Supporting Information

Alkyl-Aryl Ketone Synthesis via Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Aryl Acids and Anhydrides

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Experimental Section

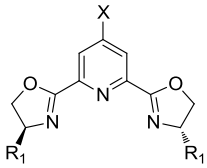
Part 1. General Information

Experiments were conducted under a nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. For product purification by flash column chromatography, silica gel (300−400 mesh) and petroleum ether (bp 60−90 ℃) were used. NMR spectra were measured on 500 MHz instruments at room temperature. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using aIon Spec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

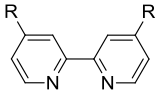
The following chemicals were purchased and used as received: Zn (99.9%, powder), NiI_2 (99.5%, Alfa Aesar), $Ni(cod)_2$ (99%, Stream), $NiCl_2$(99.5%, Alfa Aesar), $NiBr_2$ (99.5%, Alfa Aesar), $Ni(acac)_2$ (99%, Alfa Aesar), $Ni(ClO_4)_2{\cdot}6H_2O$ (99.5%, Alfa Aesar), 2,2'-bipyridine (**4a**, Aldrich) 4,4'-Di-*tert*-butyl-2,2'-bipyridine (**4b**, Aldrich), 4,4'-dimethyl-2,2'-bipyridine (**4c**, Aldrich), 4,4'-dimethoxy-2,2'-bipyridine(**4d**, Aldrich), 1,10-phenanthroline (**5a**, Aldrich), 4,7-diphenyl-1,10-phenanthroline (**5b**, Aldrich), DMA (99.8%, Super Dry, with molecular sieves), DMF (99.8%, Super Dry, with molecular sieves), Dioxane (99.5%, Super Dry, with molecular sieves), THF (99.5%, Super Dry, with molecular sieves), CH_3CN (99.5%, Super Dry, with molecular sieves), $MgCl_2$ (99%, Alfa Aesar), TBAI (99%, Aladdin), Boc_2O (99%, Aladdin), 2-iodopropane (TCI), iodocyclohexane (TCI) 2,3,4,6-Tetra-O-acetyl-alpha-D glucopyranosyl bromide (98%, Aladdin), 2,3,4,6-Tetra-O-acetyl-alpha-D-galactopyranosyl bromide(93%, Aladdin), benzoic anhydride (Alfa Asear). Ligands 3a[1], 3b[2], 3c[3], 5c[4], 6[5], L-1[6], were synthesized according to the literature procedures. The anhydrides were prepared based on reported procedures[7].

Part 2. Details of Optimization of Glycosyl Bromides

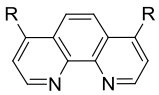
A typical procedure for optimization reactions of glycosyl bromide with benzoic anhydride: To a flame-dried Schlenk tube equipped with a stir bar was loaded benzoic anhydride (51.0 mg, 0.225 mmol, 150%), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), glycosyl bromide (61.7 mg, 0.15 mmol, 100%), $MgCl_2$ (28.6mg, 0.3mmol, 200%), ligand (0.018 mmol, 12%) and Ni sources (0.015 mmol, 10%). The tube was evacuated and refilled nitrogen (N_2) three time. Solvent (0.5 mL) was added via syringe. After the reaction mixture was allowed to stir for 12 hours under N_2 atmosphere at 25 °C, the suspension was partitioned between Na_2CO_3 (saturated) and EtOAc. The organic phase was dried (over $MgSO_4$) and filtered. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash column chromatography provided the product as oil or solid.



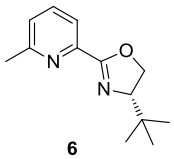
3a: X = Cl, R = *t*Bu
3b: X = H, R = *t*Bu
3c: X = H, R = *i*Pr



4a: R = H
4b: R = *t*Bu
4c: R = Me
4d: R = OMe



5a: R = H
5b: R = Ph
5c: R = Br



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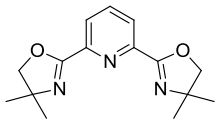

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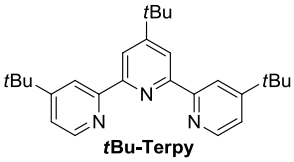
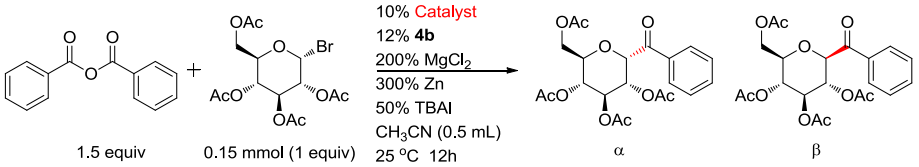


***t*Bu-Terpy**

Table S1: Screening of catalysts

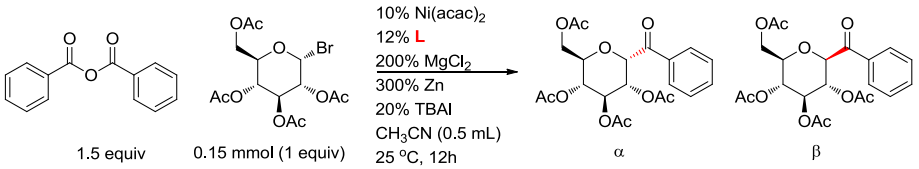


1.5 equiv | 0.15 mmol (1 equiv) | α | β

Entry	Catalyst	Yield (%)[a]	α/β
1	$Ni(COD)_2$	20	4.6/1
2	NiI_2	trace	2.85/1
3	$NiBr_2$	20	3.3/1
4	$NiCl_2$	trace	ND[b]
5	$Ni(acac)_2$	25	7/1
6	$Ni(ClO_4)_2$ 6H_2O	22	5.5/1
7	$NiBr_2$·dimethoxyethane	21	5/1
8	none	ND[b]	

[a] Determined by NMR using trimethyl(phenyl)silane as the internal standard. [b] Not detected.

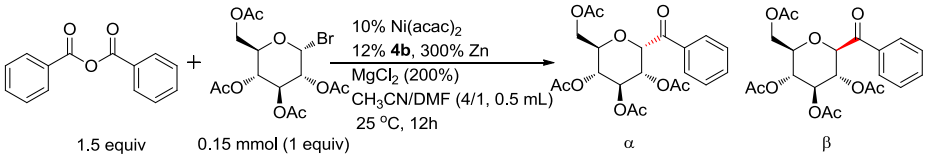
Table S2: Screening of ligands



Entry	Ligands	Yield(%)[a]	α/β
1	3b	14	4.7/1
2	4a	37	4.3/1
3	4b	25	7/1
4	4c	29	4.2/1
5	4d	28	4/1
6	5a	62	5.5/1
7	5b	31	4/1
8	L-1	21	4.9/1
9	*tBu-Terpy*	trace[b]	

[a] Determined by NMR using trimethyl(phenyl)silane as the internal standard. [b] Not detected.

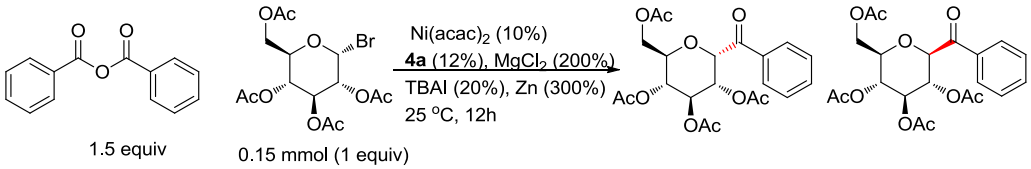
Table S3: Screening of additives



Entry	TBAI	Yield(%)[a]	α/β
1	none	none[b]	
2	10	34	3.9/1
3	20	67	2.7/1
4	30	59	3.5/1
5	40	55	3.1/1
6	50	54	2.5/1

[a] Determined by NMR using trimethyl(phenyl)silane as the internal standard. [b] Not detected.

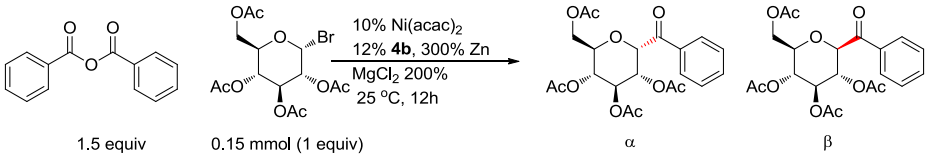
Table S4: Solvent screening



Entry	Solvent (0.5 mL)	Yield(%)[a]	α/β
1	CH_3CN	37	4.3/1
2	THF	17	1.6/1
3	DMF	trace[b]	
4	DMSO	ND[b]	
5	CH_3CN/DMF (4/1)	68	3.2/1
6	CH_3CN/THF (4/1)	47	2.5/1
7	CH_3CN/THF (4/1)	51	2.3/1
8	CH_3CN/THF (2/3)	36	2.8/1
9	CH_3CN/THF (4/1)	37	2.7/1

[a] Determined by NMR using trimethyl(phenyl)silane as the internal standard. [b] Not detected.

Table S4: Catalysts and Solvent screening



Entry	Catalysts	Solvent (0.5 mL)	Yield(%)[a]	α/β
1	$Ni(acac)_2$	CH_3CN/DMF (4/1)	68	3.2/1
2	$Ni(COD)_2$	CH_3CN/DMF (4/1)	35	3.9/1
3	$Ni(ClO_4)_2$ $6H_2O$	CH_3CN/DMF (4/1)	78	3.1/1
4[b]	$Ni(ClO_4)_2$ $6H_2O$	CH_3CN/DMF (4/1)	83[b]	2.7/1
5	$Ni(ClO_4)_2$ $6H_2O$	CH_3CN/DMF (9/1, 1 mL)[c]	90	2.7/1

[a] Determined by NMR using trimethyl(phenyl)silane as the internal standard. [b] 20°C.

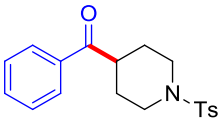
Part 3. Ketone Synthesis via Reductive Coupling.

***General procedure A* for ketone synthesis via reductive coupling of alkyl bromides with aryl acids:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl acids (0.225 mmol, 150%), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), alkyl bromides (0.150 mmol, 100%), $MgCl_2$ (35.7 mg, 0.380 mmol, 250%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (2.8 mg, 0.011 mmol, 7%) and $Ni(acac)_2$ (1.9 mg, 0.015 mmol, 5%). The tube was evacuated and refilled nitrogen (N_2) three time. Boc_2O (98.2 mg, 0.45 mmol) and CH_3CN/DMF (1:4, 1 mL) was then added via syringe. After the reaction mixture was stirred for 12 hours under N_2 atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

***General procedure B* for ketone synthesis via reductive coupling of alkyl iodides with aryl acids:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl acids (0.45 mmol), followed by addition of zinc power (58.8 mg, 0.9 mmol, 300%), $MgCl_2$ (57.2 mg, 0.6 mmol, 200%), 2,2'-bipyridine (5.6 mg, 0.036 mmol, 12%) and $Ni(ClO_4)_2.6H_2O$ (11 mg, 0.030 mmol, 10%). The tube was evacuated and refilled nitrogen (N_2) three time. Boc_2O (196.4mg, 0.9 mmol, 300%), alkyl iodides (0.3 mmol, 100%) and CH_3CN/DMF (4:1, 1 mL) was added via syringe. After the reaction mixture was stirred for 12 hours under N_2 atmosphere at 25 °C， it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

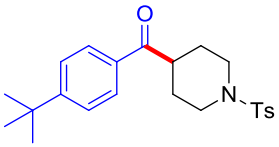
***General procedure C* for ketone synthesis via reductive coupling of glycosyl bromides with aryl anhydrides:** To a flame-dried Schlenk tube equipped with a stir bar was loaded aryl anhydrides (0.45 mmol, 150%), followed by addition of zinc power (58.8 mg, 0.9 mmol, 300%), TBAI (22.2 mg, 0.06 mmol, 20%), glycosyl bromides (0.300 mmol, 100%), $MgCl_2$ (57.2 mg, 0.6 mmol), 2,2'-bipyridine (5.6 mg, 0.036 mmol, 12%) and $Ni(ClO4)_2{\cdot}6H_2O$ (11 mg, 0.03 mmol, 10%). The tube was evacuated and refilled nitrogen (N_2) three time. CH_3CN/DMF (9:1, 1 mL) was added via syringe. After the reaction mixture was stirred for 12 hours under N_2 atmosphere at 25 °C, the suspension was washed with Na_2CO_3 (saturated) and extracted by EtOAc. The organic phase was dried (over $MgSO_4$) and filtered. The mixture was concentrated under reduced pressure, and the residue was

loaded onto a silica column. Flash column chromatography provided the product as a solid or oil.



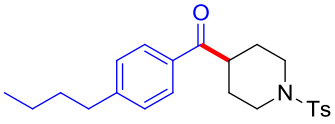
Phenyl(1-tosylpiperidin-4-yl)methanone (2a).

According to the general procedure A, the title compound was obtained in (45.3 mg, 0.132 mmol) 88% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



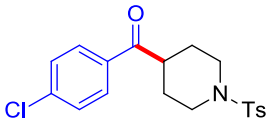
(4-(*tert*-Butyl)phenyl)(1-tosylpiperidin-4-yl)methanone (2b)

According to the general procedure A, this compound was obtained in (50.3 mg, 0.126 mmol) 84% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



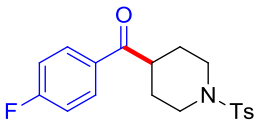
(4-Butylphenyl)(1-tosylpiperidin-4-yl)methanone (2c).

According to the general procedure A, this compound was obtained in (46.1 mg, 0.116 mmol) 77% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.76 (dt, *J* = 12.2, 4.3 Hz, 2H), 3.20–3.14 (m, 1H), 2.65–2.62 (t, *J* = 7.8 Hz, 2H), 2.51 (td, *J* = 11.4, 3.4 Hz, 2H), 2.44 (s, 3H), 1.94–1.83 (m, 4H), 1.61–1.55 (m, 2H), 1.33 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ201.0, 149.0, 143.5, 133.14, 133.08, 129.6, 128.7, 128.3, 127.7, 45.6, 42.1, 35.6, 33.1, 27.9, 22.2, 21.5, 13.8. HRMS (ESI): calcd for $C_{23}H_{29}NO_3S$ $[M]^+$ 399.1868, found 399.1868. m.p. 119–120 °C.



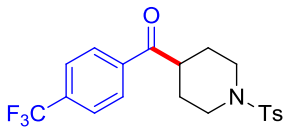
(4-Chlorophenyl)(1-tosylpiperidin-4-yl)methanone (2d).

According to the general procedure A, this compound was obtained in (39.6 mg, 0.105 mmol) 70% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



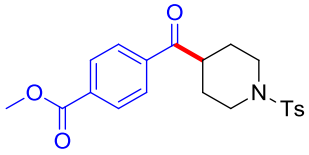
(4-Fluorophenyl)(1-tosylpiperidin-4-yl)methanone (2e).

According to the general procedure A, this compound was obtained in (41.7 mg, 0.116 mmol) 77% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



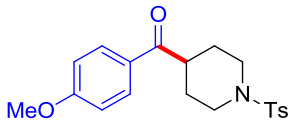
(1-Tosylpiperidin-4-yl)(4-(trifluoromethyl)phenyl)methanone

According to the general procedure A, this compound was obtained in (21.6 mg, 0.053 mmol) 35% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.94 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.77 (dt, *J* = 12.0, 3.4 Hz, 2H),3.20-3.14 (m , 1H), 2.52 (td, *J* = 11.6, 3.1 Hz, 2H), 2.45 (s, 3H), 1.98–1.81 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$):δ200.4, 143.7, 138.3, 134.8, 134.5, 134.3, 134.0, 133.0, 129.7, 128.5, 127.6, 126.7, 125.82, 125.80, 125.77, 125.74, 124.5, 122.3, 120.2, 45.4, 42.6, 27.6, 21.5. HRMS (ESI): calcd for C20H20F3NO3S $[M]^+$ 411.1116, found 411.1091.



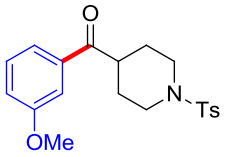
Methyl 4-(1-tosylpiperidine-4-carbonyl)benzoate (2g)

According to the general procedure A, this compound was obtained in (24.1 mg, 0.06 mmol) 40% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ8.07 (d, *J* = 8.5 Hz, 2H) 7.87 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 3.78–3.74 (m, 2H), 3.24-3.18 (m, 1H), 2.51 (td, *J* = 11.5, 3.1 Hz, 2H), 2.44 (s, 3H), 1.98-1.86 (m, 4H), 1.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ201.0, 166.1, 143.7, 138.9, 134.0, 133.0, 130.0, 129.7, 128.0, 127.7, 52.5, 45.5, 42.7, 27.7, 21.6. HRMS (ESI): calcd for $C_{21}H_{23}NO_5S$ $[M]^+$ 401.1297, found 401.1263. m.p. 173-174 °C.



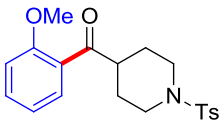
(4-Methoxyphenyl)(1-tosylpiperidin-4-yl)methanone (2h).

According to the general procedure A, this compound was obtained in (44.8 mg, 0.12 mmol) 80% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



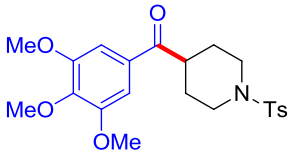
(3-Methoxyphenyl)(1-tosylpiperidin-4-yl)methanone (2i).

According to the general procedure A, this compound was obtained in (44.8 mg, 0.12 mmol) 80% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



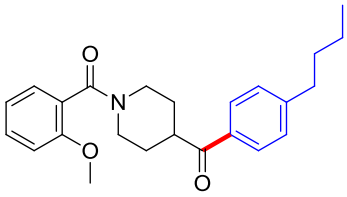
(2-Methoxyphenyl)(1-tosylpiperidin-4-yl)methanone (2j).

According to the general procedure A, this compound was obtained in 53% yield (29.7 mg, 0.080 mmol) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.65 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.44-7.41(m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 3.67 (dt, *J* = 11.9, 4.1 Hz, 2H), 3.12-3.18(m, 1H), 2.49 (td, *J* = 11.4, 2.9 Hz, 2H), 2.44 (s, 3H), 1.93 (dd, *J* = 13.5, 3.9 Hz, 2H), 1.80-1.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ204.4, 157.5, 143.4, 133.4, 133.1, 130.1, 129.6, 127.9, 127.7, 120.9, 111.3, 55.5, 46.7, 45.7, 27.3, 21.5. HRMS (ESI): calcd for $C_{20}H_{23}NO_4S$ $[M]^+$ 373.1348, found 373.1344. m.p. 111–112 °C.



(1-Tosylpiperidin-4-yl)(3,4,5-trimethoxyphenyl)methanone (2k).

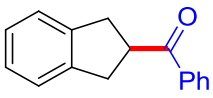
According to the general procedure A, this compound was obtained in 58% yield (37.7 mg, 0.087 mmol as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether).[8]



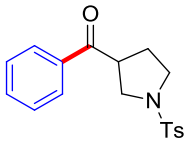
(4-(4-butylbenzoyl)piperidin-1-yl)(2-methoxyphenyl)-methanone (8)

According to the general procedure A, this compound was obtained in (45.5 mg, 0.12 mmol) 80% yield as colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.85 (dd, *J* = 8.3, 3.3 Hz, 2H), 7.33–7.20

(m, 4H), 6.96 (m, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.79–4.71 (m, 1H), 3.82 (d, *J* = 2.5 Hz, 3H), 3.58 (dd, *J* = 13.9, 3.8 Hz, 1H), 3.52–3.44 (m, 1H), 3.18–2.97 (m, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.98 (m, 1H), 1.85–1.69 (m, 3H), 1.62-1.59 (m, 2H), 1.36-1.31 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 201.3, 167.7, 167.6, 155.24, 155.16, 148.88, 148.85, 133.2, 130.22, 130.17, 128.7, 128.3, 127.7, 127.6, 125.9, 125.8, 120.8, 120.7, 110.8, 110.7, 55.5, 55.4, 46.6, 46.0, 43.2, 43.1, 41.11, 41.10, 35.5, 33.1, 28.63, 28.57, 28.52, 28.46 22.2, 13.8. HRMS (ESI): calcd for $C_{24}H_{29}NO_3$ $[M]^+$ 379.2147, found 379.2147.

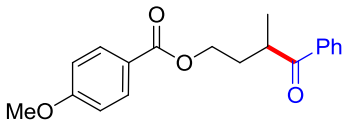


(2,3-Dihydro-1H-inden-2-yl)(phenyl)methanone (9). According to the general procedure A, this compound was obtained in (27.7 mg, 0.125 mmol) 83% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether).[8]



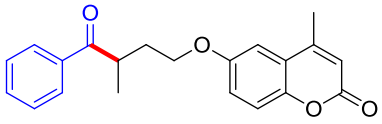
Phenyl(1-tosylpyrrolidin-3-yl)methanone (10)

According to the general procedure A, this compound was obtained in (34.5 mg, 0.105 mmol) 70% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$):δ7.88–7.84 (m, 2H), 7.75–7.70 (m, 2H), 7.60–7.56 (m, 1H), 7.50–7.45 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.93 (p, *J* = 7.7 Hz, 1H), 3.71 (dd, *J* = 10.1, 8.0 Hz, 1H), 3.47 (ddd, *J* = 9.8, 7.6, 6.4 Hz, 1H), 3.38 (dd, *J* = 10.1, 7.3 Hz, 1H), 3.25 (ddd, *J* = 9.9, 8.1, 6.0 Hz, 1H), 2.45 (s, 3H), 2.22–2.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ198.1, 143.6, 135.5, 133.6, 133.2, 129.7, 128.8, 128.3, 127.7, 50.0, 47.5, 45.0, 28.5, 21.5. HRMS (ESI): calcd for $C_{18}H_{19}NO_3S$ $[M]^+$ 329.1086, found 329.1079. m.p. 109–110 °C.



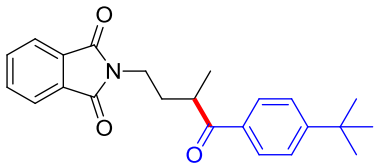
3-Methyl-4-oxo-4-phenylbutyl 4-methoxybenzoate (11)

According to the general procedure A, this compound was obtained in (29.5 mg, 0.0945 mmol) 63% yield as colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). [8]



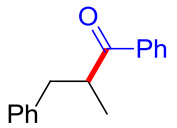
4-Methyl-6-(3-methyl-4-oxo-4-phenylbutoxy)-2H-chromen-2-one (12)

According to the general procedure A, this compound was obtained in (23.2 mg, 0.069 mmol) 46% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.98–7.97 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.43 (m, 3H), 6.77 (dd, *J* = 6.3, 2.5 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H),6.10 (q, *J* = 1.2 Hz, 1H), 4.09 (ddd, *J* = 9.5, 6.8, 5.4 Hz, 1H), 4.02 (ddd, *J* = 9.5, 6.9, 5.3 Hz, 1H), 3.83–3.76 (m, 1H), 2.42–2.38 (m, 1H), 2.36 (d, *J* = 1.3 Hz, 1H), 1.96 (ddt, *J* = 14.3, 6.9, 5.6 Hz, 1H), 1.28 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ203.4, 161.7, 161.2, 155.1, 152.4, 136.2, 133.0, 128.6, 128.2, 125.4, 113.5, 112.1, 111.9, 101.5, 66.2, 37.1, 32.5, 18.6, 17.8. HRMS (ESI): calcd for $C_{21}H_{20}O_4$ $[M]^+$ 336.1362, found 336.1335. m.p. 127–128 ^oC.



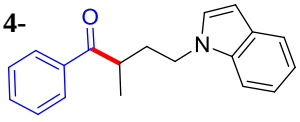
2-(4-(4-(*tert*-Butyl)phenyl)-3-methyl-4-oxobutyl)isoindoline-1,3-dione (13)

According to the general procedure A, this compound was obtained in (21.8 mg, 0.06 mmol) 40% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether).[8]



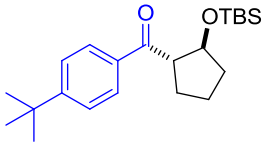
2-Methyl-1,3-diphenylpropan-1-one(1a)henyl(1-tosylpyrrolidin-3-yl)methanone (14)

According to the general procedure A, this compound was obtained in (24.9 mg, 0.111 mmol) 74% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether). [8]

4-  **(1*H*-Indol-1-yl)-2-methyl-1-phenylbutan-1-one (15)**

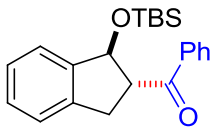
According to the general procedure A, this compound was obtained in (45.7 mg, 0.165 mmol) 55% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$):δ7.81–7.76 (m, 2H), 7.67 (d, *J* = 7.65Hz, 1H), 7.56–7.53 (m, 1H), 7.42–7.39 (t, *J* = 7.74, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.18 (dt, *J* = 8.1, 7.0, 1.2Hz, 1H),7.12 (dt, *J* = 7.9, 7.0, 1.0Hz, 1H),

7.03 (d, *J* = 3.1 Hz, 1H), 6.51 (d, *J* = 3.1 Hz, 1H), 4.26–4.13 (m, 2H), 3.36–3.29 (m, 1H), 2.50–2.43 (m, 1H), 2.00-1.92 (m, 1H), 1.24 (d, *J* =7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$):δ203.1, 135.84, 135.80, 133.0, 128.60, 128.57, 128.2, 127.8, 121.5, 120.9, 119.3, 109.4, 101.2, 44.1, 37.6, 33.4, 17.8. HRMS (ESI): calcd for $C_{19}H_{19}NO$ $[M]^+$ 277.1467, found 277.1455.



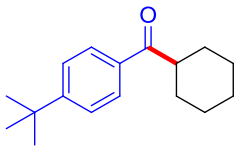
(2-(*tert*-Butyldimethylsilyloxy)cyclopentyl)(4-*tert*-butylphenyl)methanone (16).

According to the general procedure A, this compound was obtained in (52.4 mg, 0.146 mmol) 97% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether).[8]



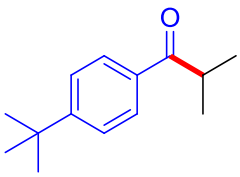
(1-((*tert*-Butyldimethylsilyl)oxy)-2,3-dihydro-1H-inden-2-yl)(phenyl)methanone (17).

According to the general procedure A, this compound was obtained in (45.5 mg, 0.129 mmol) 86% yield as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether).[8]



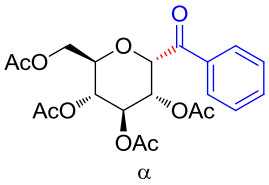
(4-*tert*-Butylphenyl)(cyclohexyl)methanone (18).

According to the general procedure B, this compound was obtained in (32.3 mg, 0.132 mmol) 88% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether).[8]



1-(4-*tert*-Butylphenyl)-2-methylpropan-1-one (19).

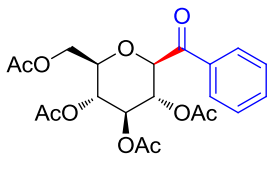
According to the general procedure B, this compound was obtained in (16.9 mg, 0.0825 mmol) 55% yield as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether). [9]



α

(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-benzoyltetrahydro-2H-pyran-3,4,5-triyl triacetate (α-21).

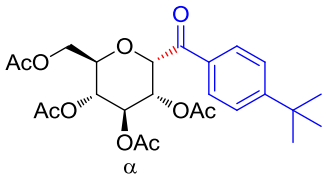
According to the general procedure C, this compound was obtained in (117.7 mg, 0.27 mmol) 90% yield and ratio of α to β (3.4:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.94–7.92 (m, 2H), 7.59(t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.87 (t, *J* = 9.4 Hz, 1H), 5.59 (d, *J* = 6.4 Hz, 1H), 5.25 (dd, *J* = 9.8, 6.3 Hz, 1H), 5.06 (t, *J* = 9.2 Hz, 1H), 4.21–4.17 (m, 2H), 3.99 (dd, *J* = 13.9, 3.9 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H) 1.96 (s, 3H), 1.78 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ195.9, 170.4, 170.1, 169.8, 169.6, 135.7, 134.0, 128.7, 128.6, 71.9, 71.2, 70.2, 69.3, 68.4, 61.9, 20.6, 20.5, 20.3. HRMS (ESI): calcd for $C_{21}H_{24}O_{10}$ $[M]^+$ 436.1369, found 436.1369.



β

(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-benzoyltetrahydro-2H-pyran-3,4,5-triyl triacetate (β-21).

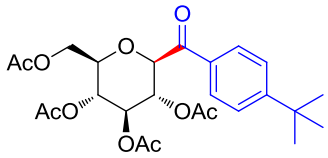
^{1}H NMR (500 MHz, $CDCl_3$): δ7.99–7.97 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 5.50 (t, *J* = 9.6 Hz, 1H), 5.36 (t, *J* = 9.4 Hz, 1H), 5.16 (t, *J* = 9.7 Hz, 1H), 4.75 (d, *J* = 9.8 Hz, 1H), 4.24 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.15 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.91 (ddd, *J* = 10.0, 5.6, 2.3 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H) 2.02 (s, 3H), 1.84 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ191.9, 170.52, 170.47, 169.4, 168.9, 134.9, 134.0, 129.3, 128.6, 77.7, 76.7, 74.2, 68.9, 68.2, 62.3, 20.69, 20.64, 20.58, 20.4. HRMS (ESI): calcd for $C_{21}H_{24}O_{10}$ $[M]^+$ 436.1369, found 436.1368. m.p. 127-128°C.



α

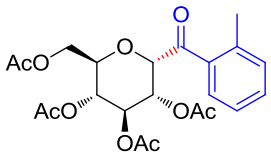
(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-(tert-butyl)benzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-22).

According to the general procedure C, this compound was obtained in (122.6 mg, 0.249 mmol) 83% yield and ratio of α to β (2.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.90 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 5.93 (t, *J* = 9.4 Hz, 1H), 5.60 (d, *J* = 6.3 Hz, 1H), 5.29–5.24 (m, 1H), 5.09 (t, *J* = 9.3 Hz, 1H), 4.22–4.18 (m, 2H), 4.00 (dd, *J* = 13.8, 3.4 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ195.3, 170.5, 170.2, 169.9, 169.7, 158.0, 133.2, 128.7, 125.8, 71.9, 71.2, 70.4 , 69.4 , 68.5 , 61.9 , 35.2, 31.04 , 30.95, 20.69, 20.61, 20.60, 20.4. HRMS (ESI): calcd for $C_{25}H_{32}O_{10}$ $[M]^+$ 492.1995, found 492.1994. m.p. 139–140 °C.



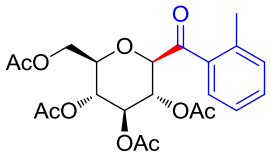
β

(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-(tert-butyl)benzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-22). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.91 (d, *J* 8.5, 2H), 7.48 (d, *J* = 8.4 Hz, 2 H), 5.49 (t, *J* = 9.6 Hz, 1H), 5.35 (t, *J* = 9.4 Hz, 1H), 5.15 (t, *J* = 9.7 Hz, 1H), 4.73 (d, *J* = 9.9 Hz, 1H), 4.24 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.14 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.90 (ddd, *J* = 10.1, 5.5, 2.4 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.82 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ191.3, 170.52, 170.47, 169.3, 168.9, 157.9, 132.3, 129.2, 125.5, 77.6, 76.6, 74.2, 68.9, 68.2, 62.2, 35.2, 31.0, 29.6, 20.66, 20.62, 20.56, 20.4. HRMS (ESI): calcd for $C_{25}H_{32}O_{10}$ $[M]^+$ 492.1995, found 492.1993. m.p. 128-129 °C.



α

(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-(2-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-23). According to the general procedure C, this compound was obtained in (102.6 mg, 0.228 mmol) 76% yield and ratio of α to β (1.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.55 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 8.1 Hz, 2H), 5.75 (t, *J* = 9.3 Hz, 1H), 5.51 (d, *J* = 6.7 Hz, 1H), 5.19 (dd, *J* = 9.8, 6.7 Hz, 1H), 5.09 (t, *J* = 9.4 Hz, 1H), 4.61 (ddd, *J* = 10.0, 4.8, 2.2 Hz, 1H), 4.25 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.10 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.51 (s, 3H), 2.05 (s, 6H), 2.02 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ201.1, 170.6, 169.82, 169.79, 169.6, 138.5, 137.2, 132.0, 128.5, 125.8, 72.8, 71.9, 70.1, 69.6, 68.3, 62.0, 20.8, 20.68, 20.67, 20.62, 20.0. HRMS (ESI):calcd for $C_{22}H_{26}O_{10}$ $[M]^+$ 450.1526, found 450.1526. m.p. 122–123 °C.

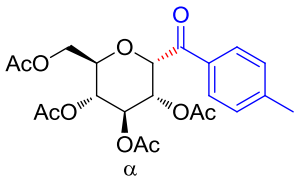


β

(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-(2-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-23). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.70 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 9.4 Hz, 2H), 5.40 (t, *J* = 9.6 Hz, 1H), 5.31 (t, *J* = 9.4 Hz, 1H), 5.12 (t, *J* = 9.7 Hz, 1H), 4.70 (d, *J* = 9.8 Hz, 1H), 4.21 (dd, *J* = 12.3, 6.1 Hz, 1H), 4.12 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.84 (ddd, *J* = 10.1, 5.5, 2.4 Hz, 2H), 2.45 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ194.9, 170.5, 170.4, 169.3, 168.9, 140.0, 135.2, 132.2, 132.1, 129.4, 125.4, 78.3, 76.4, 74.2, 69.1, 68.2, 62.2, 21.3, 20.63, 20.58, 20.53, 20.2. HRMS (ESI):calcd for $C_{22}H_{26}O_{10}$ $[M]^+$ 450.1526, found 450.1526.

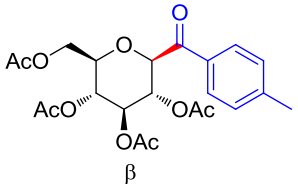
m.p. 109-110 °C

(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl



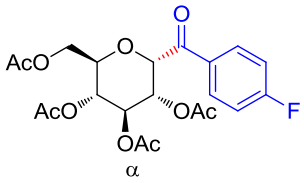
triacetate (α-24).

According to the general procedure C, this compound was obtained in (112.1 mg, 0.249 mmol) 83% yield and ratio of α to β (3.2:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.83 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.89 (t, *J* = 9.3 Hz, 1H), 5.57 (d, *J* = 6.3 Hz,) 1H, 5.24 (dd, *J* = 9.8, 6.4 Hz, 1H), 5.06 (t, *J* = 9.3 Hz, 1H), 4.21–4.15 (m, 2H), 4.00–3.96 (m, 1H), 2.39 (s, 3H), 2.00 (s, 3H) 1.99 (s, 3H), 1.97 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ195.3, 170.4, 170.1, 169.8, 169.6, 145.1, 133.2, 129.4, 128.8, 71.8, 71.0, 70.3, 69.3, 68.5, 61.8, 21.6, 20.6, 20.5, 20.4. HRMS (ESI): calcd for $C_{22}H_{26}O_{10}$ $[M]^+$ 450.1526, found 450.1522.



(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-24).

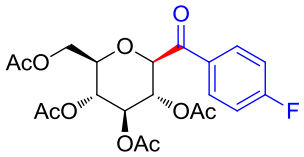
^{1}H NMR (500 MHz, $CDCl_3$): δ7.87 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.48 (t, *J* = 9.6 Hz, 1H), 5.34 (t, *J* = 9.4 Hz, 1H), 5.15 (t, *J* = 9.7 Hz, 1H), 4.71 (d, *J* = 9.8 Hz, 1H), 4.23 (dd, *J* = 12.5, 5.7 Hz, 1H), 4.14 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.89 (ddd, *J* = 10.1, 5.5, 2.4 Hz, 2H), 2.41 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ191.4, 170.52, 170.45, 169.3, 168.9, 145.0, 132.4, 129.4, 129.3, 77.7, 76.6, 74.2, 68.9, 68.2, 62.2, 21.7, 20.68, 20.62, 20.56, 20.4. HRMS (ESI): calcd for $C_{22}H_{26}O_{10}$ $[M]^+$ 450.1526, found 450.1523. m.p. 108-109 °C.



(*2R,3R,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-fluorobenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-25).

According to the general procedure C, this compound was obtained in (113.1 mg, 0.249 mmol) 83% yield and ratio of α to β (3.4:1) as a white solid. Purification of the crude material was performed by column chromatography. (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ8.01–7.98 (m, 2H), 7.13(t, *J* = 8.6 Hz, 2H), 5.88 (t, *J* = 9.2 Hz, 1H), 5.54 (d, *J* = 6.3 Hz, 1H), 5.23 (dd, *J* = 9.6, 6.2 Hz, 1H), 5.06 (t, *J* = 9.4 Hz, 1H), 4.18 (dd, *J* = 12.4, 4.9 Hz, 1H), 4.10 (ddd, *J* = 9.9, 4.9, 2.2 Hz, 1H), 3.98 (dd, *J* = 12.4, 2.3 Hz, 1H), 2.03 (s, 6H), 1.97 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ194.0, 170.4, 170.1, 169.8, 169.6, 167.2 , 165.1, 131.99, 131.97, 131.63, 131.55, 116.0, 115.9, 72.0, 71.3, 70.1, 69.3, 68.4, 61.8, 20.61, 20.58, 20.52, 20.4. HRMS (ESI): calcd for $C_{21}H_{23}FO_{10}$ $[M]^+$ 454.1275, found 454.1274. m.p. 88–89°C.

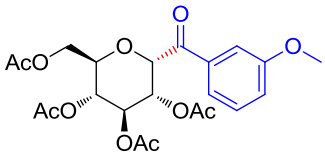
(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-fluorobenzoyl)tetrahydro-2H-pyran-3,4,5-triyl



β

triacetate (β-25).

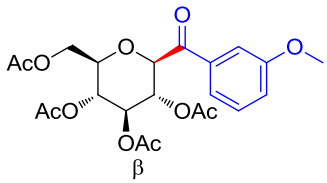
^{1}H NMR (500 MHz, $CDCl_3$): δ8.04–8.01 (m, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 5.47 (t, *J* = 9.6 Hz, 1H), 5.34 (t, *J* = 9.4 Hz, 1H), 5.15 (t, *J* = 9.7 Hz, 1H), 4.67 (d, *J* = 9.9 Hz, 1H), 4.23 (dd, *J* = 12.5, 5.4 Hz, 1H), 4.15 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.90 (ddd, *J* = 10.1, 5.6, 2.4 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ190.4, 170.44, 170.40, 169.3, 168.9 , 167.2, 165.1, 132.13, 132.06, 131.20, 131.17, 115.9, 115.7, 78.1, 76.7, 74.0, 68.8, 68.1, 62.2, 20.66, 20.60, 20.5, 20.4.HRMS (ESI): calcd for $C_{21}H_{23}FO_{10}$ $[M]^+$ 454.1275, found 454.1274. m.p. 128-129 °C.



α

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-(3-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-26).

According to the general procedure C, this compound was obtained in (111.9 mg, 0.24 mmol) 80% yield and ratio of α to β (3.7:1). as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.51 (d, *J* = 7.8 Hz, 1H), 7.47 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.14 (dd, *J* = 8.2, 2.2 Hz, 1H) 5.89 (t, *J* = 9.4 Hz, 1H), 5.59 (d, *J* = 6.4 Hz, 1H), 5.29–5.24 (m, 1H), 5.07 (t, *J* = 9.4 Hz, 1H), 4.24–4.19 (m, 2H), 4.02 (dd, *J* = 14.1, 4.0 Hz, 1H), 3.84 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ195.8, 170.5, 170.1, 169.8, 169.6, 159.9, 137.0, 129.8, 121.3, 120.8, 112.5, 72.0, 71.3, 70.3, 69.3, 68.5, 61.9, 55.4, 20.7, 20.6, 20.4. HRMS (ESI): calcd for $C_{22}H_{26}O_{11}$ $[M]^+$ 466.1475, found 466.1474.



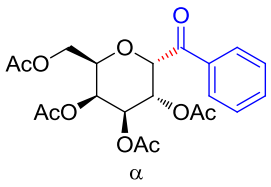
β

(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(3-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-26).

^{1}H NMR (500 MHz, $CDCl_3$): δ7.56 (d, *J* 7.6 Hz, 1H), 7.5 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.49 (t, *J* = 9.6 Hz, 1H), 5.35 (t, *J* = 9.4 Hz, 1H), 5.15 (t, *J* = 9.4 Hz, 1H), 4.72 (d, *J* = 9.8 Hz, 1H), 4.22 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.14 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.91 (ddd, *J* = 10.0, 5.6, 2.3 Hz, 1H), 3.84 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ191.6, 170.6, 170.5, 169.4 , 168.9, 159.8, 136.1, 129.5, 121.8, 120.3, 113.7, 77.7, 76.7, 74.2, 68.9, 68.2, 62.2, 55.4, 20.63, 20.57, 20.4. HRMS (ESI): calcd for $C_{22}H_{26}O_{11}$ $[M]^+$ 466.1475, found 466.1474.

m.p. 103-104 °C.

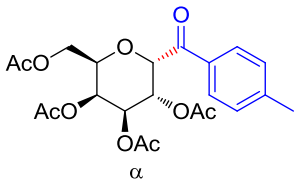
(*2R,3S,4S,5R,6S*)-2-(Acetoxymethyl)-6-benzoyltetrahydro-2H-pyran-3,4,5-triyl triacetate (α-



α

27).

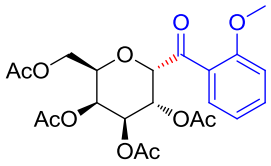
According to the general procedure C, this compound was obtained in (109.9 mg, 0.252 mmol) 84% yield and ratio of α to β (4.5:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.91 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* =7.8 Hz, 2H), 5.75 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.68 (d, *J* = 6.4 Hz, 1H), 5.53–5.48 (m, 2H), 4.52 (ddd, *J* = 7.2, 5.8, 1.7 Hz, 1H), 4.07 (qd, *J* = 11.5, 6.4 Hz, 2H), 2.15 (s, 3H), 1.99 (s, 3H), 1.90 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ196.5, 170.3, 170.0, 169.7, 136.1, 133.9, 128.7, 128.6, 71.2, 71.0, 67.9, 67.7, 66.8, 61.7, 20.63, 20.58, 20.5, 20.4. HRMS (ESI):calcd for $C_{21}H_{24}O_{10}$ $[M]^+$ 436.1369, found 436.1367. m.p. 102–103 °C.



α

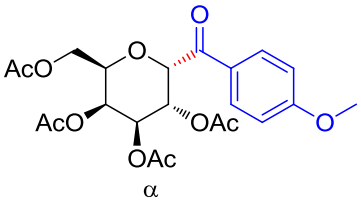
(*2R,3S,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-methylbenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-28).

According to the general procedure C, this compound was obtained in (121.5 mg, 0.27 mmol) 90% yield and ratio of α to β (4.2:1). Colorless oil. Purification by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.80 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.75 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.63 (d, *J* = 6.4 Hz, 1H), 5.51–5.45 (m, 2H), 4.50 (td, *J* = 6.5, 1.8 Hz, 1H), 4.08–4.00 (m, 2H), 2.39 (s, 3H), 2.13 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ195.9, 170.29, 170.26, 170.0, 169.6, 144.9, 133.5, 129.4, 128.7, 71.0, 70.9, 67.8 , 67.7, 66.8, 61.6, 21.6, 20.57, 20.52, 20.44, 20.39. HRMS (ESI):calcd for $C_{22}H_{26}O_{10}$ $[M]^+$ 450.1526, found 450.1525.



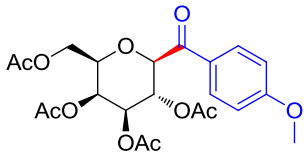
(*2R,3S,4S,5R,6S*)-2-(Acetoxymethyl)-6-(2-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-29).

According to the general procedure C, this compound was obtained in (90.9 mg, 0.195 mmol) 65% yield and ratio of α to β (4.5:1) as a colorless oil. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.58 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.9, 7.4, 1.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.83 (d, *J* = 6.6 Hz, 1H), 5.59 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.52–5.49 (m, 2H), 4.68 (td, *J* = 6.5, 2.0 Hz, 1H), 4.12–4.03 (m, 2H), 3.85 (s, 3H), 2.12 (s, 3H), 1.98 (s, 3H), 1.76 (s, 3H,) 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ199.5, 170.4, 170.0, 169.9, 169.7, 158.2, 134.3, 130.6, 127.6, 121.0, 111.5, 74.0, 70.8, 68.1, 67.9, 66.6, 61.7, 55.6, 20.64, 20.60, 20.58, 20.3. HRMS (ESI): calcd for $C_{22}H_{26}O_{11}$ $[M]^+$ 466.1475, found 466.1472.


α

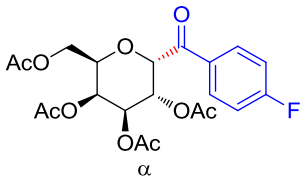
(*2R,3S,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-30).

According to the general procedure C, this compound was obtained in (104.9 mg, 0.225 mmol) 75% yield and ratio of α to β (3.6:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.92–7.90 (m, 2H), 6.93–6.91 (m, 2H), 5.79 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.62 (d, *J* = 6.4 Hz, 1H), 5.50 (dd, *J* = 3.4, 1.5 Hz, 1H) , 5.46 (dd, *J* = 10.1, 6.3 Hz, 1H), 4.50 (td, *J* = 6.4, 1.7 Hz, 1H), 4.08–4.00 (m, 2H), 3.85 (s, 3H), 2.13 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ194.5, 170.4, 170.3, 170.0, 169.7, 164.1, 132.2, 131.1, 128.9, 113.9, 70.8, 67.9, 67.7, 66.9, 61.7, 55.5, 20.6, 20.55, 20.50, 20.48. HRMS (ESI): calcd for $C_{22}H_{26}O_{11}$ $[M]^+$ 466.1475, found 466.1477. m.p. 145–146 °C


β

(*2R,3S,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-methoxybenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (β-30).

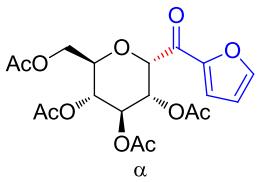
^{1}H NMR (500 MHz, $CDCl_3$): δ8.02–8.00 (m, 2H), 6.95–6.93 (m, 2H), 5.67 (t, *J* = 10.0 Hz, 1H), 5.50 (d, *J* = 3.3 Hz, 1H), 5.19 (dd, *J* = 10.1, 3.4 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.16–4.08 (m, 2H), 3.88 (s, 3H), 2.19 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ194.5, 170.4, 170.3, 170.1, 169.7, 164.1, 132.2, 131.1, 129.0, 113.9, 70.9, 67.9, 67.8, 66.9, 61.7, 55.5, 20.6, 20.55, 20.51, 20.48. HRMS (ESI): calcd for $C_{22}H_{26}O_{11}$ $[M]^+$ 466.1475, found 466.1474.


α

(*2R,3S,4S,5R,6S*)-2-(Acetoxymethyl)-6-(4-fluorobenzoyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (α-31).

According to the general procedure C, this compound was obtained in (110.4 mg, 0.243 mmol) 81% yield and ratio of α to β (5.8:1) as a white solid. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.98–7.95 (m, 2H), 7.13 (t, *J* = 8.5 Hz, 2H), 5.74 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.60 (d, *J* = 6.2 Hz, 1H), 5.50–5.45 (m, 2H), 4.40 ((td, *J* = 6.2, 1.6 Hz, 1H), 4.11–3.98 (m, 2H), 2.13 (s, 3H), 1.98 (s, 3H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ194.6, 170.34, 170.3, 170.0, 169.7, 167.2, 165.1, 132.34, 132.31,

131.64, 131.57, 116.0, 115.9, 71.4, 71.1, 67.8, 67.7, 66.9, 61.6, 20.65, 20.60, 20.54, 20.51. HRMS (ESI): calcd for $C_{21}H_{23}FO_{10}$ $[M]^+$ 454.1275, found 454.1271. m.p. 107–108 °C.



α

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

Following the general procedure C except that $Ni(ClO_4)_2$ (20 mol%), 4b (20 mol%) and furan-2-carbonyl chloride (150 mol%) were used. Purification of the crude material was performed by column chromatography (SiO_2: 30% ethyl acetate in petroleum ether). The yield of the title compound was estimated to be 25% (for α product only) due to inseparable impurities using trimehtyl(phenyl)silane as the internal standard. For the same reason, the ratio of α to β was not determined. ^{1}H NMR (500 MHz, Chloroform-*d*) for the α anomer: δ 7.65 (s, 1H), 7.31 (d, *J* = 14.0 Hz, 1H), 6.58(s, 1H), 5.79 (t, *J* = 9.2 Hz, 1H), 5.42 (d, *J* = 6.6 Hz, 1H), 5.30 (t, *J* = 8.0 Hz, 1H), 5.09 (t, *J* = 9.3 Hz, 1H), 4.57-4.55 (m, 1H), 4.27 (dd, *J* = 25.9, 9.0 Hz, 1H), 4.22 (dd, *J* = 4.6 Hz, 1H), 4.08 (d, *J* = 12.6 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H),2.02(s, 3H), 1.83 (s, 3H), 1.25 (s, 3H).

References

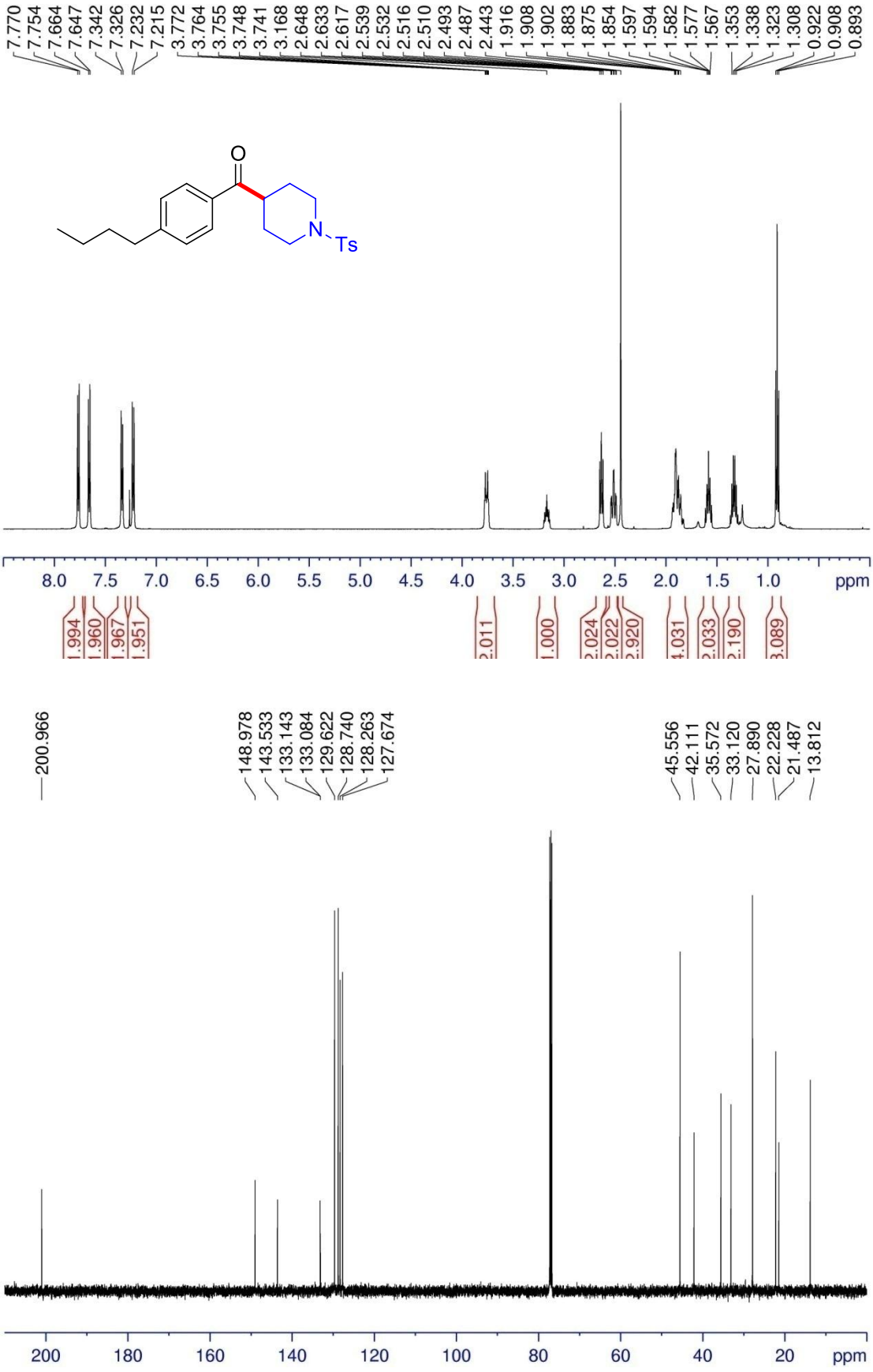
(1) Battilocchio, C.; Baumann, M.; Baxendale, IR.; Kitching, MO.; Ley, S. V.; Tappin, N. D. C.; Biava, M. *Synthesis*. **2012**, *44*, 635.

(2) Redlich, M.; Hossain, M. M. *Tetrahedron Letters*. **2004**, *45*, 8987–8990.

(3) (a) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics*. **1991**, *10*, 500. (b)

Nishiyama, H.; Soeda, N.; Naito, T.; Motoyama, Y. *Tetrahedron Asymm.* **1998**, *9*, 2865. (c) Müller, P.; Chappellet, S. *Helv. Chim. Acta* . **2005**, *88*, 1010.
(4) Kawashima, T.; Takao, T.; Suzuki, H. *J. Am. Chem. Soc.* **2007**, *129*, 11006.
(5) De Crisci, A.; Chung, K.; Oliver, A.; Waymouth, R. *Organometallics*. **2013**, *32*, 2257.
(6) Bandgar, B. P.; Pandit, S. S. *Tetrahedron Letters.* **2003**, *44*, 2331.
(7) (a) Bartoli, G.; Bosco, M.; Carlone, A. *Synthesis* **2007**, *22*, 3489. (b) Cirriez, V.; Rasson, C.; Riant, O. *Adv. Synth. Catal*. **2013**, *355*, 3137.
(8) (a) Yin, H.; Zhao, C.; You, H.; Lin, K.; Gong, H. G.*Chem. Commun*. **2012**, *48*, 7034–7036. (b) Wu, F.; Lu, W.; Qian, Q.; Ren, Q.; Gong, H. G. *Org. Lett*. **2012**, *14*, 3044-3047.
(9) Kondo, T. *J. Org. Chem.* 1990, *55*, 1286.

Spectral Data for New Compounds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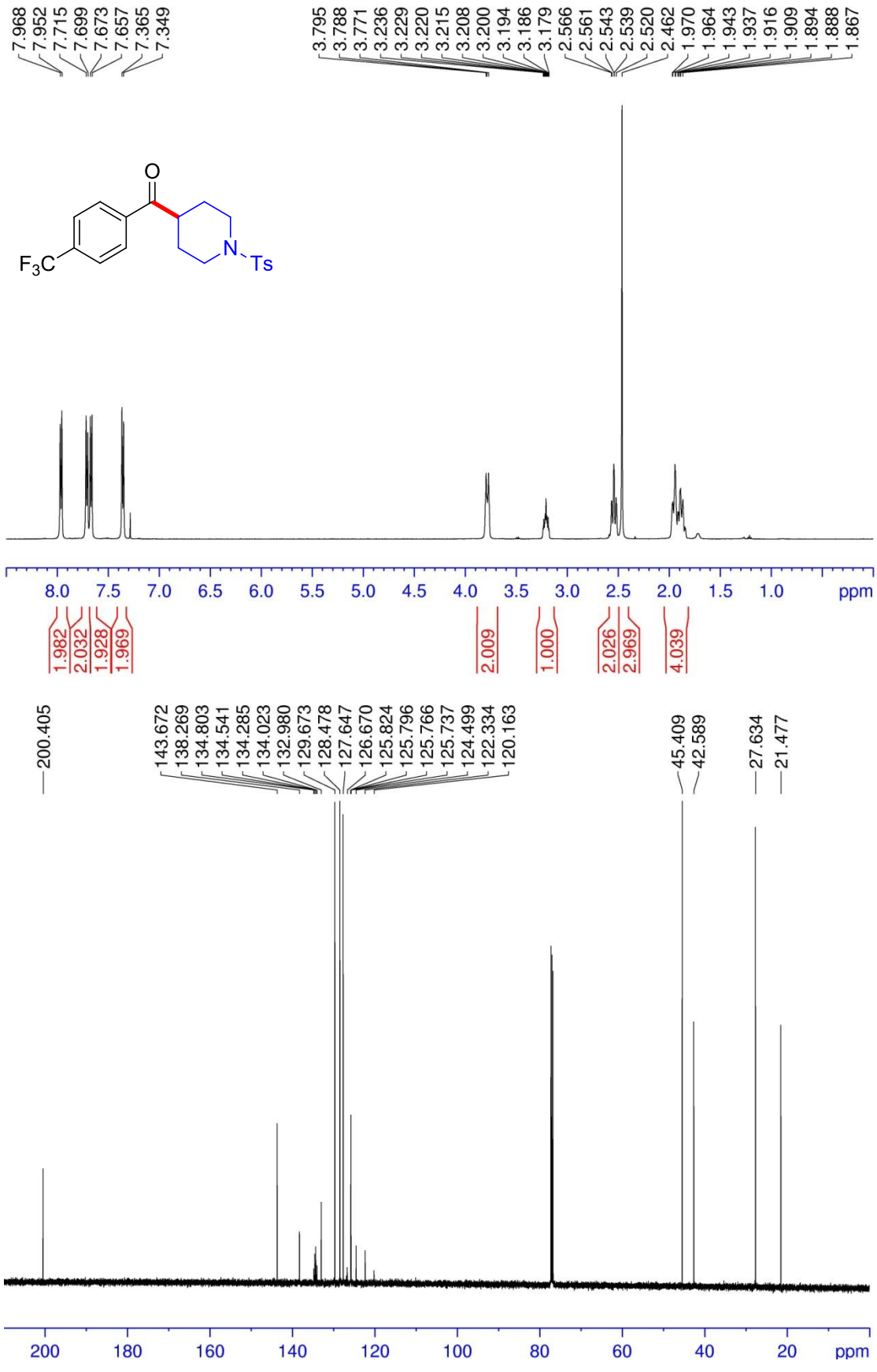
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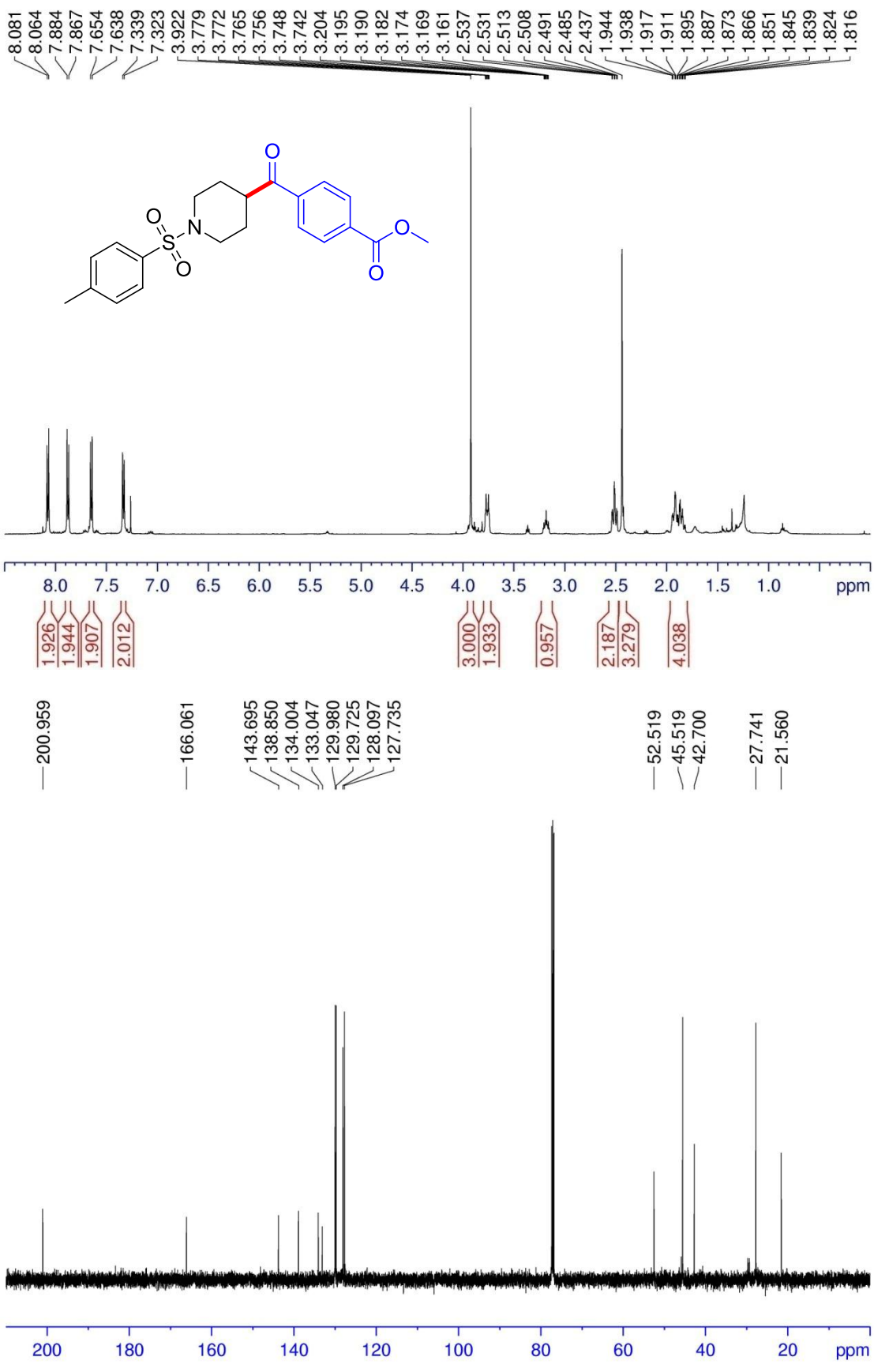
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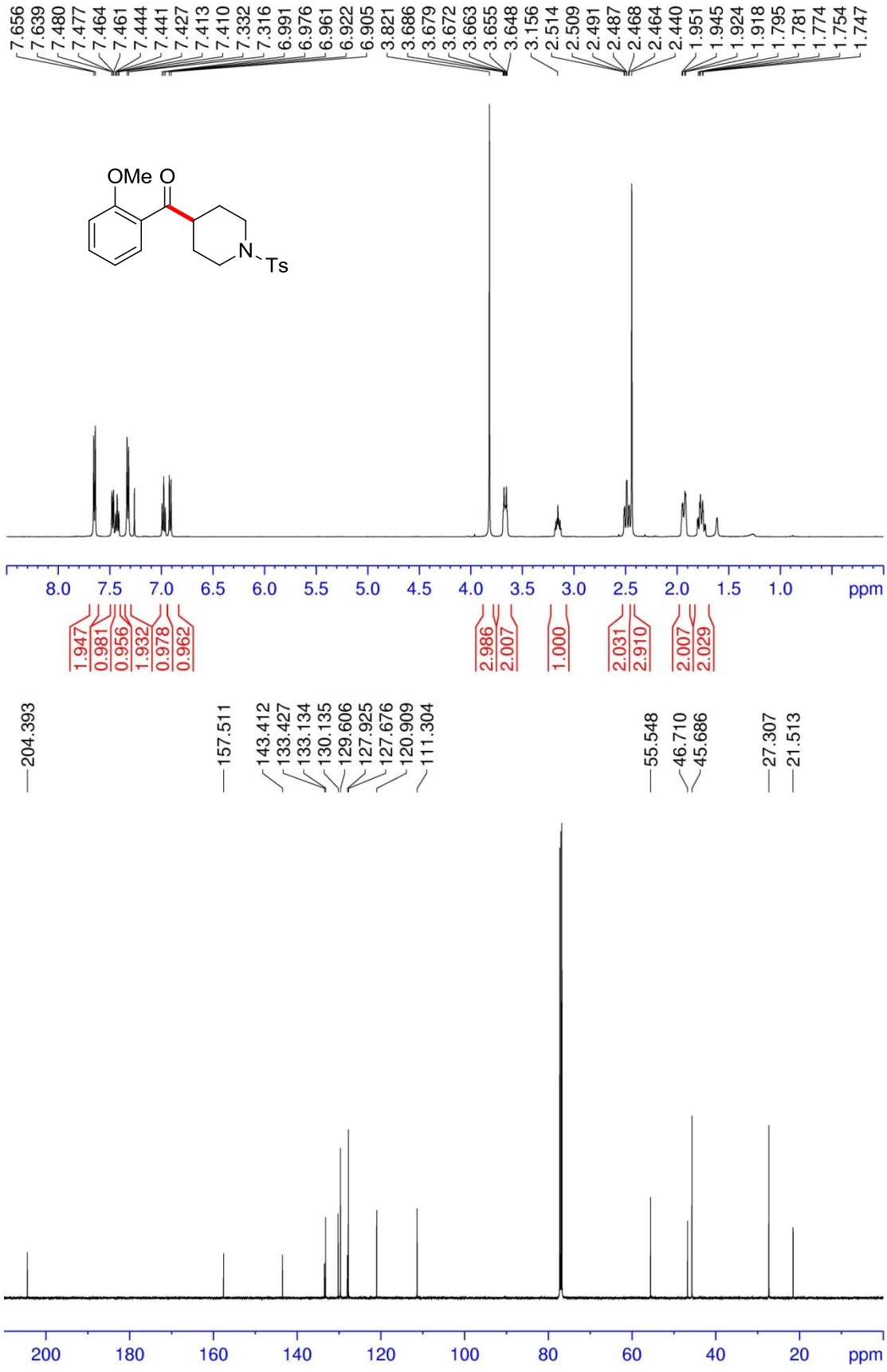
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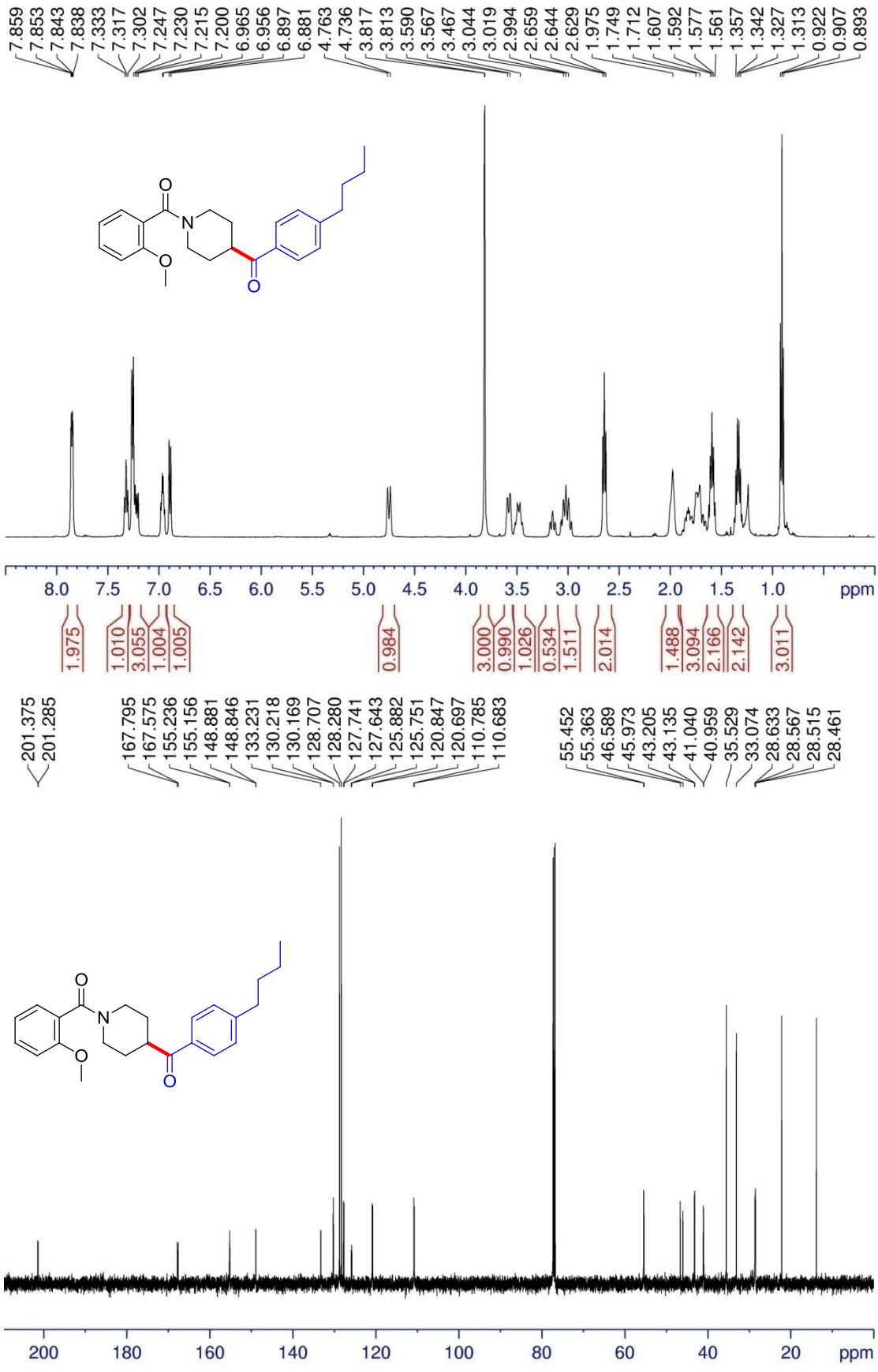
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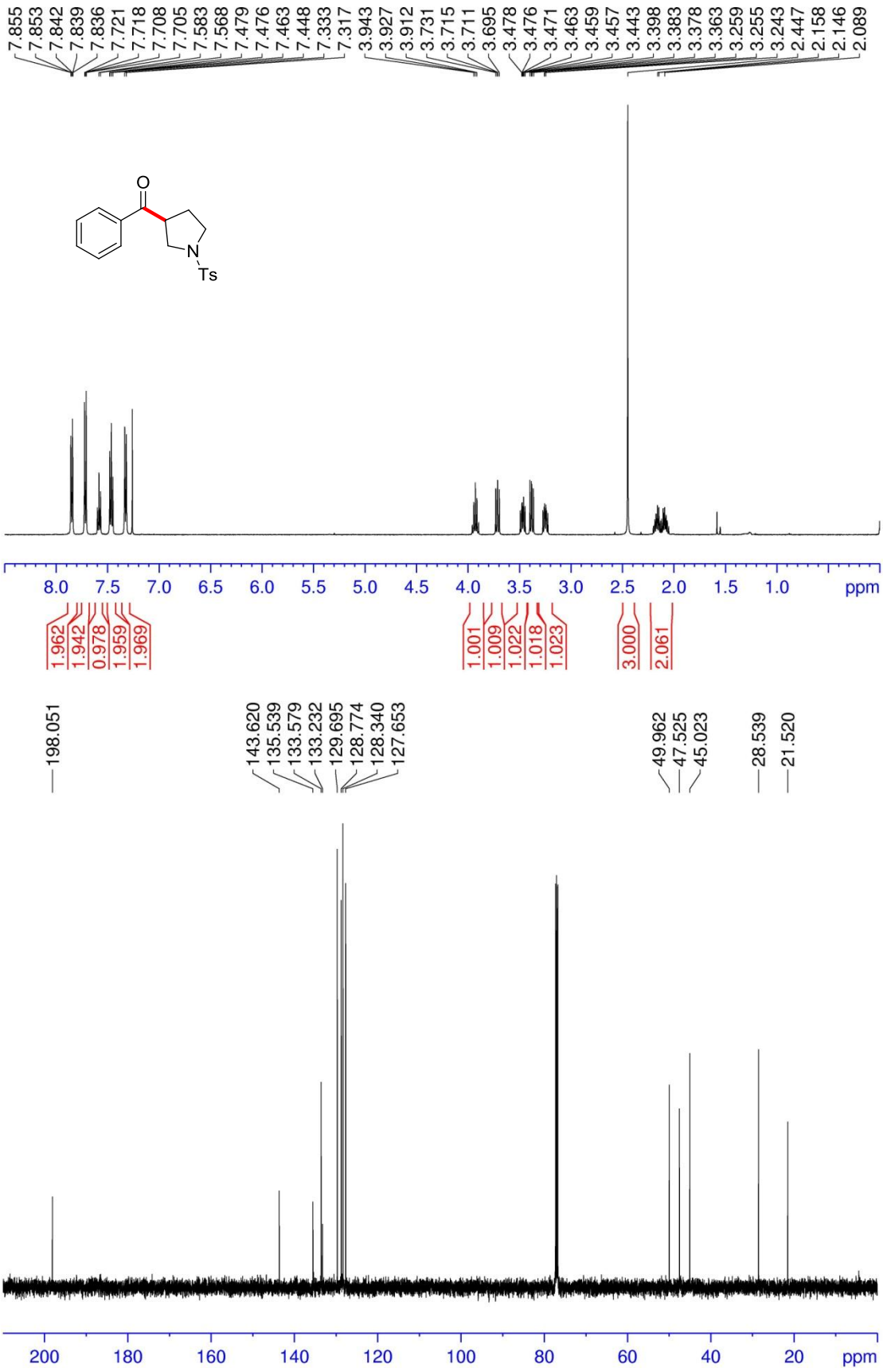
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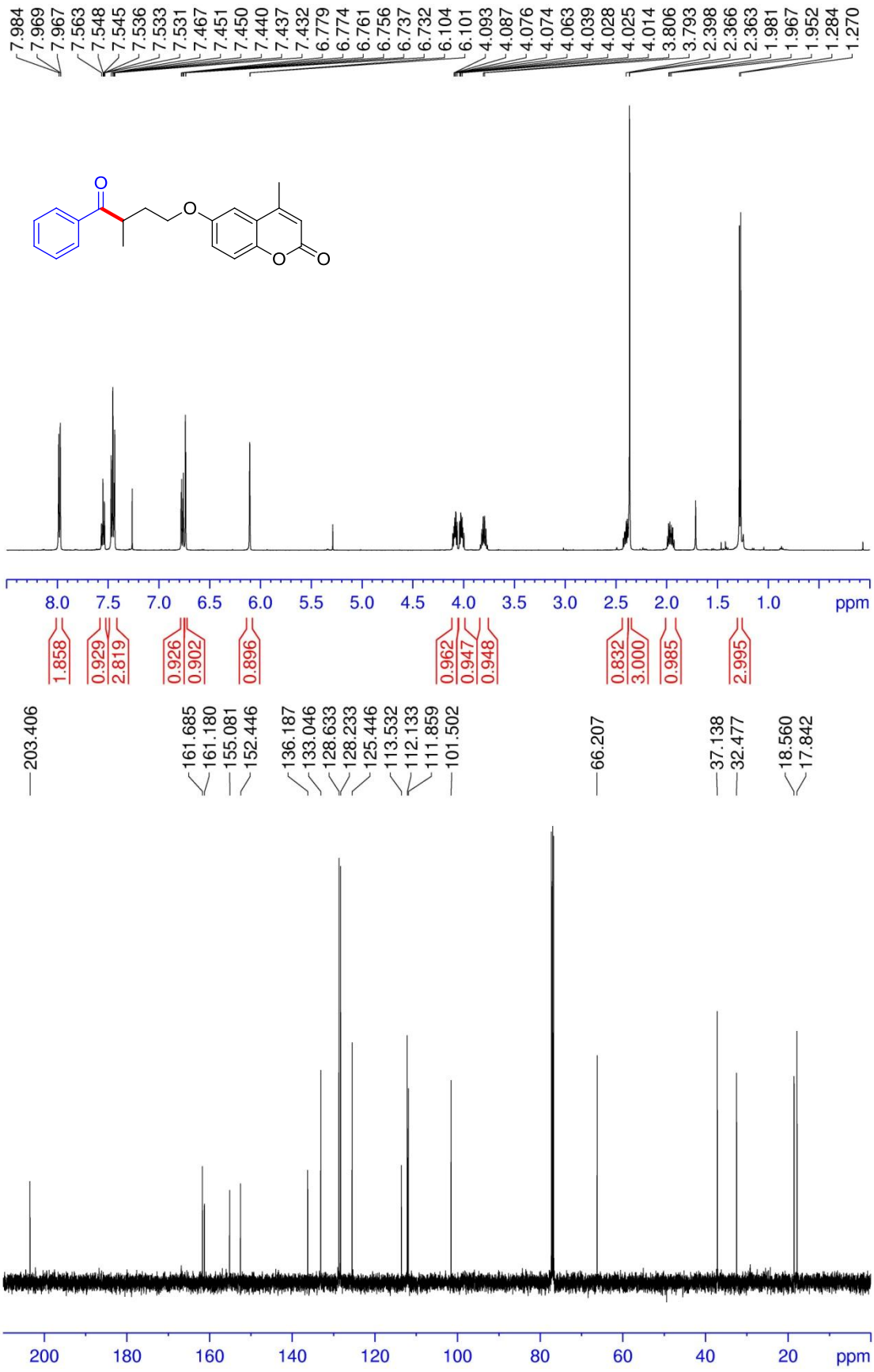
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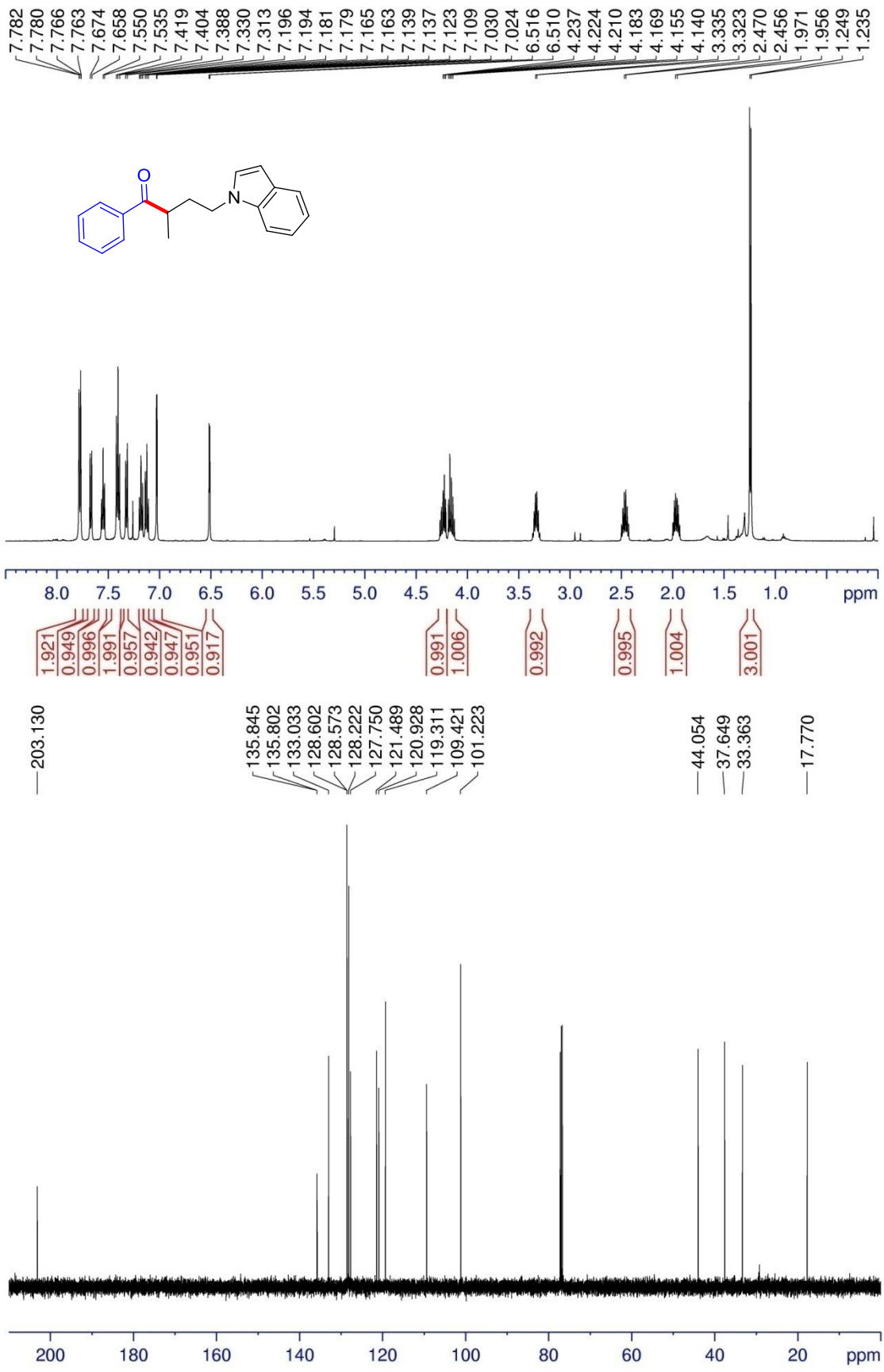
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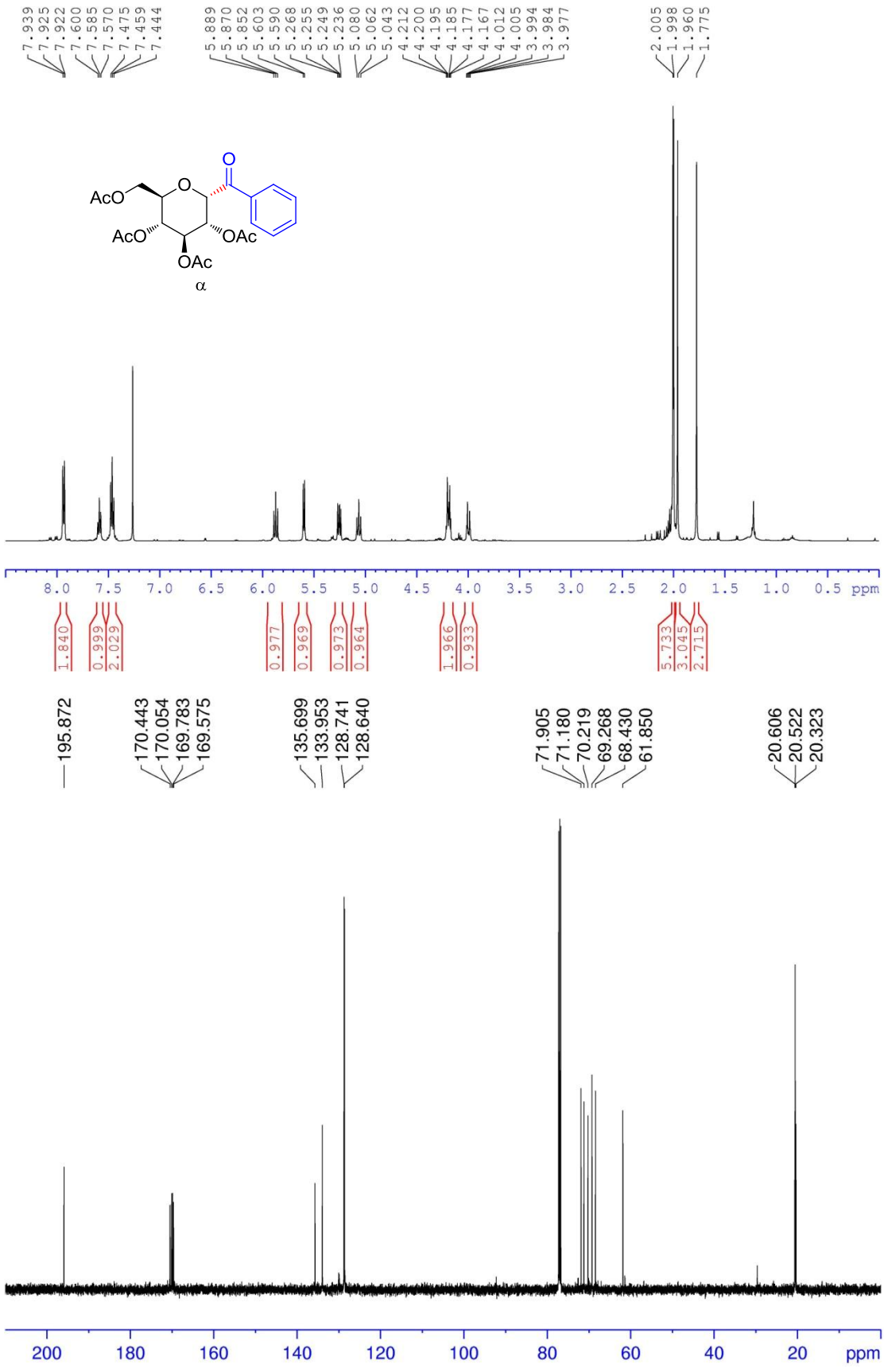
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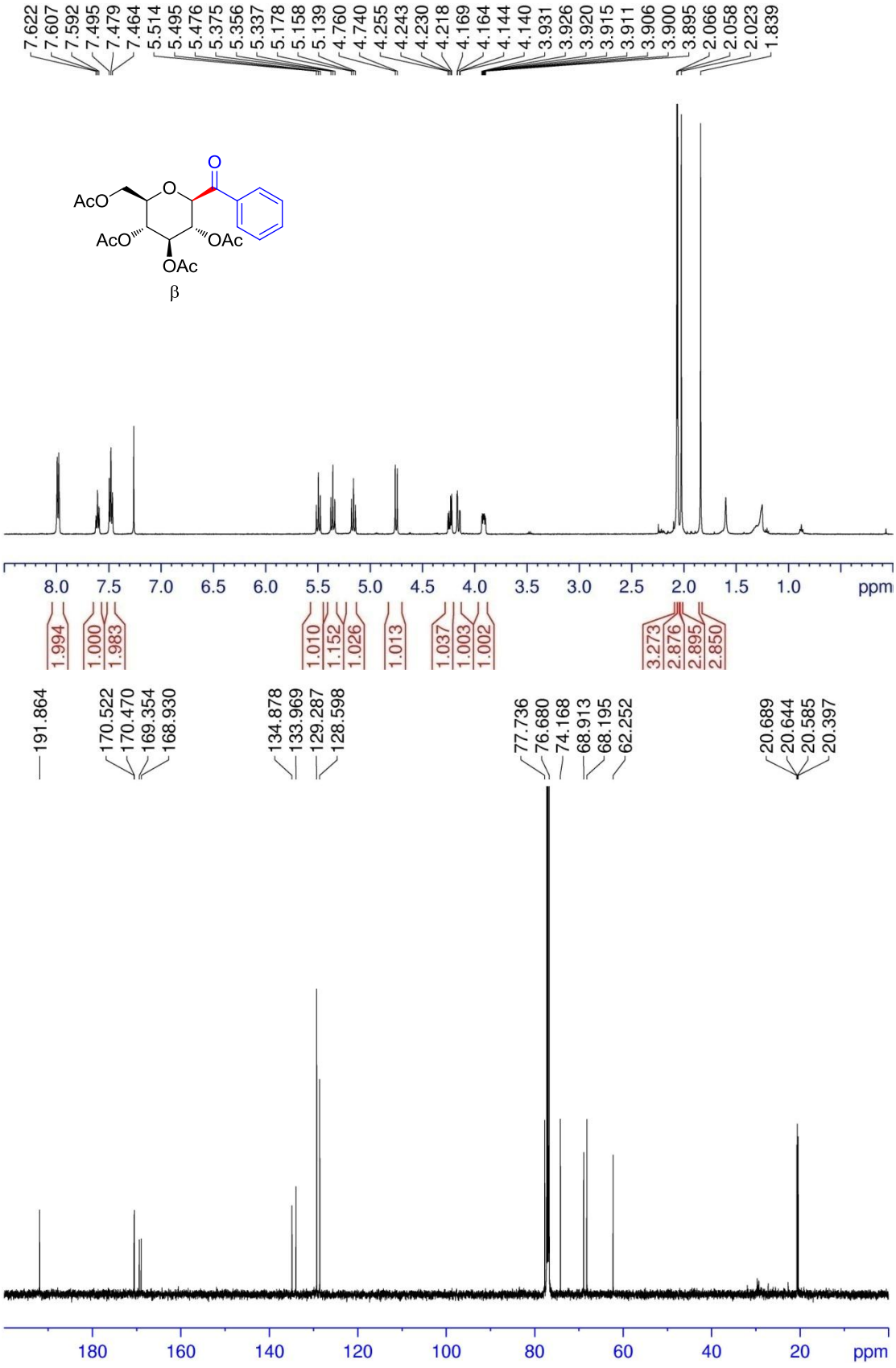
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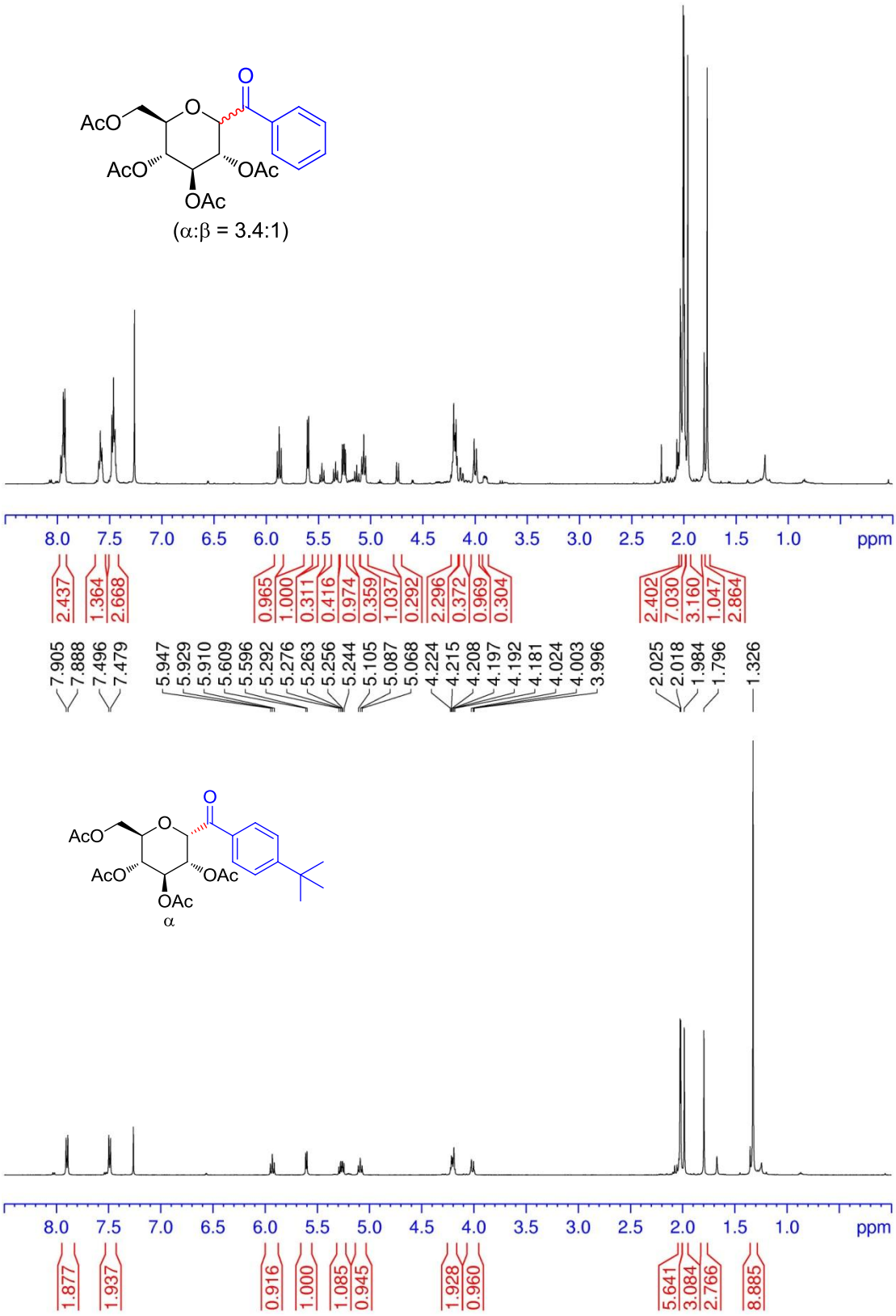
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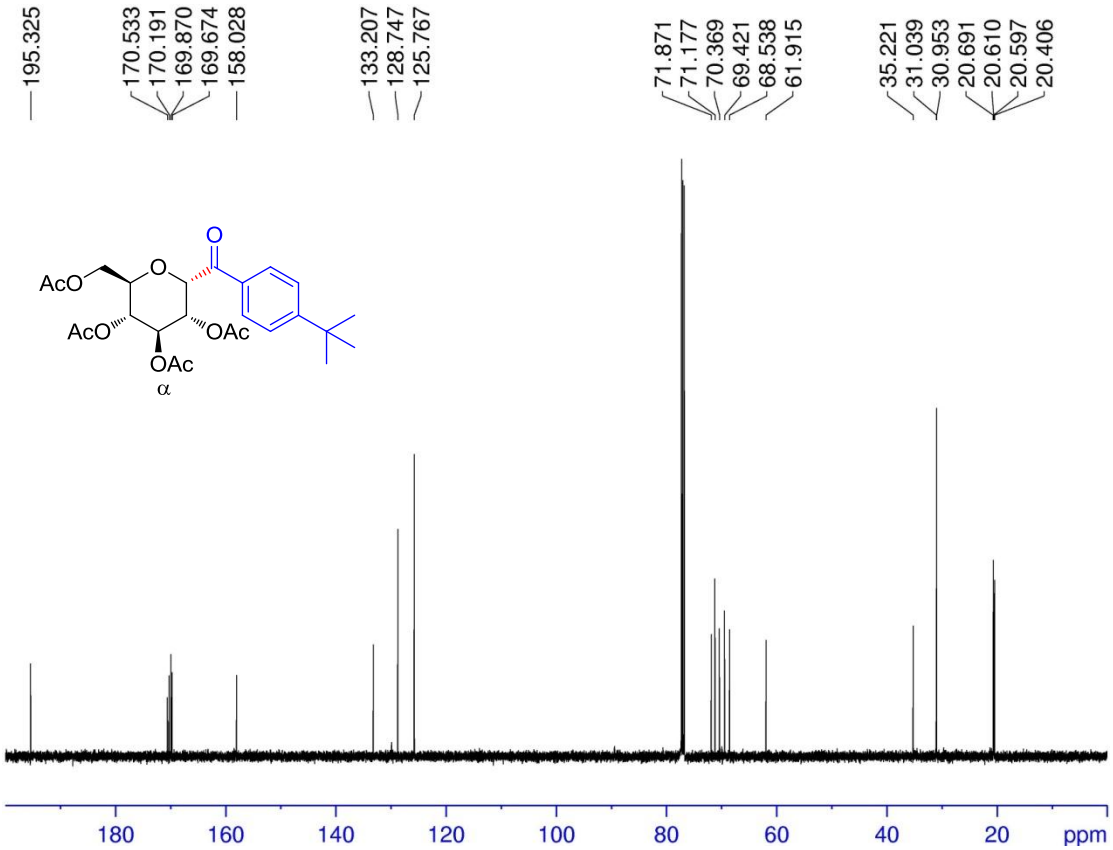
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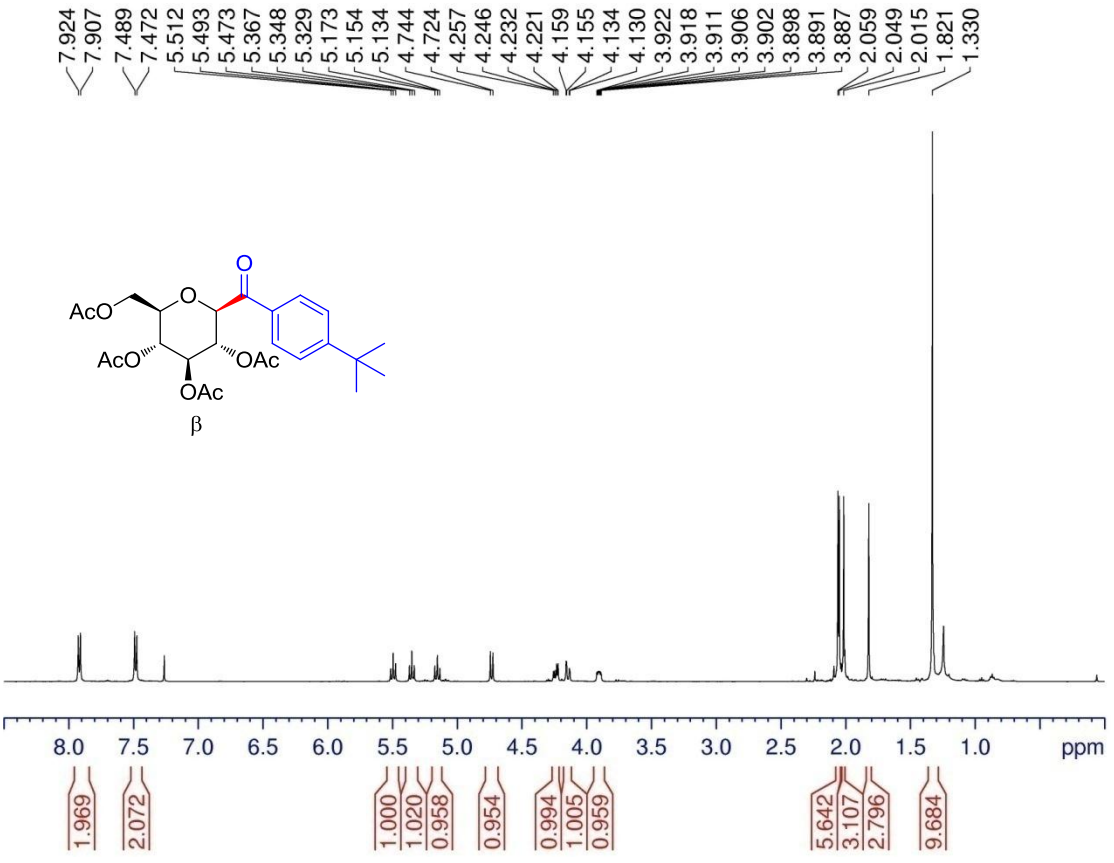
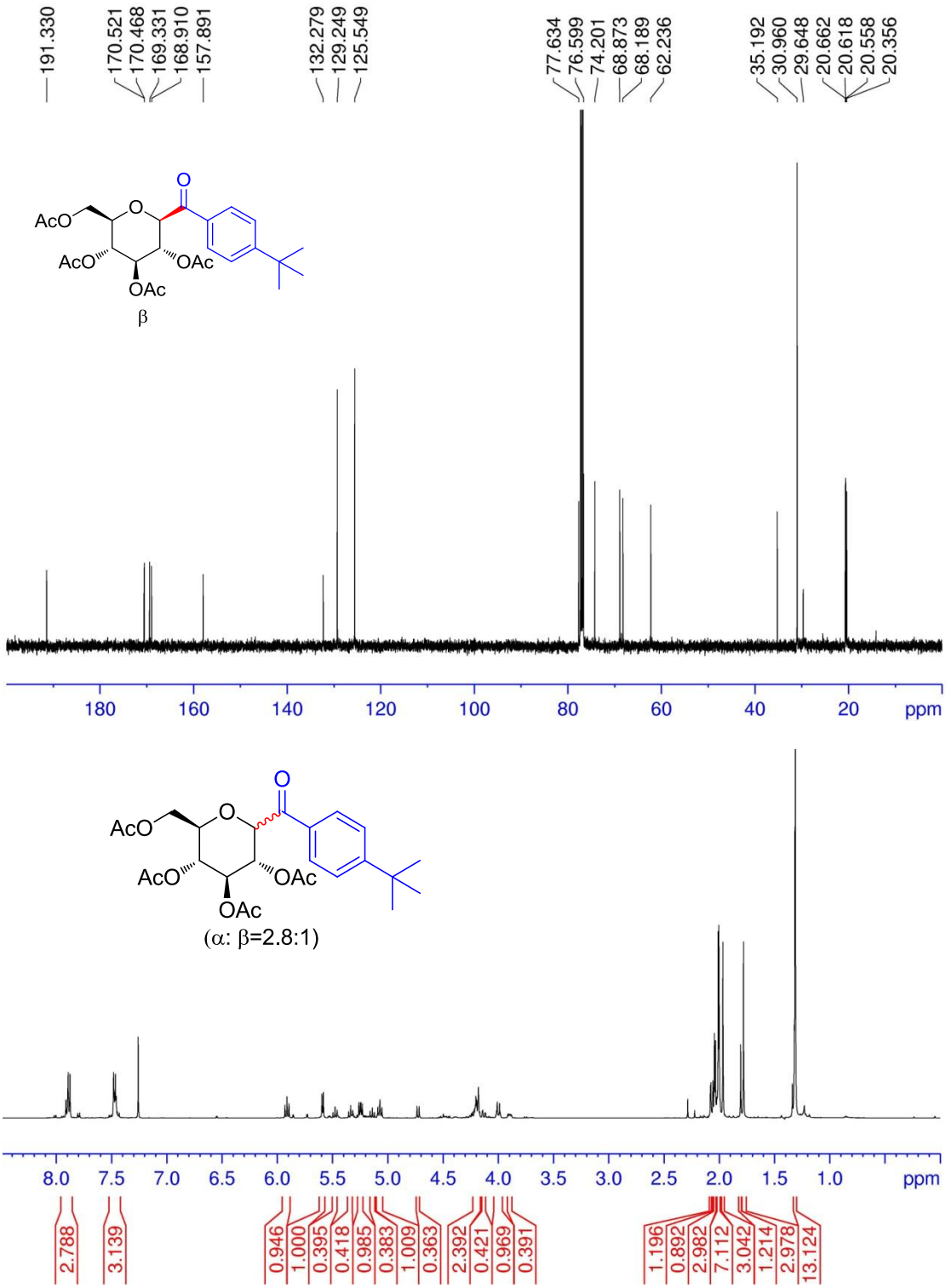
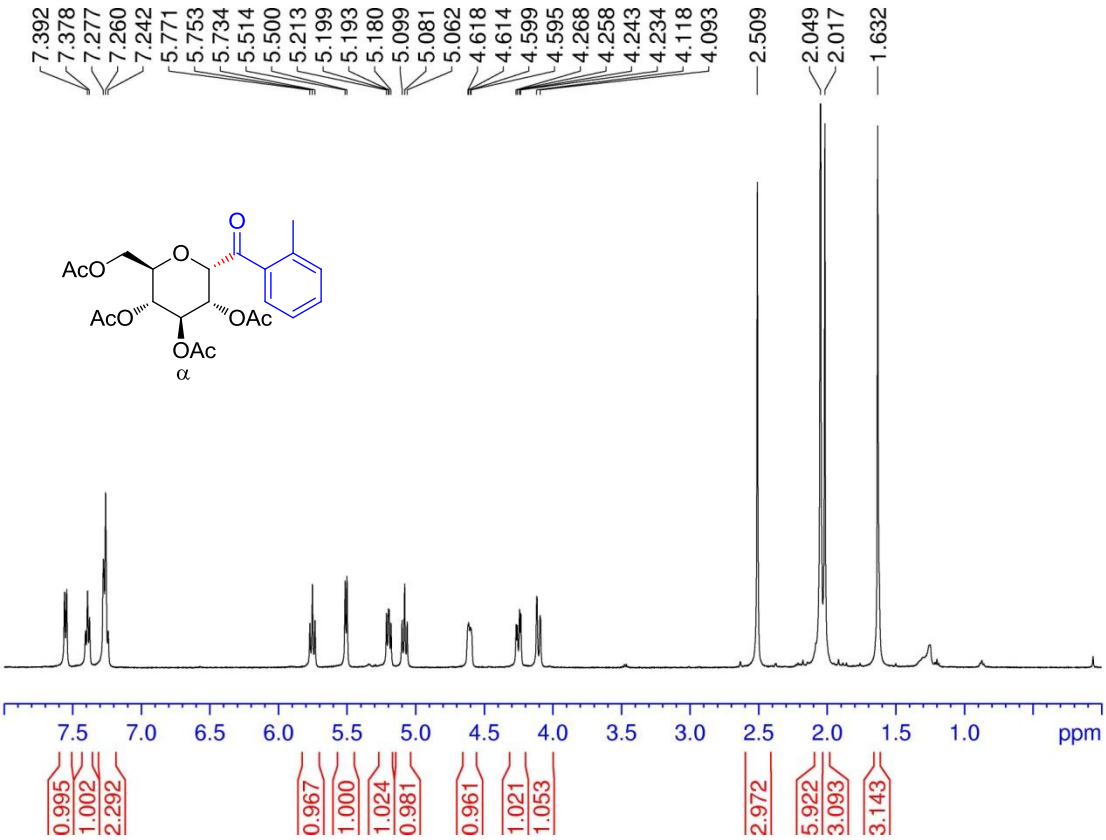
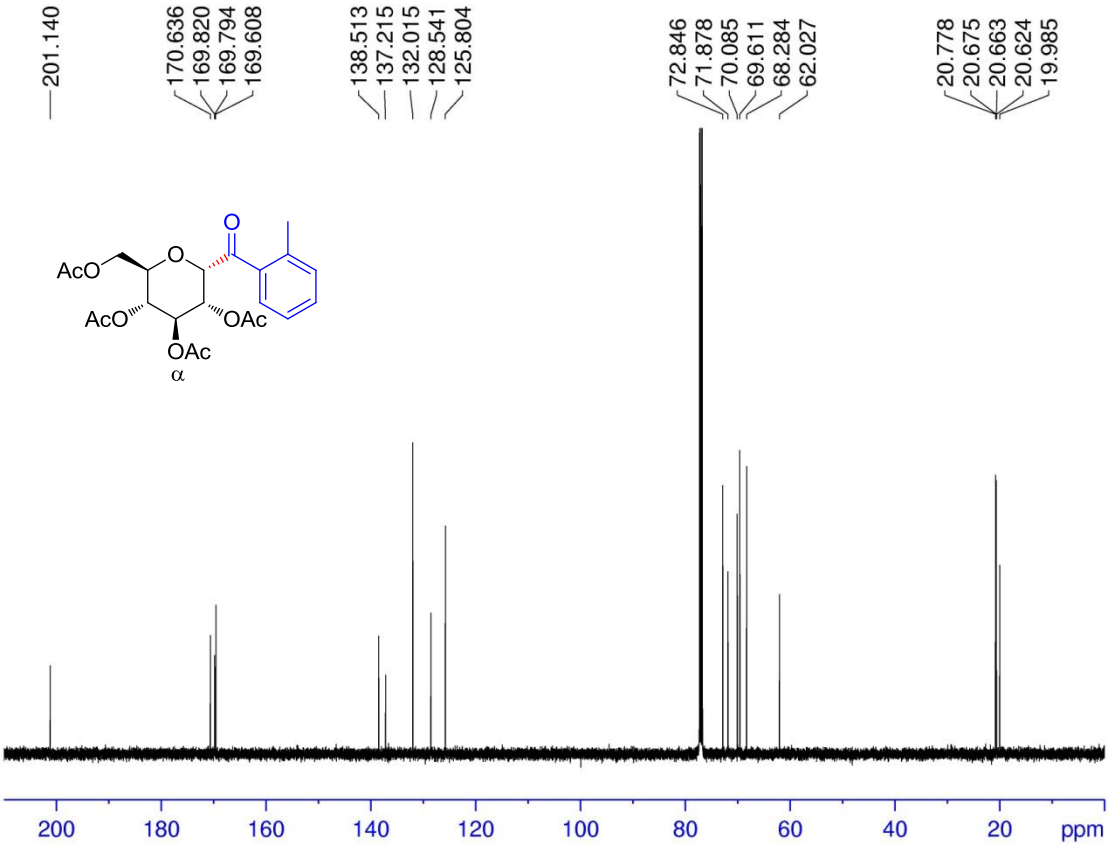
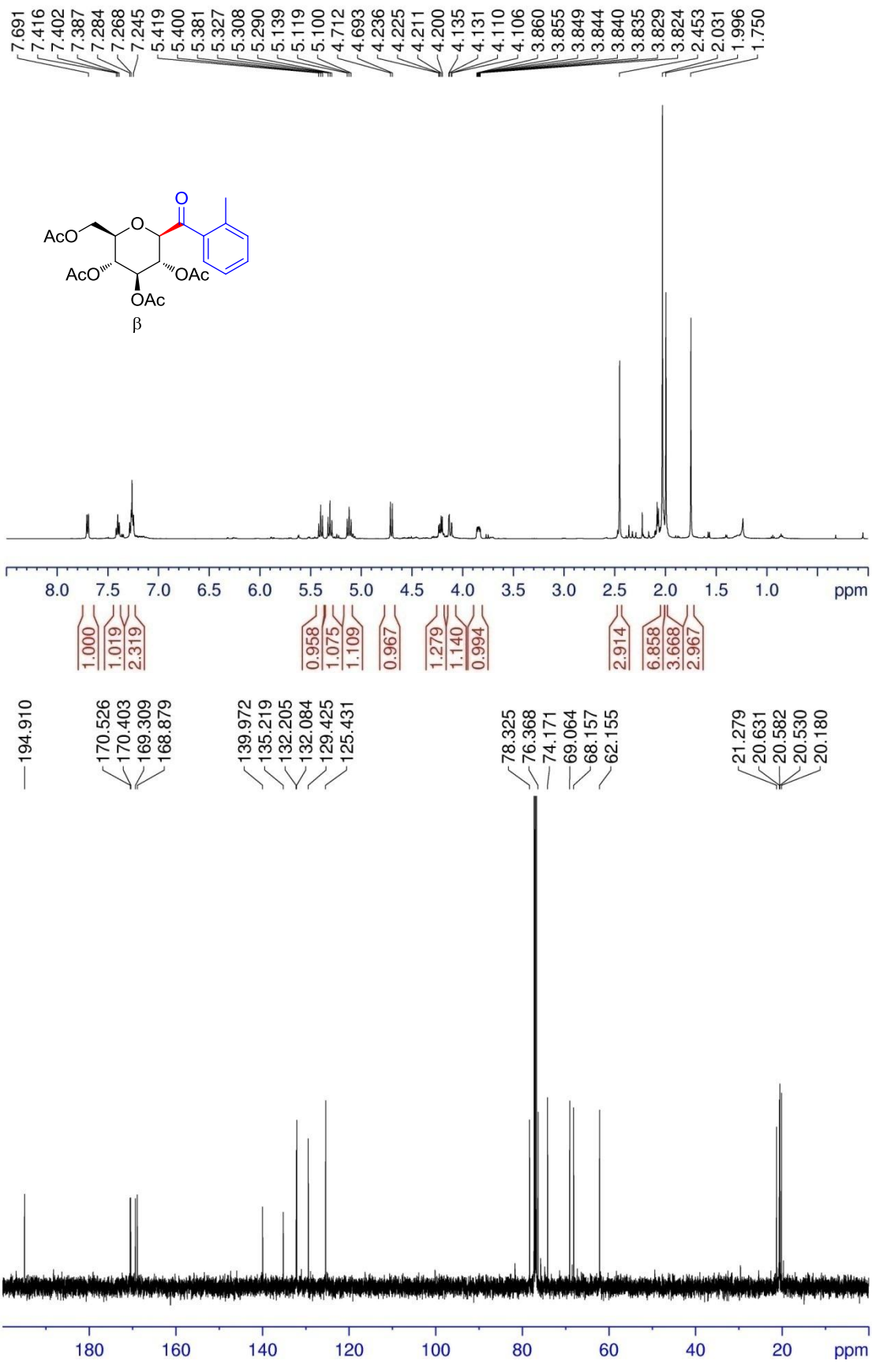
ppm

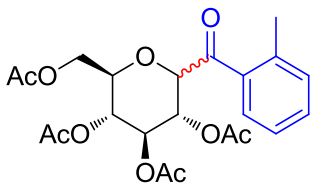

7.924
7.907
7.489
7.472
5.512
5.493
5.473
5.367
5.348
5.329
5.173
5.154
5.134
4.744
4.724
4.257
4.246
4.232
4.221
4.159
4.155
4.134
4.130
3.922
3.918
3.911
3.906
3.902
3.898
3.891
3.887
2.059
2.049
2.015
1.821
1.330
AcO
AcO
OAc
OAc
O
O
β
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.969
2.072
1.000
1.020
0.958
0.954
0.994
1.005
0.959
5.642
3.107
2.796
9.684


191.330
170.521
170.468
169.331
168.910
157.891
132.279
129.249
125.549
77.634
76.599
74.201
68.873
68.189
62.236
35.192
30.960
29.648
20.662
20.618
20.558
20.356
AcO
AcO
OAc
OAc
O
O
β
180
160
140
120
100
80
60
40
20
ppm
AcO
AcO
OAc
OAc
O
O
(α: β=2.8:1)
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
ppm
2.788
3.139
0.946
1.000
0.395
0.418
0.985
0.383
1.009
0.363
2.392
0.421
0.969
0.391
1.196
0.892
2.982
7.112
3.042
1.214
2.978
13.124


7.392
7.378
7.277
7.260
7.242
5.771
5.753
5.734
5.514
5.500
5.213
5.199
5.193
5.180
5.099
5.081
5.062
4.618
4.614
4.599
4.595
4.268
4.258
4.243
4.234
4.118
4.093
2.509
2.049
2.017
1.632
AcO
AcO
OAc
OAc
O
O
α
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
ppm
0.995
1.002
2.292
0.967
1.000
1.024
0.981
0.961
1.021
1.053
2.972
5.922
3.093
3.143

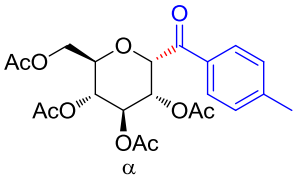

201.140
170.636
169.820
169.794
169.608
138.513
137.215
132.015
128.541
125.804
72.846
71.878
70.085
69.611
68.284
62.027
20.778
20.675
20.663
20.624
19.985
AcO
AcO
OAc
OAc
O
O
α
200
180
160
140
120
100
80
60
40
20
ppm


7.691
7.416
7.402
7.387
7.284
7.268
7.245
5.419
5.400
5.381
5.327
5.308
5.290
5.139
5.119
5.100
4.712
4.693
4.236
4.225
4.211
4.200
4.135
4.131
4.110
4.106
3.860
3.855
3.849
3.844
3.840
3.835
3.829
3.824
2.453
2.031
1.996
1.750
AcO
AcO
OAc
OAc
O
O
β
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
ppm
1.000
1.019
2.319
0.958
1.075
1.109
0.967
1.279
1.140
0.994
2.914
6.858
3.668
2.967
194.910
170.526
170.403
169.309
168.879
139.972
135.219
132.205
132.084
129.425
125.431
78.325
76.368
74.171
69.064
68.157
62.155
21.279
20.631
20.582
20.530
20.180
180
160
140
120
100
80
60
40
20
ppm

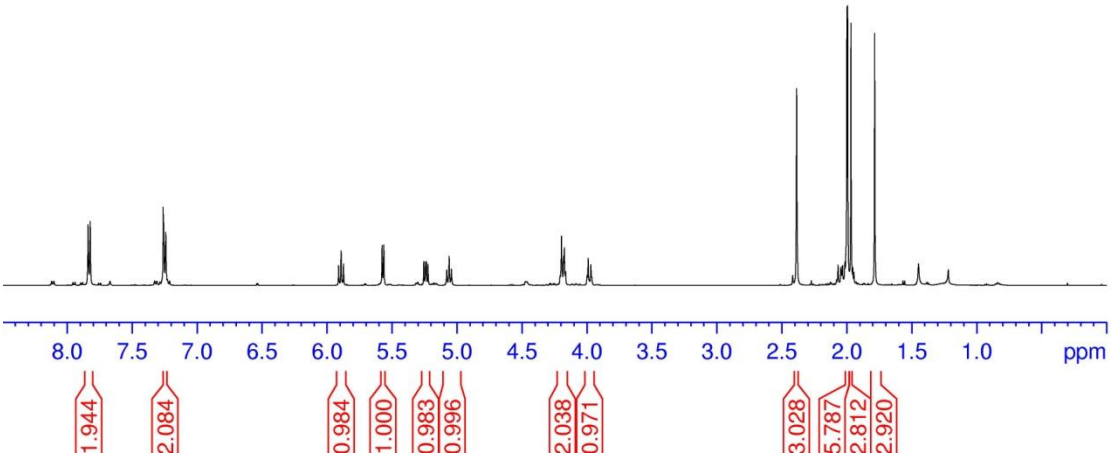

O
AcO
O
AcO
OAc
OAc

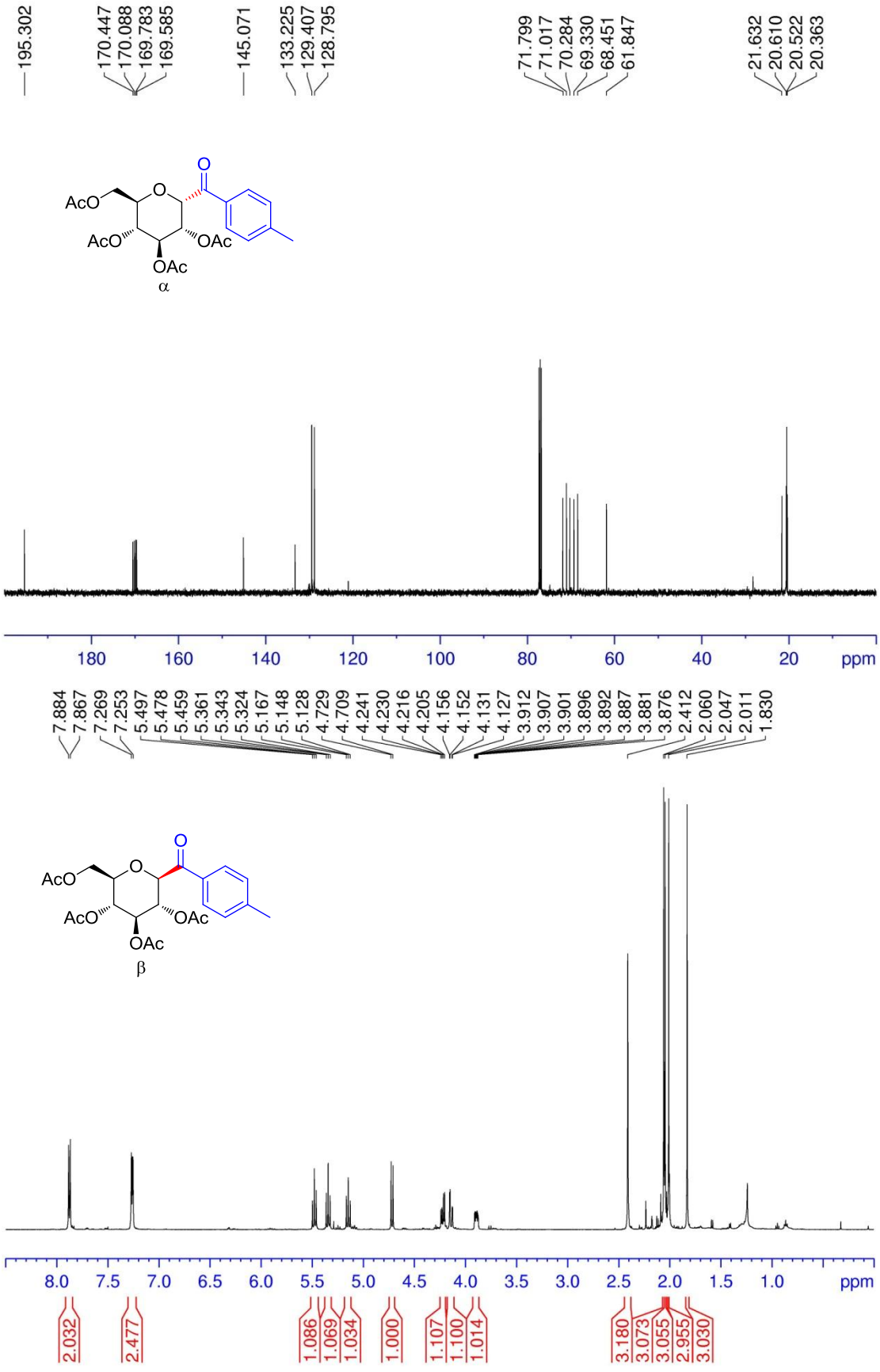
(α: β=1.8:1)

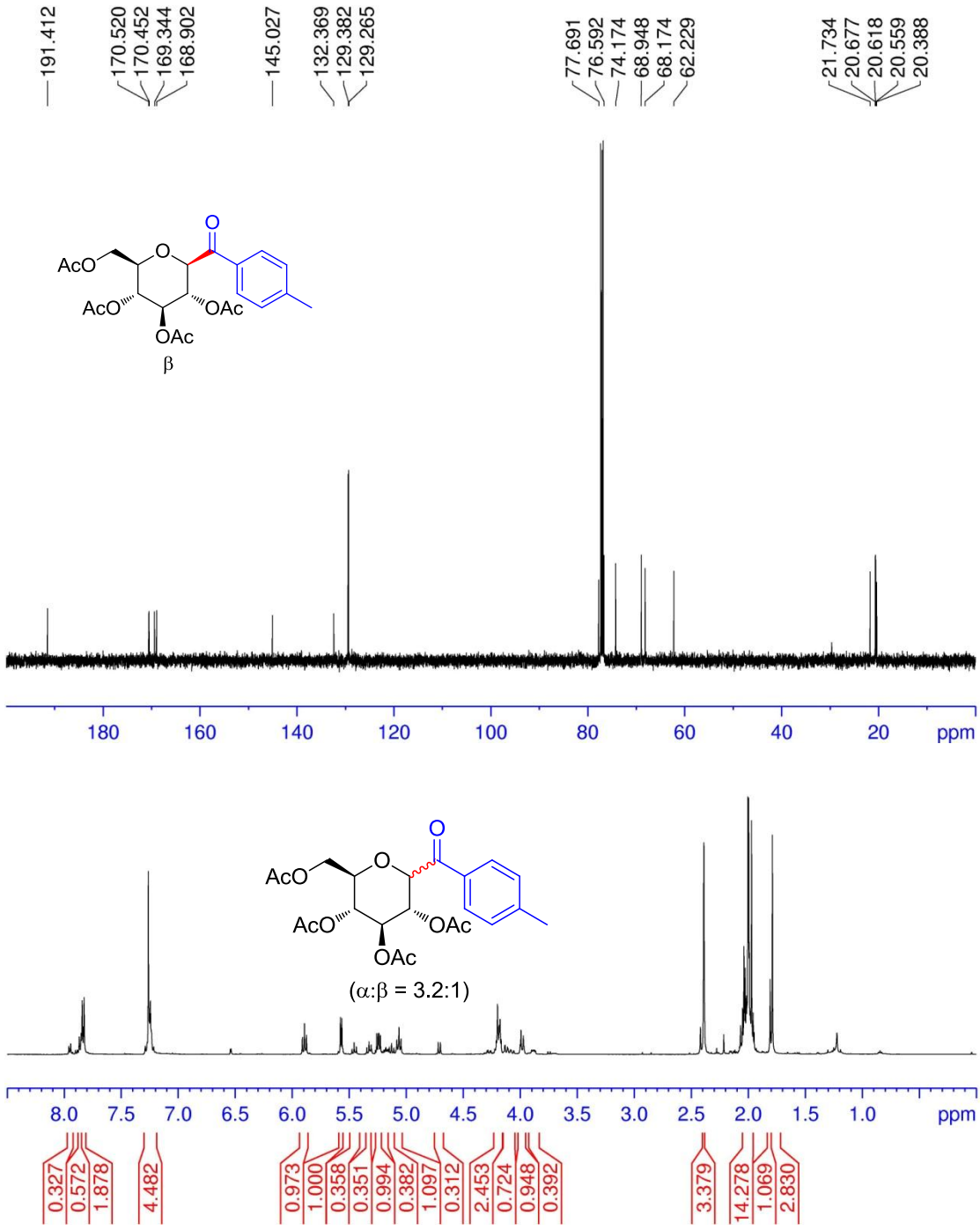
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.979 1.713 3.123 0.679 5.212 1.752 1.897 0.961 1.213 2.104 1.144 1.859 1.000 1.762 3.696 3.355 1.046 5.340 3.107 27.370 3.056 5.406
7.838 7.822 7.257 7.240 5.910 5.891 5.872 5.575 5.563 5.257 5.244 5.237 5.224 5.080 5.062 5.043 4.208 4.197 4.181 4.175 4.166 3.999 3.992 3.979 3.971 3.965 2.388 2.001 1.994 1.969 1.787

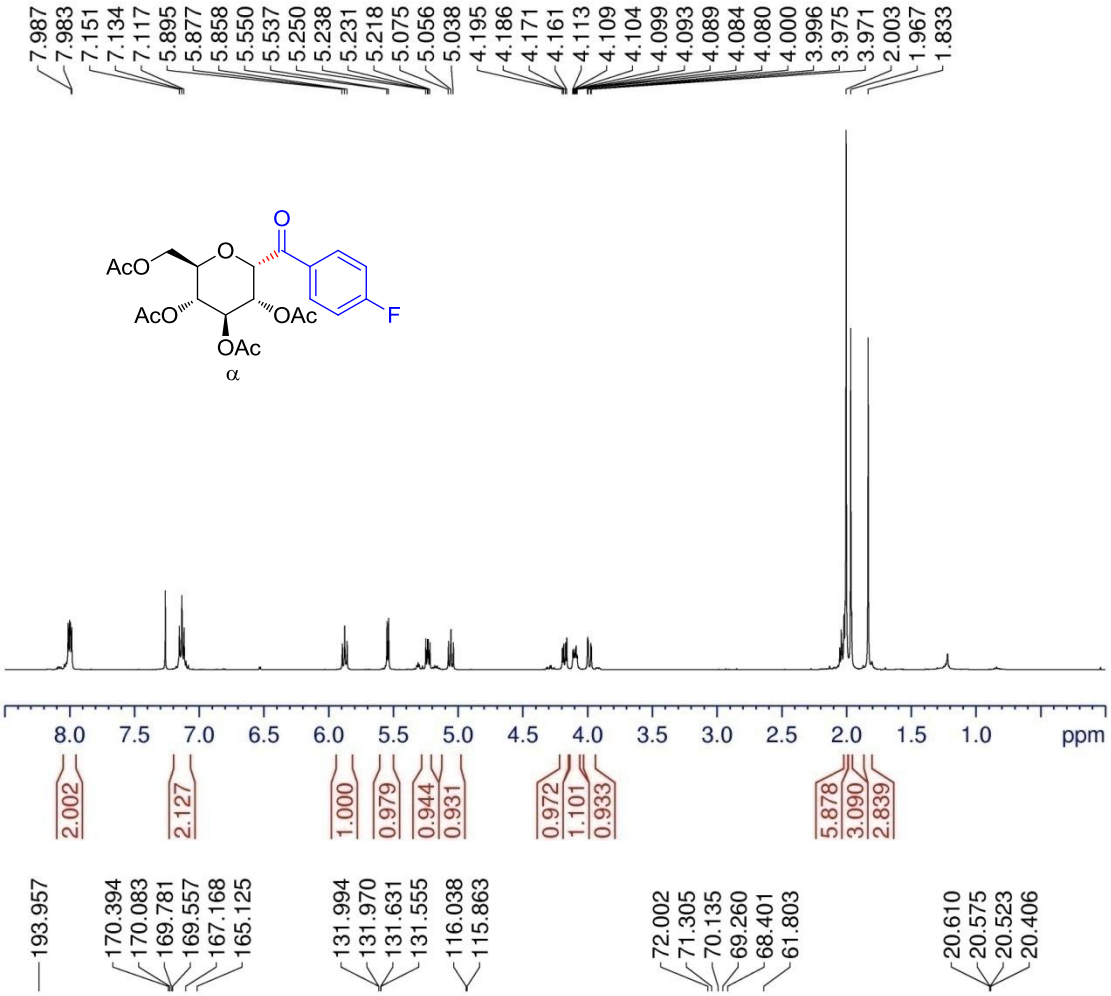

O
AcO
O
AcO
OAc
OAc

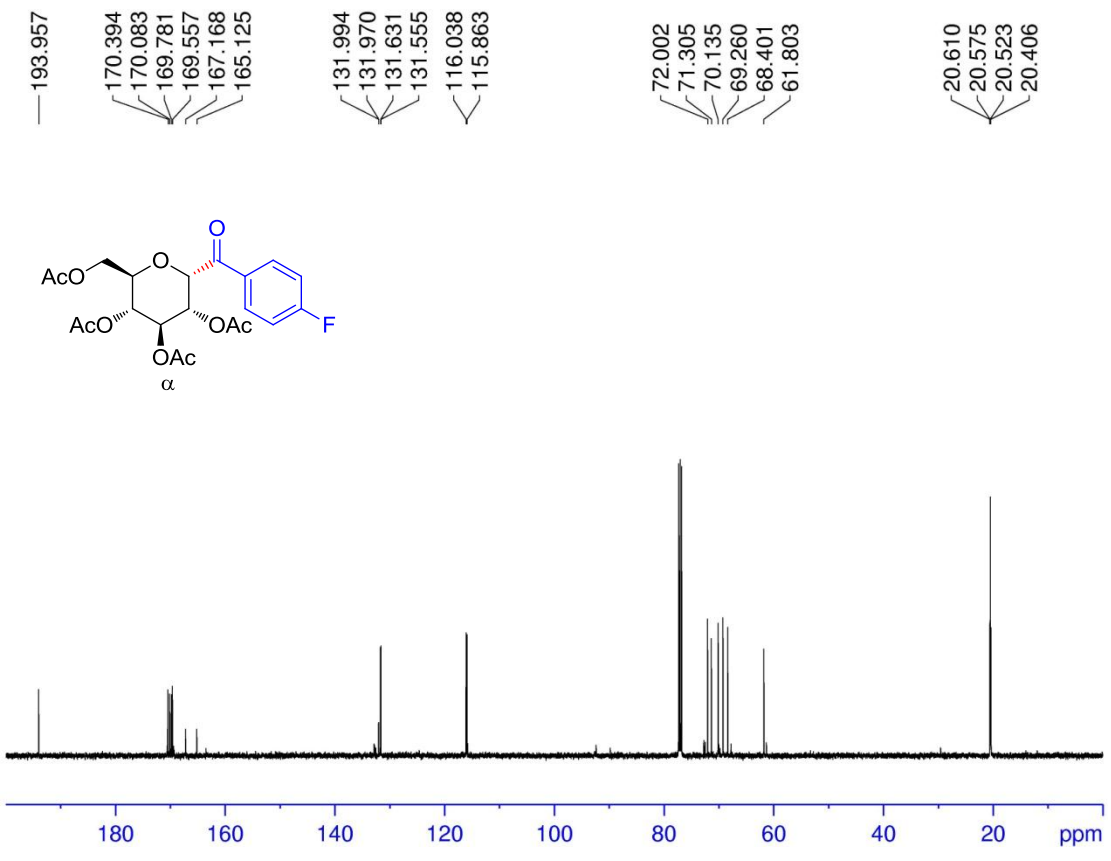
α

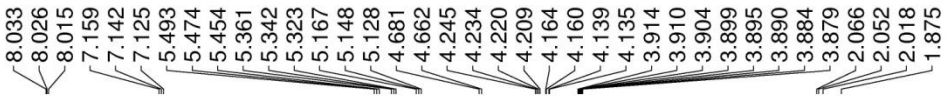

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.944 2.084 0.984 1.000 0.983 0.996 2.038 0.971 3.028 5.787 2.812 2.920

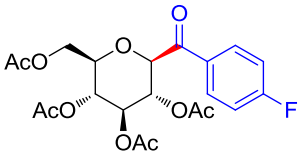

195.302
170.447
170.088
169.783
169.585
145.071
133.225
129.407
128.795
71.799
71.017
70.284
69.330
68.451
61.847
21.632
20.610
20.522
20.363
AcO
AcO
OAc
OAc
O
α
180
160
140
120
100
80
60
40
20
ppm
7.884
7.867
7.269
7.253
5.497
5.478
5.459
5.361
5.343
5.324
5.167
5.148
5.128
4.729
4.709
4.241
4.230
4.216
4.205
4.156
4.152
4.131
4.127
3.912
3.907
3.901
3.896
3.892
3.887
3.881
3.876
2.412
2.060
2.047
2.011
1.830
AcO
AcO
OAc
OAc
O
β
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
ppm
2.032
2.477
1.086
1.069
1.034
1.000
1.107
1.100
1.014
3.180
3.073
3.055
2.955
3.030


191.412
170.520
170.452
169.344
168.902
145.027
132.369
129.382
129.265
77.691
76.592
74.174
68.948
68.174
62.229
21.734
20.677
20.618
20.559
20.388
AcO
AcO
OAc
OAc
O
O
β
180
160
140
120
100
80
60
40
20
ppm
AcO
AcO
OAc
OAc
O
O
(α:β = 3.2:1)
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
ppm
0.327
0.572
1.878
4.482
0.973
1.000
0.358
0.351
0.994
0.382
1.097
0.312
2.453
0.724
0.948
0.392
3.379
14.278
1.069
2.830

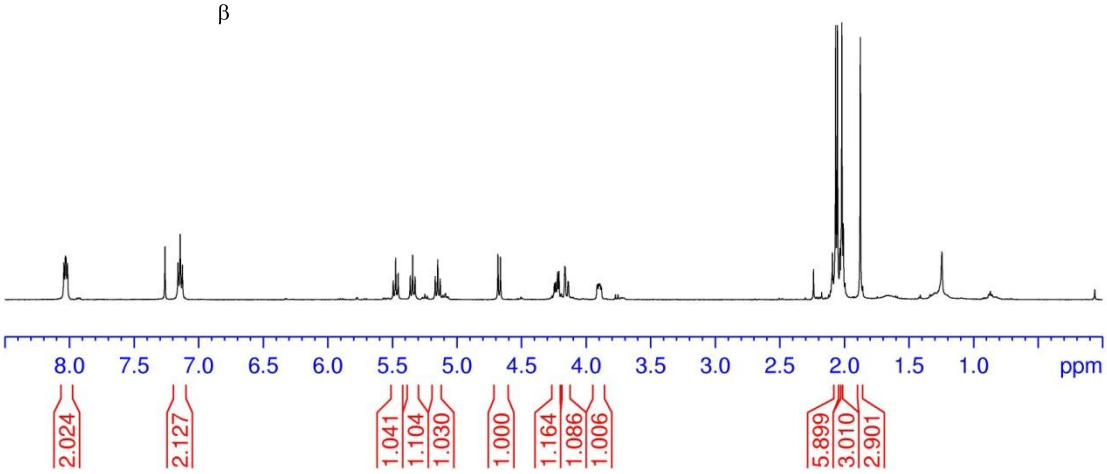

7.987
7.983
7.151
7.134
7.117
5.895
5.877
5.858
5.550
5.537
5.250
5.238
5.231
5.218
5.075
5.056
5.038
4.195
4.186
4.171
4.161
4.113
4.109
4.104
4.099
4.093
4.089
4.084
4.080
4.000
3.996
3.975
3.971
2.003
1.967
1.833
AcO
AcO
OAc
OAc
O
O
F
α
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.002
2.127
1.000
0.979
0.944
0.931
0.972
1.101
0.933
5.878
3.090
2.839


193.957
170.394
170.083
169.781
169.557
167.168
165.125
131.994
131.970
131.631
131.555
116.038
115.863
72.002
71.305
70.135
69.260
68.401
61.803
20.610
20.575
20.523
20.406
AcO
AcO
OAc
OAc
O
O
F
α
180
160
140
120
100
80
60
40
20
ppm

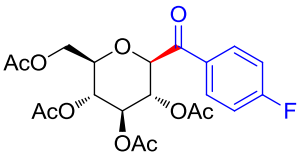

8.033
8.026
8.015
7.159
7.142
7.125
5.493
5.474
5.454
5.361
5.342
5.323
5.167
5.148
5.128
4.681
4.662
4.245
4.234
4.220
4.209
4.164
4.160
4.139
4.135
3.914
3.910
3.904
3.899
3.895
3.890
3.884
3.879
2.066
2.052
2.018
1.875


O
O
AcO
AcO
OAc
OAc
F

β

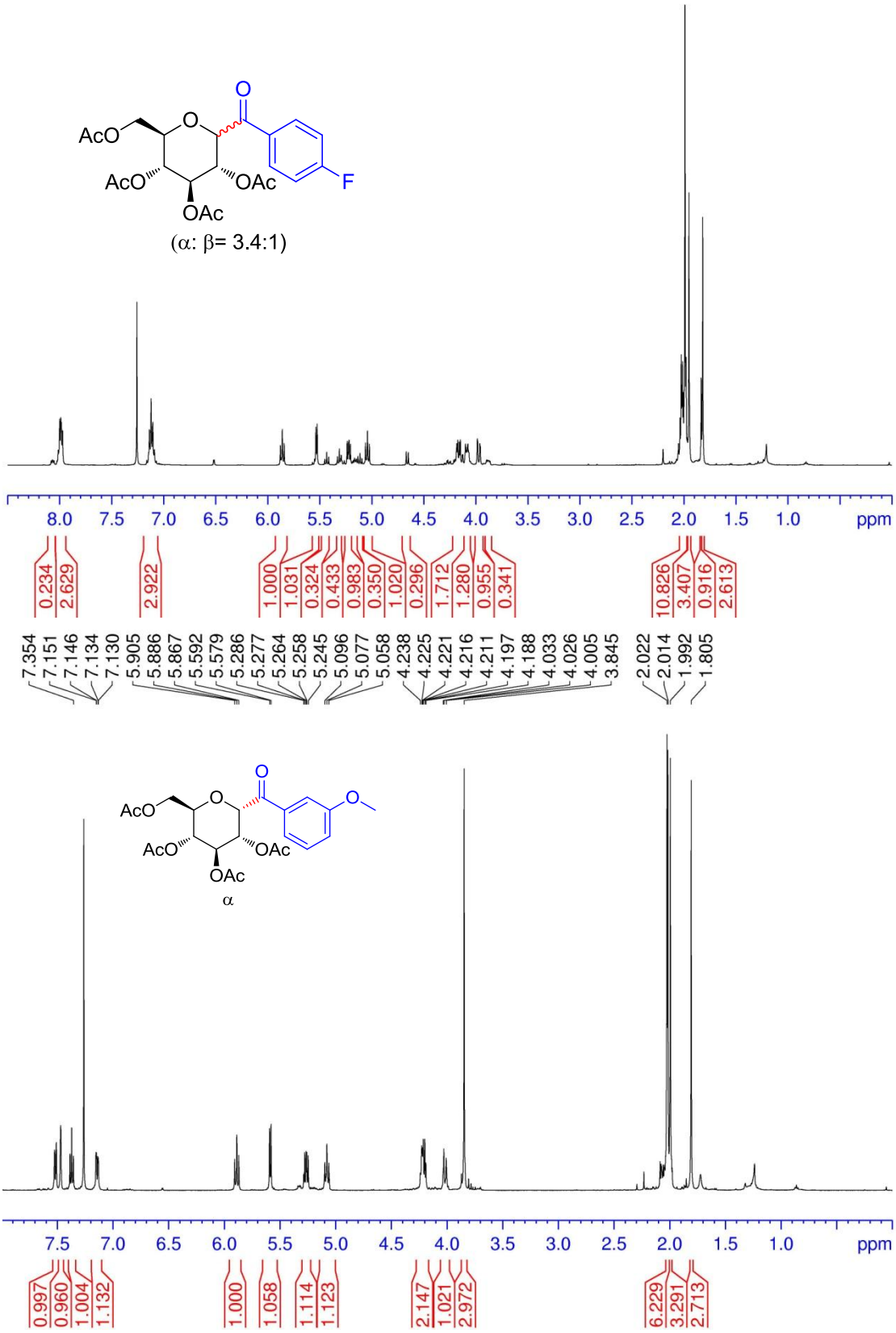

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.024
2.127
1.041
1.104
1.030
1.000
1.164
1.086
1.006
5.899
3.010
2.901

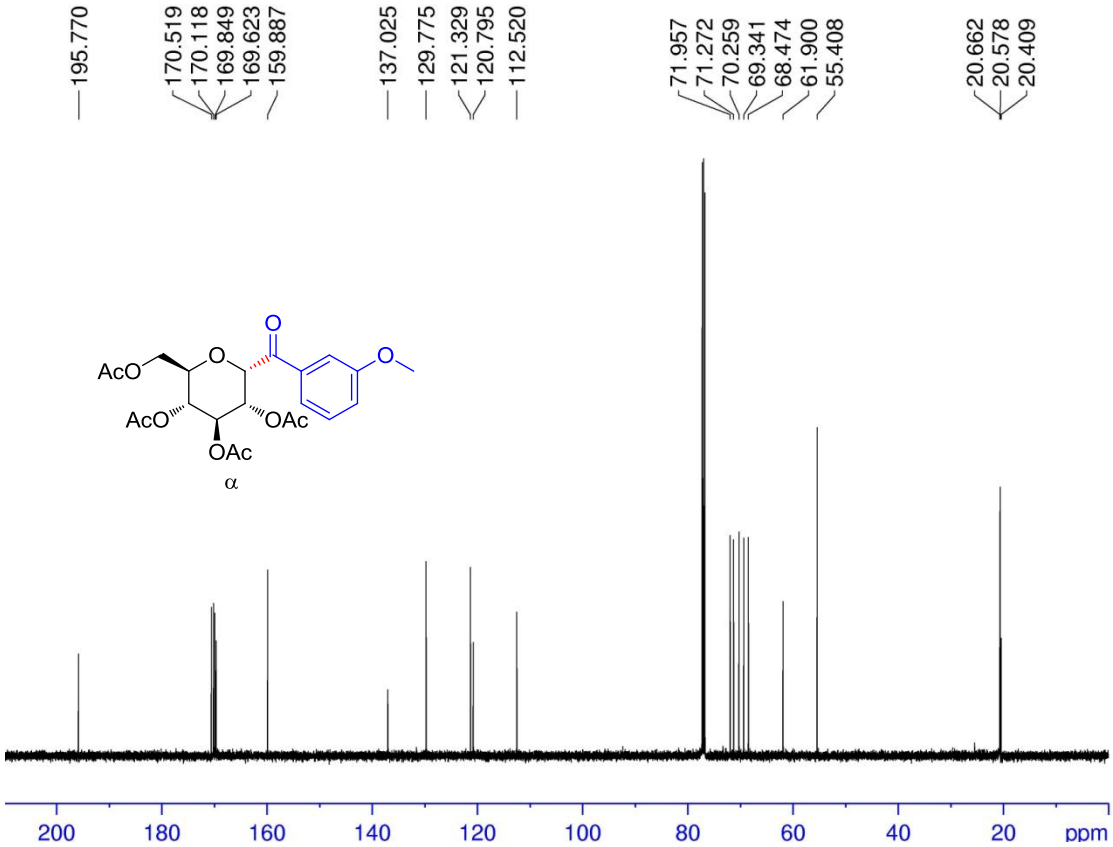

190.371
170.436
170.396
169.331
168.929
167.152
165.112
132.129
132.056
131.196
131.174
115.885
115.710
78.108
76.670
74.027
68.846
68.088
62.184
20.662
20.603
20.547
20.420

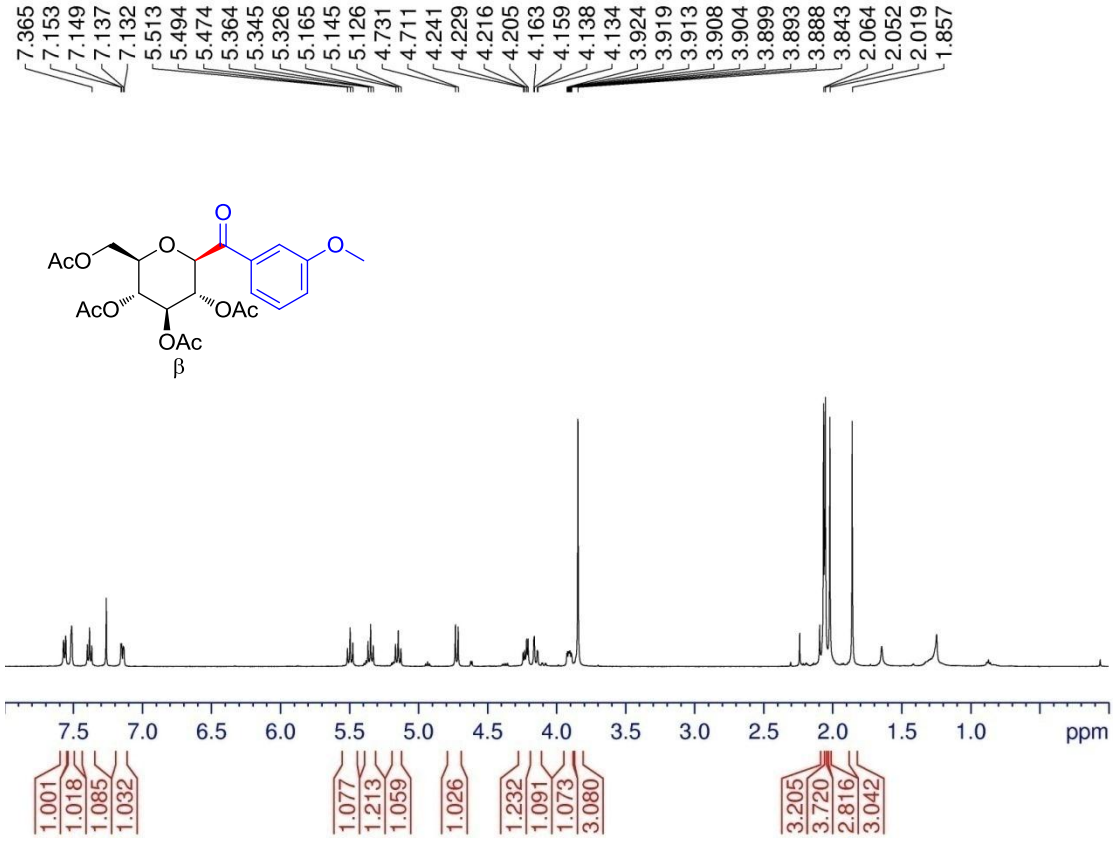

O
O
AcO
AcO
OAc
OAc
F

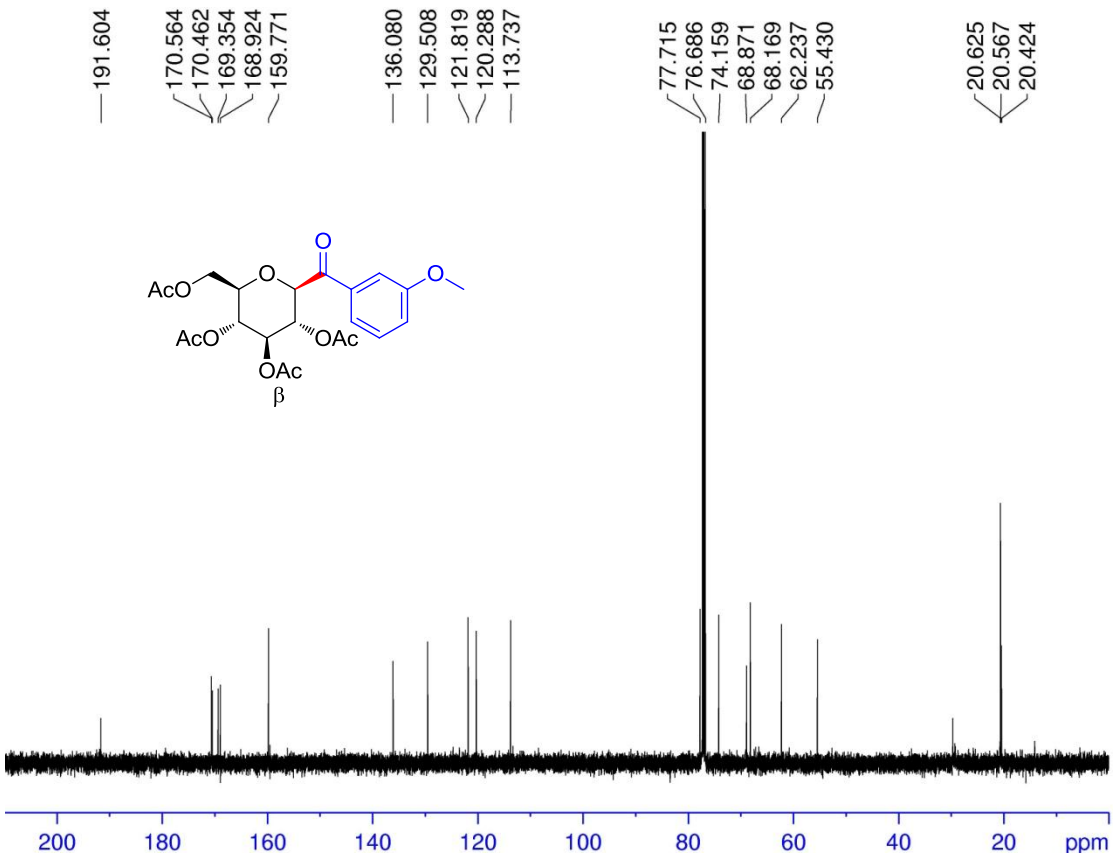
β

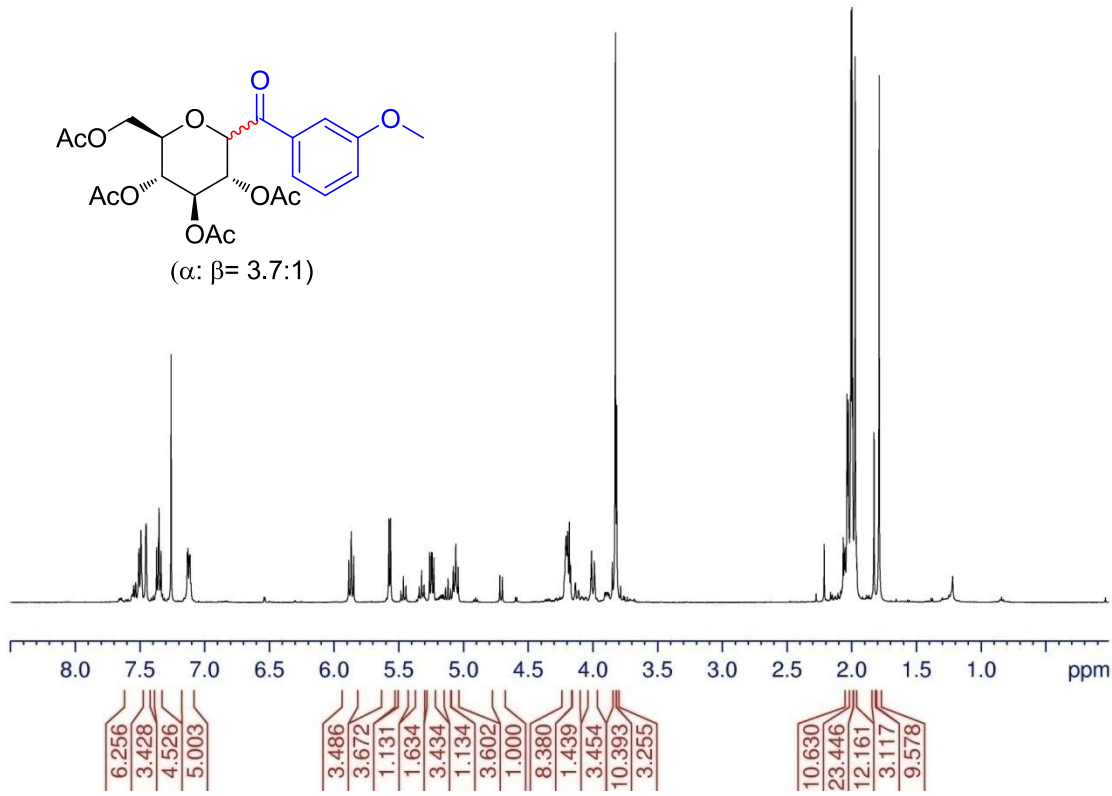
180
160
140
120
100
80
60
40
20
0
ppm

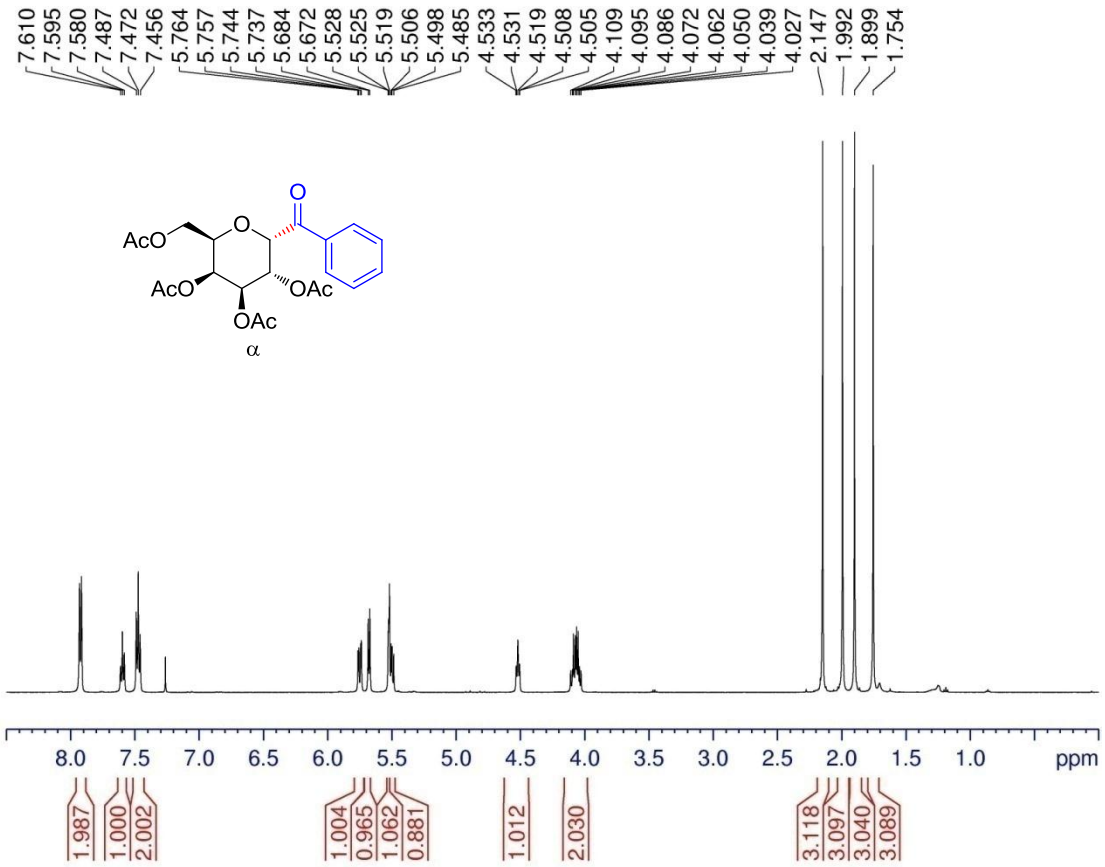

AcO
AcO
OAc
OAc
O
O
F
(α: β= 3.4:1)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.234 2.629 2.922 1.000 1.031 0.324 0.433 0.983 0.350 1.020 0.296 1.712 1.280 0.955 0.341 10.826 3.407 0.916 2.613
7.354 7.151 7.146 7.134 7.130 5.905 5.886 5.867 5.592 5.579 5.286 5.277 5.264 5.258 5.245 5.096 5.077 5.058 4.238 4.225 4.221 4.216 4.211 4.197 4.188 4.033 4.026 4.005 3.845 2.022 2.014 1.992 1.805
AcO
AcO
OAc
OAc
O
O
α
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 ppm
0.997 0.960 1.004 1.132 1.000 1.058 1.114 1.123 2.147 1.021 2.972 6.229 3.291 2.713

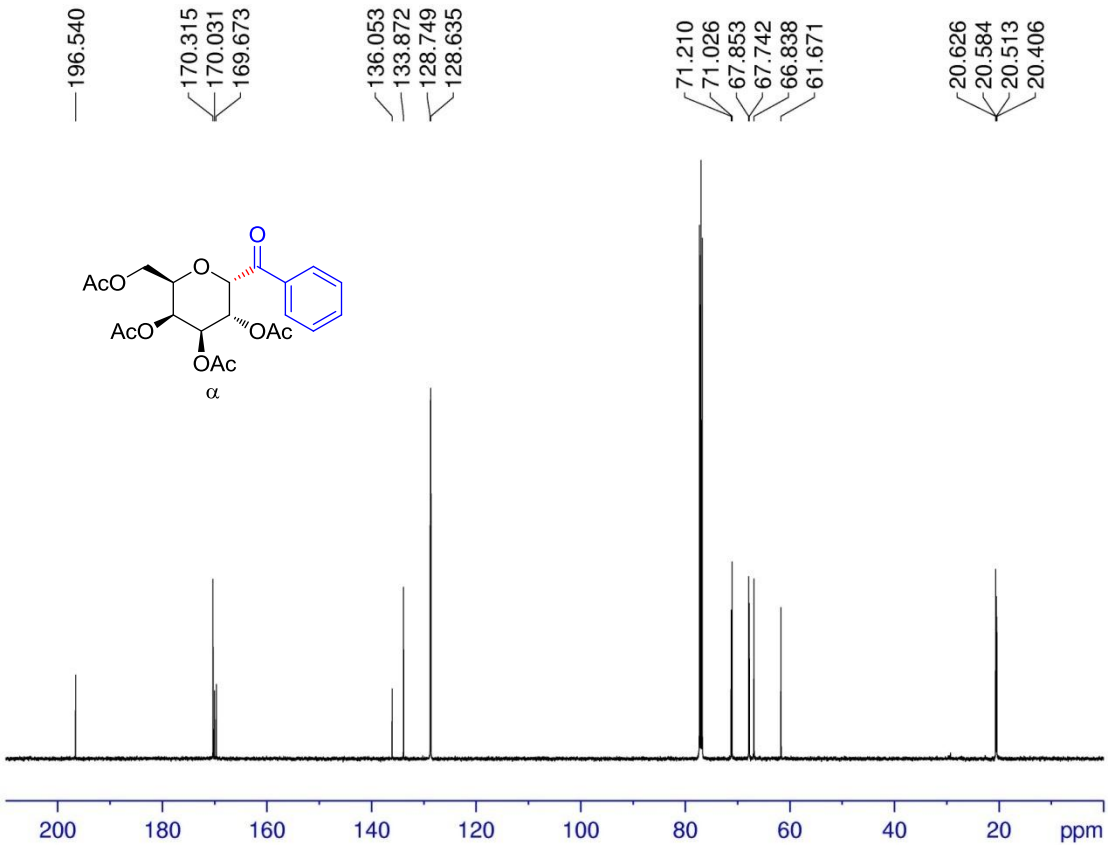

195.770
170.519
170.118
169.849
169.623
159.887
137.025
129.775
121.329
120.795
112.520
71.957
71.272
70.259
69.341
68.474
61.900
55.408
20.662
20.578
20.409
AcO
AcO
OAc
OAc
O
O
O
α
200
180
160
140
120
100
80
60
40
20
ppm

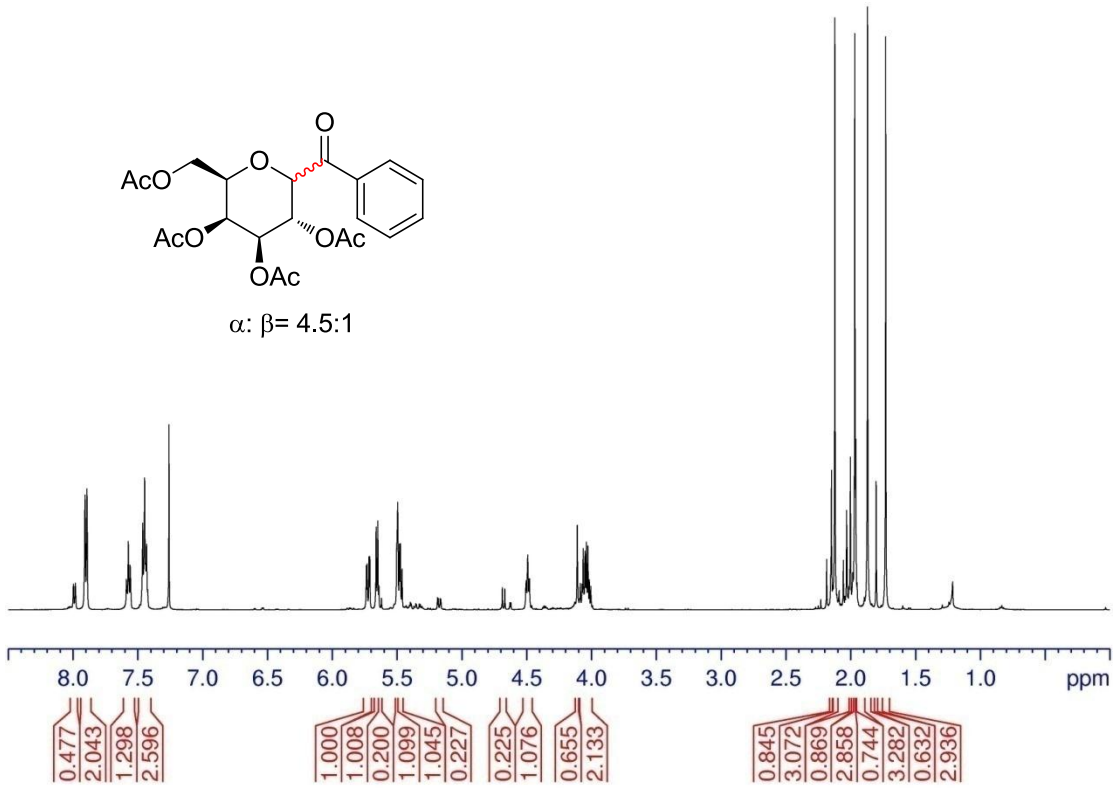

7.365
7.153
7.149
7.137
7.132
5.513
5.494
5.474
5.364
5.345
5.326
5.165
5.145
5.126
4.731
4.711
4.241
4.229
4.216
4.205
4.163
4.159
4.138
4.134
3.924
3.919
3.913
3.908
3.904
3.899
3.893
3.888
3.843
2.064
2.052
2.019
1.857
AcO
AcO
OAc
OAc
O
O
O
β
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.001
1.018
1.085
1.032
1.077
1.213
1.059
1.026
1.232
1.091
1.073
3.080
3.205
3.720
2.816
3.042

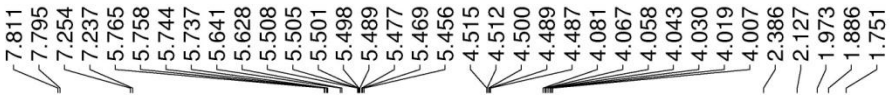

191.604
170.564
170.462
169.354
168.924
159.771
136.080
129.508
121.819
120.288
113.737
77.715
76.686
74.159
68.871
68.169
62.237
55.430
20.625
20.567
20.424
AcO
AcO
OAc
OAc
β
200
180
160
140
120
100
80
60
40
20
ppm

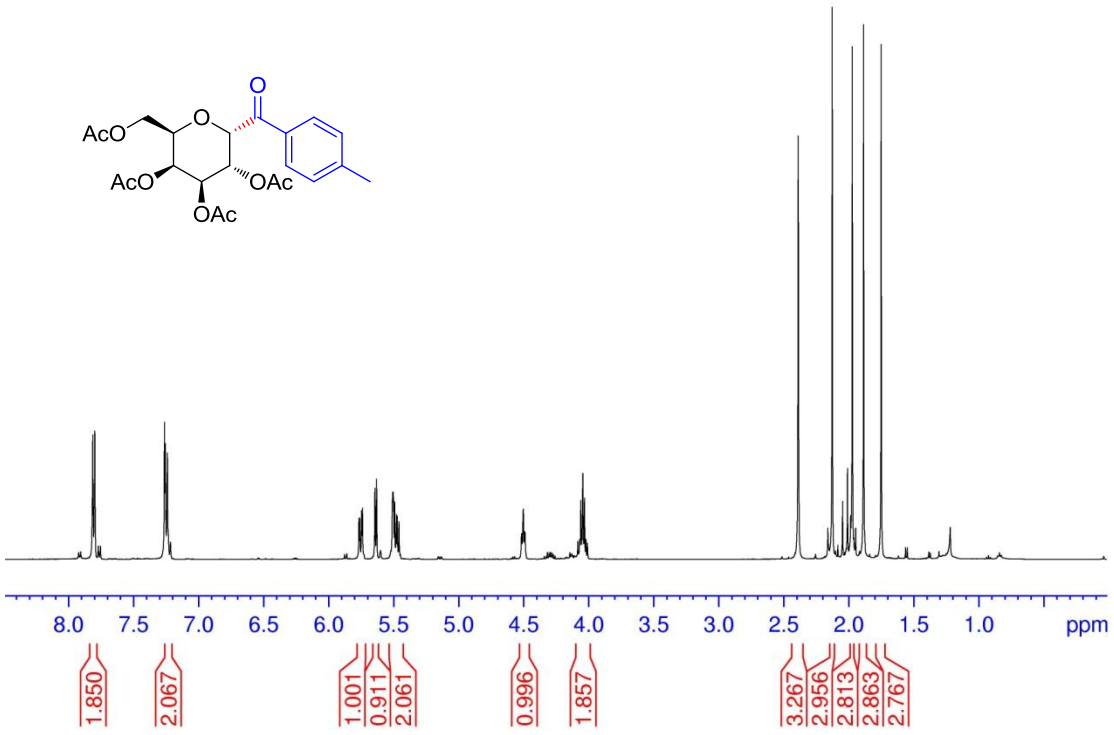

AcO
AcO
OAc
OAc
(α: β= 3.7:1)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.256
3.428
4.526
5.003
3.486
3.672
1.131
1.634
3.434
1.134
3.602
1.000
8.380
1.439
3.454
10.393
3.255
10.630
23.446
12.161
3.117
9.578

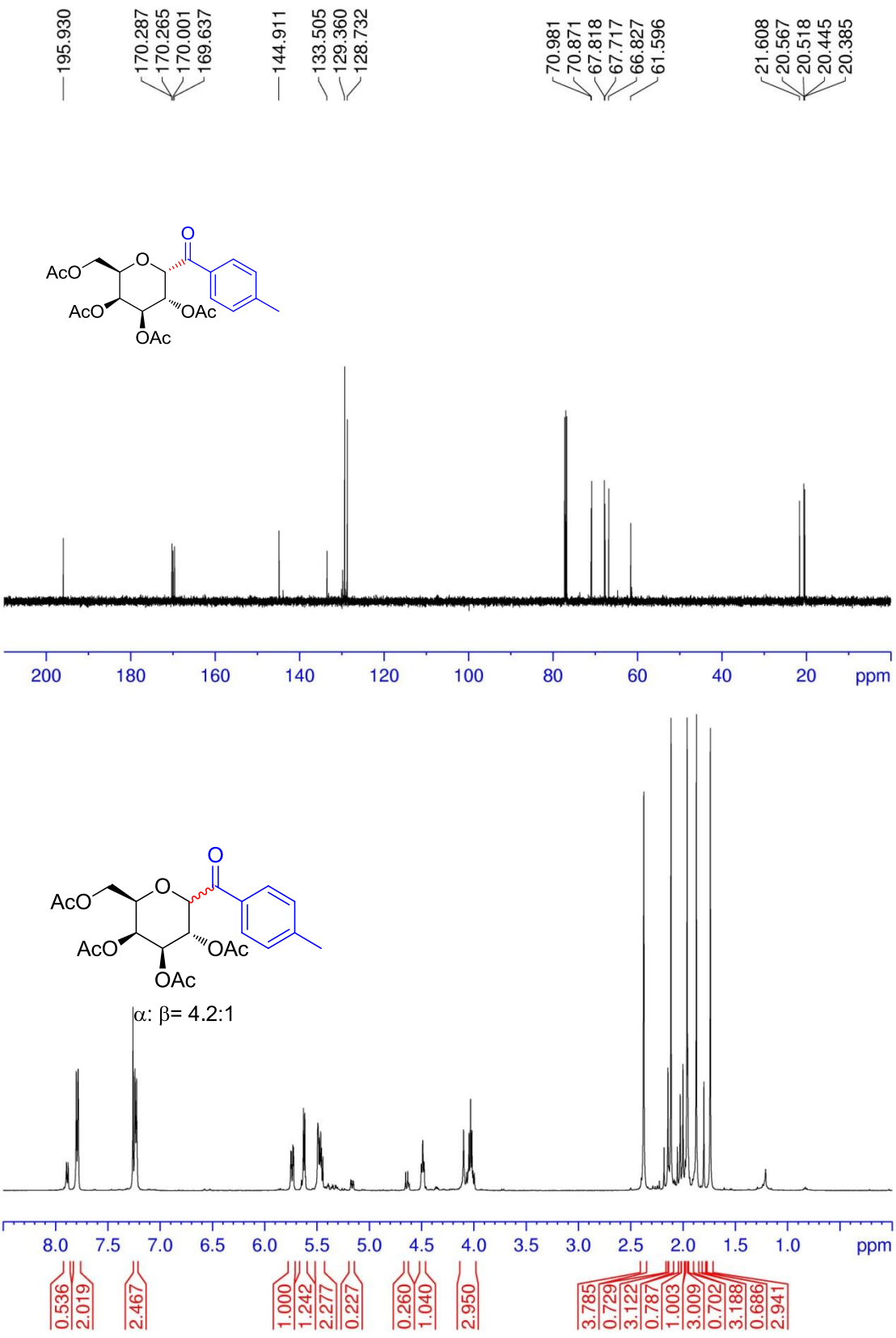

7.610
7.595
7.580
7.487
7.472
7.456
5.764
5.757
5.744
5.737
5.684
5.672
5.528
5.525
5.519
5.506
5.498
5.485
4.533
4.531
4.519
4.508
4.505
4.109
4.095
4.086
4.072
4.062
4.050
4.039
4.027
2.147
1.992
1.899
1.754
AcO
AcO
OAc
OAc
O
O
α
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.987
1.000
2.002
1.004
0.965
1.062
0.881
1.012
2.030
3.118
3.097
3.040
3.089

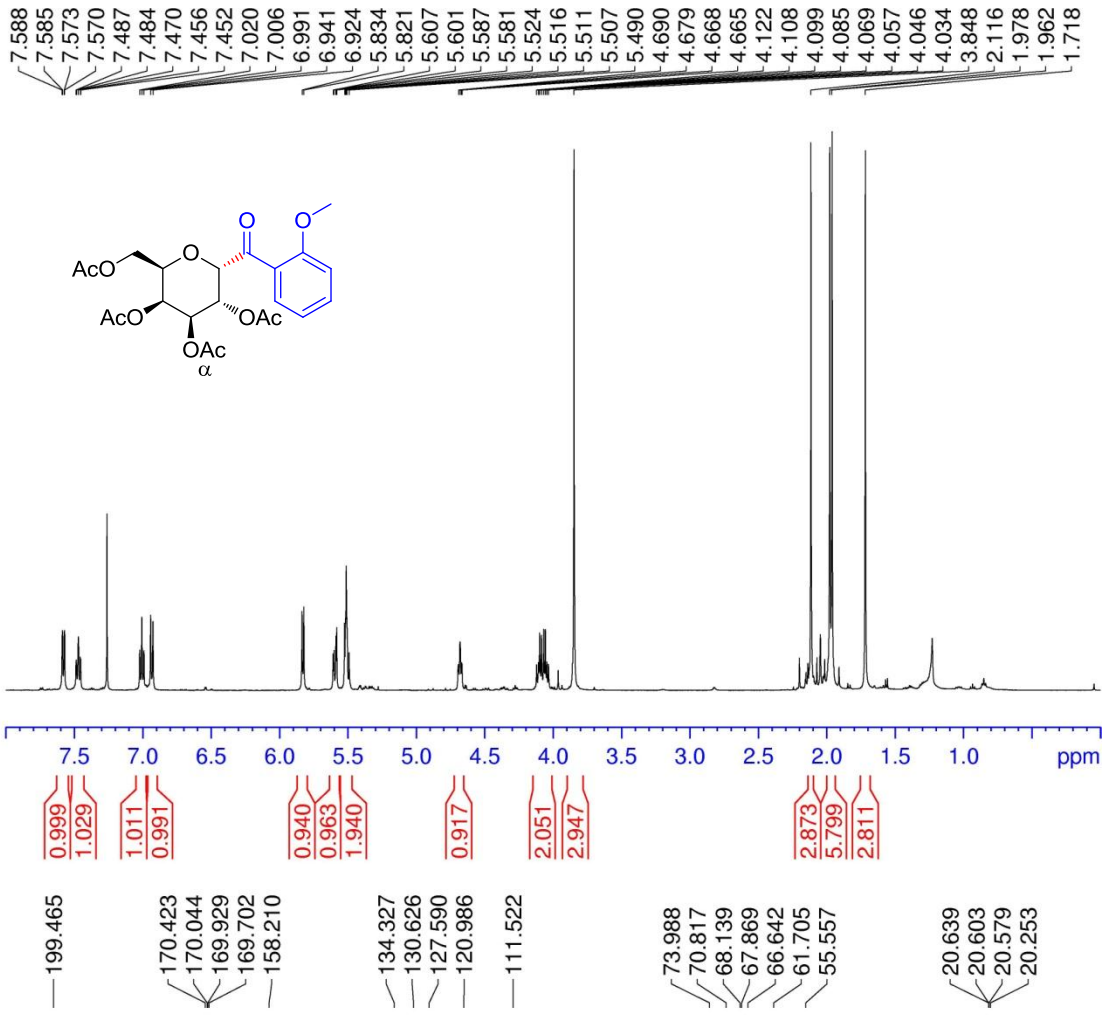

196.540
170.315
170.031
169.673
136.053
133.872
128.749
128.635
71.210
71.026
67.853
67.742
66.838
61.671
20.626
20.584
20.513
20.406
AcO
AcO
OAc
OAc
O
O
α
200
180
160
140
120
100
80
60
40
20
ppm

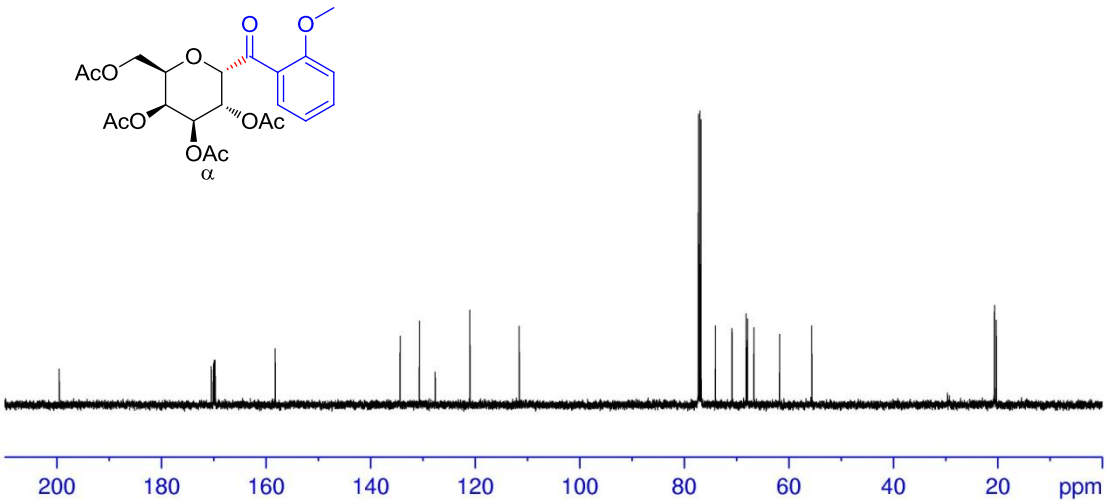

AcO
AcO
OAc
OAc
O
O
α: β= 4.5:1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.477 2.043 1.298 2.596
1.000 1.008 0.200 1.099 1.045 0.227
0.225 1.076
0.655 2.133
0.845 3.072 0.869 2.858 0.744 3.282 0.632 2.936

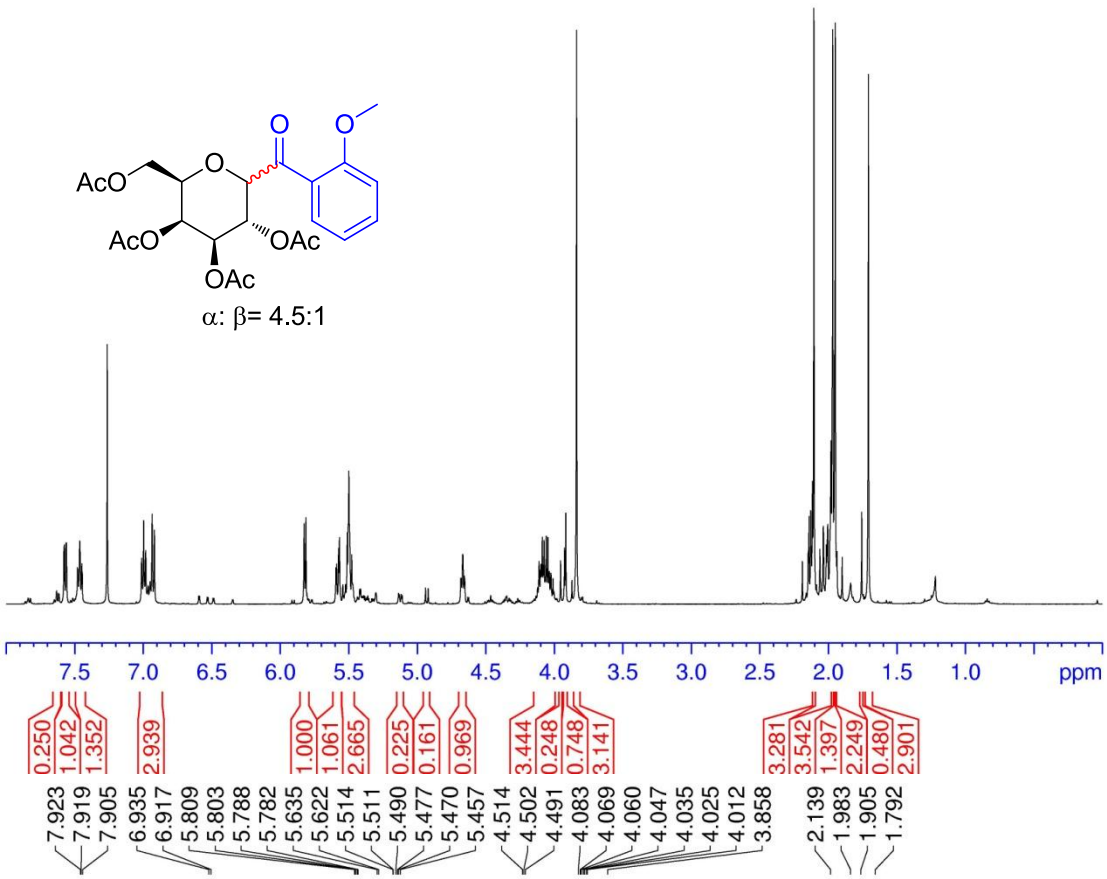

7.811 7.795 7.254 7.237 5.765 5.758 5.744 5.737 5.641 5.628 5.508 5.505 5.501 5.498 5.489 5.477 5.469 5.456 4.515 4.512 4.500 4.489 4.487 4.081 4.067 4.058 4.043 4.030 4.019 4.007 2.386 2.127 1.973 1.886 1.751

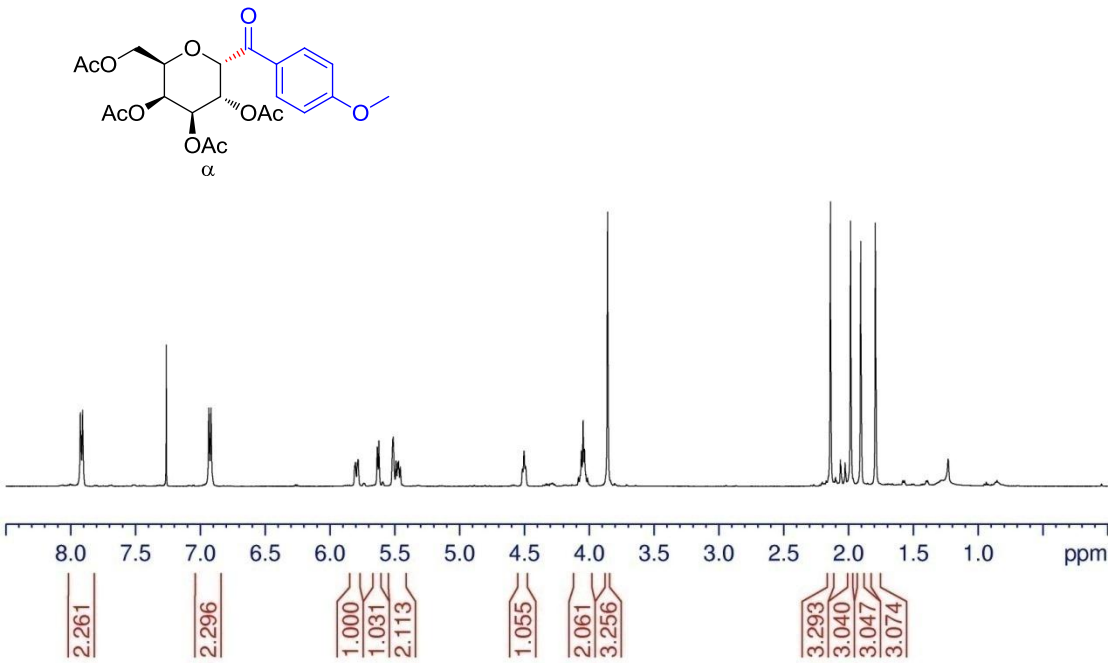

AcO
AcO
OAc
OAc
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.850 2.067
1.001 0.911 2.061
0.996 1.857
3.267 2.956 2.813 2.863 2.767

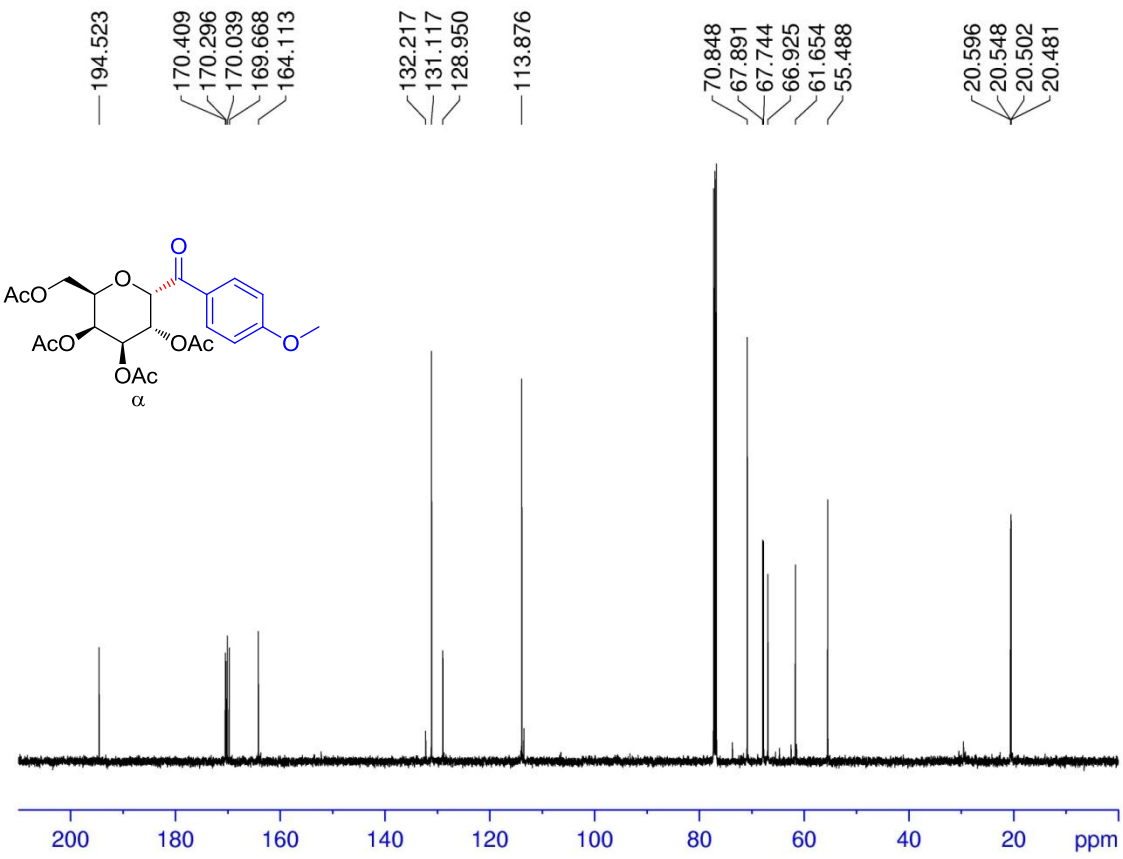

195.930
170.287
170.265
170.001
169.637
144.911
133.505
129.360
128.732
70.981
70.871
67.818
67.717
66.827
61.596
21.608
20.567
20.518
20.445
20.385
AcO
AcO
OAc
OAc
O
200
180
160
140
120
100
80
60
40
20
ppm
AcO
AcO
OAc
OAc
O
α: β= 4.2:1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.536
2.019
2.467
1.000
1.242
2.277
0.227
0.260
1.040
2.950
3.785
0.729
3.122
0.787
1.003
3.009
0.702
3.188
0.686
2.941

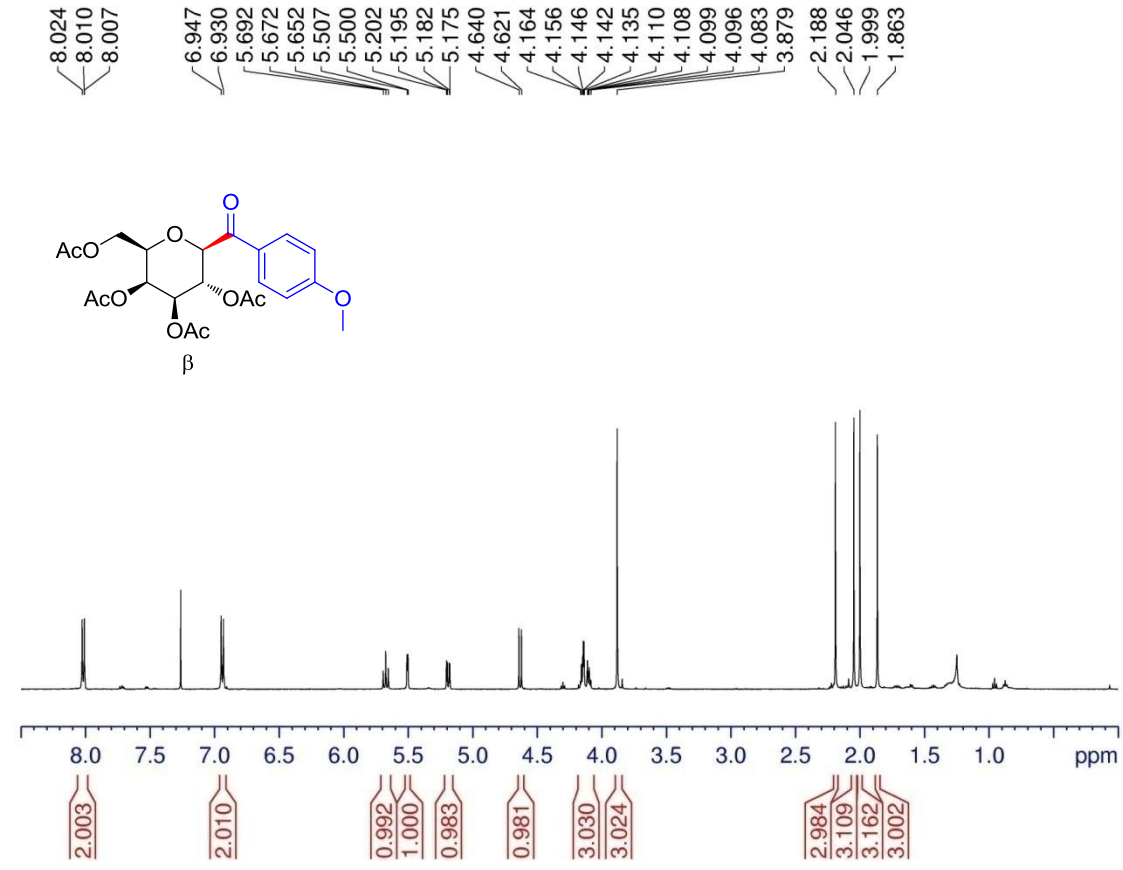

7.588
7.585
7.573
7.570
7.487
7.484
7.470
7.456
7.452
7.020
7.006
6.991
6.941
6.924
5.834
5.821
5.607
5.601
5.587
5.581
5.524
5.516
5.511
5.507
5.490
4.690
4.679
4.668
4.665
4.122
4.108
4.099
4.085
4.069
4.057
4.046
4.034
3.848
2.116
1.978
1.962
1.718
AcO
AcO
OAc
OAc
α
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.999
1.029
1.011
0.991
0.940
0.963
1.940
0.917
2.051
2.947
2.873
5.799
2.811
199.465
170.423
170.044
169.929
169.702
158.210
134.327
130.626
127.590
120.986
111.522
73.988
70.817
68.139
67.869
66.642
61.705
55.557
20.639
20.603
20.579
20.253

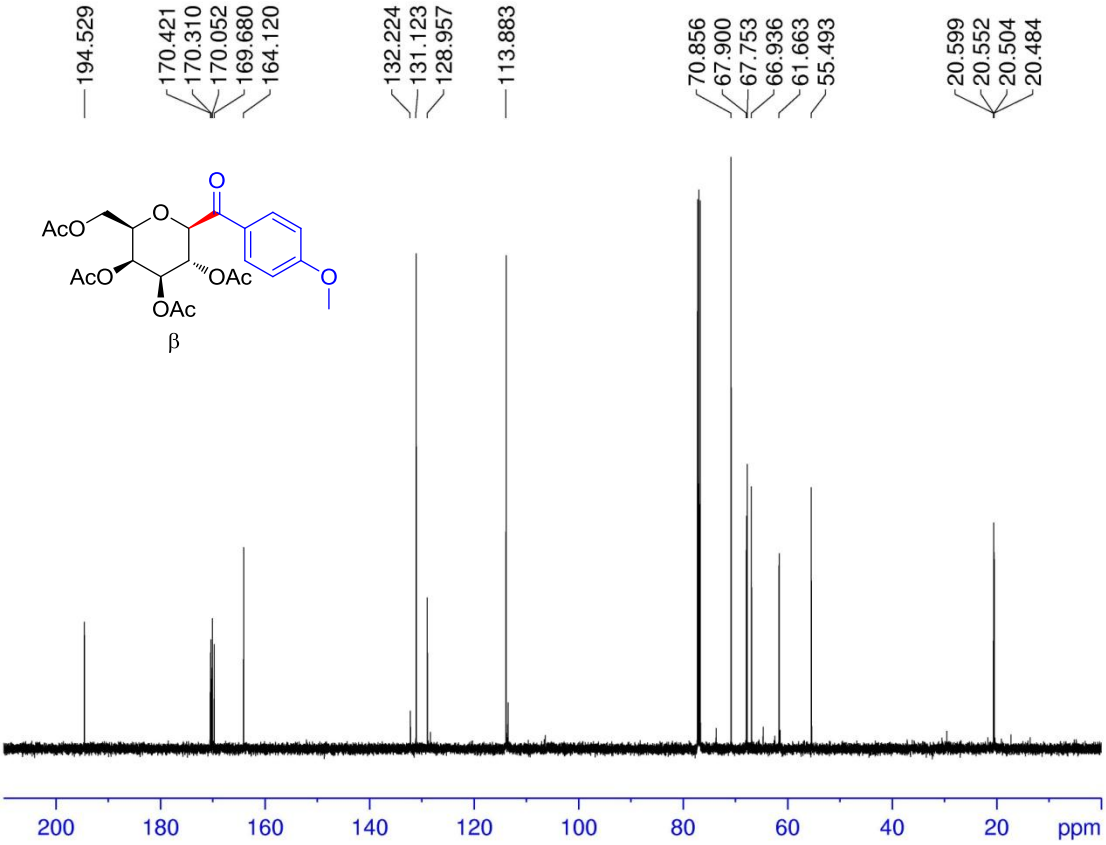

AcO
AcO
OAc
OAc
α
O
O
200
180
160
140
120
100
80
60
40
20
ppm

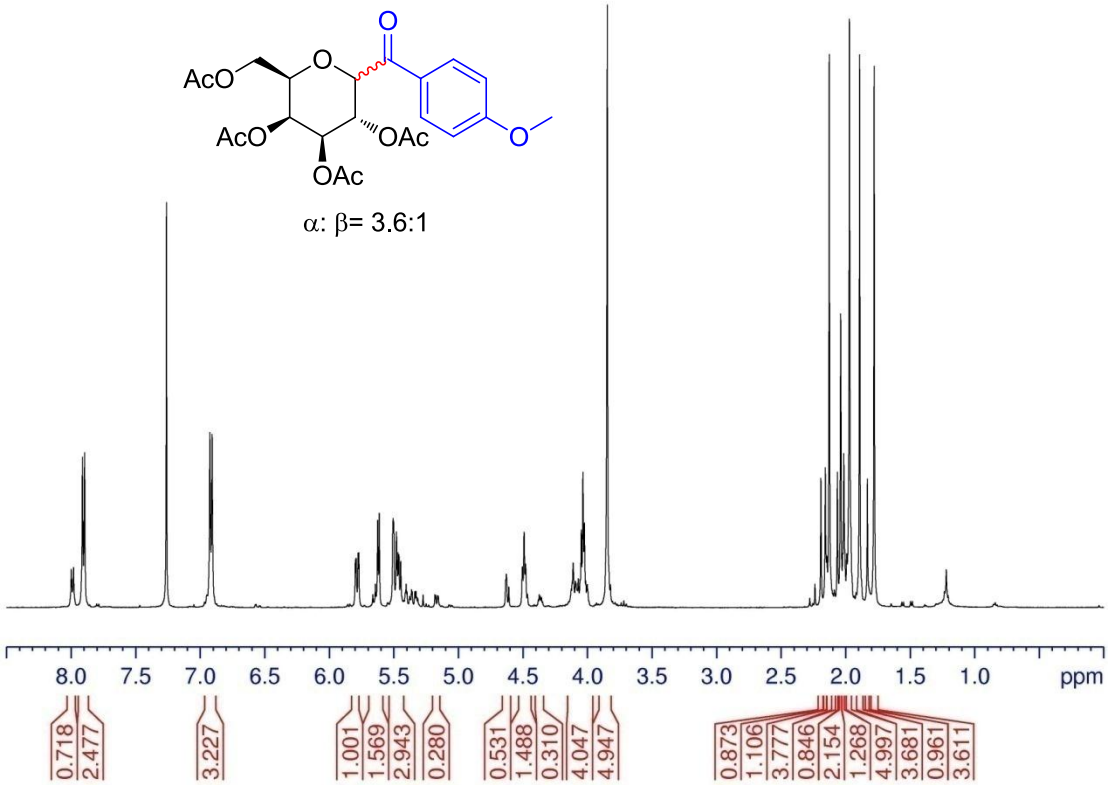

AcO
AcO
OAc
OAc
O
O
α: β= 4.5:1
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.250 1.042 1.352 2.939 1.000 1.061 2.665 0.225 0.161 0.969 3.444 0.248 0.748 3.141 3.281 3.542 1.397 2.249 0.480 2.901
7.923 7.919 7.905 6.935 6.917 5.809 5.803 5.788 5.782 5.635 5.622 5.514 5.511 5.490 5.477 5.470 5.457 4.514 4.502 4.491 4.083 4.069 4.060 4.047 4.035 4.025 4.012 3.858 2.139 1.983 1.905 1.792

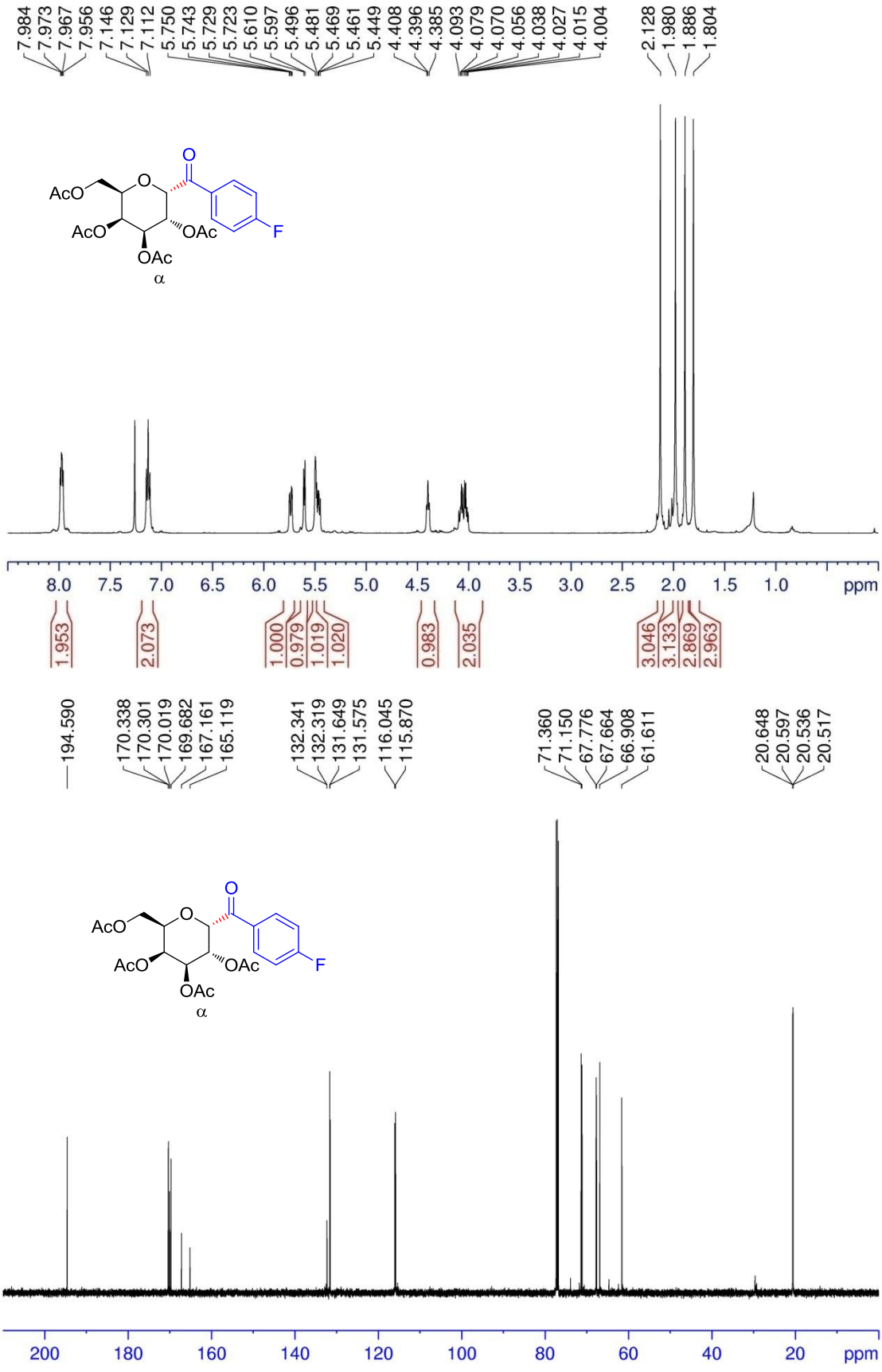

AcO
AcO
OAc
OAc
α
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.261 2.296 1.000 1.031 2.113 1.055 2.061 3.256 3.293 3.040 3.047 3.074

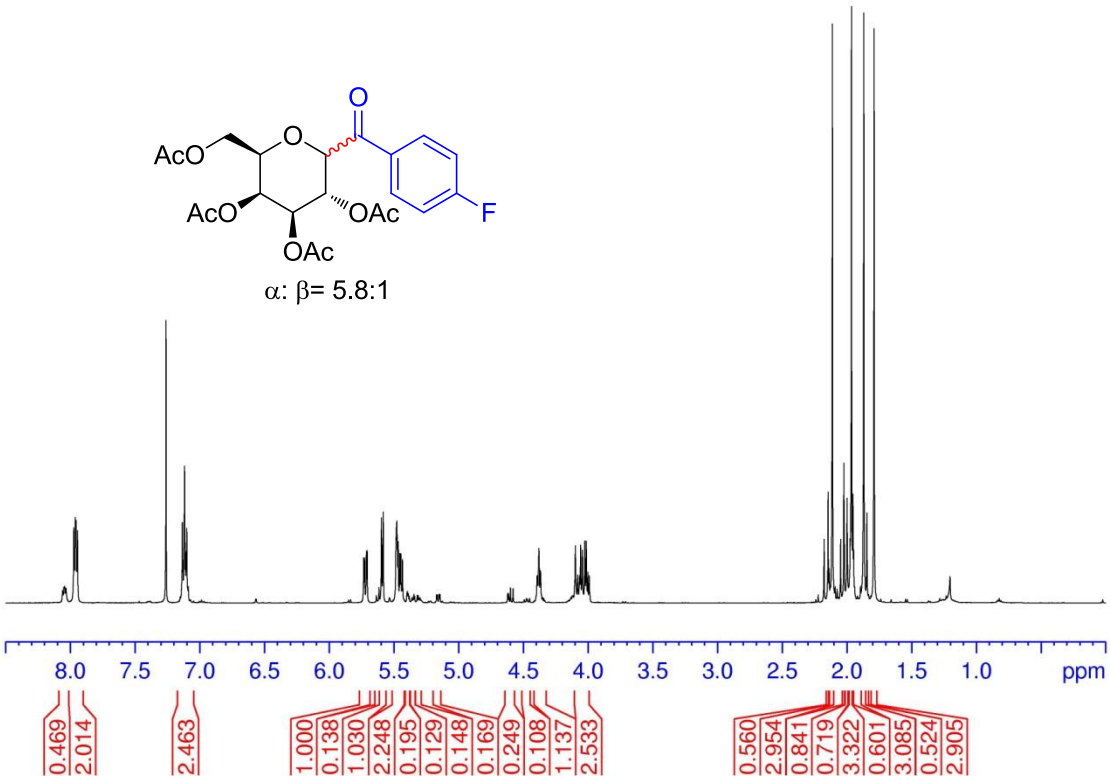

194.523
170.409
170.296
170.039
169.668
164.113
132.217
131.117
128.950
113.876
70.848
67.891
67.744
66.925
61.654
55.488
20.596
20.548
20.502
20.481
AcO
AcO
OAc
OAc
O
O
α
200
180
160
140
120
100
80
60
40
20
ppm

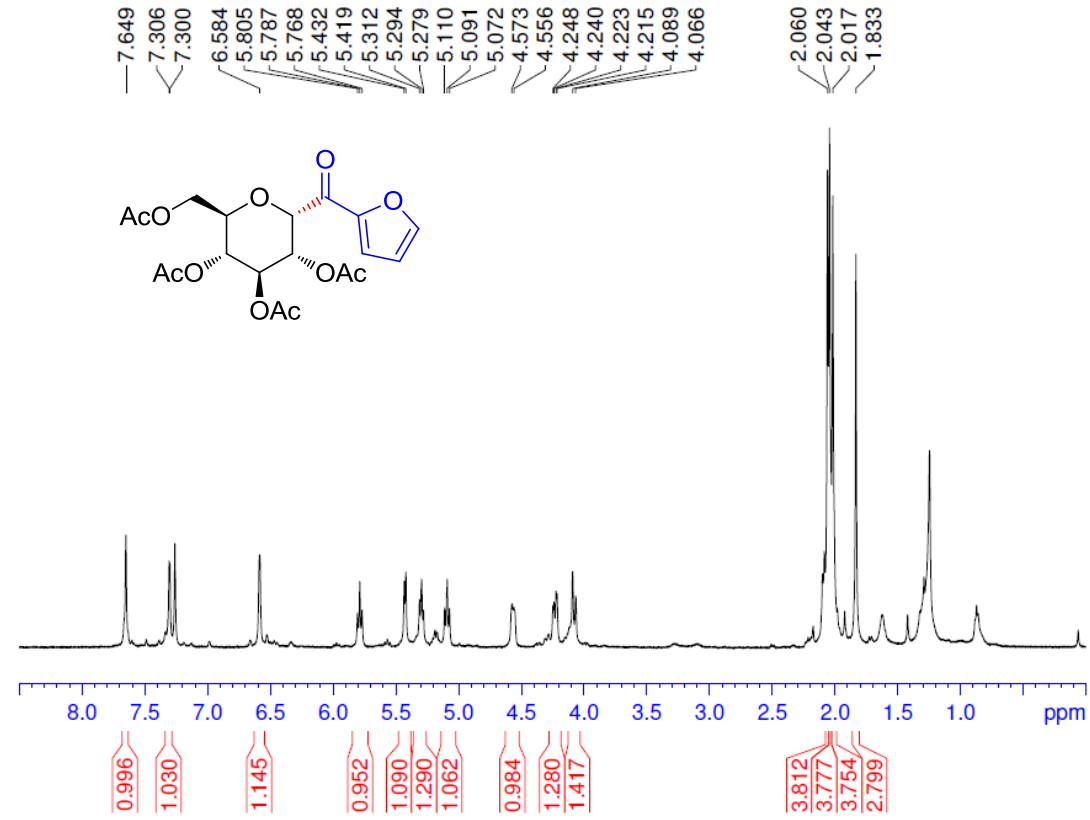

8.024
8.010
8.007
6.947
6.930
5.692
5.672
5.652
5.507
5.500
5.202
5.195
5.182
5.175
4.640
4.621
4.164
4.156
4.146
4.142
4.135
4.110
4.108
4.099
4.096
4.083
3.879
2.188
2.046
1.999
1.863
AcO
AcO
OAc
OAc
O
O
β
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.003
2.010
0.992
1.000
0.983
0.981
3.030
3.024
2.984
3.109
3.162
3.002


194.529
170.421
170.310
170.052
169.680
164.120
132.224
131.123
128.957
113.883
70.856
67.900
67.753
66.936
61.663
55.493
20.599
20.552
20.504
20.484
AcO
AcO
OAc
OAc
O
O
β
200
180
160
140
120
100
80
60
40
20
ppm


AcO
AcO
OAc
OAc
O
O
α: β= 3.6:1
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
ppm
0.718
2.477
3.227
1.001
1.569
2.943
0.280
0.531
1.488
0.310
4.047
4.947
0.873
1.106
3.777
0.846
2.154
1.268
4.997
3.681
0.961
3.611


7.984
7.973
7.967
7.956
7.146
7.129
7.112
5.750
5.743
5.729
5.723
5.610
5.597
5.496
5.481
5.469
5.461
5.449
4.408
4.396
4.385
4.093
4.079
4.070
4.056
4.038
4.027
4.015
4.004
2.128
1.980
1.886
1.804
AcO
AcO
OAc
OAc
O
O
F
α
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
ppm
1.953
2.073
1.000
0.979
1.019
1.020
0.983
2.035
3.046
3.133
2.869
2.963
194.590
170.338
170.301
170.019
169.682
167.161
165.119
132.341
132.319
131.649
131.575
116.045
115.870
71.360
71.150
67.776
67.664
66.908
61.611
20.648
20.597
20.536
20.517
AcO
AcO
OAc
OAc
O
O
F
α
200
180
160
140
120
100
80
60
40
20
ppm


AcO
O
AcO
OAc
OAc
F
α: β= 5.8:1
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 ppm
0.469 2.014 2.463 1.000 0.138 1.030 2.248 0.195 0.129 0.148 0.169 0.249 0.108 1.137 2.533 0.560 2.954 0.841 0.719 3.322 0.601 3.085 0.524 2.905


7.649 7.306 7.300 6.584 5.805 5.787 5.768 5.432 5.419 5.312 5.294 5.279 5.110 5.091 5.072 4.573 4.556 4.248 4.240 4.223 4.215 4.089 4.066 2.060 2.043 2.017 1.833
AcO
O
O
AcO
OAc
OAc
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.996 1.030 1.145 0.952 1.090 1.290 1.062 0.984 1.280 1.417 3.812 3.777 3.754 2.799