Supporting Information for

"Catch-and-Release" of HNO with Pyrazolones

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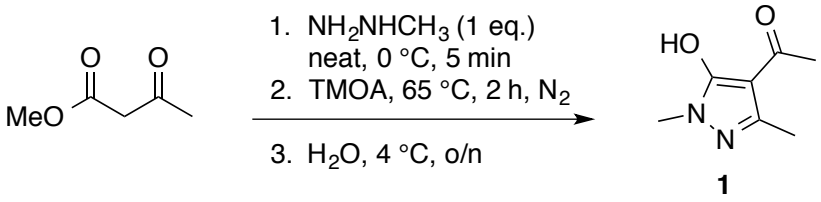
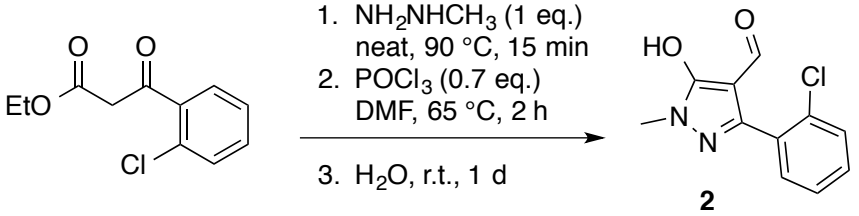
Synthetic Schemes

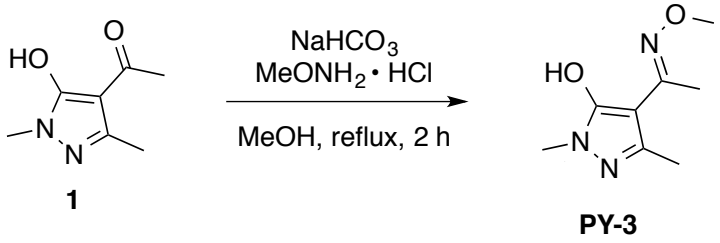
Scheme S1. Synthesis of 4-Acetyl-1,3-dimethylpyrazolone (1)



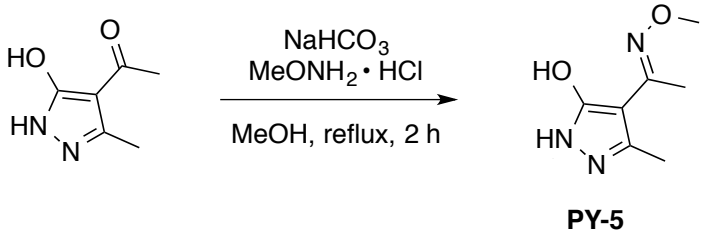
Scheme S2. Synthesis of 3-(2-Chlorophenyl)-4-formyl-1-methylpyrazolone (2)



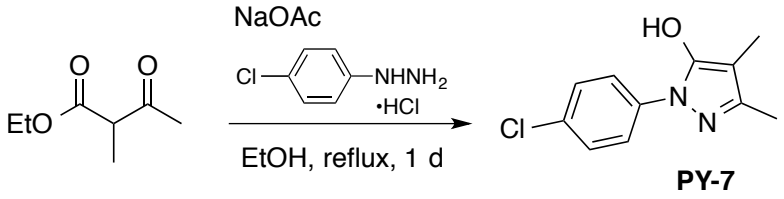
Scheme S3. Synthesis of 4-(Acetyl-*O*-methoxyoxime)-1,3-dimethylpyrazolone (PY-3)



Scheme S4. Synthesis of 4-(Acetyl-*O*-methoxyoxime)-3-methylpyrazolone (PY-5)

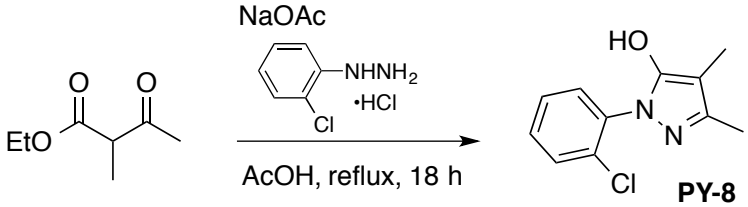


Scheme S5. Synthesis of 4-Methyl-*N*-(4-chlorophenyl)-3-methylpyrazolone (PY-7)



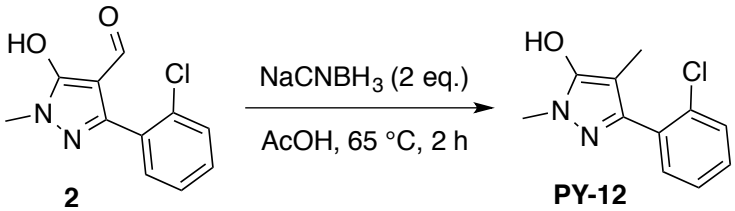
PY-7

Scheme S6. Synthesis of 4-Methyl-*N*-(2-chlorophenyl)-3-methylpyrazolone (PY-8)



PY-8

Scheme S7. Synthesis of 4-Methyl-*N*-methyl-3-(2-chlorophenyl)pyrazolone (PY-12)



2 **PY-12**

UV-vis Determined pK_a of HAPY-6

Ultraviolet-visible (UV-vis) absorption spectra were obtained using a diode array spectrometer. Buffered solutions (0.1 M) for UV-vis experiments were prepared from $NaPO_3H_2/Na_2PO_3H/Na_3PO_4$ (pH 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0).

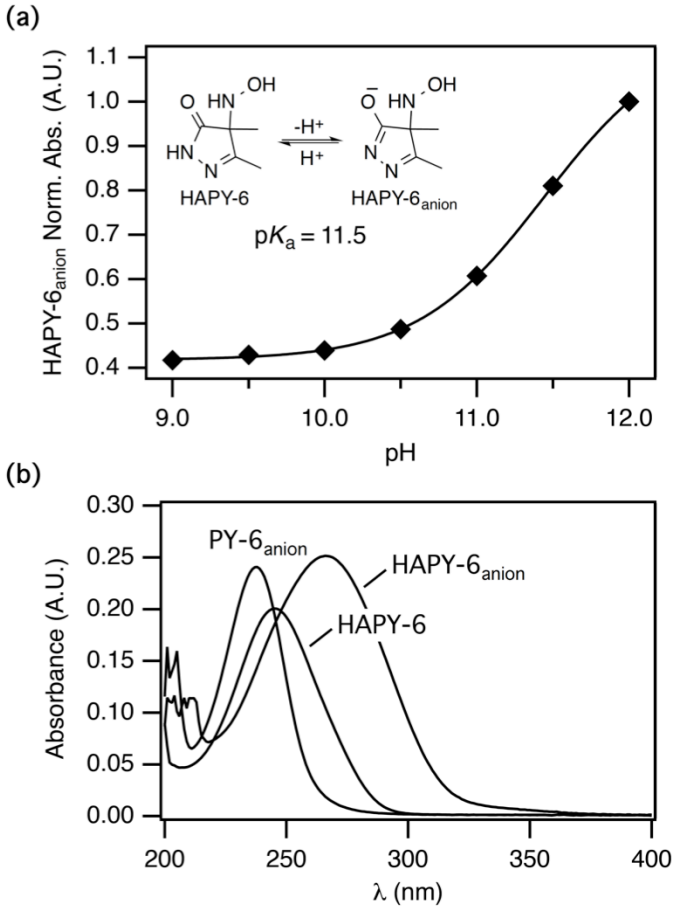
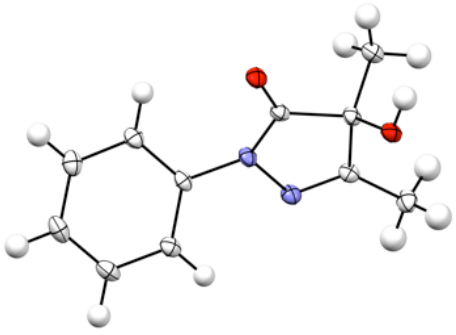


Figure S1. (a) Plot of the concentration of HAPY-6_{anion} (λ_{max} = 266 nm) as a function of pH. The solid curve is a calculated best fit to a sigmoid function. (b) Initial UV-vis spectra of HAPY-6 in pH 9.0 and pH 12.0 compared with the expected byproduct of HNO release, PY-6_{anion}, at pH 12.0.

Single-Crystal X-Ray Crystallography

All reflection intensities were measured at 110(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012). The program CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012) was used to refine the cell dimensions. Data reduction was done using the program CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012). The structure was solved with the program SHELXS-97 (Sheldrick, 2008) and was refined on F^2 with SHELXL-97 (Sheldrick, 2008). Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.36.20, Agilent Technologies, 2012). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43, AFIX 137 or AFIX 147 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C or O atoms.

The structure is ordered



PY-2$_{OH}$: Fw = 204.23, colorless irregular block, 0.55 × 0.38 × 0.19 mm^3, triclinic, *P*-1 (no. 2), a = 6.9967(3), b = 8.5345(5), c = 9.7334(6) Å, α = 110.752(5), β = 94.833(4), γ = 106.902(5)°, V = 508.51(5) Å^3, Z = 2, D_x = 1.334 g cm^{-3}, μ = 0.094 mm^{-1}, abs. corr. range: 0.966–0.987. 6277 Reflections were measured up to a resolution of

(sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 2332 Reflections were unique (R_{int} = 0.0210), of which 2063 were observed [$I > 2\sigma(I)$]. 139 Parameters were refined. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0350/0.0976. $R1/wR2$ [all refl.]: 0.0399/0.1011. S = 1.059. Residual electron density found between –0.23 and 0.35 e Å^{-3}.

Density Functional Theory (DFT) Calculations

All calculations were performed at the B3LYP/6-31G* level with an SM8 solvation model for aqueous solvation using Spartan '14 modeling software.[1] Optimized geometries and vibrational frequencies were calculated for each reactant and product independently, and free energies are given for 298.15 K.

Table S1. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Nitroxyl (HNO)

B3LYP/6-31G* Energy (E): -130.470851 hartrees
Entropy Correction (Hv-TSv): -19.0649 kJ/mol
G° = E + "entropy correction": -81876.18923 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms)		
		X	Y	Z
N	7	0.5680553	0.1586597	0.0000000
O	8	-0.6301148	-0.0406719	0.0000000
H	1	1.0645314	-0.7852429	0.0000000

Table S2. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Nitroxyl (HNO)

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	1565	20.87	**2**	1652	93.41	**3**	2940	62.00

Table S3. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Water (H_2O)

B3LYP/6-31G* Energy (E): -76.423559 hartrees
Entropy Correction (Hv-TSv): 6.5320 kJ/mol
G° = E + "entropy correction": -47954.9099 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
H	1	0.0000000	-0.2976214	-0.7243625
O	8	0.0000000	-0.3250377	0.2494010
H	1	0.0000000	0.6226591	0.4749616

Table S4. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Water (H_2O)

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	1677	110.10	**2**	3688	21.14	**3**	3778	84.71

Table S5. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Hydronium (H_3O^+)

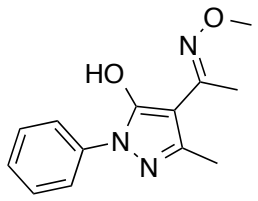
B3LYP/6-31G* Energy (E): -76.853354 hartrees
Entropy Correction (Hv-TSv): 41.0536 kJ/mol
G° = E + "entropy correction": -48216.35927 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
H	1	0.2212214	0.0000000	-0.8952325
O	8	0.2542327	0.0000000	0.0897557
H	1	-0.2377271	-0.7945454	0.4027384
H	1	-0.2377271	0.7945454	0.4027384

Table S6. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Hydronium (H_3O^+)

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	1082	495.92	**3**	1694	132.51	**5**	3621	519.14
2	1683	131.89	**4**	3555	83.48	**6**	3622	519.02

Table S7. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-1



PY-1

B3LYP/6-31G* Energy (E): -819.063789 hartrees
Entropy Correction (Hv-TSv): 593.6595 kJ/mol
G° = E + "entropy correction": -513828.0111 kcal/mol

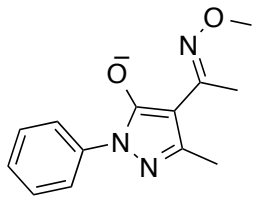
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.0871638	-0.4580564	0.2122397
C	6	-0.0636156	0.2755546	-0.0876464
N	7	-1.1482101	-0.4837613	0.2241276
N	7	-0.7475821	-1.7157646	0.7148325
C	6	0.5806836	-1.6993132	0.7099278
C	6	1.3126104	-2.9080556	1.2006235
H	1	1.9323130	-2.6797126	2.0741340
H	1	1.9717968	-3.3227835	0.4309135
H	1	0.5890499	-3.6760667	1.4846787
C	6	2.4410749	0.0480357	0.0104945
N	7	2.5039287	1.2348280	-0.5146796
O	8	3.8104584	1.7210969	-0.6941023
C	6	3.6374492	-0.7727021	0.3990201
H	1	4.5650719	-0.2400914	0.1964479
H	1	3.6434253	-1.7177815	-0.1531426
H	1	3.5956342	-1.0217433	1.4641223
C	6	3.7449648	3.0130085	-1.3045828
H	1	3.2688472	2.9607942	-2.2896587
H	1	4.7830032	3.3328302	-1.4136398
H	1	3.2046990	3.7234865	-0.6695527
O	8	-0.1628993	1.5078744	-0.6098399
H	1	0.7865376	1.7928542	-0.7450680
C	6	-2.5354003	-0.1957249	0.0850639
C	6	-5.2742824	0.3115746	-0.1690959
C	6	-2.9980489	1.1246046	0.0307135
C	6	-3.4414918	-1.2614098	0.0208271
C	6	-4.8042339	-1.0012895	-0.1022510
C	6	-4.3651147	1.3669795	-0.1027382
H	1	-2.2996952	1.9484376	0.0892735
H	1	-3.0668937	-2.2758815	0.0749875

H	1	-5.4989478	-1.8341673	-0.1505906
H	1	-4.7155919	2.3935833	-0.1456589
H	1	-6.3367040	0.5087628	-0.2701802

Table S8. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-1

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	30	0.23	**32**	715	99.26	**63**	1459	334.71
2	33	0.78	**33**	766	83.34	**64**	1482	57.86
3	50	3.92	**34**	775	54.26	**65**	1492	78.87
4	69	1.14	**35**	845	0.25	**66**	1496	1.72
5	82	2.22	**36**	854	0.32	**67**	1505	14.90
6	85	2.01	**37**	914	233.21	**68**	1508	8.52
7	126	1.83	**38**	927	5.11	**69**	1509	12.68
8	158	1.36	**39**	972	0.83	**70**	1523	59.98
9	173	2.92	**40**	995	0.48	**71**	1529	76.94
10	212	0.23	**41**	1006	2.40	**72**	1534	45.07
11	237	0.70	**42**	1019	1.70	**73**	1540	12.52
12	248	2.69	**43**	1037	43.44	**74**	1549	93.18
13	274	1.78	**44**	1054	87.82	**75**	1607	876.46
14	286	2.45	**45**	1063	0.28	**76**	1648	17.62
15	302	14.68	**46**	1066	344.97	**77**	1655	171.60
16	335	13.68	**47**	1071	2.23	**78**	1661	38.61
17	352	0.43	**48**	1088	54.45	**79**	3056	111.82
18	362	0.55	**49**	1099	24.04	**80**	3072	20.93
19	404	1.41	**50**	1118	19.85	**81**	3084	13.14
20	419	0.32	**51**	1148	12.09	**82**	3125	49.49
21	449	28.26	**52**	1180	2.37	**83**	3131	6.70
22	463	26.41	**53**	1190	0.50	**84**	3142	8.76
23	520	6.32	**54**	1212	1.90	**85**	3156	22.11
24	542	0.48	**55**	1219	25.21	**86**	3174	106.77
25	600	28.71	**56**	1256	68.74	**87**	3181	875.98
26	629	0.26	**57**	1349	26.91	**88**	3199	2.69
27	649	10.92	**58**	1369	2.81	**89**	3209	0.52
28	654	5.85	**59**	1373	61.52	**90**	3218	26.42
29	691	21.40	**60**	1383	94.09	**91**	3231	32.17
30	706	2.31	**61**	1421	51.21	**92**	3252	2.80
31	707	7.75	**62**	1435	32.60	**93**	3266	1.35

Table S9. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-1$_{anion}$



PY-1$_{anion}$

B3LYP/6-31G* Energy (E): -818.591456 hartrees
Entropy Correction (Hv-TSv): 559.3385 kJ/mol
G° = E + "entropy correction": -513539.8209 kcal/mol

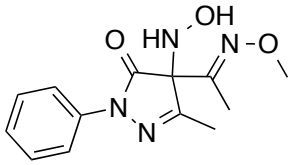
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.0413380	-0.2404651	0.1380892
C	6	-0.1393269	0.5512025	-0.0433794
N	7	-1.2031753	-0.3616604	0.1555978
N	7	-0.7423973	-1.6493189	0.4107325
C	6	0.5804145	-1.5633352	0.4110811
C	6	1.3533720	-2.8284664	0.6314983
H	1	1.8279155	-2.8606546	1.6192000
H	1	2.1450933	-2.9530380	-0.1149146
H	1	0.6680419	-3.6782628	0.5627761
C	6	2.4109696	0.2377362	0.0342045
N	7	2.6442558	1.2715884	-0.7230983
O	8	4.0326232	1.6367288	-0.6574269
C	6	3.5140608	-0.4387426	0.8151040
H	1	4.1293426	0.3161667	1.3138306
H	1	4.1845123	-0.9989005	0.1525964
H	1	3.1111067	-1.1172289	1.5650840
C	6	4.2251706	2.8049231	-1.4488498
H	1	3.9592333	2.6273889	-2.4980535
H	1	5.2903696	3.0381429	-1.3733572
H	1	3.6333255	3.6482203	-1.0724254
O	8	-0.2985039	1.7791404	-0.2879009
C	6	-2.5956807	-0.1415550	0.0980185
C	6	-5.3919047	0.2245714	-0.0080896
C	6	-3.1396548	1.1328132	-0.1469884
C	6	-3.4710198	-1.2265906	0.2913158
C	6	-4.8496350	-1.0384031	0.2375801
C	6	-4.5237357	1.3000102	-0.1978091
H	1	-2.4646084	1.9642392	-0.2941583

H	1	-3.0460758	-2.2042262	0.4795761
H	1	-5.5007576	-1.8945240	0.3899734
H	1	-4.9178014	2.2943697	-0.3894650
H	1	-6.4668676	0.3681305	-0.0503423

Table S10. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-1_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	16	0.41	**31**	747	49.39	**61**	1435	45.87
2	42	1.25	**32**	762	52.34	**62**	1479	88.57
3	44	8.71	**33**	763	84.99	**63**	1487	347.36
4	81	2.24	**34**	846	220.92	**64**	1494	49.81
5	89	7.82	**35**	854	140.00	**65**	1498	21.13
6	111	0.16	**36**	855	45.51	**66**	1499	5.44
7	150	2.17	**37**	907	5.49	**67**	1506	49.78
8	156	0.78	**38**	964	0.10	**68**	1515	134.02
9	169	4.19	**39**	978	0.88	**69**	1523	21.26
10	206	1.55	**40**	1006	25.59	**70**	1537	21.00
11	228	3.13	**41**	1014	6.61	**71**	1537	278.51
12	249	0.84	**42**	1036	50.25	**72**	1559	269.75
13	270	5.26	**43**	1049	112.26	**73**	1571	551.34
14	291	2.57	**44**	1055	15.23	**74**	1623	240.69
15	298	2.09	**45**	1061	84.22	**75**	1637	122.45
16	346	12.59	**46**	1067	0.73	**76**	1658	230.26
17	353	1.76	**47**	1081	238.40	**77**	3040	156.75
18	370	6.93	**48**	1092	21.54	**78**	3063	50.34
19	396	4.24	**49**	1100	43.28	**79**	3075	22.64
20	419	0.01	**50**	1158	1.49	**80**	3098	76.41
21	451	68.25	**51**	1179	0.93	**81**	3120	16.40
22	464	13.16	**52**	1180	2.02	**82**	3129	18.28
23	522	5.69	**53**	1191	0.41	**83**	3147	32.85
24	558	0.62	**54**	1201	0.84	**84**	3159	27.77
25	609	36.70	**55**	1223	12.04	**85**	3199	19.26
26	632	1.05	**56**	1335	423.32	**86**	202	16.66
27	647	7.53	**57**	1352	71.90	**87**	3209	29.67
28	667	32.08	**58**	1365	59.44	**88**	3235	30.56
29	703	4.24	**59**	1391	138.73	**89**	3251	5.06
30	704	11.36	**60**	1414	9.06	**90**	3256	9.48

Table S11. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-1



HAPY-1

B3LYP/6-31G* Energy (E): -949.560389 hartrees
Entropy Correction (Hv-TSv): 639.1283 kJ/mol
G° = E + "entropy correction": -595704.9348 kcal/mol

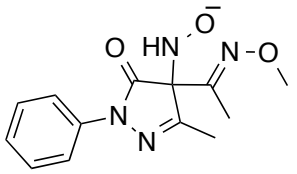
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.0639329	-0.0863496	0.4900204
C	6	-0.2392076	0.7109256	0.2736413
N	7	-1.2404253	-0.2293610	0.1490905
N	7	-0.7506639	-1.5483685	0.2299369
C	6	0.5209355	-1.5114092	0.4200677
O	8	-0.3589544	1.9333473	0.2324030
C	6	1.3359479	-2.7451277	0.5770011
H	1	1.7683876	-2.7917979	1.5840137
H	1	2.1685015	-2.7567514	-0.1336008
H	1	0.7108883	-3.6271654	0.4251715
C	6	2.0958626	0.1818373	-0.6093115
N	7	3.3141312	0.1232105	-0.2156869
O	8	4.2371190	0.3445380	-1.2472646
C	6	1.6242359	0.4283042	-2.0123874
H	1	1.2858321	1.4653858	-2.1222327
H	1	0.7735617	-0.2173345	-2.2551072
H	1	2.4243849	0.2463049	-2.7301620
C	6	5.5643100	0.2263813	-0.7175134
H	1	5.7389419	0.9668077	0.0692271
H	1	6.2277979	0.4173109	-1.5629176
H	1	5.7437491	-0.7793896	-0.3247562
N	7	1.5187321	0.1270728	1.8763323
H	1	2.3929038	-0.3973713	1.9719817
O	8	1.9613500	1.4968668	2.0340057
H	1	1.2989067	1.8555898	2.6498427
C	6	-2.6365865	-0.0439986	-0.0478155
C	6	-5.3947609	0.2622861	-0.4422363
C	6	-3.4713716	-1.1700753	-0.0934802
C	6	-3.1848728	1.2387020	-0.1990033
C	6	-4.5585847	1.3773801	-0.3947854
C	6	-4.8407360	-1.0092505	-0.2902648

H	1	-3.0403236	-2.1554003	0.0223837
H	1	-2.5422649	2.1065112	-0.1623943
H	1	-4.9715993	2.3748902	-0.5109604
H	1	-5.4749934	-1.8896793	-0.3241846
H	1	-6.4623387	0.3830062	-0.5957517

Table S12. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-1

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	27	0.23	**35**	709	15.43	**69**	1393	275.98
2	29	0.37	**36**	749	25.63	**70**	1429	20.77
3	34	0.40	**37**	766	13.64	**71**	1442	15.30
4	83	4.24	**38**	775	59.53	**72**	1488	3.66
5	88	4.16	**39**	834	80.46	**73**	1490	11.15
6	95	2.98	**40**	860	0.02	**74**	1495	18.68
7	109	2.42	**41**	891	91.08	**75**	1504	7.09
8	123	0.37	**42**	908	113.44	**76**	1505	2.57
9	126	7.16	**43**	931	5.83	**77**	1509	7.76
10	137	1.17	**44**	951	79.45	**78**	1516	11.63
11	158	4.16	**45**	978	0.00	**79**	1517	14.42
12	169	7.50	**46**	1001	1.01	**80**	1534	38.13
13	186	4.20	**47**	1009	4.86	**81**	1541	198.09
14	197	3.72	**48**	1017	0.20	**82**	1642	0.81
15	231	8.91	**49**	1020	6.12	**83**	1659	104.74
16	253	31.42	**50**	1034	12.07	**84**	1691	124.21
17	279	3.44	**51**	1045	41.44	**85**	1702	457.96
18	289	41.99	**52**	1056	361.95	**86**	1779	18.21
19	307	48.89	**53**	1061	46.18	**87**	3064	101.91
20	326	25.70	**54**	1080	12.44	**88**	3070	6.45
21	339	19.59	**55**	1081	20.59	**89**	3075	3.88
22	366	9.12	**56**	1097	13.18	**90**	3129	5.09
23	385	9.64	**57**	1130	4.00	**91**	3138	47.03
24	420	0.60	**58**	1163	98.37	**92**	3143	8.77
25	425	20.81	**59**	1189	2.09	**93**	3175	6.88
26	452	3.79	**60**	1190	0.09	**94**	3179	20.46
27	494	19.92	**61**	1212	5.43	**95**	3185	6.93
28	516	2.46	**62**	1215	16.49	**96**	3207	2.75
29	530	5.16	**63**	1243	18.56	**97**	3215	28.22
30	593	27.90	**64**	1283	28.14	**98**	3230	33.61
31	621	8.78	**65**	1299	236.05	**99**	3263	0.46
32	631	0.54	**66**	1353	28.85	**100**	3270	3.48
33	660	50.43	**67**	1366	36.55	**101**	3442	39.54
34	697	2.26	**68**	1377	62.28	**102**	3714	97.56

Table S13. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-1$_{anion}$



HAPY-1 $_{anion}$

B3LYP/6-31G* Energy (E): -949.073224 hartrees
Entropy Correction (Hv-TSv): 595.3271 kJ/mol
G° = E + "entropy correction": Not a ground state structure; HNO is dissociated

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.0214091	-0.1571378	-0.2418336
C	6	-0.2097519	0.5647410	-0.4462345
N	7	-1.2183146	-0.3865459	-0.1867631
N	7	-0.6879684	-1.6253974	0.1469285
C	6	0.6238100	-1.4894948	0.1117294
O	8	-0.4362384	1.7591017	-0.7750128
C	6	1.4758425	-2.6769185	0.4213738
H	1	2.1330056	-2.4844335	1.2761106
H	1	2.1332761	-2.9251359	-0.4184093
H	1	0.8314792	-3.5318636	0.6460040
C	6	2.3647372	0.3459400	-0.4758830
N	7	3.3632689	-0.4588540	-0.2535859
O	8	4.6030172	0.1877153	-0.5318817
C	6	2.5837684	1.7607122	-0.9593730
H	1	3.1822046	2.3181304	-0.2300227
H	1	1.6352280	2.2700151	-1.1163234
H	1	3.1668447	1.7475798	-1.8865645
C	6	5.6609478	-0.7353628	-0.2727489
H	1	5.6645765	-1.0541235	0.7760335
H	1	6.5820887	-0.1917828	-0.4961351
H	1	5.5870078	-1.6189226	-0.9173902
N	7	0.7492864	1.0344728	2.2311922
H	1	1.7762160	0.7853203	2.1133852
O	8	0.6256630	2.2511769	2.1080485
C	6	-2.6226410	-0.2321559	-0.2014021
C	6	-5.4320806	0.0015406	-0.2150673

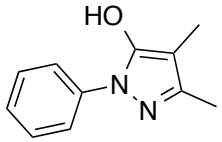
C	6	-3.2344019	0.9737642	-0.5864039
C	6	-3.4341817	-1.3171117	0.1757170
C	6	-4.8212249	-1.1945907	0.1659633
C	6	-4.6257346	1.0766866	-0.5881506
H	1	-2.6097311	1.8082664	-0.8715913
H	1	-2.9561548	-2.2418577	0.4721800
H	1	-5.4242128	-2.0478765	0.4628041
H	1	-5.0748328	2.0190565	-0.8893220
H	1	-6.5134279	0.0942735	-0.2205125

Table S14. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-1_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	2	0.28	**34**	665	110.32	**67**	1441	77.83
2	18	0.14	**35**	692	4.94	**68**	1471	500.43
3	34	3.08	**36**	704	11.11	**69**	1480	27.72
4	46	7.93	**37**	737	37.43	**70**	1489	12.46
5	62	2.92	**38**	764	53.30	**71**	1498	52.46
6	79	10.99	**39**	770	42.84	**72**	1501	2.64
7	88	1.27	**40**	851	225.74	**73**	1505	503.18
8	91	8.15	**41**	854	1.58	**74**	1511	29.70
9	106	2.31	**42**	890	186.90	**75**	1520	255.51
10	130	3.80	**43**	910	5.25	**76**	1534	18.80
11	144	1.71	**44**	965	0.13	**77**	1537	55.56
12	162	4.62	**45**	978	0.78	**78**	1540	149.85
13	170	2.28	**46**	1014	7.64	**79**	1561	52.05
14	212	3.66	**47**	1019	22.97	**80**	1572	116.86
15	218	2.64	**48**	1038	96.23	**81**	1602	670.36
16	241	4.12	**49**	1053	252.10	**82**	1621	262.52
17	254	23.24	**50**	1058	75.10	**83**	1638	79.99
18	262	5.54	**51**	1073	2.85	**84**	1659	231.84
19	294	17.73	**52**	1075	9.68	**85**	2933	43.62
20	319	4.22	**53**	1088	55.89	**86**	3048	158.56
21	340	17.66	**54**	1096	28.48	**87**	3067	44.30
22	350	1.87	**55**	1102	118.89	**88**	3068	29.35
23	380	13.09	**56**	1158	7.64	**89**	3112	68.62
24	393	0.62	**57**	1178	3.03	**90**	3117	16.26
25	419	0.06	**58**	1180	0.54	**91**	3124	16.04
26	434	7.78	**59**	1200	10.02	**92**	3149	36.44
27	476	74.97	**60**	1203	1.42	**93**	3165	28.99
28	496	61.84	**61**	1232	24.38	**94**	3195	5.78
29	523	5.61	**62**	1338	453.64	**95**	3202	10.07
30	564	2.33	**63**	1349	7.93	**96**	3210	31.36

31	611	32.08	**64**	1364	18.14	**97**	3229	35.15
32	633	0.48	**65**	1378	261.74	**98**	3252	3.86
33	658	15.88	**66**	1431	21.43	**99**	3261	7.67

Table S15. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-2



PY-2

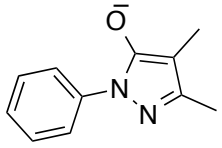
B3LYP/6-31G* Energy (E): -611.117576 hartrees
Entropy Correction (Hv-TSv): 457.2947 kJ/mol
G° = E + "entropy correction": -383372.4829 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.1225504	0.1528301	0.3568273
C	6	0.9272259	0.8410004	0.2653613
N	7	-0.0788429	-0.0606165	0.0263349
N	7	0.4364668	-1.3386332	-0.0555839
C	6	1.7466909	-1.1991077	0.1424989
C	6	3.4884350	0.7182159	0.6082297
H	1	3.4500363	1.6063280	1.2504923
H	1	4.0050531	1.0023207	-0.3174947
H	1	4.1226819	-0.0110011	1.1225173
C	6	2.6425378	-2.3959032	0.1351472
H	1	3.1765132	-2.5027597	1.0870542
H	1	3.4016929	-2.3230346	-0.6525512
H	1	2.0582706	-3.3042645	-0.0333340
C	6	-1.4674844	0.1566178	-0.1843021
C	6	-4.2109983	0.5168441	-0.6164062
C	6	-2.1929693	-0.7877473	-0.9227621
C	6	-2.1188945	1.2770635	0.3470062
C	6	-3.4838143	1.4522461	0.1190631
C	6	-3.5578803	-0.6054159	-1.1298831
H	1	-1.6763431	-1.6545416	-1.3157656
H	1	-1.5668890	2.0010319	0.9305245
H	1	-3.9788428	2.3253991	0.5329286
H	1	-4.1093133	-1.3449140	-1.7024438
H	1	-5.2736902	0.6581987	-0.7859690
O	8	0.6465056	2.1668639	0.3607940
H	1	1.4913022	2.6529789	0.4317162

Table S16. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for enol of PY-2

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	31	2.99	**25**	774	48.41	**49**	1448	7.62
2	57	1.17	**26**	822	2.26	**50**	1484	138.98
3	66	4.86	**27**	850	0.42	**51**	1492	43.05
4	106	0.15	**28**	923	5.48	**52**	1508	9.26
5	125	1.89	**29**	969	0.61	**53**	1509	27.00
6	164	6.73	**30**	977	50.59	**54**	1519	12.54
7	222	54.07	**31**	992	0.63	**55**	1525	14.09
8	227	6.17	**32**	1017	7.02	**56**	1537	108.07
9	235	55.78	**33**	1026	81.51	**57**	1551	217.77
10	279	2.51	**34**	1057	5.24	**58**	1633	212.09
11	294	27.52	**35**	1064	3.91	**59**	1649	66.34
12	339	3.13	**36**	1080	2.04	**60**	1661	69.69
13	350	10.32	**37**	1099	54.28	**61**	3047	61.73
14	399	2.51	**38**	1112	1.56	**62**	3059	40.58
15	420	1.40	**39**	1121	127.06	**63**	3099	29.99
16	516	5.34	**40**	1187	18.57	**64**	3110	16.14
17	566	21.78	**41**	1190	1.09	**65**	3125	24.91
18	608	7.51	**42**	1211	0.28	**66**	3150	20.63
19	630	0.35	**43**	1243	110.23	**67**	3206	0.24
20	654	2.15	**44**	1328	64.54	**68**	3216	25.58
21	666	14.36	**45**	1357	41.53	**69**	3227	35.93
22	688	5.30	**46**	1369	4.24	**70**	3247	5.10
23	706	20.88	**47**	1416	272.46	**71**	3267	1.21
24	742	58.88	**48**	1438	112.34	**72**	3676	240.49

Table S17. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-2_{anion}



PY-2_{anion}

B3LYP/6-31G* Energy (E): -610.654618 hartrees
Entropy Correction (Hv-TSv): 425.1610 kJ/mol
G° = E + "entropy correction": -383089.6528 kcal/mol

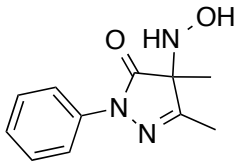
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.1728663	0.2358654	0.4538906
C	6	0.9766007	0.9853925	0.4540959
N	7	-0.0160307	0.0653284	0.0160514
N	7	0.5257457	-1.1924461	-0.2442987
C	6	1.8262128	-1.0607008	0.0253448
C	6	3.5141416	0.7728354	0.8451327
H	1	3.4086559	1.8176222	1.1592336
H	1	4.2437135	0.7506808	0.0225115
H	1	3.9680800	0.2218178	1.6811854
C	6	2.7375860	-2.2346342	-0.1434214
H	1	3.2487202	-2.4834294	0.7952988
H	1	3.5189254	-2.0318774	-0.8868652
H	1	2.1684599	-3.1100880	-0.4703671
C	6	-1.3964928	0.2640981	-0.1755972
C	6	-4.1726379	0.6021774	-0.5730418
C	6	-2.1866133	-0.7896022	-0.6738015
C	6	-2.0179069	1.4921154	0.1209485
C	6	-3.3896071	1.6466861	-0.0800147
C	6	-3.5547742	-0.6153203	-0.8668224
H	1	-1.7033019	-1.7320225	-0.8986633
H	1	-1.4052122	2.2981611	0.5014999
H	1	-3.8426442	2.6053594	0.1579587
H	1	-4.1384651	-1.4462559	-1.2532664
H	1	-5.2391649	0.7340099	-0.7258435
O	8	0.7531433	2.2042270	0.7588514

Table S18. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-2_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	42	0.04	**24**	762	69.07	**47**	1424	33.45
2	48	0.47	**25**	828	1.38	**48**	1476	137.25
3	61	6.87	**26**	856	0.04	**49**	1495	88.25
4	141	5.39	**27**	905	5.85	**50**	1505	4.79
5	145	3.99	**28**	963	0.14	**51**	1509	106.04
6	163	1.30	**29**	968	72.37	**52**	1521	8.56
7	212	9.57	**30**	976	1.07	**53**	1525	39.49
8	216	1.35	**31**	1013	10.61	**54**	1535	340.57
9	269	0.06	**32**	1020	98.48	**55**	1543	393.07
10	297	20.60	**33**	1056	1.27	**56**	1607	333.43
11	336	4.18	**34**	1056	2.17	**57**	1635	83.29
12	362	3.07	**35**	1076	1.12	**58**	1657	267.98

13	388	2.93	**36**	1091	5.44	**59**	3021	156.26
14	422	0.05	**37**	1105	64.24	**60**	3050	71.70
15	524	5.75	**38**	1139	110.61	**61**	3057	60.54
16	573	37.07	**39**	1150	43.25	**62**	3099	24.45
17	629	6.69	**40**	1176	0.86	**63**	3106	35.50
18	632	7.94	**41**	1200	1.07	**64**	3140	30.38
19	647	3.24	**42**	1315	75.29	**65**	3192	21.49
20	662	20.67	**43**	1341	378.03	**66**	3205	24.77
21	706	10.18	**44**	1355	122.44	**67**	3227	27.64
22	730	11.63	**45**	1365	64.77	**68**	3248	7.99
23	761	67.05	**46**	1418	10.45	**69**	3249	8.00

Table S19. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-2



HAPY-2

B3LYP/6-31G* Energy (E): -741.635611 hartrees
Entropy Correction (Hv-TSv): 507.8082 kJ/mol
G° = E + "entropy correction": -465261.6516 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.0161767	0.0452028	0.1943700
C	6	0.6729899	0.7849498	0.1911063
N	7	-0.2972683	-0.1858562	0.0513906
N	7	0.2601273	-1.4768462	-0.0789356
C	6	1.5434213	-1.3790149	-0.0262766
O	8	0.4988254	2.0000667	0.2987924
C	6	2.7343876	0.2189836	1.5410064
H	1	2.9570282	1.2751040	1.7036802
H	1	3.6724088	-0.3444284	1.5401906
H	1	2.1150097	-0.1438793	2.3674034
N	7	2.7905458	0.4681273	-0.9952550
H	1	3.6122847	-0.1423931	-1.0423555
O	8	3.3883890	1.7651380	-0.7487484
H	1	2.8534671	2.3531064	-1.3080297

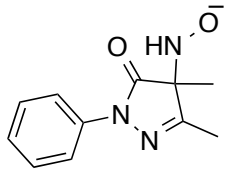
C	6	2.4244736	-2.5709806	-0.1539292
H	1	3.0900016	-2.6605798	0.7117954
H	1	3.0579115	-2.4923223	-1.0461661
H	1	1.8207289	-3.4769776	-0.2369940
C	6	-1.7113854	-0.0595583	0.0042242
C	6	-4.5080376	0.1334114	-0.0871999
C	6	-2.4943611	-1.2146547	-0.1376554
C	6	-2.3323787	1.1953480	0.1009018
C	6	-3.7236885	1.2778737	0.0542909
C	6	-3.8824875	-1.1101880	-0.1826809
H	1	-2.0089846	-2.1784822	-0.2111539
H	1	-1.7302199	2.0859052	0.2106387
H	1	-4.1915778	2.2548293	0.1302724
H	1	-4.4751223	-2.0131073	-0.2936607
H	1	-5.5900248	0.2099211	-0.1230802

Table S20. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-2

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	18	0.17	**28**	758	25.04	**55**	1398	268.05
2	39	2.57	**29**	775	60.34	**56**	1419	8.51
3	89	0.38	**30**	824	32.55	**57**	1441	26.00
4	95	9.50	**31**	860	0.02	**58**	1491	17.41
5	143	10.46	**32**	892	34.42	**59**	1495	11.49
6	152	3.46	**33**	898	15.39	**60**	1502	10.55
7	169	1.41	**34**	928	6.00	**61**	1504	0.80
8	202	21.89	**35**	956	47.06	**62**	1517	7.66
9	233	25.21	**36**	977	0.00	**63**	1524	5.68
10	238	15.14	**37**	998	0.89	**64**	1540	215.38
11	248	43.33	**38**	1016	0.21	**65**	1641	0.33
12	265	4.85	**39**	1020	27.06	**66**	1658	121.68
13	286	35.88	**40**	1028	28.75	**67**	1686	174.60
14	306	24.70	**41**	1050	10.16	**68**	1695	424.49
15	337	13.63	**42**	1060	4.50	**69**	3063	8.25
16	368	3.77	**43**	1090	30.76	**70**	3075	16.09
17	385	3.69	**44**	1116	19.44	**71**	3121	5.21
18	418	0.01	**45**	1138	25.14	**72**	3145	20.17
19	459	1.94	**46**	1156	65.38	**73**	3169	19.09
20	527	5.97	**47**	1169	66.32	**74**	3169	1.40
21	578	35.11	**48**	1189	0.04	**75**	3207	2.87
22	614	19.29	**49**	1210	5.24	**76**	3216	27.71
23	621	9.02	**50**	1263	93.76	**77**	3229	33.64
24	631	0.62	**51**	1325	228.24	**78**	3263	0.65

25	666	20.84	**52**	1352	15.19	**79**	3270	3.28
26	708	16.91	**53**	1364	23.42	**80**	3431	18.00
27	739	14.60	**54**	1369	33.68	**81**	3727	110.14

Table S21. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-2$_{anion}$



HAPY-2$_{anion}$

B3LYP/6-31G* Energy (E): -741.128834 hartrees
Entropy Correction (Hv-TSv): 472.3790 kJ/mol
G° = E + "entropy correction": -464952.1122 kcal/mol

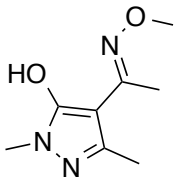
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.5851225	-1.8410150	-0.6197223
C	6	-0.8742383	-0.3633975	-0.7956171
N	7	-0.0355121	0.2992146	0.0807645
N	7	0.8736889	-0.5848576	0.6978832
C	6	0.6139977	-1.7798839	0.2827816
C	6	1.4055153	-2.9445603	0.7616526
H	1	0.7606522	-3.6549387	1.2943702
H	1	2.1977787	-2.6084607	1.4347797
H	1	1.8546016	-3.4835739	-0.0800410
O	8	-1.6892290	0.1603122	-1.5601201
C	6	-0.4185344	-2.5795818	-1.9387354
H	1	-1.4179523	-2.6942216	-2.3698320
H	1	0.0044723	-3.5747330	-1.7660285
H	1	0.2303553	-2.0469064	-2.6421870
N	7	-1.7607184	-2.4126529	0.2493755
H	1	-1.3790081	-3.3699158	0.4147602
O	8	-2.9309768	-2.5559829	-0.5124102
C	6	0.1052156	1.6892137	0.3313896
C	6	0.4211168	4.4293966	0.8661404
C	6	1.2038182	2.1439144	1.0774891
C	6	-0.8398397	2.6136198	-0.1418705
C	6	-0.6703675	3.9716346	0.1278788
C	6	1.3532210	3.5043547	1.3385028
H	1	1.9226777	1.4233990	1.4454247
H	1	-1.6856117	2.2636904	-0.7167978
H	1	-1.4113673	4.6712110	-0.2479444

H	1	2.2098924	3.8363245	1.9172339
H	1	0.5414747	5.4883966	1.0708794

Table S22. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-2_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	34	4.68	**27**	752	34.30	**53**	1388	205.26
2	45	8.86	**28**	768	49.72	**54**	1408	6.93
3	95	11.20	**29**	794	25.81	**55**	1432	18.95
4	118	11.21	**30**	846	22.36	**56**	1456	24.31
5	144	5.80	**31**	855	0.08	**57**	1492	12.67
6	157	11.89	**32**	915	47.36	**58**	1497	26.33
7	180	23.17	**33**	921	5.15	**59**	1502	1.47
8	191	1.97	**34**	968	100.47	**60**	1507	4.60
9	219	1.17	**35**	970	0.27	**61**	1532	7.26
10	261	8.70	**36**	985	1.32	**62**	1540	225.31
11	265	3.52	**37**	1017	1.00	**63**	1639	10.47
12	273	9.77	**38**	1025	27.45	**64**	1656	128.86
13	311	11.84	**39**	1039	11.73	**65**	1672	142.86
14	324	12.54	**40**	1049	3.48	**66**	1690	466.97
15	367	2.25	**41**	1060	4.30	**67**	3058	47.77
16	385	1.95	**42**	1090	22.56	**68**	3062	12.81
17	417	46.28	**43**	1109	5.04	**69**	3089	129.42
18	421	4.82	**44**	1133	18.48	**70**	3121	8.91
19	522	26.70	**45**	1160	147.86	**71**	3130	9.18
20	540	102.86	**46**	1174	11.14	**72**	3139	33.78
21	579	33.33	**47**	1184	0.08	**73**	3167	11.43
22	615	18.89	**48**	1210	3.48	**74**	3208	4.48
23	632	0.35	**49**	1284	110.65	**75**	3216	26.52
24	662	74.89	**50**	1338	353.54	**76**	3232	30.45
25	670	26.11	**51**	1353	1.71	**77**	3260	1.00
26	705	15.59	**52**	1366	4.99	**78**	3260	4.41

Table S23. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-3



PY-3

B3LYP/6-31G* Energy (E): -627.325837 hartrees
Entropy Correction (Hv-TSv): 461.1102 kJ/mol
G° = E + "entropy correction": -393542.4007 kcal/mol

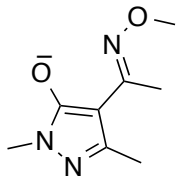
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.2117165	-0.3782990	0.2462173
C	6	-1.3804963	0.2784643	-0.1632792
N	7	-2.4375791	-0.4139166	0.2985989
N	7	-2.0337805	-1.5237325	1.0072797
C	6	-0.7012002	-1.5037328	0.9784114
C	6	0.0466954	-2.5962676	1.6767293
H	1	0.7457341	-2.2019945	2.4212847
H	1	0.6253607	-3.2080483	0.9755823
H	1	-0.6661328	-3.2496960	2.1865172
C	6	1.1294478	0.0974972	-0.0699223
N	7	1.1680806	1.1917473	-0.7706509
O	8	2.4705308	1.6458672	-1.0568078
C	6	2.3462076	-0.6450003	0.4049565
H	1	3.2526653	-0.2477427	-0.0491260
H	1	2.2610682	-1.7085304	0.1669553
H	1	2.4375174	-0.5628602	1.4939823
C	6	2.3821808	2.8257731	-1.8589235
H	1	1.8818318	2.6209890	-2.8118639
H	1	3.4150725	3.1273586	-2.0432778
H	1	1.8534343	3.6256731	-1.3289804
O	8	-1.5297495	1.4058440	-0.8864367
H	1	-0.5966072	1.6984320	-1.0758074
C	6	-3.8491973	-0.1271563	0.1019346
H	1	-4.3561877	-0.0896454	1.0681966
H	1	-4.3132448	-0.8993898	-0.5165407
H	1	-3.9399353	0.8383663	-0.3950294

Table S24. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-3

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	22	0.10	**25**	717	8.59	**49**	1503	63.32
2	34	1.49	**26**	761	61.57	**50**	1506	7.25
3	75	5.05	**27**	893	9.55	**51**	1509	3.93
4	89	1.13	**28**	912	227.67	**52**	1511	15.30
5	115	2.52	**29**	1015	13.69	**53**	1515	29.04
6	122	0.22	**30**	1017	25.68	**54**	1523	20.72
7	156	5.66	**31**	1061	84.39	**55**	1529	26.72
8	170	3.88	**32**	1068	145.82	**56**	1533	32.97

9	214	0.26	**33**	1072	37.34	**57**	1554	172.19
10	225	3.12	**34**	1075	165.19	**58**	1632	461.76
11	245	0.97	**35**	1117	29.60	**59**	1649	152.86
12	265	12.90	**36**	1168	80.26	**60**	3054	113.30
13	311	18.64	**37**	1174	11.28	**61**	3068	26.96
14	331	4.08	**38**	1177	3.10	**62**	3081	9.36
15	351	0.30	**39**	1220	12.35	**63**	3094	68.74
16	376	2.06	**40**	1267	30.10	**64**	3122	52.39
17	391	1.78	**41**	1363	12.40	**65**	3126	13.34
18	452	40.97	**42**	1391	52.96	**66**	3144	7.21
19	543	1.05	**43**	1423	47.18	**67**	3151	25.58
20	593	32.78	**44**	1433	58.16	**68**	3165	15.66
21	598	0.28	**45**	1447	257.45	**69**	3173	25.43
22	642	21.72	**46**	1472	66.74	**70**	3195	12.92
23	665	12.34	**47**	1481	17.45	**71**	3203	3.38
24	679	74.44	**48**	1491	54.63	**72**	3264	754.22

Table S25. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-3$_{anion}$



PY-3$_{anion}$

B3LYP/6-31G* Energy (E): -626.848205 hartrees
Entropy Correction (Hv-TSv): 426.5004 kJ/mol
G° = E + "entropy correction": -393250.9542 kcal/mol

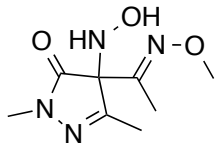
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.3346942	-0.2609653	0.0973249
C	6	-1.5699444	0.1997584	-0.4797535
N	7	-2.5424000	-0.5428637	0.1781073
N	7	-2.0303789	-1.3968058	1.1365803
C	6	-0.7117221	-1.2344043	1.0734404
C	6	0.1376431	-2.0141835	2.0315224
H	1	0.8874638	-1.3801724	2.5172620
H	1	0.6761595	-2.8363911	1.5443308
H	1	-0.5049207	-2.4499974	2.8026253
C	6	0.9983652	0.2001395	-0.2479022
N	7	1.1321513	1.4161998	-0.6979328
O	8	2.5035344	1.6685108	-1.0551299
C	6	2.1841575	-0.7288520	-0.1209954

H	1	2.7803008	-0.6888713	-1.0378414
H	1	1.8672733	-1.7566830	0.0508188
H	1	2.8492221	-0.4202722	0.6944233
C	6	2.5906919	2.9872791	-1.5840300
H	1	1.9744194	3.1015521	-2.4843166
H	1	3.6442279	3.1332571	-1.8364705
H	1	2.2808203	3.7375897	-0.8463813
O	8	-1.8386159	1.0385592	-1.3949349
C	6	-3.9689709	-0.4637713	-0.0374820
H	1	-4.1381616	0.2646574	-0.8321890
H	1	-4.4902361	-0.1389822	0.8701586
H	1	-4.3763856	-1.4342876	-0.3412344

Table S26. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-3_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	38	2.89	**24**	755	74.88	**47**	1494	21.72
2	70	9.18	**25**	765	29.76	**48**	1497	6.24
3	83	4.77	**26**	842	326.98	**49**	1508	3.22
4	96	1.68	**27**	910	4.07	**50**	1510	108.99
5	96	2.43	**28**	1001	20.77	**51**	1518	7.97
6	129	0.43	**29**	1018	33.93	**52**	1519	19.51
7	135	3.21	**30**	1051	20.32	**53**	1532	279.28
8	157	0.17	**31**	1053	12.51	**54**	1537	44.50
9	205	1.34	**32**	1065	263.30	**55**	1547	348.01
10	209	2.43	**33**	1072	7.02	**56**	1556	285.76
11	260	15.34	**34**	1089	91.99	**57**	1617	309.46
12	275	2.81	**35**	1166	15.03	**58**	3039	159.48
13	300	9.96	**36**	1175	1.76	**59**	3056	101.19
14	329	4.23	**37**	1176	2.12	**60**	3060	111.76
15	343	5.81	**38**	1214	4.04	**61**	3073	18.82
16	375	8.10	**39**	1266	50.70	**62**	3098	78.98
17	395	4.97	**40**	1378	76.21	**63**	3110	23.50
18	450	59.72	**41**	1399	78.77	**64**	3115	44.53
19	555	2.46	**42**	1414	11.11	**65**	3125	18.00
20	597	43.61	**43**	1433	12.25	**66**	3141	36.08
21	611	13.11	**44**	1453	40.44	**67**	3158	28.58
22	650	7.22	**45**	1474	65.64	**68**	3174	7.86
23	687	0.44	**46**	1483	350.71	**69**	3193	20.20

Table S27. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-3



HAPY-3

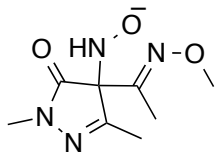
B3LYP/6-31G* Energy (E): -757.822294 hartrees
Entropy Correction (Hv-TSv): 506.6847 kJ/mol
G° = E + "entropy correction": -475419.2093 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.4111603	0.1041208	0.4470887
C	6	-1.5883892	0.9838121	-0.0358315
N	7	-2.5584909	0.1104262	-0.4213701
N	7	-2.1847825	-1.2360739	-0.3080871
C	6	-0.9897666	-1.2873857	0.1708483
O	8	-1.6580260	2.2153714	-0.0611850
C	6	-0.2925146	-2.5708186	0.4495690
H	1	-0.1118135	-2.6856895	1.5256516
H	1	0.6829038	-2.6071418	-0.0469285
H	1	-0.9049513	-3.4088517	0.1105242
C	6	0.8685781	0.3549938	-0.3493739
N	7	1.9506335	0.2648761	0.3321381
O	8	3.1025254	0.4809399	-0.4401179
C	6	0.7683663	0.6308088	-1.8213250
H	1	0.5529442	1.6921151	-1.9932739
H	1	-0.0489088	0.0559450	-2.2683874
H	1	1.7005015	0.3804069	-2.3289710
C	6	4.2587311	0.3077303	0.3892907
H	1	4.2579340	1.0236861	1.2171601
H	1	5.1114274	0.4964859	-0.2655344
H	1	4.3116646	-0.7120693	0.7833482
N	7	-0.3059603	0.2309312	1.9120659
H	1	0.4950551	-0.3408744	2.1928522
O	8	0.1331940	1.5685075	2.2559190
H	1	-0.6539719	1.9339646	2.6961316
C	6	-3.8753482	0.4365458	-0.9385315
H	1	-3.9564017	1.5227103	-0.9778217
H	1	-4.6524413	0.0331807	-0.2843899
H	1	-4.0015319	0.0213463	-1.9414587

Table S28. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-3

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	32	0.43	**28**	690	3.91	**55**	1484	5.55
2	55	1.01	**29**	755	35.08	**56**	1493	10.18
3	75	2.16	**30**	763	8.43	**57**	1497	21.20
4	89	4.99	**31**	860	87.93	**58**	1501	2.85
5	94	1.66	**32**	896	147.81	**59**	1505	7.99
6	96	2.61	**33**	930	68.32	**60**	1514	18.18
7	109	0.98	**34**	961	27.47	**61**	1514	16.64
8	131	3.03	**35**	1006	7.31	**62**	1516	1.66
9	147	7.03	**36**	1025	17.00	**63**	1532	28.44
10	162	4.20	**37**	1031	62.72	**64**	1541	14.90
11	165	4.78	**38**	1045	24.87	**65**	1676	140.74
12	171	2.10	**39**	1056	324.32	**66**	1687	492.57
13	207	7.90	**40**	1067	59.43	**67**	1771	20.29
14	246	10.64	**41**	1082	14.25	**68**	3064	3.51
15	267	35.38	**42**	1094	14.86	**69**	3064	108.06
16	299	10.54	**43**	1177	2.90	**70**	3072	5.21
17	311	5.07	**44**	1181	2.21	**71**	3089	60.87
18	325	2.02	**45**	1211	15.68	**72**	3122	6.79
19	345	106.84	**46**	1227	33.61	**73**	3131	8.66
20	361	8.81	**47**	1253	101.70	**74**	3137	48.09
21	394	6.47	**48**	1286	8.41	**75**	3159	16.07
22	421	26.24	**49**	1306	78.29	**76**	3169	8.34
23	496	28.87	**50**	1381	65.60	**77**	3178	23.83
24	510	5.90	**51**	1424	86.86	**78**	3179	2.32
25	576	20.50	**52**	1427	54.09	**79**	3198	2.37
26	598	36.28	**53**	1444	37.42	**80**	3444	39.50
27	628	10.21	**54**	1472	19.27	**81**	3712	95.73

Table S29. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-3_{anion}



HAPY-3_{anion}

B3LYP/6-31G* Energy (E): -757.331535 hartrees
Entropy Correction (Hv-TSv): 464.0413 kJ/mol
G° = E + "entropy correction": Not a ground state structure; HNO is dissociated

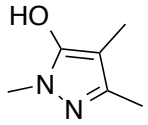
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.0872656	0.0684498	0.3658208
C	6	1.2979246	0.8315112	0.6024001
N	7	2.2709033	-0.1340585	0.8091683
N	7	1.7938754	-1.4257887	0.6464609
C	6	0.4940703	-1.3033009	0.4319634
O	8	1.5440824	2.0742055	0.6299941
C	6	-0.3294275	-2.5357479	0.2448249
H	1	-0.8626694	-2.5103062	-0.7120475
H	1	-1.0951830	-2.6341128	1.0212262
H	1	0.3249818	-3.4125133	0.2697758
C	6	-1.2538124	0.6009183	0.2050941
N	7	-2.2474037	-0.2369475	0.2378647
O	8	-3.4847387	0.4384561	0.0169207
C	6	-1.4615905	2.0784945	-0.0155002
H	1	-1.8421149	2.2501671	-1.0297131
H	1	-0.5288079	2.6242506	0.1236331
H	1	-2.2265246	2.4587568	0.6691172
C	6	-4.5355779	-0.5268662	0.0480426
H	1	-4.4116873	-1.2760519	-0.7425309
H	1	-5.4553654	0.0384819	-0.1200850
H	1	-4.5839222	-1.0334565	1.0190078
N	7	0.9485974	0.2827475	-2.1685213
H	1	1.2896092	1.2103046	-1.7895147
O	8	1.9250200	-0.4569775	-2.3279562
C	6	3.6978831	0.1061294	0.7552683
H	1	3.8761549	1.1392343	1.0567862
H	1	4.0857019	-0.0473567	-0.2594004
H	1	4.2126989	-0.5720706	1.4397845

Table S30. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-3_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	29	0.25	**27**	616	73.08	**53**	1490	576.63
2	38	0.42	**28**	665	36.57	**54**	1492	24.13
3	52	0.35	**29**	682	15.63	**55**	1499	3.12
4	70	3.26	**30**	755	20.87	**56**	1502	22.45
5	86	7.65	**31**	766	15.27	**57**	1516	37.33
6	93	12.20	**32**	870	353.72	**58**	1525	107.40
7	111	14.29	**33**	945	30.05	**59**	1534	36.54
8	121	4.40	**34**	1007	15.24	**60**	1535	21.37

9	126	14.51	**35**	1023	16.04	**61**	1539	14.14
10	152	7.67	**36**	1053	238.06	**62**	1560	92.75
11	155	1.58	**37**	1055	137.41	**63**	1571	528.20
12	164	1.70	**38**	1069	4.81	**64**	1581	98.10
13	207	0.17	**39**	1074	3.10	**65**	1627	185.42
14	227	1.71	**40**	1101	102.31	**66**	2976	35.41
15	246	38.60	**41**	1153	6.63	**67**	3046	159.94
16	251	15.09	**42**	1172	3.49	**68**	3057	117.23
17	269	16.85	**43**	1185	53.54	**69**	3063	38.81
18	310	6.36	**44**	1219	4.99	**70**	3065	22.68
19	331	30.82	**45**	1267	29.93	**71**	3109	69.76
20	357	6.31	**46**	1351	74.95	**72**	3120	18.55
21	383	1.90	**47**	1397	89.78	**73**	3121	22.07
22	396	0.51	**48**	1424	26.41	**74**	3137	39.41
23	450	27.37	**49**	1438	28.86	**75**	3143	37.69
24	561	2.89	**50**	1452	62.57	**76**	3165	28.54
25	581	79.57	**51**	1461	603.10	**77**	3181	3.45
26	600	26.89	**52**	1474	52.39	**78**	3185	8.56

Table S31. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-4



PY-4

B3LYP/6-31G* Energy (E): -419.379039 hartrees
Entropy Correction (Hv-TSv): 326.8122 kJ/mol
G° = E + "entropy correction": -263086.0114 kcal/mol

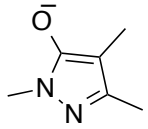
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.7239106	0.3076125	0.1668687
C	6	-0.4797297	0.9893448	0.0611517
N	7	-1.4518539	0.1006997	-0.2659170
N	7	-0.9444521	-1.1698650	-0.3642765
C	6	0.3630098	-1.0341897	-0.1147889
C	6	2.0774420	0.8678795	0.4864347
H	1	2.0064582	1.7868117	1.0807486
H	1	2.6628199	1.1043045	-0.4117460
H	1	2.6669962	0.1594699	1.0786204
C	6	1.2681189	-2.2242216	-0.1518605

H	1	1.7798839	-2.3719851	0.8071372
H	1	2.0468256	-2.1164824	-0.9165081
H	1	0.6943423	-3.1281054	-0.3739173
O	8	-0.8208944	2.2996057	0.2353313
N	7	-0.0007461	2.8220369	0.3208369
C	6	-2.8777055	0.3539588	-0.3810899
H	1	-3.0322903	1.3816949	-0.7114779
H	1	-3.3901363	0.2037703	0.5747163
H	1	-3.2919992	-0.3323399	-1.1202638

Table S32. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-4

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	30	0.12	**18**	857	10.77	**35**	1510	32.30
2	66	0.39	**19**	1004	62.18	**36**	1516	8.48
3	115	0.75	**20**	1015	5.22	**37**	1524	1.77
4	119	15.42	**21**	1063	4.76	**38**	1529	15.73
5	168	13.50	**22**	1076	6.54	**39**	1535	23.22
6	203	105.04	**23**	1087	10.50	**40**	1567	122.04
7	229	4.67	**24**	1121	195.15	**41**	1632	156.41
8	272	10.59	**25**	1193	14.57	**42**	3044	62.38
9	284	20.48	**26**	1225	62.64	**43**	3052	44.96
10	291	10.71	**27**	1285	28.68	**44**	3082	74.81
11	371	0.39	**28**	1311	75.92	**45**	3096	36.96
12	556	12.39	**29**	1415	98.14	**46**	3104	17.12
13	569	12.08	**30**	1429	121.29	**47**	3116	32.00
14	603	5.57	**31**	1449	4.10	**48**	3145	24.36
15	650	1.56	**32**	1472	36.42	**49**	3162	15.88
16	693	4.09	**33**	1500	33.51	**50**	3198	5.90
17	730	35.49	**34**	1509	32.28	**51**	3692	220.42

Table S33. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-4_{anion}



PY-4_{anion}

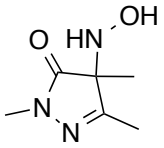
B3LYP/6-31G* Energy (E): -418.909769 hartrees
Entropy Correction (Hv-TSv): 295.4126 kJ/mol
G° = E + "entropy correction": -262799.0449 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.6948843	0.4201498	0.3085493
C	6	-0.5340356	1.1247330	0.3729937
N	7	-1.4609388	0.2467705	-0.1885770
N	7	-0.9021361	-0.9531029	-0.5911495
C	6	0.3964831	-0.8238997	-0.2842223
C	6	2.0146416	0.9412946	0.7857945
H	1	2.7450431	1.0826949	-0.0254231
H	1	2.4948658	0.2822624	1.5236082
H	1	1.8706660	1.9177436	1.2637127
C	6	1.3446436	-1.9423536	-0.5820399
H	1	1.8475834	-2.3007844	0.3257564
H	1	2.1345081	-1.6316254	-1.2786021
H	1	0.8043331	-2.7826340	-1.0294037
O	8	-0.8380649	2.2909054	0.8184417
C	6	-2.8782399	0.4783549	-0.3305169
H	1	-3.1917360	0.3955491	-1.3775224
H	1	-3.0777956	1.4898056	0.0286376
H	1	-3.4647051	-0.2358636	0.2599628

Table S34. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-4_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	58	2.80	**17**	884	7.23	**33**	1509	185.01
2	74	0.12	**18**	994	39.45	**34**	1521	20.79
3	119	0.48	**19**	1016	12.97	**35**	1521	5.53
4	129	10.05	**20**	1055	29.31	**36**	1523	24.16
5	165	0.91	**21**	1060	3.22	**37**	1538	141.29
6	203	10.83	**22**	1080	1.17	**38**	1556	131.94
7	257	0.42	**23**	1155	86.10	**39**	1585	315.63
8	260	16.92	**24**	1191	1.87	**40**	3013	158.50
9	296	9.46	**25**	1259	72.87	**41**	3044	97.53
10	367	4.57	**26**	1308	79.07	**42**	3047	72.14
11	569	39.99	**27**	1388	96.05	**43**	3053	130.48
12	592	12.01	**28**	1419	2.92	**44**	3089	31.87
13	612	5.33	**29**	1429	24.21	**45**	3098	42.31
14	650	0.93	**30**	1458	77.28	**46**	3104	53.41
15	738	10.41	**31**	1480	209.44	**47**	3134	34.36
16	761	33.18	**32**	1505	4.77	**48**	3167	10.07

Table S35. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-4



HAPY-4

B3LYP/6-31G* Energy (E): -549.89706 hartrees
Entropy Correction (Hv-TSv): 376.6585 kJ/mol
G° = E + "entropy correction": -344975.3307 kcal/mol

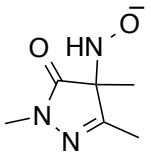
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.6674974	-0.0312016	0.2081174
C	6	-0.5732141	0.8736346	0.1660289
N	7	-1.6275977	0.0417863	-0.0540181
N	7	-1.2521411	-1.3016038	-0.2243723
C	6	0.0305132	-1.3773154	-0.1035355
O	8	-0.6244446	2.1023471	0.3060451
C	6	1.3235318	-0.0041299	1.5958698
H	1	1.6603111	1.0093295	1.8223900
H	1	2.1868379	-0.6764463	1.6180184
H	1	0.6187408	-0.3236712	2.3701152
N	7	1.5557045	0.3364823	-0.9185137
H	1	2.3018885	-0.3652952	-0.9494583
O	8	2.2909875	1.5422003	-0.5842923
H	1	1.8345244	2.2194901	-1.1112639
C	6	0.7597784	-2.6674931	-0.2355038
H	1	1.3401742	-2.8860519	0.6681470
H	1	1.4646004	-2.6380902	-1.0757288
H	1	0.0514905	-3.4807230	-0.4081954
C	6	-3.0238089	0.4081661	-0.1969990
H	1	-3.6343621	-0.1292852	0.5327235
H	1	-3.3819217	0.1733043	-1.2030979
H	1	-3.1037844	1.4811849	-0.0224786

Table S36. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-4

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	62	5.71	**21**	760	22.89	**41**	1492	18.15
2	88	11.70	**22**	847	43.49	**42**	1495	13.76
3	97	15.63	**23**	891	19.29	**43**	1509	9.81

4	130	5.37	**24**	939	25.60	**44**	1513	11.24
5	139	12.94	**25**	965	31.05	**45**	1521	1.88
6	168	0.28	**26**	1024	47.74	**46**	1532	8.00
7	206	69.21	**27**	1033	3.95	**47**	1543	18.21
8	214	24.00	**28**	1052	29.65	**48**	1669	210.81
9	248	4.68	**29**	1067	70.06	**49**	1677	448.01
10	256	6.15	**30**	1138	3.80	**50**	3062	10.19
11	270	26.74	**31**	1158	29.01	**51**	3075	17.46
12	311	14.92	**32**	1179	2.57	**52**	3087	61.46
13	328	13.61	**33**	1248	113.47	**53**	3119	7.11
14	357	4.13	**34**	1259	24.02	**54**	3144	21.22
15	409	11.21	**35**	1335	51.97	**55**	3156	18.41
16	575	20.86	**36**	1372	51.17	**56**	3165	13.26
17	585	40.67	**37**	1423	31.30	**57**	3166	10.87
18	610	6.67	**38**	1427	80.26	**58**	3196	3.16
19	622	3.76	**39**	1447	60.59	**59**	3433	19.99
20	742	14.36	**40**	1473	18.53	**60**	3722	104.49

Table S37. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-4$_{anion}$



HAPY-4$_{anion}$

B3LYP/6-31G* Energy (E): -549.389029 hartrees
Entropy Correction (Hv-TSv): 341.0871 kJ/mol
G° = E + "entropy correction": -344665.0384 kcal/mol

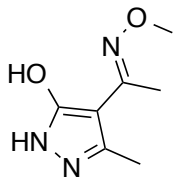
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.5432454	-0.5334428	-0.1322298
C	6	-0.9702601	0.9245379	-0.0008716
N	7	0.1330444	1.5965676	0.4273200
N	7	1.2815950	0.7911809	0.4877507
C	6	0.9364003	-0.4052621	0.1425796
C	6	1.9247615	-1.5166368	0.1202060
H	1	1.6515057	-2.2897245	0.8499816
H	1	2.9192178	-1.1352786	0.3647358
H	1	1.9565019	-1.9975274	-0.8639804
O	8	-2.0764501	1.4342318	-0.2325479
C	6	-0.9161180	-1.1262694	-1.4855654

H	1	-1.9989014	-1.2813192	-1.4884047
H	1	-0.4254366	-2.0958613	-1.6238354
H	1	-0.6334576	-0.4761163	-2.3209763
N	7	-1.1508515	-1.3030395	1.0646519
H	1	-0.6697767	-2.2196969	0.9409594
O	8	-2.5348735	-1.5291215	0.8861759
C	6	0.2612520	3.0212057	0.6709507
H	1	0.6104355	3.2039516	1.6910040
H	1	-0.7237901	3.4685721	0.5351626
H	1	0.9684468	3.4690483	-0.0330666

Table S38. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-4_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	64	11.66	**20**	752	18.12	**39**	1471	44.92
2	79	0.35	**21**	803	29.37	**40**	1493	10.98
3	113	14.69	**22**	862	11.13	**41**	1496	22.44
4	123	8.82	**23**	943	87.51	**42**	1500	3.16
5	144	7.52	**24**	968	36.52	**43**	1512	9.09
6	169	17.18	**25**	1022	13.81	**44**	1529	4.51
7	177	1.22	**26**	1036	18.10	**45**	1540	15.22
8	247	10.61	**27**	1049	7.19	**46**	1661	308.37
9	253	5.87	**28**	1066	36.65	**47**	1674	385.58
10	268	18.82	**29**	1117	22.19	**48**	3057	13.43
11	296	5.49	**30**	1164	24.59	**49**	3059	46.02
12	312	10.33	**31**	1169	8.31	**50**	3082	81.05
13	357	2.93	**32**	1248	87.60	**51**	3103	106.21
14	403	14.07	**33**	1270	17.28	**52**	3115	12.91
15	559	80.55	**34**	1344	73.82	**53**	3130	23.45
16	580	23.97	**35**	1405	14.88	**54**	3136	29.82
17	587	25.07	**36**	1419	116.74	**55**	3150	21.38
18	608	2.36	**37**	1432	7.13	**56**	3164	12.21
19	686	74.56	**38**	1451	15.32	**57**	3191	4.53

Table S39. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-5



PY-5

B3LYP/6-31G* Energy (E): -588.01246 hartrees
Entropy Correction (Hv-TSv): 391.2127 kJ/mol
G° = E + "entropy correction": -368889.6087 kcal/mol

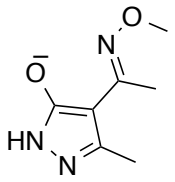
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.7796140	-0.3777535	0.2542232
C	6	-1.9453394	0.2748677	-0.1660934
N	7	-2.9923681	-0.4228846	0.3037214
N	7	-2.6007109	-1.5228842	1.0285410
C	6	-1.2689904	-1.4983019	0.9991359
C	6	-0.5179078	-2.5821689	1.7071310
H	1	0.1771001	-2.1794777	2.4508123
H	1	0.0651319	-3.1963464	1.0118701
H	1	-1.2293269	-3.2349895	2.2194956
C	6	0.5625838	0.0947998	-0.0654699
N	7	0.6005916	1.1785570	-0.7819402
O	8	1.9024583	1.6315985	-1.0718533
C	6	1.7789790	-0.6378384	0.4248813
H	1	2.6880788	-0.2318612	-0.0157719
H	1	1.7070153	-1.7017436	0.1834914
H	1	1.8532190	-0.5578960	1.5152806
C	6	1.8123587	2.8012924	-1.8889049
H	1	1.3134307	2.5834523	-2.8397091
H	1	2.8447020	3.1032234	-2.0761727
H	1	1.2811750	3.6065311	-1.3696061
H	1	-3.9754845	-0.2111343	0.1749576
O	8	-2.1036530	1.3941550	-0.8999366
H	1	-1.1734291	1.6868031	-1.0980833

Table S40. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-5

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	33	1.51	**22**	725	5.67	**43**	1492	35.93
2	73	3.95	**23**	755	36.43	**44**	1500	21.15

3	107	0.52	**24**	785	16.05	**45**	1507	7.11
4	123	2.06	**25**	909	216.01	**46**	1508	1.77
5	131	0.92	**26**	1002	24.90	**47**	1523	50.13
6	171	3.39	**27**	1005	63.80	**48**	1525	54.39
7	215	0.07	**28**	1060	163.27	**49**	1533	37.65
8	223	0.04	**29**	1066	223.66	**50**	1550	131.23
9	249	0.79	**30**	1073	1.80	**51**	1615	435.28
10	296	21.67	**31**	1086	19.87	**52**	1651	167.08
11	328	7.62	**32**	1108	23.57	**53**	3054	113.57
12	349	0.89	**33**	1143	17.99	**54**	3068	23.25
13	359	4.65	**34**	1179	2.41	**55**	3080	9.26
14	408	3.20	**35**	1220	9.79	**56**	3122	52.40
15	446	41.41	**36**	1255	97.67	**57**	3126	13.45
16	469	116.89	**37**	1332	8.36	**58**	3143	7.08
17	543	0.05	**38**	1408	16.76	**59**	3151	25.27
18	562	6.51	**39**	1422	69.35	**60**	3173	24.30
19	598	29.48	**40**	1443	303.53	**61**	3196	12.22
20	651	87.10	**41**	1444	38.59	**62**	3283	690.65
21	685	20.61	**42**	1484	22.88	**63**	3602	262.74

Table S41. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-5$_{anion}$



PY-5$_{anion}$

B3LYP/6-31G* Energy (E): -587.534096 hartrees
Entropy Correction (Hv-TSv): 355.5968 kJ/mol
G° = E + "entropy correction": -368597.9434 kcal/mol

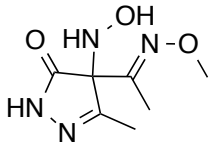
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.9483545	-0.3252580	0.0668253
C	6	-2.1846271	0.1432293	-0.5021595
N	7	-3.1384302	-0.6311003	0.1334290
N	7	-2.6370704	-1.4981195	1.0830477
C	6	-1.3204277	-1.3236420	1.0236699

C	6	-0.4654010	-2.1160239	1.9658167
H	1	0.2809817	-1.4861849	2.4619818
H	1	0.0770980	-2.9264504	1.4635803
H	1	-1.1049322	-2.5689024	2.7294542
C	6	0.3836614	0.1477886	-0.2655238
N	7	0.5156371	1.3758495	-0.6825143
O	8	1.8876679	1.6383713	-1.0335552
C	6	1.5703995	-0.7831263	-0.1645514
H	1	2.1621629	-0.7238259	-1.0832846
H	1	1.2539988	-1.8141342	-0.0125523
H	1	2.2395566	-0.4913326	0.6536921
C	6	1.9763834	2.9738319	-1.5184447
H	1	1.3645221	3.1178585	-2.4176107
H	1	3.0310281	3.1285861	-1.7611115
H	1	1.6628257	3.6998679	-0.7582788
H	1	-4.1403707	-0.5409830	0.0115610
O	8	-2.4663093	1.0037002	-1.3934711

Table S42. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-5_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	41	3.17	**21**	737	21.79	**41**	1483	257.20
2	86	7.80	**22**	773	25.41	**42**	1492	5.80
3	99	0.09	**23**	806	32.93	**43**	1498	6.04
4	103	4.21	**24**	847	323.79	**44**	1509	28.56
5	133	0.56	**25**	993	110.63	**45**	1510	61.13
6	148	8.07	**26**	1005	3.48	**46**	1519	20.35
7	182	3.67	**27**	1052	38.09	**47**	1539	36.47
8	203	0.51	**28**	1055	157.99	**48**	1547	504.23
9	239	25.51	**29**	1071	0.92	**49**	1552	392.07
10	274	3.42	**30**	1082	60.04	**50**	1618	333.90
11	287	2.61	**31**	1100	114.19	**51**	3039	159.00
12	329	7.24	**32**	1117	0.90	**52**	3056	49.27
13	363	13.12	**33**	1186	2.00	**53**	3073	19.85
14	406	12.73	**34**	1209	7.52	**54**	3098	79.21
15	433	63.34	**35**	1246	4.95	**55**	3109	22.57
16	455	74.50	**36**	1353	24.10	**56**	3125	18.20
17	552	2.95	**37**	1396	97.12	**57**	3141	35.87
18	590	24.77	**38**	1416	5.53	**58**	3157	28.06
19	622	13.95	**39**	1437	42.64	**59**	3194	20.16
20	669	19.37	**40**	1478	171.09	**60**	3598	91.18

Table S43. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-5



HAPY-5

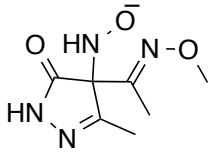
B3LYP/6-31G* Energy (E): -718.508674 hartrees
Entropy Correction (Hv-TSv): 436.148 kJ/mol
G° = E + "entropy correction": -450766.4176 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.5488549	-0.0087294	0.2966453
C	6	-1.7267288	0.8757830	-0.1846993
N	7	-2.6779534	-0.0082044	-0.5827926
N	7	-2.3182464	-1.3525688	-0.4735570
C	6	-1.1275857	-1.4021806	0.0163923
O	8	-1.8059484	2.1045011	-0.2029808
C	6	-0.4319475	-2.6849130	0.3024980
H	1	-0.2620499	-2.7999768	1.3802743
H	1	0.5480581	-2.7214621	-0.1847925
H	1	-1.0404730	-3.5235534	-0.0422009
C	6	0.7253335	0.2418650	-0.5083225
N	7	1.8124673	0.1579845	0.1660064
O	8	2.9570116	0.3746046	-0.6178078
C	6	0.6149579	0.5107946	-1.9809948
H	1	0.4563406	1.5811067	-2.1591741
H	1	-0.2388798	-0.0218305	-2.4111505
H	1	1.5247947	0.2074508	-2.5007872
C	6	4.1211686	0.2044737	0.2004180
H	1	4.1264605	0.9203995	1.0283668
H	1	4.9672743	0.3954420	-0.4623339
H	1	4.1810197	-0.8151659	0.5942052
N	7	-0.4365070	0.1165113	1.7602777
H	1	0.3653749	-0.4557015	2.0371990
O	8	0.0025082	1.4545650	2.1033947
H	1	-0.7771808	1.8117802	2.5632944
H	1	-3.5892628	0.2264404	-0.9620430

Table S44. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-5

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	22	0.40	**25**	644	10.62	**49**	1440	3.70
2	69	0.50	**26**	751	16.51	**50**	1482	7.26
3	84	6.70	**27**	763	29.93	**51**	1494	10.68
4	94	2.24	**28**	771	28.47	**52**	1498	17.91
5	107	1.65	**29**	875	73.80	**53**	1503	1.40
6	117	1.96	**30**	898	127.44	**54**	1504	9.41
7	146	5.84	**31**	929	99.14	**55**	1514	8.33
8	156	1.31	**32**	997	15.51	**56**	1515	17.12
9	161	1.45	**33**	1012	4.43	**57**	1532	28.05
10	169	2.81	**34**	1029	20.34	**58**	1683	40.40
11	195	0.05	**35**	1047	32.07	**59**	1699	661.42
12	251	15.62	**36**	1056	367.58	**60**	1768	19.84
13	277	10.47	**37**	1079	17.17	**61**	3063	82.20
14	309	6.08	**38**	1082	28.89	**62**	3064	26.50
15	319	16.94	**39**	1103	30.23	**63**	3069	2.86
16	342	62.99	**40**	1178	2.53	**64**	3121	7.41
17	353	63.09	**41**	1195	72.07	**65**	3130	8.65
18	407	6.58	**42**	1210	11.83	**66**	3136	48.34
19	415	7.01	**43**	1284	18.18	**67**	3168	8.49
20	468	83.46	**44**	1297	70.56	**68**	3175	9.05
21	512	12.01	**45**	1306	46.84	**69**	3177	17.27
22	518	95.25	**46**	1380	50.74	**70**	3445	38.86
23	584	23.42	**47**	1401	82.80	**71**	3596	211.53
24	600	33.21	**48**	1427	22.04	**72**	3712	96.51

Table S45. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-5_{anion}



HAPY-5_{anion}

B3LYP/6-31G* Energy (E): -718.017094 hartrees
Entropy Correction (Hv-TSv): 390.2085 kJ/mol
G° = E + "entropy correction": Not a ground state structure; HNO is dissociated

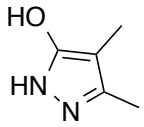
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.8897996	-0.0602097	-0.3755040
C	6	-2.1403720	0.4651086	-0.8926977
N	7	-3.0637703	-0.4846269	-0.5049160
N	7	-2.5341821	-1.5414715	0.2082488
C	6	-1.2334508	-1.2994091	0.2584175
O	8	-2.4449829	1.5052057	-1.5492058
C	6	-0.3454993	-2.2635734	0.9760941
H	1	0.2079265	-1.7668265	1.7814772
H	1	0.4048671	-2.6974744	0.3078198
H	1	-0.9566355	-3.0641779	1.4038529
C	6	0.4293010	0.5143274	-0.5686257
N	7	1.4619714	-0.2287839	-0.3027021
O	8	2.6739920	0.5051555	-0.4851190
C	6	0.5677570	1.9433334	-1.0322508
H	1	0.9590270	2.5572568	-0.2119993
H	1	-0.3948145	2.3366768	-1.3580932
H	1	1.2964940	2.0101347	-1.8460412
C	6	3.7715652	-0.3612935	-0.2023398
H	1	3.7404422	-0.7198888	0.8332440
H	1	4.6678317	0.2444917	-0.3563794
H	1	3.7865801	-1.2227483	-0.8803739
N	7	-1.5177289	1.3686555	1.8136065
H	1	-2.0739699	1.9453067	1.1192516
O	8	-2.3087944	0.7394192	2.5201555
H	1	-4.0637551	-0.4245880	-0.6559201

Table S46. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-5_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	-43	9.32	**24**	592	60.63	**47**	1477	44.06
2	-23	5.04	**25**	612	46.13	**48**	1492	422.03
3	37	0.02	**26**	673	43.84	**49**	1494	326.15
4	69	7.21	**27**	751	4.92	**50**	1499	9.72
5	82	6.97	**28**	758	26.54	**51**	1505	9.83
6	85	9.82	**29**	798	48.47	**52**	1521	122.49
7	102	5.76	**30**	873	321.76	**53**	1532	26.68
8	116	2.85	**31**	994	75.95	**54**	1534	28.44
9	140	13.05	**32**	1020	7.15	**55**	1559	137.63
10	147	6.69	**33**	1055	315.63	**56**	1570	66.82

11	191	13.72	**34**	1070	5.24	**57**	1579	581.46
12	221	26.61	**35**	1077	3.01	**58**	1630	193.38
13	226	33.74	**36**	1092	85.53	**59**	2955	46.71
14	251	14.40	**37**	1115	3.85	**60**	3046	154.17
15	271	24.63	**38**	1117	51.06	**61**	3063	41.50
16	301	2.37	**39**	1174	2.32	**62**	3066	24.39
17	319	7.10	**40**	1206	4.41	**63**	3108	70.93
18	358	23.17	**41**	1256	28.29	**64**	3121	23.51
19	400	4.16	**42**	1340	54.49	**65**	3123	21.35
20	443	57.34	**43**	1391	78.61	**66**	3144	35.69
21	457	38.81	**44**	1422	34.21	**67**	3163	28.67
22	499	46.78	**45**	1442	65.03	**68**	3179	2.18
23	561	6.17	**46**	1468	506.54	**69**	3604	125.20

Table S47. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-6



PY-6

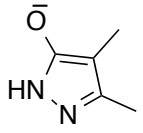
B3LYP/6-31G* Energy (E): -380.066128 hartrees
Entropy Correction (Hv-TSv): 257.5155 kJ/mol
G° = E + "entropy correction": -238433.3682 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.0012941	-0.6332998	0.0008509
C	6	-1.1319720	0.1690625	-0.0008776
N	7	-0.7232614	1.4601851	-0.0007344
N	7	0.6407509	1.5700133	-0.0000300
C	6	1.0674297	0.3027823	-0.0021440
H	1	-1.3124565	2.2840479	-0.0019890
C	6	2.5304030	-0.0053629	-0.0012923
H	1	2.8175404	-0.5974393	0.8763593
H	1	3.1115569	0.9207396	0.0081250
H	1	2.8216184	-0.5834513	-0.8865503
C	6	0.0730538	-2.1305192	0.0015701
H	1	-0.8785170	-2.5844753	0.3018988
H	1	0.8270675	-2.4916253	0.7101548
H	1	0.3309510	-2.5403349	-0.9833823
O	8	-2.4716296	-0.0968927	0.0107040
H	1	-2.5928740	-1.0596865	-0.0935414

Table S48. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-6

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	107	0.54	**15**	770	5.10	**29**	1508	7.09
2	149	3.63	**16**	961	28.59	**30**	1514	17.49
3	172	20.86	**17**	1006	63.24	**31**	1525	4.11
4	195	120.92	**18**	1065	1.53	**32**	1530	3.01
5	233	2.14	**19**	1085	2.57	**33**	1554	192.56
6	276	23.17	**20**	1109	147.03	**34**	1633	158.23
7	289	6.36	**21**	1145	18.46	**35**	3046	55.26
8	332	28.88	**22**	1156	98.10	**36**	3055	38.10
9	429	66.66	**23**	1222	40.20	**37**	3099	39.21
10	506	25.80	**24**	1363	93.42	**38**	3105	14.06
11	568	15.16	**25**	1415	117.86	**39**	3115	37.48
12	672	9.45	**26**	1440	34.55	**40**	3145	24.02
13	697	5.55	**27**	1453	3.72	**41**	3610	244.42
14	708	26.22	**28**	1499	20.40	**42**	3693	201.57

Table S49. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-6_{anion}



PY-6_{anion}

B3LYP/6-31G* Energy (E): -379.595625 hartrees
Entropy Correction (Hv-TSv): 223.0236 kJ/mol
G° = E + "entropy correction": -238146.3671 kcal/mol

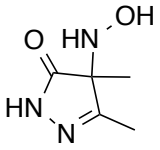
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.5055753	-0.2929715	0.0094368
C	6	-1.6958443	0.4786730	0.0310258
N	7	-1.2333856	1.7879491	0.0146000
N	7	0.1432923	1.9066690	-0.0096111
C	6	0.5606684	0.6332797	-0.0140311
H	1	-1.8115821	2.6192789	0.0377488
C	6	2.0259655	0.3327436	-0.0418937
H	1	2.3369844	-0.2536002	0.8327180
H	1	2.5998043	1.2649098	-0.0509318
H	1	2.3047904	-0.2504693	-0.9293832

C	6	-0.4480373	-1.7892726	0.0139251
H	1	-1.4671978	-2.1918933	0.0546738
H	1	0.0993244	-2.1976523	0.8763337
H	1	0.0316277	-2.2078543	-0.8834214
O	8	-2.9408349	0.1602103	0.0588103

Table S-50. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-6_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	22	1.49	**14**	792	9.27	**27**	1506	4.77
2	98	14.75	**15**	930	27.34	**28**	1510	158.45
3	116	19.85	**16**	988	99.94	**29**	1521	5.87
4	154	0.59	**17**	1059	0.02	**30**	1522	34.16
5	213	29.17	**18**	1079	1.07	**31**	1538	344.05
6	256	5.18	**19**	1100	39.91	**32**	1589	342.40
7	282	0.88	**20**	1151	22.90	**33**	3016	138.65
8	431	63.46	**21**	1182	59.35	**34**	3044	67.14
9	540	20.70	**22**	1285	36.81	**35**	3048	68.66
10	584	39.29	**23**	1382	52.25	**36**	3090	31.54
11	670	15.41	**24**	1414	41.68	**37**	3099	42.34
12	712	4.09	**25**	1424	13.72	**38**	3134	33.88
13	750	4.88	**26**	1483	201.85	**39**	3598	78.35

Table S-51. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-6



HAPY-6

B3LYP/6-31G* Energy (E): -510.583141 hartrees
Entropy Correction (Hv-TSv): 307.2283 kJ/mol
G° = E + "entropy correction": -320322.0869 kcal/mol

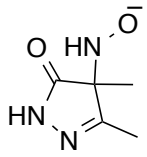
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.1231117	-0.2841939	-0.2004076
C	6	-0.5695334	1.1804075	-0.0493404
N	7	0.5740192	1.8688917	0.2043141
N	7	1.7211724	1.0733400	0.3064389

C	6	1.3639491	-0.1497289	0.1014574
H	1	0.6520336	2.8642383	0.3828779
C	6	2.3389161	-1.2732784	0.1361728
H	1	2.0866292	-1.9919373	0.9259469
H	1	3.3438520	-0.8908740	0.3276289
H	1	2.3410928	-1.8205552	-0.8132553
O	8	-1.7099599	1.6472889	-0.1405069
C	6	-0.3857942	-0.7933624	-1.6248209
H	1	-1.4567545	-0.7631111	-1.8342776
H	1	-0.0357026	-1.8250926	-1.7289102
H	1	0.1360561	-0.1775020	-2.3641289
N	7	-0.7478580	-1.0779252	0.8818552
H	1	-0.3211791	-2.0090747	0.8535154
O	8	-2.1281272	-1.3655358	0.5397668
H	1	-2.6192221	-0.7693255	1.1298996

Table S-52. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-6

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	72	1.11	**18**	762	20.41	**35**	1445	3.26
2	107	11.46	**19**	772	25.94	**36**	1494	15.81
3	146	4.39	**20**	848	43.93	**37**	1496	12.60
4	167	0.16	**21**	889	27.51	**38**	1505	8.08
5	211	11.25	**22**	951	45.77	**39**	1517	6.96
6	222	3.03	**23**	995	11.99	**40**	1528	6.63
7	248	10.05	**24**	1033	46.22	**41**	1678	33.73
8	259	69.69	**25**	1055	14.43	**42**	1687	694.59
9	297	16.35	**26**	1092	48.60	**43**	3062	9.32
10	328	46.33	**27**	1130	9.10	**44**	3075	15.38
11	345	8.86	**28**	1160	39.22	**45**	3117	7.78
12	425	5.85	**29**	1216	114.02	**46**	3145	20.50
13	496	146.70	**30**	1308	10.75	**47**	3164	22.65
14	561	31.22	**31**	1333	52.49	**48**	3164	2.31
15	582	27.74	**32**	1371	47.68	**49**	3432	19.67
16	629	12.17	**33**	1402	74.86	**50**	3596	180.30
17	719	2.54	**34**	1433	11.92	**51**	3723	106.80

Table S-53. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-6$_{anion}$



HAPY-6$_{anion}$

B3LYP/6-31G* Energy (E): -510.074697 hartrees
Entropy Correction (Hv-TSv): 271.0122 kJ/mol
G° = E + "entropy correction": -320011.6896 kcal/mol

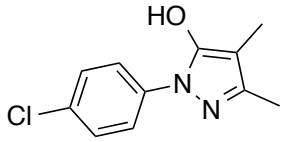
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	-0.4927162	0.0571893	-0.0258868
C	6	-0.9209071	1.5173689	0.0957674
N	7	0.1644597	2.1619140	0.5993900
N	7	1.3110047	1.3644929	0.6975040
C	6	0.9744477	0.1744040	0.3220017
H	1	0.2596872	3.1648622	0.7270012
C	6	1.9563979	-0.9428053	0.3309540
H	1	1.6436007	-1.7258667	1.0337293
H	1	2.9395489	-0.5716188	0.6304642
H	1	2.0349519	-1.4081767	-0.6580721
O	8	-2.0035828	2.0417263	-0.1941132
C	6	-0.8021749	-0.5218591	-1.4011459
H	1	-1.8841000	-0.6740782	-1.4558142
H	1	-0.3070144	-1.4910060	-1.5266485
H	1	-0.4799470	0.1354452	-2.2163044
N	7	-1.1669328	-0.7167229	1.1328865
H	1	-0.6860714	-1.6357450	1.0274271
O	8	-2.5406521	-0.9295239	0.8808598

Table S-54. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-6$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	76	8.82	**17**	719	7.34	**33**	1431	19.99
2	125	12.45	**18**	780	27.70	**34**	1455	5.73
3	145	6.77	**19**	809	53.11	**35**	1495	14.89
4	172	4.57	**20**	865	13.04	**36**	1496	17.26
5	185	25.56	**21**	952	87.88	**37**	1505	3.94
6	221	7.30	**22**	994	23.53	**38**	1531	6.69
7	262	4.31	**23**	1038	16.96	**39**	1670	88.81

8	292	9.81	**24**	1051	2.60	**40**	1682	667.30
9	297	13.96	**25**	1089	39.43	**41**	3058	18.37
10	327	11.68	**26**	1112	4.41	**42**	3059	36.26
11	411	4.12	**27**	1166	39.26	**43**	3101	108.12
12	466	141.37	**28**	1218	98.16	**44**	3115	13.73
13	552	40.23	**29**	1316	21.79	**45**	3130	24.43
14	572	63.13	**30**	1342	60.57	**46**	3135	27.95
15	584	17.67	**31**	1391	35.34	**47**	3164	12.86
16	686	62.14	**32**	1408	9.04	**48**	3582	164.09

Table S-55. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-7



PY-7

B3LYP/6-31G* Energy (E): -1070.713457 hartrees
Entropy Correction (Hv-TSv): 428.275 kJ/mol
G° = E + "entropy correction": -671779.9705 kcal/mol

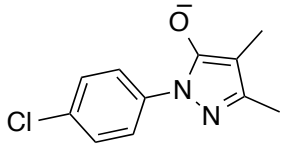
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.1469309	0.1991542	0.3509865
C	6	0.9368068	0.8625249	0.2877277
N	7	-0.0503943	-0.0546695	0.0203817
N	7	0.4953009	-1.3172743	-0.1063928
C	6	1.8016649	-1.1536564	0.0909005
C	6	3.5008279	0.7844591	0.6203555
H	1	4.0244202	1.0753723	-0.2990946
H	1	4.1407686	0.0675226	1.1452472
H	1	3.4403161	1.6738718	1.2589193
C	6	2.7273231	-2.3259204	0.0367473
H	1	3.2532179	-2.4651693	0.9890382
H	1	3.4927047	-2.1930456	-0.7366409
H	1	2.1694585	-3.2398206	-0.1827363
C	6	-1.4435647	0.1275925	-0.1706938
C	6	-4.1867605	0.4048679	-0.5628041
C	6	-2.1664704	-0.8699977	-0.8394864
C	6	-2.1117259	1.2622779	0.3084588
C	6	-3.4836204	1.4032004	0.1042086
C	6	-3.5375350	-0.7349192	-1.0326464
H	1	-1.6449124	-1.7487209	-1.1959934

H	1	-1.5713562	2.0334560	0.8389297
H	1	-3.9991341	2.2823034	0.4738905
H	1	-4.0937156	-1.5083043	-1.5501446
Cl	17	-5.9270524	0.5801524	-0.8146434
O	8	0.6272398	2.1765554	0.4300985
H	1	1.4592615	2.6781875	0.5353866

Table S-56. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-7

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	31	2.54	**25**	708	6.82	**49**	1440	85.08
2	44	0.95	**26**	712	24.19	**50**	1449	19.47
3	58	0.91	**27**	747	29.68	**51**	1454	81.98
4	98	1.17	**28**	827	5.20	**52**	1498	82.49
5	128	0.86	**29**	833	5.96	**53**	1500	28.60
6	137	1.59	**30**	845	52.12	**54**	1509	13.56
7	171	8.02	**31**	960	2.21	**55**	1518	42.80
8	224	18.57	**32**	971	0.90	**56**	1528	65.32
9	233	66.59	**33**	977	85.97	**57**	1536	124.34
10	254	7.88	**34**	1025	35.37	**58**	1546	360.14
11	260	12.47	**35**	1029	85.17	**59**	1630	98.68
12	286	40.50	**36**	1063	3.70	**60**	1643	191.78
13	318	3.92	**37**	1081	2.01	**61**	1651	14.55
14	332	5.01	**38**	1095	85.71	**62**	3049	60.60
15	371	1.71	**39**	1104	45.85	**63**	3060	38.99
16	409	0.82	**40**	1121	107.44	**64**	3101	29.35
17	423	0.73	**41**	1140	7.31	**65**	3111	14.96
18	489	72.68	**42**	1188	30.69	**66**	3123	25.41
19	518	10.88	**43**	1211	0.17	**67**	3151	19.93
20	568	26.19	**44**	1246	108.70	**68**	3237	3.78
21	609	3.66	**45**	1328	39.76	**69**	3238	2.91
22	642	0.23	**46**	1337	23.93	**70**	3258	0.51
23	654	1.34	**47**	1355	50.24	**71**	3277	1.90
24	688	4.67	**48**	1416	314.96	**72**	3678	254.39

Table S-57. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-7_{anion}



PY-7_{anion}

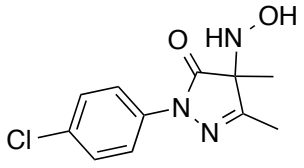
B3LYP/6-31G* Energy (E): -1070.252293 hartrees
Entropy Correction (Hv-TSv): 396.8443 kJ/mol
G° = E + "entropy correction": -671498.0981 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.1946860	0.2838020	0.4359125
C	6	0.9825510	1.0062959	0.4480322
N	7	0.0078511	0.0632125	0.0148065
N	7	0.5754042	-1.1816594	-0.2547642
C	6	1.8742019	-1.0192859	0.0053024
C	6	3.5277727	0.8483567	0.8167531
H	1	4.2564484	0.8221205	-0.0063419
H	1	3.9915539	0.3201282	1.6622015
H	1	3.4063037	1.8967990	1.1122662
C	6	2.8130204	-2.1694426	-0.1750890
H	1	3.3358874	-2.4094906	0.7593047
H	1	3.5842002	-1.9424254	-0.9219920
H	1	2.2645479	-3.0574721	-0.5031799
C	6	-1.3744179	0.2299787	-0.1593881
C	6	-4.1424053	0.4993190	-0.5187974
C	6	-2.1464147	-0.8418914	-0.6470979
C	6	-2.0220140	1.4430469	0.1430328
C	6	-3.3980138	1.5727298	-0.0368584
C	6	-3.5197750	-0.7087685	-0.8255335
H	1	-1.6473002	-1.7738842	-0.8790494
H	1	-1.4270581	2.2658989	0.5154843
H	1	-3.8838491	2.5130149	0.2016573
H	1	-4.0999910	-1.5441342	-1.2022381
Cl	17	-5.8818819	0.6661331	-0.7405949
O	8	0.7286919	2.2176179	0.7561712

Table S-58. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-7$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	41	0.54	**24**	710	23.03	**47**	1422	11.69
2	49	1.63	**25**	730	10.57	**48**	1431	40.20
3	66	0.11	**26**	763	57.25	**49**	1455	47.97
4	111	3.71	**27**	835	8.70	**50**	1486	184.58
5	119	6.79	**28**	840	18.12	**51**	1505	5.52
6	144	0.17	**29**	842	45.76	**52**	1514	120.43
7	174	0.03	**30**	956	0.24	**53**	1522	7.56
8	220	1.68	**31**	968	0.14	**54**	1530	431.26
9	254	0.81	**32**	975	99.84	**55**	1531	171.27
10	257	8.06	**33**	1020	3.33	**56**	1544	365.46
11	266	15.14	**34**	1023	104.94	**57**	1606	282.14
12	319	2.69	**35**	1057	0.42	**58**	1626	149.89
13	348	8.36	**36**	1079	1.14	**59**	1647	183.01
14	378	2.59	**37**	1098	87.53	**60**	3022	156.52
15	396	1.07	**38**	1104	17.32	**61**	3052	69.31
16	425	0.03	**39**	1114	12.82	**62**	3057	59.30
17	491	78.12	**40**	1148	47.73	**63**	3101	23.41
18	519	9.45	**41**	1156	103.79	**64**	3106	35.12
19	578	44.08	**42**	1197	2.27	**65**	3141	29.75
20	634	9.78	**43**	1313	41.86	**66**	3228	6.16
21	647	2.77	**44**	1328	0.84	**67**	3233	5.06
22	649	9.64	**45**	1350	153.51	**68**	3252	12.51
23	702	0.23	**46**	1355	440.78	**69**	3256	1.49

Table S-59. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-7



HAPY-7

B3LYP/6-31G* Energy (E): -1201.231562 hartrees
Entropy Correction (Hv-TSv): 478.7001 kJ/mol
G° = E + "entropy correction": -753669.2042 kcal/mol

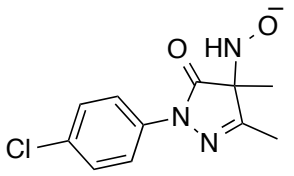
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.7769855	0.0734007	0.1852081
C	6	1.4174387	0.7828539	0.1953124
N	7	0.4689417	-0.2113990	0.0624142
N	7	1.0536506	-1.4896300	-0.0742113
C	6	2.3346470	-1.3616343	-0.0324991
O	8	1.2121547	1.9921314	0.3057915
C	6	3.5044012	0.2621569	1.5248401
H	1	3.7092888	1.3223552	1.6840992
H	1	4.4524696	-0.2841381	1.5162414
H	1	2.8995808	-0.1108878	2.3574634
N	7	3.5282170	0.5148003	-1.0122642
H	1	4.3631615	-0.0765175	-1.0707819
O	8	4.0963516	1.8254844	-0.7707427
H	1	3.5520284	2.3983802	-1.3368225
C	6	3.2418540	-2.5326761	-0.1684802
H	1	3.9102694	-2.6124444	0.6960293
H	1	3.8723010	-2.4337670	-1.0607405
H	1	2.6587625	-3.4515686	-0.2561509
C	6	-0.9442866	-0.1175298	0.0281684
C	6	-3.7270813	0.0081553	-0.0380896
C	6	-1.7025138	-1.2892183	-0.1103153
C	6	-1.5958534	1.1209709	0.1336159
C	6	-2.9877866	1.1794142	0.1002418
C	6	-3.0923446	-1.2266853	-0.1439568
H	1	-1.1994714	-2.2431280	-0.1915062
H	1	-1.0184684	2.0279878	0.2410289
H	1	-3.4897170	2.1370264	0.1818724
H	1	-3.6744346	-2.1346503	-0.2522999
Cl	17	-5.4913476	0.0886939	-0.0812267

Table S-60. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-7

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	24	0.06	**28**	712	0.47	**55**	1370	51.55
2	33	1.22	**29**	713	10.33	**56**	1397	305.58
3	70	0.64	**30**	741	12.63	**57**	1421	8.23
4	88	4.50	**31**	758	31.31	**58**	1442	18.42
5	128	8.58	**32**	826	52.25	**59**	1460	7.11
6	140	0.91	**33**	839	0.67	**60**	1491	16.29
7	145	6.68	**34**	848	58.45	**61**	1495	14.48
8	183	0.43	**35**	892	31.86	**62**	1507	9.18
9	224	48.43	**36**	898	30.75	**63**	1519	8.42

10	228	1.64	**37**	956	53.65	**64**	1526	4.34
11	240	1.80	**38**	970	0.39	**65**	1535	402.65
12	252	3.31	**39**	976	0.41	**66**	1629	2.18
13	259	20.78	**40**	1020	29.03	**67**	1648	49.64
14	268	64.38	**41**	1023	24.15	**68**	1687	138.66
15	317	7.66	**42**	1031	37.95	**69**	1697	448.28
16	319	6.15	**43**	1052	11.19	**70**	3065	7.36
17	334	30.59	**44**	1098	68.25	**71**	3075	15.78
18	386	16.19	**45**	1102	33.11	**72**	3122	4.77
19	399	1.59	**46**	1126	24.48	**73**	3146	19.61
20	421	0.16	**47**	1150	8.45	**74**	3169	17.51
21	432	14.95	**48**	1157	75.82	**75**	3170	2.61
22	508	50.15	**49**	1170	64.03	**76**	3236	3.56
23	524	10.99	**50**	1209	6.92	**77**	3242	2.95
24	580	31.40	**51**	1267	84.17	**78**	3269	0.46
25	615	18.67	**52**	1324	226.29	**79**	3274	4.62
26	622	7.06	**53**	1334	5.44	**80**	3432	18.60
27	645	0.64	**54**	1349	7.92	**81**	3726	108.20

Table S-61. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-7$_{anion}$



HAPY-7$_{anion}$

B3LYP/6-31G* Energy (E): -1200.725219 hartrees
Entropy Correction (Hv-TSv): 441.7324 kJ/mol
G° = E + "entropy correction": -753360.3049 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms)		
		X	Y	Z
C	6	2.0163014	0.3394052	0.1477668
C	6	0.6710296	1.0231604	0.2777659
N	7	-0.2755822	0.0687389	-0.0484915
N	7	0.3082644	-1.2030962	-0.2302067
C	6	1.5843375	-1.0811307	-0.0725480
O	8	0.4435130	2.1920972	0.6009742
C	6	2.9477287	0.6039421	1.3194044
H	1	3.3166921	1.6289950	1.2145568
H	1	3.8014922	-0.0807744	1.2859500
H	1	2.4511379	0.4869038	2.2887888

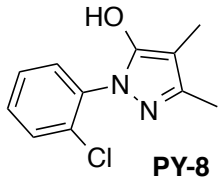
N	7	2.6154928	0.8316134	-1.2263691
H	1	3.4409156	0.1926845	-1.2678103
O	8	3.1067641	2.1390282	-1.1240479
C	6	2.4846453	-2.2579280	-0.2037196
H	1	3.0726231	-2.4040749	0.7094484
H	1	3.1949953	-2.1076477	-1.0262410
H	1	1.8975772	-3.1581045	-0.3997391
C	6	-1.6860478	0.1696036	-0.1135305
C	6	-4.4703474	0.3065651	-0.2621748
C	6	-2.4438544	-0.9883174	-0.3493711
C	6	-2.3427577	1.4009380	0.0444668
C	6	-3.7332190	1.4643111	-0.0293988
C	6	-3.8319092	-0.9204205	-0.4238685
H	1	-1.9348690	-1.9345875	-0.4746130
H	1	-1.7650800	2.2954191	0.2293589
H	1	-4.2338987	2.4182615	0.0949025
H	1	-4.4087715	-1.8199666	-0.6067134
Cl	17	-6.2271733	0.3943814	-0.3545402

Table S-62. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-7_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	20	2.70	**27**	660	64.97	**53**	1349	1.12
2	36	7.77	**28**	707	0.26	**54**	1387	221.71
3	72	12.90	**29**	713	12.31	**55**	1413	6.64
4	103	7.14	**30**	754	22.15	**56**	1427	21.76
5	124	1.95	**31**	793	18.23	**57**	1449	14.48
6	131	11.12	**32**	836	1.12	**58**	1461	15.25
7	149	10.19	**33**	845	64.70	**59**	1491	13.27
8	174	0.88	**34**	847	33.94	**60**	1494	24.01
9	176	25.32	**35**	914	73.55	**61**	1507	5.55
10	228	2.32	**36**	964	0.31	**62**	1532	54.46
11	238	12.24	**37**	972	39.78	**63**	1533	384.50
12	255	1.34	**38**	973	70.51	**64**	1626	7.69
13	263	14.14	**39**	1023	5.02	**65**	1646	66.18
14	306	6.26	**40**	1027	53.14	**66**	1671	141.39
15	318	1.89	**41**	1041	11.55	**67**	1690	463.20
16	325	17.49	**42**	1049	2.09	**68**	3058	45.74
17	375	16.01	**43**	1098	43.31	**69**	3062	11.02
18	396	4.03	**44**	1104	46.34	**70**	3081	136.99
19	400	26.96	**45**	1114	2.42	**71**	3120	8.90
20	422	0.30	**46**	1145	12.63	**72**	3128	9.51
21	486	183.93	**47**	1159	144.32	**73**	3139	31.79

22	520	18.23	**48**	1174	13.14	**74**	3168	11.42
23	537	51.60	**49**	1206	5.90	**75**	3236	4.08
24	579	34.57	**50**	1284	96.96	**76**	3244	2.51
25	618	14.70	**51**	1329	70.85	**77**	3267	0.65
26	645	0.71	**52**	1341	316.91	**78**	3268	3.03

Table S-63. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-8



PY-8

B3LYP/6-31G* Energy (E): -1070.706172 hartrees
Entropy Correction (Hv-TSv): 427.4027 kJ/mol
G° = E + "entropy correction": -671775.6076 kcal/mol

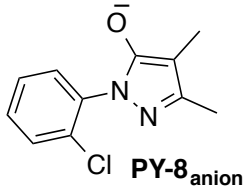
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.0102059	-0.4648007	0.5621577
C	6	0.8635377	0.2502545	0.8563888
N	7	-0.1056050	-0.1063171	-0.0393297
N	7	0.3793226	-1.0244047	-0.9509619
C	6	1.6409416	-1.2352406	-0.5732994
C	6	3.3339922	-0.4244936	1.2646933
H	1	4.1199995	0.0222200	0.6435480
H	1	3.6713936	-1.4286113	1.5469951
H	1	3.2847875	0.1613801	2.1895681
C	6	2.5036537	-2.1992028	-1.3219940
H	1	2.8642192	-3.0042009	-0.6702461
H	1	3.3887390	-1.7037016	-1.7388054
H	1	1.9430103	-2.6501610	-2.1450038
C	6	-1.4109972	0.4355684	-0.1823846
C	6	-3.9687940	1.5256670	-0.5372636
C	6	-2.3996267	0.2732937	0.7990635
C	6	-1.7338488	1.1308744	-1.3531600
C	6	-3.0043379	1.6684441	-1.5357814
C	6	-3.6685348	0.8271255	0.6305761
H	1	-0.9667111	1.2356262	-2.1123342
H	1	-3.2346011	2.2052625	-2.4498877
H	1	-4.4128526	0.6935593	1.4073530
H	1	-4.9590208	1.9504075	-0.6647259
Cl	17	-2.0854466	-0.6722956	2.2503228

O	8	0.5754934	1.1934759	1.7887655
H	1	1.3710803	1.3402708	2.3357458

Table S-64. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-8

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	33	1.56	**25**	702	28.48	**49**	1435	58.60
2	53	10.05	**26**	727	15.42	**50**	1458	3.26
3	62	0.43	**27**	748	48.96	**51**	1479	50.69
4	81	2.65	**28**	776	45.14	**52**	1500	21.68
5	143	2.66	**29**	831	3.91	**53**	1503	2.91
6	158	1.75	**30**	878	1.11	**54**	1511	14.49
7	160	1.75	**31**	955	2.38	**55**	1515	50.77
8	195	77.30	**32**	980	33.42	**56**	1522	42.11
9	203	44.37	**33**	989	0.02	**57**	1533	87.81
10	230	5.37	**34**	1025	67.61	**58**	1543	178.45
11	253	2.27	**35**	1050	91.76	**59**	1630	9.50
12	280	5.61	**36**	1062	1.53	**60**	1638	231.04
13	299	11.39	**37**	1067	10.90	**61**	1648	4.59
14	322	5.88	**38**	1085	0.50	**62**	3050	58.68
15	376	2.72	**39**	1105	88.77	**63**	3057	41.89
16	425	17.39	**40**	1128	31.28	**64**	3103	38.19
17	457	1.77	**41**	1155	10.96	**65**	3108	9.74
18	479	11.22	**42**	1192	2.07	**66**	3116	39.14
19	525	2.43	**43**	1194	21.12	**67**	3148	21.28
20	570	19.59	**44**	1244	118.32	**68**	3222	0.23
21	607	6.05	**45**	1291	23.08	**69**	3230	8.15
22	651	10.33	**46**	1326	18.02	**70**	3239	8.46
23	660	9.53	**47**	1348	17.11	**71**	3245	8.15
24	692	2.66	**48**	1416	181.44	**72**	3690	218.80

Table S-65. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-8_{anion}



PY-8_{anion}

B3LYP/6-31G* Energy (E): -1070.23931 hartrees
Entropy Correction (Hv-TSv): 396.2348 kJ/mol
G° = E + "entropy correction": -671490.0968 kcal/mol

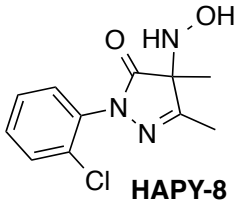
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.0488394	-0.4547807	0.6732204
C	6	0.8850112	0.2325763	1.0919322
N	7	-0.1051665	-0.1773655	0.1626278
N	7	0.4155817	-0.9969108	-0.8432390
C	6	1.6949486	-1.1614089	-0.4941640
C	6	3.3789927	-0.3759652	1.3555536
H	1	4.1609339	0.0787658	0.7290756
H	1	3.7604503	-1.3598536	1.6650657
H	1	3.2878349	0.2398132	2.2582559
C	6	2.5777630	-2.0380294	-1.3259581
H	1	2.9783519	-2.8769486	-0.7425796
H	1	3.4400100	-1.4833596	-1.7176142
H	1	2.0150523	-2.4448066	-2.1716801
C	6	-1.3729743	0.4104668	-0.0279127
C	6	-3.8806924	1.6273616	-0.4793853
C	6	-2.3800156	0.3869379	0.9508520
C	6	-1.6760306	1.0259198	-1.2538388
C	6	-2.9114976	1.6212338	-1.4846631
C	6	-3.6132640	1.0059542	0.7379666
H	1	-0.9044936	1.0166202	-2.0159943
H	1	-3.1082025	2.0901976	-2.4434522
H	1	-4.3594092	0.9720800	1.5241633
H	1	-4.8439575	2.1000091	-0.6407624
Cl	17	-2.1629646	-0.5002093	2.4600389
O	8	0.6748985	1.0617018	2.0324920

Table S-66. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-8_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	42	5.88	**24**	725	28.55	**47**	1418	4.51
2	52	1.53	**25**	738	6.64	**48**	1435	32.61
3	84	6.30	**26**	757	49.08	**49**	1475	21.02
4	84	1.72	**27**	777	63.54	**50**	1485	181.03
5	148	0.62	**28**	845	4.83	**51**	1506	34.36
6	156	4.15	**29**	867	1.99	**52**	1508	185.60
7	164	3.46	**30**	938	2.44	**53**	1522	20.69
8	193	1.66	**31**	962	0.14	**54**	1524	125.77
9	225	3.93	**32**	977	49.40	**55**	1532	23.99
10	249	9.04	**33**	1019	60.89	**56**	1547	287.80
11	276	10.69	**34**	1048	104.71	**57**	1605	385.20

12	292	2.54	**35**	1057	1.00	**58**	1624	44.59
13	328	0.79	**36**	1069	3.17	**59**	1646	91.07
14	378	15.86	**37**	1079	1.38	**60**	3016	160.71
15	424	17.04	**38**	1115	22.08	**61**	3049	72.08
16	456	4.16	**39**	1128	31.23	**62**	3050	67.77
17	477	6.66	**40**	1158	30.16	**63**	3097	27.67
18	537	1.32	**41**	1160	57.61	**64**	3102	38.30
19	583	34.24	**42**	1183	0.22	**65**	3139	30.81
20	626	10.27	**43**	1284	27.21	**66**	3219	5.10
21	651	7.88	**44**	1319	5.77	**67**	3232	5.07
22	653	22.24	**45**	1338	28.59	**68**	3236	13.96
23	704	19.67	**46**	1360	260.49	**69**	3249	9.33

Table S-67. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-8



HAPY-8

B3LYP/6-31G* Energy (E): -1201.222966 hartrees
Entropy Correction (Hv-TSv): 477.8088 kJ/mol
G° = E + "entropy correction": -753664.0231 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	2.2817321	-0.0177457	0.2688175
C	6	1.0272969	0.8396164	0.4837288
N	7	-0.0175173	0.0889766	0.0003750
N	7	0.3972948	-1.1364559	-0.5714507
C	6	1.6791582	-1.2113101	-0.4553921
O	8	0.9481848	1.9609140	0.9870888
C	6	2.9099090	-0.4133844	1.6133213
H	1	3.2373575	0.4831657	2.1428553
H	1	3.7757557	-1.0620810	1.4486435
H	1	2.1905218	-0.9516564	2.2386700
N	7	3.1771564	0.7022694	-0.6645613
H	1	3.9335794	0.0583216	-0.9165962
O	8	3.8893644	1.7413134	0.0532837

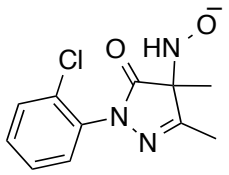
H	1	3.4344628	2.5490270	-0.2392482
C	6	2.4424833	-2.3813923	-0.9682229
H	1	3.0255412	-2.8490391	-0.1671004
H	1	3.1482463	-2.0796454	-1.7517812
H	1	1.7567019	-3.1206404	-1.3875296
C	6	-1.3846274	0.4664273	-0.0590371
C	6	-4.0718109	1.2421372	-0.2090304
C	6	-2.3756730	-0.2535516	0.6237485
C	6	-1.7604804	1.5871168	-0.8065502
C	6	-3.0942273	1.9800705	-0.8767881
C	6	-3.7148700	0.1227208	0.5415044
H	1	-0.9896113	2.1404116	-1.3314190
H	1	-3.3670089	2.8525395	-1.4606602
H	1	-4.4629190	-0.4546876	1.0725257
H	1	-5.1149983	1.5348998	-0.2661351
Cl	17	-1.9472110	-1.6342617	1.6261022

Table S-68. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-8

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	24	1.40	**28**	708	31.62	**55**	1372	38.87
2	39	4.70	**29**	724	7.40	**56**	1408	169.47
3	63	0.06	**30**	745	29.75	**57**	1421	8.41
4	73	2.94	**31**	759	12.81	**58**	1443	8.99
5	113	9.93	**32**	776	55.50	**59**	1483	20.65
6	126	0.41	**33**	831	39.27	**60**	1488	22.04
7	154	6.40	**34**	874	3.43	**61**	1495	8.18
8	161	3.77	**35**	892	21.56	**62**	1511	9.25
9	198	0.74	**36**	904	27.12	**63**	1517	12.44
10	223	4.58	**37**	952	14.33	**64**	1527	42.97
11	229	26.30	**38**	956	39.48	**65**	1530	90.28
12	245	16.24	**39**	990	0.20	**66**	1631	8.34
13	256	52.21	**40**	1024	36.95	**67**	1646	25.04
14	283	2.93	**41**	1030	19.93	**68**	1675	68.78
15	287	11.26	**42**	1052	57.78	**69**	1697	440.03
16	318	37.46	**43**	1055	43.89	**70**	3065	9.35
17	344	27.38	**44**	1070	11.31	**71**	3075	16.52
18	351	8.64	**45**	1106	41.17	**72**	3121	6.60
19	405	14.31	**46**	1132	26.33	**73**	3144	19.96
20	460	2.85	**47**	1153	33.09	**74**	3166	12.90
21	463	5.31	**48**	1157	28.06	**75**	3168	8.29
22	491	12.20	**49**	1187	59.09	**76**	3222	0.30
23	539	8.66	**50**	1194	5.22	**77**	3230	8.64

24	579	32.79	**51**	1266	37.45	**78**	3239	9.21
25	613	14.87	**52**	1299	2.17	**79**	3245	6.28
26	624	6.84	**53**	1326	114.70	**80**	3433	18.29
27	656	21.89	**54**	1341	3.46	**81**	3721	109.56

Table S-69. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-8$_{anion}$



HAPY-8$_{anion}$

B3LYP/6-31G* Energy (E): -1200.71576 hartrees
Entropy Correction (Hv-TSv): 441.9393 kJ/mol
G° = E + "entropy correction": -753354.3198 kcal/mol

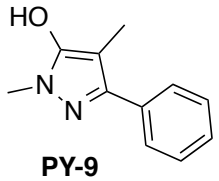
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.9840536	-0.0650869	0.2881352
C	6	0.7259482	0.7356831	0.5833366
N	7	-0.2968389	0.0623918	-0.0418269
N	7	0.1214935	-1.1533489	-0.6245823
C	6	1.3906675	-1.2627719	-0.4109039
O	8	0.5976840	1.7712501	1.2421687
C	6	2.8105354	-0.3559995	1.5333240
H	1	3.3214159	0.5733963	1.8032577
H	1	3.5631840	-1.1209815	1.3161559
H	1	2.2000641	-0.7036349	2.3738781
N	7	2.7687141	0.7423455	-0.7893335
H	1	3.4987068	0.0378942	-1.0307676
O	8	3.4280650	1.8479496	-0.2182222
C	6	2.1454816	-2.4460290	-0.9052102
H	1	2.6399054	-2.9693711	-0.0790047
H	1	2.9281333	-2.1422900	-1.6114255
H	1	1.4642719	-3.1380090	-1.4064551
C	6	-1.6611018	0.4493766	-0.1131967
C	6	-4.3398360	1.2587538	-0.3043321
C	6	-2.6841014	-0.3150891	0.4674749
C	6	-2.0037113	1.6336447	-0.7764955
C	6	-3.3313368	2.0427185	-0.8661520
C	6	-4.0179606	0.0779681	0.3624964

H	1	-1.2045136	2.2184096	-1.2190578
H	1	-3.5725907	2.9644478	-1.3848655
H	1	-4.7879755	-0.5370791	0.8138943
H	1	-5.3782075	1.5643815	-0.3793295
Cl	17	-2.3101503	-1.7709206	1.3770394

Table S-70. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-8_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	12	7.91	**27**	673	60.24	**53**	1341	71.96
2	41	7.61	**28**	706	31.19	**54**	1398	137.72
3	70	10.73	**29**	723	1.59	**55**	1405	6.93
4	77	0.38	**30**	752	45.95	**56**	1428	14.34
5	130	16.54	**31**	769	51.50	**57**	1454	12.49
6	151	5.98	**32**	798	23.06	**58**	1477	19.15
7	162	6.04	**33**	851	29.97	**59**	1491	11.04
8	172	10.19	**34**	870	1.47	**60**	1495	23.05
9	192	13.06	**35**	914	56.87	**61**	1506	4.25
10	198	6.77	**36**	949	3.05	**62**	1527	139.31
11	239	4.20	**37**	961	78.64	**63**	1533	5.86
12	260	1.85	**38**	978	0.12	**64**	1628	9.56
13	269	2.89	**39**	1024	18.65	**65**	1643	31.55
14	285	7.60	**40**	1040	22.92	**66**	1664	119.52
15	306	6.00	**41**	1051	4.97	**67**	1688	408.66
16	333	12.67	**42**	1055	78.58	**68**	3058	39.31
17	349	11.50	**43**	1069	15.42	**69**	3060	22.44
18	402	7.51	**44**	1109	19.52	**70**	3100	120.02
19	442	24.33	**45**	1118	26.98	**71**	3117	13.39
20	460	4.71	**46**	1149	32.06	**72**	3130	12.27
21	486	7.53	**47**	1164	57.36	**73**	3139	34.33
22	534	17.23	**48**	1187	14.04	**74**	3163	11.16
23	554	78.09	**49**	1191	28.01	**75**	3216	7.50
24	581	39.70	**50**	1277	26.70	**76**	3228	6.54
25	614	12.72	**51**	1301	3.26	**77**	3239	11.18
26	653	32.07	**52**	1335	92.87	**78**	3247	4.88

Table S-71. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-9



PY-9

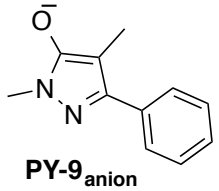
B3LYP/6-31G* Energy (E): -611.119386 hartrees
Entropy Correction (Hv-TSv): 460.2285 kJ/mol
G° = E + "entropy correction": -383372.9175 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2279980	-0.5972430	0.4991380
C	6	2.4013577	0.1075204	0.2694476
N	7	2.1039122	1.2267176	-0.4360540
N	7	0.7658943	1.3160387	-0.6797098
C	6	0.2371656	0.2116743	-0.1255479
C	6	3.0174180	2.2813104	-0.8472432
H	1	2.6416284	2.7180891	-1.7726173
H	1	4.0051926	1.8525931	-1.0188724
H	1	3.0916560	3.0615029	-0.0835099
C	6	1.1030536	-1.8674621	1.2876683
H	1	1.1123806	-2.7673902	0.6595223
H	1	0.1767964	-1.8845898	1.8704190
H	1	1.9266650	-1.9656083	2.0053586
C	6	-1.2186751	-0.0085336	-0.2003982
C	6	-4.0079908	-0.3934044	-0.3544722
C	6	-1.7694665	-1.3008983	-0.2096477
C	6	-2.0956528	1.0882743	-0.2786995
C	6	-3.4724796	0.8973322	-0.3570598
C	6	-3.1498683	-1.4904623	-0.2825808
H	1	-4.1299724	1.7600045	-0.4136283
H	1	-3.5517949	-2.4992946	-0.2905957
H	1	-5.0823659	-0.5399752	-0.4100304
H	1	-1.1151326	-2.1651687	-0.1852482
H	1	-1.6785141	2.0898479	-0.2747765
O	8	3.6960940	-0.1133755	0.6334065
H	1	3.7647008	-1.0174995	0.9957315

Table S-72. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-9

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	47	0.88	**25**	791	21.17	**49**	1471	20.84
2	79	2.01	**26**	822	19.14	**50**	1480	38.19
3	81	3.96	**27**	861	0.65	**51**	1493	54.14
4	110	1.86	**28**	930	5.04	**52**	1511	36.13
5	133	12.86	**29**	969	0.76	**53**	1518	2.64
6	171	0.03	**30**	994	0.41	**54**	1528	24.11
7	197	95.33	**31**	1016	17.31	**55**	1530	9.66
8	224	36.49	**32**	1017	1.38	**56**	1557	11.27
9	254	1.91	**33**	1039	125.37	**57**	1566	156.26
10	271	10.77	**34**	1065	22.36	**58**	1611	122.58
11	295	5.48	**35**	1072	5.55	**59**	1640	13.01
12	327	8.54	**36**	1080	6.02	**60**	1665	10.27
13	331	4.50	**37**	1112	3.05	**61**	3046	57.58
14	391	0.88	**38**	1151	150.03	**62**	3088	77.89
15	419	0.08	**39**	1186	32.76	**63**	3097	35.82
16	513	4.33	**40**	1189	0.02	**64**	3124	24.91
17	576	12.15	**41**	1212	0.15	**65**	3168	13.03
18	614	6.99	**42**	1263	37.10	**66**	3201	3.39
19	633	0.17	**43**	1281	20.68	**67**	3202	4.58
20	660	0.54	**44**	1308	59.11	**68**	3209	11.43
21	672	19.80	**45**	1338	30.54	**69**	3221	38.19
22	712	19.17	**46**	1366	3.17	**70**	3227	41.21
23	719	33.13	**47**	1409	242.41	**71**	3234	13.79
24	747	27.00	**48**	1452	2.57	**72**	3686	233.62

Table S-73. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-9_{anion}



PY-9_{anion}

B3LYP/6-31G* Energy (E): -610.65229 hartrees
Entropy Correction (Hv-TSv): 427.8126 kJ/mol
G° = E + "entropy correction": -383087.5582 kcal/mol

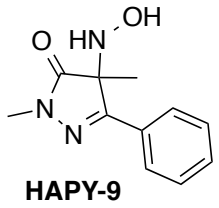
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.3873872	-0.6600497	0.4897516
C	6	2.6076012	0.0428783	0.3189587
N	7	2.2356149	1.2318268	-0.3061037
N	7	0.8880471	1.3234881	-0.5463574
C	6	0.3798171	0.1753032	-0.0567854
C	6	3.1283292	2.2806060	-0.7441372
H	1	3.1363312	2.3695207	-1.8367973
H	1	4.1297505	2.0210210	-0.3964293
H	1	2.8324021	3.2463104	-0.3212992
C	6	1.3116520	-1.9830485	1.1889925
H	1	1.1618477	-2.8371274	0.5105789
H	1	0.5066699	-2.0259792	1.9339693
H	1	2.2604707	-2.1597804	1.7102829
C	6	-1.0762991	-0.0387740	-0.1342891
C	6	-3.8784665	-0.4051650	-0.3002595
C	6	-1.6504389	-1.3191218	-0.0362381
C	6	-1.9455505	1.0541851	-0.3237955
C	6	-3.3230140	0.8732176	-0.4083032
C	6	-3.0324851	-1.4983433	-0.1151773
H	1	-3.9646119	1.7380241	-0.5528181
H	1	-3.4423410	-2.5012523	-0.0365185
H	1	-4.9535061	-0.5446702	-0.3605654
H	1	-1.0055811	-2.1815766	0.0867416
H	1	-1.5096619	2.0447466	-0.4012644
O	8	3.8160354	-0.2462400	0.6378631

Table S-74. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-9_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	1	1.15	**24**	786	19.28	**47**	1450	183.48
2	76	0.82	**25**	846	9.80	**48**	1462	7.39
3	92	3.36	**26**	858	0.38	**49**	1480	1.45
4	110	0.58	**27**	922	4.26	**50**	1500	92.30
5	126	1.88	**28**	961	0.77	**51**	1511	351.61
6	142	7.47	**29**	981	0.42	**52**	1522	5.39
7	200	0.46	**30**	1003	16.69	**53**	1530	26.04
8	254	0.57	**31**	1015	3.27	**54**	1544	1.76
9	274	10.12	**32**	1032	29.67	**55**	1558	34.52
10	284	10.15	**33**	1045	38.75	**56**	1570	609.40
11	330	21.56	**34**	1062	6.26	**57**	1633	1.82

12	343	2.74	**35**	1063	9.58	**58**	1660	28.89
13	379	6.84	**36**	1107	8.28	**59**	3008	142.59
14	419	0.11	**37**	1181	0.15	**60**	3048	49.14
15	514	1.44	**38**	1188	2.26	**61**	3059	167.43
16	575	29.13	**39**	1206	8.54	**62**	3095	49.50
17	632	0.25	**40**	1220	59.81	**63**	3117	44.87
18	641	5.76	**41**	1279	79.65	**64**	3176	8.26
19	673	26.18	**42**	1293	67.68	**65**	3200	6.32
20	684	6.66	**43**	1334	12.97	**66**	3208	11.91
21	708	28.16	**44**	1364	0.31	**67**	3220	32.72
22	741	30.66	**45**	1388	74.48	**68**	3227	47.41
23	770	34.57	**46**	1426	47.60	**69**	3236	19.36

Table S-75. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-9



HAPY-9

B3LYP/6-31G* Energy (E): -741.63449 hartrees
Entropy Correction (Hv-TSv): 512.2117 kJ/mol
G° = E + "entropy correction": -465259.8957 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.0125600	-0.6692558	0.2153561
C	6	2.2888911	0.1852619	0.1244898
N	7	1.8650175	1.4731938	-0.0042953
N	7	0.4813263	1.5965305	-0.0566489
C	6	-0.0506499	0.4161510	0.0453318
O	8	3.4623994	-0.2001839	0.1589396
C	6	2.6909867	2.6592805	-0.1446975
H	1	2.5273393	3.1264055	-1.1192492
H	1	3.7319206	2.3478749	-0.0583799
H	1	2.4552136	3.3790341	0.6425725
C	6	0.9685895	-1.3720509	1.5822995
H	1	1.8616314	-1.9893731	1.6969529
H	1	0.0870029	-2.0093915	1.6773197

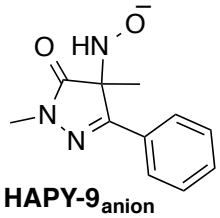
H	1	0.9429793	-0.6355219	2.3916157
N	7	1.0024272	-1.5491405	-0.9795268
H	1	0.0837359	-1.9931988	-1.0413619
O	8	1.8786507	-2.6809718	-0.7545329
H	1	2.6695788	-2.4413727	-1.2667492
C	6	-1.5097912	0.2501149	0.0075625
C	6	-4.3131036	-0.0041323	-0.0819019
C	6	-2.1250484	-1.0059323	0.1494981
C	6	-2.3317816	1.3800373	-0.1813970
C	6	-3.7137825	1.2521718	-0.2237262
C	6	-3.5137396	-1.1300527	0.1029770
H	1	-4.3281243	2.1353549	-0.3693306
H	1	-3.9660717	-2.1102211	0.2153978
H	1	-5.3937440	-0.1003443	-0.1163385
H	1	-1.5285805	-1.8968204	0.3074828
H	1	-1.8661609	2.3525189	-0.2936337

Table S-76. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-9

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	29	0.39	**28**	760	20.04	**55**	1430	20.23
2	62	3.14	**29**	789	18.32	**56**	1438	140.57
3	79	1.65	**30**	815	31.56	**57**	1472	11.39
4	100	0.67	**31**	861	0.64	**58**	1490	7.37
5	105	0.20	**32**	884	34.06	**59**	1511	8.02
6	143	0.81	**33**	940	36.34	**60**	1515	12.53
7	157	2.20	**34**	942	5.86	**61**	1517	8.48
8	183	0.44	**35**	968	37.31	**62**	1526	10.90
9	223	1.18	**36**	980	0.71	**63**	1539	43.71
10	255	2.56	**37**	1006	0.88	**64**	1545	1.46
11	266	6.62	**38**	1017	5.32	**65**	1603	48.55
12	279	3.37	**39**	1025	65.12	**66**	1640	3.62
13	310	11.46	**40**	1033	11.63	**67**	1662	1.22
14	320	3.11	**41**	1062	4.10	**68**	1681	795.96
15	340	9.81	**42**	1064	135.20	**69**	3085	16.47
16	354	7.95	**43**	1119	5.91	**70**	3090	70.78
17	416	0.28	**44**	1130	10.54	**71**	3157	18.45
18	422	23.86	**45**	1176	2.86	**72**	3161	15.35
19	448	147.96	**46**	1194	4.76	**73**	3178	19.31
20	498	3.47	**47**	1195	20.31	**74**	3198	2.19
21	614	54.69	**48**	1218	4.14	**75**	3208	1.03
22	629	2.34	**49**	1247	59.82	**76**	3216	13.54
23	653	18.67	**50**	1263	116.76	**77**	3227	38.36

24	665	49.07	**51**	1336	71.94	**78**	3237	30.74
25	674	16.46	**52**	1357	77.75	**79**	3240	9.05
26	707	40.21	**53**	1371	7.72	**80**	3467	32.15
27	745	27.03	**54**	1383	90.70	**81**	3722	110.52

Table S-77. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-9$_{anion}$



HAPY-9$_{anion}$

B3LYP/6-31G* Energy (E): -741.126974 hartrees
Entropy Correction (Hv-TSv): 474.0132 kJ/mol
G° = E + "entropy correction": -464950.5545 kcal/mol

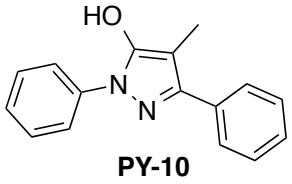
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2764962	-0.7474886	0.1782950
C	6	2.5265486	0.1224540	0.1656210
N	7	2.1171916	1.3534442	-0.2534907
N	7	0.7397602	1.4532432	-0.3931339
C	6	0.2169947	0.2958418	-0.1071504
O	8	3.6894455	-0.1837435	0.4594785
C	6	2.9359409	2.5369040	-0.4460429
H	1	2.8715108	2.8824925	-1.4814572
H	1	3.9658407	2.2641707	-0.2148596
H	1	2.6069866	3.3381188	0.2207626
C	6	1.1497547	-1.5371552	1.4763380
H	1	1.8133722	-2.4036164	1.3724180
H	1	0.1265930	-1.8819308	1.6430550
H	1	1.4525048	-0.9490498	2.3494737
N	7	1.4101965	-1.6521582	-1.0980736
H	1	0.4570413	-2.0649519	-1.1307571
O	8	2.3126587	-2.7060934	-0.8801456
C	6	-1.2432139	0.1325789	-0.1335099
C	6	-4.0521725	-0.1135134	-0.1959353
C	6	-1.8589997	-1.1309869	-0.0905173
C	6	-2.0694527	1.2729757	-0.2037348
C	6	-3.4533379	1.1496905	-0.2367667
C	6	-3.2485835	-1.2504401	-0.1242023
H	1	-4.0672163	2.0436126	-0.2894513

H	1	-3.6955463	-2.2394061	-0.0941441
H	1	-5.1332434	-0.2088874	-0.2178957
H	1	-1.2474177	-2.0258434	-0.0452331
H	1	-1.5996532	2.2497380	-0.2289403

Table S-78. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-9_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	47	4.15	**27**	755	30.53	**53**	1406	38.11
2	74	7.31	**28**	779	41.54	**54**	1421	35.94
3	81	4.74	**29**	802	26.73	**55**	1450	60.70
4	95	5.86	**30**	839	17.72	**56**	1470	29.72
5	107	6.44	**31**	860	0.01	**57**	1486	5.84
6	130	8.06	**32**	938	3.62	**58**	1508	2.33
7	152	7.60	**33**	955	108.59	**59**	1514	9.40
8	179	15.28	**34**	974	87.76	**60**	1535	2.40
9	214	4.73	**35**	975	27.71	**61**	1539	38.46
10	252	6.49	**36**	989	1.56	**62**	1544	7.73
11	263	6.51	**37**	1016	1.41	**63**	1592	67.38
12	277	4.43	**38**	1030	54.48	**64**	1637	3.13
13	303	11.82	**39**	1035	7.56	**65**	1660	7.84
14	320	21.60	**40**	1061	49.67	**66**	1674	755.80
15	350	1.39	**41**	1063	9.44	**67**	3051	56.49
16	354	13.33	**42**	1111	30.58	**68**	3086	94.21
17	407	22.28	**43**	1116	4.88	**69**	3119	9.41
18	418	0.14	**44**	1170	2.05	**70**	3152	79.69
19	495	31.91	**45**	1187	0.09	**71**	3156	18.29
20	551	169.96	**46**	1204	19.59	**72**	3158	44.21
21	606	53.37	**47**	1216	0.40	**73**	3195	3.30
22	630	2.32	**48**	1257	90.64	**74**	3203	8.21
23	649	15.82	**49**	1268	72.49	**75**	3212	0.20
24	663	33.94	**50**	1336	41.51	**76**	3219	36.89
25	706	25.65	**51**	1362	105.34	**77**	3231	33.54
26	710	54.56	**52**	1370	37.73	**78**	3239	15.47

Table S-79. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-10



PY-10

B3LYP/6-31G* Energy (E): -802.857405 hartrees
Entropy Correction (Hv-TSv): 591.8378 kJ/mol
G° = E + "entropy correction": -503658.7947 kcal/mol

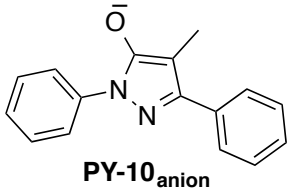
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.6190253	-1.5419797	-0.4078239
C	6	-0.7627205	-1.5676442	-0.3403067
N	7	-1.2101896	-0.3088748	-0.0367705
N	7	-0.1536048	0.5523998	0.1129437
C	6	0.9405550	-0.1864878	-0.1083434
C	6	1.5006064	-2.6963825	-0.7842054
H	1	0.9598387	-3.4141770	-1.4124238
H	1	1.8810409	-3.2458470	0.0859163
H	1	2.3647230	-2.3610609	-1.3655826
C	6	2.2664195	0.4566920	-0.0613719
C	6	4.7831802	1.7181873	0.0323677
C	6	3.4134765	-0.2538861	0.3290590
C	6	2.4035742	1.8152623	-0.3970127
C	6	3.6478726	2.4379771	-0.3494189
C	6	4.6598900	0.3714472	0.3733615
H	1	3.7322454	3.4871297	-0.6172362
H	1	5.5328870	-0.1954986	0.6823726
H	1	3.3283444	-1.2938586	0.6241404
H	1	1.5213391	2.3701210	-0.6986160
H	1	5.7530943	2.2050815	0.0642763
C	6	-2.5372962	0.1459544	0.2047603
C	6	-5.1230323	1.0886885	0.7023162
C	6	-2.7344581	1.2177707	1.0838086
C	6	-3.6313975	-0.4472634	-0.4355218
C	6	-4.9182968	0.0237368	-0.1744576
C	6	-4.0244075	1.6852435	1.3241675
H	1	-1.8744415	1.6717303	1.5608996
H	1	-3.4790075	-1.2640530	-1.1284014
H	1	-5.7619109	-0.4436996	-0.6728570
H	1	-4.1673822	2.5163474	2.0078957
H	1	-6.1265651	1.4526225	0.8979332

O	8	-1.6503479	-2.5780193	-0.5216694
H	1	-1.1530541	-3.4176595	-0.5741992

Table S-80. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-10

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	33	0.21	**32**	775	46.75	**63**	1366	6.51
2	37	1.16	**33**	785	2.99	**64**	1370	5.28
3	64	7.57	**34**	794	30.19	**65**	1413	405.59
4	71	0.70	**35**	853	0.55	**66**	1450	1.55
5	91	0.44	**36**	861	0.82	**67**	1482	41.49
6	145	2.02	**37**	927	5.59	**68**	1486	76.62
7	156	0.37	**38**	933	4.54	**69**	1495	64.93
8	186	2.61	**39**	969	1.18	**70**	1512	18.32
9	241	89.46	**40**	971	0.54	**71**	1520	3.40
10	249	34.21	**41**	981	83.63	**72**	1532	101.95
11	261	1.79	**42**	994	0.32	**73**	1551	213.65
12	272	4.47	**43**	996	0.29	**74**	1560	7.10
13	304	21.66	**44**	1017	1.11	**75**	1611	224.36
14	311	1.79	**45**	1019	0.06	**76**	1641	18.21
15	343	4.61	**46**	1032	49.91	**77**	1651	32.05
16	397	11.68	**47**	1057	11.15	**78**	1660	80.33
17	418	0.03	**48**	1066	9.39	**79**	1665	2.02
18	420	1.18	**49**	1073	0.86	**80**	3048	55.86
19	431	1.74	**50**	1102	94.39	**81**	3099	31.57
20	500	5.30	**51**	1112	3.01	**82**	3129	20.36
21	530	5.37	**52**	1115	20.28	**83**	3202	3.89
22	627	24.00	**53**	1146	67.51	**84**	3209	1.06
23	629	3.79	**54**	1190	0.98	**85**	3209	9.29
24	633	1.09	**55**	1192	0.08	**86**	3218	22.75
25	648	6.75	**56**	1211	13.44	**87**	3220	31.39
26	664	2.78	**57**	1212	1.78	**88**	3227	44.42
27	684	10.88	**58**	1224	95.98	**89**	3230	36.73
28	706	23.97	**59**	1266	36.12	**90**	3235	14.81
29	712	36.75	**60**	1322	42.29	**91**	3246	4.83
30	721	13.62	**61**	1338	40.01	**92**	3263	1.62
31	749	54.81	**62**	1358	42.80	**93**	3678	247.95

Table S-81. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-10$_{anion}$



PY-10$_{anion}$

B3LYP/6-31G* Energy (E): -802.396021 hartrees
Entropy Correction (Hv-TSv): 559.9689 kJ/mol
G° = E + "entropy correction": -503376.889 kcal/mol

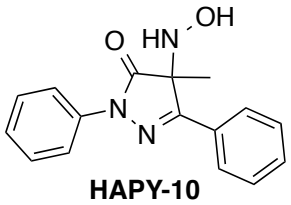
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.5877823	-1.6487395	-0.5006172
C	6	-0.8220144	-1.7396280	-0.4572379
N	7	-1.2498622	-0.4490629	-0.0484478
N	7	-0.1831551	0.4068535	0.1546939
C	6	0.9086299	-0.3221948	-0.1225465
C	6	1.4466011	-2.7899562	-0.9539548
H	1	0.8112985	-3.5315763	-1.4526901
H	1	1.9573597	-3.3145024	-0.1321617
H	1	2.2231495	-2.4776978	-1.6633283
C	6	2.2291824	0.3272171	-0.0217897
C	6	4.7393409	1.6118817	0.1782162
C	6	3.4130714	-0.4144293	0.1366930
C	6	2.3341554	1.7307083	-0.0720907
C	6	3.5701037	2.3630683	0.0288553
C	6	4.6521531	0.2210286	0.2327917
H	1	3.6185338	3.4474429	-0.0162790
H	1	5.5484665	-0.3797918	0.3568734
H	1	3.3588974	-1.4950530	0.2021845
H	1	1.4237230	2.3078141	-0.1948343
H	1	5.7032688	2.1060004	0.2516160
C	6	-2.5586502	0.0282472	0.1754316
C	6	-5.1533108	1.0400719	0.6278965
C	6	-2.7455969	1.3419436	0.6438939
C	6	-3.6893078	-0.7742876	-0.0635151
C	6	-4.9668576	-0.2626744	0.1644642
C	6	-4.0294093	1.8344226	0.8645367
H	1	-1.8710045	1.9536050	0.8256370
H	1	-3.5379165	-1.7834009	-0.4216525
H	1	-5.8227922	-0.9035756	-0.0287253
H	1	-4.1445891	2.8521298	1.2269159
H	1	-6.1517268	1.4282331	0.8020086

O	8	-1.5995240	-2.7140975	-0.7228374

Table S-82. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-10$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	23	0.02	**31**	767	78.68	**61**	1358	85.32
2	30	1.13	**32**	787	25.05	**62**	1364	25.98
3	56	3.46	**33**	807	0.83	**63**	1366	33.17
4	80	3.31	**34**	855	0.02	**64**	1431	68.17
5	90	2.46	**35**	859	0.65	**65**	1461	127.51
6	165	2.61	**36**	907	4.90	**66**	1482	6.70
7	182	2.19	**37**	927	3.99	**67**	1496	77.64
8	192	0.87	**38**	962	0.13	**68**	1515	18.17
9	241	0.42	**39**	965	2.04	**69**	1518	379.82
10	264	5.04	**40**	977	54.29	**70**	1534	36.86
11	265	1.94	**41**	978	12.57	**71**	1536	364.43
12	287	1.61	**42**	983	1.00	**72**	1560	47.56
13	325	26.81	**43**	1014	9.71	**73**	1592	582.92
14	361	2.42	**44**	1016	0.34	**74**	1634	14.54
15	395	10.61	**45**	1027	70.91	**75**	1639	40.39
16	416	4.75	**46**	1056	3.08	**76**	1656	287.35
17	419	0.42	**47**	1063	5.42	**77**	1662	5.37
18	420	0.86	**48**	1073	1.64	**78**	3016	146.13
19	508	4.23	**49**	1095	12.10	**79**	3069	46.62
20	531	3.06	**50**	1106	38.44	**80**	3105	41.48
21	629	19.03	**51**	1112	37.47	**81**	3202	14.01
22	633	0.16	**52**	1162	39.01	**82**	3203	0.48
23	635	16.90	**53**	1179	0.98	**83**	3208	32.52
24	671	13.25	**54**	1184	0.10	**84**	3210	13.70
25	682	11.48	**55**	1198	21.34	**85**	3222	31.88
26	689	19.35	**56**	1208	3.84	**86**	3228	42.54
27	704	10.82	**57**	1228	108.56	**87**	3230	32.71
28	709	25.68	**58**	1312	7.95	**88**	3237	20.69
29	734	30.88	**59**	1336	70.24	**89**	3250	5.94
30	761	51.57	**60**	1339	384.45	**90**	3251	11.55

Table S-83. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-10



HAPY-10

B3LYP/6-31G* Energy (E): -933.372296 hartrees
Entropy Correction (Hv-TSv): 642.0662 kJ/mol
G° = E + "entropy correction": -585546.0586 kcal/mol

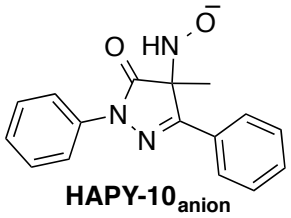
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.6850904	-1.4545779	-0.2182886
C	6	-0.8513867	-1.4496239	-0.1897632
N	7	-1.2322829	-0.1256317	-0.1167440
N	7	-0.1319754	0.7339636	-0.0702362
C	6	0.9628826	0.0406611	-0.1070471
O	8	-1.5872908	-2.4352332	-0.2214676
C	6	1.1636317	-2.0868864	-1.5354078
H	1	0.7536342	-3.0951320	-1.6183335
H	1	2.2527805	-2.1473983	-1.5798884
H	1	0.8204587	-1.4957583	-2.3903047
N	7	1.1245847	-2.1166907	1.0346444
H	1	2.1285027	-1.9586819	1.1440246
O	8	1.0462816	-3.5529657	0.8786509
H	1	0.2487414	-3.7790549	1.3868325
C	6	2.2684791	0.7128273	-0.0503085
C	6	4.7395962	2.0551694	0.0855368
C	6	3.4796683	0.0026086	-0.1220755
C	6	2.3217714	2.1146356	0.0918799
C	6	3.5417087	2.7744032	0.1564857
C	6	4.7028734	0.6695156	-0.0531301
H	1	3.5605634	3.8543372	0.2654562
H	1	5.6249166	0.1001397	-0.1112976
H	1	3.4826797	-1.0742238	-0.2419299
H	1	1.3941304	2.6718797	0.1519862
H	1	5.6912117	2.5746515	0.1384401
C	6	-2.5355596	0.4408332	-0.0386223
C	6	-5.0806281	1.6034625	0.1264071
C	6	-2.6679045	1.8290255	0.1069274
C	6	-3.6806154	-0.3670378	-0.1039676
C	6	-4.9411877	0.2236066	-0.0203399
C	6	-3.9361121	2.3990698	0.1882407

H	1	-1.7800972	2.4447934	0.1559613
H	1	-3.5787873	-1.4369623	-0.2152150
H	1	-5.8199457	-0.4121162	-0.0713553
H	1	-4.0236929	3.4752117	0.3022628
H	1	-6.0666718	2.0520643	0.1911934

Table S-84. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-10

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	18	0.15	**35**	760	20.39	**69**	1356	10.14
2	34	1.10	**36**	775	60.41	**70**	1365	32.57
3	49	1.51	**37**	790	14.26	**71**	1370	2.08
4	68	1.22	**38**	803	31.92	**72**	1375	98.29
5	78	0.35	**39**	858	0.20	**73**	1412	195.60
6	99	4.89	**40**	859	0.49	**74**	1430	15.55
7	120	0.25	**41**	884	46.68	**75**	1492	7.80
8	165	4.60	**42**	901	26.37	**76**	1504	4.37
9	187	10.66	**43**	929	5.12	**77**	1507	16.11
10	215	12.99	**44**	943	3.40	**78**	1513	3.99
11	232	2.28	**45**	952	42.81	**79**	1525	18.14
12	253	45.76	**46**	976	0.04	**80**	1541	203.93
13	260	10.32	**47**	980	0.52	**81**	1546	21.97
14	264	0.32	**48**	999	0.76	**82**	1612	48.12
15	277	37.31	**49**	1007	0.75	**83**	1639	2.64
16	303	52.80	**50**	1015	3.39	**84**	1649	19.73
17	329	9.01	**51**	1017	24.37	**85**	1658	105.97
18	346	21.08	**52**	1018	10.46	**86**	1663	2.26
19	373	0.49	**53**	1023	48.25	**87**	1700	678.40
20	411	6.84	**54**	1060	5.25	**88**	3084	14.02
21	415	0.03	**55**	1063	4.99	**89**	3157	17.73
22	419	0.07	**56**	1101	53.68	**90**	3177	17.63
23	495	2.25	**57**	1113	34.32	**91**	3208	2.99
24	501	15.13	**58**	1119	2.52	**92**	3208	1.33
25	531	3.25	**59**	1141	28.12	**93**	3216	26.99
26	631	2.62	**60**	1170	162.37	**94**	3217	10.55
27	631	1.05	**61**	1190	0.54	**95**	3227	36.18
28	638	37.52	**62**	1196	0.03	**96**	3230	34.23
29	674	24.42	**63**	1198	67.28	**97**	3236	31.94
30	675	11.16	**64**	1212	4.62	**98**	3239	8.30
31	681	61.98	**65**	1219	1.50	**99**	3263	0.96
32	705	35.67	**66**	1254	81.02	**100**	3272	3.90
33	708	17.94	**67**	1323	250.44	**101**	3467	31.71
34	741	23.21	**68**	1349	62.33	**102**	3721	111.77

Table S-85. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-10$_{anion}$



HAPY-10$_{anion}$

B3LYP/6-31G* Energy (E): -932.875214 hartrees
Entropy Correction (Hv-TSv): 598.8653 kJ/mol
G° = E + "entropy correction": Not a ground state structure; HNO is dissociated

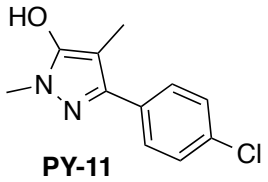
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	0.6208385	-1.2860540	0.6656423
C	6	-0.8112153	-1.3671016	0.6841239
N	7	-1.2444588	-0.0938899	0.2585264
N	7	-0.1771051	0.7648798	0.0290382
C	6	0.9193137	0.0612257	0.2928946
O	8	-1.5620971	-2.3170827	1.0284011
N	7	0.6796230	-2.1687163	-1.6363697
H	1	1.1648782	-1.2484115	-1.8398544
O	8	1.5486646	-3.0650790	-1.6038462
C	6	-2.5582049	0.3835152	0.0503369
C	6	-5.1541459	1.3879612	-0.3792844
C	6	-3.6778669	-0.4515827	0.2084836
C	6	-2.7524241	1.7240395	-0.3259289
C	6	-4.0391680	2.2132490	-0.5371203
C	6	-4.9584101	0.0578721	-0.0067834
H	1	-3.5230971	-1.4813578	0.4989275
H	1	-1.8843208	2.3586941	-0.4496016
H	1	-4.1637464	3.2522055	-0.8286242
H	1	-5.8084707	-0.6065086	0.1208261
H	1	-6.1549597	1.7735803	-0.5451710
C	6	1.4940225	-2.3292042	1.2652167
H	1	2.3282155	-1.8969897	1.8276544
H	1	1.9223784	-2.9959827	0.4916114
H	1	0.9073198	-2.9630433	1.9403888
C	6	2.2425797	0.6976480	0.1675166
C	6	4.7643040	1.9264876	-0.0846158
C	6	2.3955678	2.0779643	0.3881807
C	6	3.3758414	-0.0546104	-0.1893711
C	6	4.6238540	0.5571211	-0.3127798
C	6	3.6426168	2.6846743	0.2625202

H	1	1.5199800	2.6572093	0.6622742
H	1	3.2684785	-1.1150869	-0.3976961
H	1	5.4839347	-0.0429939	-0.5949038
H	1	3.7383065	3.7514281	0.4426956
H	1	5.7371308	2.3994048	-0.1775215

Table S-86. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-10$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	24	0.20	**34**	714	24.95	**67**	1359	663.49
2	37	2.61	**35**	740	68.67	**68**	1366	359.05
3	40	4.61	**36**	764	54.79	**69**	1372	10.15
4	59	0.68	**37**	772	104.57	**70**	1379	472.29
5	68	2.60	**38**	786	25.83	**71**	1454	146.69
6	91	4.47	**39**	808	2.19	**72**	1473	22.88
7	116	7.08	**40**	856	0.05	**73**	1487	20.82
8	140	36.06	**41**	867	1.00	**74**	1499	7.83
9	159	5.47	**42**	912	4.68	**75**	1510	32.03
10	168	7.33	**43**	939	5.26	**76**	1527	172.23
11	209	5.17	**44**	966	0.04	**77**	1536	16.13
12	225	1.57	**45**	971	101.83	**78**	1539	306.12
13	244	6.36	**46**	976	7.07	**79**	1550	97.27
14	262	4.18	**47**	981	1.02	**80**	1560	19.45
15	268	7.48	**48**	994	5.65	**81**	1604	697.37
16	287	99.77	**49**	1015	6.73	**82**	1636	5.62
17	324	18.20	**50**	1016	0.35	**83**	1640	56.14
18	332	2.43	**51**	1032	78.78	**84**	1658	250.28
19	379	2.93	**52**	1058	3.62	**85**	1663	8.35
20	394	8.37	**53**	1065	14.28	**86**	2937	117.92
21	420	0.25	**54**	1079	105.37	**87**	2951	70.12
22	420	0.26	**55**	1096	15.59	**88**	3077	54.72
23	445	2.59	**56**	1110	29.61	**89**	3126	30.43
24	509	5.55	**57**	1120	53.45	**90**	3198	4.91
25	528	5.55	**58**	1152	33.70	**91**	3203	8.56
26	631	6.30	**59**	1181	0.25	**92**	3206	0.82
27	631	0.21	**60**	1185	0.52	**93**	3210	31.51
28	637	29.34	**61**	1203	8.34	**94**	3214	20.24
29	666	44.84	**62**	1215	0.47	**95**	3222	45.41
30	679	34.67	**63**	1233	105.36	**96**	3228	35.64
31	684	26.18	**64**	1325	165.56	**97**	3231	30.28
32	697	7.33	**65**	1339	34.94	**98**	3253	3.93
33	705	11.43	**66**	1344	178.07	**99**	3258	8.56

Table S-87. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-11



PY-11

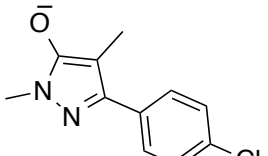
B3LYP/6-31G* Energy (E): -1070.715916 hartrees
Entropy Correction (Hv-TSv): 430.195 kJ/mol
G° = E + "entropy correction": -671781.0547 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2518005	-0.5980621	0.5122775
C	6	2.4249337	0.1091910	0.2888789
N	7	2.1298133	1.2256819	-0.4223208
N	7	0.7950345	1.3109130	-0.6762665
C	6	0.2645184	0.2071882	-0.1224044
C	6	3.0448283	2.2802394	-0.8311217
H	1	2.6728788	2.7153555	-1.7587098
H	1	4.0334008	1.8514617	-0.9975443
H	1	3.1152361	3.0612414	-0.0679351
C	6	1.1243018	-1.8658631	1.3041563
H	1	1.1179793	-2.7666788	0.6773598
H	1	0.2065188	-1.8733620	1.9004758
H	1	1.9560881	-1.9707971	2.0110970
C	6	-1.1898147	-0.0102012	-0.2084521
C	6	-3.9619952	-0.3771073	-0.3807061
C	6	-1.7523254	-1.2966452	-0.1777530
C	6	-2.0587659	1.0877278	-0.3387105
C	6	-3.4361190	0.9134118	-0.4270946
C	6	-3.1317532	-1.4872732	-0.2593203
H	1	-4.0953446	1.7688897	-0.5225919
H	1	-3.5524999	-2.4864577	-0.2368829
H	1	-1.1117487	-2.1683842	-0.1125449
H	1	-1.6395924	2.0874155	-0.3676247
Cl	17	-5.7125828	-0.6030888	-0.4773068
O	8	3.7175608	-0.1062282	0.6623692
H	1	3.7876485	-1.0085682	1.0286761

Table S-88. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-11

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	41	1.01	**25**	715	9.45	**49**	1448	46.20
2	54	0.62	**26**	743	12.97	**50**	1454	23.81
3	78	1.60	**27**	749	44.35	**51**	1472	29.57
4	87	0.88	**28**	823	12.10	**52**	1480	98.96
5	133	11.68	**29**	837	6.80	**53**	1510	34.40
6	150	9.99	**30**	851	42.41	**54**	1518	2.61
7	174	1.03	**31**	955	1.68	**55**	1527	29.72
8	201	116.27	**32**	975	0.34	**56**	1530	14.29
9	227	1.99	**33**	1016	25.42	**57**	1550	51.29
10	238	9.56	**34**	1024	106.41	**58**	1565	154.50
11	275	8.15	**35**	1046	93.02	**59**	1605	95.89
12	283	5.76	**36**	1073	7.58	**60**	1631	43.34
13	296	10.72	**37**	1080	6.90	**61**	1651	1.59
14	319	2.78	**38**	1097	91.83	**62**	3046	54.73
15	359	1.13	**39**	1139	7.00	**63**	3089	77.45
16	409	1.67	**40**	1150	137.82	**64**	3098	35.21
17	422	0.16	**41**	1185	31.01	**65**	3124	25.08
18	481	61.39	**42**	1209	0.09	**66**	3168	12.52
19	519	10.82	**43**	1264	44.87	**67**	3202	4.21
20	578	3.72	**44**	1281	18.84	**68**	3226	4.77
21	612	4.57	**45**	1308	55.33	**69**	3231	3.34
22	644	1.23	**46**	1331	15.20	**70**	3240	10.53
23	661	0.51	**47**	1337	17.37	**71**	3245	5.00
24	706	2.80	**48**	1402	203.52	**72**	3687	230.58

Table 3-89. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-11_{anion}



PY-11_{anion}

B3LYP/6-31G* Energy (E): -1070.249995 hartrees
Entropy Correction (Hv-TSv): 400.0009 kJ/mol
G° = E + "entropy correction": -671495.9016 kcal/mol

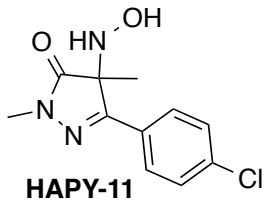
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.4250965	-0.6924571	0.4543984
C	6	2.6377142	0.0309382	0.3114764
N	7	2.2488660	1.2493368	-0.2427793
N	7	0.9009310	1.3453544	-0.4538949
C	6	0.4038333	0.1659918	-0.0304670
C	6	3.1195936	2.3547442	-0.5736850
H	1	3.0771841	2.5854211	-1.6439065
H	1	4.1352147	2.0593725	-0.3052537
H	1	2.8412982	3.2551339	-0.0152845
C	6	1.3870493	-2.0765982	1.0287998
H	1	1.0197794	-2.8348430	0.3224716
H	1	0.7681769	-2.1570887	1.9333641
H	1	2.4079439	-2.3635767	1.3073333
C	6	-1.0509396	-0.0421594	-0.1247114
C	6	-3.8398327	-0.3695892	-0.3197644
C	6	-1.6754536	-1.2409101	0.2635885
C	6	-1.8787253	0.9869129	-0.6192540
C	6	-3.2564871	0.8332999	-0.7189639
C	6	-3.0576782	-1.4097020	0.1703812
H	1	-3.8721947	1.6399439	-1.1017165
H	1	-3.5162460	-2.3430436	0.4784494
H	1	-1.0788006	-2.0590494	0.6460662
H	1	-1.4123823	1.9169838	-0.9243198
Cl	17	-5.5872521	-0.5684468	-0.4350212
O	8	3.8533111	-0.2659694	0.5926930

Table S-90. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-11$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	20	0.17	**24**	721	0.37	**47**	1423	79.97
2	53	0.16	**25**	748	24.25	**48**	1438	17.32
3	57	1.08	**26**	776	35.56	**49**	1455	42.29
4	108	0.20	**27**	835	4.52	**50**	1461	81.02
5	122	12.91	**28**	848	17.85	**51**	1504	534.06
6	139	0.05	**29**	850	34.38	**52**	1517	5.80
7	235	0.56	**30**	951	0.02	**53**	1525	20.50
8	238	0.38	**31**	976	0.14	**54**	1530	3.65
9	250	0.74	**32**	1014	60.33	**55**	1541	16.93
10	255	12.33	**33**	1025	13.09	**56**	1554	54.52
11	290	7.64	**34**	1044	36.80	**57**	1568	679.71
12	306	14.51	**35**	1053	30.99	**58**	1622	4.27

13	314	0.57	**36**	1072	0.38	**59**	1649	4.75
14	381	5.06	**37**	1102	66.37	**60**	3021	132.30
15	385	4.72	**38**	1138	16.65	**61**	3060	49.26
16	421	0.08	**39**	1171	1.49	**62**	3061	167.52
17	487	89.03	**40**	1207	8.22	**63**	3100	46.68
18	520	4.91	**41**	1220	45.96	**64**	3117	41.89
19	580	18.84	**42**	1282	105.10	**65**	3176	7.67
20	639	3.48	**43**	1293	55.23	**66**	3225	3.37
21	654	4.14	**44**	1331	4.96	**67**	3231	4.32
22	677	2.80	**45**	1336	8.76	**68**	3239	11.57
23	720	14.72	**46**	1388	73.42	**69**	3258	7.60

Table S-91. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-11



HAPY-11

B3LYP/6-31G* Energy (E): -1201.230331 hartrees
Entropy Correction (Hv-TSv): 480.9956 kJ/mol
G° = E + "entropy correction": -753667.8831 kcal/mol

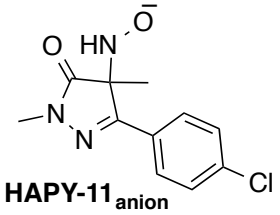
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.7456823	-0.6788200	0.2144890
C	6	3.0286965	0.1651453	0.1129251
N	7	2.6149644	1.4577745	-0.0133936
N	7	1.2340914	1.5920486	-0.0521997
C	6	0.6923159	0.4168513	0.0551792
O	8	4.1984846	-0.2298326	0.1391310
C	6	3.4487285	2.6384016	-0.1566082
H	1	3.2792916	3.1105660	-1.1275954
H	1	4.4880555	2.3191341	-0.0811883
H	1	3.2254139	3.3563943	0.6357755
C	6	1.7097332	-1.3847856	1.5798629
H	1	2.6020638	-2.0046604	1.6856240
H	1	0.8281522	-2.0215208	1.6798203
H	1	1.6922063	-0.6511661	2.3919213
N	7	1.7149915	-1.5560907	-0.9819664
H	1	0.7932286	-1.9960883	-1.0315031
O	8	2.5889624	-2.6917181	-0.7707863

H	1	3.3697030	-2.4596622	-1.3015316
C	6	-0.7688461	0.2716010	0.0303977
C	6	-3.5592270	0.0693836	-0.0284572
C	6	-1.4066537	-0.9696437	0.1937991
C	6	-1.5735207	1.4121454	-0.1663263
C	6	-2.9573688	1.3185353	-0.1951346
C	6	-2.7966755	-1.0775060	0.1638517
H	1	-3.5663170	2.2022616	-0.3467142
H	1	-3.2762776	-2.0409970	0.2923746
H	1	-0.8308444	-1.8724597	0.3580895
H	1	-1.0965560	2.3764063	-0.2967558
Cl	17	-5.3209297	-0.0516556	-0.0637007

Table S-92. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-11

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	22	0.71	**28**	712	5.66	**55**	1367	68.06
2	54	1.08	**29**	729	11.70	**56**	1432	87.50
3	69	2.03	**30**	745	27.42	**57**	1436	85.10
4	84	3.70	**31**	763	27.43	**58**	1448	14.18
5	92	0.78	**32**	817	37.51	**59**	1472	10.30
6	113	6.46	**33**	836	10.96	**60**	1509	5.86
7	133	2.25	**34**	853	35.56	**61**	1514	12.71
8	154	2.92	**35**	884	39.30	**62**	1517	18.92
9	208	3.30	**36**	940	44.65	**63**	1528	7.14
10	222	3.08	**37**	960	1.17	**64**	1538	10.75
11	234	39.38	**38**	969	44.45	**65**	1539	81.29
12	240	1.80	**39**	988	0.18	**66**	1596	29.48
13	280	74.87	**40**	1020	79.49	**67**	1629	17.16
14	289	1.09	**41**	1035	75.53	**68**	1649	45.56
15	294	8.06	**42**	1039	42.26	**69**	1684	816.60
16	319	10.97	**43**	1068	116.69	**70**	3088	74.78
17	350	45.62	**44**	1097	104.65	**71**	3092	12.86
18	357	2.90	**45**	1130	9.05	**72**	3160	15.38
19	376	2.67	**46**	1150	9.57	**73**	3161	15.70
20	420	0.19	**47**	1175	2.66	**74**	3199	2.06
21	427	23.05	**48**	1195	18.11	**75**	3205	21.30
22	481	62.22	**49**	1220	3.29	**76**	3235	5.68
23	513	9.20	**50**	1249	59.32	**77**	3237	0.08
24	620	56.91	**51**	1264	133.16	**78**	3249	10.65
25	637	4.31	**52**	1330	35.96	**79**	3250	2.16
26	662	27.79	**53**	1341	30.73	**80**	3464	30.44
27	669	11.35	**54**	1355	98.71	**81**	3721	113.44

Table S-93. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-11$_{anion}$



HAPY-11$_{anion}$

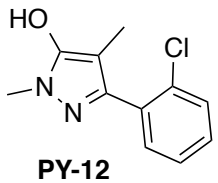
B3LYP/6-31G* Energy (E): -1200.723566 hartrees
Entropy Correction (Hv-TSv): 449.1237 kJ/mol
G° = E + "entropy correction": -753357.501 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2948369	-0.6741042	0.4013380
C	6	2.5510678	0.1403525	0.1227574
N	7	2.1487305	1.1913447	-0.6484319
N	7	0.7733111	1.2562336	-0.8046996
C	6	0.2425771	0.2445727	-0.1800840
O	8	3.7118643	-0.0733711	0.4930840
C	6	2.9751961	2.2545045	-1.1928803
H	1	2.6779548	3.2200050	-0.7751465
H	1	2.8808814	2.2895291	-2.2814557
H	1	4.0086214	2.0384710	-0.9212023
C	6	1.1790899	-1.0345834	1.8782796
H	1	1.8821904	-1.8565906	2.0512189
H	1	0.1717026	-1.3667804	2.1384257
H	1	1.4333279	-0.1928264	2.5316034
N	7	1.4074698	-1.9193954	-0.5465835
H	1	0.4525575	-2.3157270	-0.4393963
O	8	2.3118557	-2.8649306	-0.0392392
C	6	-1.2184887	0.0976314	-0.1607725
C	6	-4.0133177	-0.1134340	-0.1642467
C	6	-2.0281232	1.1635366	-0.6040221
C	6	-1.8560979	-1.0735617	0.2835377
C	6	-3.2461754	-1.1848821	0.2821598
C	6	-3.4131302	1.0653329	-0.6101957
H	1	-3.7213462	-2.0972228	0.6242933
H	1	-4.0219523	1.8944206	-0.9523826
H	1	-1.5475368	2.0737028	-0.9437378
H	1	-1.2677857	-1.9191182	0.6216110
Cl	17	-5.7692809	-0.2431095	-0.1638320

Table S-94. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-11$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	45	5.78	**27**	704	33.21	**53**	1365	123.57
2	59	0.92	**28**	715	12.76	**54**	1415	21.07
3	76	14.51	**29**	734	8.13	**55**	1421	46.59
4	86	5.27	**30**	759	33.68	**56**	1446	21.10
5	113	2.11	**31**	801	68.36	**57**	1459	72.74
6	122	9.83	**32**	839	15.43	**58**	1509	2.40
7	159	1.68	**33**	843	14.23	**59**	1522	12.15
8	173	17.87	**34**	852	30.98	**60**	1534	3.90
9	180	7.24	**35**	959	131.63	**61**	1537	23.06
10	225	2.97	**36**	970	21.04	**62**	1538	58.38
11	243	4.35	**37**	978	1.00	**63**	1585	44.72
12	251	8.41	**38**	991	83.05	**64**	1625	27.91
13	286	16.22	**39**	1021	51.66	**65**	1647	18.21
14	300	9.12	**40**	1037	37.13	**66**	1650	284.15
15	324	1.00	**41**	1047	7.50	**67**	1685	540.97
16	359	8.61	**42**	1096	85.24	**68**	3061	51.84
17	377	5.79	**43**	1101	113.06	**69**	3098	94.98
18	408	27.73	**44**	1126	89.27	**70**	3122	9.14
19	424	0.63	**45**	1144	14.20	**71**	3150	103.01
20	459	43.71	**46**	1184	4.45	**72**	3169	18.03
21	501	30.53	**47**	1205	17.36	**73**	3190	31.64
22	509	55.21	**48**	1216	1.26	**74**	3205	3.06
23	553	164.16	**49**	1258	49.23	**75**	3221	10.21
24	617	36.64	**50**	1299	105.40	**76**	3235	0.52
25	638	9.18	**51**	1335	3.18	**77**	3241	7.54
26	663	18.91	**52**	1340	14.60	**78**	3248	4.14

Table S-95. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for Enol of PY-12



PY-12

B3LYP/6-31G* Energy (E): -1070.710534 hartrees
Entropy Correction (Hv-TSv): 430.0694 kJ/mol
G° = E + "entropy correction": -671777.7074 kcal/mol

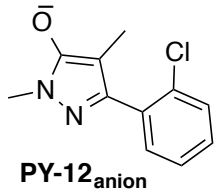
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2687381	-0.6845066	0.1740961
C	6	2.4040455	0.1142365	0.2069352
N	7	2.0374216	1.3981192	-0.0316850
N	7	0.6897942	1.5029493	-0.2132336
C	6	0.2332420	0.2450688	-0.1018371
C	6	2.8908524	2.5753940	-0.0612848
H	1	2.6800865	3.1568968	-0.9607480
H	1	3.9305955	2.2500359	-0.0733531
H	1	2.7173946	3.2012915	0.8183437
C	6	1.2095492	-2.1597120	0.4349228
H	1	1.4419363	-2.7571421	-0.4549806
H	1	0.2124100	-2.4588550	0.7716120
H	1	1.9108717	-2.4509551	1.2268217
C	6	-1.2251275	0.0071254	-0.1759793
C	6	-4.0272737	-0.3746367	-0.1991932
C	6	-2.0733285	0.7245014	0.6876360
C	6	-1.8384950	-0.8897698	-1.0655857
C	6	-3.2187280	-1.0910967	-1.0791011
C	6	-3.4529592	0.5436595	0.6804692
H	1	-3.6487194	-1.7942695	-1.7833899
H	1	-4.0752217	1.1123322	1.3638434
H	1	-5.1009555	-0.5327519	-0.2098827
H	1	-1.6148840	1.4298166	1.3725620
Cl	17	-0.8825452	-1.7625516	-2.2715532
O	8	3.7150271	-0.1678176	0.4452569
H	1	3.8162730	-1.1373627	0.4993081

Table S-96. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for Enol of PY-12

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	43	1.76	**25**	724	8.88	**49**	1448	2.08
2	44	0.19	**26**	746	23.37	**50**	1465	13.12
3	72	2.89	**27**	752	12.51	**51**	1477	23.21
4	90	2.02	**28**	778	45.69	**52**	1482	132.11
5	132	5.38	**29**	825	23.41	**53**	1510	27.72
6	136	13.90	**30**	883	0.47	**54**	1517	11.95
7	163	1.16	**31**	957	2.39	**55**	1521	5.71
8	182	15.13	**32**	988	0.06	**56**	1527	35.01
9	215	104.55	**33**	1014	13.45	**57**	1547	4.34
10	228	2.29	**34**	1030	60.36	**58**	1572	155.87
11	259	8.57	**35**	1054	125.21	**59**	1611	85.55

12	292	14.03	**36**	1072	6.55	**60**	1623	51.88
13	298	4.58	**37**	1078	5.33	**61**	1654	4.04
14	314	4.46	**38**	1088	77.05	**62**	3049	52.48
15	357	2.83	**39**	1149	14.18	**63**	3093	72.20
16	421	17.71	**40**	1161	120.35	**64**	3100	30.00
17	453	5.87	**41**	1185	6.57	**65**	3130	20.38
18	473	10.76	**42**	1192	0.23	**66**	3165	17.12
19	522	2.36	**43**	1256	27.32	**67**	3205	2.94
20	576	9.99	**44**	1288	30.38	**68**	3214	0.37
21	615	5.83	**45**	1294	12.45	**69**	3223	11.67
22	654	18.62	**46**	1308	85.09	**70**	3234	20.78
23	662	3.25	**47**	1333	2.74	**71**	3241	9.03
24	707	25.78	**48**	1408	214.27	**72**	3690	242.69

Table S-97. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for PY-12$_{anion}$



PY-12$_{anion}$

B3LYP/6-31G* Energy (E): -1070.242766 hartrees
Entropy Correction (Hv-TSv): 399.4654 kJ/mol
G° = E + "entropy correction": -671491.4933 kcal/mol

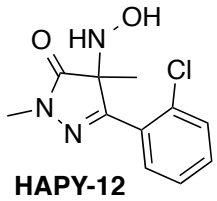
Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.4297665	-0.7280154	0.1634182
C	6	2.6149212	0.0488761	0.2374611
N	7	2.1806109	1.3596018	0.0499032
N	7	0.8227485	1.4658153	-0.1409676
C	6	0.3855910	0.1931895	-0.0742168
C	6	3.0180163	2.5356561	-0.0124193
H	1	2.9909902	2.9942252	-1.0077092
H	1	4.0387684	2.2204458	0.2115265
H	1	2.6975543	3.2836594	0.7204662
C	6	1.3895340	-2.2063190	0.3924421
H	1	1.5828029	-2.7953073	-0.5159923
H	1	0.4166419	-2.5331395	0.7781964
H	1	2.1559981	-2.4936633	1.1240491
C	6	-1.0719389	-0.0432802	-0.1509590
C	6	-3.8863172	-0.4072599	-0.1659528
C	6	-1.9236168	0.7043382	0.6875471

C	6	-1.6971193	-0.9591548	-1.0139833
C	6	-3.0795610	-1.1527327	-1.0224326
C	6	-3.3043341	0.5343600	0.6842625
H	1	-3.5093976	-1.8735835	-1.7088584
H	1	-3.9199002	1.1300703	1.3508681
H	1	-4.9608276	-0.5598796	-0.1726420
H	1	-1.4543899	1.4257288	1.3481327
Cl	17	-0.7550505	-1.8676836	-2.2077211
O	8	3.8385088	-0.2759476	0.4455808

Table S-98. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for PY-12$_{anion}$

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	34	0.98	**24**	736	2.04	**47**	1436	61.72
2	55	0.74	**25**	749	27.75	**48**	1449	113.42
3	72	0.46	**26**	769	10.05	**49**	1461	9.73
4	92	0.92	**27**	776	67.65	**50**	1471	17.52
5	124	0.08	**28**	852	10.10	**51**	1503	419.71
6	133	12.14	**29**	878	0.93	**52**	1512	15.06
7	163	1.23	**30**	947	2.75	**53**	1522	7.30
8	178	0.69	**31**	975	0.21	**54**	1524	24.77
9	226	0.83	**32**	1010	12.77	**55**	1551	159.30
10	254	2.59	**33**	1031	26.05	**56**	1564	269.46
11	287	9.44	**34**	1050	101.13	**57**	1590	177.55
12	303	11.69	**35**	1056	26.17	**58**	1616	9.37
13	317	11.82	**36**	1074	2.95	**59**	1650	4.57
14	352	2.44	**37**	1089	42.89	**60**	3022	134.55
15	419	18.92	**38**	1145	8.52	**61**	3066	62.38
16	455	17.71	**39**	1186	0.22	**62**	3069	138.62
17	471	11.45	**40**	1220	55.00	**63**	3105	46.12
18	528	0.72	**41**	1230	8.34	**64**	3143	49.99
19	581	28.23	**42**	1273	86.46	**65**	3181	15.45
20	635	2.09	**43**	1284	3.70	**66**	3213	2.54
21	655	20.92	**44**	1306	56.17	**67**	3223	13.37
22	691	4.95	**45**	1331	2.35	**68**	3234	22.73
23	712	32.68	**46**	1394	75.57	**69**	3243	9.36

Table S-99. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-12



HAPY-12

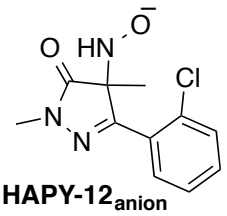
B3LYP/6-31G* Energy (E): -1201.220982 hartrees
Entropy Correction (Hv-TSv): 481.3899 kJ/mol
G° = E + "entropy correction": -753661.9222 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2191291	-0.8757850	0.0806324
C	6	2.5003867	-0.0413677	0.2509508
N	7	2.0972747	1.1632027	0.7498347
N	7	0.7147166	1.2685746	0.8905761
C	6	0.1790996	0.1531967	0.5204658
O	8	3.6624157	-0.3781222	0.0053310
C	6	2.9339191	2.3069961	1.0667669
H	1	2.6840903	3.1536684	0.4223967
H	1	3.9698295	2.0122475	0.8992419
H	1	2.7982690	2.5981430	2.1109020
C	6	1.2911929	-2.1395399	0.9487114
H	1	2.1717872	-2.7187327	0.6637892
H	1	0.4040342	-2.7601559	0.7983481
H	1	1.3693946	-1.8852040	2.0106885
N	7	1.0128659	-1.1158829	-1.3672839
H	1	0.0789286	-1.5225818	-1.4733599
O	8	1.8748288	-2.1956326	-1.8046529
H	1	2.5431161	-1.7301722	-2.3356671
C	6	-1.2899593	-0.0257394	0.4982282
C	6	-4.0845419	-0.4156443	0.5093985
C	6	-1.8855061	-1.0343100	1.2782063
C	6	-2.1444001	0.7795207	-0.2791539
C	6	-3.5250510	0.5898983	-0.2769111
C	6	-3.2637844	-1.2287637	1.2895626
H	1	-4.1498393	1.2265665	-0.8927613
H	1	-3.6923379	-2.0088390	1.9095908
H	1	-5.1603033	-0.5580134	0.5067946
H	1	-1.2516414	-1.6521557	1.9031232
Cl	17	-1.5053065	2.0530868	-1.3293838

Table S-100. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-12

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	25	0.48	**28**	704	46.11	**55**	1370	68.11
2	55	0.84	**29**	739	22.31	**56**	1426	12.59
3	72	3.93	**30**	745	19.10	**57**	1432	134.85
4	86	1.01	**31**	759	34.30	**58**	1469	6.97
5	93	0.77	**32**	776	51.07	**59**	1473	43.71
6	116	6.40	**33**	820	23.69	**60**	1508	5.85
7	139	1.32	**34**	884	19.71	**61**	1513	12.67
8	154	0.29	**35**	888	17.28	**62**	1520	14.44
9	180	13.14	**36**	936	42.18	**63**	1527	9.70
10	233	66.64	**37**	964	5.40	**64**	1532	18.53
11	247	24.96	**38**	967	25.94	**65**	1542	27.71
12	258	5.82	**39**	997	0.16	**66**	1619	4.12
13	269	18.32	**40**	1023	60.47	**67**	1643	17.46
14	281	7.98	**41**	1034	57.59	**68**	1650	18.67
15	294	5.30	**42**	1054	76.73	**69**	1687	658.97
16	316	19.37	**43**	1062	89.02	**70**	3078	15.61
17	336	3.31	**44**	1090	14.36	**71**	3090	62.15
18	354	17.69	**45**	1127	8.45	**72**	3152	15.92
19	411	17.74	**46**	1162	6.34	**73**	3162	15.84
20	412	7.39	**47**	1178	2.14	**74**	3168	15.31
21	455	10.88	**48**	1200	3.15	**75**	3198	2.12
22	464	12.86	**49**	1205	8.80	**76**	3219	2.05
23	515	1.60	**50**	1250	99.47	**77**	3232	13.69
24	612	43.58	**51**	1257	50.85	**78**	3243	8.51
25	636	8.31	**52**	1304	6.33	**79**	3256	5.41
26	653	21.57	**53**	1318	25.10	**80**	3435	23.83
27	690	3.09	**54**	1347	55.81	**81**	3719	108.69

Table S-101. B3LYP/6-31G* Optimized Geometries, Energies, and Entropy Corrections for HAPY-12$_{anion}$



HAPY-12$_{anion}$

B3LYP/6-31G* Energy (E): -1200.713193 hartrees
Entropy Correction (Hv-TSv): 445.1987 kJ/mol
G° = E + "entropy correction": -753351.93 kcal/mol

Atom	Atomic Number	Cartesian Coordinates (Angstroms) X	Y	Z
C	6	1.2678813	-0.6989743	-0.2354491
C	6	2.5292334	0.0969556	0.0547601
N	7	2.1175863	1.3808600	0.2674859
N	7	0.7324748	1.5103648	0.3040883
C	6	0.2183360	0.3409755	0.0831598
O	8	3.7025328	-0.2962609	0.0947223
C	6	2.9447879	2.5293061	0.5919196
H	1	2.7925998	3.3268526	-0.1400153
H	1	3.9843059	2.2016374	0.5655375
H	1	2.7017690	2.9065684	1.5888003
C	6	1.2394100	-2.0391026	0.4799732
H	1	1.9850129	-2.6691929	-0.0157334
H	1	0.2622363	-2.5181390	0.3723935
H	1	1.4765982	-1.9560601	1.5464223
N	7	1.2244901	-0.8711379	-1.8056417
H	1	0.2585456	-1.2601583	-1.8911308
O	8	2.1197043	-1.8624342	-2.2267148
C	6	-1.2488857	0.1630544	0.0443132
C	6	-4.0508320	-0.2145894	0.0956645
C	6	-1.8516645	-0.7734254	0.9067195
C	6	-2.1060999	0.9079187	-0.7885184
C	6	-3.4879794	0.7222490	-0.7685295
C	6	-3.2298558	-0.9636736	0.9376613
H	1	-4.1093499	1.3122248	-1.4324461
H	1	-3.6560395	-1.6896661	1.6218398
H	1	-5.1270949	-0.3526332	0.1063234
H	1	-1.2121141	-1.3347802	1.5779229
Cl	17	-1.4775890	2.1012609	-1.9355283

Table S-102. B3LYP/6-31G* Calculated IR Frequencies (cm^{-1}, uncorrected) and Intensities for HAPY-12_{anion}

	cm^{-1}	Intensity		cm^{-1}	Intensity		cm^{-1}	Intensity
1	28	3.36	**27**	700	17.42	**53**	1353	88.59
2	49	6.93	**28**	704	63.01	**54**	1403	20.11
3	69	7.36	**29**	743	21.64	**55**	1425	51.66
4	74	2.40	**30**	754	36.49	**56**	1455	69.44
5	86	11.16	**31**	773	56.16	**57**	1466	40.04
6	119	13.00	**32**	791	25.81	**58**	1504	2.19
7	142	13.15	**33**	836	7.01	**59**	1508	8.68
8	148	1.23	**34**	884	0.20	**60**	1518	20.09
9	178	0.45	**35**	958	5.36	**61**	1524	3.17
10	196	26.46	**36**	961	121.91	**62**	1529	19.66
11	246	2.74	**37**	984	40.74	**63**	1586	56.26
12	251	6.92	**38**	989	41.89	**64**	1613	15.15
13	277	2.66	**39**	1028	76.77	**65**	1624	46.87
14	300	21.30	**40**	1044	11.10	**66**	1647	7.71
15	312	2.98	**41**	1055	49.67	**67**	1674	666.74
16	343	0.69	**42**	1077	44.26	**68**	3055	49.35
17	370	48.33	**43**	1086	27.25	**69**	3063	129.14
18	406	20.66	**44**	1120	30.48	**70**	3088	83.27
19	435	5.01	**45**	1151	6.68	**71**	3124	6.92
20	452	8.11	**46**	1171	2.36	**72**	3144	32.70
21	468	4.29	**47**	1190	1.12	**73**	3156	19.19
22	514	46.17	**48**	1217	13.27	**74**	3199	3.48
23	535	153.02	**49**	1264	93.62	**75**	3222	0.43
24	606	51.78	**50**	1280	28.01	**76**	3233	8.45
25	643	26.57	**51**	1295	10.08	**77**	3243	10.71
26	652	16.14	**52**	1319	12.08	**78**	3247	9.89

Reference

(1) Shao Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio Jr., R. A.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C-P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W. Z.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock III, H. L.; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F.; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006***, 8*, 3172–3191.

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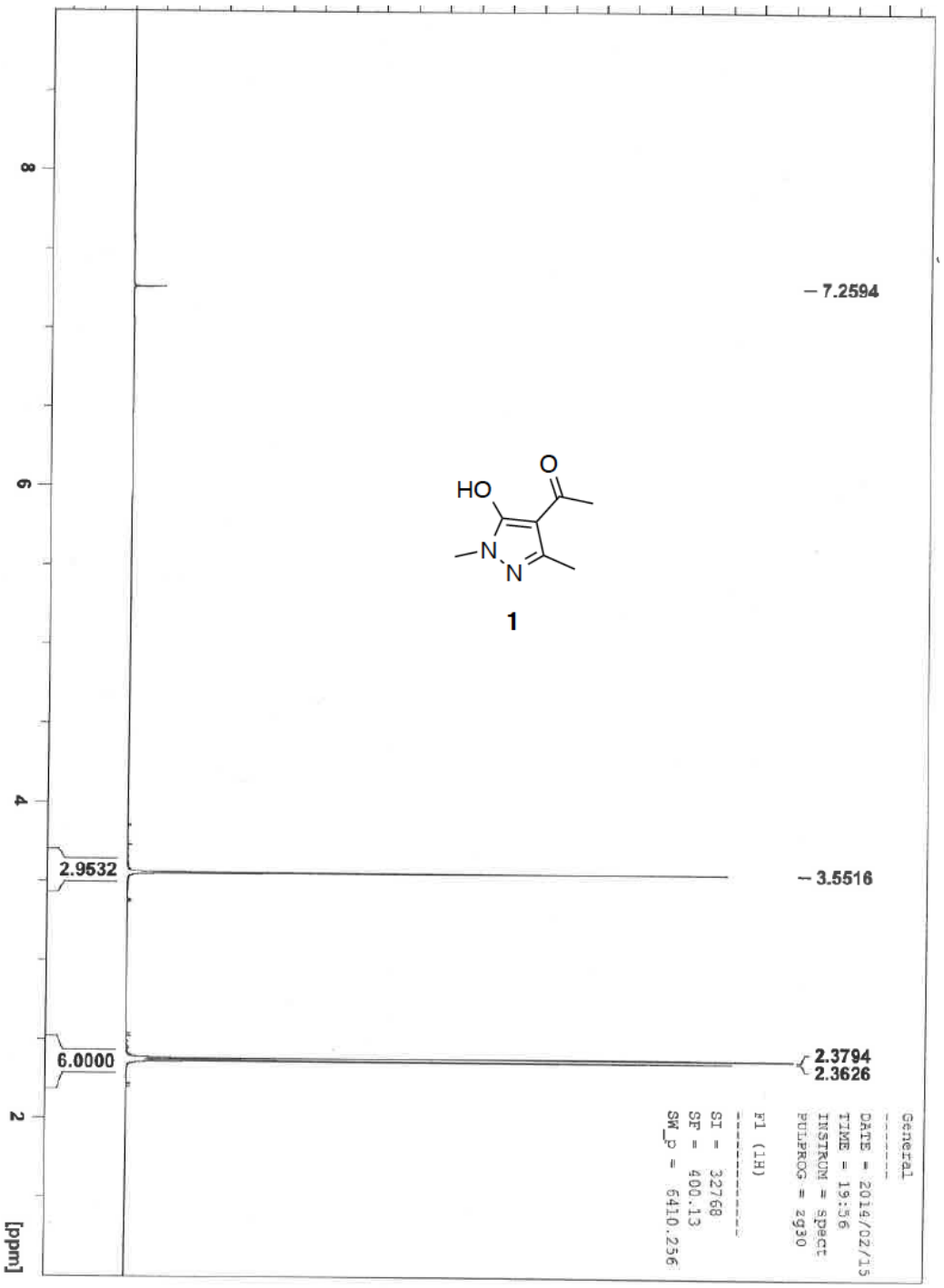

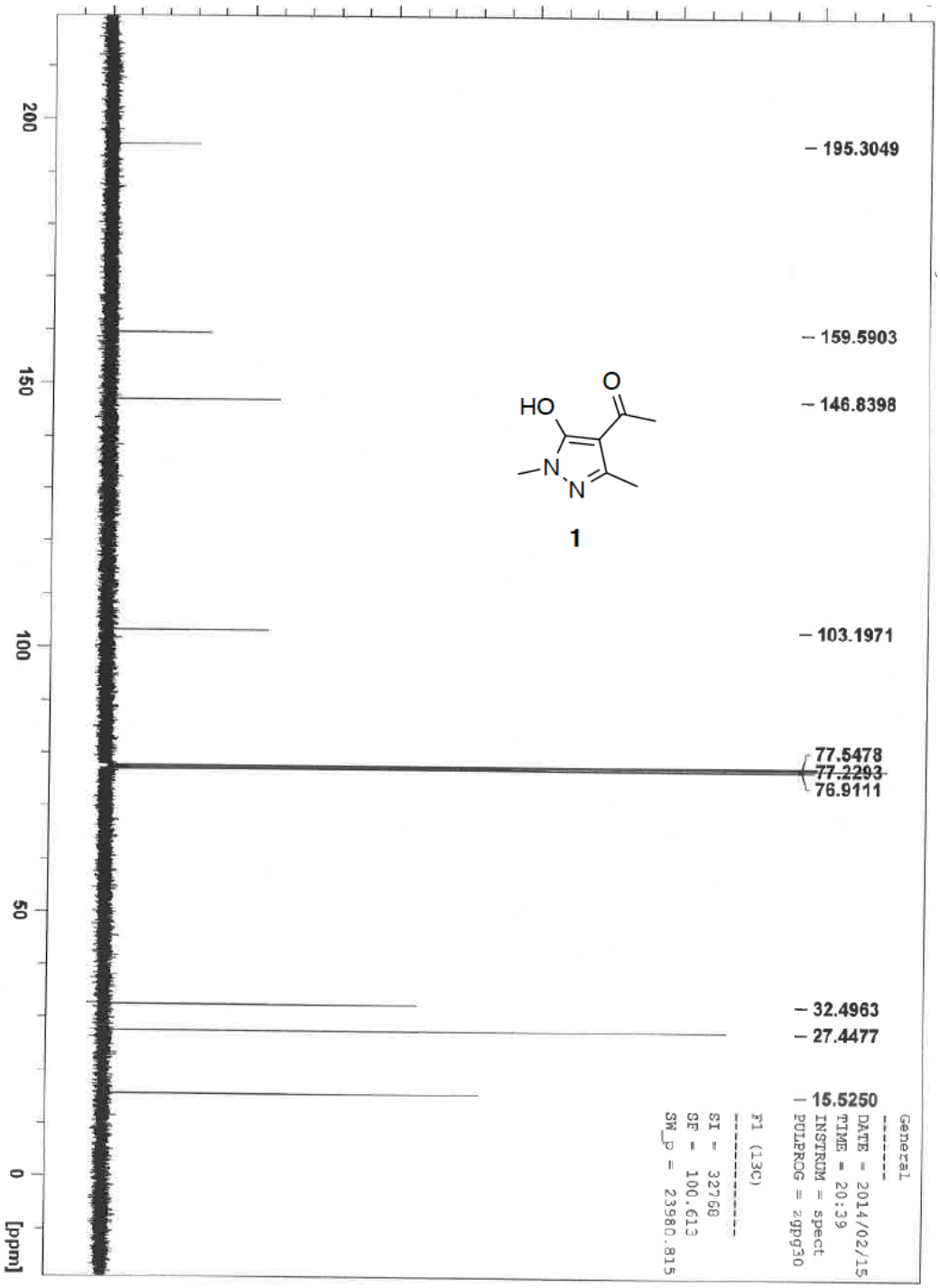
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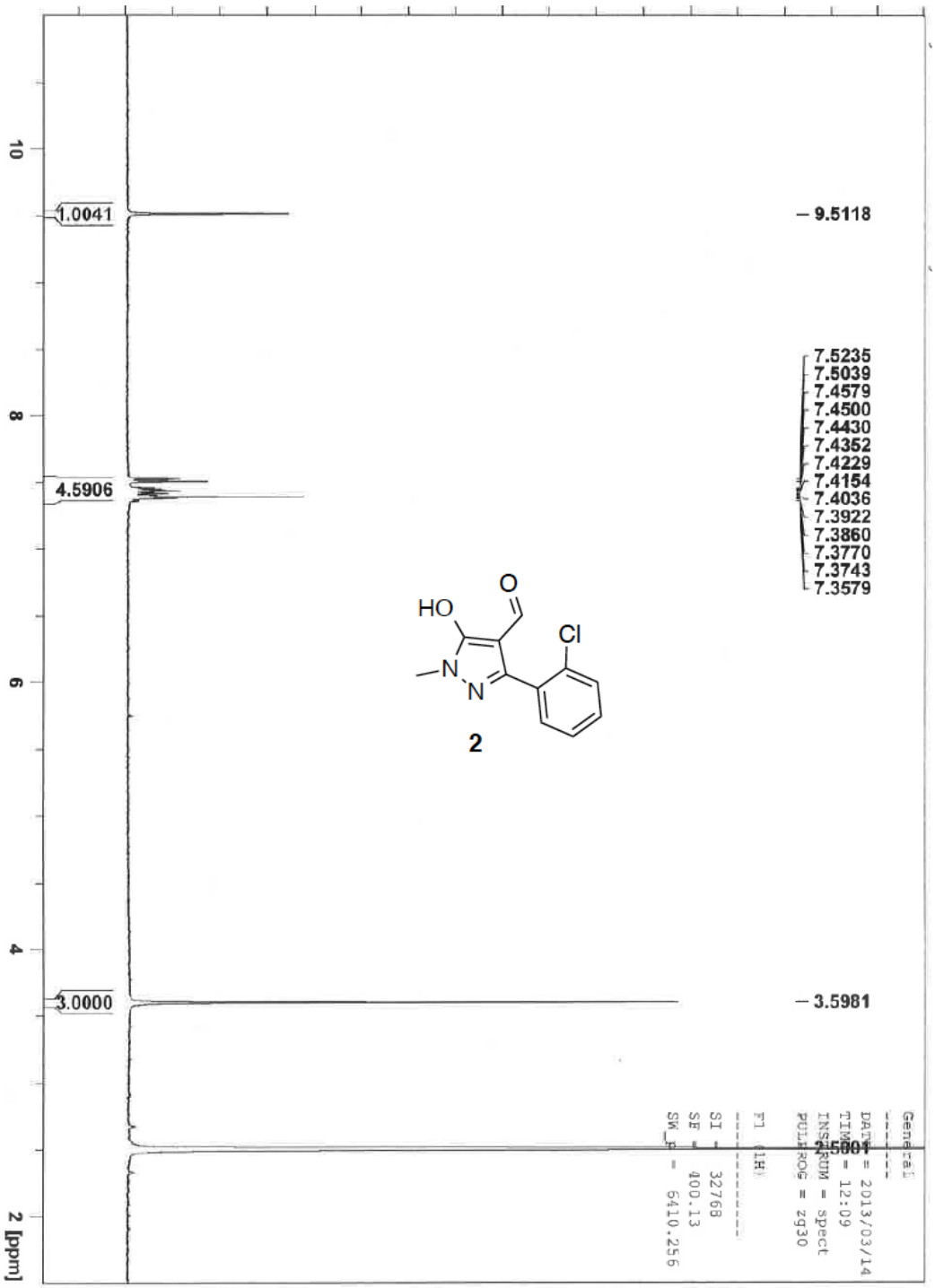
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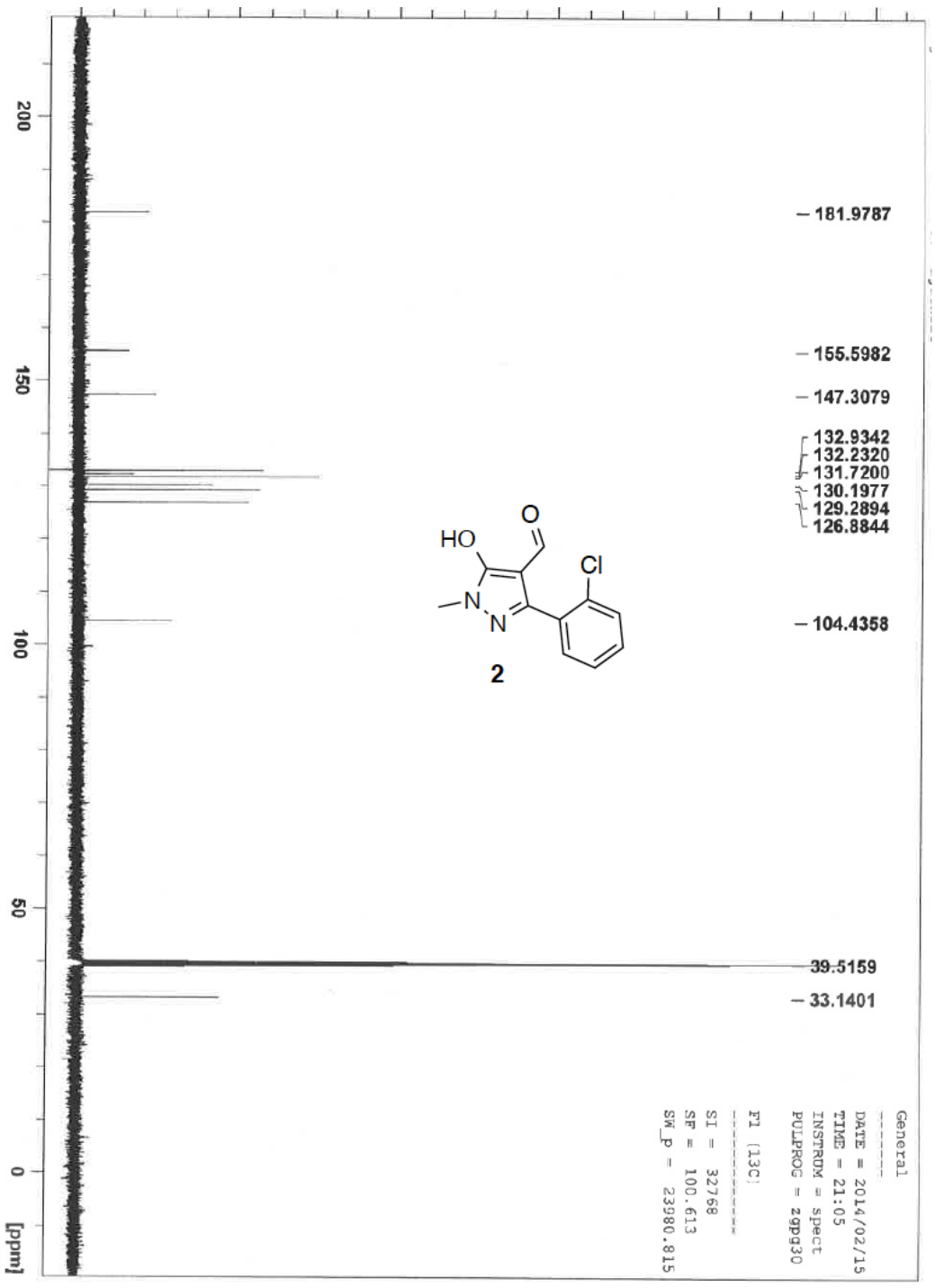
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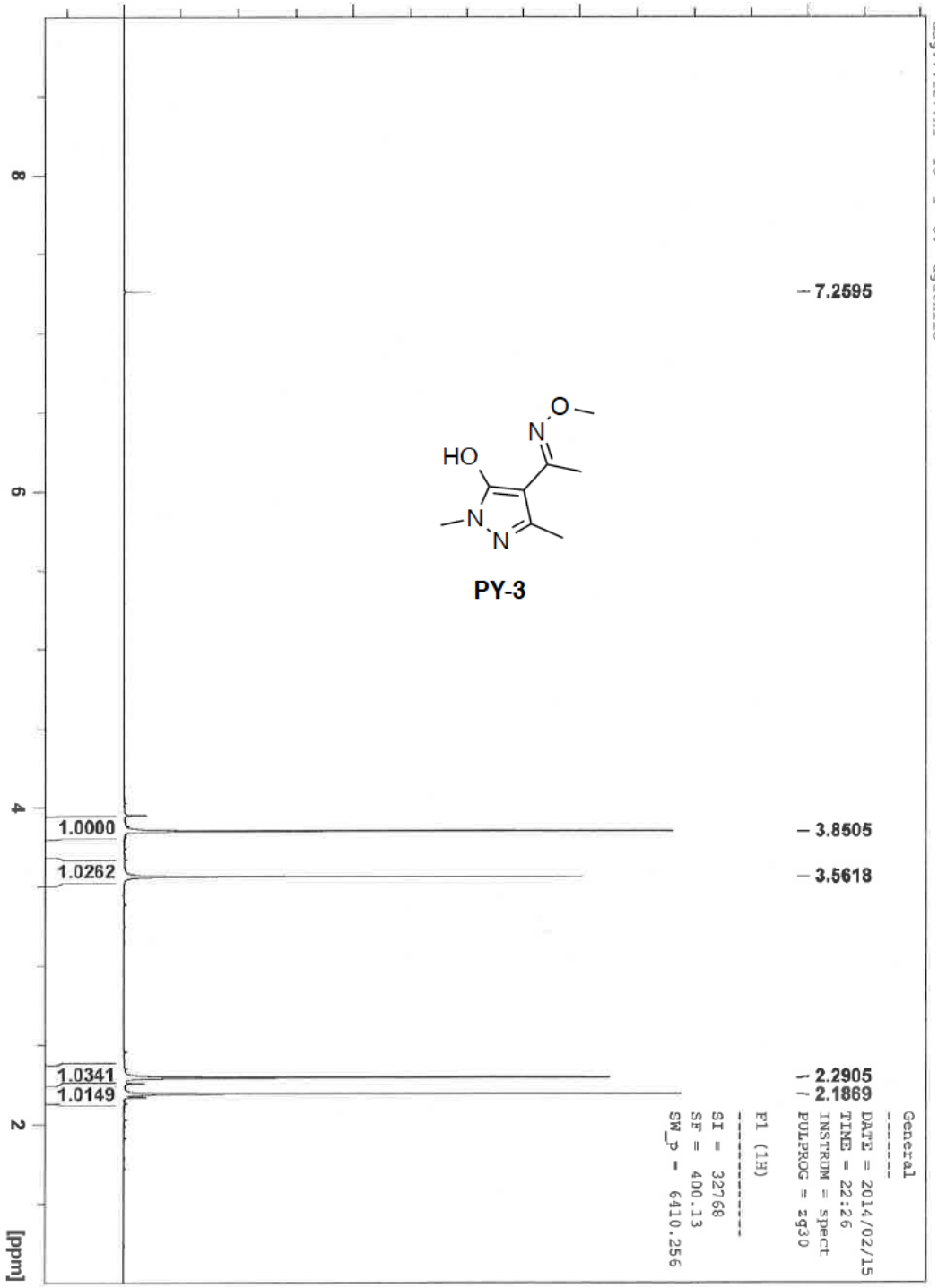
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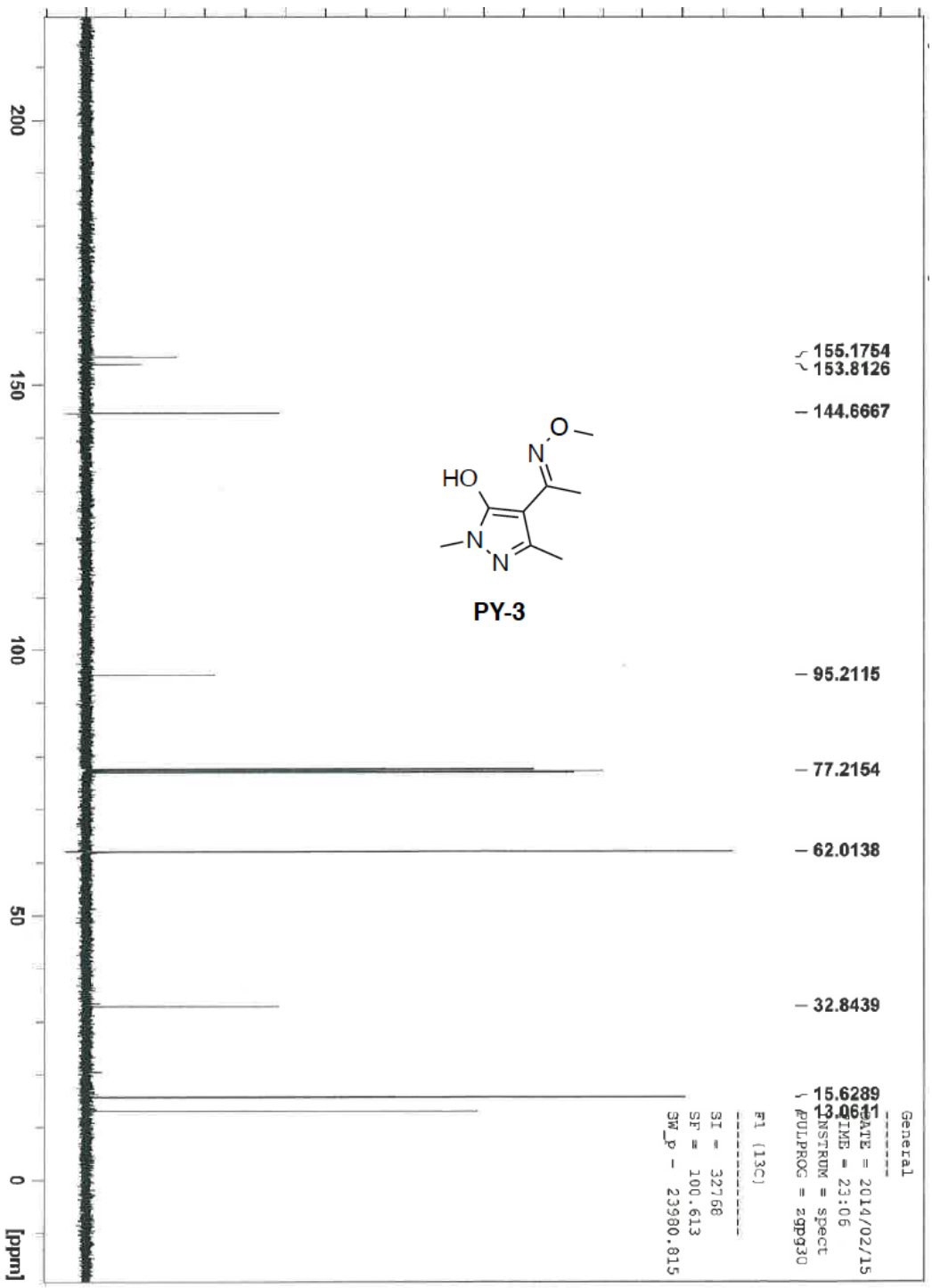
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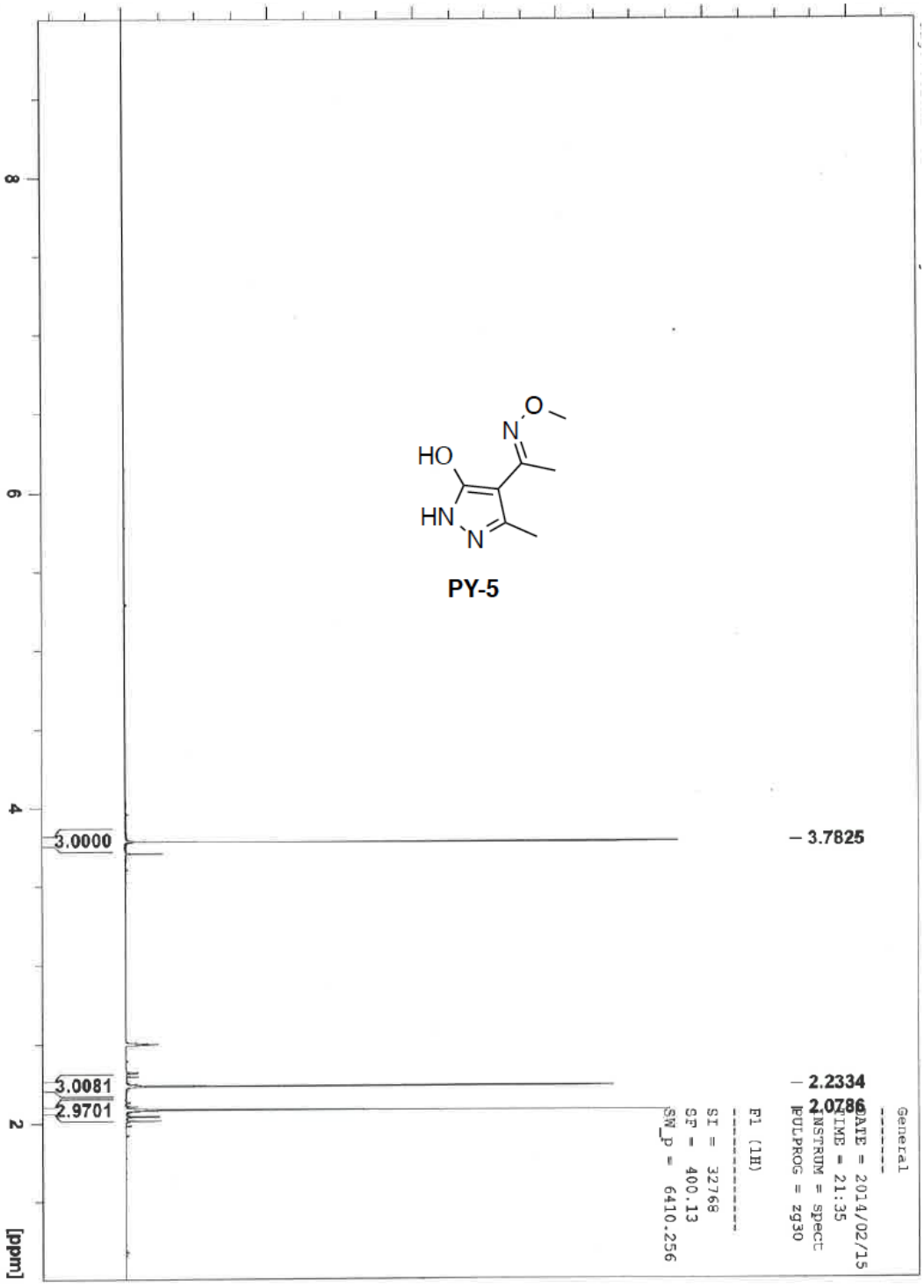
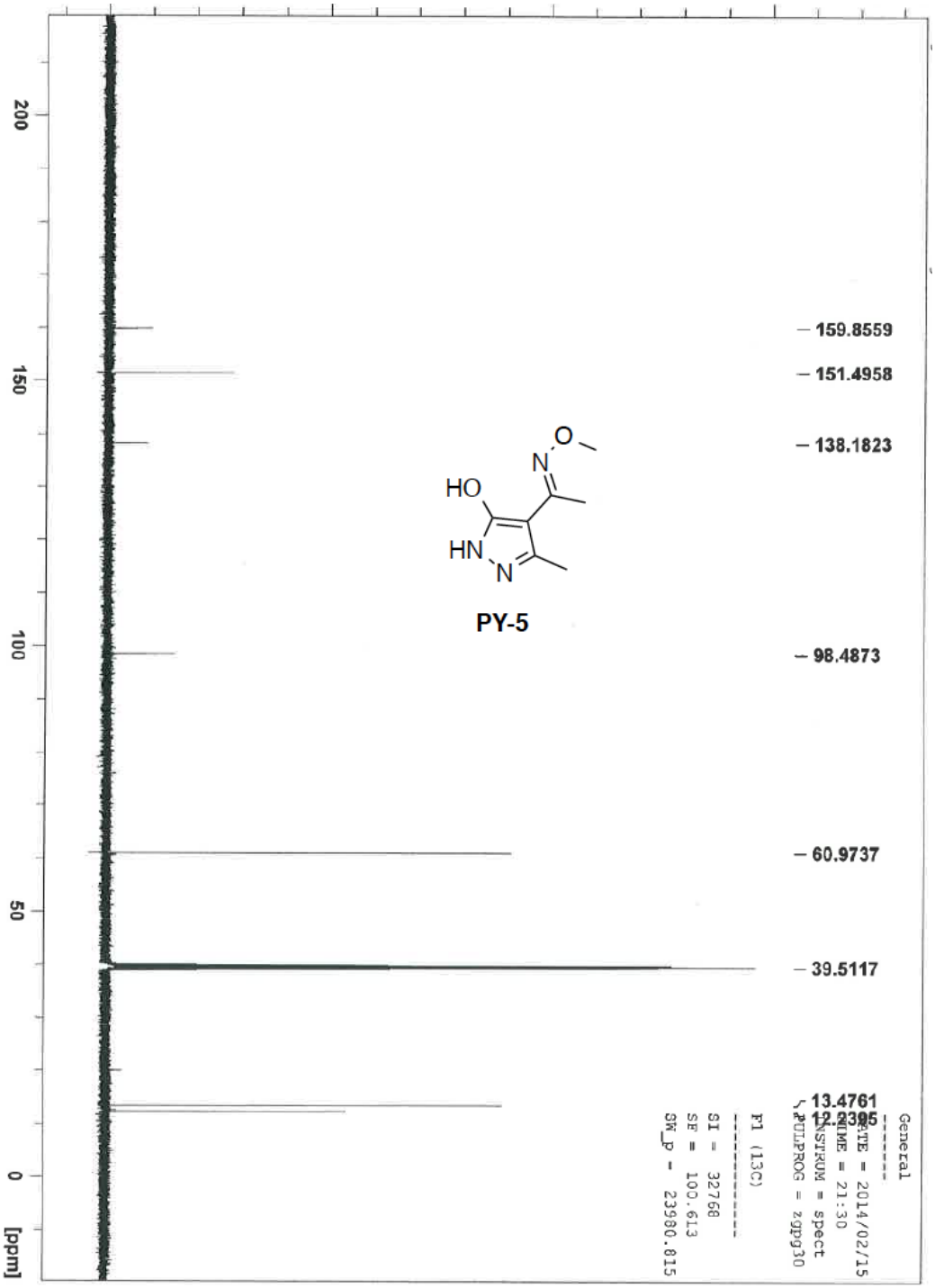
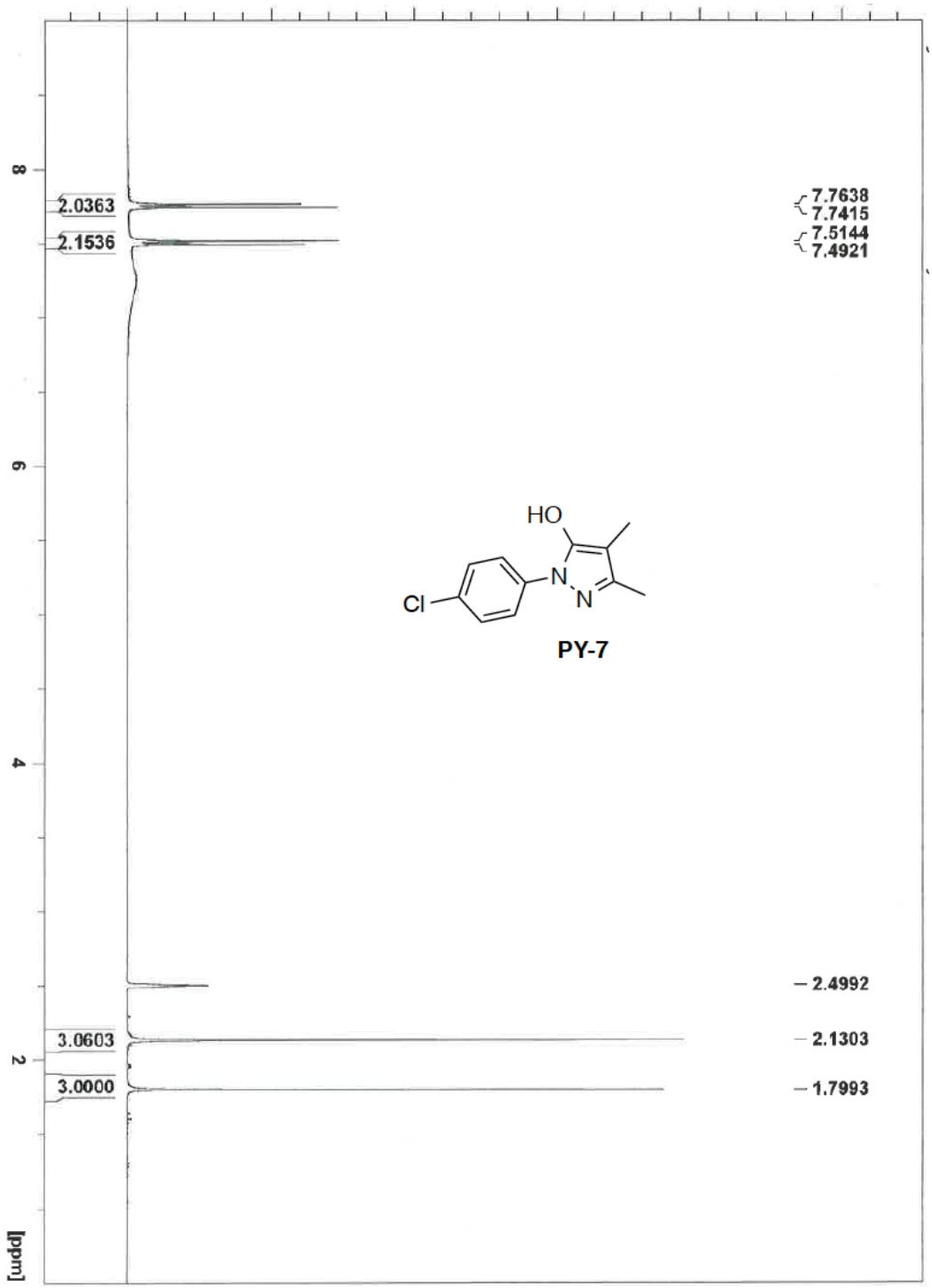
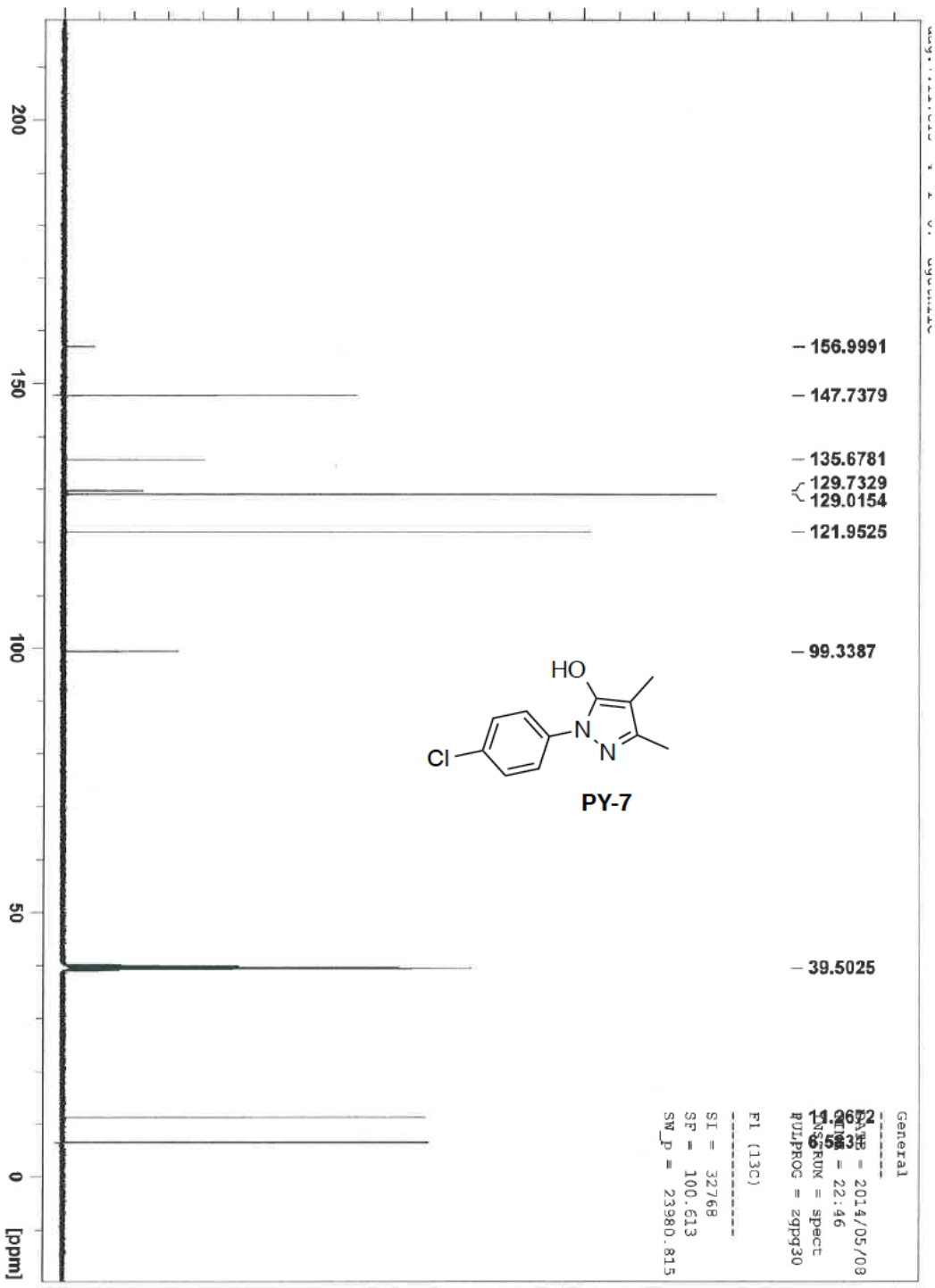
DATE = 2014/02/15
TIME = 23:06
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

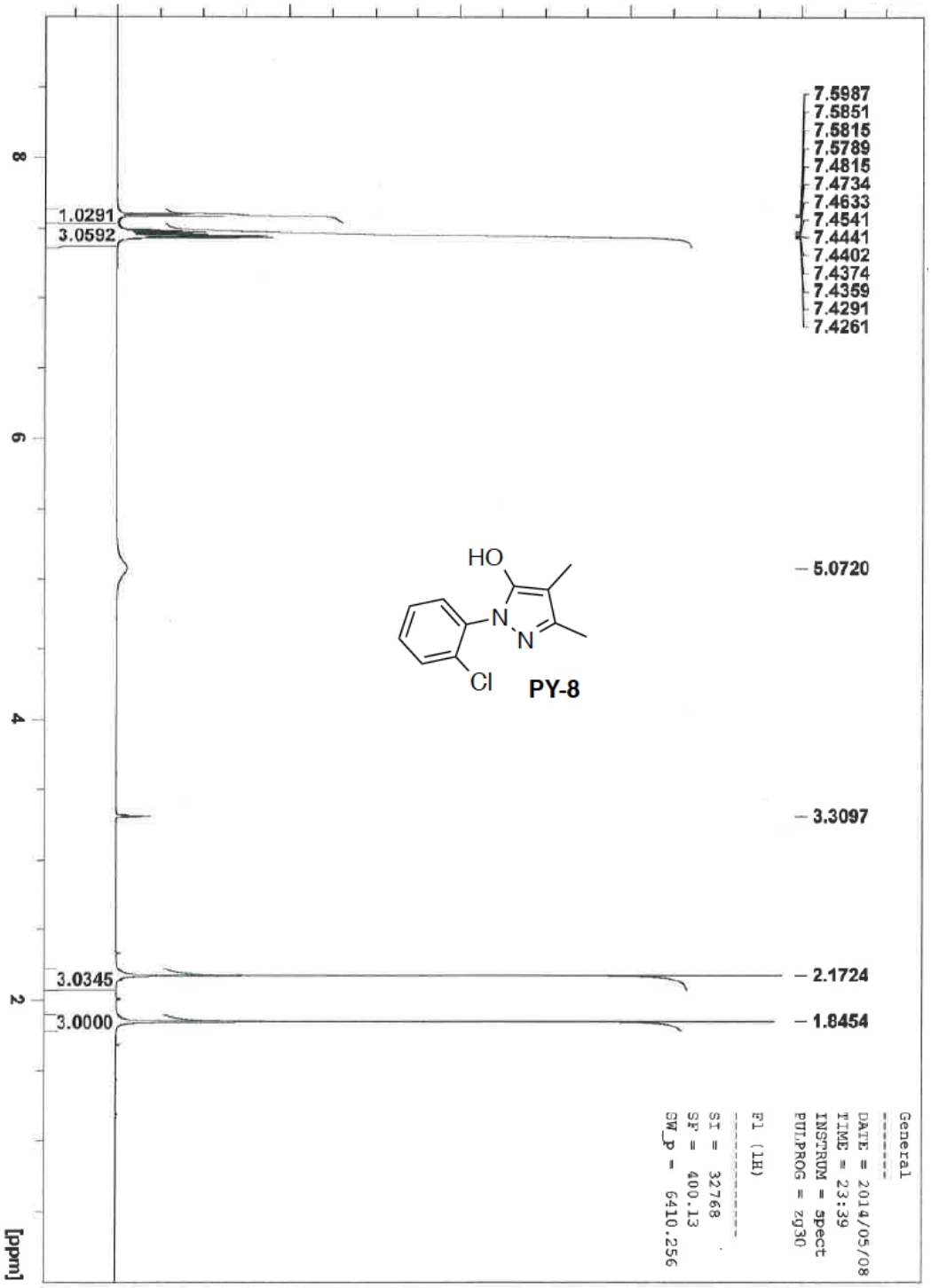

HO
N
O
HN
N
PY-5
3.0000
3.0081
2.9701
3.7825
2.2334
2.0786
Solvent
Creation_DATE = 2014/02/15
Creation_TIME = 21:35
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256
8
6
4
2
[ppm]

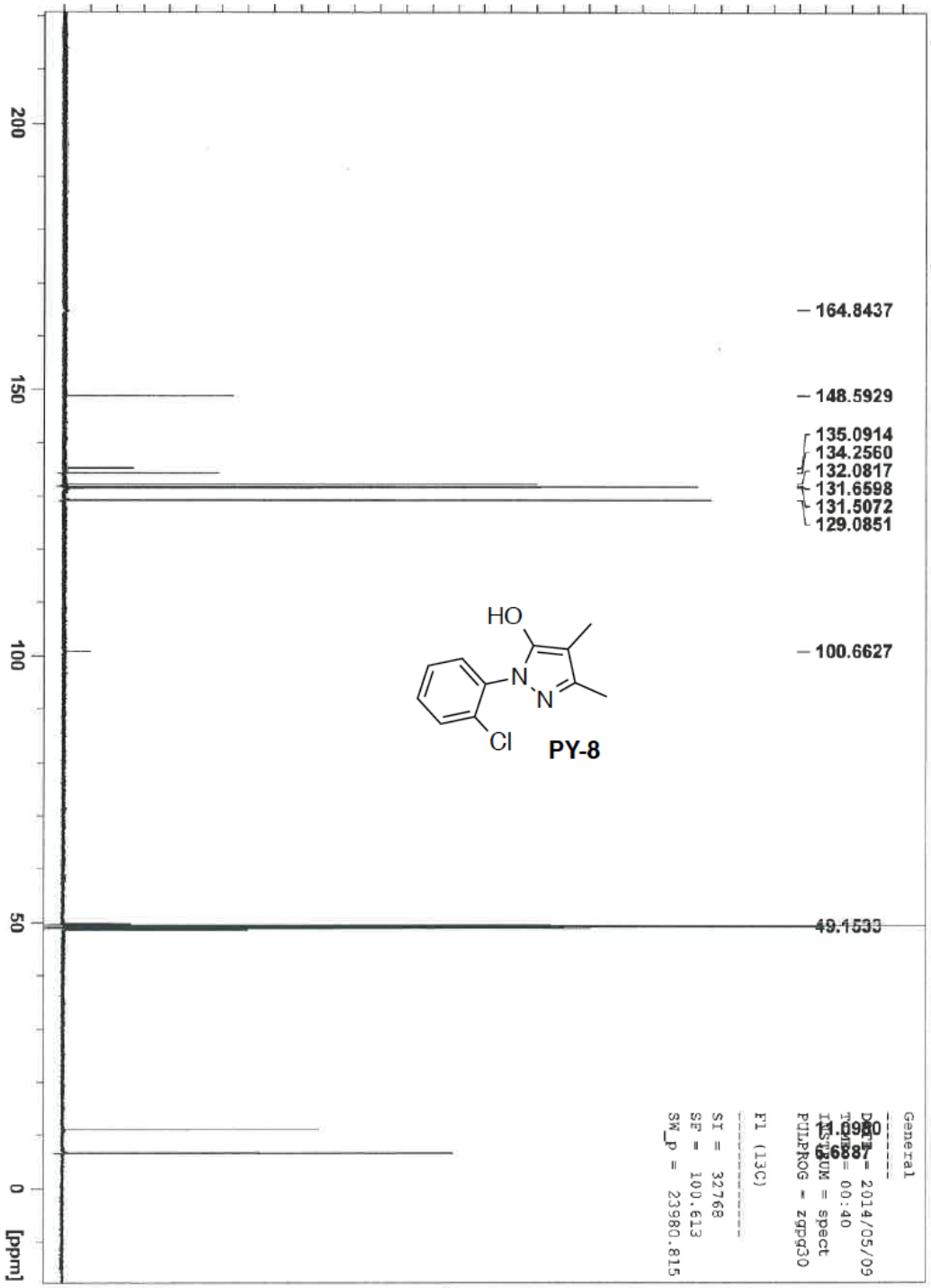

159.8559
151.4958
138.1823
98.4873
60.9737
39.5117
13.4761
12.2395
HO
HN
N
O
N
PY-5
200
150
100
50
0
[ppm]
General
DATE = 2014/02/15
TIME = 21:30
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

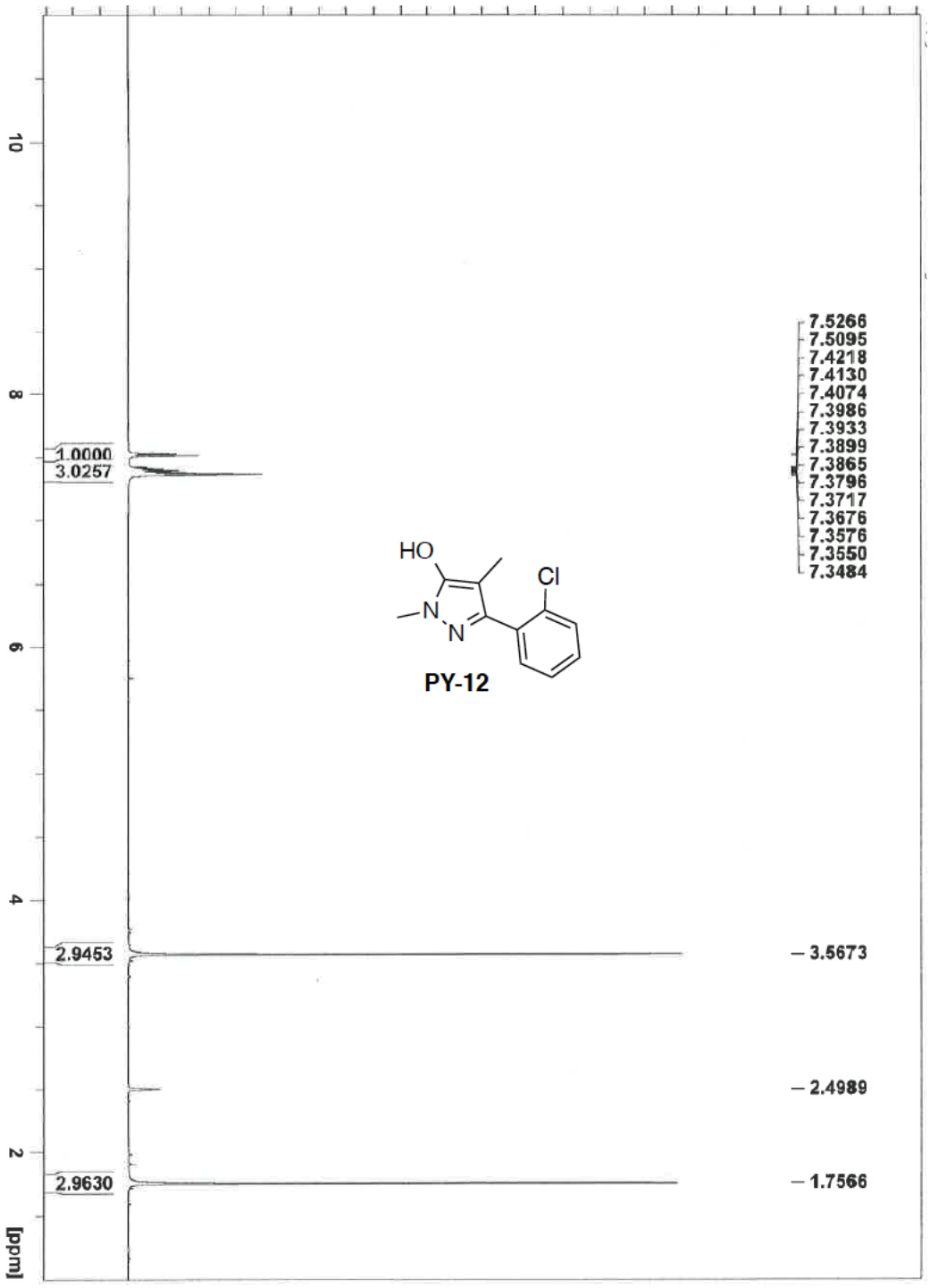

8
6
4
2
[ppm]
2.0363
2.1536
3.0603
3.0000
7.7638
7.7415
7.5144
7.4921
2.4992
2.1303
1.7993
HO
N
N
Cl

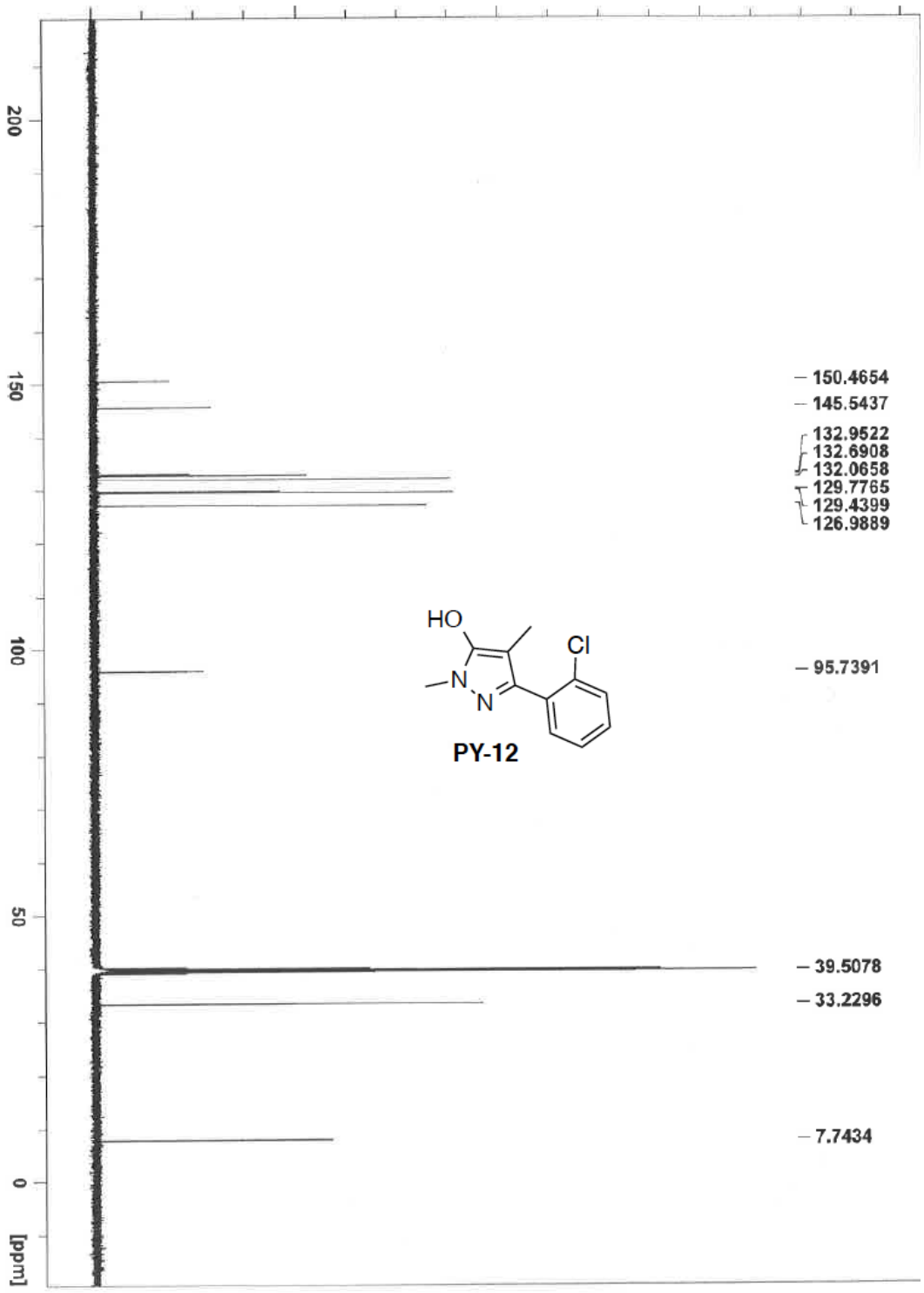
PY-7

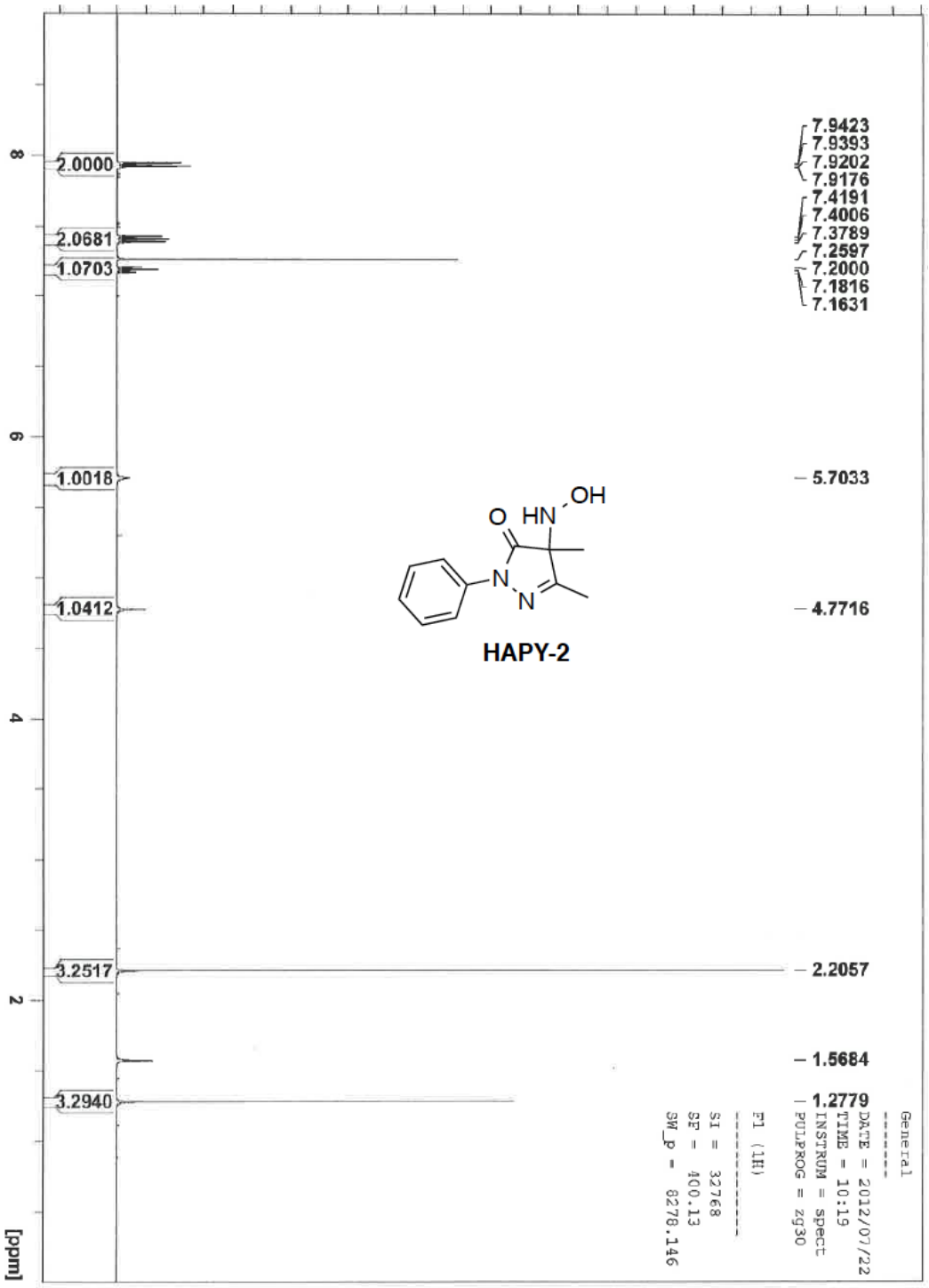

156.9991
147.7379
135.6781
129.7329
129.0154
121.9525
99.3387
39.5025
HO
N
N
Cl
PY-7
200
150
100
50
0
[ppm]

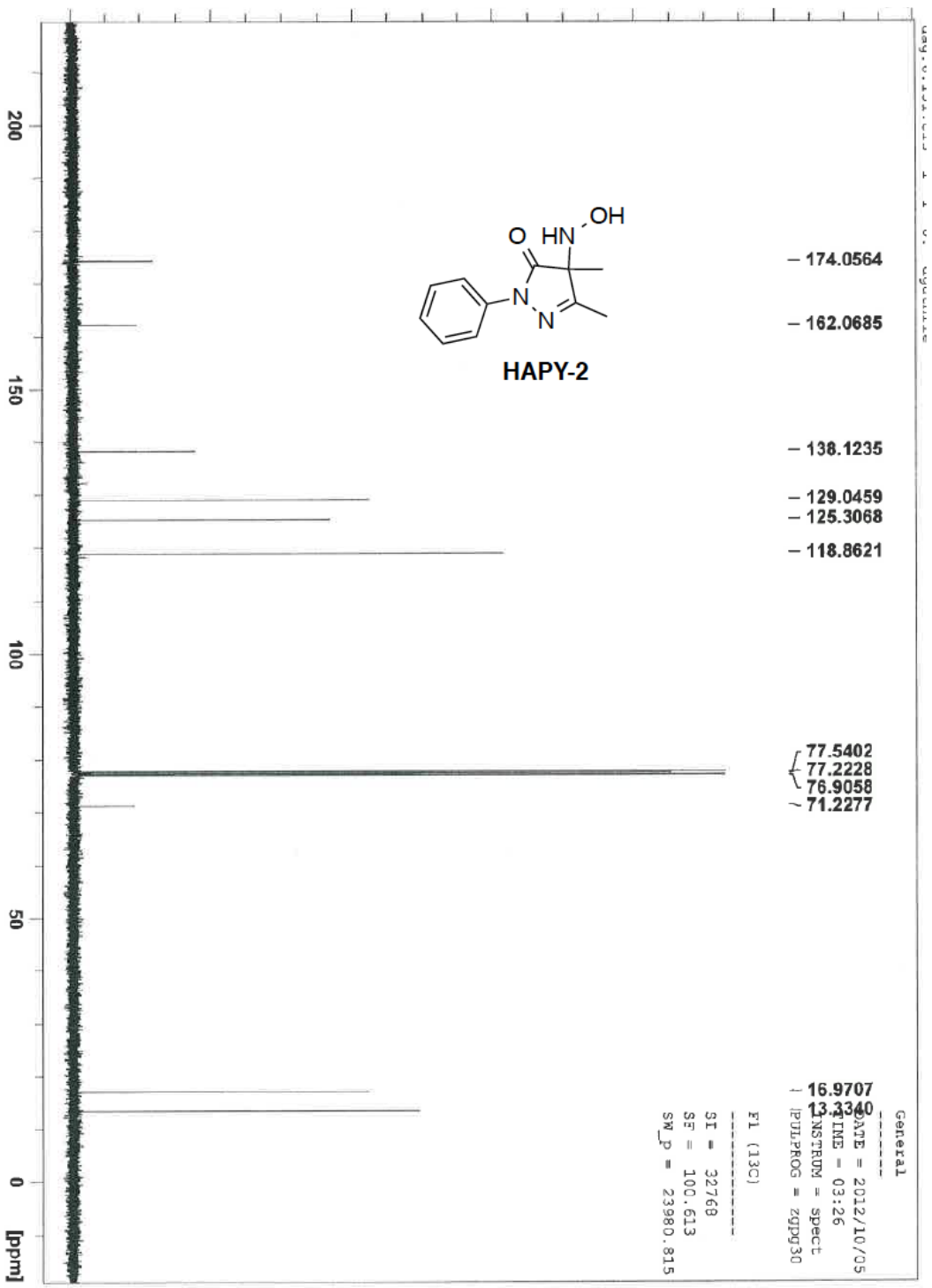

7.5987
7.5851
7.5815
7.5789
7.4815
7.4734
7.4633
7.4541
7.4441
7.4402
7.4374
7.4359
7.4291
7.4261
1.0291
3.0592
5.0720
3.3097
3.0345
3.0000
2.1724
1.8454
HO
N
N
Cl
PY-8
[ppm]
General
DATE = 2014/05/08
TIME = 23:39
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256

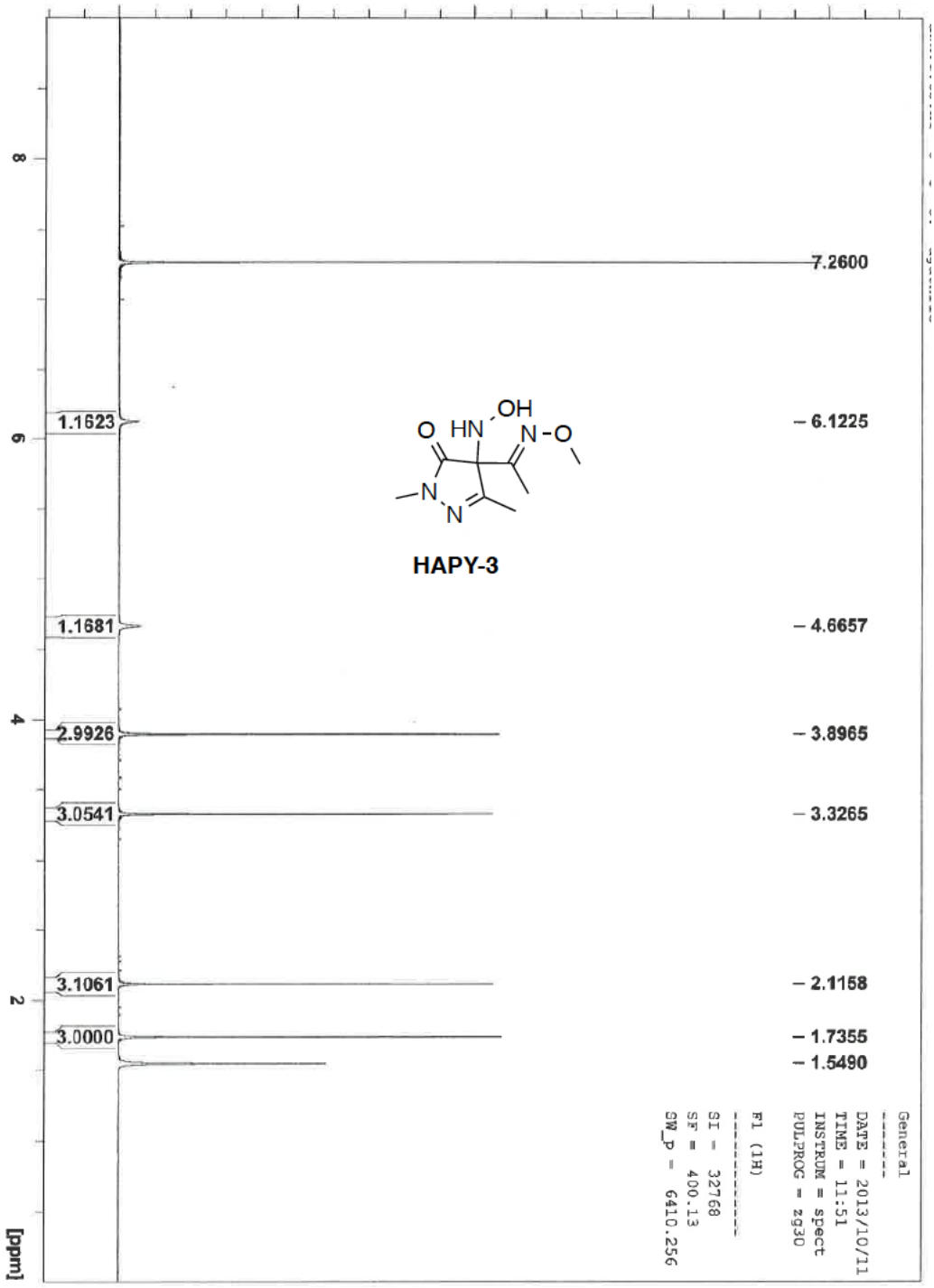

164.8437
148.5929
135.0914
134.2560
132.0817
131.6598
131.5072
129.0851
100.6627
49.1533
11.0980
8.6887
HO
N
N
Cl
PY-8
200
150
100
50
0
[ppm]
General
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815
PULPROG = zgpg30
NS = spect
TIME= 00:40
DATE= 2014/05/09

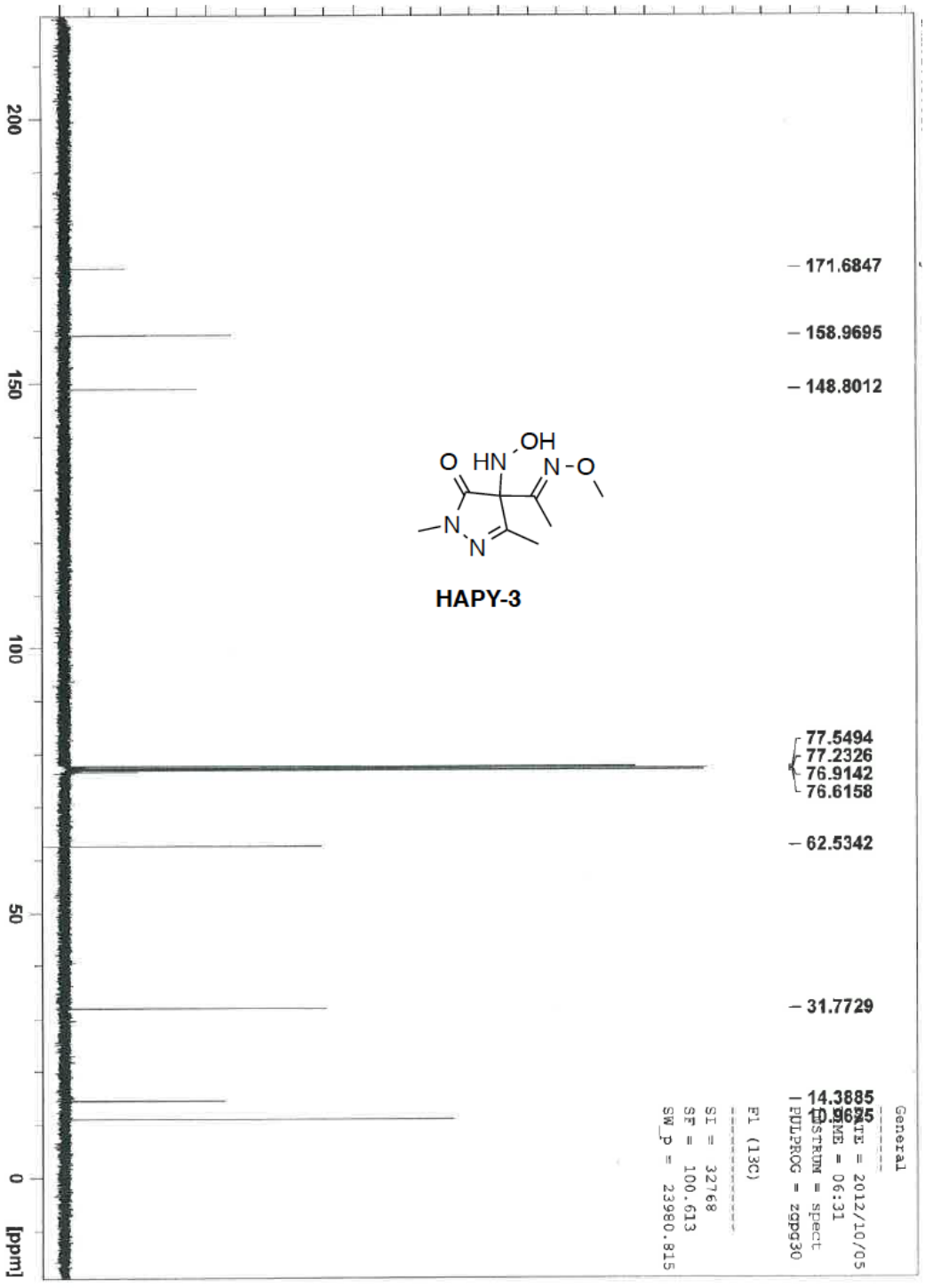

10
8
6
4
2
[ppm]
1.0000
3.0257
2.9453
2.9630
7.5266
7.5095
7.4218
7.4130
7.4074
7.3986
7.3933
7.3899
7.3865
7.3796
7.3717
7.3676
7.3576
7.3550
7.3484
3.5673
2.4989
1.7566
HO
Cl
N
N
PY-12

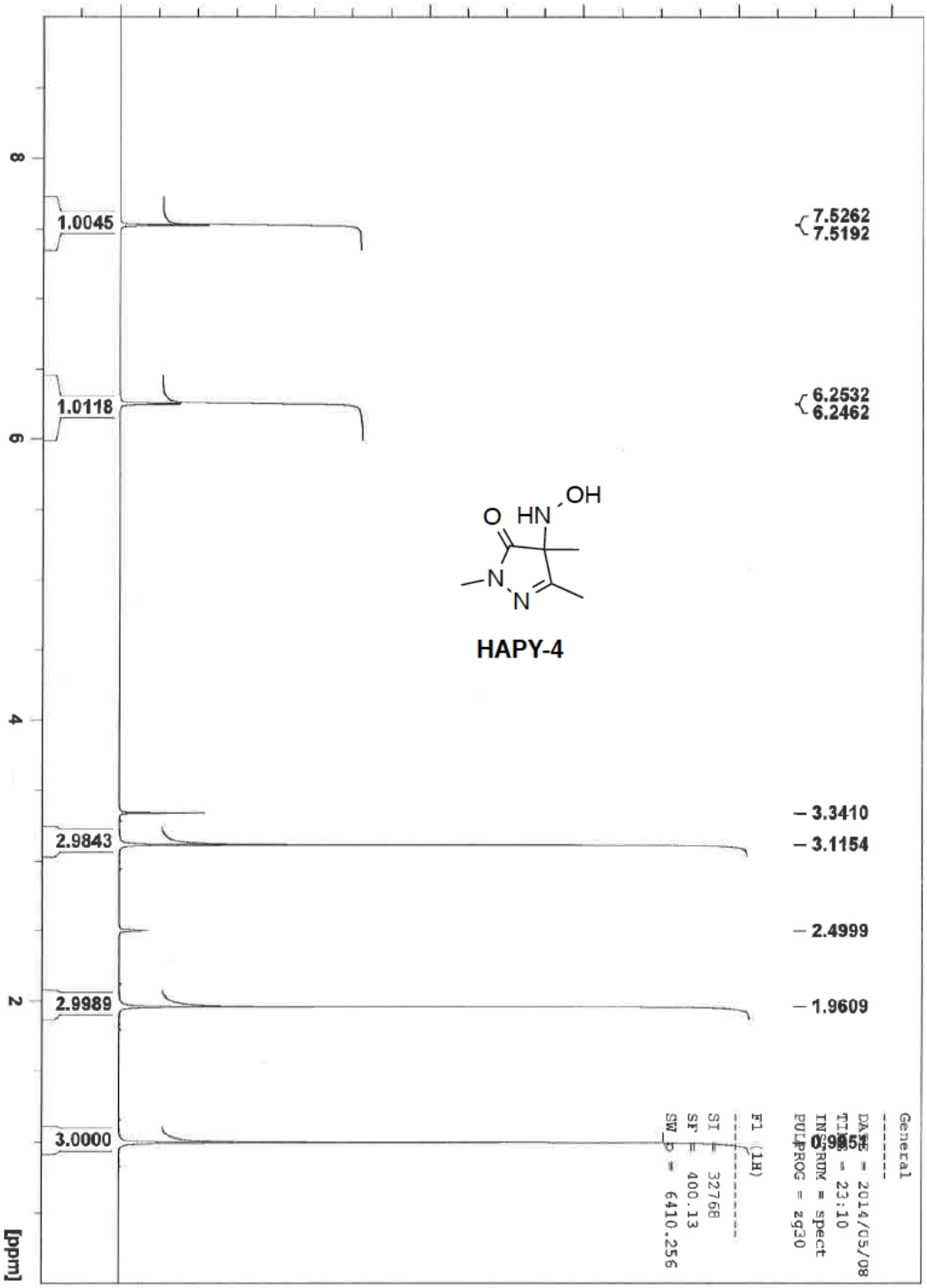

200
150
100
50
0
[ppm]
150.4654
145.5437
132.9522
132.6908
132.0658
129.7765
129.4399
126.9889
95.7391
39.5078
33.2296
7.7434
HO
Cl
N
N
PY-12

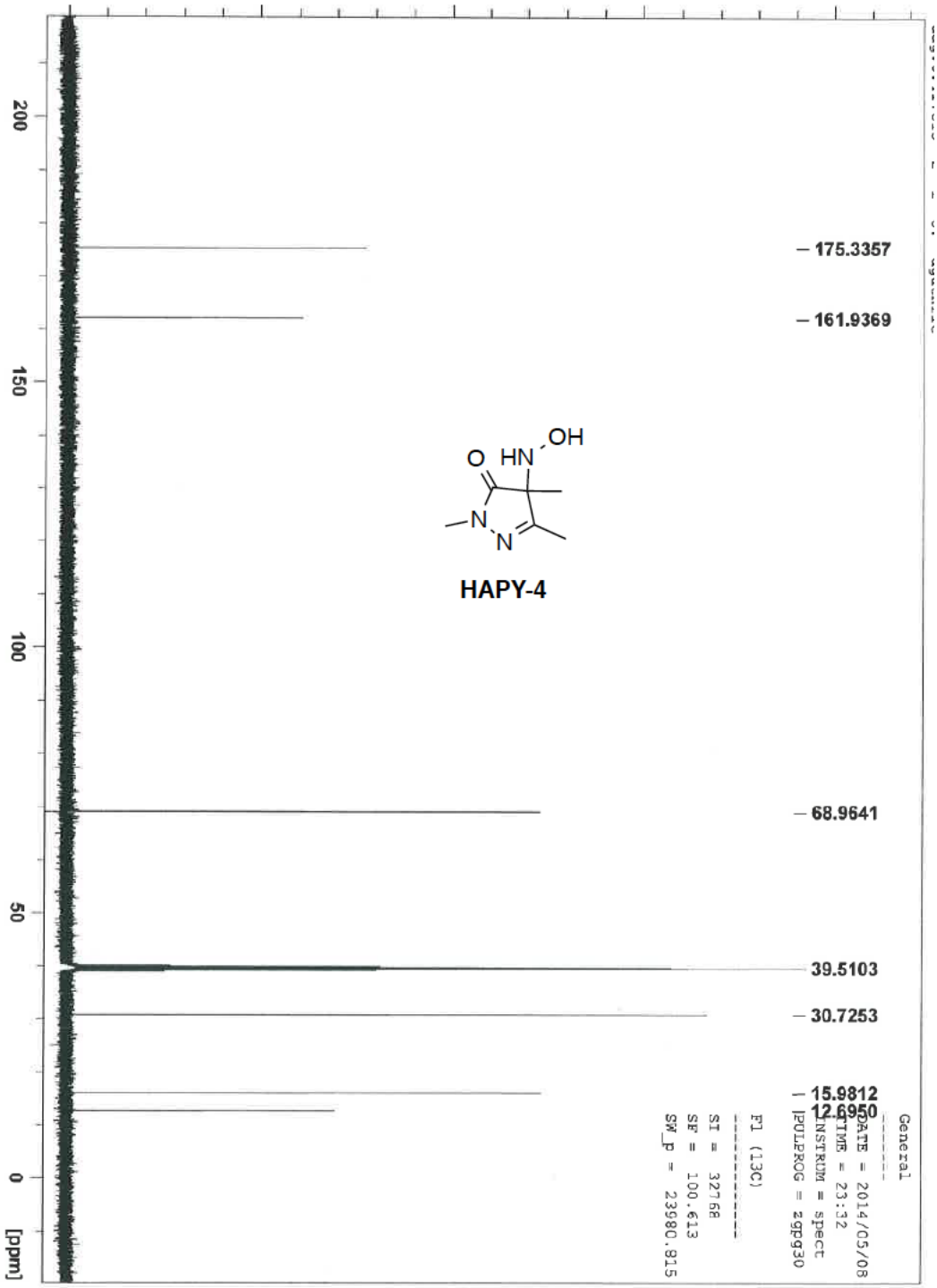

7.9423
7.9393
7.9202
7.9176
7.4191
7.4006
7.3789
7.2597
7.2000
7.1816
7.1631
2.0000
2.0681
1.0703
1.0018
1.0412
3.2517
3.2940
5.7033
4.7716
2.2057
1.5684
1.2779
O HN OH
N N
HAPY-2
[ppm]
8
6
4
2
General
DATE = 2012/07/22
TIME = 10:19
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6276.146

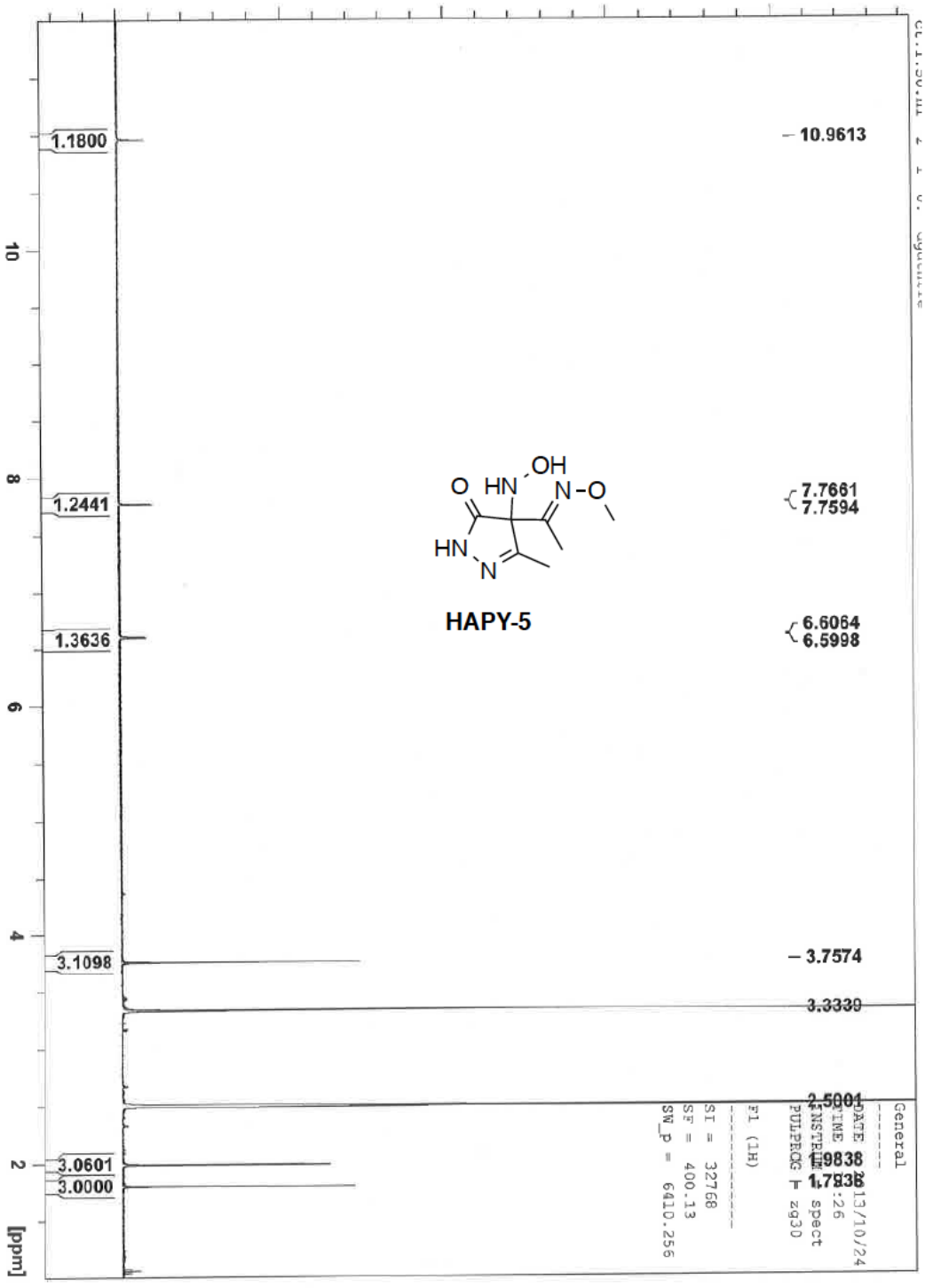

OH
O HN
N
N
HAPY-2
174.0564
162.0685
138.1235
129.0459
125.3068
118.8621
77.5402
77.2228
76.9058
71.2277
16.9707
13.3340
200
150
100
50
0
[ppm]
General
DATE = 2012/10/05
TIME = 03:26
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

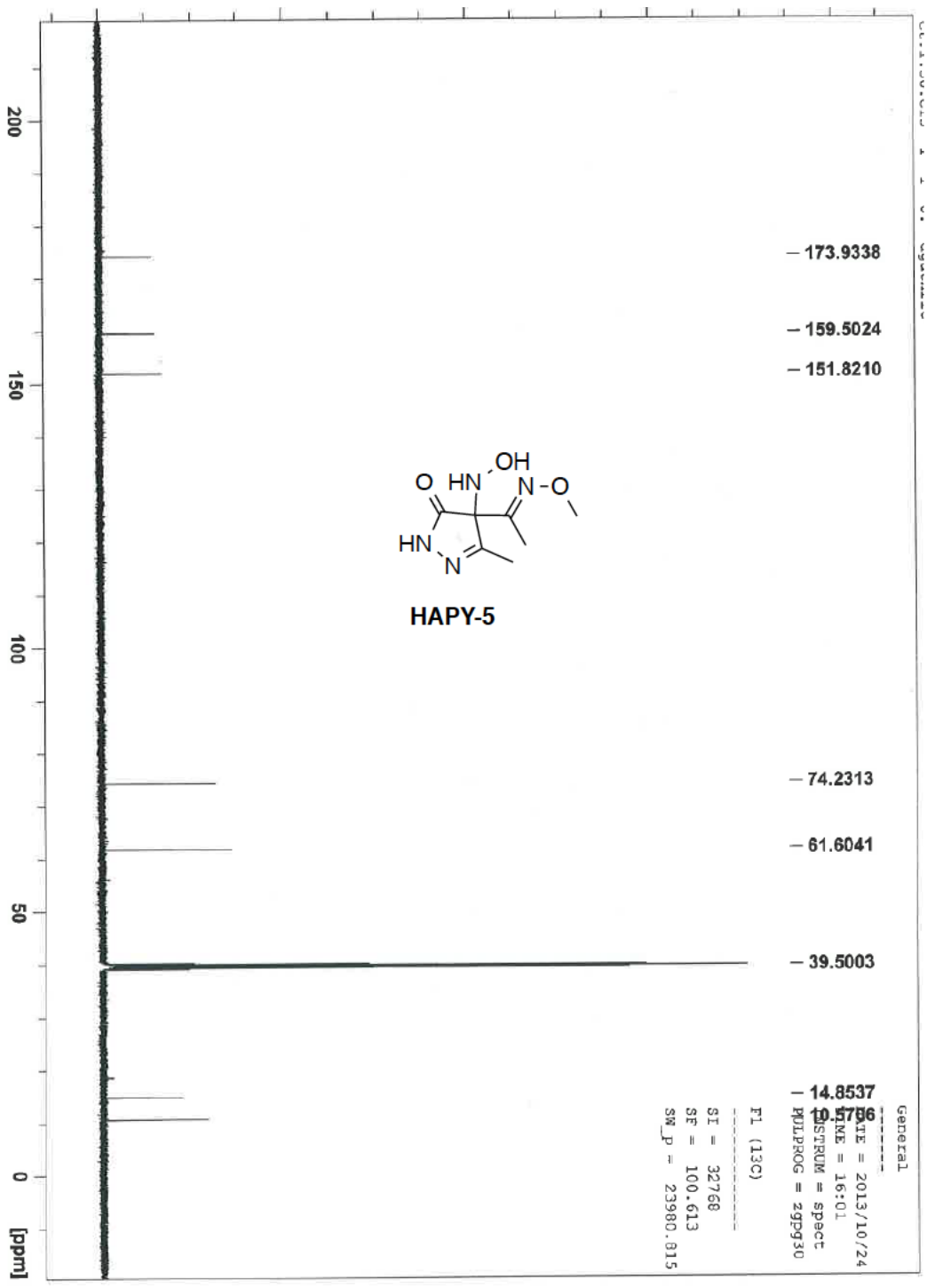

HAPY-3
7.2600
6.1225
4.6657
3.8965
3.3265
2.1158
1.7355
1.5490
1.1623
1.1681
2.9926
3.0541
3.1061
3.0000
[ppm]
General
DATE = 2013/10/11
TIME = 11:51
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256

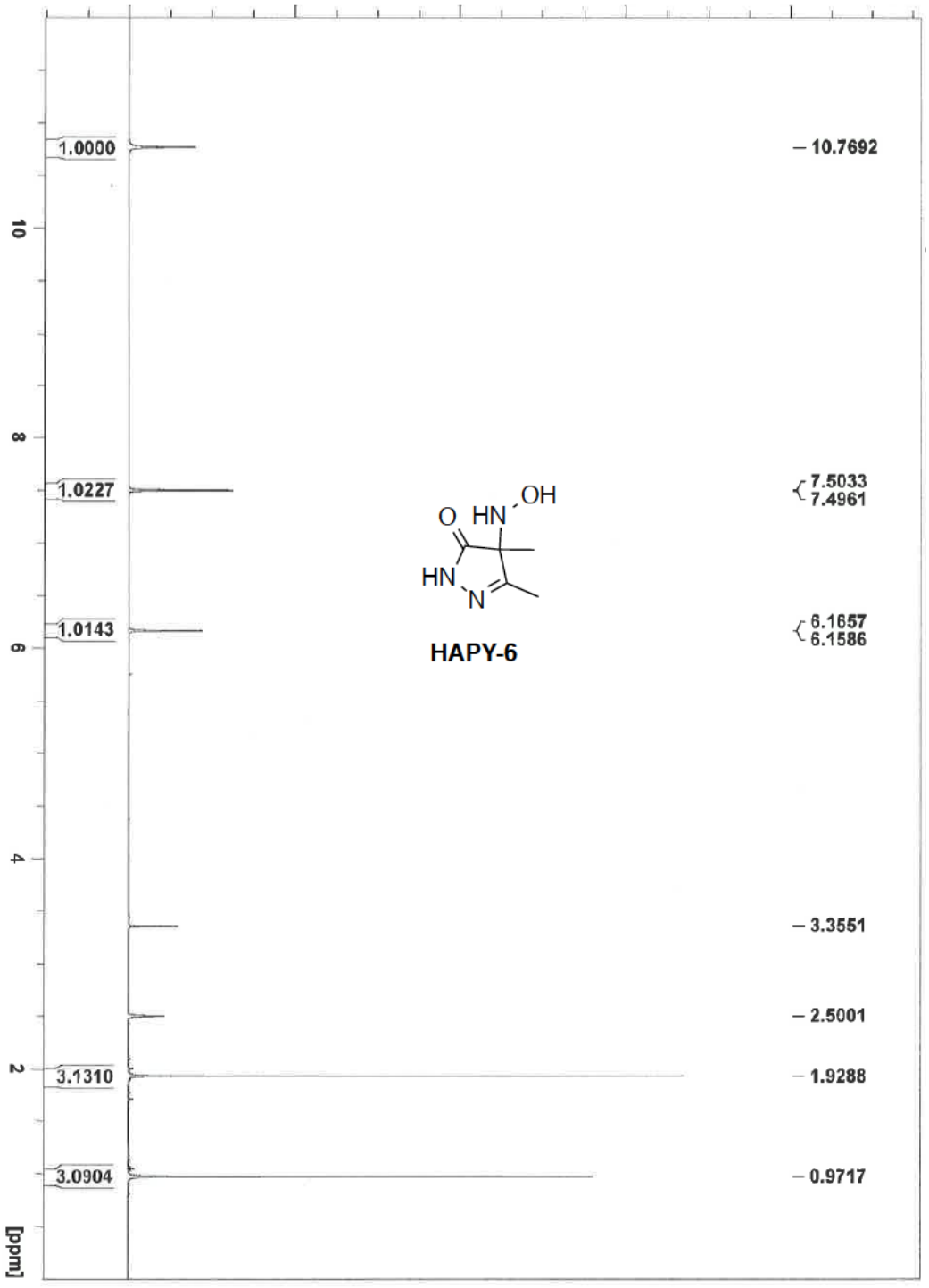

171.6847
158.9695
148.8012
77.5494
77.2326
76.9142
76.6158
62.5342
31.7729
14.3885
10.9625
HAPY-3
200
150
100
50
0
[ppm]
General
DATE = 2012/10/05
TIME = 06:31
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

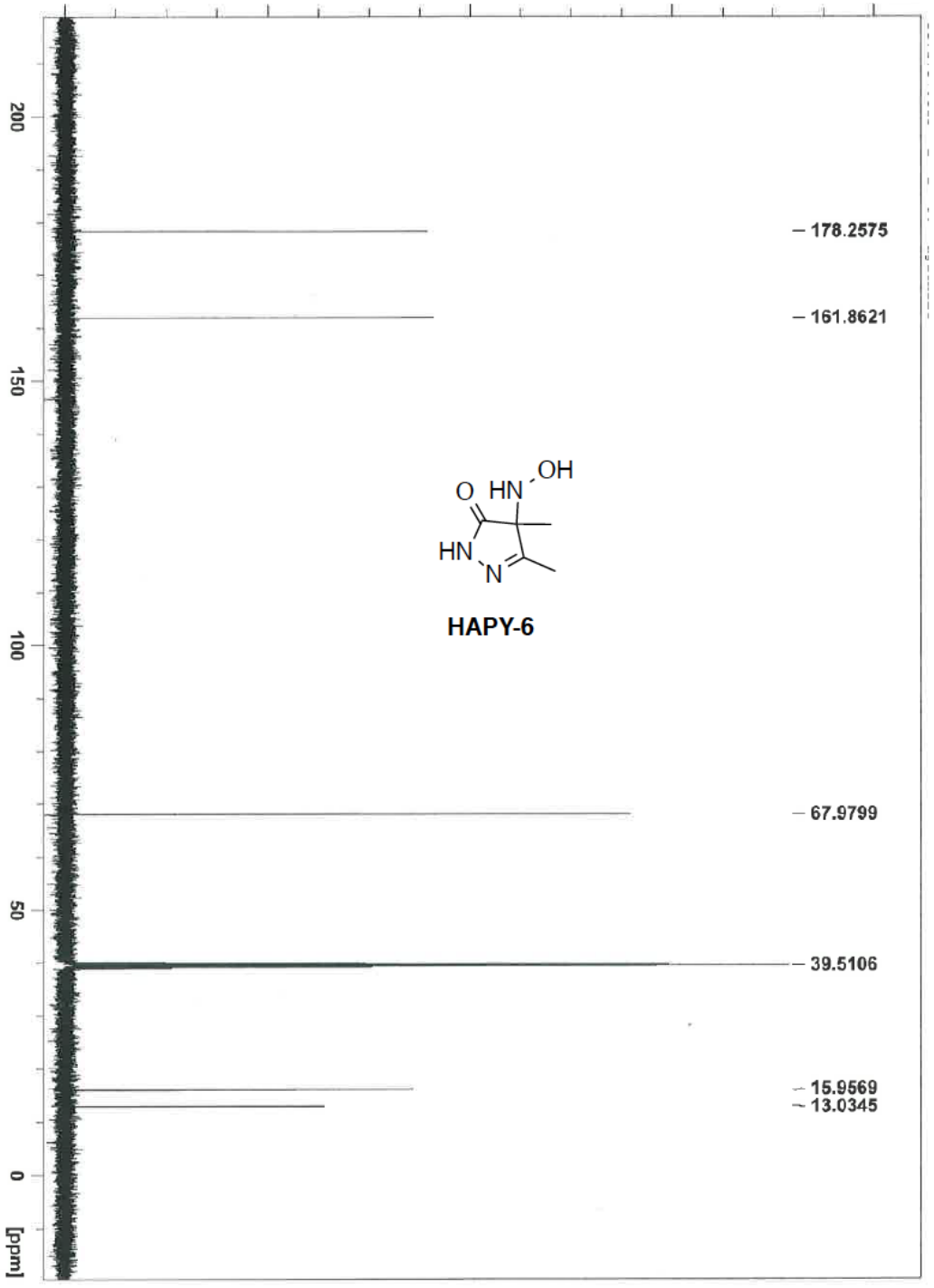

8
6
4
2
[ppm]
1.0045
1.0118
2.9843
2.9989
3.0000
7.5262
7.5192
6.2532
6.2462
3.3410
3.1154
2.4999
1.9609
0.9957
O
HN
OH
N
N
HAPY-4
General
DATE = 2014/05/08
TIME = 23:10
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_h = 6410.256


175.3357
161.9369
68.9641
39.5103
30.7253
15.9812
12.6950
HAPY-4
200
150
100
50
0
[ppm]
General
DATE = 2014/05/08
TIME = 23:32
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

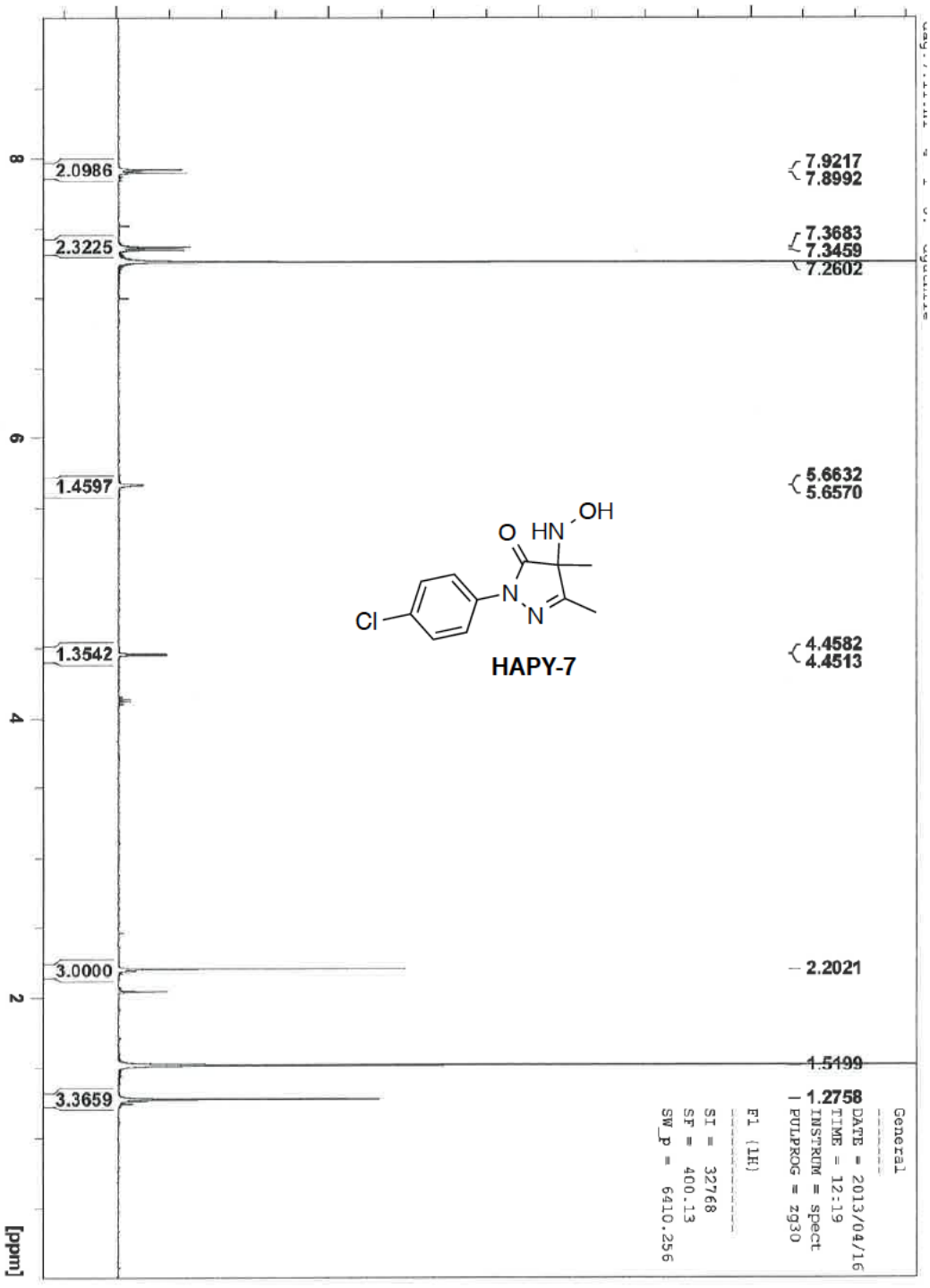

10.9613
7.7661
7.7594
6.6064
6.5998
3.7574
3.3339
2.5001
1.9838
1.7838
1.2441
1.3636
3.1098
3.0601
3.0000
HAPY-5
10
8
6
4
2
[ppm]
General
DATE 13/10/24
TIME :26
INSTRUM spect
PULPROG zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256

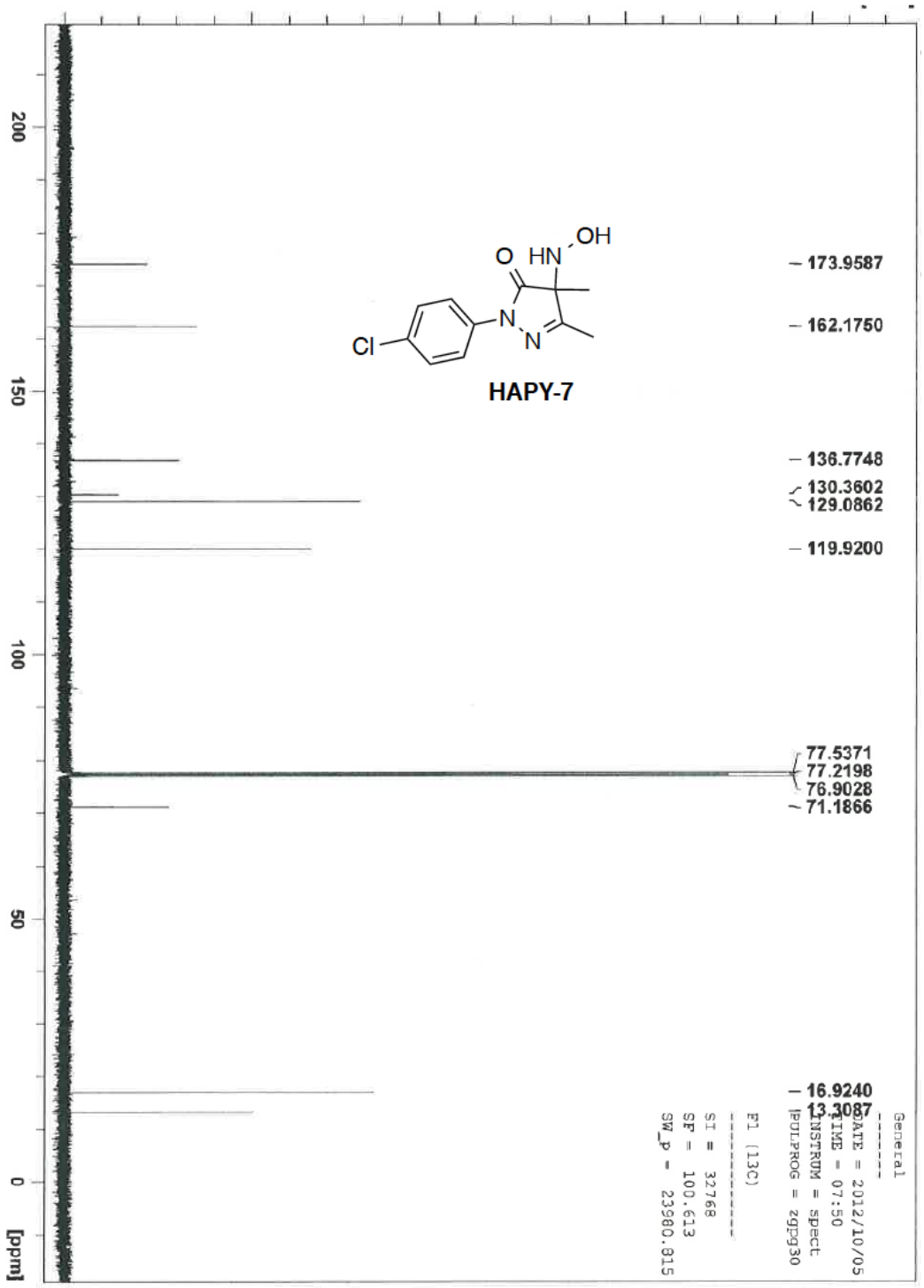

200
150
100
50
0
[ppm]
173.9338
159.5024
151.8210
74.2313
61.6041
39.5003
14.8537
10.5796
O
HN
OH
N-O
HN
N
HAPY-5
General
DATE = 2013/10/24
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

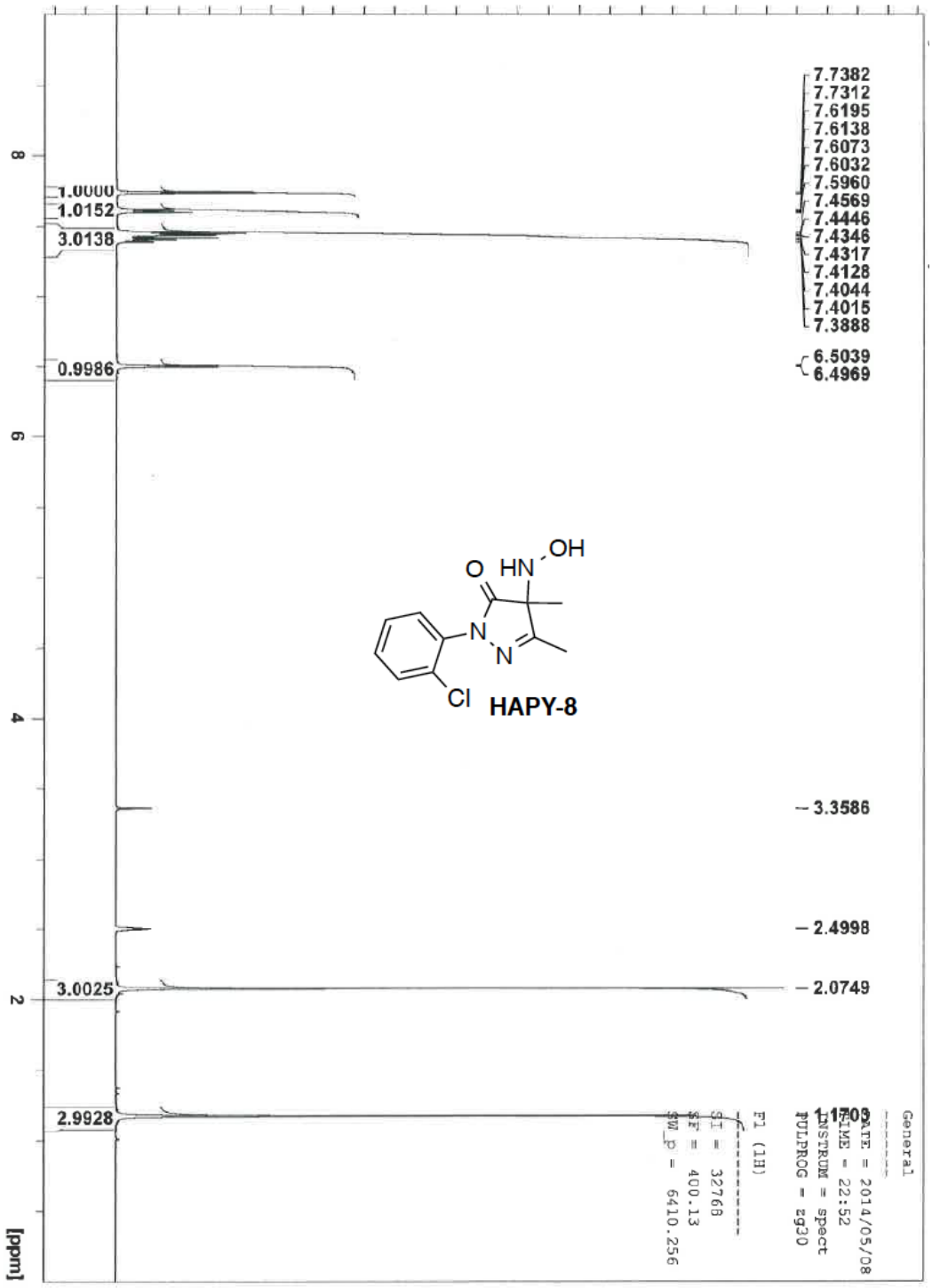

1.0000
1.0227
1.0143
3.1310
3.0904
10.7692
7.5033
7.4961
6.1657
6.1586
3.3551
2.5001
1.9288
0.9717
HAPY-6
[ppm]

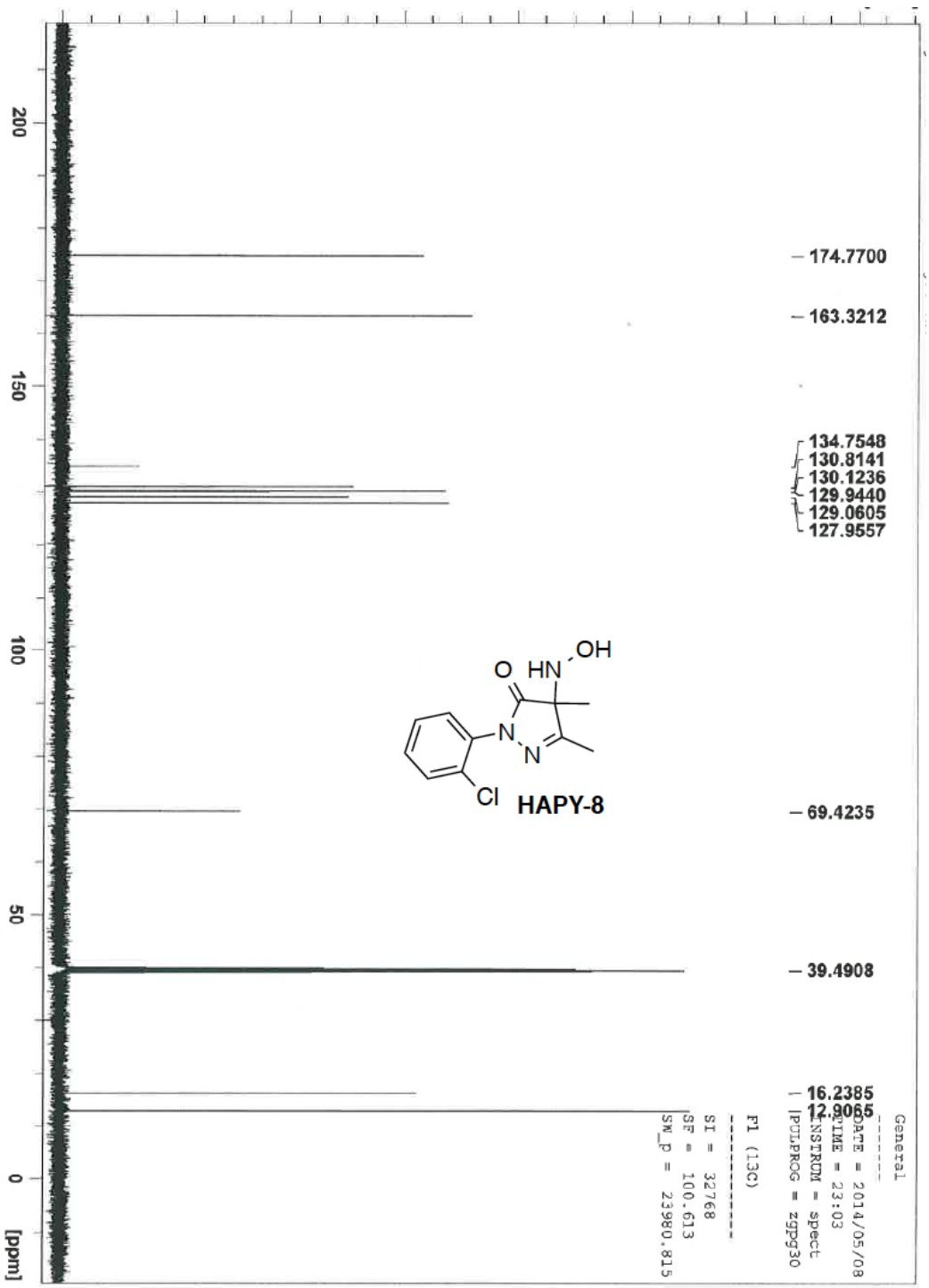

200
150
100
50
0
[ppm]
178.2575
161.8621
67.9799
39.5106
15.9569
13.0345
O
HN
OH
HN
N

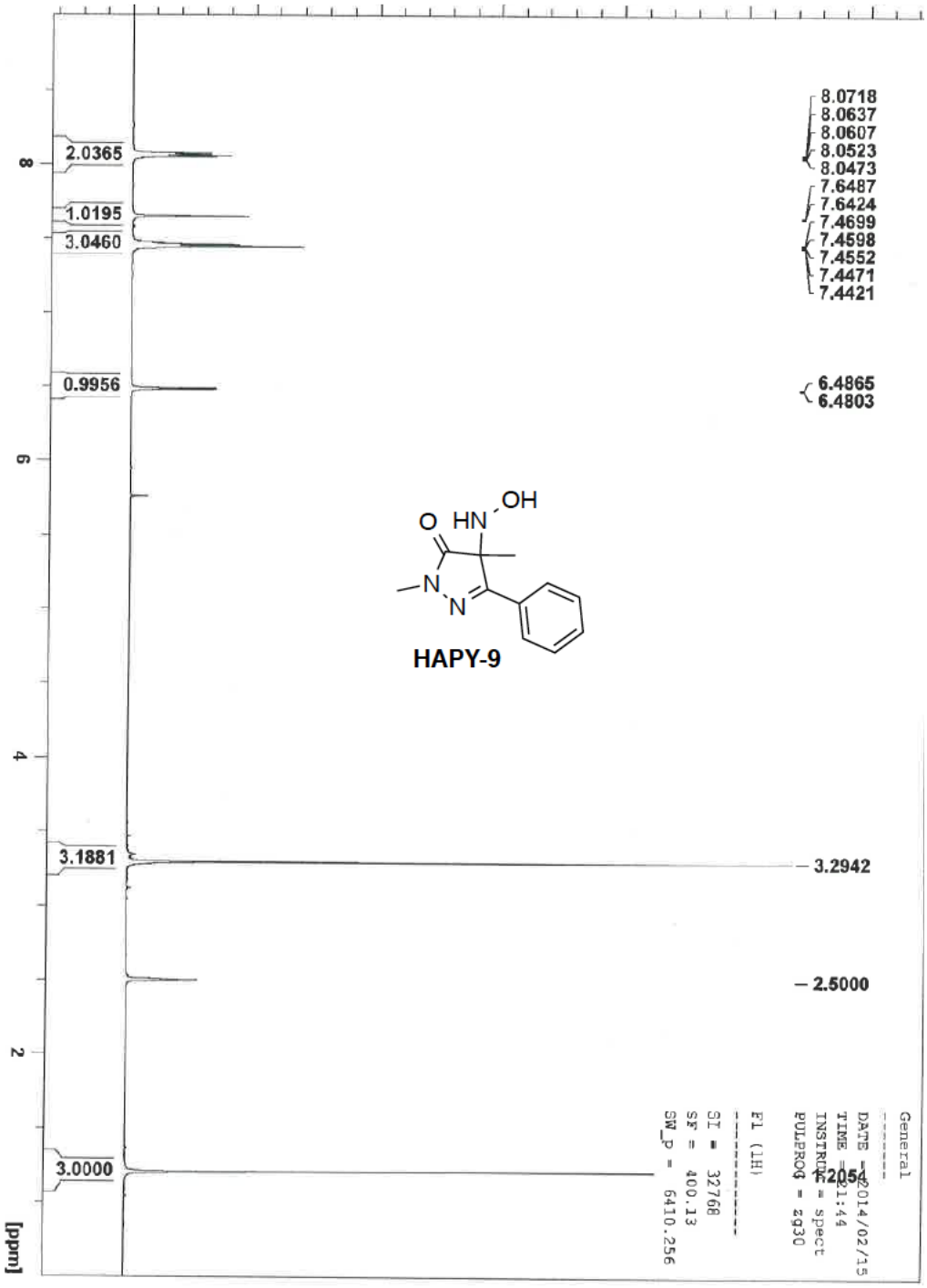
HAPY-6

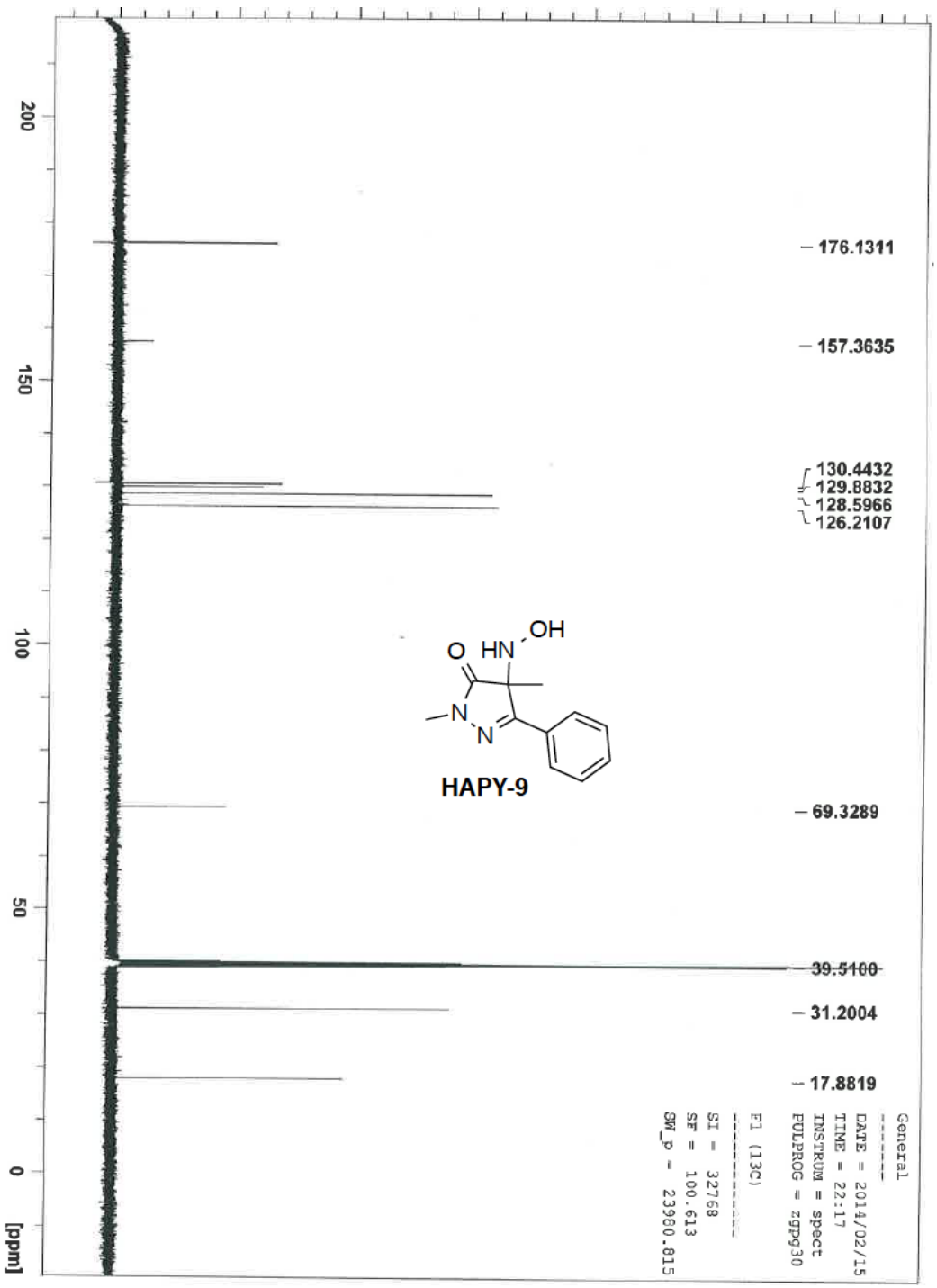

8
6
4
2
[ppm]
2.0986
2.3225
1.4597
1.3542
3.0000
3.3659
7.9217
7.8992
7.3683
7.3459
7.2602
5.6632
5.6570
4.4582
4.4513
2.2021
1.5499
1.2758
O
HN
OH
N
N
Cl
HAPY-7
General
DATE = 2013/04/16
TIME = 12:19
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256

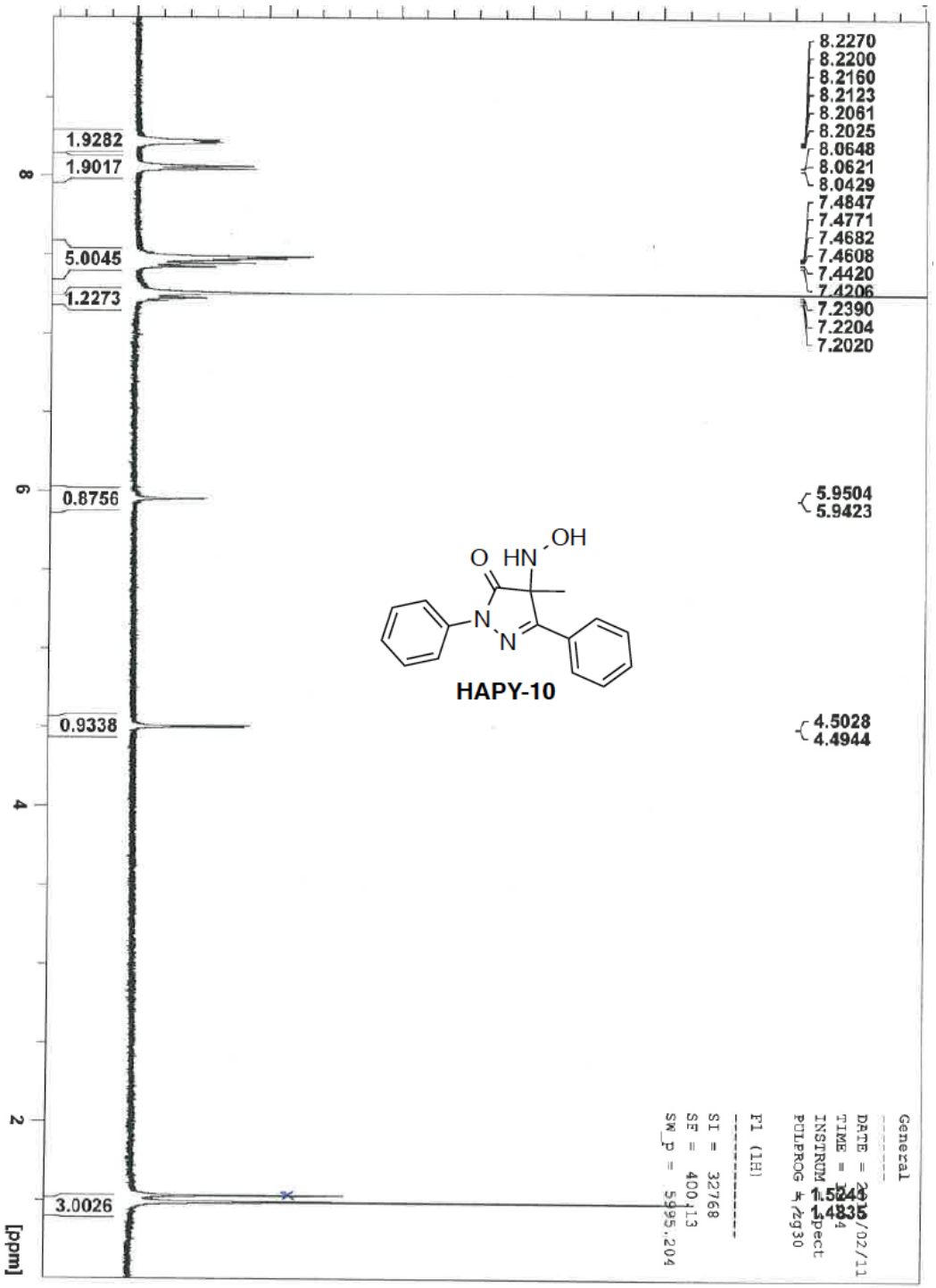

HAPY-7
O
HN
OH
N
N
Cl
173.9587
162.1750
136.7748
130.3602
129.0862
119.9200
77.5371
77.2198
76.9028
71.1866
16.9240
13.3087
200
150
100
50
0
[ppm]
General
DATE = 2012/10/05
TIME = 07:50
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815

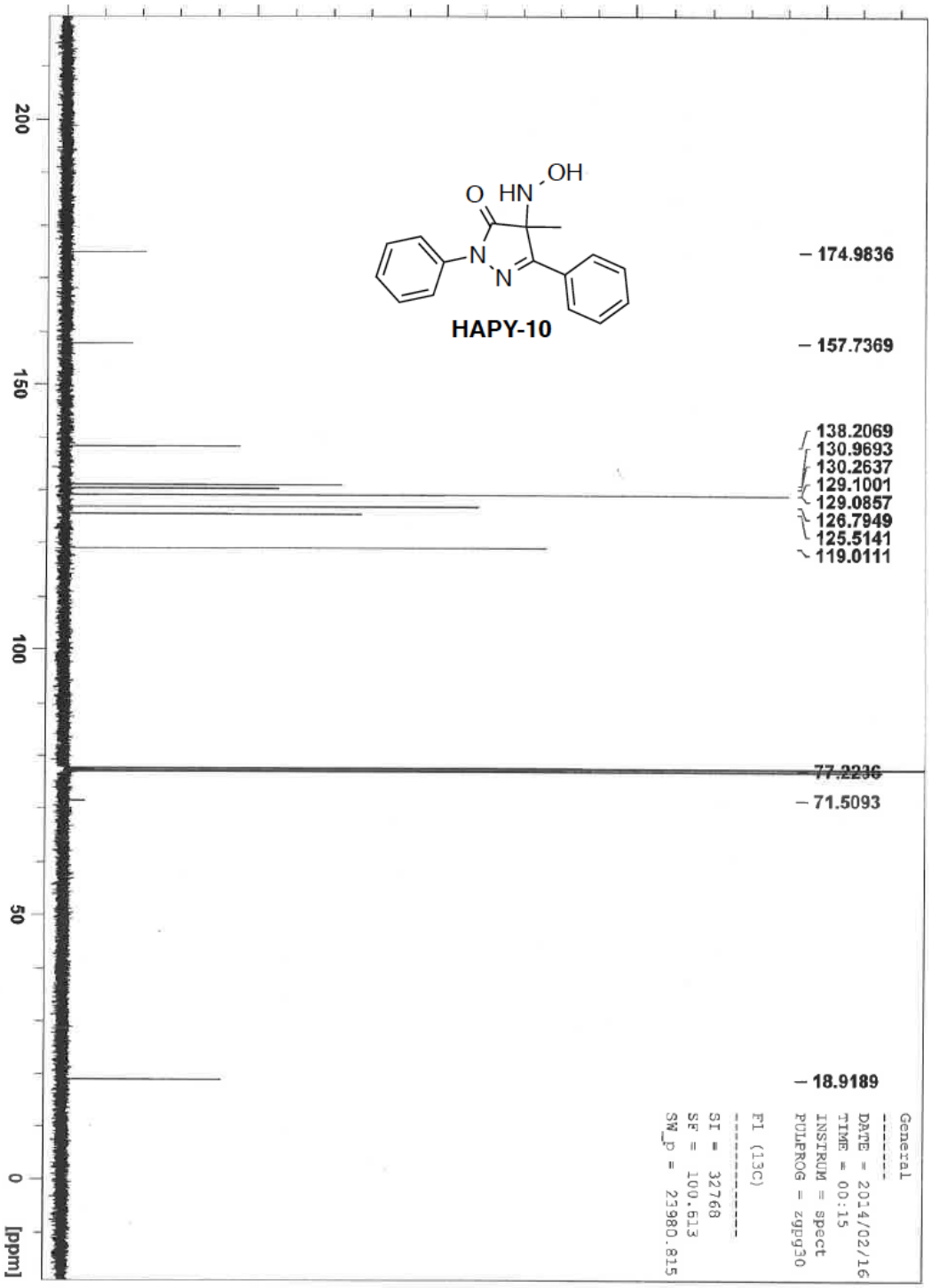

7.7382
7.7312
7.6195
7.6138
7.6073
7.6032
7.5960
7.4569
7.4446
7.4346
7.4317
7.4128
7.4044
7.4015
7.3888
6.5039
6.4969
1.0000
1.0152
3.0138
0.9986
3.0025
2.9928
3.3586
2.4998
2.0749
1.1703
O
HN
OH
N
N
Cl
HAPY-8
[ppm]
8
6
4
2
General
DATE = 2014/05/08
TIME = 22:52
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256

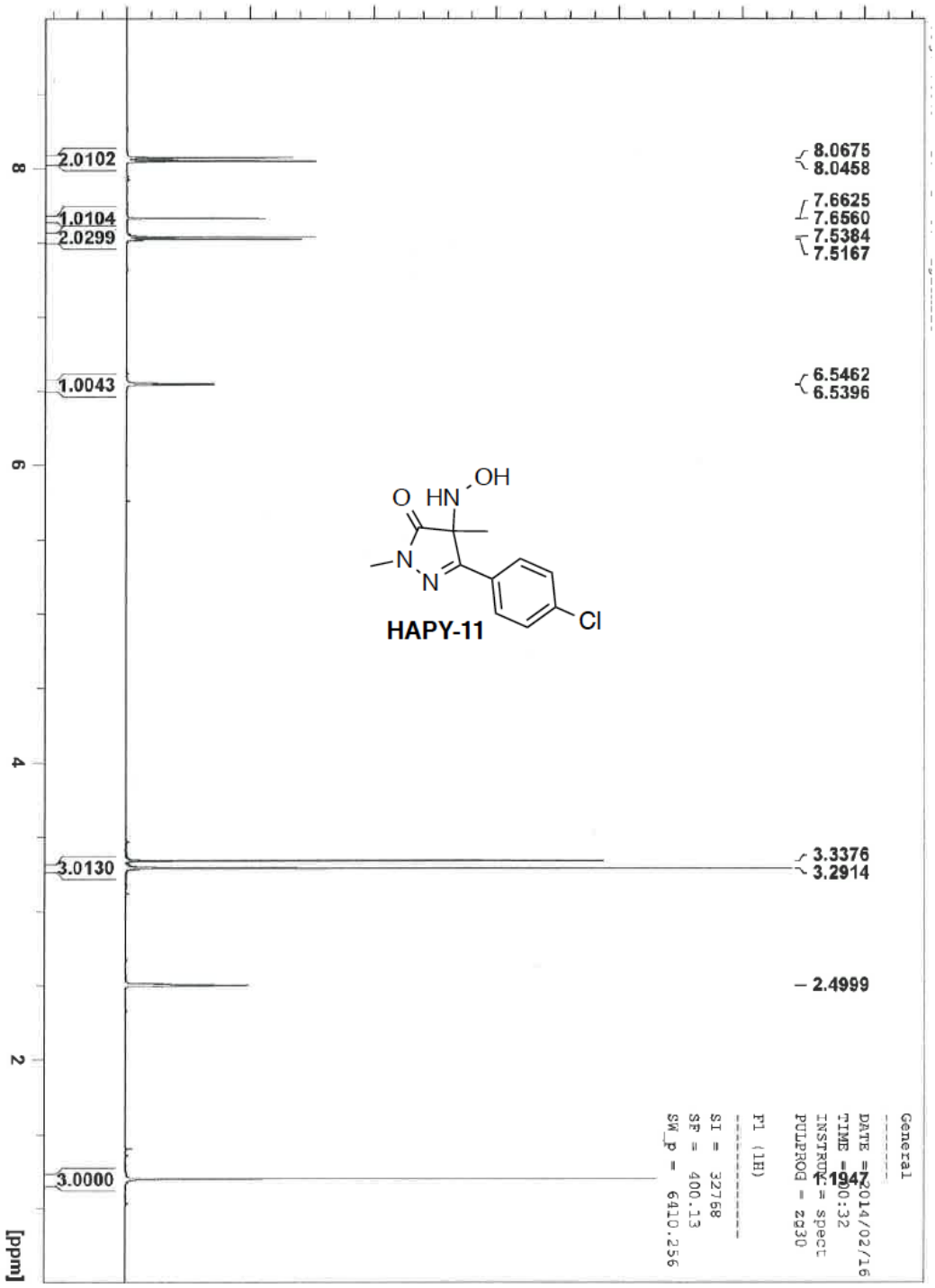

174.7700
163.3212
134.7548
130.8141
130.1236
129.9440
129.0605
127.9557
69.4235
39.4908
16.2385
12.9065
HAPY-8
200
150
100
50
0
[ppm]
General
DATE = 2014/05/08
TIME = 23:03
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815


8.0718
8.0637
8.0607
8.0523
8.0473
7.6487
7.6424
7.4699
7.4598
7.4552
7.4471
7.4421
6.4865
6.4803
3.2942
2.5000
3.2054
2.0365
1.0195
3.0460
0.9956
3.1881
3.0000
8
6
4
2
[ppm]
O
HN
OH
N
N
HAPY-9
General
DATE = 2014/02/15
TIME = 21:44
INSTRUM = spect
PULPROG = zg30
FL (1H)
SI = 32768
SF = 400.13
SW_p = 6410.256


200
150
100
50
0
[ppm]
176.1311
157.3635
130.4432
129.8832
128.5966
126.2107
69.3289
39.5100
31.2004
17.8819
OH
HN
O
N
N
HAPY-9
General
DATE = 2014/02/15
TIME = 22:17
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815


8.2270
8.2200
8.2160
8.2123
8.2061
8.2025
8.0648
8.0621
8.0429
7.4847
7.4771
7.4682
7.4608
7.4420
7.4206
7.2390
7.2204
7.2020
1.9282
1.9017
5.0045
1.2273
0.8756
0.9338
3.0026
5.9504
5.9423
4.5028
4.4944
O HN OH
N
N
HAPY-10
8
6
4
2
[ppm]
General
F1 (1H)
SI = 32768
SW_p = 5995.204


HAPY-10
174.9836
157.7369
138.2069
130.9693
130.2637
129.1001
129.0857
126.7949
125.5141
119.0111
77.2236
71.5093
18.9189
200
150
100
50
0
[ppm]
General
DATE = 2014/02/16
TIME = 00:15
INSTRUM = spect
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 100.613
SW_p = 23980.815


2.0102
1.0104
2.0299
1.0043
3.0130
3.0000
8.0675
8.0458
7.6625
7.6560
7.5384
7.5167
6.5462
6.5396
3.3376
3.2914
2.4999
1.1947
O HN OH
N N
Cl
HAPY-11
8
6
4
2
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SI = 32768
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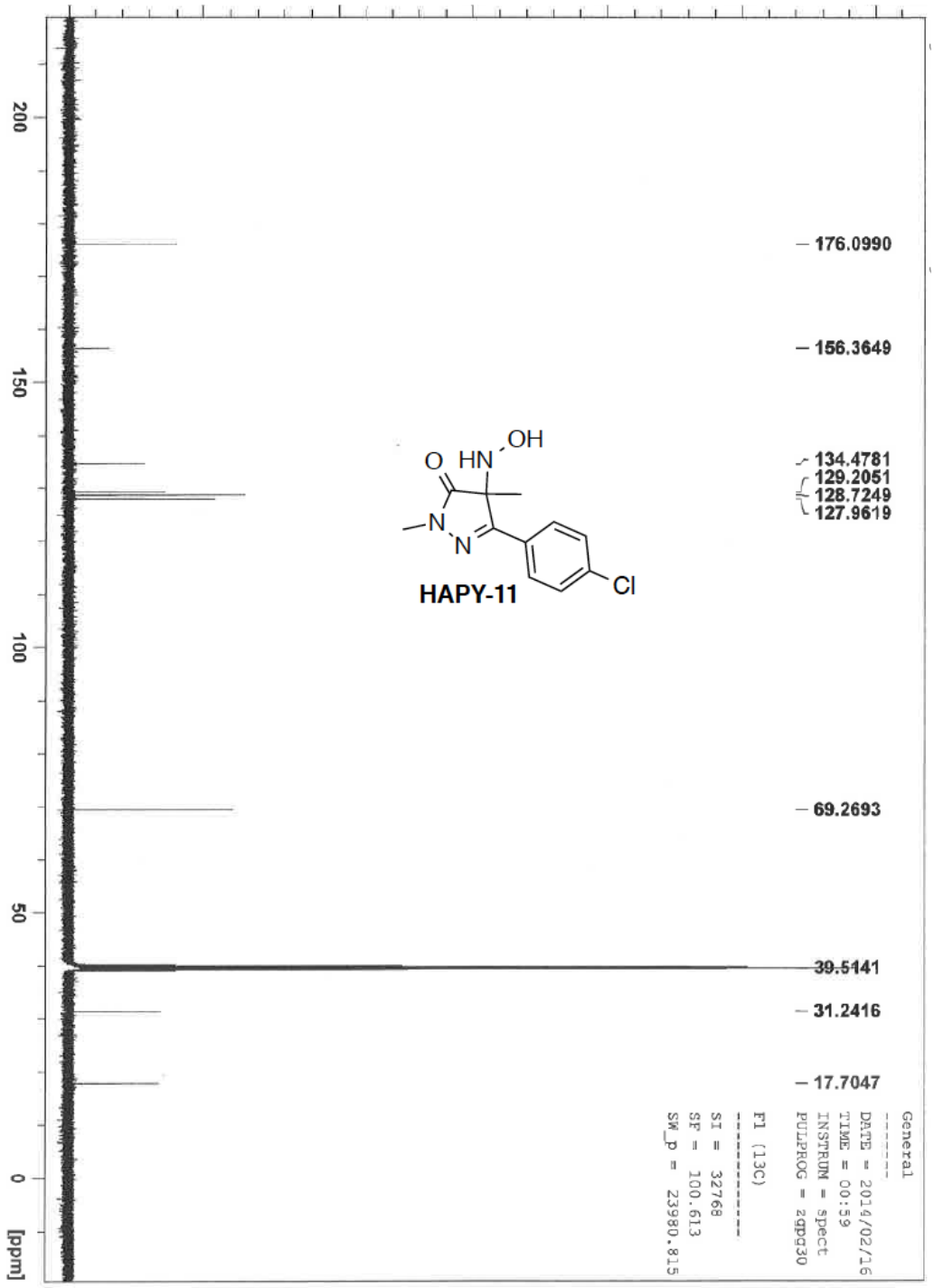
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HAPY-11
Cl
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HN
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N
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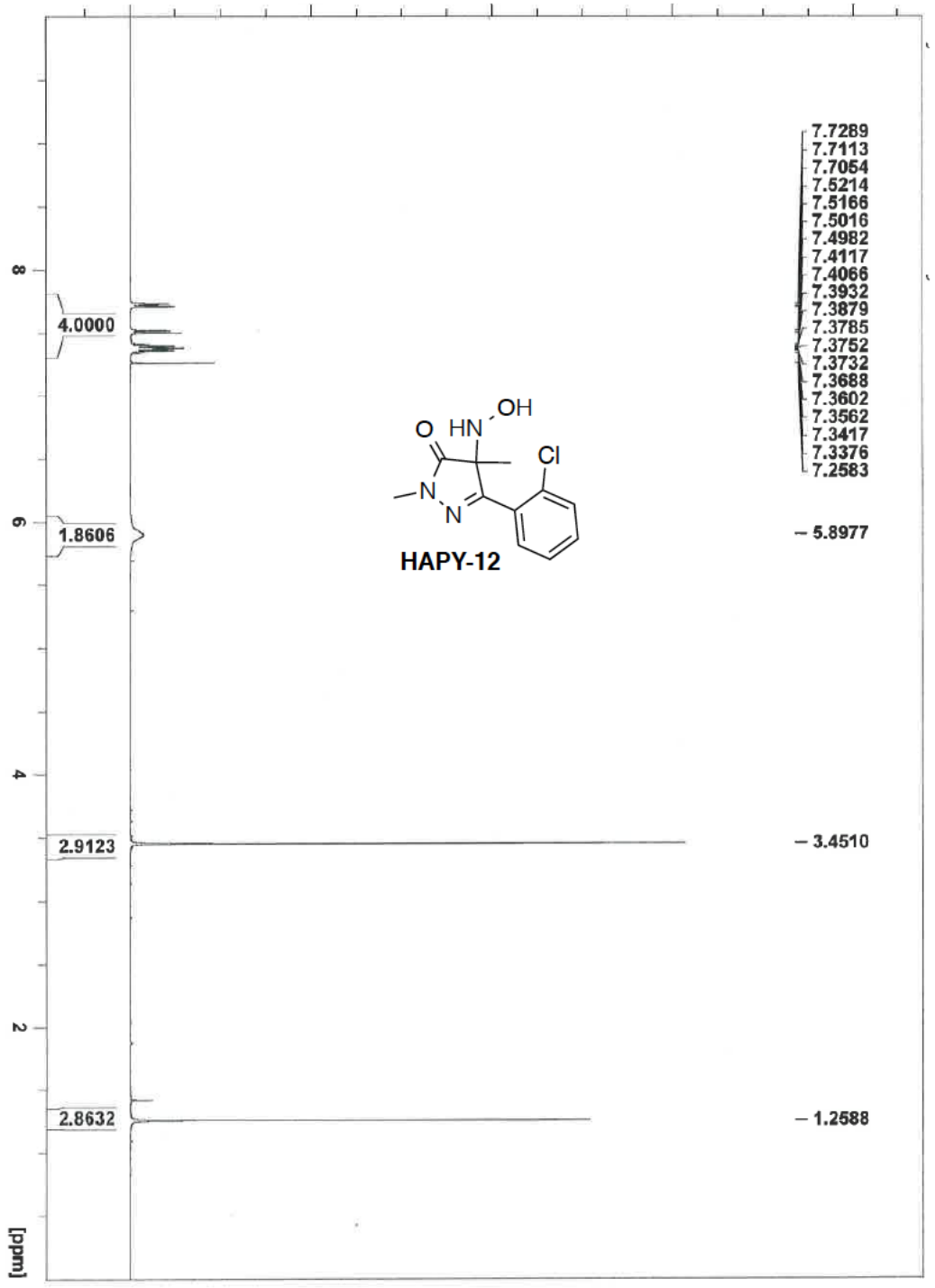
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7.3785
7.3752
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7.3688
7.3602
7.3562
7.3417
7.3376
7.2583
4.0000
1.8606
2.9123
2.8632
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OH
O HN
Cl
N
N
HAPY-12
8
6
4
2
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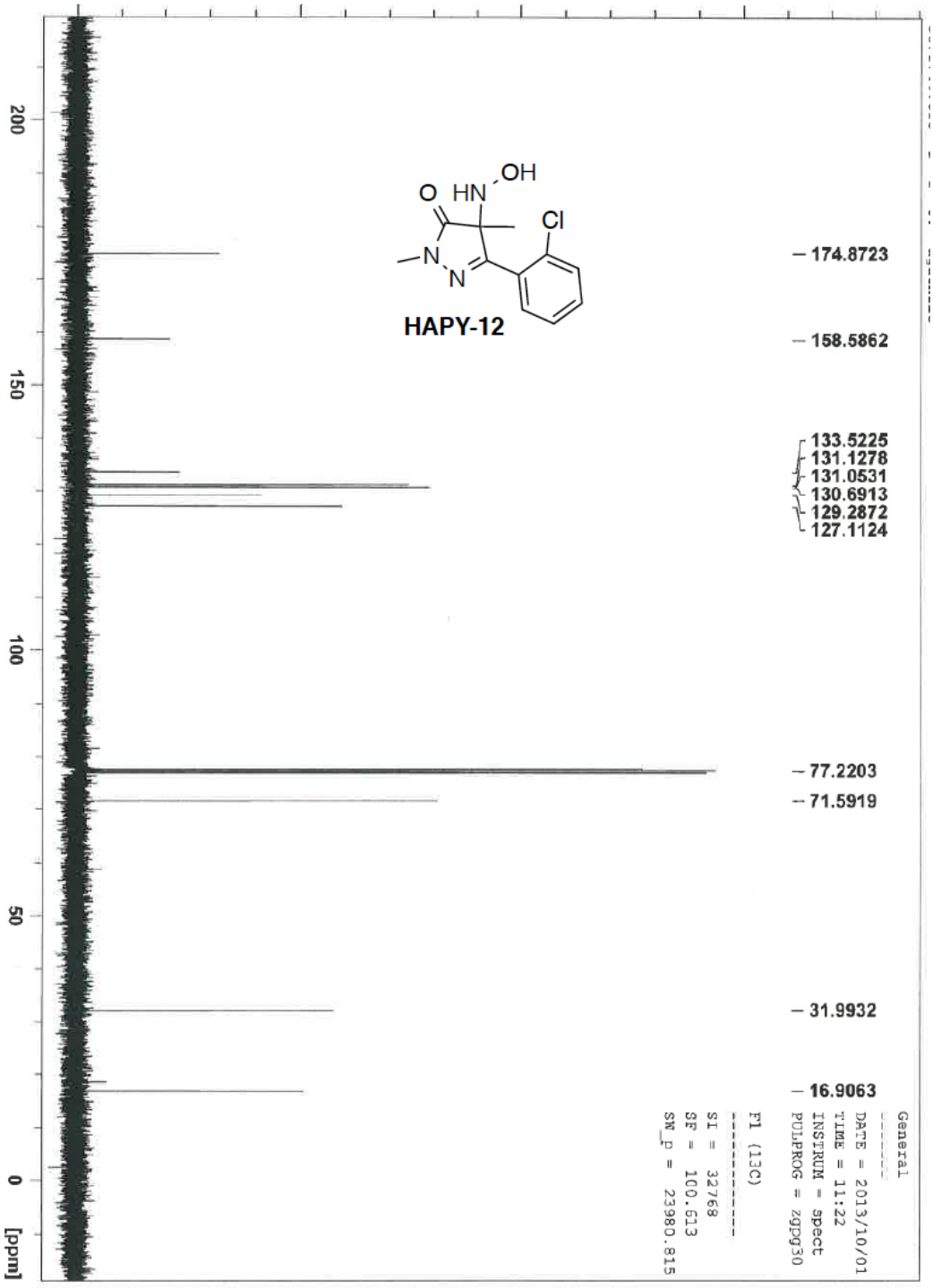
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31.9932
16.9063
200
150
100
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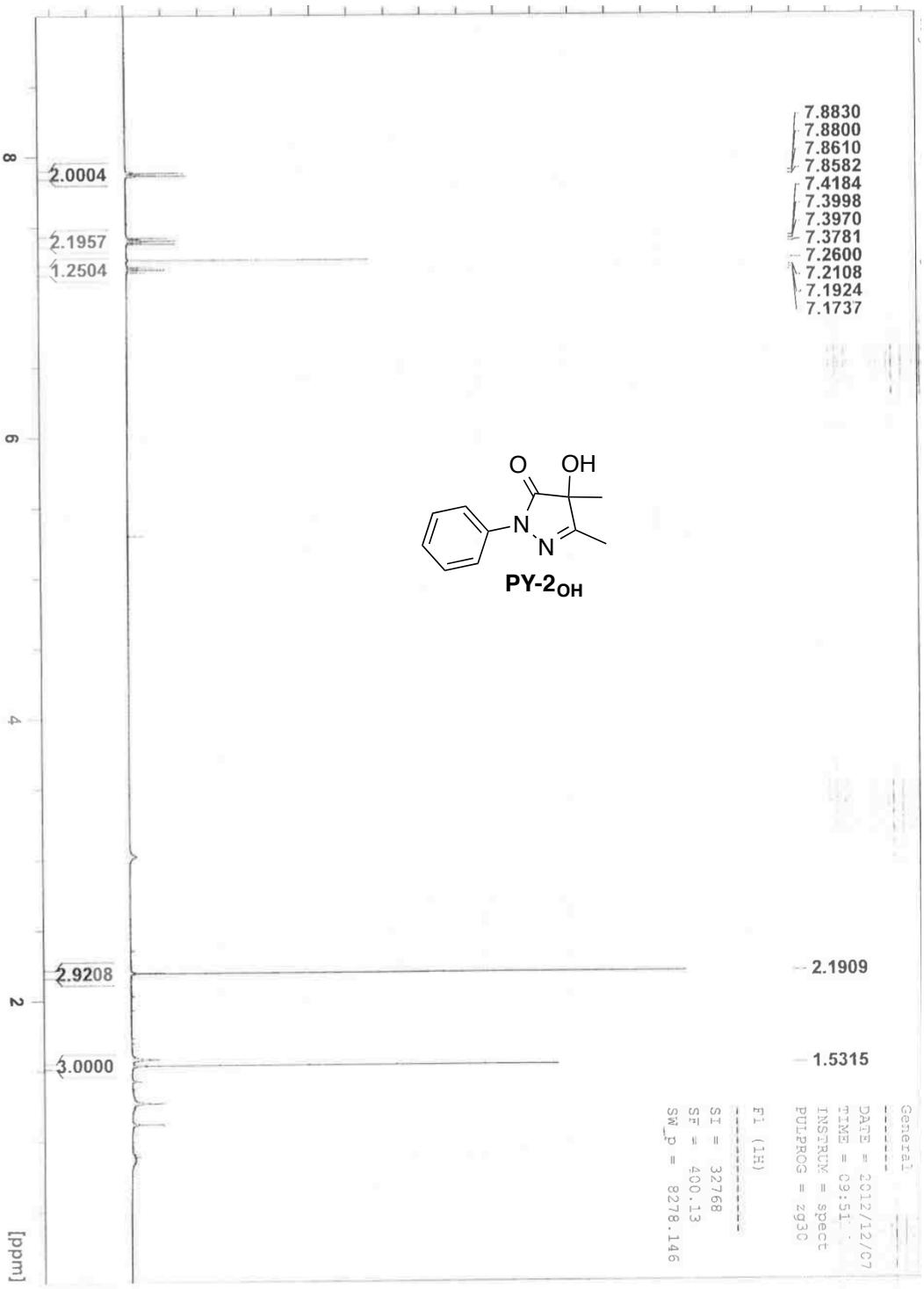
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2.0004
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N
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4
2
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