- Supporting Information –

Excited-State Dynamics of 4-hydroxyisoindoline-1,3-dione and Its Derivative as Fluorescent Probe

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1. Materials and methods

All starting materials and reagents were purchased from Sigma Aldrich and used as received without any further purification. BHID and probe BHID-Bpin were synthesized following our reported procedure[1].

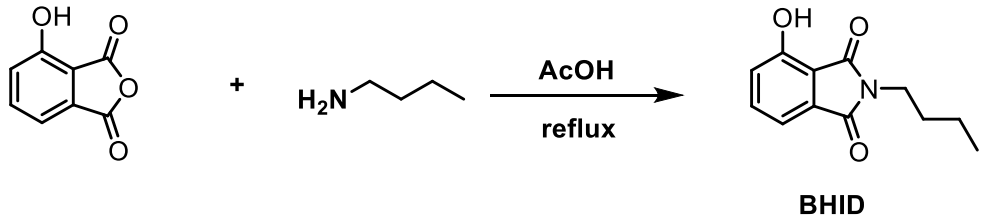

Fig. S1. Synthetic route to achieve the BHID

Synthesis of BHID 3-Hydroxyphthalic anhydride (0.77 g, 4.69 mmol, 1.0 equiv.) was dissolved in acetic acid (40 mL), then butylamine (0.51 g, 7.04 mmol, 1.5 equiv.) was added. The mixture was further heated under reflux for 2.5 hours, TLC was used to monitor the reaction until the 3-hydroxyphthalic anhydride was consumed. The solvent was removed under vacuum, the crude product was purified by silica chromatography using elute solvents (PE/EtOAc = 10/1, v/v). BHID was then obtained as a white solid (0.90 g, yield 88%).^{1}H NMR (500 MHz, $CDCl_3$) δH 7.64 (s, 1H), 7.57 – 7.54 (m, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 3.63 (t, J = 7.2 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.39 – 1.32 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δC 170.7, 168.1, 154.7, 136.4, 132.3, 122.6, 116.0, 114.8, 37.8, 30.7, 20.2, 13.7.

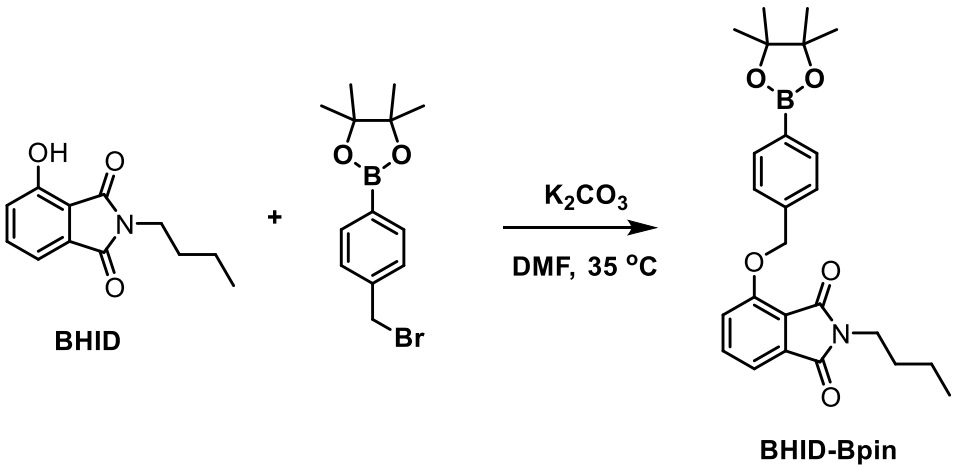

Fig. S2. Synthetic route to achieve BHID-Bpin

Synthesis of BHID-Bpin BHID (0.30 g, 1.37 mmol, 1.0 equiv.), 4-bromomethylphenylboronic acid pinacol ester (0.49 g, 1.64 mmol, 1.2 equiv.) and K_2CO_3 (0.38 g, 2.74mmol, 2.0 equiv.) were dissolved in dry DMF (7 mL). The mixture was then stirred for 6 hours at 35 °C. TLC was used to monitor the reaction until the BHID consumed. The solvent was removed under vacuum, the crude product was purified by silica chromatography using elute solvents (PE/EtOAc = 20/1, v/v). BHID-Bpin was then obtained as a white solid (0.194 g, 33%). ^{1}H NMR (500 MHz, $CDCl_3$) δH 7.82 (d, *J* = 7.7 Hz, 2H), 7.55-7.52 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 2H), 3.66 (t, *J* = 7.2Hz, 2H), 1.68 – 1.62 (m, 2H), 1.39 - 1.33 (m, 14H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δC 168.3, 167.1, 155.6, 139.1, 135.8, 135.3, 134.6, 126.1, 119.6, 118.3, 115.8, 84.0, 71.0, 37.8, 30.8, 25.0, 20.2, 13.8.

2. NMR results

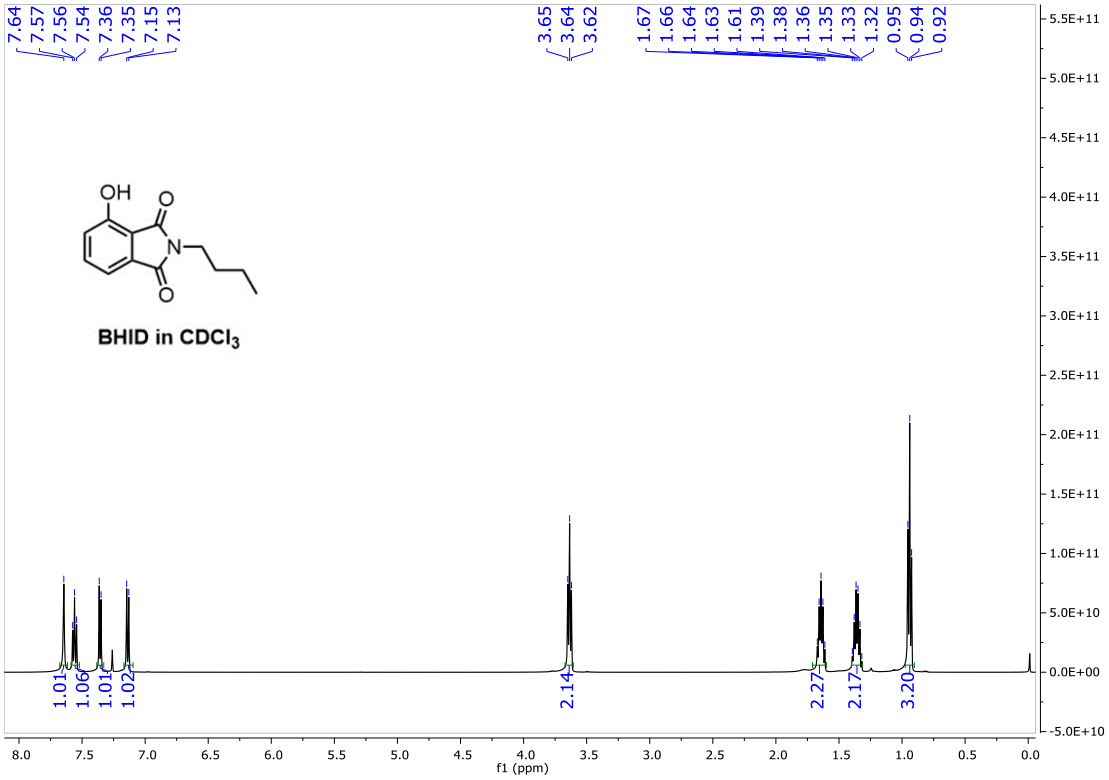

Fig. S3. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of BHID

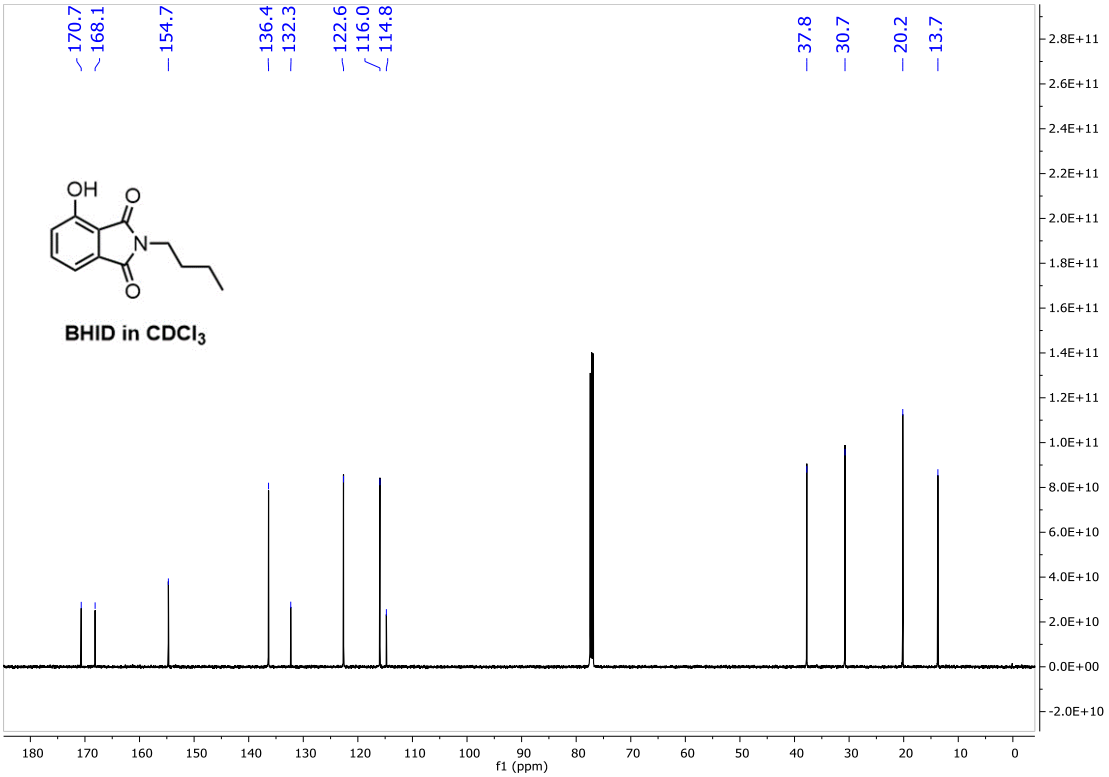

Fig. S4. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of BHID

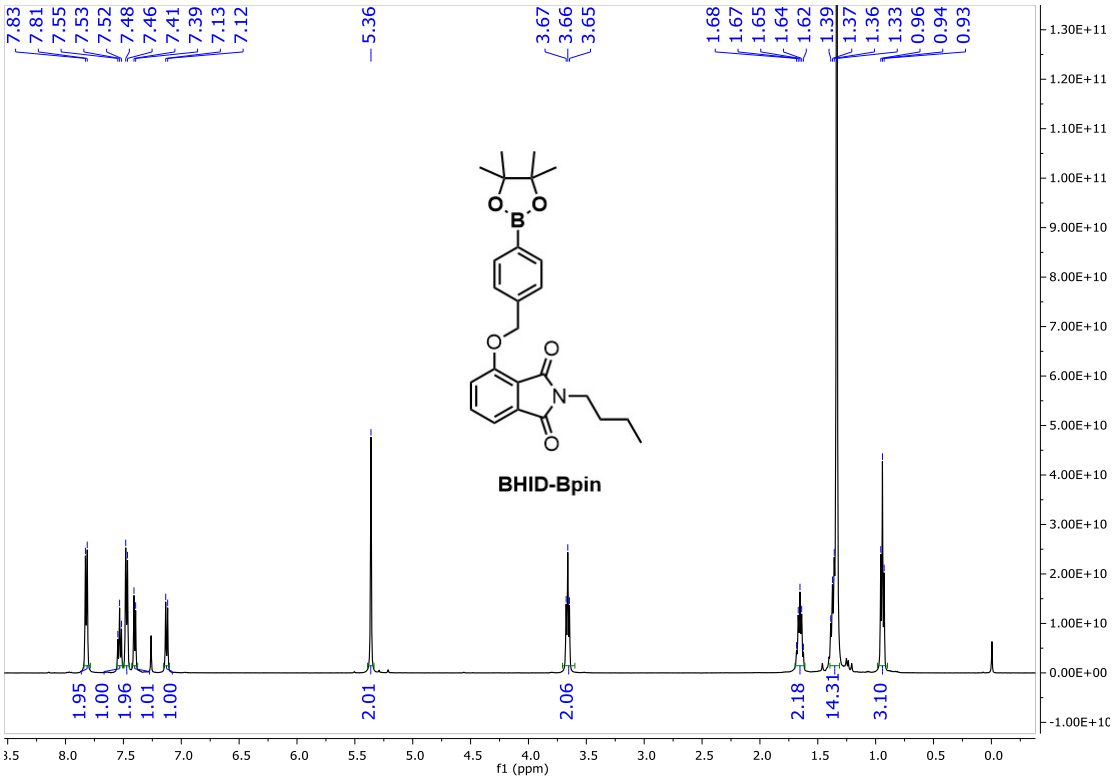

Fig. S5. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of BHID-Bpin

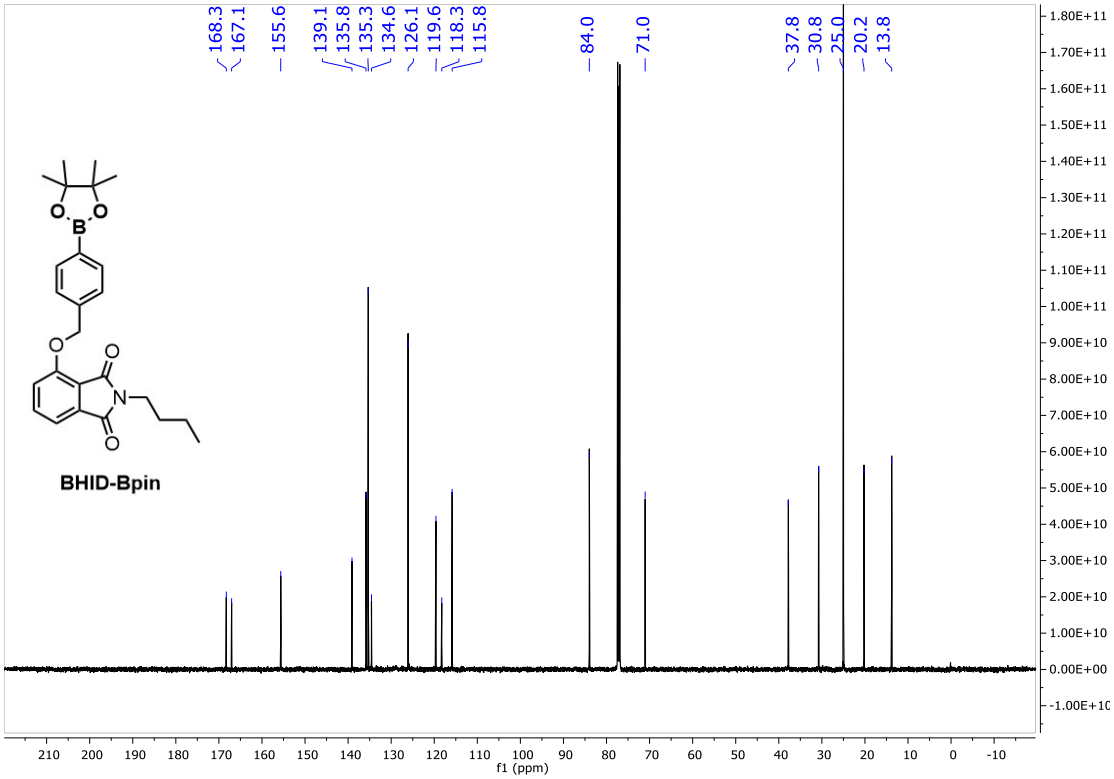

Fig. S6. ^{13}C NMR (126 MHz, $CDCl_3$) of BHID-Bpin

3. Results

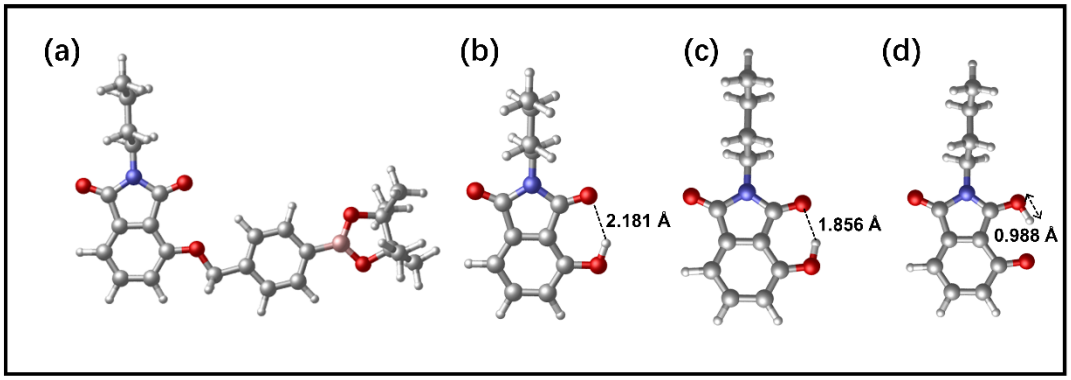

Fig. S7. The optimized structures of the BHID-Bpin (a); enol-BHID in the S_0 (b), in the S_1 (c), keto-BHID in the S_1 (d) in acetonitrile at DFT//CAM-B3LYP//6-31+G(d,p) level.

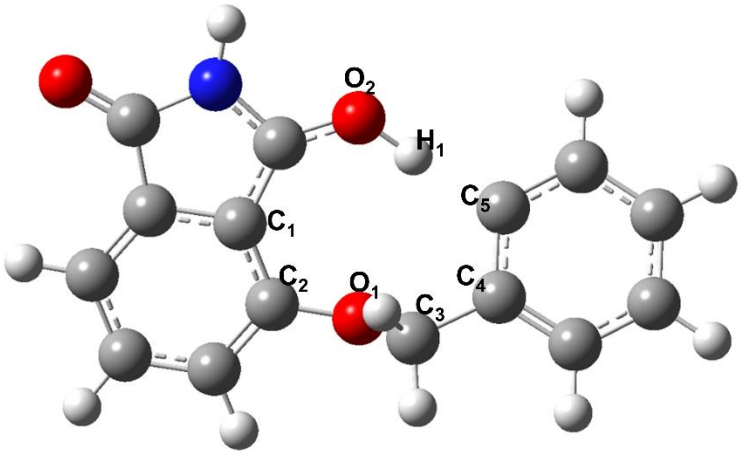

Fig. S8. The truncated model of BHID-Bpin in acetonitrile for high level quantum chemistry calculation for locating the minimum energy conical intersection (MECI).

Table S1. Key configurational parameters for the truncated model for BHID-Bpin in acetonitrile (shown in Fig. S8) at FC, TS and MECI points.

	O_2---H_1 (Å)	$C_2O_1C_3C_4$ (°)	$C_1C_2O_1C_3$ (°)	$O_1C_3C_4C_5$ (°)
FC	2.924	179.9	-179.9	0.0
TS	2.542	-159.2	147.1	32.2
MECI	1.054	-144.9	82.8	57.4

Table S2. The vertical excitation energy (VE) of the truncated model for BHID-Bpin in acetonitrile (shown in Fig. S8) at FC point calculated with CASSCF(4,4) and CASSCF(8,8) calculation level.

Methods	CASSCF(4,4)//6-31G(d,p)	CASSCF(8,8)//6-31G(d,p)	CASSCF(8,8)// aug-cc-pVDZ
VE (eV)	4.23	4.23	4.07

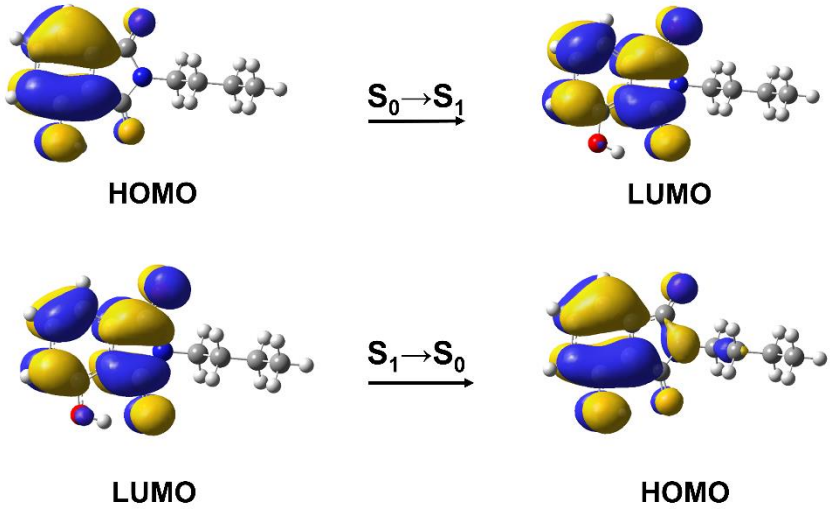

Fig. S9. Orbitals and the relevant transitions involved in BHID in acetonitrile at TD-DFT//CAM-B3LYP//6-31+G(d,p) level.

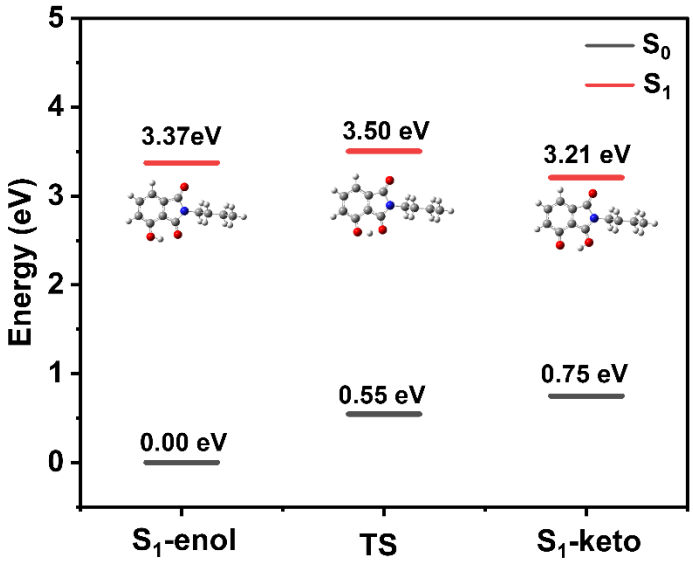

Fig. S10. The energy diagram of the critical points of the BHID system in acetonitrile.

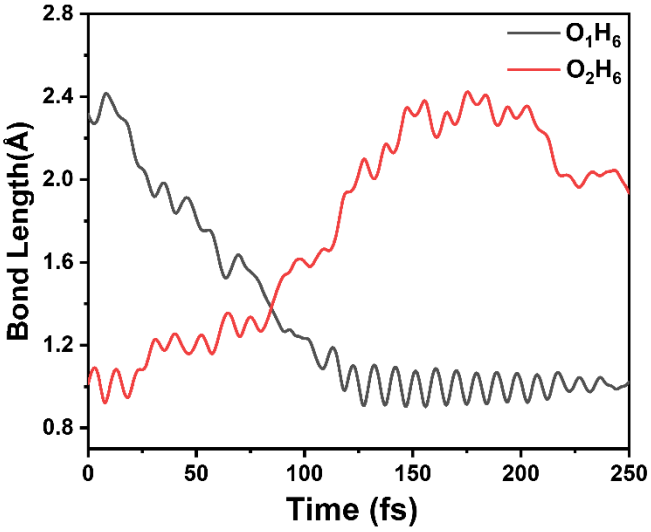

Fig. S11. The time evolution of the O_1–H_6 and O_2–H_6 distances averaged over 7 trajectories within the 250fs for BHID system in acetonitrile at TDDFT//CAM-B3LYP//6-31+G(d,p) level.

Table S3 Calculated vertical transition energy and transition oscillator strength (*f*) of BHID-Bpin in water at TD-DFT//CAM-B3LYP //6-31+G(d,p) level.

Electronic transition	Energy (nm, eV)	Contrib.[a]	*f* [b]
$S_0 \rightarrow S_1$	303 (4.08)	H→L (73%)	0.1248
$S_1 \rightarrow S_0$	364 (3.40)	L→H (79%)	0.1379

[a] H means the HOMO, L means the LUMO; [b] *f* means the transition oscillator strength.

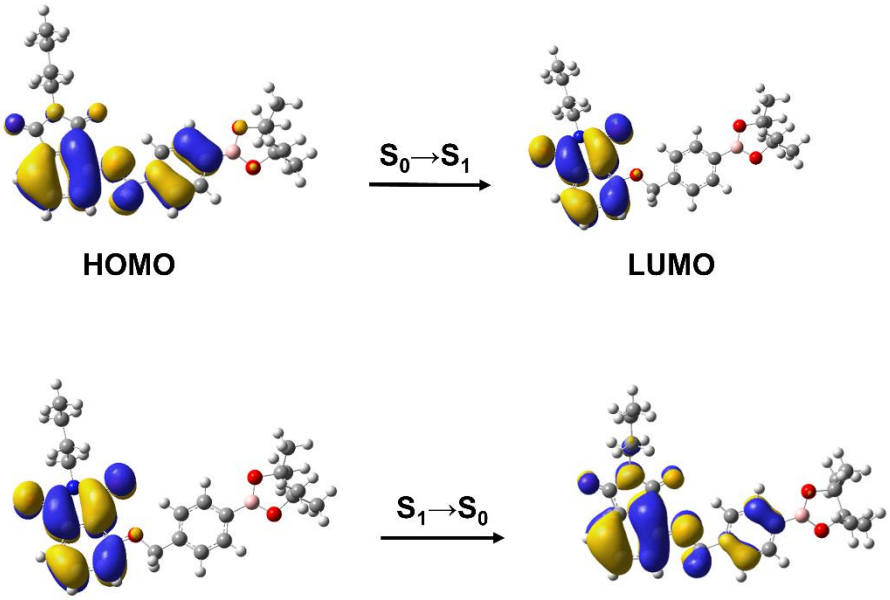

Fig. S12. Orbitals and the relevant transitions involved in the first excited state of BHID-Bpin in water at TD-DFT//CAM-B3LYP //6-31+G(d,p) level.

Table S4 Calculated vertical transition energy and transition oscillator strength (*f*) of enol- and keto-BHID in water at TD-DFT//CAM-B3LYP //6-31+G(d,p) level.

Geometry	Electronic transition	Energy (nm, eV)	Contrib.[a]	*f* [b]
enol	$S_0 \rightarrow S_1$	301 (4.11)	H→L (83%)	0.1344
	$S_1 \rightarrow S_0$	368 (3.37)	L→H (88%)	0.1629
keto	$S_1 \rightarrow S_0$	505 (2.45)	L→H (96%)	0.2706

[a] H means the HOMO, L means the LUMO; [b] *f* means the transition oscillator strength.

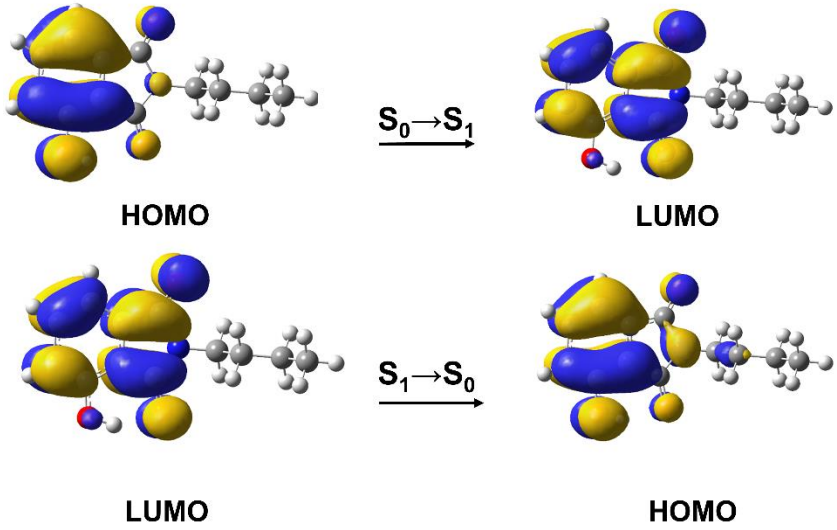

Fig. S13. Orbitals and the relevant transitions involved in BHID in water at TD-DFT//CAM-B3LYP//6-31+G(d,p) level.

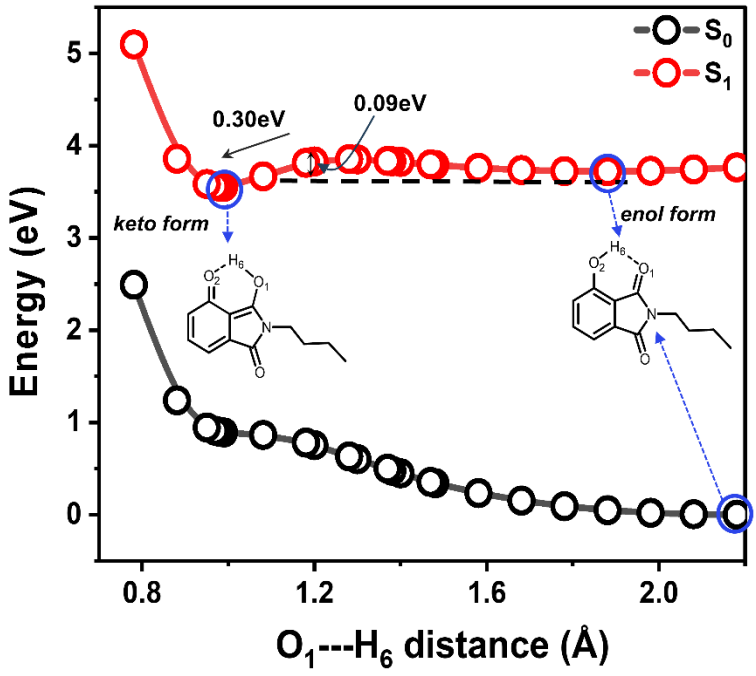

Fig. S14. The calculated potential energy curves of S_1 and S_0 of BHID in water computed at

TDDFT//CAM-B3LYP//6-31+G(d,p) level.

Table S5 Calculated vertical transition energy and transition oscillator strength (*f*) of enol-BHID cluster with one H_2O molecule at TD-DFT//CAM-B3LYP //6-31+G(d,p) level.

Geometry	Electronic transition	Energy (nm, eV)	Contrib.[a]	*f* [b]
Enol-BHID-H_2O	$S_0 \rightarrow S_1$	256 (4.85)	H→L (95%)	0.2439

[a] H means the HOMO, L means the LUMO; [b] *f* means the transition oscillator strength.

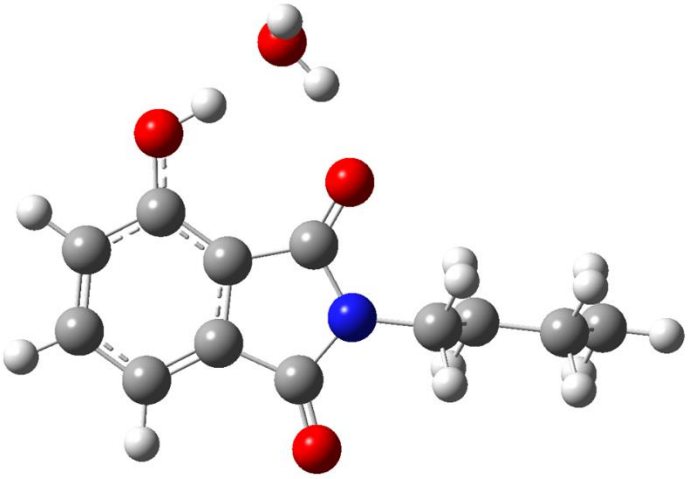

Fig. S15. The most stable structure in S_0 of enol-BHID-H_2O complex in water optimized at TD-DFT//CAM-B3LYP//6-31+G(d,p) level.

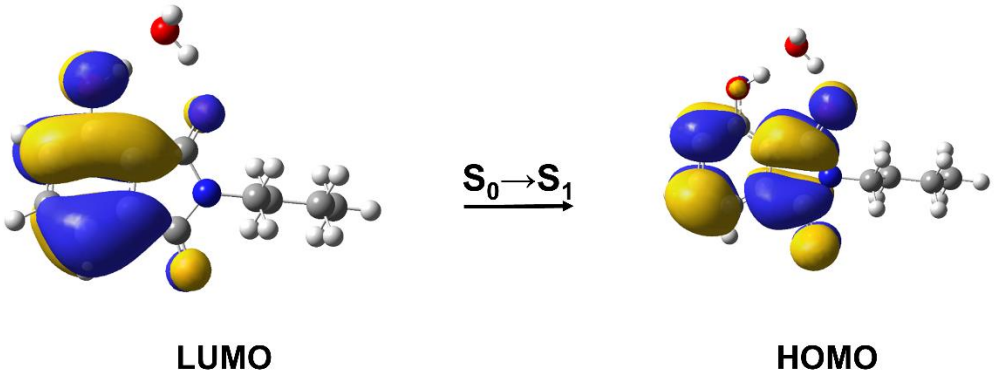

Fig. S16. Orbitals and the relevant transitions involved in enol-BHID-H_2O in water at TD-DFT//CAM-B3LYP//6-31+G(d,p) level.

4. Cartesian coordinates of the optimized structure of BHID and BHID-Bpin.

Table S6 Cartesian coordinates of equilibrium structure of enol-BHID in the S_0 (left) and S_1 (right) optimized with DFT//CAM-B3LYP//6-31+G(d,p) and TD-DFT//CAM- B3LYP //6-31+G(d,p) method, respectively.

DFT//CAM- B3LYP //6-31+G(d,p)				TD-DFT//CAM- B3LYP/ /6-31+G(d,p)			
	X	Y	Z		X	Y	Z
C	-1.44067000	1.03582300	-0.02471000	C	-1.410040000000	1.096841000000	-0.020095000000
C	-1.54352000	-0.35125100	-0.06351900	C	-1.497584000000	-0.314036000000	-0.074353000000
C	-2.73372200	-1.00677500	0.19538400	C	-2.711289000000	-1.033554000000	0.193326000000
C	-3.84856500	-0.21297400	0.50471600	C	-3.853407000000	-0.311822000000	0.519984000000
C	-3.73563500	1.17142500	0.54161400	C	-3.751817000000	1.089306000000	0.570101000000
C	-2.52319500	1.83181400	0.27602400	C	-2.561668000000	1.808312000000	0.307898000000
C	-0.02324300	1.37236400	-0.35625100	C	-0.046986000000	1.436490000000	-0.349213000000
C	-0.23346500	-0.91665000	-0.40954700	C	-0.243305000000	-0.897397000000	-0.421132000000
H	-4.79681000	-0.69598700	0.71342300	H	-4.785862000000	-0.820544000000	0.728163000000
H	-4.61538700	1.75804800	0.78367700	H	-4.641155000000	1.656451000000	0.823757000000
H	-2.45126000	2.91253900	0.30795300	H	-2.564205000000	2.890820000000	0.363218000000
N	0.63177700	0.15587500	-0.57139100	N	0.607099000000	0.182862000000	-0.583149000000
C	2.04243500	0.03443600	-0.91333000	C	2.008912000000	0.071849000000	-0.922613000000
H	2.14608100	-0.86004700	-1.53175300	H	2.120044000000	-0.805537000000	-1.564575000000
H	2.30077900	0.90244600	-1.52421000	H	2.275063000000	0.967090000000	-1.488682000000
O	0.05031000	-2.09974200	-0.53674900	O	0.012204000000	-2.122083000000	-0.551101000000
O	0.50203300	2.46390300	-0.43989100	O	0.535167000000	2.522887000000	-0.443136000000
O	-2.84567800	-2.35104300	0.15828300	O	-2.656902000000	-2.347522000000	0.112631000000
H	-1.98263900	-2.73904400	-0.07358900	H	-1.728861000000	-2.614165000000	-0.137410000000
C	2.94348700	-0.04987500	0.31592300	C	2.898647000000	-0.058348000000	0.319248000000
C	4.41754900	-0.17755100	-0.06254800	C	4.374900000000	-0.174287000000	-0.053772000000
H	2.64109000	-0.91065000	0.92391000	H	2.587373000000	-0.939758000000	0.891025000000
H	2.79507900	0.84511000	0.93132000	H	2.742295000000	0.816338000000	0.960248000000
C	5.33222700	-0.25999900	1.15689200	C	5.277685000000	-0.299980000000	1.170861000000
H	4.55566900	-1.06979800	-0.68564500	H	4.516995000000	-1.044591000000	-0.705932000000
H	4.70804500	0.68019200	-0.68166800	H	4.670496000000	0.704543000000	-0.639626000000
H	6.38118200	-0.35110500	0.86080700	H	6.328950000000	-0.381025000000	0.880048000000
H	5.23713900	0.63463600	1.78102600	H	5.177656000000	0.572287000000	1.825047000000
H	5.08318100	-1.12714400	1.77744100	H	5.023476000000	-1.188449000000	1.758156000000

Table S7 Cartesian coordinates of equilibrium structure of BHID-Bpin in the S_0 (left) and S_1 (right) optimized with DFT//CAM-B3LYP //6-31+G(d,p) and TD-DFT//CAM-B3LYP //6-31+G(d,p) method, respectively.

DFT//CAM- B3LYP //6-31+G(d,p)				TD-DFT//CAM-B3LYP //6-31+G(d,p)			
	X	Y	Z		X	Y	Z
C	-5.09464600	-1.59217500	-0.15491000	C	-5.180189000000	-1.470224000000	-0.165426000000
C	-3.75573800	-1.21255000	-0.15968600	C	-3.779409000000	-1.168201000000	-0.171119000000
C	-2.74967200	-2.15010300	0.06310400	C	-2.818878000000	-2.221365000000	0.068077000000
C	-3.14544700	-3.47943700	0.28829500	C	-3.268039000000	-3.517135000000	0.288331000000
C	-4.49195500	-3.83283100	0.28728900	C	-4.652662000000	-3.771066000000	0.278541000000
C	-5.50114600	-2.89170200	0.06452000	C	-5.612867000000	-2.771245000000	0.055890000000
C	-5.91367900	-0.37437100	-0.42159600	C	-5.892289000000	-0.252188000000	-0.427728000000
C	-3.69274900	0.24600500	-0.43008500	C	-3.579373000000	0.235316000000	-0.435525000000
H	-2.40471400	-4.24799400	0.46618200	H	-2.575054000000	-4.326837000000	0.469011000000
H	-4.75528900	-4.86999600	0.46526100	H	-4.988292000000	-4.788026000000	0.451490000000
H	-6.54869000	-3.16870100	0.06391700	H	-6.668606000000	-3.016818000000	0.054747000000
N	-5.01767800	0.67206700	-0.57307700	N	-4.885831000000	0.733073000000	-0.583119000000
C	-5.40325000	2.04964500	-0.84167900	C	-5.171578000000	2.123855000000	-0.840027000000
H	-4.61455000	2.49081400	-1.45523900	H	-4.368398000000	2.509238000000	-1.472972000000
H	-6.31959600	2.01620800	-1.43546500	H	-6.117815000000	2.165481000000	-1.383283000000
O	-2.72858600	0.97949400	-0.52682000	O	-2.553232000000	0.929947000000	-0.531569000000
O	-7.12433000	-0.28045200	-0.50169200	O	-7.104344000000	-0.011470000000	-0.523334000000
O	-1.47392800	-1.72198900	0.04797100	O	-1.562087000000	-1.823391000000	0.054104000000
C	-5.61488900	2.86453500	0.43181200	C	-5.263950000000	2.945992000000	0.452994000000
C	-6.01820800	4.30609900	0.12944700	C	-5.557278000000	4.416919000000	0.166375000000
H	-4.69073500	2.85437900	1.02149000	H	-4.320372000000	2.852610000000	1.001346000000
H	-6.38897700	2.38326800	1.04109400	H	-6.052283000000	2.523381000000	1.085928000000
C	-6.23257900	5.13452500	1.39368400	C	-5.647064000000	5.252122000000	1.441276000000
H	-5.24450500	4.77612700	-0.49020300	H	-4.772893000000	4.822815000000	-0.483977000000
H	-6.93710900	4.30699900	-0.46983600	H	-6.497263000000	4.497290000000	-0.393001000000
H	-6.52043400	6.16158800	1.15157100	H	-5.857492000000	6.300860000000	1.212683000000
H	-7.02308400	4.70358300	2.01695100	H	-6.443993000000	4.886044000000	2.096856000000
H	-5.31911100	5.17624100	1.99609000	H	-4.708357000000	5.213763000000	2.003512000000
C	0.90027700	-1.94032400	0.19253300	C	0.814340000000	-2.028397000000	0.202746000000
C	0.99519100	-0.57416600	-0.06549500	C	0.896056000000	-0.670516000000	-0.100897000000
C	2.06896300	-2.68003100	0.39265000	C	1.984625000000	-2.750650000000	0.447308000000
C	2.24505000	0.03828700	-0.12138600	C	2.141413000000	-0.049570000000	-0.160210000000
H	0.09272100	0.00530800	-0.22198200	H	-0.009167000000	-0.103063000000	-0.288016000000
C	3.31015900	-2.06117400	0.33600100	C	3.220388000000	-2.120807000000	0.387116000000
H	2.00556100	-3.74615200	0.59459500	H	1.928657000000	-3.809238000000	0.686625000000
C	3.42468100	-0.68725500	0.07750600	C	3.324539000000	-0.756387000000	0.080995000000
H	2.30279400	1.10368900	-0.32421700	H	2.192443000000	1.008490000000	-0.399446000000

H	4.20723600	-2.65174400	0.49574400	H	4.120532000000	-2.695809000000	0.581868000000
O	4.98458400	1.35257000	-0.16159600	O	4.867778000000	1.286622000000	-0.227405000000
B	4.81440300	0.00475300	0.01584600	B	4.708701000000	-0.052286000000	0.013229000000
O	6.00290200	-0.66680700	0.13441200	O	5.900787000000	-0.703985000000	0.188107000000
C	7.06091300	0.32586300	0.25834100	C	6.945560000000	0.306161000000	0.284463000000
C	6.40222900	1.59321500	-0.39034900	C	6.287547000000	1.531452000000	-0.440432000000
C	6.59549800	1.67050500	-1.90272900	C	6.509940000000	1.534095000000	-1.950807000000
H	5.95894400	2.46499400	-2.29952600	H	5.872241000000	2.299219000000	-2.400032000000
H	7.63214000	1.90196100	-2.15878600	H	7.548727000000	1.765083000000	-2.198582000000
H	6.31708600	0.73351700	-2.39169200	H	6.252166000000	0.569910000000	-2.396301000000
C	6.78076100	2.91533400	0.25624400	C	6.639289000000	2.888624000000	0.145688000000
H	7.85657200	3.09161800	0.16857700	H	7.714774000000	3.072236000000	0.070191000000
H	6.26185100	3.73151600	-0.25264800	H	6.122579000000	3.672221000000	-0.414070000000
H	6.50772600	2.94174800	1.31173500	H	6.344853000000	2.965499000000	1.192945000000
C	8.29833300	-0.19103300	-0.45627100	C	8.203566000000	-0.231169000000	-0.376953000000
H	9.08997700	0.56342200	-0.44649300	H	8.986602000000	0.532178000000	-0.387813000000
H	8.67208800	-1.07976400	0.05837900	H	8.575280000000	-1.088662000000	0.189478000000
H	8.08484200	-0.45938400	-1.49151100	H	8.015553000000	-0.553019000000	-1.401819000000
C	7.34057400	0.48444100	1.75078200	C	7.190487000000	0.541967000000	1.772769000000
H	7.61810200	-0.48859700	2.16320300	H	7.469655000000	-0.406017000000	2.238942000000
H	8.16473500	1.17945300	1.92806600	H	8.002624000000	1.255020000000	1.933180000000
H	6.45981100	0.84465800	2.28839100	H	6.294067000000	0.917455000000	2.272686000000
C	-0.42318200	-2.65768400	0.26403400	C	-0.500013000000	-2.759277000000	0.272602000000
H	-0.46763300	-3.44365200	-0.49895500	H	-0.559558000000	-3.537746000000	-0.495384000000
H	-0.54410100	-3.12756900	1.24707600	H	-0.640082000000	-3.225249000000	1.253390000000

Table S8 Cartesian coordinates of equilibrium structure of truncated BHID-Bpin model in the S_0 (left) and the S_1 transition state (right) optimized with TD-DFT//CAM- B3LYP //6-31G(d,p) method.

TD-DFT//CAM- B3LYP //6-31G(d,p)				TD-DFT//CAM- B3LYP //6-31G(d,p)			
	X	Y	Z		X	Y	Z
C	3.07882000	0.35710200	-0.00000300	C	-3.04135900	0.28541200	-0.03274400
C	1.75706400	-0.07581000	0.00000800	C	-1.70165500	-0.03472900	0.16548400
C	0.70808500	0.84021800	-0.00000200	C	-0.73616600	0.96086200	0.23780800
C	1.04206100	2.20328200	-0.00004300	C	-1.15578600	2.28609800	0.05475600
C	2.37285100	2.60998700	-0.00005800	C	-2.49648900	2.58235300	-0.16908200
C	3.42429300	1.69194700	-0.00003700	C	-3.47212800	1.58307200	-0.21044800
C	3.96075700	-0.84745700	0.00002800	C	-3.81697000	-0.98927200	-0.07944400
C	1.74844900	-1.56186500	0.00003100	C	-1.56560800	-1.51461300	0.17193100
H	0.26405000	2.95549200	-0.00005800	H	-0.43046500	3.09022900	0.08452700
H	2.58900400	3.67282600	-0.00009200	H	-2.78541800	3.61929200	-0.30173300
H	4.46003800	2.00923200	-0.00005000	H	-4.51658000	1.81402000	-0.38249100
N	3.09556900	-1.93222800	0.00007500	N	-2.87250600	-1.99667800	0.07019000
O	0.81945500	-2.33918200	0.00001600	O	-0.57212800	-2.20815600	0.19090400
O	5.17074400	-0.89935500	0.00001400	O	-5.01013900	-1.14641200	-0.21263000
O	-0.54340900	0.35306800	0.00003200	O	0.53125100	0.59690600	0.51925400
C	-2.92239600	0.44915400	0.00000100	C	2.84477500	0.49698500	-0.04167700
C	-2.91905000	-0.94308300	-0.00011700	C	2.76651200	-0.88970000	-0.17243700
C	-4.13971600	1.13127800	0.00011400	C	4.09379600	1.10722300	0.05459500
C	-4.12321500	-1.64274000	-0.00012300	C	3.93169300	-1.64820400	-0.22363400
H	-1.97434400	-1.47416800	-0.00018700	H	1.79606800	-1.37457600	-0.21222700
C	-5.33876800	0.43127700	0.00010000	C	5.25652200	0.34762600	-0.01121100
H	-4.14903400	2.21792500	0.00021100	H	4.15817900	2.18342500	0.18838500
C	-5.33385000	-0.96118900	-0.00001500	C	5.17788100	-1.03294300	-0.15638300
H	-4.11113900	-2.72805500	-0.00020900	H	3.86564200	-2.72802400	-0.31221000
H	-6.27896800	0.97317100	0.00018800	H	6.22369700	0.83386500	0.06512900
H	3.40316300	-2.89457100	0.00003500	H	-3.09623900	-2.98070700	0.01809600
C	-1.64502500	1.25057600	-0.00001200	C	1.60122600	1.34521100	-0.05844600
H	-1.59904500	1.89551800	-0.88604100	H	1.77387700	2.27140600	0.50154300
H	-1.59907800	1.89559400	0.88596300	H	1.32531600	1.62409900	-1.08252200
H	-6.27011300	-1.50967100	-0.00001700	H	6.08413100	-1.62726500	-0.21246300

Table S9 Cartesian coordinates of MECI of truncated BHID-Bpin model located between the S_0 and S_1 state optimized with SA2-CASSCF(4,4)//6-31G(d,p) method.

SA2-CASSCF(4,4) //6-31G(d,p)			
	X	Y	Z
C	2.8428050735	0.1734020199	-0.0540555658
C	1.4324533905	0.1382920382	-0.0853239639
C	0.7234732230	1.3300431367	-0.2512726333
C	1.4354466248	2.5104668569	-0.3650542253
C	2.8295763738	2.5279881988	-0.3137381691
C	3.5492532973	1.3490395842	-0.1591870331
C	3.3386191406	-1.2031473586	0.0760706445
C	1.0421716955	-1.2369409620	0.0282584533
H	0.8859463063	3.4192438113	-0.5061897779
H	3.3453009234	3.4632585351	-0.4038432915
H	4.6204511871	1.3436011880	-0.1278995034
N	2.1831719646	-1.9830482880	0.1007811725
O	-0.0936331026	-1.8543731246	0.1002973998
O	4.4773959455	-1.6291017733	0.1536137461
O	-0.6405722887	1.3351738844	-0.3776779144
C	-2.7171387558	0.4789140380	0.4212205615
C	-2.5403306021	-0.8315338468	-0.0354618072
C	-4.0018089677	0.9913650459	0.5022972419
C	-3.6271356302	-1.6172877551	-0.4068004210
H	-1.0307464422	-1.3898900456	-0.0337156583
C	-5.0970148095	0.2098576698	0.1435082832
H	-4.1572957142	2.0024571154	0.8322971463
C	-4.9085106477	-1.0884519628	-0.3101585914
H	-3.4828607615	-2.6185527136	-0.7637409956
H	-6.0870226433	0.6180963257	0.2094603844
H	2.1810501040	-2.9691611700	0.2154306836
C	-1.5124443601	1.2860335442	0.7955059683
H	-1.7649271905	2.2990881773	1.0717967150
H	-0.9650182961	0.8259582828	1.6104121775
H	-5.7550610379	-1.6864824523	-0.5915500267

Table S10 Cartesian coordinates of the transition state of the BHID in the S_1 (left) and equilibrium structure of keto-BHID on the S_1 state (right) state optimized with TD-DFT//CAM-B3LYP //6-31+G(d,p) method.

TD-DFT//CAM- B3LYP //6-31+G(d,p)				TD-DFT//CAM- B3LYP //6-31+G(d,p)			
	X	Y	Z		X	Y	Z
C	-1.435974000000	1.122418000000	-0.009334000000	C	-1.457443000000	1.065001000000	-0.016626000000
C	-1.509519000000	-0.268105000000	-0.062944000000	C	-1.521052000000	-0.330570000000	-0.066829000000
C	-2.670254000000	-1.069103000000	0.185896000000	C	-2.715172000000	-1.105019000000	0.193603000000
C	-3.850130000000	-0.380438000000	0.519640000000	C	-3.874154000000	-0.341156000000	0.519493000000
C	-3.785359000000	1.019439000000	0.577414000000	C	-3.798365000000	1.052258000000	0.567135000000
C	-2.622190000000	1.790198000000	0.323815000000	C	-2.621522000000	1.778578000000	0.307407000000
C	-0.061767000000	1.457138000000	-0.342305000000	C	-0.093371000000	1.439423000000	-0.342675000000
C	-0.264569000000	-0.844364000000	-0.407770000000	C	-0.236344000000	-0.839839000000	-0.411528000000
H	-4.770324000000	-0.913661000000	0.723014000000	H	-4.802992000000	-0.860432000000	0.726218000000
H	-4.691559000000	1.558491000000	0.833579000000	H	-4.695227000000	1.610045000000	0.817241000000
H	-2.672445000000	2.871070000000	0.390548000000	H	-2.621139000000	2.861534000000	0.357286000000
N	0.598447000000	0.187576000000	-0.577773000000	N	0.600117000000	0.188314000000	-0.576936000000
C	2.005498000000	0.076547000000	-0.921784000000	C	2.014887000000	0.106373000000	-0.915887000000
H	2.115939000000	-0.791586000000	-1.576300000000	H	2.142857000000	-0.734242000000	-1.601771000000
H	2.264613000000	0.975214000000	-1.485212000000	H	2.256731000000	1.028899000000	-1.446814000000
O	-0.105923000000	-2.117168000000	-0.517457000000	O	0.106102000000	-2.101488000000	-0.556686000000
O	0.530056000000	2.532726000000	-0.442530000000	O	0.470067000000	2.525859000000	-0.438631000000
O	-2.464551000000	-2.342688000000	0.066600000000	O	-2.622919000000	-2.364483000000	0.110600000000
H	-1.305181000000	-2.451320000000	-0.233050000000	H	-0.710614000000	-2.628326000000	-0.380945000000
C	2.897392000000	-0.059038000000	0.314031000000	C	2.898968000000	-0.055010000000	0.320810000000
C	4.373579000000	-0.165314000000	-0.062806000000	C	4.379188000000	-0.121147000000	-0.050054000000
H	2.593079000000	-0.946095000000	0.881339000000	H	2.608941000000	-0.966359000000	0.856103000000
H	2.739718000000	0.809539000000	0.963134000000	H	2.721504000000	0.787965000000	0.997906000000
C	5.279859000000	-0.296912000000	1.158627000000	C	5.280389000000	-0.277464000000	1.172013000000
H	4.518344000000	-1.029590000000	-0.722402000000	H	4.543777000000	-0.959710000000	-0.737550000000
H	4.663921000000	0.719576000000	-0.642079000000	H	4.656245000000	0.788146000000	-0.597055000000
H	6.330738000000	-0.371522000000	0.864931000000	H	6.334035000000	-0.322112000000	0.882394000000
H	5.177697000000	0.569941000000	1.819633000000	H	5.158140000000	0.564104000000	1.861623000000
H	5.030273000000	-1.190854000000	1.739492000000	H	5.044853000000	-1.195373000000	1.720490000000

Table S11 Cartesian coordinates of the enol-BHID-H2O complex in S_0 optimized with DFT//CAM-B3LYP //6-31+G(d,p) method.

DFT//CAM-B3LYP //6-31+G(d,p) method.			
	X	Y	Z
C	1.19487600	-1.44130000	-0.08814600
C	1.43531400	-0.05930400	-0.01889500
C	2.70898700	0.40678500	0.31323400
C	3.69713800	-0.56926000	0.57172900
C	3.43194100	-1.92295300	0.49712200
C	2.15250400	-2.39275200	0.15761200
C	-0.23405500	-1.64303500	-0.44707500
C	0.15177900	0.61876200	-0.32321200
H	4.68861600	-0.21569300	0.83303300
H	4.22834000	-2.62963200	0.70439100
H	1.92947700	-3.45135200	0.09645600
N	-0.78659700	-0.37389600	-0.56657900
C	-2.18162600	-0.11460600	-0.89686300
H	-2.21043500	0.81454000	-1.46986800
H	-2.50966400	-0.92834600	-1.54742500
O	-0.12496300	1.81035200	-0.37068100
O	-0.83796100	-2.68491500	-0.61394100
O	3.10802700	1.67817800	0.42776700
H	2.47683900	2.39258100	0.14953300
C	-3.07224600	-0.01746100	0.33900400
C	-4.53110800	0.24811900	-0.02651500
H	-2.70045200	0.78472500	0.98710400
H	-2.99706400	-0.95093500	0.90901800
C	-5.43592400	0.34507300	1.19917200
H	-4.59626500	1.17803400	-0.60484800
H	-4.89074200	-0.55184500	-0.68546900
H	-6.47394200	0.53583300	0.91205500
H	-5.41430100	-0.58382900	1.77855700
H	-5.11700300	1.15757300	1.86040000
O	1.65929600	3.79428400	-0.21651900
H	1.91425100	4.23918600	-1.03473400
H	0.83784700	3.29483200	-0.39816700

5. References

(1) L. Wu, X. Tian, D. J. Lee, J. Yoon, C. S. Lim, H. M. Kim and T. D. James, *Chem. Commun.,* 2021, **57**, 11084-11087.