Electronic Supplementary Material (ESI) for Dalton Transactions.

Theoretical study on the electronic structures and photophysical properties of phosphorescent iridium(III) complexes with -CH_3/H and tBu substituents

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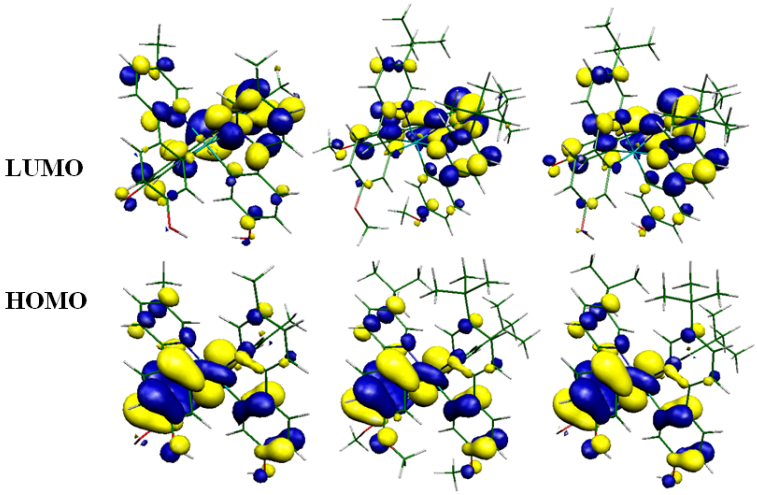

Fig. S1 Orbital composition distribution of HOMO and LUMO for complexes **3**, **5** and **6**.

Table S1 Main optimized bond lengths of the complex **1** at the PBE0, B3LYP，Cam-B3LYP，M062X and M052X level, respectively, together with the experimental values.

Item	PBE0	B3LYP	Cam-b3LYP	M062X	M052X	Exp.[19]
Bond length/Å						
Ir-N1	2.152	2.190	2.171	2.199	2.177	2.135
Ir-C1	2.012	2.026	2.022	1.997	2.006	2.021
Ir-N2	2.150	2.189	2.169	2.192	2.178	2.139
Ir-C2	2.007	2.025	2.019	1.997	2.002	2.003
Ir-N3	2.149	2.191	2.169	2.201	2.182	2.126
Ir-C3	2.007	2.028	2.018	1.996	2.001	2.004

Table S2 Calculated wavelength (nm)/energies (eV), largest oscillator strength (*f*) and dominant orbital excitations of the singlet vertical absorptions for **1**-**6**

	State	λ_{cal}	*f*	Configuration	Character	Exp.[19]
1	S_{25}	287	0.3163	H-2->L+5 (46%)	MLCT/LLCT/ILCT	291
				H-5->LUMO (28%)	ILCT/LLCT	
2	S_{28}	286	0.2237	H-5->L+2 (42%)	MLCT/LLCT/ILCT	
				H-2->L+5 (19%)	MLCT/LLCT	
3	S_{27}	285	0.2877	H-5->LUMO (30%)	MLCT/LLCT/ILCT	
				H-5->L+2 (24%)	LLCT/ILCT	
				H-2->L+5 (17%)	MLCT/LLCT/ILCT	
4	S_{23}	293	0.3023	H-4->L+1 (39%)	MLCT/LLCT/ILCT	
				H-2->L+5 (21%)	LLCT/ILCT	
5	S_{25}	287	0.2415	H-5->LUMO (67%)	MLCT/LLCT/ILCT	
6	S_{27}	286	0.2840	H-5->LUMO (63%)	MLCT/LLCT/ILCT	
				H-5->L+1 (12%)	MLCT/ILCT/LLCT	

Table S3 Molecular orbital composition (%) of **1** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.43	2	3	50	45	π*(L1+L2)
L+4	-0.48	2	51	23	25	π*(L3+L2+L1)
L+3	-0.74	2	44	25	28	π*(L3+L2+L1)
L+2	-0.99	5	11	51	34	π*(L2+L1+L3)
L+1	-1.03	4	24	35	37	π*(L1+L2+L3)
LUMO	-1.13	2	62	11	25	π*(L3+L1+L2)
HOMO	-5.17	38	12	30	20	d(Ir)+π(L2+L1+L3)
H-1	-5.31	26	5	33	36	d(Ir)+π(L1+L2)
H-2	-5.37	39	41	7	13	d(Ir)+π(L3+L1)
H-3	-5.64	17	5	19	60	d(Ir)+π(L1+L2)
H-4	-5.72	16	18	59	7	d(Ir)+π(L2+L3)
H-5	-5.83	1	76	3	19	π(L3+L1)

Table S4 Molecular orbital composition (%) of **2** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.19	2	2	31	65	π*(L1+L2)
L+4	-0.24	2	47	40	11	π*(L3+L2)
L+3	-0.5	3	49	27	22	π*(L3+L2+L1)
L+2	-0.73	5	1	19	76	π*(L1+L2)
L+1	-0.77	4	25	60	11	π*(L2+L3)
LUMO	-0.86	2	71	18	9	π*(L3+L2)
HOMO	-4.89	35	7	20	37	d(Ir)+π(L1+L2)
H-1	-5.03	25	4	41	30	d(Ir)+π(L2+L1)
H-2	-5.13	34	49	9	8	d(Ir)+π(L3)
H-3	-5.48	15	62	19	4	d(Ir)+π(L3+L2)
H-4	-5.51	22	6	18	54	d(Ir)+π(L1+L2)
H-5	-5.68	18	21	42	19	d(Ir)+π(L2+L3+L1)

Table S5 Molecular orbital composition (%) of **3** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.25	2	66	3	30	π*(L3+L1)
L+4	-0.29	2	8	51	39	π*(L2+L1)
L+3	-0.55	3	24	44	30	π*(L2+L1+L3)
L+2	-0.79	5	77	2	17	π*(L3+L1)
L+1	-0.82	4	8	29	58	π*(L1+L2)
LUMO	-0.9	2	12	65	21	π*(L2+L1+L3)
HOMO	-4.98	36	35	10	19	d(Ir)+π(L3+L1)
H-1	-5.13	26	32	5	37	d(Ir)+π(L1+L3)
H-2	-5.19	31	8	48	13	d(Ir)+π(L2+L1)
H-3	-5.57	21	57	13	10	d(Ir)+ π(L3+L2)
H-4	-5.59	19	4	42	35	d(Ir)+ π(L2+L1)
H-5	-5.75	18	17	30	35	d(Ir)+π(L1+L2+L3)

Table S6 Molecular orbital composition (%) of **4** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.51	2	1	55	43	π*(L2+L1)
L+4	-0.56	2	54	17	28	π*(L3+L1+L2)
L+3	-0.81	2	44	26	28	π*(L3+L1+L2)
L+2	-0.91	4	1	53	42	π*(L2+L1)
L+1	-0.96	4	29	30	37	π*(L1+L2+L3)
LUMO	-1.06	2	67	14	17	π*(L3+L1+L2)
HOMO	-5.16	38	9	31	22	d(Ir)+π(L2+L1)
H-1	-5.27	26	4	30	40	d(Ir)+π(L1+L2)
H-2	-5.34	38	42	8	12	d(Ir)+π(L3+L1)
H-3	-5.61	16	4	7	73	d(Ir)+π(L1)
H-4	-5.71	16	5	72	6	d(Ir)+π(L2)
H-5	-5.84	1	96	2	1	π(L3)

Table S7 Molecular orbital composition (%) of **5** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.28	1	65	2	32	π*(L3+L1)
L+4	-0.33	1	11	48	39	π*(L2+L1)
L+3	-0.59	2	23	48	27	π*(L2+L1+L3)
L+2	-0.66	5	71	1	23	π*(L3+L1)
L+1	-0.7	4	14	28	54	π*(L1+L2+L3)
LUMO	-0.8	2	11	68	19	π*(L2+L1)
HOMO	-4.89	34	40	6	20	d(Ir)+π(L3+L1)
H-1	-5	25	28	4	42	d(Ir)+π(L1+L3)
H-2	-5.11	34	7	51	8	d(Ir)+π(L2)
H-3	-5.47	14	4	64	18	d(Ir)+π(L2+L3)
H-4	-5.5	22	54	5	19	d(Ir)+π(L3+L1)
H-5	-5.66	19	19	20	42	d(Ir)+π(L1+L2+L3)

Table S8 Molecular orbital composition (%) of **6** in the ground state

MO	Energy(ev)	Composition (100%)				Assign
		Ir	L3	L2	L1	
L+5	-0.33	1	64	2	32	π*(L3+L1)
L+4	-0.38	1	9	53	36	π*(L2+L1)
L+3	-0.64	2	25	43	30	π*(L2+L1+L3)
L+2	-0.71	4	74	2	19	π*(L3+L1)
L+1	-0.75	4	9	33	54	π*(L1+L2)
LUMO	-0.83	2	13	62	23	π*(L2+L1+L3)
HOMO	-4.98	35	37	9	19	d(Ir)+π(L3+L1)
H-1	-5.1	26	30	5	39	d(Ir)+π(L1+L3)
H-2	-5.17	31	7	50	12	π(L2+L1)
H-3	-5.56	20	58	12	10	d(Ir)+π(L3+L2)
H-4	-5.58	18	3	43	35	d(Ir)+π(L2+L1)
H-5	-5.73	19	17	30	35	d(Ir)+π(L1+L2+L3)

Table S9 Cartesian coordinates for the optimized structures of **1** in the ground state

C	3.22557400	-1.51902400	-2.25218700	H	1.87034800	2.52747200	4.30823400
H	3.40824300	-2.21067600	-1.43420000	C	-3.11672400	0.02146900	3.55234400
C	3.78657400	-1.73364700	-3.50430800	C	-3.49944100	0.82257800	2.47628800
C	3.48550200	-0.78695800	-4.49129000	H	-2.81691100	1.56552500	2.07644200
H	3.89552000	-0.89832700	-5.49281500	C	-4.76724800	0.66157800	1.92504400
C	2.66104300	0.28392500	-4.20010700	H	-5.05968600	1.29224100	1.08999600
H	2.42235100	1.00940600	-4.96998300	C	-5.65365100	-0.28236800	2.44057500
C	2.12496600	0.43171100	-2.91326600	H	-6.64308900	-0.39559800	2.00653100
C	4.65897200	-2.92369800	-3.77609800	C	-5.25990700	-1.07613800	3.51635800
H	4.78187800	-3.53894400	-2.87957500	H	-5.94153300	-1.81519400	3.92995700
H	5.65702000	-2.62054400	-4.11444600	C	-3.99355400	-0.93005900	4.07219900
H	4.23008700	-3.55977200	-4.55946100	H	-3.66817900	-1.53494900	4.91307500
C	1.22172000	1.49241800	-2.47799300	C	3.41035200	-1.96170700	1.62501100
C	0.79064400	1.42523600	-1.12332900	H	4.01585600	-1.05990000	1.65615700
C	-0.12420600	2.40171300	-0.70522900	C	3.82153400	-3.11743400	2.27530800
H	-0.49821300	2.40080700	0.31439800	C	2.96315100	-4.22047600	2.18333400
C	-0.58521700	3.37770500	-1.58008600	H	3.22696000	-5.15494700	2.67409000
C	-0.14201600	3.44721200	-2.90057400	C	1.77837200	-4.12450400	1.47821300
H	-0.51659100	4.22934900	-3.55294500	H	1.11247500	-4.97831500	1.41776900
C	0.76631000	2.49864700	-3.34121800	C	1.42885000	-2.92294800	0.84448500
H	1.10608700	2.54213900	-4.37319400	C	5.11015500	-3.16669900	3.04235000
C	-2.79810300	4.02471100	-1.05264000	H	5.66169000	-2.22579500	2.95253400
C	-3.34474700	2.83394900	-1.53208000	H	5.76071200	-3.97269000	2.68256200
H	-2.70815100	2.08250300	-1.98684700	H	4.93140300	-3.34598300	4.10936300
C	-4.71824800	2.62234500	-1.42475800	C	0.21678900	-2.68283300	0.07273600
H	-5.13656100	1.69257000	-1.80250500	C	0.06359400	-1.37108100	-0.45736900
C	-5.54653800	3.57967000	-0.84528000	C	-1.09821600	-1.12075900	-1.19673000
H	-6.61619200	3.40701300	-0.76802700	H	-1.27939600	-0.14016400	-1.62538700
C	-4.98641600	4.76459100	-0.36722800	C	-2.05841400	-2.10600000	-1.39811400
H	-5.61893900	5.52123100	0.08974400	C	-1.90059100	-3.39299000	-0.87251000
C	-3.62010600	4.99106500	-0.46796800	H	-2.65380500	-4.15467100	-1.04519300
H	-3.16706100	5.90726800	-0.10156100	C	-0.75874000	-3.66725200	-0.13982200
C	4.23558800	1.51523000	-0.03153000	H	-0.63332100	-4.66907400	0.26436700
H	4.34666100	1.01938000	-0.99195600	C	-4.37117800	-2.27427700	-1.92174200
C	5.20581600	2.39472700	0.42948300	C	-5.15599200	-2.65369800	-3.00885000
C	4.96473400	2.98837700	1.67502800	H	-4.73324600	-2.58993000	-4.00690600
H	5.68501700	3.69053200	2.08956400	C	-6.45661100	-3.09969200	-2.79494800
C	3.81123300	2.69192100	2.37576300	H	-7.06678200	-3.39469400	-3.64462500
H	3.62367000	3.16219100	3.33473300	C	-6.97225600	-3.17495700	-1.50302400
C	2.87460000	1.79190200	1.84629800	H	-7.98621700	-3.52817900	-1.33791300
C	6.43519000	2.69577200	-0.37627900	C	-6.17873100	-2.78836600	-0.42457000
H	6.45988300	2.10701300	-1.29844700	H	-6.57195300	-2.82963100	0.58778600
H	7.34896400	2.47399000	0.18780500	C	-4.87956800	-2.33194200	-0.62373600
H	6.47664600	3.75493100	-0.65742100	H	-4.26938000	-2.01094900	0.21480300
C	1.61969300	1.39791100	2.47305600	Ir	1.54852500	-0.08612300	-0.04115200
C	0.79372200	0.51207500	1.72521200	N	2.43555300	-0.47876600	-1.95860600
C	-0.42061800	0.12754700	2.30991300	N	3.11812600	1.21682000	0.64318000

H	-1.08474600	-0.54973300	1.78156700	N	2.26896100	-1.86202600	0.93246200
C	-0.79137200	0.59164200	3.57029600	O	-1.46998400	4.34008100	-1.13336400
C	0.03093500	1.45571200	4.29718100	O	-1.92749900	0.17027400	4.21519100
H	-0.28810200	1.79281500	5.27795400	O	-3.12494900	-1.77315300	-2.19736100
C	1.23298800	1.85315500	3.74133800	H	1.87034800	2.52747200	4.30823400

Table S10 Cartesian coordinates for the optimized structures of **2** in the ground state

C	-1.87333800	-2.35392300	1.35406300	H	-0.51936700	4.04224600	-3.01574400
H	-1.96848100	-2.67890400	0.32127400	C	-1.83364200	-1.26854100	-2.41338700
C	-2.43871700	-3.09233100	2.38450000	H	-2.50416200	-0.44716900	-2.17595500
C	-2.25132000	-2.59390700	3.68067800	C	-2.10882900	-2.13000700	-3.46697100
H	-2.66839600	-3.12817500	4.53192900	C	-1.17736000	-3.15153400	-3.69347000
C	-1.53235800	-1.43203700	3.88321200	H	-1.33603800	-3.85938300	-4.50442100
H	-1.38128700	-1.05558800	4.88902400	C	-0.05417700	-3.25875200	-2.89579300
C	-0.98709800	-0.73759300	2.79142000	H	0.66821300	-4.04643500	-3.08070300
C	-3.19889100	-4.35776100	2.11516100	C	0.16008900	-2.34791900	-1.85011900
H	-3.24348300	-4.57302300	1.04299300	C	-3.33358700	-1.95964900	-4.31684200
H	-4.22889100	-4.29519500	2.48682200	H	-3.95564300	-1.13499700	-3.95541000
H	-2.72888400	-5.21794300	2.60699700	H	-3.94932800	-2.86708400	-4.32123700
C	-0.20462300	0.48482900	2.86207100	H	-3.06835800	-1.74279000	-5.35868800
C	0.27709800	0.99383700	1.62641500	C	1.30202700	-2.33588500	-0.94727600
C	1.04761400	2.16531500	1.66881500	C	1.32406200	-1.29477700	0.02856000
H	1.42773300	2.56907900	0.73717500	C	2.42496100	-1.25766100	0.88577700
C	1.33026700	2.80583800	2.87521000	H	2.50525900	-0.48738200	1.64750000
C	0.84456400	2.29028900	4.08772800	C	3.46105100	-2.19278600	0.80059100
H	1.07945800	2.80975500	5.01130200	C	3.42485500	-3.21152900	-0.16090200
C	0.08493600	1.13956800	4.07119700	H	4.21761000	-3.94701100	-0.23919000
H	-0.28417000	0.74773500	5.01639700	C	2.34053700	-3.26894000	-1.02446600
C	-3.07970700	1.24377000	0.32933300	H	2.31954900	-4.06103800	-1.76971800
H	-3.19562800	0.41645800	1.02448600	Ir	-0.25143300	-0.05022800	-0.00539800
C	-4.10705200	2.15689500	0.13351800	N	-1.18353100	-1.22127200	1.53863400
C	-3.85345400	3.18994100	-0.77826800	N	-1.89764900	1.30542000	-0.29608800
H	-4.61830900	3.93828400	-0.97580300	N	-0.75333700	-1.37009700	-1.62934300
C	-2.63304300	3.26840000	-1.42122500	O	2.06902700	3.93797800	2.98385900
H	-2.43819200	4.07623500	-2.11825200	O	3.52427800	2.19374400	-3.31322900
C	-1.63806300	2.31089500	-1.16974700	O	4.47123600	-2.03449200	1.69395700
C	-5.40868100	2.04036400	0.87081100	C	5.53348200	-2.95420800	1.66135200
H	-5.42066600	1.15693100	1.51670900	H	6.22174900	-2.65059800	2.45267300
H	-6.25689100	1.96199000	0.18001000	H	5.19055200	-3.97946400	1.85685200
H	-5.58717300	2.91715300	1.50492300	H	6.06166900	-2.93308300	0.69809400
C	-0.30825500	2.28483100	-1.75748300	C	2.59164500	4.49640800	1.80080200
C	0.54824100	1.23735900	-1.32356100	H	3.27006800	3.80048000	1.29066800
C	1.84781300	1.20863300	-1.85195400	H	1.79503400	4.78799200	1.10420400
H	2.52074000	0.42446900	-1.52424000	H	3.14767100	5.38463800	2.10764700
C	2.28170900	2.16529700	-2.76936000	C	4.43382000	1.19106400	-2.92297900
C	1.42005800	3.19046700	-3.19218300	H	4.63416000	1.22384400	-1.84416800
H	1.78289400	3.92018100	-3.90913900	H	4.06868100	0.18931400	-3.18401000
C	0.13847600	3.24172000	-2.68443700	H	5.35730800	1.39399400	-3.46919900

Table S11 Cartesian coordinates for the optimized structures of **3** in the ground state

C	0.43992000	3.04736300	0.40317100	C	0.52765100	-4.34460300	0.11931600
H	0.89280700	2.68955900	1.32408400	C	-0.65688800	-4.76318800	0.73761000
C	0.39853800	4.40386300	0.11195500	H	-0.81932300	-5.82083000	0.91856400
C	-0.19730600	4.75910300	-1.10570300	C	-1.58767500	-3.80806300	1.10129600
H	-0.25824200	5.80664500	-1.39375700	H	-2.50712900	-4.13795900	1.57974100
C	-0.69961200	3.78487900	-1.94629900	C	0.60995900	0.15468900	3.03794200
H	-1.15046500	4.06432500	-2.89226600	H	-0.47573100	0.14557600	3.08390900
C	-0.62237600	2.43014200	-1.58572500	C	1.37066700	0.21292400	4.19786000
C	0.97247000	5.42398400	1.05077400	C	2.76138100	0.21319000	4.02876300
H	1.37312800	4.95148100	1.95301800	H	3.41299600	0.25680600	4.89905000
H	0.21563600	6.15375600	1.36298100	C	3.30904700	0.15074600	2.76179600
H	1.78854700	5.98514800	0.57977200	H	4.38648100	0.14302000	2.63715300
C	-1.09986600	1.30736500	-2.37586500	C	2.47658300	0.09129500	1.63363800
C	-0.88303600	0.01423000	-1.82217100	C	0.72832400	0.26261600	5.55295700
C	-1.31872300	-1.07828200	-2.57829400	H	-0.36309100	0.27757400	5.47410300
H	-1.16592500	-2.08690000	-2.19526600	H	1.03618800	1.15493100	6.11124900
C	-1.93815100	-0.91401600	-3.81673600	H	1.00535000	-0.60956600	6.15722600
C	-2.14784800	0.36397800	-4.34879800	C	2.91643200	0.00886800	0.24892800
H	-2.63228700	0.46651500	-5.31442100	C	1.88738300	-0.07202900	-0.73563200
C	-1.72600000	1.46133700	-3.62262300	C	2.29102600	-0.17594800	-2.07032200
H	-1.88814100	2.45192100	-4.04148700	H	1.55527500	-0.24713000	-2.86579700
C	-2.73836000	0.89169300	1.15365200	C	3.63942700	-0.19547400	-2.42538000
H	-2.35234400	1.86634800	0.86690700	C	4.63906000	-0.11167000	-1.44775500
C	-3.99433100	0.76736600	1.73179600	H	5.69051400	-0.12500400	-1.73047700
C	-4.40146600	-0.53303100	2.05760000	C	4.26786700	-0.00984300	-0.11805400
H	-5.37596300	-0.69750500	2.51286300	H	5.05001500	0.05276800	0.63518800
C	-3.57462100	-1.60852800	1.79543900	Ir	0.00994100	-0.02074700	-0.02410300
H	-3.89871200	-2.61396200	2.04115200	N	-0.05287200	2.09622100	-0.39996000
C	-2.31773400	-1.40706800	1.20390200	N	-1.92593200	-0.14301600	0.90444500
C	-4.86396900	1.96496500	1.97882400	N	1.13140000	0.10412800	1.80572600
H	-4.35761200	2.88976900	1.68556300	O	-2.36121800	-1.97089600	-4.55574300
H	-5.13609100	2.05286900	3.03756400	O	1.41942000	-5.30722400	-0.22970600
H	-5.79832800	1.90320900	1.40797300	O	3.94112000	-0.30143000	-3.74599700
C	-1.35837700	-2.44476200	0.85970300	H	-2.14684400	-2.78002200	-4.06990900
C	-0.15710400	-2.00471400	0.23464800	H	4.90300700	-0.29192700	-3.84338100
C	0.76636200	-2.99248200	-0.12412000	H	2.18051700	-4.87337100	-0.64098200
H	1.69562100	-2.70078800	-0.61288500	C	0.52765100	-4.34460300	0.11931600

Table S12 Cartesian coordinates for the optimized structures of **4** in the ground state

C	2.60352600	-1.11774600	-2.14024600	C	-0.60272300	-1.26157600	-0.40455200
H	2.81785000	-1.78938100	-1.31450600	C	-1.77953400	-1.10597200	-1.14659300
C	3.22742600	-1.27492600	-3.37693700	H	-2.04480500	-0.14002400	-1.56463900
C	2.86367400	-0.34902400	-4.36002300	C	-2.64790600	-2.16977500	-1.36512700
H	3.30306900	-0.39727300	-5.35133500	C	-2.37944200	-3.44414400	-0.85414700
C	1.93142900	0.64025800	-4.08648500	H	-3.06229000	-4.26670100	-1.03956300
H	1.65301100	1.34644400	-4.86116100	C	-1.22023300	-3.62576400	-0.11994800
C	1.34524700	0.72884300	-2.82051500	H	-1.00749700	-4.61702300	0.27370400
C	0.34115500	1.69992300	-2.39706900	C	-4.93696300	-2.52798200	-1.89286100

C	-0.10076700	1.59170800	-1.04857300	C	-5.68833400	-2.96881000	-2.98052900
C	-1.09871400	2.48872200	-0.64071200	H	-5.27294600	-2.86828300	-3.97866600
H	-1.48218000	2.45674900	0.37489700	C	-6.94741300	-3.52154900	-2.76694000
C	-1.62949700	3.42343300	-1.52035600	H	-7.53143700	-3.86445600	-3.61702800
C	-1.17995100	3.53064600	-2.83648500	C	-7.45465300	-3.64157400	-1.47506600
H	-1.61215400	4.27840200	-3.49360600	H	-8.43601300	-4.07750700	-1.31053300
C	-0.18831200	2.66397200	-3.26594200	C	-6.69521300	-3.19278300	-0.39613400
H	0.15943900	2.73679900	-4.29367500	H	-7.08353400	-3.26696800	0.61621600
C	-3.90480400	3.90560000	-1.09370000	C	-5.43814900	-2.63069400	-0.59493500
C	-4.33780400	2.67970200	-1.59989300	H	-4.85608500	-2.26249700	0.24410600
H	-3.62339800	1.97119600	-2.00521000	Ir	0.76477800	0.14189200	0.03640200
C	-5.69823200	2.37640500	-1.58190400	N	1.71352500	-0.16118000	-1.86373300
H	-6.02713200	1.41880400	-1.97789900	N	2.22706300	1.53818900	0.76092600
C	-6.62525000	3.27742000	-1.06542700	N	1.63174200	-1.57470900	0.99261400
H	-7.68371100	3.03345900	-1.05741100	O	-2.59750000	4.30595000	-1.07973600
C	-6.17842400	4.49873300	-0.55999900	O	-2.81821400	0.13975500	4.21127800
H	-6.88916600	5.21262800	-0.15172300	O	-3.73641000	-1.92493500	-2.16704300
C	-4.82670700	4.81628300	-0.57174900	C	5.50101600	3.17193400	-0.21961500
H	-4.46131700	5.76177400	-0.18251800	C	6.30214200	1.89710800	-0.53323700
C	3.32962400	1.91620900	0.10875800	C	5.05113800	3.82848800	-1.53546800
H	3.45222600	1.46899500	-0.87275500	C	6.41878600	4.14842000	0.52037200
C	4.27244300	2.81056500	0.61178600	H	6.63852100	1.40812900	0.38848400
C	3.99848500	3.32507800	1.88354700	H	5.70877900	1.17244200	-1.10195400
H	4.67948100	4.02931300	2.35110500	H	7.18845500	2.14286000	-1.13073100
C	2.85049100	2.94998400	2.56356300	H	4.48119600	4.74384600	-1.34177600
H	2.64637400	3.36496400	3.54458000	H	5.92364800	4.09148200	-2.14584200
C	1.95082800	2.04480600	1.99032600	H	4.41682300	3.16042700	-2.12809800
C	0.70840100	1.56836800	2.58354300	H	7.28782200	4.38189000	-0.10465400
C	-0.05629600	0.65974000	1.79849700	H	5.91116300	5.09367100	0.74464900
C	-1.26279700	0.20405900	2.34673600	H	6.79168600	3.72508100	1.46046300
H	-1.88042800	-0.49329200	1.78889500	C	4.63163000	-2.60745600	3.06237000
C	-1.68529600	0.62400600	3.60632400	C	5.74377900	-2.17411700	2.09224800
C	-0.92179500	1.50969200	4.37065600	C	4.50152800	-1.56705700	4.18702000
H	-1.28001300	1.81159400	5.34939500	C	5.03078800	-3.94707400	3.68634500
C	0.27227700	1.97593700	3.85187500	H	5.85895400	-2.89877400	1.27768000
H	0.86149700	2.67065400	4.44579400	H	5.53624300	-1.19502600	1.64584700
C	-3.97346200	-0.06553200	3.50371700	H	6.70222700	-2.10197400	2.62069200
C	-4.37296600	0.74744800	2.44260900	H	3.71725700	-1.85359500	4.89618000
H	-3.72786600	1.54768100	2.09435600	H	5.44701500	-1.48382900	4.73672900
C	-5.60679600	0.52315300	1.83925700	H	4.25234900	-0.57394200	3.79788500
H	-5.91226200	1.16052200	1.01389800	H	5.98030500	-3.83453800	4.22122600
C	-6.44431500	-0.49558900	2.29017600	H	4.28446500	-4.29716600	4.40880000
H	-7.40682100	-0.66085000	1.81449100	H	5.16956300	-4.72638200	2.92774200
C	-6.03572000	-1.29909100	3.35302800	C	4.22768800	-2.40883800	-3.58902900
H	-6.68038500	-2.09532300	3.71699500	C	5.38882500	-2.26385500	-2.59104400
C	-4.80133700	-1.09041600	3.95948600	C	3.52390900	-3.75706300	-3.36121600
H	-4.46484200	-1.70280300	4.79049200	C	4.80560500	-2.39732400	-5.00657600
C	2.77783400	-1.58292600	1.67804000	H	5.91192400	-1.31079100	-2.73219600
H	3.28743700	-0.62502800	1.71767900	H	5.04227500	-2.30770000	-1.55247600
C	3.30894200	-2.70795800	2.30610000	H	6.11488800	-3.07352600	-2.73329200
C	2.55236000	-3.87907300	2.18815700	H	2.69259700	-3.88805100	-4.06258800
H	2.89024100	-4.80156100	2.64983900	H	4.23025200	-4.58290500	-3.50937600
C	1.35774400	-3.87944500	1.48551400	H	3.11979000	-3.83976200	-2.34657700
H	0.77834900	-4.79323700	1.40925600	H	5.51646900	-3.22314600	-5.12010500
C	0.89184200	-2.70799400	0.87953300	H	4.02524800	-2.52766600	-5.76520900
C	-0.33637500	-2.56191100	0.10910700	H	5.34390600	-1.46642700	-5.22053100

Table S13 Cartesian coordinates for the optimized structures of **5** in the ground state

C	1.60357100	-1.61738000	-1.57592300	O	-4.06866800	3.31284500	-2.70217500
H	1.83802300	-1.92386100	-0.56088800	O	-4.52862300	1.15407400	3.57538200
C	2.31542400	-2.12369200	-2.66140700	O	-4.65666900	-3.07157900	-1.47152900
C	1.91220000	-1.65708400	-3.91790800	C	3.90610500	3.39035900	-1.09556300
H	2.41058200	-2.00159500	-4.81876400	C	4.86958200	2.21544200	-0.85840700
C	0.86898700	-0.75294800	-4.03348400	C	3.52664000	3.44579200	-2.58477900
H	0.56343000	-0.40555800	-5.01456400	C	4.63060000	4.68891500	-0.73241300
C	0.20300800	-0.28719700	-2.89307300	H	5.16012700	2.15274800	0.19686400
C	-0.90024900	0.65849300	-2.86350100	H	4.42047000	1.25703300	-1.14183100
C	-1.42373200	0.97411300	-1.58096500	H	5.78111000	2.34485200	-1.45465900
C	-2.49839000	1.87412000	-1.52762000	H	2.84093500	4.27690800	-2.78296300
H	-2.91609500	2.12309500	-0.55857600	H	4.42363200	3.58766600	-3.20007200
C	-3.03188900	2.43857500	-2.68611300	H	3.03630200	2.52385800	-2.91534700
C	-2.50120800	2.11723000	-3.94597400	H	5.52703100	4.79534100	-1.35330600
H	-2.93615200	2.57131200	-4.83066000	H	4.00064300	5.56844200	-0.90854500
C	-1.44509500	1.23393200	-4.02381700	H	4.95132500	4.69801700	0.31601200
H	-1.04381700	0.98876100	-5.00471000	C	3.42456000	-1.01992000	3.83553800
C	1.85074600	2.06404200	-0.44990900	C	4.51820800	-0.67416000	2.81093100
H	2.11176700	1.31261300	-1.18867800	C	3.05649300	0.24178600	4.63394600
C	2.64458000	3.19313300	-0.25773500	C	3.98608700	-2.06124600	4.80652500
C	2.19541300	4.08709700	0.72093100	H	4.80214600	-1.55681700	2.22584200
H	2.75260500	4.99367800	0.93624400	H	4.19139200	0.10296400	2.11102800
C	1.02999300	3.83409400	1.42650700	H	5.41469000	-0.30400700	3.32323100
H	0.69132300	4.54023200	2.17716000	H	2.28522000	0.02060800	5.37996200
C	0.28396100	2.67708200	1.17304200	H	3.93863500	0.62987800	5.15773000
C	-0.95695800	2.28880900	1.82370900	H	2.67425500	1.03746200	3.98546500
C	-1.53764200	1.06666800	1.38945900	H	4.87488600	-1.65824600	5.30453300
C	-2.74933700	0.68240700	1.98440000	H	3.26094600	-2.32230600	5.58588300
H	-3.21351200	-0.24217700	1.65950500	H	4.28459700	-2.98101700	4.28981500
C	-3.35847700	1.46665400	2.96391300	C	3.45036100	-3.11934300	-2.43297800
C	-2.76937900	2.67056700	3.38318300	C	4.53600500	-2.46750400	-1.56010500
H	-3.26528000	3.25981100	4.14805300	C	2.90348500	-4.36623100	-1.71828000
C	-1.57885200	3.06980000	2.81223600	C	4.09166300	-3.56079500	-3.75100400
H	-1.13246800	4.00594400	3.14044500	H	4.94862300	-1.57596500	-2.04671600
C	1.54813100	-0.73590400	2.16101000	H	4.14413800	-2.16651700	-0.58206800
H	1.91579800	0.25851300	1.92681900	H	5.35875800	-3.17202800	-1.38691400
C	2.18591600	-1.53651500	3.10671500	H	2.12796800	-4.85284800	-2.32001600
C	1.61032400	-2.79408400	3.32029800	H	3.70950500	-5.09045500	-1.54753100
H	2.04357900	-3.48288500	4.03890300	H	2.46452000	-4.11948400	-0.74549700
C	0.47699900	-3.17888000	2.62163800	H	4.89996200	-4.27181400	-3.54686700
H	0.03937600	-4.15502100	2.80180600	H	3.36943300	-4.06067400	-4.40680200
C	-0.10619400	-2.31674600	1.68634300	H	4.52631200	-2.71540200	-4.29734200
C	-1.29145600	-2.58411700	0.88393100	C	-5.42015900	-4.25004700	-1.41278600
C	-1.68847100	-1.55267100	-0.01931800	H	-6.23463200	-4.11948800	-2.12812800
C	-2.83336400	-1.78985500	-0.78160200	H	-4.83006000	-5.13216600	-1.69677800
H	-3.19189300	-1.04454700	-1.48583700	H	-5.84372200	-4.41237200	-0.41195300
C	-3.56262200	-2.97790700	-0.67270200	C	-4.64490300	3.66979100	-1.46719000
C	-3.16019700	-3.98241100	0.21747300	H	-5.06230100	2.79718500	-0.94829400
H	-3.71300300	-4.91009600	0.31463300	H	-3.91712000	4.15889100	-0.80690300

C	-2.02455600	-3.77021800	0.98591800	H	-5.44911700	4.37012800	-1.70184700
H	-1.71951300	-4.55178300	1.67850400	C	-5.16689400	-0.04362800	3.19771900
Ir	-0.51540500	0.07827000	-0.02989500	H	-5.43770500	-0.04049400	2.13385500
N	0.60256600	-0.73908000	-1.67477700	H	-4.53611400	-0.91918700	3.39885300
N	0.73087900	1.80627600	0.23009000	H	-6.07435100	-0.10409300	3.80207800
N	0.46320900	-1.10191400	1.47375800	O	-4.06866800	3.31284500	-2.70217500

Table S14 Cartesian coordinates for the optimized structures of **6** in the ground state

C	1.38254600	-1.42522000	-1.71741700	H	-1.59538700	-4.81357700	1.41232400
H	1.65778100	-1.79369700	-0.73397700	Ir	-0.79829100	0.00153300	-0.00619000
C	2.10232800	-1.79659600	-2.85095900	N	0.32342300	-0.61171200	-1.73010700
C	1.64206600	-1.26161500	-4.05972500	N	0.32501400	1.79931300	0.33599000
H	2.14294600	-1.49925300	-4.99308100	N	0.30748500	-1.19360800	1.39487500
C	0.53690600	-0.42668700	-4.08664900	O	-4.66427700	3.11791900	-2.31293200
H	0.18677700	-0.02730200	-5.03241100	O	-4.74407400	0.48656400	3.75917100
C	-0.13519400	-0.09938200	-2.90273900	O	-4.71544800	-3.41004300	-1.56246400
C	-1.30567000	0.75419900	-2.78100500	C	3.33144300	3.70180100	-0.96435500
C	-1.81924400	0.93051400	-1.46495100	C	4.38246800	2.58565200	-0.84203800
C	-2.95626200	1.73360800	-1.33303200	C	2.89931700	3.83516400	-2.43419300
H	-3.38717000	1.89019900	-0.34448100	C	3.97477700	5.02053200	-0.52768700
C	-3.56078500	2.33736300	-2.43520100	H	4.71301000	2.46944400	0.19676700
C	-3.04366100	2.15759000	-3.72390700	H	3.99172500	1.61963800	-1.18109300
H	-3.53194900	2.63694300	-4.56616000	H	5.26141000	2.82264500	-1.45401300
C	-1.92137700	1.36706600	-3.88307500	H	2.15392500	4.62926100	-2.55241100
H	-1.52580400	1.22536400	-4.88638000	H	3.76433000	4.08051900	-3.06246200
C	1.39721700	2.18761300	-0.35900200	H	2.46062300	2.90712900	-2.81628700
H	1.68439100	1.51524000	-1.16167400	H	4.83997700	5.23644100	-1.16434000
C	2.11677200	3.35388200	-0.10702600	H	3.27881700	5.86235000	-0.62004700
C	1.64316400	4.13882300	0.95031000	H	4.32992800	4.97831200	0.50875200
H	2.14412900	5.06459600	1.21559500	C	3.27973900	-1.01597300	3.73686000
C	0.52459500	3.75171900	1.67073900	C	4.34431400	-0.55683100	2.72659200
H	0.16425200	4.37513100	2.48197700	C	2.83009400	0.18537300	4.58512200
C	-0.14696000	2.56474200	1.35508400	C	3.91317500	-2.05444700	4.66610700
C	-1.33275800	2.04026300	2.01470100	H	4.68699500	-1.39513000	2.10886400
C	-1.83997600	0.81007100	1.50766600	H	3.96193700	0.22130200	2.05656100
C	-2.99493500	0.30602500	2.11504600	H	5.21387100	-0.14467000	3.25296300
H	-3.42284500	-0.62833800	1.75198600	H	2.07447800	-0.11493200	5.31938100
C	-3.62134900	0.97073500	3.16885400	H	3.68504400	0.60819700	5.12684800
C	-3.10917400	2.17779100	3.66001700	H	2.39766600	0.98084000	3.96864500
H	-3.61286100	2.67619600	4.48197900	H	4.77025800	-1.60988600	5.18400600
C	-1.96942800	2.69971700	3.07703400	H	3.20822700	-2.39950100	5.43129400
H	-1.57730100	3.64009000	3.45820700	H	4.27813700	-2.92819100	4.11338900
C	1.37117100	-0.78577700	2.09162700	C	3.30090300	-2.73400100	-2.72112200
H	1.66189000	0.24446500	1.91064500	C	4.35306700	-2.09877300	-1.79650400

C	2.07670900	-1.58567800	2.98837100	C	2.83979500	-4.07349900	-2.12298400
C	1.59893900	-2.89249000	3.13668200	C	3.95480000	-3.00930500	-4.07763000
H	2.08967400	-3.58428600	3.81423100	H	4.70518900	-1.14255500	-2.20089500
C	0.48945700	-3.32281500	2.42660900	H	3.95479900	-1.91366800	-0.79255300
H	0.12695700	-4.33673900	2.55829700	H	5.21933700	-2.76367700	-1.69324700
C	-0.16862000	-2.45689100	1.54583200	H	2.09160600	-4.55132100	-2.76499600
C	-1.34491400	-2.76566500	0.74616500	H	3.69167400	-4.75718300	-2.02201000
C	-1.84297500	-1.71303300	-0.07788100	H	2.39405900	-3.94467800	-1.13076300
C	-2.98513600	-1.98639700	-0.83711600	H	4.80897400	-3.68244400	-3.94427100
H	-3.41481500	-1.22508700	-1.48140700	H	3.25935700	-3.49245600	-4.77361000
C	-3.60896000	-3.23283700	-0.79395700	H	4.32782300	-2.09017800	-4.54459600
C	-3.10675600	-4.25765900	0.01831000	H	-4.90639100	3.14824800	-1.37648300
H	-3.59679700	-5.22959800	0.04748000	H	-5.03246400	-4.31538900	-1.44169900
C	-1.97758000	-4.01440700	0.78123200	H	-4.97518600	-0.34591200	3.32348500