Supporting Information

Solvent-polarity-dependent conformation and ESIPT behaviors for 2-(benzimidazol-2-yl)-3-hydroxychromone: A novel dynamical mechanism

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Table S1. The optimized energies (Hartree) and percentage (in brackets) of BI3HC-A, BI3HC-B and BI3HC-C conformations via Cam-B3LYP and PBE0 functionals in S_0 state in CYC, TOL, CHL and ACE solvents based on Boltzmann distribution.

Cam-B3LYP	BI3HC-A	BI3HC-B	BI3HC-C
CYC	-950.7165 (57.84%)	-950.7102 (0.07%)	-950.7162 (42.09%)
TOL	-950.7173 (42.09%)	-950.7115 (0.09%)	-950.7176 (57.82%)
CHL	-950.7208 (20.12%)	-950.7161 (0.14%)	-950.7221 (79.74%)
ACE	-950.7248 (4.42%)	-950.7217 (0.17%)	-950.7277 (95.41%)
PBE0	BI3HC-A	BI3HC-B	BI3HC-C
CYC	-950.0984 (60.37%)	-950.0925 (0.11%)	-950.0980 (39.52%)
TOL	-950.09947 (51.52%)	-950.0938 (0.13%)	-950.09941 (48.35%)
CHL	-950.1027 (18.47%)	-950.0982 (0.16%)	-950.1041 (81.37%)
ACE	-950.1067 (3.99%)	-950.1037 (0.17%)	-950.1097 (95.84%)

Table S2. Parameters of bond lengths (Å) and bong angles (°) involved in hydrogen bond O_1-$H_2\cdots N_4$ for BI3HC-C fluorophore in CYC, TOL, CHL and ACE solvents in S_0 and S_1 states.

	CYC		TOL		CHL		ACE	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O_1-H_2	0.9895	1.0067	0.9898	1.0068	0.9909	1.0069	0.9922	1.0070
$H_2\cdots N_4$	1.7983	1.7169	1.7954	1.7146	1.7863	1.7123	1.7765	1.7094
$\sigma(O_1H_2N_4)$	145.55	147.93	145.60	147.94	145.90	148.03	146.24	148.14

Table S3. Parameters of bond lengths (Å) and bong angles (°) involved in hydrogen bond $O_1\cdots H_2$-O_3 for BI3HC-A-T and hydrogen bond $O_1\cdots H_2$-N_4 for BI3HC-C-T in CYC, TOL, CHL and ACE solvents in S_0 and S_1 states.

BI3HC-A-T	CYC		TOL		CHL		ACE	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
$O_1\cdots H_2$	1.9485	2.0770	1.9500	2.0792	1.9622	2.0886	1.9714	2.0987
H_2-O_3	0.9892	0.9778	0.9890	0.9777	0.9880	0.9773	0.9874	0.9771
$\sigma(O_1H_2O_3)$	120.56	116.30	120.51	116.21	120.09	115.85	119.74	115.49
BI3HC-C-T	CYC		TOL		CHL		ACE	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
$O_1\cdots H_2$	1.8985	2.0208	1.9030	2.0285	1.9209	2.0479	1.9467	2.0758
H_2-N_4	1.0242	1.0180	1.0239	1.0174	1.0226	1.0166	1.0212	1.0159
$\sigma(O_1H_2N4)$	127.08	122.16	126.96	121.93	126.44	121.40	125.75	120.61

Table S4. Simulated BCP parameters involved in hydrogen bond O_1-$H_2\cdots N_3$ as well as predicted hydrogen bonding energy E(HB) (kcal/mol) for BI3HC-C fluorophore in CYC, TOL, CHL and ACE solvents in S_0 and S_1 states.

Solvent	States	ρ(r)	V(r)	G(r)	K(r)	E(HB)
CYC	S_0	0.04180	-0.03646	003181	-0.00465	-8.582
	S_1	0.05055	-0.04732	0.03777	-0.00955	-10.534
TOL	S_0	0.04209	-0.03682	0.03201	0.00480	-8.647
	S_1	0.05084	-0.04769	0.03796	0.00973	-10.599
CHL	S_0	0.04303	-0.03793	0.03264	0.00529	-8.857
	S_1	0.05117	-0.04807	0.03814	0.00993	-10.673
ACE	S_0	0.04407	-0.03916	0.03331	0.00584	-9.089
	S_1	0.05156	-0.04851	0.03834	0.01017	-10.760

ρ(r): Density of all electrons.

V(r): Potential energy density.

G(r): Lagrangian kinetic energy.

K(r): Hamiltonian kinetic energy.

E(HB): Hydrogen bonding energy based on -223.08*ρ(r)+0.7423.

Table S5. Theoretical vertical excitation energies (λ nm), oscillator strength (*f*) and transition compositions for BI3HC-C fluorophore in CYC, TOL, CHL and ACE solvents.

	Transition	λ	f	Composition	CI (%)
CYC	$S_0 \rightarrow S_1$	372.38	0.6954	H → L	98.15
	$S_0 \rightarrow S_2$	352.17	0.0001	H-3 → L	95.99
	$S_0 \rightarrow S_3$	317.47	0.0141	H-1 → L	94.23
TOL	$S_0 \rightarrow S_1$	373.82	0.7148	H → L	98.20
	$S_0 \rightarrow S_2$	350.39	0.0000	H-3 → L	96.04
	$S_0 \rightarrow S_3$	318.88	0.0144	H-1 → L	94.87
CHL	$S_0 \rightarrow S_1$	374.13	0.7191	H → L	98.17
	$S_0 \rightarrow S_2$	344.30	0.0000	H-3 → L	96.19
	$S_0 \rightarrow S_3$	323.26	0.0138	H-1 → L	96.36
ACE	$S_0 \rightarrow S_1$	373.47	0.7108	H → L	98.11
	$S_0 \rightarrow S_2$	336.75	0.0000	H-3 → L	96.35
	$S_0 \rightarrow S_3$	328.46	0.0127	H-1 → L	97.37

Table S6. Theoretical vertical excitation energies (λ nm), oscillator strength (*f*) and transition compositions of the first transition ($S_0 \rightarrow S_1$) for BI3HC-A and BI3HC-C fluorophores in CYC, TOL, CHL and ACE solvents via Cam-B3LYP functional level.

BI3HC-A	Transition	λ	f	Composition	CI (%)
CYC	$S_0 \rightarrow S_1$	334.91	0.9127	H → L	91.64
TOL	$S_0 \rightarrow S_1$	336.01	0.9271	H → L	91.70
CHL	$S_0 \rightarrow S_1$	335.54	0.9113	H → L	91.89
ACE	$S_0 \rightarrow S_1$	334.28	0.8781	H → L	92.10
BI3HC-C	Transition	λ	f	Composition	CI (%)
CYC	$S_0 \rightarrow S_1$	334.37	0.7722	H → L	94.08
TOL	$S_0 \rightarrow S_1$	335.64	0.7891	H → L	94.06
CHL	$S_0 \rightarrow S_1$	335.90	0.7871	H → L	93.94
ACE	$S_0 \rightarrow S_1$	335.34	0.7753	H → L	93.76

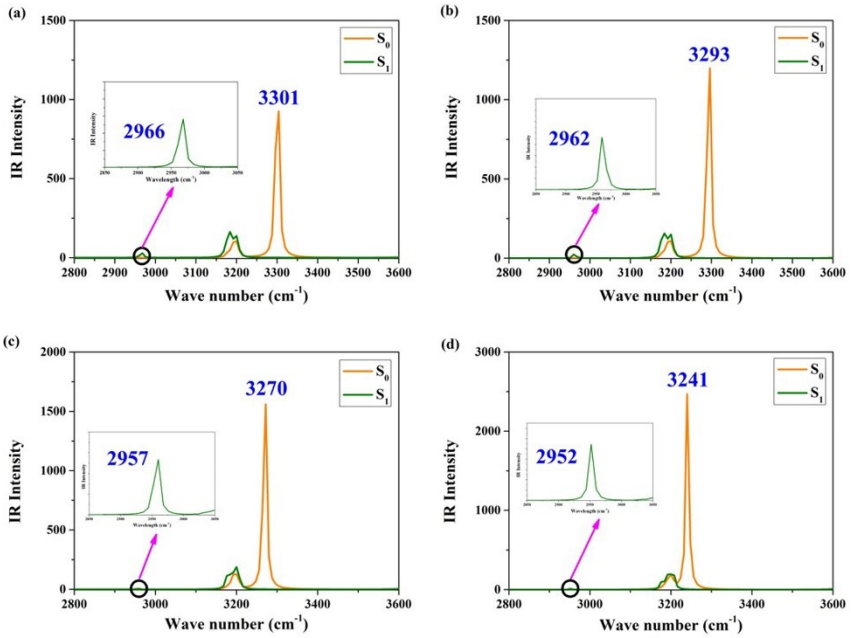

Figure S1. Simulated IR vibrational spectra related to O_1-H_2 stretching vibration for BI3HC-C form in S_0 and S_1 states. (a) CYC; (b) TOL; (c) CHL; (d) ACE.

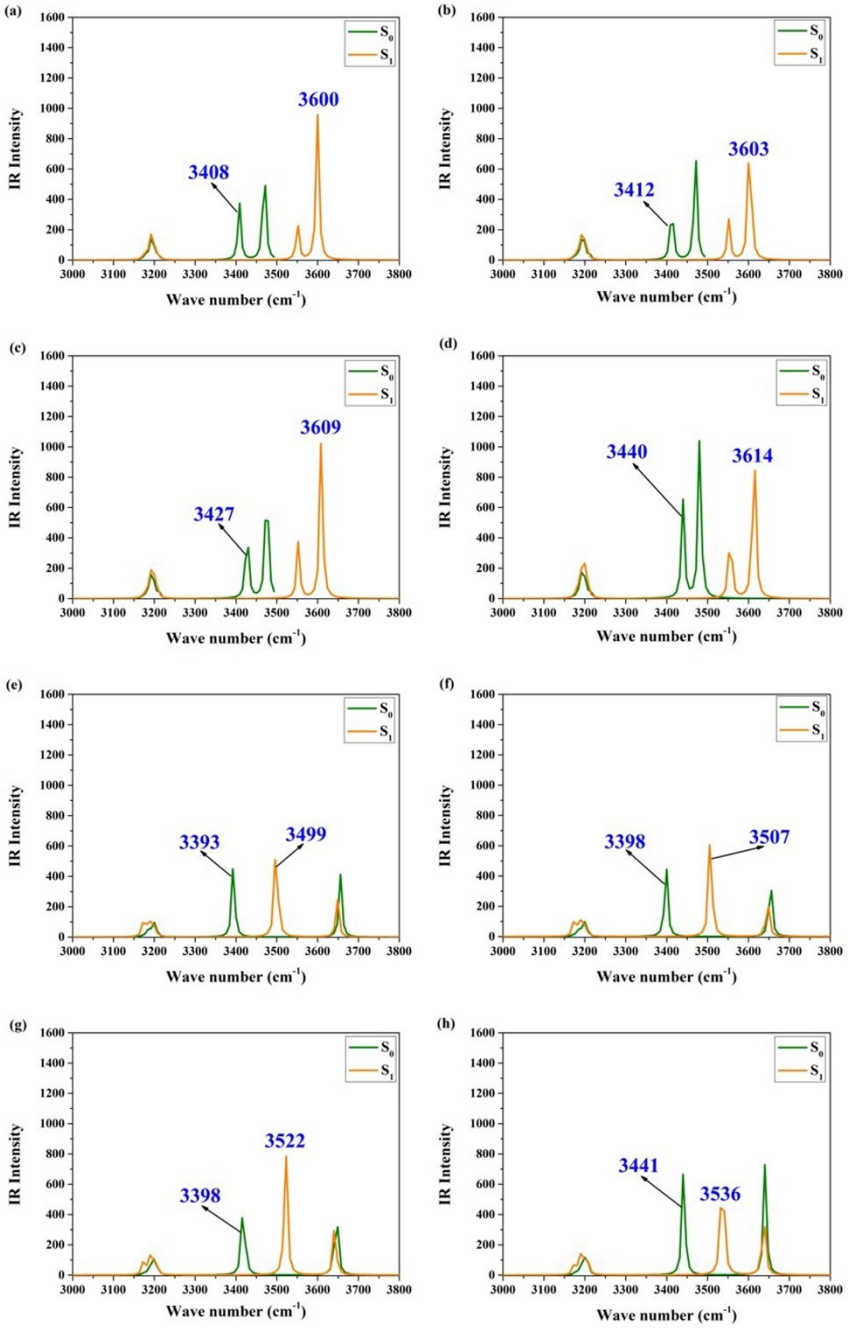

Figure S2. Simulated IR vibrational spectra related to H_2-O_3 stretching vibration for BI3HC-A-T ((a) CYC; (b) TOL; (c) CHL; (d) ACE) and related to H_2-N_4 stretching vibration for BI3HC-C-T ((e) CYC; (f) TOL; (g) CHL; (h) ACE) in S_0 and S_1 states.

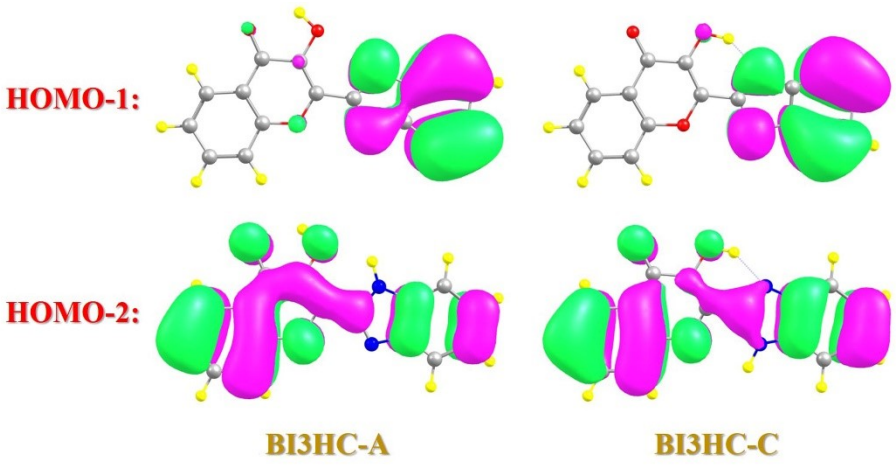

Figure S3. View of HOMO-1 and HOMO-2 orbitals for BI3HC-A and BI3HC-C forms.

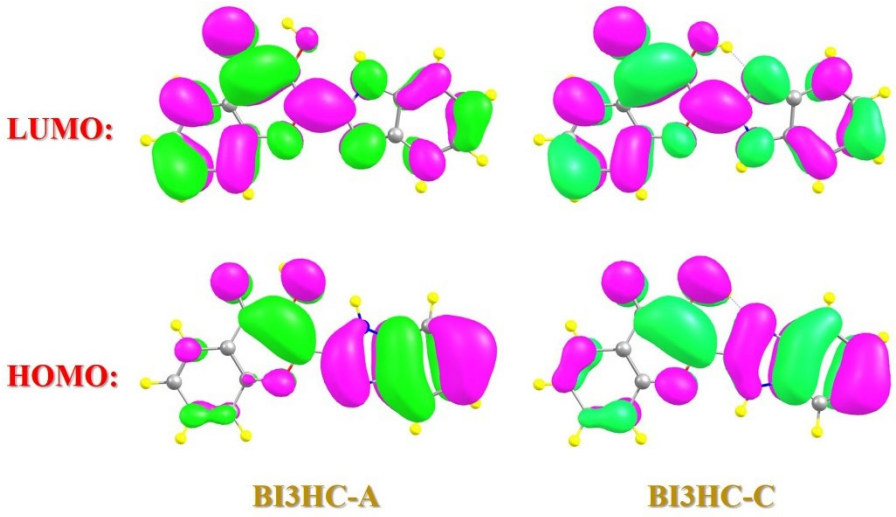

Figure S4. View of HOMO and LUMO orbitals for BI3HC-A and BI3HC-C forms based on TDDFT/D3-Cam-B3LYP/6-311+G(d,p) level.

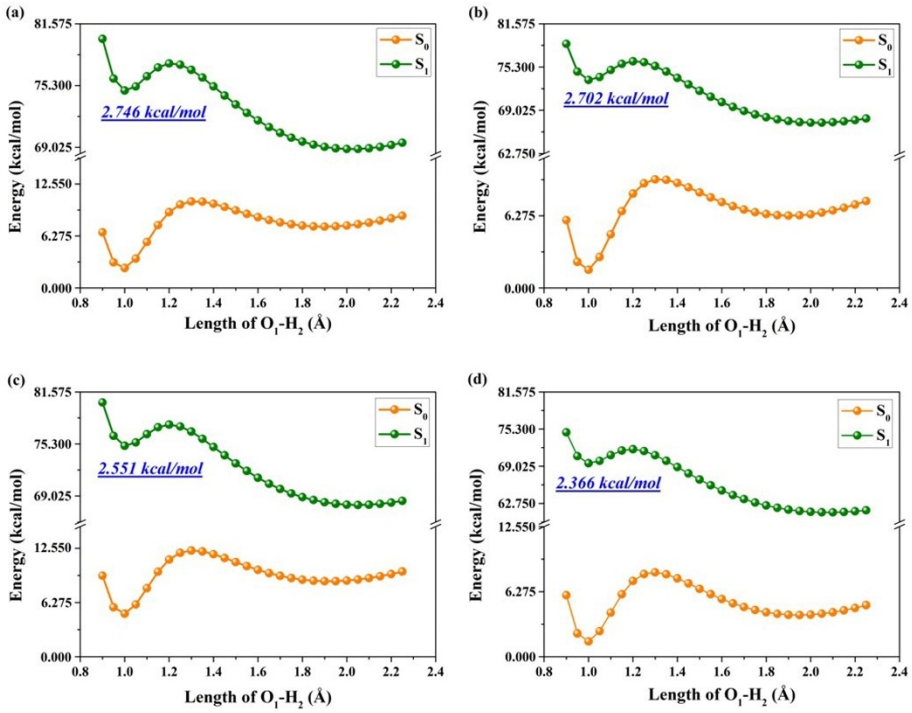

Figure S5. The constructed S_0-state and S_1-state PECs along with O_1-H_2···N_4 for BI3HC-C. (a) CYC; (b) TOL; (c) CHL; (d) ACE.

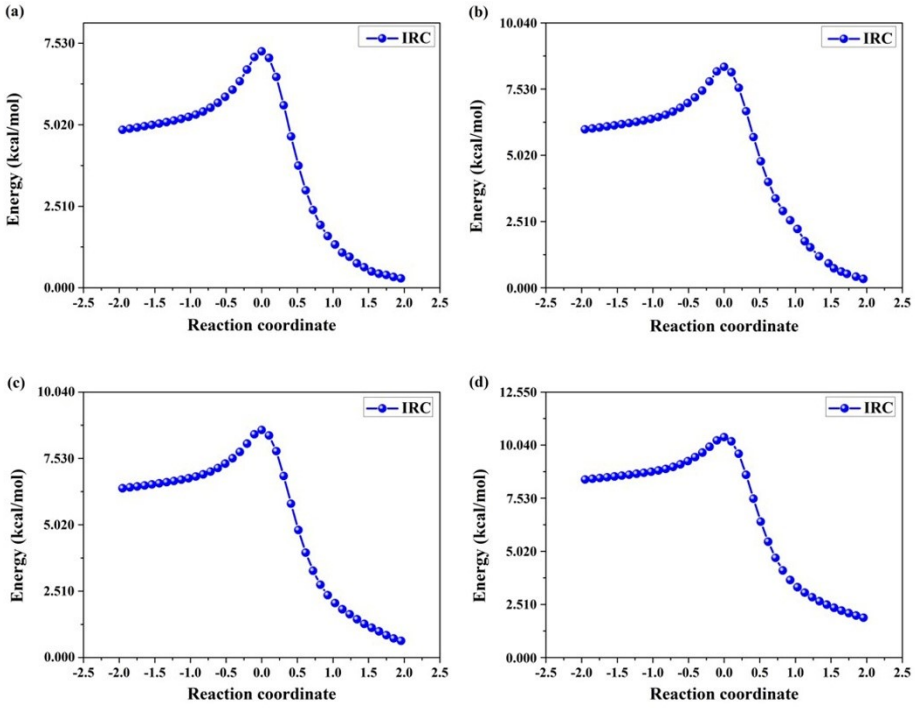

Figure S6. Energy profile along the excited state IRC for BI3HC-C form based on TDDFT/B3LYP-D3/6-311+G(d,p) level. (a) CYC; (b) TOL; (c) CHL; (d) ACE.

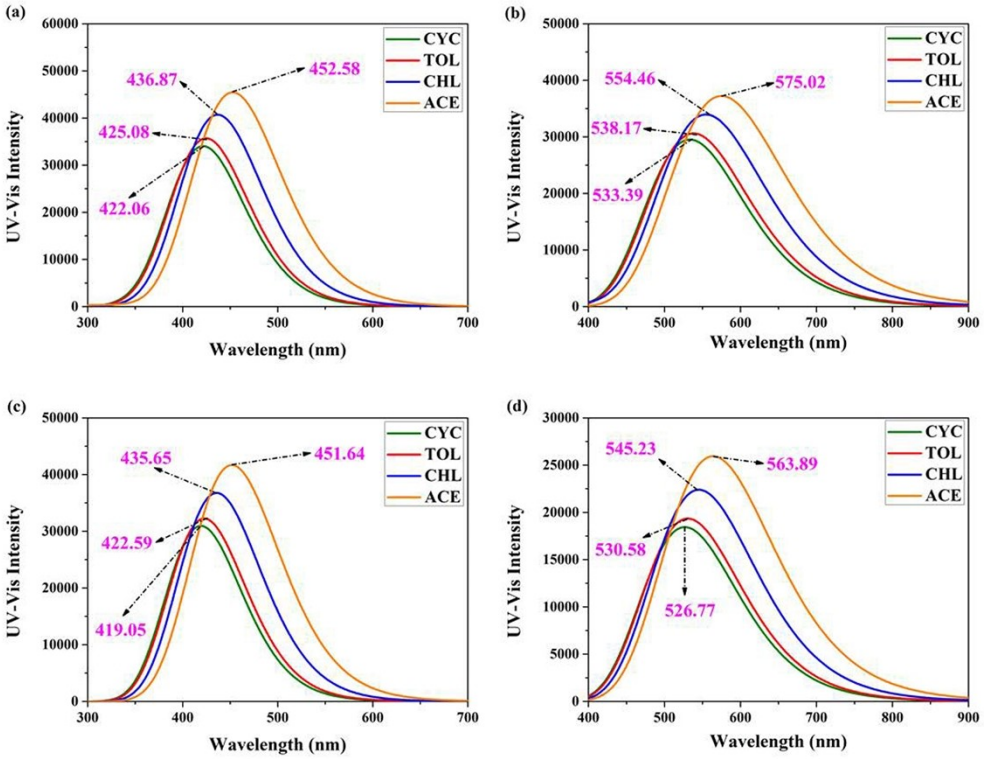

Figure S7. Our simulated emission spectra for BI3HC-A (a), BI3HC-A-T (b), BI3HC-C (c) and BI3HC-C-T (d) structures in CYC, TOL, CHL and ACE solvents.

The relative coordinates of TS forms in this work:

TS for BI3HC-A in CYC：

	X	Y	Z
C	5.22974100	-0.96537200	-0.00035000
C	4.56558100	0.24971200	-0.00021700
C	3.14464600	0.29463400	0.00004800
C	2.43405800	-0.94464500	0.00012600
C	3.10767700	-2.15390700	-0.00002100
C	4.51017200	-2.16647900	-0.00024500
H	6.31332800	-0.98667900	-0.00054200
H	5.10766300	1.18699300	-0.00030800
C	2.38140700	1.47658800	0.00016000
H	2.53420100	-3.07241700	0.00005200
H	5.03291900	-3.11524900	-0.00035900
C	0.28772700	0.12331400	0.00033000
C	0.92060400	1.35420200	0.00026700
C	-3.26337100	0.49455600	-0.00009900
C	-3.08096600	-0.93155200	0.00003700

C	-4.21243200	-1.78028200	-0.00007600
C	-5.46161900	-1.19162300	-0.00031800
C	-5.61525500	0.21739000	-0.00045800
C	-4.51825500	1.08332500	-0.00035300
C	-1.11637200	-0.06749900	0.00024300
H	-4.08334200	-2.85537200	0.00002900
H	-6.34954100	-1.81235500	-0.00040900
H	-6.61498900	0.63558400	-0.00065400
H	-4.65025200	2.15830300	-0.00046400
H	-1.69387400	1.97485700	0.00001400
O	1.05680300	-1.01957500	0.00040600
O	2.72450900	2.71866600	0.00010200
O	0.38619500	2.54660100	0.00023100
H	1.44921600	3.07232400	0.00014600
N	-1.98770300	1.00570500	0.00006500
N	-1.76450600	-1.24937700	0.00024100

TS for BI3HC-A in TOL：

	X	Y	Z
C	5.22875100	-0.96740800	0.00009100
C	4.56484800	0.24811100	0.00010800
C	3.14441000	0.29377200	0.00005600
C	2.43332900	-0.94471300	-0.00000800
C	3.10595700	-2.15439500	-0.00003000
C	4.50840100	-2.16786700	0.00002000
H	6.31229100	-0.98922800	0.00013100
H	5.10779400	1.18491600	0.00016100
C	2.38126000	1.47645900	0.00006700
H	2.53228300	-3.07278800	-0.00008300
H	5.03041800	-3.11703400	0.00000600
C	0.28673000	0.12424500	-0.00002700
C	0.92245400	1.35587300	0.00002400
C	-3.26343100	0.49467500	-0.00003600
C	-3.08012600	-0.93190400	-0.00006800
C	-4.21122600	-1.78110200	-0.00008500
C	-5.46032800	-1.19266700	-0.00007000
C	-5.61494900	0.21695900	-0.00003600
C	-4.51922300	1.08316400	-0.00001800
C	-1.11578100	-0.06580400	-0.00004500
H	-4.08233700	-2.85622400	-0.00011000
H	-6.34809700	-1.81363600	-0.00008200
H	-6.61510000	0.63412300	-0.00002200
H	-4.65114100	2.15811200	0.00001000

H	-1.69833900	1.97672300	0.00000600
O	1.05577500	-1.01835500	-0.00005500
O	2.72650100	2.71901300	0.00011600
O	0.38830300	2.54799500	0.00005300
H	1.45191100	3.07337100	0.00009200
N	-1.98933200	1.00683100	-0.00002400
N	-1.76363600	-1.24853800	-0.00007300

TS for BI3HC-A in CHL：

	X	Y	Z
C	-5.22593100	-0.97337300	-0.00051800
C	-4.56273900	0.24335300	-0.00039300
C	-3.14369000	0.29115900	-0.00004500
C	-2.43122700	-0.94506700	0.00013700
C	-3.10104600	-2.15594000	0.00002000
C	-4.50332000	-2.17201200	-0.00030300
H	-6.30931900	-0.99667900	-0.00078100
H	-5.10845800	1.17862300	-0.00055400
C	-2.38060900	1.47583800	0.00004900
H	-2.52708400	-3.07417800	0.00016800
H	-5.02322400	-3.12230100	-0.00039400
C	-0.28383800	0.12708500	0.00037100
C	-0.92784300	1.36102100	0.00022700
C	3.26348300	0.49500900	-0.00002900
C	3.07773900	-0.93286200	0.00014100
C	4.20799800	-1.78343100	0.00006200
C	5.45701400	-1.19560000	-0.00019100
C	5.61417100	0.21553800	-0.00036400
C	4.52165900	1.08263100	-0.00028400
C	1.11389200	-0.06039700	0.00031400
H	4.07988700	-2.85869300	0.00019100
H	6.34432400	-1.81724000	-0.00026300
H	6.61536300	0.63006200	-0.00056300
H	4.65327300	2.15744800	-0.00041500
H	1.71094600	1.98209700	0.00002800
O	-1.05274300	-1.01490600	0.00044400
O	-2.73213600	2.72015500	-0.00009200
O	-0.39448400	2.55226600	0.00016700
H	-1.46113800	3.07646400	0.00001500
N	1.99372100	1.01000300	0.00011300
N	1.76143000	-1.24620800	0.00035200

TS for BI3HC-A in ACE：

	X	Y	Z
C	5.22290300	-0.98045800	0.00038700
C	4.56093700	0.23773300	0.00034100
C	3.14314100	0.28828100	0.00008500
C	2.42885000	-0.94553200	-0.00009700
C	3.09546400	-2.15780900	-0.00005300
C	4.49761600	-2.17706700	0.00018500
H	6.30610900	-1.00570300	0.00058400
H	5.11035300	1.17093700	0.00049900
C	2.38029400	1.47493400	0.00002900
H	2.52124900	-3.07594100	-0.00020200
H	5.01502500	-3.12864800	0.00022900
C	0.28087300	0.13093000	-0.00025800
C	0.93334300	1.36704800	-0.00014800
C	-3.26362800	0.49551800	-0.00000800
C	-3.07533400	-0.93349700	-0.00012900
C	-4.20464900	-1.78587800	-0.00006700
C	-5.45394900	-1.19907000	0.00011400
C	-5.61363000	0.21328500	0.00024700
C	-4.52414400	1.08172900	0.00019400
C	-1.11196800	-0.05358100	-0.00024800
H	-4.07709500	-2.86130400	-0.00016500
H	-6.34061200	-1.82158700	0.00016300
H	-6.61578700	0.62525300	0.00039800
H	-4.65573200	2.15624100	0.00029900
H	-1.72379000	1.98807800	-0.00004200
O	1.04928700	-1.01101000	-0.00033700
O	2.73836100	2.72126100	0.00014500
O	0.40140900	2.55746300	-0.00012100
H	1.47311700	3.07994400	0.00002500
N	-1.99806700	1.01359000	-0.00011400
N	-1.75936200	-1.24336000	-0.00027600

TS for BI3HC-C in CYC：

	X	Y	Z
C	5.27090300	-0.79370000	0.00007500
C	4.52693000	0.38600700	0.00010100
C	3.11728000	0.35745600	0.00005100
C	2.50438800	-0.91024800	-0.00001400
C	3.22601100	-2.08913200	-0.00003000
C	4.63101700	-2.02981100	0.00000800

H	6.35365800	-0.74452200	0.00010700
H	5.00906300	1.35531600	0.00015400
C	2.33677700	1.59541300	0.00006000
H	2.70026900	-3.03601800	-0.00007600
H	5.20459000	-2.94858100	-0.00001400
C	0.33509700	0.05645000	-0.00002400
C	0.87362000	1.38800400	0.00002900
C	-3.12740100	-0.95051400	-0.00005100
C	-3.16700700	0.47710300	-0.00004600
C	-4.39757200	1.15034300	-0.00003400
C	-5.55092800	0.37641400	-0.00002300
C	-5.49975400	-1.03224900	-0.00002600
C	-4.28617400	-1.72008400	-0.00003800
C	-1.05321400	-0.12995800	-0.00004900
H	-4.43632000	2.23222900	-0.00002900
H	-6.51773500	0.86573500	-0.00001200
H	-6.42592200	-1.59432600	-0.00001500
H	-4.25009800	-2.80237700	-0.00003500
H	-1.40094300	-2.22392200	-0.00004400
O	1.11691900	-1.04467800	-0.00005400
O	2.83486300	2.73272200	0.00010400
O	0.06056800	2.38748100	0.00004800
H	-1.06462400	1.93782300	-0.00000500
N	-1.78816300	-1.29266800	-0.00005500
N	-1.88477700	0.94488100	-0.00005200

TS for BI3HC-C in TOL：

	X	Y	Z
C	5.27081800	-0.79270300	-0.00013300
C	4.52637000	0.38647500	-0.00007300
C	3.11670500	0.35762400	0.00003100
C	2.50391900	-0.91028400	0.00006100
C	3.22633000	-2.08883600	0.00000400
C	4.63091600	-2.02905000	-0.00009200
H	6.35353400	-0.74326900	-0.00021200
H	5.00886600	1.35559700	-0.00010300
C	2.33527800	1.59462600	0.00009500
H	2.70101800	-3.03595600	0.00003300
H	5.20470700	-2.94768800	-0.00013500
C	0.33463400	0.05535400	0.00010700
C	0.87362600	1.38721700	0.00009500
C	-3.12688400	-0.95095100	-0.00001000
C	-3.16616100	0.47733900	-0.00004000

C	-4.39682000	1.15098100	-0.00012600
C	-5.55008100	0.37727500	-0.00018000
C	-5.49912300	-1.03189900	-0.00014800
C	-4.28597200	-1.72018800	-0.00006300
C	-1.05292800	-0.13098700	0.00008000
H	-4.43535100	2.23286500	-0.00015100
H	-6.51689700	0.86656600	-0.00024900
H	-6.42552800	-1.59357900	-0.00019100
H	-4.24987900	-2.80241200	-0.00003800
H	-1.40237400	-2.22545600	0.00010000
O	1.11725000	-1.04531400	0.00014900
O	2.83357200	2.73330500	0.00010700
O	0.06063000	2.38761200	0.00006800
H	-1.06265600	1.93867000	0.00003900
N	-1.78844800	-1.29355400	0.00006800
N	-1.88452600	0.94468000	0.00002700

TS for BI3HC-C in CHL：

	X	Y	Z
C	5.27017900	-0.78992100	0.00015700
C	4.52438500	0.38773900	0.00012600
C	3.11463100	0.35798100	0.00003600
C	2.50199800	-0.91050900	-0.00001600
C	3.22673100	-2.08814700	0.00001400
C	4.63003500	-2.02692700	0.00010000
H	6.35278200	-0.73991300	0.00022800
H	5.00810500	1.35624900	0.00017300
C	2.33034100	1.59182200	0.00000500
H	2.70266400	-3.03592200	-0.00003000
H	5.20441700	-2.94519000	0.00012400
C	0.33308200	0.05217000	-0.00007900
C	0.87380900	1.38489300	-0.00003100
C	-3.12478700	-0.95225600	-0.00005600
C	-3.16337000	0.47831400	-0.00001800
C	-4.39451700	1.15288900	0.00003900
C	-5.54719400	0.37955000	0.00005300
C	-5.49652700	-1.03138900	0.00001200
C	-4.28470600	-1.72082600	-0.00004200
C	-1.05198500	-0.13368800	-0.00008700
H	-4.43275100	2.23474700	0.00007000
H	-6.51423500	0.86834600	0.00009600
H	-6.42357800	-1.59197000	0.00002400
H	-4.24813400	-2.80282400	-0.00007100

H	-1.40593700	-2.22955000	-0.00012600
O	1.11794000	-1.04707800	-0.00010300
O	2.82991800	2.73512500	0.00002400
O	0.06080100	2.38852600	-0.00001100
H	-1.05620400	1.94195600	-0.00002300
N	-1.78899600	-1.29584300	-0.00010100
N	-1.88372400	0.94460200	-0.00004600

TS for BI3HC-C in ACE：

	X	Y	Z
C	5.26867800	-0.78794500	0.00040300
C	4.52185700	0.38847300	0.00025300
C	3.11191400	0.35801700	-0.00001200
C	2.49897000	-0.91095900	-0.00011100
C	3.22575700	-2.08793500	0.00003100
C	4.62777100	-2.02542500	0.00029200
H	6.35119100	-0.73792300	0.00061200
H	5.00712400	1.35627800	0.00034600
C	2.32479300	1.58831000	-0.00011900
H	2.70269600	-3.03619600	-0.00005100
H	5.20249300	-2.94345200	0.00041000
C	0.33126400	0.04939900	-0.00027700
C	0.87447300	1.38278800	-0.00017700
C	-3.12159400	-0.95352600	-0.00008600
C	-3.16018100	0.47979200	0.00003000
C	-4.39219800	1.15471800	0.00026800
C	-5.54368000	0.38110900	0.00036900
C	-5.49254400	-1.03203100	0.00024000
C	-4.28213700	-1.72216100	0.00001500
C	-1.05095200	-0.13538000	-0.00026500
H	-4.43084400	2.23652600	0.00036400
H	-6.51133500	0.86861600	0.00054900
H	-6.42013000	-1.59169600	0.00032500
H	-4.24436600	-2.80395400	-0.00007200
H	-1.40764900	-2.23228800	-0.00035300
O	1.11791800	-1.04837900	-0.00035900
O	2.82718700	2.73718900	-0.00009300
O	0.06097400	2.39051800	-0.00010500
H	-1.04859900	1.94677600	-0.00007500
N	-1.78886100	-1.29721100	-0.00027300
N	-1.88290300	0.94567000	-0.00011700