Electronic Supplementary Information

# Thermal conversion of primary alcohols to disulfides via xanthate intermediates: an extension to Chugaev elimination

**Wei He,[a] Yong Ding,[a] Jianzhuo Tu,[a] Chuqiang Que[a], Zhanhui Yang,*[a] and Jiaxi Xu*[a]**

**Fax: +86 10 64435565**

**E-mail: zhyang@mail.buct.edu.cn (Zhanhui Yang)**

**Email.: jxxu@mail.buct.edu.cn (Jiaxi Xu)**

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry,

Faculty of Science, Beijing University of Chemical Technology,

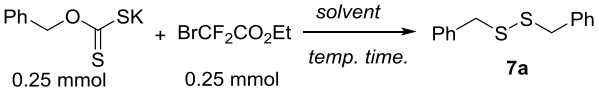
Beijing 100029, People's Republic of China

## Contents

# 1. Further condition optimization.

To a 15-mL heavy-wall reaction tube was sequentially added potassium xanthates **9** (0.25 mmol), ethyl bromodifluoroacetate (**10a**) (55.3 mg, 0.25 mmol), and different solvents (1.0 mL). The tube was sealed and immersed into a preheated oil-bath at different temperatures, and heated for different time. Upon cooling to room temperature, mesitylene (0.125 mmol, 21 mg) was added. The reaction mixture was diluted with ethyl acetate (5 mL) and washed with brine (5 mL x 3). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was submitted to $^1$H NMR analysis to determine the yields of **7a**.

**Table S1. Further optimization of reaction conditions**



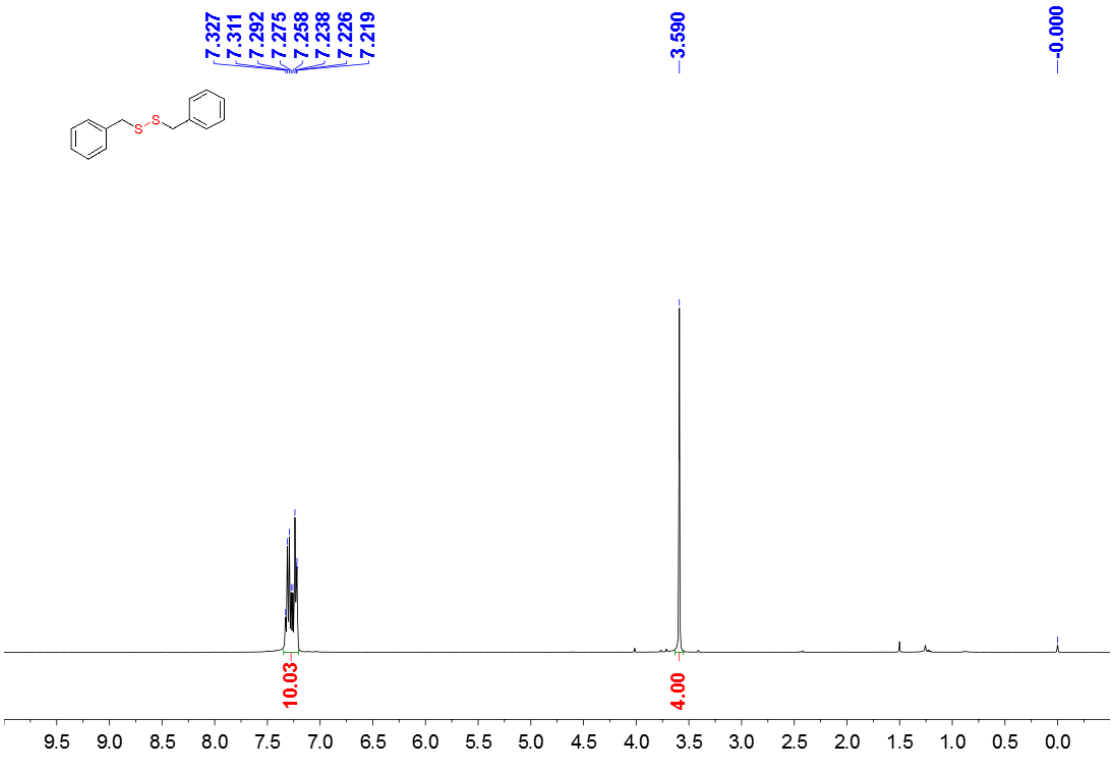

| Entry | Solvent | Temp. (°C) | Time (h) | **9a**:**10a** | Yield (%) |
|---|---|---|---|---|---|
| 1 | MeCN | 80 | 1 | 1:1 | 38 |
| 2 | DMF | 80 | 1 | 1:1 | 40 |
| 3[a] | DMF | 80 | 1 | 1:1 | 30 |
| 4 | DMSO | 80 | 1 | 1:1 | 18 |
| 5[a] | DMSO | 80 | 1 | 1:1 | 13 |
| 6 | THF | 80 | 1 | 1:1 | trace |
| 7 | DCM | 60 | 1 | 1:1 | n.r. |
| 8 | Acetone | 65 | 1 | 1:1 | 10 |
| 9 | EA | 80 | 1 | 1:1 | trace |
| 10[b] | $MeNO_2$ | 80 | 1 | 1:1 | 35 |
| 11[b] | EtOH | 80 | 1 | 1:1 | n.p. |
| 12[b] | DMF | 80 | 1 | 1:1 | 14 |
| 13 | $MeNO_2$ | 80 | 1 | 1:1 | 45 |
| 14 | $MeNO_2$ | 80 | 1 | 1:2 | 32 |
| 15 | $MeNO_2$ | 80 | 2 | 1:1 | 50 |
| 16 | $MeNO_2$ | 80 | 3 | 1:1 | 50 |
| 17 | $MeNO_2$ | 80 | 6 | 1:1 | 50 |
| 18 | $MeNO_2$ | 80 | 2 | 1:1.2 | 41 |
| 19 | $MeNO_2$ | 80 | 2 | 1:1.5 | 28 |
| 20[c] | $MeNO_2$ | 80 | 2 | 1:1 | 37 |
| 21[d] | $MeNO_2$ | 80 | 0.5 | 1:1 | 45 |
| 22 | $MeNO_2$ | 60 | 12 | 1:1 | 50 |
| 23 | $MeNO_2$ | 100 | 1 | 1:1 | 53 |
| 24 | $MeNO_2$ | 110 | 1 | 1:1 | 60/58[f] |
| 25 | $MeNO_2$ | 110 | 1.5 | 1:1 | 50 |
| 26 | $MeNO_2$ | 110 | 2 | 1:1 | 58 |
| 27[d] | $MeNO_2$ | 110 | 1/3 | 1:1 | 46 |
| 28[e] | $MeNO_2$ | 110 | 1 | 1:1 | 50 |

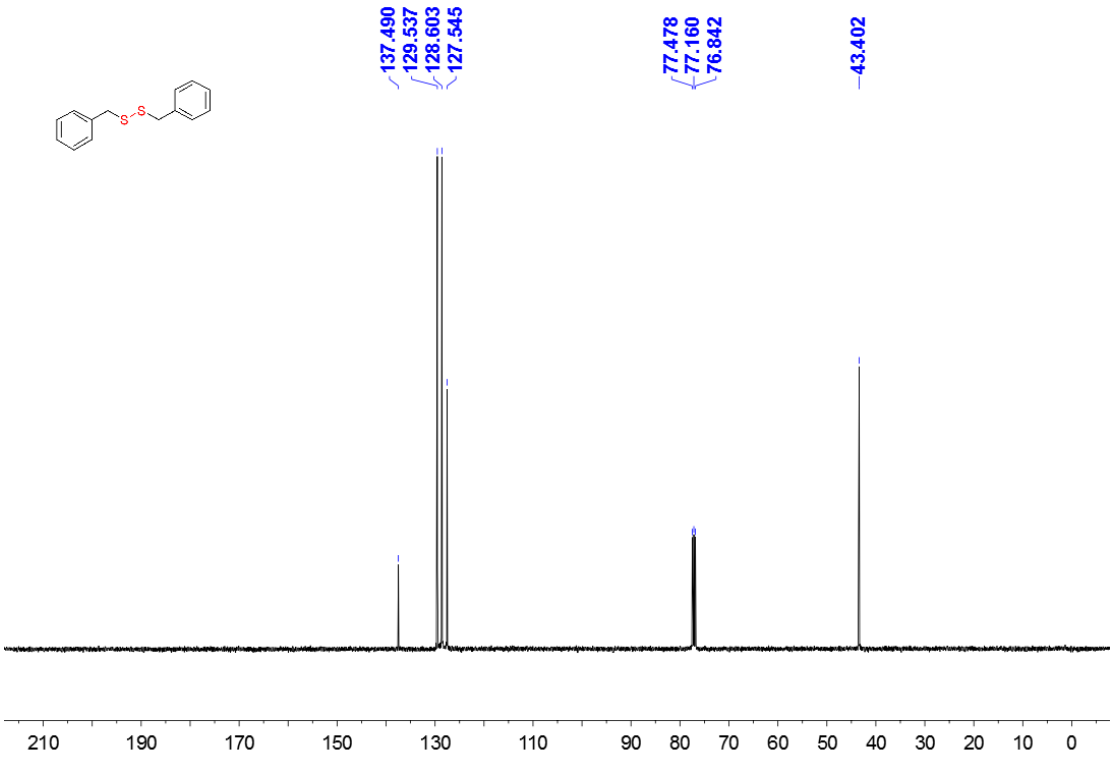
| | | | | | |
|---|---|---|---|---|---|
| 29 | HMPA | 110 | 1 | 1:1 | n.p |
| 30 | NMP | 110 | 1 | 1:1 | 48 |
| 31[g] | $MeNO_2$ | 110 | 1 | 1:1 | 54 |

Reaction conditions: 0.25 mmol of **9a**, 1 mL of anhydrous solvent, reflux in air. NMR yields using 1,3,5-trimethoxybenzene as an internal standard. [a]Under $N_2$. [b]Commercial reagent, unanhydrous. [c]Reaction with 2 mL of $MeNO_2$. [d]Microwave irradiation. [e]Reaction with 0.5 mL of $MeNO_2$. [f]Isolated yields. [g]In degassed nitromethane and under nitrogen atmosphere. [n. r = no reaction; n. p. = no product.]

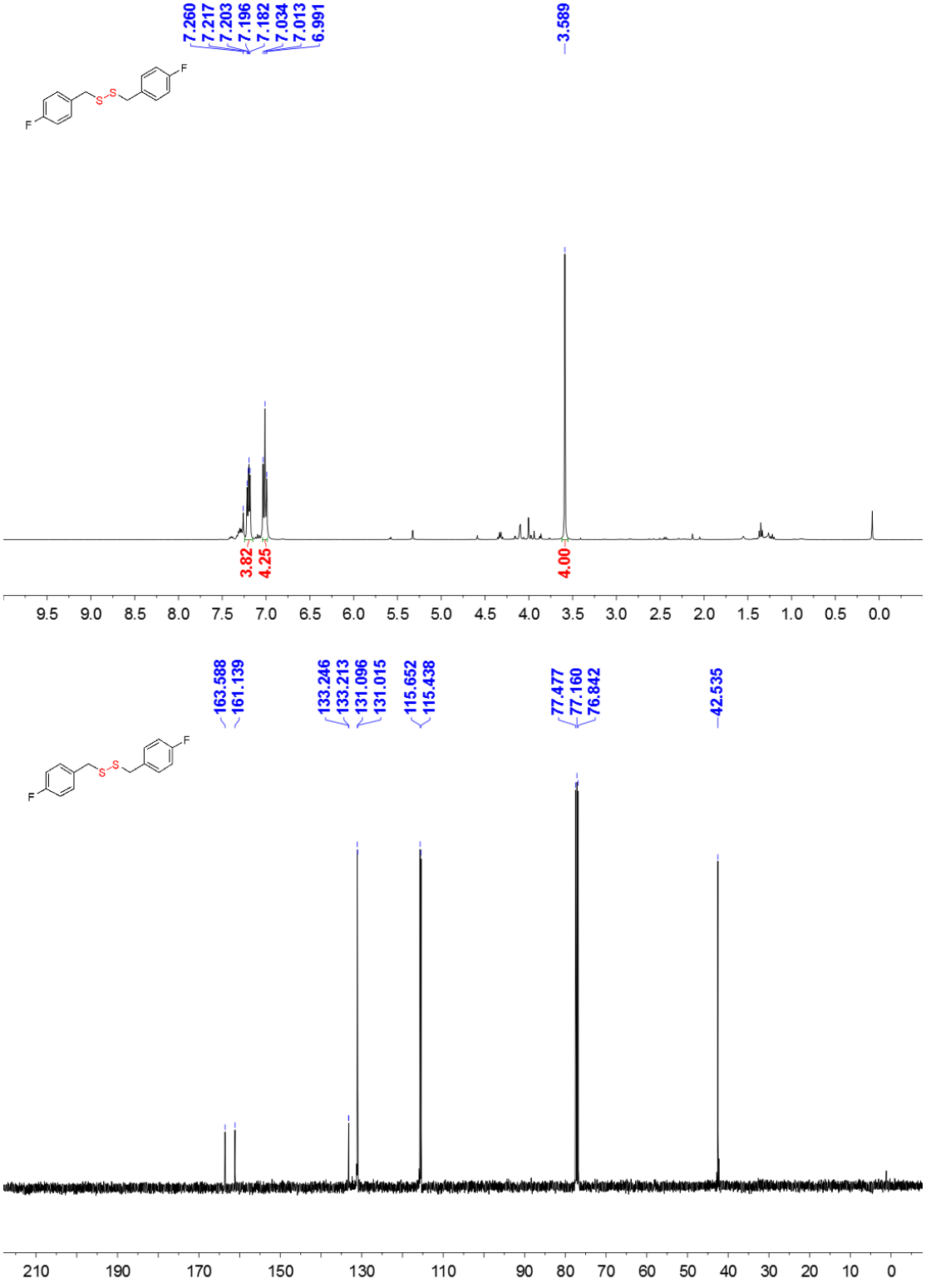
# 2. Copies of $^{1}H$ and $^{13}C$ NMR Spectra of Products

**1,2-dibenzyldisulfane (7a)**

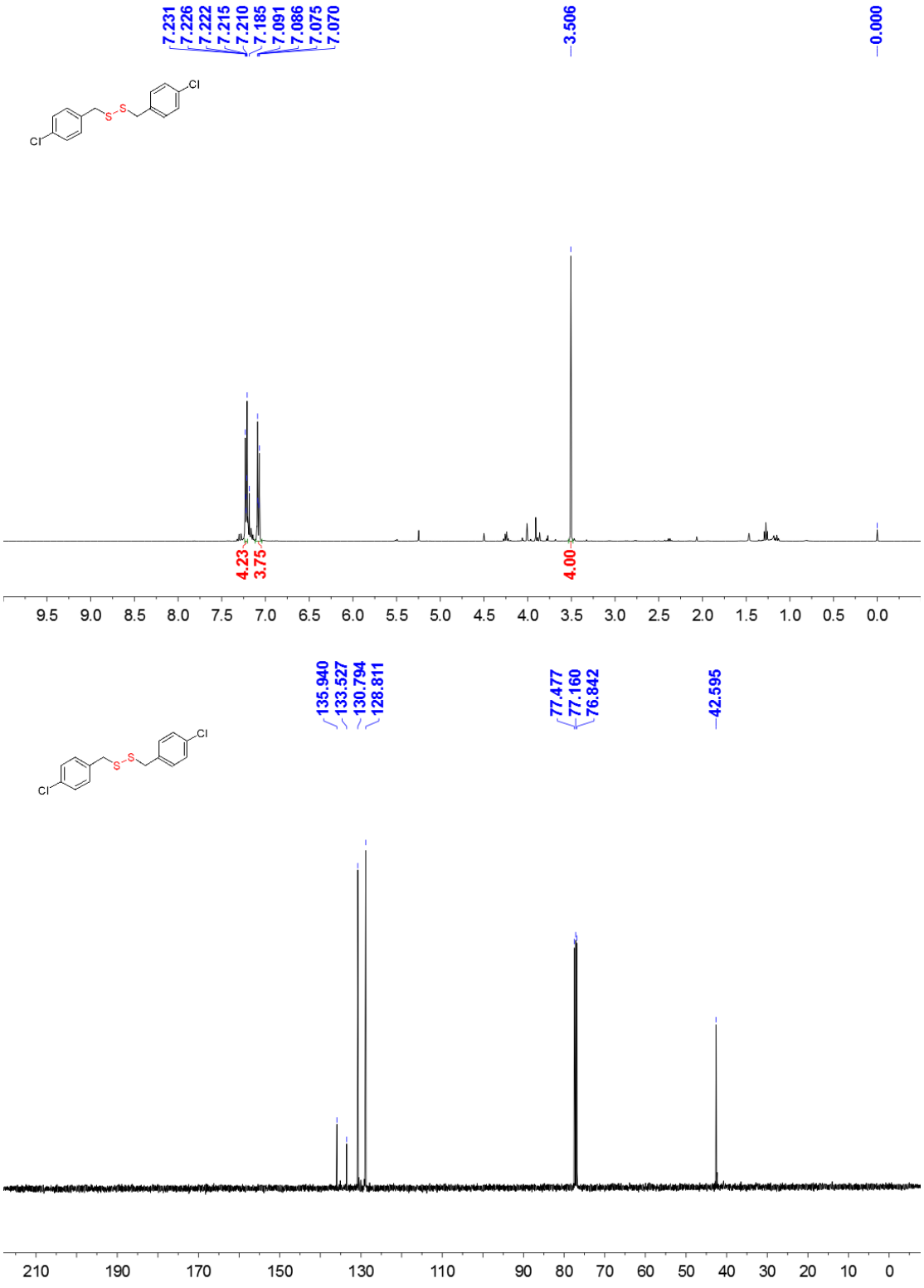


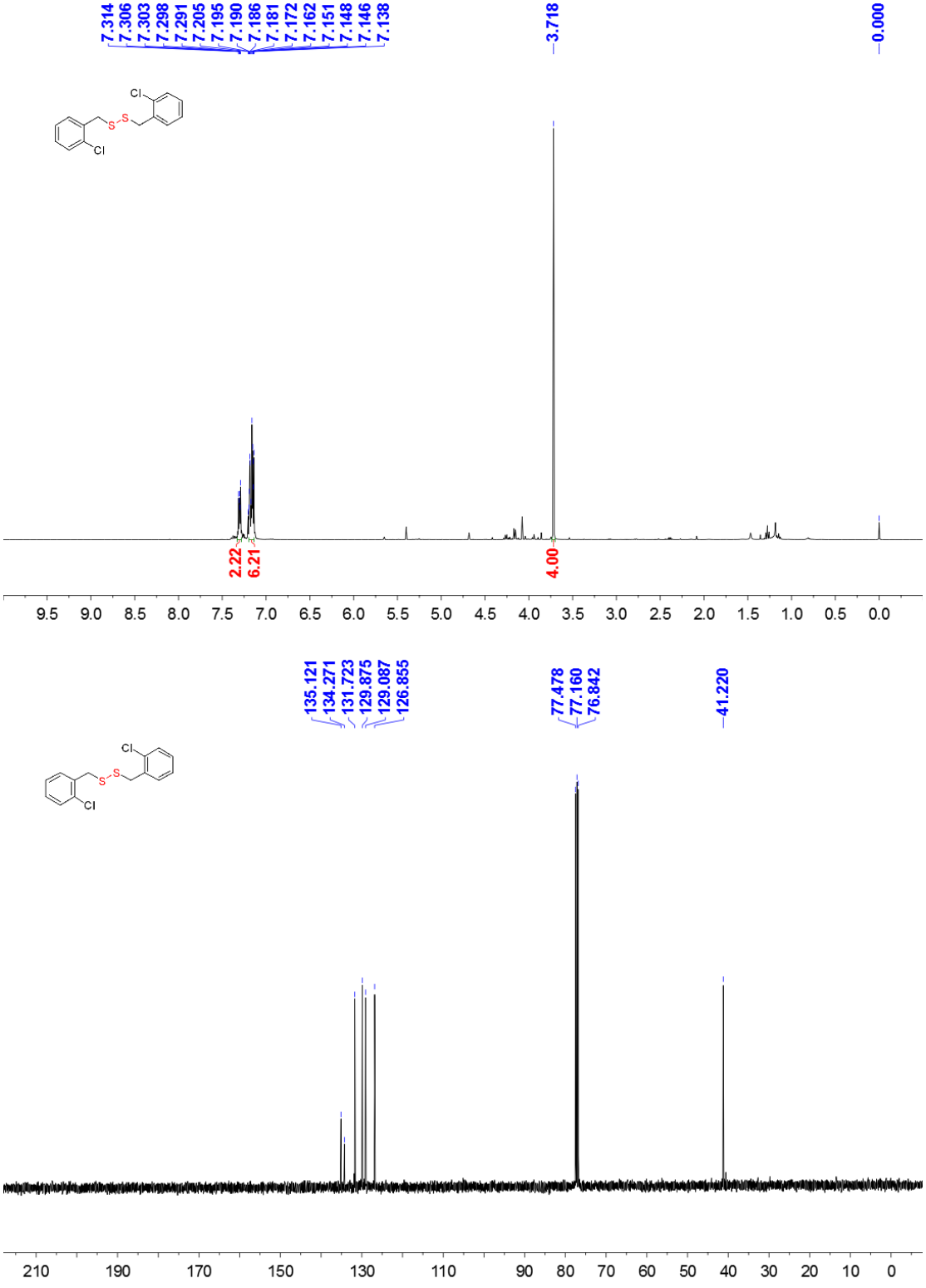
**1,2-bis(4-fluorobenzyl)disulfane (7b)**



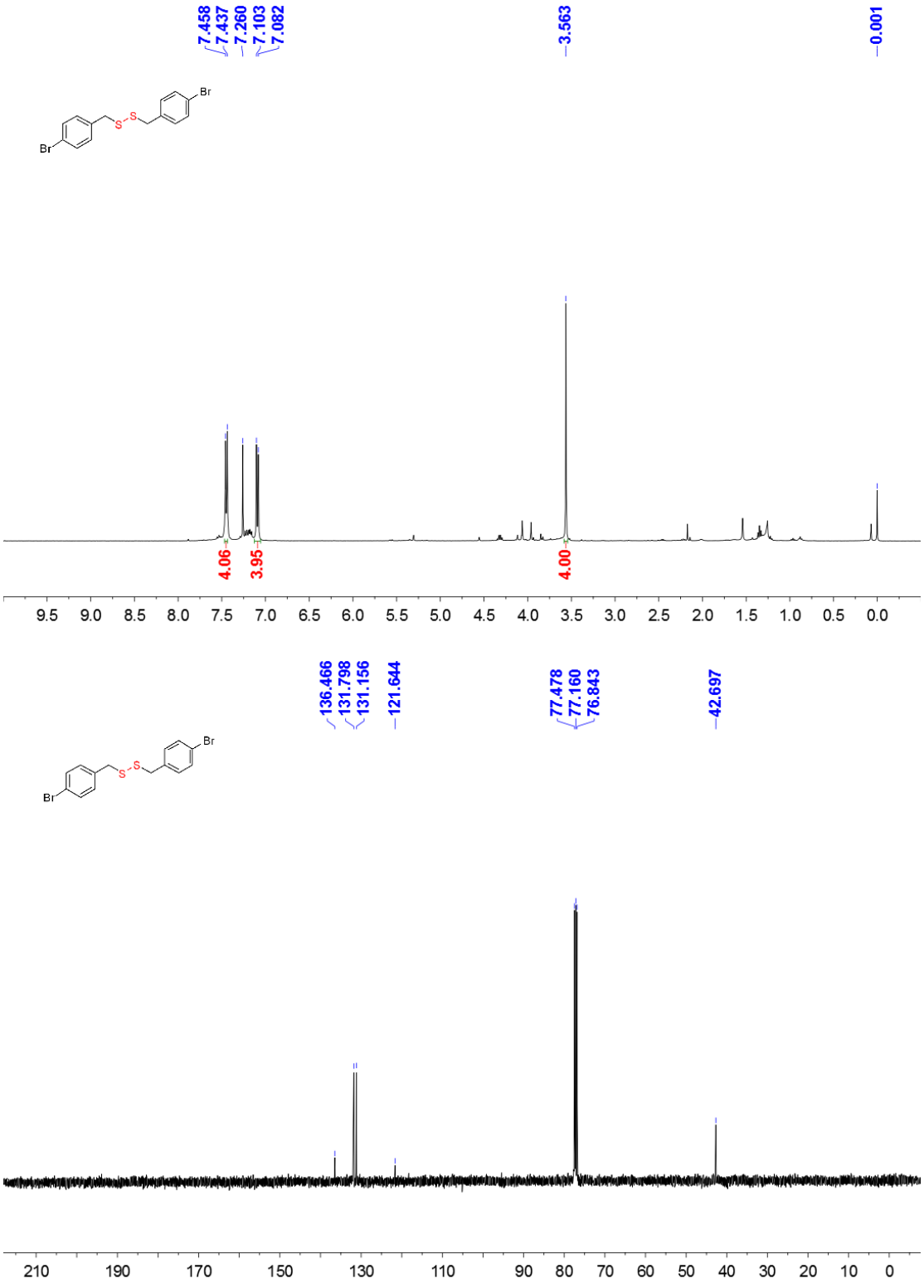
**1,2-bis(4-chlorobenzyl)disulfane (7c)**



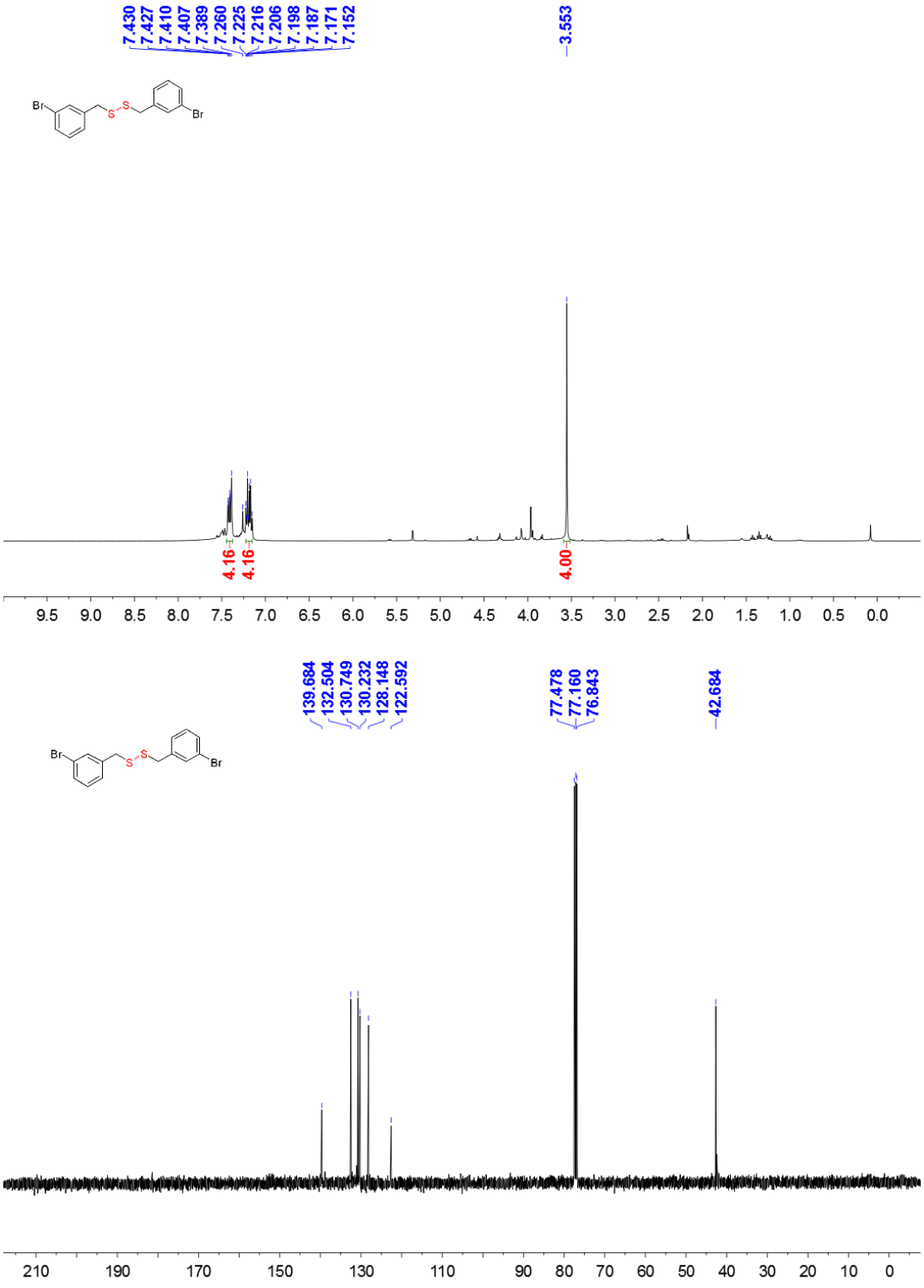
**1,2-bis(2-chlorobenzyl)disulfane (7d)**



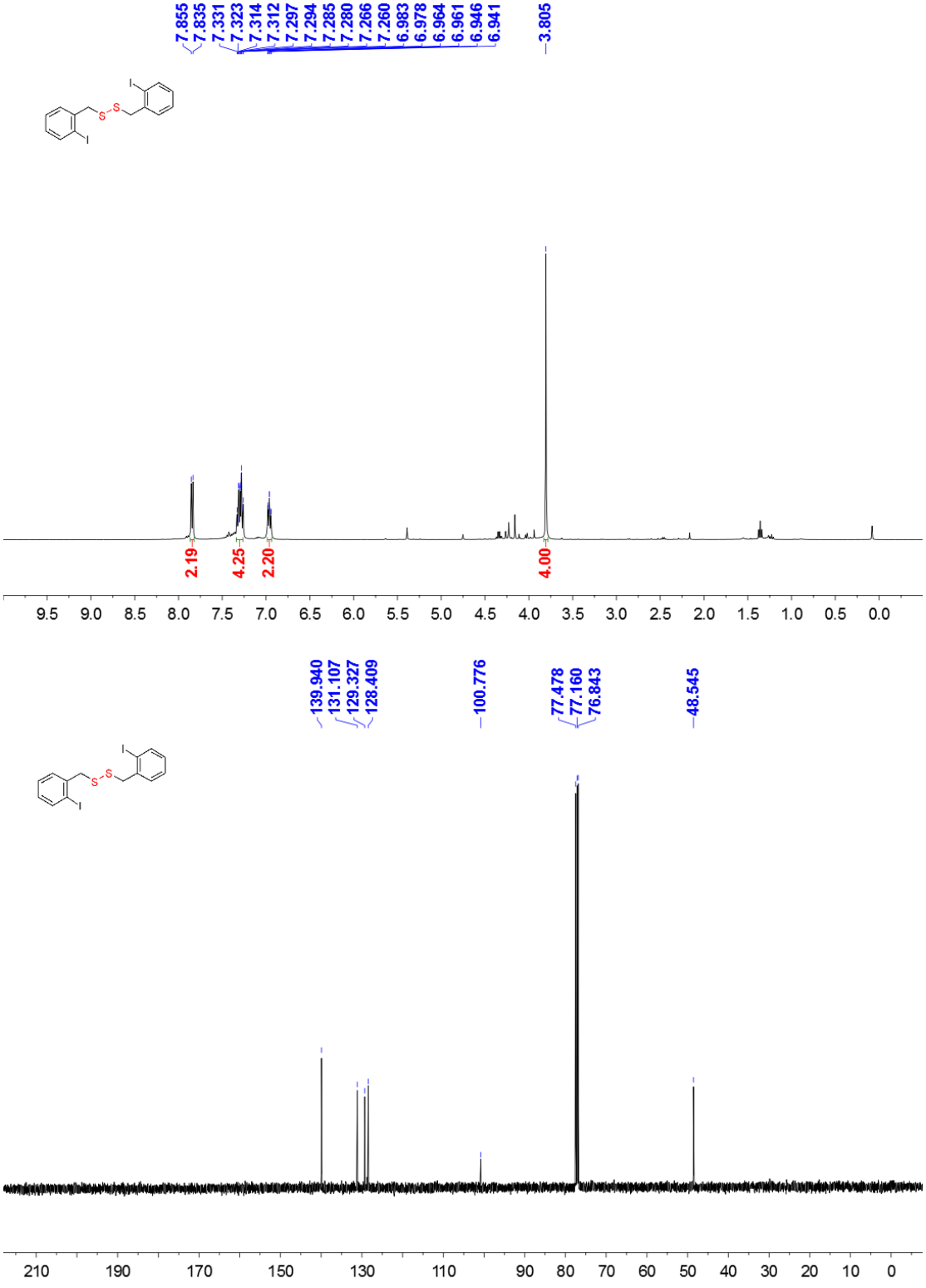
**1,2-bis(4-bromobenzyl)disulfane (7e)**



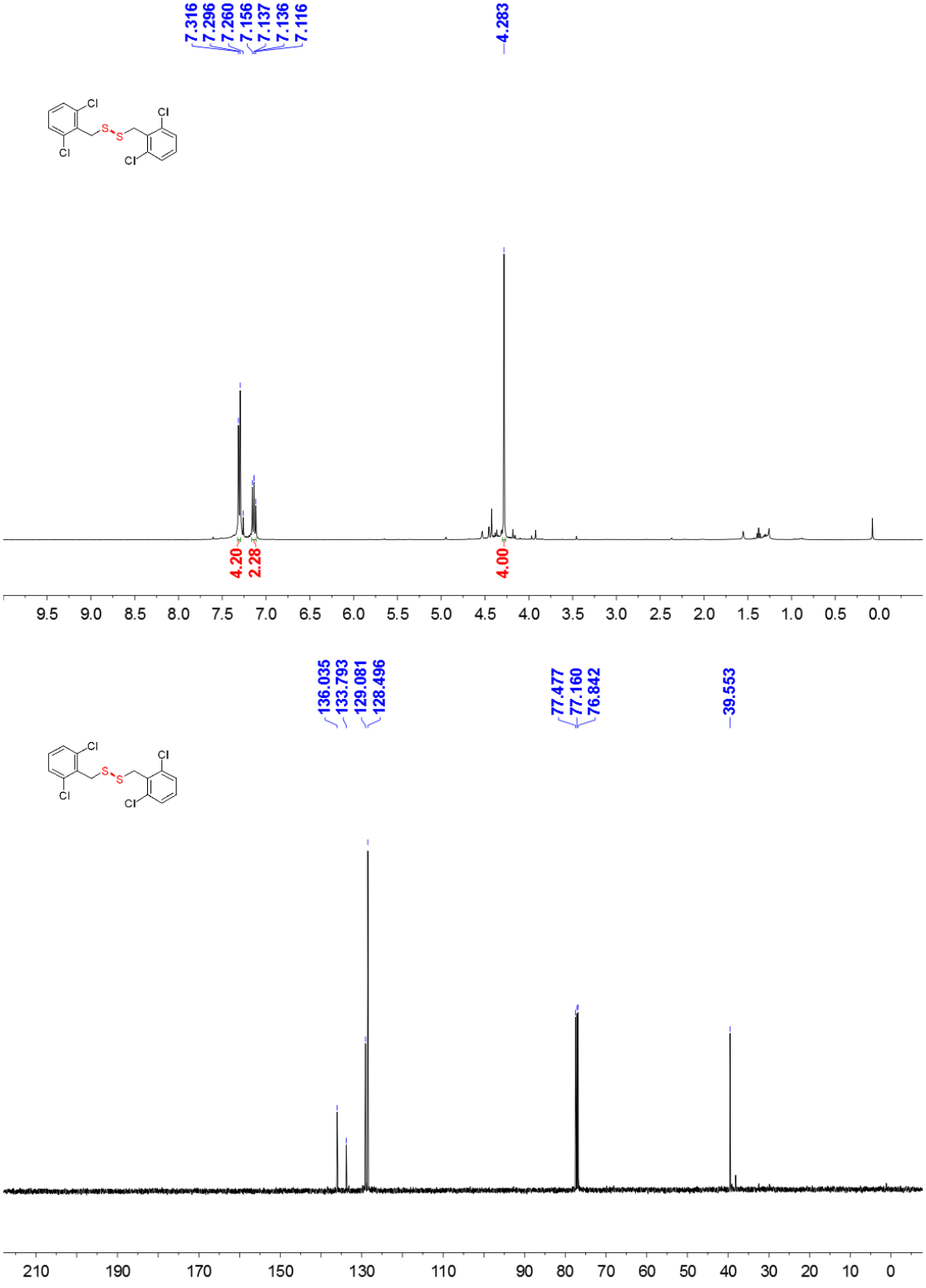
**1,2-bis(3-bromobenzyl)disulfane (7f)**



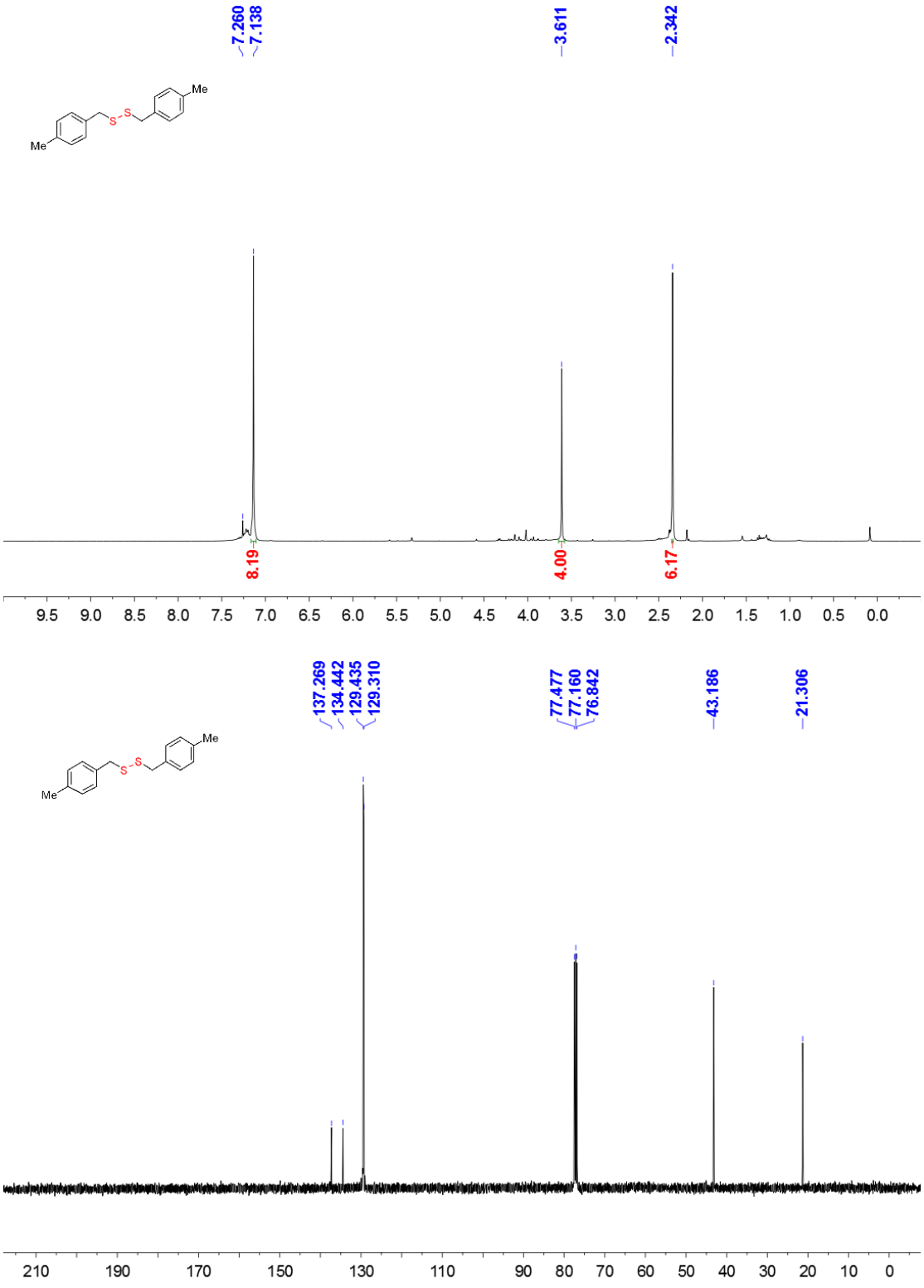
**1,2-bis(2-iodobenzyl)disulfane (7g)**



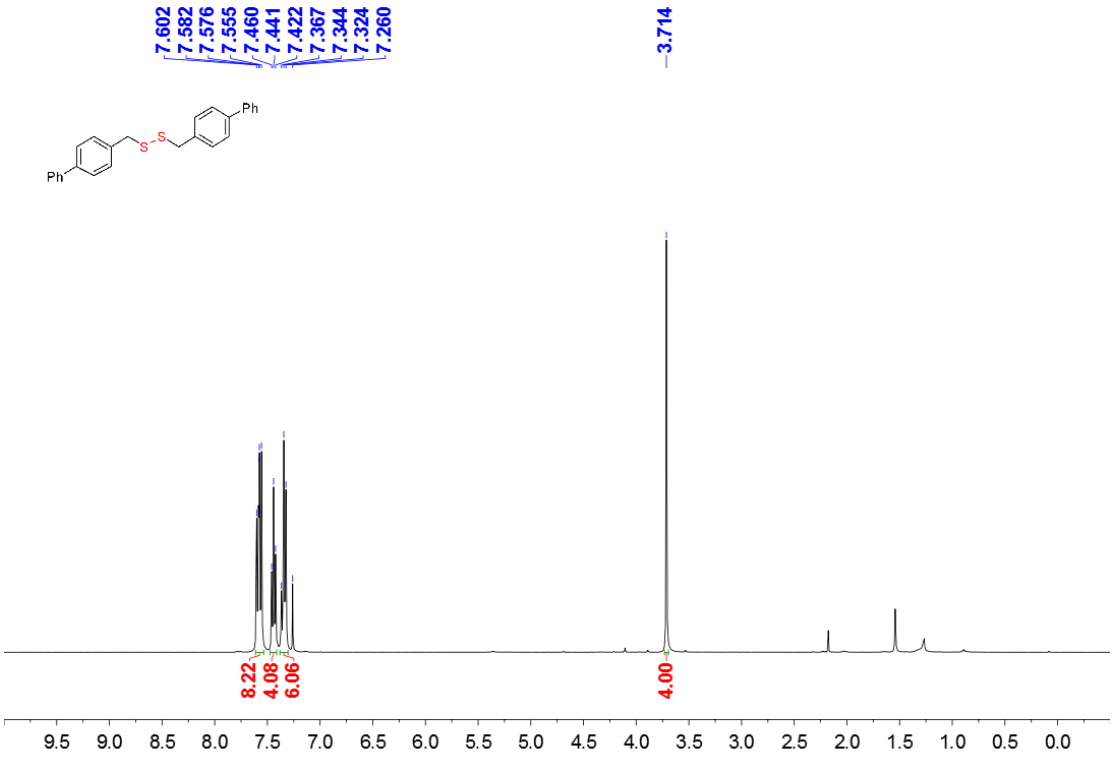
**1,2-bis(2,6-dichlorobenzyl)disulfane (7h)**

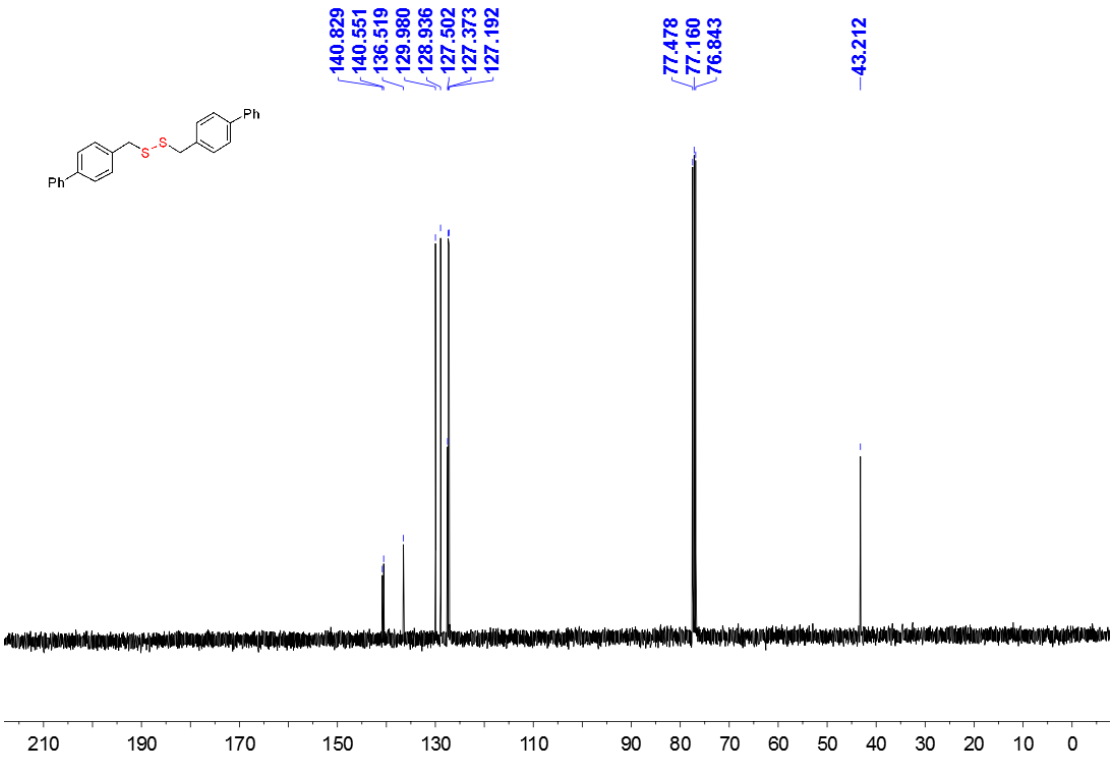


**1,2-bis(4-methylbenzyl)disulfane (7i)**

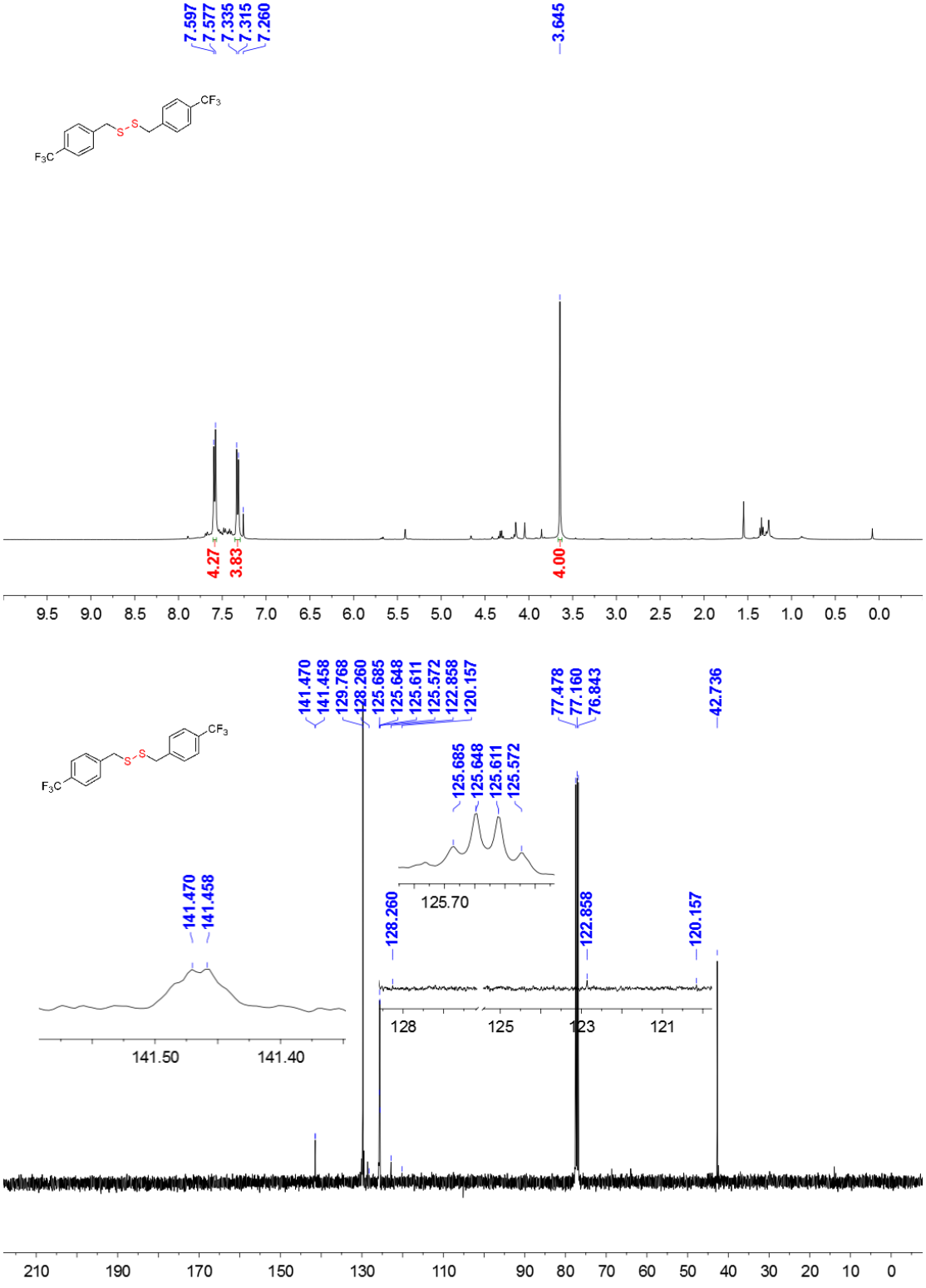


**1,2-bis([1,1'-biphenyl]-4-ylmethyl)disulfane (7j)**

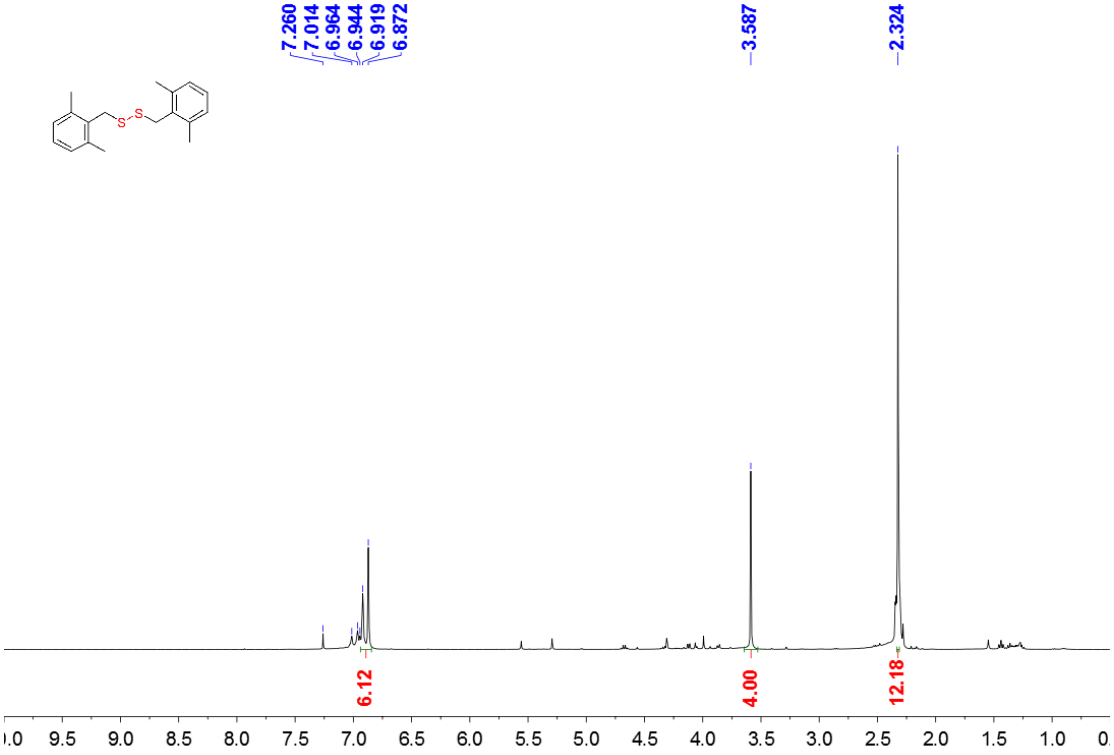


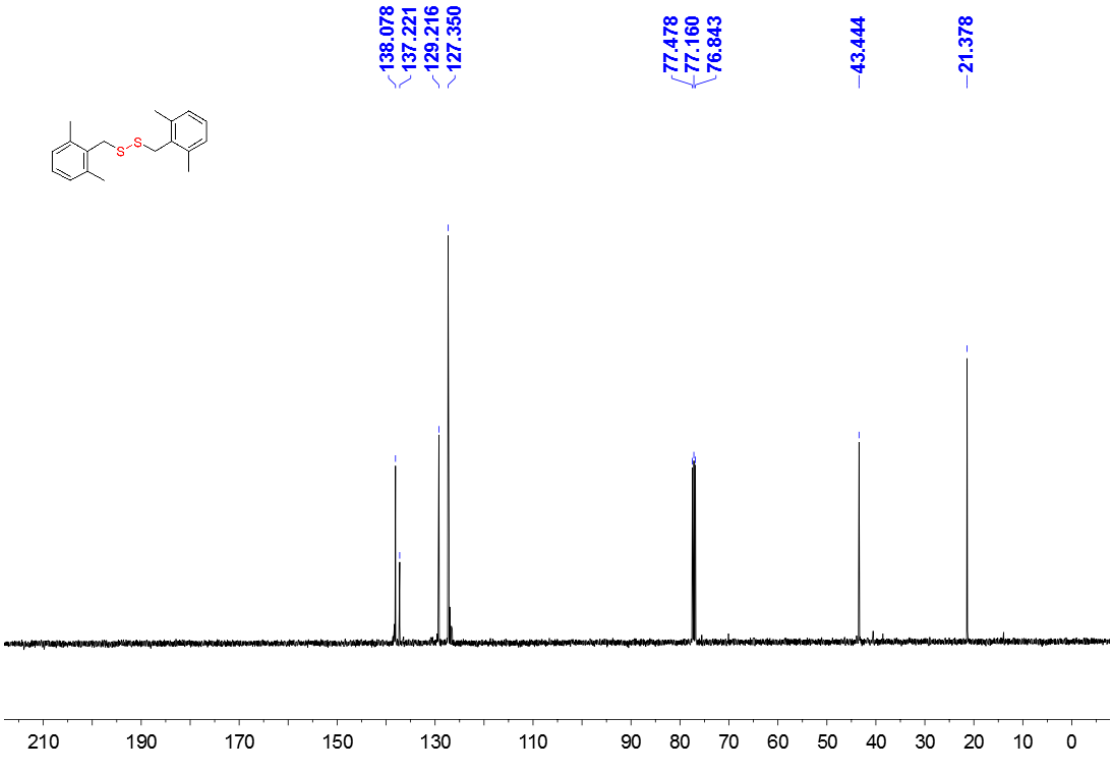



**1,2-bis([1,1'-biphenyl]-4-ylmethyl)disulfane (7k)**

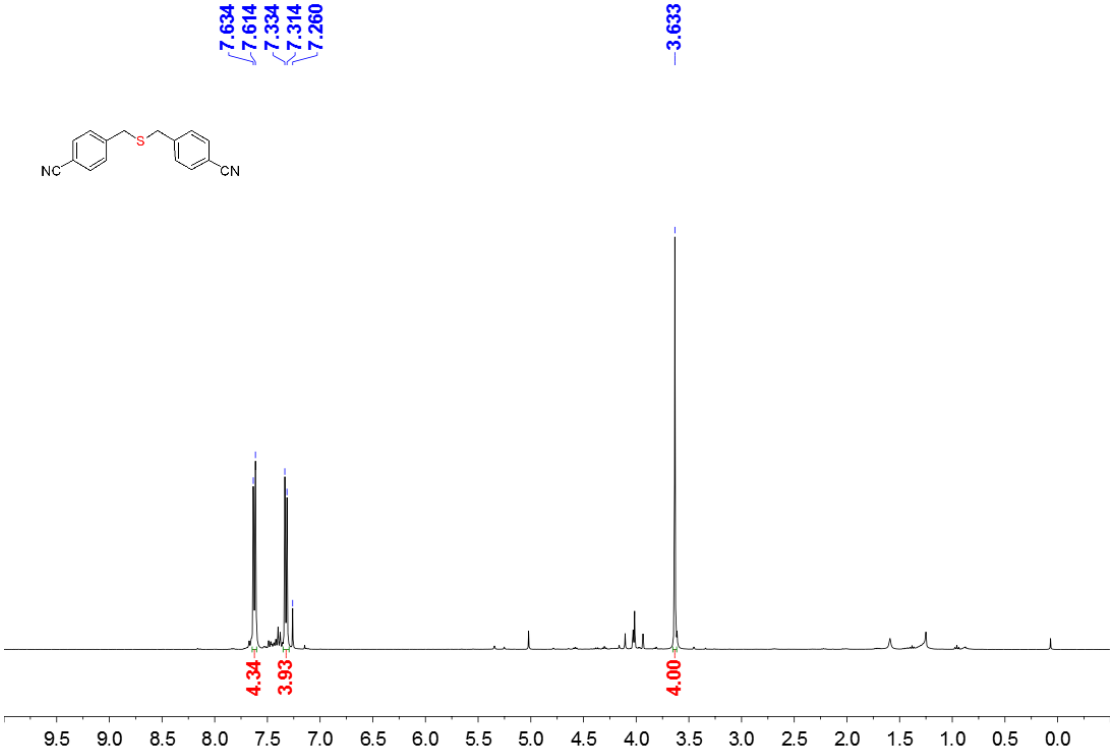


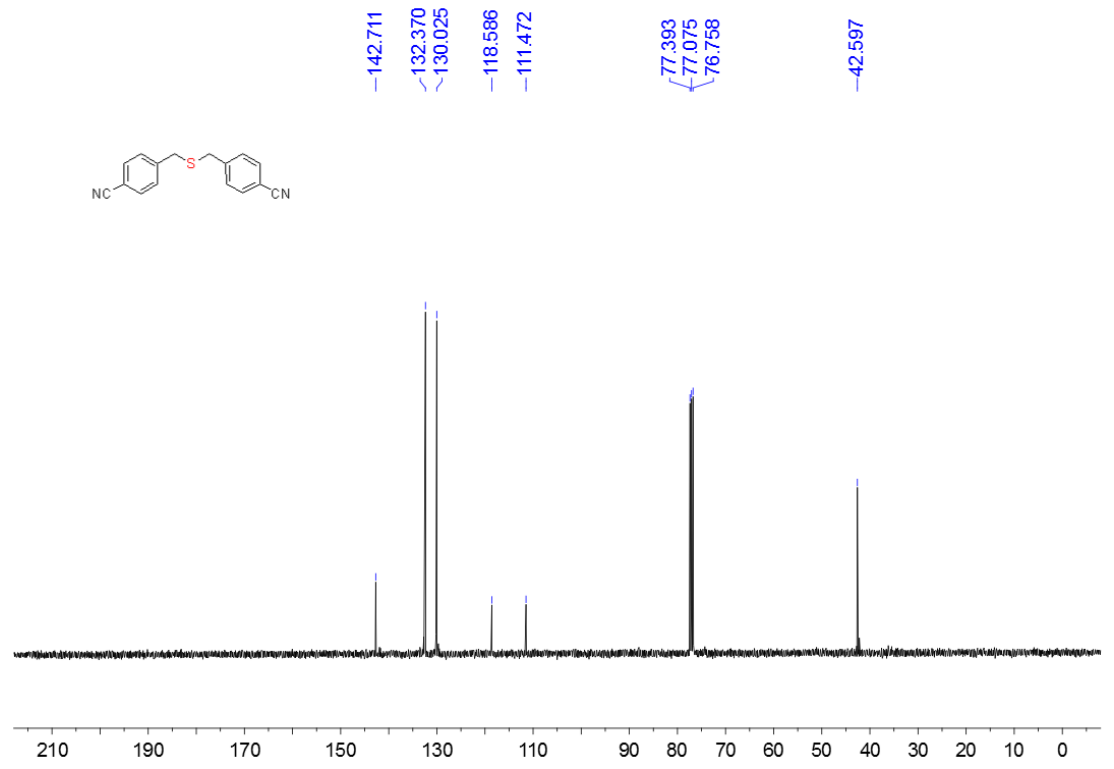
**1,2-bis(2,6-dimethylbenzyl)disulfane (7l)**



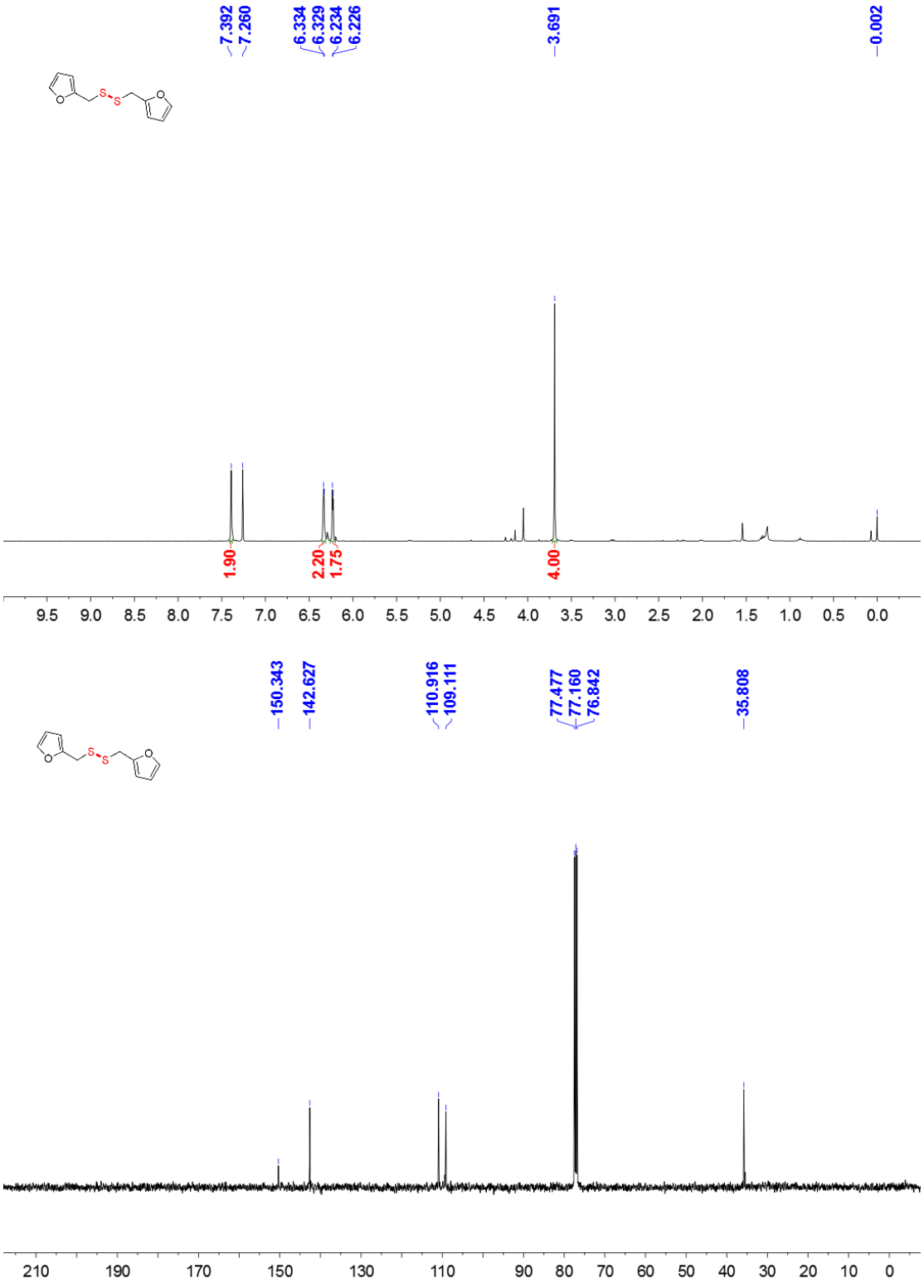



**4,4'-(thiobis(methylene))dibenzonitrile (7m)**

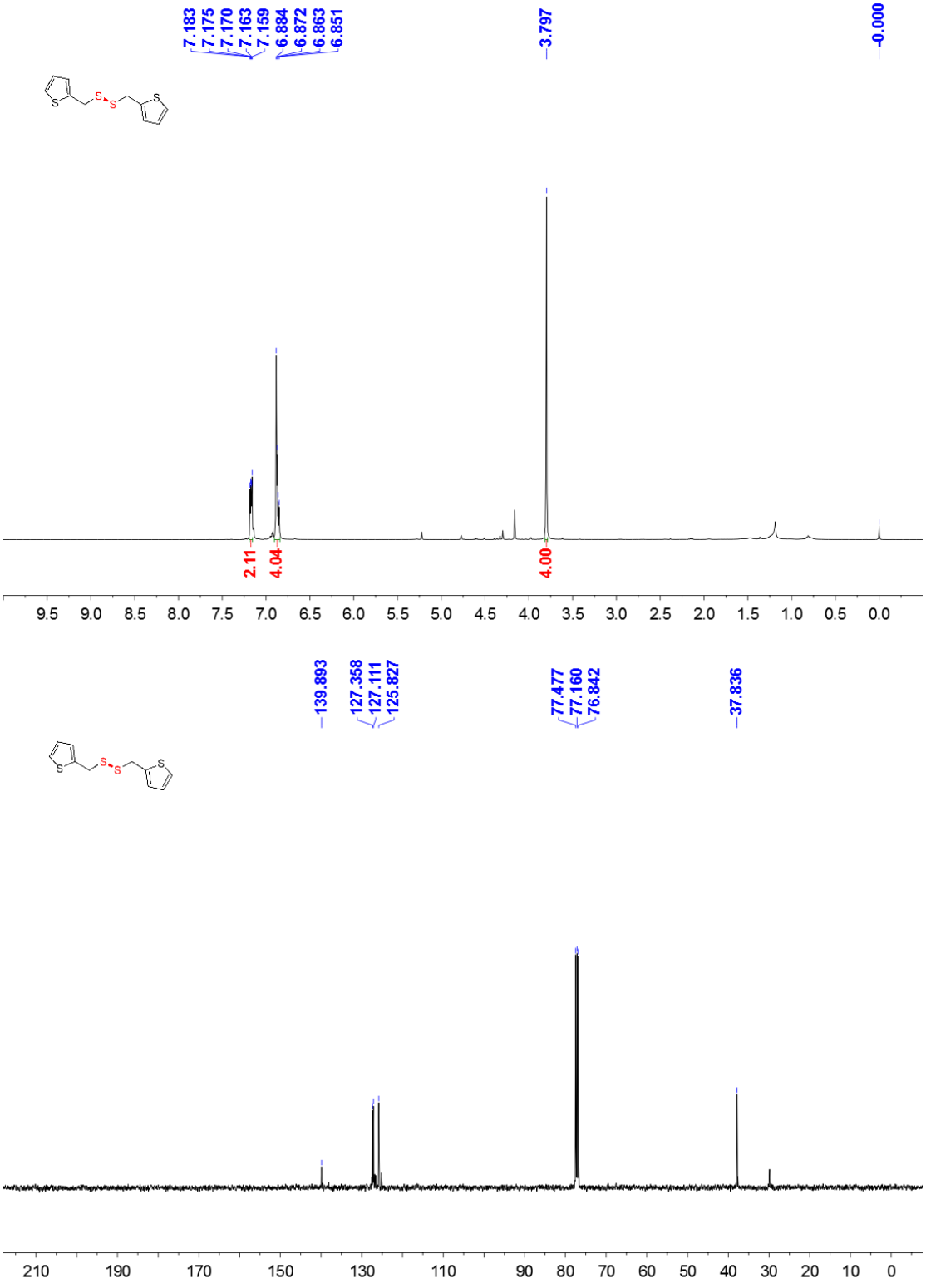


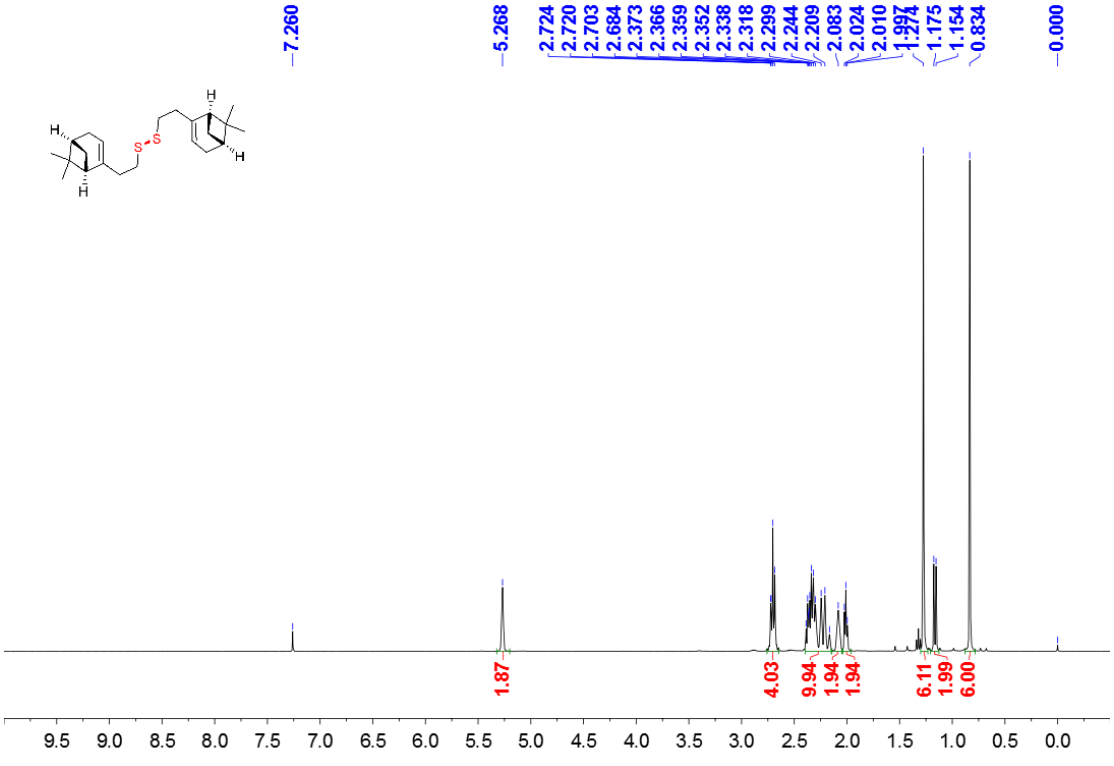
**1,2-bis(furan-2-ylmethyl)disulfane (7n)**

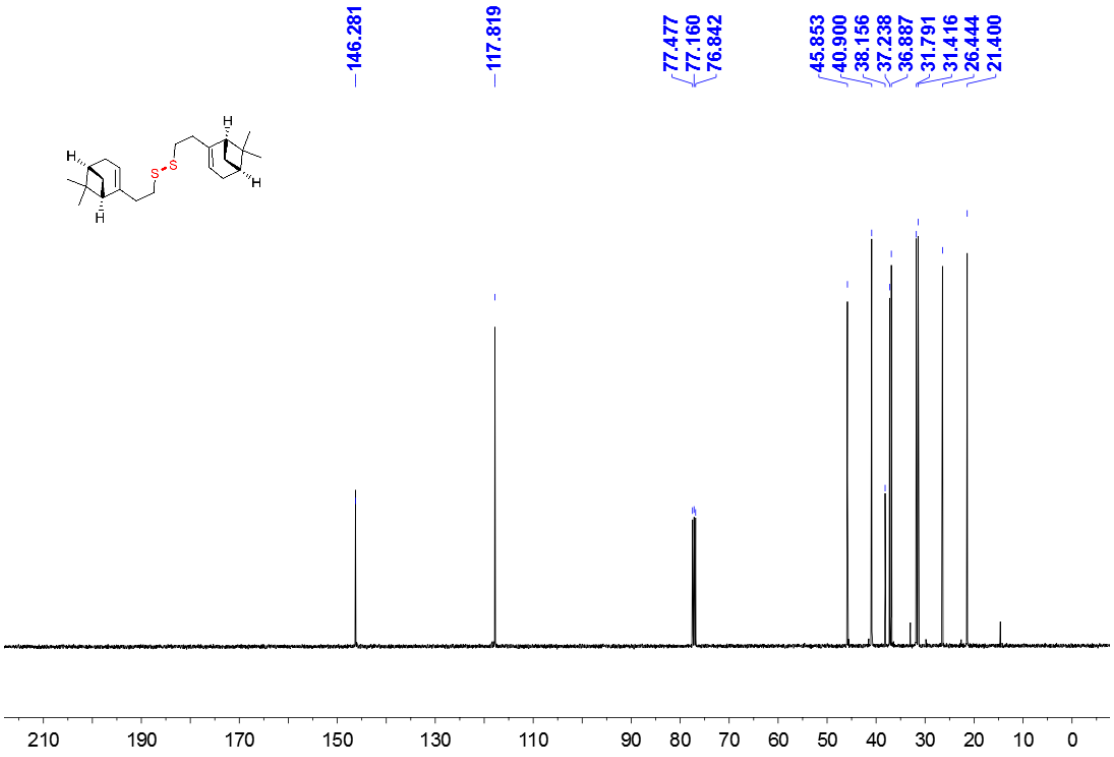


**1,2-bis(thiophen-2-ylmethyl)disulfane (7o)**

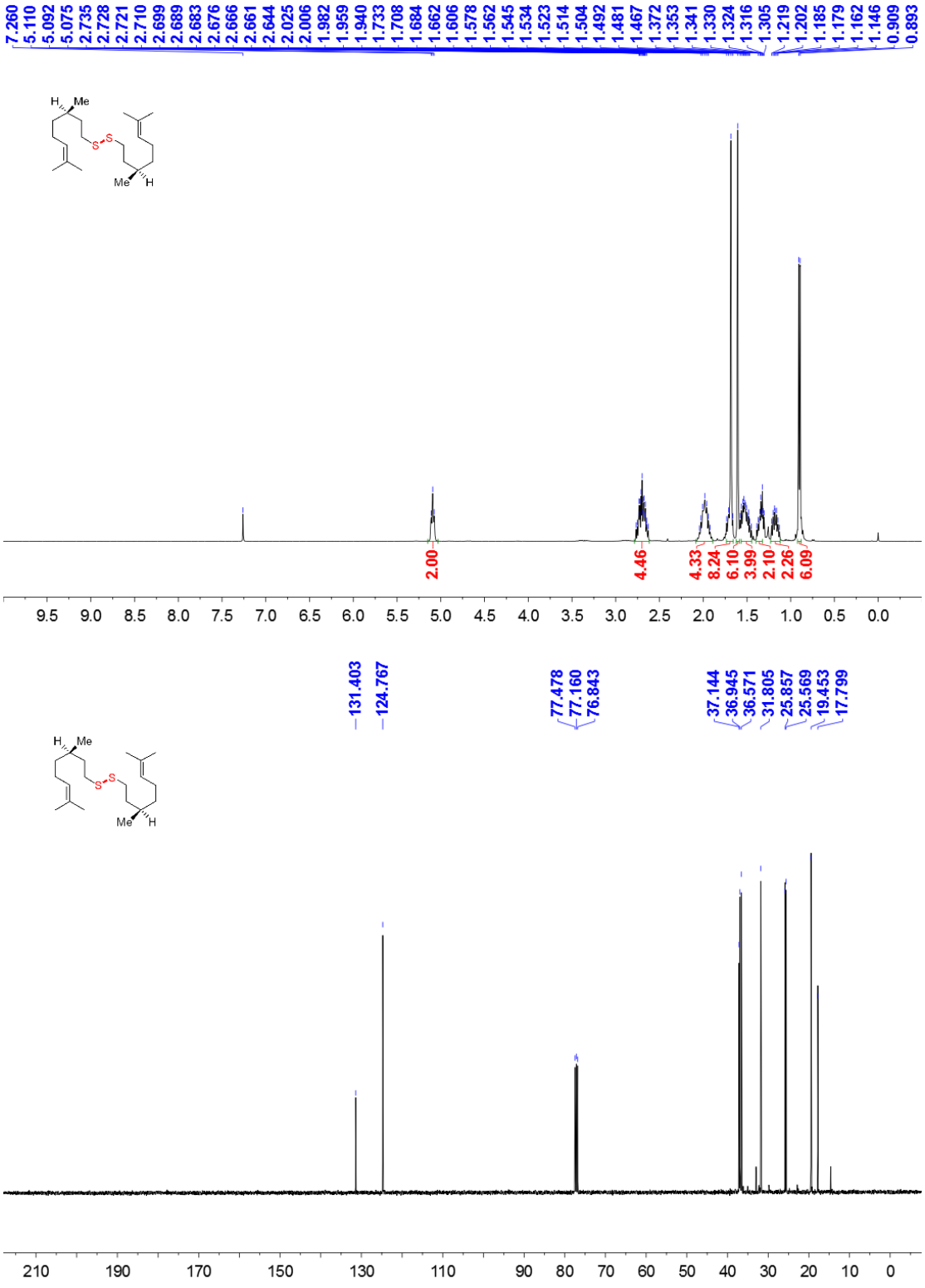


**1,2-bis(2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)disulfane (7p)**

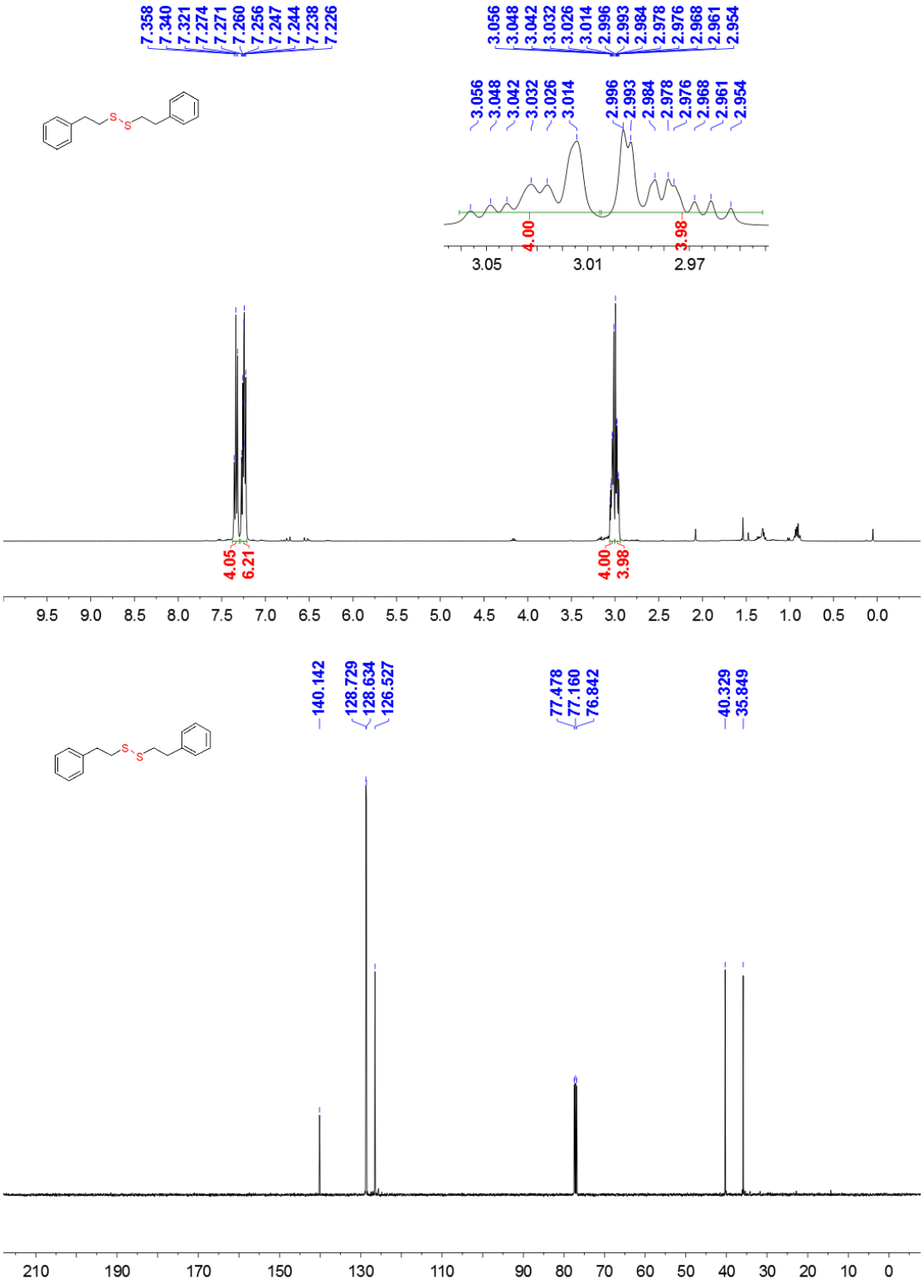


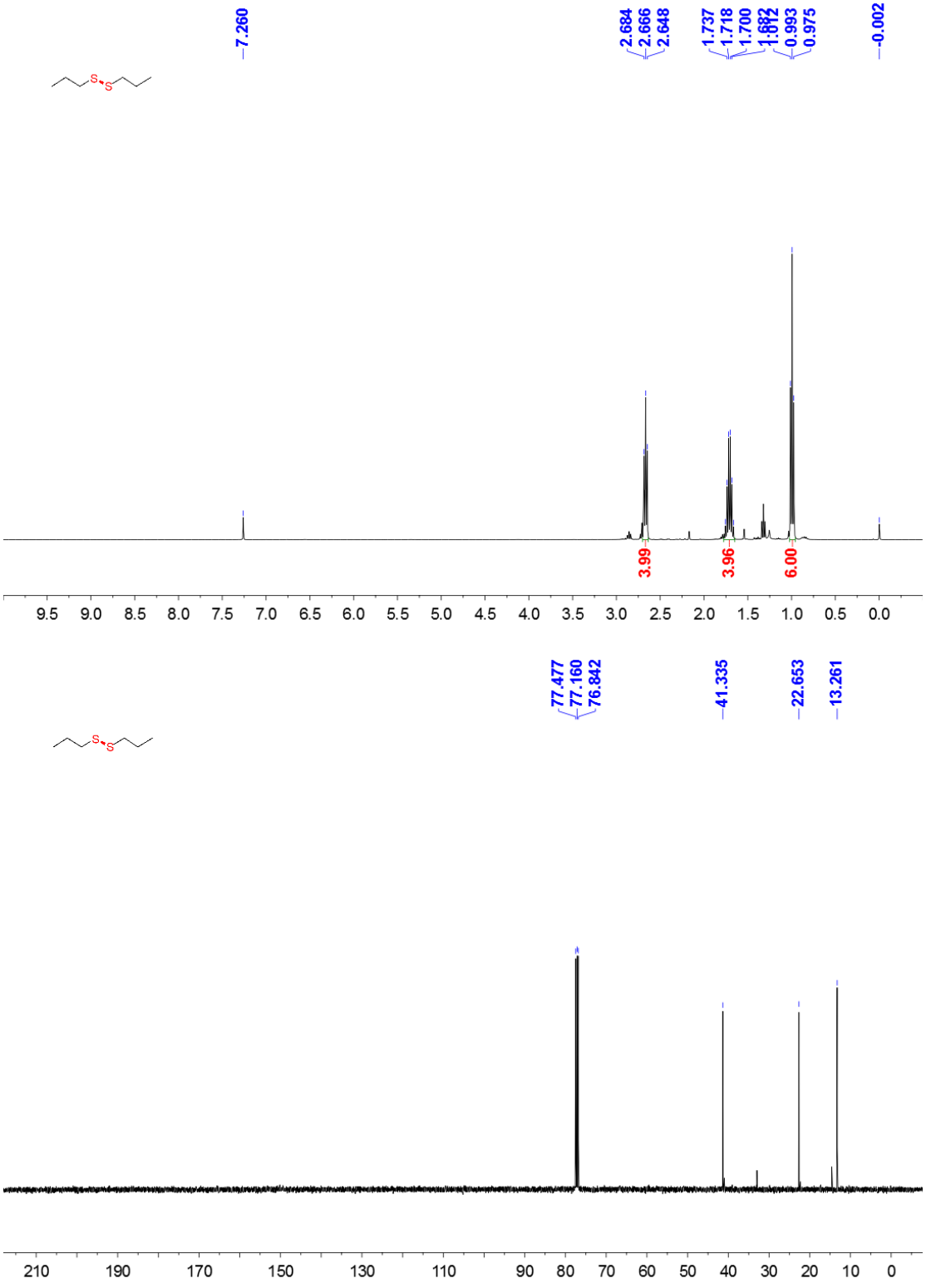
**1,2-bis((R)-3,7-dimethyloct-6-en-1-yl)disulfane (7q)**



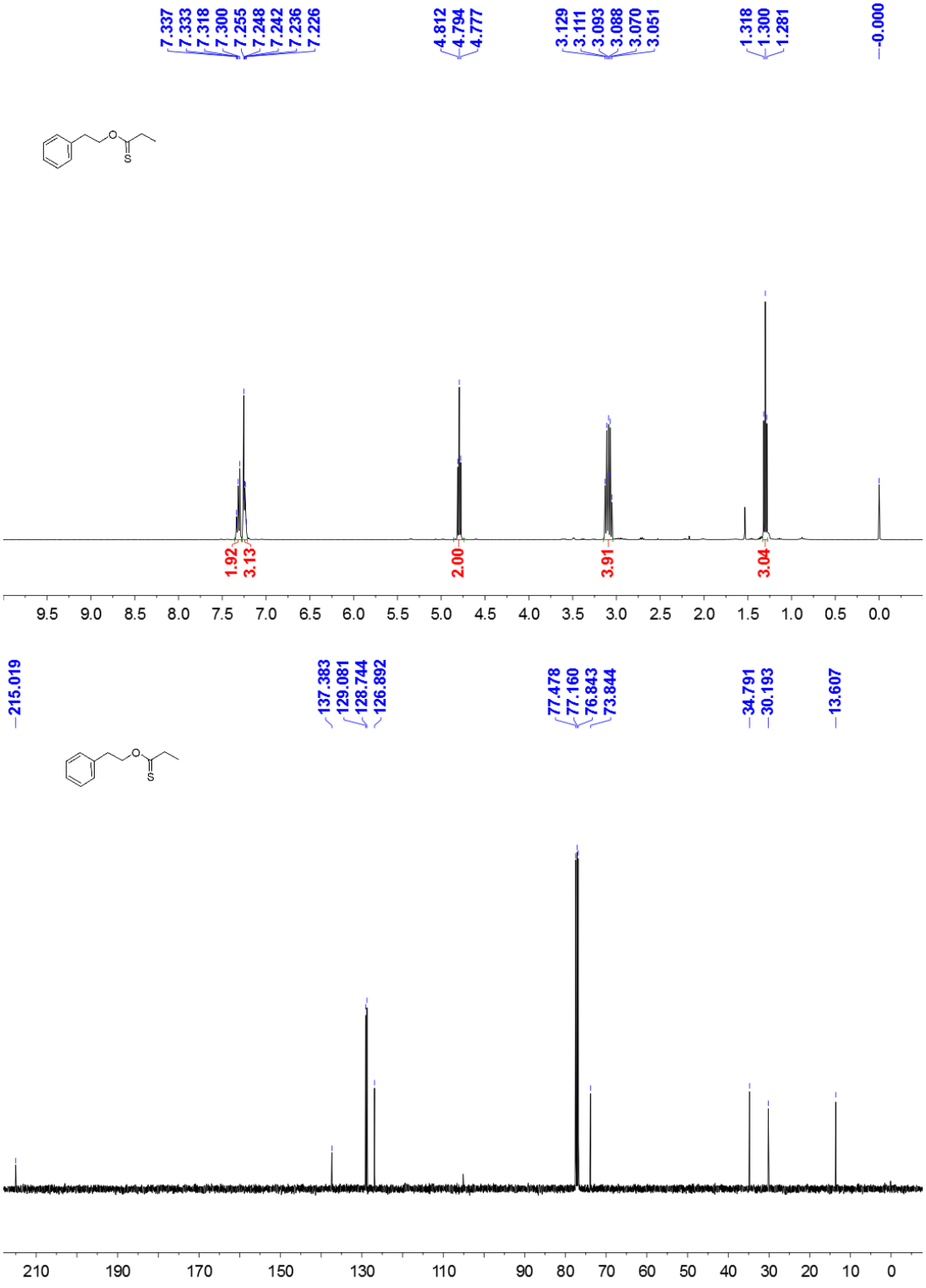
**1,2-diphenethyldisulfane (7r)**



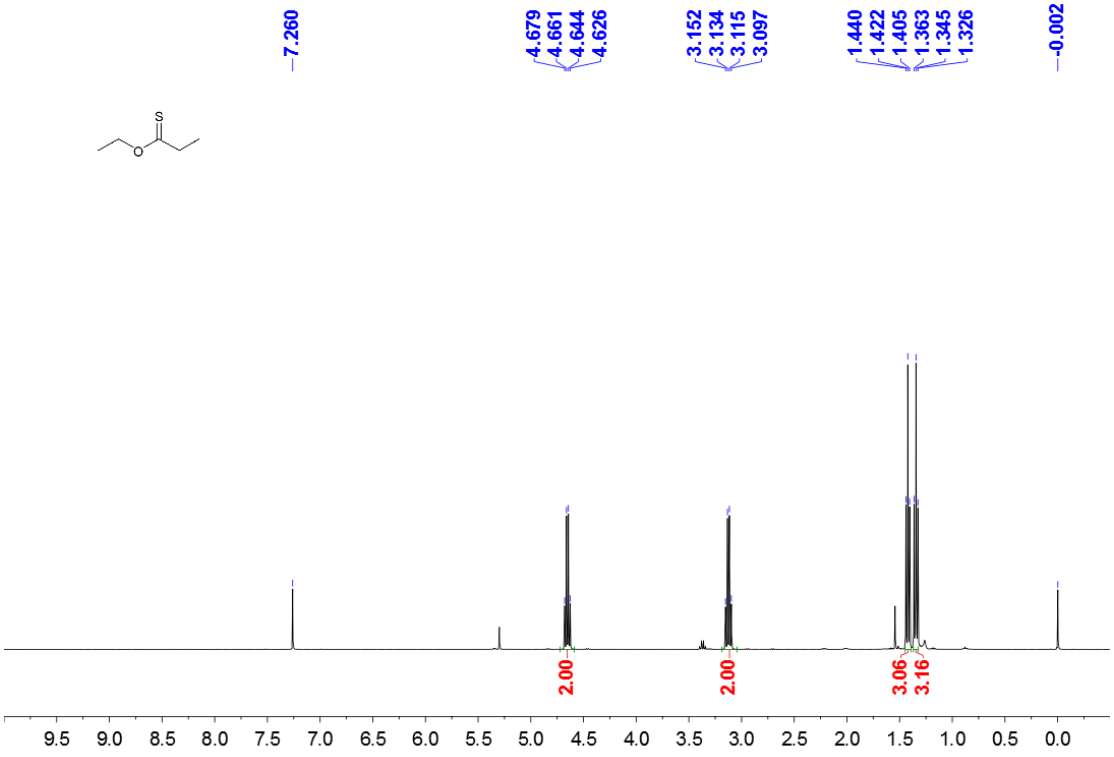
**1,2-dipropyldisulfane (7s)**

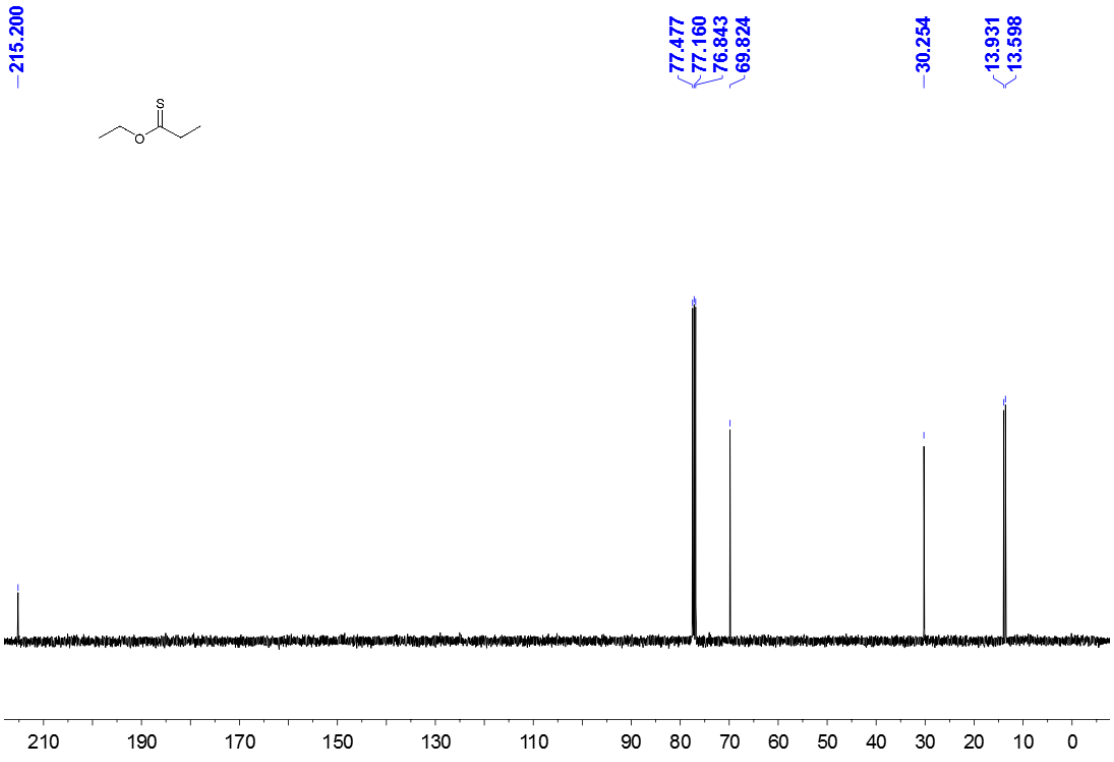


**O-phenethyl propanethioate (14t)**



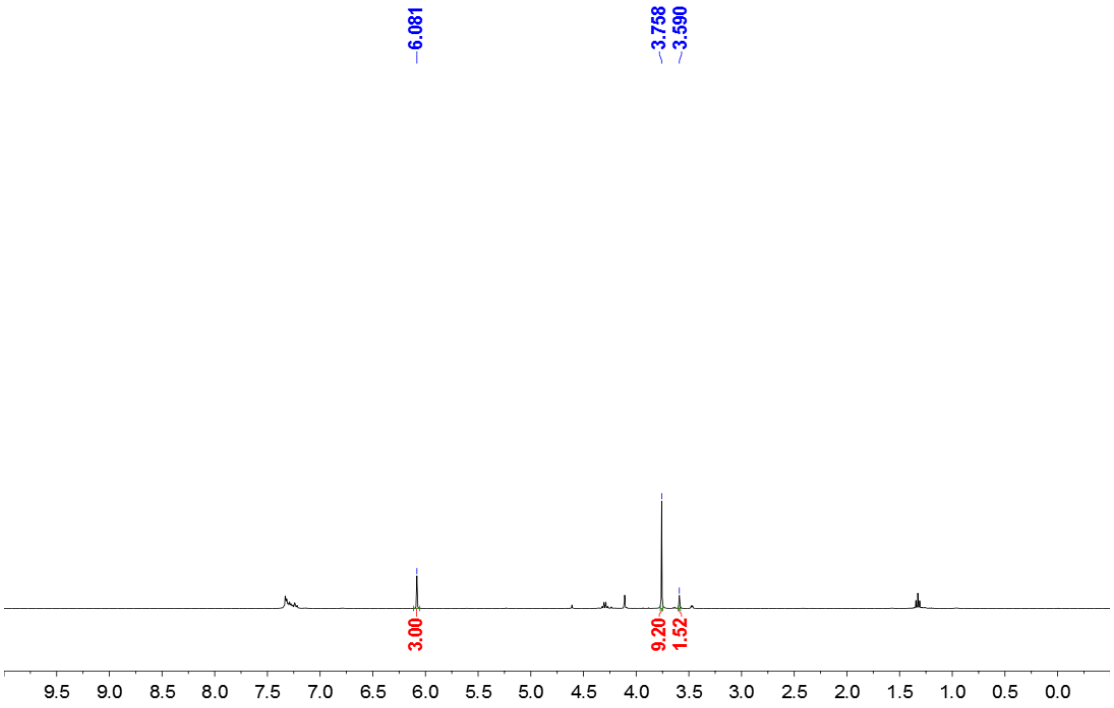
**O-ethyl propanethioate (14u)**



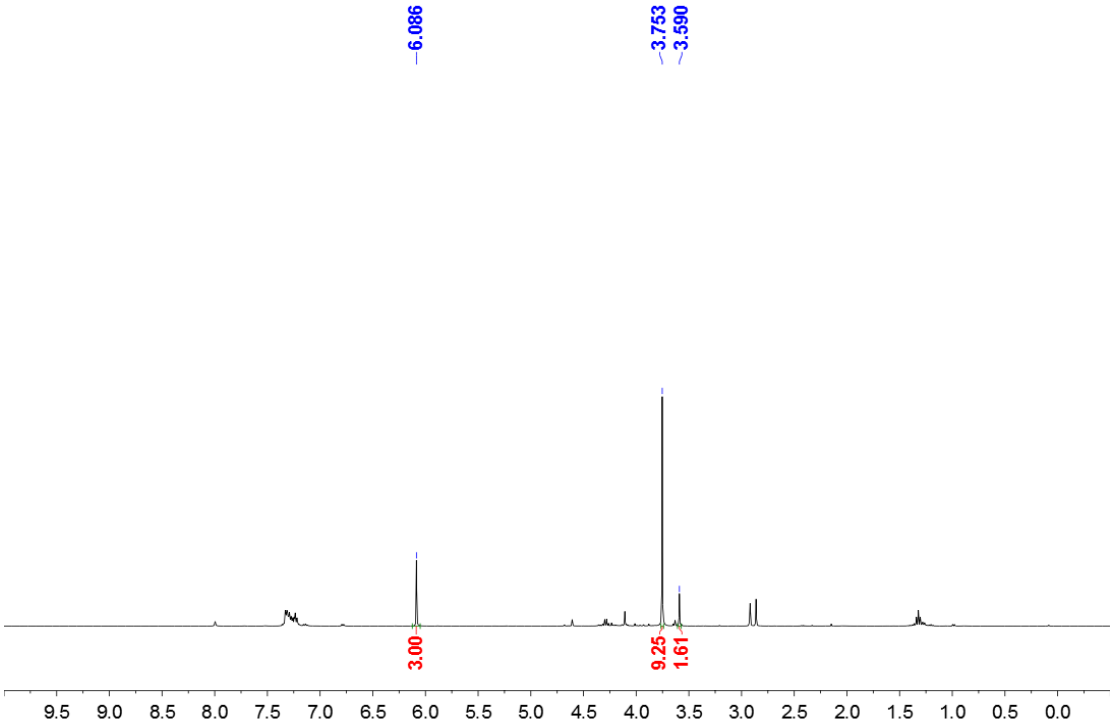



# 3. Copies of $^1$H NMR of crude reaction mixtures in the condition optimization and radical probing experiments

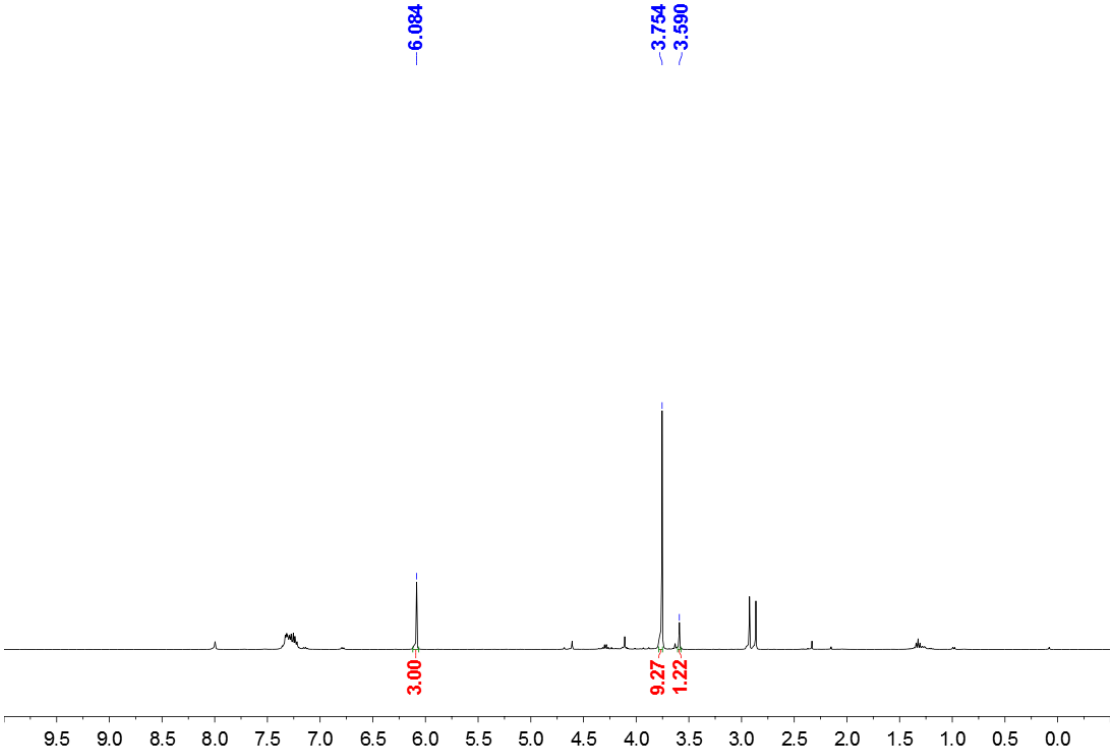
**Entry 1, Table S1:** yield = 1.52/4.00 = 0.38 (38%).



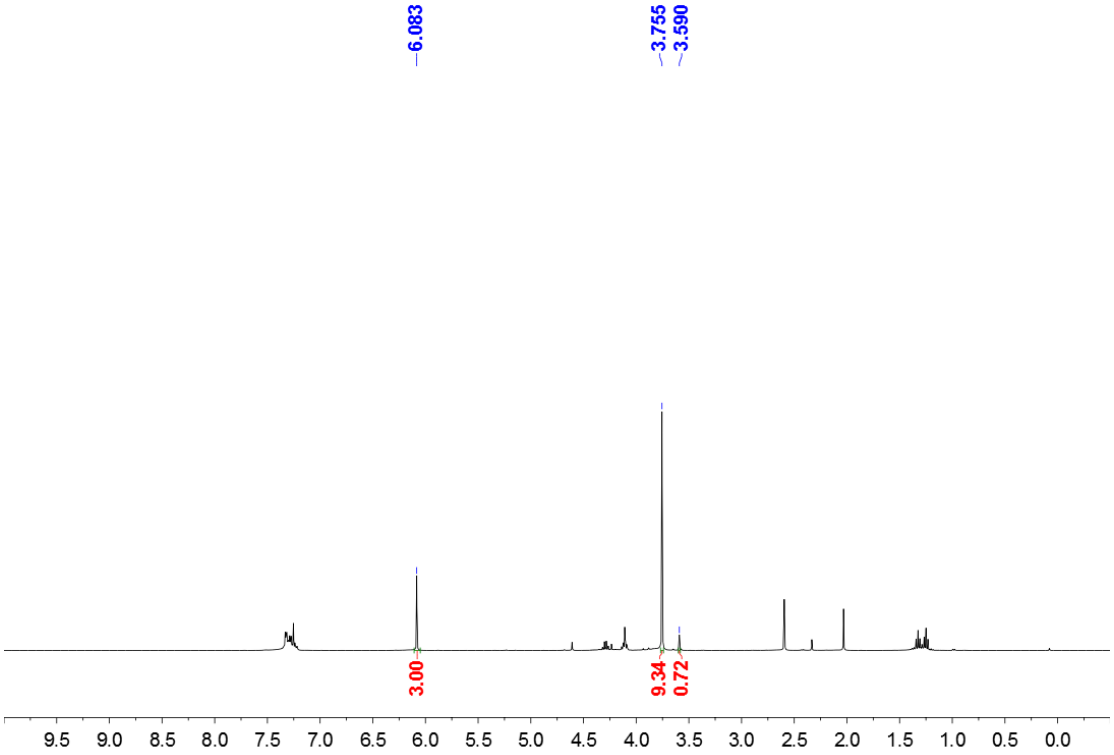

**Entry 2, Table S1:** yield = 1.61/4.00 = 0.40 (40%).



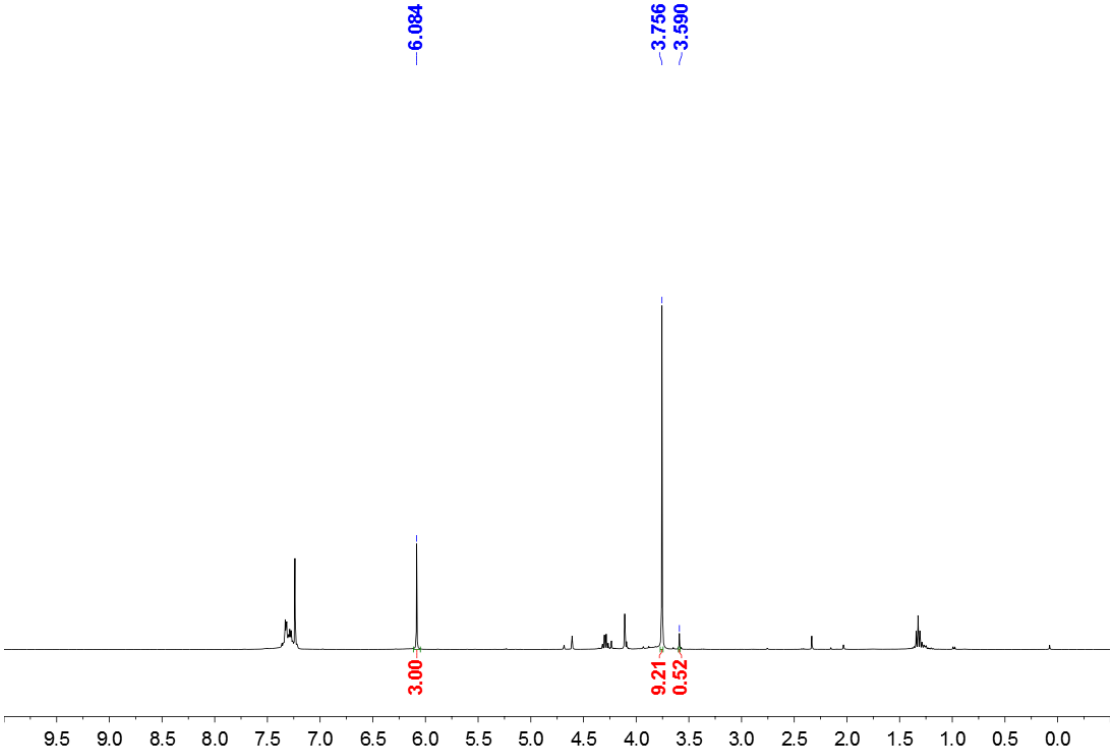
**Entry 3, Table S1:** yield = 1.22/4.00 = 0.30 (30%).



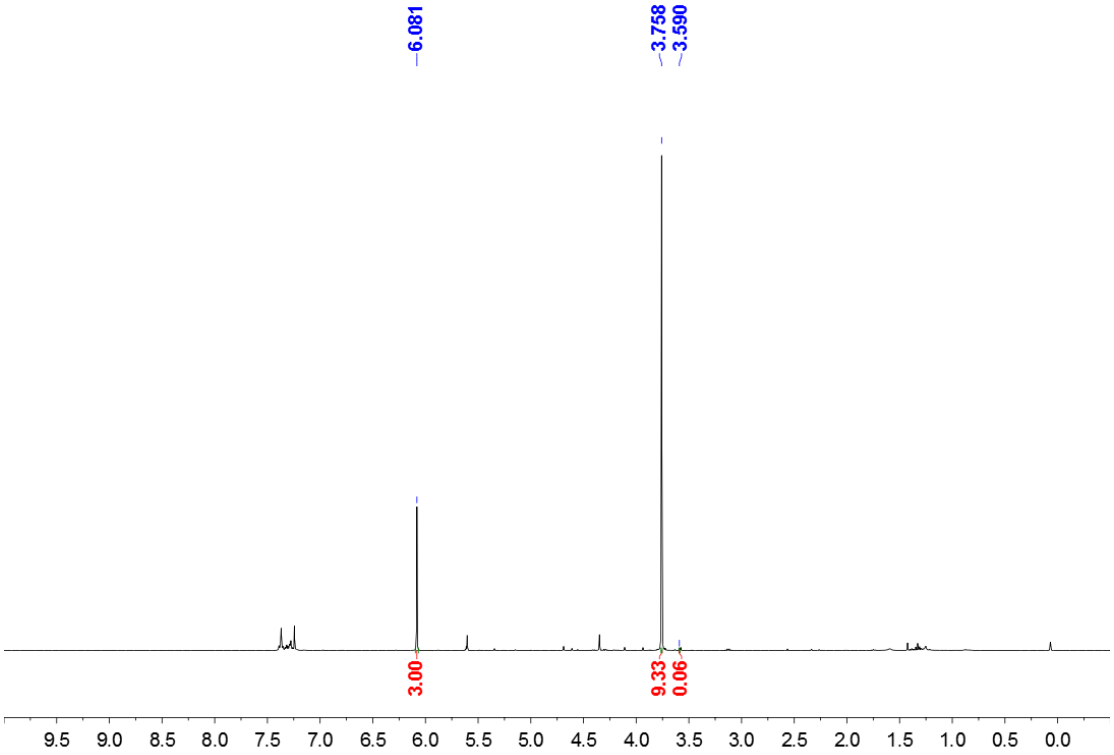

**Entry 4, Table S1:** yield = 0.72/4.00 = 0.18 (18%).



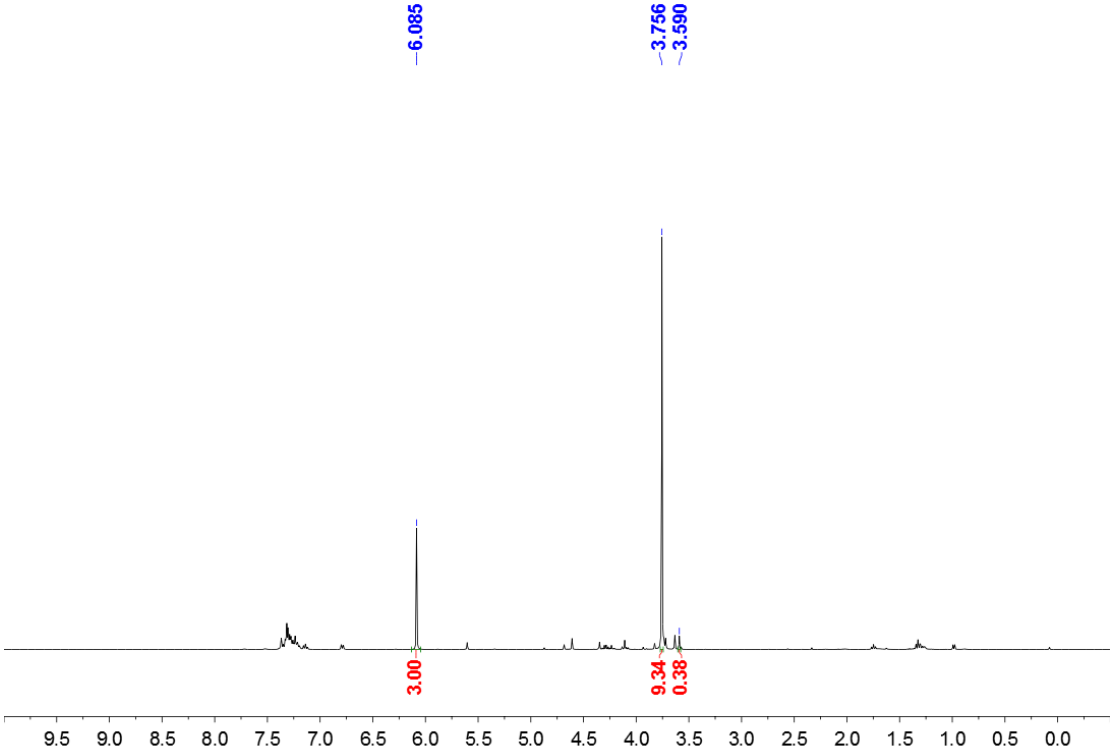
**Entry 5, Table S1:** yield = 0.52/4.00 = 0.13 (13%).



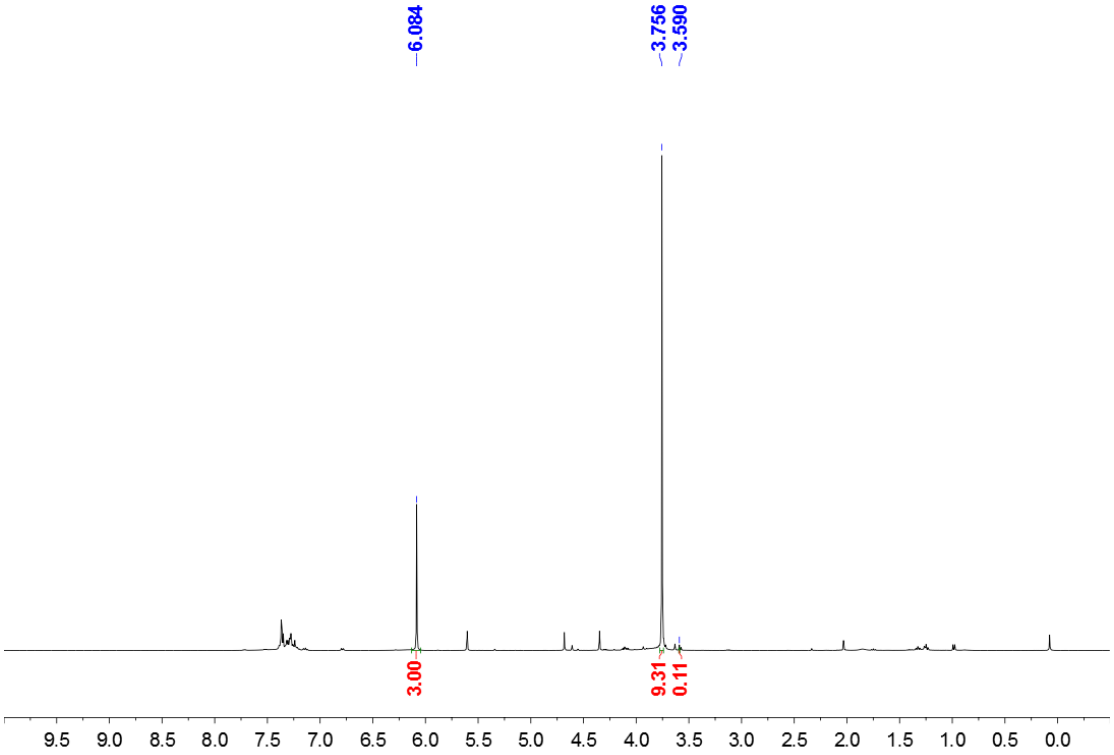

**Entry 6, Table S1:** yield = 0.06/4.00 = 0.02 (2%, trace).



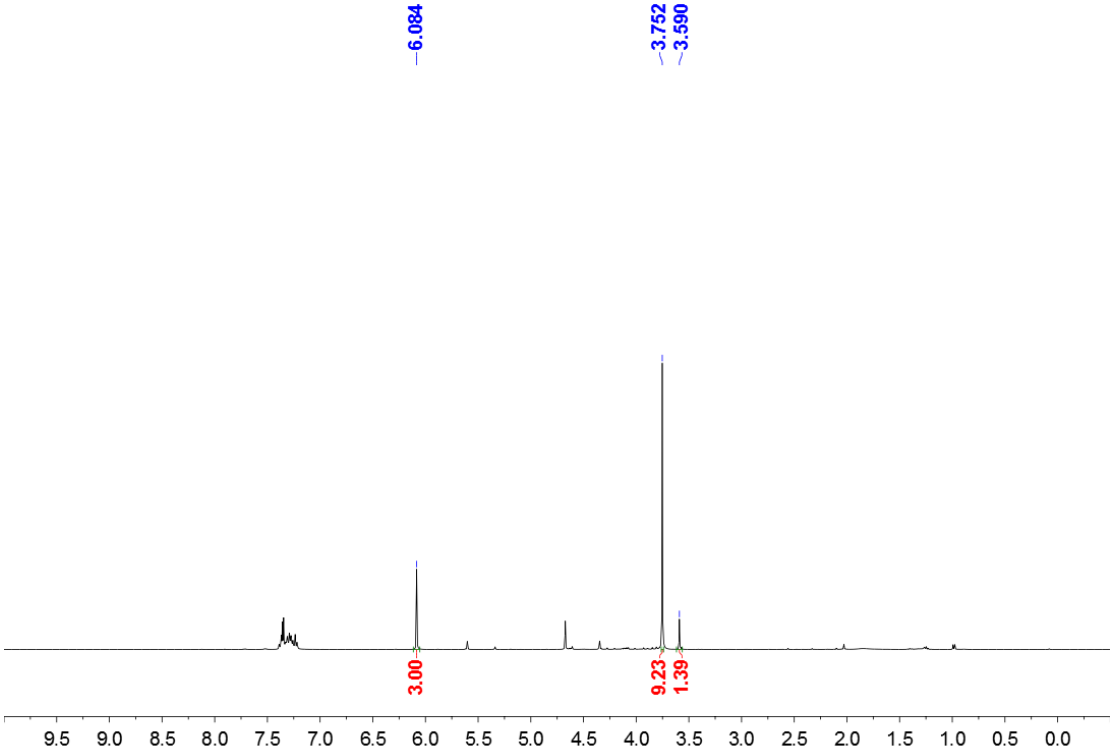
**Entry 8, Table S1:** yield = 0.38/4.00 = 0.10 (10%).



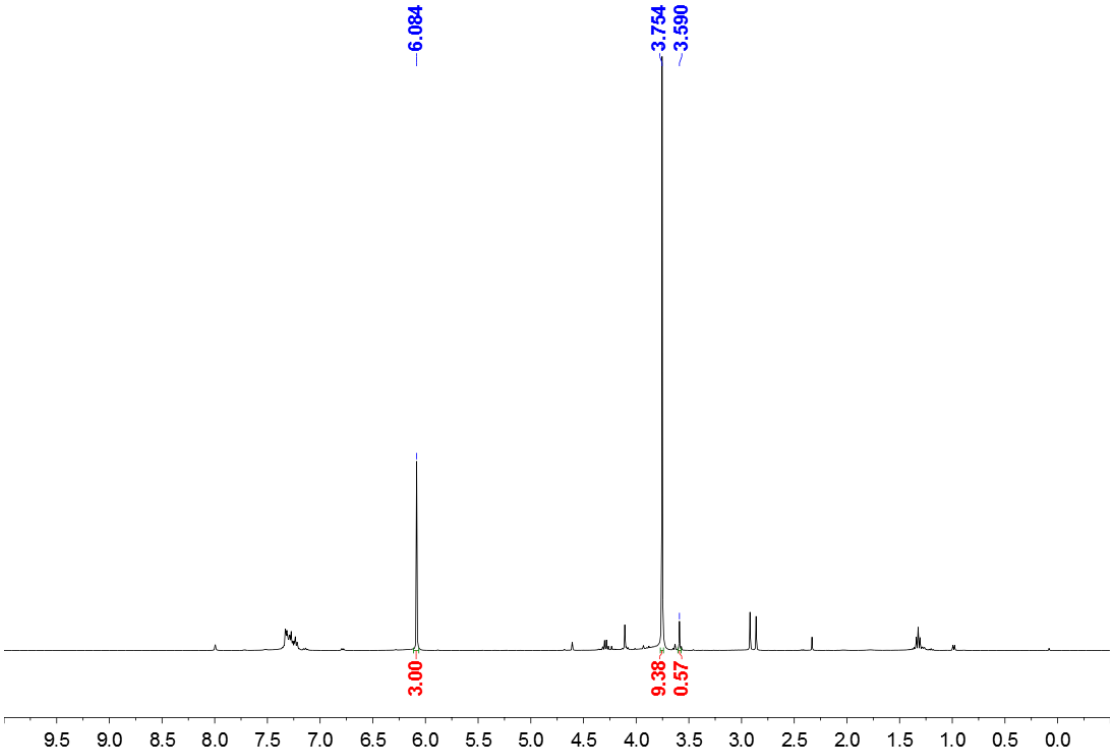

**Entry 9, Table S1:** yield = 0.11/4.00 = 0.03 (3%, trace).



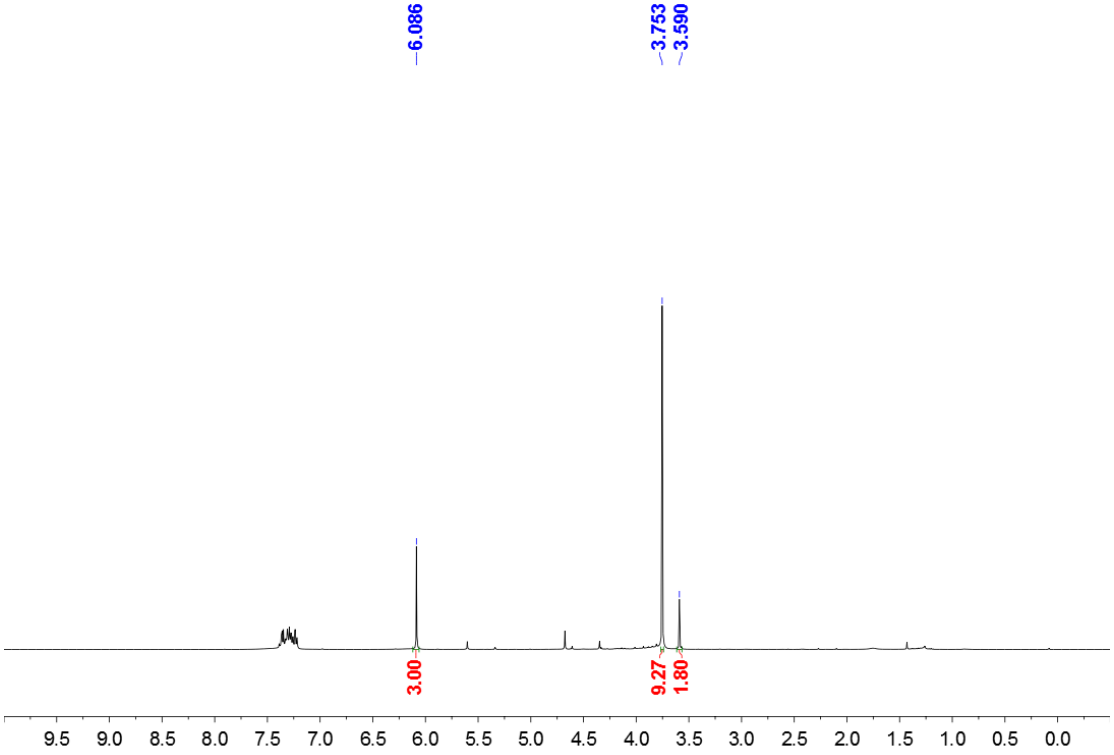
**Entry 10, Table S1:** yield = 1.39/4.00 = 0.35 (35%).



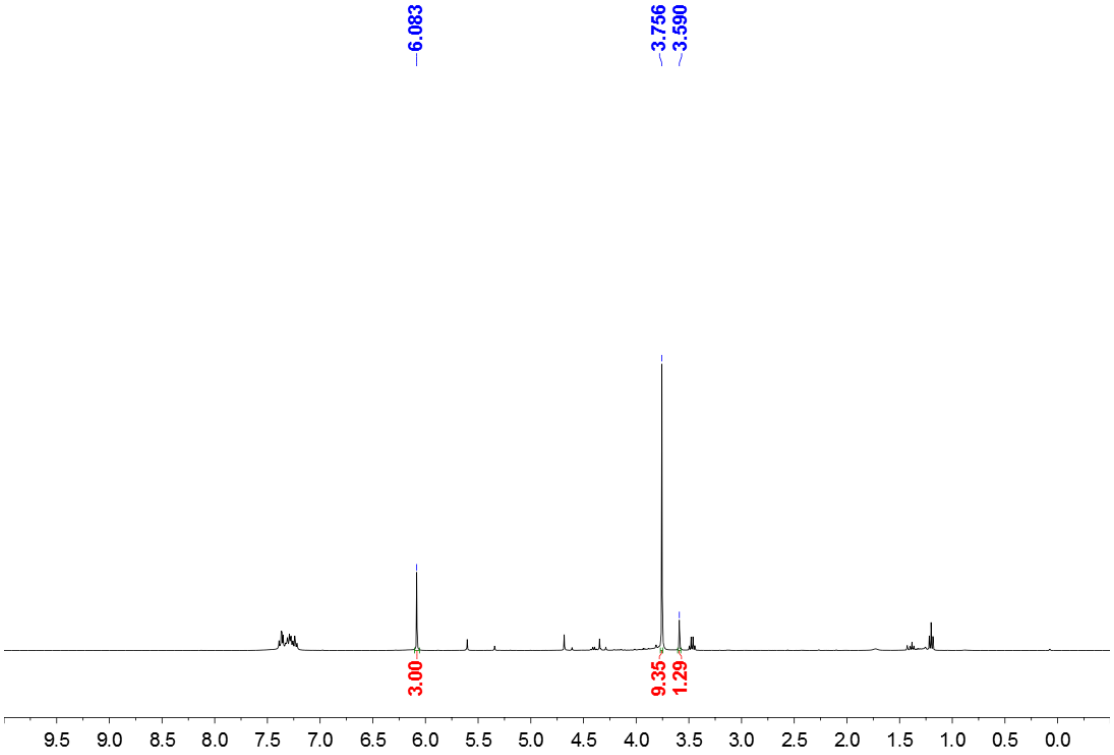

**Entry 12, Table S1:** yield = 0.57/4.00 = 0.14 (14%).



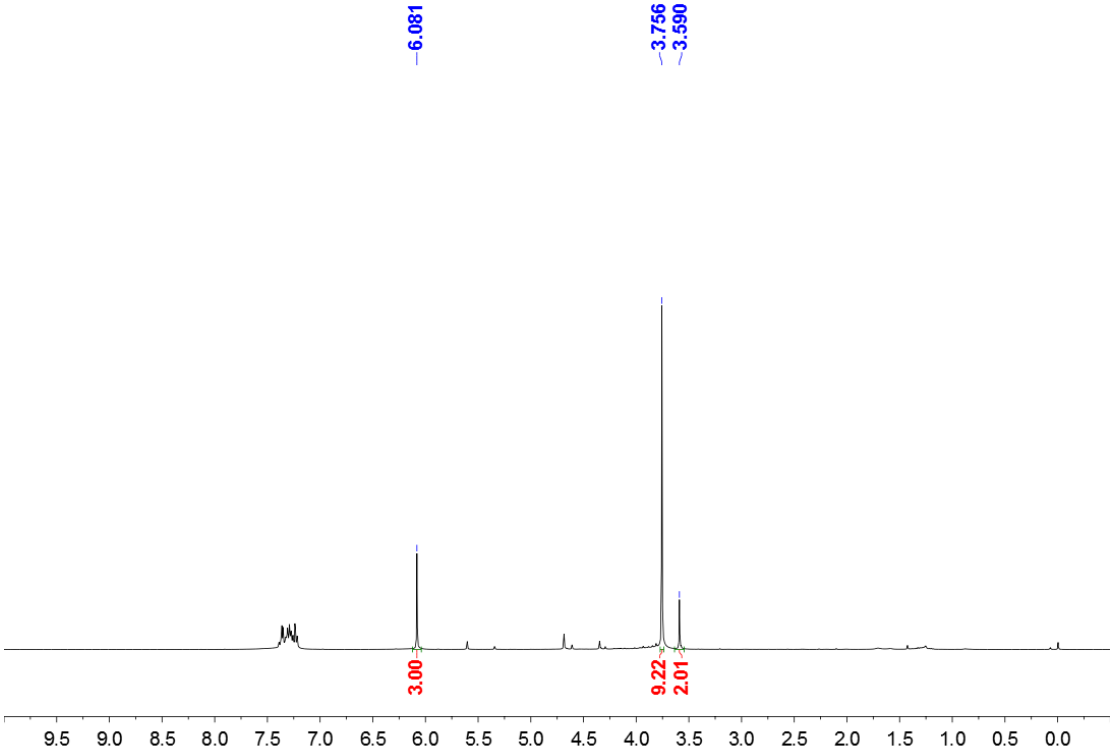
**Entry 13, Table S1:** yield = 1.80/4.00 = 0.45 (45%).



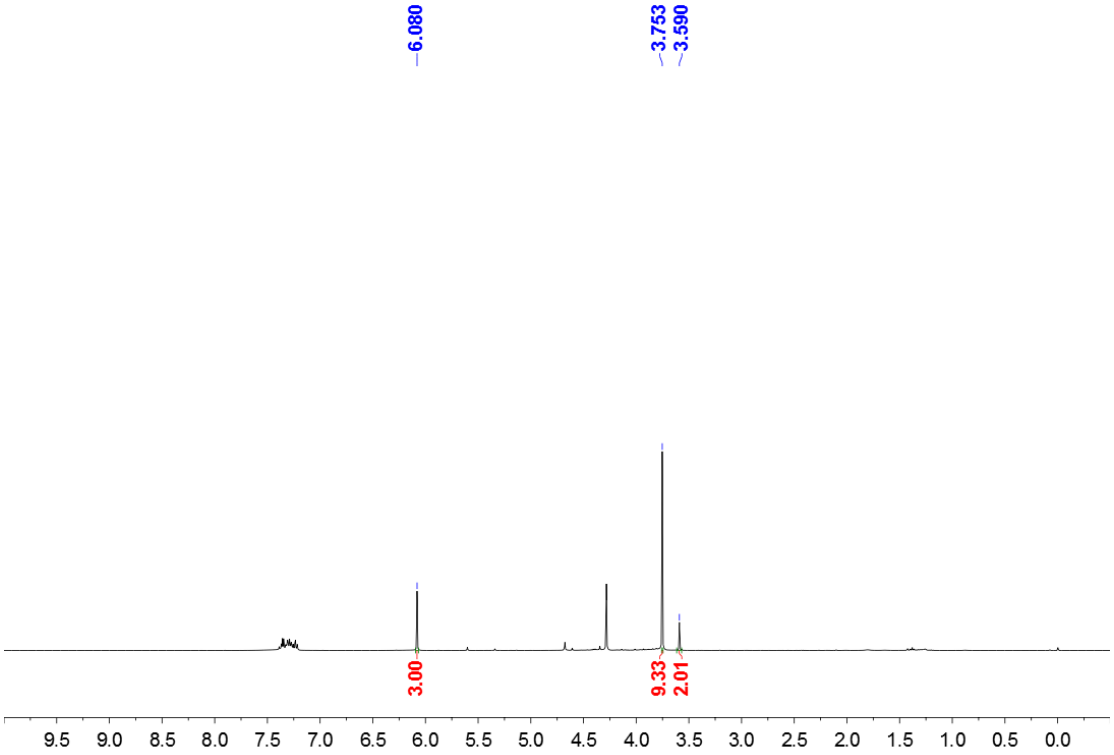

**Entry 14, Table S1:** yield = 1.29/4.00 = 0.32 (32%).



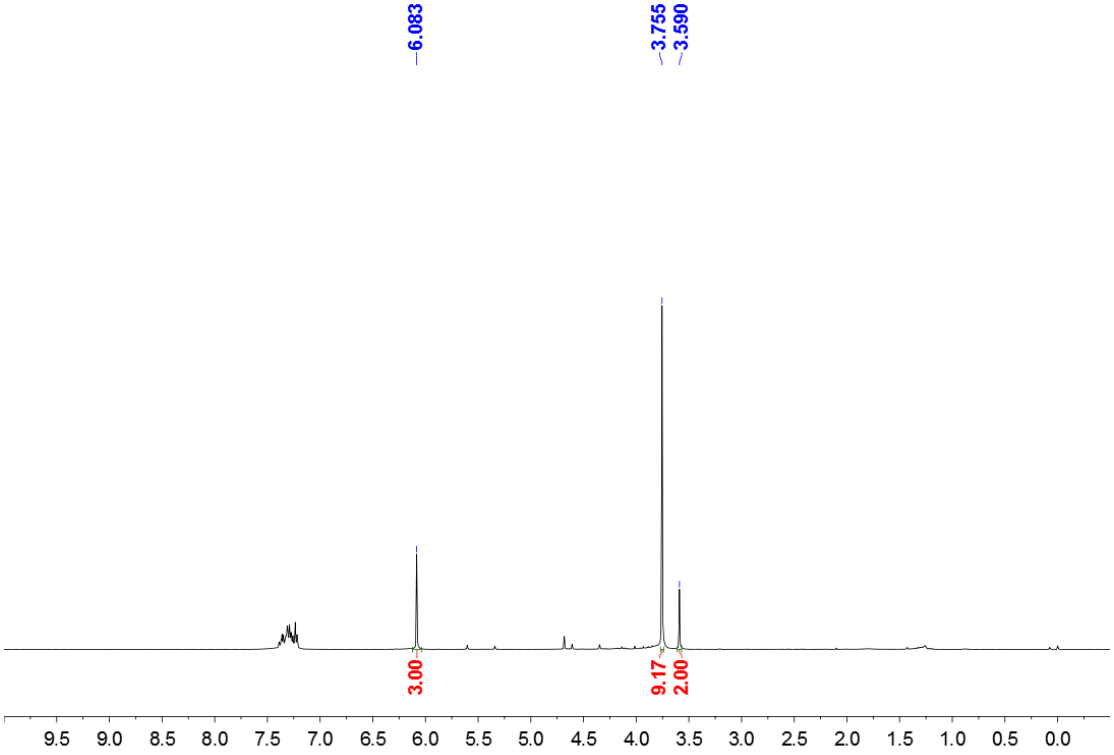
**Entry 15, Table S1:** yield = 2.01/4.00 = 0.50 (50%).



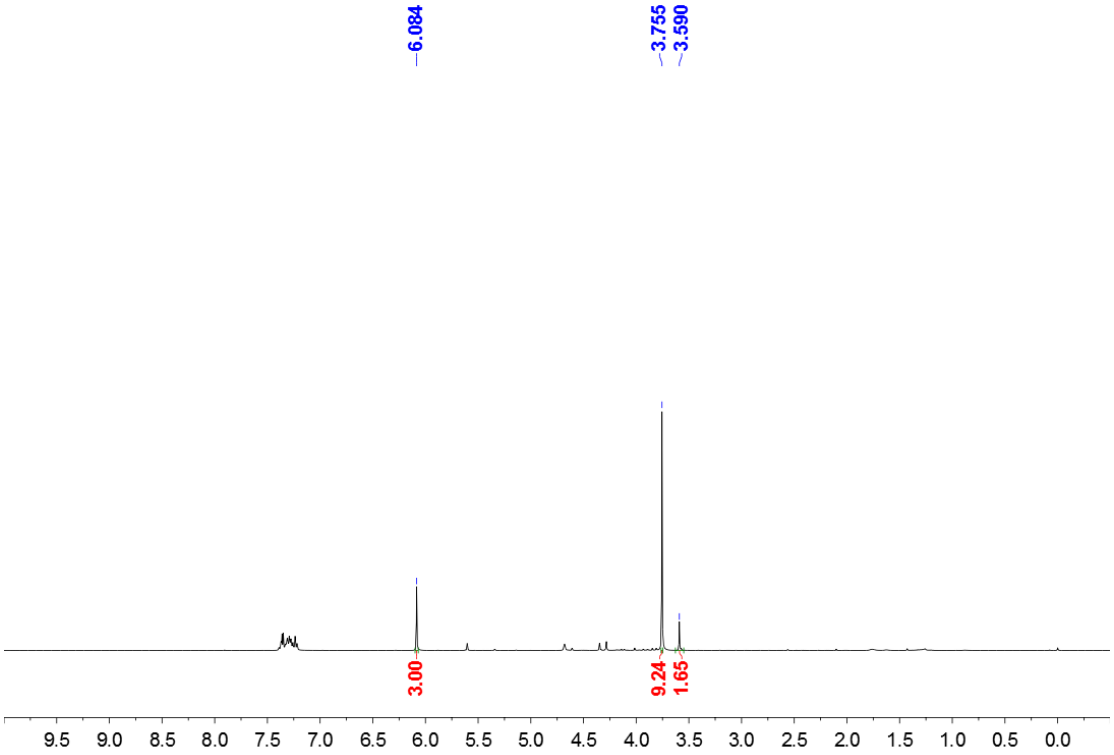

**Entry 16, Table S1:** yield = 2.01/4.00 = 0.50 (50%).



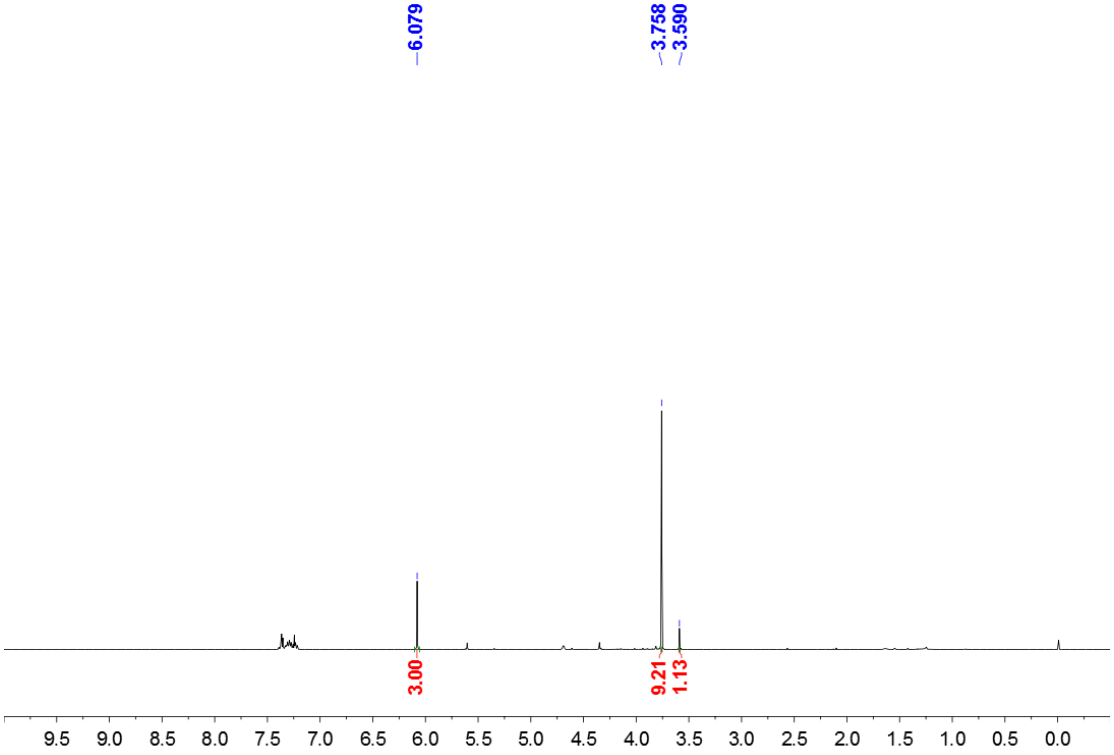
**Entry 17, Table S1:** yield = 2.00/4.00 = 0.50 (50%).



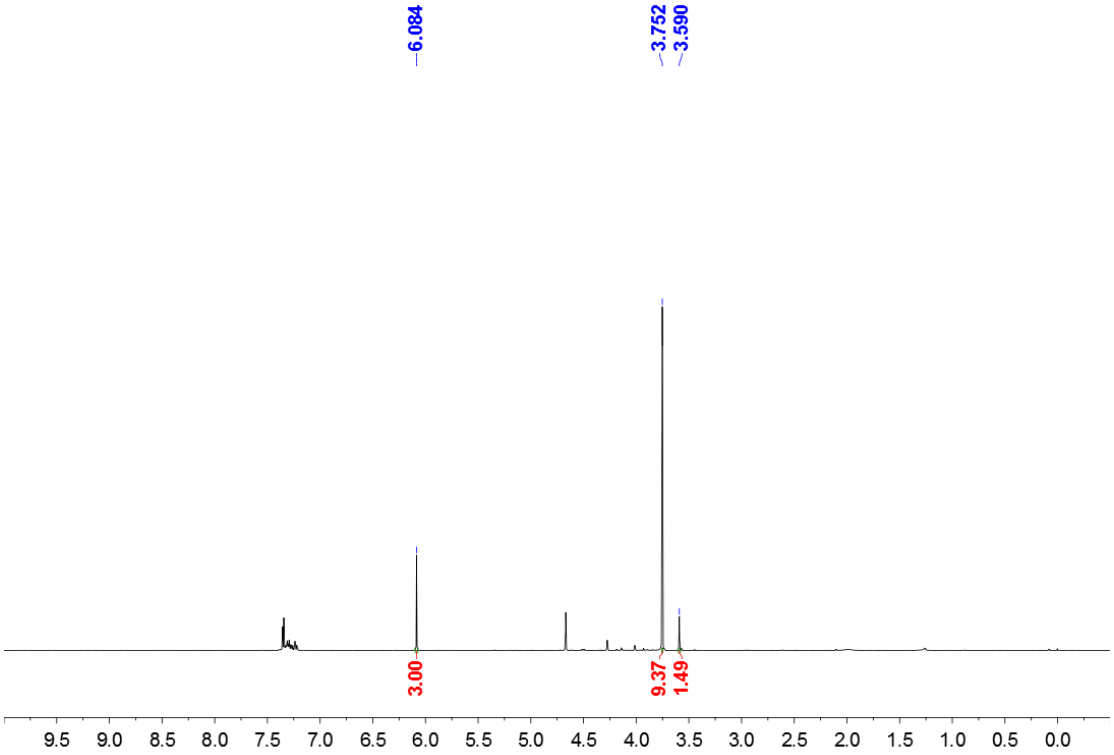

**Entry 18, Table S1:** yield = 1.65/4.00 = 0.41 (41%).



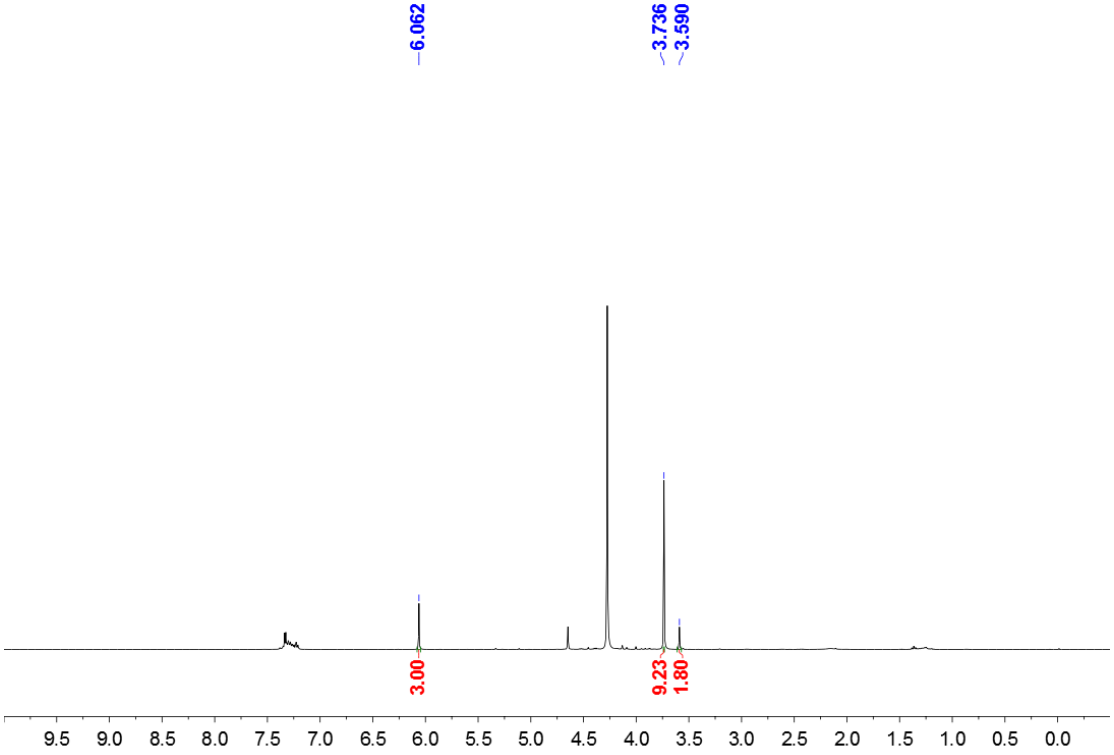
**Entry 19, Table S1:** yield = 1.13/4.00 = 0.28 (28%).



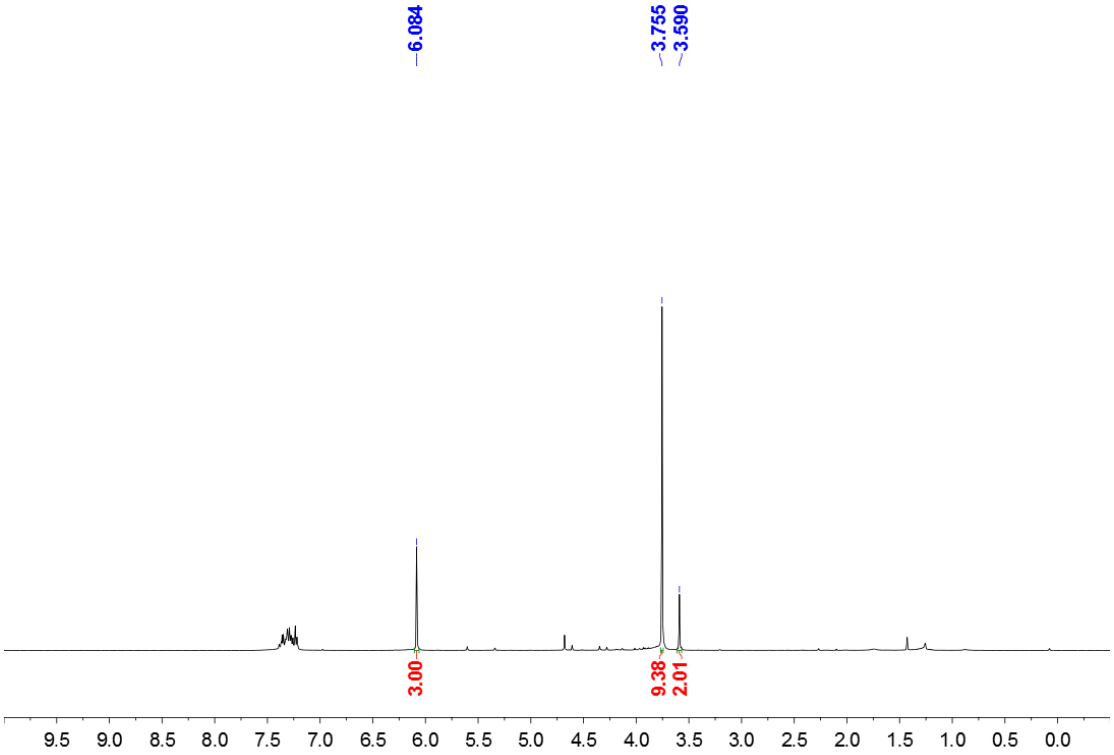

**Entry 20, Table S1:** yield = 1.49/4.00 = 0.37 (37%).



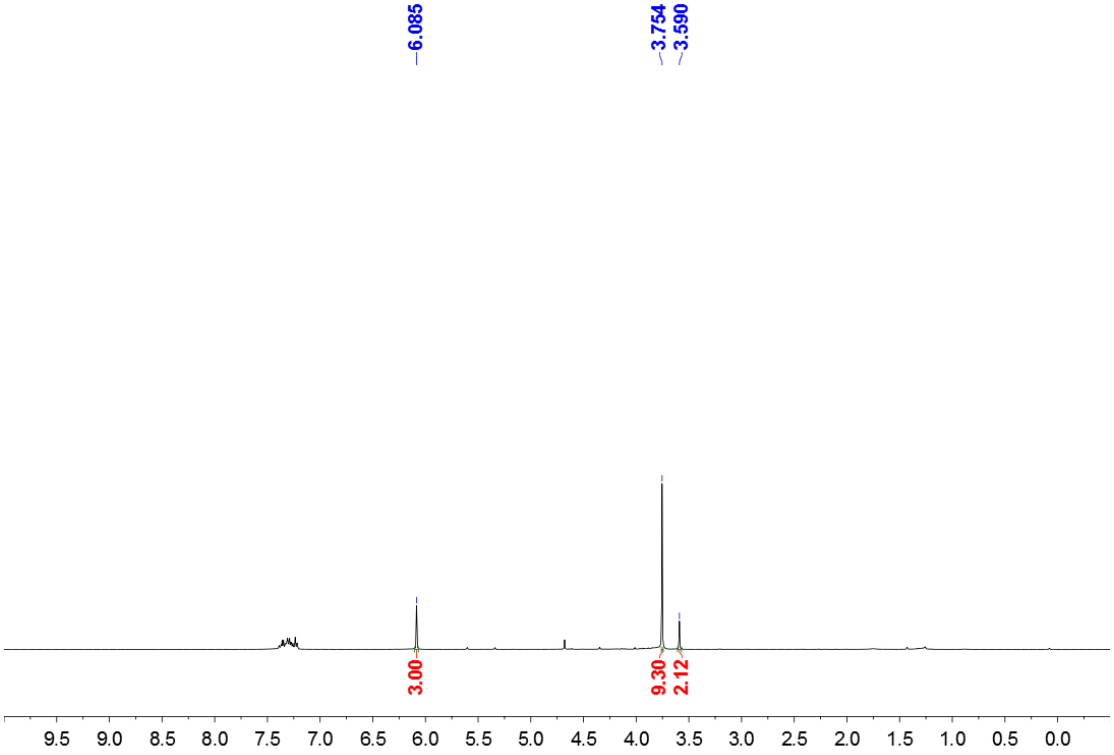
**Entry 21, Table S1:** yield = 1.80/4.00 = 0.45 (45%).



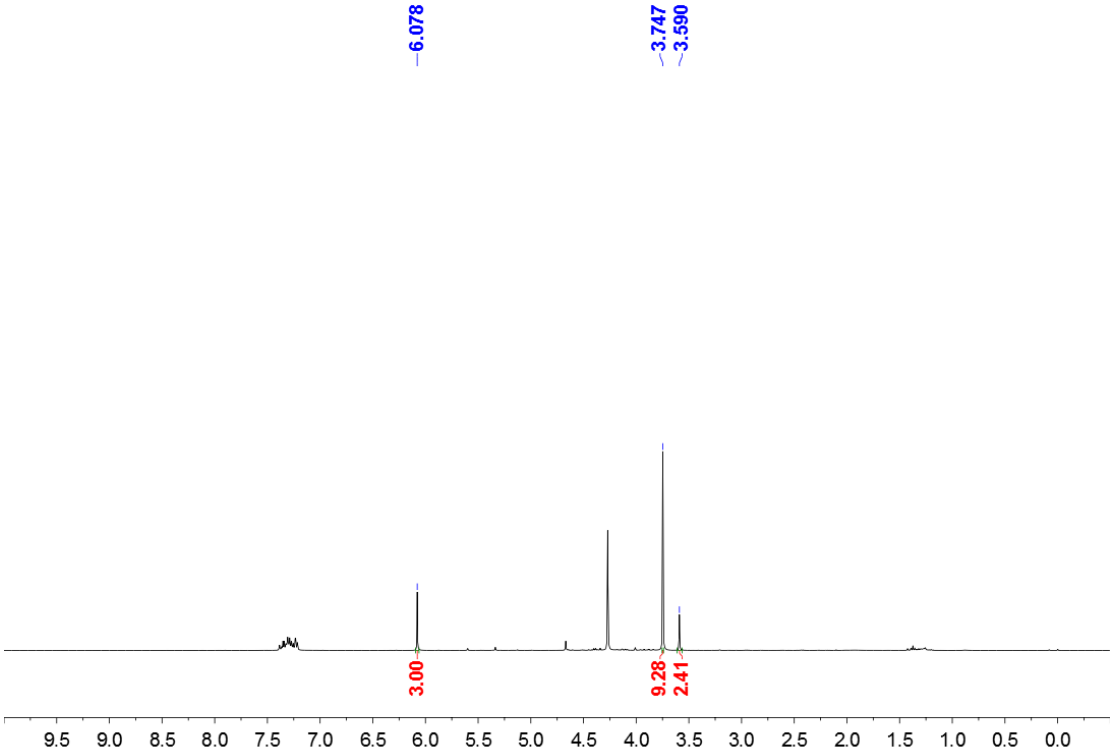

**Entry 22, Table S1:** yield = 2.01/4.00 = 0.50 (50%).



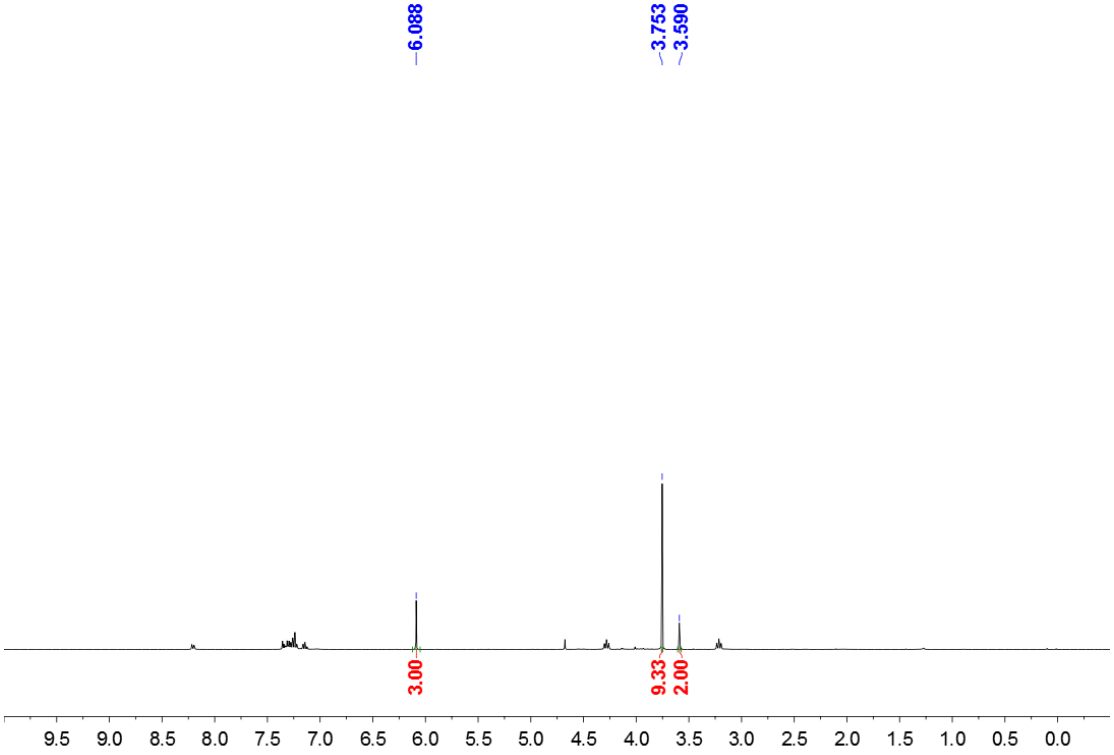
**Entry 23, Table S1:** yield = 2.12/4.00 = 0.53 (53%).



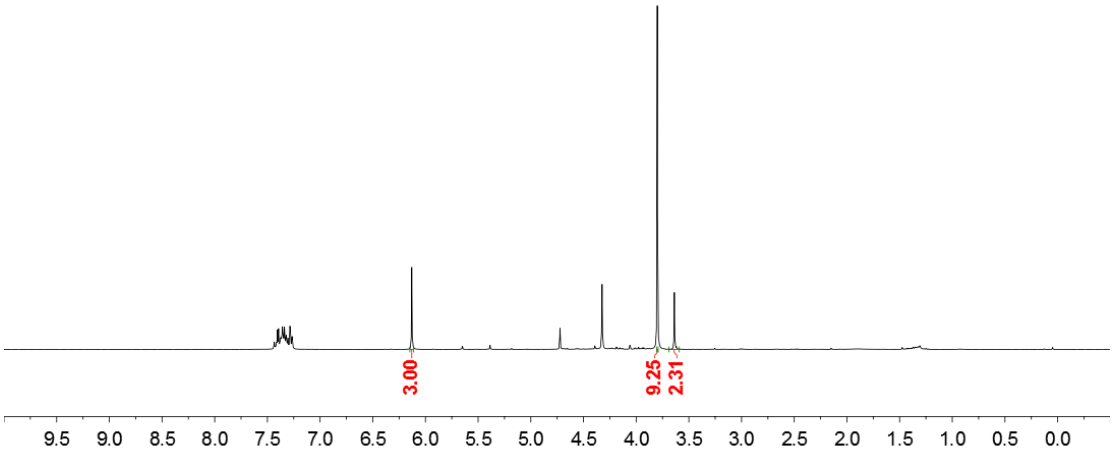

**Entry 24, Table S1:** yield = 2.41/4.00 = 0.60 (60%).



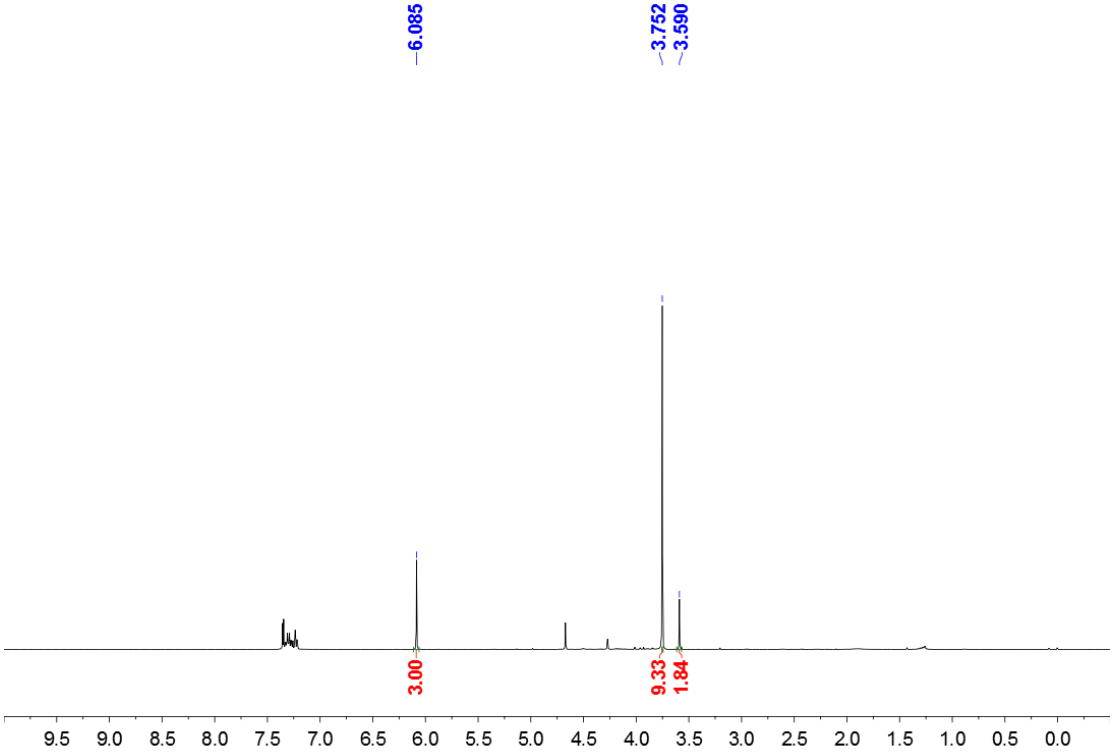
**Entry 25, Table S1:** yield = 2.00/4.00 = 0.50 (50%).



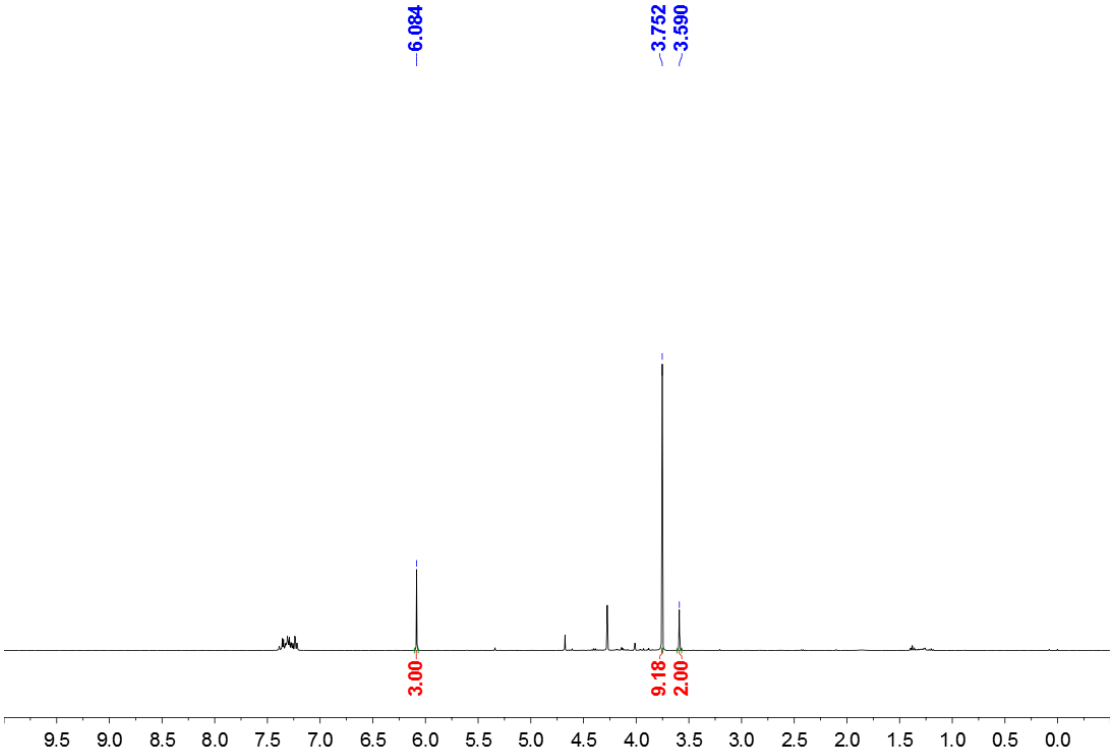

**Entry 26, Table S1:** yield = 2.31/4.00 = 0.58 (58%).



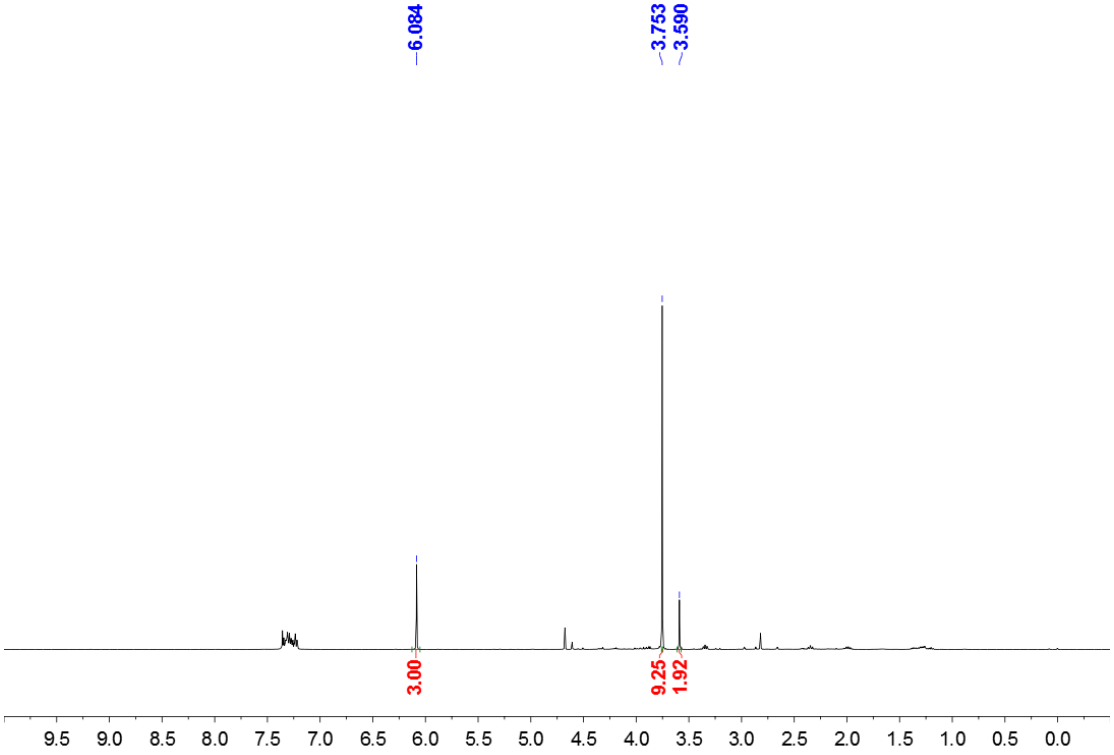
**Entry 27, Table S1:** yield = 1.84/4.00 = 0.46 (46%).



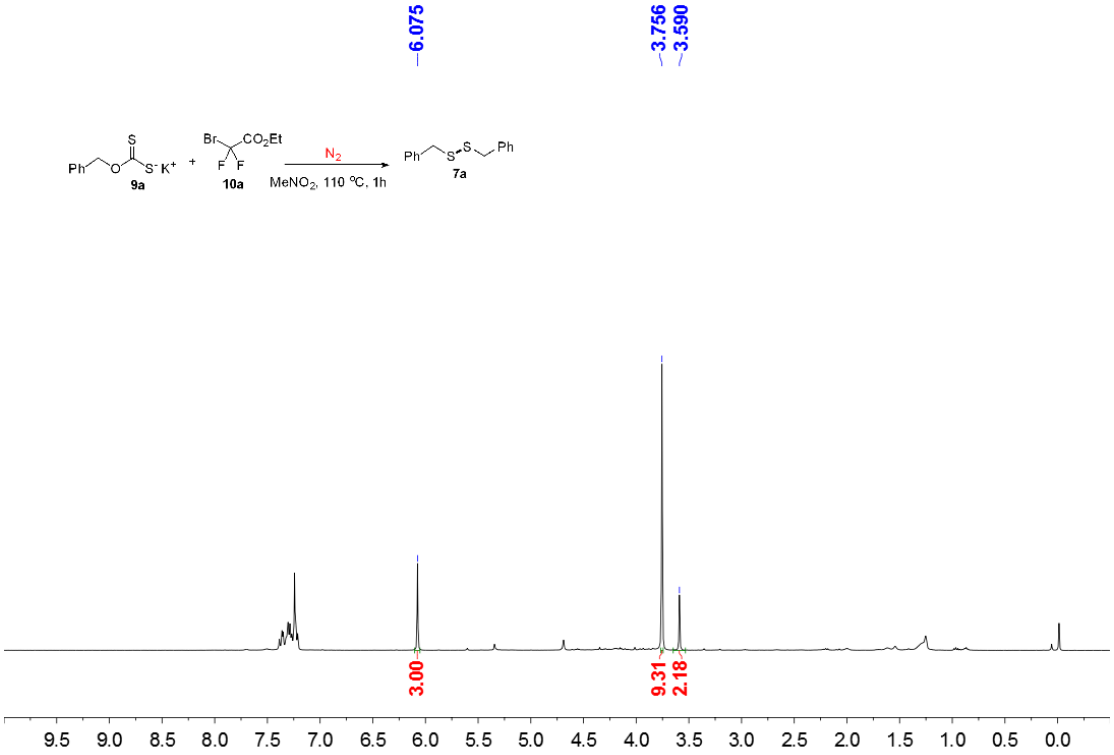

**Entry 28:** yield = 2.00/4.00 = 0.50 (50%).



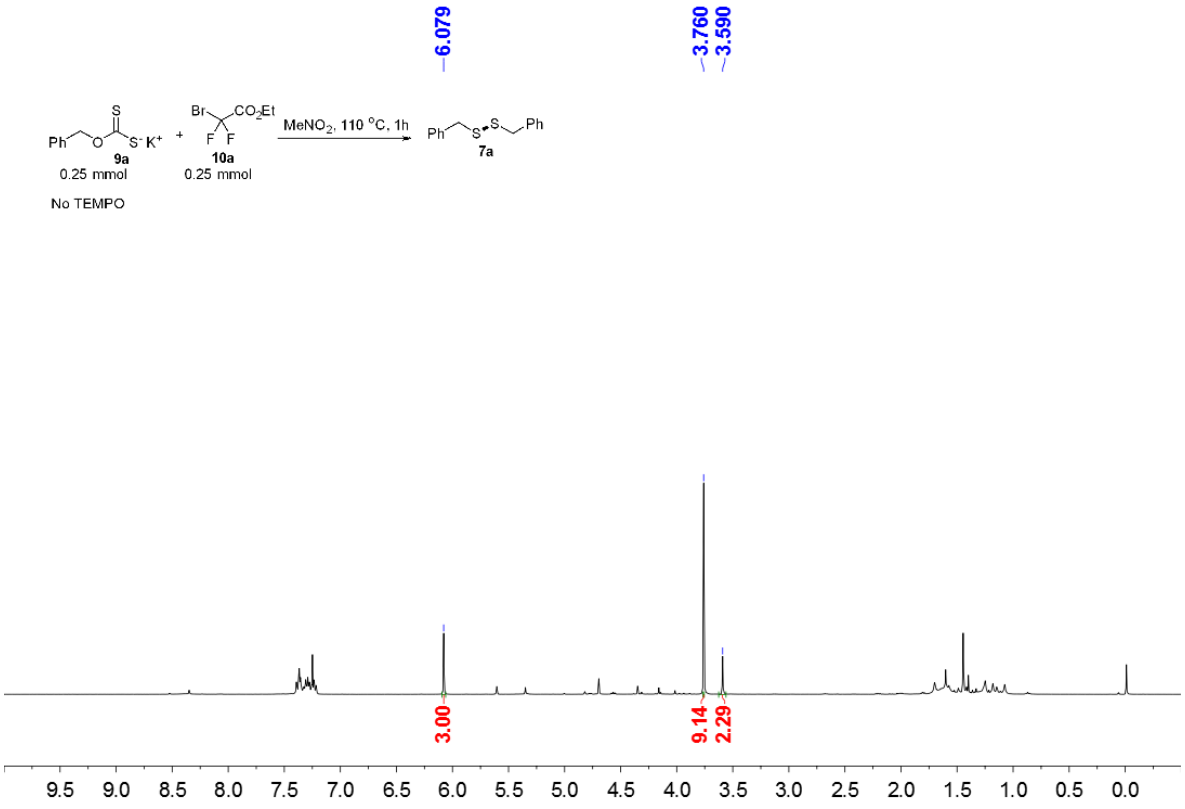
**Entry 30, Table S1:** yield = 1.92/4.00 = 0.48 (48%).



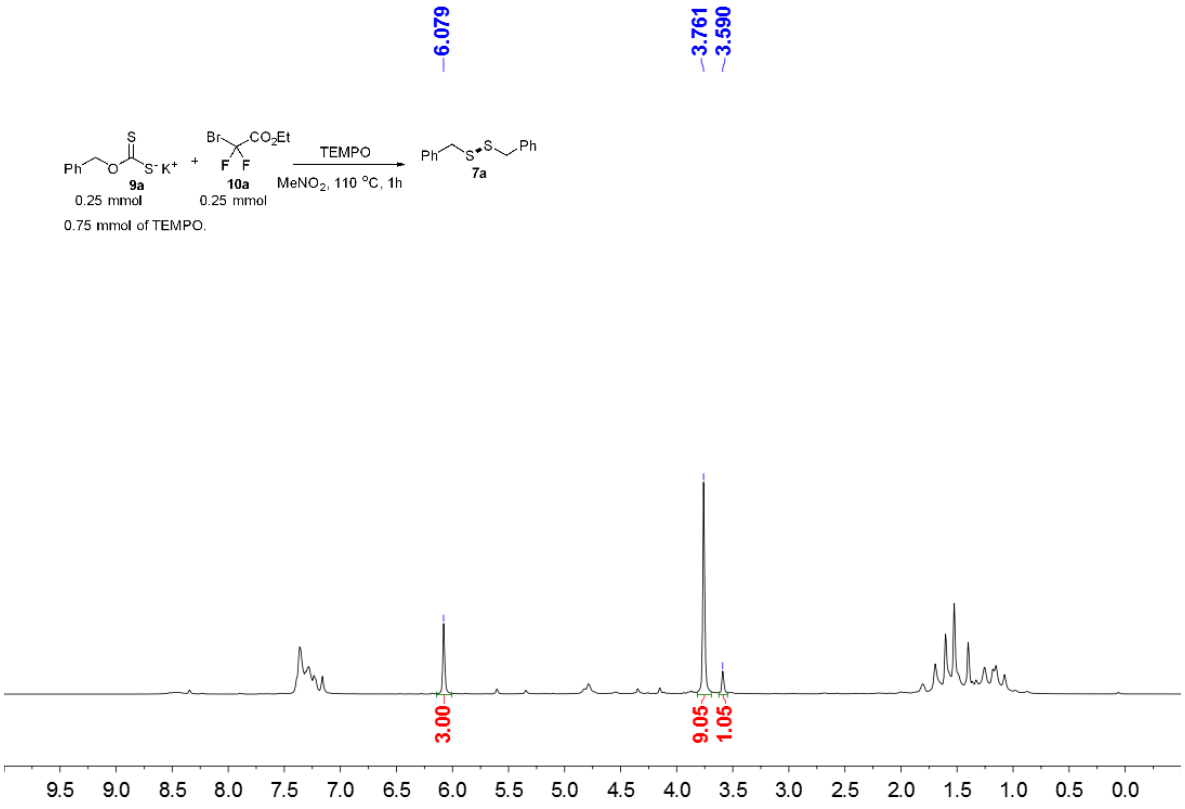

**Entry 31, Table S1:** yield = 2.18/4.00 = 0.54 (54%).



No TEMPO: yield = 2.29/4.00 = 0.57 (57%).




3 equivalents of TEMPO: yield = 1.05/4.00 = 0.26 (26%).



4 equivalents of TEMPO: yield = 0.68/4.00 = 0.17 (17%).