2.106
2.040
1.992
AcO
AcO
OAc
OAc
O
11
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
1.00
1.04
1.02
1.03
1.01
1.04
1.05
1.00
3.01
3.05
3.05
3.03

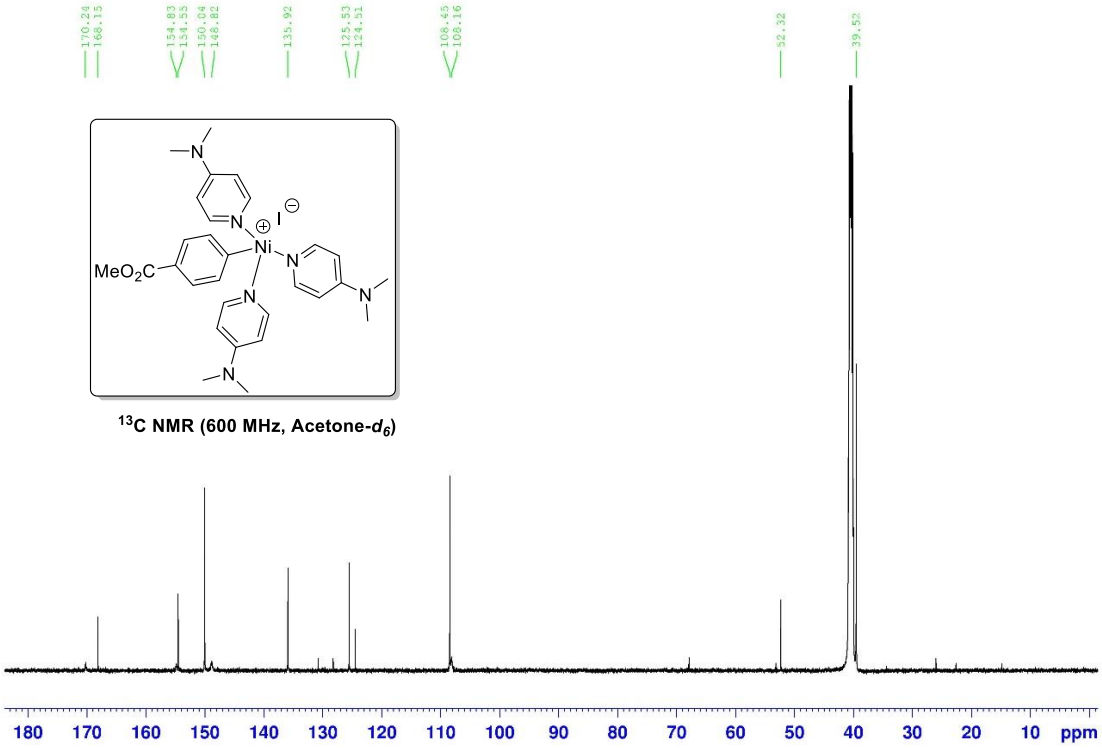

170.73
170.36
170.32
169.69
135.35
129.17
128.55
126.55
75.86
71.29
69.77
69.29
66.92
62.50
21.03
20.83
20.79
20.77
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.965
7.949
7.940
7.923
7.298
7.282
7.245
7.229
5.233
5.230
5.224
5.218
5.212
5.208
4.902
4.886
4.874
4.869
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
4.004
4.003
3.995
3.968
3.948
3.944
3.932
3.925
3.917
3.909
3.902
3.888
3.762
3.740
2.945
2.703
2.696
2.689
2.677
2.058
2.051
2.041
2.035
2.023
2.019
CO2Me
AcO
AcO
OAc
13
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
2.00
2.85
2.88
2.00
2.43
2.43
3.46
1.44
9.86
7.42
1.46
1.03
1.42
1.02
3.42
1.48
7.47
7.41
7.47





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



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