Electronic Supplementary Material (ESI) for

Understanding the structure and reactivity of the C-S linkage in biologically active 5-arylthio-5*H*-chromenopyridines

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NMR spectra fo

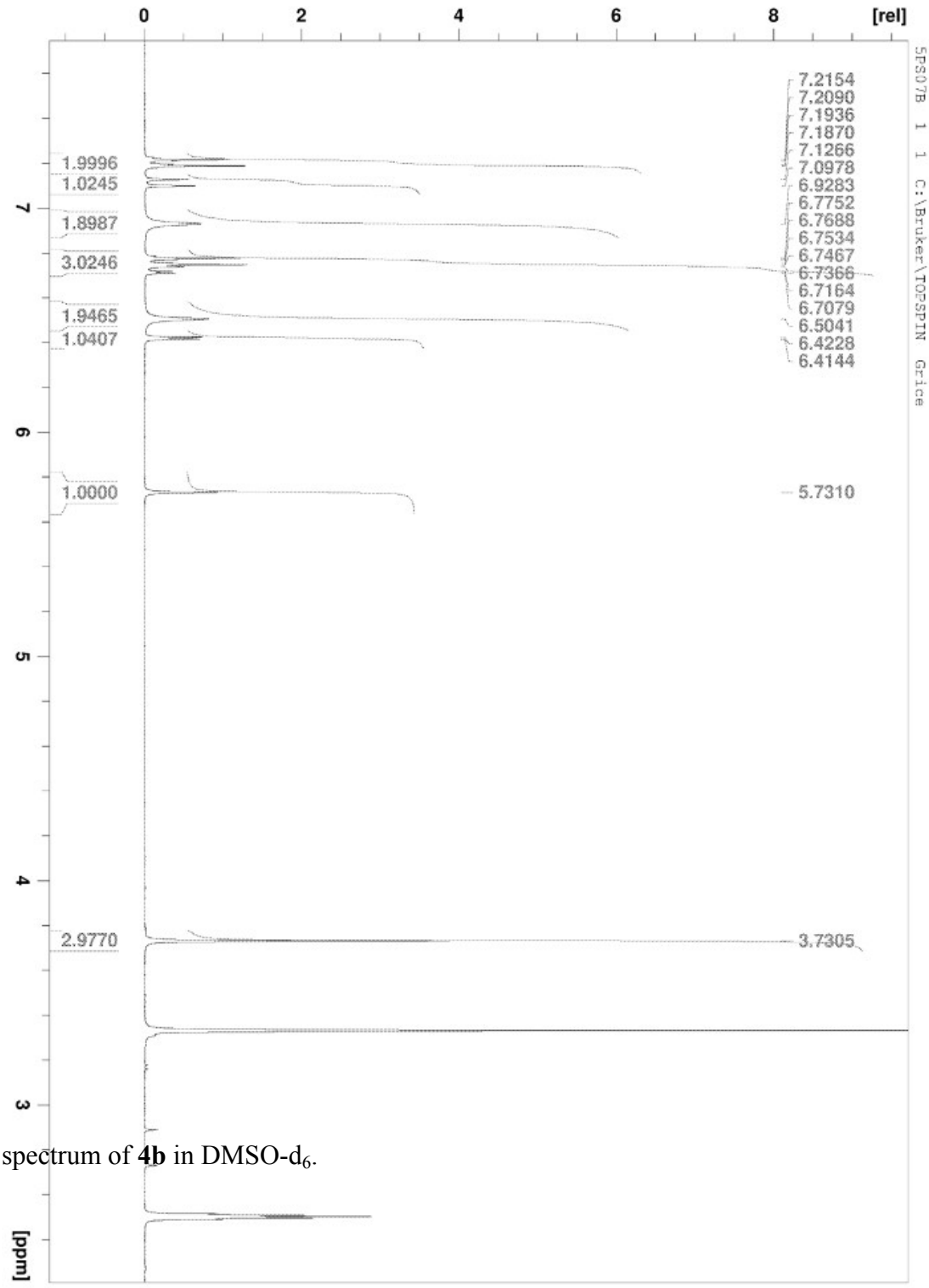

Figure S1. ^{1}H NMR spectrum of **4b** in DMSO-d_6.

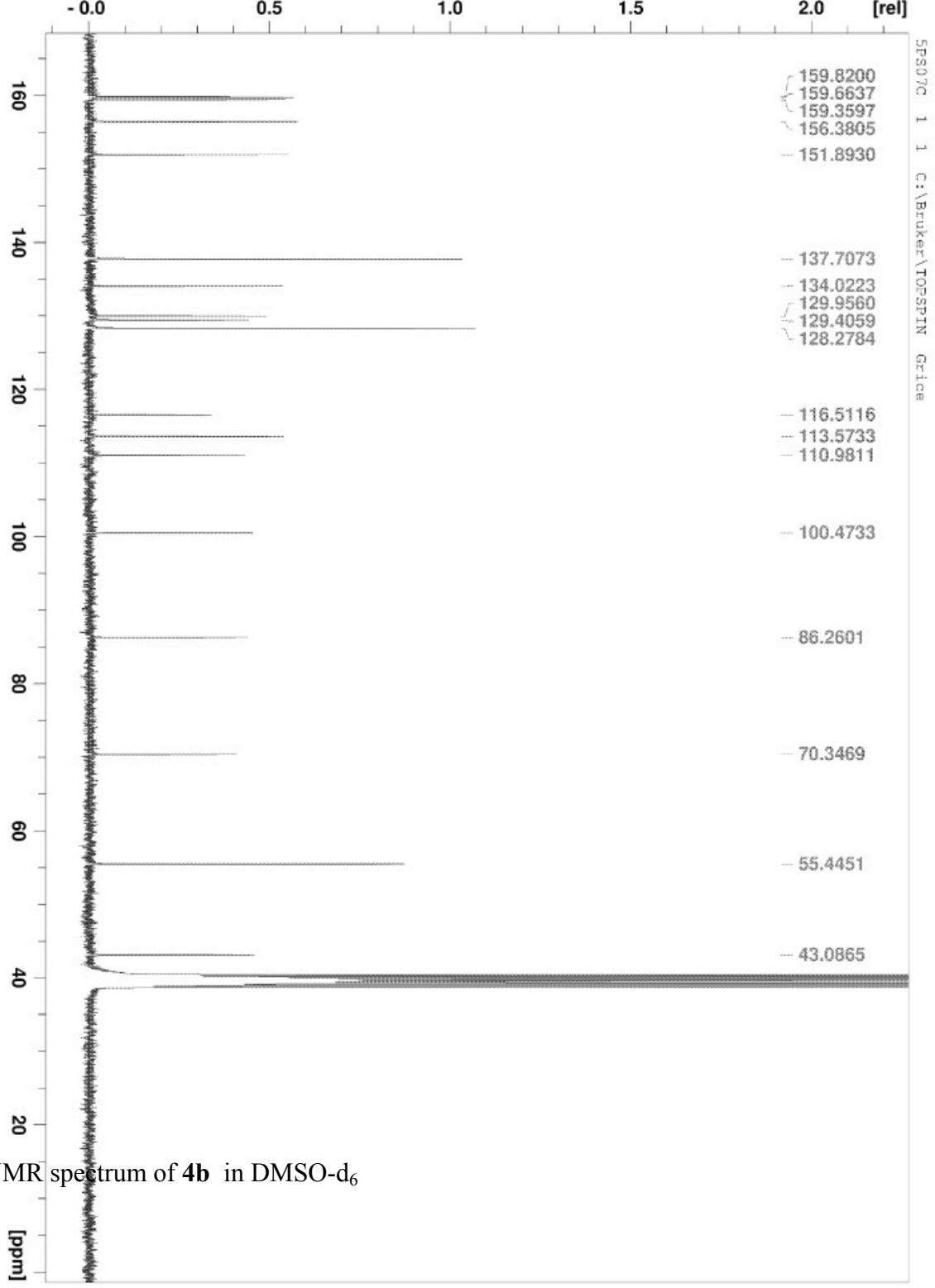

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in DMSO-d_6

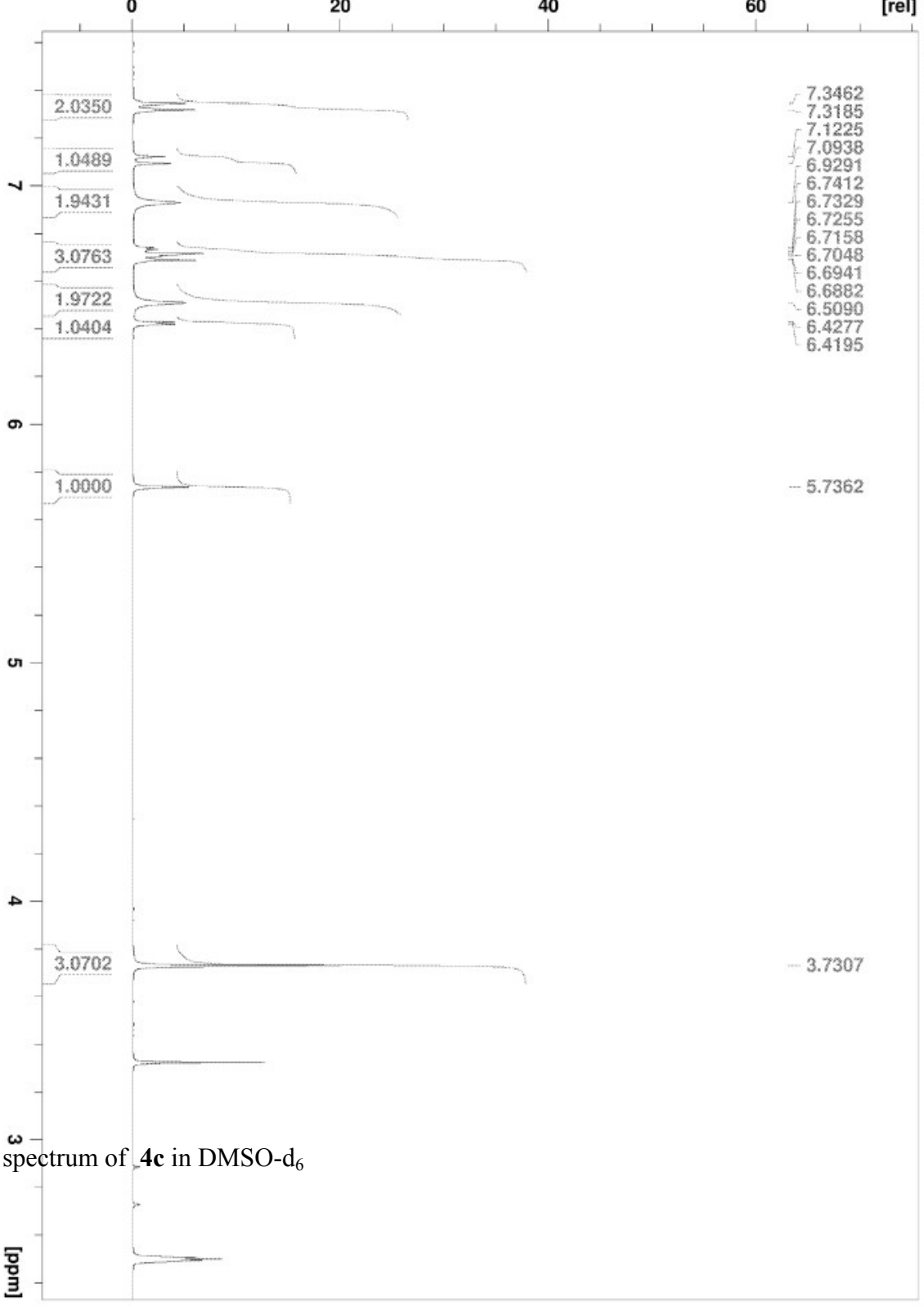

Figure S3. ^{1}H NMR spectrum of **4c** in DMSO-d_6

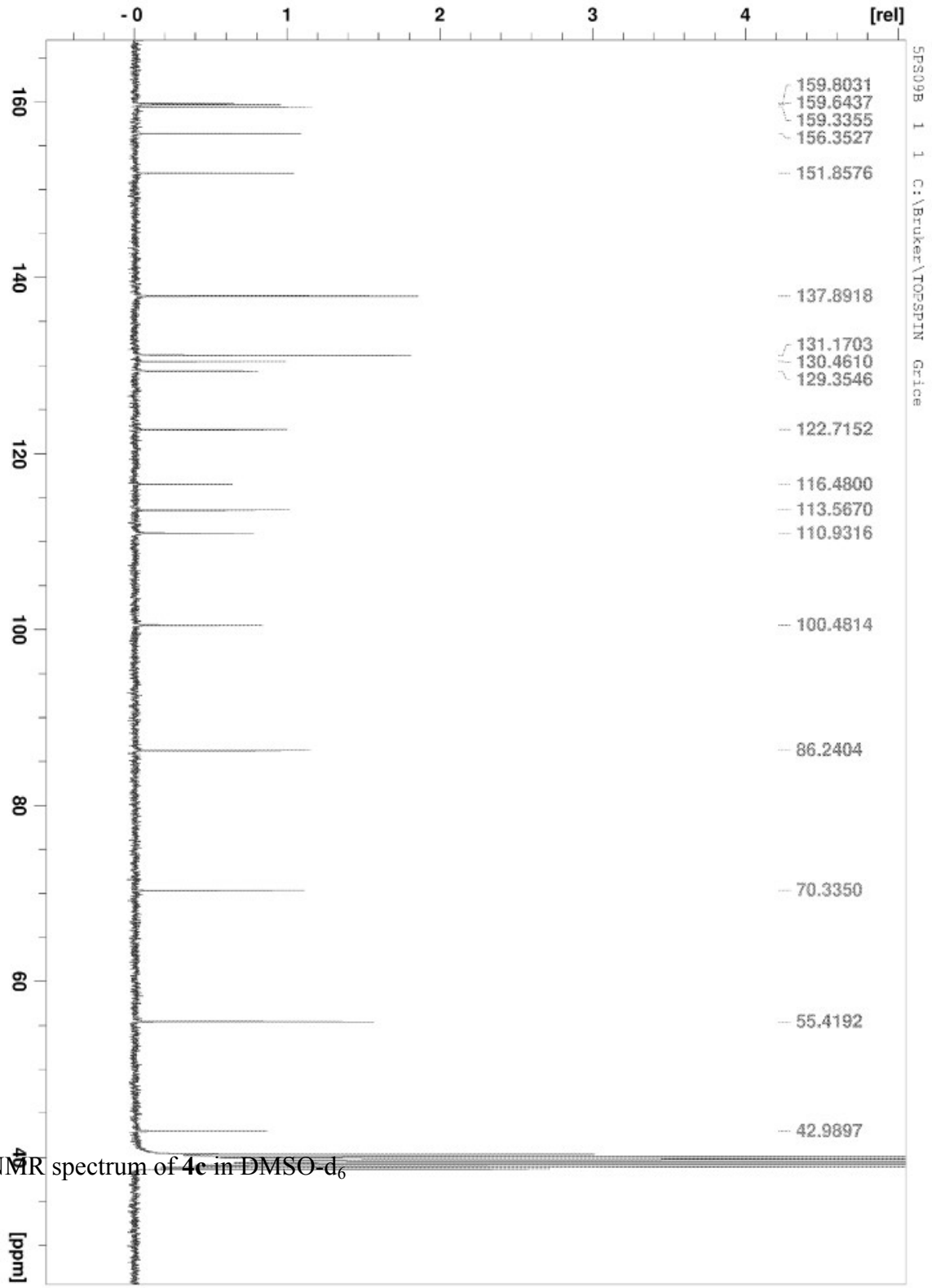

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in DMSO-d_6

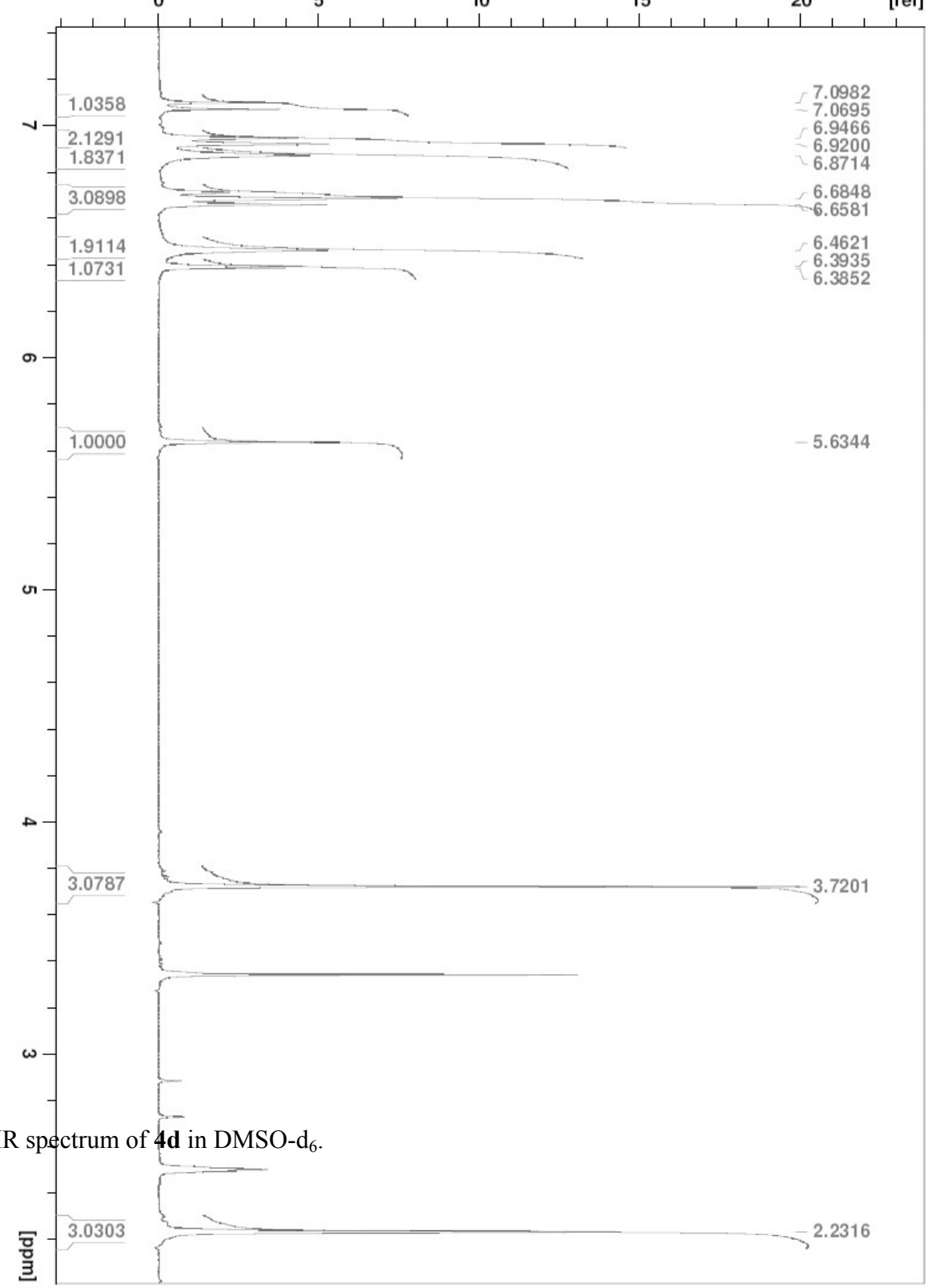

Figure S5. ^{1}H NMR spectrum of **4d** in DMSO-d_6.

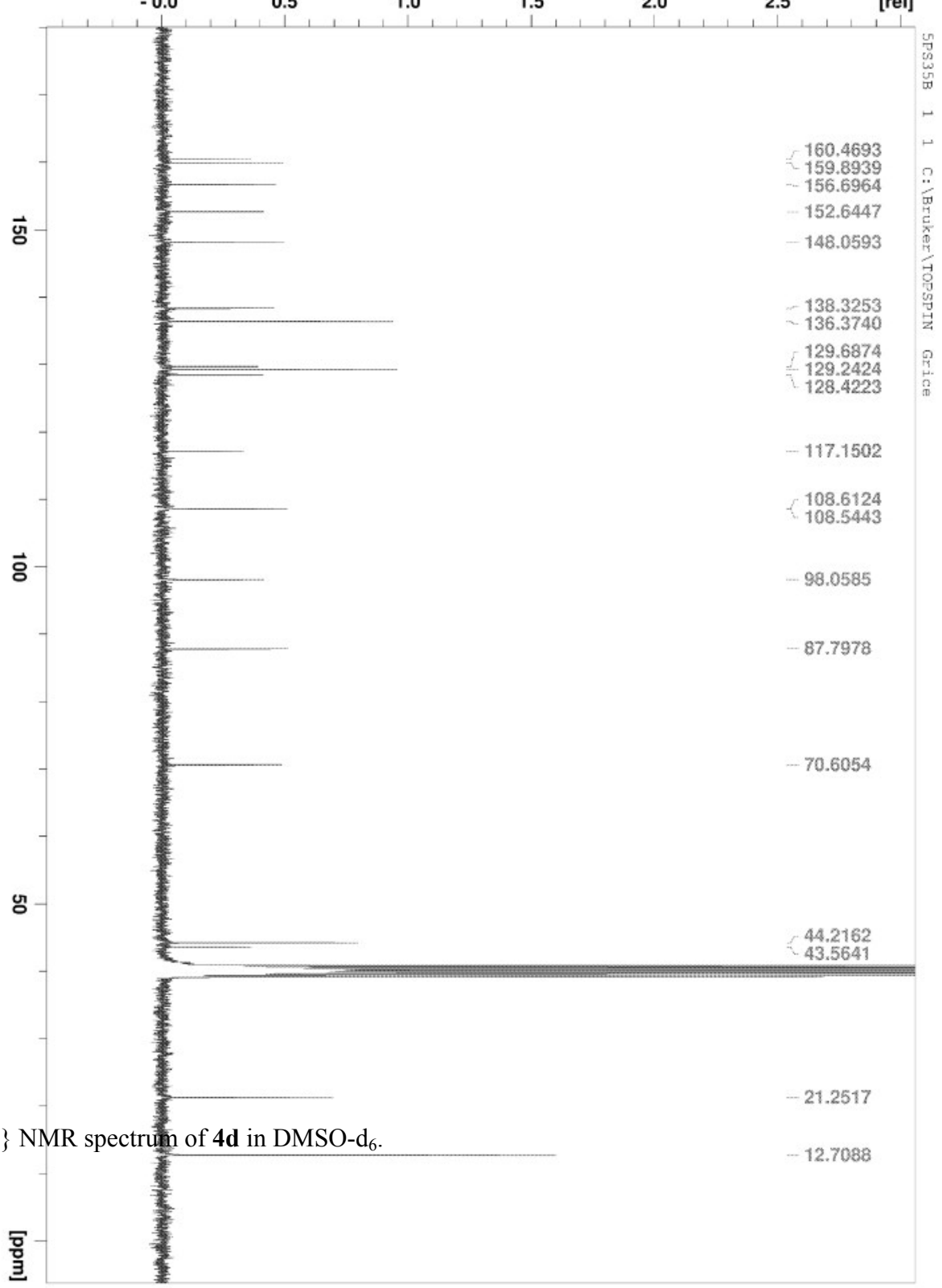

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in DMSO-d_6.

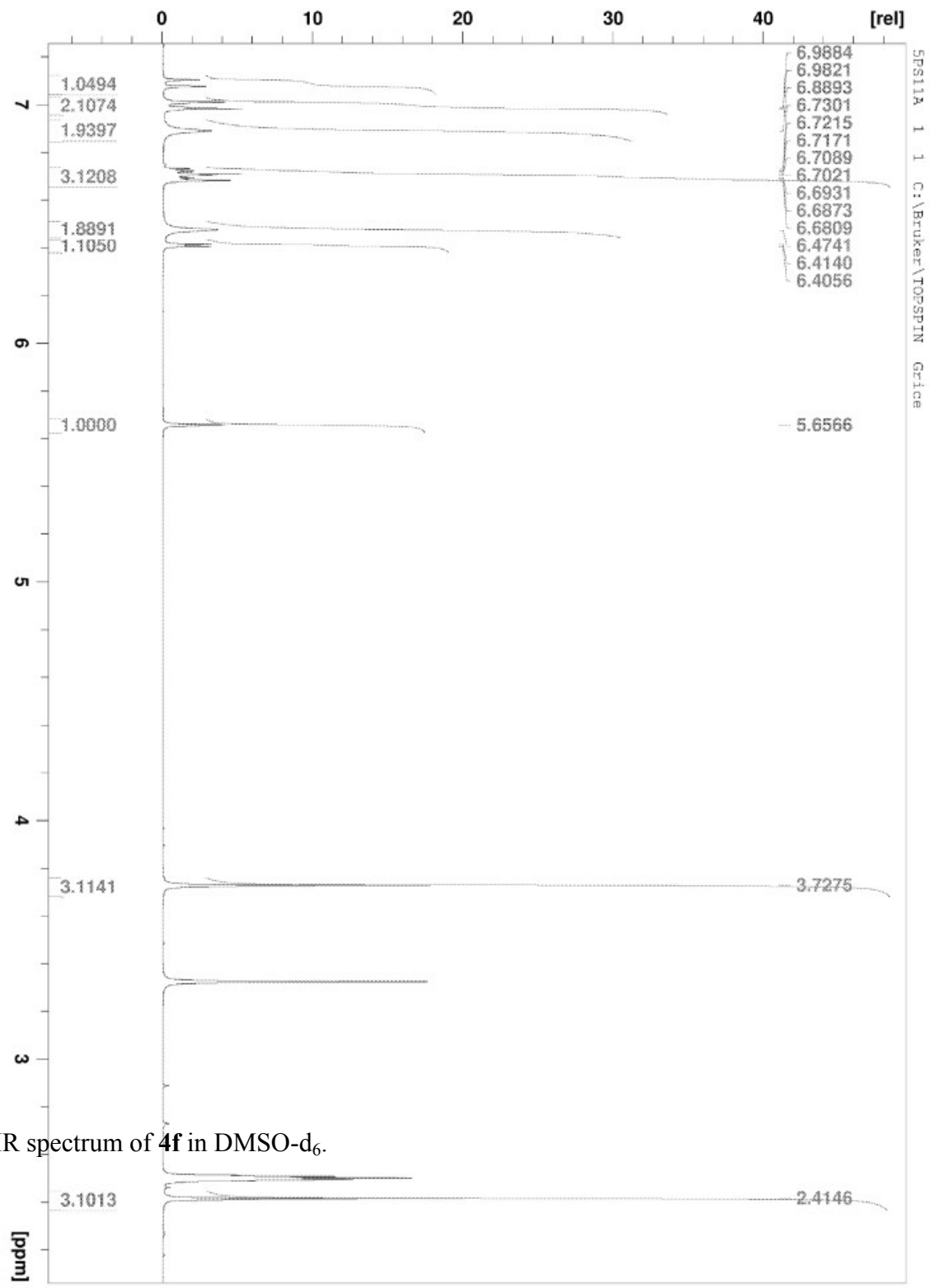

Figure S7. ^{1}H NMR spectrum of **4f** in DMSO-d_6.

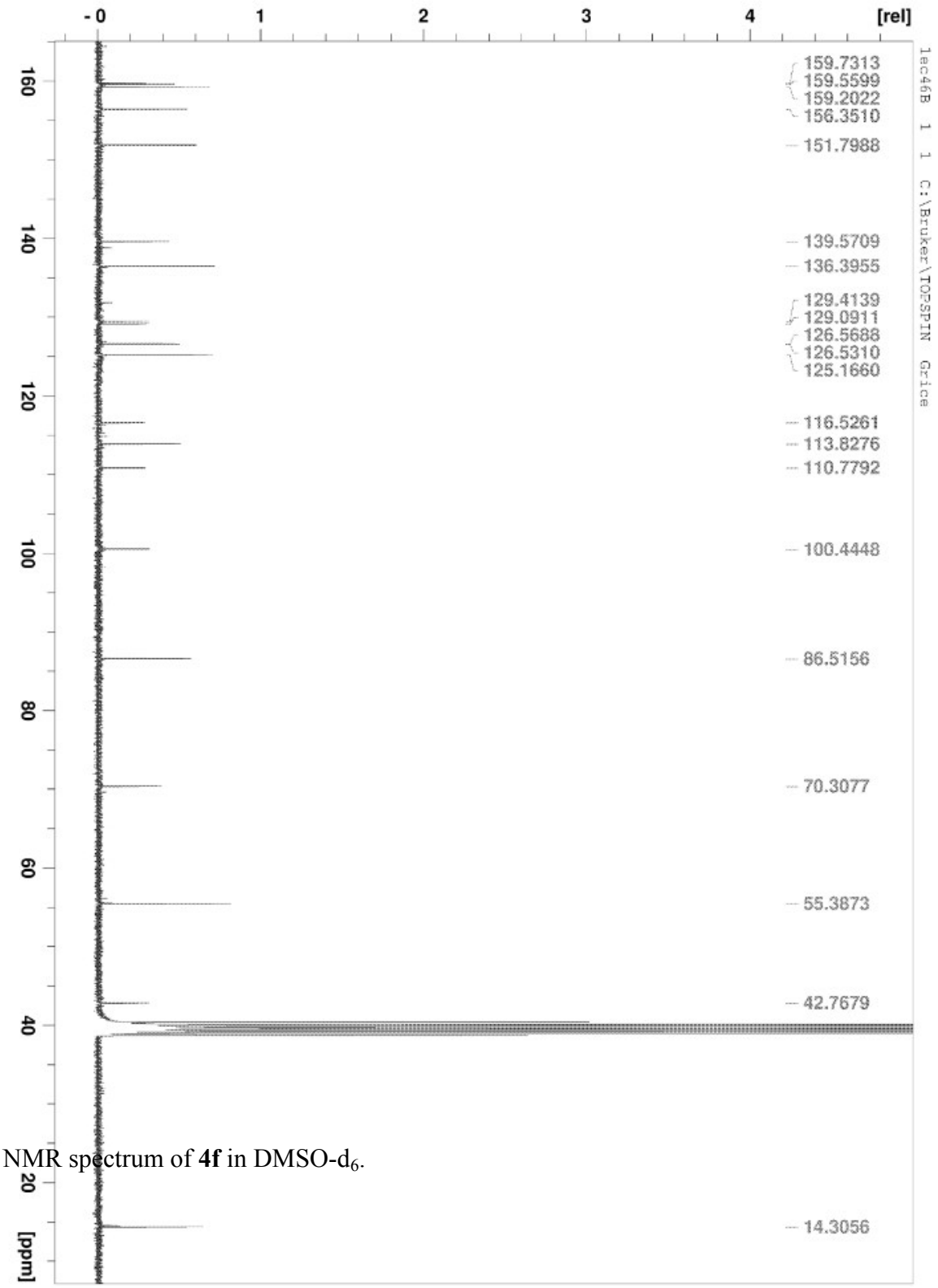

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** in DMSO-d_6.

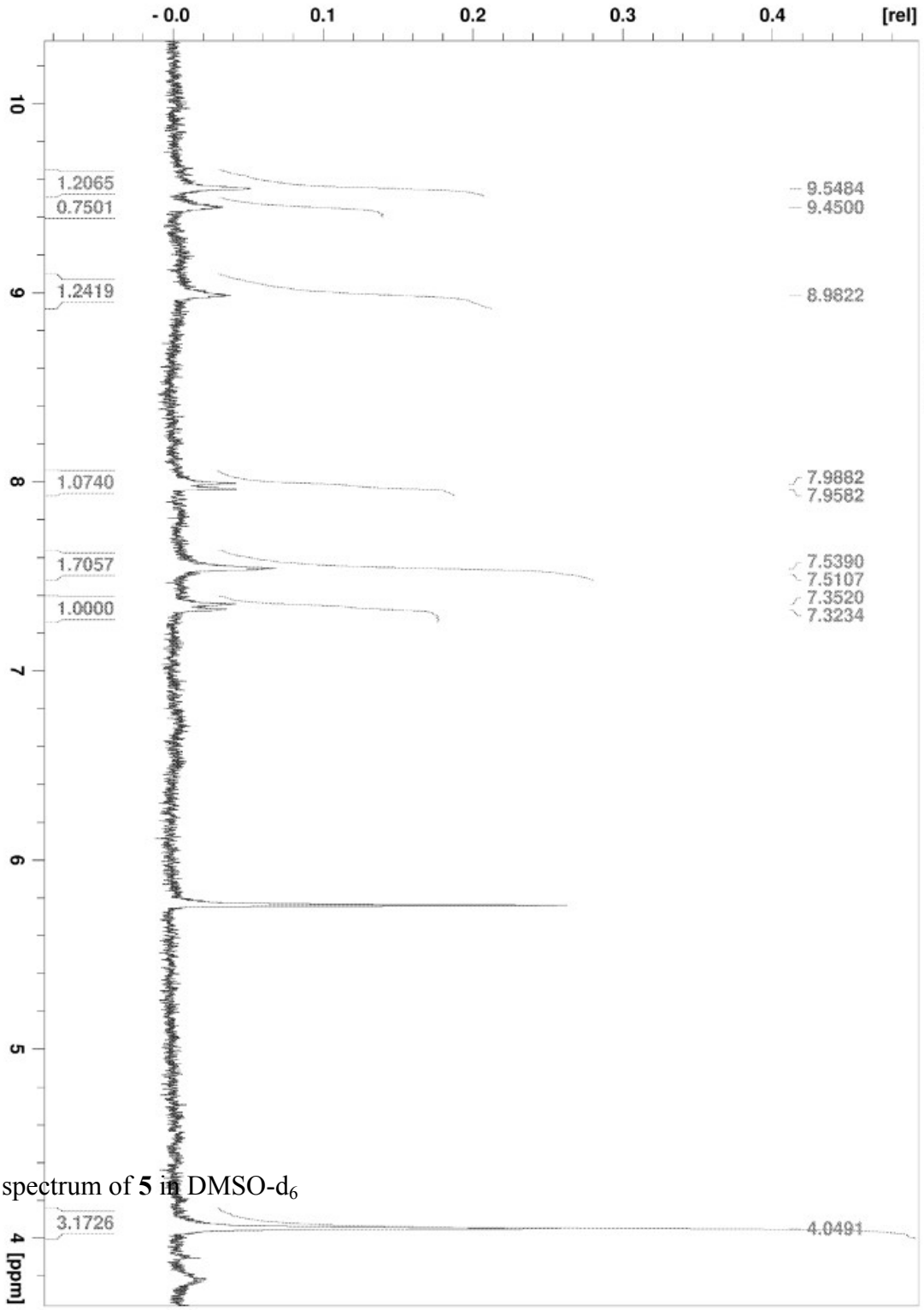

Figure S9. ^{1}H NMR spectrum of **5** in DMSO-d_6

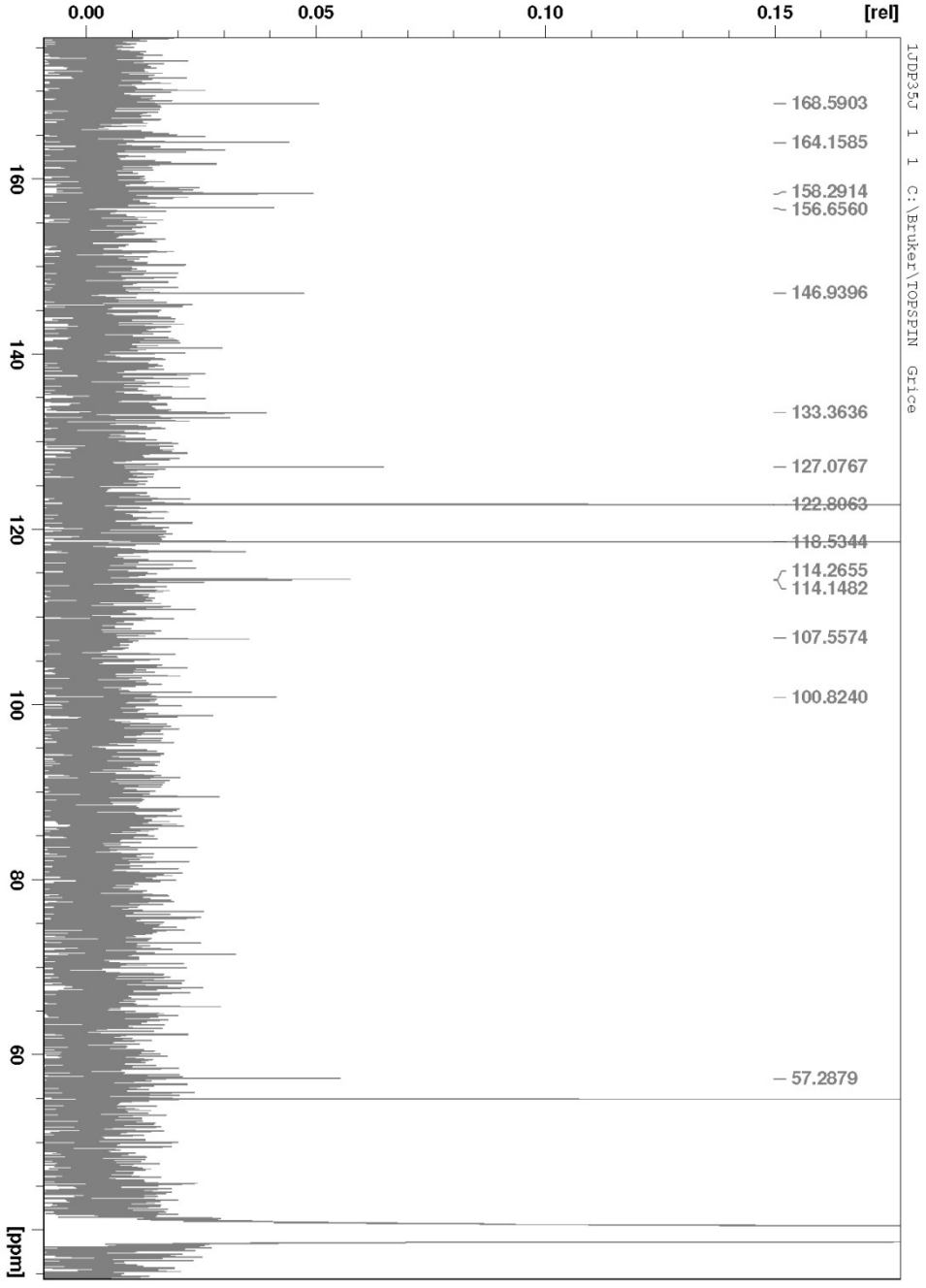

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in DMSO-d_6.

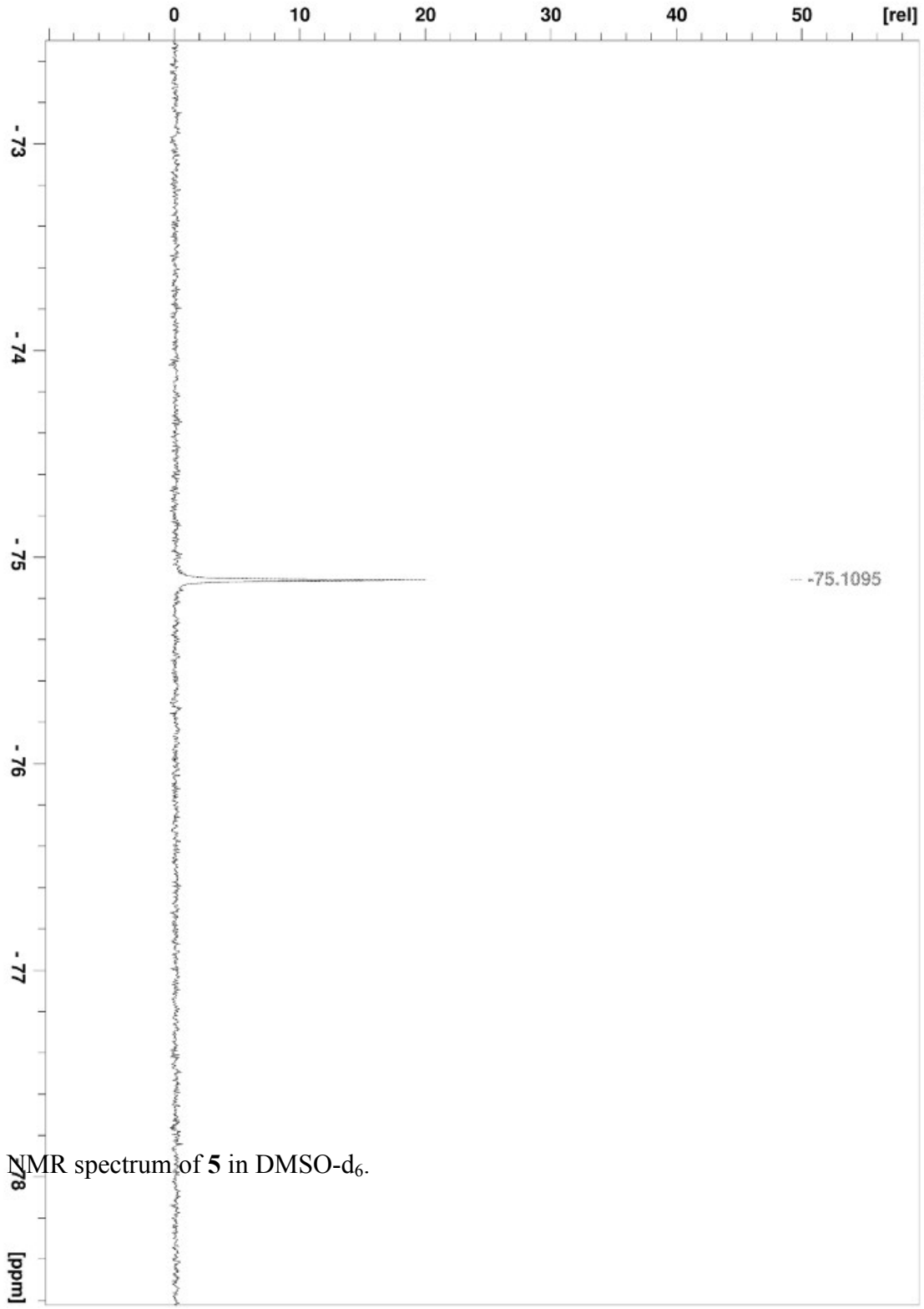

Figure S11. $^{19}F\{^{1}H\}$ NMR spectrum of **5** in DMSO-d_6.

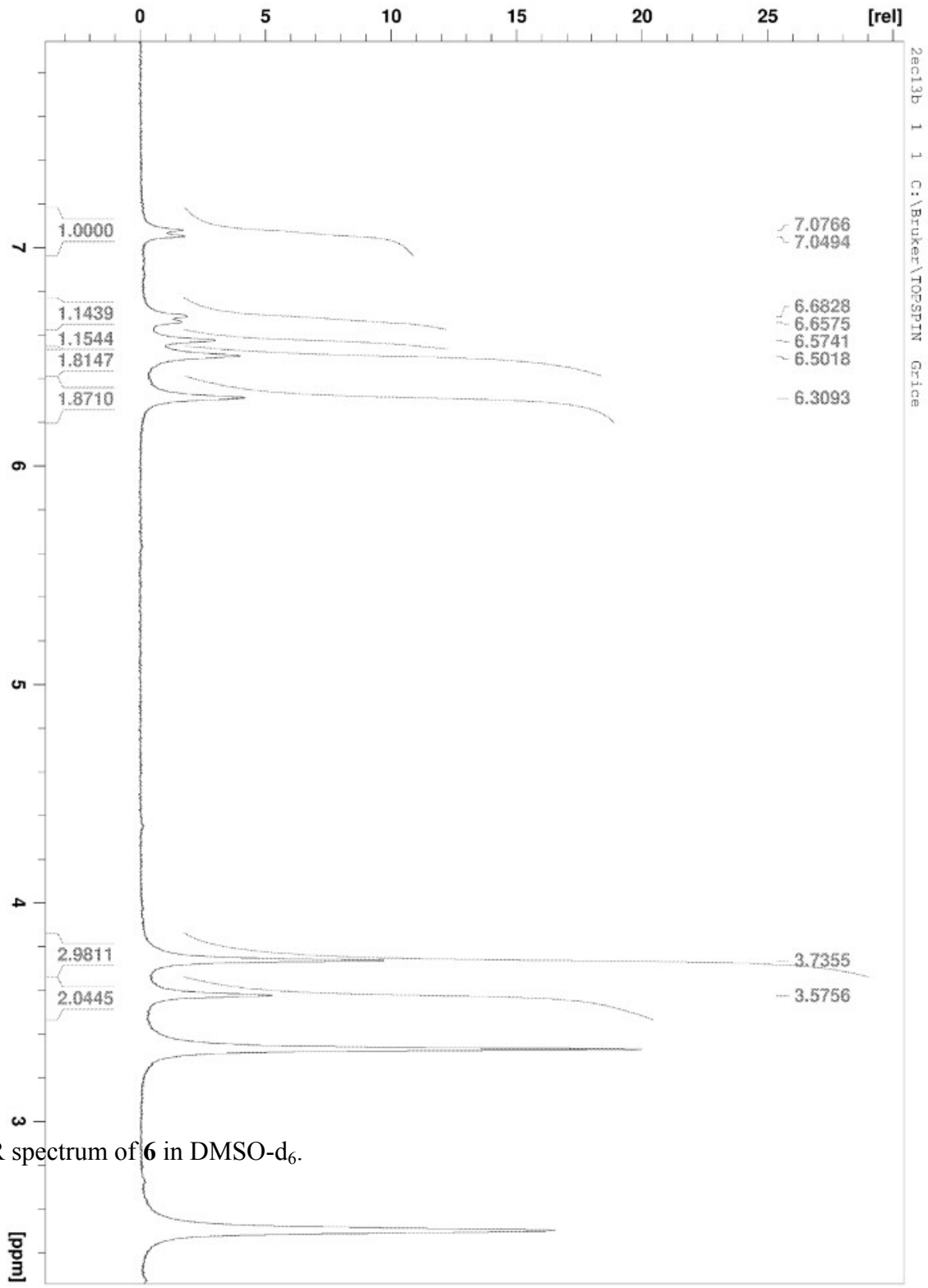

Figure S12. ^{1}H NMR spectrum of **6** in DMSO-d_6.

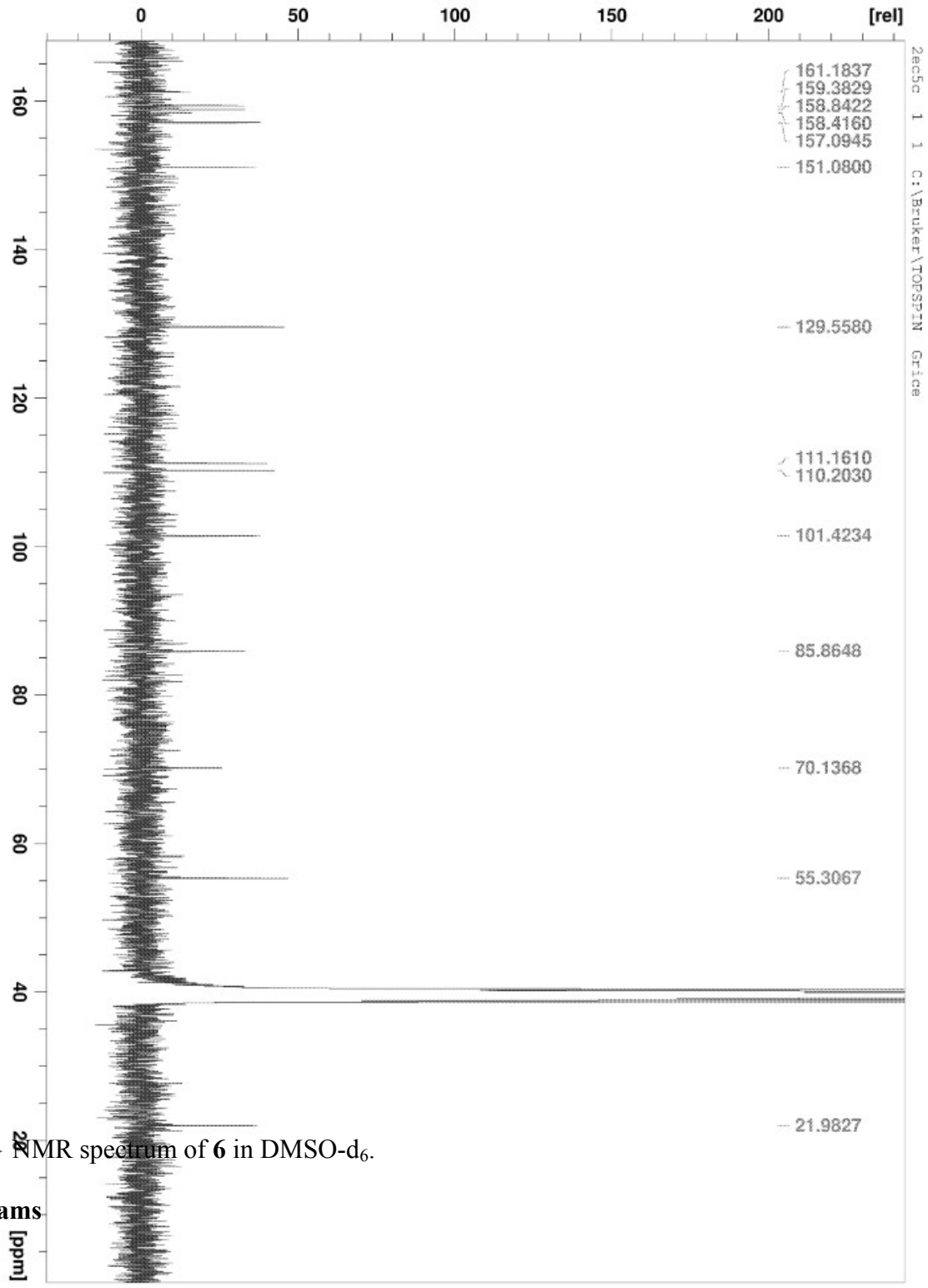

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in DMSO-d_6.

Cyclic voltammograms

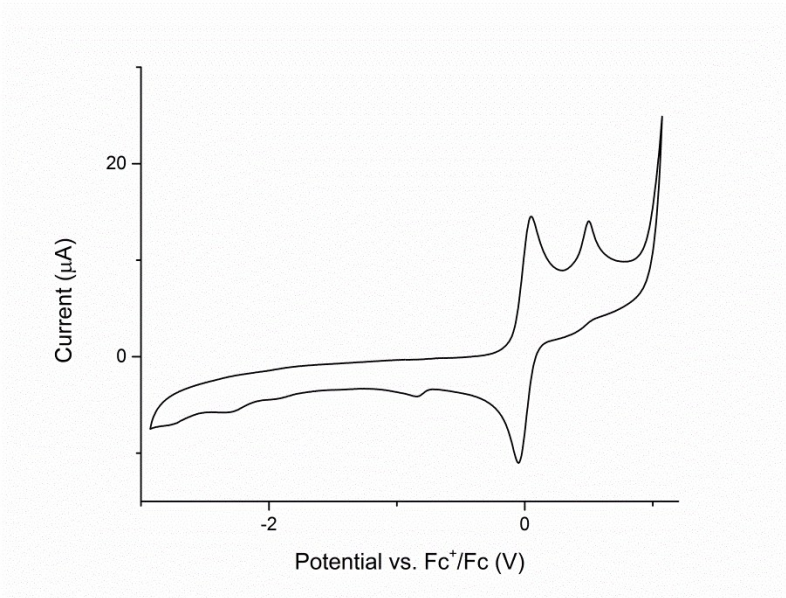

Figure S14. Cyclic voltammogram of **4d** (3 mM) in DMSO under Ar gas at 250 mV/s. Tetrabutylammonium hexafluorophosphate was the supporting electrolyte (0.24 M), and ferrocene (6 mM) was added as an internal reference. The primary signal from **4d** is the irreversible oxidation at 0.50 V vs Fc^+/Fc. The irreversibility is likely due to C−S bond cleavage upon oxidation.

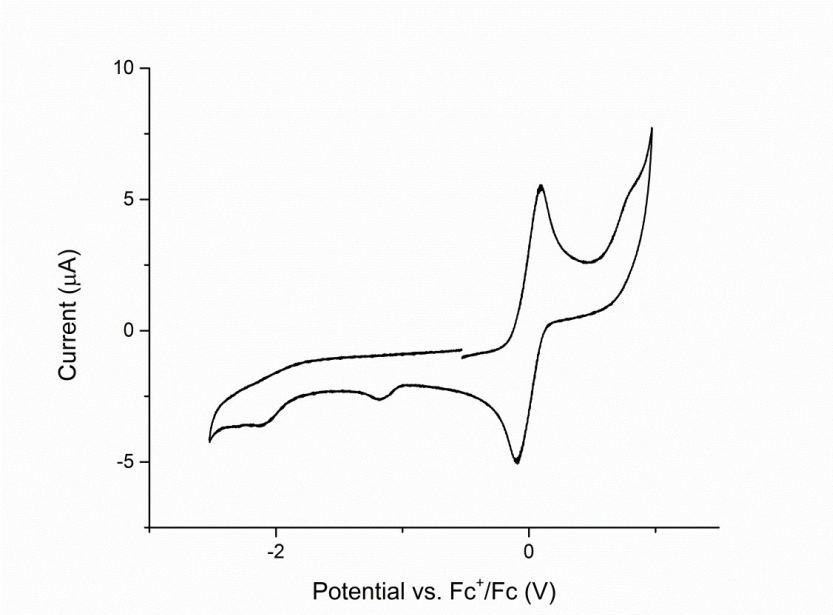

Figure S15. Cyclic voltammogram of **3e** (1.7 mM) in DMSO under Ar gas at 250 mV/s. Tetrabutylammonium hexafluorophosphate was the supporting electrolyte (0.21 M), and ferrocene (5 mM) was added as an internal reference. The primary signal from **3e** is the irreversible oxidation at 0.79 V vs Fc^+/Fc. The reduction peaks are due to reduction of species formed upon oxidation.

Crystallographic Information and Tables

Data for 4e (CCDC 1577117)

A pale yellow needle-like specimen of $C_{21}H_{18}N_4O_3S$, approximate dimensions 0.136 mm x 0.160 mm x 0.343 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 10.45 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 46344 reflections to a maximum θ angle of 30.54° (0.70 Å resolution), of which 5803 were independent (average redundancy 7.986, completeness = 99.9%, R_{int} = 3.38%, R_{sig} = 2.06%) and 4575(78.84%) were greater than $2\sigma(F^2)$. The final cell constants of a = 21.6226(4) Å, b = 14.4826(4) Å, c = 13.0479(3) Å, β = 112.052(2)°, volume = 3787.05(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 865 reflections above 20 σ(I) with 3.485° < 2θ < 67.59°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.949. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9340 and 0.9730. The final anisotropic full-matrix least-squares refinement on F^2 with 280 variables converged at R1 = 3.93%, for the observed data and wR2 = 10.53% for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was 0.333 $e^-/Å^3$ and the largest hole was -0.743 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.426 g/cm^3 and F(000), 1696 e^-.

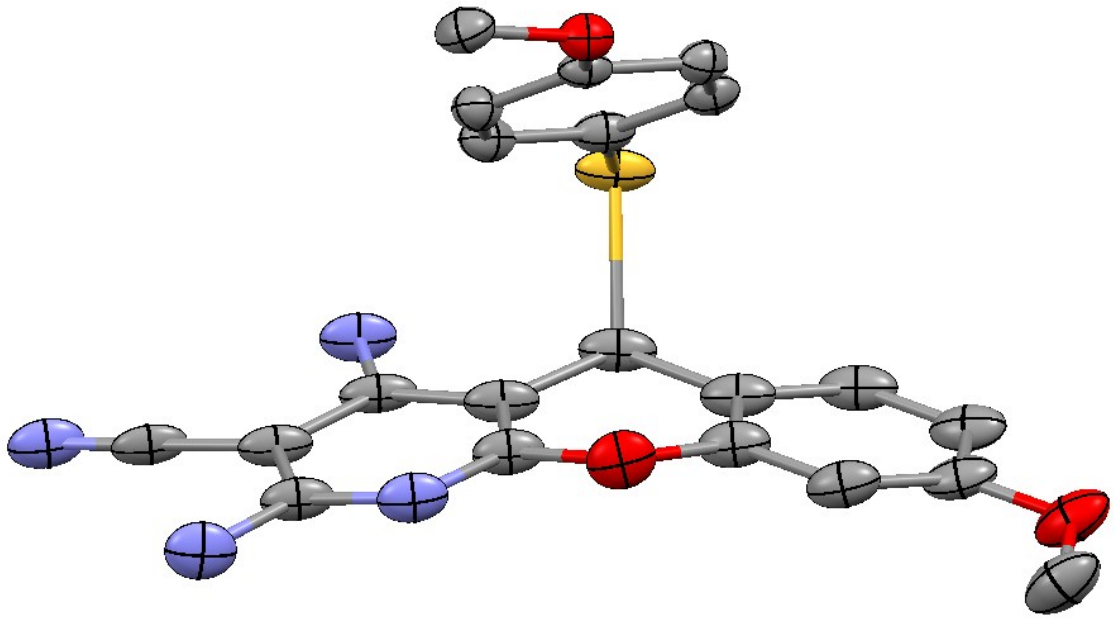

Figure S16. Structure of compound **4e** (CCDC 1577117) with ellipsoids at 50% and hydrogen atoms excluded for clarity. The image was generated with Mercury.[1]

Table S1. Sample and crystal data for compound 4a (CCDC 1575965)

Identification code	rds610

Chemical formula	$C_{20}H_{15}FN_4O_2S$	
Formula weight	394.42 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.224 x 0.288 mm	
Crystal habit	pale yellow plate	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 14.6027(7) Å	α = 90°
	b = 7.1994(4) Å	β = 107.694(2)°
	c = 18.1327(10) Å	γ = 90°
Volume	1816.12(17) $Å^3$	
Z	4	
Density (calculated)	1.443 g/cm^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	816	

Table S2. Data collection and structure refinement for rds610.

Theta range for data collection	2.14 to 30.51°	
Index ranges	-19<=h<=20, -10<=k<=10, -23<=l<=25	
Reflections collected	34880	
Independent reflections	5533 [R(int) = 0.0353]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9920 and 0.9410	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5533 / 0 / 270	
Goodness-of-fit on F^2	1.025	
Final R indices	4391 data; $I>2\sigma(I)$	R1 = 0.0377, wR2 = 0.0930
	all data	R1 = 0.0553, wR2 = 0.1018
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0492P)^2+0.7375P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.415 and -0.249 $eÅ^{-3}$	
R.M.S. deviation from mean	0.056 $eÅ^{-3}$	

Table S3. Sample and crystal data for compound 4e (CCDC 1577117)

Identification code	rds526
Chemical formula	$C_{21}H_{18}N_4O_3S$
Formula weight	406.45 g/mol

Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.136 x 0.160 x 0.343 mm	
Crystal habit	pale yellow needle	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 21.6226(4) Å	α = 90°
	b = 14.4826(4) Å	β = 112.052(2)°
	c = 13.0479(3) Å	γ = 90°
Volume	3787.05(16) $Å^3$	
Z	8	
Density (calculated)	1.426 g/cm^3	
Absorption coefficient	0.203 mm^{-1}	
F(000)	1696	

Table S4. Data collection and structure refinement for 4e (CCDC 1577117)

Theta range for data collection	1.74 to 30.54°	
Index ranges	-30<=h<=30, -20<=k<=20, -18<=l<=18	
Reflections collected	46344	
Independent reflections	5803 [R(int) = 0.0338]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9730 and 0.9340	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5803 / 2 / 280	
Goodness-of-fit on F^2	1.029	
Δ/σ_{max}	0.001	
Final R indices	4575 data; I>2σ(I)	R1 = 0.0393, wR2 = 0.0945
	all data	R1 = 0.0560, wR2 = 0.1053
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0428P)^2+3.4981P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.333 and -0.743 $eÅ^{-3}$	
R.M.S. deviation from mean	0.048 $eÅ^{-3}$	

Density Functional Theory
Sample Input Calculation

```
%chk=SP123DMSO.chk
%nprocshared=8
%mem=48MW
# opt freq=noraman rb3lyp/6-311+g(d,p) scrf=(solvent=dmso)
```

SP123DMSO

0 1

S	0.14024777	0.11324263	-2.64599357
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O	-0.56439660	-0.95102298	1.40757554
O	-5.24110106	-1.62236977	0.74548828
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N	5.86942931	-1.79503907	0.01847709
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H	2.30572080	-1.24982484	-2.63188216
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H	3.30235931	-1.18926485	3.74511269
H	4.67112656	-1.51309197	2.73971804

Output coordinates and ΔG_{298K}:

Compound **3a**

Charge: 0, Singlet

Total energy: -1089845.7 kcal/mol

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H	3.06610089	-0.58346425	-2.65985804
N	-4.67915321	-1.25805996	0.39443633
N	4.19680128	-1.75047791	2.74695804
H	3.78362010	-1.60548580	3.65429793
H	5.20017872	-1.72704302	2.66094787
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C	3.08004663	-1.22856799	-0.73719504
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H	-5.58728253	-1.96779364	-1.35405098
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H	-4.21264897	-1.89337506	2.33308941
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C	0.88564472	2.05046065	-1.19239945
C	2.04878025	2.50390095	-0.55223577
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C	1.97567166	3.45667527	0.46262004
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C	0.72665611	3.94452401	0.82942479
H	2.86381732	3.82083675	0.96710015
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H	-7.12014127	-0.06581566	-1.74335244
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H	-4.01459989	0.65732915	2.33777069
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H	-5.13662056	0.04336270	3.56342634
F	0.64937746	4.86740468	1.80962364

Compound **3e**
Charge: 0, Singlet
Total energy: -1099415.8 kcal/mol

O	-0.06492301	-0.71135005	1.32812510
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N	4.61168035	-1.41350611	0.65695305
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N	-6.49921950	-2.00889515	0.36710403
C	3.32861025	-1.39079611	0.15223101
C	-1.74553214	-1.30108510	-0.28985502
C	0.65226805	-1.40200511	-0.88264107
C	2.22594417	-1.02369208	0.95299608
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C	-5.36611538	-1.78851114	0.48773004
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C	-3.11968424	-1.57357012	-0.48522904
C	-0.74624806	-1.34706410	-1.40070110
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C	-3.45554126	-1.15785809	1.90260415
C	0.93837107	-1.04604308	0.43190303
C	3.04621723	-1.76290414	-1.19139809
H	3.84432630	-2.04301116	-1.86282014
C	5.74618345	-1.82920014	-0.17196701
H	5.45040940	-2.69054721	-0.77706706
H	6.52193449	-2.19083217	0.50598004
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H	4.13493432	-1.42302011	2.69865821
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C	4.96744838	0.52551504	2.24220717
H	4.04099531	1.02135108	1.94398015
H	5.78667943	0.96038007	1.66528413
H	5.14292839	0.74459306	3.29954725
H	-4.59339935	-1.95745415	-1.85027614
H	-3.08031323	-1.58601812	-2.52190319
H	-3.84698930	-0.68303305	3.83661929
H	-5.24603340	-1.09356908	2.92742922
H	1.57909012	-2.04466415	-2.70878321
S	-0.98997908	0.09844601	-2.67110820
C	-0.87621807	1.55620312	-1.64493713
C	-2.02414415	2.12013416	-1.06538408
C	0.35672903	2.17885116	-1.43349111
C	-1.93536915	3.26709525	-0.29115402
H	-2.99098923	1.66008813	-1.22913709
C	0.45802604	3.33313026	-0.65613505
H	1.25107109	1.76394213	-1.88201214
C	-0.69253005	3.88115130	-0.07918101
H	-2.81987322	3.70549929	0.15589701
H	1.42805611	3.78921229	-0.51322204
O	-0.70760405	5.00219938	0.69267105
C	0.52668404	5.68019346	0.94510607
H	0.27226102	6.53138051	1.57310112
H	1.23058809	5.03266839	1.47524711
H	0.97864807	6.03495844	0.01465900
H	-0.94015807	-2.19060617	-2.06807216

Compound **4a**
Charge: 0, Singlet
Total energy: -1028345.0 kcal/mol

S	-0.15463409	0.74204137	2.50406767
O	0.54846279	-0.82978686	-1.30644793
N	-1.58284115	-1.00143586	-1.93934013
N	-3.72240115	-1.17100461	-2.75103784
C	-0.75048972	-0.94496645	-0.90686270
O	5.18737107	-1.66203880	-0.53163386
C	-3.37981894	-1.25899627	-0.35329926
C	-1.09240004	-1.00920771	0.44370065
C	-2.46971892	-1.16573644	0.73078716
C	1.32388635	-1.14267807	0.96874015
C	2.83430725	-1.21540926	-0.95453836

H	2.94241452	-1.13791994	-2.02689550
C	1.56359030	-1.05480157	-0.39725218
C	-2.88461821	-1.15437594	-1.68157157
N	-2.90791367	-1.25791454	2.01474208
N	-5.90014646	-1.54314706	0.07689135
C	-0.05089894	-0.91140663	1.51139779
H	-0.25611385	-1.61170147	2.32492736
C	-4.76301812	-1.41496206	-0.11587386
C	3.90705578	-1.48637925	-0.10904141
C	3.69324229	-1.60476706	1.27612836
H	4.53446676	-1.82816748	1.92050076
F	0.37271025	4.87860348	-1.68604064
C	0.00327566	1.97675945	1.21907473
C	2.42321875	-1.43235147	1.79316681
H	2.26975354	-1.51157815	2.86375823
C	-1.13603299	2.49790741	0.59262729
H	-2.11842133	2.14317336	0.87715014
C	-1.01803048	3.47805959	-0.39051665
H	-1.88877893	3.89202720	-0.88329349
C	1.26885377	2.45723611	0.85807495
H	2.15273472	2.06938675	1.34821978
C	0.25095354	3.92116889	-0.72739628
C	1.40063477	3.43598940	-0.12461572
H	2.37122425	3.81849706	-0.41471753
C	5.46980888	-1.55108746	-1.93001710
H	6.54025355	-1.71753771	-2.02893766
H	5.21806237	-0.55464034	-2.30356568
H	4.92740833	-2.30940430	-2.50147267
H	-3.30513515	-1.25480303	-3.66511465
H	-2.34554040	-0.83838674	2.74101394
H	-4.67676377	-1.47931010	-2.65239506
H	-3.90217156	-1.23057982	2.18969430

Compound **4e**
Charge: 0, Singlet
Total energy: -1037915.8 kcal/mol

S	0.13288355	0.02618673	-2.64768687
O	-0.57248022	4.90694842	0.68497016
O	-0.54433286	-0.77982974	1.38129272
O	-5.20121382	-1.68346116	0.81843197
N	2.87467763	-1.89449493	-1.81721052
N	1.59078182	-0.85794528	2.02106177
N	3.73588921	-0.89682921	2.83614810
N	5.88141623	-1.83058229	0.11082927
C	-0.33052993	3.79244184	-0.05716075
C	-1.45866665	3.16784913	-0.60871948

H	-2.43743243	3.59409854	-0.42259663
C	-1.31606121	2.02551576	-1.38136349
H	-2.19333374	1.55455439	-1.80760959
C	3.36905461	-1.43871941	0.50156961
C	2.88787921	-1.07494828	1.78841869
C	0.94151118	3.26111405	-0.29517885
H	1.82832336	3.72721035	0.11182586
C	1.07659698	-1.32182162	-0.31156785
C	1.07343598	2.11186921	-1.07529349
H	2.06264693	1.71209722	-1.26204289
C	-0.04556126	1.47785414	-1.62124397
C	-1.34569583	-1.52546362	-0.78132533
C	2.44900664	-1.54790924	-0.57283566
C	4.74812133	-1.65358571	0.28704536
C	0.74908645	-0.99030776	1.00253343
C	-1.57100754	-1.16648165	0.54182328
C	-2.83837803	-1.19599162	1.12838906
H	-2.93590851	-0.90535223	2.16454485
C	0.02521064	-1.41576632	-1.37099333
H	0.21499072	-2.25937264	-2.03937413
C	0.53507290	5.59718963	1.27194830
H	1.22256614	5.96269754	0.50419626
H	1.07235199	4.95407849	1.97438164
H	0.10576332	6.44136297	1.80732777
C	-3.92247467	-1.61305966	0.36032655
C	-2.45598877	-1.95717780	-1.52451440
H	-2.31293059	-2.24771793	-2.55947283
C	-3.72357372	-2.00623285	-0.97518083
H	-4.57366590	-2.34062482	-1.55684129
C	-5.46817113	-1.29578250	2.16958691
H	-5.20127712	-0.24878518	2.33796475
H	-4.92885847	-1.93383111	2.87526805
H	-6.53942491	-1.42530624	2.30759179
H	2.30866000	-1.62125254	-2.60726731
H	3.86739219	-1.90934995	-2.00210351
H	3.32353165	-0.80602002	3.75189720
H	4.68212655	-1.24128708	2.79435810

NEt_2Chromenecation
Charge: 1, Singlet
Total energy: -632213.5 kcal/mol

O	0.35897970	1.06842896	-0.16788999
N	2.49435404	1.68752295	-0.09165626
N	3.79934992	-2.28915720	0.16040139
N	-4.31796697	0.25088041	-0.41094464
N	4.64651238	2.43710185	-0.02423867

N	6.81963982	-0.39981316	0.23005348
C	-3.05465602	-0.21030704	-0.30041002
C	1.97671710	-0.69894581	-0.01209514
C	-0.38874249	-1.22338785	-0.11610103
C	-1.94125290	0.67603854	-0.27005260
H	-2.05965233	1.74745309	-0.30822858
C	4.29181788	0.05392083	0.07343066
C	5.68141491	-0.19375761	0.15944640
C	1.65384632	0.68437291	-0.08786910
C	3.37910442	-1.02107243	0.07727273
C	0.93425899	-1.63280405	-0.02992517
H	1.13543257	-2.69647547	0.02019063
C	-1.51007796	-2.10182991	-0.13505505
H	-1.33539445	-3.16957238	-0.07736199
C	3.80806529	1.39422685	-0.01487589
C	-0.67025835	0.17014151	-0.18615661
C	-2.78323812	-1.62520871	-0.21806588
H	-3.59880438	-2.33115044	-0.21839821
C	-5.48128552	-0.65951711	-0.43331563
H	-5.24558249	-1.51968101	-1.06126171
H	-6.28296884	-0.12412026	-0.94107105
C	-4.60234002	1.69789349	-0.48176825
H	-5.56709886	1.80336292	-0.97703887
H	-3.86852782	2.16702154	-1.13937524
C	-5.95526593	-1.11253032	0.95054214
H	-5.17158749	-1.64502084	1.49352259
H	-6.80655993	-1.78812867	0.83461011
H	-6.27652711	-0.26438810	1.55750761
C	-4.63727876	2.40032932	0.87898579
H	-3.69089435	2.29652628	1.41357583
H	-5.43302419	2.00102870	1.51018745
H	-4.82647198	3.46604955	0.72781063
H	4.78190898	-2.50956009	0.22527356
H	3.16328364	-3.06861956	0.17624099
H	4.26505872	3.36871474	-0.08774644
H	5.64737526	2.32800868	0.02545155

NEt_2Chromeneradical
Charge: 0, Doublet
Total energy: -632301.3 kcal/mol

O	0.36215350	1.04381859	-0.16735212
N	2.50543517	1.67053595	-0.08213148
N	3.82659824	-2.29193252	0.17805425
N	-4.35125804	0.26540547	-0.42864634
N	4.66068783	2.47668116	-0.04971121
N	6.83733974	-0.36687566	0.19483704

C	-3.07119883	-0.22925254	-0.29508111
C	1.99632262	-0.72007630	-0.00553542
C	-0.38953562	-1.26613792	-0.09306427
C	-1.94457574	0.63276765	-0.27279542
H	-2.04607954	1.70673739	-0.32341631
C	4.30540388	0.07511718	0.07081590
C	5.69542339	-0.16744733	0.13879896
C	1.66624365	0.64901953	-0.08429617
C	3.38874580	-1.00724426	0.06799867
C	0.95707263	-1.69517571	0.00126292
H	1.16868026	-2.75242601	0.08842514
C	-1.52165130	-2.11290069	-0.09839973
H	-1.36829008	-3.18423529	-0.02347485
C	3.81520428	1.40514758	-0.00427498
C	-0.66955198	0.11576107	-0.18045465
C	-2.81100560	-1.62306045	-0.19040969
H	-3.62664935	-2.33099579	-0.17783308
C	-5.51296842	-0.62827760	-0.43502242
H	-5.28745562	-1.50384037	-1.04985607
H	-6.31793460	-0.09968590	-0.94900437
C	-4.60275055	1.70711848	-0.50496993
H	-5.56667854	1.83748174	-1.00035684
H	-3.86092738	2.16495726	-1.16541806
C	-6.00018647	-1.07145720	0.95068841
H	-5.21703371	-1.59436813	1.50428466
H	-6.85029056	-1.75148274	0.84286668
H	-6.32479342	-0.21578437	1.54664583
C	-4.62303011	2.43556405	0.84543584
H	-3.67884939	2.31595813	1.38153711
H	-5.42638089	2.06064844	1.48335547
H	-4.78803078	3.50505037	0.68534308
H	4.80806014	-2.49150941	0.05499878
H	3.20703478	-3.04685820	-0.06859809
H	4.24354279	3.38309136	0.10002460
H	5.61545757	2.37321879	0.25829601

OMeChromenecation
Charge: +1, Singlet
Total energy: -570706.8 kcal/mol

O	-0.57650160	-1.11893083	-0.00026043
N	1.56403927	-1.71754262	-0.00021390
N	3.72321483	-2.44005695	-0.00062264
C	0.71572890	-0.72681320	-0.00018970
O	-5.24520227	-0.23768240	0.00021114
C	3.35368679	-0.05941137	0.00024152
C	1.02662150	0.66877358	-0.00018520

C	2.43650359	1.00748184	-0.00015390
C	-1.35082701	1.15837040	-0.00013619
C	-2.88871662	-0.76002883	0.00000873
H	-3.02078930	-1.83178099	-0.00000021
C	-1.60847218	-0.23328672	-0.00011747
C	2.87866928	-1.40765255	-0.00013813
N	2.84291371	2.27889635	-0.00034201
N	5.88288623	0.41620237	0.00102481
C	-0.01594671	1.58357687	-0.00017026
H	0.17253282	2.65087535	-0.00021600
C	4.74484727	0.20012723	0.00069470
C	-3.96373827	0.13426047	0.00006870
C	-3.74186405	1.53961367	-0.00002853
H	-4.60420616	2.19344931	-0.00003147
C	-2.46918791	2.03671201	-0.00012946
H	-2.29659417	3.10585538	-0.00017871
C	-5.58433395	-1.63774288	0.00048321
H	-6.67030394	-1.66962142	0.00096942
H	-5.19709679	-2.12468784	0.89739277
H	-5.19785772	-2.12481542	-0.89669006
H	3.34887494	-3.37730333	-0.00011578
H	2.20008399	3.05334466	-0.00000209
H	4.72470814	-2.32128904	-0.00039937
H	3.82507733	2.51250211	-0.00074612

OMeChromeneradical
Charge: 0, Doublet
Total energy: -570800.8 kcal/mol

O	0.57150173	-1.10935942	-0.00656645
O	5.28603417	-0.27702184	-0.00440208
N	-2.85041154	2.28558019	0.02640873
N	-1.58254396	-1.70190653	0.00155722
N	-3.74802888	-2.47097780	-0.02947575
N	-5.88976353	0.40978182	-0.01278803
C	-3.36255784	-0.07393777	0.00111103
C	-2.89101484	-1.41353384	0.00537400
C	-1.03951010	0.68188588	0.00081438
C	1.35782504	1.18867519	0.00881991
C	-2.43002075	0.99432761	-0.00395309
C	-4.75011287	0.19143589	-0.00622963
C	-0.72962537	-0.69400582	-0.00318274
C	1.61290328	-0.19840038	-0.00308022
C	2.89142427	-0.73684501	-0.00800225
H	3.00379472	-1.81172873	-0.01597962
C	0.01309690	1.64022910	0.01500121
H	-0.18366480	2.70327704	0.04200986

C	3.98790700	0.13258432	-0.00084878
C	2.49436304	2.03466716	0.01639542
H	2.34352684	3.10827473	0.02593053
C	3.77724043	1.52319347	0.01129713
H	4.63817993	2.18068375	0.01686712
C	5.56416643	-1.68014654	-0.01166296
H	5.15972636	-2.15689341	-0.90896275
H	5.15912322	-2.16601627	0.88046242
H	6.64861132	-1.76608651	-0.01177280
H	-2.20709354	3.02851652	-0.19277765
H	-3.82403574	2.49894775	-0.12928819
H	-3.35714149	-3.38224445	0.15519853
H	-4.72258638	-2.34379967	0.19502519

SArFanion
Charge: -1, Singlet
Total energy: -457635.1 kcal/mol

S	2.79760516	-0.00002044	0.00017255
F	-3.16112046	0.00000232	0.00028325
C	1.02157021	-0.00000866	-0.00106678
C	0.28049413	-1.20133558	0.00011758
H	0.81003769	-2.14712389	0.00071907
C	-1.11416952	-1.21028399	0.00003444
H	-1.66862576	-2.14176007	0.00047200
C	0.28053895	1.20137365	0.00023415
H	0.81015350	2.14712842	0.00108777
C	-1.78675558	-0.00000027	-0.00050667
C	-1.11410797	1.21030481	-0.00011190
H	-1.66858512	2.14176197	0.00020619

SArFradical
Charge: 0, doublet
Total energy: -457529.4 kcal/mol

S	2.73825552	-0.00002698	0.00000003
F	-3.10849205	0.00003188	-0.00013852
C	1.01469675	-0.00001061	0.00024499
C	0.28742000	-1.22043032	-0.00002477
H	0.83127013	-2.15621810	-0.00012716
C	-1.09616873	-1.22423813	-0.00002186
H	-1.66335240	-2.14626215	-0.00010972
C	0.28744375	1.22042464	-0.00000878
H	0.83131432	2.15620060	-0.00009940
C	-1.75917804	0.00001669	0.00008622
C	-1.09614373	1.22425960	-0.00000018
H	-1.66331196	2.14629317	-0.00007121

SArOMeanion
Charge: -1, Singlet
Total energy: -467203.4 kcal/mol

S	-3.26223860	-0.21680314	0.00055275
O	2.69780123	0.53640806	-0.00149781
C	1.34454761	0.28243657	-0.00080222
C	0.50299228	1.40063636	-0.00010018
H	0.94559117	2.39124544	0.00021025
C	-0.87814524	1.24513191	0.00022380
H	-1.50529007	2.13012630	0.00076908
C	0.77224338	-0.99071722	-0.00119842
H	1.38821046	-1.88095288	-0.00189360
C	-0.61995259	-1.13152868	-0.00077287
H	-1.03791549	-2.13244875	-0.00105844
C	-1.49034760	-0.02791906	0.00001437
C	3.58872922	-0.57563613	0.00201887
H	3.45638991	-1.19600277	-0.89039330
H	3.45272764	-1.19310428	0.89587830
H	4.59329195	-0.15569982	0.00332613

SArOMeradical
Charge: 0, doublet
Total energy: -457529.4 kca/mol

S	-3.19456100	-0.22042000	0.00030600
O	2.63895800	0.53109600	-0.00077500
C	1.31960500	0.27895800	-0.00026400
C	0.47978800	1.41497200	-0.00011600
H	0.93735700	2.39684900	0.00004500
C	-0.88602900	1.26510400	0.00001400
H	-1.52680100	2.13828500	0.00035400
C	0.75528100	-1.01113900	-0.00061000
H	1.38223700	-1.89187800	-0.00107900
C	-0.61929700	-1.15301400	-0.00047300
H	-1.05386900	-2.14504000	-0.00067100
C	-1.48707600	-0.02778800	0.00010700
C	3.57202400	-0.56208700	0.00103100
H	3.45162200	-1.17434600	-0.89512700
H	3.44823700	-1.17418000	0.89682000
H	4.55674400	-0.10177800	0.00282000

$Ph_2CHSArF$
Charge: 0, Singlet
Total energy: -772528.0 kcal/mol

C	-0.88450083	-0.28572329	0.29025404
C	-0.59132377	1.20474575	0.24973607
C	-0.48302849	1.93714024	-0.93787831

C	-0.45590849	1.88365166	1.46726893
C	-0.26608266	3.31411777	-0.90774987
H	-0.54925481	1.42788151	-1.89188617
C	-0.23678964	3.26046353	1.50035037
H	-0.52549744	1.33030485	2.39825466
C	-0.14438015	3.98205255	0.31088335
H	-0.18496275	3.86397286	-1.83885659
H	-0.13327491	3.76566108	2.45419246
C	-2.35635618	-0.65088048	0.17405881
C	-3.18208994	-0.12036766	-0.82427328
C	-2.90552315	-1.56325568	1.08365355
C	-4.52298692	-0.49317115	-0.90890644
H	-2.78481624	0.59316255	-1.53576199
C	-4.24721208	-1.93260719	1.00413978
H	-2.27810591	-1.98553863	1.86167216
C	-5.06106671	-1.39901341	0.00521326
H	-5.14808729	-0.07153885	-1.68807557
H	-4.65499782	-2.63534979	1.72209339
H	-6.10496811	-1.68422835	-0.05900203
H	-0.52487700	-0.67321549	1.24349810
S	0.02269787	-1.28640498	-1.01476945
C	1.73636584	-1.06951571	-0.52065373
C	2.57875627	-0.23227035	-1.26006440
C	2.25206672	-1.77280663	0.57498459
C	3.92186981	-0.09266388	-0.91258585
H	2.18766847	0.31267756	-2.10977554
C	3.58831357	-1.63187689	0.94156452
H	1.61162092	-2.43756677	1.14190316
C	4.39281200	-0.79366265	0.18506062
H	4.58736571	0.54909441	-1.47629481
H	4.00212867	-2.16740606	1.78683229
H	0.02927099	5.05194110	0.33253025
F	5.70111221	-0.65816796	0.53385011

$Ph_2CHSArOMe$
Charge: 0, Singlet
Total energy: -782098.9 kcal/mol

C	-1.18534697	-0.29008074	0.26335882
C	-0.99075612	1.21654334	0.26895589
C	-1.00391785	1.99968196	-0.89083856
C	-0.81963242	1.85593954	1.50332823
C	-0.86969941	3.38544701	-0.81618508
H	-1.09939755	1.52368272	-1.85943630
C	-0.68274509	3.24157010	1.58107071
H	-0.79535040	1.26398408	2.41259462
C	-0.71069113	4.01262988	0.41973003

H	-0.88225905	3.97473861	-1.72643467
H	-0.54892401	3.71547276	2.54716774
C	-2.63410986	-0.74939909	0.21220137
C	-3.55908456	-0.21448412	-0.69231139
C	-3.05816287	-1.76114611	1.08331936
C	-4.87339428	-0.67961858	-0.72343396
H	-3.26107808	0.57461279	-1.37171893
C	-4.37258962	-2.22395783	1.05714759
H	-2.35324262	-2.18771198	1.78941361
C	-5.28569876	-1.68487789	0.15100772
H	-5.57614949	-0.25223395	-1.42998990
H	-4.68224230	-3.00329133	1.74445513
H	-6.30892694	-2.04229264	0.12858803
H	-0.74708979	-0.68837277	1.17849523
S	-0.28809564	-1.18272799	-1.12644179
C	1.43453658	-0.88557857	-0.72149417
C	2.17622171	0.07359985	-1.42619421
C	2.07487178	-1.63766989	0.26581917
C	3.51999993	0.27538117	-1.14505975
H	1.69729651	0.66263518	-2.19861265
C	3.42236424	-1.43570206	0.56536486
H	1.52243754	-2.39520571	0.80972019
C	4.15170867	-0.47424646	-0.14327302
H	4.09628968	1.01414115	-1.68958056
H	3.88663689	-2.03412396	1.33733434
O	5.46890775	-0.20052613	0.06474945
C	6.16926124	-0.92431274	1.08079237
H	7.18581180	-0.53686256	1.07120446
H	5.72239238	-0.75377796	2.06419667
H	6.18476338	-1.99564560	0.86204181
H	-0.60151111	5.08979538	0.47579823

Ph_2CHcation
Charge: +1, singlet
Total energy: -314867.3 kcal/mol

C	-0.00005129	1.01014915	0.00016949
H	-0.00024065	2.09773274	0.00052858
C	1.28734200	0.42313666	0.03976915
C	1.54318072	-0.92488844	0.41490291
C	2.38930822	1.26375513	-0.28487084
C	2.83576798	-1.41093696	0.41028688
H	0.73786652	-1.55484012	0.76465964
C	3.67526537	0.75809017	-0.31206064
H	2.20400476	2.30059489	-0.53888035
C	3.89844703	-0.57887377	0.03271574
H	3.03112975	-2.43104388	0.71564027

H	4.50650295	1.39596271	-0.58398687
H	4.90867105	-0.97104930	0.03099694
C	-1.28722967	0.42297250	-0.03967688
C	-2.38924861	1.26369992	0.28476862
C	-1.54320105	-0.92501981	-0.41482105
C	-3.67523611	0.75817230	0.31187020
H	-2.20395207	2.30056597	0.53869177
C	-2.83581029	-1.41095684	-0.41024471
H	-0.73797769	-1.55509582	-0.76459666
C	-3.89848332	-0.57880676	-0.03279879
H	-4.50642366	1.39617889	0.58364020
H	-3.03114573	-2.43107127	-0.71558140
H	-4.90874116	-0.97089439	-0.03117269

Ph_2CHradical
Charge: 0, doublet
Total energy: -314979.2 kcal/mol

C	-0.00000915	1.02072320	0.00010072
H	0.00000140	2.10744702	0.00014978
C	1.30474639	0.42530286	0.01777453
C	1.58075495	-0.92373665	0.36259304
C	2.42014482	1.25444934	-0.28110310
C	2.88217635	-1.40945015	0.37188269
H	0.77765344	-1.58059021	0.66632385
C	3.71550880	0.76012713	-0.27700549
H	2.24355494	2.29606404	-0.52803944
C	3.95827349	-0.57997215	0.04361351
H	3.06206616	-2.44226253	0.64953915
H	4.54234788	1.41812532	-0.52052135
H	4.97043292	-0.96732299	0.05059547
C	-1.30473024	0.42529441	-0.01770828
C	-2.42018430	1.25444443	0.28108143
C	-1.58072997	-0.92376411	-0.36250634
C	-3.71553110	0.76012940	0.27689244
H	-2.24356248	2.29605832	0.52800871
C	-2.88215046	-1.40946208	-0.37188471
H	-0.77760106	-1.58062788	-0.66615005
C	-3.95827902	-0.57998533	-0.04372198
H	-4.54238939	1.41813318	0.52033607
H	-3.06201509	-2.44228429	-0.64953265
H	-4.97043206	-0.96734184	-0.05076040

CH_3SArF
Charge: 0, Singlet
Total energy: -482577.5 kcal/mol

C	2.99216325	-0.56254387	0.94817455

H	2.65006757	-0.10442660	1.87548437
S	2.31461266	0.33739927	-0.50073894
C	0.54682042	0.15812540	-0.24173965
C	-0.07433471	-1.07627286	-0.37368071
C	-0.22035725	1.27713200	0.04330367
C	-1.43650372	-1.19514187	-0.20512396
H	0.50860115	-1.95566001	-0.61566265
C	-1.58782850	1.16959007	0.19571597
H	0.25448994	2.24371810	0.15015836
C	-2.15813736	-0.06562563	0.07240187
H	-1.93584633	-2.15046359	-0.30108884
H	-2.20060919	2.03387793	0.41620091
F	-3.49706254	-0.17855928	0.22853515
H	4.07683113	-0.47445582	0.87736697
H	2.71529336	-1.61552423	0.91823721

$CH_3SArOMe$
Charge: 0, Singlet
Total energy: -492147.6 kcal/mol

C	3.41351146	0.06564104	1.17570458
H	3.00012615	0.86437572	1.79099704
S	2.79492108	0.19417848	-0.54887750
C	1.02483645	0.00587844	-0.30961539
C	0.44358841	-1.26843408	-0.23080344
C	0.19699066	1.12680208	-0.23930295
C	-0.92674683	-1.41215817	-0.07135767
H	1.06961868	-2.15067720	-0.29612608
C	-1.18467528	0.99518184	-0.08462995
H	0.62884325	2.11849493	-0.30550349
C	-1.75145187	-0.28013689	0.00279551
H	-1.37882709	-2.39508631	-0.00885470
H	-1.79703858	1.88510639	-0.03523187
H	4.49772906	0.17268448	1.12211279
H	3.16733116	-0.90696437	1.60099981
O	-3.08263119	-0.52327189	0.15548989
C	-3.97905412	0.58832305	0.23817922
H	-4.97131638	0.15861193	0.35836137
H	-3.74699335	1.21826988	1.10147861
H	-3.94915403	1.18792014	-0.67593208

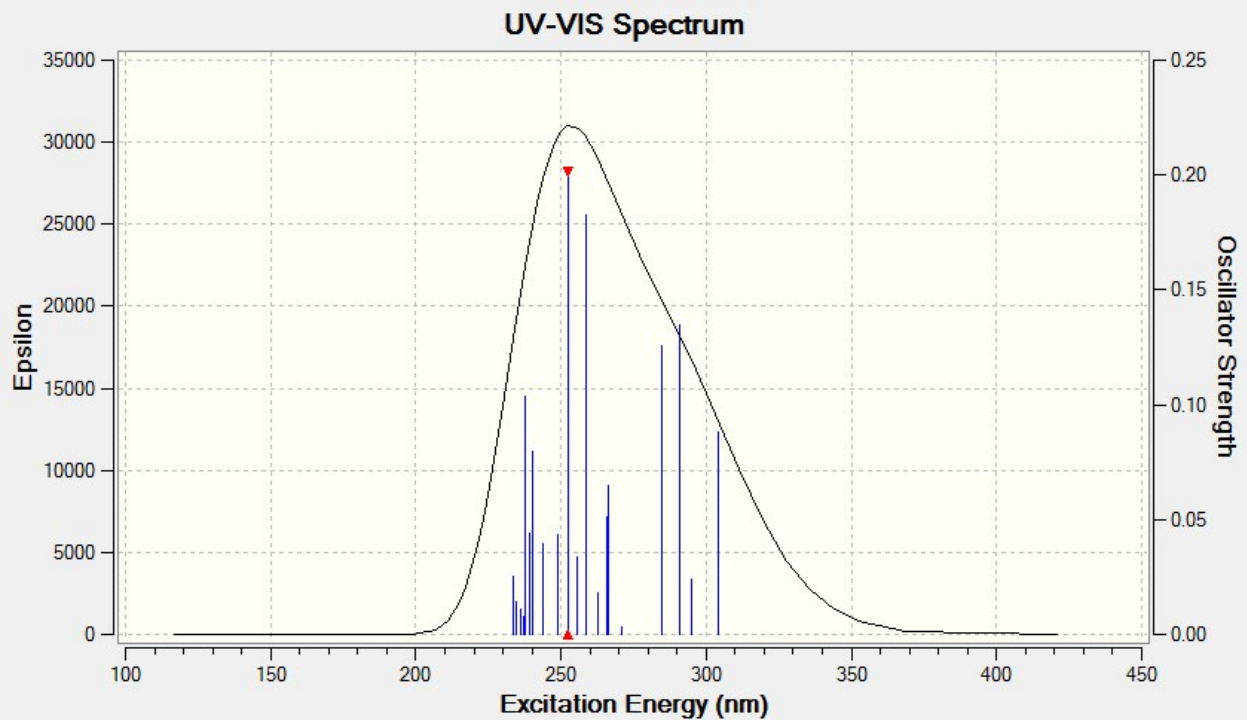
CH_3cation
Charge: +1, Singlet
Total energy: -24844.8 kcal/mol

C	0.00000000	0.00000000	0.00002000
H	0.00000000	1.08806300	-0.00004100
H	-0.94229000	-0.54403100	-0.00004100
H	0.94229000	-0.54403100	-0.00004100

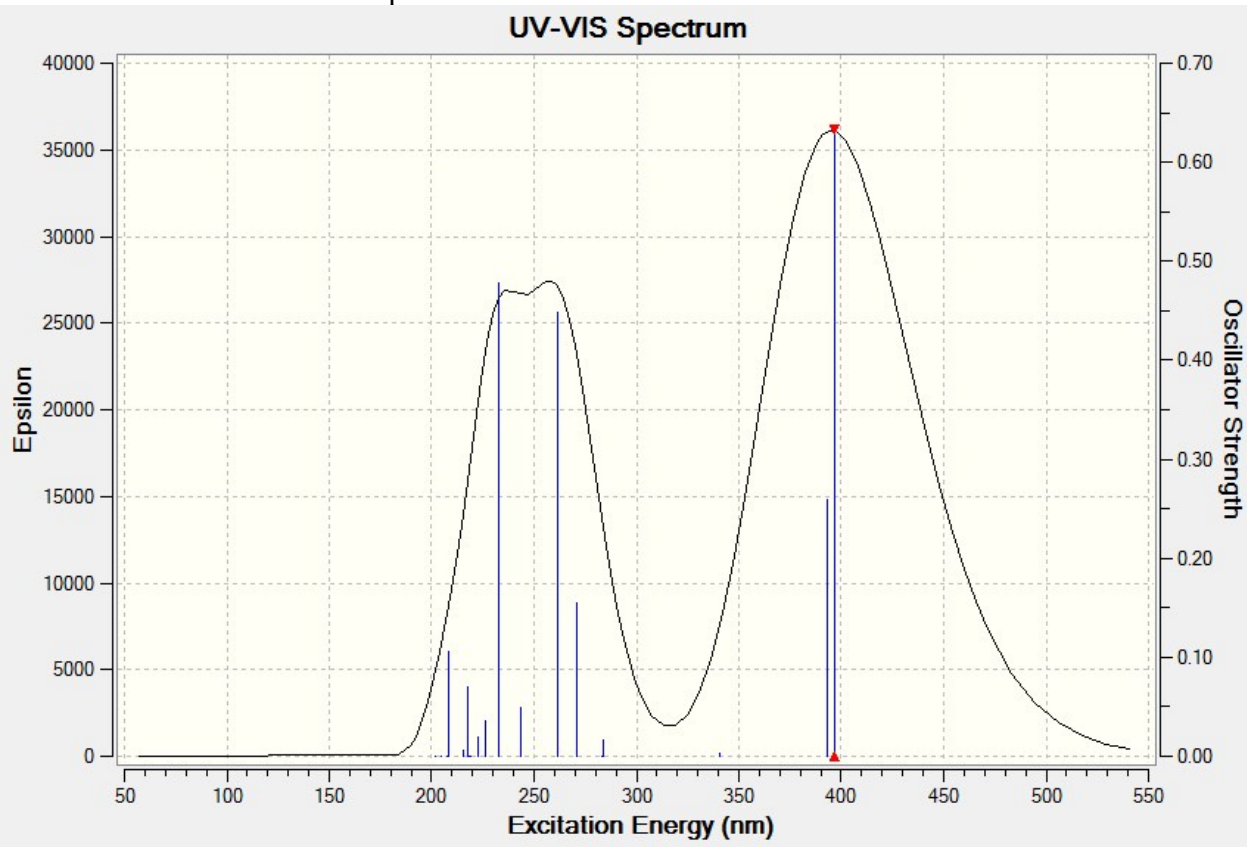
CH_3radical
Charge: 0, Doublet
Total energy: -25003.1 kcal/mol

C	0.00000000	0.00000000	0.00002100
H	0.00000000	1.08110900	-0.00004300
H	-0.93626800	-0.54055500	-0.00004300
H	0.93626800	-0.54055500	-0.00004300

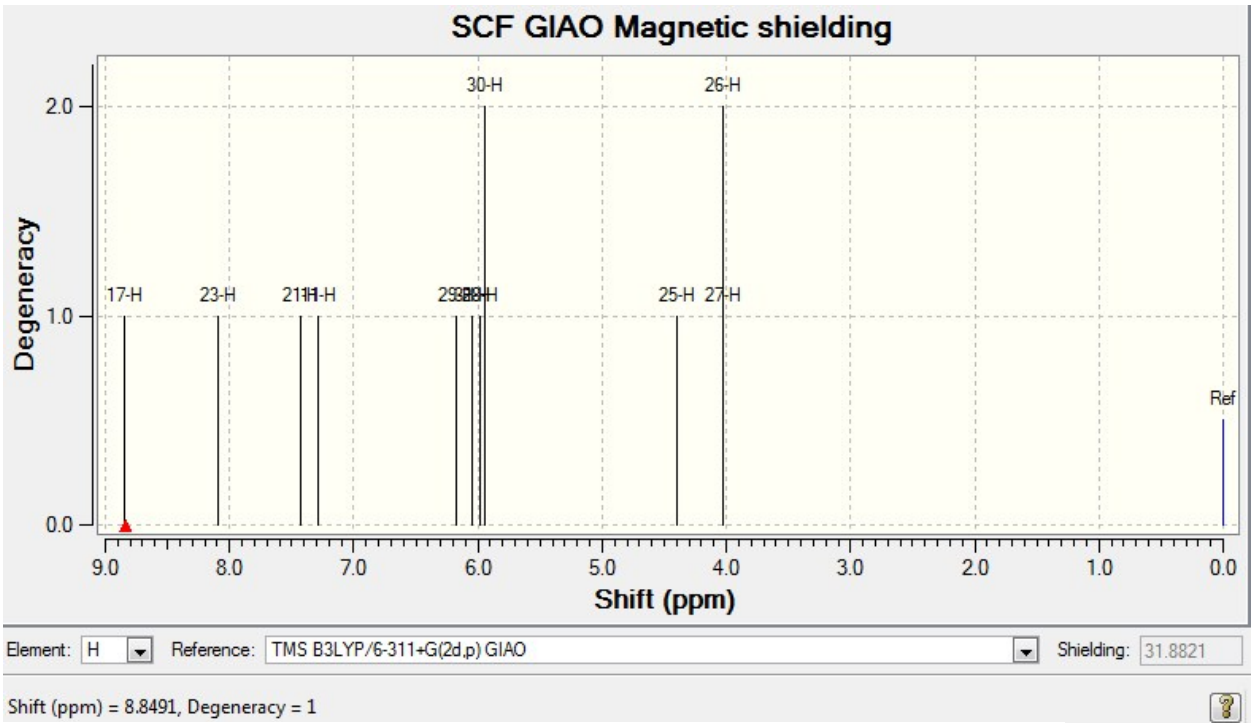
Calculated UV-Vis and NMR
Calculated TD-DFT UV-Vis spectrum of **4a**

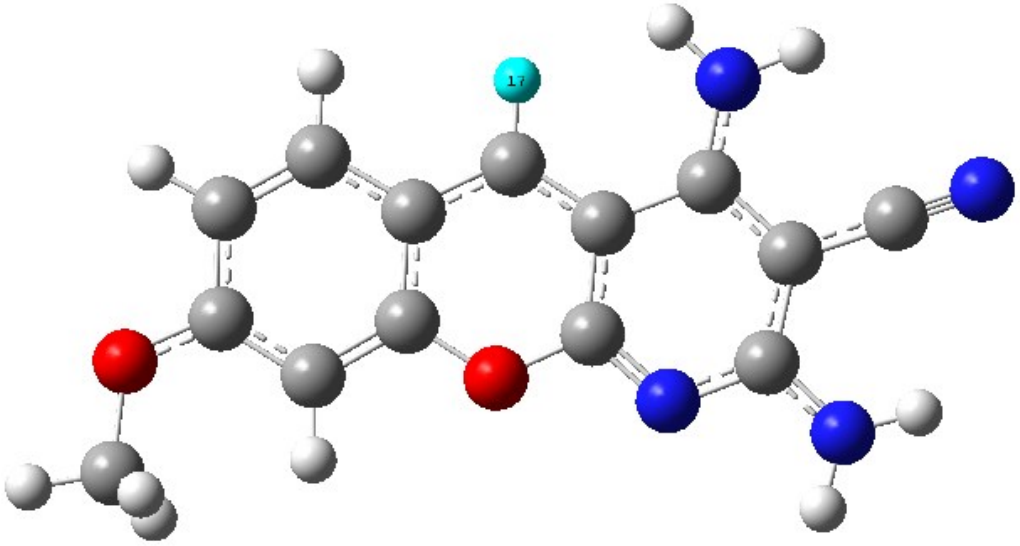


Calculated TD-DFT UV-Vis spectrum of **5**



Output from NMR calculation of compound **5** showing the most downfield proton (H17) as being the proton connected to the carbocation site:





1. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.

Table S5. HOMO and LUMO gap calculated energies from DFT

Compound	HOMO (hartree)	LUMO (hartree)	HOMO (eV)	LUMO (eV)	Gap (eV)	Gap (nm)
3a	-0.2284	-0.0551	-6.216	-1.499	4.72	263
3e	-0.2248	-0.0544	-6.118	-1.480	4.64	267
4a	-0.2012	-0.0528	-5.475	-1.436	4.04	307
4e	-0.2002	-0.0521	-5.447	-1.419	4.03	308
5	-0.2602	-0.1334	-7.081	-3.630	3.45	359
6	-0.2223	-0.0514	-6.049	-1.400	4.65	267