Electronic Supplementary Material (ESI) for RSC Advances

Conformational Analysis via Calculations and NMR Spectroscopy for Isomers of the Mono(imino)pyridine Ligand, 2-{(2,6-Me_2-C_6H_3)NC(*i*-Pr)}C_5H_4N

Timothy J. Dudley, Jennifer E. Beck, Earl E. P. Santos, Kathryn A. Johnston, William S. Kassel, William G. Dougherty, Walter J. Boyko, and Deanna L. Zubris**

Below is an example set of input parameters used to perform B3LYP/6-31G* stationary point searches in GAMESS.

```
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE DFTTYP=B3LYP MAXIT=99 $END
$SYSTEM TIMLIM=6000 MEMORY=6553600 PARALL=.TRUE. $END
$DFT NRAD0=96 NLEB0=302 $END
$SCF DIRSCF=.TRUE. $END
$STATPT OPTTOL=0.001 NSTEP=40 METHOD=RFO HSSEND=.T. $END
$FORCE NVIB=2 $END
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1-E_A

Nuclear Rep. Energy = 1391.1038607821 a.u.

MP2/6-311+G** Energy = -767.2549960219 a.u.

Nuclear Coordinates (Bohr)

N	2.2149100357	5.1050002695	0.4575215589
N	0.0593184988	0.4771936064	1.4391586205
C	0.7413206077	3.9393605885	-1.2538142956
C	-0.3940834575	5.2475989926	-3.2613269041
H	-1.5852533366	4.2644123557	-4.6120841429
C	-0.0211649311	7.8474084174	-3.4730329065
H	-0.9122652206	8.9037274500	-4.9926938541
C	1.5069619889	9.0555858304	-1.7031911355
H	1.8662555910	11.0743801031	-1.7956365308
C	2.5822349732	7.5880246284	0.2111579819
C	0.3102363154	1.1439267294	-0.8630567559
C	-0.2962145486	-1.9534286508	2.4489714965
C	-2.7720579486	-2.8059218383	2.9924377933
C	-3.0678000657	-5.1509584056	4.1753495699
H	-4.9704895737	-5.8222835627	4.5733258629
C	-0.9887613286	-6.5993766834	4.8944092055
H	-1.2573858777	-8.4146663644	5.8167655628
C	1.4366452849	-5.6508854156	4.5010816384
H	3.0709748054	-6.7153680645	5.1536229192
C	1.8323350095	-3.3191336221	3.3216091631
C	-5.0395968531	-1.1642601810	2.4313592503
H	-6.7104169824	-1.8699405566	3.4273015376
H	-5.5058300488	-1.0919781620	0.4131318954
H	-4.6962714356	0.7883369903	3.0352400870
C	4.4618698241	-2.2334860421	3.0772675929
H	5.7371892015	-3.1075976950	4.4530259065
H	4.4448622902	-0.1870261810	3.3931352918
H	5.2801400741	-2.5425129329	1.1965744954
H	3.8055679886	8.4567316649	1.6212148221
C	0.2487257345	-0.5106984482	-3.2645961301
H	0.6444343563	0.7609737580	-4.8507943297
C	2.3458302521	-2.5293415428	-3.2914491364
H	2.0512975597	-3.9453510199	-1.8165180030
H	4.2152227882	-1.6819128209	-3.0248276968
H	2.3448286973	-3.4990733306	-5.1229526664
C	-2.3522175260	-1.7203687447	-3.7608570717
H	-2.3335470332	-2.6784220260	-5.5984266222
H	-3.8658880421	-0.3061356100	-3.7999555024
H	-2.8129705163	-3.1251154549	-2.3165772938

1-TS$_A$

Nuclear Rep. Energy = 1381.2081297050 a.u.

MP2/6-311+G** Energy = -767.2313640872 a.u.

Nuclear Coordinates (Bohr)

N	1.4844537100	4.3643980359	0.9231940657
N	-0.0200391149	-0.5401503478	0.3171933579
C	0.7234055318	3.5903422122	-1.3760319321
C	0.3965682004	5.2870132775	-3.3866958581
H	-0.2105541781	4.6347458762	-5.2315292343
C	0.8446900972	7.8545610562	-2.9862448366
H	0.5833943170	9.2020491744	-4.5145431096
C	1.6323604714	8.6505176991	-0.6063855275
H	2.0123990801	10.6274156980	-0.2063668674
C	1.9313665288	6.8178210365	1.2747456384
C	0.2194511678	0.7723861324	-1.6282372051
C	-0.1837834738	-2.1136743311	2.3174206513
C	-2.5772557145	-2.9786505226	3.1744371462
C	-2.6584715180	-4.5935026902	5.2580854613
H	-4.4961092201	-5.2410774408	5.9177979131
C	-0.4680554065	-5.3920295555	6.4861411099
H	-0.5780671483	-6.6617285455	8.0955622897
C	1.8659962777	-4.5135869292	5.6282631825
H	3.5923616658	-5.0951487719	6.5837957495
C	2.0664035511	-2.8623030500	3.5848991963
C	-4.9578720039	-2.1288039002	1.8627275425
H	-6.6344865656	-2.8379320318	2.8459205938
H	-5.0451722591	-2.8126964448	-0.0976620835
H	-5.0978792956	-0.0599705818	1.7774288709
C	4.5784331973	-1.8507192556	2.7077295915
H	6.0985057329	-2.4443817544	3.9798549759
H	4.5484882327	0.2223194069	2.6340726012
H	5.0652366048	-2.5112877721	0.7977368215
H	2.5623533176	7.3566851275	3.1589973067
C	0.0006650390	-0.3526591985	-4.3118093861
H	1.1849232564	0.7908867843	-5.5742501507
C	0.9792390626	-3.0799508937	-4.3899053410
H	-0.1054172225	-4.2937714699	-3.1130039647
H	2.9682352088	-3.1836245139	-3.8229666321
H	0.8163466092	-3.8463967724	-6.3071865790
C	-2.7530395991	-0.2085650784	-5.2625852922
H	-2.8797526273	-0.8996864077	-7.2113975638
H	-3.5063325524	1.7198315997	-5.2161592177
H	-3.9829889611	-1.3886748568	-4.0868227362

1-Z_A

Nuclear Rep. Energy = 1413.0699020177 a.u.

MP2/6-311+G** Energy = -767.2651824209 a.u.

Nuclear Coordinates (Bohr)

N	2.0047725059	3.0517940866	0.9333545626
N	0.0597909303	-1.8816568578	-0.7768474563
C	0.5032529278	2.7550504148	-1.0930553058
C	-0.7531880869	4.7971450089	-2.2295365148
H	-1.9470035824	4.5048232958	-3.8715383228
C	-0.4679717436	7.2051661432	-1.2010909405
H	-1.4364752096	8.8125292739	-2.0363687244
C	1.0824161485	7.5097332807	0.9054811043
H	1.3702781082	9.3504586735	1.7665725451
C	2.2780079864	5.3715650174	1.8881764124
C	0.2392582073	0.1126276689	-2.1189119555
C	-0.0726977587	-2.0178305124	1.8880063371
C	-2.4374063735	-1.7814068941	3.0956924213
C	-2.5732776720	-2.2171966041	5.7008308735
H	-4.3950680105	-2.0352159915	6.6372278949
C	-0.4392290113	-2.8851580490	7.0894393238
H	-0.5813930974	-3.2252142405	9.1101233224
C	1.8779907893	-3.1353766670	5.8570167263
H	3.5565398979	-3.6621566834	6.9219529095
C	2.1016020655	-2.7251171551	3.2596450480
C	-4.7788713586	-1.1054519083	1.6097441854
H	-6.4685698505	-1.2550048230	2.7941866400
H	-5.0253294219	-2.3571119163	-0.0253034310
H	-4.7047563053	0.8334258524	0.8724297968
C	4.6097597799	-2.9615218762	1.9333219663
H	6.0519608592	-3.7388606612	3.1974541657
H	5.2541752390	-1.1036377713	1.2731650897
H	4.4730758992	-4.1880296312	0.2666025423
H	3.5208051795	5.5293193428	3.5207673850
C	0.1690548869	-0.2092682559	-5.0029739635
H	0.7611627306	1.5834391996	-5.8600969797
C	2.0234996904	-2.2754190618	-5.8595678564
H	1.5184137284	-4.0881954073	-5.0038621347
H	3.9654766017	-1.8239068316	-5.3002278613
H	1.9754061640	-2.4755032494	-7.9211833200
C	-2.5351618988	-0.8150010240	-5.9036173692
H	-2.5875828977	-0.9951863969	-7.9670847642
H	-3.8926465621	0.6530326096	-5.3576377368
H	-3.1705255704	-2.6021526851	-5.0751803934

1-E_B

Nuclear Rep. Energy = 1388.7147029633 a.u.

MP2/6-311+G** Energy = -767.2677693454 a.u.

	Nuclear Coordinates (Bohr)		
N	-5.1453763763	0.2800285903	2.7657512478
N	0.7743713183	1.4515041389	-0.2290590374
C	-3.1043607197	1.5642041121	1.9658240397
C	-2.8576582672	4.1832250545	2.3317139328
H	-1.1745420108	5.1253969578	1.6443231665
C	-4.7814547916	5.4859375795	3.5581131436
H	-4.6317623549	7.5119872984	3.8639178628
C	-6.9011179949	4.1518721976	4.3877474229
H	-8.4493562923	5.0897961163	5.3556488669
C	-6.9829086757	1.5563036651	3.9405942410
C	-1.0521595152	0.1097599832	0.6336652038
C	2.8905932328	0.5025335388	-1.5460538012
C	5.0784962025	-0.2224316668	-0.1991730118
C	7.2197295649	-0.9532505888	-1.5662257056
H	8.9055005369	-1.5204348635	-0.5342809811
C	7.2316140854	-0.9458330342	-4.1994594064
H	8.9144215991	-1.5158041343	-5.2297494559
C	5.0802685978	-0.1587540865	-5.5000059845
H	5.0876005563	-0.1021470781	-7.5555019739
C	2.8978927067	0.5925687063	-4.2141632149
C	5.1160904727	-0.1661222396	2.6535530337
H	7.0450076124	-0.3858142089	3.3686994529
H	3.9696598556	-1.6831858049	3.4816193346
H	4.3533411036	1.6195834657	3.3771109555
C	0.6062710046	1.5252312836	-5.6361740316
H	-0.9778907114	0.1881495522	-5.5415262618
H	1.0497783669	1.8211907620	-7.6355245867
H	-0.0804752280	3.3132784913	-4.8440564245
H	-8.6006524495	0.4416743566	4.5551122344
C	-1.2304802921	-2.7659312960	0.3609454886
H	0.5336528632	-3.3249515510	-0.5691931970
C	-3.4240016352	-3.5888063454	-1.3761332439
H	-5.2506965483	-3.1565866017	-0.5176062548
H	-3.3122499830	-5.6327917849	-1.7023905015
H	-3.3243238836	-2.6540812418	-3.2219005723
C	-1.3516888654	-4.1576821121	2.9208264158
H	0.1593182585	-3.5460422594	4.1992473852
H	-1.1207091169	-6.1929207180	2.6046871739
H	-3.1635216784	-3.8349850562	3.8528564961

1-TS_B

Nuclear Rep. Energy = 1376.6305538353 a.u.

MP2/6-311+G** Energy = -767.2339127081 a.u.

Nuclear Coordinates (Bohr)

N	-4.8817780895	-1.5050289806	2.7286584028
N	0.8698084335	-0.1056795005	-0.5433302577
C	-3.0552293760	-0.0693460139	1.7042206007
C	-3.0357362649	2.5735370926	1.9392081579
H	-1.5194438135	3.6563224057	1.0853565022
C	-4.9736338079	3.7478247537	3.2733563861
H	-5.0043581044	5.7913827915	3.4783291843
C	-6.8692635294	2.2576365859	4.3403241547
H	-8.4177653210	3.0907246747	5.3989363199
C	-6.7289909897	-0.3548238201	4.0122440491
C	-0.9539037164	-1.3817905809	0.2668540061
C	2.8273138553	1.2868868642	-1.4024871804
C	4.9729050910	1.6855516755	0.1655955747
C	6.9662016589	3.1288584418	-0.7799537168
H	8.6070723842	3.4284422428	0.4238395421
C	6.9028028043	4.1797057615	-3.1972407792
H	8.4789743742	5.2964135556	-3.8914254873
C	4.7814029784	3.7706556321	-4.7081191188
H	4.7010333688	4.5739655366	-6.6002008813
C	2.7288159772	2.3436714010	-3.8713975630
C	5.0491201580	0.5480109886	2.7758127214
H	6.8142154726	1.0314839508	3.7400173659
H	4.9053442778	-1.5237455022	2.7170805031
H	3.4754534114	1.2145647927	3.9557516433
C	0.4448392673	1.8942964064	-5.5136466197
H	0.1562453736	-0.1276203367	-5.8930724336
H	0.6428432879	2.8589027426	-7.3329286686
H	-1.3000537757	2.5801662108	-4.6192350136
H	-8.1688174819	-1.5853964040	4.8172499828
C	-1.0509148927	-4.2585638559	-0.1822859978
H	0.6161497329	-4.6213174599	-1.3591828859
C	-3.3948241395	-5.1077500856	-1.6838325391
H	-5.1151622614	-4.9133586868	-0.5602747876
H	-3.1844478676	-7.0979274022	-2.2251218281
H	-3.6180284061	-4.0059130655	-3.4257957875
C	-0.7334417832	-5.7729489892	2.2852539340
H	0.9618079582	-5.1749545265	3.3171229750
H	-0.5221656405	-7.7872586819	1.8430204407
H	-2.3725008785	-5.5418011625	3.5194093725

1-Z_B

Nuclear Rep. Energy = 1414.3074368605 a.u.

MP2/6-311+G** Energy = -767.2687942118 a.u.

Nuclear Coordinates (Bohr)

N	-3.2459634318	-0.9819961095	3.4304006883
N	1.2862230963	-1.4846065305	-1.4560905653
C	-2.3151599993	-0.1519150722	1.2127505499
C	-2.8163531258	2.2867952123	0.3009955553
H	-2.0510329980	2.9039230281	-1.4947543590
C	-4.3118822725	3.9038526372	1.7443493675
H	-4.7353698663	5.7973769742	1.0707187446
C	-5.2478824515	3.0560081756	4.0558432984
H	-6.4159409817	4.2546991641	5.2439518214
C	-4.6527510461	0.5995344669	4.8084644675
C	-0.7584604224	-2.0189076562	-0.2764102202
C	2.5402830563	0.8680267352	-1.4568086612
C	3.9523052115	1.6744295059	0.6613096094
C	5.3495875041	3.9101832193	0.4591089287
H	6.4423971456	4.5396320485	2.0831016480
C	5.3787459761	5.3204668267	-1.7653253260
H	6.4795491585	7.0504353794	-1.8786332962
C	4.0197495320	4.4680114336	-3.8561748505
H	4.0615313736	5.5342137331	-5.6140735534
C	2.6158154040	2.2341096517	-3.7515029281
C	4.0371539084	0.1273108398	3.0600521892
H	5.4027832907	0.9289515010	4.3913074557
H	4.5972119994	-1.8307287424	2.6684820673
H	2.2028346866	0.0400621909	4.0206566005
C	1.1989177557	1.2661353090	-6.0309471063
H	1.6881489166	-0.7108960193	-6.4171126118
H	1.6332145821	2.3951898949	-7.7093072423
H	-0.8596741463	1.3123580067	-5.7584675161
H	-5.3489072028	-0.1414648874	6.5979782861
C	-1.6629588692	-4.7610323452	-0.4524759905
H	-0.6268410074	-5.5194171786	-2.0787174838
C	-4.5107003437	-4.9964355115	-0.9881188217
H	-5.6427784911	-4.3624891344	0.6225891239
H	-4.9911631760	-6.9768494494	-1.3625869234
H	-5.0670167772	-3.8888104184	-2.6496981909
C	-0.8794595774	-6.3184311208	1.8850394673
H	1.1686443453	-6.2229810611	2.1771533105
H	-1.3909517105	-8.3076889763	1.6013349047
H	-1.8192392084	-5.6278307586	3.5892321575

1-Z_B'

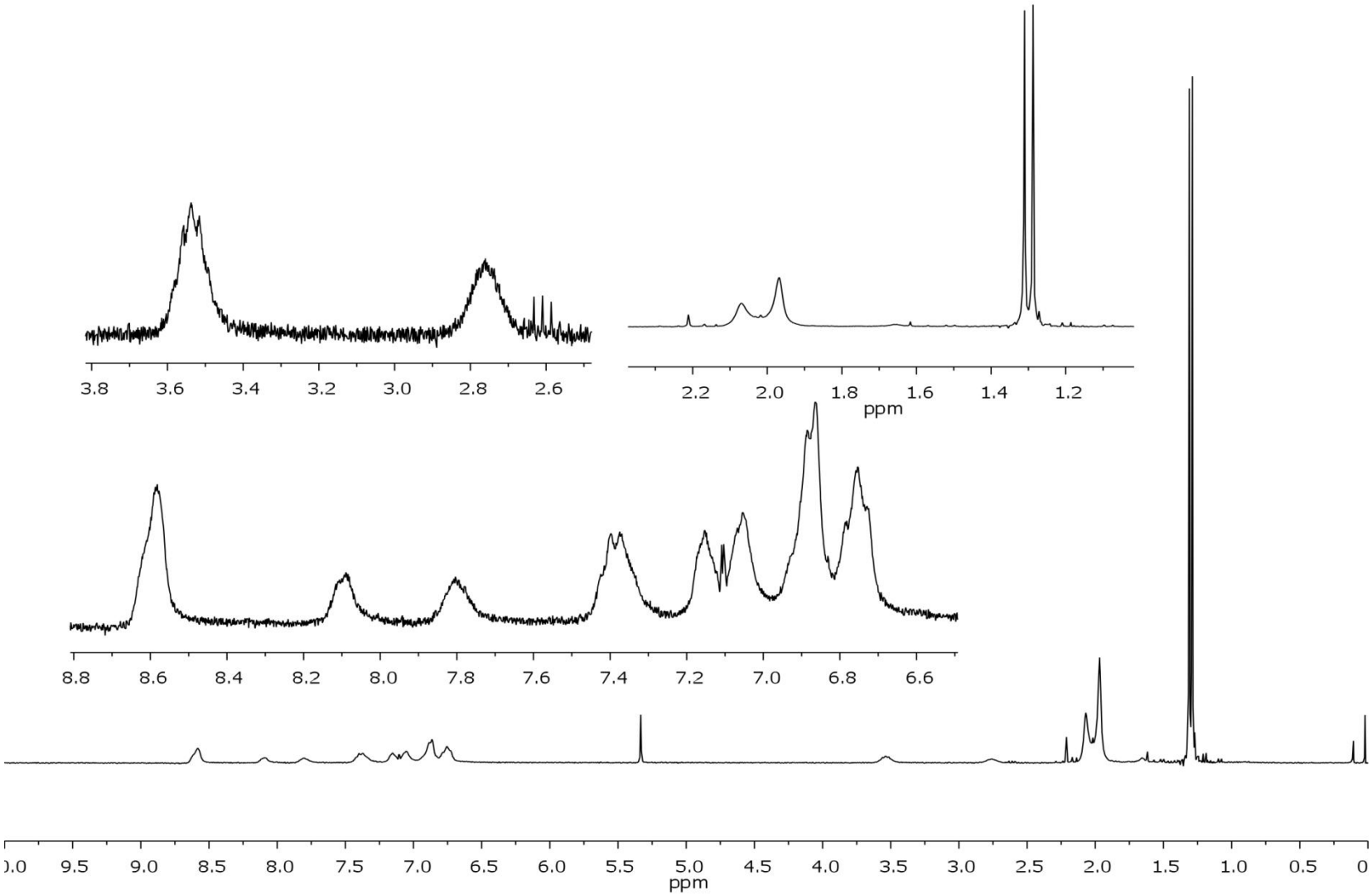
Nuclear Rep. Energy = 1411.4694154064 a.u.

MP2/6-311+G** Energy = -767.2707939500 a.u.

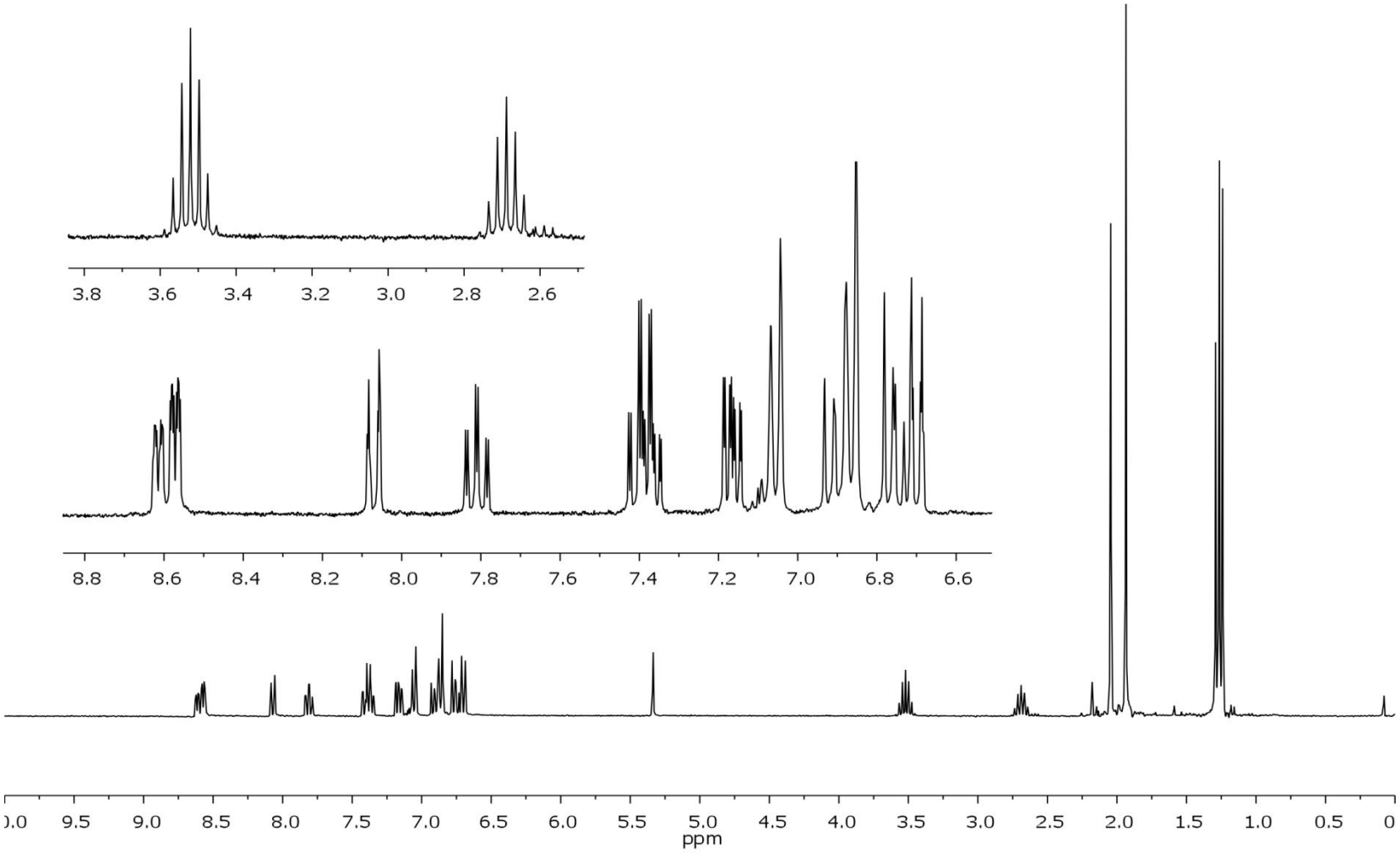
Nuclear Coordinates (Bohr)

N	-3.6031216435	0.4914232431	3.8451955426
N	0.6130838022	-1.8842268851	-0.8234480991
C	-2.3564316149	0.7853134287	1.6462347942
C	-1.9923948006	3.1697885773	0.5432962215
H	-0.9936935134	3.3548494433	-1.2334430494
C	-2.9374845616	5.2981302655	1.7731487915
H	-2.6877950669	7.1624016441	0.9476219938
C	-4.2013899940	4.9961520526	4.0639691202
H	-4.9651794437	6.6031372381	5.0873124343
C	-4.4773088854	2.5509978026	5.0144068057
C	-1.4415207780	-1.6265060549	0.4221269911
C	2.5022239749	-0.0437093621	-1.1877494751
C	4.2216856511	0.5427293037	0.7693263469
C	6.2102821025	2.2030047620	0.2376141457
H	7.5409137595	2.6573704785	1.7376786347
C	6.5188932535	3.2596261507	-2.1551191054
H	8.0763487208	4.5459248361	-2.5268093100
C	4.8347694533	2.6207664861	-4.0789168527
H	5.0804338317	3.4060610175	-5.9635216830
C	2.8348724405	0.9509101170	-3.6444310536
C	3.9708056290	-0.6438296440	3.3539801693
H	5.6050973549	-0.1740059689	4.5320353501
H	3.8441939878	-2.7092812513	3.2221906789
H	2.2726600619	-0.0068974999	4.3588797578
C	1.0500829369	0.2011046396	-5.7406285028
H	0.9375686515	-1.8620792965	-5.9105337663
H	1.6686091499	0.9794638767	-7.5548032455
H	-0.8885491594	0.8639260298	-5.4005912085
H	-5.4557712074	2.2267397204	6.7961538505
C	-3.1755711388	-3.9111280823	0.7146376768
H	-3.7305836614	-3.9528532321	2.7112465664
C	-1.8759876798	-6.4029585642	0.0284214789
H	-1.3227703969	-6.4396192484	-1.9647481094
H	-3.1634202007	-7.9886465378	0.3790223414
H	-0.1608345788	-6.6947133594	1.1480652293
C	-5.6115791151	-3.5229216726	-0.8465405507
H	-6.6136441146	-1.7994726745	-0.2915658226
H	-6.8970085264	-5.1223857486	-0.5669177963
H	-5.1777736173	-3.4016201615	-2.8704370836

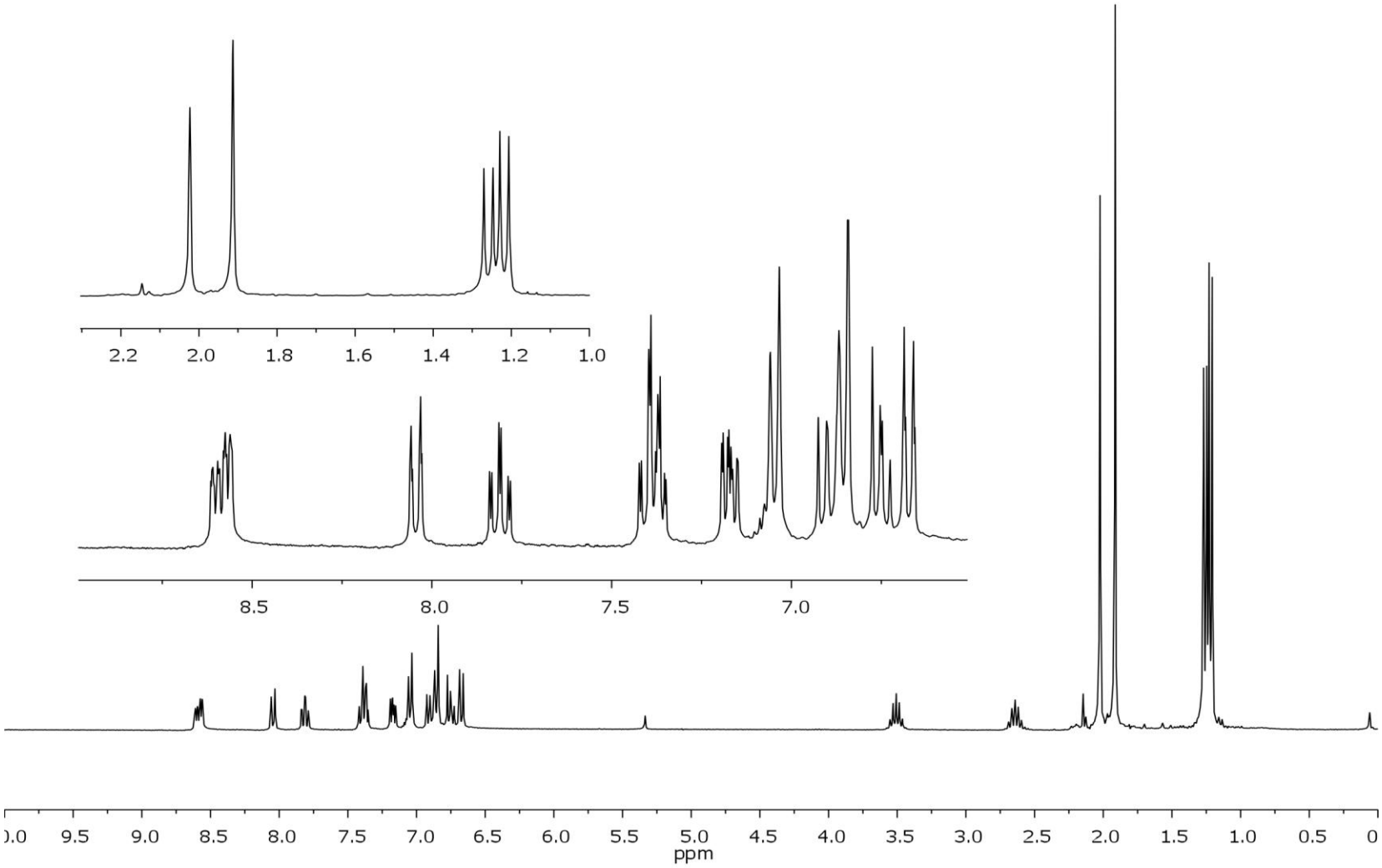
300 MHz ^{1}H spectrum of (**1**) in CD_2Cl_2 at 20 ºC



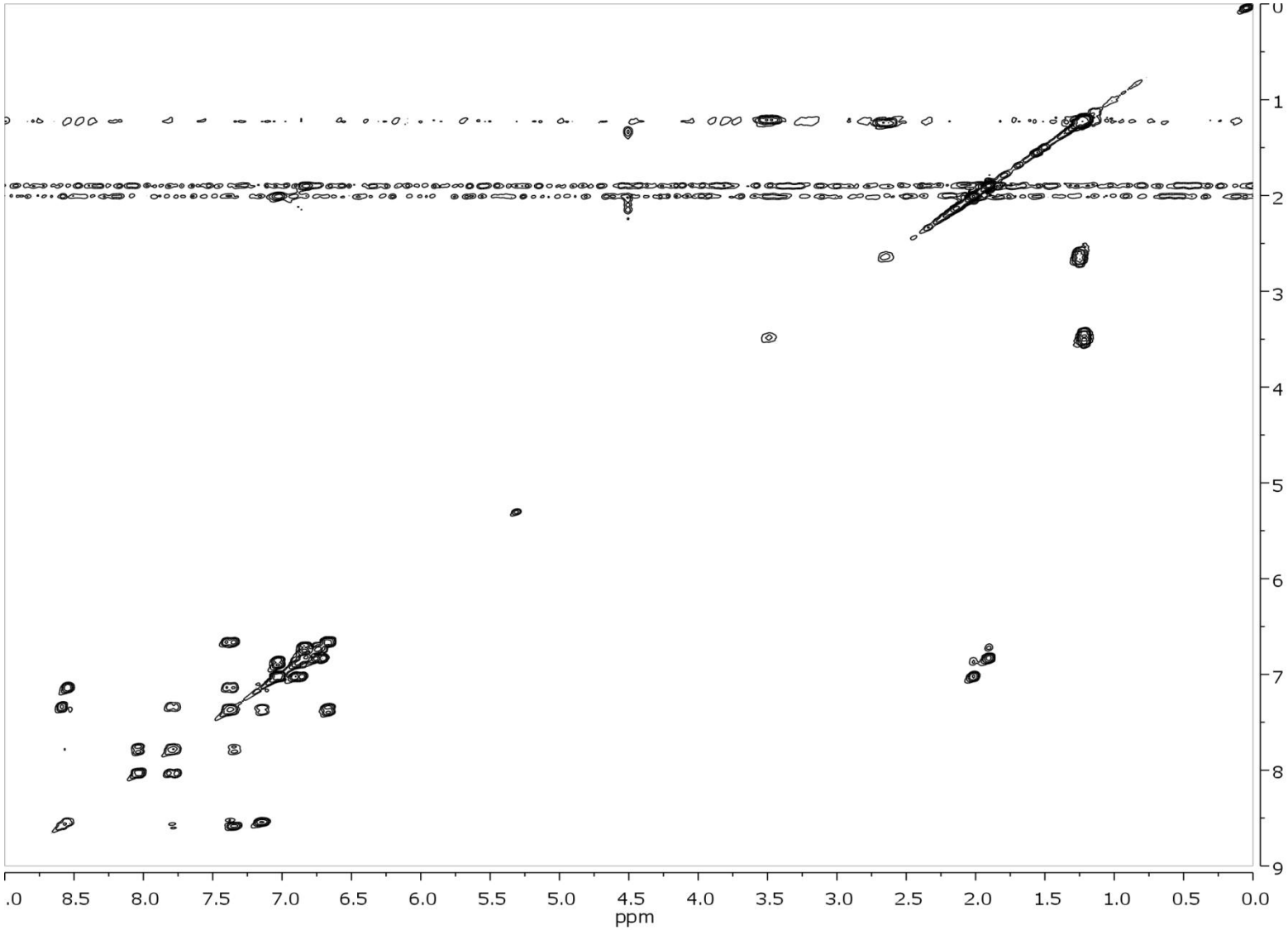
300 MHz ^{1}H spectrum of (**1**) in CD_2Cl_2 at -40 ºC



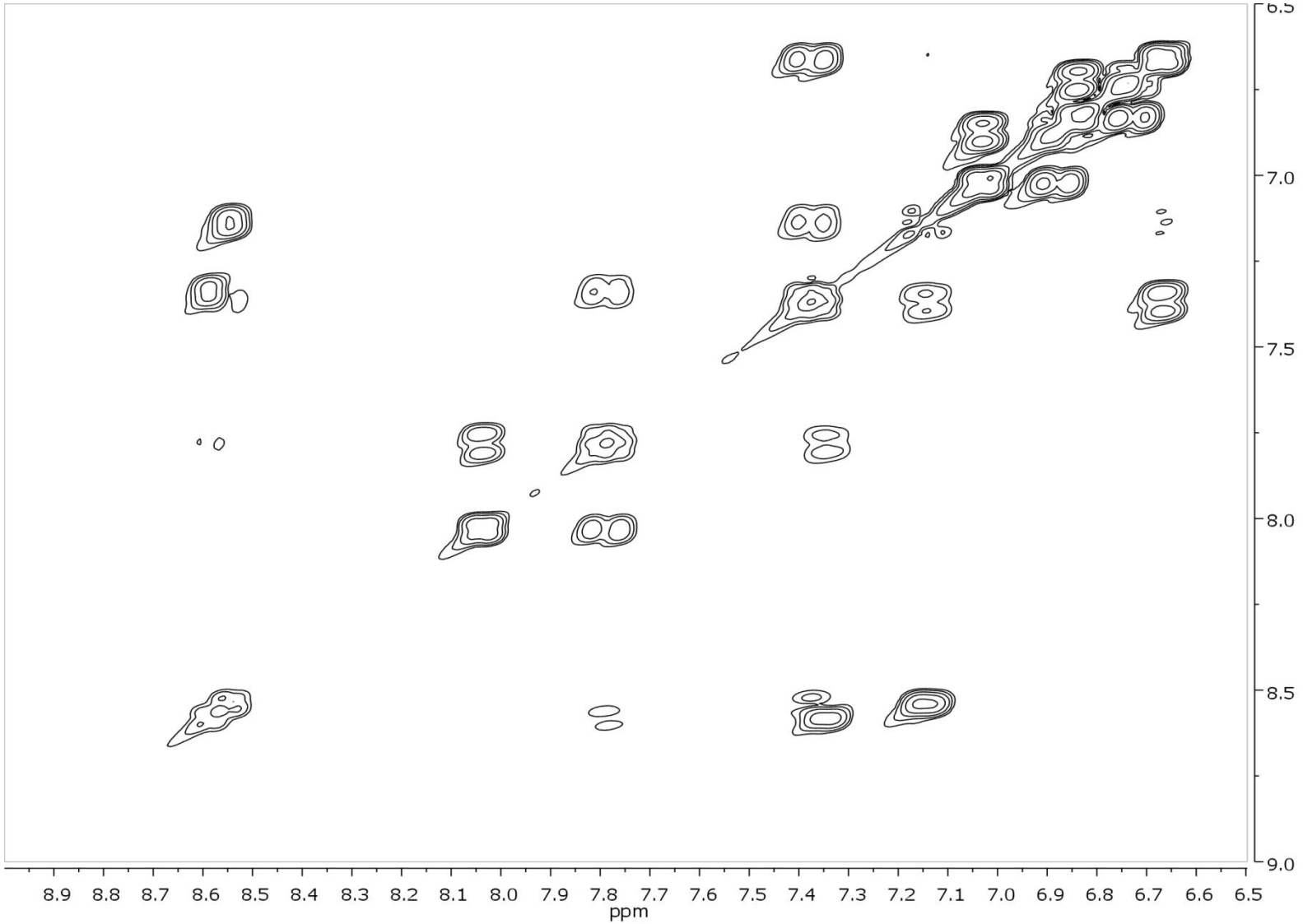
300 MHz ^{1}H spectrum of (**1**) in CD_2Cl_2 at -60 ºC



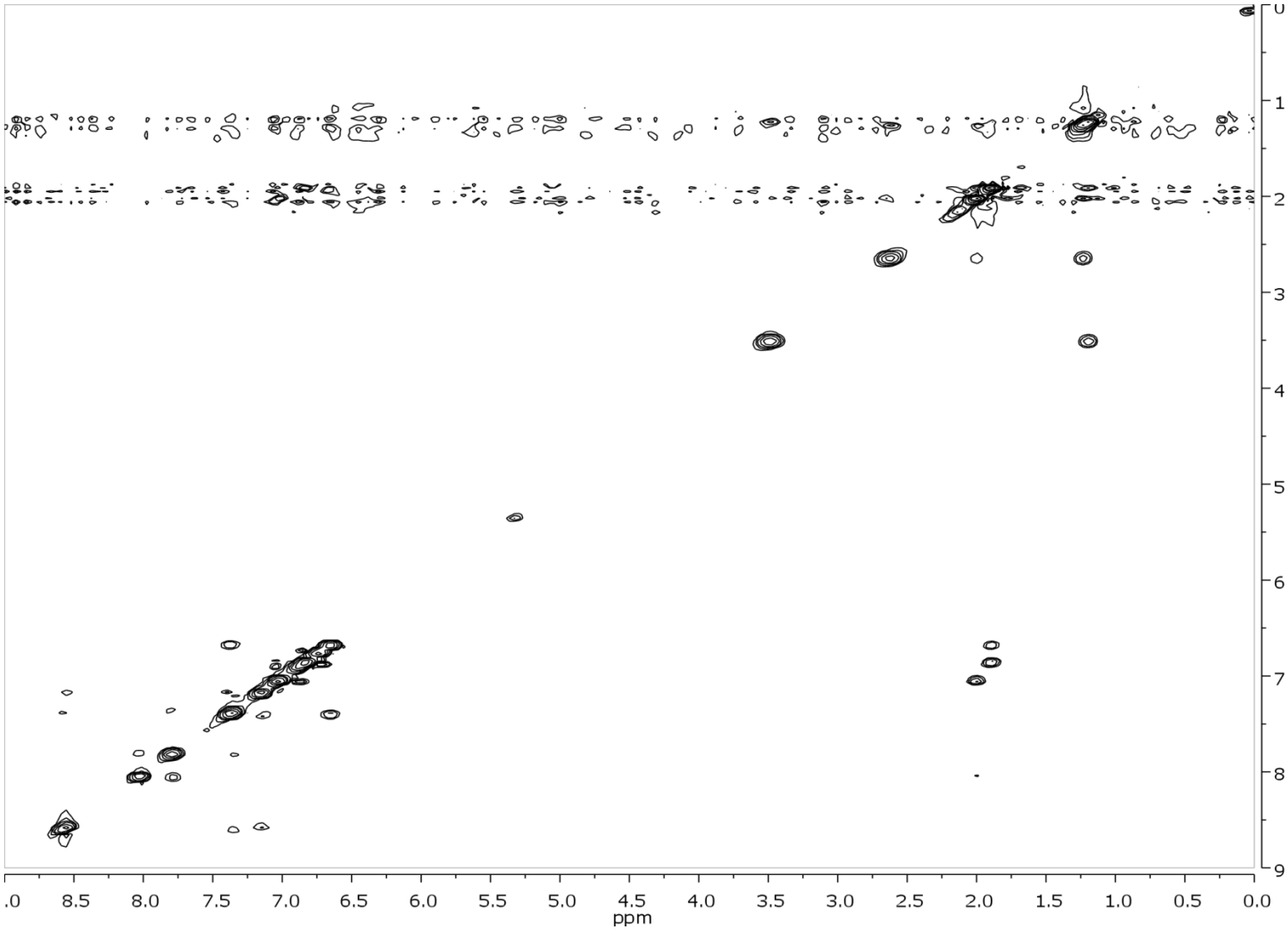
300 MHz ^{1}H gCOSY 2D map of (**1**) in CD_2Cl_2 at -40 ºC



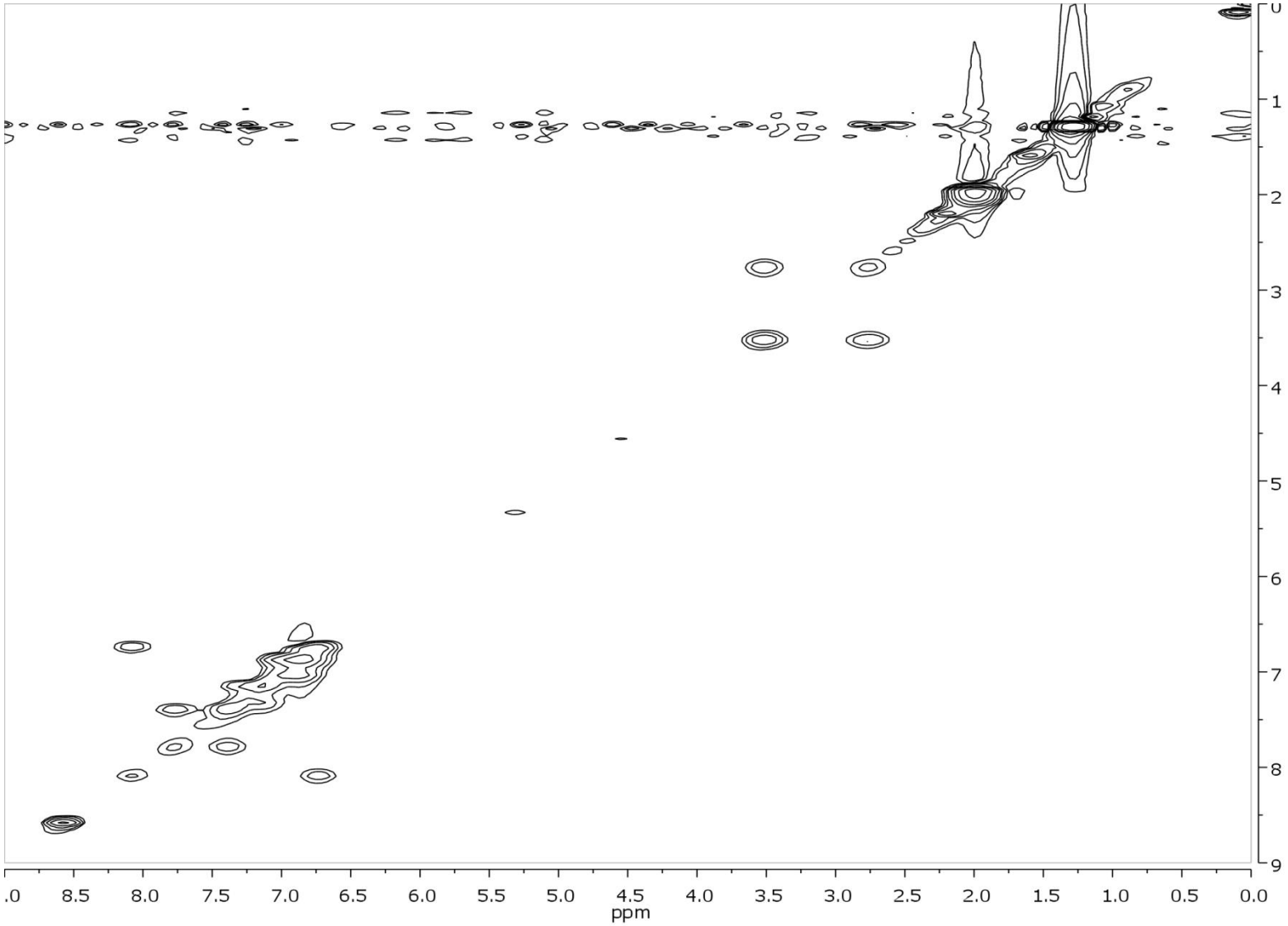
300 MHz ^{1}H gCOSY 2D map of (**1**) in CD_2Cl_2 at -40 ºC, aromatic region expansion



300 MHz ^{1}H NOESY 2D map of (**1**) in CD_2Cl_2 at -40 ºC, 1.2 s mixing time



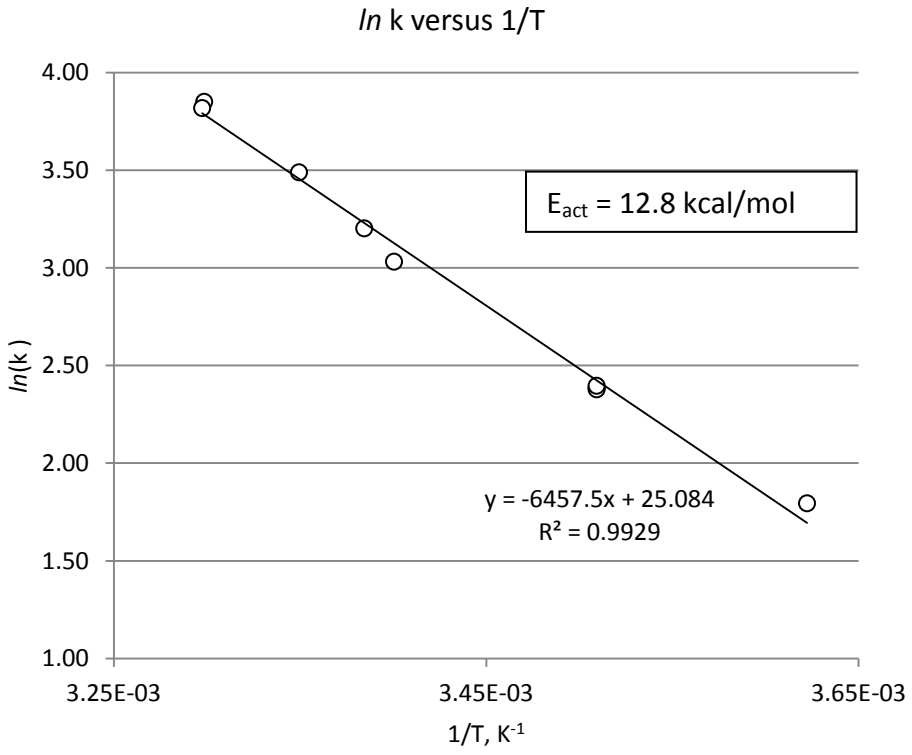
300 MHz ^{1}H EXSY 2D map of (**1**) in CD_2Cl_2 at 30 ºC, 0.5 s mixing time



Tabulated data for determination of $\Delta G^{\ddagger}$ and E_a for **1** via NMR line shape analysis

300 MHz ^{1}H NMR spectra of **1** were collected in methylene chloride-d_2 solvent over a range of temperatures from 0 °C (273 K) to 30 °C (303 K). Temperature calibrations were performed using the standard methanol sample and software provided by Varian (now Agilent). Line shape analysis was carried out by using the commercially available program WINDNMR. Line broadening of the Me_a signals was modelled, and k, $\Delta G^{\ddagger}$, and E_a were calculated over the range of temperatures using methods described by J. Sandström.[1]

T, (K)	1/T, (1/K)	k, (1/s)	*ln*(k)	$\Delta G^{\ddagger}$ (kcal/mol)
276.07	3.62E-03	6.02	1.7951	15.13
284.96	3.51E-03	10.89	2.3877	15.30
284.96	3.51E-03	10.79	2.3786	15.30
284.96	3.51E-03	10.99	2.3968	15.29
294.08	3.40E-03	20.74	3.0322	15.43
295.47	3.38E-03	24.60	3.2027	15.40
298.56	3.35E-03	32.78	3.4897	15.40
303.17	3.30E-03	47.02	3.8506	15.43
303.27	3.30E-03	45.54	3.8185	15.45



[1] "Dynamic NMR Spectroscopy," Sandström, J., Academic Press, New York, 1982.