Electronic Supplementary Information

Dual emission of ESIPT-capable 2-(2-hydroxyphenyl)-4-(1*H*-pyrazol-1-yl)pyrimidines: interplay of fluorescence and phosphorescence

Nikita A. Shekhovtsov,*[a] Elena B. Nikolaenkova,[b] Alexey A. Ryadun,[a] Sofia N. Vorobyeva,[a] Viktor P. Krivopalov [b] and Mark B. Bushuev *[a]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia. E-mail addresses: shekhovtsov@niic.nsc.ru (Nikita A. Shekhovtsov), bushuev@niic.nsc.ru (Mark B. Bushuev). Fax: +7 383 330 94 89; Tel: +7 383 316 51 43.
[b] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia.

Table of Contents

NMR and IR spectral data

HL¹

Figure S1. ¹H NMR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL¹**).

HL^1

Figure S2. ^{13}C NMR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL^1**).

Figure S3. IR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL^1**).
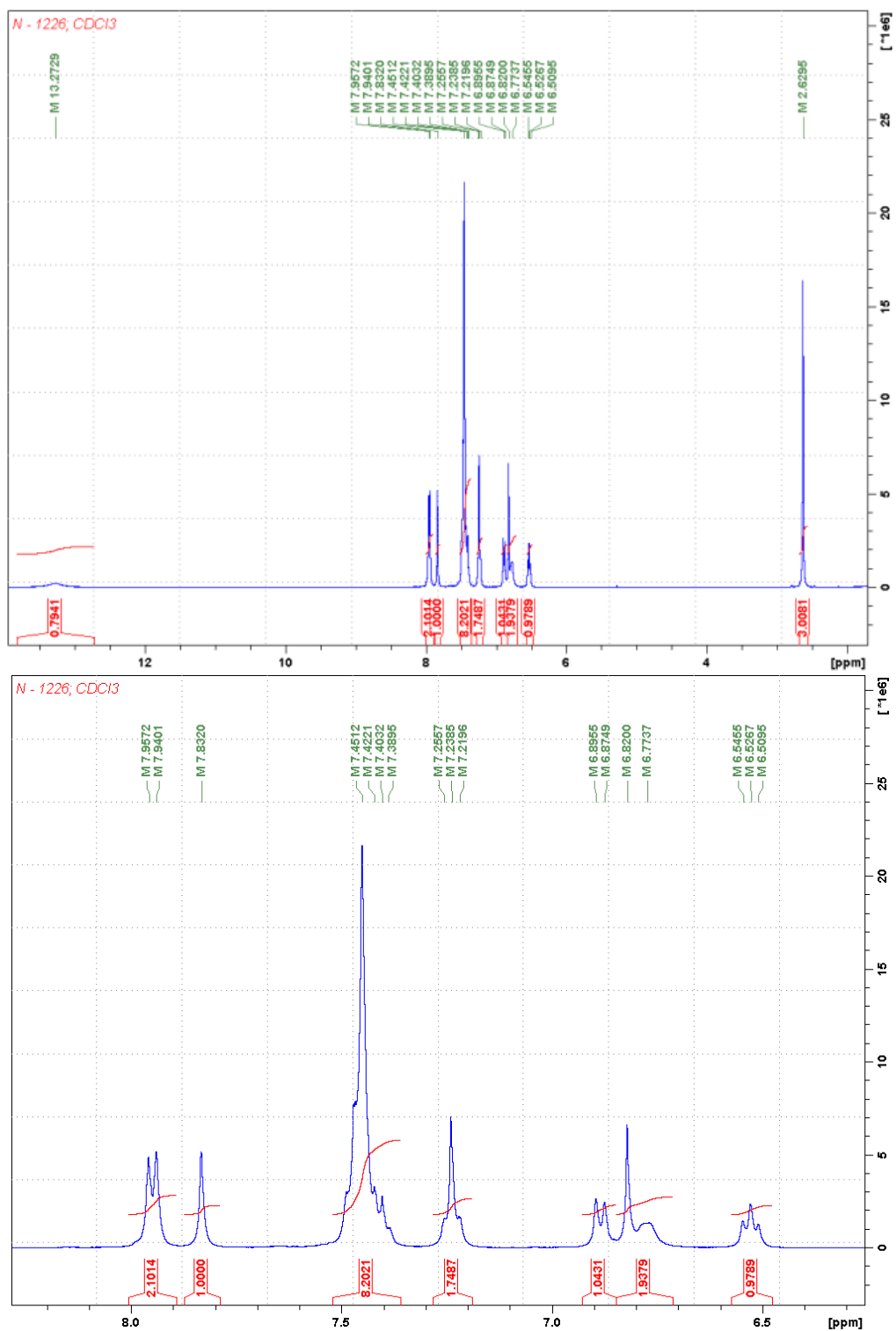
Figure S4. ^{1}H NMR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL²**).
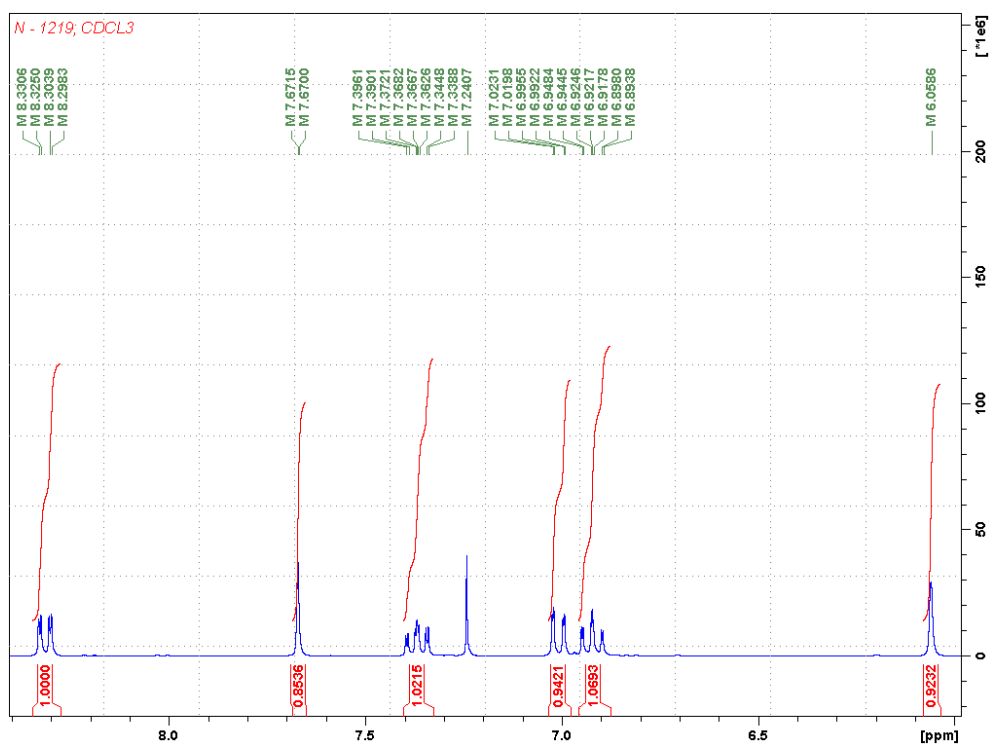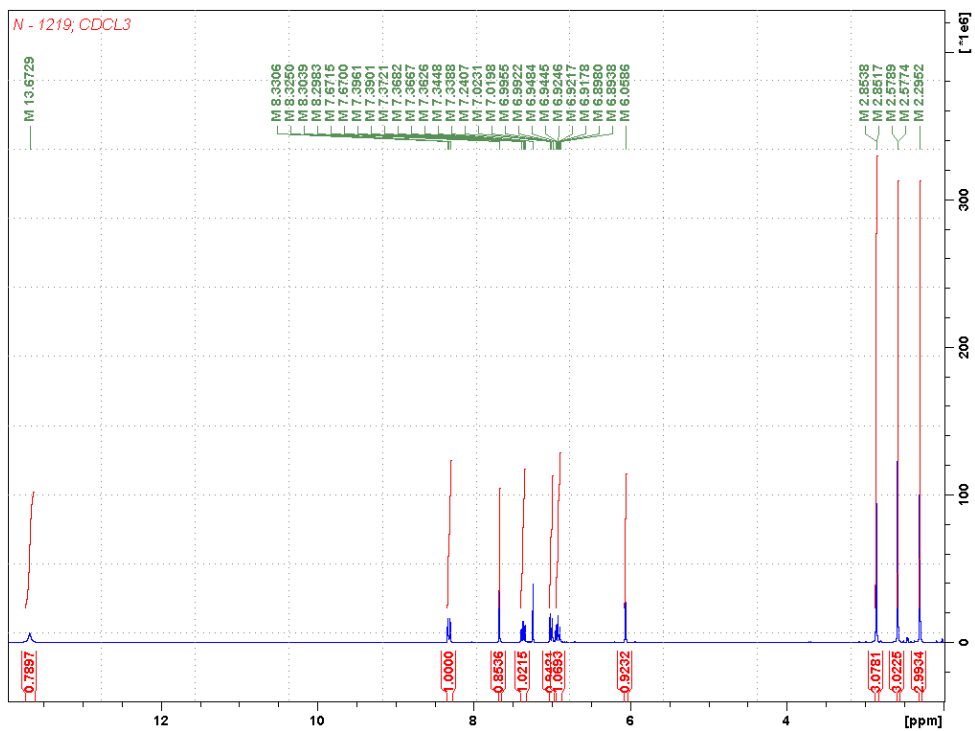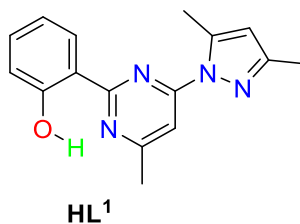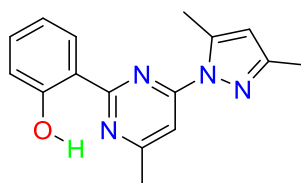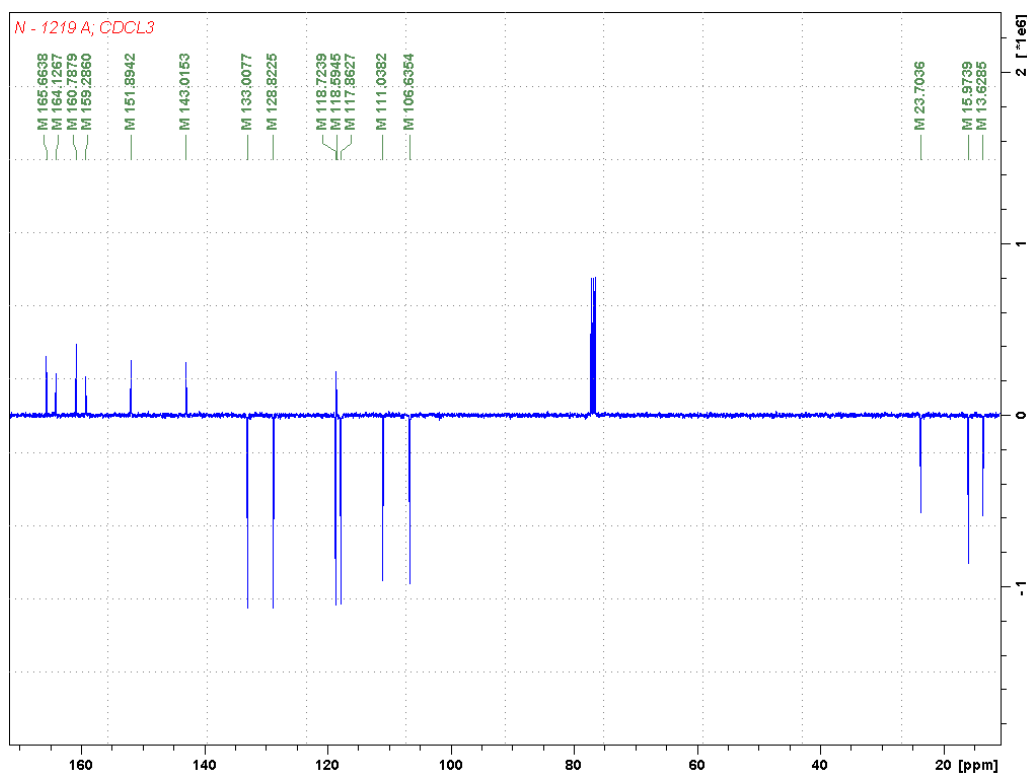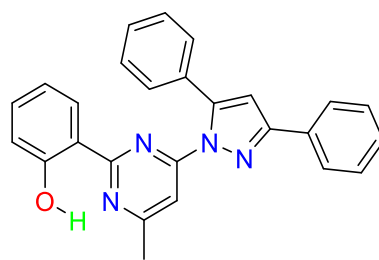
HL²
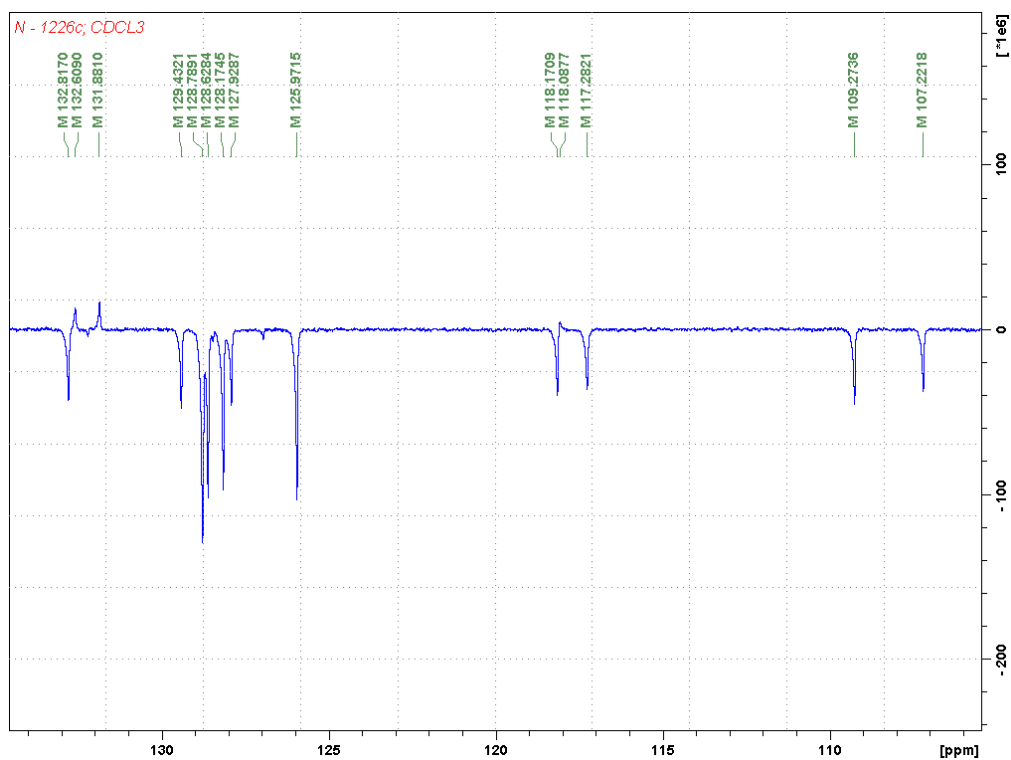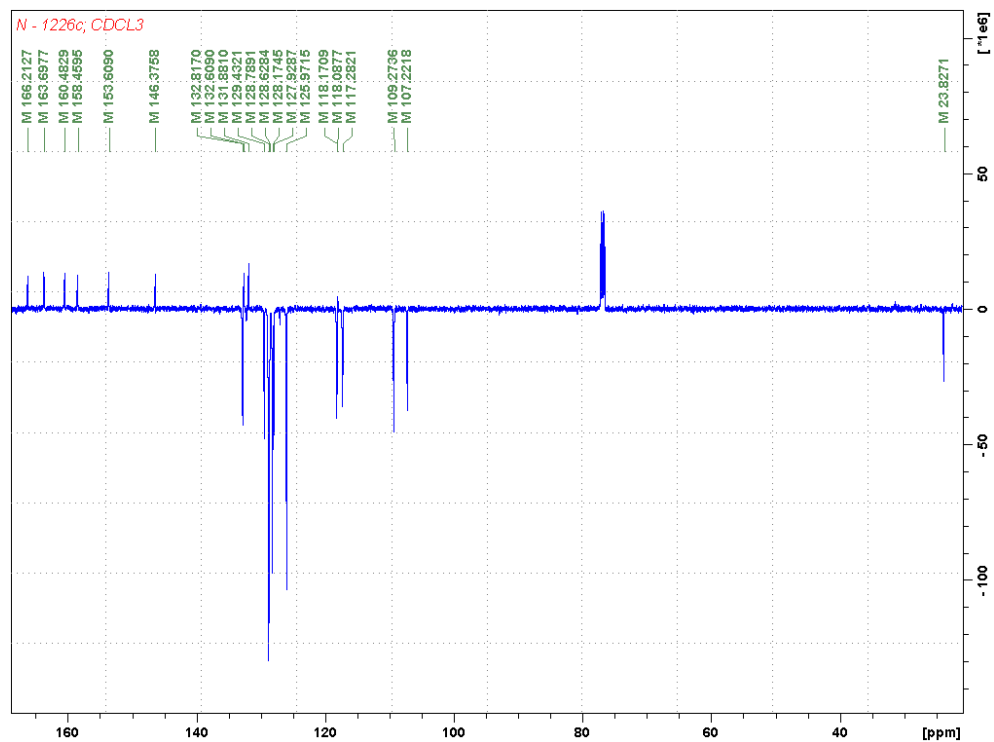
Figure S5. ¹³C NMR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL²**).
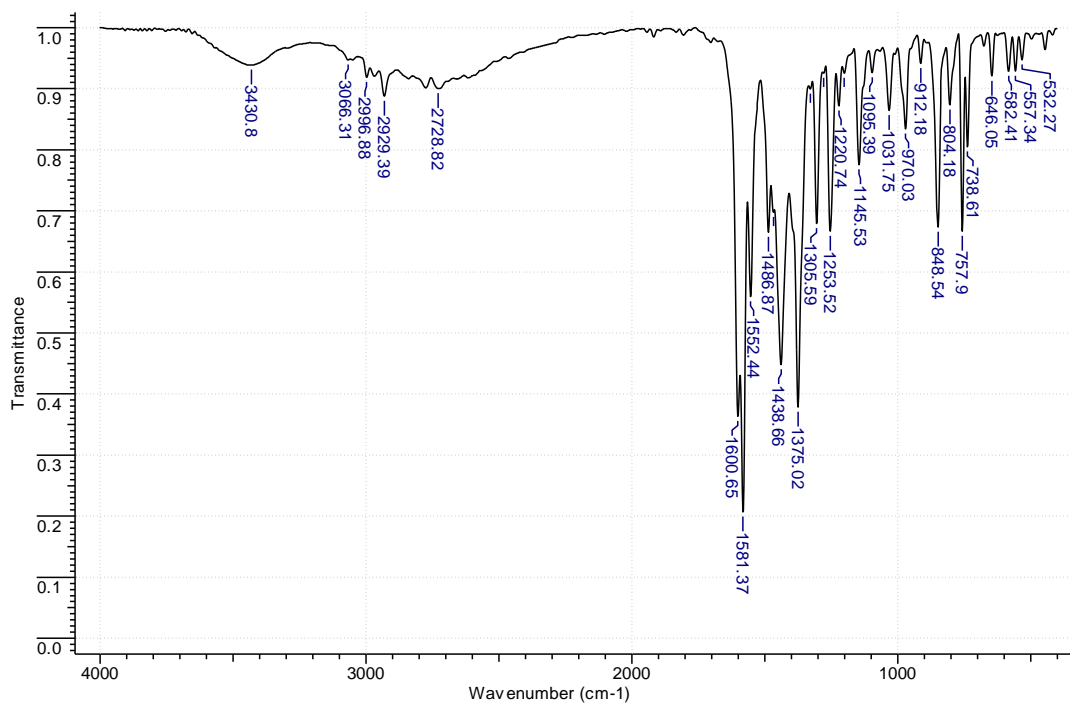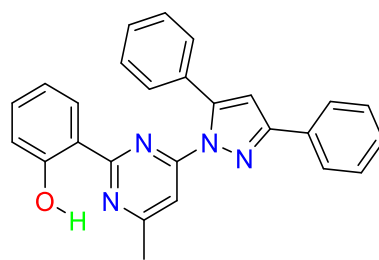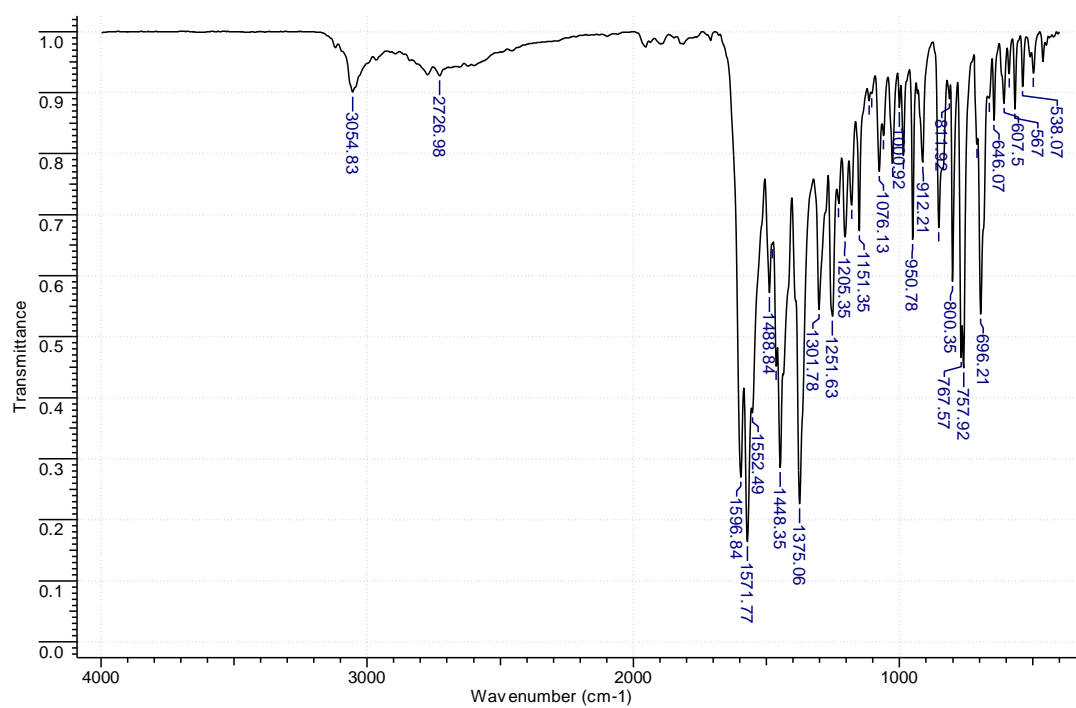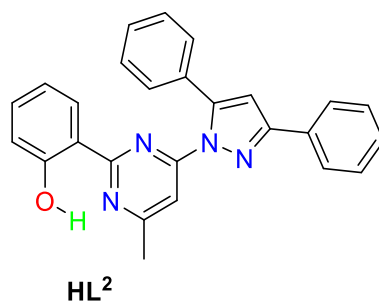
Figure S6. IR spectrum of 2-(2-hydroxyphenyl)-4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**HL²**).

Structural data

Table S1. Crystal data and structure refinement for **HL^1** and **HL^2**.

Complex	HL^1	HL^2
Empirical formula	$C_{16}H_{16}N_4O$	$C_{26}H_{20}N_4O$
Formula weight	280.33	404.46
Crystal system	monoclinic	triclinic
Space group, Z	P2$_1$/n, 4	P-1, 2
a(Å)	15.0005(5)	10.0306(9)
b(Å)	5.2660(2)	10.1285(9)
c(Å)	18.7118(7)	12.2622(10)
α/°	90	94.126(3)
β/°	113.3110(10)	113.697(3)
γ/°	90	109.740(3)
V(Å3)	1357.44(9)	1042.06(16)
dCalc(g/cm3)	1.372	1.289
μ/mm^{-1}	0.090	0.081
F(000)	592.0	424.0
Crystal size (mm)	0.160 × 0.100 × 0.050	0.080 × 0.080 × 0.030
2Θ range for data collection/°	4.462 - 61.042	3.738 - 52.808
Index ranges	-21 ≤ h ≤ 21 -7 ≤ k ≤ 7 -26 ≤ l ≤ 26	-12 ≤ h ≤ 12 -12 ≤ k ≤ 12 -15 ≤ l ≤ 15
Reflections collected	17280	20705
Independent reflections (Rint)	4138 [R$_{int}$ = 0.0616]	4276 [R$_{int}$ = 0.0352]
Completeness to theta = 50.5°	99.9 %	99.9 %
Data / restraints / parameters	4138/0/194	4276/0/282
Goodness-of-fit on F2	1.042	1.029
Final R indices (I>=2σ (I))	R$_1$ = 0.0586, wR$_2$ = 0.1410	R$_1$ = 0.0451, wR$_2$ = 0.1172
R indices (all data)	R$_1$ = 0.0990, wR$_2$ = 0.1648	R$_1$ = 0.0689, wR$_2$ = 0.1327
Largest diff. peak and hole (e/Å3)	0.32/-0.27	0.13/-0.20

Table S2. Bond lengths and angles in the structure of **HL¹**.
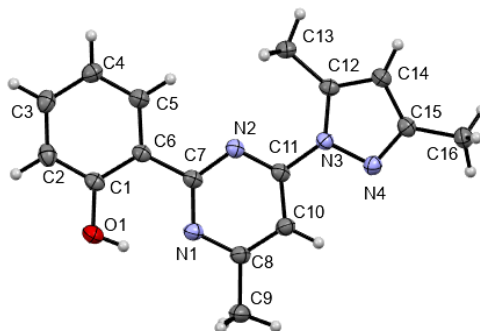
Distance	*d*, Å	Angle	ω
O1−C1	1.353(2)	C11−N2−C7	116.52(15)
N2−C11	1.323(2)	N4−N3−C11	117.86(14)
N2−C7	1.341(2)	N4−N3−C12	111.94(13)
N3−N4	1.3820(19)	C12−N3−C11	130.20(15)
N3−C11	1.400(2)	C15 −N4 −N3	104.71(14)
N3−C12	1.382(2)	C7−N1−C8	117.31(15)
N4−C15	1.320(2)	N2 −C11 −N3	116.83(15)
N1−C7	1.350(2)	N2 −C11 −C10	122.97(16)
N1−C8	1.351(2)	C10 −C11 −N3	120.20(16)
C11−C10	1.395(2)	N3 −C12 −C13	126.23(15)
C12−C14	1.366(2)	C14 −C12 −N3	105.29(15)
C12−C13	1.482(2)	C14 −C12 −C13	128.47(16)
C7−C6	1.475(2)	N2 −C7 −N1	124.97(16)
C5−C6	1.401(2)	N2 −C7 −C6	117.53(15)
C5−C4	1.379(3)	N1 −C7 −C6	117.50(15)
C1−C6	1.411(2)	C4 −C5 −C6	121.52(17)
C1−C2	1. 395(3)	O1 −C1 −C6	122.93(16)
C15−C14	1.416(2)	O1 −C1 −C2	117.29(16)
C15−C16	1.494(2)	C2 −C1 −C6	119.78(16)
C8−C10	1.372(2)	N4 −C15 −C14	111.25(16)
C8−C9	1.498(2)	N4 −C15 −C16	120.86(16)
C3−C4	1.394(3)	C14 −C15 −C16	127.89(16)
C3−C2	1.377(3)	C5 −C6 −C7	119.49(15)
		C5 −C6 −C1	118.31(16)
		C1 −C6 −C7	122.20(15)
		C12 −C14 −C15	106.81(15)
		N1 −C8 −C10	121.16(15)
		N1 −C8 −C9	116.16(16)
		C10 −C8 −C9	122.68(16)
		C8 −C10 −C11	117.04(16)
		C2 −C3 −C4	120.42(17)
		C5 −C4−C3	119.41(17)
		C3 −C2 −C1	120.55(17)

Table S3. Bond lengths and angles in the structure of **HL²**.
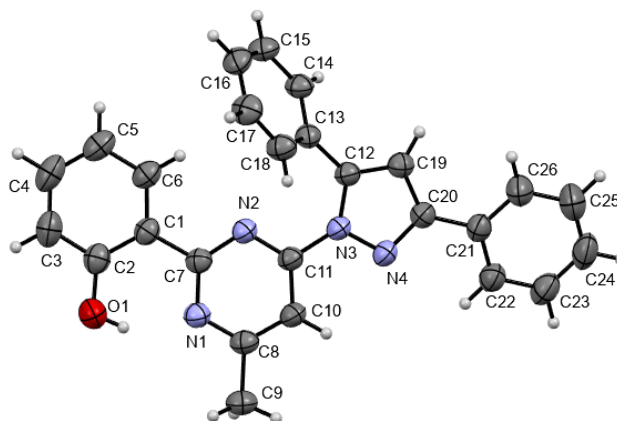
Distance	*d*, Å	Angle	ω
N2−C11	1.3246(18)	C11−N2−C7	115.98(13)
N2−C7	1.3436(19)	N4−N3−C11	116.93(11)
O1−C2	1.353(2)	N4−N3−C12	111.67(12)
N3−N4	1.3725(16)	C12−N3−C11	131.08(12)
N3−C11	1.4077(19)	C7−N1−C8	117.90(13)
N3−C12	1.3842(18)	C20−N4−N3	105.03(12)
N1−C7	1.3426(18)	N2 −C11 −N3	116.60(12)
N1−C8	1.3466(19)	N2 −C11 −C10	123.46(14)
N4−C20	1.3259(19)	C10 −C11 −N3	119.94(13)
C11−C10	1.3872(19)	N2 −C7 −C1	117.42(13)
C12−C19	1.358(2)	N1 −C7 −N2	124.85(14)
C1−C6	1.400(2)	N1 −C7 −C1	117.73(14)
C1−C2	1.407(2)	N4−C20 −C21	120.36(13)
C21−C22	1.391(2)	N4−C20 −C19	110.77(13)
C21−C26	1.380(2)	C19−C20 −C21	128.86(14)
C14−C15	1.381(2)	C14−C13 −C12	119.32(14)
C6−C5	1.377(2)	C14−C13 −C18	118.75(14)
C22−C23	1.376(2)	C18−C13 −C12	121.80(13)
C18−C17	1.377(2)	N1−C8 −C10	120.85(14)
C2−C3	1.393(2)	N1−C8 −C9	117.14(14)
C7−C1	1.473(2)	C10−C8 −C9	122.01(14)
C20−C21	1.473(2)	N3−C12 −C13	126.07(13)
C20−C19	1.412(2)	C19−C12 −N3	105.50(13)
C13−C12	1.477(2)	C19−C12 −C13	128.22(13)
C13−C14	1.386(2)	C6−C1 −C7	119.71(14)
C13−C18	1.394(2)	C6−C1 −C2	118.44(15)
C8−C10	1.373(2)	C2−C1 −C7	121.85(14)
C8−C9	1.495(2)	C8−C10 −C11	116.92(14)
C15−C16	1.370(2)	C22−C21 −C20	121.29(14)
C16−C17	1.382(2)	C26−C21 −C20	120.34(15)
C5−C4	1.382(3)	C26−C21 −C22	118.36(16)
C3−C4	1.373(3)	C15−C14 −C13	120.72(15)
C23−C24	1.370(3)	C12−C19−C20	107.03(13)
C26−C25	1.382(3)	C5−C6 −C1	121.35(17)

C24–C25	1.374(3)	C23–C22 –C21	120.82(17)
		C17–C18 –C13	119.96(15)
		O1–C2 –C1	123.21(15)
		O1–C2 –C3	117.31(16)
		C3–C2 –C1	119.48(16)
		C16–C15 –C14	120.21(15)
		C15–C16 –C17	119.60(15)
		C18–C17 –C16	120.71(16)
		C6–C5 –C4	119.46(18)
		C4–C3 –C2	120.60(18)
		C24–C23 –C22	120.25(18)
		C3–C4 –C5	120.65(17)
		C21–C26 –C25	120.43(18)
		C23–C24 –C25	119.59(18)
		C24–C25 –C26	120.54(19)
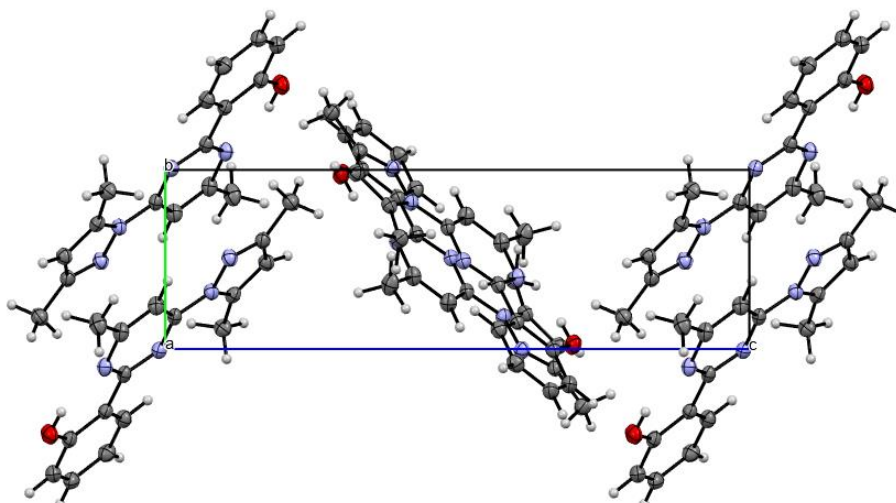
Figure S7. Packing of **HL¹** (view along the *a* axis).
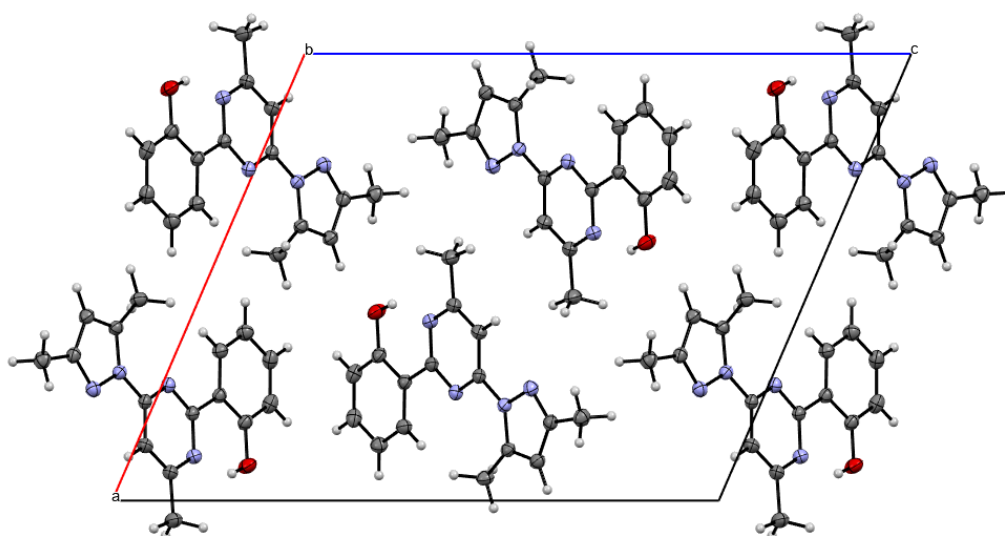
Figure S8. Packing of **HL¹** (view along the *b* axis).
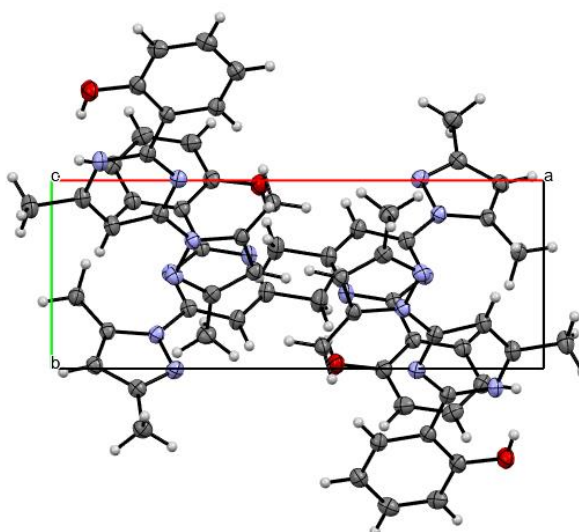
Figure S9. Packing of **HL¹** (view along the *c* axis).
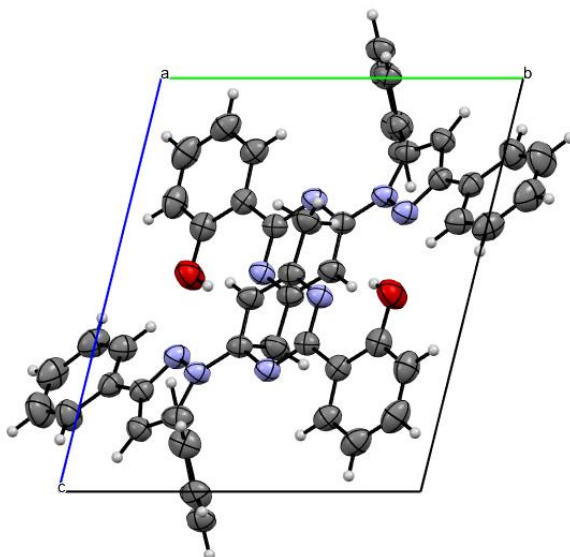
Figure S10. Packing of **HL²** (view along the *a* axis).
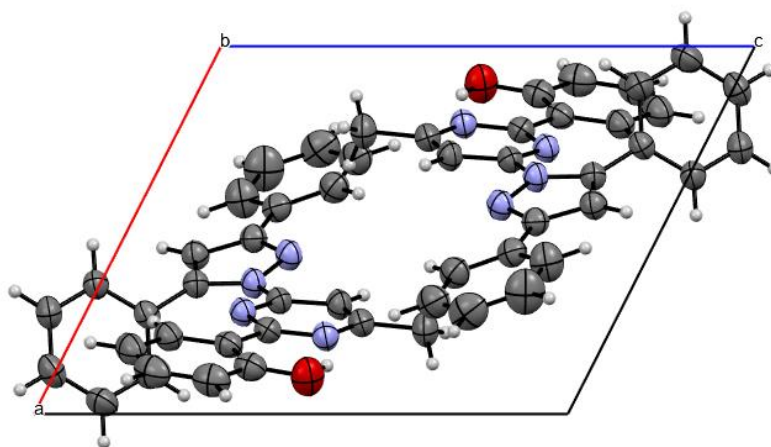
Figure S11. Packing of **HL²** (view along the *b* axis).
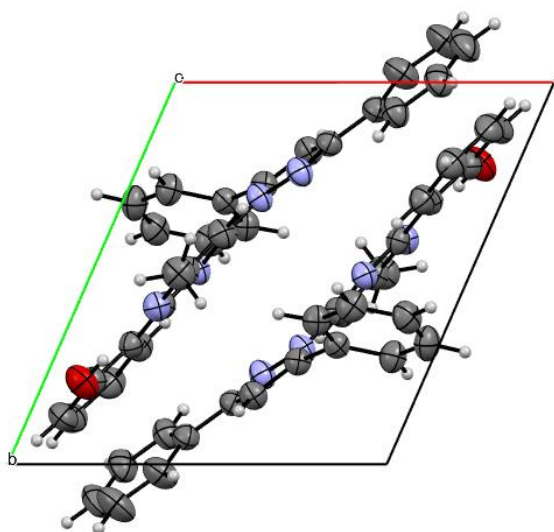
Figure S12. Packing of **HL²** (view along the *c* axis).
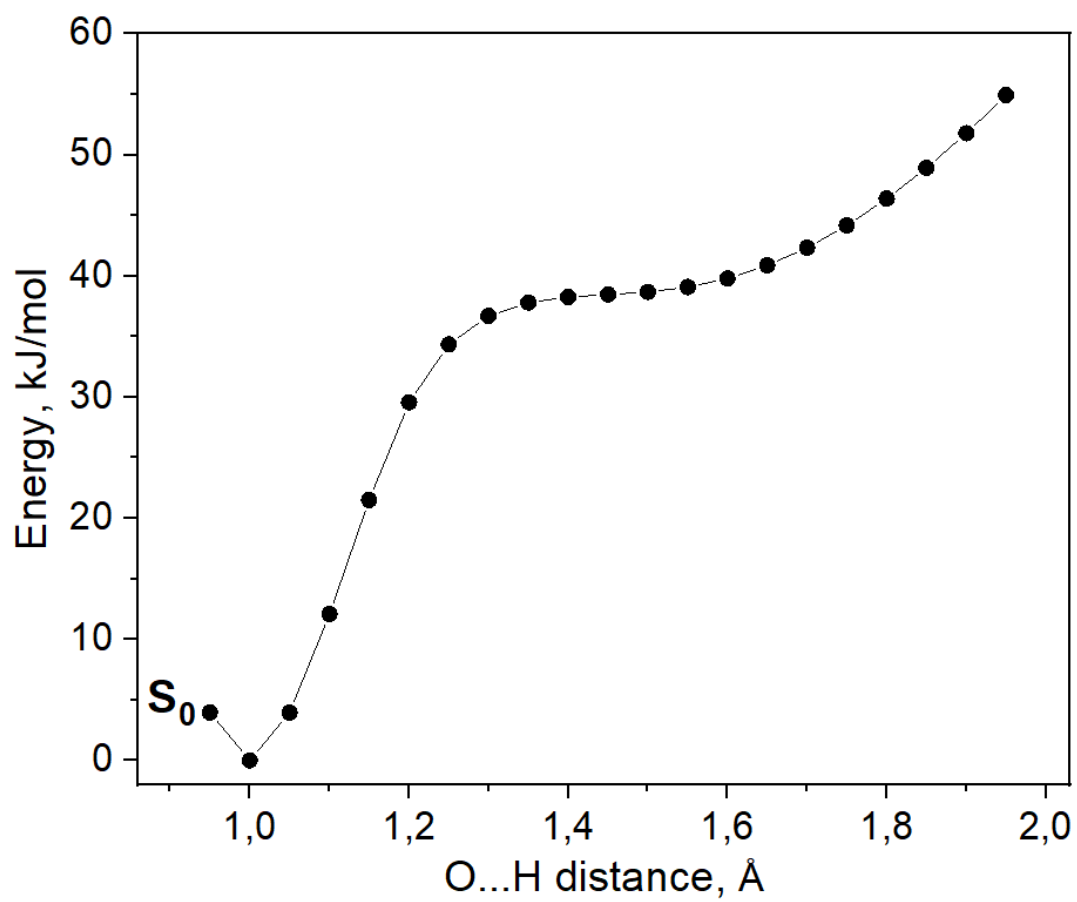
Figure S13. The potential energy curve of the ground state of **HL²**.

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	54,37201		
Adj. R-Square	0,99818		
		Value	Standard Error
	y0	4	0
C	A1	804329,86325	7150,49913
	t1	5,45873	0,00749

Speed Mode is On

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	216,75376		
Adj. R-Square	0,99798		
		Value	Standard Error
	y0	18,11753	1,93014
S1	A1	2253,74798	18,10635
	t1	0,17822	0,00182
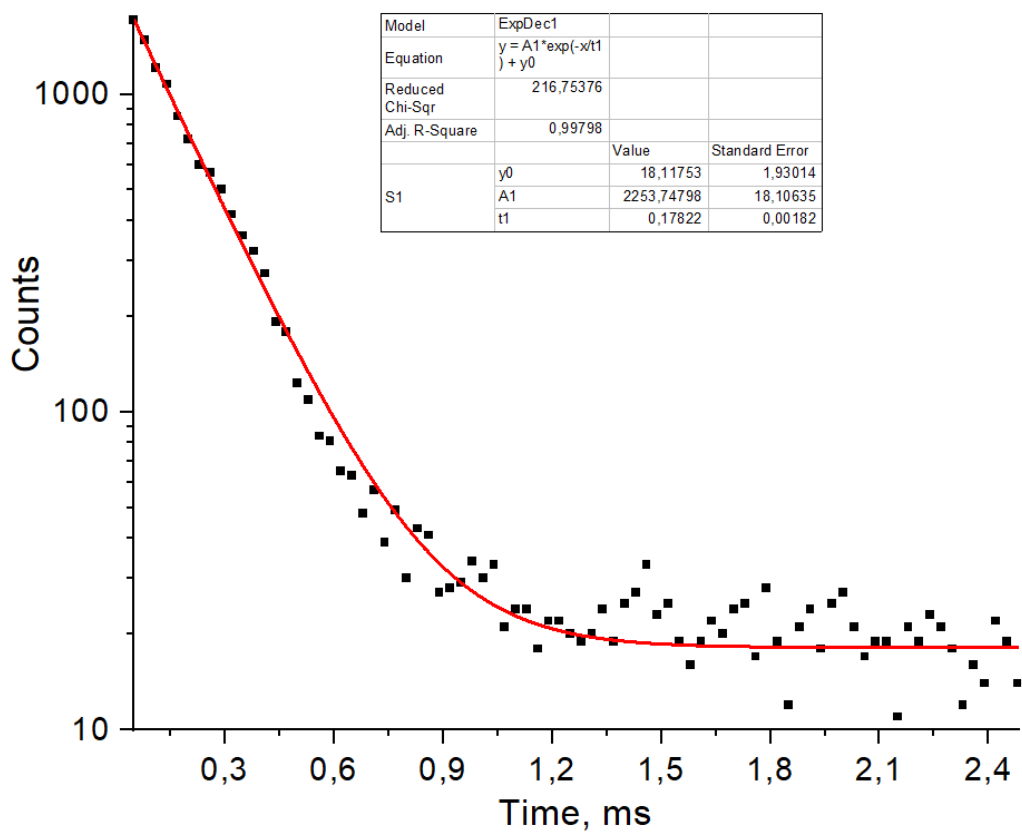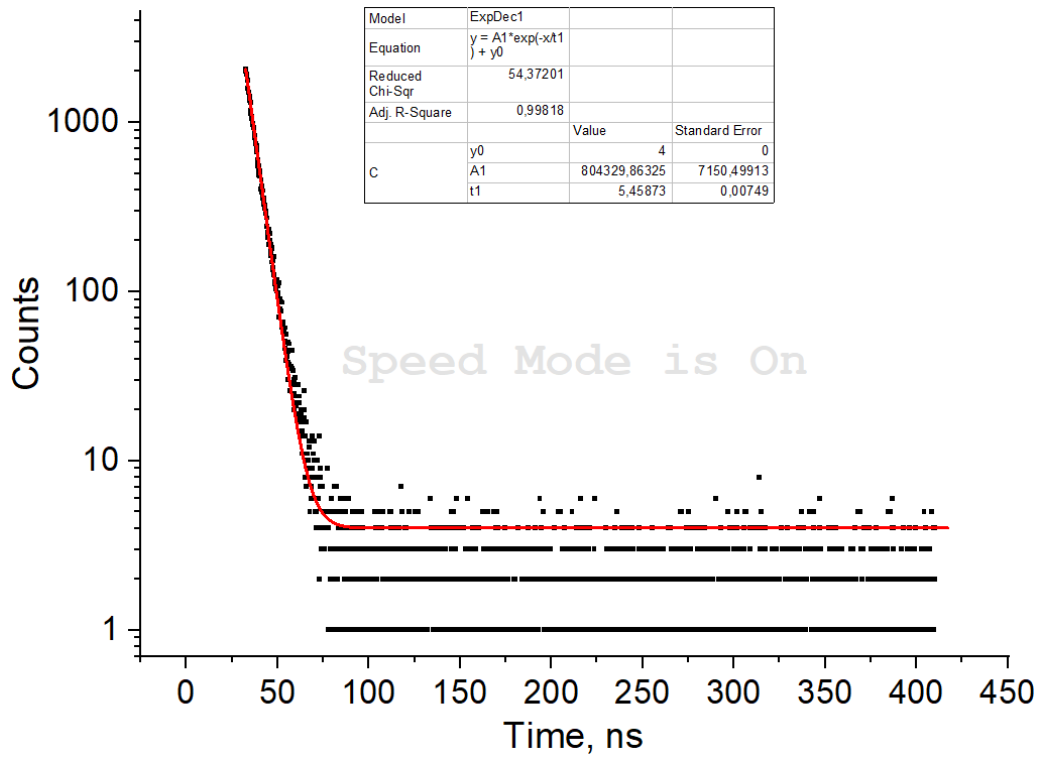
Figure S14. Photoluminescence decay curves for **HL[1]**.

15

Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	15,6798		
Adj. R-Square	0,99044		
		Value	Standard Error
	y0	4,85689	0,07245
	A1	450,6475	32,11752
C	t1	17,47079	0,41668
	A2	2435450,1	187290,11797
	t2	3,42948	0,03196

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2,89404		
Adj. R-Square	0,97272		
		Value	Standard Error
	y0	0,25264	0,24676
S1	A1	337,15152	32,10923
	t1	0,02839	0,00128

Figure S15. Photoluminescence decay curves for **HL²**.
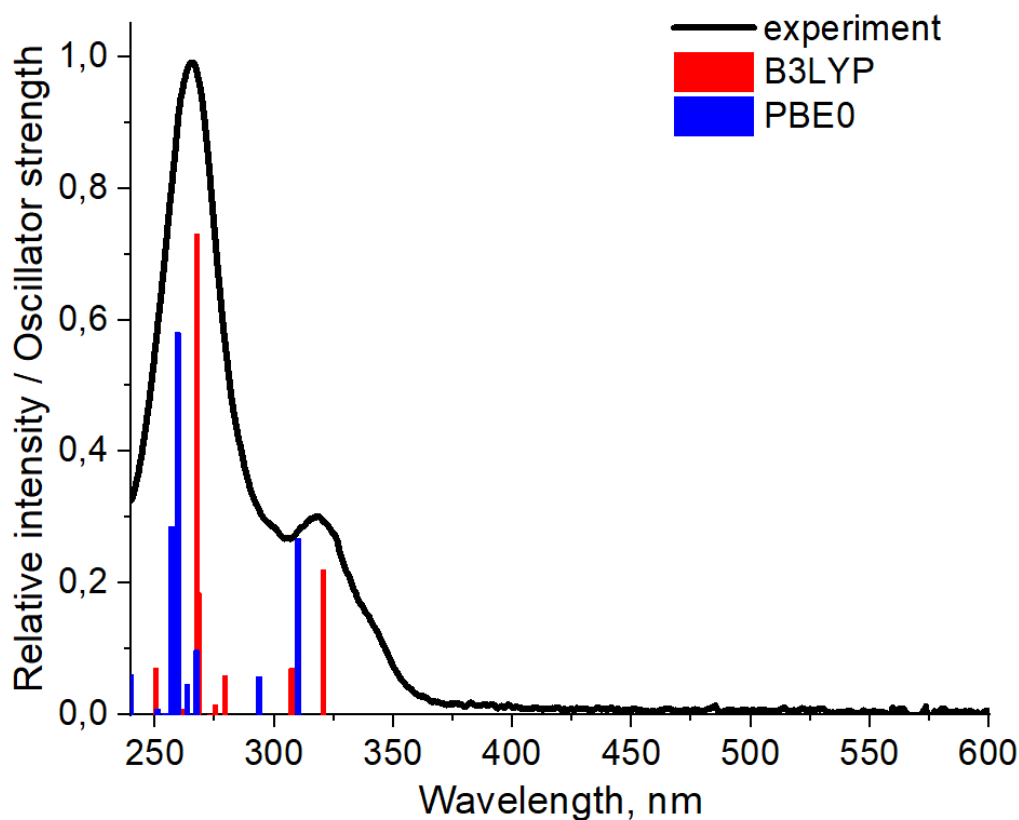
Figure S16. Comparison of the experimental absorption spectrum of **HL**[1] with those computed using PBE0 and B3LYP functionals.
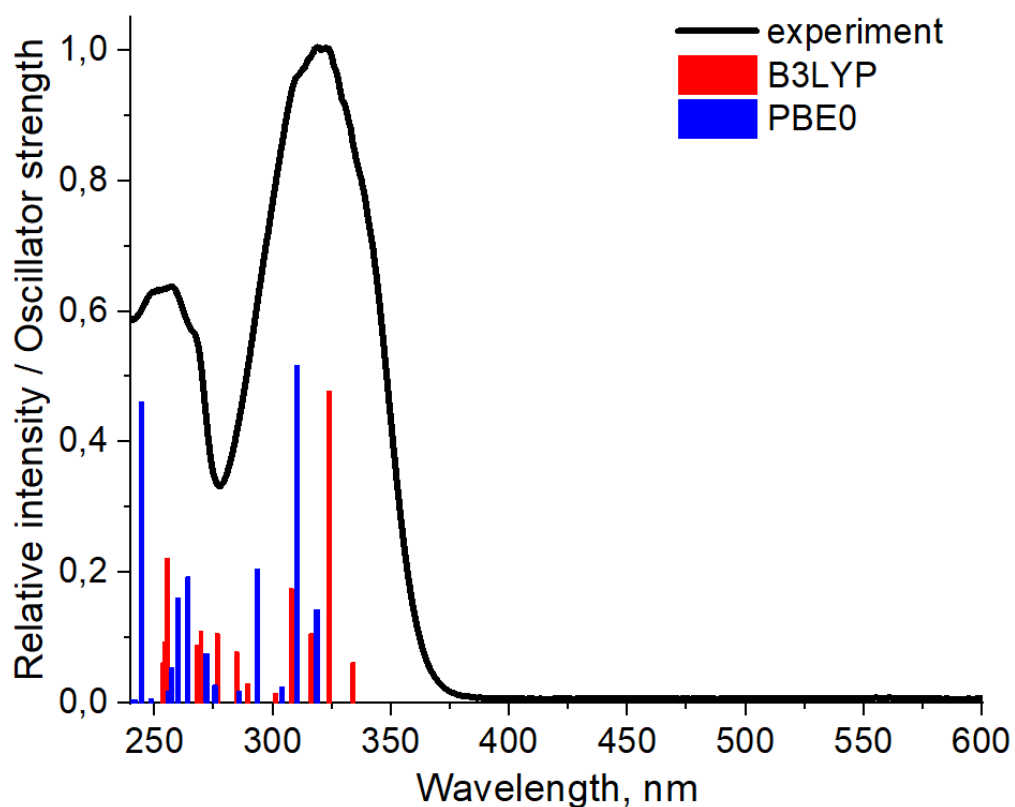
Figure S17. Comparison of the experimental absorption spectrum of **HL**[2] with those computed using PBE0 and B3LYP functionals.

Table S4. Optimized geometry of the **S$_0$ state** of **HL^1** (**enol form**, **S$_0^E$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory **in MeCN continuum solvation model**.

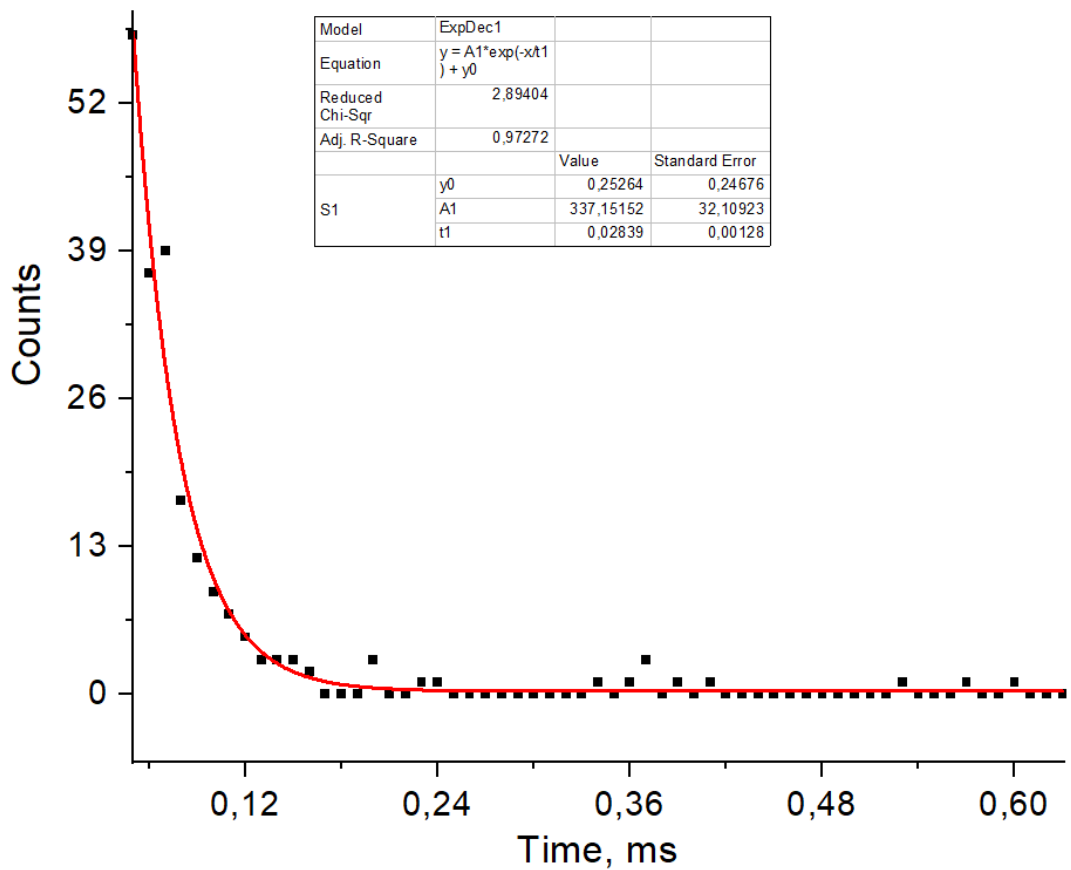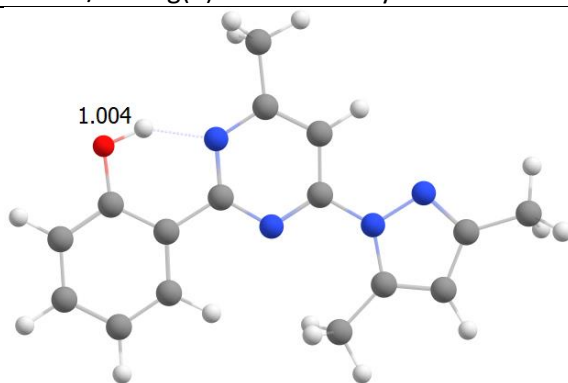|			
O	6.453660000000	5.076798000000	5.112313000000
H	6.001742000000	4.312322000000	5.580919000000
N	7.753639000000	2.659857000000	8.393390000000
N	7.504897000000	0.943068000000	9.951920000000
N	6.734591000000	-0.076854000000	10.467048000000
N	6.063285000000	3.143414000000	6.793488000000
C	6.994931000000	1.679643000000	8.876495000000
C	8.713372000000	1.063799000000	10.626643000000
C	7.262969000000	3.366342000000	7.360956000000
C	9.353741000000	4.729612000000	7.371366000000
H	9.683439000000	4.117532000000	8.202378000000
C	7.650141000000	5.255843000000	5.721137000000
C	7.448439000000	-0.594676000000	11.456118000000
C	8.089586000000	4.457514000000	6.811274000000
C	8.692230000000	0.085213000000	11.593807000000
H	9.475803000000	-0.115762000000	12.311490000000
C	9.791355000000	2.057034000000	10.341048000000
H	10.176739000000	1.955005000000	9.322611000000
H	10.609463000000	1.890784000000	11.047657000000
H	9.433847000000	3.085004000000	10.448448000000
C	5.293689000000	2.148838000000	7.283837000000
C	5.728548000000	1.373075000000	8.348817000000
H	5.129590000000	0.572351000000	8.756993000000
C	9.715495000000	6.527031000000	5.807312000000
H	10.338435000000	7.326736000000	5.415868000000
C	10.163792000000	5.747207000000	6.884682000000
H	11.133655000000	5.935360000000	7.334998000000
C	6.929680000000	-1.741510000000	12.264177000000
H	6.856714000000	-1.471576000000	13.324236000000
H	7.601177000000	-2.605213000000	12.193298000000
H	5.938694000000	-2.040623000000	11.911646000000
C	8.473271000000	6.283361000000	5.233114000000
H	8.112470000000	6.877914000000	4.399119000000
C	3.963886000000	1.934132000000	6.622682000000
H	3.358627000000	2.845316000000	6.690654000000
H	3.415704000000	1.109957000000	7.085066000000
H	4.104155000000	1.714293000000	5.558185000000

Table S5. Optimized geometry of the **S₀ state** of **HL¹** (**enol form**, **S₀ᴱ**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
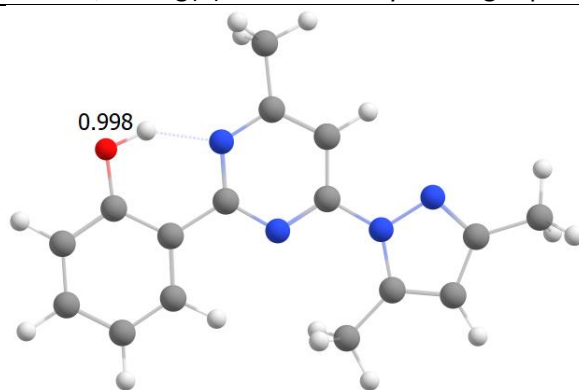
O	6.459257000000	5.086982000000	5.107273000000
H	5.998883000000	4.328911000000	5.564049000000
N	7.755256000000	2.660049000000	8.394040000000
N	7.509791000000	0.943339000000	9.953698000000
N	6.738884000000	-0.074024000000	10.465825000000
N	6.061147000000	3.140214000000	6.796452000000
C	6.999266000000	1.680794000000	8.877914000000
C	8.717234000000	1.064184000000	10.627532000000
C	7.263276000000	3.368371000000	7.359626000000
C	9.351926000000	4.728378000000	7.371732000000
H	9.678773000000	4.114552000000	8.202334000000
C	7.648269000000	5.256970000000	5.719839000000
C	7.449662000000	-0.593031000000	11.453874000000
C	8.087345000000	4.457414000000	6.810568000000
C	8.694844000000	0.085091000000	11.593972000000
H	9.478132000000	-0.116746000000	12.311969000000
C	9.792402000000	2.059616000000	10.338009000000
H	10.173713000000	1.958392000000	9.317777000000
H	10.614261000000	1.897636000000	11.042117000000
H	9.431894000000	3.086957000000	10.443221000000
C	5.297326000000	2.145290000000	7.290891000000
C	5.731732000000	1.369359000000	8.355136000000
H	5.140496000000	0.566332000000	8.770854000000
C	9.714958000000	6.524821000000	5.809882000000
H	10.339809000000	7.324209000000	5.419990000000
C	10.162448000000	5.743923000000	6.887411000000
H	11.132329000000	5.931157000000	7.338420000000
C	6.923572000000	-1.740055000000	12.257008000000
H	6.843875000000	-1.474192000000	13.318037000000
H	7.589042000000	-2.608864000000	12.185599000000
H	5.933211000000	-2.029709000000	11.895538000000
C	8.475319000000	6.284133000000	5.234799000000
H	8.111121000000	6.876417000000	4.401229000000
C	3.965545000000	1.928895000000	6.630728000000
H	3.359089000000	2.839514000000	6.697703000000
H	3.417523000000	1.104380000000	7.094196000000
H	4.103844000000	1.708479000000	5.565948000000

Table S6. Optimized geometry of the **S$_1$ state** of **HL[1]** (**keto form**, **S$_1^K$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
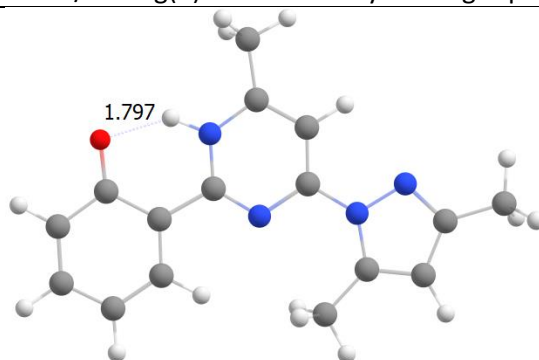
O	6.494866000000	5.100385000000	5.091247000000
H	5.847707000000	3.727248000000	6.052380000000
N	7.787983000000	2.671516000000	8.397275000000
N	7.493934000000	0.914682000000	9.970281000000
N	6.733899000000	-0.104655000000	10.492928000000
N	6.100017000000	3.113541000000	6.838740000000
C	6.969538000000	1.636870000000	8.897963000000
C	8.700558000000	1.043320000000	10.638446000000
C	7.295658000000	3.345573000000	7.394343000000
C	9.322662000000	4.747104000000	7.329130000000
H	9.657659000000	4.141301000000	8.163038000000
C	7.612601000000	5.273277000000	5.660599000000
C	7.453742000000	-0.617575000000	11.484435000000
C	8.092260000000	4.475440000000	6.784369000000
C	8.689759000000	0.064627000000	11.615398000000
H	9.478971000000	-0.127126000000	12.329671000000
C	9.786484000000	2.034881000000	10.359158000000
H	10.181909000000	1.933499000000	9.344993000000
H	10.598876000000	1.859452000000	11.071884000000
H	9.438267000000	3.065121000000	10.471321000000
C	5.246903000000	2.099546000000	7.295453000000
C	5.731130000000	1.349771000000	8.369489000000
H	5.139980000000	0.545701000000	8.788297000000
C	9.730452000000	6.570211000000	5.761598000000
H	10.363188000000	7.366427000000	5.379502000000
C	10.157282000000	5.786613000000	6.835984000000
H	11.121915000000	5.961882000000	7.300954000000
C	6.929373000000	-1.764095000000	12.290731000000
H	6.846642000000	-1.498129000000	13.351749000000
H	7.593686000000	-2.634324000000	12.222045000000
H	5.939284000000	-2.054992000000	11.928606000000
C	8.494813000000	6.325069000000	5.186795000000
H	8.126718000000	6.911078000000	4.350789000000
C	3.939603000000	1.931010000000	6.603809000000
H	3.315188000000	2.835873000000	6.665932000000
H	3.380397000000	1.109107000000	7.059693000000
H	4.060500000000	1.700856000000	5.533818000000

Table S7. Optimized geometry of the **S₂ state** of **HL¹** (**keto form**, **S₂ᴷ**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
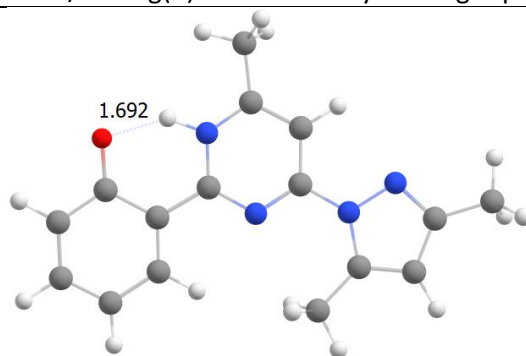

O	6.568009000000	4.891750000000	5.029478000000
H	5.859405000000	3.729178000000	6.034465000000
N	7.782064000000	2.632656000000	8.411703000000
N	7.516383000000	0.916948000000	9.950136000000
N	6.736190000000	-0.096175000000	10.460629000000
N	6.064886000000	3.128351000000	6.867260000000
C	7.004508000000	1.671363000000	8.894156000000
C	8.736902000000	1.009461000000	10.611894000000
C	7.301518000000	3.373213000000	7.390038000000
C	9.274921000000	4.861498000000	7.431565000000
H	9.585592000000	4.335745000000	8.328655000000
C	7.664777000000	5.194754000000	5.633344000000
C	7.452925000000	-0.638859000000	11.432580000000
C	8.103694000000	4.485133000000	6.820805000000
C	8.710431000000	0.018428000000	11.565016000000
H	9.499627000000	-0.205429000000	12.270121000000
C	9.819847000000	1.994564000000	10.322330000000
H	10.178689000000	1.911368000000	9.292045000000
H	10.652322000000	1.808975000000	11.008136000000
H	9.472805000000	3.024228000000	10.455073000000
C	5.257400000000	2.155451000000	7.319811000000
C	5.707374000000	1.375859000000	8.398461000000
H	5.108712000000	0.587575000000	8.826692000000
C	9.706411000000	6.606785000000	5.791547000000
H	10.312266000000	7.412929000000	5.387512000000
C	10.102662000000	5.924853000000	6.921663000000
H	11.027434000000	6.168362000000	7.434828000000
C	6.920040000000	-1.788657000000	12.226929000000
H	6.856046000000	-1.536847000000	13.292657000000
H	7.571089000000	-2.666803000000	12.136224000000
H	5.921277000000	-2.058587000000	11.873184000000
C	8.497830000000	6.248970000000	5.153397000000
H	8.164910000000	6.762249000000	4.256416000000
C	3.938894000000	1.948815000000	6.647451000000
H	3.755014000000	2.703568000000	5.877424000000
H	3.123903000000	1.991685000000	7.381264000000
H	3.897650000000	0.956727000000	6.177951000000

Table S8. Optimized geometry of the **T$_1$ state** of **HL^1** (**enol form**, **T$_1^E$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
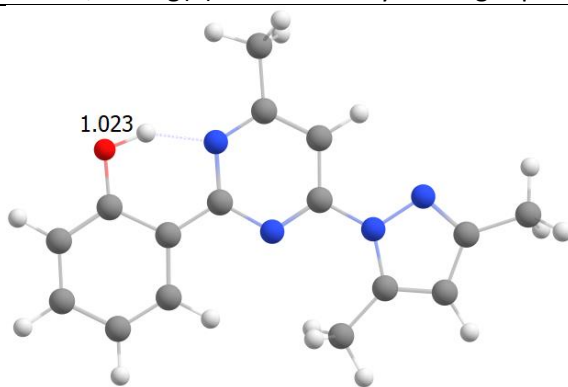

|			
O	6.441606000000	5.080399000000	5.137685000000
H	6.012162000000	4.294075000000	5.632431000000
N	7.792846000000	2.663250000000	8.418465000000
N	7.533286000000	0.934879000000	9.956061000000
N	6.752004000000	-0.082663000000	10.448304000000
N	6.053906000000	3.154718000000	6.786914000000
C	7.039816000000	1.693803000000	8.880635000000
C	8.732740000000	1.040192000000	10.640574000000
C	7.295619000000	3.398689000000	7.363722000000
C	9.371675000000	4.763066000000	7.382344000000
H	9.732274000000	4.166021000000	8.209860000000
C	7.625812000000	5.298469000000	5.702905000000
C	7.450851000000	-0.618817000000	11.437912000000
C	8.079244000000	4.447206000000	6.843243000000
C	8.697307000000	0.049100000000	11.597104000000
H	9.473543000000	-0.165140000000	12.319362000000
C	9.813057000000	2.034426000000	10.368179000000
H	10.198083000000	1.943050000000	9.347989000000
H	10.631115000000	1.863521000000	11.074909000000
H	9.453760000000	3.061911000000	10.480068000000
C	5.311886000000	2.173784000000	7.267731000000
C	5.759216000000	1.378360000000	8.348669000000
H	5.168426000000	0.571808000000	8.756748000000
C	9.671172000000	6.595066000000	5.769316000000
H	10.294718000000	7.396368000000	5.388342000000
C	10.126627000000	5.787308000000	6.867530000000
H	11.100777000000	5.996239000000	7.302739000000
C	6.908338000000	-1.772285000000	12.221490000000
H	6.818339000000	-1.520207000000	13.285175000000
H	7.567022000000	-2.646090000000	12.146140000000
H	5.919598000000	-2.049639000000	11.845731000000
C	8.428734000000	6.332910000000	5.209701000000
H	8.041265000000	6.914812000000	4.379234000000
C	3.970935000000	1.916899000000	6.638504000000
H	3.787603000000	2.619618000000	5.822198000000
H	3.170763000000	2.018884000000	7.381790000000
H	3.919321000000	0.894144000000	6.245483000000

Table S9. Optimized geometry of the **T$_1$ state** of **HL^1** (**keto form**, **T$_1$^{K}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
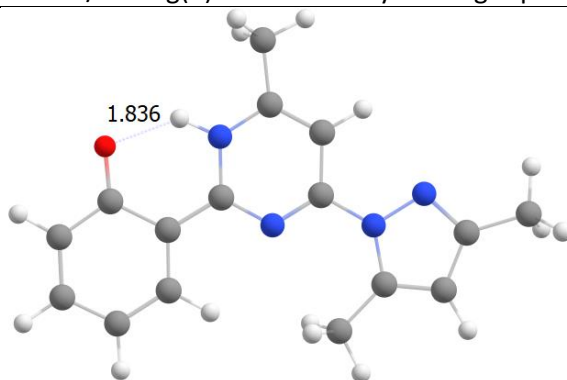

O	6.513518000000	5.094879000000	5.119693000000
H	5.757748000000	3.691417000000	6.030823000000
N	7.752703000000	2.651262000000	8.396060000000
N	7.514906000000	0.938455000000	9.960220000000
N	6.739326000000	-0.075675000000	10.468580000000
N	6.038464000000	3.096386000000	6.814793000000
C	7.013213000000	1.679612000000	8.883384000000
C	8.717533000000	1.054122000000	10.638063000000
C	7.299242000000	3.381408000000	7.362081000000
C	9.355627000000	4.739261000000	7.357276000000
H	9.712314000000	4.145572000000	8.190288000000
C	7.642364000000	5.280013000000	5.680089000000
C	7.446295000000	-0.599368000000	11.462651000000
C	8.098619000000	4.448663000000	6.817861000000
C	8.689582000000	0.072688000000	11.607456000000
H	9.470449000000	-0.130869000000	12.327888000000
C	9.791727000000	2.048770000000	10.346258000000
H	10.171965000000	1.947262000000	9.324690000000
H	10.615726000000	1.889547000000	11.048844000000
H	9.431166000000	3.077282000000	10.449675000000
C	5.256933000000	2.091600000000	7.307493000000
C	5.710233000000	1.345197000000	8.357362000000
H	5.130753000000	0.540416000000	8.782697000000
C	9.749691000000	6.575946000000	5.771025000000
H	10.385757000000	7.369994000000	5.393310000000
C	10.162705000000	5.777860000000	6.846815000000
H	11.130823000000	5.955732000000	7.308461000000
C	6.908347000000	-1.745282000000	12.260645000000
H	6.820693000000	-1.482896000000	13.322146000000
H	7.566941000000	-2.619877000000	12.192516000000
H	5.918609000000	-2.027630000000	11.890992000000
C	8.505592000000	6.323859000000	5.201509000000
H	8.127931000000	6.905985000000	4.366336000000
C	3.931915000000	1.885566000000	6.638683000000
H	3.318665000000	2.792634000000	6.707769000000
H	3.389244000000	1.060366000000	7.104809000000
H	4.067085000000	1.659929000000	5.573601000000

Table S10. Optimized geometry of **HL[1]** near S_0/S_1 conical intersection in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
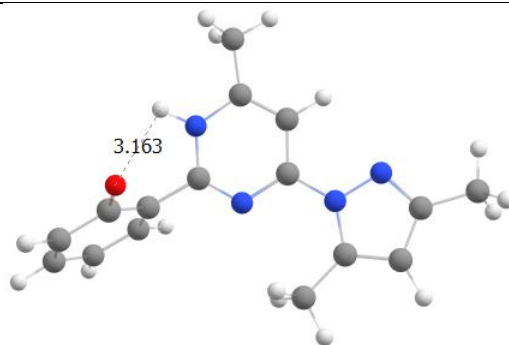

|			
O	6.713953000000	4.745803000000	5.024107000000
H	5.958058000000	4.700374000000	8.094712000000
N	7.697269000000	2.112313000000	7.255488000000
N	7.301791000000	-0.189229000000	7.646196000000
N	6.584367000000	-1.166476000000	8.293441000000
N	6.244157000000	3.729353000000	8.133758000000
C	6.904400000000	1.133622000000	7.818569000000
C	8.333401000000	-0.722682000000	6.892865000000
C	7.346514000000	3.345334000000	7.409357000000
C	9.297950000000	4.905862000000	7.533701000000
H	9.593100000000	4.424108000000	8.461627000000
C	7.774584000000	5.089501000000	5.611839000000
C	7.163121000000	-2.315153000000	7.953130000000
C	8.182274000000	4.467162000000	6.862222000000
C	8.257087000000	-2.091100000000	7.080858000000
H	8.910447000000	-2.829414000000	6.636231000000
C	9.294626000000	0.045928000000	6.043646000000
H	8.781486000000	0.636481000000	5.279163000000
H	9.963676000000	-0.665676000000	5.549440000000
H	9.894779000000	0.745687000000	6.631711000000
C	5.397065000000	2.771137000000	8.710815000000
C	5.748984000000	1.454318000000	8.558503000000
H	5.150253000000	0.663942000000	8.990236000000
C	9.735634000000	6.573093000000	5.804661000000
H	10.351605000000	7.377749000000	5.412121000000
C	10.090502000000	5.956475000000	7.013989000000
H	10.978363000000	6.274721000000	7.550687000000
C	6.640119000000	-3.613840000000	8.481748000000
H	7.407252000000	-4.146461000000	9.057210000000
H	6.323927000000	-4.276004000000	7.666294000000
H	5.780820000000	-3.434376000000	9.134144000000
C	8.607916000000	6.164847000000	5.115745000000
H	8.310583000000	6.627129000000	4.180038000000
C	4.201559000000	3.287464000000	9.441879000000
H	4.489478000000	3.938591000000	10.280163000000
H	3.614899000000	2.457285000000	9.842578000000
H	3.549546000000	3.876192000000	8.780173000000

Table S11. Optimized geometry of the **S₀ state** of **HL²** (**enol form**, **S₀ᴱ**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory **in MeCN continuum solvation model**.
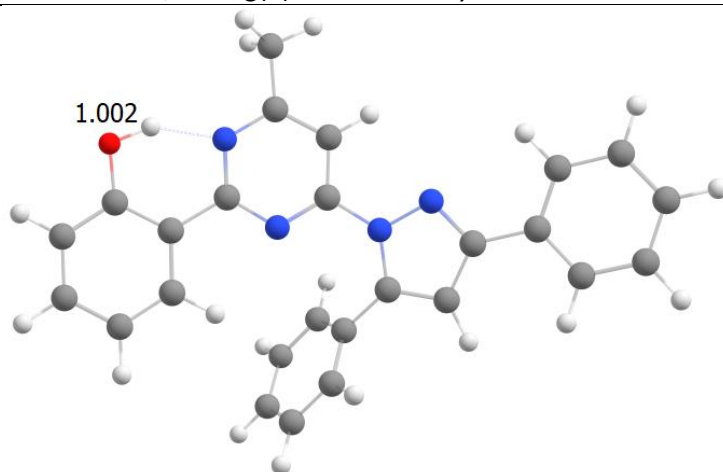
N	-1.118332000000	-0.427285000000	-0.125682000000
O	-4.816718000000	-2.563633000000	-0.225090000000
H	-3.892770000000	-2.879249000000	-0.000194000000
N	1.170516000000	-0.207631000000	0.208692000000
N	-2.247882000000	-2.489327000000	0.205714000000
N	2.388782000000	-0.805975000000	0.058853000000
C	0.020060000000	-1.016930000000	0.213339000000
C	-2.231247000000	-1.176523000000	-0.096902000000
C	3.266755000000	0.191098000000	-0.049688000000
C	0.160567000000	2.118344000000	0.450198000000
C	-1.083776000000	-3.093552000000	0.520400000000
C	1.267042000000	1.175999000000	0.205299000000
C	-3.508035000000	-0.516675000000	-0.418953000000
C	0.106742000000	-2.374093000000	0.549395000000
H	1.049158000000	-2.832142000000	0.815437000000
C	4.702897000000	-0.075061000000	-0.222580000000
C	-0.077633000000	3.157965000000	-0.458745000000
H	0.527486000000	3.230667000000	-1.357842000000
C	2.606138000000	1.452300000000	0.032443000000
H	3.045874000000	2.438799000000	0.026693000000
C	-3.528147000000	0.869468000000	-0.675304000000
H	-2.591449000000	1.411532000000	-0.622291000000
C	5.215317000000	-1.376170000000	-0.074045000000
H	4.539006000000	-2.186922000000	0.176869000000
C	-0.627460000000	2.024975000000	1.608489000000
H	-0.443280000000	1.226065000000	2.320640000000
C	-4.732983000000	-1.232903000000	-0.467495000000
C	-1.101510000000	4.080574000000	-0.223488000000
H	-1.284295000000	4.875432000000	-0.941143000000
C	-1.889677000000	3.975576000000	0.924697000000
H	-2.689345000000	4.688391000000	1.105025000000
C	-1.144176000000	-4.557464000000	0.843097000000
H	-1.830535000000	-4.731357000000	1.679374000000
H	-0.158692000000	-4.949708000000	1.104783000000
H	-1.530229000000	-5.115251000000	-0.017836000000
C	-1.646538000000	2.946211000000	1.841853000000
H	-2.254102000000	2.860630000000	2.738365000000
C	-4.709421000000	1.533941000000	-0.976276000000

H	-4.699458000000	2.603089000000	-1.165206000000
C	-5.923113000000	-0.556105000000	-0.777024000000
H	-6.846325000000	-1.126872000000	-0.810564000000
C	6.576913000000	-1.624400000000	-0.242772000000
H	6.957782000000	-2.635069000000	-0.123679000000
C	-5.911704000000	0.811513000000	-1.028932000000
H	-6.843325000000	1.319106000000	-1.264184000000
C	5.587576000000	0.968611000000	-0.540948000000
H	5.211429000000	1.979200000000	-0.667377000000
C	7.451439000000	-0.578425000000	-0.559578000000
H	8.512388000000	-0.773020000000	-0.689073000000
C	6.950981000000	0.718410000000	-0.707328000000
H	7.620796000000	1.537164000000	-0.955040000000

Table S12. Optimized geometry of the S_0 state of **HL^2** (**enol form**, S_0^E) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
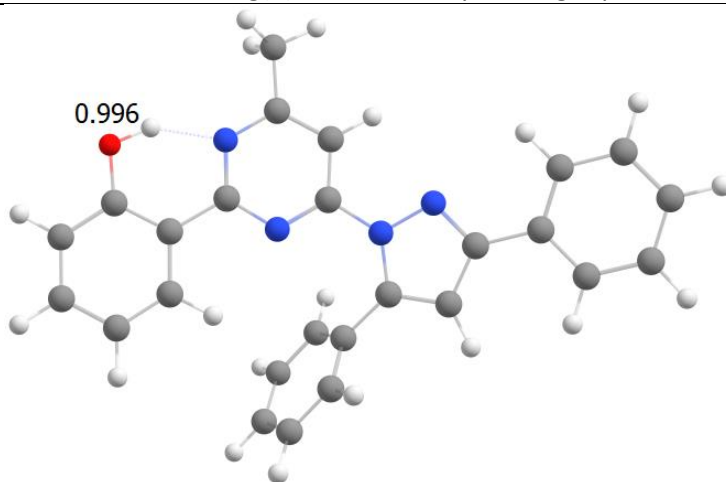
N	-1.127404000000	-0.431868000000	-0.093719000000
O	-4.835594000000	-2.572101000000	-0.128404000000
H	-3.912271000000	-2.906047000000	0.037630000000
N	1.167940000000	-0.204128000000	0.189900000000
N	-2.230129000000	-2.519234000000	0.168401000000
N	2.390768000000	-0.798438000000	0.071368000000
C	0.024085000000	-1.022283000000	0.183866000000
C	-2.235393000000	-1.193335000000	-0.080799000000
C	3.267243000000	0.197729000000	-0.034016000000
C	0.150316000000	2.131190000000	0.369280000000
C	-1.051661000000	-3.119335000000	0.426627000000
C	1.259038000000	1.180468000000	0.169573000000
C	-3.518899000000	-0.532886000000	-0.355442000000
C	0.134362000000	-2.394751000000	0.452685000000
H	1.091956000000	-2.850601000000	0.662056000000
C	4.705658000000	-0.068149000000	-0.180704000000
C	-0.077285000000	3.135761000000	-0.579666000000
H	0.529641000000	3.164828000000	-1.480086000000
C	2.599872000000	1.457649000000	0.019869000000
H	3.032606000000	2.446992000000	0.006300000000
C	-3.541335000000	0.854258000000	-0.610235000000
H	-2.599633000000	1.389069000000	-0.599983000000
C	5.193064000000	-1.386149000000	-0.171303000000
H	4.490907000000	-2.204832000000	-0.053945000000

|			
C	-0.643904000000	2.089721000000	1.525491000000
H	-0.470293000000	1.314933000000	2.266399000000
C	-4.747922000000	-1.245776000000	-0.362634000000
C	-1.093299000000	4.075566000000	-0.384379000000
H	-1.267041000000	4.843311000000	-1.133439000000
C	-1.885267000000	4.022474000000	0.763423000000
H	-2.679597000000	4.748288000000	0.913805000000
C	-1.092158000000	-4.598028000000	0.688818000000
H	-1.748013000000	-4.812987000000	1.540146000000
H	-0.095910000000	-4.995748000000	0.899561000000
H	-1.505693000000	-5.122543000000	-0.180289000000
C	-1.655672000000	3.026495000000	1.718980000000
H	-2.270783000000	2.977672000000	2.613028000000
C	-4.728506000000	1.524063000000	-0.862668000000
H	-4.719077000000	2.592900000000	-1.053734000000
C	-5.945497000000	-0.559159000000	-0.620765000000
H	-6.868885000000	-1.129861000000	-0.619911000000
C	6.556055000000	-1.637287000000	-0.311890000000
H	6.917420000000	-2.662199000000	-0.302845000000
C	-5.935652000000	0.807336000000	-0.867300000000
H	-6.873301000000	1.320851000000	-1.064497000000
C	5.617369000000	0.987841000000	-0.334911000000
H	5.261872000000	2.013814000000	-0.348591000000
C	7.457770000000	-0.578628000000	-0.463854000000
H	8.520603000000	-0.776288000000	-0.572941000000
C	6.982357000000	0.734595000000	-0.474696000000
H	7.673583000000	1.564653000000	-0.593180000000

Table S13. Optimized geometry of the S_1 **state** of **HL^2** (**keto form**, S_1^K) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.

N	-1.169819000000	-0.383387000000	-0.072486000000
O	-4.863685000000	-2.559027000000	-0.236153000000
H	-3.146843000000	-2.919531000000	0.126398000000
N	1.169330000000	-0.224386000000	0.194416000000
N	-2.227702000000	-2.453437000000	0.184178000000
N	2.394704000000	-0.821172000000	0.080640000000
C	0.036708000000	-1.027934000000	0.229729000000
C	-2.237265000000	-1.136007000000	-0.072538000000
C	3.273697000000	0.177361000000	-0.061487000000
C	0.185877000000	2.134791000000	0.359729000000

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C	-1.052635000000	-3.145831000000	0.472034000000
C	1.265179000000	1.162324000000	0.131037000000
C	-3.577541000000	-0.526913000000	-0.362175000000
C	0.112785000000	-2.381568000000	0.492686000000
H	1.069712000000	-2.841550000000	0.704540000000
C	4.708615000000	-0.096340000000	-0.204045000000
C	0.042007000000	3.221747000000	-0.514941000000
H	0.681913000000	3.284946000000	-1.390541000000
C	2.611271000000	1.432363000000	-0.047750000000
H	3.046847000000	2.419646000000	-0.090316000000
C	-3.615732000000	0.832696000000	-0.565663000000
H	-2.687262000000	1.389619000000	-0.514693000000
C	5.198904000000	-1.410927000000	-0.109438000000
H	4.497853000000	-2.218992000000	0.070908000000
C	-0.654918000000	2.054383000000	1.482269000000
H	-0.544581000000	1.224257000000	2.172627000000
C	-4.807523000000	-1.306022000000	-0.417699000000
C	-0.928514000000	4.199258000000	-0.283054000000
H	-1.031226000000	5.030405000000	-0.975826000000
C	-1.764876000000	4.106877000000	0.831899000000
H	-2.518813000000	4.867740000000	1.015732000000
C	-1.158421000000	-4.607372000000	0.744770000000
H	-1.796406000000	-4.819198000000	1.615928000000
H	-0.167434000000	-5.023532000000	0.945277000000
H	-1.587628000000	-5.154519000000	-0.107464000000
C	-1.622188000000	3.030211000000	1.713993000000
H	-2.265192000000	2.952153000000	2.586667000000
C	-4.831865000000	1.516045000000	-0.833666000000
H	-4.814841000000	2.590826000000	-0.980462000000
C	-6.026435000000	-0.568515000000	-0.700053000000
H	-6.938522000000	-1.155239000000	-0.742582000000
C	6.560827000000	-1.671506000000	-0.245605000000
H	6.922198000000	-2.693892000000	-0.169727000000
C	-6.030917000000	0.802195000000	-0.901900000000
H	-6.963769000000	1.319427000000	-1.108764000000
C	5.621184000000	0.945551000000	-0.439330000000
H	5.264355000000	1.967972000000	-0.521679000000
C	7.461756000000	-0.626969000000	-0.477721000000
H	8.523696000000	-0.831859000000	-0.582873000000
C	6.984325000000	0.682951000000	-0.573729000000
H	7.674005000000	1.503116000000	-0.755282000000

Table S14. Optimized geometry of the S_2 state of HL^2 (**keto form**, S_2^K) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
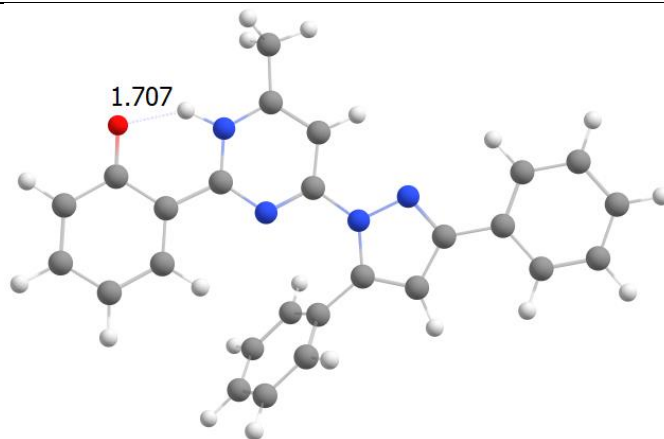
N	1.118715000000	0.409493000000	-0.074540000000
O	4.763199000000	2.587153000000	-0.099074000000
H	3.109489000000	2.965070000000	0.089605000000
N	-1.167823000000	0.201813000000	0.144810000000
N	2.166987000000	2.511788000000	0.113143000000
N	-2.398551000000	0.792514000000	0.067858000000
C	-0.037683000000	1.022485000000	0.133149000000
C	2.234933000000	1.167714000000	-0.072017000000
C	-3.273333000000	-0.207018000000	-0.035683000000
C	-0.143258000000	-2.141838000000	0.273511000000
C	1.010829000000	3.174605000000	0.306206000000
C	-1.256788000000	-1.188362000000	0.108451000000
C	3.557317000000	0.530085000000	-0.278235000000
C	-0.180669000000	2.415570000000	0.326306000000
H	-1.148233000000	2.867927000000	0.475312000000
C	-4.712681000000	0.051300000000	-0.139957000000
C	0.126078000000	-3.077235000000	-0.732694000000
H	-0.447309000000	-3.046533000000	-1.654698000000
C	-2.596284000000	-1.466590000000	-0.018029000000
H	-3.025129000000	-2.457608000000	-0.040647000000
C	3.623456000000	-0.828905000000	-0.468812000000
H	2.704122000000	-1.403595000000	-0.472620000000
C	-5.207158000000	1.367866000000	-0.094922000000
H	-4.505507000000	2.187629000000	0.017770000000
C	0.606494000000	-2.177456000000	1.459609000000
H	0.400422000000	-1.453751000000	2.242574000000
C	4.777423000000	1.312956000000	-0.271393000000
C	1.136353000000	-4.029897000000	-0.561439000000
H	1.339159000000	-4.746956000000	-1.352395000000
C	1.880052000000	-4.057332000000	0.618743000000
H	2.664159000000	-4.797497000000	0.753995000000
C	1.071495000000	4.655804000000	0.497962000000
H	1.678333000000	4.922647000000	1.373901000000
H	0.066569000000	5.058950000000	0.644322000000
H	1.517053000000	5.155315000000	-0.372787000000
C	1.610676000000	-3.127454000000	1.630582000000
H	2.185665000000	-3.143392000000	2.552322000000
C	4.876002000000	-1.510225000000	-0.654340000000
H	4.873287000000	-2.586653000000	-0.791272000000

|			
C	6.007828000000	0.609793000000	-0.463797000000
H	6.915899000000	1.204895000000	-0.454859000000
C	-6.574233000000	1.613999000000	-0.194130000000
H	-6.939640000000	2.636994000000	-0.157406000000
C	6.052263000000	-0.786318000000	-0.652192000000
H	7.008750000000	-1.282202000000	-0.791981000000
C	-5.625832000000	-1.006523000000	-0.287866000000
H	-5.266917000000	-2.030712000000	-0.328540000000
C	-7.476104000000	0.553987000000	-0.339847000000
H	-8.542377000000	0.748303000000	-0.416492000000
C	-6.994443000000	-0.757147000000	-0.386228000000
H	-7.685085000000	-1.588495000000	-0.500052000000

Table S15. Optimized geometry of the **T₁ state** of **HL²** (**enol form**, **T₁ᴱ**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
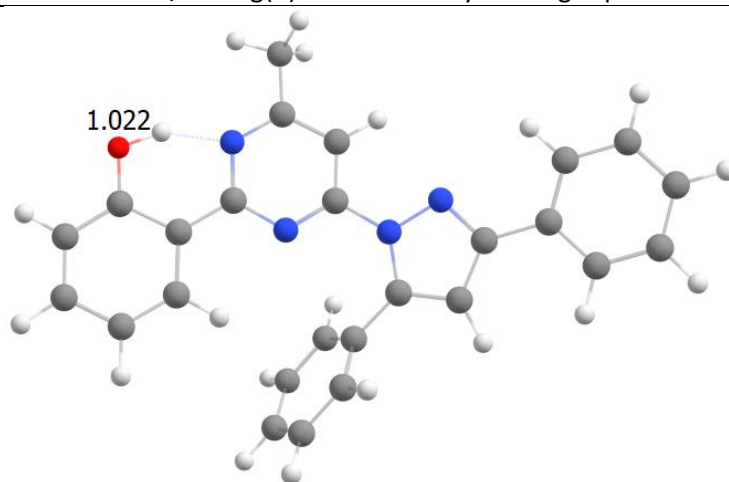
N	-1.116122000000	-0.393614000000	-0.118289000000
O	-4.800979000000	-2.580057000000	-0.130474000000
H	-3.837181000000	-2.870580000000	0.047692000000
N	1.171605000000	-0.181682000000	0.190566000000
N	-2.246617000000	-2.522430000000	0.189348000000
N	2.384580000000	-0.788945000000	0.062984000000
C	0.010518000000	-0.984058000000	0.182423000000
C	-2.256637000000	-1.159124000000	-0.090717000000
C	3.273766000000	0.198297000000	-0.044880000000
C	0.175524000000	2.155272000000	0.381245000000
C	-1.091740000000	-3.104454000000	0.462781000000
C	1.277405000000	1.198780000000	0.173026000000
C	-3.488067000000	-0.530087000000	-0.365689000000
C	0.116238000000	-2.366387000000	0.487873000000
H	1.069429000000	-2.822228000000	0.714238000000
C	4.708164000000	-0.085628000000	-0.195022000000
C	-0.048909000000	3.168868000000	-0.558881000000
H	0.558001000000	3.202649000000	-1.459160000000
C	2.621536000000	1.464130000000	0.014755000000
H	3.064985000000	2.448879000000	0.002810000000
C	-3.565265000000	0.873141000000	-0.645398000000
H	-2.645215000000	1.443163000000	-0.639646000000
C	5.180183000000	-1.409351000000	-0.178549000000
H	4.468252000000	-2.218422000000	-0.053476000000
C	-0.618976000000	2.108466000000	1.537433000000

H	-0.448023000000	1.326467000000	2.271256000000
C	-4.781783000000	-1.272434000000	-0.375931000000
C	-1.060599000000	4.111937000000	-0.355548000000
H	-1.229554000000	4.888023000000	-1.097286000000
C	-1.852496000000	4.053256000000	0.792222000000
H	-2.640826000000	4.784116000000	0.950933000000
C	-1.087578000000	-4.579506000000	0.753709000000
H	-2.105010000000	-4.977288000000	0.738726000000
H	-0.641076000000	-4.779200000000	1.735332000000
H	-0.486417000000	-5.115645000000	0.008925000000
C	-1.625829000000	3.048520000000	1.739809000000
H	-2.238312000000	2.996988000000	2.635733000000
C	-4.770859000000	1.478316000000	-0.897909000000
H	-4.790370000000	2.546352000000	-1.099639000000
C	-5.990336000000	-0.614771000000	-0.640094000000
H	-6.897906000000	-1.210380000000	-0.631869000000
C	6.539672000000	-1.678148000000	-0.321570000000
H	6.888191000000	-2.707540000000	-0.306692000000
C	-6.011040000000	0.746366000000	-0.901328000000
H	-6.944314000000	1.259192000000	-1.106429000000
C	5.633134000000	0.957527000000	-0.359226000000
H	5.289959000000	1.987671000000	-0.379088000000
C	7.454358000000	-0.632125000000	-0.483134000000
H	8.514408000000	-0.843563000000	-0.593957000000
C	6.994502000000	0.686676000000	-0.501313000000
H	7.695371000000	1.507615000000	-0.627392000000

Table S16. Optimized geometry of the **T$_1$ state** of **HL^2** (**keto form**, **T$_1^K$**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory in the gas phase.
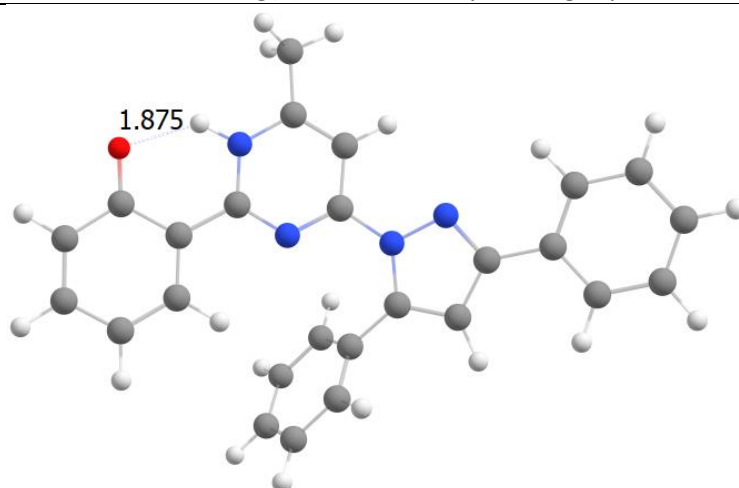
N	-1.128987000000	-0.450950000000	-0.102535000000
O	-4.851256000000	-2.513209000000	-0.176386000000
H	-3.087724000000	-3.026543000000	0.199064000000
N	1.172485000000	-0.202543000000	0.183466000000
N	-2.196552000000	-2.529907000000	0.234339000000
N	2.396032000000	-0.786390000000	0.049933000000
C	0.035373000000	-1.019326000000	0.185960000000
C	-2.238848000000	-1.165918000000	-0.081123000000
C	3.270682000000	0.222175000000	-0.055633000000
C	0.139905000000	2.114028000000	0.403368000000
C	-0.991945000000	-3.163341000000	0.474176000000

C	1.255506000000	1.180776000000	0.174851000000
C	-3.511554000000	-0.524419000000	-0.377575000000
C	0.154406000000	-2.427212000000	0.462555000000
H	1.120613000000	-2.875870000000	0.644477000000
C	4.707905000000	-0.037415000000	-0.204330000000
C	-0.087528000000	3.159449000000	-0.501980000000
H	0.532190000000	3.234490000000	-1.391011000000
C	2.597624000000	1.471193000000	0.006118000000
H	3.023473000000	2.463831000000	-0.003028000000
C	-3.544101000000	0.843115000000	-0.642632000000
H	-2.614415000000	1.398922000000	-0.623359000000
C	5.204168000000	-1.352837000000	-0.177582000000
H	4.506194000000	-2.172690000000	-0.044417000000
C	-0.672939000000	2.016890000000	1.545024000000
H	-0.500447000000	1.213067000000	2.254333000000
C	-4.785714000000	-1.263910000000	-0.401073000000
C	-1.115264000000	4.081076000000	-0.280638000000
H	-1.282449000000	4.882225000000	-0.995856000000
C	-1.925094000000	3.969801000000	0.850872000000
H	-2.725079000000	4.684552000000	1.024636000000
C	-1.059912000000	-4.634179000000	0.741294000000
H	-1.691843000000	-4.842927000000	1.614368000000
H	-0.062439000000	-5.038481000000	0.927963000000
H	-1.497877000000	-5.165331000000	-0.113913000000
C	-1.697378000000	2.933809000000	1.764643000000
H	-2.321067000000	2.841956000000	2.649750000000
C	-4.750122000000	1.511378000000	-0.921181000000
H	-4.718200000000	2.580196000000	-1.114512000000
C	-5.994128000000	-0.530668000000	-0.692669000000
H	-6.912632000000	-1.109588000000	-0.700458000000
C	6.567940000000	-1.599817000000	-0.320755000000
H	6.933474000000	-2.623303000000	-0.297658000000
C	-5.980657000000	0.829216000000	-0.948583000000
H	-6.900709000000	1.363171000000	-1.165637000000
C	5.616880000000	1.019267000000	-0.379394000000
H	5.256258000000	2.043324000000	-0.408354000000
C	7.465280000000	-0.540622000000	-0.492830000000
H	8.528621000000	-0.734942000000	-0.603830000000
C	6.981974000000	0.770174000000	-0.521266000000
H	7.668499000000	1.602046000000	-0.655604000000