Electronic Supplementary Material (ESI) for RSC Advances.

Novel phosphorescent iridium(III) complexes containing 2-thienyl quinazoline ligand: synthesis, photophysical properities and theoretical calculation

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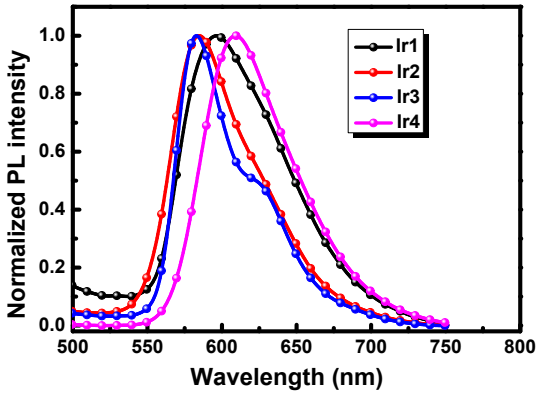

Figure. S1 Photoluminescence spectra of complexes **Ir1-Ir4** in 2 wt% PMMA films at room temperature

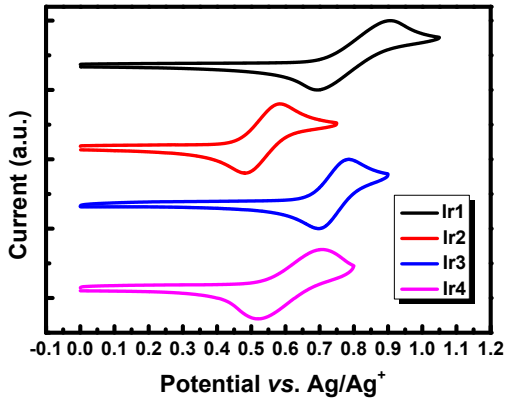

Figure. S2 Cyclic voltammogram of complexes **Ir1-Ir4** in deoxygenated DCM solutions at room temperature.

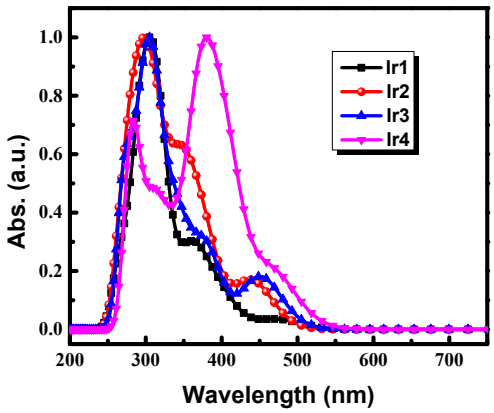

Fig. S3 The simulated absorption spectra of **complexes** Ir1-Ir4 in DCM.

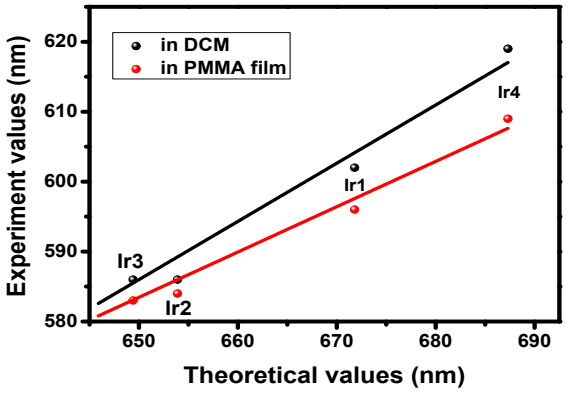

Figure. S4 The relationship between the theoretical and experimental values of the maximum phosphorescence emissions.

Table S1 XRD experimental details

	Ir1	**Ir2**	**Ir3**	**Ir4**
Empirical formula	$C_{30}H_{18}IrN_5O_2S_2$	$C_{40}H_{36}IrN_7O_2S_2$	$C_{46}H_{34}IrN_5O_4S_2$	$C_{54}H_{36}IrN_7O_2S_2$
Formula weight	736.81	903.08	977.10	1071.22
Temperature (K)	296	296	296	296
Mo $K\alpha$ radiation (Å)	λ = 0.71073	λ = 0.71073	λ = 0.71073	λ = 0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 11.3735 (11) Å	a = 9.324 (5) Å	a = 27.554 (13) Å	a = 14.908 (3) Å
	α = 90.000 °	α = 106.650 (8) °	α = 90.000 °	α = 90.000 °
	b = 12.2222 (11) Å	b = 12.900 (7) Å	b = 17.381 (8) Å	b = 14.425 (3) Å
	β = 93.385 (1) °	β = 94.335 (8) °	β = 122.764 (7) °	β = 94.332 (4) °
	c = 121.987 (2) Å	c = 18.496 (10) Å	c = 23.473 (11) Å	c = 23.345 (5) Å
	γ = 90.000 °	γ = 91.856 (7) °	γ = 90.000 °	γ = 90.000 °
Volume (Å^3)	3051.1 (5)	2122 (2)	9453 (8)	4684 Å^3
Z, Calculated density	4	2	8	4
D_x (Mg/m^3)	1.604	1.413	1.373	1.421
μ (mm^{-1})	4.55	3.29	2.96	2.80
F(000)	1432	900	3888	2136
Crystal size (mm)	0.26 × 0.24 × 0.22	0.28 × 0.25 × 0.22	0.27 × 0.25 × 0.22	0.26 × 0.24 × 0.22
Theta range for data collection	2.5° - 27.2°	1.2° - 25.0°	1.5° - 25.0°	1.6° - 25.0°
Limiting indices	h = -13 → 11	h = -10 → 11	h = -27 → 32	h = -17 → 12
	k = -14 → 14	k = -15 → 15	k = -20 → 20	k = -17 → 17
	l = -26 → 20	l = -21 → 12	l = -27 → 22	l = -27 → 27
No. of mearured, independent and observed [$I > 2\sigma(I)$] reflections	16314, 5383, 4171	11715, 7432, 6271	25823, 8342, 6649	27285, 8827, 6894
R_{int}	0.031	0.026	0.033	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595	0.595	0.595
Refinement method	Refinement on F^2	Refinement on F^2	Refinement on F^2	Refinement on F^2
Least-squares matrix	full	full	full	full
Data / restraints / parameters	5383 / 0 / 361	7432 / 0 / 469	8342 / 72 / 515	8827 / 48 / 595
Goodness-of-fit on F^2	1.02	0.97	1.05	1.02
R[$F^2 > 2\sigma(F^2)$]	0.026	0.031	0.027	0.029
wR(F^2)	0.060	0.065	0.066	0.072
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e A^{-3})	0.81, -0.72	0.84, -0.95	0.61, -0.51	1.03, -0.53

Table S2 Selected bond lengths of complexes **Ir1**-**Ir4**

Ir1	Bond length (Å)	**Ir2**	Bond length (Å)	**Ir3**	Bond length (Å)	**Ir4**	Bond length (Å)
Ir-C30	2.001(4)	Ir-C15	1.980(4)	Ir-C18	1.983(3)	Ir-C22	1.984(4)
Ir-C21	1.986(4)	Ir-C32	1.966(3)	Ir-C38	1.975(4)	Ir-C46	1.963(4)
Ir-N1	2.049(3)	Ir-N1	2.100(4)	Ir-N3	2.101(3)	Ir-N4	2.083(3)
Ir-N3	2.044(3)	Ir-N4	2.083(4)	Ir-N1	2.077(3)	Ir-N1	2.087(3)
Ir-N5	2.129(3)	Ir-N7	2.150(4)	Ir-N5	2.157(5)	Ir-N7	2.164(3)
Ir-O1	2.148(2)	Ir-O1	2.158(3)	Ir-O3	2.149(4)	Ir-O1	2.138(3)

Table S3 Selected bond angles of complexes **Ir1**-**Ir4**

Ir1	Bond angle (°)	**Ir2**	Bond angle (°)	**Ir3**	Bond angle (°)	**Ir4**	Bond angle (°)
C30-Ir-C21	86.9(2)	C15-Ir-C32	92.6(2)	C18-Ir-C38	93.0(2)	C22-Ir-C46	95.3(2)
C30-Ir-N1	80.6(2)	C15-Ir-N1	79.3(1)	C18-Ir-N3	79.5(1)	C22-Ir-N4	79.7(1)
C30-Ir-N3	95.1(1)	C15-Ir-N4	92.7(1)	C18-Ir-N1	93.5(1)	C22-Ir-N1	94.4(1)
C30-Ir-N5	173.6(1)	C15-Ir-N7	171.5(1)	C18-Ir-N5	169.7(2)	C22-Ir-N7	165.8(1)
C30-Ir-O1	98.2(1)	C15-Ir-O1	95.3(1)	C18-Ir-O3	93.2(2)	C22-Ir-O1	90.2(1)
C21-Ir-N1	96.1(1)	C32-Ir-N1	99.0(1)	C38-Ir-N3	94.6(1)	C46-Ir-N4	95.7(1)
C21-Ir-N3	80.0(1)	C32-Ir-N4	79.6(1)	C38-Ir-N1	79.6(1)	C46-Ir-N1	79.7(1)
C21-Ir-N5	98.5(1)	C32-Ir-N7	95.7(1)	C38-Ir-N5	96.5(2)	C46-Ir-N7	98.3(1)
C21-Ir-O1	172.3(1)	C32-Ir-O1	172.0(1)	C38-Ir-O3	173.4(2)	C46-Ir-O1	173.8(1)
N1-Ir-N3	174.4(1)	N1-Ir-N4	171.8(1)	N3-Ir-N1	170.8(1)	N4-Ir-N1	172.2(1)
N1-Ir-N5	95.4(1)	N1-Ir-N7	101.2(1)	N3-Ir-N5	103.5(1)	N4-Ir-N7	103.0(1)
N1-Ir-O1	90.4(1)	N1-Ir-O1	82.9(1)	N3-Ir-O3	84.5(1)	N4-Ir-O1	82.5(1)
N3-Ir-N5	89.2(1)	N4-Ir-N7	87.0(1)	N1-Ir-N5	84.5(1)	N1-Ir-N7	84.0(1)
N3-Ir-O1	93.8(1)	N4-Ir-O1	99.7(1)	N1-Ir-O3	102.1(1)	N1-Ir-O1	102.7(1)
N5-Ir-O1	76.8(1)	N7-Ir-O1	76.3(1)	N5-Ir-O1	77.4(2)	N7-Ir-O1	76.4(1)

Table S4 Orbital composition analysis for **Ir1–Ir4** at their lowest singlet state (S_0) geometries

Complex	Orbital	Ir	C^N (1)				C^N (2)				N^O
			total	QZ	Th	substituent	total	QZ	Th	substituent	
Ir1	LUMO	1.7%	5.5%	3.9%	1.6%	--	91.8%	66.4%	17.0%	--	0.9%
	HOMO	33.0%	35.8%	22.7%	13.1%	--	27.7%	25.4%	10.4%	--	3.6%
Ir2	LUMO+1	2.2%	81.1%	59.6%	13.9%	7.6%	0.7%	0.5%	0.0%	0.2%	16.0%
	LUMO	3.0%	0.4%	0.1%	0.2%	0.0%	95.7%	71.4%	15.8%	8.5%	0.9%
	HOMO	34.7%	32.6%	7.7%	24.8%	0.1%	29.6%	7.1%	22.4%	0.1%	3.1%
Ir3	LUMO+1	3.3%	89.6%	69.5%	16.3%	3.8%	4.1%	7.9%	20.9%	0.0%	3.0%
	LUMO	3.5%	4.7%	3.4%	1.1%	0.2%	90.9%	71.2%	19.1%	0.6%	0.9%
	HOMO	34.3%	33.9%	9.0%	24.8%	0.0%	28.9%	3.4%	0.7%	0.0%	3.0%
Ir4	LUMO+1	3.6%	0.8%	0.5	0.3	0.0	94.3%	69.5%	13.8	11.0	1.4%
	LUMO	2.5%	94.5%	72.3	10.7	11.5	0.5%	0.2	0.2	0.0	2.5%
	HOMO	34.5%	30.4%	7.8	22.6	0.0	32.0%	7.8	23.9	0.3	3.1%

Table S5 Orbital composition analysis for **Ir1–Ir4** at their first excited triplet state (T_1) geometries.

Complex	Orbital	Ir	C^N (1)				C^N (2)				N^O
			total	QZ	Th	substituent	total	QZ	Th	substituent	
Ir1	LUMO+4	5.7	71.4	43.7	27.6	--	21.7	13.8	7.8	--	1.2
	LUMO	1.5	96.8	88.4	8.3	--	1.2	0.7	0.5	--	0.5
	HOMO	28.0	48.3	15.8	32.5	--	20.4	5.4	15.0	--	3.4
	HOMO-1	2.5	42.9	18.6	24.3	--	53.4	19.2	34.3	--	1.1
Ir2	LUMO+4	1.9	61.4	44.1	16.1	1.2	34.1	25.6	7.8	0.6	2.6
	LUMO	4.2	91.6	62.4	23.8	5.4	0.5	0.3	0.2	0.0	3.7
	HOMO	28.8	49.1	18.7	30.4	0.1	20.1	5.1	14.9	0.1	1.9
	HOMO-1	20.6	33.5	19.3	10.3	3.9	43.2	20.4	20.5	2.3	2.8
Ir3	LUMO	4.90	5.08	3.34	1.60	0.15	88.84	55.77	30.46	2.62	1.18
	HOMO	29.34	25.65	7.09	18.54	0.02	42.24	15.30	26.92	0.02	2.77
	HOMO-1	17.70	40.74	17.71	22.58	0.45	38.35	21.05	16.61	0.69	3.21
Ir4	LUMO	4.4	0.8	0.4	0.3	0.0	93.9	71.4	14.7	7.9	0.9
	HOMO	30.4	28.6	7.5	20.9	0.1	38.1	12.7	25.4	0.1	2.8
	HOMO-1	12.1	19.0	8.3	6.1	4.6	67.5	18.7	4.4	44.3	1.4
	HOMO-3	2.3	57.5	6.5	19.7	31.4	39.1	14.4	16.8	10.9	1.0

2. Characterizations: ^{1}H-NMR, ^{13}C-NMR, and MADIL-TOF-MS spectra

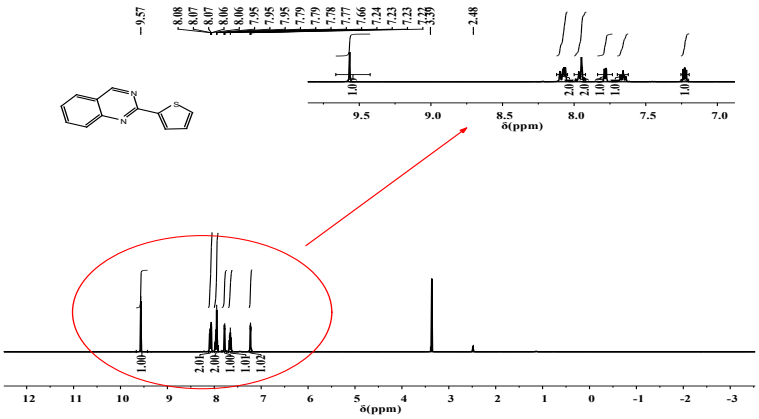

Figure S5. ^{1}H NMR of **L1** in DMSO

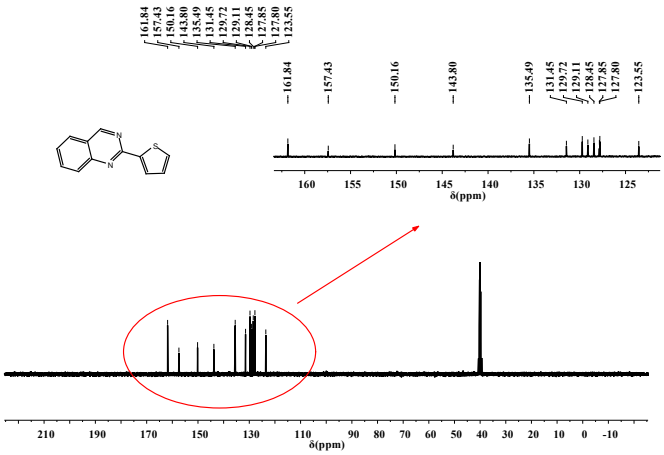

Figure S6. ^{13}C NMR of **L1** in DMSO

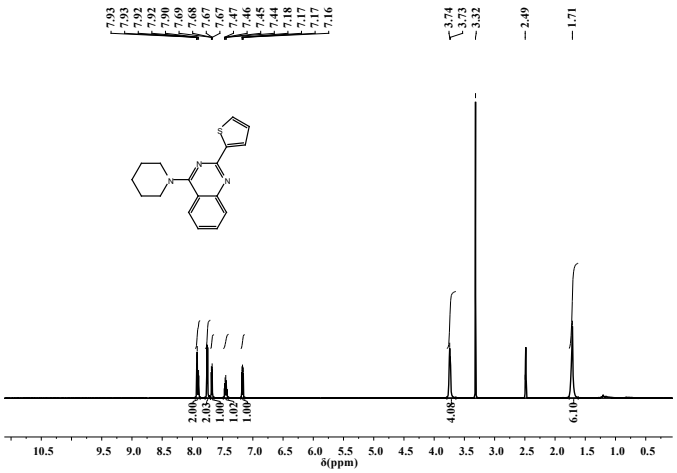

Figure S7. ^{1}H NMR of **L2** in DMSO

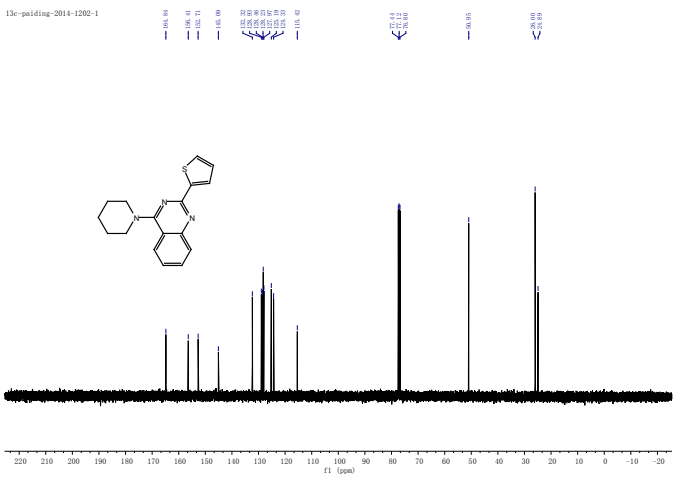

Figure S8. ^{13}C NMR of **L2** in DMSO

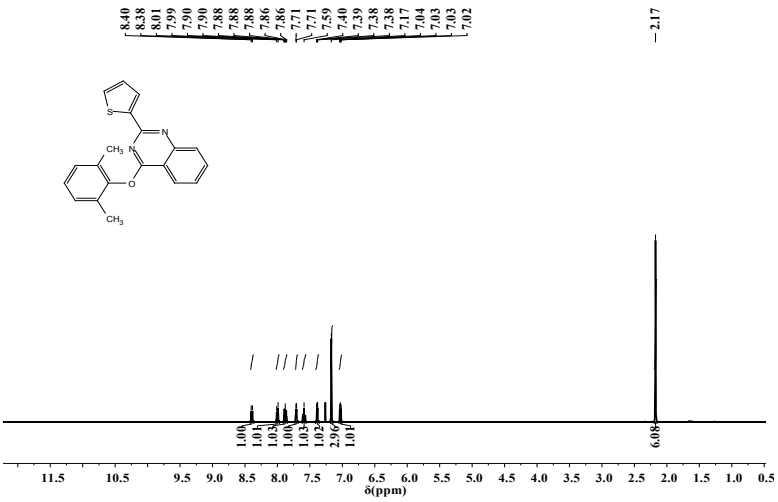

Figure S9. ^{1}H NMR of **L3** in $CDCl_3$

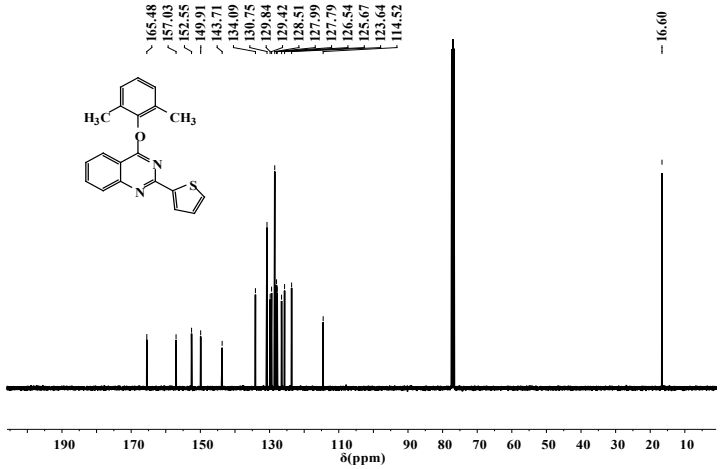

Figure S10. ^{13}C NMR of **L3** in $CDCl_3$

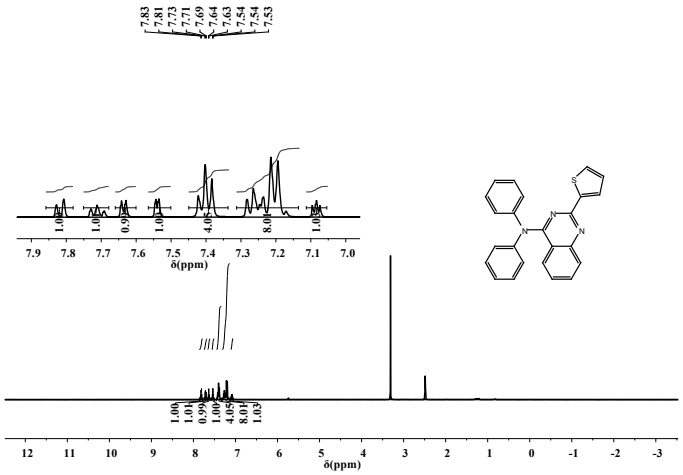

Figure S11. [1]H NMR of **L4** in DMSO

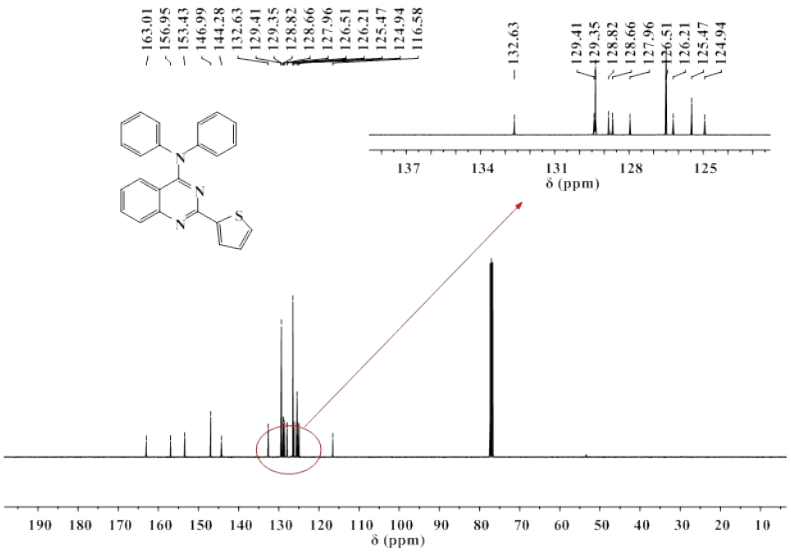

Figure S12. [13]C NMR of **L4** in $CDCl_3$

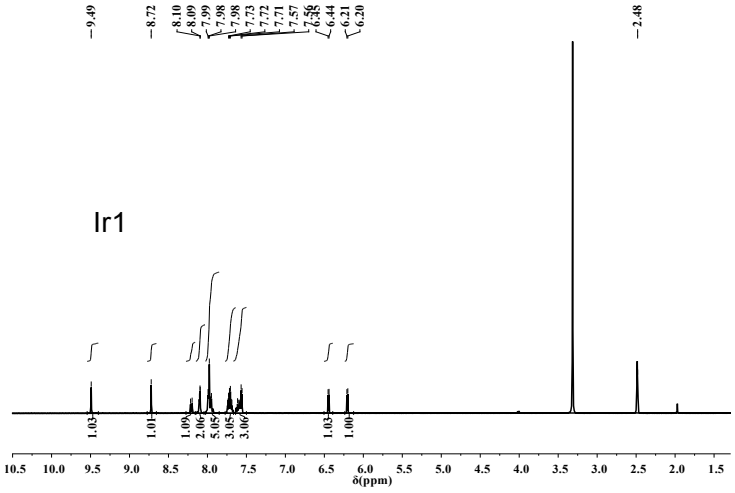

Figure S13. [1]H NMR of **Ir1** in DMSO

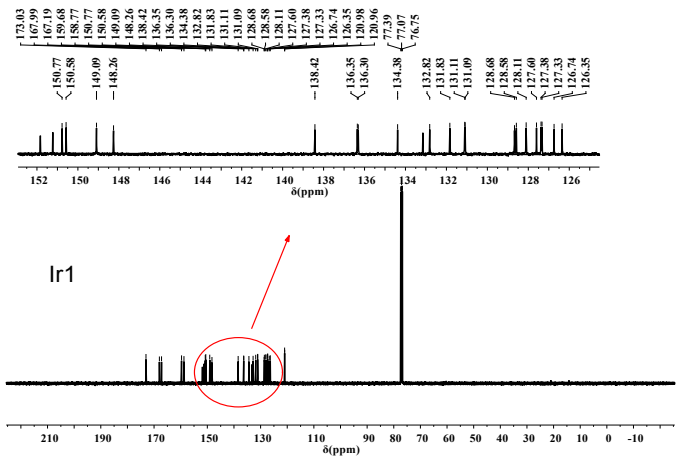

Figure S14. ^{13}C NMR of **Ir1** in $CDCl_3$

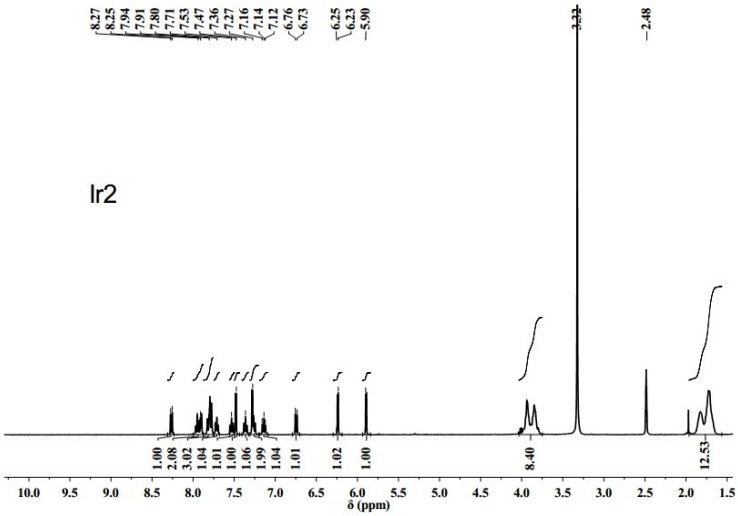

Figure S15. ^{1}H NMR of **Ir2** in DMSO

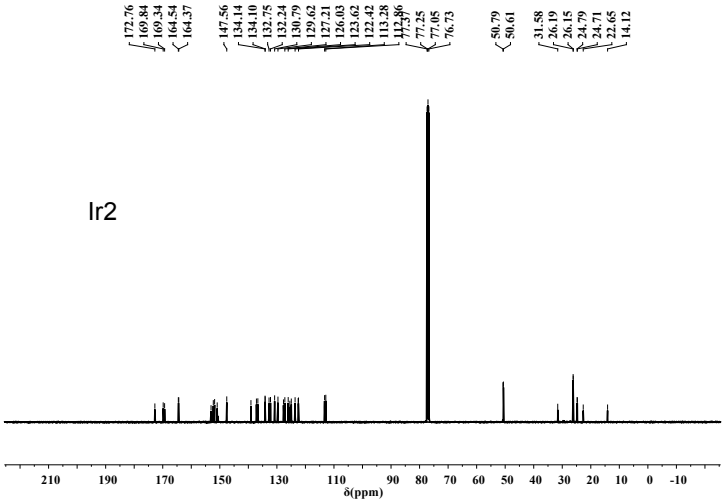

Figure S16. ^{13}C NMR of **Ir2** in $CDCl_3$

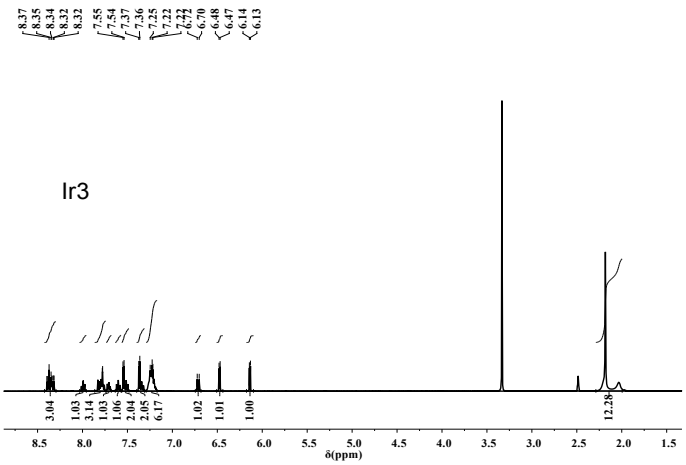

Figure S17. ^{1}H NMR of **Ir3** in DMSO

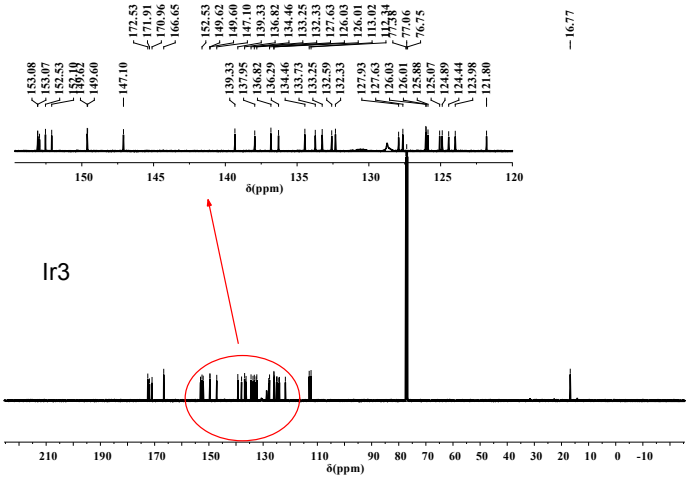

Figure S18. ^{13}C NMR of **Ir3** in $CDCl_3$

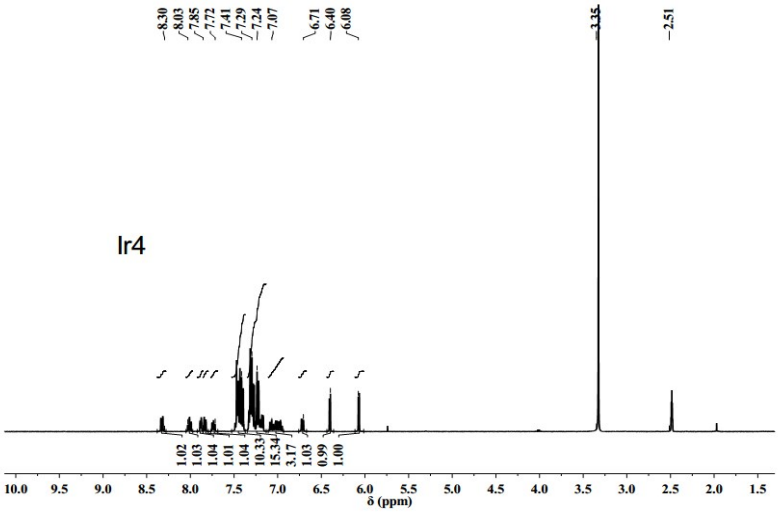

Figure S19. ^{1}H NMR of **Ir4** in DMSO

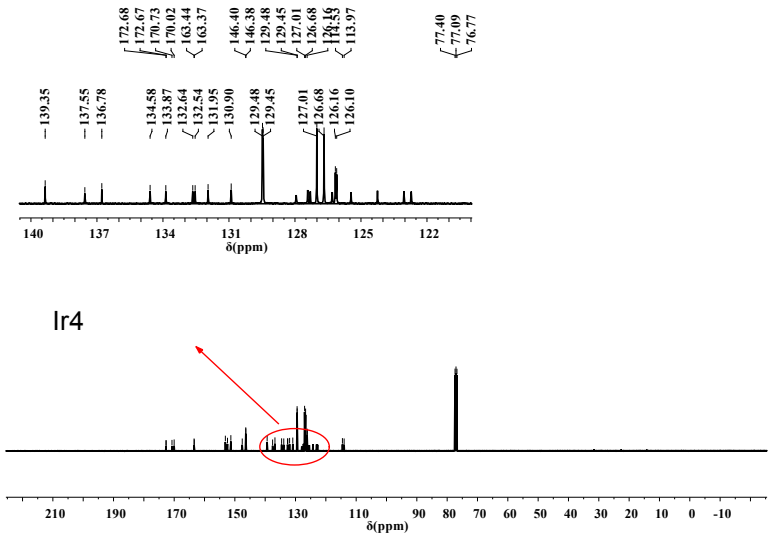

Figure S20. ^{13}C NMR of **Ir4** in $CDCl_3$

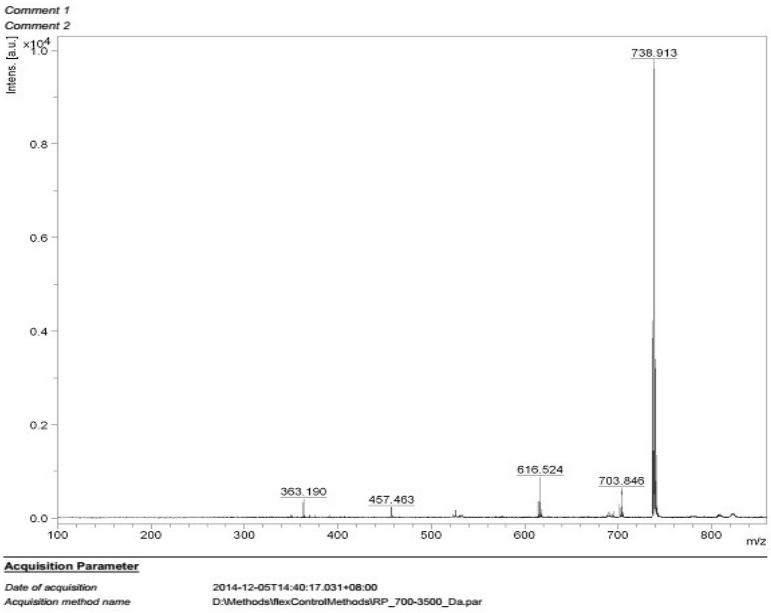

Figure S21. MALDI-TOF spectrum of **Ir1**

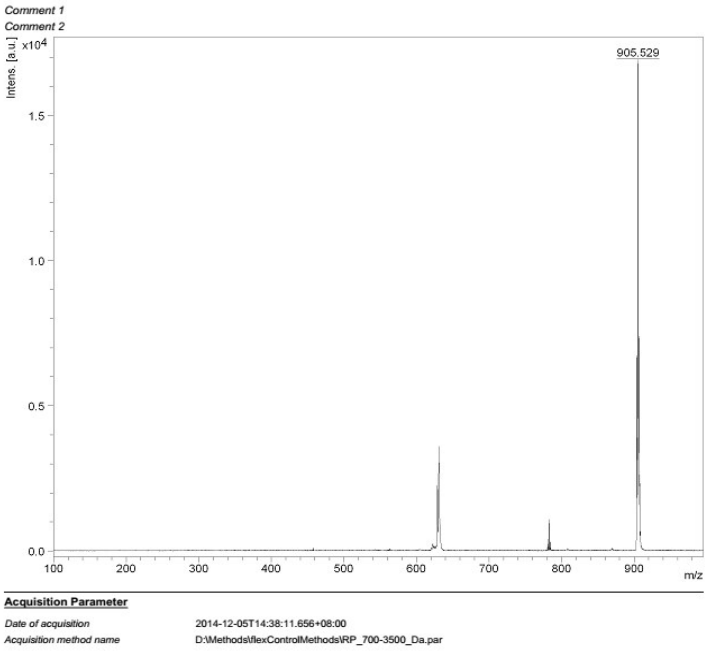

Figure S22. MALDI-TOF spectrum of **Ir2**

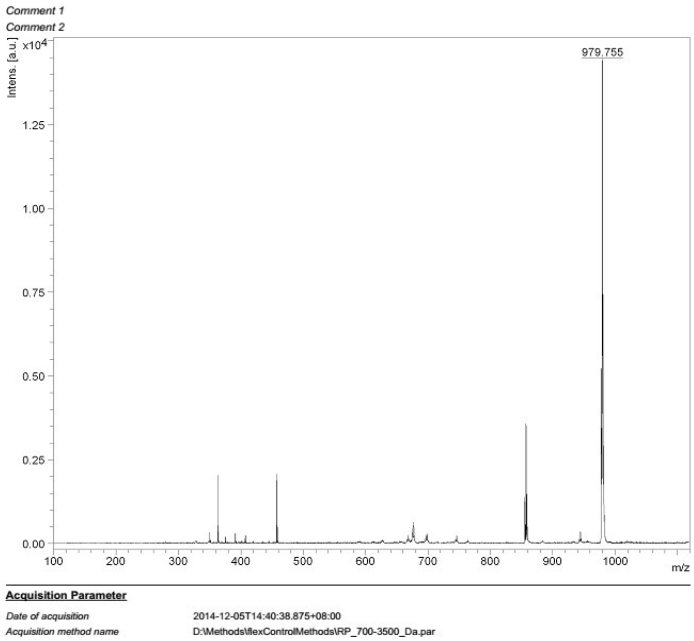

Figure S23. MALDI-TOF spectrum of **Ir3**

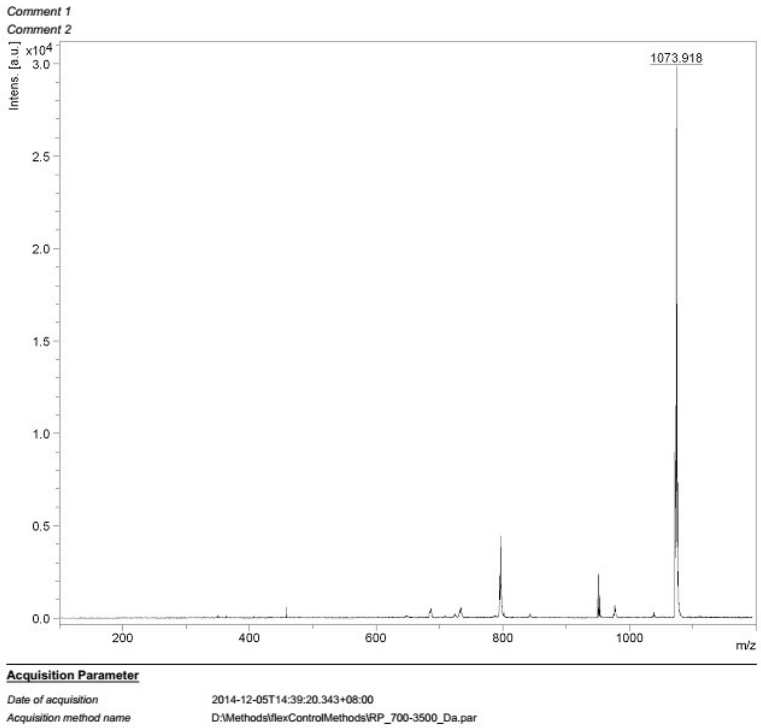

Figure S24. MALDI-TOF spectrum of **Ir4**