

Supporting Information File 2

for

Synthesis and in vitro cytotoxicity of acetylated 3-fluoro, 4-fluoro and 3,4-difluoro analogs of D-glucosamine and D-galactosamine

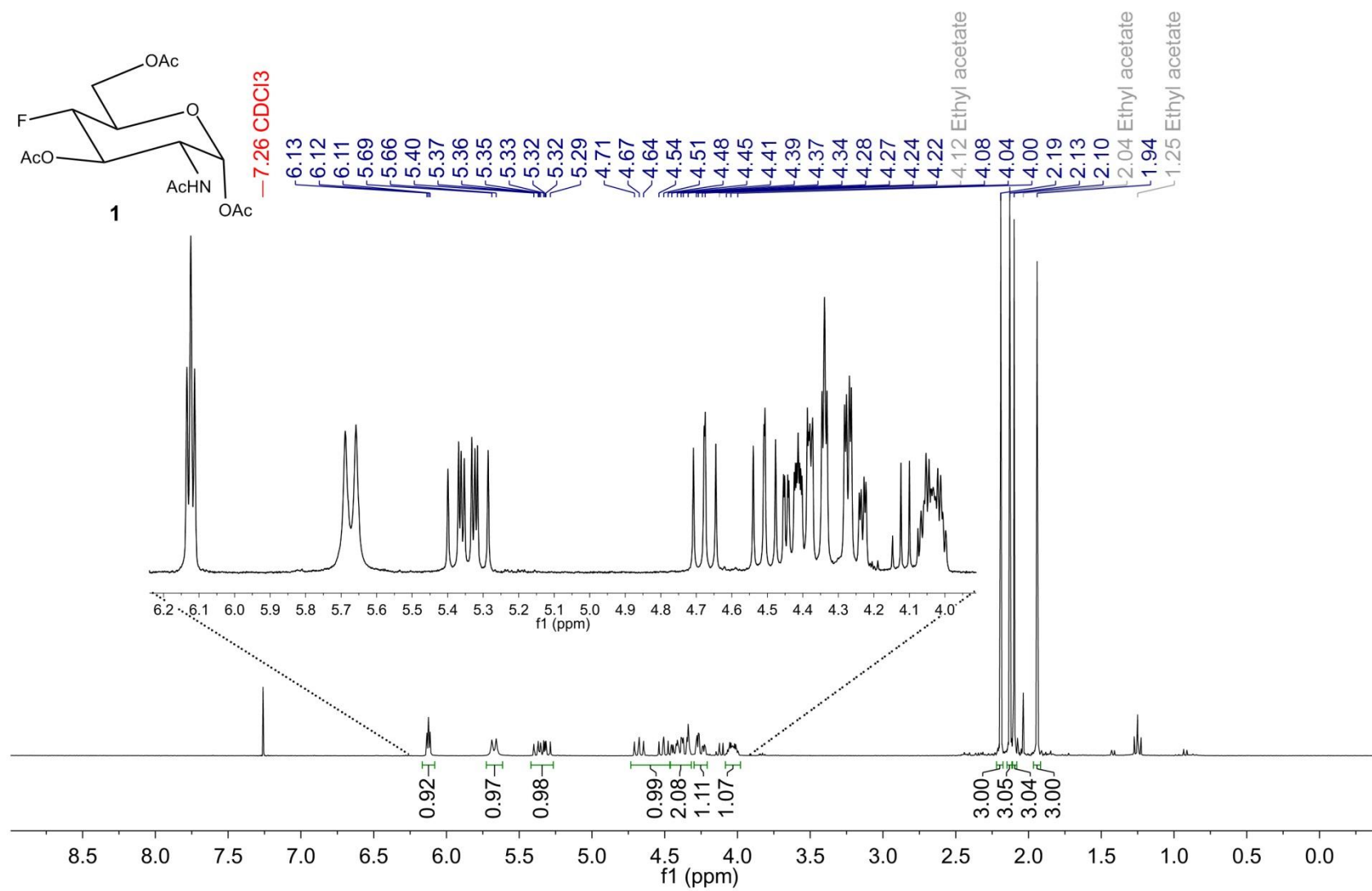
Štěpán Horník¹, Lucie Červenková Šťastná¹, Petra Cuřínová¹, Jan Sýkora¹, Kateřina Káňová², Roman Hrstka², Ivana Císařová³, Martin Dračinský⁴ and Jindřich Karban^{*1}

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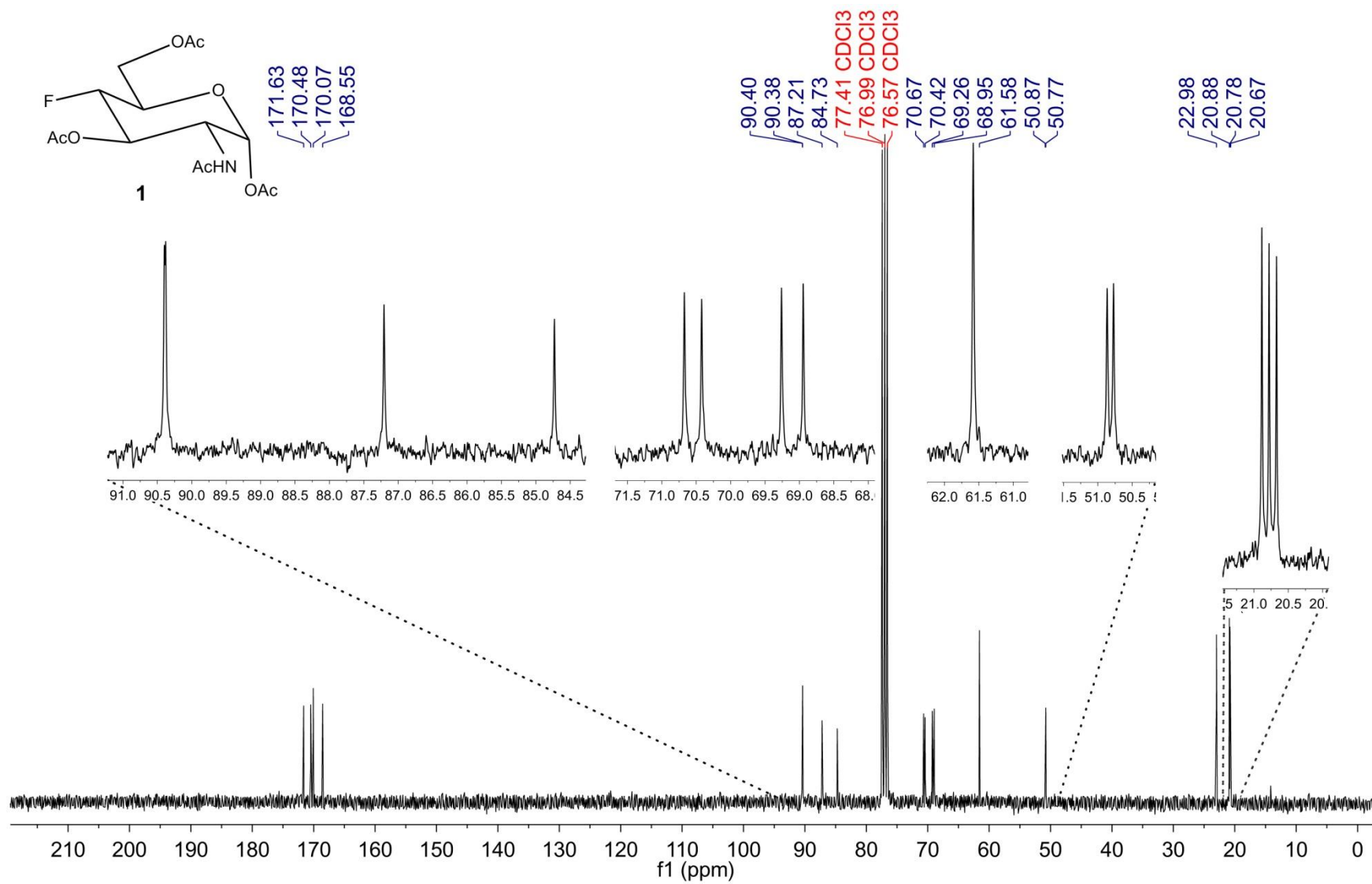
Email: Jindřich Karban - karban@icpf.cas.cz

* Corresponding author

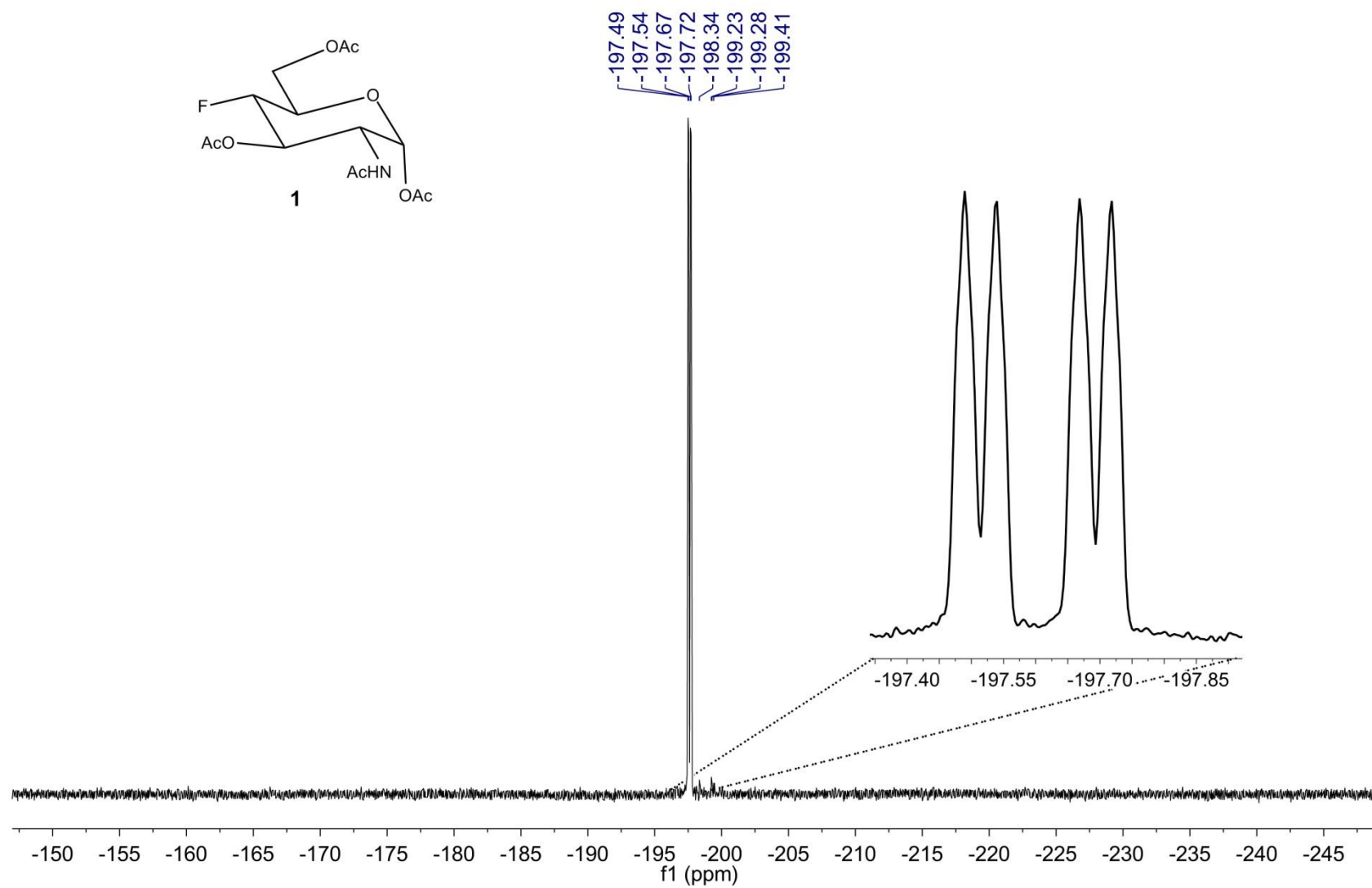
NMR spectra for compounds 1, 2, 4–8, 12, 18–22, 25, 26, 28, 29, 31, 40–46, and 48–51



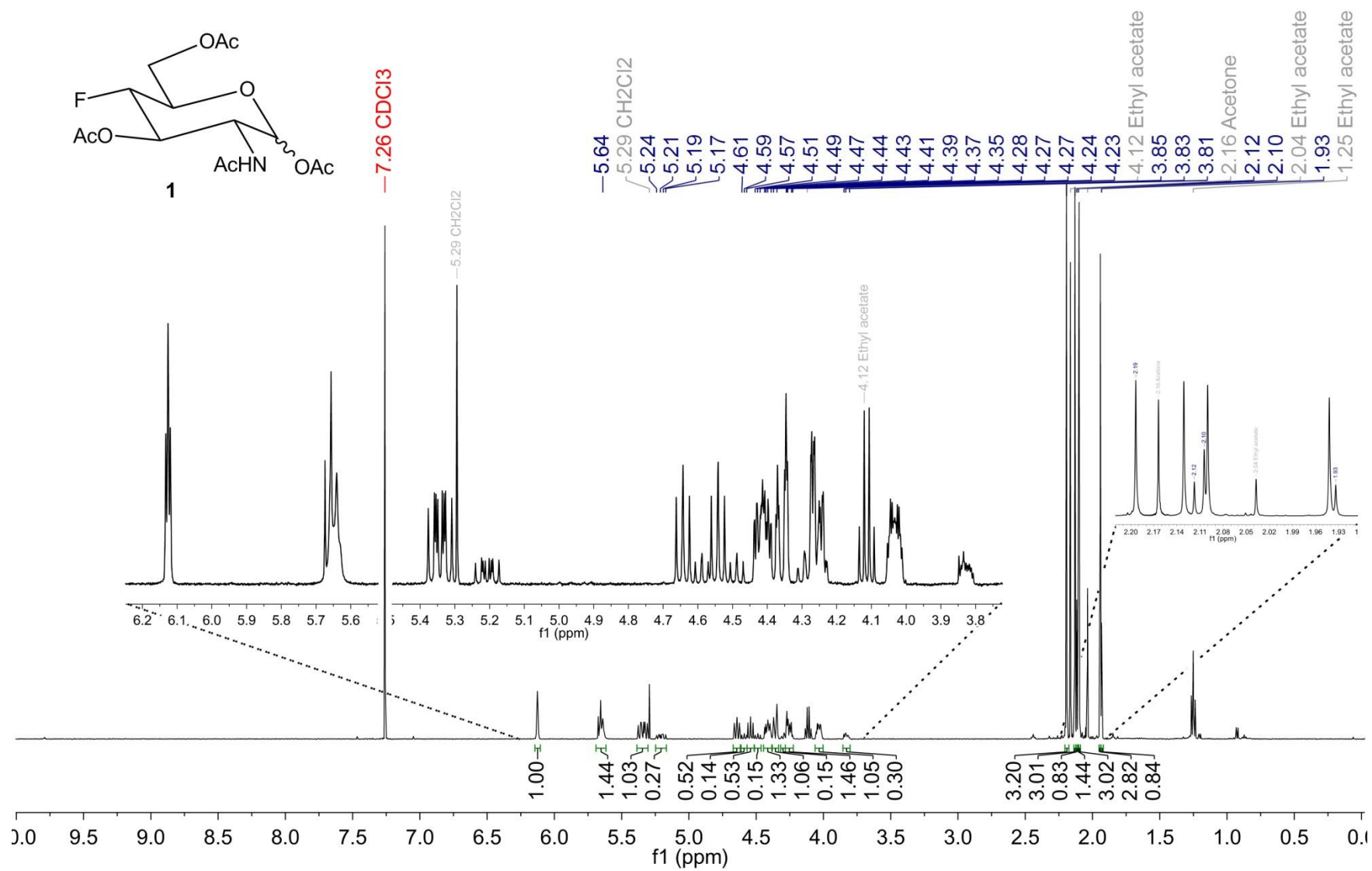
¹H NMR (300 MHz, CDCl₃) of **1a** (α-anomer).



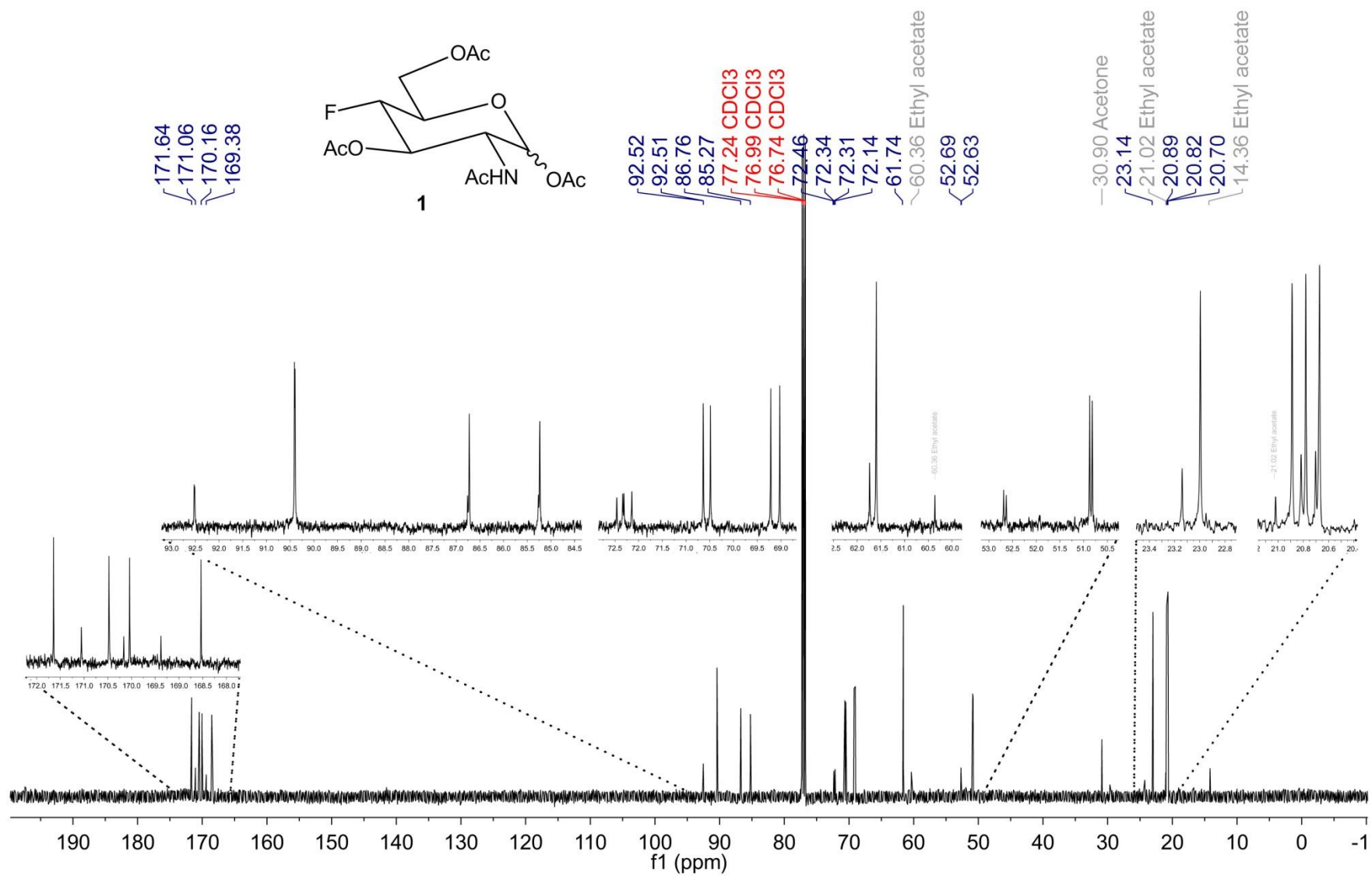
¹³C {¹H} NMR (75 MHz, CDCl₃) of **1α** (α-anomer).



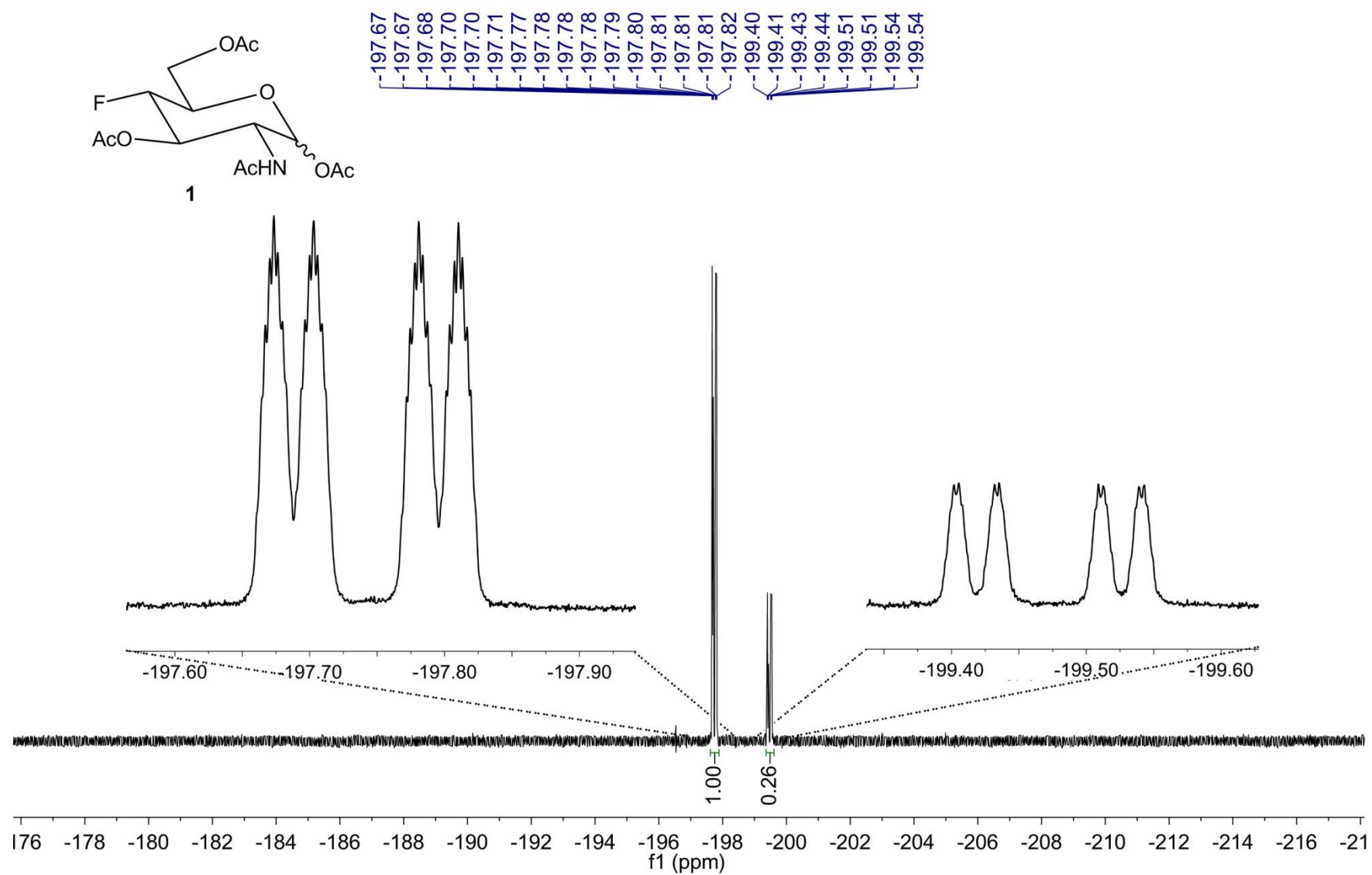
^{19}F NMR (282 MHz, CDCl_3) of **1α** (α-anomer).



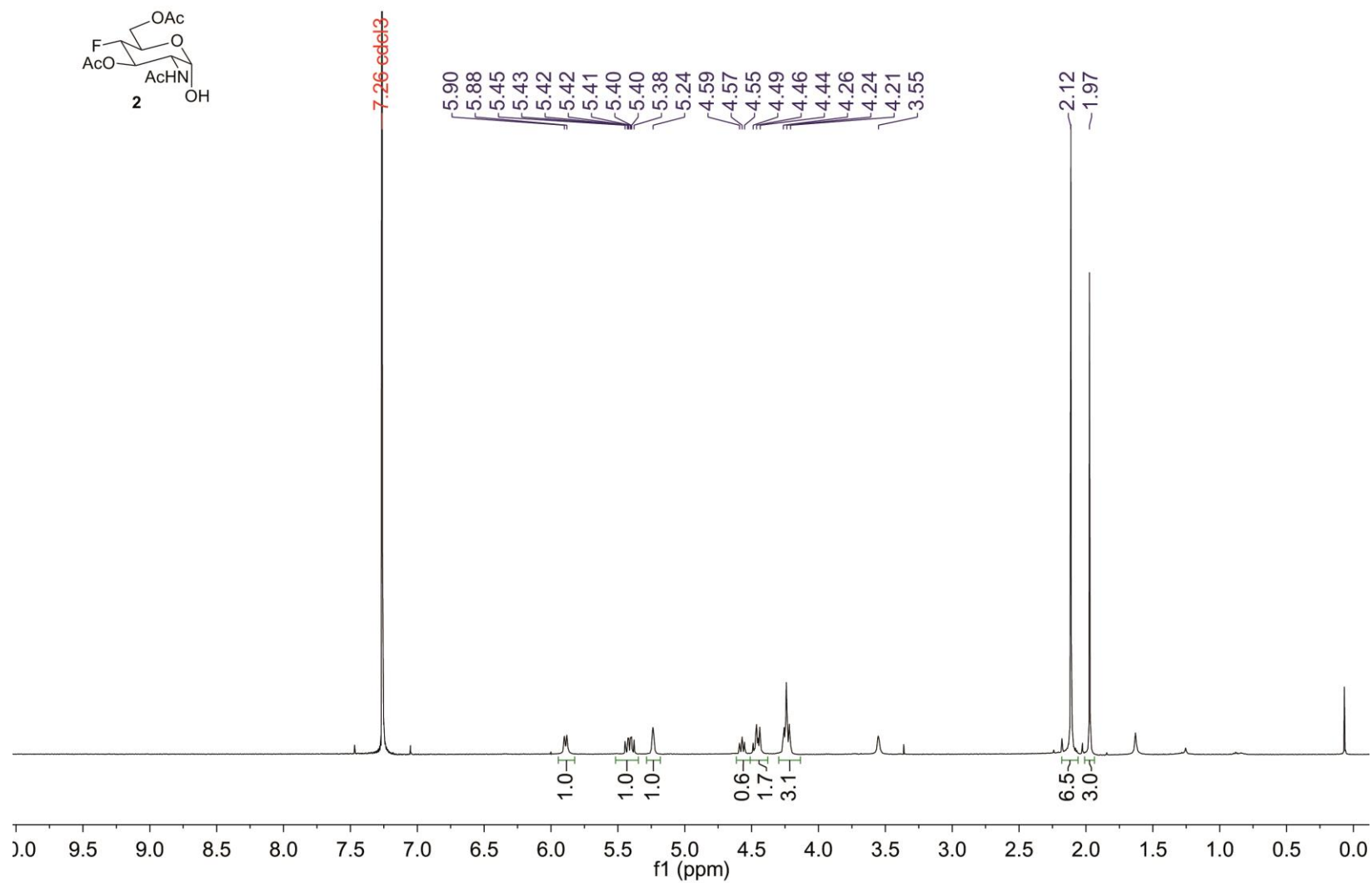
¹H NMR (500 MHz, CDCl₃) of **1** (α -anomer/ β -anomer ca 1:0.3).



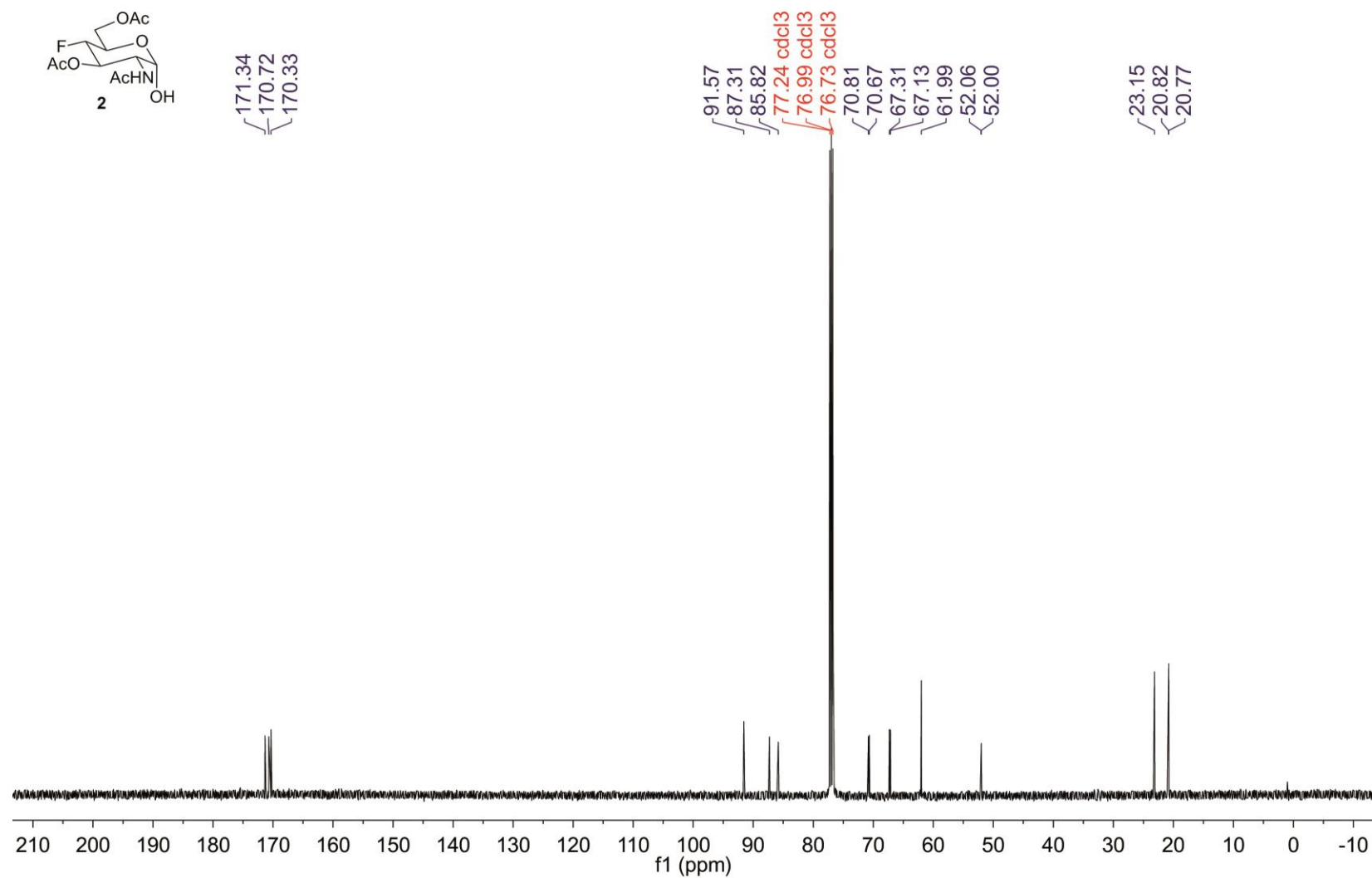
^{13}C { ^1H } NMR (125 MHz, CDCl_3) of **1** (α -anomer/ β -anomer ca 1:0.3).



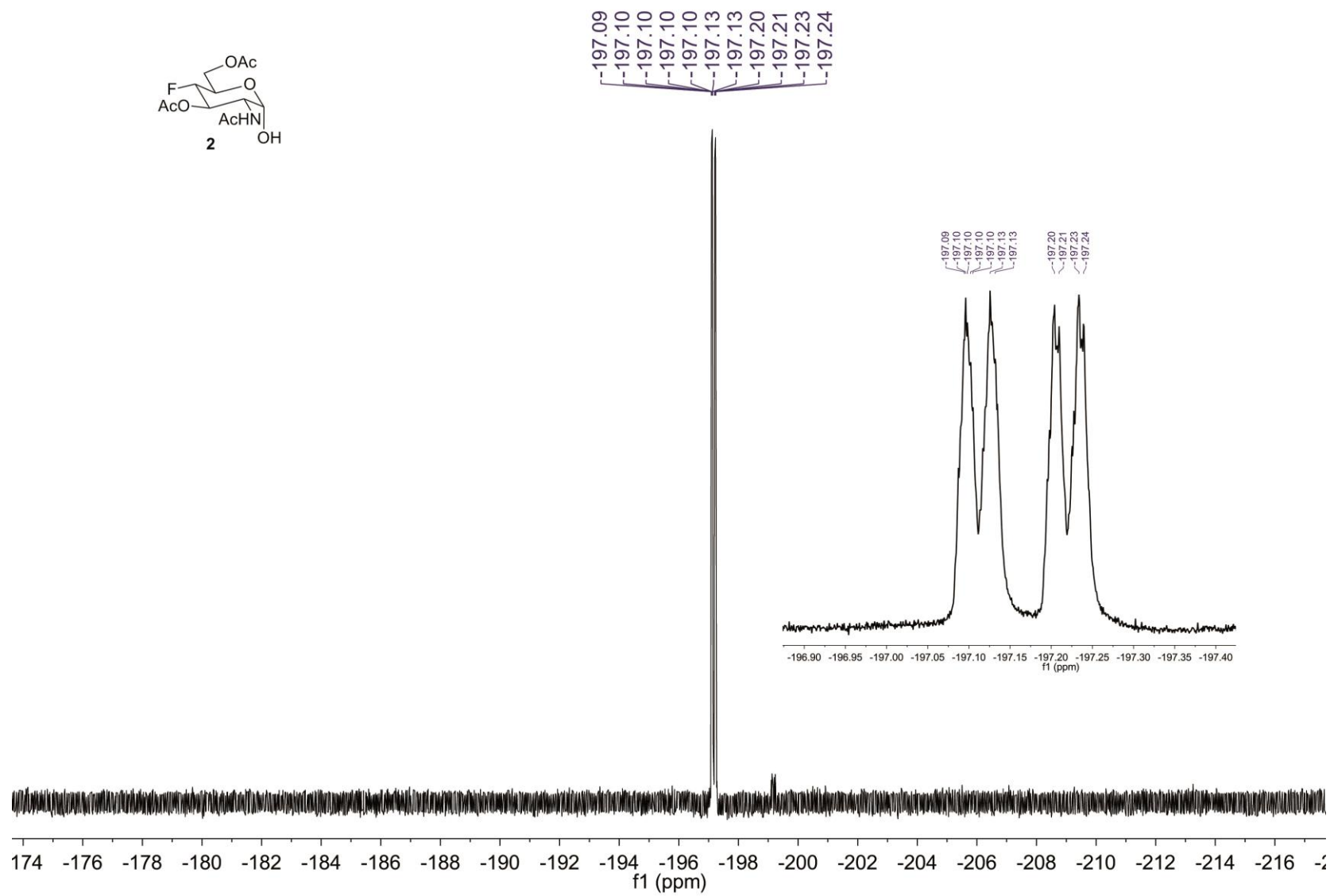
^{19}F NMR (470 MHz, CDCl_3) of **1** (α -anomer/ β -anomer ca 1:0.3)



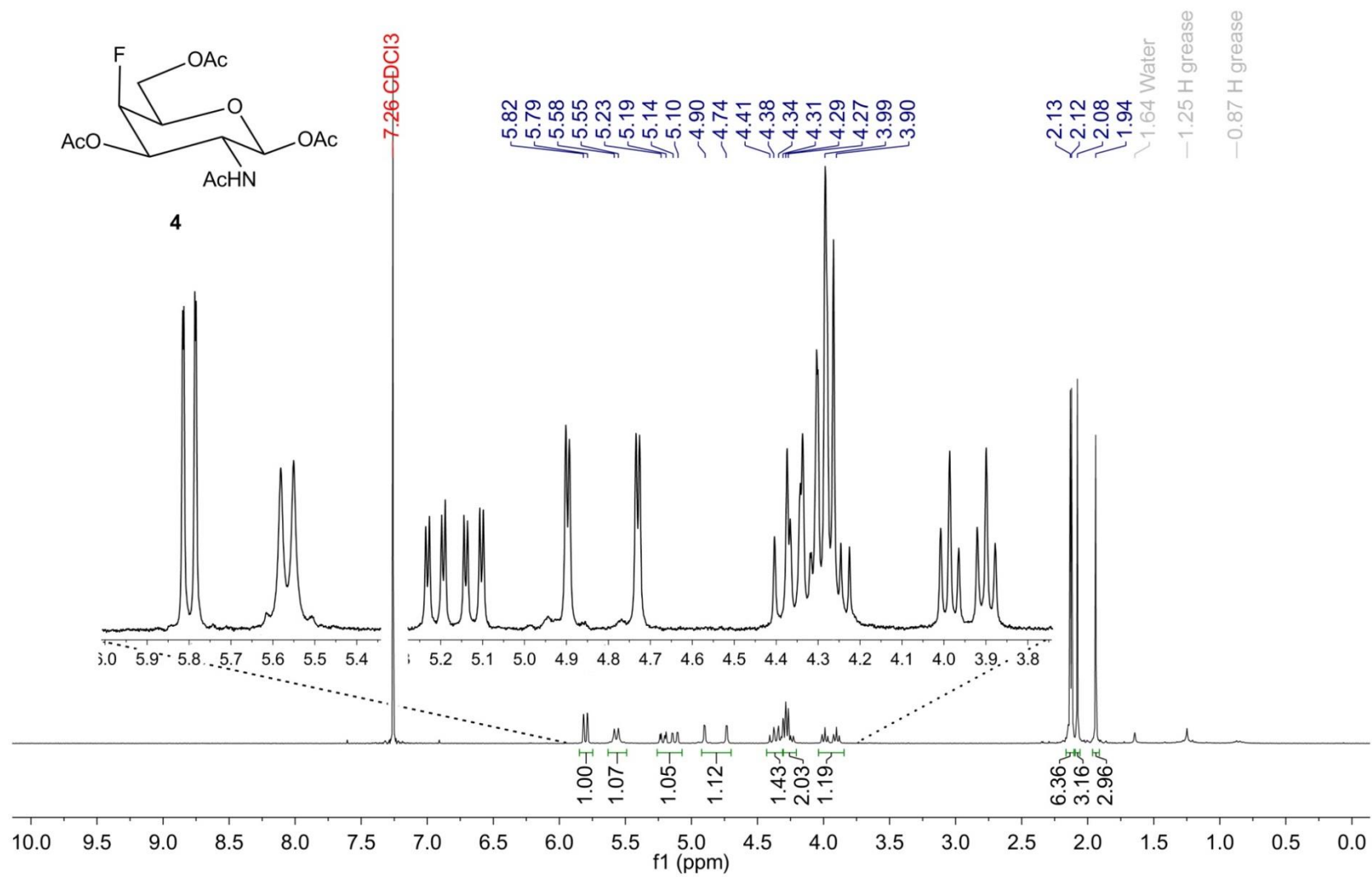
¹H NMR (500 MHz, CDCl₃) of **2** (α-anomer)



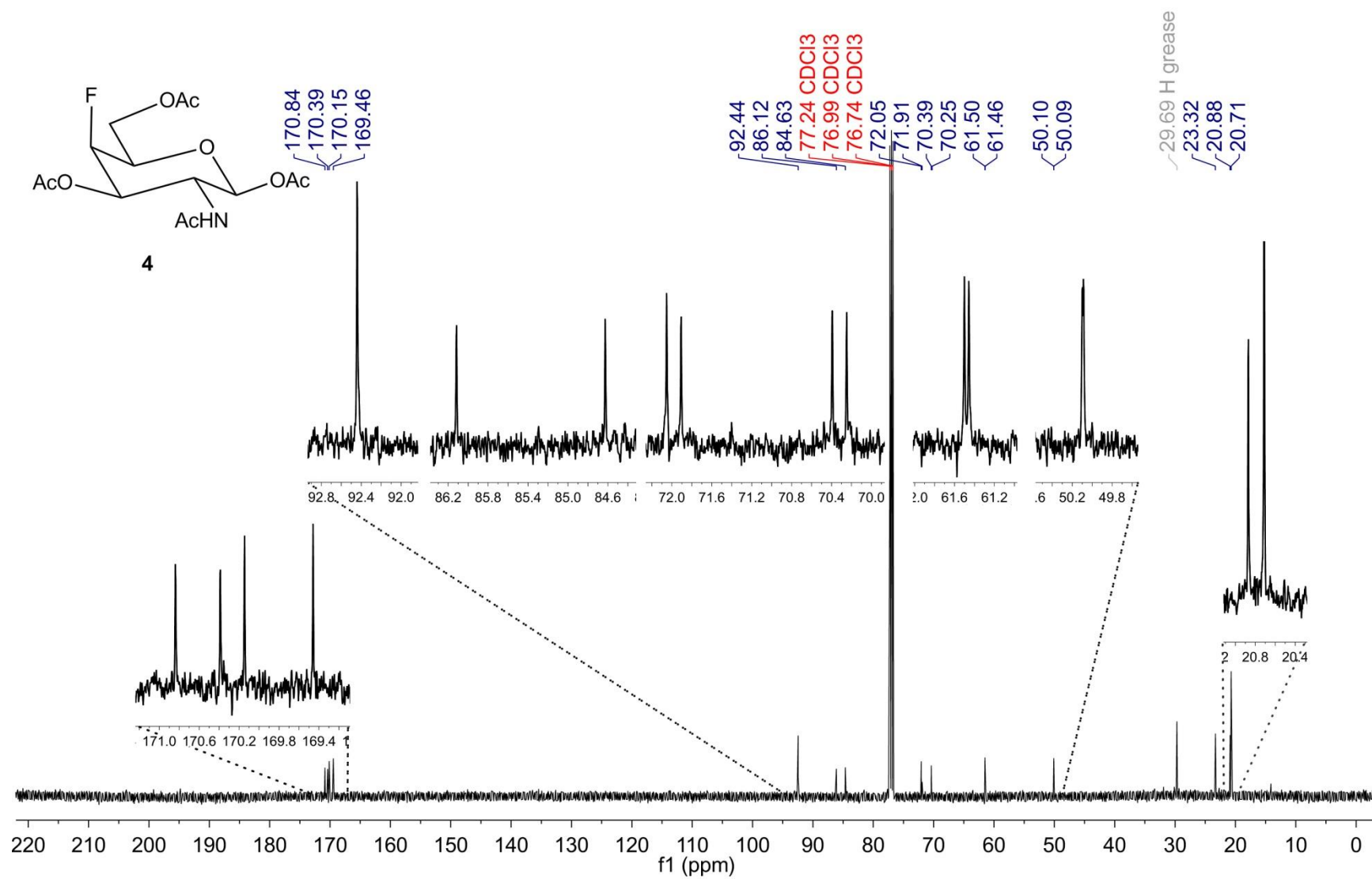
^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of **2** (α-anomer)



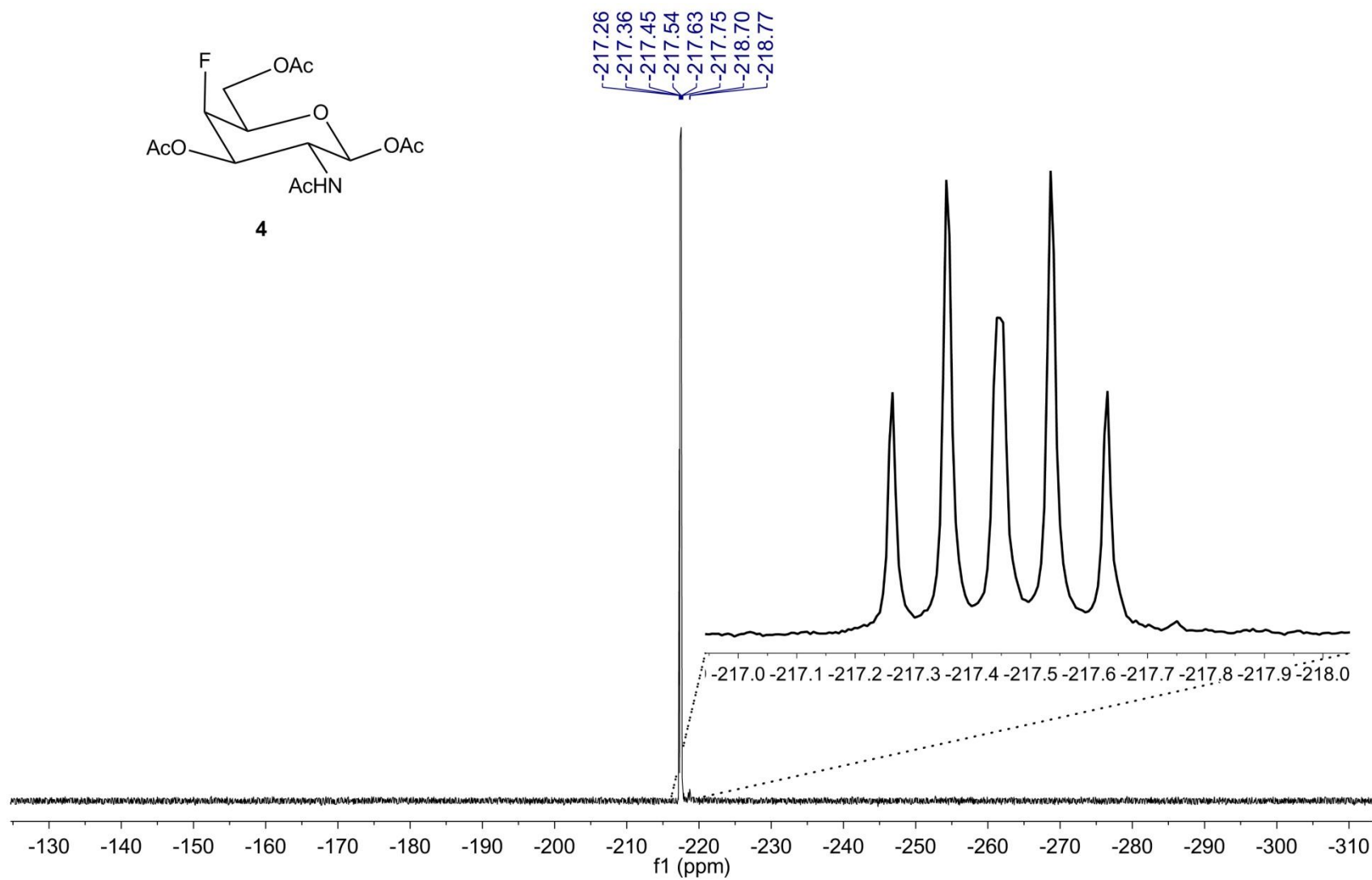
^{19}F NMR (470 MHz, CDCl_3) of **2** (α-anomer)



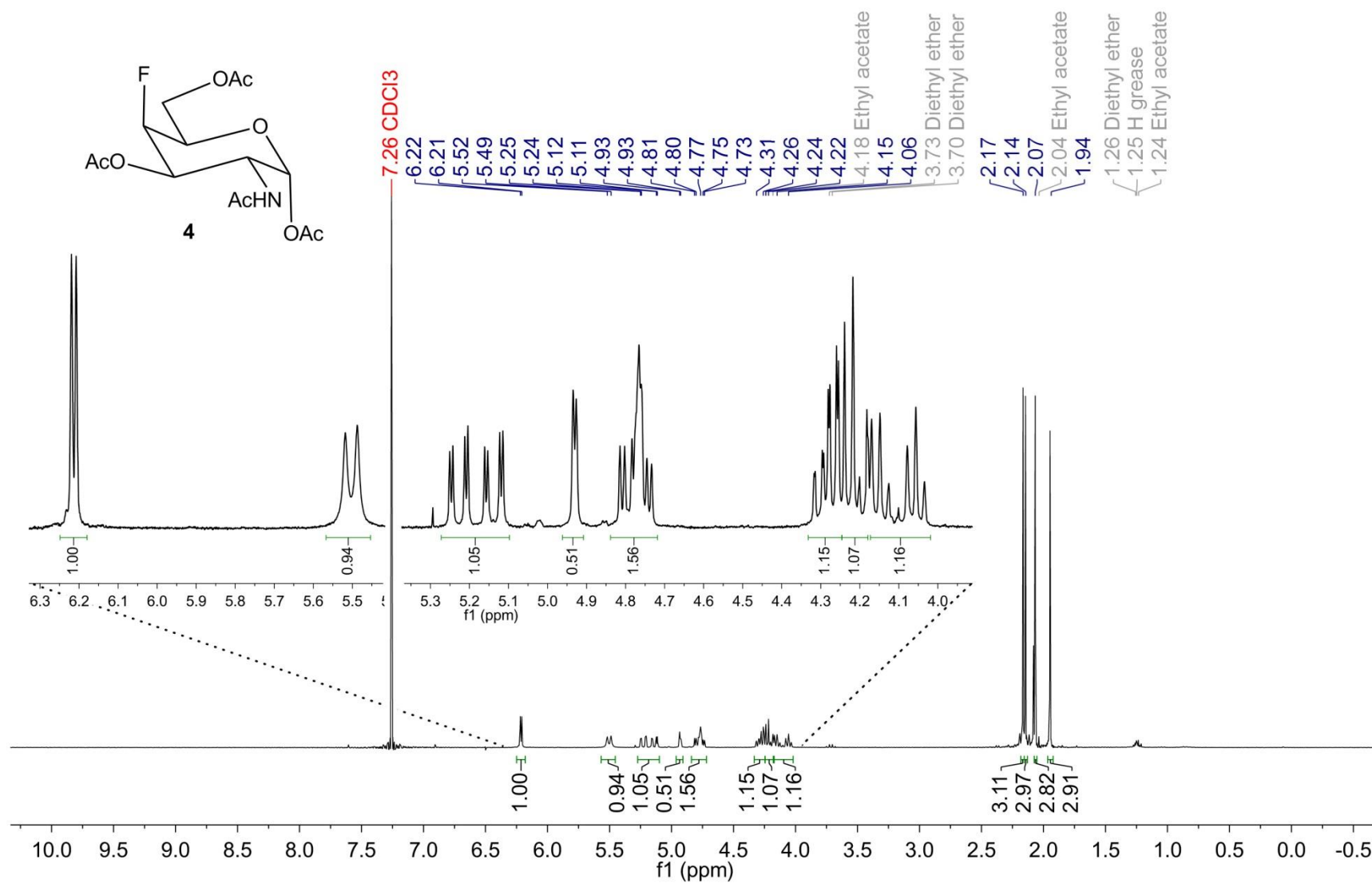
¹H NMR (300 MHz, CDCl₃) of **4β** (β-anomer).



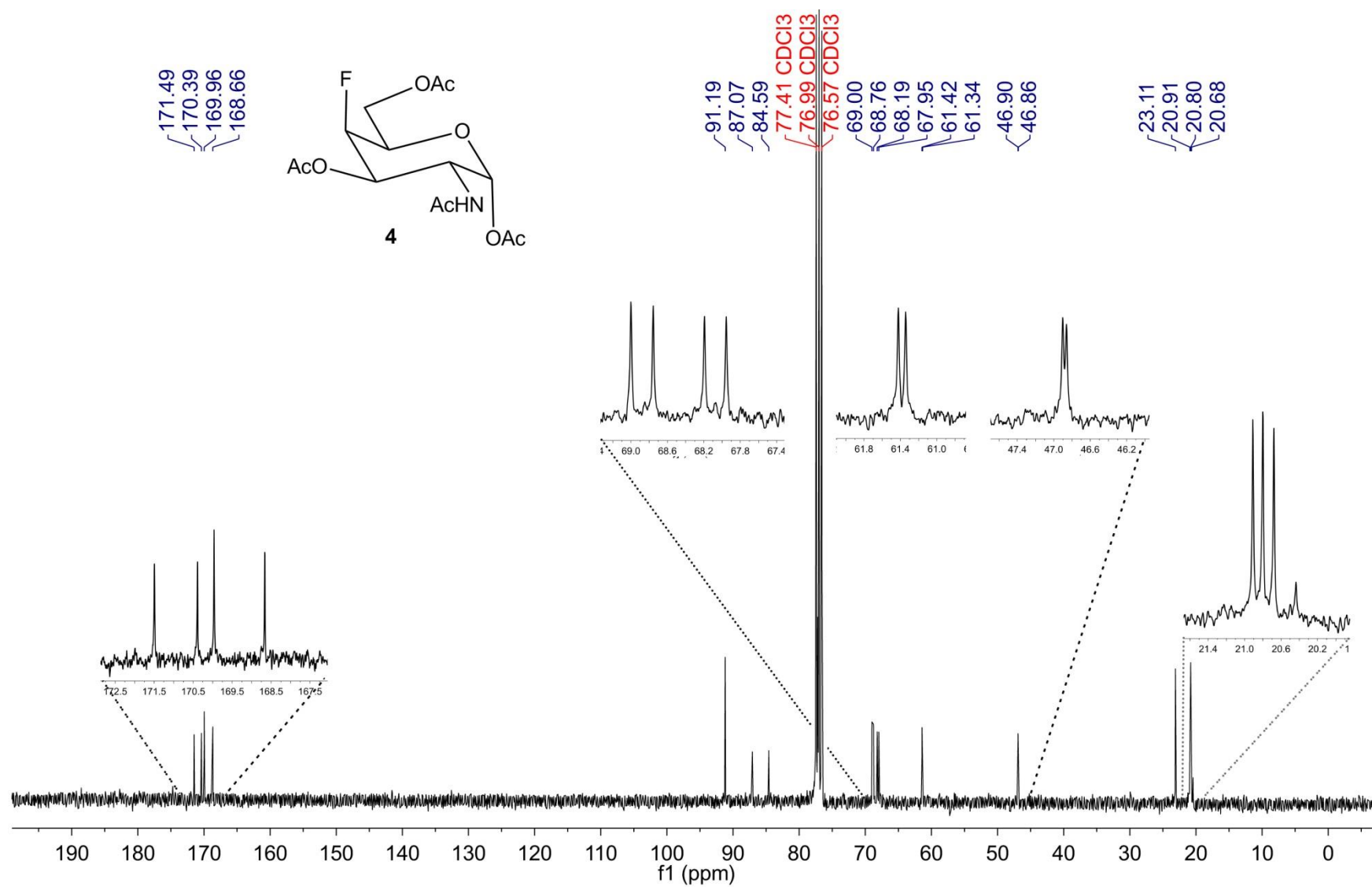
¹³C {¹H} NMR (75 MHz, CDCl₃) of **4β** (β-anomer).



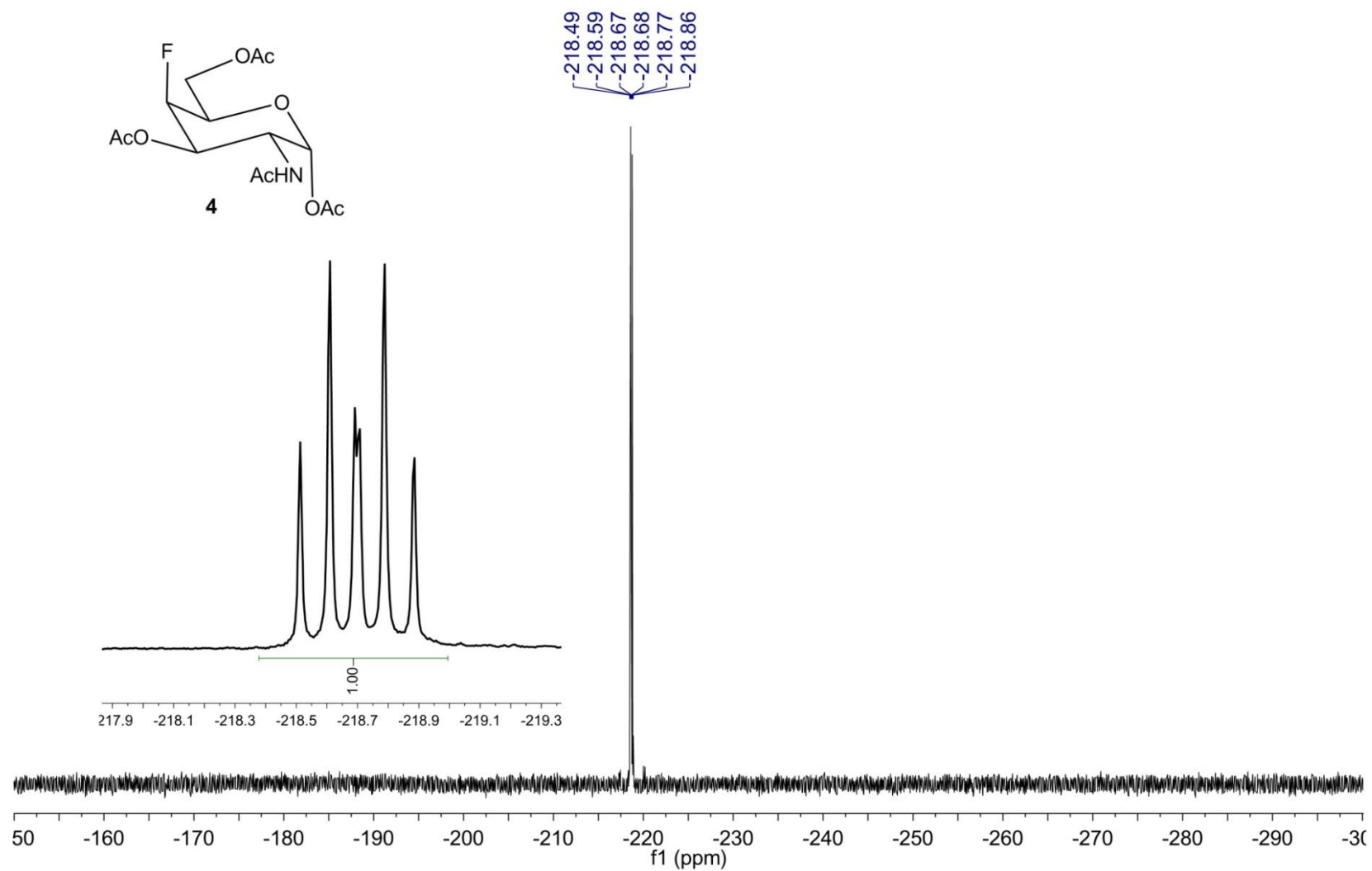
¹⁹F NMR (282 MHz, CDCl₃) of **4**β (β-anomer).



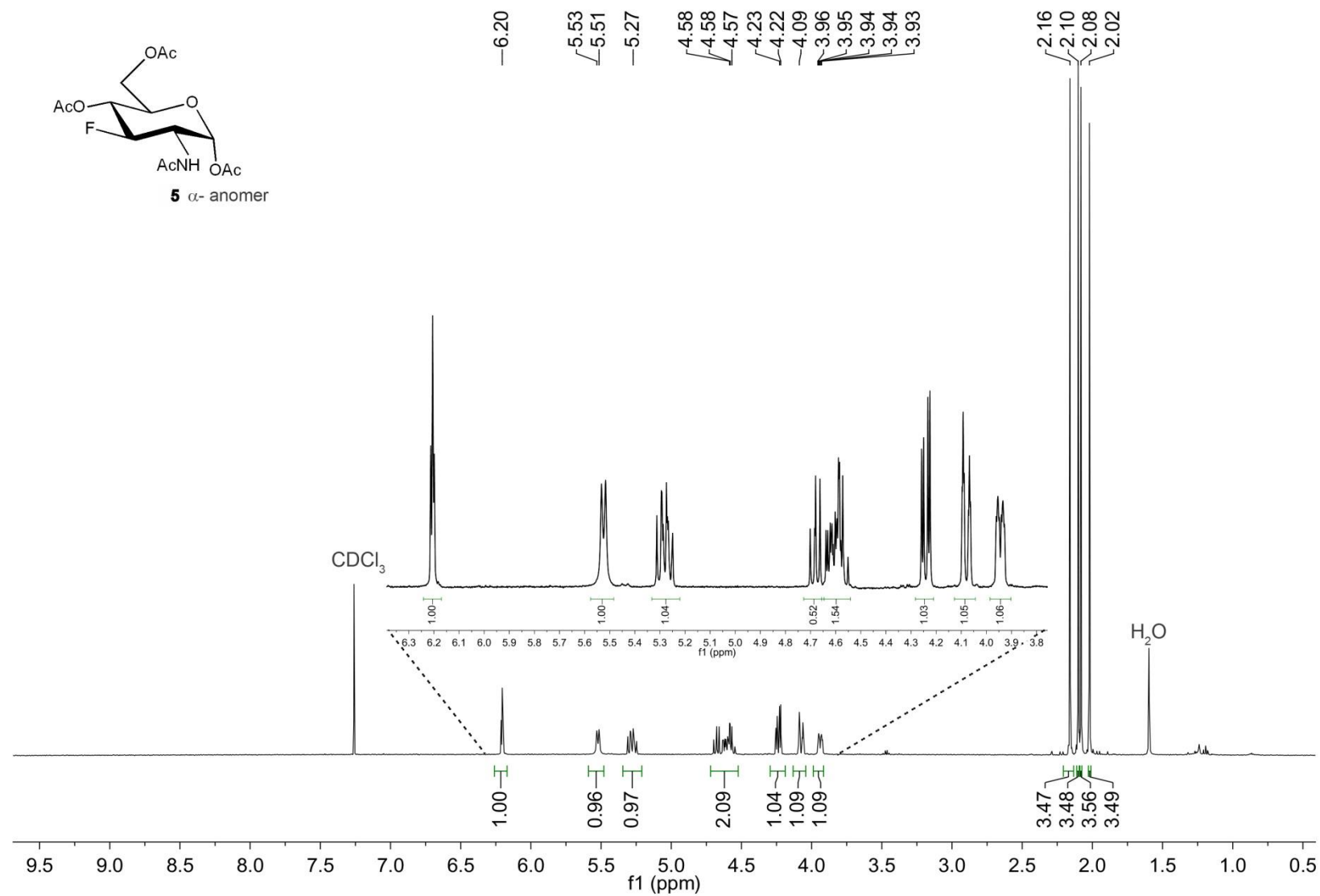
¹H NMR (300 MHz, CDCl₃) of **4α** (α-anomer).



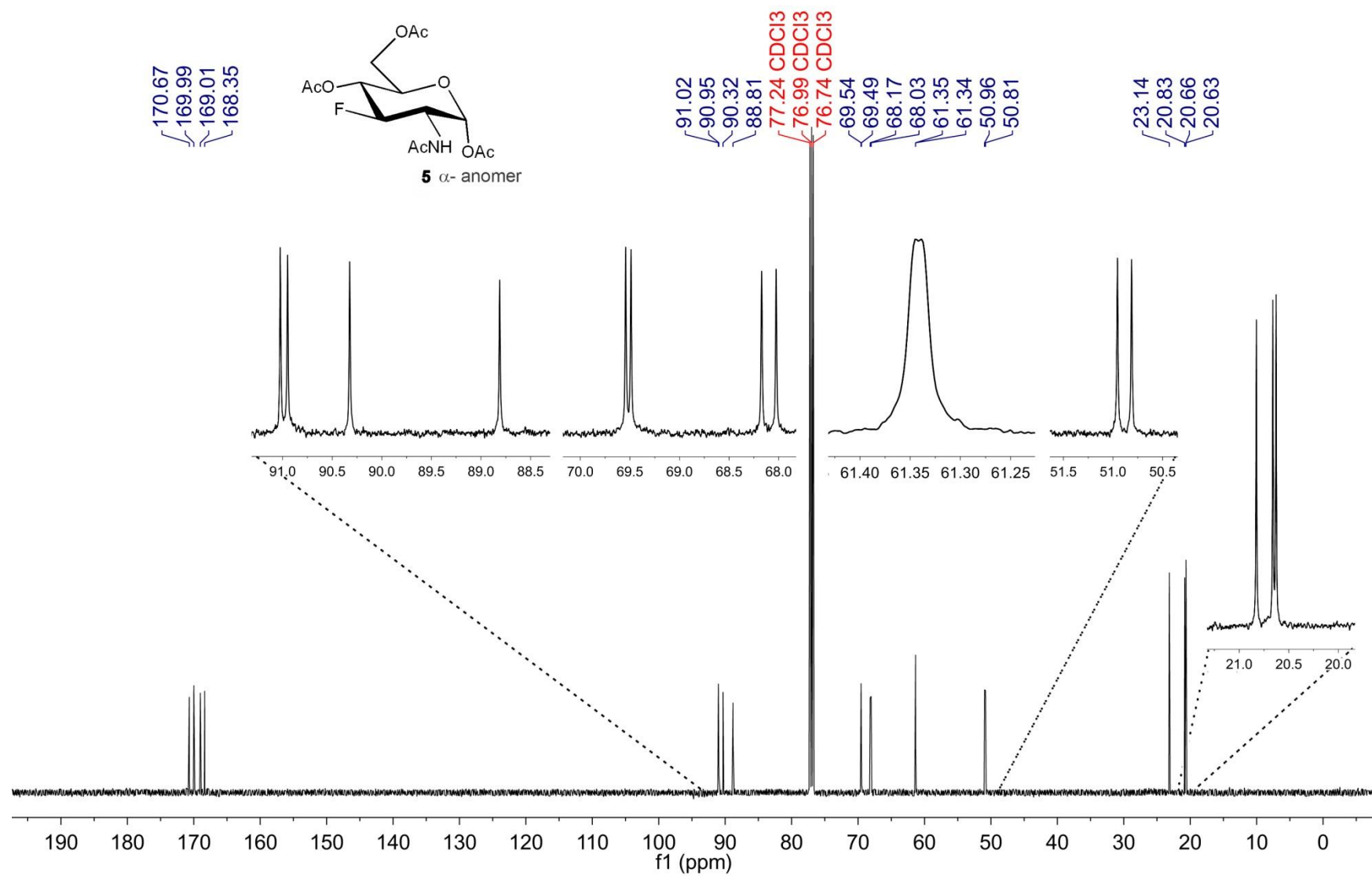
¹³C {¹H} NMR (75 MHz, CDCl₃) of **4α** (α-anomer).



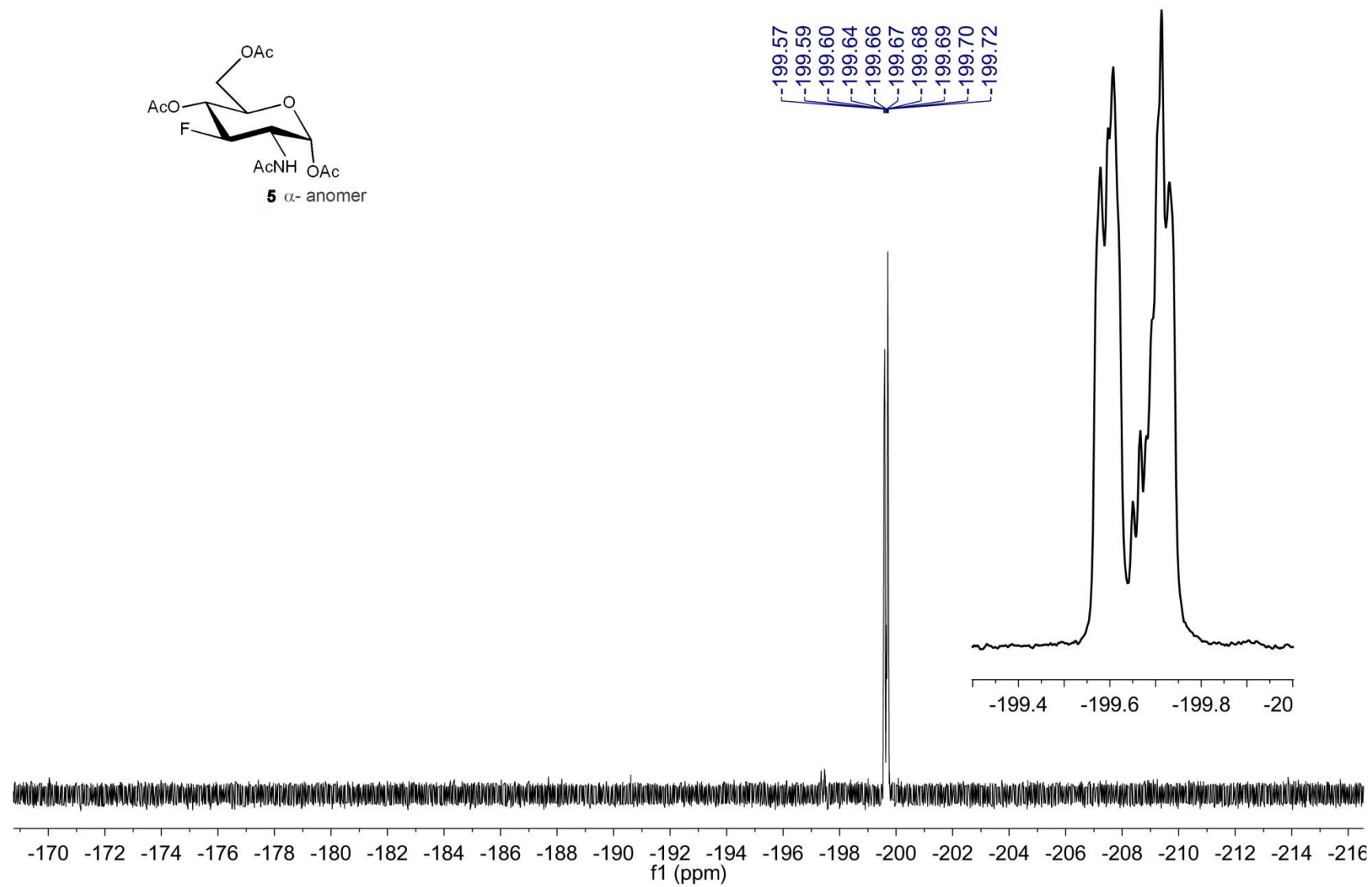
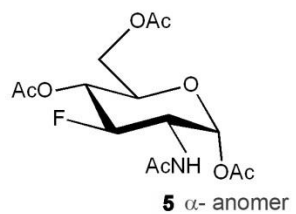
^{19}F NMR (282 MHz, CDCl_3) of **4 α** (α -anomer).



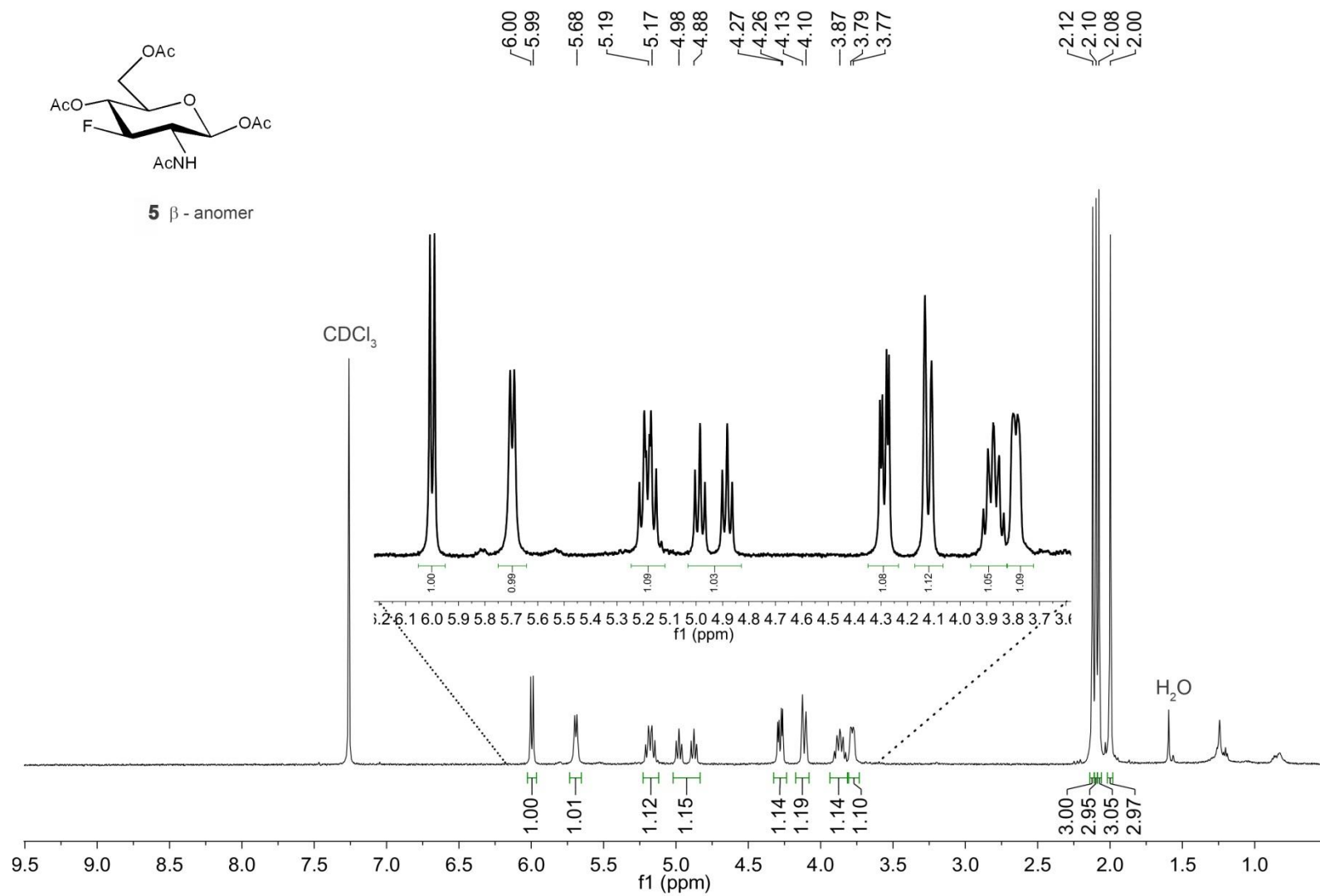
¹H NMR (500 MHz, CDCl₃) of **5** α (α -anomer).



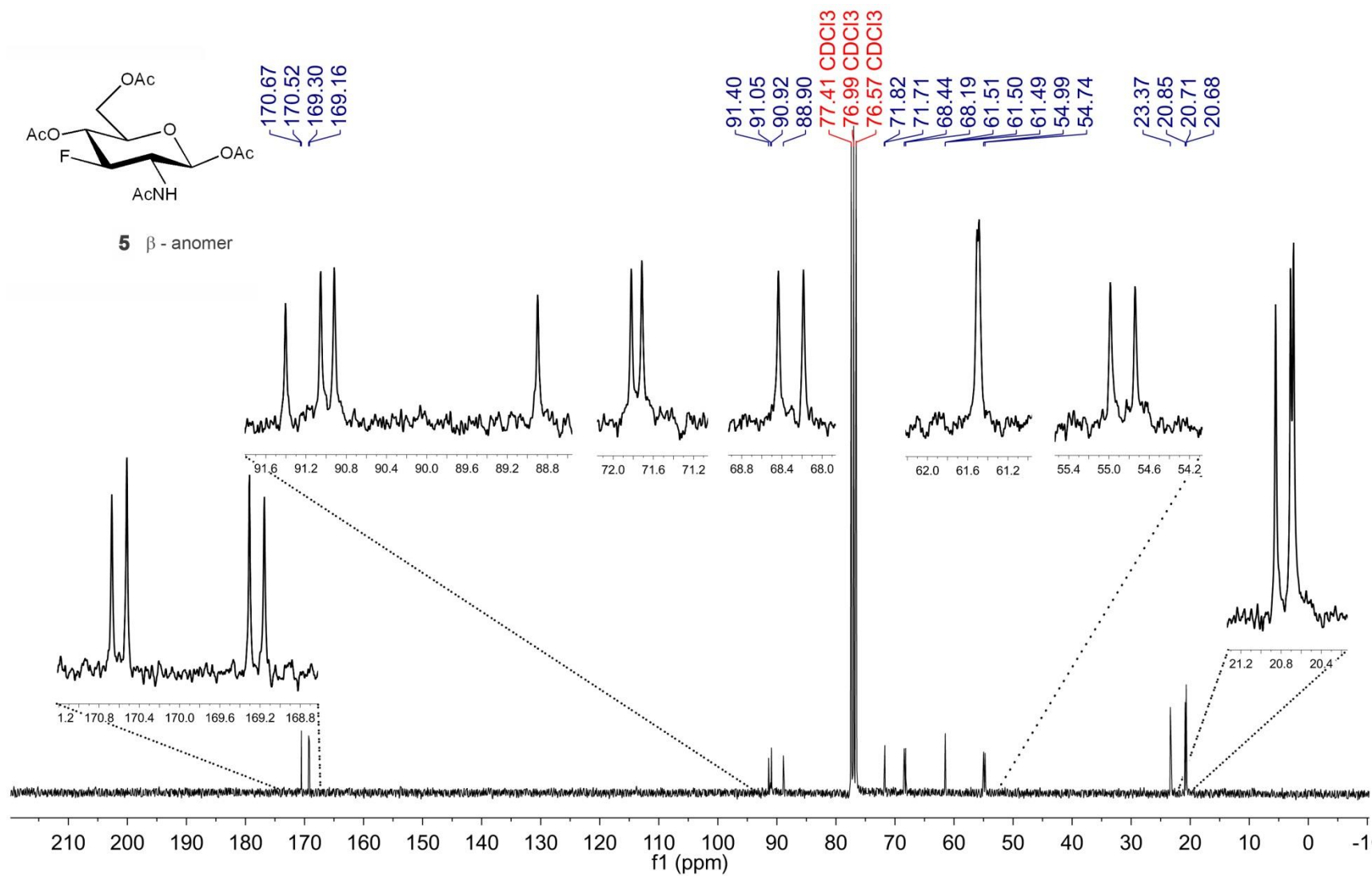
^{13}C { ^1H } NMR (125 MHz, CDCl₃) of **5** α (α -anomer).



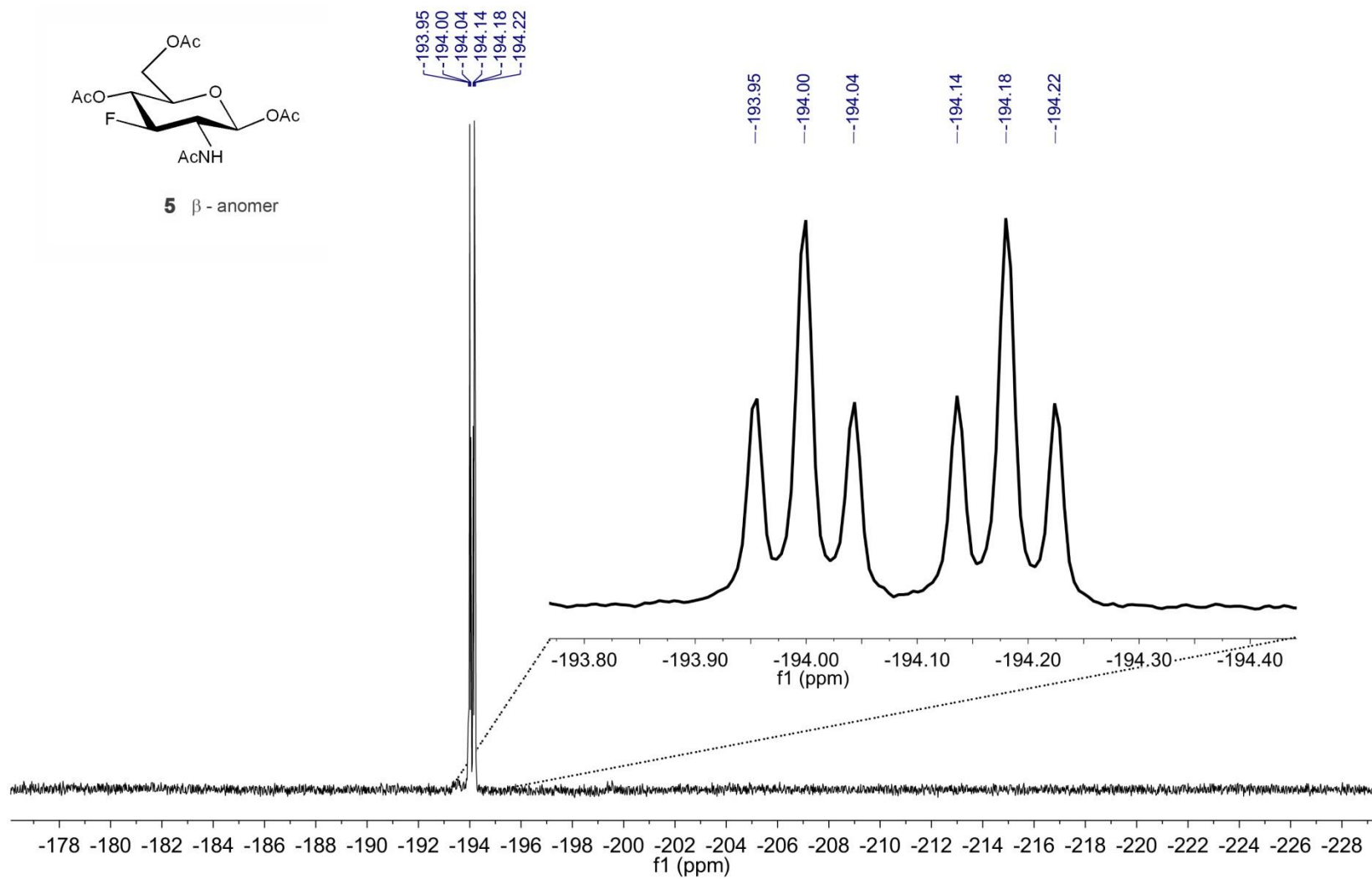
^{19}F NMR (470 MHz, CDCl_3) of **5α** (α-anomer).



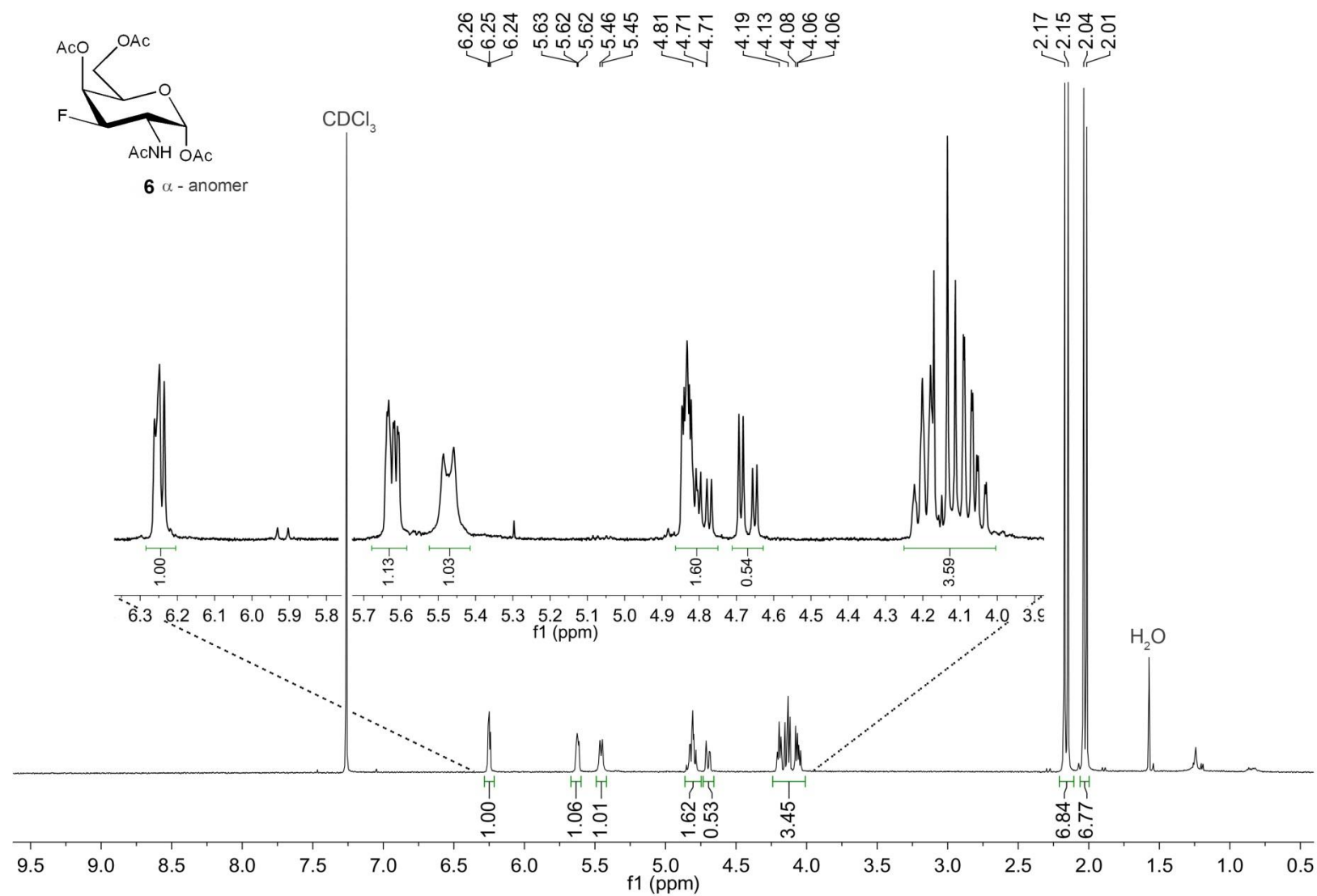
^1H NMR (300 MHz, CDCl_3) of **5** β -anomer.



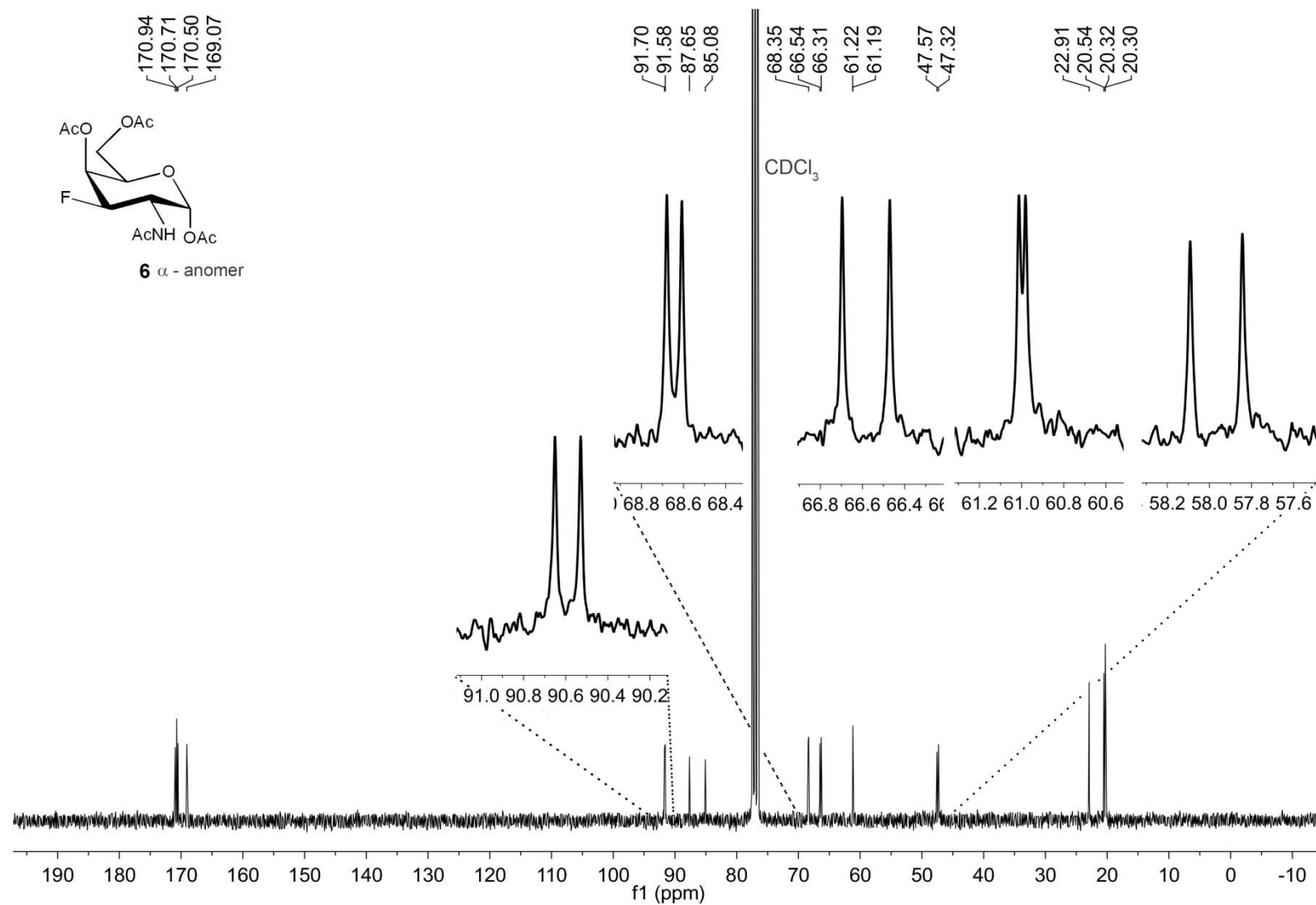
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **5** β (β -anomer).



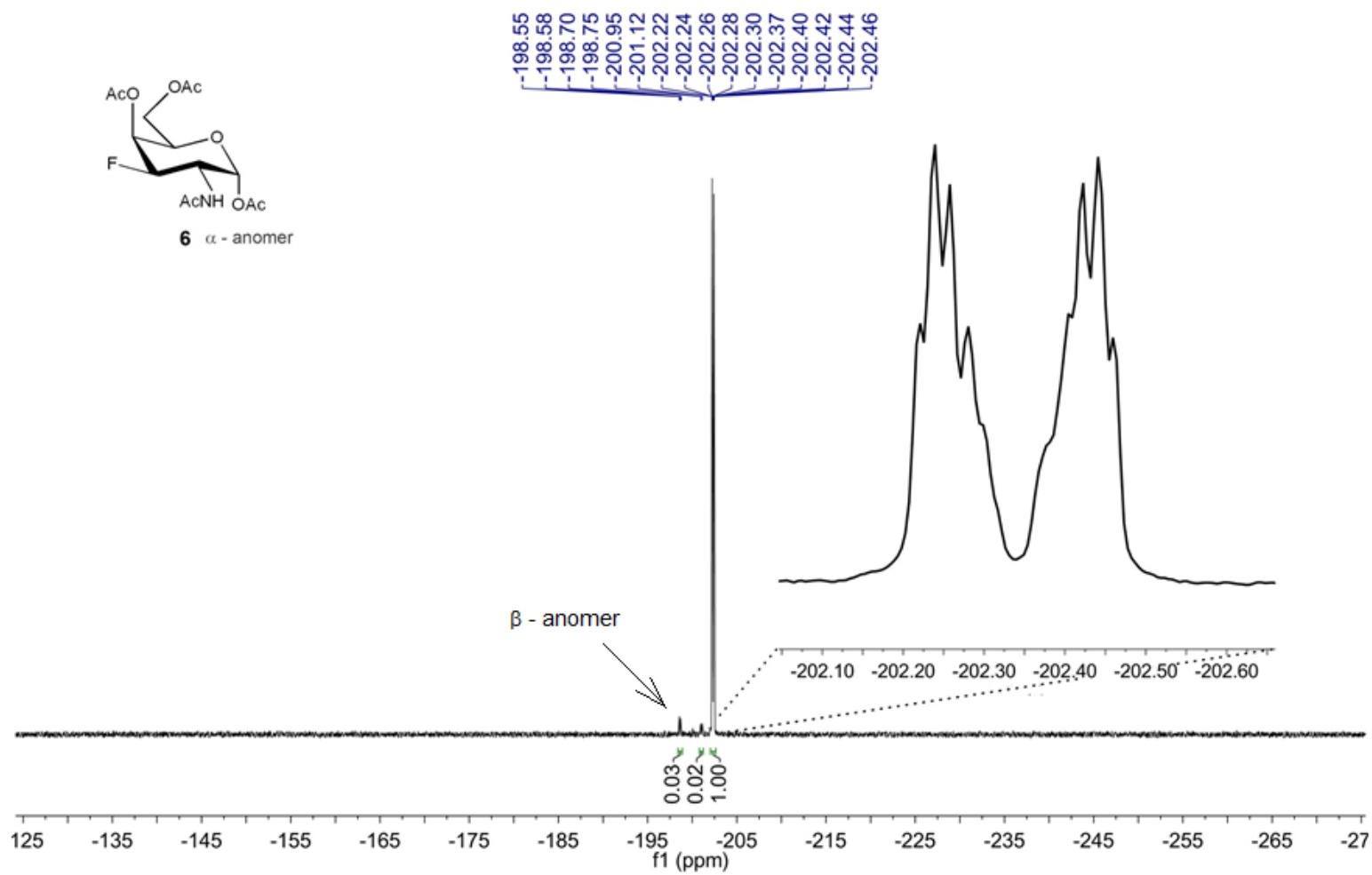
^{19}F NMR (282 MHz, CDCl_3) of **5 β** (β -anomer).



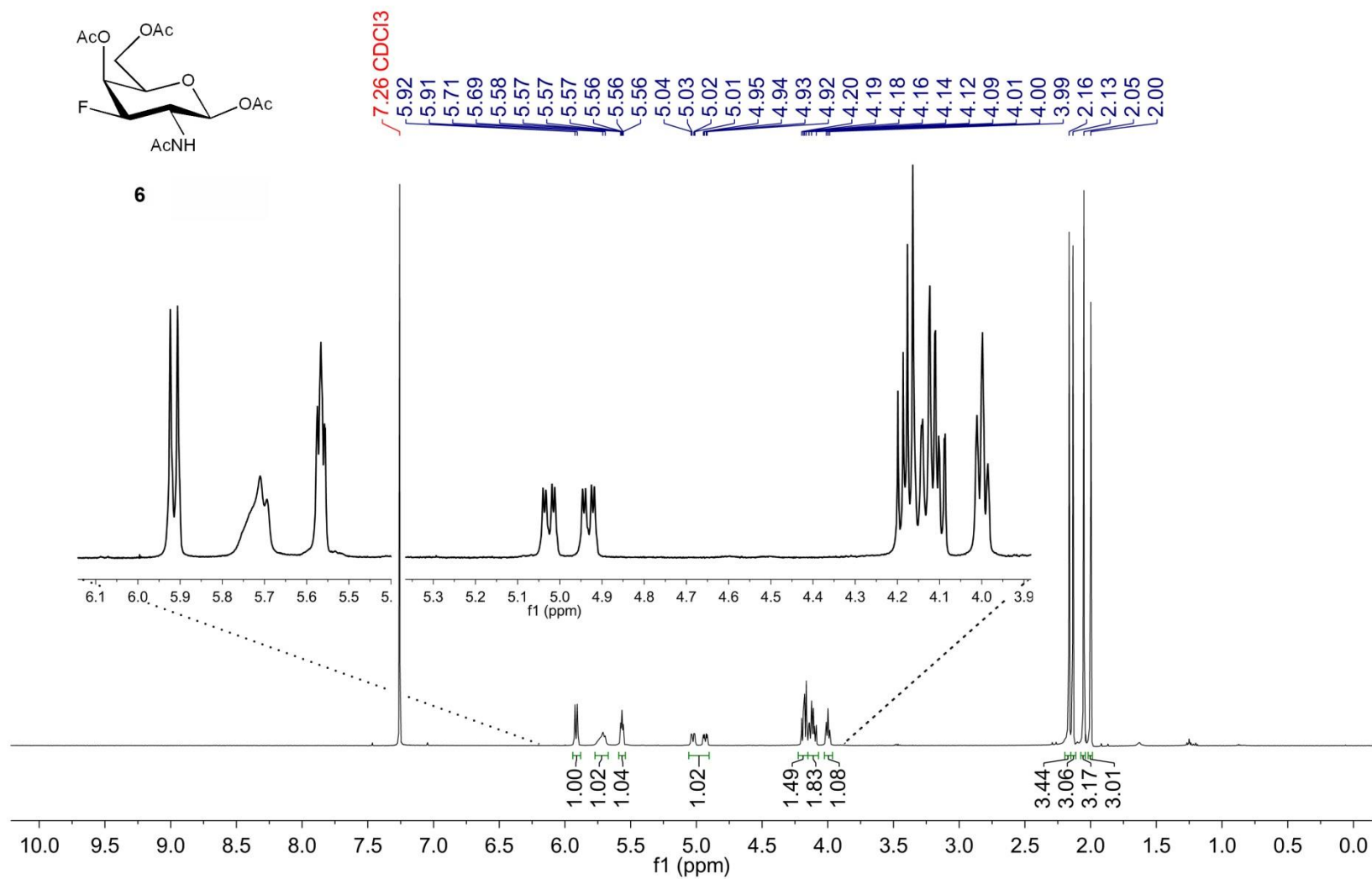
^1H NMR (300 MHz, CDCl_3) of **6** (α -anomer).



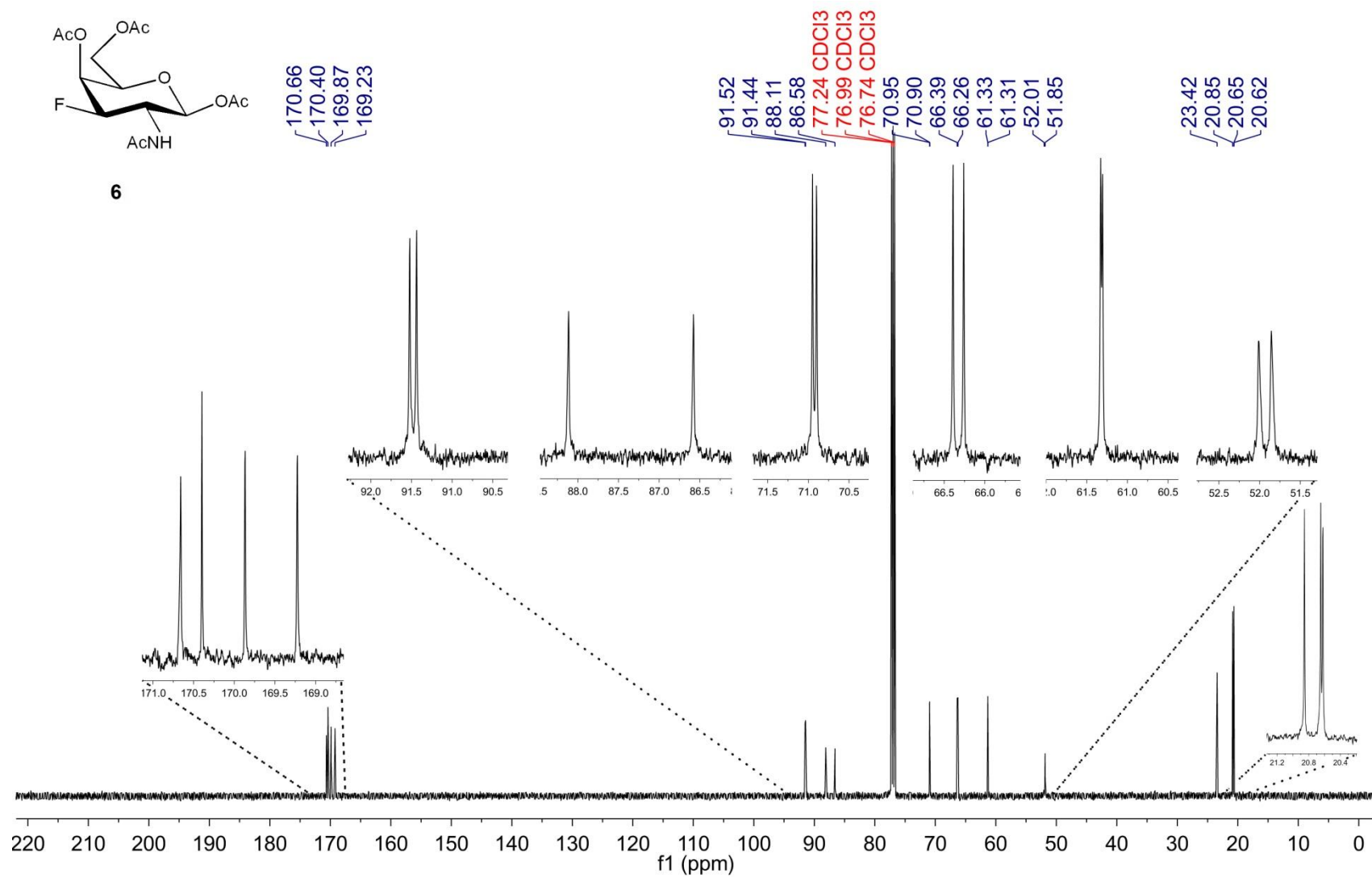
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **6** (α -anomer).



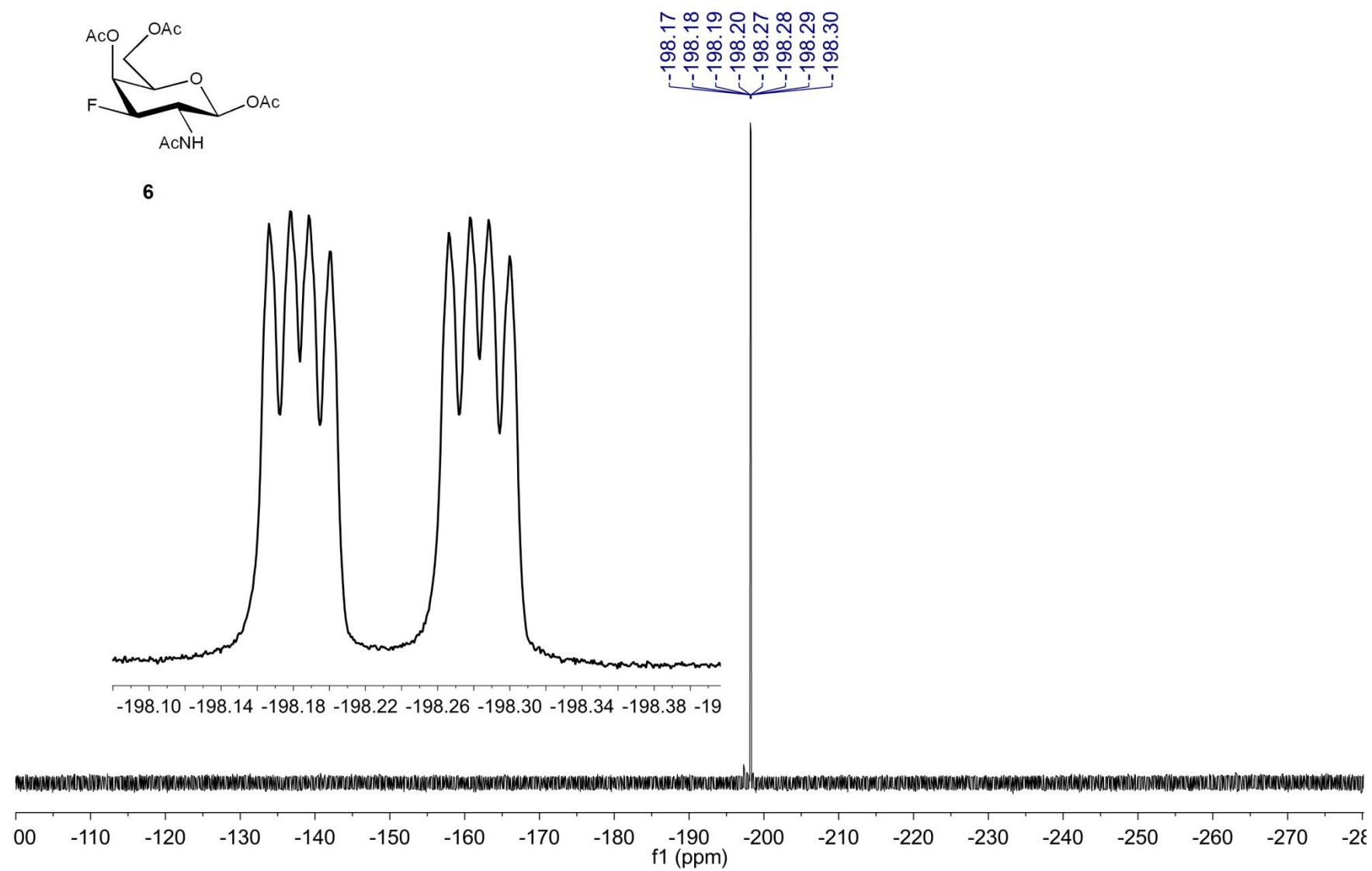
^{19}F NMR (282 MHz, CDCl_3) of **6** (α -anomer + cca 3 % β -anomer).



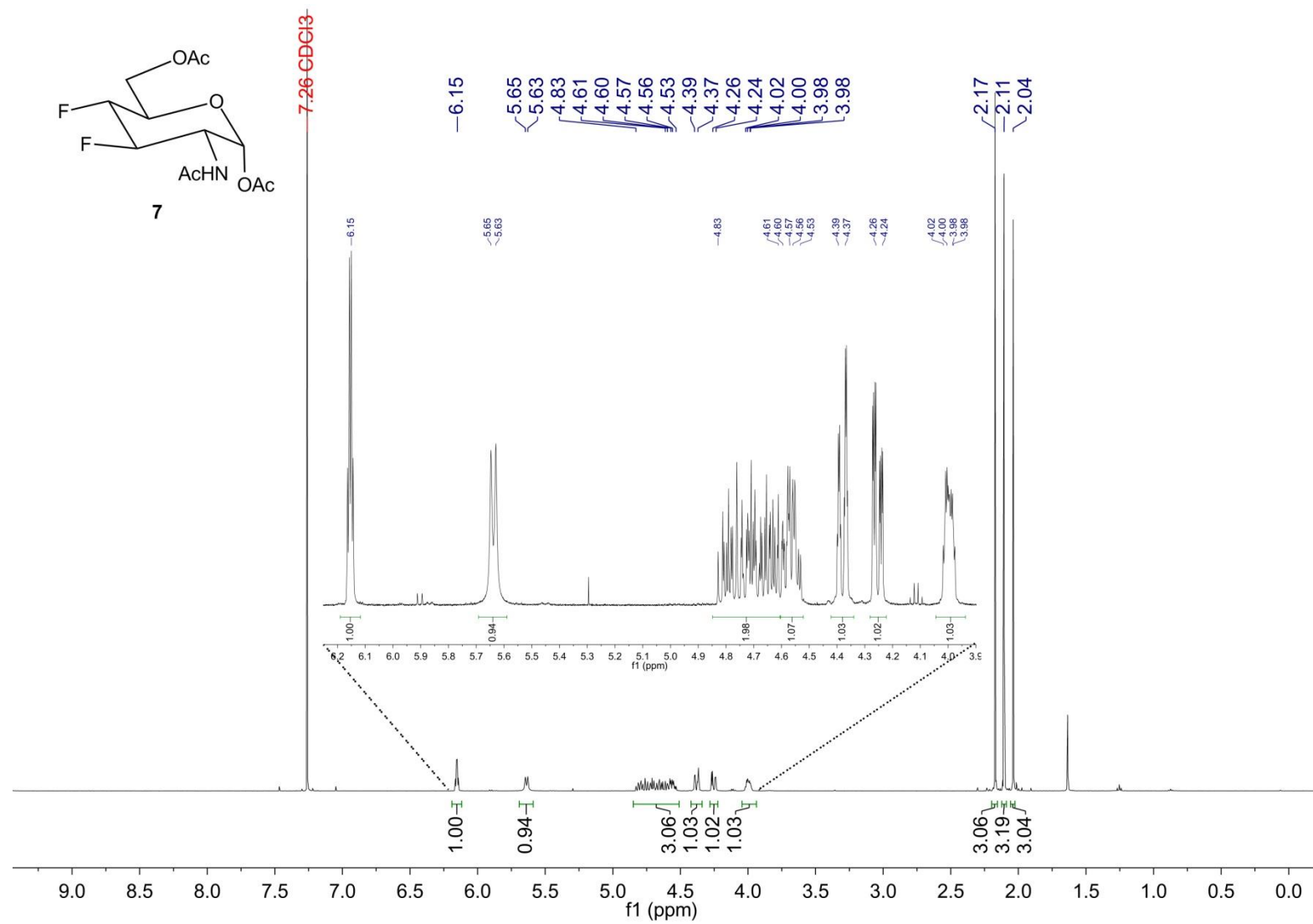
^1H NMR (500 MHz, CDCl_3) of **6** (β -anomer).



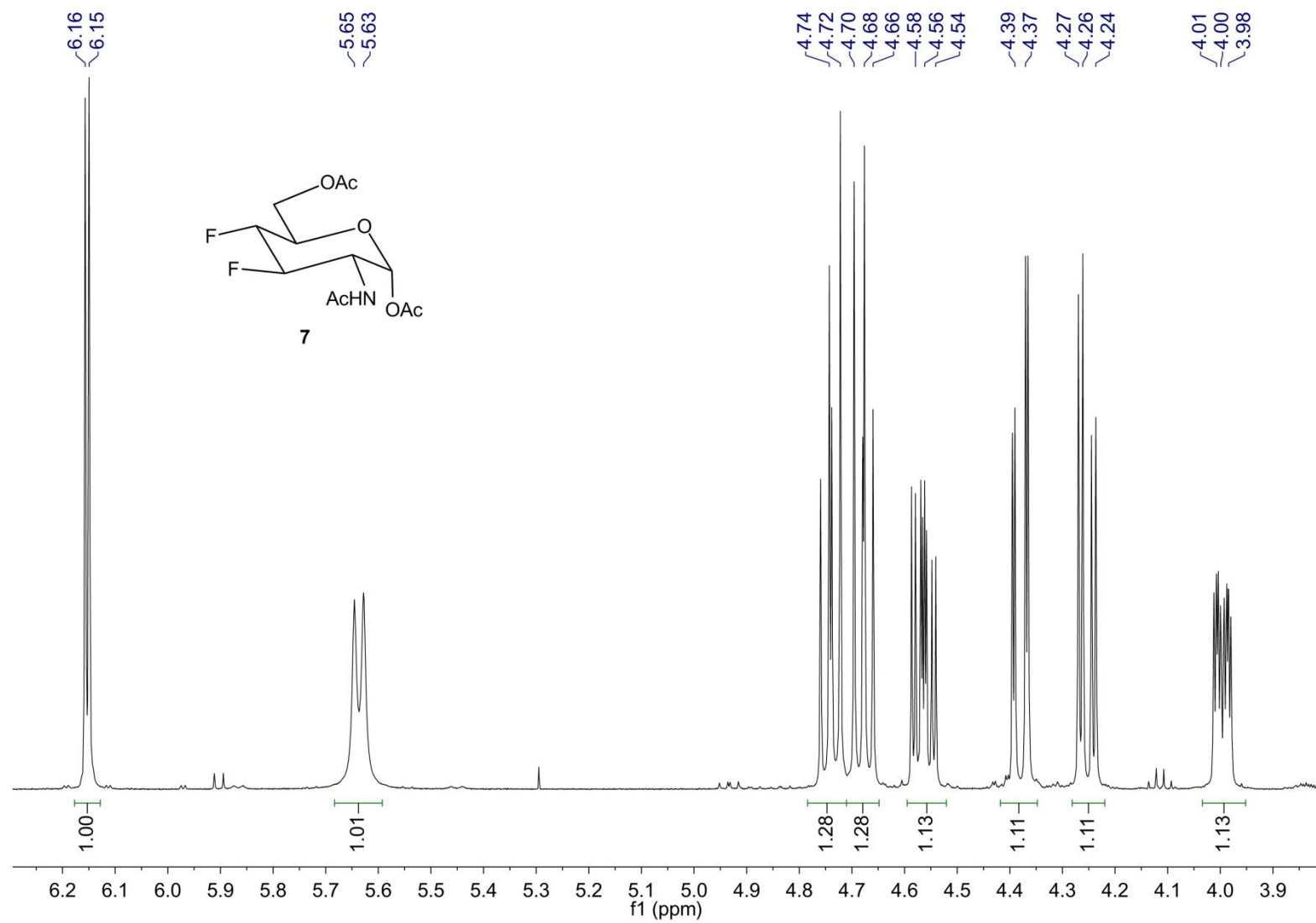
^{13}C { ^1H } NMR (125 MHz, CDCl_3) of **6** (β-anomer).



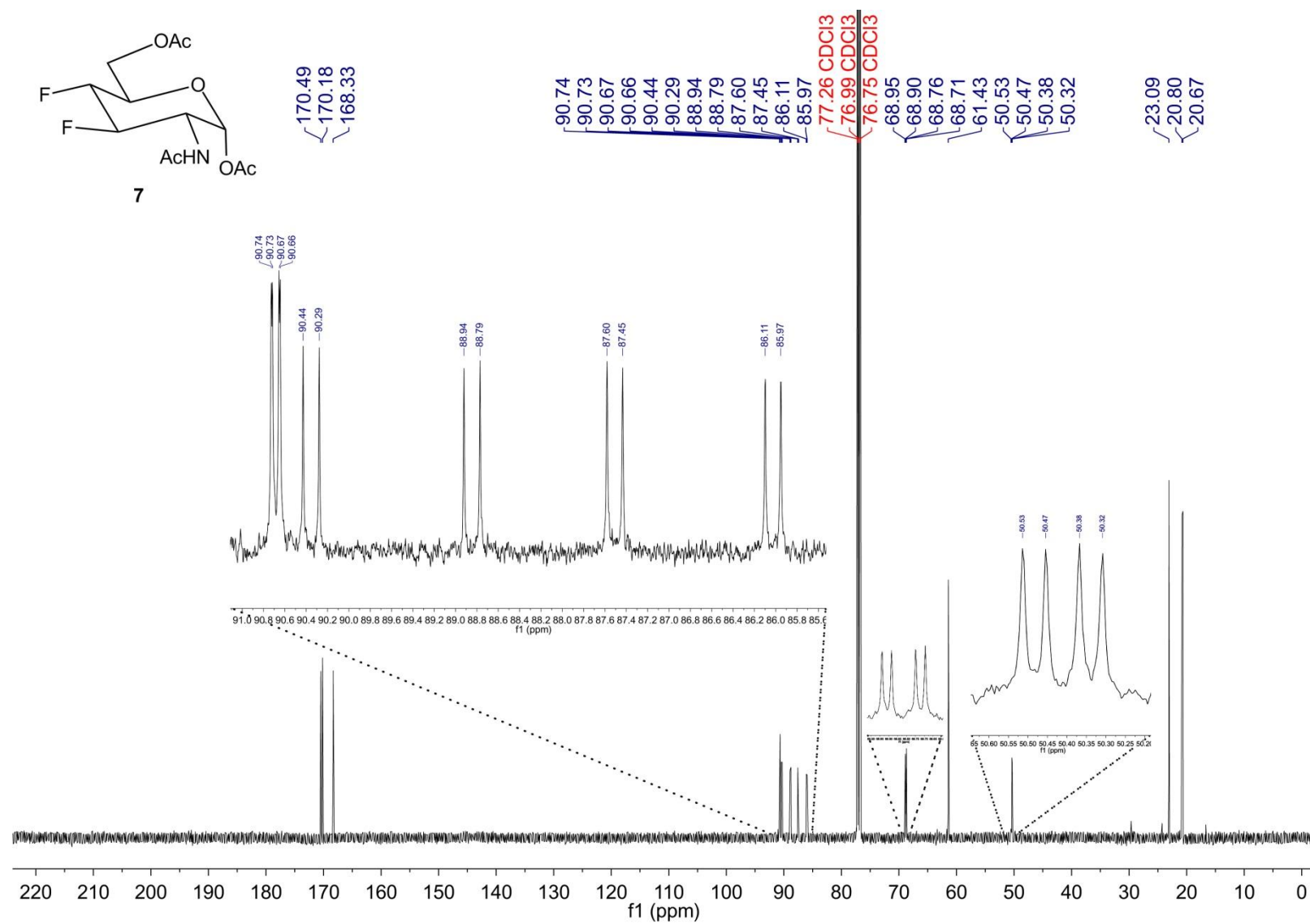
^{19}F NMR (470 MHz, CDCl_3) of **6** (β-anomer).



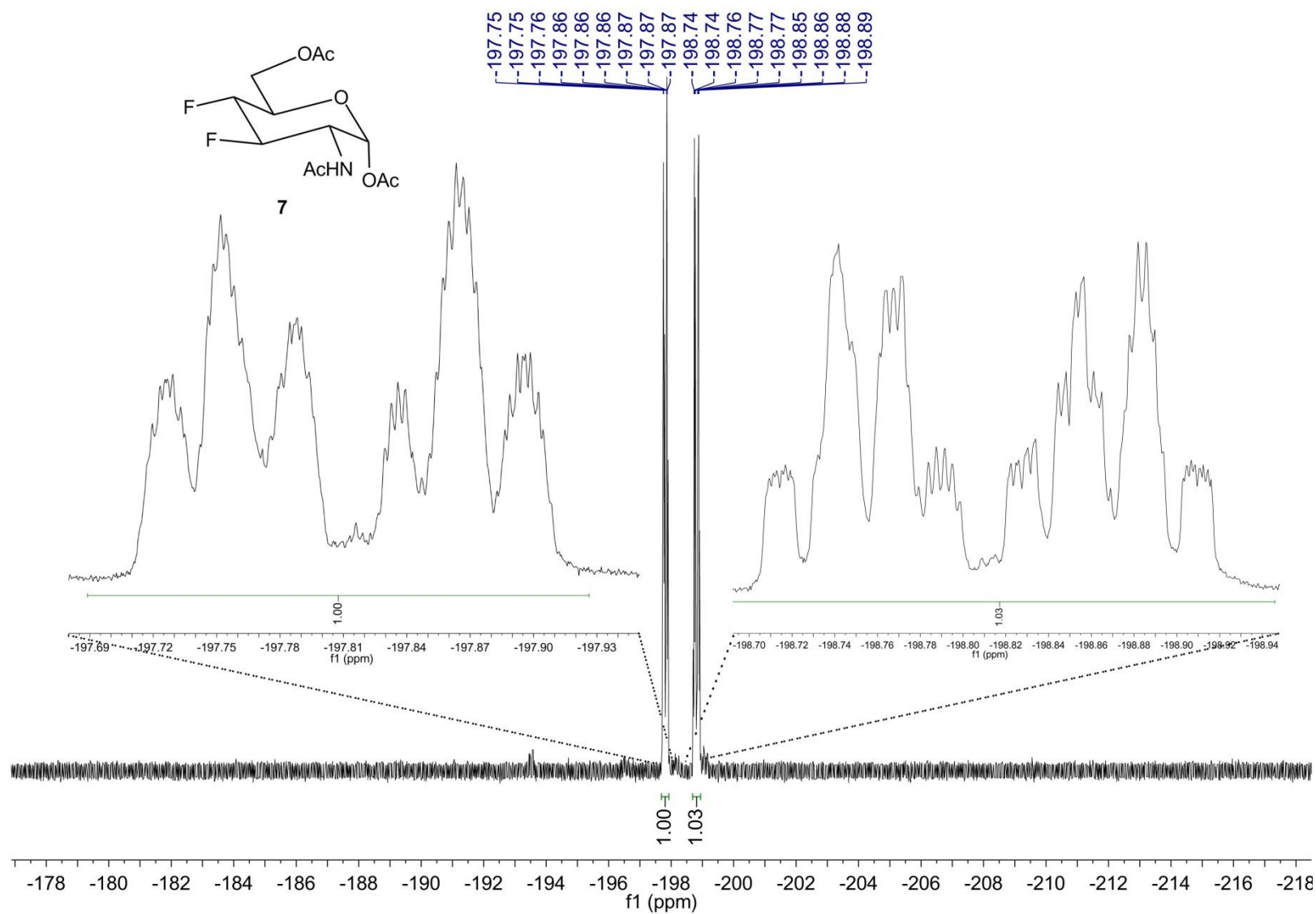
¹H NMR (500 MHz, CDCl₃) of 7 (α-anomer).



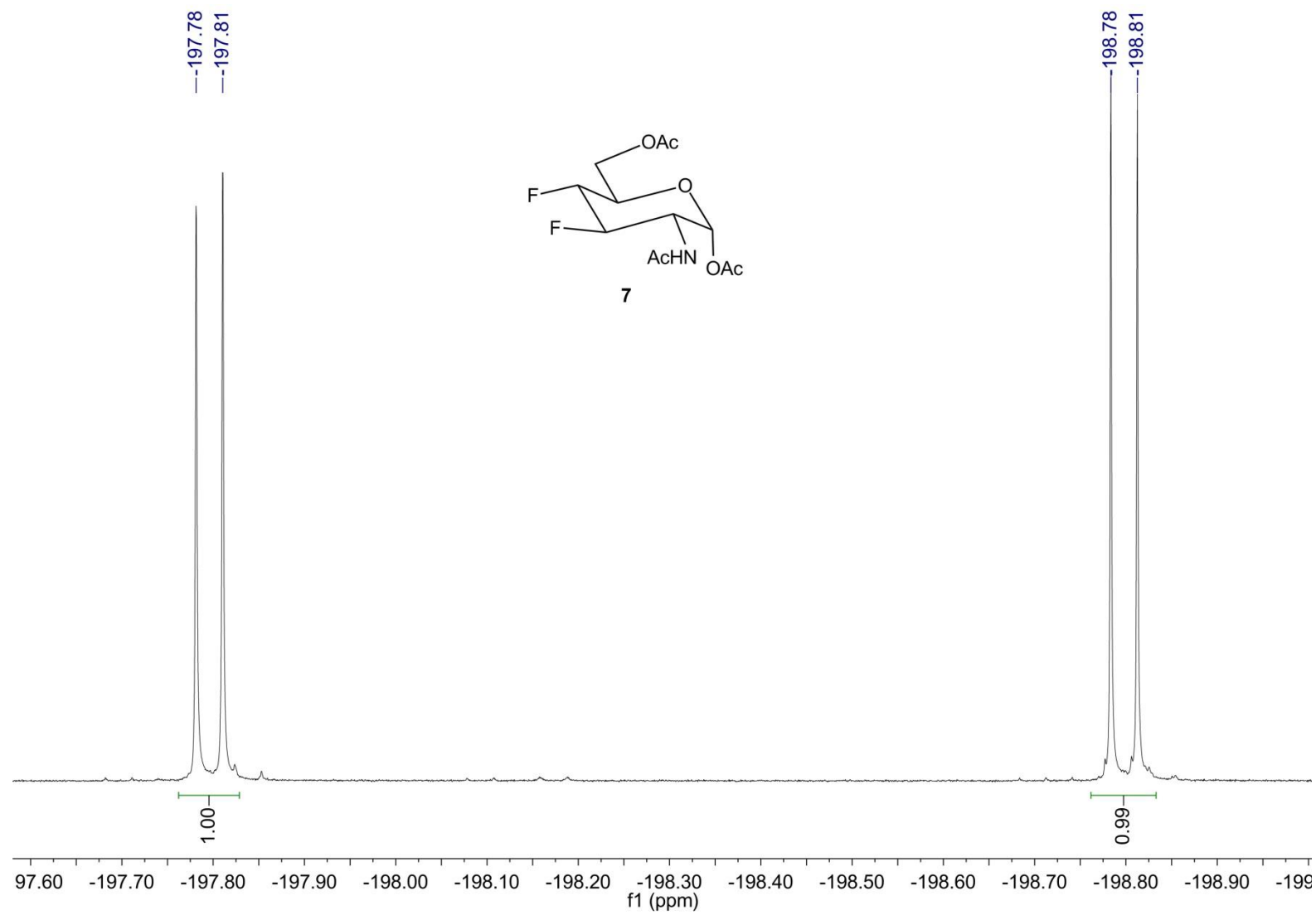
Detail of $^1\text{H} \{^{19}\text{F}\}$ NMR (500 MHz, CDCl_3) of **7** (α-anomer).



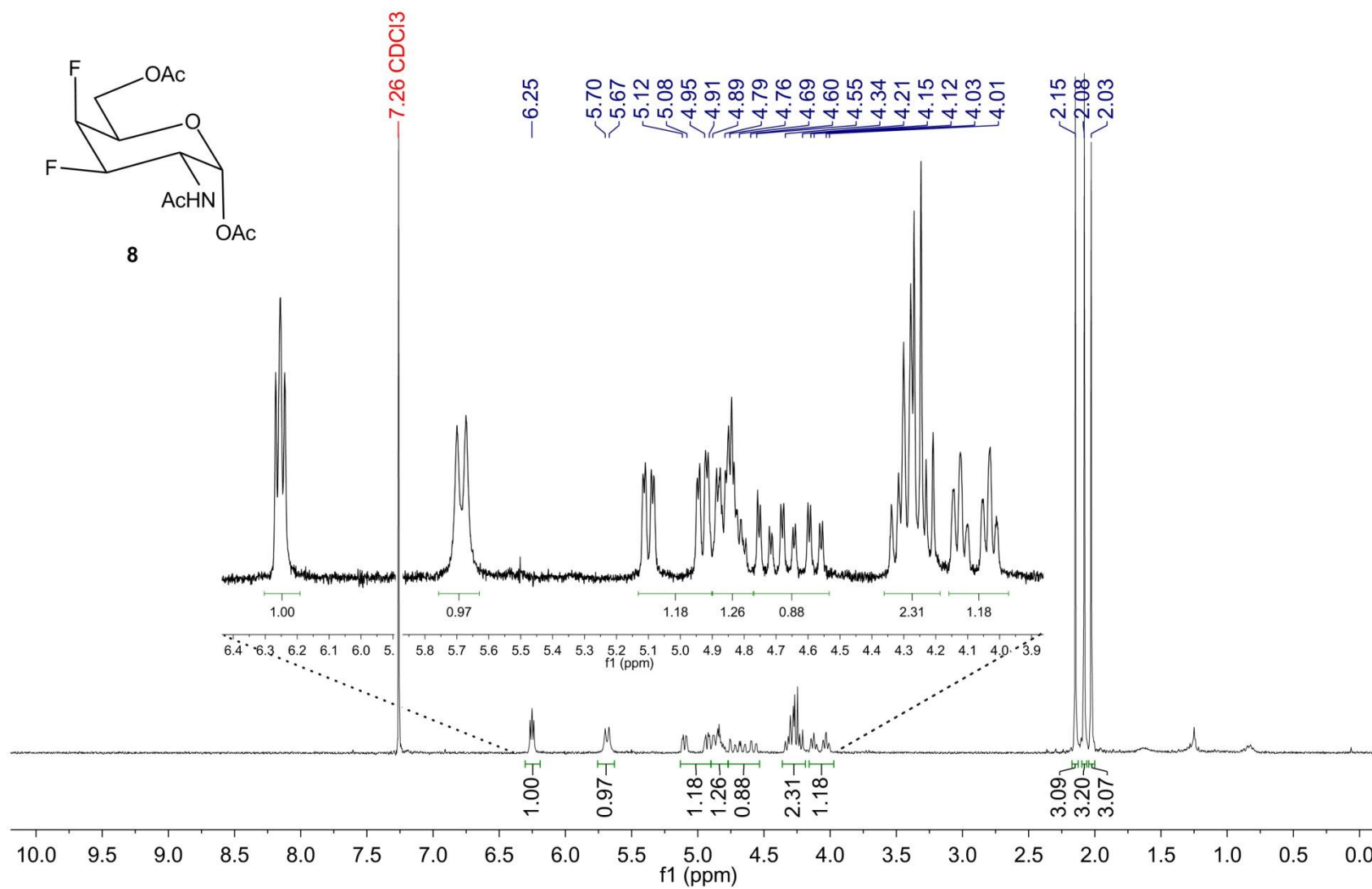
¹³C {¹H} NMR (125 MHz, CDCl₃) of **7** (α-anomer).



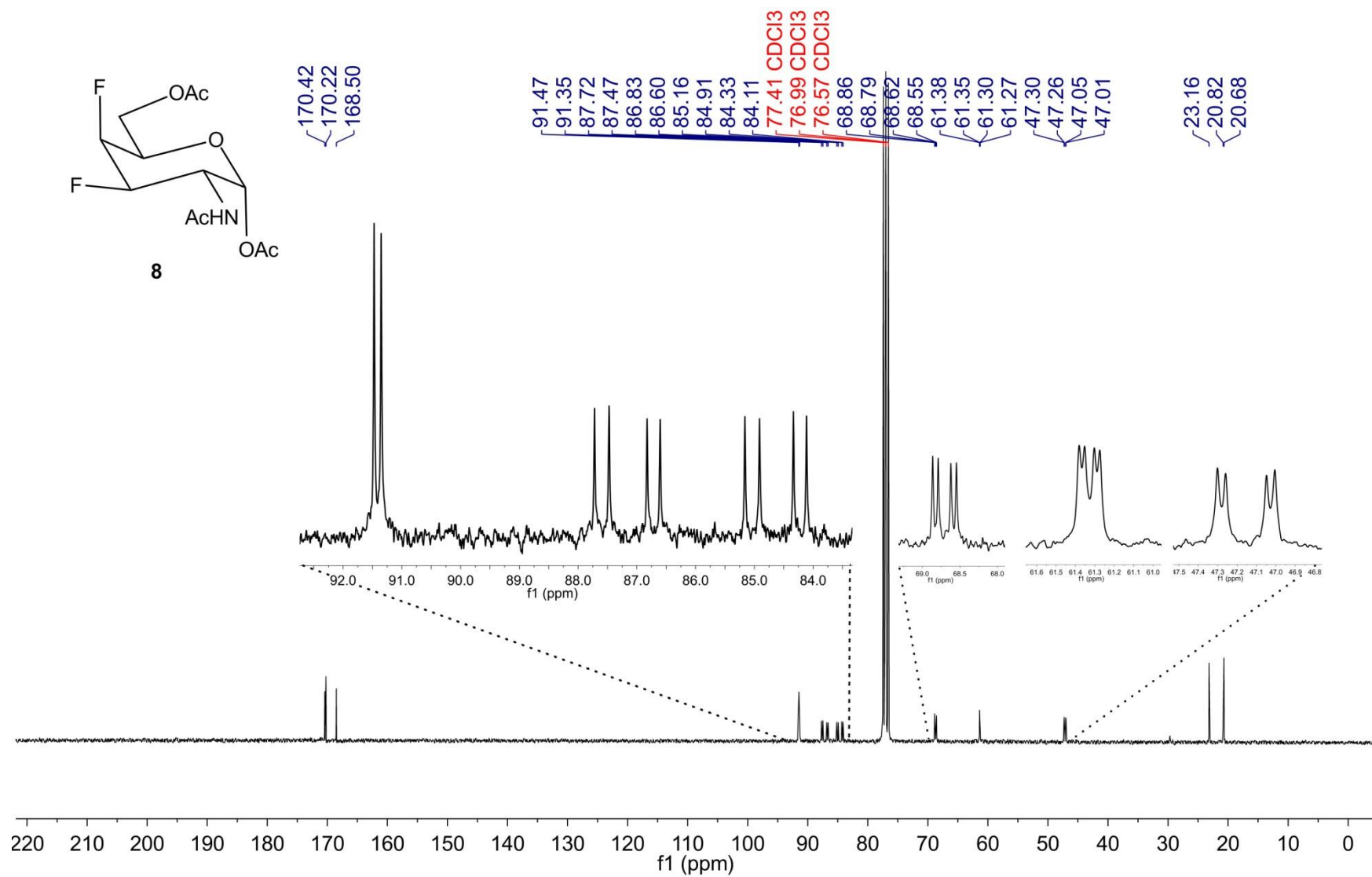
¹⁹F NMR (470 MHz, CDCl₃) of **7** (α-anomer).



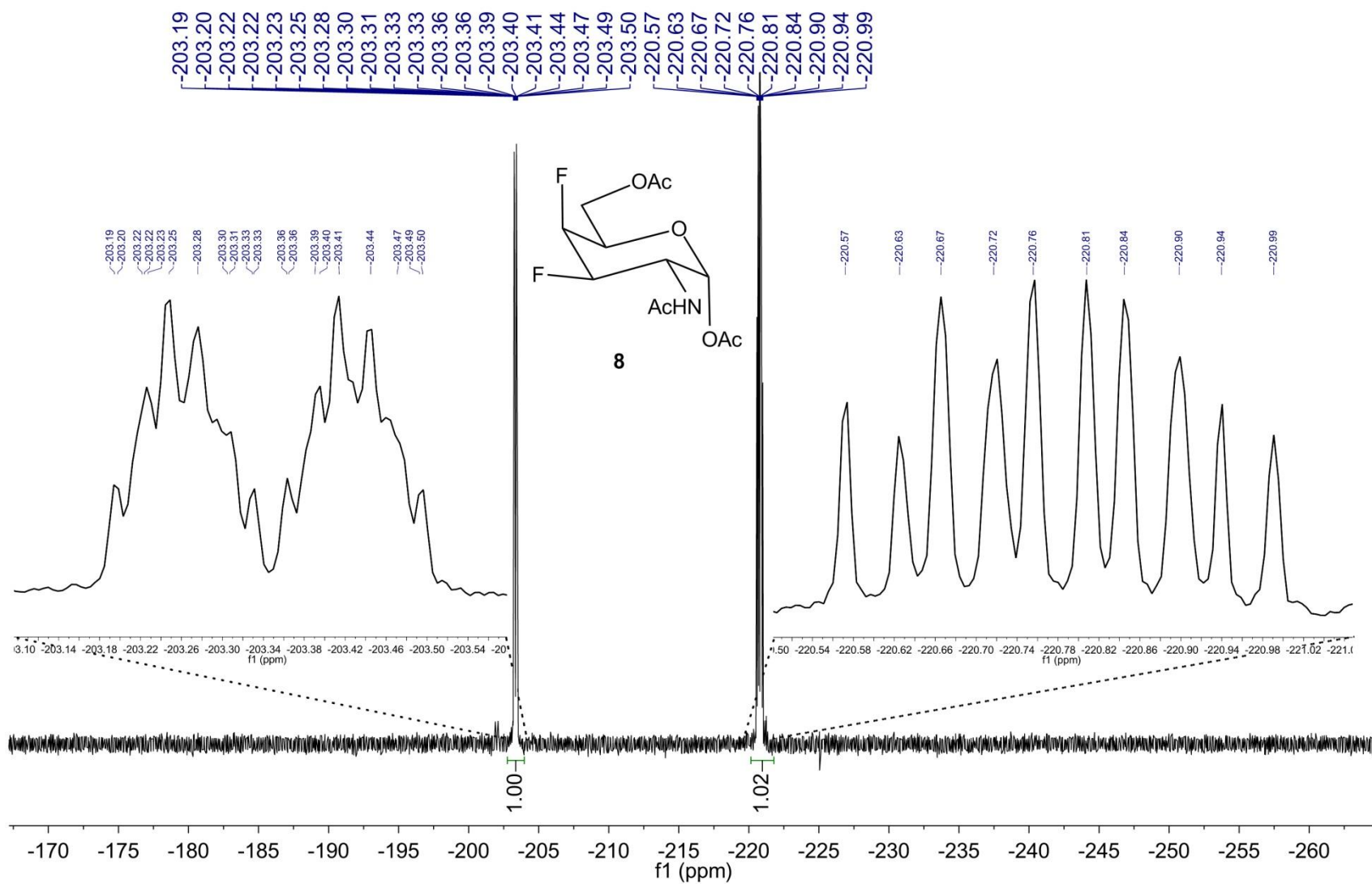
^{19}F { ^1H } NMR (470 MHz, CDCl_3) of **7** (α-anomer).



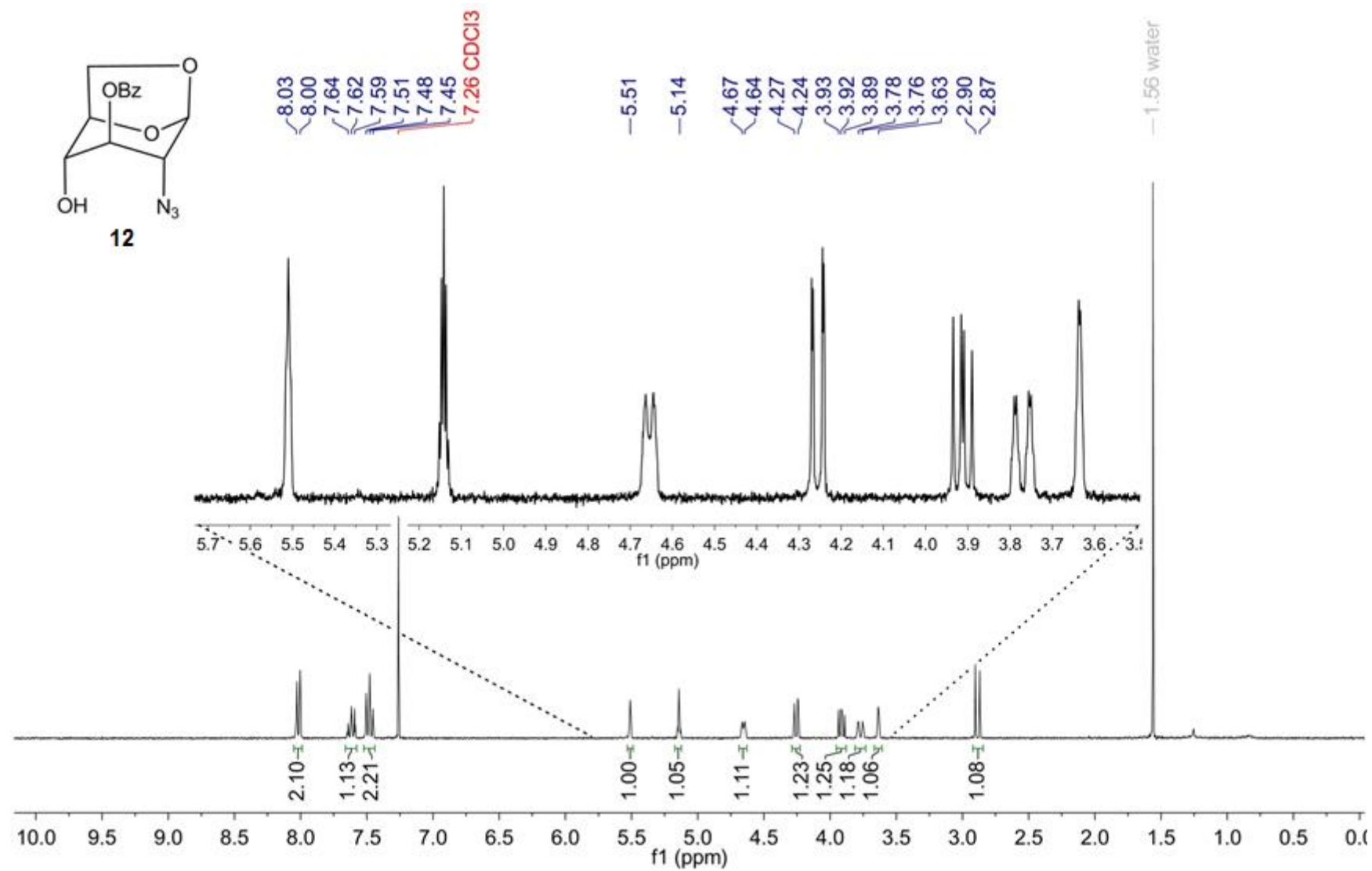
¹H NMR (300 MHz, CDCl₃) of **8** (α-anomer).



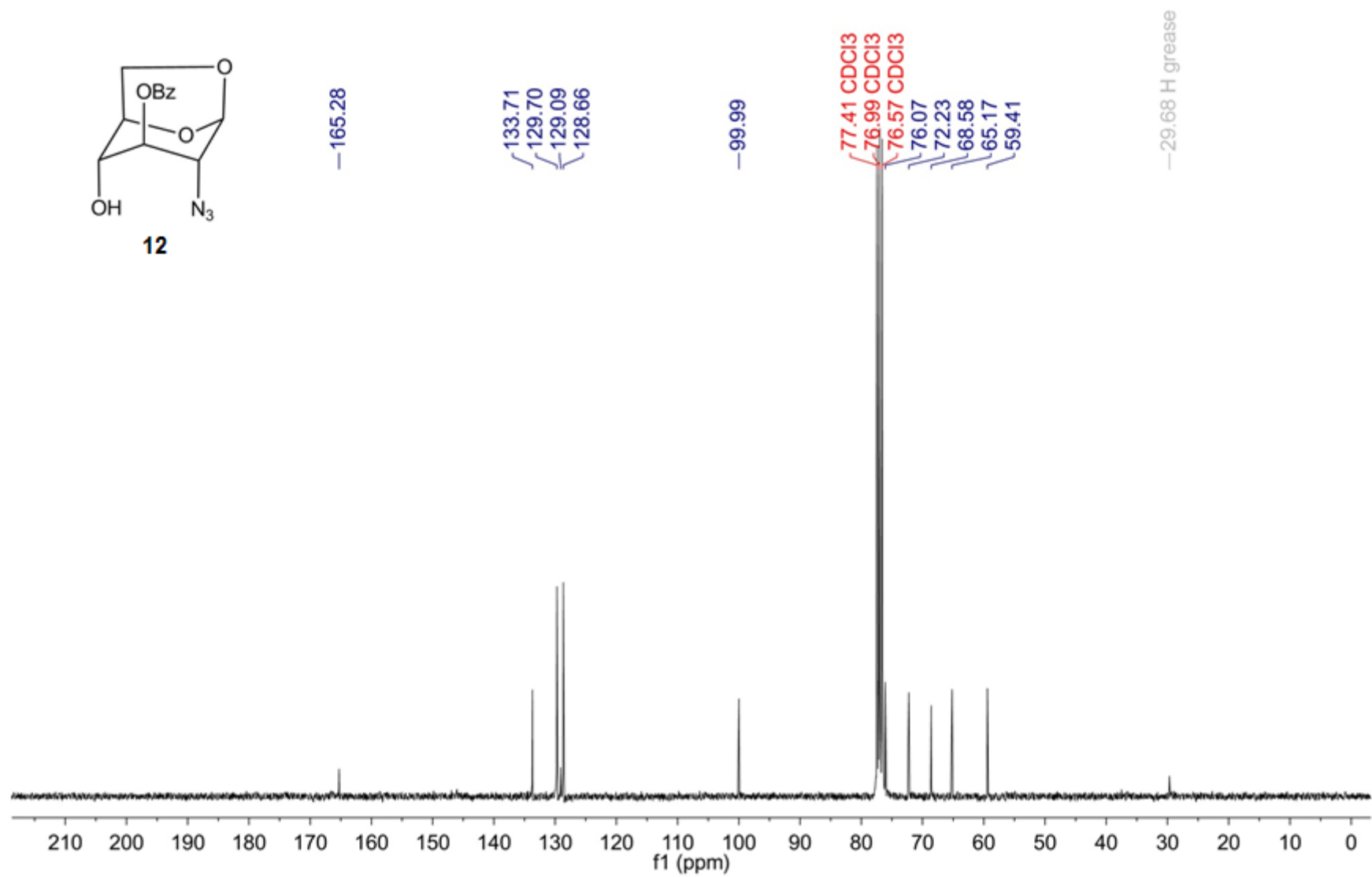
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **8** (α-anomer).



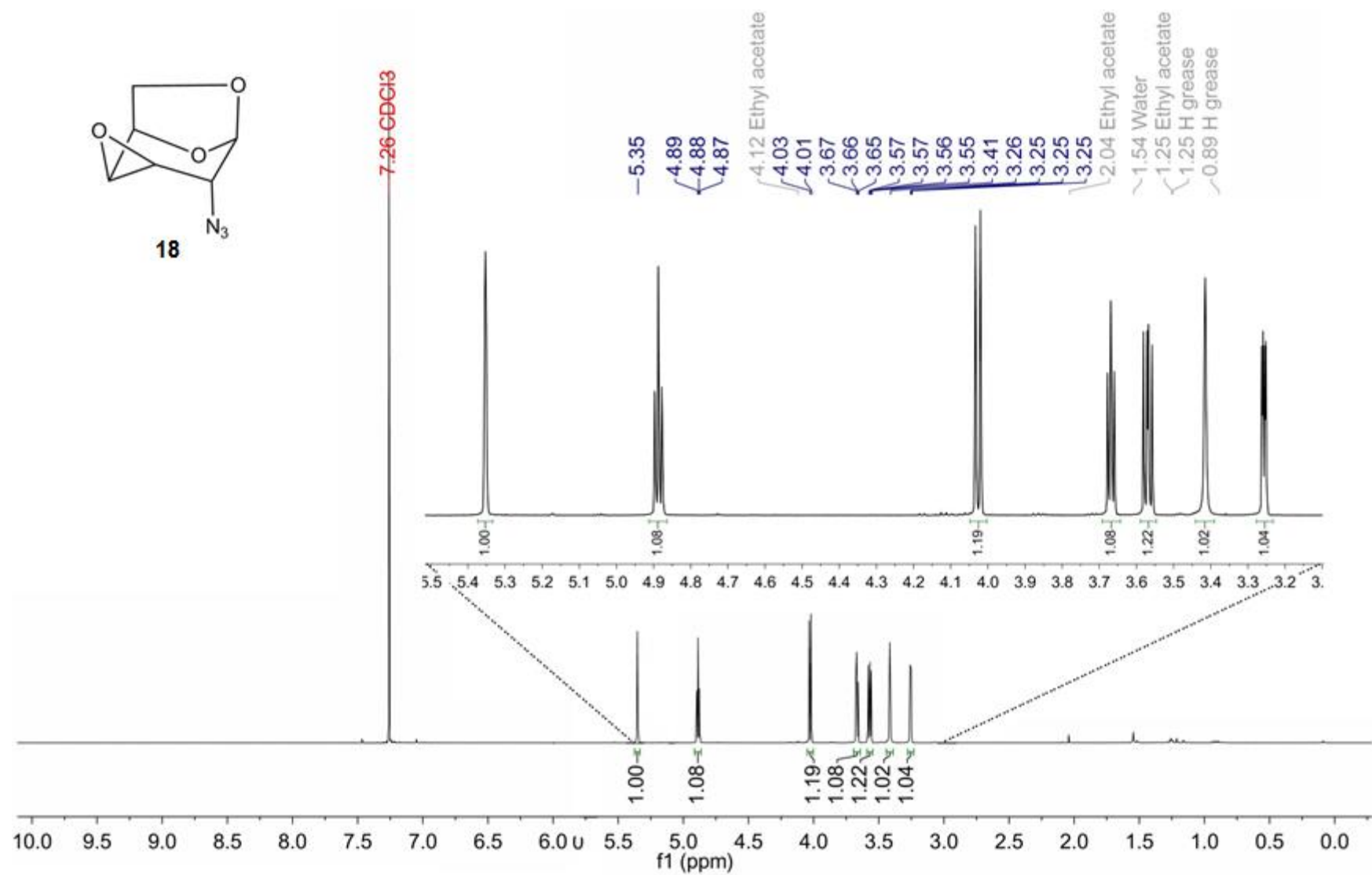
¹⁹F NMR (282 MHz, CDCl₃) of **8** (α-anomer)

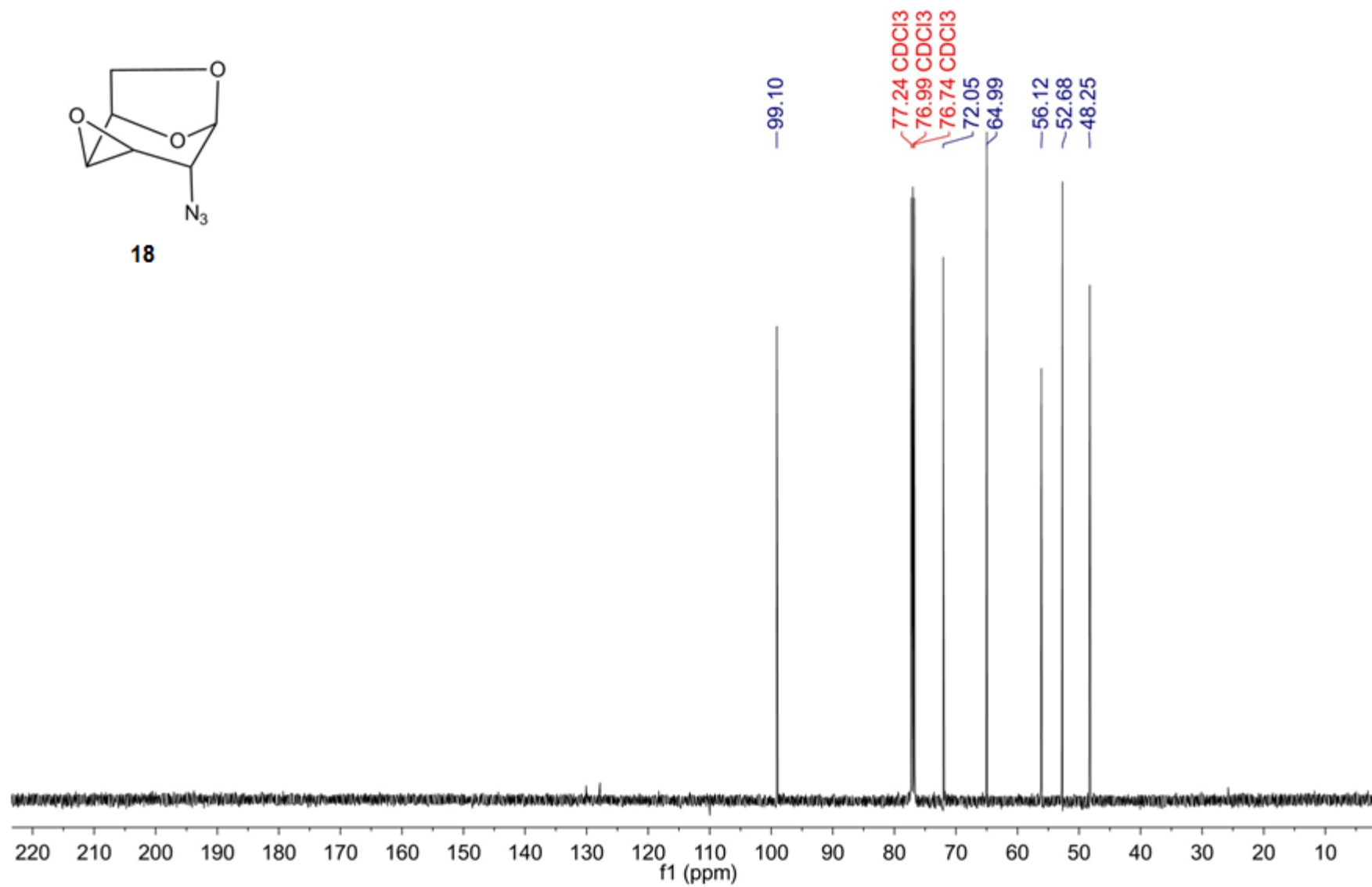
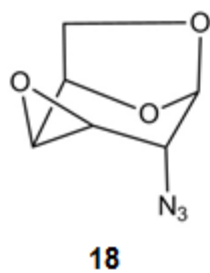


¹H NMR (500 MHz, CDCl₃) of **12**.

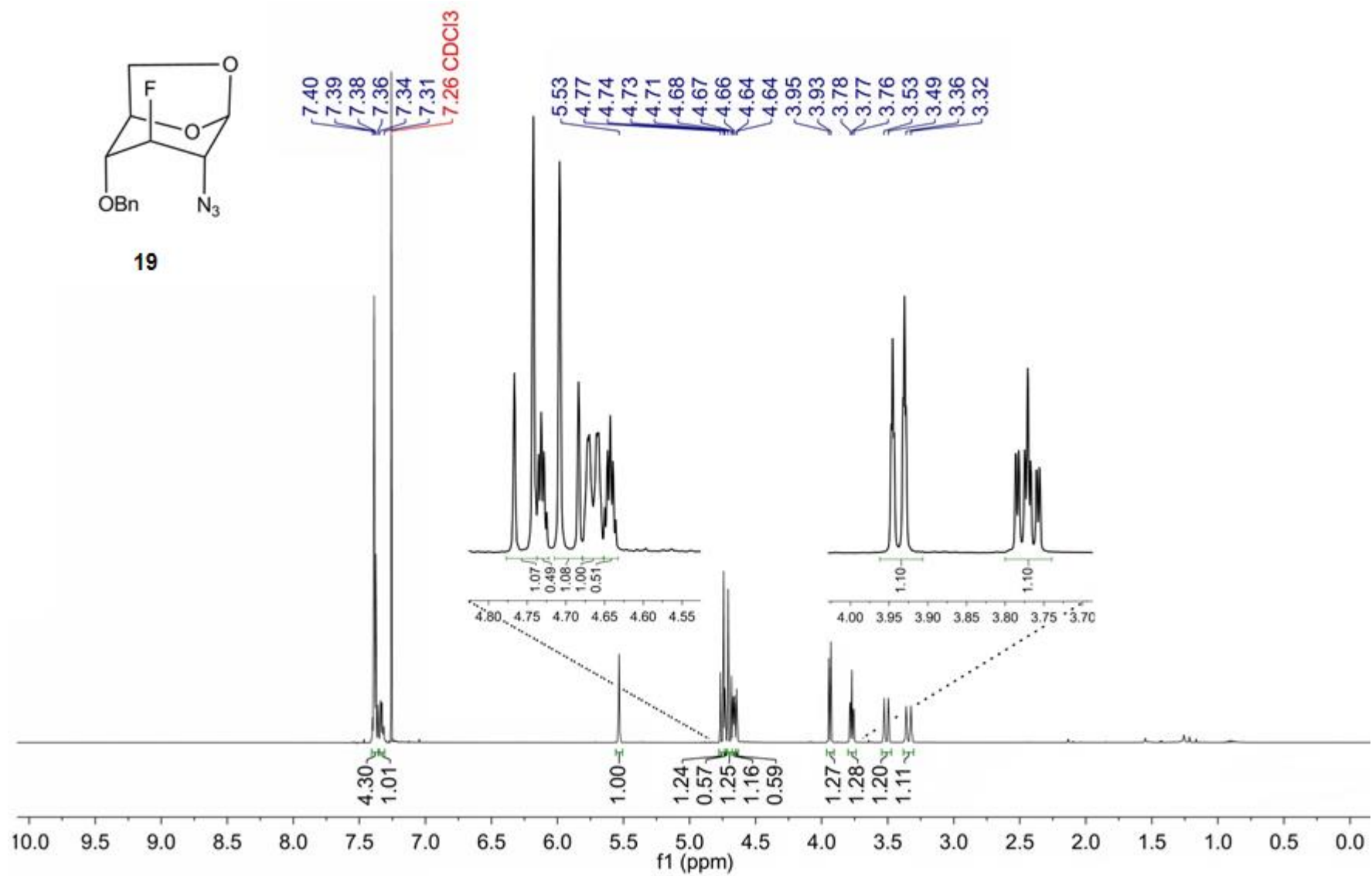


¹³C {¹H} NMR (125 MHz, CDCl₃) of **12**.

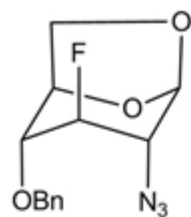




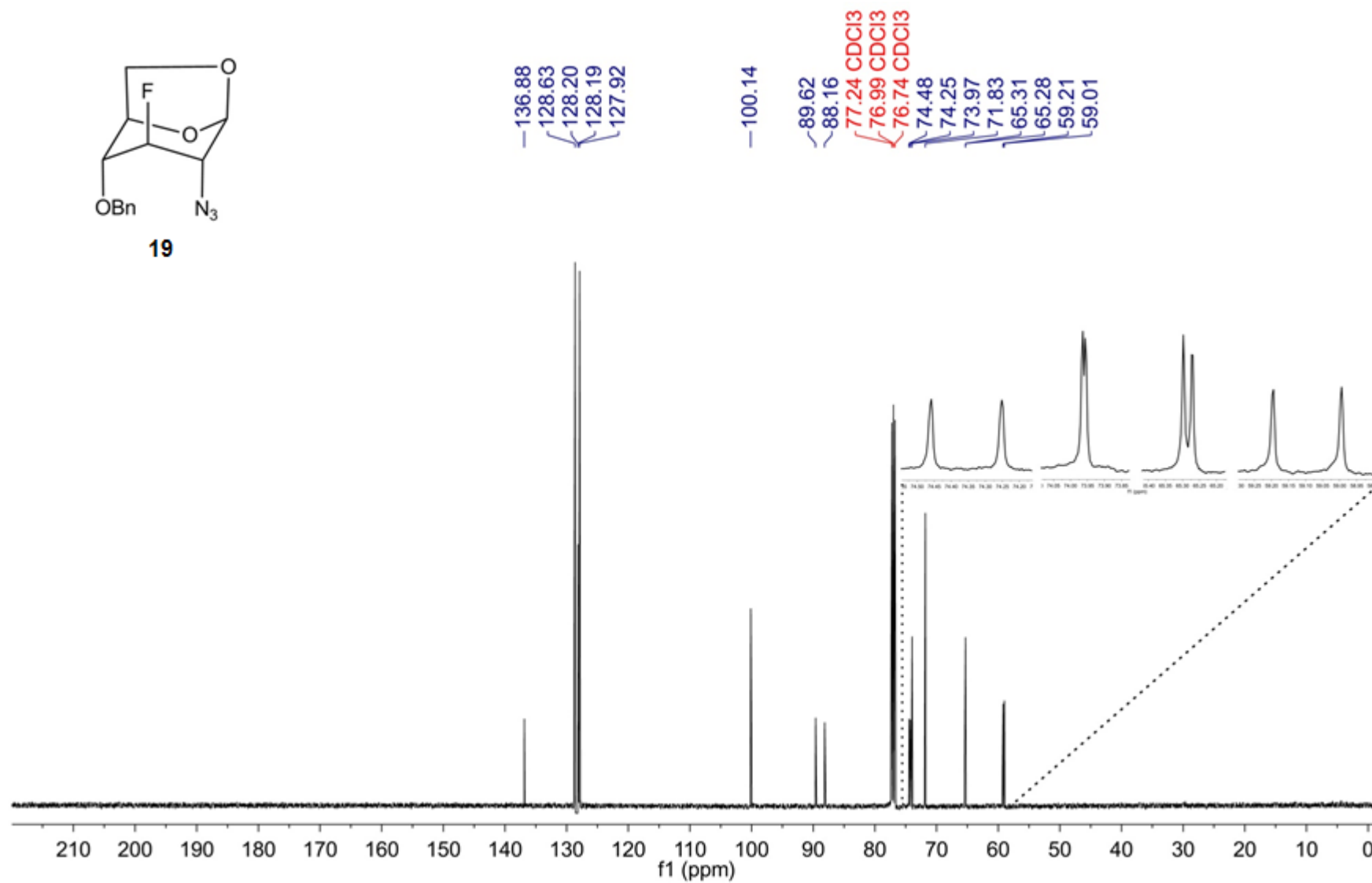
¹³C NMR (125 MHz, CDCl₃) of **18**.



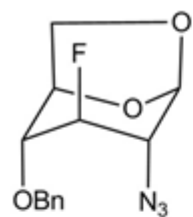
¹H NMR (500 MHz, CDCl₃) of **19**.



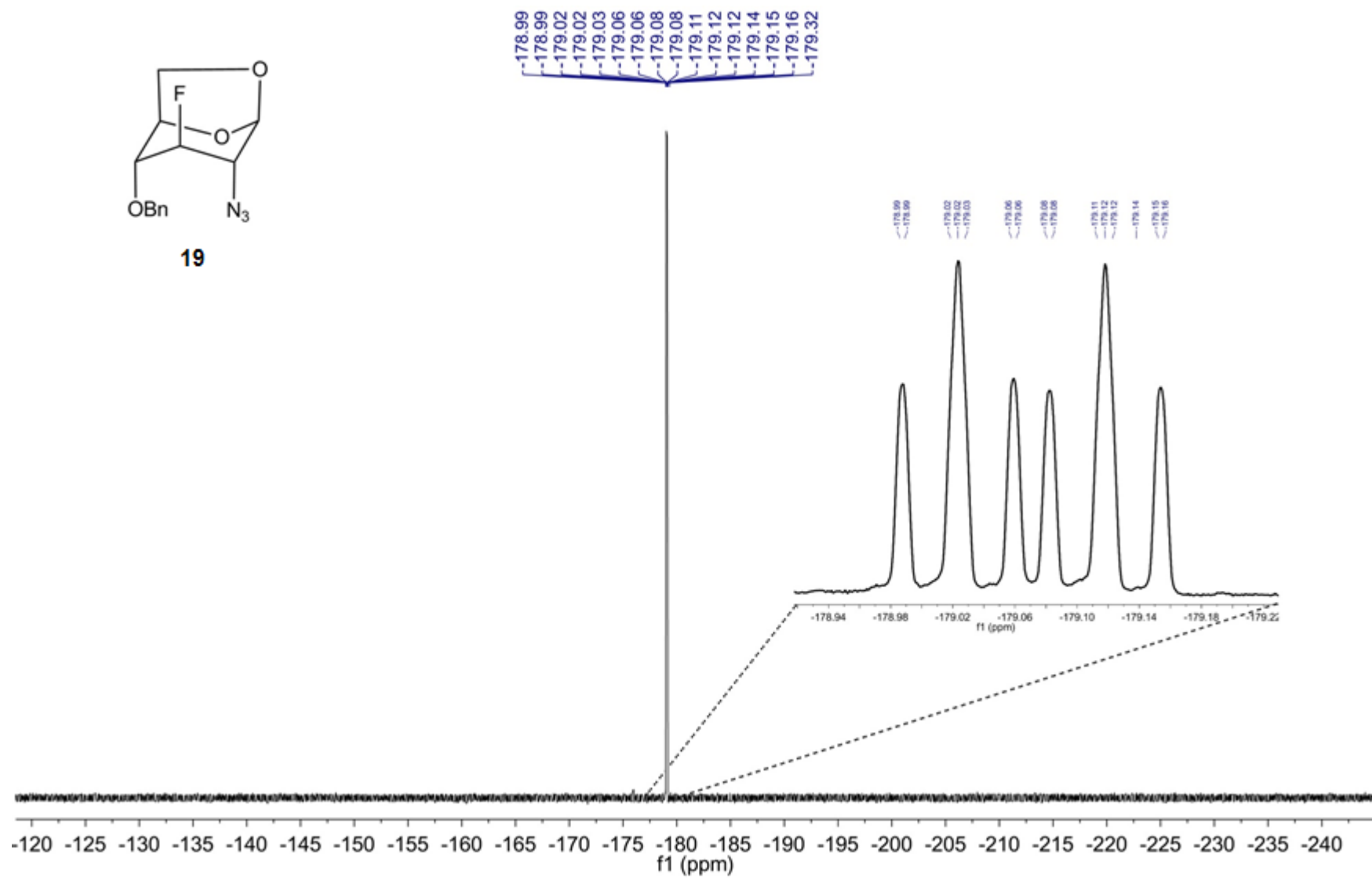
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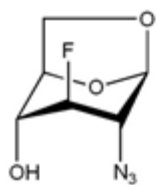
¹³C {¹H} NMR (125 MHz, CDCl₃) of **19**



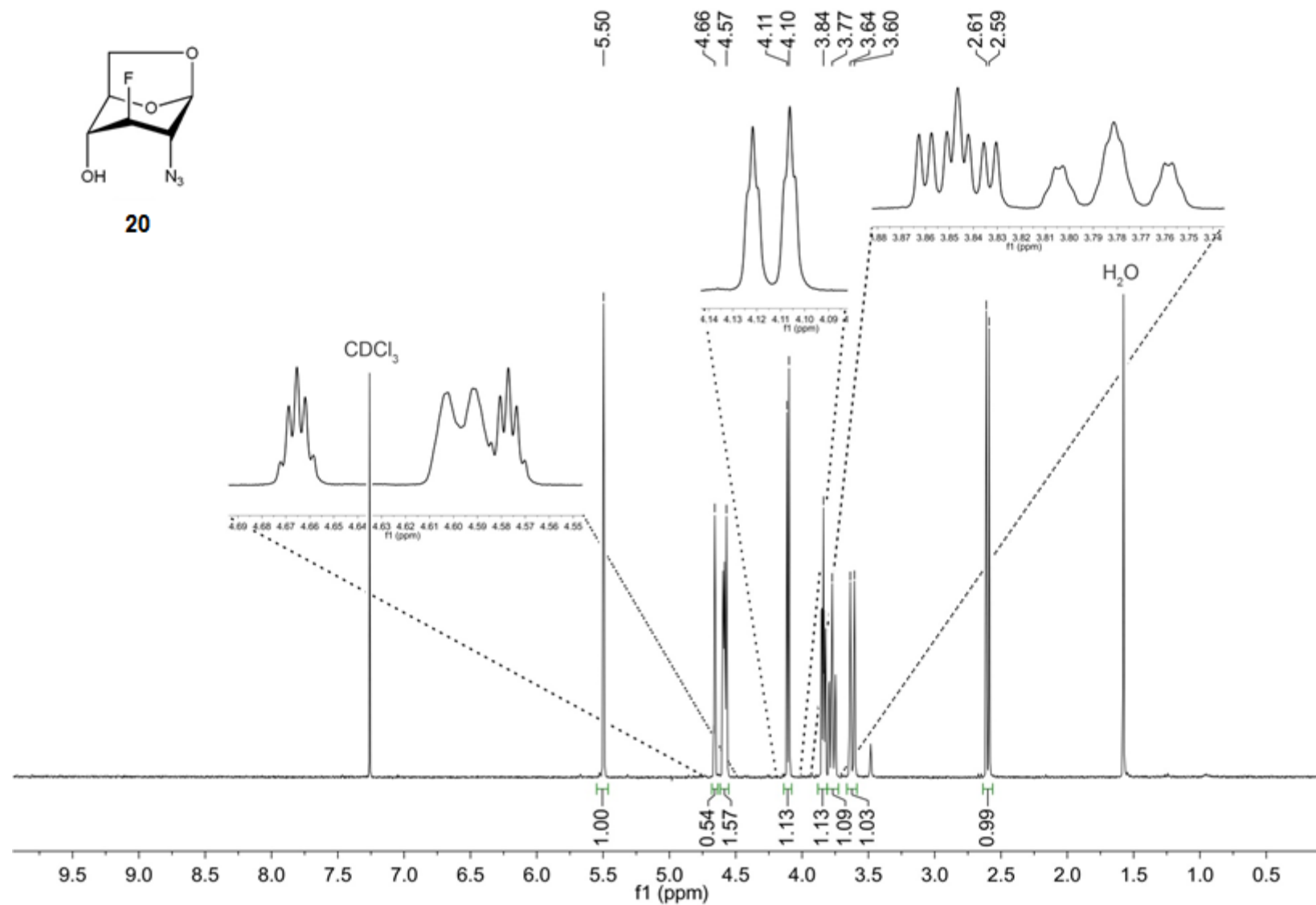
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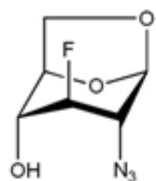
¹⁹F NMR (470 MHz, CDCl₃) of **19**



20

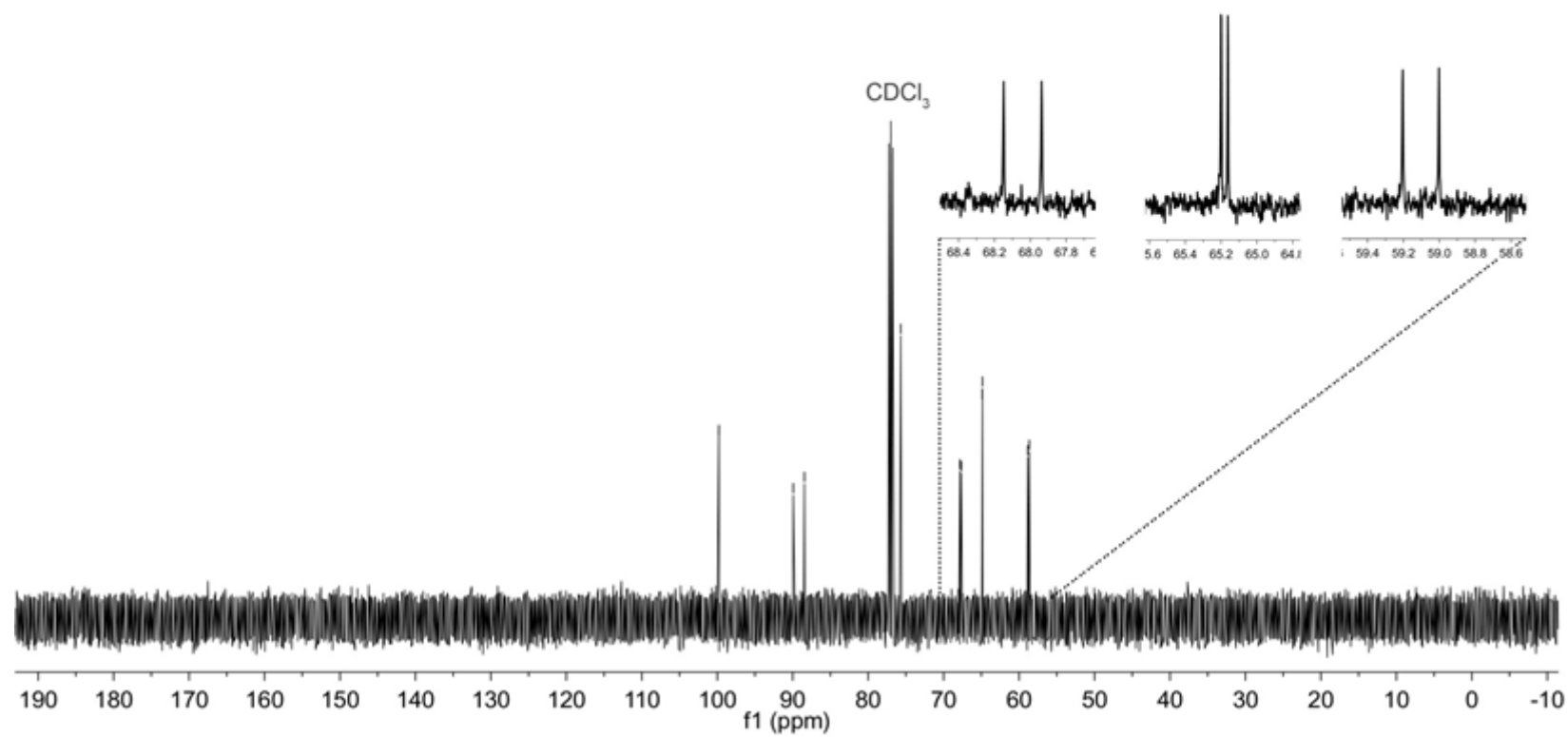


¹H NMR (300 MHz, CDCl₃) of **20**

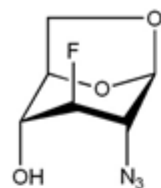


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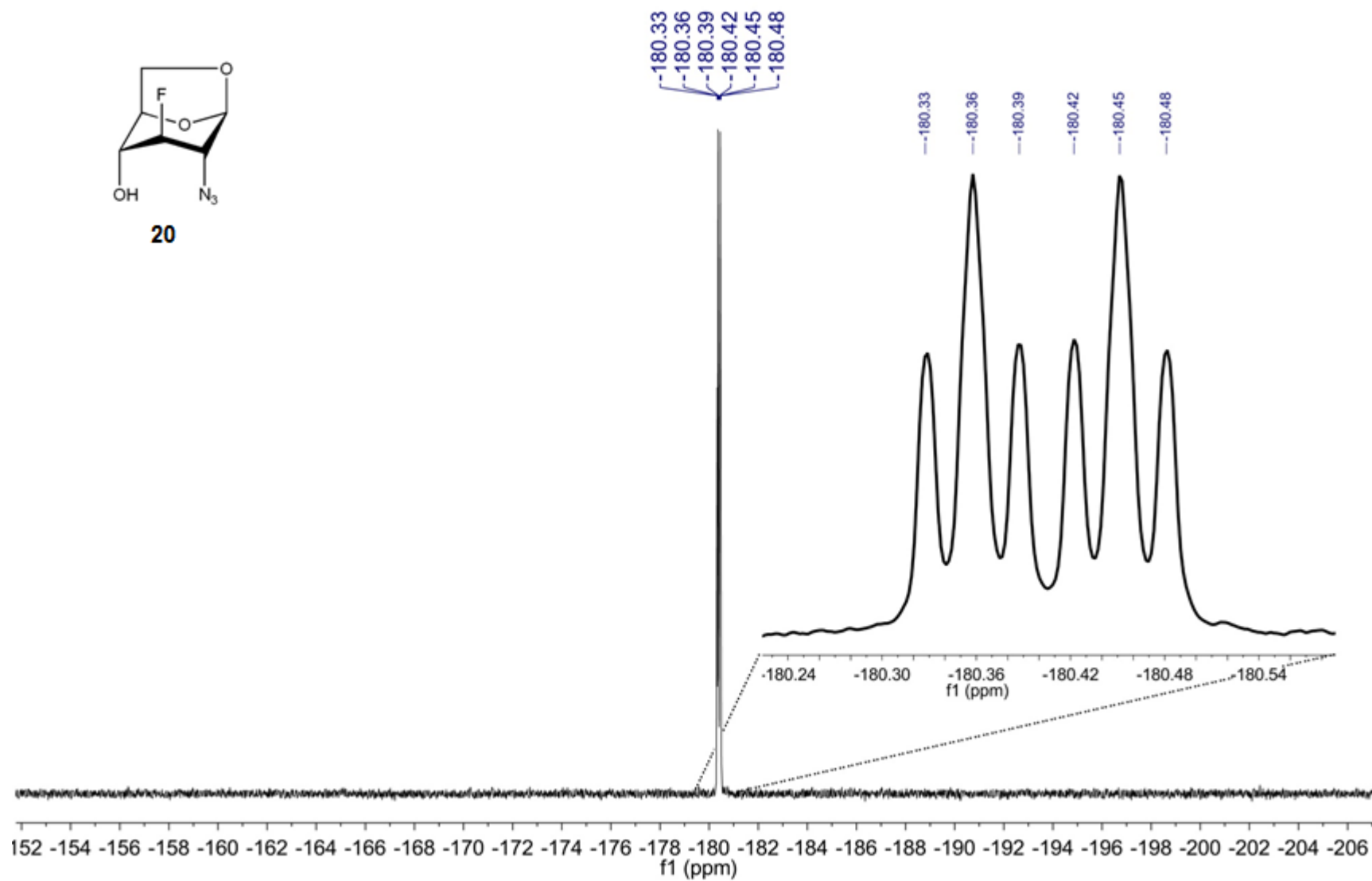
— 99.78
 ~ 89.93
 ~ 88.45
 — 75.69
 ~ 67.64
 — 64.85
 ~ 58.86
 ~ 58.65



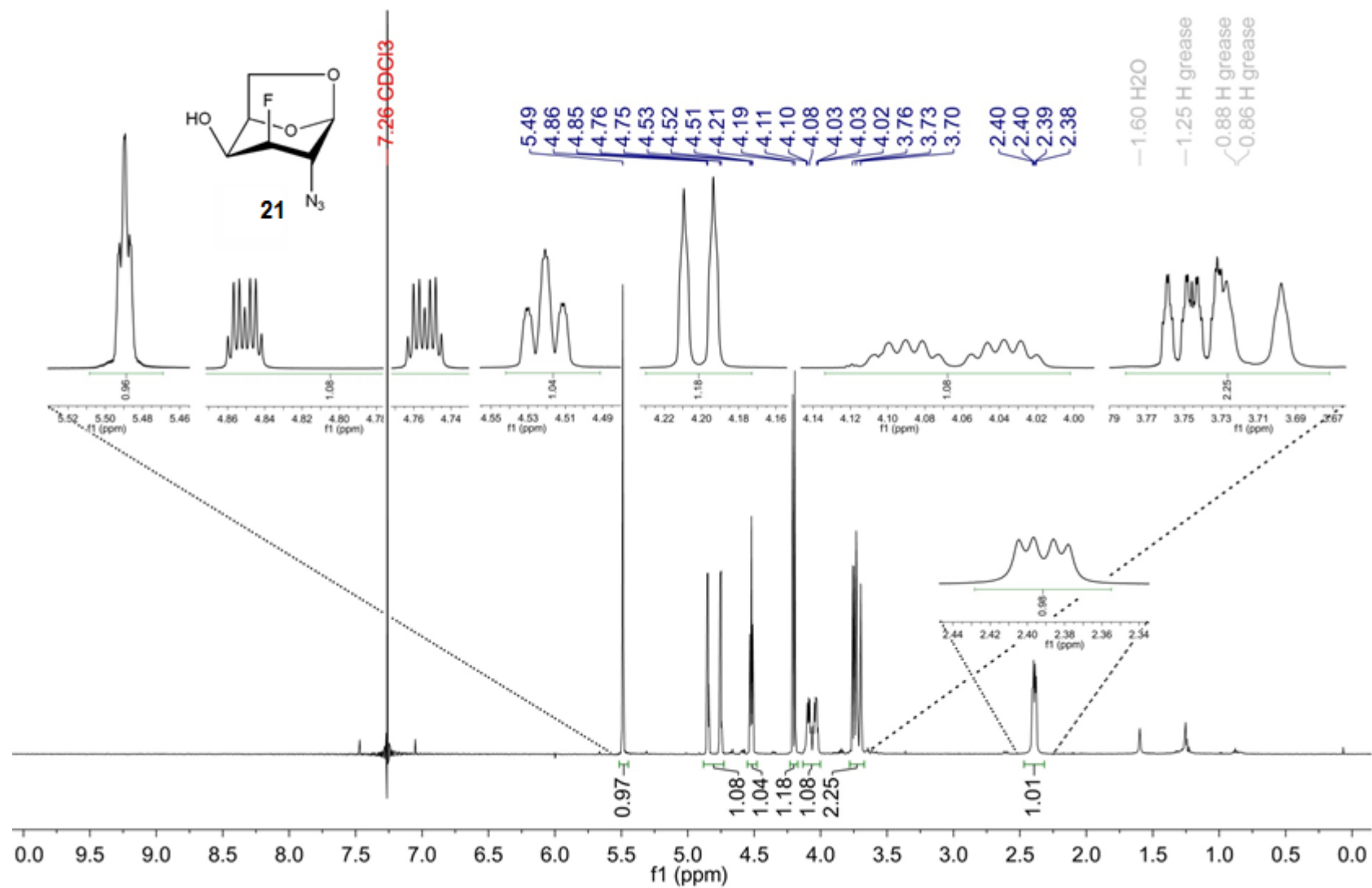
$^{13}\text{C} \{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **20**



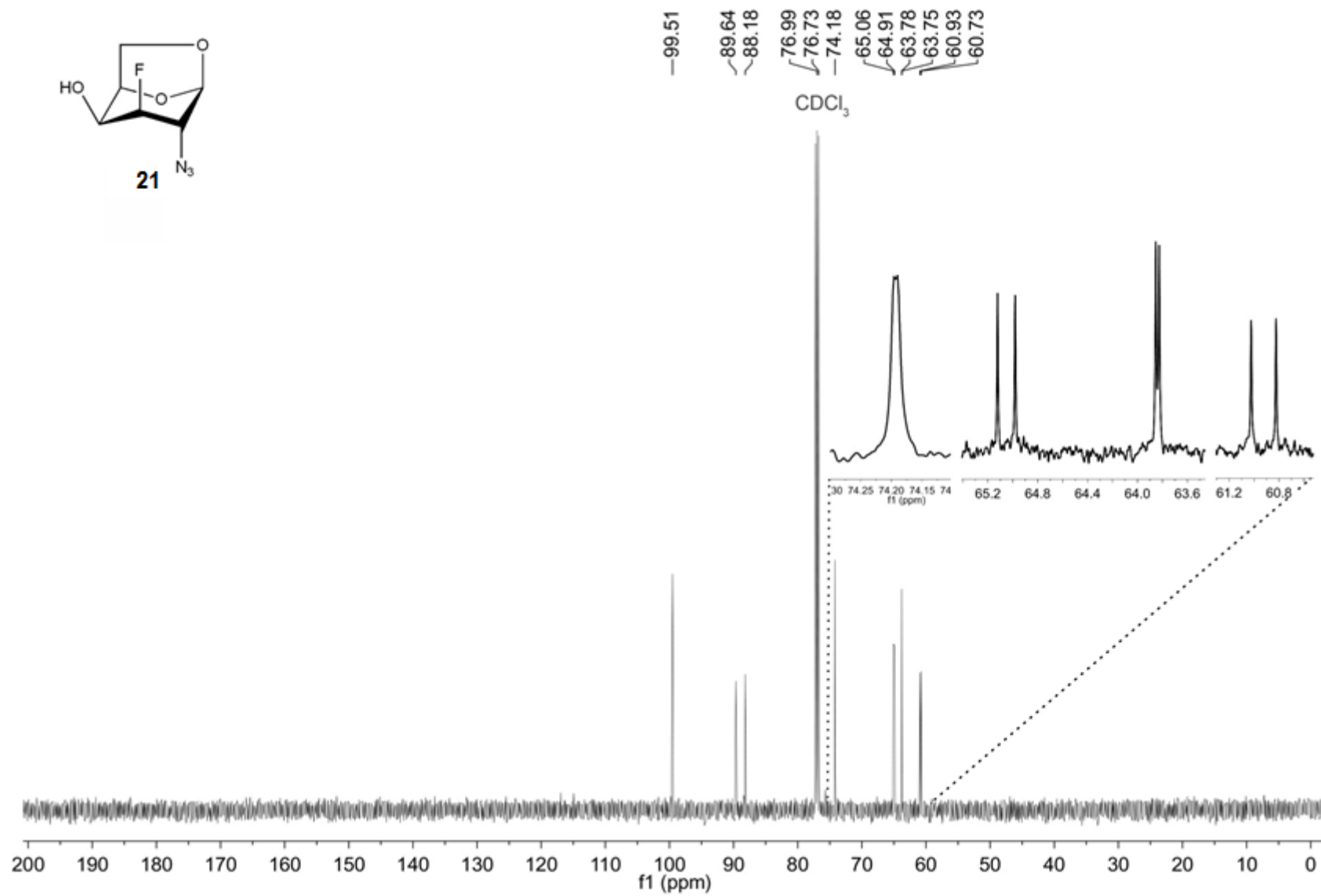
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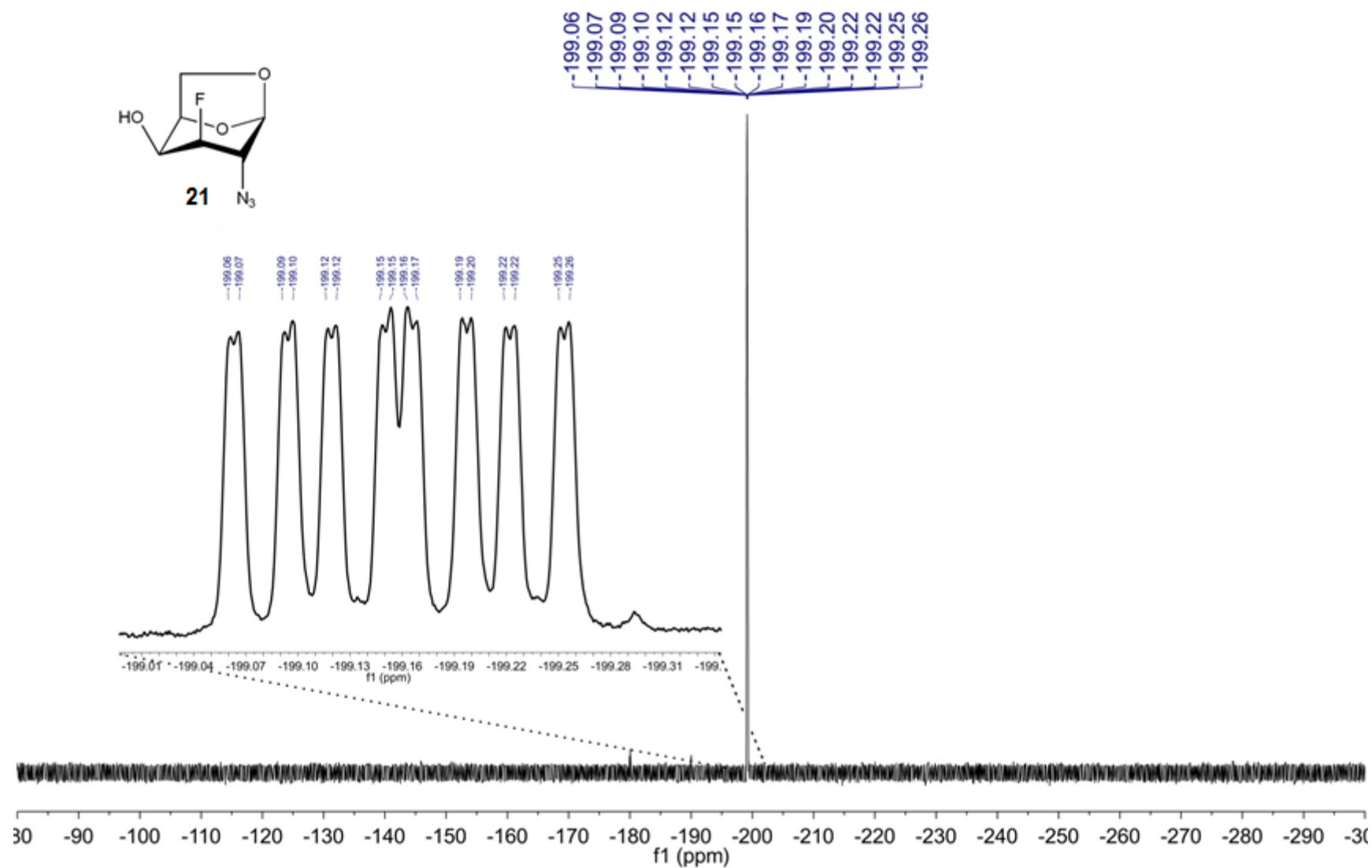
¹⁹F NMR (282 MHz, CDCl₃) of **20**



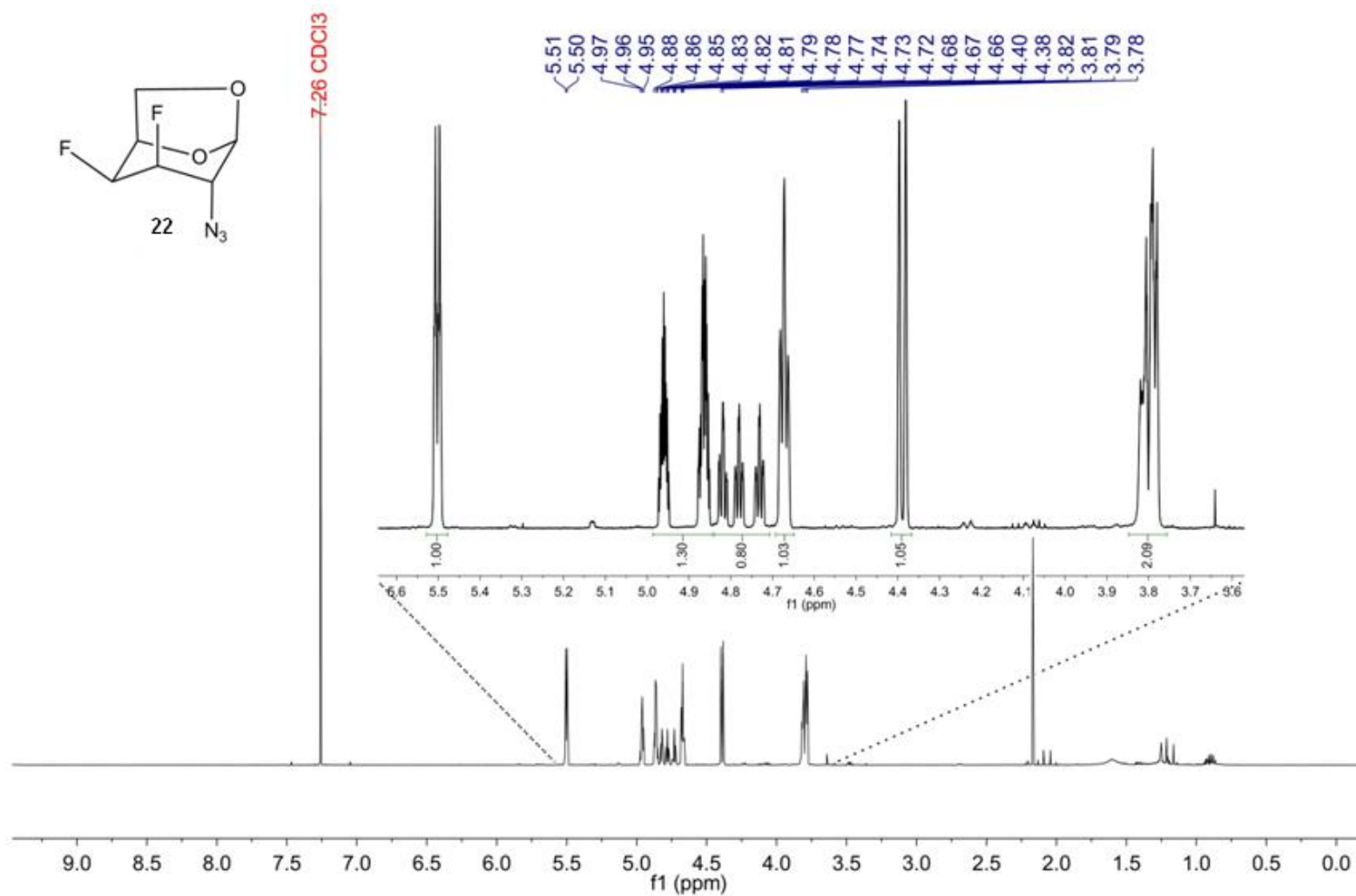
^1H NMR (300 MHz, CDCl_3) of **21**.



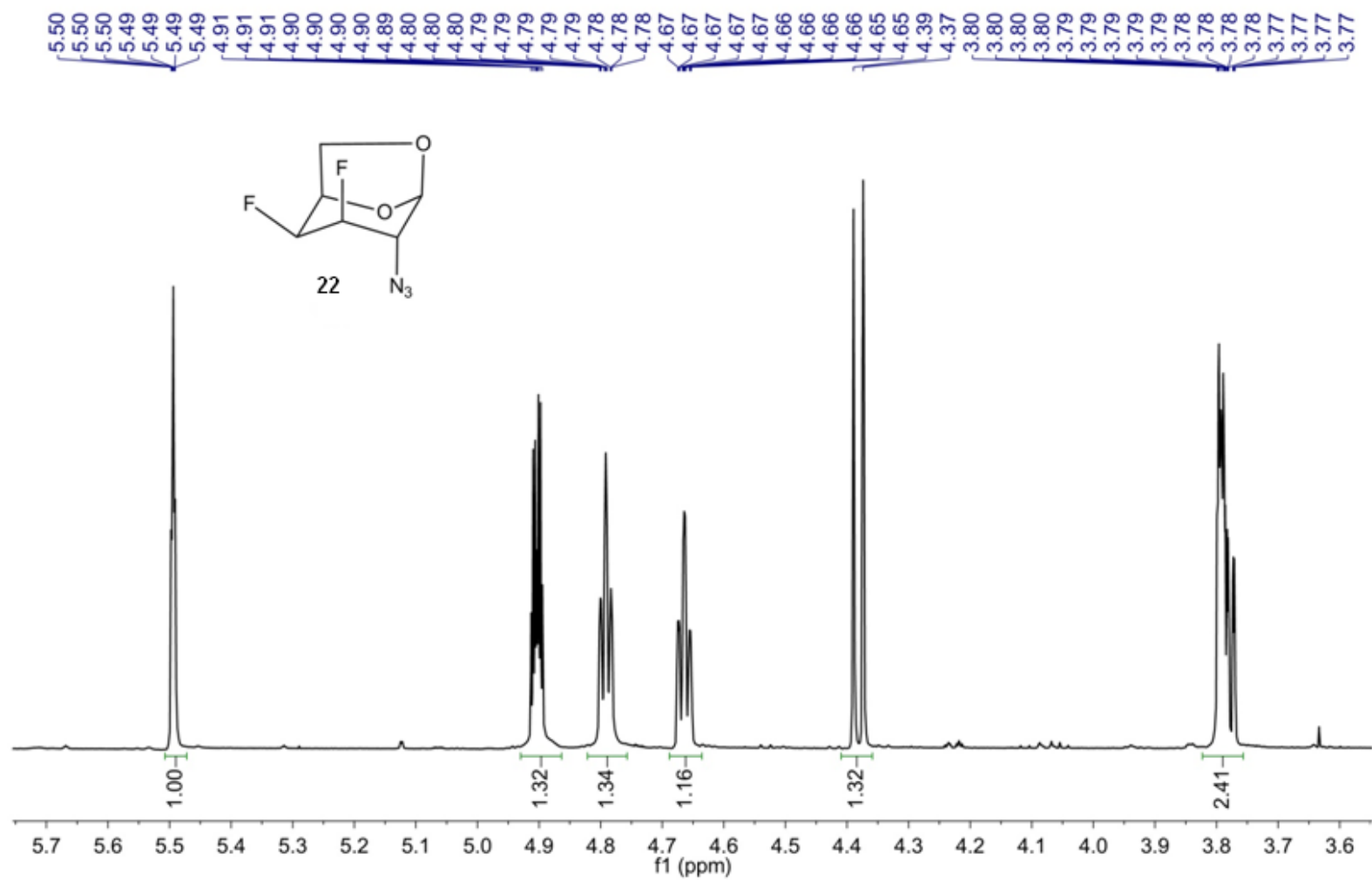
¹³C {¹H} NMR (75 MHz, CDCl₃) of **21**



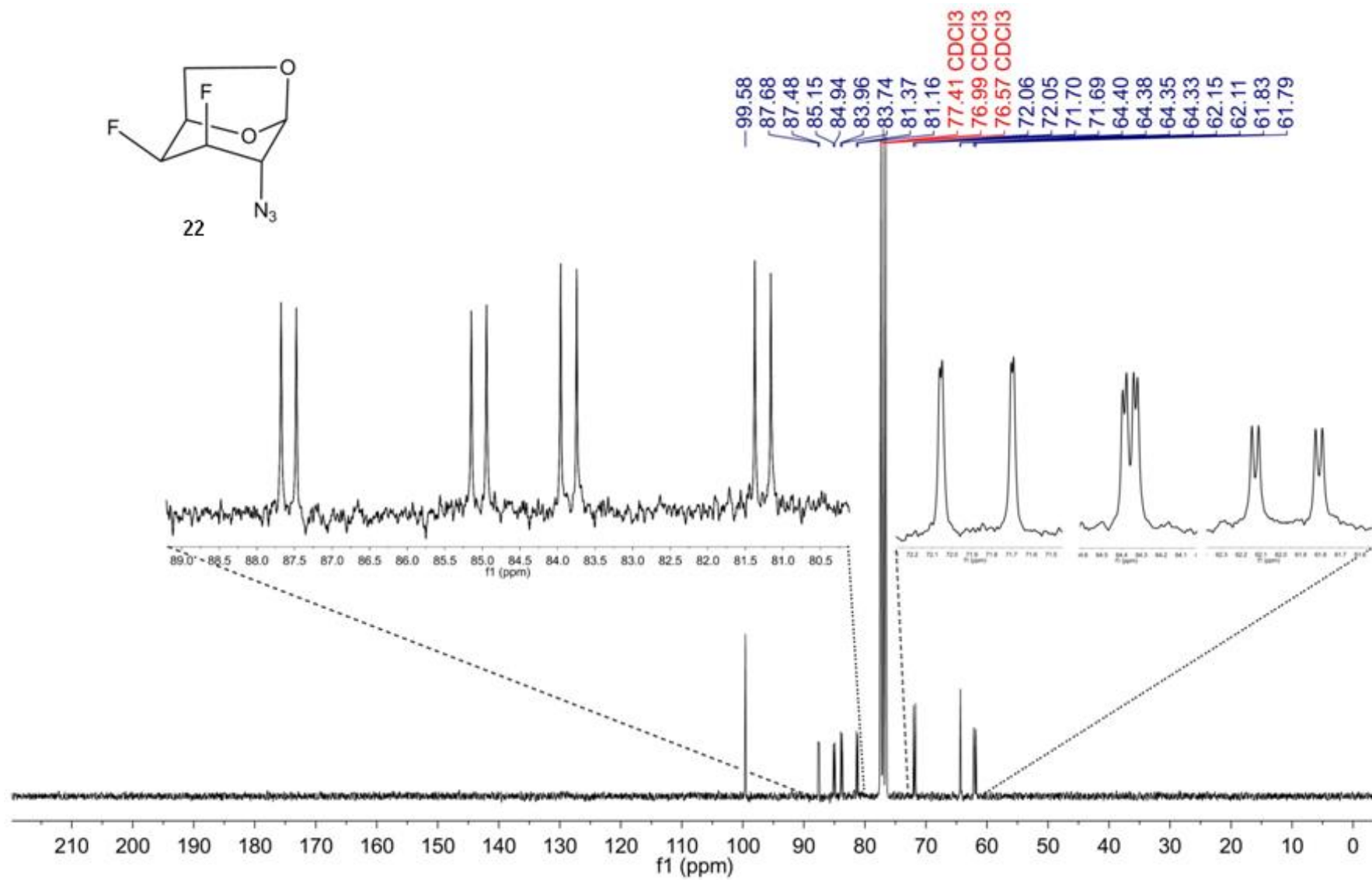
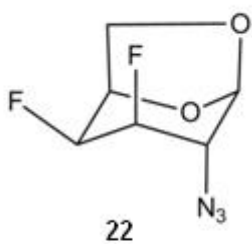
^{19}F NMR (282 MHz, CDCl_3) of **21**



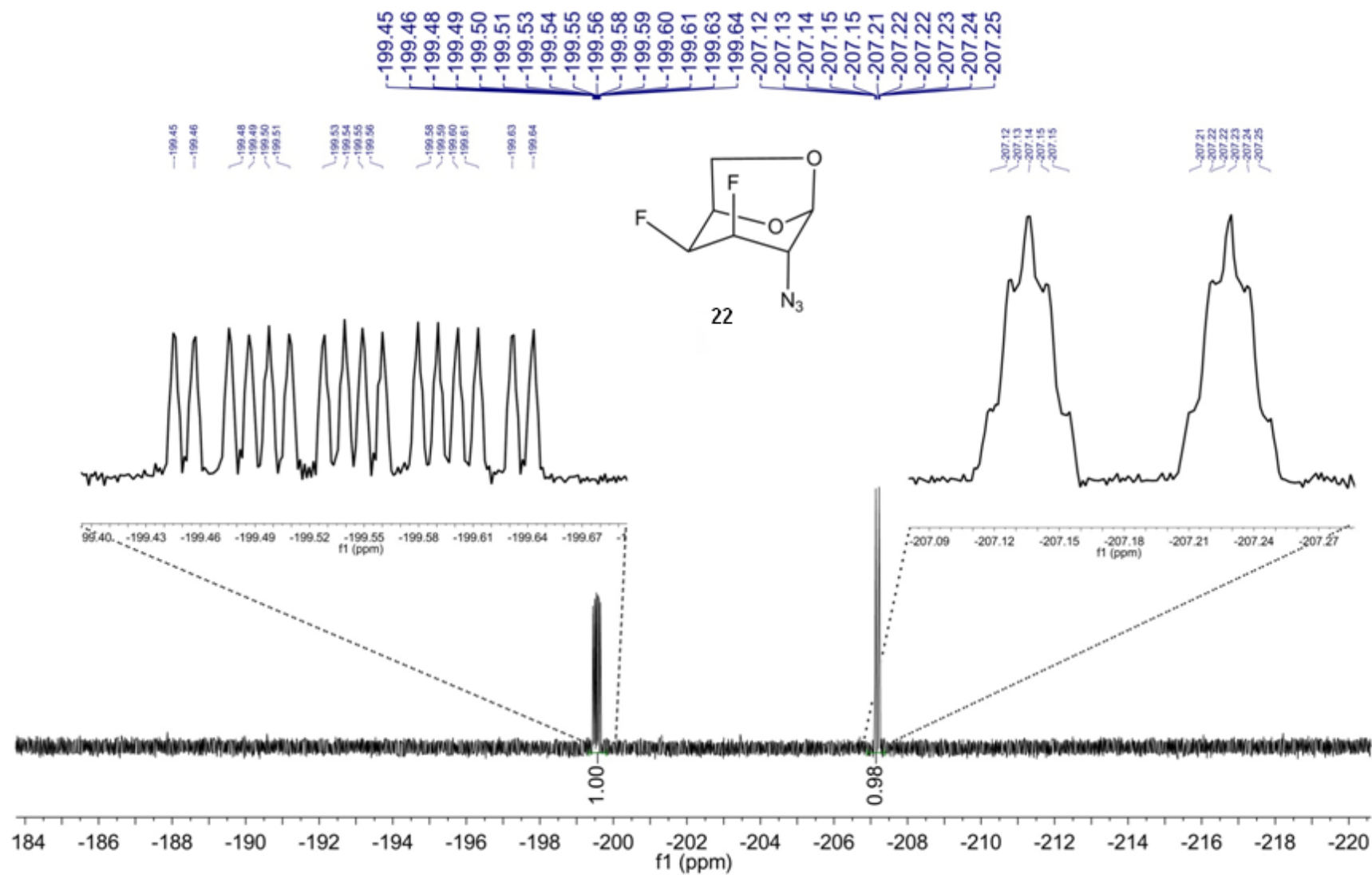
¹H NMR (500 MHz, CDCl₃) of 22



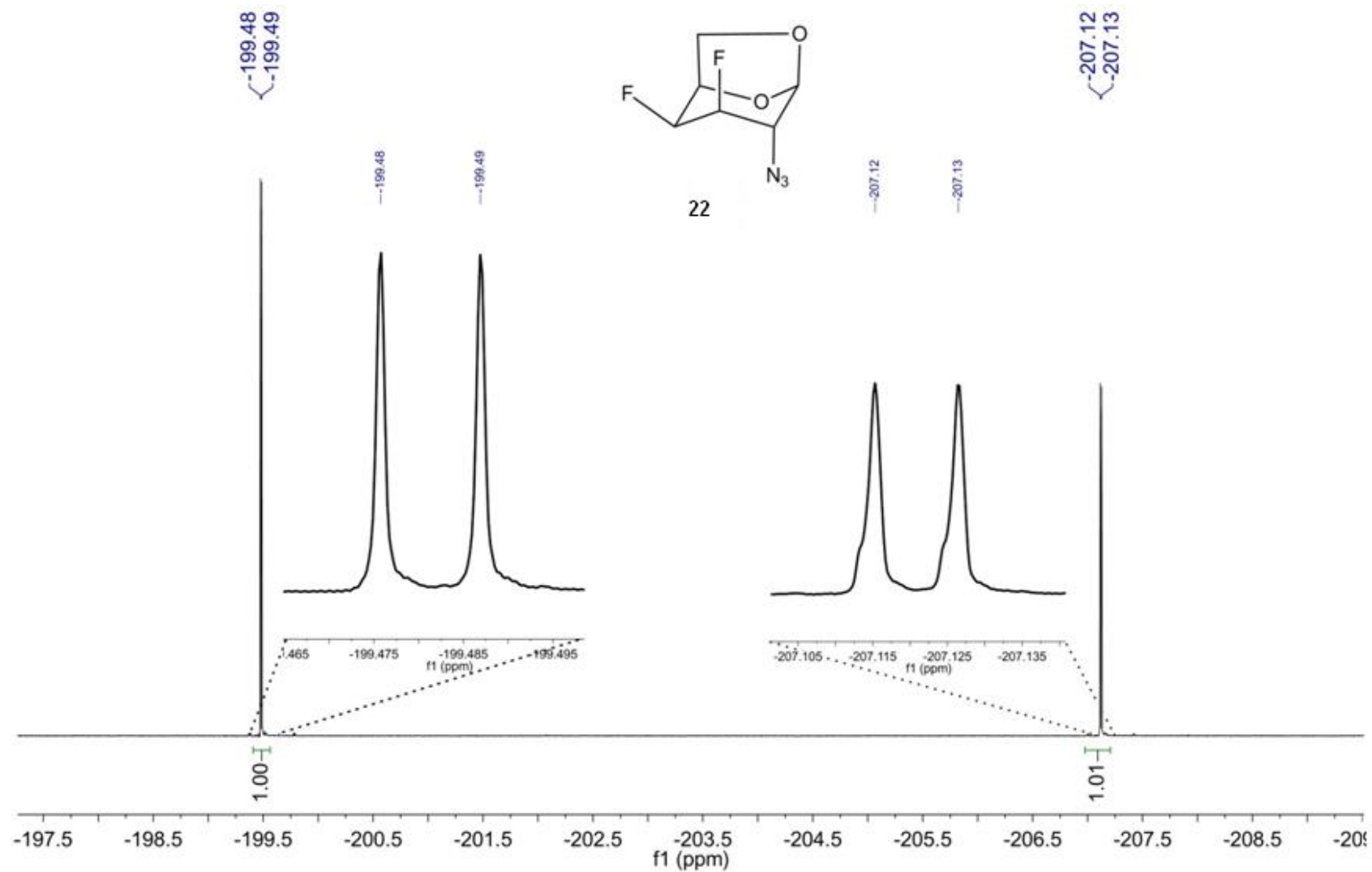
1H $\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) of 22



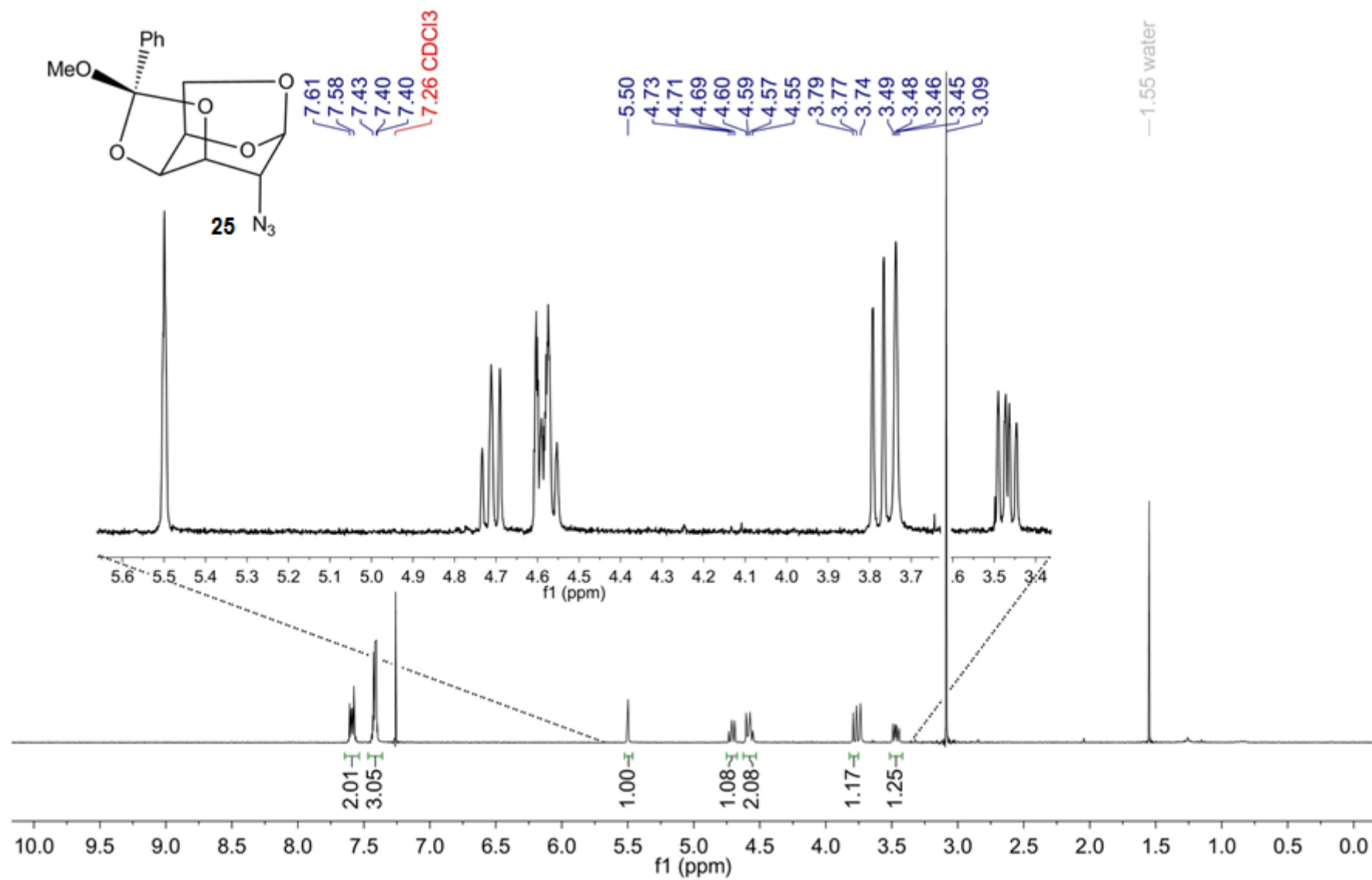
¹³C {¹H} NMR (75 MHz, CDCl₃) of 22



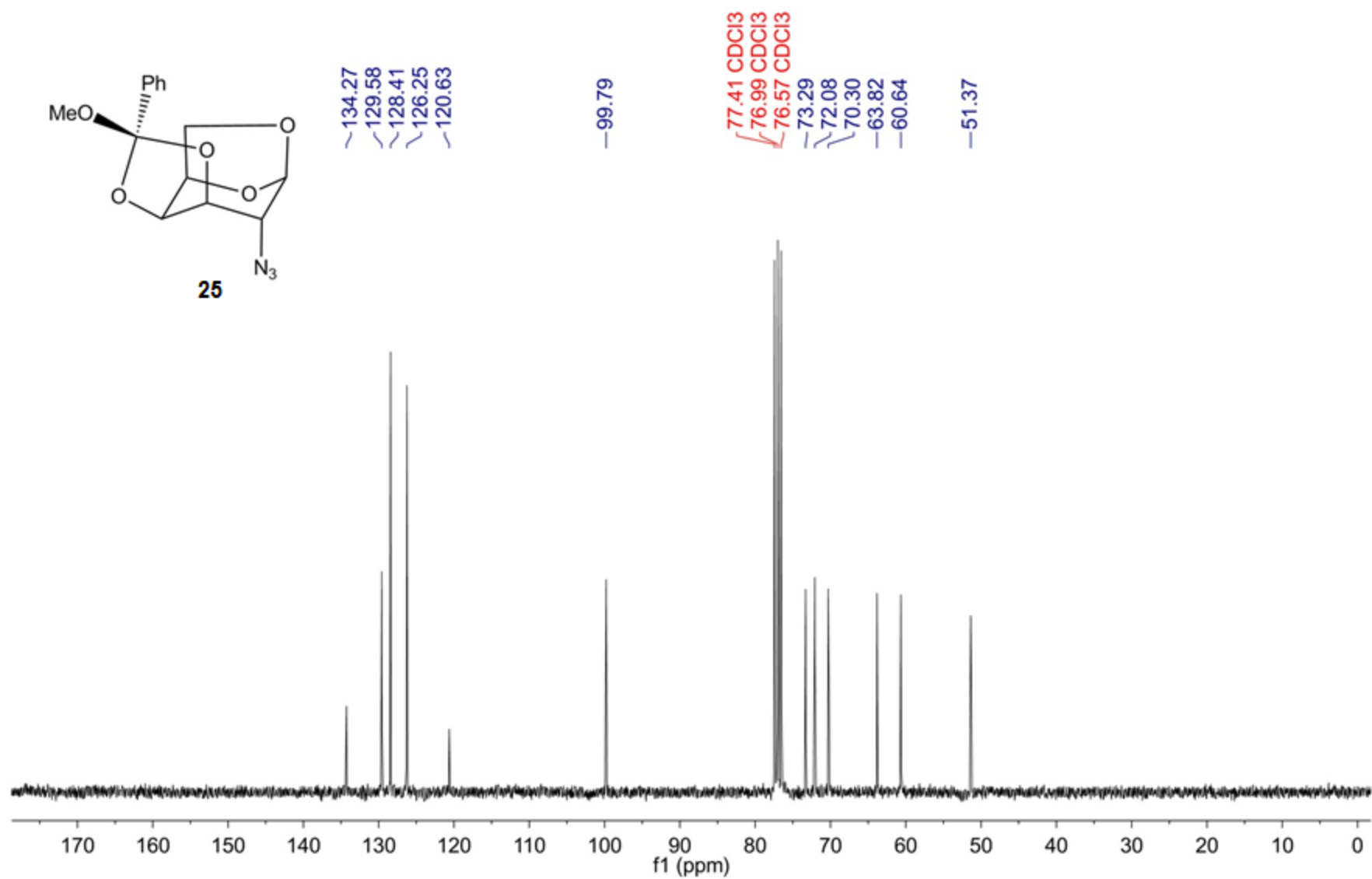
^{19}F NMR (470 MHz, CDCl_3) of 22



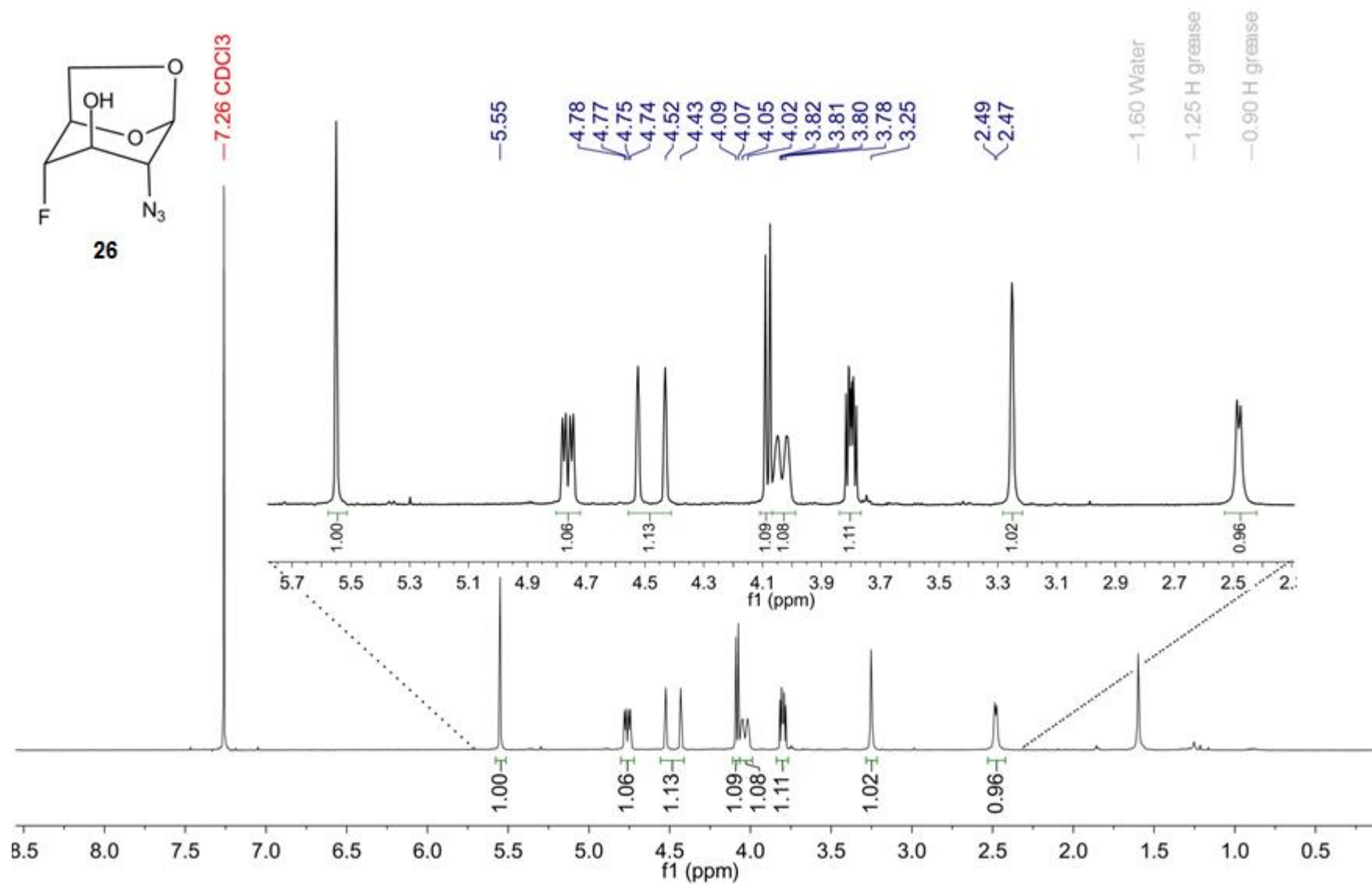
¹⁹F {¹H} NMR (470 MHz, CDCl₃) of 22



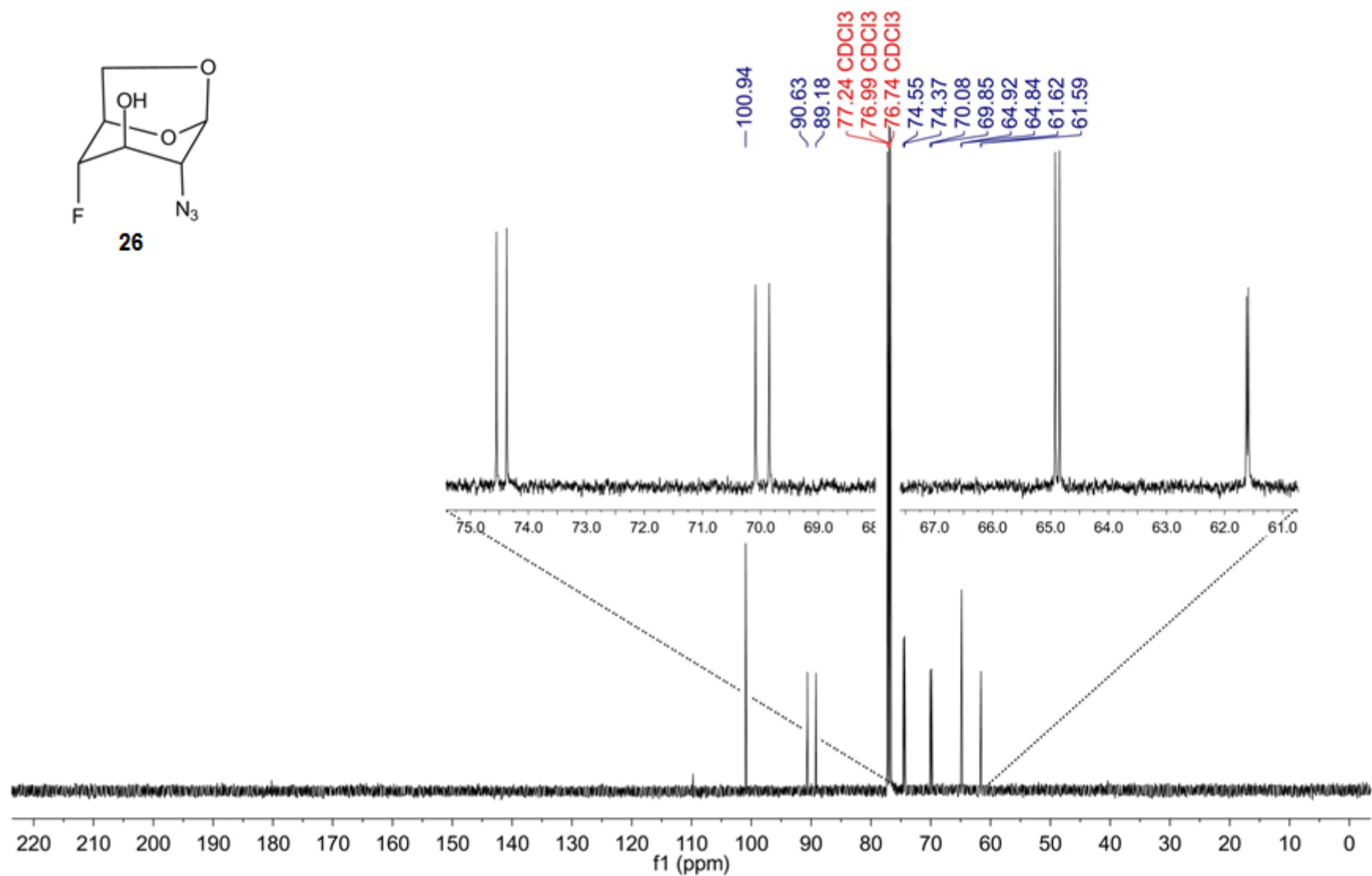
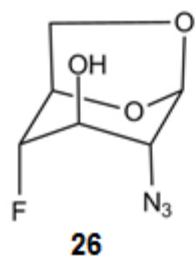
¹H NMR (500 MHz, CDCl₃) of **25**



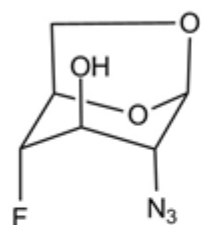
¹³C {¹H} NMR (125 MHz, CDCl₃) of **25**



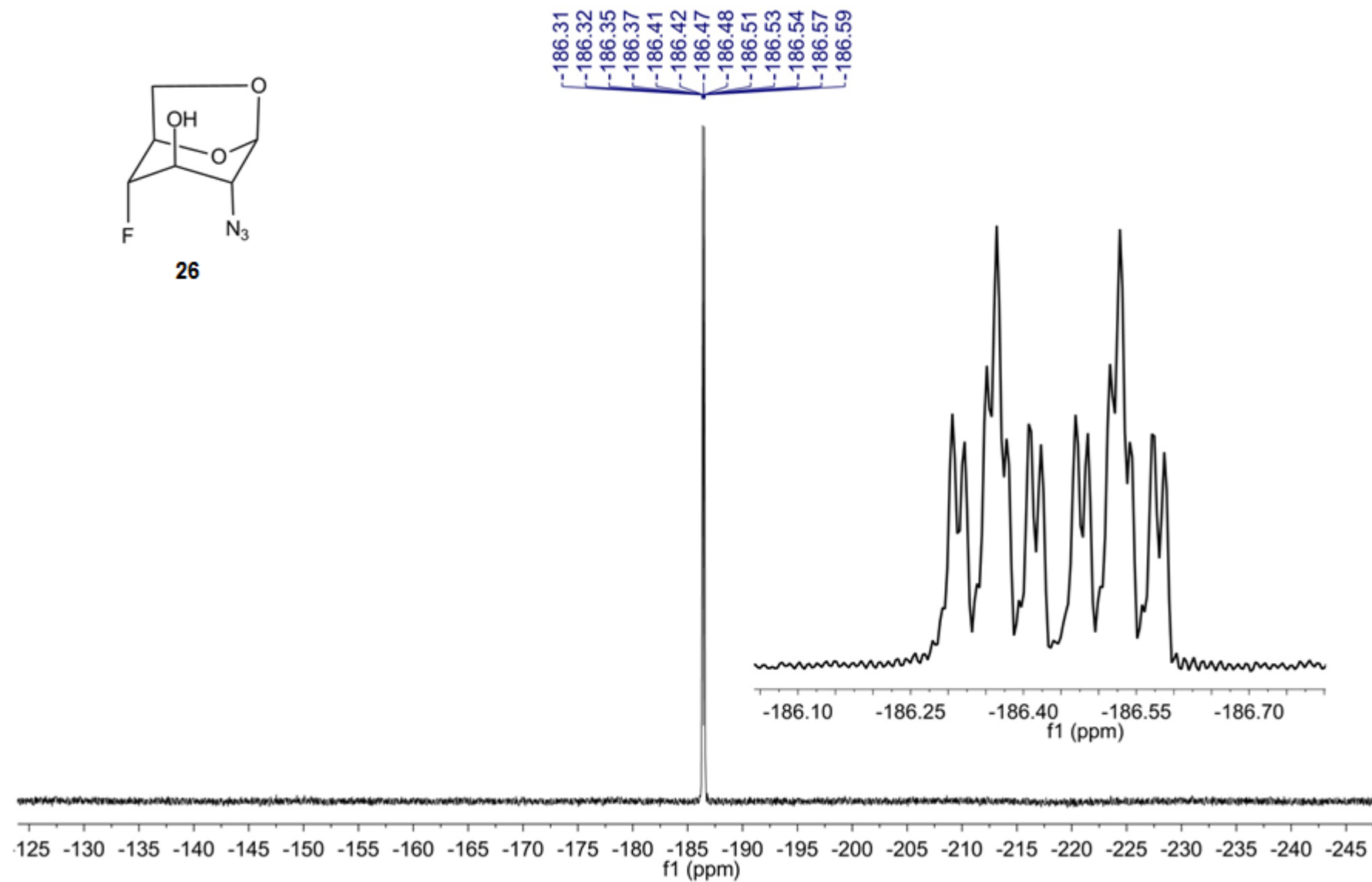
¹H NMR (300 MHz, CDCl₃) of **26**



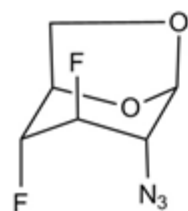
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **26**



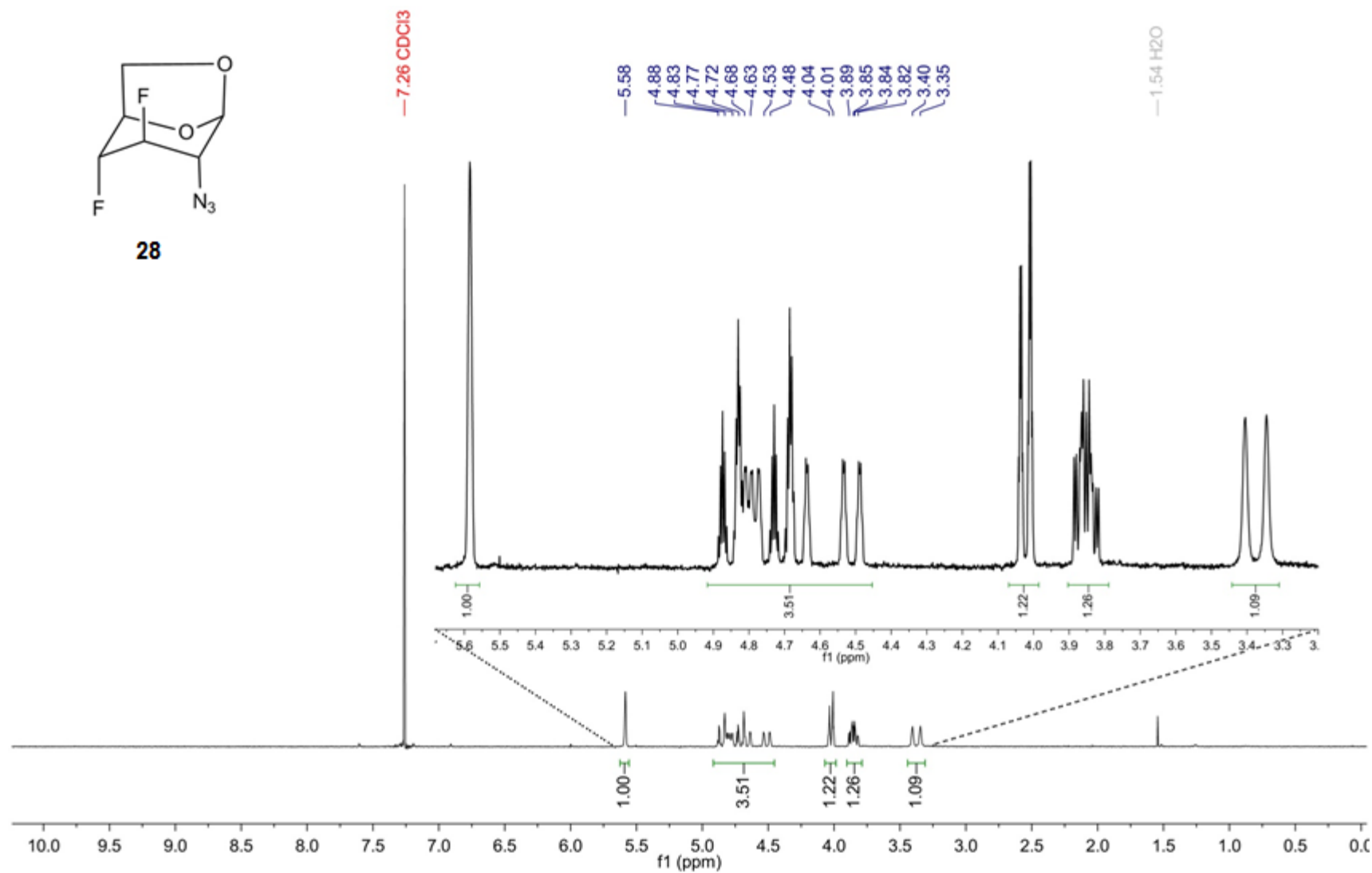
26



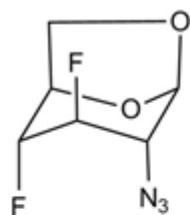
¹⁹F NMR (282 MHz, CDCl₃) of **26**



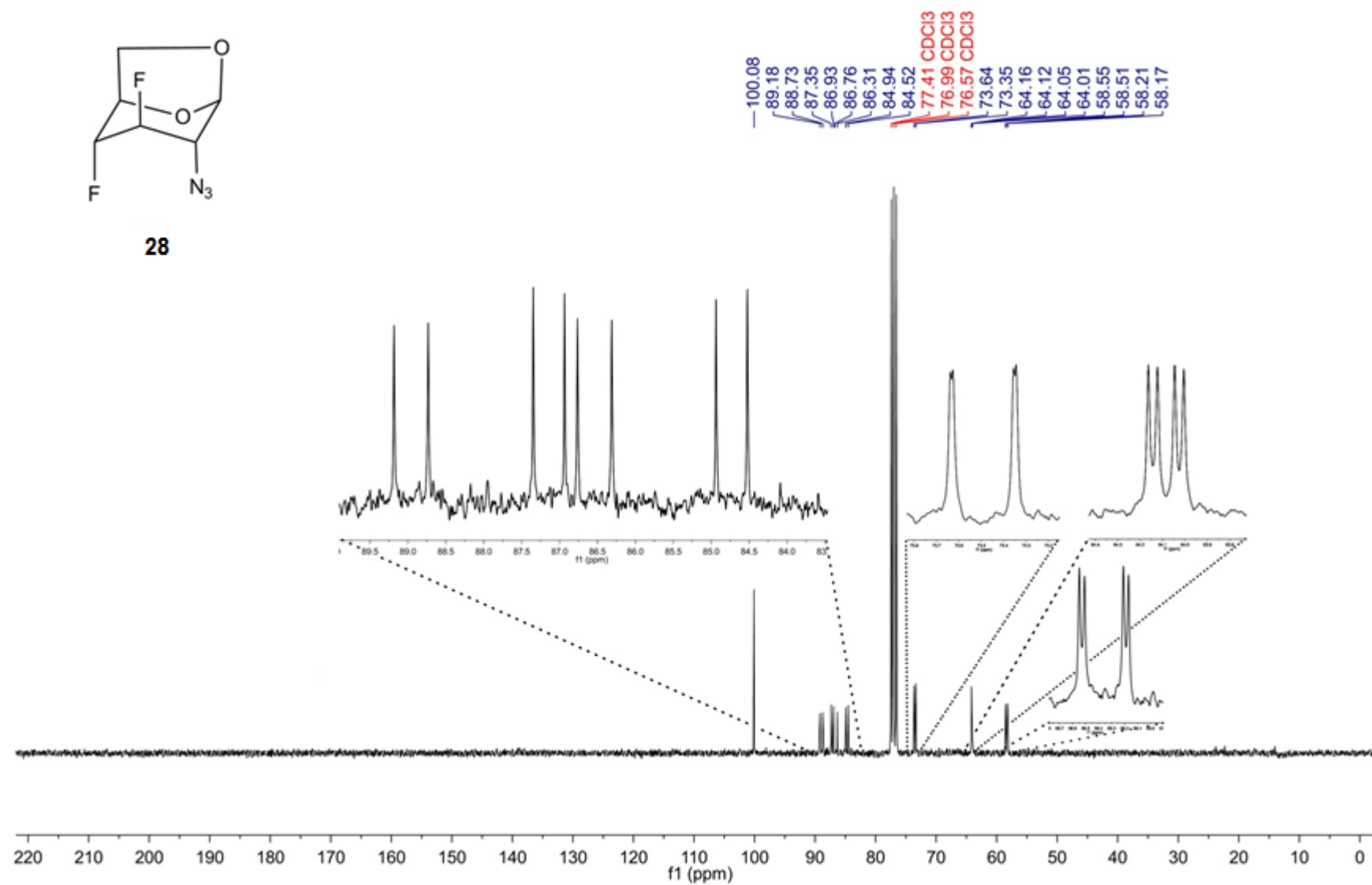
28



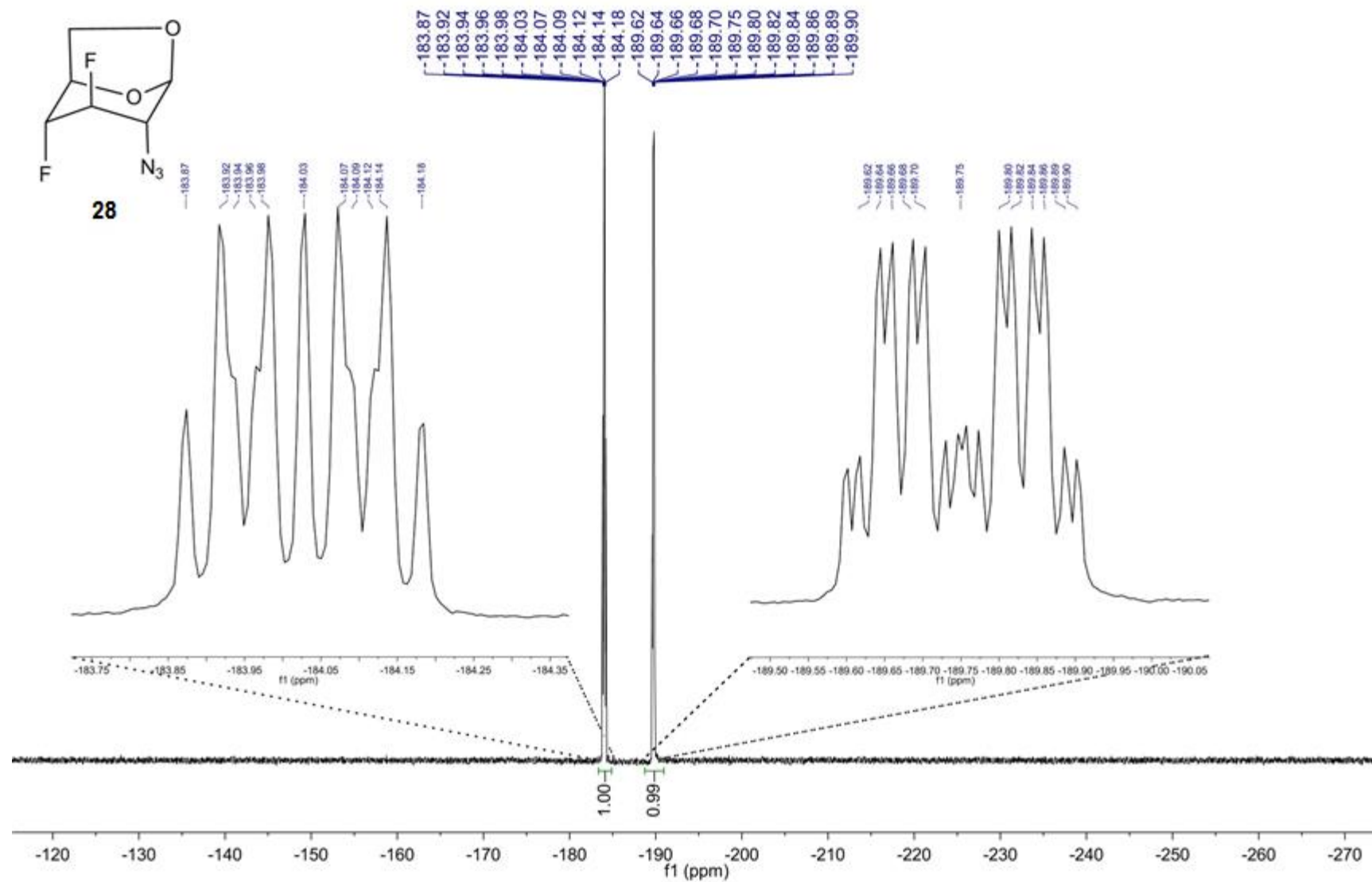
¹H NMR (300 MHz, CDCl₃) of **28**



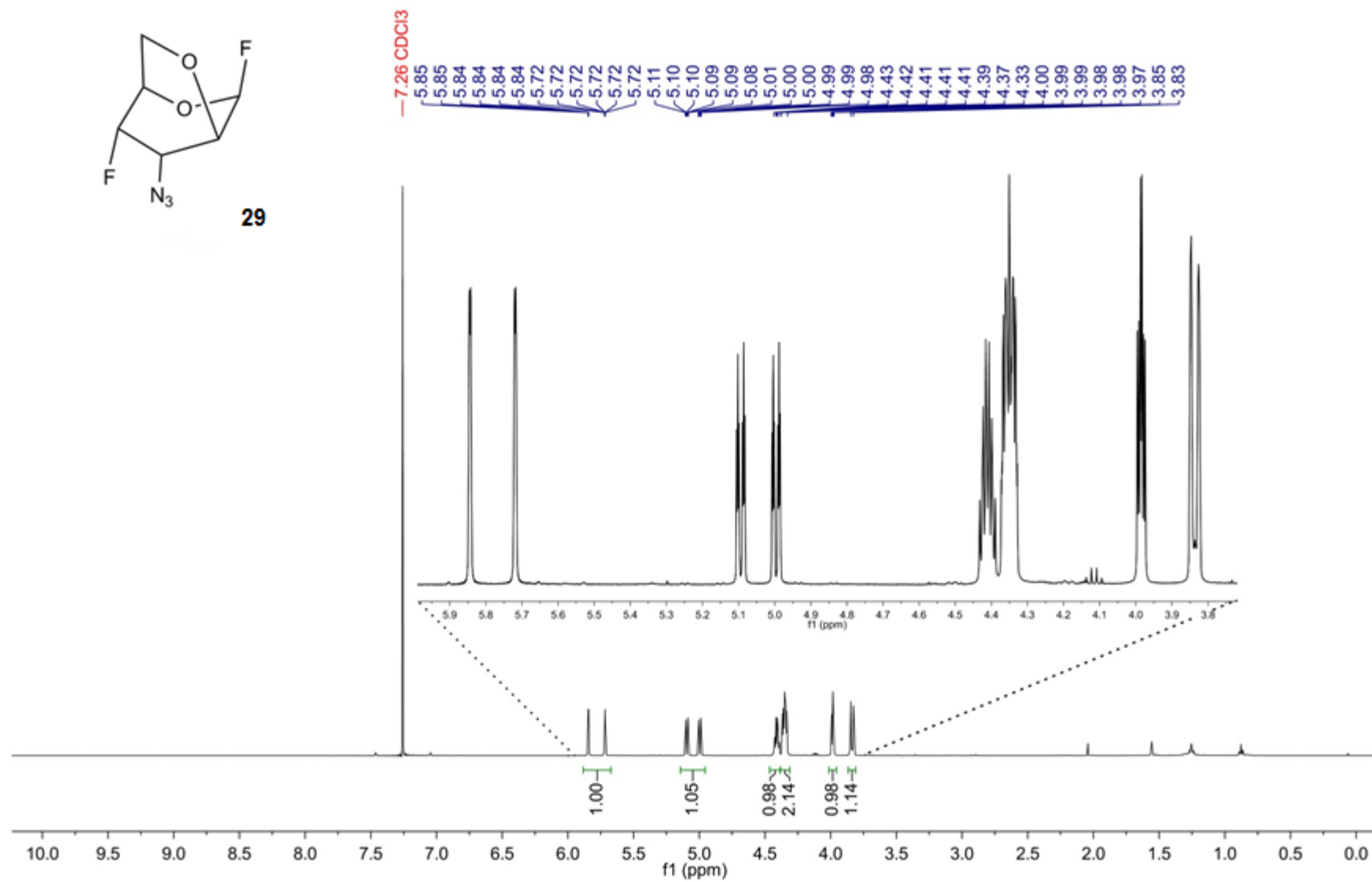
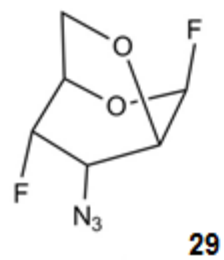
28



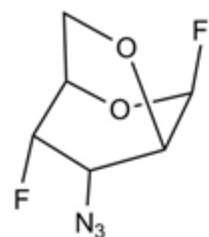
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **28**



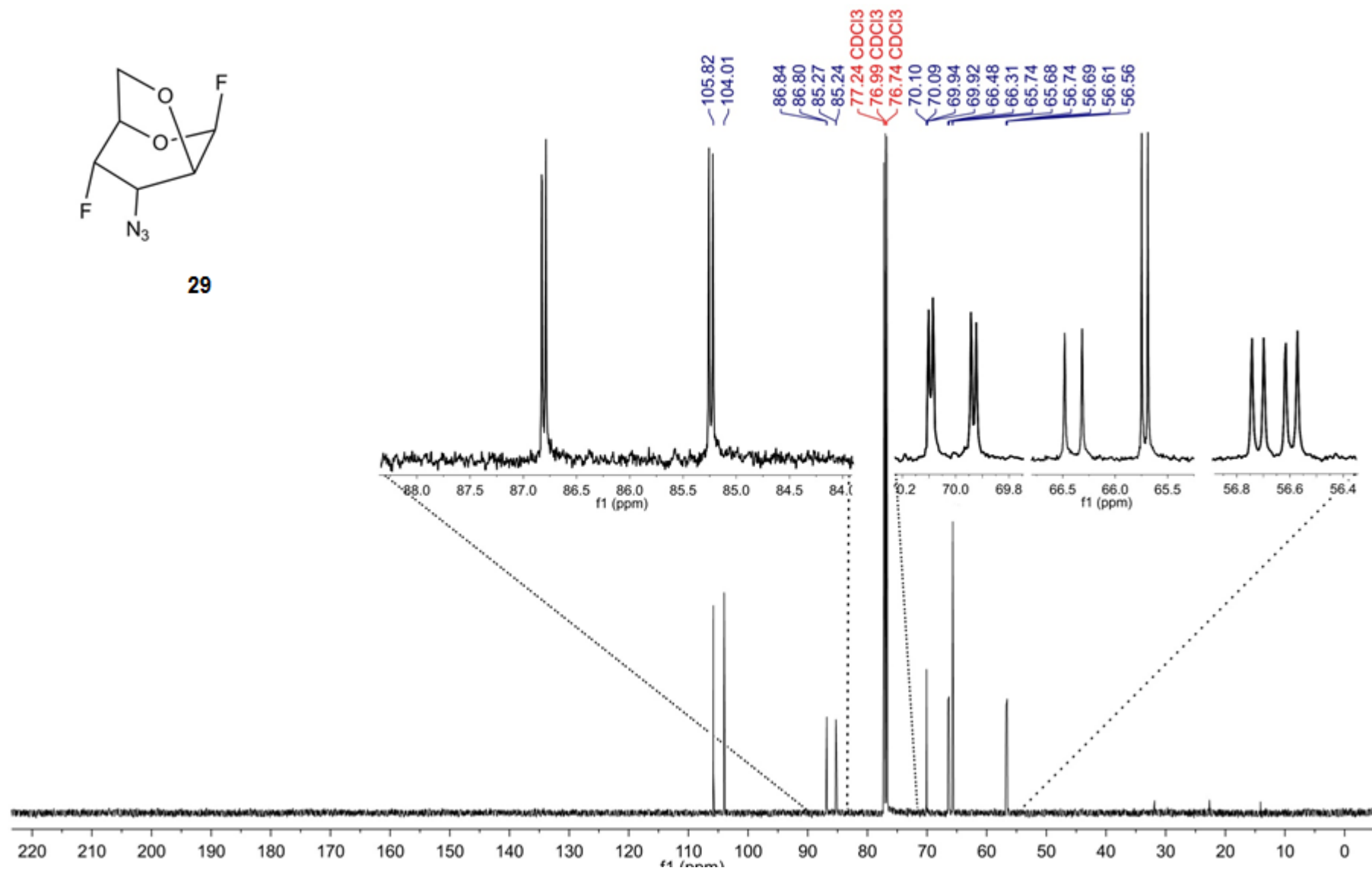
^{19}F NMR (282 MHz, CDCl_3) of **28**



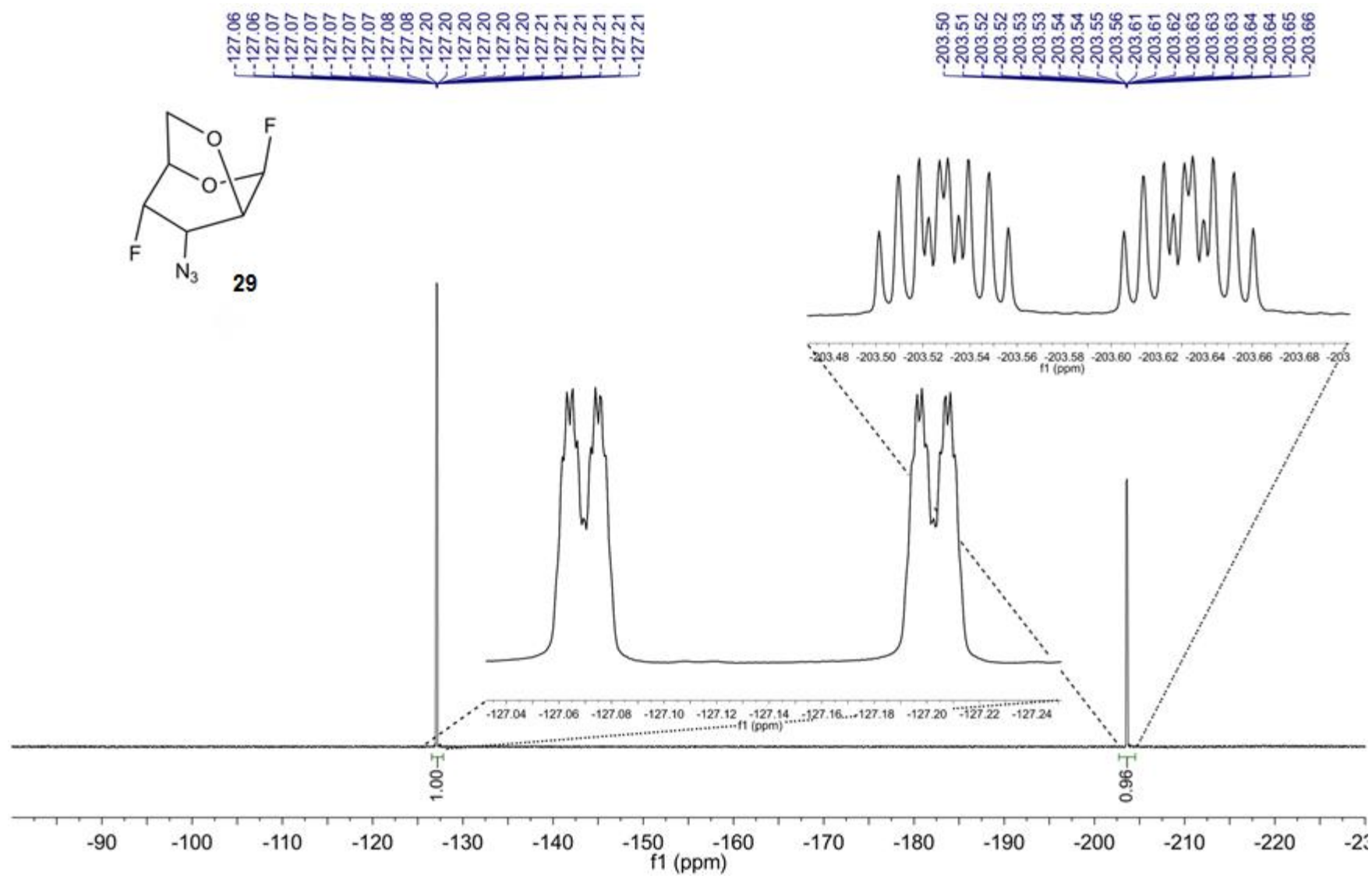
¹H NMR (500 MHz, CDCl₃) of **29**



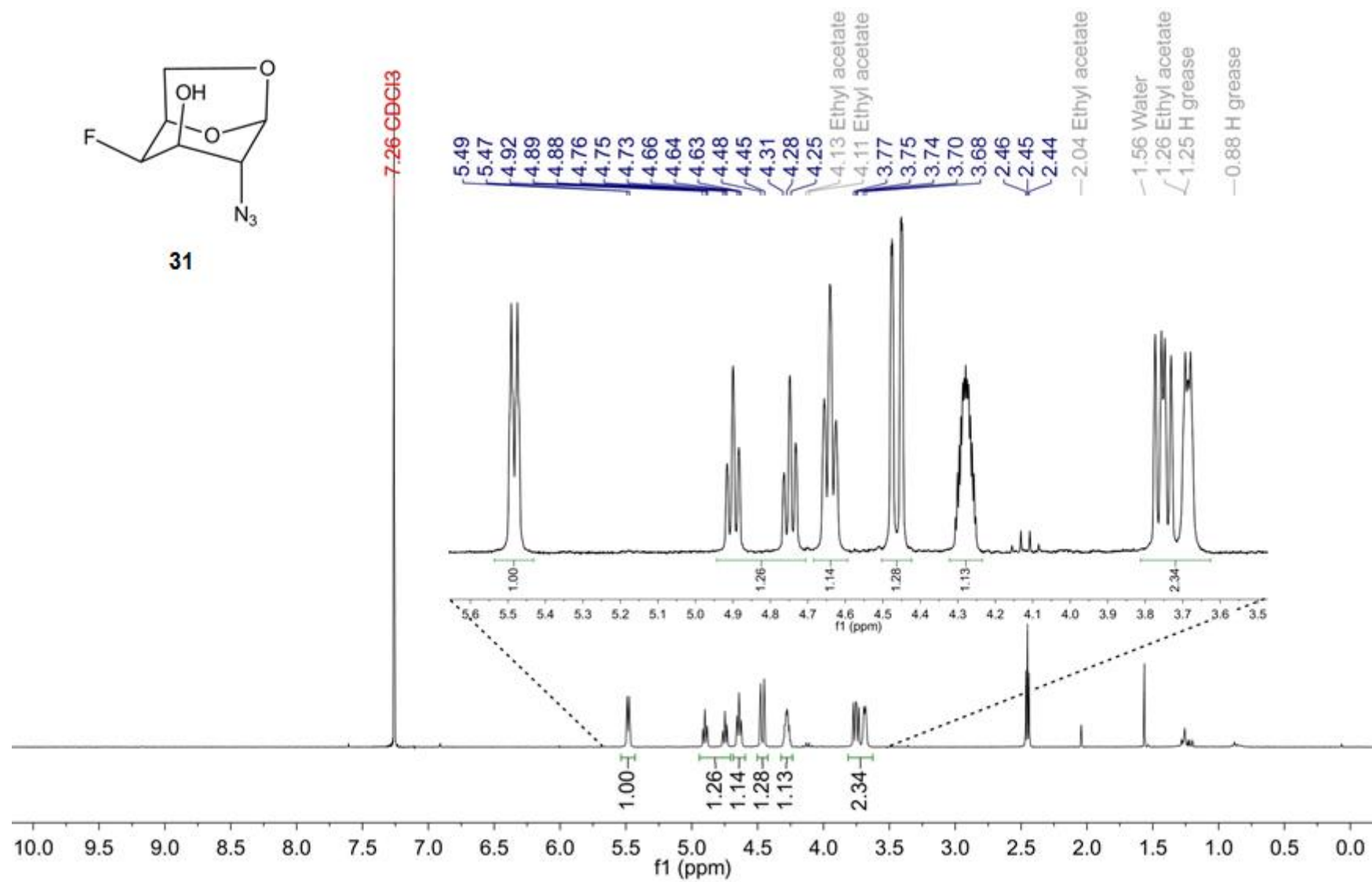
29



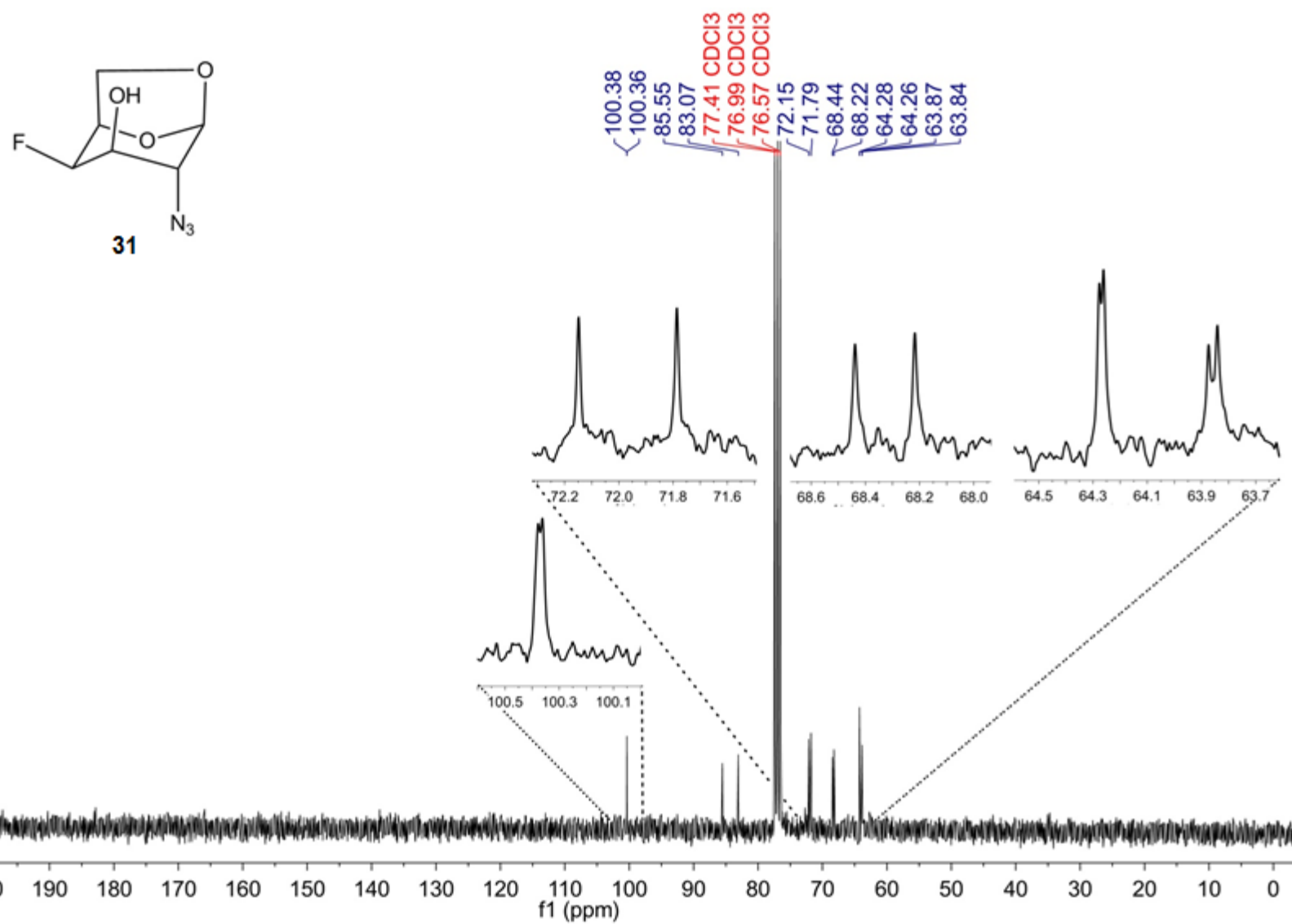
^{13}C { 1H } NMR (75 MHz, $CDCl_3$) of **29**



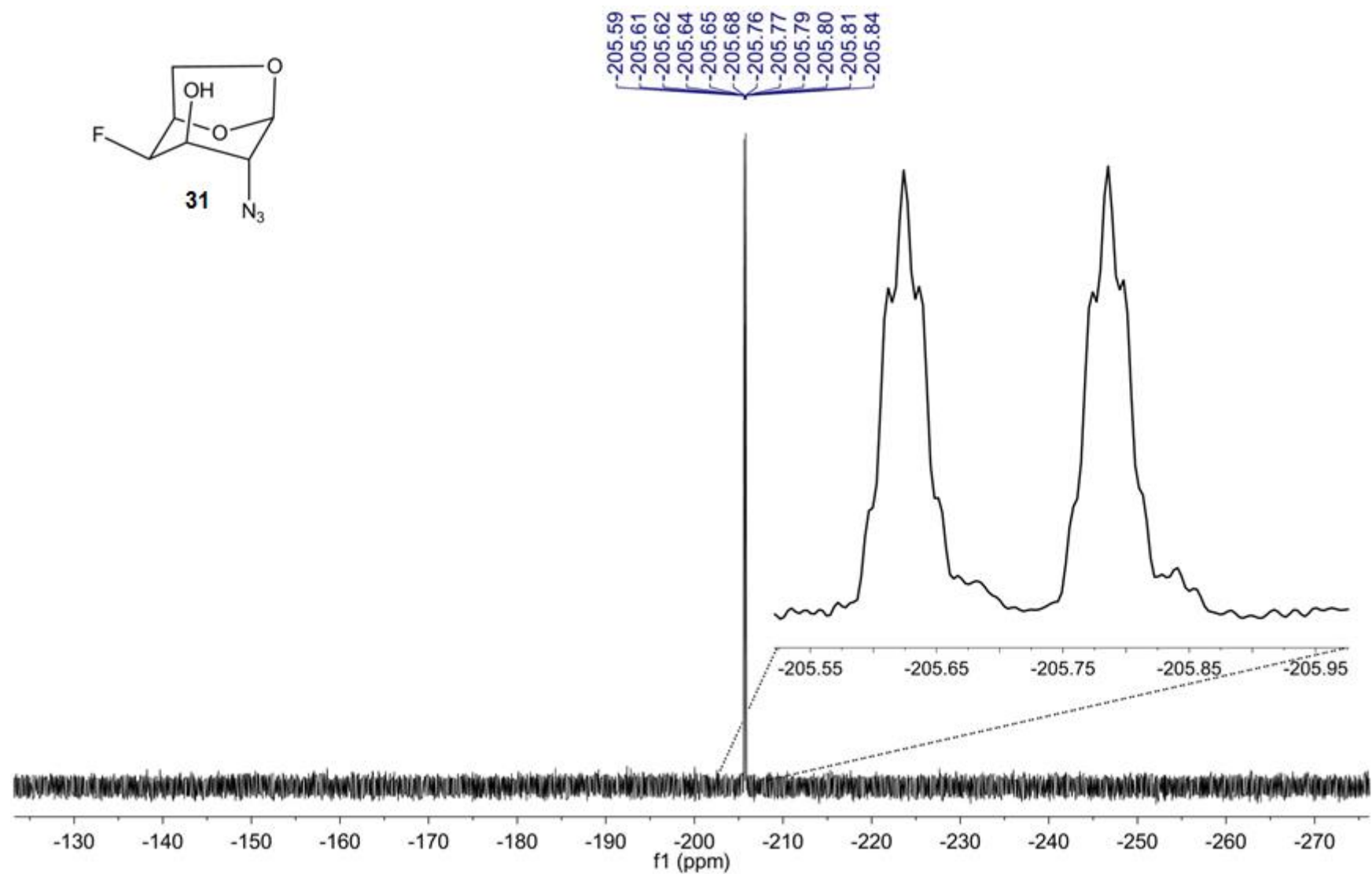
^{19}F NMR (470 MHz, CDCl_3) of **29**



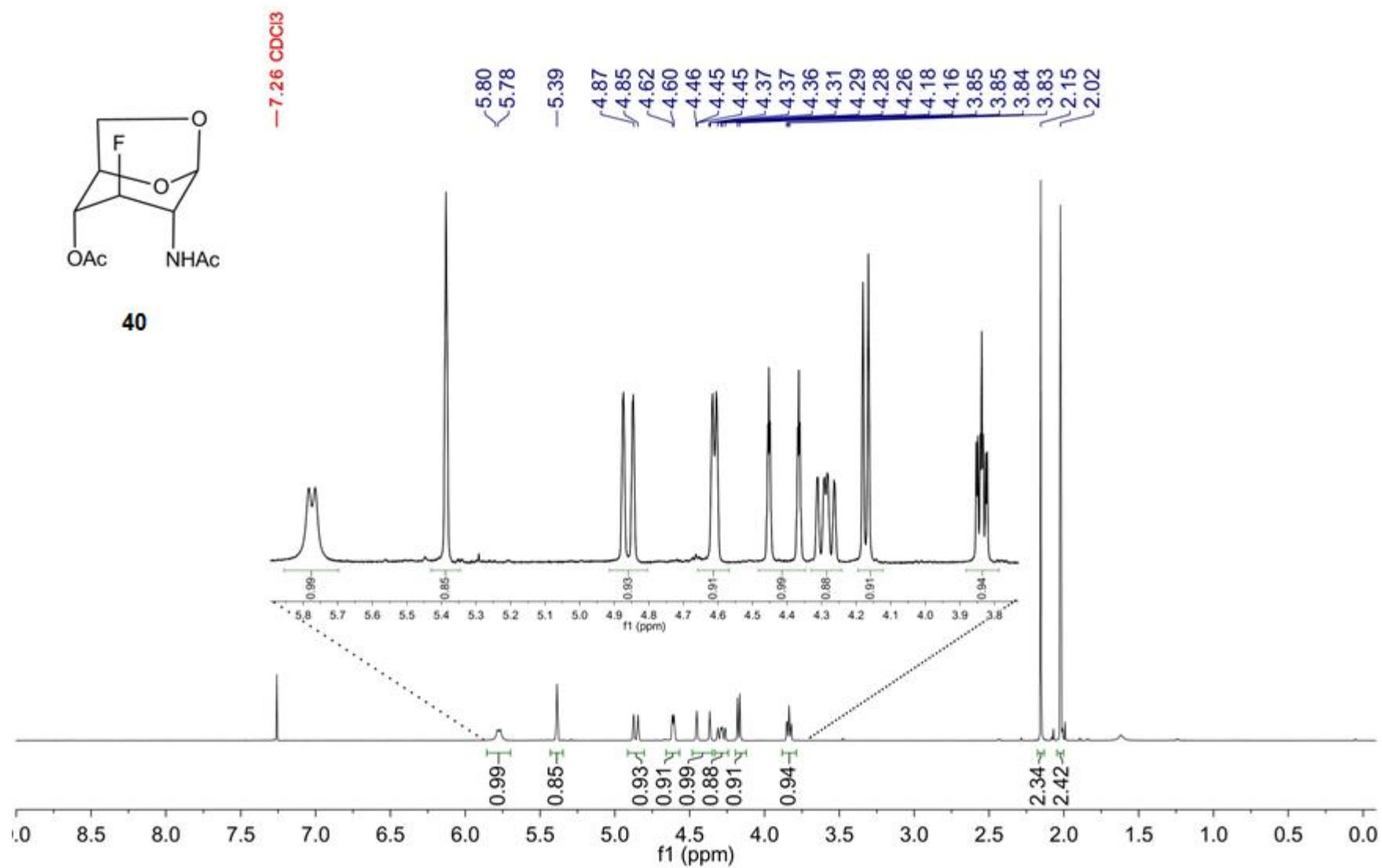
¹H NMR (300 MHz, CDCl₃) of **31**



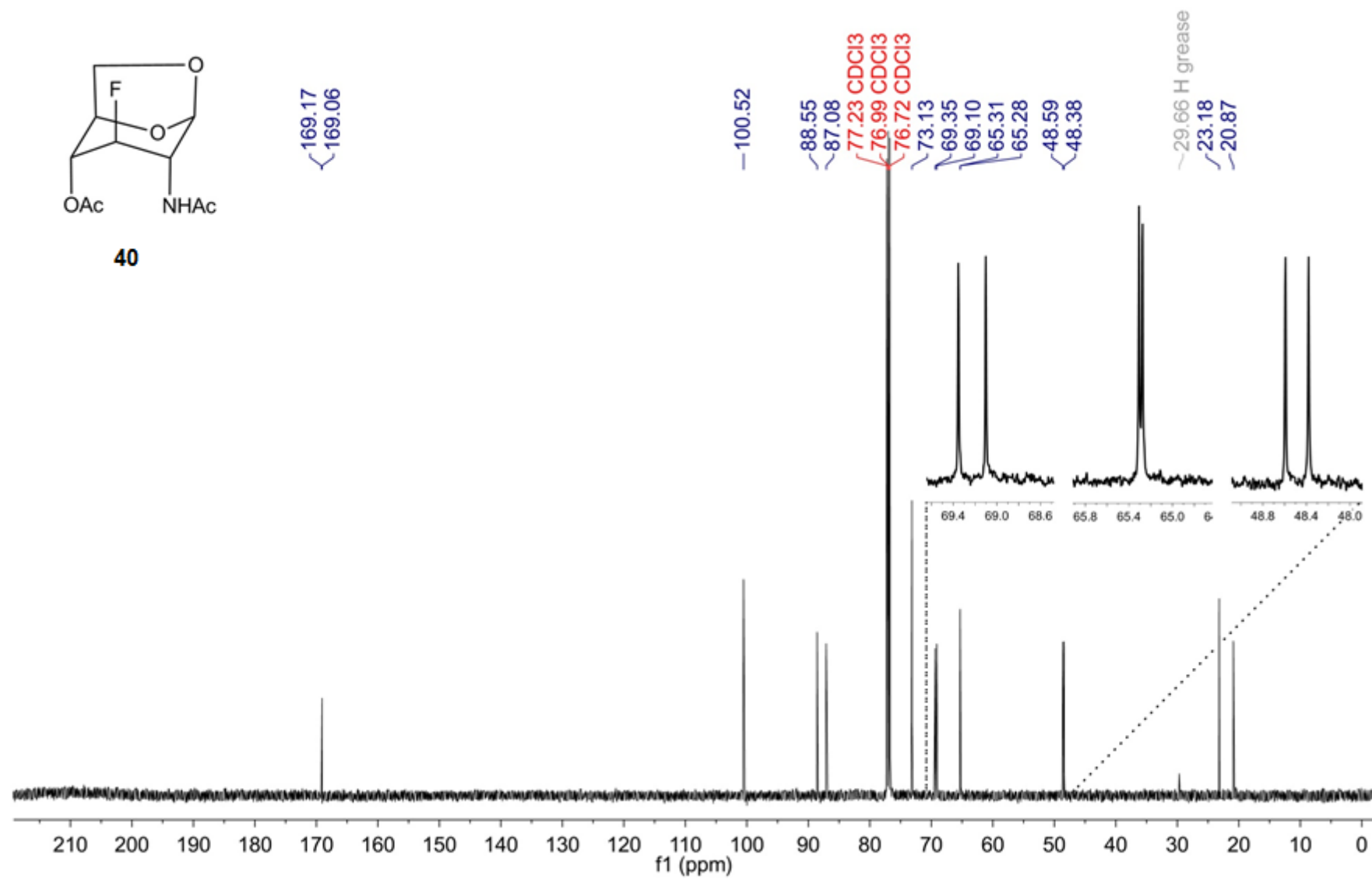
¹³C {¹H} NMR (75 MHz, CDCl₃) of **31**



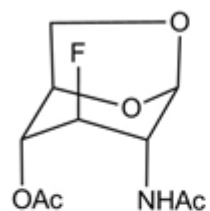
¹⁹F NMR (282 MHz, CDCl₃) of **31**



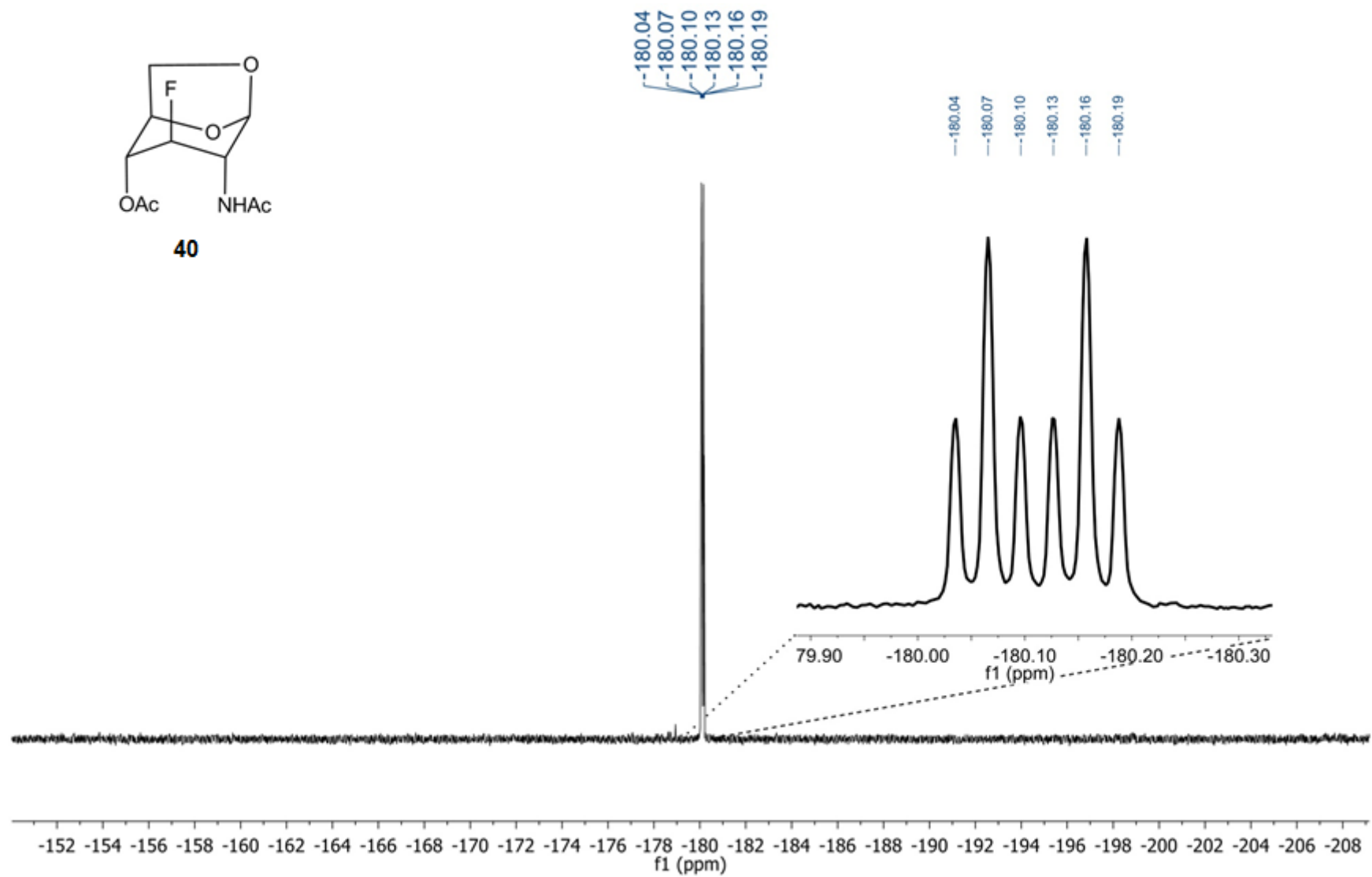
^1H NMR (500 MHz, CDCl_3) of **40**



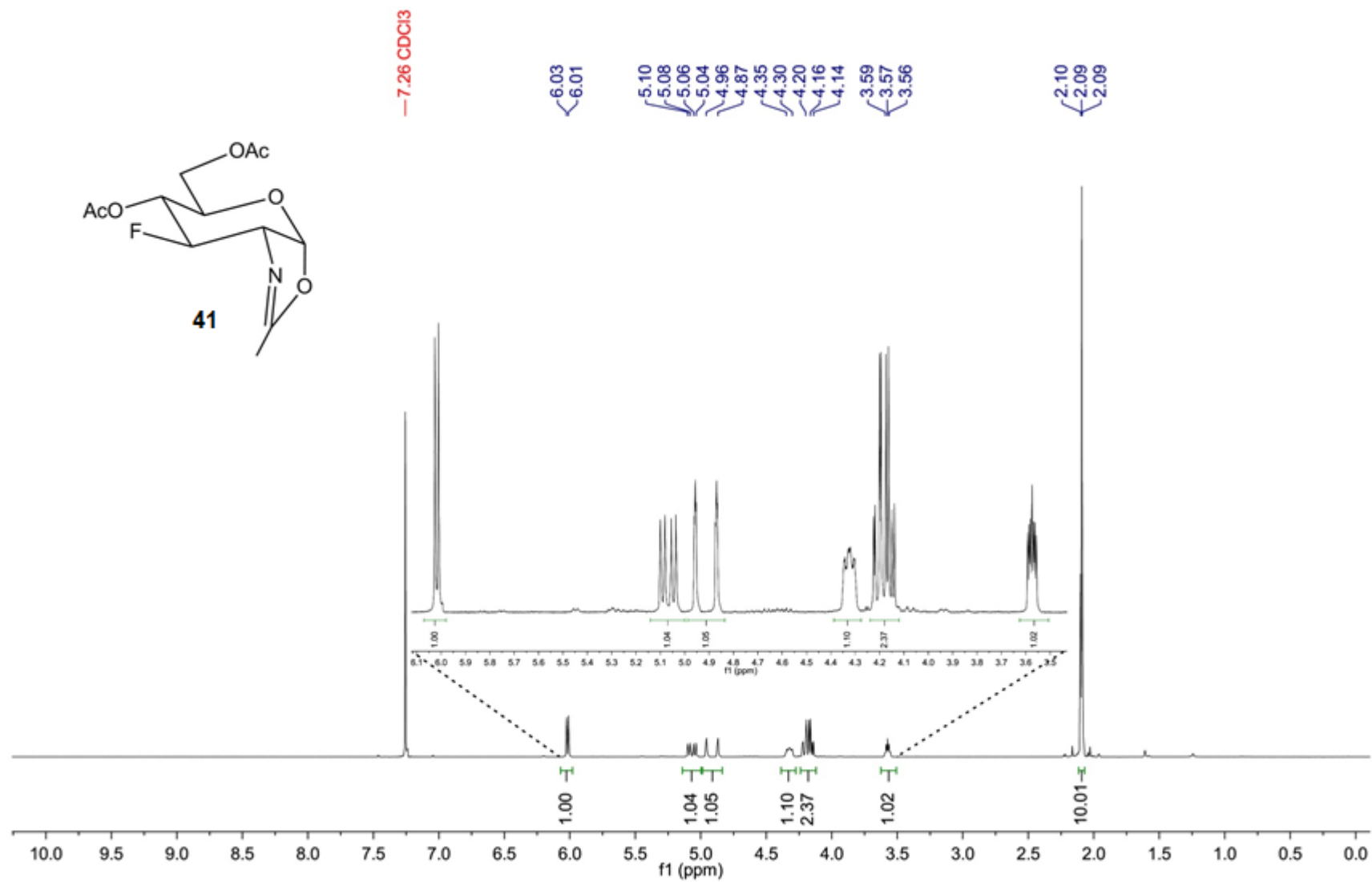
^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of **40**



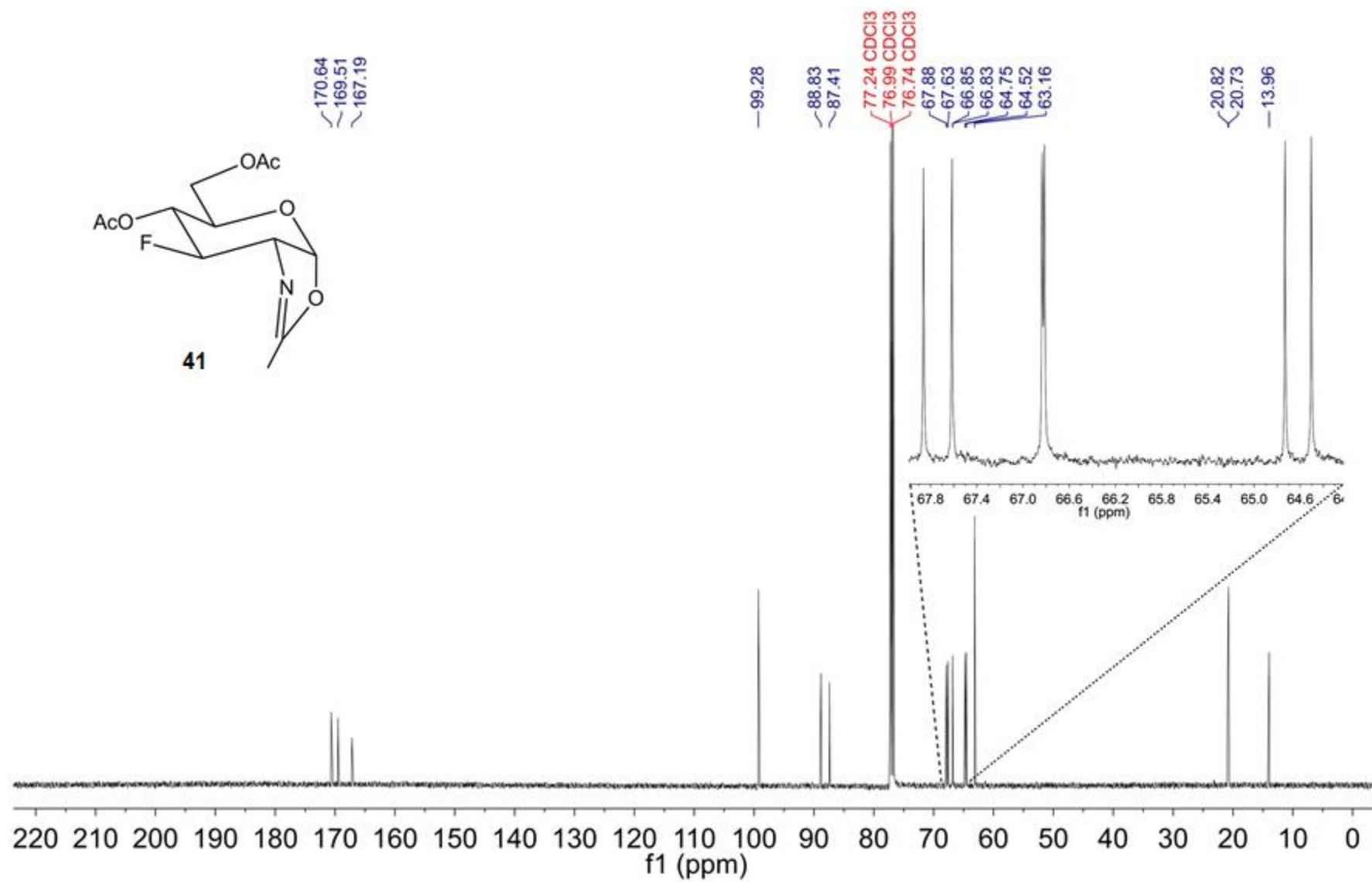
40



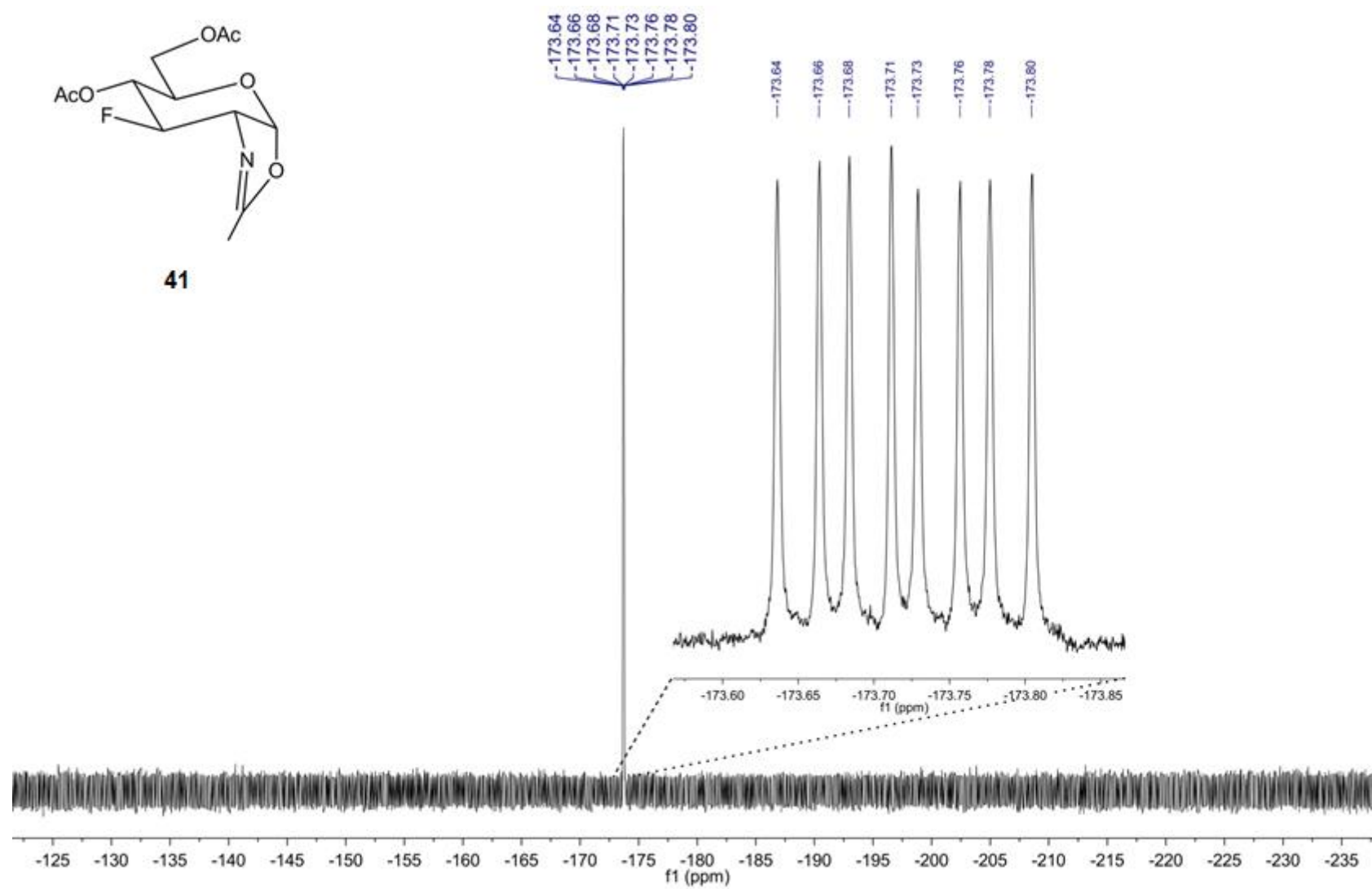
^{19}F NMR (470 MHz, CDCl_3) of **40**



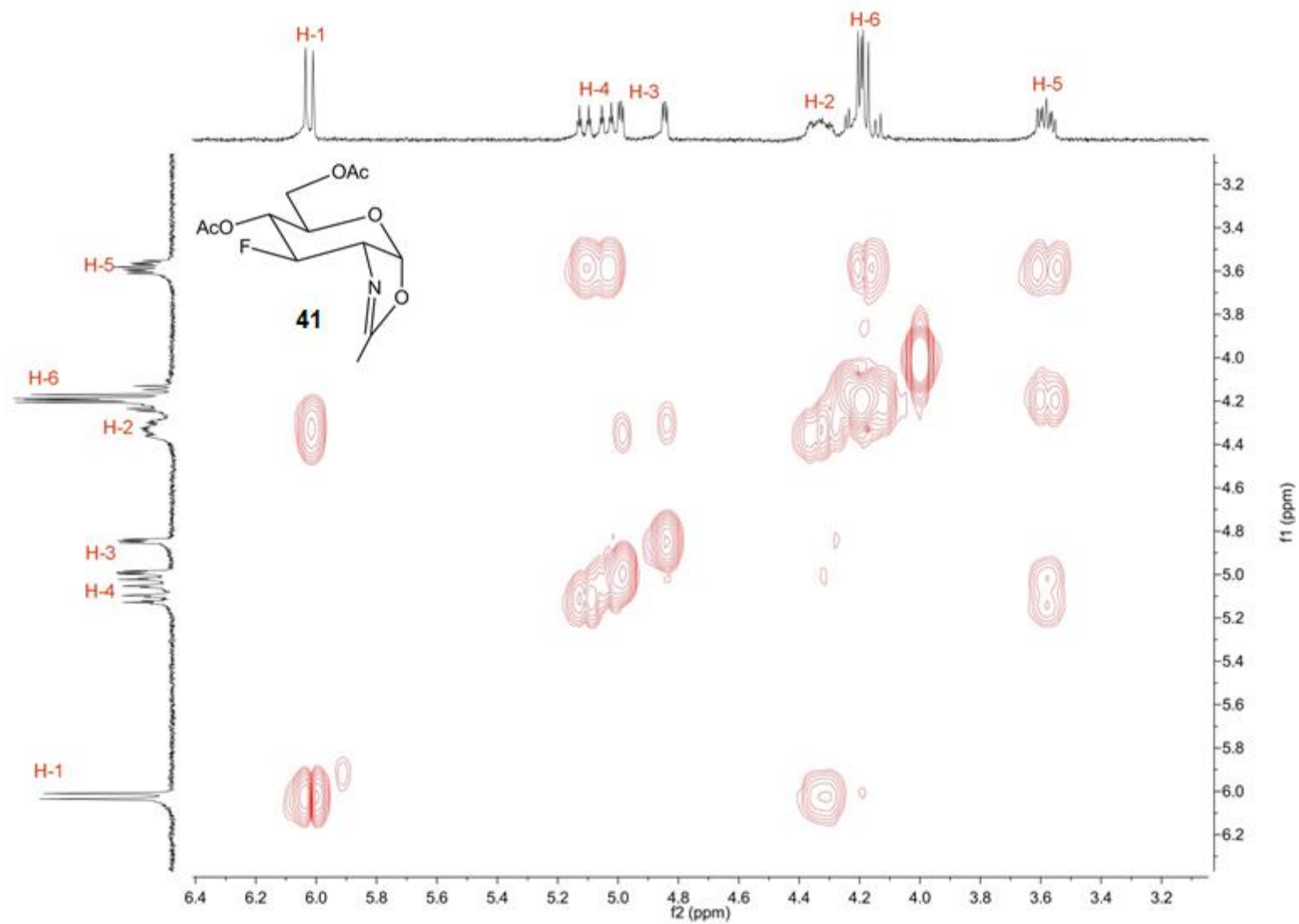
¹H NMR (500 MHz, CDCl₃) of **41**



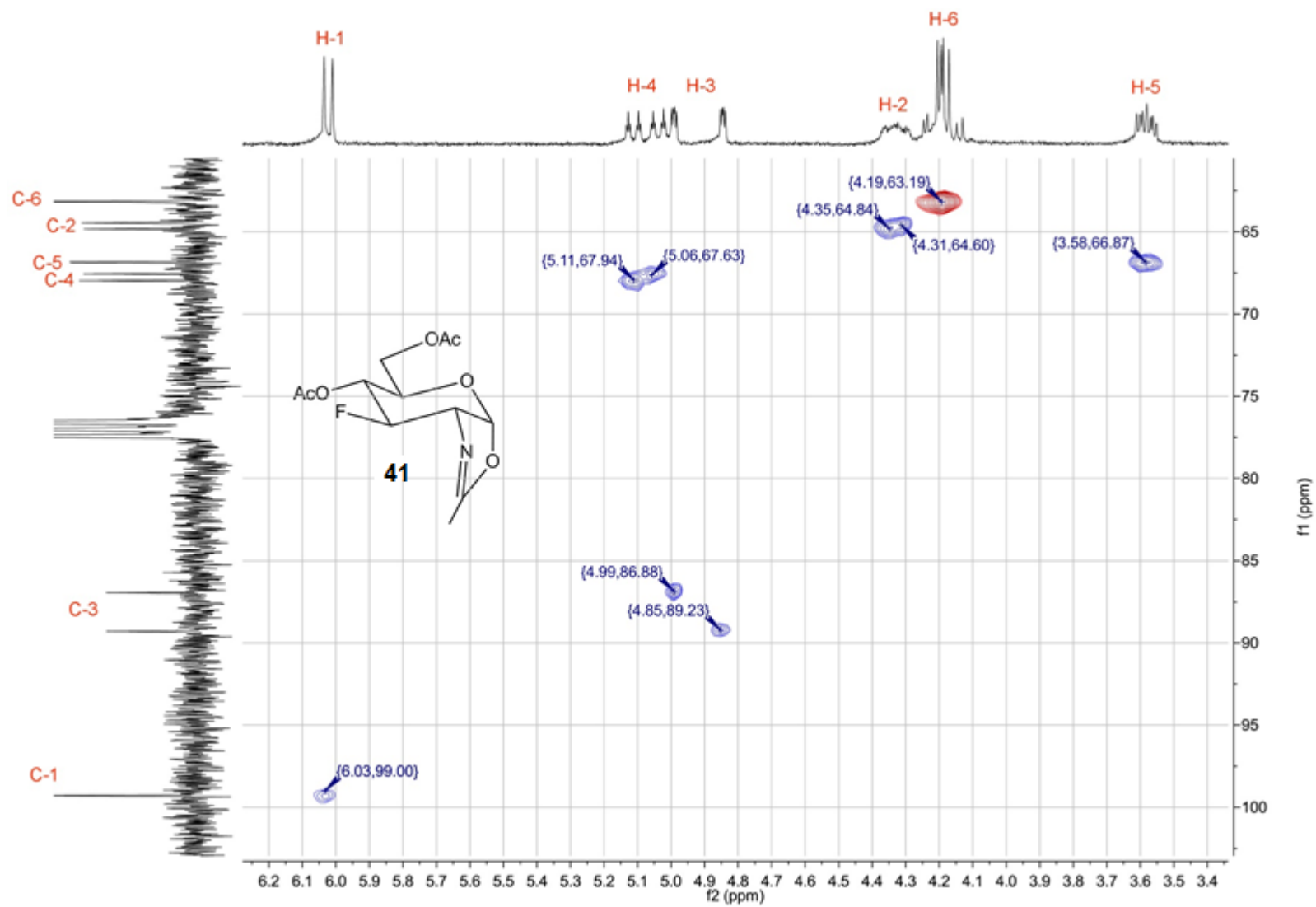
^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of **41**



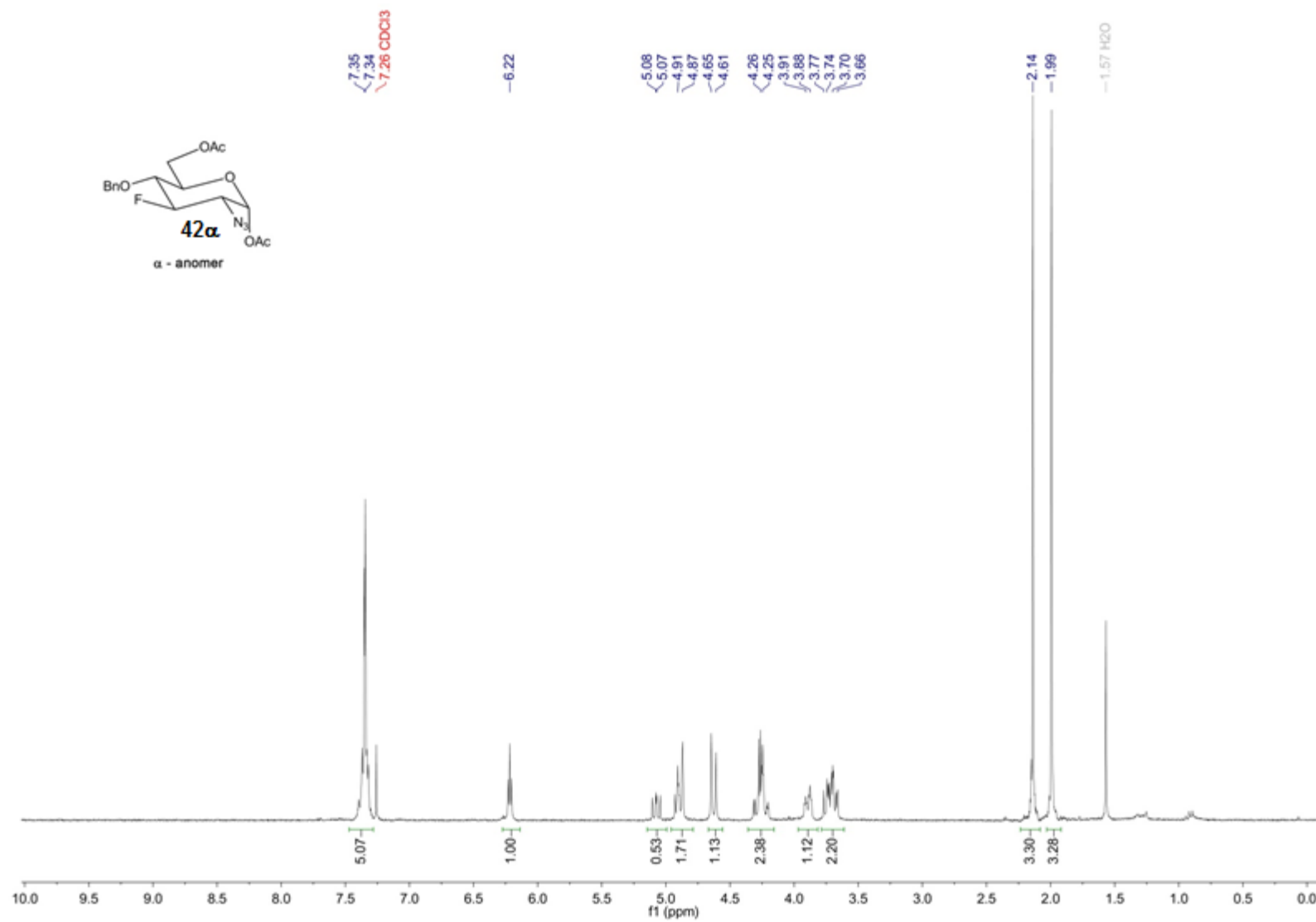
^{19}F NMR (470 MHz, CDCl_3) of **41**



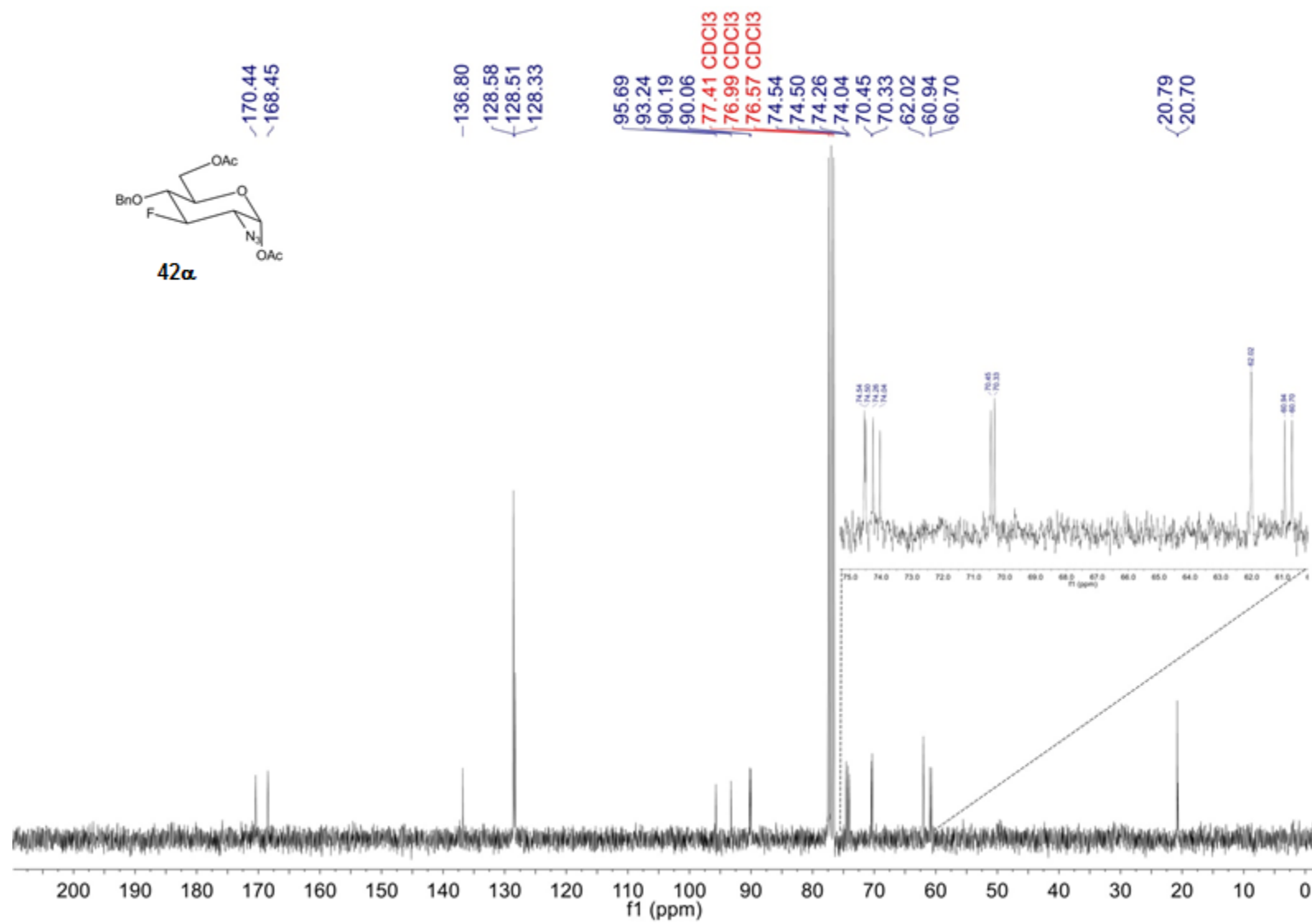
gCOSY NMR (500 MHz, CDCl₃) of **41**



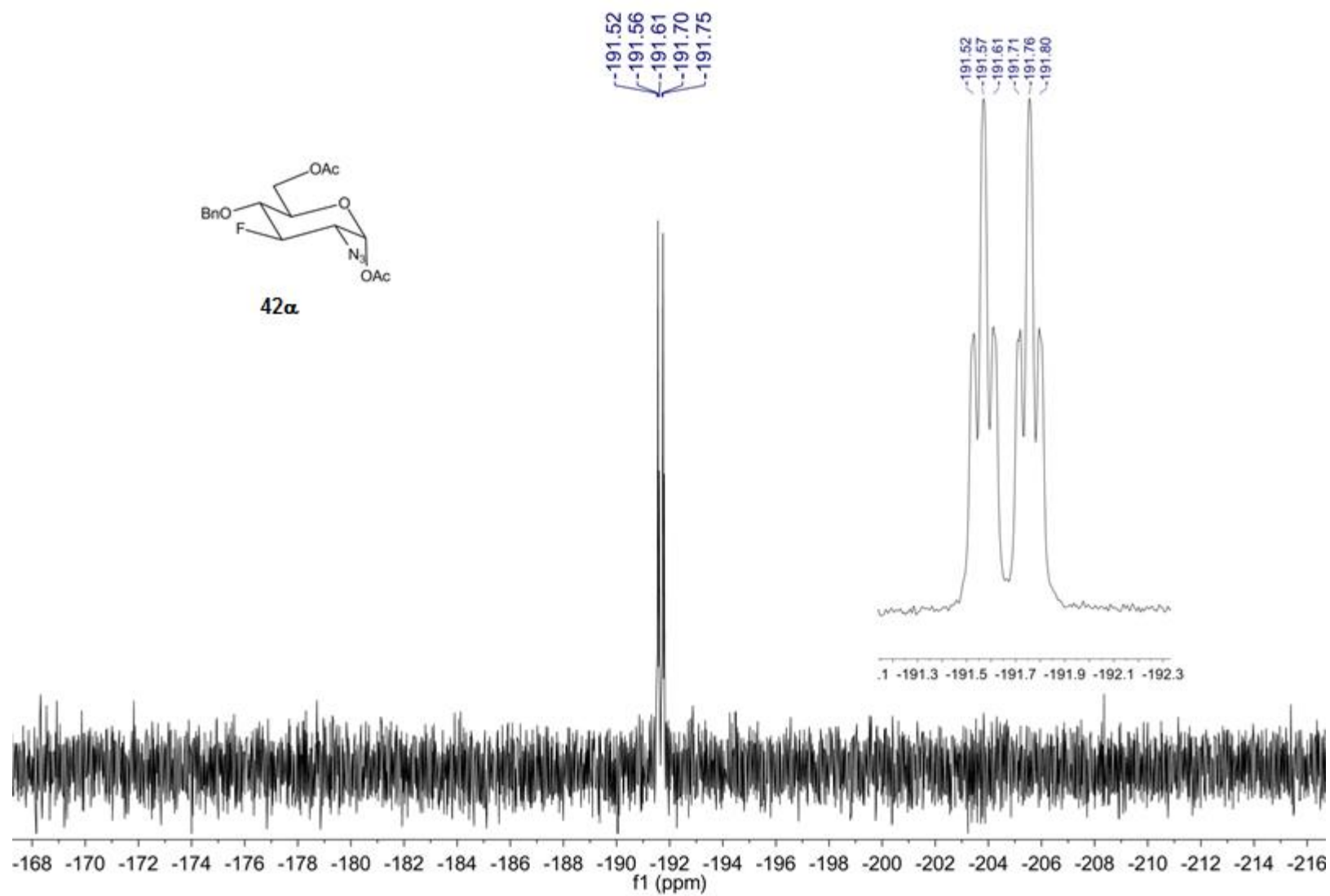
gHSQC NMR (500 MHz, CDCl_3) of **41**



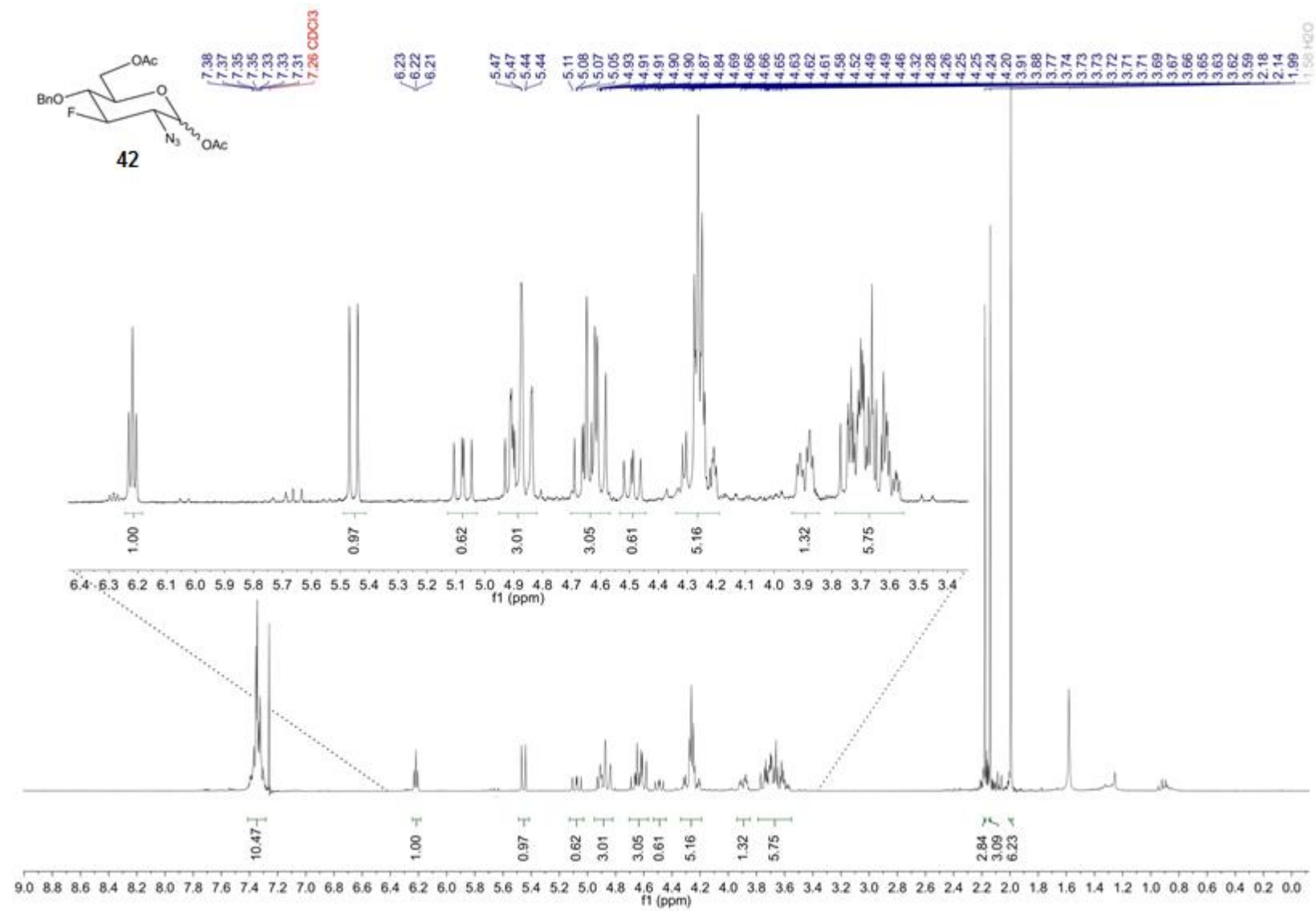
¹H NMR (300 MHz, CDCl₃) of **42α** (α-anomer)



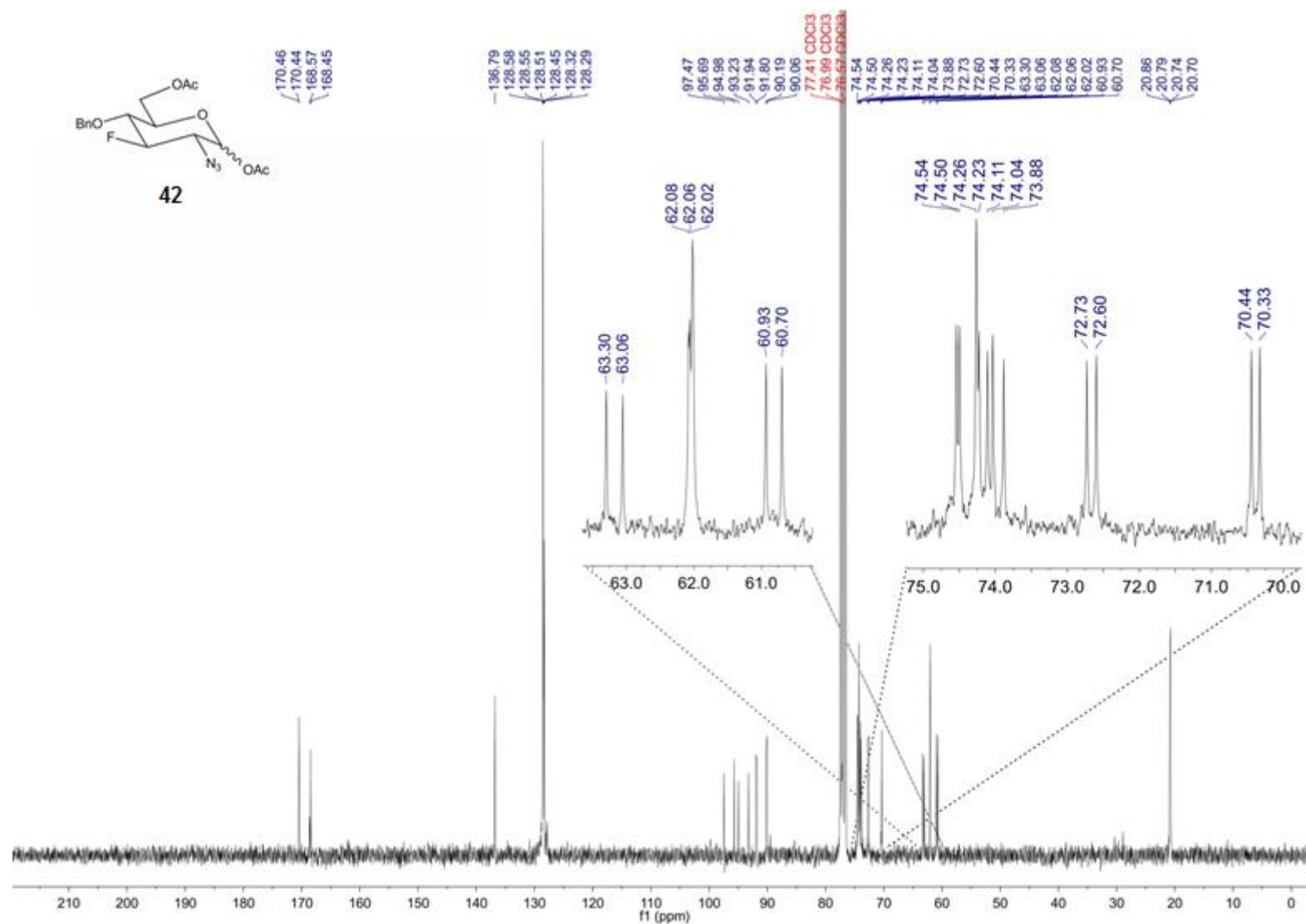
¹³C {¹H} NMR (75 MHz, CDCl₃) of **42 α** (α-anomer)



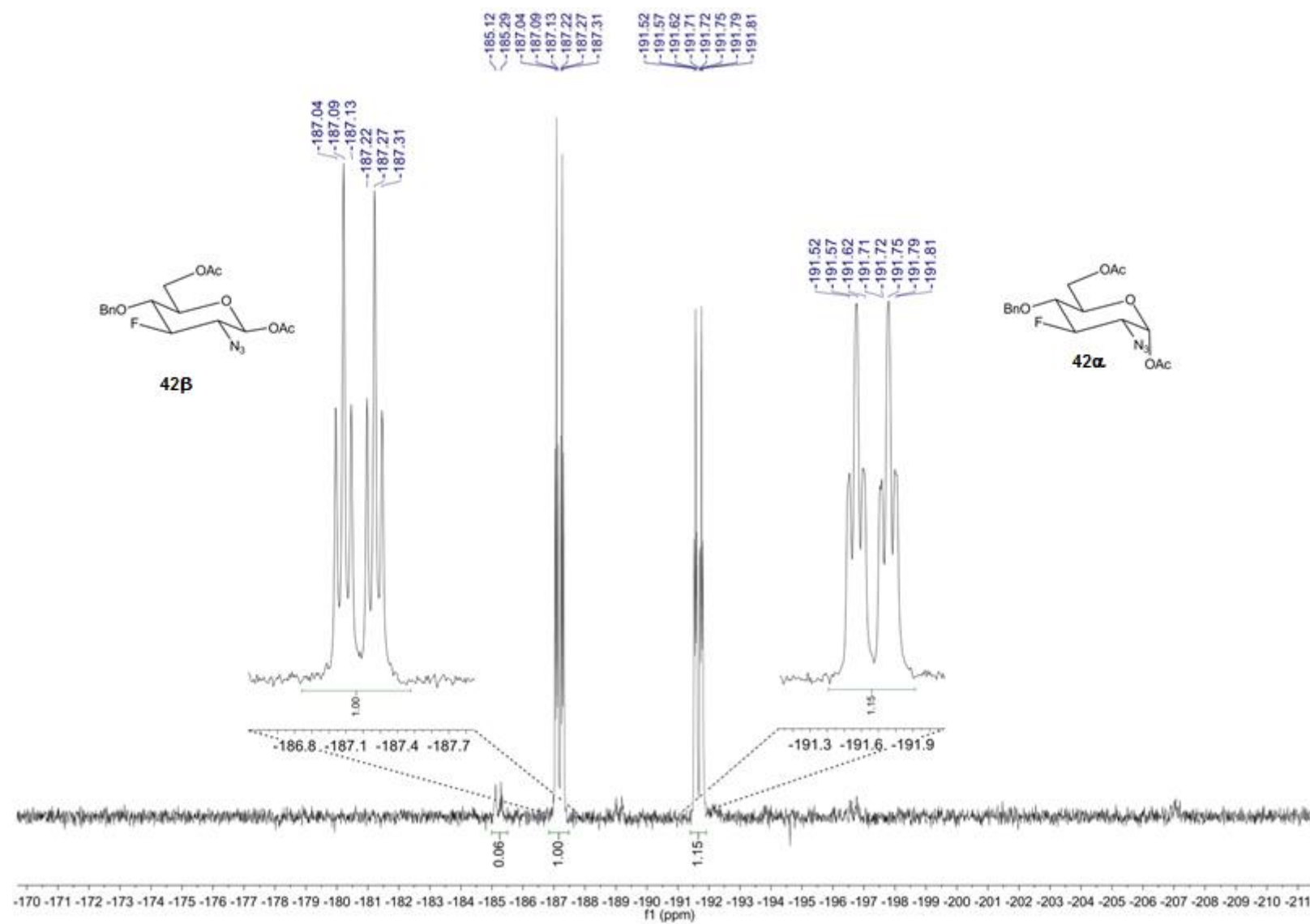
¹⁹F NMR (470 MHz, CDCl₃) of **42a** (α-anomer)



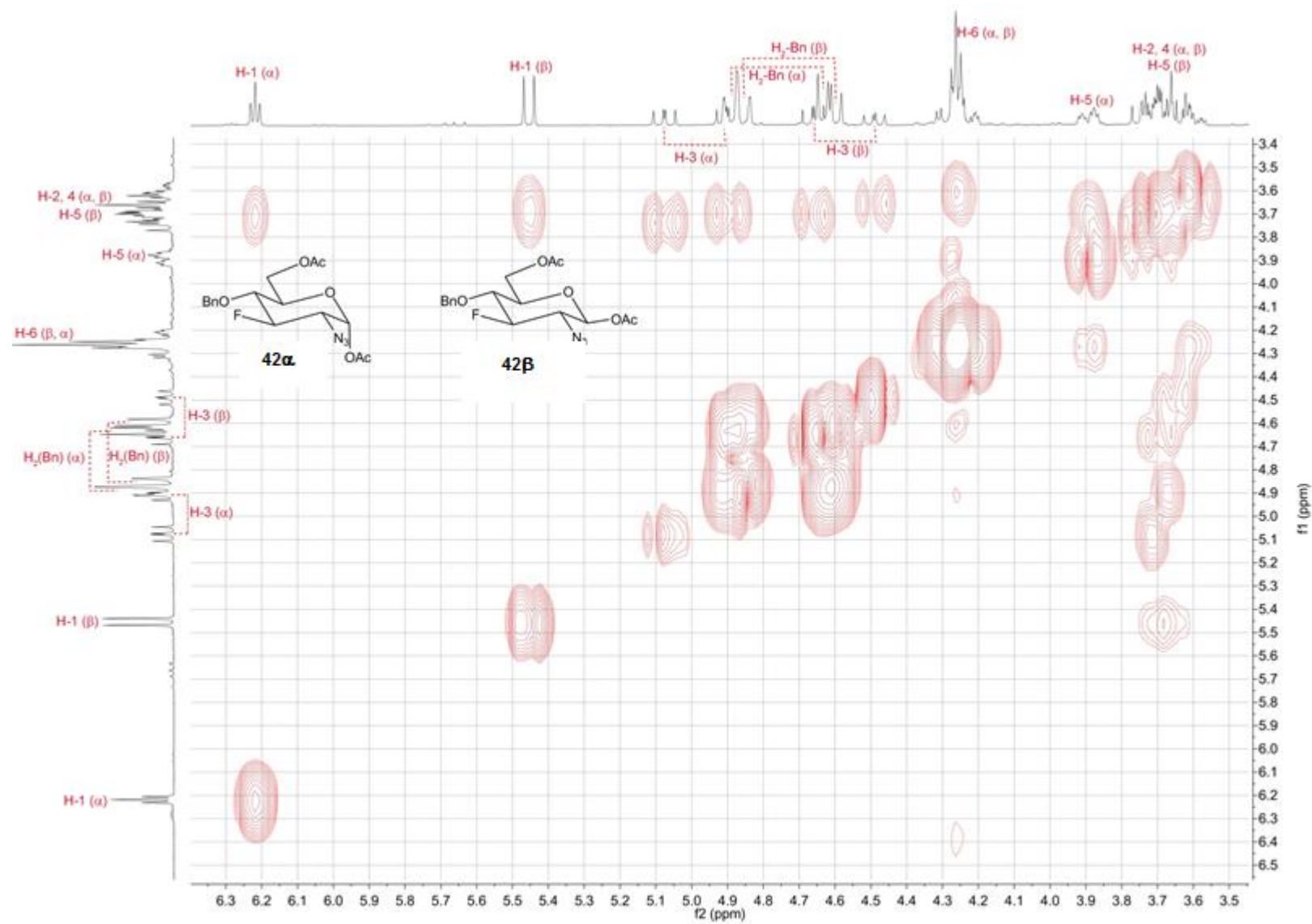
¹H NMR (300 MHz, CDCl₃) of **42** (α-anomer+β-anomer)



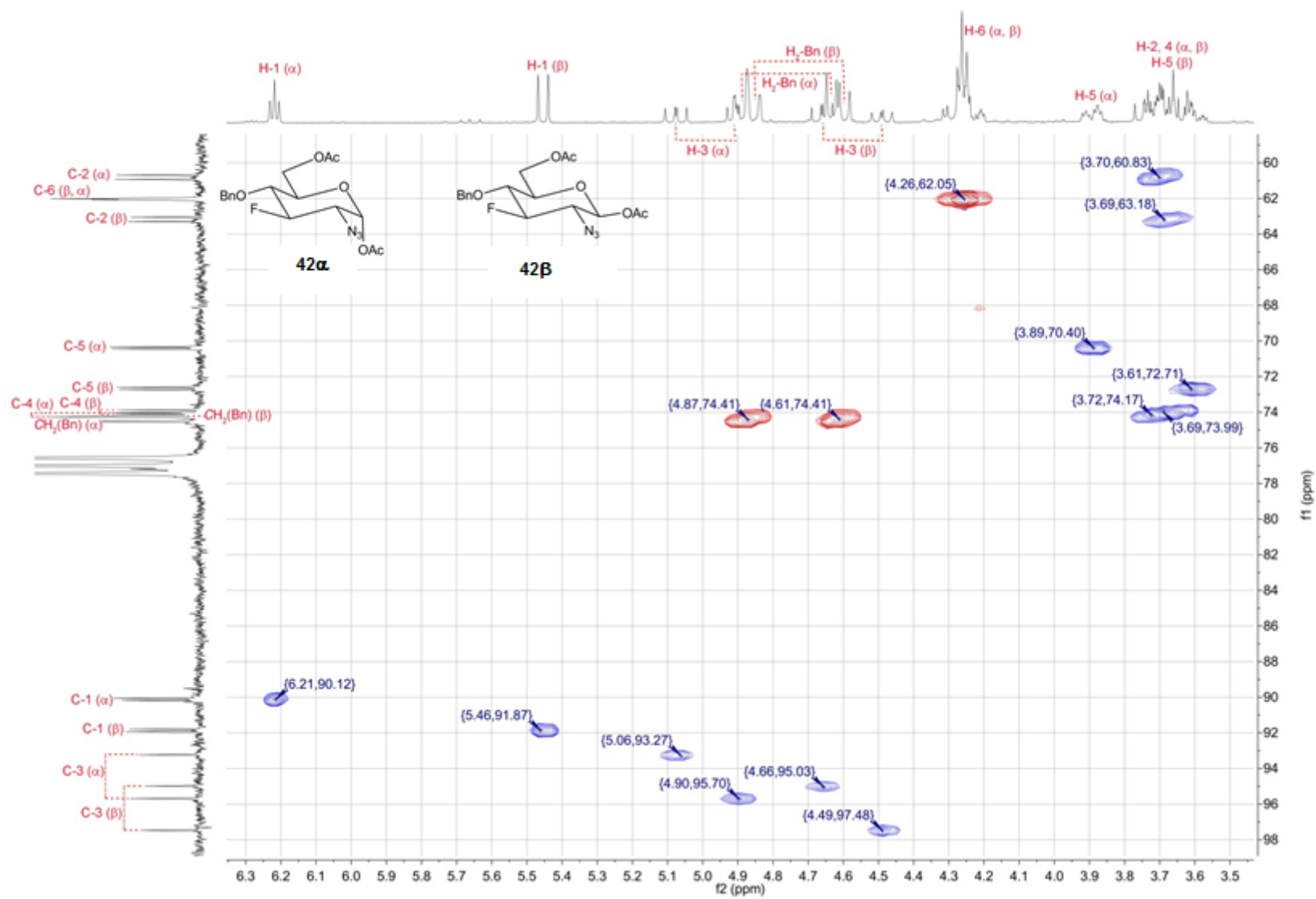
^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of **42** (α -anomer+ β -anomer)



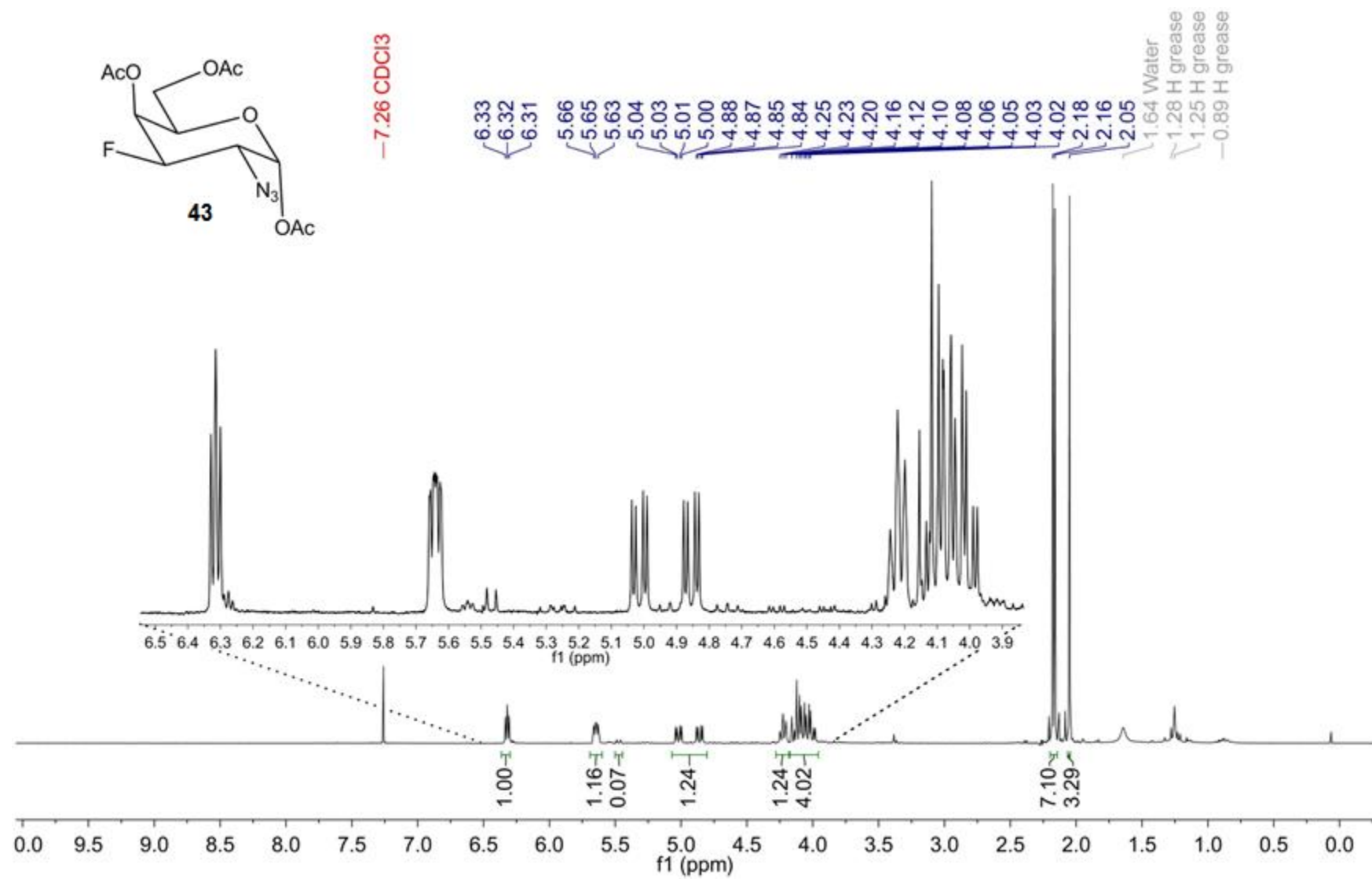
^{19}F NMR (282 MHz, CDCl_3) of **42** (α -anomer + β -anomer)



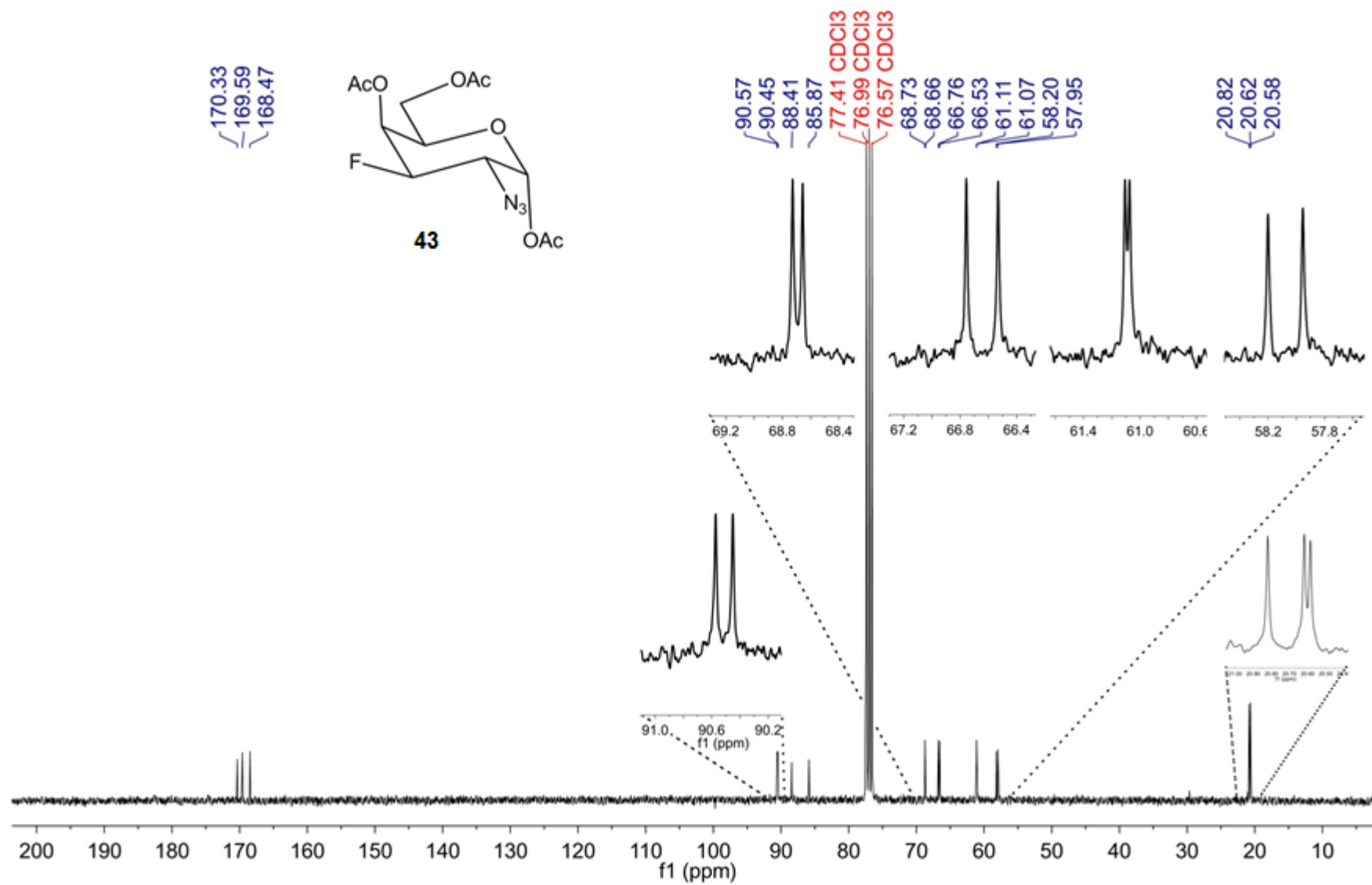
gCOSY NMR (300 MHz, CDCl₃) of **42** (α -anomer/ β -anomer ca 1:1)



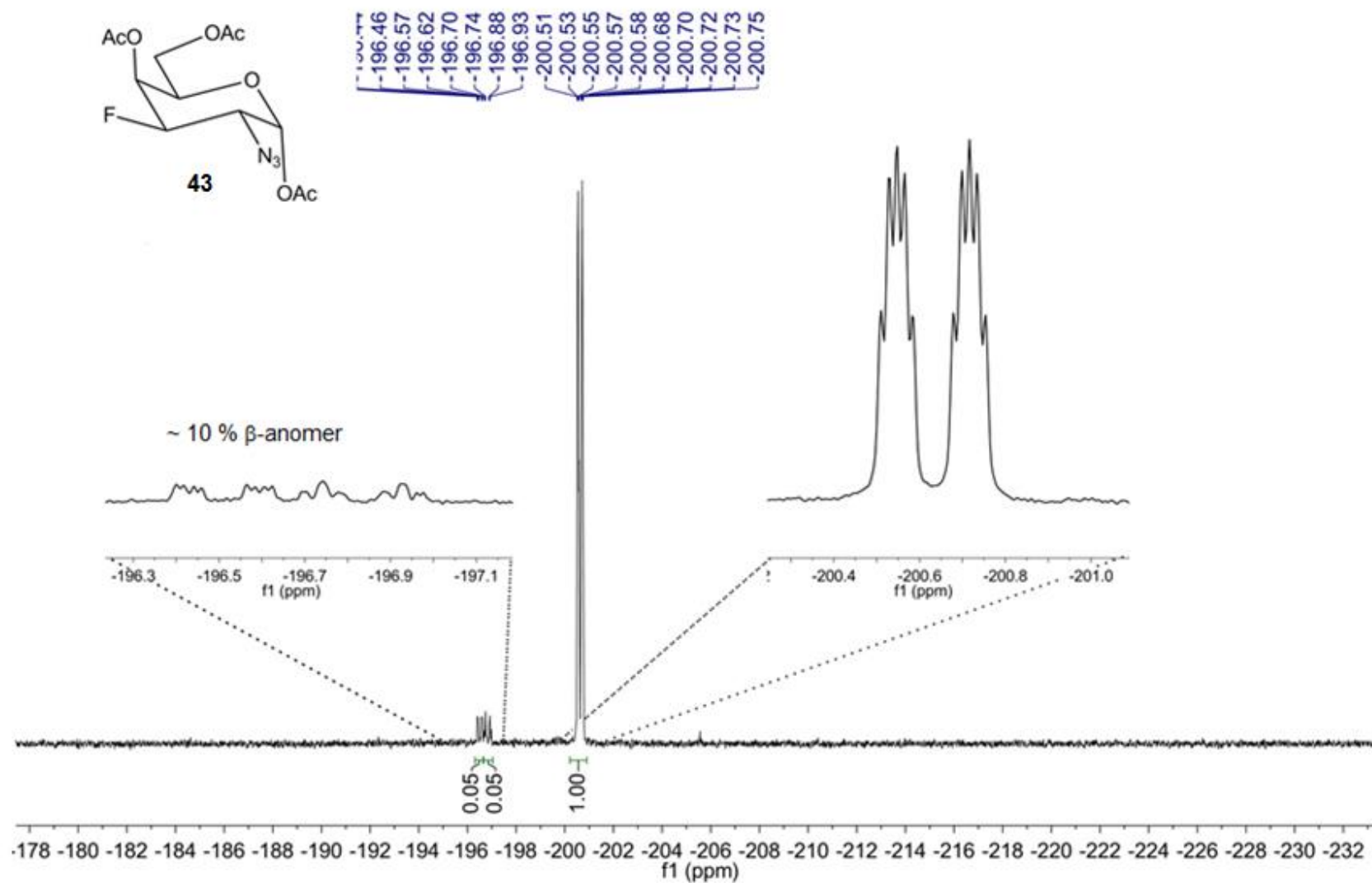
gHSQC NMR (300 MHz, CDCl₃) of **42** (α -anomer/ β -anomer ca 1:1)



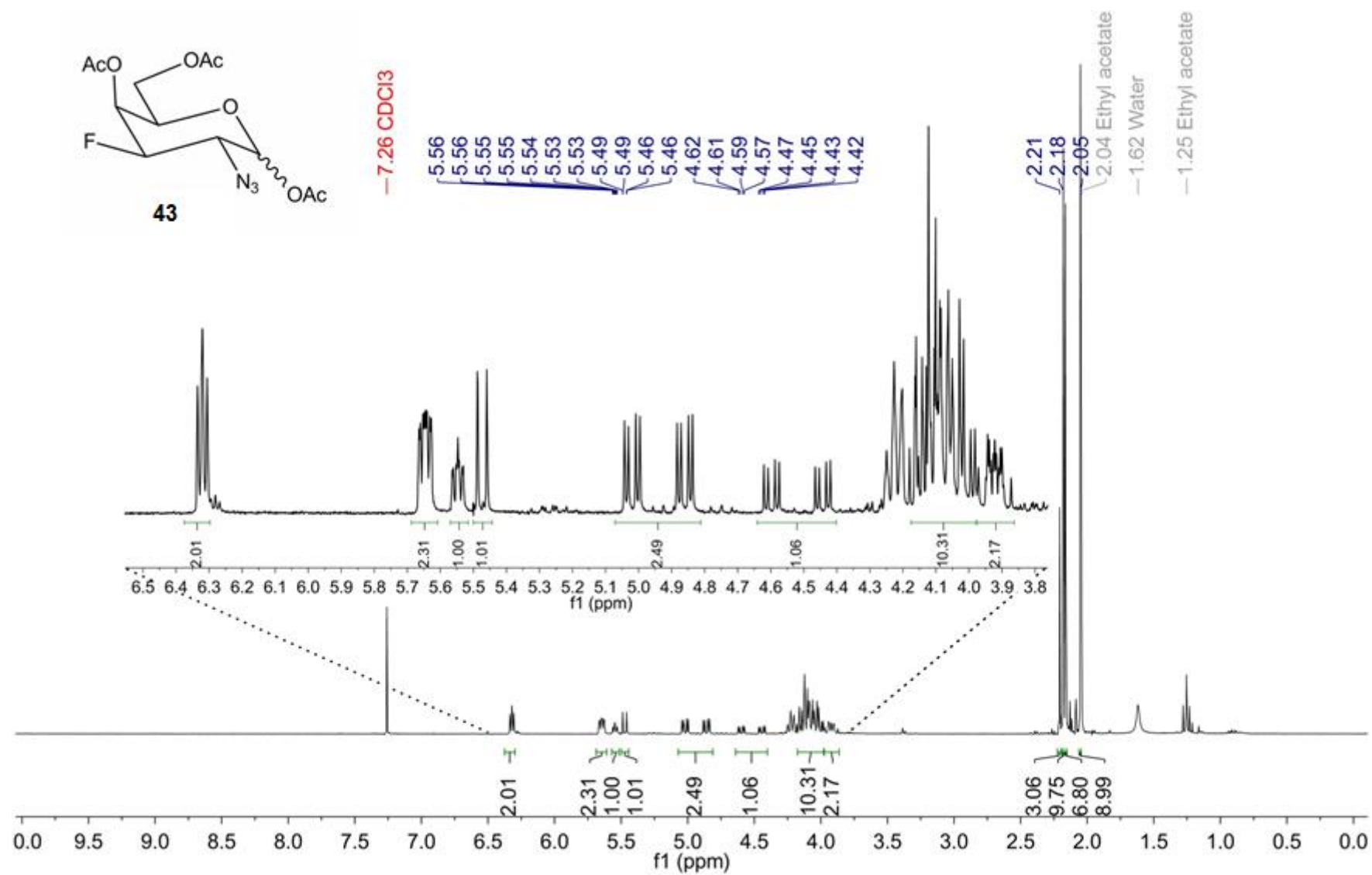
1H NMR (300 MHz, $CDCl_3$) of **43** (α -anomer and ca. 10% β -anomer)



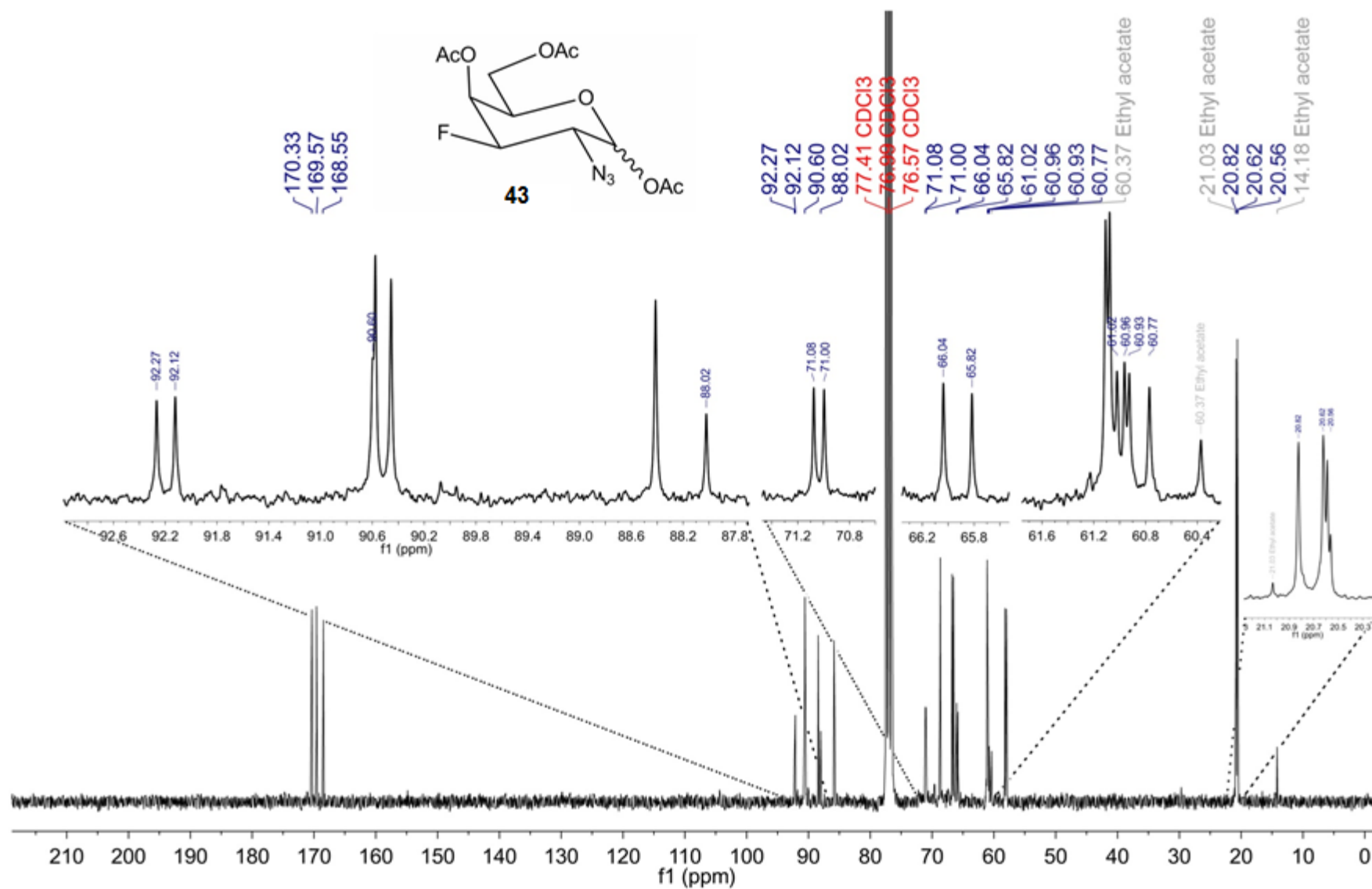
¹³C {¹H} NMR (75 MHz, CDCl₃) of **43** (α-anomer and ca. 10% β-anomer).



¹⁹F NMR (282 MHz, CDCl₃) of **43** (α-anomer and ca. 10% β-anomer)



¹H NMR (300 MHz, CDCl₃) of **43** (α/β ca 3:7)



¹³C {¹H} NMR (75 MHz, CDCl₃) of **43** (α/β ca 3:7)

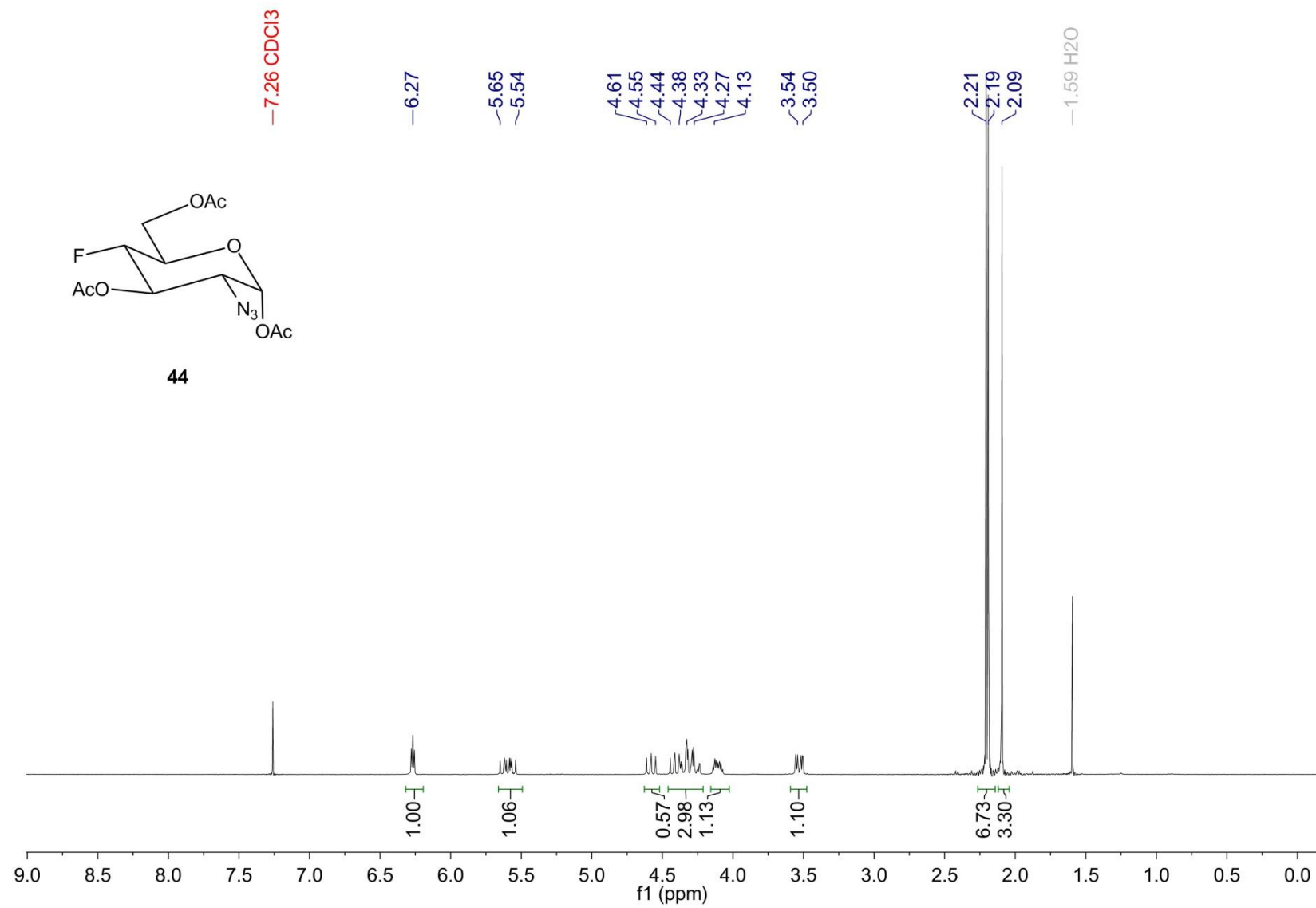


Figure SII-90. ¹H NMR (300 MHz, CDCl₃) of **44** (α-anomer)

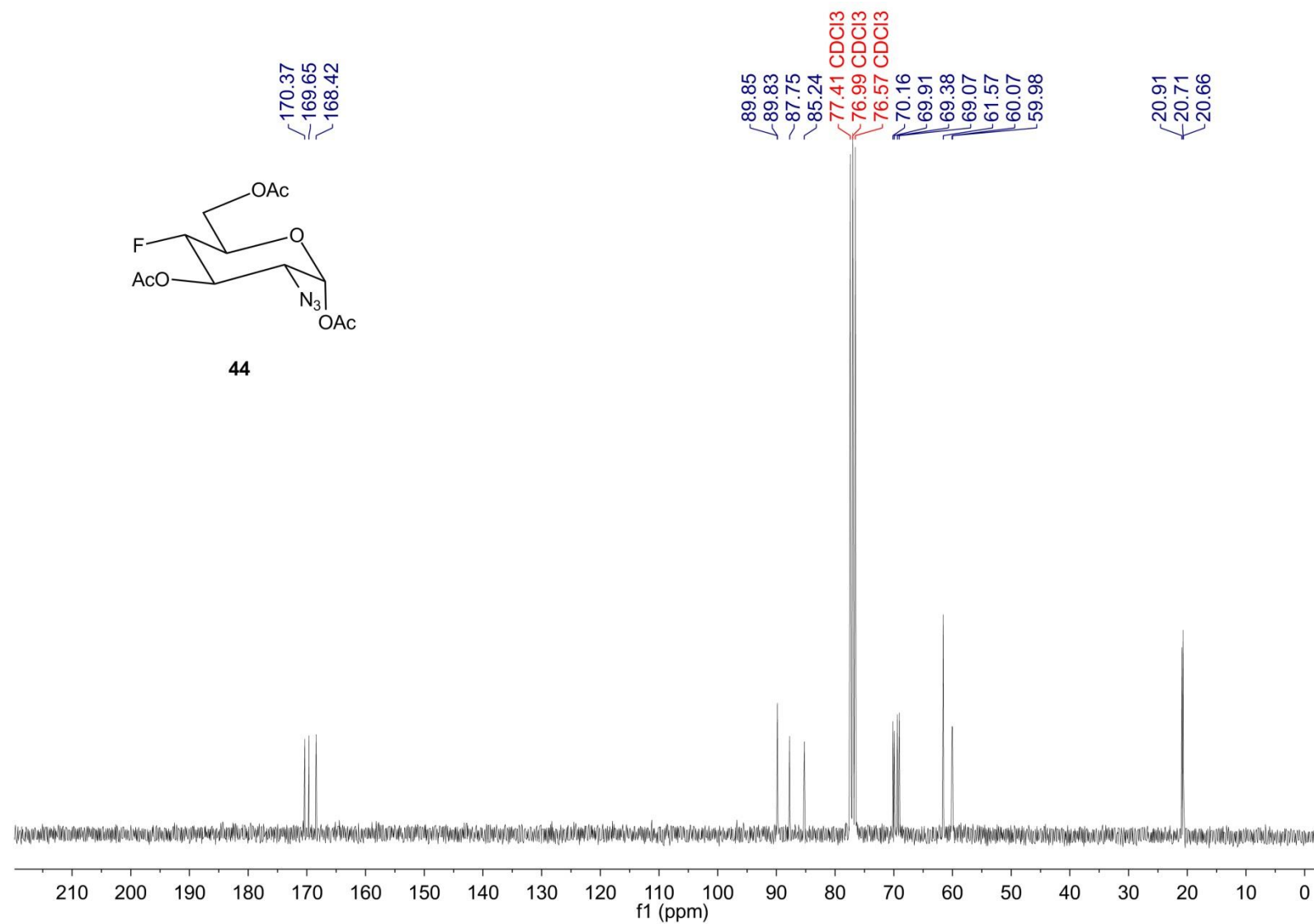
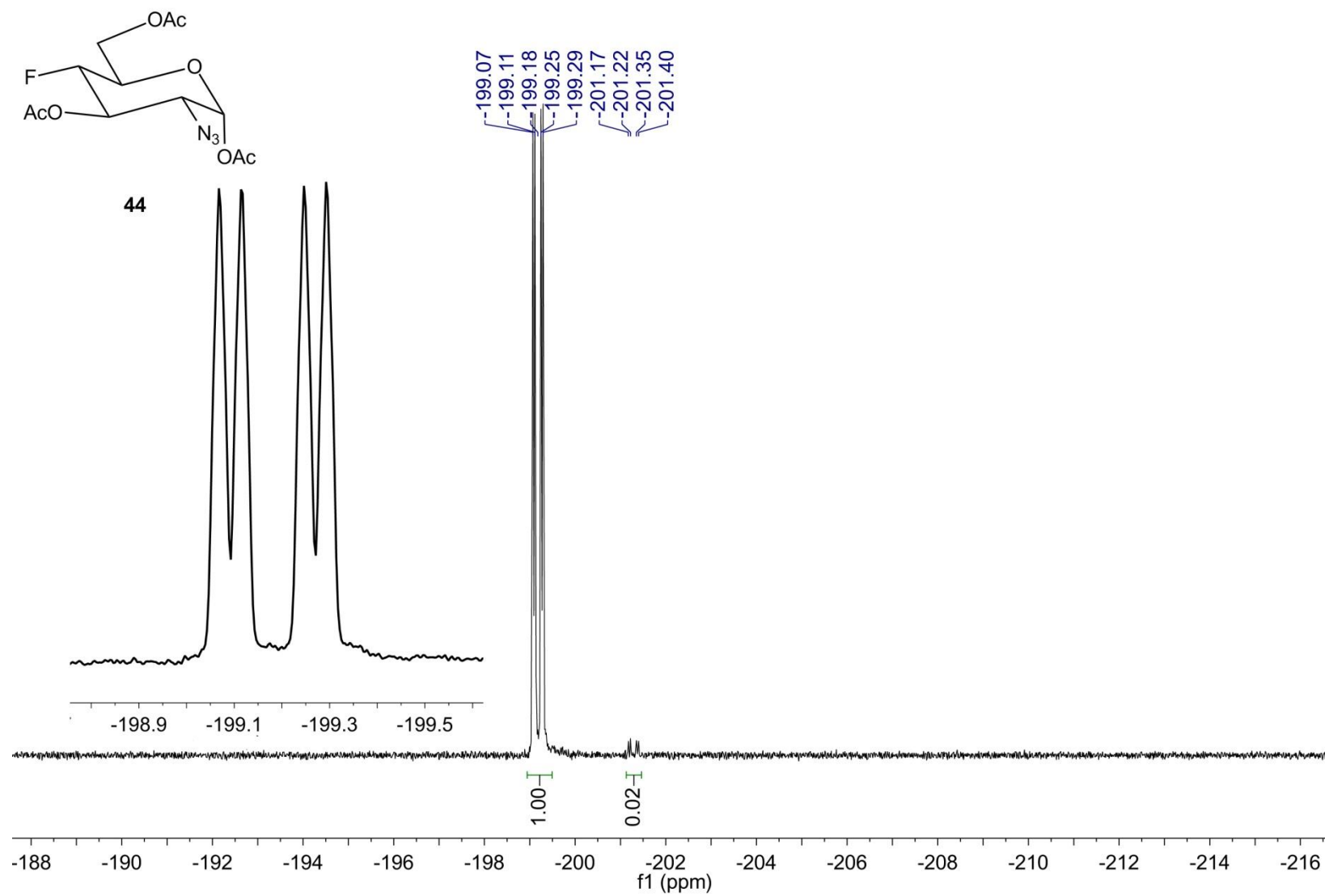
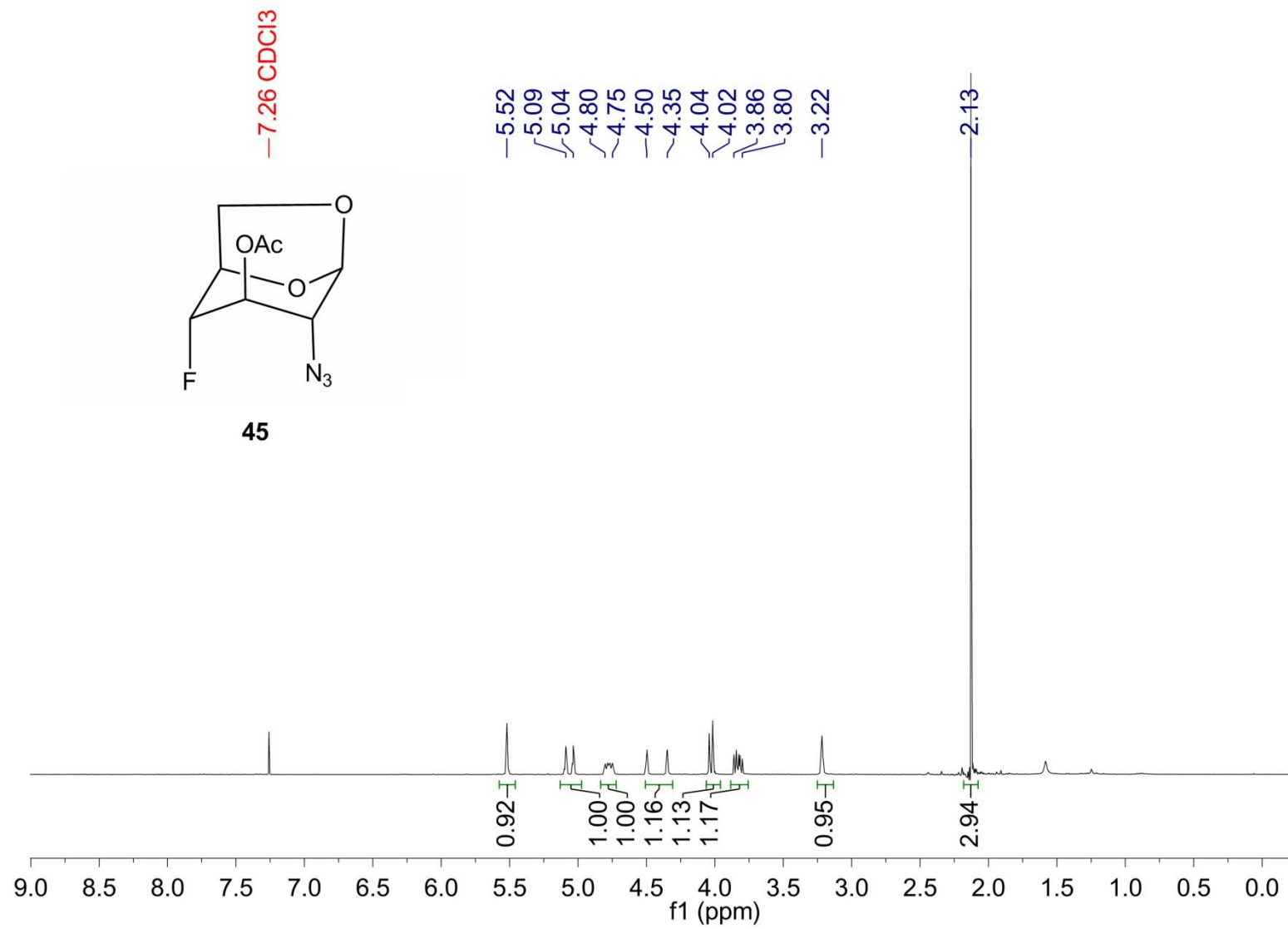


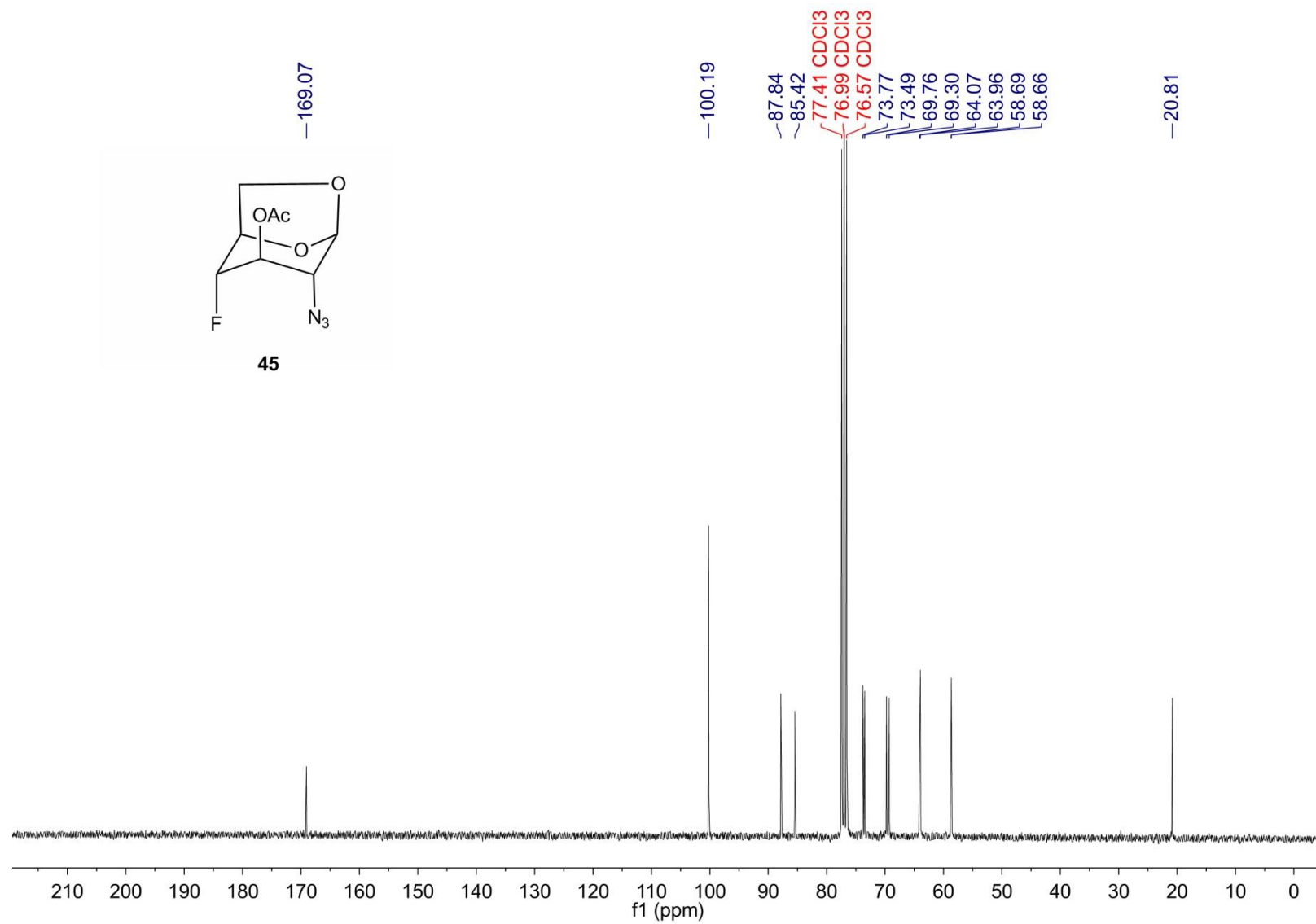
Figure SII-91. ¹³C {¹H} NMR (75 MHz, CDCl₃) of **44** (α-anomer)



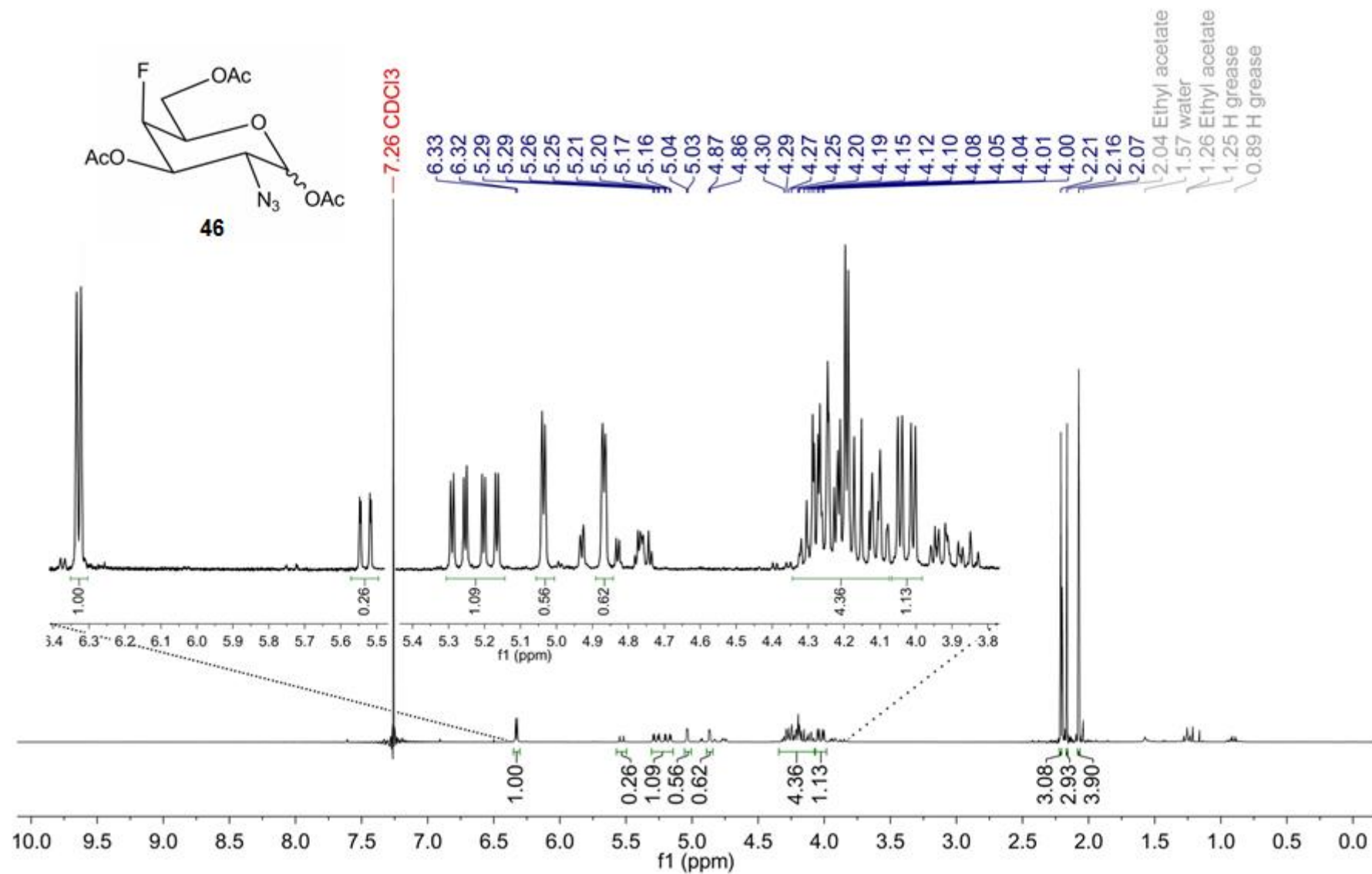
^{19}F NMR (282 MHz, CDCl_3) of **44** (α -anomer)



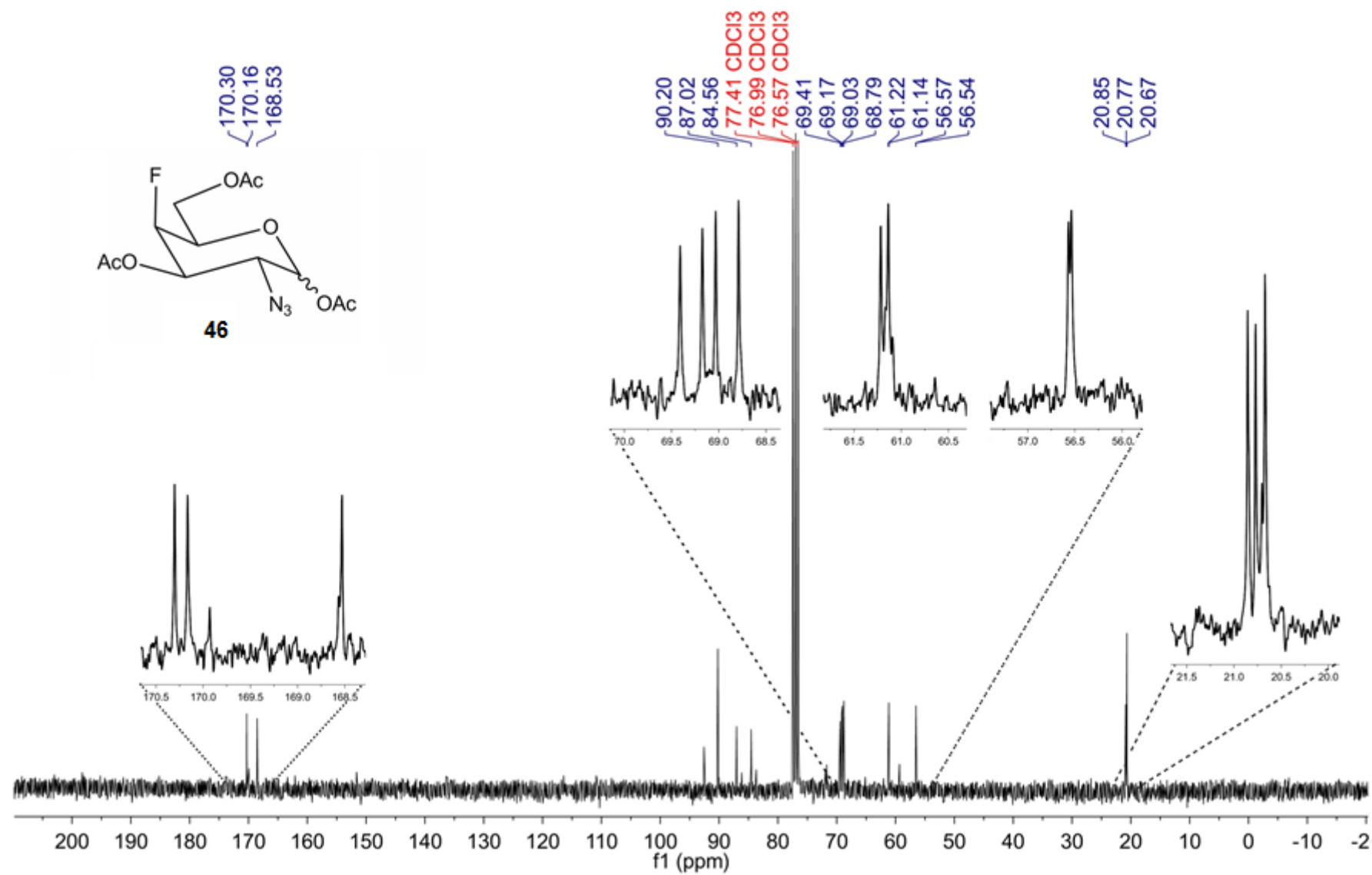
¹H NMR (300 MHz, CDCl₃) of **45**



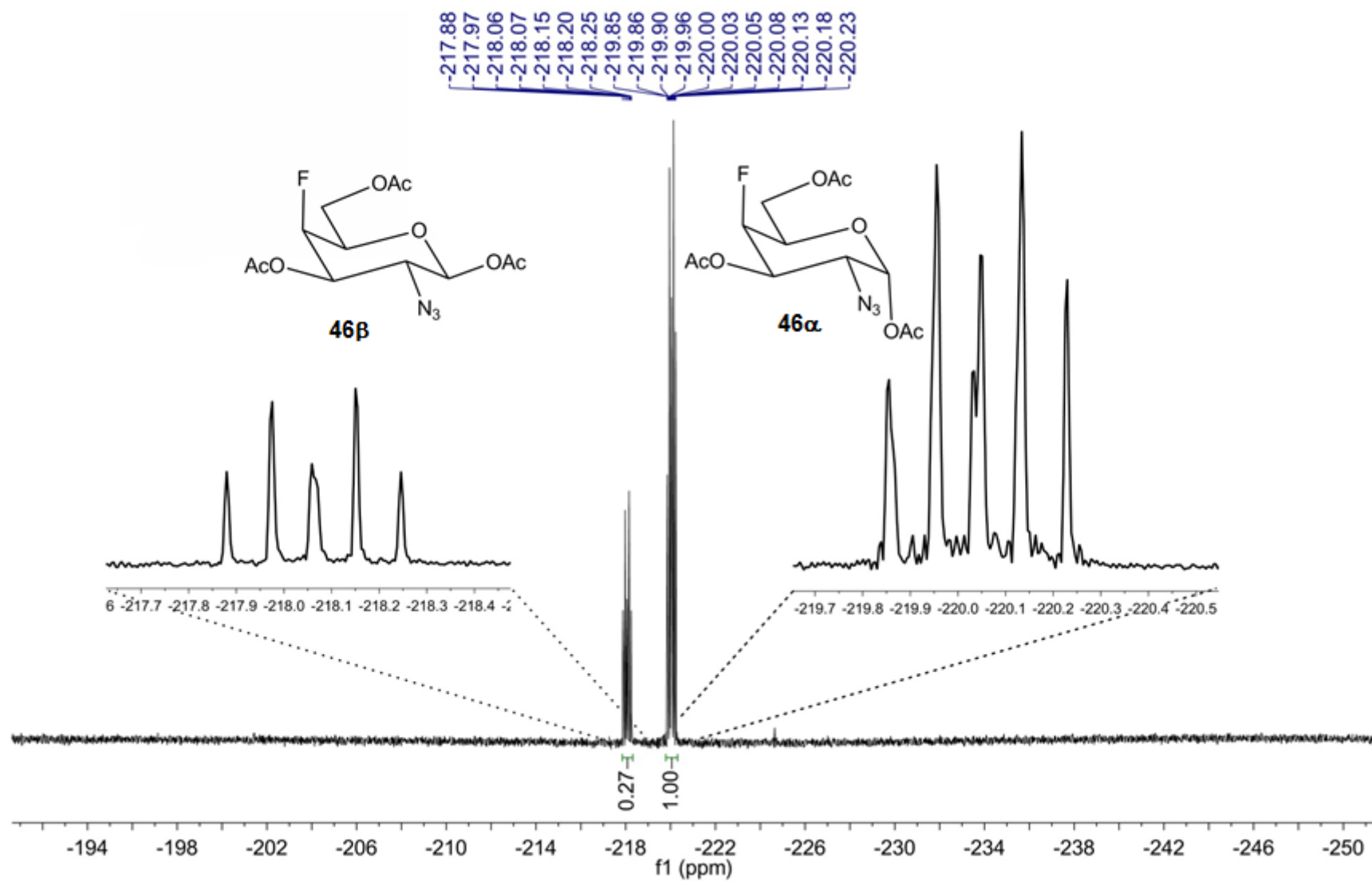
¹³C {¹H} NMR (75 MHz, CDCl₃) of **45**



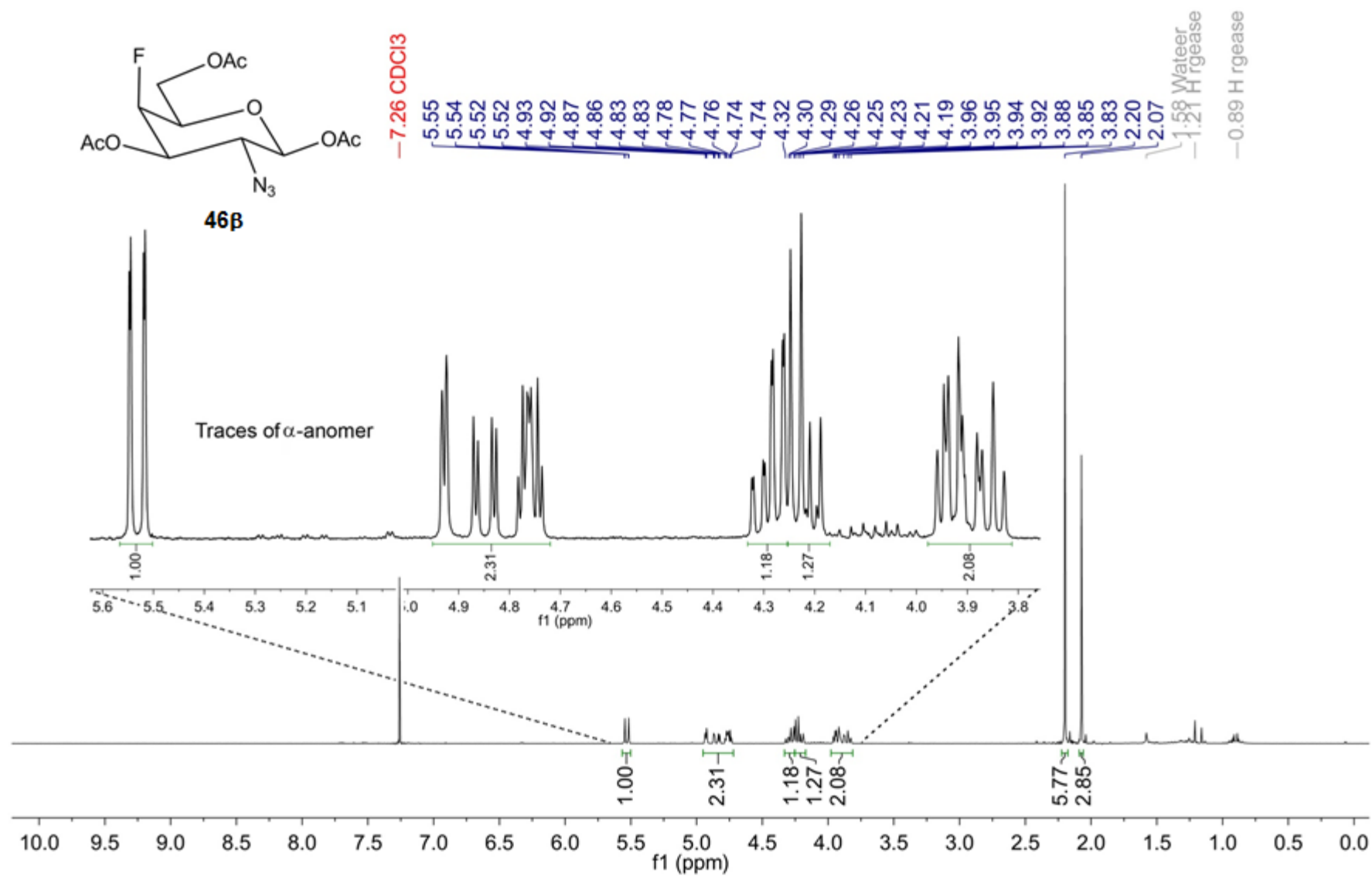
¹H NMR (300 MHz, CDCl₃) of **46** (α-anomer/β-anomer ca 1:0.3)



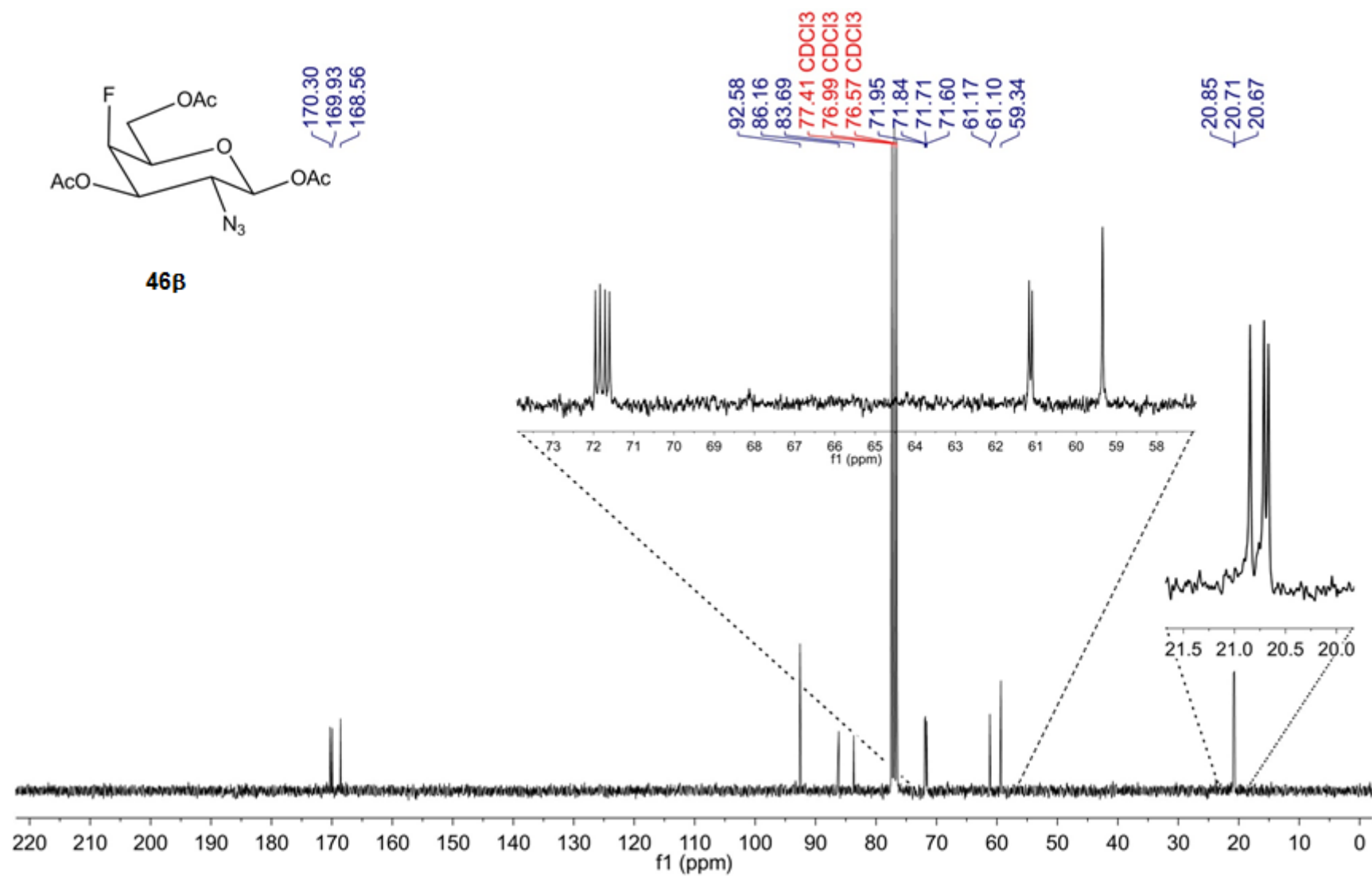
^{13}C { ^1H } NMR (75 MHz, CDCl_3) of **46** (α -anomer/ β -anomer ca 1:0.3)



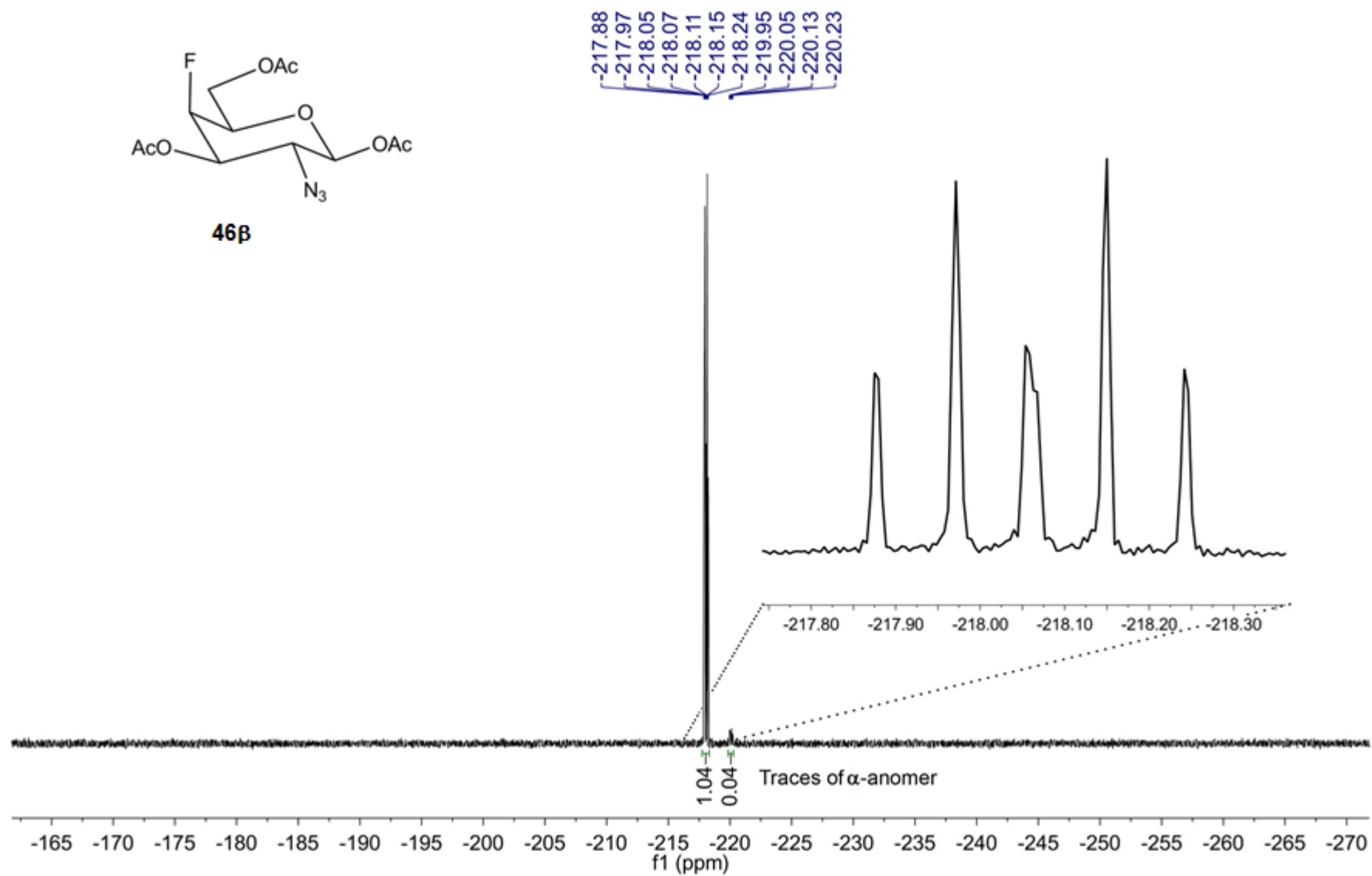
^{19}F NMR (282 MHz, CDCl_3) of **46** (α -anomer/ β -anomer ca 1:0.3)



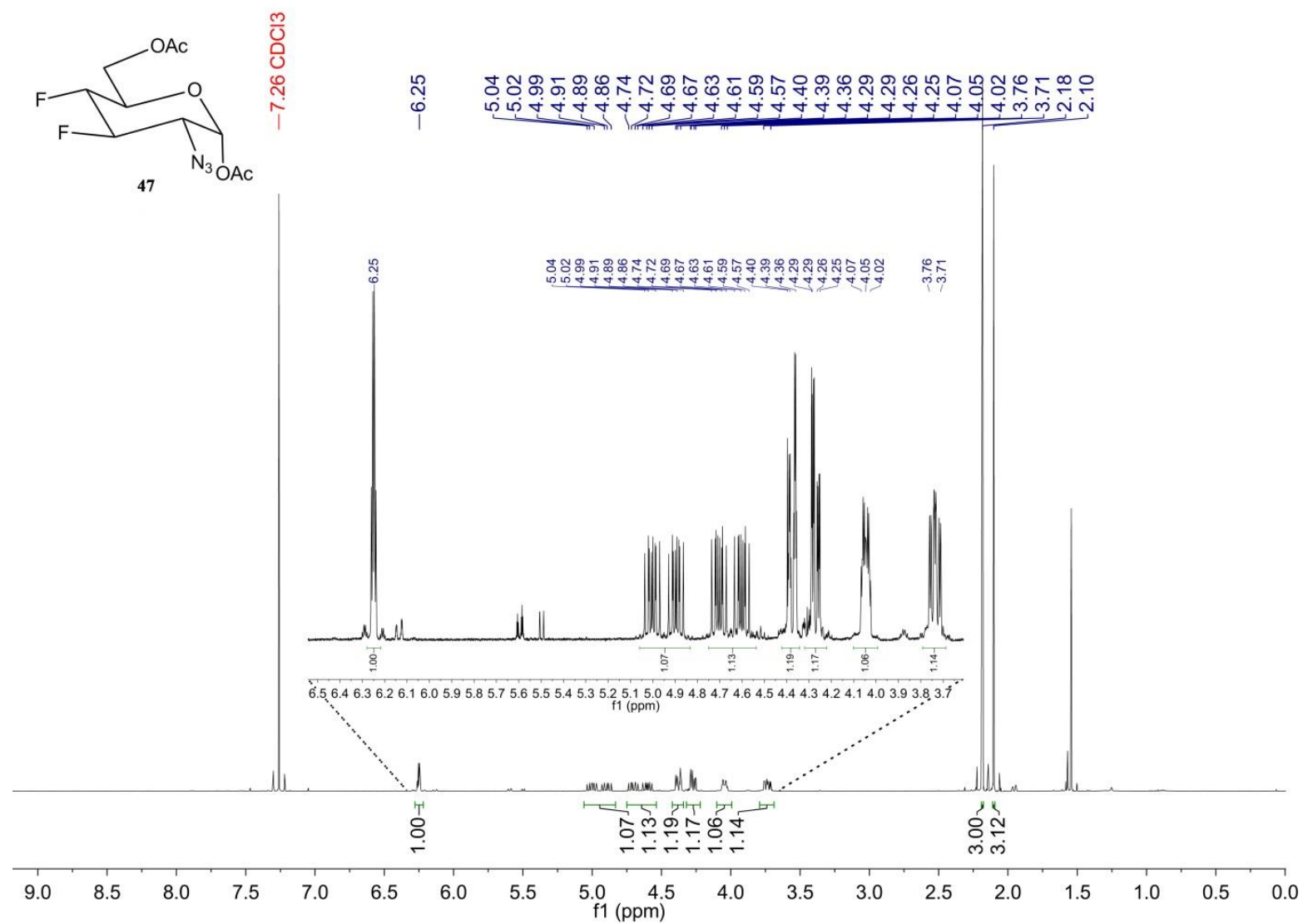
1H NMR (300 MHz, $CDCl_3$) of **46 β** (β -anomer)



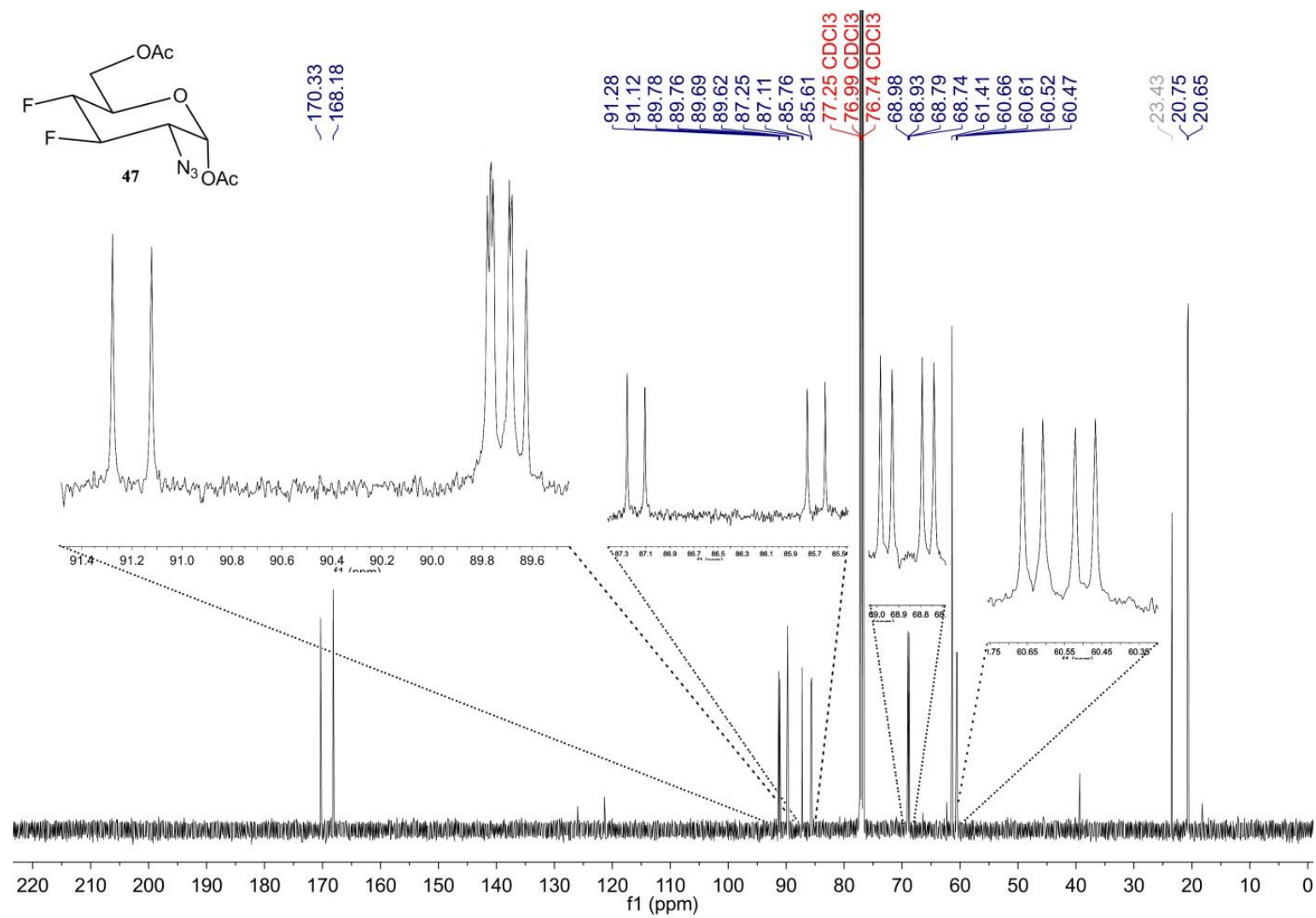
^{13}C { 1H } NMR (75 MHz, $CDCl_3$) of **46β** (β-anomer)



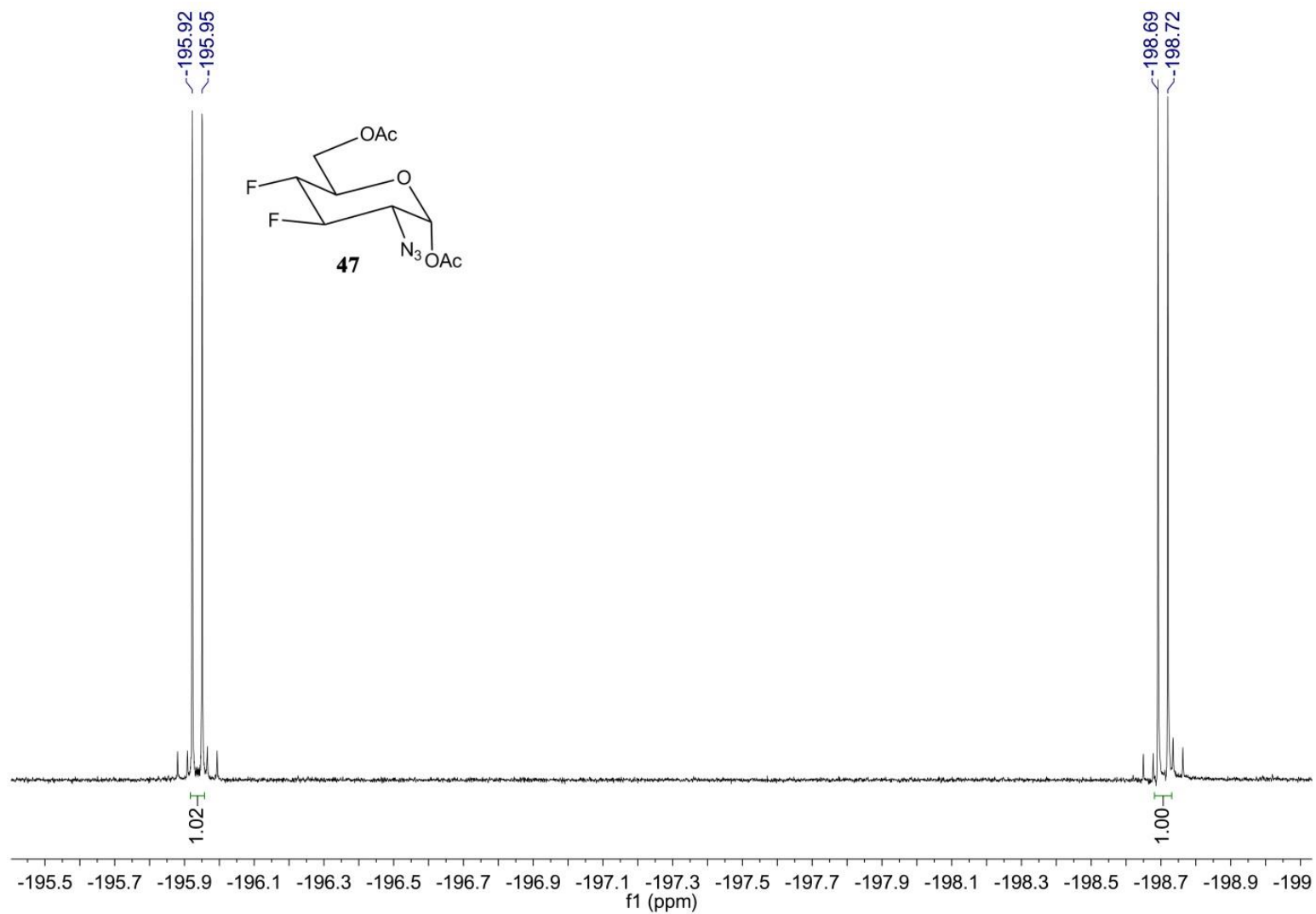
¹⁹F NMR (282 MHz, CDCl₃) of **46** (β-anomer + ca 4% α-anomer)



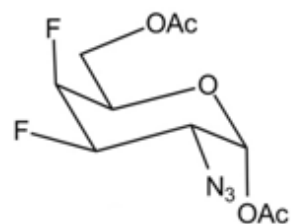
¹H {¹⁹F} NMR (500 MHz, CDCl₃) of **47** (α-anomer), ca 5% impurities



¹³C {¹H} NMR (125 MHz, CDCl₃) of **47**. (α-anomer), ca 5% impurities

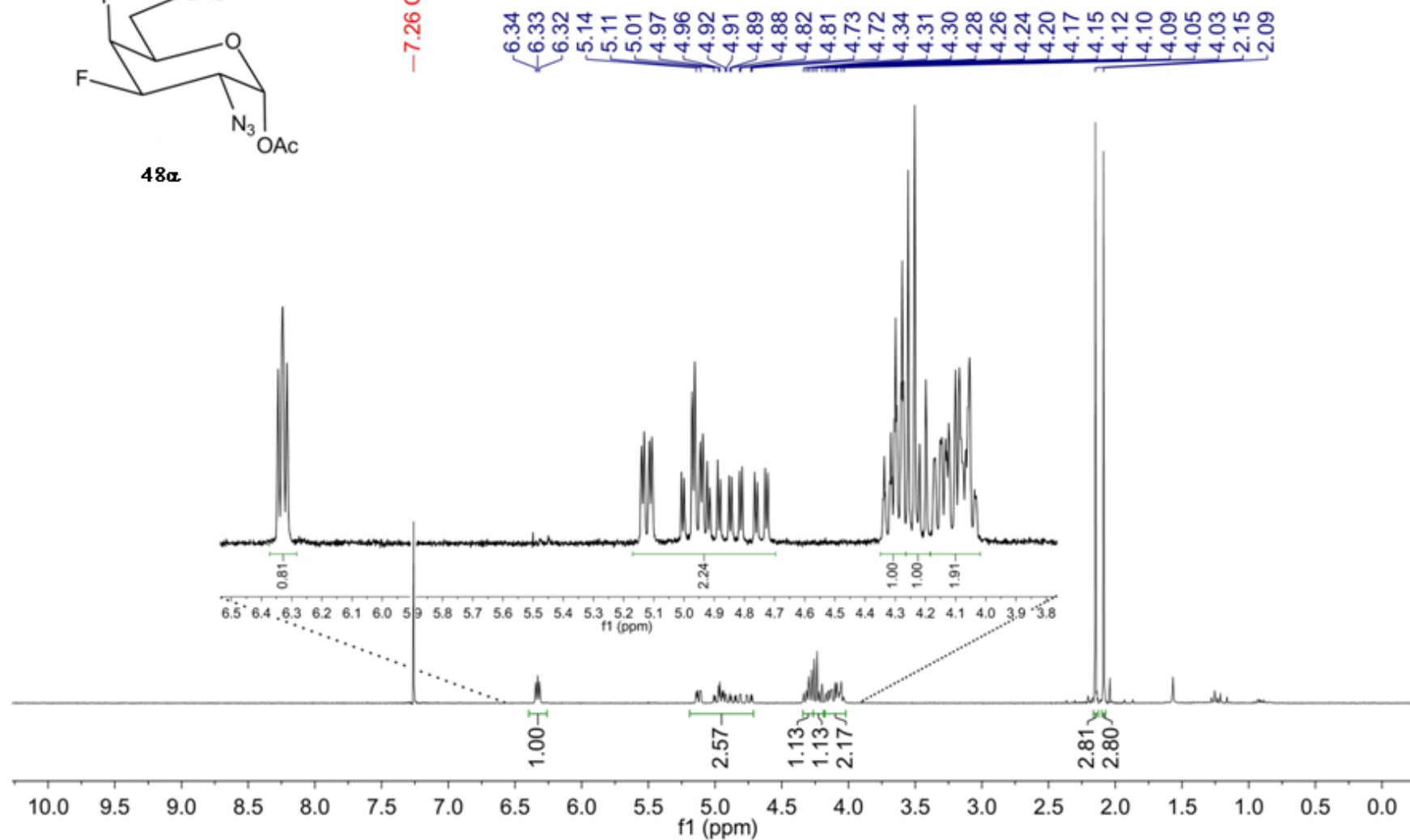


¹⁹F {¹H} NMR (470 MHz, CDCl₃) of **47**. (α -anomer), ca 5% impurities

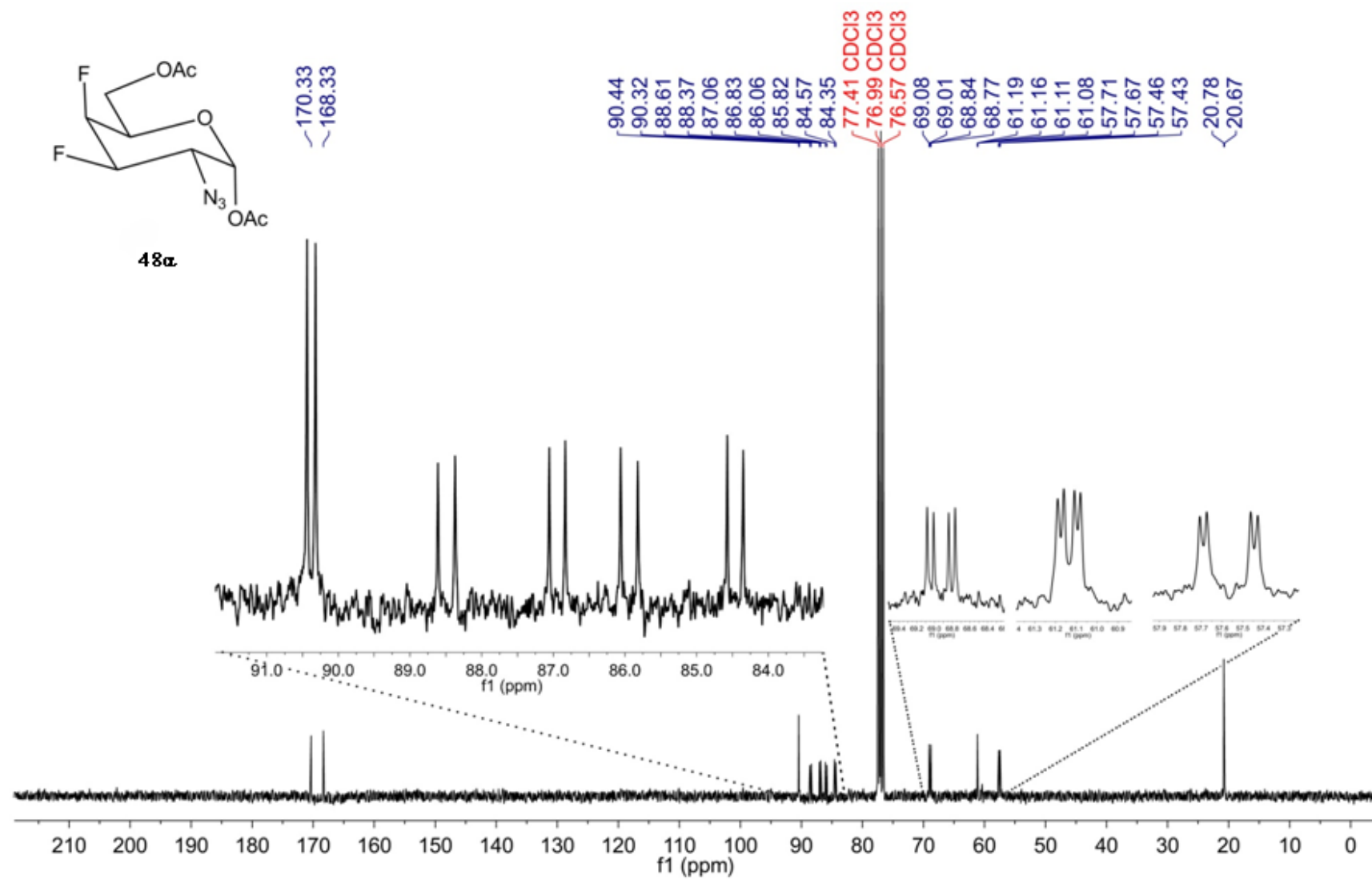


48 α

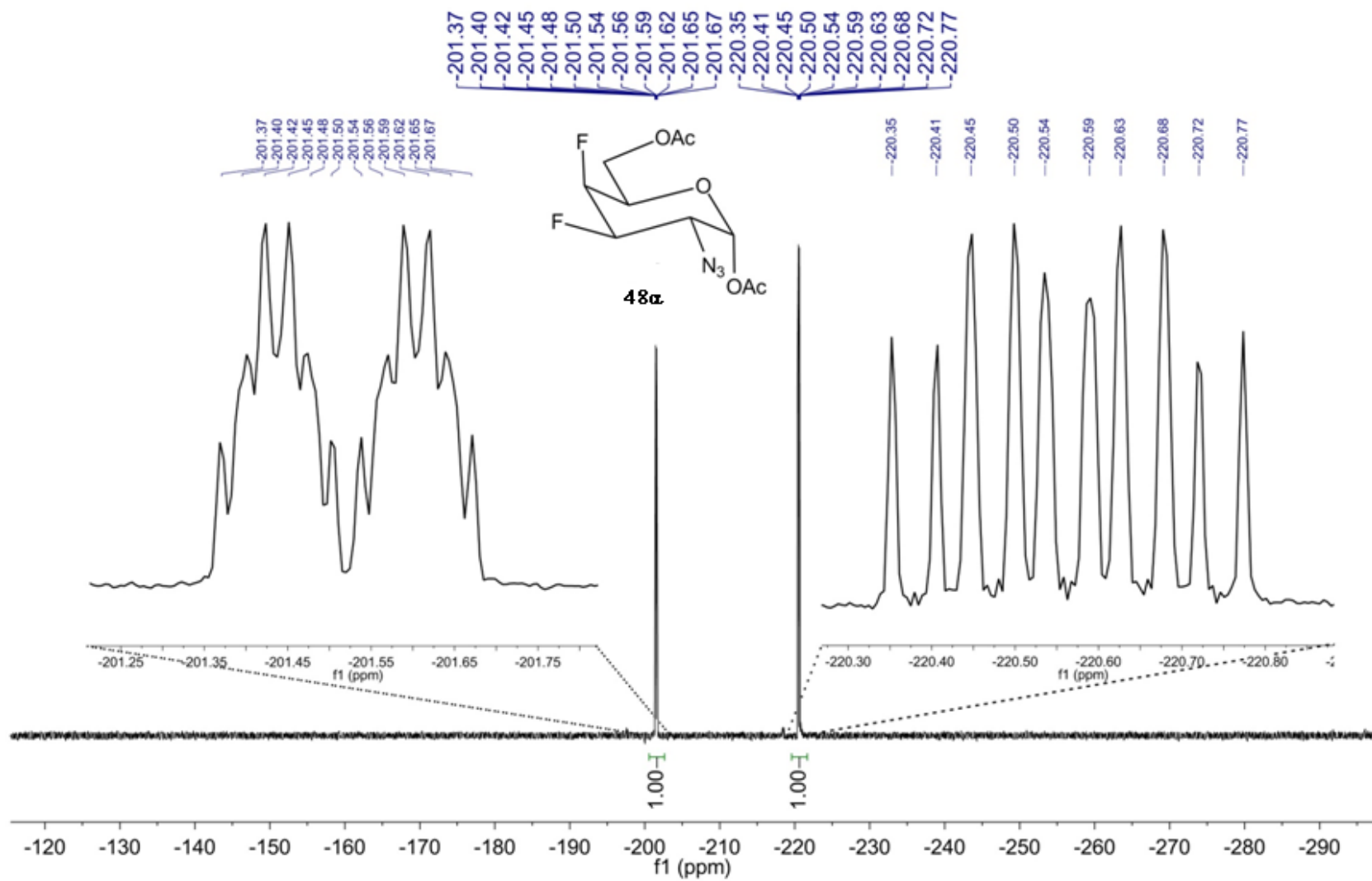
—7.26 CDCl₃



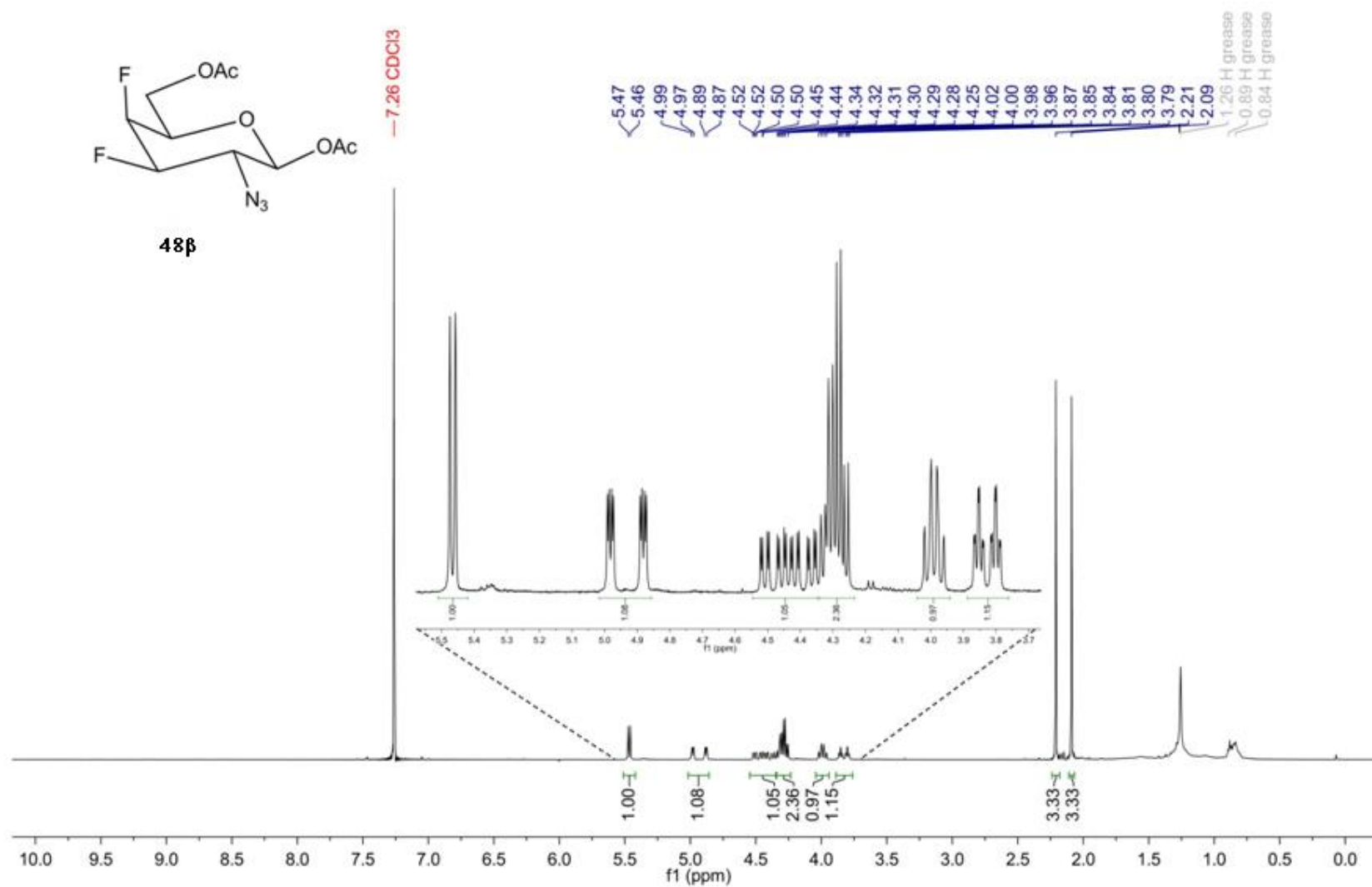
¹H NMR (300 MHz, CDCl₃) of **48** (α -anomer)



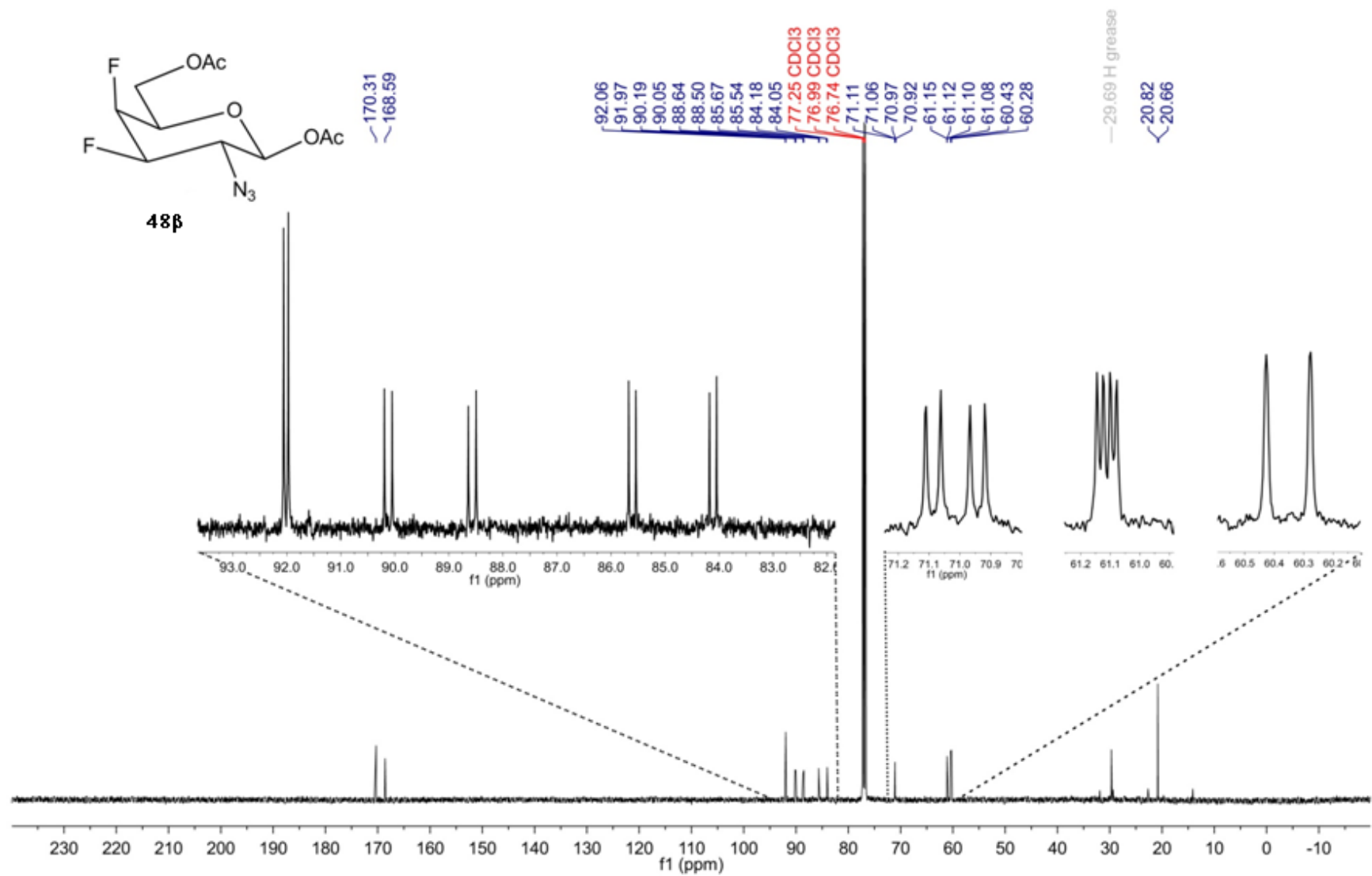
¹³C {¹H} NMR (75 MHz, CDCl₃) of **48** (α-anomer)



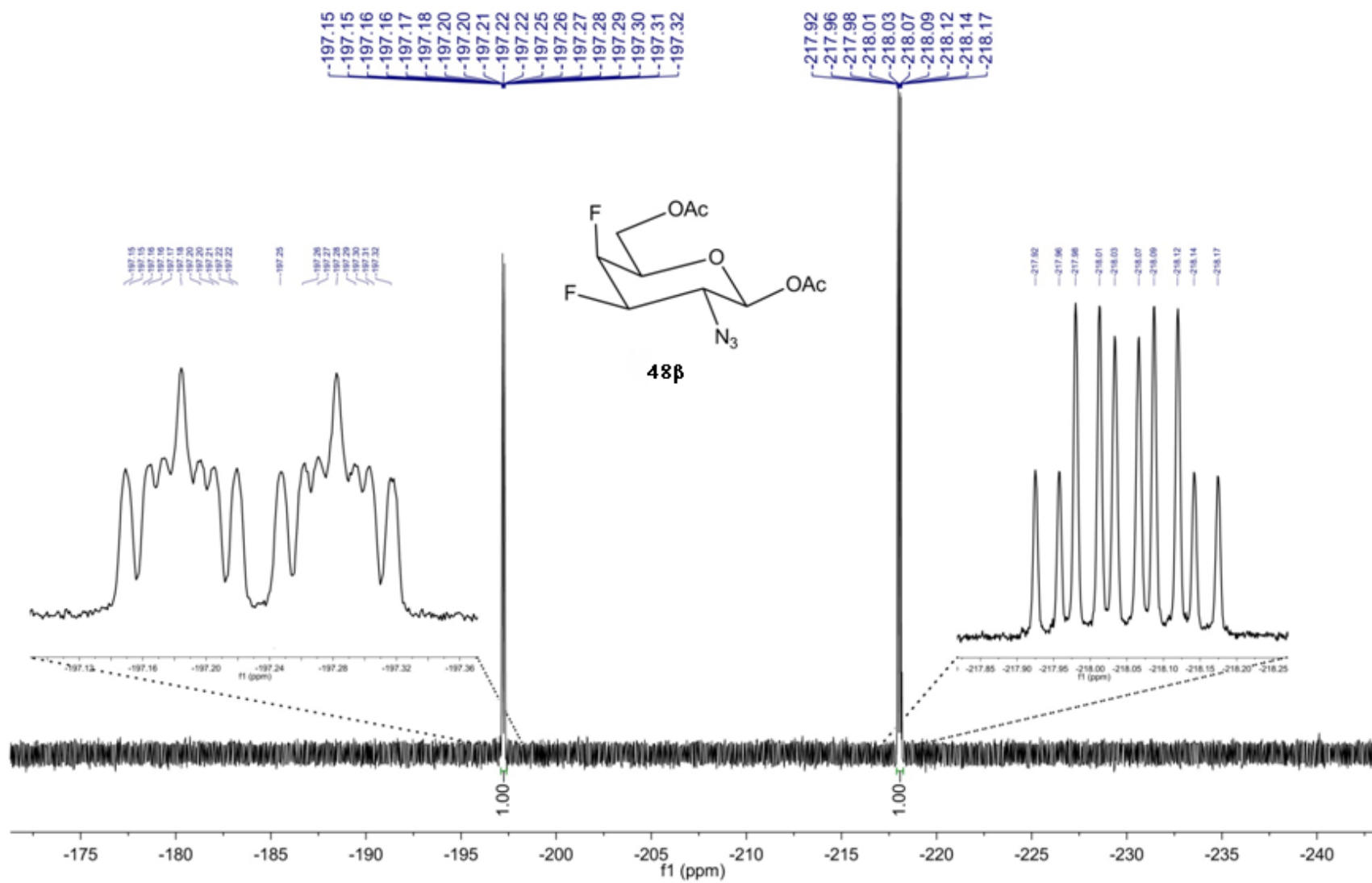
^{19}F NMR (282 MHz, CDCl_3) of **48** (α -anomer)



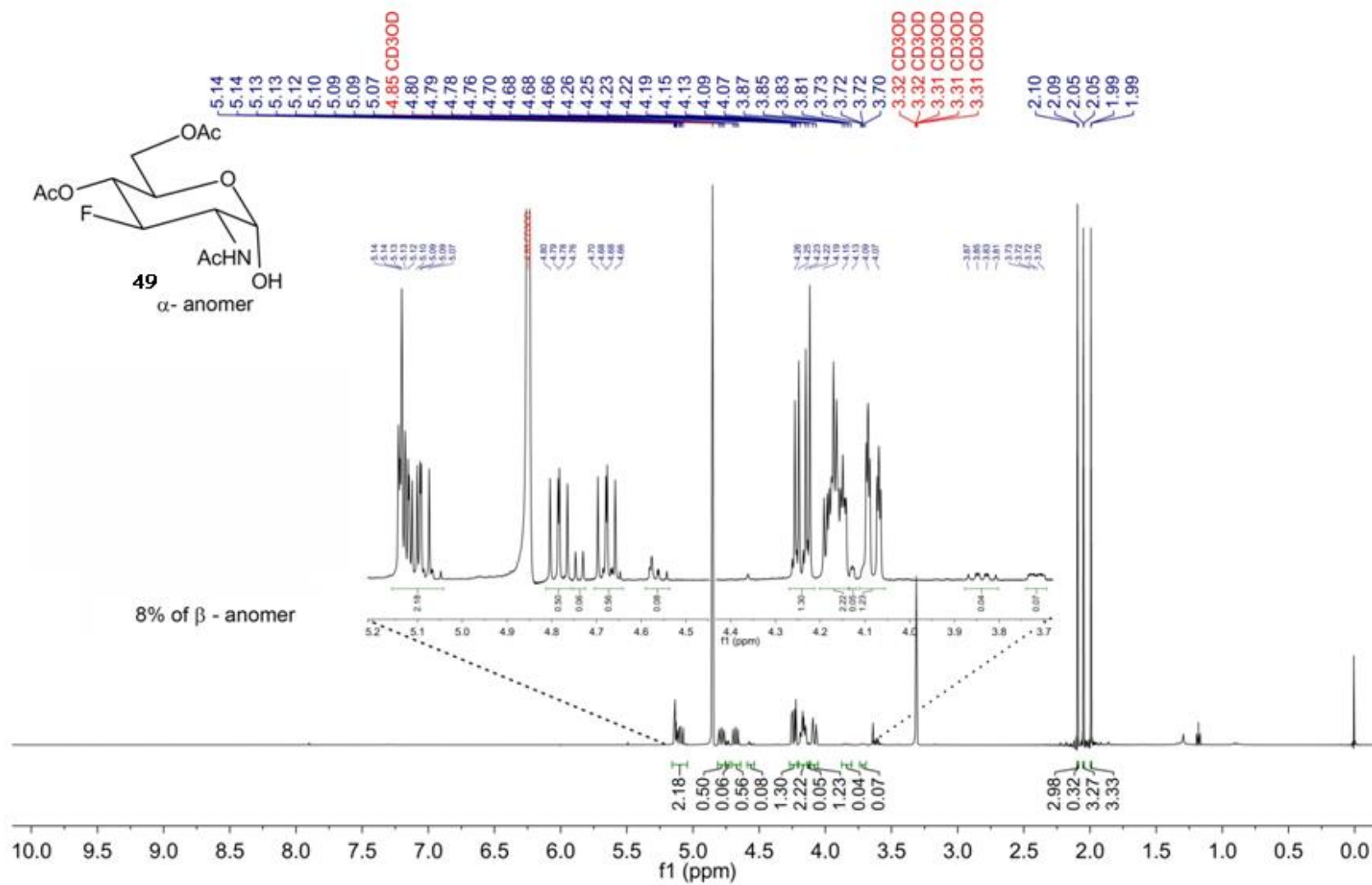
¹H NMR (500 MHz, CDCl₃) of **48** (β-anomer)



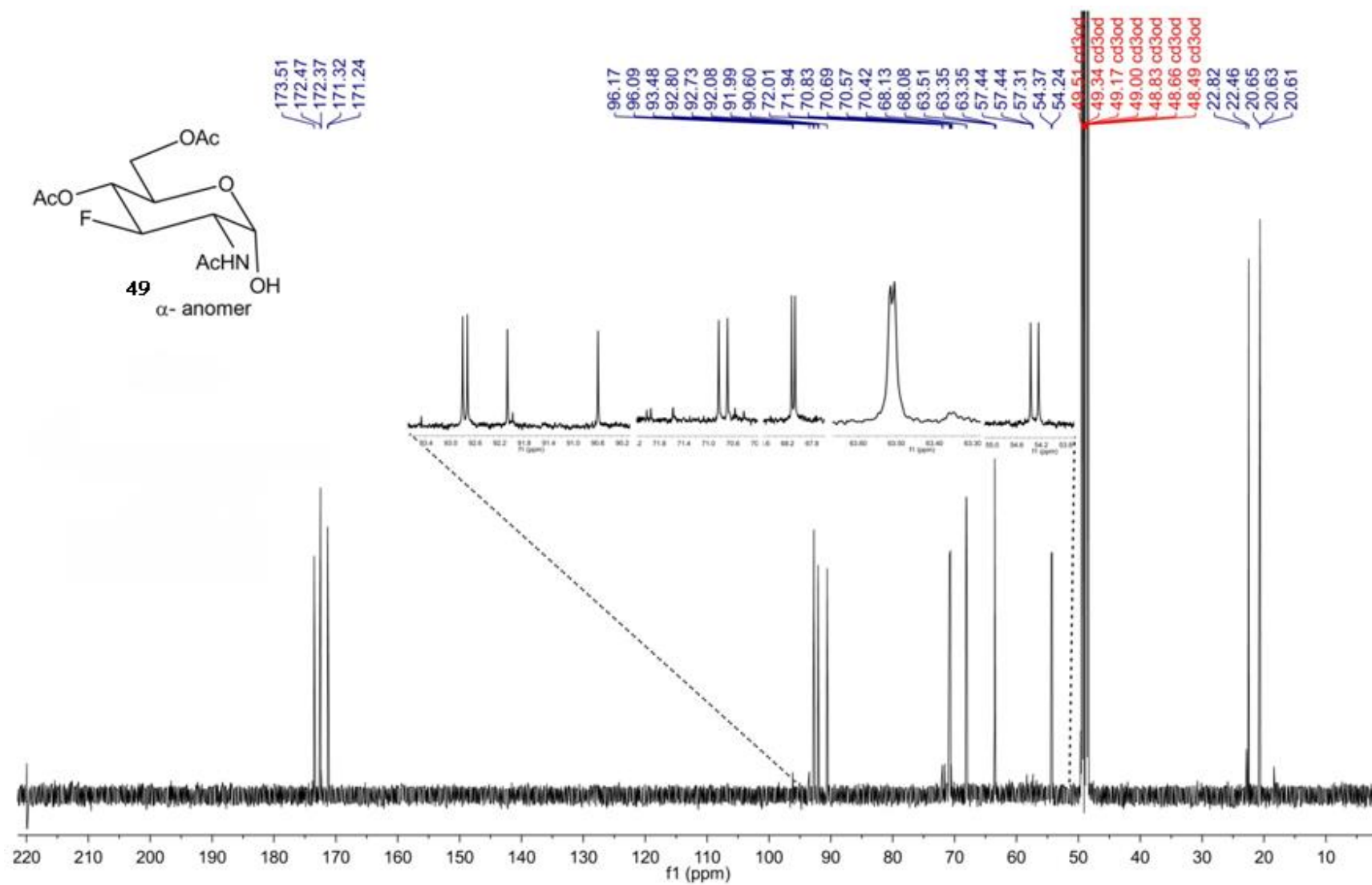
$^{13}\text{C} \{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of **48** (β -anomer)



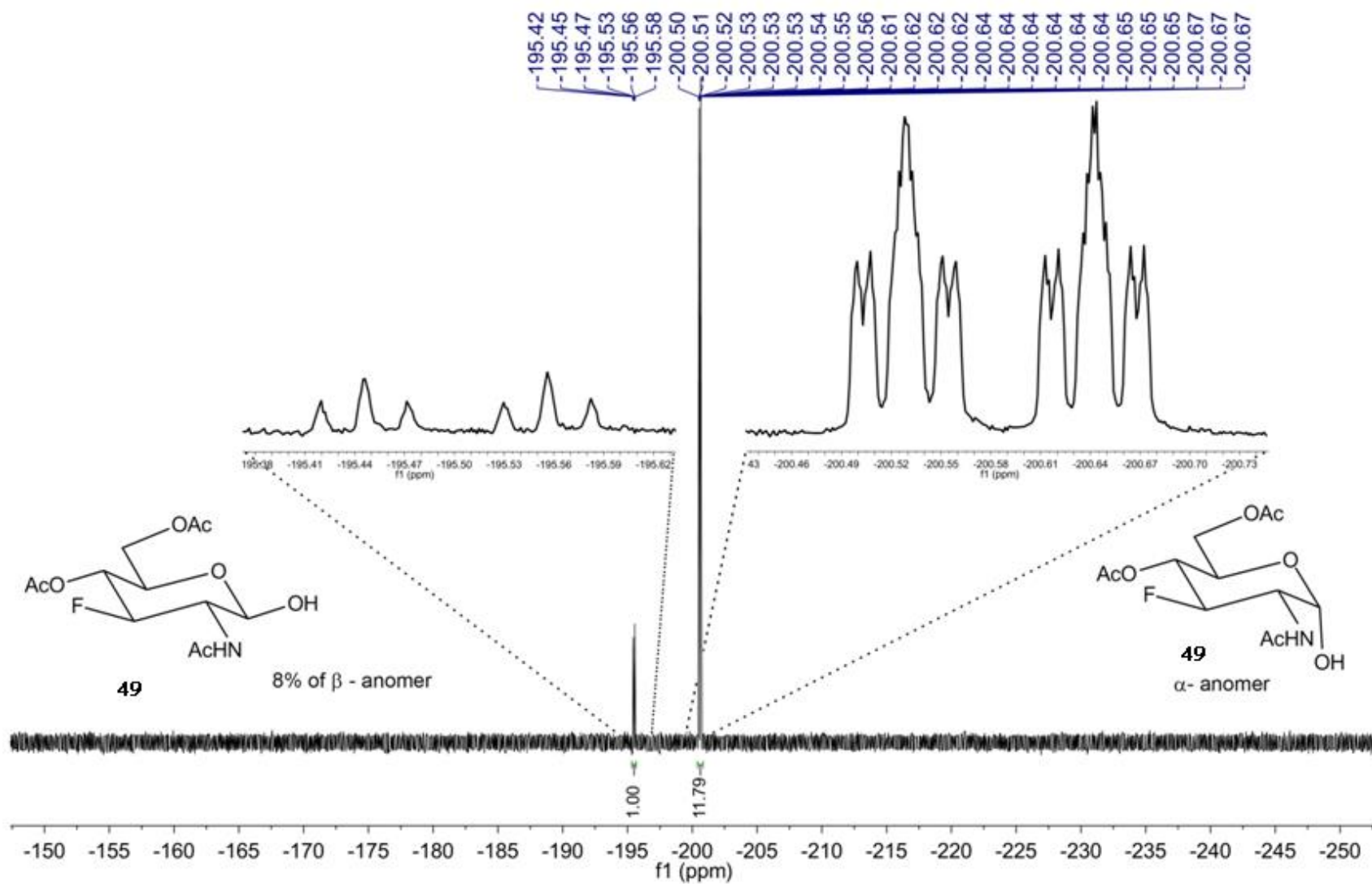
¹⁹F NMR (470 MHz, CDCl₃) of **48** (β-anomer)



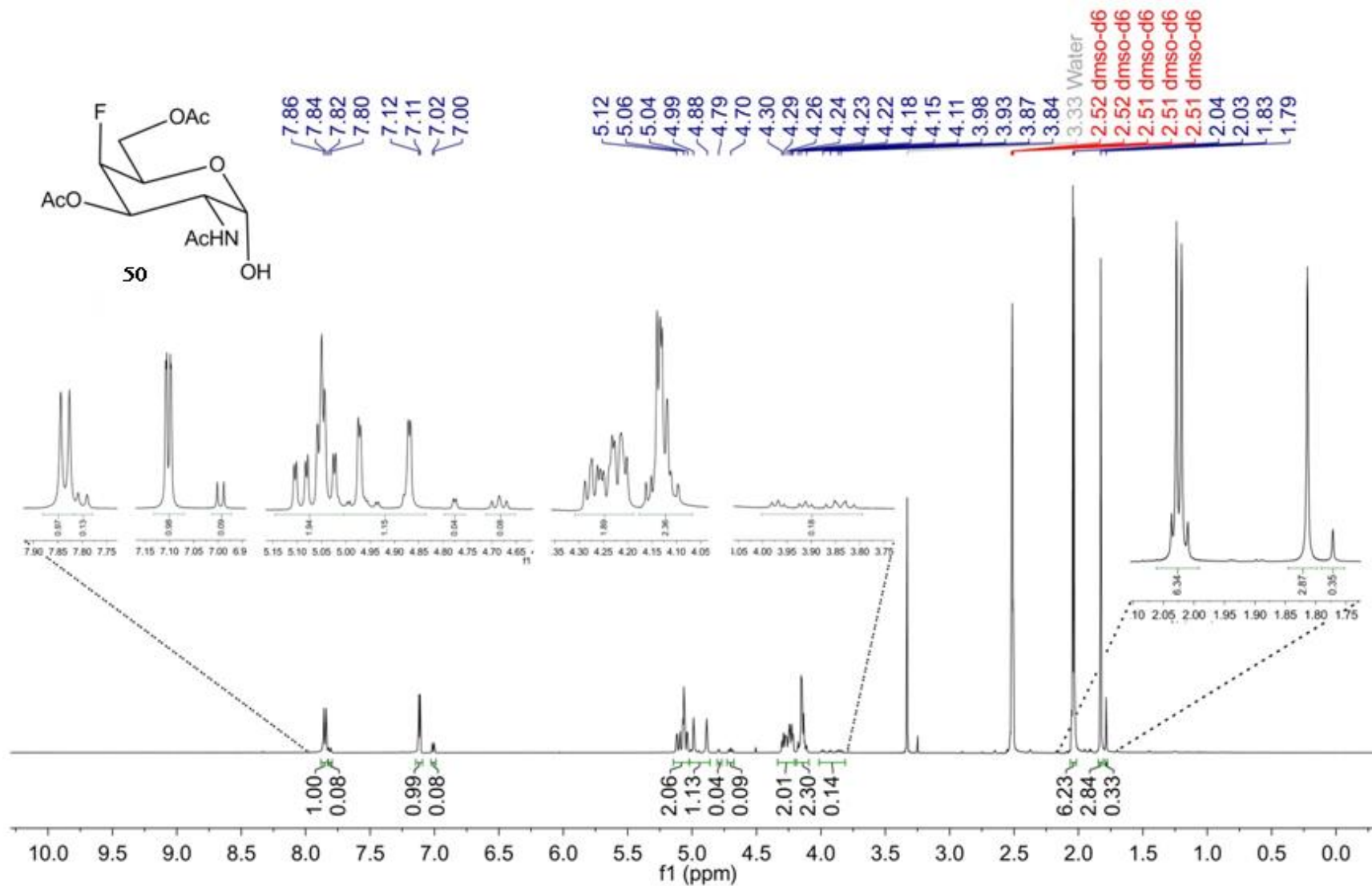
^1H NMR (500 MHz, CD_3OD) of **49** (α-anomer and ca 8% β-anomer)



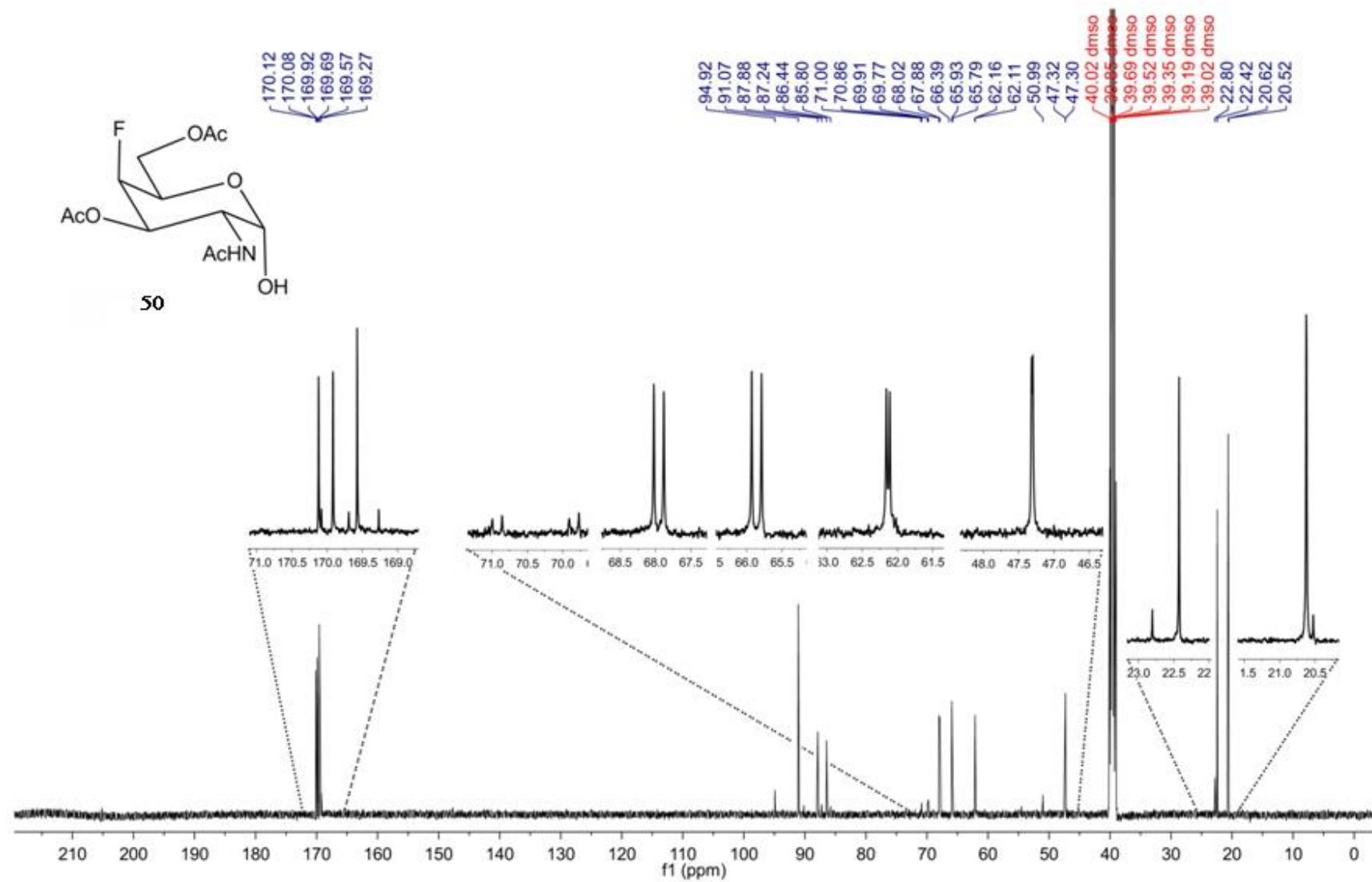
¹³C {¹H} NMR (125 MHz, CD₃OD) of **49** (α-anomer and ca 8% β-anomer)



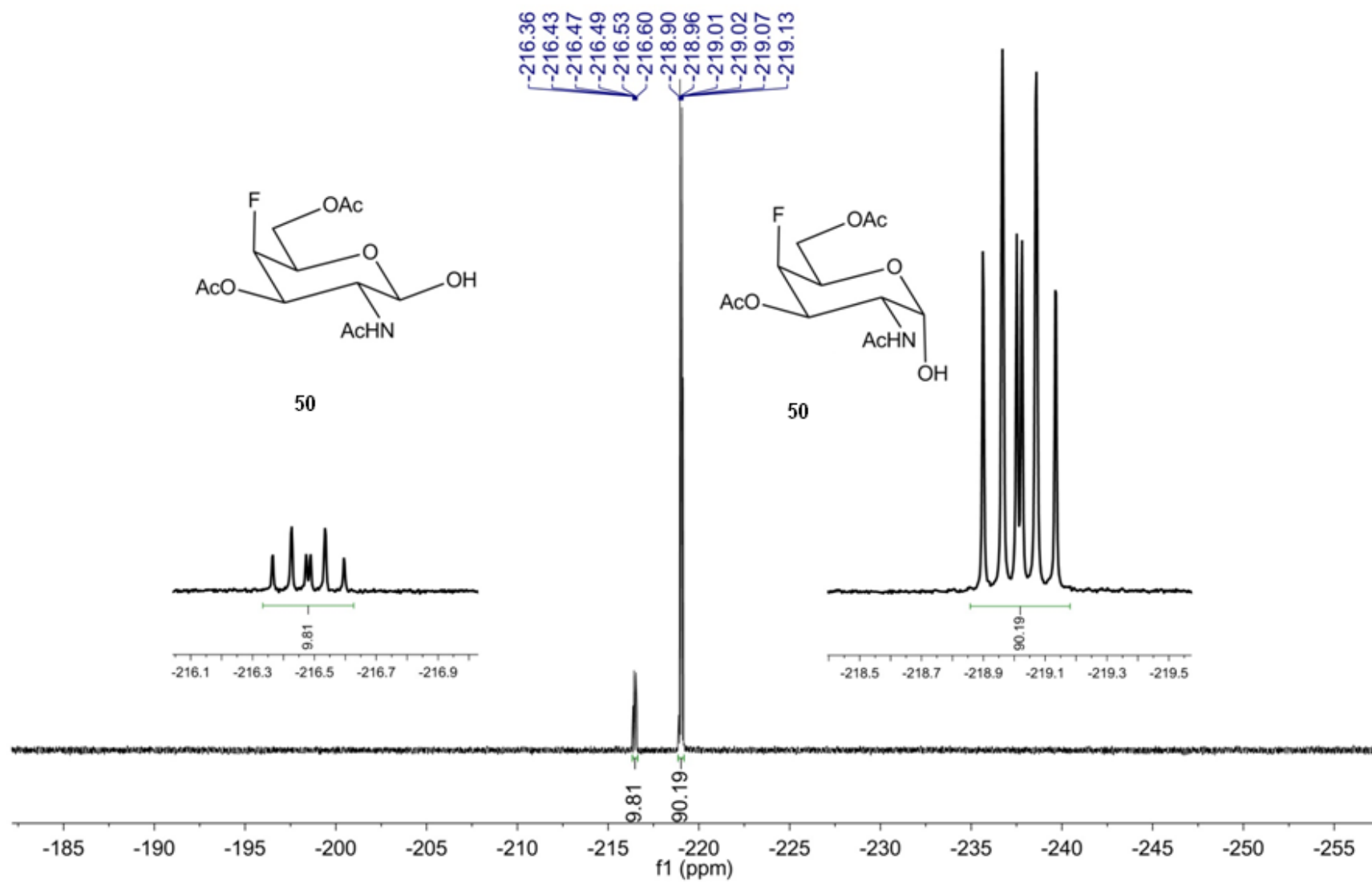
^{19}F NMR (470 MHz, CD_3OD) of **49** (α -anomer and ca 8% β -anomer)



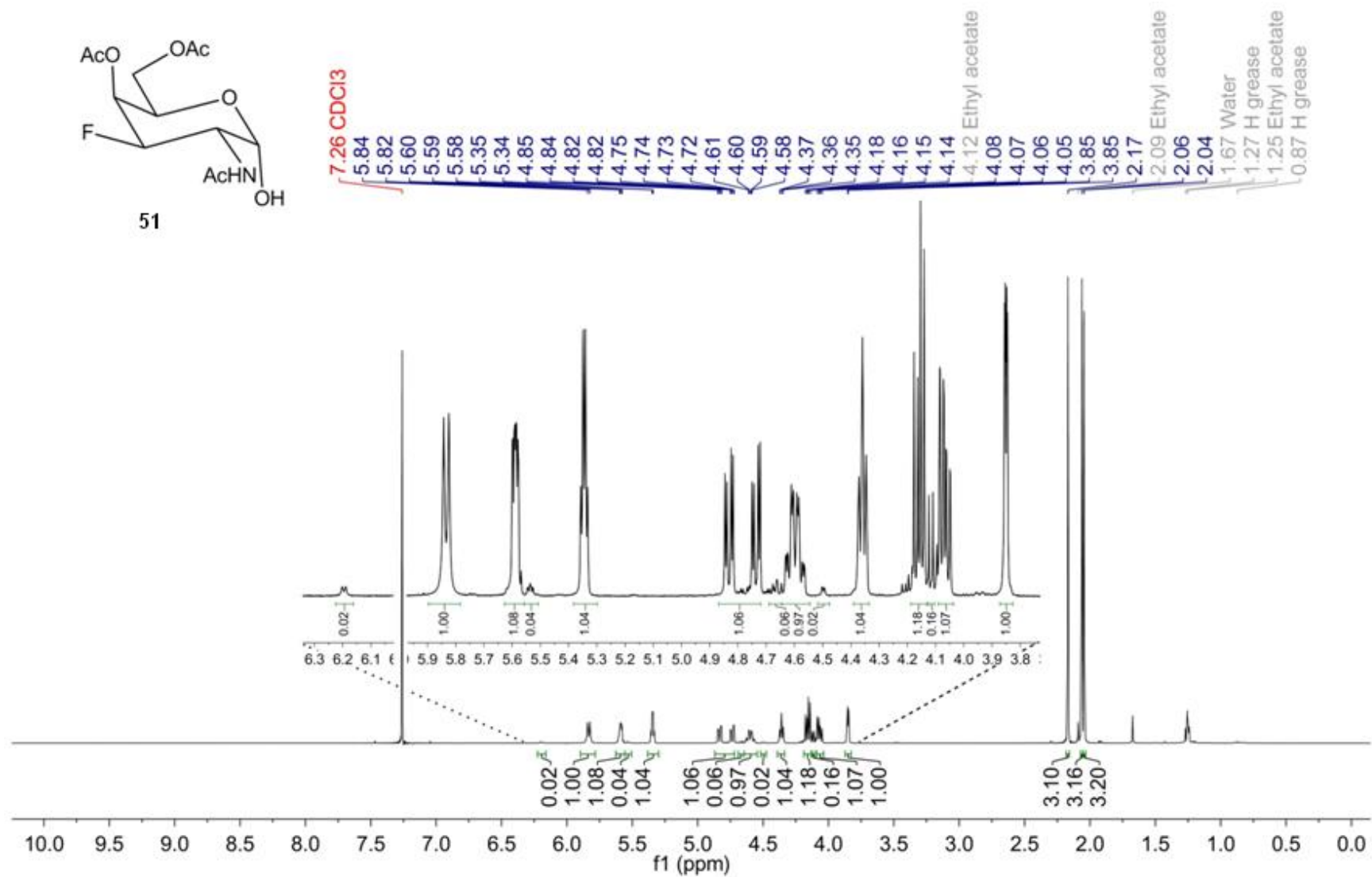
^1H NMR (500 MHz, CDCl_3) of **50** (α -anomer and ca. 10% β -anomer)



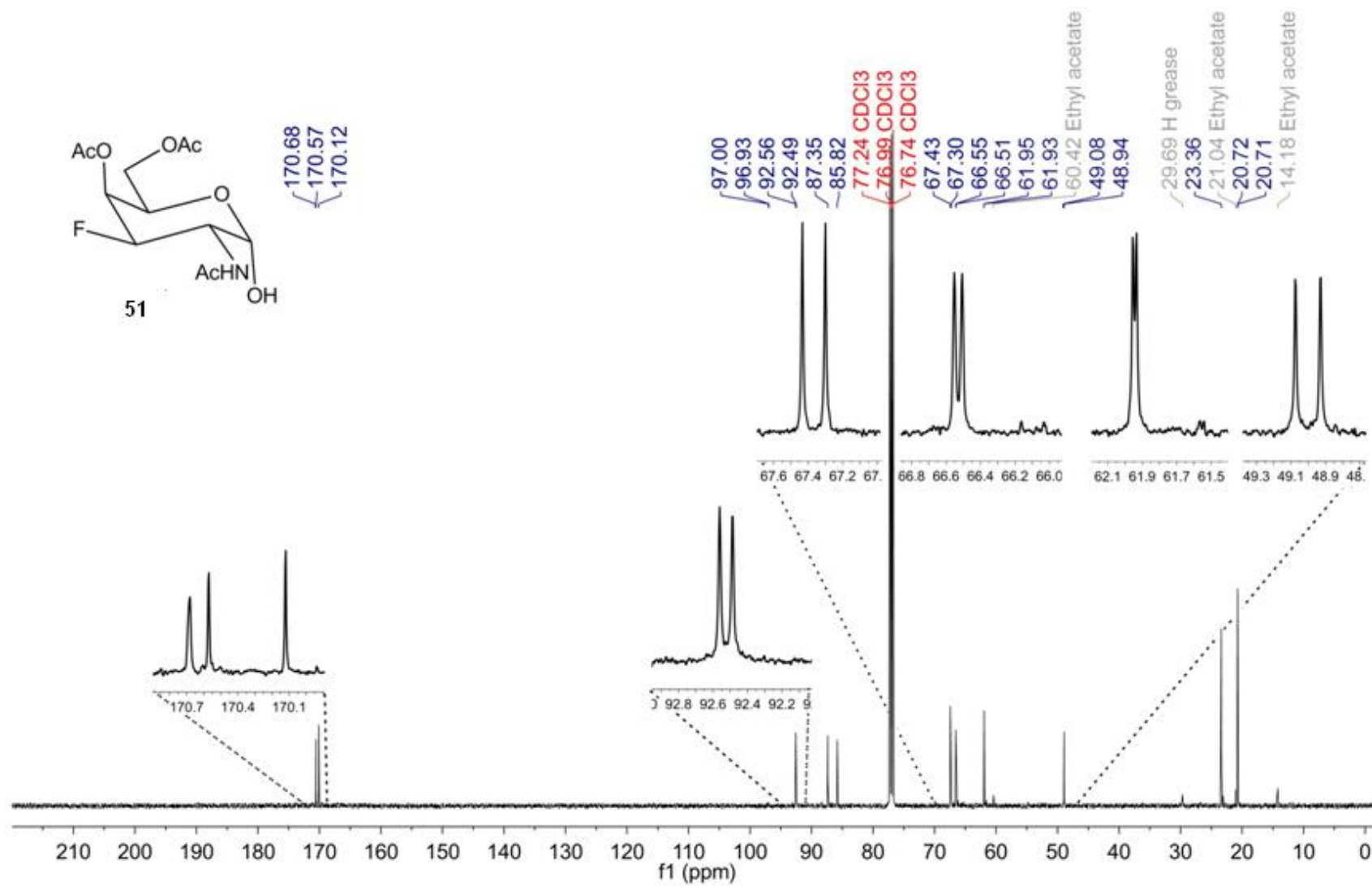
¹³C {¹H} NMR (125 MHz, CDCl₃) of **50** (α-anomer and ca. 10% β-anomer)



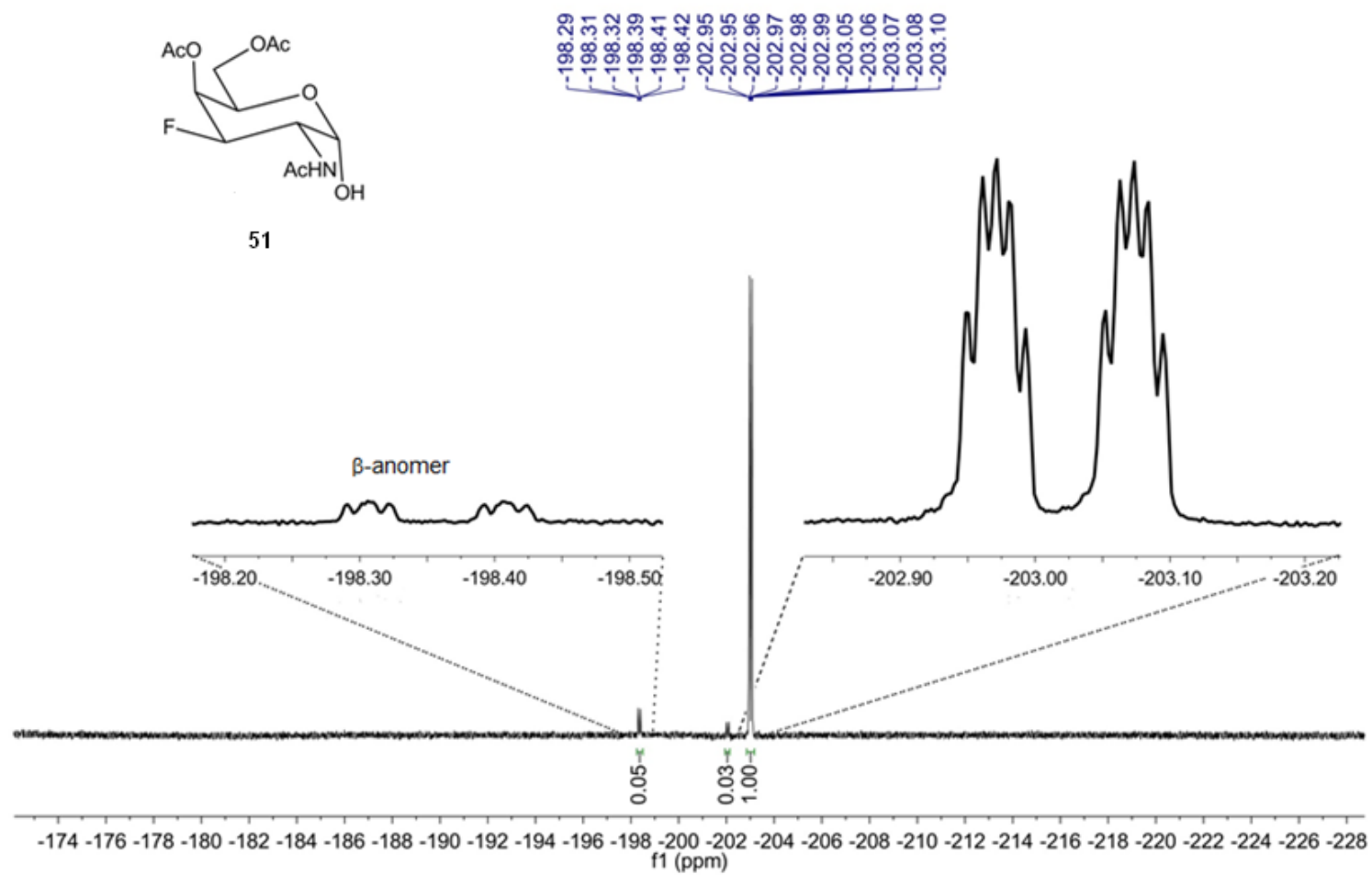
^{19}F NMR (470 MHz, CDCl_3) of **50** (α -anomer and ca. 10% β -anomer)



^1H NMR (500 MHz, CDCl_3) of **51** (α -anomer and ca. 5% β -anomer)



¹³C {¹H} NMR (125 MHz, CDCl₃) of **51** (α-anomer and ca. 5% β-anomer)



^{19}F NMR (470 MHz, CDCl_3) of **51** (α -anomer and ca. 5% β -anomer)