

SUPPORTING INFORMATION

Fine tuning of emission color of iridium(III) complexes from yellow to red via substituent effect on 2-phenylbenzothiazole ligands: synthesis, photophysical, electrochemical and DFT study

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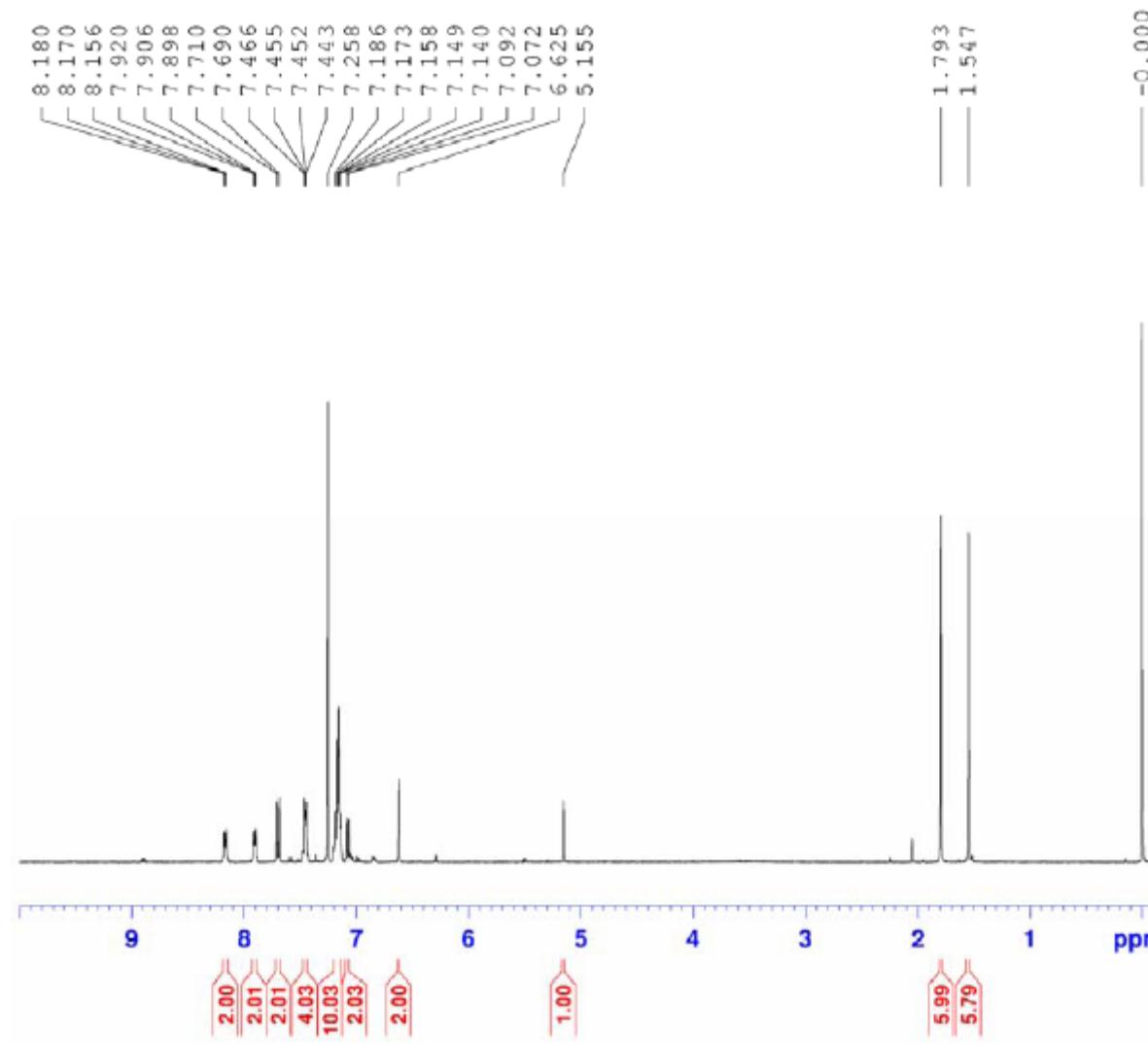


Figure S1. ¹H NMR Spectrum of 7a

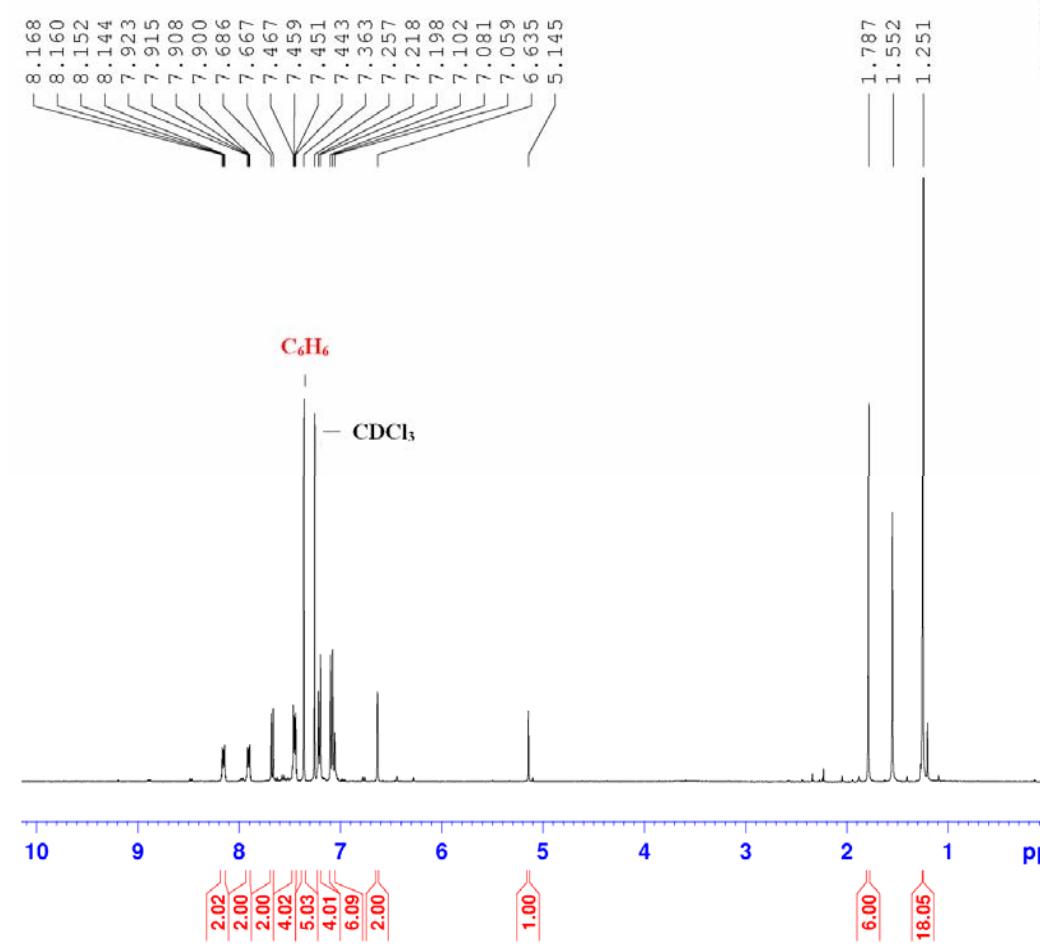


Figure S2. ¹H NMR Spectrum of **7b**

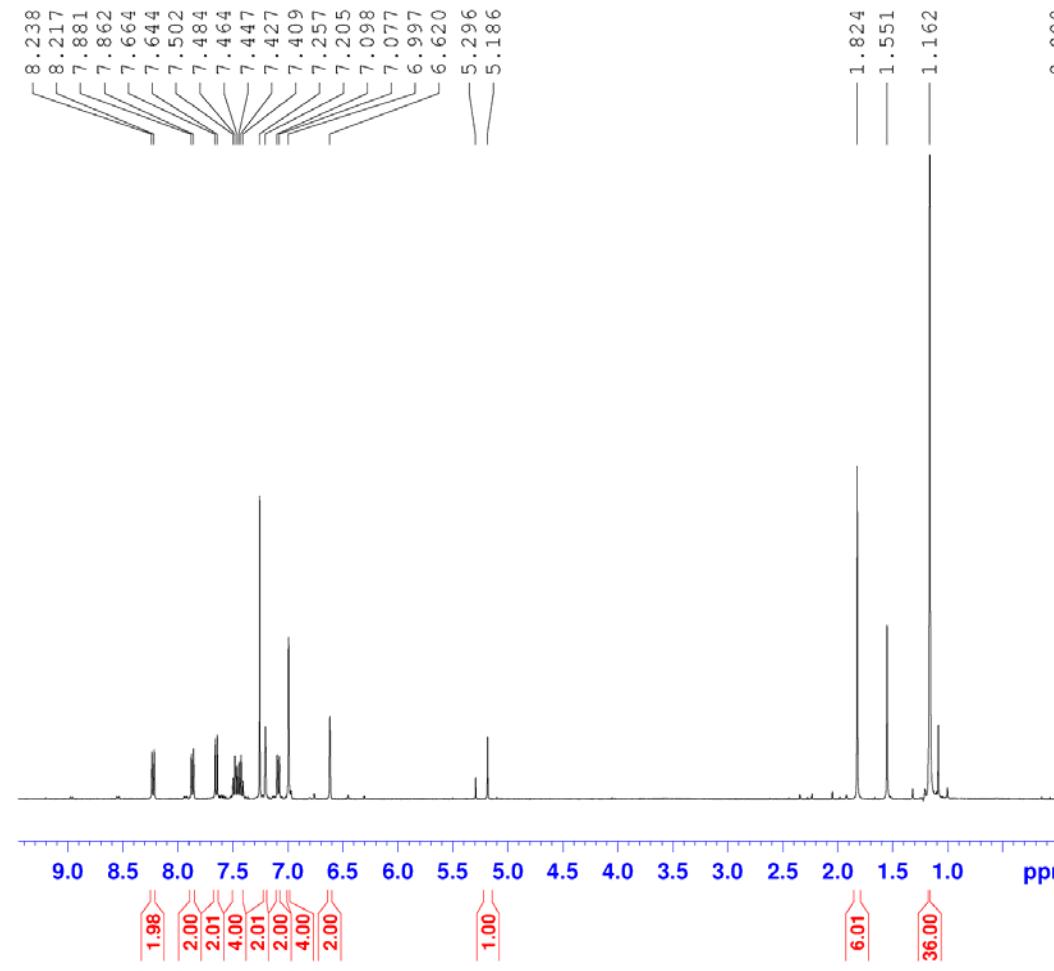


Figure S3. ^1H NMR Spectrum of **7c**

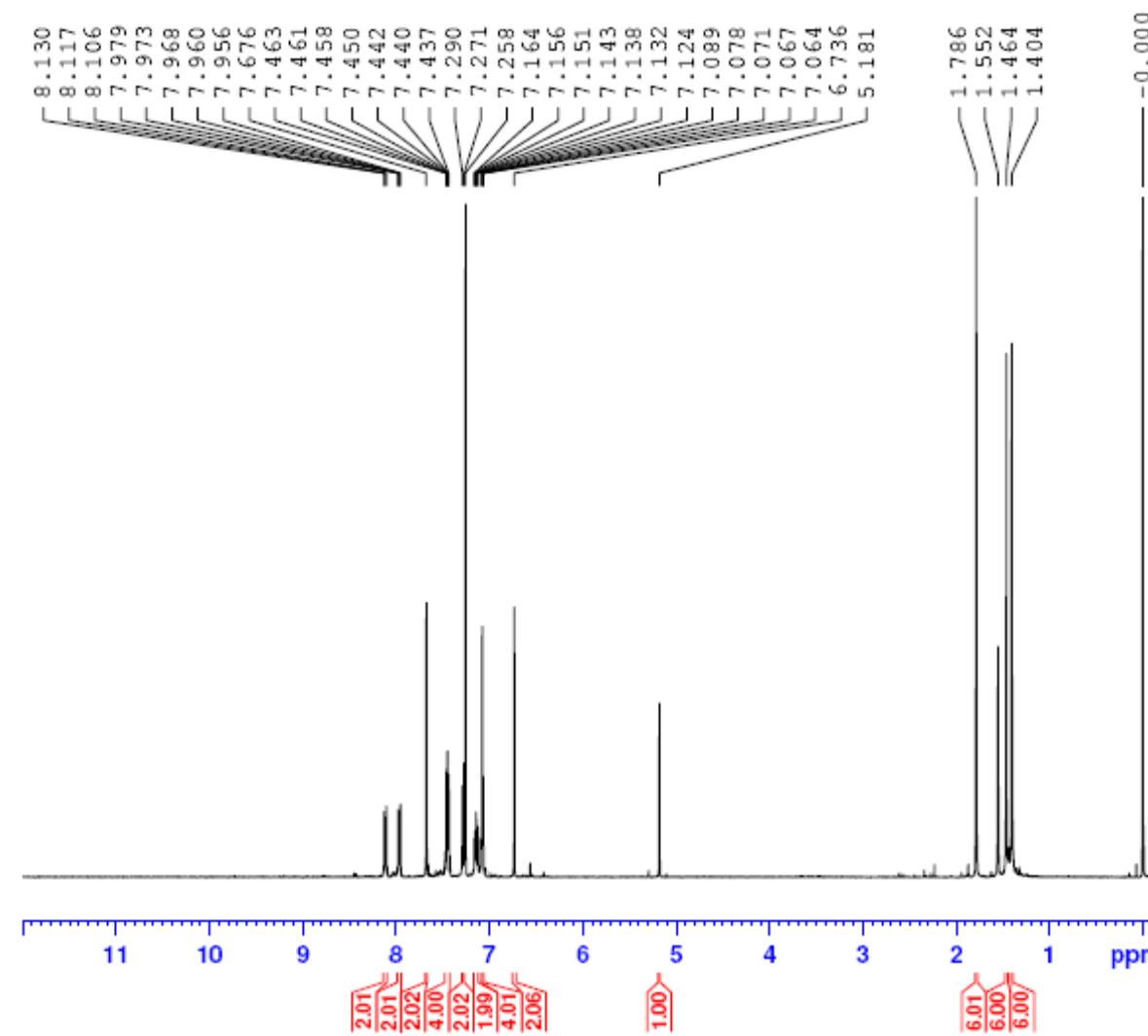


Figure S4. ¹H NMR Spectrum of 7d

Figure S5. Optimized structures and the numbering of important atoms of $(\text{pbt})_2\text{Ir}(\text{acac})$ and **7a~7d**, calculation is conducted at the level of B3LYP/LANL2DZ/6-31(d,p).

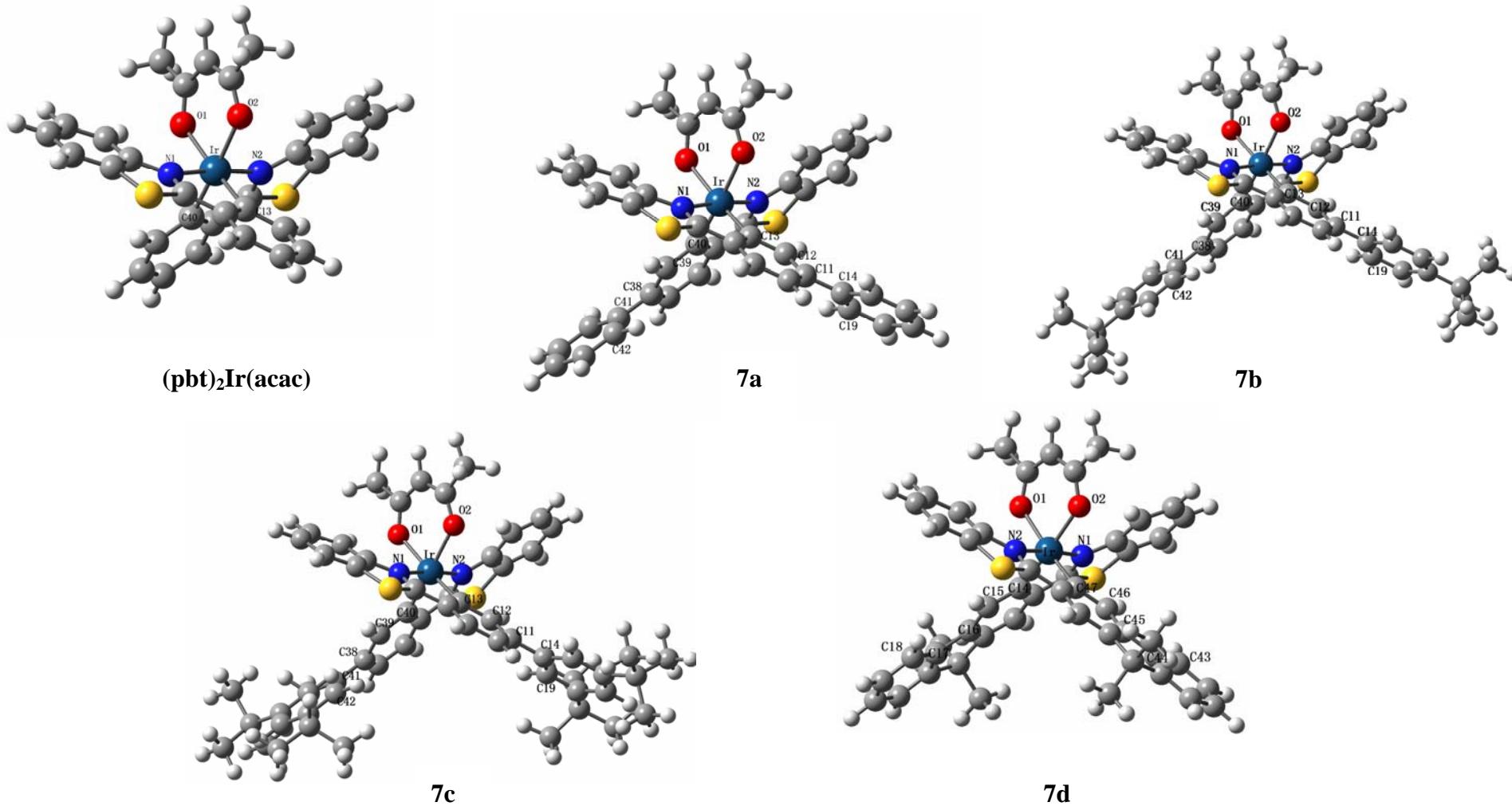


Table S1. Optimized Geometry Parameters of the Five Complexes using B3LYP method^a

(pbt) ₂ Ir(acac)	7a	7b	7c		7d
Bond Length (Å)					
Ir-O1	2.202	2.200	2.199	2.200 (2.157)	Ir-O1
Ir-O2	2.202	2.200	2.199	2.200 (2.131)	Ir-O2
Ir-N1	2.082	2.083	2.084	2.084 (2.045)	Ir-N2
Ir-N2	2.082	2.083	2.084	2.084 (2.044)	Ir-N1
Ir-C13	2.010	2.011	2.010	2.010 (1.992)	Ir-C47
Ir-C40	2.009	2.011	2.010	2.010 (1.992)	Ir-C14
Bond Angle (deg)					
O1-Ir-O2	86.2	86.4	86.2	86.1 (87.8)	O1-Ir-O2
N1-Ir-N2	174.8	174.8	175.1	175.0 (173.2)	N2-Ir-N1
C13-Ir-C40	94.8	94.8	94.5	94.0 (91.9)	C47-Ir-C14
N2-Ir-C13	96.5	96.4	96.6	96.6 (95.0)	N1-Ir-C47
N1-Ir-C40	96.5	96.4	96.7	96.6 (94.7)	N2-Ir-C14
N2-Ir-C40	80.0	80.0	80.0	80.0 (80.0)	N1-Ir-C14
N1-Ir-C13	80.0	80.0	80.0	80.0980.8)	N2-Ir-C47
Torsion Angle (deg)					
N1-Ir-C13-C40	95.7	95.7	96.0	96.0(94.4)	N2-Ir-C47-C14
N2-Ir-C40-C13	95.7	95.7	96.0	96.0 (94.7)	N1-Ir-C14-C47
N1-Ir-C40-O1	98.4	98.1	98.1	98.6 (96.5)	N2-Ir-C14-O1
N2-Ir-O1-C40	80.0	80.0	80.0	79.9 (79.9)	N1-Ir-O1-C14
N1-Ir-O1-O2	84.8	85.1	84.9	84.4 (85.9)	N2-Ir-O1-O2
N2-Ir-O2-O1	84.8	85.1	84.9	84.5 (87.7)	N1-Ir-O2-O1
N1-Ir-O2-C13	80.0	80.0	80.0	80.0 (80.9)	N2-Ir-O2-C47
N2-Ir-C13-O2	98.4	98.1	98.1	98.7 (99.1)	N1-Ir-C47-O2
C40-Ir-N1-O1	-90.5	-90.4	-90.6	-91.0 (-92.0)	C14-Ir-N2-O1
C40-Ir-N2-O1	90.3	90.2	90.4	90.9 (91.9)	C14-Ir-N1-O1
C13-Ir-N1-C40	-93.7	-93.7	-93.5	-92.9 (-91.2)	C47-Ir-N2-C14
C13-Ir-N2-C40	93.7	93.7	93.5	92.9 (91.0)	C47-Ir-N1-C14
O2-Ir-N1-C13	-90.3	-90.2	-90.4	-90.7 (-89.4)	O2-Ir-N2-C47
O2-Ir-N2-C13	90.5	90.4	90.6	90.9 (89.6)	O2-Ir-N1-C47
O1-Ir-N1-O5	-85.4	-85.7	-85.5	-85.3 (-87.4)	O1-Ir-N2-O2
O1-Ir-N2-O5	85.4	85.7	85.5	85.3 (87.5)	O1-Ir-N1-O2
C12-C11-C14-C19	/	-37.8	-37.1	-38.0 (-34.4)	C46-C45-C44-C43
C39-C38-C41-C42	/	-37.9	-37.0	-37.5 (-43.6)	C15-C16-C17-C18
The values in parentheses are derived from crystal data.					

^a The values in parentheses are derived from crystal data.

Table S2. Molecular orbital compositions in the ground state for complex **(pbt)₂Ir(acac)**, derived from DFT/B3LYP calculation

MO	Energy (eV)	Contribution (%)				
		Ir-d	bt ^a	phen-1 ^b	acac	assignment
LUMO+2	-0.71	1.5	7.2	2.8	87.8	$\pi^*(\text{acac})$
LUMO+1	-1.60	2.7	67.4	27.9	1.2	$\pi^*(\text{C}^\wedge\text{N})$
LUMO	-1.60	3.2	68.0	27.0	1.4	$\pi^*(\text{C}^\wedge\text{N})$
HOMO	-5.02	49.0	10.2	34.2	5.3	d(Ir) + $\pi(\text{C}^\wedge\text{N})$
HOMO-1	-5.37	38.7	12.4	7.2	42.8	d(Ir) + $\pi(\text{acac})$
HOMO-2	-5.81	2.7	40.9	34.2	21.6	$\pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-3	-5.85	48.7	27.4	17.6	5.2	d(Ir) + $\pi(\text{C}^\wedge\text{N})$
HOMO-4	-6.18	16.1	23.5	37.3	22.5	d(Ir) + $\pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-5	-6.21	27.2	39.0	32.1	1.7	d(Ir) + $\pi(\text{C}^\wedge\text{N})$

^a bt represents for benzothiazole moiety.

^b phenyl-1 represents for the phenyl group bonded to Ir atom directly.

Table S3. Molecular orbital compositions in the ground state for complex **7a**, derived from DFT/B3LYP calculation

MO	Energy (eV)	Contribution (%)					assignment
		Ir-d	bt ^a	phen-1 ^b	phen-2 ^c	acac	
LUMO+2	-0.72	1.5	7.1	3.0	0.1	87.5	$\pi^*(\text{acac})$
LUMO+1	-1.71	2.5	59.6	27.8	8.5	0.9	$\pi^*(\text{C}^{\wedge}\text{N})$
LUMO	-1.71	3.1	60.0	26.8	8.3	1.3	$\pi^*(\text{C}^{\wedge}\text{N})$
HOMO	-5.05	46.8	11.4	33.6	2.0	4.8	d(Ir)+ $\pi(\text{C}^{\wedge}\text{N})$
HOMO-1	-5.35	37.3	14.1	9.4	3.0	35.8	d(Ir)+ $\pi(\text{acac} + \text{C}^{\wedge}\text{N})$
HOMO-2	-5.64	0.7	27.1	30.3	16.6	24.6	$\pi(\text{C}^{\wedge}\text{N} + \text{acac})$
HOMO-3	-5.69	23.5	19.9	30.9	20.0	4.6	d(Ir) + $\pi(\text{C}^{\wedge}\text{N})$
HOMO-4	-6.05	52.1	23.7	12.9	8.1	2.8	d(Ir)+ $\pi(\text{C}^{\wedge}\text{N} + \text{acac})$
HOMO-5	-6.16	23.7	35.0	10.0	5.2	25.5	d(Ir)+ $\pi(\text{C}^{\wedge}\text{N} + \text{acac})$

^a bt represents for benzothiazole moiety.

^b phenyl-1 represents for the phenyl group bonded to Ir atom directly.

^c phenyl-2 represents for the substituent introduced to the *para*-site of phenyl-1.

Table S4. Molecular orbital compositions in the ground state for complex **7b**, derived from DFT/B3LYP calculation

MO	Energy (eV)	Contribution (%)						
		Ir-d	bt ^a	phen-1 ^b	phen-2 ^c	sub ^d	acac	assignment
LUMO+2	-0.69	1.5	7.1	3.0	7.1	0	87.5	$\pi^*(\text{acac})$
LUMO+1	-1.66	2.5	59.5	27.5	8.0	1.0	0.9	$\pi^*(\text{C}^\wedge\text{N})$
LUMO	-1.67	3.1	60.0	26.5	7.8	0.9	1.27	$\pi^*(\text{C}^\wedge\text{N})$
HOMO	-5.00	46.3	11.7	33.6	2.2	0.1	4.8	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-1	-5.31	35.9	14.6	11.4	4.8	0.6	32.4	$d(\text{Ir}) + \pi(\text{acac} + \text{C}^\wedge\text{N})$
HOMO-2	-5.55	2.6	22.5	26.2	18.9	2.5	26.5	$\pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-3	-5.59	18.7	15.9	30.6	26.1	3.5	4.2	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-4	-5.99	55.0	22.6	10.1	7.5	1.1	3.1	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-5	-6.11	23.6	34.1	7.0	7.4	1.1	26.5	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$

^a bt represents for benzothiazole moiety.

^b phenyl-1 represents for the phenyl group bonded to Ir atom directly.

^c phenyl-2 represents for the substituent introduce to the *para*-site of phenyl-1.

^d sub represents for the substituent on phenyl-2.

Table S5. Molecular orbital compositions in the ground state for complex **7c**, derived from DFT/B3LYP calculation

MO	Energy (eV)	Contribution (%)						
		Ir-d	bt ^a	phen-1 ^b	phen-2 ^c	sub ^d	acac	assignment
LUMO+2	-0.73	1.5	7.0	2.9	0.1	0	87.8	$\pi^*(\text{acac})$
LUMO+1	-1.67	2.7	59.8	27.2	8.0	0.8	1.1	$\pi^*(\text{C}^\wedge\text{N})$
LUMO	-1.68	2.7	60.1	27.2	7.6	0.8	1.1	$\pi^*(\text{C}^\wedge\text{N})$
HOMO	-5.05	47.0	11.8	33.7	2.6	0.1	4.7	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-1	-5.36	35.4	15.1	11.8	4.9	0.3	31.9	$d(\text{Ir}) + \pi(\text{acac} + \text{C}^\wedge\text{N})$
HOMO-2	-5.59	3.3	22.9	26.2	18.3	1.4	27.3	$\pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-3	-5.64	18.9	16.9	31.4	25.3	1.9	4.7	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-4	-6.03	53.0	25.1	10.1	7.6	0.7	3.0	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-5	-6.14	21.8	36.1	5.8	10.9	1.5	23.7	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$

^a bt represents for benzothiazole moiety.

^b phenyl-1 represents for the phenyl group bonded to Ir atom directly.

^c phenyl-2 represents for the substituent introduced to the *para*-site of phenyl-1.

^d sub represents substituents on phenyl-2.

Table S6. Molecular orbital compositions in the ground state for complex **7d**, derived from DFT/B3LYP calculation

MO	Energy (eV)	Contribution (%)						
		Ir-d	bt ^a	phen-1 ^b	phen-2 ^c	sub ^d	acac	assignment
LUMO+2	-0.68	1.5	7.2	3.0	0.2	0	87.4	$\pi^*(\text{acac})$
LUMO+1	-1.70	2.9	56.5	26.3	11.3	1.6	1.1	$\pi^*(\text{C}^\wedge\text{N})$
LUMO	-1.71	2.4	55.8	27.4	11.2	1.6	0.9	$\pi^*(\text{C}^\wedge\text{N})$
HOMO	-4.92	41.9	12.5	33.3	2.7	3.3	3.9	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-1	-5.25	30.7	17.8	19.1	10.9	0.3	21.1	$d(\text{Ir}) + \pi(\text{acac} + \text{C}^\wedge\text{N})$
HOMO-2	-5.47	9.8	17.7	19.8	12.3	0.6	39.1	$\pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-3	-5.56	19.9	14.6	33.4	25.1	1.5	4.6	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N})$
HOMO-4	-5.95	58.1	22.6	9.0	6.1	0.2	3.3	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$
HOMO-5	-6.10	22.0	28.6	19.3	1.5	1.6	26.6	$d(\text{Ir}) + \pi(\text{C}^\wedge\text{N} + \text{acac})$

^a bt represents for benzothiazole moiety,

^b phenyl-1 for the phenyl group bonded to Ir atom directly,

^c phenyl-2 for the substituent introduced to the parasite of phenyl-1,

^d sub represents methylene for the linkage group between phenyl-1 and phenyl-2.