Electronic Supporting Information

3, 6-Di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) mediated metal-free mild oxidation of thiols to disulfides in aqueous medium

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Table S1 Crystallographic data of compound **2t** and **H_2pytz**

	Compound 2t	**H_2pytz**
Empirical formula	$C_{12}H_{16}N_2S_4$	$C_{12}H_{10}N_6$
Formula weight	316.51	238.26
T/K	150(2)	120(2)
Crystal system	Monoclinic	Triclinic
Space group	*P*2(1)/n	P-1
a/Å	12.0283 (13)	8.1982(6)
b/Å	8.2692 (9)	8.2816(6)
c/Å	14.3216 (15)	8.8622(6)
α/°	90	102.040(2)
β/°	102.017 (2)	111.9550(10)
γ/°	90	90.162(2)
Z	4	2
V/ Å^3	1393.3 (3)	543.61(7)
D calcd/ g cm^{-3}	1.509	1.456
μ/ mm^{-1}	0.665	0.096
F(000)	664	248
Crystal size/ mm^3	0.34×0.24×0.07	0.42×0.30×0.22
Reflections collected	6151	6902
Independent reflections	2624	2116
parameters /Restraints	163/0	180/0
Goodness-of-fit , S^a	1.118	1.030
Final R indices [$I>2\sigma(I)$]	$R1^a$ = 0.0319	$R1^a$ = 0.0327
	$wR_2{}^b$ = 0.0890	$wR_2{}^b$ = 0.0931
R indices (all data)	$R1^a$ = 0.0355	$R1^a$ = 0.0342
	$wR_2{}^b$ = 0.1007	$wR_2{}^b$ = 0.0945

$^aS = [\sum w(Fo^2 - Fc^2)/(N-P)]^{1/2}$ where N is the number of data and *P* the total number of parameters refined. $^bR_1(F) = \Sigma||F_o| - |F_c||\Sigma|F_o|$. $^cwR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected Bond distances (Å) and Bond Angles (°) for 2-aminocyclopent-1-enecarbothioic dithioperoxyanhydride (**2t**)

	2t
S2–S3	2.0112(7)
S1–C6	1.671(2)
S2–C6	1.8069(19)
S3–C7	1.793(2)
S4–C7	1.669(2)
N1–C1	1.319(3)
N2–C12	1.321(3)
C6–S2–S3	107.28(7)
C7–S3–S2	106.41(7)

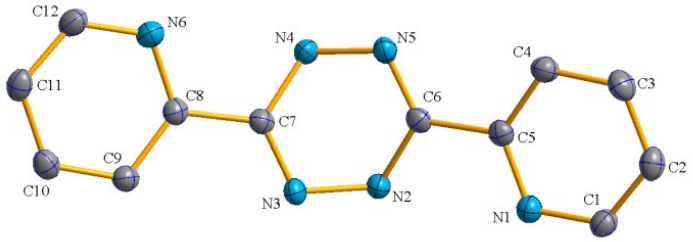
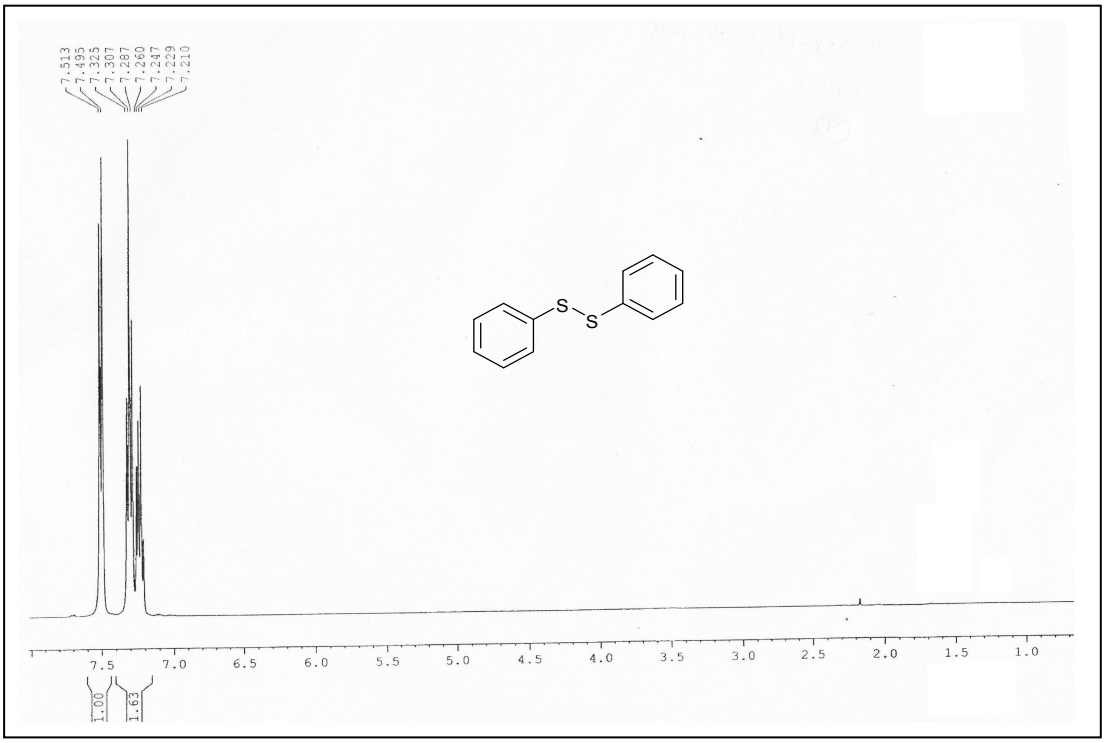


Fig. S1 ORTEP representation of the 3, 6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (**H_2pytz**) showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Oxidation of 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2pytz) to 3,6-Di(pyridin-2-yl)-1,2,4,5-tetrazine (Pytz)

The H_2pytz (0.48 g, 2 mmol) was dissolved in hot ethanol (50 ml) and excess sodium nitrite (0.69g, 10 mmol) in 5 ml water was added to this solution followed by drop wise addition of 2% aqueous hydrochloric acid until the solution reached approximately pH 3 under stirring condition. The solution turned red and 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine slowly crystallized upon cooling of the solution to room temperature. The product was filtered off and washed with water followed by ethanol. Yellow solid, yield (214 mg, 60%), mp: 193-194 °C, FT-IR (KBr, ν_{max}/cm^{-1}): 3336 w, 3323 s, 3298 w, 3059 w, 1590 m, 1566 m, 1472 m, 1445 s, 1385 s, 1287 m, 1252 w, 1155 w, 1113 m, 993 m, 882 m, 785 s, 744 s, 679 m. ^{1}H NMR δ_H (300 MHz, $CDCl_3$): 8.573 (t, 4H, J = 8.0 Hz), 8.052 (d, 2H, J = 8.0 Hz), 7.762−7.728 (m, 2H), 7.338 (dd, 2H, J = 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.60, 147.69, 146.85, 139.92, 125.06, 121.52. HRMS (ESI-TOF): m/z 261.1530 ($M+Na^+$).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6.5
6.0
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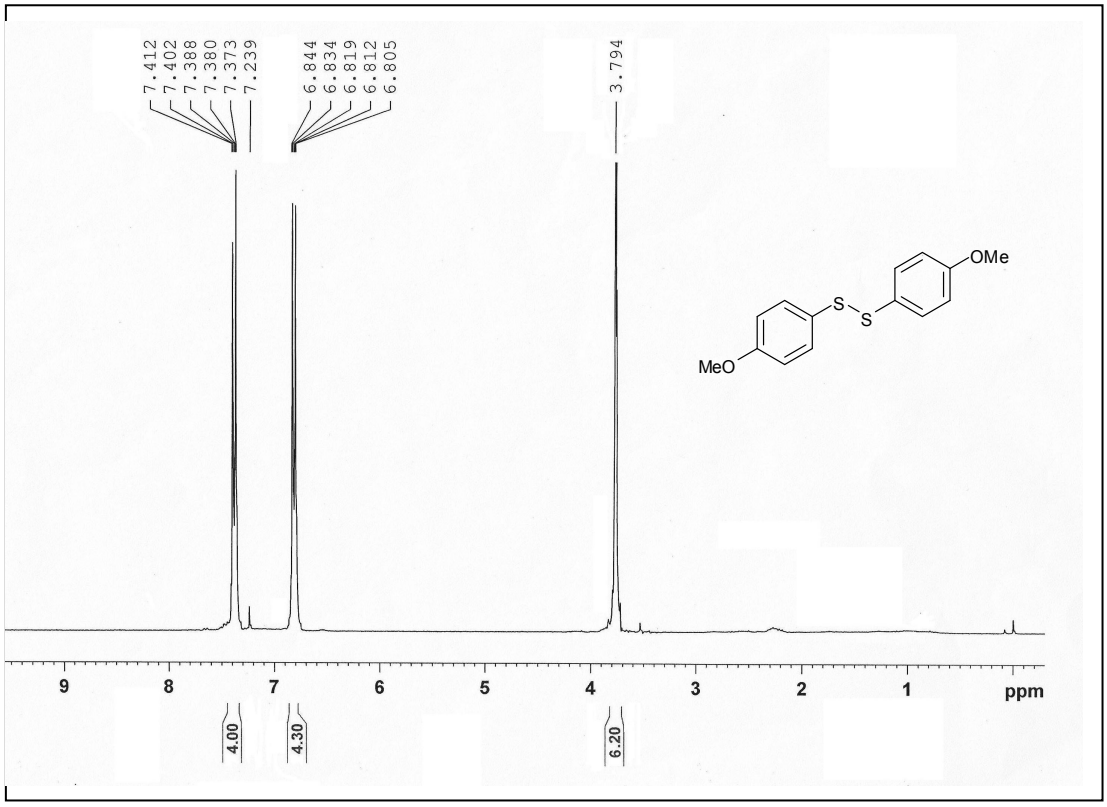
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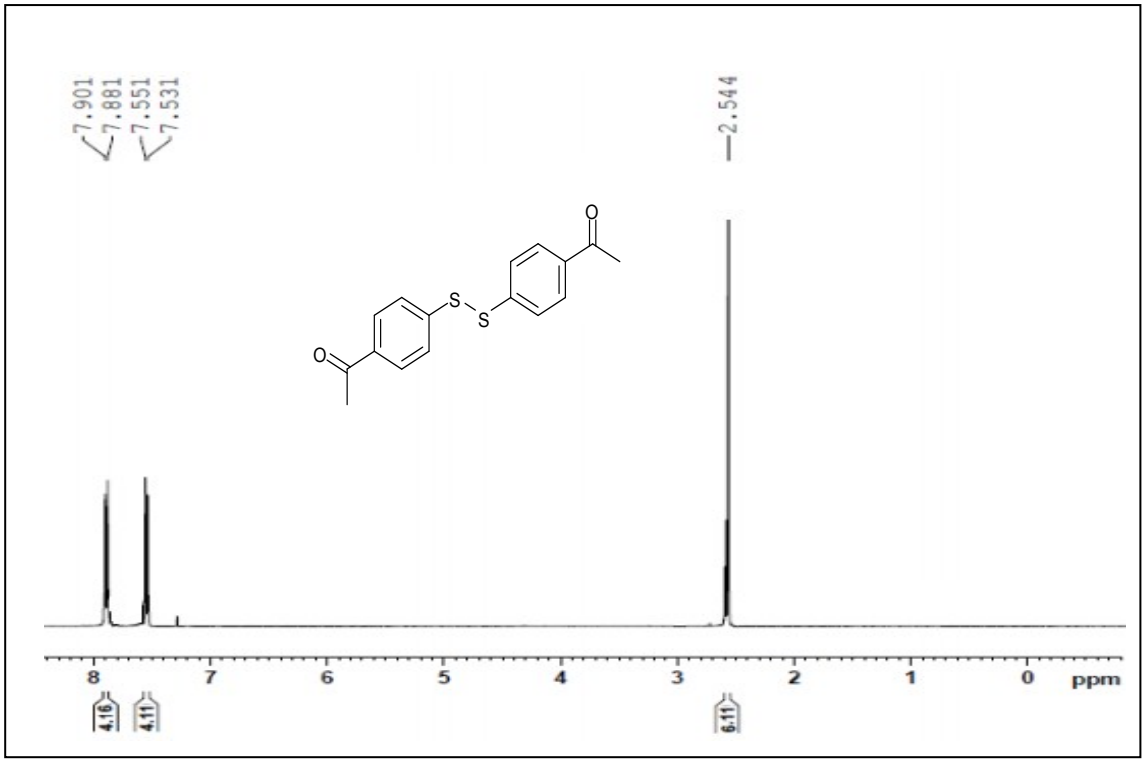
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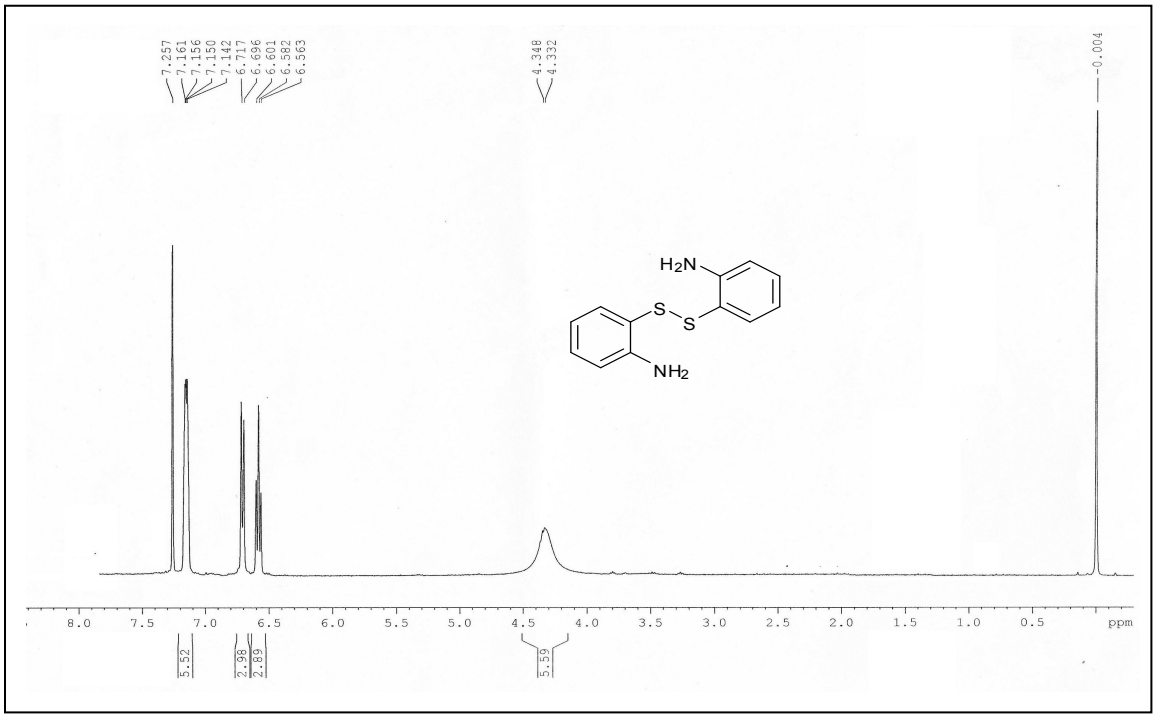
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H2N
S
S
NH2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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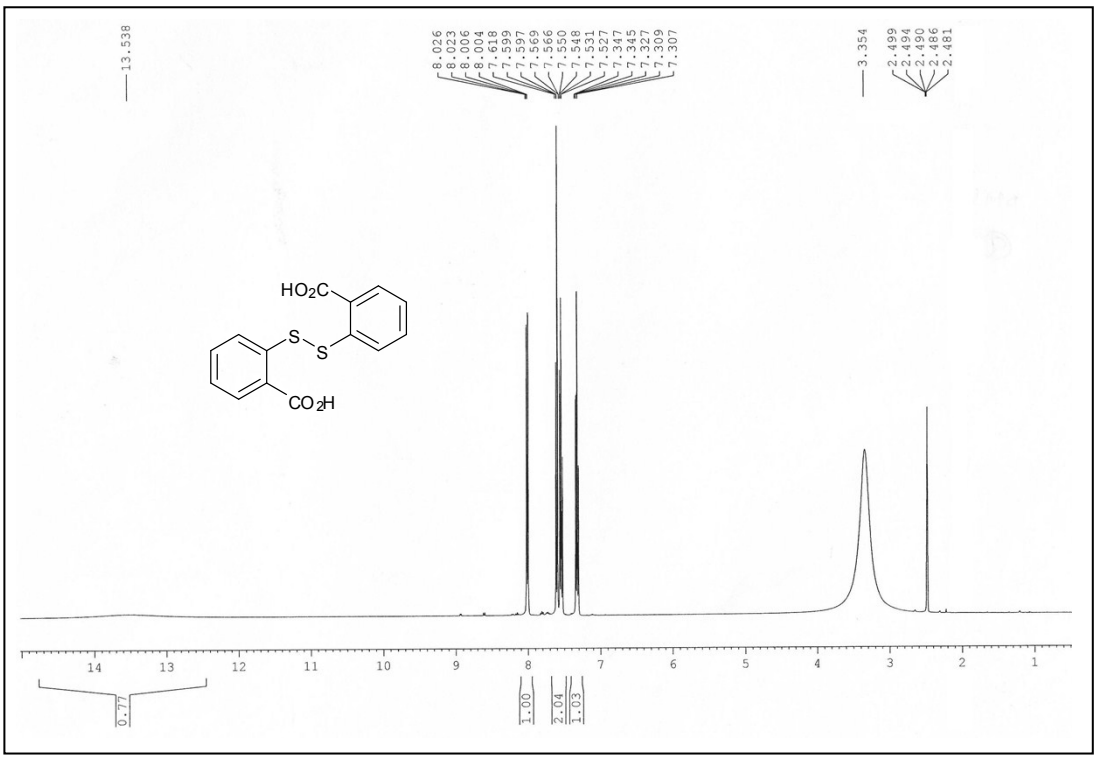
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7.597
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7.566
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7.548
7.531
7.527
7.347
7.345
7.327
7.309
7.307
3.354
2.499
2.494
2.490
2.486
2.481
HO2C
S
S
CO2H
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8
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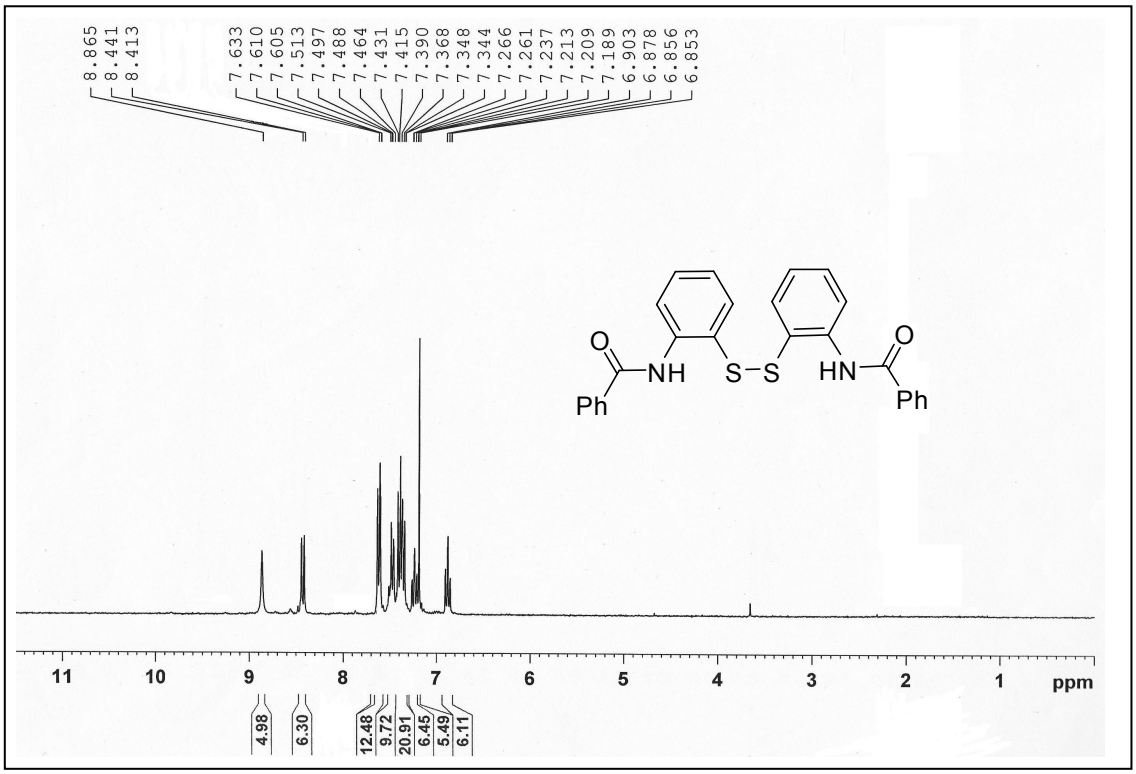
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7.368
7.348
7.344
7.266
7.261
7.237
7.213
7.209
7.189
6.903
6.878
6.856
6.853
O
NH
S–S
HN
O
Ph
Ph
11
10
9
8
7
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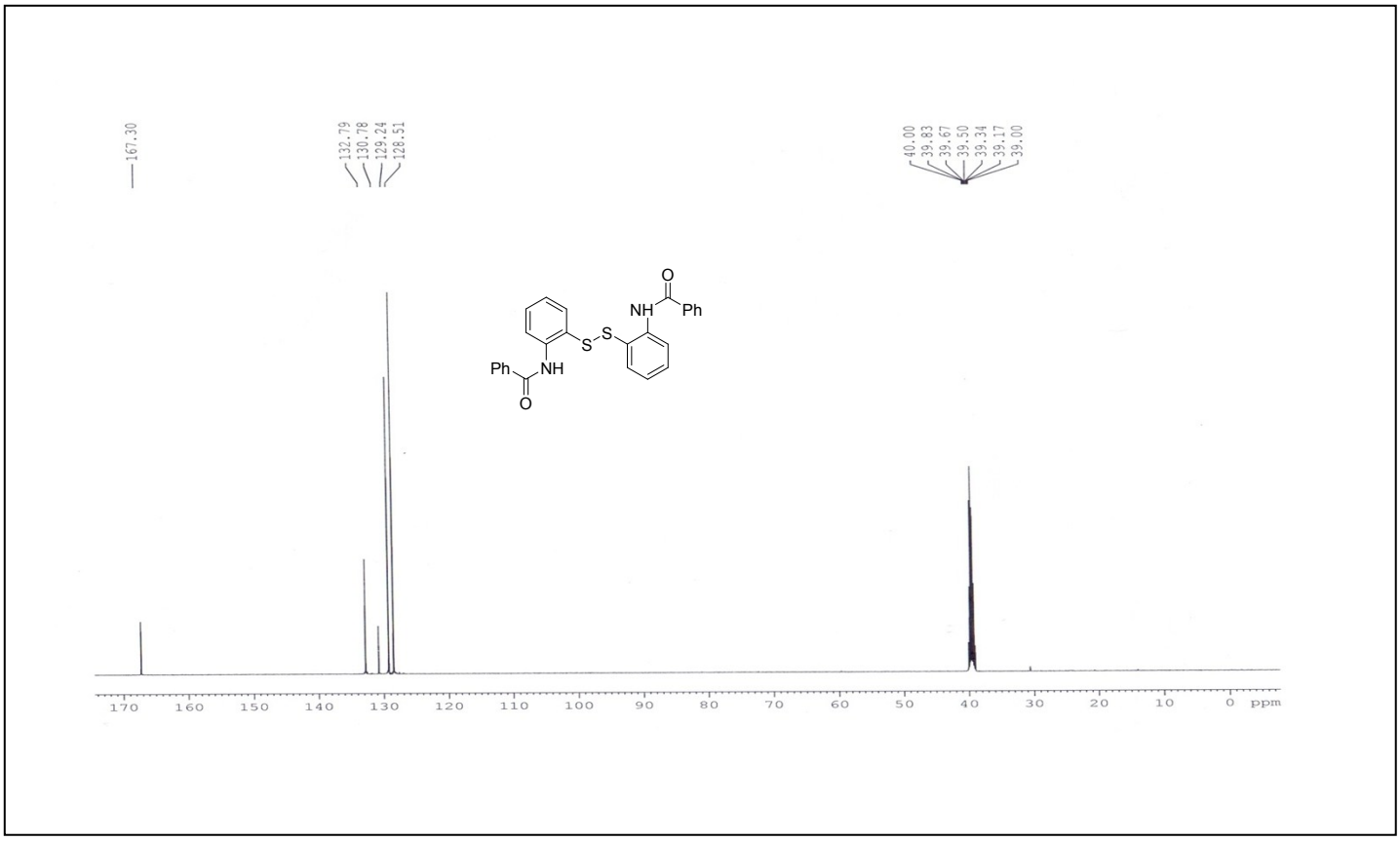
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Ph
S
S
Ph
NH
O
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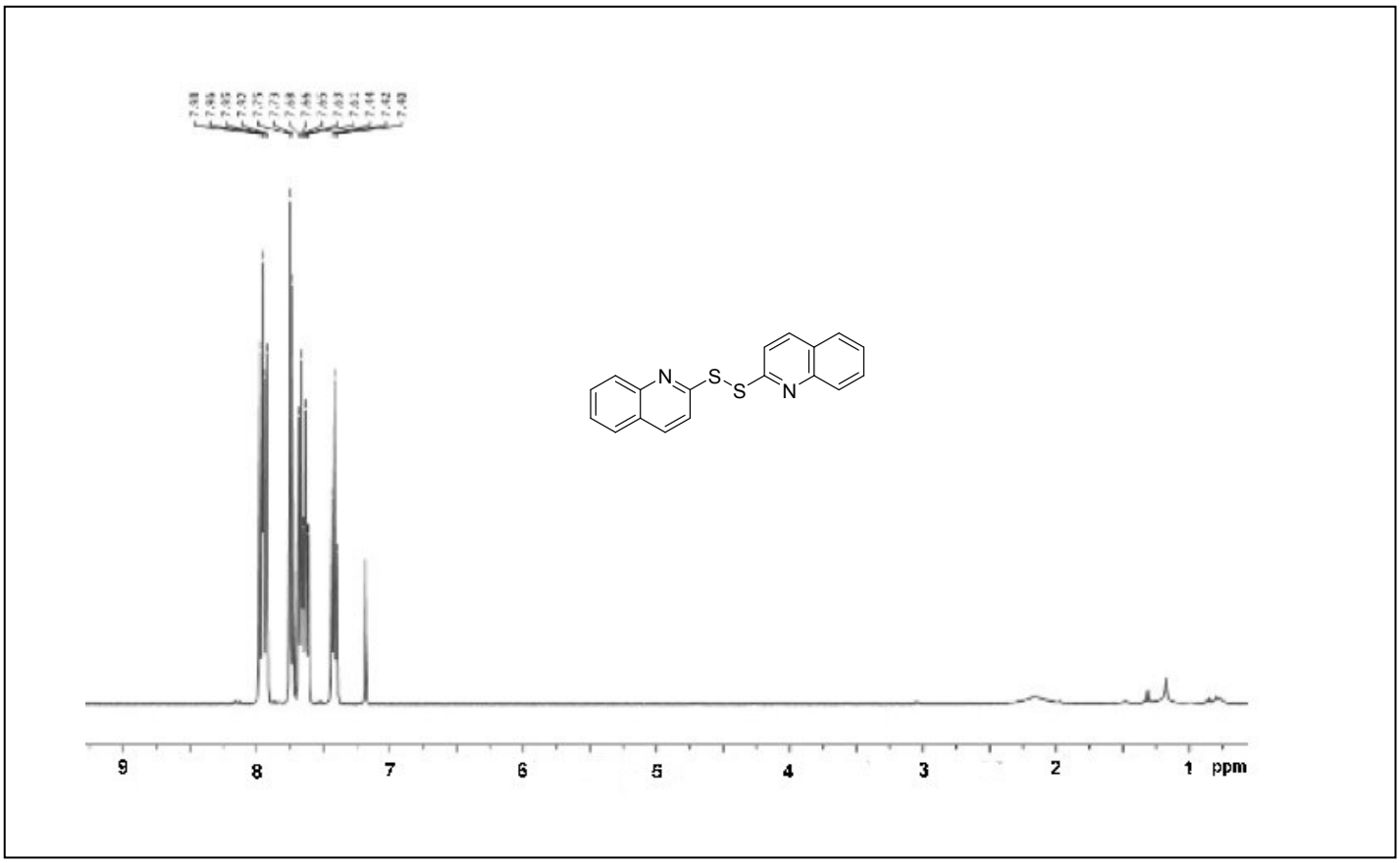
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S
N
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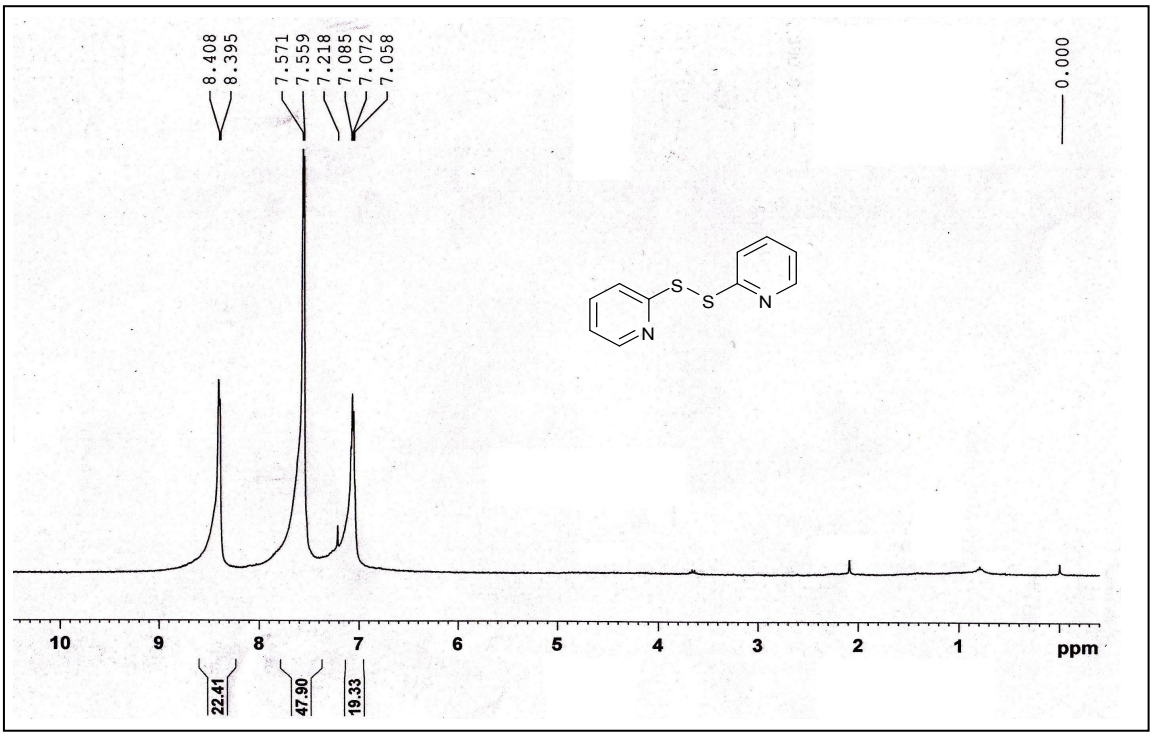
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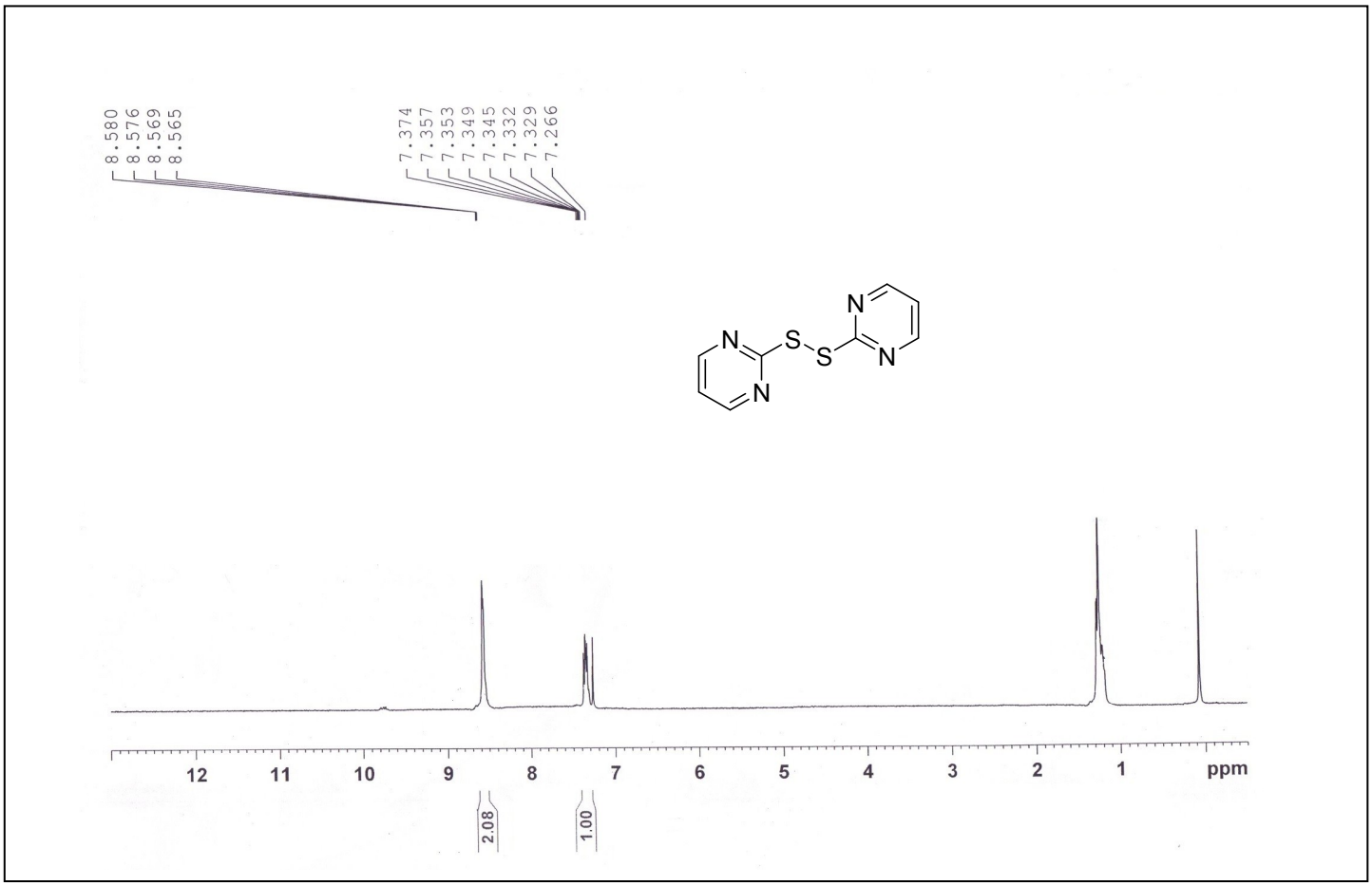
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11
10
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8
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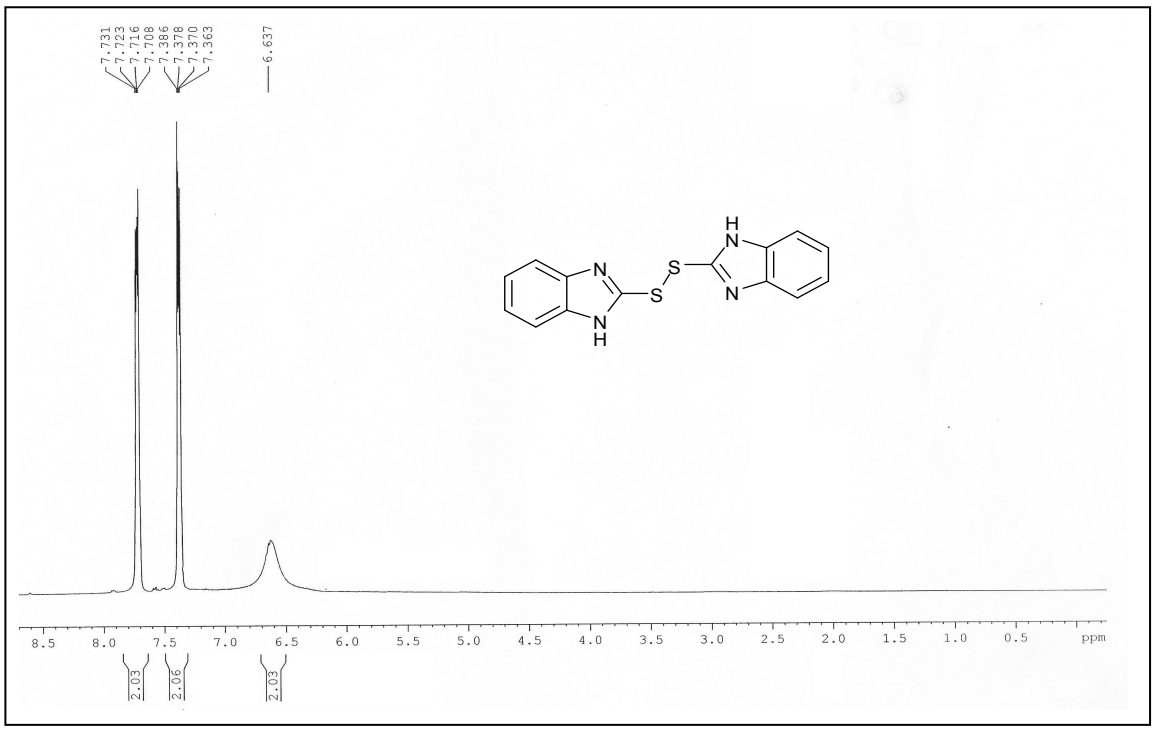
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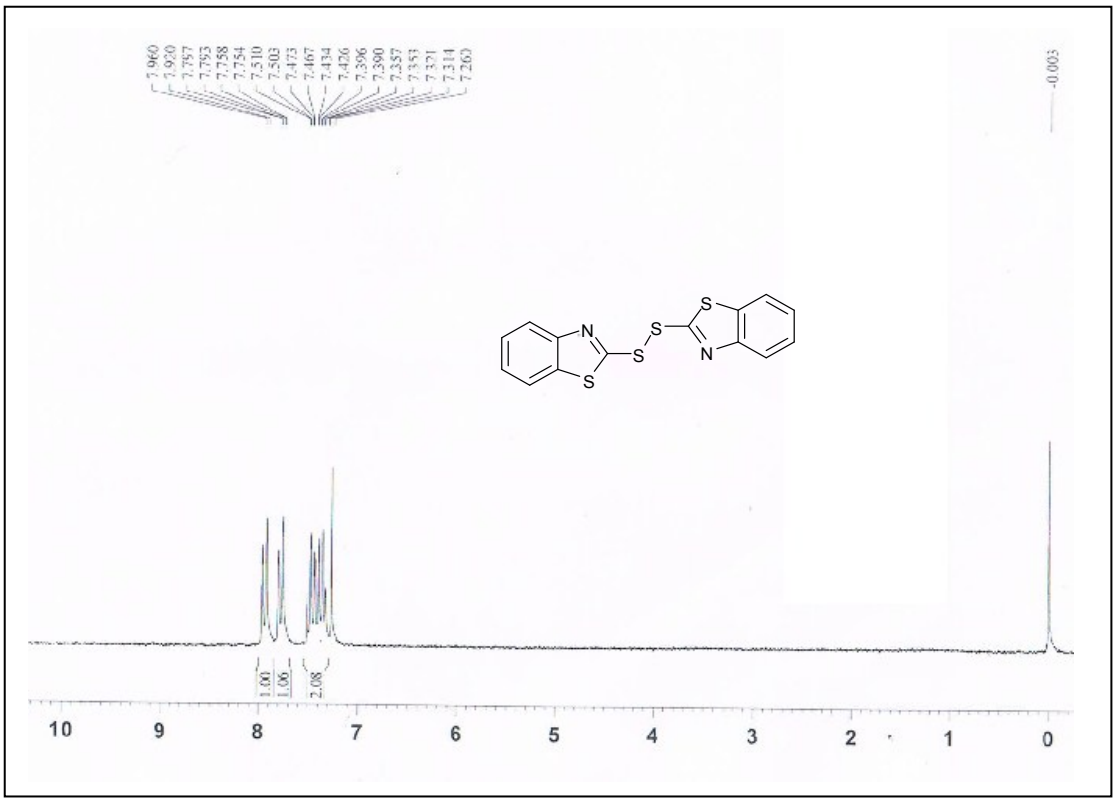
H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S
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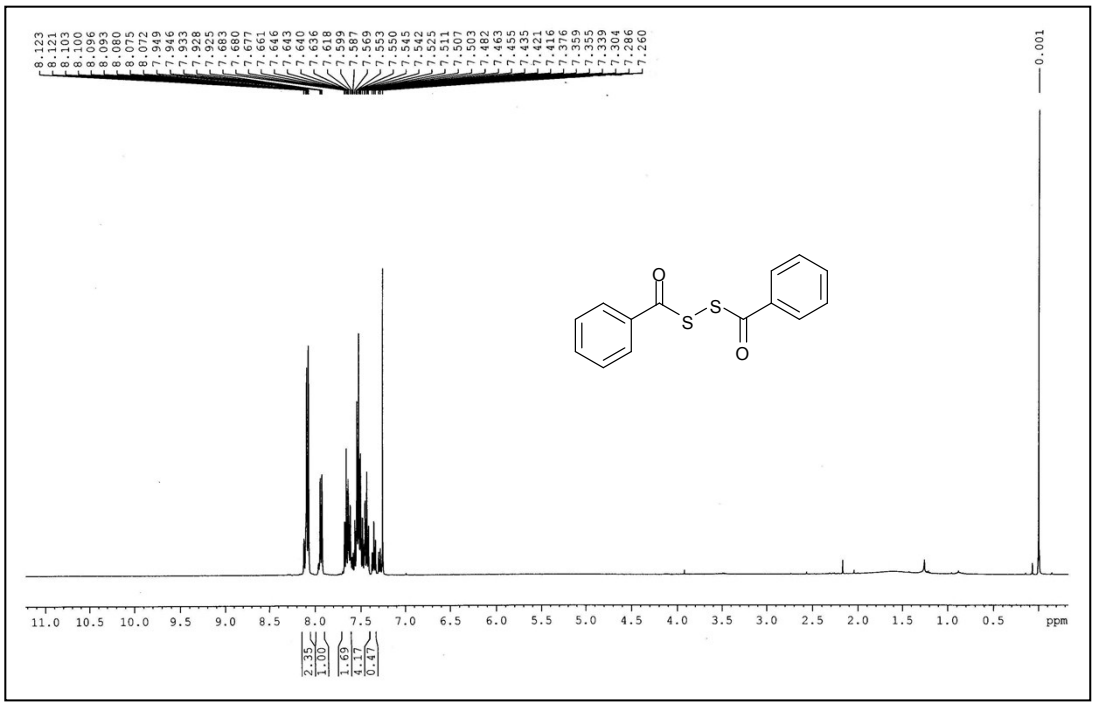
S
N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7.677
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7.643
7.640
7.636
7.618
7.589
7.587
7.569
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7.542
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7.416
7.376
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7.355
7.339
7.304
7.286
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S
S
O
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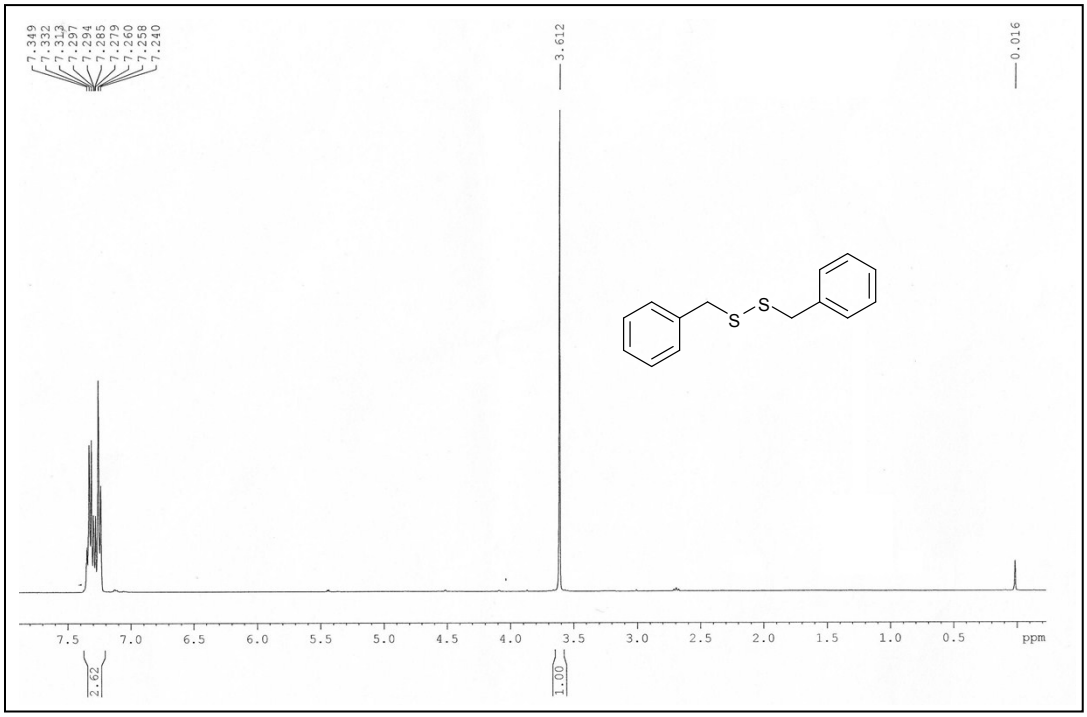
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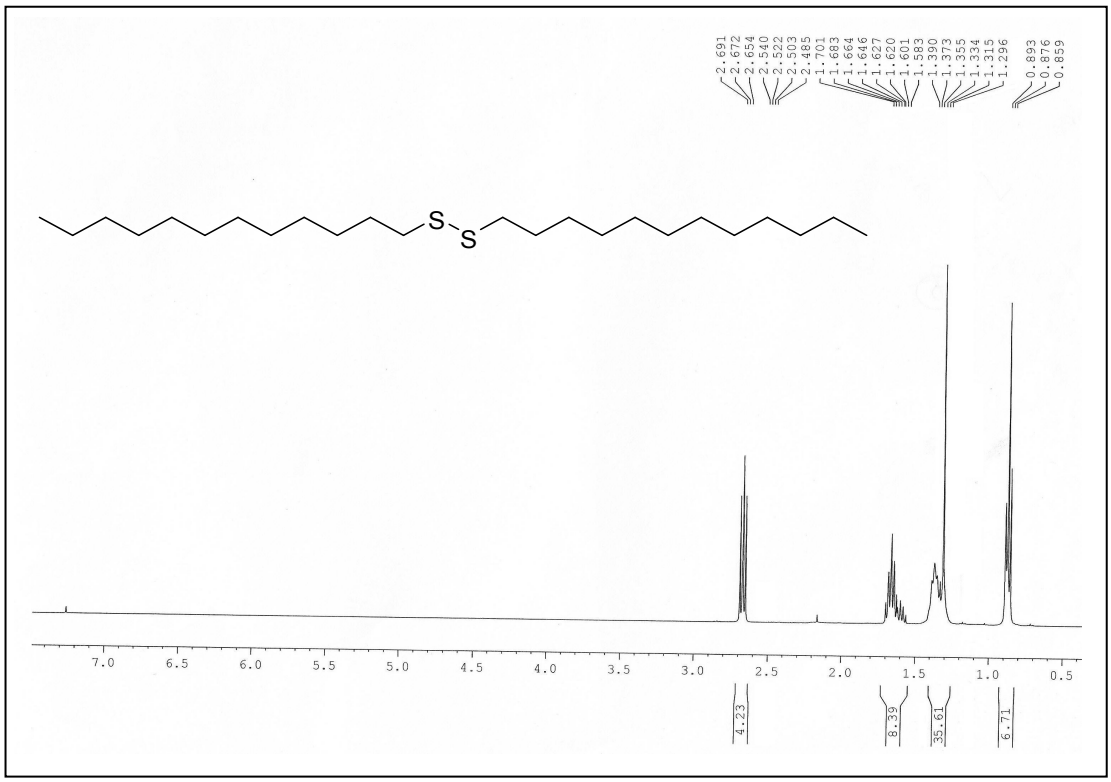
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1.296
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S
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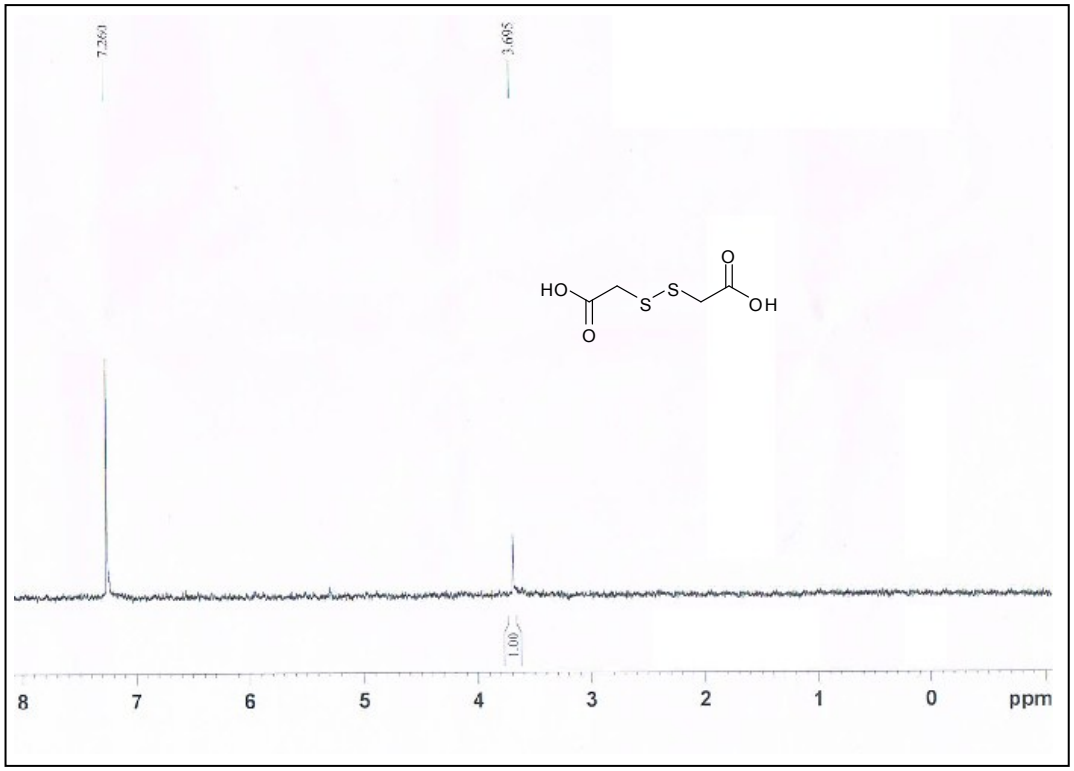
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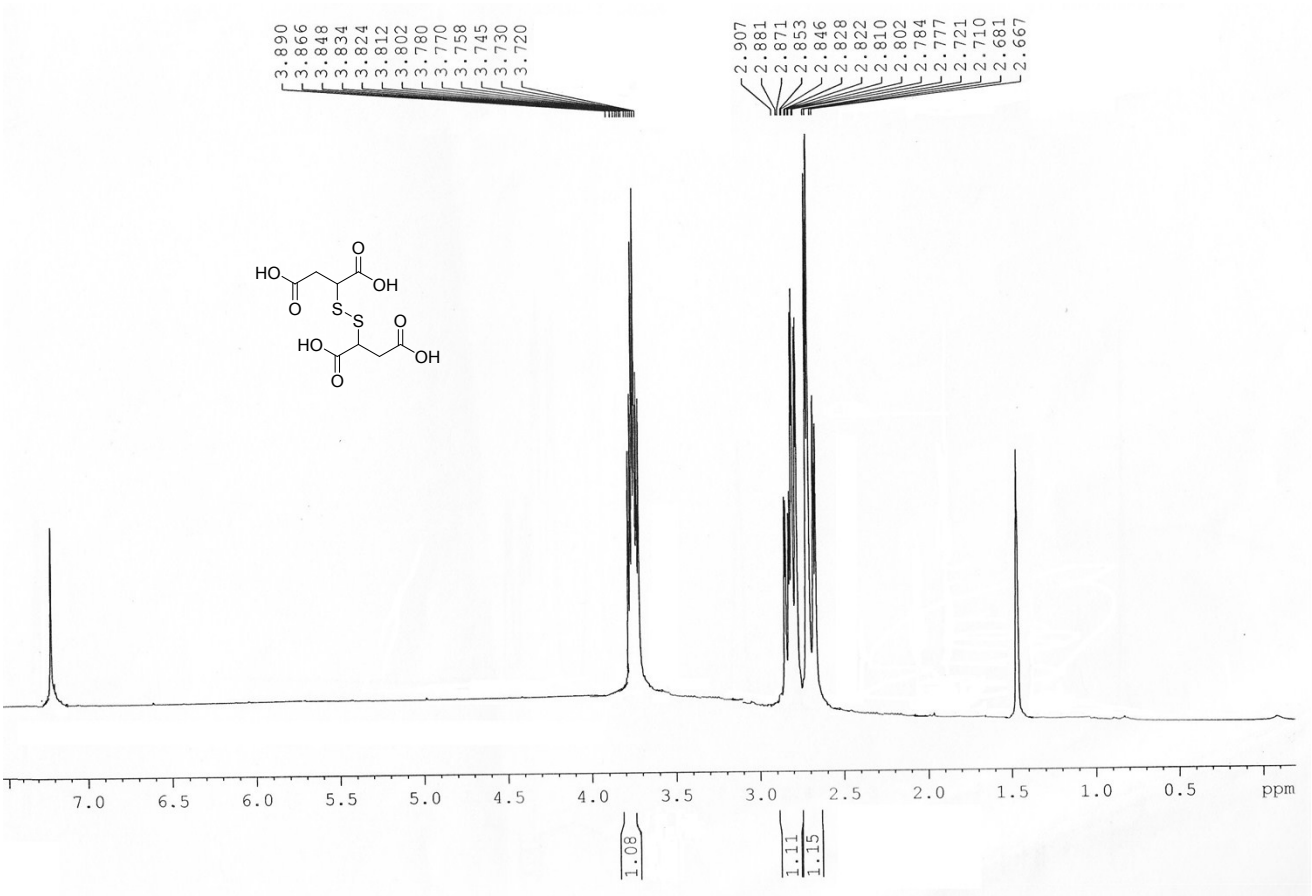
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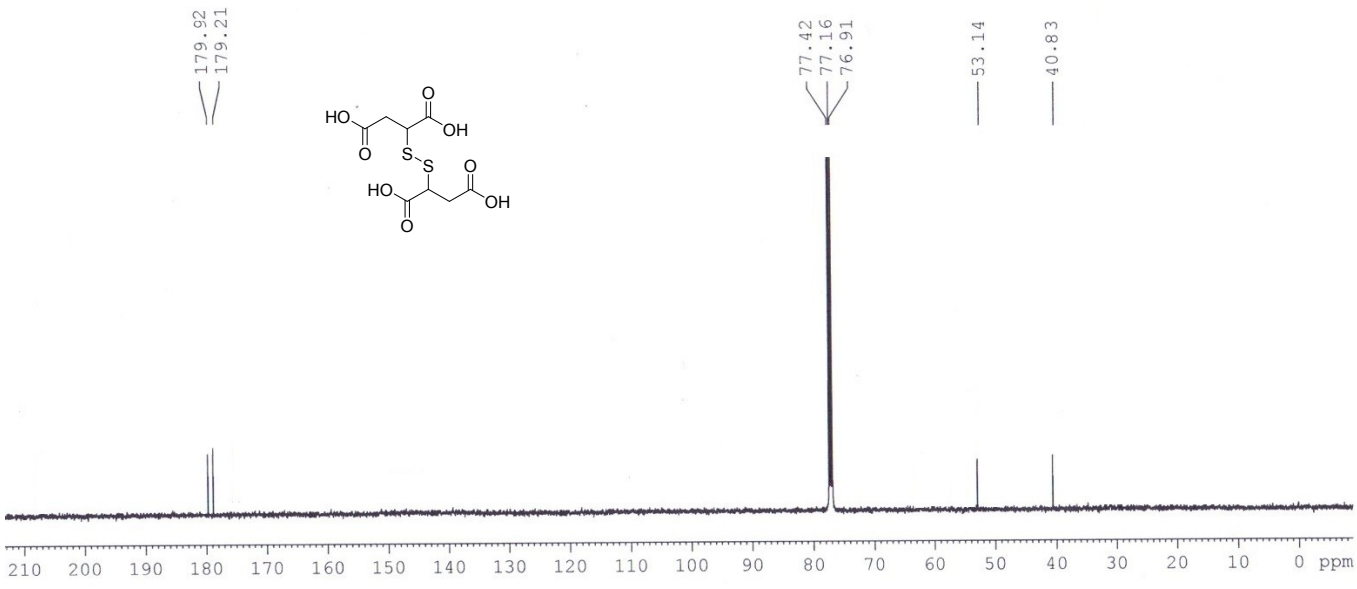
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200
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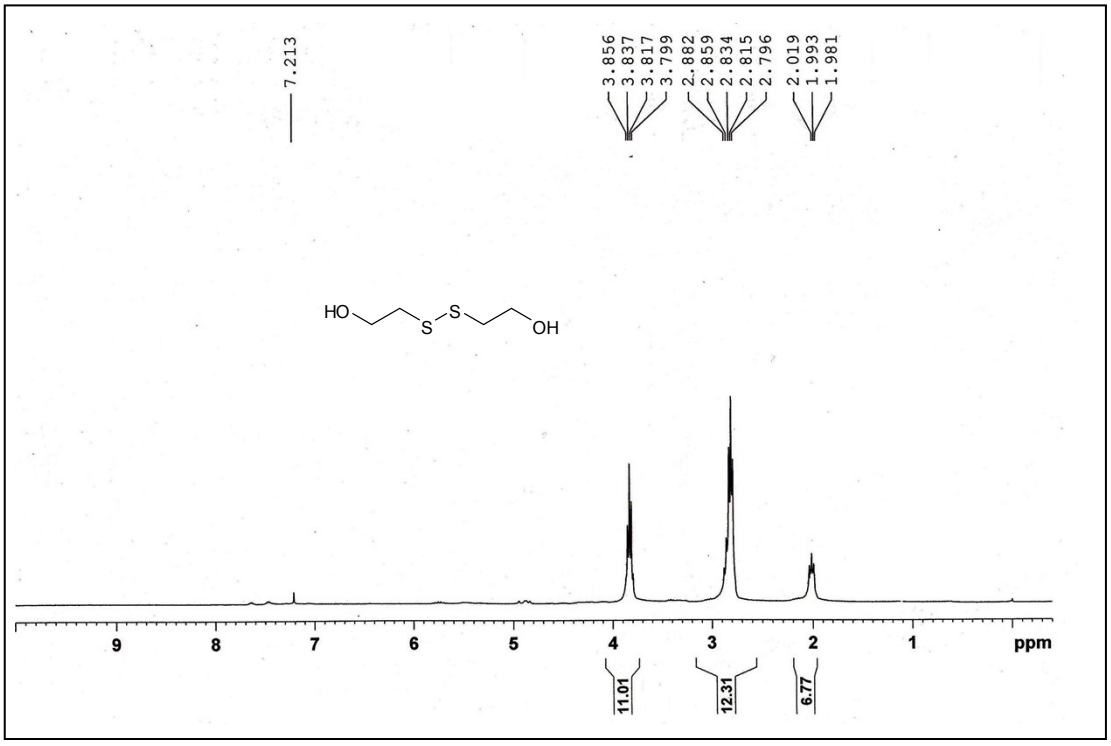
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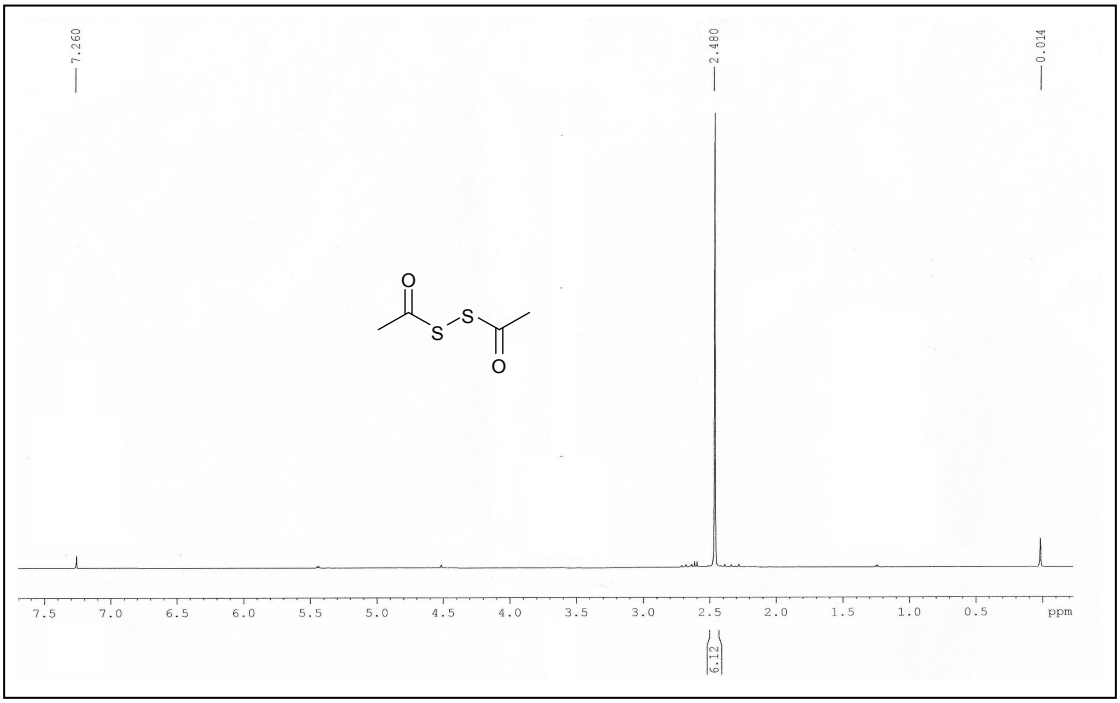
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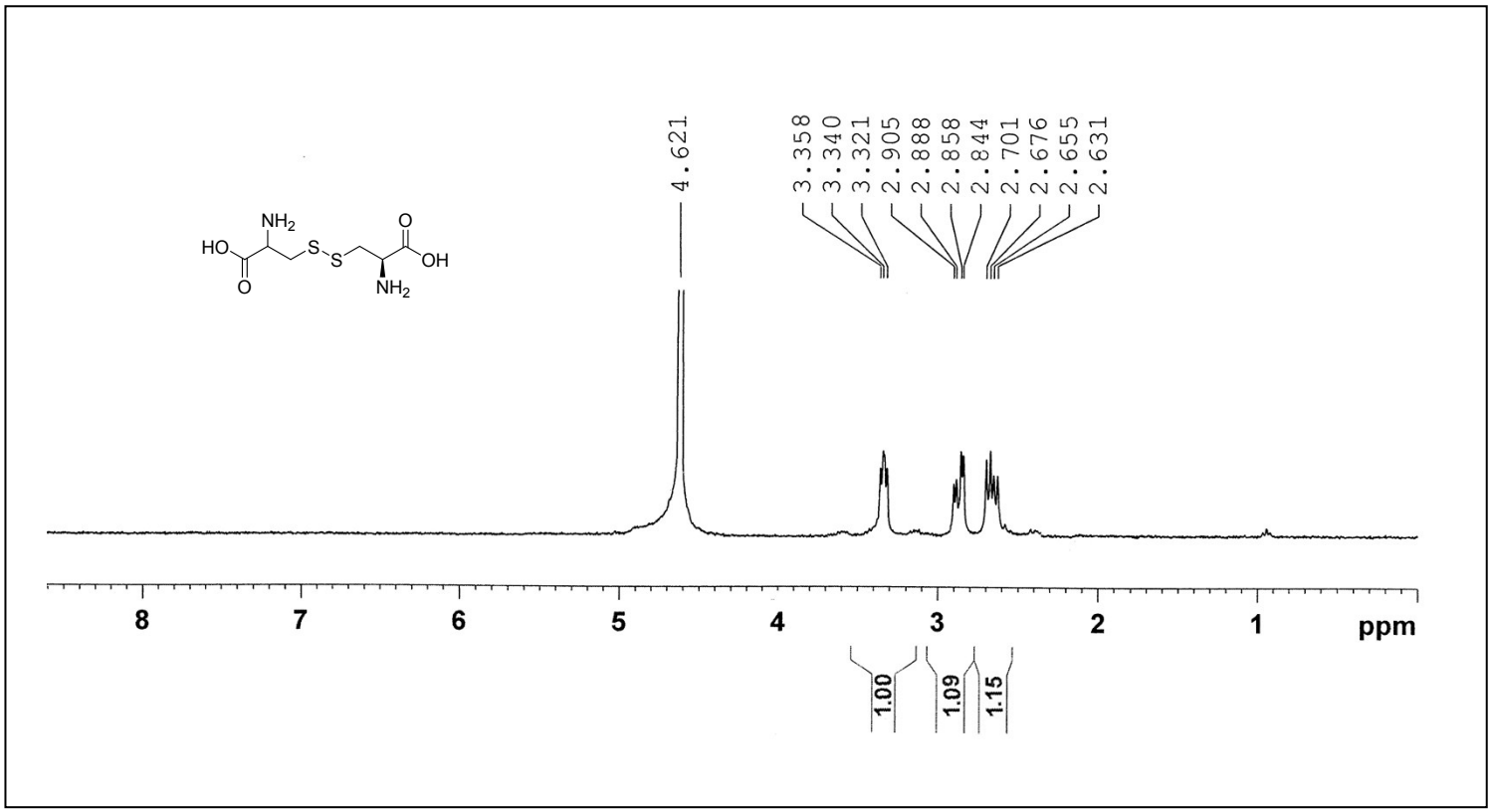
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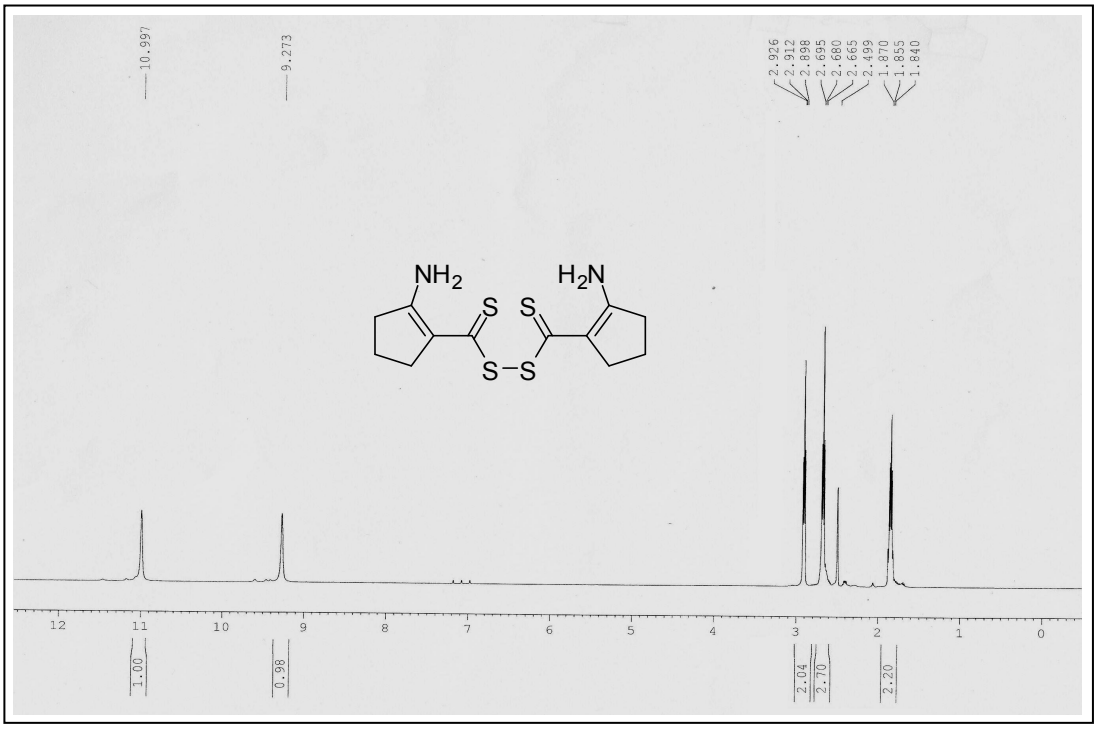
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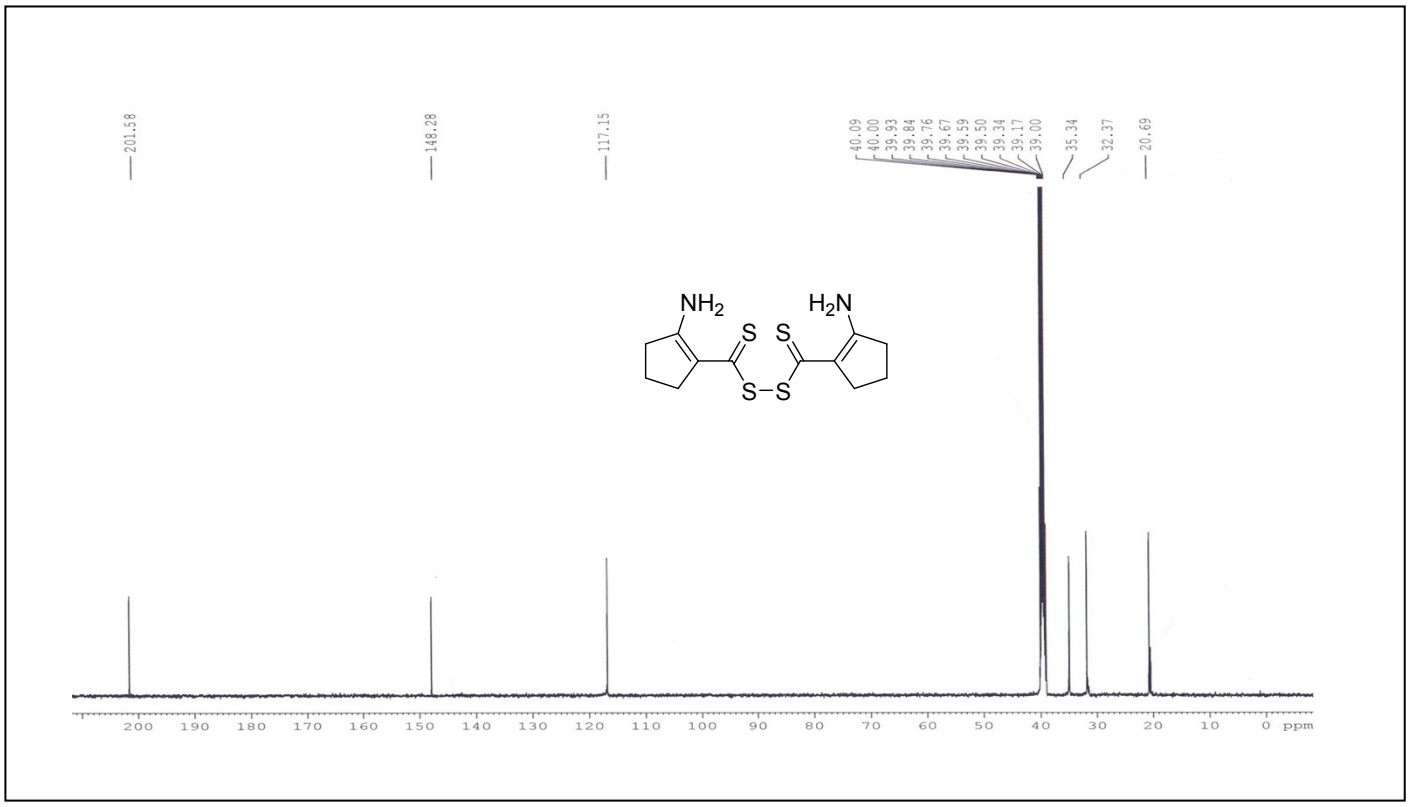
2.20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39.59
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39.34
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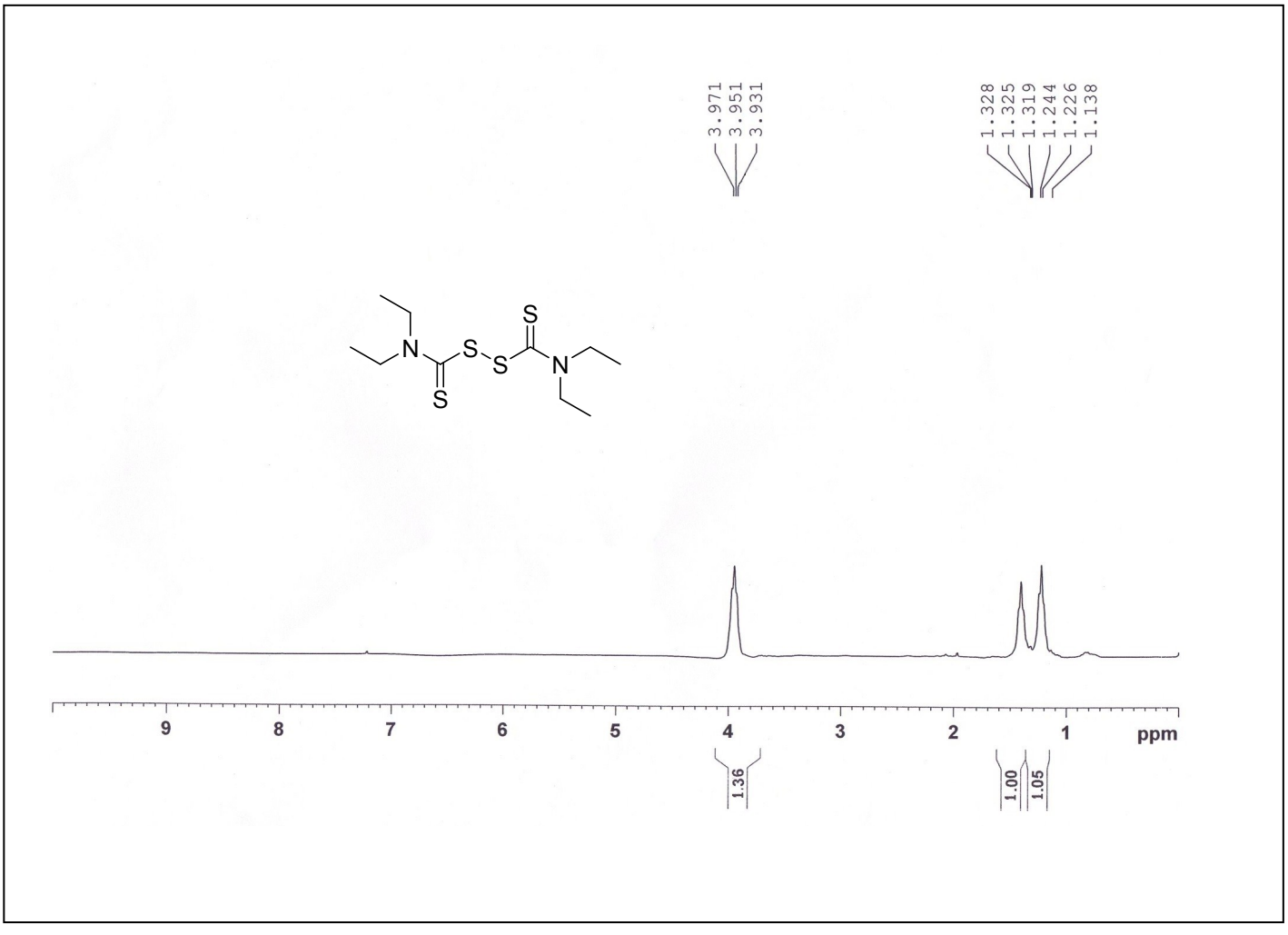
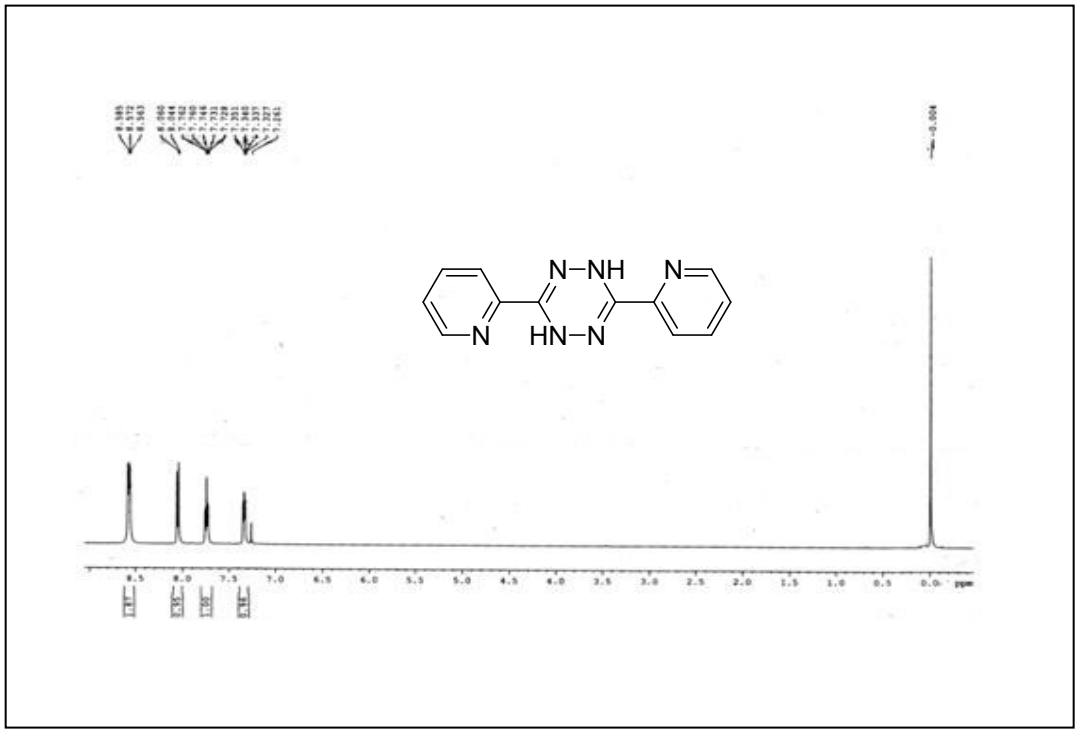
39.00
35.34
32.37
20.69
NH2
H2N
S
S
S–S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3.971
3.951
3.931
1.328
1.325
1.319
1.244
1.226
1.138
N
S
S
S
S
N
9 8 7 6 5 4 3 2 1 ppm
1.36
1.00
1.05


N–NH
N
N
HN–N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm