

Thioamidation of *gem*-dibromoalkene in a water medium

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Entry	Table of Contents	Page
1.	Figure S1. ^1H NMR Spectrum of 3aa	3
2.	Figure S2. ^{13}C NMR Spectrum of 3aa	4
3.	Figure S3. ^1H NMR Spectrum of 3ba	5
4.	Figure S4. ^{13}C NMR Spectrum of 3ba	6
5.	Figure S5. ^1H NMR Spectrum of 3ca	7
6.	Figure S6. ^{13}C NMR Spectrum of 3ca	8
7.	Figure S7. ^1H NMR Spectrum of 3da	9
8.	Figure S8. ^{13}C NMR Spectrum of 3da	10
9.	Figure S9. ^{19}F NMR Spectrum of 3da	11
10.	Figure S10. ^1H NMR Spectrum of 3ea	12
11.	Figure S11. ^{13}C NMR Spectrum of 3ea	13
12.	Figure S12. ^{19}F NMR Spectrum of 3ea	14
13.	Figure S13. ^1H NMR Spectrum of 3fa	15
14.	Figure S14. ^{13}C NMR Spectrum of 3fa	16
15.	Figure S15. APT Spectrum of 3fa	17
16.	Figure S16. ^1H NMR Spectrum of 3ga	18
17.	Figure S17. ^{13}C NMR Spectrum of 3ga	19
18.	Figure S18. ^1H NMR Spectrum of 3ha	20
19.	Figure S19. ^{13}C NMR Spectrum of 3ha	21
20.	Figure S20. ^1H NMR Spectrum of 3ia	22
21.	Figure S21. ^{13}C NMR Spectrum of 3ia	23
22.	Figure S22. ^1H NMR Spectrum of 3ja	24
23.	Figure S23. ^{13}C NMR Spectrum of 3ja	25
24.	Figure S24. ^1H NMR Spectrum of 3ka	26
25.	Figure S25. ^{13}C NMR Spectrum of 3ka	27
26.	Figure S26. ^1H NMR Spectrum of 3ma	28
27.	Figure S27. ^{13}C NMR Spectrum of 3ma	29
28.	Figure S28. ^1H NMR Spectrum of 3na	30
29.	Figure S29. ^{13}C NMR Spectrum of 3na	31
30.	Figure S30. ^1H NMR Spectrum of 3oa	32
31.	Figure S31. ^{13}C NMR Spectrum of 3oa	33
32.	Figure S32. ^1H NMR Spectrum of 3pa	34
33.	Figure S33. ^{13}C NMR Spectrum of 3pa	35
34.	Figure S34. ^1H NMR Spectrum of 3ob	36
35.	Figure S35. ^{13}C NMR Spectrum of 3ob	37
36.	Figure S36. ^1H NMR Spectrum of 3oc	38
37.	Figure S37. ^{13}C NMR Spectrum of 3oc	39
38.	Figure S38. ^1H NMR Spectrum of 3od	40
39.	Figure S39. ^{13}C NMR Spectrum of 3od	41
40.	Figure S40. ^1H NMR Spectrum of 3oe	42

41. Figure S41. ^{13}C NMR Spectrum of 3oe	43
42. Figure S42. ^1H NMR Spectrum of 3of	44
43. Figure S43. ^{13}C NMR Spectrum of 3of	45
44. Figure S44. ^1H NMR Spectrum of 3og	46
45. Figure S45. ^{13}C NMR Spectrum of 3og	47
46. Figure S46. ^1H NMR Spectrum of 4ka	48
47. Figure S47. ^{13}C NMR Spectrum of 4ka	49
48. Figure S48. ^1H NMR Spectrum of 4ma	50
49. Figure S49. ^{13}C NMR Spectrum of 4ma	51
50. Single crystal X-ray structure data of 3oa	52
51. Scaled up procedure for the synthesis of thioamide (3oa)	54
52. Control experimental procedure for the synthesis of thioamide	54

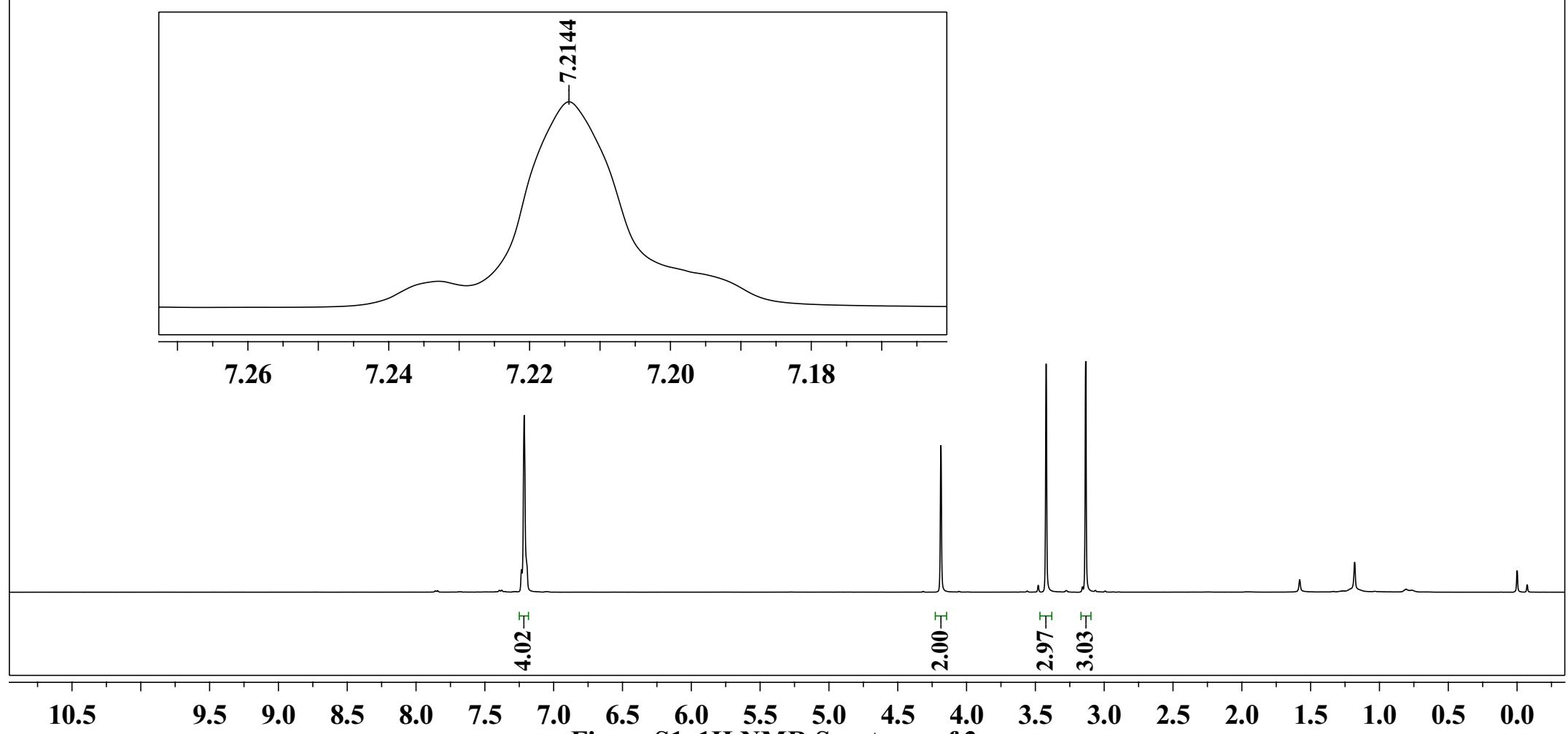
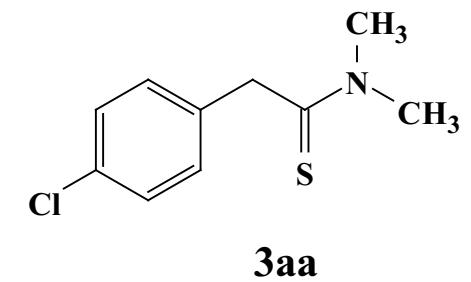


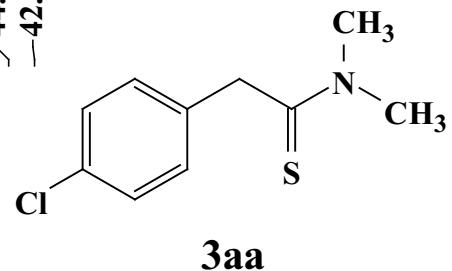
Figure S1. ^1H NMR Spectrum of 3aa

-200.05

134.19
132.83
129.58
128.94

77.35
77.10
76.84

50.05
44.89
42.31



3aa

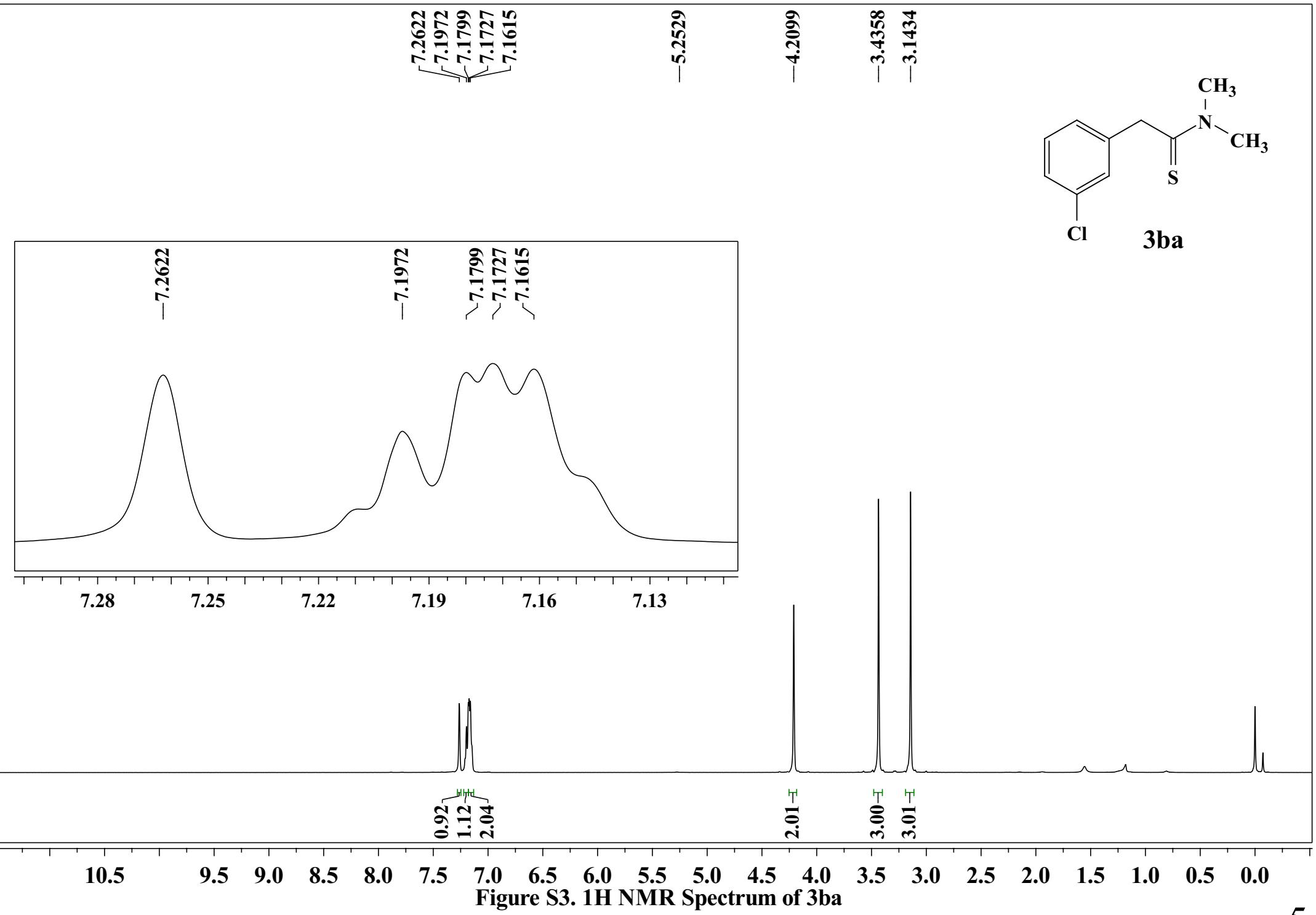
134.19
132.83

129.58
128.94

135 134 133 132 131 130 129 128 127

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Figure S2. ^{13}C NMR Spectrum of 3aa

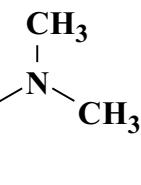


—198.42

136.65
133.46
129.01
127.13
126.18
125.38

76.37
76.11
75.86

—49.19
—43.83
—41.36



3ba

—136.65

—133.46

—129.01

—127.13

—126.18

—125.38

139

137

135

133

131

129

127

125

123

200

190

180

170

160

150

140

130

120

110

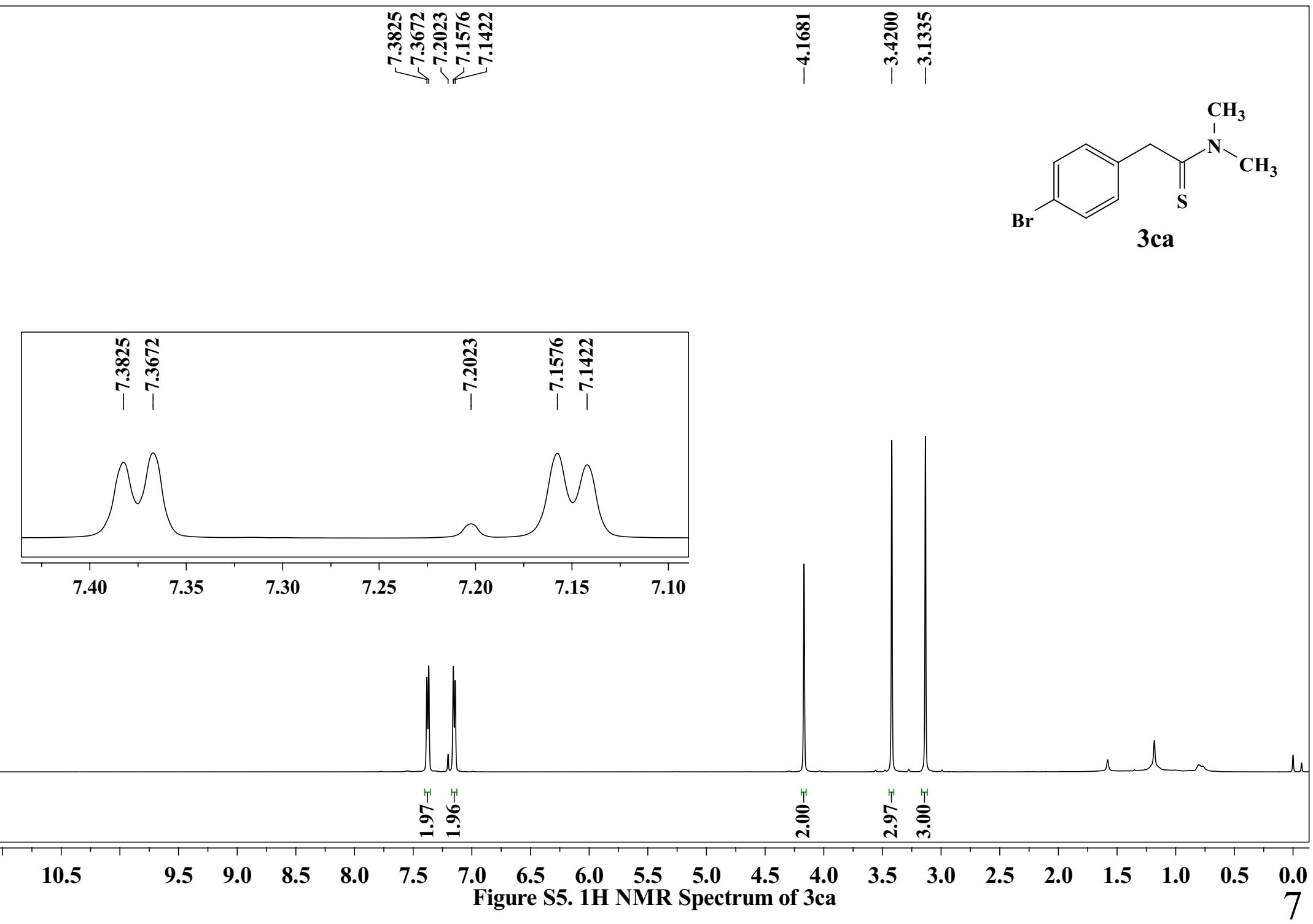
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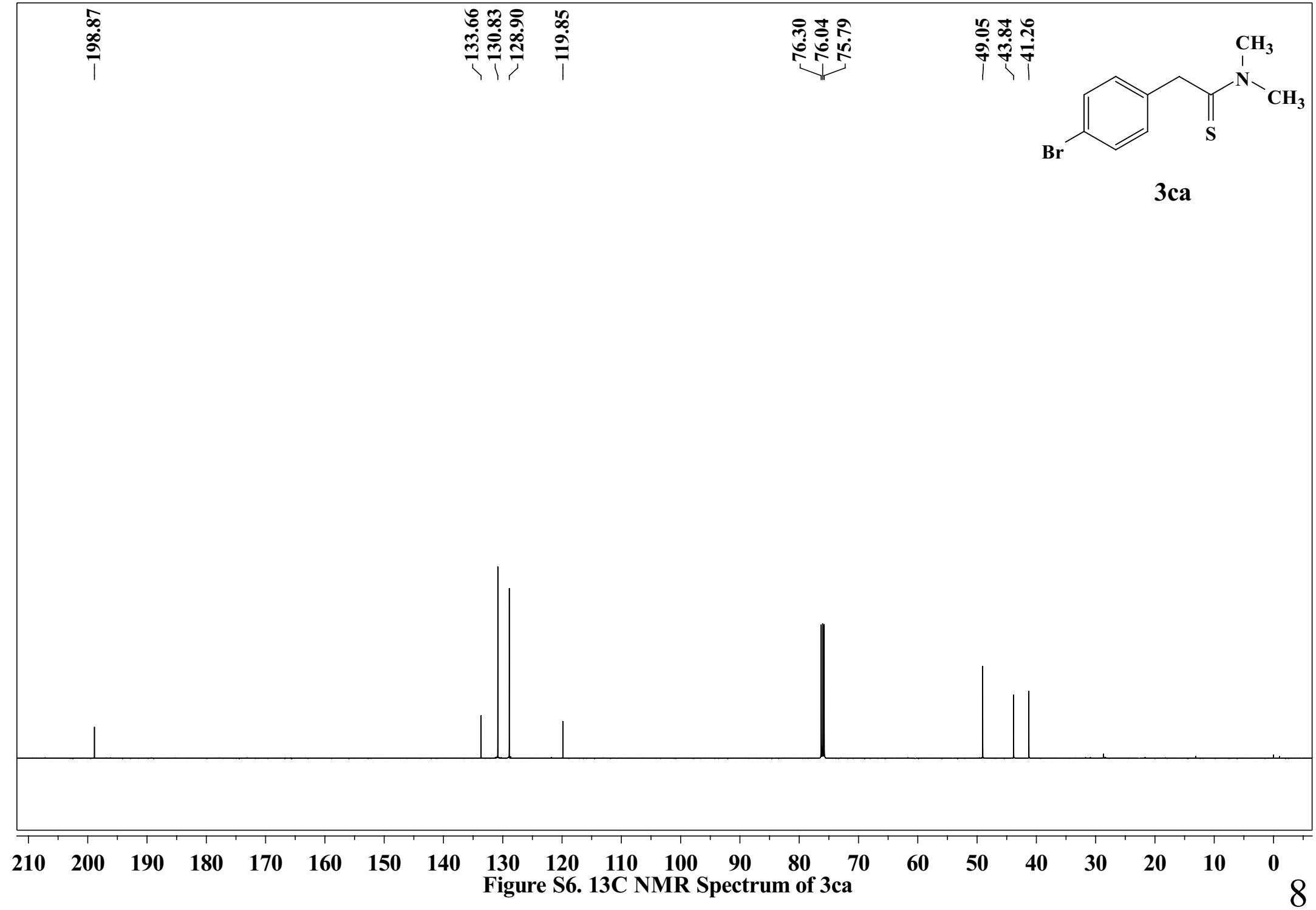
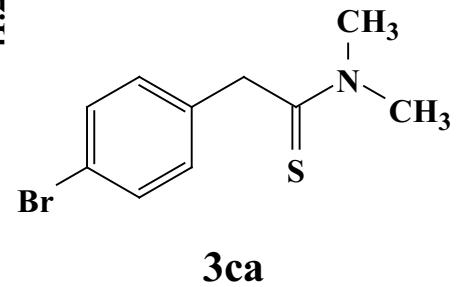
90

80

6

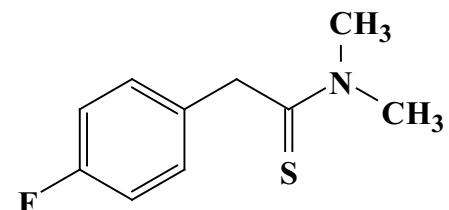
Figure S4. ¹³C NMR Spectrum of 3ba





7.2519
7.2398
7.2281
6.9632
6.9469
6.9311

-4.1952
-3.4303
-3.1455



3da

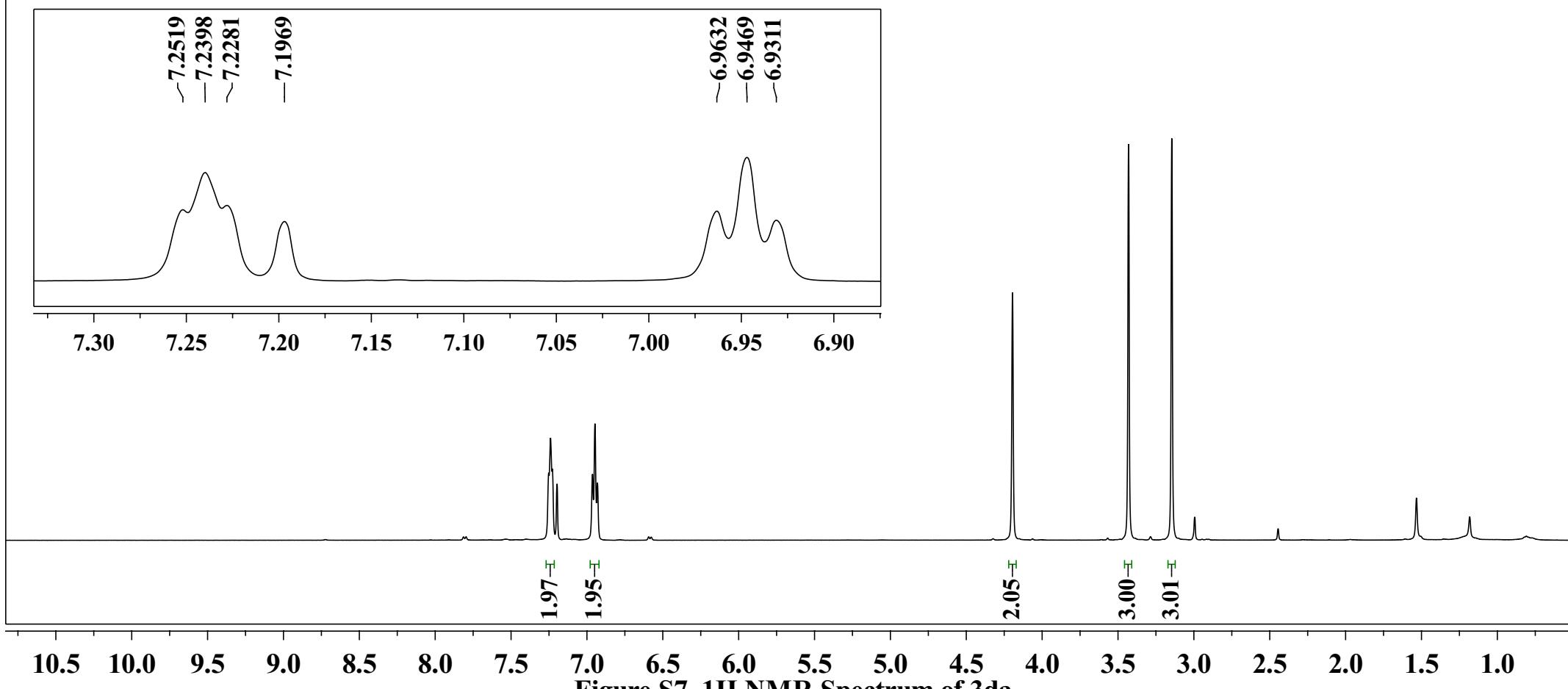
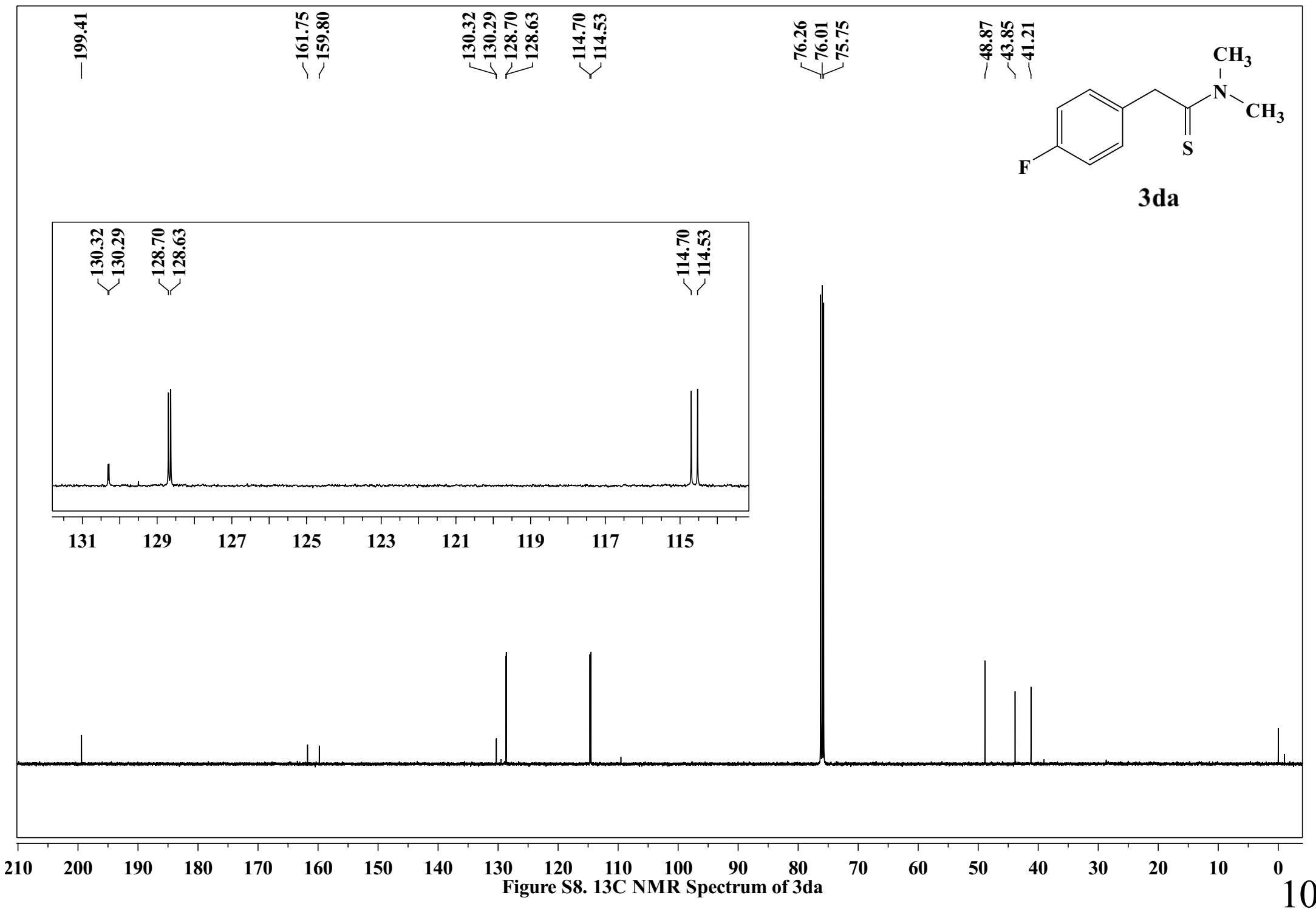


Figure S7. ¹H NMR Spectrum of 3da



-115.68

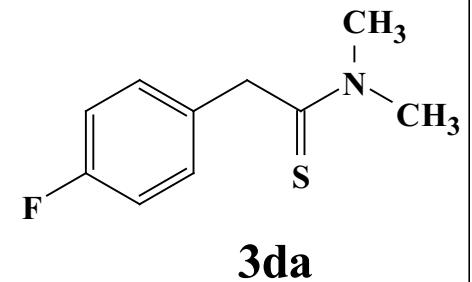
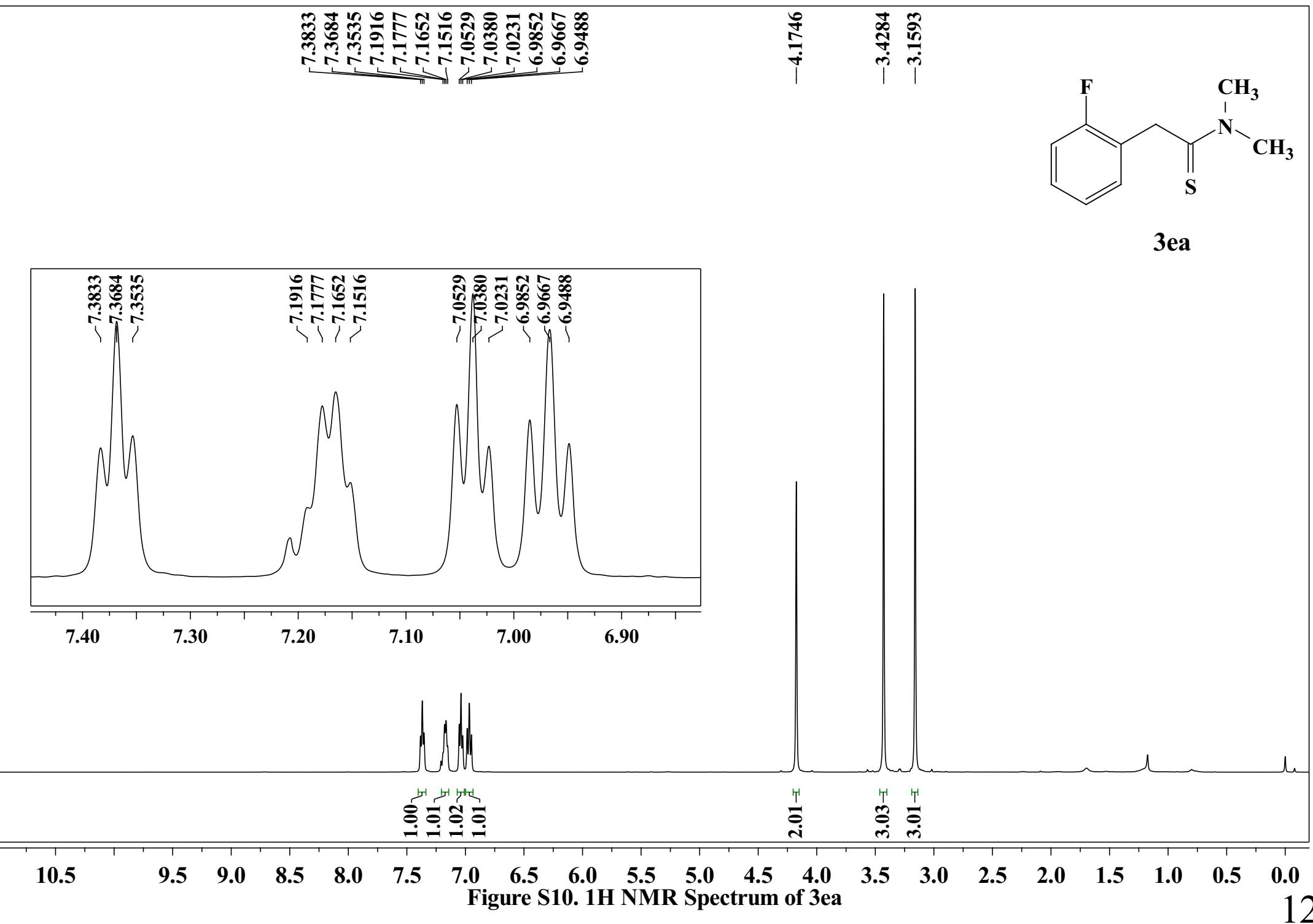


Figure S9. ¹⁹F NMR Spectrum of 3da



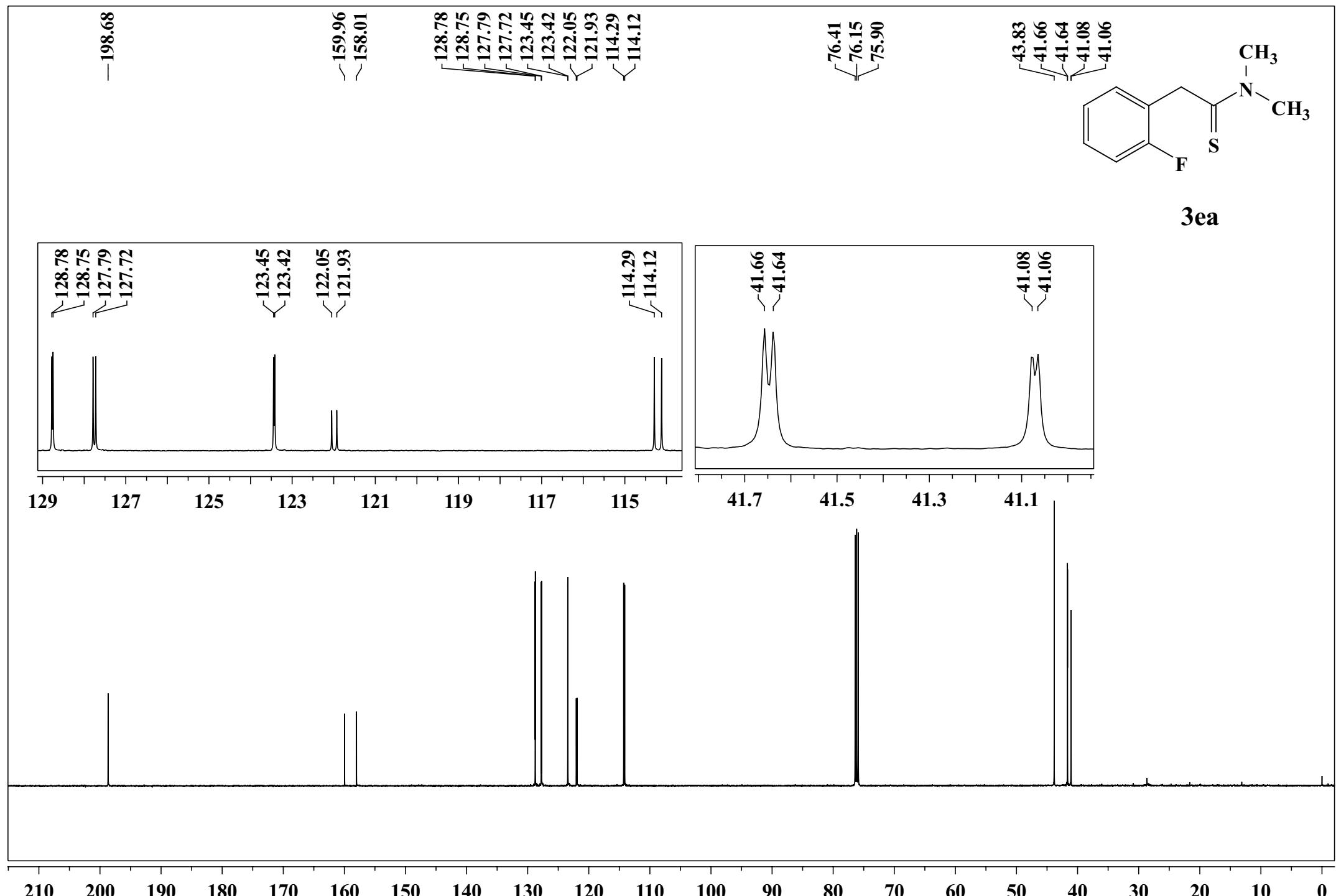
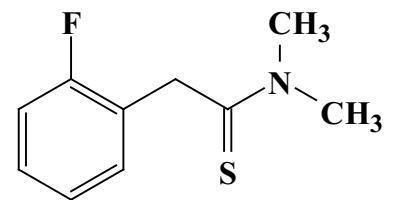
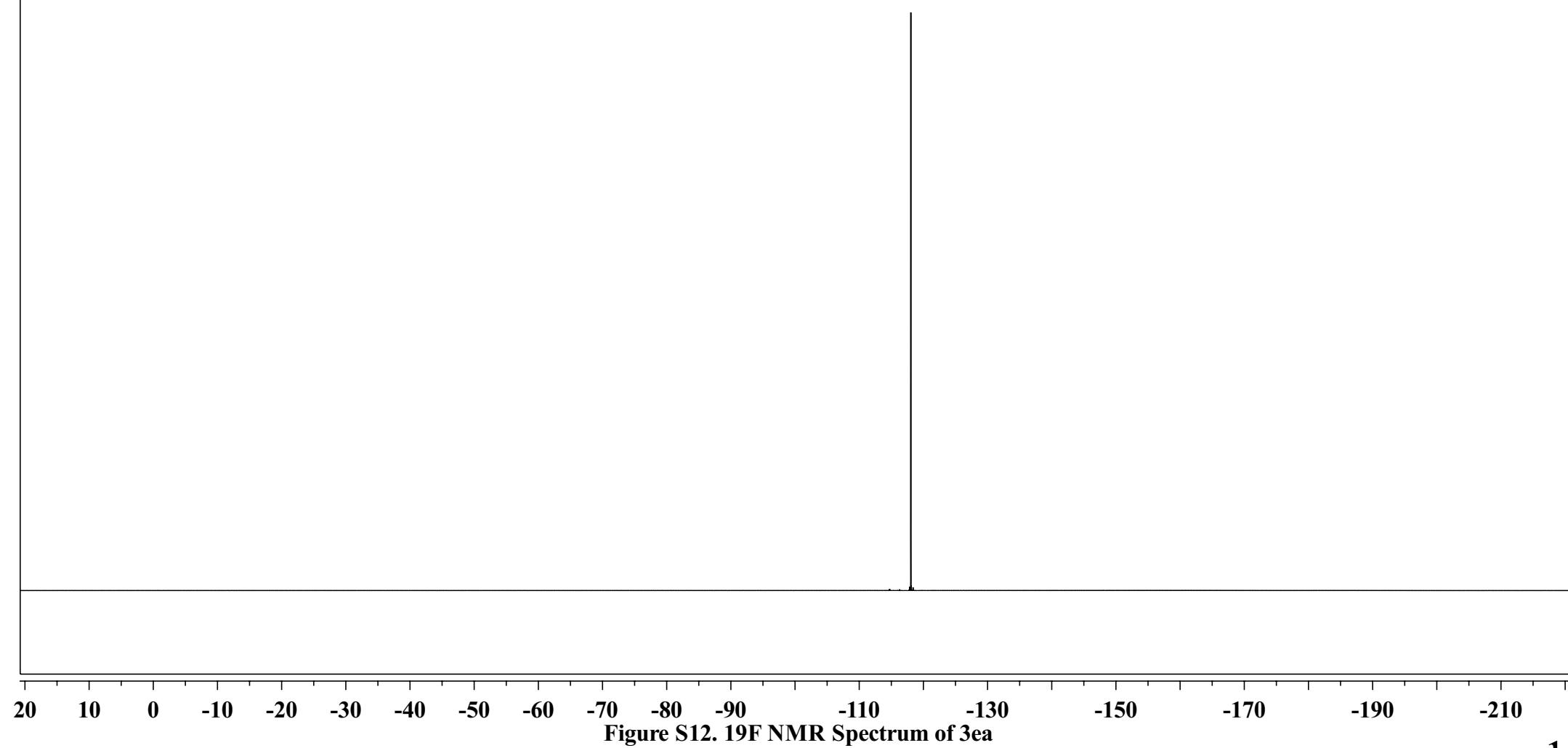


Figure S11. ^{13}C NMR Spectrum of **3ea**



3ea



8.1873
8.1718

7.5313
7.5155

-4.3779

-3.5263
-3.2826

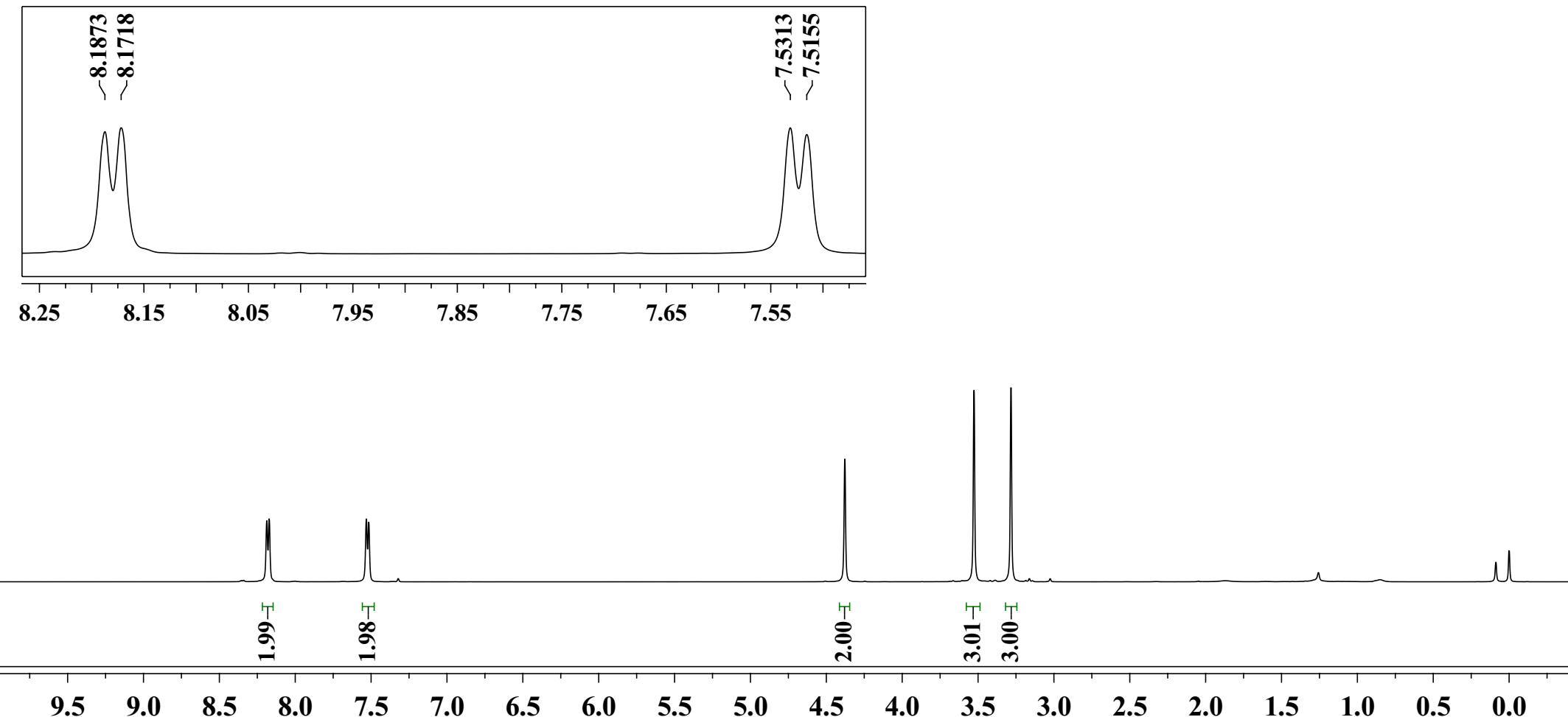
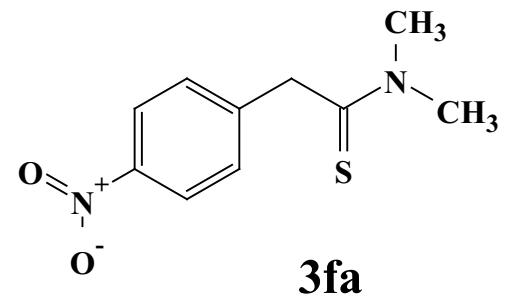


Figure S13. ¹H NMR Spectrum of 3fa

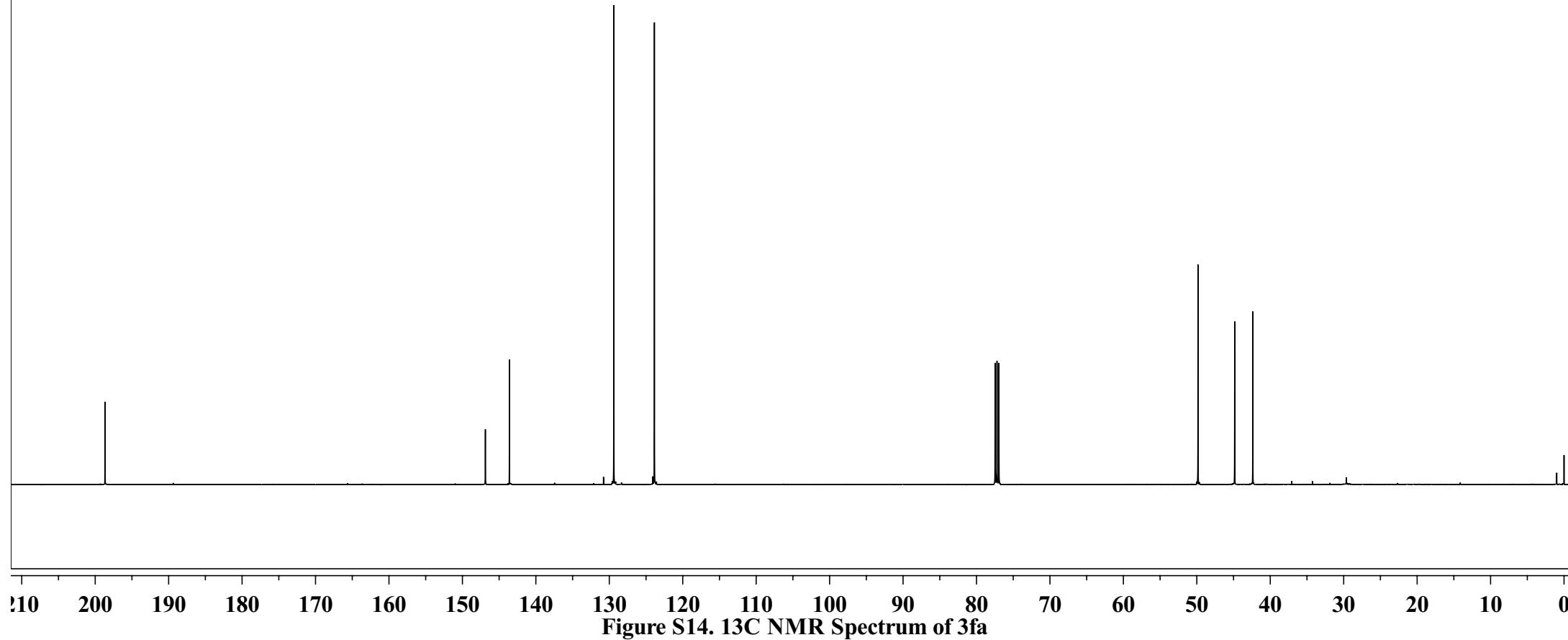
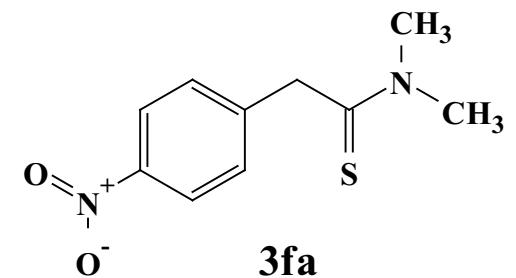
-198.66

-146.87
-143.60

-129.39
-123.86

77.46
77.21
76.95

-49.84
-44.84
-42.37



-198.67

-146.88
-143.60

-129.39
-123.86

77.46
77.21
76.95

-49.84
-44.84
-42.37

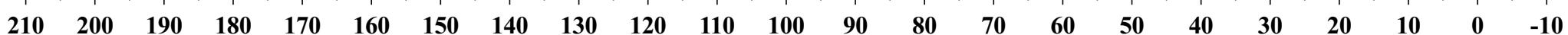
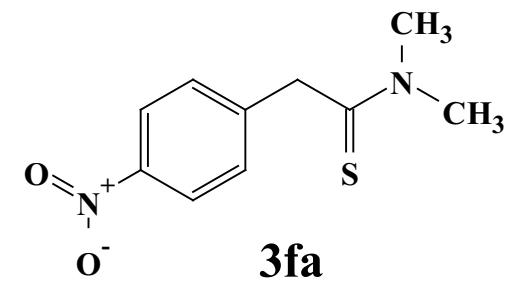


Figure S15. APT Spectrum of 3fa

8.0397
8.0235
7.5587
7.5438
7.5288
7.4108
7.3954
7.3799
7.3335
7.3183
7.1984

-4.3792
-3.4815
-3.3290

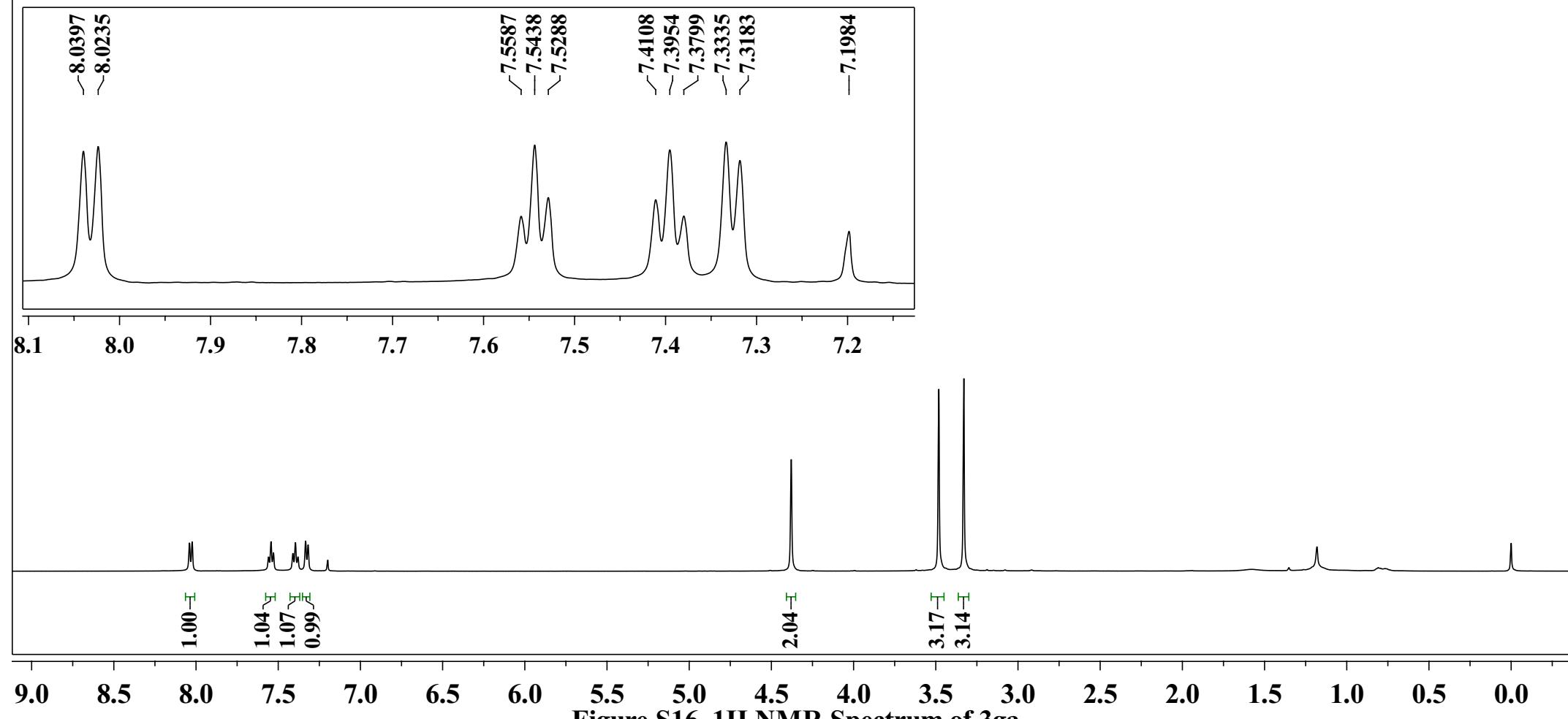
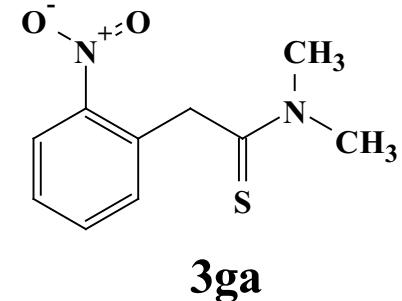


Figure S16. ¹H NMR Spectrum of 3ga

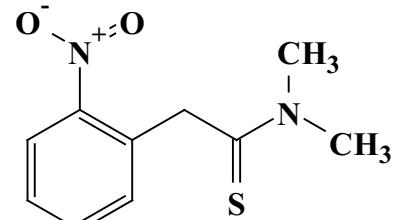
-198.19

-147.33

132.59
131.95
131.61
127.17
124.19

76.29
76.03
75.78

45.51
43.83
41.04

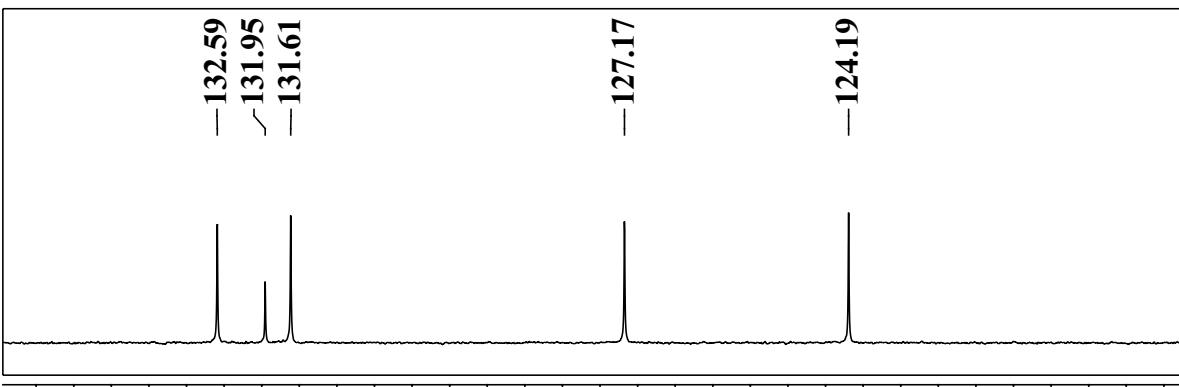


3ga

-132.59
-131.95
-131.61

-127.17

-124.19



135 133 131 129 127 125 123 121

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Figure S17. ¹³C NMR Spectrum of 3ga

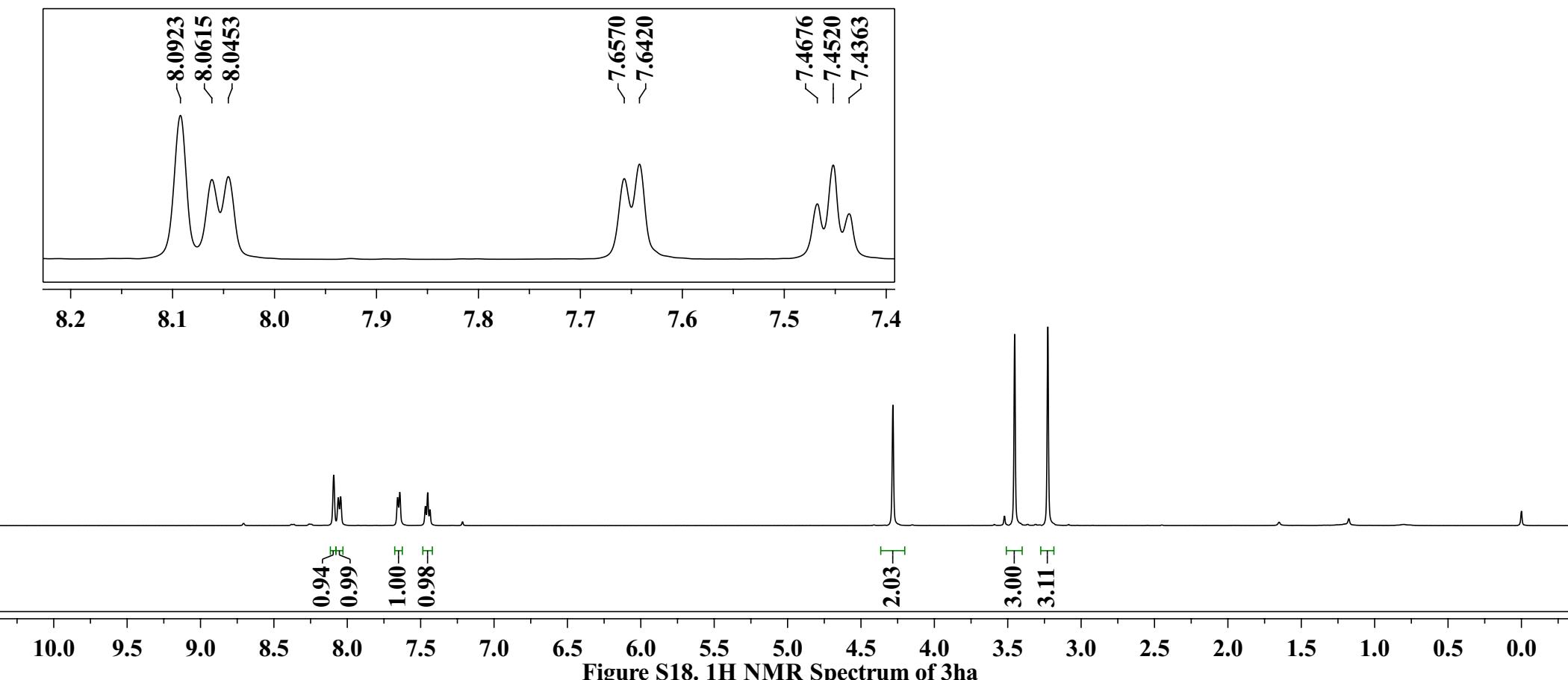
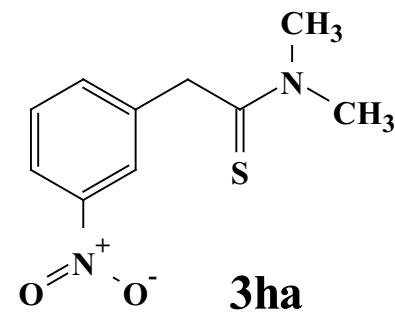
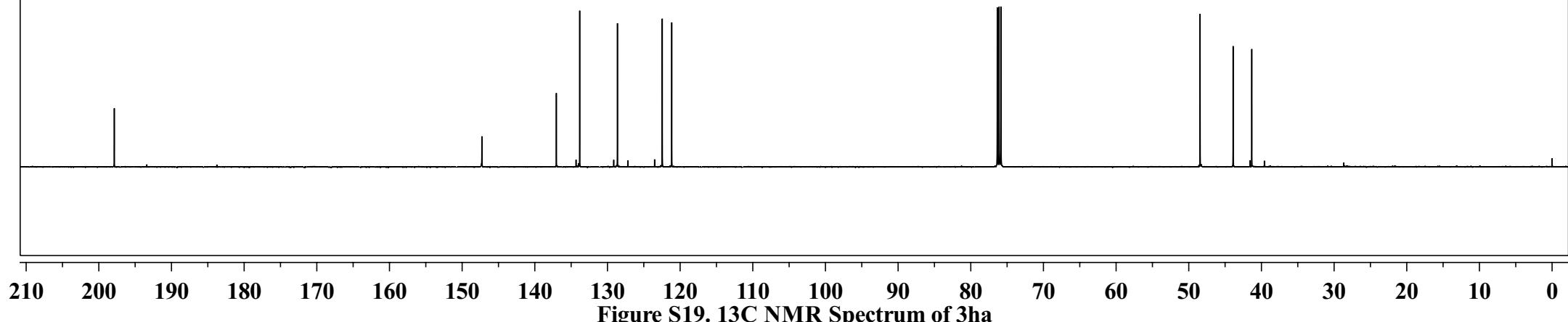
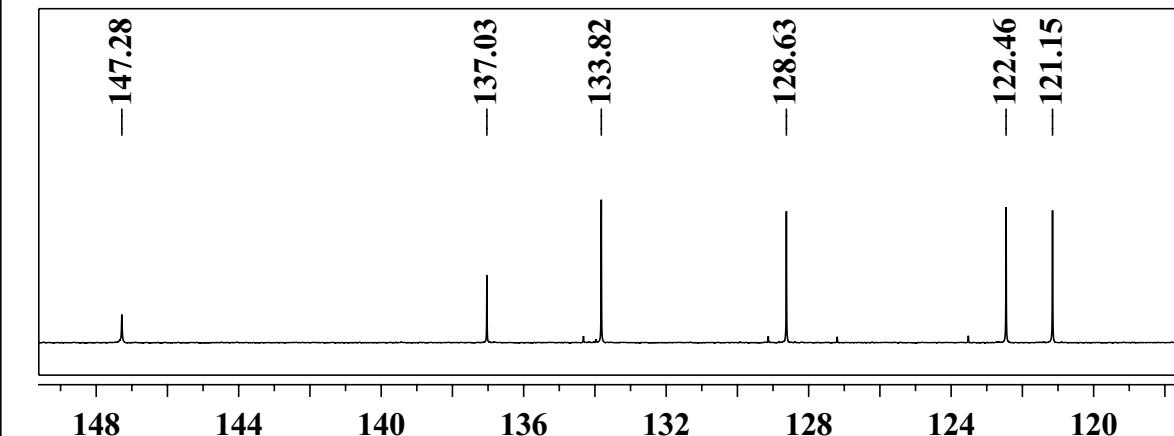
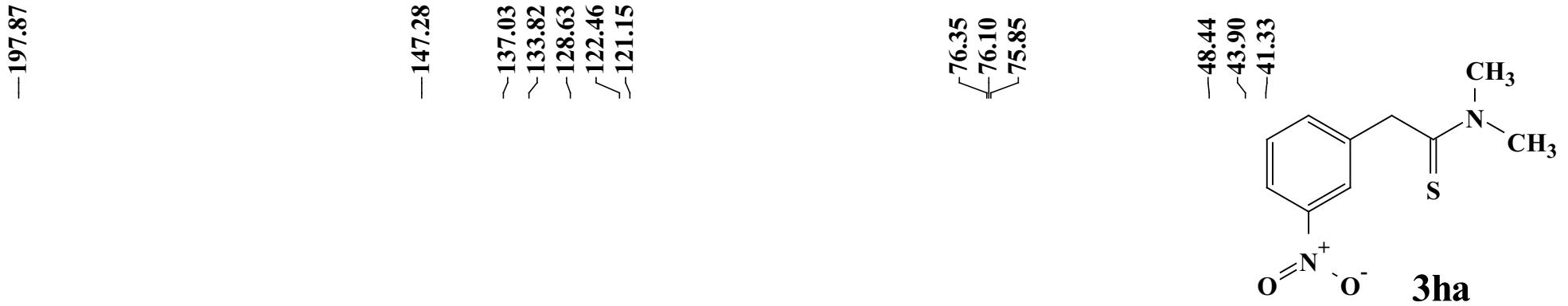
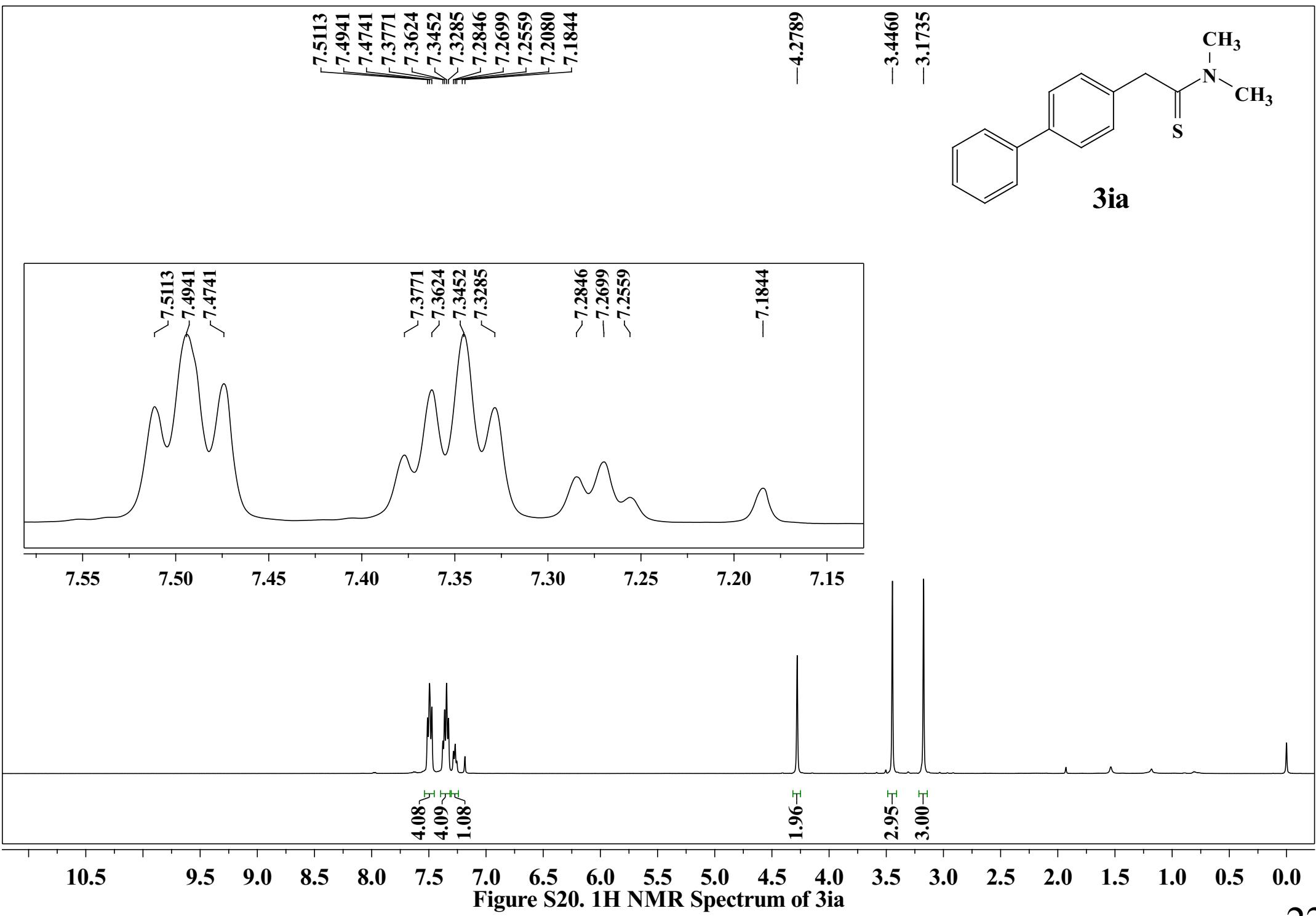


Figure S18. ¹H NMR Spectrum of **3ha**



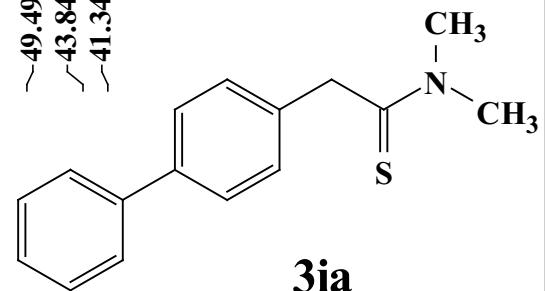


—199.45

139.57
138.82
133.64
127.75
127.50
126.45
126.27
125.96

76.28
76.03
75.77

~49.49
~43.84
~41.34



3ia

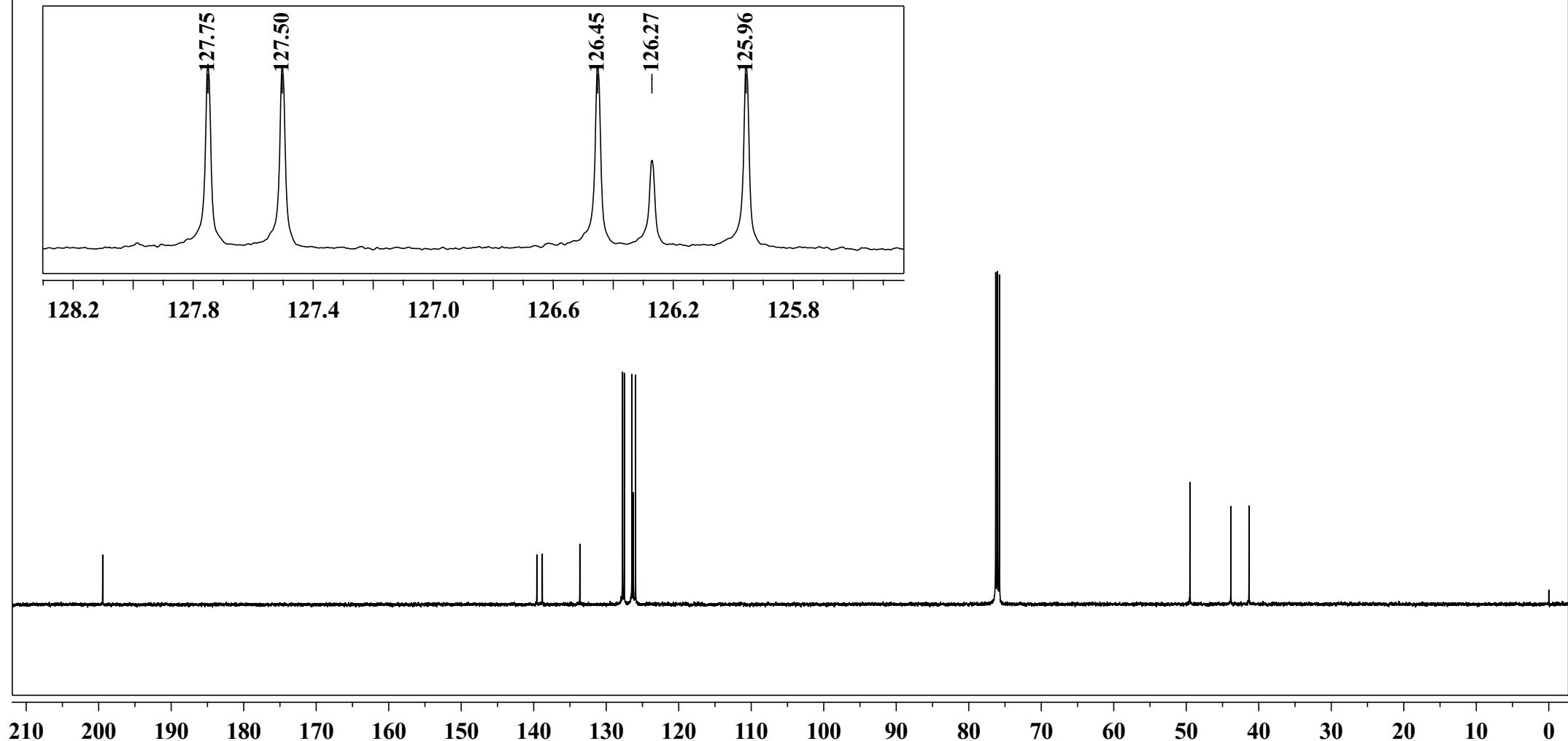
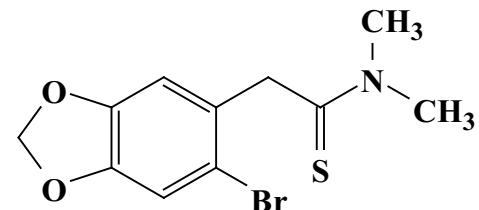


Figure S21. ¹³C NMR Spectrum of 3ia



3ja

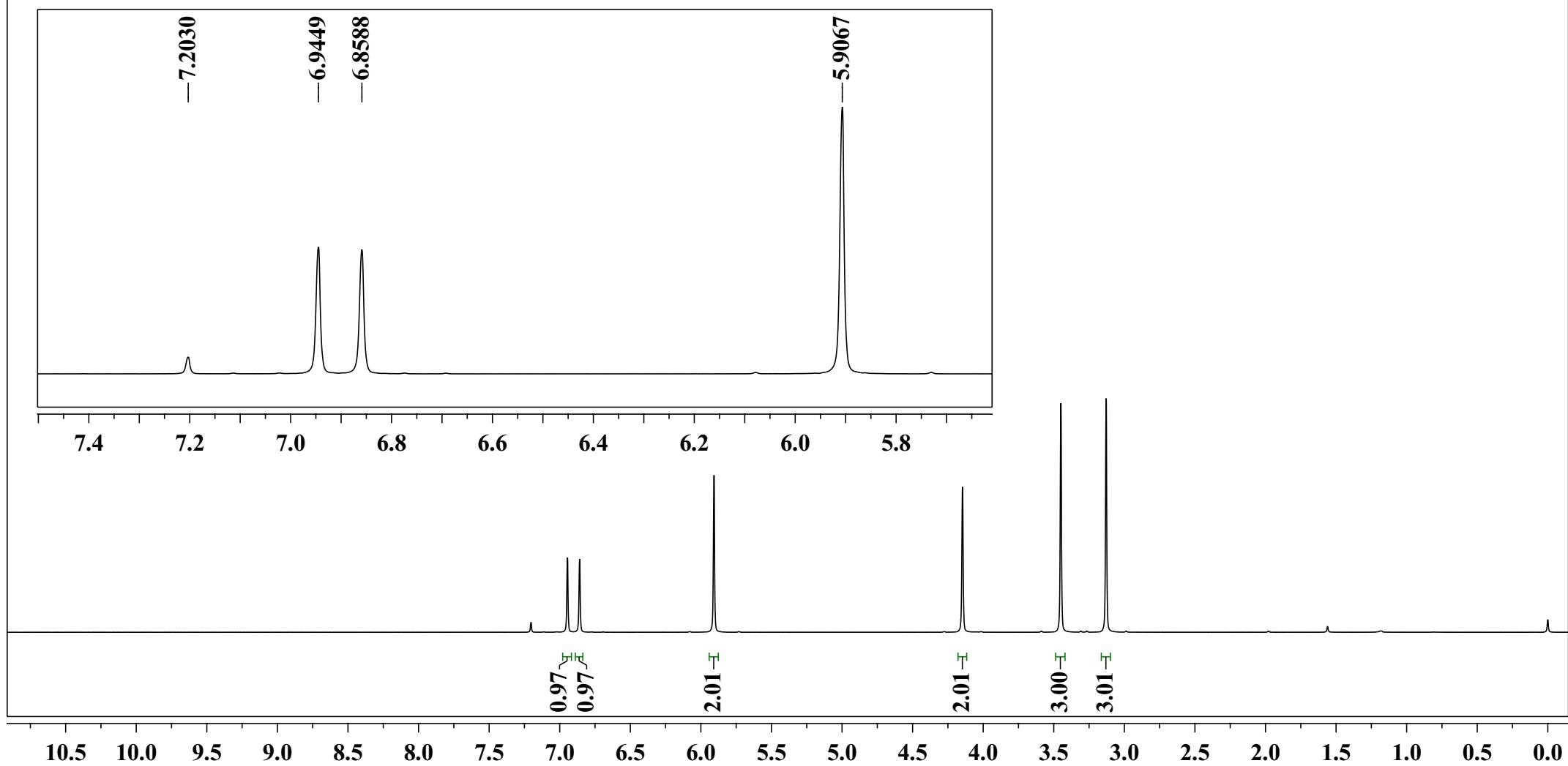
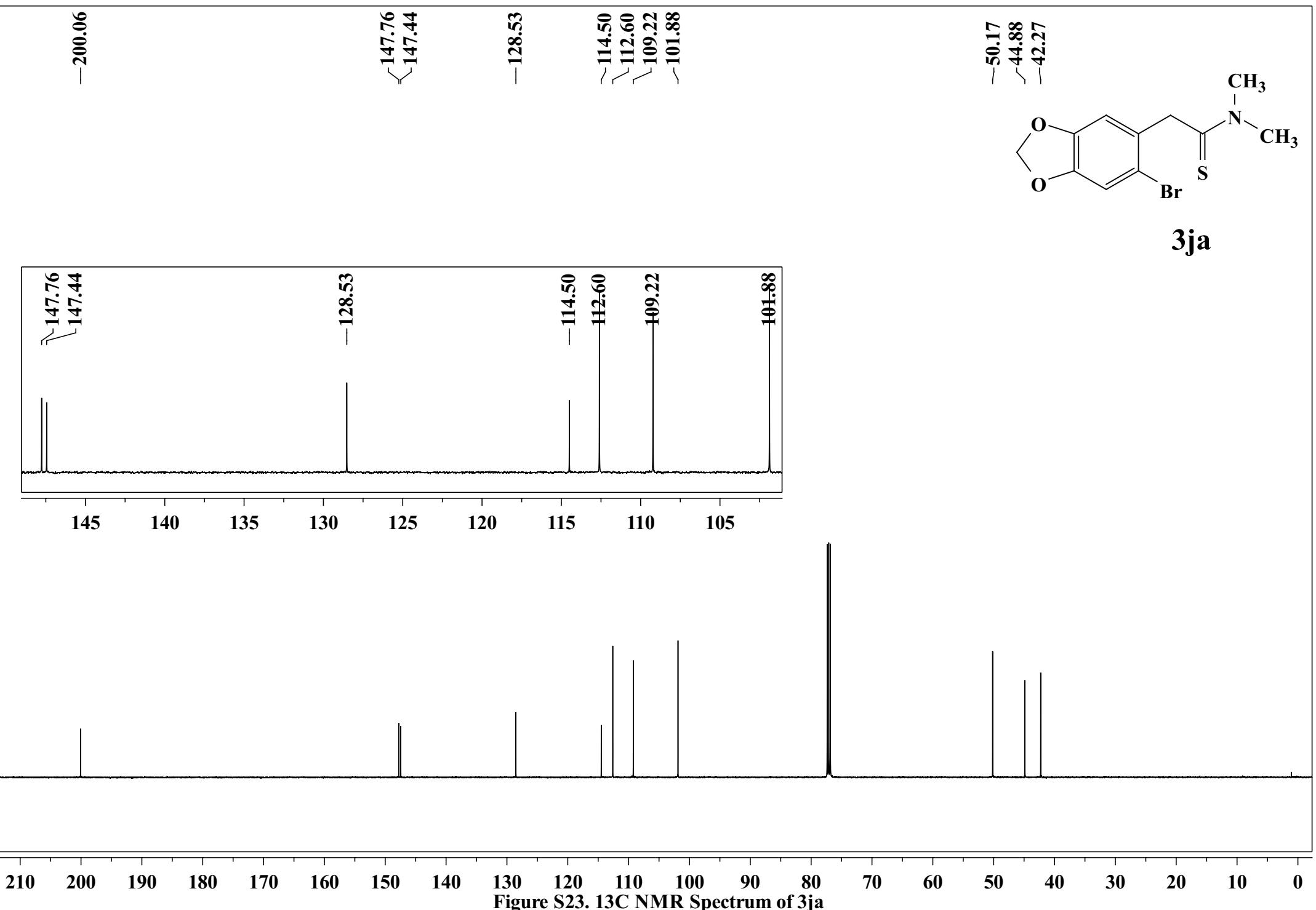
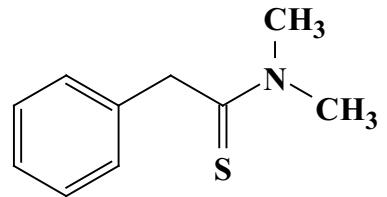


Figure S22. ^1H NMR Spectrum of 3ja





3ka

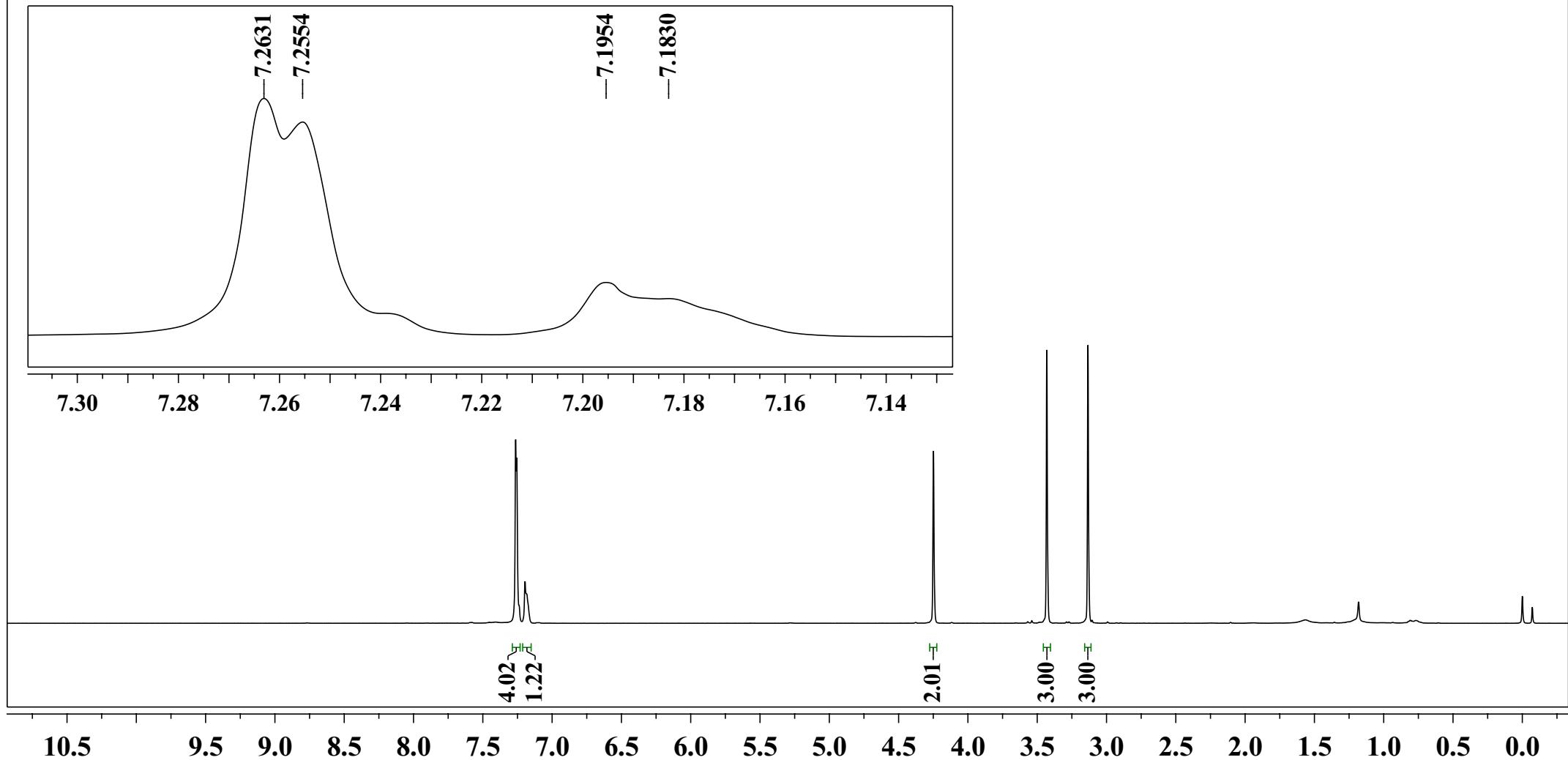


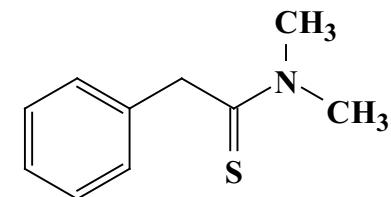
Figure S24. ¹H NMR Spectrum of 3ka

-199.54

134.59
127.78
127.04
125.93

76.28
76.03
75.77

49.90
43.82
41.29



3ka

-134.59

-127.78

-127.04

-125.93

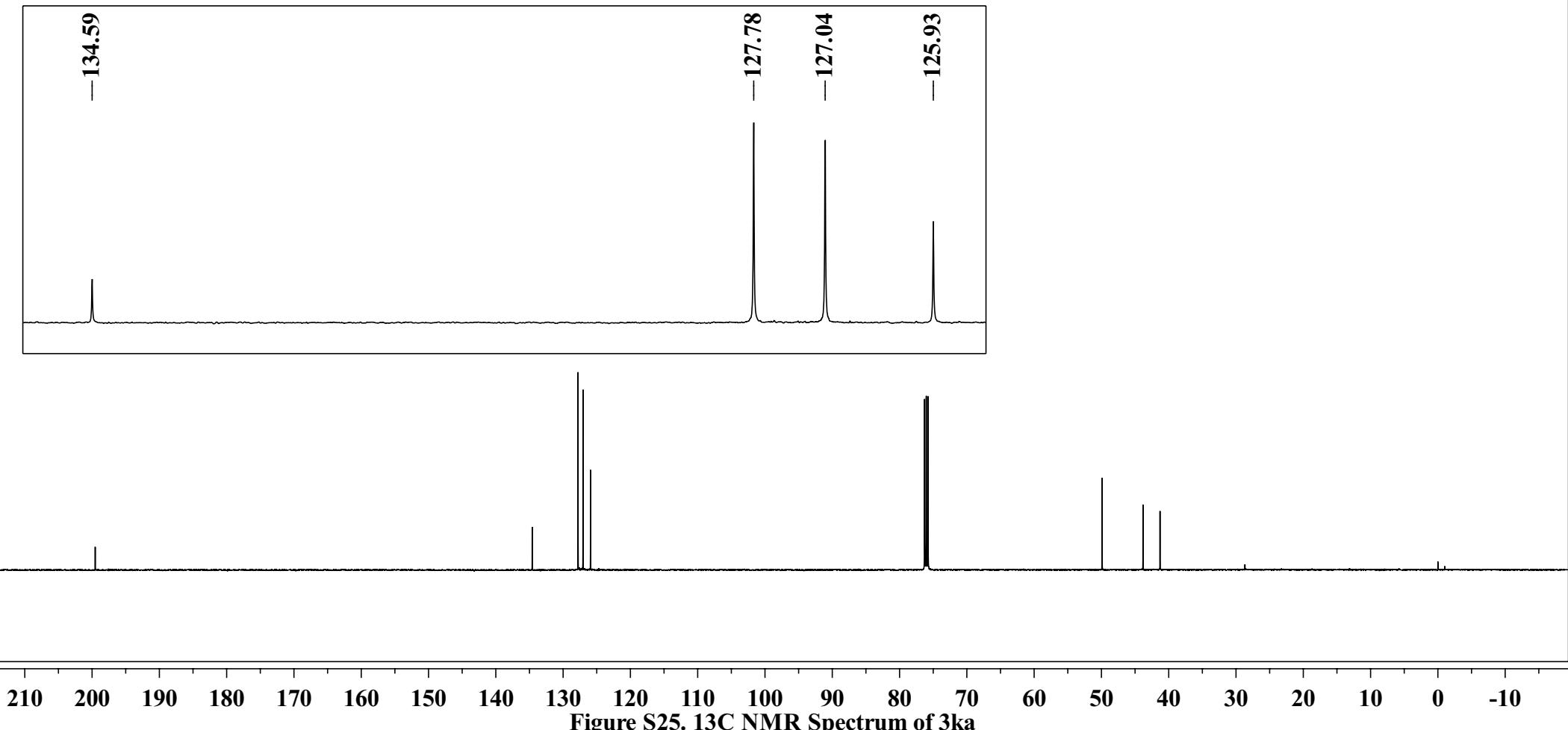
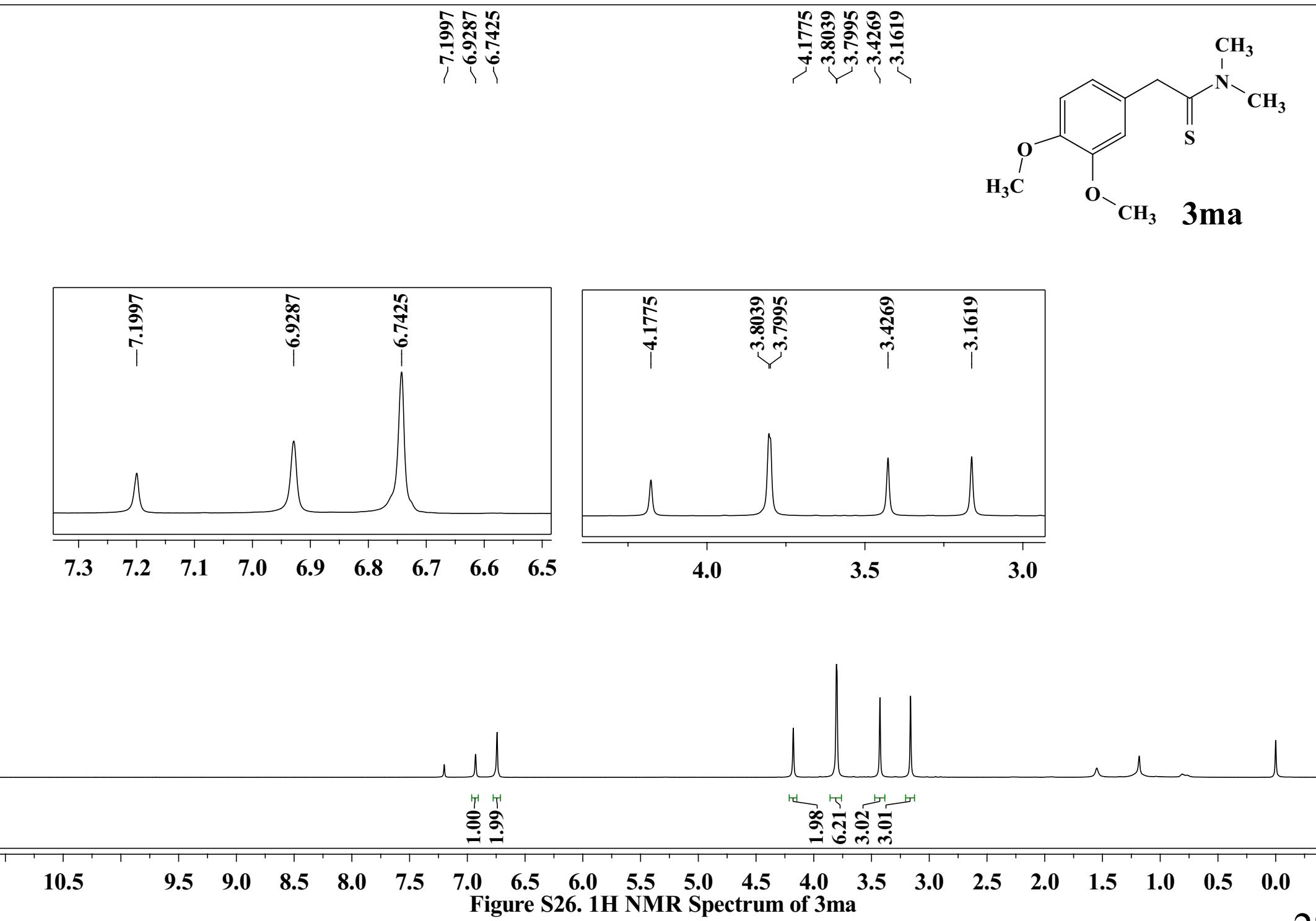
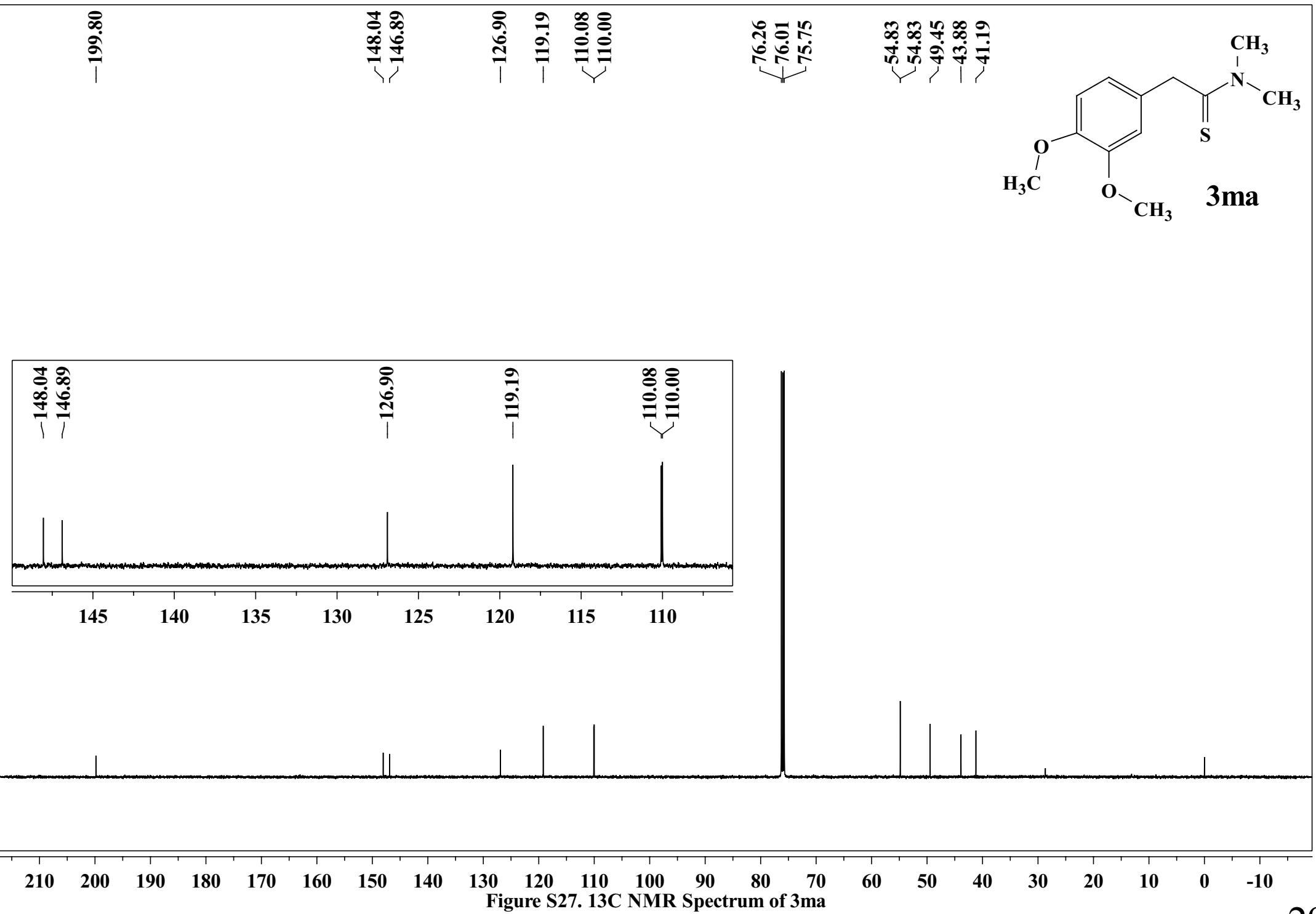
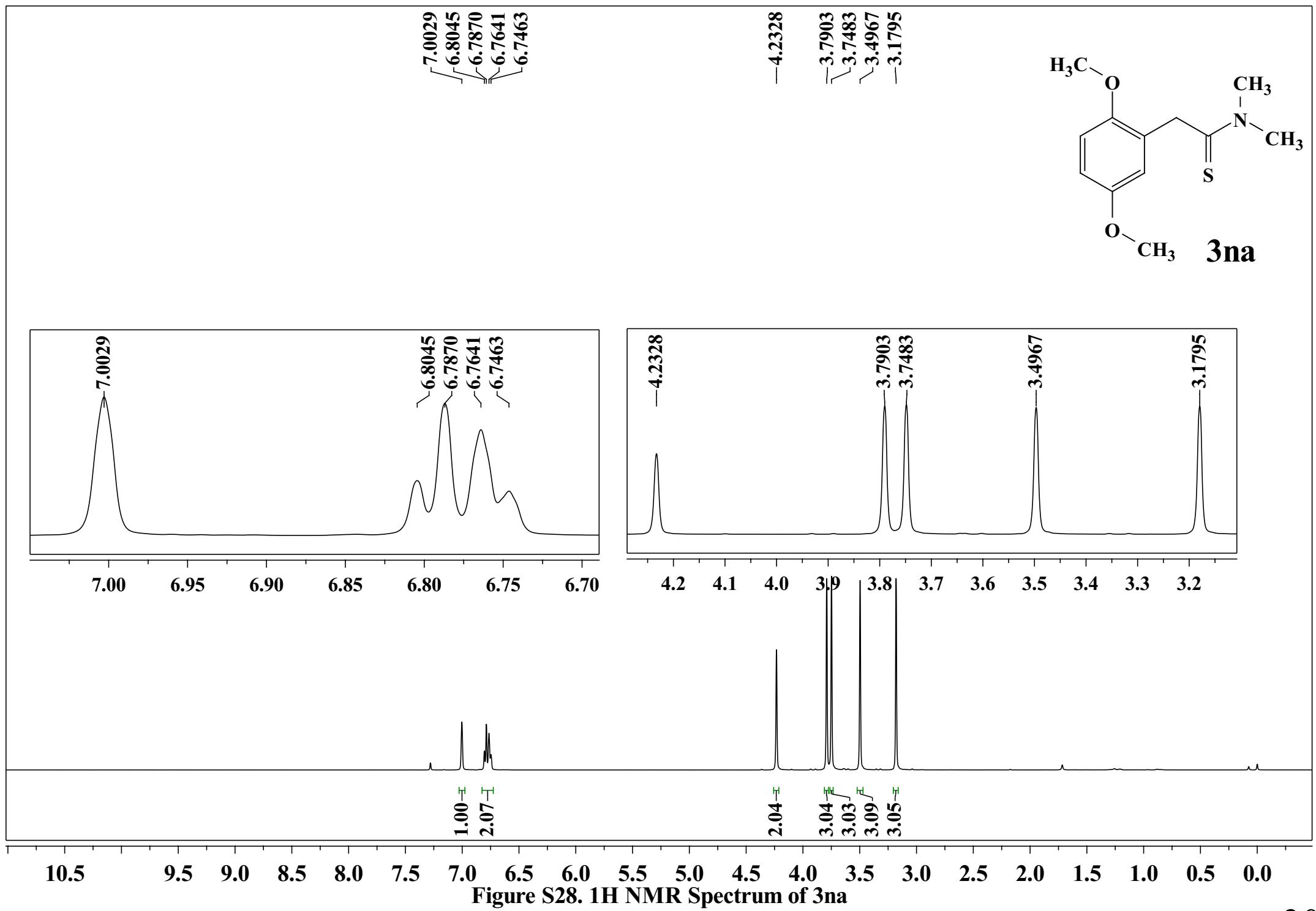


Figure S25. ¹³C NMR Spectrum of 3ka







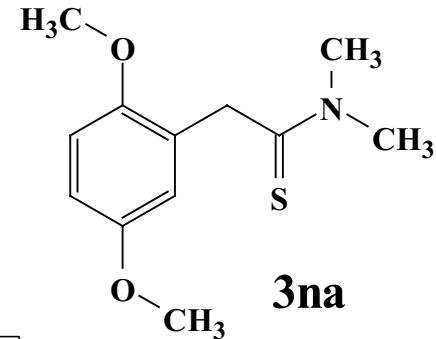
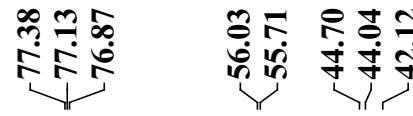
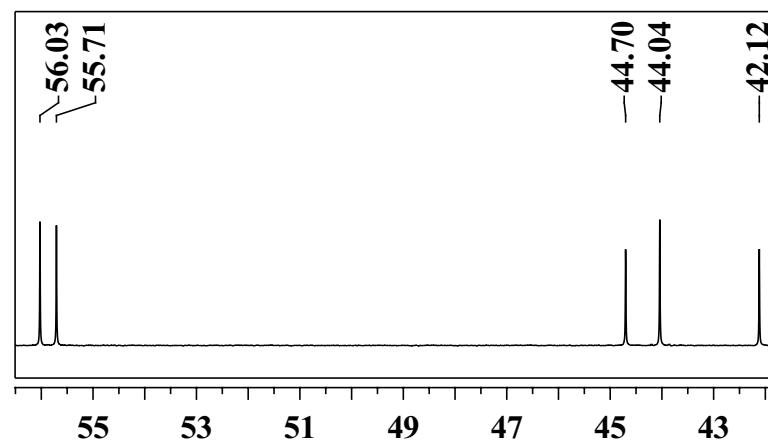
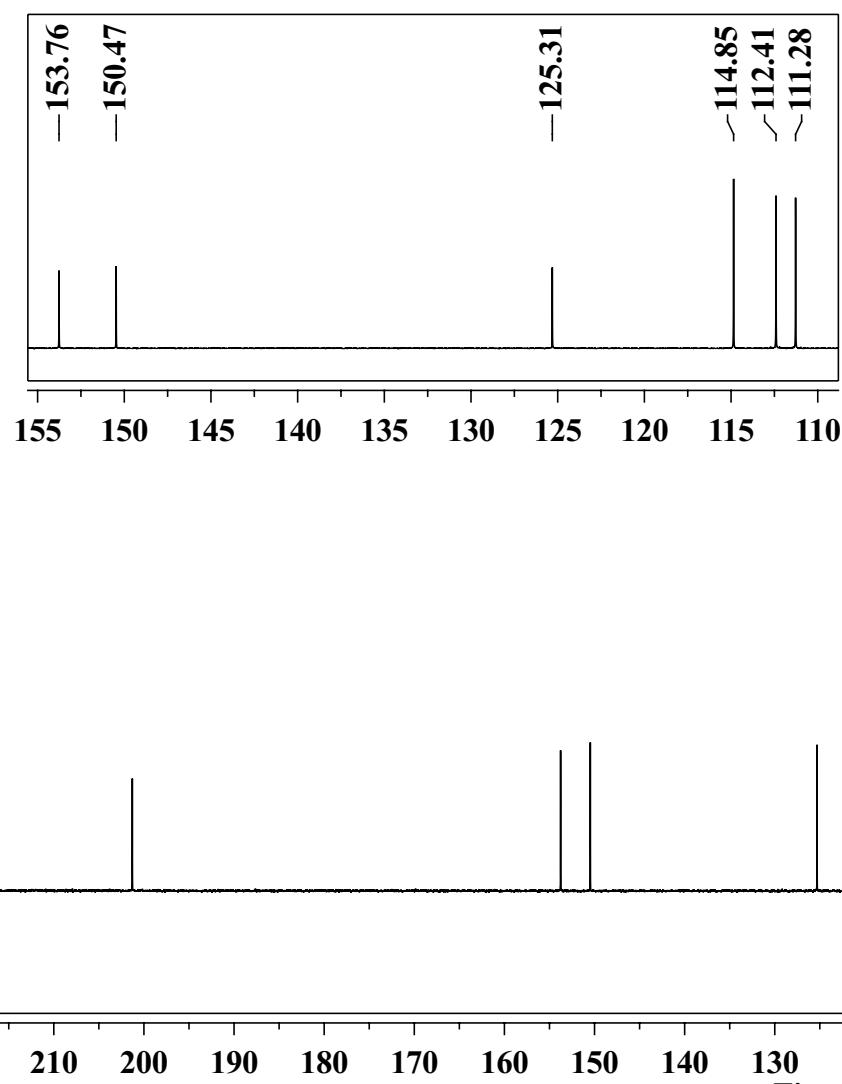
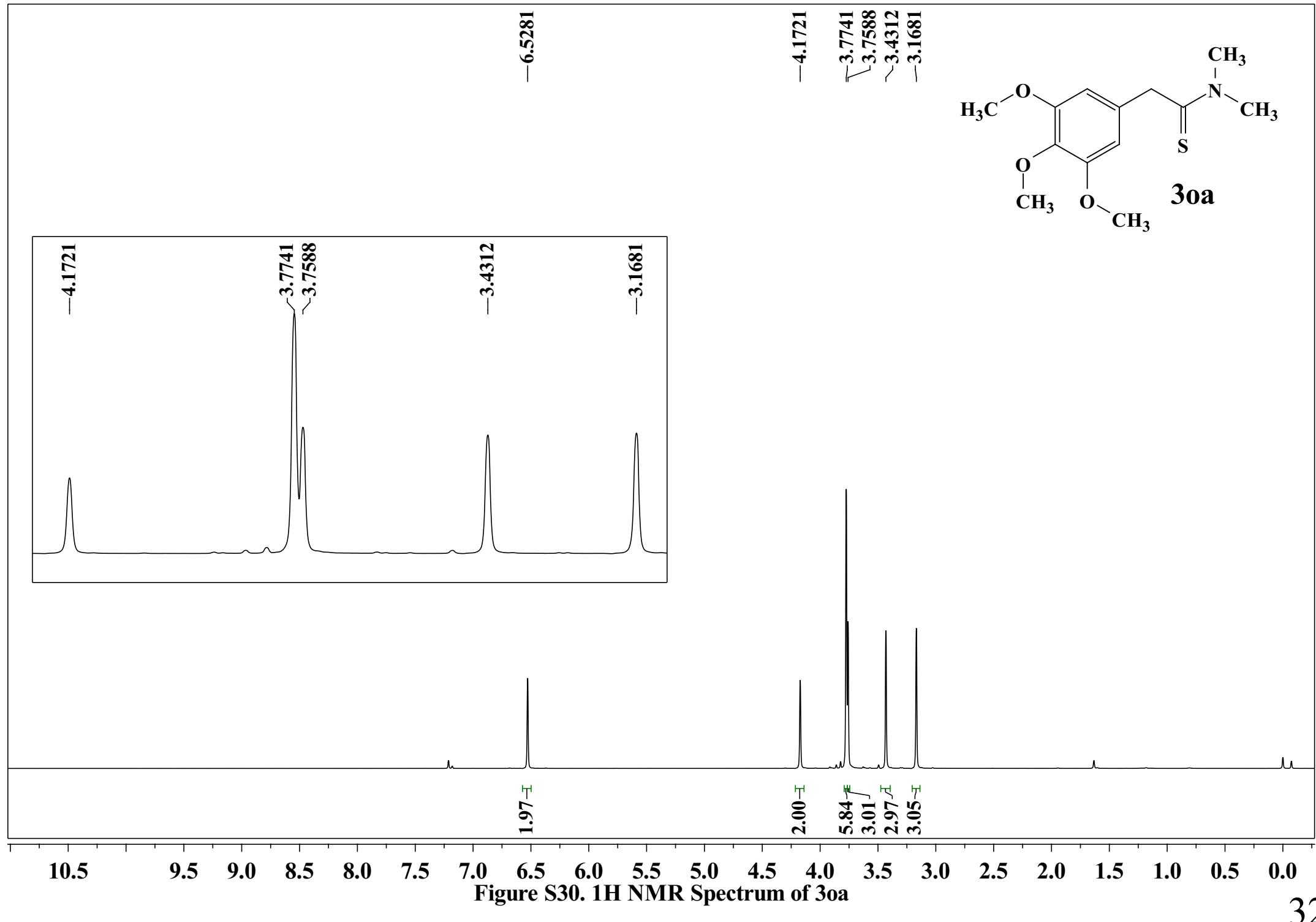


Figure S29. ^{13}C NMR Spectrum of 3na



—199.26

—152.35

—135.74

—130.14

—103.97

76.31
76.06
75.81

59.84
55.12
50.06
43.88
41.31

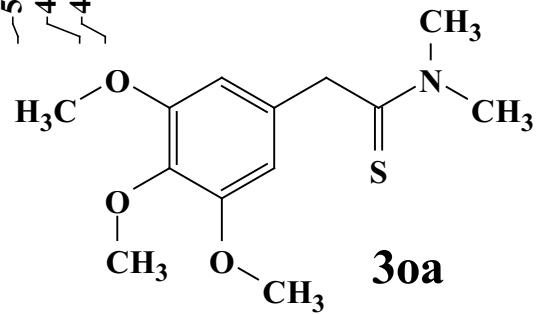
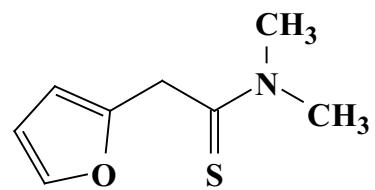
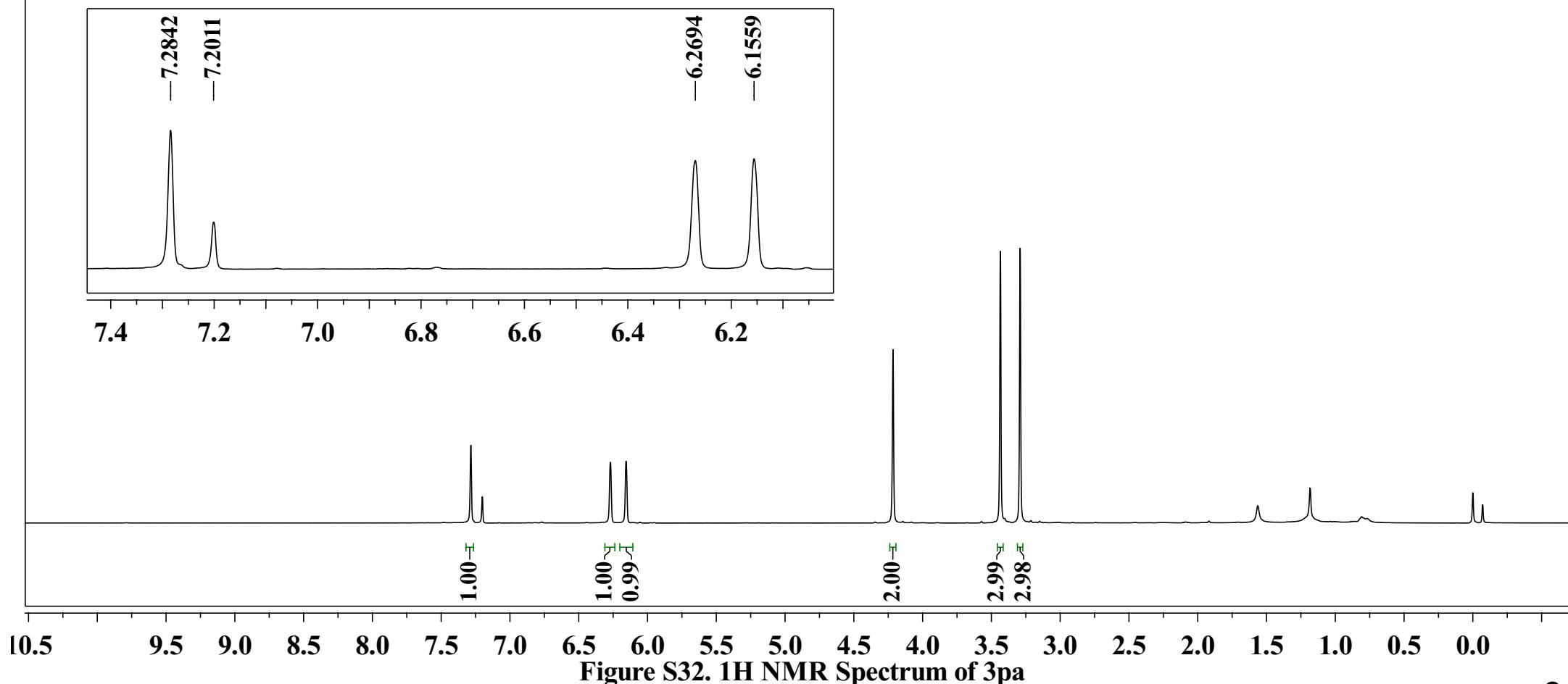


Figure S31. ¹³C NMR Spectrum of 3oa



3pa



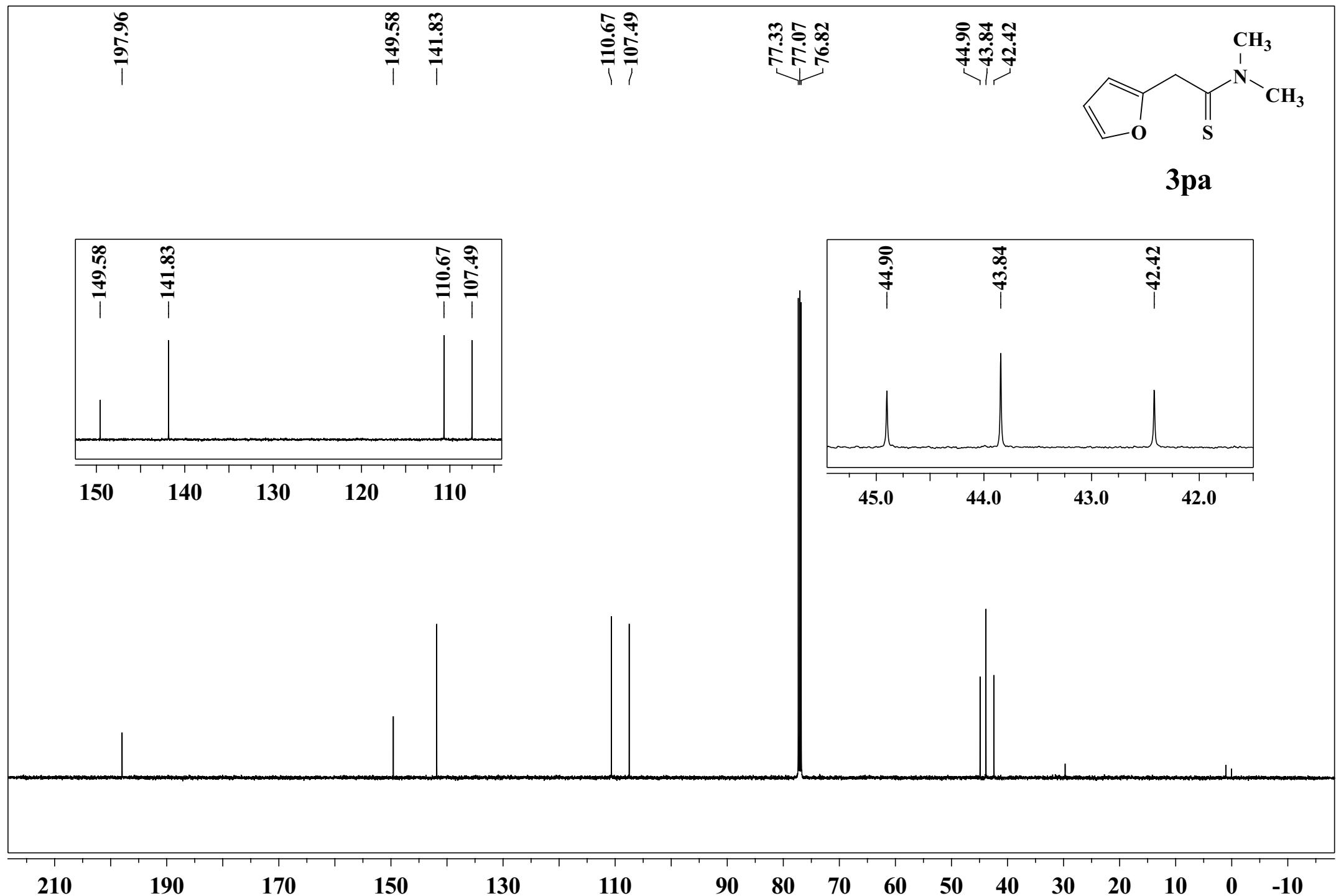


Figure S33. ^{13}C NMR Spectrum of **3pa**

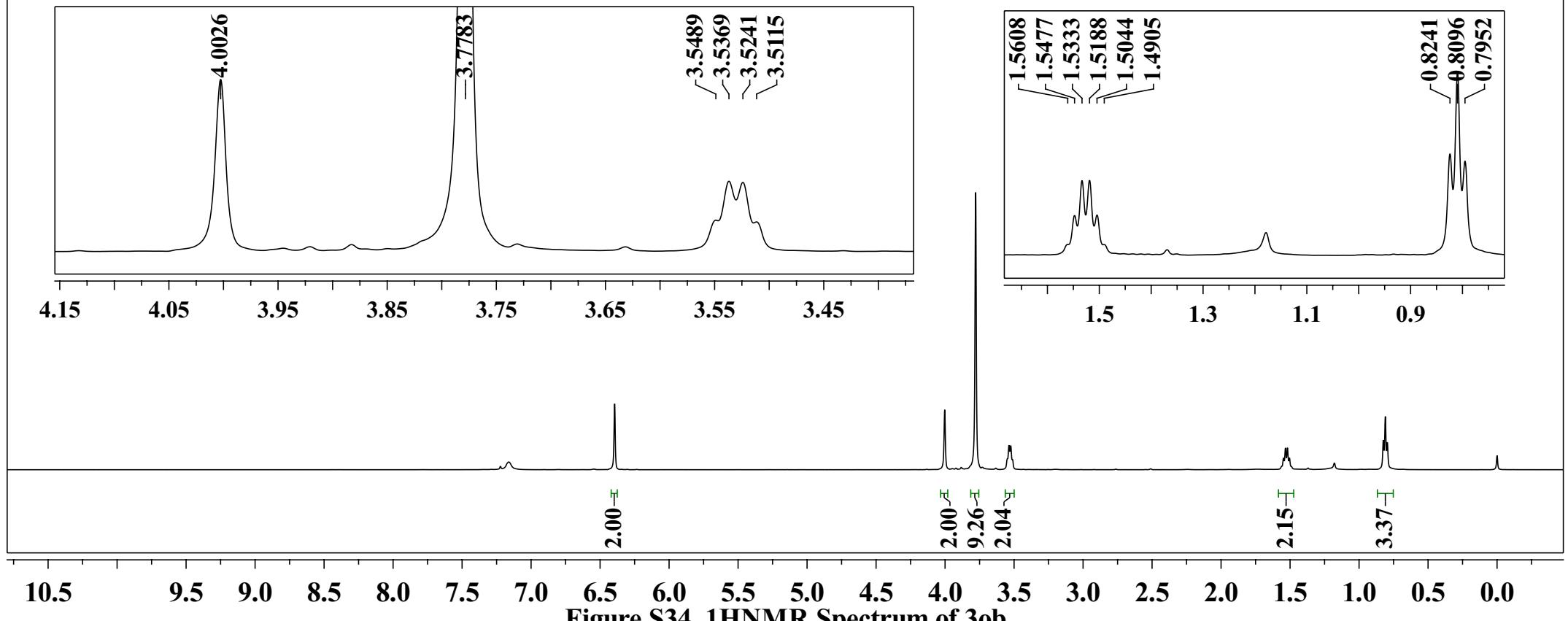
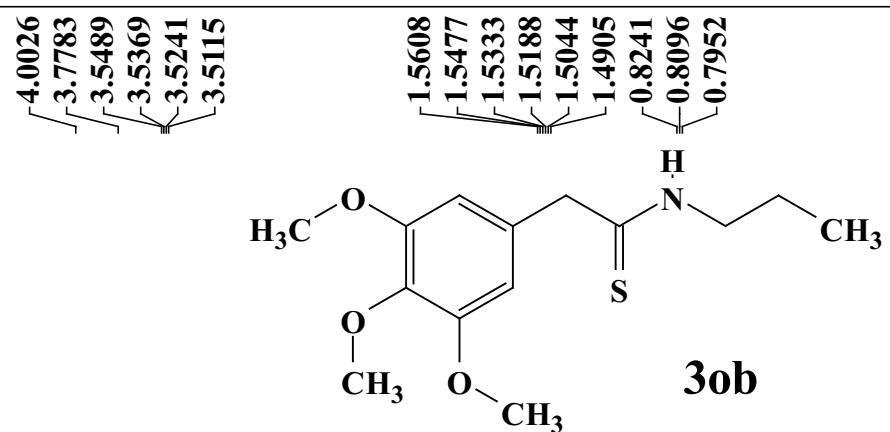


Figure S34. ^1H NMR Spectrum of 3ob

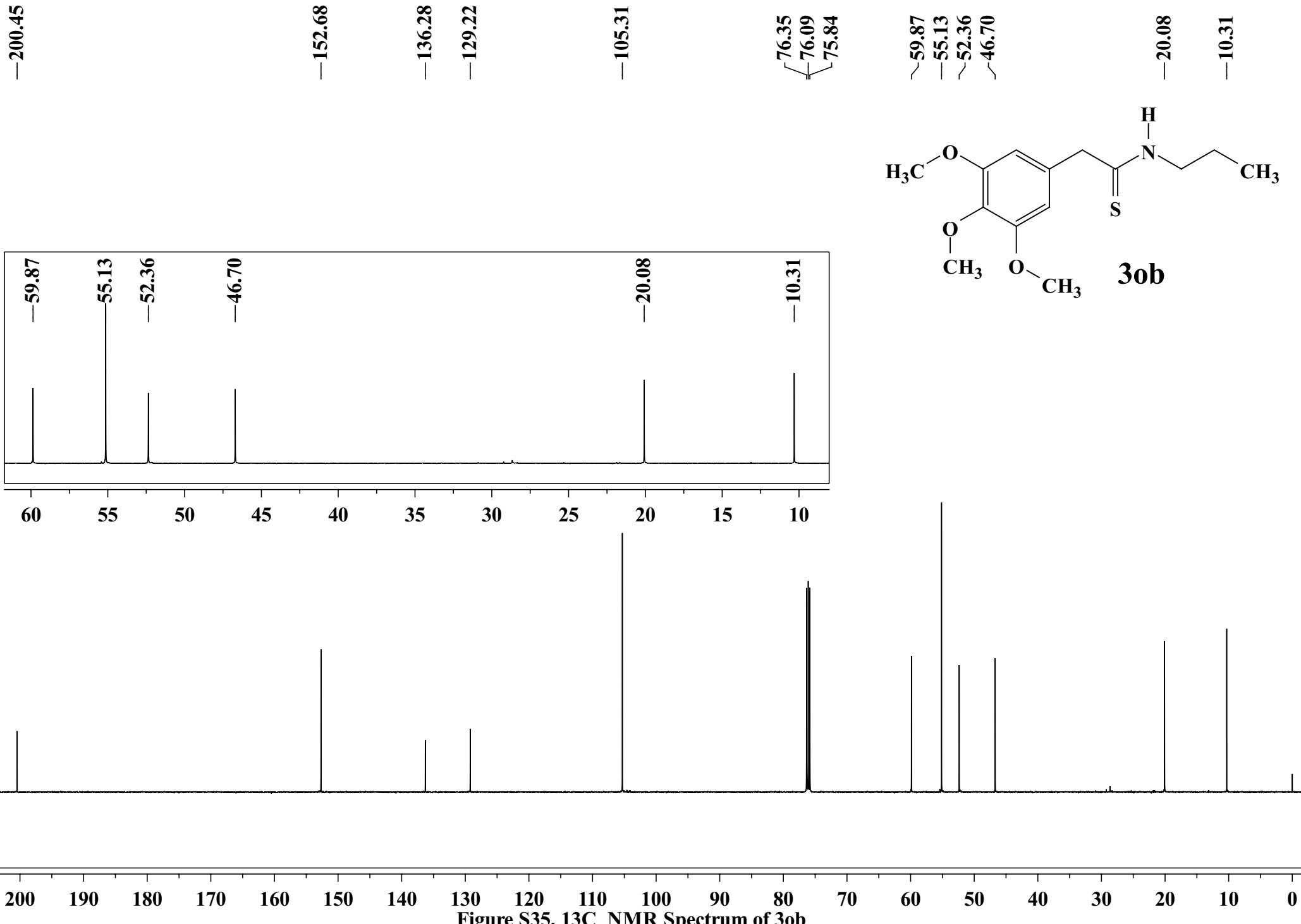


Figure S35. ^{13}C NMR Spectrum of **3ob**

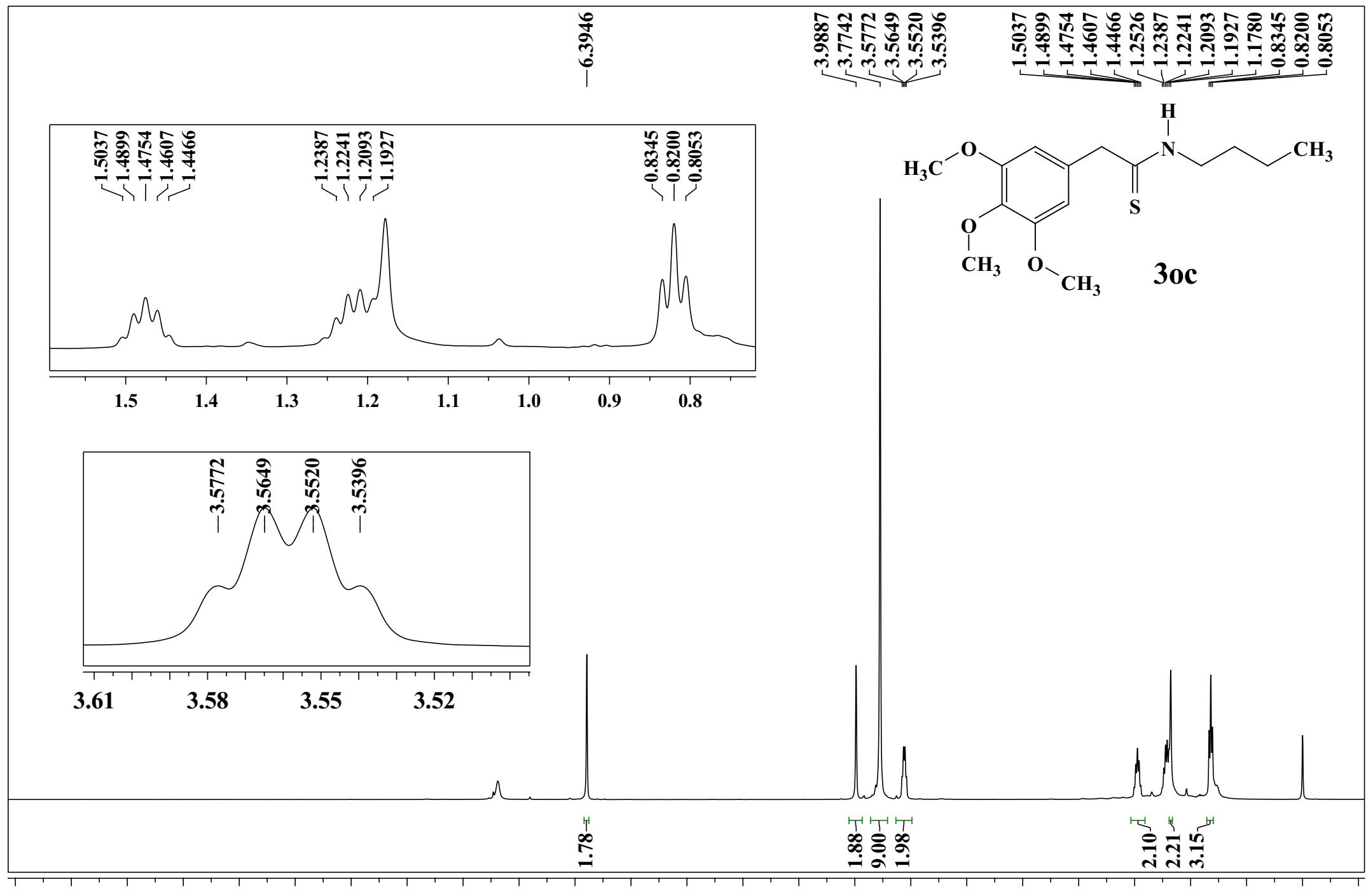


Figure S36. ^1H NMR Spectrum of **3oc**

-201.353

-153.752

-137.460

-130.199

-106.439

77.328
77.073
76.819

-60.896
-56.191
-53.420
-45.893

-29.804
-20.079
-13.683

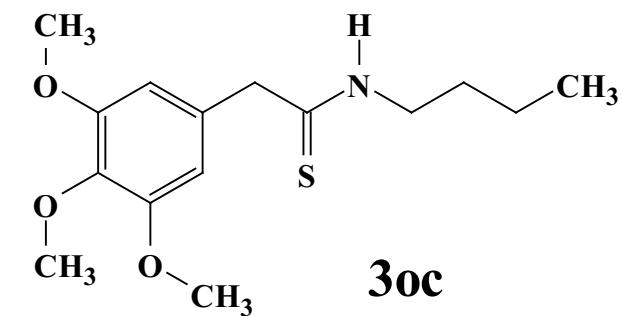
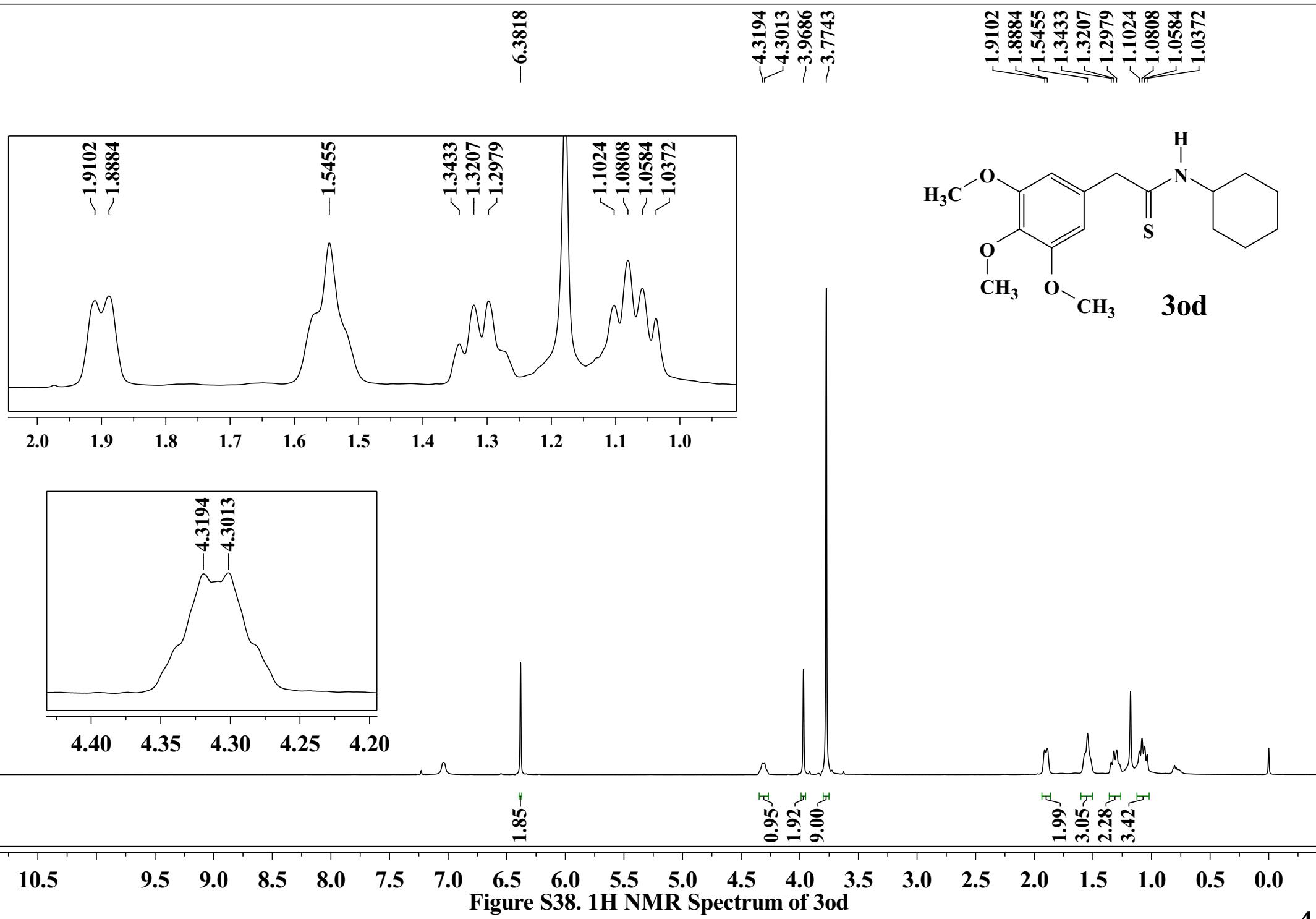


Figure S37. ¹³C NMR Spectrum of **3oc**



-198.78

-152.61

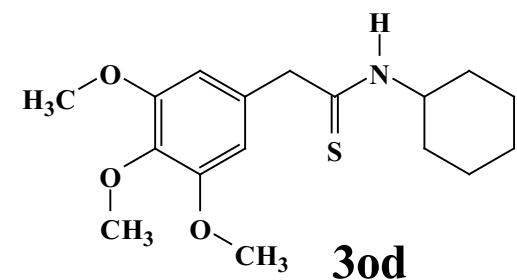
-136.19

-129.43

-105.15

59.87
55.13
53.09
52.49

30.08
28.66
24.27
23.37



-198.78

-152.61

-136.19

-129.43

-105.15

59.87
55.13
53.09
52.49

30.08
28.66
24.27
23.37

200

190

180

170

160

150

140

130

120

110

100

90

80

70

60

50

40

30

20

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Figure S39. ¹³C NMR Spectrum of 3od

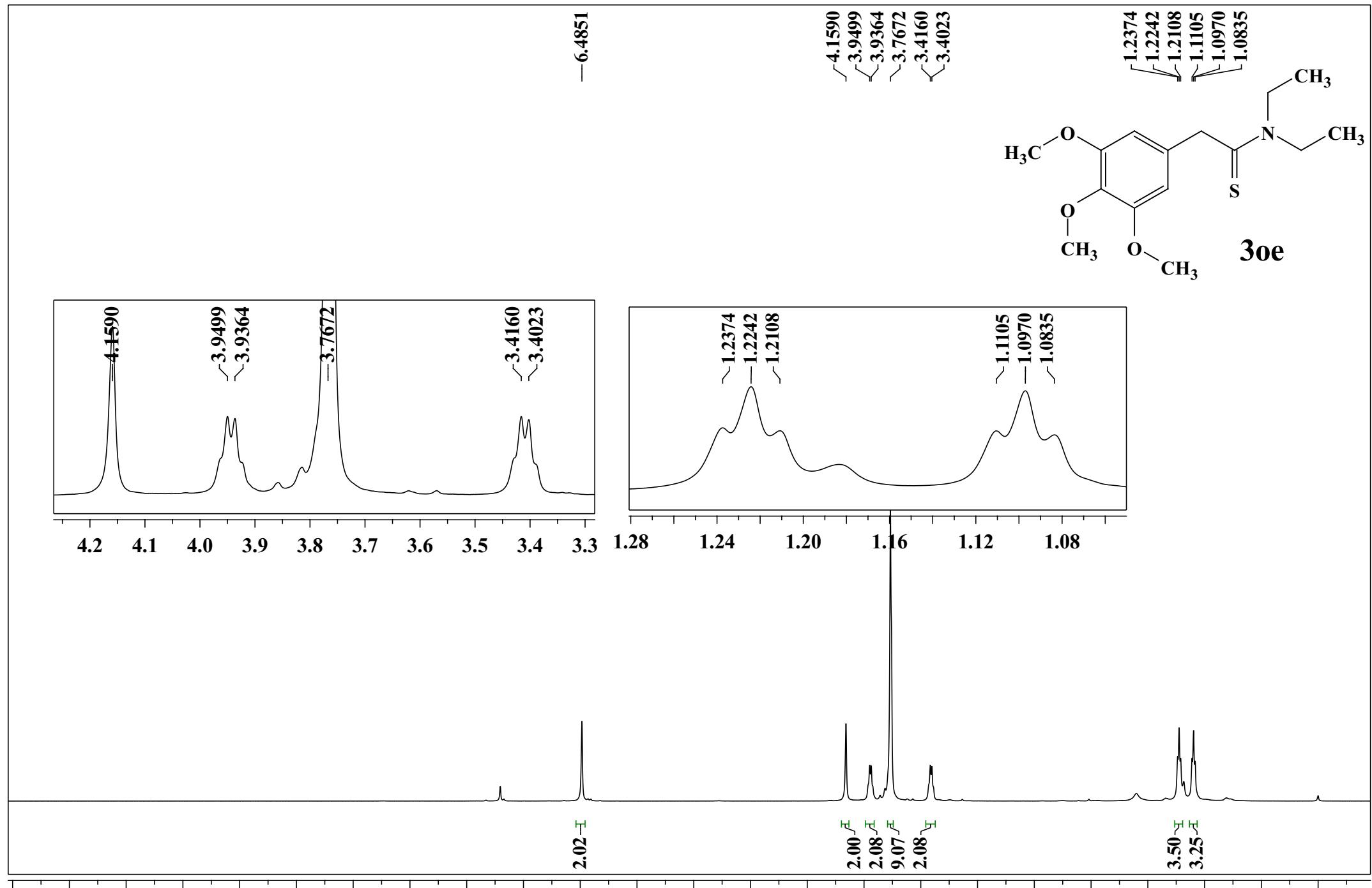


Figure S40. ¹H NMR Spectrum of **3oe**

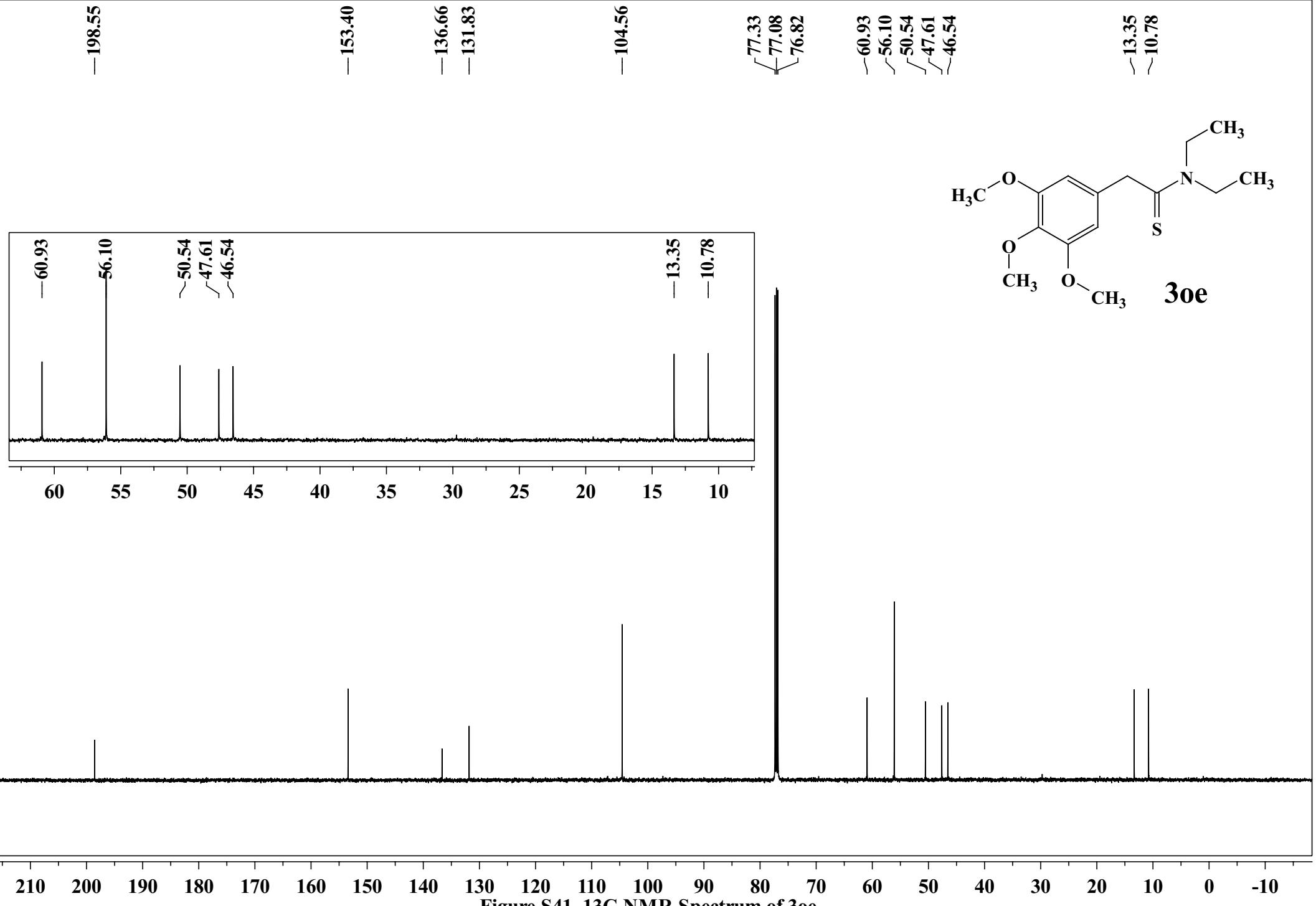
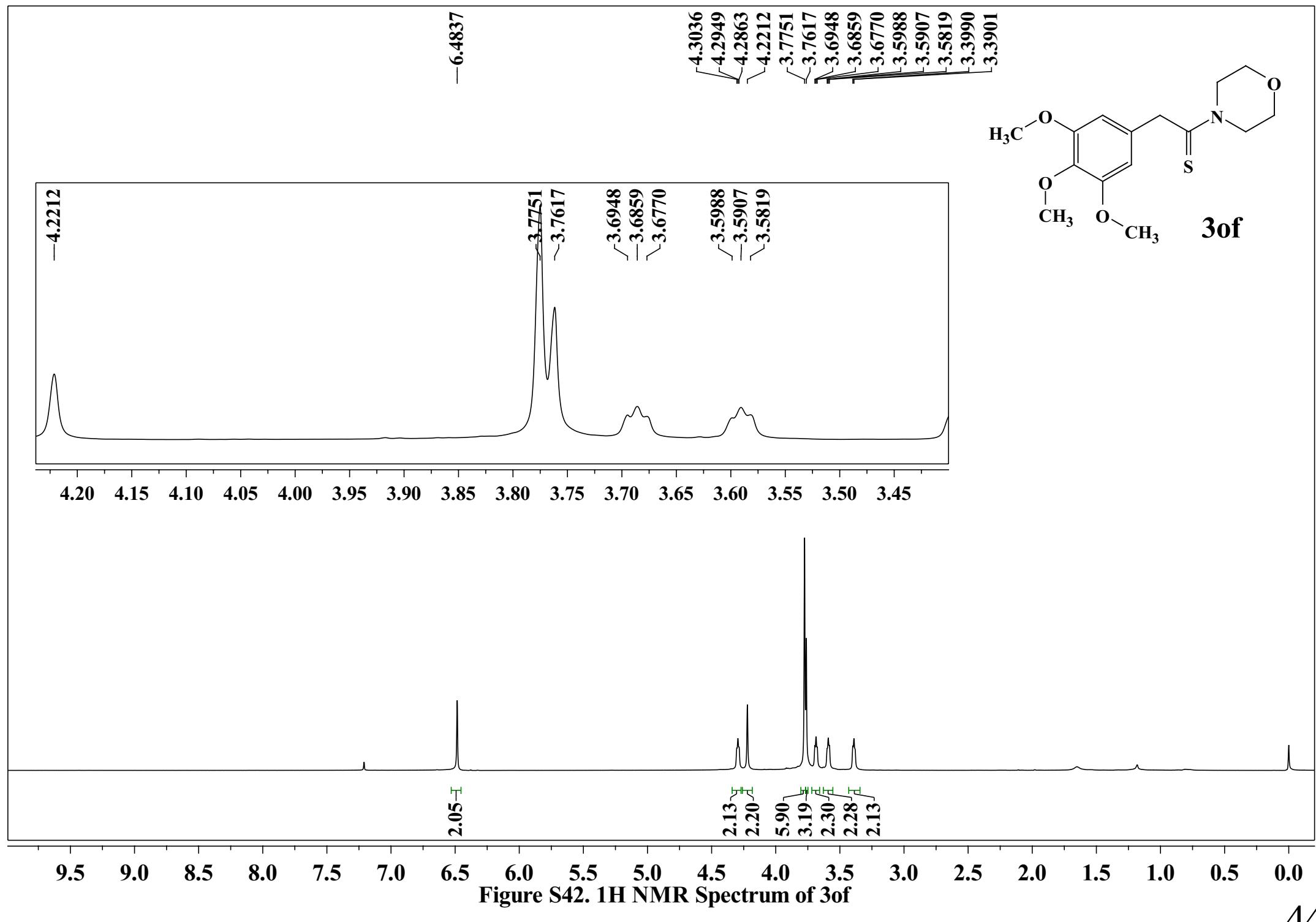


Figure S41. ^{13}C NMR Spectrum of **3oe**



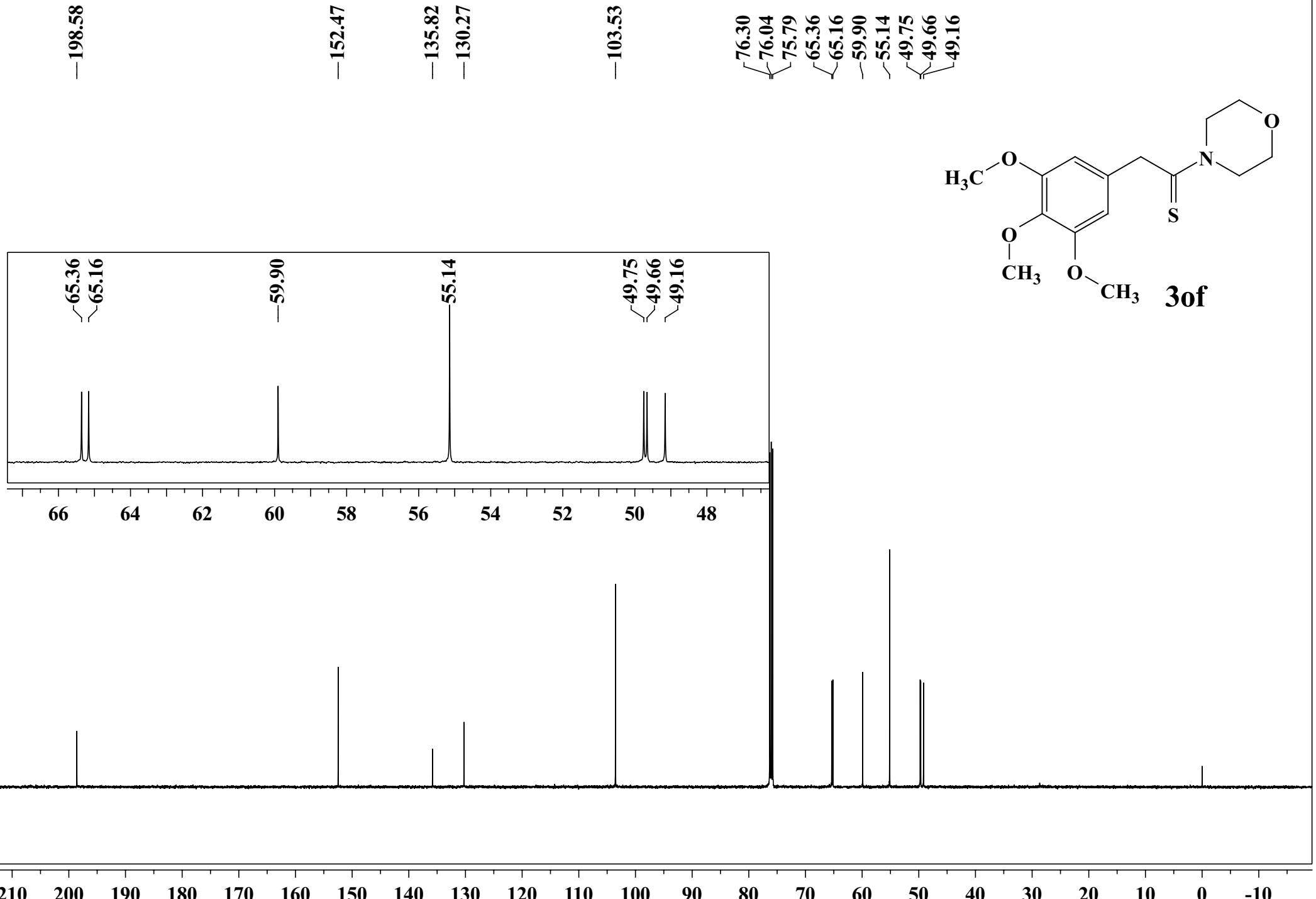
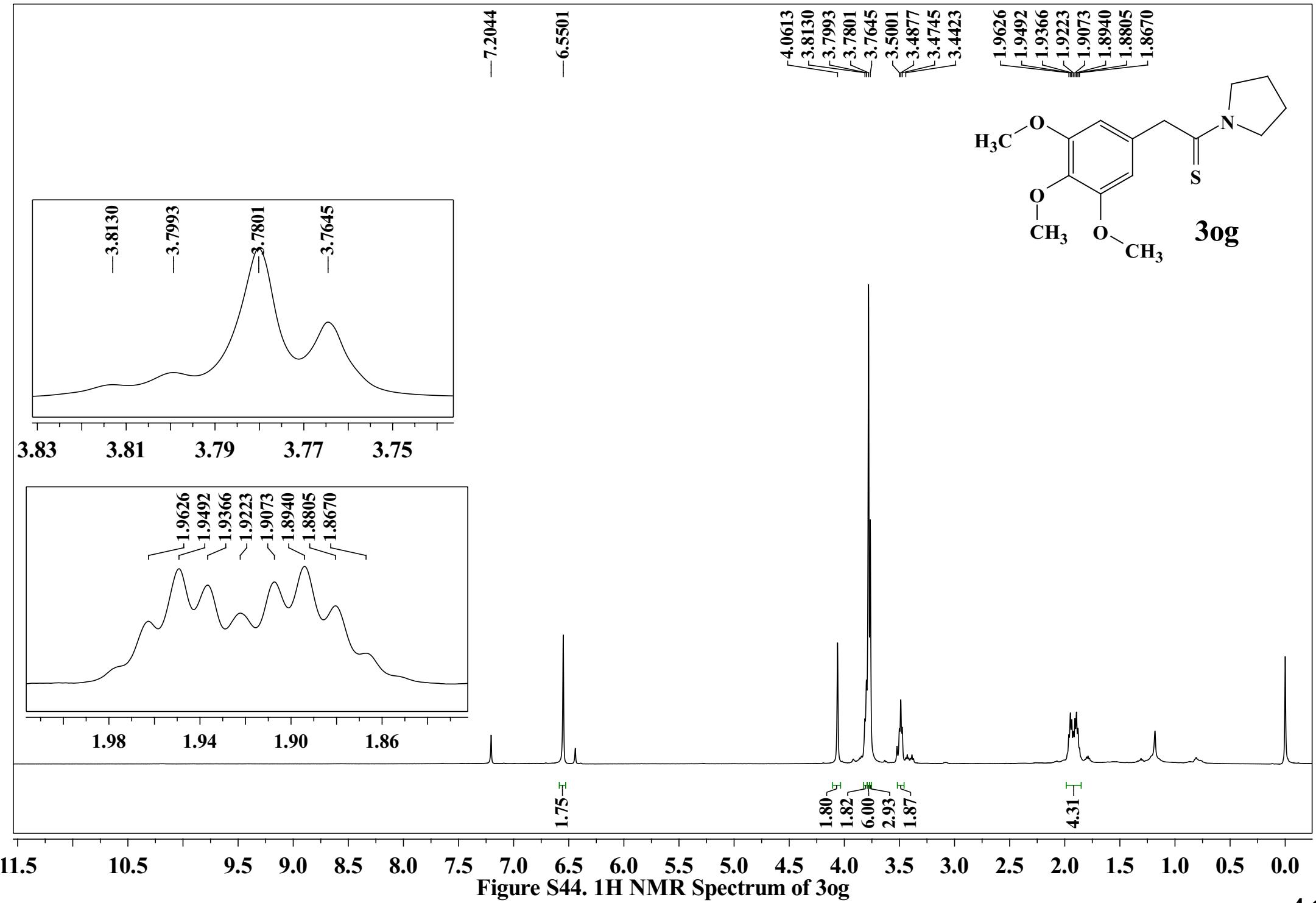
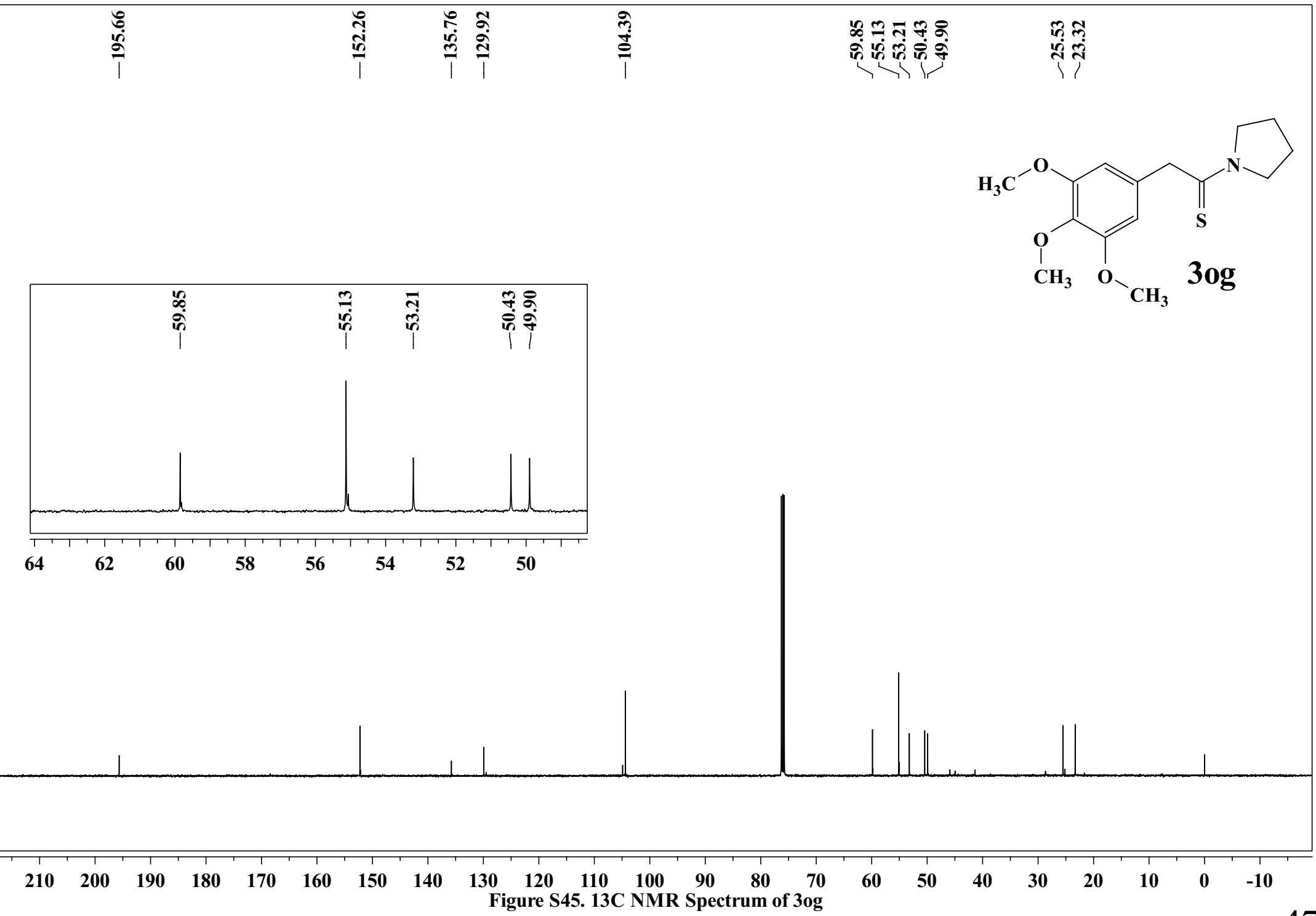


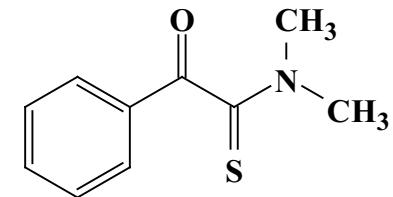
Figure S43. ^{13}C NMR Spectrum of **3of**





7.9854
7.9700
7.6238
7.6092
7.5948
7.5014
7.4867
7.4719

-3.5594
-3.2322



4ka

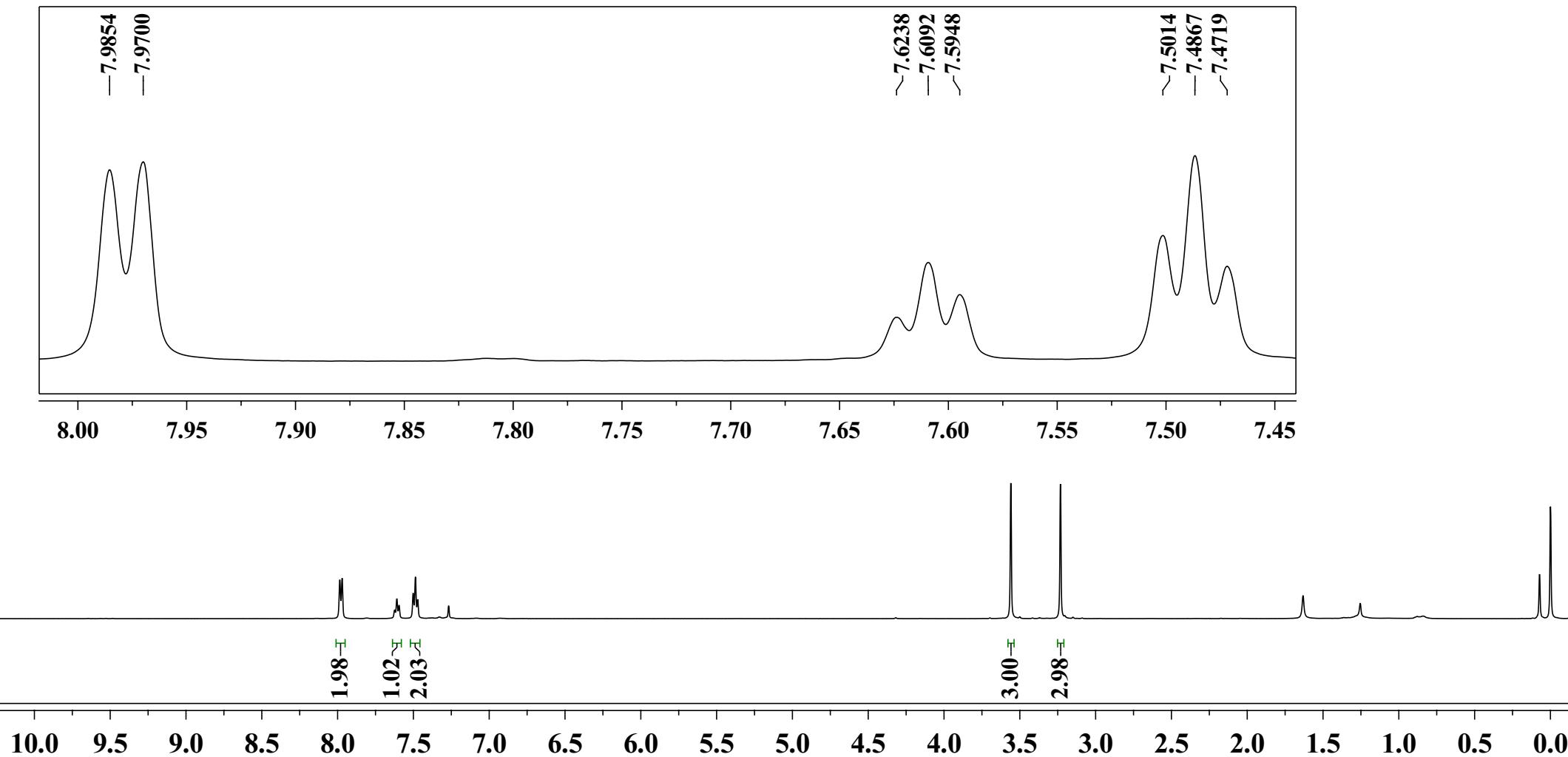
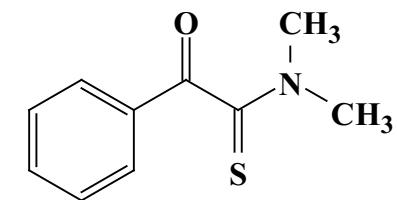


Figure S46. ¹H NMR of Spectrum of 4ka

—196.72
—188.42

134.26
133.11
129.88
128.86

—42.47
—40.42



4ka

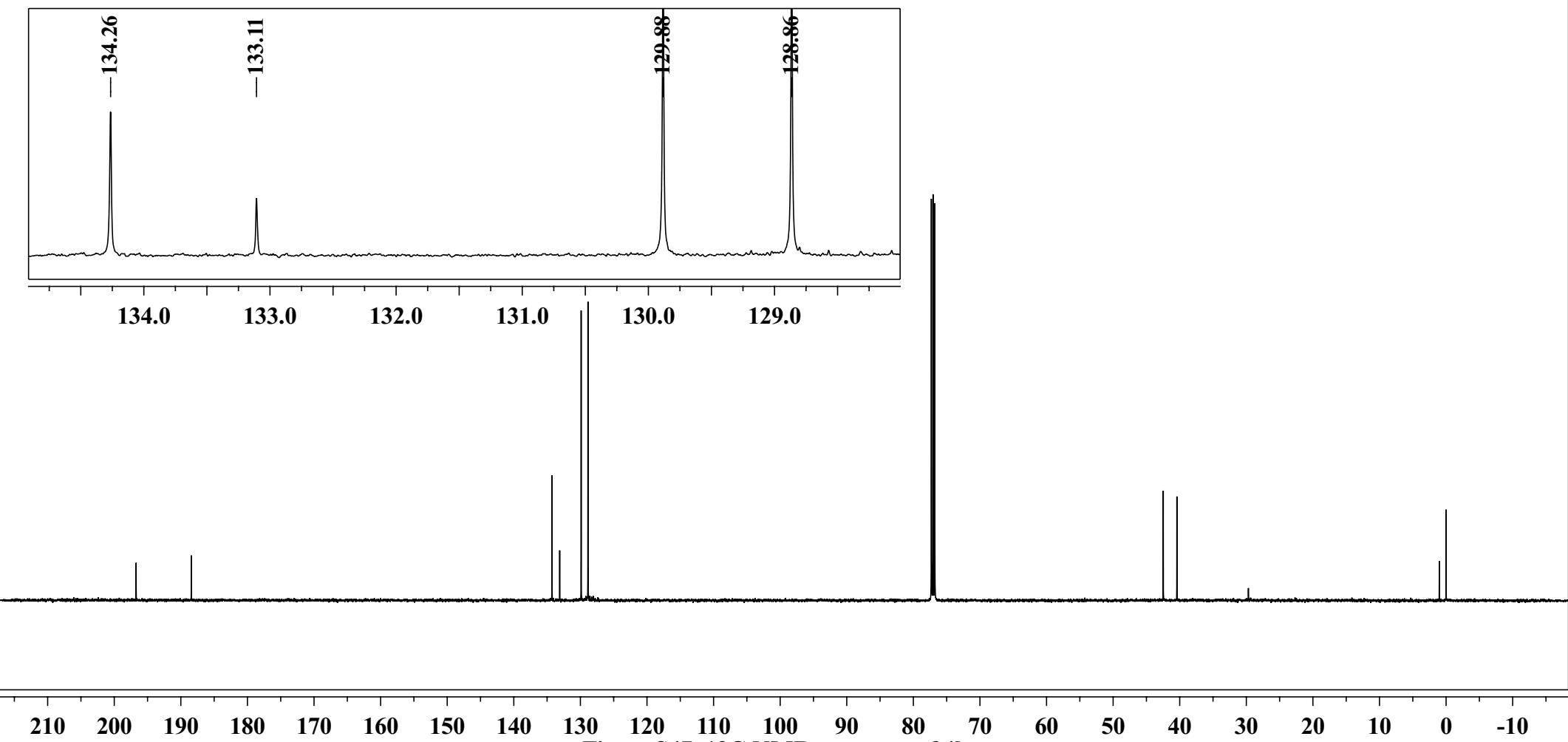
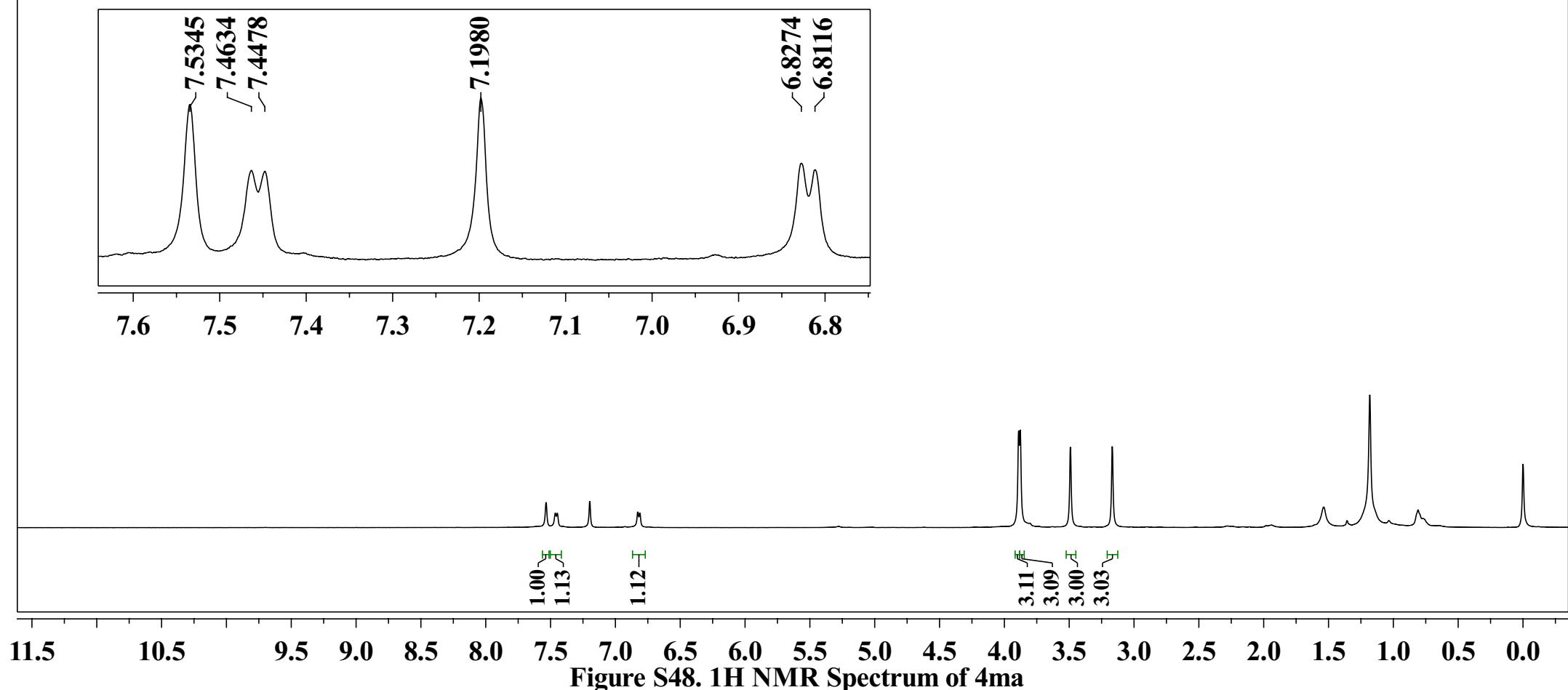
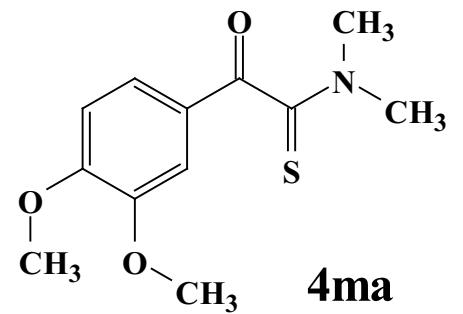


Figure S47. ¹³C NMR spectrum of 4ka



-197.10
-187.91

-154.33
-149.40

126.17
125.64
110.99
110.26

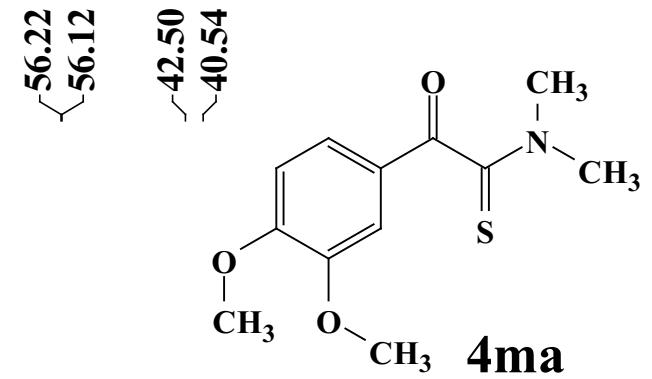


Figure S49. ¹³C NMR Spectrum of 4ma

Single crystal X-ray structure of 3oa

Datablock: shelx

Bond precision: C-C = 0.0040 Å

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

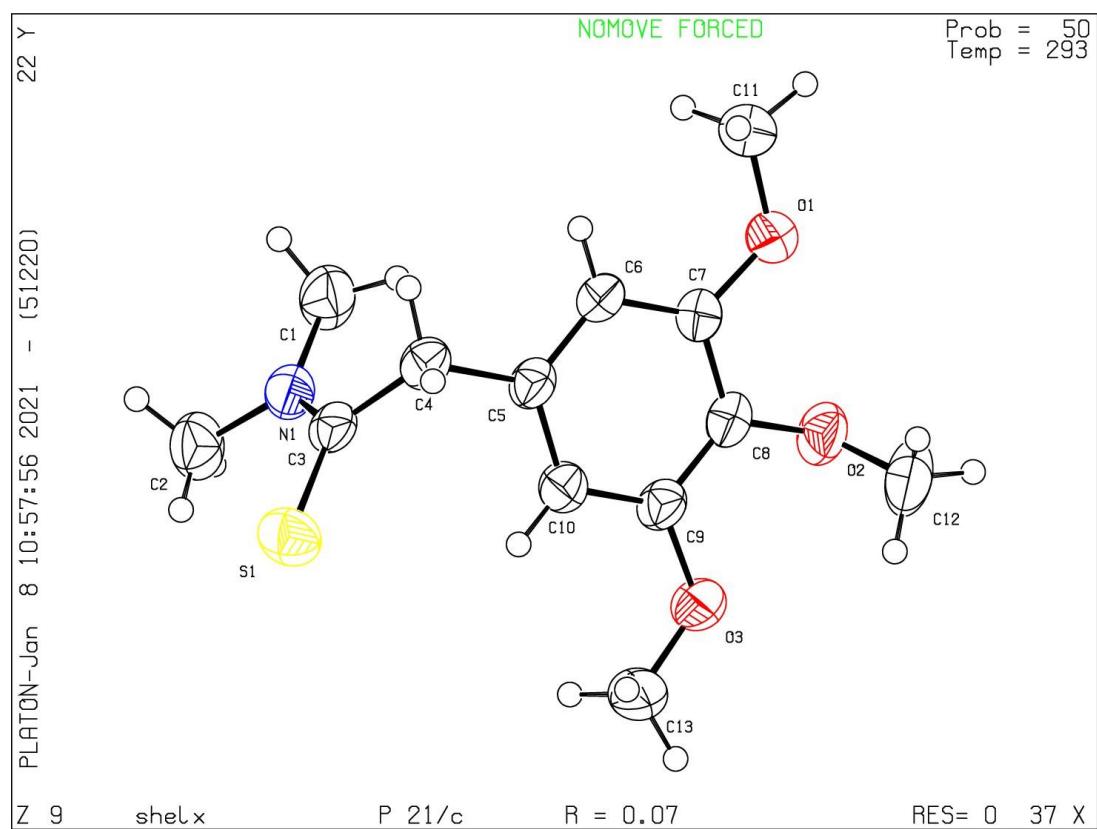
Theta (max)= 27.569

R(reflections)= 0.0679(2215)

wR2(reflections)= 0.1974(3270)

S = 1.069

Npar= 168



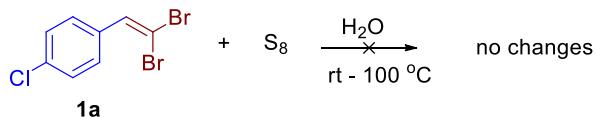
Scaled up procedure for the synthesis of thioamide (**3oa**):

To a stirred solution of **1o** (1g, 2.84 mmol, 1.0 equiv) in 10-12 mL of amine **2** (40 wt% in H₂O), 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 NaHCO₃, 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:

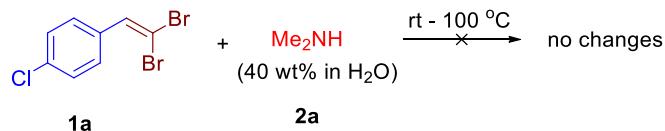
Expt. 1:

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.



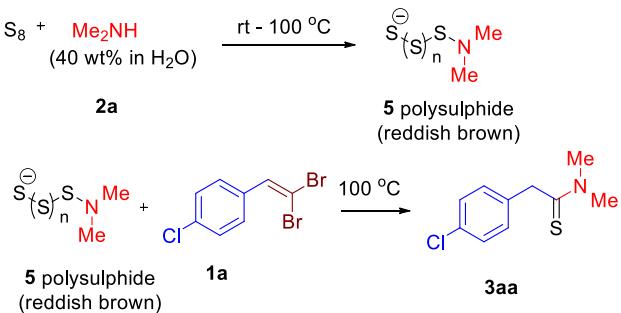
Expt. 2:

1,1 dibromoalkene **1a** (0.148 g, 0.5 mmol, 1.0 equiv) was added to previously stirred solution of 5 mL of Me₂NH **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.



Expt. 3:

To a stirred solution of 5 mL of Me₂NH **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 NaHCO₃. 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