Supporting Information

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S18 Dammarane derivative **25**[a]

S19 Dammarane derivative **25b**

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S21 20-*O*-[2'',3'',4''-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-3,6-di-*O*-acetyl-12-*O*-allyl-protopanaxatriol (**28**)

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S26 Ginsenoside Rh1 (**3**)

S27 6,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-*tert*-butyldimethylsilyl-12-*O*-allyl-protopanaxatriol (**31**)

S27 Ginsenoside Rg1 (**4**)

S29 3,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-6-*O*-acetyl-12-*O*-allyl-protopanaxatriol (**32**)

S30 3,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-6-*O*-acetyl-protopanaxatriol (**33**)

S31 Ginsenoside Ia (**5**)

S31 3-*O*-Chloroacetyl-12-*O*-allyl-protopanaxadiol (**34**)

S32 20-*O*-(2',3',4'-Tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-allyl-protopanaxadiol (**35**)

S33 20-*O*-(2',3',4'-Tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-acetyl-protopanaxadiol (**36**)

S34 20-*O*-(2',3',4'-Tri-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-acetyl protopanaxadiol (**37**)

S35 20-*O*-[2'',3'',4''-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-3-*O*-chloroacetyl-12-*O*-acetyl-protopanaxadiol (**38**)

S36 20-*O*-[2'',3'',4''-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (**39**)

S37 2-*O*-(2-Azidomethyl)benzoyl-3,4,6-tri-*O*-benzoyl-D-glucopyanose (**S4**)

S38 2-*O*-(2-Azidomethyl)benzoyl-3,4,6-tri-*O*-benzoyl-D-glucopyanosyl *ortho*-cyclopropylethynylbenzoate (**40**)

S39 3-*O*-(3''',4''',6'''-Tri-*O*-benzoyl-β-D-glucopyranosyl)-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (**41**)

S40 2-*O*-(2-Azidomethyl)benzoyl-3-*O*-allyl-4,6-*O*-benzylidene-D-glucopyranosyl *ortho*-hexynylbenzoate (**43**)

S41 3-*O*-[2'''-*O*-(2-Azidomethyl)benzoyl-3'''-*O*-allyl-4''',6'''-*O*-benzylidene-β-D-glucopyranosyl]-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (**44**)

S42 3-*O*-(3'''-*O*-Allyl-4''',6'''-*O*-benzylidene-β-D-glucopyranosyl)-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (**45**)

S43 3-*O*-[2'''',3'''',4'''',6''''-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3'''-*O*-allyl-4''',6'''-*O*-benzylidene-β-D-glucopyranosyl]-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (**47**)

S44 Ginsenoside Rb2 (**6**)

S45 Comparison of the ^{13}C NMR data of the synthetic ginsenosides **1**-**6** with those reported for the natural products

S53-S142 ^{1}H and ^{13}C NMR Spectra

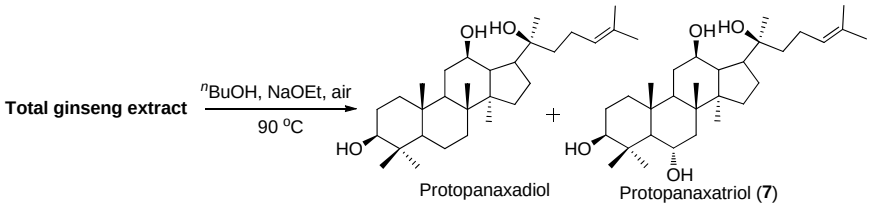
Page	*Compound*	*Solvent*
S53-54	^{1}H and ^{13}C NMR of **8**	$CDCl_3$
S55-56	^{1}H and ^{13}C NMR of **9**	$CDCl_3$

S57-58	^{1}H and ^{13}C NMR of **10**	$CDCl_3$
S59-60	^{1}H and ^{13}C NMR of **11**	$CDCl_3$
S61-62	^{1}H and ^{13}C NMR of **12**	$CDCl_3$
S63-64	^{1}H and ^{13}C NMR of **13**	$CDCl_3$
S65-66	^{1}H and ^{13}C NMR of **14**	$CDCl_3$
S67-68	^{1}H and ^{13}C NMR of **15**	$CDCl_3$
S69-70	^{1}H and ^{13}C NMR of **16**	$CDCl_3$
S71-72	^{1}H and ^{13}C NMR of the major isomer of **19**	$CDCl_3$
S73-74	^{1}H and ^{13}C NMR of the minor isomer of **19**	$CDCl_3$
S75-76	^{1}H and ^{13}C NMR of **20α**	$CDCl_3$
S77-78	^{1}H and ^{13}C NMR of **21β**	$CDCl_3$
S79-80	^{1}H and ^{13}C NMR of **22**	$CDCl_3$
S81-82	^{1}H and ^{13}C NMR of **23**	$CDCl_3$
S83-84	^{1}H and ^{13}C NMR of **24a**	$CDCl_3$
S85-86	^{1}H and ^{13}C NMR of **24b**	$CDCl_3$
S87-88	^{1}H and ^{13}C NMR of **25a**	$CDCl_3$
S89-90	^{1}H and ^{13}C NMR of **25b**	$CDCl_3$
S91-92	^{1}H and ^{13}C NMR of **26**	$CDCl_3$
S93-94	^{1}H and ^{13}C NMR of **27α**	$CDCl_3$
S95-96	^{1}H and ^{13}C NMR of **28**	$CDCl_3$
S97-98	^{1}H and ^{13}C NMR of **1**	C_5D_5N
S99-100	^{1}H and ^{13}C NMR of **29**	$CDCl_3$
S101-102	^{1}H and ^{13}C NMR of **2**	C_5D_5N
S103-104	^{1}H and ^{13}C NMR of **30**	$CDCl_3$
S105-106	^{1}H and ^{13}C NMR of **3**	C_5D_5N
S107-108	^{1}H and ^{13}C NMR of **31**	$CDCl_3$
S109-110	^{1}H and ^{13}C NMR of **4**	C_5D_5N
S111-112	^{1}H and ^{13}C NMR of **32**	$CDCl_3$
S113-114	^{1}H and ^{13}C NMR of **33**	$CDCl_3$
S115-116	^{1}H and ^{13}C NMR of **5**	C_5D_5N
S117-118	^{1}H and ^{13}C NMR of **34**	$CDCl_3$
S119-120	^{1}H and ^{13}C NMR of **35**	$CDCl_3$
S121-122	^{1}H and ^{13}C NMR of **36**	$CDCl_3$
S123-124	^{1}H and ^{13}C NMR of **37**	$CDCl_3$
S125-126	^{1}H and ^{13}C NMR of **38**	$CDCl_3$
S127-128	^{1}H and ^{13}C NMR of **39**	$CDCl_3$
S129-130	^{1}H and ^{13}C NMR of **40β**	$CDCl_3$
S131-132	^{1}H and ^{13}C NMR of **41**	$CDCl_3$

S133-134	^{1}H and ^{13}C NMR of **43α**	$CDCl_3$
S135-136	^{1}H and ^{13}C NMR of **44**	$CDCl_3$
S137-138	^{1}H and ^{13}C NMR of **45**	$CDCl_3$
S139-140	^{1}H and ^{13}C NMR of **47**	$CDCl_3$
S141-142	^{1}H and ^{13}C NMR of **6**	C_5D_5N

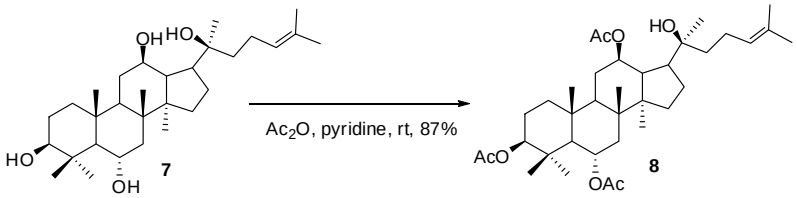
Experimental Section

Protopanaxatriol (7) and protopanaxadiol



To a solution of the total extract of ginseng (60.0 g) in ^{n}BuOH (700 mL) was added NaOEt (60 g, 0.9 mol) at rt. The resulting mixture was heated to 90 °C and stirred vigorously, and to which air was bubbled. After stirring at the same temperature for 3 d, the reaction mixture was cooled down, and the solvent was removed under reduced pressure. The residue was dissolved in EtOAc. The resulting solution was washed with water and brine, respectively, and was then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 30:1 to 25:1) to afford **7** (8.0 g) and protopanaxadiol (2.0 g) as white solids.[S1]

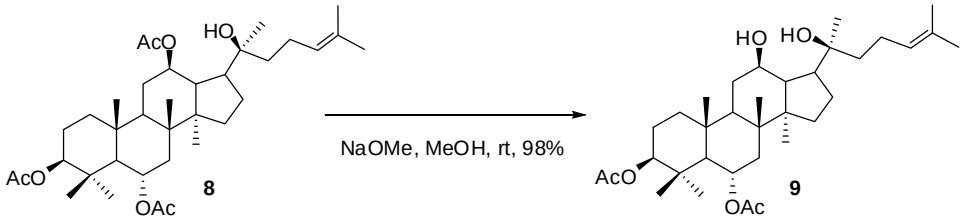
3,6,12-Tri-*O*-acetyl-protopanaxatriol (8)



To a solution of protopanaxatriol **7** (500 mg, 1.05 mmol) in dry pyridine (3 mL) was added Ac_2O (3 mL) dropwise at 0 °C under Ar atmosphere. The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) to give compound **8** (550 mg, 87%) as a white solid: $[\alpha]^{25}_D$ = 22.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38-5.30 (m, 1 H), 5.16 (m, 1 H), 4.74 (m, 1 H), 4.50 (dd, *J* = 4.8, 11.4 Hz, 1 H), 2.04 (s, 9 H), 1.71 (s, 3 H), 1.64 (s, 3 H), 1.15 (s, 3 H), 1.13 (s, 3 H), 1.02 (s, 3 H), 1.00 (s, 3 H), 0.97 (s, 3 H), 0.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.0, 169.5, 131.2, 125.0, 79.9, 75.9, 73.5, 70.1,

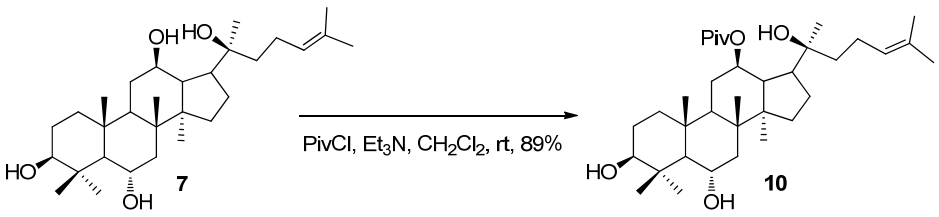
58.5, 52.8, 52.3, 49.1, 42.0, 44.3, 40.4, 39.1, 37.9, 37.6, 35.9, 31.2, 30.1, 27.9, 26.9, 25.6, 23.0, 22.1, 21.8, 21.3, 21.1, 17.5, 17.0 (2 C), 16.7, 16.6; HRMS (MALDI) calcd for $C_{36}H_{58}O_7Na$ $[M+Na]^+$ 625.4096, found 625.4075.

3,6-Di-*O*-acetyl-protopanaxatriol (9)



Compound **8** (100 mg, 0.17 mmol) was treated with a solution of MeOH (10 mL) containing a catalytic amount of NaOMe. The resulting mixture was stirred at room temperature for 30 min, H^+ resin was then added to quench the reaction. The resin was removed by filtration. The solvent was evaporated to give the crude product, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 2:1) to provide **9** (91 mg, 98%) as a white solid: $[\alpha]^{25}_D$ = 40.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31-5.24 (m, 1 H), 5.09 (t, *J* = 5.1 Hz, 1 H), 4.40 (dd, *J* = 3.9, 8.7 Hz, 1 H), 4.19 (bs, 2 H), 3.54-3.48 (m, 1 H), 1.98 (s, 3 H), 1.97 (s, 3 H), 1.66 (s, 3 H), 1.60 (s, 3 H), 1.19 (s, 3 H), 1.11 (s, 3 H), 0.96 (s, 3 H), 0.94 (s, 3 H), 0.85 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.1, 131.6, 124.8, 80.2, 74.1, 70.5, 70.3, 58.6, 53.4, 51.3, 49.3, 47.2, 42.3, 40.6, 39.2, 38.2, 37.6, 34.4, 30.8, 30.2, 29.6, 26.7, 26.3, 25.6, 23.1, 22.2, 21.9, 21.2, 17.6, 17.0, 16.8, 16.7, 16.6; HRMS (MALDI) calcd for $C_{34}H_{56}O_6Na$ $[M+Na]^+$ 583.3969, found 583.3961.

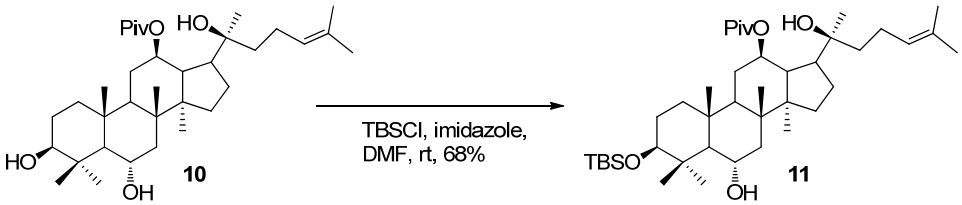
12-*O*-Pivaloyl-protopanaxatriol (10)



To a solution of **7** (200 mg, 0.42 mmol) in dry CH_2Cl_2 (4 mL) was added Et_3N (292 μL, 2.10 mmol) and PivCl (129 μL, 1.05 mmol) successively at 0 °C under an

atmosphere of Ar. The mixture was stirred at room temperature for 2 h. Water was added to quench the reaction. The mixture was diluted with ethyl acetate (300 mL), and was then washed with water and brine, respectively. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to provide **10** (187 mg, 89%) as a white solid: $[\alpha]^{25}_D$ = 11.2 (*c* 4.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.06 (m, 1 H), 4.76-4.70 (m, 1 H), 4.05-4.00 (m, 1 H), 3.12 (dd, *J* = 4.5, 8.1 Hz, 1 H), 2.14-1.81 (m, 8 H), 1.64 (s, 3 H), 1.55 (s, 3 H), 1.25 (s, 3 H), 1.14 (s, 9 H), 1.05 (s, 3 H), 1.03 (s, 3 H), 0.92 (s, 3 H), 0.91 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 131.1, 124.9, 78.2, 76.4, 73.2, 68.2, 60.8, 53.3, 52.5, 49.0, 46.5, 43.8, 40.6, 39.1, 39.0, 38.9, 38.4, 35.7, 30.8, 30.7, 27.4, 27.0, 26.7, 25.8, 25.7, 22.1, 17.6, 17.1 (2 C), 17.0, 15.4; HRMS (MALDI) calcd for $C_{35}H_{60}O_5Na$ $[M+Na]^+$ 583.4330, found 583.4346.

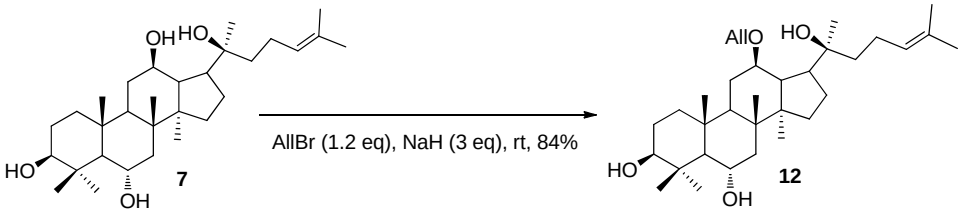
3-*O*-*tert*-Butyldimethysilyl-12-*O*-pivaloyl-protopanaxatriol (11)



To a solution of triol **10** (300 mg, 0.54 mmol) and imidazole (74 mg, 1.08 mmol) in dry DMF (2 mL) was added TBSCl (162 mg, 1.08 mmol) at room temperature under Ar. After being stirred at the same temperature for 24 h, the mixture was diluted with ethyl acetate (300 mL). The organic phase was washed with water and brine, respectively, and was then dried over Na_2SO_4 and concentration. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to afford **11** (245 mg, 68%) as a white solid: $[\alpha]^{25}_D$ = 18.2 (*c* 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.10 (m, 1 H), 4.77 (m, 1 H), 4.07 (m, 1 H), 3.15 (dd, *J* = 5.4, 9.9 Hz, 1 H), 2.18-1.84 (m, 7 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.19 (s, 3 H), 1.17 (s, 9 H), 1.09 (s, 3 H), 1.06 (s, 3 H), 0.95 (s, 3 H), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.86 (s, 9 H), 0.00 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 131.1, 125.0, 79.0, 76.5, 73.2, 68.5, 61.1, 53.4,

52.6, 49.2, 46.6, 43.9, 40.6, 39.8, 39.1, 38.8, 38.5, 35.7, 30.9, 27.5, 27.2, 27.1, 26.8, 25.9, 25.7, 25.6, 22.2, 18.0, 17.6, 17.2, 17.1 (2 C), 15.9, -3.7, -5.0; HRMS (MALDI) calcd for $C_{41}H_{74}O_5SiNa$ $[M+Na]^+$ 697.5198, found 697.5220.

12-*O*-Allyl-protopanaxatriol (12)

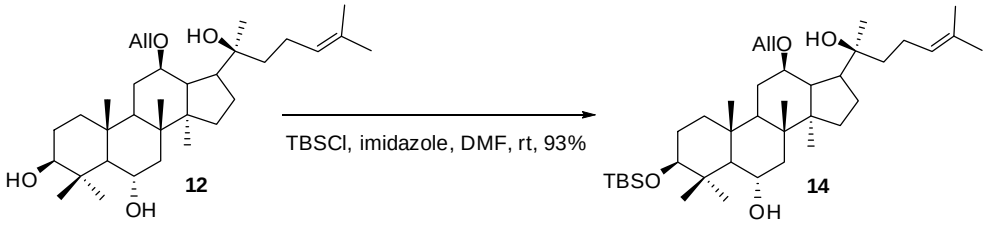


To a mixture of **7** (50 mg, 0.1 mmol) and 60% NaH (12 mg, 0.3 mmol) in dry DMF (6 mL) was added AllBr (10 μL, 0.12 mmol) at 0 ^oC under Ar atmosphere. The ice bath was removed and the mixture was stirred at room temperature for 10 min. Saturated aqueous NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with ethyl acetate (100 mL×3). The organic layers were combined, washed with water and brine, respectively, and dried over Na_2SO_4. The solvent was removed under vacuum to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 2:1) to afford compound **12** (40 mg, 84%) as a white solid: $[\alpha]^{25}_D$ = 19.7 (*c* 5.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.82-5.71 (m, 1 H), 5.17-5.00 (m, 1 H), 4.05-3.95 (m, 2 H), 3.78 (dd, *J* = 6.0, 12.0 Hz, 1 H), 3.23 (m, 1 H), 3.05-3.02 (m, 1 H), 1.55 (s, 3 H), 1.48 (s, 3 H), 1.18 (s, 3 H), 0.97 (s, 3 H), 0.93 (s, 3 H), 0.85 (s, 3 H), 0.80 (s, 3 H), 0.78 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5, 130.8, 125.3, 117.9, 79.2, 78.2, 72.3, 68.8, 68.1, 60.8, 53.7, 51.5, 49.2, 46.6, 45.5, 40.7, 39.1, 39.0, 38.6, 35.5, 30.8, 30.7, 26.7, 26.6, 26.4, 25.8, 25.6, 22.1, 17.5, 17.0, 16.8, 15.4; HRMS (MALDI) calcd for $C_{33}H_{56}O_4Na$ $[M+Na]^+$ 539.4071, found 539.4072.

3,6-Di-*O*-acetyl-12-*O*-allyl-protopanaxatriol (13)

To a solution of **12** (50 mg, 0.1 mmol) in dry pyridine (0.5 mL) was added Ac_2O (0.5 mL) dropwise at 0 °C under Ar atmosphere. The mixture was stirred at room temperature for 30 min, and the solvent was then removed under vaccum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) to give **13** (53 mg, 84%) as a white solid: $[\alpha]^{25}_D$ = 27.0 (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91-5.78 (m, 1 H), 5.33-5.08 (m, 5 H), 4.43 (dd, *J* = 5.1, 11.1 Hz, 1 H), 4.15 (dd, *J* = 5.7, 12.0 Hz, 1 H), 3.85 (dd, *J* = 6.0, 12.0 Hz, 1 H), 3.37 (td, *J* = 4.8, 10.2 Hz, 1 H), 2.00 (s, 3 H), 1.98 (s, 3 H), 1.63 (s, 3 H), 1.55 (s, 3 H), 1.06 (s, 3 H), 1.04 (s, 3 H), 0.97 (s, 3 H), 0.96 (s, 3 H), 0.86 (s, 3 H), 0.85 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.0, 133.4, 130.8, 125.3, 118.0, 79.9, 79.1, 72.2, 70.2, 68.9, 58.5, 53.7, 51.5, 49.1, 45.5, 42.1, 40.5, 39.2, 38.1, 37.5, 35.5, 30.8, 30.1, 26.6, 26.4, 25.8, 25.6, 23.0, 22.1, 21.8, 21.1, 17.5, 17.0, 16.8, 16.6; HRMS (MALDI) calcd for $C_{37}H_{60}O_6Na$ $[M+Na]^+$ 623.4282, found 623.4271.

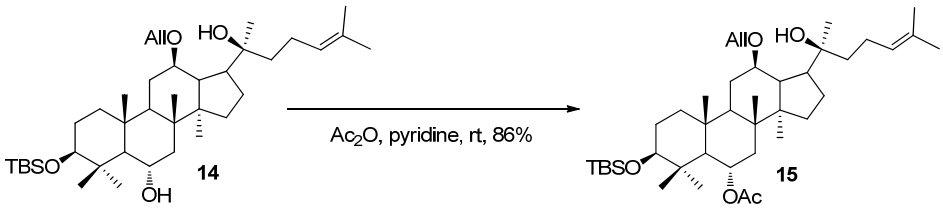
3-*O*-*tert*-Butyldimethylsilyl-12-*O*-allyl-protopanaxatriol (14)



A similar procedure as that used for **10→11** was applied. Thus, treatment of **12** (853 mg, 1.65 mmol) with TBSCl (274 mg, 1.8 mmol) and imidazole (122 mg, 1.8 mmol) in DMF (5 mL) at rt followed by purification on silica gel (petroleum ether/EtOAc, 9:1) led to **14** (969 mg, 93%) as a white solid: $[\alpha]^{25}_D$ = 16.4 (*c* 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91-5.80 (m, 1 H), 5.27-5.10 (m, 4 H), 4.17-4.02 (m, 2 H), 3.86 (dd, *J* = 6.0, 11.7 Hz, 1 H), 3.33 (m, 1 H), 3.13 (m, 1 H), 2.16 (m, 1 H), 2.01 (m, 3 H), 1.83 (m, 2 H), 1.65 (s, 3 H), 1.58 (s, 3 H), 1.20 (s, 3 H), 1.07 (s, 3 H), 1.02 (s, 3 H),

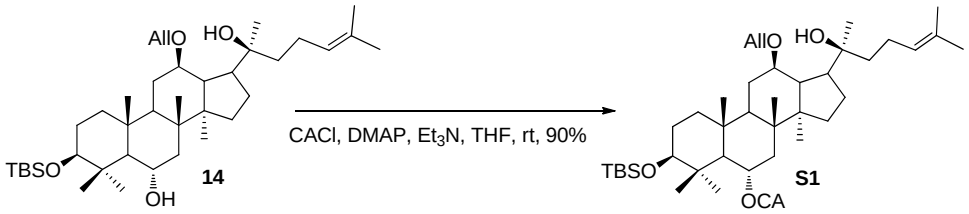
0.91 (s, 3 H), 0.89 (s, 3 H), 0.86 (s, 9 H), 0.00 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5, 130.9, 125.4, 118.0, 79.4, 79.0, 72.3, 68.9, 68.4, 61.0, 53.8, 51.6, 49.3, 46.7, 45.6, 40.8, 39.8, 38.9, 38.7, 35.6, 31.0, 30.8, 27.3, 26.7, 26.4, 25.9, 25.8, 25.7, 22.1, 18.0, 17.6, 17.2, 17.1, 16.8, 15.9, -3.7, -5.0; HRMS (MALDI) calcd for $C_{39}H_{70}O_4SiNa$ $[M+Na]^+$ 653.4936, found 653.4956.

3-*O*-*tert*-Butyldimethylsilyl-6-*O*-acetyl-12-*O*-allyl-protopanaxatriol (15)



A similar procedure as that used for **12→13** was applied to convert **14** to **15**. Thus treatment of **14** (965 mg, 1.5 mmol) with Ac_2O (2 mL) in dry pyridine (2 mL) and purification on silica gel (petrolium ether/EtOAc, 9:1) gave **15** (885 mg, 86%) as a white solid: $[\alpha]^{25}_D$ = 29.6 (*c* 2.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90-5.78 (m, 1 H), 5.24-5.08 (m, 5 H), 4.15 (dd, *J* = 5.4, 11.7 Hz, 1 H), 3.83 (dd, *J* = 5.7, 12.0 Hz, 1 H), 3.32 (m, 1 H), 3.14 (dd, *J* = 4.5, 10.5 Hz, 1 H), 2.15 (m, 1 H), 2.04 (s, 3 H), 1.62 (s, 3 H), 1.55 (s, 3 H), 1.05 (s, 3 H), 1.03 (s, 6 H), 0.93 (s, 3 H), 0.84 (s, 3 H), 0.74 (s, 3 H), 0.02 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 133.4, 130.7, 125.3, 118.0, 79.1, 78.6, 72.3, 70.5, 68.8, 58.5, 53.7, 51.5, 49.2, 45.5, 42.2, 40.5, 39.2, 39.1, 38.4, 35.5, 30.7, 30.5, 27.1, 26.6, 26.3, 25.7, 25.6, 22.1, 21.8, 17.9, 17.5, 17.0, 16.7, 15.9, -3.8, -5.2; HRMS (MALDI) calcd for $C_{41}H_{72}O_5SiNa$ $[M+Na]^+$ 695.5041, found 695.5001.

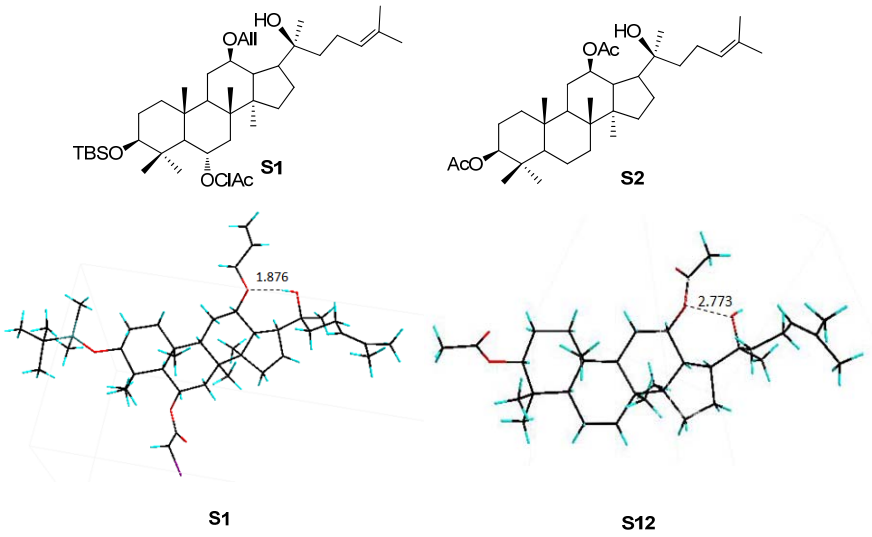
3-*O*-*tert*-Butyldimethylsilyl-6-*O*-chloroacetyl-12-*O*-allyl-protopanaxatriol (S1)



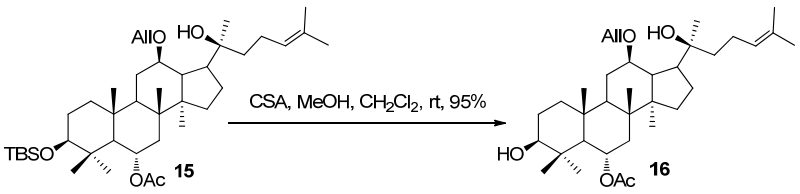
To a solution of **14** (350 mg, 0.55 mmol), DMAP (7 mg, 0.055 mmol), and DIPEA

(144 μL, 0.82 mmol) in dry THF (12 mL) was added $ClCH_2COCl$ (64 μL, 0.62 mmol) slowly at 0 °C under Ar atmosphere. The ice bath was removed and the mixture was stirred at room temperature for 1 h. Ethanol was added at 0 °C to quench the reaction. The mixture was diluted with ethyl acetate, and was then washed with water and brine, respectively. The organic phase was dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to provide **S1** (351 mg, 90%) as a white solid: $[\alpha]^{25}_D$ = 24.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.82 (m, 1 H), 5.41-5.37 (m, 1 H), 5.27-5.09 (m, 4 H), 4.16 (dd, *J* = 5.2, 11.6 Hz, 1 H), 4.00 (s, 2 H), 3.86 (dd, *J* = 6.0, 11.6 Hz, 1 H), 3.36-3.32 (dd, *J* = 5.2, 9.6 Hz, 1 H), 3.17 (dd, *J* = 4.8, 11.2 Hz, 1 H), 1.69 (s, 3 H), 1.58 (s, 3 H), 1.09 (s, 3 H), 1.07 (s, 3 H), 1.05 (s, 3 H), 0.97 (s, 3 H), 0.88 (s, 3 H), 0.86 (s, 9 H), 0.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 133.6, 130.9, 125.5, 118.1, 79.3, 78.7, 73.5, 72.4, 69.0, 58.6, 53.9, 51.7, 49.4, 45.8, 42.2, 41.5, 40.8, 39.5, 38.7, 35.7, 30.9, 30.8, 27.2, 26.8, 26.5, 26.0, 25.9, 25.8, 22.3, 18.1, 17.6, 17.2, 17.0, 16.9, 16.2; HRMS (MALDI) calcd for $C_{41}H_{71}O_5SiClNa$ $[M+Na]^+$ 729.4652, found 729.4644.

ORTEP drawing of the protopanaxatriol and diol derivatives S1 and S2[S2]

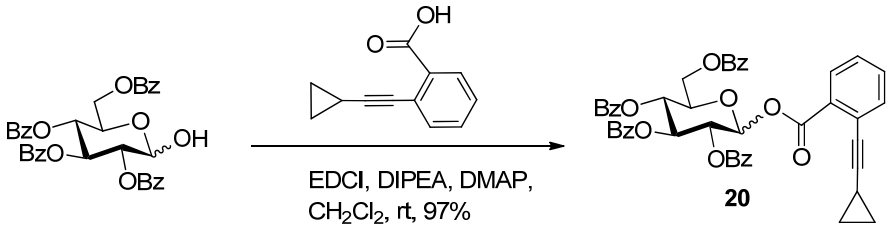


6-*O*-Acetyl-12-*O*-allyl-protopanaxatriol (16)



To compound **15** (500 mg, 0.74 mmol) in MeOH (4 mL) was added CSA (345 mg, 1.48 mmol). The mixture was stirred at room temperature for 15 h; TLC showed that the starting material was consumed completely. Evaporation of the solvent under reduced pressure gave a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to provide **16** (364 mg, 95%) as a white solid: $[\alpha]^{25}_{D}$ = 24.0 (*c* 9.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90-5.77 (m, 1 H), 5.32-5.07 (m, 5 H), 4.14 (dd, *J* = 5.4, 11.7 Hz, 1 H), 3.84 (dd, *J* = 6.0, 12.0 Hz, 1 H), 3.33-3.28 (m, 1 H), 3.14 (dd, *J* = 5.1, 11.1 Hz, 1 H), 2.16 (m, 1 H), 1.98 (s, 3 H), 1.62 (s, 3 H), 1.54 (s, 3 H), 1.14 (s, 3 H), 1.05 (s, 3 H), 1.03 (s, 3 H), 0.92 (s, 3 H), 0.84 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 133.4, 130.7, 125.3, 117.9, 79.1, 77.7, 72.3, 70.4, 68.8, 58.4, 53.7, 51.5, 49.2, 45.5, 42.2, 40.5, 39.3, 38.6, 38.5, 35.5, 30.7, 30.2, 26.7, 26.6, 26.3, 25.7, 25.6, 22.0, 21.8, 17.5, 16.9, 16.7 (2 C), 15.5; HRMS (MALDI) calcd for $C_{35}H_{58}O_5Na$ $[M+Na]^+$ 581.4176, found 581.4183.

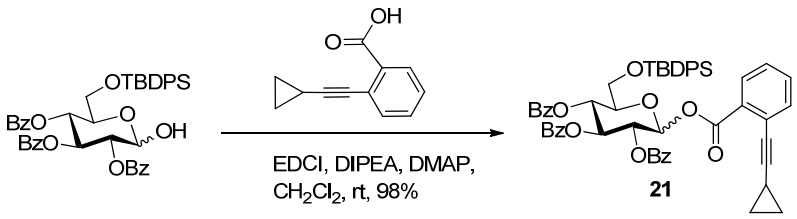
2,3,4,6-Tetra-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (20)



To a solution of 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose[S3] (2.16 g, 3.6 mmol), *ortho*-cyclopropylethynylbenzoic acid (970 mg, 4.8 mmol),[S4] and DMAP (488 mg, 4.8 mmol) in dry dichloromethane (5 mL), was added EDCI (955 mg, 5.1 mmol) and DIPEA (1.3 mL, 7.2 mmol) successively. The mixture was stirred at room temperature for 3 h, and was then diluted with ethyl acetate (300 mL). The mixture was washed with water and saturated brine, respectively, and was then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue, which was purified

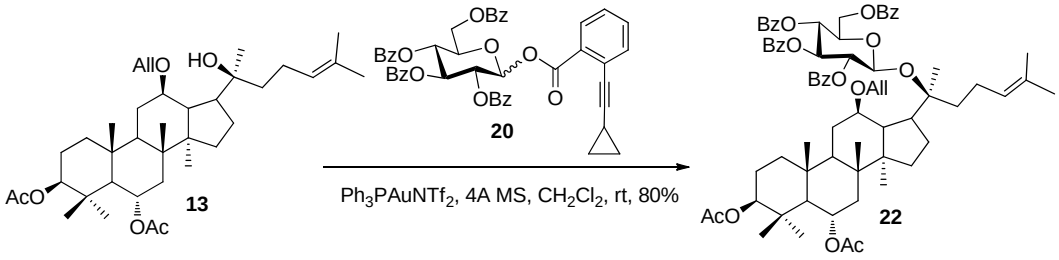
by silica gel column chromatograph (petroleum ether/EtOAc/CH_2Cl_2, 9:1:1) to provide **20** (2.82 g, 97%) as a white foam. The α isomer: $[\alpha]^{25}_D$ = 105.9 (*c* 5.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2 H), 7.92-7.87 (m, 6 H), 7.44-7.28 (m, 17 H), 6.94 (d, *J* = 3.3 Hz, 1 H), 6.38 (dd, *J* = 9.6, 9.9 Hz, 1 H), 5.94 (dd, *J* = 9.9, 10.2 Hz, 1 H), 5.76 (dd, *J* = 3.3, 9.9 Hz, 1 H), 4.80-4.66 (m, 2 H), 4.54 (dd, *J* = 3.3, 6.0 Hz, 1 H), 1.56 (m, 1 H), 0.84 (d, *J* = 6.6 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 165.7, 165.2, 165.0, 163.8, 134.6, 133.4 (2 C), 133.2, 133.0, 132.3, 130.6, 130.0, 129.8, 129.7, 129.6 (2 C), 129.4, 128.7, 128.6, 128.4, 128.3, 128.2, 127.2, 125.2, 100.3, 90.0, 74.4, 70.6, 70.4 (3 C), 68.7, 62.3, 9.02, 9.00, 0.62; HRMS (MALDI) calcd for $C_{46}H_{36}O_{11}Na$ $[M+Na]^+$ 787.2137, found 787.2150.

2,3,4-Tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (21)



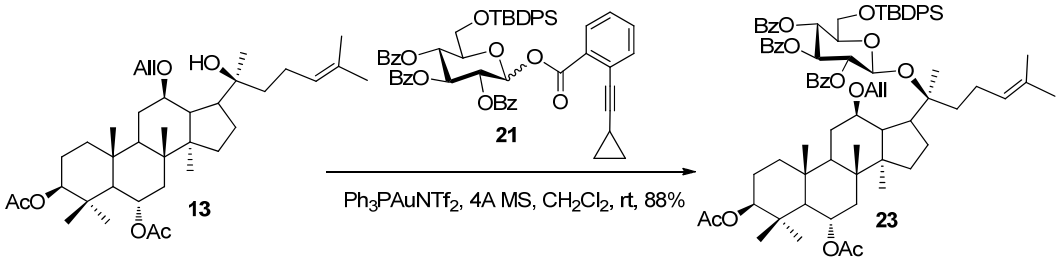
A similar procedure as that used for the synthesis of **20** was applied. Thus, treatment of 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-D-glucopyranose[S5] (3.0 g, 4.1 mmol), *ortho*-cyclopropylethynylbenzoic acid (1.52 g, 8.2 mmol), DIPEA (1.44 mL, 8.2 mmol), and DMAP (1 g, 8.2 mmol) in dry dichloromethane (24 mL) with EDCI (1.57 g, 8.2 mmol) followed by silica gel column chromatography (petroleum ether/EtOAc, 12:1) afforded **21** (3.6 g, 98%) as a white foam. The β isomer: $[\alpha]^{25}_D$ = 43.8 (*c* 4.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01-7.86 (m, 6 H), 7.69-7.11 (m, 23 H), 6.32 (d, *J* = 7.8 Hz, 1 H), 5.97-5.79 (m, 3 H), 4.08 (m, 1 H), 3.93 (m, 2 H), 1.50 (m, 1 H), 1.04 (s, 9 H), 0.87 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 165.0, 164.8, 163.3, 135.6, 135.5, 134.3, 133.3, 133.2, 133.1, 132.9, 132.8, 132.4, 130.9, 129.7, 129.5, 129.4, 129.0, 128.8, 128.3 (2 C), 128.2, 127.6, 127.5, 127.0, 125.7, 100.4, 92.4, 75.6, 74.2, 73.3, 71.0, 68.5, 62.2, 26.6, 19.1, 8.9 (2 C), 0.6; HRMS (MALDI) calcd for $C_{55}H_{50}O_{10}SiNa$ $[M+Na]^+$ 921.3066, found 921.3032.

20-*O*-(2',3',4',6'-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,6-di-*O*-acetyl-12-*O*-allyl -protopanaxatriol (22)



To a flask, donor **20** (160 mg, 0.2 mmol), acceptor **13** (60 mg, 0.1 mmol), PPh_3AuNTf_2 (12 mg, 0.02 mmol), and activated 4Å MS were added. The flask was evacuated and refilled with Ar, and this process was repeated for three times. Dry CH_2Cl_2 was added, and the resulting mixture was stirred at room temperature for 30 min. Filtration followed by evaporation led to a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to provide glycoside **22** (93 mg, 80%) as a white solid: $[\alpha]^{25}_D$ = 26.4 (*c* 3.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2 H), 7.95-7.89 (m, 4 H), 7.85 (d, *J* = 7.5 Hz, 2 H), 7.57-7.25 (m, 12 H), 5.92 (t, *J* = 9.6 Hz, 1 H), 5.82-5.76 (m, 1 H), 5.64 (t, *J* = 9.9 Hz, 1 H), 5.55 (dd, *J* = 8.1, 9.6 Hz, 1 H), 5.30 (m, 1 H), 5.18-5.05 (m, 3 H), 4.96 (m, 1 H), 4.56 (m, 1 H), 4.45 (dd, *J* = 4.2, 12.0 Hz, 2 H), 4.13 (m, 1 H), 3.98 (dd, *J* = 5.4, 12.0 Hz, 1 H), 3.74 (dd, *J* = 5.7, 12.0 Hz, 1 H), 3.13 (m, 1 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.56 (s, 6 H), 1.18 (s, 3 H), 1.00 (s, 3 H), 0.92 (s, 3 H), 0.89 (s, 6 H), 0.74 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.0, 166.1, 165.8, 165.2, 165.0, 135.3, 133.3, 133.1, 133.0, 130.6, 129.7 (2 C), 129.5, 129.4, 128.8 (2 C), 128.3, 128.2 (2 C), 125.0, 116.2, 95.4, 84.2, 80.1, 78.7, 73.4, 72.1, 71.7, 70.4, 70.0, 69.2, 63.6, 58.5, 51.7, 49.0, 47.6, 46.9, 42.0, 40.3, 39.1, 39.0, 38.0, 37.6, 30.5, 30.2, 27.6, 25.9, 25.6, 23.0, 22.6, 21.9, 21.2, 20.4, 17.8 (2 C), 16.9, 16.7, 16.6; HRMS (MALDI) calcd for $C_{71}H_{86}O_{15}Na$ $[M+Na]^+$ 1201.5859, found 1201.5824.

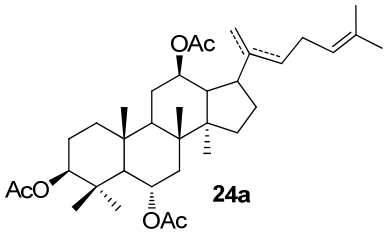
20-*O*-(2',3',4'-Tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3,6 -di-*O*-acetyl-12-*O*-allyl-protopanaxatriol (23)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **13** (58 mg, 0.096 mmol) and **21** (130 mg, 0.145 mmol) with PPh_3AuNTf_2 (11 mg, 0.015 mmol) in dry CH_2Cl_2 (1 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 12:1) led to **23** (112 mg, 88%) as a white solid: $[\alpha]^{25}_D$ = 11.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2 H), 7.84 (d, *J* = 7.2 Hz, 4 H), 7.65-7.16 (m, 19 H), 5.85-5.76 (m, 2 H), 5.60 (t, *J* = 9.0 Hz, 1 H), 5.50 (dd, *J* = 7.8, 9.6 Hz, 1 H), 5.31 (m, 1 H), 5.16-5.02 (m, 4 H), 4.46 (dd, *J* = 4.5, 10.5 Hz, 1 H), 3.96 (dd, *J* = 5.7, 12.3 Hz, 1 H), 3.84-3.70 (m, 4 H), 3.14 (m, 1 H), 2.04 (s, 3 H), 2.02 (s, 3 H), 1.59 (s, 6 H), 1.25 (s, 3 H), 1.01 (s, 12 H), 0.96 (s, 3 H), 0.90 (s, 3 H), 0.89 (s, 3 H), 0.78 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 169.9, 165.9, 165.0 (2 C), 135.5, 135.4 (2 C), 133.0, 132.9, 132.8 (2 C), 130.4, 129.7 (2 C), 129.4, 129.2, 129.1, 128.2, 128.1, 127.5, 125.2, 116.0, 95.4, 83.6, 80.2, 78.9, 74.8, 73.8, 72.4, 70.4, 69.6, 69.4, 63.0, 58.6, 51.8, 49.2, 47.5, 46.6, 42.2, 40.3, 39.5, 39.1, 38.1, 37.6, 30.9, 30.2, 27.7, 26.5, 26.0, 25.6, 23.1, 21.9, 21.2, 21.1, 19.0, 18.0, 17.8, 16.9, 16.8, 16.6; HRMS (MALDI) calcd for $C_{80}H_{100}O_{14}Na$ $[M+Na]^+$ 1335.6775, found 1335.6754.

3,6,12-Tri-*O*-acetyl-dammar-20(21),24-diene and

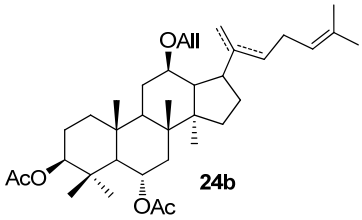
3,6,12-tri-*O*-acetyl-dammar-20(22),24-diene (24a)



To a suspension of the trifluoroacetimidate donor **17** (96 mg, 0.13 mmol), acceptor **8** (50 mg, 0.083 mmol), and activated 4Å MS in dry CH_2Cl_2 was added TMSOTf (0.083

mL, 0.0083 mmol, 0.1 M) at room temperature. The resulting mixture was stirred at the same temperature for 30 min. Filtration followed by evaporation led to a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 30:1) to provide **24a** (44 mg, 91%; an inseparable mixture of the $\Delta^{20,21}$ and $\Delta^{20,22}$ isomers) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (td, *J* = 4.2, 10.6 Hz, 1 H), 5.15 (t, *J* = 6.9 Hz, 0.3 H), 5.04 (t, *J* = 7.0 Hz, 1.4 H), 4.93-4.86 (m, 1 H), 4.72 (s, 0.3 H), 4.62 (s, 0.3 H), 4.44 (dd, *J* = 4.4, 11.5 Hz, 1 H), 2.67-2.43 (m, 2.3 H), 2.02 (d, *J* = 1.2 Hz, 6 H), 1.81 (s, 3 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.53 (s, 3 H), 1.14 (s, 3 H), 1.00 (s, 3 H), 0.98 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.5, 170.1, 152.1, 136.9, 131.4, 131.0, 124.4, 123.2, 123.2, 108.0, 79.9, 73.8, 70.2, 58.4, 50.9, 50.7, 49.6, 49.1, 47.4, 46.3, 42.3, 40.7, 39.2, 38.2, 37.6, 31.9, 30.2, 29.3, 28.3, 28.0, 27.1, 26.6, 25.6, 23.1, 21.9, 21.2, 21.0, 20.9, 17.6, 17.1, 17.1, 16.7, 16.6, 16.4, 12.2; HRMS (MALDI) calcd for $C_{36}H_{56}O_6Na$ $[M+Na]^+$ 607.3996, found 607.3969.

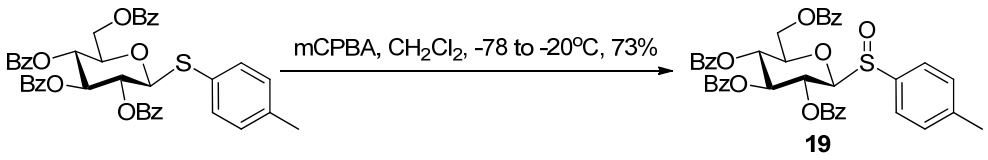
3,6-Di-*O*-acetyl-12-*O*-allyl-dammar-20(21),24-diene and
3,6-di-*O*-acetyl-12-*O*-allyl-dammar-20(22),24-diene (24b)



24b

Compound **24b** (30 mg, 74%; an inseparable mixture of the $\Delta^{20,21}$ and $\Delta^{20,22}$ isomers), a colorless oil, was isolated upon treatment of **17** and **13** in the presence of TMSOTf: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86-5.73 (m, 1 H), 5.38-5.30 (m, 1 H), 5.21-5.05 (m, 3 H), 4.80 (s, 0.4 H), 4.65 (s, 0.4 H), 4.48 (dd, *J* = 5.4, 11.1 Hz, 1 H), 3.98-3.82 (m, 2 H), 3.21 (m, 1 H), 2.68 (t, *J* = 6.9 Hz, 1 H), 2.54-2.45 (m, 1 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 2.68-0.89 (m, 39 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.4, 153.8, 138.3, 135.7, 131.4, 131.1, 125.0, 123.9, 122.7, 116.2, 116.0, 107.4, 80.5, 80.2, 80.1, 71.3, 71.0, 70.8, 60.6, 59.0, 50.1, 50.0, 48.7, 48.0, 42.8, 41.1, 39.6, 38.6, 38.0, 30.6, 28.9, 28.7, 27.3, 26.6, 25.9, 22.2, 21.3, 17.0, 14.4, 12.9; HRMS (MALDI) calcd for $C_{37}H_{58}O_5Na$ $[M+Na]^+$ 605.4187, found 605.4177.

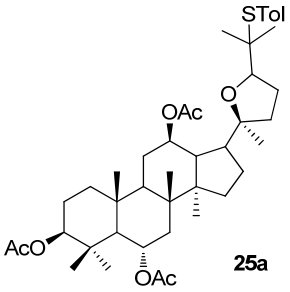
_p_-Tolylsulfenyl 2,3,4,6-tetra-_O_-benzoyl-β-D-glucopyranoside (19)



19

To a solution of *p*-tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside[S6] (1.43 g, 2.03 mmol) in dry dichloromethane (25 mL) was added *m*-chloroperoxybenzoic acid (550 mg, 3.20 mmol) at -78°C. The mixture was warmed gradually to -20°C, and was stirred at this temperature for 3h. After addition of $Na_2S_2O_3$ to quench the reaction, the mixture was diluted with EtOAc (300 mL), and was then washed with water and brine, respectively. The organic phase was dried over Na_2SO_4 and condensation under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to provide **19** (1.06 g, 73%; a difficult-to-separate 4:5 mixture of the diastereoisomers) as a white solid. The major isomer: $[\alpha]^{25}_D$ = -10.2 (*c* 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2 H), 7.88-7.79 (m, 6 H), 7.62-7.22 (m, 14 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 6.00 (t, *J* = 9.3 Hz, 1 H), 5.71 (t, *J* = 9.6 Hz, 1 H), 5.61 (t, *J* = 9.6 Hz, 1 H), 4.94 (d, *J* = 9.9 Hz, 1 H), 4.74 (m, 1 H), 4.44 (dd, *J* = 4.2, 12.3 Hz, 1 H), 4.26 (m, 1 H), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 165.5, 164.8, 164.7, 142.1, 134.6, 133.4, 133.3, 133.2, 133.0, 129.7, 129.6, 129.4, 129.3, 128.4, 128.3, 128.2 (2 C), 125.7, 92.6, 73.7, 68.3, 67.6, 62.1, 21.2; HRMS (MALDI) calcd for $C_{41}H_{34}O_{10}SNa$ $[M+Na]^+$ 741.1777, found 741.1765. The minor isomer: $[\alpha]^{25}_D$ = 13.1 (*c* 6.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.77 (m, 10 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.50-7.21 (m, 11 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 5.98 (t, *J* = 9.6 Hz, 1 H), 5.79 (t, *J* = 9.6 Hz, 1 H), 5.56 (t, *J* = 9.6 Hz, 1 H), 4.94 (d, *J* = 9.9 Hz, 1 H), 4.73 (d, *J* = 12.0 Hz, 1 H), 4.39 (m, 1 H), 4.25 (d, *J* = 9.3 Hz, 1 H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, CDCl3) δ 165.6, 165.5, 164.9, 164.8, 145.6, 133.5, 133.3, 133.2, 133.1, 131.3, 130.4, 129.8, 129.7, 129.6, 129.4, 129.2, 128.8, 128.3, 128.2 (2 C), 89.0, 76.5, 73.6, 68.1, 67.6, 61.8, 21.5.

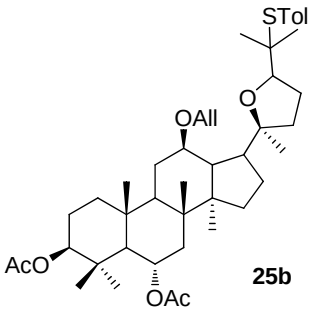
Dammarane derivative 25a



25a

To a suspension of **19** (120 mg, 0.166 mmol), **8** (48 mg, 0.08 mmol), DTBMP (21 mg, 0.10 mmol), and activated 4Å MS in dry dichloromethane (1 mL) was added Tf_2O (15 μL, 0.091 mmol) at -78 °C. The mixture was stirred and the temperature was warmed gradually to room temperature in 2h. After addition of triethylamine for neutralization, insoluble materials were removed by filtration (Celite) and washed with CH_2Cl_2. Evaporation of the solvent led to a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 12:1) to provide **25a** (28 mg, 47%) as a colorless oil: $[\alpha]^{25}_D$ = 26.0 (*c* 2.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (m, 2 H), 7.13 (d, *J* = 6.6 Hz, 2 H), 5.35 (m, 1 H), 4.83 (m, 1 H), 4.48 (m, 1 H), 3.71 (m, 1 H), 2.36 (s, 3 H), 2.05 (s, 6 H), 2.01 (s, 3 H), 1.16 (s, 6 H), 1.12 (s, 3 H), 1.02 (s, 3 H), 0.98 (s, 3 H), 0.94 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (75 MHz, CDCl3) δ 170.8, 170.5, 170.1, 138.6, 137.6, 129.1, 128.2, 85.4, 85.1, 83.8, 82.4, 80.0, 75.1, 70.3, 58.5, 52.1, 51.8, 51.1, 50.9, 49.8, 49.0, 45.8, 45.6, 42.1, 40.4, 39.5, 39.2, 38.0, 37.7, 30.8, 30.7, 30.3, 28.1, 27.9, 25.5, 25.4, 24.4, 24.2, 23.1, 22.5, 22.0, 21.8, 21.2 (2 C), 17.3, 17.0, 16.8; HRMS (MALDI) calcd for $C_{43}H_{64}O_7SNa$ $[M+Na]^+$ 747.4275, found 747.4265.

Dammarane derivative 25b

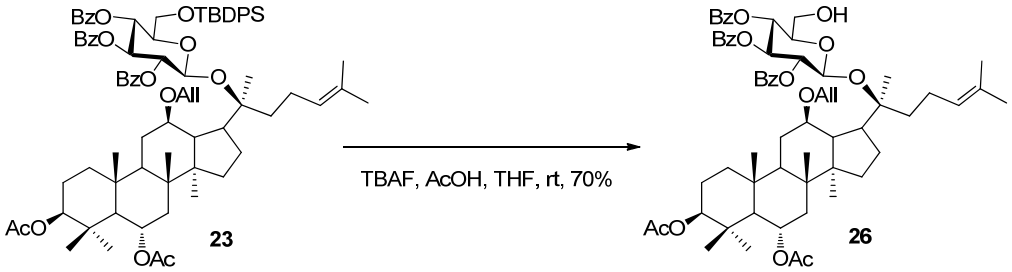


25b

Compound **25b** (43 mg, 72%), a white solid, was isolated upon treatment of **19** and **13** in the presence of Tf_2O and DTBMP: $[\alpha]^{25}_D$ = 21.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.45 (m, 2 H), 7.13 (m, 2 H), 5.90 (m, 1 H), 5.33 (m, 1 H), 5.25-5.11

(m, 2 H), 4.45 (m, 1 H), 4.05 (m, 1 H), 3.83 (m, 1 H), 3.71 (m, 1 H), 3.26 (m, 1 H), 2.35 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 1.16 (s, 6 H), 1.10 (s, 3 H), 1.03 (s, 3 H), 1.00 (s, 3 H), 0.92 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (75 MHz, $CHCl_3$) δ 171.0, 170.1, 138.5, 137.7, 137.6, 135.3, 135.3, 129.1, 128.4, 116.3, 86.4, 86.0, 83.5, 82.3, 80.2, 79.0, 70.4, 69.3, 58.6, 51.6, 51.4, 51.3, 51.2, 49.9, 49.2, 47.7, 47.4, 42.3, 40.6, 39.7, 39.6, 39.3, 38.2, 37.7, 30.8, 30.2, 28.1, 27.9, 27.5, 25.8, 25.5, 25.3, 24.3, 24.0, 23.1, 22.4, 22.0, 21.3, 21.2, 21.0, 17.4 (2 C), 17.0, 16.8, 16.7; HRMS (MALDI) calcd for $C_{44}H_{66}O_6SNa$ $[M+Na]^+$ 745.4484, found 745.44723.

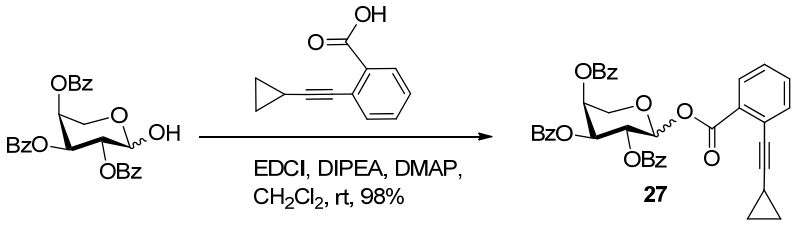
20-*O*-(2',3',4'-Tri-*O*-benzoyl-β-D-glucopyranosyl)-3,6-di-*O*-acetyl-12-*O*-allyl-protopanaxatriol (26)



To a solution of **23** (170 mg, 0.13 mmol) in dry THF (2 mL) was added TBAF in THF (3.9 mL, 3.9 mmol) and AcOH (300 μL, 5.2 mmol) under an atmosphere of Ar at room temperature. The mixture was stirred at room temperature for another 10 h, TLC showed that the reaction reached completion. The mixture was diluted by EtOAc (300 mL), and was then washed with water and brine, respectively. The organic phase was dried over Na_2SO_4 and condensation under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) to provide **26** (98 mg, 70%) as a white solid: $[\alpha]^{25}_D$ = 2.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 4 H), 7.84 (d, *J* = 7.2 Hz, 2 H), 7.54-7.25 (m, 9 H), 5.92-5.79 (m, 2 H), 5.52 (dd, *J* = 7.8, 9.9 Hz, 1 H), 5.40 (t, *J* = 9.6 Hz, 1 H), 5.30-5.24 (m, 1 H), 5.20-5.00 (m, 4 H), 4.46 (dd, *J* = 4.5, 10.8 Hz, 1 H), 4.01 (dd, *J* = 5.1, 12.3 Hz, 1 H), 3.80-3.69 (m, 4 H), 3.23 (m, 1 H), 2.62 (brs, 1 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.69 (s, 3 H), 1.67 (s, 3 H), 1.14 (s, 3 H), 1.01 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 6 H), 0.81 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.1, 165.8, 165.7, 164.9, 135.2, 133.4,

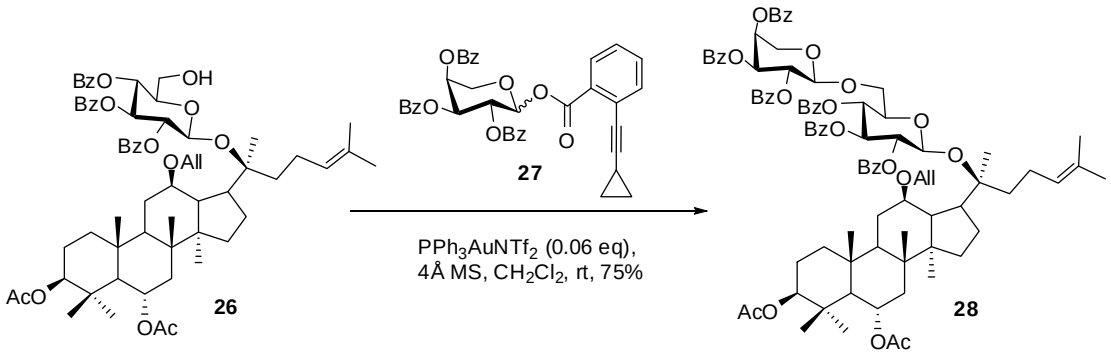
133.0, 132.0, 129.8, 129.7, 129.6, 129.4, 128.9, 128.7, 128.4, 128.3, 128.2, 125.1, 116.2, 95.1, 84.4, 80.2, 78.7, 74.8, 73.2, 71.9, 70.4, 69.9, 69.2, 62.2, 58.5, 51.7, 49.0, 47.0, 46.5, 42.0, 40.3, 39.2, 39.1, 38.0, 37.6, 30.4, 30.2, 27.5, 25.7, 25.6, 23.0, 22.5, 21.9, 21.2, 20.2, 18.0, 17.8, 16.9, 16.7, 16.6; HRMS (MALDI) calcd for $C_{64}H_{82}O_{14}Na$ $[M+Na]^+$ 1097.5597, found 1097.5616.

2,3,4-Tri-*O*-benzoyl-L-arabinopyranosyl *ortho*-cyclopropylethynlbenzoate (27)



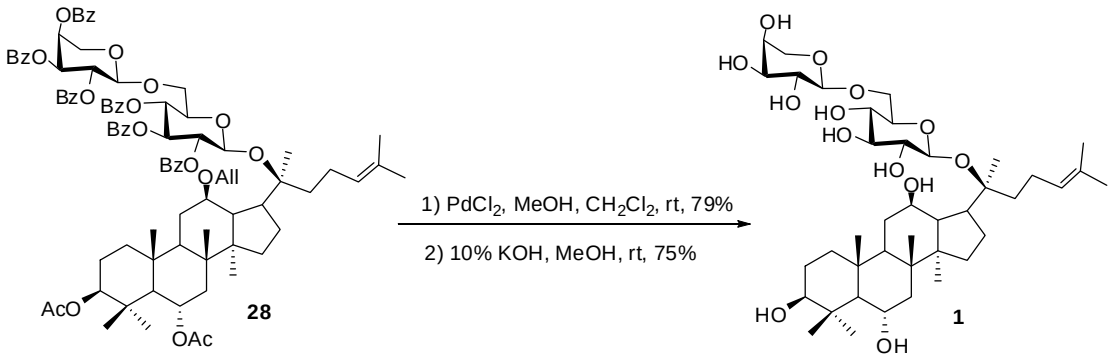
A similar procedure as that used for the synthesis of **20** was applied. Thus, treatment of 2,3,4-tri-*O*-benzoyl-L-arabinopyranose[S7] (150 mg, 0.324 mmol), *ortho*-cyclopropylethynylbenzoic acid (120.6 mg, 0.648 mmol), DIPEA (0.11 mL, 0.648 mmol), and DMAP (79 mg, 0.648 mmol) in dry dichloromethane (4 mL) with EDCI (124 mg, 0.648 mmol) followed by silica gel column chromatography (petroleum ether/EtOAc, 9:1) led to **27** (200 mg, 98%) as a white foam. The α isomer: $[\alpha]^{25}_D$ = 124.8 (*c* 4.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 4 H), 7.98 (d, *J* = 7.5 Hz, 2 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.58-7.25 (m, 11 H), 7.18 (t, *J* = 6.9 Hz, 1 H), 6.33 (d, *J* = 5.1 Hz, 1 H), 5.93 (dd, *J* = 5.1, 6.3 Hz, 1 H), 5.82 (m, 2 H), 4.49 (dd, *J* = 5.7, 12.6 Hz, 1 H), 4.16 (m, 1 H), 1.52 (m, 1 H), 0.86 (d, *J* = 6.6 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 165.3, 165.0, 163.8, 134.2, 133.5, 133.4, 133.3, 132.1, 130.5, 130.0, 129.8 (2 C), 129.1, 128.9, 128.7, 128.4 (2 C), 128.3, 126.9, 125.3, 100.3, 92.0, 74.1, 69.5, 68.8, 67.3, 62.2, 8.8, 0.6; HRMS (MALDI) calcd for $C_{38}H_{30}O_9Na$ $[M+Na]^+$ 653.1784, found 653.1782.

20-*O*-[2",3",4"-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-3,6-di-*O*-acetyl-12-*O*-allyl-protopanaxatriol (28)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **26** (100 mg, 0.093 mmol) and **27** (144 mg, 0.232 mmol) with PPh_3AuNTf_2 (4 mg, 0.0054 mmol) in dry CH_2Cl_2 (3 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 4:1) led to **28** (105 mg, 75%) as a white solid: $[\alpha]^{25}_D$ = 44.8 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-7.87 (m, 10 H), 7.78 (d, *J* = 7.5 Hz, 2 H), 7.58-7.23 (m, 18 H), 5.86-5.78 (m, 2 H), 5.64-5.59 (m, 3 H), 5.53 (t, *J* = 9.6 Hz, 1 H), 5.40 (dd, *J* = 8.1, 9.3 Hz, 1 H), 5.30 (m, 1 H), 5.17-5.05 (m, 3 H), 4.98 (d, *J* = 7.5 Hz, 1 H), 4.82 (d, *J* = 4.2 Hz, 1 H), 4.46 (dd, *J* = 4.5, 10.8 Hz, 1 H), 4.27 (dd, *J* = 6.3, 12.3 Hz, 1 H), 4.08 (d, *J* = 10.2 Hz, 1 H), 3.96-3.90 (m, 2 H), 3.81-3.70 (m, 3 H), 3.14 (m, 1 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.63 (s, 3 H), 1.55 (s, 3 H), 1.08 (s, 3 H), 1.00 (s, 3 H), 0.90 (s, 9 H), 0.73 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 170.0, 165.8, 165.5, 165.4, 165.1, 164.9, 135.4, 133.4, 133.3, 133.2, 133.0, 132.9, 130.5, 129.9, 129.8 (2 C), 129.6 (2 C), 129.3, 129.2, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2 (2 C), 125.3, 116.3, 99.6, 95.5, 84.1, 80.2, 78.7, 77.2, 73.6, 73.2, 72.3, 70.4, 69.7, 69.6, 69.4, 67.5, 58.6, 51.7, 49.1, 47.5, 46.9, 42.1, 40.3, 39.2, 39.1, 38.0, 37.6, 30.7, 30.2, 29.6, 27.7, 26.0, 25.6, 23.1, 22.7, 22.0, 21.3, 20.3, 17.9 (2 C), 16.9, 16.7 (2 C); HRMS (MALDI) calcd for $C_{90}H_{102}O_{21}Na$ $[M+Na]^+$ 1541.6806, found 1541.6807.

Ginsenoside F3 (1)

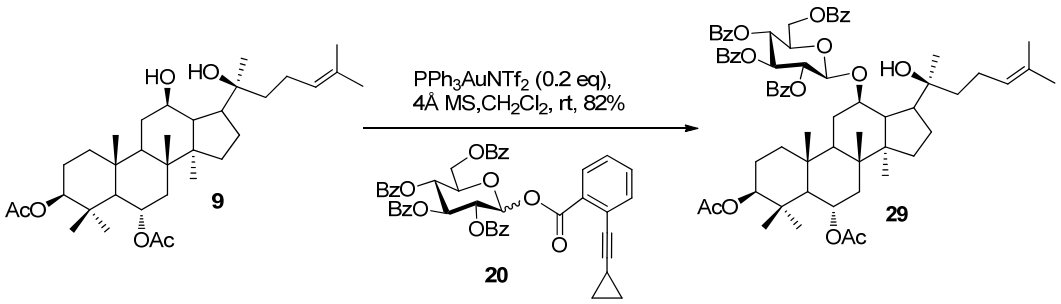


To a solution of compound **28** (100 mg, 0.066 mmol) in a mixed solvent of dichloromethane and MeOH (10 mL, v/v = 1:1) was added $PdCl_2$ (6 mg, 0.034 mmol) under Ar atmosphere at room temperature. The mixture was stirred at the same temperature for 10 h, and was then filtered through a pad of silica gel. The filtrate was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to provide the deallylated product (77 mg, 79%) as a white solid.

To a solution of freshly prepared 10% KOH/MeOH (0.2 g KOH in 2.5 mL MeOH) was added the above deallylated product (148 mg, 0.1 mmol) at room temperature. The mixture was stirred at the same temperature for 12 h, and then H^+-resin was added to adjust the pH value to 7~8. Filtration followed by concentration led to a residue, which was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 10:1) to provide **1** (58 mg, 75%) as a white solid: $[\alpha]^{25}_D$ = 24.9 (*c* 1.2, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5) δ 5.56 (s, 1 H), 5.34 (m, 1 H), 5.15 (d, *J* = 7.5 Hz, 1 H), 5.02 (d, *J* = 6.0 Hz, 1 H), 4.73 (d, *J* = 10.8 Hz, 1 H), 4.49-4.20 (m, 8 H), 4.11-4.06 (m, 2 H), 3.98 (t, *J* = 8.4 Hz, 1 H), 3.82 (d, *J* = 11.4 Hz, 1 H), 3.55 (dd, *J* = 5.1, 10.8 Hz, 1 H), 2.61 (m, 1 H), 2.42 (m, 1 H), 2.00 (s, 3 H), 1.67 (s, 3 H), 1.63 (s, 6 H), 1.46 (s, 3 H), 1.10 (s, 3 H), 1.02 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 131.2, 126.0, 104.7, 98.2, 83.5, 79.3, 78.6, 76.8, 74.2, 71.9, 70.3, 69.3, 68.7, 67.8, 65.7, 61.8, 51.7, 51.4, 50.0, 49.2, 47.6, 41.3, 40.4, 39.4, 36.2, 32.1, 30.9, 30.8, 28.2, 26.7, 25.9, 23.3, 22.4, 18.0, 17.7, 17.5 (2 C), 16.6; HRMS (MALDI) calcd for $C_{41}H_{70}O_{13}Na$ $[M+Na]^+$ 793.4787, found 793.4703.

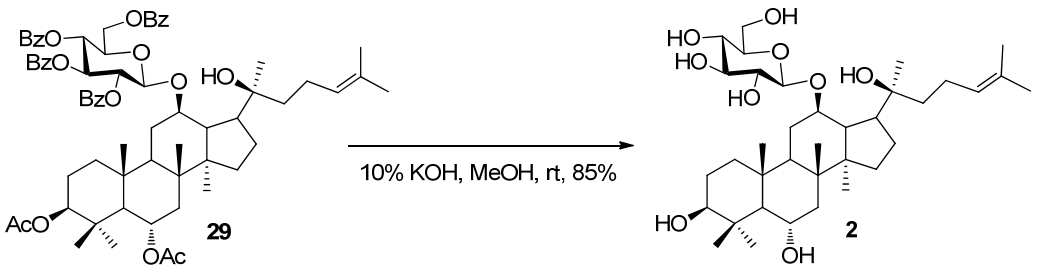
12-*O*-(2',3',4',6'-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,6-di-*O*-acetyl-protopana

xatriol (29)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **9** (50 mg, 0.084 mmol) and **20** (132 mg, 0.17 mmol) with PPh_3AuNTf_2 (12.6 mg, 0.017 mmol) in dry CH_2Cl_2 (2 mL) at the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 4:1) led to **29** (78 mg, 82%) as a white solid: $[\alpha]^{25}_D$ = 31.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-7.80 (m, 8 H), 7.59-7.25 (m, 12 H), 5.96 (t, *J* = 7.5 Hz, 1 H), 5.60 (t, *J* = 7.2 Hz, 1 H), 5.49 (dd, *J* = 6.0, 7.2 Hz, 1 H), 5.29-5.15 (m, 2 H), 5.04 (d, *J* = 6.0 Hz, 1 H), 4.61 (d, *J* = 3.9 Hz, 2 H), 4.42 (dd, *J* = 3.6, 8.7 Hz, 1 H), 4.21-4.11 (m, 2 H), 3.93-3.87 (m, 1 H), 2.34-2.27 (m, 1 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.70 (s, 3 H), 1.65 (s, 3 H), 1.14 (s, 3 H), 1.00 (s, 3 H), 0.90 (s, 3 H), 0.86 (s, 3 H), 0.84 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 170.2, 166.1, 165.9, 165.3, 164.6, 133.6, 133.4, 130.7, 129.9, 129.5, 128.6, 128.4, 126.1, 97.2, 80.0, 78.2, 72.9 (2 C), 72.6, 72.2, 70.3, 63.4, 58.7, 53.6, 52.0, 49.3, 45.5, 42.3, 40.6, 39.2, 38.1, 37.8, 36.0, 31.1, 30.5, 29.8, 27.1, 26.9, 26.4, 26.0, 23.2, 22.5, 22.1, 21.4, 17.9, 17.2, 16.9, 16.8; HRMS (MALDI) calcd for $C_{68}H_{82}O_{15}Na$ $[M+Na]^+$ 1161.5546, found 1161.5583.

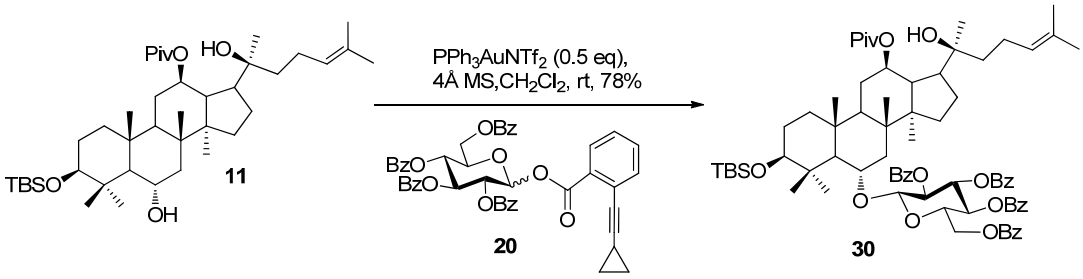
Chikusetsusaponin L10 (2)



A similar procedure as that used for the synthesis of **1** from the deallylated intermediate was adopted. Thus treatment of **29** (60 mg, 0.053 mmol) with 10%

KOH/MeOH (2 mL) followed by silica gel chromatography (CH_2Cl_2/MeOH, 10:1) provided **2** (31 mg, 85%) as a white solid: $[\alpha]^{25}_D$ = 14.3 (*c* 0.6, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5) δ 5.36-5.30 (m, 2 H), 4.52 (d, *J* = 8.4 Hz, 1 H), 4.40-4.30 (m, 4 H), 4.26 (t, *J* = 9.0 Hz, 1 H), 4.14 (dd, *J* = 7.8, 8.7 Hz, 1 H), 4.06 (m, 1 H), 3.56 (dd, *J* = 5.4, 10.8 Hz, 1 H), 2.60 (m, 1 H), 2.37 (m, 2 H), 2.24 (m, 1 H), 2.00 (s, 3 H), 1.65 (s, 6 H), 1.44 (s, 3 H), 1.34 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 130.6, 126.4, 100.4, 78.6, 78.4, 78.3, 77.5, 75.2, 73.0, 71.0, 67.5, 62.4, 61.6, 54.0, 52.0, 49.7, 47.1, 46.2, 40.9, 40.3, 39.3, 38.9, 36.3, 31.9, 31.1, 28.0, 27.8, 27.0, 26.6, 25.8, 22.8, 17.6, 17.4, 17.2 (2 C), 16.4; HRMS (MALDI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4292.

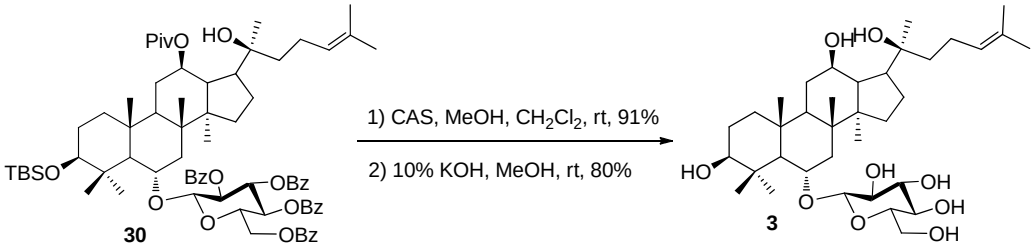
6-*O*-(2',3',4',6'-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-*tert*-butyldimethylsily-12-*O*-pivaloyl-protopanaxatriol (30)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **11** (20 mg, 0.03 mmol) and **22** (46 mg, 0.06 mmol) with PPh_3AuNTf_2 (11 mg, 0.015 mmol) in dry CH_2Cl_2 (1 mL) at the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 10:1) led to **35** (29 mg, 78%) as a white solid: $[\alpha]^{25}_D$ = 14.8 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.4 Hz, 2 H), 7.92 (t, *J* = 6.0 Hz, 4 H), 7.80 (d, *J* = 5.4 Hz, 2 H), 7.56-7.23 (m, 12 H), 5.94 (t, *J* = 7.2 Hz, 1 H), 5.67 (t, *J* = 7.2 Hz, 1 H), 5.62 (t, *J* = 6.9 Hz, 1 H), 5.17 (m, 2 H), 4.75-4.70 (m, 1 H), 4.63 (dd, *J* = 1.8, 9.3 Hz, 1 H), 4.53 (dd, *J* = 2.1, 9.0 Hz, 1 H), 4.25 (m, 1 H), 4.05 (dd, *J* = 6.0, 7.5 Hz, 1 H), 2.99 (dd, *J* = 3.9, 8.1 Hz, 1 H), 2.22 (bs, 1 H), 2.05-1.93 (m, 4 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.18 (s, 9 H), 1.09 (s, 3 H), 0.95 (s, 3 H), 0.90 (s, 3 H), 0.88 (s, 3 H), 0.83 (s, 3 H), 0.70 (s, 9 H), 0.65 (s, 3 H), 0.10 (s, 3 H), 0.21 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 166.0,

165.8, 165.2, 165.1, 133.4, 133.2, 133.0, 131.1, 129.8, 129.7 (2 C), 129.5, 129.2, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 125.1, 102.6, 80.5, 79.3, 73.3, 73.1, 72.1, 69.5, 59.9, 53.4, 52.5, 49.0, 43.8, 40.6, 39.2, 39.1, 30.2, 27.1, 25.8 (2 C), 22.2, 17.9, 17.6, 17.2, 17.1, 16.8, 15.9, -3.8, -5.3; HRMS (MALDI) calcd for $C_{75}H_{100}O_{14}SiNa$ $[M+Na]^+$ 1275.6775, found 1275.6796.

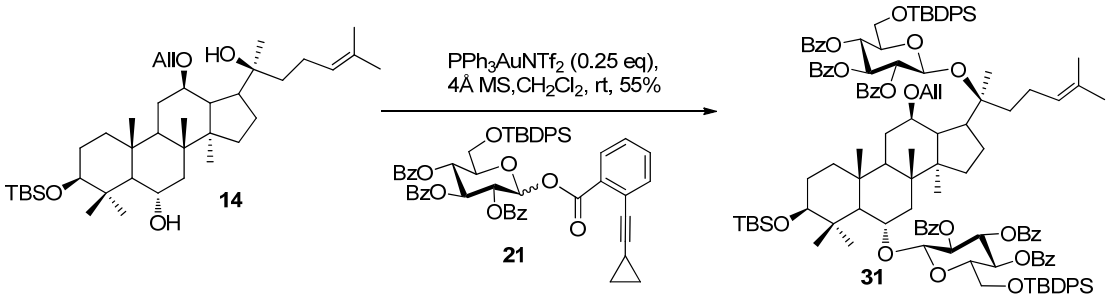
Ginsenoside Rh1 (3)



To a solution of **30** (70 mg, 0.056 mmol) in MeOH (10 mL) was added CSA (23 mg, 0.01 mmol). After being stirred at room temperature for 10 h, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 3:1) to provide the 3-ol derivative (57 mg, 91%) as a white solid.

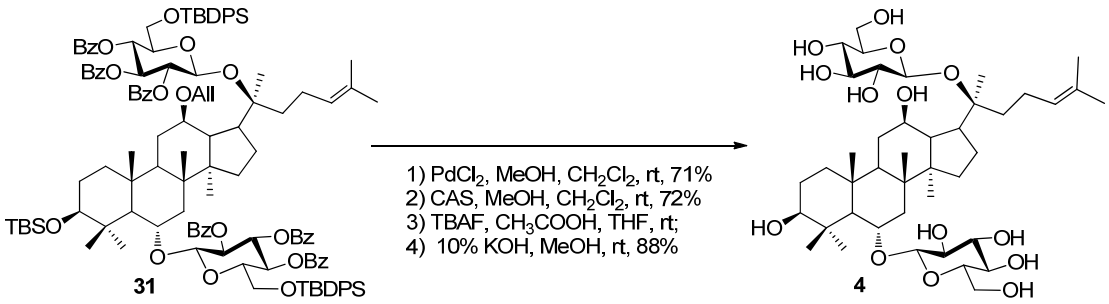
The above compound (60 mg, 0.053 mmol) was treated with a solution of freshly prepared 10% KOH in MeOH (0.2 g KOH in 2.5 mL MeOH). The resulting mixture was stirred at room temperature for 12 h, and was then neutralized with $^+$H resin. The resin was removed by filtration. The filtrate was concentrated to give a residue, which was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 10:1) to provide **3** (27 mg, 80%) as a white solid: $[\alpha]^{25}_D$ = 23.6 (*c* 0.8, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5) δ 5.34 (m, 1 H), 5.08 (d, *J* = 7.8 Hz, 1 H), 4.59 (d, *J* = 10.8 Hz, 1 H), 4.48-4.38 (m, 2 H), 4.33-4.23 (m, 2 H), 4.16 (t, *J* = 7.8 Hz, 1 H), 3.98-3.90 (m, 2 H), 3.58 (dd, *J* = 4.8, 11.1 Hz, 1 H), 2.57 (m, 2 H), 2.32 (m, 2 H), 2.11 (s, 3 H), 1.67 (s, 3 H), 1.64 (s, 6 H), 1.41 (s, 3 H), 1.19 (s, 3 H), 1.04 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 130.8, 126.3, 106.1, 80.1, 79.7, 78.6, 78.2, 75.5, 73.0, 71.9, 71.1, 63.1, 61.5, 54.8, 51.7, 50.2, 48.3, 45.3, 41.1, 40.4, 39.7, 39.4, 35.8, 32.1, 31.8, 31.3, 28.0, 27.1, 26.9, 25.8, 23.0, 17.7 (2 C), 17.4, 16.8, 16.4; HRMS (MALDI) calcd for $C_{36}H_{62}O_9Na$ $[M+Na]^+$ 661.4286, found 661.4300.

6,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-*tert*-butyldimethylsilyl-12-*O*-allyl-protopanaxatriol (31)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **14** (70 mg, 0.11 mmol) and **21** (300 mg, 0.33 mmol) with PPh_3AuNTf_2 (20.5 mg, 0.03 mmol) in dry CH_2Cl_2 (4 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 12:1) led to **31** (125 mg, 55%) as a white solid: $[\alpha]^{25}_D$ = 2.7 (*c* 4.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.78 (m, 12 H), 7.63-7.16 (m, 38 H), 5.86-5.69 (m, 4 H), 5.61-5.46 (m, 3 H), 5.14-4.97 (m, 4 H), 4.04-3.62 (m, 9 H), 3.05-2.98 (m, 2 H), 1.60 (s, 6 H), 1.26 (s, 3 H), 0.99 (s, 9 H), 0.98 (s, 9 H), 0.88 (s, 3 H), 0.80 (s, 3 H), 0.76 (s, 3 H), 0.73 (s, 9 H), 0.71 (s, 3 H) 0.60 (s, 3 H), -0.08 (s, 3 H), -0.18 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.1, 165.0, 164.9 (2 C), 135.5 (2 C), 135.4, 135.3, 133.0, 132.9, 132.8, 132.7, 130.4, 129.7, 129.6, 129.5 (2 C), 129.3, 129.2, 129.0, 128.9, 128.2, 128.1, 128.0, 127.6, 127.5, 125.2, 115.9, 102.3, 95.4, 83.6, 80.2, 79.5, 79.1, 74.9, 74.8, 74.0, 73.9, 72.5, 72.2, 69.6, 69.5, 69.3, 63.5, 63.1, 59.9, 51.8, 49.3, 47.6, 46.6, 44.6, 40.5, 39.5, 39.2, 39.0, 38.5, 30.9, 30.4, 29.6, 27.7, 27.0, 26.7, 26.5, 26.0, 25.8, 25.6, 23.2, 21.5, 19.0, 18.9, 17.9, 17.8, 17.2, 17.0, 15.8, -3.8, -5.3; HRMS (MALDI) calcd for $C_{125}H_{150}O_{20}Si_3Na$ $[M+Na]^+$ 2077.9942, found 2077.9921.

Ginsenoside Rg1 (4)



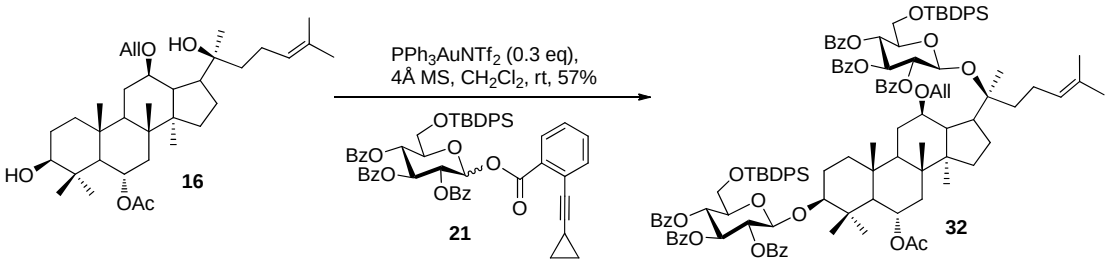
To a solution of compound **31** (200 mg, 0.097 mmol) in a mixed solvent of dichloromethane and MeOH (20 mL, v/v = 1:1) was added $PdCl_2$ (8 mg, 0.045 mmol) under Ar atmosphere at room temperature. The mixture was stirred at the same temperature for 10 h, and was then filtered through a pad of silica gel. The filtrate was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to provide the 12-ol derivative (139 mg, 71%).

The above compound (175 mg, 0.087 mmol) in a mixed solvent of dichloromethane and MeOH (30 mL, v/v = 1:1) was added CSA (40 mg, 0.17 mmol). After being stirred at room temperature for 20 h, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to provide the 3-ol derivative (118 mg, 72%) as a white solid.

To a solution of the above compound (80 mg, 0.042 mmol) in dry THF (3 mL) was added TBAF in THF (1.26 mL, 1.26 mmol) and AcOH (96 μL, 1.68 mmol) under an atmosphere of Ar at room temperature. The mixture was stirred at room temperature for another 48 h, TLC showed that the reaction reached completion. The mixture was diluted by EtOAc (300 mL), and was then washed with water and brine, respectively. The organic phase was dried over Na_2SO_4 and condensation under reduced pressure. The above crude product was treated with a solution of the freshly prepared 10% KOH in MeOH (0.2 g KOH in 2.5 mL MeOH). The resulting mixture was stirred at room temperature for 12 h, and was then neutralized with $^{+}$H resin. Filtration and concentration led to a residue, which was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 10:1) to provide **4** (30 mg, 88%) as a white solid: $[\alpha]^{25}_{D}$ = 27.8 (*c* 1.4, MeOH); ^{1}H NMR (400 MHz, C_6D_5N) δ 5.22 (t, *J* = 7.0 Hz, 1 H),

5.15 (d, *J* = 7.7 Hz, 1 H), 5.00 (d, *J* = 7.8 Hz, 1 H), 4.54-3.87 (m, 14 H), 3.54-3.45 (m, 1 H), 2.05 (s, 3 H), 1.59 (s, 3 H), 1.56 (s, 6 H), 1.14 (s, 3 H), 1.02 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_5N) δ 131.4, 126.5, 106.5, 98.7, 83.8, 80.6, 80.1, 79.8, 79.2, 78.7, 78.6, 76.0, 75.6, 72.4, 72.2, 70.7, 63.6, 63.4, 61.9, 52.0, 51.9, 50.5, 49.7, 45.6, 41.6, 40.8, 40.2, 40.0, 36.6, 32.2, 31.5, 31.2, 28.4, 27.1, 26.2, 23.7, 22.8, 18.2, 18.0, 17.7, 16.8; HRMS (MALDI) calcd for $C_{42}H_{72}O_{14}Na$ $[M+Na]^+$ 823.4814, found 823.4831.

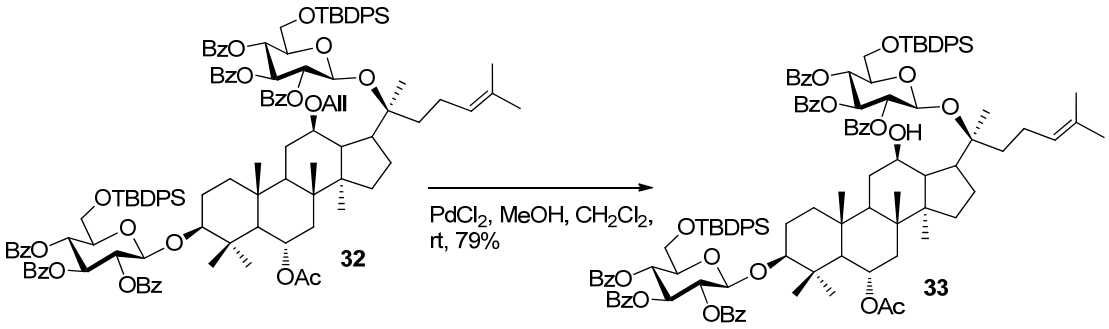
3,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-6-*O*-acetyl-12-*O*-allyl-protopanaxatriol (32)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **16** (80 mg, 0.14 mmol) and **21** (384 mg, 0.43 mmol) with PPh_3AuNTf_2 (32 mg, 0.04 mmol) in dry CH_2Cl_2 (4 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 6:1) led to **32** (162 mg, 57%) as a white solid: $[\alpha]^{25}_D$ = 24.0 (*c* 9.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 4 H), 7.85 (m, 8 H), 7.69-7.19 (m, 38 H), 5.89-5.78 (m, 3 H), 5.56 (m, 3 H), 4.50 (t, *J* = 8.7 Hz, 1 H), 5.16-5.04 (m, 5 H), 4.85 (d, *J* = 7.8 Hz, 1 H), 3.87-3.80 (m, 8 H), 3.12 (m, 2 H), 2.02 (m, 6 H), 1.83 (s, 3 H), 1.59 (s, 6 H), 1.26 (s, 6 H), 1.03 (s, 9 H), 1.01 (s, 9 H), 0.93 (s, 3 H), 0.86 (s, 6 H), 0.76 (s, 3 H), 0.69 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 166.1, 165.2 (2 C), 135.7 (2 C), 135.6, 133.4, 133.2, 133.1 (2 C), 133.0, 130.6, 129.9, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.5, 128.4, 128.3, 127.8, 127.7, 125.5, 116.3, 103.8, 95.6, 89.6, 83.8, 79.1, 75.3, 75.1, 74.0, 73.4, 72.6, 72.5, 70.6, 69.9, 69.5, 63.2, 63.0, 59.1, 52.0, 49.6, 47.7, 46.9, 42.4, 40.6, 39.8, 39.0, 38.7, 31.1, 30.0, 29.8, 27.9, 26.8, 26.2, 25.8, 23.3, 21.9, 21.2, 19.3, 19.2, 18.3, 18.0, 17.0 (2 C), 16.2; HRMS (MALDI) calcd for

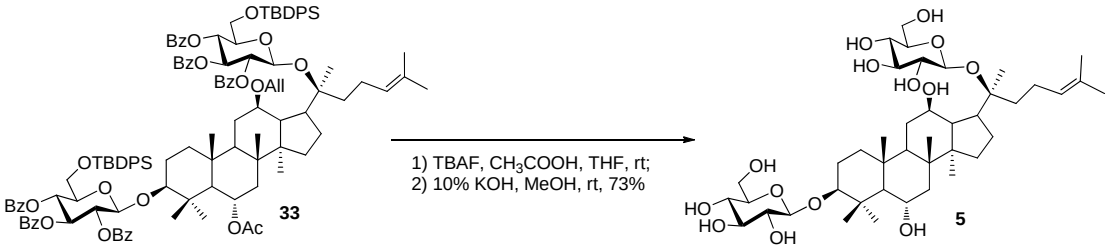
$C_{121}H_{138}O_{21}Si_2Na$ $[M+Na]^+$ 2005.9161, found 2005.9254.

3,20-Di-*O*-(2',3',4'-tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-6-*O*-acetyl-protopanaxatriol (33)



A similar procedure as that used for the deallylation of **28** was applied to remove the allyl group on **32**. Thus, treatment of **32** (150 mg, 0.076 mmol) with $PdCl_2$ (6 mg, 0.034 mmol) in CH_2Cl_2/MeOH (6 mL/6 mL) at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 6:1) led to the desired 12-ol **33** (105 mg, 79%) as a white solid: $[\alpha]^{25}_D$ = 7.9 (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.80 (m, 12 H), 7.73-7.19 (m, 38 H), 5.93-5.85 (m, 2 H), 5.72 (t, *J* = 9.6 Hz, 1 H), 5.62-5.54 (m, 2 H), 5.50 (t, *J* = 9.0 Hz, 1 H), 5.23 (m, 2 H), 5.07 (m, 1 H), 4.90 (d, *J* = 7.8 Hz, 1 H), 4.36 (bs, 1 H), 3.89-3.75 (m, 6 H), 3.21-3.09 (m, 2 H), 2.21 (m, 1 H), 2.02 (m, 5 H), 1.82 (s, 3 H), 1.63 (s, 3 H), 1.57 (s, 3 H), 1.27 (s, 3 H), 1.04 (s, 3 H), 0.92 (s, 3 H), 0.87 (s, 3 H), 0.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 166.2, 166.1, 165.2, 165.1, 164.9, 135.7 (2 C), 135.6, 135.5, 133.3, 133.2, 133.0, 132.9, 132.7, 131.6, 129.9 (2 C), 129.8, 129.4, 129.3, 129.1, 129.0, 128.5, 128.4 (2 C), 128.3, 127.8 (2 C), 124.6, 103.6, 95.2, 89.9, 85.2, 75.5, 75.2, 73.8, 73.5, 72.7, 72.6, 70.8, 69.6, 69.3, 62.9, 58.9, 52.3, 50.9, 49.0, 48.0, 42.3, 40.7, 38.9, 38.6, 35.4, 30.3, 29.8, 26.7, 25.8, 22.8, 21.9, 19.3, 19.2, 17.9, 17.2, 16.8, 16.4; HRMS (MALDI) calcd for $C_{118}H_{134}O_{21}Si_2Na$ $[M+Na]^+$ 1965.8848, found 1965.8875.

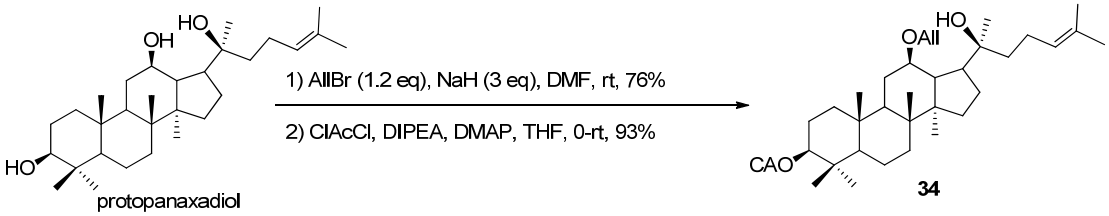
Ginsenoside Ia (5)



To a solution of **33** (98 mg, 0.05 mmol) in dry THF (1 mL) was added TBAF in THF (1.5 mL, 1.5 mmol) and acetic acid (113 μL, 2.0 mmol) at room temperature. After being stirred at the same temperature for 10 h, the mixture was diluted with ethyl acetate (300 mL). The organic phase was washed with water and brine, respectively, and was then dried with Na_2SO_4 and concentrated under reduced pressure.

The above crude product was treated with freshly prepared 10% KOH in MeOH (0.2 g KOH in 2.5 mL MeOH). The mixture was stirred at room temperature for 20 h, and was then neutralized with H^+ resin. Filtration and concentration led to a residue, which was purified by C18 reversed phase column chromatography (MeOH/H_2O, 2:1) to provide **5** (29 mg, 73%) as a white solid: $[\alpha]^{25}_D$ = 19.8 (*c* 0.9, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5) δ 5.59 (s, 1 H), 5.25-5.20 (m, 2 H), 5.04 (d, *J* = 7.8 Hz, 1 H), 4.65 (d, *J* = 9.9 Hz, 1 H), 4.54 (d, *J* = 10.2 Hz, 1 H), 4.46-3.96 (m, 12 H), 3.49 (m, 1 H), 2.60-2.33 (m, 5 H), 2.09 (s, 3 H), 1.64 (s, 3 H), 1.60 (s, 6 H), 1.44 (s, 3 H), 1.07 (s, 3 H), 1.01 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 130.9, 125.9, 107.2, 98.3, 89.4, 83.2, 79.3, 78.8, 78.4, 78.3, 75.9, 75.1, 71.9, 71.6, 70.1, 67.5, 63.1, 62.9, 61.8, 51.6, 51.3, 49.8, 49.1, 47.5, 41.1, 40.5, 39.1, 38.8, 36.1, 31.4, 30.9, 30.7, 26.6, 25.8, 23.2, 22.3, 17.7, 17.6, 17.4 (2 C), 17.0; HRMS (MALDI) calcd for $C_{42}H_{72}O_{14}Na$ $[M+Na]^+$ 823.4814, found 823.4831.

3-*O*-Chloroacetyl-12-*O*-allyl-protopanaxadiol (34)

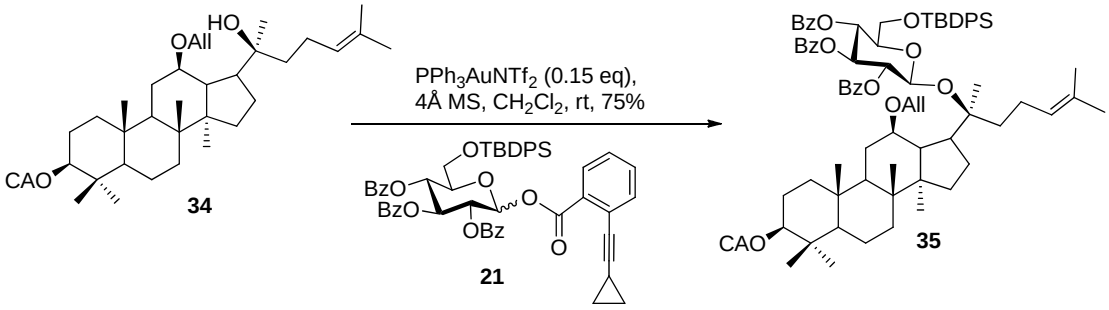


A similar procedure as that used for **7→12** was applied. Thus, treatment of protopanaxadiol (2.38 g, 5.17 mmol) with AllBr (0.9 mL, 10.34 mmol) and 60% NaH

(1.04 g, 25.85 mmol) in DMF (25 mL) at 0 °C to rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 5:1) led to 12-*O*-allyl-protopanaxadiol (2.0 g, 76%) a white foam: $[\alpha]_D^{28}$ = 5.84 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95-5.86 (m, 1 H), 5.30-5.13 (m, 4 H), 4.20 (dd, *J* = 5.6, 12 Hz, 1 H), 3.88 (dd, *J* = 6.0, 12.0 Hz, 1 H), 3.37 (m, 1 H), 3.20 (m, 1 H), 2.21 (m, 1 H), 1.69 (s, 3 H), 1.62 (s, 3 H), 1.10 (s, 3 H), 0.98 (s, 6 H), 0.88 (s, 6 H), 0.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 130.9, 125.6, 118.0, 79.6, 78.6, 72.4, 69.0, 55.8, 53.9, 51.9, 50.0, 46.1, 38.9, 34.7, 31.0, 25.8, 22.3, 17.7, 16.2, 15.7, 15.4; HRMS (MALDI) calcd for $C_{33}H_{56}O_3Na$ $[M+Na]^+$: 523.4112, found 523.4122.

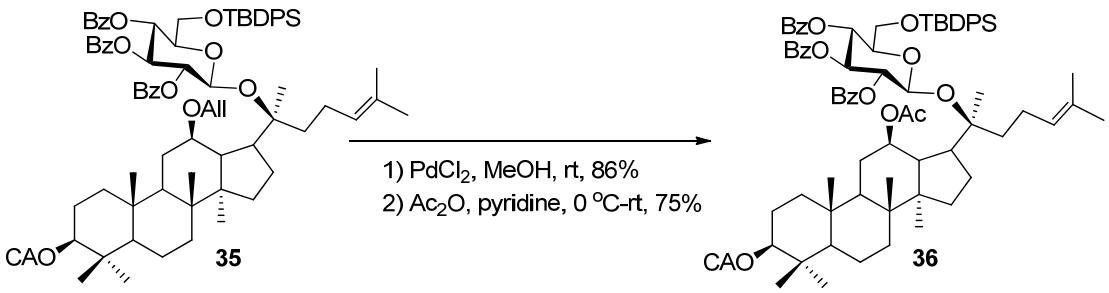
To a solution of the above compound (200 mg, 0.40 mmol), DMAP (8 mg, 0.065 mmol), and DIPEA (108 μL, 0.62 mmol) in dry THF (12 mL) was added $ClCH_2COCl$ (64 μL, 0.618 mmol) slowly at 0 °C under Ar atmosphere. The ice bath was removed and the mixture was stirred at room temperature for 1 h. Ethanol was added at 0 °C to quench the reaction. The mixture was diluted with ethyl acetate, and was then washed with water and brine, respectively. The organic phase was dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to provide **34** (220 mg, 93%) as a white foam: $[\alpha]_D^{28}$ = 26.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94-5.86 (m, 1 H), 5.30-5.15 (m, 4 H), 4.59 (dd, *J* = 5.2, 10.4 Hz, 1 H), 4.21 (dd, *J* = 5.2, 12.0 Hz, 1 H), 4.10 (AB, 2 H), 3.91 (dd, *J* = 6.4, 12.0 Hz, 1 H), 3.41-3.34 (m, 1 H), 1.74 (s, 3 H), 1.62 (s, 3 H), 1.11 (s, 3 H), 0.99 (s, 3 H), 0.92 (s, 3 H), 0.88 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 133.7, 130.8, 125.6, 118.0, 83.0, 79.5, 72.4, 69.1, 55.8, 53.9, 51.8, 49.8, 46.1, 41.2, 39.8, 38.0, 37.1, 35.7, 34.5, 31.0, 27.9, 27.0, 26.6, 26.0, 25.8, 23.4, 22.3, 18.0, 17.7, 16.9, 16.4, 16.2, 15.7; HRMS (MALDI) calcd for $C_{35}H_{57}O_4Na$ $[M+Na]^+$ 599.3835, found 599.3838.

20-*O*-(2',3',4'-Tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-allyl-protopanaxadiol (35)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **34** (100 mg, 0.17 mmol) and **21** (280 mg, 0.31 mmol) with PPh_3AuNTf_2 (16 mg, 0.022 mmol) in dry CH_2Cl_2 (4 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2, 20:1:0.5) led to **35** (167 mg, 75%) as a white foam: $[\alpha]_D^{28}$ = 9.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2 H), 7.94 (d, *J* = 6.8 Hz, 2 H), 7.87 (d, *J* = 7.2 Hz, 2 H), 7.80 (d, *J* = 6.4 Hz, 2 H), 7.67-7.37 (m, 15 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 5.98 (t, *J* = 9.6 Hz, 1 H), 5.89-5.78 (m, 2 H), 5.50-5.41 (m, 2 H), 5.18-5.04 (m, 3 H), 4.56 (dd, *J* = 4.2, 10.8 Hz, 1 H), 4.34-4.20 (m, 3 H), 4.02 (dd, *J* = 5.6, 12.8 Hz, 1 H), 3.93 (d, *J* = 2.8 Hz, 2 H), 3.82 (dd, *J* = 5.6, 12.4 Hz, 1 H), 3.27-3.20 (m, 1 H), 1.62 (s, 3 H), 1.61 (s, 3 H), 1.40 (s, 3 H), 1.06 (s, 9 H), 0.91 (s, 3 H), 0.90 (s, 3 H), 0.89 (s, 3 H), 0.88 (s, 3 H), 0.84 (s, 3 H); ^{13}C NMR (75 MHz, C_2D_6CO) δ 167.7, 166.3, 165.7, 165.6, 137.1, 136.4, 136.2, 134.2, 134.1, 133.9, 133.6, 130.8 (2 C), 130.6, 130.5, 130.4, 130.3, 129.4, 129.3, 128.6, 126.4, 115.8, 95.7, 84.5, 83.2, 80.0, 75.1, 74.9, 73.5, 70.3, 70.0, 63.6, 56.5, 53.0, 50.8, 47.8, 41.9, 40.5, 40.4, 39.0, 38.7, 37.8, 35.3, 32.4, 28.2, 27.0, 26.0, 24.3, 24.2, 22.3, 19.7, 18.9, 18.8, 18.0, 16.8, 16.6, 16.2; HRMS (MALDI) calcd for $C_{78}H_{97}O_{12}SiClNa$ $[M+Na]^+$ 1311.6387, found 1311.6330.

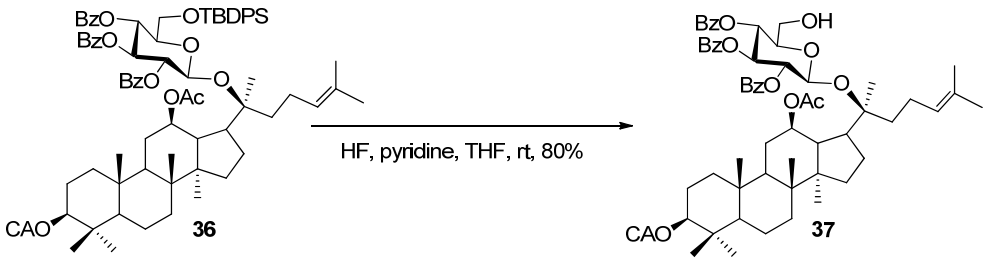
20-*O*-(2',3',4'-Tri-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-acetyl-protopanaxadiol (36)



To a solution of **35** (80 mg, 0.062 mmol) in MeOH/CH_2Cl_2 (7 mL/7 mL) was added $PdCl_2$ (6 mg, 0.034 mmol). The mixture was stirred at room temperature overnight. Filtration followed by evaporation led to a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to provide the corresponding 12-ol (66 mg, 86%) as a white foam.

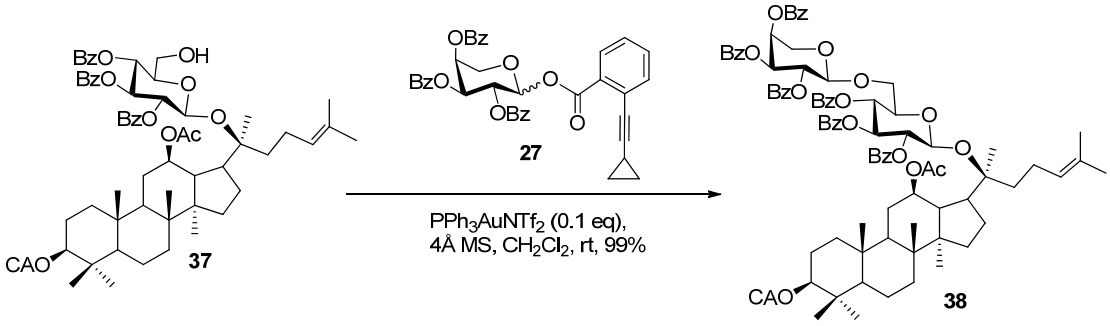
To a solution of the above product (1073 mg, 0.858 mmol) and DMAP (21 mg, 0.172 mmol) in dry pyridine (6 mL) was added Ac_2O (6 mL) slowly at 0 °C under Ar atmosphere. The ice bath was removed and the mixture was stirred at room temperature for 3 h. Concentrated and purification by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2, 8:1:0.5) afforded **36** (832 mg, 75%) as a white foam: $[\alpha]_D^{28}$ = 9.8 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2 H), 7.89-7.86 (m, 4 H), 7.71 (d, *J* = 6.8 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.53 (m, 2 H), 7.40-7.20 (m, 11 H), 5.91 (t, *J* = 10.0 Hz, 1 H), 5.74 (t, *J* = 5.6 Hz, 1 H), 5.51 (dd, *J* = 8.0, 9.6 Hz, 1 H), 5.09 (d, *J* = 7.6 Hz, 1 H), 5.00 (m, 1 H), 4.60 (dd, *J* = 6.0, 10.4 Hz, 1 H), 4.10 (AB, 2 H), 3.90-3.84 (m, 3 H), 1.70 (s, 3 H), 1.58 (s, 3 H), 1.23 (s, 3 H), 1.05 (s, 9 H), 0.98 (s, 3 H), 0.89 (s, 3 H), 0.88 (s, 3 H), 0.87 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 166.9, 165.9, 164.9, 164.6, 135.5, 135.3, 133.0 (2 C), 132.9, 132.7, 131.1, 129.8, 129.7, 129.6, 129.5, 129.4, 129.2, 129.0, 128.2, 128.1 (2 C)127.5, 124.4, 94.8, 83.0, 82.8, 74.8, 74.7, 73.6, 72.4, 69.2, 62.6, 55.7, 53.0, 49.9, 46.8, 44.6, 41.1, 39.7, 39.4, 38.2, 37.9, 36.8, 34.3, 31.9, 28.6, 27.8, 26.5, 26.3, 25.6, 23.6, 23.5, 23.3, 21.4, 19.0, 18.0, 17.6, 16.3, 16.1, 15.3; HRMS (MALDI) calcd for $C_{78}H_{99}O_{12}SiClNa$ $[M+Na]^+$ 1313.6496, found 1313.6487.

20-*O*-(2',3',4'-Tri-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-chloroacetyl-12-*O*-acetyl-protopanaxadiol (37)



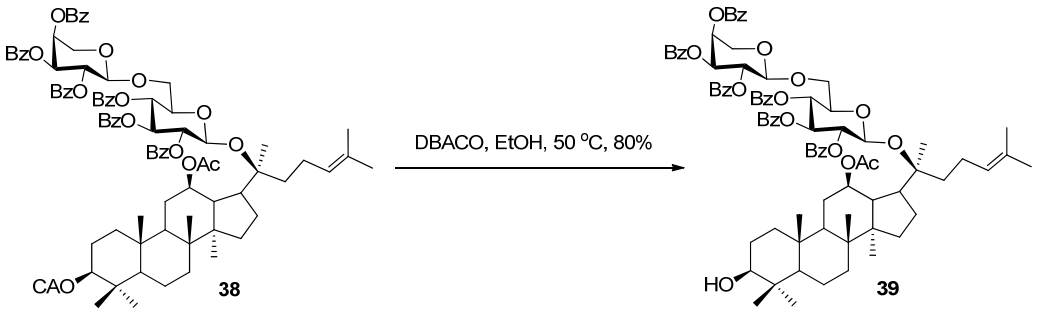
To a solution of **36** (260 mg, 0.2 mmol) in a dry mixed solvent of pyridine/THF (20 mL, v/v = 1 : 1) was added HF/pyridine (2 mL, 77 mmol) at 0 ^{o}C. The mixture was warmed to rt, and the stirring was continued for 6 h. A saturated $NaHCO_3$ solution was added to quench the reaction. The resultant solution was diluted with EtOAc. The organic layer, after being washed with water, saturated aqueous $CuSO_4$, and brine, respectively, was dried with Na_2SO_4 and concentration. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 5:1) to afford **37** (169 mg, 80%) as a white foam: $[\alpha]_D^{28}$ = 10.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2 H), 7.94 (m, 2 H), 7.84 (m, 2 H), 7.54 (m, 2 H), 7.43-7.35 (m, 5 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 5.94 (t, *J* = 9.6 Hz, 1 H), 5.50-5.41 (m, 2 H), 5.04 (m, 2 H), 4.72 (td, *J* = 4.8, 10.8 Hz, 1 H), 4.56 (dd, *J* = 5.6, 10.8 Hz, 1 H), 4.08 (AB, 2 H), 3.80-3.69 (m, 3 H), 2.55 (m, 1 H), 1.78 (s, 3 H), 1.67 (s, 3 H), 1.60 (s, 3 H), 1.18 (s, 3 H), 0.88 (s, 3 H), 0.86 (s, 6 H), 0.85 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 166.9, 165.8 (2 C), 164.6, 133.5, 133.1, 133.0, 132.1, 129.8, 129.7, 129.6, 129.4, 128.8, 128.6, 128.4, 128.2 (2 C), 124.1, 95.0, 83.2, 83.0, 74.9, 74.5, 73.1, 72.0, 69.8, 61.7, 55.6, 52.9, 49.7, 46.8, 44.9, 41.2, 39.9, 39.3, 38.2, 37.9, 36.8, 34.2, 31.6, 28.6, 27.8, 26.1, 25.6, 23.3, 23.1, 22.5, 21.6, 18.0, 17.8 (2 C), 16.3, 16.0, 15.3; HRMS (MALDI) calcd for $C_{61}H_{77}O_{13}ClNa$ $[M+Na]^+$ 1075.4964, found 1075.1945.

20-*O*-[2”,3”,4”-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2’,3’,4’-tri-*O*-benzoyl-β-D-glucopyranosyl]-3-*O*-chloroacetyl-12-*O*-acetyl-protopanaxadiol (38)



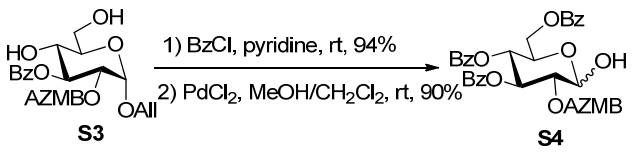
A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **37** (582 mg, 0.55 mmol) and **27** (700 mg, 1.11 mmol) with PPh_3AuNTf_2 (41 mg, 0.055 mmol) in dry CH_2Cl_2 (8 mL) in the presence of 4Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 5:1) led to **38** (816 mg, 99%) as a white foam: $[\alpha]_D^{28}$ = 57.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.02 (m, 4 H), 7.99-7.96 (m, 4 H), 7.89 (m, 2 H), 7.78 (m, 2 H), 7.58-7.46 (m, 8 H), 7.44-7.23 (m, 10 H), 5.87 (t, *J* = 9.6 Hz, 1 H), 5.65-5.60 (m, 3 H), 5.52 (t, *J* = 10.0 Hz, 1 H), 5.41 (dd, *J* = 8.0, 9.6 Hz, 1 H), 5.02 (m, 2 H), 4.85 (d, *J* = 4.4 Hz, 1 H), 4.68-4.61 (m, 1 H), 4.56 (dd, *J* = 5.6, 10.8 Hz, 1 H), 4.31 (dd, *J* = 6.0, 12.0 Hz, 1 H), 4.06-3.98 (m, 4 H), 3.84-3.78 (m, 2 H), 1.73 (s, 3 H), 1.63 (s, 3 H), 1.52 (s, 3 H), 1.09 (s, 3 H), 0.87 (s, 3 H), 0.86 (s, 6 H), 0.79 (s, 3 H), 0.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 167.1, 165.9, 165.6 (2 C), 165.1, 164.9, 164.8, 133.4, 133.1, 131.4, 130.0, 129.9 (2 C), 129.8, 129.6, 129.3, 129.0, 128.6, 128.5, 124.6, 99.4, 95.3, 83.3, 83.1, 74.9, 73.6, 69.8, 55.8, 52.9, 49.9, 47.3, 45.0, 41.3, 39.6, 39.4, 38.4, 38.1, 36.9, 34.3, 31.8, 28.7, 28.0, 26.4, 25.7, 23.4, 23.3, 22.7, 21.6, 18.1, 17.8, 16.4, 16.2, 15.4; HRMS (MALDI) calcd for $C_{87}H_{97}O_{20}ClNa$ $[M+Na]^+$ 1519.6150, found 1519.6154.

20-*O*-[2",3",4"-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (39)



A solution of **38** (100 mg, 0.0667 mmol) and DBACO (112 mg, 1.0 mmol) in ethanol (30 mL) was stirred at 50 °C for 2 d. Concentration and purification by silica gel column chromatography (petroleum ether/EtOAc 2:1) afforded **39** (76 mg, 80%) as a white foam: $[\alpha]_D^{28}$ = 40.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2 H), 8.04 (d, *J* = 7.6 Hz, 2 H), 7.98 (d, *J* = 8.0 Hz, 4 H), 7.89 (d, *J* = 7.6 Hz, 2 H), 7.77 (d, *J* = 7.2 Hz, 2 H), 7.60-7.45 (m, 7 H), 7.43-7.24 (m, 11 H), 5.86 (t, *J* = 9.6 Hz, 1 H), 5.64-5.59 (m, 3 H), 5.51 (t, *J* = 9.6 Hz, 1 H), 5.41 (dd, *J* = 8.4, 9.2 Hz, 1 H), 5.01-4.96 (m, 2 H), 4.84 (d, *J* = 4.4 Hz, 1 H), 4.68-4.60 (m, 1 H), 4.30 (dd, *J* = 5.6, 11.6 Hz, 1 H), 4.08 (d, *J* = 10.8 Hz, 1 H), 4.00 (m, 1 H), 3.83-3.77 (m, 2 H), 3.18 (m, 1 H), 1.74 (s, 3 H), 1.62 (s, 3 H), 1.52 (s, 3 H), 1.08 (s, 3 H), 0.95 (s, 3 H), 0.86 (s, 3 H), 0.75 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 165.9, 165.6, 165.5, 165.1, 164.9, 164.7, 133.4, 133.3, 133.2, 133.1, 133.0, 131.3, 129.9 (2 C), 129.8 (2 C), 129.6, 129.4, 129.3 (2 C), 129.1, 129.0, 128.6, 128.4, 128.3, 128.2 (2 C), 124.6, 99.4, 95.3, 83.3, 78.8, 75.1, 73.6, 73.2, 72.5, 69.8, 69.6, 69.5, 67.5, 67.3, 60.3, 55.8, 53.0, 50.0, 47.2, 45.0, 39.6, 39.4, 38.9, 38.7, 37.0, 34.4, 31.8, 28.7, 28.0, 27.2, 26.3, 25.6, 23.2, 22.5, 21.6, 18.2, 17.9, 17.7, 16.1, 15.4, 15.3; HRMS (MALDI) calcd for $C_{85}H_{96}O_{19}Na$ $[M+Na]^+$ 1443.6471, found 1443.6438.

2-*O*-(2-Azidomethyl)benzoyl-3,4,6-tri-*O*-benzoyl-D-glucopyranose (S4)

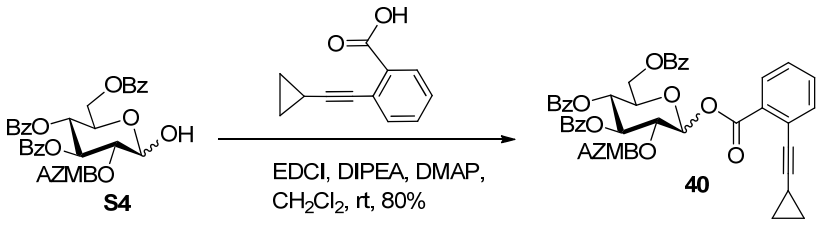


To a solution of **S3**[S9] (4.1 g, 10.8 mmol) in dry pyridine (30 mL) was added BzCl (7 mL, 60.4 mmol) dropwise at 0 °C. The reaction mixture was warmed to rt and was stirred overnight before EtOAc was added to dilute the reaction. The resultant mixture

was washed with 1 N HCl, saturated $NaHCO_3$, and brine, successively, and was then dried over Na_2SO_4. Concentration to yield a residue which was further purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to afford the benzoylated intermediate (7.0 g, 94%) as a white foam.

A similar procedure as that used for the deallylation of **28** was applied to remove the anomeric allyl group. Thus, treatment of above product (6.7 g, 9.7 mmol) with $PdCl_2$ (512 mg, 2.89 mmol) in CH_2Cl_2/MeOH (60 mL/60mL) at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 4:1) led to **S4** (5.18 g, 90%) as a white foam: $[\alpha]_D^{28}$ = 59.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.98 (m, 3.6 H), 7.94-7.87 (m, 5.0 H), 7.53-7.27 (m, 14.8 H), 6.29 (t, *J* = 9.6 Hz, 1 H), 5.96 (t, *J* = 9.6 Hz, 0.2 H), 5.79-5.72 (m, 2.2 H), 5.50 (dd, *J* = 8.0, 9.6 Hz, 0.2 H), 5.41 (dd, *J* = 3.6, 10.4 Hz, 1 H), 5.14 (d, *J* = 6.4 Hz, 0.2 H), 4.74-4.60 (m, 5.4 H), 4.50 (dd, *J* = 4.8, 12.0 Hz, 0.2 H), 4.43 (dd, *J* = 4.4, 12.4 Hz, 1 H), 4.19-4.08 (m, 0.2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.5, 166.1, 166.0, 165.8, 165.4 (2 C), 137.6 (2 C), 133.6, 133.5, 133.4, 133.3 (2 C), 131.8, 131.2, 129.9, 129.8 (2 C), 129.7, 129.5, 129.4, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 127.7, 127.5, 95.8, 90.4, 73.9, 72.8, 72.4 (2 C), 70.4, 69.6, 69.5, 67.7, 63.1, 62.9, 53.2, 52.8; HRMS (MALDI) calcd for $C_{35}H_{29}N_3O_{10}Na$ $[M+Na]^+$ 674.1745, found 674.1754.

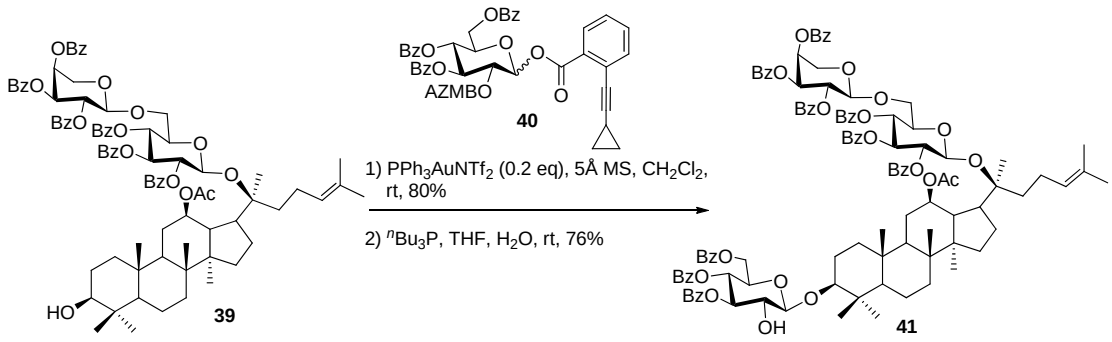
2-*O*-(2-Azidomethyl)benzoyl-3,4,6-tri-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (40)



A similar procedure as that used for the synthesis of **20** was applied. Thus, treatment of **S4** (2.0 g, 3.07 mmol), *ortho*-cyclopropylethynylbenzoic acid (1.03 g, 5.53 mmol), DIPEA (1.4 mL, 7.89 mmol), and DMAP (674 mg, 5.52 mmol) in dry dichloromethane (10 mL) with EDCI (1.1 g, 5.74 mmol) followed by silica gel column chromatography (petroleum ether/EtOAc, 8:1 to 4:1) provided **40** (2.3 g, 80%)

as a white foam. The pure β anomer was obtained for characterization: $[\alpha]_D^{28}$ = 36.2 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2 H), 8.00 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.93-7.90 (m, 4 H), 7.85 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.53-7.25 (m, 15 H), 6.38 (d, *J* = 8.0 Hz, 1 H), 6.06 (t, *J* = 9.6 Hz, 1 H), 5.88-5.82 (m, 2 H), 4.70 (dd, *J* = 2.4, 12.4 Hz, 1 H), 4.55-4.49 (m, 3 H), 4.43-4.39 (m, 1 H), 1.53-1.47 (m, 1 H), 0.88-0.86 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.0, 164.4 (2 C), 162.6, 136.8, 133.7, 132.8, 132.4, 131.9, 130.2 (2 C), 129.1, 127.9, 127.7, 127.4, 126.8, 126.3, 125.1, 100.0, 91.7, 73.5, 72.5, 72.3, 70.4, 68.3, 62.0, 52.0, 8.3; HRMS (MALDI) calcd for $C_{47}H_{37}N_3O_{11}Na$ $[M+Na]^+$ 842.2311, found 842.2320.

3-*O*-(3'",4'",6'"-Tri-*O*-benzoyl-β-D-glucopyranosyl)-20-*O*-[2",3",4"-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (41)

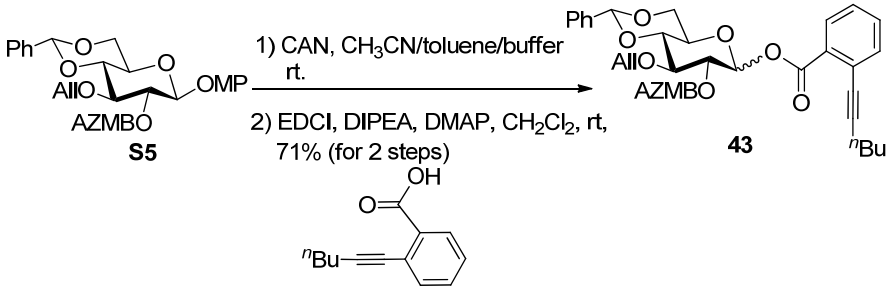


A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **39** (20 mg, 0.014 mmol) and **40** (23 mg, 0.028 mmol) with PPh_3AuNTf_2 (3 mg, 0.004 mmol) in dry CH_2Cl_2 (2 mL) in the presence of 5Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 3:1) led to the desired trisaccharide (23 mg, 80%) as a white foam.

A similar procedure as that used for **44→45** was applied. Thus, treatment of the above trisaccharide (200 mg, 0.097 mmol) with Bu_3P (85 μL, 0.3 mmol) in THF/H_2O (2 mL/0.02 mL) at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 3:1) led to **41** (145 mg, 76%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-7.87 (m, 16 H), 7.77 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.61-7.46 (m, 10

H), 7.45-7.24 (m, 17 H), 5.86 (t, *J* = 9.6 Hz, 1 H), 5.66-5.60 (m, 4 H), 5.51 (AB, 2 H), 5.42 (dd, *J* = 8.0, 9.6 Hz, 1 H), 5.02-4.96 (m, 2 H), 4.84 (d, *J* = 4.4 Hz, 1 H), 4.70-4.63 (m, 1 H), 4.59 (d, *J* = 7.6 Hz, 1 H), 4.54-4.51 (m, 2 H), 4.30 (dd, *J* = 6.0, 12.0 Hz, 1 H), 4.09-4.05 (m, 2 H), 4.02-3.98 (m, 1 H), 3.88-3.78 (m, 3 H), 3.12 (dd, *J* = 4.0, 11.6 Hz, 1 H), 2.55 (brs, 1 H), 1.78 (s, 3 H), 1.64 (s, 3 H), 1.54 (s, 3 H), 1.10 (s, 3 H), 0.97 (s, 3 H), 0.84 (s, 3 H), 0.79 (s, 3 H), 0.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.4, 165.9, 165.6, 165.5, 165.1, 164.9, 164.7, 133.4, 133.3, 133.1, 131.3, 130.0, 129.9 (2 C), 129.8, 129.7, 129.4, 129.3, 129.2, 129.1, 128.9, 128.6 (2 C), 128.5, 128.4, 128.3, 128.2, 124.7, 105.1, 95.4, 90.4, 83.4, 75.1, 73.7, 73.3, 72.6, 72.1, 70.0, 69.9, 69.8, 67.6, 63.5, 56.1, 53.0, 50.0, 45.1, 39.7, 39.4, 39.2, 36.6, 34.4, 31.7, 28.0, 26.3, 25.6, 23.3, 22.5, 21.6, 18.1, 17.9, 17.8, 16.3, 16.0, 15.4; HRMS (MALDI) calcd for $C_{112}H_{118}O_{27}Na$ $[M+Na]^+$ 1917.7753, found: 1917.7750.

2-*O*-(2-Azidomethyl)benzoyl-3-*O*-allyl-4,6-*O*-benzylidene-D-glucopyranosyl *ortho*-hexynylbenzoate (43)

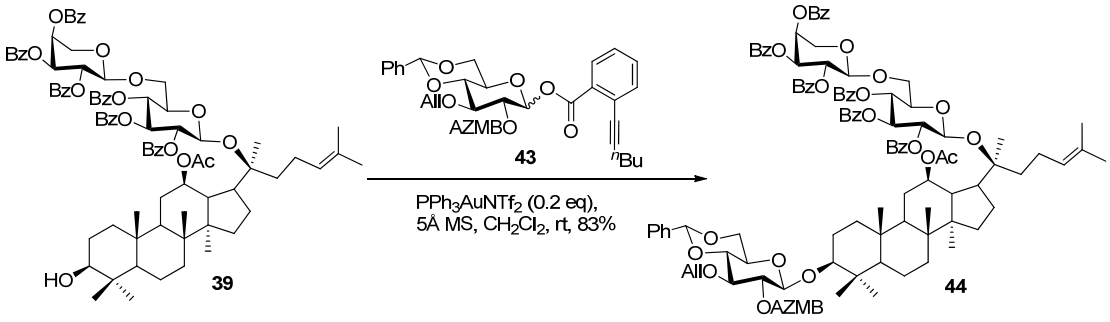


To a solution of **S5**[S8] (1.07 g, 1.87 mmol) in CH_3CN/toluene/buffer H_2O (37 mL, v/v/v, 25:6:6) was added CAN (3.07 g, 5.60 mmol) at room temperature. After being stirred at the same temperature for 15 min, the mixture was diluted with CH_2Cl_2. The organic phase was washed with saturated $NaHCO_3$ and brine, respectively, and dried with Na_2SO_4. Concentration under reduced pressure yielded the crude lactol product, which was put forward to synthesize donor **43** without further purification.

A similar procedure as that used for the synthesis of **20** was applied. Thus, treatment of the above lactol, *ortho*-hexynylbenzoic acid (453 mg, 2.24 mmol), and DMAP (23 mg, 0.19 mmol) in dry dichloromethane (12 mL) with EDCI (644 mg, 3.36 mmol) followed by silica gel column chromatography (petroleum ether/EtOAc,

40:3) led to **43** (860 mg, 71%) as a white foam. The pure α-isomer was obtained for characterization: $[\alpha]_D^{24}$ = 106.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 1 H), 7.87 (d, *J* = 7.6 Hz, 1 H), 7.56-7.27 (m, 12 H), 6.74 (d, *J* = 3.6 Hz, 1 H), 5.89-5.79 (m, 1 H), 5.65 (s, 1 H), 5.41 (dd, *J* = 4.4, 9.6 Hz, 1 H), 5.25 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.10 (d, *J* = 10.4 Hz, 1 H), 4.81 (AB, 2 H), 4.46-4.36 (m, 2 H), 4.29-4.18 (m, 3 H), 3.90-3.80 (m, 2 H), 2.50-2.40 (m, 2 H), 1.57-1.49 (m, 2 H), 1.38-1.32 (m, 2 H), 0.87 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.4, 137.6, 137.0, 135.2, 134.6, 132.9, 132.3, 131.0, 130.9, 130.0, 129.3, 129.0, 128.2, 127.9, 127.3, 125.9, 125.1, 116.8, 101.3, 97.1, 90.8, 81.7, 79.9, 75.9, 73.6, 71.9, 68.7, 65.3, 52.8, 30.7, 29.7, 22.0, 19.7, 13.6; HRMS (MALDI) calcd for $C_{37}H_{37}N_3O_8Na$ $[M+Na]^+$ 674.2484, found 674.2473.

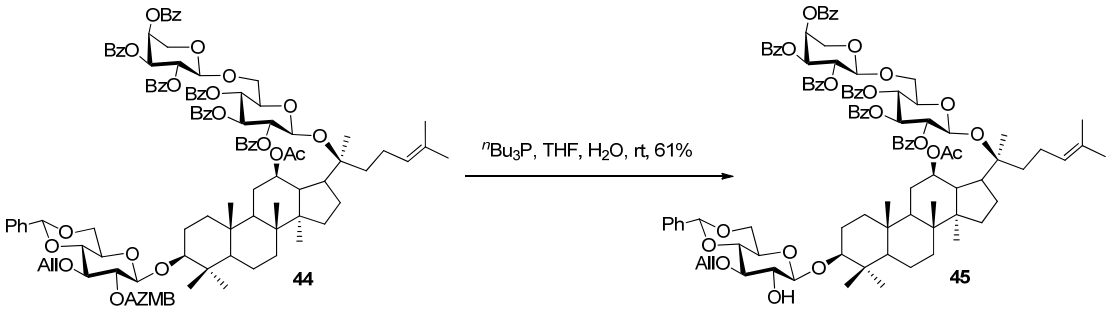
3-*O*-[2'''-*O*-(2-Azidomethyl)benzoyl-3'''-*O*-allyl-4''',6'''-*O*-benzylidene-β-D-glucopyranosyl]-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (44)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **39** (106 mg, 0.075 mmol) and **43** (73 mg, 0.11 mmol) with PPh_3AuNTf_2 (11 mg, 0.015 mmol) in dry CH_2Cl_2 (4 mL) in the presence of 5Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 5:1) led to **44** (116 mg, 83%) as a white foam: $[\alpha]_D^{23}$ = 41.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.03 (m, 5 H), 7.98 (d, *J* = 6.8 Hz, 4 H), 7.89 (d, *J* = 7.2 Hz, 2 H), 7.77 (d, *J* = 7.2 Hz, 2 H), 7.55-7.22 (m, 26 H), 5.87 (t, *J* = 9.2 Hz, 1 H), 5.78-5.71 (m, 1 H), 5.66-5.58 (m, 4 H), 5.52 (t, *J* = 9.6 Hz, 1 H), 5.42 (dd, *J* = 8.0, 9.2 Hz, 1 H), 5.32 (t, *J* = 8.0 Hz, 1 H), 5.19 (d, *J* = 16.8 Hz, 1 H), 5.04-4.97 (m, 3 H), 4.91-4.78 (m, 3 H),

4.69-4.63 (m, 2 H), 4.38-4.28 (m, 3 H), 4.15-4.07 (m, 2 H), 4.00 (m, 1 H), 3.87-3.79 (m, 5 H), 3.51 (m, 1 H), 3.06 (m, 1 H), 1.74 (s, 3 H), 1.63 (s, 3 H), 1.52 (s, 3 H), 1.08 (s, 3 H), 0.82 (s, 3 H), 0.73 (s, 6 H), 0.68 (s, 3 H), 0.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 135.9, 165.6 (2 C), 165.1, 164.9 (2 C), 164.8, 138.0, 137.3, 134.7, 133.5, 133.4, 133.1, 132.9, 131.4, 130.9, 129.8, 129.4, 129.0, 128.5, 128.3, 127.9, 126.0, 124.7, 117.1, 103.7, 101.2, 99.4, 95.4, 90.0, 83.4, 81.5, 78.7, 75.1, 73.8, 73.6, 73.2, 72.5, 69.8, 69.7, 68.8, 67.6, 66.2, 56.1, 52.9, 50.0, 47.3, 45.1, 39.4, 39.0, 38.8, 36.7, 34.4, 31.8, 29.7, 28.8, 27.7, 26.0, 25.7, 23.3, 22.5, 21.6, 18.0, 17.8, 16.1, 15.4; HRMS (MALDI) calcd for $C_{109}H_{119}N_3O_{25}Na$ $[M+Na]^+$ 1892.8046, found 1892.8025.

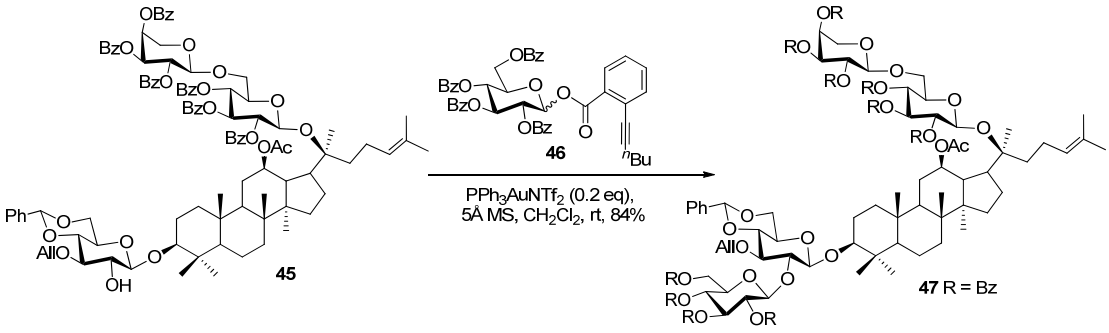
3-*O*-(3'''-*O*-Allyl-4''',6'''-*O*-benzylidene-β-D-glucopyranosyl)-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (45)



To a solution of **44** (202 mg, 0.108 mmol) in THF/H_2O (2 mL/0.2 mL) was added ^{n}Bu_3P (10% in hexane, 280 μL, 0.114 mmol). The mixture was stirred at room temperature for 4 h, and was then diluted with CH_2Cl_2. The solution was washed with saturated aqueous $NaHCO_3$, water, and brine, respectively, and was then dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 2:1) to provide **45** (113 mg, 61%) as a white foam: $[\alpha]_D^{24}$ = 35.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2 H), 8.04 (d, *J* = 7.2 Hz, 2 H), 7.98 (d, *J* = 7.6 Hz, 4 H), 7.89 (d, *J* = 7.6 Hz, 2 H), 7.77 (d, *J* = 7.2 Hz, 2 H), 7.59-7.23 (m, 23 H), 5.98-5.90 (m, 1 H), 5.86 (t, *J* = 9.6 Hz, 1 H), 5.65-5.60 (m, 3 H), 5.53-5.47 (m, 2 H), 5.42 (t, *J* = 8.8 Hz, 1 H), 5.32 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.18 (d, *J* = 10.4 Hz, 1 H), 5.01-4.96 (m, 2 H), 4.84 (d, *J* = 4.4

Hz, 1 H), 4.66-4.60 (m, 1 H), 4.46-4.40 (m, 2 H), 4.31-4.25 (m, 3 H), 4.12-4.06 (m, 1 H), 4.00 (m, 1 H), 3.83-3.75 (m, 3 H), 3.64-3.56 (m, 3 H), 3.45-3.39 (m, 1 H), 3.16 (dd, *J* = 4.0, 11.2 Hz, 1 H), 2.53 (brs, 1 H), 1.73 (s, 3 H), 1.62 (s, 3 H), 1.52 (s, 3 H), 1.08 (s, 3 H), 1.01 (s, 3 H), 0.86 (s, 3 H), 0.82 (s, 3 H), 0.77 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 165.9, 165.6 (2 C), 165.1, 164.9, 164.8, 137.4, 135.0, 133.5, 133.4, 133.1, 131.4, 129.9, 129.7, 129.4, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 126.0, 124.7, 117.2, 105.5, 101.2, 99.4, 95.4, 89.9, 83.4, 81.3, 80.2, 75.1, 74.8, 73.6, 73.2, 72.5, 69.8, 69.7, 68.8, 67.6, 67.3, 66.4, 56.2, 53.0, 50.1, 47.3, 45.1, 39.7, 39.4, 39.2, 38.8, 36.7, 34.5, 31.8, 28.8, 28.0, 26.4, 26.0, 25.7, 23.3, 22.5, 21.6, 18.0, 17.8, 16.4, 16.1, 15.4; HRMS (MALDI) calcd for $C_{101}H_{114}O_{24}Na$ $[M+Na]^+$ 1733.7637, found 1733.7592.

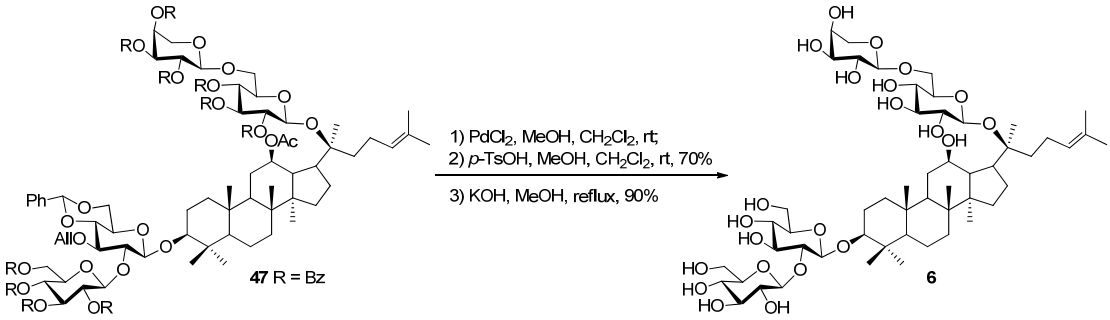
3-*O*-[2'''',3'''',4'''',6''''-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3'''-*O*-allyl-4'''',6'''-*O*-benzylidene-β-D-glucopyranosyl]-20-*O*-[2'',3'',4''-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→6)-2',3',4'-tri-*O*-benzoyl-β-D-glucopyranosyl]-12-*O*-acetyl-protopanaxadiol (47)



A similar procedure as that used for the synthesis of **22** was applied. Thus, treatment of **45** (87 mg, 0.051 mmol) and **46** (125 mg, 0.16 mmol) with PPh_3AuNTf_2 (12 mg, 0.016 mmol) in dry CH_2Cl_2 (2.5 mL) in the presence of 5Å MS at rt followed by purification by silica gel column chromatography (petroleum ether/EtOAc, 4:1 to 3:1) led to **47** (98 mg, 84%) as a white foam: $[\alpha]_D^{24}$ = 19.6 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.95 (m, 12 H), 7.90 (d, *J* = 7.2 Hz, 4 H), 7.83 (d, *J* = 7.6 Hz, 2 H), 7.78 (d, *J* = 7.2 Hz, 2 H), 7.58-7.23 (m, 35 H), 5.99-5.83 (m, 3 H), 5.75-5.64 (m, 4 H), 5.24 (d, *J* = 17.2 Hz, 1 H), 5.14 (d, *J* = 10.4 Hz, 1 H), 5.02-4.98 (m, 2 H), 4.85 (d,

J = 3.6 Hz, 1 H), 4.64 (d, *J* = 9.2 Hz, 2 H), 4.48 (m, 2 H), 4.30-4.25 (m, 3 H), 4.16-4.08 (m, 2 H), 4.00 (m, 1 H), 3.89-3.82 (m, 3 H), 3.75 (t, *J* = 10.0 Hz, 1 H), 3.60-3.49 (m, 2 H), 3.32 (m, 1 H), 3.07 (m, 1 H), 1.74 (s, 3 H), 1.63 (s, 3 H), 1.53 (s, 3 H), 1.14 (s, 3 H), 1.09 (s, 3 H), 0.83 (s, 3 H), 0.76 (s, 3 H), 0.73 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 166.2, 165.9, 165.6, 165.2, 165.1 (2 C), 164.9, 164.8, 137.3, 135.0, 133.5, 133.4, 133.3, 133.1, 133.0, 131.4, 129.9 (2 C), 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 126.0, 124.7, 116.9, 104.2, 101.1, 100.9, 99.4, 95.4, 90.6, 83.4, 81.9, 81.6, 78.0, 75.2, 73.7, 73.6, 73.3, 72.5, 72.3, 72.0, 69.8, 69.7, 69.5, 68.8, 67.6, 67.3, 65.6, 63.3, 60.4, 56.2, 53.0, 50.0, 47.4, 45.1, 39.7, 39.4, 38.8, 36.6, 34.5, 31.8, 29.7, 28.8, 27.6, 26.4, 26.1, 25.7, 23.3, 22.4, 21.6, 18.0, 17.8, 16.0 (2 C), 15.4; HRMS (MALDI) calcd for $C_{135}H_{140}O_{33}Na$ $[M+Na]^+$ 2311.9225, found 2311.9169.

Ginsenoside Rb2 (6)



To a solution of **47** (68 mg, 0.0297 mmol) in CH_2Cl_2/MeOH (15 mL/15 mL) was added $PdCl_2$ (2.6 mg, 0.0148 mmol). The mixture was stirred at room temperature for 7 h, and then Et_3N was added (0.1 mL). Filtration through a pad of Celite and concentrated of the filtrate led to the deallylated product, which was used for the next step without further purification.

To a solution of the above crude product in CH_2Cl_2/MeOH (3.6 mL/2.4 mL) was added *p*-TsOH (12 mg, 0.063 mmol). The mixture was stirred at room temperature overnight and was diluted with EtOAc. The mixture was washed with saturated $NaHCO_3$, water, and brine, successively. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified

by silica gel column chromatography (petroleum ether/EtOAc, 1:1 to petroleum ether/EtOAc/MeOH, 1:1:0.1) to afford the debenzylidenated product (45 mg, 70% for two steps) as a white foam.

To a solution of the above product (40 mg, 0.018 mmol) in MeOH (2.5 mL) was added KOH (130 mg, 2.14 mmol). The mixture was refluxed overnight, and was then neutralized with $^{+}$H resin. Filtration and concentration led to a residue, which was purified by RP-18 silica gel column chromatography (H_2O/MeOH, 1:4) to afford **6** (18 mg, 90%) as a white solid: $[\alpha]_D^{22}$ = 13.3 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, C_5D_5N) δ 5.32 (d, *J* = 7.6 Hz, 1 H), 5.24 (m, 1 H), 4.87 (d, *J* = 6.0 Hz, 1 H), 4.80 (d, *J* = 7.2 Hz, 1 H), 4.55 (d, *J* = 10.4 Hz, 1 H), 1.56 (s, 3 H), 1.53 (s, 6 H), 1.13 (s, 3 H), 0.98 (s, 3 H), 0.87 (s, 3 H), 0.81 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (100 MHz, C_5D_5N) δ 131.2, 126.0, 106.2, 105.2, 104.7, 98.2, 89.0, 83.5, 79.3, 78.4, 78.3, 78.2, 78.0, 77.2, 76.8, 75.0, 74.2, 72.2, 71.9, 71.7 (2 C), 70.2, 69.3, 68.6, 65.7, 62.9, 62.7, 56.4, 51.7, 51.5, 50.3, 49.5, 40.1, 39.7, 39.2, 37.0, 36.2, 35.2, 30.8 (2 C), 28.2, 26.8, 26.7, 25.9, 23.3, 22.4, 18.5, 17.9, 17.4, 16.7, 16.3, 16.1; HRMS (MALDI) calcd for $C_{53}H_{90}O_{22}Na$ $[M+Na]^+$ 1101.5808, found 1101.5816.

Comparison of the ^{13}C NMR data of the synthetic ginsenosides 1-6 with those reported for the natural products.

C	Synthetic ginsenoside F3 (**1**)	Reported data[S10]
1	39.4	39.4
2	28.2	28.2
3	78.6	78.5
4	40.4	40.4
5	61.8	61.8
6	67.8	67.8
7	47.6	47.5
8	41.3	41.2
9	50.0	49.9
10	39.4	39.4
11	30.8	30.7
12	70.3	70.2
13	49.2	49.1
14	51.4	51.4

15	30.9	30.8
16	26.7	26.7
17	51.7	51.7
18	17.5	17.5
19	17.5	17.5
20	83.5	83.5
21	22.4	22.3
22	36.2	36.2
23	23.3	23.2
24	126.0	126.0
25	131.2	131.2
26	25.9	25.8
27	18.0	17.9
28	32.1	32.0
29	16.6	16.5
30	17.7	17.7
1’	98.2	98.0
2’	75.0	74.9
3’	79.3	79.2
4’	72.2	72.1
5’	76.8	76.7
6’	69.3	69.1
1’’	104.7	104.6
2’’	71.9	71.8
3’’	74.2	74.1
4’’	68.7	68.6
5’’	65.7	65.6

C	Synthetic chikusetsusaponin L10 (**2**)	Reported data[S11]
1	38.9	39.0
2	27.8	27.9
3	78.3	78.3
4	40.3	40.2
5	61.6	61.6
6	67.5	67.5
7	47.1	47.1
8	40.9	41.0
9	49.7	49.7
10	39.3	39.3
11	28.0	27.9

12	78.4	78.3
13	46.2	46.2
14	52.0	52.0
15	31.1	31.1
16	26.6	26.6
17	54.0	54.1
18	17.2	17.2
19	17.2	17.2
20	73.0	73.1
21	26.6	26.6
22	36.3	36.3
23	22.8	22.8
24	126.4	126.4
25	130.6	130.5
26	25.8	25.8
27	17.6	17.6
28	31.9	31.8
29	16.4	16.4
30	17.4	17.2
1’	100.4	100.4
2’	75.2	75.1
3’	78.6	78.3
4’	71.0	70.9
5’	77.5	77.7
6’	62.4	62.8

C	Synthetic gensinoside Rh1 (**3**)	Reported data[S12]
1	38.9	39.0
2	27.8	27.9
3	78.3	78.3
4	40.3	40.2
5	61.6	61.6
6	67.5	67.5
7	47.1	47.1
8	40.9	41.0
9	49.7	49.7
10	39.3	39.3
11	28.0	27.9
12	78.4	78.3
13	46.2	46.2
14	52.0	52.0
15	31.1	31.1

16	26.6	26.6
17	54.0	54.1
18	17.2	17.2
19	17.2	17.2
20	73.0	73.1
21	26.6	26.6
22	36.3	36.3
23	22.8	22.8
24	126.4	126.4
25	130.6	130.5
26	25.8	25.8
27	17.6	17.6
28	31.9	31.8
29	16.4	16.4
30	17.4	17.2
1’	100.4	100.4
2’	75.2	75.1
3’	78.6	78.3
4’	71.0	70.9
5’	77.5	77.7
6’	62.4	62.8

C	Synthetic ginsenoside Rg1 (**4**)	Reported data[S12]
1	39.5	39.9
2	28.0	28.4
3	78.8	79.2
4	40.4	40.8
5	61.5	61.8
6	80.2	80.6
7	45.2	45.6
8	41.2	41.6
9	50.1	50.5
10	39.8	40.2
11	31.0	31.5
12	70.4	70.7
13	49.2	49.7
14	51.5	51.9
15	30.8	31.2
16	26.7	27.1
17	51.8	52.0
18	17.6	18.1
19	17.6	18.1

20	83.5	83.8
21	22.5	22.8
22	36.2	36.6
23	23.4	23.7
24	126.0	126.5
25	131.1	131.4
26	25.9	26.2
27	17.9	18.3
28	31.8	32.2
29	16.5	16.9
30	17.2	17.7
6-Glc 1’	106.0	106.5
2’	75.5	76.0
3’	79.7	80.1
4’	71.9	72.4
5’	78.3	78.7
6’	63.2	63.4
20-Glc 1’’	98.3	98.7
2’’	75.2	75.6
3’’	79.2	79.8
4’’	71.6	72.2
5’’	78.2	78.6
6’’	63.2	63.6

C	Synthetic ginsenoside Ia (**5**)	Reported data[S13]
1	39.1	39.1
2	26.6	26.7
3	89.4	89.4
4	40.5	40.5
5	61.8	61.8
6	67.5	67.5
7	47.5	47.5
8	41.1	41.1
9	49.8	49.8
10	38.8	38.9
11	30.9	30.9
12	70.1	70.1
13	49.1	49.1
14	51.3	51.3
15	30.7	30.8
16	26.7	26.7
17	51.6	51.5

18	17.6	17.6
19	17.4	17.4
20	83.2	83.2
21	22.3	22.4
22	36.1	36.2
23	23.2	23.2
24	125.9	125.9
25	130.9	130.9
26	25.8	25.8
27	17.7	17.8
28	31.4	31.4
29	17.0	16.9
30	17.4	17.4
3-Glc 1’	107.2	107.2
2’	75.9	75.8
3’	78.8	78.7
4’	71.9	71.9
5’	78.4	78.3
6’	63.1	63.1
20-Glc 1”	98.3	98.2
2”	75.1	75.1
3”	79.3	79.3
4”	71.6	71.6
5”	78.3	78.2
6”	62.9	62.9

^{13}C NMR signal*	Synthetic G-Rb2 (**6**)	Authentic G-Rb2 [S14]	Reported data [S15]
1	16.1	16.1	
2	16.3	16.3	
3	16.7	16.7	
4	17.4	17.4	
5	18.0	18.0	
6	18.5	18.5	
7	22.4	22.4	22.4
8	23.3	23.3	23.2
9	25.9	25.9	
10	26.7	26.7	
11	26.8	26.8	26.9
12	28.2	28.2	
13(2)	30.8	30.8	
14	35.2	35.2	
15	36.2	36.2	36.2

16	37.0	37.0	
17	39.2	39.2	
18	39.7	39.7	
19	40.1	40.1	
20	49.5	49.5	
21	50.3	50.3	
22	51.5	51.5	
23	51.7	51.7	51.7
24	56.4	56.4	
25	62.7	62.7	
26	62.9	62.9	
27	65.7	65.7	
28	68.6	68.7	
29	69.3	69.3	
30	70.2	70.2	
31(2)	71.7	71.7	
32	71.9	71.9	
33	72.2	72.2	
34	74.2	74.2	
35	75.0	75.0	
36	77.0	76.9	
37	77. 3	77.3	
38	78.0	78.0	
39	78.2	78.2	
40	78.3	78.4	
41	78.4	78.4	
42	79.3	79.3	
43	83.5	83.5	83.5
44	89.0	89.0	
45	98.2	98.2	98.1
46	104.7	104. 8	104.6
47	105.2	105.2	105.1
48	106.2	106.2	106.1
49	126.0	126.0	126.0
50	131.2	131.2	131.1

*The ^{13}C signals are numbered from the highest to the lowest.

References

[S1] The spectroscopic data of the obtained two compounds are identical to those of the authentic samples which are commercially available.

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[S14] An authentic sample was purchased from Shanhai Yuanye Company (www.shyuanye.com).

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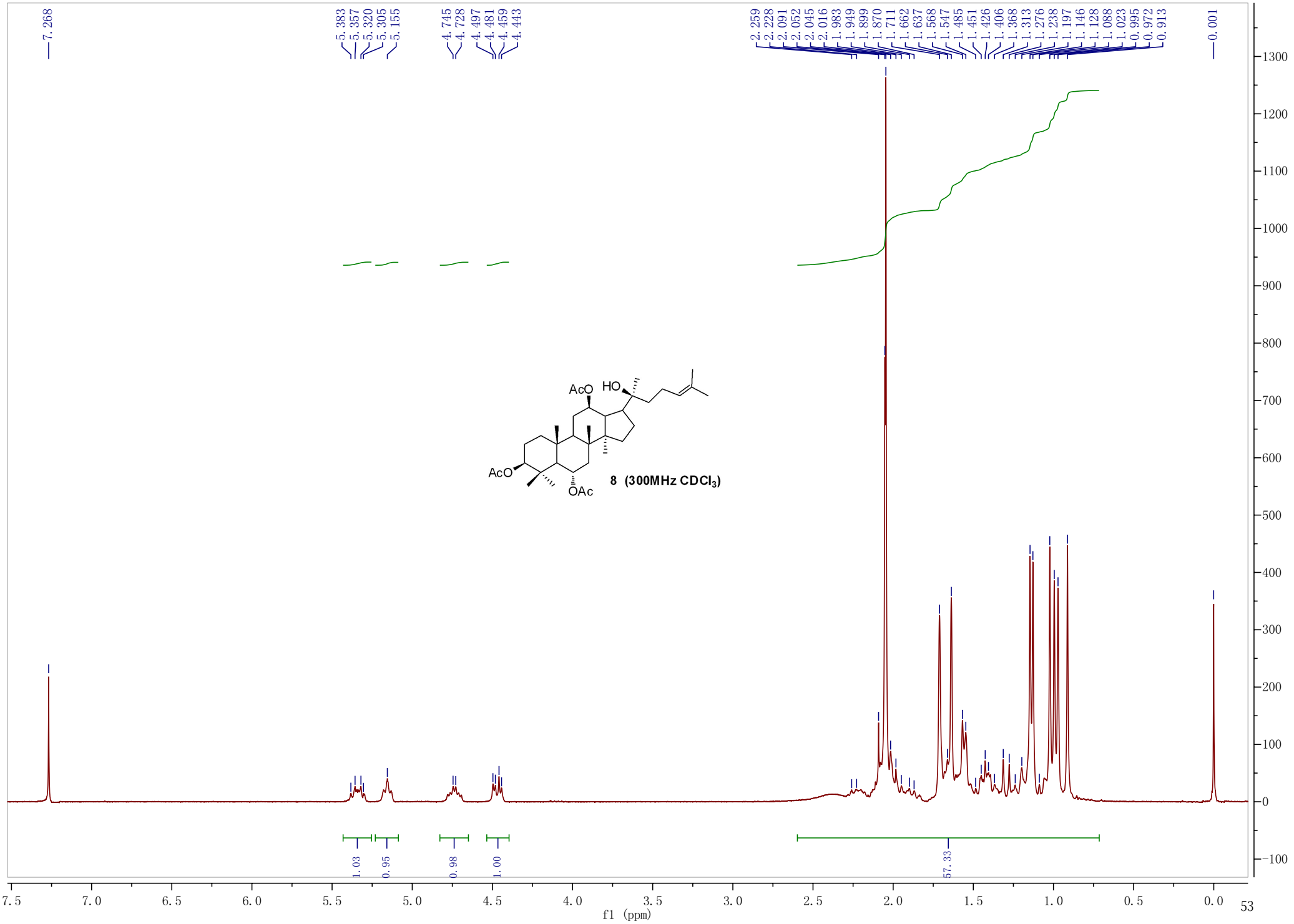

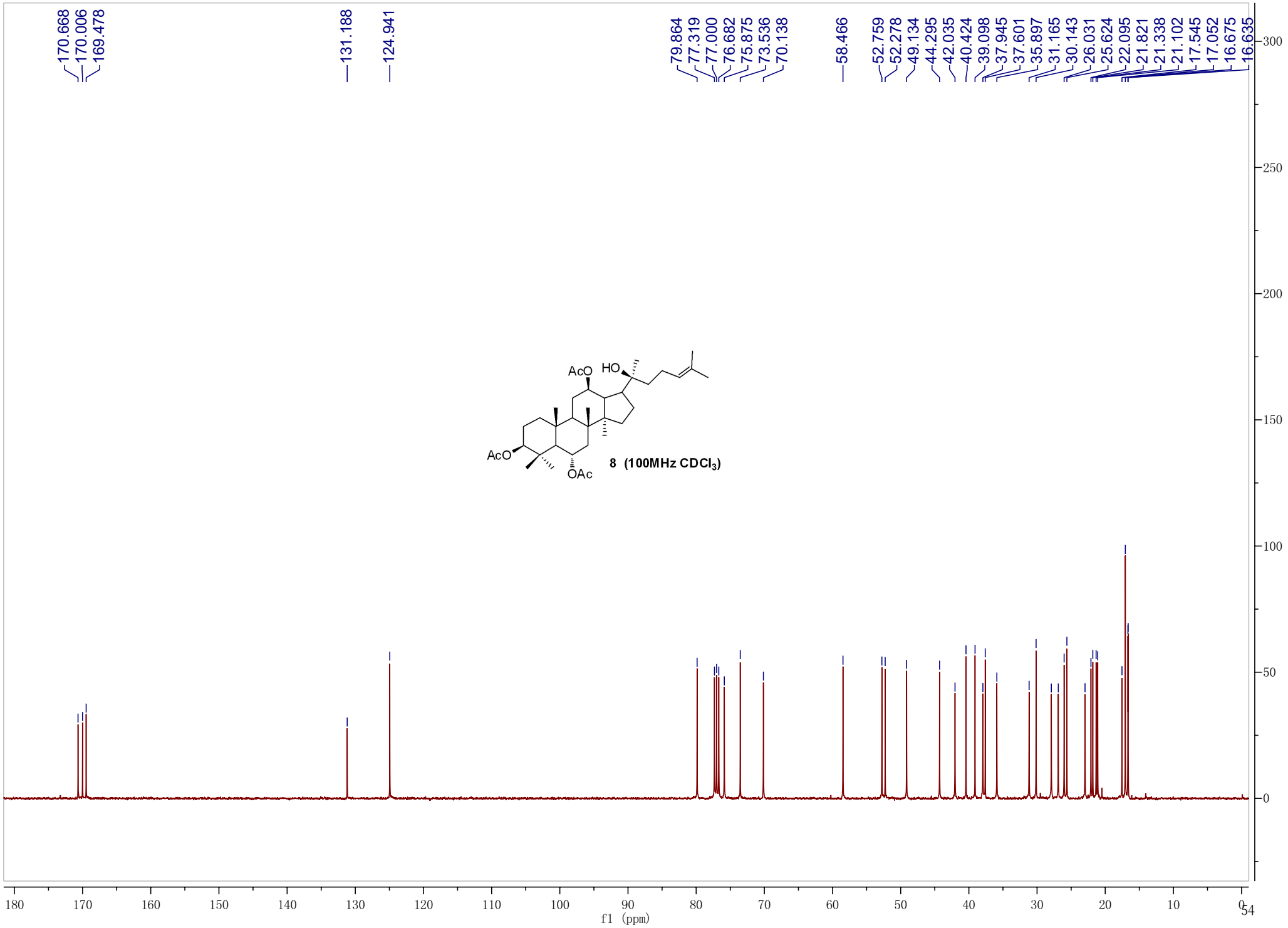
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169.478
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77.319
77.000
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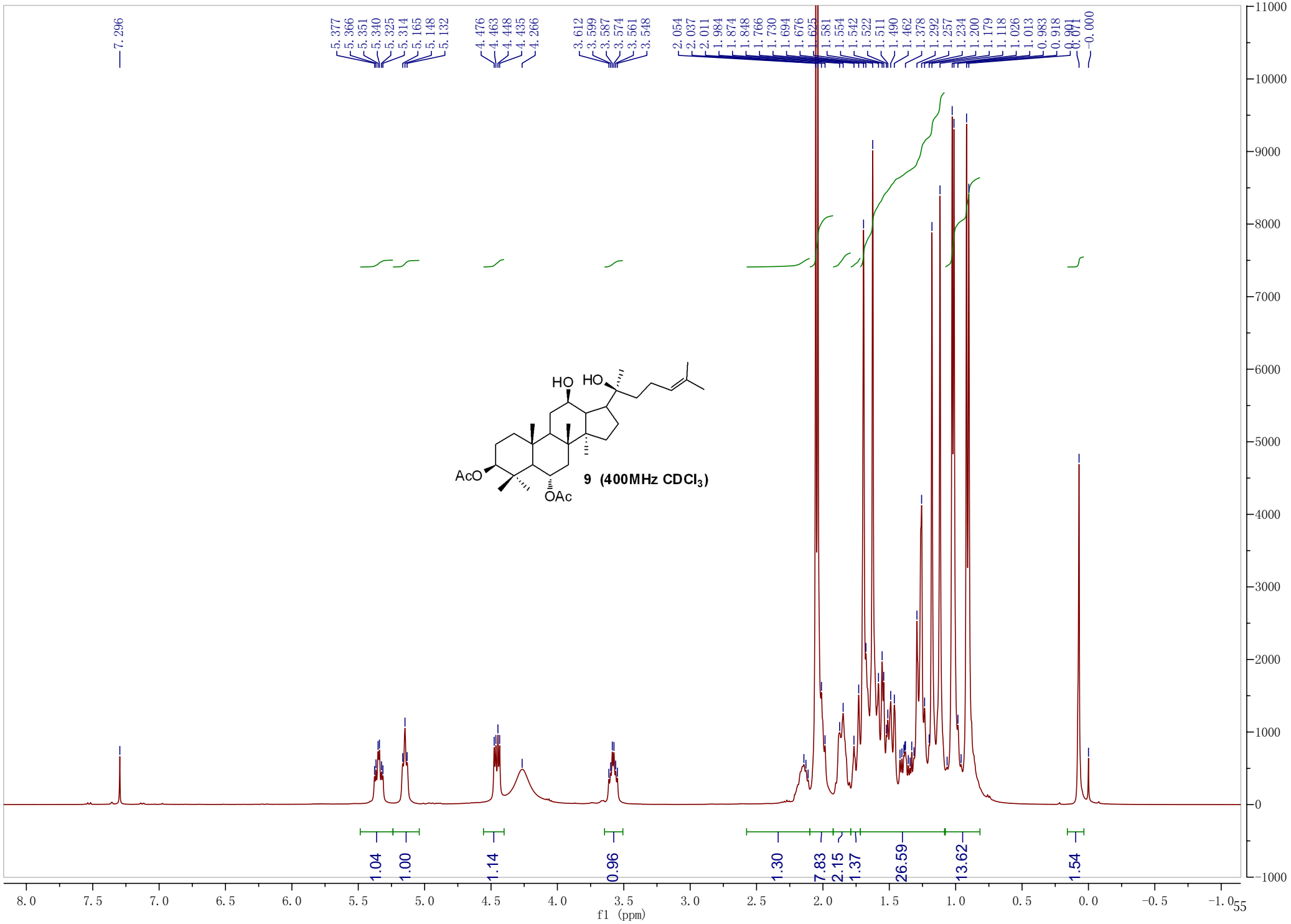
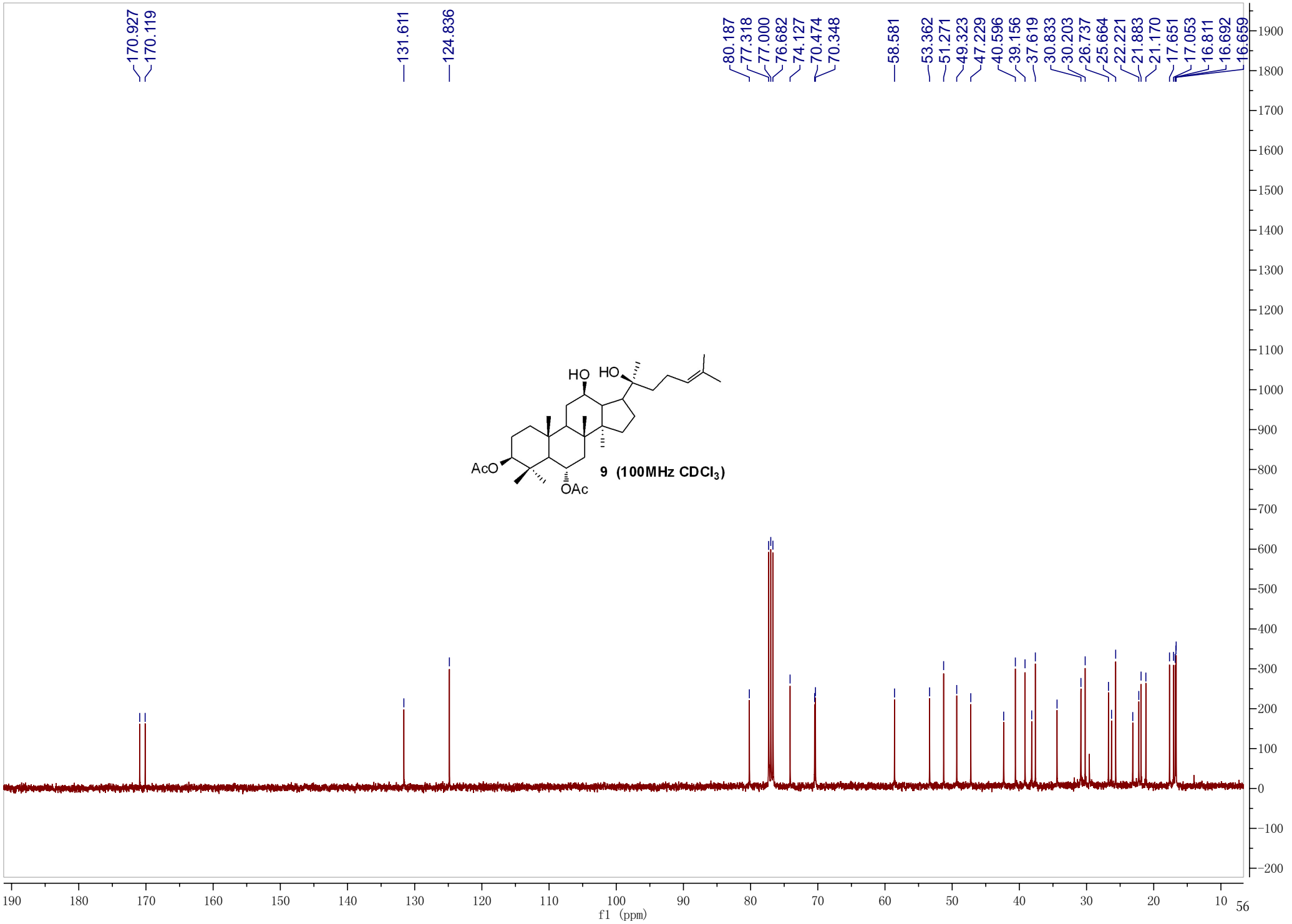
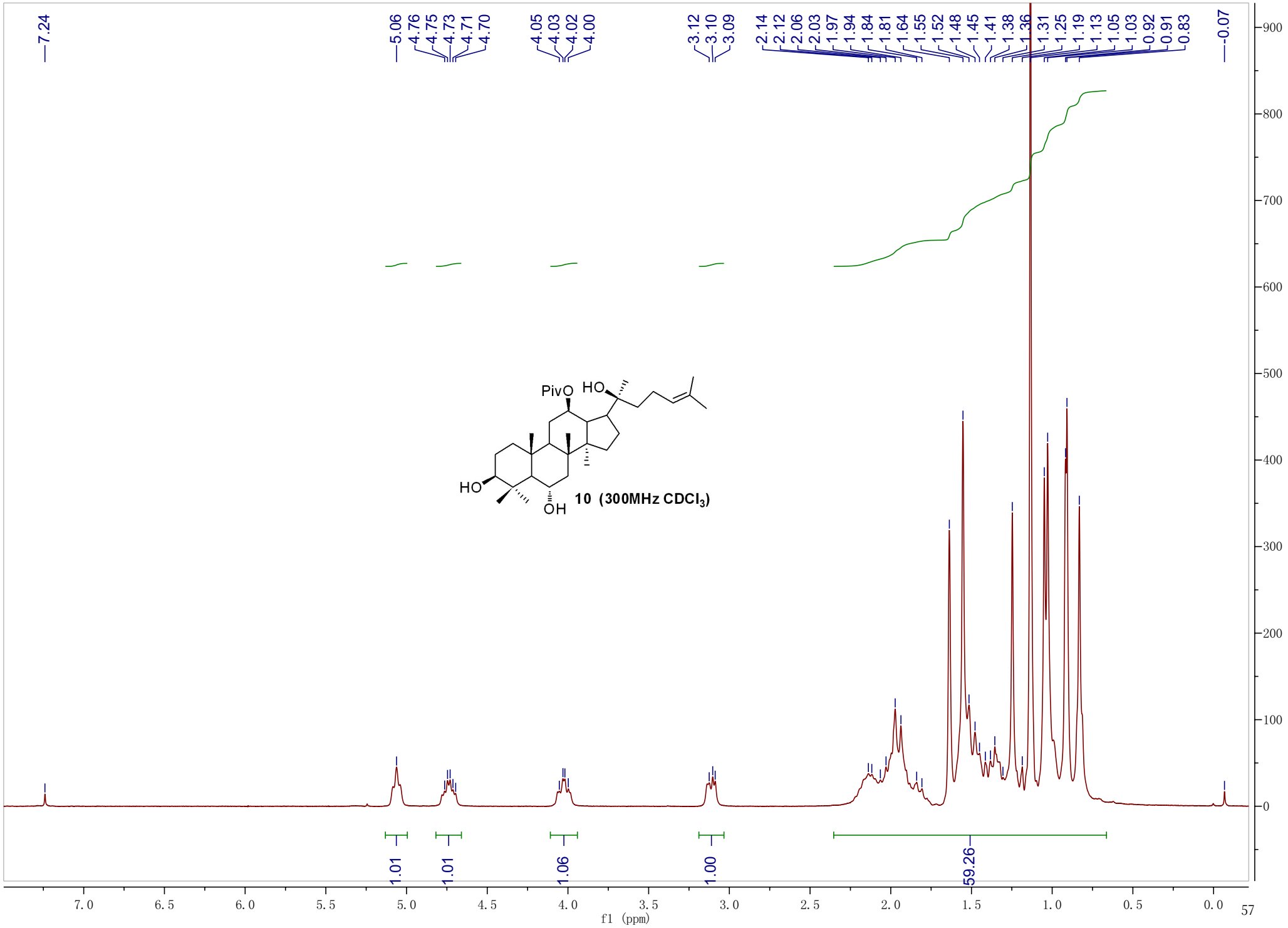
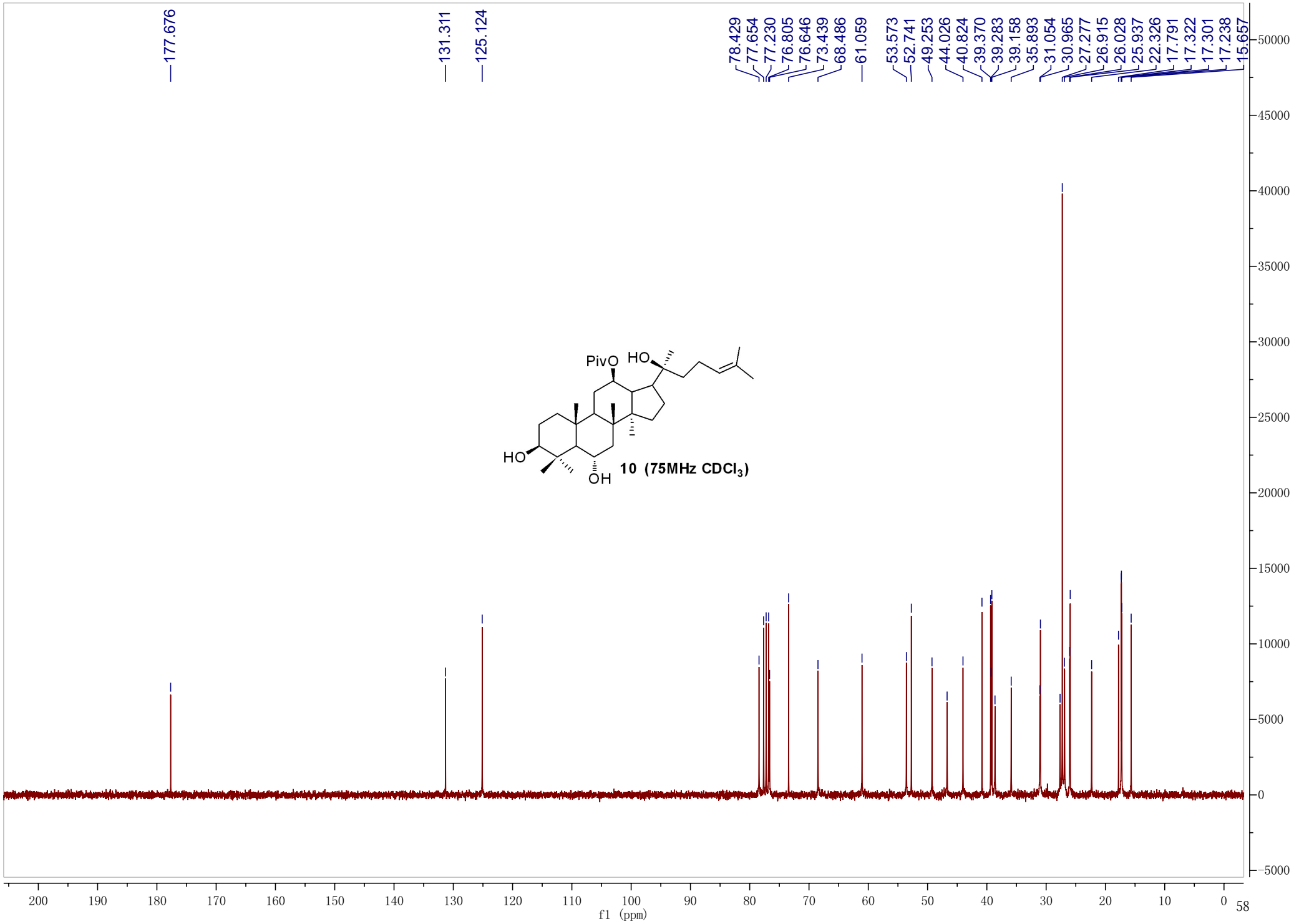
75.875
73.536
70.138
58.466
52.759
52.278
49.134
44.295
42.035
40.424
39.098
37.945
37.601
35.897
31.165
30.143
26.031
25.624
22.095
21.821
21.338
21.102
17.545
17.052
16.675
16.635
AcO
HO
AcO
OAc
8 (100MHz CDCl3)
f1 (ppm)





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77.230
76.805
76.646
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68.486
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53.573
52.741
49.253
44.026
40.824
39.370
39.283
39.158
35.893
31.054
30.965
27.277
26.915
26.028
25.937
22.326
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17.301
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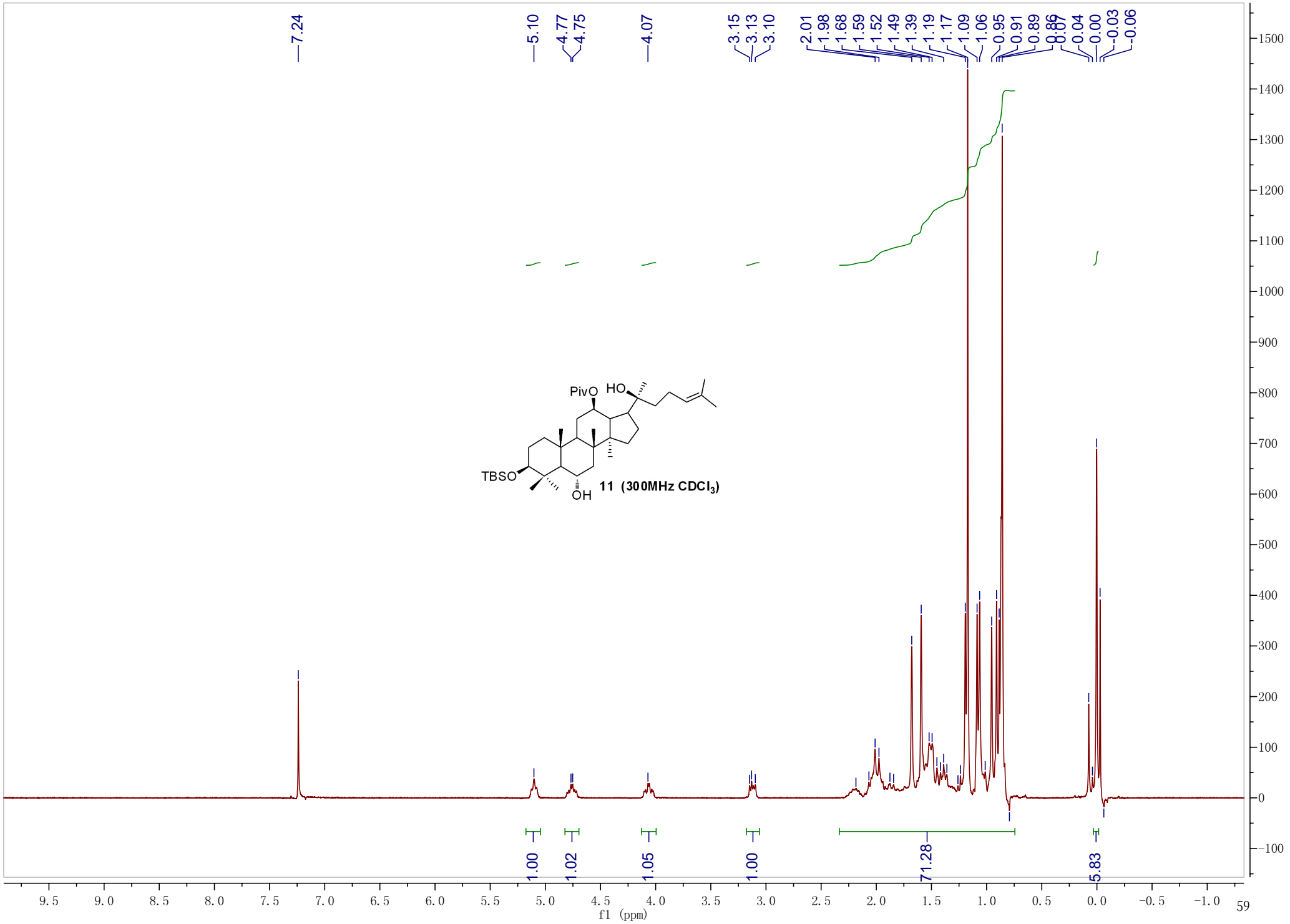
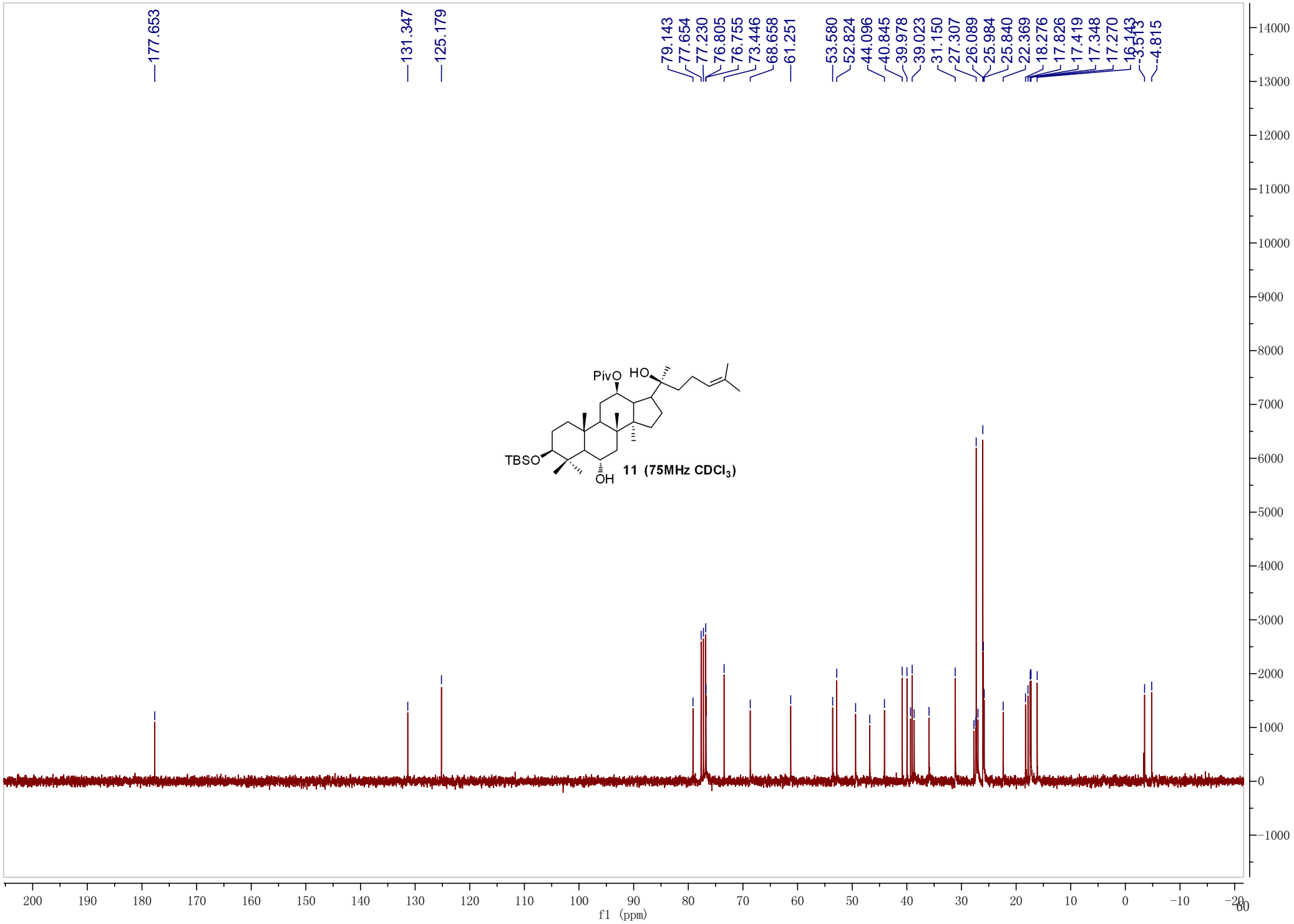
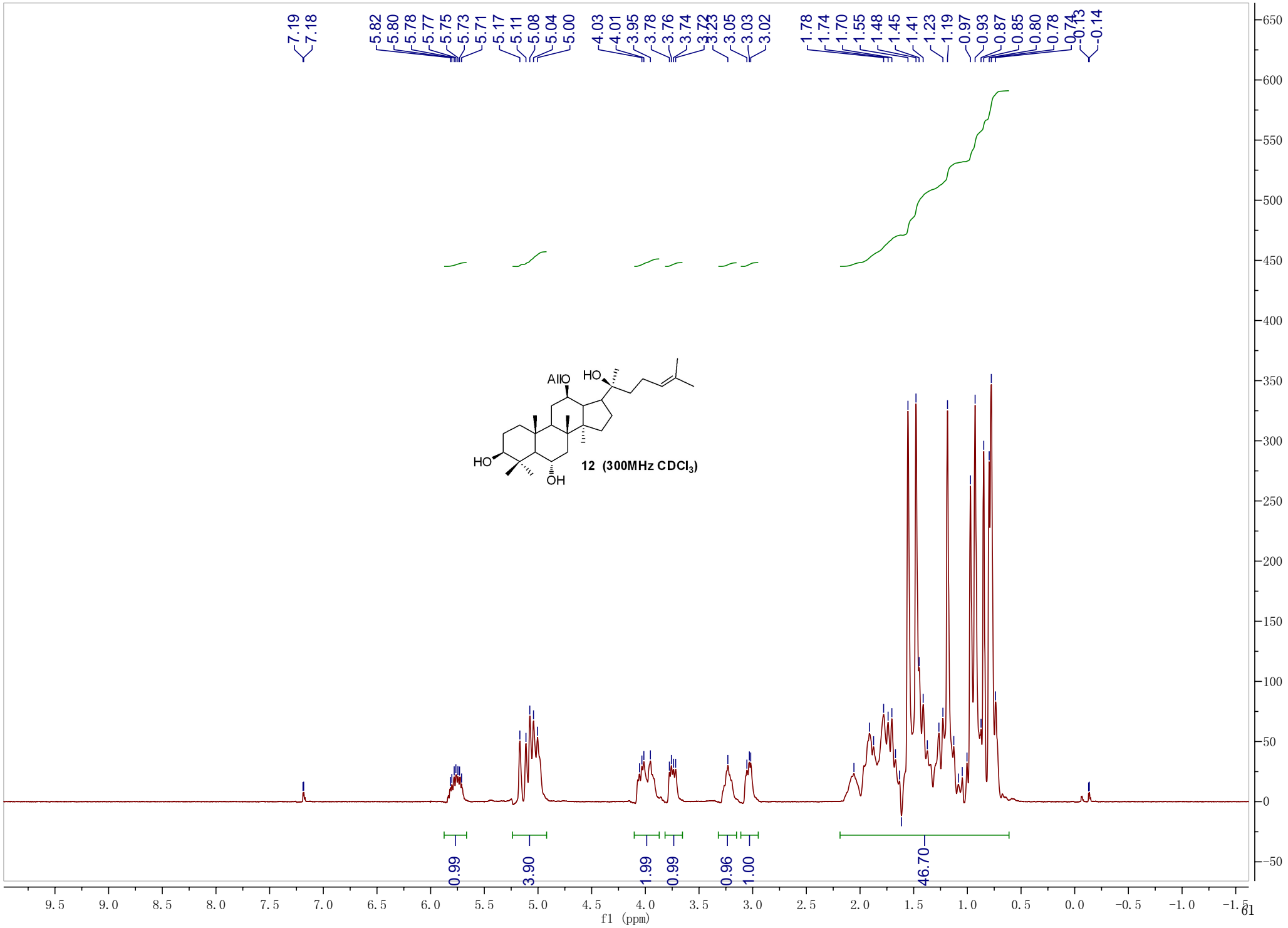
PivO
HO
HO
OH
10 (75MHz CDCl3)
f1 (ppm)



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5.82
5.80
5.78
5.77
5.75
5.73
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5.17
5.11
5.08
5.04
5.00
4.03
4.01
3.95
3.78
3.76
3.74
3.72
3.23
3.05
3.03
3.02
1.78
1.74
1.70
1.55
1.48
1.45
1.41
1.23
1.19
0.97
0.93
0.87
0.85
0.80
0.78
0.74
0.13
-0.14
AllO
HO
HO
OH
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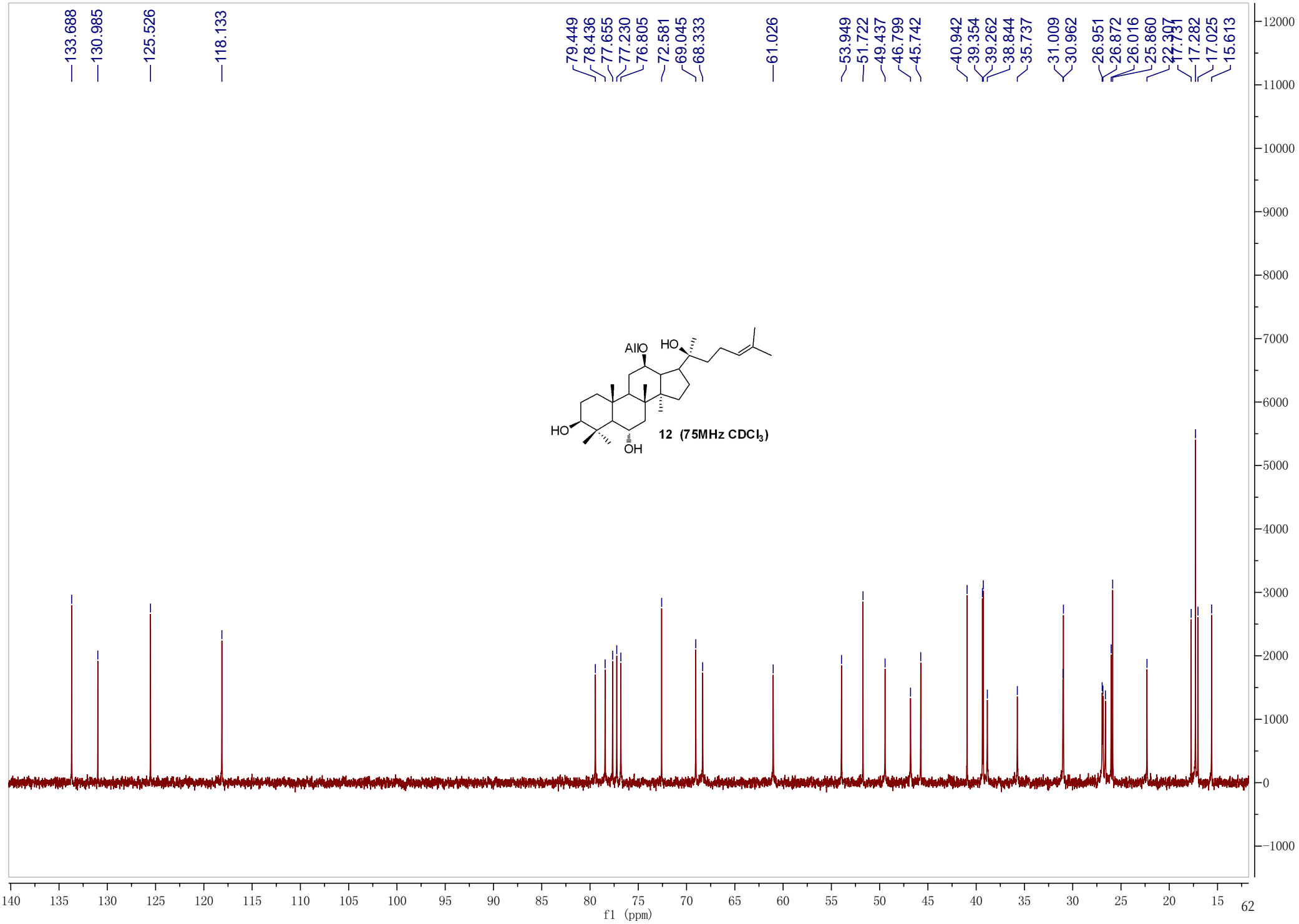
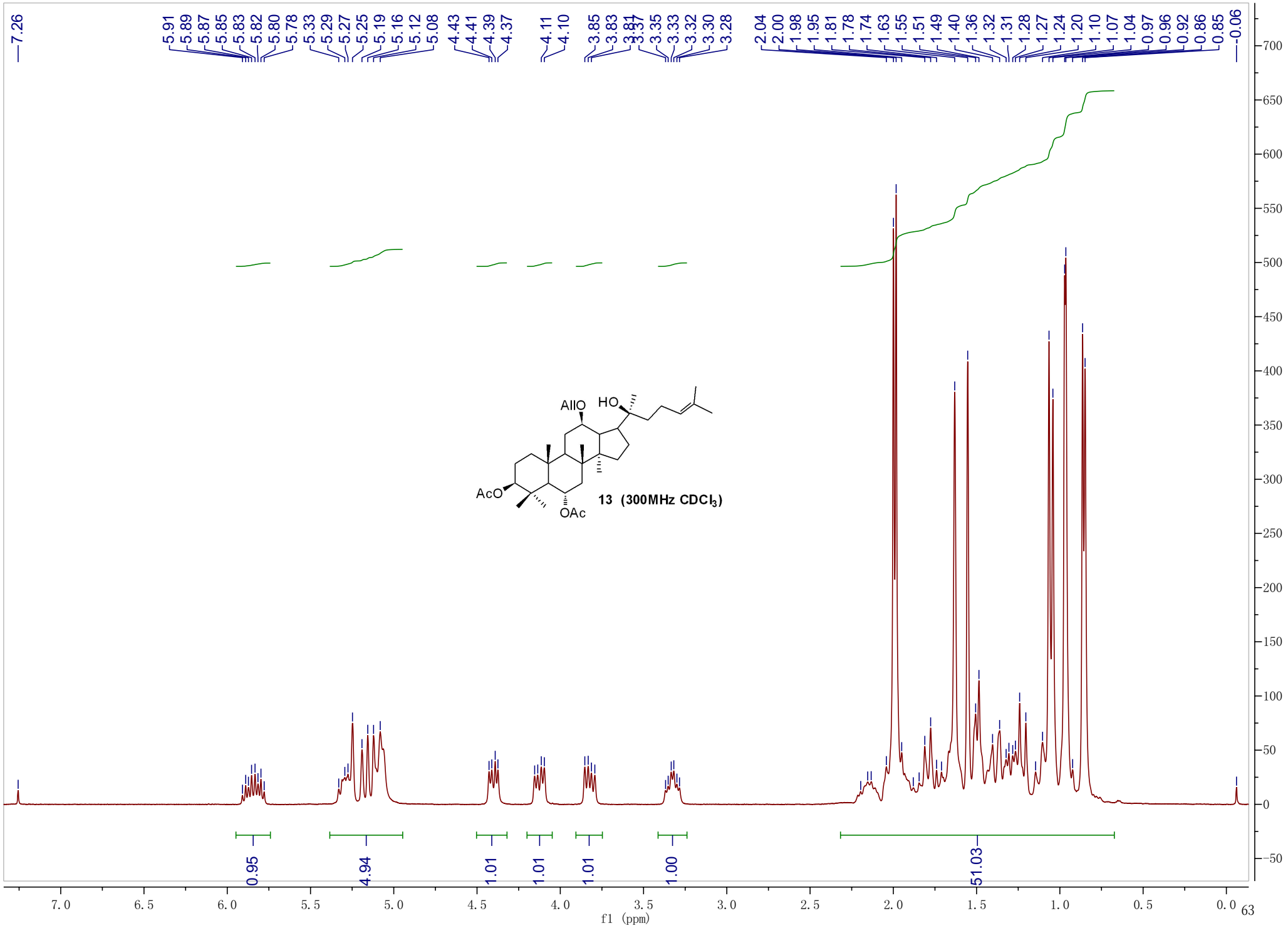
1.99
0.99
0.96
1.00
46.70
f1 (ppm)

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5.82
5.80
5.78
5.33
5.29
5.27
5.25
5.19
5.16
5.12
5.08
4.43
4.41
4.39
4.37
4.11
4.10
3.85
3.83
3.81
3.37
3.35
3.33
3.32
3.30
3.28
2.04
2.00
1.98
1.95
1.81
1.78
1.74
1.63
1.55
1.51
1.49
1.40
1.36
1.32
1.31
1.28
1.27
1.24
1.20
1.10
1.07
1.04
0.97
0.96
0.92
0.86
0.85
-0.06
AllO
HO
AcO
OAc
13 (300MHz CDCl3)
0.95
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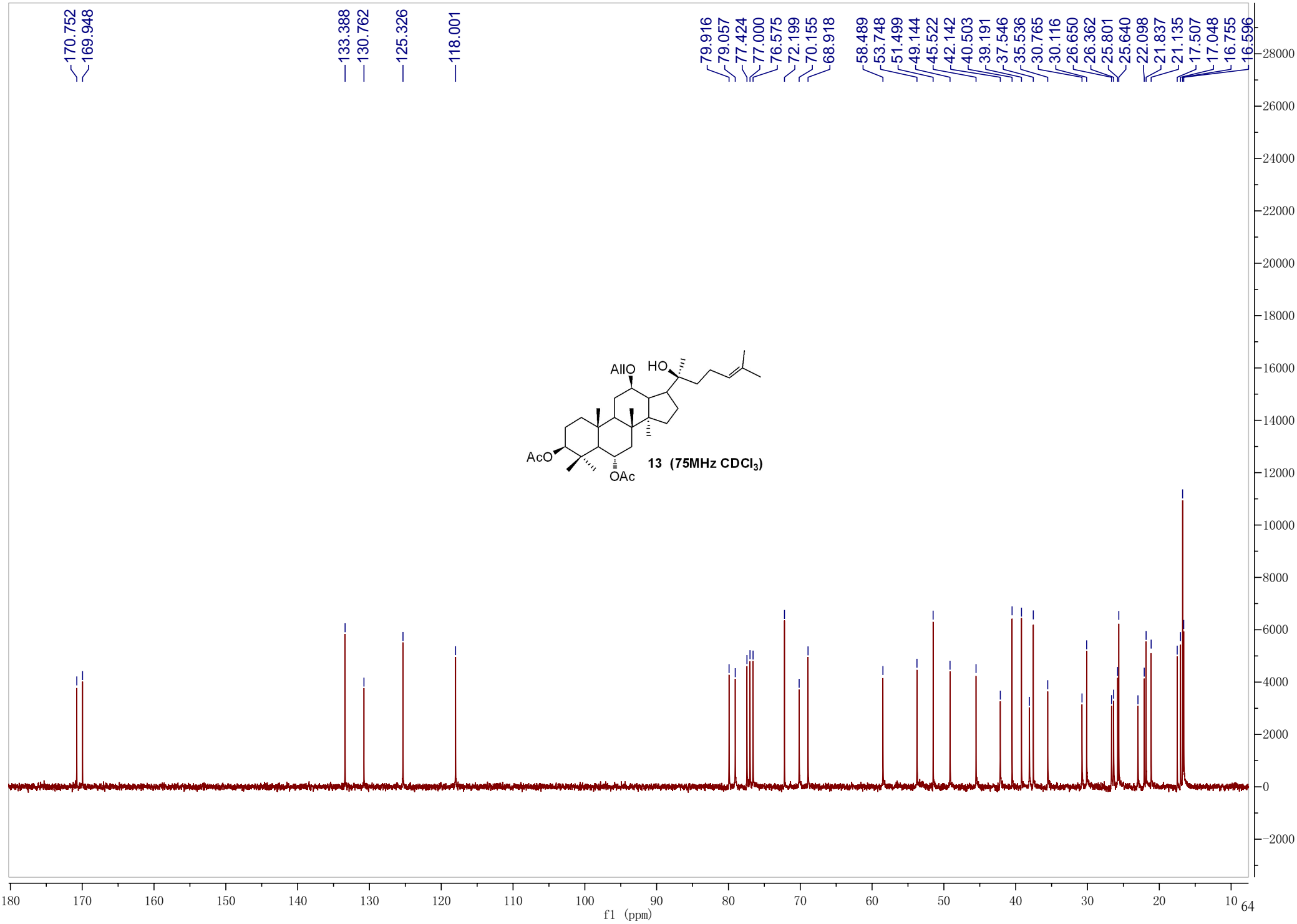
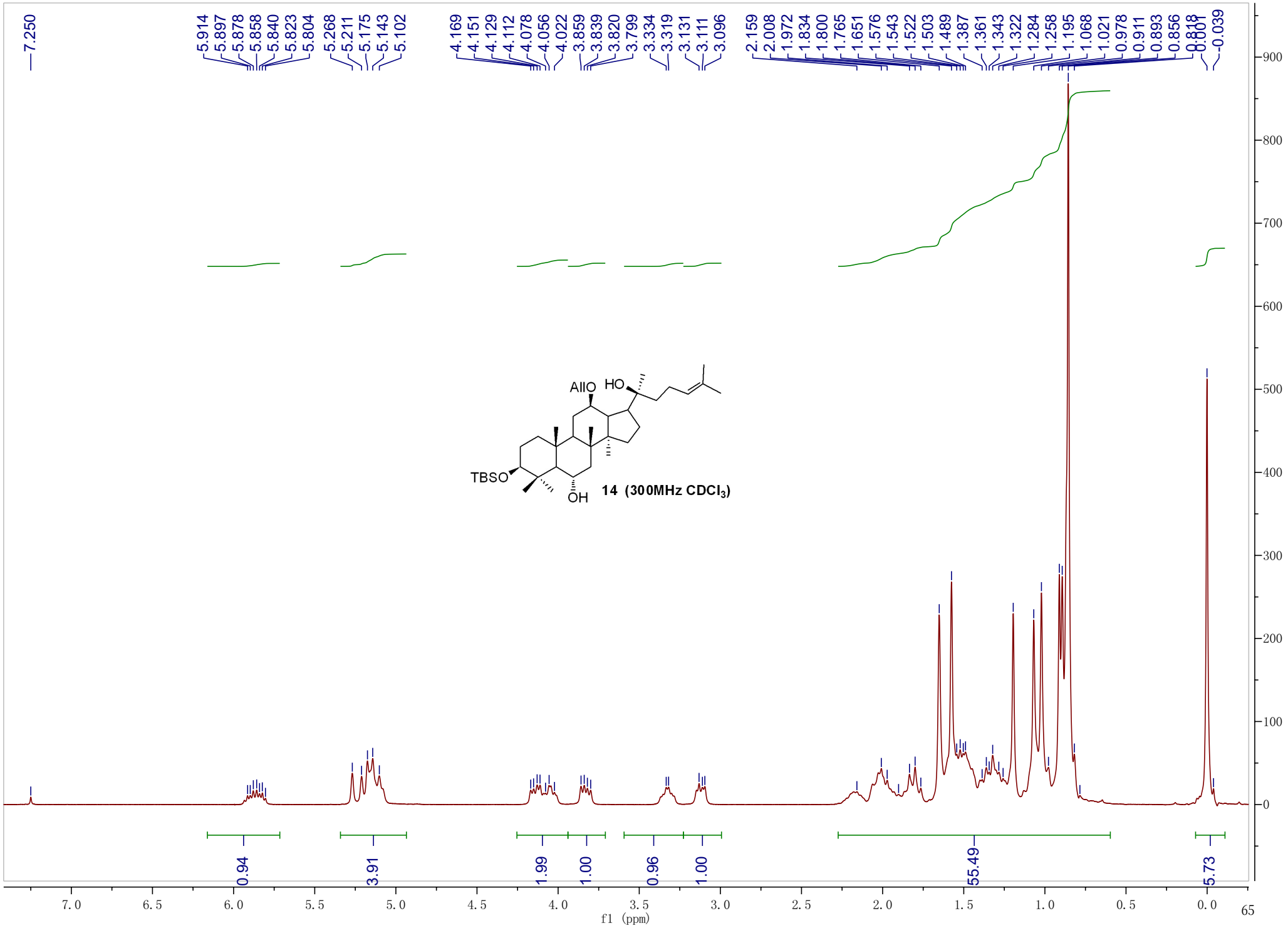
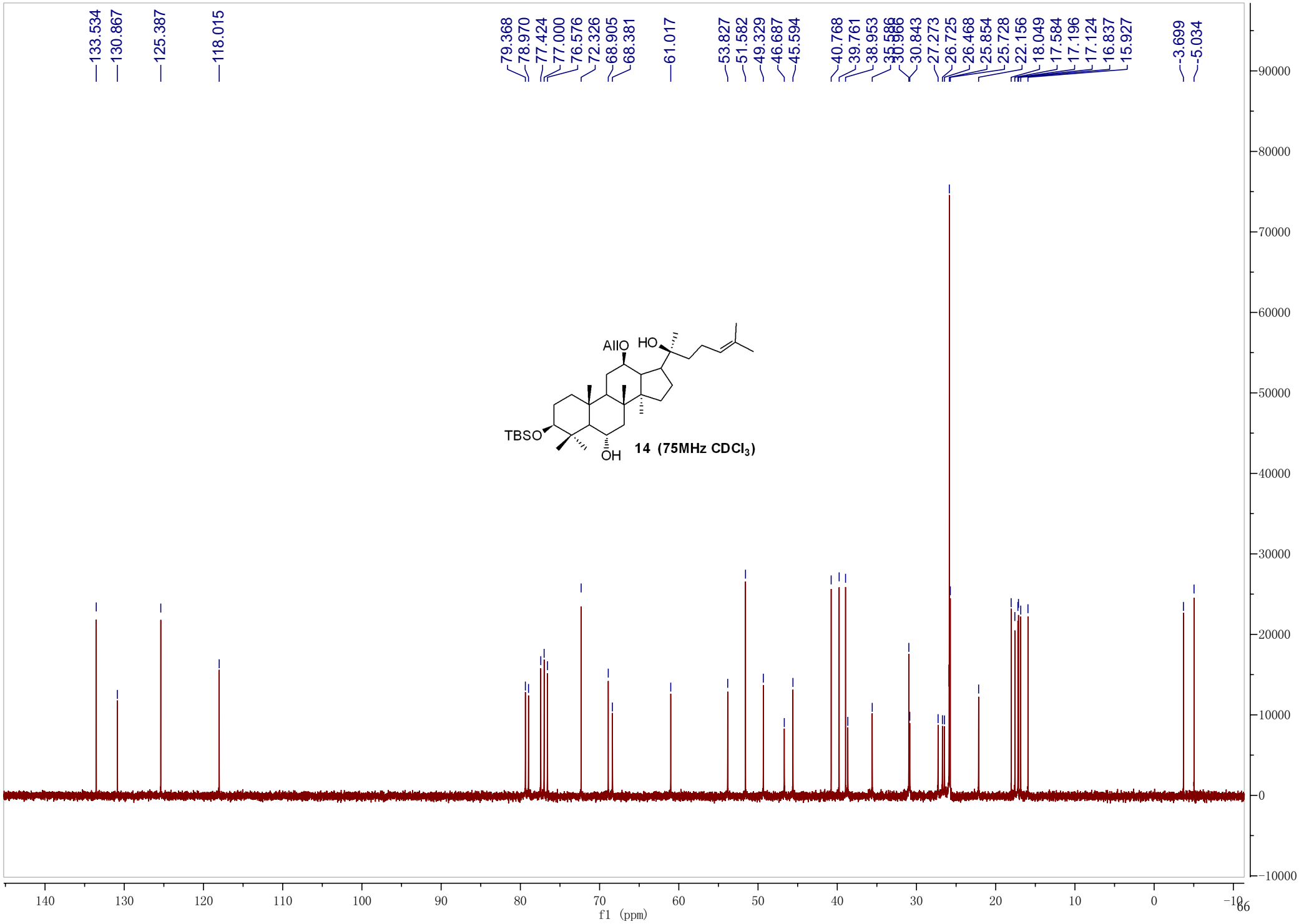
1.01
1.01
1.01
1.00
51.03
f1 (ppm)
63



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61.017
53.827
51.582
49.329
46.687
45.594
40.768
39.761
38.953
35.586
30.966
30.843
27.273
26.725
26.468
25.854
25.728
22.156
18.049
17.584
17.196
17.124
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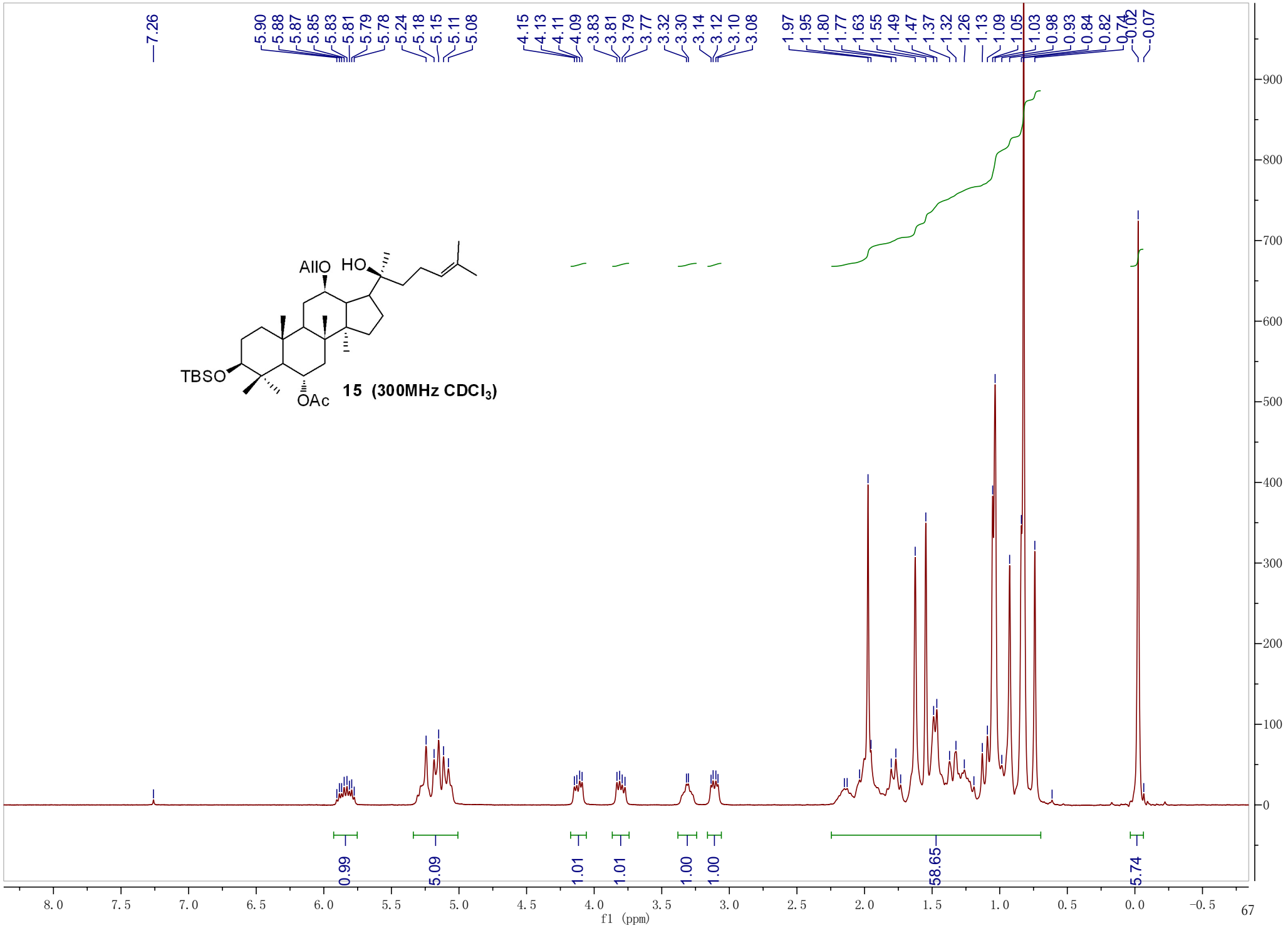
15.927
-3.699
-5.034
AllO
HO
TBSO
OH
14 (75MHz CDCl3)
f1 (ppm)


7.26
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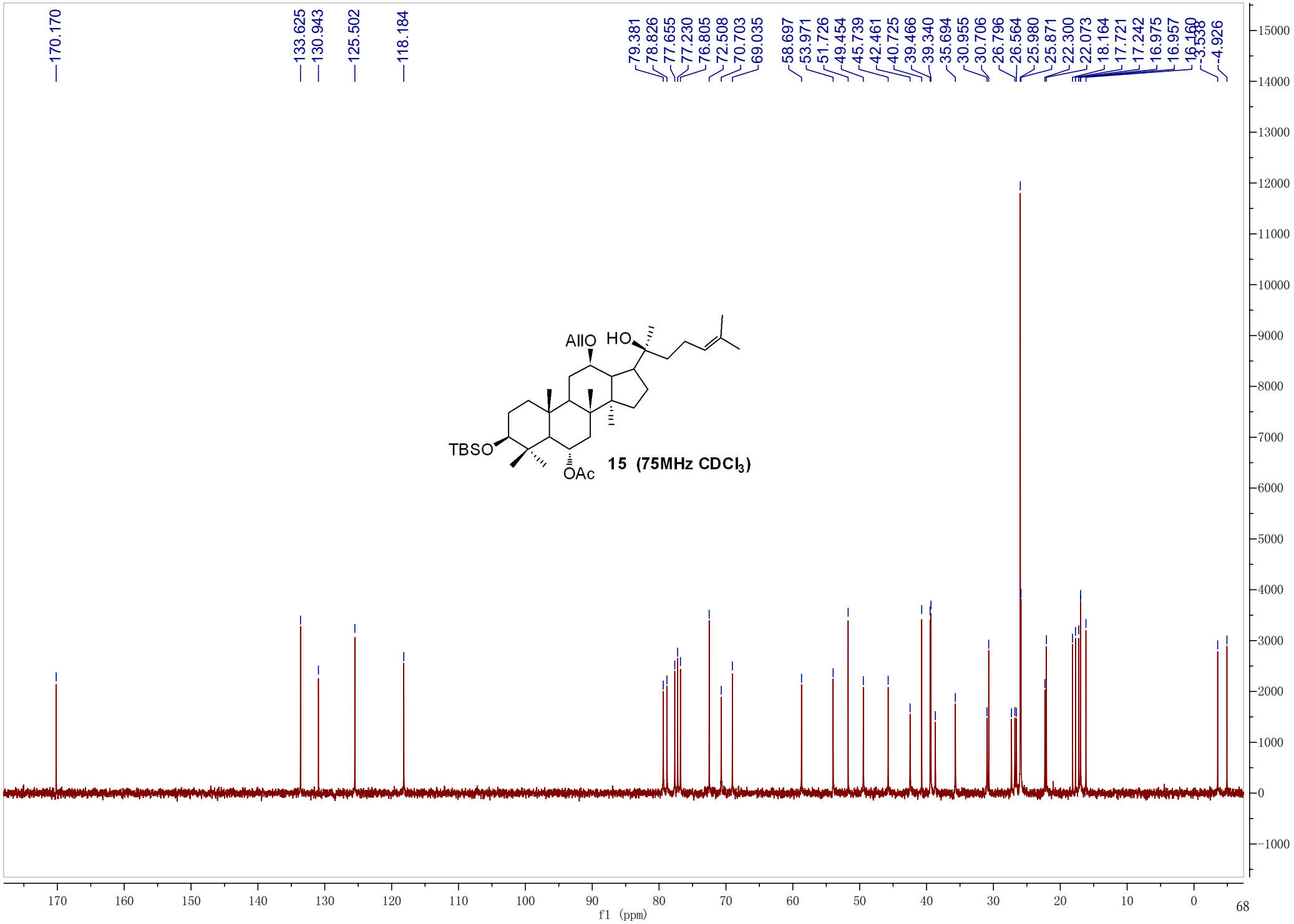
5.88
5.87
5.85
5.83
5.81
5.79
5.78
5.24
5.18
5.15
5.11
5.08
4.15
4.13
4.11
4.09
3.83
3.81
3.79
3.77
3.32
3.30
3.14
3.12
3.10
3.08
1.97
1.95
1.80
1.77
1.63
1.55
1.49
1.47
1.37
1.32
1.26
1.13
1.09
1.05
1.03
0.98
0.93
0.84
0.82
0.74
0.02
-0.07
AllO
HO
TBSO
OAc
15 (300MHz CDCl3)
0.99
5.09
1.01
1.01
1.00
1.00
58.65
5.74
f1 (ppm)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79.381
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77.230
76.805
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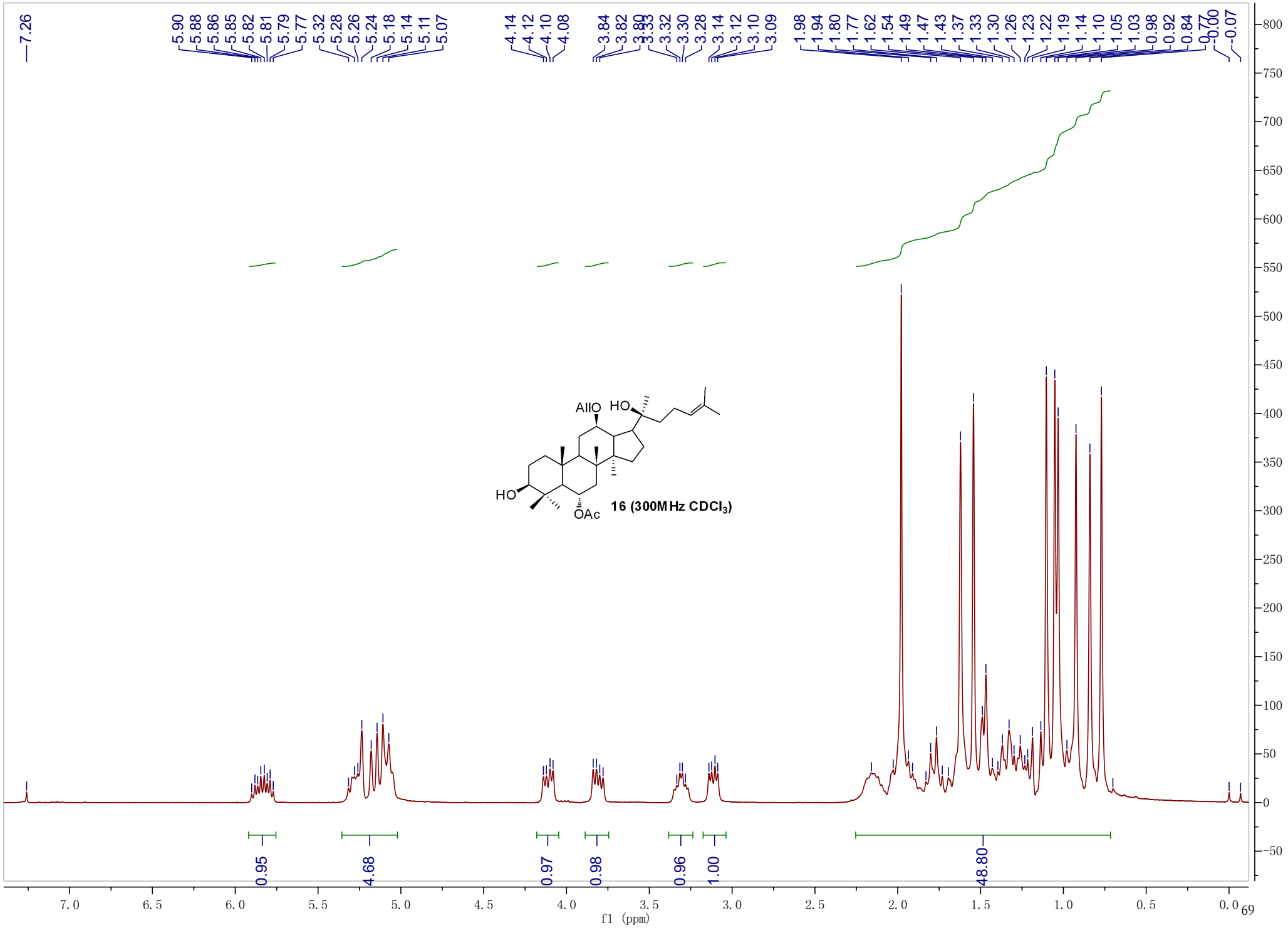
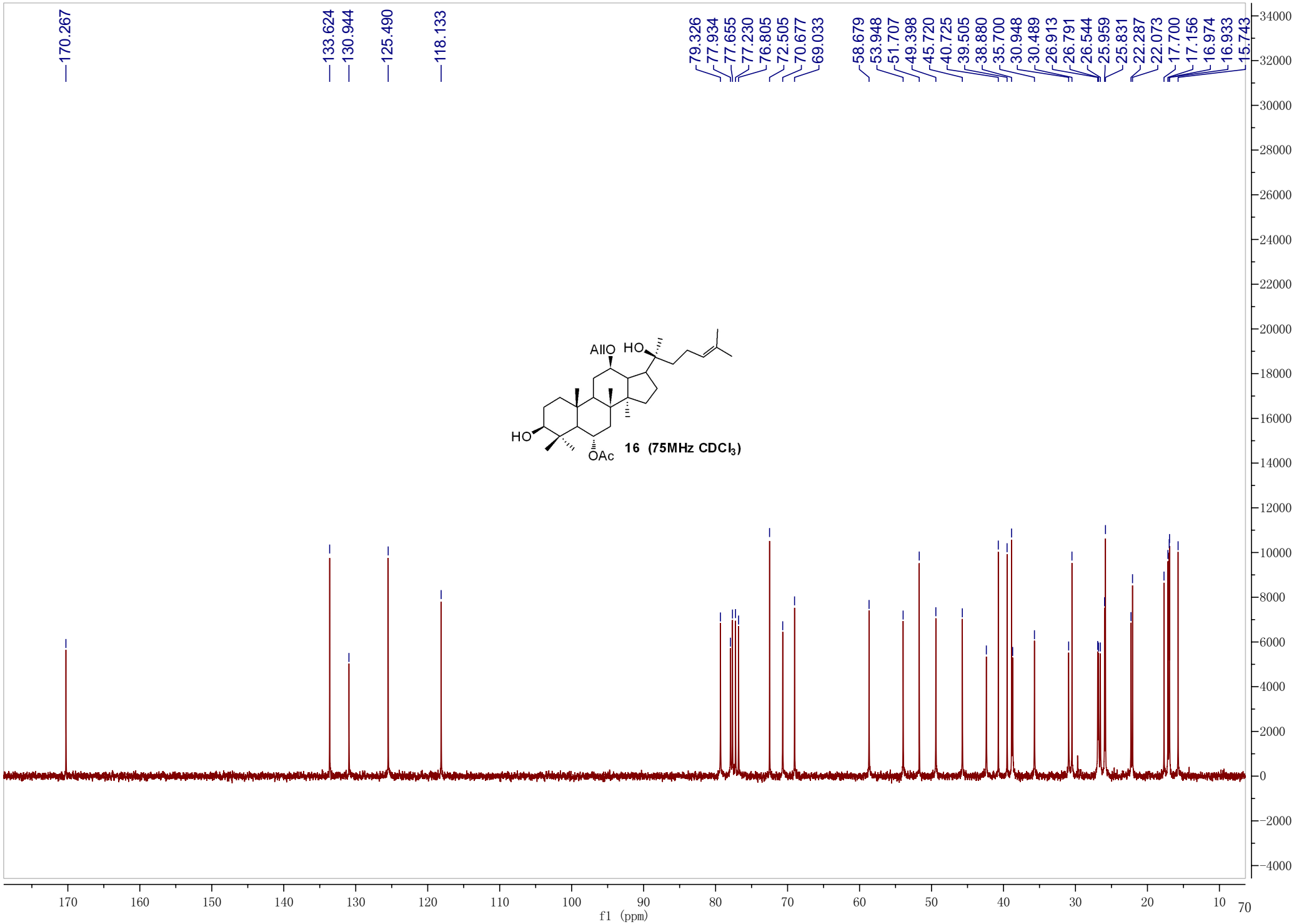
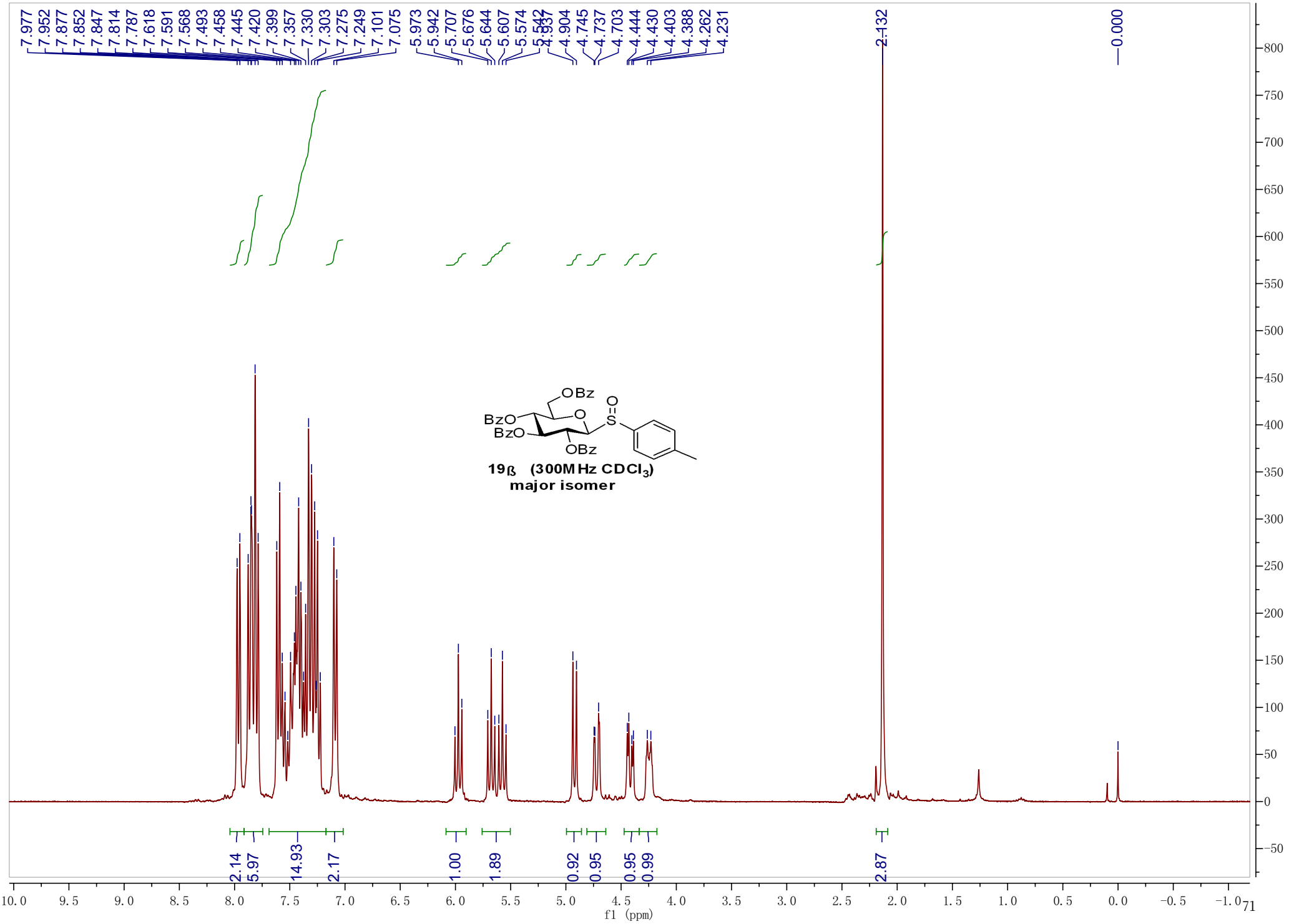
70.703
69.035
58.697
53.971
51.726
49.454
45.739
42.461
40.725
39.466
39.340
35.694
30.955
30.706
26.796
26.564
25.980
25.871
22.300
22.073
18.164
17.721
17.242
16.975
16.957
16.160
-3.538
-4.926
AllO
HO
TBSO
OAc
15 (75MHz CDCl3)
f1 (ppm)



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7.847
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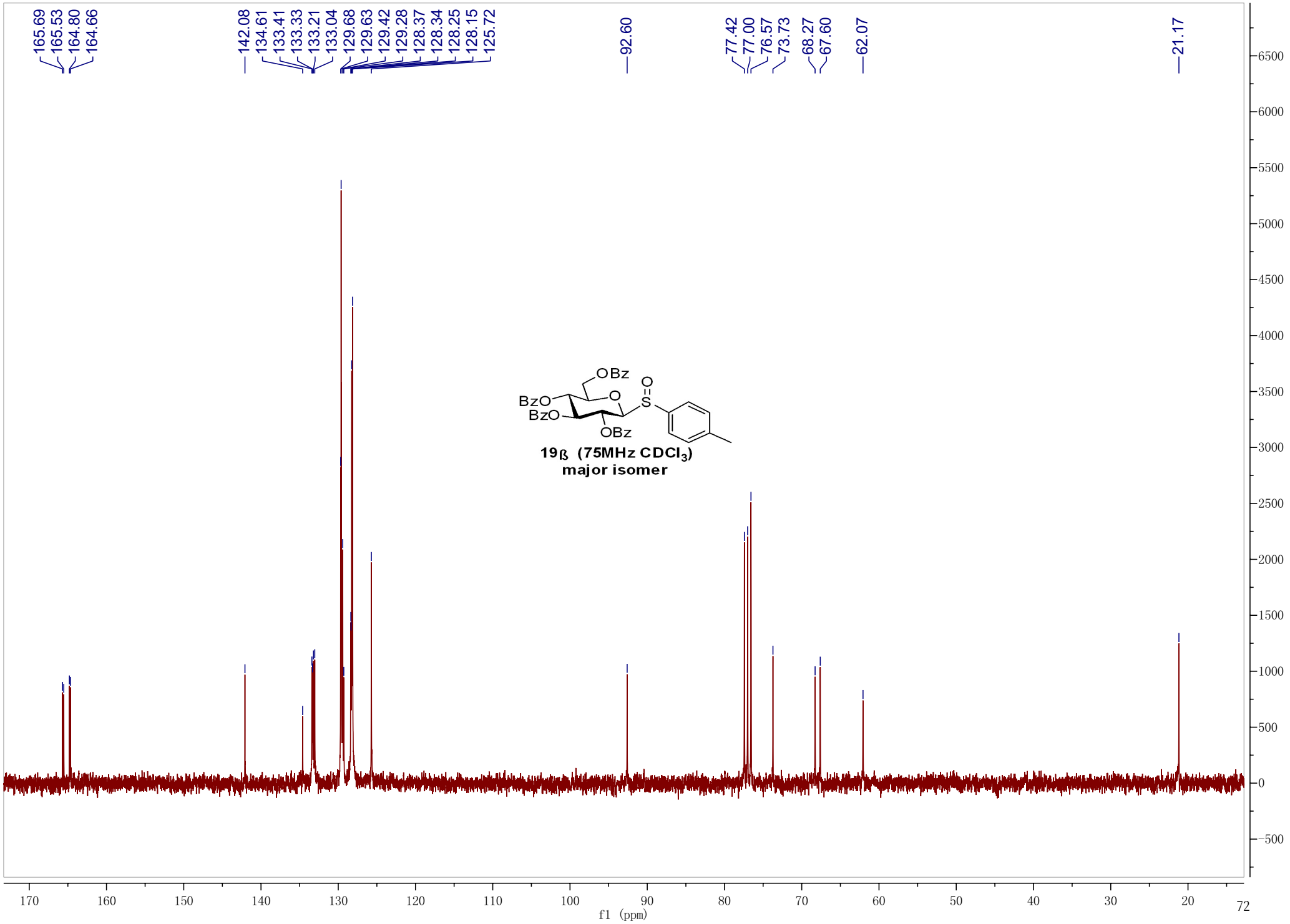
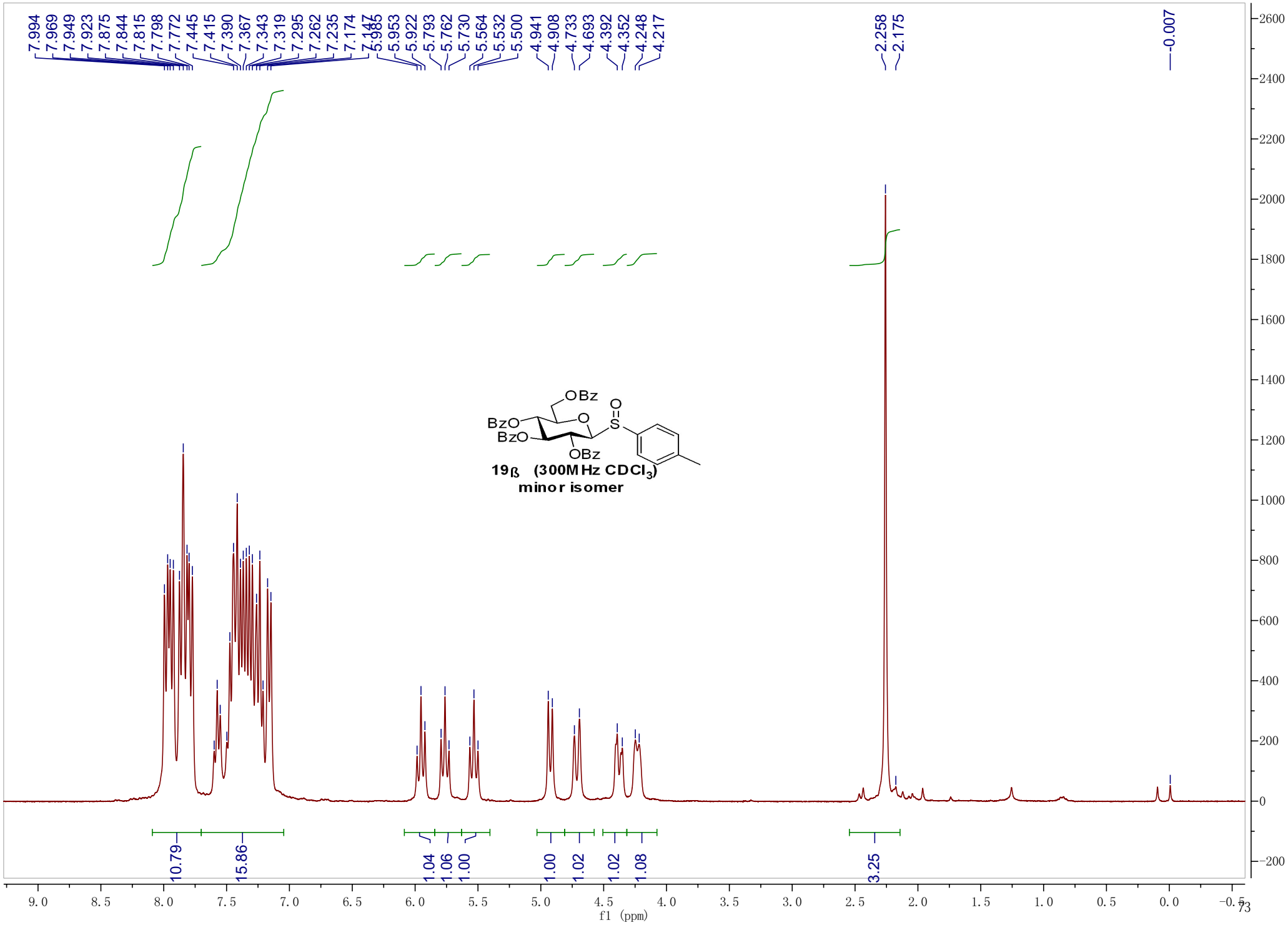
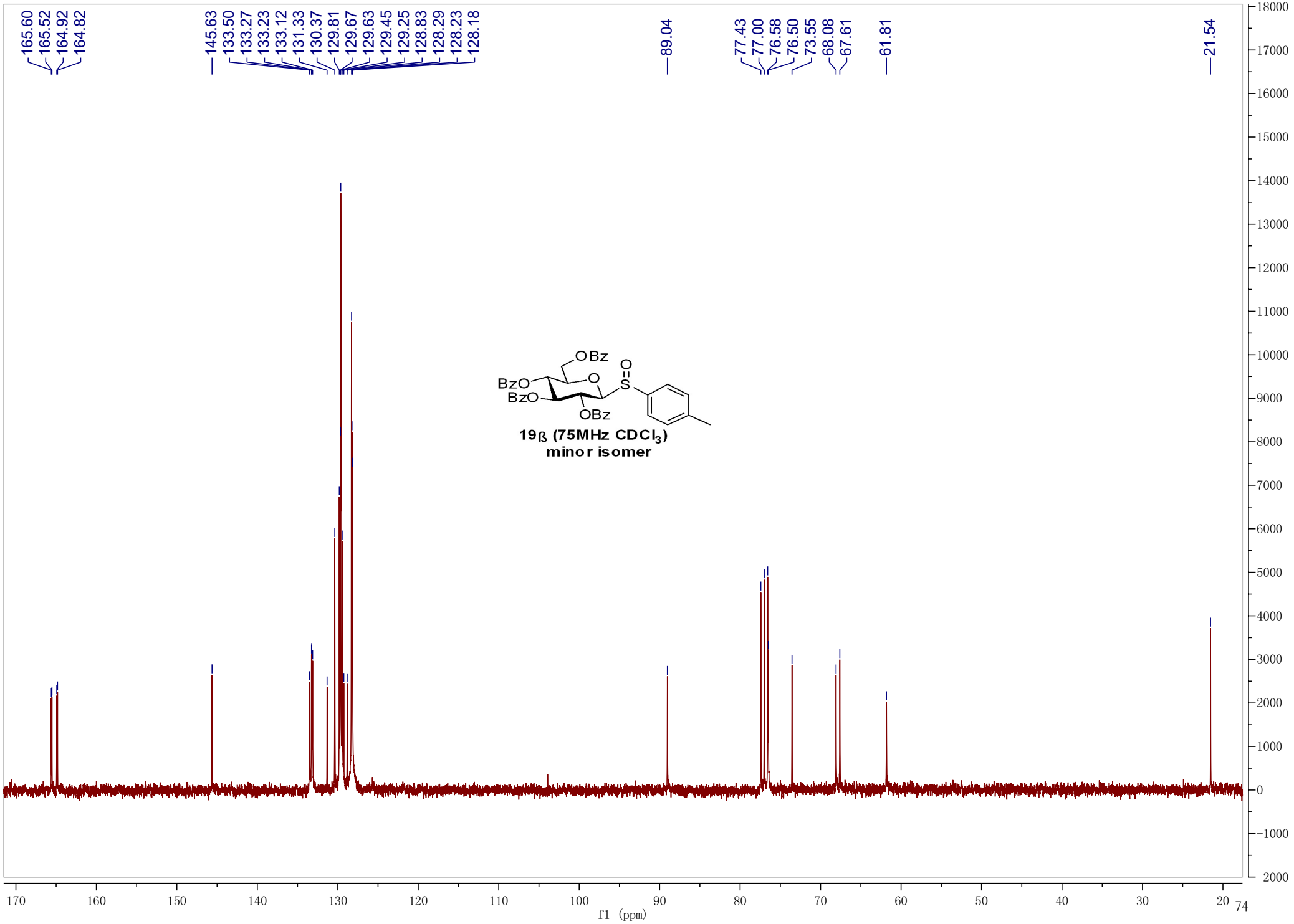
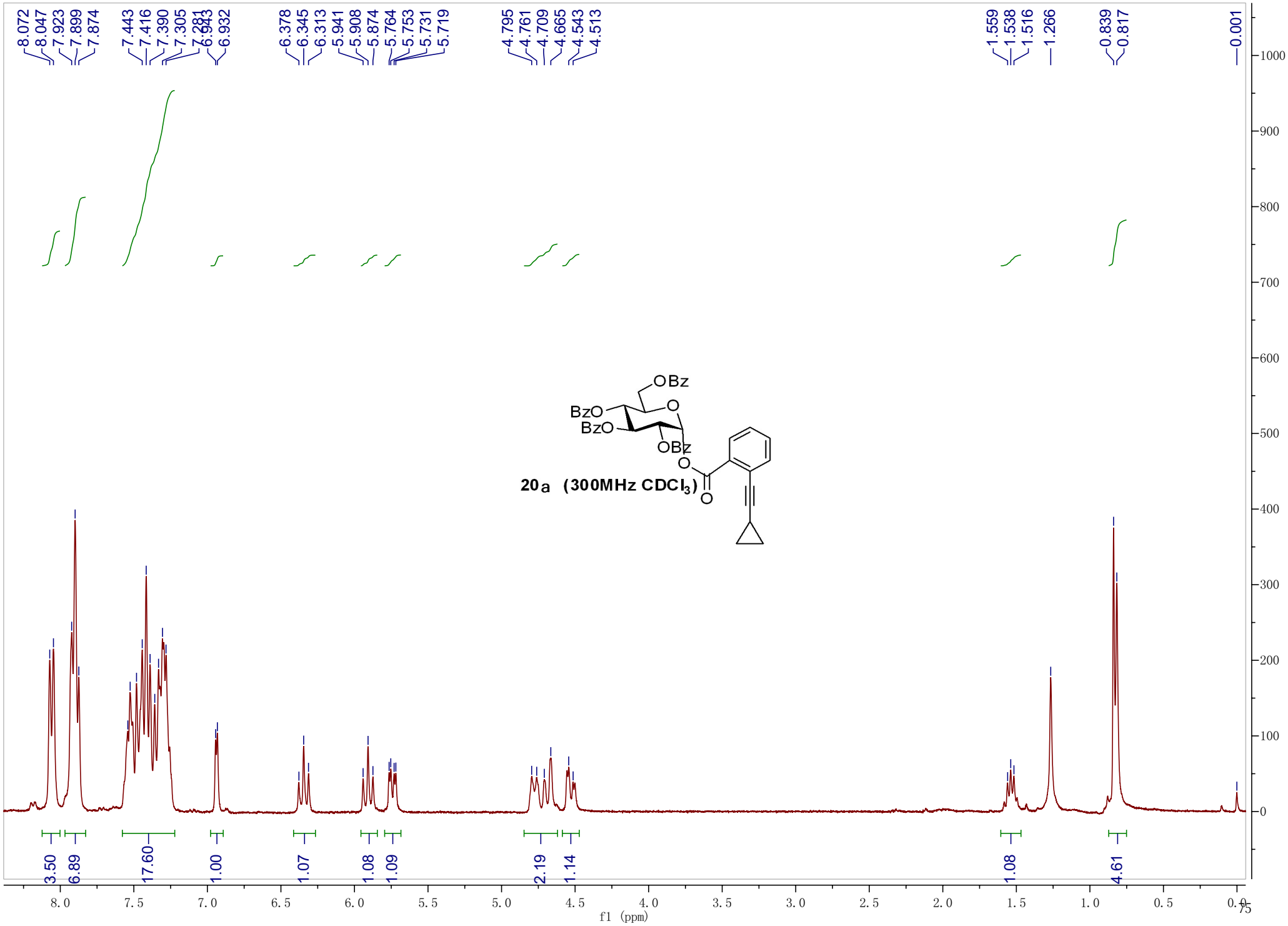
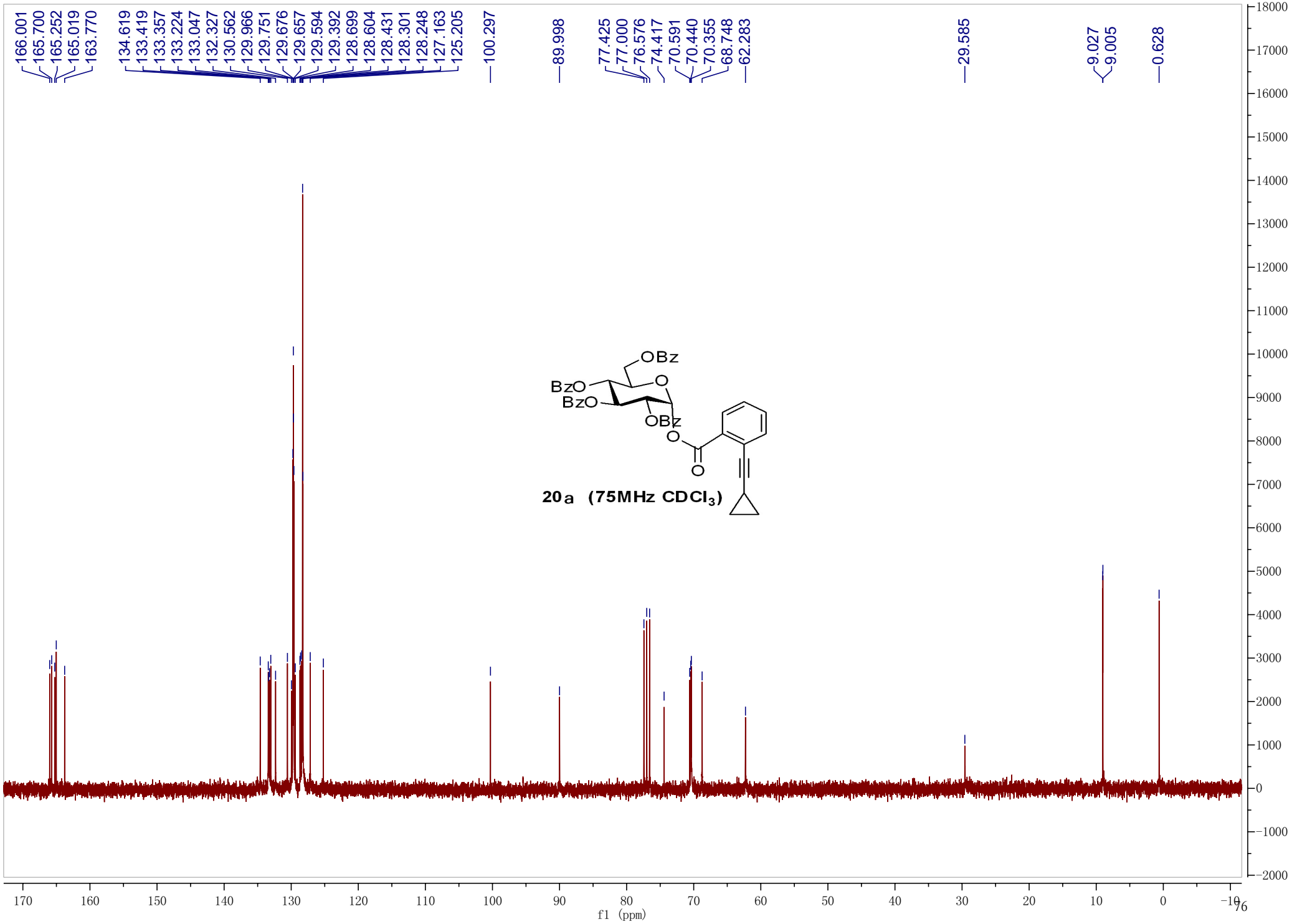
7.787
7.618
7.591
7.568
7.493
7.458
7.445
7.420
7.399
7.357
7.330
7.303
7.275
7.249
7.101
7.075
5.973
5.942
5.707
5.676
5.644
5.607
5.574
5.542
4.937
4.904
4.745
4.737
4.703
4.444
4.430
4.403
4.388
4.262
4.231
2.132
0.000
OBz
BzO
BzO
O
S
O
OBz
19ß (300MHz CDCl3)
major isomer
2.14
5.97
14.93
2.17
1.00
1.89
0.92
0.95
0.95
0.99
2.87
f1 (ppm)







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133.357
133.224
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129.751
129.676
129.657
129.594
129.392
128.699
128.604
128.431
128.301
128.248
127.163
125.205
100.297
89.998
77.425
77.000
76.576
74.417
70.591
70.440
70.355
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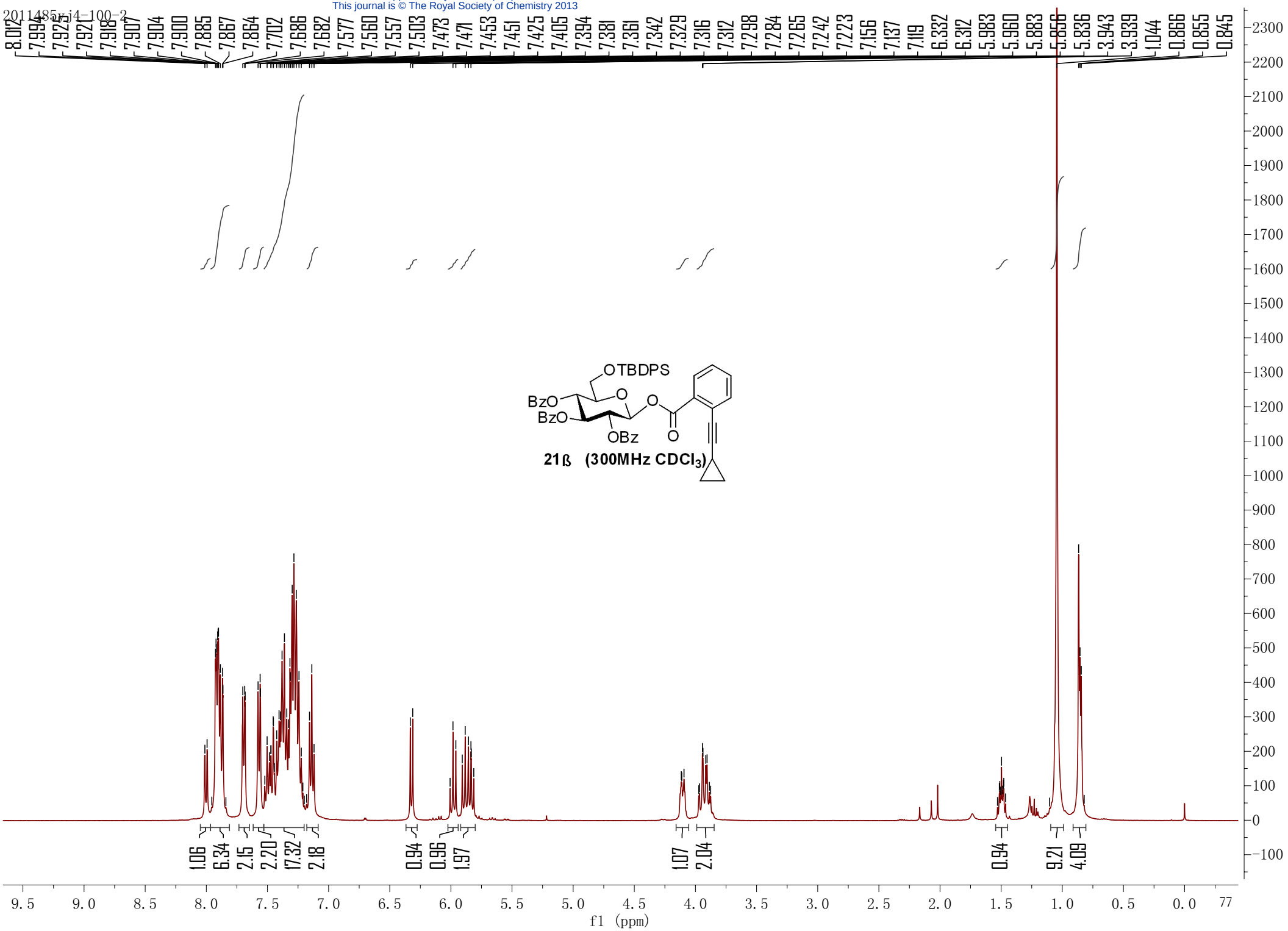
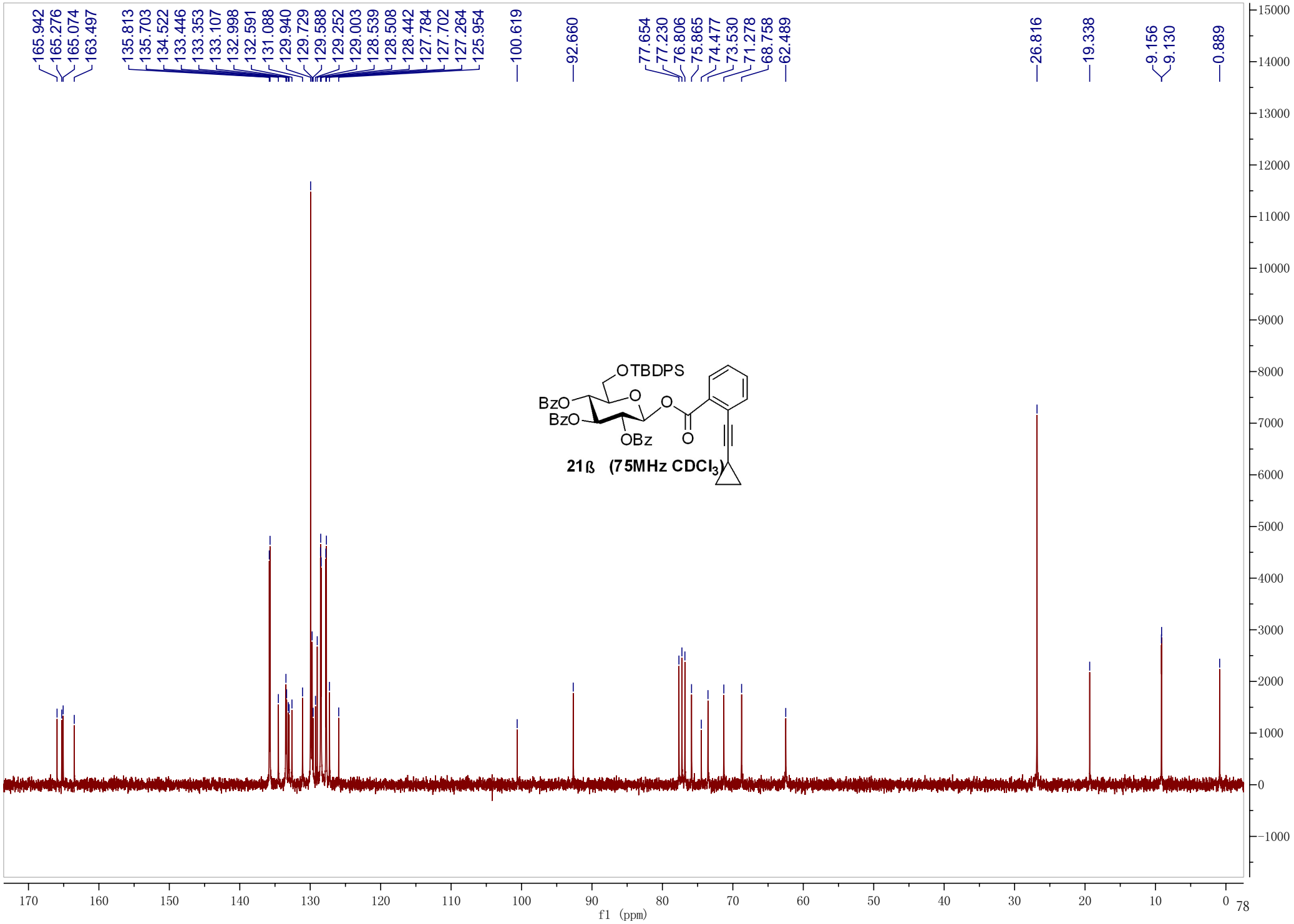
OBz
O
O
20a (75MHz CDCl3)
f1 (ppm)

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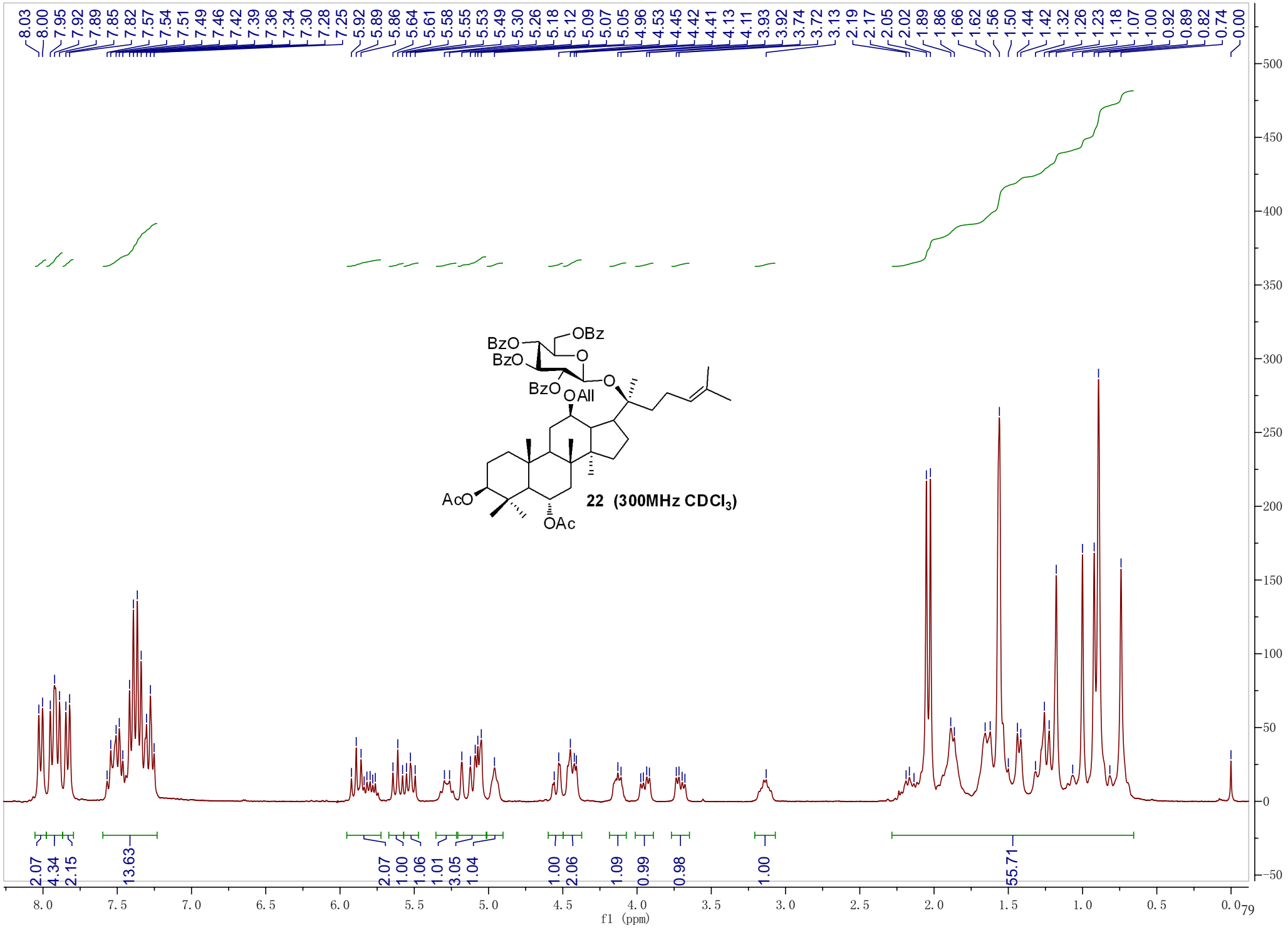
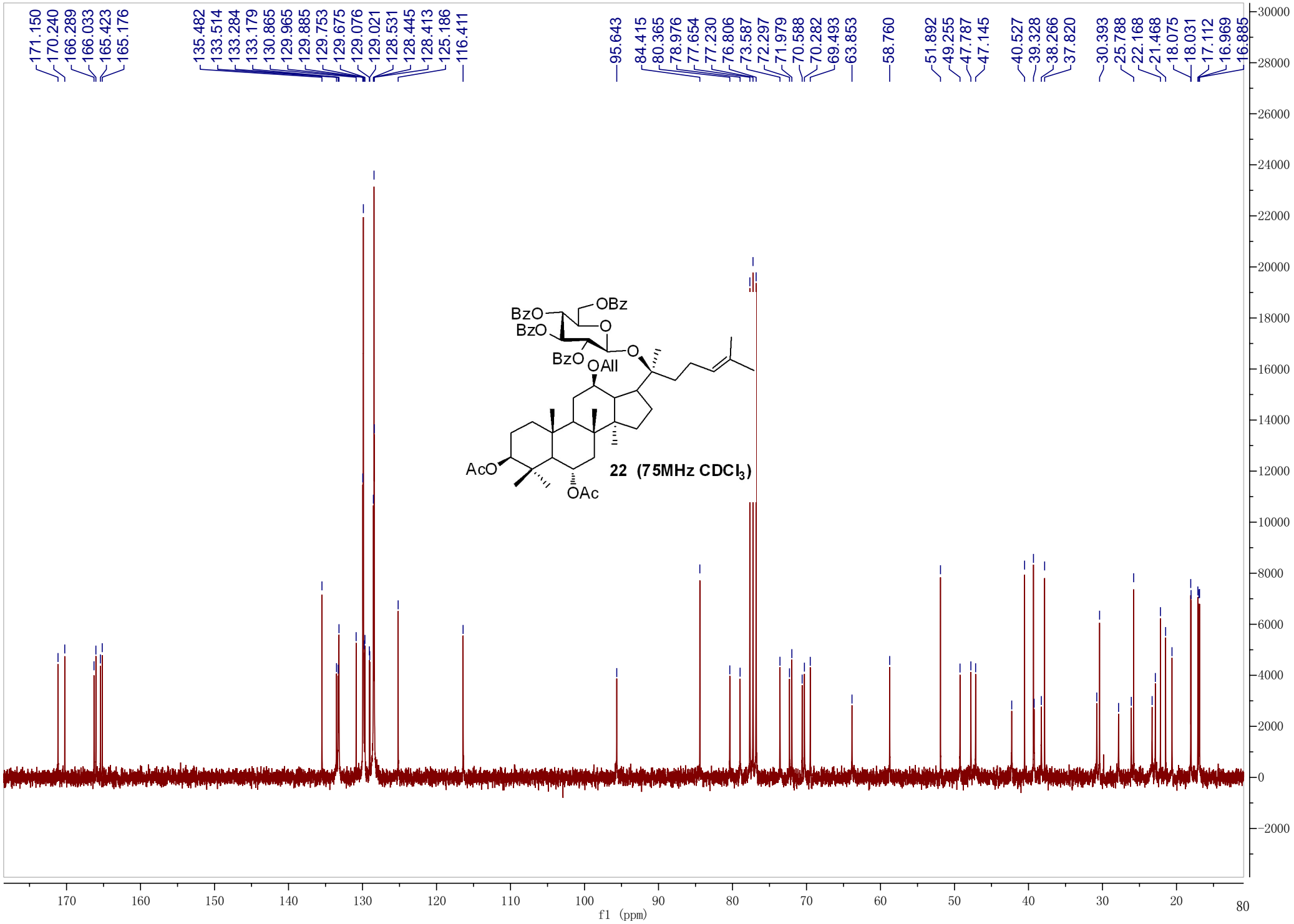
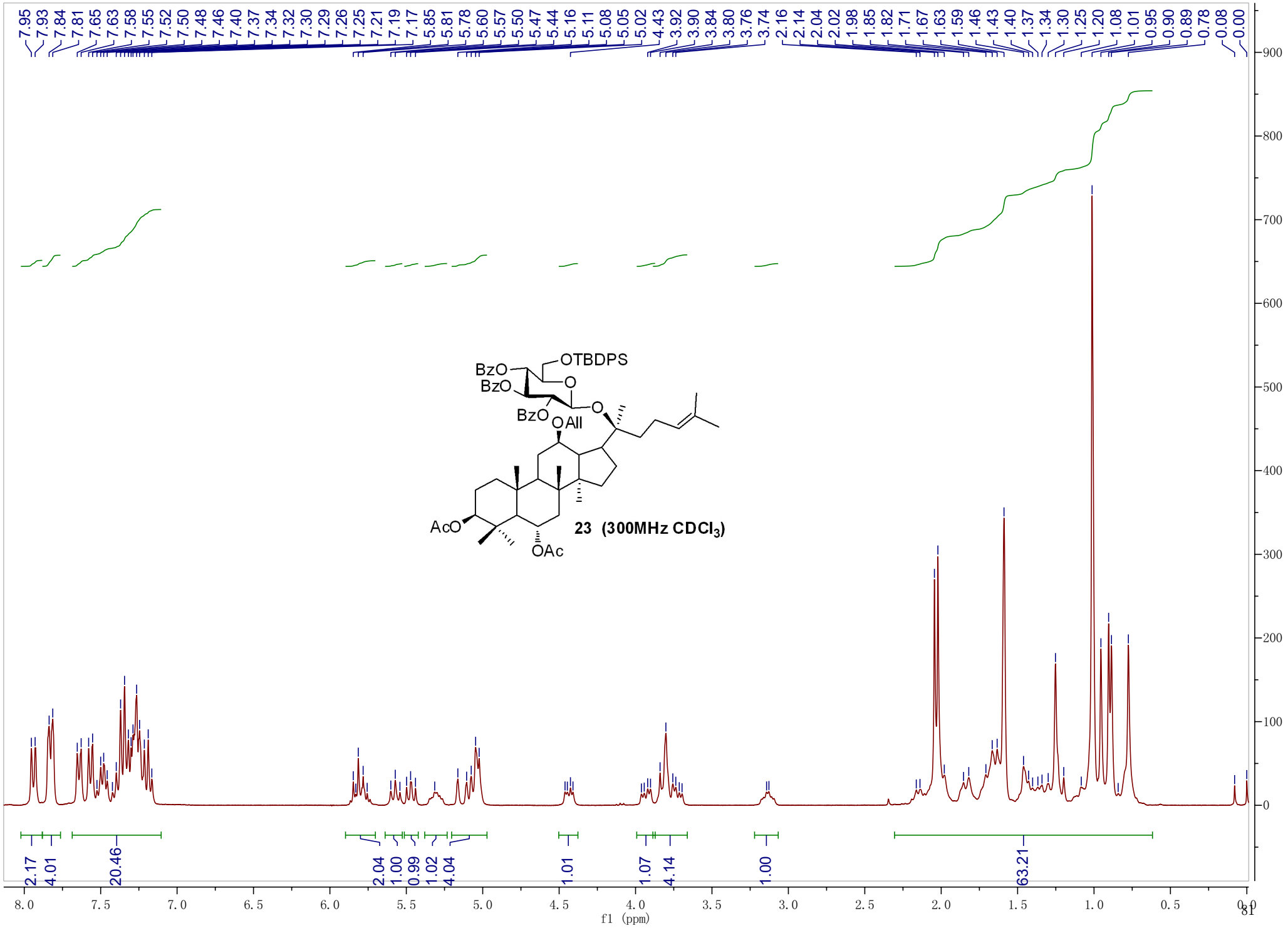
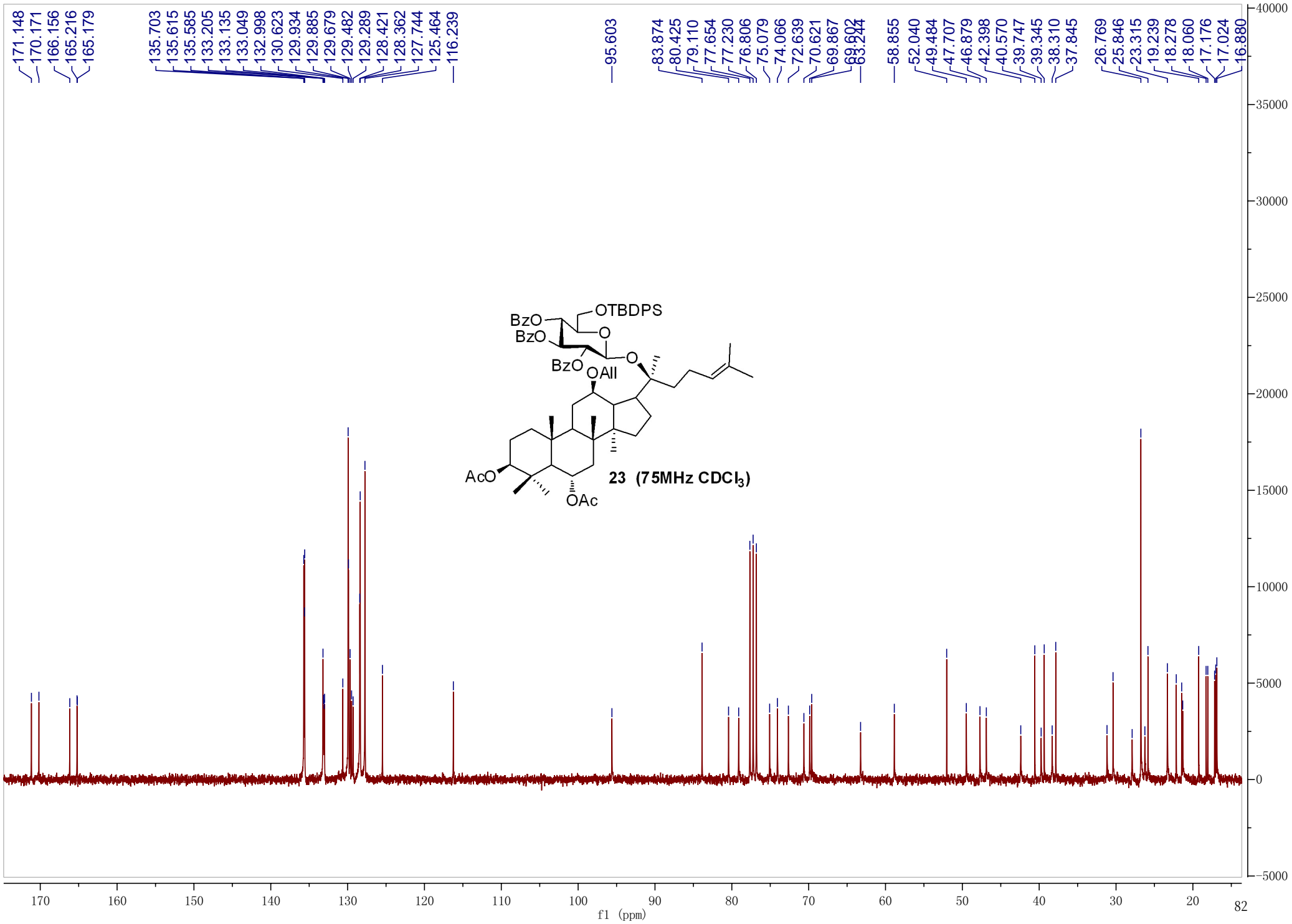
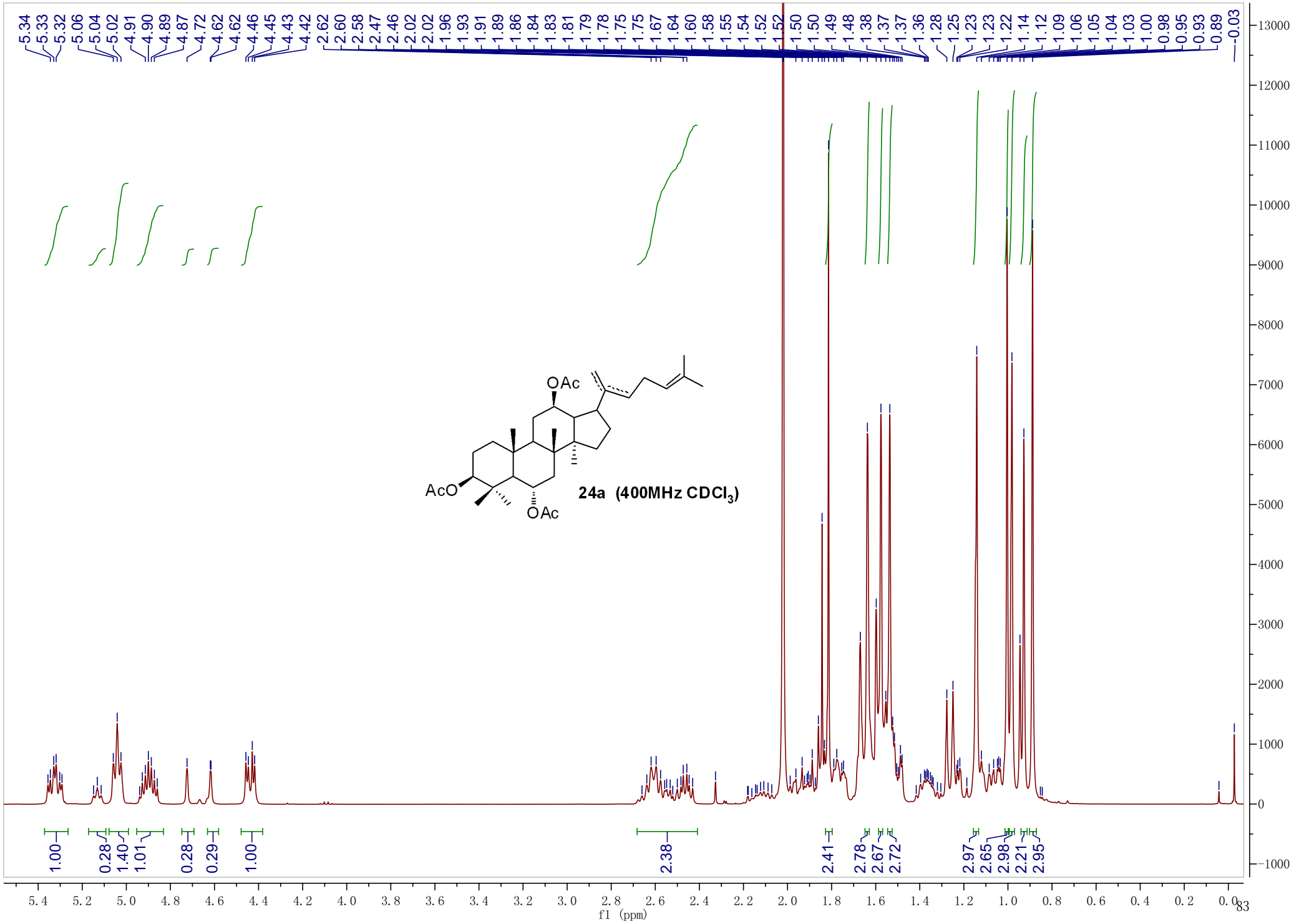
135.813
135.703
134.522
133.446
133.353
133.107
132.998
132.591
131.088
129.940
129.729
129.588
129.252
129.003
128.539
128.508
128.442
127.784
127.702
127.264
125.954
100.619
92.660
77.654
77.230
76.806
75.865
74.477
73.530
71.278
68.758
62.489
26.816
19.338
9.156
9.130
0.889
OTBDPS
BzO
BzO
OBz
O
O
O
21ß (75MHz CDCl3)
f1 (ppm)

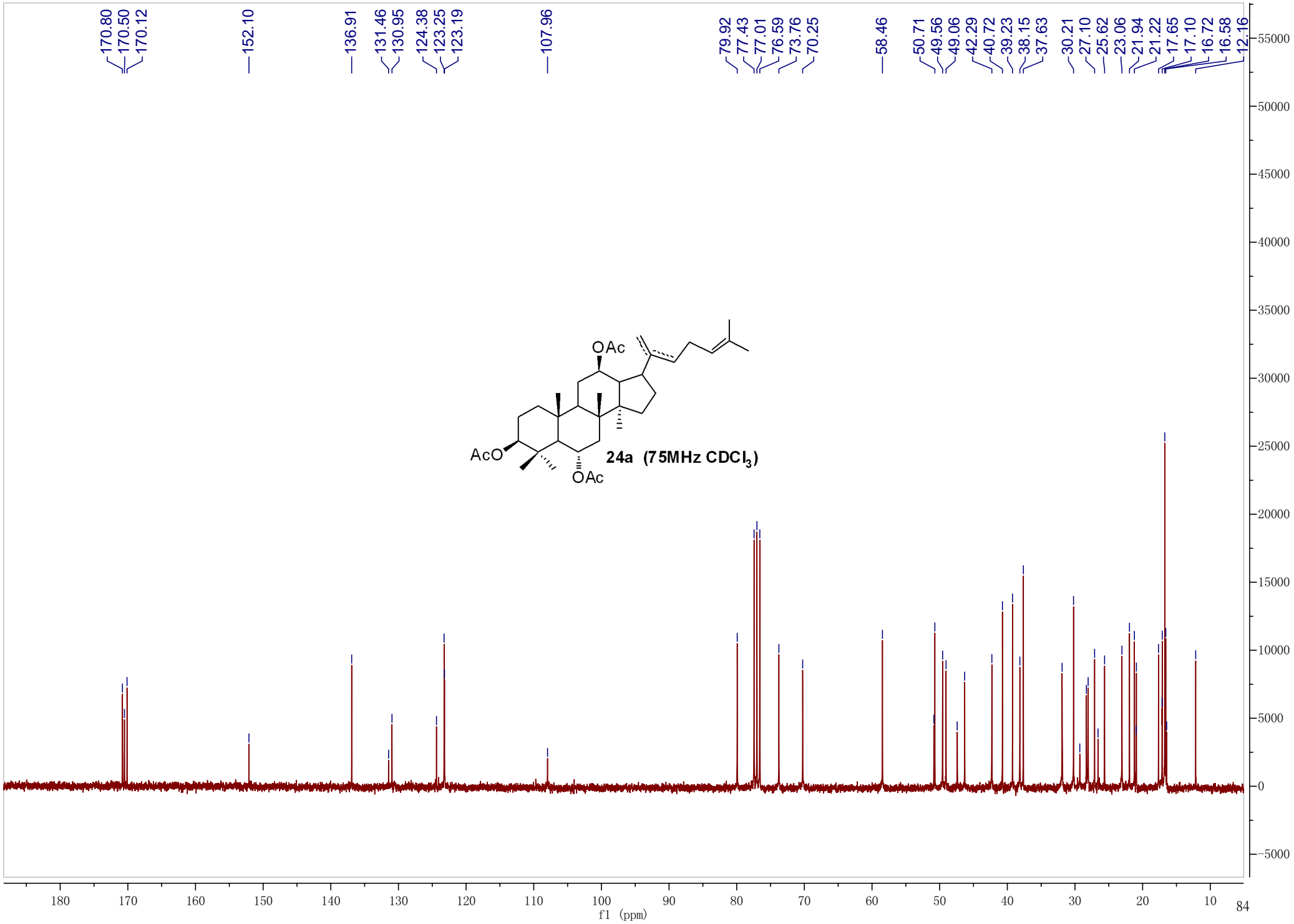

8.03 8.00 7.95 7.92 7.89 7.85 7.82 7.57 7.54 7.51 7.49 7.46 7.42 7.39 7.36 7.34 7.30 7.28 7.25
5.92 5.89 5.86 5.64 5.61 5.58 5.55 5.53 5.49 5.30 5.26 5.18 5.12 5.09 5.07 5.05 4.96 4.53 4.45 4.42 4.41 4.13 4.11 3.93 3.92 3.74 3.72 3.13
2.19 2.17 2.05 2.02 1.89 1.86 1.66 1.62 1.56 1.50 1.44 1.42 1.32 1.26 1.23 1.18 1.07 1.00 0.92 0.89 0.82 0.74 0.00
BzO
BzO
OBz
O
BzO
O
OAll
AcO
OAc
22 (300MHz CDCl3)
2.07 4.34 2.15 13.63 2.07 1.00 1.06 1.01 3.05 1.04 1.00 2.06 1.09 0.99 0.98 1.00 55.71
f1 (ppm)

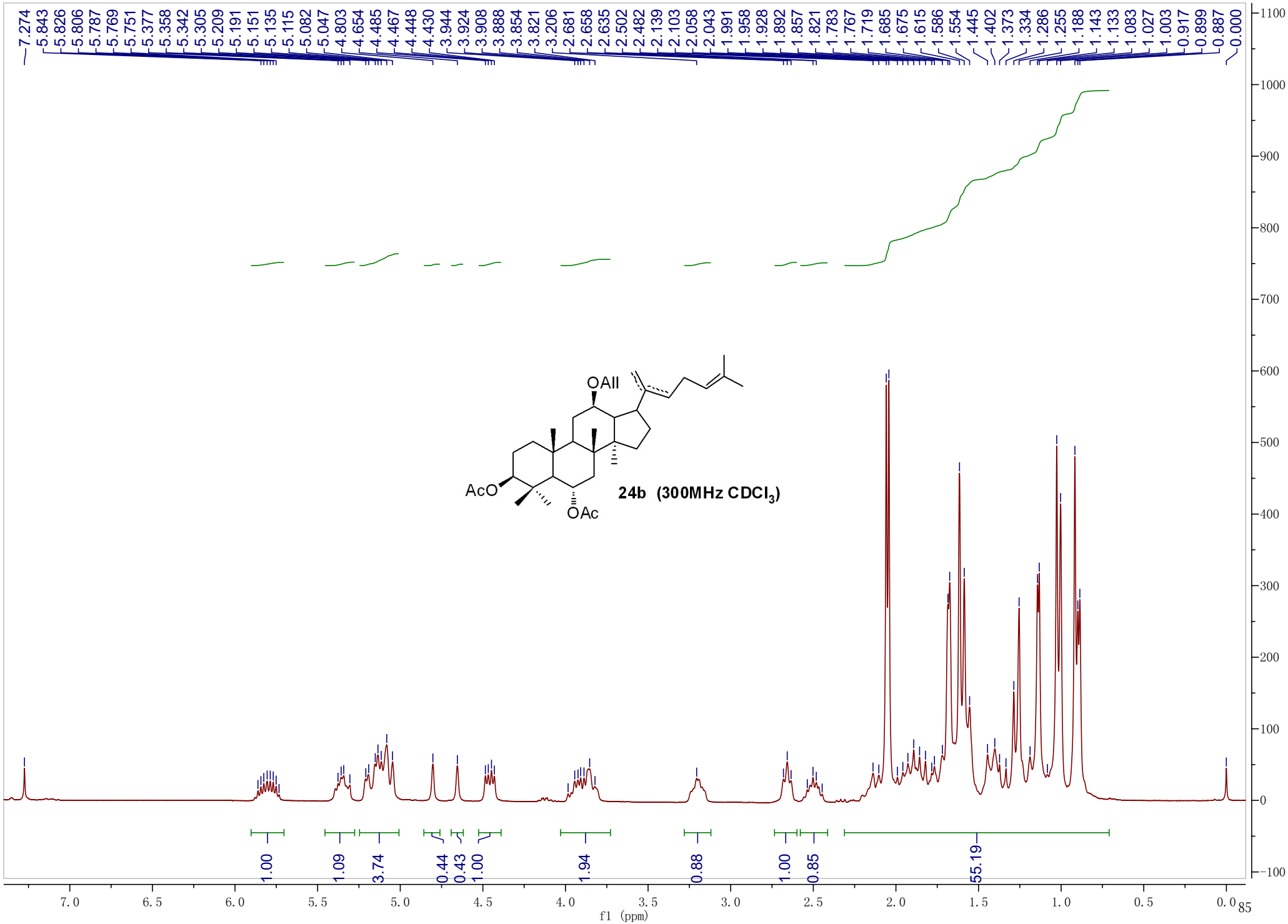


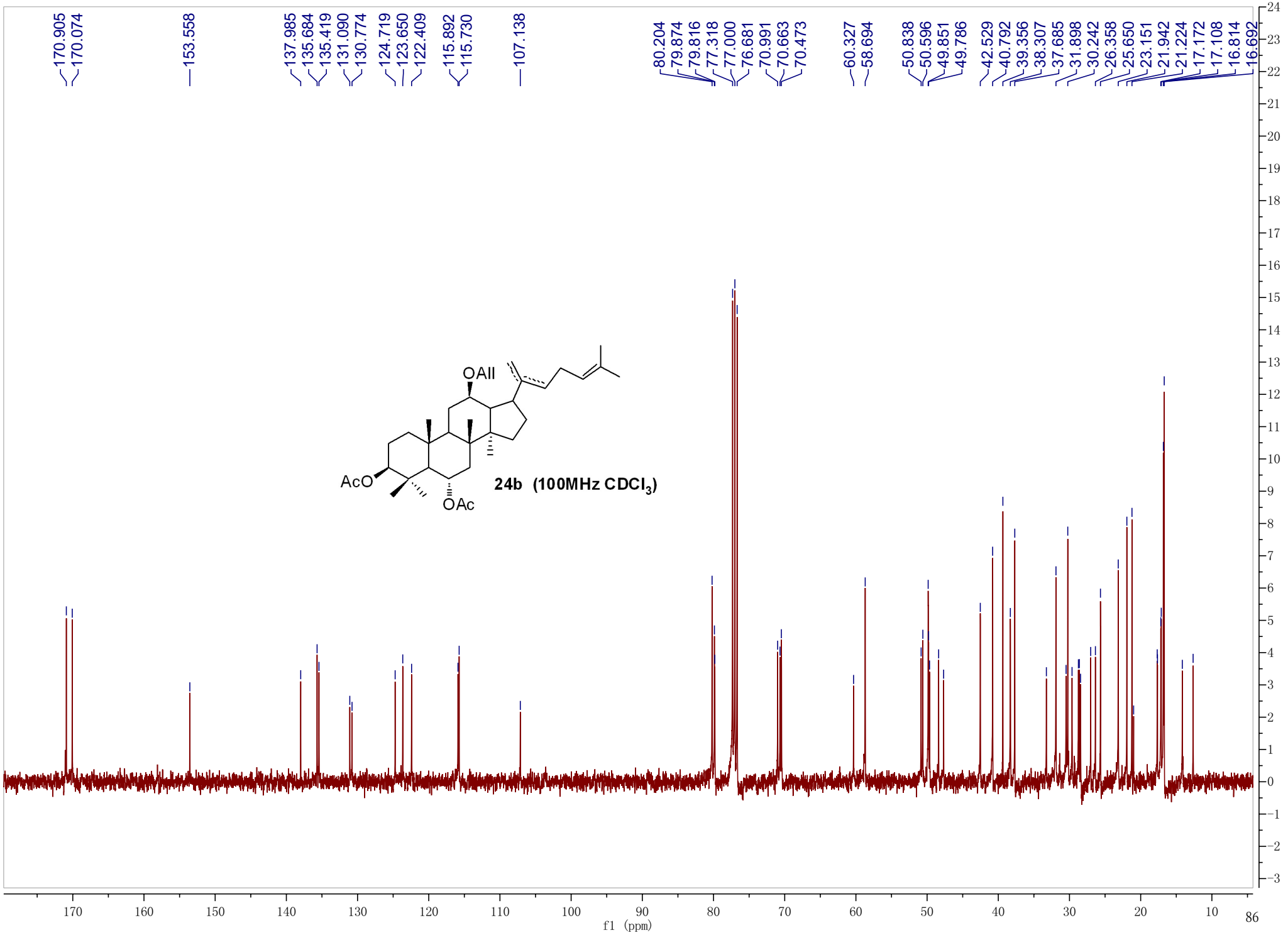

7.95 7.93 7.84 7.81 7.65 7.63 7.58 7.55 7.52 7.50 7.48 7.46 7.40 7.37 7.34 7.32 7.30 7.29 7.26 7.25 7.21 7.19 7.17 5.85 5.81 5.78 5.60 5.57 5.50 5.47 5.44 5.16 5.11 5.08 5.05 5.02 4.43 3.92 3.90 3.84 3.80 3.76 3.74 2.16 2.14 2.04 2.02 1.98 1.85 1.82 1.71 1.67 1.63 1.59 1.46 1.43 1.40 1.37 1.34 1.30 1.25 1.20 1.08 1.01 0.95 0.90 0.89 0.78 0.08 0.00
BzO
BzO
OTBDPS
O
BzO
OAll
O
AcO
OAc
23 (300MHz CDCl3)
2.17 4.01 20.46 2.04 1.00 0.99 1.02 4.04 1.01 1.07 4.14 1.00 63.21
f1 (ppm)

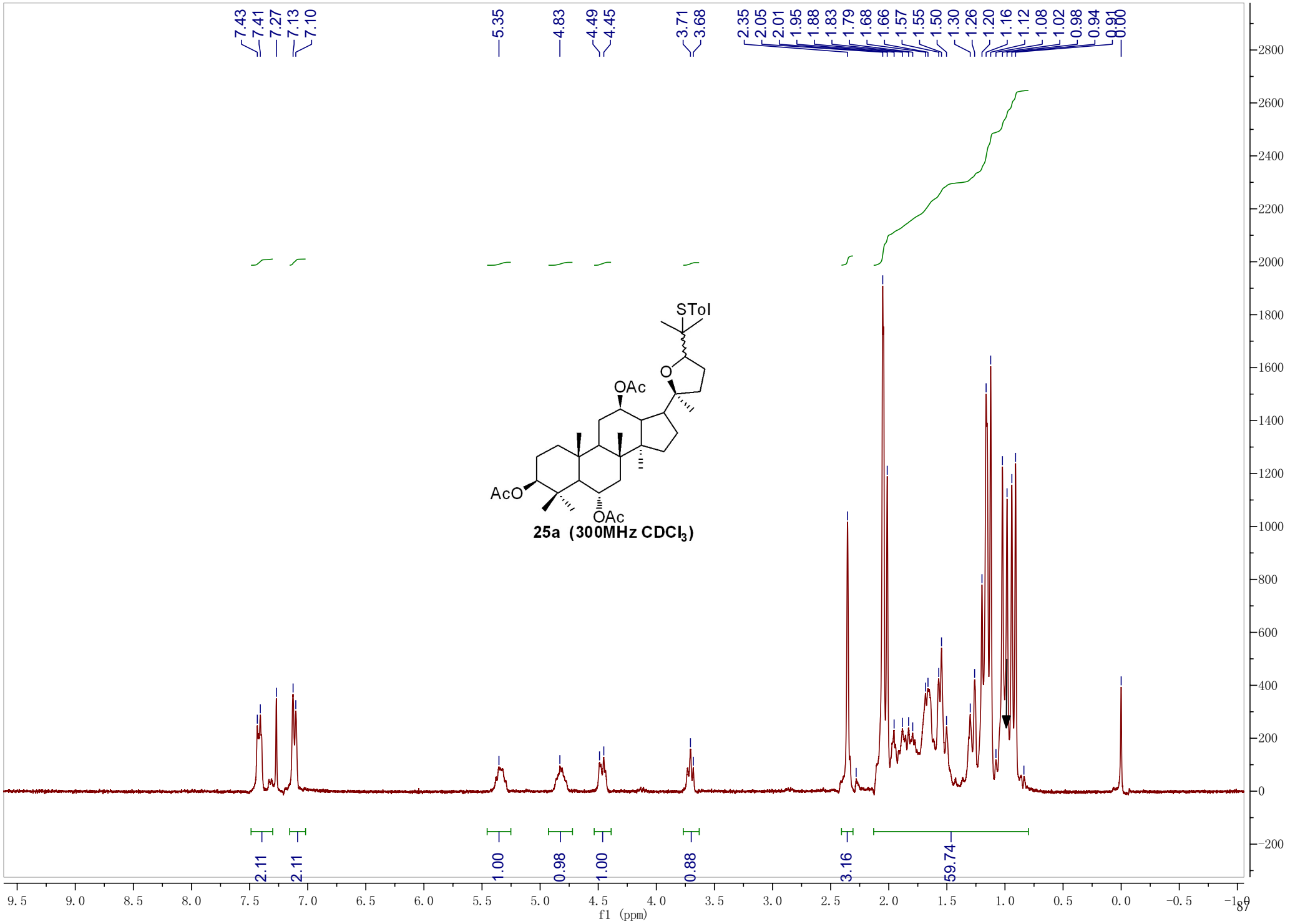


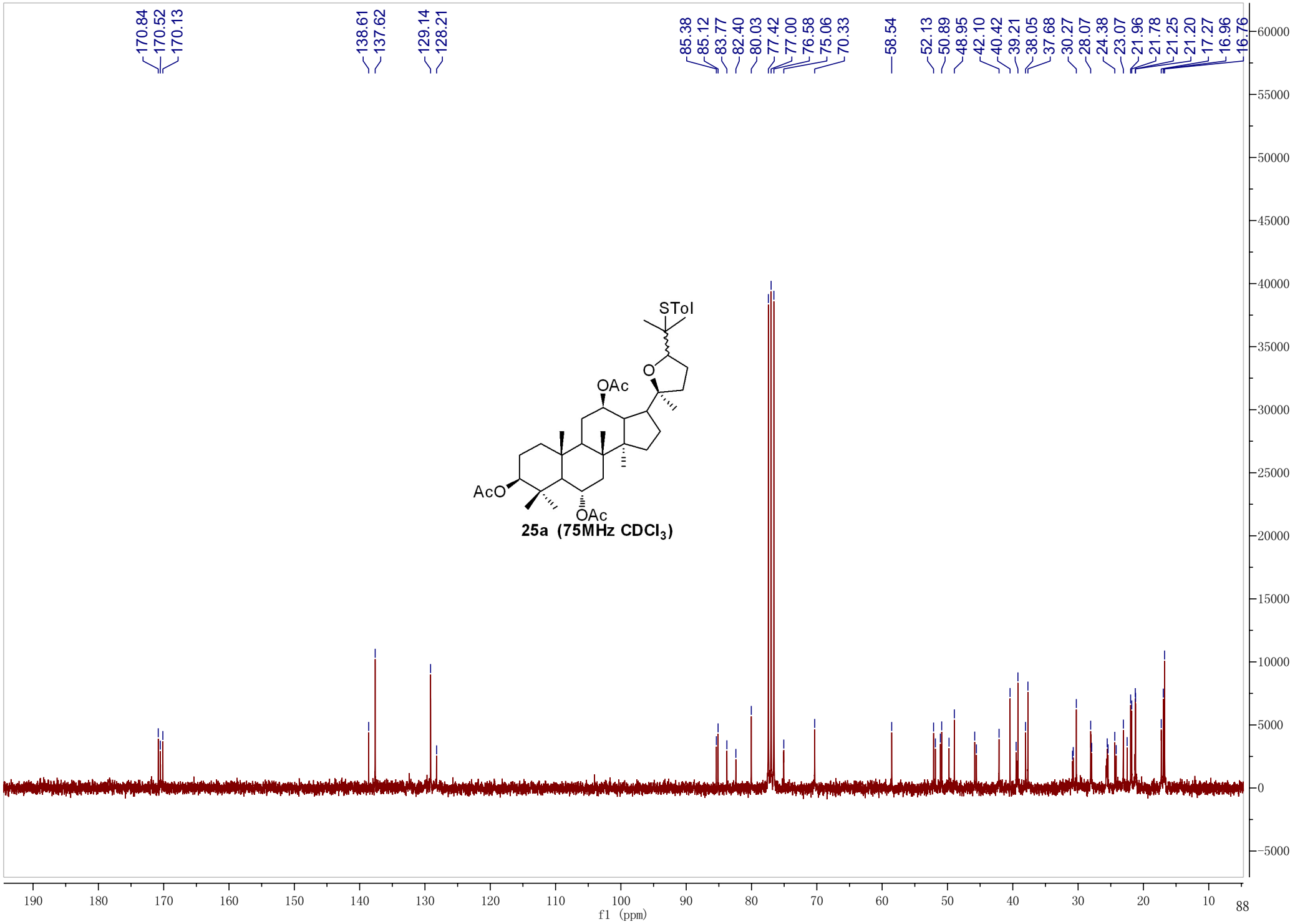

5.34 5.33 5.32 5.06 5.04 5.02 4.91 4.90 4.89 4.87 4.72 4.62 4.62 4.46 4.45 4.43 4.42 2.62 2.60 2.58 2.47 2.46 2.02 2.02 1.96 1.93 1.91 1.89 1.86 1.84 1.83 1.81 1.79 1.78 1.75 1.75 1.67 1.64 1.60 1.58 1.55 1.54 1.52 1.52 1.50 1.50 1.49 1.48 1.38 1.37 1.37 1.36 1.28 1.25 1.23 1.23 1.22 1.14 1.12 1.09 1.06 1.05 1.04 1.03 1.00 0.98 0.95 0.93 0.89 -0.03
OAc
AcO
OAc
24a (400MHz CDCl3)
1.00 0.28 1.40 1.01 0.28 0.29 1.00 2.38 2.41 2.78 2.67 2.72 2.97 2.65 2.98 2.21 2.95
f1 (ppm)

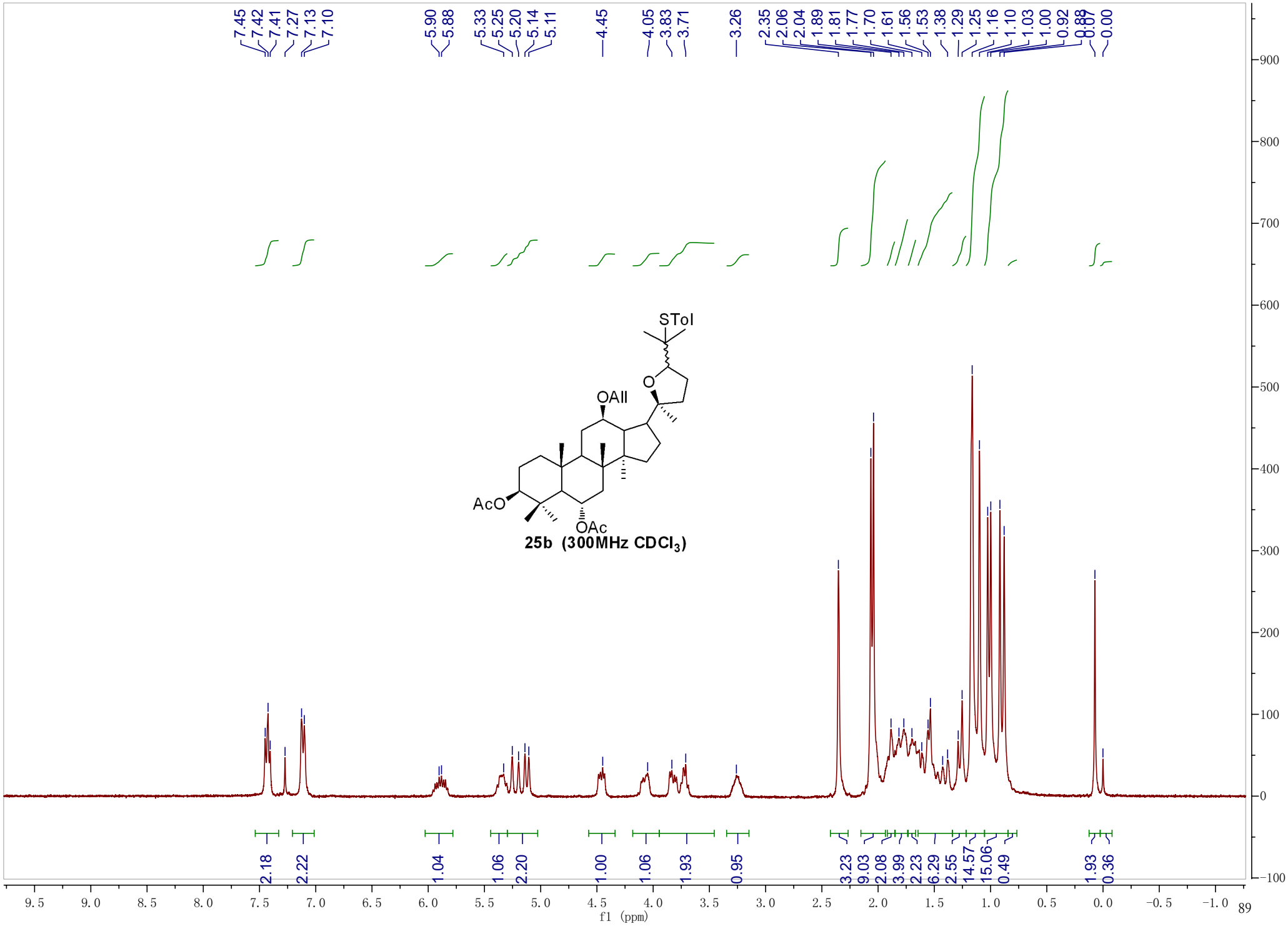

170.80
170.50
170.12
152.10
136.91
131.46
130.95
124.38
123.25
123.19
107.96
79.92
77.43
77.01
76.59
73.76
70.25
58.46
50.71
49.56
49.06
42.29
40.72
39.23
38.15
37.63
30.21
27.10
25.62
23.06
21.94
21.22
17.65
17.10
16.72
16.58
12.16
OAc
AcO
OAc
24a (75MHz CDCl3)
f1 (ppm)

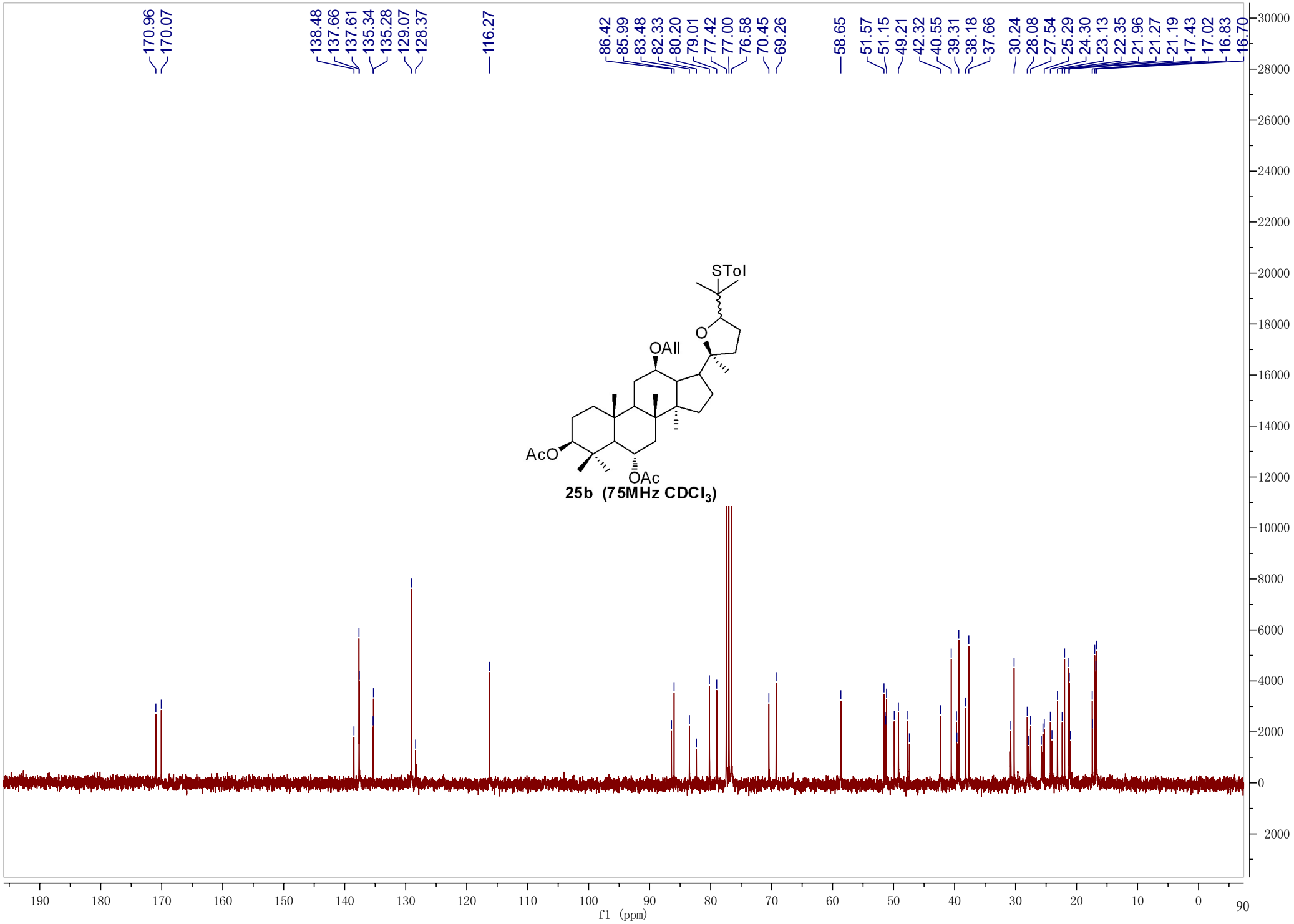


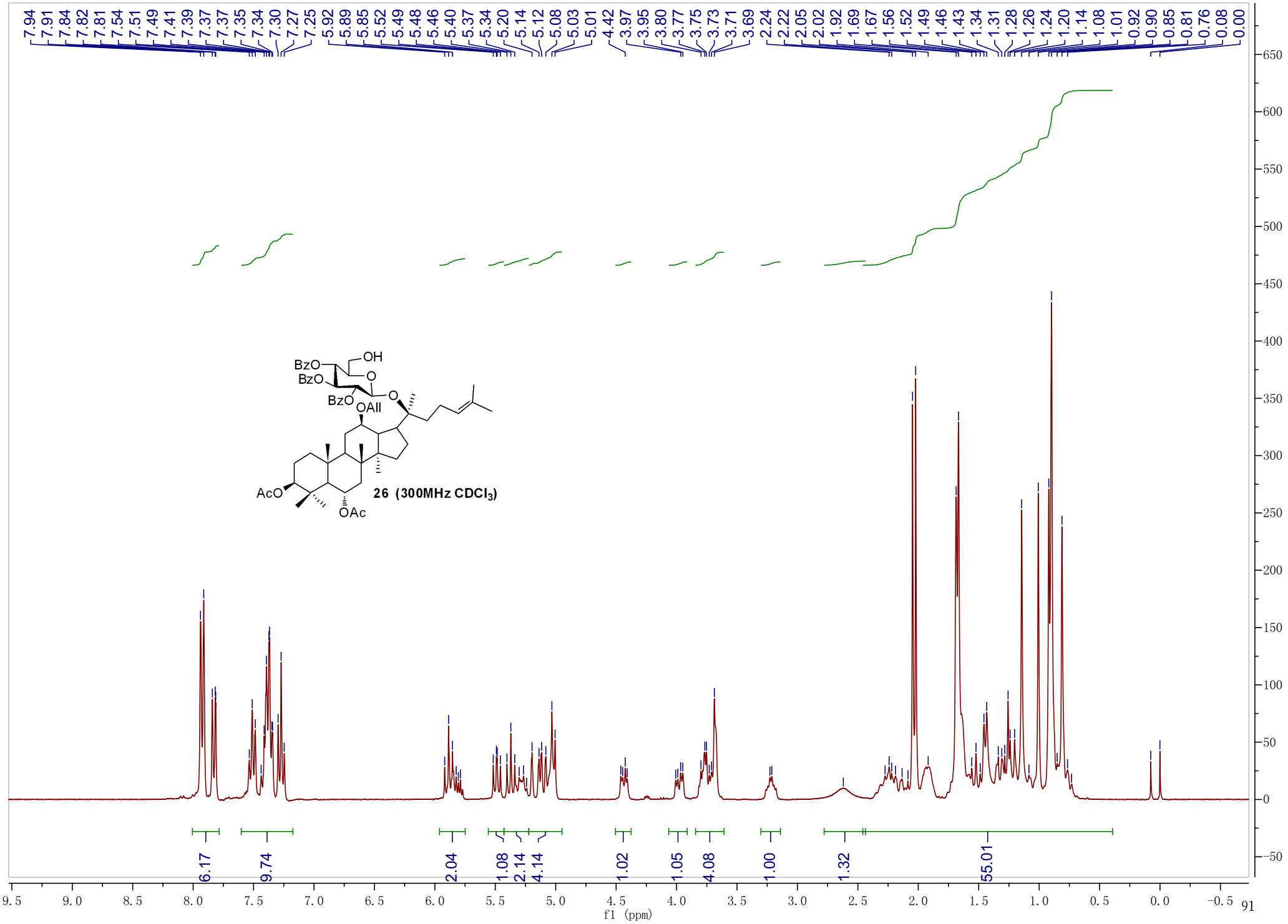


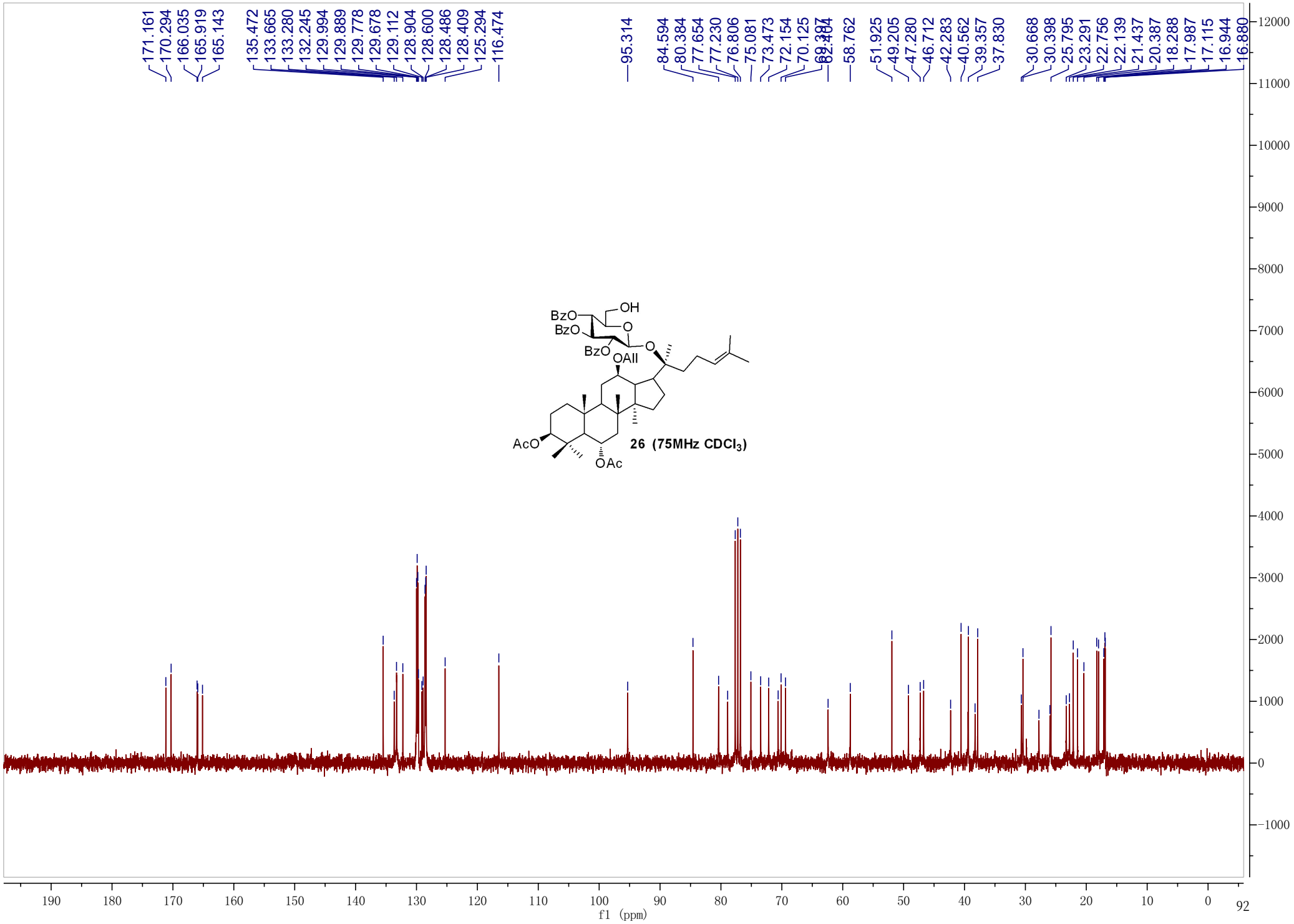

7.43
7.41
7.27
7.13
7.10
5.35
4.83
4.49
4.45
3.71
3.68
2.35
2.05
2.01
1.95
1.88
1.83
1.79
1.68
1.66
1.57
1.55
1.50
1.30
1.26
1.20
1.16
1.12
1.08
1.02
0.98
0.94
0.91
0.00
STol
O
OAc
AcO
OAc
25a (300MHz CDCl3)
2.11
2.11
1.00
0.98
1.00
0.88
3.16
59.74
f1 (ppm)

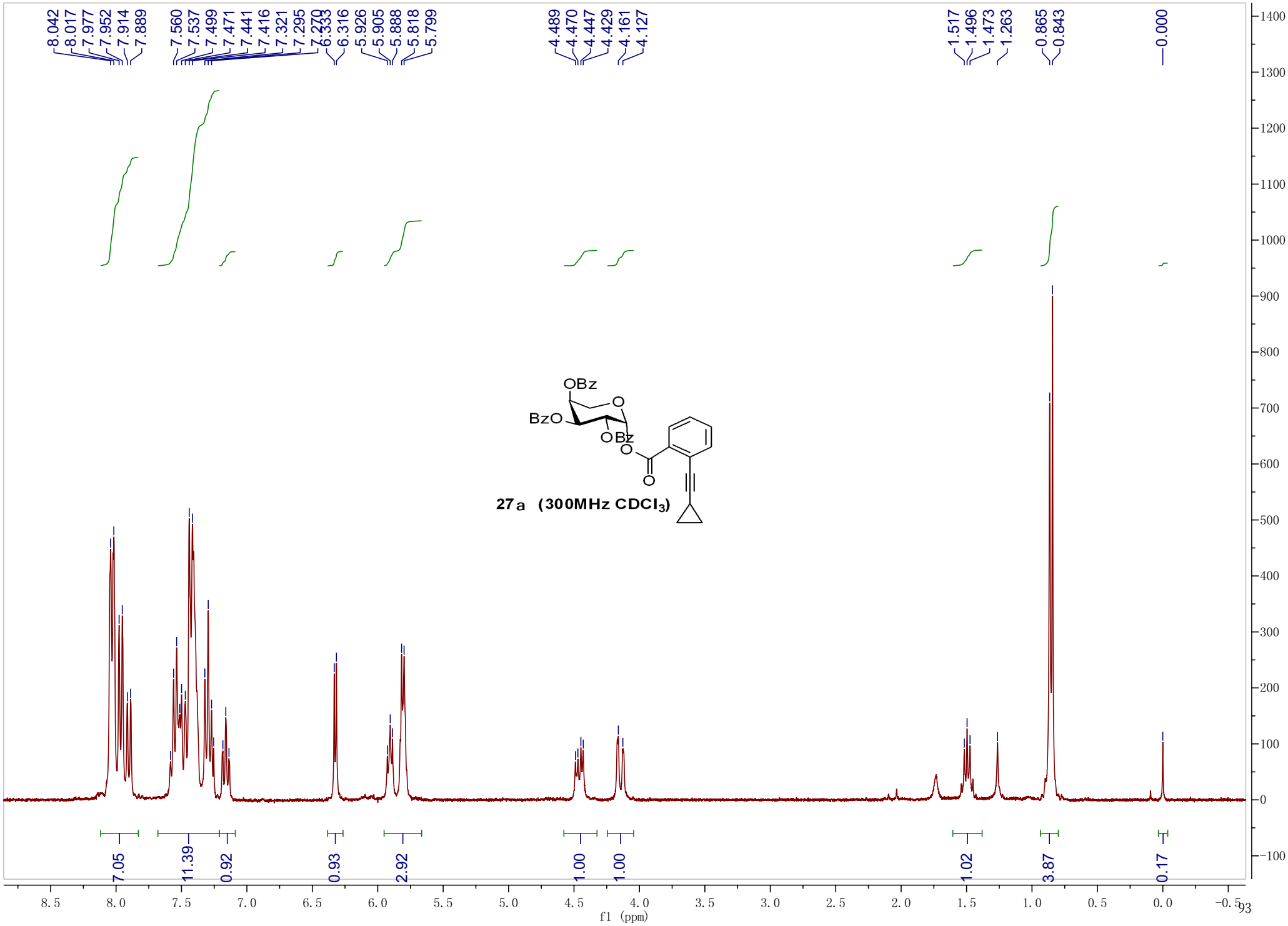


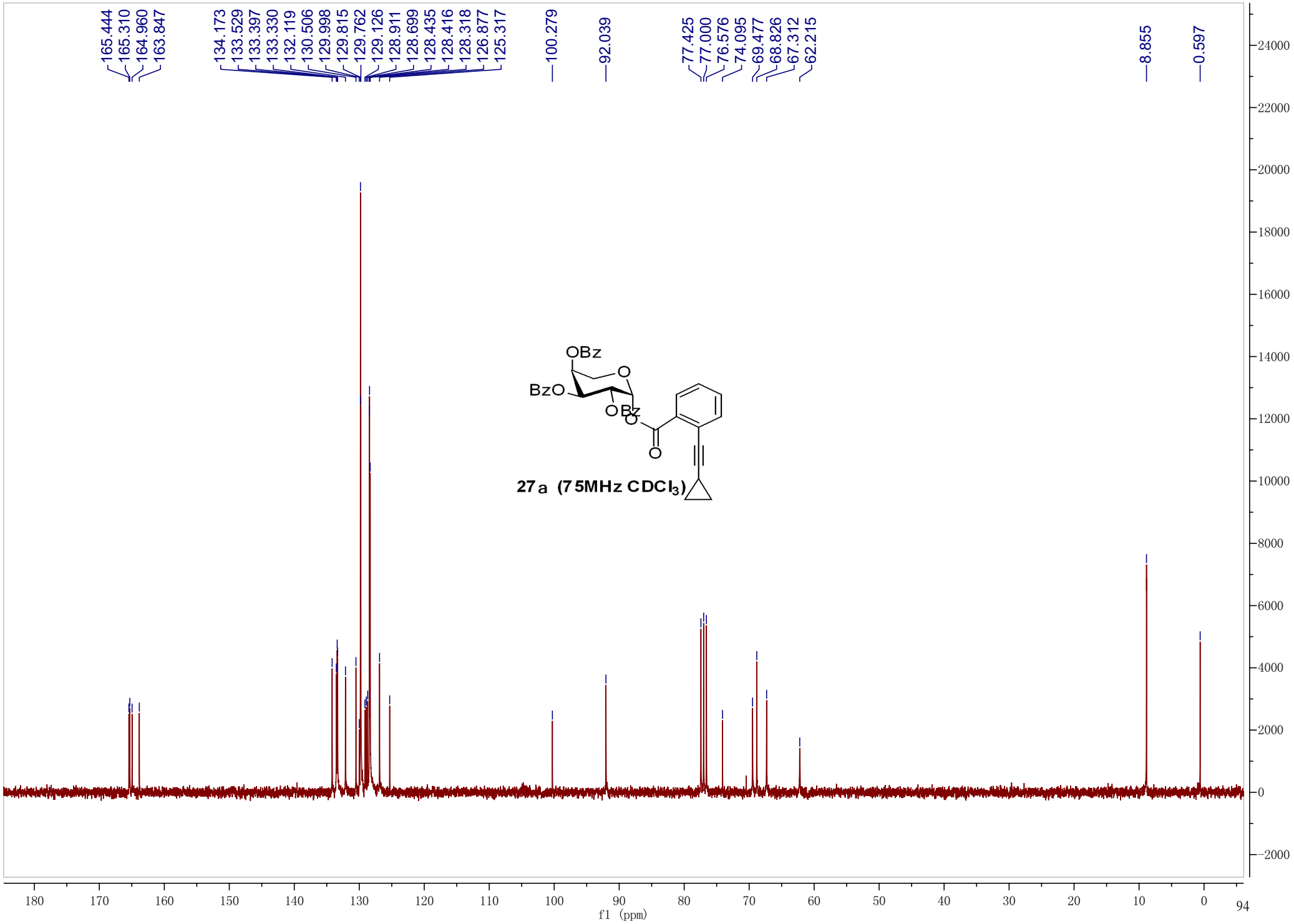


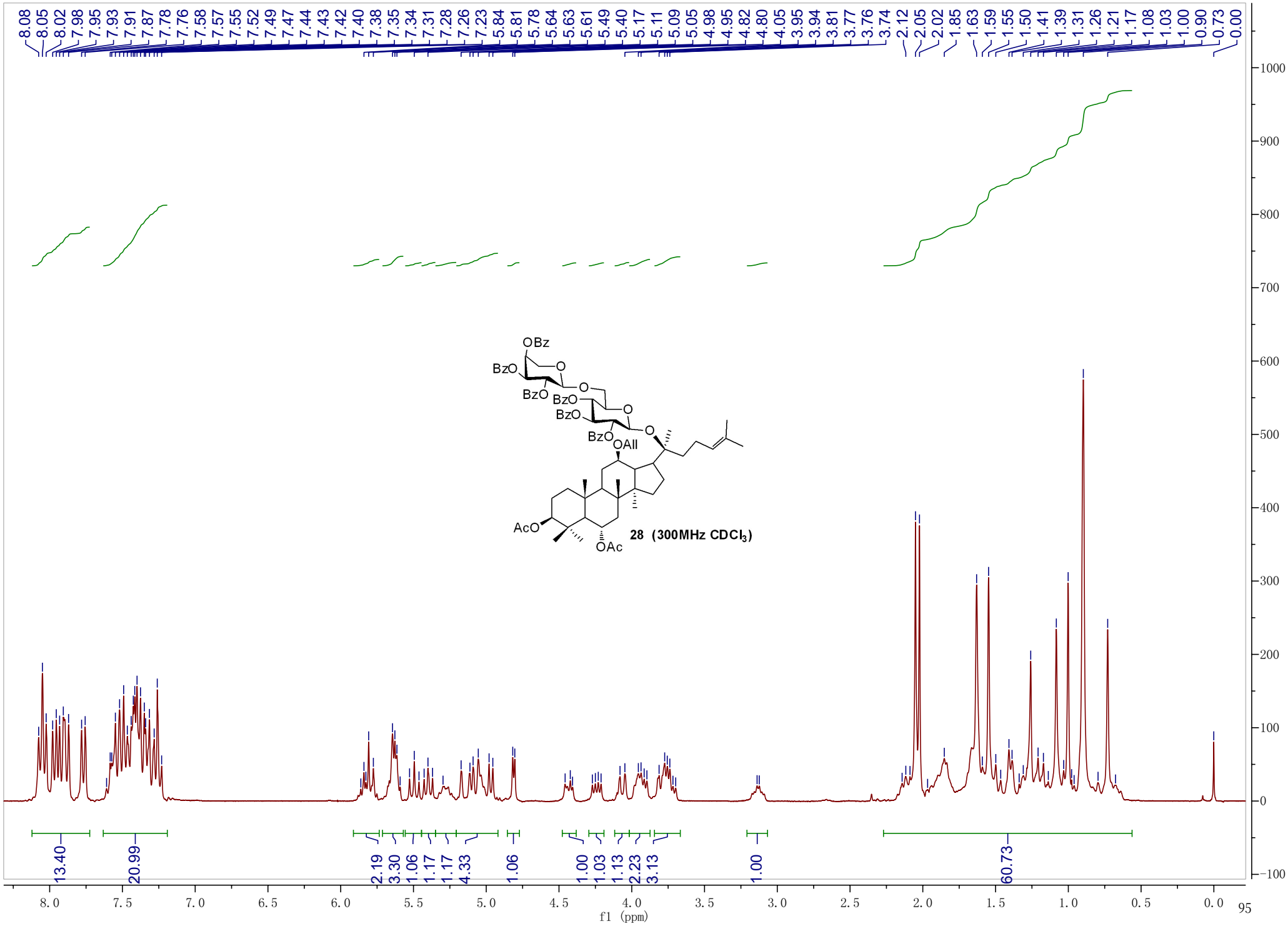


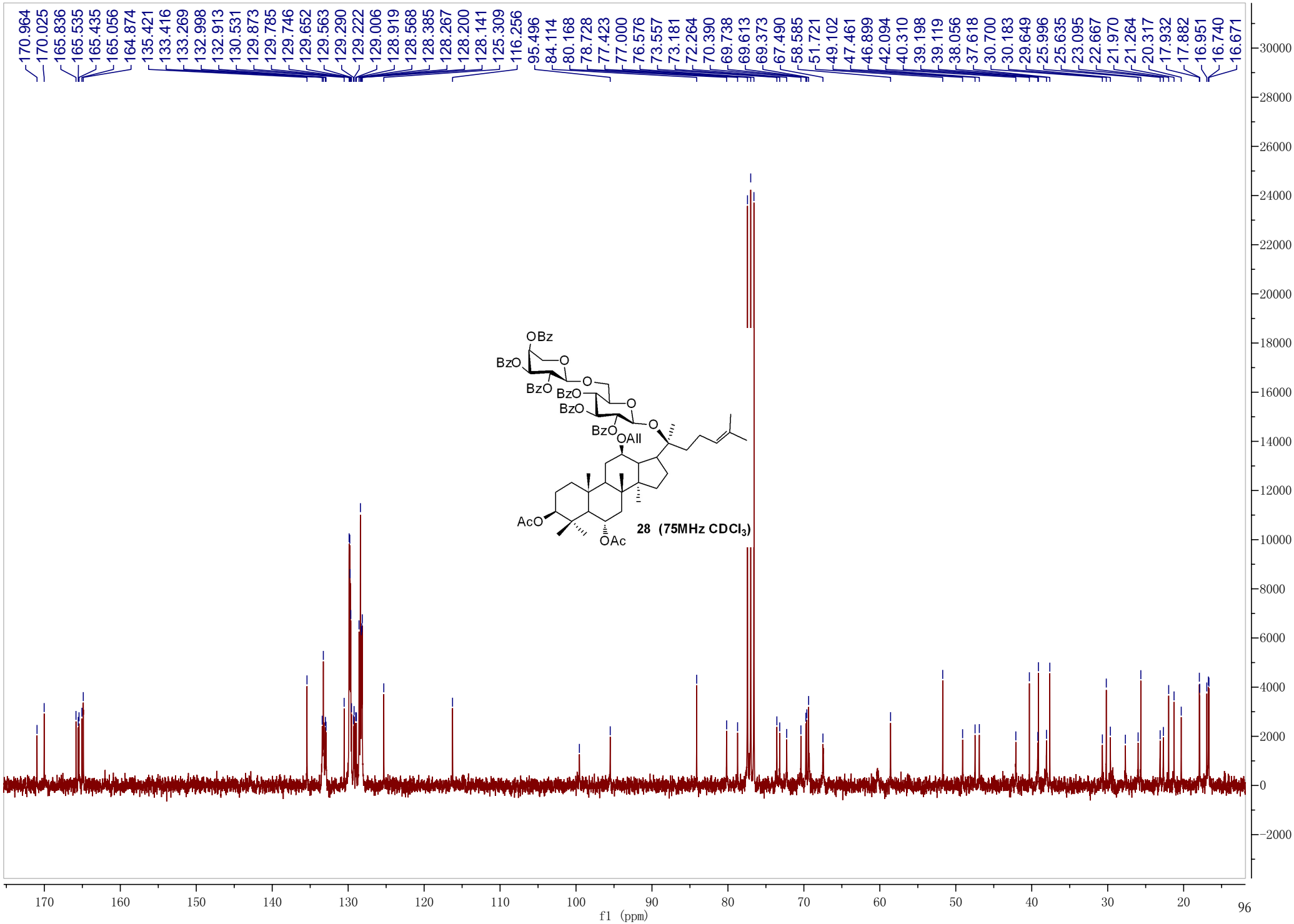

7.94 7.91 7.84 7.82 7.81 7.54 7.51 7.49 7.41 7.39 7.37 7.37 7.35 7.34 7.30 7.27 7.25
5.92 5.89 5.85 5.52 5.49 5.48 5.46 5.40 5.37 5.34 5.20 5.14 5.12 5.08 5.03 5.01
4.42 3.97 3.95 3.80 3.77 3.75 3.73 3.71 3.69
2.24 2.22 2.05 2.02 1.92 1.69 1.67 1.56 1.52 1.49 1.46 1.43 1.34 1.31 1.28 1.26 1.24 1.20 1.14 1.08 1.01 0.92 0.90 0.85 0.81 0.76 0.08 0.00
BzO
BzO
BzO
OH
O
O
OAll
AcO
OAc
26 (300MHz CDCl3)
6.17
9.74
2.04
1.08
2.14
4.14
1.02
1.05
4.08
1.00
1.32
55.01
f1 (ppm)

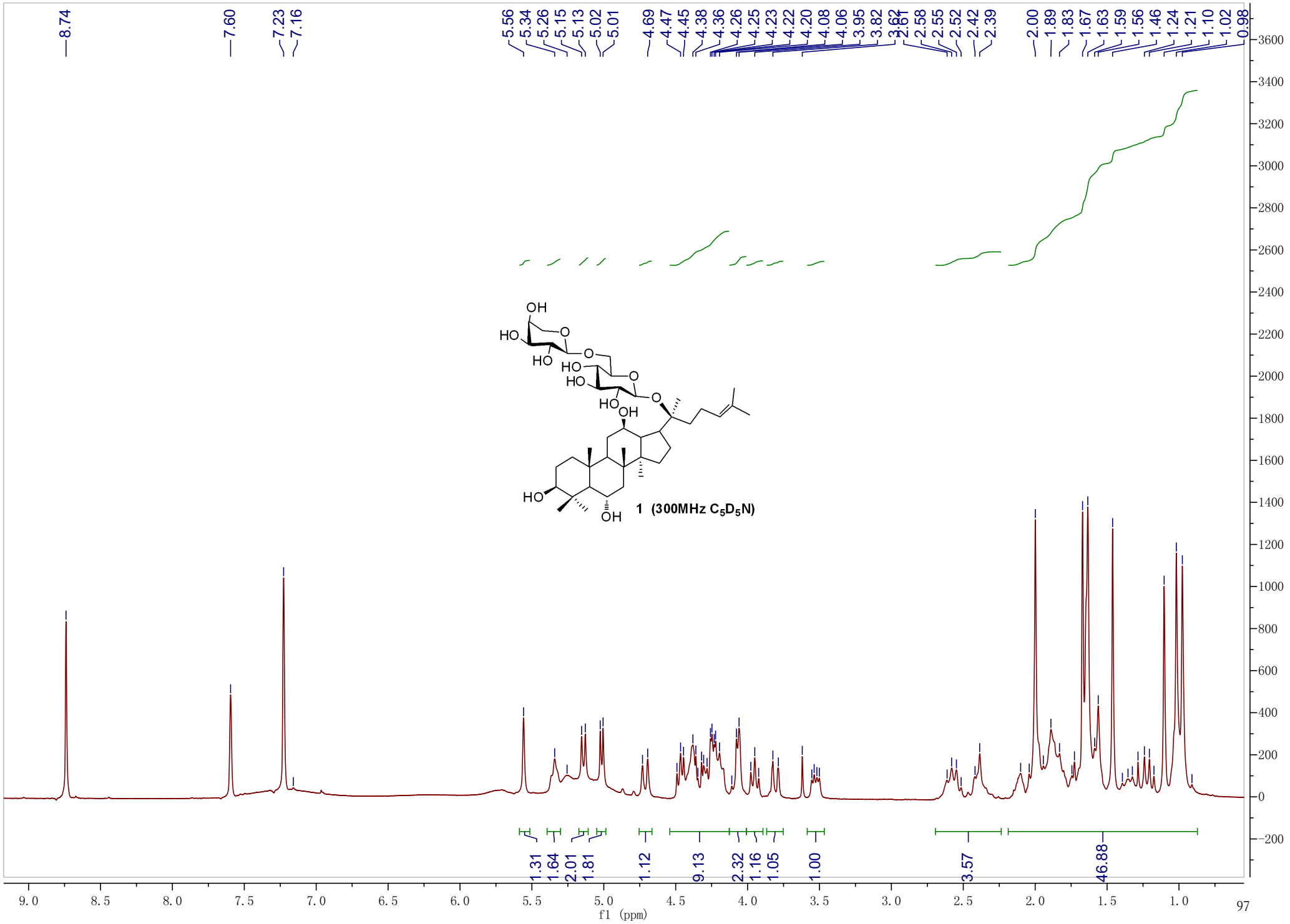



8.042
8.017
7.977
7.952
7.914
7.889
7.560
7.537
7.499
7.471
7.441
7.416
7.321
7.295
7.270
6.333
6.316
5.926
5.905
5.888
5.818
5.799
4.489
4.470
4.447
4.429
4.161
4.127
1.517
1.496
1.473
1.263
0.865
0.843
0.000
OBz
BzO
OBz
O
O
O
27a (300MHz CDCl3)
7.05
11.39
0.92
0.93
2.92
1.00
1.00
1.02
3.87
0.17
f1 (ppm)




8.08 8.05 8.02 7.98 7.95 7.93 7.91 7.87 7.78 7.76 7.58 7.57 7.55 7.52 7.49 7.47 7.44 7.43 7.42 7.40 7.38 7.35 7.34 7.31 7.28 7.26 7.23 5.84 5.81 5.78 5.64 5.63 5.61 5.49 5.40 5.17 5.11 5.09 5.05 4.98 4.95 4.82 4.80 4.05 3.95 3.94 3.81 3.77 3.76 3.74 2.12 2.05 2.02 1.85 1.63 1.59 1.55 1.50 1.41 1.39 1.31 1.26 1.21 1.17 1.08 1.03 1.00 0.90 0.73 0.00
OBz
BzO
BzO
BzO
BzO
BzO
BzO
OAll
AcO
OAc
28 (300MHz CDCl3)
13.40
20.99
2.19
3.30
1.06
1.17
1.17
4.33
1.06
1.00
1.03
1.13
2.23
3.13
1.00
60.73
f1 (ppm)
95





1 (300MHz C_5D_5N)

Electronic Supplementary Material (ESI) for Chemical Science
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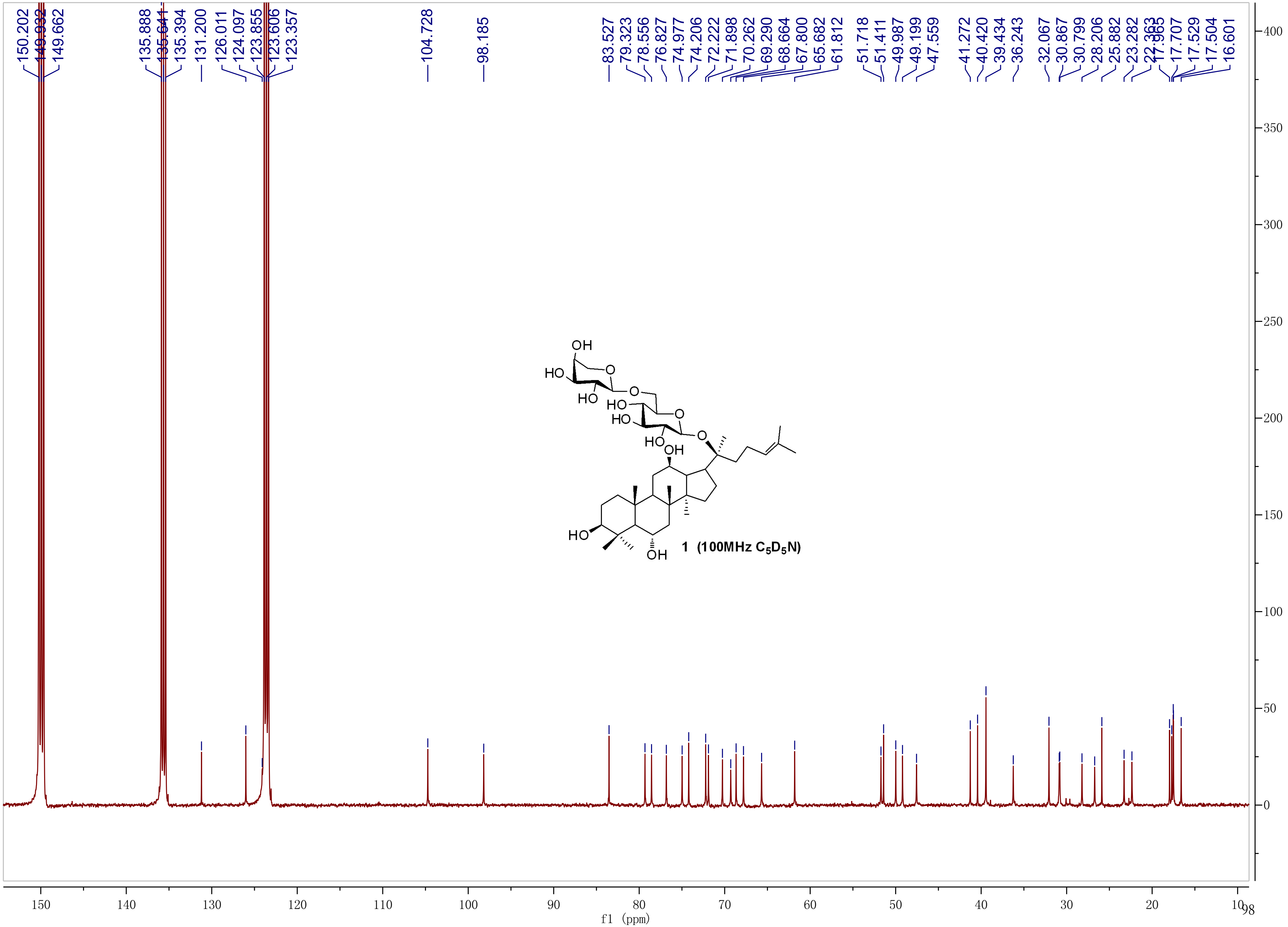
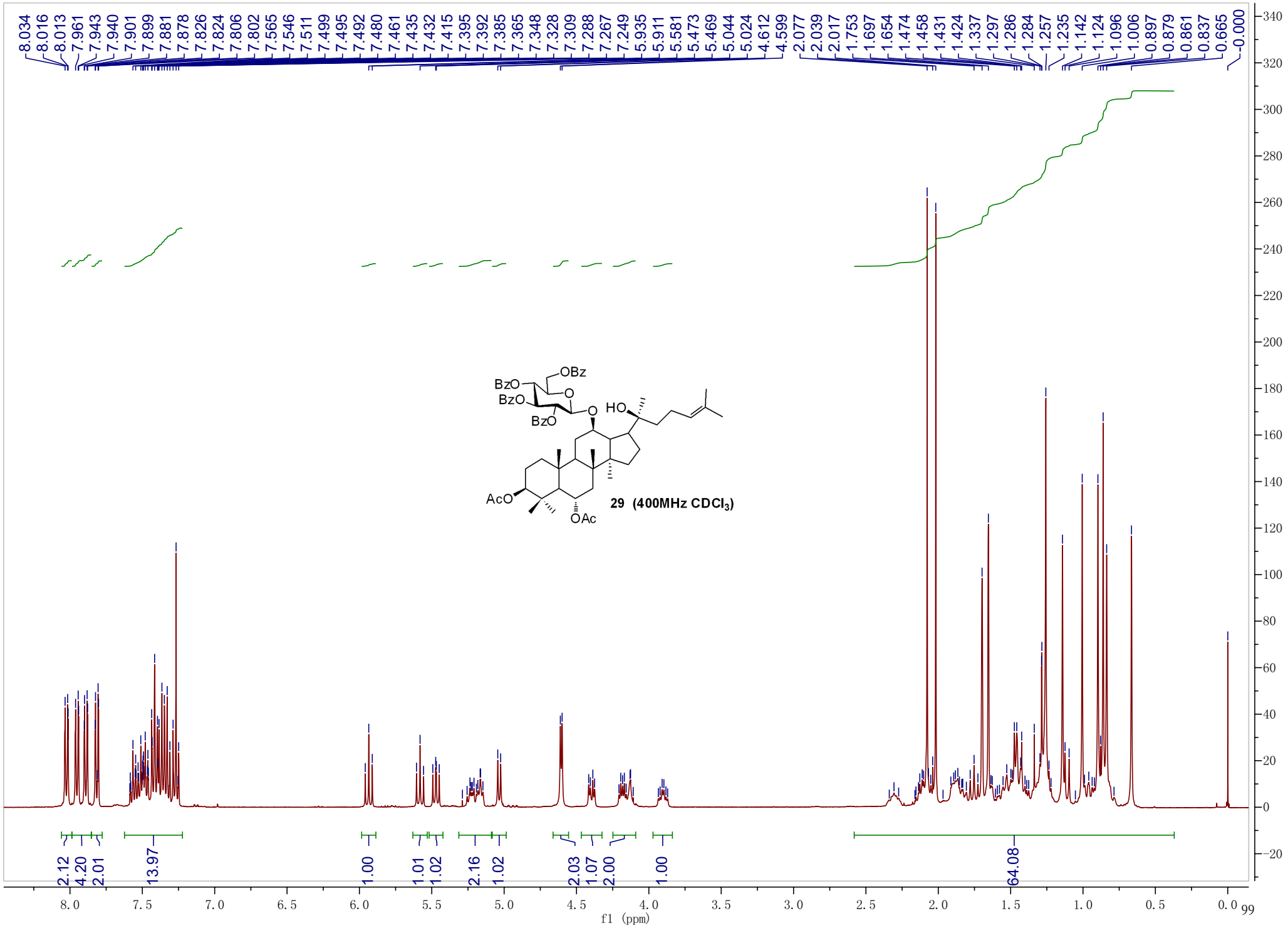
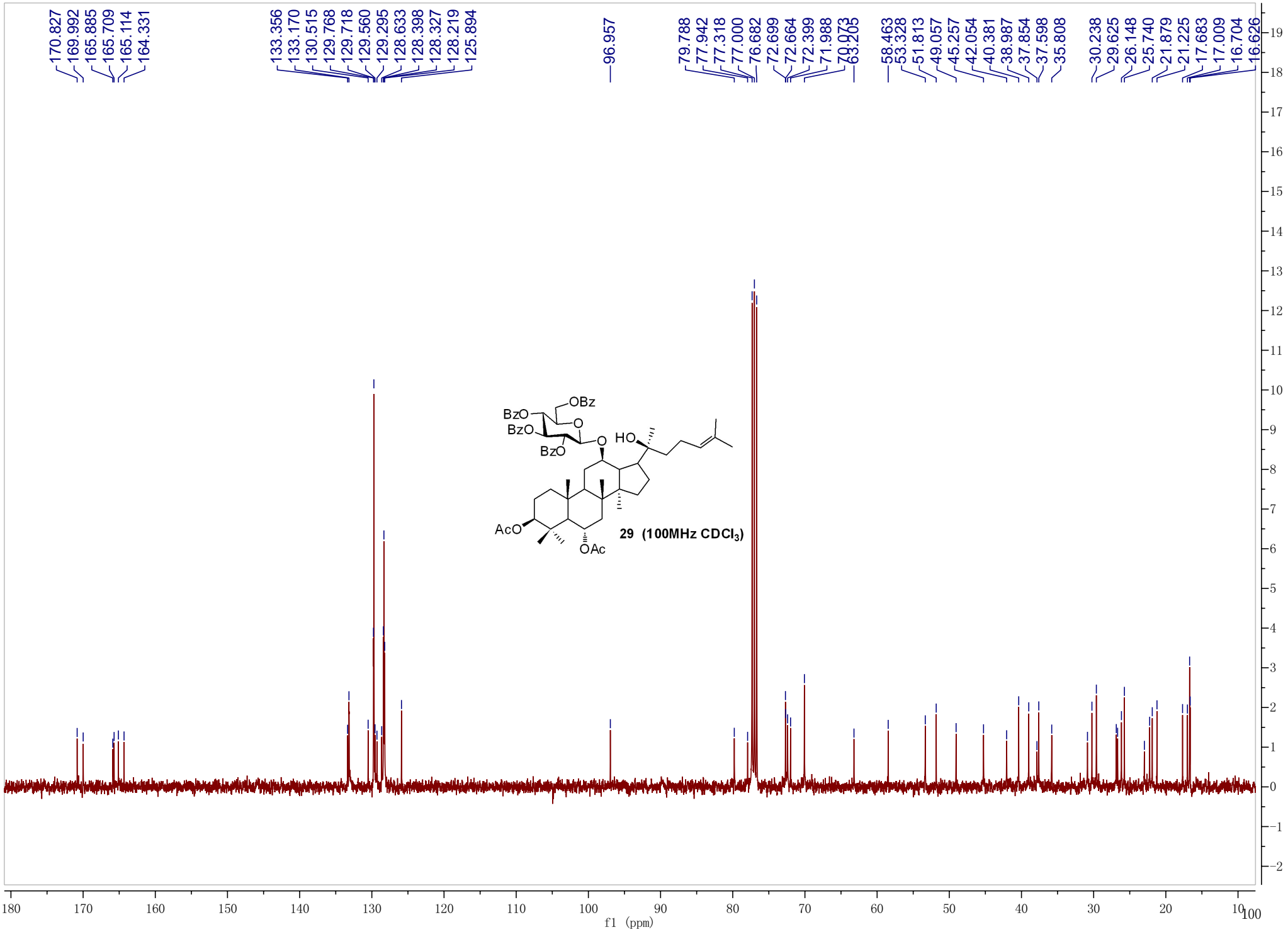
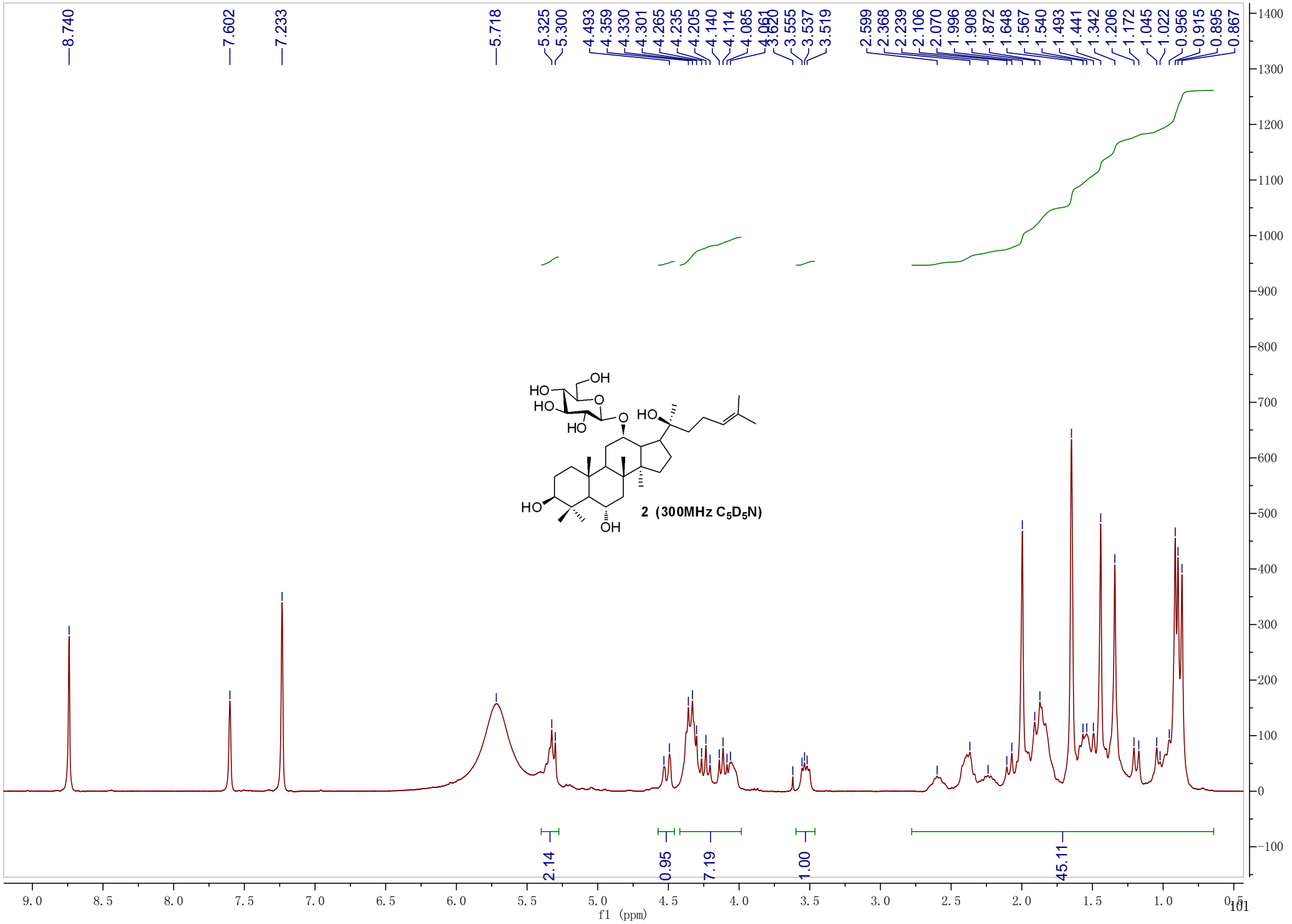
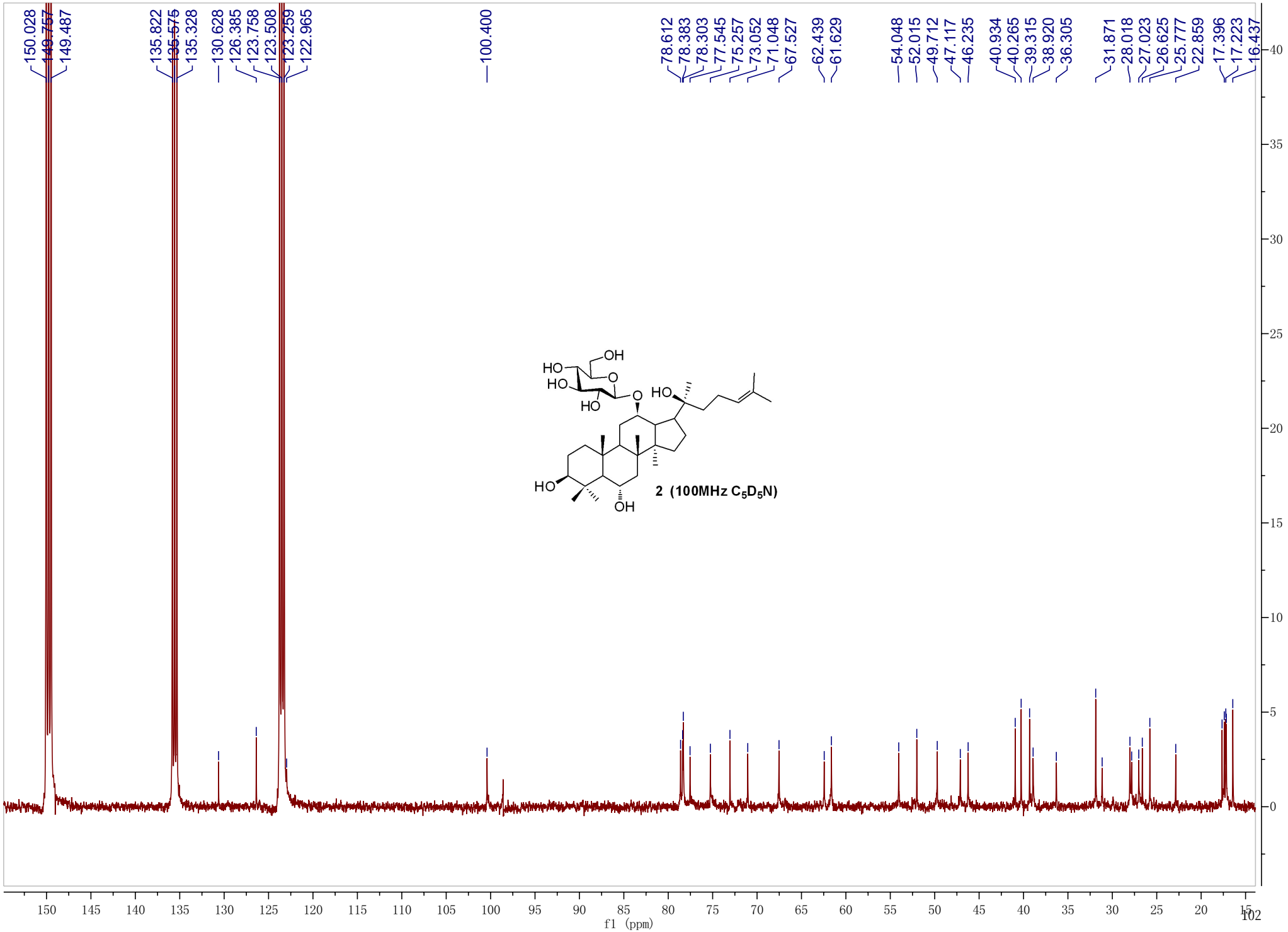







8.740
7.602
7.233
5.718
5.325
5.300
4.493
4.359
4.330
4.301
4.265
4.235
4.205
4.140
4.114
4.085
4.061
3.620
3.555
3.537
3.519
2.599
2.368
2.239
2.106
2.070
1.996
1.908
1.872
1.648
1.567
1.540
1.493
1.441
1.342
1.206
1.172
1.045
1.022
0.956
0.915
0.895
0.867
HO
OH
O
HO
HO
HO
HO
OH
2 (300MHz C5D5N)
2.14
0.95
7.19
1.00
45.11
f1 (ppm)


150.028
149.757
149.487
135.822
135.575
135.328
130.628
126.385
123.758
123.508
123.259
122.965
100.400
78.612
78.383
78.303
77.545
75.257
73.052
71.048
67.527
62.439
61.629
54.048
52.015
49.712
47.117
46.235
40.934
40.265
39.315
38.920
36.305
31.871
28.018
27.023
26.625
25.777
22.859
17.396
17.223
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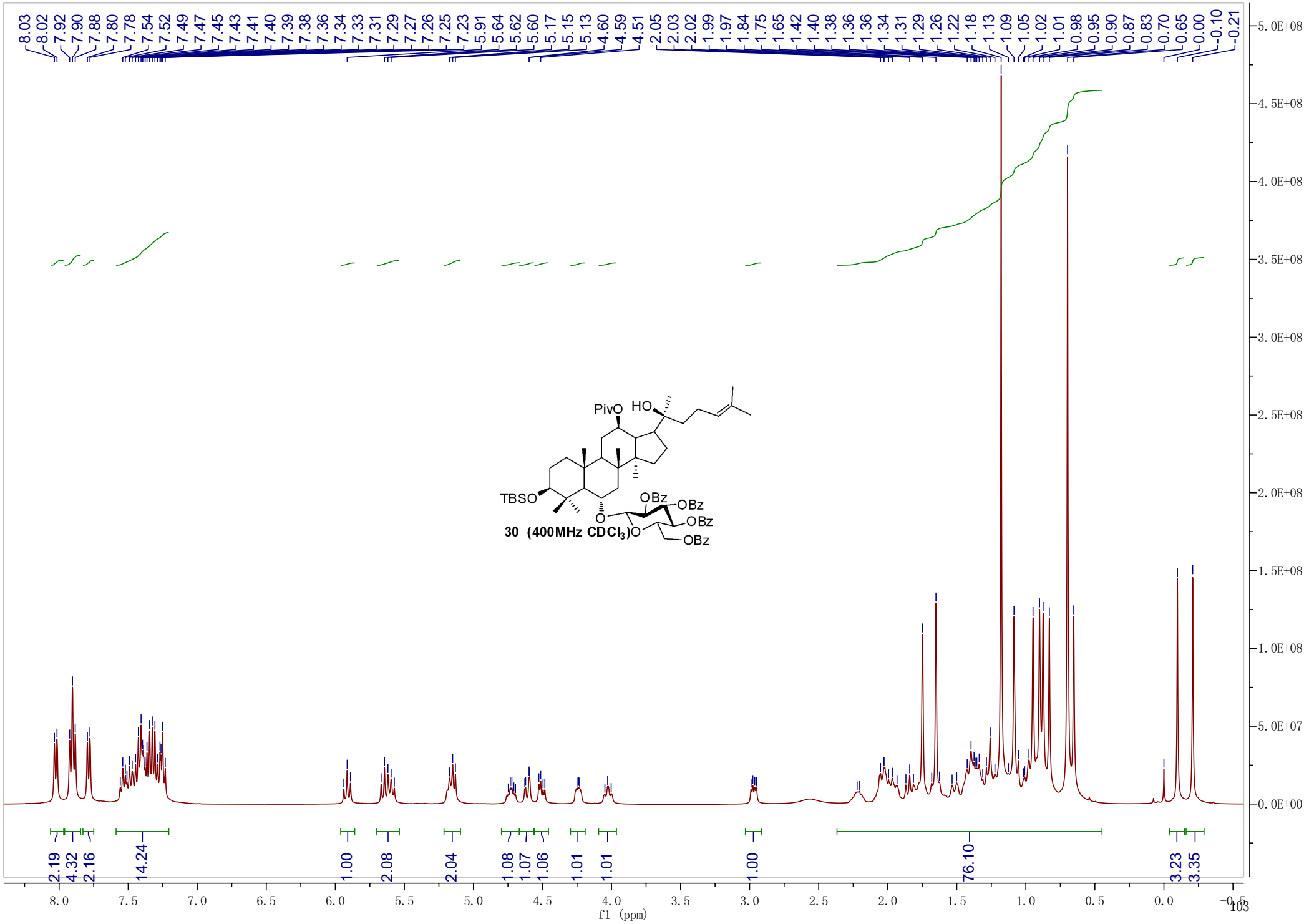
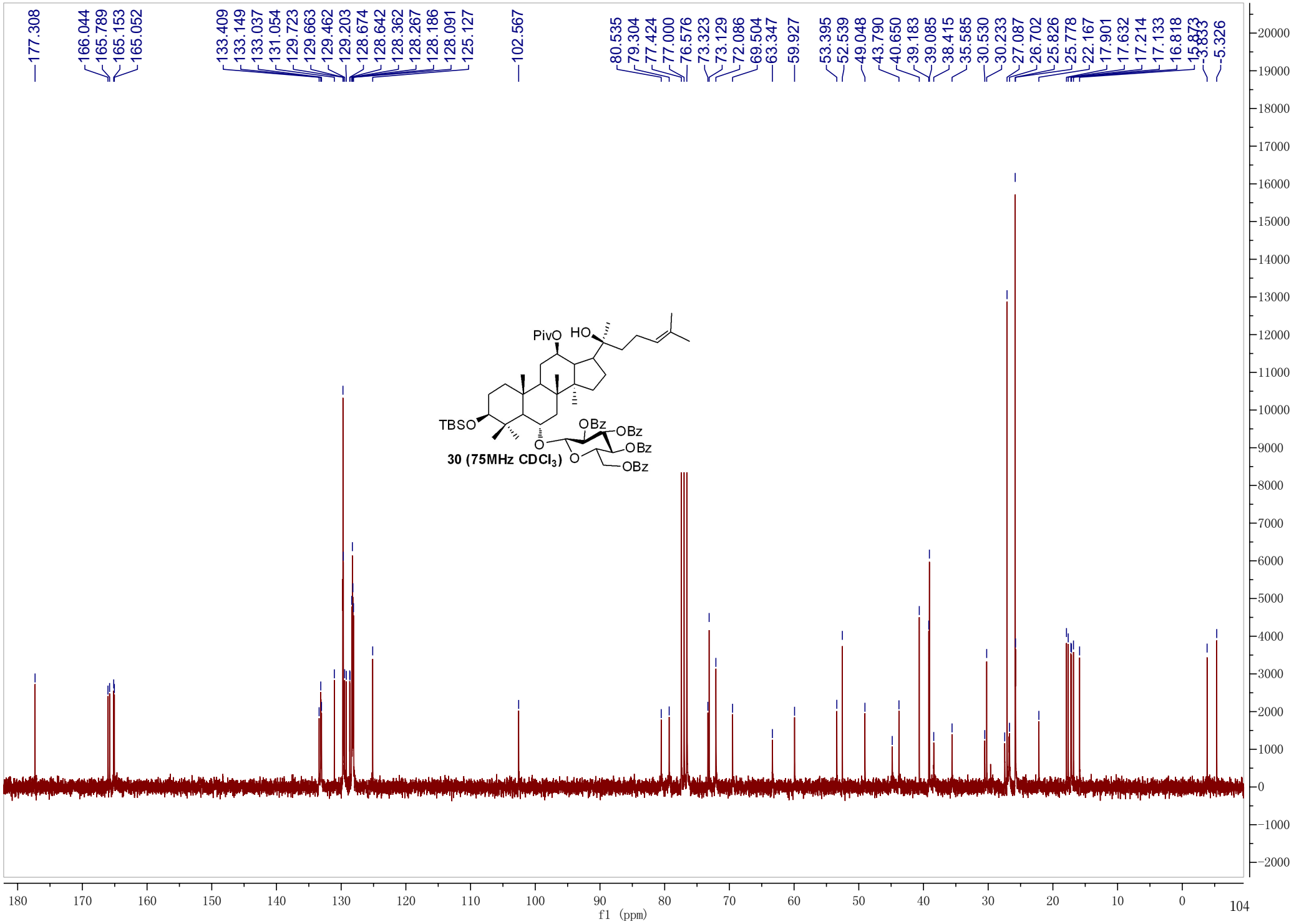
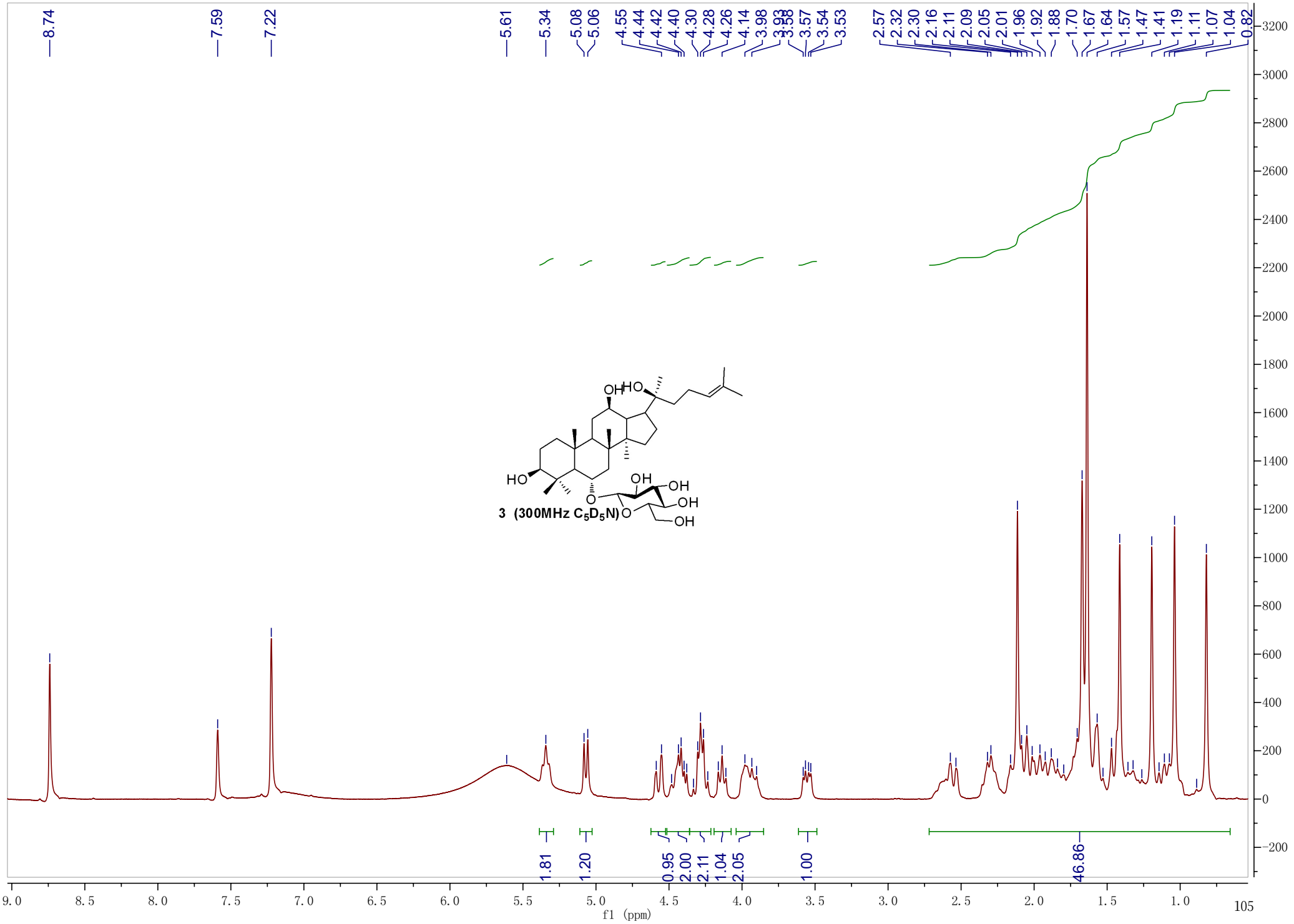
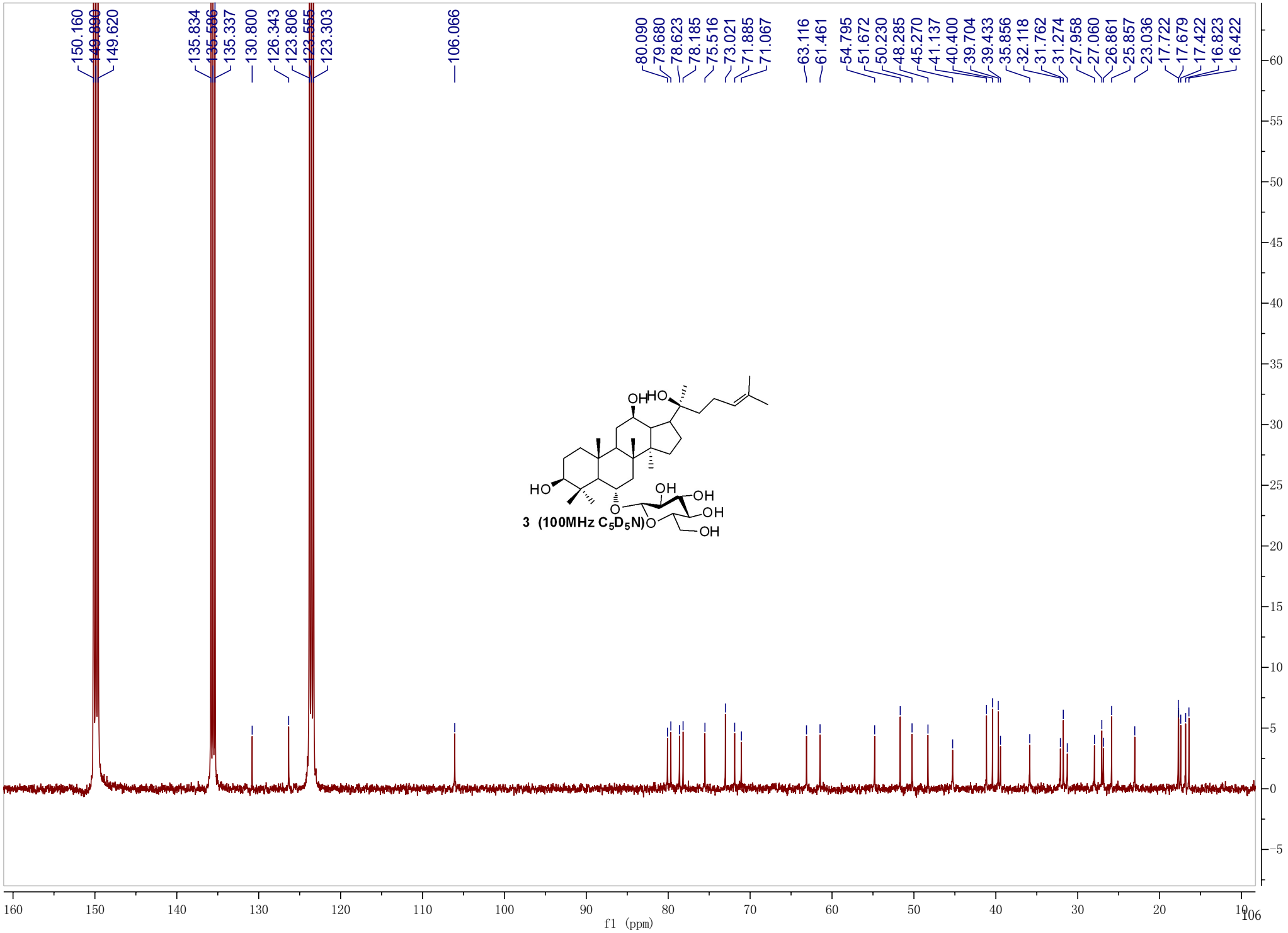
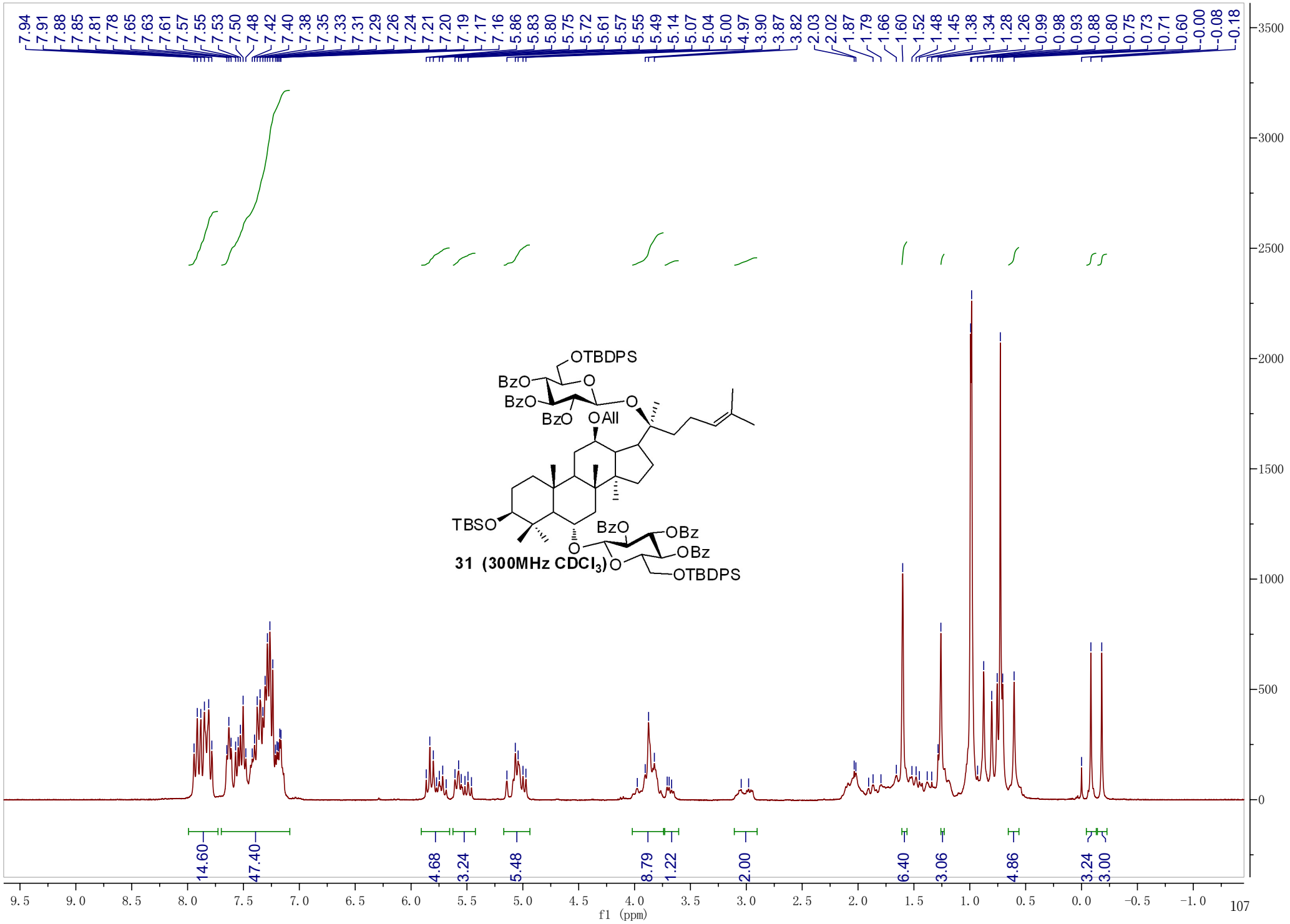
HO
HO
HO
OH
O
O
HO
HO
OH
2 (100MHz C5D5N)
f1 (ppm)

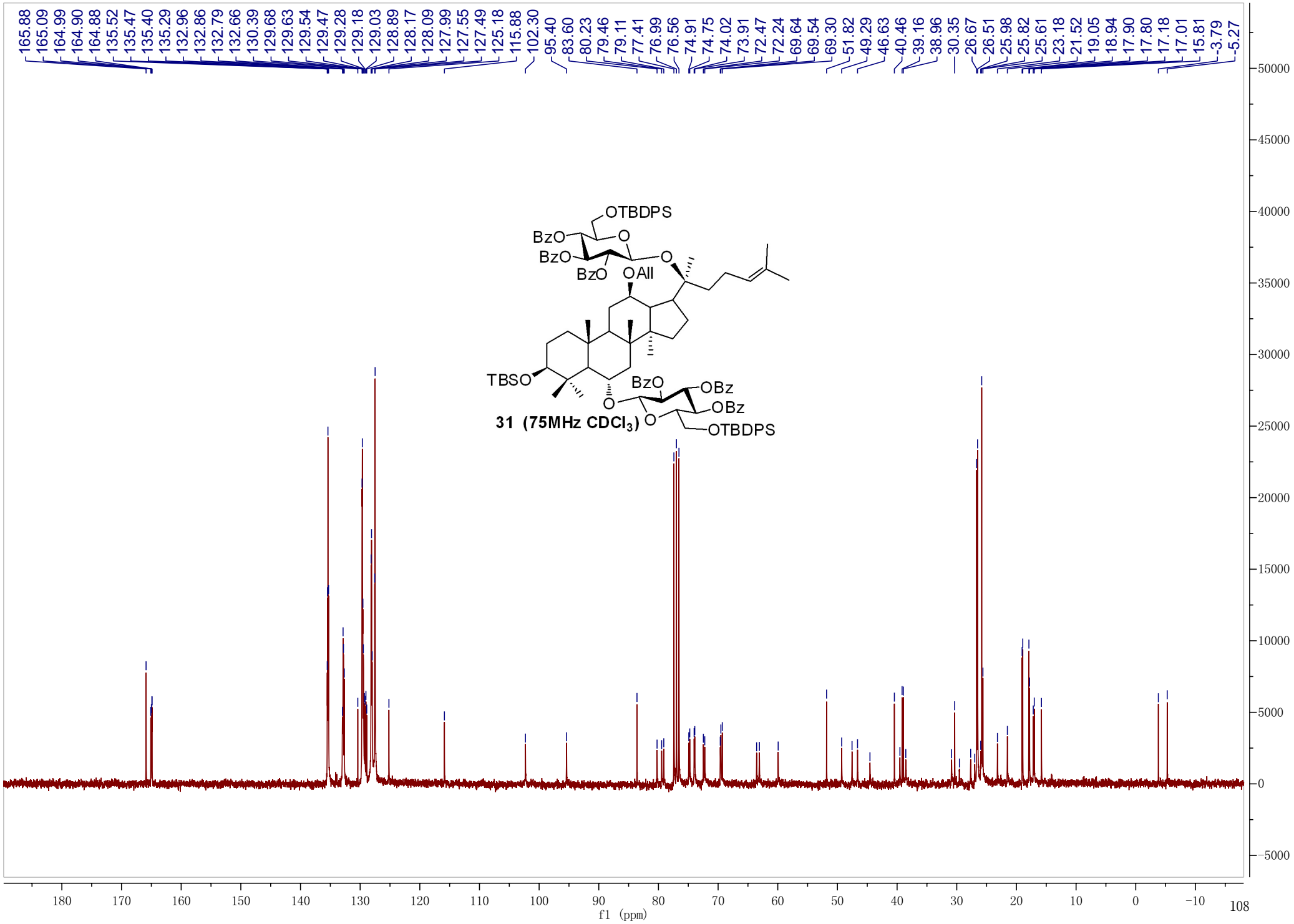


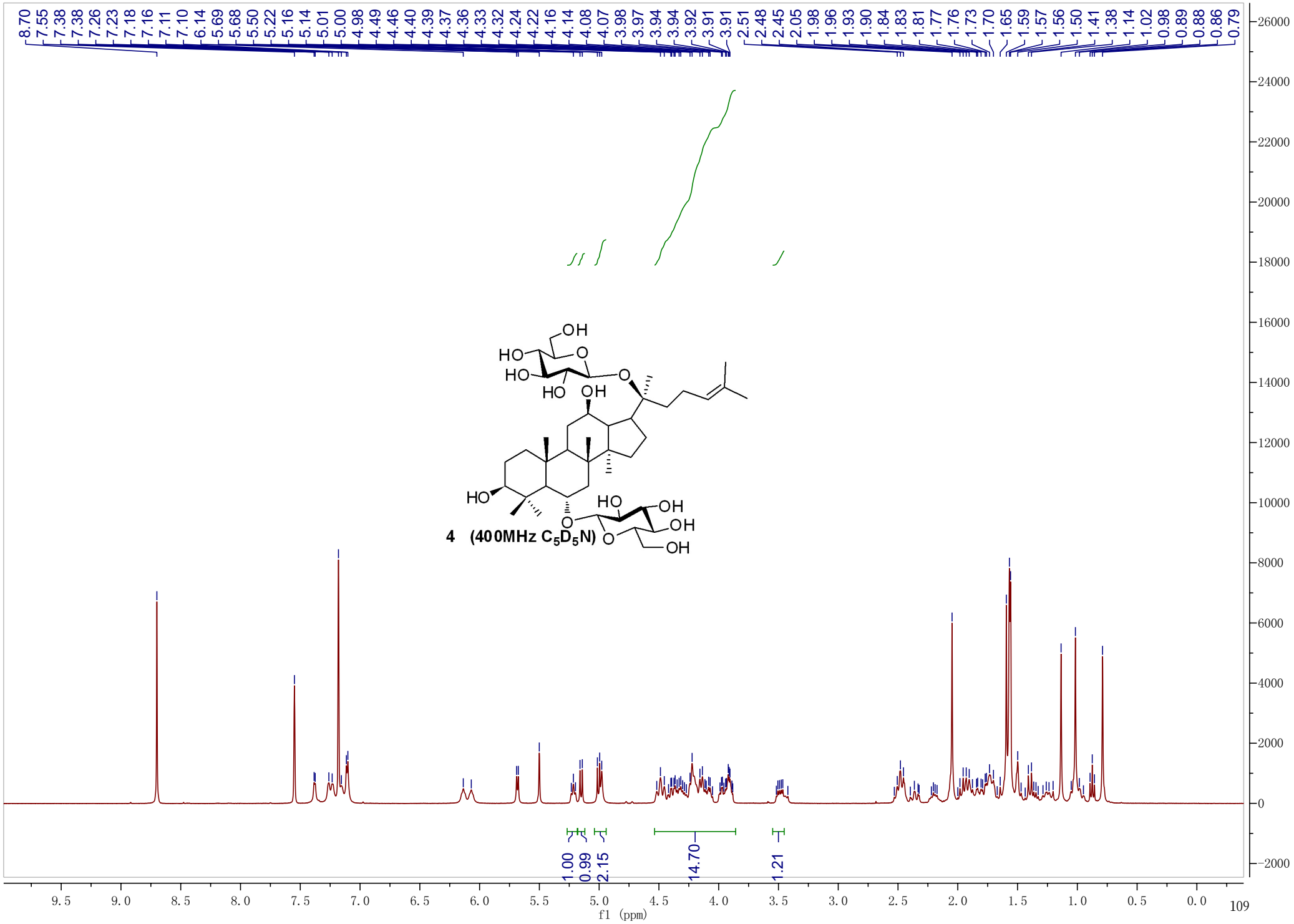

177.308
166.044
165.789
165.153
165.052
133.409
133.149
133.037
131.054
129.723
129.663
129.462
129.203
128.674
128.642
128.362
128.267
128.186
128.091
125.127
102.567
80.535
79.304
77.424
77.000
76.576
73.323
73.129
72.086
69.504
63.347
59.927
53.395
52.539
49.048
43.790
40.650
39.183
39.085
38.415
35.585
30.530
30.233
27.087
26.702
25.826
25.778
22.167
17.901
17.632
17.214
17.133
16.818
15.873
-3.833
-5.326
PivO
HO
TBSO
OBz
OBz
OBz
OBz
O
O
30 (75MHz CDCl3)
f1 (ppm)
104

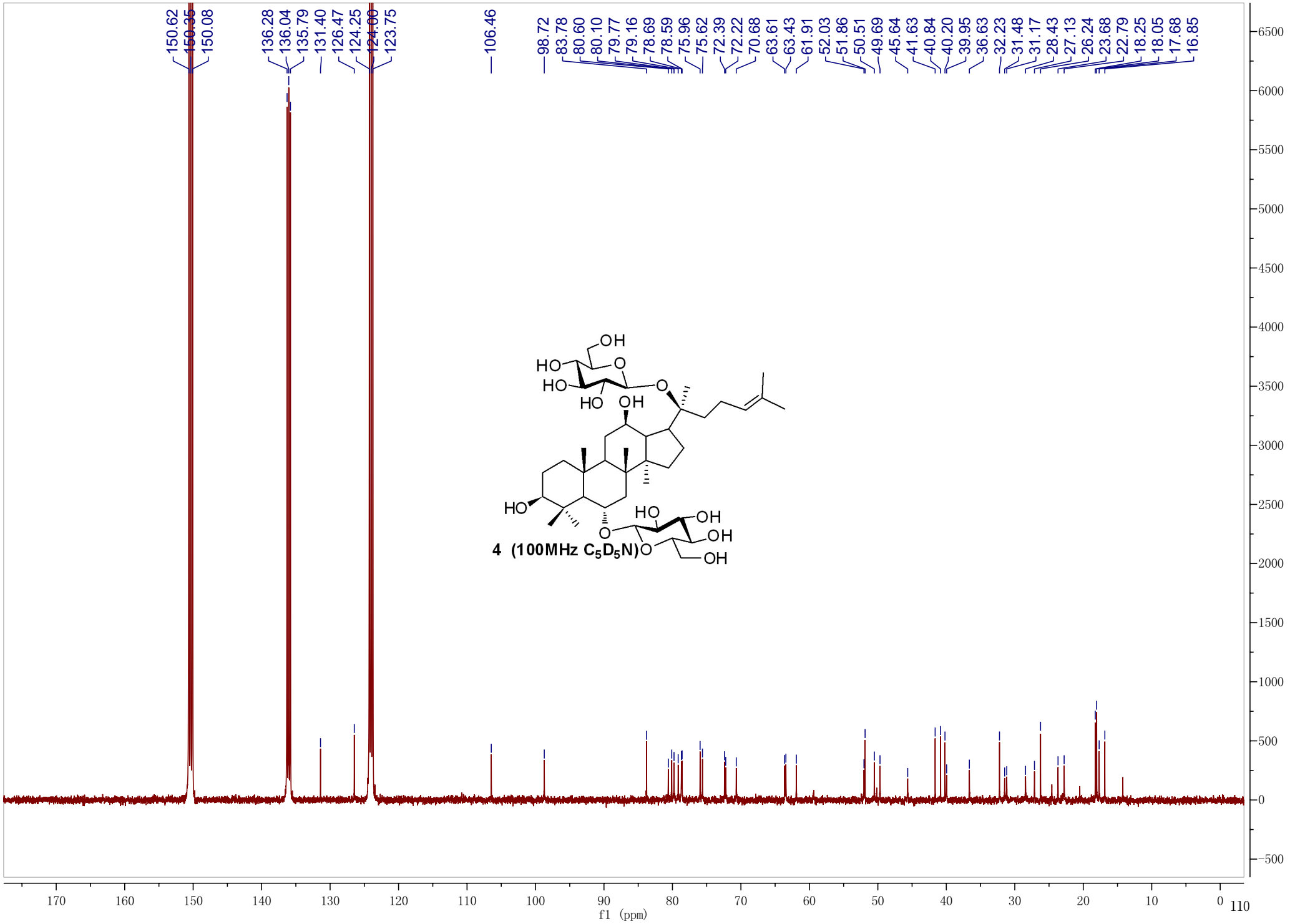


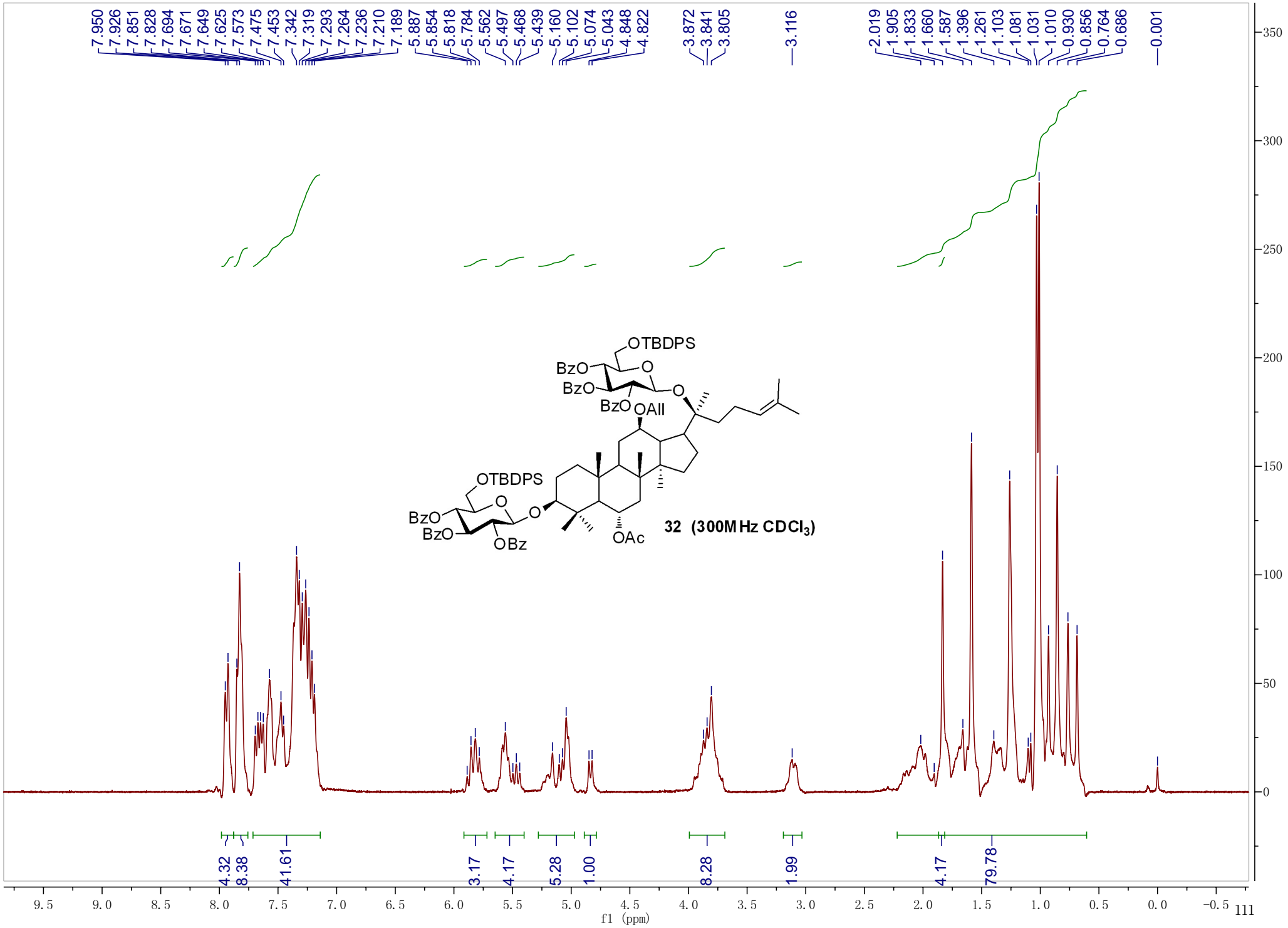

150.160
149.890
149.620
135.834
135.596
135.337
130.800
126.343
123.806
123.555
123.303
106.066
80.090
79.680
78.623
78.185
75.516
73.021
71.885
71.067
63.116
61.461
54.795
51.672
50.230
48.285
45.270
41.137
40.400
39.704
39.433
35.856
32.118
31.762
31.274
27.958
27.060
26.861
25.857
23.036
17.722
17.679
17.422
16.823
16.422
HO
OH
HO
OH
OH
OH
OH
O
O
3 (100MHz C5D5N)
f1 (ppm)

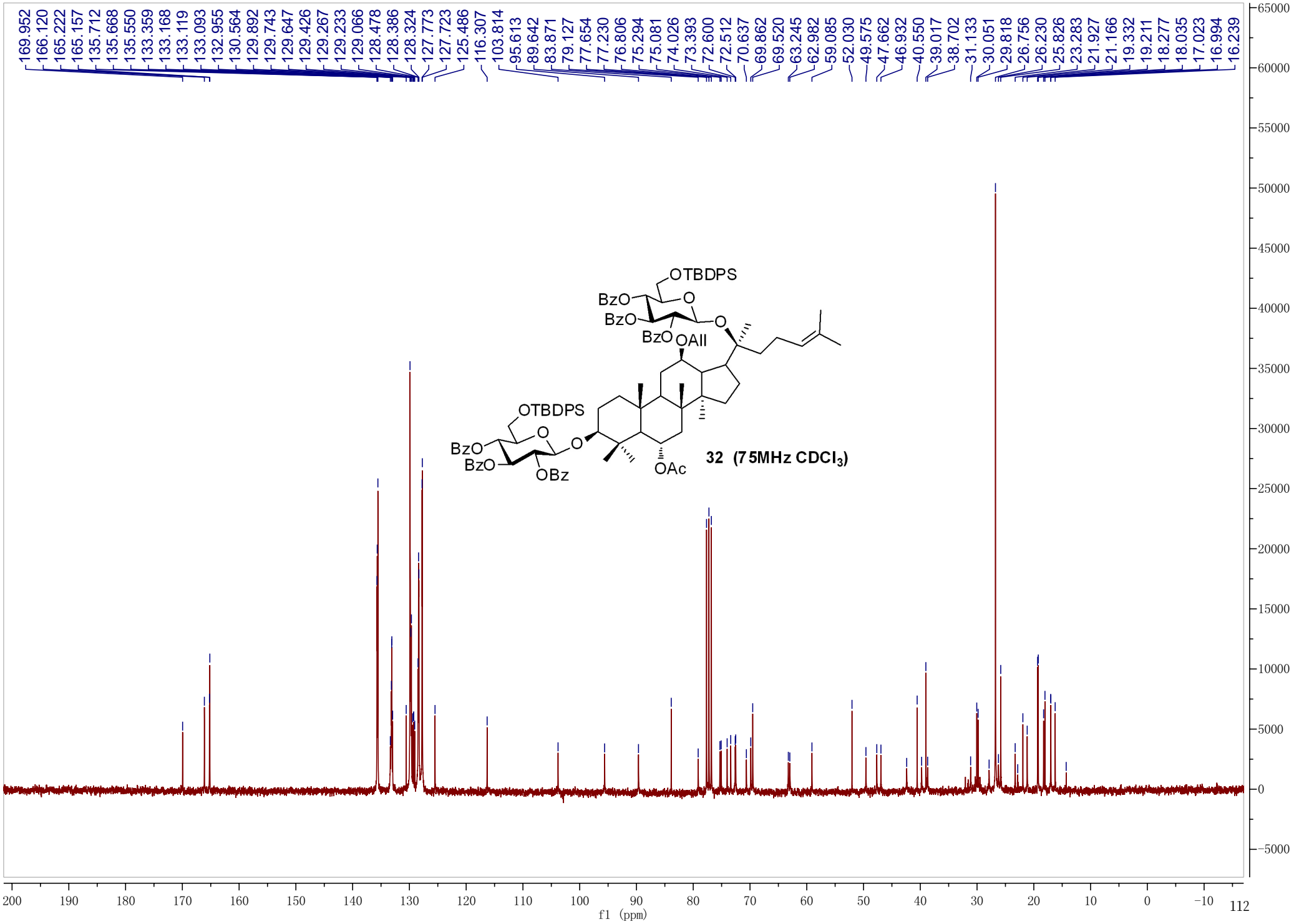


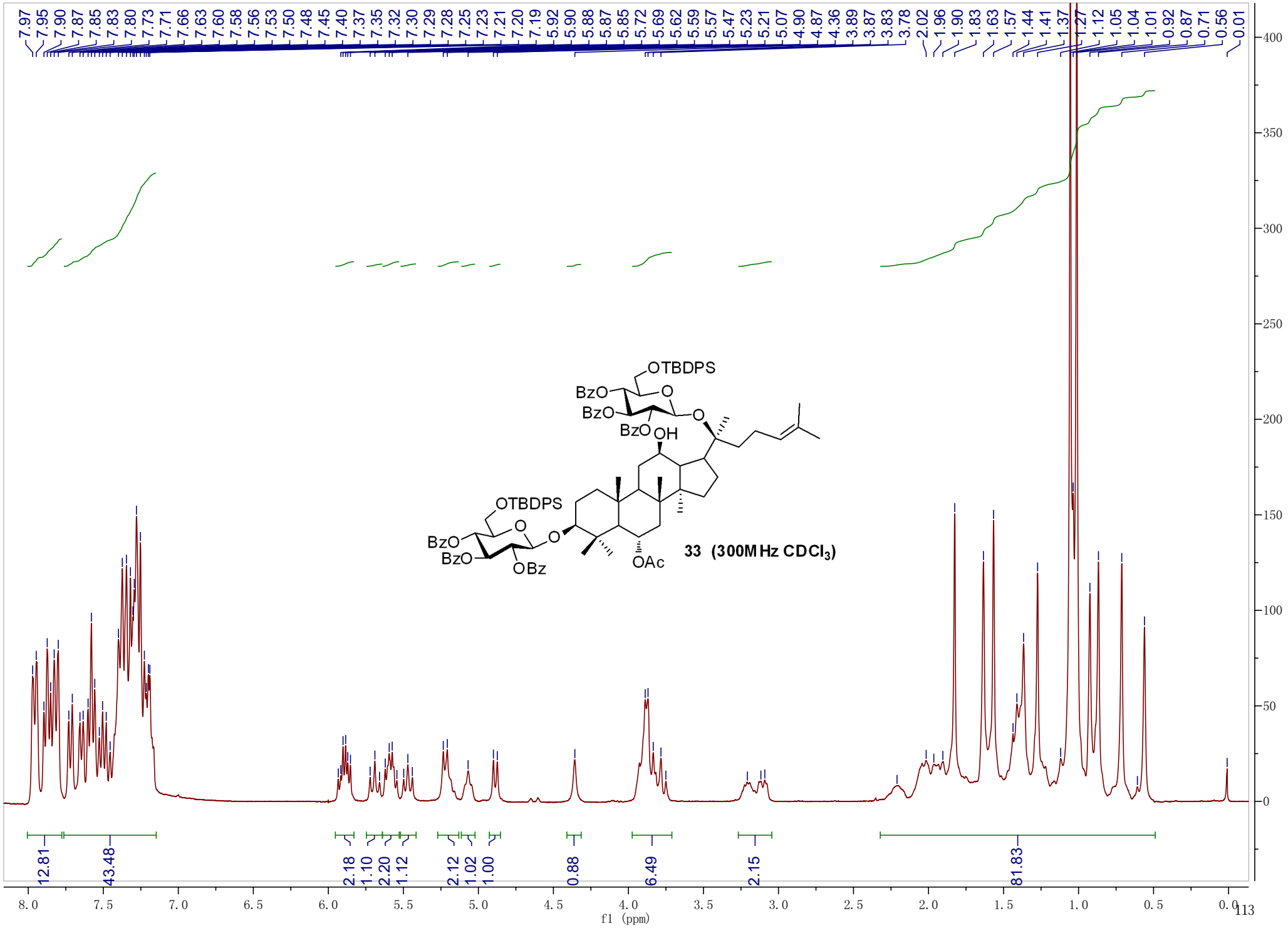


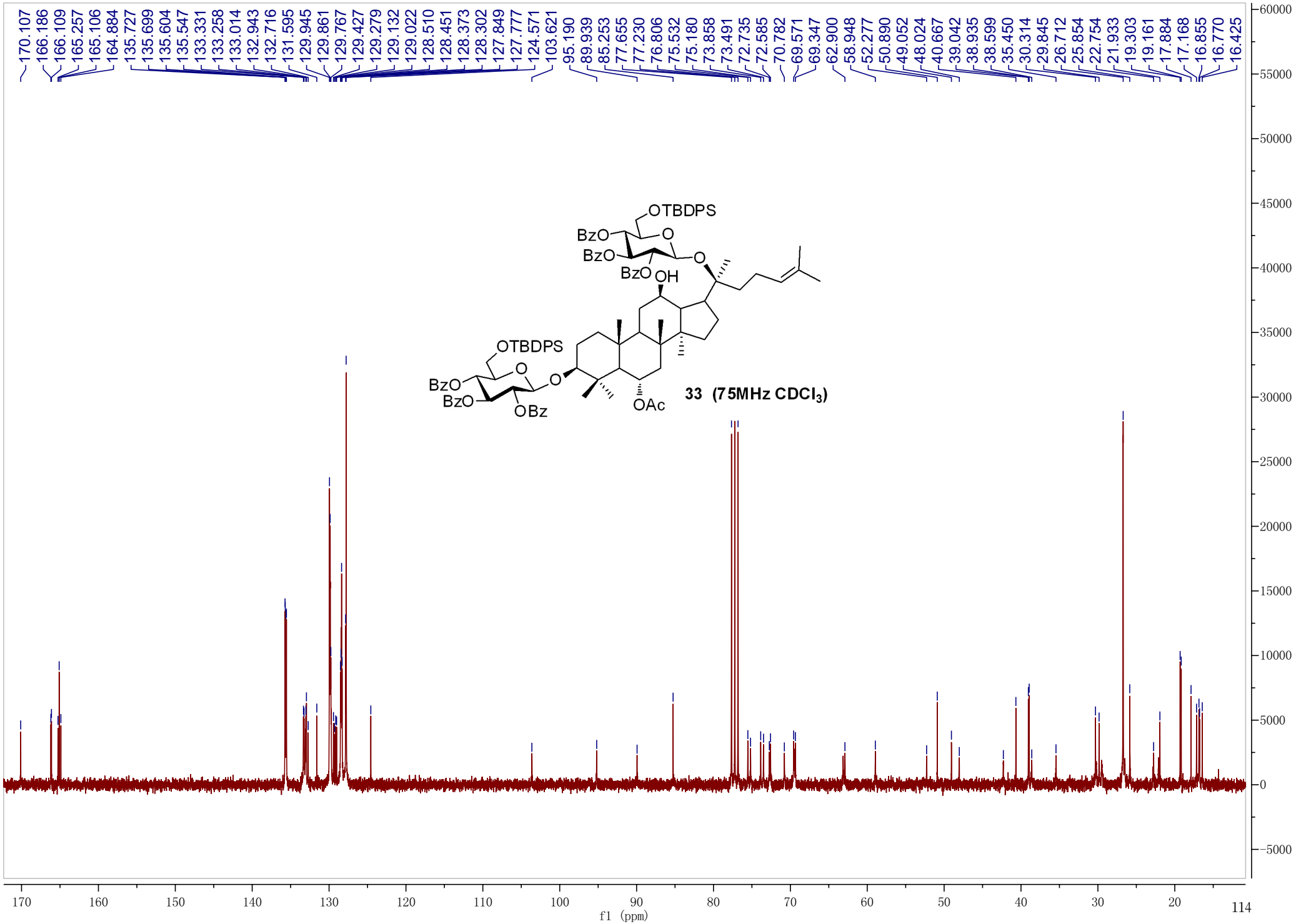

8.70 7.55 7.38 7.38 7.26 7.23 7.18 7.16 7.11 7.10 6.14 5.69 5.68 5.50 5.22 5.16 5.14 5.01 5.00 4.98 4.49 4.46 4.40 4.39 4.37 4.36 4.33 4.32 4.24 4.22 4.16 4.14 4.08 4.07 3.98 3.97 3.94 3.94 3.92 3.91 3.91 2.51 2.48 2.45 2.05 1.98 1.96 1.93 1.90 1.84 1.83 1.81 1.77 1.76 1.73 1.70 1.65 1.59 1.57 1.56 1.50 1.41 1.38 1.14 1.02 0.98 0.89 0.88 0.86 0.79
4 (400MHz C5D5N)
1.00
0.99
2.15
14.70
1.21
f1 (ppm)
109

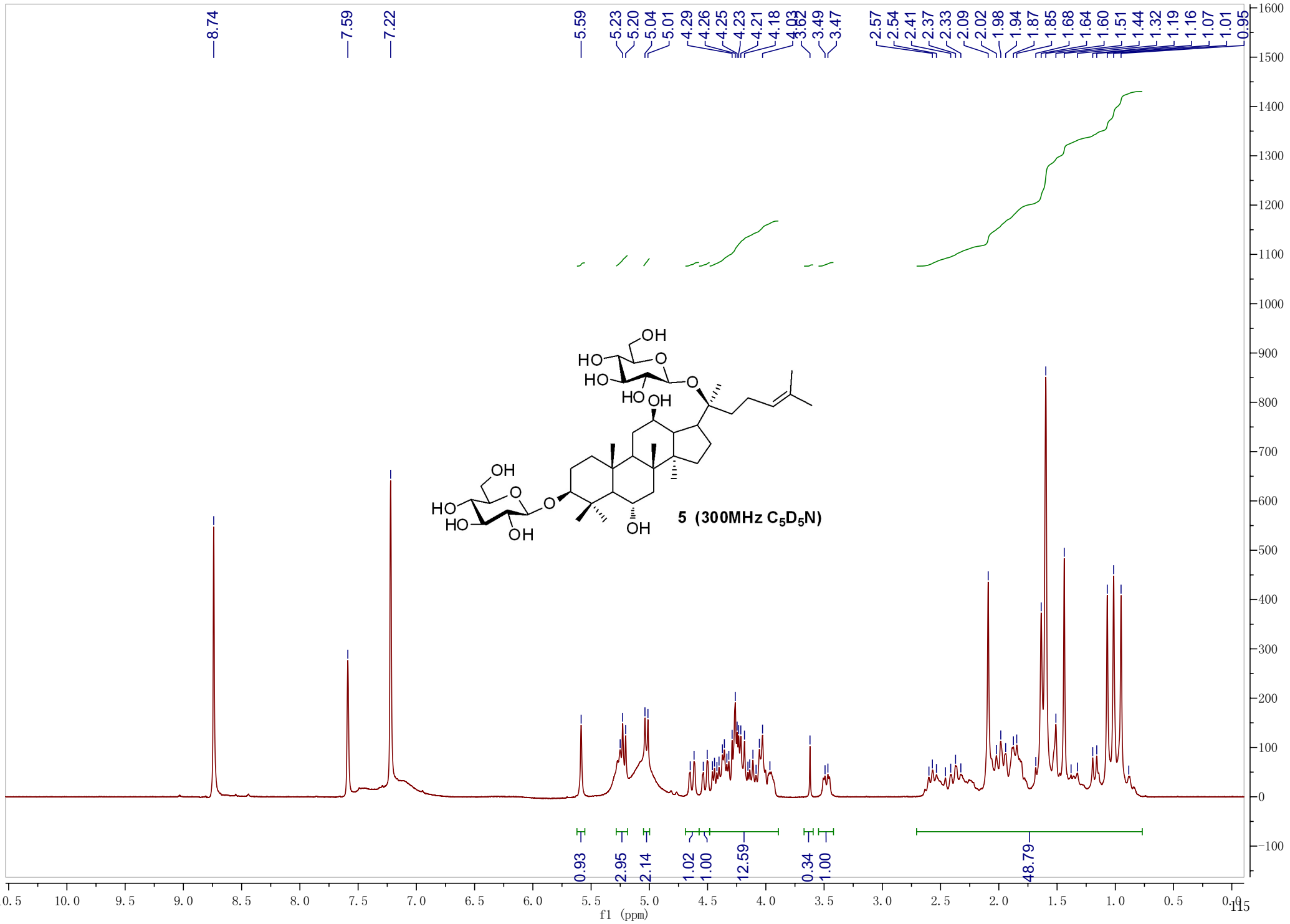







OTBDPS
BzO
BzO
BzO
O
O
OH
OTBDPS
BzO
BzO
OBz
O
O
OAc
33 (300MHz CDCl3)
f1 (ppm)




8.74
7.59
7.22
5.59
5.23
5.20
5.04
5.01
4.29
4.26
4.25
4.23
4.21
4.18
4.03
3.82
3.49
3.47
2.57
2.54
2.41
2.37
2.33
2.09
2.02
1.98
1.94
1.87
1.85
1.68
1.64
1.60
1.51
1.44
1.32
1.19
1.16
1.07
1.01
0.95
OH
HO
HO
O
HO
OH
OH
HO
HO
O
O
OH
OH
5 (300MHz C5D5N)
0.93
2.95
2.14
1.02
1.00
12.59
0.34
1.00
48.79
f1 (ppm)

Electronic Supplementary Material (ESI) for Chemical Science
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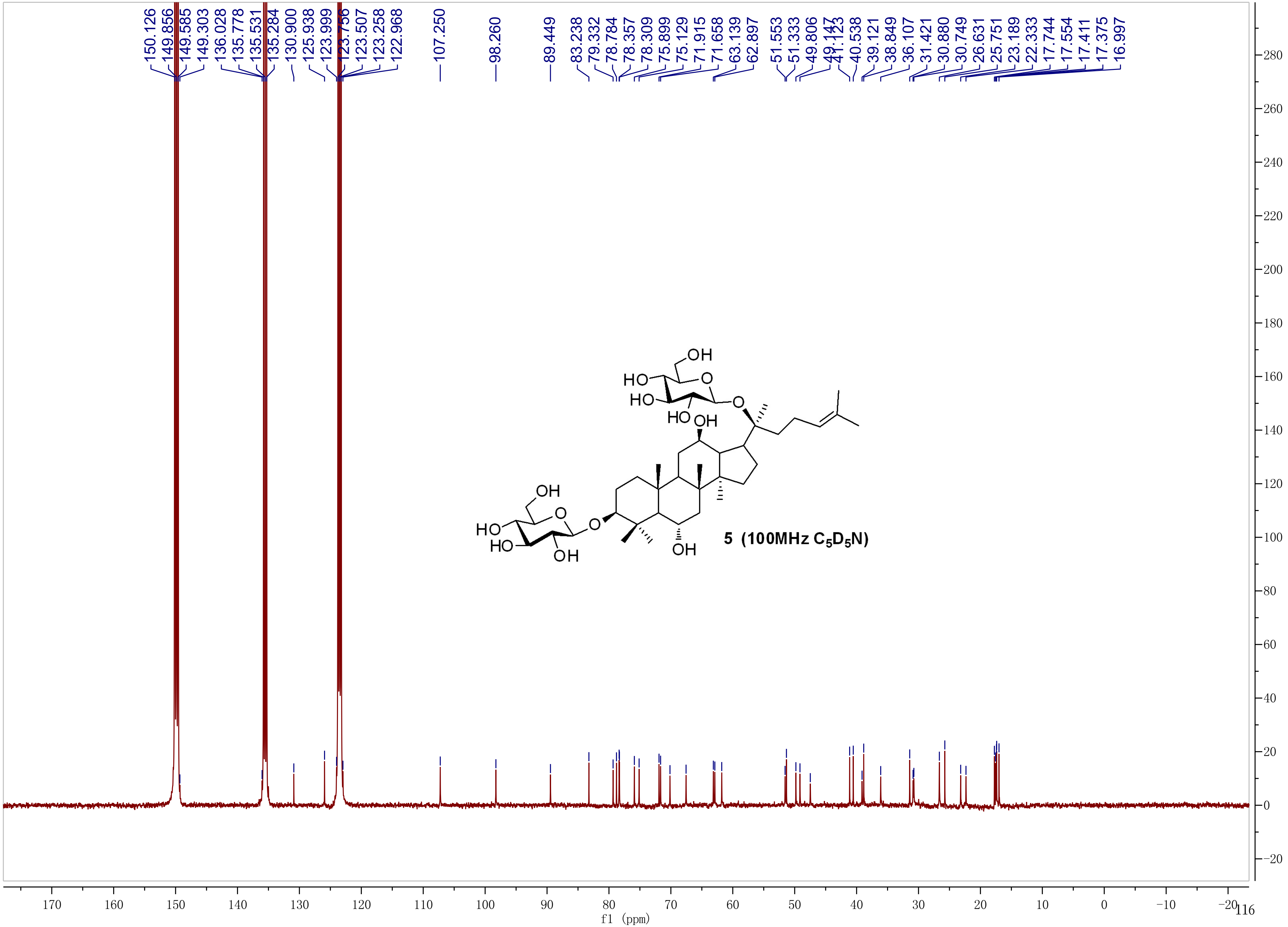
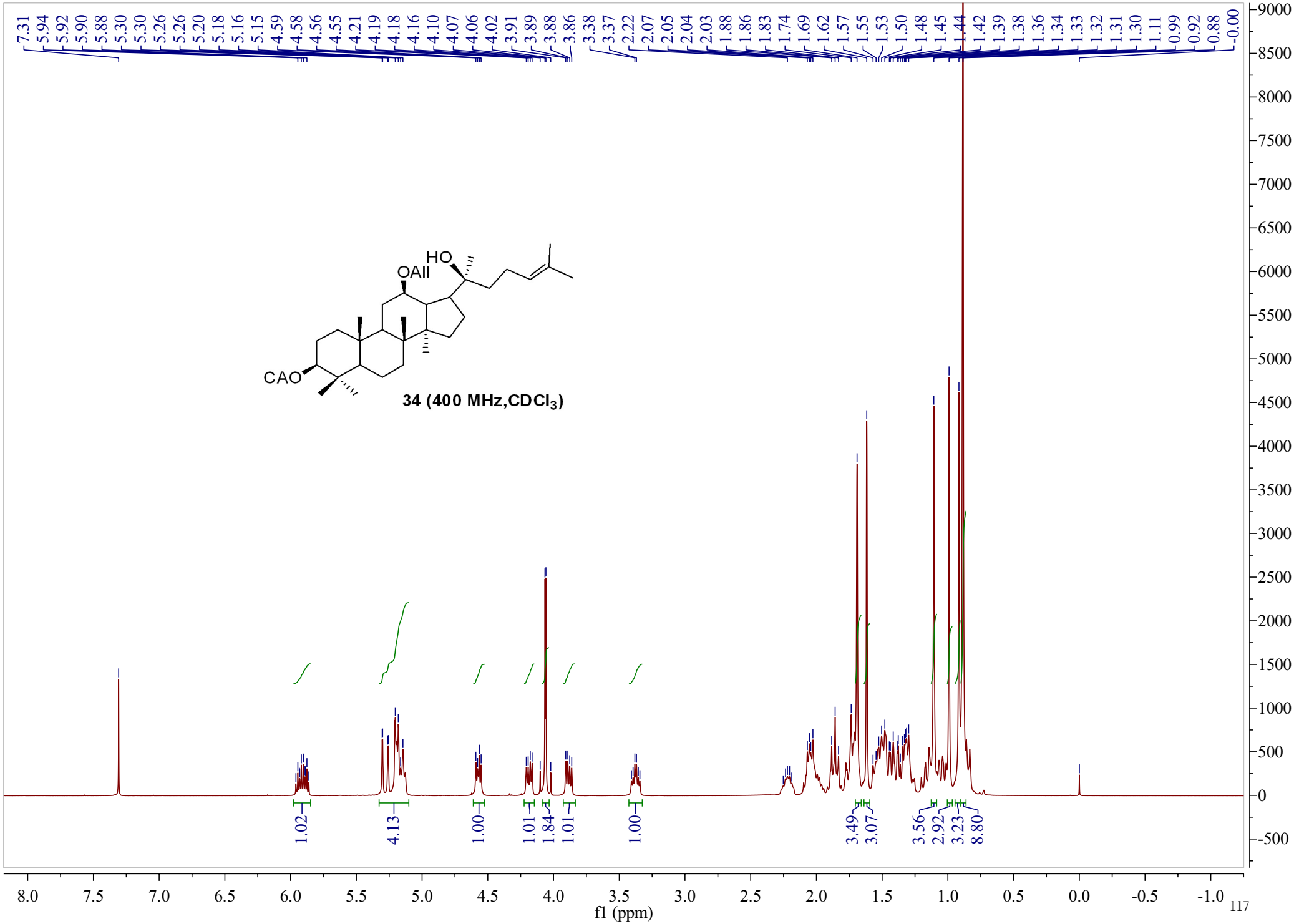
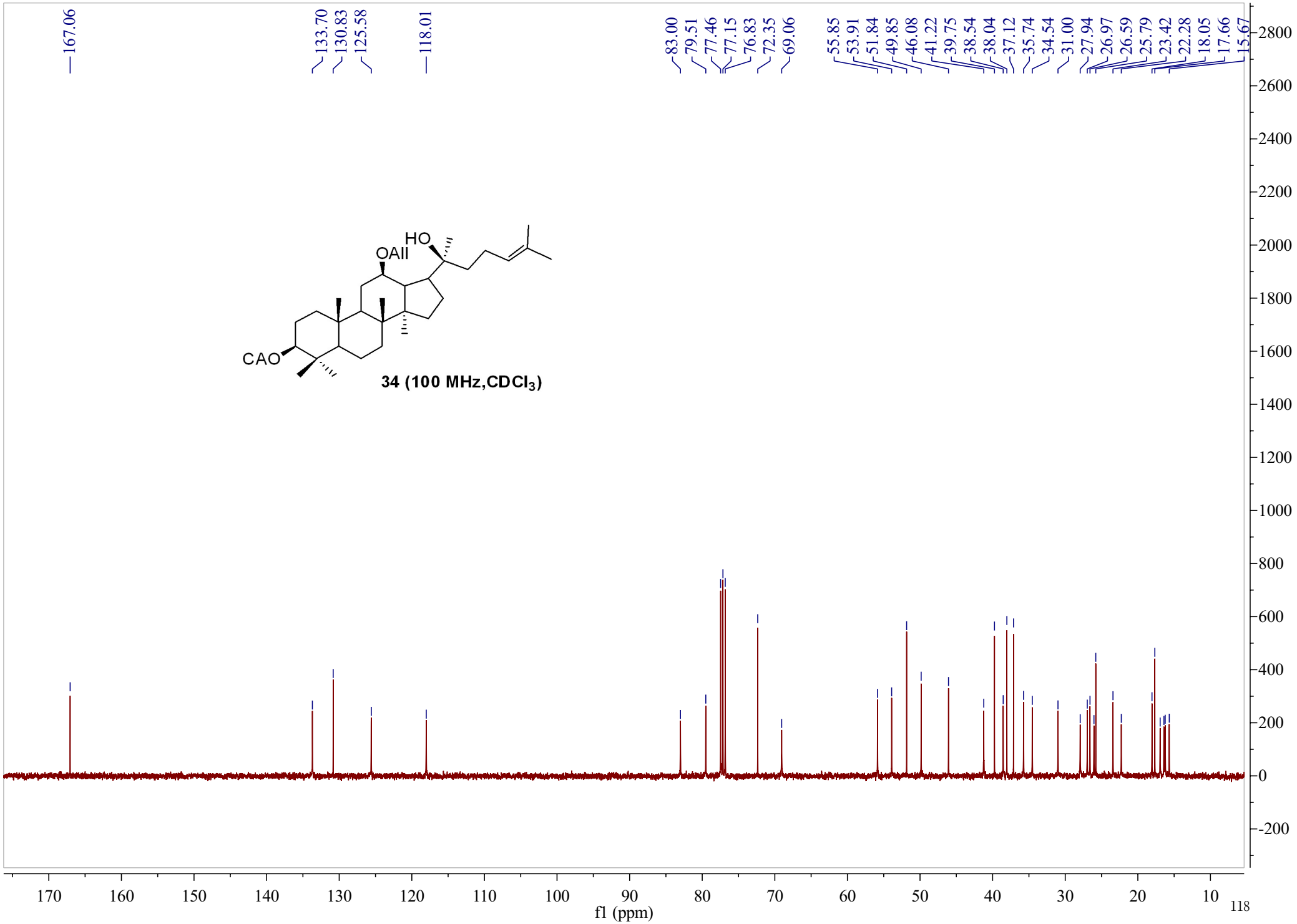
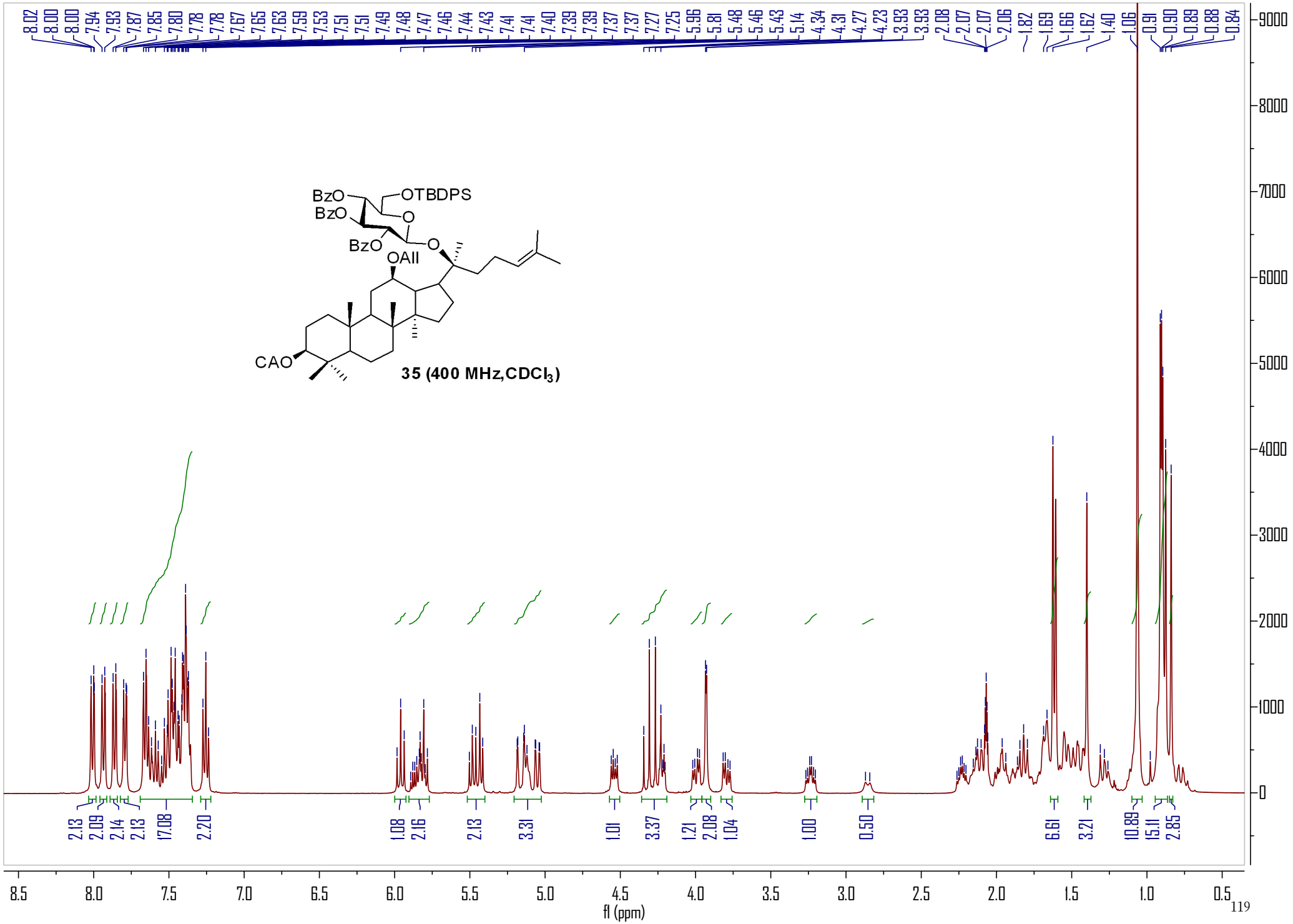






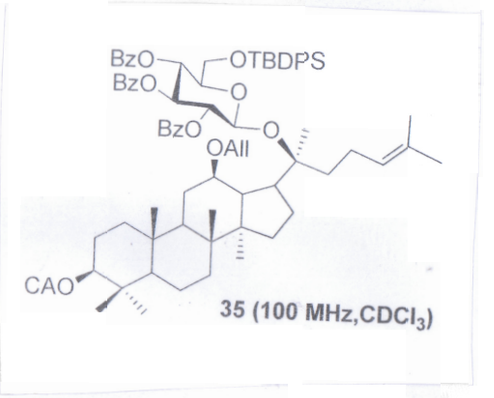

BzO
BzO
BzO
OTBDPS
O
O
OAll
CAO
35 (400 MHz,CDCl3)
f1 (ppm)

2-12

Pulse Sequence: s2pul

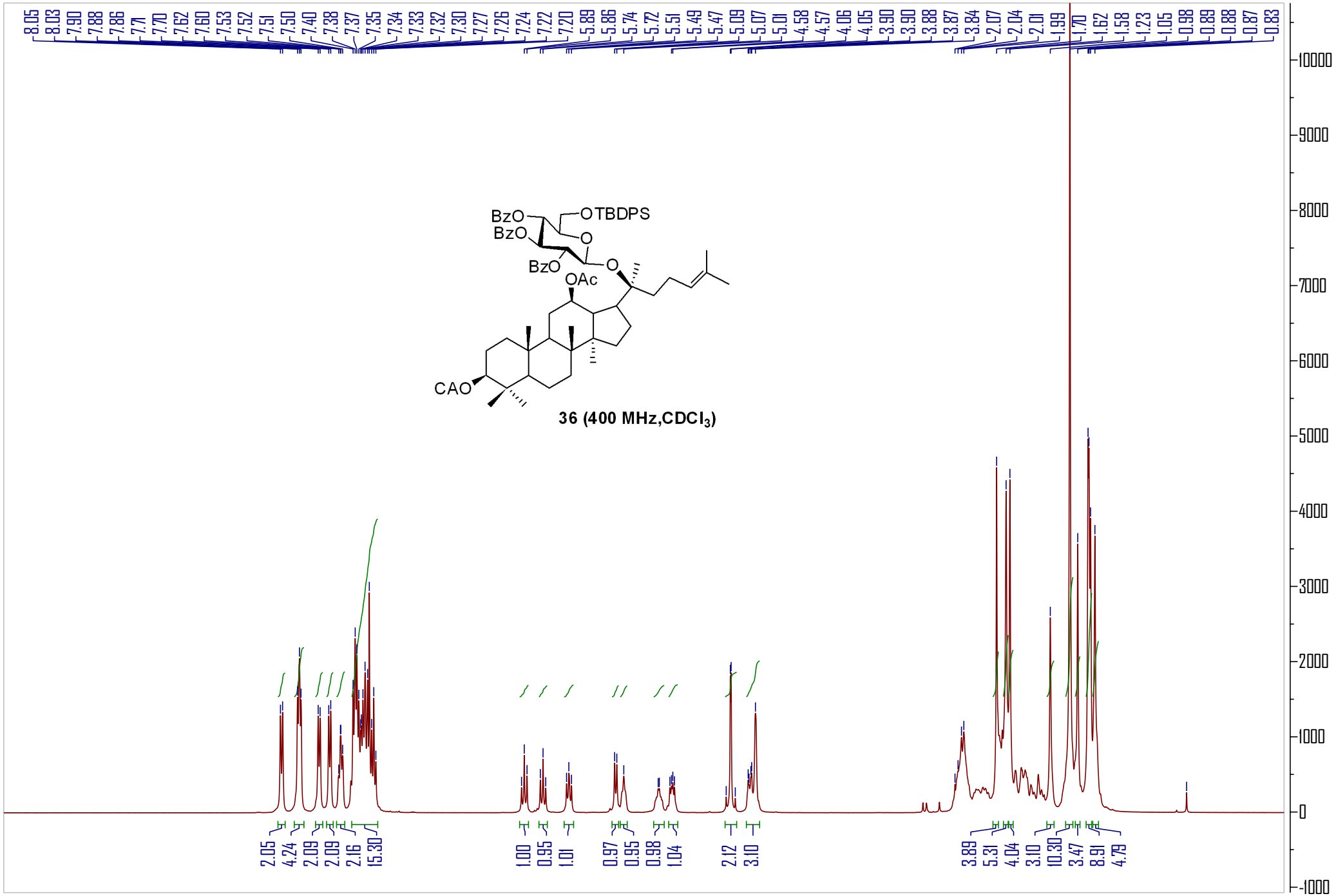
206.130

167.678 166.264 165.663 165.610 137.066 136.397 136.168 134.214 134.070 133.941 133.910 133.568 130.808 130.785 130.572 130.511 130.458 130.359 130.283 129.409 129.272 128.618 128.557 126.367 115.836 95.732 84.501 83.216 80.030 75.088 74.883 73.506 70.267 70.009 63.614 56.482 52.961 50.787 47.844 41.936 40.537 40.385 39.039 38.727 37.761 35.283 32.424 30.629 30.378 30.120 29.861 29.603 29.352 29.093 28.820 28.188 27.055 25.953 24.303 24.204 22.737 19.733 18.927 18.843 18.030 16.760 16.608 16.251



35 (100 MHz,$CDCl_3$)

200 180 160 140 120 100 80 60 40 20 0 ppm

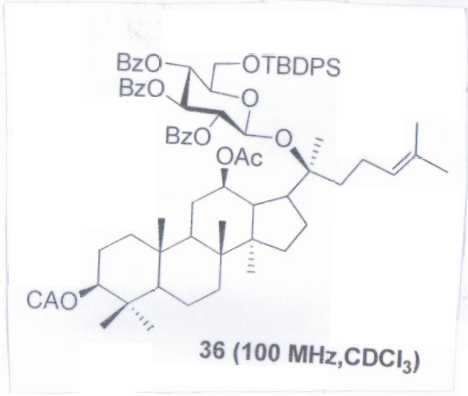

BzO
BzO
OTBDPS
O
BzO
O
OAc
CAO
36 (400 MHz,CDCl3)
f1 (ppm)

2-20

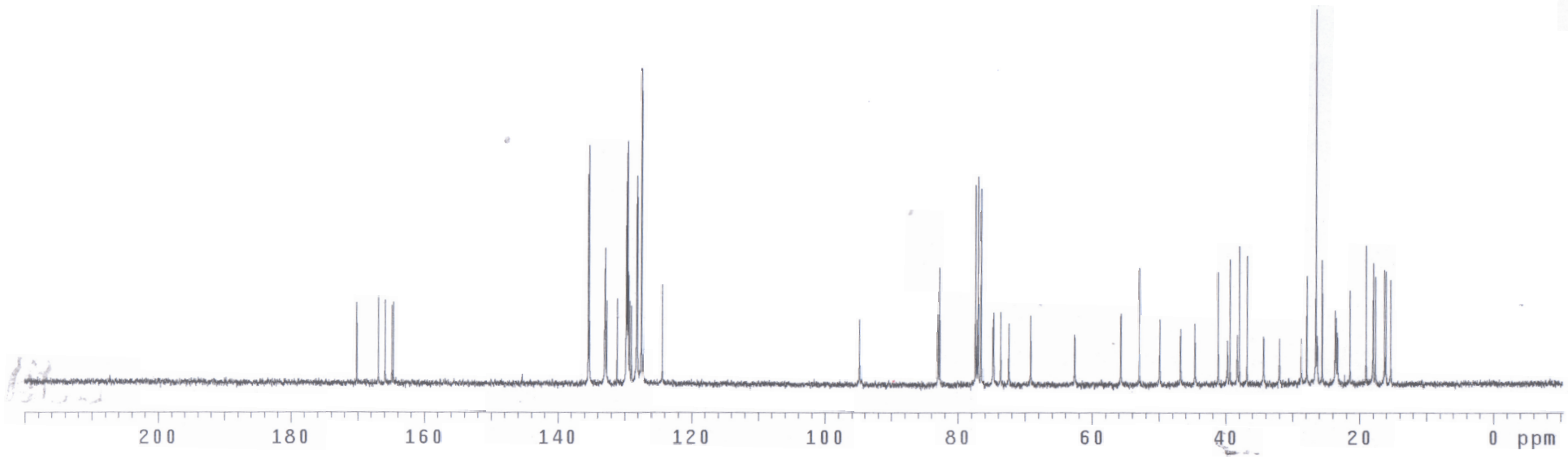
Pulse Sequence: s2pul

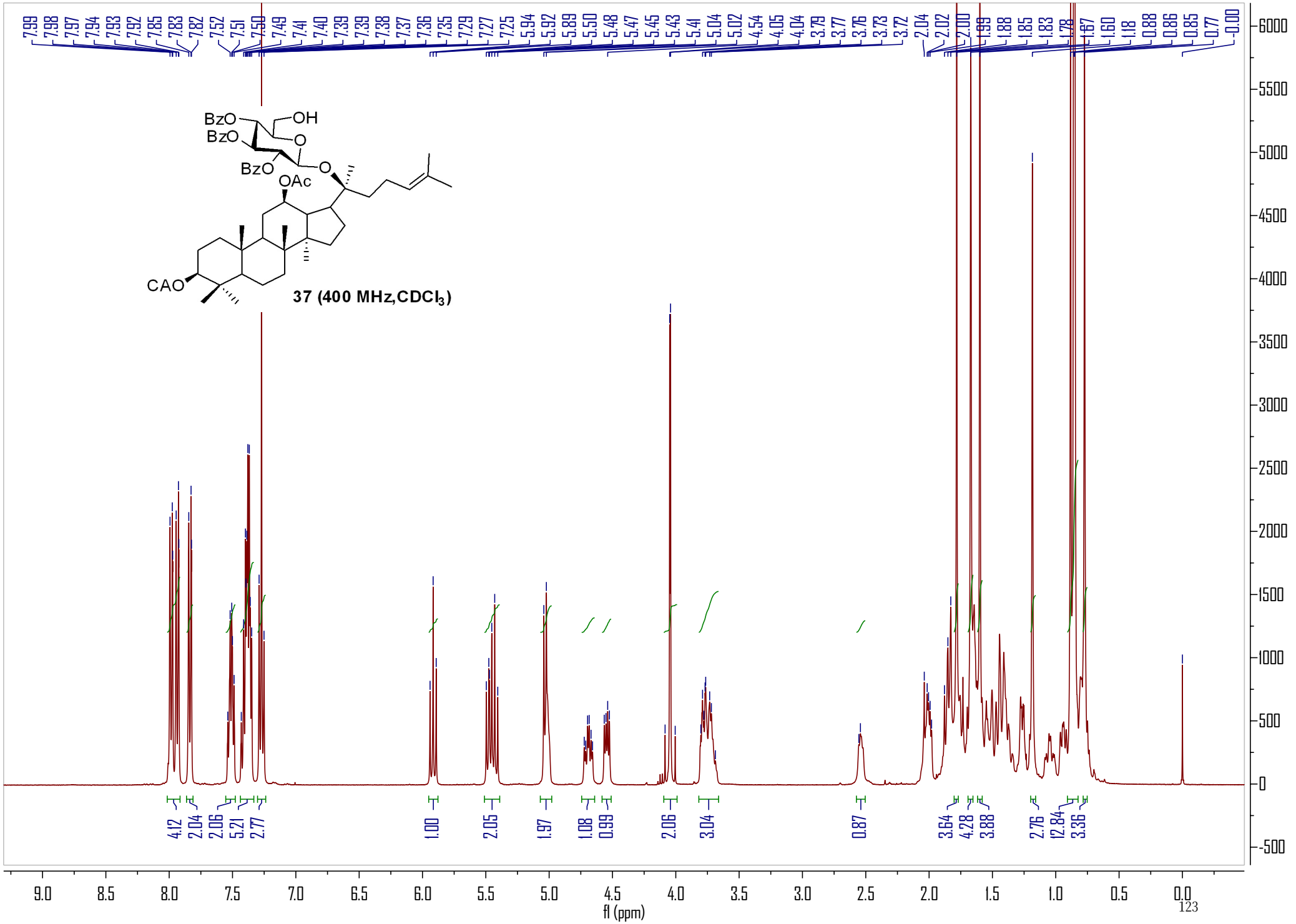
170.146
166.906
165.894
164.875
164.646

135.471
135.310
133.004
132.958
132.905
132.698
131.127
129.787
129.679
129.572
129.465
129.411
129.235
128.974
128.208
128.139
128.093
127.473
124.378
94.843
82.983
82.777
77.421
77.199
77.000
76.579
74.786
74.694
73.652
72.426
69.185
62.604
55.717
52.959
49.910
46.799
44.631
41.122
39.720
39.352
38.249
37.935
36.778
34.311
31.921
28.657
27.807
26.466
26.274
25.554
23.631
23.516
23.294
21.440
19.011
17.962
17.640
16.276
16.069
15.342



36 (100 MHz,$CDCl_3$)





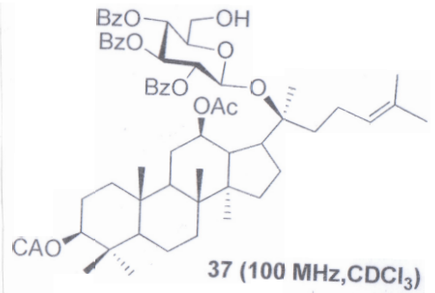
2011526-2-60

Pulse Sequence: s2pul

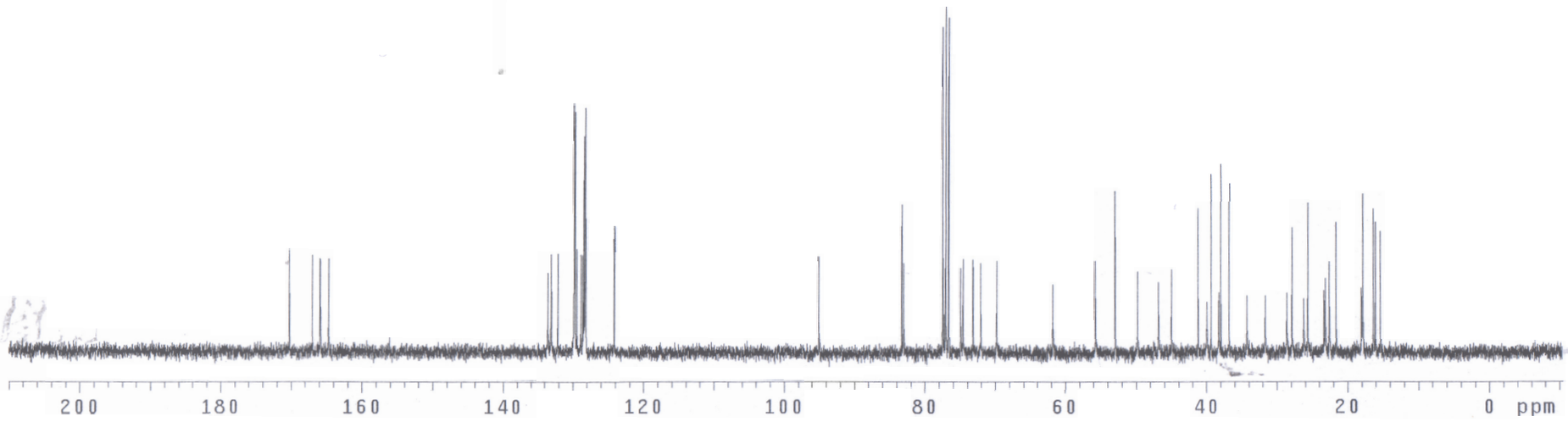
170.198
166.937
165.858
165.783
164.643

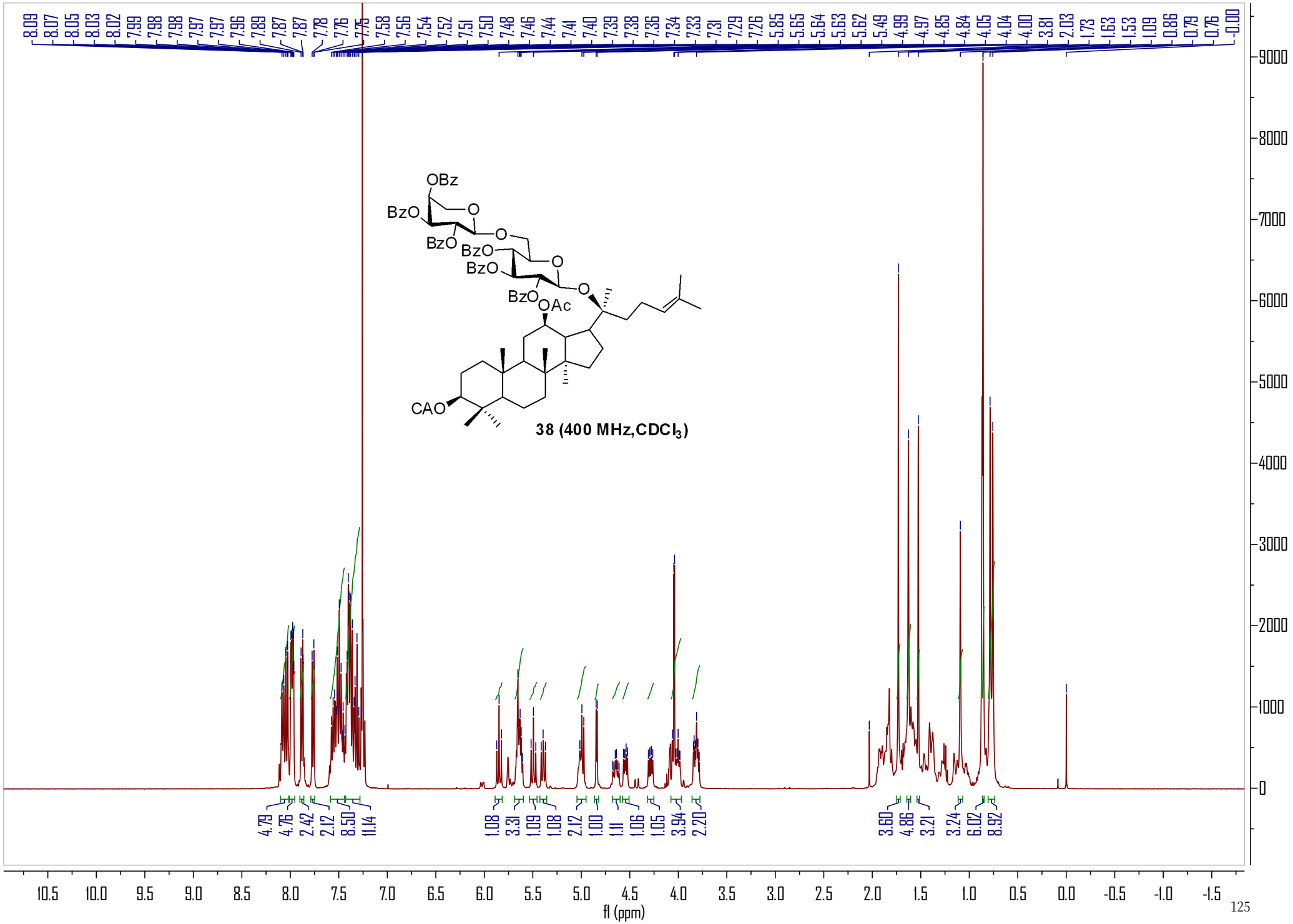
133.527
133.082
133.044
132.123
129.784
129.731
129.655
129.384
128.825
128.553
128.395
128.221
128.184
124.131

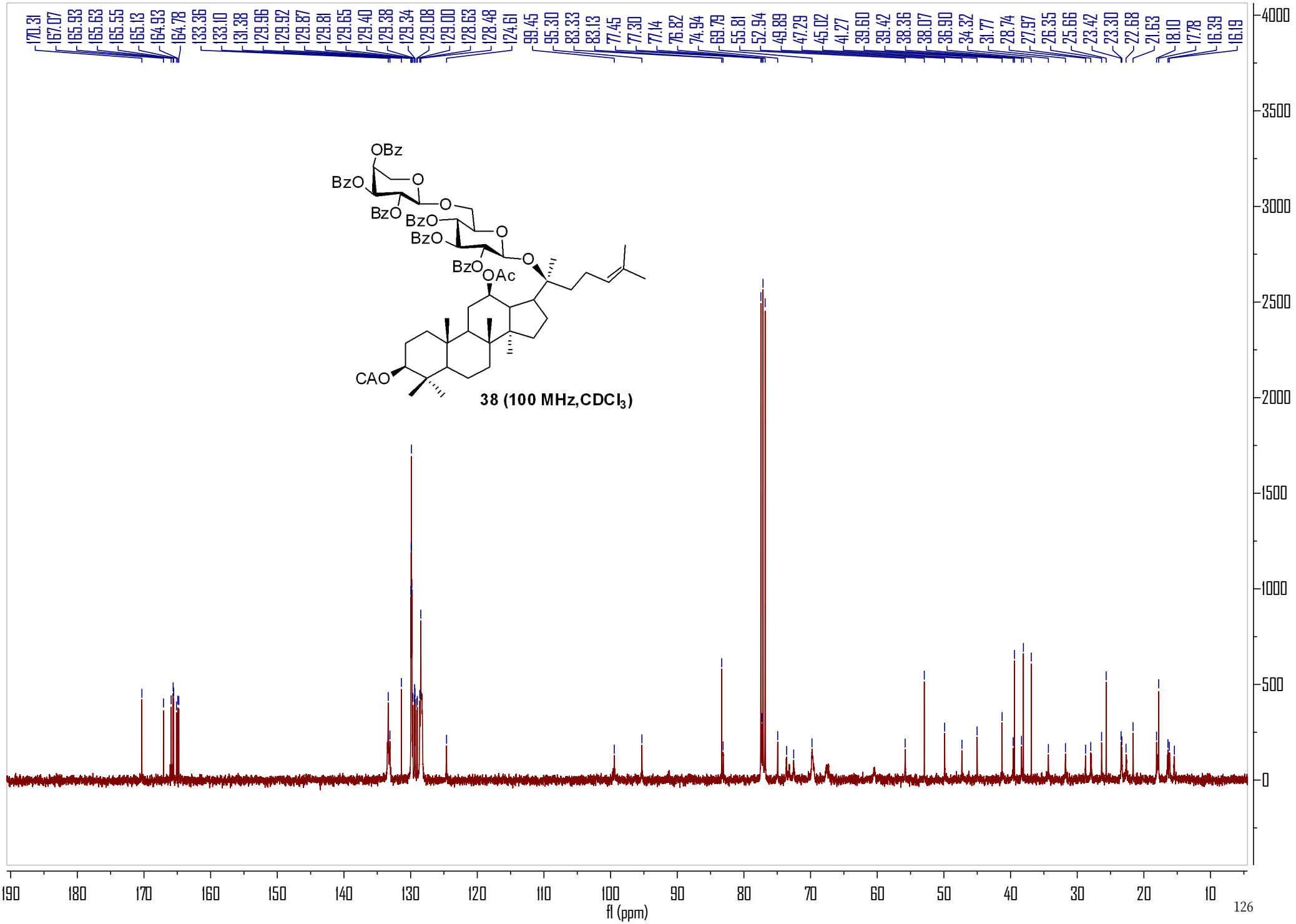
95.007
83.234
82.970
77.423
77.204
77.000
76.577
74.887
74.540
73.143
72.034
69.755
61.740
55.657
52.880
49.710
46.767
44.933
41.152
39.914
39.310
38.216
37.937
36.760
34.216
31.620
28.556
27.816
26.148
25.575
23.281
23.084
22.541
21.583
17.960
17.786
17.764
16.285
16.005
15.303

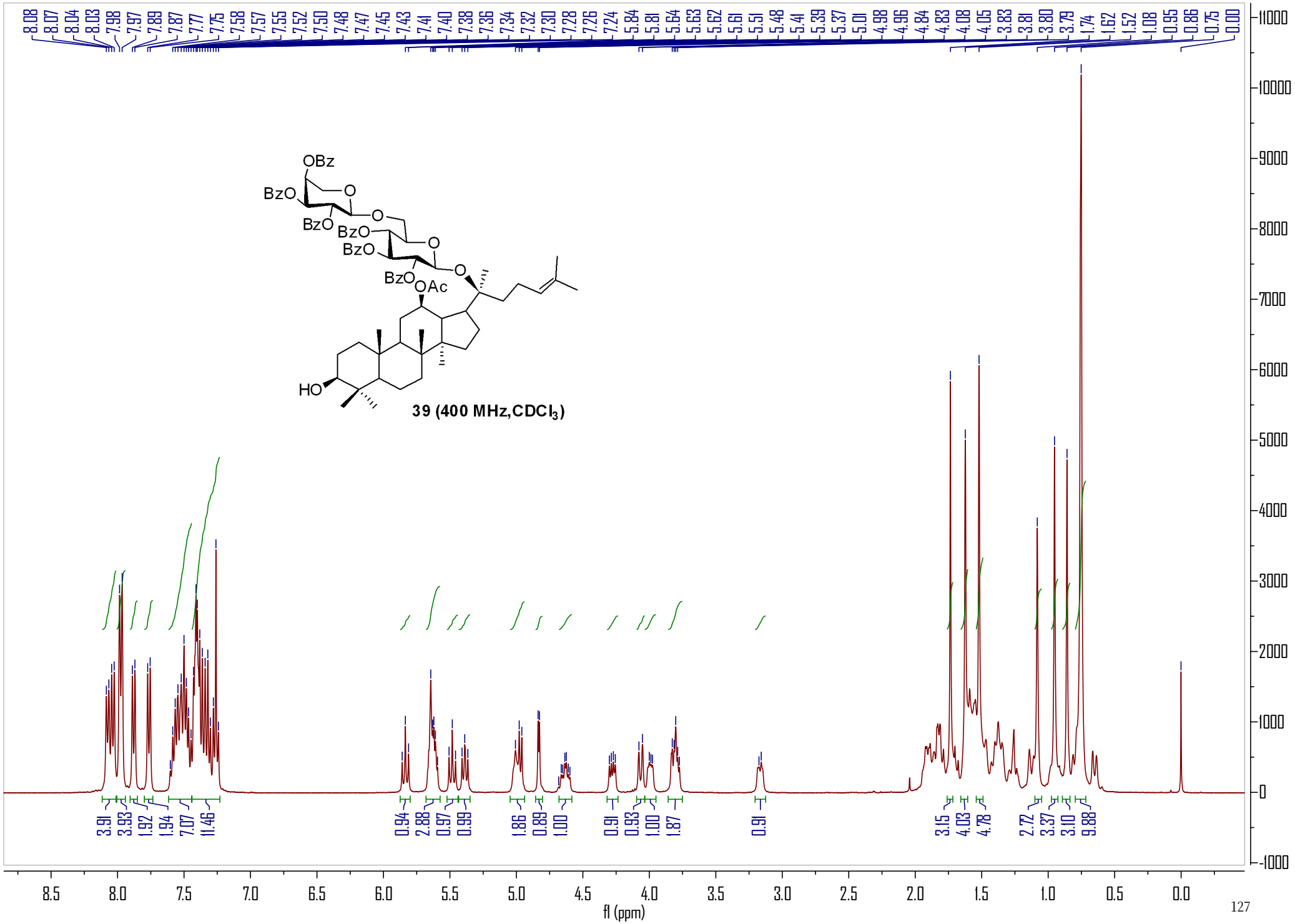


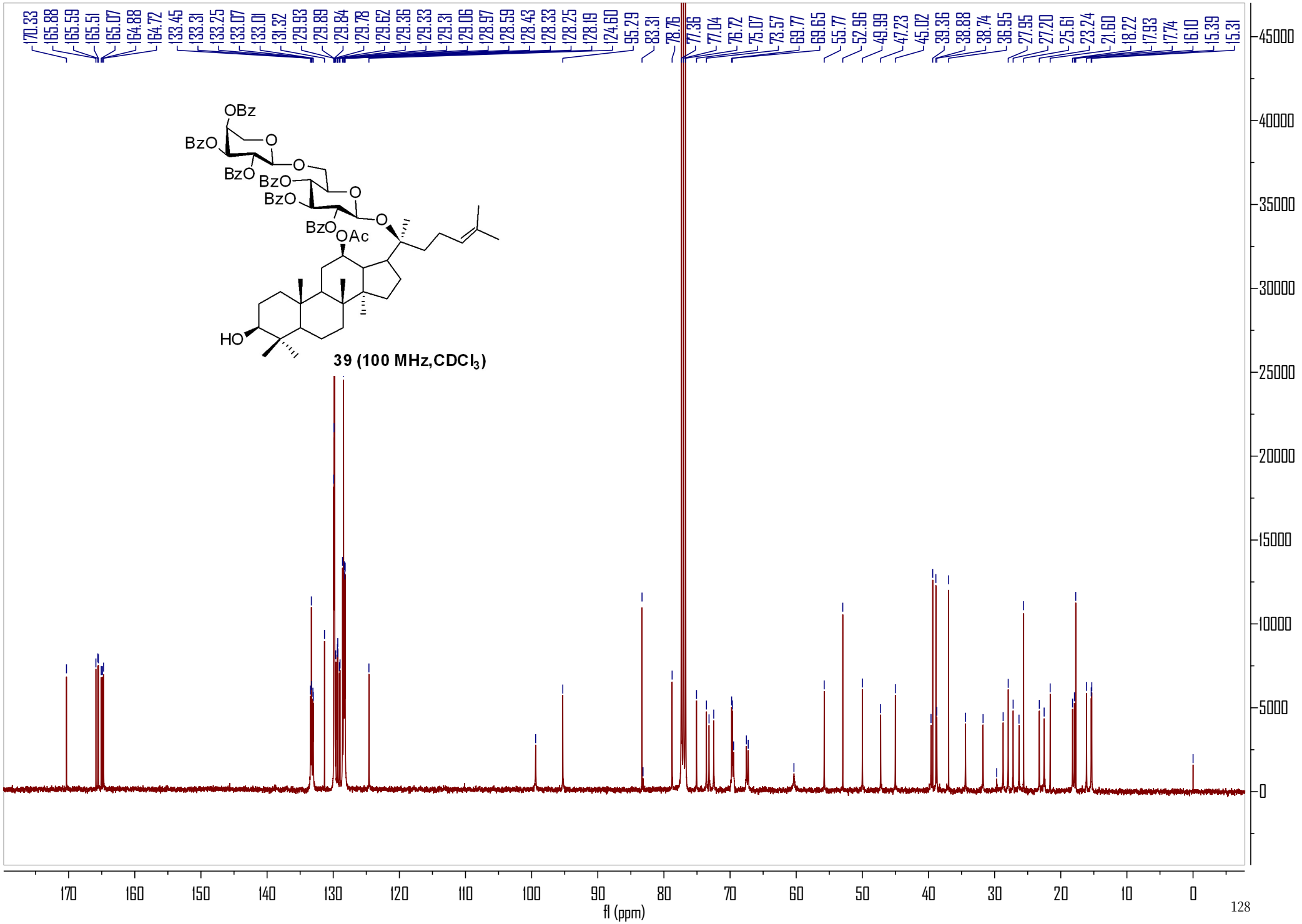
37 (100 MHz,$CDCl_3$)

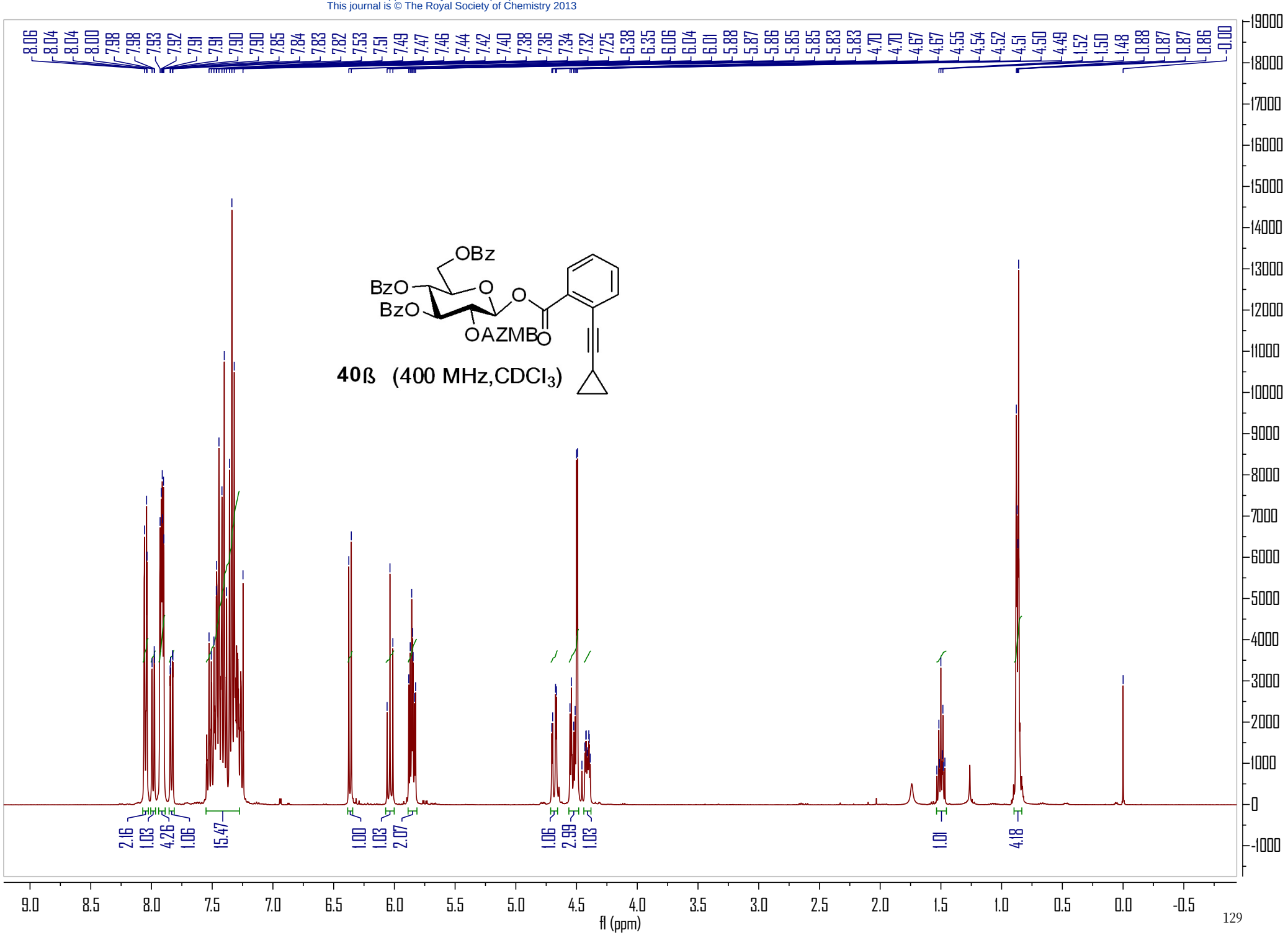


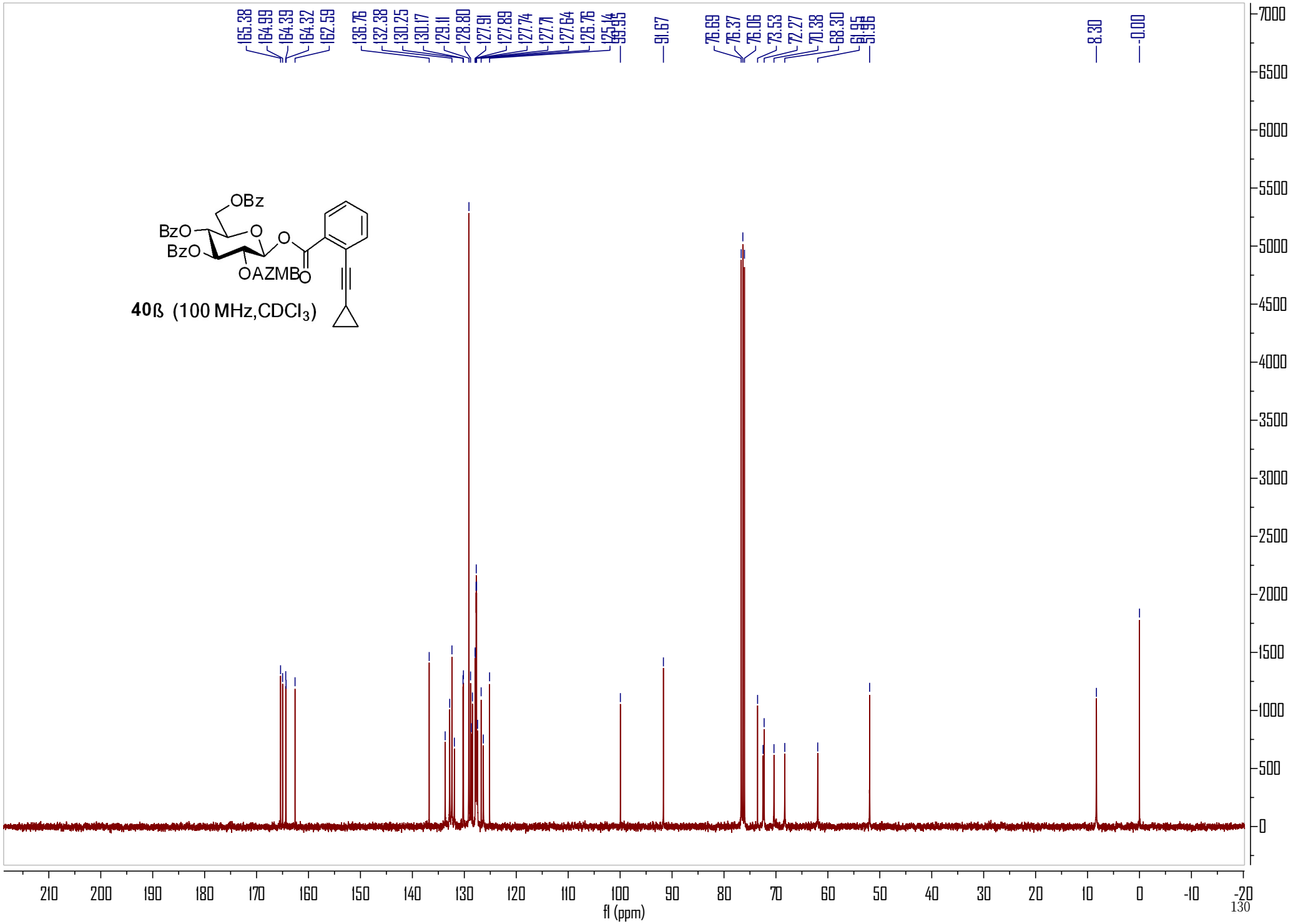


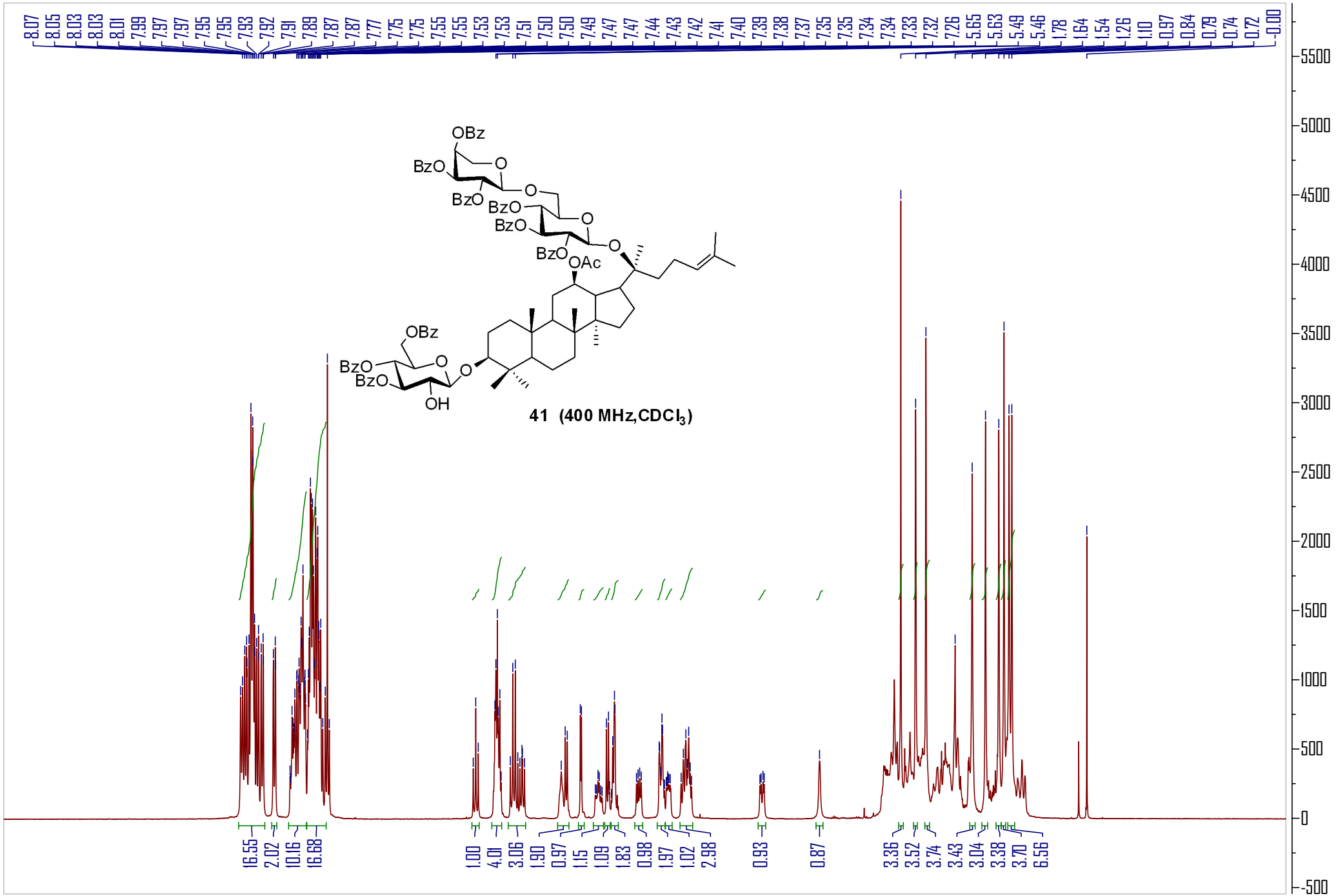

170.31
167.07
165.93
165.63
165.55
165.13
164.93
164.78
133.36
133.10
131.38
129.96
129.92
129.87
129.81
129.65
129.40
129.38
129.34
129.08
129.00
128.63
128.48
124.61
99.45
95.30
83.33
83.13
77.45
77.30
77.14
76.82
74.94
69.79
55.81
52.94
49.89
47.29
45.02
41.27
39.60
39.42
38.36
38.07
36.90
34.32
31.77
28.74
27.97
26.35
25.66
23.42
23.30
22.68
21.63
18.10
17.78
16.39
16.19
OBz
BzO
O
BzO
O
BzO
BzO
O
BzO
OAc
CAO
38 (100 MHz,CDCl3)
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

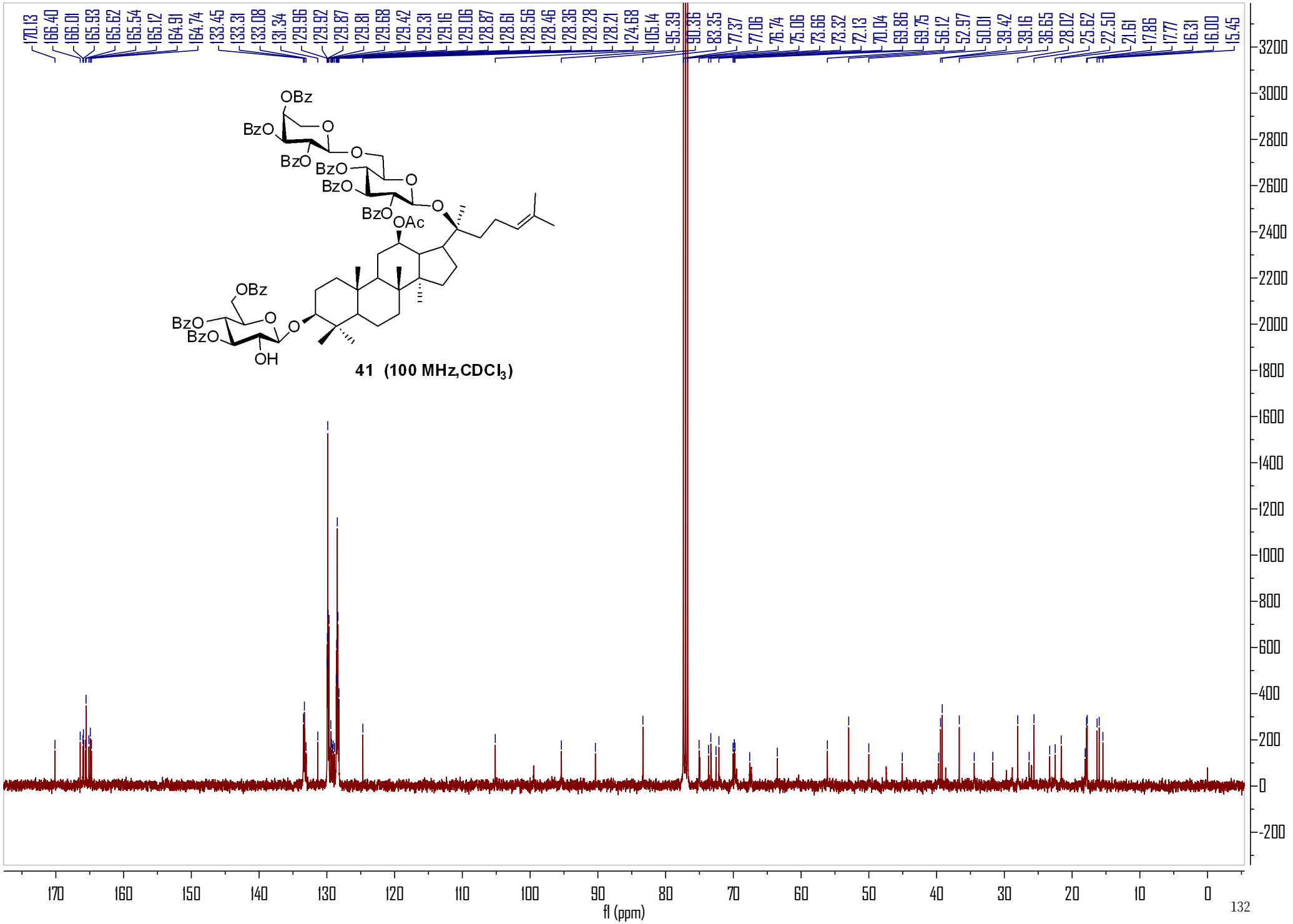

OBz
BzO
BzO
BzO
BzO
BzO
BzO
OAc
HO
39 (400 MHz,CDCl3)
f1 (ppm)

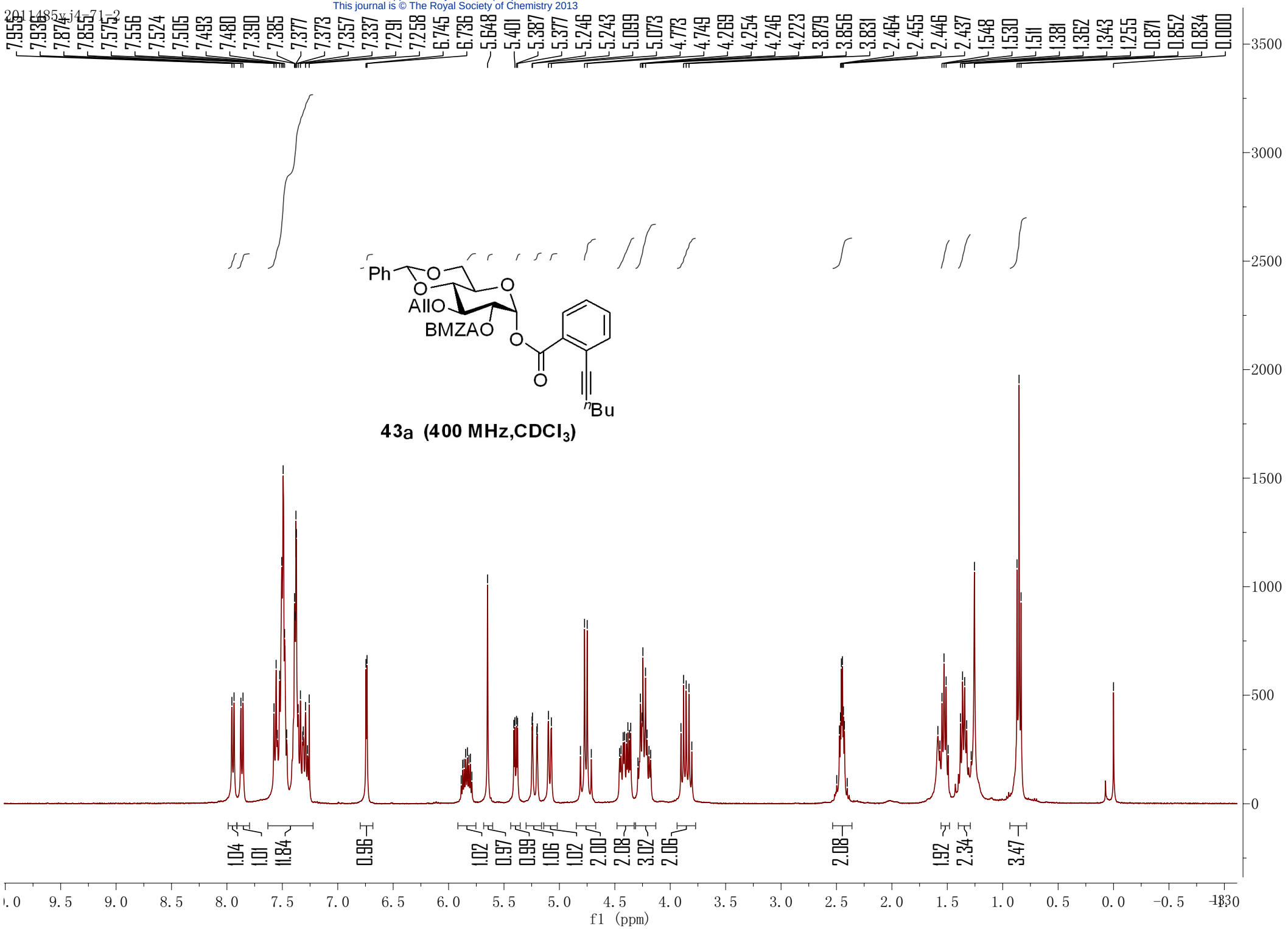

170.33
165.88
165.59
165.51
165.07
164.88
164.72
133.45
133.31
133.25
133.07
133.01
131.32
129.93
129.89
129.84
129.78
129.62
129.36
129.33
129.31
129.06
128.97
128.59
128.43
128.33
128.25
128.19
124.60
95.29
83.31
78.76
77.36
77.04
76.72
75.07
73.57
69.77
69.65
55.77
52.96
49.99
47.23
45.02
39.36
38.88
38.74
36.95
27.95
27.20
25.61
23.24
21.60
18.22
17.93
17.74
16.10
15.39
15.31
OBz
BzO
BzO
BzO
BzO
BzO
OAc
HO
39 (100 MHz,CDCl3)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

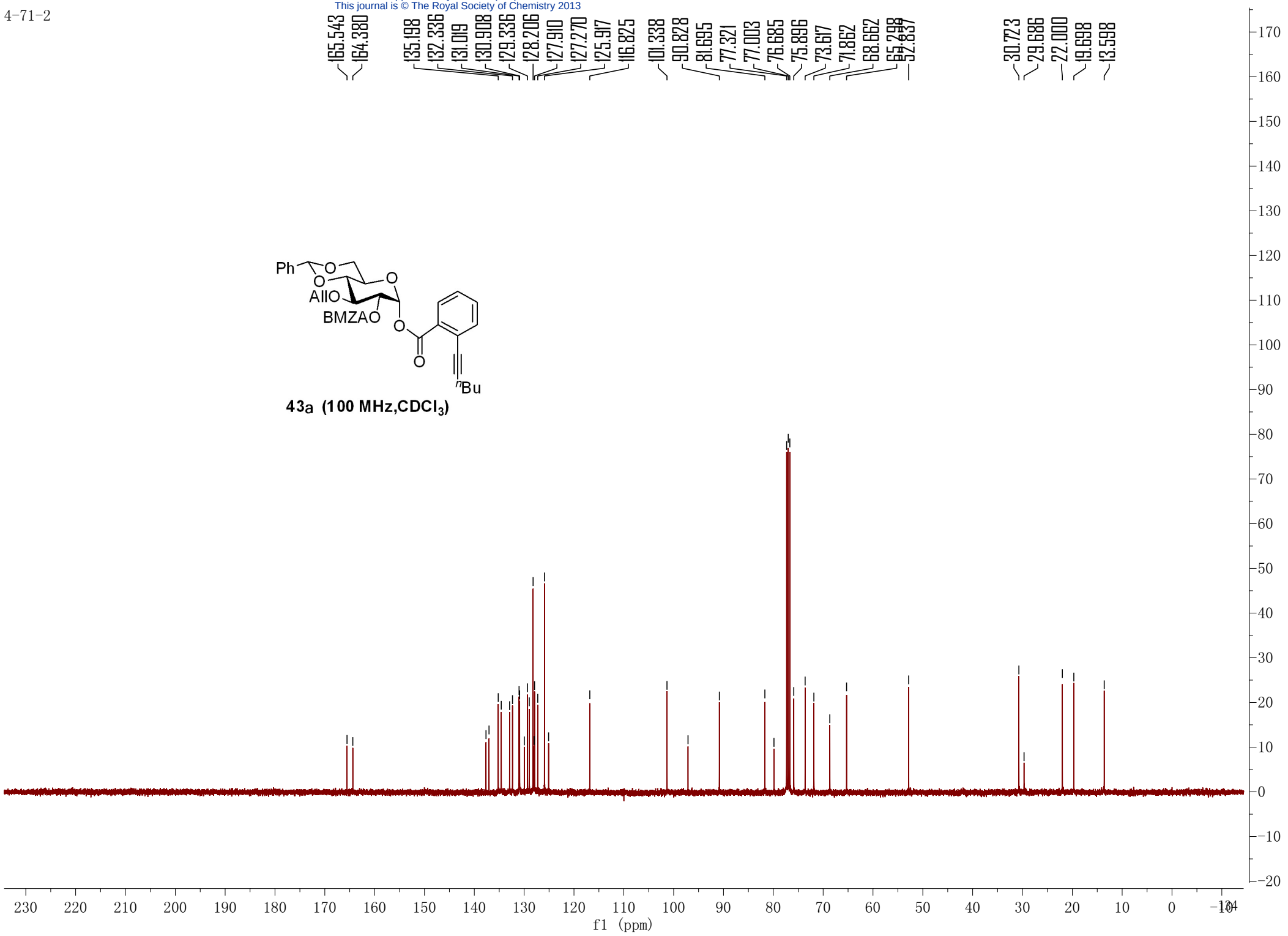

OBz
BzO
BzO
O
O
OAZMB
O
40ß (400 MHz,CDCl3)
f1 (ppm)

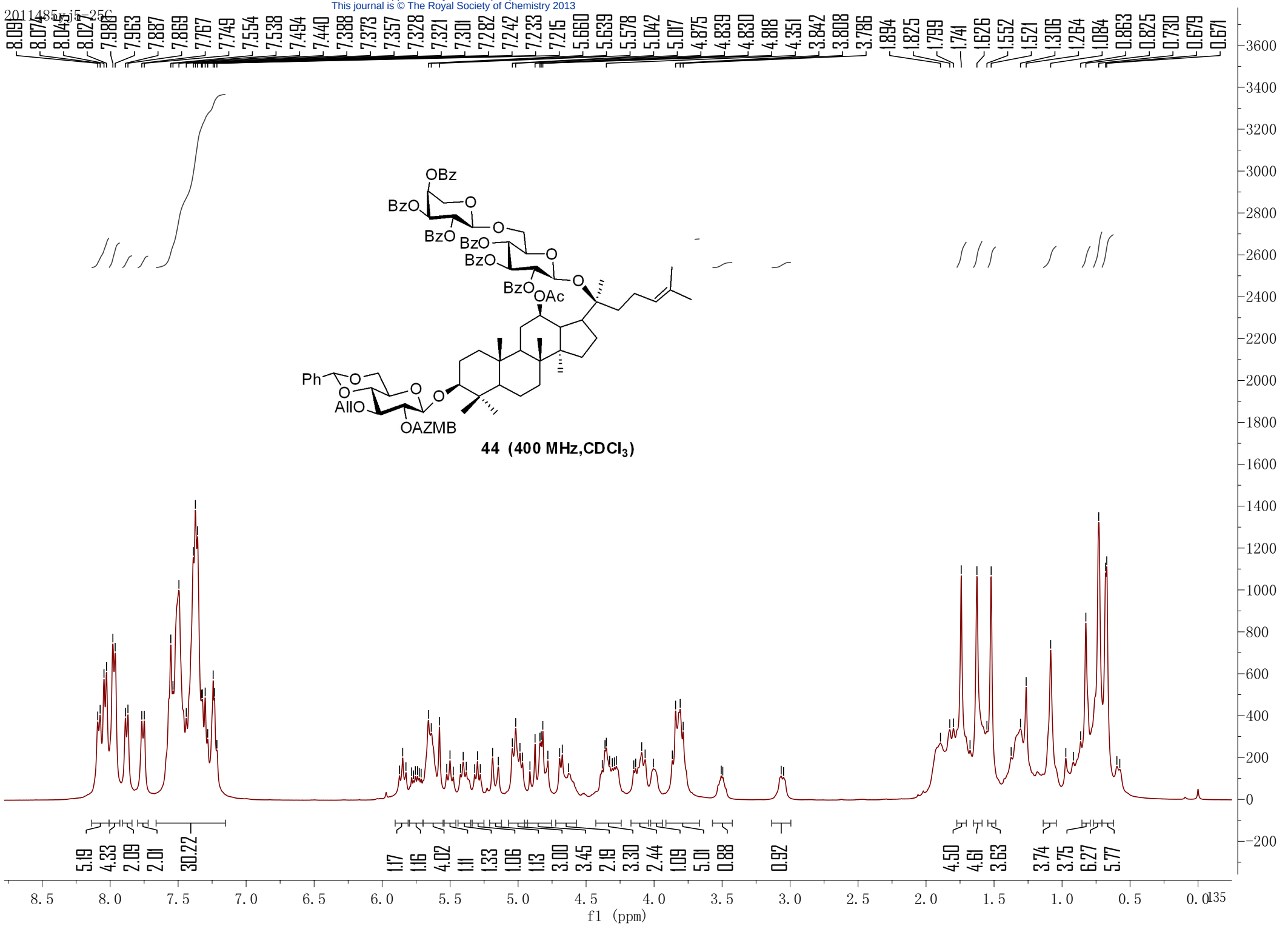


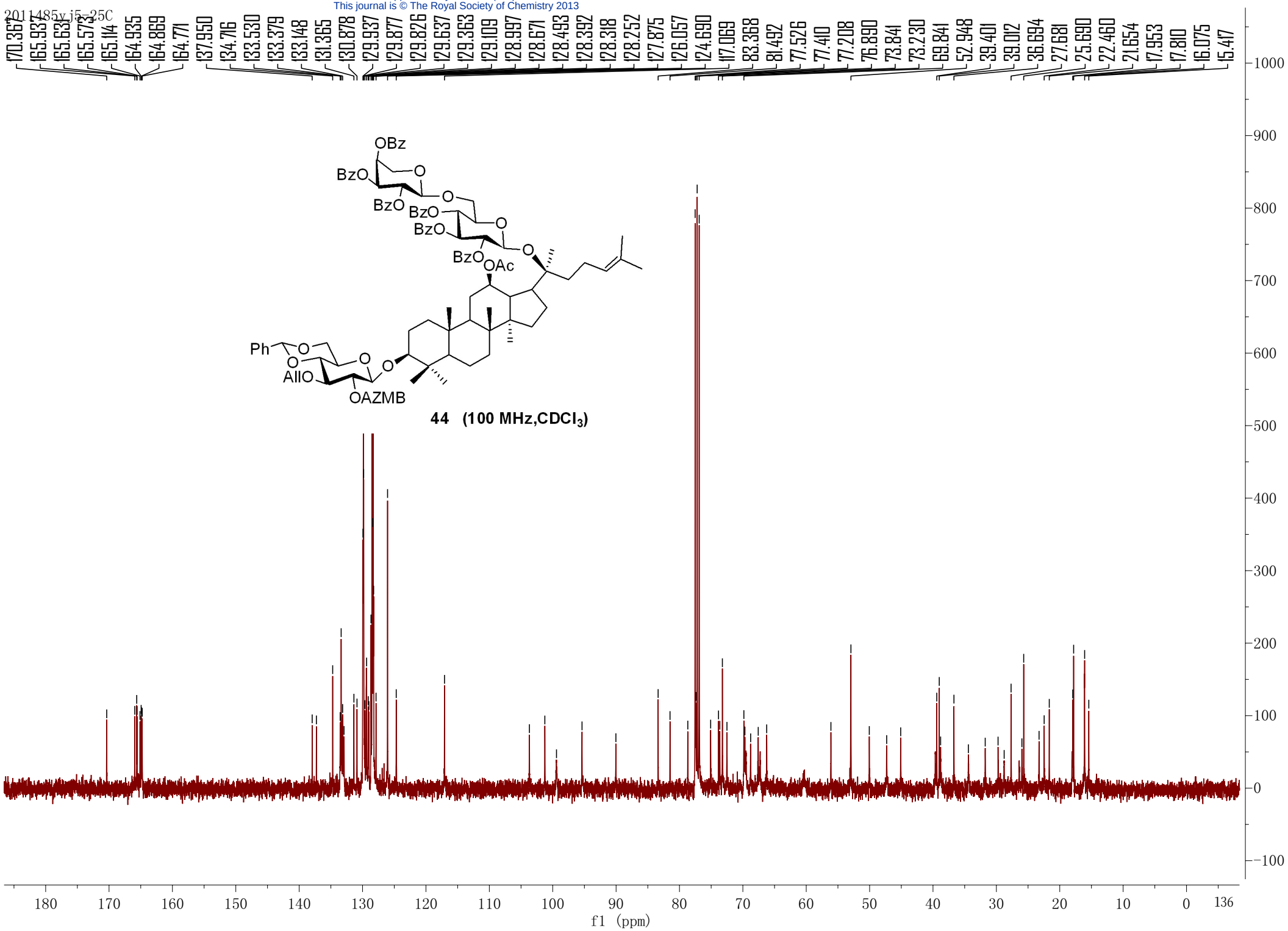

OBz
BzO
O
BzO
BzO
BzO
BzO
OAc
OBz
BzO
BzO
OH
41 (400 MHz,CDCl3)
f1 (ppm)

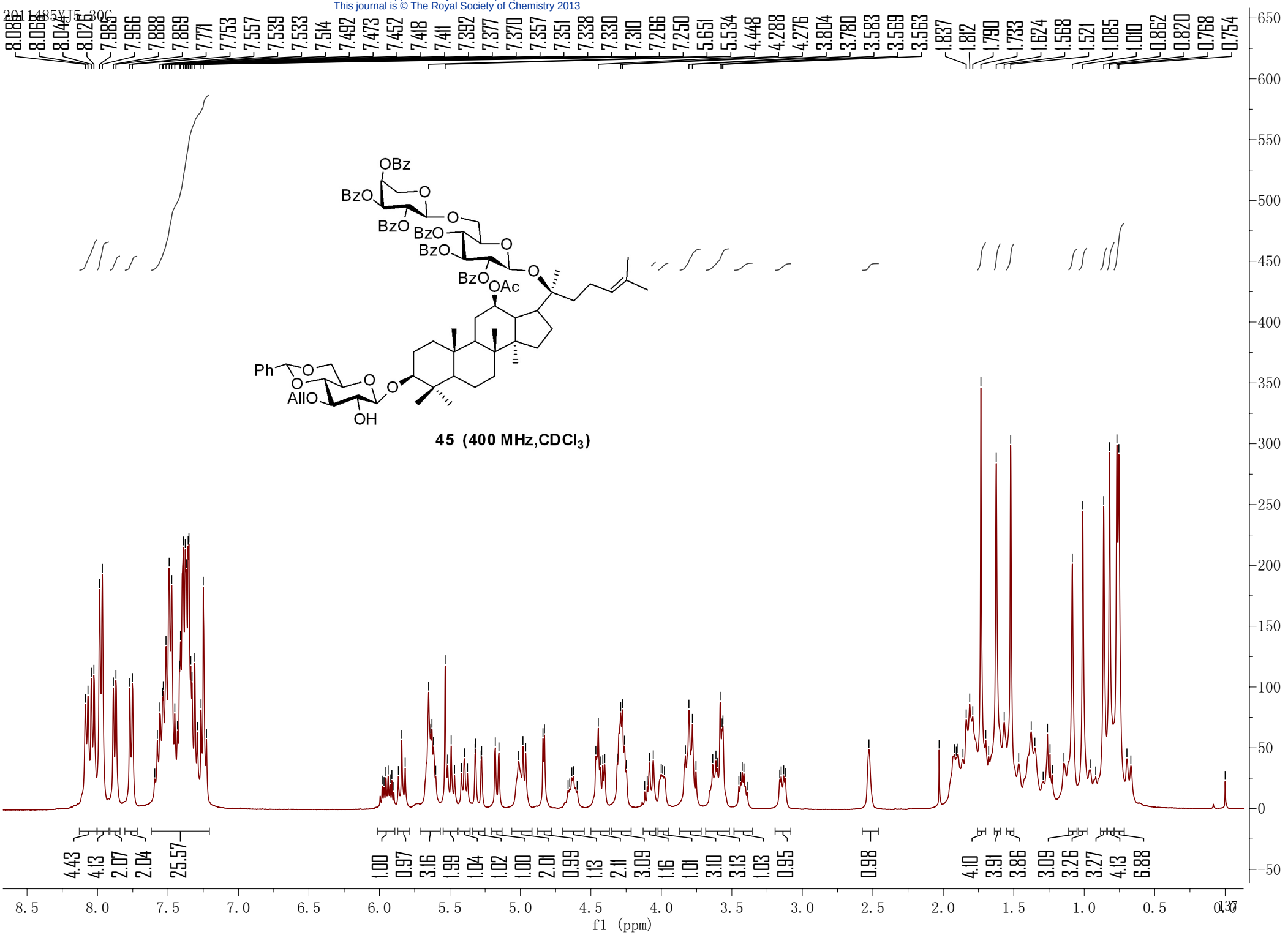

170.13
166.40
166.01
165.93
165.62
165.54
165.12
164.91
164.74
133.45
133.31
133.08
131.34
129.96
129.92
129.87
129.81
129.68
129.42
129.31
129.16
129.06
128.87
128.61
128.56
128.46
128.36
128.28
128.21
124.68
105.14
95.39
90.36
83.35
77.37
77.06
76.74
75.06
73.66
73.32
72.13
70.04
69.86
69.75
56.12
52.97
50.01
39.42
39.16
36.65
28.02
25.62
22.50
21.61
17.86
17.77
16.31
16.00
15.45
OBz
BzO
O
BzO
O
BzO
BzO
O
BzO
OAc
OBz
BzO
O
BzO
O
OH
41 (100 MHz,CDCl3)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

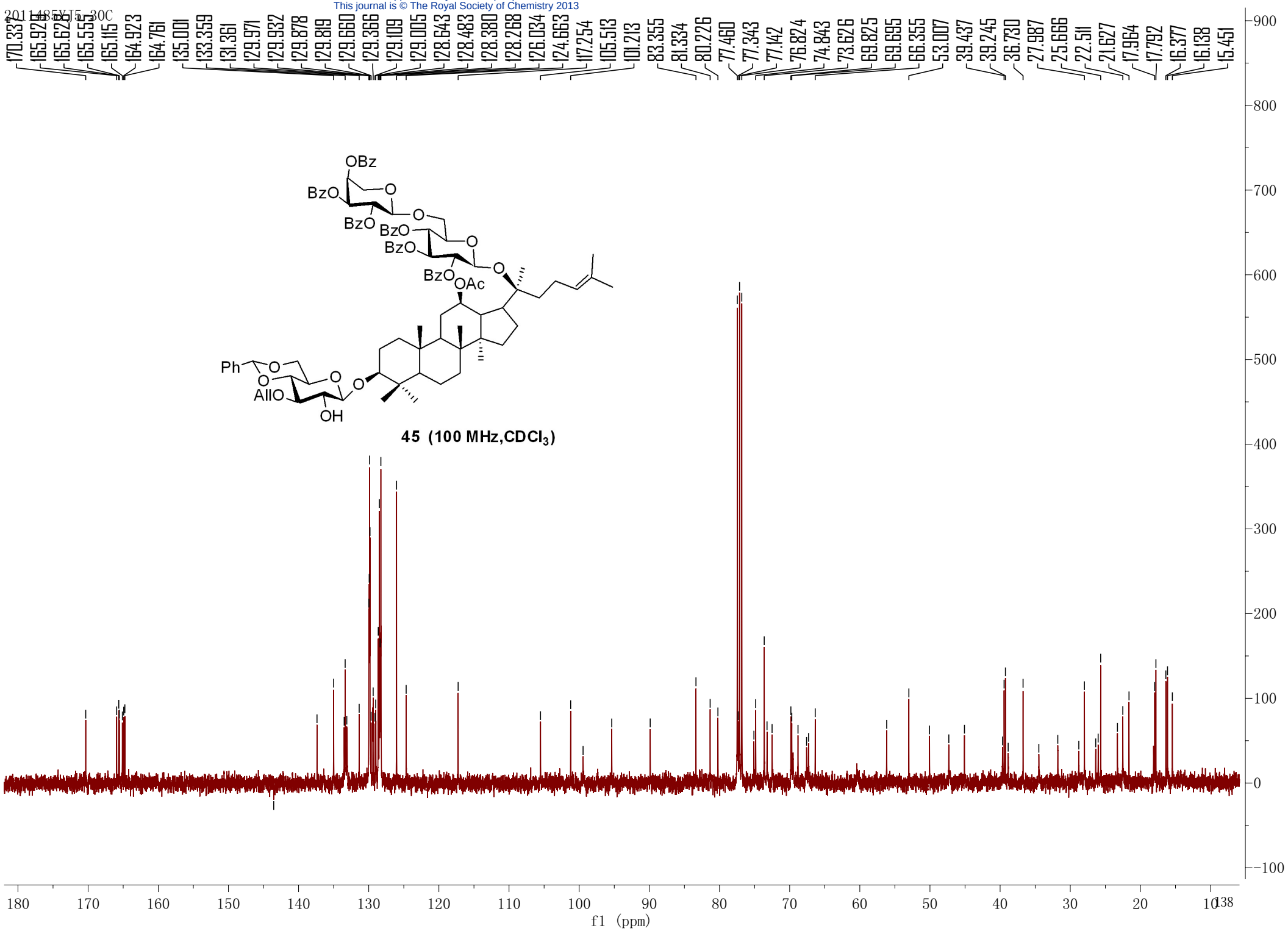


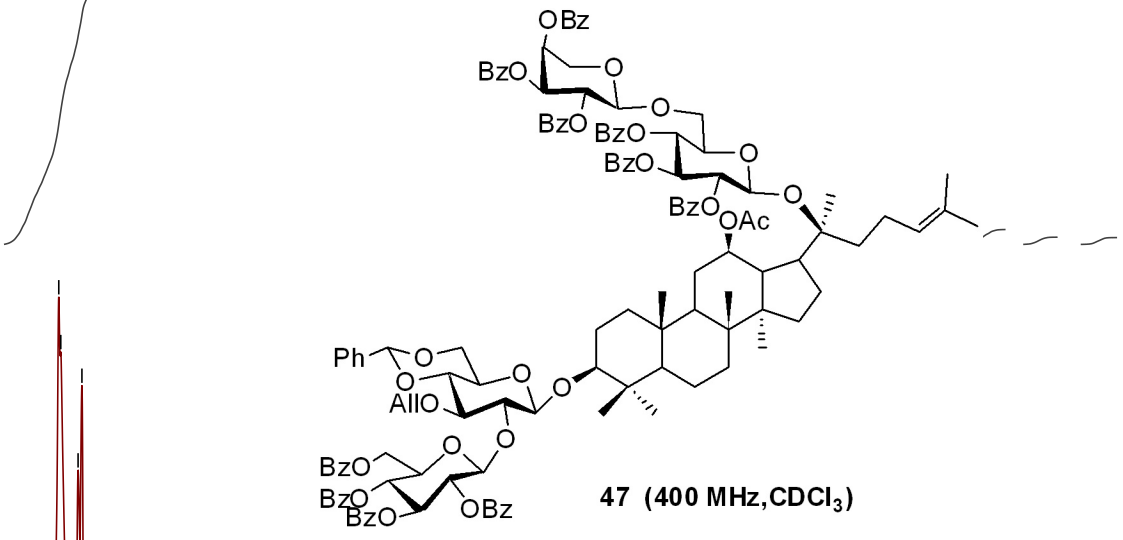












47 (400 MHz,$CDCl_3$)

f1 (ppm)