Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

1,2,4-Dithiazole-5-ones and 5-thiones§ as Efficient Sulfurizing Agents of Phosphorus (III) Compounds – A Kinetic Comparative Study

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Electronic Supplementary Information

The observed rate constants (k_{obs}) for reaction of 3-methoxy-1,2,4-dithiazol-5-one (**1**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 290 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.010	6.62	4.04	3.54	5.34
0.025	13.94	10.66	8.30	13.42
0.050	30.24	21.36	16.92	27.30
0.075	45.10	32.50	25.94	41.10
0.100	59.53	42.85	34.56	54.76
k **(l·mol^{-1}·s^{-1})**	596.6	432.3	346.9	550.2

The observed rate constants (k_{obs}) for reaction of 3-methyl-1,2,4-dithiazol-5-one (**2**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 320 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.010	0.02218	0.02106	0.01315	0.0170
0.020	0.04373	0.03010	0.02866	0.0380
0.030	0.06368	0.06949	0.04492	0.0612
0.040	0.08649	0.08132	0.06285	0.0740
0.050	0.10240	0.10100	0.07709	0.0935
k **(l·mol^{-1}·s^{-1})**	2.03	2.11	1.62	1.87

The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-one (**3a**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 350 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	0.0643	–	0.0202	–
0.010	0.1067	0.0358	0.0443	0.0789
0.015	–	0.0468	0.0660	–
0.020	0.2002	0.0847	0.0877	0.1183
0.025	0.2527	0.105	–	–
0.030	0.2854	0.119	0.1343	0.1979
0.035	–	0.142	–	–
0.040	0.3908	0.164	–	0.2453
0.050	0.5645	0.188	–	0.2907
k **(l·mol^{-1}·s^{-1})**	10.64	3.97	4.48	5.51

The observed rate constants (k_{obs}) for reaction of 3-(4-methoxyphenyl)-1,2,4-dithiazol-5-one (**3b**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 390 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	–	0.0143	0.0109	
0.010	–	0.0277	0.0165	0.100
0.015	–	0.0459	0.0267	0.132
0.020	0.199	0.0605	0.0344	0.158
0.025	0.228	0.0810	–	
0.030	0.269	0.0914	–	0.205
0.035	–	0.110	–	
0.040	0.345	0.121	–	0.264
0.045	0.377	–	–	
0.050	0.407	–	–	0.328
k (l·mol^{-1}·s^{-1})	7.11	3.13	1.61	5.55

The observed rate constants (k_{obs}) for reaction of 3-(4-methylphenyl)-1,2,4-dithiazol-5-one (**3c**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 365 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	–	0.0129	0.0120	
0.010	0.115	0.0285	0.0260	0.0805
0.015	–	0.0418	0.0370	0.105
0.020	0.196	0.0596	0.0503	0.125
0.025	–	0.0715	–	
0.030	0.275	0.0841	–	0.166
0.035	0.313	0.0950	–	
0.040	0.361	0.111	–	0.210
0.045	0.389	0.141	–	
0.050	0.427	0.147	–	0.245
k (l·mol^{-1}·s^{-1})	7.83	3.02	2.52	4.12

The observed rate constants (k_{obs}) for reaction of 3-(4-chlorophenyl)-1,2,4-dithiazol-5-one (**3d**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 335 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	0.164	0.0656	0.0627	
0.010	0.295	0.1349	0.1142	0.2612
0.015	–	0.2023		0.3721
0.020	0.564	0.2625	0.2192	0.5274
0.025	–	0.3283		
0.030	0.838	0.3927	0.3337	0.7334
0.035	–	–		
0.040	1.113	0.5350	0.4373	0.9524
0.045	–	–		
0.050	1.331	0.6032	0.5463	1.167
k (l·mol^{-1}·s^{-1})	26.3	12.3	10.8	22.6

The observed rate constants (k_{obs}) for reaction of 3-(3-chlorophenyl)-1,2,4-dithiazol-5-one (**3e**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 365 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	–	0.0991	0.107	0.1304
0.010	0.319	0.1791	0.215	0.2386
0.015	–	0.2739	0.339	0.4000
0.020	0.626	0.3768	0.423	0.6056
0.025	0.786	0.4701	–	
0.030	0.915	0.5697	–	0.8691
0.035	1.093	–	–	
0.040	1.268	0.7606	–	1.156
0.045	–	–	–	
0.050	1.549	0.8661	–	1.341
k **(l·mol^{-1}·s^{-1})**	31.0	17.8	21.4	28.0

The observed rate constants (k_{obs}) for reaction of 3-phenoxy-1,2,4-dithiazol-5-one (**4a**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 327 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.0025	5.173	–	–	–
0.0050	11.91	–	5.628	13.75
0.0075	18.55	–	–	–
0.0100	24.53	17.1	10.60	31.00
0.0125	30.72	–	–	–
0.0150	37.00	–	16.65	48.02
0.0175	40.31	–	–	–
0.0200	48.94	33.5	22.31	63.97
0.0225	54.92	–	–	–
0.0250	60.29	–	28.17	81.60
0.0300	–	52.5	33.79	99.78
0.0350	–	–	39.79	120.9
0.0400	–	74.5	45.16	137.0
0.0450	–	–	50.46	159.3
0.0500	–	99.1	56.22	175.9
k **(l·mol^{-1}·s^{-1})**	2 430	1 882	1 125	3 626

The observed rate constants (k_{obs}) for reaction of 3-(4-methoxyphenoxy)-1,2,4-dithiazol-5-one (**4b**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 327 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	DCM	THF	TOL
0.0025	4.13			
0.0050	9.12	5.48	–	10.00
0.0075	13.90		–	
0.0100	19.25	10.73	4.12	21.23
0.0125	23.67		–	
0.0150	27.20		5.38	33.61
0.0175	29.48		–	
0.0200	32.38	21.22	13.71	48.92
0.0225	35.32		–	
0.0250	39.14		16.14	
0.0300	–	31.25	19.55	66.28
0.0350	–		27.14	
0.0400	–	37.27	30.91	89.53
0.0450	–		34.10	
0.0500	–	46.88	36.27	119.1
k (l·mol^{-1}·s^{-1})	1 587	909.1	720.9	2 362

The observed rate constants (k_{obs}) for reaction of 3-(4-methylphenoxy)-1,2,4-dithiazol-5-one (**4c**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 327 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	DCM	THF	TOL
0.0025	4.87	–	–	
0.0050	11.49	6.4	6.30	11.79
0.0075	17.93	–	–	
0.0100	30.00	14.6	12.42	25.24
0.0125	23.49	–	–	
0.0150	34.88	21.1	18.41	38.41
0.0175	–	–	–	
0.0200	46.51	30.1	24.11	54.29
0.0225	52.49	–	–	
0.0250	58.00	–	29.94	
0.0300	–	47.0	34.61	77.241
0.0350	–	–	40.33	
0.0400	–	–	45.19	101.95
0.0450	–	69.9	51.10	
0.0500	–	78.4	56.61	124.9
k (l·mol^{-1}·s^{-1})	2 306	1 550	1 148	2 515

The observed rate constants (k_{obs}) for reaction of 3-(4-chlorophenoxy)-1,2,4-dithiazol-5-one (**4d**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 327 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	DCM	THF	TOL
0.0025	7.672	–	–	
0.0050	17.07	–	10.63	26.597
0.0075	25.19	–	–	
0.0100	34.42	25.8	20.98	53.988
0.0125	44.75	–	–	
0.0150	53.58	–	32.82	80.804
0.0175	62.47	–	–	
0.0200	70.75	56.8	43.22	122.1
0.0225	79.26	–	–	
0.0250	90.02	73.6	52.25	
0.0300	–	90.4	63.78	165.9
0.0350	–	–	74.00	
0.0400	–	133.1	85.26	224.7
0.0450	–	145.4	96.06	
0.0500	–	162.8	109.0	293.7
k (l·mol^{-1}·s^{-1})	3 630	3 184	2 141	5 843

The observed rate constants (k_{obs}) for reaction of 3-(3-chlorophenoxy)-1,2,4-dithiazol-5-one (**4e**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 325 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	DCM	THF	TOL
0.0025	7.97	–	–	
0.0050	14.54	10.04	11.85	23.481
0.0075	23.11	–	–	
0.0100	34.61	27.99	21.73	53.181
0.0125	43.95	–	–	
0.0150	54.42	44.71	33.72	73.613
0.0175	63.67	–	–	
0.0200	74.62	61.22	45.61	110.0
0.0225	84.03	–	–	
0.0250	94.65	80.17	55.69	
0.0300	–	96.36	67.15	155.5
0.0350	–	118.65	81.43	
0.0400	–	135.71	91.50	219.6
0.0450	–	161.31	105.4	
0.0500	–	189.78	122.1	295.8
k (l·mol^{-1}·s^{-1})	3 932	3 475	2 333	5 907

The observed rate constants (k_{obs}) for reaction of 3-[(3-trifluoromethyl)phenoxy]-1,2,4-dithiazol-5-one (**4f**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 331 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.0025	11.50	–	–	
0.0050	21.21	12.50	6.988	22.651
0.0075	29.80	–	–	
0.0100	41.70	32.88	22.47	
0.0125	53.46	–	–	
0.0150	63.44	57.37	36.20	89.171
0.0175	72.52	–	–	
0.0200	86.42	74.20	48.28	136.4
0.0225	95.94	–	–	
0.0250	111.0	98.59	62.25	155.0
0.0300	–	120.8	76.53	
0.0350	–	144.9	–	
0.0400	–	176.5	104.68	258.1
0.0450	–	200.2	–	
0.0500	–	225.2	138.53	328.6
k (l·mol^{-1}·s^{-1})	4 372	4 283	2 624	6 737

The observed rate constants (k_{obs}) for reaction of 3-phenylthio-1,2,4-dithiazol-5-one (**5a**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	–	1.354	2.480	2.057
0.010	4.889	2.689	3.981	3.998
0.015	–	4.020	4.592	5.999
0.020	7.847	4.990	5.735	7.996
0.025	9.904	6.312	6.996	10.061
0.030	12.256	7.640	–	13.200
0.035	13.996	8.526	9.281	15.469
0.040	16.091	9.653	10.417	17.410
0.045	18.206	10.957	11.483	19.267
0.050	19.670	12.252	13.955	20.067
k (l·mol^{-1}·s^{-1})	384	237.6	238.6	426.2

The observed rate constants (k_{obs}) for reaction of 3-(4-methylphenylthio)-1,2,4-dithiazol-5-one (**5c**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 320 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	DCM	THF	TOL
0.005	1.684	0.966	1.672	1.393
0.01	2.982	2.008	2.727	2.672
0.015	4.598	2.945	3.921	4.003
0.02	6.228	3.842	4.869	5.277
0.025	7.667	4.721	6.102	6.609
0.03	10.125	5.724	–	7.932
0.035	–	6.800	7.443	9.338
0.04	12.944	7.614	8.471	10.551
0.045	–	8.666	9.552	11.855
0.05	16.081	9.269	10.863	12.875
k **(l·mol^{-1}·s^{-1})**	327	187.3	195.9	259.2

The observed rate constants (k_{obs}) for reaction of 3-(4-chlorophenylthio)-1,2,4-dithiazol-5-one (**5d**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	DCM	THF	TOL
0.005	3.503	2.584	3.965	3.946
0.01	6.799	5.484	6.271	8.145
0.015	10.535	7.815	8.248	12.273
0.02	14.013	10.616	10.844	16.400
0.025	17.159	12.801	12.510	20.520
0.03	22.523	15.091	–	24.796
0.035	25.983	18.063	16.704	29.149
0.04	–	21.021	18.517	33.612
0.045	32.861	25.282	20.802	37.165
0.05	–	26.383	22.828	40.826
k **(l·mol^{-1}·s^{-1})**	748	537.5	415.2	829.4

The observed rate constants (k_{obs}) for reaction of 3-(3-nitro-phenylthio)-1,2,4-dithiazol-5-one (**5g**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	DCM	THF	TOL
0.005	8.007	8.268	7.962	21.307
0.01	15.407	18.085	14.445	40.187
0.015	21.963	29.164	19.484	58.601
0.02	30.254	37.699	26.562	80.550
0.025	37.849	47.650	31.804	100.05
0.03	–	55.445	–	117.86
0.035	53.587	68.611	50.414	136.41
0.04	–	76.859	57.354	157.78
0.045	68.098	84.548	62.288	169.58
0.05	–	90.345	66.230	193.91
k **(l·mol^{-1}·s^{-1})**	1515	1870	1369	3807

The observed rate constants (k_{obs}) for reaction of 3-(4-nitrophenylthio)-1,2,4-dithiazol-5-one (**5h**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	7.873	9.259	6.579	22.017
0.01	16.194	20.287	15.115	44.539
0.015	25.055	32.996	20.318	65.233
0.02	32.396	42.861	27.924	84.764
0.025	32.916	52.106	32.265	110.01
0.03	–	64.206	–	126.43
0.035	52.192	73.361	46.783	148.99
0.04	–	83.310	50.836	173.53
0.045	71.129	94.193	60.673	194.79
0.05	–	97.678	69.338	222.70
k (l·mol^{-1}·s^{-1})	1576	2022	1335	4374

The observed rate constants (k_{obs}) for reaction of 1,2,4-dithiazol-3-thione (**6**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 400 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^2 \cdot k_{obs}$, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.01	–	0.119	–	
0.02	–	0.274	0.057	
0.03	0.37	0.446	–	
0.04	0.47	0.577	–	
0.05	0.587	0.772	–	
0.06	0.702	0.990	–	
0.07	0.853	1.16	0.119	
0.08	0.975	1.36	0.137	
0.09	1.09	1.55	0.162	
0.10	1.23	1.66	0.174	0.691
$10^2 \cdot k$ (l·mol^{-1}·s^{-1})	12.36	17.78	1.52	6.91

The observed rate constants (k_{obs}) for reaction of 1,2,4-dithiazol-3-thione(**6**) with triethyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 400 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.010	14.32			
0.015	21.24			
0.020	28.24			
0.025	35.93			
0.035	47.43			
0.040	59.07			
0.045	62.34			
0.050	70.83			
k (l·mol^{-1}·s^{-1})	1 408			

The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-thione (**7a**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 465 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^4 \cdot k_{obs}$, (s^{-1})			
	ACN	DCM	THF	TOL
0.005	–		1.32	–
0.01	10.6	2.28	2.38	–
0.015	–		4.17	–
0.02	18.6	4.07	5.23	7.27
0.025	–		6.78	–
0.03	26.0	6.43	8.04	–
0.035	–		9.20	–
0.04	33.1	9.03	10.8	14.3
0.045	–		12.0	–
0.05	41.1	10.9	13.1	–
0.06	46.3		–	20.9
0.07	57.7		–	–
0.08	68.5		–	27.0
0.09	80.2		–	–
0.10	82.1		–	31.9
k (l·mol^{-1}·s^{-1})	0.0828	0.0222	0.0266	0.0310

The observed rate constants (k_{obs}) for reaction of 3-(4-methoxyphenyl)-1,2,4-dithiazol-5-thione (**7b**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 450 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^4 \cdot k_{obs}$, (s^{-1})			
	ACN	DCM	THF	TOL
0.005	–			–
0.01	5.62			–
0.015	–			–
0.02	10.7	6.75	4.12	3.26
0.025	–			–
0.03	18.2			4.61
0.035	–			–
0.04	22.4	9.03	7.71	6.42
0.045	–			–
0.05	29.2	10.9	9.24	8.72
0.06	34.0	12.8		10.9
0.07	38.9		12.4	12.7
0.08	47.4	16.6		14.5
0.09	51.8			17.1
0.1	56.1	21.2	24.6	18.2
k (l·mol^{-1}·s^{-1})	0.0571	0.0184	0.0250	0.0196

The observed rate constants (k_{obs}) for reaction of 3-(4-methylphenyl)-1,2,4-dithiazol-5-thione (**7c**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 460 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^4 \cdot k_{obs}$, (s^{-1})			
	ACN	DCM	THF	TOL
0.005	–		–	
0.01	6.05		1.70	
0.015	–		3.11	
0.02	11.8	5.76	–	3.41
0.025	–		4.90	
0.03	17.6		5.96	5.00
0.035	–		6.16	
0.04	22.3	8.89	7.32	6.65
0.045	–		8.22	
0.05	26,2		9.25	8.57
0.06	31.3	11.7	–	
0.07	38.6		–	
0.08	44.3	15.5	–	
0.09	49.0		–	15.1
0.10	52.5	18.2	–	16.7
k (l·mol^{-1}·s^{-1})	0.0524	0.0158	0.0179	0.0167

The observed rate constants (k_{obs}) for reaction of 3-(4-chlorophenyl)-1,2,4-dithiazol-5-thione (**7d**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 450 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	DCM	THF	TOL
0.005	–			
0.01	0.00230			0.00092
0.015	–			
0.02	0.00466	0.00219	0.00190	0.00190
0.025	–			
0.03	0.071.4			0.00285
0.035	–			
0.04	0.087.2		0.00356	0.00397
0.045	–			
0.05	0.0113	0.00499	0.00405	0.00587
0.06	0.0136	0.00589		
0.07	–		0.00583	
0.08	0.0186	0.00875		
0.09	0.0210			0.0082
0.1	–	0.00896	0.00765	0.0104
k (l·mol^{-1}·s^{-1})	0.2325	0.0909	0.0722	0.0997

The observed rate constants (k_{obs}) for reaction of 3-(3-chlorophenyl)-1,2,4-dithiazol-5-thione (**7e**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 450 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.005	–			
0.01	0.00303		0.00135	0.00141
0.015	–			
0.02	0.00691	0.00240		0.00309
0.025	–			
0.03	0.0104	0.00324	0.00355	0.00447
0.035	–			
0.04	0.0114			0.00608
0.045	–			
0.05	0.0189		0.00570	0.00739
0.06	0.0226	0.00643		
0.07	0.0249	0.00722	0.00645	
0.08	0.0283			
0.09	0.0314	0.0108		0.0137
0.1	0.0345		0.0122	0.0152
k (l·mol^{-1}·s^{-1})	0.3566	0.1155	0.1139	0.1530

The observed rate constants (k_{obs}) for reaction of 3-dimethylamino-1,2,4-dithiazol-3-thione (**9**) with triphenyl phosphite in acetonitrile, dichloromethane, THF and toluene at 25 °C (λ = 400 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs}, (s^{-1})			
	ACN	**DCM**	**THF**	**TOL**
0.01	0.02267	0.02091	0.00994	0.0201
0.02	0.04957	0.03033	–*	0.0324
0.03	0.07573	0.06859	–*	0.0534
0.04	0.1022	0.09060	–*	0.0717
0.05	0.1273	0.1093	–*	0.0860
k (l·mol^{-1}·s^{-1})	2.62	2.37	0.99	1.71

* Consecutive reaction appears.

The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-one (**3a**) with tris(subst. phenyl) phosphites in acetonitrile at 25 °C (λ = 379 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^4 \cdot k_{obs}$, (s^{-1})				
	3-Cl	**4-Cl**	**H**	**4-CH$_3$**	**4-OCH$_3$**
0.005	28.33	–	643	–	1429
0.01	39.88	30.72	1067	1938	2991
0.015		33.84	–	2969	4565
0.02	59.23	40.29	2002	4135	6097
0.025	82.60	44.35	–	5014	7765
0.03	93.04	–	2854	–	9297
0.035		47.96	–	7085	
0.04	123.3	52.02	3908	8180	12225
0.045		–	–	–	
0.05	157.7	54.43	5645	9753	14513
$10^4 \cdot k$ (l·mol^{-1}·s^{-1})	2880	6055	106400	198200	295900

The observed rate constants (k_{obs}) for reaction of 3-phenoxy-1,2,4-dithiazol-5-one (**4a**) with tris(subst. phenyl) phosphites in acetonitrile at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})				
	3-Cl	**4-Cl**	**H**	**4-CH$_3$**	**4-OCH$_3$**
0.0025	–	–	5.173	–	–
0.005	2.161	3.398	11.91	12.81	17.81
0.0075	–	–	18.55	–	–
0.01	4.672	7.908	24.53	30.68	40.43
0.0125	–	–	30.72	–	–
0.015	–	12.45	37.00	48.42	69.25
0.0175	–	–	40.31	–	–
0.02	7.183	17.70	48.94	79.88	95.33
0.0225	–	–	54.92	–	–
0.025	9.411	22.15	60.29	106.2	127.0
0.03	11.45	27.29	–	128.8	156.0
0.04	16.66	38.07	–	174.4	187.5
0.05	20.73	46.77	–	231.1	–
k (l·mol^{-1}·s^{-1})	410.5	978.4	2430	4899	5097

The observed rate constants (k_{obs}) for reaction of 3-phenylthio-1,2,4-dithiazol-5-one (**5a**) with tris(subst. phenyl) phosphites in acetonitrile at 25 °C (λ = 340 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})				
	3-Cl	**4-Cl**	**H**	**4-CH$_3$**	**4-OCH$_3$**
0.005	0,2437	0.883	–	3.433	4.849
0.01	0.5569	1.566	4.889	7.086	8.667
0.015	–	2.001	–	10.91	14.05
0.02	1.254	2.671	7.847	14.21	18.71
0.025	1.459	3.14	9.904	18.02	25.50
0.03	1,784	3.901	12.256	21.50	27.94
0.035	–	–	13.996	–	–
0.04	2.349	–	16.091	28.99	39.76
0.045	–	–	18.206	–	–
0.05	2.796	6.291	19.670	36.54	48.16
k (l·mol^{-1}·s^{-1})	57.24	120.0	384	732.9	984.2

The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-thione (**7a**) with tris(subst. phenyl) phosphites in acetonitrile at 25 °C (λ = 379 nm).

$c_{phosphite}$, (mol·l^{-1})	$10^4 \cdot k_{obs}$, (s^{-1})				
	3-Cl	**4-Cl**	**H**	**4-CH$_3$**	**4-OCH$_3$**
0.01	4.69	–	10.6	29.2	166
0.02	1.27	2.30	18.6	66.5	344
0.03	1.48	3.95	26.0	96.2	524
0.04	2.06	5.51	33.1	128	635
0.05	2.35	7.23	41.1	158	887
0.06	3.47	8.64	46.3	172	1095
0.07	–	9.59	57.7	198	1254
0.08	3.95	10.9	68.5	225	1415
0.09	–	–	80.2	248	1601
0.10	2.59	–	82.1	274	1709
$10^4 \cdot k$ (l·mol^{-1}·s^{-1})	48.0	143.6	828	2631	17710

The observed rate constants (k_{obs}) for reaction of 3-(subst.phenoxy)-1,2,4-dithiazol-5-ones (**4a-f**) with triphenyl phosphite in acetonitrile at 25 °C.

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})					
	4a	**4b**	**4c**	**4d**	**4e**	**4f**
0.0025	5.173	4.13	4.87	7.672	7.97	11.50
0.005	11.91	9.12	11.49	17.07	14.54	21.21
0.0075	18.55	13.90	17.93	25.19	23.11	29.80
0.01	24.53	19.25	30.00	34.42	34.61	41.70
0.0125	30.72	23.67	23.49	44.75	43.95	53.46
0.015	37.00	27.20	34.88	53.58	54.42	63.44
0.0175	40.31	29.48	–	62.47	63.67	72.52
0.02	48.94	32.38	46.51	70.75	74.62	86.42
0.0225	54.92	35.32	52.49	79.26	84.03	95.94
0.025	60.29	39.14	58.00	90.02	94.65	111.0
k (l·mol^{-1}·s^{-1})	2430	1587	2306	3630	3932	4372

The observed rate constants (k_{obs}) for reaction of 3-(subst.phenylthio)-1,2,4-dithiazol-5-ones (**5a,c,d,g,h**) with triphenyl phosphite in acetonitrile at 25 °C.

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})				
	5a	**5c**	**5d**	**5g**	**5h**
0.005	–	1.684	3.503	8.007	7.873
0.01	4.889	2.982	6.799	15.407	16.194
0.015	–	4.598	10.535	21.963	25.055
0.02	7.847	6.228	14.013	30.254	32.396
0.025	9.904	7.667	17.159	37.849	32.916
0.03	12.256	10.125	22.523	–	–
0.035	13.996	–	25.983	53.587	52.192
0.04	16.091	12.944	–	–	–
0.045	18.206	–	32.861	68.098	71.129
0.05	19.670	16.081	–	–	–
k (l·mol^{-1}·s^{-1})	384	327	748	1515	1576

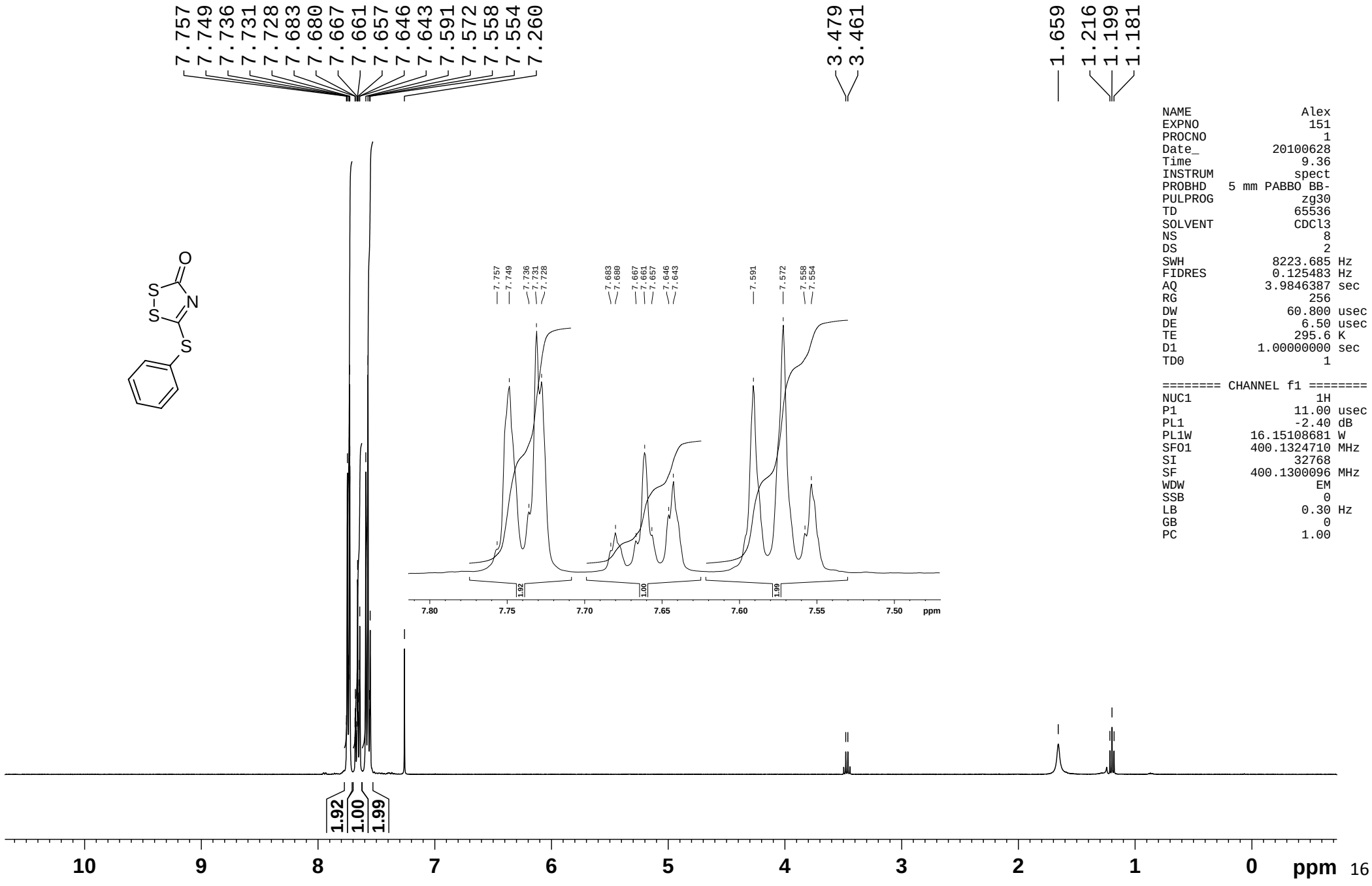
The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-thione (**7a**) with tris(subst. phenyl) phosphines in acetonitrile at 25 °C (λ = 425 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	4-Cl	**H**	**4-CH$_3$**	**4-OCH$_3$**
0.001	0.5658		53.69	116.3
0.002	1.145		106.26	234.48
0.003	1.685		174.74	383.83
0.004	2.266			515.55
0.005	2.783	49.88	294.53	665.42
0.01		95.39		
0.015		149.69		
0.02		200.24		
0.025		263.25		
k (l·mol^{-1}·s^{-1})	555.5	10630	58310	137900

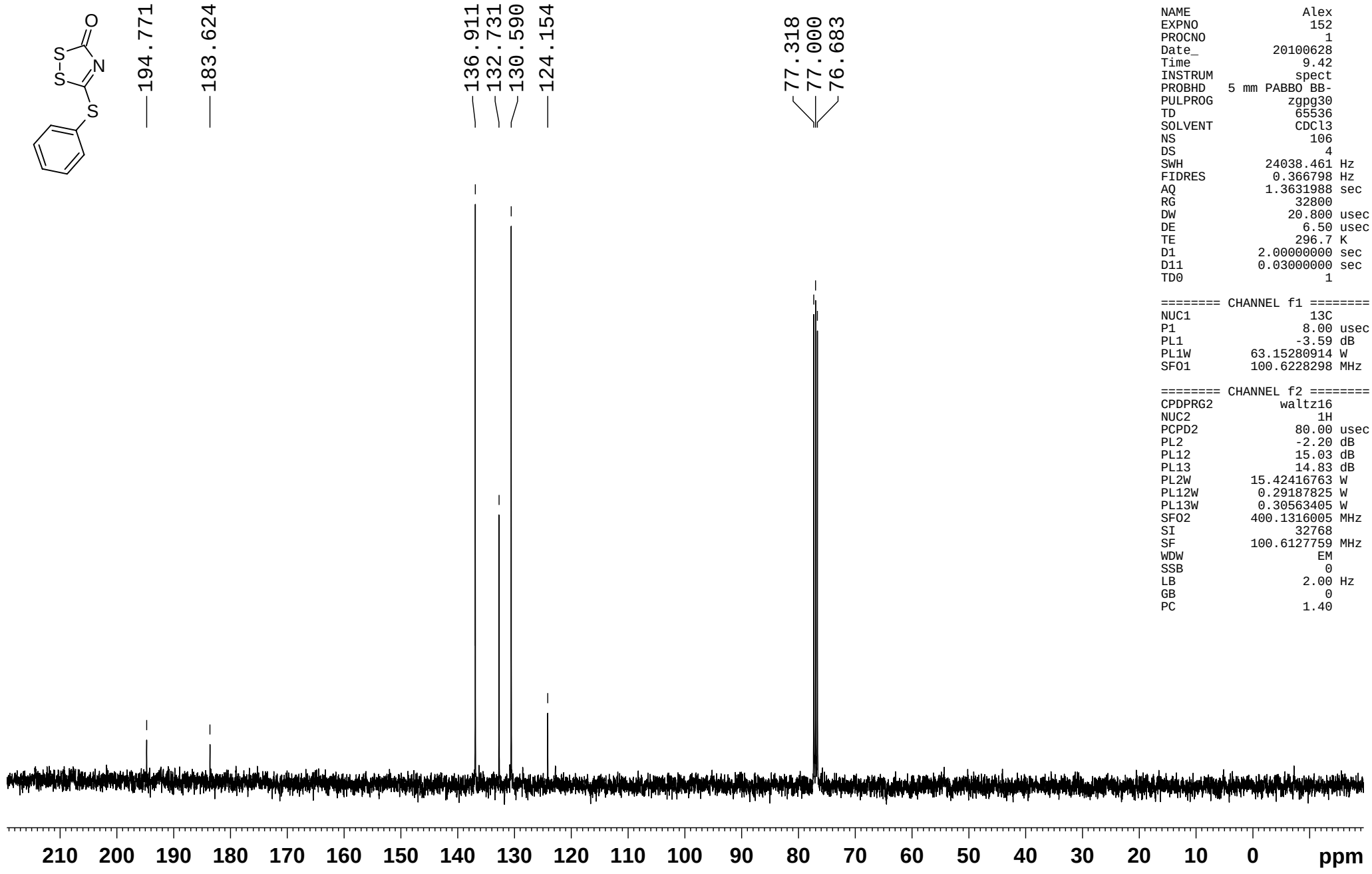
The observed rate constants (k_{obs}) for reaction of 3-phenyl-1,2,4-dithiazol-5-thione (**7a**) with triphenylphosphine, methyl diphenylphosphonite, dimethyl phenylphosphonite, trimethylphosphite in acetonitrile at 25 °C (λ = 425 nm).

$c_{phosphite}$, (mol·l^{-1})	k_{obs} , (s^{-1})			
	PPh_3	**$PPh_2(OMe)$**	**$PPh(OMe)_2$**	**$P(OMe)_3$**
0.001		130.15	82.892	
0.002		256.89	190.56	
0.003		419.79	313.49	
0.004		562.21	433.23	
0.005		783.06	558.9	
0.01	103.31			11.55
0.02	220.79			22.20
0.03	348.26			33.80
0.04	480.75			45.31
0.05	608.65			57.04
k (l·mol^{-1}·s^{-1})	12 710	161 100	119 500	1 141

3-phenylthio-1,2,4-dithiazole-5-one (5a)



3-phenylthio-1,2,4-dithiazole-5-one (5a)

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EXPNO                 152
PROCNO                  1
Date_            20100628
Time                 9.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     106
DS                       4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   32800
DW                20.800 usec
DE                 6.50 usec
TE                296.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -3.59 dB
PL1W         63.15280914 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.20 dB
PL12               15.03 dB
PL13               14.83 dB
PL2W         15.42416763 W
PL12W         0.29187825 W
PL13W         0.30563405 W
SFO2        400.1316005 MHz
SI                 32768
SF          100.6127759 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
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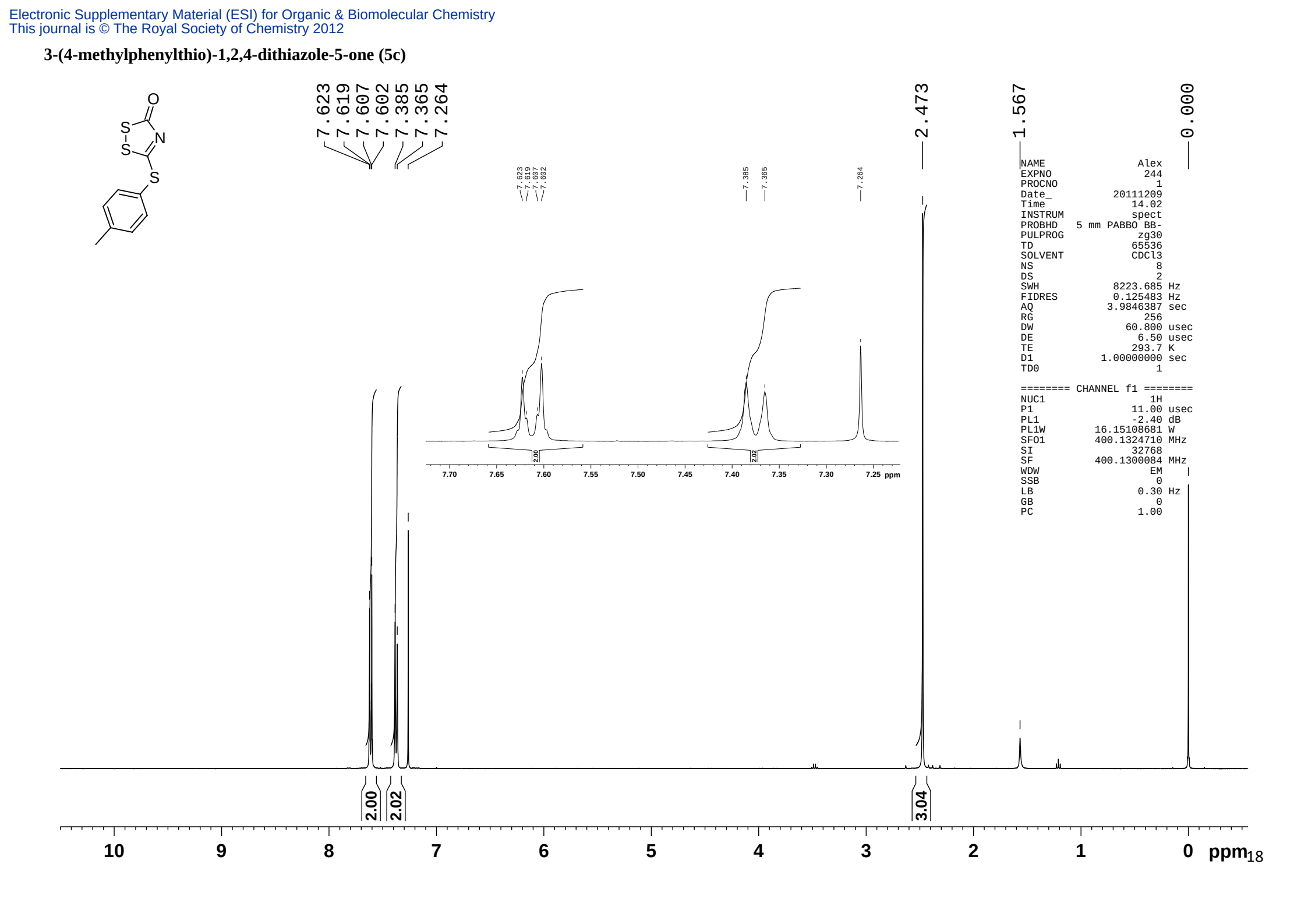
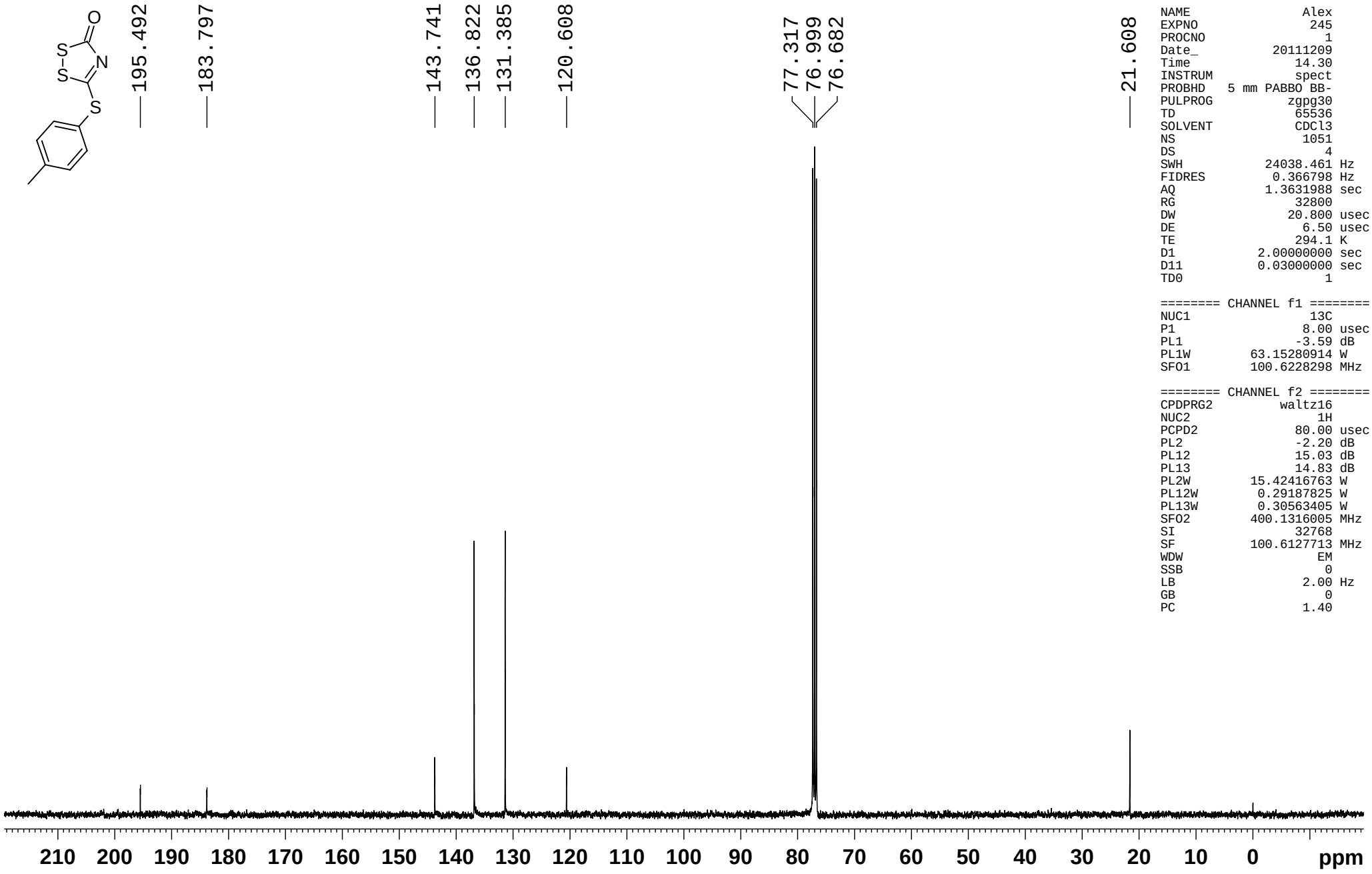
3-(4-methylphenylthio)-1,2,4-dithiazole-5-one (5c)



NAME	Alex
EXPNO	244
PROCNO	1
Date_	20111209
Time	14.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	256
DW	60.800 usec
DE	6.50 usec
TE	293.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.00 usec
PL1	-2.40 dB
PL1W	16.15108681 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300084 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

3-(4-methylphenylthio)-1,2,4-dithiazole-5-one (5c)

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NAME                Alex
EXPNO                245
PROCNO                 1
Date_           20111209
Time                14.30
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1051
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 32800
DW                20.800 usec
DE                 6.50 usec
TE                294.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
PL1               -3.59 dB
PL1W        63.15280914 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -2.20 dB
PL12               15.03 dB
PL13               14.83 dB
PL2W        15.42416763 W
PL12W        0.29187825 W
PL13W        0.30563405 W
SFO2       400.1316005 MHz
SI                 32768
SF         100.6127713 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
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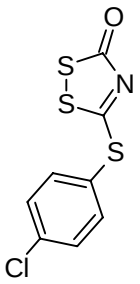
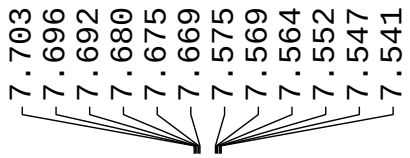
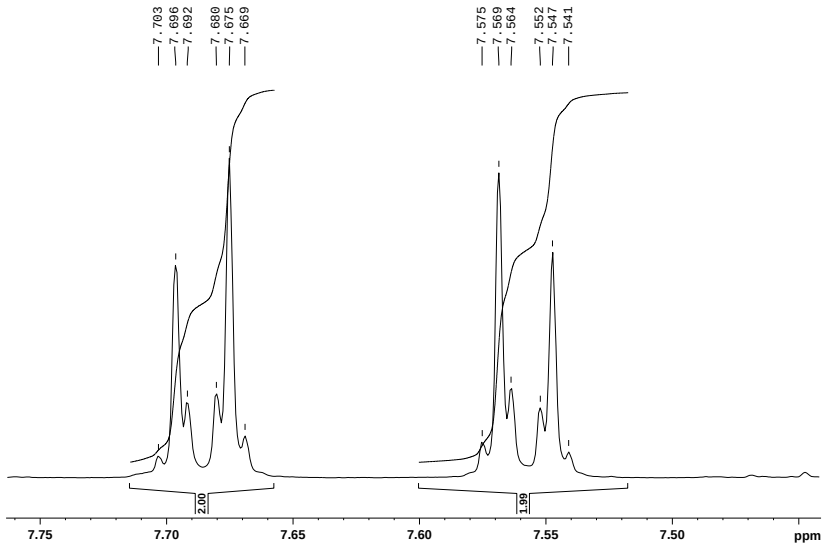
3-(4-chlorophenylthio)-1,2,4-dithiazole-5-one (5d





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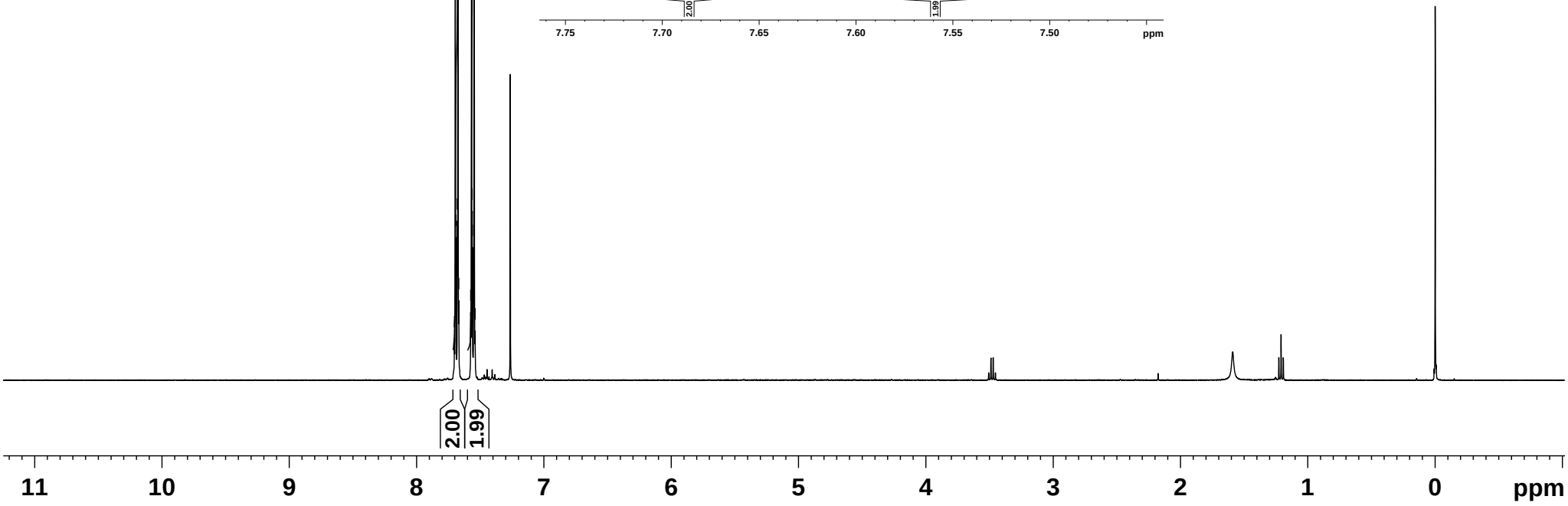
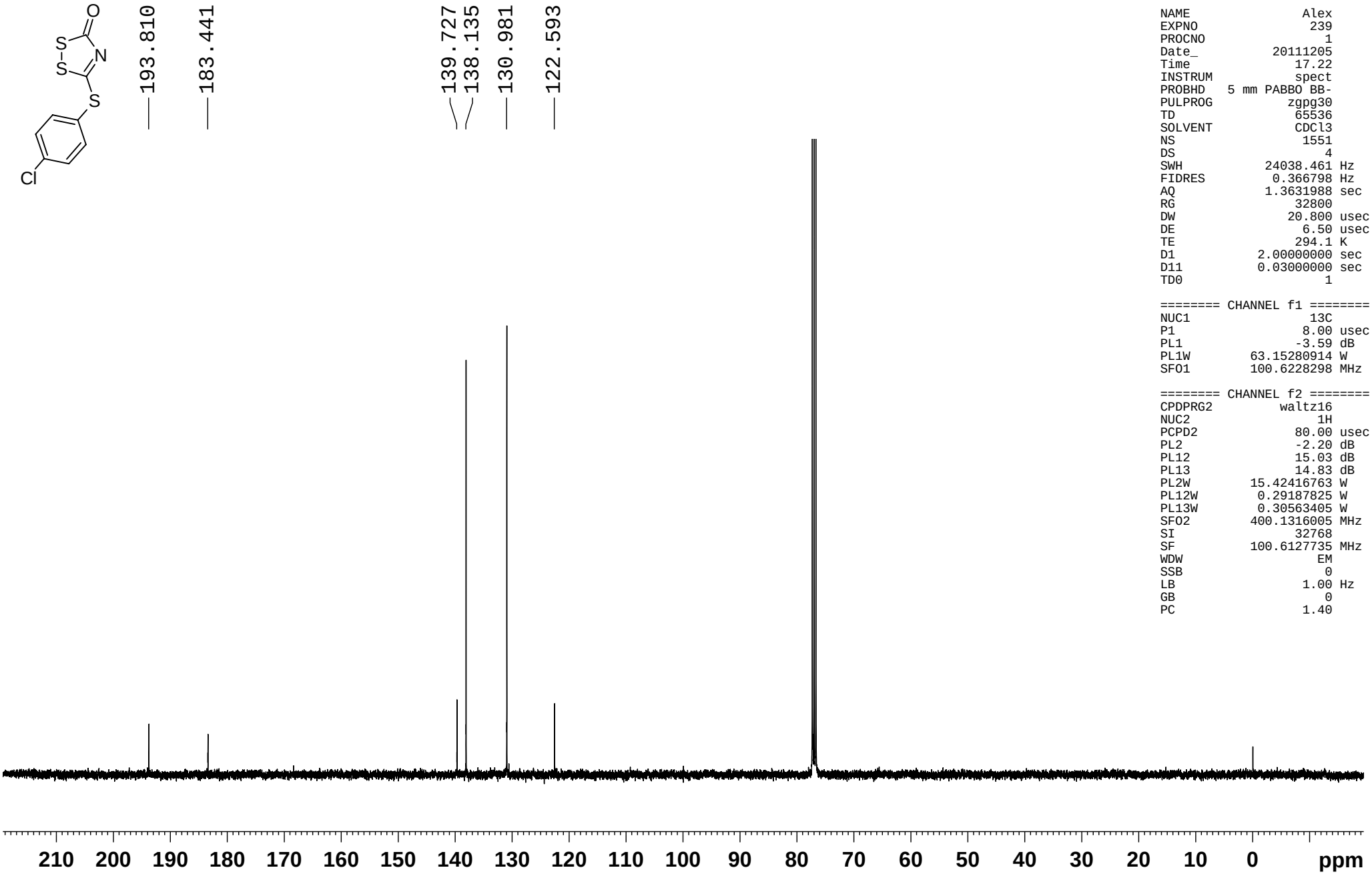
EXPNO                237
PROCNO                 1
Date_           20111205
Time               16.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.50 usec
TE                293.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.00 usec
PL1               -2.40 dB
PL1W        16.15108681 W
SFO1        400.1324710 MHz
SI                 32768
SF          400.1300079 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



3-(4-chlorophenylthio)-1,2,4-dithiazole-5-one (5d)




```
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PROCNO                 1
Date_           20111205
Time               17.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1551
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                32800
DW               20.800 usec
DE                6.50 usec
TE               294.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
PL1               -3.59 dB
PL1W        63.15280914 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -2.20 dB
PL12               15.03 dB
PL13               14.83 dB
PL2W        15.42416763 W
PL12W        0.29187825 W
PL13W        0.30563405 W
SFO2       400.1316005 MHz
SI                32768
SF         100.6127735 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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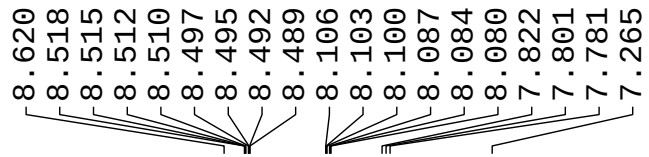
3-(3-nitrophenylthio)-1,2,4-dithiazole-5-one 5g




```
NAME                Alex
EXPNO                231
PROCNO                 1
Date_           20111020
Time               15.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   287
DW                60.800 usec
DE                 6.50 usec
TE                294.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.00 usec
PL1               -2.40 dB
PL1W        16.15108681 W
SFO1        400.1324710 MHz
SI                 32768
SF          400.1300096 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
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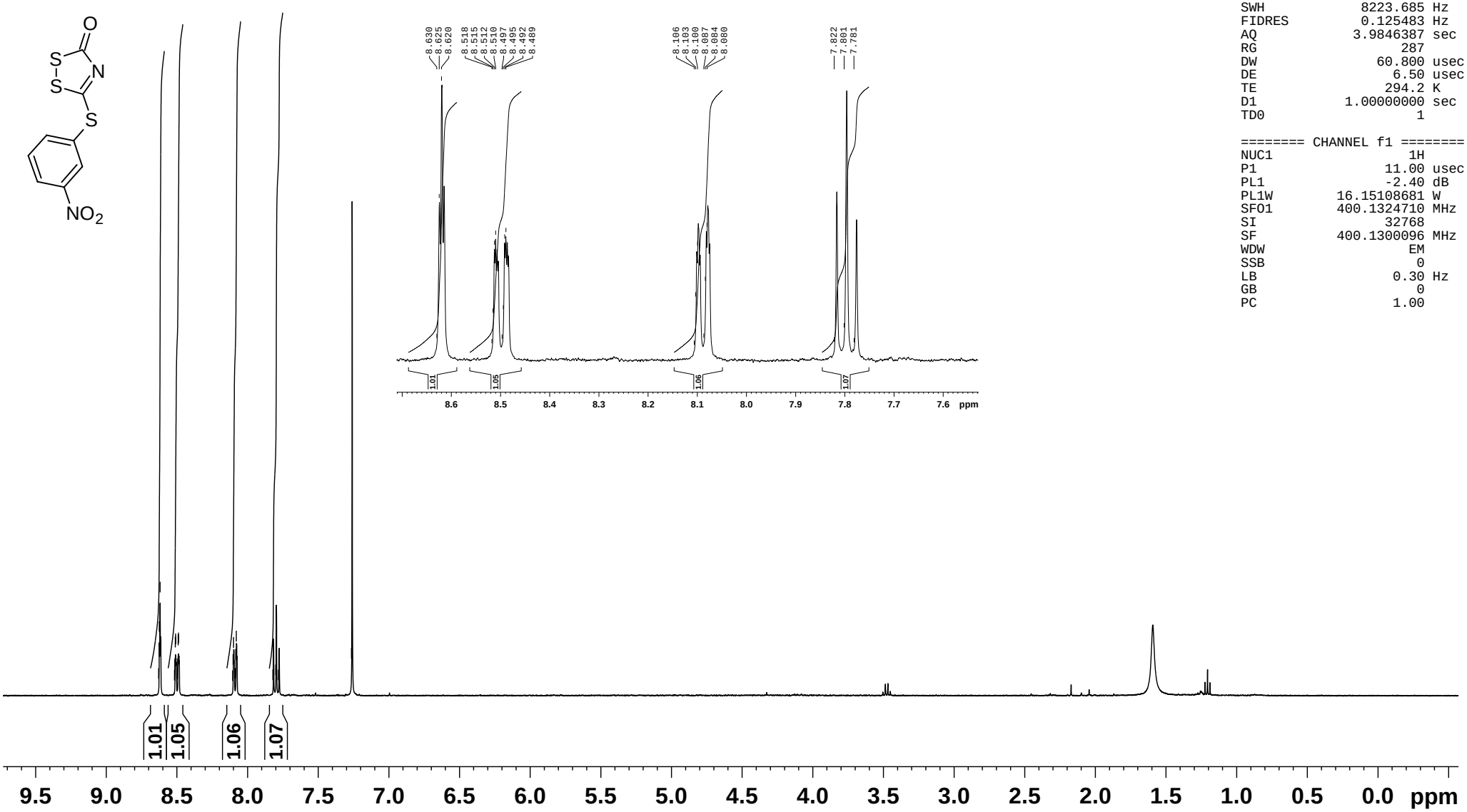
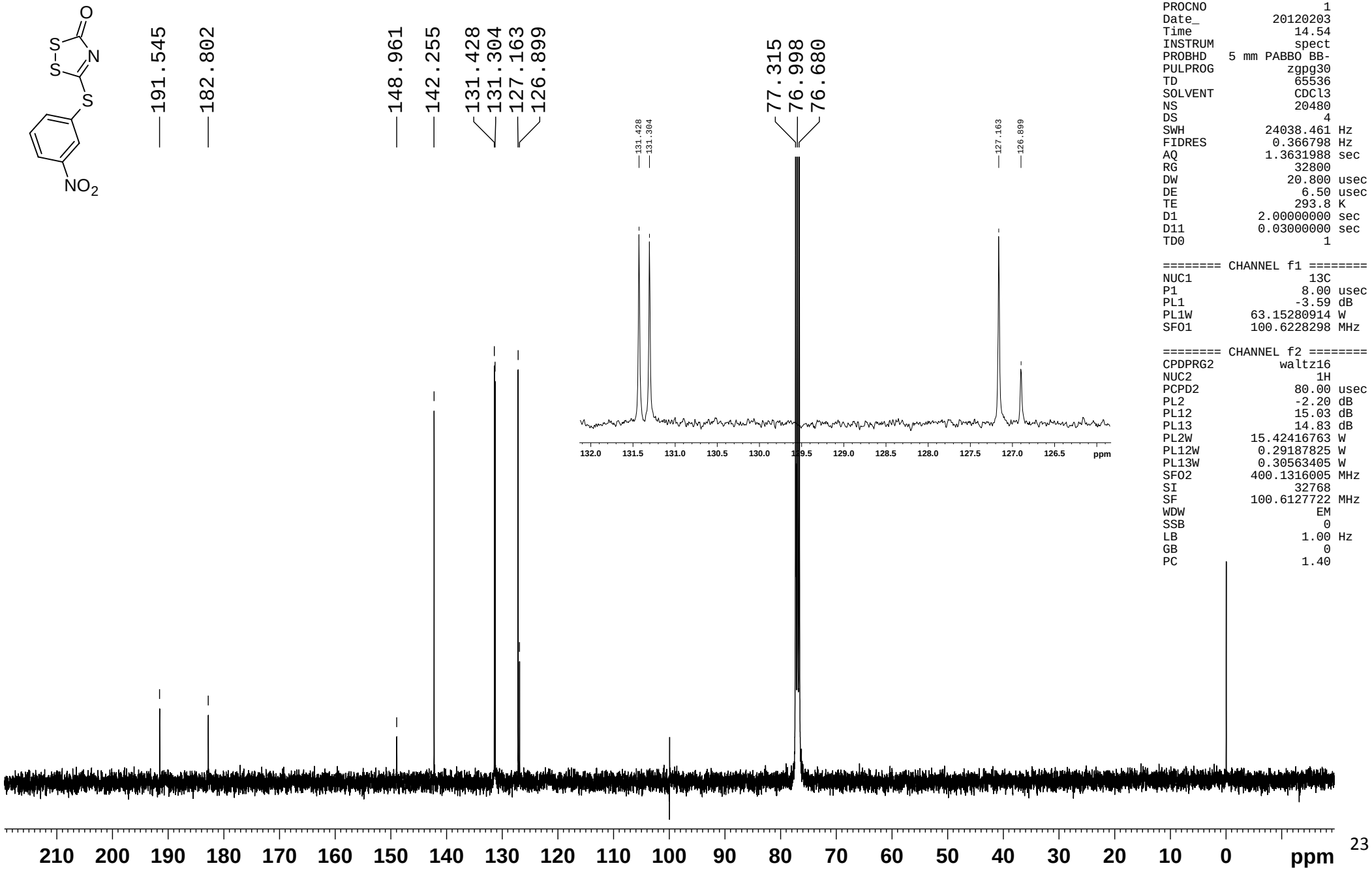
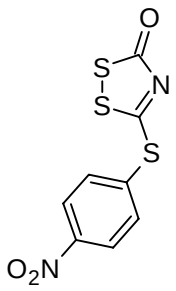
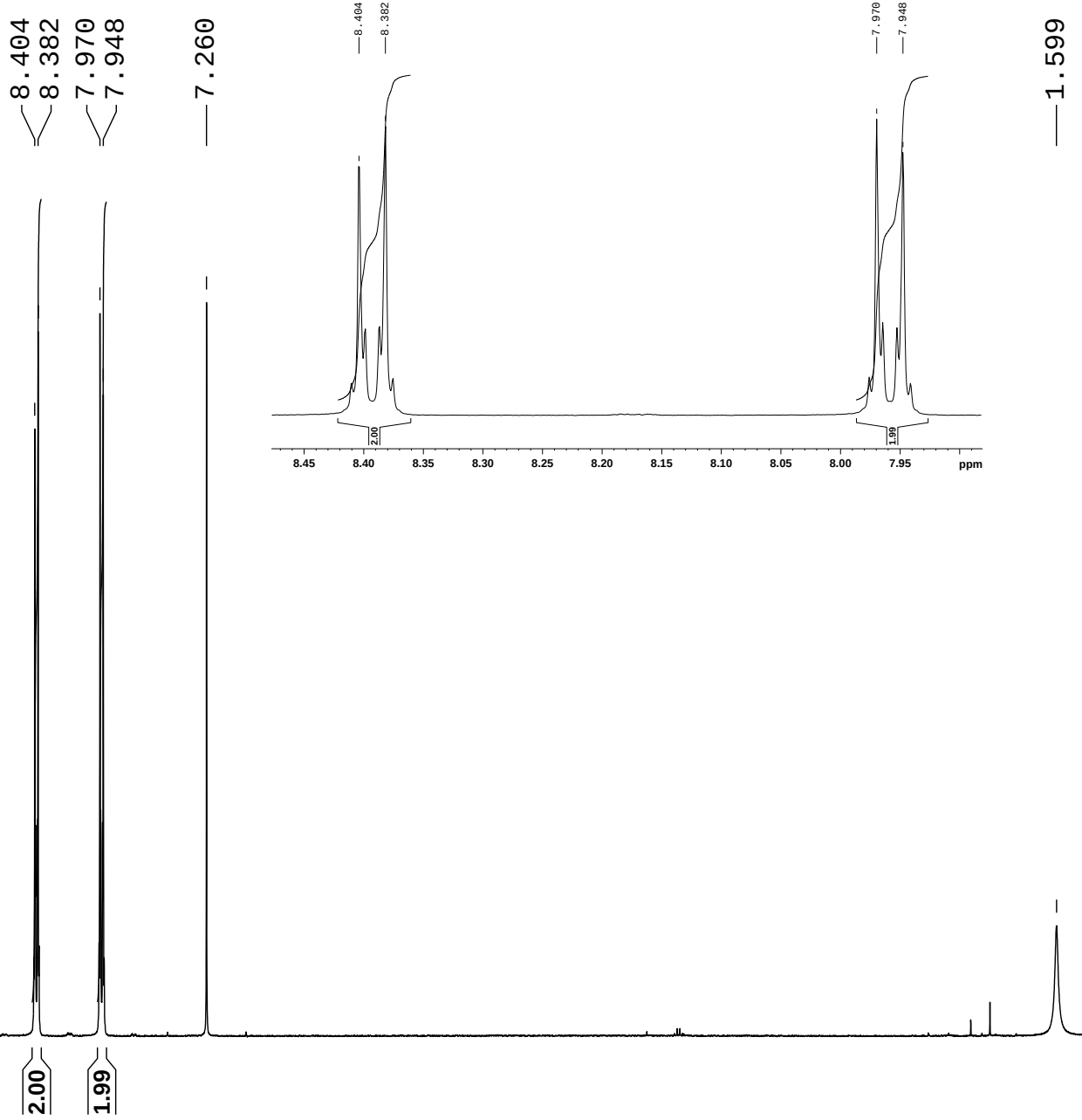


3-(3-nitrophenylthio)-1,2,4-dithiazole-5-one 5g



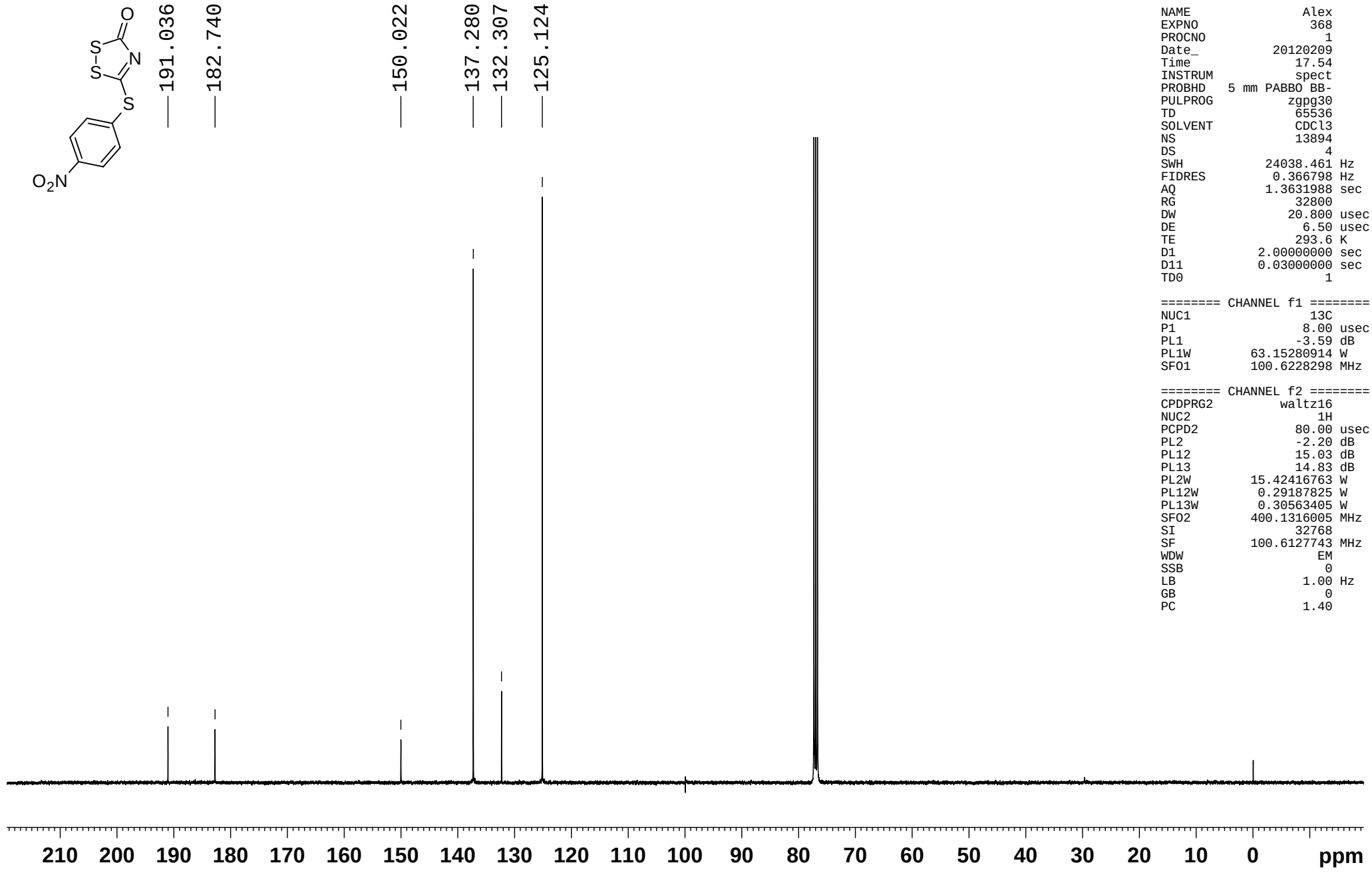
3-(4-nitrophenylthio)-1,2,4-dithiazole-5-one (5h)





NAME	Alex
EXPNO	223
PROCNO	1
Date_	20111012
Time	15.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	322
DW	60.800 usec
DE	6.50 usec
TE	294.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.00 usec
PL1	-2.40 dB
PL1W	16.15108681 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

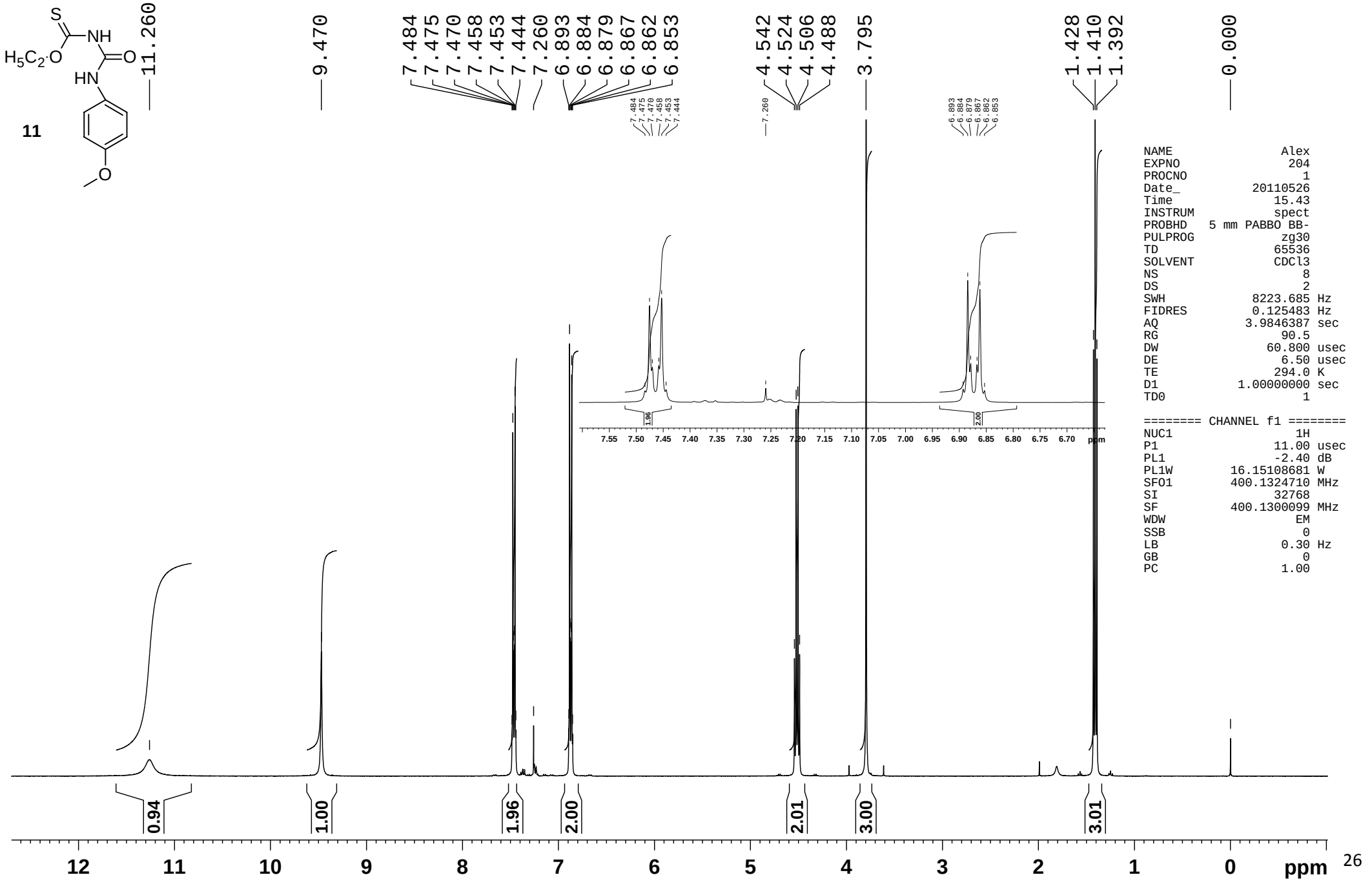
3-(4-nitrophenylthio)-1,2,4-dithiazole-5-one (5h)

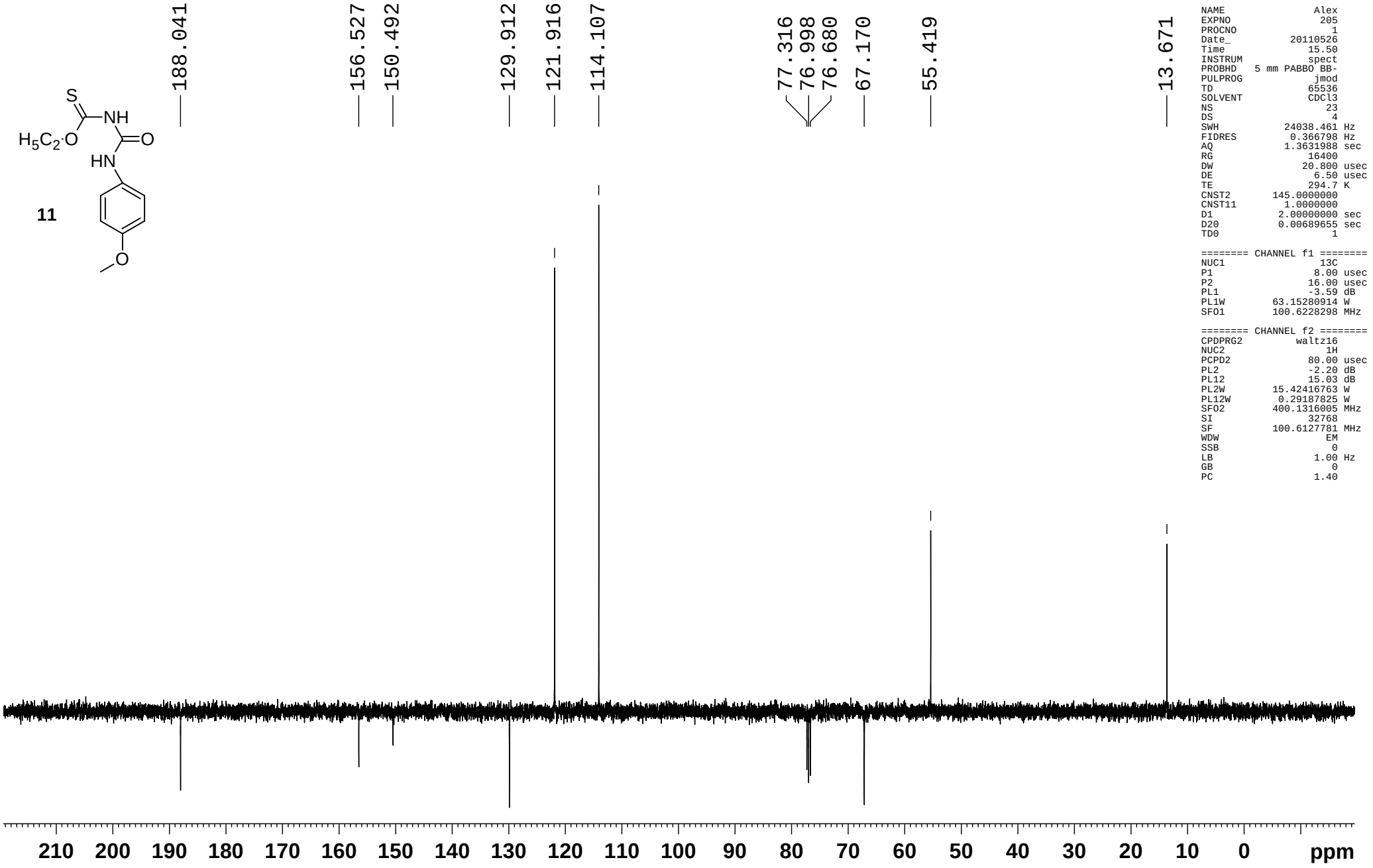


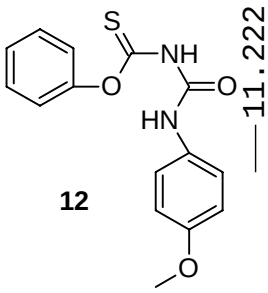

```
NAME                Alex
EXPNO                368
PROCNO                 1
Date_           20120209
Time               17.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                13894
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                32800
DW               20.800 usec
DE                6.50 usec
TE                293.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -3.59 dB
PL1W        63.15280914 W
SFO1       100.6228298 MHz

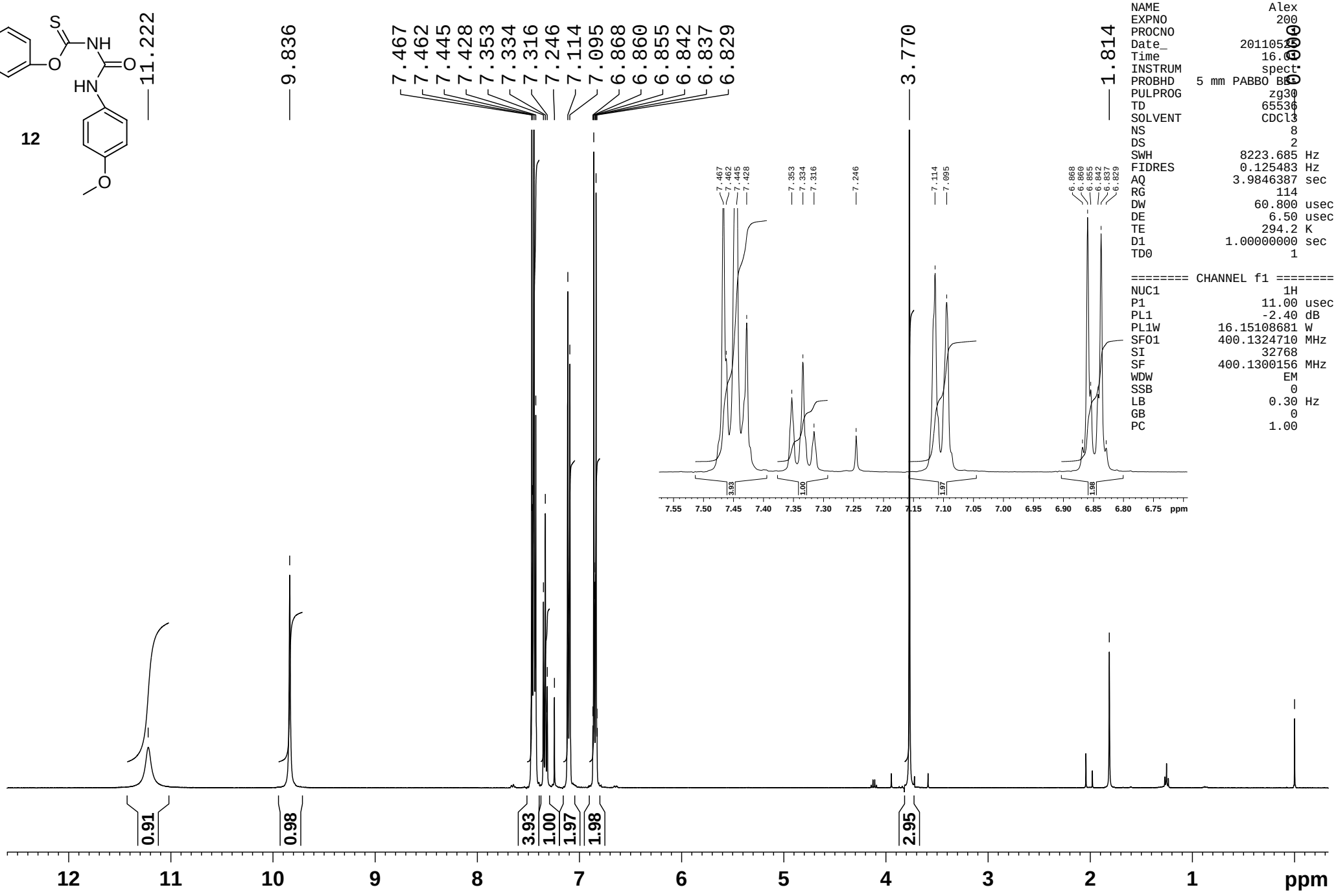
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -2.20 dB
PL12               15.03 dB
PL13               14.83 dB
PL2W        15.42416763 W
PL12W        0.29187825 W
PL13W        0.30563405 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127743 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```





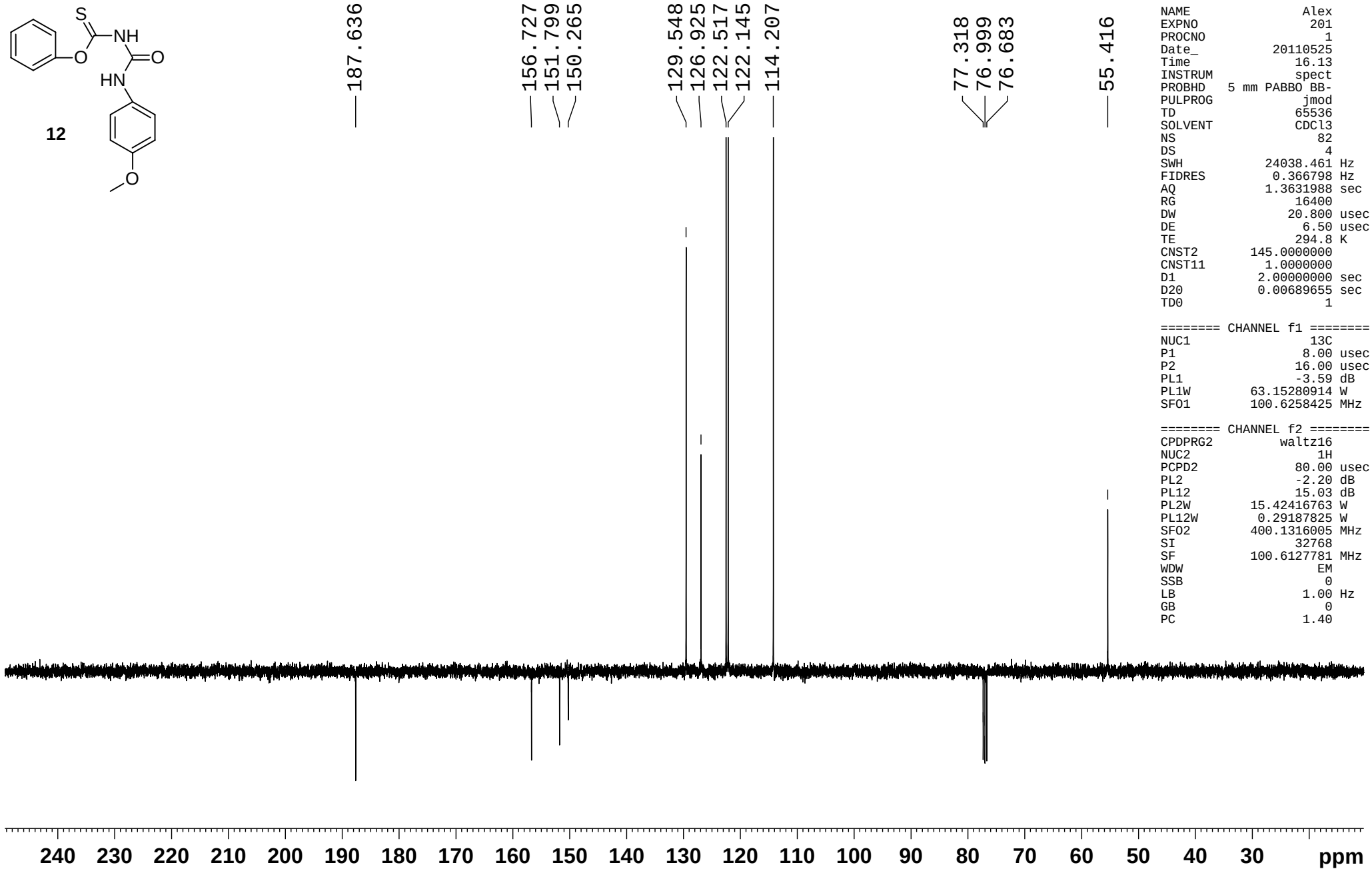


12

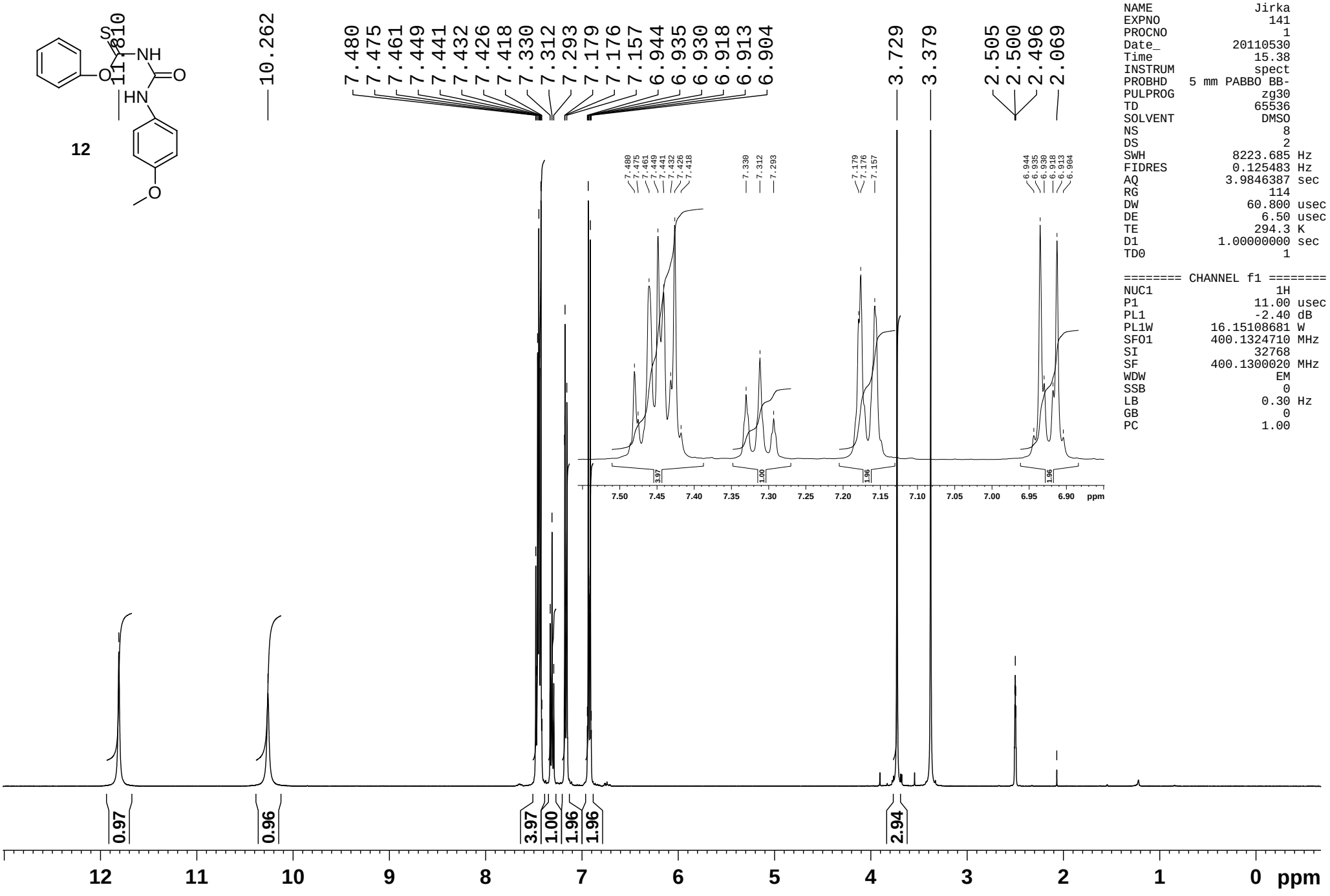



```
NAME                 Alex
EXPNO                 200
PROCNO                  1
Date_          20110525
Time                16.00
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   114
DW                60.800 usec
DE                 6.50 usec
TE                294.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                -2.40 dB
PL1W          16.15108681 W
SFO1          400.1324710 MHz
SI                 32768
SF            400.1300156 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

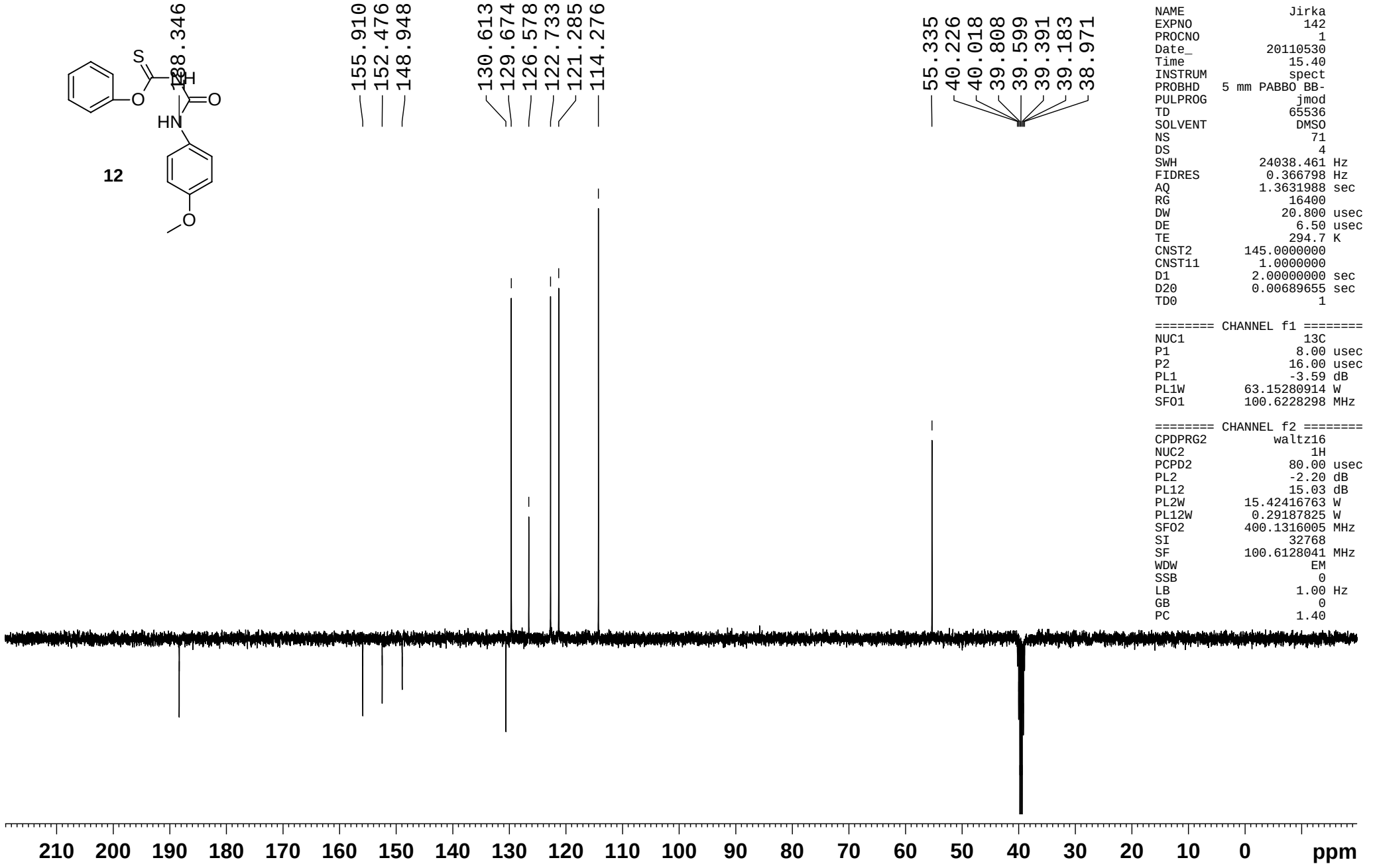


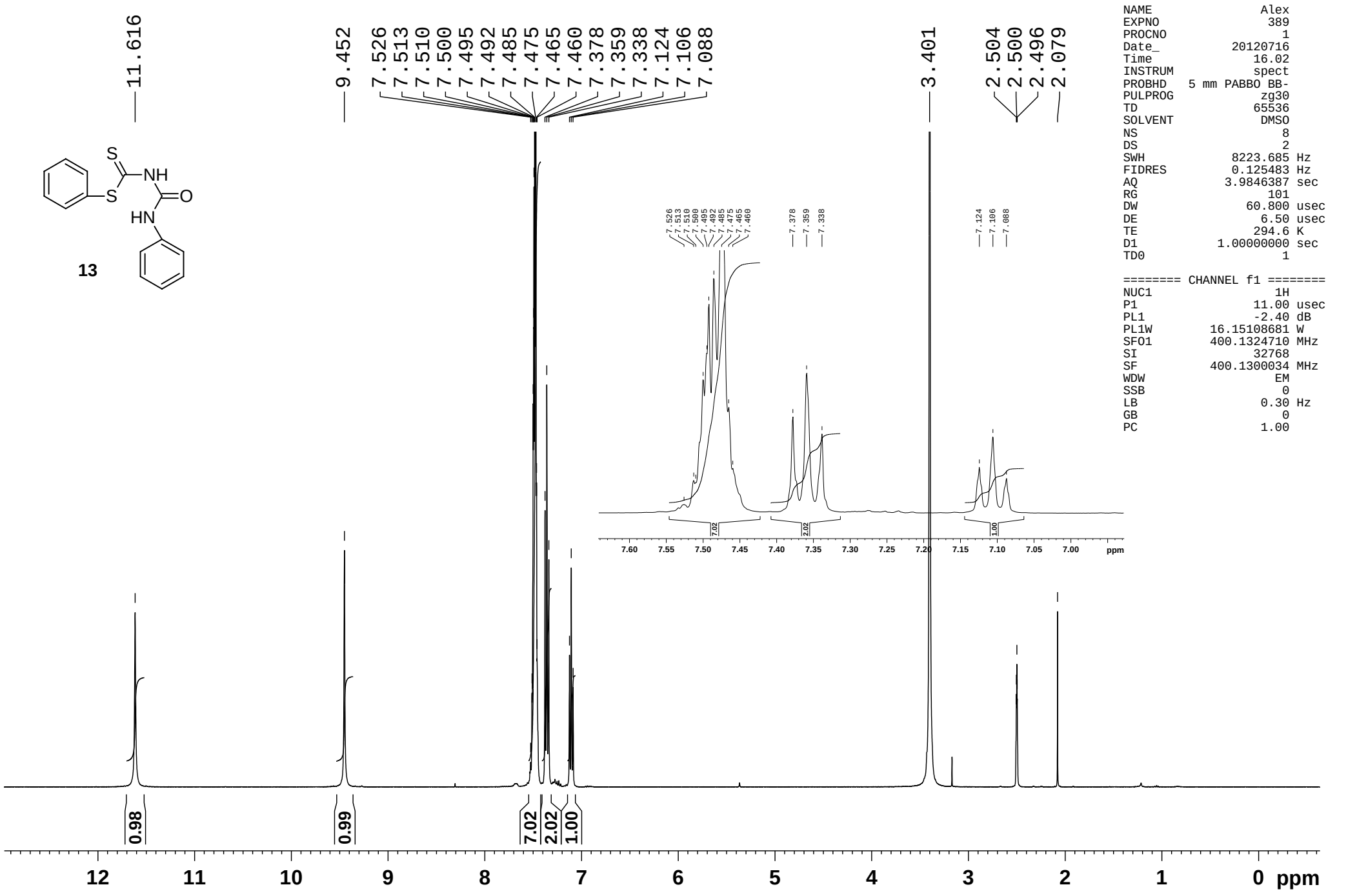
12

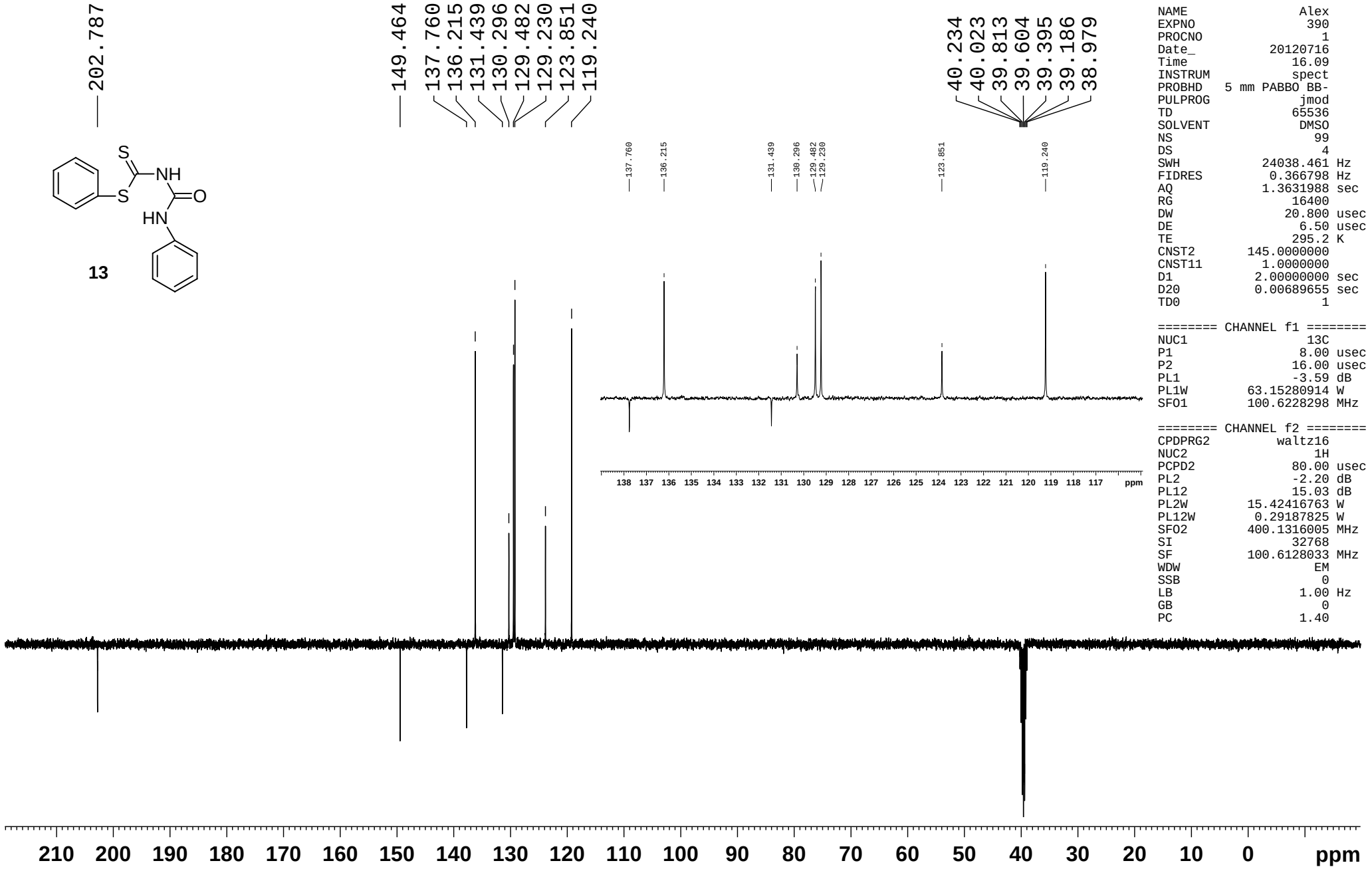



```
NAME                Jirka
EXPNO                 141
PROCNO                  1
Date_            20110530
Time                15.38
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT               DMSO
NS                       8
DS                       2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                     114
DW                60.800 usec
DE                 6.50 usec
TE                294.3 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.00 usec
PL1                 -2.40 dB
PL1W          16.15108681 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1300020 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```







NAME	Alex
EXPNO	390
PROCNO	1
Date_	20120716
Time	16.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	jmod
TD	65536
SOLVENT	DMSO
NS	99
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	16400
DW	20.800 usec
DE	6.50 usec
TE	295.2 K
CNST2	145.0000000
CNST11	1.0000000
D1	2.00000000 sec
D20	0.00689655 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
P2	16.00 usec
PL1	-3.59 dB
PL1W	63.15280914 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.20 dB
PL12	15.03 dB
PL2W	15.42416763 W
PL12W	0.29187825 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6128033 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40