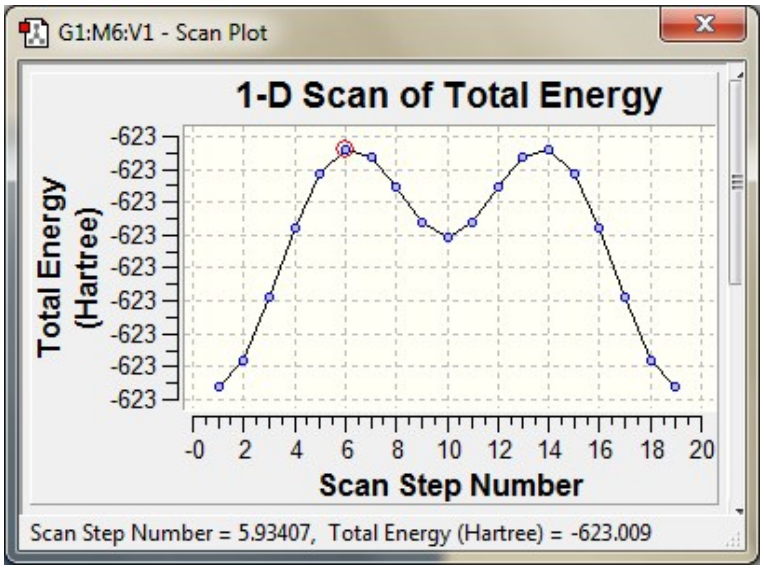
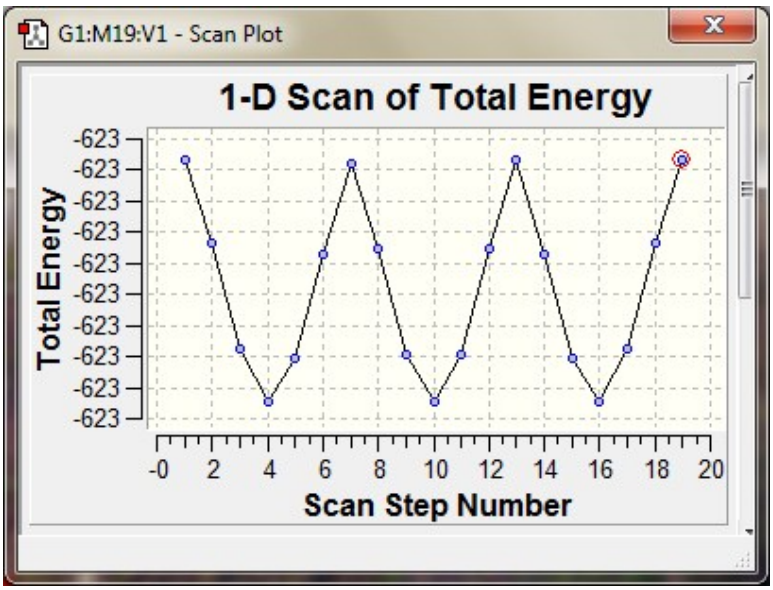
Electronic Supplementary Material (ESI) for RSC Advances.

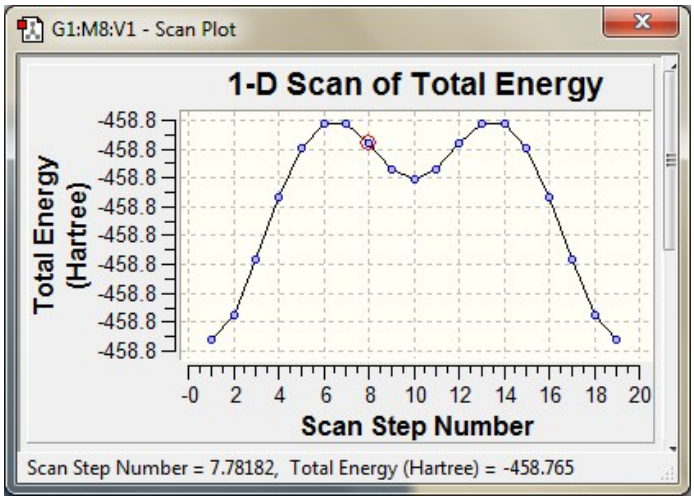


(a)

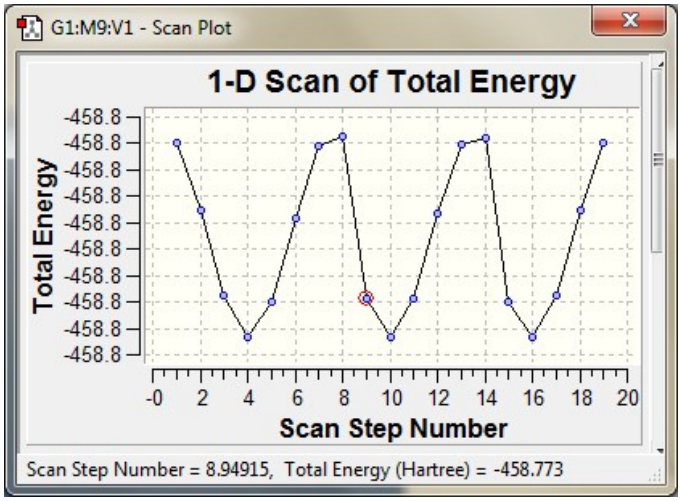


(b)

Fig S1 Potential energy surface of 2-methoxy-5-nitrophenol for the rotations (a) T(C2-C1-O10-H11) (b) T(C1-012-C13-H14)



(a)



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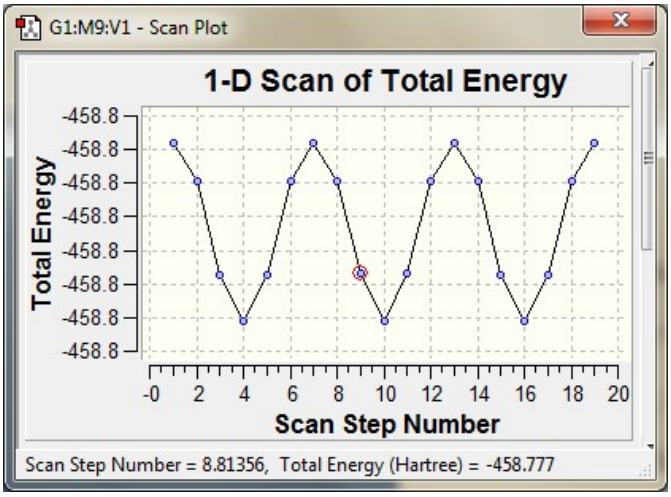

(c)

Fig. S2: Potential energy surface of 2-methoxy-4-methylphenol for the rotations T(C2-C1-O10-H11) (b) T(C1-012-C13-H14) (c) T(C3-C4-C17-H19)

Table S1: Optimized parameters of 2-methoxy-5-nitrophenol by HF and B3LYP method using 6-31G(d,p) basis set

Bond length (Å)	Values		Exp. value[a]	Bond angles (°)	Values		Exp. value[a]	Dihedral angles (°)	Values		Exp. value[a]
	HF	B3LYP			HF	B3LYP			HF	B3LYP	
	6-31G(d,p)	6-311G(d,p)			6-31G(d,p)	6-311G(d,p)			6-31G(d,p)	6-311G(d,p)	
C1-C2	1.4152	1.3963	1.411	C2-C1-C6	119.3388	120.1954	-	C6-C1-C2-C3	0.0051	-0.0003	-
C1-C6	1.3822	1.3726	1.406	C2-C1-O10	119.1637	120.483	-	C6-C1-C2-O12	180.0029	-180.0	-
C1-O10	1.3752	1.3652	1.359	C6-C1-O10	121.4975	119.3216	-	O10-C1-C2-C3	180.0026	179.9999	-
C2-C3	1.3889	1.3828	1.402	C1-C2-C3	120.8663	120.5607	-	O10-C1-C2-O12	0.0004	0.0001	-
C2-O12	1.3872	1.3666	-	C 1-C2-O12	112.357	114.0585	-	C2-C1-C6-C5	-0.0061	0.0001	-
C3-C4	1.3955	1.3876	1.384	C3-C2-O12	126.7767	125.3808	-	C2-C1-C6-H9	179.9946	-179.9999	-
C3-H7	1.0812	1.0699	1.080	C2-C3-C4	119.6101	119.7001	-	O10-C1-C6-C5	179.9965	-180.0	-
C4-C5	1.3877	1.38	1.387	C2-C3-H7	120.8147	120.8311	-	O10-C1-C6-H9	-0.0028	0.0	-
C4-H8	1.0788	1.0686	1.080	C 4-C3-H7	119.5752	119.4688	-	C2-C1-O10-H11	-0.0079	-0.0006	-
C 5-C6	1.3945	1.3893	1.383	C3-C4-C5	118.9771	118.8292	-	C6-C1-O10-H11	-180.0105	-180.0004	-
C5-N17	1.4578	1.4442	1.464	C3-C4-H8	122.2656	121.0098	-	C1-C2-C3-C4	-0.0006	0.0003	-
C6-H9	1.078	1.0682	1.080	C5-C4-H8	118.7572	120.161	-	C1-C2-C3-H7	-180.0007	-179.9997	-
O10-H11	0.9987	0.9526	0.969	C4-C5-C6	122.1024	122.1988	-	O12-C2-C3-C4	-179.998	180.0	-
O12-C13	1.4624	1.4353	-	C4-C5-N17	119.1316	119.0316	-	O12-C2-C3-H7	0.0019	0.0	-
C13-H14	1.0954	1.081	-	C6-C5-N17	118.766	118.7696	-	C1-C2-O12-C13	-180.0357	-179.997	-
C13-H15	1.0896	1.0754	-	C1-C6-C5	119.1052	118.5158	-	C3-C2-O12-C13	-0.0381	0.0033	-
C13-H16	1.0954	1.081	-	C1-C6-H9	120.9823	120.0145	-	C2-C3-C4-C5	-0.0029	-0.0001	-
N17-O18	1.286	1.2277	1.241	C5-C6-H9	119.9124	121.4697	-	C2-C3-C4-H8	179.9999	180.0	-

N17-O19	1.2849	1.226	1.225	C1-O10-H11	106.5788	112.9224	-	H7-C3-C4-C5	179.9973	-180.0001	-
				C2-O12-C13	118.5404	122.073	-	H7-C3-C4-H8	0.0	-0.0001	-
				O12-C13-H14	110.9344	110.5495	-	C3-C4-C5-C6	0.0018	-0.0001	-
				O12-C13-H15	105.2106	105.4803	-	C3-C4-C5-N17	-179.9968	180.0	-
				O12-C13-H16	110.9404	110.5494	-	H8-C4-C5-C6	179.9992	-180.0001	-
				H14-C13-H15	109.980	109.9442	-	H8-C4-C5-N17	0.0006	-0.0001	-
				H14-C13-H16	109.707	110.2727	-	C4-C5-C6-C1	0.0027	0.0001	-
				H15-H13-H16	109.987	109.9441	-	C4-C5-C6-H9	-179.998	180.0001	-
				C5-N17-H18	117.2745	118.2688	-	N17-C5-C6-C1	-179.9987	180.0	-
				C5-N17-H19	117.3286	118.3387	-	N17-C5-C6-H9	0.0006	0.0	-
				H18-N17-H19	125.396	123.3925	-	C4-C5-N17-H18	0.0011	-0.0005	-
								C4-C5-N17-H19	180.0011	179.9995	-
								C6-C5-N17-H18	-179.9975	179.9995	-
								C6-C5-N17-H19	0.0024	-0.0005	-
								C2-O12-C13-H14	61.070	61.1915	-
								C2-O12-C13-H15	179.962	179.9957	-
								C2-O12-C13-H16	-61.135	-61.2002	-

[a]Refer the ref of [11]

Table S2: Optimized parameters of 2-methoxy-4-methylphenol by HF and B3LYP method using 6-31G(d,p) basis set.

Bond length (Å)	Values		Exp. value[a]	Bond angles (°)	Values		Exp. value[a]	Dihedral angles (°)	Values	
	HF	B3LYP			HF	B3LYP			HF	B3LYP
	6-31G(d,p)	6-311G(d,p)			6-31G(d,p)	6-311G(d,p)			6-31G(d,p)	6-311G(d,p)
C1-C2	1.4098	1.3927	1.384	C2-C1-C6	118.9903	119.6045	121.8	C6-C1-C2-C3	0.0001	0.0
C1-C6	1.3859	1.3744	1.396	C2-C1-O10	119.1861	120.4141	116.6	C6-C1-C2-O12	180.0002	-180.0
C1-O10	1.3825	1.3717	1.369	C6-C1-O10	121.8236	119.9814	123.7	O10-C1-C2-C3	-180.0001	180.0
C2-C3	1.3841	1.3785	1.395	C1-C2-C3	120.9077	120.516	119.2	O10-C1-C2-O12	0.0	0.0
C2-O12	1.3997	1.3804	-	C1-C2-O12	112.3003	114.0995	-	C2-C1-C6-C5	-0.0001	0.0
C3-C4	1.4085	1.3989	1.384	C3-C2-O12	126.792	125.3845	-	C2-C1-C6-H9	-180.0002	180.0
C3-H7	1.0833	1.0725	-	C2-C3-C4	120.2356	120.3792	119.7	O10-C1-C6-C5	180.0001	-180.0
C4-C5	1.3953	1.3856	1.387	C2-C3-H7	120.4847	120.2756	-	O10-C1-C6-H9	0.0	0.0
C4-C17	1.5188	1.5102	1.508	C4-C3-H7	119.2797	119.3452	-	C2-C1-O10-H11	-0.0002	0.0
C5-C6	1.4004	1.3925	1.383	C3-C4-C5	118.6028	118.5043	120.1	C6-C1-O10-H11	-180.000	180.0
C5-H8	1.0841	1.073	-	C3-C4-C17	119.8975	119.9598	120.5	C1-C2-C3-C4	0.0	0.0
C6-H9	1.0819	1.0711	-	C5-C4-C17	121.4997	121.5359	121.8	C1-C2-C3-H7	180.0	-180.0
O10-H11	0.9987	0.9524	0.969	C4-C5-C6	121.069	121.0546	121.4	O12-C2-C3-C4	-180.0001	180.0
O12-C13	1.4562	1.4287	-	C4-C5-H8	119.569	119.7716	-	O12-C2-C3-H7	-0.0001	0.0001
C13-H14	1.0965	1.0819	-	C6-C5-H8	119.3621	119.1738	-	C1-C2-O12-C13	-180.000	-180.0
C13-H15	1.0904	1.0763	-	C1-C6-C5	120.1947	119.9415	117.7	C3-C2-O12-C13	-0.0002	-0.0001
C13-H16	1.0965	1.0819	-	C1-C6-H9	118.4515	118.6452	-	C2-C3-C4-C5	-0.0001	0.0
C17-H18	1.0971	1.0852	1.090[b]	C5-C6-H9	121.3539	121.4133	-	C2-C3-C4-C17	-180.001	179.9999
C17-H19	1.0971	1.0852	1.090_b	C1-O10-H11	105.8897	112.2173	-	H7-C3-C4-C5	-180.0001	179.9999

C17-H20	1.0942	1.0824	1.090[b]	C2-O12-C13	118.0552	121.4883	-	H7-C3-C4-C17	-0.001	-0.0001
				O12-C13-H14	111.2683	110.8104	-	C3-C4-C5-C6	0.0002	0.0
				O12-C13-H15	105.4192	105.7673	-	C3-C4-C5-H8	180.0002	-180.0
				O12-C13-H16	111.2684	110.8104	-	C17-C4-C5-C6	180.0011	-179.9999
				H14-C13-H15	109.7758	109.7532	-	C17-C4-C5-C8	0.0011	0.0001
				H14-C13-H16	109.2693	109.8681	-	C3-C4-C17-H18	-60.0466	-59.9985
				H15-C13-H16	109.7759	109.7533	-	C3-C4-C17-H19	60.0189	59.9956
				C4-C17-H18	111.0782	111.3565	-	C3-C4-C17-H20	-180.013	179.9986
				C4-C17-H19	111.0783	111.3566	-	C5-C4-C17-H18	119.9525	120.0015
				C4-C17-H20	110.6541	111.0716	-	C5-C4-C17-H19	-119.982	-120.0044
				H18-C17-H19	107.8693	107.5172	-	C5-C4-C17-H20	-0.0146	-0.0014
				H18-C17-H20	108.0152	107.676	-	C4-C5-C6-C1	-0.0001	0.0
				H19-C17-H20	108.0155	107.6761	-	C4-C5-C6-H9	180.0001	-180.0
								H8-C5-C6-C1	-180.0001	180.0
								H8-C5-C6-H9	0.0	0.0
								C2-O12-C13-H14	61.0553	61.1179
								C2-O12-C13-H15	-179.998	180.0
								C2-O12-C13-H16	-61.053	-61.1179

[a] Ref reference[11]
[b] Ref reference[12]

Table S3: Second order perturbation theory analysis of Fock matrix in NBO basis for 2-methoxy-5-nitrophenol by B3LYP method using 6-31G(d,p) basis set.

Donor(i)	Type	Acceptor(j)	Type	$E^{(2)}$ (kJ mol^{-1})	$\varepsilon_j - \varepsilon_i$[a] (a.u.)	F(i,j)[b] (a.u)
C1 - C2	σ	C1 - C6	σ *	16.98704	1.33	0.066
		C2 - C3	σ *	18.15856	1.30	0.067
	π	C3 - C4	π *	80.3328	0.29	0.068
		C5 - C6	π *	90.45808	0.29	0.071
C1 - C6	σ	C1 - C2	σ *	16.86152	1.26	0.064
		C5 - C6	σ *	13.8072	1.31	0.059
		C5 - N17	σ *	15.4808	1.03	0.056
C3 - C4	σ	C2 - C3	σ *	15.02056	1.28	0.060
		C2 – O12	σ *	19.91584	0.99	0.061
		C4 - C5	σ *	13.72352	1.29	0.058
		C5 - N17	σ *	17.69832	1.00	0.059
	π	C1 - C2	π *	93.97264	0.25	0.070
C5 - C6	π	C1 - C2	π *	41.67264	0.26	0.067
		N17 - O19	π *	27.196	0.13	0.057
N17 - O19	Π	N17 - O19	π *	39.62248	0.27	0.055
LP(1)O10	n_1	C1 - C2	σ *	20.58528	1.11	0.066
LP(2)O10	n_2	C1 - C2	π *	142.507	0.28	0.095
LP(1)O12	n_1	C2 - C3	σ *	25.2713	1.15	0.075
		O10 - H11	σ *	26.5684	0.89	0.068
LP(2)O12	n_2	C1 - C2	π *	111.6291	0.31	0.088
		C13 - H14	σ *	19.7903	0.72	0.054
		C13 - H16	σ *	19.8321	0.72	0.054
LP(2)O18	n_2	N17 - O19	σ *	83.1360	0.57	0.096
LP(3)O18	n_3	N17 - O19	π *	755.0446	0.10	0.124

$E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).
[a] Energy difference between donor and acceptor i and j NBO orbitals.
[b] F (i, j) is the Fock matrix element between i and j NBO orbitals.

Table S4: Second order perturbation theory analysis of Fock matrix in NBO basis for 2-methoxy-4-methylphenol by B3LYP method using 6-31G(d,p) basis set.

Donor(i)	Type	Acceptor(j)	Type	$E^{(2)}$ ($kJmol^{-1}$)	$\varepsilon_j - \varepsilon_i$[a] (a.u.)	F(i,j)[b] (a.u)
C1 - C6	Π	C 2 - C3	π*	88.1150	0.27	0.069
		C4 - C5	π*	75.5630	0.29	0.065
C2 - C3		C1 - C6	π*	79.0776	0.28	0.067
		C4 - C5	π*	80.0399	0.30	0.068
C4 - C5		C1 - C6	π*	89.5376	0.26	0.068
		C2 - C3	π*	84.3494	0.25	0.065
C3 - C4	σ	C2 - C3	σ*	14.4348	1.26	0.059
		C2 - O12	σ*	14.8950	0.96	0.052
		C3 - H7	σ*	8.1588	1.19	0.043
		C4 - C5	σ*	15.0205	1.28	0.061
LP(2)O10	n_2	C1 - C6	π*	86.0648	0.32	0.078
LP(2)O12		C2 - C3	π*	85.2280	0.31	0.077
		C13 - H14	σ*	18.9535	0.75	0.054
		C13 - H16	σ*	24.4345	0.75	0.061
LP(1)O10	n_1	C1 - C2	σ*	18.4096	1.13	0.063
LP(1)O12		C2 - C3	σ*	16.5268	1.14	0.060

$E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).

[a] Energy difference between donor and acceptor i and j NBO orbitals.

[b] F (i, j) is the Fock matrix element between i and j NBO orbitals.

Table S5: Calculated chemical shifts of carbon atoms of 2-methoxy-5-nitrophenol and 2-methoxy-4-methylphenol using B3LYP/6-31G(d,p) method and basis set.

Atoms	Chemical shifts of 2-methoxy-5-nitrophenol (ppm)			Chemical shifts of 2-methoxy-4-methylphenol (ppm)			Experimental chemical shifts [a] (ppm)	
	In gas phase	In DMSO	$CDCl_3$	In gas phase	In DMSO	$CDCl_3$	2-methoxy phenol	4-nitrophenol
C1	113.4941	113.4	112.4206	112.1776	111.4501	111.5099	148.523	176.12
C2	117.4975	120.2722	119.5185	112.4858	112.9394	112.8489	150.60	117.56
C3	76.1632	78.1177	77.5124	77.4659	78.5899	78.2154	115.17	126.5
C4	82.4601	83.819	83.4055	93.2688	94.757	94.317	111 .65	132.46
C5	112.5195	113.4216	113.189	89.2535	88.5542	88.7023	120.74	126.50
C6	77.5025	75.9572	76.4644	80.483	79.3891	79.6929	116.19	117.56
C13	32.3098	33.0565	32.8594	31.012	31.3778	31.2735	-	-
C17	-	-	-	1.9936	1.5234	1.6697	-	-

[a] Refer the reference [25]

Table S6: Calculated chemical shifts of hydrogen atoms of 2-methoxy-5-nitrophenol and 2-methoxy-4-methylphenol using B3LYP/6-31G(d,p) method and basis set.

Atoms	Chemical shifts of 2-methoxy-5-nitrophenol (ppm)			Chemical shifts of 2-methoxy-4-methylphenol (ppm)			Experimental chemical shifts [b] (ppm)			
							2-methoxy phenol		2-methylphenol	
	In gas phase	In DMSO	In $CDCl_3$	In gas phase	In DMSO	In $CDCl_3$	In DMSO	In $CDCl_3$	In DMSO	In $CDCl_3$
H7	5.0212	5.5868	5.4115	4.7539	5.1827	5.0343	6.75	6.850	7.032	7.114
H8	6.5672	6.8101	6.7302	5.335	5.6138	5.5183	6.75	6.850	6.669	6.842
H9	6.4004	6.388	6.3917	5.1463	5.313	5.2594	6.9	6.911	6.753	6.761
H11	5.0218	5.9532	5.6633	4.6935	5.4165	5.1824	8.823	5.59	9.153	4.604
H14	2.8797	3.1075	3.0455	2.7142	2.8834	2.8345	3.750	3.886	-	-
H15	3.3776	3.6332	3.5721	3.1288	3.3535	3.2938			-	-
H16	2.8772	3.1049	3.043	2.7142	2.884	2.835			-	-
H18	-	-	-	1.4026	1.4877	1.4595	-	-	2.250	2.092
H19	-	-	-	1.4024	1.4816	1.4593	-	-		
H20	-	-	-	0.7674	0.8563	0.8279	-	-		

[b] Refer the reference [26]

Table S7: Excitation energy (in eV), Wavelength (nm), Oscillator strength (f) and main configuration of 2-methoxy-5-nitrophenol (MNP) and 2-methoxy-4-methylphenol (MMP) calculated at PCM-TD-B3LYP/6-31G(d,p) method and basis set.

Compounds		PCM-TD-B3LYP/6-31G(d,p)									Assign.
		Cyclohexane(CHX)			Tetrahydrofuran(THF)			Acetonitrile(ACN)			
		Excitation energy/ Wave length	Oscillator strength	Main Contribution	Excitation energy/ Wave length	Oscillator strength	Main Contribution	Excitation energy	Oscillator strength	Main Contribution	
MNP	1	3.1024 / 399.64	0.1038	H →L (94.64%)	2.9879/ 414.96	0.1063	H →L (93.54%)	2.9518 / 420.04	0.1042	H →L (92.22%)	π→π*
MMP	1	4.6117/ 268.85	0.1038	H →L (85.14%)	4.9859 / 248.67	0.0807	H →L (79.47%)	4.6263/ 268	0.0970	H →L (84.97%)	π→π*
	2	5.5197 / 224.62	0.0962	H →L+1 (74.11%)	5.7422 / 215.92	0.1402	H →L+1 (80.67%)	5.5430/ 223.68	0.0852	H →L+1 (72.42%)	π→π*