Supporting information:

N-Acetyl-L-phenylalanine Racemization during TBTU Amidation: An In-Depth Study for the Synthesis of Anti-Inflammatory 2-(*N*-Acetyl)-L-phenylalanylamido-2 -deoxy-D-glucose (NAPA)

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NMR spectra (400 MHz $CDCl_3$)

All ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400, operating at 400.13 MHz for the proton and 100.61 MHz for the carbon spectra. $CDCl_3$ signal is at 7.26 ppm.

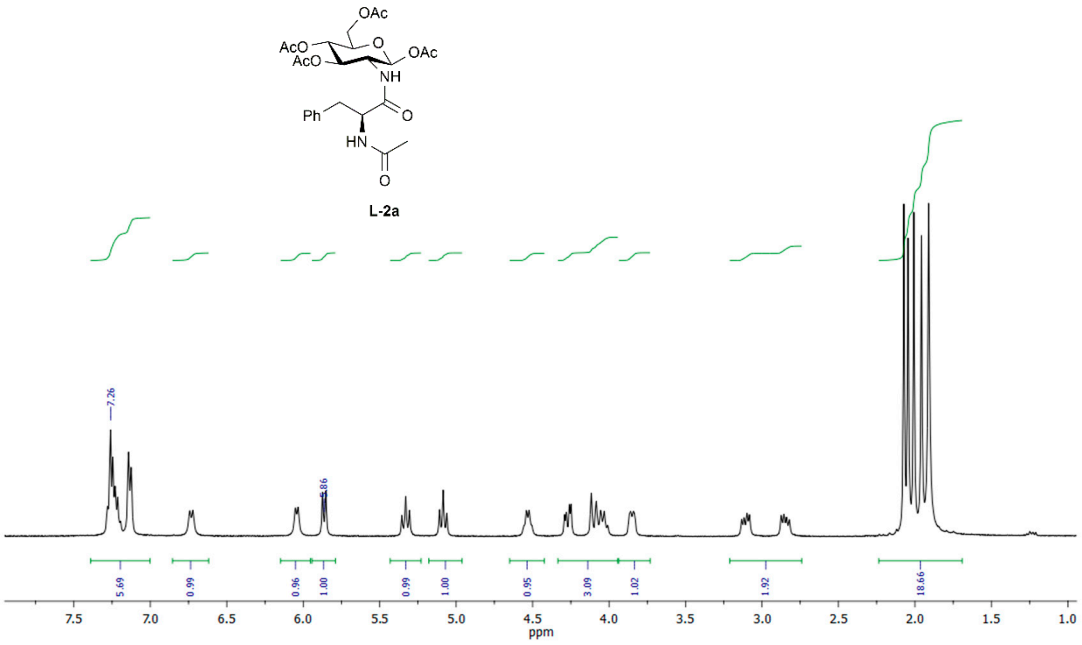


Figure S1. ^1H NMR for compound **L-2a**. L-H-1 at 5.86 ppm.

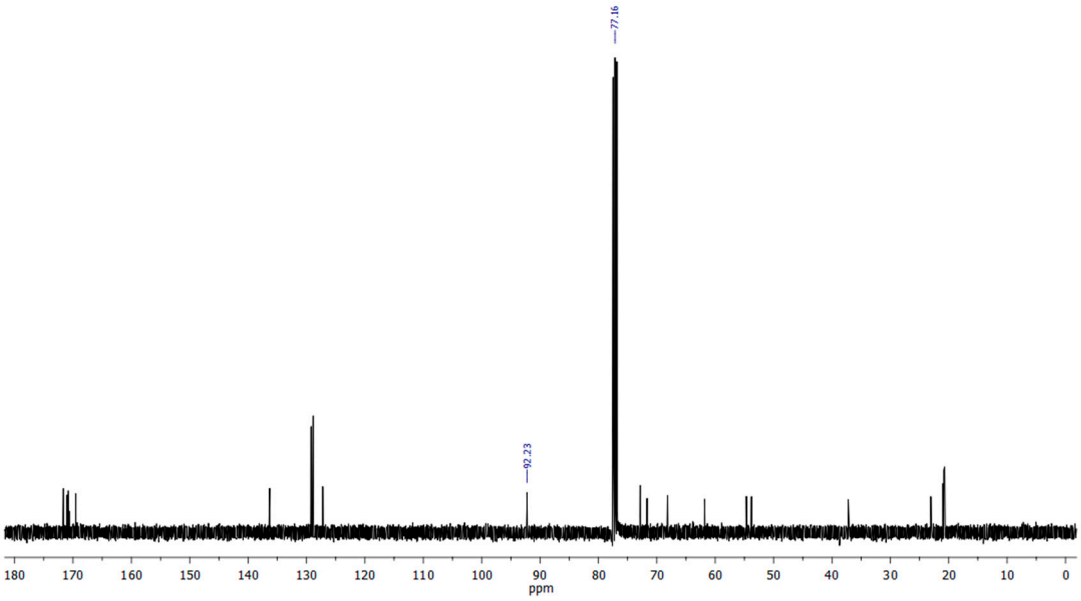


Figure S2. ^{13}C NMR for compound **L-2a**.

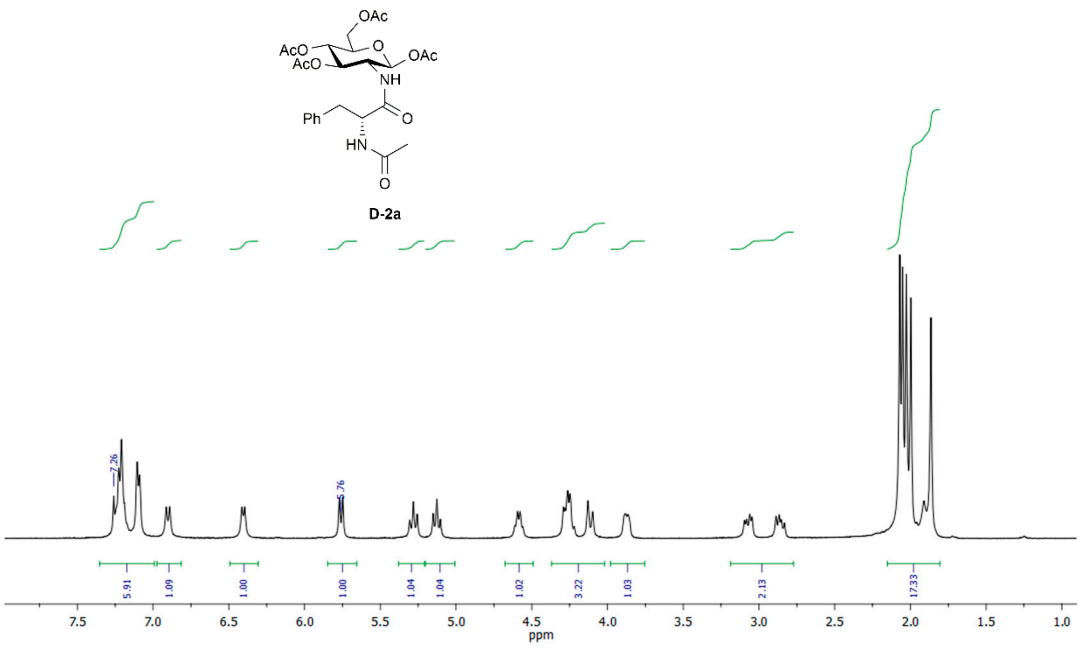


Figure S3. ^{1}H NMR for compound **D-2a**. D-H-1 at 5.76 ppm.

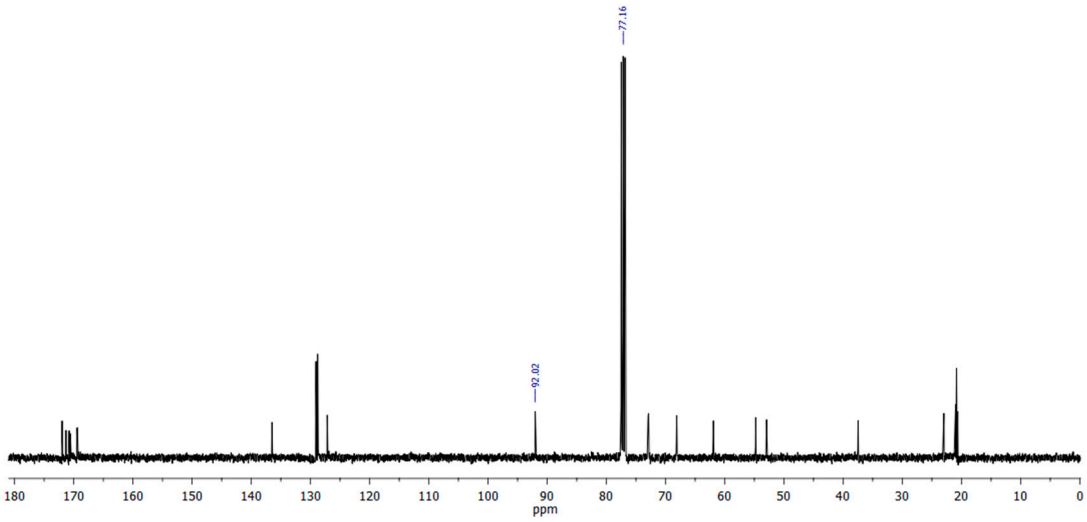


Figure S4. ^{13}C NMR for compound **D-2a**.

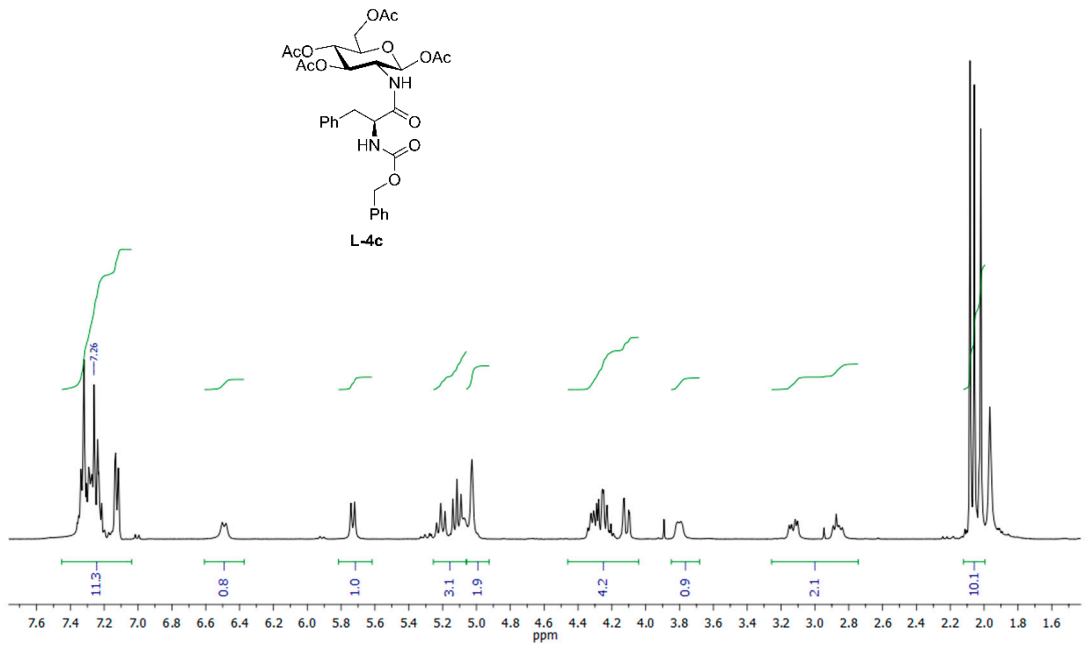


Figure S5. ^{1}H NMR for compound **L-4c**.

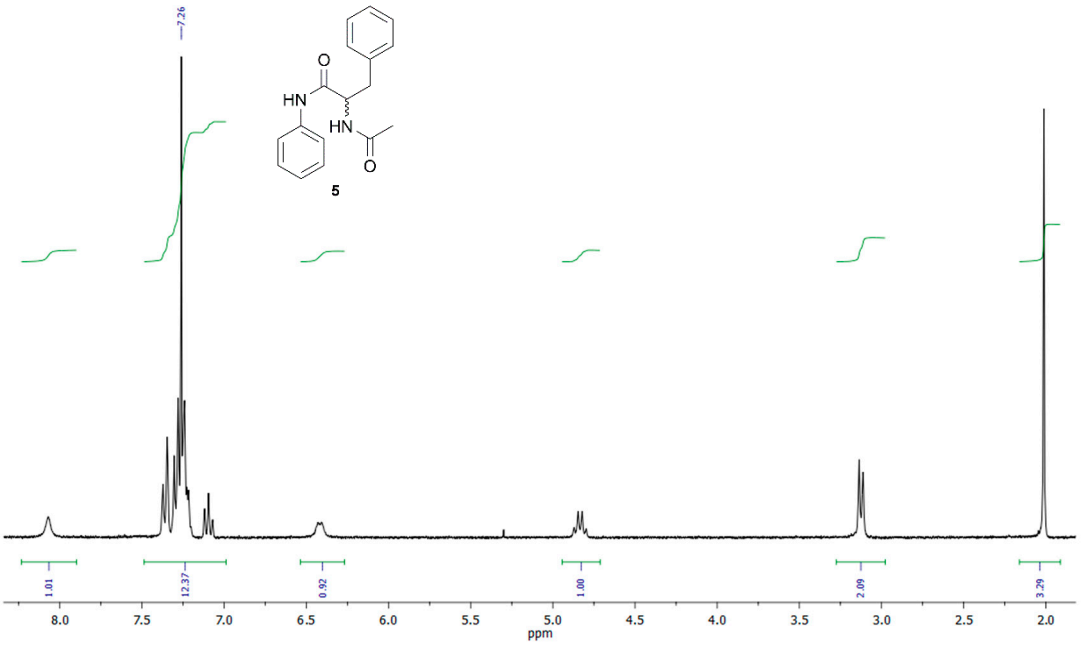
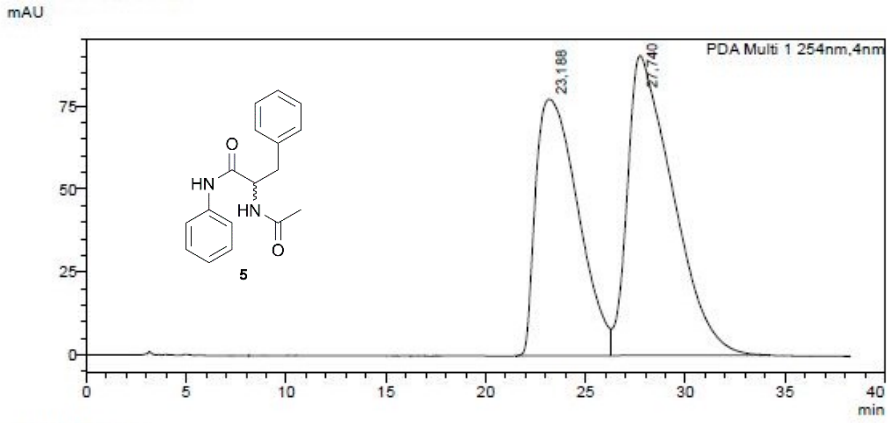


Figure S6. ^{1}H NMR for compound **5**.

HPLC chromatogram

Column: Chiralpak, IA, Daicel chemical industries (H-iPrOH-95-5, 1 ml/min).

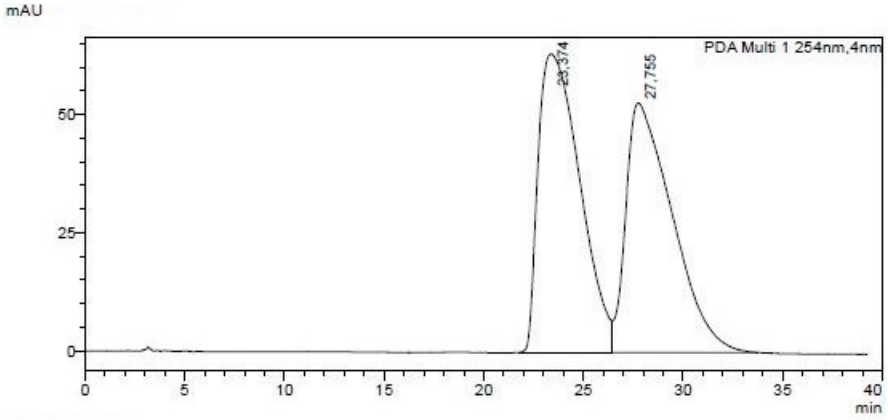


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23,188	11376371	77277	44,280
2	27,740	14315807	90342	55,720
Total		25692178	167619	100,000

Figure S7. Chromatogram of compound **5** from pure *N*-Ac-L-phe with TBTU/DIPEA.

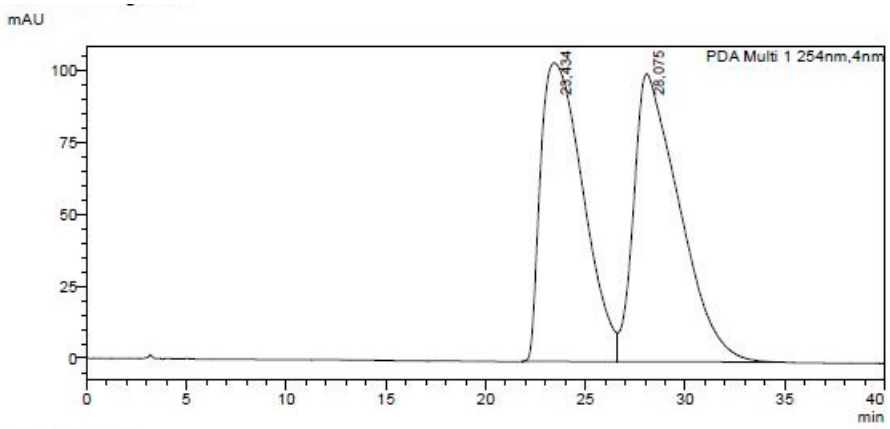


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23,374	9185655	63175	51,737
2	27,755	8569018	52814	48,263
Total		17754673	115989	100,000

Figure S8. Chromatogram of compound **5** from pure N-Ac-D-phe with TBTU/DIPEA.

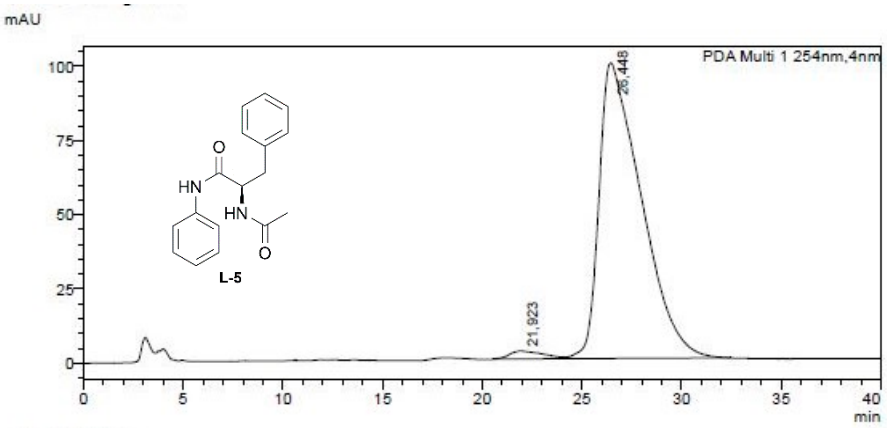


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23,434	15355208	103812	49,085
2	28,075	15927992	100077	50,915
Total		31283201	203889	100,000

Figure S9. Chromatogram of compound **5** from N-Ac-L-phe:N-Ac-D-phe=1:1 with TBTU/DIPEA.



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	21,923	314557	2620	2,096
2	26,448	14690309	99582	97,904
Total		15004866	102203	100,000

Figure S10. Chromatogram of compound **L-5** from pure N-Ac-L-phe and pyridine.