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Supporting Information

Design and Synthesis of the First Spiro Bis(isoxazoline) Derivatives as Asymmetric Ligands

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2,2-dibut-3-enyl-1,3-propanediol (2)

To a solution of diethyl dibut-3-enylmalonate (**1**) (31.9 g, 119 mmol) in THF (265 mL) was added $LiAlH_4$ (9.0 g, 158 mmol) at 0 °C, and the reaction mixture was stirred for 3.5 h at rt. The reaction mixture was quenched by addition of Na_2SO_4-$10H_2O$. After addition of 10-15 % aq.H_2SO_4 to the reaction mixture, this mixture was extracted with ethyl acetate, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate =2/1) to give 2,2-dibut-3-enyl-1,3-propanediol (**2**) (20.1 g, 109 mmol, 92 %) as white solid. IR (nujol) 3335, 1641, 1393, 1053, 1011, 907, 467, 421 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.97-2.02 (m, 4H), 1.34 (t, *J*=8.5Hz, 2H), 1.34 (dd, *J*=7.0, 5.0Hz, 2H), 2.35 (br-s, 2H), 3.60 (s, 4H), 4.96 (dd, *J*=10.0, 2.0Hz, 2H), 5.04 (ddd, *J*=17.0, 2.0, 1.0Hz, 2H), 5.82 (ddt, *J*=17.0, 10.0, 7.0Hz, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 27.298, 29.886, 41.003, 68.388, 114.299, 138.693 ; Mass m/z (relative intensity) 185(M^++1, 10, bp), 167(10) ; HR-MS (M^++1) calcd for $C_{11}H_{21}O_2$ 185.1542, found 185.1540;

2,2-dibut-3-enyl malonaldehyde

To a solution of $(COCl)_2$ (18.3 mL, 56.5 mmol) in CH_2Cl_2 (179 mL) was added a solution of DMSO (20.8 mL, 294 mmol) in CH_2Cl_2 (56 mL) slowly at –78 °C, and the reaction mixture was stirred for 30 min. To the reaction mixture was added a solution of 2,2-dibut-3-enyl-1,3-propanediol (**2**) (10.4 g, 56.5 mmol) in CH_2Cl_2 at –78 °C, and the reaction mixture was stirred for 30 min. To the above mixture was added

triethylamine (70.6 mL, 508 mmol) at –78°C. After stirring for 1.5 hr at rt, the reaction mixture was quenched by the addition of sat. NH_4Cl aq. and extracted with CH_2Cl_2, and dried over Na_2SO_4 and concentrated. This crude mixture was directly used the next reaction. IR (neat) 3080, 2978, 2926, 2849, 1728, 1713, 1641, 1452, 995, 916 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.54-2.06 (m, 8H), 5.00 (d, *J*=10.5Hz, 2H), 5.15 (d, *J*=17.4Hz, 2H), 5.75 (ddt, *J*=17.4, 10.5, 5.2Hz, 2H), 9.75 (s, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 28.14, 30.24, 64.62, 115.85, 136.77, 201.09.

2,2-dibut-3-enyl malonodioxime (3)

To the above crude mixture was added NH_2OH-HCl (15.7 g, 225.8 mmol) and Pyridine (150 mL) at 0°C and the reaction mixture was stirred for 7 days at rt. (To the reaction mixture was added NH_2OH-HCl (9.0 g, 129.5 mmol) once two days.) The reaction mixture was diluted with ethyl acetate, washed with *1N* HCl aq. to remove Pyridine, washed with sat. $NaHCO_3$ aq., brine, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate=4/1) to give 2,2-dibut-3-enyl malonodioxime (**3**) (9.93 g, 47.2 mmol, 87 % in 2 steps) as white solid. IR (KBr) 3199, 2887, 1639, 1450, 1425, 1323, 1302, 974, 955, 924, 762 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.66-1.82 (m, 4H), 1.94-2.11 (m, 4H), 4.94 (dd, *J*=10.2, 1.8Hz, 2H), 4.99 (dd, *J*=17.1, 1.6Hz, 2H), 6.01 (ddt, *J*=17.1, 10.2, 6.4Hz, 2H), 7.34 (s, 2H), 8.76 (br-s, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 28.237, 35.226, 45.659, 115.008, 137.506, 153.535 ; Mass m/z (FAB) 211$(M+H)^+$; HR-MS (EI) (M^++1) calcd for $C_{11}H_{19}N_2O_2$ 211.1447, found 211.1451.

SPRIXs (4-6)

To a solution of 2,2-dibut-3-enyl malonodioxime (**3**) (4.78 g, 22.7 mmol) in CH_2Cl_2 (455 mL) was added aq.NaOCl (>5.0 %, 34 mL) at 0°C, and stirred for 2 h. The reacton mixture was quenched by the addition of H_2O, and extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, and concentrated. The residure was purified by silicagel column chromatography (hexane/ethyl acetate=2/1~1/1~1/2) to give SPRIXs (**4-6**) (3.46 g, 16.8 mmol, totally 74 %) as white solid. (*M, S, S*)-SPRIX (**4**), 36 %, (*M, R, R*)-SPRIX (**5**), 13 %, (*M, S, R*)-SPRIX (**6**), 25 %.

(±)-(*M, S, S*)-SPRIX (4)

IR (KBr) 2974, 2930, 2864, 1452, 1445, 1339, 1269, 1205, 887, 839, 800 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.70-1.88 (m, 2H), 2.05-2.27 (m, 2H), 2.63 (dd, 2H, *J*=19.8, 7.3Hz), 3.77-4.00 (m, 4H), 4.55 (m, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 27.13, 40.51, 43.97, 55.08, 74.94, 174.98 ; Mass m/z (FAB) 207 $(M+H)^+$; HR-MS (EI) (M^+) calcd for $C_{11}H_{14}O_2N_2$ 206.1055, found 206.1073. Each enantiomer was separated using DAICEL CHIRALPAK AD (EtOH, 3.0 mL/min, 21 min, 29 min) $[\alpha]_D^{26}$ (+)-(*M, S, S*)-SPRIX, +234 (c 0.406, $CHCl_3$).

(±)-(*M, R, R*)-SPRIX (5)

IR (KBr) 2945, 2880, 1468, 1337, 1273, 1082, 885, 856, 812, 791 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.50-1.68 (m, 2H), 2.16-2.33 (m, 4H), 2.73-2.84 (m, 2H), 3.88-4.03 (m, 4H), 4.52-4.66 (m, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 26.42, 40.83, 41.95, 53.89, 75.87, 172.66 ; Mass m/z (FAB) 207 $(M+H)^+$; HR-MS (EI) (M^+) calcd for $C_{11}H_{14}O_2N_2$ 206.1055, found 206.1058. Each enantiomer was separated using DAICEL CHIRALPAK AD (EtOH, 4.5 mL/min, 30 min, 66 min) $[\alpha]_D^{26}$ +121 (c 0.148, $CHCl_3$) (second peak).

(±)-(*M, S, R*)-SPRIX (6)

IR (KBr) 2924, 2858, 1460, 1441, 1348, 1273, 891, 831, 808, 787 cm^{-1} ; ^{1}H-NMR (270MHz, $CDCl_3$) : δ 1.54-1.84 (m, 2H), 2.02-2.35 (m, 4H), 2.40-2.55 (m, 1H), 2.84 (dd, 1H, *J*=13.2, 7.6Hz), 3.80-4.00 (m, 3H), 4.11-4.22 (m, 1H), 4.50-4.70 (m, 2H) ; ^{13}C-NMR (67.5MHz, $CDCl_3$) : δ 24.92, 27.45, 40.61, 41.36, 41.46, 53.12, 55.01, 75.06, 76.20, 171.64, 173.80 ; Mass m/z (FAB) 207 $(M+H)^+$; HR-MS (M^+) calcd for $C_{11}H_{14}O_2N_2$ 206.1055, found 206.1076. Each enantiomer was separated using DAICEL CHIRALPAK AD (EtOH, 3.0 mL/min, 33 min, 39 min) $[\alpha]_D^{26}$ +133 (c 0.286, $CHCl_3$) (second peak).

Asymmetric catalytic Michael reaction of diisopropylzinc with cyclohexenone

The mixture of a chiral SPRIX (**4**) (71.3 μmol) and $Cu(acac)_2$ (35.6 μmol) in 2.3 mL of toluene was stirred at 55 °C for 2 h. To this solution was added the toluene solution of diisopropylzinc (1.1 M, 0.85 mL) at –30°C and the mixture was stirred for

30 min at –30°C. To the mixture was added cyclohexenone (70 μl, 0.71 mmol) at –30°C, and the reaction mixture was stirred for 3h. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and extracted with Et_2O, and dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane/acetone=30/1) to give the Michael adduct (79.3 mg, 0.56 mmol, 79 % yield, 49 % ee) as colorless oil.

Figure 1 ab initio calculations.

After the conformation search, each conformer was minimized by MM2. The ab initio calculations were carried out on all conformers at the HF/3-21G level with Gaussian 94. The most stable conformer was calculated at the HF/6-31G level.

Isoxazoline

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

O							
N	1	r2					
C	2	r3	1	a3			
C	3	r4	2	a4	1	t4	0
C	1	r5	2	a5	3	t5	0
H	5	r6	1	a6	4	t6	0
H	5	r7	1	a7	4	t7	0
H	4	r8	3	a8	5	t8	0
H	4	r9	3	a9	5	t9	0
H	3	r10	2	a10	4	t10	0

Variables:

r2	1.33353
r3	1.25988
r4	1.49494
r5	1.42711
r6	1.1143
r7	1.11535
r8	1.11276
r9	1.11367
r10	1.09787
a3	112.88692
a4	113.62535
a5	107.58427
a6	109.35109
a7	108.04831
a8	111.79959
a9	110.40762
a10	122.30669

t4	-0.32463
t5	8.19014
t6	-121.84875
t7	120.00501
t8	-118.16274
t9	117.83664
t10	179.20274

Final structure in terms of initial Z-matrix:

O
N,1,r2
C,2,r3,1,a3
C,3,r4,2,a4,1,t4,0
C,1,r5,2,a5,3,t5,0
H,5,r6,1,a6,4,t6,0
H,5,r7,1,a7,4,t7,0
H,4,r8,3,a8,5,t8,0
H,4,r9,3,a9,5,t9,0
H,3,r10,2,a10,4,t10,0

Variables:

r2=1.37164781
r3=1.25150413
r4=1.50295783
r5=1.42044368
r6=1.08018652
r7=1.08365328
r8=1.08327888
r9=1.08561848
r10=1.07272643
a3=109.9955072
a4=114.36337828
a5=110.04399908
a6=108.03355931
a7=108.61731669
a8=112.7830017
a9=110.87323189
a10=119.54500767
t4=0.47167331
t5=9.06470086
t6=-122.00074281
t7=119.72371785
t8=-119.69960954
t9=119.11990497
t10=178.52705516

Molecular Orbital Coefficients

			15	16	17	18	19
			O	O	O	O	O
						nextHOMO	HOMO
EIGENVALUES --			-0.54395	-0.52783	-0.51194	-0.45532	-0.37593
1 1	O	1S	-0.01747	-0.00490	0.03549	0.03318	0.00035
2		2S	0.04088	0.00988	-0.08361	-0.07568	-0.00262
3		2PX	0.02960	0.01071	-0.12266	0.16887	0.00652
4		2PY	-0.28862	0.04094	0.38076	0.12767	-0.04550

5		2PZ	-0.06274	-0.20892	-0.00954	-0.01360	0.41155
6		3S	0.07621	0.02548	-0.14001	-0.15617	0.00541
7		3PX	0.01504	0.01321	-0.10600	0.11596	0.00420
8		3PY	-0.20457	0.03222	0.28918	0.08728	-0.03367
9		3PZ	-0.04678	-0.16318	-0.00580	-0.01144	0.35612
10		4XX	0.00597	-0.00418	0.00993	0.00305	0.00024
11		4YY	-0.01876	0.00384	0.01480	0.00450	-0.00225
12		4ZZ	0.00576	-0.00216	-0.01001	-0.00077	0.00106
13		4XY	-0.00188	0.00047	-0.01116	0.02213	-0.00037
14		4XZ	0.00373	0.01500	0.00009	0.00301	0.00277
15		4YZ	-0.00482	-0.00813	0.00261	-0.00072	0.01194
16	2 N	1S	0.01089	0.00236	-0.00167	-0.07786	0.00380
17		2S	-0.02264	-0.00415	0.01015	0.17072	-0.00847
18		2PX	0.03087	-0.05095	0.18786	-0.30630	-0.00188
19		2PY	0.12853	0.01206	0.00328	-0.36081	0.02311
20		2PZ	-0.06648	-0.26744	-0.05563	-0.02331	-0.29982
21		3S	-0.06008	-0.00817	-0.03237	0.36641	-0.01857
22		3PX	0.01044	-0.02270	0.08416	-0.21572	-0.00383
23		3PY	0.06261	0.00084	0.02500	-0.23618	0.02034
24		3PZ	-0.04131	-0.17562	-0.03385	-0.01675	-0.22079
25		4XX	-0.01533	-0.00107	0.02212	-0.01583	0.00103
26		4YY	0.01460	0.00030	-0.01051	-0.01836	0.00309
27		4ZZ	0.00037	0.00210	-0.00297	0.01043	-0.00335
28		4XY	0.00789	-0.00312	0.00927	-0.00316	-0.00317
29		4XZ	-0.00221	-0.01331	-0.00390	0.00087	0.00854
30		4YZ	-0.00537	-0.01992	-0.00390	-0.00328	-0.03599
31	3 C	1S	-0.03332	0.00999	0.00705	0.02613	-0.00241
32		2S	0.07535	-0.01882	-0.01612	-0.07015	0.00786
33		2PX	0.30359	-0.09529	-0.02340	0.12846	-0.02290
34		2PY	-0.05091	-0.02413	0.05352	0.17817	-0.01013
35		2PZ	-0.06857	-0.18640	-0.02859	-0.03323	-0.30927
36		3S	0.07283	-0.03701	-0.00956	-0.03677	0.00081
37		3PX	0.15499	-0.06331	0.01926	0.05636	-0.01579
38		3PY	-0.02015	-0.01202	0.02555	0.02190	0.00695
39		3PZ	-0.04064	-0.12124	-0.02003	-0.02240	-0.25720
40		4XX	-0.01220	-0.00004	-0.00599	0.00247	0.00175
41		4YY	0.00731	-0.00084	0.00488	-0.00275	-0.00065
42		4ZZ	-0.00091	0.00151	-0.00001	0.00298	-0.00045
43		4XY	0.01740	-0.00238	-0.00670	0.02822	-0.00001
44		4XZ	-0.00063	-0.00316	-0.00031	0.00029	0.00113
45		4YZ	0.00345	0.01854	0.00401	0.00126	0.02763
46	4 C	1S	-0.00017	0.00021	0.02717	-0.01680	-0.00346
47		2S	-0.00113	-0.00476	-0.05531	0.03381	0.00794
48		2PX	-0.25845	0.07101	-0.12389	-0.19467	0.02980
49		2PY	0.01300	0.00542	0.29843	-0.06105	-0.01999
50		2PZ	-0.00273	-0.07505	0.01043	0.03240	0.11192
51		3S	-0.00470	0.01679	-0.11135	0.07596	0.02522
52		3PX	-0.12547	0.02870	-0.07514	-0.14004	0.03529
53		3PY	0.00707	-0.01548	0.16712	-0.02911	-0.01189
54		3PZ	0.00194	-0.05295	0.00684	0.02420	0.09432
55		4XX	0.01177	-0.00554	-0.00805	0.00703	0.00283
56		4YY	-0.00909	0.00111	-0.00524	-0.00128	0.00483
57		4ZZ	-0.00204	0.00385	0.01276	-0.00474	-0.00686
58		4XY	0.01898	-0.00386	0.01226	0.00587	-0.00131

59		4XZ	0.00004	0.00988	0.00011	-0.00093	0.00828
60		4YZ	-0.00085	-0.00743	0.00803	0.00200	0.01860
61 5	C	1S	0.01769	-0.00443	0.00191	-0.01430	-0.00284
62		2S	-0.04085	0.01059	-0.00426	0.03439	0.01086
63		2PX	0.26235	-0.09799	0.15012	-0.08776	-0.01086
64		2PY	-0.06708	0.02288	-0.25777	-0.15361	0.02068
65		2PZ	0.09294	0.30995	0.01281	-0.01393	-0.11307
66		3S	-0.02836	0.00113	-0.00565	0.03942	-0.00538
67		3PX	0.13268	-0.04671	0.08719	-0.03696	0.01528
68		3PY	-0.05477	0.01411	-0.09046	-0.06997	0.00228
69		3PZ	0.04004	0.15673	0.00008	-0.01297	-0.07039
70		4XX	-0.00249	-0.01106	0.00920	0.00367	0.00376
71		4YY	-0.01667	0.00211	-0.01455	0.00412	0.00696
72		4ZZ	0.01936	0.00854	0.01015	-0.00395	-0.01052
73		4XY	-0.00750	0.00076	0.02356	0.00822	0.00000
74		4XZ	-0.00023	0.03386	-0.00143	0.00231	-0.02087
75		4YZ	0.00110	0.00244	0.00500	0.00401	-0.00998
76 6	H	1S	0.06466	-0.19831	0.07599	-0.01706	0.07263
77		2S	0.05233	-0.17103	0.05609	-0.02519	0.06861
78 7	H	1S	0.11374	0.17393	0.05976	-0.01436	-0.10202
79		2S	0.09743	0.14962	0.05037	-0.01667	-0.12292
80 8	H	1S	-0.02056	-0.02892	0.10835	-0.01432	0.07525
81		2S	-0.01739	-0.01038	0.10367	-0.02006	0.07712
82 9	H	1S	-0.01137	0.05251	0.05081	-0.03917	-0.09531
83		2S	-0.00942	0.04254	0.05179	-0.04293	-0.11191
84 10	H	1S	-0.16267	0.03126	0.02513	-0.08029	0.00500
85		2S	-0.12892	0.02055	0.03466	-0.06670	0.00513
			20	21	22	23	24
			V	V	V	V	V
EIGENVALUES --			0.17402	0.23247	0.27264	0.27797	0.29657
1 1	O	1S	0.00560	-0.01484	-0.03193	0.03848	-0.00113
2		2S	-0.00325	0.03816	0.05817	-0.05448	-0.01370
3		2PX	-0.00367	-0.00016	-0.03063	0.03892	-0.03855
4		2PY	-0.01300	0.04792	0.07796	-0.09370	0.04002
5		2PZ	0.11921	-0.01076	-0.05411	-0.06803	-0.00980
6		3S	-0.07529	0.12977	0.31459	-0.44741	0.04201
7		3PX	-0.01505	-0.05399	0.03263	-0.06191	-0.03185
8		3PY	-0.02872	0.10638	0.14281	-0.22071	0.07965
9		3PZ	0.14612	-0.01755	-0.10952	-0.13110	-0.01532
10		4XX	0.00668	0.00927	-0.01662	0.02419	-0.00977
11		4YY	0.00100	0.00588	-0.00038	0.00187	-0.00464
12		4ZZ	0.00194	-0.00508	-0.00225	0.00828	-0.00287
13		4XY	-0.00069	-0.00111	0.00446	-0.00959	-0.00629
14		4XZ	0.01731	0.00122	-0.00292	-0.00308	-0.00101
15		4YZ	0.00502	0.00145	0.00616	0.00269	0.00000
16 2	N	1S	0.00088	-0.00853	0.01588	-0.01805	0.01397
17		2S	-0.00095	0.02844	-0.04111	0.05942	-0.01248
18		2PX	-0.01883	0.00249	-0.08980	0.11120	-0.00593
19		2PY	0.00107	0.03295	0.00620	0.01056	-0.00778
20		2PZ	-0.41296	-0.00854	0.08097	0.04910	0.00372
21		3S	-0.00803	0.11437	-0.07820	-0.01376	-0.33315
22		3PX	-0.03322	0.01389	-0.02772	-0.02522	0.01965
23		3PY	0.00512	0.12419	-0.00624	-0.00110	-0.10786
24		3PZ	-0.61184	-0.01411	0.17930	0.12454	0.02294

25		4XX	-0.00122	0.00264	0.00906	-0.00776	0.01100
26		4YY	0.00085	0.00512	-0.00423	0.00498	-0.00462
27		4ZZ	0.00114	-0.00189	-0.00085	0.00329	0.00355
28		4XY	0.00017	-0.00035	-0.00901	0.01261	-0.00101
29		4XZ	-0.00768	-0.00176	0.00634	0.00492	0.00048
30		4YZ	0.00331	0.00220	0.00300	0.00195	-0.00088
31 3	C	1S	-0.00186	-0.01335	-0.03931	0.07925	0.01272
32		2S	-0.00136	0.07677	0.03344	-0.09290	0.00849
33		2PX	0.02086	-0.03500	-0.09555	0.13923	-0.04414
34		2PY	-0.00491	0.04375	0.07065	-0.13220	-0.01230
35		2PZ	0.35190	0.02665	-0.07641	-0.05911	-0.02235
36		3S	0.03668	-0.00577	0.75793	-1.26948	-0.13702
37		3PX	0.03397	-0.22108	-0.46339	0.81052	-0.26907
38		3PY	0.00674	0.11605	0.23635	-0.50022	-0.37677
39		3PZ	0.64572	0.05026	-0.35483	-0.30025	-0.02396
40		4XX	0.00015	0.00225	-0.00523	0.00964	0.01224
41		4YY	-0.00250	0.01378	-0.00053	0.00257	0.00164
42		4ZZ	0.00107	-0.00167	-0.00136	-0.00023	-0.00336
43		4XY	0.00149	0.00476	0.01063	-0.01222	0.00346
44		4XZ	0.00230	-0.00052	0.01454	0.00785	0.00058
45		4YZ	0.03009	-0.00088	-0.00809	-0.00473	-0.00045
46 4	C	1S	0.00049	-0.07853	0.03196	-0.02283	-0.11736
47		2S	-0.00359	0.05577	-0.02992	0.05111	0.04799
48		2PX	0.01336	0.02535	-0.03152	0.00125	0.04104
49		2PY	-0.00227	0.15901	0.04503	-0.02483	0.08466
50		2PZ	0.03374	-0.00731	0.21147	0.13154	0.00375
51		3S	0.00149	1.55549	-0.52087	0.14137	2.41507
52		3PX	0.06405	0.02014	-0.02547	-0.10965	0.33248
53		3PY	-0.02834	0.61542	0.11619	0.28933	0.07862
54		3PZ	0.19090	-0.06865	0.82738	0.51993	0.04211
55		4XX	-0.00509	0.00630	0.00881	-0.01405	-0.01594
56		4YY	-0.00250	-0.00471	-0.00700	0.00904	-0.00279
57		4ZZ	0.00730	-0.01461	0.00047	0.00494	-0.00182
58		4XY	-0.00047	-0.00213	-0.00134	-0.00001	0.00646
59		4XZ	-0.02553	0.00010	0.00769	0.00608	-0.00027
60		4YZ	-0.02083	-0.00446	-0.01196	-0.00670	0.00124
61 5	C	1S	0.00253	-0.06277	0.01116	-0.03338	0.10826
62		2S	0.00254	0.06315	-0.01926	0.01301	-0.05966
63		2PX	-0.01401	0.14998	-0.04447	-0.00596	-0.11636
64		2PY	-0.03758	0.03493	0.08553	-0.06771	-0.06993
65		2PZ	0.03672	0.03851	0.17753	0.13294	0.00537
66		3S	-0.07366	1.17408	-0.20831	0.76331	-2.16943
67		3PX	-0.05079	0.59753	-0.29608	-0.05111	-0.34756
68		3PY	-0.10361	0.00164	0.38300	-0.35407	-0.49718
69		3PZ	0.11032	0.18096	0.58188	0.38873	0.04326
70		4XX	0.00225	-0.00301	0.00174	0.00328	0.00734
71		4YY	0.00230	0.00386	-0.00318	0.00340	0.00710
72		4ZZ	-0.00208	-0.01310	-0.00296	-0.00309	0.00658
73		4XY	0.00010	0.00363	0.00978	-0.01454	-0.00163
74		4XZ	-0.01202	0.00183	-0.01236	-0.00750	-0.00031
75		4YZ	-0.00694	-0.00033	0.01036	0.00687	-0.00113
76 6	H	1S	0.02495	-0.01215	0.03186	0.02052	0.01248
77		2S	0.21662	-0.84748	1.01932	0.18650	1.22109
78 7	H	1S	-0.02665	-0.00928	-0.02707	-0.01540	0.00967

79		2S	-0.17202	-0.94445	-0.58430	-0.87033	0.98330
80	8 H	1S	-0.07194	-0.02664	-0.03224	0.00859	0.02028
81		2S	-0.32486	-1.13485	-0.77013	-0.68028	-1.08126
82	9 H	1S	0.08759	-0.00837	0.00888	0.02174	0.00785
83		2S	0.43185	-0.99250	1.12391	0.47018	-0.97085
84	10 H	1S	-0.00020	-0.00279	-0.03875	0.04323	0.04503
85		2S	-0.01537	-0.40073	-1.01013	1.80270	0.02267

Total atomic charges:

		1
1	O	-0.508965
2	N	-0.064771
3	C	0.020247
4	C	-0.435938
5	C	0.013066
6	H	0.185305
7	H	0.174814
8	H	0.197912
9	H	0.199894
10	H	0.218437

Sum of Mulliken charges= 0.00000

Oxazoline

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

O							
C	1	r2					
N	2	r3	1	a3			
C	3	r4	2	a4	1	t4	0
C	1	r5	2	a5	3	t5	0
H	5	r6	1	a6	4	t6	0
H	5	r7	1	a7	4	t7	0
H	4	r8	3	a8	5	t8	0
H	4	r9	3	a9	5	t9	0
H	2	r10	1	a10	3	t10	0

Variables:

r2	1.36454
r3	1.27693
r4	1.48142
r5	1.41881
r6	1.11376
r7	1.11376
r8	1.11407
r9	1.1136
r10	1.09468
a3	117.02034
a4	106.08256
a5	108.35732
a6	107.9742
a7	107.80593
a8	108.28742
a9	108.31611

a10	116.35888
t4	-0.08494
t5	0.59932
t6	-120.17256
t7	119.77266
t8	120.358
t9	-120.43342
t10	179.77318

Final structure in terms of initial Z-matrix:

O
C,1,r2
N,2,r3,1,a3
C,3,r4,2,a4,1,t4,0
C,1,r5,2,a5,3,t5,0
H,5,r6,1,a6,4,t6,0
H,5,r7,1,a7,4,t7,0
H,4,r8,3,a8,5,t8,0
H,4,r9,3,a9,5,t9,0
H,2,r10,1,a10,3,t10,0

Variables:

r2=1.33780812
r3=1.24612287
r4=1.46044945
r5=1.42641482
r6=1.08087054
r7=1.0810143
r8=1.08344356
r9=1.08332971
r10=1.07277693
a3=119.64556011
a4=106.38412264
a5=106.32580922
a6=108.34550201
a7=108.33238217
a8=109.8617291
a9=109.91795805
a10=114.92491189
t4=0.13847626
t5=0.2265967
t6=-120.91514272
t7=120.80884578
t8=120.86814158
t9=-120.8905401
t10=-179.90936711

Molecular Orbital Coefficients

			15	16	17	18	19
			O	O	O	O	O
						nextHOMO	HOMO
EIGENVALUES --			-0.56727	-0.53069	-0.51775	-0.43287	-0.37839
1 1	O	1S	-0.02950	-0.00031	0.03251	-0.01270	0.00004
2		2S	0.07000	0.00062	-0.07299	0.02735	0.00006
3		2PX	-0.19641	0.00025	0.15385	-0.04532	0.00058

4		2PY	-0.10503	-0.00232	0.37537	0.14118	0.00080
5		2PZ	0.00591	-0.27604	-0.00174	-0.00014	-0.34167
6		3S	0.11468	0.00158	-0.12936	0.08678	-0.00087
7		3PX	-0.14658	0.00037	0.11287	-0.03776	0.00030
8		3PY	-0.08371	-0.00165	0.28685	0.10288	0.00056
9		3PZ	0.00434	-0.21570	-0.00137	-0.00007	-0.31442
10		4XX	-0.01055	-0.00002	0.00165	-0.00452	0.00003
11		4YY	0.00048	-0.00013	0.01915	0.00404	0.00009
12		4ZZ	0.00523	-0.00004	-0.00655	-0.00168	0.00000
13		4XY	-0.01320	0.00007	0.00341	0.00454	-0.00001
14		4XZ	0.00001	0.00684	0.00010	0.00000	-0.00330
15		4YZ	0.00028	-0.01830	-0.00005	0.00002	-0.01068
16	2 C	1S	-0.00617	0.00012	-0.02402	0.03757	-0.00003
17		2S	0.02184	-0.00019	0.05382	-0.09256	0.00008
18		2PX	0.28616	-0.00142	0.06854	-0.01304	0.00024
19		2PY	0.16740	0.00212	-0.09884	-0.08143	-0.00055
20		2PZ	0.00100	-0.24237	-0.00249	0.00026	0.23357
21		3S	-0.02232	-0.00013	0.05472	-0.04295	0.00028
22		3PX	0.13534	-0.00074	0.03113	0.00580	0.00027
23		3PY	0.04121	0.00039	0.01762	0.04719	-0.00050
24		3PZ	0.00050	-0.14599	-0.00135	0.00037	0.16319
25		4XX	-0.04117	0.00001	0.00260	-0.02264	0.00010
26		4YY	0.02727	-0.00004	-0.00197	0.02578	-0.00028
27		4ZZ	-0.00223	0.00005	-0.00240	0.00076	0.00018
28		4XY	-0.00033	0.00019	-0.01974	-0.02678	0.00006
29		4XZ	0.00017	-0.01512	-0.00018	0.00000	0.00610
30		4YZ	-0.00022	-0.00329	0.00000	0.00016	0.04021
31	3 N	1S	0.00620	0.00026	-0.00355	-0.07040	0.00012
32		2S	-0.01176	-0.00046	0.01236	0.15401	-0.00023
33		2PX	-0.24574	-0.00077	-0.02991	-0.25993	0.00119
34		2PY	-0.19385	-0.00039	0.10546	0.42147	-0.00168
35		2PZ	-0.00154	-0.21517	-0.00155	0.00211	0.38632
36		3S	-0.05837	-0.00144	-0.00618	0.28341	-0.00079
37		3PX	-0.13643	-0.00075	-0.02149	-0.18103	0.00088
38		3PY	-0.08922	-0.00003	0.06657	0.33412	-0.00137
39		3PZ	-0.00083	-0.14127	-0.00101	0.00165	0.33050
40		4XX	-0.02064	0.00001	-0.00017	-0.00550	0.00000
41		4YY	0.02174	-0.00004	-0.00380	-0.02383	0.00018
42		4ZZ	0.00045	0.00013	0.00410	0.01093	-0.00012
43		4XY	0.01542	0.00002	0.01089	0.01493	-0.00005
44		4XZ	-0.00007	0.00217	0.00007	0.00006	-0.00630
45		4YZ	0.00011	0.02153	0.00016	-0.00021	-0.03360
46	4 C	1S	0.00123	-0.00014	0.02469	0.02107	0.00007
47		2S	-0.00593	0.00014	-0.05207	-0.04320	-0.00019
48		2PX	0.25044	-0.00049	0.09762	0.16186	-0.00060
49		2PY	0.05262	-0.00148	0.32584	-0.15348	0.00128
50		2PZ	-0.00708	-0.03410	0.00053	-0.00152	-0.15035
51		3S	0.00974	0.00103	-0.06794	-0.06591	-0.00050
52		3PX	0.12982	-0.00089	0.03743	0.05843	-0.00055
53		3PY	0.02718	-0.00119	0.16921	-0.05110	0.00081
54		3PZ	-0.00371	-0.04865	0.00016	-0.00078	-0.09108
55		4XX	-0.00990	-0.00002	0.00079	-0.02125	-0.00015
56		4YY	-0.00333	0.00004	-0.01763	0.01967	-0.00026
57		4ZZ	0.01730	-0.00003	0.01693	-0.00192	0.00039

58		4XY	0.01187	0.00001	0.00614	-0.01317	0.00002
59		4XZ	-0.00015	0.00855	0.00028	-0.00007	-0.02778
60		4YZ	-0.00037	-0.00927	0.00023	-0.00013	-0.01214
61 5	C	1S	0.01993	-0.00008	0.00488	-0.02232	0.00019
62		2S	-0.04189	0.00021	-0.01048	0.04762	-0.00060
63		2PX	0.17457	-0.00143	-0.04257	-0.01960	-0.00003
64		2PY	-0.03846	0.00249	-0.30253	0.20330	-0.00142
65		2PZ	0.00287	0.32215	0.00164	0.00006	0.10867
66		3S	-0.03662	-0.00002	-0.03935	0.10059	-0.00025
67		3PX	0.06443	-0.00069	0.00992	0.00645	-0.00081
68		3PY	-0.03098	0.00096	-0.13141	0.13915	-0.00039
69		3PZ	0.00160	0.16673	0.00084	-0.00011	0.07303
70		4XX	-0.01198	-0.00042	0.02364	-0.00003	-0.00015
71		4YY	0.00070	-0.00002	-0.02645	0.00749	-0.00023
72		4ZZ	0.01042	0.00040	0.00929	-0.00554	0.00037
73		4XY	-0.00038	0.00021	-0.00245	0.00365	-0.00004
74		4XZ	-0.00024	0.03225	0.00021	0.00009	0.01996
75		4YZ	-0.00029	-0.01751	0.00012	-0.00020	-0.00799
76 6	H	1S	0.03751	-0.18686	0.06080	-0.03803	-0.08415
77		2S	0.03510	-0.15961	0.04945	-0.04479	-0.08713
78 7	H	1S	0.03933	0.18655	0.06168	-0.03671	0.08532
79		2S	0.03646	0.15927	0.05039	-0.04335	0.08929
80 8	H	1S	0.08788	0.01553	0.08964	-0.02341	0.11508
81		2S	0.06694	-0.00292	0.08407	-0.01154	0.13326
82 9	H	1S	0.08183	-0.01615	0.09216	-0.02525	-0.11391
83		2S	0.06224	0.00272	0.08639	-0.01365	-0.13165
84 10	H	1S	-0.20146	0.00044	-0.00926	-0.06900	0.00033
85		2S	-0.14857	0.00035	-0.01287	-0.07030	0.00034
			20	21	22	23	24
			V	V	V	V	V
EIGENVALUES --			0.19855	0.23760	0.27568	0.28067	0.30561
1 1	O	1S	-0.00039	-0.01644	-0.05563	0.00028	-0.01359
2		2S	0.00029	0.02150	0.05849	0.00002	-0.00591
3		2PX	0.00050	0.03258	0.11311	-0.00090	0.03298
4		2PY	0.00068	0.02665	0.05844	-0.00014	0.05356
5		2PZ	-0.17369	-0.00027	-0.00030	-0.11468	0.00019
6		3S	0.00519	0.24610	0.73923	-0.00507	0.24998
7		3PX	0.00174	0.01671	0.23868	-0.00236	0.08823
8		3PY	0.00128	0.17664	0.10098	-0.00053	0.10531
9		3PZ	-0.24539	-0.00047	-0.00022	-0.22584	0.00053
10		4XX	-0.00019	0.00263	-0.02196	0.00009	-0.01874
11		4YY	-0.00019	0.00770	-0.01649	0.00015	-0.00653
12		4ZZ	-0.00020	-0.01378	-0.02684	0.00028	-0.01007
13		4XY	0.00016	-0.00533	0.01027	-0.00010	0.00004
14		4XZ	-0.01884	0.00010	0.00012	0.00078	0.00002
15		4YZ	0.00547	0.00002	0.00015	0.00903	-0.00003
16 2	C	1S	0.00022	-0.01020	0.07658	-0.00089	0.00563
17		2S	-0.00019	0.07571	-0.10452	0.00122	-0.00512
18		2PX	0.00071	-0.00557	0.20174	-0.00296	-0.00815
19		2PY	-0.00029	0.00788	0.05507	0.00008	0.00675
20		2PZ	0.41402	-0.00047	-0.00006	0.10670	-0.00110
21		3S	-0.00325	-0.27358	-1.26376	0.01581	-0.10098
22		3PX	0.00271	-0.21676	0.94533	-0.01327	-0.00736
23		3PY	-0.00105	-0.03304	0.21345	0.00065	0.09031

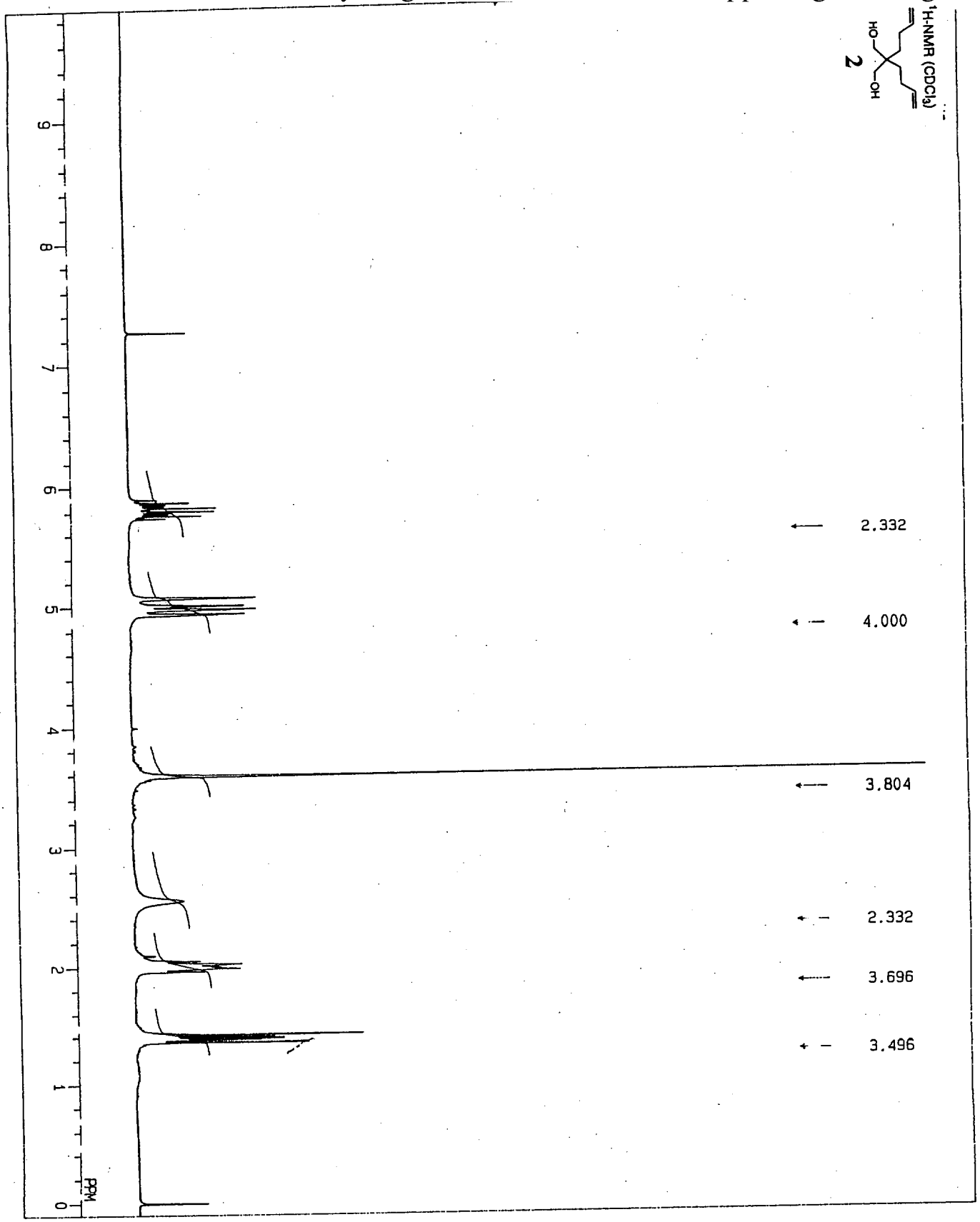
24		3PZ	0.75086	-0.00119	-0.00091	0.22953	-0.00033
25		4XX	0.00004	0.00216	0.01773	-0.00019	0.00036
26		4YY	0.00008	-0.00374	-0.00140	0.00003	-0.00047
27		4ZZ	-0.00005	0.00276	-0.00550	0.00004	-0.00105
28		4XY	-0.00003	0.00196	0.00093	-0.00018	-0.00905
29		4XZ	-0.02341	0.00005	0.00007	0.00165	0.00002
30		4YZ	-0.01628	0.00012	-0.00004	-0.00651	0.00001
31 3	N	1S	0.00003	-0.01316	-0.03858	0.00081	0.00248
32		2S	0.00023	0.01950	0.06276	-0.00148	0.01822
33		2PX	-0.00037	0.03450	0.10743	-0.00197	-0.02761
34		2PY	0.00056	-0.02468	-0.04833	0.00089	0.03429
35		2PZ	-0.33141	0.00101	-0.00109	-0.14957	0.00023
36		3S	-0.00178	0.28309	0.38735	-0.00748	-0.11441
37		3PX	-0.00159	0.01971	0.21281	-0.00270	-0.10240
38		3PY	0.00099	-0.23130	-0.02465	0.00056	0.02901
39		3PZ	-0.54537	0.00145	-0.00271	-0.34269	0.00092
40		4XX	0.00003	0.00536	-0.00480	0.00020	0.01337
41		4YY	0.00012	0.01081	0.00212	-0.00004	0.00360
42		4ZZ	0.00005	-0.01132	-0.01143	0.00014	0.00117
43		4XY	0.00012	0.00492	-0.00663	0.00010	0.00111
44		4XZ	-0.02137	-0.00003	0.00002	0.00193	0.00002
45		4YZ	-0.00018	-0.00001	-0.00001	-0.00602	0.00005
46 4	C	1S	-0.00009	-0.06580	0.04671	-0.00035	-0.11509
47		2S	0.00004	0.06012	-0.04015	0.00087	0.05959
48		2PX	-0.00043	0.11250	0.05418	-0.00085	0.11700
49		2PY	0.00084	0.09583	-0.00253	0.00180	0.04071
50		2PZ	-0.05458	-0.00062	0.00216	0.21996	-0.00078
51		3S	0.00235	1.21322	-0.66114	0.00042	2.27233
52		3PX	-0.00175	0.45132	0.39948	-0.00077	0.53099
53		3PY	0.00286	0.47245	-0.05476	0.00944	-0.07192
54		3PZ	-0.25242	-0.00472	0.00714	0.76128	-0.00241
55		4XX	0.00023	0.00325	0.02133	-0.00034	-0.00656
56		4YY	0.00011	0.00021	-0.00573	0.00007	-0.00949
57		4ZZ	-0.00034	-0.01496	-0.00723	0.00019	-0.00513
58		4XY	-0.00008	-0.00381	-0.00699	0.00006	0.00315
59		4XZ	0.02790	-0.00012	-0.00015	0.00052	-0.00005
60		4YZ	-0.00057	-0.00013	-0.00032	-0.02091	0.00007
61 5	C	1S	0.00005	-0.07288	0.04501	-0.00055	0.11192
62		2S	0.00010	0.06386	-0.04693	0.00010	-0.06690
63		2PX	0.00150	0.16068	0.13540	-0.00229	-0.09383
64		2PY	0.00111	-0.08552	0.05079	0.00182	0.03973
65		2PZ	-0.05711	0.00166	0.00409	0.25404	-0.00040
66		3S	-0.00011	1.40991	-0.53689	0.00888	-2.16395
67		3PX	0.00595	0.57425	0.64157	-0.01494	-0.39674
68		3PY	0.00229	-0.41399	0.24721	0.00854	-0.14051
69		3PZ	-0.19522	0.00837	0.01437	0.90416	0.00003
70		4XX	-0.00005	0.00022	0.01720	-0.00009	0.00862
71		4YY	-0.00009	0.00030	-0.01050	0.00013	0.00969
72		4ZZ	0.00015	-0.01644	-0.00769	-0.00003	0.00158
73		4XY	-0.00003	0.00292	0.00530	-0.00014	0.00405
74		4XZ	0.01433	0.00005	-0.00001	-0.00577	-0.00001
75		4YZ	0.00223	-0.00008	0.00018	0.02002	-0.00012
76 6	H	1S	-0.02337	-0.01366	-0.01873	0.03711	-0.00015
77		2S	-0.27870	-1.05060	0.07522	1.10916	1.07477

78	7	H	1S	0.02353	-0.01356	-0.01935	-0.03632	0.00006
79			2S	0.27827	-1.05540	0.04619	-1.10399	1.07213
80	8	H	1S	-0.06052	-0.01273	-0.02376	0.02644	-0.00231
81			2S	-0.40796	-0.94041	0.10603	0.93030	-1.16465
82	9	H	1S	0.05987	-0.01348	-0.02528	-0.02600	-0.00230
83			2S	0.40134	-0.94286	0.08241	-0.93220	-1.16416
84	10	H	1S	0.00046	0.00878	0.06225	-0.00061	0.00247
85			2S	0.00350	-0.14242	1.89528	-0.02505	0.05029

Total atomic charges:

		1
1	O	-0.601967
2	C	0.383003
3	N	-0.513680
4	C	-0.187368
5	C	-0.034001
6	H	0.183055
7	H	0.182784
8	H	0.185827
9	H	0.185889
10	H	0.216457

Sum of Mulliken charges= 0.00000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OH
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3.496
PPM
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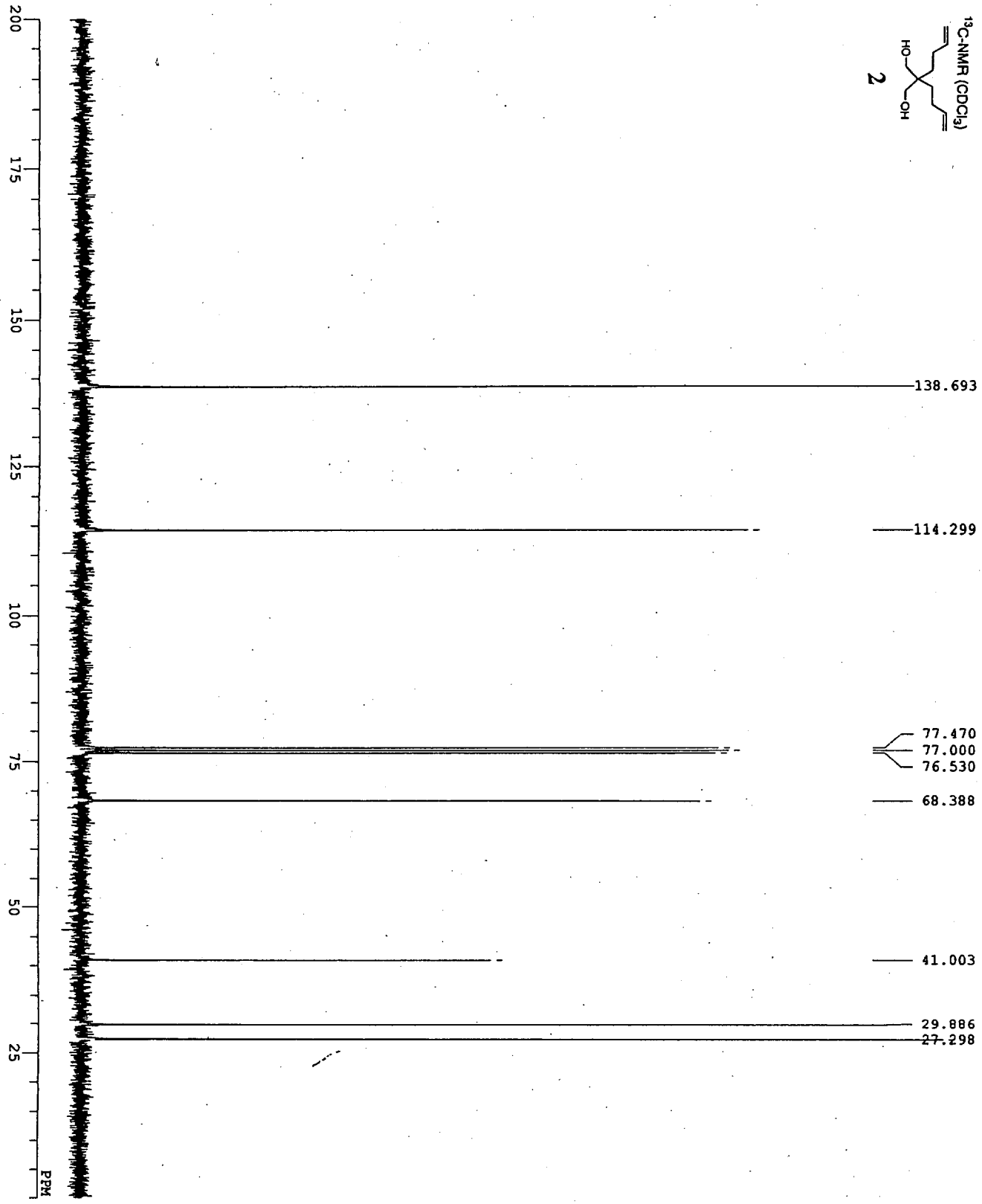
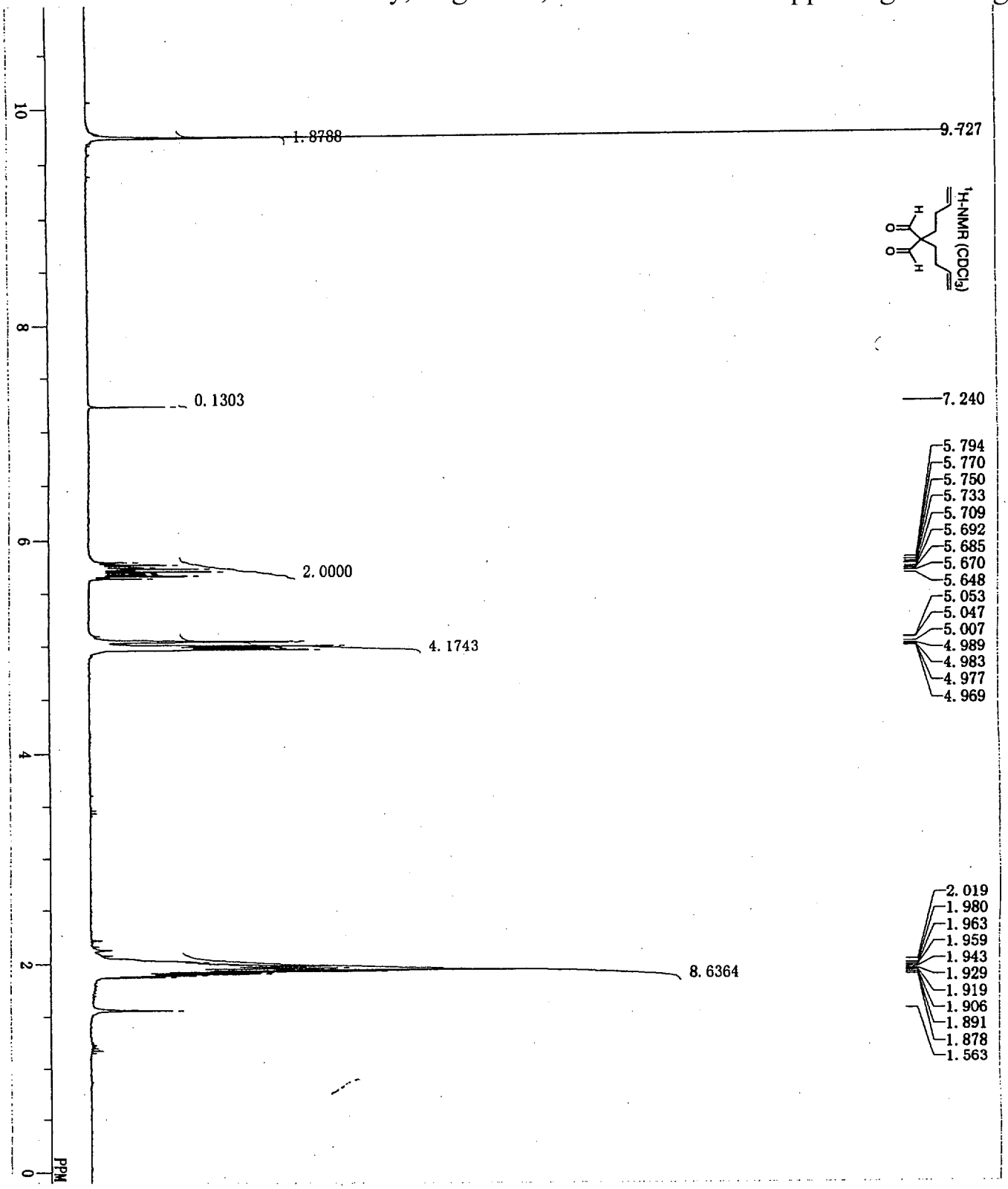
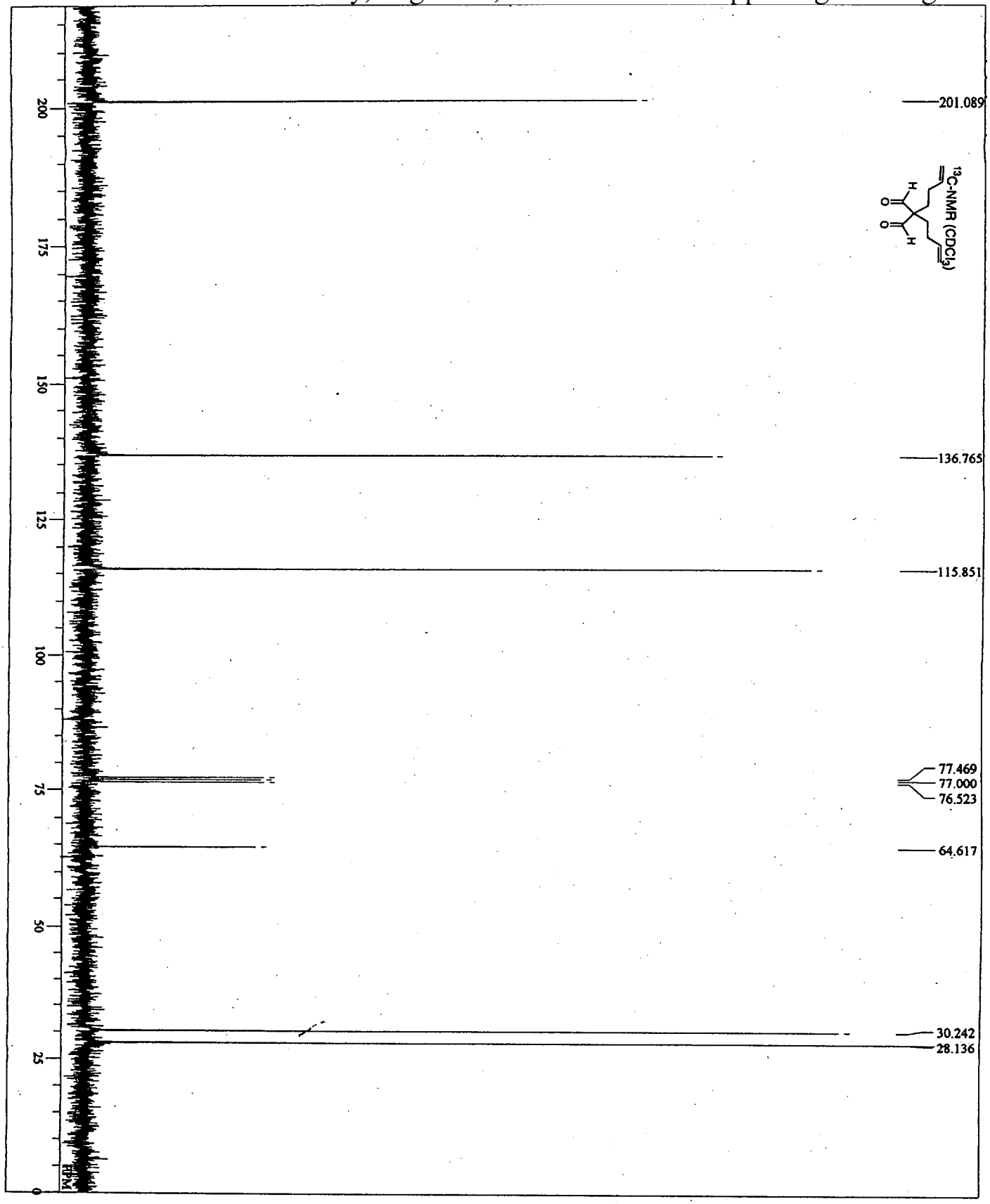
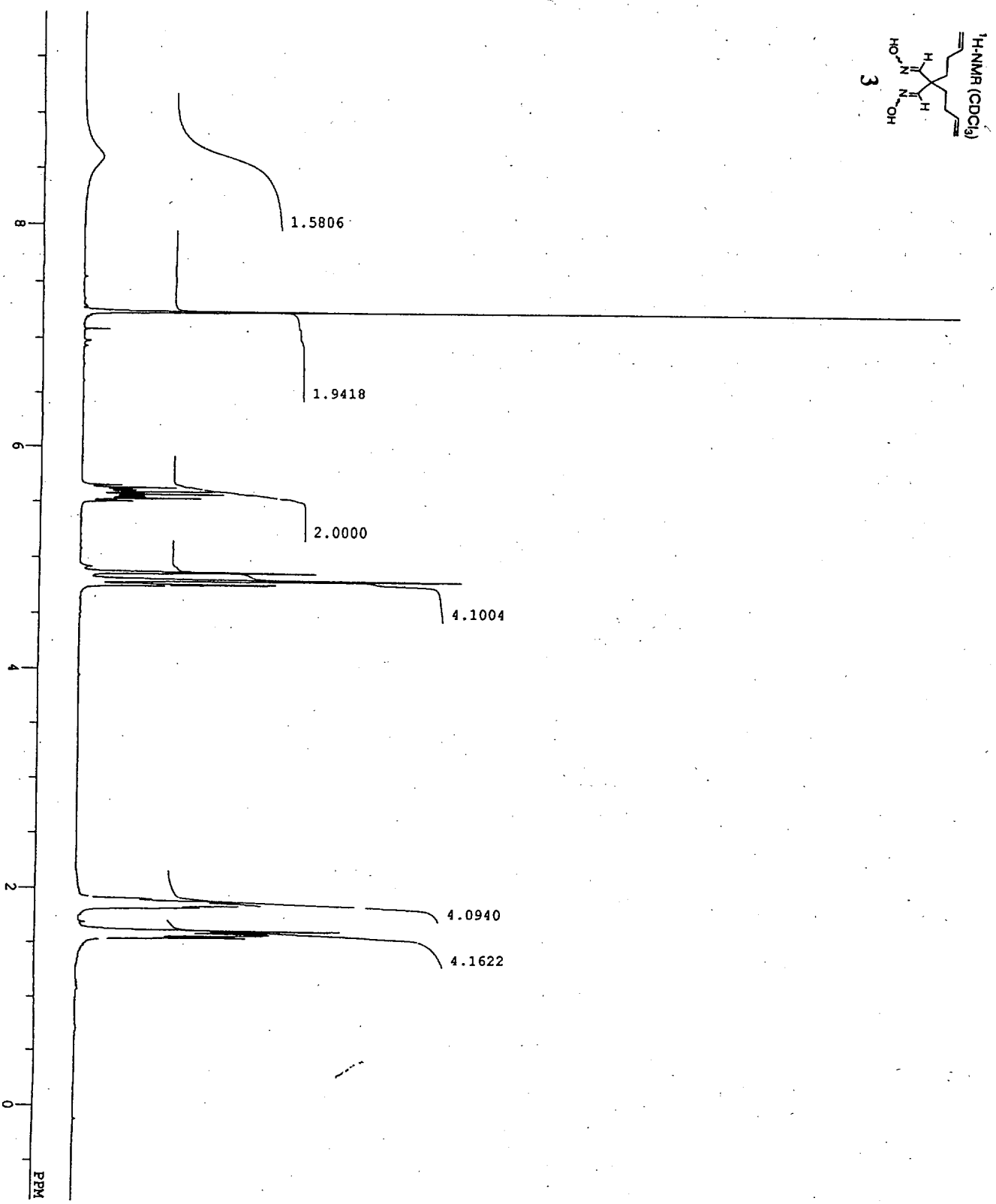
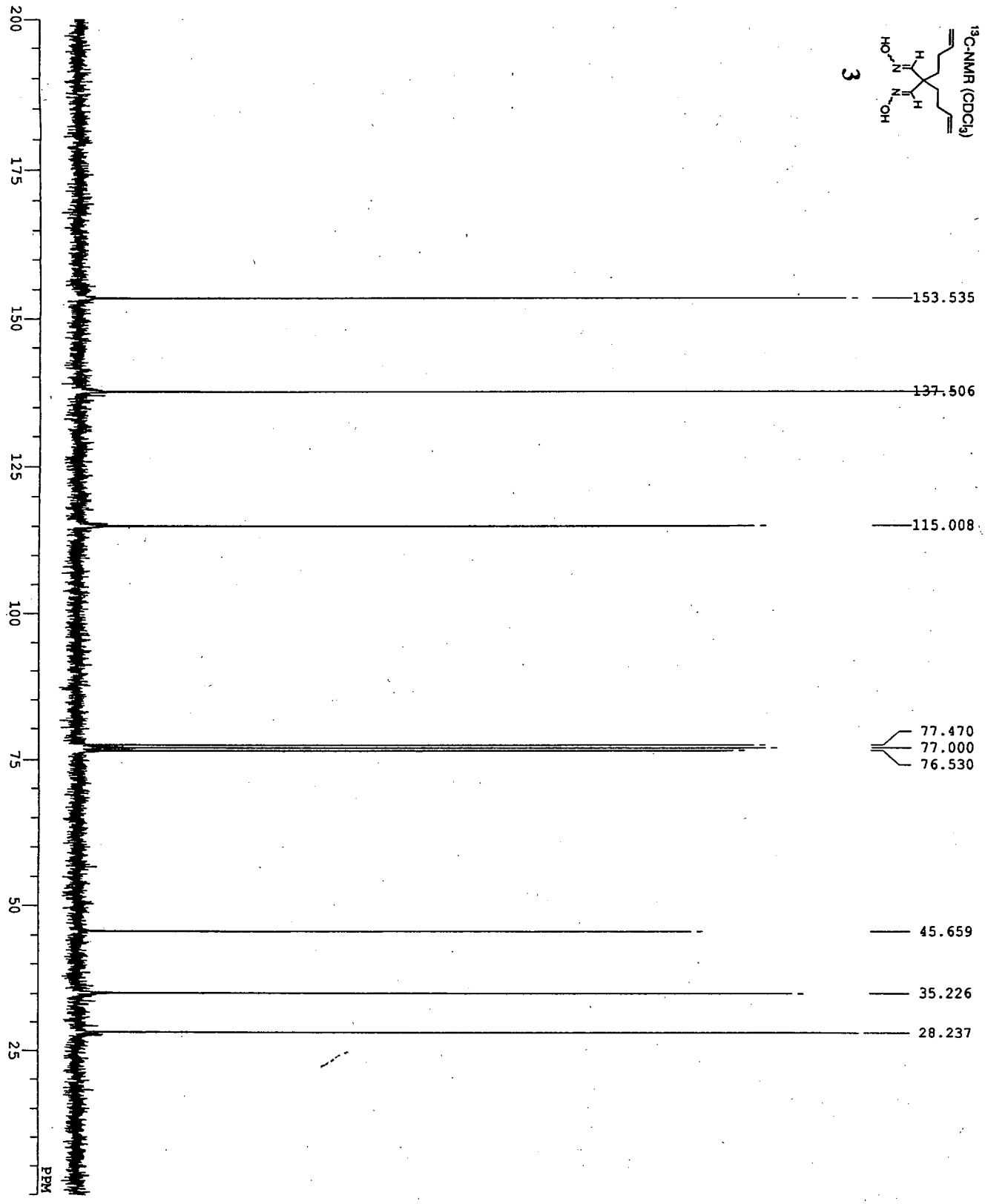
2
3
4
5
6
7
8
9

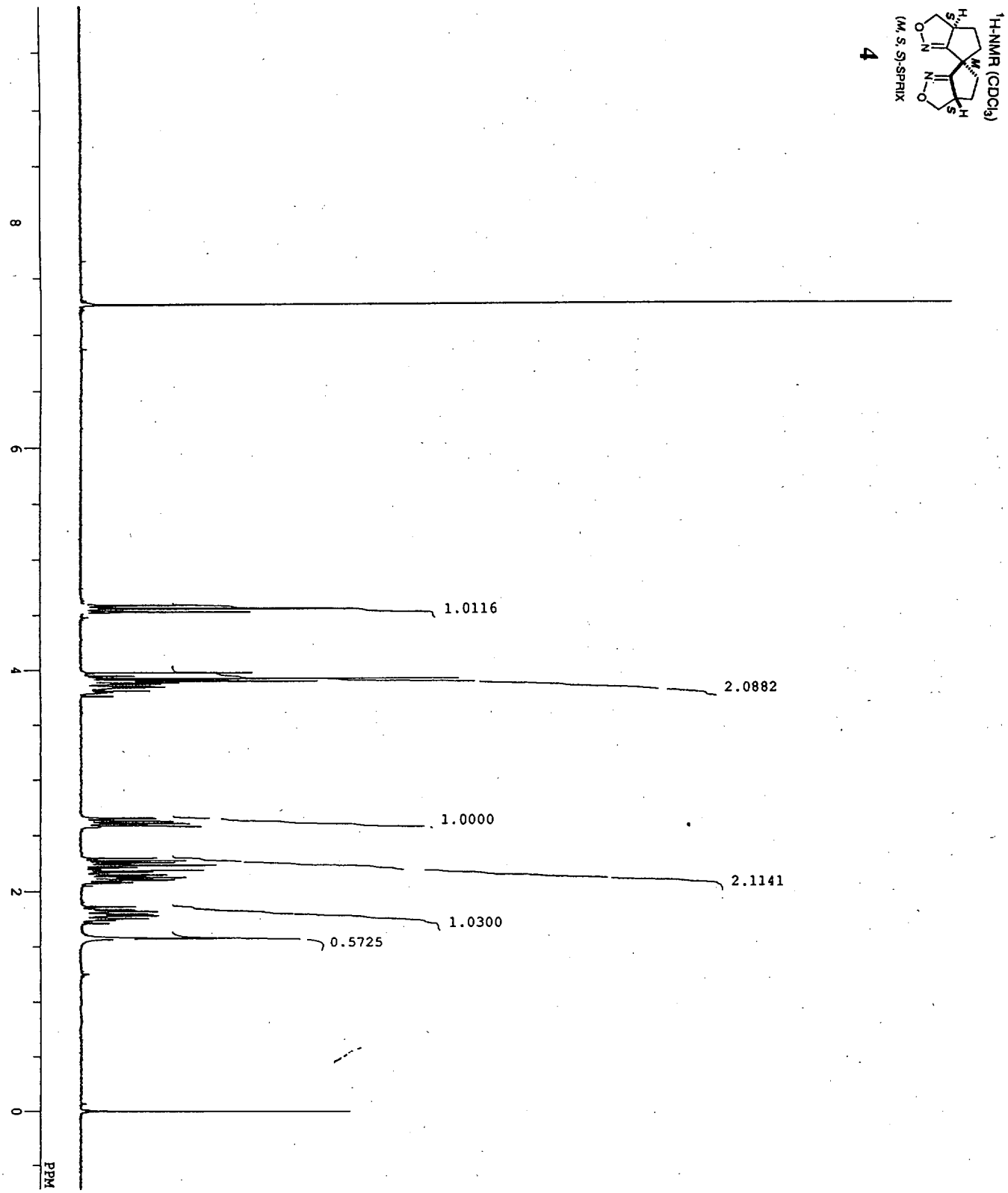


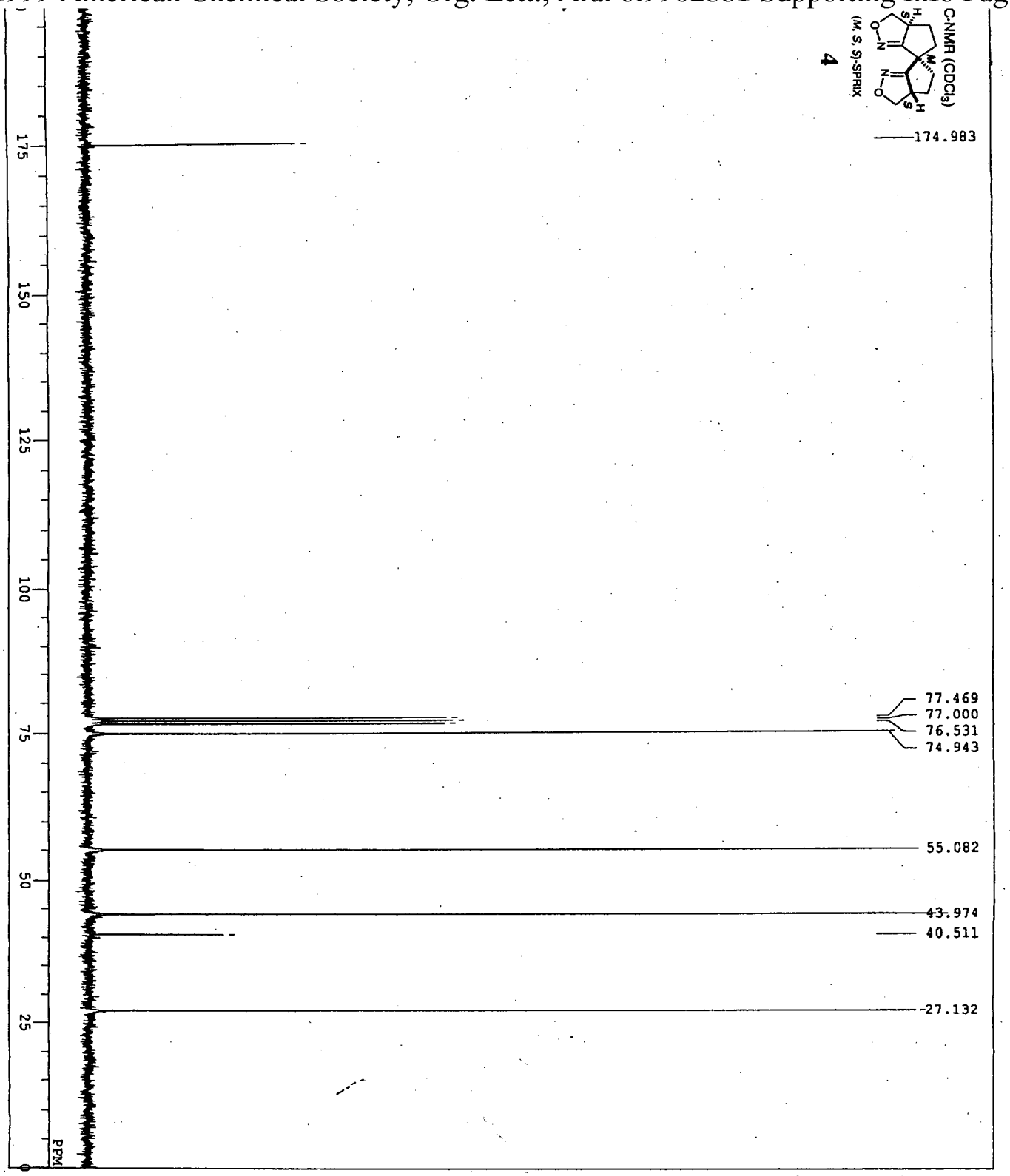


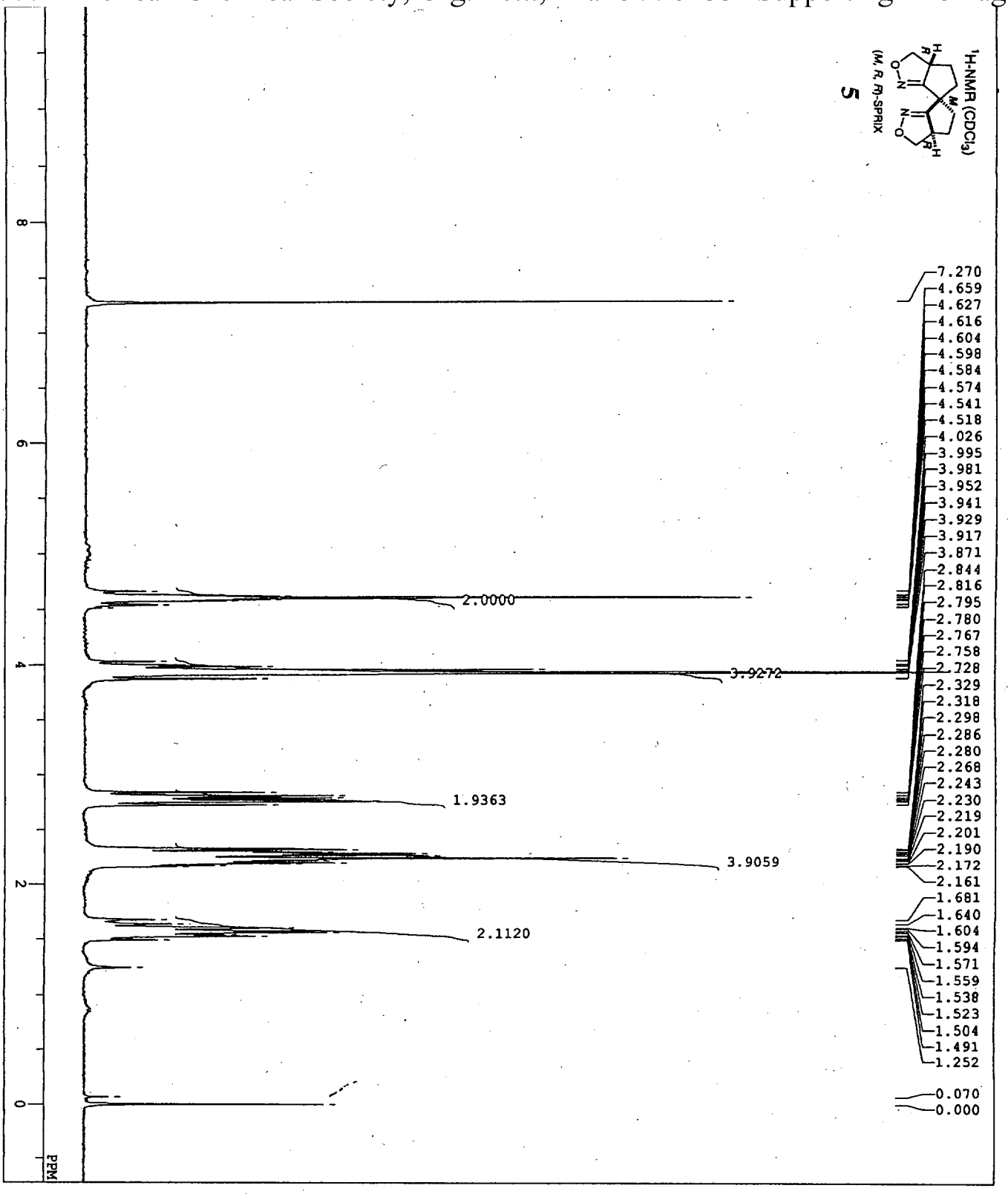


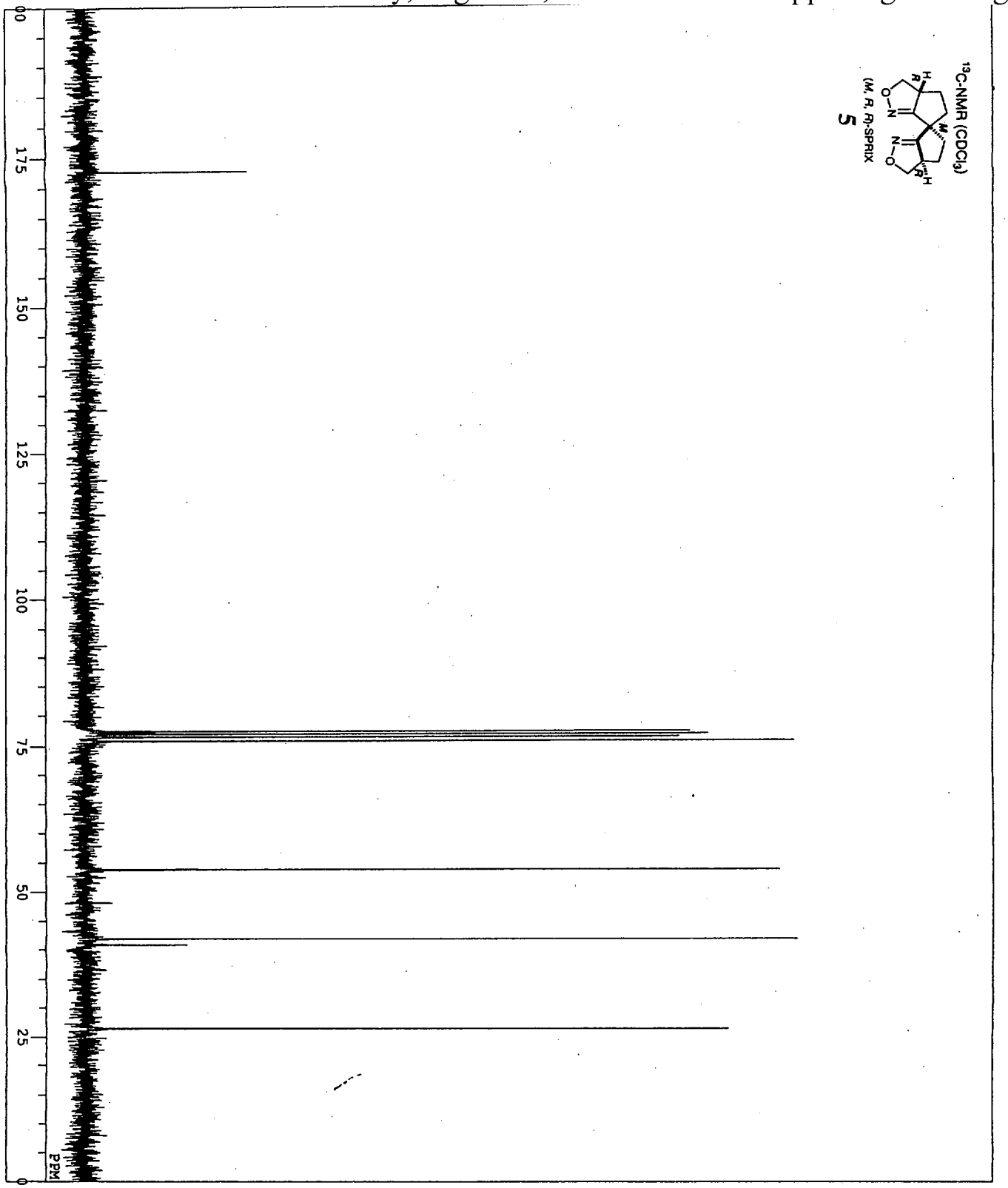


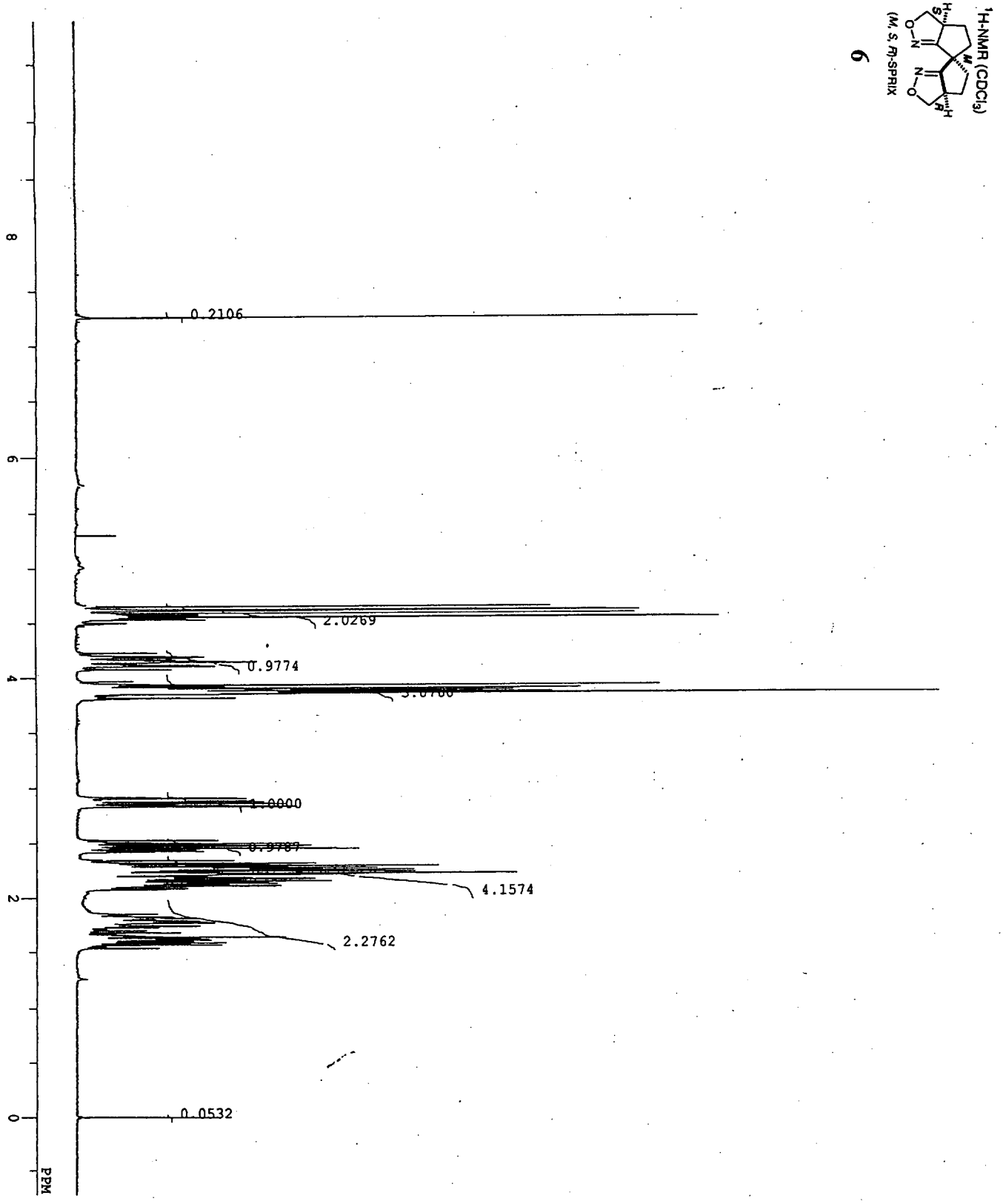


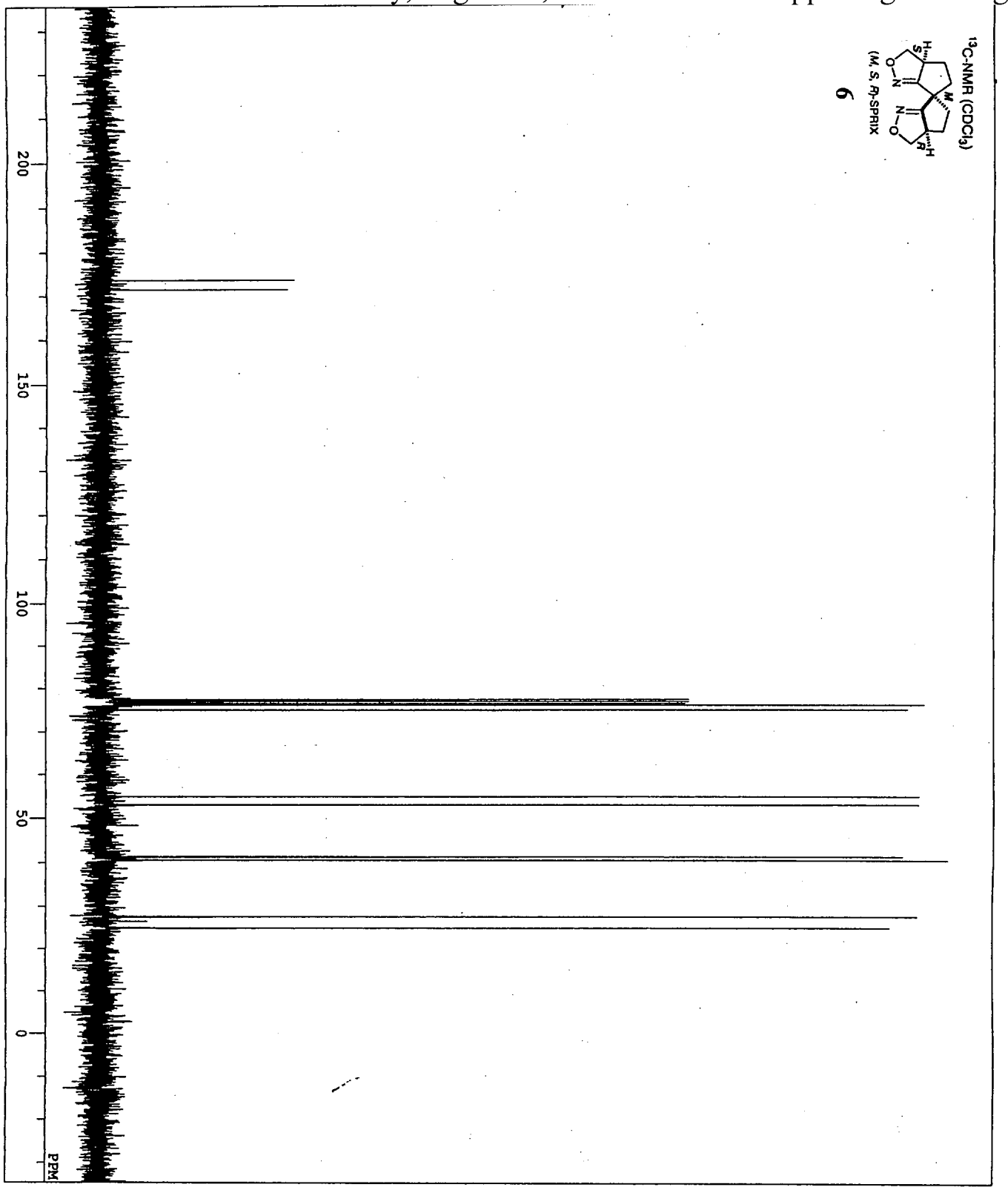




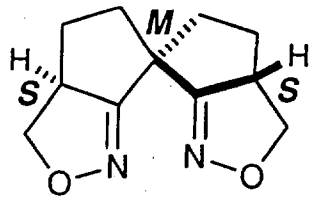




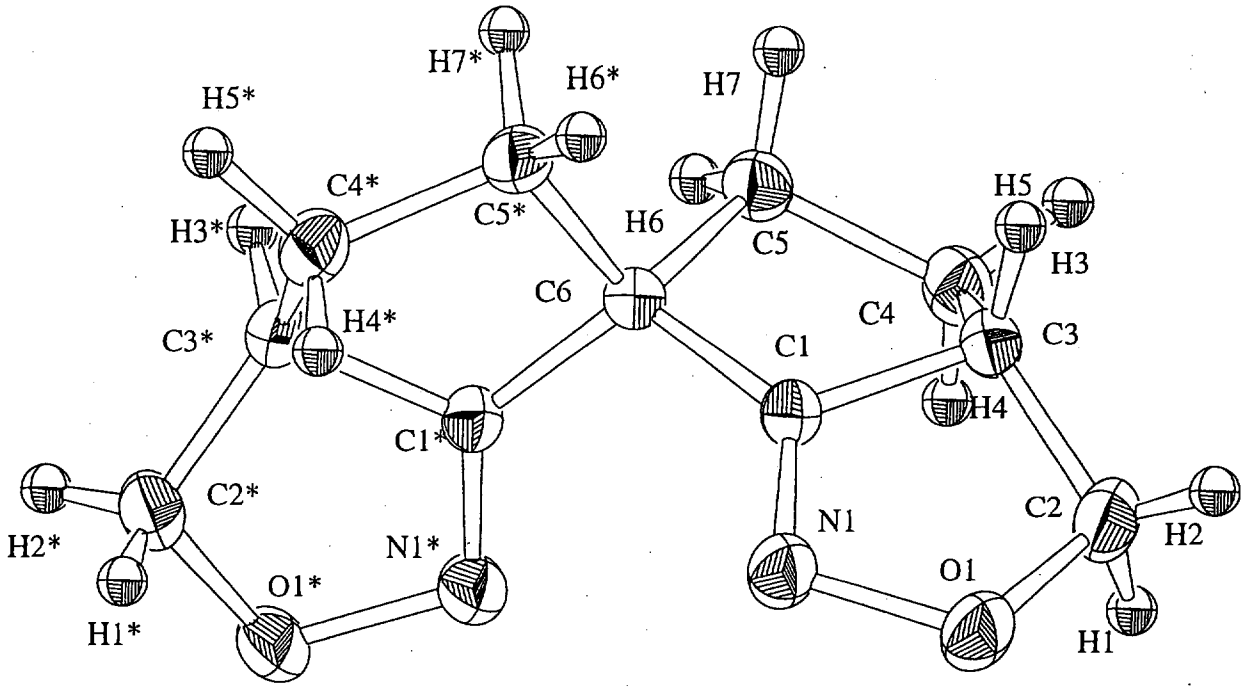




X-ray Structure Report



(*M*, *S*, *S*)-SPRIX



Experimental

Data Collection

A colorless prismatic crystal of $C_{11}H_{14}O_2N_2$ having approximate dimensions of 0.85 x 0.63 x 0.45 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection , obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $39.44 < 2\theta < 40.00°$ corresponded to a C-centered monoclinic cell with dimensions:

a = 10.860(3) $\AA$
b = 10.154(2) $\AA$ $\beta = 121.57(1)°$
c = 10.865(3) $\AA$
V = 1020.7(5) $\AA^3$

For Z = 4 and F.W. = 206.24, the calculated density is 1.34 g/cm^3. Based on the systematic absences of:

hkl: h+k $\neq$ 2n
h0l: l $\neq$ 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2/c (#15)

The data were collected at a temperature of -75 $\pm$ 1°C using the ω-2θ scan technique to a maximum 2θ value of 60.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.22° with a take-off angle of 6.0°. Scans of $(1.63 + 0.30 \tan\theta)°$ were made at a speed of 8.0°/min (in omega). The weak reflections ($I < 5.0\sigma(I)$) were rescanned (maximum of 10 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 258 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Data Reduction

Of the 1559 reflections which were collected, 1490 were unique ($R_{int} = 0.014$). The intensities of three representative reflection were measured after every 150 reflections. Over the course of data collection, the standards increased by 0.6%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.9 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging

from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.83158e-06).

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[3] was based on 1490 observed reflections ($I > 0.00\sigma(I)$) and 98 variable parameters and converged (largest parameter shift was 0.05 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.053$$

$$R_w = \sqrt{\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2} = 0.062$$

The standard deviation of an observation of unit weight[4] was 1.34. The weighting scheme was based on counting statistics and included a factor (p = 0.060) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and -0.20 $e^-/\AA^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5] . Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SAPI91: Fan Hai-Fu (1991). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized: $\Sigma w(|Fo| - |Fc|)^2$

where $w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$

$\sigma_c(Fo)$ = e.s.d. based on counting statistics

p = p-factor

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\Sigma w(|Fo| - |Fc|)^2/(No - Nv)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{11}H_{14}O_2N_2$
Formula Weight	206.24
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.85 X 0.63 X 0.45 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	24 (39.4 - 40.0°)
Omega Scan Peak Width at Half-height	0.22°
Lattice Parameters	a = 10.860(3)Å b = 10.154(2) Å c = 10.865(3) Å β = 121.57(1)°
	V = 1020.7(5) Å^3
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.342 g/cm^3
F_{000}	440.00
μ(MoKα)	0.94 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated

Attenuator	Zr foil (factors = 1.00, 3.40, 11.34, 38.03)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	258 mm
Temperature	-75.0°C
Scan Type	ω-2θ
Scan Rate	8.0°/min (in ω) (up to 10 scans)
Scan Width	$(1.63 + 0.30 \tan \theta)°$
$2\theta_{max}$	60.0°
No. of Reflections Measured	Total: 1559 Unique: 1490 (R_{int} = 0.014)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9584 - 0.9981) Decay (0.65% increase) Secondary Extinction (coefficient: 1.83158e-06)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SAPI91)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0600
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	1490
No. Variables	98
Reflection/Parameter Ratio	15.20
Residuals: R; Rw	0.053 ; 0.062

Residuals: R1	0.041
No. of Reflections to calc R1	1232
Goodness of Fit Indicator	1.34
Max Shift/Error in Final Cycle	0.05
Maximum peak in Final Diff. Map	0.37 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.20 $e^-/\AA^3$

Table 1. Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
O(1)	0.72215(9)	0.22795(8)	0.70802(9)	2.75(2)	1.0000
N(1)	0.87116(10)	0.18812(10)	0.7793(1)	2.35(2)	1.0000
C(1)	0.8744(1)	0.07532(10)	0.7306(1)	1.70(2)	1.0000
C(2)	0.6392(1)	0.1437(1)	0.5817(1)	2.97(2)	1.0000
C(3)	0.7318(1)	0.0223(1)	0.6124(1)	2.03(2)	1.0000
C(4)	0.7753(1)	-0.0271(1)	0.5068(1)	2.34(2)	1.0000
C(5)	0.9234(1)	-0.0909(1)	0.6088(1)	2.11(2)	1.0000
C(6)	1.0000	-0.0054(1)	0.7500	1.68(2)	0.5000
H(1)	0.629(2)	0.199(2)	0.496(2)	3.3(3)	1.0000
H(2)	0.553(2)	0.127(2)	0.582(2)	4.3(4)	1.0000
H(3)	0.704(2)	-0.053(1)	0.652(2)	2.7(3)	1.0000
H(4)	0.787(2)	0.048(2)	0.460(2)	3.1(3)	1.0000
H(5)	0.699(2)	-0.088(2)	0.428(2)	4.4(4)	1.0000
H(6)	0.981(1)	-0.101(1)	0.563(2)	2.6(3)	1.0000
H(7)	0.906(2)	-0.181(2)	0.633(2)	2.7(3)	1.0000

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.0274(4)	0.0310(4)	0.0392(5)	0.0072(3)	0.0128(4)	-0.0063(3)
N(1)	0.0245(5)	0.0278(5)	0.0305(5)	0.0025(3)	0.0100(4)	-0.0057(4)
C(1)	0.0192(4)	0.0229(5)	0.0197(4)	-0.0003(3)	0.0082(3)	-0.0002(3)
C(2)	0.0231(5)	0.0343(6)	0.0413(7)	0.0060(4)	0.0070(5)	-0.0077(5)
C(3)	0.0189(5)	0.0237(5)	0.0309(5)	-0.0013(3)	0.0106(4)	-0.0030(4)
C(4)	0.0263(5)	0.0313(6)	0.0242(5)	-0.0020(4)	0.0082(4)	-0.0064(4)
C(5)	0.0251(5)	0.0245(5)	0.0286(5)	-0.0010(4)	0.0127(4)	-0.0067(4)
C(6)	0.0193(6)	0.0195(6)	0.0230(6)	0.0000	0.0096(5)	0.0000

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond Lengths($\AA$)

atom	atom	distance	atom	atom	distance
O(1)	N(1)	1.439(1)	O(1)	C(6)	1.460(1)
N(1)	C(3)	1.270(1)	C(1)	C(4)	1.569(1)
C(1)	C(5)	1.539(2)	C(1)	H(1)	0.99(1)
C(1)	H(6)	1.00(2)	C(2)	C(3)	1.502(1)
C(2)	C(5)	1.536(2)	C(2)	C(6)	1.513(2)
C(2)	H(2)	1.00(1)	C(3)	C(4)	1.509(1)
C(5)	H(4)	0.96(2)	C(5)	H(7)	1.03(2)
C(6)	H(5)	0.95(2)	C(6)	H(8)	1.04(2)

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	O(1)	C(6)	107.94(8)	O(1)	N(1)	C(3)	107.31(8)
C(4)	C(1)	C(5)	106.86(8)	C(4)	C(1)	H(1)	113.6(8)
C(4)	C(1)	H(6)	108.9(9)	C(5)	C(1)	H(1)	112.1(9)
C(5)	C(1)	H(6)	107.7(8)	H(1)	C(1)	H(6)	107(1)
C(3)	C(2)	C(5)	99.97(8)	C(3)	C(2)	C(6)	99.50(8)
C(3)	C(2)	H(2)	108.2(9)	C(5)	C(2)	C(6)	122.0(1)
C(5)	C(2)	H(2)	110.6(8)	C(6)	C(2)	H(2)	113.9(8)
N(1)	C(3)	C(2)	116.04(9)	N(1)	C(3)	C(4)	130.68(9)
C(2)	C(3)	C(4)	112.12(8)	C(1)	C(4)	C(1)	112.8(1)
C(1)	C(4)	C(3)	100.75(5)	C(1)	C(4)	C(3)	114.49(5)
C(1)	C(4)	C(3)	114.49(5)	C(1)	C(4)	C(3)	100.75(5)
C(3)	C(4)	C(3)	114.2(1)	C(1)	C(5)	C(2)	102.37(9)
C(1)	C(5)	H(4)	109.4(9)	C(1)	C(5)	H(7)	115.5(10)
C(2)	C(5)	H(4)	108.5(10)	C(2)	C(5)	H(7)	113(1)
H(4)	C(5)	H(7)	107(1)	O(1)	C(6)	C(2)	104.98(9)
O(1)	C(6)	H(5)	103(1)	O(1)	C(6)	H(8)	104.2(9)
C(2)	C(6)	H(5)	113(1)	C(2)	C(6)	H(8)	112.6(9)
H(5)	C(6)	H(8)	117(1)				

Table 5. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	N(1)	C(3)	C(2)	3.8(1)	O(1)	N(1)	C(3)	C(4)	170.38(9)
O(1)	C(6)	C(2)	C(3)	-17.4(1)	O(1)	C(6)	C(2)	C(5)	-125.5(1)
N(1)	O(1)	C(6)	C(2)	21.1(1)	N(1)	C(3)	C(2)	C(5)	134.1(1)
N(1)	C(3)	C(2)	C(6)	9.0(1)	N(1)	C(3)	C(4)	C(1)	-153.8(1)
N(1)	C(3)	C(4)	C(1)	84.8(1)	N(1)	C(3)	C(4)	C(3)	-30.62(10)
C(1)	C(4)	C(1)	C(5)	136.85(9)	C(1)	C(4)	C(3)	C(2)	13.2(1)
C(1)	C(4)	C(3)	C(2)	-108.20(9)	C(1)	C(5)	C(2)	C(3)	41.3(1)
C(1)	C(5)	C(2)	C(6)	149.2(1)	C(2)	C(3)	C(4)	C(3)	136.38(9)
C(2)	C(5)	C(1)	C(4)	-35.6(1)	C(3)	N(1)	O(1)	C(6)	-15.8(1)
C(3)	C(4)	C(1)	C(5)	14.3(1)	C(3)	C(4)	C(1)	C(5)	-108.69(10)
C(4)	C(3)	C(2)	C(5)	-34.9(1)	C(4)	C(3)	C(2)	C(6)	-160.09(9)

Table 6. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
O(1)	H(2)	2.57(2)	65606	O(1)	H(1)	2.84(1)	45505
O(1)	H(6)	2.88(2)	65606	O(1)	H(4)	2.89(2)	65607
O(1)	H(7)	2.90(2)	4	O(1)	H(6)	3.22(1)	45505
O(1)	C(1)	3.378(2)	45505	O(1)	H(8)	3.44(2)	65607
O(1)	C(2)	3.460(1)	65606	N(1)	H(8)	2.79(2)	8
N(1)	H(1)	2.80(1)	4	N(1)	H(2)	2.96(1)	65606
N(1)	C(3)	3.045(2)	75602	N(1)	N(1)	3.179(2)	75602
N(1)	H(8)	3.20(2)	65607	N(1)	H(7)	3.21(2)	4
N(1)	H(1)	3.35(1)	75602	N(1)	H(5)	3.38(2)	8
N(1)	C(1)	3.412(2)	75602	N(1)	C(1)	3.462(2)	4
N(1)	C(6)	3.489(2)	8	N(1)	H(4)	3.50(2)	65607
N(1)	H(4)	3.51(2)	4	N(1)	C(5)	3.544(2)	4
N(1)	H(4)	3.58(2)	75602	C(1)	H(6)	2.59(1)	75602
C(1)	C(3)	2.589(2)	75602	C(1)	C(1)	2.615(2)	75602
C(1)	H(1)	3.15(2)	75602	C(1)	H(1)	3.22(1)	75603
C(1)	H(5)	3.28(2)	54505	C(1)	H(7)	3.47(2)	64607
C(1)	H(2)	3.50(1)	75602	C(1)	C(2)	3.556(2)	75602
C(2)	H(5)	3.08(2)	65603	C(2)	H(1)	3.50(1)	75602
C(2)	H(4)	3.57(2)	4	C(3)	C(3)	2.534(2)	75602
C(3)	H(1)	2.65(1)	75602	C(3)	H(1)	3.17(1)	4
C(3)	H(6)	3.31(2)	75602	C(3)	H(4)	3.34(2)	4
C(3)	H(8)	3.35(2)	65607	C(3)	H(4)	3.45(2)	75602
C(3)	C(5)	3.511(2)	75602	C(3)	H(7)	3.53(2)	4
C(3)	H(8)	3.59(2)	8	C(4)	H(6)	2.11(2)	75602