Thioamidation of *gem*-dibromoalkene in a water medium

Jigarkumar K. Vankar,[a] Ankush Gupta,[a] Jaydeepbhai P. Jadav,[a] Shankara H. Nanjegowda[b] and Guddeangadi N. Gururaja [a *]

[a] School of Chemical Sciences, Central University of Gujarat, Gandhinagar 382030, India.
[b] Institution of excellence, University of Mysore, Mysuru 570 006, India.

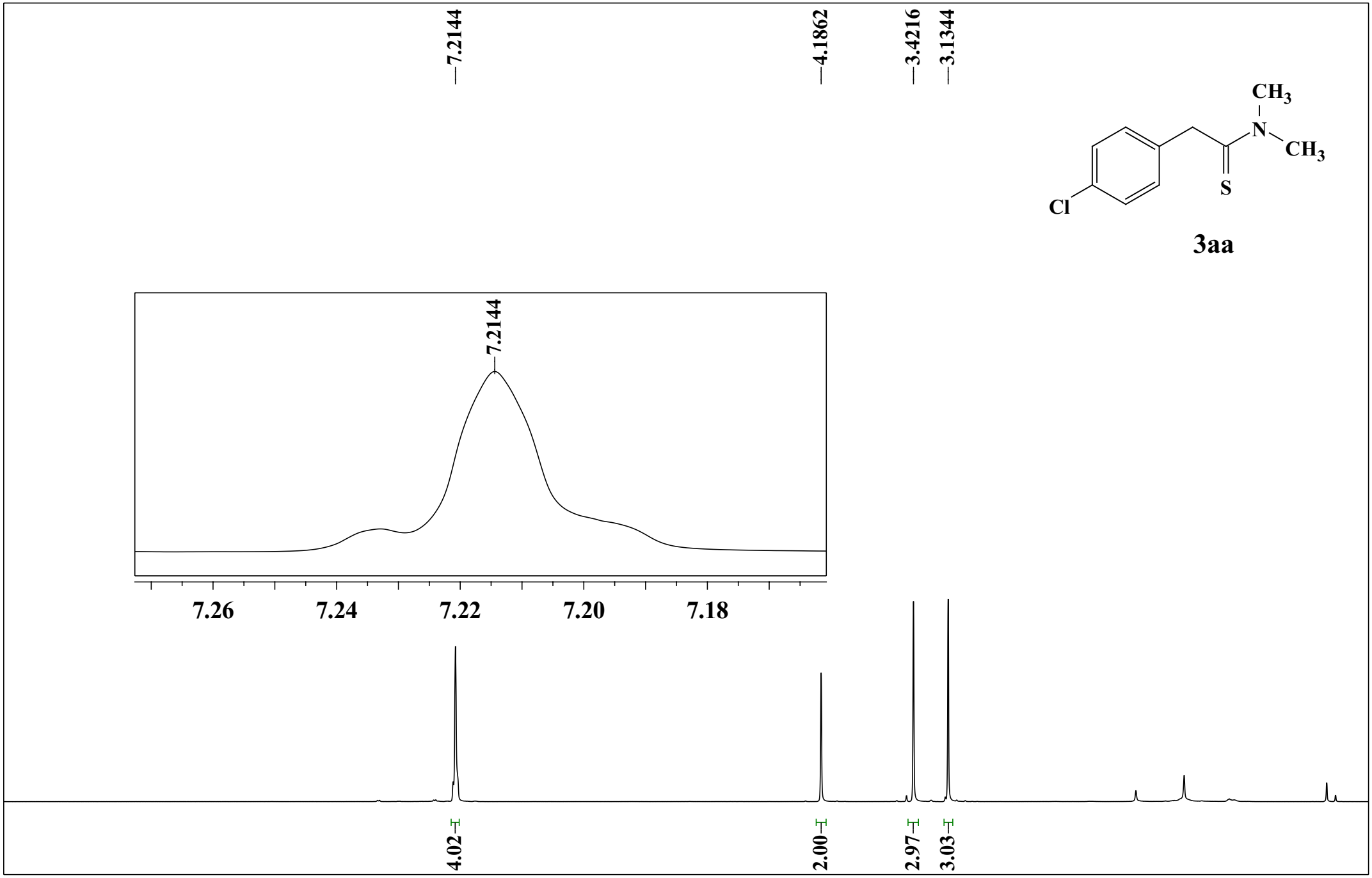


Figure S1. 1H NMR Spectrum of 3aa

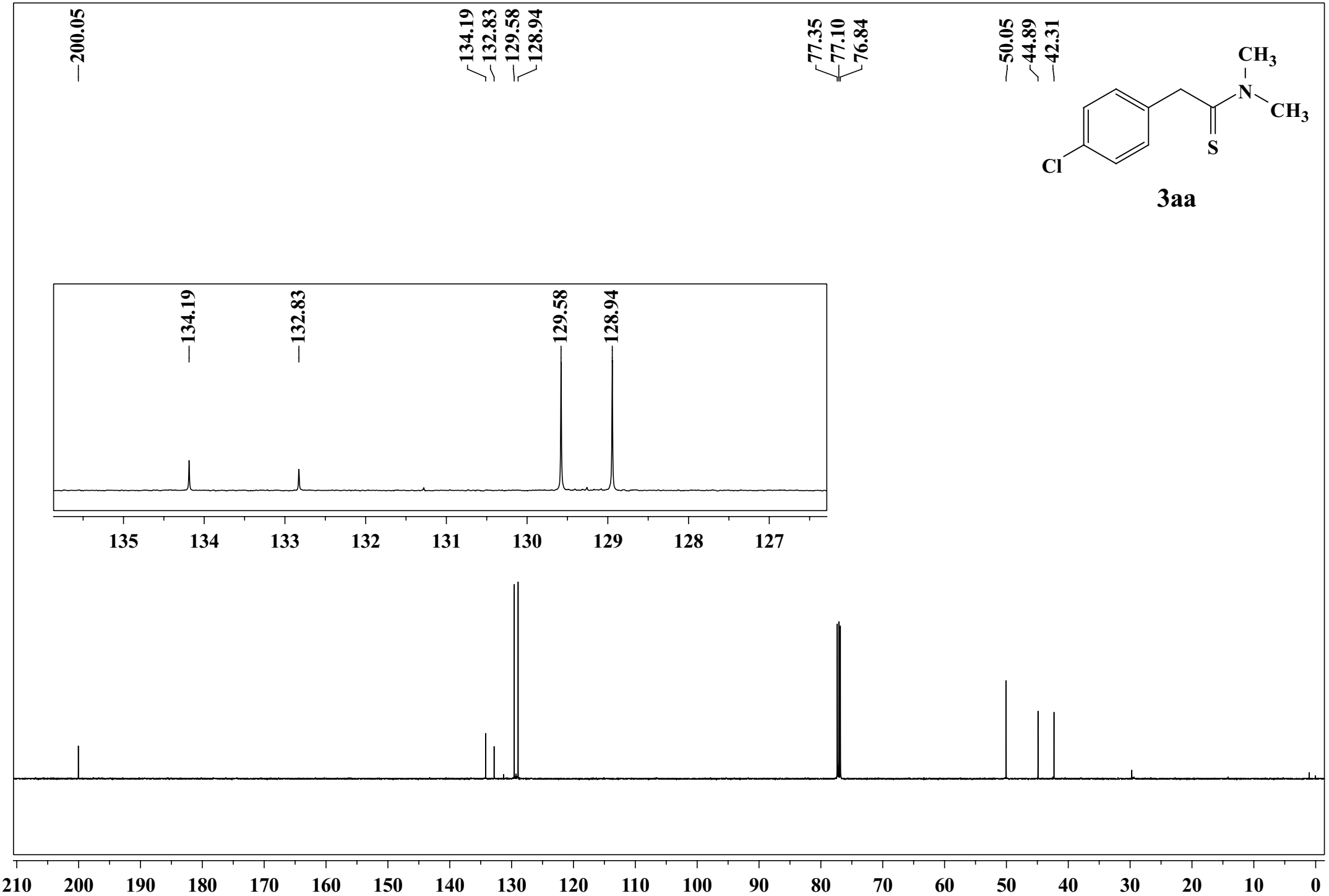


Figure S2. 13C NMR Spectrum of 3aa

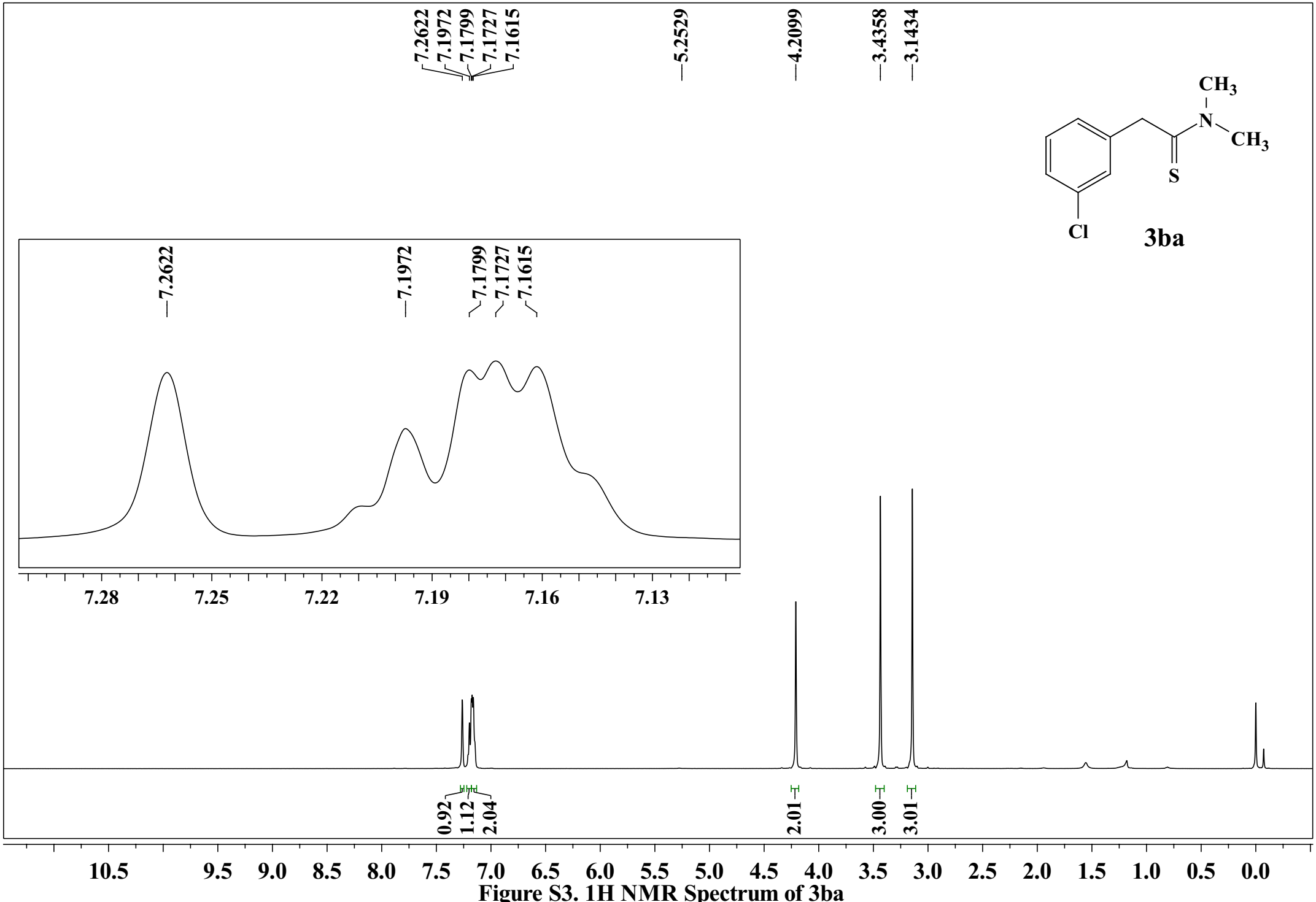


Figure S3. 1H NMR Spectrum of 3ba

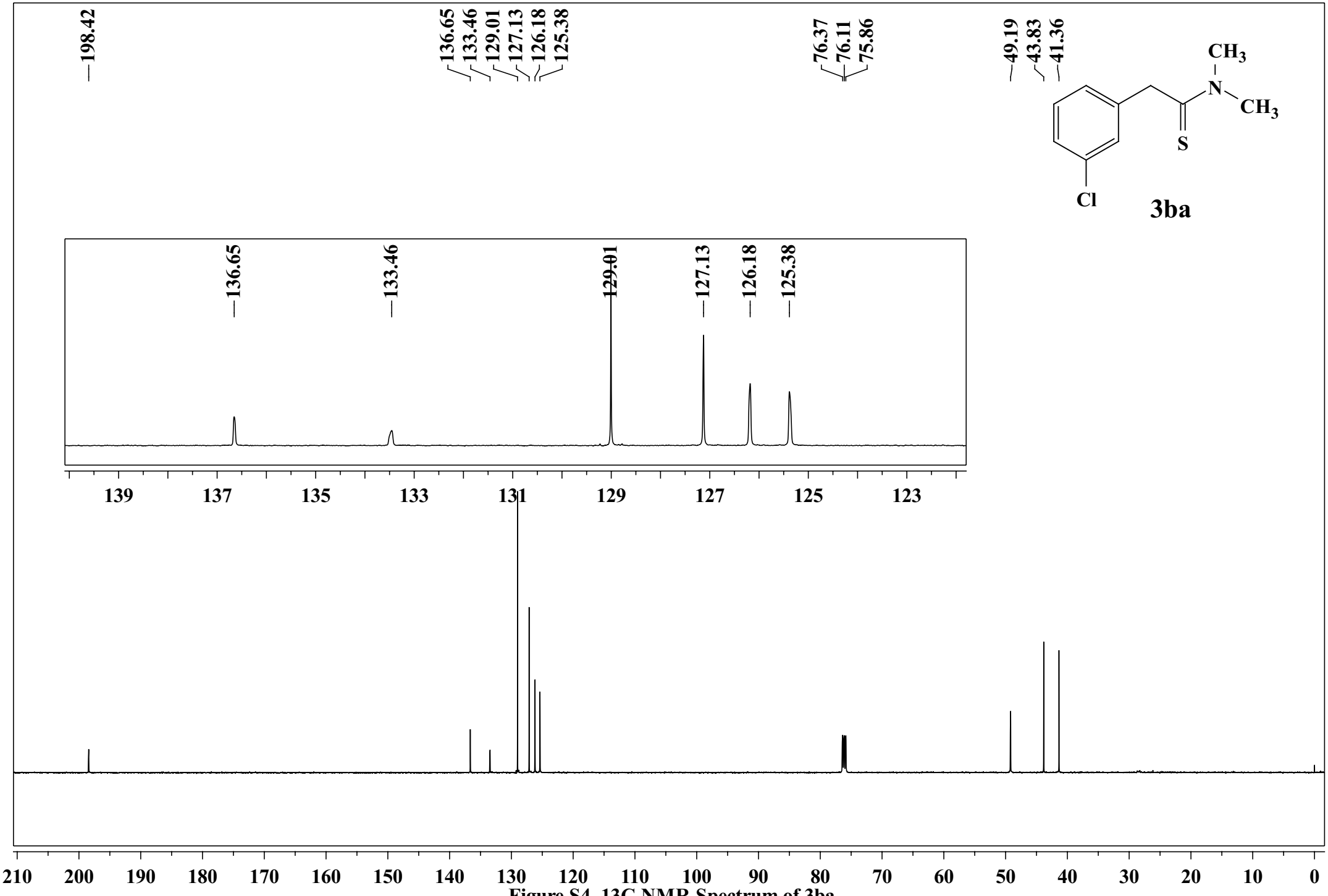


Figure S4. 13C NMR Spectrum of 3ba

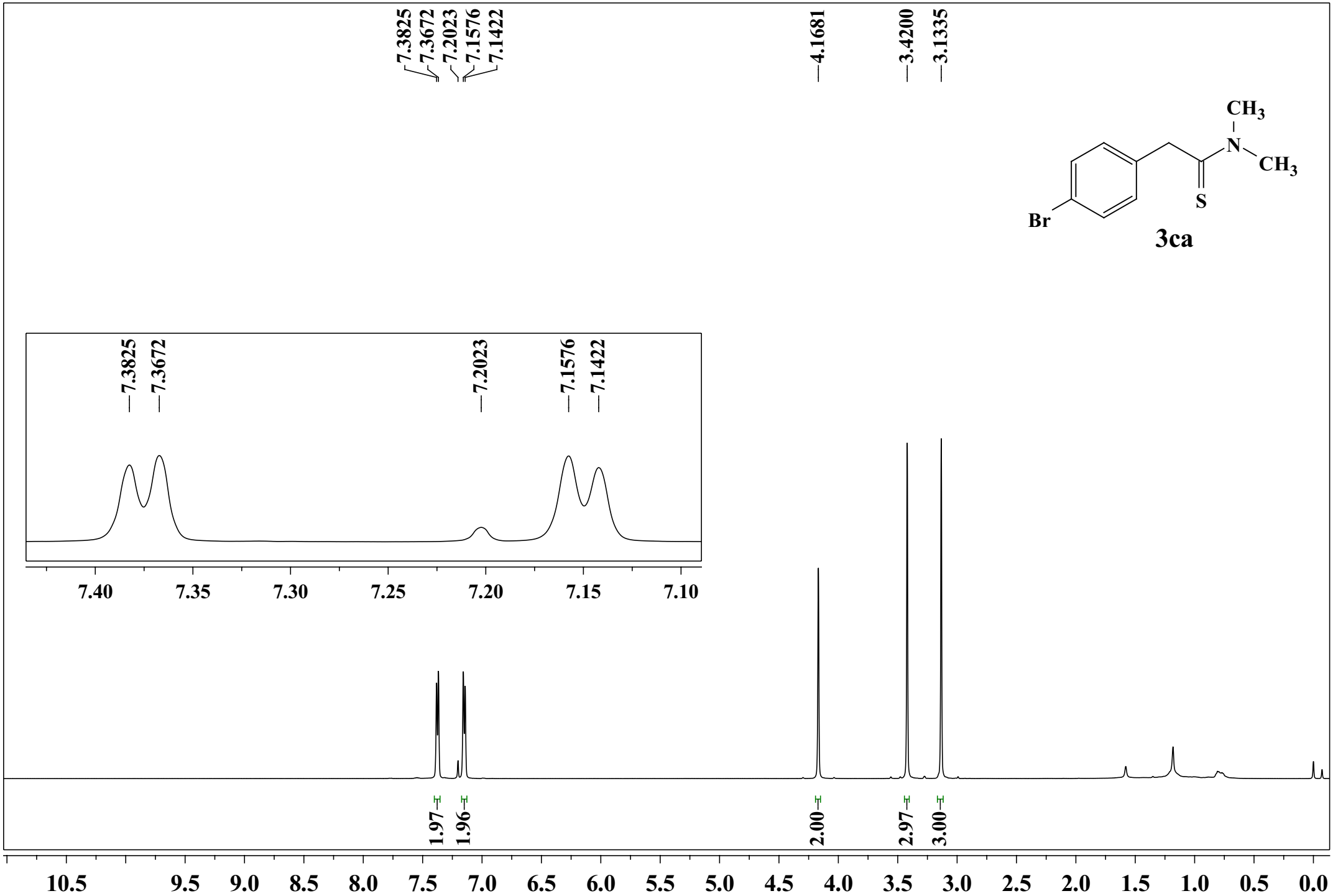


Figure S5. 1H NMR Spectrum of 3ca

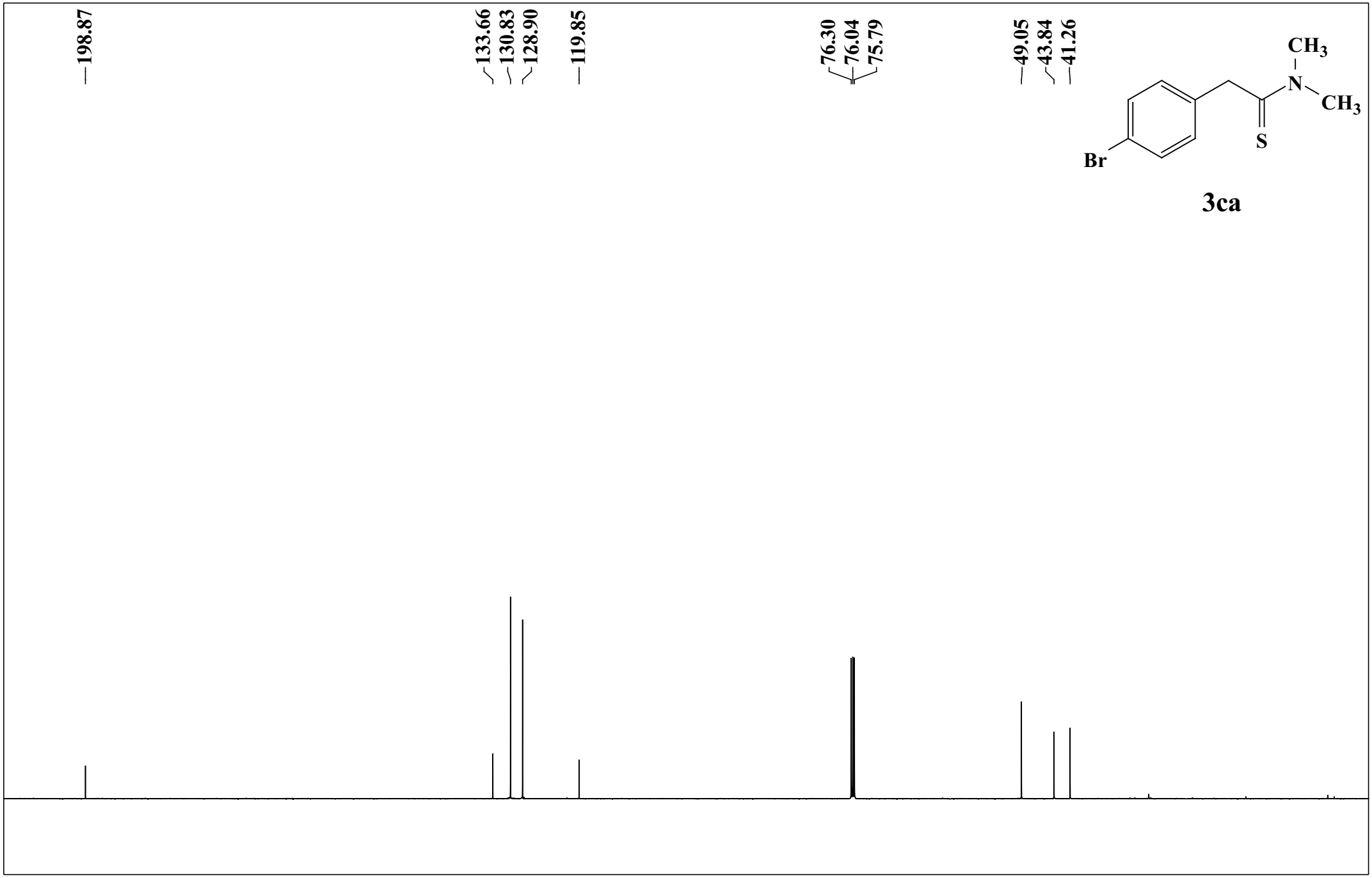


Figure S6. 13C NMR Spectrum of 3ca

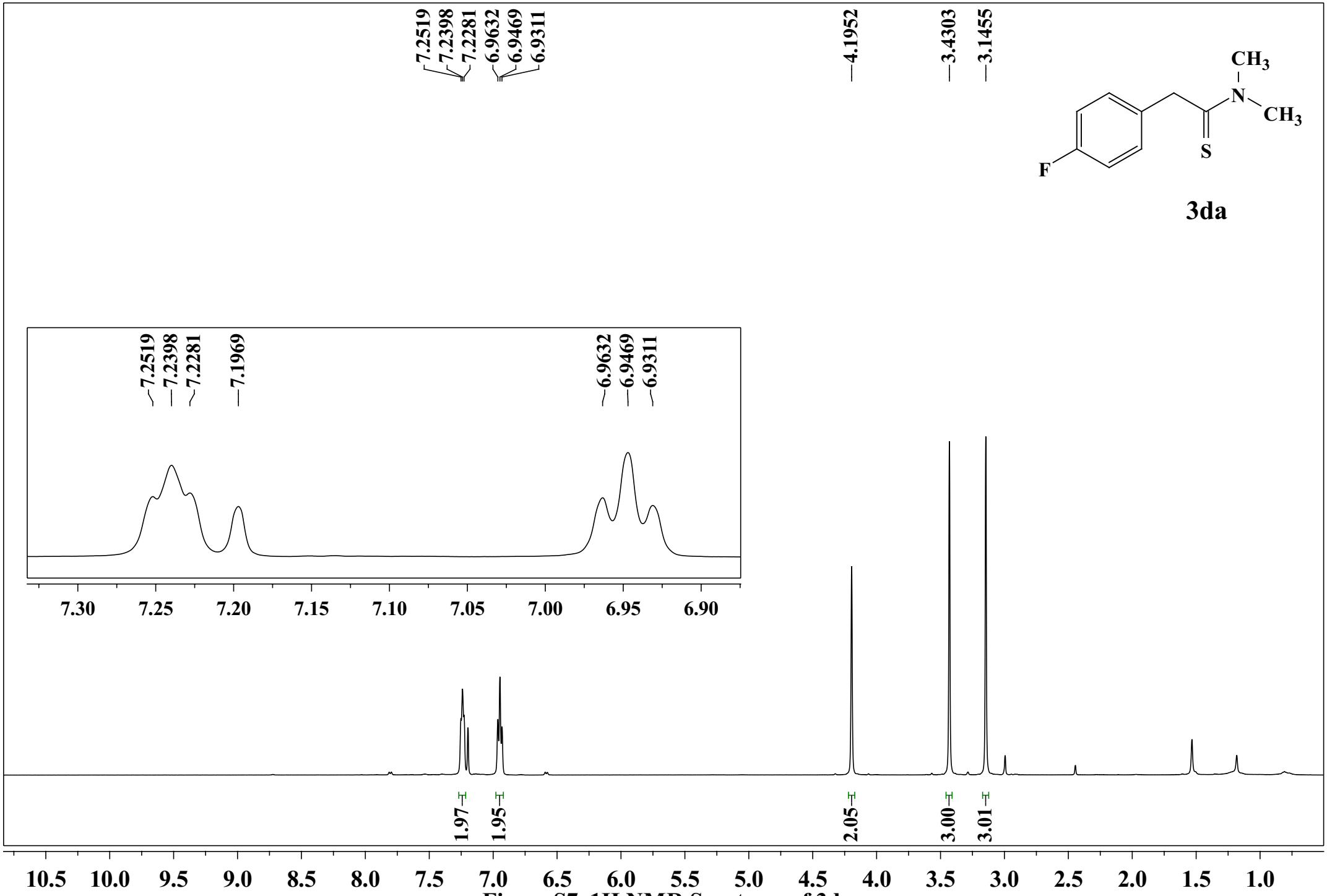


Figure S7. 1H NMR Spectrum of 3da

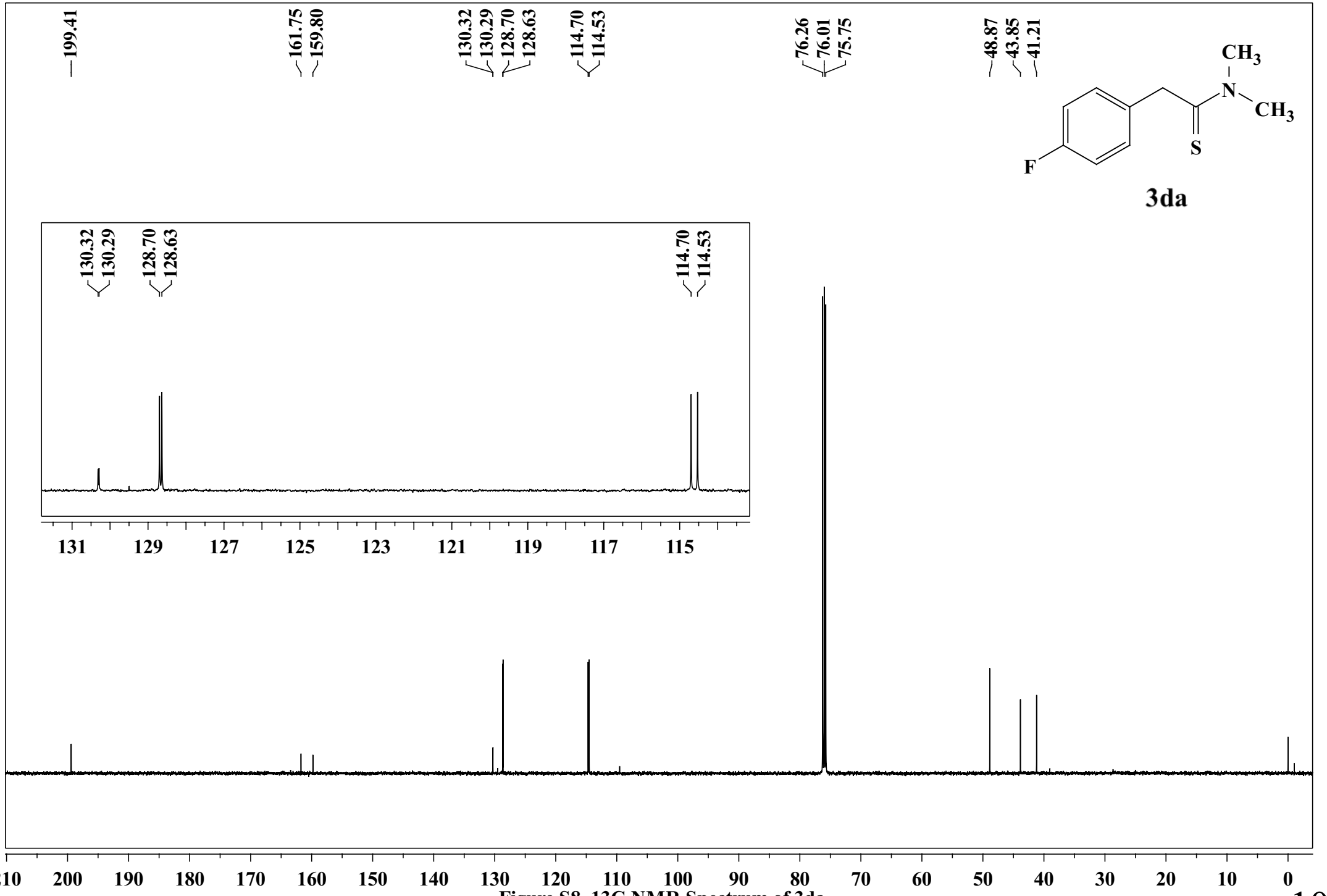


Figure S8. 13C NMR Spectrum of 3da

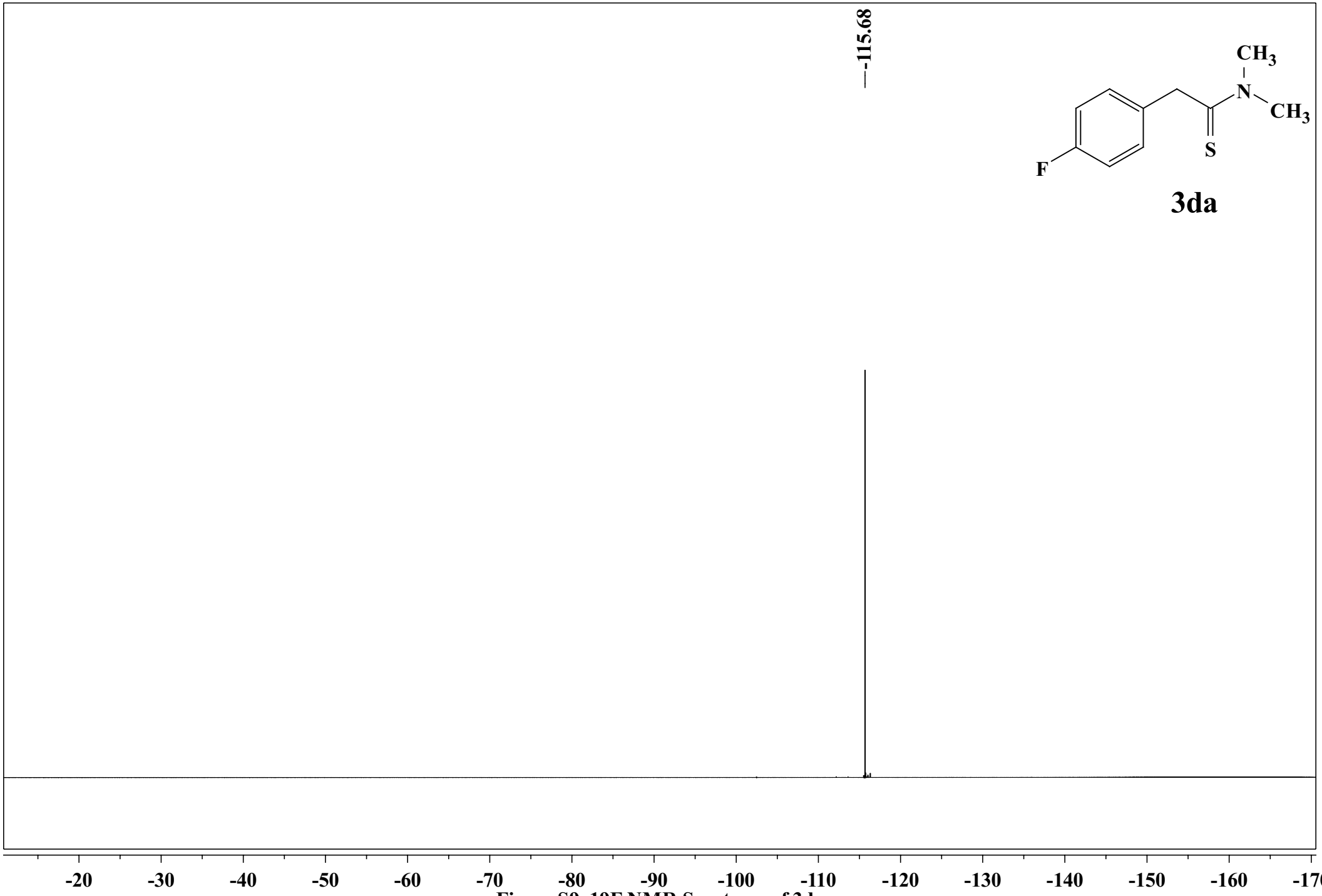


Figure S9. 19F NMR Spectrum of 3da

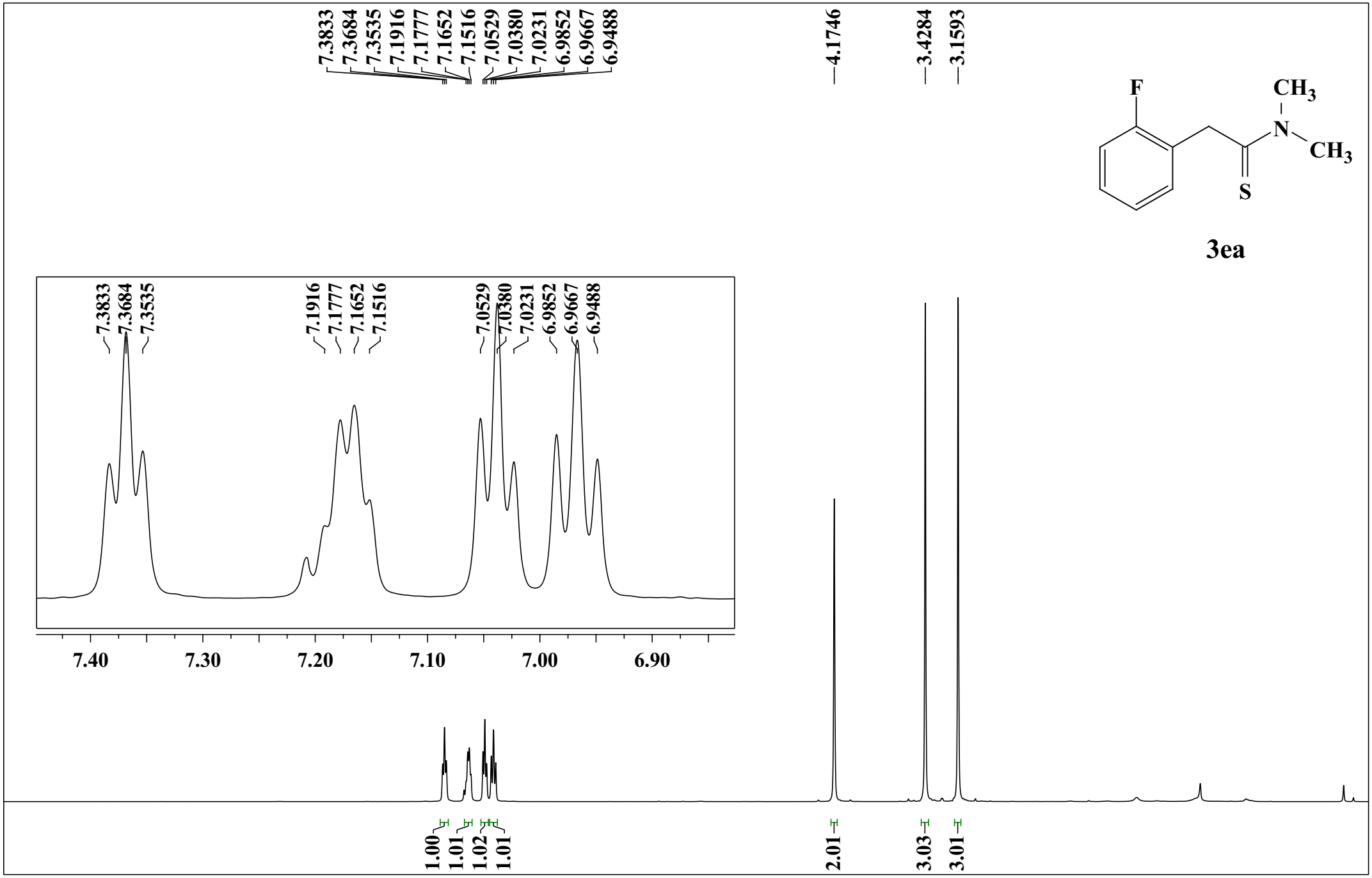


Figure S10. 1H NMR Spectrum of 3ea

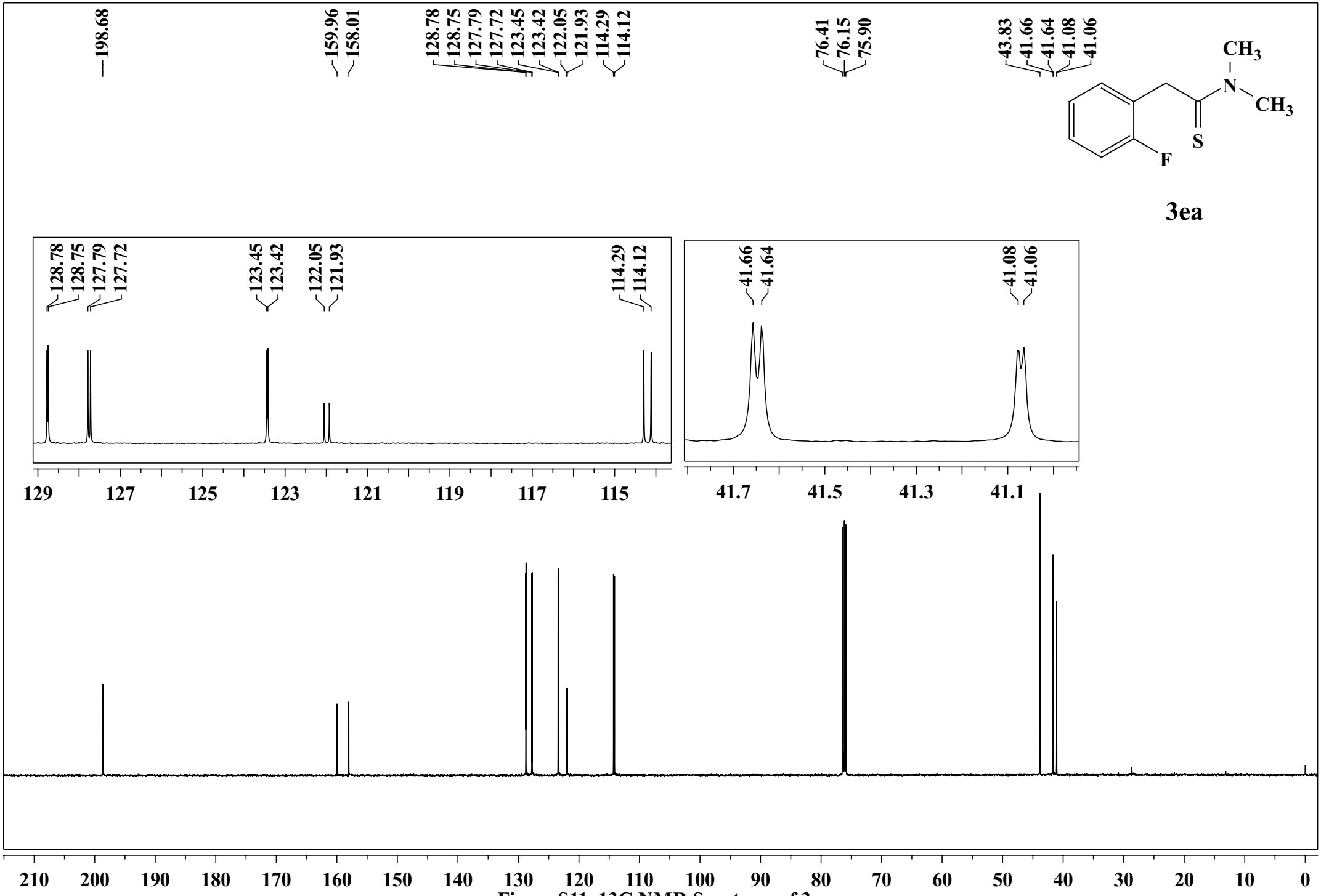


Figure S11. 13C NMR Spectrum of 3ea

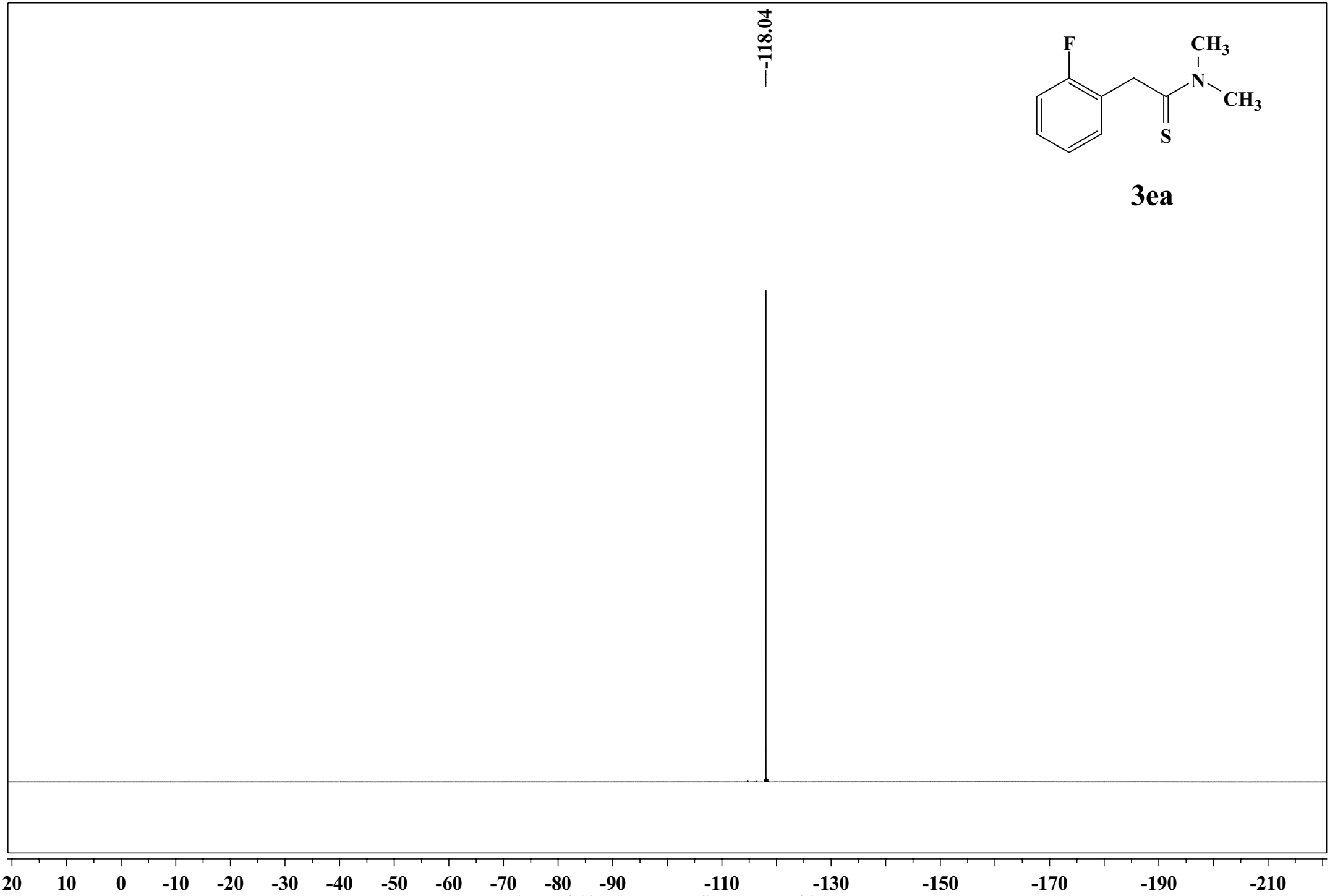


Figure S12. 19F NMR Spectrum of 3ea

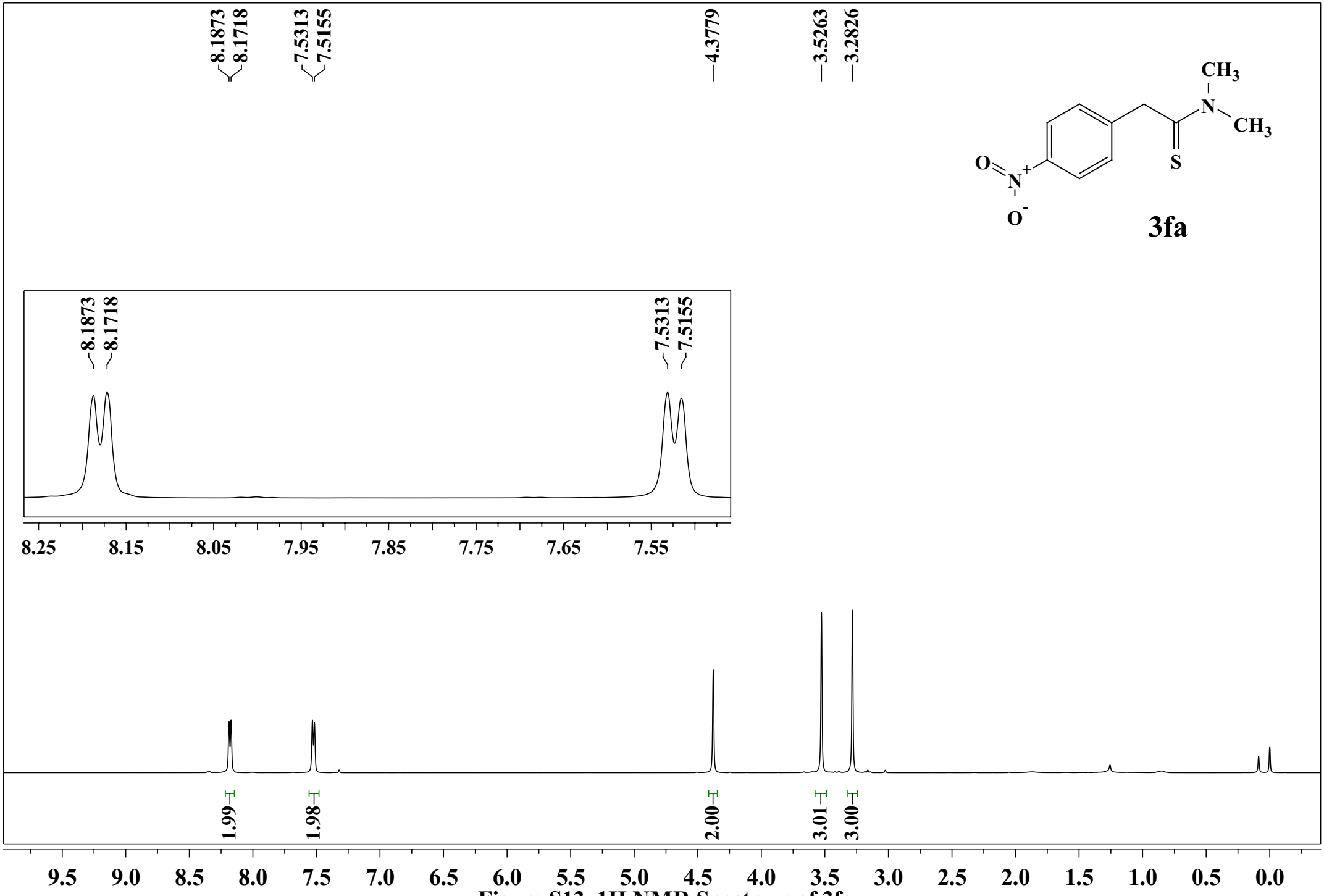


Figure S13. 1H NMR Spectrum of 3fa

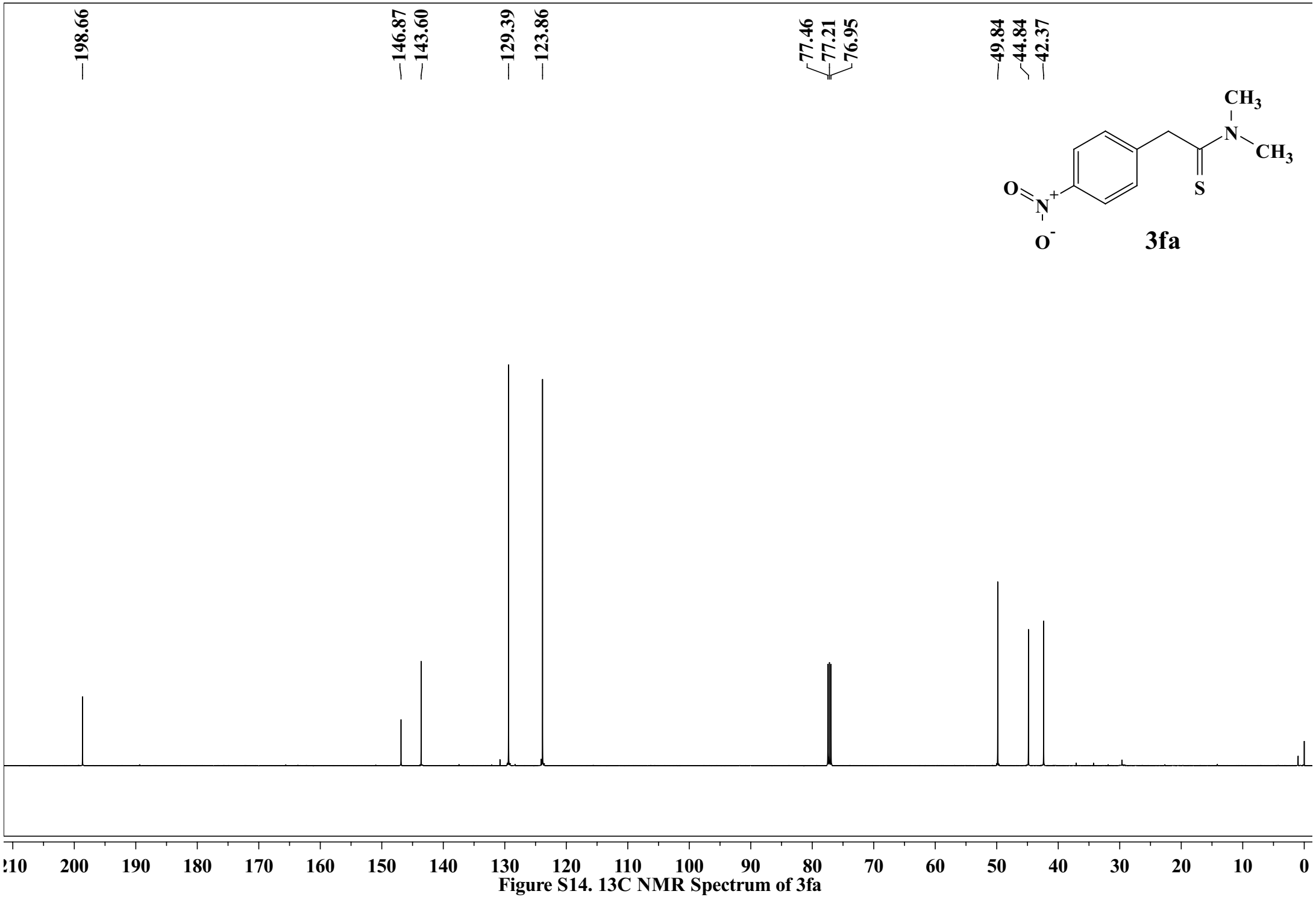


Figure S14. 13C NMR Spectrum of 3fa

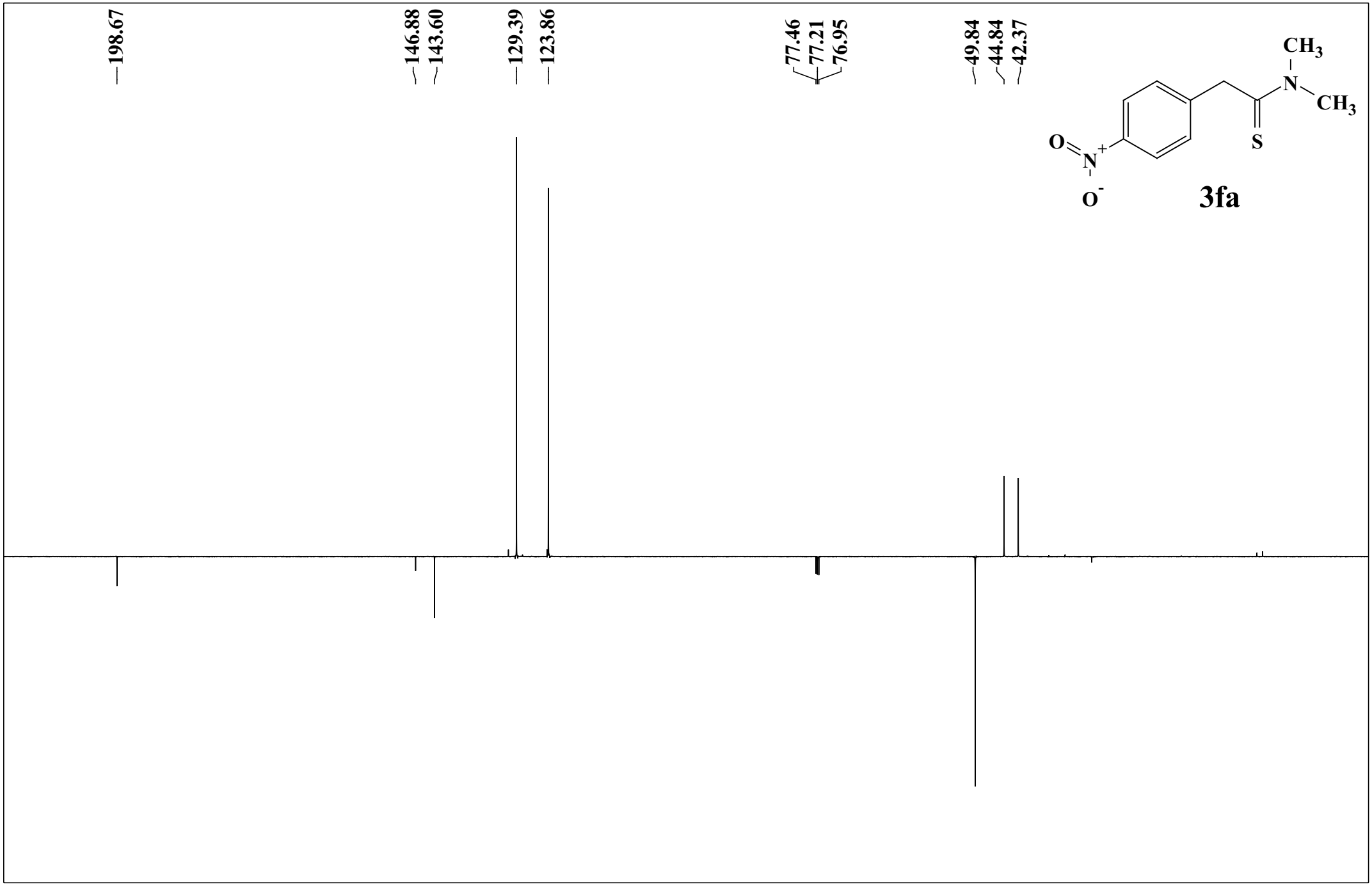


Figure S15. APT Spectrum of 3fa

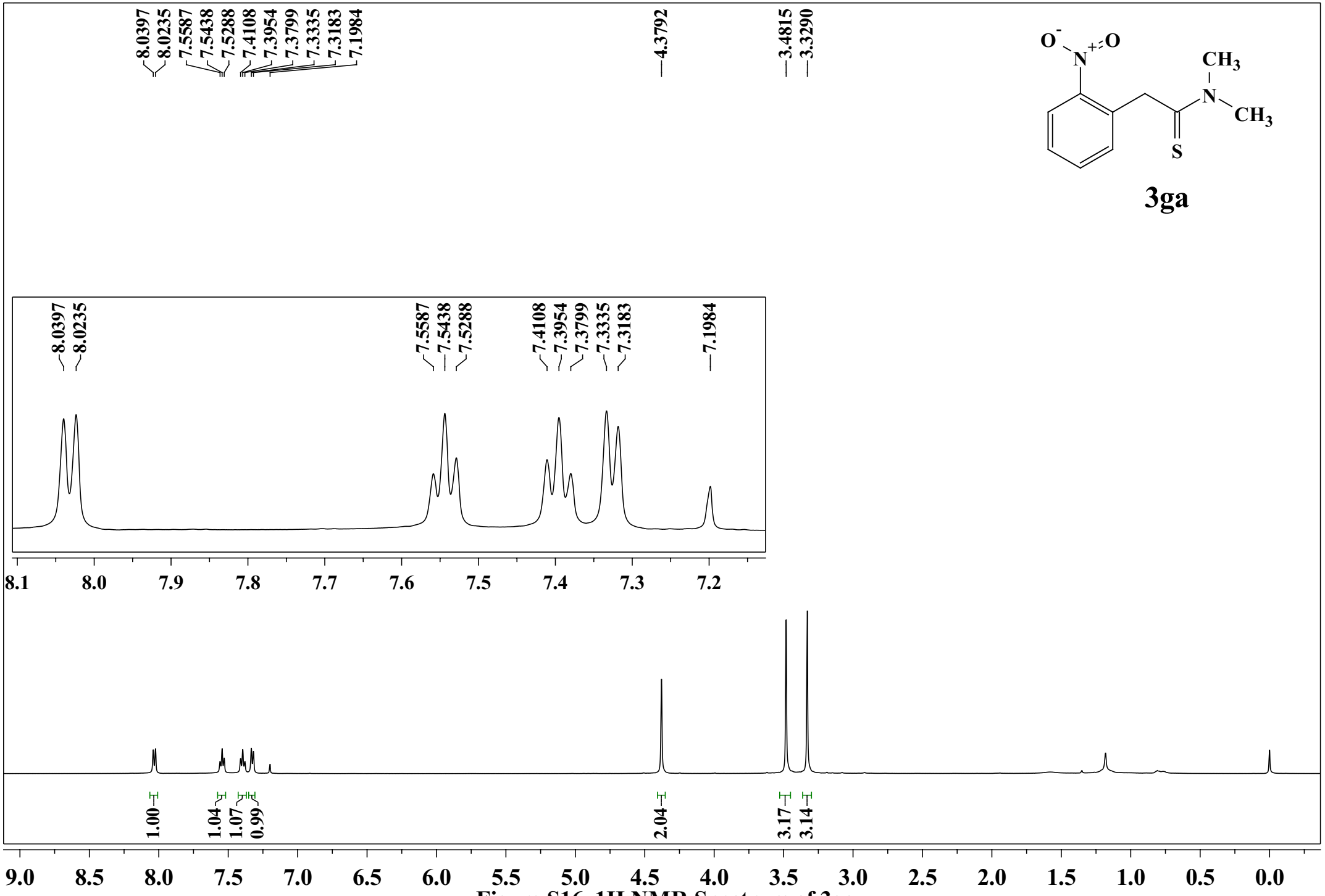


Figure S16. 1H NMR Spectrum of 3ga

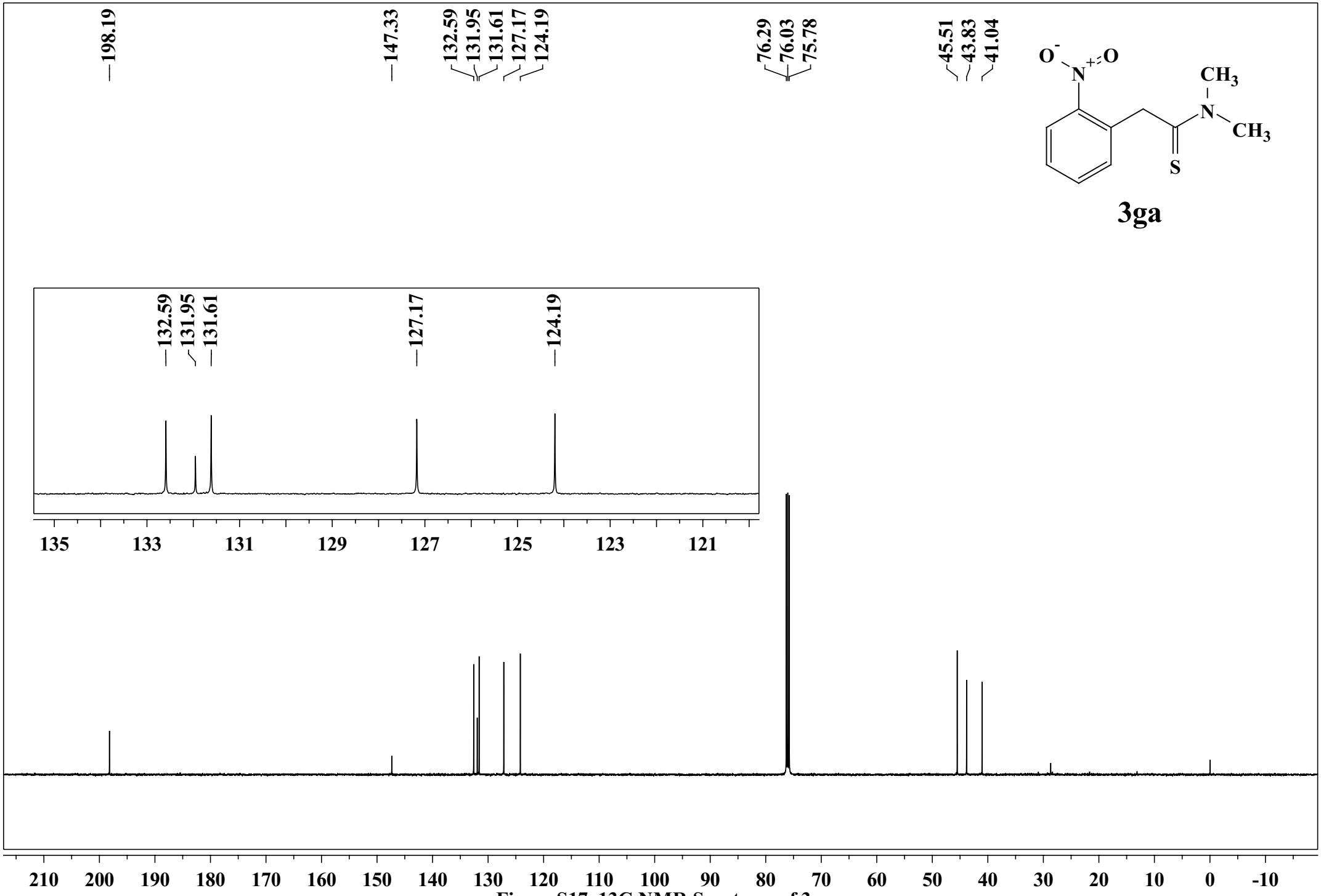


Figure S17. 13C NMR Spectrum of 3ga

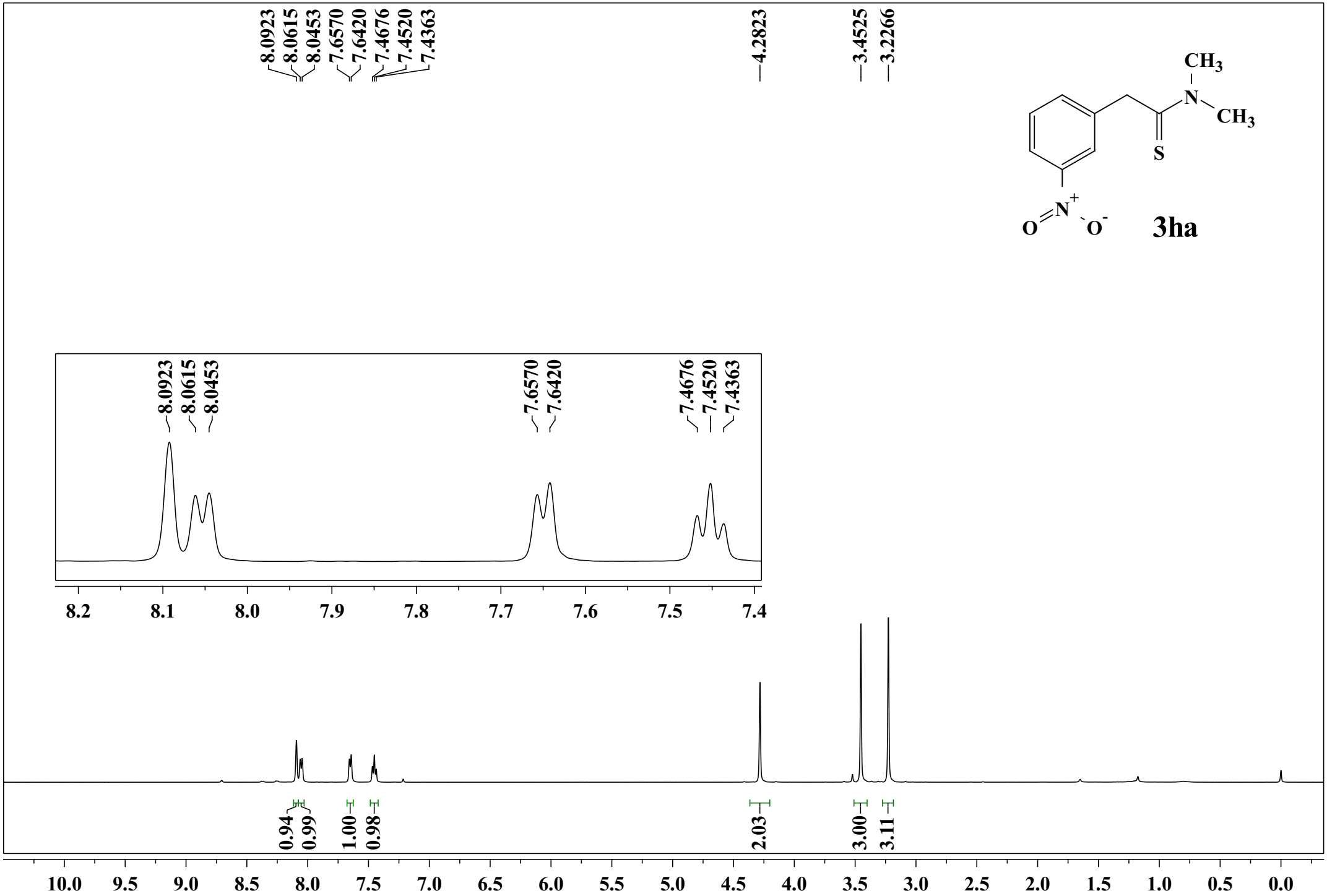


Figure S18. 1H NMR Spectrum of 3ha

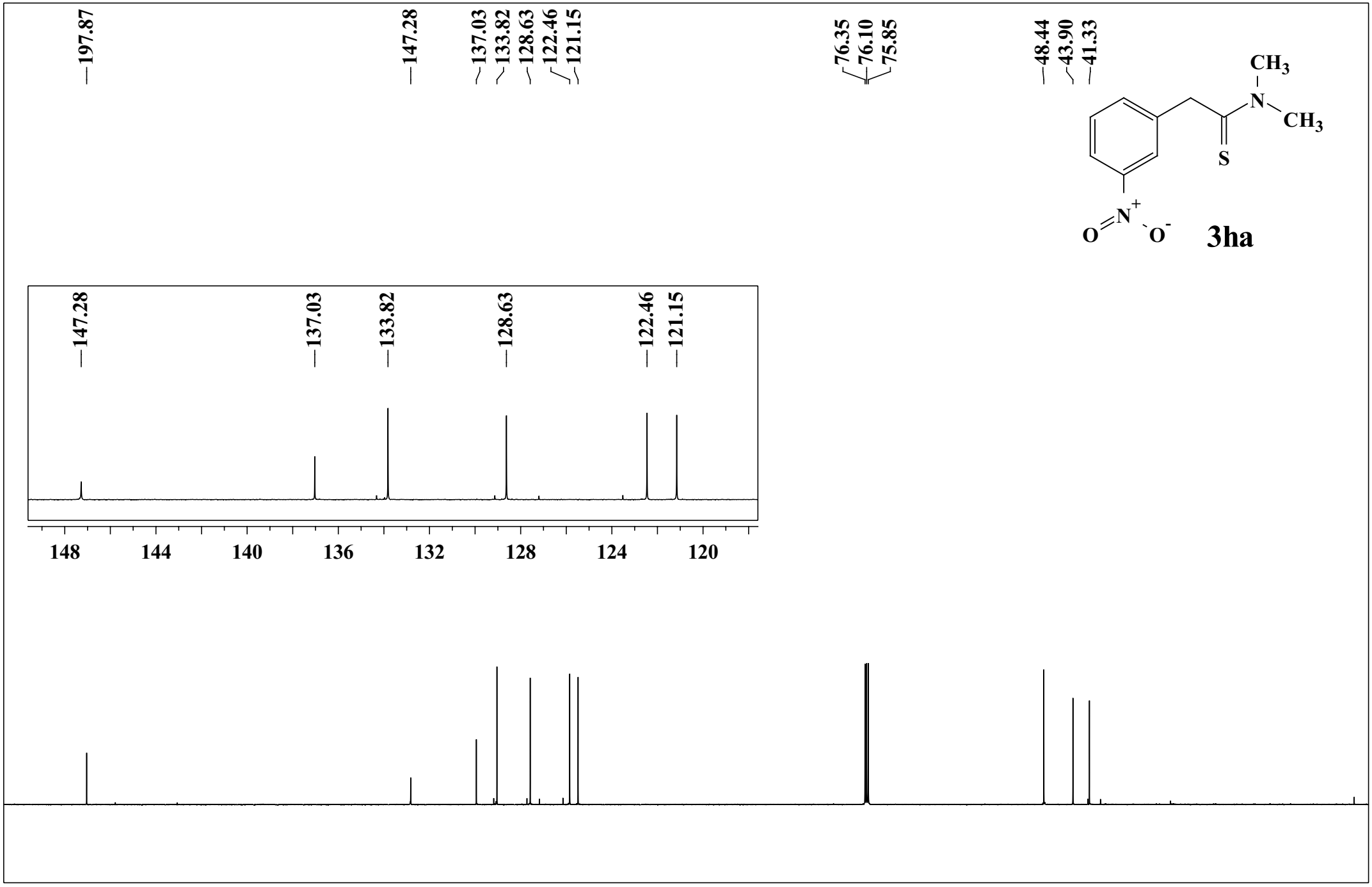


Figure S19. 13C NMR Spectrum of 3ha

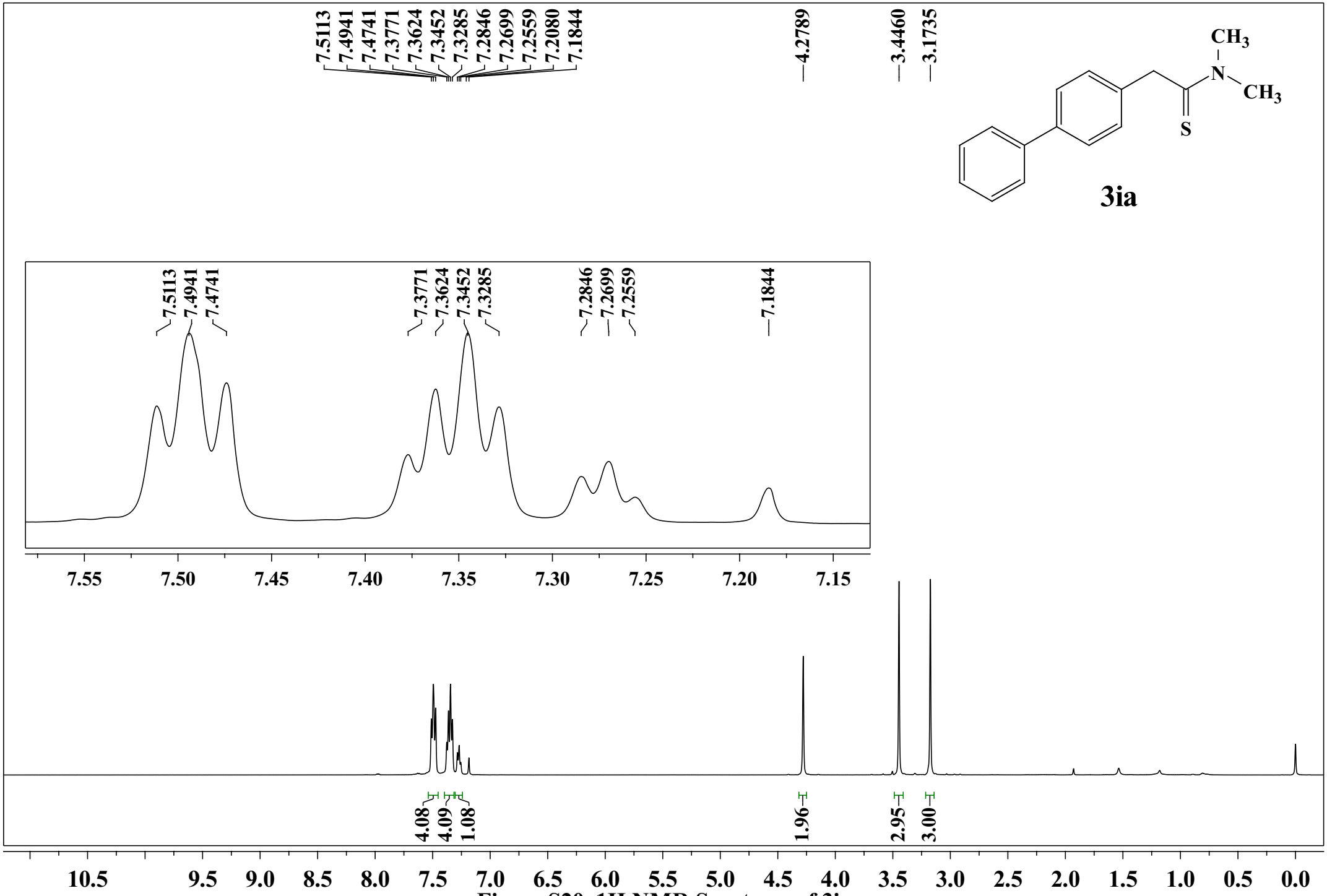


Figure S20. 1H NMR Spectrum of 3ia

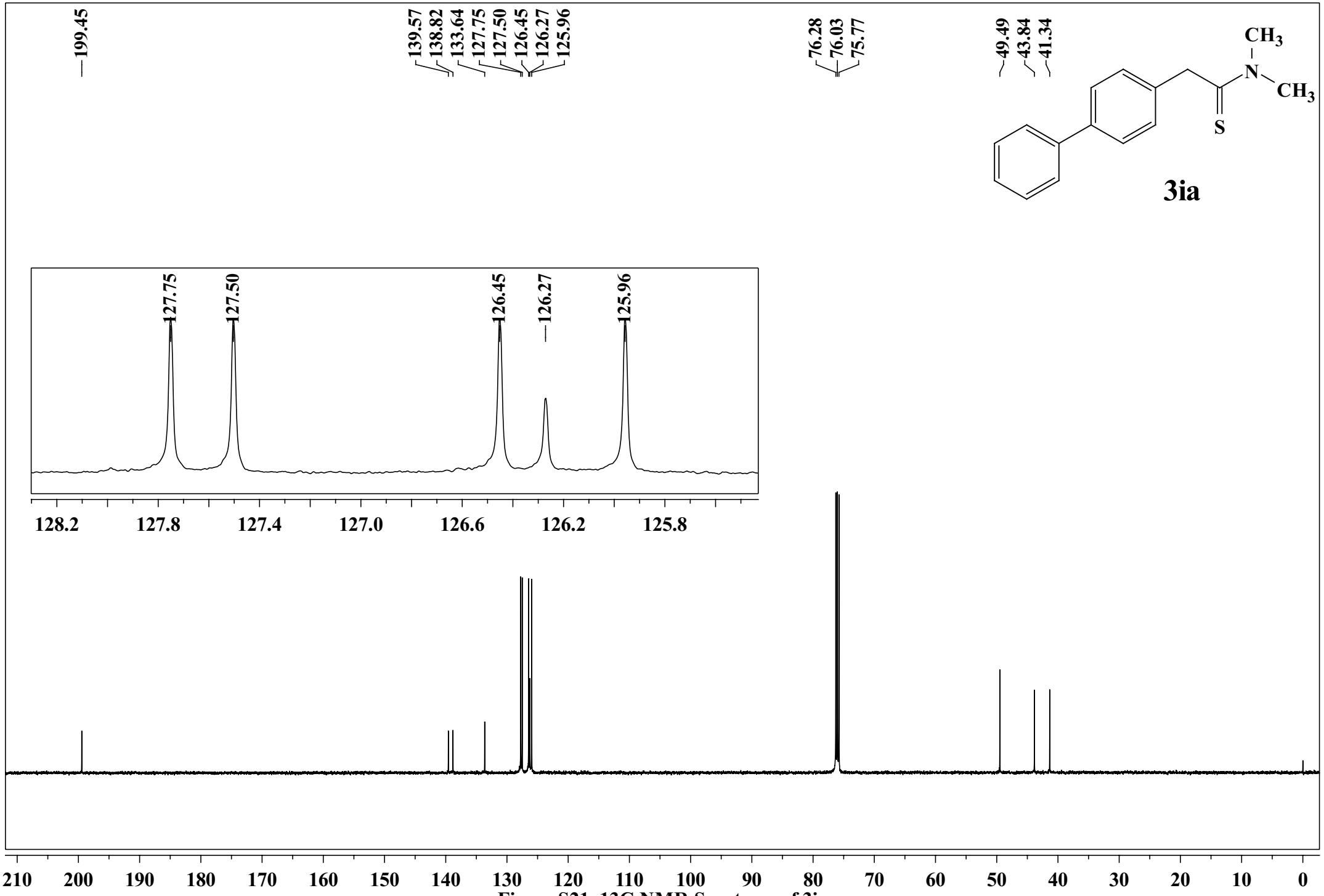


Figure S21. 13C NMR Spectrum of 3ia

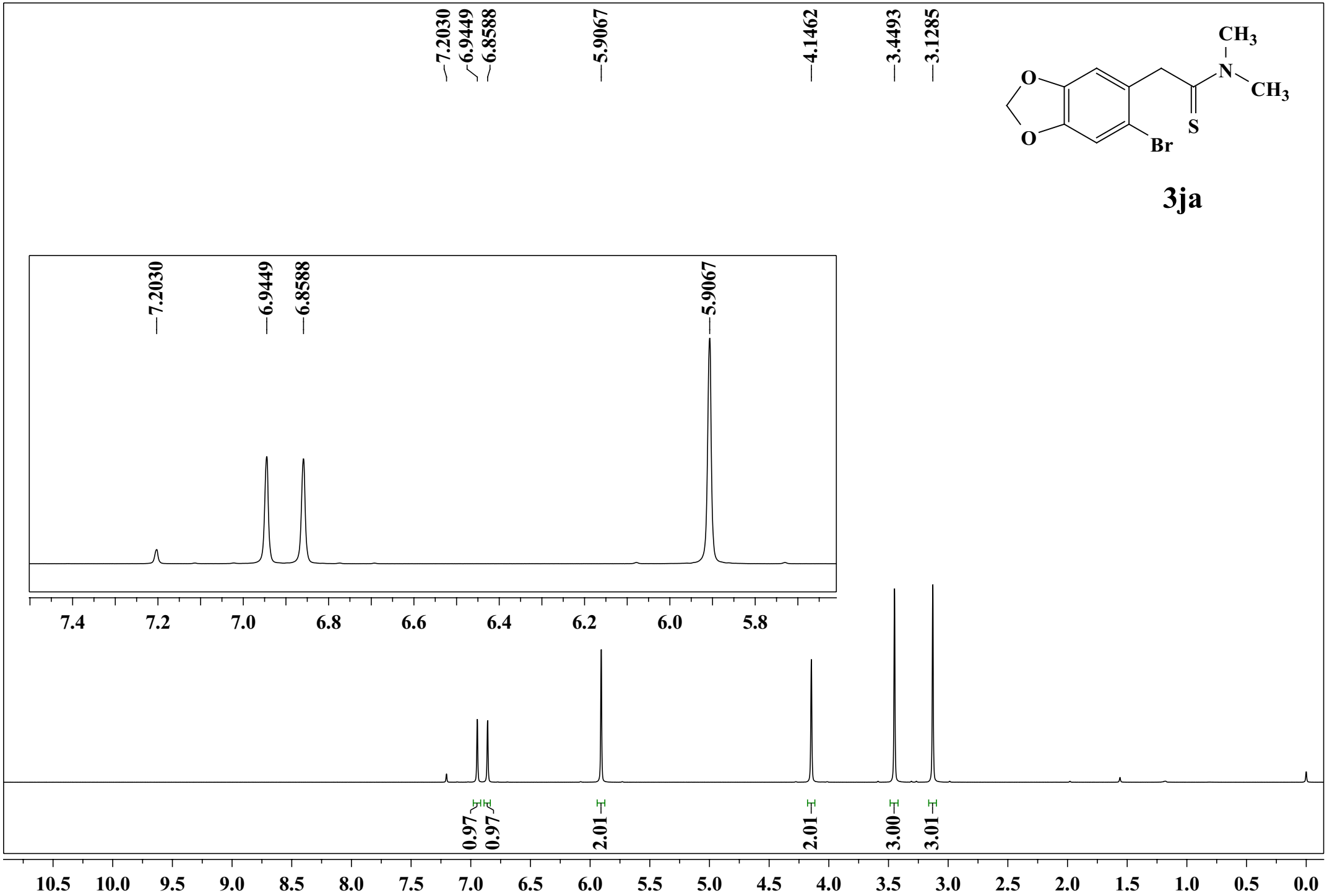


Figure S22. 1H NMR Spectrum of 3ja

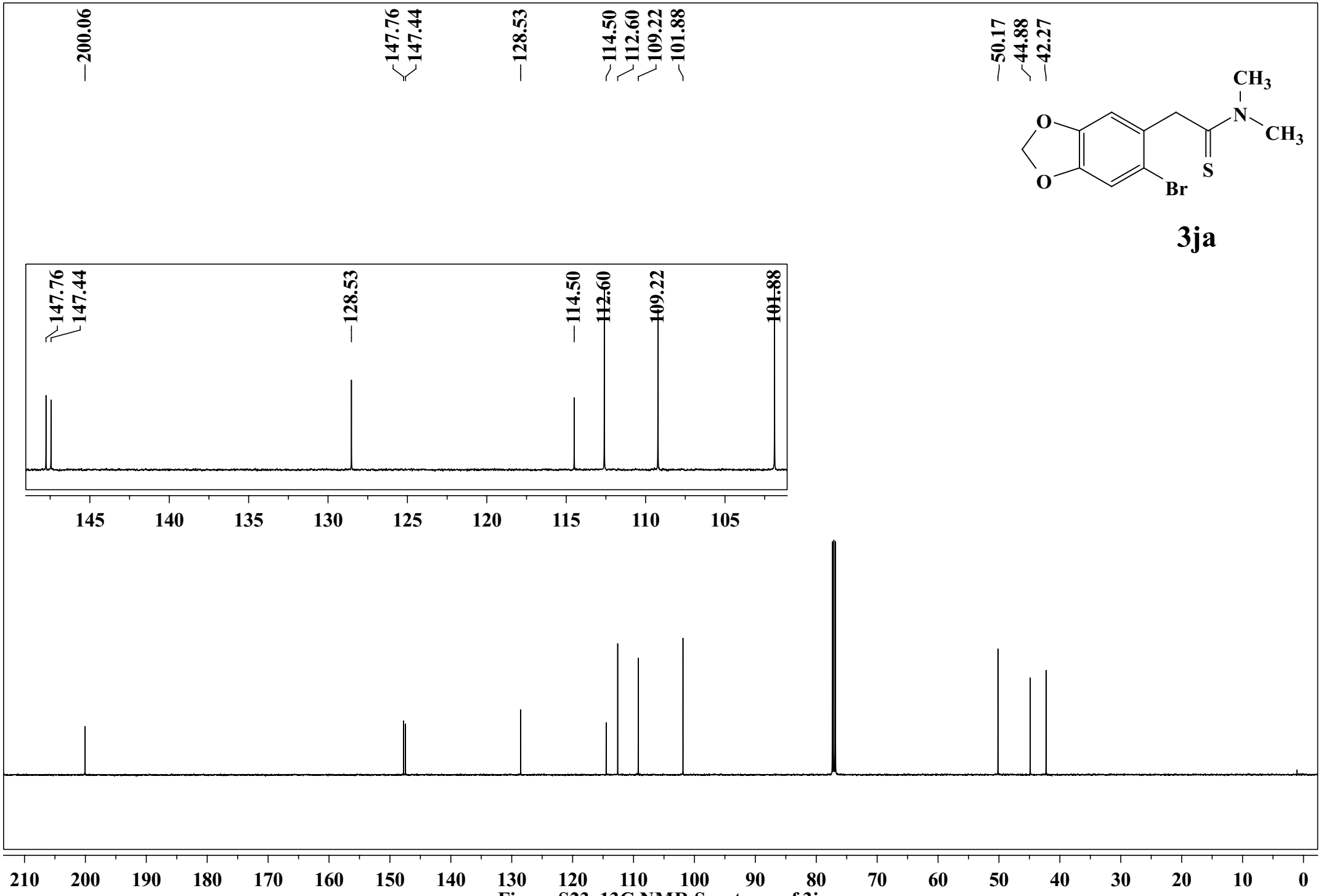


Figure S23. 13C NMR Spectrum of 3ja

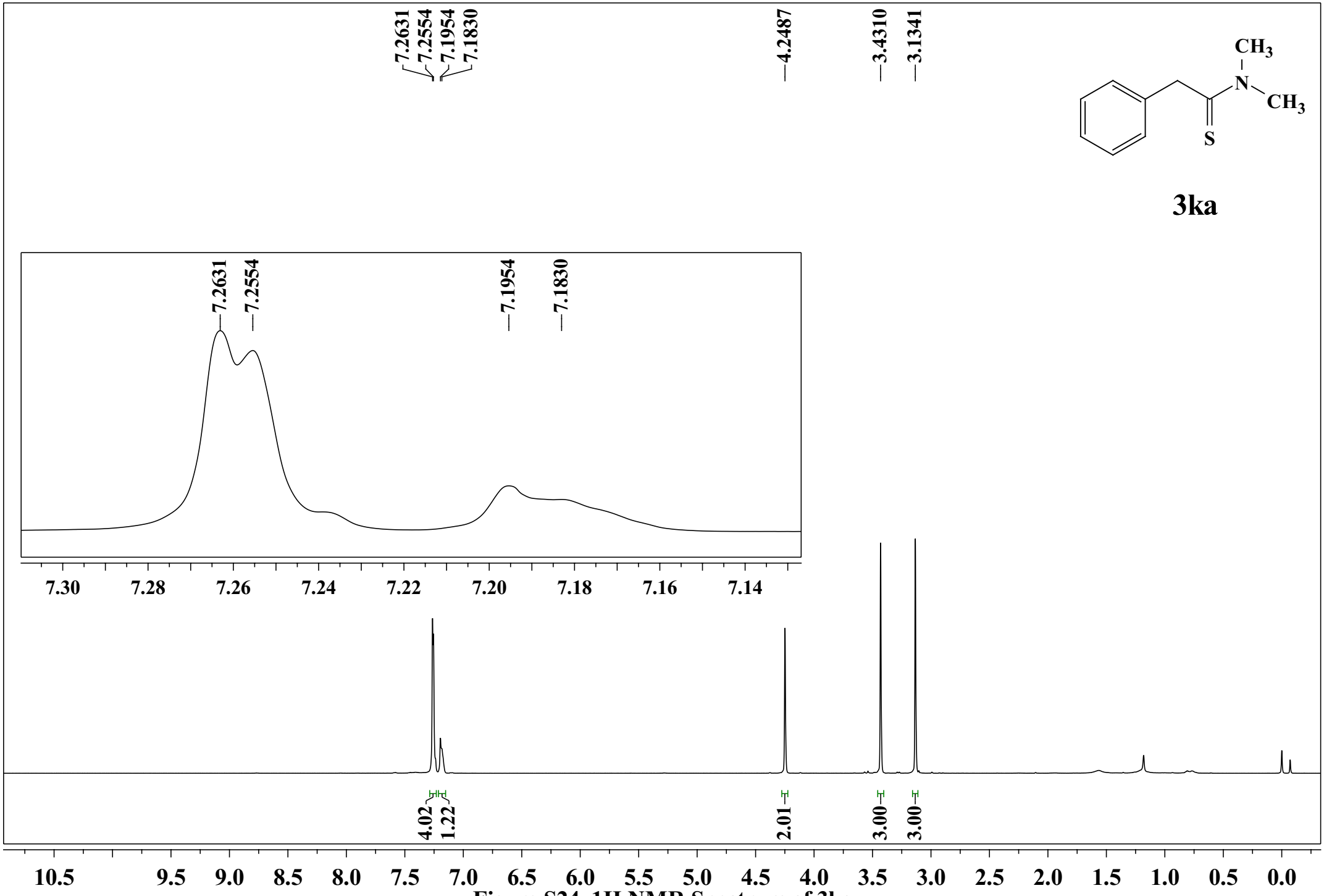


Figure S24. 1H NMR Spectrum of 3ka

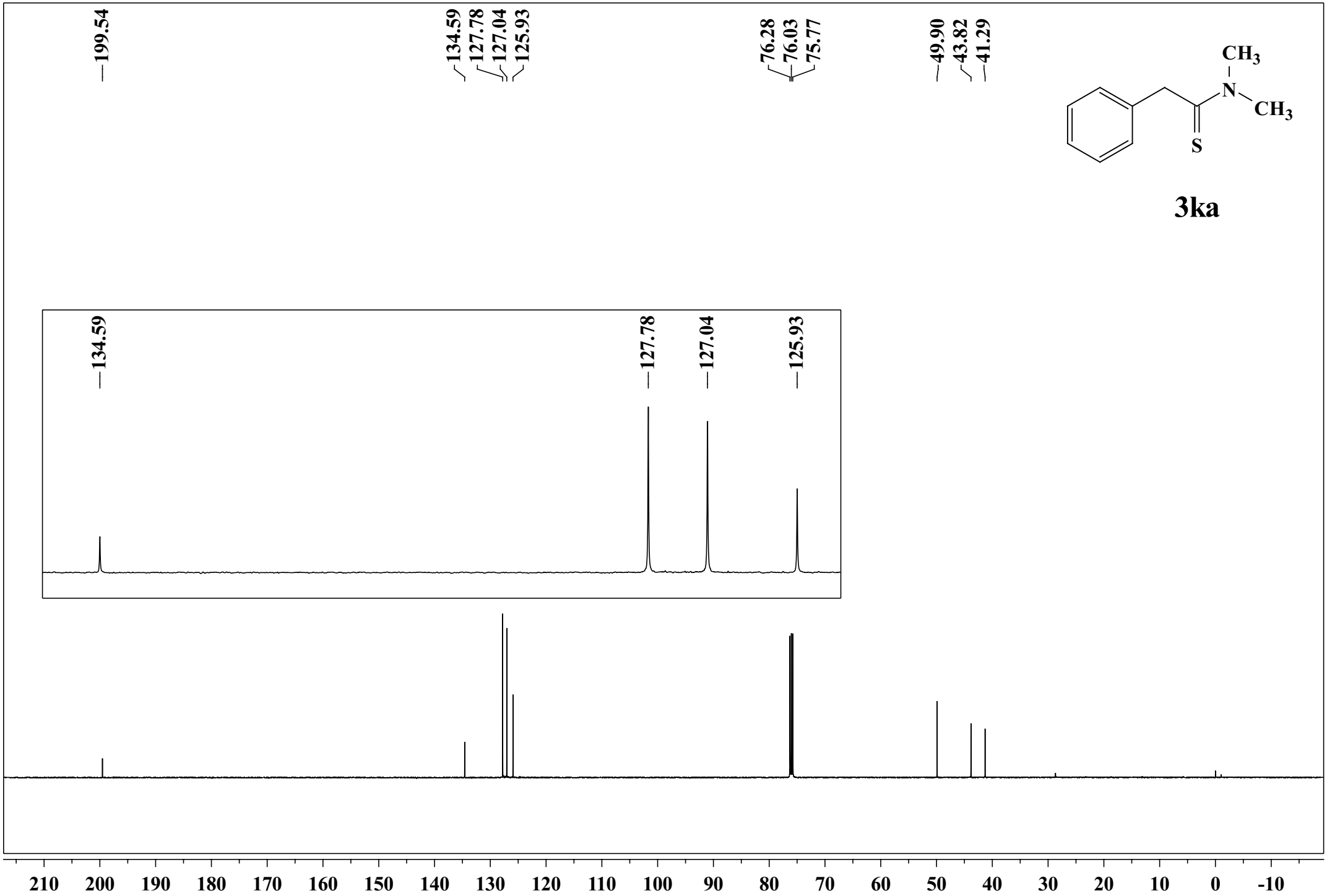


Figure S25. 13C NMR Spectrum of 3ka

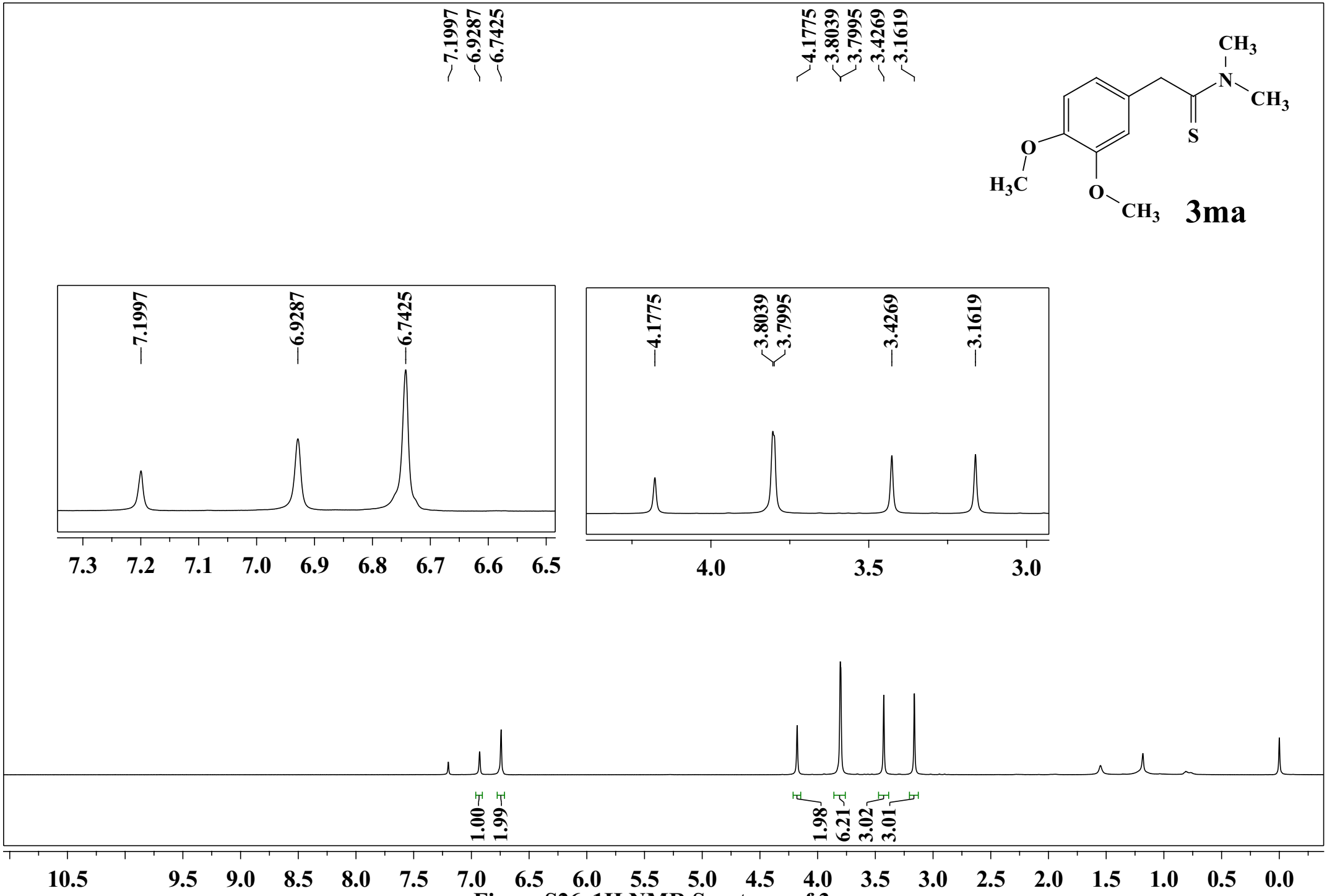


Figure S26. 1H NMR Spectrum of 3ma

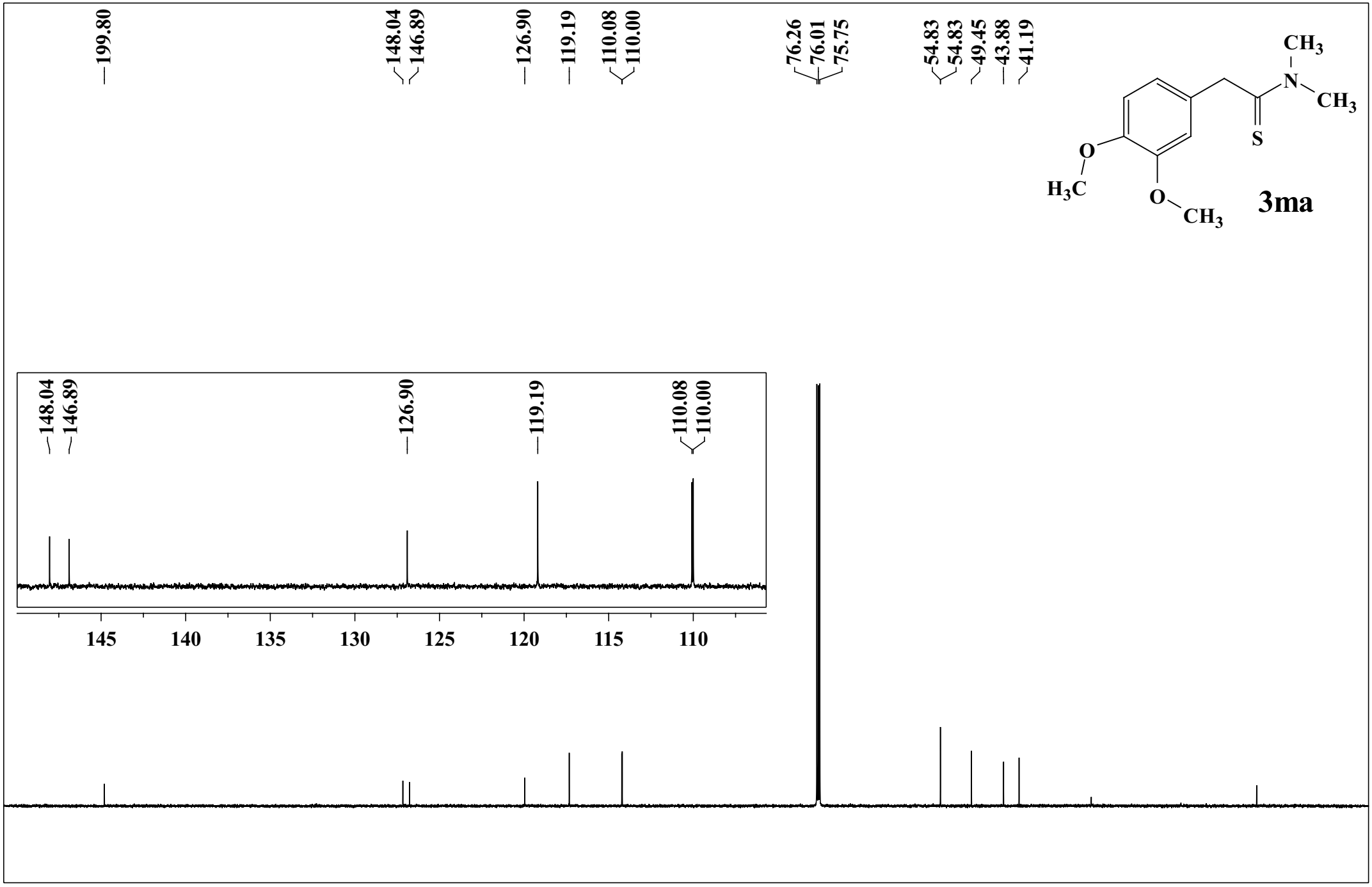


Figure S27. 13C NMR Spectrum of 3ma

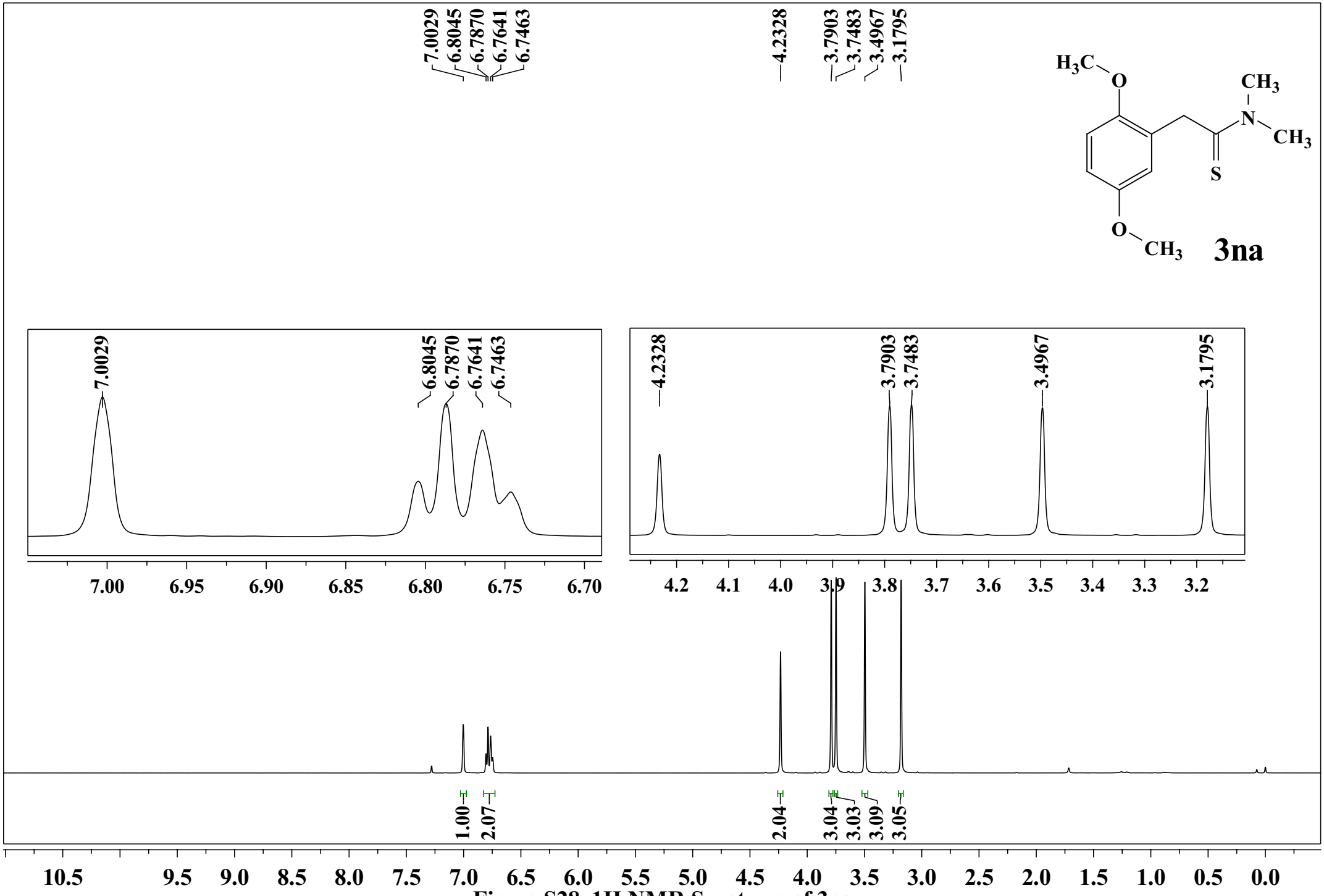


Figure S28. 1H NMR Spectrum of 3na

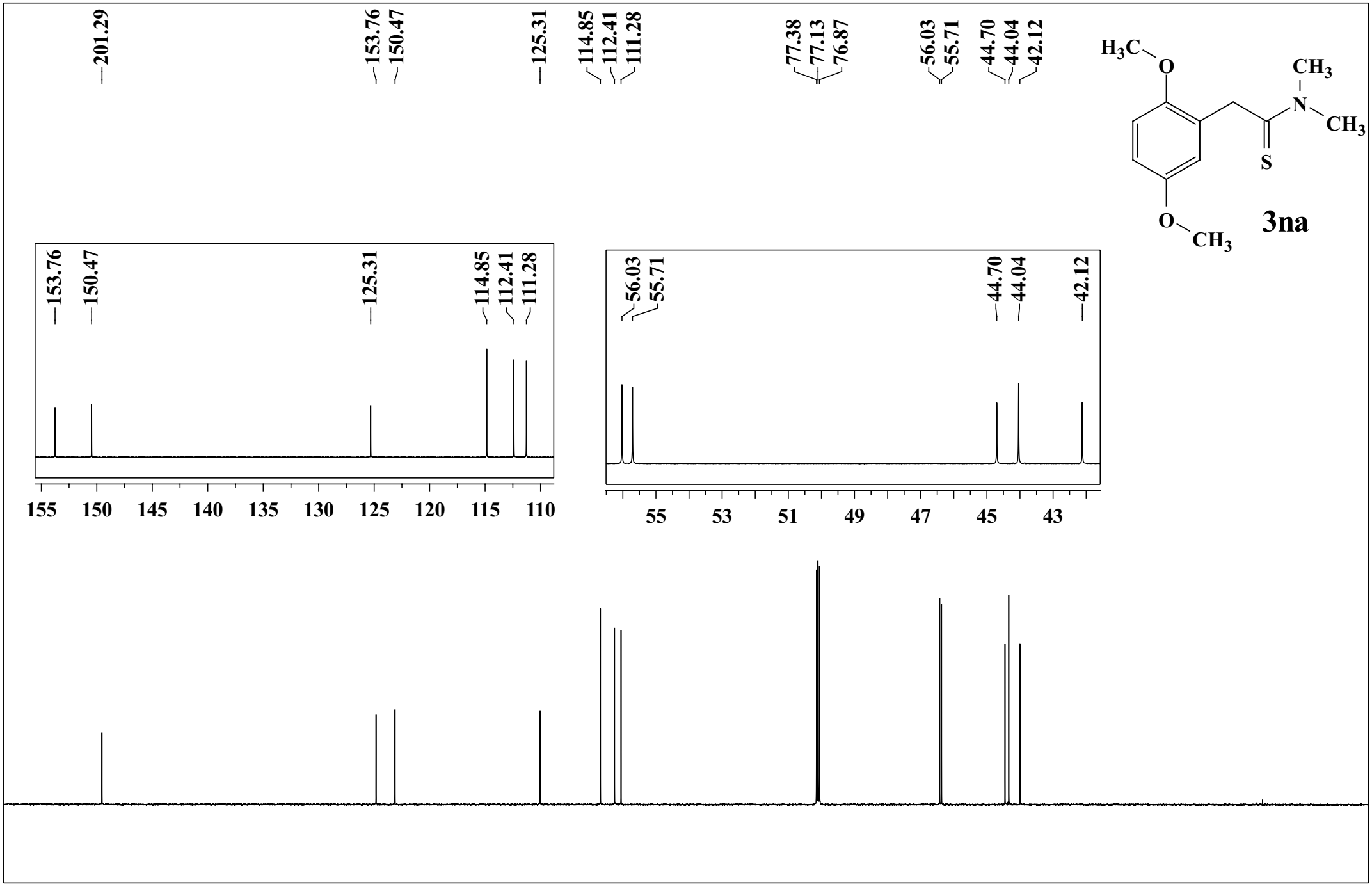


Figure S29. 13C NMR Spectrum of 3na

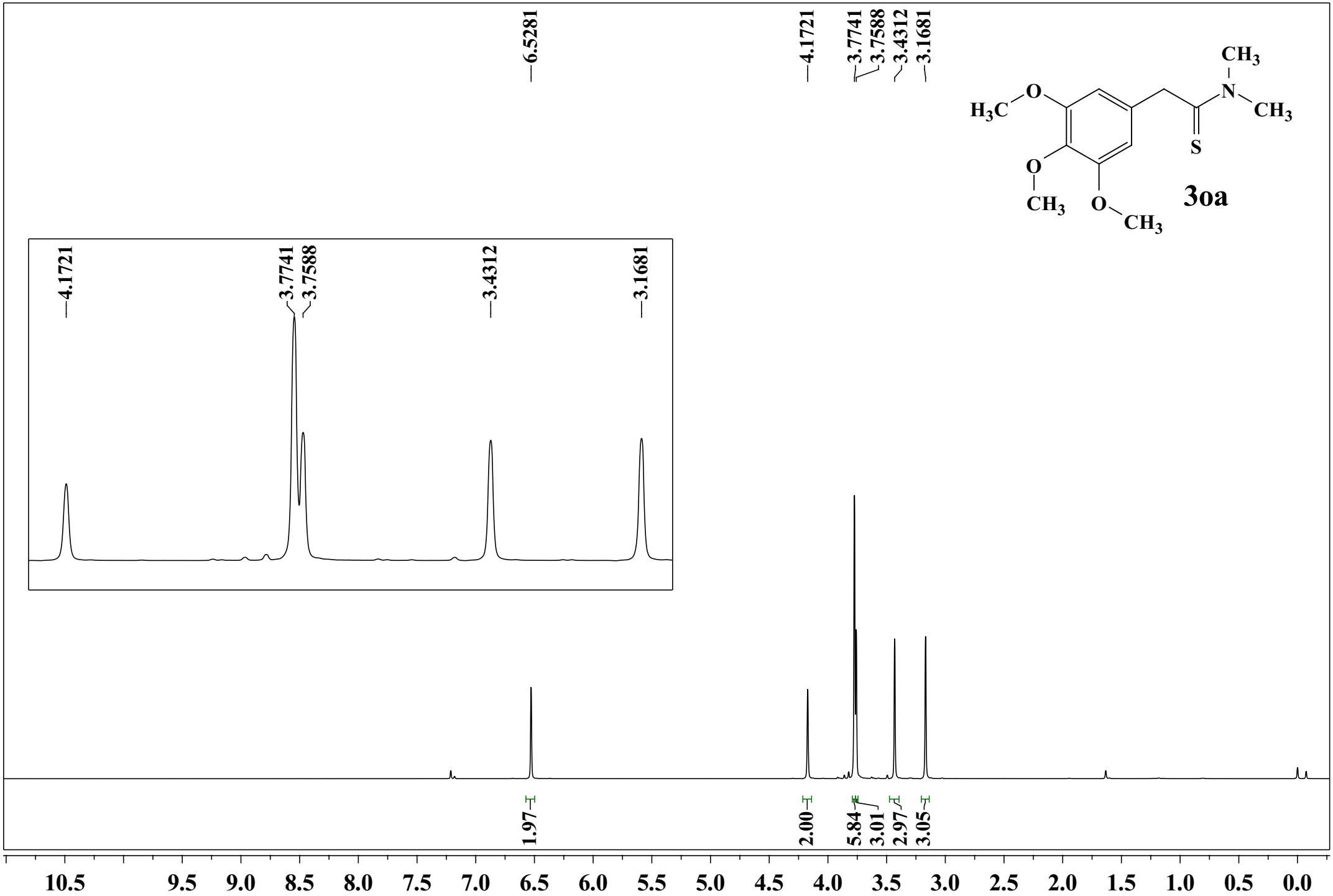


Figure S30. 1H NMR Spectrum of 3oa

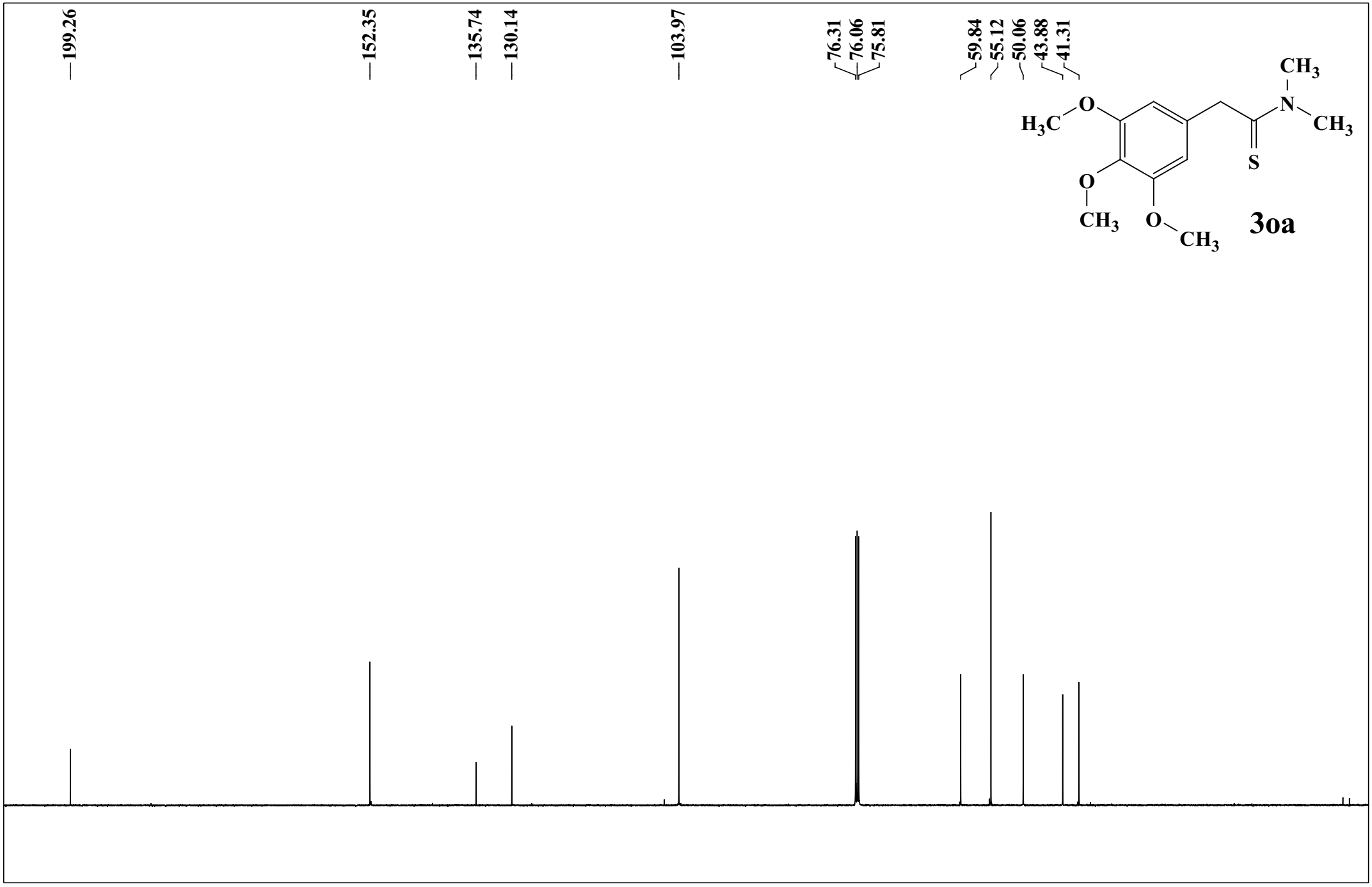


Figure S31. 13C NMR Spectrum of 3oa

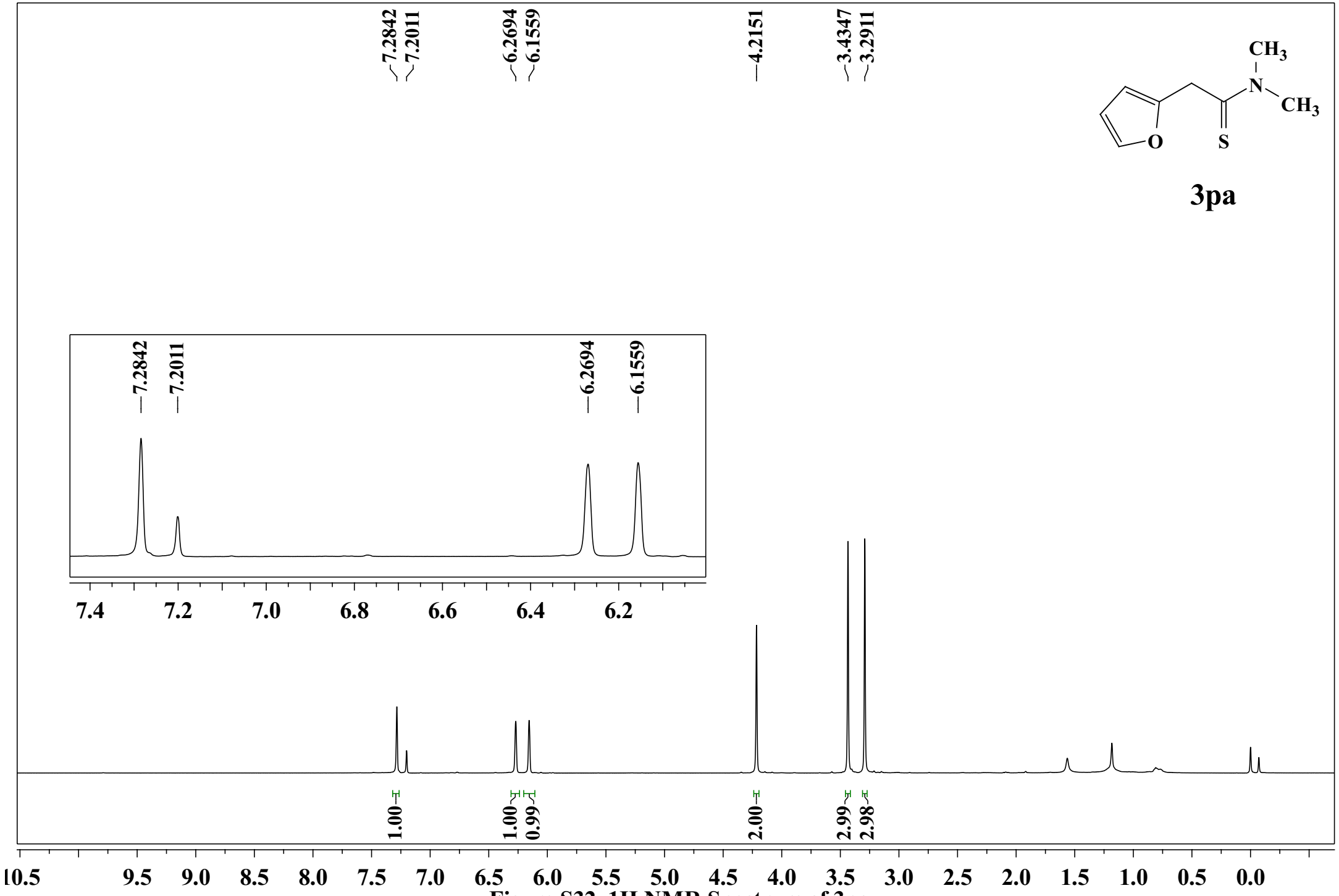


Figure S32. 1H NMR Spectrum of 3pa

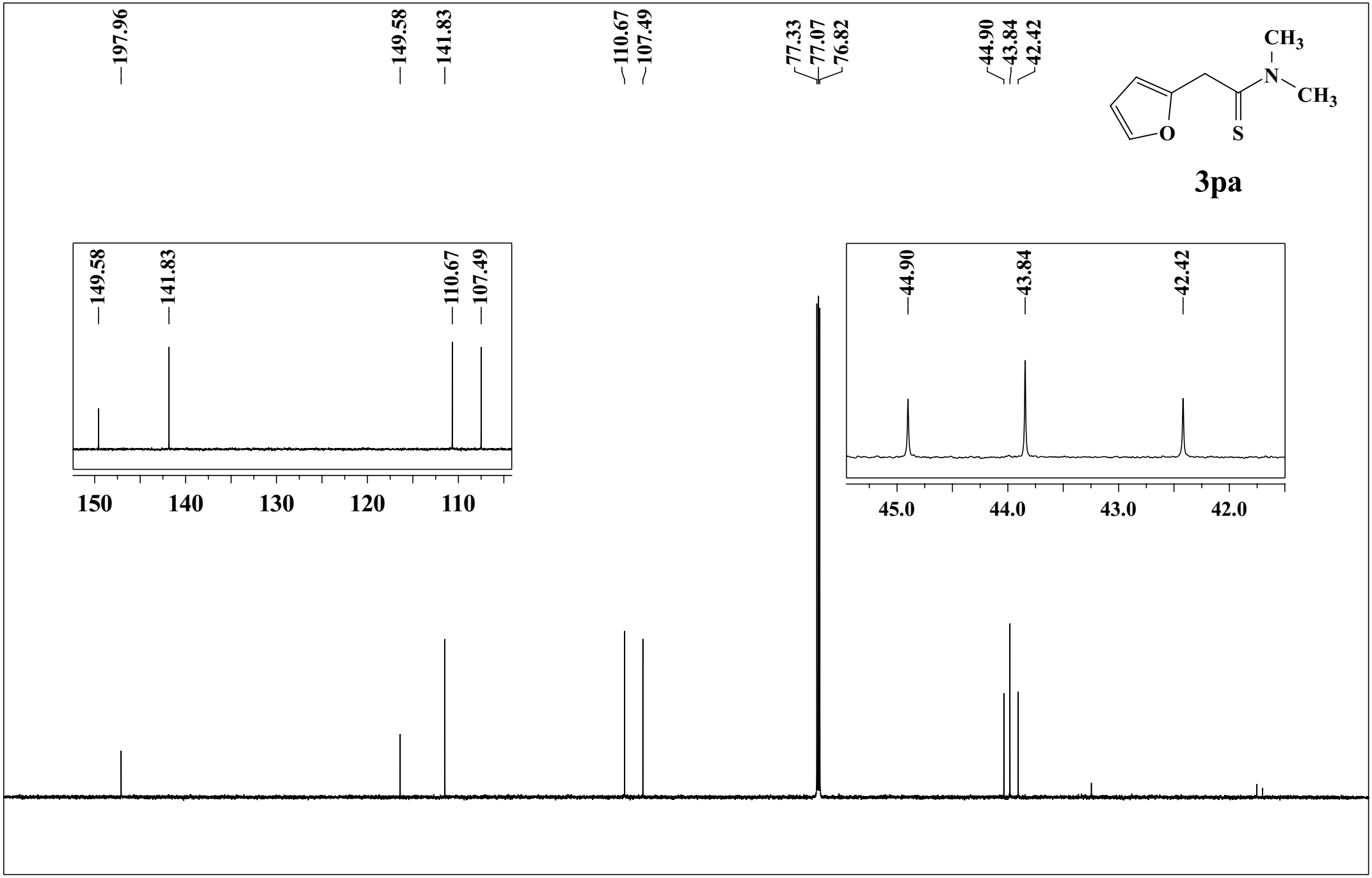


Figure S33. 13C NMR Spectrum of 3pa

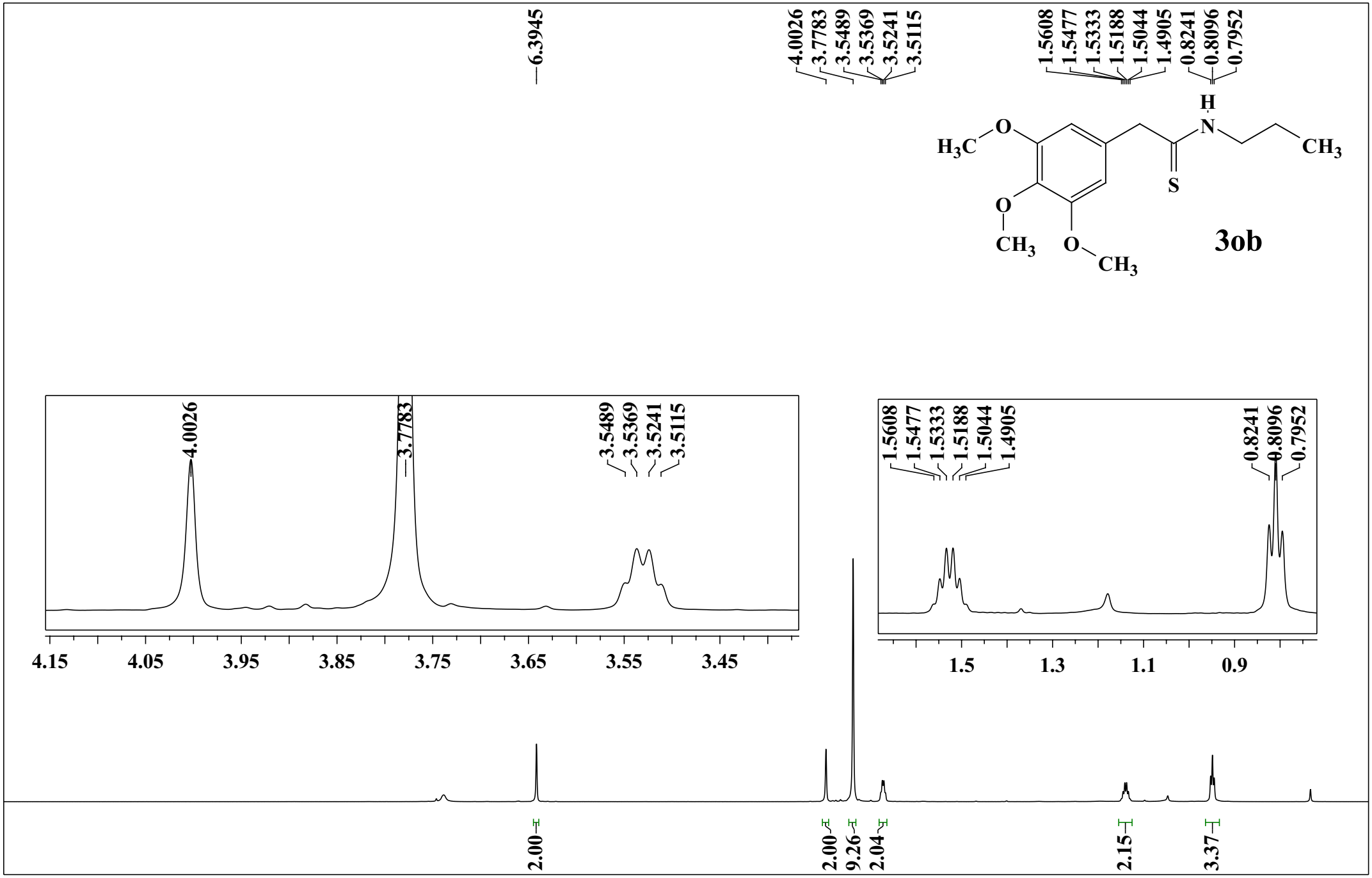


Figure S34. 1HNMR Spectrum of 3ob

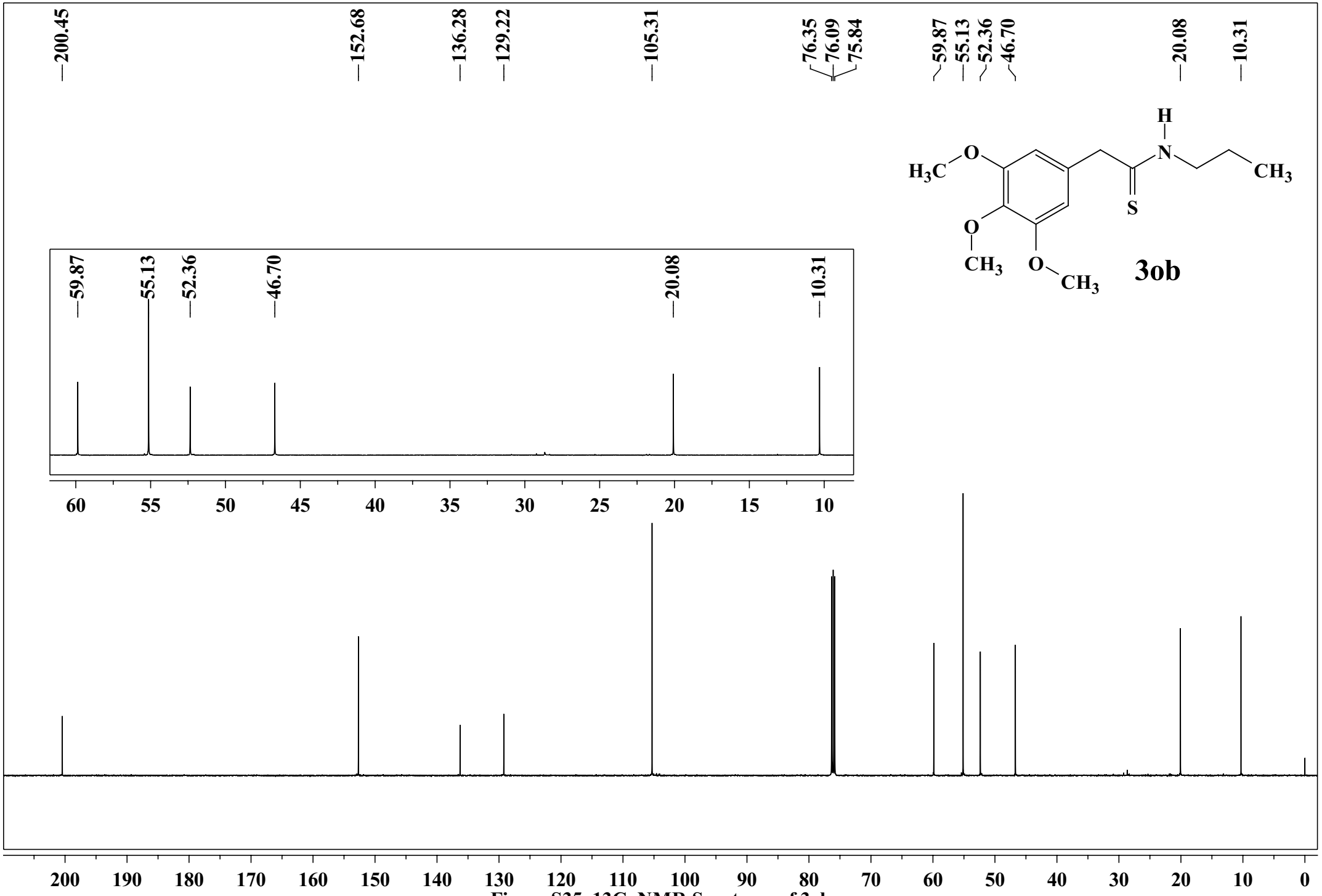


Figure S35. 13C NMR Spectrum of 3ob

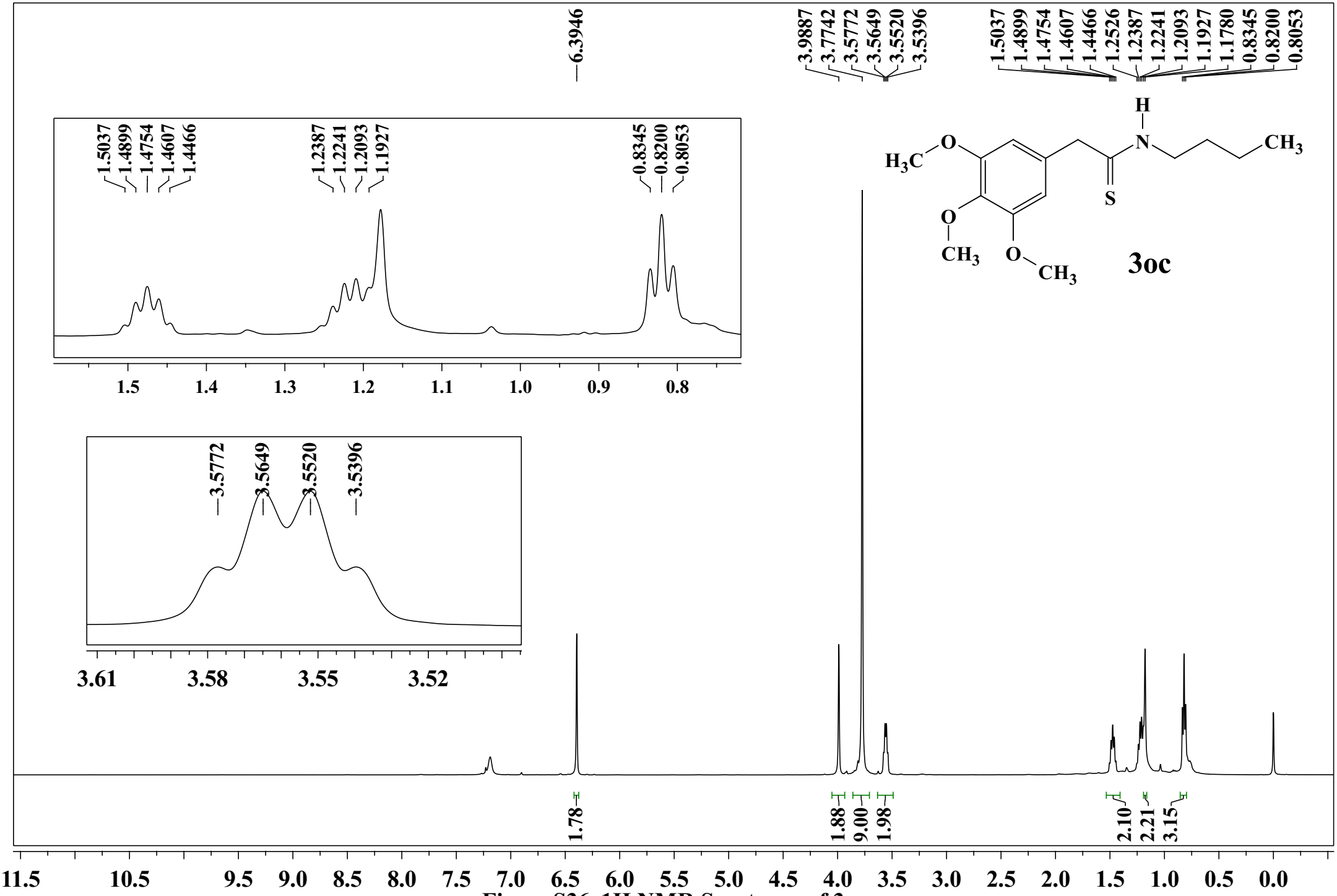


Figure S36. 1H NMR Spectrum of 3oc

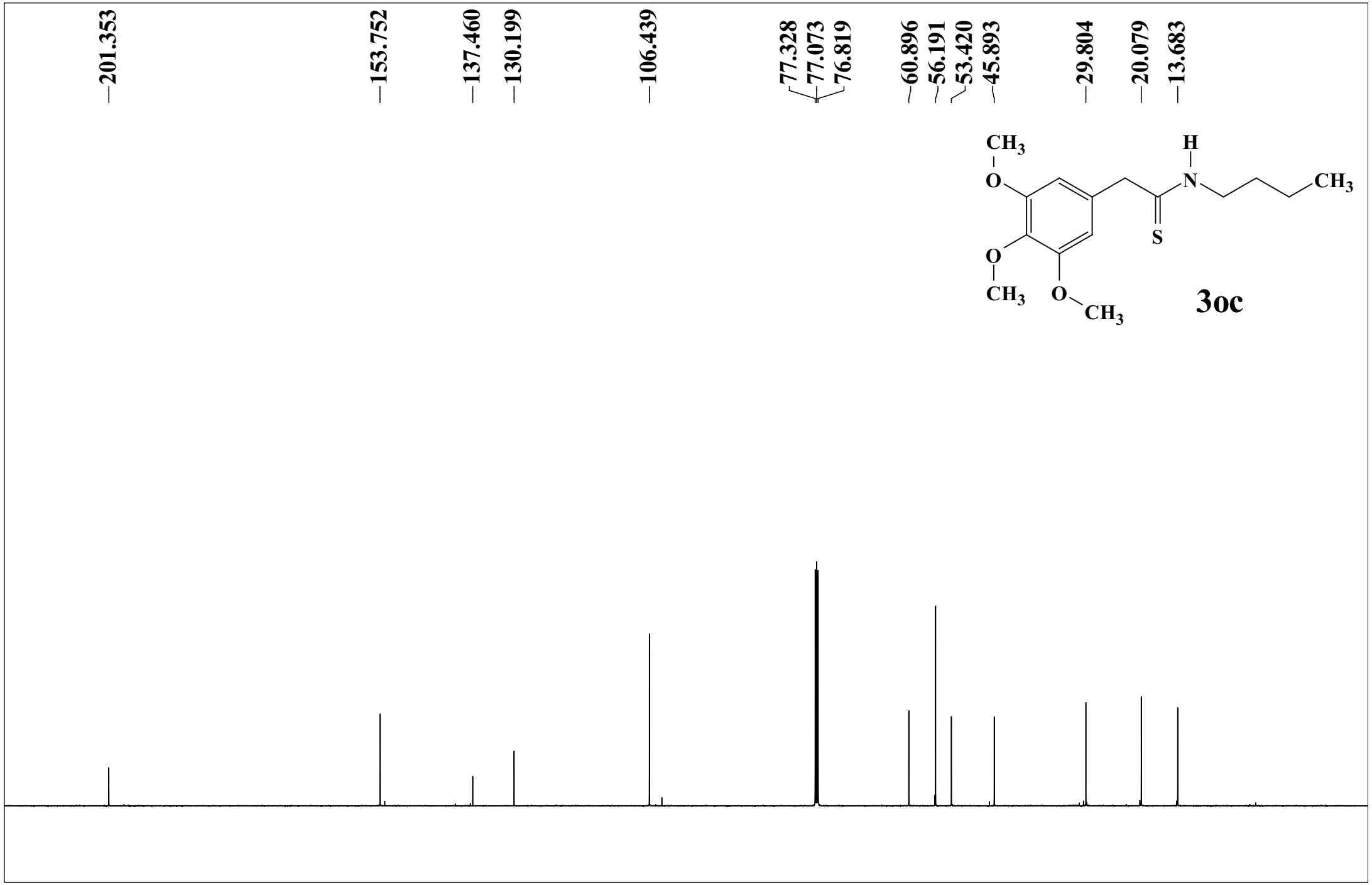


Figure S37. 13C NMR Spectrum of 3oc

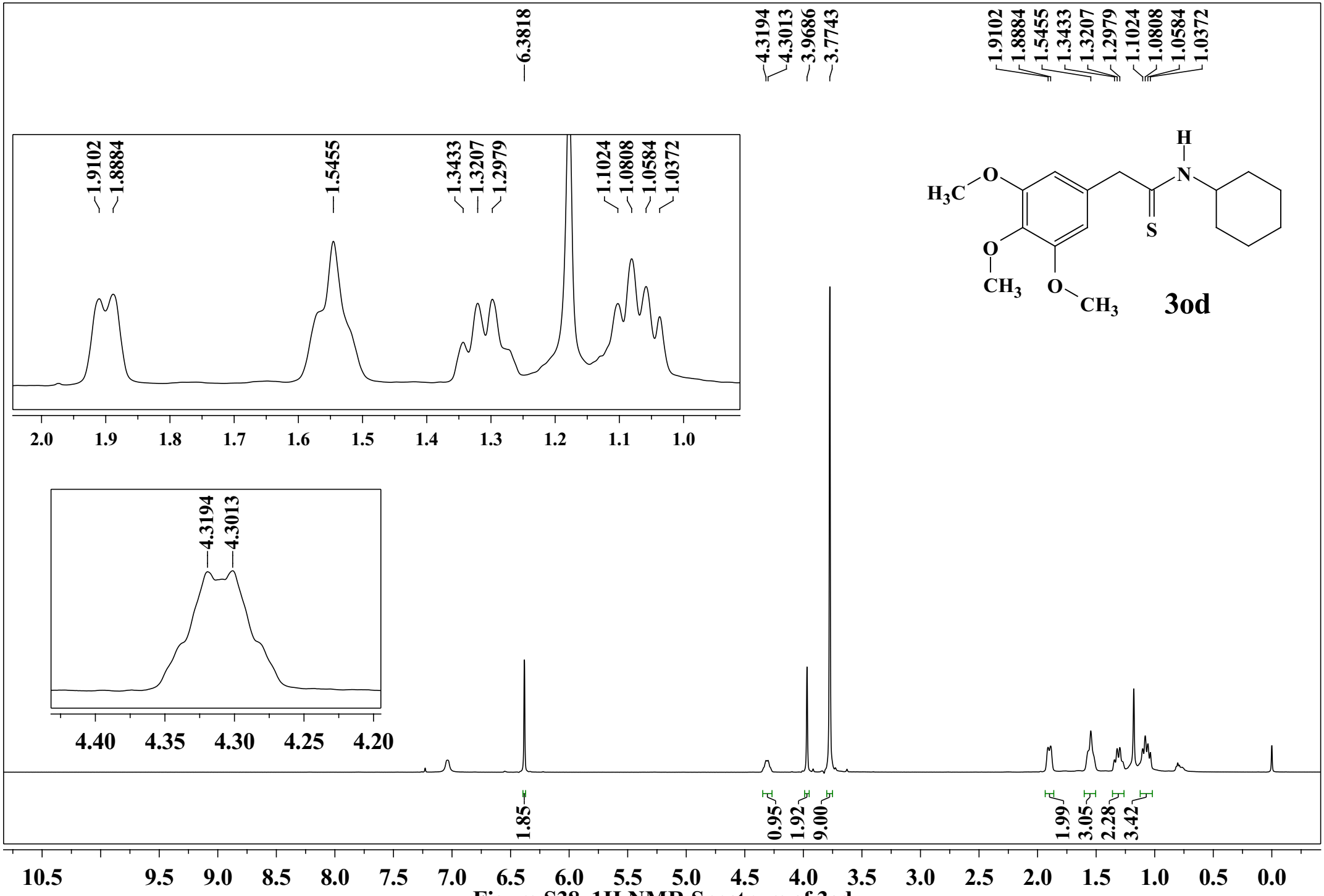


Figure S38. 1H NMR Spectrum of 3od

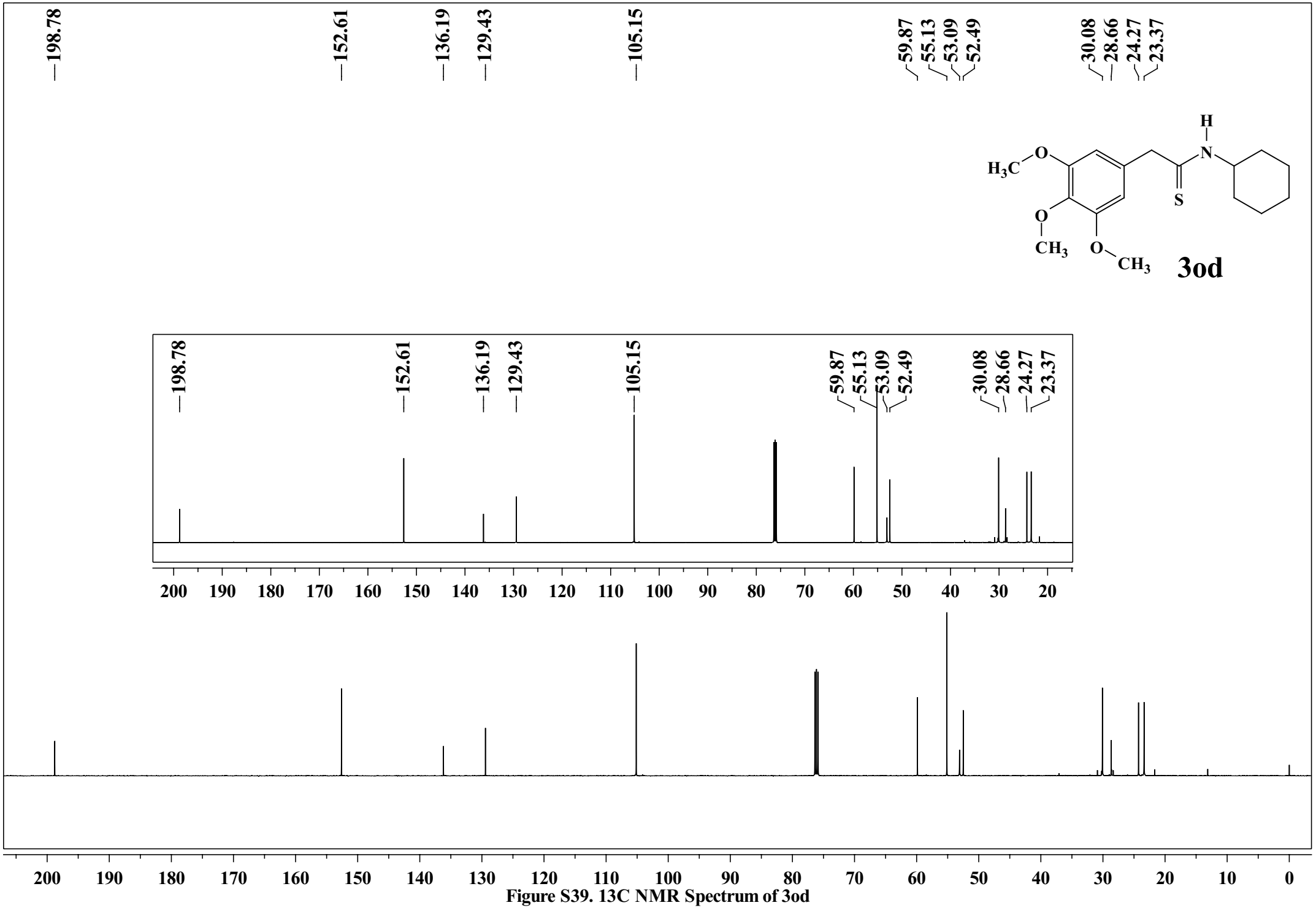


Figure S39. 13C NMR Spectrum of 3od

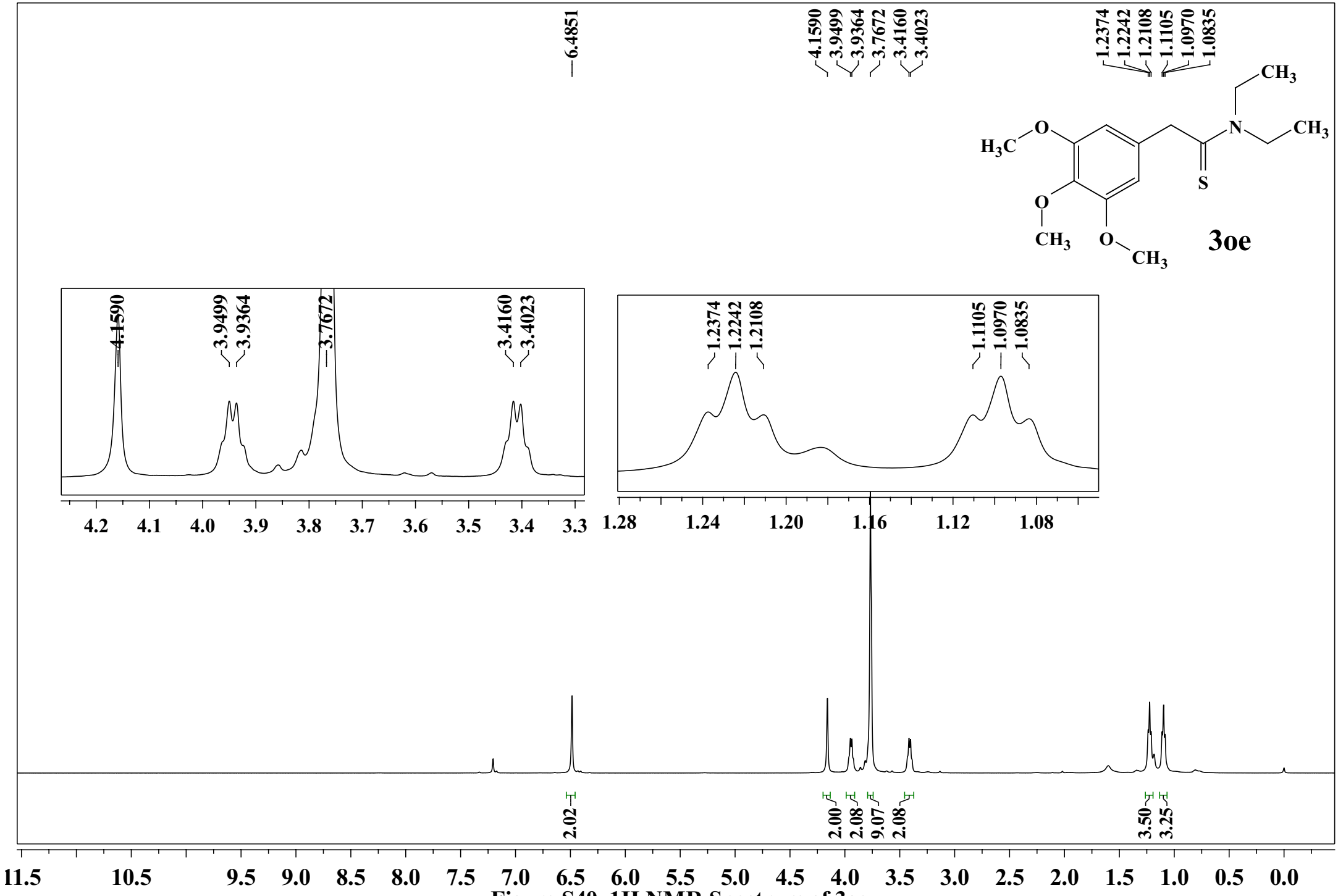


Figure S40. 1H NMR Spectrum of 3oe

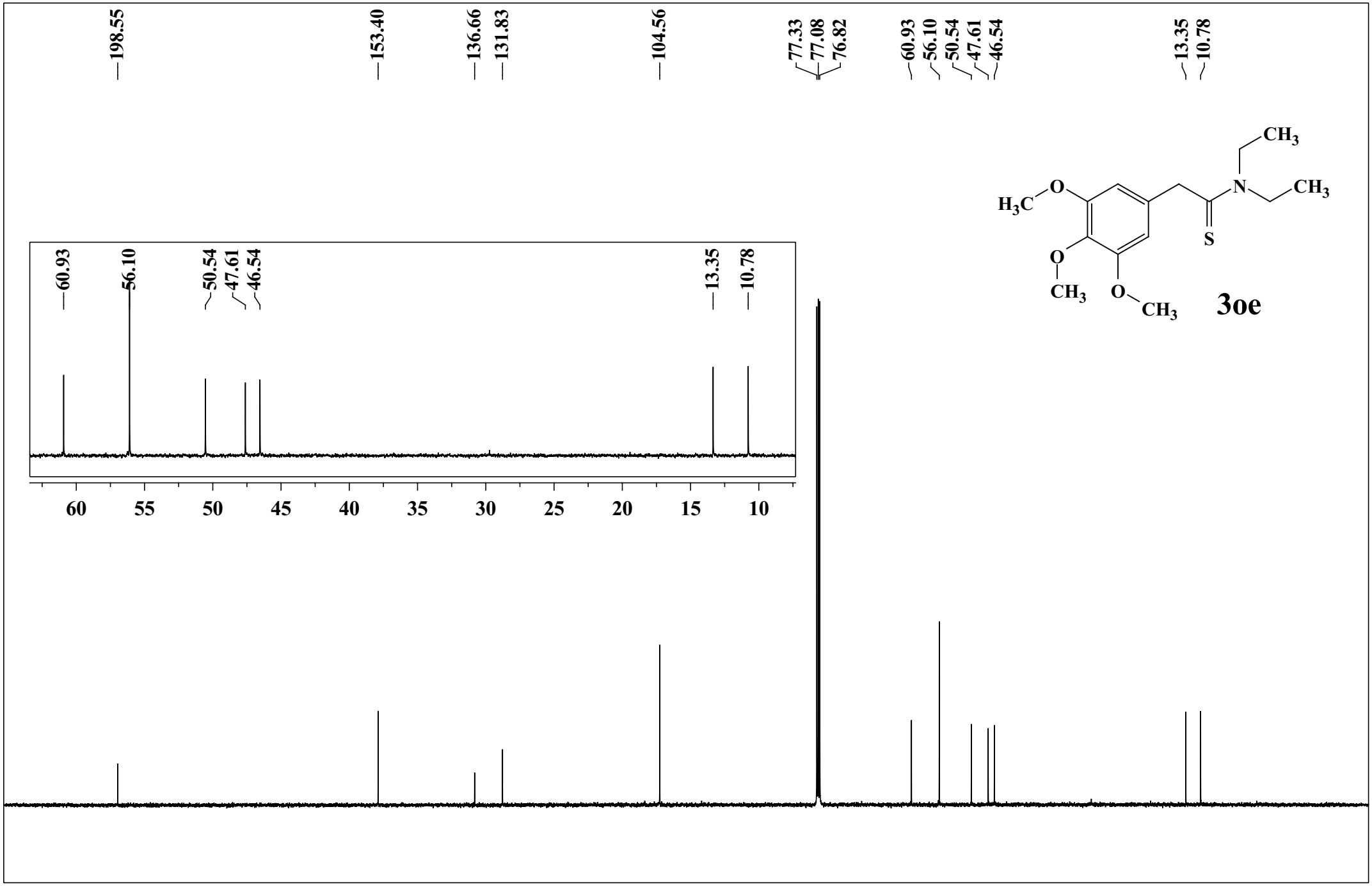


Figure S41. 13C NMR Spectrum of 3oe

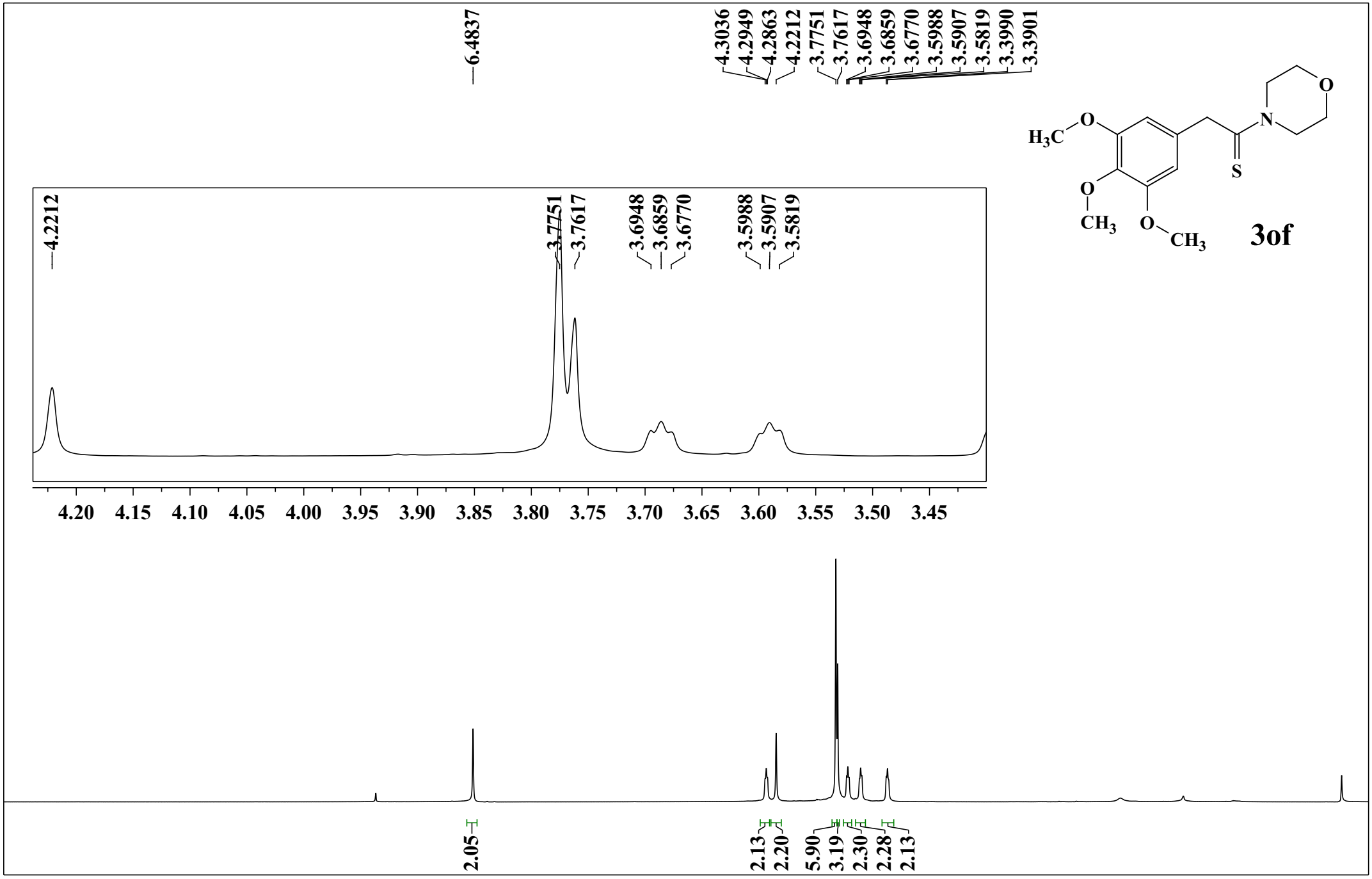


Figure S42. 1H NMR Spectrum of 3of

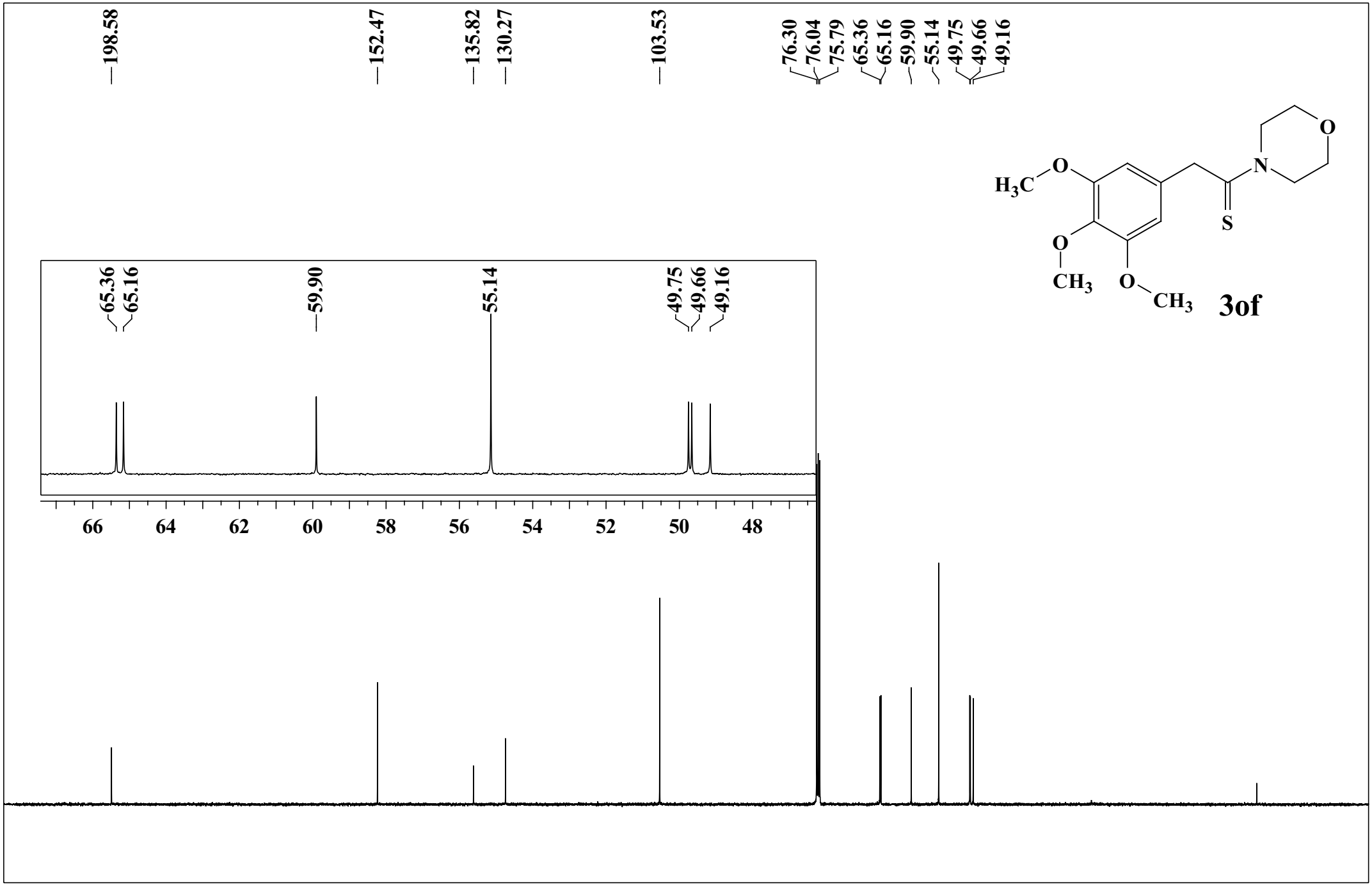


Figure S43. 13C NMR Spectrum of 3of

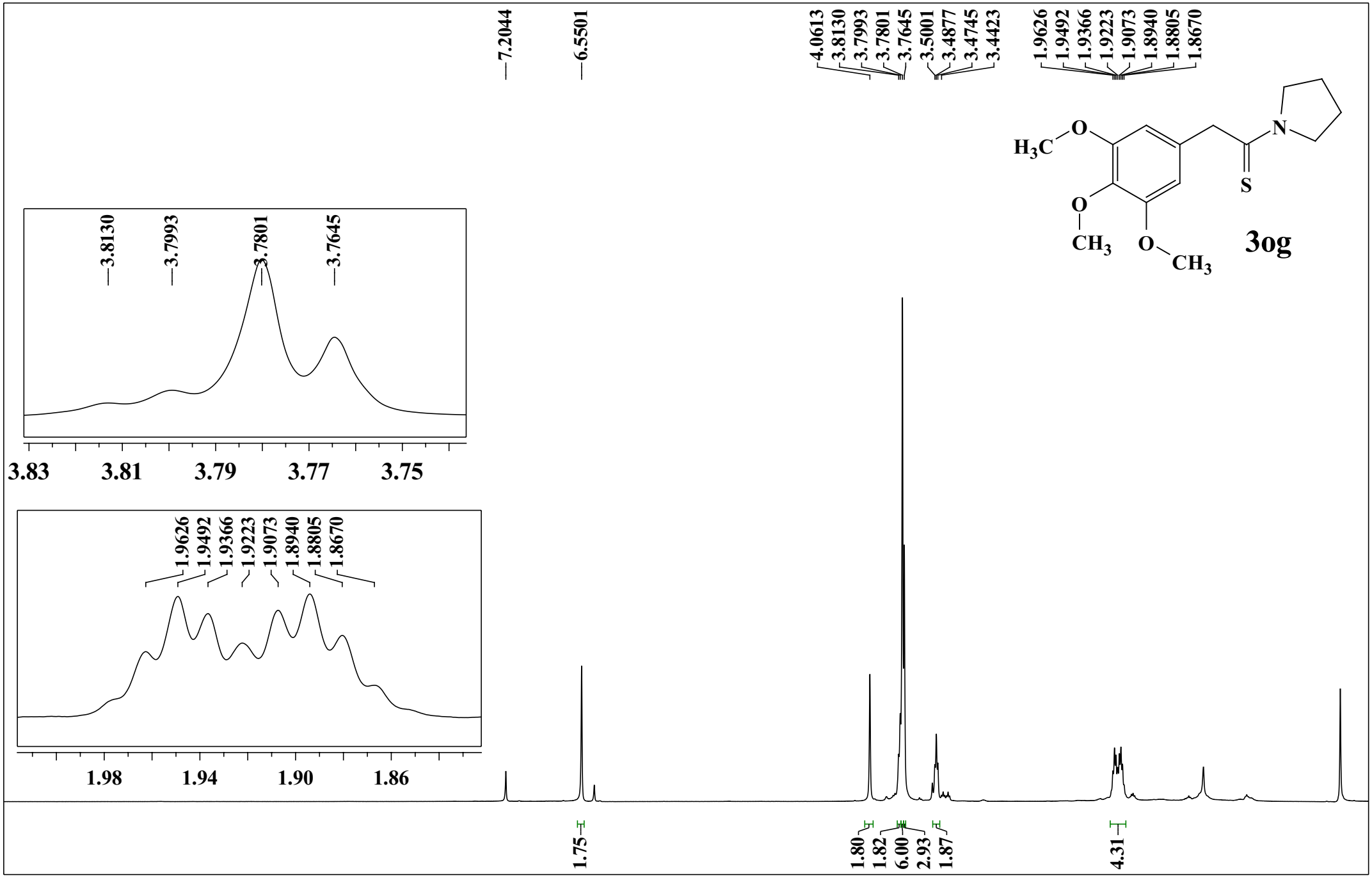


Figure S44. 1H NMR Spectrum of 3og

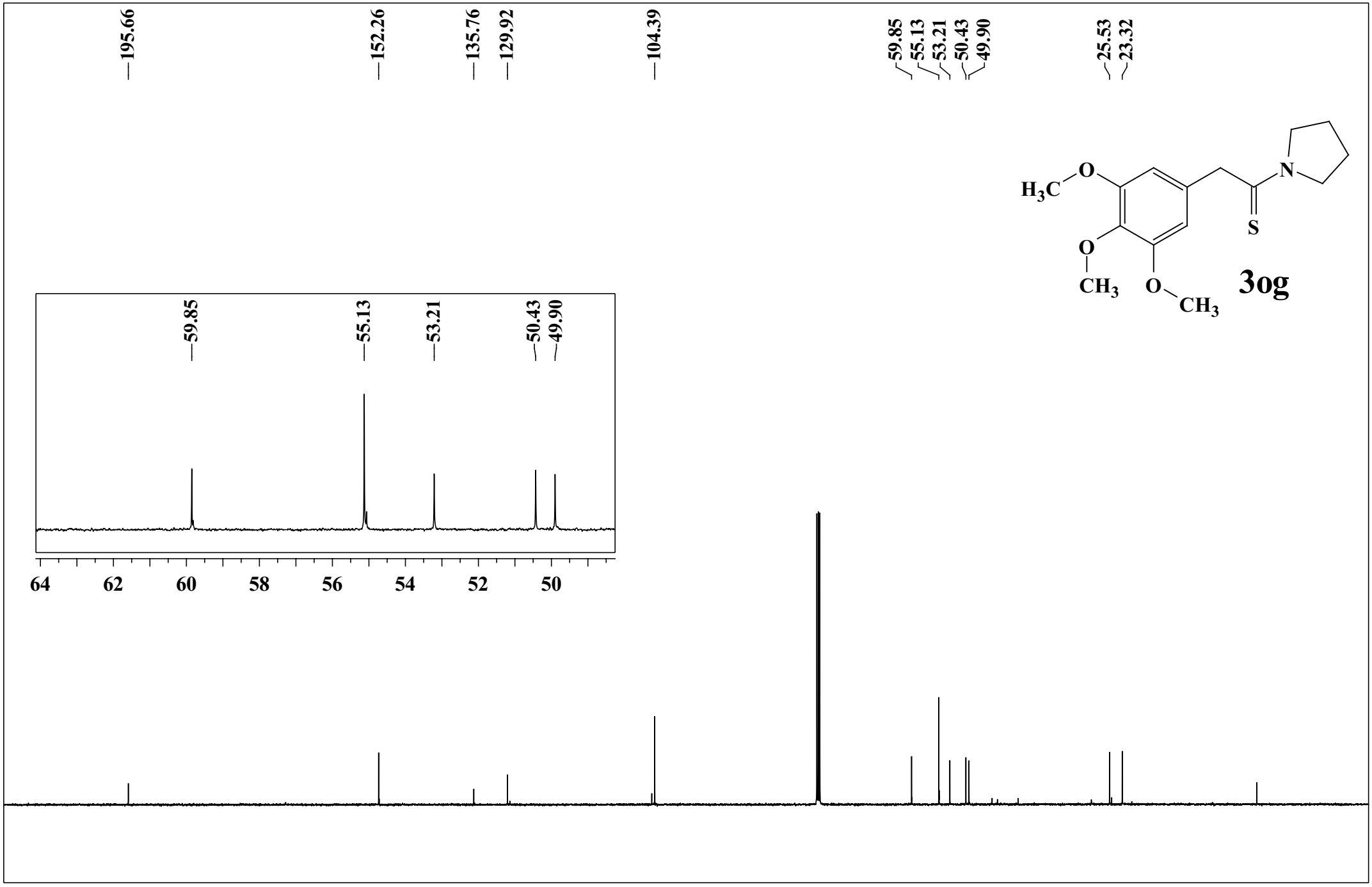


Figure S45. 13C NMR Spectrum of 3og

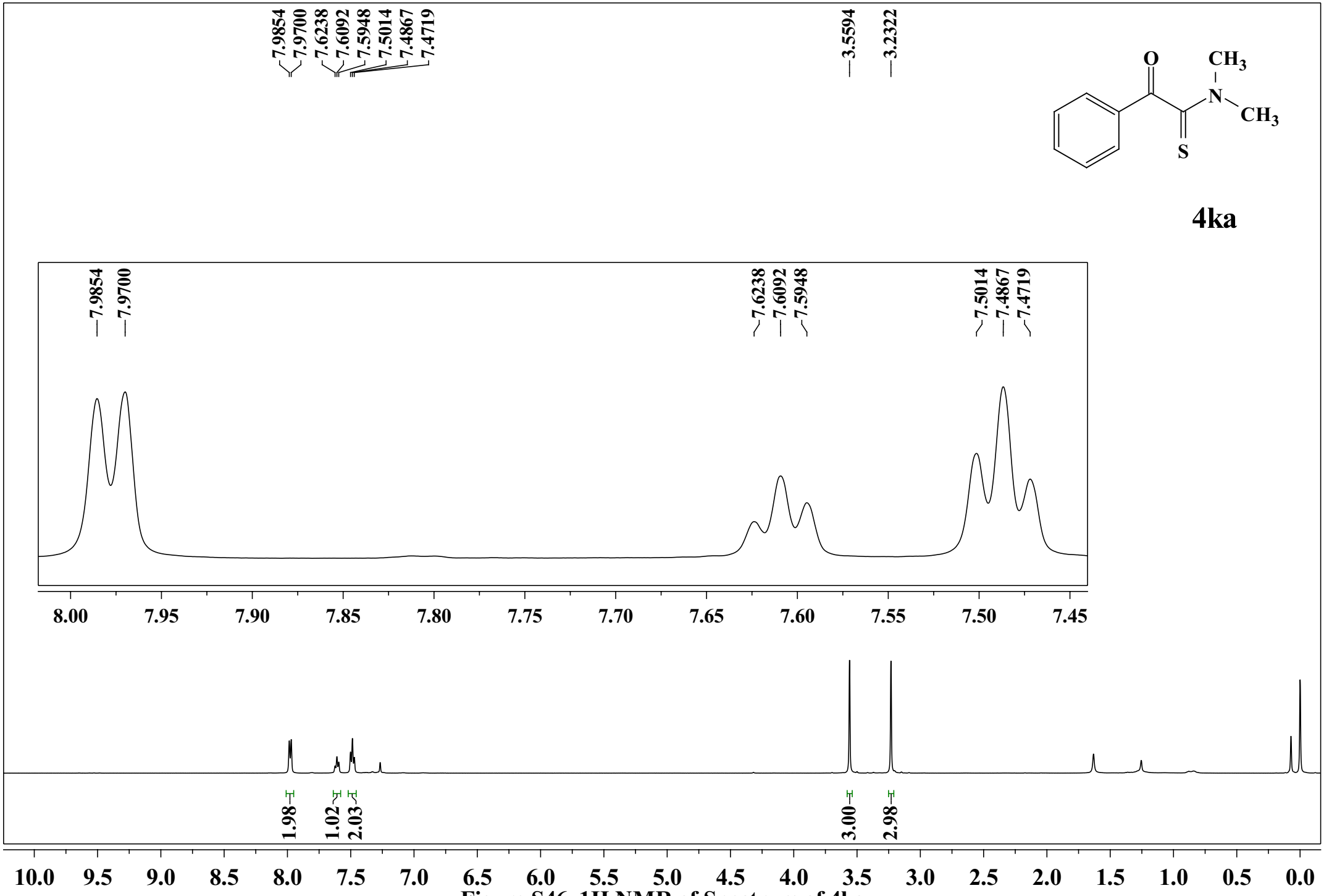


Figure S46. 1H NMR of Spectrum of 4ka

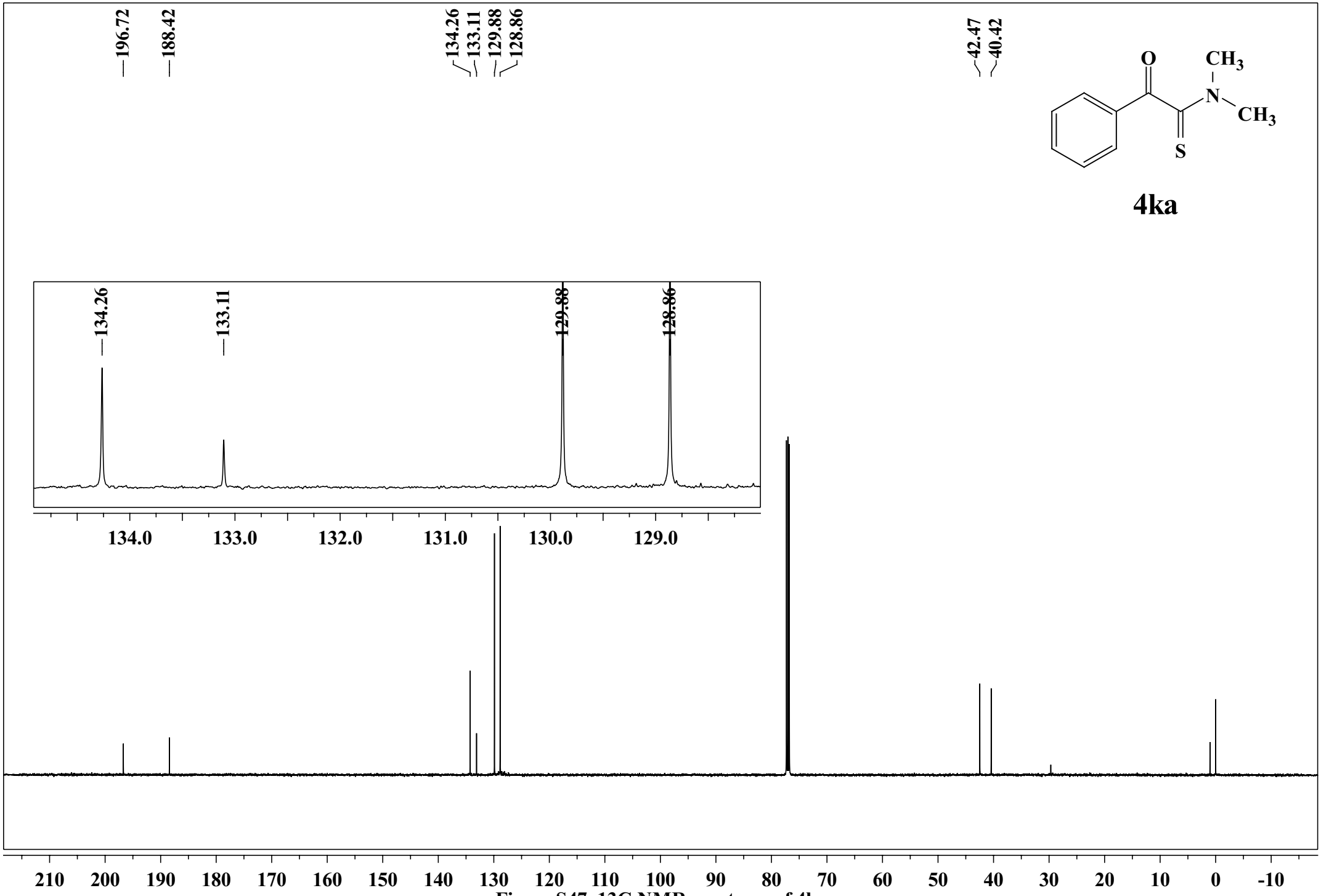


Figure S47. 13C NMR spectrum of 4ka

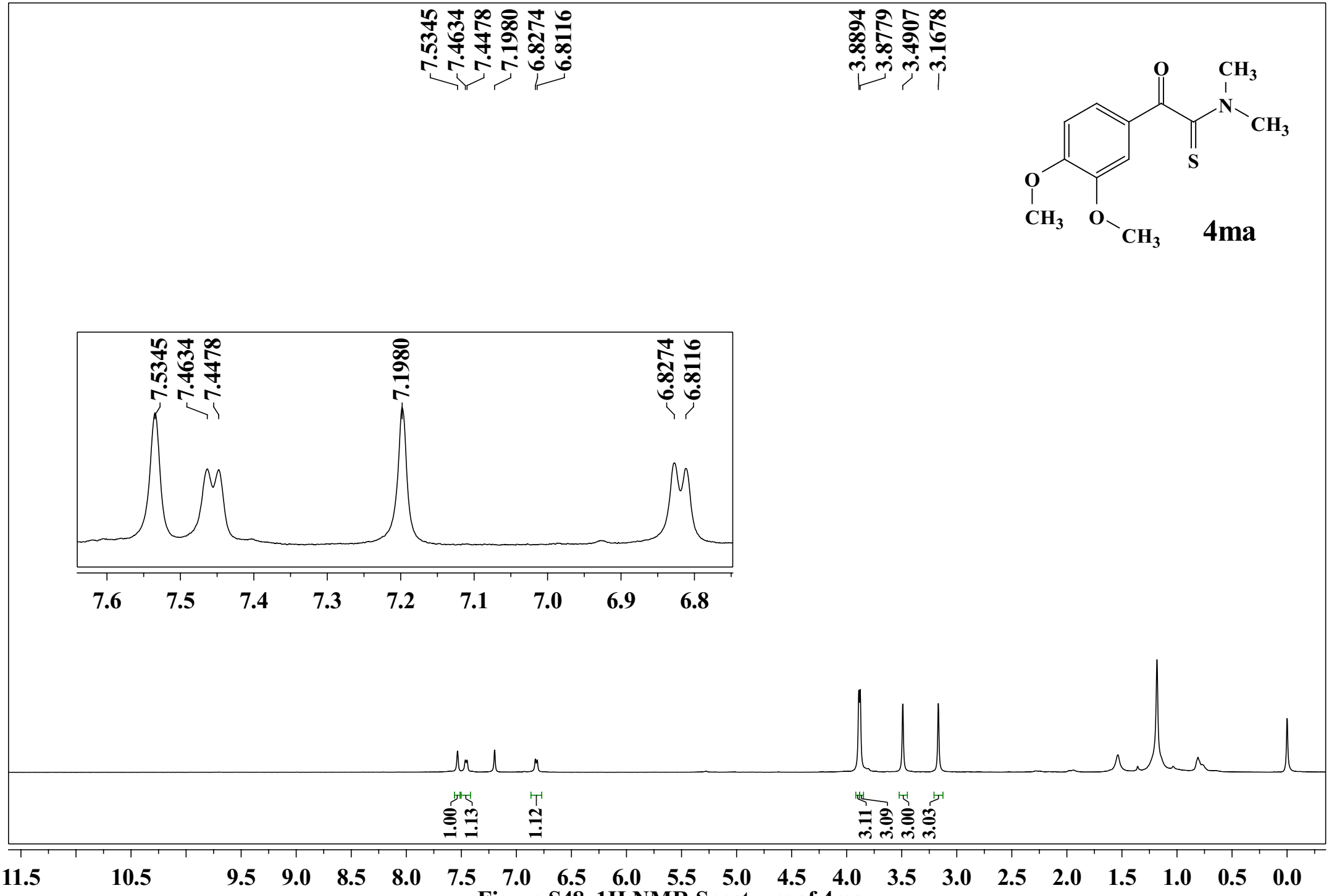


Figure S48. 1H NMR Spectrum of 4ma

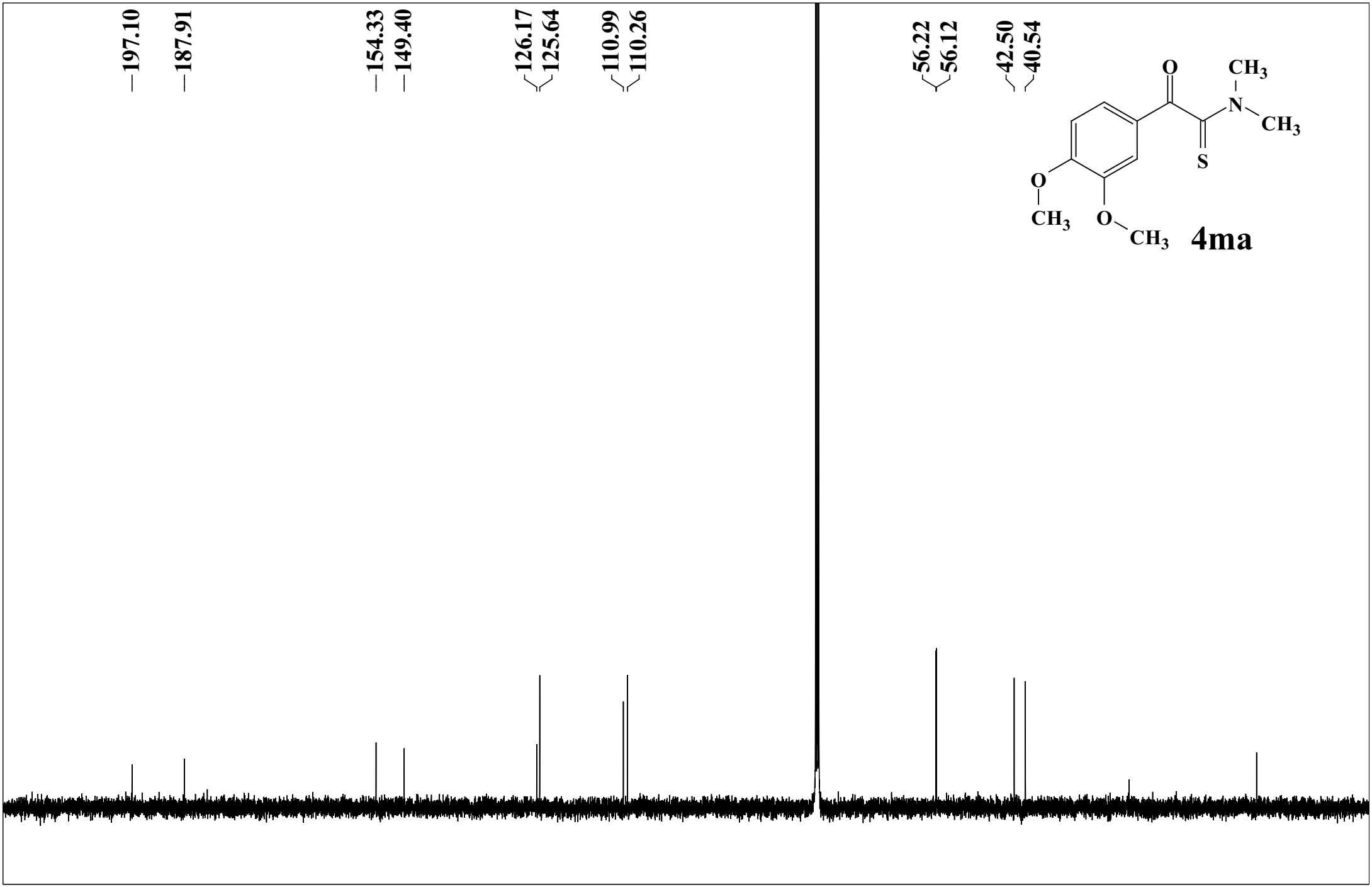


Figure S49. 13C NMR Spectrum of 4ma

Single crystal X-ray structure of 3oa

Datablock: shelx

Bond precision: C-C = 0.0040 A Wavelength=0.71075

Cell:	a=14.183(18)	b=7.331(9)	c=14.82(2)
	alpha=90	beta=111.951(11)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	1429(3)	1430(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H19 N O3 S	?
Sum formula	C13 H19 N O3 S	C13 H19 N O3 S
Mr	269.35	269.35
Dx,g cm-3	1.252	1.251
Z	4	4
Mu (mm-1)	0.227	0.227
F000	576.0	576.0
F000'	576.75	
h,k,lmax	18,9,19	18,9,19
Nref	3314	3270
Tmin,Tmax	0.950,0.967	
Tmin'	0.949	

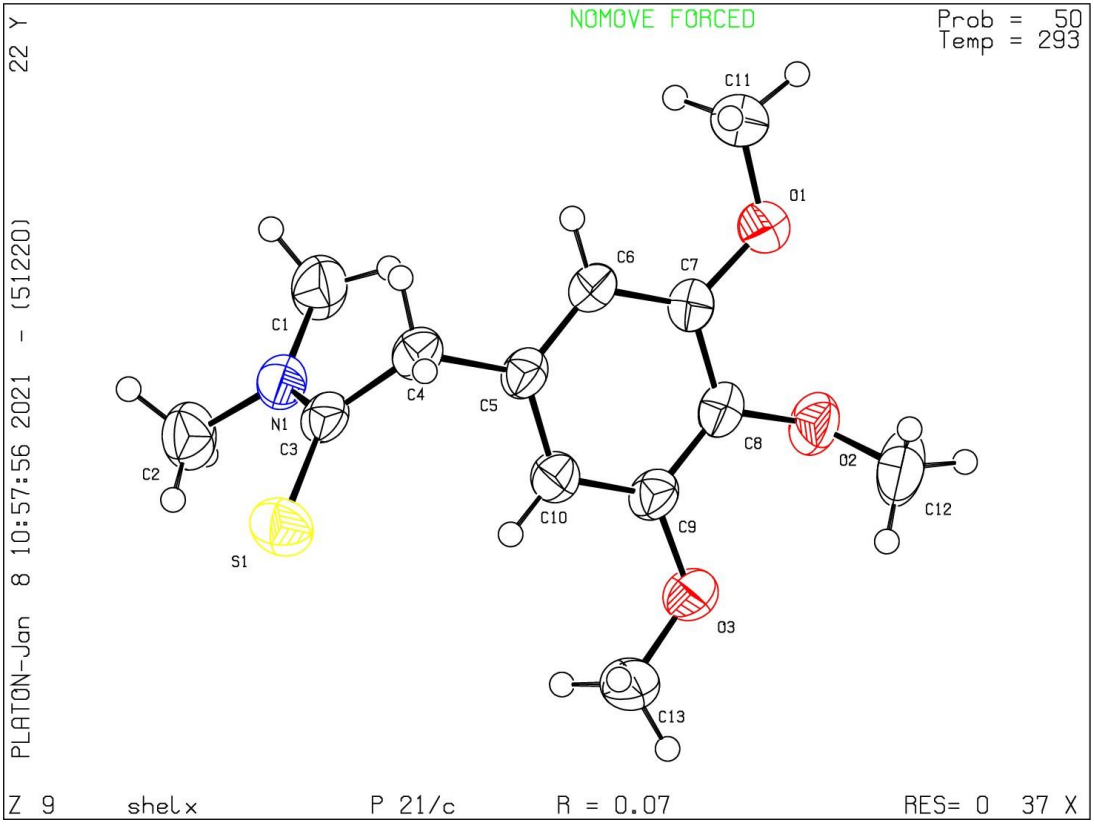
Correction method= Not given

Data completeness= 0.987 Theta(max)= 27.569

R(reflections)= 0.0679(2215) wR2(reflections)= 0.1974(3270)

S = 1.069 Npar= 168

Datablock shelx - ellipsoid plot

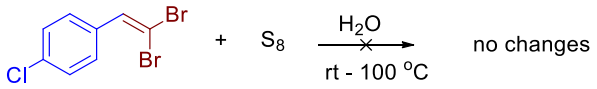


Scaled up procedure for the synthesis of thioamide (3oa):

To a stirred solution of **1o** (1g, 2.84 mmol, 1.0 equiv) in 10-12 mL of amine **2** (40 wt% in H_2O), elemental sulphur (10 equiv) was added. The reaction mixture was refluxed at 100 °C until the completion of the reaction. After completion of the reaction as determined TLC, the reaction mixture was cooled to room temperature. Subsequently, quenched with saturated $NaHCO_3$, diluted with water, and extracted with chloroform. The combined organic phase is evaporated under reduced pressure. The product from resulted crude was separated using silica gel column chromatography.

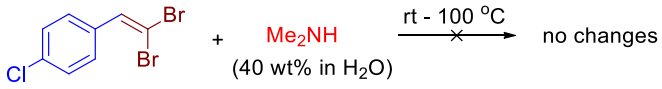
Control experimental procedure for the synthesis of thioamide:

Expt. 1:
1,1 dibromoalkene **1a** (0.148 g, 0.5 mmol, 1.0 equiv) was added to previously stirred solution of solid elemental sulphur (0.1603 g, 5 mmol, 10 equiv) in 5 mL of water at rt. The reaction mixture is slowly heated to 100 °C. The reaction mixture was continued to reflux at 100 °C for 24h.



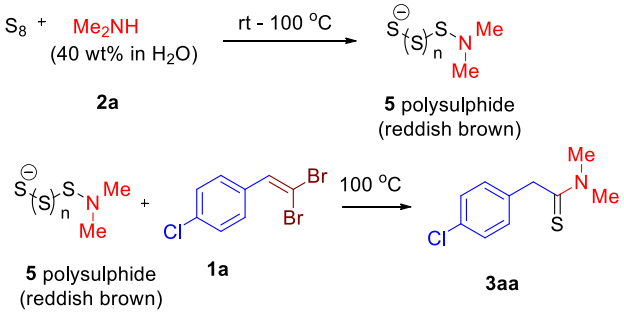
1a

Expt. 2:
1,1 dibromoalkene **1a** (0.148 g, 0.5 mmol, 1.0 equiv) was added to previously stirred solution of 5 mL of Me_2NH **2a** in water at rt. The reaction mixture is slowly heated to 100 °C. The reaction mixture was continued to reflux at 100 °C for 24h.



1a **2a**

Expt. 3:
To a stirred solution of 5 mL of Me_2NH **2a** in water, solid elemental sulphur (0.1603 g, 5 mmol, 10 equiv) was added at rt. The reaction mixture is slowly heated to 100 °C, during this colour of reaction mixture changes to reddish-brown indicating the formation of polysulphide.[1,2] 1,1 dibromoalkene **1a** (0.148 g, 0.5 mmol, 1.0 equiv) was added to polysulphide solution. The reaction mixture was continued to reflux at 100 °C. The reaction was monitored by TLC to ensure the formation of the required product. After completion, the reaction mixture was cooled to room temperature and quenched with saturated $NaHCO_3$. After the workup procedure, the crude was purified using silica gel column chromatography.



1. M. Carmack, *J. Heterocyclic Chem*., 1989, **26**, 1319-1323
2. T. B. Nguyen, M. Q. Tran, L. Ermolenko and A. Al-Mourabit, *Org. Lett*., 2014, **16**, 310-313