Electronic Supplementary Information

ESIPT-capable 4-(2-hydroxyphenyl)-2-(pyridin-2-yl)-1*H*-imidazoles with single and double proton transfer: synthesis, selective reduction of the imidazolic OH group and luminescence

Nikita A. Shekhovtsov [1,*], Elena B. Nikolaenkova [2], Alexey A. Ryadun [1], Denis G. Samsonenko [1], Alexsei Ya. Tikhonov [2,*] Mark B. Bushuev [1,*]

[1] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia.
[2] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia.
Correspondence: shekhovtsov@niic.nsc.ru (Nikita A. Shekhovtsov), alyatikh@nioch.nsc.ru (Alexsei Ya. Tikhonov), bushuev@niic.nsc.ru (Mark B. Bushuev).

Table of Contents

Spectral data 3
Figure S1 3
Figure S2 3
Figure S3 4
Figure S4 5
Figure S5 5
Figure S6 6
Figure S7 7
Figure S8 7
Structural data 8
Table S1 8
Table S2 9
Figure S9 12
Figure S10 12
Figure S11 12
Photophysical data 13
Figure S12 13
Figure S13 13
Figure S14 14
Figure S15 15
Theoretical data 16
Table S3 16
Table S4 17
Table S5 18
Table S6 19
Table S7 20
Table S8 21
Table S9 22
Table S10 23
Table S11 24
Table S12 25
Table S13 26
Table S14 27
Table S15 28
Table S16 29

Spectral data

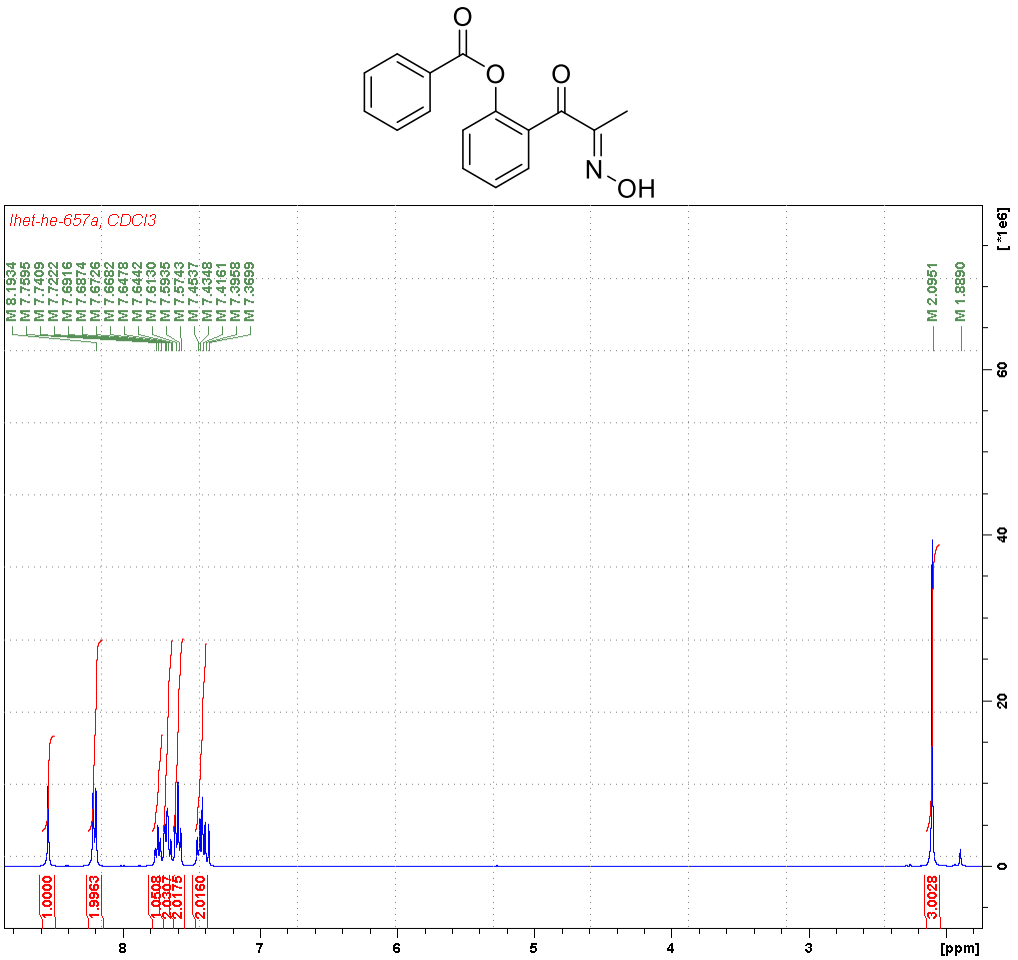


Figure S1. ^{1}H NMR spectrum of 1-(2-benzoyloxyphenyl)-2-(hydroxyimino)propan-1-one (in $CDCl_3$).

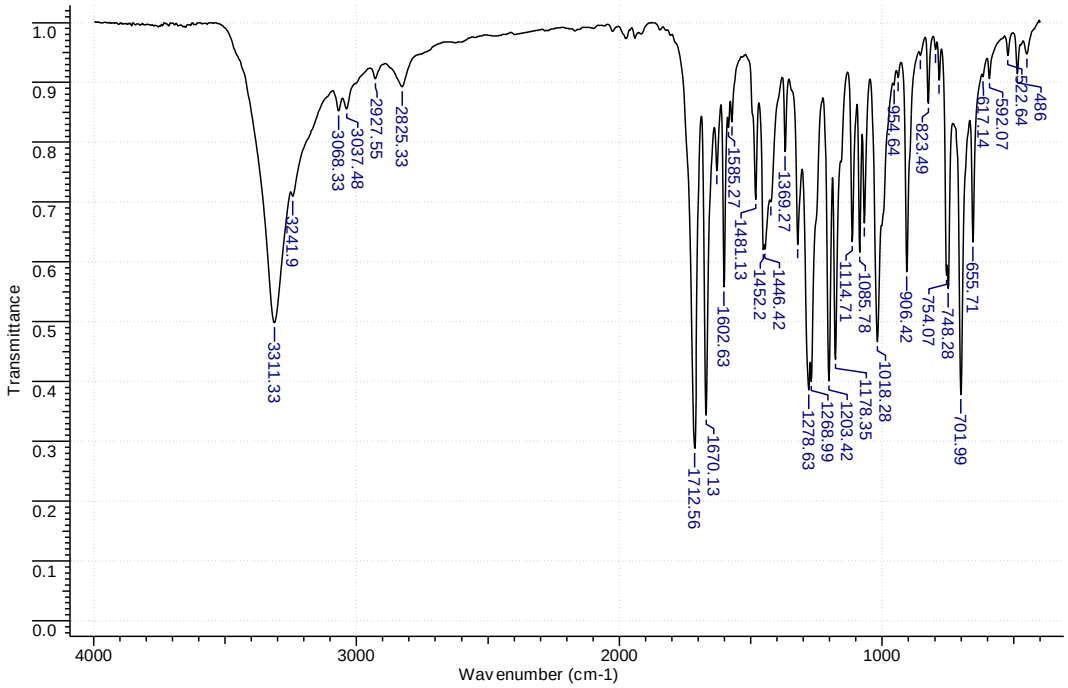


Figure S2. IR spectrum of 1-(2-benzoyloxyphenyl)-2-(hydroxyimino)propan-1-one (in KBr).

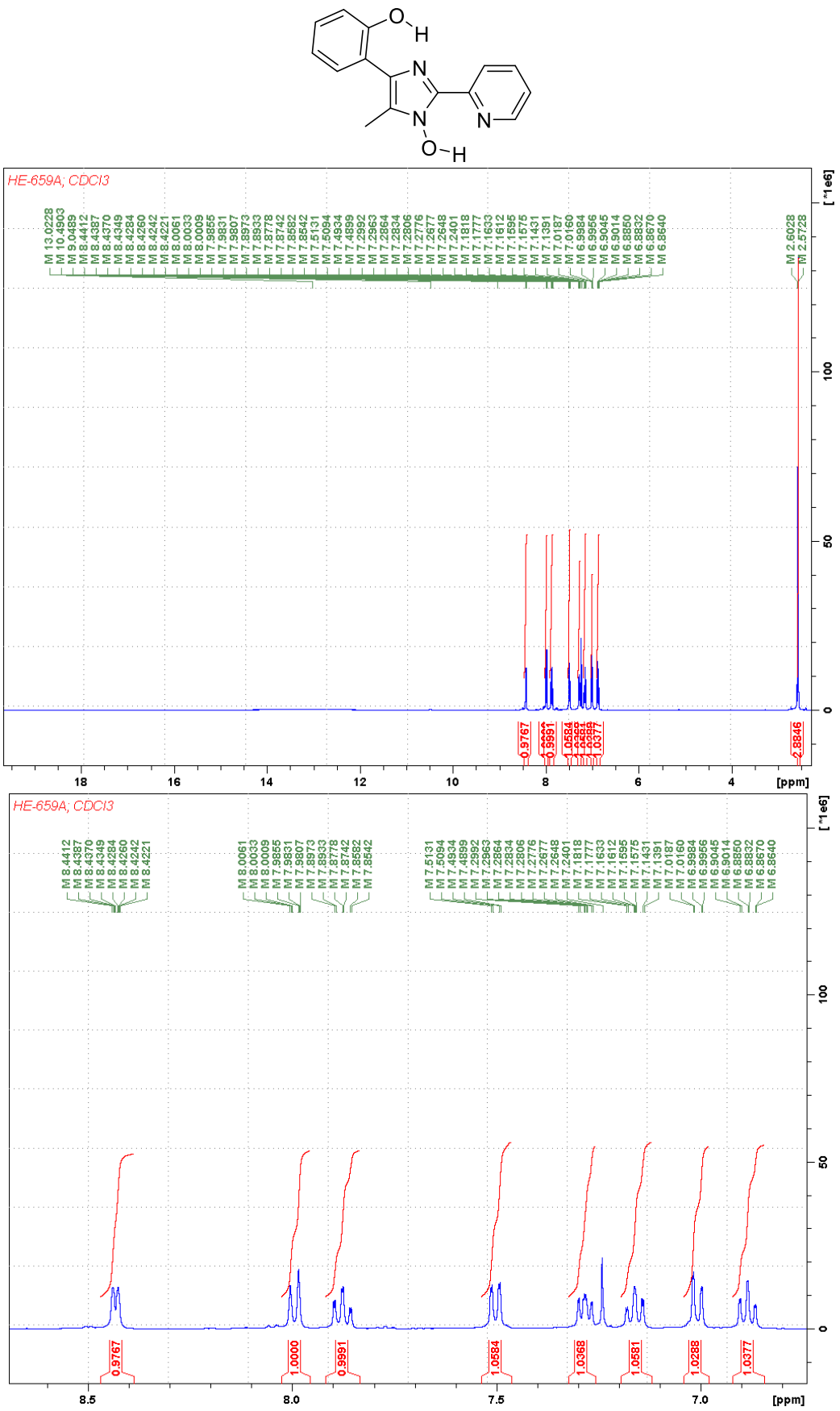


Figure S3. ^{1}H NMR spectrum of 1-hydroxy-4-(2-hydroxyphenyl)-5-methyl-2-(pyridin-2-yl)-1*H*-imidazole (in $CDCl_3$).

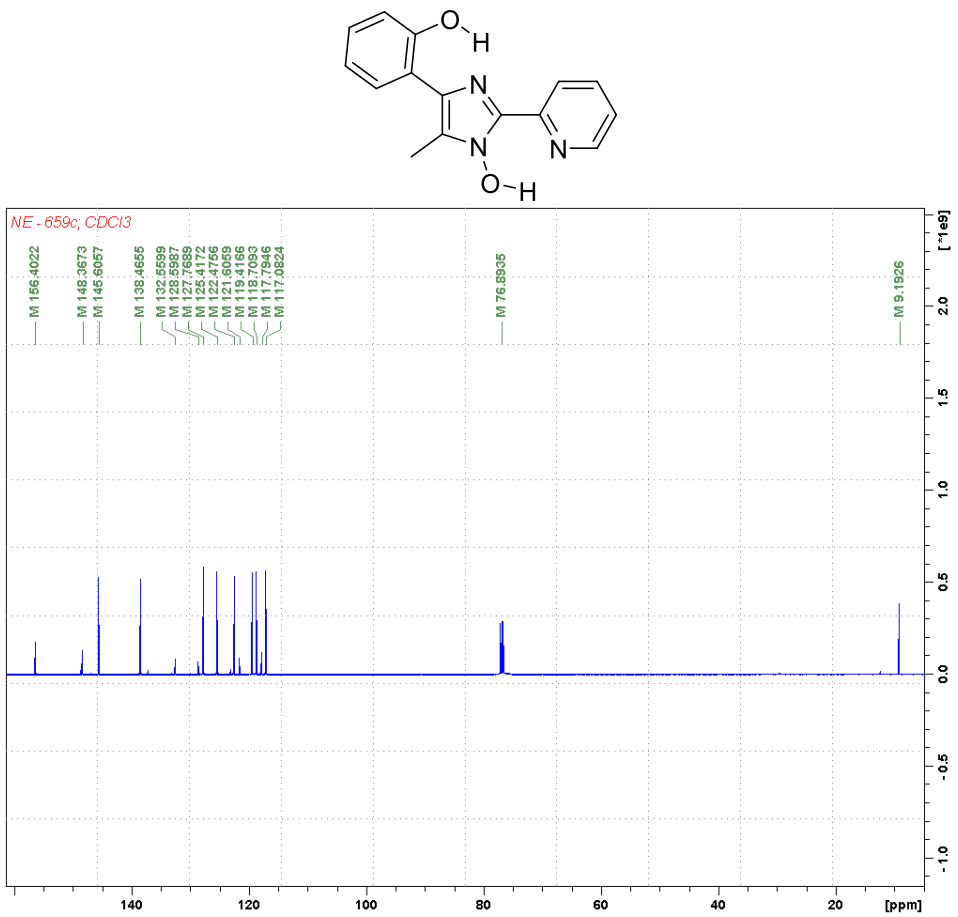


Figure S4. ^{13}C NMR spectrum of 1-hydroxy-4-(2-hydroxyphenyl)-5-methyl-2-(pyridin-2-yl)-1*H*-imidazole (in $CDCl_3$).

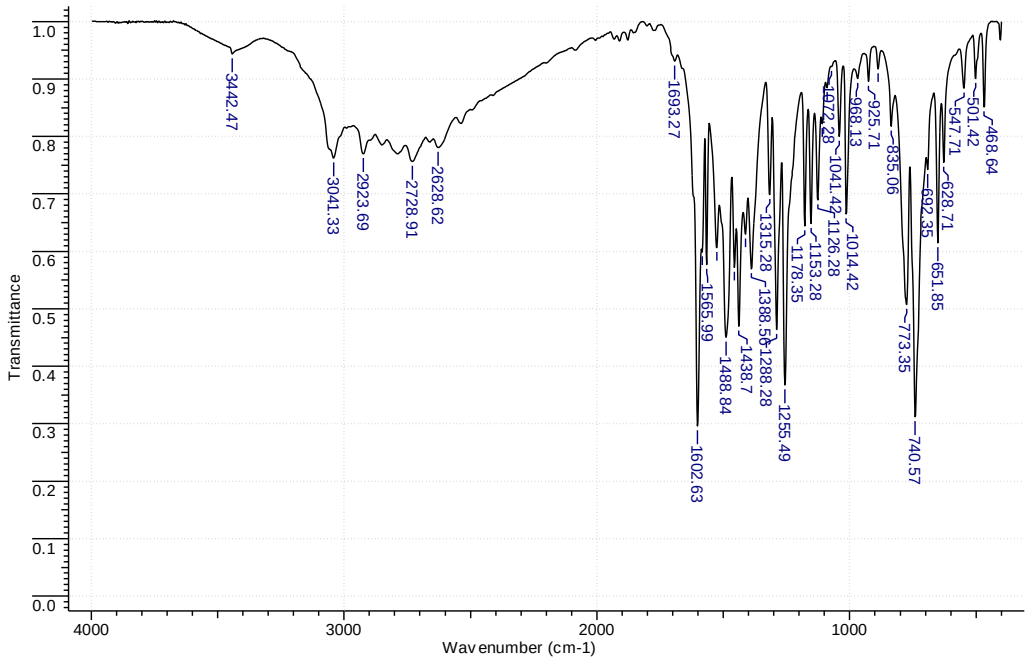
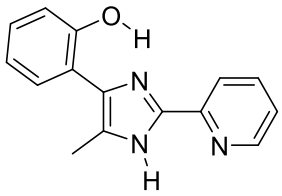


Figure S5. IR spectrum of 1-hydroxy-4-(2-hydroxyphenyl)-5-methyl-2-(pyridin-2-yl)-1*H*-imidazole (in KBr)**.**



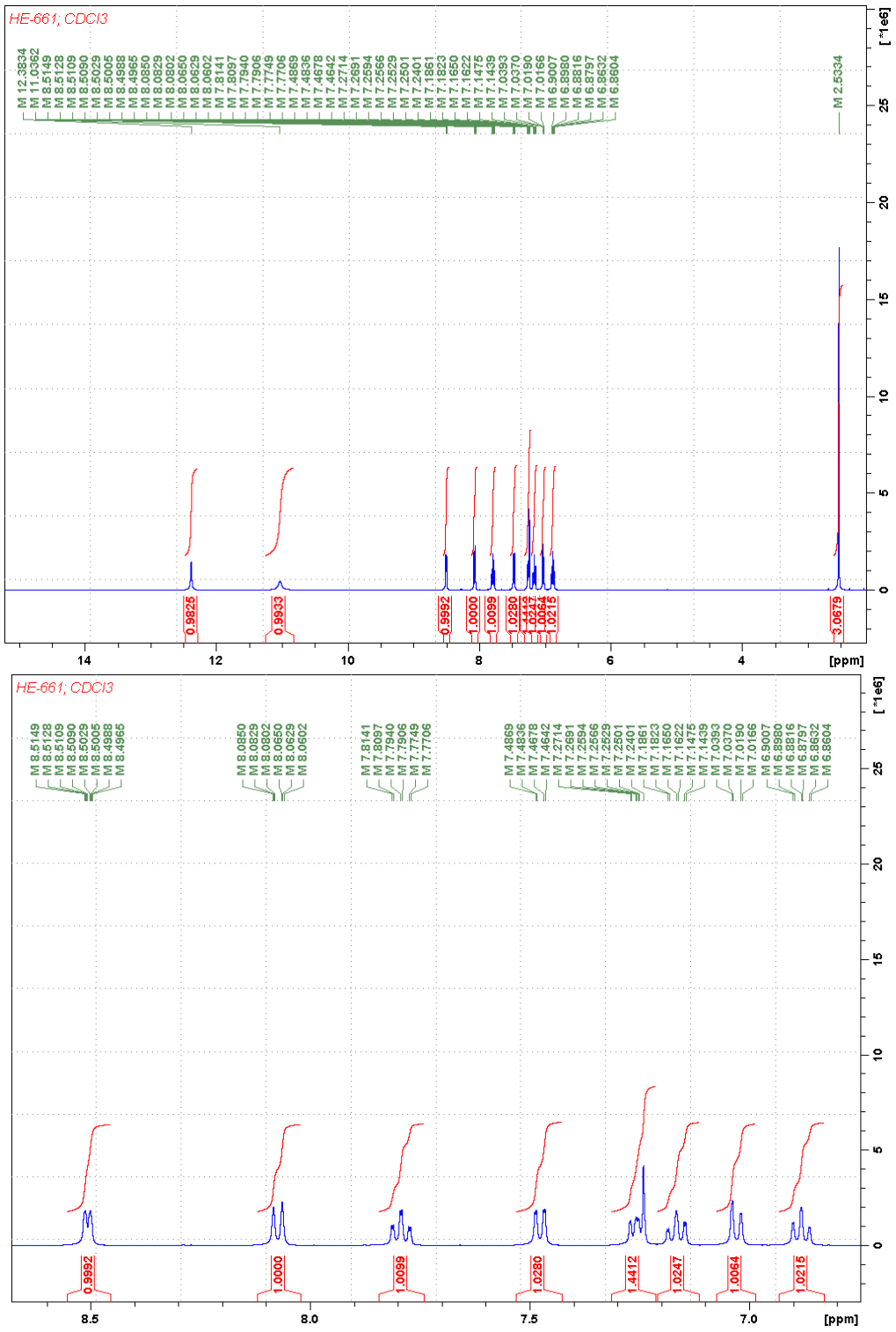
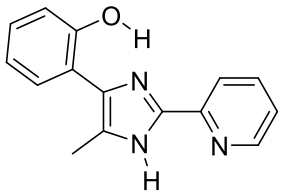


Figure S6. ^{1}H NMR spectrum of 4-(2-hydroxyphenyl)-5-methyl-2-(pyridin-2-yl)-1*H*-imidazole (in $CDCl_3$).



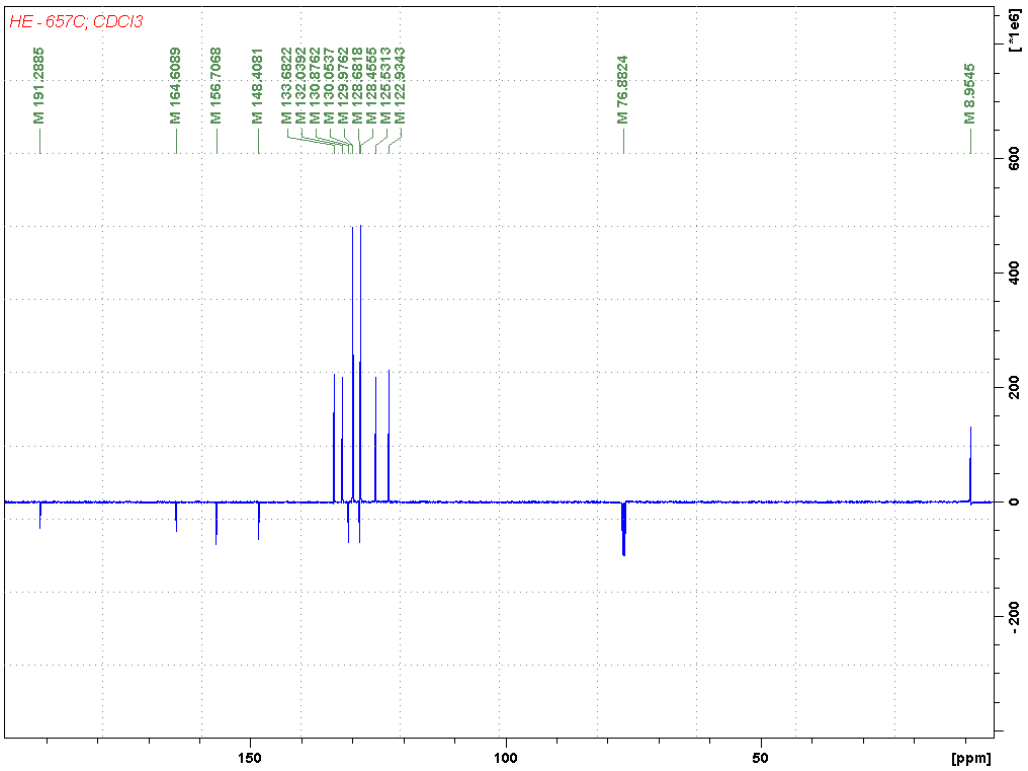


Figure S7. ^{13}C NMR spectrum of 1-(2-benzoyloxyphenyl)-2-(hydroxyimino)propan-1-one (in $CDCl_3$).

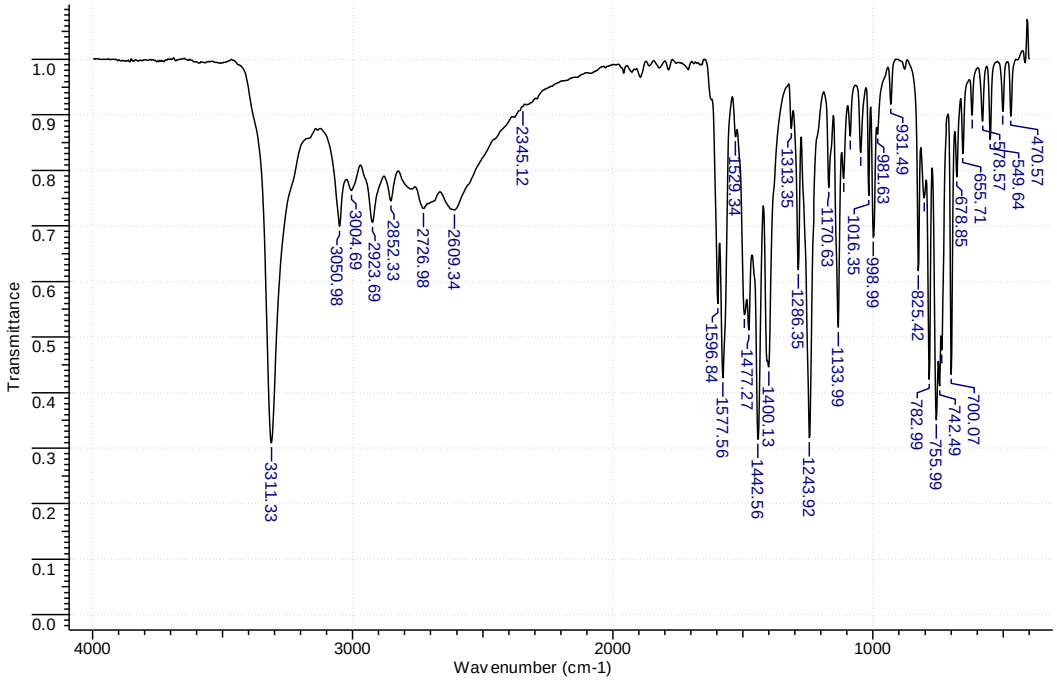


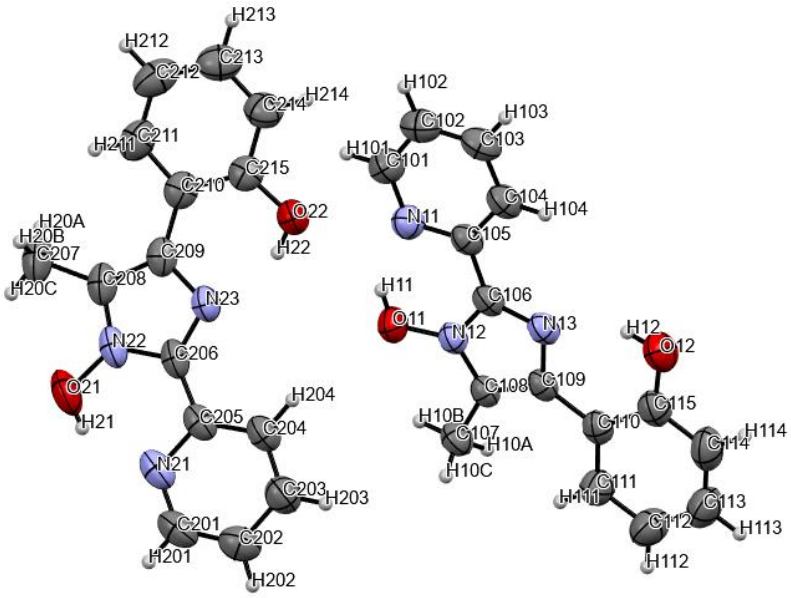
Figure S8. IR spectrum of 4-(2-hydroxyphenyl)-5-methyl-2-(pyridin-2-yl)-1*H*-imidazole (in KBr).

Structural data

Table S1. Crystal data and structure refinement for $\mathbf{L^{OH,OH}}$.

Identification code	$\mathbf{L^{OH,OH}}$
Empirical formula	$C_{15}H_{13}N_3O_2$
Formula weight	267.28
Crystal system	*Monoclinic*
Space group	$P2_1/c$
a, Å	13.0513(5)
b, Å	7.2703(4)
c, Å	27.5672(12)
β, deg.	90.491(4)
V, Å^3	2615.7(2)
Z	8
D(calc.), g/cm^3	1.357
μ, mm^{-1}	0.093
F(000)	1120
Crystal size, mm	0.47 × 0.11 × 0.05
θ range for data collection, deg.	2.14–29.13
Index ranges	$-16 \le h \le 17$, $-9 \le k \le 9$, $-25 \le l \le 36$
Reflections collected / independent	13699 / 5878
R_{int}	0.0195
Reflections with $I > 2\sigma(I)$	3781
Goodness-of-fit on F^2	1.040
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1191$
R indices (all data)	$R_1 = 0.0875$, $wR_2 = 0.1332$
Largest diff. peak / hole, *e*/Å^3	0.172 / −0.178

Table S2. Bond lengths and angles for $\mathbf{L^{OH,OH}}$.



Bond	*d*, Å	Bond	*d*, Å
O(11)-H(11)	0.8200	O(21)-H(21)	0.8200
O(11)-N(12)	1.3826(16)	O(21)-N(22)	1.3832(18)
O(12)-H(12)	0.8200	O(22)-H(22)	0.8200
O(12)-C(115)	1.355(2)	O(22)-C(215)	1.3560(18)
N(11)-C(101)	1.336(2)	N(21)-C(201)	1.339(2)
N(11)-C(105)	1.3475(19)	N(21)-C(205)	1.349(2)
N(12)-C(106)	1.3582(19)	N(22)-C(206)	1.353(2)
N(12)-C(108)	1.3556(19)	N(22)-C(208)	1.353(2)
N(13)-C(106)	1.3241(19)	N(23)-C(206)	1.330(2)
N(13)-C(109)	1.3802(19)	N(23)-C(209)	1.376(2)
C(101)-H(101)	0.9300	C(201)-H(201)	0.9300
C(101)-C(102)	1.369(2)	C(201)-C(202)	1.370(3)
C(102)-H(102)	0.9300	C(202)-H(202)	0.9300
C(102)-C(103)	1.384(2)	C(202)-C(203)	1.376(3)
C(103)-H(103)	0.9300	C(203)-H(203)	0.9300
C(103)-C(104)	1.372(2)	C(203)-C(204)	1.374(2)
C(104)-H(104)	0.9300	C(204)-H(204)	0.9300
C(104)-C(105)	1.388(2)	C(204)-C(205)	1.388(2)
C(105)-C(106)	1.452(2)	C(205)-C(206)	1.455(2)
C(107)-H(10A)	0.9600	C(207)-H(20A)	0.9600
C(107)-H(10B)	0.9600	C(207)-H(20B)	0.9600

C(107)-H(10C)	0.9600	C(207)-H(20C)	0.9600
C(107)-C(108)	1.485(2)	C(207)-C(208)	1.490(2)
C(108)-C(109)	1.393(2)	C(208)-C(209)	1.393(2)
C(109)-C(110)	1.464(2)	C(209)-C(210)	1.466(2)
C(110)-C(111)	1.389(2)	C(210)-C(211)	1.396(2)
C(110)-C(115)	1.407(2)	C(210)-C(215)	1.412(2)
C(111)-H(111)	0.9300	C(211)-H(211)	0.9300
C(111)-C(112)	1.380(2)	C(211)-C(212)	1.376(3)
C(112)-H(112)	0.9300	C(212)-H(212)	0.9300
C(112)-C(113)	1.368(3)	C(212)-C(213)	1.375(3)
C(113)-H(113)	0.9300	C(213)-H(213)	0.9300
C(113)-C(114)	1.367(3)	C(213)-C(214)	1.370(3)
C(114)-H(114)	0.9300	C(214)-H(214)	0.9300
C(114)-C(115)	1.399(3)	C(214)-C(215)	1.385(2)
Angle	ω, deg.	Angle	ω, deg.
N(12)-O(11)-H(11)	109.5	N(22)-O(21)-H(21)	109.5
C(115)-O(12)-H(12)	109.5	C(215)-O(22)-H(22)	109.5
C(101)-N(11)-C(105)	117.87(14)	C(201)-N(21)-C(205)	118.01(16)
C(106)-N(12)-O(11)	126.15(13)	C(206)-N(22)-O(21)	125.28(15)
C(108)-N(12)-O(11)	123.03(12)	C(208)-N(22)-O(21)	123.53(14)
C(108)-N(12)-C(106)	110.80(13)	C(208)-N(22)-C(206)	111.19(14)
C(106)-N(13)-C(109)	107.10(13)	C(206)-N(23)-C(209)	106.83(13)
N(11)-C(101)-H(101)	118.4	N(21)-C(201)-H(201)	118.5
N(11)-C(101)-C(102)	123.24(17)	N(21)-C(201)-C(202)	122.94(17)
C(102)-C(101)-H(101)	118.4	C(202)-C(201)-H(201)	118.5
C(101)-C(102)-H(102)	120.7	C(201)-C(202)-H(202)	120.6
C(101)-C(102)-C(103)	118.64(16)	C(201)-C(202)-C(203)	118.72(18)
C(103)-C(102)-H(102)	120.7	C(203)-C(202)-H(202)	120.6
C(102)-C(103)-H(103)	120.3	C(202)-C(203)-H(203)	120.1
C(104)-C(103)-C(102)	119.31(16)	C(204)-C(203)-C(202)	119.74(18)
C(104)-C(103)-H(103)	120.3	C(204)-C(203)-H(203)	120.1
C(103)-C(104)-H(104)	120.6	C(203)-C(204)-H(204)	120.8
C(103)-C(104)-C(105)	118.74(16)	C(203)-C(204)-C(205)	118.46(16)
C(105)-C(104)-H(104)	120.6	C(205)-C(204)-H(204)	120.8
N(11)-C(105)-C(104)	122.20(14)	N(21)-C(205)-C(204)	122.12(16)
N(11)-C(105)-C(106)	115.43(13)	N(21)-C(205)-C(206)	115.43(15)
C(104)-C(105)-C(106)	122.37(15)	C(204)-C(205)-C(206)	122.44(14)
N(12)-C(106)-C(105)	123.33(14)	N(22)-C(206)-C(205)	123.20(14)

N(13)-C(106)-N(12)	108.69(13)	N(23)-C(206)-N(22)	108.54(15)
N(13)-C(106)-C(105)	127.97(14)	N(23)-C(206)-C(205)	128.24(14)
H(10A)-C(107)-H(10B)	109.5	H(20A)-C(207)-H(20B)	109.5
H(10A)-C(107)-H(10C)	109.5	H(20A)-C(207)-H(20C)	109.5
H(10B)-C(107)-H(10C)	109.5	H(20B)-C(207)-H(20C)	109.5
C(108)-C(107)-H(10A)	109.5	C(208)-C(207)-H(20A)	109.5
C(108)-C(107)-H(10B)	109.5	C(208)-C(207)-H(20B)	109.5
C(108)-C(107)-H(10C)	109.5	C(208)-C(207)-H(20C)	109.5
N(12)-C(108)-C(107)	120.69(13)	N(22)-C(208)-C(207)	120.98(16)
N(12)-C(108)-C(109)	103.96(13)	N(22)-C(208)-C(209)	103.70(14)
C(109)-C(108)-C(107)	135.32(14)	C(209)-C(208)-C(207)	135.31(18)
N(13)-C(109)-C(108)	109.45(13)	N(23)-C(209)-C(208)	109.74(15)
N(13)-C(109)-C(110)	120.08(14)	N(23)-C(209)-C(210)	120.26(14)
C(108)-C(109)-C(110)	130.47(14)	C(208)-C(209)-C(210)	130.00(15)
C(111)-C(110)-C(109)	122.45(15)	C(211)-C(210)-C(209)	122.72(17)
C(111)-C(110)-C(115)	116.60(15)	C(211)-C(210)-C(215)	116.64(16)
C(115)-C(110)-C(109)	120.95(15)	C(215)-C(210)-C(209)	120.63(14)
C(110)-C(111)-H(111)	118.6	C(210)-C(211)-H(211)	118.9
C(112)-C(111)-C(110)	122.79(18)	C(212)-C(211)-C(210)	122.3(2)
C(112)-C(111)-H(111)	118.6	C(212)-C(211)-H(211)	118.9
C(111)-C(112)-H(112)	120.2	C(211)-C(212)-H(212)	120.0
C(113)-C(112)-C(111)	119.6(2)	C(213)-C(212)-C(211)	120.03(18)
C(113)-C(112)-H(112)	120.2	C(213)-C(212)-H(212)	120.0
C(112)-C(113)-H(113)	120.0	C(212)-C(213)-H(213)	120.3
C(114)-C(113)-C(112)	120.01(18)	C(214)-C(213)-C(212)	119.34(19)
C(114)-C(113)-H(113)	120.0	C(214)-C(213)-H(213)	120.3
C(113)-C(114)-H(114)	119.6	C(213)-C(214)-H(214)	119.3
C(113)-C(114)-C(115)	120.80(19)	C(213)-C(214)-C(215)	121.42(19)
C(115)-C(114)-H(114)	119.6	C(215)-C(214)-H(214)	119.3
O(12)-C(115)-C(110)	122.19(16)	O(22)-C(215)-C(210)	122.54(15)
O(12)-C(115)-C(114)	117.59(17)	O(22)-C(215)-C(214)	117.30(16)
C(114)-C(115)-C(110)	120.21(18)	C(214)-C(215)-C(210)	120.16(16)

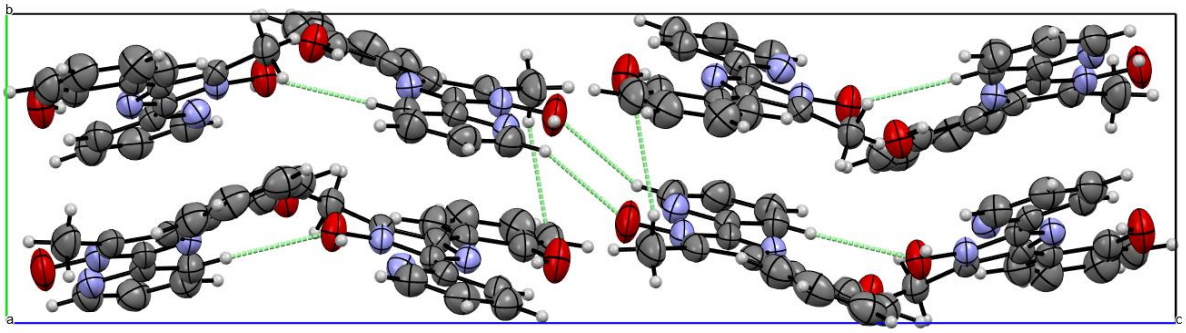


Figure S9. Packing of $\mathbf{L}^{\mathbf{OH,OH}}$ (view along the *a* axis).

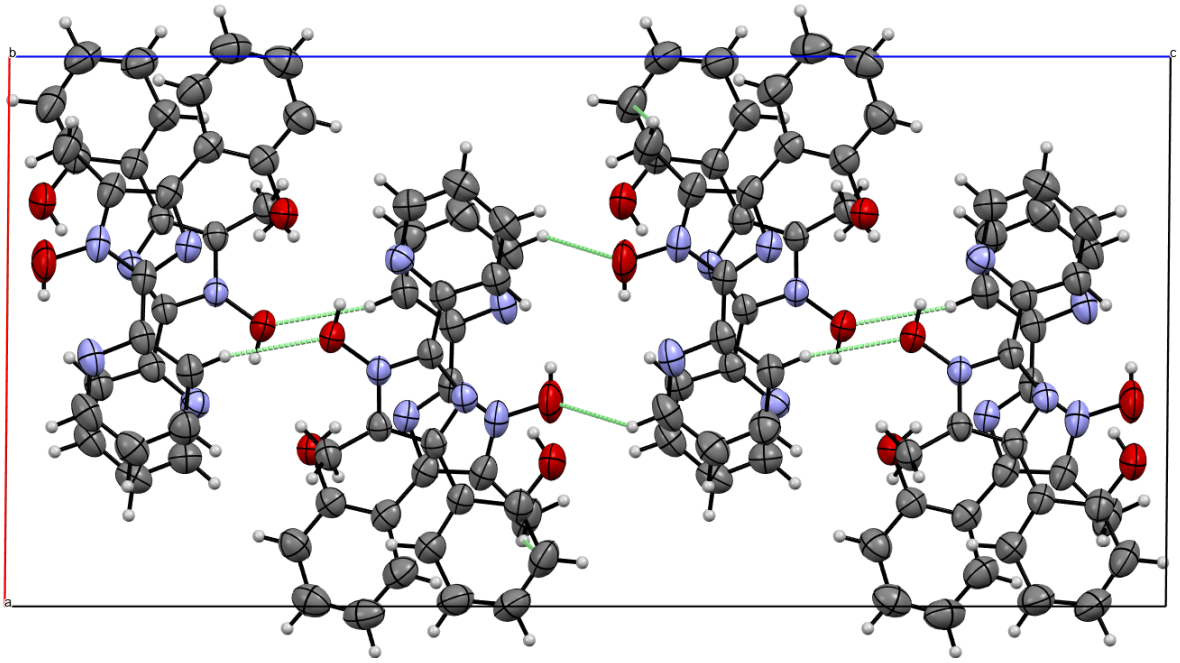


Figure S10. Packing of $\mathbf{L}^{\mathbf{OH,OH}}$ (view along the *b* axis).

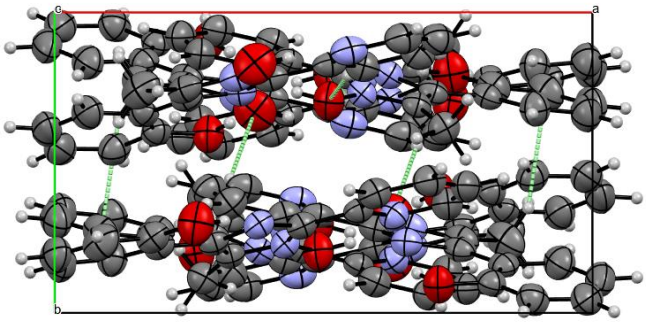


Figure S11. Packing of $\mathbf{L}^{\mathbf{OH,OH}}$ (view along the *c* axis).

Photophysical data

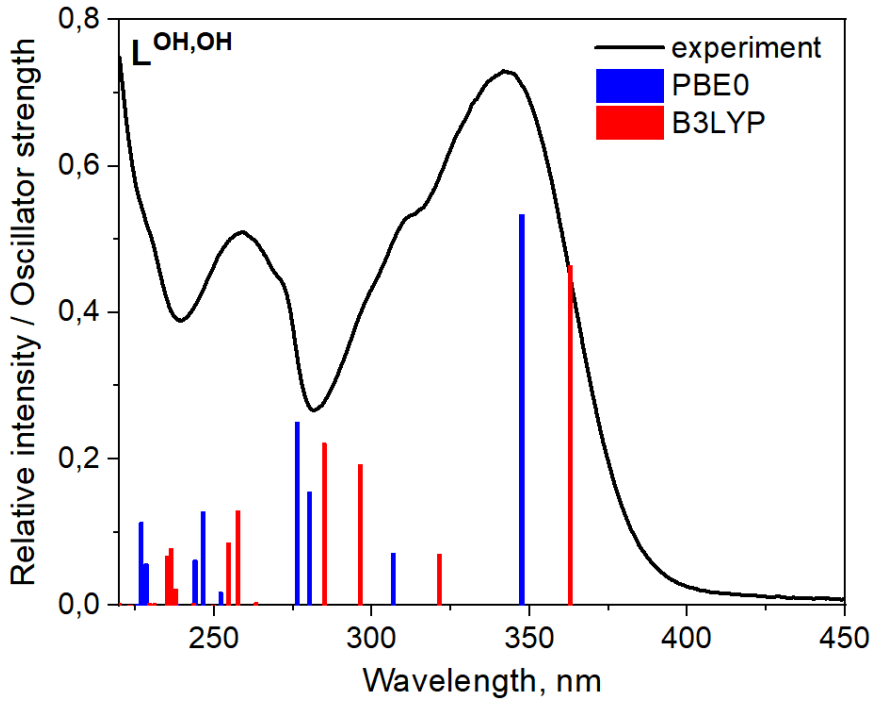


Figure S12. Comparison of the experimental absorption spectrum of $\mathbf{L}^{OH,OH}$ with those computed using PBE0 and B3LYP functionals.

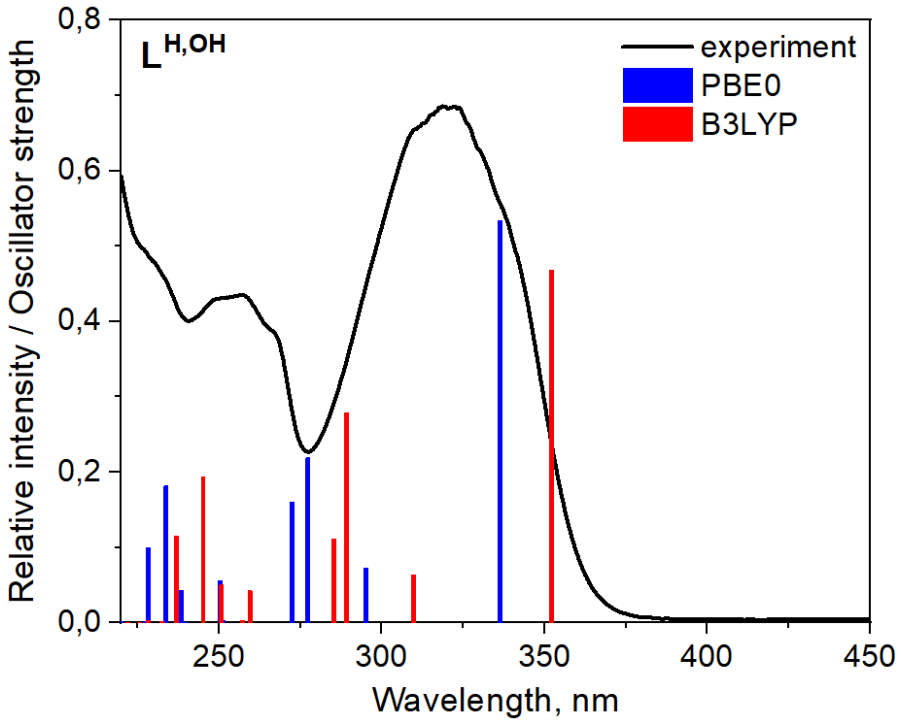


Figure S13. Comparison of the experimental absorption spectrum of $\mathbf{L}^{H,OH}$ with those computed using PBE0 and B3LYP functionals.

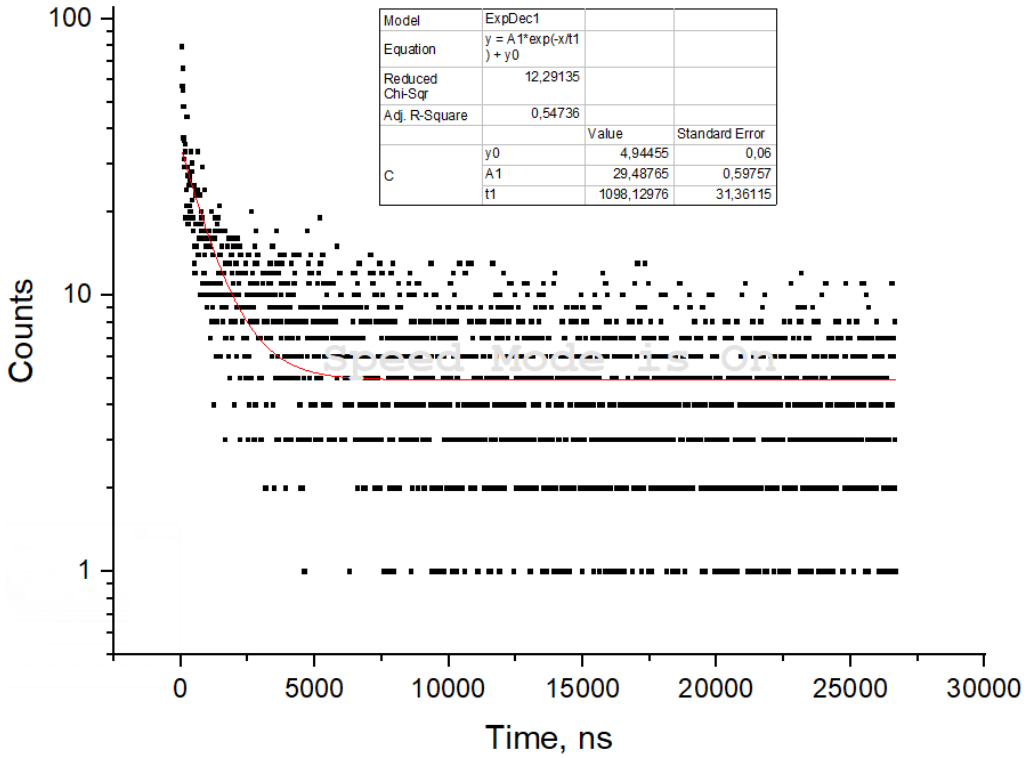


Figure S14. Photoluminescence decay curve for $\mathbf{L^{H,OH}}$.

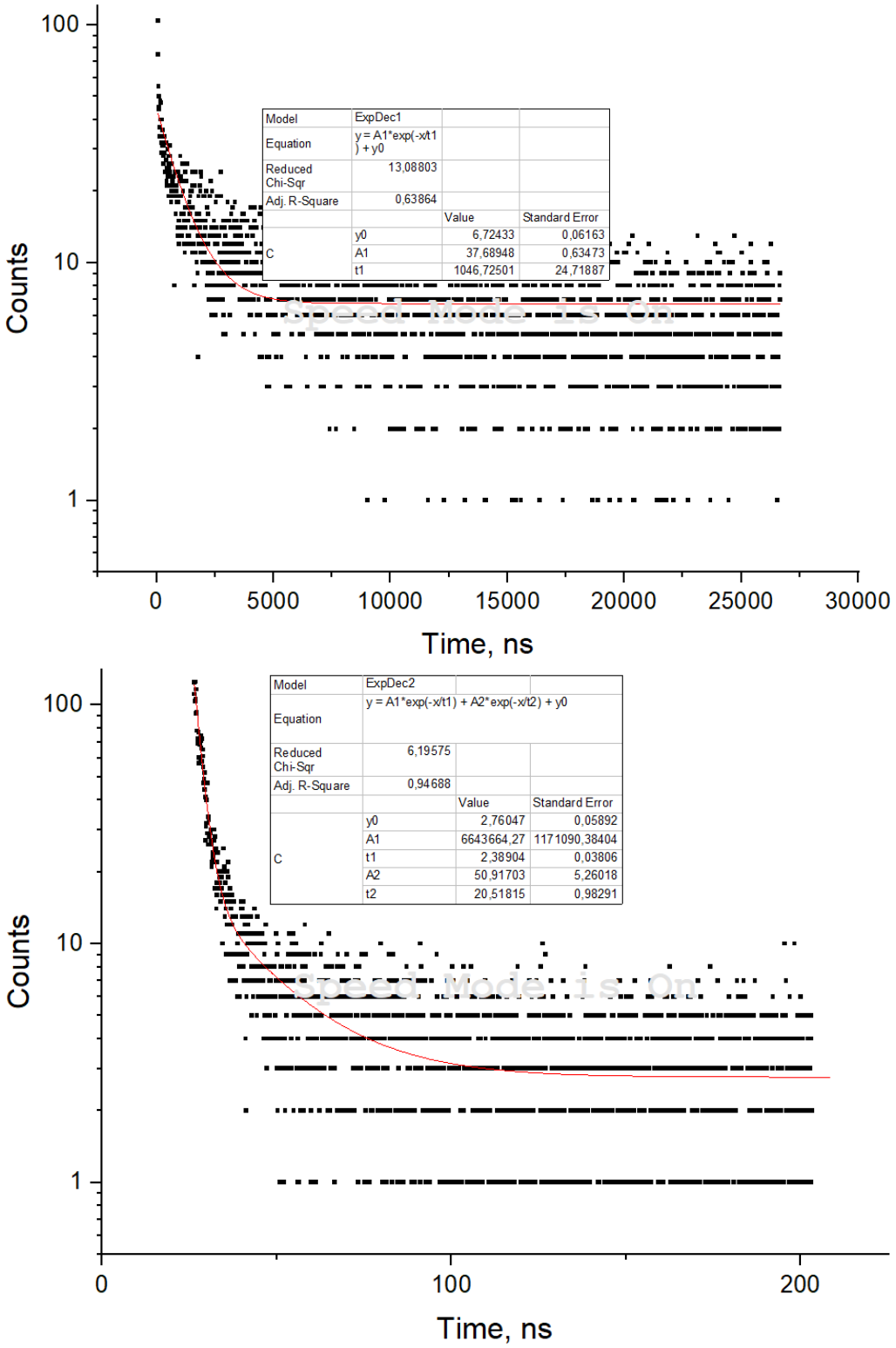
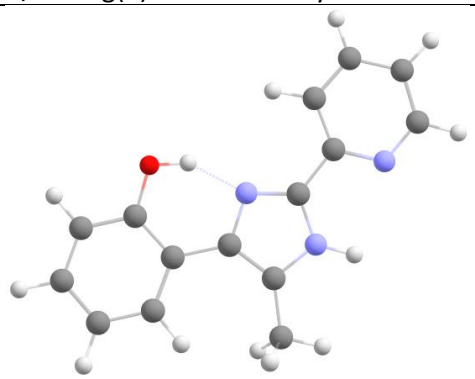


Figure S15. Photoluminescence decay curves for $\mathbf{L^{OH,OH}}$.

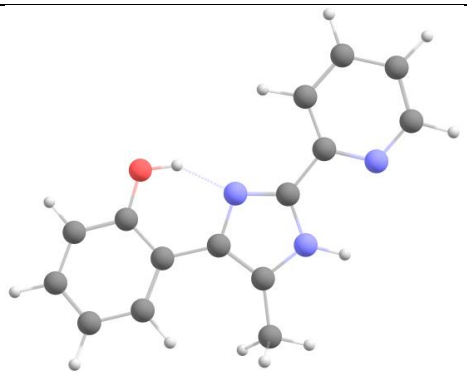
Theoretical data

Table S3. Optimized geometry of the **S_0 state** of **$L^{H,OH}$** (***N*-$L^{H,OH}$ form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model.**



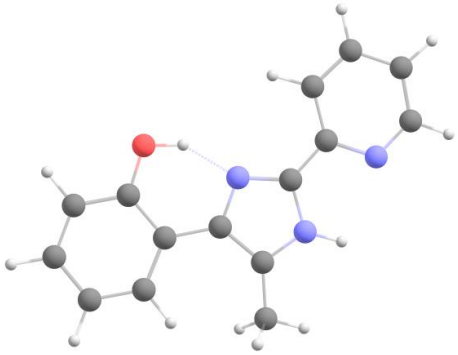
N	0.154602000000	-0.327532000000	-0.028976000000
C	1.253141000000	0.405811000000	-0.006470000000
C	-0.915083000000	0.542549000000	-0.008188000000
H	-3.245774000000	1.944987000000	-0.190102000000
C	-0.434023000000	1.850876000000	0.032257000000
N	0.926463000000	1.718995000000	0.028119000000
H	1.609212000000	2.466225000000	0.053500000000
C	2.633622000000	-0.059486000000	-0.014297000000
H	4.547823000000	-2.851404000000	-0.084168000000
N	3.571391000000	0.901203000000	0.016135000000
C	2.938141000000	-1.423891000000	-0.051148000000
C	4.849301000000	0.521111000000	0.010809000000
C	4.274952000000	-1.800236000000	-0.055962000000
C	5.256380000000	-0.811286000000	-0.024336000000
H	2.140521000000	-2.159136000000	-0.075614000000
H	5.585437000000	1.322031000000	0.035892000000
H	6.312595000000	-1.061331000000	-0.026896000000
C	-1.081068000000	3.189899000000	0.082401000000
H	-1.629570000000	3.411173000000	-0.840505000000
H	-1.787067000000	3.261683000000	0.916733000000
C	-3.399414000000	0.874878000000	-0.111578000000
H	-0.329912000000	3.973619000000	0.215761000000
C	-2.284190000000	0.024979000000	-0.022201000000
C	-2.528103000000	-1.370332000000	0.054486000000
C	-3.838991000000	-1.856201000000	0.057355000000
C	-4.701113000000	0.387806000000	-0.110816000000
C	-4.920399000000	-0.987815000000	-0.022611000000
H	-3.985186000000	-2.931279000000	0.120969000000
H	-5.536758000000	1.078240000000	-0.181759000000
H	-5.932016000000	-1.385382000000	-0.020359000000
O	-1.533485000000	-2.282397000000	0.129114000000
H	-0.667542000000	-1.790889000000	0.078495000000

Table S4. Optimized geometry of the **S_0 state** of **$L^{H,OH}$** (***N*-$L^{H,OH}$ form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



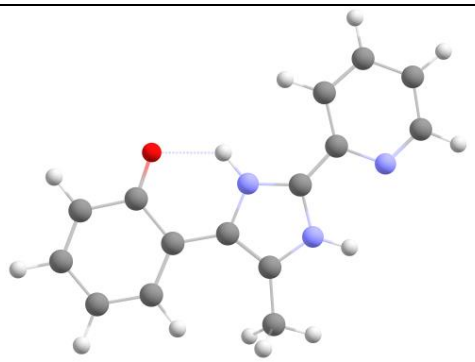
N	-1.142467000000	0.307306000000	-3.002752000000
C	-0.095718000000	1.078464000000	-3.228272000000
C	-0.660009000000	-0.916686000000	-2.594297000000
H	-0.130111000000	-3.196620000000	-1.213189000000
C	0.732962000000	-0.877168000000	-2.586888000000
N	1.047133000000	0.395175000000	-2.980663000000
H	1.966744000000	0.799897000000	-3.097824000000
C	-0.083507000000	2.461675000000	-3.678776000000
H	-2.090108000000	5.044062000000	-4.551231000000
N	1.132364000000	3.007783000000	-3.838765000000
C	-1.272680000000	3.156700000000	-3.922139000000
C	1.193839000000	4.272333000000	-4.251182000000
C	-1.187071000000	4.473174000000	-4.352051000000
C	0.070225000000	5.049944000000	-4.522851000000
H	-2.226429000000	2.662108000000	-3.770229000000
H	2.193972000000	4.684960000000	-4.370786000000
H	0.181613000000	6.076845000000	-4.857264000000
C	1.787827000000	-1.883834000000	-2.291704000000
H	1.935040000000	-2.028778000000	-1.213863000000
H	1.531700000000	-2.855532000000	-2.725903000000
C	-1.151391000000	-3.150704000000	-1.576822000000
H	2.748323000000	-1.573264000000	-2.716665000000
C	-1.576949000000	-2.010943000000	-2.277034000000
C	-2.934975000000	-1.948447000000	-2.676772000000
C	-3.789486000000	-3.023466000000	-2.414214000000
C	-2.005755000000	-4.212178000000	-1.310536000000
C	-3.331214000000	-4.147608000000	-1.742721000000
H	-4.820659000000	-2.942552000000	-2.745830000000
H	-1.643179000000	-5.077716000000	-0.763388000000
H	-4.013252000000	-4.970498000000	-1.544268000000
O	-3.461319000000	-0.887219000000	-3.316239000000
H	-2.775260000000	-0.175472000000	-3.342017000000

Table S5. Optimized geometry of the **T_1 state** of **$L^{H,OH}$** (***N*-$L^{H,OH}$ form**, **T_1^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



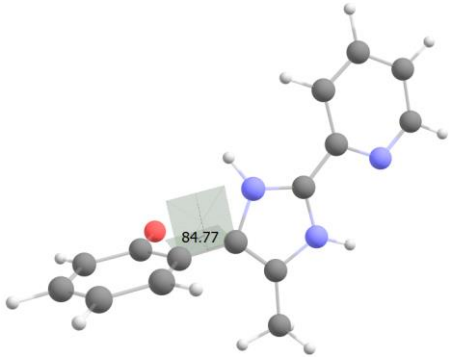
N	0.121619000000	-0.075677000000	-4.090932000000
C	0.159237000000	1.067937000000	-3.334976000000
C	-0.041392000000	-1.109837000000	-3.244828000000
H	-0.617868000000	-3.401353000000	-1.867887000000
C	-0.102466000000	-0.639018000000	-1.888385000000
N	0.006758000000	0.712238000000	-1.986757000000
H	0.039149000000	1.405617000000	-1.252261000000
C	0.316888000000	2.382376000000	-3.722694000000
H	0.740463000000	4.435919000000	-6.415873000000
N	0.315942000000	3.307876000000	-2.678945000000
C	0.471860000000	2.777280000000	-5.096195000000
C	0.464097000000	4.571545000000	-3.010104000000
C	0.621965000000	4.106060000000	-5.387231000000
C	0.620978000000	5.047624000000	-4.327900000000
H	0.464501000000	2.016553000000	-5.870761000000
H	0.461875000000	5.282053000000	-2.182688000000
H	0.737408000000	6.110337000000	-4.513446000000
C	-0.231482000000	-1.312738000000	-0.573799000000
H	-1.231071000000	-1.744147000000	-0.429109000000
H	0.498831000000	-2.121753000000	-0.460770000000
C	-0.406574000000	-3.566353000000	-2.917531000000
H	-0.062714000000	-0.596468000000	0.236040000000
C	-0.110172000000	-2.463111000000	-3.745481000000
C	0.120324000000	-2.709846000000	-5.133157000000
C	0.080246000000	-4.025323000000	-5.619607000000
C	-0.451478000000	-4.855238000000	-3.411253000000
C	-0.199812000000	-5.081040000000	-4.772857000000
H	0.268450000000	-4.178005000000	-6.677932000000
H	-0.685559000000	-5.684346000000	-2.750359000000
H	-0.230990000000	-6.092515000000	-5.169633000000
O	0.380361000000	-1.740483000000	-6.004857000000
H	0.341290000000	-0.864759000000	-5.510884000000

Table S6. Optimized geometry of the **T_1 state** of **$L^{H,OH}$** (***T*-$L^{H,OH}$ form**, **T_1^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



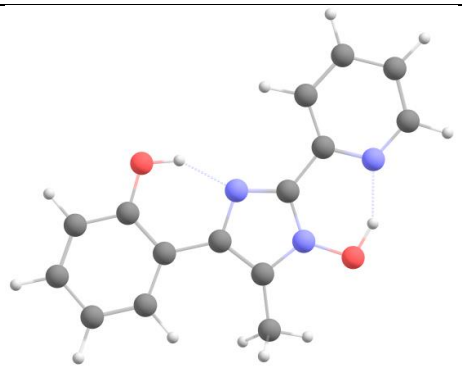
N	-0.104130000000	-0.077890000000	-4.090866000000
C	-0.045145000000	1.085772000000	-3.378701000000
C	-0.051182000000	-1.177881000000	-3.242785000000
H	-0.152065000000	-3.490643000000	-1.812554000000
C	0.035913000000	-0.674144000000	-1.943495000000
N	0.027142000000	0.689167000000	-2.050695000000
H	0.097541000000	1.382365000000	-1.318361000000
C	-0.050015000000	2.421273000000	-3.771174000000
H	-0.181794000000	4.545819000000	-6.427138000000
N	0.028705000000	3.318084000000	-2.724940000000
C	-0.127849000000	2.847286000000	-5.131339000000
C	0.030262000000	4.604662000000	-3.032574000000
C	-0.123134000000	4.194586000000	-5.400000000000
C	-0.042063000000	5.115238000000	-4.334165000000
H	-0.190676000000	2.117986000000	-5.935152000000
H	0.093613000000	5.289333000000	-2.186404000000
H	-0.035708000000	6.186356000000	-4.507088000000
C	0.132565000000	-1.329396000000	-0.614164000000
H	-0.787977000000	-1.867095000000	-0.355514000000
H	0.961885000000	-2.044335000000	-0.576260000000
C	-0.120418000000	-3.634474000000	-2.885846000000
H	0.305835000000	-0.579259000000	0.163050000000
C	-0.081319000000	-2.513629000000	-3.741813000000
C	-0.078369000000	-2.746784000000	-5.197658000000
C	-0.087713000000	-4.118785000000	-5.651276000000
C	-0.133208000000	-4.923313000000	-3.377712000000
C	-0.112827000000	-5.166012000000	-4.775191000000
H	-0.078982000000	-4.264719000000	-6.727353000000
H	-0.166206000000	-5.760270000000	-2.685903000000
H	-0.122509000000	-6.189231000000	-5.142102000000
O	-0.066338000000	-1.809323000000	-6.033846000000
H	-0.105602000000	-0.224226000000	-5.098116000000

Table S7. Optimized geometry of $\mathbf{L^{H,OH}}$ near S_0/S_1 conical intersection in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



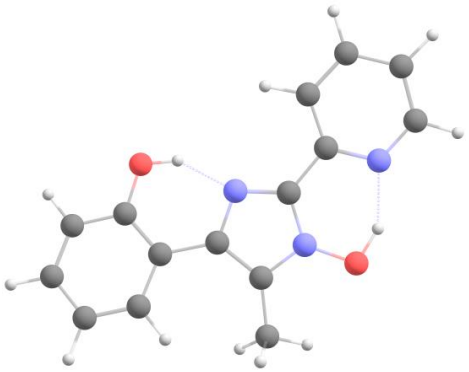
N	-0.305971000000	-0.037272000000	-4.019431000000
C	-0.071671000000	1.114771000000	-3.314699000000
C	0.076517000000	-1.120526000000	-3.219580000000
H	-1.986216000000	-2.800214000000	-2.880325000000
C	0.459618000000	-0.655260000000	-2.021128000000
N	0.352022000000	0.729339000000	-2.082550000000
H	0.573797000000	1.403536000000	-1.364503000000
C	-0.242016000000	2.457670000000	-3.703776000000
H	-1.176723000000	4.526003000000	-6.232906000000
N	0.100622000000	3.367200000000	-2.731070000000
C	-0.714414000000	2.853897000000	-4.985635000000
C	-0.009404000000	4.647960000000	-3.041397000000
C	-0.814457000000	4.196688000000	-5.262723000000
C	-0.450552000000	5.136600000000	-4.277076000000
H	-1.001135000000	2.116144000000	-5.731113000000
H	0.269113000000	5.345396000000	-2.251263000000
H	-0.512119000000	6.203868000000	-4.459404000000
C	0.908637000000	-1.351594000000	-0.793244000000
H	0.216408000000	-1.198009000000	0.044593000000
H	0.974015000000	-2.424661000000	-0.981300000000
C	-1.182407000000	-3.243766000000	-3.465413000000
H	1.900819000000	-0.998287000000	-0.484289000000
C	-0.053145000000	-2.510757000000	-3.705078000000
C	1.010747000000	-3.071693000000	-4.514602000000
C	0.839161000000	-4.414461000000	-5.015558000000
C	-1.315189000000	-4.563139000000	-3.957979000000
C	-0.296498000000	-5.139781000000	-4.725438000000
H	1.659559000000	-4.828934000000	-5.594156000000
H	-2.221612000000	-5.123349000000	-3.753289000000
H	-0.410266000000	-6.155281000000	-5.094919000000
O	2.031076000000	-2.401948000000	-4.782716000000
H	-0.220109000000	-0.049955000000	-5.013214000000

Table S8. Optimized geometry of the **S_0 state** of **$L^{OH,OH}$** (***N,N*-$L^{H,OH}$ form**, **$S_0^{N,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.



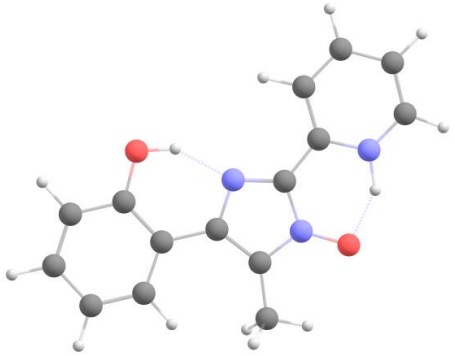
N	-0.170318000000	-0.049413000000	-4.064017000000
C	-0.084930000000	1.054424000000	-3.331537000000
C	-0.066182000000	-1.115928000000	-3.211206000000
C	0.098176000000	-0.652883000000	-1.900436000000
C	0.304502000000	-1.301095000000	-0.580403000000
N	0.071327000000	0.701741000000	-2.027446000000
C	-0.136888000000	2.431619000000	-3.780158000000
N	-0.009692000000	3.363480000000	-2.815837000000
C	-0.306413000000	2.768949000000	-5.126816000000
C	-0.046101000000	4.653554000000	-3.154393000000
C	-0.341765000000	4.113502000000	-5.466565000000
C	-0.209651000000	5.079320000000	-4.467172000000
H	-0.407013000000	1.987814000000	-5.872654000000
H	0.060664000000	5.364747000000	-2.339723000000
H	-0.471746000000	4.409520000000	-6.503515000000
H	-0.232924000000	6.138987000000	-4.698454000000
H	-0.623311000000	-1.734233000000	-0.187884000000
H	1.047379000000	-2.101524000000	-0.651051000000
H	0.662105000000	-0.566034000000	0.144878000000
C	-0.112358000000	-2.483649000000	-3.727076000000
C	-0.019986000000	-2.728746000000	-5.120395000000
C	-0.247175000000	-3.593468000000	-2.876878000000
C	-0.027819000000	-4.039458000000	-5.605193000000
C	-0.260436000000	-4.895487000000	-3.363048000000
C	-0.142795000000	-5.117616000000	-4.736095000000
H	-0.358967000000	-3.432982000000	-1.810221000000
H	0.052415000000	-4.188968000000	-6.678673000000
H	-0.367580000000	-5.729031000000	-2.674812000000
O	0.080924000000	-1.733308000000	-6.029553000000
H	-0.004159000000	-0.869329000000	-5.544356000000
O	0.193620000000	1.554501000000	-0.975316000000
H	0.153327000000	2.463401000000	-1.434090000000
H	-0.150331000000	-6.129724000000	-5.132292000000

Table S9. Optimized geometry of the **S_0 state** of **$L^{OH,OH}$** (***N,N*-$L^{H,OH}$ form**, **$S_0^{N,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



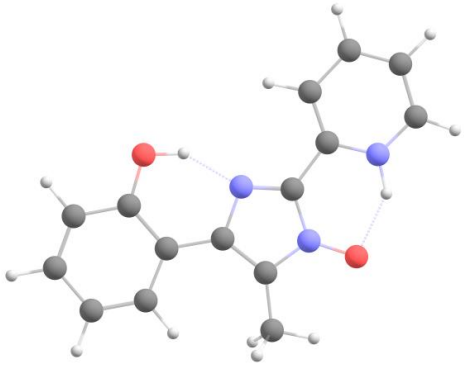
N	-0.187803000000	-0.038195000000	-4.061322000000
C	-0.091463000000	1.060320000000	-3.320704000000
C	-0.078752000000	-1.108653000000	-3.219575000000
C	0.103706000000	-0.653749000000	-1.905901000000
C	0.338835000000	-1.311852000000	-0.596010000000
N	0.078419000000	0.699984000000	-2.019875000000
C	-0.146468000000	2.434467000000	-3.765019000000
N	0.000660000000	3.374959000000	-2.811162000000
C	-0.341208000000	2.763985000000	-5.113005000000
C	-0.039988000000	4.660634000000	-3.163572000000
C	-0.379379000000	4.103175000000	-5.463302000000
C	-0.226119000000	5.078478000000	-4.474700000000
H	-0.459624000000	1.972070000000	-5.844698000000
H	0.083147000000	5.378970000000	-2.356515000000
H	-0.528740000000	4.390516000000	-6.500592000000
H	-0.251069000000	6.136606000000	-4.714169000000
H	-0.589523000000	-1.698462000000	-0.157152000000
H	1.034625000000	-2.149274000000	-0.706040000000
H	0.765903000000	-0.594640000000	0.110034000000
C	-0.126756000000	-2.475893000000	-3.733975000000
C	0.026194000000	-2.726376000000	-5.120154000000
C	-0.319044000000	-3.577069000000	-2.884960000000
C	0.030598000000	-4.040903000000	-5.595330000000
C	-0.323862000000	-4.880475000000	-3.362731000000
C	-0.137904000000	-5.109704000000	-4.726874000000
H	-0.489441000000	-3.405013000000	-1.827368000000
H	0.161311000000	-4.192976000000	-6.662861000000
H	-0.478698000000	-5.709475000000	-2.678129000000
O	0.175920000000	-1.743039000000	-6.027743000000
H	0.061244000000	-0.879164000000	-5.561972000000
O	0.216478000000	1.540060000000	-0.959233000000
H	0.181323000000	2.447728000000	-1.400853000000
H	-0.136622000000	-6.124357000000	-5.116926000000

Table S10. Optimized geometry of the **S_0 state** of **$L^{OH,OH}$** (***T,N*-$L^{H,OH}$ form**, **$S_0^{T,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



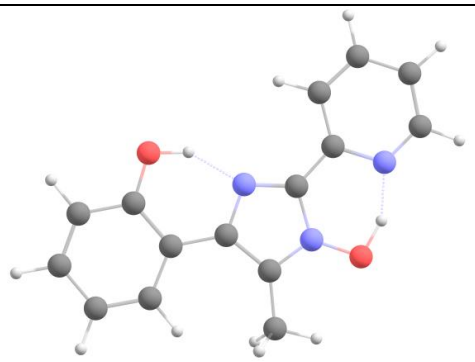
N	-0.004844000000	-0.517430000000	-0.005024000000
C	1.142560000000	0.179694000000	-0.001537000000
C	-1.006920000000	0.389319000000	-0.002891000000
C	-0.464287000000	1.703048000000	0.002722000000
C	-1.032469000000	3.072657000000	0.011401000000
N	0.877241000000	1.532694000000	0.003145000000
C	2.456834000000	-0.330783000000	-0.002765000000
N	3.475405000000	0.573466000000	0.001690000000
C	2.785487000000	-1.703919000000	-0.008239000000
C	4.771695000000	0.218993000000	0.001128000000
C	4.108621000000	-2.077697000000	-0.008797000000
C	5.133385000000	-1.105518000000	-0.004020000000
H	1.979406000000	-2.428594000000	-0.012089000000
H	5.486160000000	1.035110000000	0.004948000000
H	4.368868000000	-3.132470000000	-0.013031000000
H	6.180294000000	-1.385634000000	-0.004396000000
H	-1.637806000000	3.268192000000	-0.881477000000
H	-1.662040000000	3.245508000000	0.891932000000
H	-0.205117000000	3.787661000000	0.030831000000
C	-2.401904000000	-0.040679000000	-0.004334000000
C	-2.727753000000	-1.422333000000	0.008793000000
C	-3.462810000000	0.880690000000	-0.018307000000
C	-4.067074000000	-1.824872000000	0.010314000000
C	-4.789281000000	0.475174000000	-0.017408000000
C	-5.089589000000	-0.888502000000	-0.002407000000
H	-3.241906000000	1.941492000000	-0.031242000000
H	-4.273869000000	-2.891144000000	0.021250000000
H	-5.583130000000	1.216492000000	-0.028685000000
O	-1.796391000000	-2.391081000000	0.020294000000
H	-0.906107000000	-1.953366000000	0.013024000000
O	1.789217000000	2.475297000000	0.007725000000
H	-6.124285000000	-1.221908000000	-0.001277000000
H	3.103330000000	1.572186000000	0.005465000000

Table S11. Optimized geometry of the **S_1 state** of **$L^{OH,OH}$** (***T,N*-$L^{H,OH}$ form**, **$S_1^{T,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



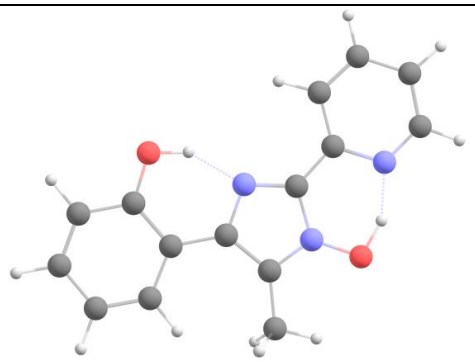
N	-0.046645000000	-0.060188000000	-4.012483000000
C	-0.040176000000	1.007716000000	-3.267741000000
C	-0.045876000000	-1.161106000000	-3.149734000000
C	-0.038404000000	-0.705035000000	-1.831728000000
N	-0.034964000000	0.662279000000	-1.923130000000
C	-0.037820000000	2.394104000000	-3.795981000000
N	-0.024984000000	3.340152000000	-2.846035000000
C	-0.046742000000	2.706979000000	-5.125019000000
C	-0.020068000000	4.685736000000	-3.138864000000
C	-0.041622000000	4.120284000000	-5.485092000000
C	-0.028550000000	5.062137000000	-4.494553000000
H	-0.056710000000	1.923922000000	-5.869648000000
H	-0.009346000000	5.368375000000	-2.302126000000
H	-0.048073000000	4.410237000000	-6.529965000000
H	-0.024454000000	6.121618000000	-4.734434000000
C	-0.034067000000	-1.349219000000	-0.495778000000
H	-0.923192000000	-1.971106000000	-0.339194000000
H	0.852952000000	-1.976103000000	-0.347365000000
H	-0.028362000000	-0.561897000000	0.263224000000
C	-0.052271000000	-2.487713000000	-3.700205000000
C	-0.059362000000	-2.699921000000	-5.120042000000
C	-0.051782000000	-3.632645000000	-2.870670000000
C	-0.065465000000	-4.005680000000	-5.633023000000
C	-0.057836000000	-4.909209000000	-3.391198000000
C	-0.064743000000	-5.095381000000	-4.785772000000
H	-0.046466000000	-3.499203000000	-1.795682000000
H	-0.070722000000	-4.121222000000	-6.712372000000
H	-0.057249000000	-5.766939000000	-2.725414000000
H	-0.069533000000	-6.099875000000	-5.199858000000
O	-0.060551000000	-1.706067000000	-6.004081000000
H	-0.055767000000	-0.842590000000	-5.504498000000
O	-0.028112000000	1.481879000000	-0.922972000000
H	-0.021119000000	2.991541000000	-1.875077000000

Table S12. Optimized geometry of the **T_1 state** of **$L^{OH,OH}$** (***N,N*-$L^{H,OH}$ form**, **$T_1^{N,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



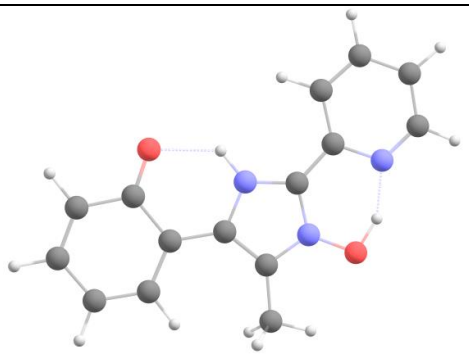
N	-0.111049000000	-0.082521000000	-4.123081000000
C	-0.058432000000	1.052595000000	-3.403157000000
C	-0.039548000000	-1.133279000000	-3.244586000000
C	0.063258000000	-0.646280000000	-1.903564000000
C	0.168558000000	-1.282055000000	-0.569002000000
N	0.049573000000	0.685759000000	-2.031918000000
C	-0.093413000000	2.384351000000	-3.804770000000
N	-0.015927000000	3.330850000000	-2.778820000000
C	-0.201142000000	2.790065000000	-5.172645000000
C	-0.044526000000	4.610576000000	-3.102262000000
C	-0.227891000000	4.124475000000	-5.470653000000
C	-0.148169000000	5.078868000000	-4.415968000000
H	-0.259280000000	2.028721000000	-5.944285000000
H	0.018359000000	5.311694000000	-2.271490000000
H	-0.309175000000	4.455747000000	-6.501985000000
H	-0.166363000000	6.144930000000	-4.613446000000
H	-0.702189000000	-1.912963000000	-0.355847000000
H	1.065775000000	-1.907245000000	-0.492582000000
H	0.225294000000	-0.504944000000	0.196840000000
C	-0.072666000000	-2.481413000000	-3.723273000000
C	-0.181911000000	-2.732236000000	-5.132247000000
C	-0.001851000000	-3.601855000000	-2.859769000000
C	-0.214873000000	-4.053233000000	-5.602999000000
C	-0.035593000000	-4.892549000000	-3.340616000000
C	-0.143125000000	-5.117160000000	-4.724578000000
H	0.081201000000	-3.442165000000	-1.791879000000
H	-0.298195000000	-4.203530000000	-6.674989000000
H	0.020713000000	-5.730685000000	-2.652533000000
O	-0.255073000000	-1.759532000000	-6.033083000000
H	-0.219331000000	-0.880163000000	-5.542463000000
O	0.125169000000	1.559717000000	-1.007802000000
H	0.082857000000	2.487379000000	-1.529198000000
H	-0.170173000000	-6.133523000000	-5.108419000000

Table S13. Optimized geometry of the **T_1 state** of **$L^{OH,OH}$** (***T,N*-$L^{H,OH}$ form**, **$T_1^{T,N}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



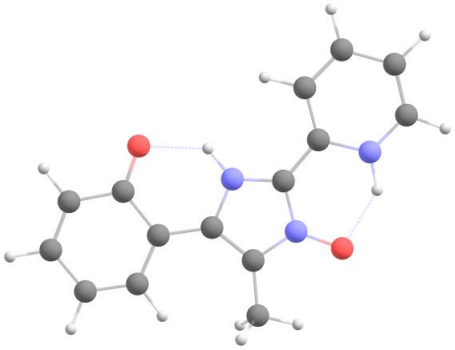
N	-0.111049000000	-0.082521000000	-4.123081000000
C	-0.058432000000	1.052595000000	-3.403157000000
C	-0.039548000000	-1.133279000000	-3.244586000000
C	0.063258000000	-0.646280000000	-1.903564000000
C	0.168558000000	-1.282055000000	-0.569002000000
N	0.049573000000	0.685759000000	-2.031918000000
C	-0.093413000000	2.384351000000	-3.804770000000
N	-0.015927000000	3.330850000000	-2.778820000000
C	-0.201142000000	2.790065000000	-5.172645000000
C	-0.044526000000	4.610576000000	-3.102262000000
C	-0.227891000000	4.124475000000	-5.470653000000
C	-0.148169000000	5.078868000000	-4.415968000000
H	-0.259280000000	2.028721000000	-5.944285000000
H	0.018359000000	5.311694000000	-2.271490000000
H	-0.309175000000	4.455747000000	-6.501985000000
H	-0.166363000000	6.144930000000	-4.613446000000
H	-0.702189000000	-1.912963000000	-0.355847000000
H	1.065775000000	-1.907245000000	-0.492582000000
H	0.225294000000	-0.504944000000	0.196840000000
C	-0.072666000000	-2.481413000000	-3.723273000000
C	-0.181911000000	-2.732236000000	-5.132247000000
C	-0.001851000000	-3.601855000000	-2.859769000000
C	-0.214873000000	-4.053233000000	-5.602999000000
C	-0.035593000000	-4.892549000000	-3.340616000000
C	-0.143125000000	-5.117160000000	-4.724578000000
H	0.081201000000	-3.442165000000	-1.791879000000
H	-0.298195000000	-4.203530000000	-6.674989000000
H	0.020713000000	-5.730685000000	-2.652533000000
O	-0.255073000000	-1.759532000000	-6.033083000000
H	-0.219331000000	-0.880163000000	-5.542463000000
O	0.125169000000	1.559717000000	-1.007802000000
H	0.082857000000	2.487379000000	-1.529198000000
H	-0.170173000000	-6.133523000000	-5.108419000000

Table S14. Optimized geometry of the **T_1 state** of **$L^{OH,OH}$** (***N,T*-$L^{H,OH}$ form**, **$T_1^{N,T}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



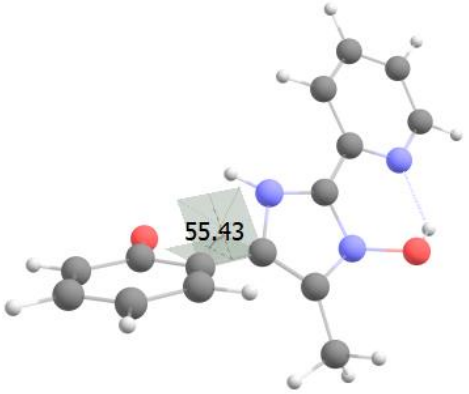
N	-0.107298000000	-0.070292000000	-4.076267000000
C	-0.056692000000	1.095212000000	-3.381974000000
C	-0.037604000000	-1.167452000000	-3.220463000000
C	0.061552000000	-0.653419000000	-1.925845000000
C	0.167501000000	-1.278235000000	-0.584862000000
N	0.047566000000	0.698731000000	-2.056656000000
C	-0.093356000000	2.426239000000	-3.804208000000
N	-0.016932000000	3.365049000000	-2.787525000000
C	-0.200607000000	2.830744000000	-5.167879000000
C	-0.045523000000	4.651629000000	-3.107769000000
C	-0.227164000000	4.169928000000	-5.460096000000
C	-0.148470000000	5.123199000000	-4.413647000000
H	-0.259857000000	2.085704000000	-5.956775000000
H	0.017563000000	5.345756000000	-2.271412000000
H	-0.308447000000	4.498349000000	-6.492802000000
H	-0.167043000000	6.188783000000	-4.613244000000
H	-0.703413000000	-1.906804000000	-0.366799000000
H	1.065614000000	-1.901123000000	-0.503895000000
H	0.223835000000	-0.495115000000	0.174324000000
C	-0.072108000000	-2.504253000000	-3.714081000000
C	-0.184502000000	-2.745221000000	-5.165793000000
C	-0.002156000000	-3.621878000000	-2.858985000000
C	-0.215471000000	-4.116203000000	-5.614750000000
C	-0.036511000000	-4.913983000000	-3.348346000000
C	-0.144152000000	-5.163748000000	-4.738790000000
H	0.080877000000	-3.474889000000	-1.788797000000
H	-0.298606000000	-4.263914000000	-6.687437000000
H	0.020037000000	-5.748180000000	-2.654539000000
O	-0.252411000000	-1.808200000000	-6.003079000000
O	0.125721000000	1.563351000000	-1.015321000000
H	0.084492000000	2.488580000000	-1.512994000000
H	-0.169407000000	-6.187975000000	-5.101415000000
H	-0.185094000000	-0.230064000000	-5.080413000000

Table S15. Optimized geometry of the **T_1 state** of **$L^{OH,OH}$** (***T,T*-$L^{H,OH}$ form**, **$T_1^{T,T}$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



N	-0.102192000000	-0.064340000000	-4.011442000000
C	-0.049785000000	1.072301000000	-3.294203000000
C	-0.034326000000	-1.170656000000	-3.178261000000
C	0.065388000000	-0.672432000000	-1.877635000000
C	0.170904000000	-1.306098000000	-0.543548000000
N	0.054126000000	0.695287000000	-1.971688000000
C	-0.090267000000	2.404168000000	-3.765805000000
N	-0.019116000000	3.421875000000	-2.811789000000
C	-0.196418000000	2.772457000000	-5.118776000000
C	-0.050463000000	4.729866000000	-3.166598000000
C	-0.228856000000	4.098020000000	-5.487201000000
C	-0.152988000000	5.109240000000	-4.472706000000
H	-0.252872000000	1.993994000000	-5.874674000000
H	0.011100000000	5.438196000000	-2.347217000000
H	-0.310860000000	4.374683000000	-6.532783000000
H	-0.175757000000	6.162852000000	-4.726525000000
H	-0.700461000000	-1.932983000000	-0.320503000000
H	1.070160000000	-1.927404000000	-0.457879000000
H	0.226273000000	-0.508243000000	0.202218000000
C	-0.071871000000	-2.494044000000	-3.710220000000
C	-0.184786000000	-2.699946000000	-5.166439000000
C	-0.003783000000	-3.627959000000	-2.879951000000
C	-0.218212000000	-4.060085000000	-5.646539000000
C	-0.040398000000	-4.909768000000	-3.398191000000
C	-0.148567000000	-5.127080000000	-4.793749000000
H	0.079527000000	-3.499281000000	-1.806996000000
H	-0.301725000000	-4.184123000000	-6.722209000000
H	0.014717000000	-5.759716000000	-2.723689000000
O	-0.251266000000	-1.742863000000	-5.982608000000
O	0.129772000000	1.526199000000	-0.968735000000
H	-0.175672000000	-6.142724000000	-5.179727000000
H	0.057196000000	3.084708000000	-1.840701000000
H	-0.180127000000	-0.215605000000	-5.019900000000

Table S16. Optimized geometry of $\mathbf{L^{OH,OH}}$ near S_0/S_1 conical intersection in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in the gas phase**.



N	-0.150139000000	-0.078830000000	-4.036393000000
C	0.007242000000	1.082177000000	-3.339741000000
C	0.105821000000	-1.146964000000	-3.177735000000
C	0.400496000000	-0.667104000000	-1.955045000000
C	0.736982000000	-1.332350000000	-0.674497000000
N	0.398285000000	0.747387000000	-2.065253000000
C	-0.190429000000	2.412980000000	-3.779466000000
N	0.146362000000	3.384118000000	-2.877484000000
C	-0.683025000000	2.727860000000	-5.068301000000
C	0.025827000000	4.649088000000	-3.257088000000
C	-0.797734000000	4.054296000000	-5.427818000000
C	-0.429450000000	5.051786000000	-4.512789000000
H	-0.976821000000	1.935683000000	-5.750955000000
H	0.306580000000	5.393305000000	-2.513142000000
H	-1.175515000000	4.322274000000	-6.410711000000
H	-0.507447000000	6.105218000000	-4.758691000000
H	-0.047994000000	-1.207505000000	0.082987000000
H	0.887525000000	-2.401419000000	-0.844668000000
H	1.658463000000	-0.908240000000	-0.260830000000
C	-0.024152000000	-2.531177000000	-3.702255000000
C	0.743368000000	-2.893100000000	-4.880554000000
C	-0.912073000000	-3.419621000000	-3.152890000000
C	0.572788000000	-4.230888000000	-5.389496000000
C	-1.029350000000	-4.735337000000	-3.662551000000
C	-0.278896000000	-5.128395000000	-4.774136000000
H	-1.514865000000	-3.113516000000	-2.301092000000
H	1.165549000000	-4.508582000000	-6.256316000000
H	-1.704050000000	-5.438476000000	-3.184026000000
O	1.490984000000	-2.051432000000	-5.435343000000
H	0.160173000000	-0.165753000000	-5.007068000000
O	-0.158765226215	1.437018356216	-0.986217212986
H	0.084231226215	2.343513643784	-1.207874787014
H	-0.379106000000	-6.139621000000	-5.159629000000