Electronic Supplementary Information

Synthesis, glycosylation and NMR characterization of linear peracetylated D-galactose glycopolymers

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Table S1. Homopolymerization of **4** in DMF at 60 °C.

Run	Monomer g (mmol)	AIBN mg (%)	DMF mL	Time h	Polymer g (%)
1	***4αp*** 0.188 (0.39)	2.0 (1.1)	1.0	48	***P4αp*** 0.163 (87)
2	***4βp***[a] 0.916 (1.92)	9.2 (1.0)	4.8	48	***P4βp***[a] 0.839 (92)
3	***4αβp*** 1.860 (3.90)	18.6 (1.0)	18.0	24	***P4αβp*** 0.821 (44)
4	***4αβp*** 2.18 (4.57)	21.8 (1.0)	11.6	50	***P4αβp*** 1.99 (91)
5	***4αβpf*** 2.28 (4.76)	22.9 (1.0)	16	72	***P4αβpf*** 2.01 (88)

AIBN = azo*bis*isobutironitrile; DMF = *N*,*N*-dimethylformamide; *p* = pyranose form; *f* = furanose form; [a] as enriched β-pyranose anomer.

Table S2. Typical glycosylation data of **5** with **2** in the presence of $SnCl_4$ or $BF_3·Et_2O$ in CH_2Cl_2.

Run	Substrate mg (mmol)	**C** µL (mmol)	**2** mg (mmol)	**5** : **C** : **2** Molar ratio	***6αp*** mg (mmol) %	***6βp*** mg (mmol) %	***7αβf*** mg (mmol) %	**8** mg (mmol) %[a]	***9βp*** mg (mmol) %	***10αβp*** mg (mmol) %
1	***5αp*** 108.2 (0.240)	$SnCl_4$ 35 (0.299)	78.3 (0.269)	1:1.3:1.1	41.8 (0.061) 25.4	5.2 (0.008) 3.3	-	27.2 (0.082) 30.5	-	-
2	***5βp*** 250.9 (0.556)	$SnCl_4$ 70 (0.598)	173.1 (0.594)	1:1.1:1.1	-	111.0 (0.163) 29.3	-	85.5 (0.257) 43.2	22.3 (0.054) 9.1	-
3	***5αβf***[b] 116.2 (0.257)	$SnCl_4$ 35 (0.299)	84.0 (0.299)	1:1.2:1.2	-	-	84.4 (0.124) 48.1	7.1 (0.021) 7.3	-	-
4	***5βp*** 200.3 (0.444)	$BF_3·Et_2O$ 60 (0.473)	142.6 (0.490)	1:1.1:1.1	-	100.9 (0.148) 33.3	-	71.7 (0.215) 43.9	2.5 (0.006) 1.4	-
5	***5αβp***[d] 122.9 (0.272)	$BF_3·Et_2O$ 252 (2.042)	95.1 (0.327)	1:7.5:1.2	-	36.9 (0.054) 19.9	-	22.9 (0.069) 21.0	7.4 (0.018) 6.6	15.5 (0.038) 13.9

C = promoter; [a] yield percent with respect to **2**; [b] β/α = 1.3; [c] β/α = 2.0; [d] β/α = 2.2.

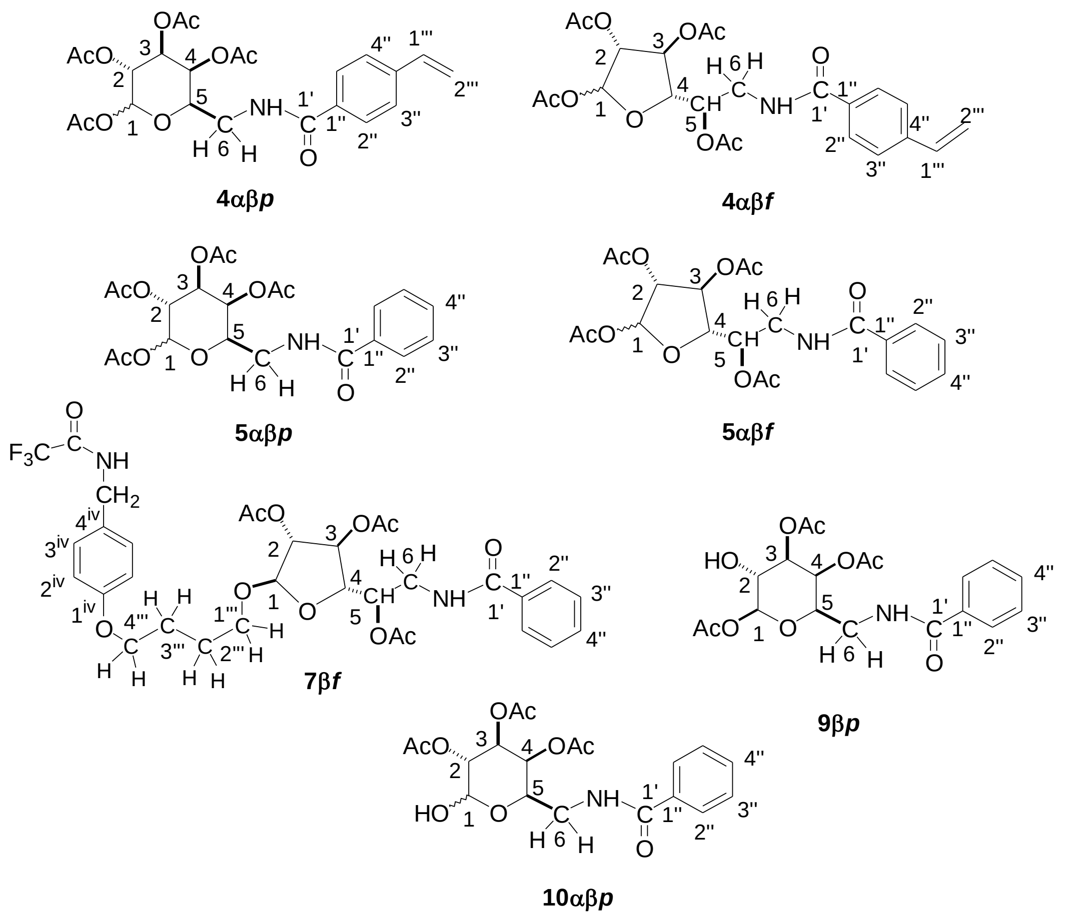


Chart S1. Numbering of the carbons of **4αβ*p***, **4αβ*f***, **5αβ*p***, **5αβ*f***, **7β*f***, **9β*p***, and **10αβ*p*** for NMR assignments.

Characterization of compounds 7αβ*f*, 8, 9β*p*, and 10αβ*p*

7αβ*f*. Oil. ν_{max}/cm^{-1} (neat) 1748 (ester), 1650 (amide).

7β*f*. δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.72-1.89 (m, 4H, H-2''' + H-3''')*, 2.07 (s, 3H, CH_3)*, 2.10 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.49-3.91 (m, 4H, H-6 + H-1''')*, 3.97 (t, 2H, *J* = 6.1, H-4''')*, 4.25 (dd, 1H, J_1 = 5.7, J_2 = 3.2, H-4), 4.43 (d, 2H, *J* = 5.6, H-1^{v})*, 4.98-5.03 (m, 1H, H-3), 5.04-5.09 (m, 2H, H-1 + H-2), 5.33 (dt, 1H, J_1 = 7.1, J_2 = 3.4, H-5), 6.81-6.91 (m, 3H, H-2^{iv} + H-6^{iv} + CH_2NH)*, 7.14-7.22 (m, 2H, H-3^{iv} + H-5^{iv}), 7.25 (bs, 1H, CF_3CONH)*, 7.38-7.53 (m, 3H, H-3'' + H.4'' + H-5'')*, 7.70-7.76 (m, 2H, H-2''+ H-6'')*. *Overlapped with those from **7α*f***. δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 20.68 (CH_3)**, 20.78 (CH_3)**, 20.91 (CH_3)**, 25.88 (C-2''' or C-3''')**, 25.94 (C-2''' or C-3''')**, 41.75 (C-6), 43.37 (C-1^{v})**, 67.34 (C-1''), 67.54 (C-4'')**, 70.62 (C-5), 76.89 (C-3), 81.33 (C-2), 81.61 (C-4), 105.59 (C-1), 114.87 (C-2^{iv})**, 115.96 (q, CF_3CO, J_{CF} = 288)**, 126.89

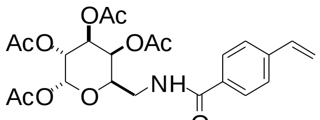
(C-2")**, 128.13 (C-4[iv]), 128.63 (C-3")**, 129.45 (C-3[iv])**, 131.65 (C-4")**, 134.07 (C-1"), 157.10 (q, CF_3*C*O, J_{CF} = 37)**, 158.86 (C-1[iv])**, 167.54 (*C*O, amide), 169.80 (*C*O, ester)**, 170.31 (*C*O, ester), 171.18 (*C*O, ester). ******Overlapped with those of **7α*f*** or not assignable to the proper anomer.

7α*f*. δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.72-1.89 (m, 4H, H-2''' + H-3''')*, 2.07 (s, 3H, CH_3)*, 2.09 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 3.35-3.45 (m, 1H, H-6), 3.49-3.91 (m, 3H, H-6 + H-1''')*, 3.97 (t, 2H, J = 6.1, H-4''')*, 4.08 (dd, 1H, J_1= 6.5, J_2= 5.2, H-4), 4.43 (d, 2H, J = 5.6, H-1[v])*, 5.14-5.17 (m, 1H, H-5), 5.21 (d, 1H, J = 4.7, H-1), 5.56 (dd, 1H, J_1= 7.2, J_2= 6.5, H-3), 6.81-6.91 (m, 3H, H-2[iv] +H-6[iv] + CH_2NH)*, 7.14-7.22 (m, 2H, H-3[iv] +H-5[iv])*, 7.25 (bs, 1H, CF_3CONH)*, 7.38-7.53 (m, 3H, H-3" + H-4" + H-5")*, 7.70-7.76 (m, 2H, H-2"+ H-6")*. *****Overlapped with those from **7β*f***. The H-2 signal around 5.0 ppm is hidden under H-3 from the β-anomer (DQF-COSY). δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 20.54 (CH_3), 20.67 (CH_3)**, 20.78 (CH_3)**, 20.91 (CH_3)**, 25.88 (C-2''' or C-3''')**, 25.94 (C-2''' or C-3''')**, 41.08 (C-6), 43.37 (C-1[v])**, 67.54 (C-4")**, 68.18 (C-1"), 71.80, 73.91, 76.46, 78.91, 99.68 (C-1), 114.87 (C-2[iv])**, 115.96 (q, *C*F_3CO, J_{CF}= 288)**, 126.89 (C-2")**, 128.06 (C-4[iv]), 128.63 (C-3")**, 129.45 (C-3[iv])**, 131.65 (C-4")**, 134.07 (C-1")**,157.10 (q, CF_3*C*O, J_{CF}= 37), 158.86 (C-1[iv])**, 167.49 (*C*O, amide), 169.80 (*C*O, ester)**, 170.37 (*C*O, ester), 171.27 (*C*O, ester). ******Overlapped with those of **7β*f*** or not assignable to the proper anomer.

8. Mp 65-66 °C (from Et_2O/pentane/-30 °C). ν_{max}/cm^{-1} (KBr) 3334 (NH amide), 1716 (ester + amide). δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.73-1.89 (m, 4H), 2.05 (s, 3H, CH_3), 3.98 (t, 2H, J = 5.9), 4.13 (t, 3H, J = 6.2), 4.45 (d, 2H, J = 5.7), 6.64 (bs, 1H, NH), 6.84-6.91 (m, 2H), 7.17-7.23 (m, 2H). δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 20.95, 25.40, 25.84, 43.47, 64.11, 67.42, 114.96, 115.93 (q, $^1J_{CF}$ = 288), 128.04, 129.48, 157.06 (q, $^2J_{CF}$ = 37), 158.97, 171.25. *m/z* (CI) 334 (M^++1, 20%), 221 (100). Anal. calcd for $C_{15}H_{18}F_3NO_4$: C, 54.05; H, 5.44; N, 4.20. Found: C, 54.26; H, 5.77; N, 4.06.

9β*p*. $[\alpha]_D^{22}$ = +17.2 (*c* 0.255, $CHCl_3$). ν_{max}/cm^{-1} (KBr) 3375 (NH + OH), 1751 (ester), 1646 (amide). δ_H (300 MHz; $CDCl_3$, Me_4Si) 2.07 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.65 (bs, 1H, OH), 3.47-3.70 (m, 2H, H-6), 3.92-4.06 (m, 2H, H-2 + H-5), 5.02 (dd, 1H, J_1 = 3.4, J_2 = 10.2, H-3), 5.41 (dd, 1H, J_1 = 0.7, J_2 = 3.4, H-4), 5.63 (d, 1H, *J* = 8.2, H-1), 6.63 (bt, 1H, *J* = 5.6, NH), 7.38-7.55 (m, 3H, aromatics), 7.72-7.79 (m, 2H, aromatics). δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 20.72 (CH_3), 20.98 (3CH_3), 39.20 (C-6), 68.35, 68.52, 72.46, 73.03, 94.44 (C-1), 127.03 (C-2"), 128.66 (C-3"), 131.74 (C-4"), 133.92 (C-1"), 167.60 (*C*O, amide), 169.28 (*C*O, ester), 170.45 (*C*O, ester), 170.83 (*C*O, ester). Anal. calcd for $C_{19}H_{23}NO_9$: C, 55.74; H, 5.66; N, 3.42. Found: C, 55.64; H, 5.56; N, 3.13.

10αβ*p*. ν_{max}/cm^{-1} (KBr): 3390 (NH + OH), 1740 (ester), 1647 (amide). δ_H (300 MHz; DMSO-*d6*, Me_4Si) 1.88 (s, CH_3β), 1.91(s, 3H, CH_3α), 2.01 (s, 3H, CH_3β), 2.03 (s, 3H, CH_3α), 2.12 (s, 3H, CH_3α), 2.13 (s, 3H, CH_3β), 3.10-3.29 (m, H-6α + H-6β), 3.44-3.64 (m, H-6α + H-6β), 4.12 (bt, 1H, *J* = 7.0, H-5β), 4.44 (bt, 1H, *J* = 7.1, H-5α), 4.78 (dd, 1H, J_1 = 7.8, J_2 = 6.5, H-1β), 4.86-4.97 (m, H-2α + H-2β), 5.09 (dd, 1H, J_1 = 10.3, J_2 = 3, H-3β), 5.18-5.30 (m, H-1α + H-3α + H-4α + H-4β), 7.11 (dd, 1H, J_1 = 4.8, J_2 = 0.9, OHα), 7.19 (d, 1H, *J* = 6.5, OHβ), 7.43-7.56 (m, aromatics), 7.52-7.56 (m, aromatics), 8.45 (bdd, 1H, J_1 = 7.1, J_2 = 4.1, NHα), 8.56 (bdd, 1H, J_1 = 6.6, J_2 = 4.8, NHβ). δ_C (75.5 MHz; DMSO-*d6*, Me_4Si) 20.31 (CH_3β), 20.36 (CH_3α), 20.47(CH_3α), 20.52 (CH_3α), 20.55 (CH_3β), 20.58 (CH_3β), 38.46 (C-6), 38.56 (C-6), 65.57 (α-anomer), 67.15 (α-anomer), 67.40 (β-anomer), 67.68 (α-anomer), 68.26 (α-anomer), 70.12 (β-anomer), 70.17 (β-anomer), 89.36 (C-1α), 94.21 (C-1β), 127.05 (C-2"), 128.18 (C-3"), 131.14 (C-4"α), 131.18 (C-4"β), 134.12 (C-1"β), 134.21 (C-1"α), 166.38 (*C*O, amide), 169.12 (*C*O, ester), 169.53 (*C*O, ester), 169.54 (*C*O, ester), 169.95 (*C*O ester).



4α*p*

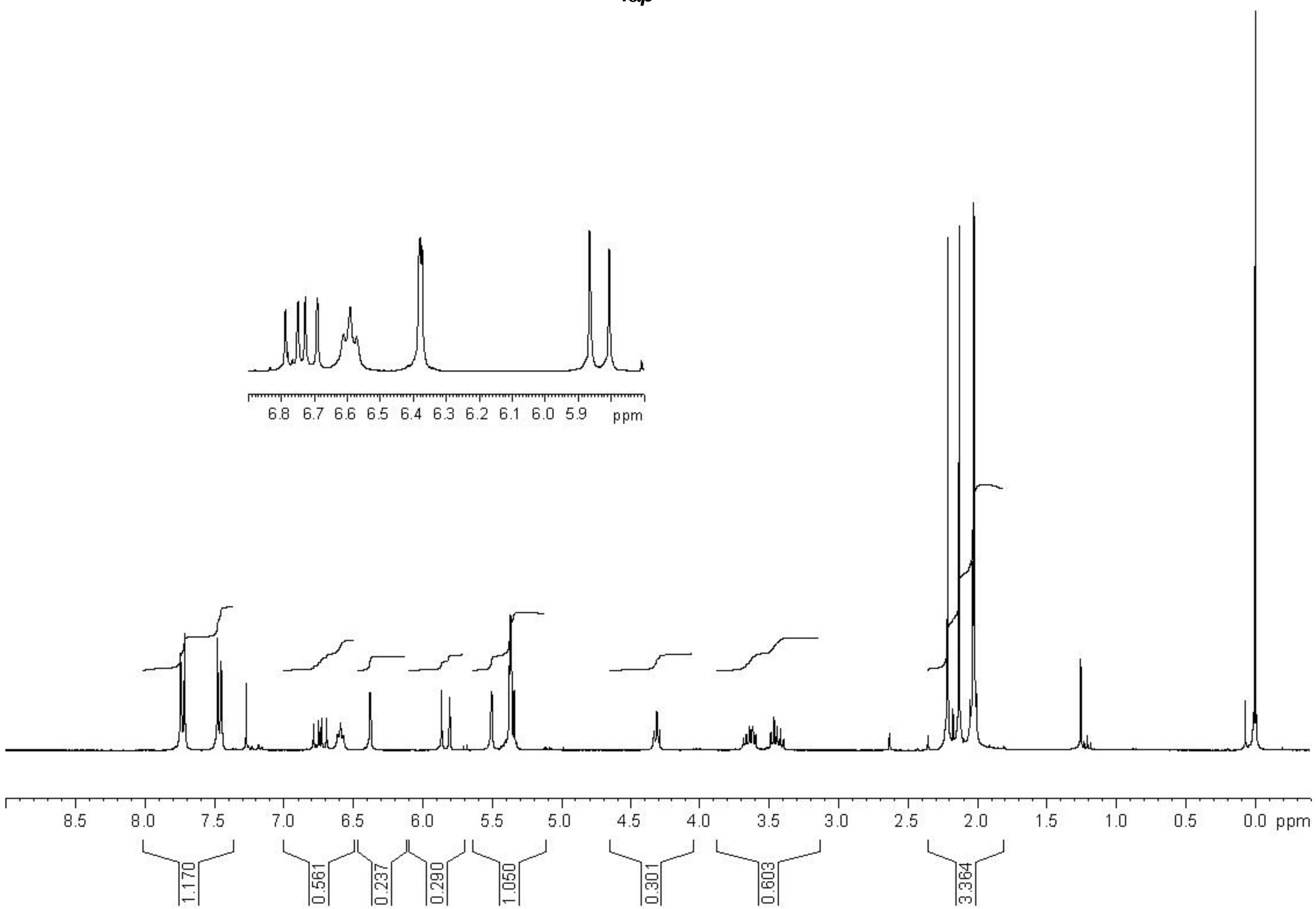
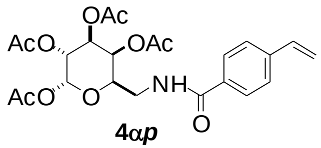


Figure S1. ^{1}H NMR spectrum of **4α*p*** in $CDCl_3$.



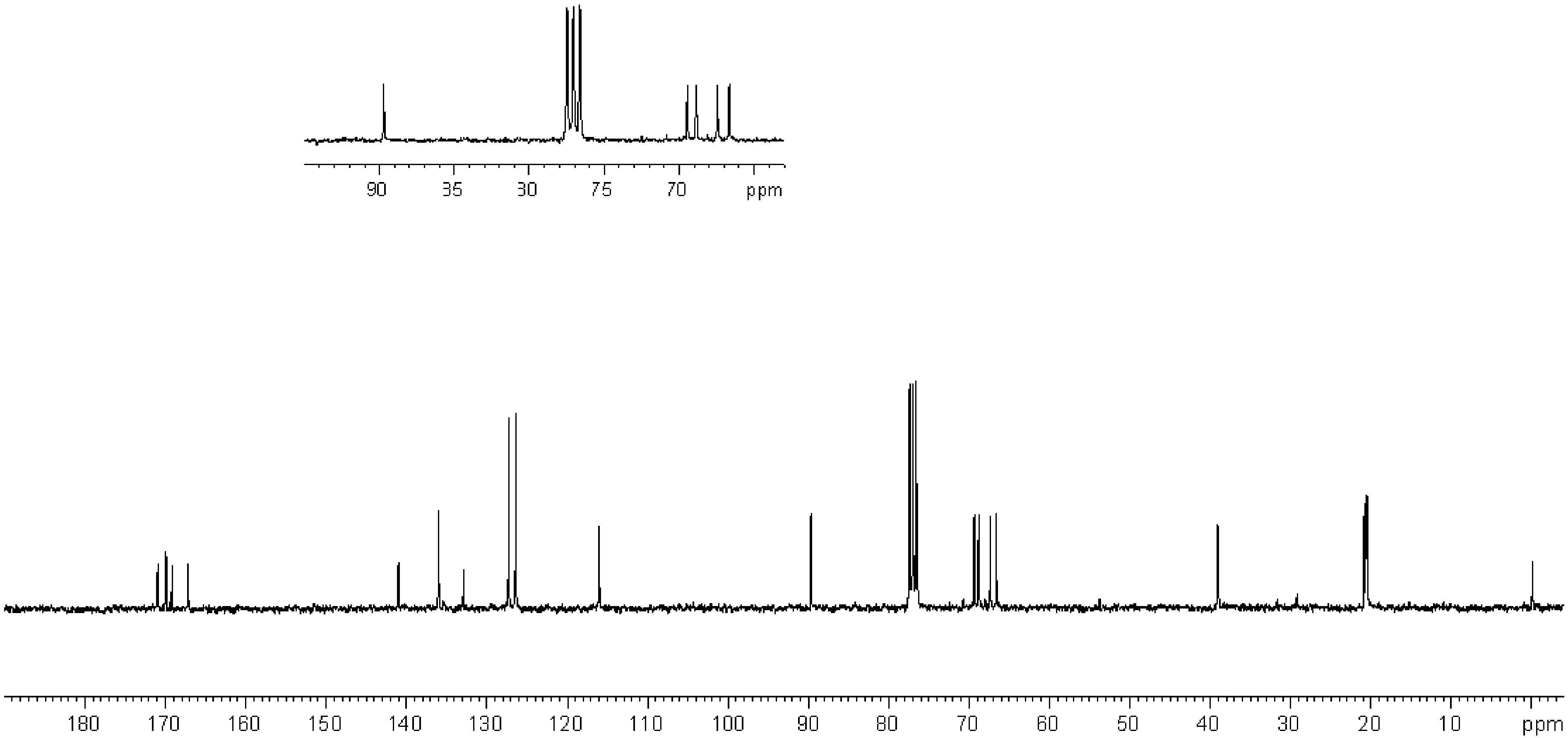


Figure S2. ^{13}C NMR spectrum of ***4αp*** in $CDCl_3$.

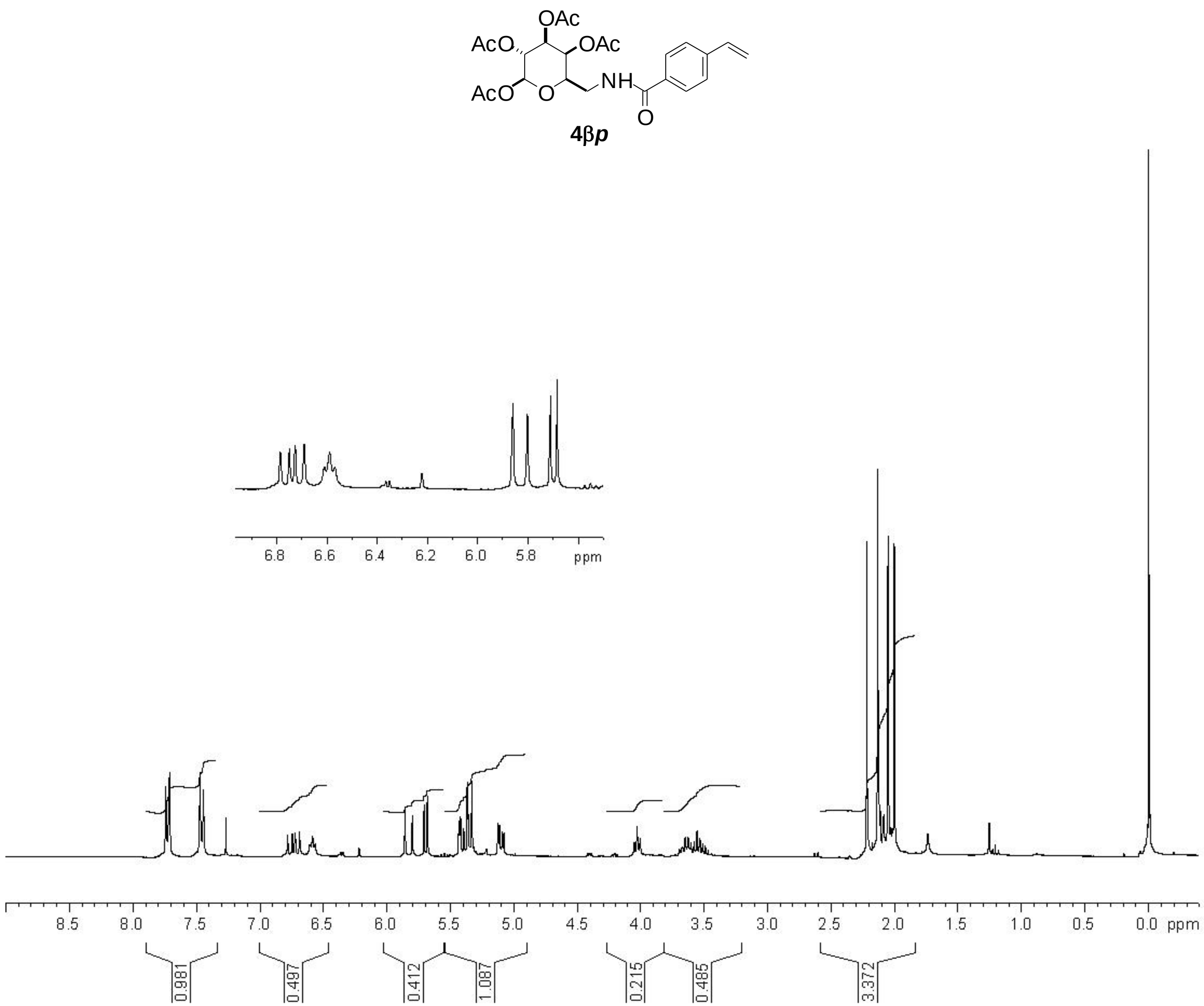
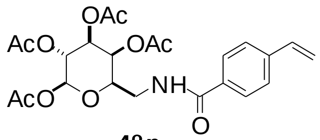


Figure S3. ^{1}H NMR spectrum of **4β*p*** containing small amounts of **4α*p***, **4α*f*** and **4β*f*** in $CDCl_3$.



4β*p*

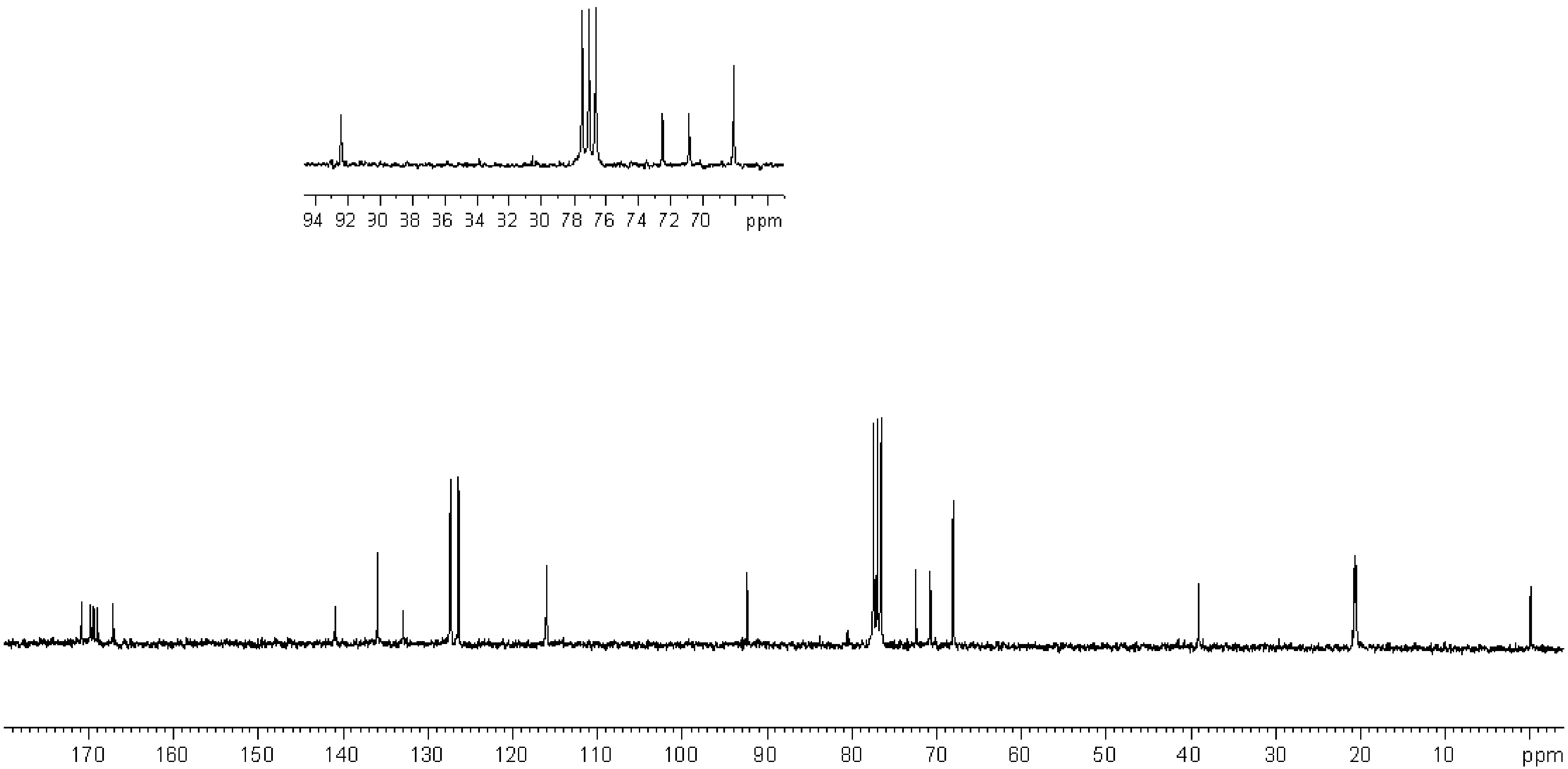


Figure S4. ^{13}C NMR spectrum of **4β*p*** containing small amounts of **4α*p***, **4α*f*** and **4β*f*** in $CDCl_3$.

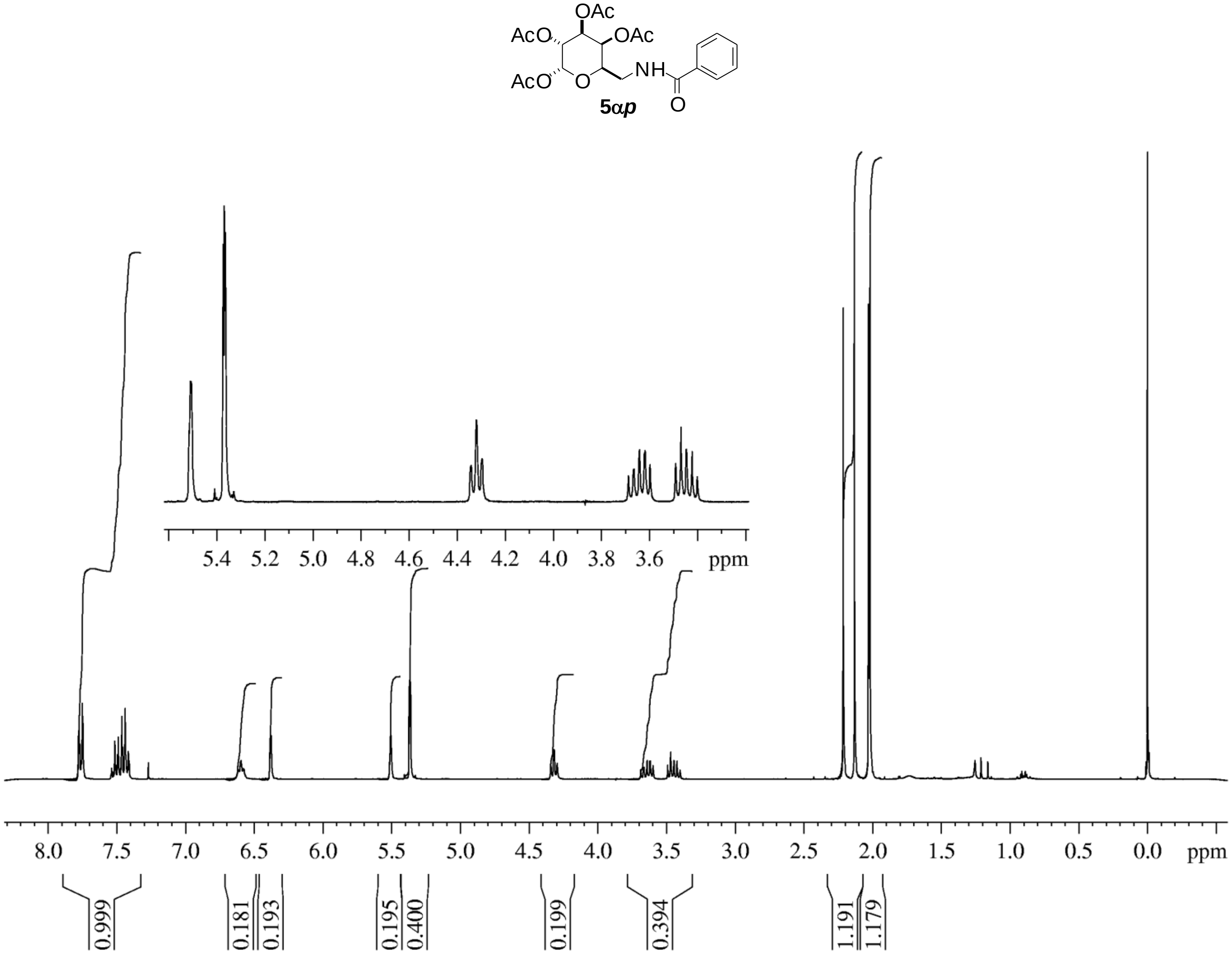


Figure S5. ^{1}H NMR spectrum of ***5αp*** in $CDCl_3$.

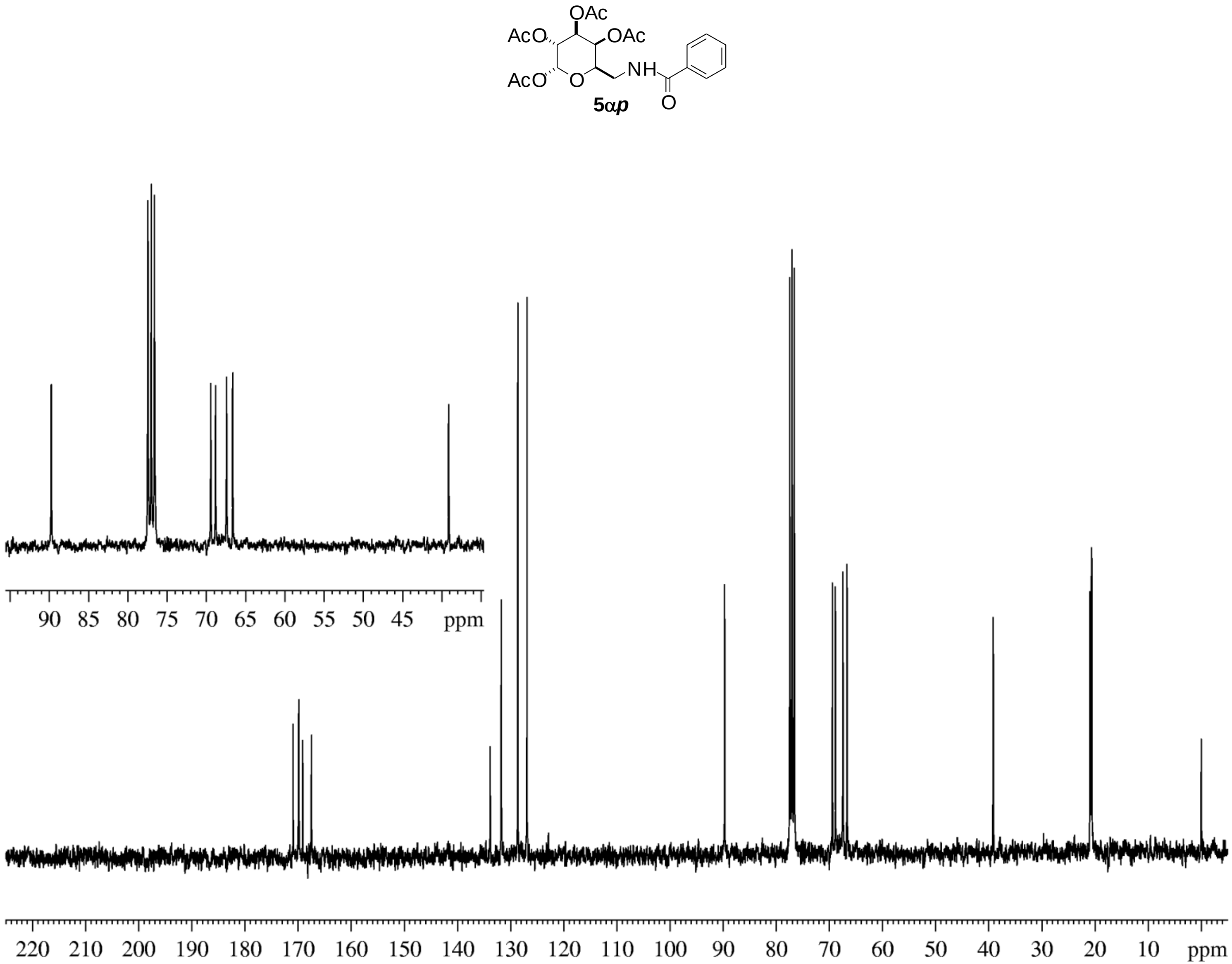


Figure S6. ^{13}C NMR spectrum of ***5αp*** in $CDCl_3$.

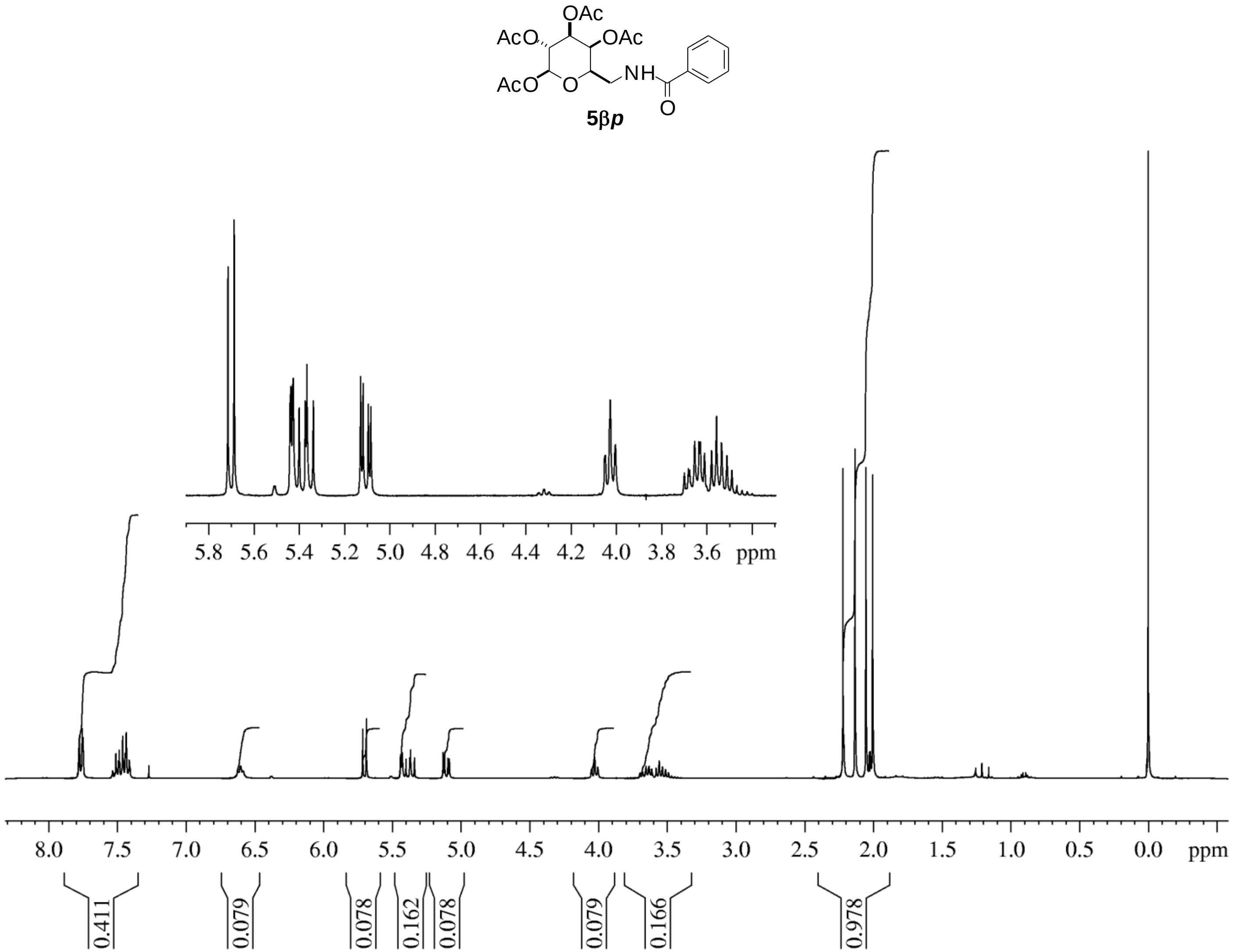
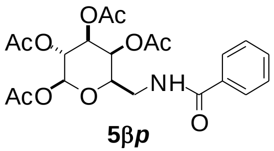


Figure S7. ^{1}H NMR spectrum of **5β*p*** in $CDCl_3$.



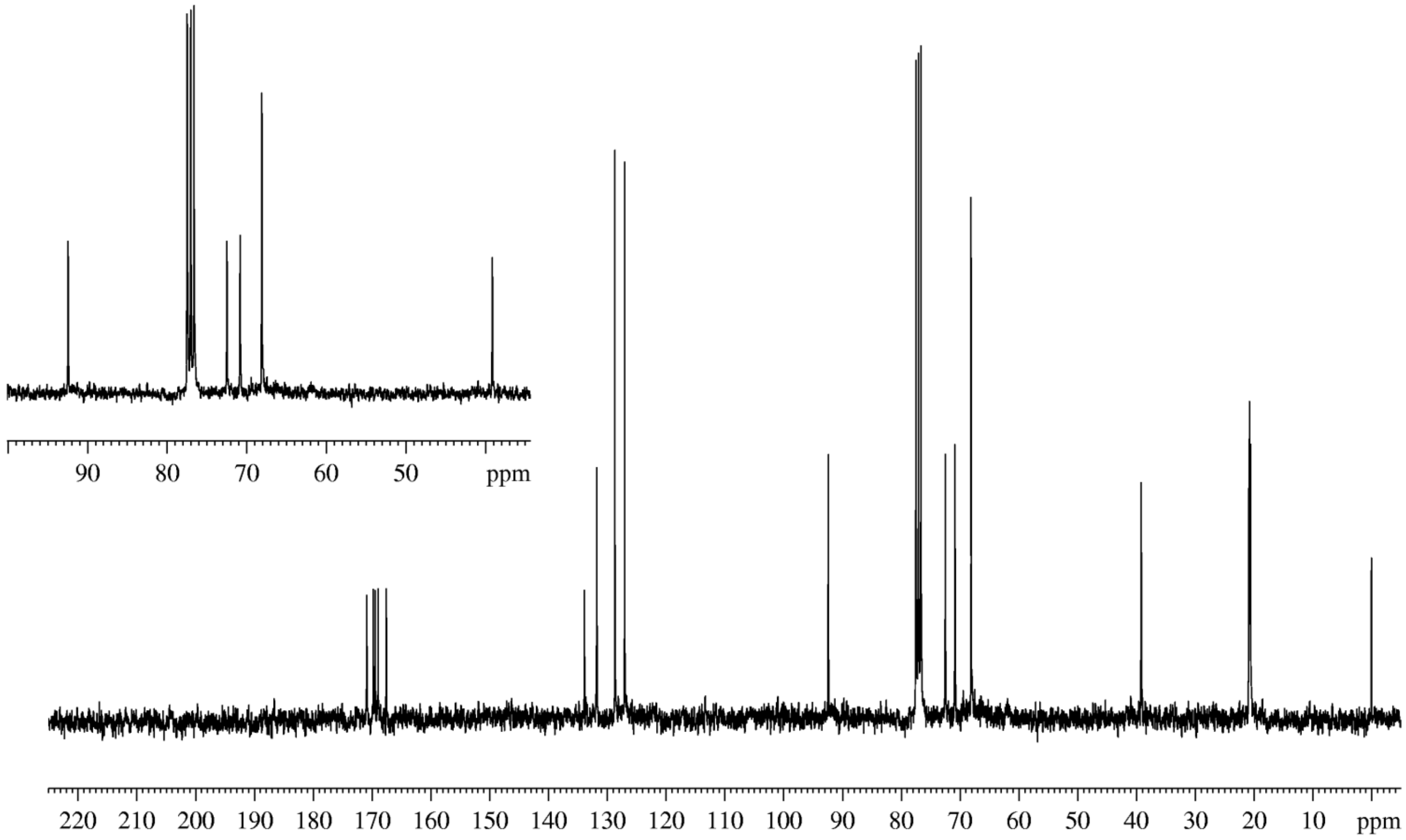
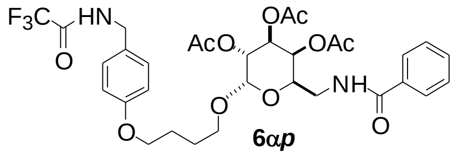


Figure S8. ^{13}C NMR spectrum of **5β*p*** in $CDCl_3$.



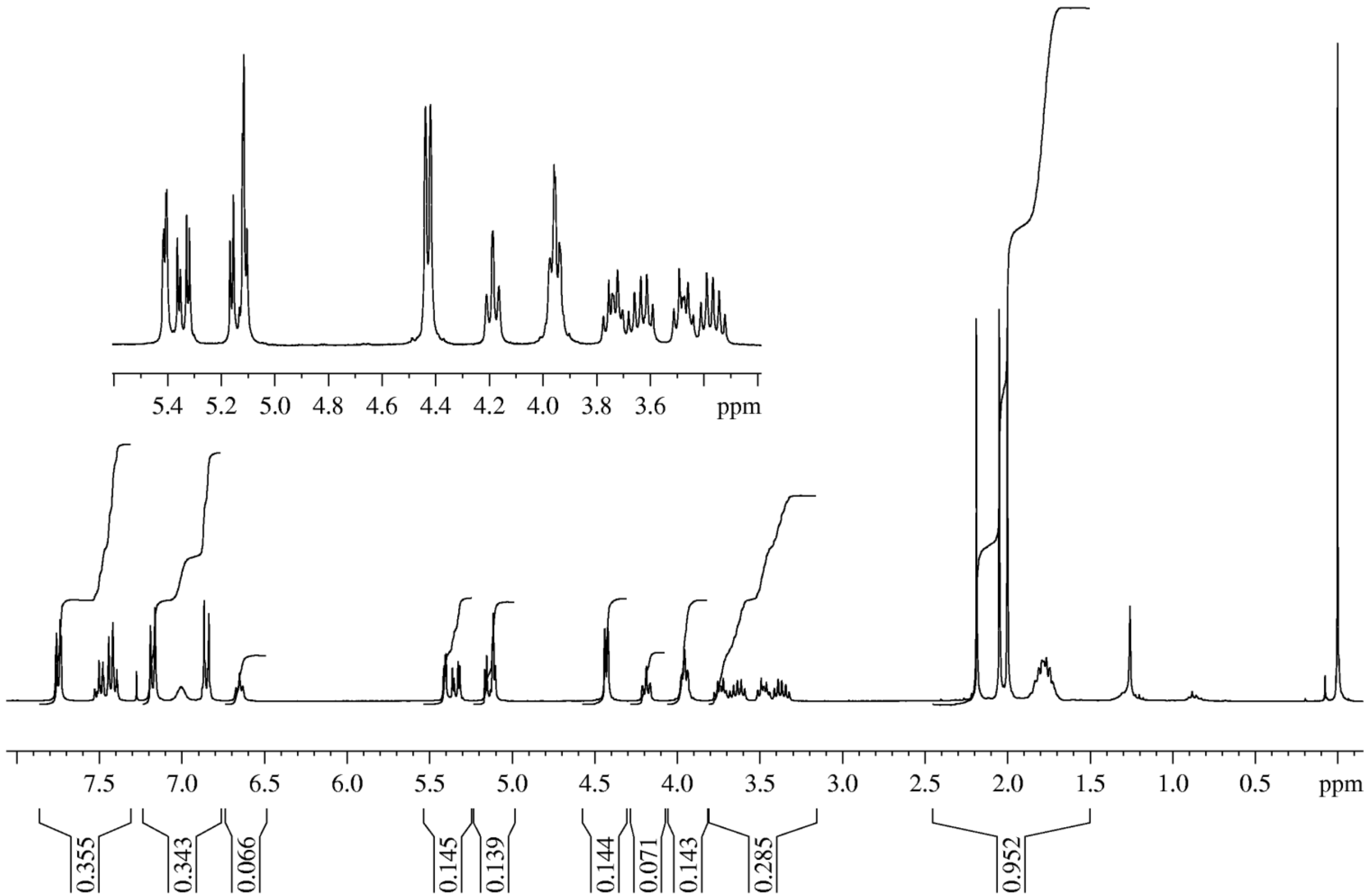


Figure S9. ^{1}H NMR spectrum of ***6αp*** in $CDCl_3$.

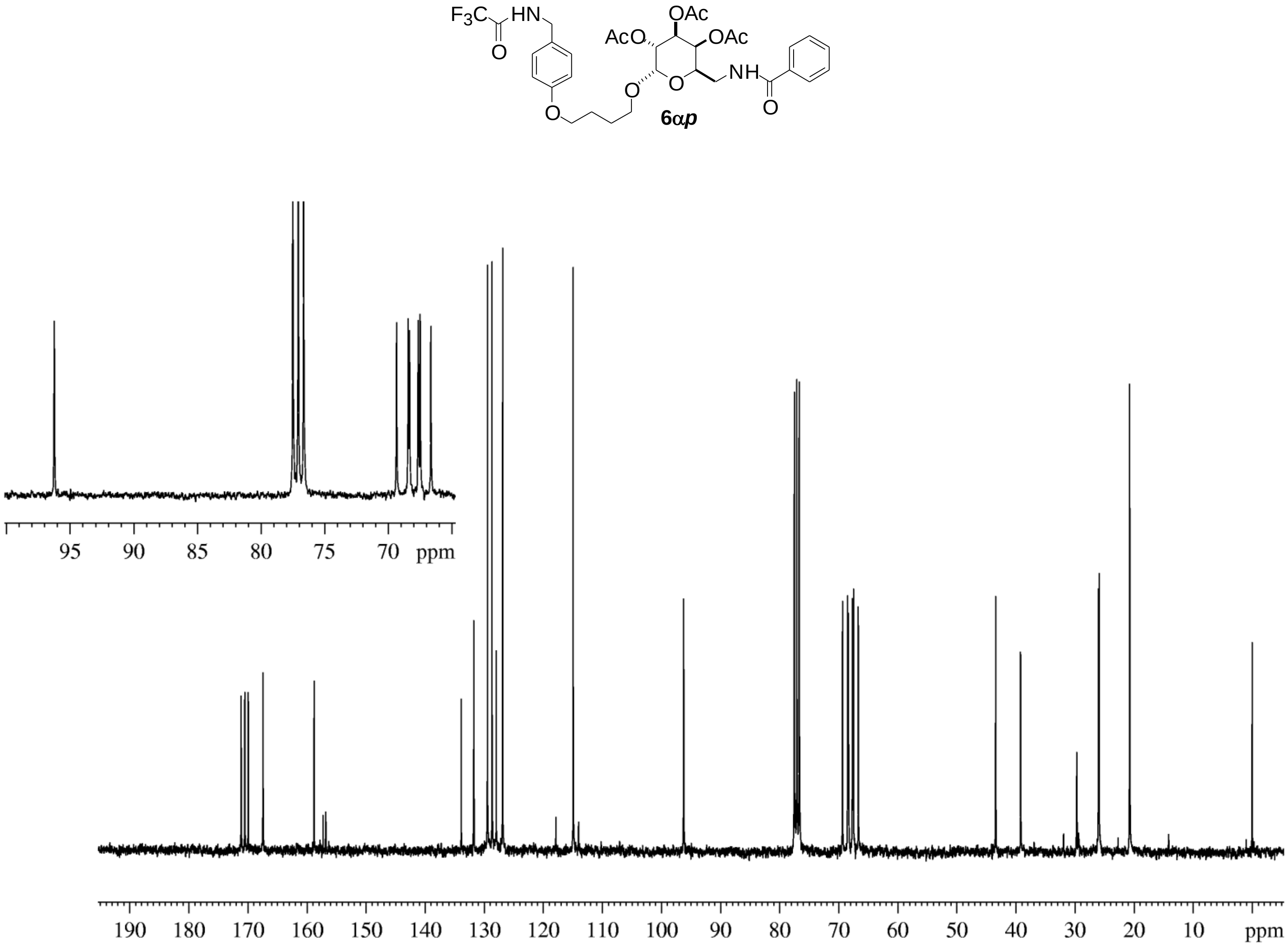


Figure S10. ^{13}C NMR spectrum of ***6αp*** in $CDCl_3$.

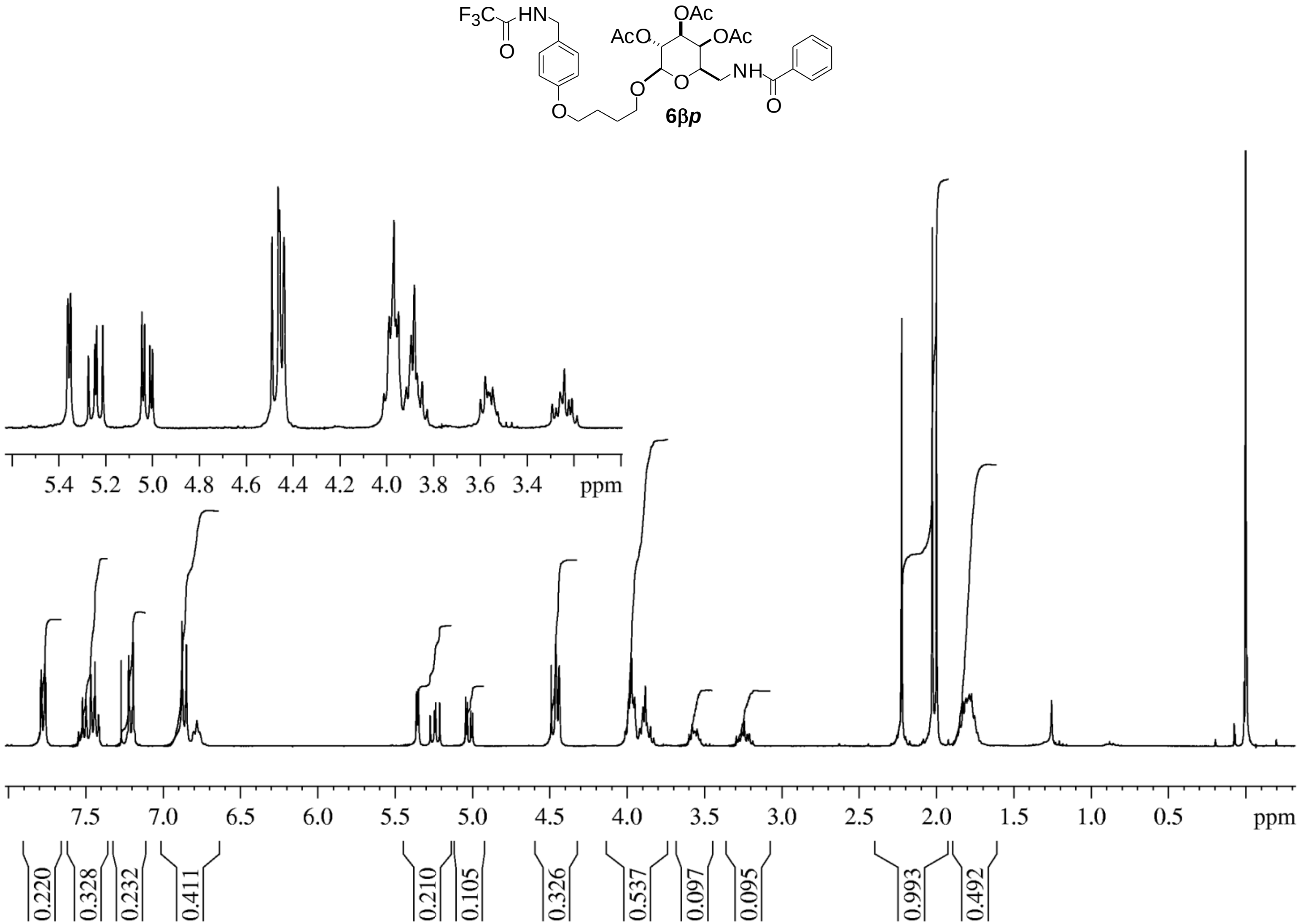
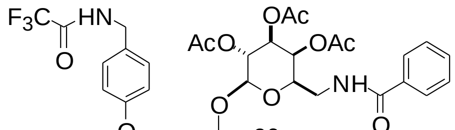


Figure S11. ^{1}H NMR spectrum of **6β*p*** in $CDCl_3$.



6β*p*

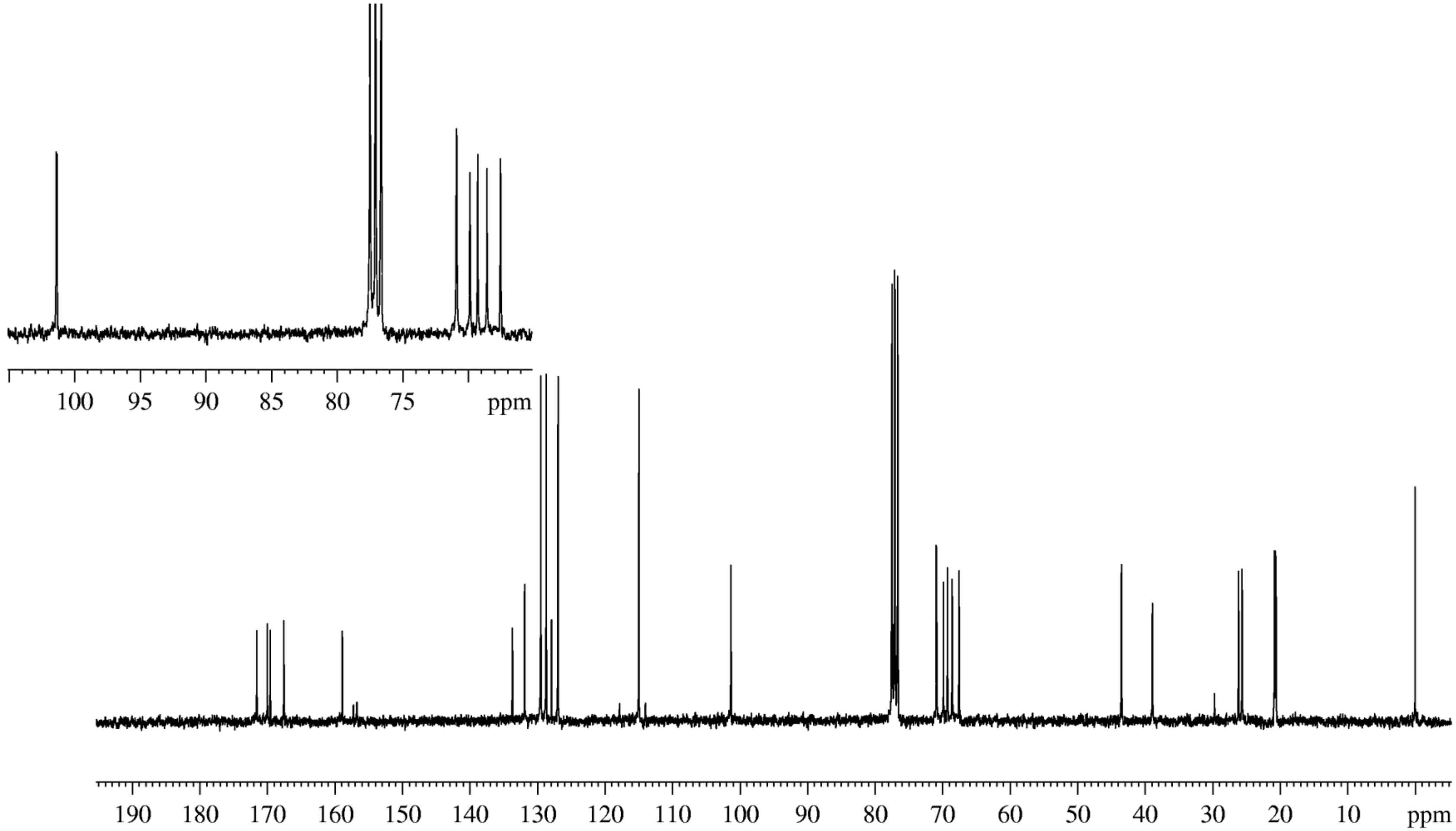
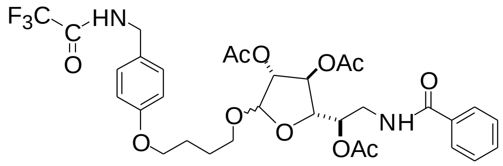


Figure S12. ^{13}C NMR spectrum of **6β*p*** in $CDCl_3$.



7αβ*f*

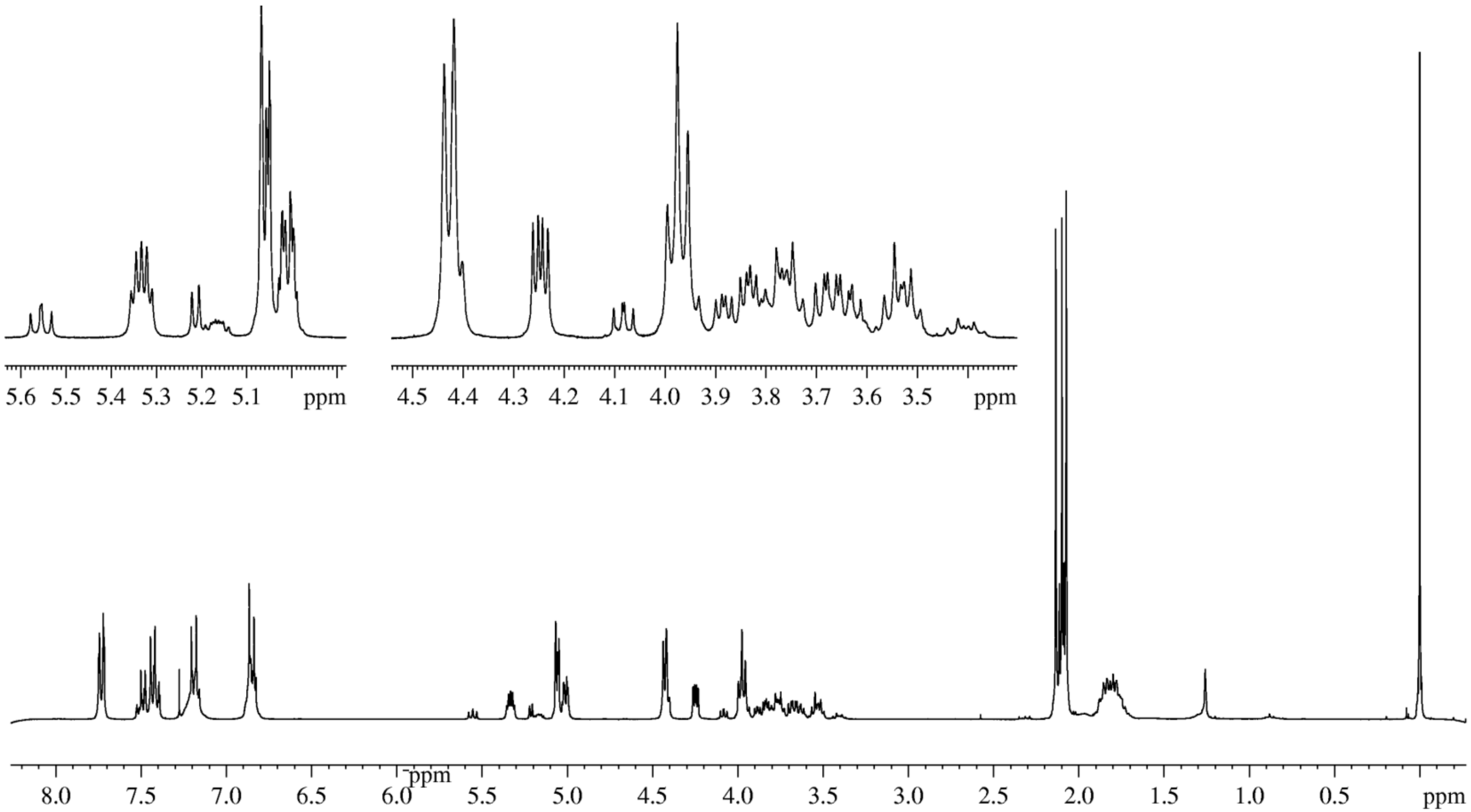
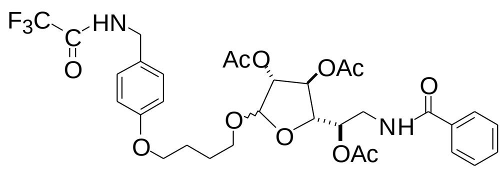


Figure S13. ^{1}H NMR spectrum of **7αβ*f*** in $CDCl_3$.



7αβ*f*

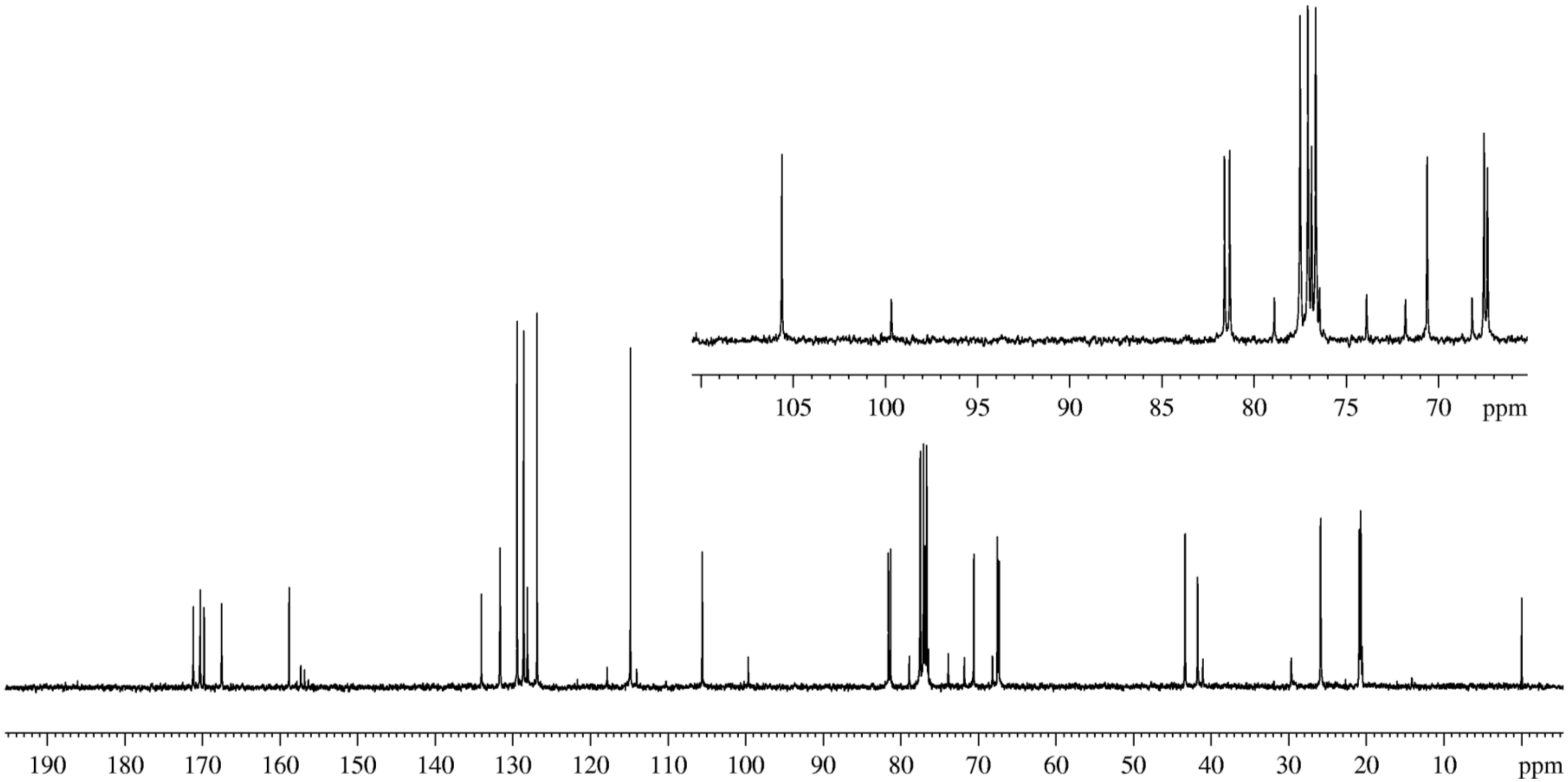
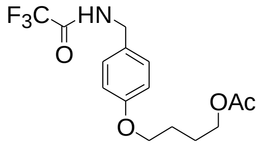


Figure S14. ^{13}C NMR spectrum of **7αβ*f*** in $CDCl_3$.



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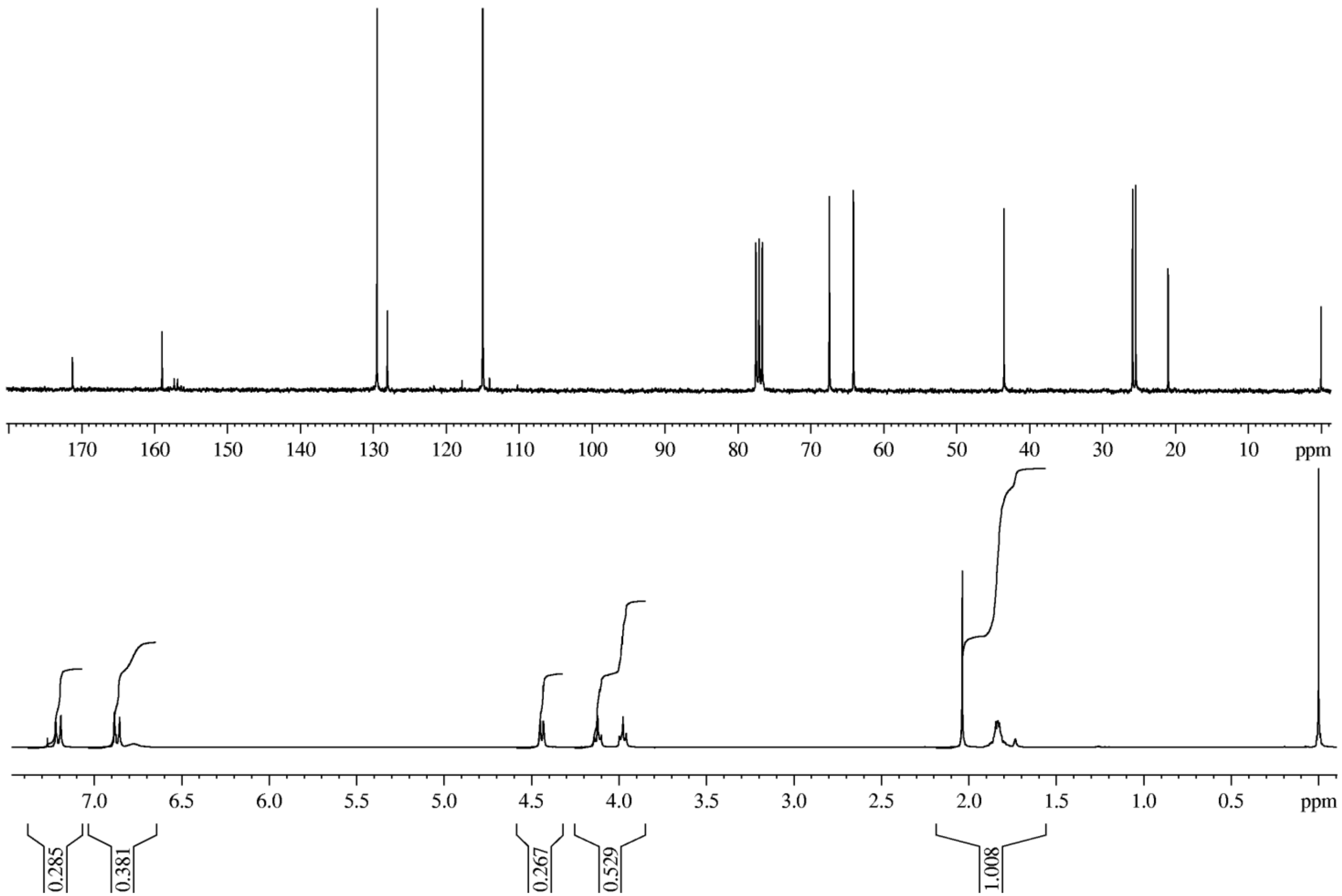


Figure S15. ^{1}H and ^{13}C NMR spectra of **8** in $CDCl_3$.

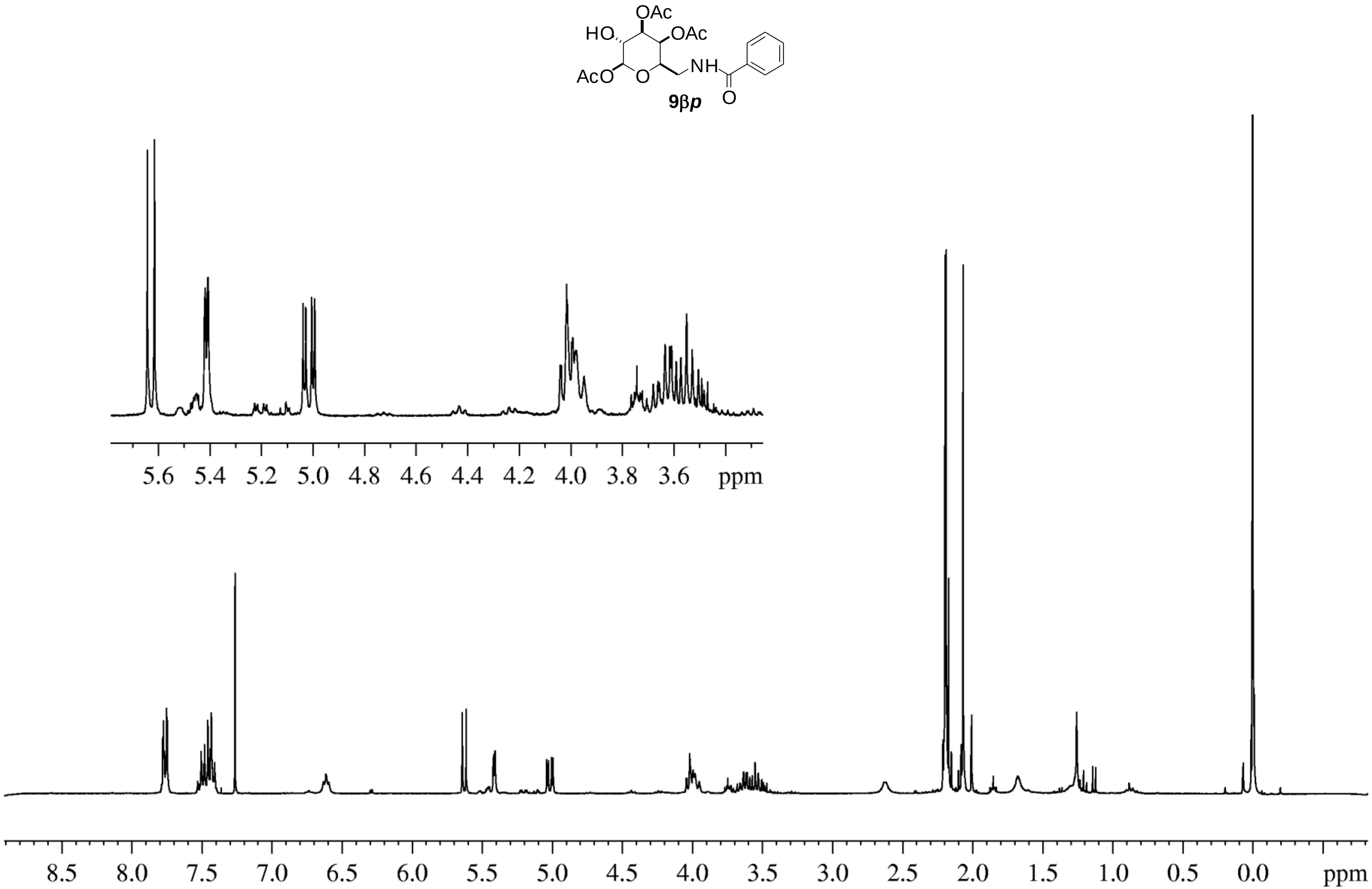
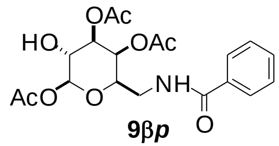


Figure S16. ^{1}H NMR spectrum of **9β*p*** in $CDCl_3$.



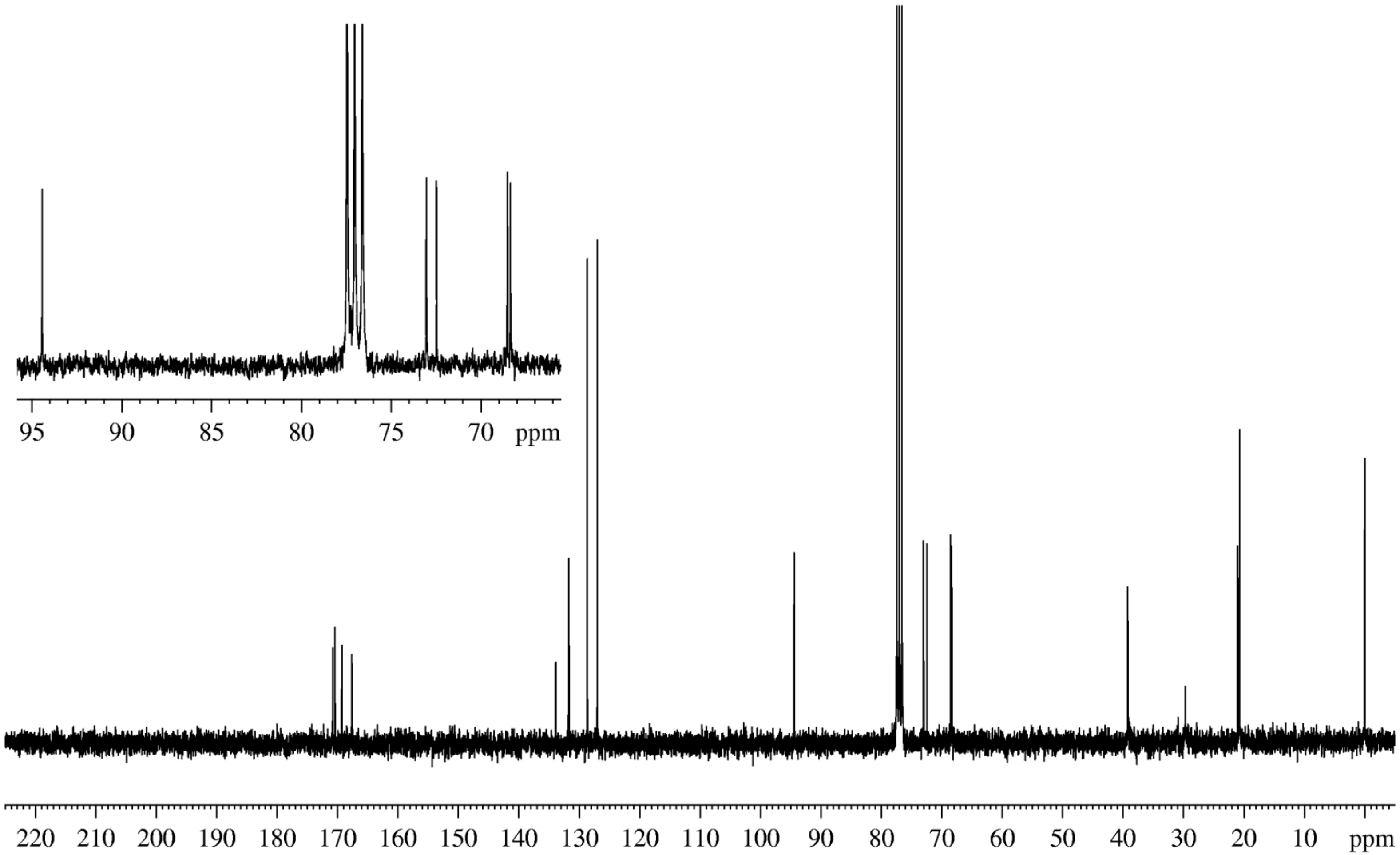
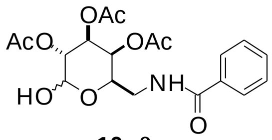


Figure S17. ^{13}C NMR spectrum of **9β*p*** in $CDCl_3$.



10αβ*p*

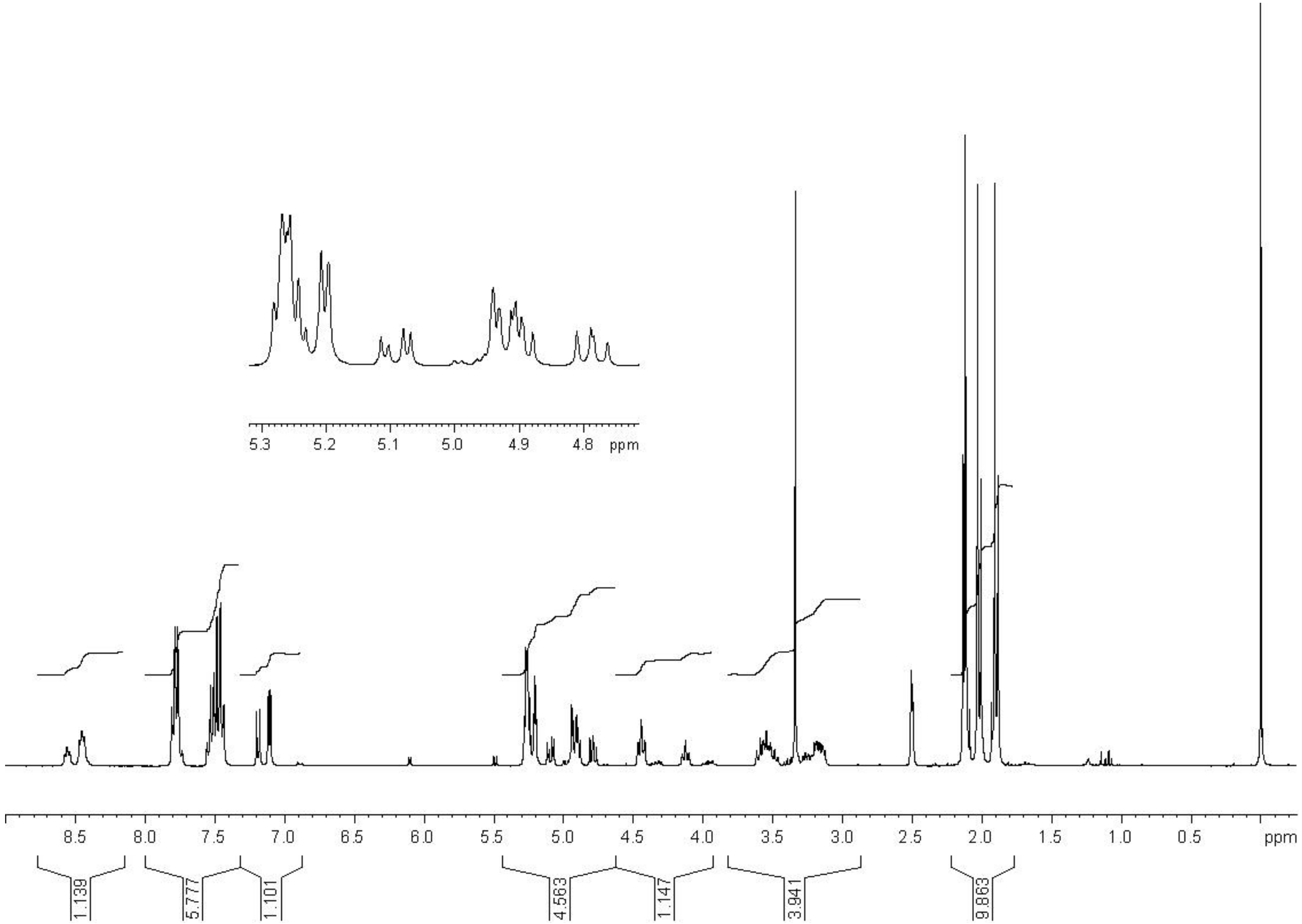
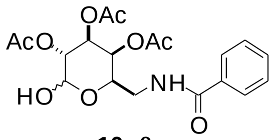


Figure S18. ^{1}H NMR spectrum of **10αβ*p*** in DMSO-*d6*.



10αβ*p*

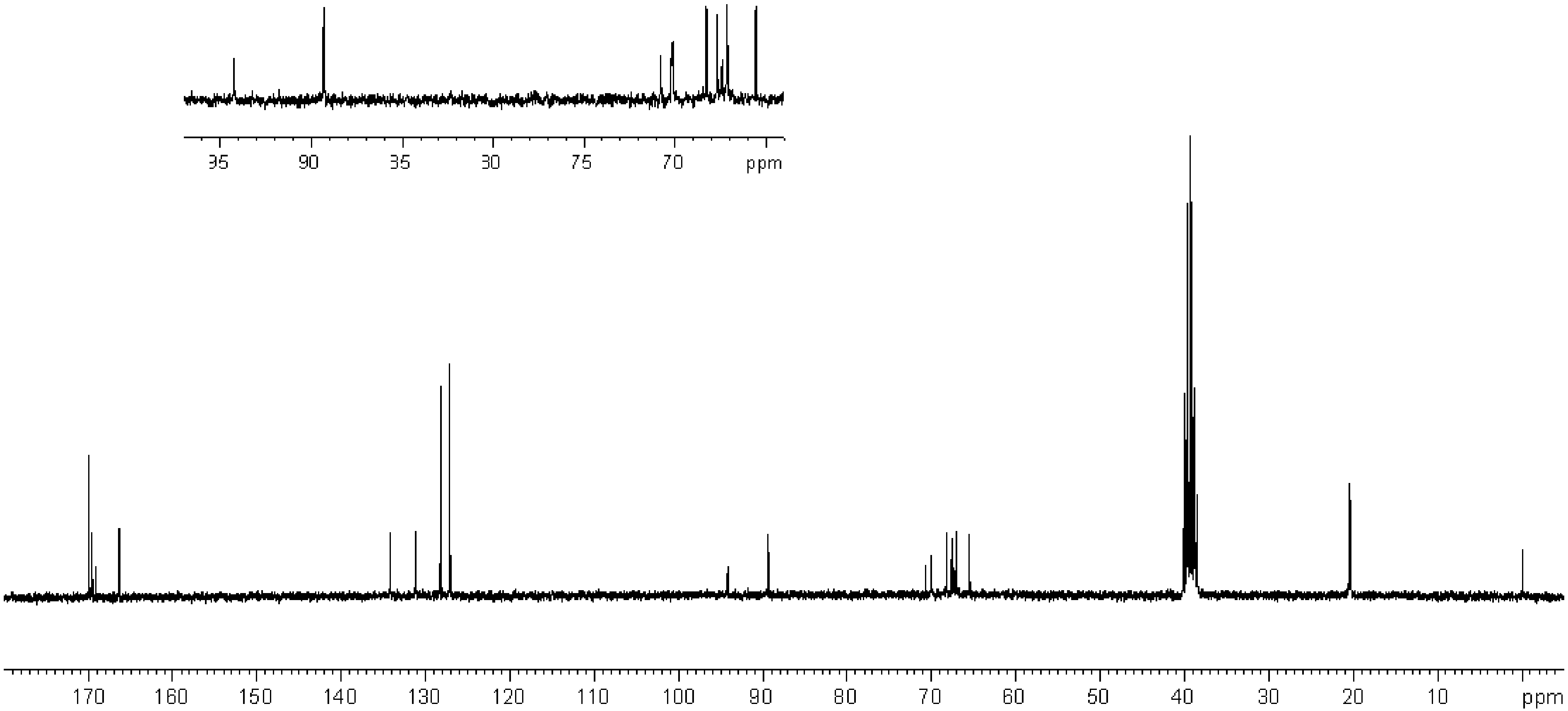
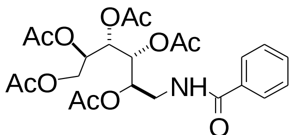


Figure S19. ^{13}C NMR spectrum of **10αβ*p*** in DMSO-*d6*.



11

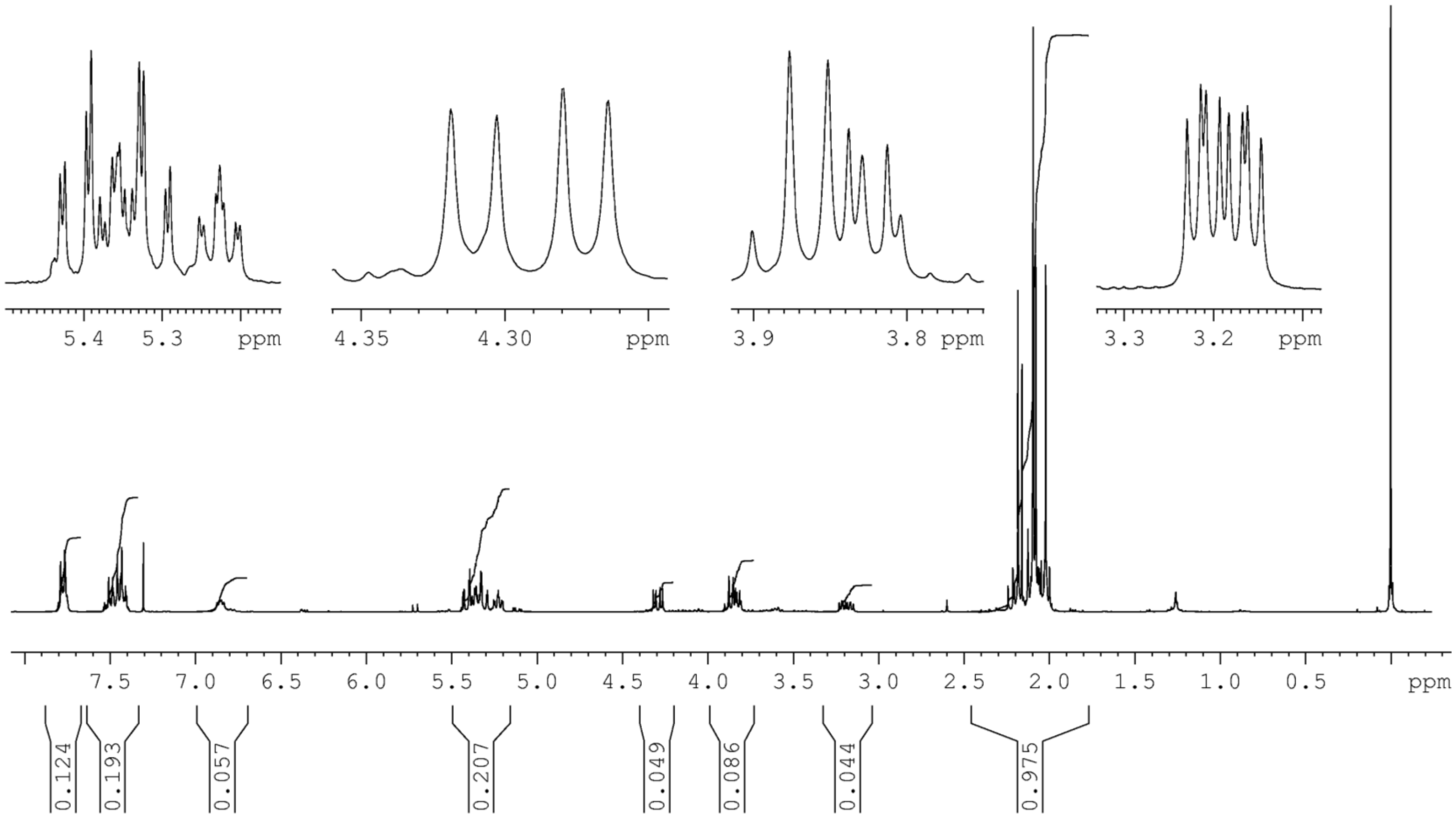
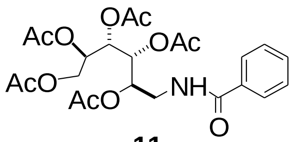


Figure S20. ^{1}H NMR spectrum of **11** in $CDCl_3$.



11

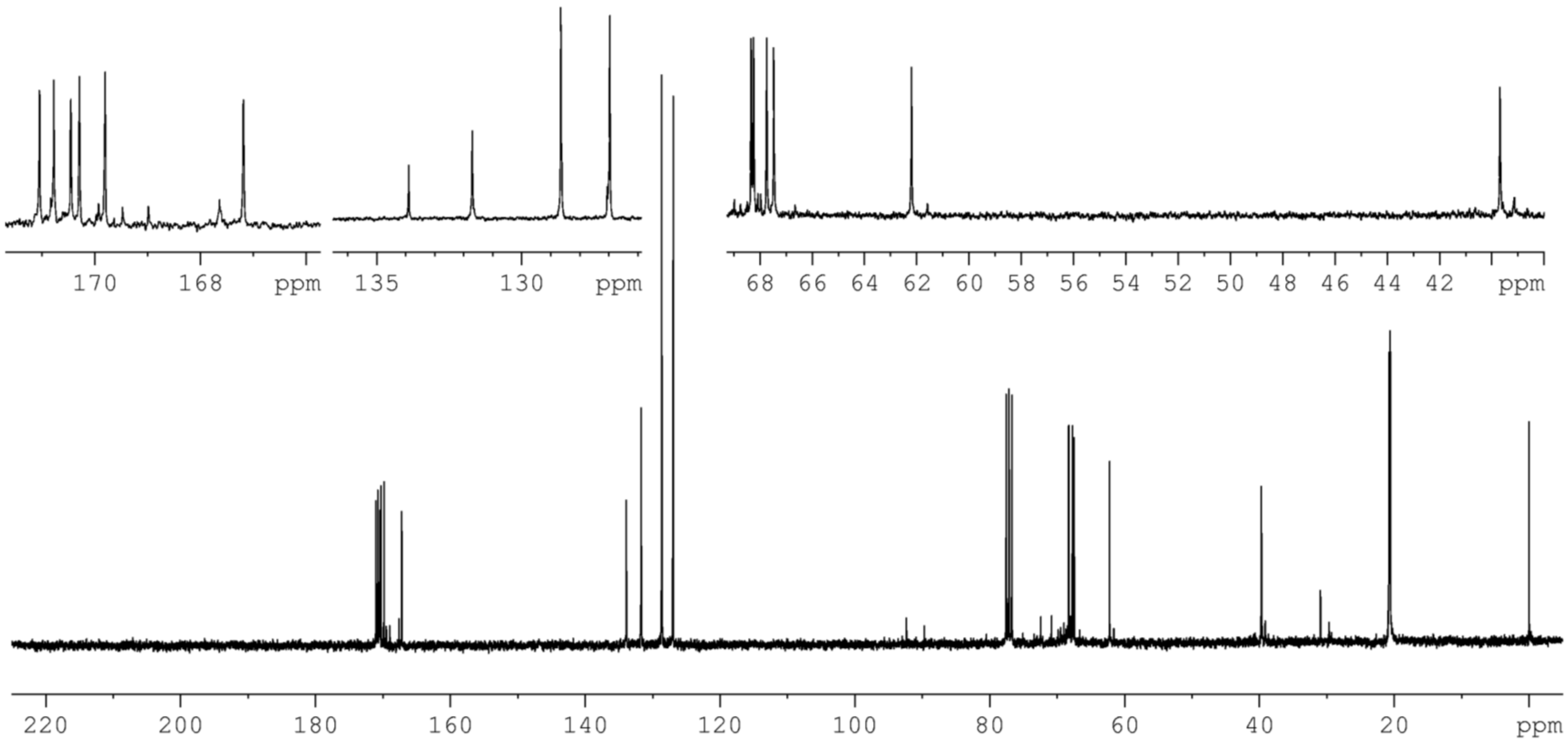


Figure S21. ^{13}C NMR spectrum of **11** in $CDCl_3$.

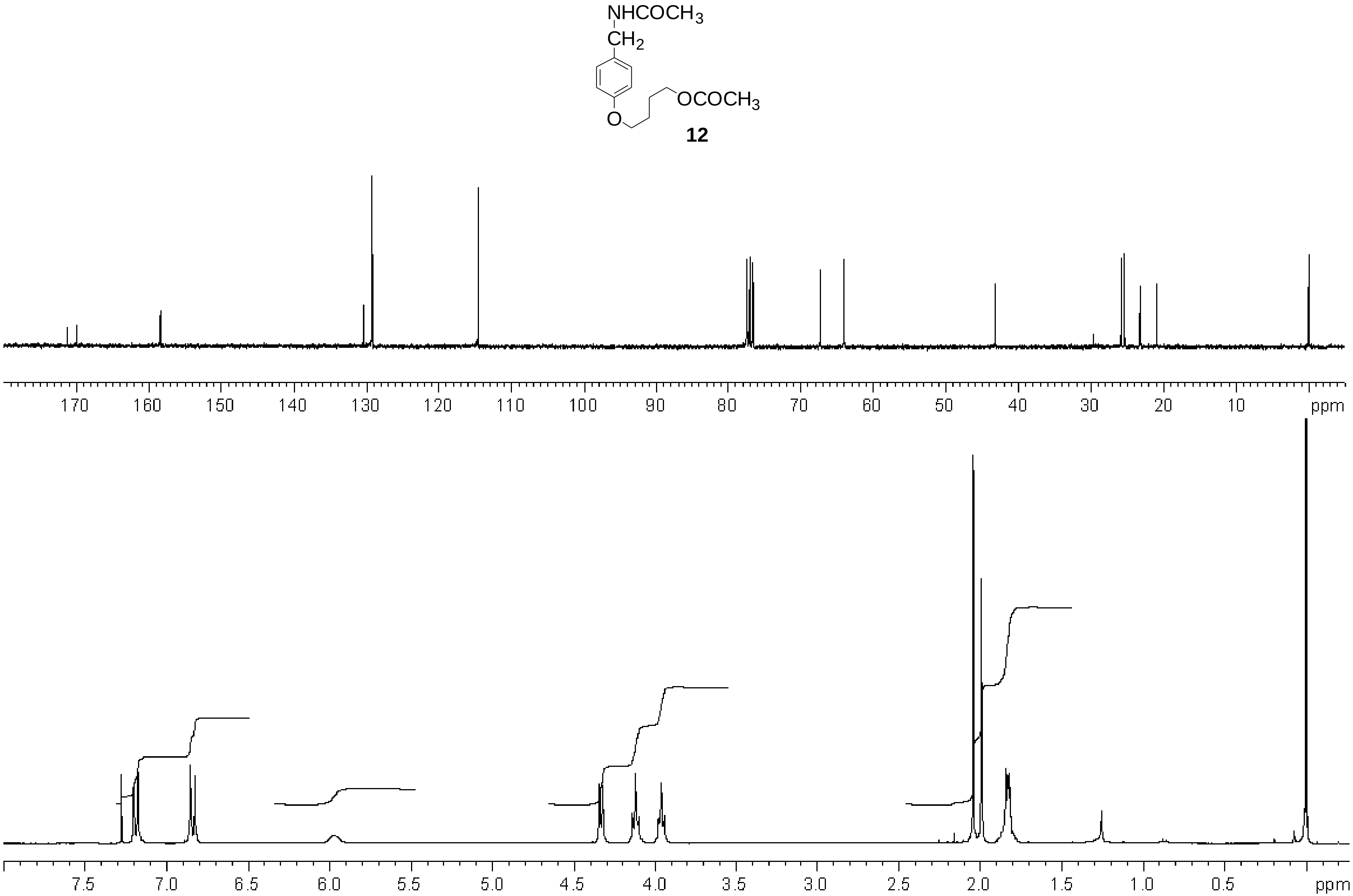


Figure S22. ^{1}H and ^{13}C NMR spectra of **12** in $CDCl_3$.