Supporting Information

Stereocontrolled Synthesis of 2-Deoxy-*C*-Glycopyranosyl Arenes Using Glycals and Aromatic Amines

Shengbiao Tang,[†, ‡] Qiannan Zheng,[†] De-Cai Xiong,*[,†,§] Shende Jiang,[‡] Qin Li,[†] and Xin-Shan Ye*[,†]

†State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Road No. 38, Beijing 100191, China

‡School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

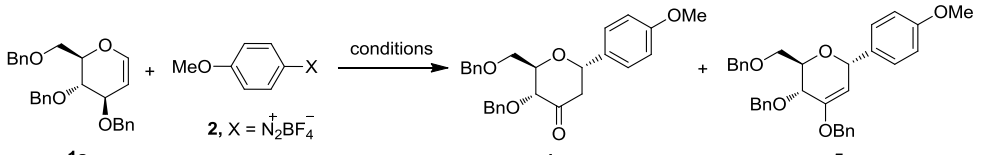
§ State key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences

Table of Contents

1) General information

All reagents were purchased as reagent grade and used without further purification unless otherwise indicated. The Pd-catalysts were purchased from Sigma-Aldrich company Ltd. THF (99.5+% extra pure) was purchased. Organic solutions were removed by rotary evaporation with a water bath temperature below 50 °C. Reactions were monitored by thin-layer chromatography (TLC) analysis, and stained by the solution of potassium permanganate or acidic ceric ammonium molybdate. Product purification was subjected by column chromatography on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at 20 ^{o}C. The residual solvent of $CDCl_3$ (7.26 ppm for ^{1}H NMR), TMS (0 ppm for ^{1}H NMR) was used as an internal standard for ^{1}H NMR spectra, and the residual solvent of $CDCl_3$ (77.16 ppm for ^{13}C NMR) was used as an internal standard for ^{13}C NMR. Chemical shifts (δ) were recorded in ppm, coupling constants (*J*) were reported in Hz. The abbreviations are as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. High resolution mass spectra were obtained using a Fourier transform ion cyclotron resonance mass spectrometer.

2) Table S1. Screening the reaction conditions[ab]

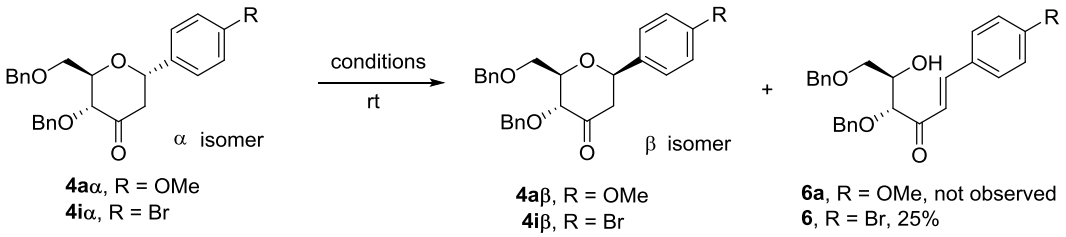


entry	substrate	solvent	catalyst (15%)	ligand (20%)	additive (10 equiv.)	**4aα**(%)	**5a** (%)
1	**2**	THF	$Pd(OAc)_2$	-	-	0	trace
2	**2**	THF	$Pd(OAc)_2$	Ph_3P	-	34	25
3	**2**	THF	$Pd(PPh_3)_4$	-	-	36	31
4	**2**	THF	$Pd(PPh_3)_4$	xanphose	-	33	30

5	**2**	THF	$Pd(dba)_2$	-	-	81	0
6	**2**	THF	$Pd(dba)_2$	Ph_3P	-	74	0
7	**2**	THF	$Pd(dba)_2$	-	$NaHCO_3$	53	26
8	**2**	THF	$Pd(dba)_2$	-	K_2CO_3	56	17
9	**2**	THF	$Pd(dba)_2$	-	K_3PO_4	46	20
10	**2**	THF	$Pd(dba)_2$	-	NaOH	0	21
11	**2**	THF	$Pd(dba)_2$	-	DMAP	0	0
12	**2**	THF	$Pd(dba)_2$	-	Et_3N	0	0
13	**2**	THF	$Pd(dba)_2$	-	H_2O	62	0
14	**2**	THF	$Pd(dba)_2$	-	AcOH	76	0
15	**2**	THF	$Pd(dba)_2$	-	2M HCl	31	0
16	**2**	Acetone	$Pd(dba)_2$	-	-	31	0
17	**2**	CH_3CN	$Pd(dba)_2$	-	-	0	0
18	**2**	DMF	$Pd(dba)_2$	-	-	0	0
19	**2**	DCM	$Pd(dba)_2$	-	-	0	0
20[c]	**3**	THF	$Pd(dba)_2$	-	$NaNO_2$+HBF_4	0	0
21[c]	**3**	MeOH	$Pd(dba)_2$	-	$NaNO_2$+HBF_4	0	0
22[c]	**3**	THF	$Pd(dba)_2$	-	^{t}Butyl nitrite +HBF_4	trace	0
23[c]	**3**	THF	$Pd(dba)_2$	-	$NOBF_4$	73	0

[a]The reactions of entries 1-19 were carried out with **1a** (21.0 mg, 0.05 mmol), **2** (22.0 mg, 0.1 mmol) and solvent (4 mL) at room temperature for 1 h; [b]Isolated yield; [c]The reactions of entries 20-23 were carried out in one-pot protocol: *p*-anisidine **3** (31.0 mg，0.25 mmol), additives (0.25 mmol of each) at 0 ^oC for 30 min, then **1a** (42.0 mg, 0.1 mmol) and $Pd(dba)_2$ (15 mol%) were added, and then stirred at r.t. for 1 h.

3) Table S2. Investigation of anomerization[ab]



4aα, R = OMe
4iα, R = Br

4aβ, R = OMe
4iβ, R = Br

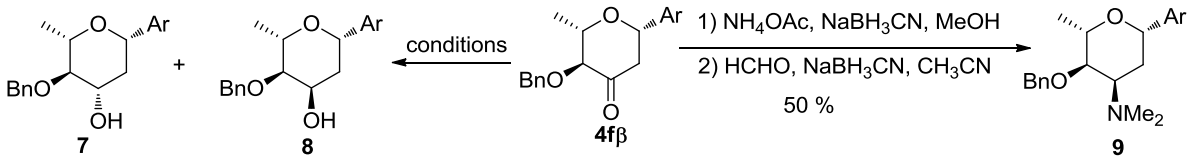
6a, R = OMe, not observed
6, R = Br, 25%

entry	catalyst	solvent	**4aβ** R = OMe yield (%)	**4iβ** R = Br yield (%)
1	HBF_4, 12.5 μL	Et_2O	0	0
2	HBF_4, 25 μL	Et_2O	trace	0
3	HBF_4, 50 μL	Et_2O	92	32
4	HBF_4, 75 μL	Et_2O	86	51
5	HBF_4, 100 μL	Et_2O	78	46
6	$BF_3{\cdot}Et_2O$, 100 μL	Et_2O	23	0
7	$SnCl_4$, 100 μL	Et_2O	45	0
8	con. HCl, 100 μL	Et_2O	0	0
9	HBF_4, 50 μL	isopropyl ether	82	50
10	HBF_4, 50 μL	$^nBu_2O$	65	trace
11	HBF_4, 50 μL	glycol dimethyl ether	0	0
12	HBF_4, 50 μL	methyl ^{t}butyl ether	0	0
13	HBF_4, 50 μL	dichloromethane	0	0
14	HBF_4, 50 μL	ethyl acetate	86	0
15	HBF_4, 50 μL	CH_3CN	trace	0
16	HBF_4, 50 μL	acetone	85	0
17	HBF_4, 50 μL	DMF	0	0
18	HBF_4, 50 μL	dichloroethene	0	0
19	HBF_4, 50 μL	octane	0	0

20	HBF_4, 50 μL	THF	50	trace
21	HBF_4, 50 μL	toluene	22	0
22	HBF_4, 50 μL	MeOH	0	0

[a]All reactions were carried out with **4aα** (10.0 mg), HBF_4 (50% V/V in Et_2O) in solvent (1 mL) at room temperature for 1 h; **4iα** (10.0 mg), HBF_4 (50% V/V in Et_2O) in solvent (1 mL) at room temperature for 5 h. [b] Isolated yield.

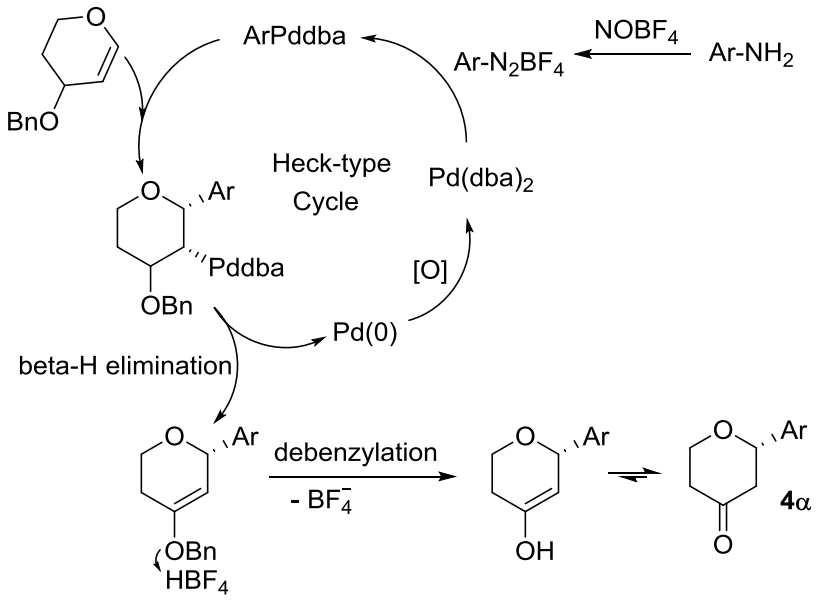
4) Table S3. Reduction and reductive-amination of the compound 4fβ



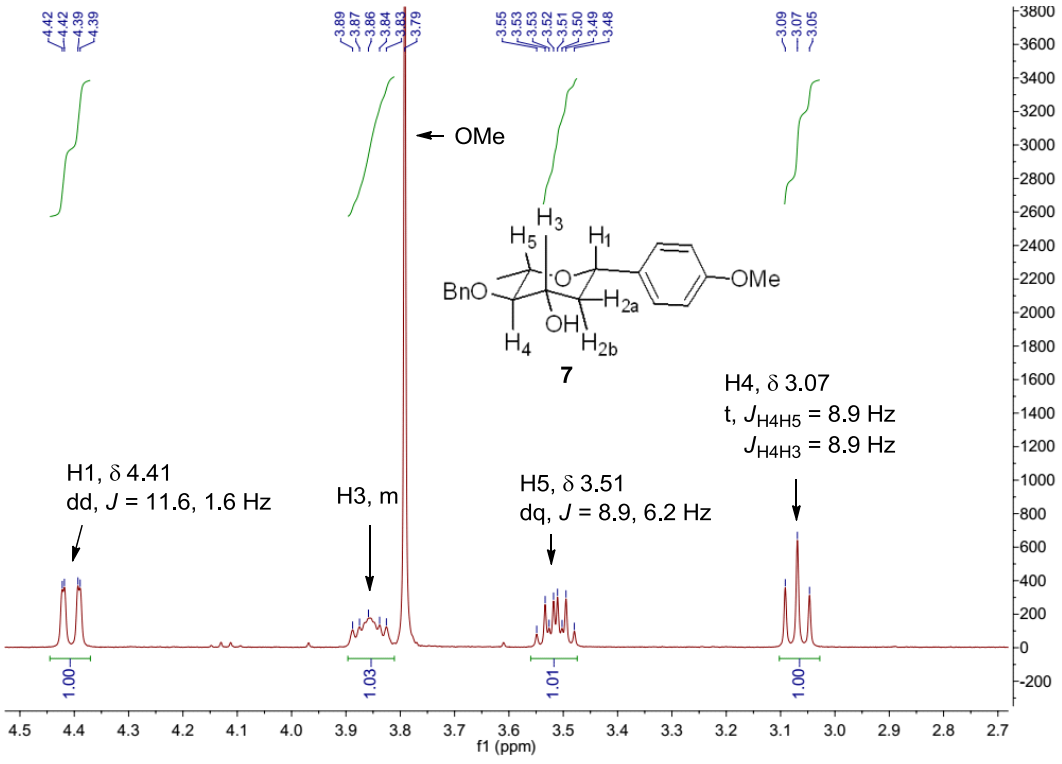
Ar = *p*-Methoxyphenyl

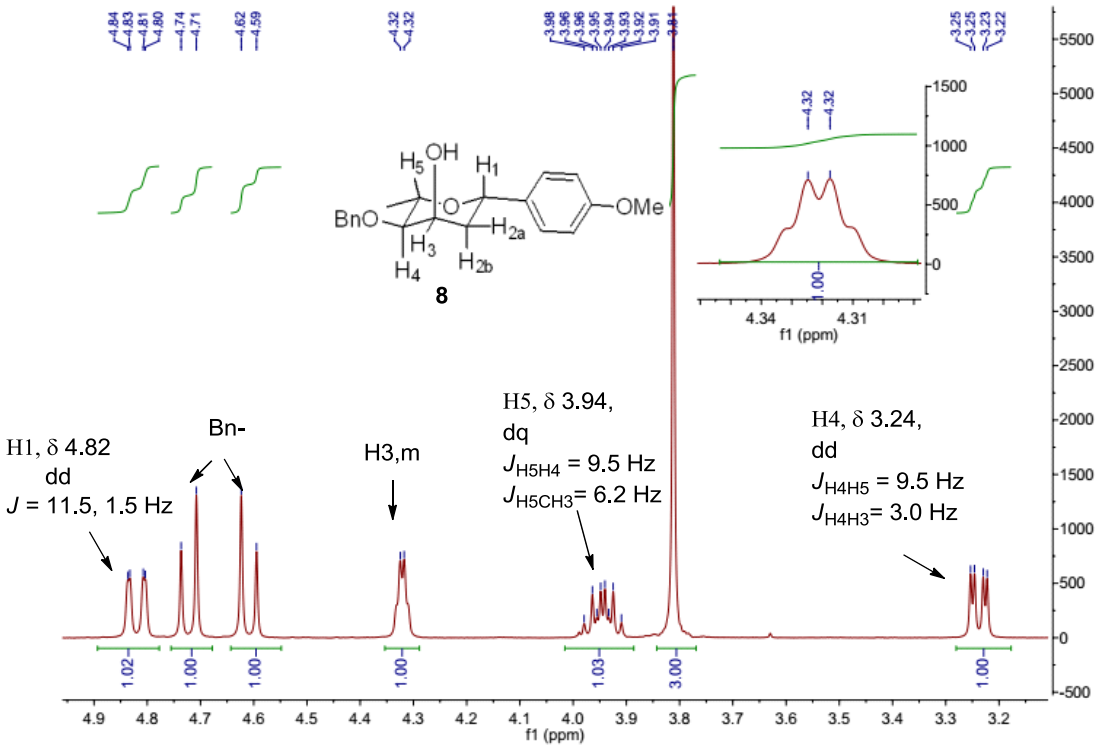
entry	conditions	**7** (%)	**8** (%)
1	$NaBH_4$, THF, rt, 1 h	42	40
2	$LiBH_4$, THF, rt, 1h	40	41
3	$LiBHEt_3$, 0 ^oC, 24 h	trace	78
4	Pd/C (10%), rt, 24 h	10	73
5	$NaBHAc_3$, MeOH, 24 h	0	0
6	$NaBHAc_3$, MeCN/AcOH = 2/1, rt, 24 h	45	36
7	$LiAlH_4$, THF, 0 ^oC, 1 h	20	25

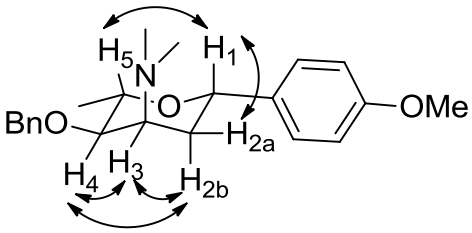
5) Scheme S1. Plausible mechanism of the arylation



6) Scheme S2. NMR analyses of compounds 7-9.



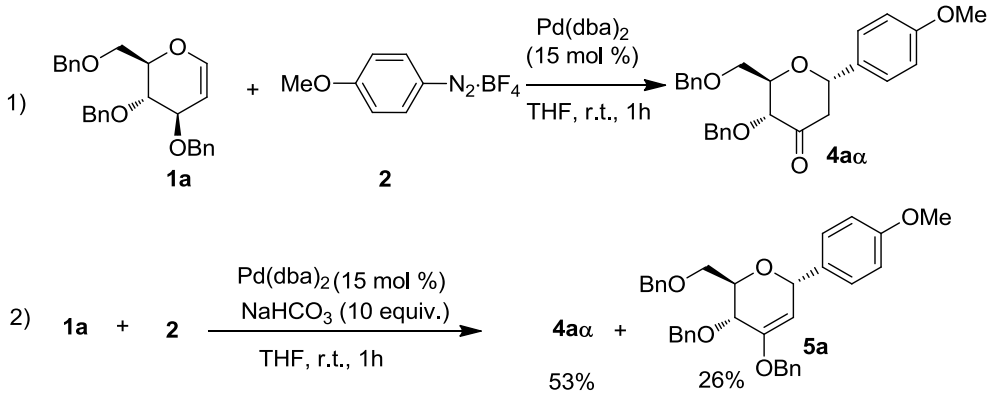




NOE analysis of the compound **9**

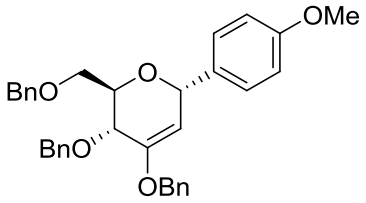
7） Experimental procedures and compound characterization data

Procedure A： The preparation of 4aα from glucal 1a and 2:



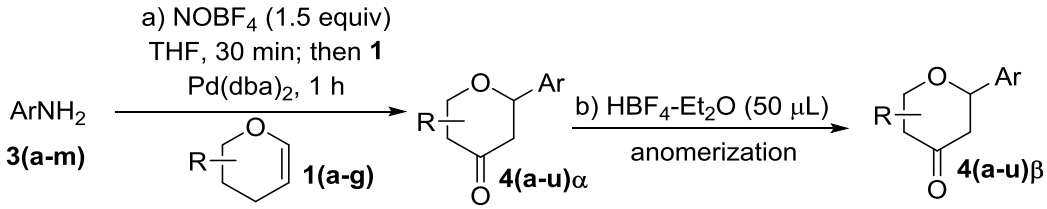
To a solution of 4-methoxybenzenediazonium tetrafluoroborate (**2**) (22.0 mg，0.1 mmol) in tetrahydrofuran (4 mL) were added the glucal **1a** (21.0 mg, 0.05 mmol) and bis(dibenzylideneacetone)palladium (4.5 mg, 15 mol%) at room temperature, and the mixture was stirred for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4aα** as a white foam (18.0 mg, 81%). R_f = 0.23 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{21}$ = +120.8 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 12H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.44 (dd, *J* = 6.2, 2.6 Hz, 1H), 4.85 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 11.1 Hz, 1H), 4.23 (d, *J* = 8.3 Hz, 1H), 3.77 (s, 3H), 3.71 – 3.61 (m, 3H), 3.09 (dd, *J* = 14.6, 2.9 Hz, 1H), 3.03 (dd, *J* = 14.7, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.86, 159.57, 138.06, 137.59, 130.80, 129.02, 128.53, 128.50, 128.35, 128.05, 127.99, 127.87, 114.19, 79.87, 75.02, 74.39, 73.71, 73.62, 69.28, 55.43, 44.24; HMRS (ESI) calcd for $C_{27}H_{29}O_5$ [M + H]$^+$ 433.2010, found 433.2007.

1-Methoxy-4-(3,4,6-tri-*O*-benzyl-2-deoxy-2,3-didehydro-α-D-glucopyranosyl) benzene (5a):

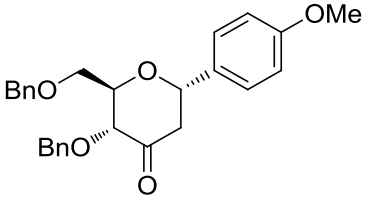


Colorless oil (6.8 mg, 26%), R_f = 0.31 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{26}$ = +34.9 (c 0.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 17H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.33 (d, *J* = 2.7 Hz, 1H, H-1), 5.00 (d, *J* = 3.4 Hz, 1H, H-2), 4.94 – 4.79 (m, 3H, Bn), 4.56 (d, *J* = 11.3 Hz, 1H, Bn), 4.54 (d, *J* = 11.3 Hz, 1H, Bn), 4.42 (d, *J* = 12.2 Hz, 1H, Bn), 4.21 (d, *J* = 6.5 Hz, 1H, H-4), 3.90 – 3.84 (m, 1H, H-5), 3.79 (s, 3H, -OMe), 3.65 (dd, *J* = 10.4, 4.6 Hz, 1H, H-6a), 3.53 (dd, *J* = 10.4, 3.5 Hz, 1H, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.53, 153.44, 138.64, 138.35, 137.06, 133.06, 129.70, 128.63, 128.45, 128.38, 128.34, 128.00, 127.97, 127.73, 127.71, 127.53, 113.75, 99.28, 73.66, 73.44, 73.36, 72.21, 71.64, 69.29, 69.10, 55.43; HMRS (ESI) calcd for $C_{34}H_{35}O_5$ $[M + H]^+$ 523.2484, found 523.2484.

Procedure B：The preparation of 4(a-u)α and 4(a-u)β



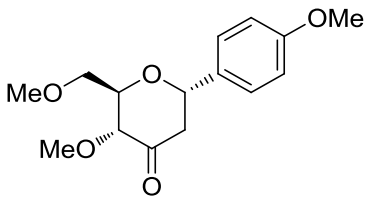
(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H -pyran-4-one (4aα):



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at

room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4aα** as a white foam (31.9 mg, 73%). R_f = 0.23 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{21}$ = +120.8 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 12H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.44 (dd, *J* = 6.2, 2.6 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.85 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 11.1 Hz, 1H), 4.23 (d, *J* = 8.3 Hz, 1H), 3.77 (s, 3H), 3.71 – 3.61 (m, 3H), 3.09 (dd, *J* = 14.6, 2.9 Hz, 1H), 3.03 (dd, *J* = 14.7, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.86, 159.57, 138.06, 137.59, 130.80, 129.02, 128.53, 128.50, 128.35, 128.05, 127.99, 127.87, 114.19, 79.87, 75.02, 74.39, 73.71, 73.62, 69.28, 55.43, 44.24; HMRS (ESI) calcd for $C_{27}H_{29}O_5$ $[M + H]^+$ 433.2010, found 433.2007.

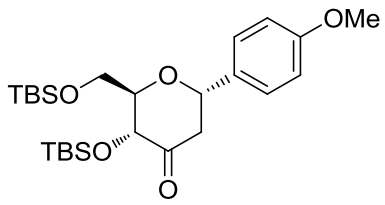
(2R,3R,6S)-3-Methoxy-2-methoxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4bα):



To a solution of *p*-anisidine (**3**) (31.0 mg，0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension

was observed. Then the glucal **1b** (19.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/3) to afford **4bα** as a white foam (18.5 mg, 65%). R_f = 0.24 (ethyl acetate/petroleum ether: 1/3); $[\alpha]_D^{17}$ = +128.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 6.85(d, *J* = 8.6 Hz, 2H), 5.42 (dd, *J* = 6.2, 2.6 Hz, 1H, H-1, $^4C_1$ (D, α)), 3.94 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 3.62 – 3.54 (m, 3H), 3.50 (s, 3H), 3.42 (s, 3H), 3.07 (dd, *J* = 14.6, 2.8 Hz, 1H), 3.01 (dd, *J* = 14.8, 6.8 Hz, 1H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.89, 159.57, 130.69, 129.03, 114.17, 81.97, 75.05, 74.16, 71.74, 59.67, 59.52, 55.39, 44.07; HMRS (ESI) calcd for $C_{15}H_{21}O_5$ [M + H]$^+$ 281.1384, found 281.1376.

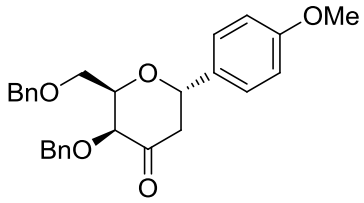
(2R,3R,6S)-3-*tert*-Butyldimethylsilyloxy-2-butyldimethylsilyloxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4cα):



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the glucal **1c** (49.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate

solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/20) to afford **4cα** as a colorless oil (30.3 mg, 63%). R_f = 0.33 (ethyl acetate/petroleum ether: 1/20); $[\alpha]_D^{17}$ = +68.3 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.39 (dd, *J* = 6.8, 2.7 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.30 (d, *J* = 9.0 Hz, 1H), 3.88 – 3.75 (m, 2H), 3.79 (s, 3H), 3.50 – 3.45 (m, 1H), 3.05 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.92 (dd, *J* = 14.6, 6.9 Hz, 1H), 0.91 (s, 9H), 0.88 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.82, 159.36, 131.34, 128.81, 114.09, 75.13, 74.62, 63.32, 55.41, 43.83, 26.07, 25.94, 18.57, 18.54, -4.12, -4.90, -5.20, -5.42; HMRS (ESI) calcd for $C_{25}H_{45}O_5Si_2$ $[M + H]^+$ 481.2801, found 481.2795.

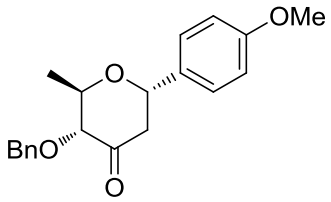
(2R,3S,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4dα):



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the galactal **1d** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica

gel (ethyl acetate/petroleum ether: 1/10) to afford **4dα** as a yellow foam (25.0 mg, 57%). R_f = 0.34 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{19}$ = +39.5 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 12H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.27 (dd, *J* = 9.5, 3.6 Hz, 1H, H-1, $^1C_4$ (D, α)), 4.93 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.5 Hz, 2H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.43 – 4.37 (m, 1H), 4.15 (d, *J* = 6.4 Hz, 1H), 3.86 – 3.76 (m, 2H), 3.80 (s, 3H), 2.80 (dd, *J* = 14.4, 3.7 Hz, 1H), 2.66 (dd, *J* = 14.1, 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.60, 159.53, 138.10, 137.60, 132.70, 128.65, 128.49, 128.12, 127.98, 127.81, 127.75, 127.60, 114.08, 79.45, 76.36, 74.68, 73.70, 72.78, 68.58, 55.44, 47.86; HMRS (ESI) calcd for $C_{27}H_{29}O_5$ $[M + H]^+$ 433.2010, found 433.2008.

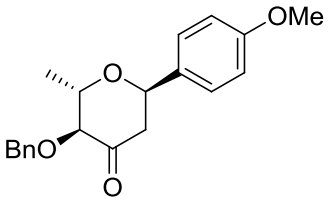
(2R,3R,6S)-3-Benzyloxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4eα):



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the 6-deoxy-glucal **1e** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4eα** as a white foam (25.5 mg, 78%). R_f = 0.35 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{19}$ = +102.8 (c 0.4, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.27 (dd, *J* = 6.4, 2.9 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.87 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 3.79 (s, 3H), 3.82 – 3.72 (m, 1H), 3.66 (d, *J* = 7.9 Hz, 1H), 3.11 (dd, *J* = 14.2, 3.1 Hz, 1H), 2.93 (dd, *J* = 13.9, 6.6 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.77, 159.52, 137.53, 131.32, 128.79, 128.57, 128.37, 128.12, 114.16, 85.03, 74.56, 73.25, 71.65, 55.44, 44.75, 18.38; HMRS (ESI) calcd for $C_{20}H_{23}O_4$ $[M + H]^+$ 327.1591, found 327.1592.

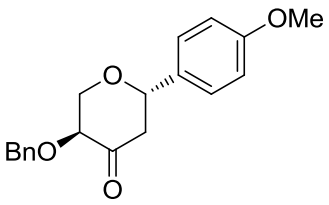
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4fα).



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4fα** as a light yellow foam (23.0 mg, 70%). R_f = 0.36 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{20}$ = -141.2 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 7H), 6.88 – 6.84 (m, 2H), 5.27 (dd, *J* = 6.7, 3.3 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.87 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 3.79 (s, 3H), 3.81 – 3.73 (m, 1H), 3.66 (dd, *J* = 8.0, 0.9 Hz, 1H), 3.11 (dd, *J* = 14.2, 3.3 Hz,

1H), 2.93 (ddd, *J* = 14.2, 6.7, 1.0 Hz, 1H), 1.28 (d, *J* = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.80, 159.52, 137.52, 131.31, 128.80, 128.57, 128.38, 128.13, 114.15, 85.03, 74.56, 73.26, 71.64, 55.44, 44.74, 18.38; HMRS (ESI) calcd for $C_{20}H_{23}O_4$ $[M + H]^+$ 327.1586, found 327.1586.

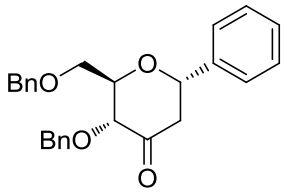
(3S,6R)-3-Benzyloxy-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4gβ).



To a solution of *p*-anisidine (**3**) (31.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the arabinal **1g** (30.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4gβ** as a white foam (17.3 mg, 55%). R_f = 0.43 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -98.2 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 7H), 6.91 – 6.87 (m, 2H), 4.95 (d, *J* = 11.9 Hz, 1H, Bn-), 4.60 (d, *J* = 12.0 Hz, 1H, Bn-), 4.60 – 4.57 (m, 1H, H-1), 4.40 (dd, *J* = 10.9, 7.2 Hz, 1H, H-5a), 4.19 (dd, *J* = 10.4, 7.3 Hz, 1H, H-5b), 3.80 (s, 3H), 3.62 (t, *J* = 10.7 Hz, 1H, H-4), 2.76 – 2.66 (m, 2H, H-2a, 2b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.15, 159.77, 137.57, 132.18, 128.75, 128.27, 128.15, 127.18, 114.23, 80.65, 79.16,

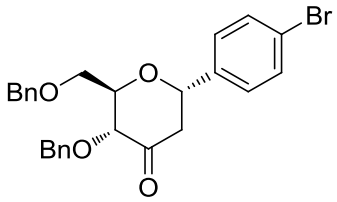
72.94, 70.72, 55.47, 49.90; HMRS (ESI) calcd for $C_{19}H_{20}O_4Na$ $[M + Na]^+$ 335.1254, found 335.1256.

(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-phenyl-tetrahydro-4H-pyran-4-one (4hα):



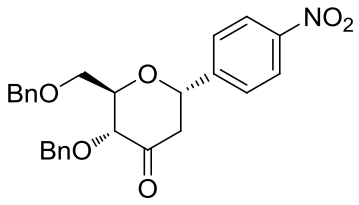
To a solution of aniline (**3b**) (23.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4hα** as a white foam (30.5 mg, 76%). R_f = 0.29 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{19}$ = +85.3 (c 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 15H), 5.48 (dd, *J* = 6.6, 3.1 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.84 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.43 (d, *J* = 11.1 Hz, 1H), 4.24 (d, *J* = 8.6 Hz, 1H), 3.76 – 3.68 (m, 2H), 3.65 (dd, *J* = 10.4, 2.2 Hz, 1H), 3.12 (dd, *J* = 14.7, 3.2 Hz, 1H), 3.03 (dd, *J* = 14.7, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.55, 138.78, 138.04, 137.54, 128.87, 128.54, 128.52, 128.36, 128.32, 128.08, 127.99, 127.89, 127.54, 79.78, 75.35, 74.85, 73.72, 73.58, 69.33, 44.15. The $^1H/^{13}C$ NMR spectroscopic data coincide with the previous report.[1]

(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-bromophenyl)-tetrahydro-4H-pyran-4-one (4iα):



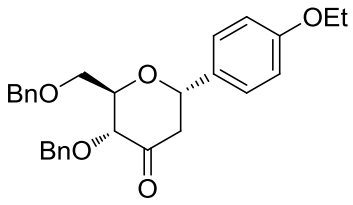
To a solution of *p*-bromoaniline (**3c**) (43.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4iα** as a white foam (37.5 mg, 78%). R_f = 0.30 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{19}$ = +104.5 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.24 (m, 12H), 5.41 (dd, *J* = 5.5, 3.9 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.82 (d, *J* = 11.2 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 8.6 Hz, 1H), 3.72 – 3.62 (m, 3H), 3.06 (dd, *J* = 14.9, 3.9 Hz, 1H), 3.01 (dd, *J* = 15.1, 6.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.10, 137.92, 137.89, 137.41, 132.01, 129.20, 128.56, 128.53, 128.34, 128.12, 127.96, 127.93, 122.47, 79.60, 75.18, 74.80, 73.74, 73.50, 69.32, 44.11; HMRS (ESI) calcd for $C_{26}H_{29}O_4NBr$ $[M + NH_4]^+$ 498.1280, found 498.1281.

(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-nitrophenyl)-tetrahydro-4H-pyran-4-one (4jα):



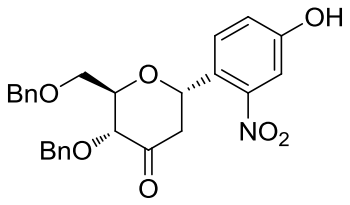
To a solution of *p*-nitroaniline (**3d**) (35.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4jα** as a white foam (32.7 mg, 73%). R_f = 0.21 (ethyl acetate/petroleum ether: 1/3); $[\alpha]_D^{23}$ = +74.1 (c 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.26 (m, 10H), 5.52 (t, *J* = 5.3 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.81 (d, *J* = 11.2 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.21 (d, *J* = 7.8 Hz, 1H), 3.82 – 3.77 (m, 1H), 3.70 (d, *J* = 2.9 Hz, 2H), 3.08 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.02 (dd, *J* = 14.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.11, 147.86, 146.46, 137.79, 137.24, 128.63, 128.60, 128.36, 128.23, 128.06, 127.94, 124.06, 79.34, 76.31, 74.58, 73.82, 73.33, 69.63, 44.40; HMRS (ESI) calcd for $C_{26}H_{29}O_6N_2$ $[M + NH_4]^+$ 465.2021, found 465.2018.

(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-ethoxyphenyl)-tetrahydro-4H-pyran-4-one (4kα):



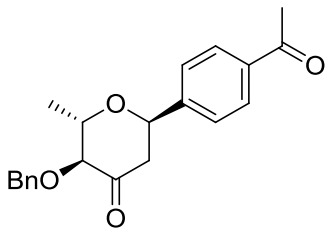
To a solution of *p*-phenetidine (**3e**) (34.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/6) to afford **4kα** as a gray foam (34.1 mg, 76%). R_f = 0.19 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = +93.8 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 1H), 7.34 – 7.25 (m, 12H), 7.05 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.98 (t, *J* = 5.7 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.79 (d, *J* = 11.2 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 7.3 Hz, 1H, H-4), 4.06 (qd, *J* = 7.0, 2.7 Hz, 2H, -O$CH_2$$CH_3$), 3.78 – 3.72 (m, 1H, H-5), 3.66 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.58 (dd, *J* = 10.7, 2.3 Hz, 1H), 3.07 (dd, *J* = 15.5, 5.4 Hz, 1H), 2.95 (dd, *J* = 15.3, 5.7 Hz, 1H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.93, 159.18, 149.48, 137.84, 137.34, 129.88, 128.55, 128.34, 128.15, 127.90, 127.86, 125.67, 118.93, 110.63, 79.17, 76.53, 73.71, 73.31, 70.75, 69.45, 64.50, 44.69, 14.68; HMRS (ESI) calcd for $C_{28}H_{31}O_5$ $[M + H]^+$ 447.2166, found 447.2165.

(2R,3R,6S)-3-Benzyloxy-2-benzyloxymethyl-6-(4-hydroxy-2-nitrophenyl)-tetrahydro-4H-pyran-4-one (4lα):



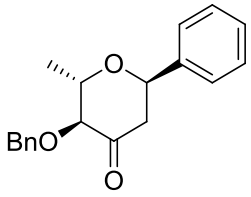
To a solution of 4-amino-3-nitrophenol (**3f**) (39.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the glucal **1a** (42.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/3) to afford **4lα** as a colorless oil (29.6 mg, 64%). R_f = 0.23 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{19}$ = +250.7 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 12H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.67 (s, 1H), 5.94 (t, *J* = 5.2 Hz, 1H, H-1, $^4C_1$ (D, α)), 4.79 (d, *J* = 11.0 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 11.0 Hz, 1H), 4.26 (d, *J* = 7.6 Hz, 1H), 3.69 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.61 – 3.55 (m, 2H), 3.08 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.98 (dd, *J* = 15.1, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.55, 156.61, 149.55, 137.62, 136.78, 129.94, 128.65, 128.60, 128.56, 128.42, 128.08, 128.00, 124.54, 119.48, 111.94, 79.34, 76.26, 73.81, 70.90, 69.08, 44.36; HMRS (ESI) calcd for $C_{26}H_{25}O_7NNa$ $[M + Na]^+$ 486.1524, found 486.1524.

(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(4-ethoxyphenyl)-tetrahydro-4H-pyran-4-one (4mα):



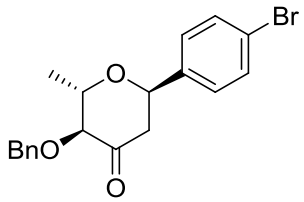
To a solution of 4-aminoacetophenone (**3g**) (34.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 1 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4mα** as a white foam (23.3 mg, 69%). R_f = 0.28 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{19}$ = -102.1 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.28 (m, 5H), 5.31 – 5.29 (m, 1H, H-1, $^1C_4$ (L, α)), 4.83 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.68 (d, *J* = 7.4 Hz, 1H), 3.15 (dd, *J* = 14.2, 4.3 Hz, 1H), 2.94 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.59 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.04, 197.68, 144.48, 137.30, 136.92, 128.85, 128.59, 128.35, 128.20, 127.35, 84.63, 74.31, 73.14, 72.84, 44.63, 26.77, 18.01; HMRS (ESI) calcd for $C_{21}H_{23}O_4$ $[M + H]^+$ 339.1591, found 339.1592.

(2S,3S,6R)-3-Benzyloxy-2-methyl-6-phenyl-tetrahydro-4H-pyran-4-one (4nα):



To a solution of aniline (**3b)** (23.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) was added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 1 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4nα** as a white foam (23.7 mg, 80%). R_f = 0.36 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{17}$ = -162.3 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 10H), 5.30 (dd, *J* = 6.6, 3.5 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.86 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 3.82 (dq, *J* = 12.6, 6.3 Hz, 1H), 3.67 (d, *J* = 7.8 Hz, 1H), 3.16 (dd, *J* = 14.2, 3.7 Hz, 1H), 2.94 (ddd, *J* = 14.2, 6.5, 0.9 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.62, 139.19, 137.43, 128.83, 128.58, 128.38, 128.25, 128.15, 127.32, 84.88, 74.81, 73.20, 72.10, 44.63, 18.24; HMRS (ESI) calcd for $C_{19}H_{20}O_3Na$ $[M + Na]^+$ 319.1305, found 319.1310.

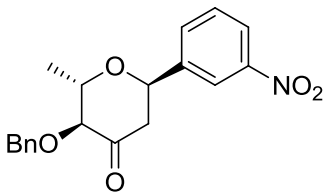
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(4-bromophenyl)-tetrahydro-4H-pyran-4-one (4oα):



To a solution of *p*-bromoaniline (**3c**) (43.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 30 min, during this period, a large amount of solid suspension

was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/12) to afford **4oα** as a white foam (28.1 mg, 75%). R_f = 0.35 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{22}$ = -98.5 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.24 (m, 7H), 5.23 (dd, *J* = 6.2, 4.0 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.84 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 3.84 – 3.76 (m, 1H), 3.66 (d, *J* = 7.6 Hz, 1H), 3.09 (dd, *J* = 14.2, 3.9 Hz, 1H), 2.92 (dd, *J* = 14.1, 6.4 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.25, 138.27, 137.31, 131.96, 129.01, 128.59, 128.36, 128.18, 122.35, 84.69, 74.22, 73.16, 72.40, 44.55, 18.13; HMRS (ESI) calcd for $C_{19}H_{19}O_3BrNa$ $[M + Na]^+$ 397.0405, found 397.0409.

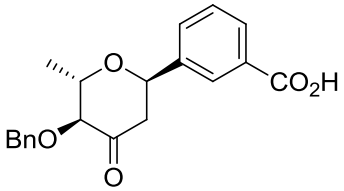
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(3-nitrophenyl)-tetrahydro-4H-pyran-4-one (4pα):



To a solution of 3-nitroaniline (**3h**) (35.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the

completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4pα** as a white foam (26.6 mg, 78%). R_f = 0.38 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{19}$ = -87.3 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.15 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.28 (m, 5H), 5.32 (t, *J* = 5.4 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.81 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 3.95 – 3.83 (m, 1H), 3.70 (d, *J* = 6.9 Hz, 1H), 3.16 (dd, *J* = 14.1, 5.0 Hz, 1H), 2.96 (ddd, *J* = 14.1, 5.9, 0.6 Hz, 1H), 1.33 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.63, 148.69, 141.67, 137.08, 132.82, 129.86, 128.61, 128.34, 128.24, 123.18, 122.22, 84.32, 73.65, 73.33, 73.02, 44.68, 17.69; HMRS (ESI) calcd for $C_{19}H_{19}O_5NNa$ [M + Na]$^+$ 364.1156, found 364.1165.

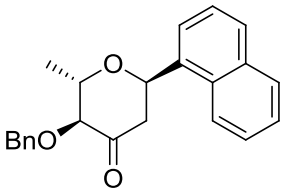
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(3-carboxyphenyl)-tetrahydro-4H-pyran-4-one (4qα):



To a solution of 3-aminobenzoic acid (**3i**) (34.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with

ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (MeOH/DCM: 1/20) to afford **4qα** as a white foam (17.0 mg, 49%). R_f = 0.24 (MeOH/DCM: 1/20); $[\alpha]_D^{20}$ = -81.8 (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.28 (m, 5H), 5.33 (t, *J* = 5.2 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.84 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 3.96 – 3.83 (m, 1H), 3.69 (d, *J* = 7.2 Hz, 1H), 3.19 (dd, *J* = 14.1, 4.6 Hz, 1H), 2.95 (dd, *J* = 13.9, 6.2 Hz, 1H), 1.32 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.19, 171.50, 140.04, 137.27, 132.28, 130.04, 129.99, 129.11, 129.04, 128.60, 128.38, 128.20, 84.55, 77.48, 77.16, 76.84, 74.21, 73.07, 72.84, 44.74, 17.90; HMRS (ESI) calcd for $C_{20}H_{24}O_5N$ $[M + NH_4]^+$ 358.1649, found 358.1652.

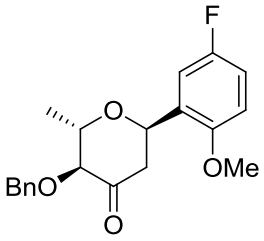
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(1-naphthyl)-tetrahydro-4H-pyran-4-one (4rα):



To a solution of α-naphthylamine (**3j**) (36.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column

chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4rα** as a white foam (20.8 mg, 60%). R_f = 0.29 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{18}$ = -278.3 (c 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.57 – 7.45 (m, 3H), 7.41 – 7.28 (m, 6H), 5.97 (dd, *J* = 6.7, 2.4 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.91 (d, *J* = 11.5 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 3.72 (d, *J* = 8.2 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.28 (dd, *J* = 14.6, 2.7 Hz, 1H), 3.13 (dd, *J* = 14.6, 6.9 Hz, 1H), 1.20 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.31, 137.55, 134.43, 134.21, 131.63, 129.51, 128.84, 128.57, 128.39, 128.13, 126.48, 126.13, 126.05, 125.01, 124.78, 85.27, 73.45, 72.69, 71.60, 44.88, 18.56; HMRS (ESI) calcd for $C_{23}H_{22}O_3Na$ $[M + Na]^+$ 369.1462, found 369.1468.

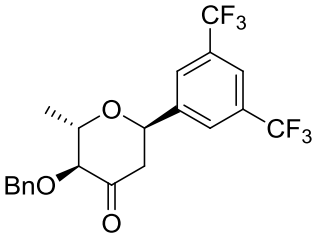
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(2-methyl-5-fluorophenyl)-tetrahydro-4H-pyran-4-one (4sα):



To a solution of 5-fluoro-2-methoxy-aniline (**3k**) (35.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4sα** as a

white foam (21.7 mg, 63%). R_f = 0.33 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -32.9 (c 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.23 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.79 (dd, *J* = 9.0, 4.3 Hz, 1H), 5.39 (dd, *J* = 7.7, 4.9 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.77 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.31 – 4.23 (m, 1H), 3.80 (s, 3H), 3.61 (dd, *J* = 4.9, 0.9 Hz, 1H), 2.89 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.79 (ddd, *J* = 14.2, 4.8, 0.9 Hz, 1H), 1.29 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.34, 157.22 (d, *J* = 239.0 Hz), 152.42, 137.30, 130.45 (d, *J* = 6.8 Hz), 128.63, 128.31, 128.19, 114.99 (d, *J* = 22.9 Hz), 114.62 (d, *J* = 24.5 Hz), 111.56 (d, *J* = 8.1 Hz), 84.14, 73.70, 72.66, 68.54, 55.97, 45.30, 16.81; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.92; HMRS (ESI) calcd for $C_{20}H_{21}O_{4w\beta}a$ $[M + Na]^+$ 367.1317, found 367.1313.

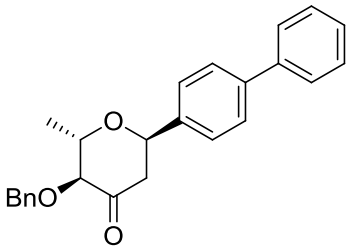
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(3,5-bis-trifluoromethylphenyl)-tetrahydro-4 H-pyran-4-one (4tα):



To a solution of 3,5-bis(trifluoromethyl)aniline (**3l)** (65.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^oC under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica

gel (ethyl acetate/petroleum ether: 1/10) to afford **4tα** as a white foam (29.8 mg, 69%). R_f = 0.31 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{17}$ = -56.4 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.82 (s, 1H), 7.38 – 7.29 (m, 5H), 5.28 (t, *J* = 5.8 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.78 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.06 (p, *J* = 6.5 Hz, 1H), 3.68 (dd, *J* = 5.9, 0.9 Hz, 1H), 3.14 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.88 (ddd, *J* = 14.0, 5.3, 0.9 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.26, 142.49, 136.97, 132.27 (q, *J* = 33.4 Hz, -CF_3), 128.69, 128.39, 128.35, 126.93 – 126.89 (m), 123.28 (q, *J* = 272.9 Hz), 122.31 – 122.21 (m), 84.01, 74.04, 73.23, 72.85, 45.04, 17.14; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84 (s, 6F); HMRS (ESI) calcd for $C_{22}H_{19}O_5F_6$ $[M + HCO_2]^-$ 477.1143, found 477.1143.

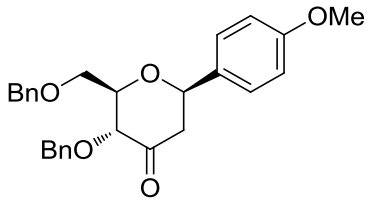
(2S,3S,6R)-3-Benzyloxy-2-methyl-6-(4-biphenyl)-tetrahydro-4H-pyran-4-one (4uα):



To a solution of 4-aminodiphenyl (**3m**) (42.0 mg, 0.25 mmol) in tetrahydrofuran (THF) (4 mL) were added nitrosonium tetrafluoroborate (44.0 mg, 0.38 mmol) at -40 ^{o}C under argon. Then, the acetonitrile-dry ice bath was removed and the mixture was stirred at room temperature for 0.5 h, during this period, a large amount of solid suspension was observed. Then the rhamnal **1f** (31.0 mg, 0.1 mmol) and bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) (8.7 mg, 0.015 mmol) were added to the reaction mixture, and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 20 mL) and the aqueous layer was extracted with ethyl acetate (20 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4uα** as a white foam (24.6 mg, 66%).

R_f = 0.26 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{21}$ = -119.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.47 – 7.40 (m, 4H), 7.37 – 7.28 (m, 6H), 5.35 (dd, *J* = 6.4, 3.5 Hz, 1H, H-1, $^1C_4$ (L, α)), 4.87 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.69 (d, *J* = 7.9 Hz, 1H), 3.19 (dd, *J* = 14.2, 3.5 Hz, 1H), 2.98 (dd, *J* = 14.2, 6.6 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.60, 141.18, 140.67, 138.13, 137.42, 128.94, 128.59, 128.39, 128.16, 127.79, 127.60, 127.57, 127.25, 84.91, 74.66, 73.25, 72.15, 44.65, 18.33; HMRS (ESI) calcd for $C_{25}H_{28}O_3N$ $[M + NH_4]^+$ 390.2064, found 390.2072.

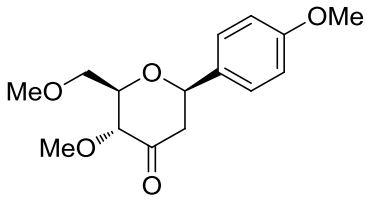
(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4aβ):



To a solution of **4aα** (10.0 mg, 0.023 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4aβ** as a white foam (9.2 mg, 92%). R_f = 0.30 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{16}$ = +105.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 12H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.63 (dd, *J* = 10.6, 2.9 Hz, 1H, H-1), 4.56 (d, *J* = 12.2 Hz, 1H), 4.50 (d, *J* = 11.1 Hz, 1H), 4.27 (d, *J* = 8.9 Hz, 1H), 3.83 – 3.81 (m, 3H), 3.81 (s, 3H, MeO-), 2.82 (dd, *J* = 13.8, 10.7 Hz, 1H), 2.71 (dd, *J* = 13.8, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.04, 159.66, 138.38, 137.63, 132.40, 128.54, 128.52, 128.39, 128.09, 127.87, 127.78, 127.24, 114.14,

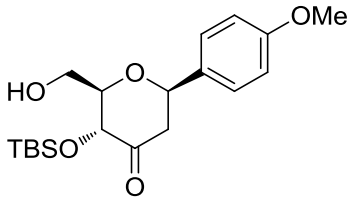
81.00, 79.90, 79.35, 73.71, 73.67, 69.39, 55.48, 50.11; HMRS (ESI) calcd for HMRS (ESI) calcd for $C_{27}H_{29}O_5$ $[M + H]^+$ 433.2010, found 433.2006.

(2R,3R,6R)-3-Methoxy-2-methoxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4bβ):



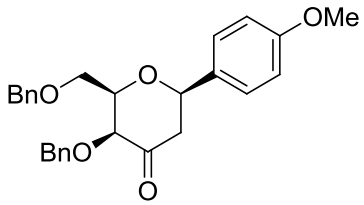
To a solution of **4bα** (10.0 mg, 0.036 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/6) to afford **4bβ** as a white foam (8.3 mg, 83%). R_f = 0.27 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{15}$ = +132.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.61 (dd, *J* = 11.3, 2.7 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.00 (d, *J* = 9.9 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.70 (m, 3H), 3.56 (s, 3H), 3.46 (s, 3H), 2.78 (ddd, *J* = 13.7, 11.3, 0.8 Hz, 1H), 2.70 (dd, *J* = 13.7, 2.8 Hz, 1H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.13, 159.68, 132.20, 127.32, 114.14, 82.09, 80.97, 79.48, 71.83, 59.89, 59.84, 55.47, 49.96; HMRS (ESI) calcd for $C_{15}H_{21}O_5$ $[M + H]^+$ 281.1384, found 281.1385.

(2R,3R,6R)-3-*Tert*-butyldimethylsilyloxy-2-hydroxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4cβ):



To a solution of **4cα** (10.0 mg, 0.021 mmol) in ether (2 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/6) to afford **4cβ** as a colorless oil (5.8 mg, 75%). R_f = 0.31 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{19}$ = +96.7 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.67 (dd, *J* = 11.2, 2.4 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.36 (d, *J* = 9.4 Hz, 1H), 4.04 – 3.95 (m, 1H), 3.89 – 3.76 (m, 1H), 3.81 (s, 3H), 3.70 – 3.64 (m, 1H), 2.76 (dd, *J* = 13.8, 11.3 Hz, 1H), 2.69 (dd, *J* = 13.8, 2.7 Hz, 1H), 2.03 – 2.00 (m, 1H, -OH), 0.94 (s, 9H), 0.20 (s,3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.44, 159.88, 132.10, 127.39, 114.25, 82.51, 79.35, 75.32, 62.71, 55.50, 49.19, 25.92, 18.62, -4.13, -5.45; HMRS (ESI) calcd for $C_{19}H_{31}O_5Si$ $[M + H]^+$ 367.1936, found 367.1938.

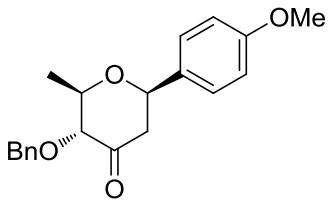
(2R,3S,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4dβ):



To a solution of **4dα** (10.0 mg, 0.023 mmol) in ether (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4dβ** as a colorless oil (6.4 mg, 64%). R_f = 0.35 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{21}$ =

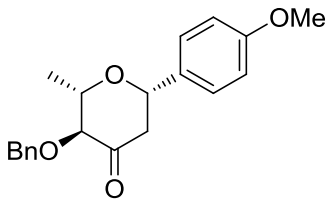
+30.5 (c 0.2, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 12H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.62 – 4.51 (m, 3H, H-1, Bn), 4.47 (d, *J* = 12.0 Hz, 1H, Bn), 4.41 (d, *J* = 11.9 Hz, 1H, Bn), 3.91 (t, *J* = 6.0 Hz, 1H, H-4), 3.86 – 3.77 (m, 3H, H-5, H-6a, H-6b), 3.80 (s, 3H), 3.20 – 3.12 (m, 1H), 2.48 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.06, 159.71, 138.19, 137.21, 132.70, 128.59, 128.53, 128.25, 128.18, 127.85, 127.42, 114.14, 80.13, 79.86, 79.69, 73.67, 72.24, 68.58, 55.48, 47.30; HMRS (ESI) calcd for $C_{27}H_{29}O_5$ $[M + H]^+$ 433.2010, found 433.2008.

(2R,3R,6R)-3-Benzyloxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4eβ):



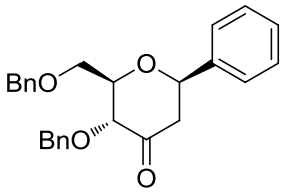
To a solution of **4eα** (10.0 mg, 0.03 mmol) in ether (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4eβ** as a white foam (9.2 mg, 92%). R_f = 0.41 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{16}$ = +187.1 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 7H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.62 (dd, *J* = 10.7, 3.3 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.54 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 3.82 – 3.74 (m, 2H), 2.76 (dd, *J* = 13.6, 11.1 Hz, 1H), 2.70 (dd, *J* = 13.7, 3.4 Hz, 1H), 1.46 – 1.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.72, 159.65, 137.59, 132.43, 128.60, 128.45, 128.17, 127.24, 114.18, 85.06, 79.11, 77.80, 73.45, 55.47, 50.14, 19.51; HMRS (ESI) calcd for $C_{20}H_{22}O_4Na$ $[M + Na]^+$ 349.1810, found 349.1817.

(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran-4-one (4fβ):



To a solution of **4fα** (10.0 mg, 0.03 mmol) in ether (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4fβ** as a white foam (9.0 mg, 90%). R_f = 0.42 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{22}$ = -224.9 (c 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 7H), 6.90 – 6.87 (m, 2H), 4.99 (d, *J* = 11.5 Hz, 1H), 4.62 (dd, *J* = 10.5, 3.5 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.54 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.74 (m, 2H), 2.79 – 2.67 (m, 2H), 1.45 (dd, *J* = 3.9, 1.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.69, 159.69, 137.64, 132.49, 128.61, 128.45, 128.17, 127.24, 114.21, 85.11, 79.12, 77.82, 73.47, 55.48, 50.15, 19.52; HMRS (ESI) calcd for $C_{20}H_{22}O_4Na$ $[M + Na]^+$ 349.1811, found 349.1815.

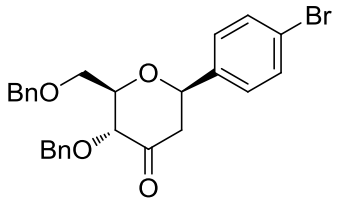
(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-phenyl-tetrahydro-4H-pyran-4-one (4hβ):



To a solution of **4hα** (10.0 mg, 0.025 mmol) in ether (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with

ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4hβ** as a white foam (6.1 mg, 61%). R_f = 0.37 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = +84.8 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 15H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.69 (t, *J* = 7.0 Hz, 1H, H-1), 4.66 (d, *J* = 12.3 Hz, 1H), 4.58 (d, *J* = 12.3 Hz, 1H), 4.50 (d, *J* = 11.1 Hz, 1H), 4.28 (d, *J* = 9.5 Hz, 1H), 3.87 – 3.81 (m, 3H), 2.76 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.84, 140.27, 138.44, 137. 66, 128.77, 128.55, 128.53, 128.40, 128.31, 128.10, 127.85, 127.79, 125.83, 81.12, 79.92, 79.57, 73.75, 73.71, 69.44, 50.18. The ^{1}H/^{13}C NMR spectroscopic data are coincide with the previous report.[1]

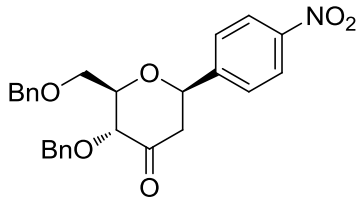
(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-bromophenyl)-tetrahydro-4H-pyran-4-one (4iβ):



To a solution of **4iα** (10.0 mg, 0.021 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4iβ** as a white foam (5.1 mg, 51%). R_f = 0.38 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = +133.6 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.24 (m, 12H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.65 (dd, *J* = 11.1, 3.3 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.57 (d, *J* = 12.2 Hz, 1H), 4.49 (d, *J* = 11.1 Hz, 1H), 4.27 – 4.23 (m, 1H), 3.86 –

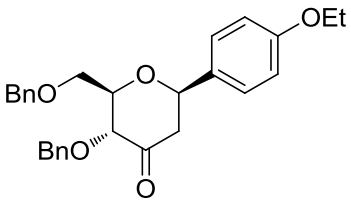
3.78 (m, 1H), 2.77 – 2.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.43, 139.19, 138.22, 137.45, 131.86, 128.55, 128.54, 128.39, 128.14, 127.85, 127.50, 122.16, 80.93, 79.67, 78.76, 73.69, 73.67, 69.22, 49.94; HMRS (ESI) calcd for $C_{26}H_{25}O_4NaBr$ $[M + Na]^+$ 503.0828, found 503.0826.

(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-nitrophenyl)-tetrahydro-4H-pyran-4-one (4jβ):



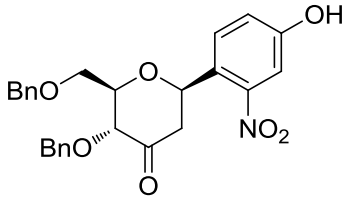
To a solution of **4jα** (10.0 mg, 0.022 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/6) to afford **4jβ** as a white foam (6.3 mg, 63%). R_f = 0.30 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{19}$ = +137.8 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.28 (m, 10H), 4.95 (d, *J* = 11.1 Hz, 1H), 4.80 (dd, *J* = 11.6, 2.5 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.65 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 4.28 (d, *J* = 9.3 Hz, 1H, H-4), 3.89 – 3.82 (m, 3H), 2.81 (dd, *J* = 13.8, 2.6 Hz, 1H), 2.68 (ddd, *J* = 13.8, 11.7, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.70, 147.80, 147.16, 138.11, 137.35, 128.59, 128.42, 128.23, 127.95, 127.87, 126.53, 124.03, 80.96, 79.54, 78.16, 73.78, 73.72, 69.16, 49.71; HMRS (ESI) calcd for $C_{26}H_{29}O_6N_2$ $[M + NH_4]^+$ 465.2021, found 465.2018.

(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-ethoxyphenyl)-tetrahydro-4H-pyran-4-one (4kβ):



To a solution of **4kα** (10.0 mg, 0.022 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4kβ** as a white foam (9.0 mg, 90%). R_f = 0.25 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = +123.6 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 12H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.61 (dd, *J* = 10.8, 2.9 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.56 (d, *J* = 12.2 Hz, 1H), 4.49 (d, *J* = 11.1 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.84 – 3.80 (m, 3H), 2.81 – 2.74 (m, 1H), 2.71 (dd, *J* = 13.8, 3.0 Hz, 1H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.12, 159.00, 138.35, 137.60, 132.18, 128.54, 128.52, 128.39, 128.09, 127.87, 127.78, 127.22, 114.67, 80.96, 79.87, 79.38, 73.68, 73.66, 69.33, 63.64, 50.10, 14.95; HMRS (ESI) calcd for $C_{28}H_{31}O_5$ $[M + H]^+$ 447.2166, found 447.2167.

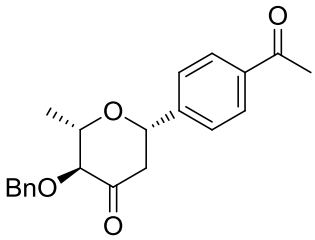
(2R,3R,6R)-3-Benzyloxy-2-benzyloxymethyl-6-(4-hydroxy-2-nitrophenyl)-tetrahydro-4H-pyran-4-one (4lβ):



To a solution of **4lα** (10.0 mg, 0.022 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with

ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/3) to afford **4lβ** as a white foam (6.2 mg, 62%). R_f = 0.25 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{20}$ = +277.1 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 11H), 7.12 (s, 1H, -OH), 7.08 (s, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.12 (d, *J* = 10.5 Hz, 1H, H-1, $^4C_1$ (D, β)), 4.97 (d, *J* = 11.2 Hz, 1H, Bn), 4.61 (d, *J* = 11.9 Hz, 1H, Bn), 4.54 (d, *J* = 11.8 Hz, 1H, Bn), 4.46 (d, *J* = 11.1 Hz, 1H, Bn), 4.07 (d, *J* = 9.9 Hz, 1H, H-4), 3.91 – 3.83 (m, 2H, H-5, H-6a), 3.77 (dd, *J* = 10.8, 5.4 Hz, 1H, H-6b), 2.93 (d, *J* = 13.5 Hz, 1H, H-2a), 2.72 – 2.63 (m, 1H, H-2b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.70, 156.40, 148.10, 137.37, 136.89, 128.73, 128.63, 128.45, 128.39, 128.25, 125.83, 120.62, 111.40, 79.88, 79.46, 74.75, 73.93, 73.69, 69.68, 48.43; HMRS (ESI) calcd for $C_{26}H_{25}O_7NNa$ $[M + Na]^+$ 486.1524, found 486.1525.

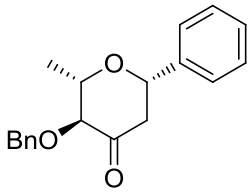
(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(4-acetylphenyl)-tetrahydro-4H-pyran-4-one (4mβ):



To a solution of **4mα** (10.0 mg, 0.029 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/5) to afford **4mβ** as a white foam (6.0 mg, 60%). R_f = 0.36 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{20}$ = -235.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.31 (m, 5H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.74 (dd, *J* = 11.4, 2.5

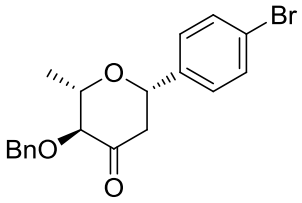
Hz, 1H, H-1, $^1C_4$ (L, β)), 4.55 (d, J = 11.4 Hz, 1H), 3.85 – 3.76 (m, 1H), 2.77 (dd, J = 13.7, 2.6 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.60 (s, 3H), 1.48 (d, J = 5.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.96, 197.75, 145.37, 137.43, 136.94, 128.87, 128.62, 128.46, 128.23, 125.85, 84.84, 78.60, 77.94, 73.50, 50.02, 26.81, 19.46; HMRS (ESI) calcd for $C_{21}H_{23}O_4$ $[M + H]^+$ 339.1591, found 339.1599.

(2S,3S,6S)-3-Benzyloxy-2-methyl-6-phenyl-tetrahydro-4H-pyran-4-one (4nβ):



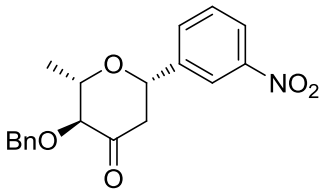
To a solution of **4nα** (10.0 mg, 0.034 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4nβ** as a white foam (4.5 mg, 45%). R_f = 0.43 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{18}$ = -86.7 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 10H), 5.00 (d, J = 11.4 Hz, 1H), 4.67 (dd, J = 8.5, 5.6 Hz, 1H, H-1), 4.55 (d, J = 11.4 Hz, 1H), 3.82 – 3.74 (m, 2H), 2.77 – 2.69 (m, 2H), 1.46 (d, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.51, 140.33, 137.63, 128.81, 128.61, 128.45, 128.33, 128.18, 125.82, 85.08, 79.35, 77.90, 73.49, 50.24, 19.50; HMRS (ESI) calcd for $C_{19}H_{20}O_3Na$ [M + Na]+ 319.1305, found 319.1310.

(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(4-bromophenyl)-tetrahydro-4H-pyran-4-one (4oβ):



To a solution of **4oα** (10.0 mg, 0.027 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4oβ** as a white foam (4.2 mg, 42%). R_f = 0.43 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{19}$ = -125.9 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.42 – 7.30 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.99 (d, *J* = 11.4 Hz, 1H), 4.64 (dd, *J* = 11.0, 3.1 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.54 (d, *J* = 11.4 Hz, 1H), 3.83 – 3.74 (m, 2H), 2.73 (dd, *J* = 13.7, 3.1 Hz, 1H), 2.67 (dd, *J* = 13.5, 11.1 Hz, 1H), 1.46 (d, *J* = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.13, 139.34, 137.47, 131.92, 128.63, 128.47, 128.23, 127.49, 122.19, 84.88, 78.57, 77.89, 76.84, 73.50, 50.09, 19.47; HMRS (ESI) calcd for HMRS (ESI) calcd for $C_{19}H_{19}O_3BrNa$ $[M + Na]^+$ 397.0405, found 397.0409.

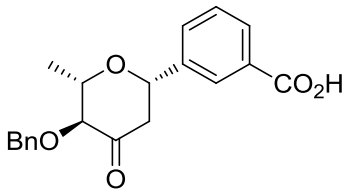
(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(3-nitrophenyl)-tetrahydro-4H-pyran-4-one (4pβ):



To a solution of **4pα** (10.0 mg, 0.029 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 3 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The

solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/5) to afford **4pβ** as a white foam (6.5 mg, 65%). R_f = 0.48 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{20}$ = -104.5 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (t, *J* = 1.8 Hz, 1H), 8.18 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.31 (m, 5H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.79 (dd, *J* = 11.6, 2.5 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.56 (d, *J* = 11.4 Hz, 1H), 3.88 – 3.76 (m, 2H), 2.81 (dd, *J* = 13.7, 2.6 Hz, 1H), 2.73 – 2.64 (m, 1H), 1.49 (d, *J* = 5.5 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.47, 148.63, 142.43, 137.34, 131.82, 129.79, 128.66, 128.50, 128.30, 123.23, 120.89, 84.70, 78.00, 77.87, 73.57, 49.92, 19.43; HMRS (ESI) calcd for $C_{19}H_{23}O_5N_2$ $[M + NH_4]^+$ 359.1602, found 359.1603.

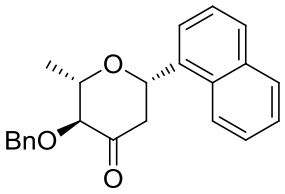
(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(3-carboxyphenyl)-tetrahydro-4H-pyran-4-one (4qβ):



To a solution of **4qα** (10.0 mg, 0.029 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with brine (10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (MeOH/DCM: 1/20) to afford **4qβ** as a white foam (5.2 mg, 52%). R_f = 0.24 (MeOH/DCM: 1/20); $[a]_D^{20}$ = -48.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.32 (m, 5H), 5.00 (d, *J* = 11.4 Hz, 1H, Bn), 4.75 (dd, *J* = 10.9, 3.1 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.56 (d, *J* = 11.4 Hz, 1H, Bn), 3.85 – 3.78 (m, 2H, H-4, H-5), 2.80 (dd, *J* = 13.7, 3.2 Hz, 1H, H-2a), 2.74 (dd, *J* = 13.6, 11.1 Hz, 1H, H-2b), 1.48 (d, *J* = 5.3 Hz, 3H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.03

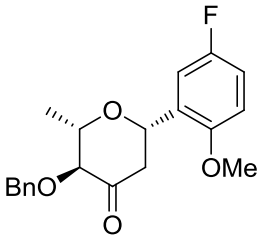
(C-3), 170.78 (-CO_2H), 141.02, 137.52, 131.22, 130.10, 129.82, 129.07, 128.64, 128.49, 128.24, 127.61, 84.94, 78.66, 78.00, 73.56 (Ph-CH_2-), 50.07, 19.47 (C-6); HMRS (ESI) calcd for $C_{20}H_{24}O_5N$ $[M + NH_4]^+$ 358.1649, found 358.1652.

(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(1-naphthyl)-tetrahydro-4H-pyran-4-one (4rβ):



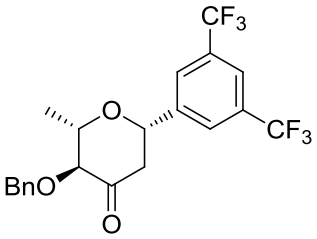
To a solution of **4rα** (10.0 mg, 0.029 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 2.5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4rβ** as a white foam (4.1 mg, 41%). R_f = 0.35 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -167.8 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.45 – 7.33 (m, 5H), 5.39 (dd, *J* = 10.6, 3.4 Hz, 1H, H-1, $^1C_4$ (L, β)), 5.04 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.87 (d, *J* = 8.7 Hz, 1H), 2.98 – 2.87 (m, 2H), 1.53 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.77, 137.61, 135.74, 133.90, 130.09, 129.12, 128.90, 128.63, 128.46, 128.20, 126.63, 125.91, 125.59, 123.14, 122.88, 85.19, 78.16, 76.47, 73.51, 49.36, 19.64; HMRS (ESI) calcd for $C_{23}H_{22}O_3Na$ $[M + Na]^+$ 369.1462, found 369.1467.

(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(2-methyl-5-fluorophenyl)-tetrahydro-4H-pyran-4-one (4sβ):



To a solution of **4sα** (10.0 mg, 0.058 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 3 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4sβ** as a white foam (4.5 mg, 45%). R_f = 0.39 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -106.0 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 7.24 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.77 (dd, *J* = 9.0, 4.3 Hz, 1H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.95 (dd, *J* = 11.5, 2.2 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.54 (d, *J* = 11.6 Hz, 1H), 3.79 (s, 3H), 3.82 – 3.72 (m, 2H), 2.87 (dd, *J* = 13.7, 2.3 Hz, 1H), 2.44 (ddd, *J* = 13.6, 11.5, 1.0 Hz, 1H), 1.46 (d, *J* = 5.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.63, δ 157.46 (d, *J* = 238.4 Hz), 151.52, 137.64, 130.80 (d, *J* = 7.1 Hz), 128.60, 128.44, 128.16, 114.60 (d, *J* = 23.0 Hz), 113.17 (d, *J* = 24.8 Hz), 111.26 (d, *J* = 8.1 Hz), 84.99, 77.68, 73.48, 73.44, 55.92, 48.66, 19.51; ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.03; HMRS (ESI) calcd for $C_{20}H_{21}O_4F$ $[M + Na]^+$ 367.1317, found 367.1308.

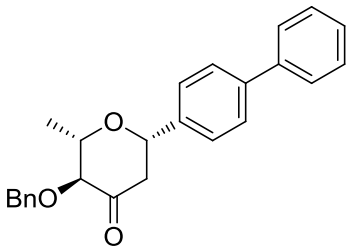
(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(3,5-bis-trifluoromethylphenyl)-tetrahydro-4 H-pyran-4-one (4tβ):



To a solution of **4tα** (10.0 mg, 0.023 mmol) in ether (Et_2O) (1mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h.

After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4tβ** as a white foam (3.6 mg, 36%). R_f = 0.37 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -94.2 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 3H), 7.43 – 7.32 (m, 5H), 5.00 (d, *J* = 11.4 Hz, 1H), 4.80 (dd, *J* = 11.7, 2.4 Hz, 1H, H-1, $^1C_4$ (L, β)), 4.56 (d, *J* = 11.4 Hz, 1H), 3.87 – 3.77 (m, 2H), 2.82 (dd, *J* = 13.7, 2.6 Hz, 1H), 2.72 – 2.62 (m, 1H), 1.49 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.12, 142.87, 137.30, 132.21(q, J = 32.1 Hz), 128.68, 128.51, 128.34, 126.93 – 126.89 (m), 123.28 (q, *J* = 272.9 Hz), 122.31 – 122.21 (m), 84.60, 78.09, 77.67, 73,60, 49.89, 19.39; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.85 (s, 6F); HMRS (ESI) calcd for $C_{22}H_{19}O_5F_6$ $[M + HCO_2]^-$ 477.1143, found 477.1144.

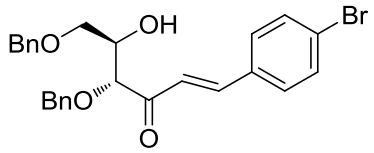
(2S,3S,6S)-3-Benzyloxy-2-methyl-6-(4-biphenyl)-tetrahydro-4H-pyran-4-one (4uβ):



To a solution of **4uα** (10.0 mg, 0.027 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (50 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **4uβ** as a white foam (3.5 mg, 35%). R_f = 0.33 (ethyl acetate/petroleum ether: 1/6); $[a]_D^{20}$ = -76.4

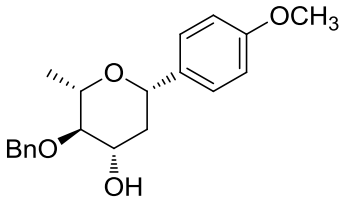
(c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 8.1 Hz, 4H), 7.47 – 7.32 (m, 10H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.72 (t, *J* = 7.1 Hz, 1H, H-1), 4.56 (d, *J* = 11.4 Hz, 1H), 3.87 – 3.76 (m, 2H), 2.79 (d, *J* = 6.6 Hz, 2H), 1.48 (d, *J* = 5.6 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.54, 141.37, 140.79, 139.23, 137.57, 128.95, 128.62, 128.47, 128.20, 127.59, 127.27, 126.32, 85.05, 79.16, 77.94, 73.49, 50.13, 19.53; HMRS (ESI) calcd for $C_{25}H_{24}O_3Na$ $[M + Na]^+$ 395.1617, found 395.1612.

(4R,5S,E)-4,6-Di(benzyloxy)-5-hydroxy1-(4-bromophenyl)-3-ono-1-hexene (6):



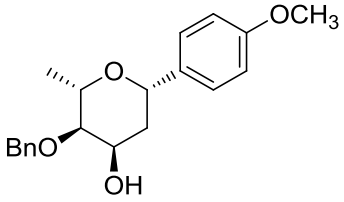
To a solution of **4iα** (10.0 mg, 0.021 mmol) in ether (Et_2O) (1 mL) was added HBF_4 (75 μL, 50% V/V in Et_2O), and the mixture was stirred at room temperature for 5 h. After the completion of the reaction, the mixture was diluted with saturated sodium bicarbonate solution (sat.$NaHCO_3$, 10 mL) and the aqueous layer was extracted with ethyl acetate (10 mL * 3). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether: 1/10) to afford **6h** as a white foam (2.5 mg, 25%). R_f = 0.13 (ethyl acetate/petroleum ether: 1/6); $[\alpha]_D^{20} = 0$ (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H, Ph-*HC*=CH), 7.51 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 10H), 7.13 (d, *J* = 16.0 Hz, 1H, Ph-HC=*CH*-CO), 4.64 (d, *J* = 11.6 Hz, 1H, Bn), 4.54 (d, *J* = 11.8 Hz, 1H, Bn), 4.50 (d, *J* = 11.8 Hz, 2H, Bn), 4.16 – 4.10 (m, 2H, H-4, H-5), 3.69 – 3.61 (m, 2H, H-6a,b), 2.63 (br, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.60, 142.55, 137.82, 137.13, 133.60, 132.29, 130.10, 128.70, 128.56, 128.34, 127.96, 125.15, 122.14, 84.14, 73.59, 73.19, 71.41, 70.31. HMRS (ESI) calcd for $C_{26}H_{26}O_4Br$ $[M + H]^+$ 481.1009, found 481.1011.

(2S,3S,4S,6S)-3-Benzyloxy-4-hydroxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran (7):



To the solution of **4fβ** (20.0 mg, 0.06 mmol) in THF (2 mL) was added $NaBH_4$ (0.6 mmol). Then, the mixture was stirred for 1 h. The solution was taken up in 20 mL of sat. NH_4Cl, then it was extracted with ethyl acetate (3*20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under rotary evaporation. The residue was purified through silica (petroleum ether/ethyl acetate: 3/1) to afford a colorless oil **7** (8.5 mg, 42%), R_f = 0.24 (ethyl acetate/petroleum ether: 1/3) and **8** (8.0 mg, 40%), R_f = 0.26 (ethyl acetate/petroleum ether: 1/3). For compound **7**, $[a]_D^{26}$ = -86.4 (c 0.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.4 Hz, 4H), 7.33 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.83 (d, *J* = 11.3 Hz, 1H, Bn), 4.74 (d, *J* = 11.4 Hz, 1H, Bn), 4.41 (dd, *J* = 11.6, 1.6 Hz, 1H, H-1), 3.89 – 3.82 (m, 1H, H-3), 3.79 (s, 3H, -OMe), 3.51 (dq, *J* = 8.9, 6.2 Hz, 1H, H-5), 3.07 (t, *J* = 8.9 Hz, 1H, H-4), 2.23 – 2.18 (m, 1H, H-2a), 2.15 (s, 1H, -OH), 1.76 (dd, *J* = 24.3, 11.6 Hz, 1H, H-2b), 1.41 (d, *J* = 6.2 Hz, 3H, -Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.33, 138.50, 133.70, 128.86, 128.23, 128.10, 127.48, 113.99, 86.64, 77.48, 75.66, 75.37, 73.02, 55.45, 40.96, 18.89. HMRS (ESI) calcd for $C_{20}H_{24}O_4Na$ $[M + Na]^+$ 351.1572, found 351.1569.

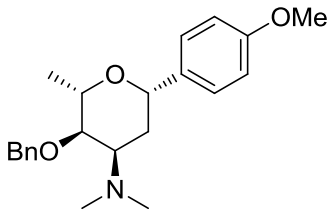
(2S,3S,4R,6S)-3-Benzyloxy-4-hydroxy-2-methyl-6-(4-methoxyphenyl)-tetrahydro -4H-pyran (8):



To the solution of **4fβ** (20.0 mg, 0.06 mmol) in THF (2 mL) was added 1 M $LiBHEt_3$ (0.6 mL, 0.6 mmol) at 0 ^{o}C. Then, the mixture was stirred 0 ^{o}C for 24 h. The solution was taken up in 20 mL of sat. NH_4Cl, and extracted with ethyl acetate (3*20

mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under rotary evaporation. The residue was purified through silica (petroleum ether/ethyl acetate: 3/1) to afford a colorless oil **8** (16.0 mg, 78%), R_f = 0.26 (ethyl acetate/petroleum ether: 1/3). $[\alpha]_D^{26}$ = -38.8 (c 0.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 5H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.79 (dd, *J* = 11.5, 1.5 Hz, 1H, H-1), 4.69 (d, *J* = 11.5 Hz, 1H, Bn), 4.58 (d, *J* = 11.5 Hz, 1H, Bn), 4.30 – 4.28 (m, 1H, H-3), 3.96 – 3.87 (m, 1H, H-5), 3.78 (s, 3H, -OMe), 3.21 (dd, *J* = 9.5, 3.0 Hz, 1H, H-4), 2.52 (s, 1H, -OH), 2.20 – 2.13 (m, 1H, H-2a), 1.80 (dd, *J* = 13.7, 12.2 Hz, 1H, H-2b), 1.31 (d, *J* = 6.2 Hz, 3H, -Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.13, 137.81, 134.45, 128.74, 128.28, 128.13, 127.42, 113.93, 80.97, 72.91, 71.69, 70.81, 64.45, 55.43, 39.21, 18.81; HMRS (ESI) calcd for $C_{20}H_{24}O_4Na$ $[M + Na]^+$ 351.1572, found 351.1574.

(2S,3S,4R,6S)-3-Benzyloxy-4-dimethylamino-2-methyl-6-(4-methoxyphenyl)-tetrahydro-4H-pyran (9):



To the solution of **4fβ** (50.0 mg, 0.15 mmol) and ammonium acetate (115.0 mg, 1.5 mmol) in methanol (4 mL) was added $NaBH_3CN$ (94.0 mg, 1.5 mmol) at room temperature. The mixture was stirred at room temperature for 24 h. The solution was taken up in 20 mL of water and extracted with ethyl acetate (3*20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under rotary evaporation. Then the residue was dissolved in acetonitrile (4 mL), and was added 45% aq. formaldehyde (1 mL) and $NaBH_3CN$ (47.0 mg, 7.5 mmol), the mixture was stirred at room temperature for 24 h. The resulting mixture was quenched with brine (20 mL) and the aqueous layer was extracted with ethyl acetate (3* 20 ml). The organic layer was washed with water then dried over Na_2SO_4, and the solvent was removed under rotary evaporation. The residue was purified through silica gel (petroleum ether/ ethyl acetate:

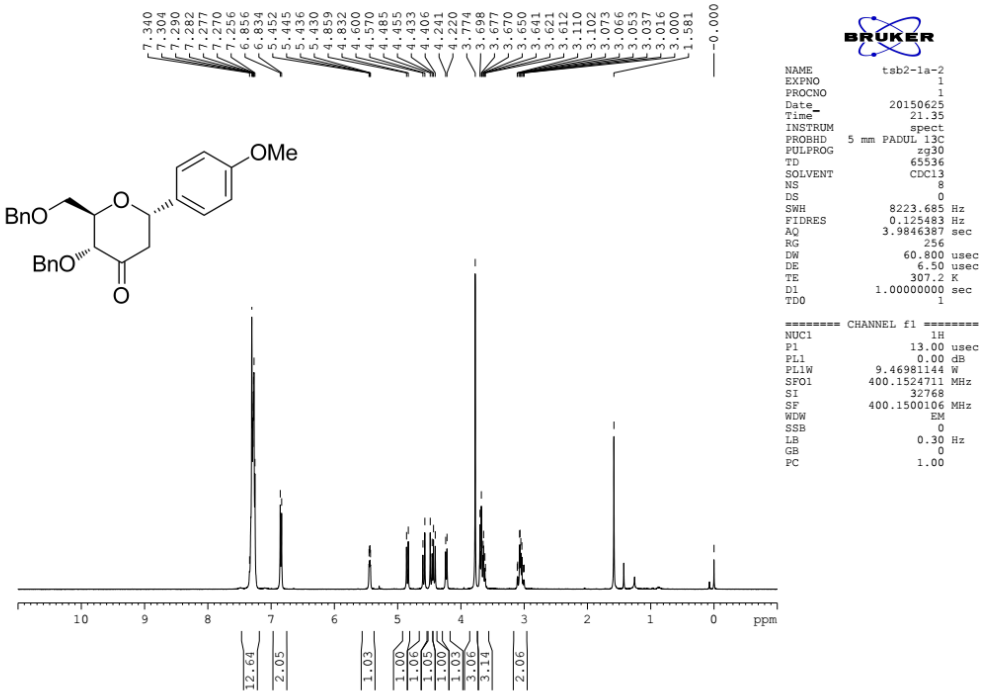
3/1) to afford a colorless oil **9** (27.1 mg, 50%), R_f = 0.40 (ethyl acetate/petroleum ether: 1/3); $[a]_D^{20}$ = -81.8 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.86 (dd, *J* = 11.1, 2.5 Hz, 1H, H-1), 4.73 (d, *J* = 11.6 Hz, 1H, Ph-*CH*$_2$-), 4.51 (d, *J* = 11.6 Hz, 1H, Ph-*CH*$_2$-), 4.30 – 4.21 (m, 1H, H-5), 3.78 (s, 3H, MeO-), 3.43 (d, *J* = 6.2 Hz, 1H, H-4), 2.75 (s, 1H, H-3), 2.44 (s, 6H, -NMe_2), 2.19 (ddd, *J* = 14.1, 4.8, 2.8 Hz, 1H, H-2a), 1.80 – 1.71 (m, 1H, H-2b), 1.30 (d, *J* = 6.3 Hz, 3H, Me-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.12, 138.40, 135.19, 128.51, 127.92, 127.40, 113.93, 83.95(br, -*C*-NMe_2), 73.27, 72.35, 71.66, 59.34, 55.44, 44.98, 37.22(br, C2), 19.24; HMRS (ESI) calcd for $C_{22}H_{30}O_3N$ $[M + H]^+$ 356.2220, found 356.2224.

8) Reference

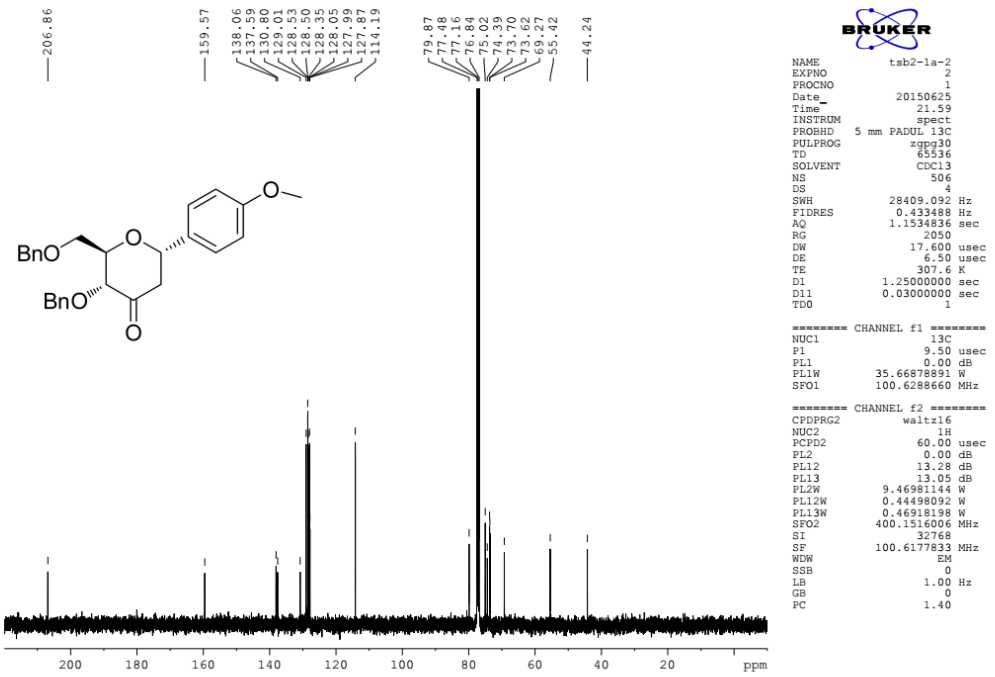
[1] C.-F. Liu, D.-C. Xiong, X.-S. Ye, *J. Org. Chem.* **2014**, *79*, 4676-4686.

9) Spectral data

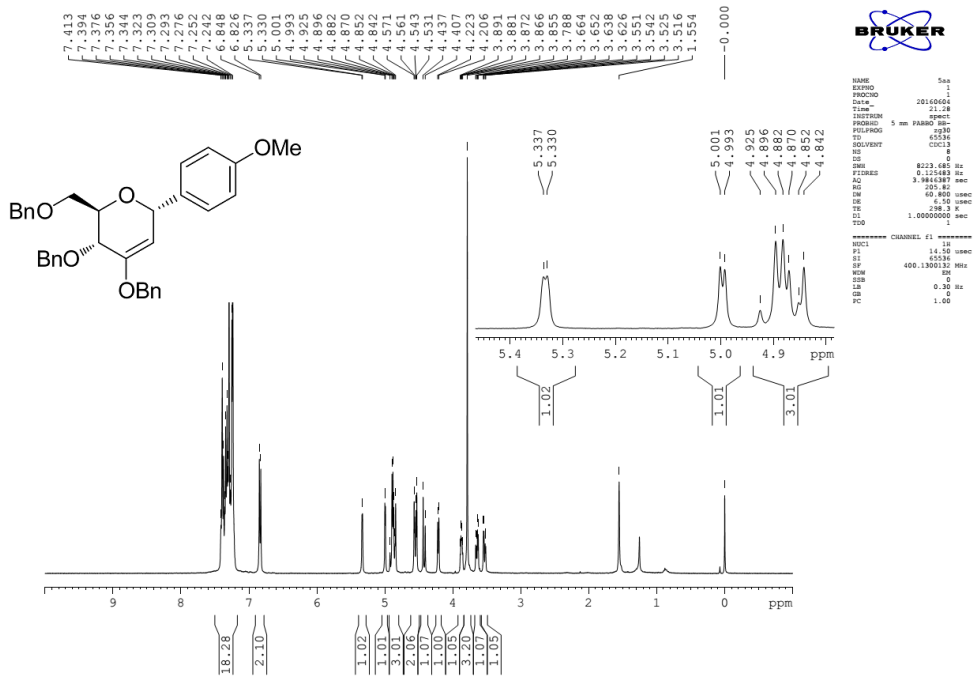
^{1}H NMR spectrum of **4aα**, 400MHz, $CDCl_3$



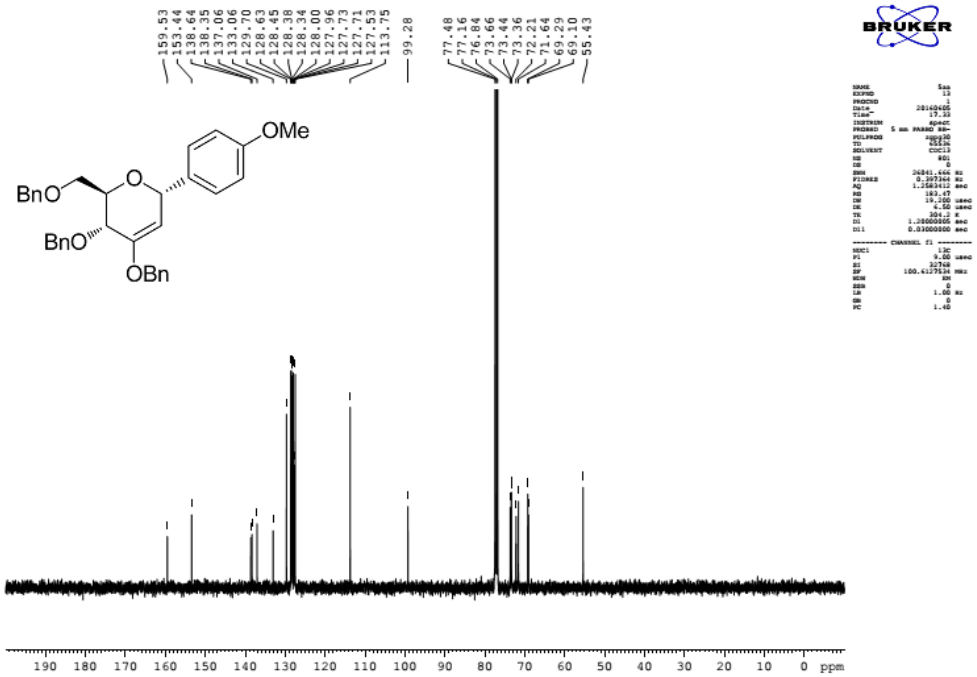
^{13}C NMR spectrum of **4aα**, 100MHz, $CDCl_3$



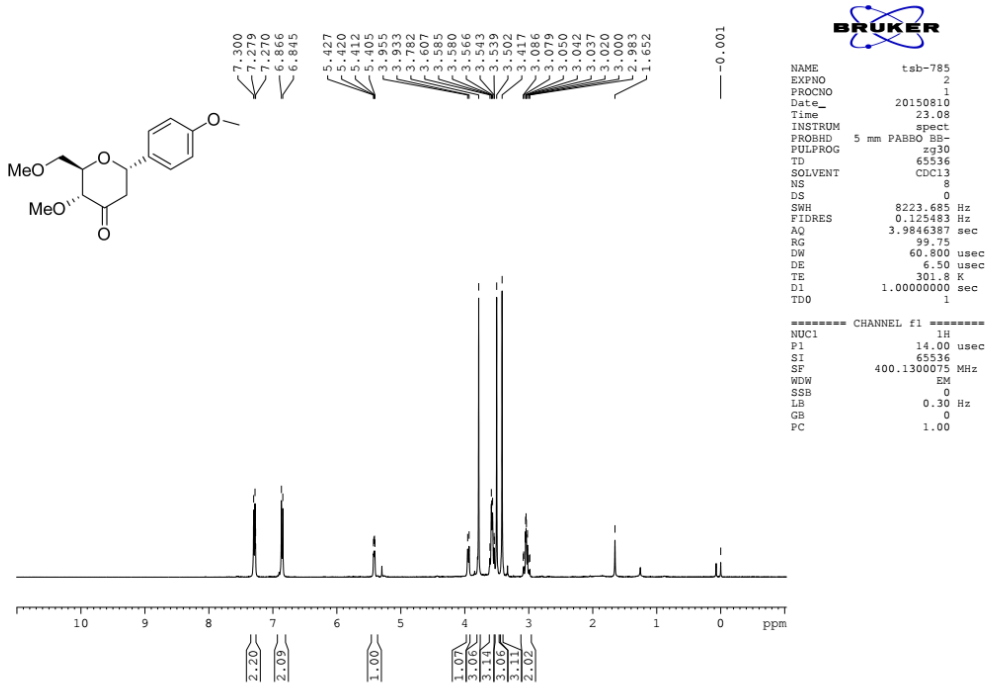
^{1}H NMR spectrum of **5a**, 400MHz, $CDCl_3$



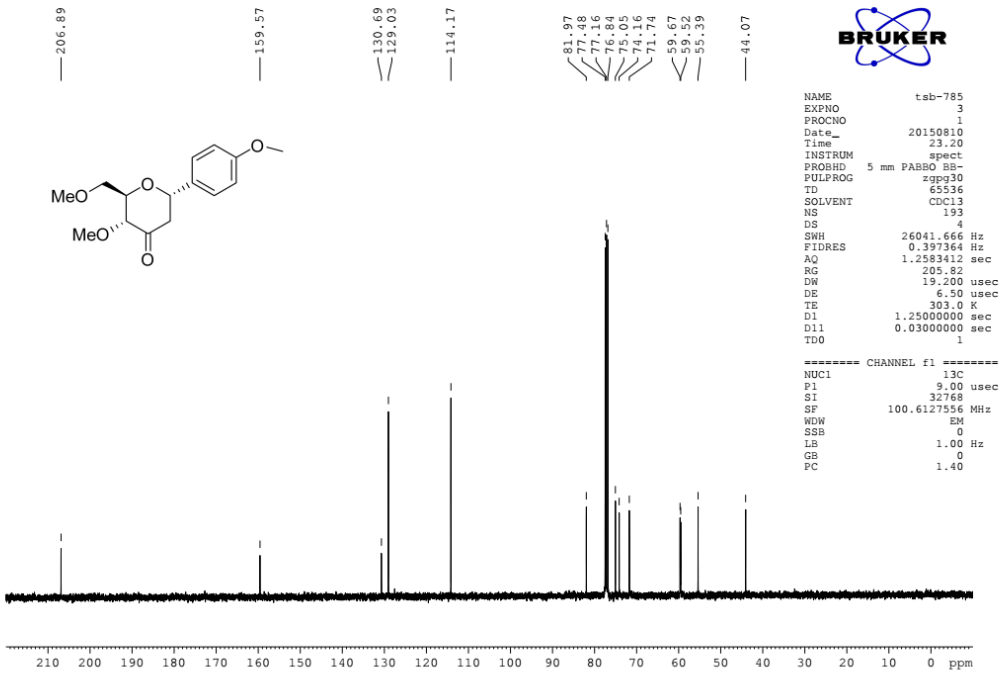
^{13}C NMR spectrum of **5a**, 100MHz, $CDCl_3$



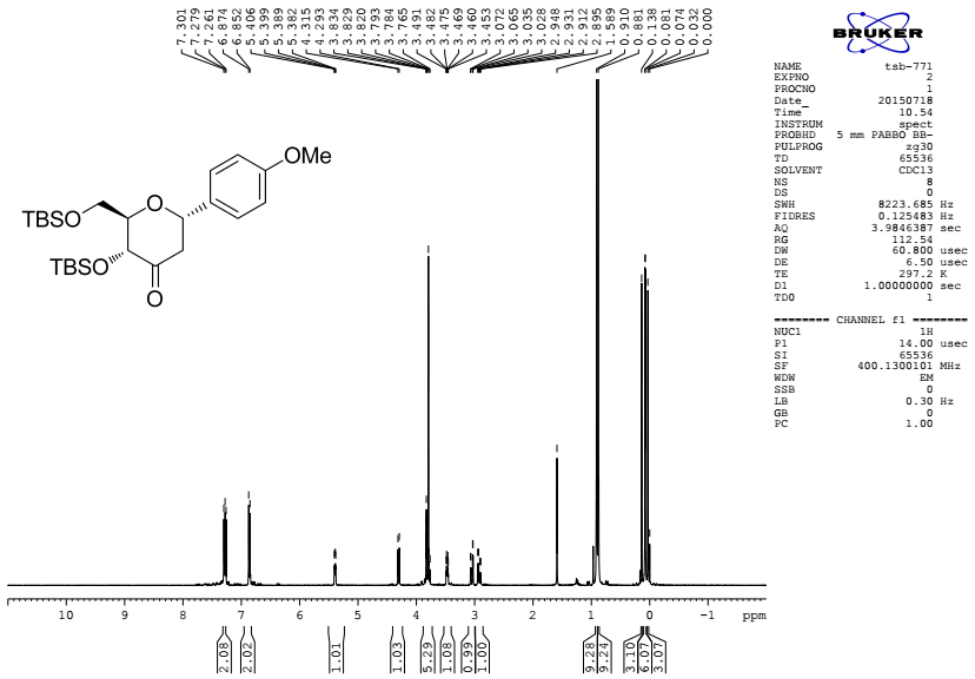
^{1}H NMR spectrum of **4bα**, 400MHz, $CDCl_3$



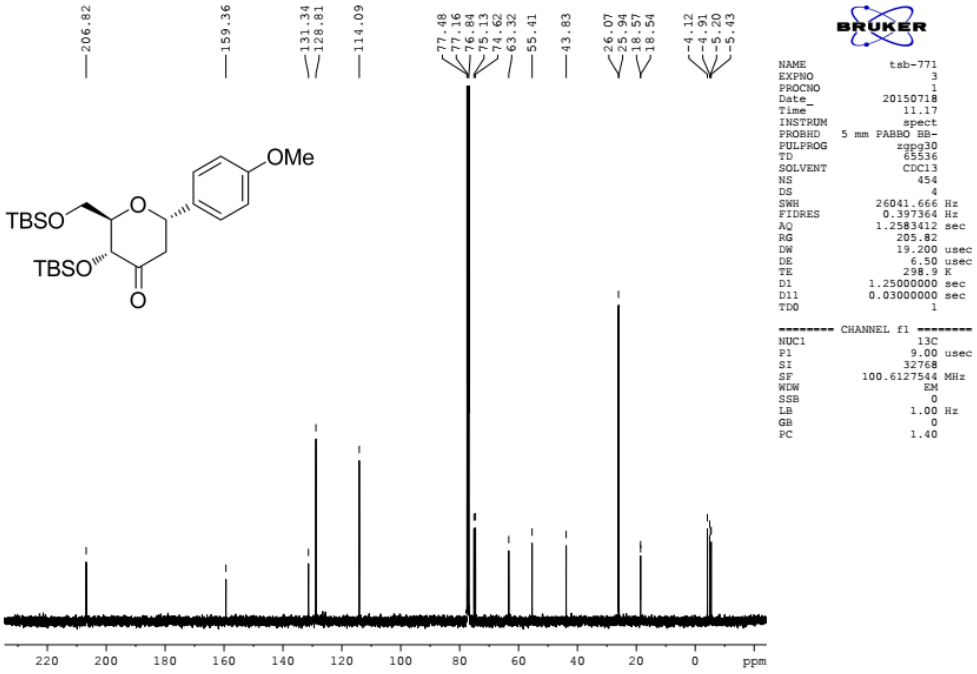
^{13}C NMR spectrum of **4bα**, 100MHz, $CDCl_3$



^{1}H NMR spectrum of **4cα**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4cα**, 100MHz, $CDCl_3$



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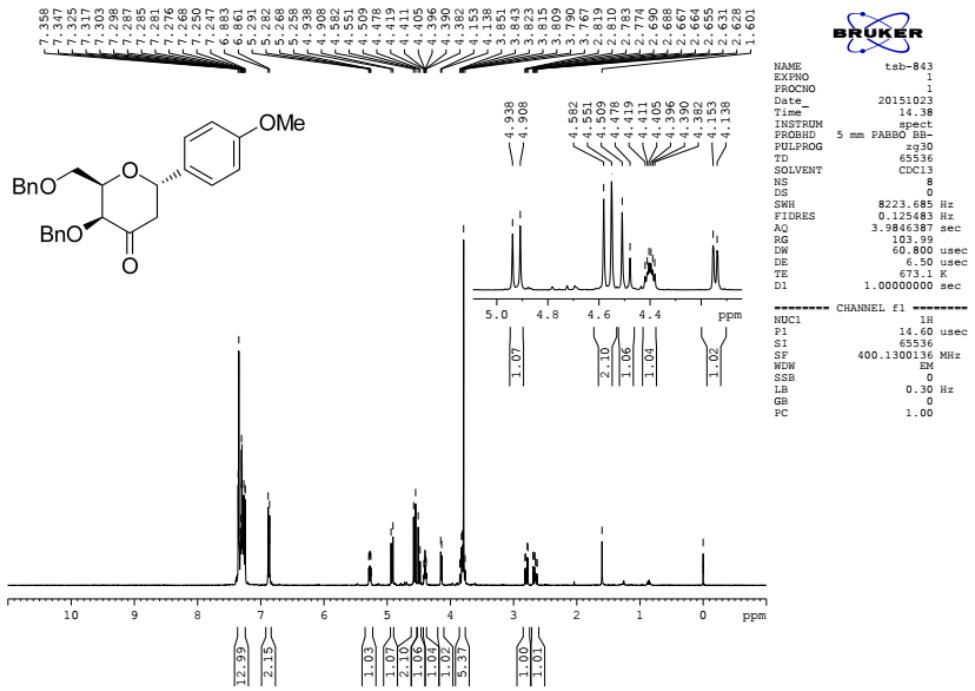

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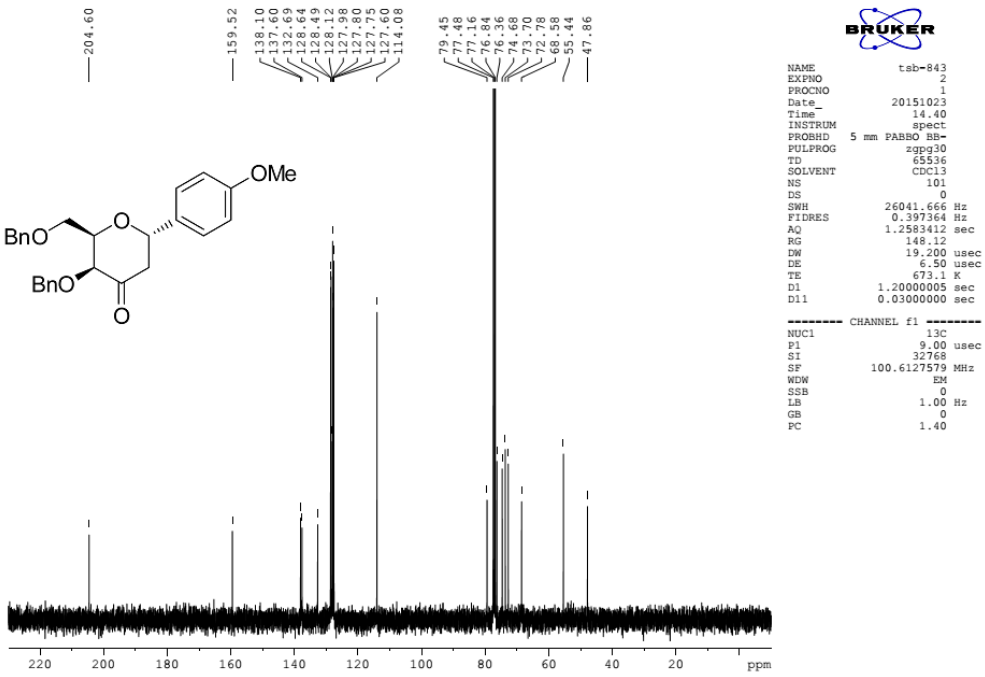
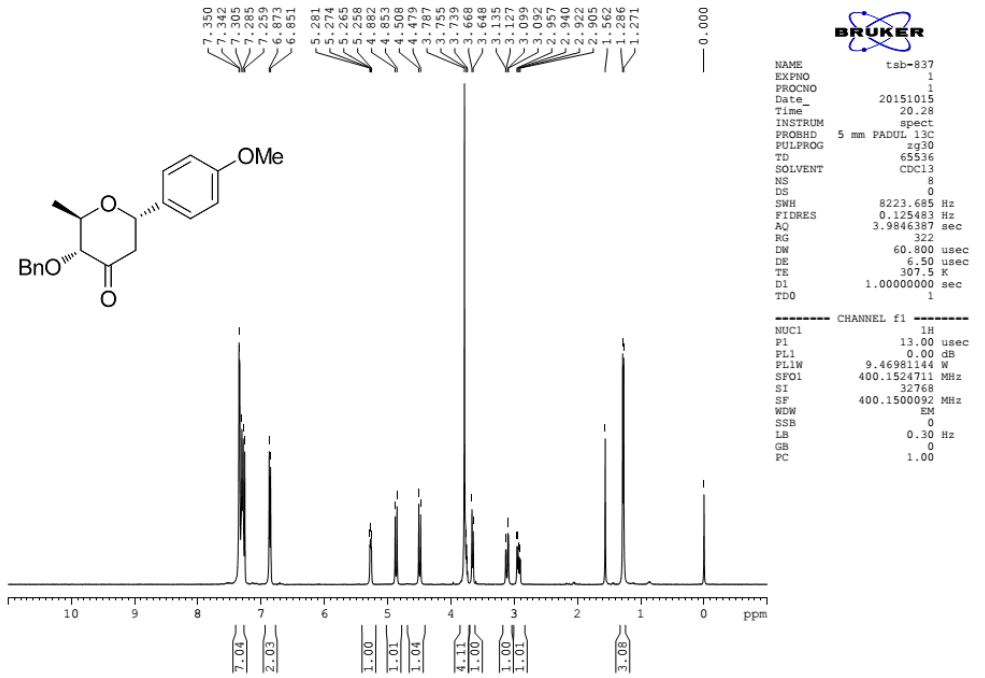
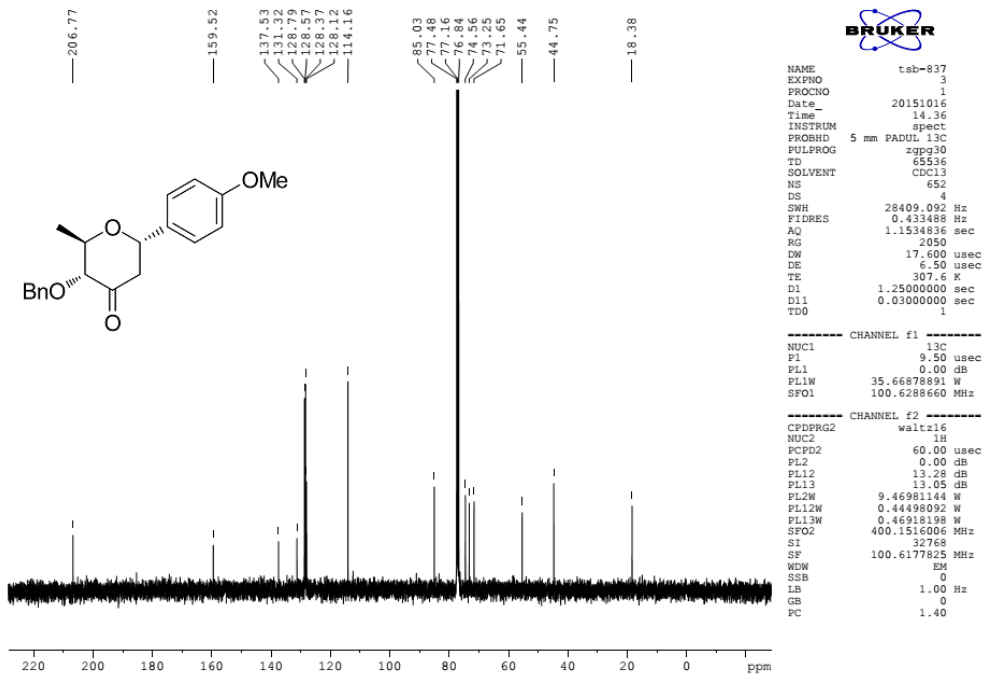


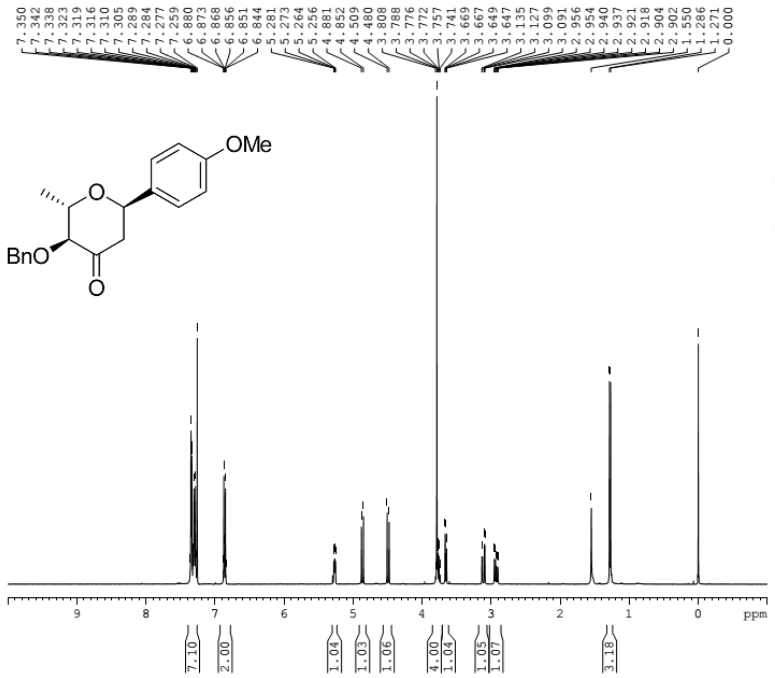
^{1}H NMR spectrum of **4eα**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4eα**, 100MHz, $CDCl_3$



^{1}H NMR spectrum of **4fα**, 400MHz, $CDCl_3$

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TE                 298.8 K
D1              1.00000000 sec
TD0                      1

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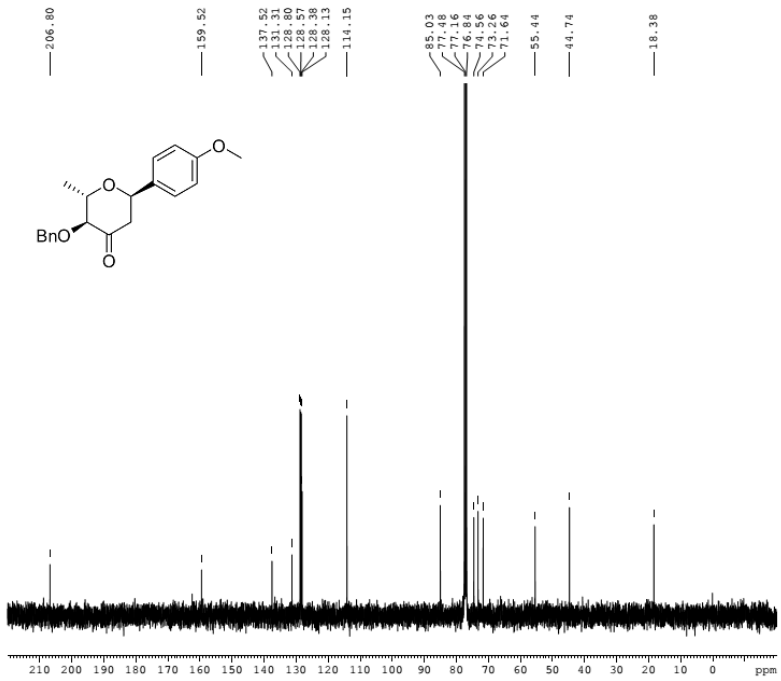
^{13}C NMR spectrum of **4fα**, 100MHz, $CDCl_3$

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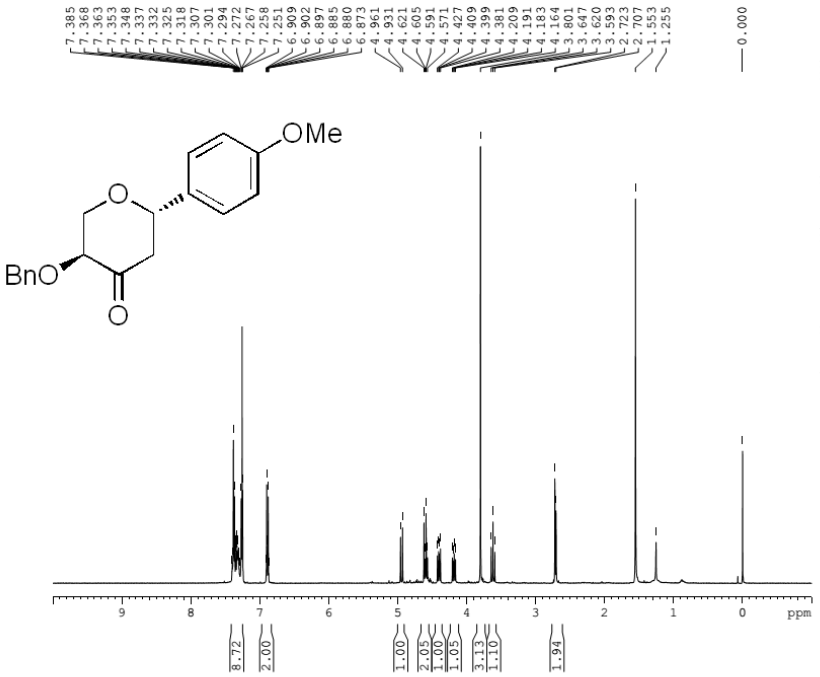
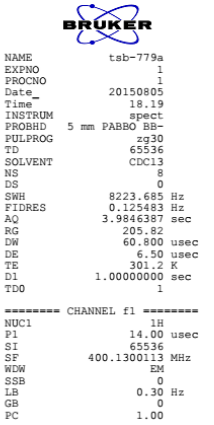
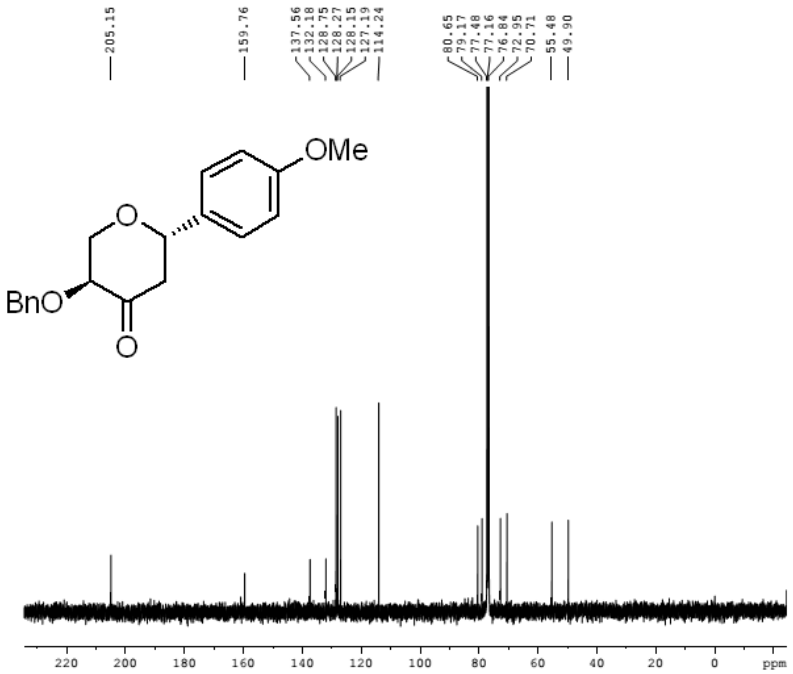
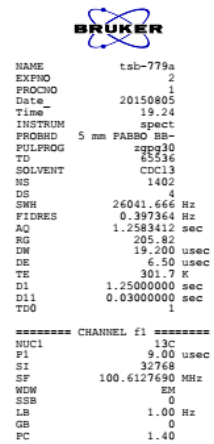
^{1}H NMR spectrum of **4gβ**, 400MHz, $CDCl_3$



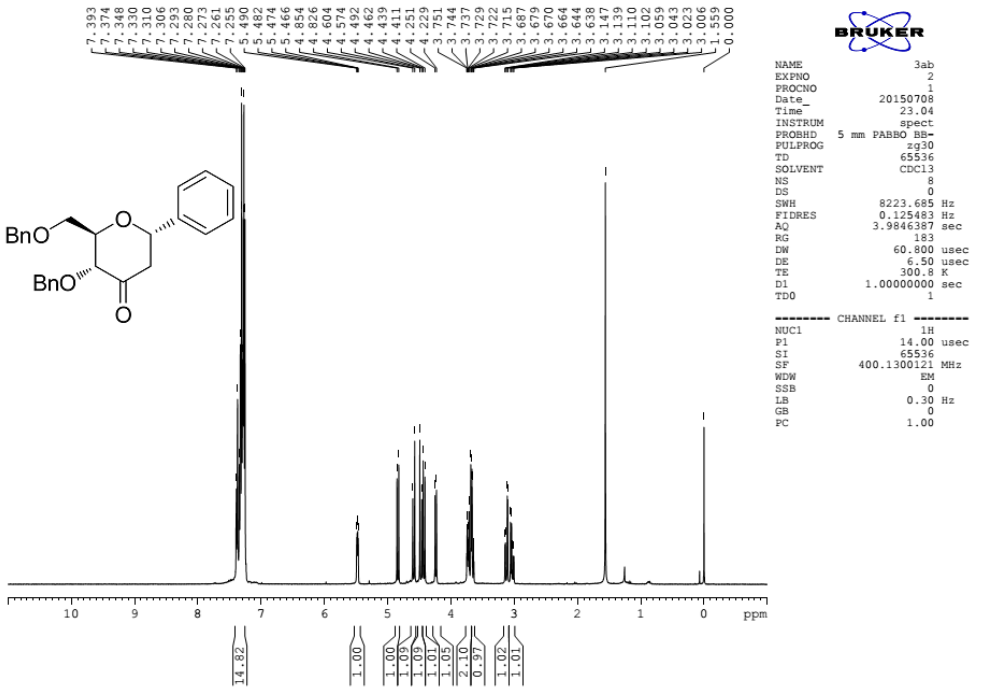


^{13}C NMR spectrum of **4gβ**, 100MHz, $CDCl_3$

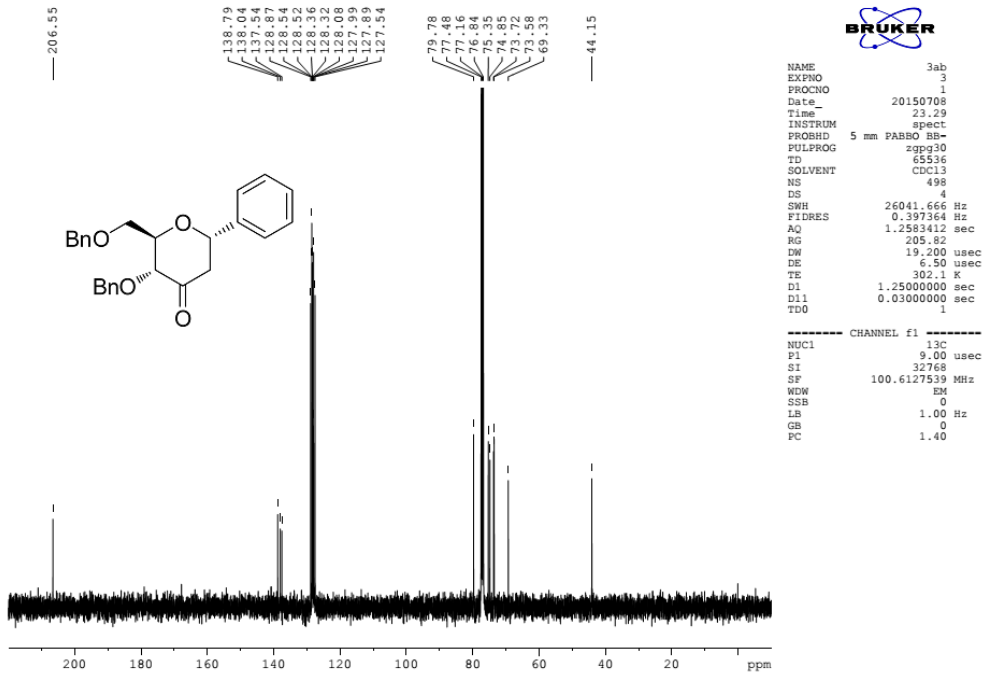




^{1}H NMR spectrum of **4hα**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4hα**, 100MHz, $CDCl_3$



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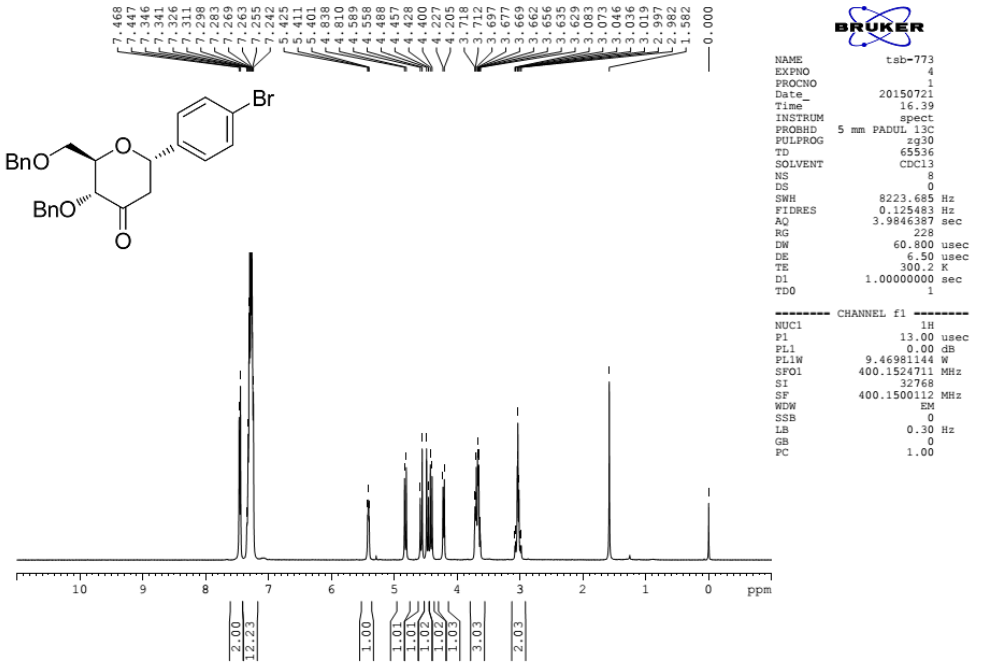
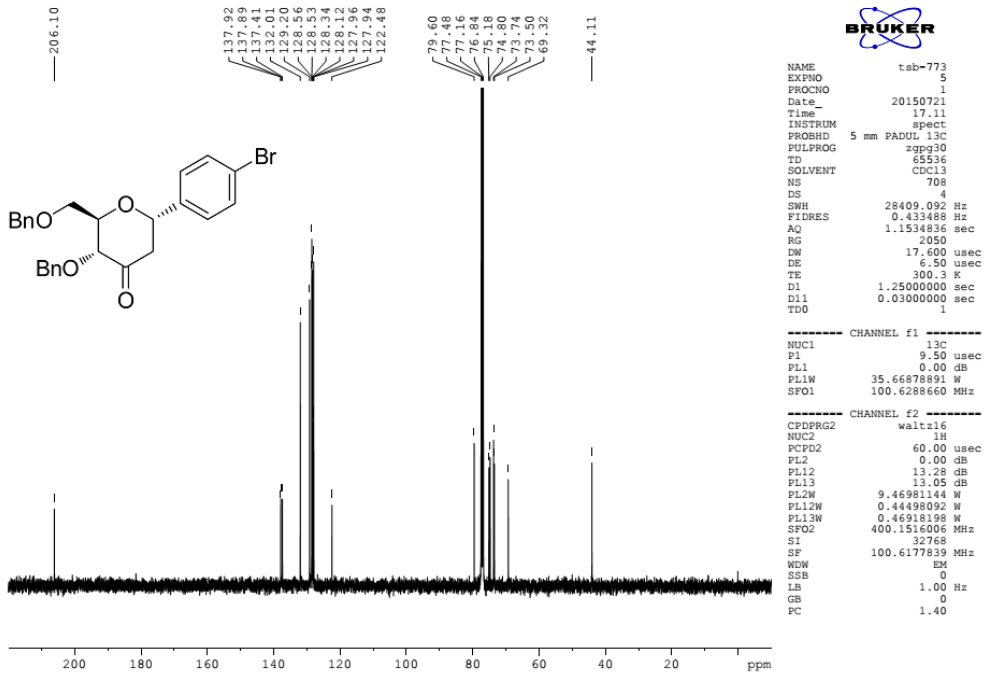


^{13}C NMR spectrum of **4iα**, 100MHz, $CDCl_3$



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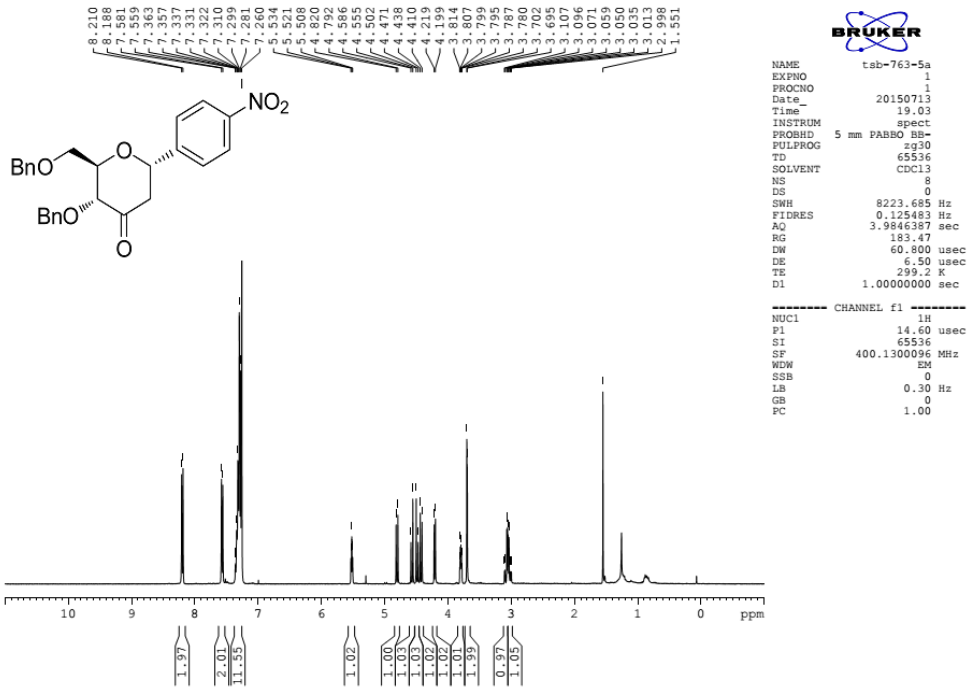
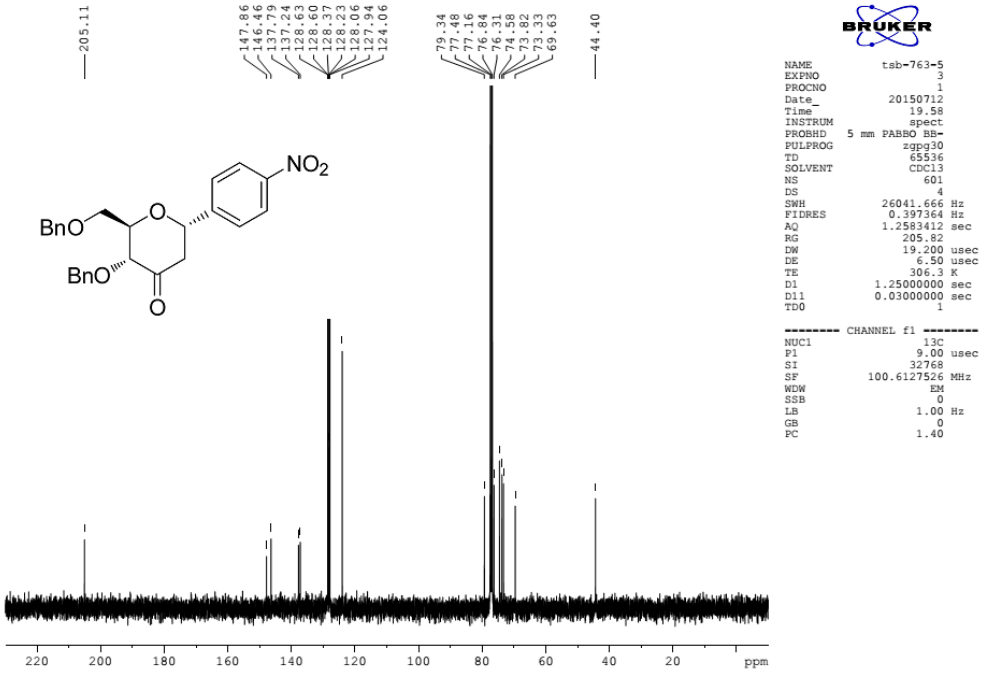
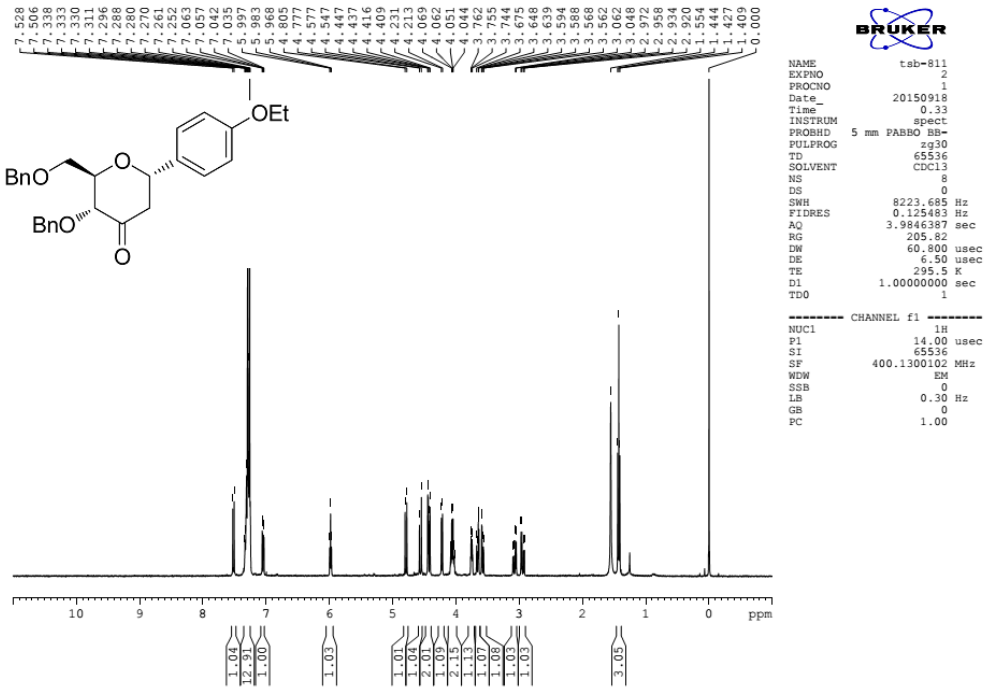


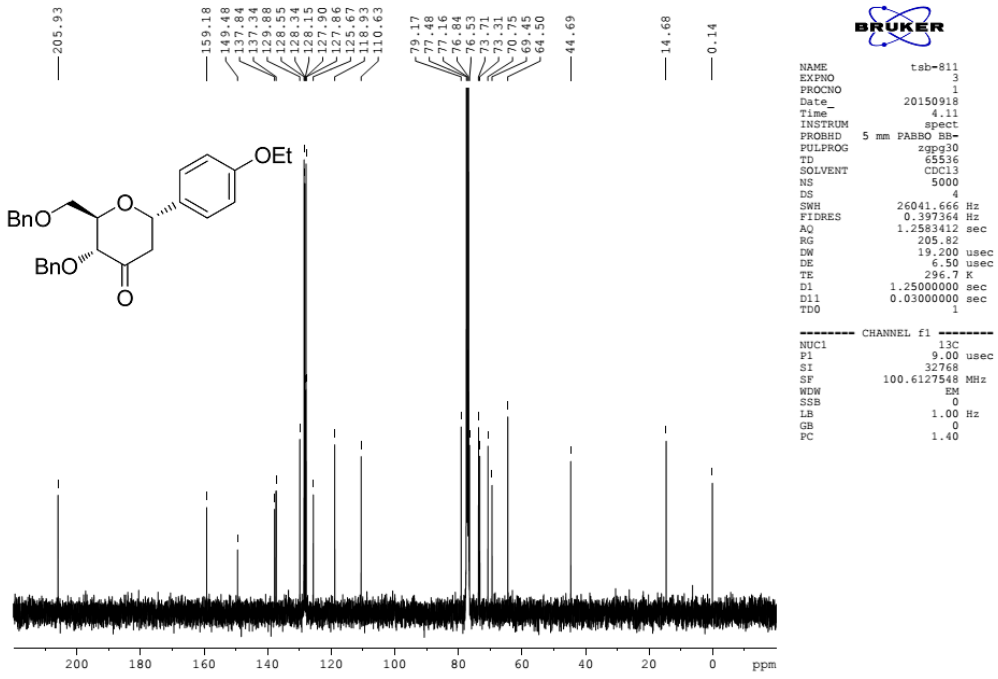
^{13}C NMR spectrum of **4jα**, 100MHz, $CDCl_3$



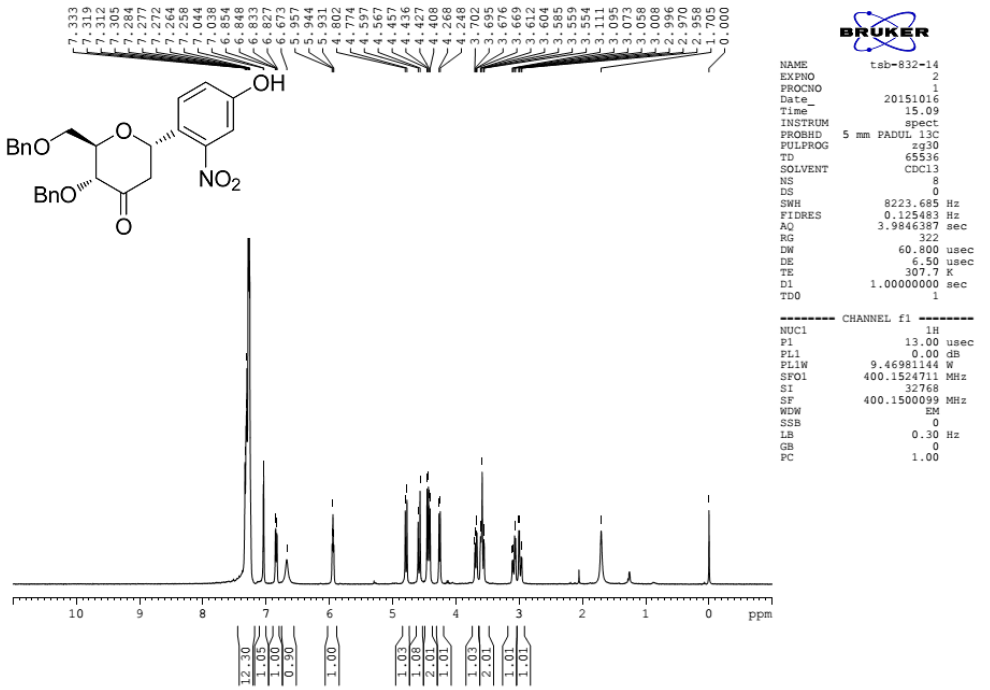
^{1}H NMR spectrum of **4kα**, 400MHz, $CDCl_3$



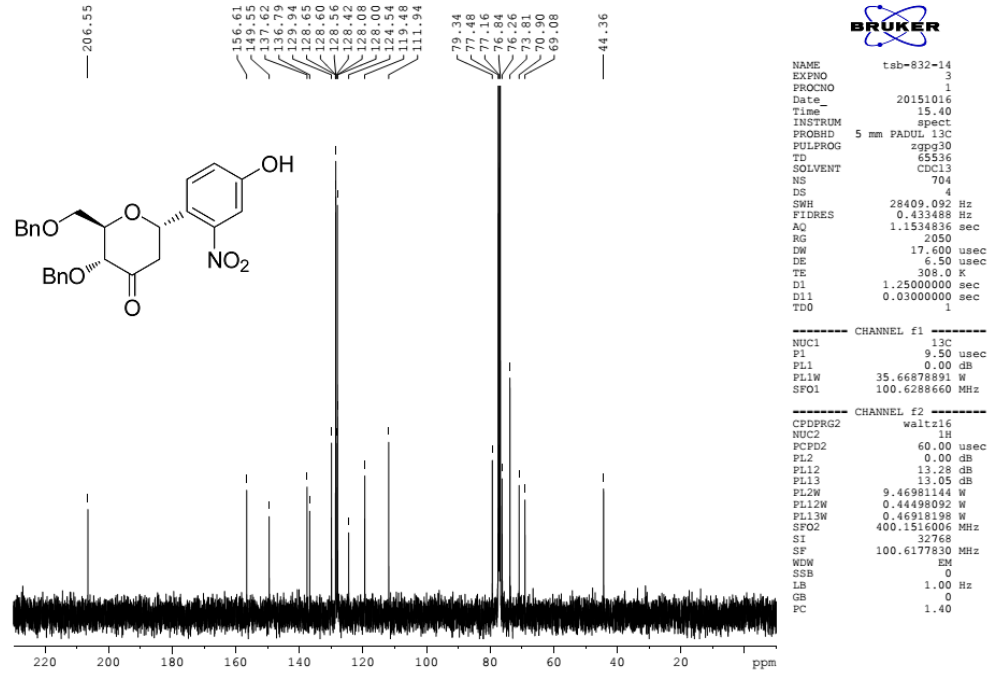
^{13}C NMR spectrum of **4kα**, 100MHz, $CDCl_3$



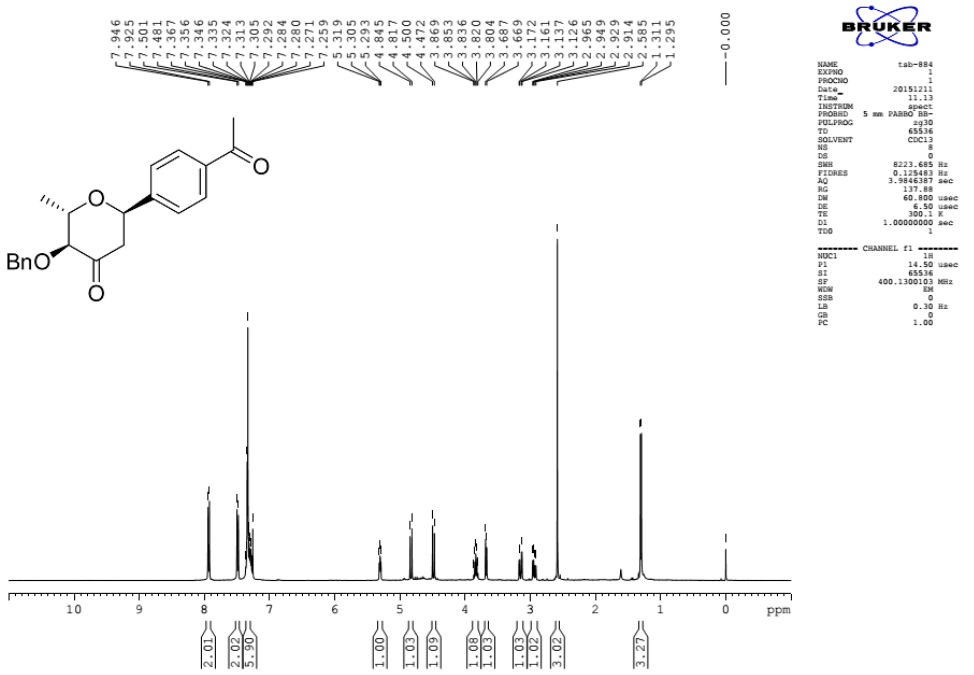
^{1}H NMR spectrum of **4lα**, 400MHz, $CDCl_3$



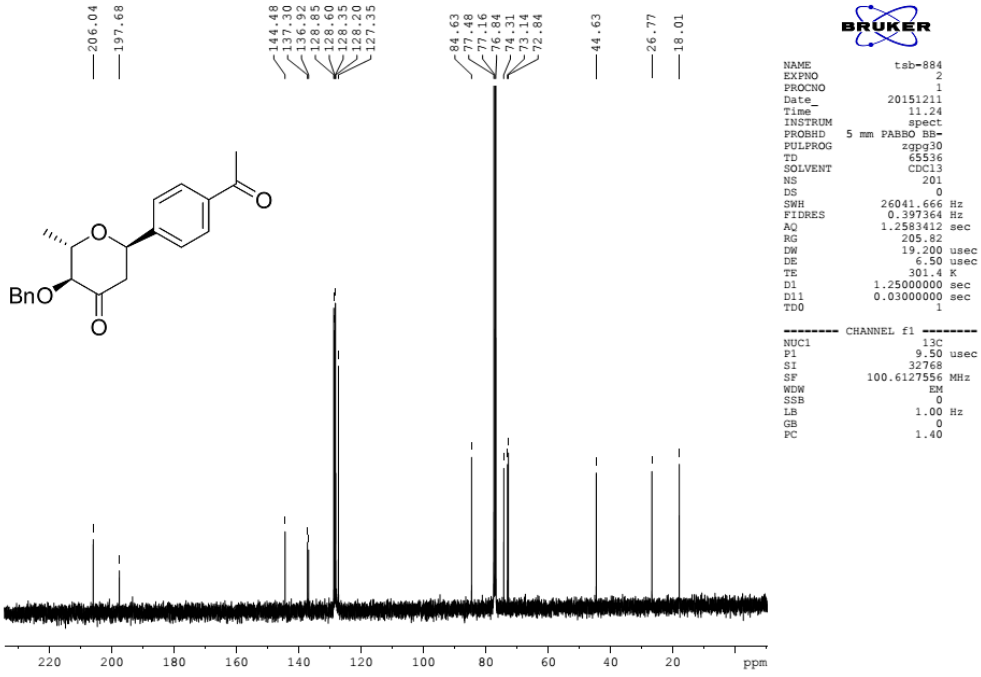
^{13}C NMR spectrum of **4lα**, 100MHz, $CDCl_3$



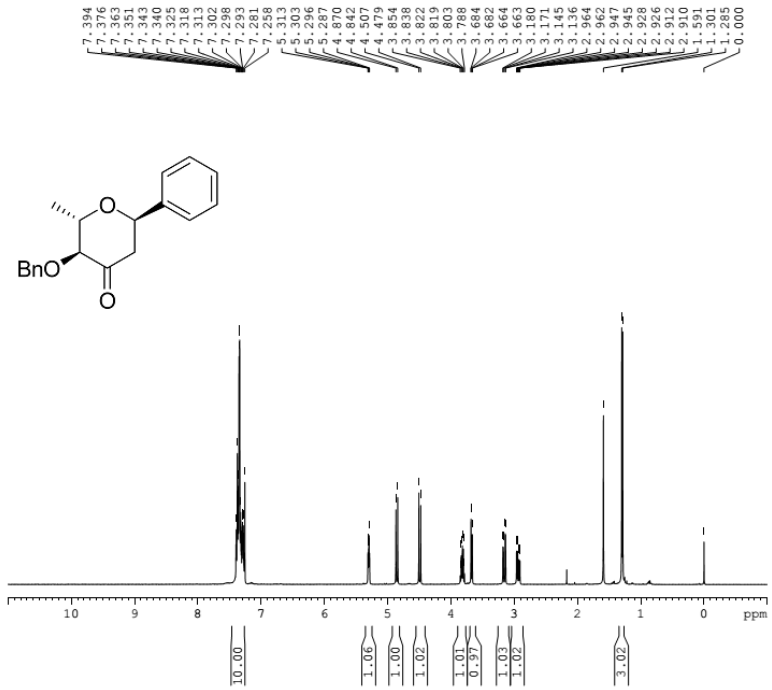
^{1}H NMR spectrum of **4mα**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4mα**, 100MHz, $CDCl_3$



^{1}H NMR spectrum of **4nα**, 400MHz, $CDCl_3$

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TD                   65536
SOLVENT              CDCl3
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SWH               8223.685 Hz
FIDRES           0.125483 Hz
AQ                3.9846387 sec
RG                   161.46
DW                 60.800 usec
DE                  6.50 usec
TE                  295.3 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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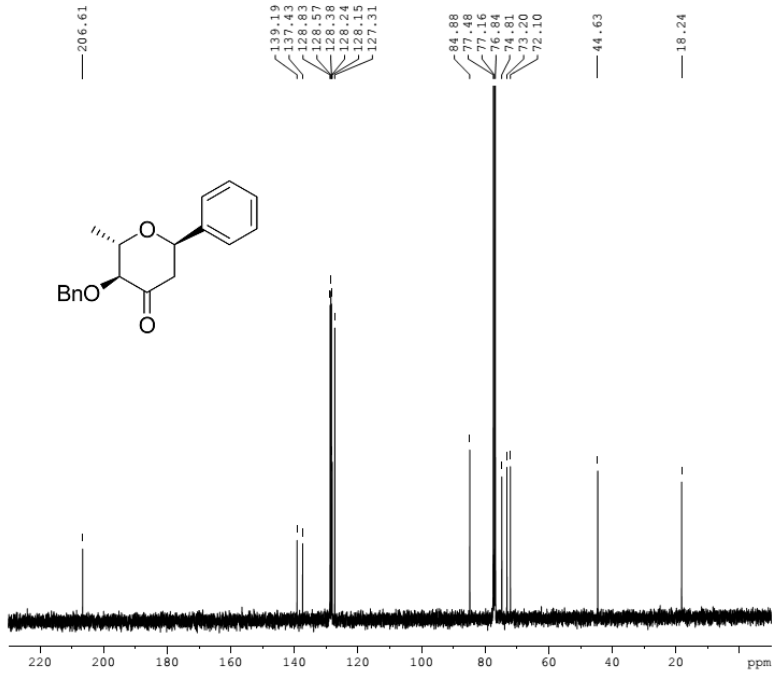
^{13}C NMR spectrum of **4nα**, 100MHz, $CDCl_3$

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FIDRES           0.397364 Hz
AQ                1.2583412 sec
RG                   205.82
DW                 19.200 usec
DE                  6.50 usec
TE                  296.7 K
D1               1.25000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
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PC                 1.40
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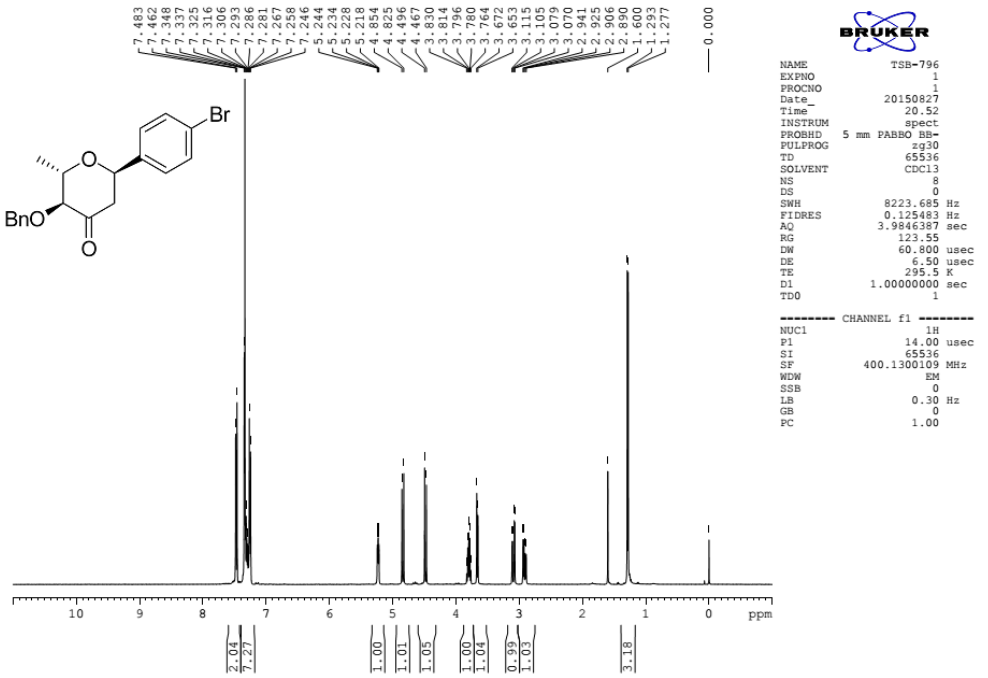
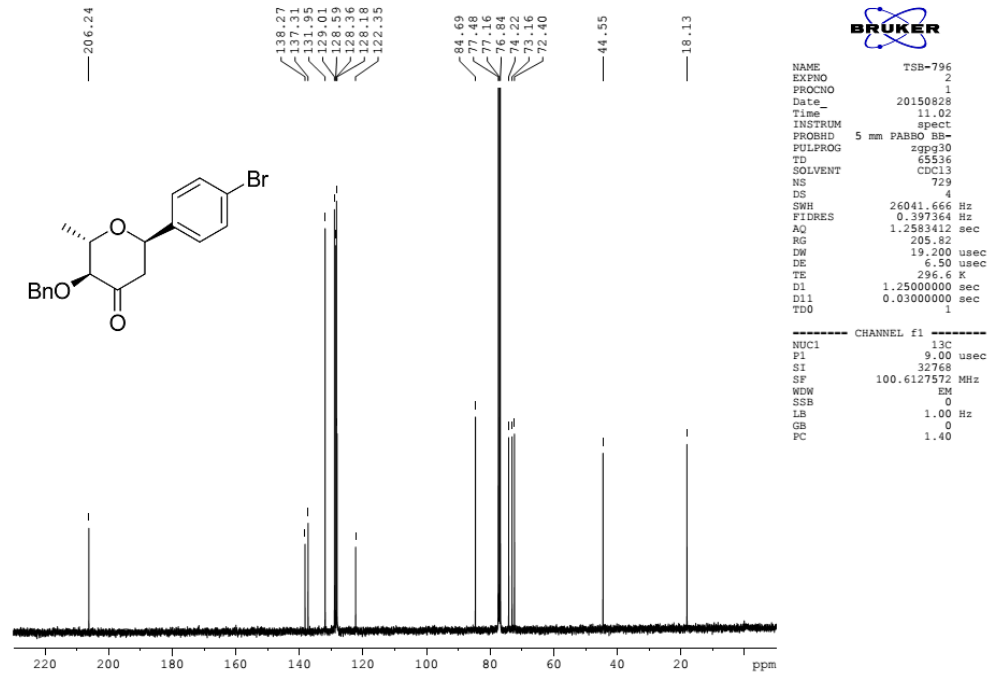
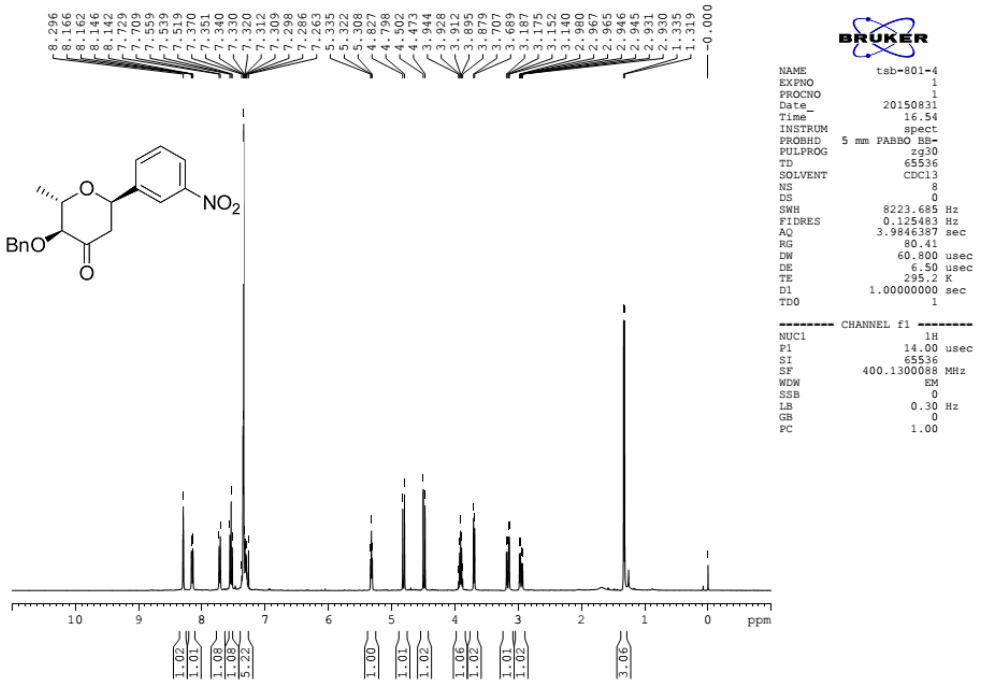
^{1}H NMR spectrum of **4oα**, 400MHz, $CDCl_3$



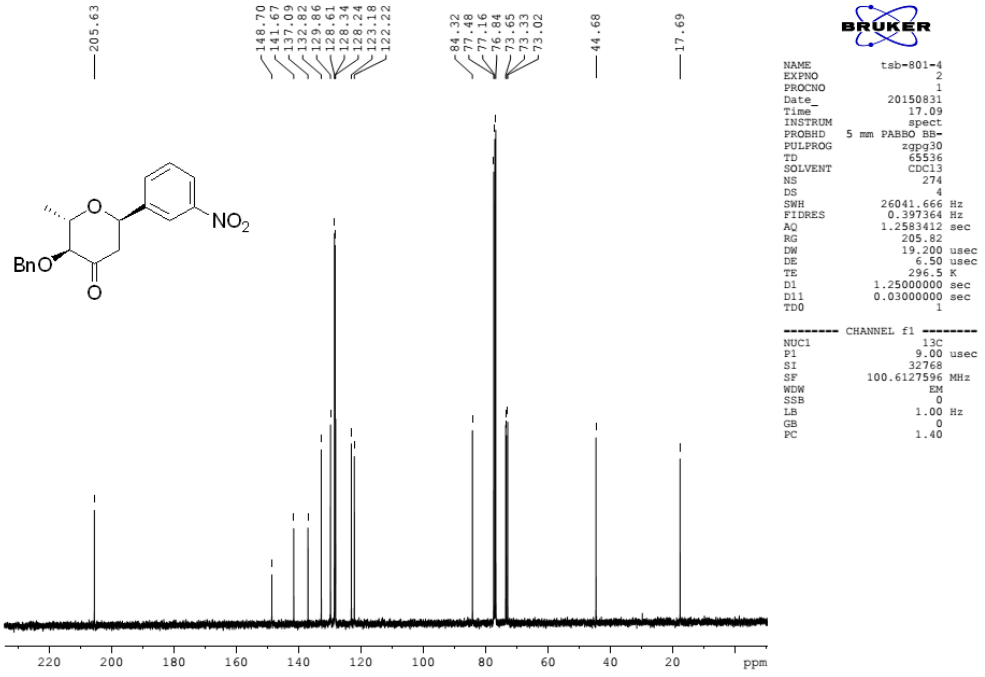
^{13}C NMR spectrum of **4oα**, 100MHz, $CDCl_3$



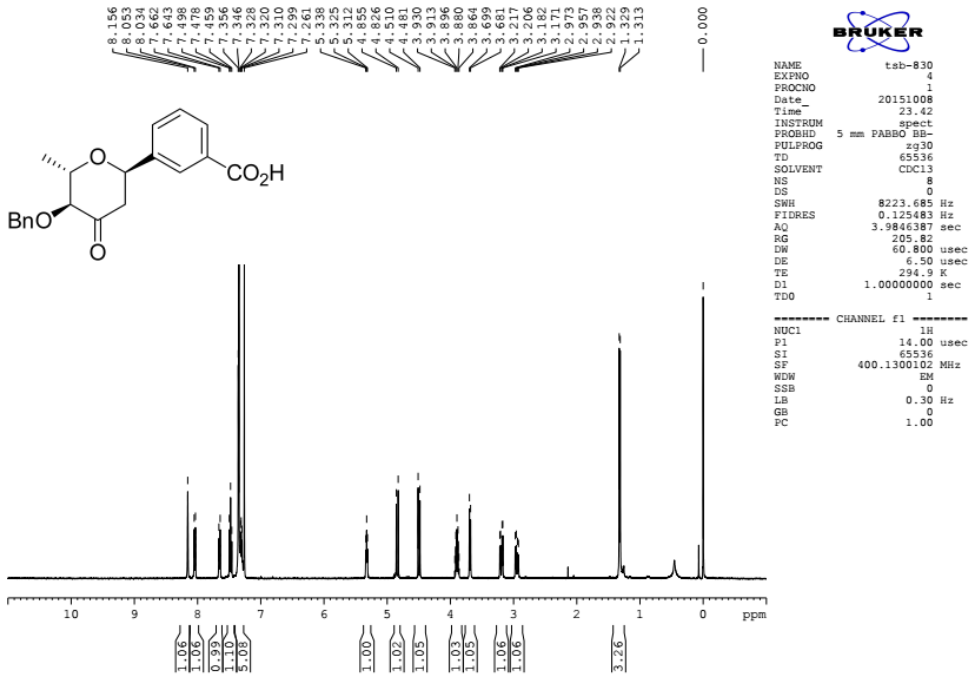
^{1}H NMR spectrum of **4pα**, 400MHz, $CDCl_3$



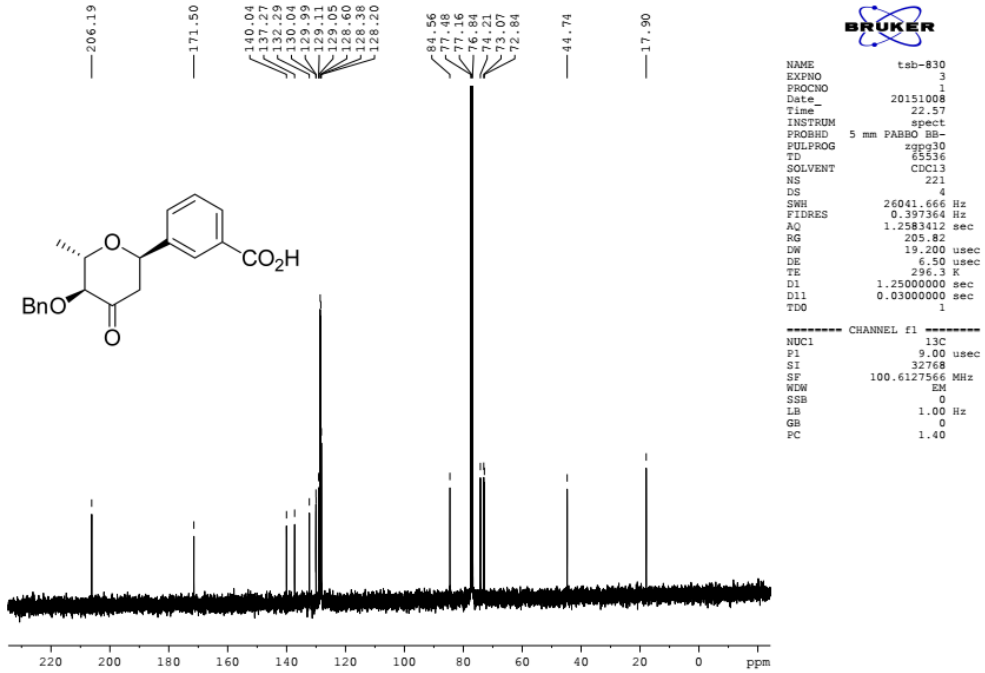
^{13}C NMR spectrum of **4pα**, 100MHz, $CDCl_3$



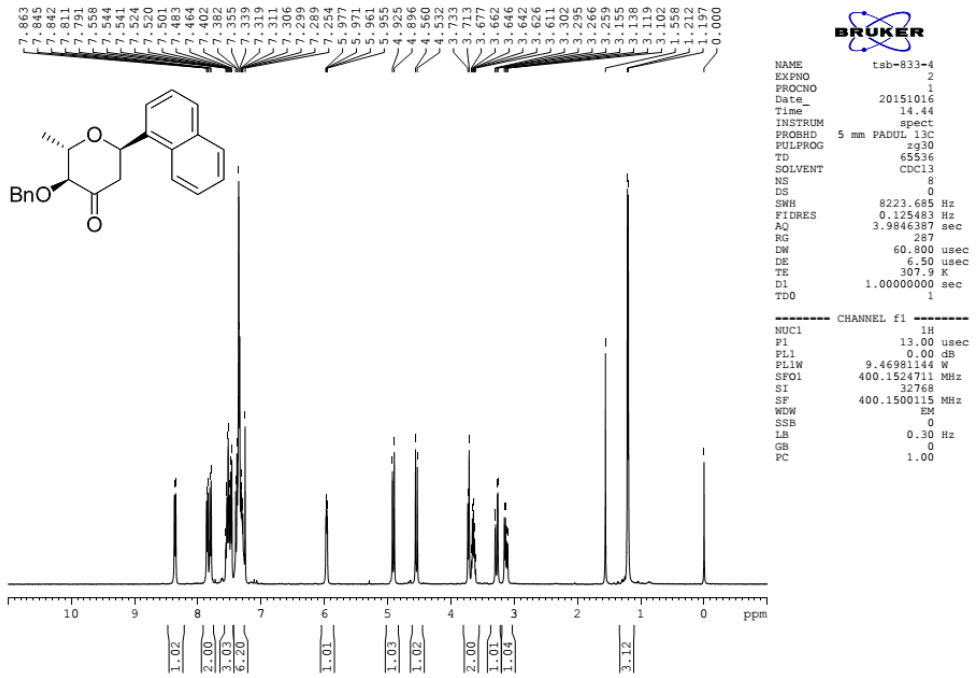
^{1}H NMR spectrum of **4qα**, 400MHz, $CDCl_3$



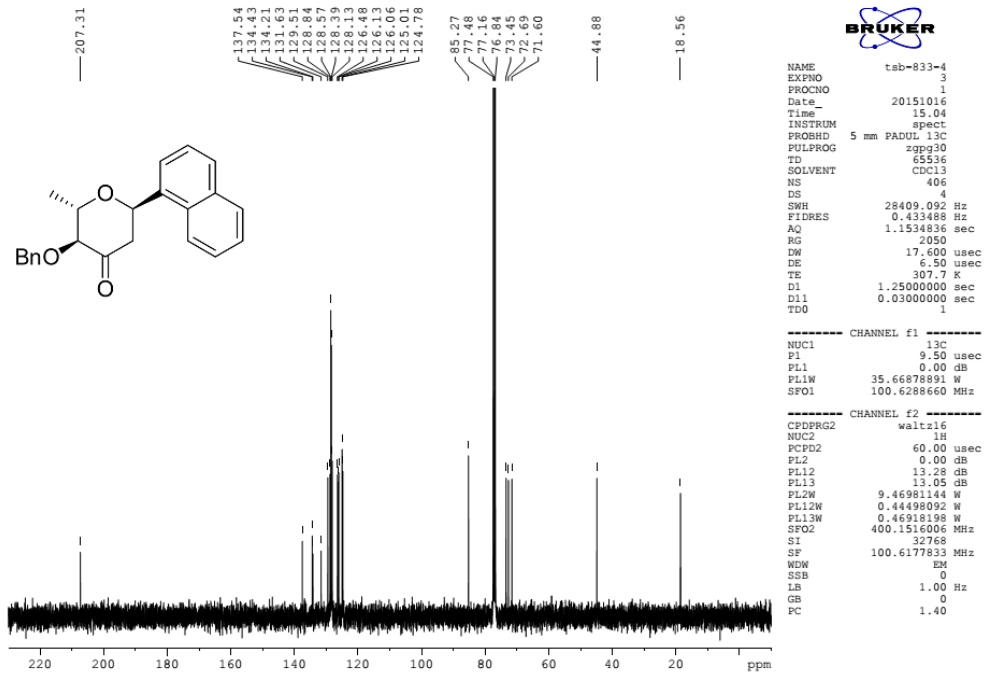
^{13}C NMR spectrum of **4qα**, 100MHz, $CDCl_3$



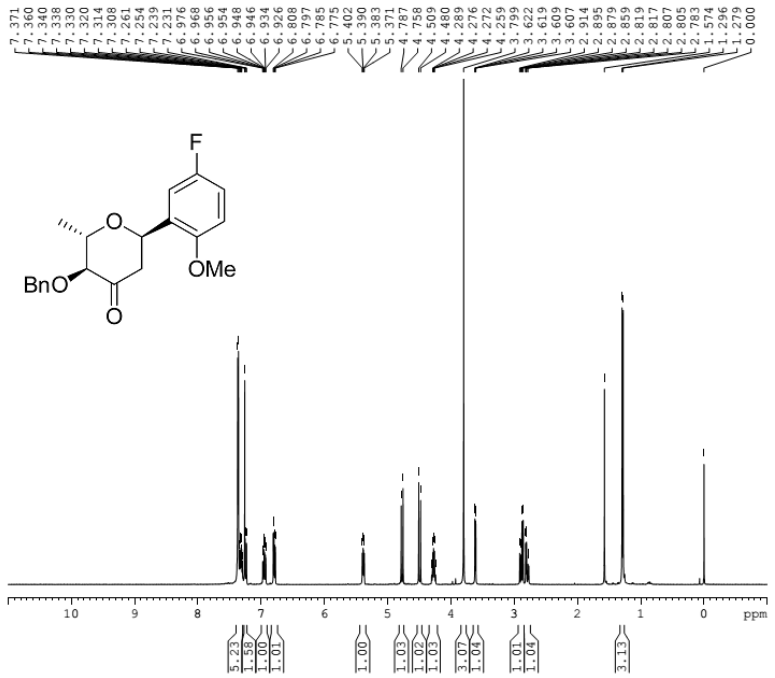
^{1}H NMR spectrum of **4rα**, 400MHz, $CDCl_3$

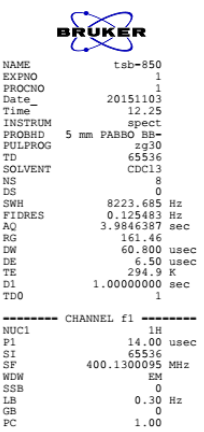


^{13}C NMR spectrum of **4rα**, 100MHz, $CDCl_3$

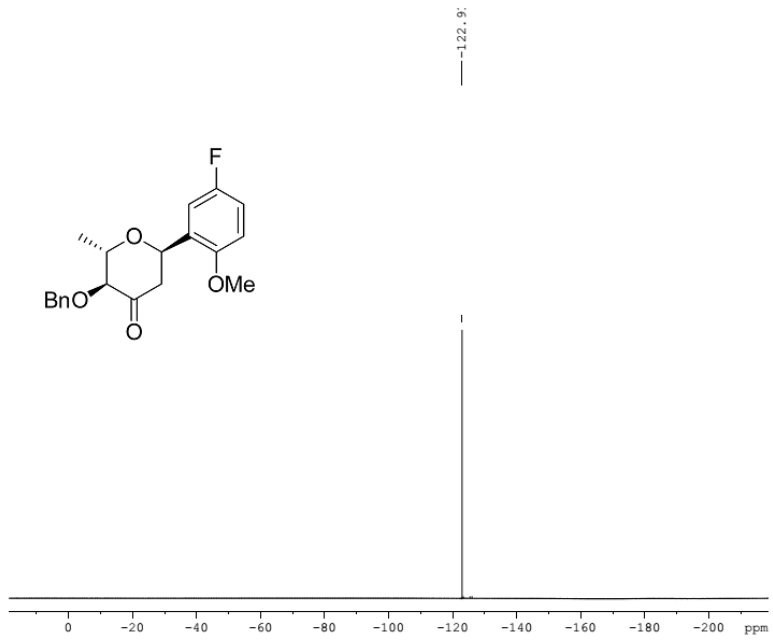


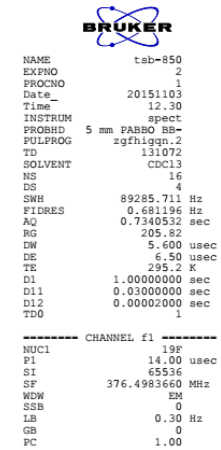
^{1}H NMR spectrum of **4sα**, 400MHz, $CDCl_3$



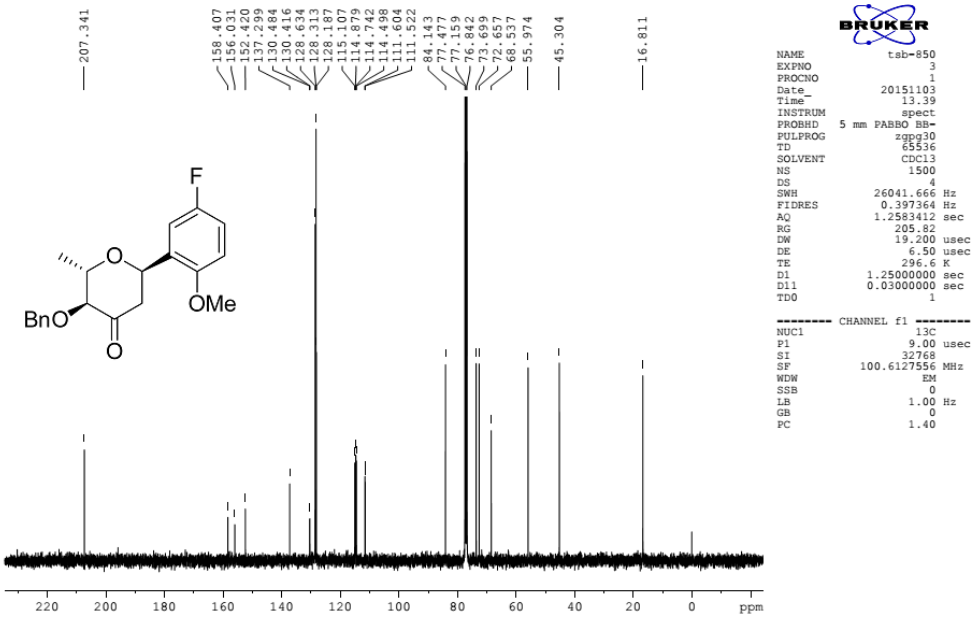


^{19}F NMR spectrum of **4sα**, 376MHz, $CDCl_3$

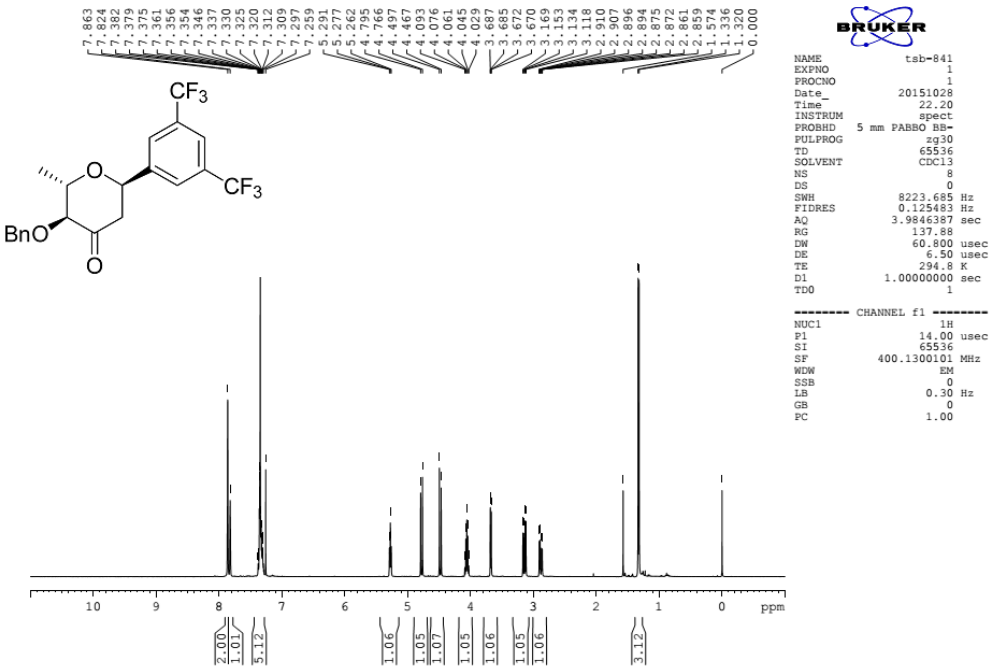




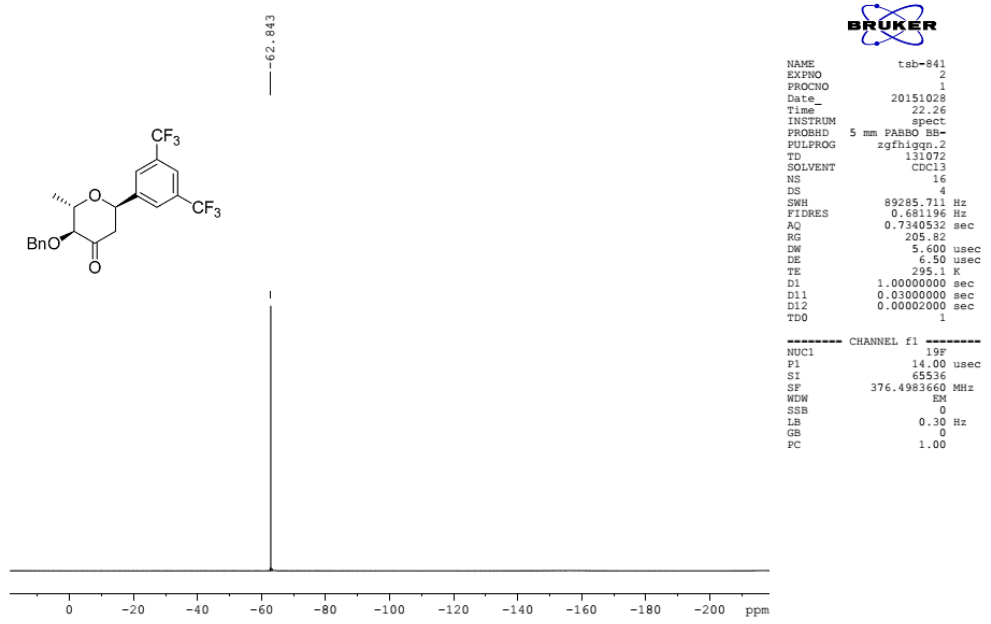
^{13}C NMR spectrum of **4sα**, 100MHz, $CDCl_3$



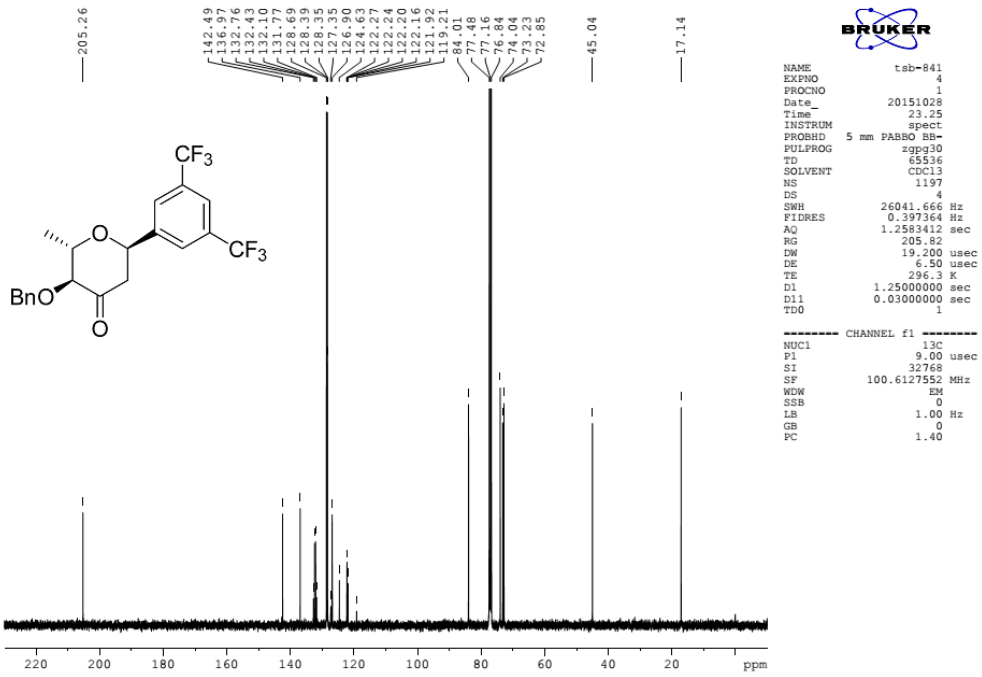
^{1}H NMR spectrum of **4tα**, 400MHz, $CDCl_3$



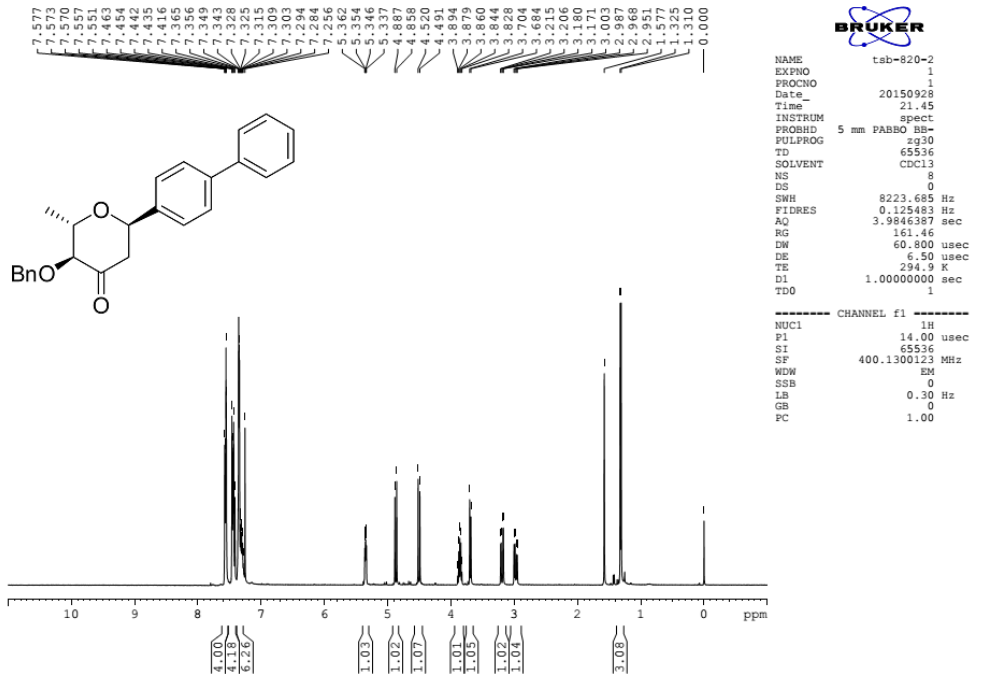
^{19}F NMR spectrum of **4tα**, 376MHz, $CDCl_3$



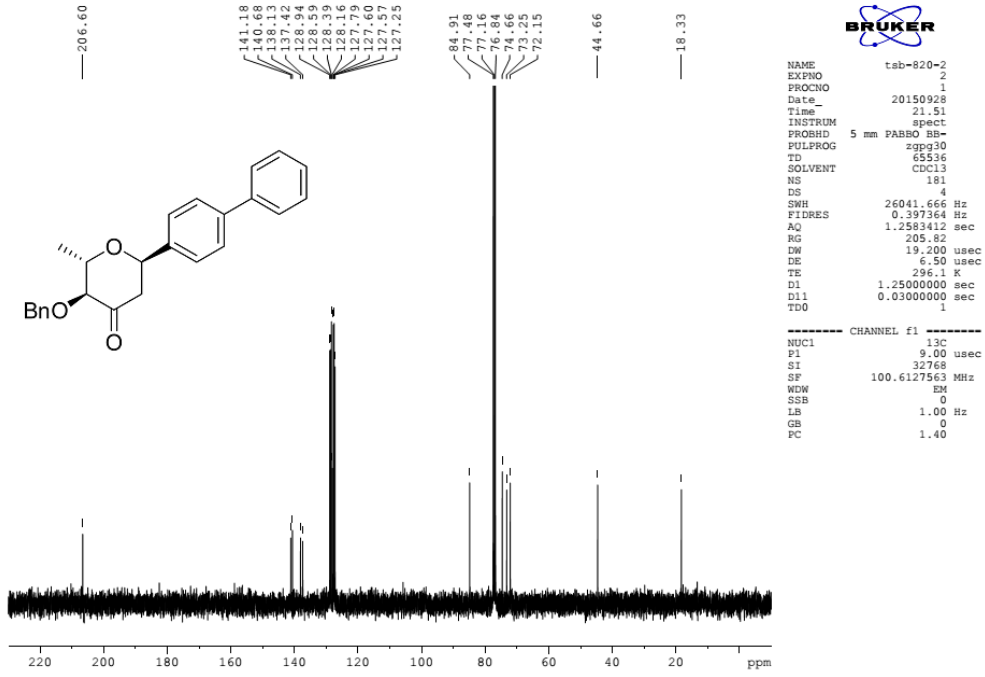
^{13}C NMR spectrum of **4tα**, 100MHz, $CDCl_3$



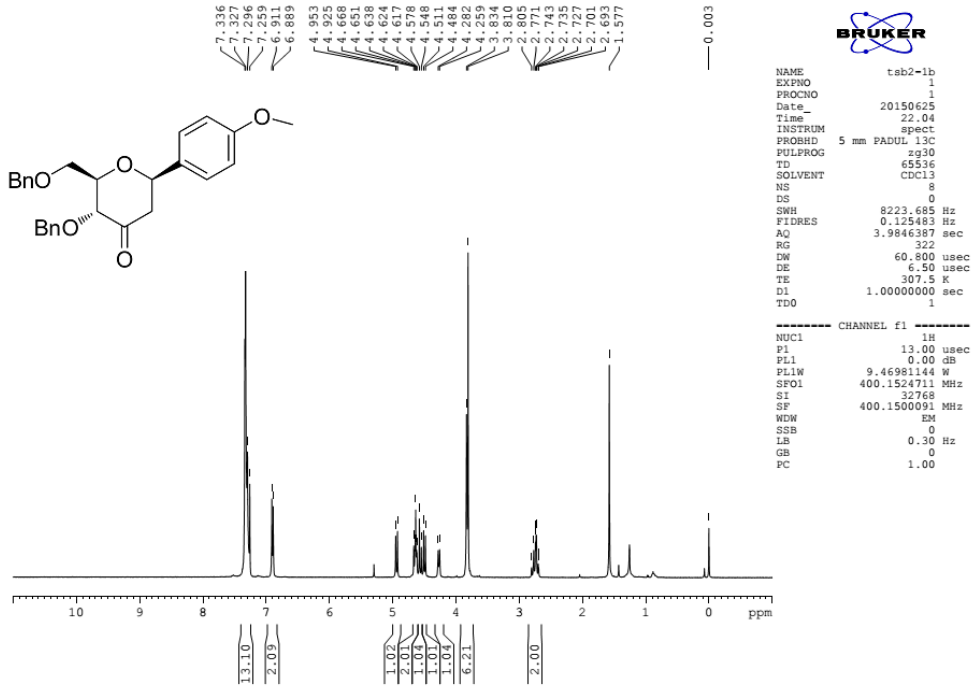
^{1}H NMR spectrum of **4uα**, 400MHz, $CDCl_3$



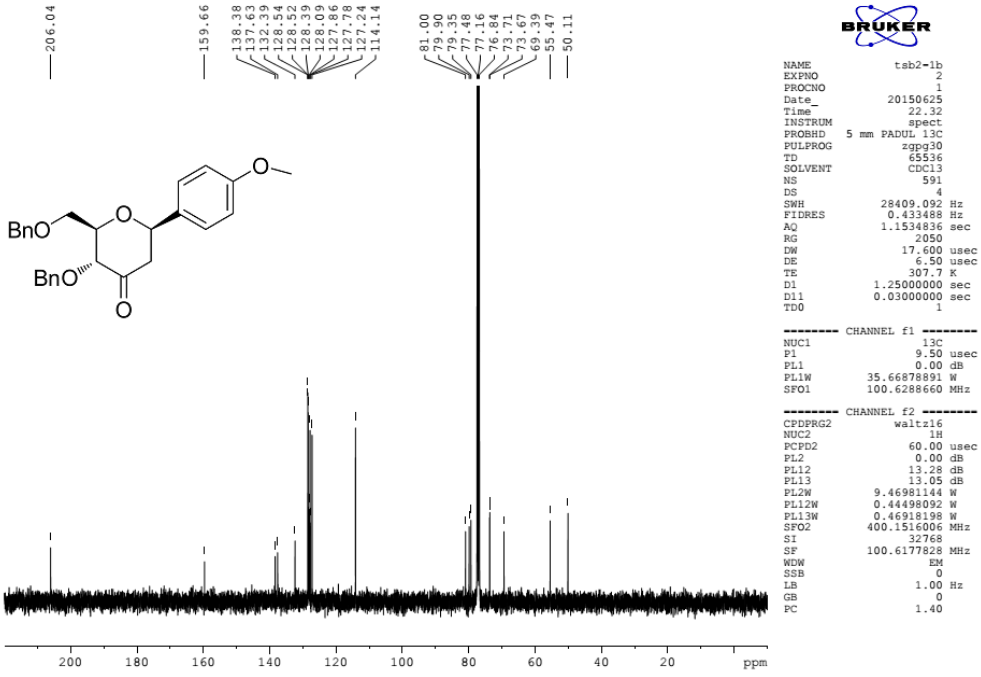
^{13}C NMR spectrum of **4uα** 100MHz, $CDCl_3$



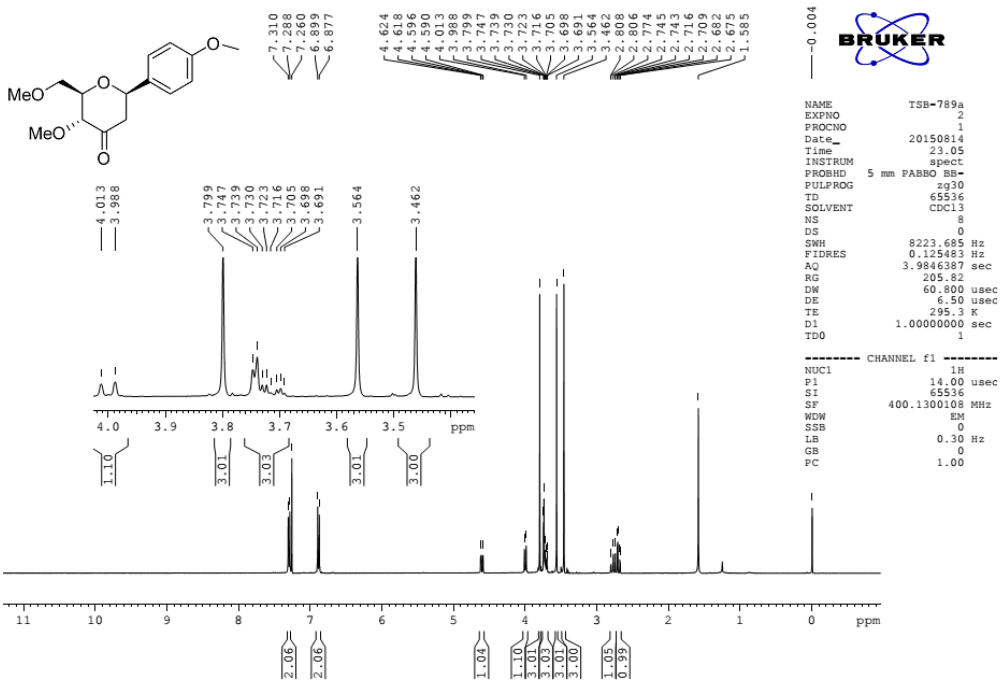
^{1}H NMR spectrum of **4aβ**, 400MHz, $CDCl_3$



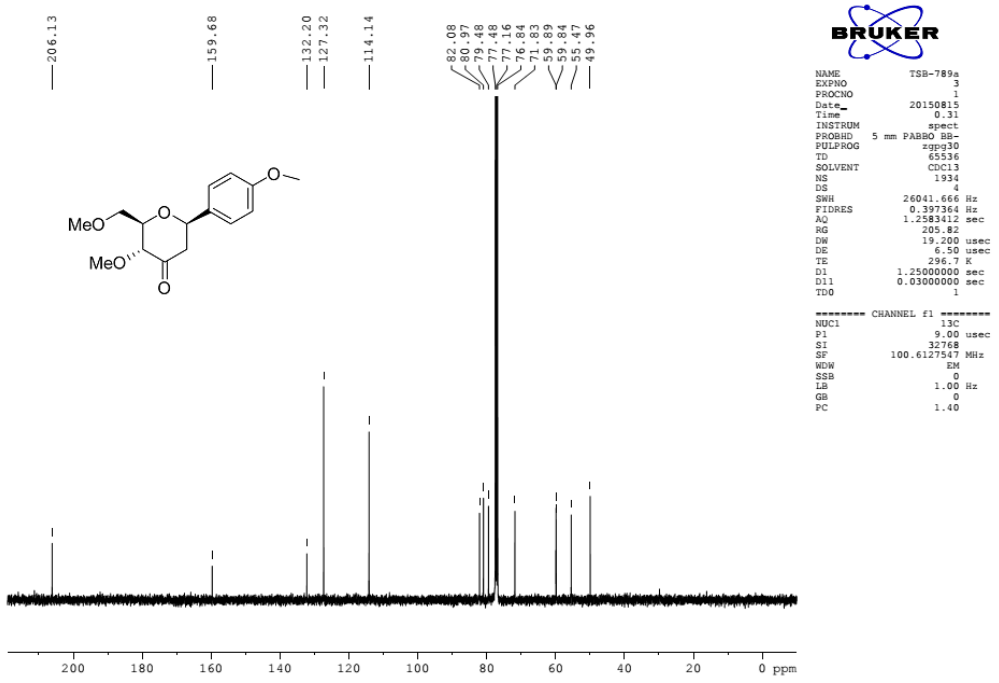
^{13}C NMR spectrum of **4aβ**, 100MHz, $CDCl_3$



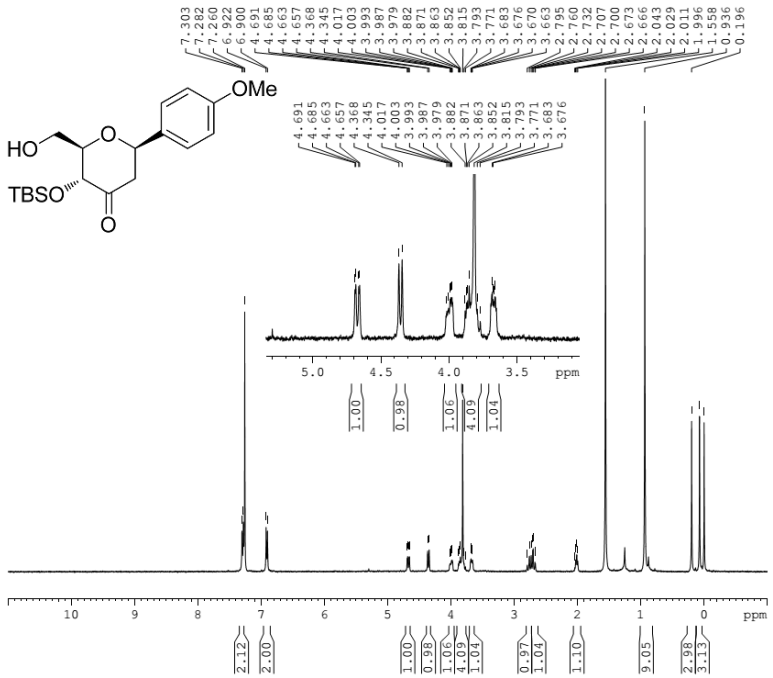
^{1}H NMR spectrum of **4bβ**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4bβ**, 100MHz, $CDCl_3$



^{1}H NMR spectrum of **4cβ**, 400MHz, $CDCl_3$

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D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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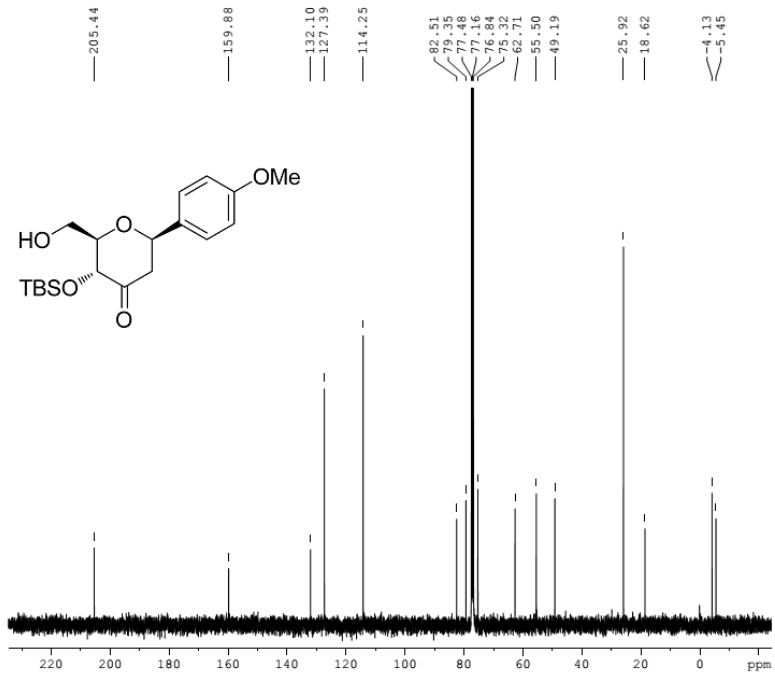
^{13}C NMR spectrum of **4cβ**, 100MHz, $CDCl_3$

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DW                  19.200 usec
DE                   6.50 usec
TE                   303.6 K
D1                1.25000000 sec
D11               0.03000000 sec
TD0                       1

-------- CHANNEL f1 --------
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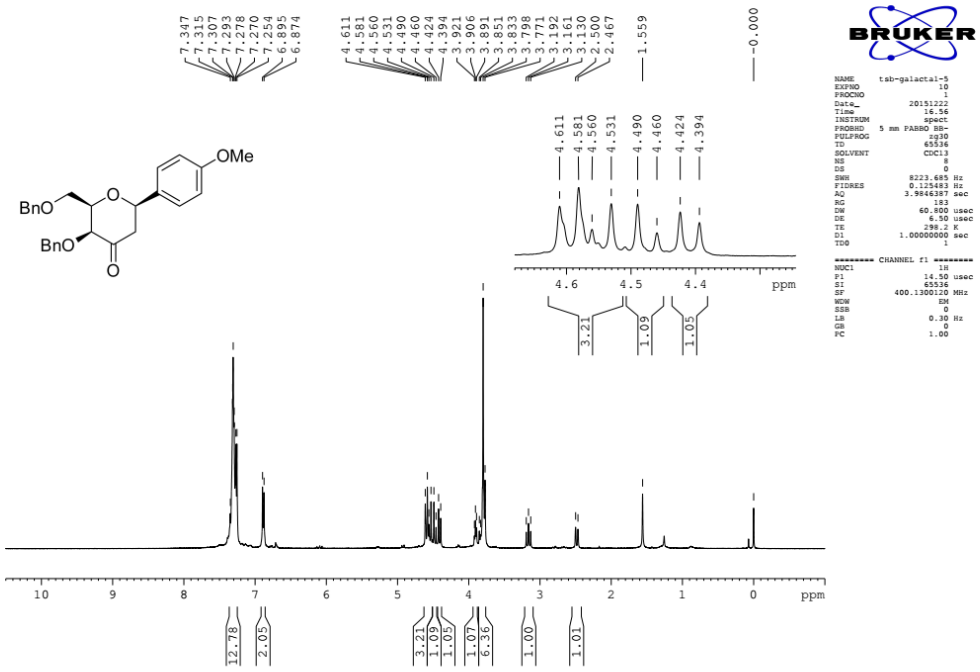
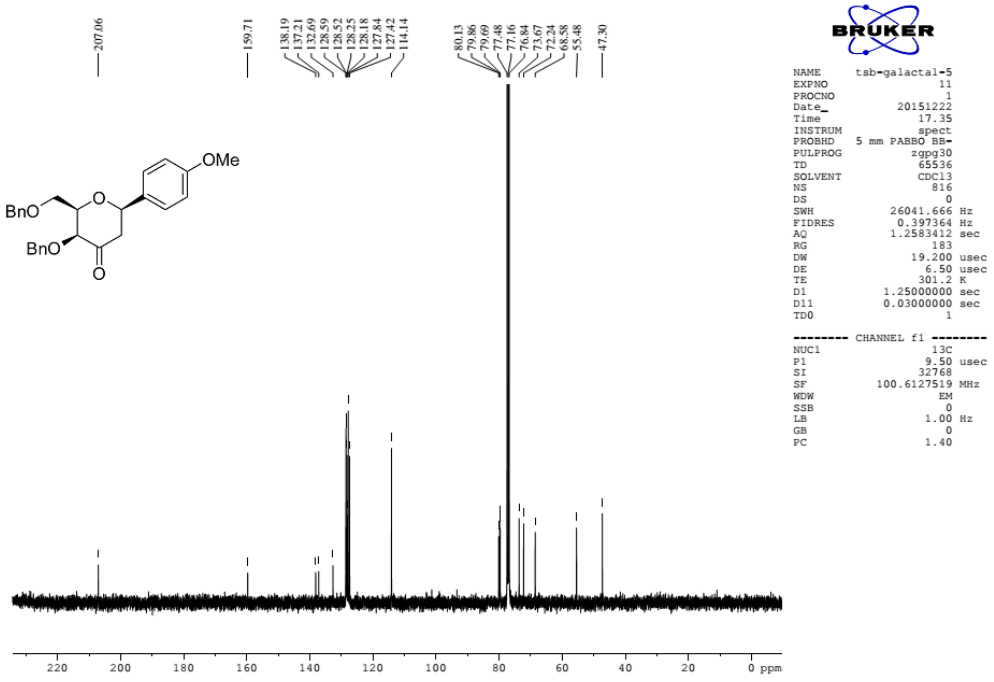
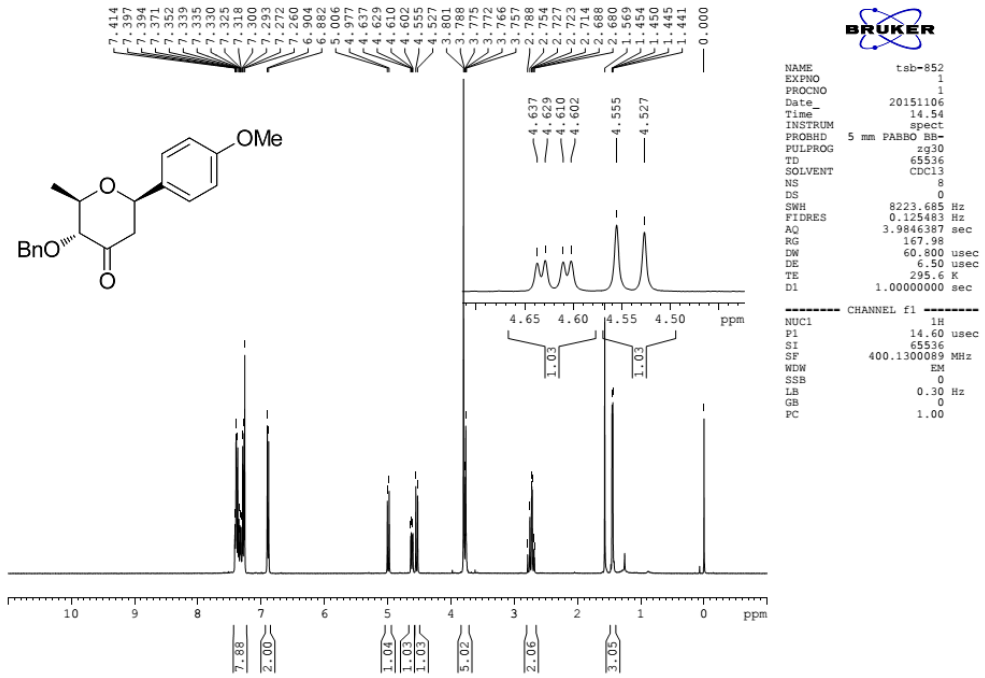
^{1}H NMR spectrum of **4dβ**, 400MHz, $CDCl_3$



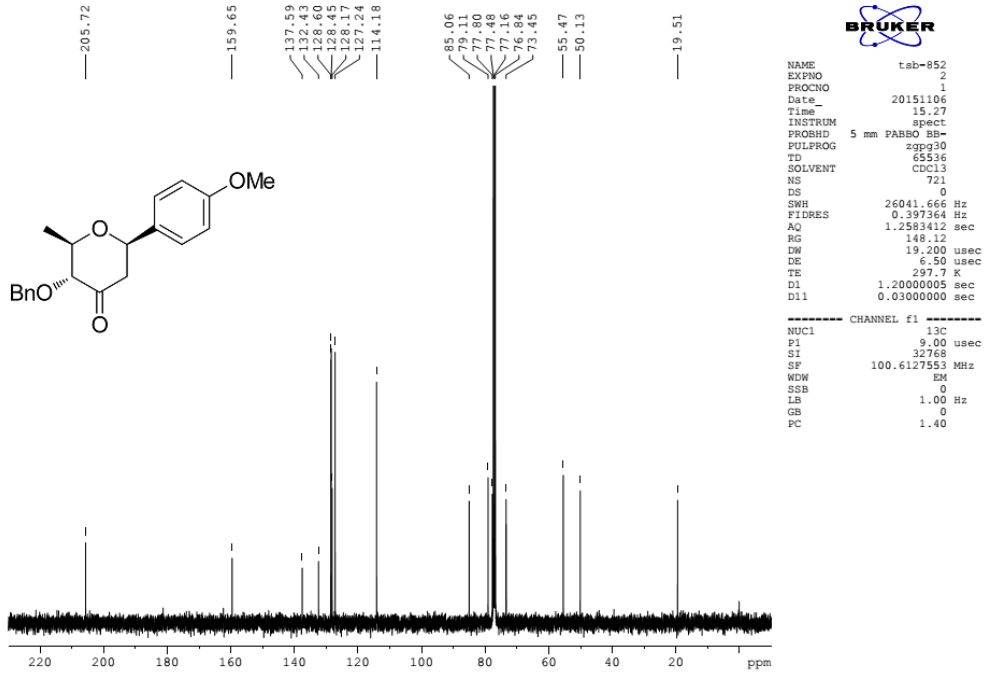
^{13}C NMR spectrum of **4dβ**, 100MHz, $CDCl_3$



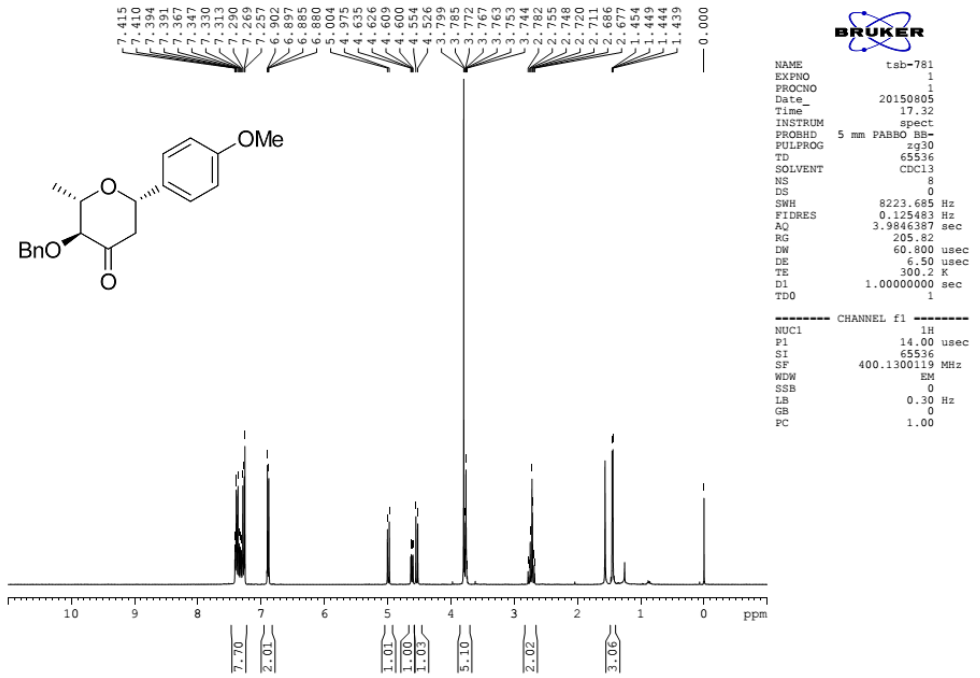
^{1}H NMR spectrum of **4eβ**, 400MHz, $CDCl_3$



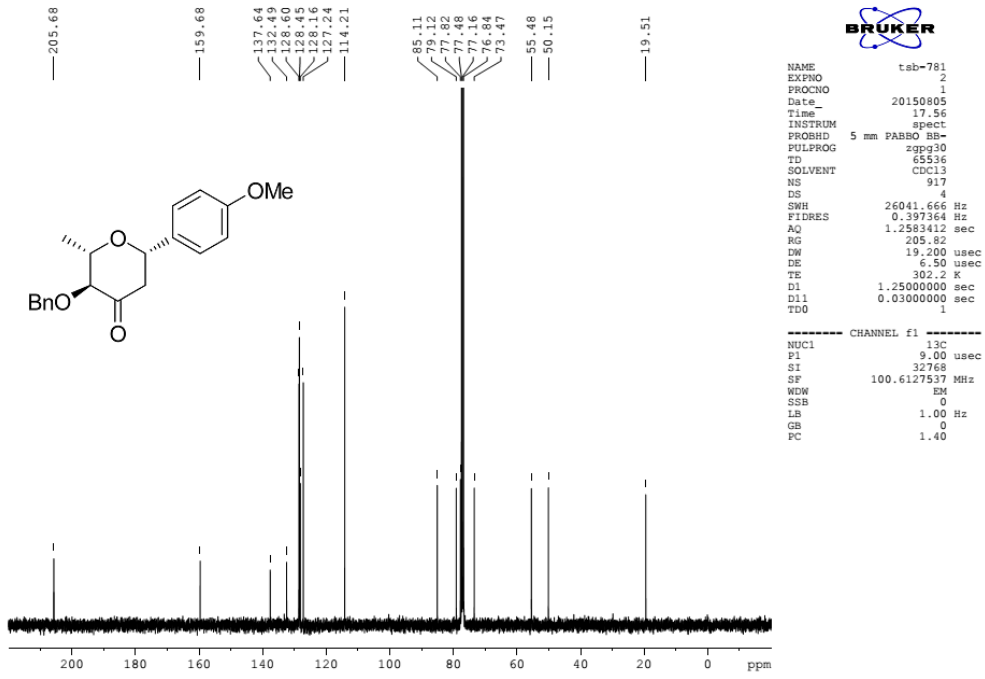
^{13}C NMR spectrum of **4eβ**, 100MHz, $CDCl_3$



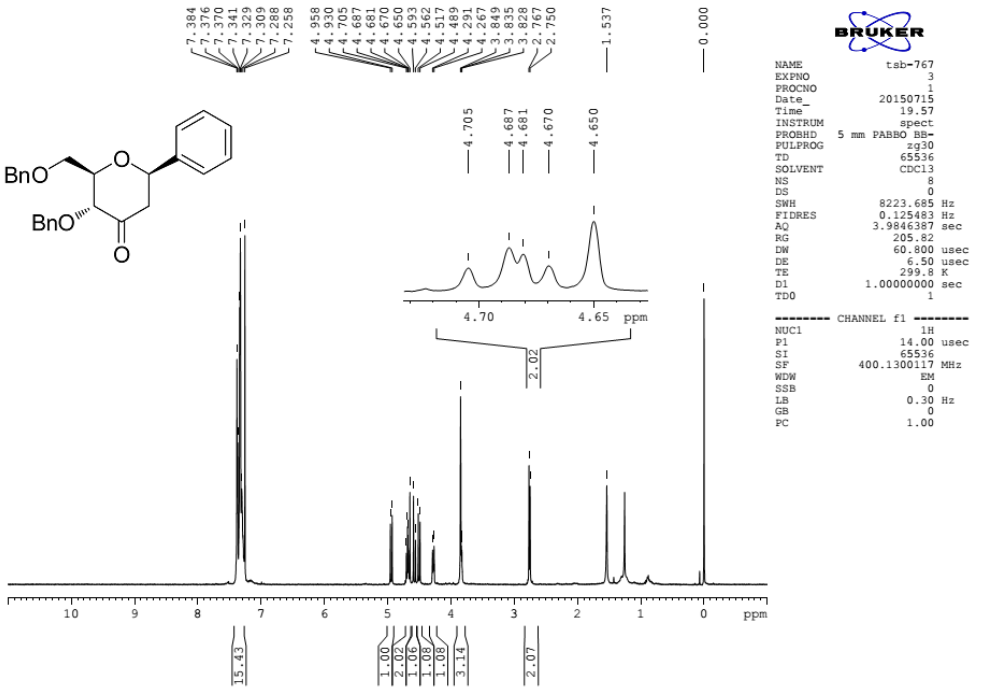
^{1}H NMR spectrum of **4fβ**, 400MHz, $CDCl_3$



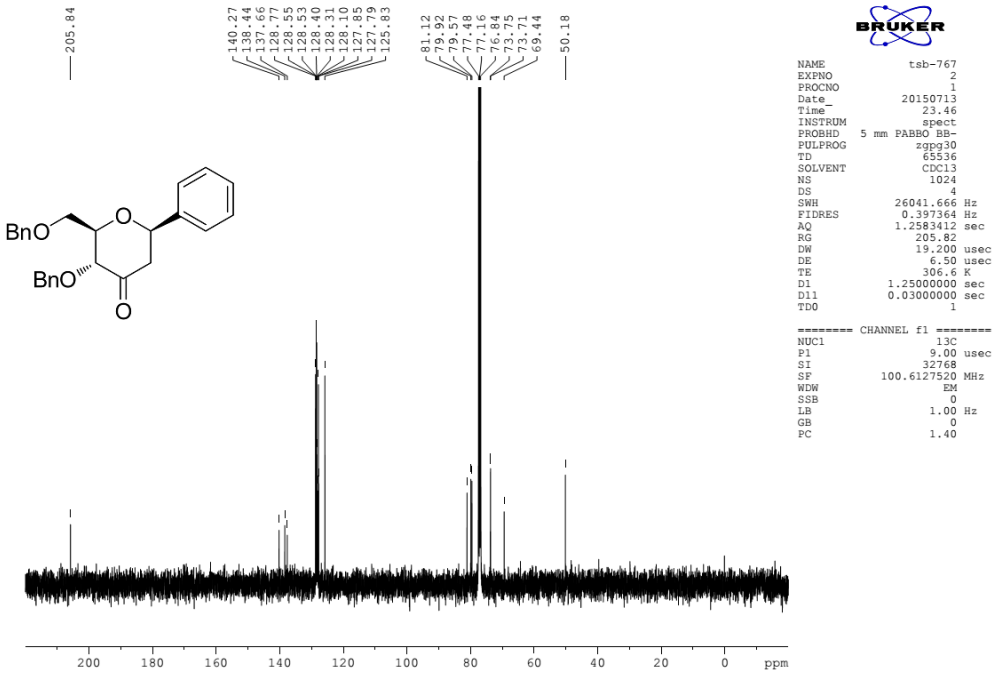
^{13}C NMR spectrum of **4fβ**, 100MHz, $CDCl_3$



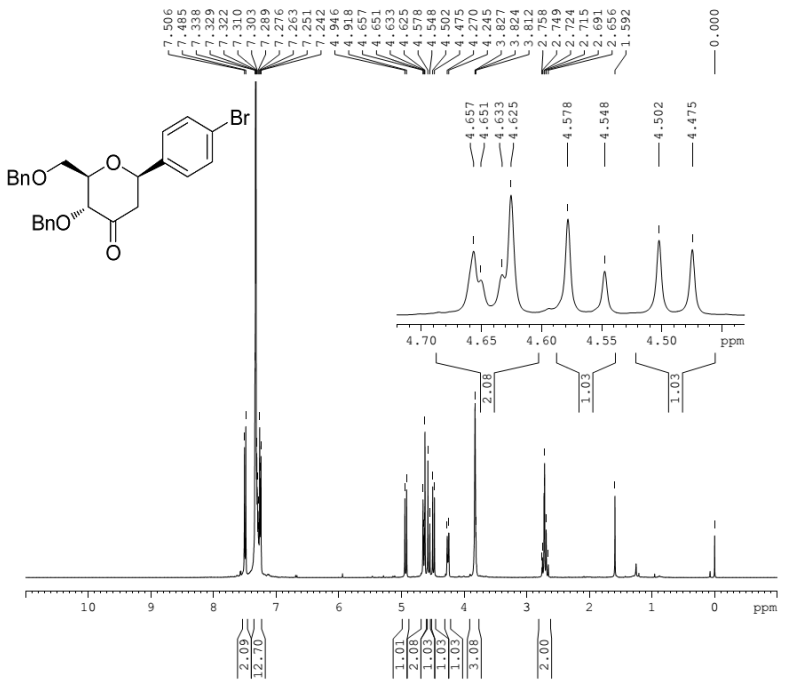
^{1}H NMR spectrum of **4hβ**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4hβ**, 100MHz, $CDCl_3$



^{1}H NMR spectrum of **4iβ**, 400MHz, $CDCl_3$

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SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 112.54
DW              60.800 usec
DE               6.50 usec
TE               294.6 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1              14.50 usec
SI                  65536
SF          400.1300127 MHz
WDW                    EM
SSB                     0
LB              0.30 Hz
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PC                   1.00
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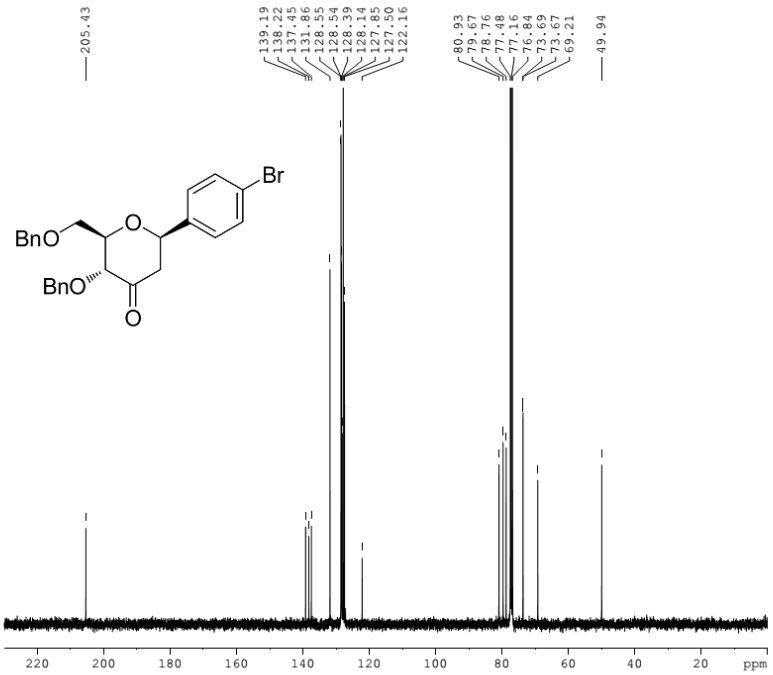
^{13}C NMR spectrum of **4iβ**, 100MHz, $CDCl_3$

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NS                    601
DS                      0
SWH           26041.666 Hz
FIDRES        0.397364 Hz
AQ            1.2583412 sec
RG                 183.47
DW              19.200 usec
DE               6.50 usec
TE               297.1 K
D1            1.20000005 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1               9.00 usec
SI                  32768
SF          100.6127579 MHz
WDW                    EM
SSB                     0
LB              1.00 Hz
GB                      0
PC                   1.40
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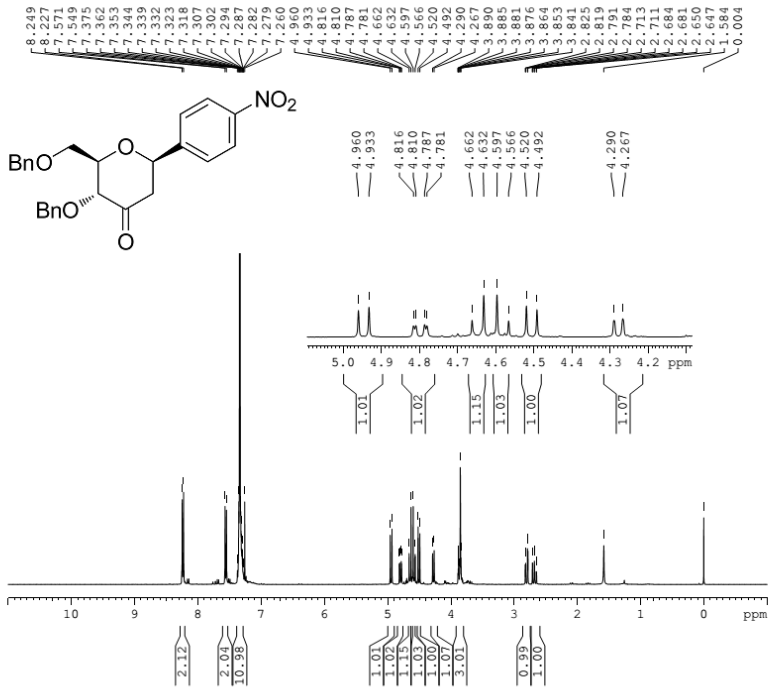
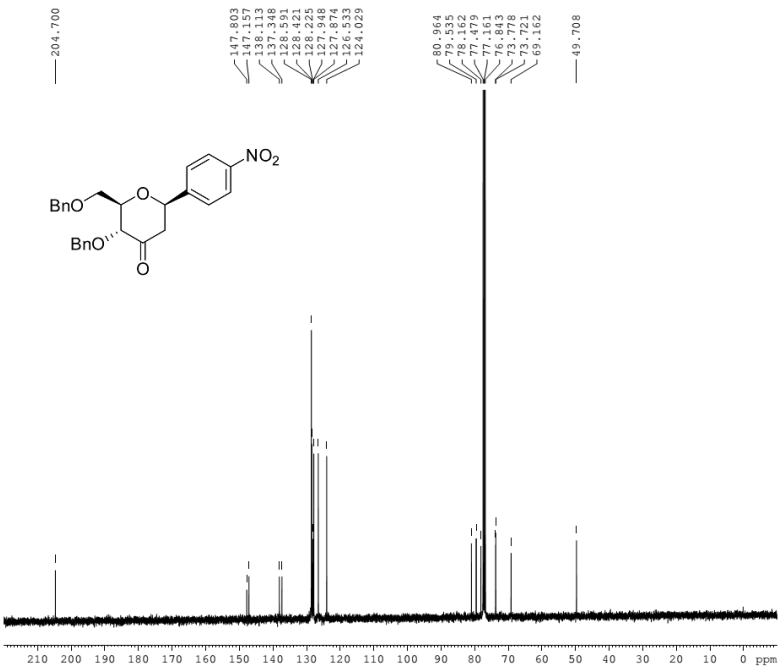
^{1}H NMR spectrum of **4jβ**, 400MHz, $CDCl_3$



BRUKER

NAME	tsb-774
EXPNO	1
PROCNO	1
Date_	20150722
Time	18.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	137.88
DW	60.800 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.00 usec
SI	65536
SF	400.1300104 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

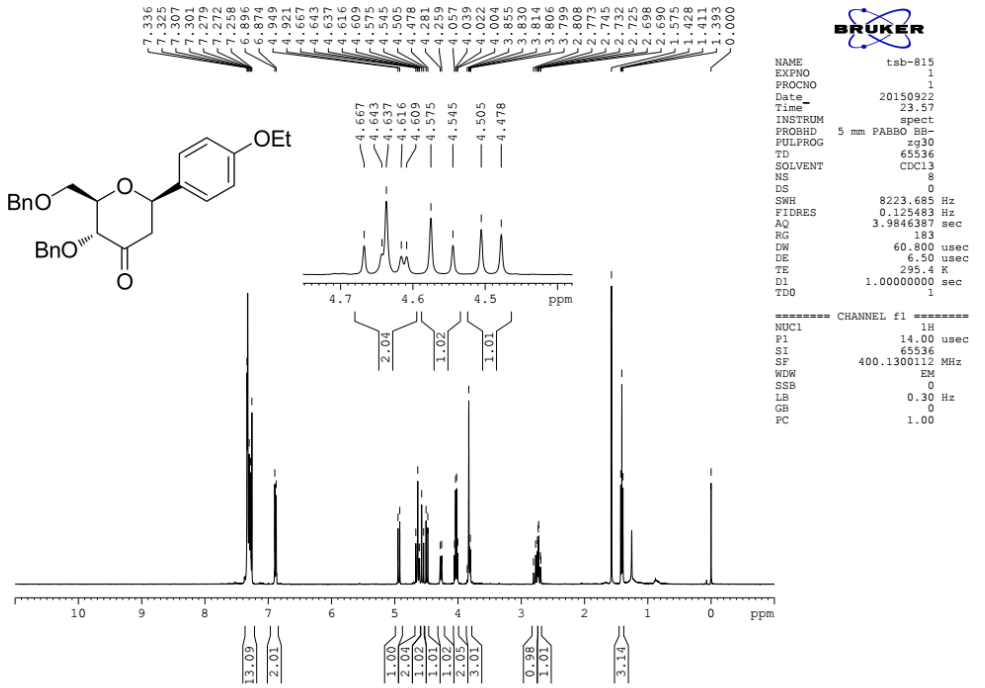
^{13}C NMR spectrum of **4jβ**, 100MHz, $CDCl_3$



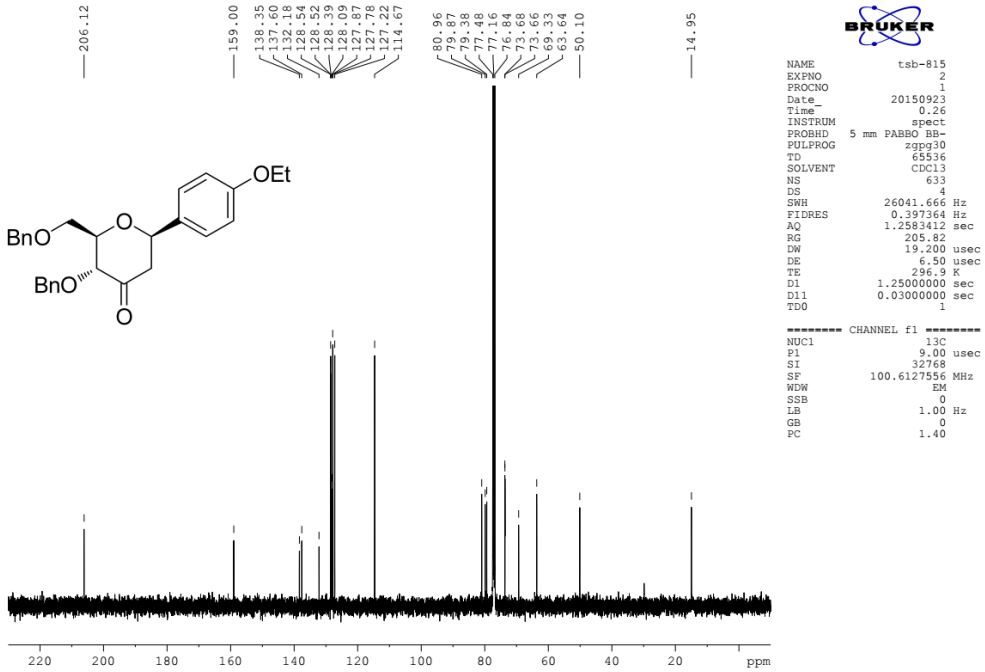
BRUKER

NAME	tsb-774
EXPNO	2
PROCNO	1
Date_	20150722
Time	18.49
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	426
DS	4
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	205.82
DW	19.200 usec
DE	6.50 usec
TE	299.7 K
D1	1.25000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.00 usec
SI	32768
SF	100.6127559 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

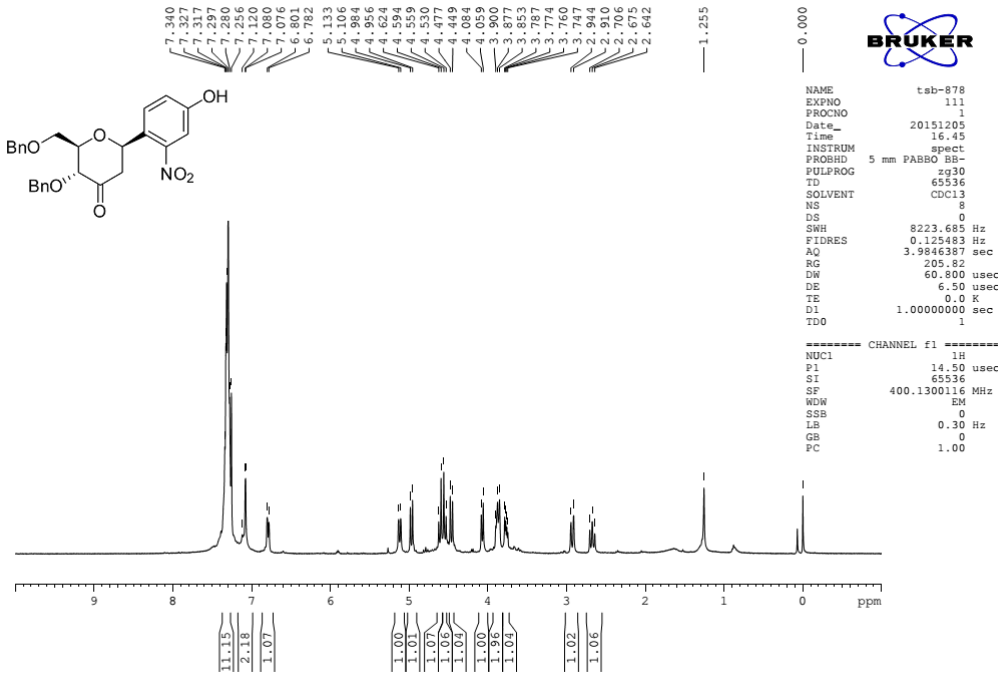
^{1}H NMR spectrum of **4kβ**, 400MHz, $CDCl_3$



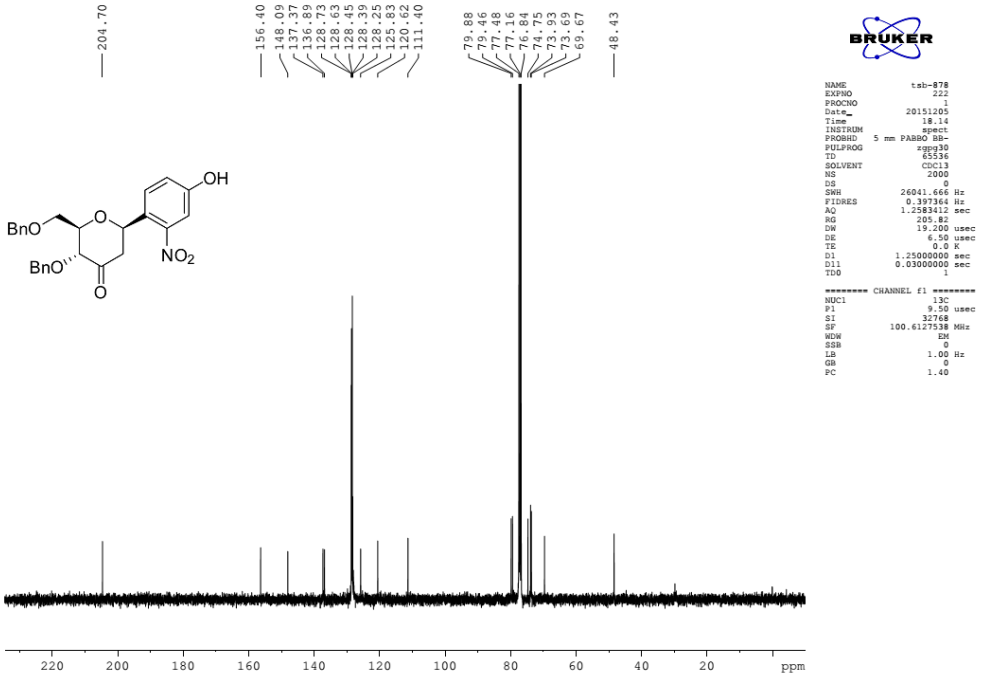
^{13}C NMR spectrum of **4kβ**, 100MHz, $CDCl_3$



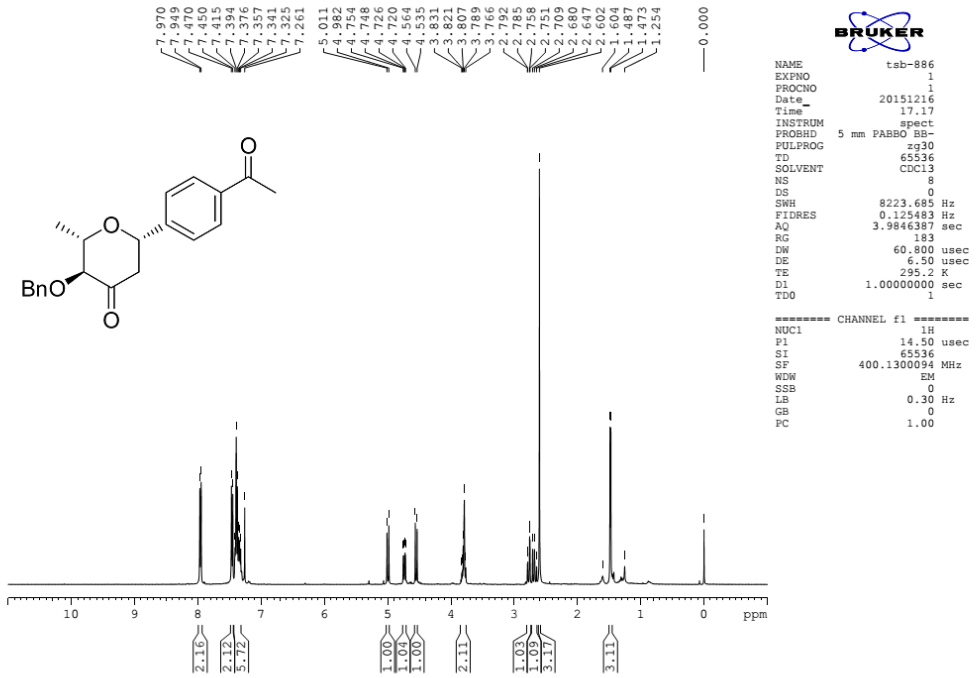
^{1}H NMR spectrum of **4lβ**, 400MHz, $CDCl_3$



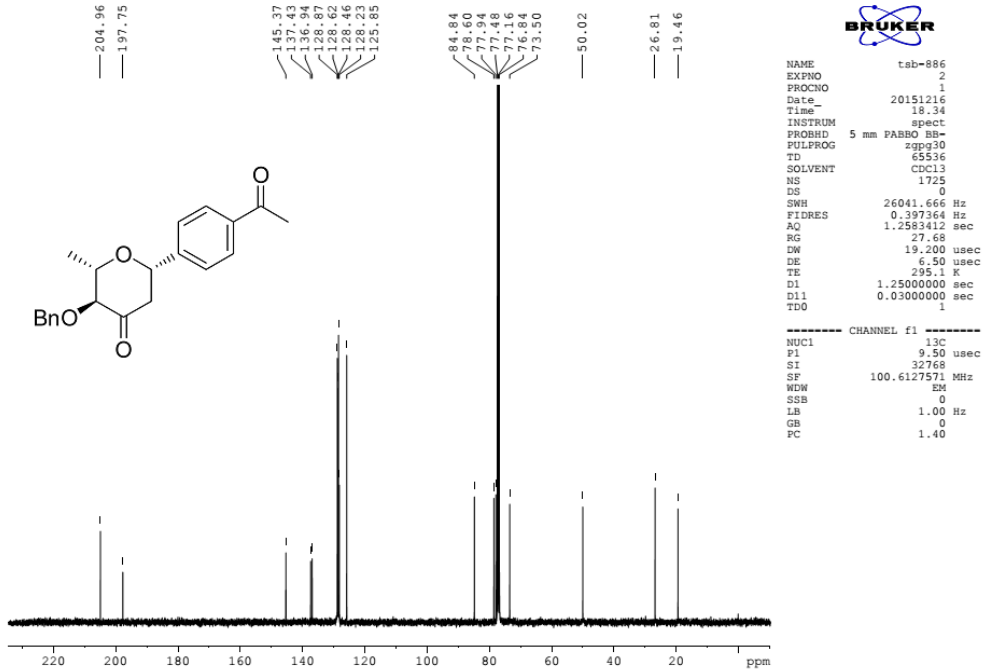
^{13}C NMR spectrum of **4lβ**, 100MHz, $CDCl_3$



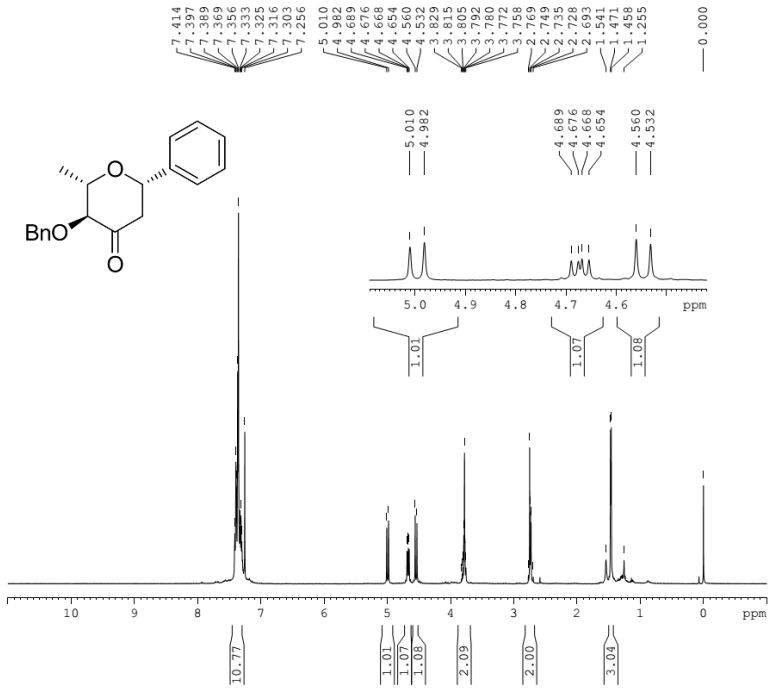
^{1}H NMR spectrum of **4mβ**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **4mβ**, 100MHz, $CDCl_3$



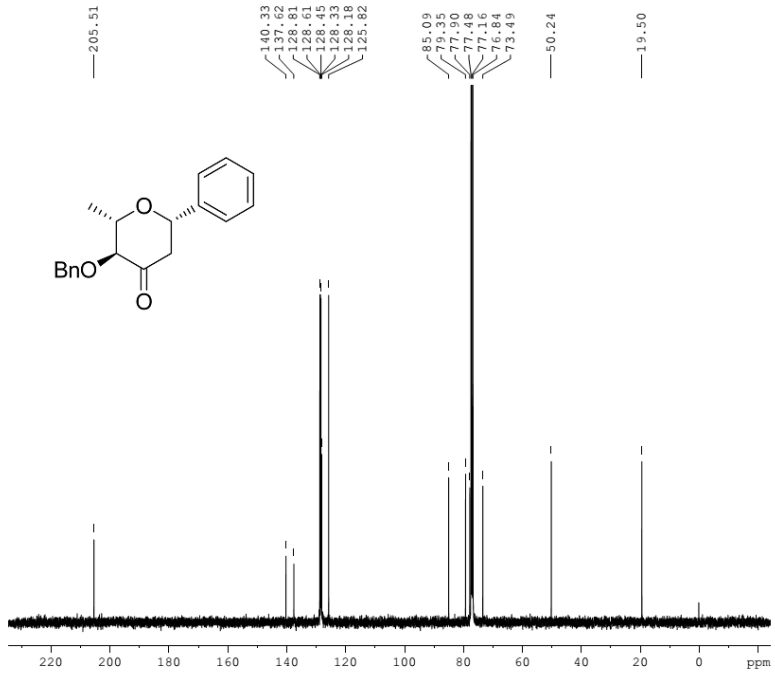
^{1}H NMR spectrum of **4nβ**, 400MHz, $CDCl_3$



BRUKER

NAME	tsb-885
EXPNO	1
PROCNO	1
Date_	20151211
Time	11.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	205.82
DW	60.800 usec
DE	6.50 usec
TE	300.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.50 usec
SI	65536
SF	400.1300115 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

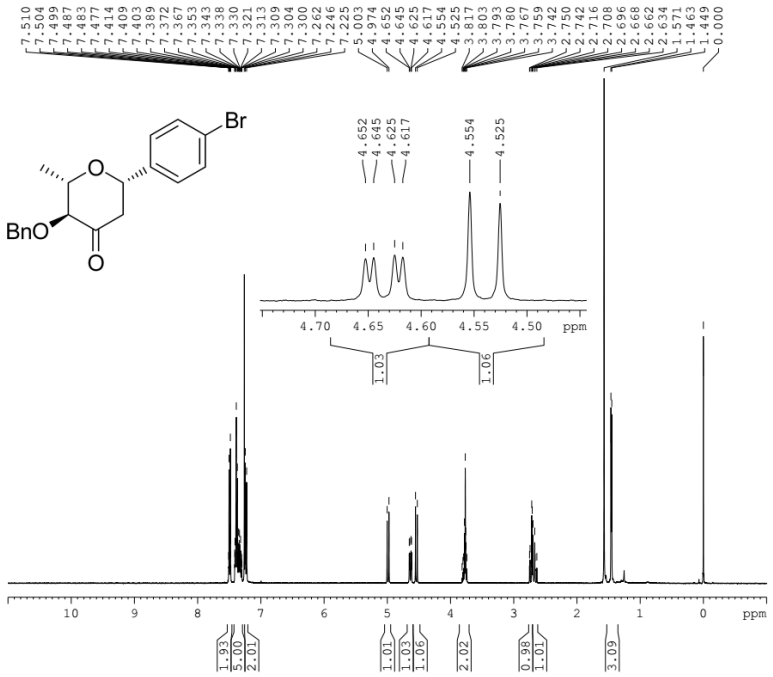
^{13}C NMR spectrum of **4nβ**, 100MHz, $CDCl_3$



BRUKER

NAME	tsb-885
EXPNO	2
PROCNO	1
Date_	20151211
Time	13.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	3000
DS	0
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	161.46
DW	19.200 usec
DE	6.50 usec
TE	302.3 K
D1	1.25000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
SI	32768
SF	100.6127535 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H NMR spectrum of **4oβ**, 400MHz, $CDCl_3$

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NAME                TSB-798
EXPNO                     3
PROCNO                    1
Date_              20150901
Time                  16.55
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                        8
DS                        0
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                   205.82
DW                   60.800 usec
DE                    6.50 usec
TE                   295.4 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
SI                    65536
SF            400.1300099 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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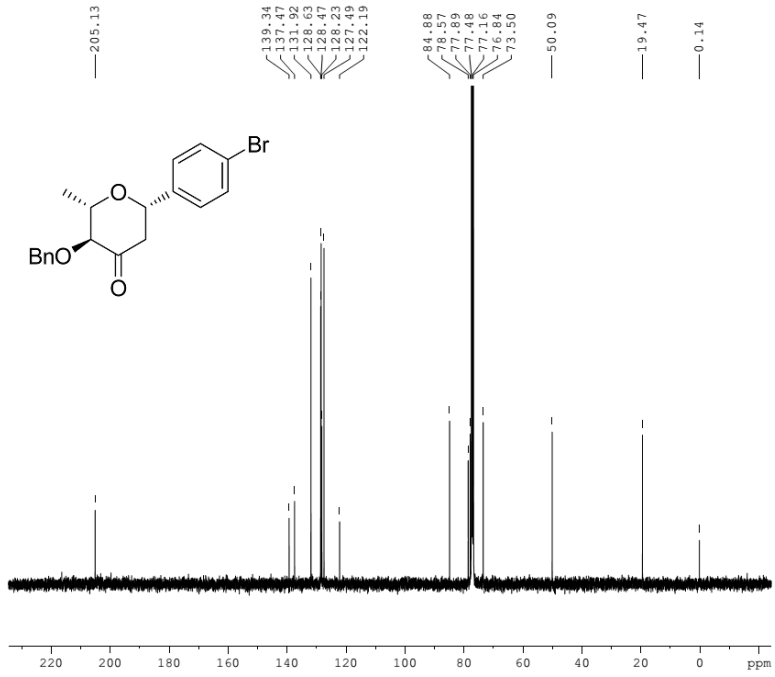
^{13}C NMR spectrum of **4oβ**, 100MHz, $CDCl_3$

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NAME                TSB-798
EXPNO                    22
PROCNO                    1
Date_              20150902
Time                   4.19
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     6000
DS                        4
SWH               26041.666 Hz
FIDRES            0.397364 Hz
AQ                1.2583412 sec
RG                   205.82
DW                   19.200 usec
DE                    6.50 usec
TE                   296.6 K
D1                1.25000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.00 usec
SI                    32768
SF            100.6127549 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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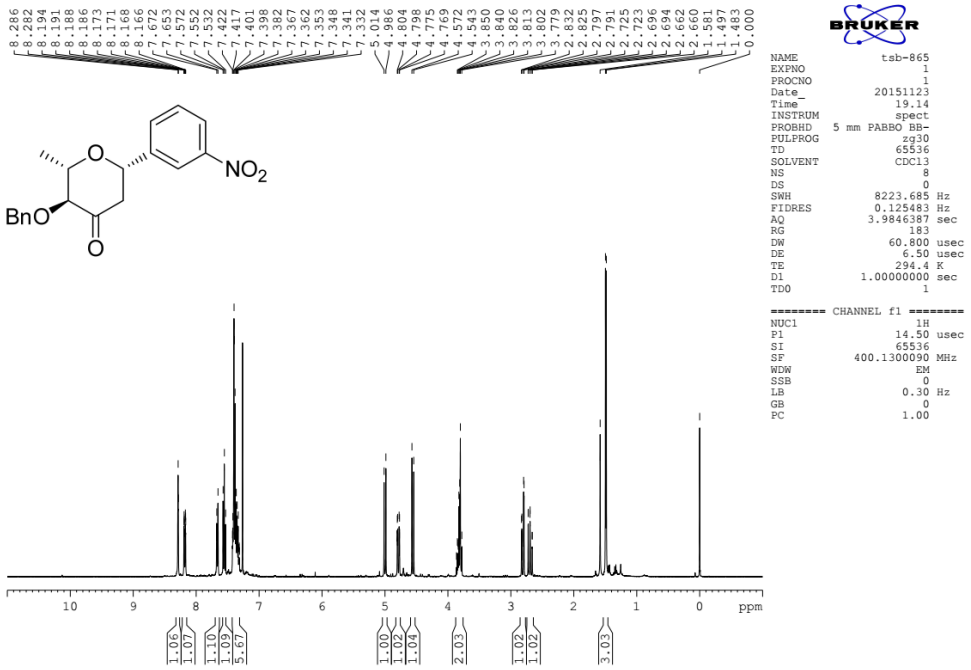
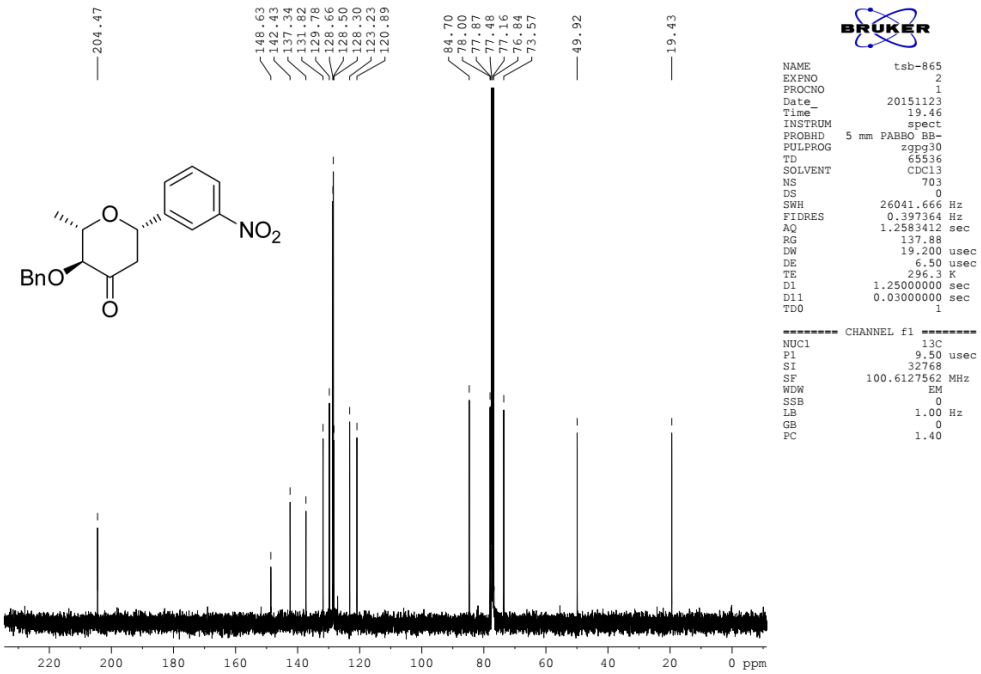
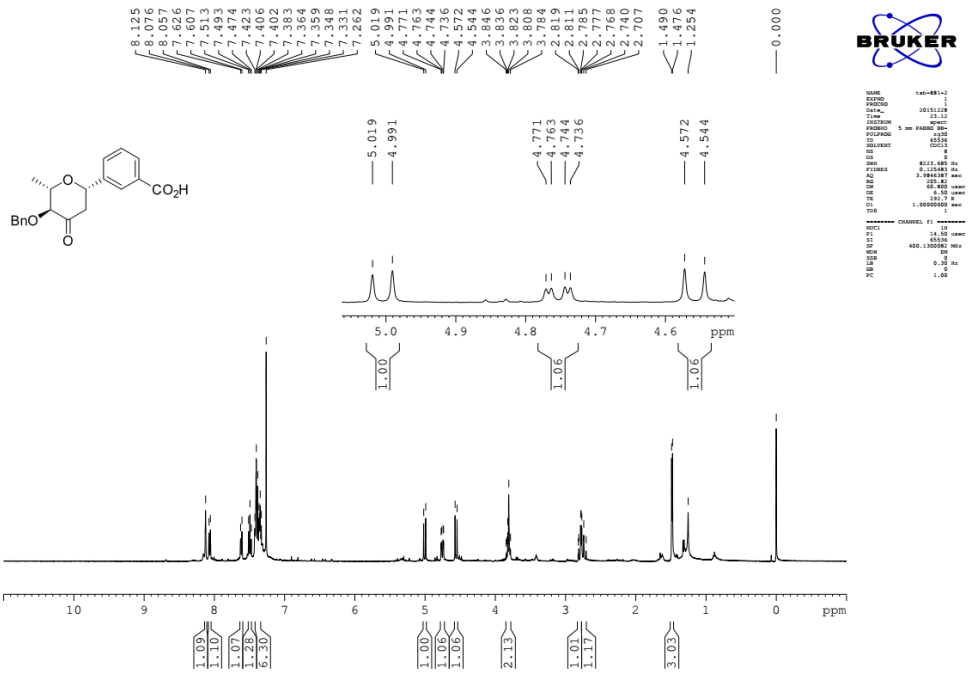
^{1}H NMR spectrum of **4pβ**, 400MHz, $CDCl_3$



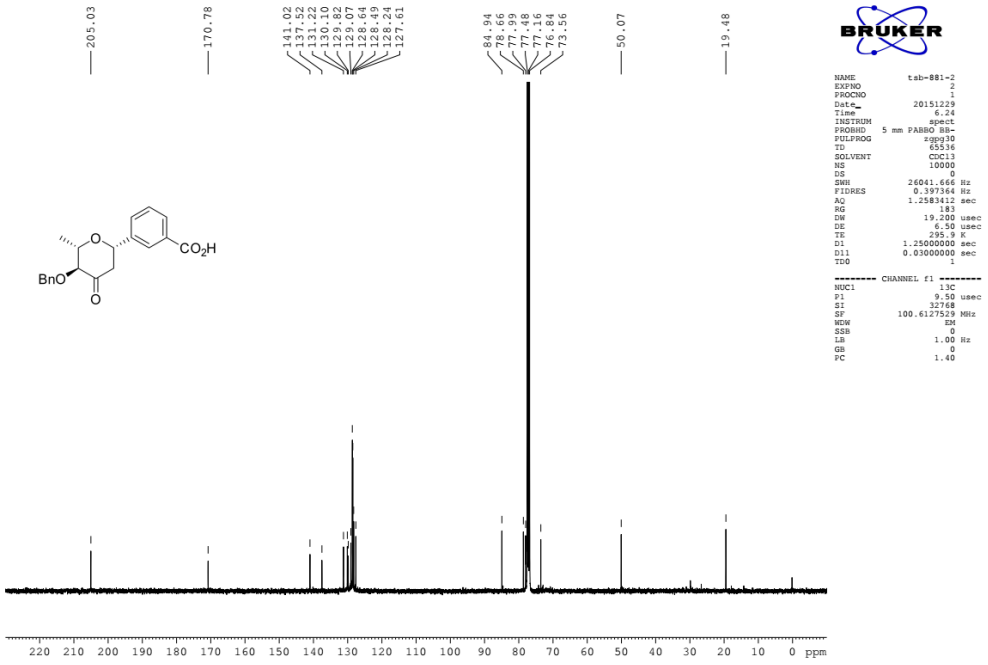
^{13}C NMR spectrum of **4pβ**, 100MHz, $CDCl_3$



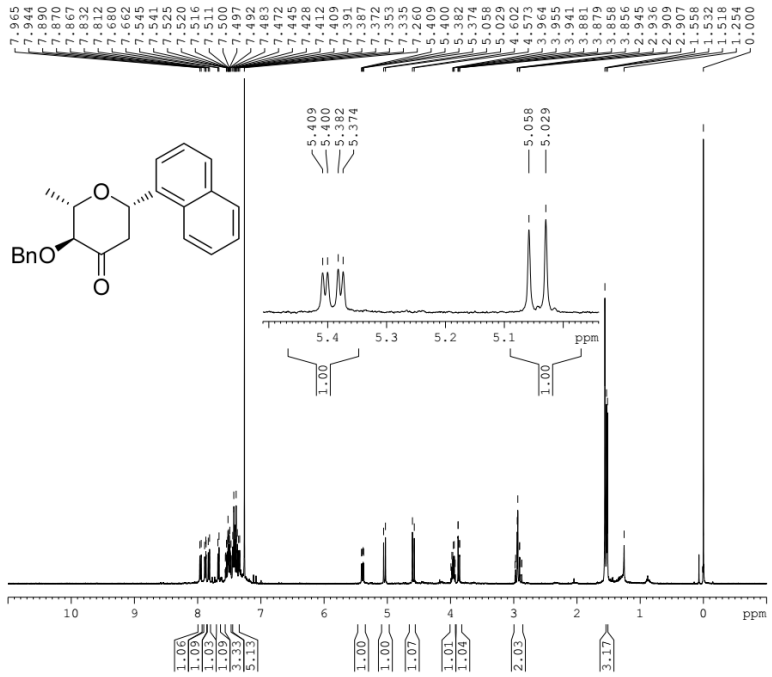
^{1}H NMR spectrum of **4qβ**, 400MHz, $CDCl_3$

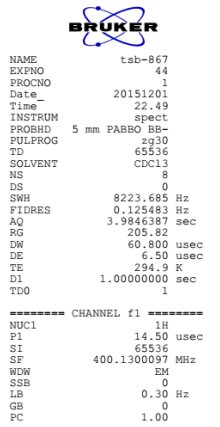


^{13}C NMR spectrum of **4qβ**, 100MHz, $CDCl_3$

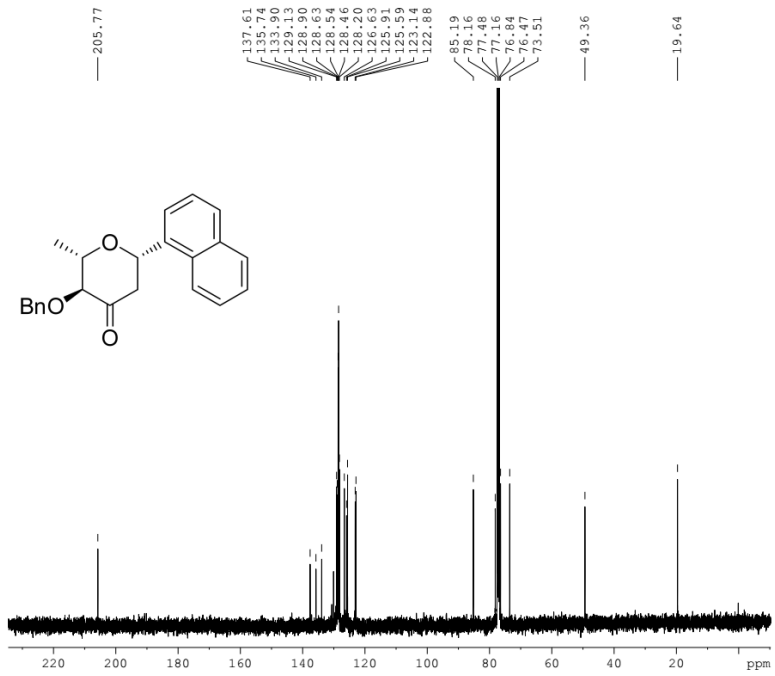


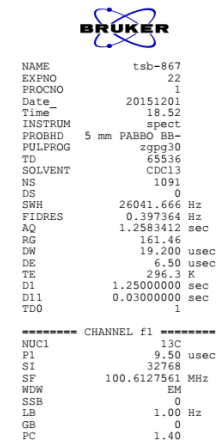
^{1}H NMR spectrum of **4rβ**, 400MHz, $CDCl_3$



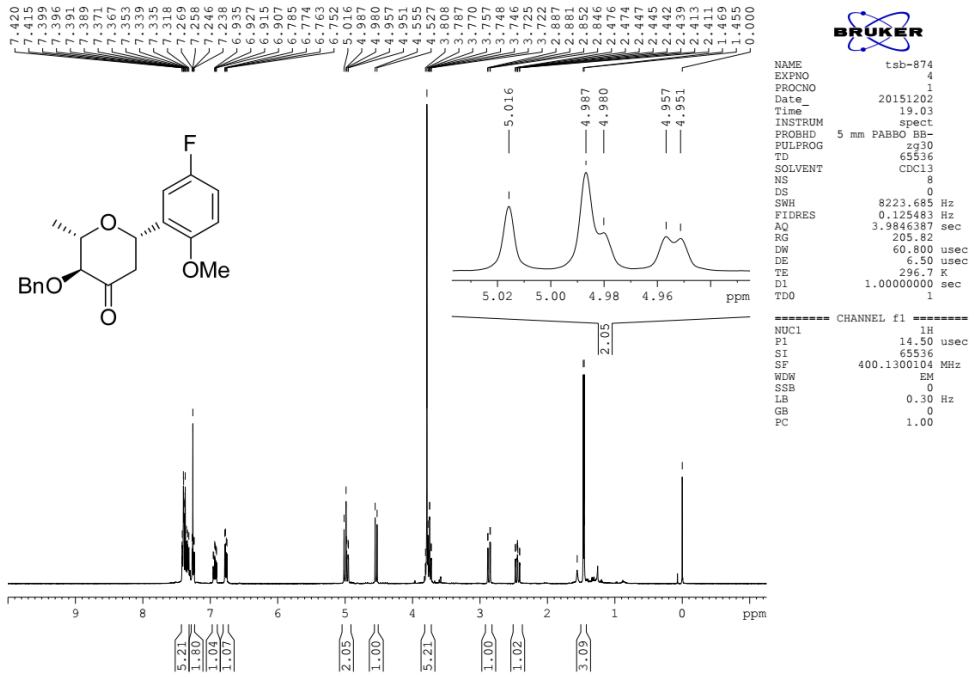


^{13}C NMR spectrum of **4rβ**, 100MHz, $CDCl_3$

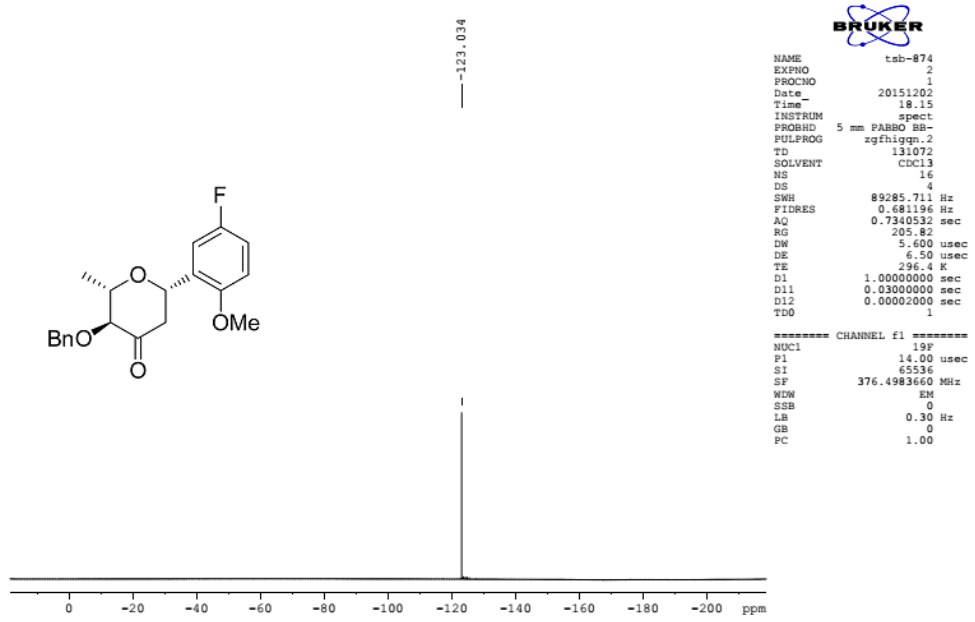




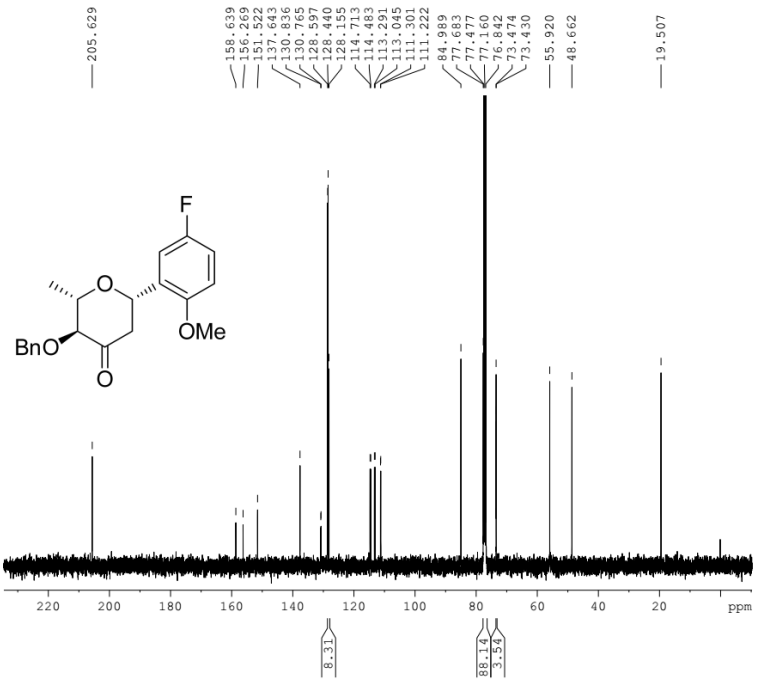
^{1}H NMR spectrum of **4sβ**, 400MHz, $CDCl_3$



^{19}C NMR spectrum of **4sβ**, 376MHz, $CDCl_3$



^{13}C NMR spectrum of **4sβ**, 100MHz, $CDCl_3$

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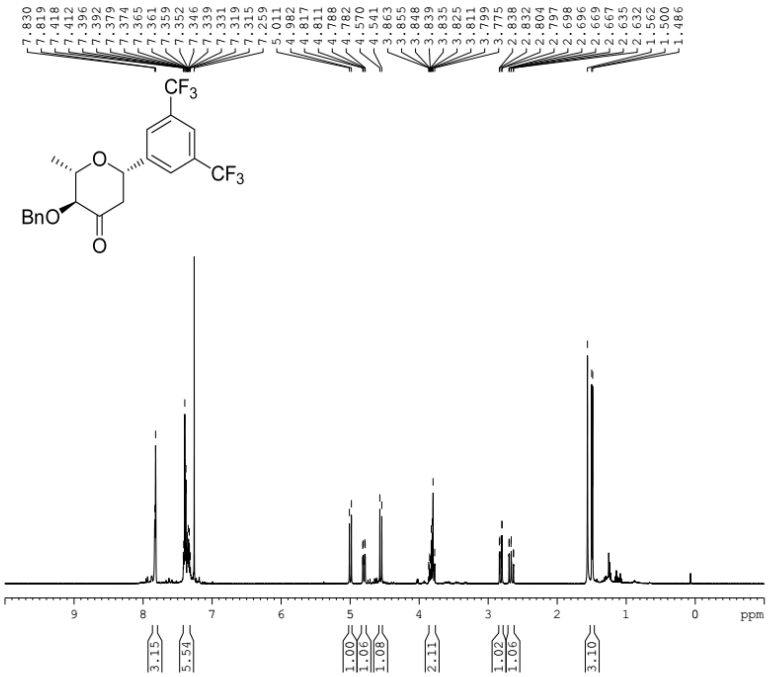
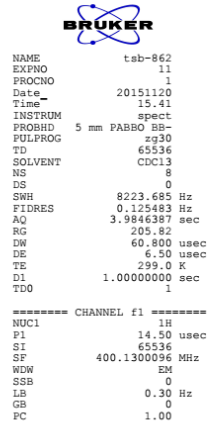
NAME                tsb-874
EXPNO                     3
PROCNO                    1
Date_              20151202
Time_                 18.59
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   968
DS                     0
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ             1.2583412 sec
RG                205.82
DW              19.200 usec
DE               6.50 usec
TE               297.5 K
D1           1.25000000 sec
D11          0.03000000 sec
TD0                    1

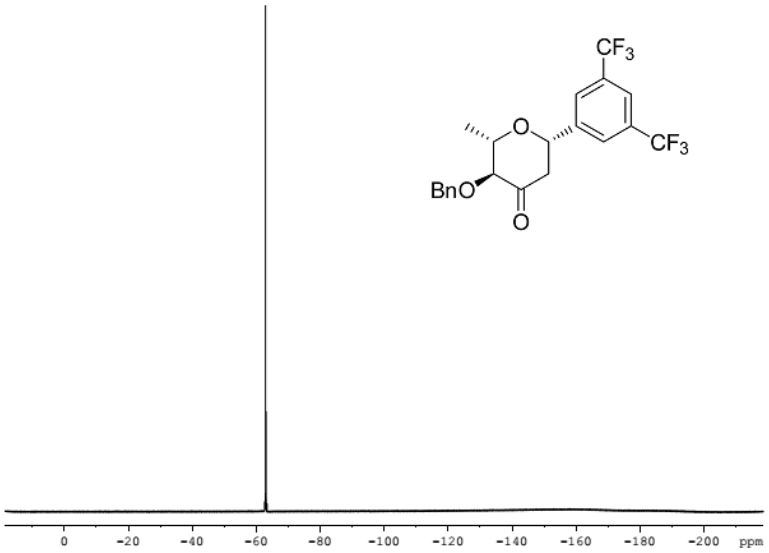
======== CHANNEL f1 ========
NUC1                 13C
P1                9.50 usec
SI                32768
SF          100.6127554 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

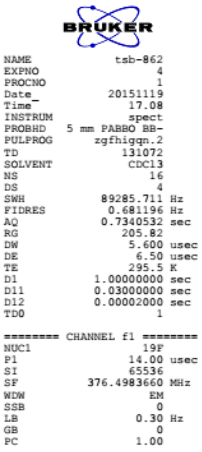
^{1}H NMR spectrum of **4tβ**, 400MHz, $CDCl_3$



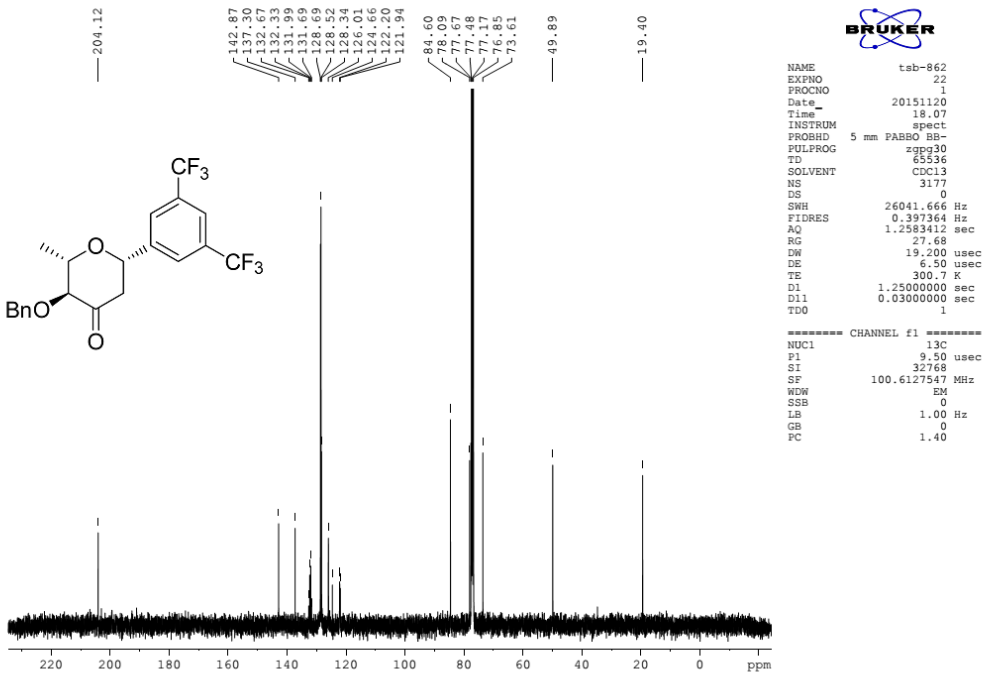


^{19}F NMR spectrum of **4tβ**, 376MHz, $CDCl_3$

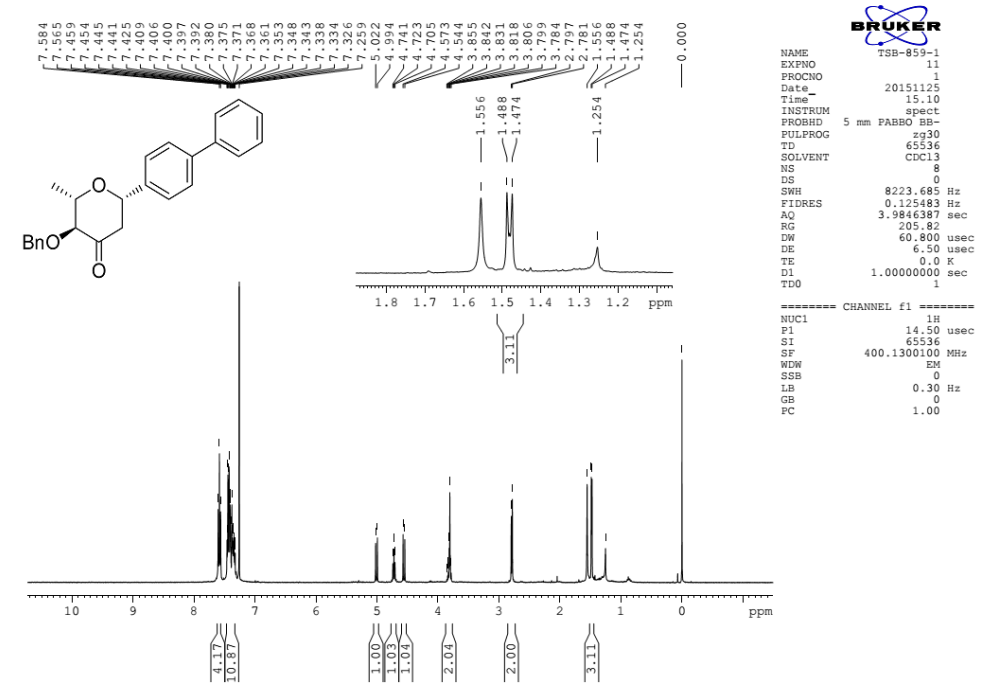




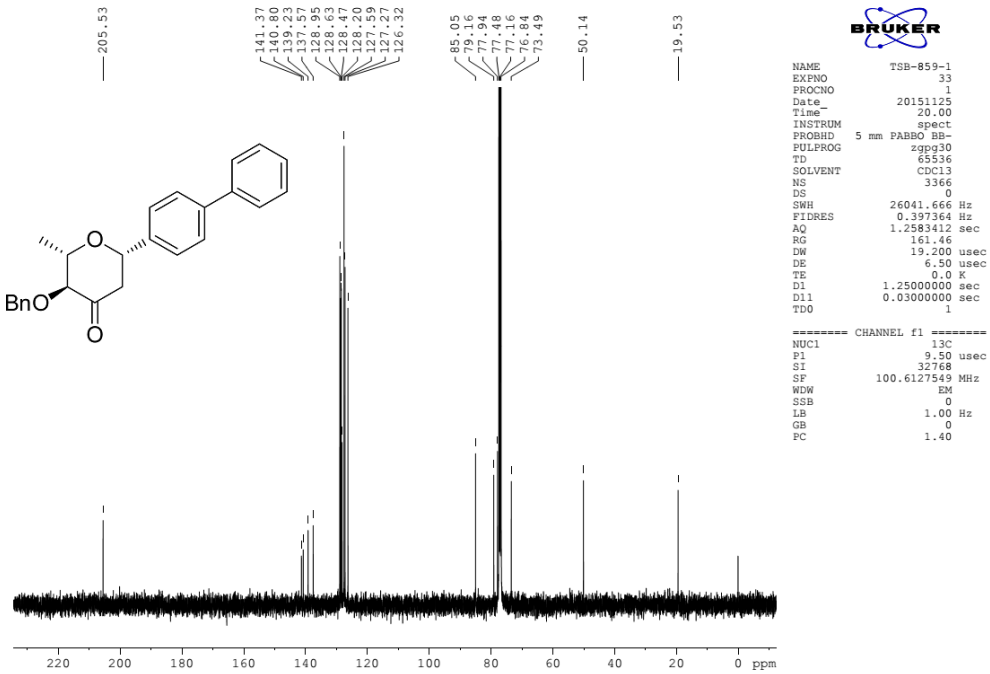
^{13}C NMR spectrum of **4tβ**, 100MHz, $CDCl_3$



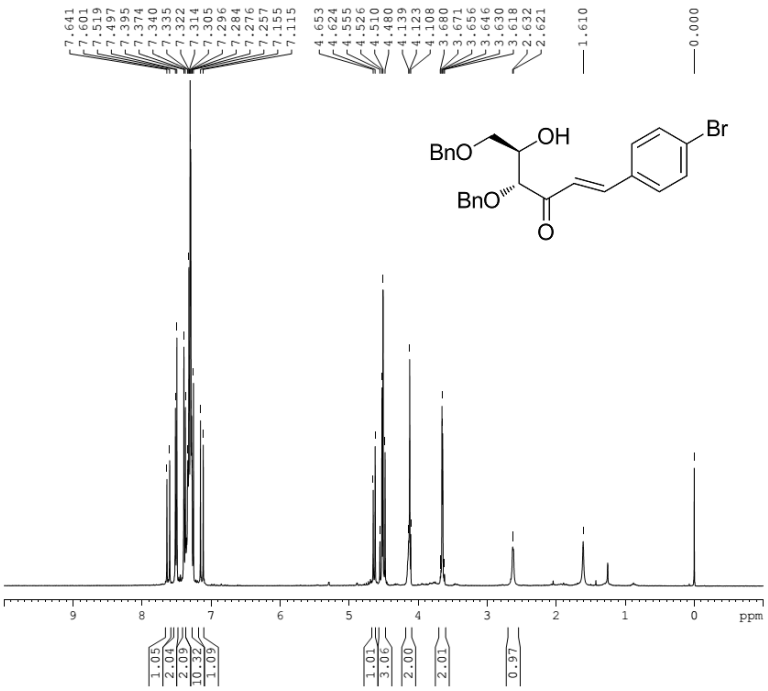
^{1}H NMR spectrum of **4uβ**, 400MHz, $CDCl_3$



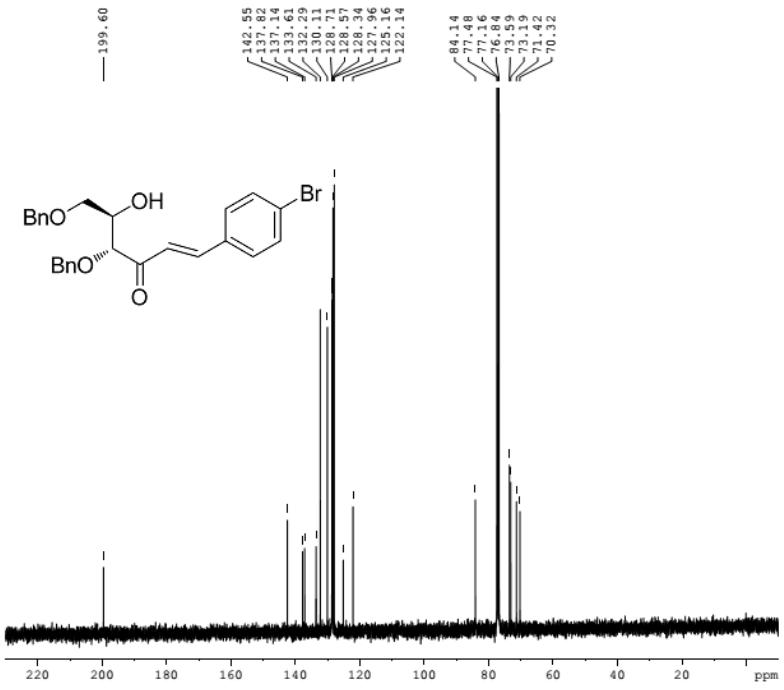
^{13}C NMR spectrum of **4uβ**, 100MHz, $CDCl_3$

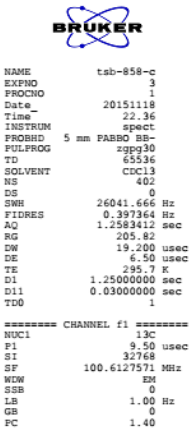


^{1}H NMR spectrum of **6**, 400MHz, $CDCl_3$

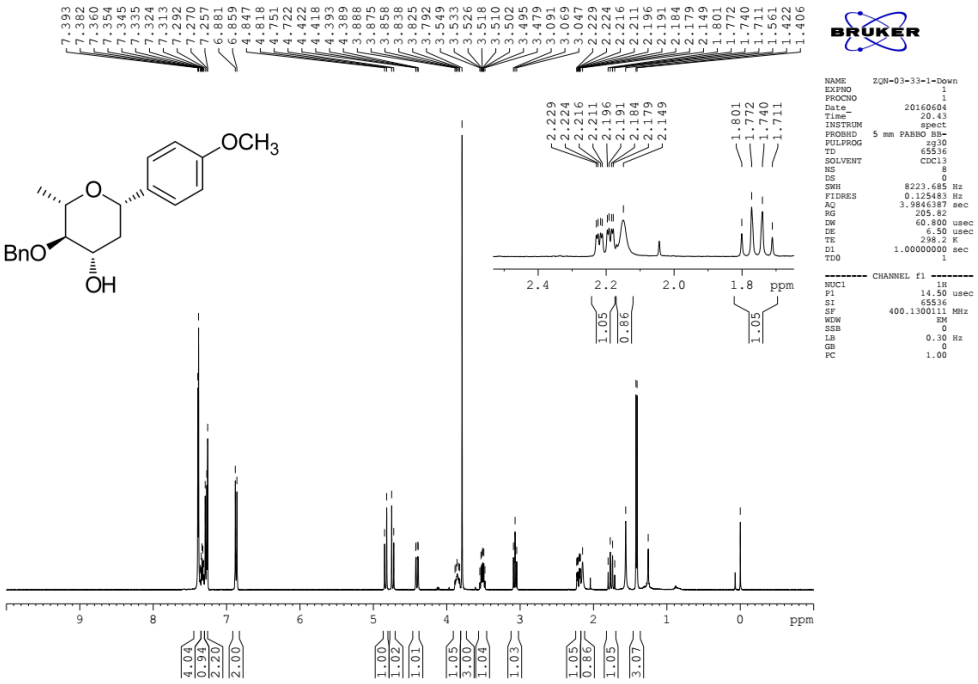


^{13}C NMR spectrum of **6**, 100MHz, $CDCl_3$

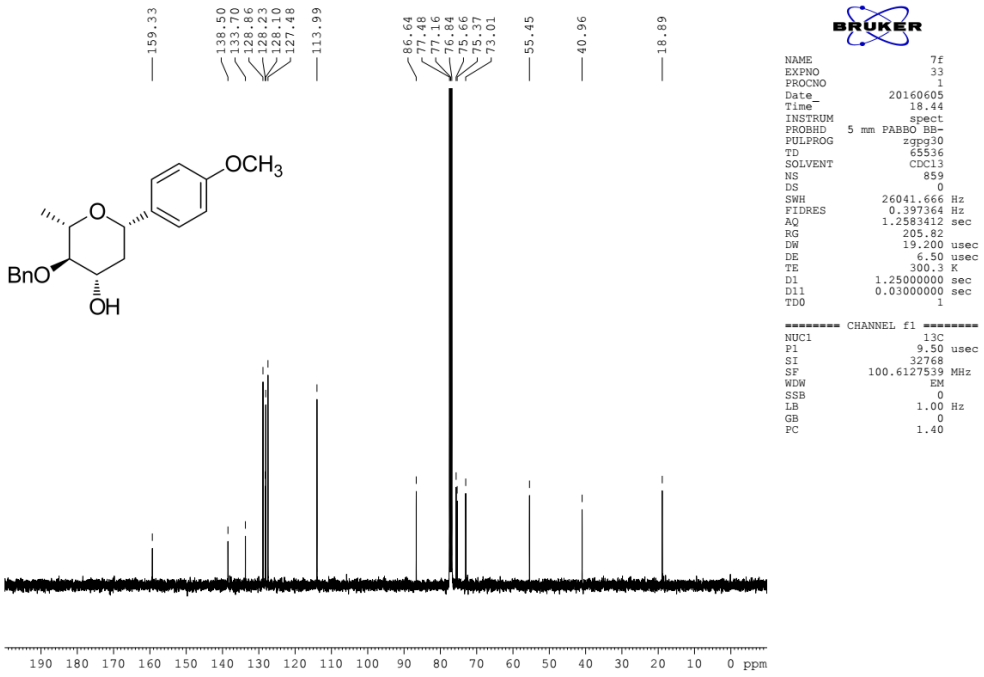




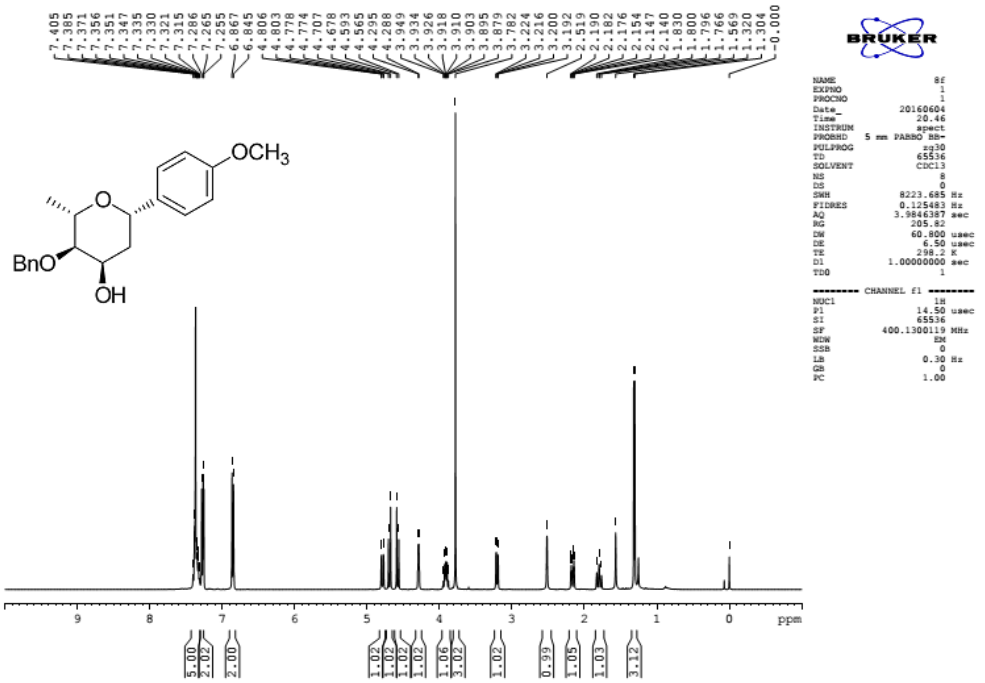
^{1}H NMR spectrum of **7**, 400MHz, $CDCl_3$



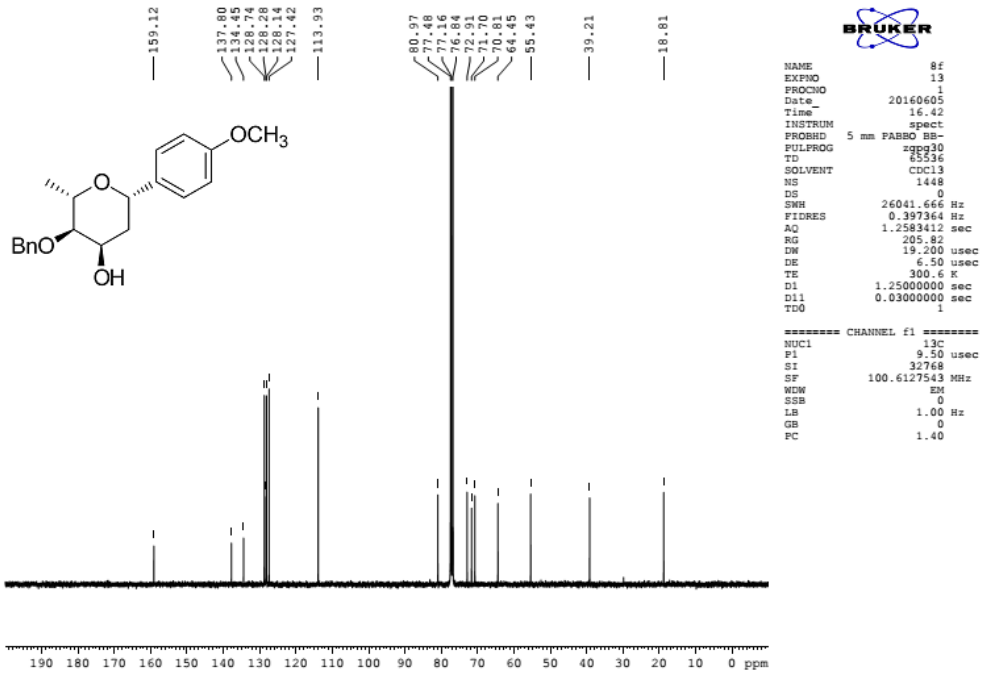
^{13}C NMR spectrum of **7**, 100MHz, $CDCl_3$



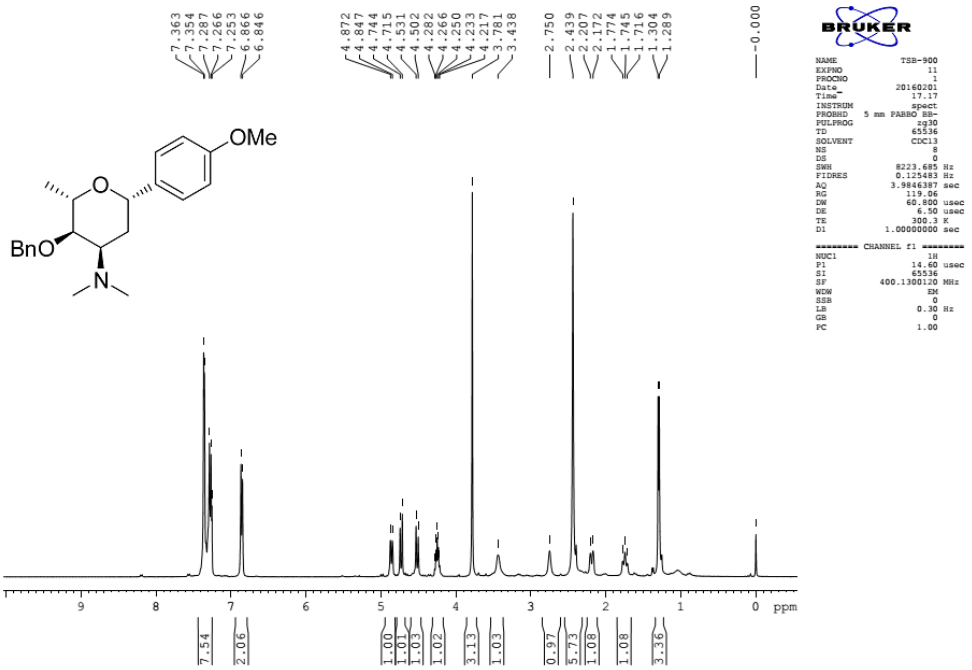
^{1}H NMR spectrum of **8**, 400MHz, $CDCl_3$



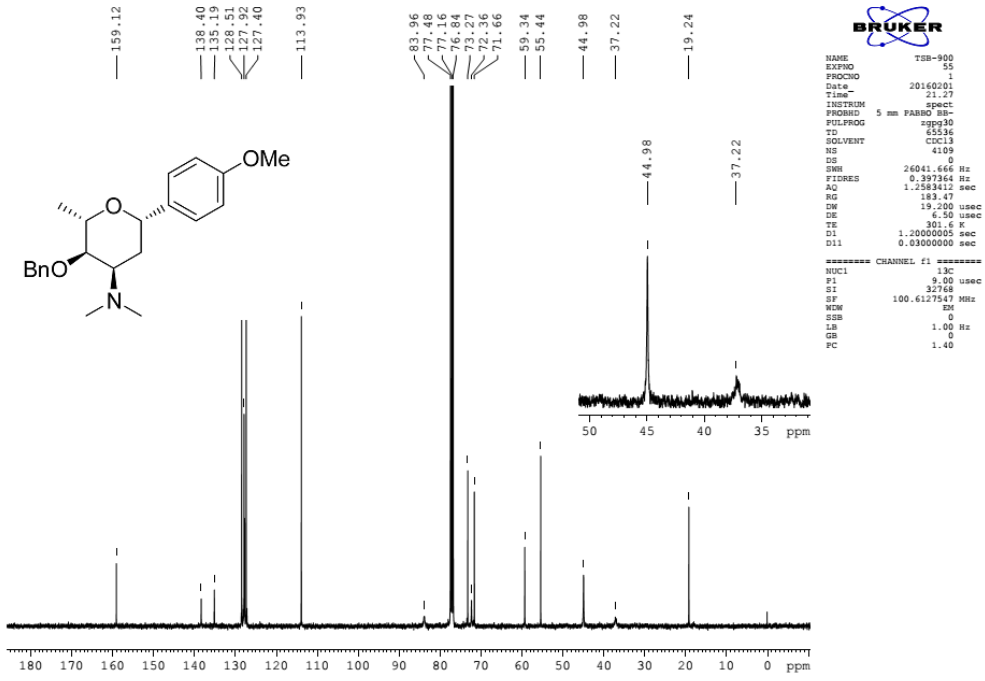
^{13}C NMR spectrum of **8**, 100MHz, $CDCl_3$



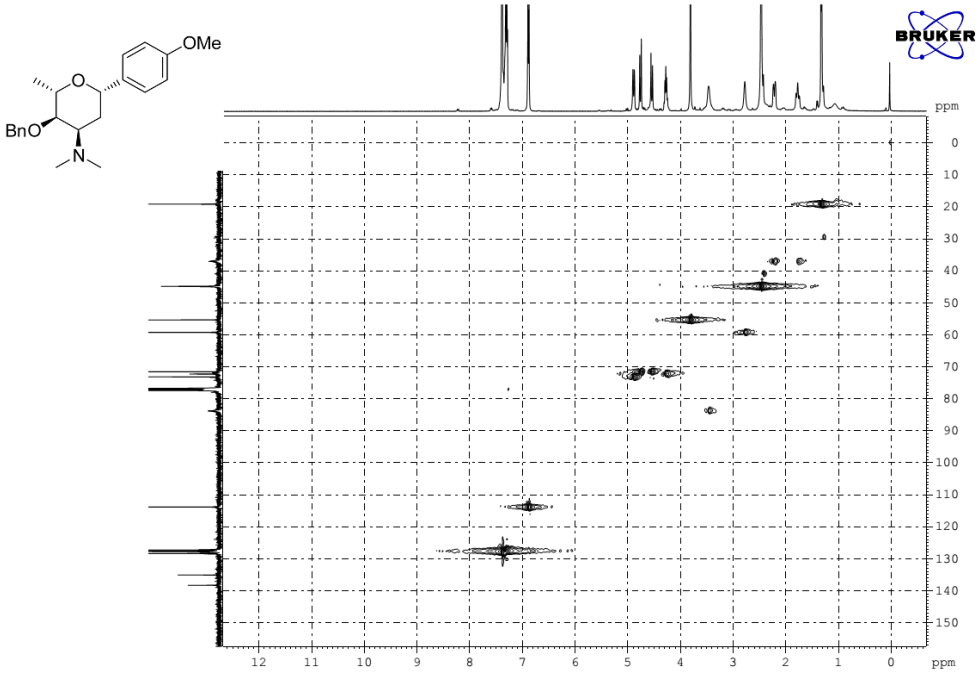
^{1}H NMR spectrum of **9**, 400MHz, $CDCl_3$



^{13}C NMR spectrum of **9**, 100MHz, $CDCl_3$



HSQC spectrum of **9**, 100MHz, $CDCl_3$



NOE spectrum of **9**, 400MHz, $CDCl_3$