

Electronic Supplementary Information for

Cyclometalated Ir(III) complex with styryl-Bodipy ligands showing Near IR absorption/emission: preparation, study of photophysical properties and application as photodynamic/luminescence imaging materials

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1.0. Experimental, Synthesis and characterization data

Singlet oxygen ($^1\text{O}_2$) quantum yields (Φ_Δ)

Φ_Δ value of the triplet photosensitizers were calculated according to a modified literature method.¹ The quantum yields were calculated with MB ($\Phi_\Delta = 0.57$ in dichloromethane) as standard.² Quantum yields for singlet oxygen generation in CH_2Cl_2 , MeOH and a mixture of MeOH:H₂O(8:2) were determined by monitoring the photooxidation of 1,3-diphenylisobenzofuran (DPBF) sensitized by the Iridium complexes. 1, 3-Diphenylisobenzofuran (DPBF) was used as the $^1\text{O}_2$ scavenger, due to its fast reaction with $^1\text{O}_2$. The absorbance of DPBF was adjusted to around 1.0 at 414 nm and 407 nm in air saturated CH_2Cl_2 , MeOH and a mixture of MeOH:H₂O(9:1), respectively. Then, the photosensitizer was added to cuvette and photosensitizer's absorbance was adjusted to around 0.2–0.3. Then, the cuvette was exposed to monochromatic light at the specific wavelength for 10 seconds depending on the efficiency of the triplet photosensitizers. The photosensitizer and MB were irradiated at the same wavelength. Absorbance was measured six times after each irradiation. Then, the slope of the curves of absorbance maxima of DPBF at 414 nm and 407 nm versus irradiation time for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) were calculated according to the equation (eqn (1)):

$$\Phi_{\Delta\text{sam}} = \Phi_{\Delta\text{std}} \left(\frac{m_{\text{sam}}}{m_{\text{std}}} \right) \left(\frac{F_{\text{std}}}{F_{\text{sam}}} \right) \left(\frac{n_{\text{sam}}}{n_{\text{std}}} \right) \quad (\text{Eq. 1})$$

where "sam" and "std" designate the "Ir(III) photosensitizers" and "MB", respectively. "m" is the slope of difference in change in absorbance of DPBF (at 414 nm) with the irradiation time, "F" is the absorption correction factor, which is given by $F = 1 - 10^{-\text{OD}}$ (OD is the absorbance at the irradiation wavelength).

Singlet oxygen quantum yield (Φ_Δ) in a mixture of MeOH:H₂O (8:2) were calculated according to the equation (eqn (1)) and compared with the results of MeOH at 407 nm.

Synthesis of 5 and 6

Method A

To a solution of **2** (250 mg, 0.555 mmol) and *p*-(*N*, *N*-dimethylamino)benzaldehyde (328 mg, 2.22 mmol) in dry toluene, acetic acid (1.5 mL) and piperidine (1.5 mL) was added under N₂ atmosphere. The reaction mixture was heated at 120°C under reflux and a Dean Stark trap was used to remove the water produced by the condensation and the reaction was monitored by TLC (CH_2Cl_2 /Petroleum ether = 1:2 as eluent). After consumption of all the starting materials, the reaction mixture was cooled to room temperature and the majority of the solvent was evaporated under reduced pressure. Water (150 mL) was added to the residue and the product

was extracted from CH₂Cl₂ (3 × 100 mL). Organic phase was dried over Na₂SO₄, evaporated under reduced pressure, and the crude products thus obtained were purified by silica gel column chromatography (CH₂Cl₂/Petroleum ether = 1:2, v/v as eluent). The first band was collected to obtain a violet solid as compound **5**. Yield: 161 mg, 50%. mp 188–190 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.55–7.49 (m, 6H), 7.32–7.30 (m, 3H), 6.73–6.68 (m, 3H), 3.07 (s, 6H), 2.69 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 154.76, 145.25, 140.86, 139.98, 135.45, 132.69, 131.99, 129.84, 129.52, 129.39, 128.77, 128.35, 125.47, 123.09, 118.95, 115.79, 112.61, 111.29, 83.25, 40.24, 30.05, 16.56, 15.02. TOF MALDI-HRMS: calcd ([C₂₈H₂₇BF₂IN₃]⁺), *m/z* = 581.1311, found, *m/z* = 581.1329.

The second band, from the silica gel column chromatography of the same reaction mixture was isolated as grayish green solid as compound **6**. Yield: 93.3 mg, 23.6%. TOF MALDI-HRMS: calcd ([C₃₇H₃₆BF₂IN₄]⁺), *m/z* = 712.2046, found, *m/z* = 712.2017.

Method B

To a solution of **2** (250 mg, 0.555 mmol) and *p*-(*N*, *N*-dimethylamino)benzaldehyde (328 mg, 2.22 mmol) in dry toluene, acetic acid (1.5 mL) and piperidine (1.5 mL) was added under N₂ atmosphere. The reaction mixture was heated at 120°C under reflux by using a Dean Stark trap and the reaction was monitored by TLC (CH₂Cl₂/Petroleum ether = 1:2 as eluent). The moment the formation of the compound **6** found to be formed on the TLC plate, the reaction mixture was cooled to room temperature and the majority of the solvent was evaporated under reduced pressure. Water (150 mL) was added to the residue and the product was extracted from CH₂Cl₂ (3 × 100 mL). Organic phase was dried over Na₂SO₄, evaporated under reduced pressure, and the crude product thus obtained was purified by silica gel column chromatography (CH₂Cl₂/Petroleum ether = 1:2, v/v as eluent). The violet solid was obtained as compound **5**. Yield: 213.5 mg, 66.2%.

Following the similar synthesis procedure, the above reaction mixture was refluxed for 12 hrs until most of compound **5** was converted to compound **6**, as visualized from TLC (CH₂Cl₂/Petroleum ether = 1:2 as eluent). After that the reaction mixture was cooled to rt, the solvent was evaporated, water (150 mL) was added and was extracted from CH₂Cl₂ (3 × 100 mL). The crude product thus obtained on evaporating the organic phase, was purified by column chromatography (silica gel, CH₂Cl₂/Petroleum ether = 1:2, v/v as eluent). The grayish green solid was obtained as compound **6**. Yield: 207.2 mg, 52.4%.

The spectral data of compound **5/6** obtained by **Method B** is superimposable with that of **Method A**.

Synthesis of L3

To a deaerated solution of compound **5** (116 mg, 0.20 mmol) and 5-ethynyl-2,2-bipyridine (36 mg, 0.20 mmol) in the mixed solvent of triethylamine (5 mL) and THF (10 mL), Pd(PPh₃)₄ (11.6 mg, 0.01 mmol, 5 mol%) and CuI (3.8 mg, 0.02 mmol, 10 mol%) were added under an Ar atmosphere. The reaction mixture was refluxed for 12 h at 85°C. Thereafter the synthetic procedure is similar to that of **L1**; a violet solid compound **L3** was obtained. Yield: 71.3 mg, 56.3%. mp 308–310 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.70 (s, 1H), 8.64 (d, 1H, *J* = 4 Hz), 8.39 (t, 2H, *J* = 8 Hz), 7.82 (dd, 2H, *J* = 20 Hz, 8 Hz), 7.51–7.49 (m, 5H), 7.42 (d, 1H, *J* = 16 Hz), 7.34–7.30 (m, 4H), 6.71–6.68 (m, 3H), 3.03 (s, 6H), 2.70 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 157.01, 155.30, 154.06, 153.36, 151.69, 151.05, 149.19, 144.91, 140.17, 139.74, 138.78, 138.69, 137.02, 136.96, 134.88, 134.51, 129.93, 129.58, 129.15, 129.03, 128.44, 123.88, 121.01, 120.12, 118.75, 113.16, 111.93, 92.39, 87.20, 39.93, 29.68, 14.66, 12.70. TOF MALDI-HRMS: calcd ([C₄₀H₃₄BF₂N₅]⁺), *m/z* = 633.2875, found, *m/z* = 633.2845.

Synthesis of **L4**

To a deaerated solution of compound **6** (142 mg, 0.20 mmol) and 5-ethynyl-2,2-bipyridine (36 mg, 0.20 mmol) in the mixed solvent of triethylamine (5 mL) and THF (10 mL), Pd(PPh₃)₄ (11.6 mg, 0.01 mmol, 5 mol%) and CuI (3.8 mg, 0.02 mmol, 10 mol%) were added under an Ar atmosphere. The reaction mixture was refluxed for 12 h at 85°C. Thereafter the synthetic procedure is similar to that of **L1**; a greyish green solid compound **L4** was obtained. Yield: 75.2 mg, 49.2%. mp 316–318 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.72 (d, 1H, *J* = 12 Hz), 8.58 (s, 1H), 8.36 (t, 2H, *J* = 8 Hz), 8.23 (d, 1H, *J* = 16 Hz), 7.85 (dd, 1H, *J* = 20 Hz, 8 Hz), 7.76 (t, 1H, *J* = 8 Hz), 7.61 (d, 2H, *J* = 8 Hz), 7.55 (t, 1H, *J* = 8 Hz), 7.50–7.41 (m, 6H), 7.28–7.21 (m, 4H), 6.70–6.62 (m, 5H), 2.98–2.96 (m, 12H), 1.50 (s, 3H), 1.39 (s, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 171.51, 155.88, 151.87, 151.52, 151.29, 150.46, 149.68, 143.92, 142.57, 140.67, 139.5, 138.89, 137.92, 137.36, 135.54, 132.35, 131.58, 129.38, 129.46, 129.33, 129.17, 127.92, 125.46, 124.85, 124.64, 124.29, 121.75, 121.45, 120.76, 120.67, 120.54, 118.87, 114.04, 112.58, 112.36, 111.29, 94.61, 89.54, 81.21, 40.36, 40.23, 30.04, 14.96, 13.01. TOF MALDI-HRMS: calcd ([C₄₉H₄₃BF₂N₆]⁺), *m/z* = 764.3610, found, *m/z* = 764.3625.

2.0. NMR and HR MS spectra

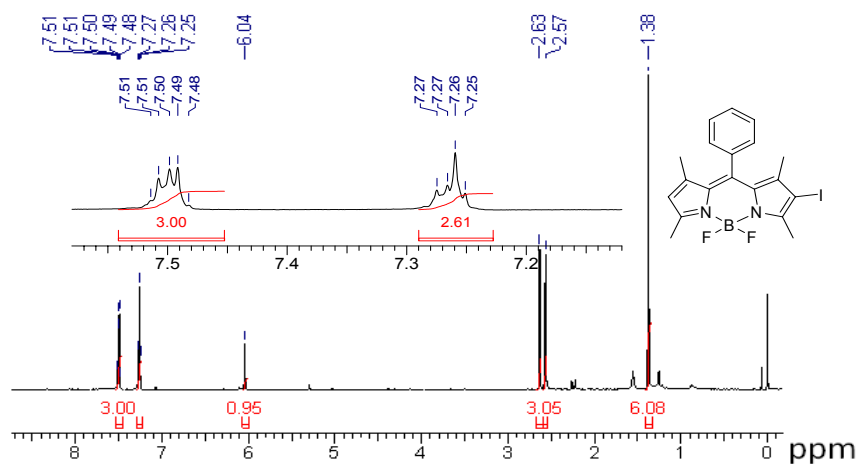


Fig. S1. ¹H NMR spectrum of Compound **2** (400 MHz, CDCl₃).

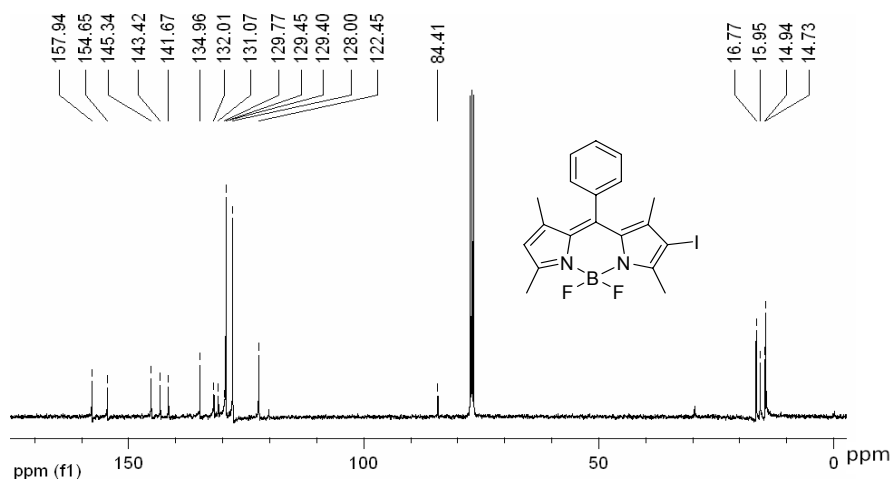


Fig. S2. ¹³C NMR spectrum of Compound **2** (100 MHz, CDCl₃).

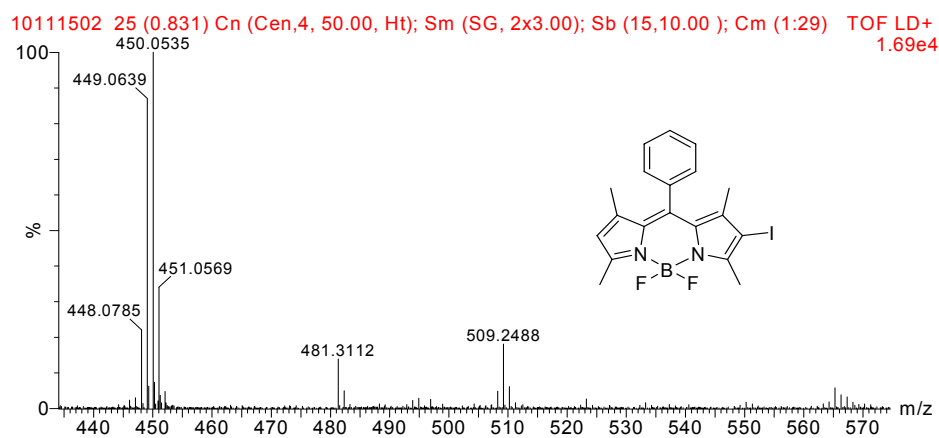


Fig. S3. MALDI-HRMS of compound **2**

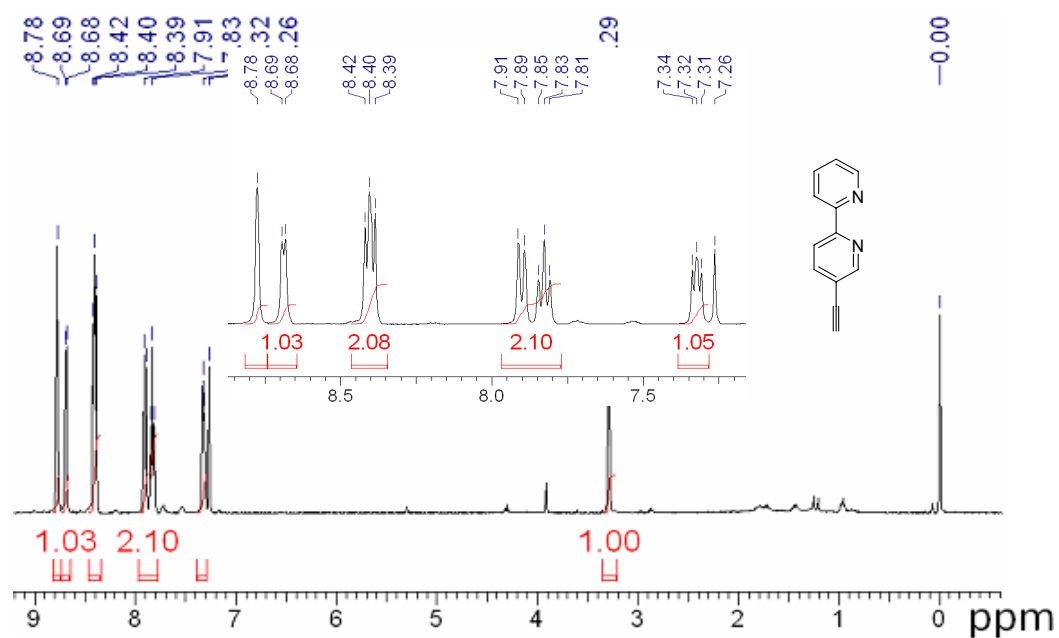


Fig. S4. ¹H NMR spectrum of 5-ethynyl-2, 2'-bipyridine (400 MHz, CDCl₃).

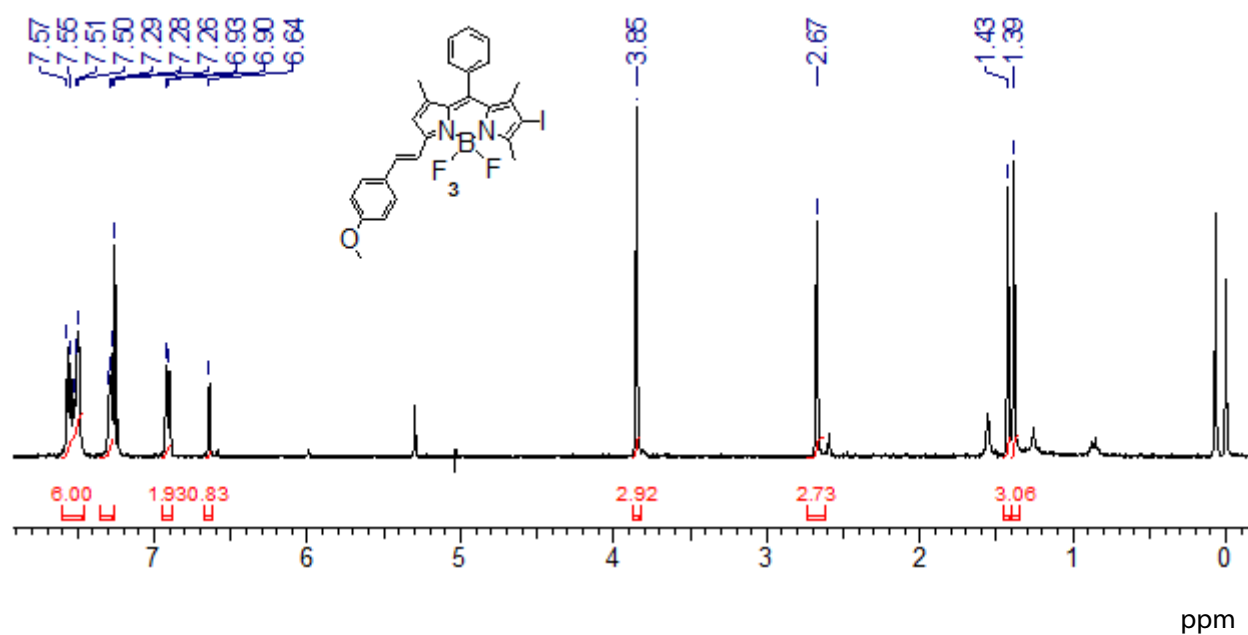


Fig. S5. ¹H NMR spectrum of Compound **3** (400 MHz, CDCl₃).

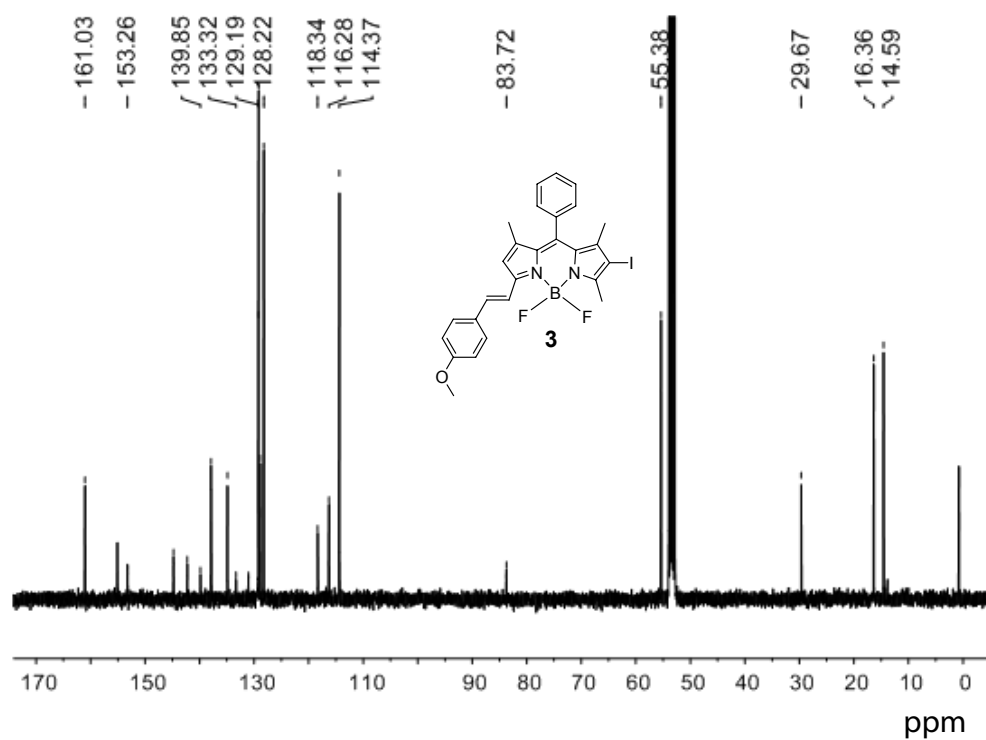


Fig. S6. ^{13}C NMR spectrum of Compound **3** (100 MHz, CDCl_3).

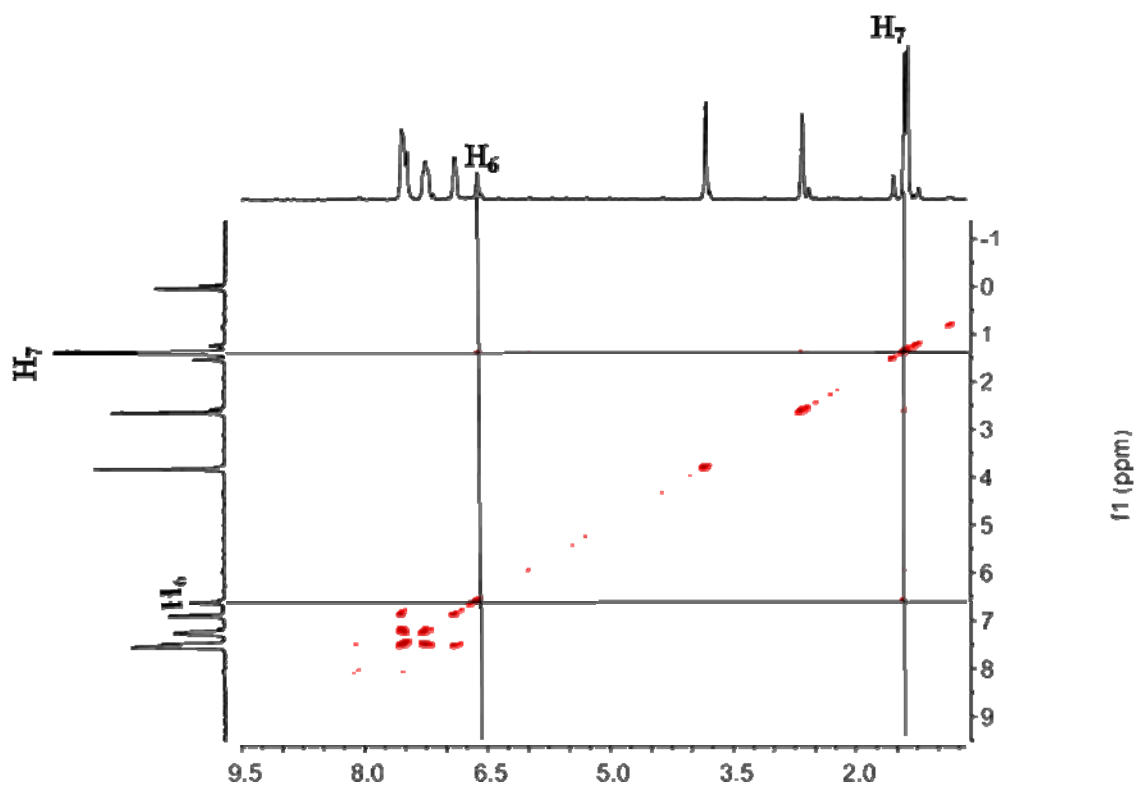


Fig. S7. ^1H - ^1H 2D g-COSY NMR of compound **3** (400 MHz, CDCl_3).

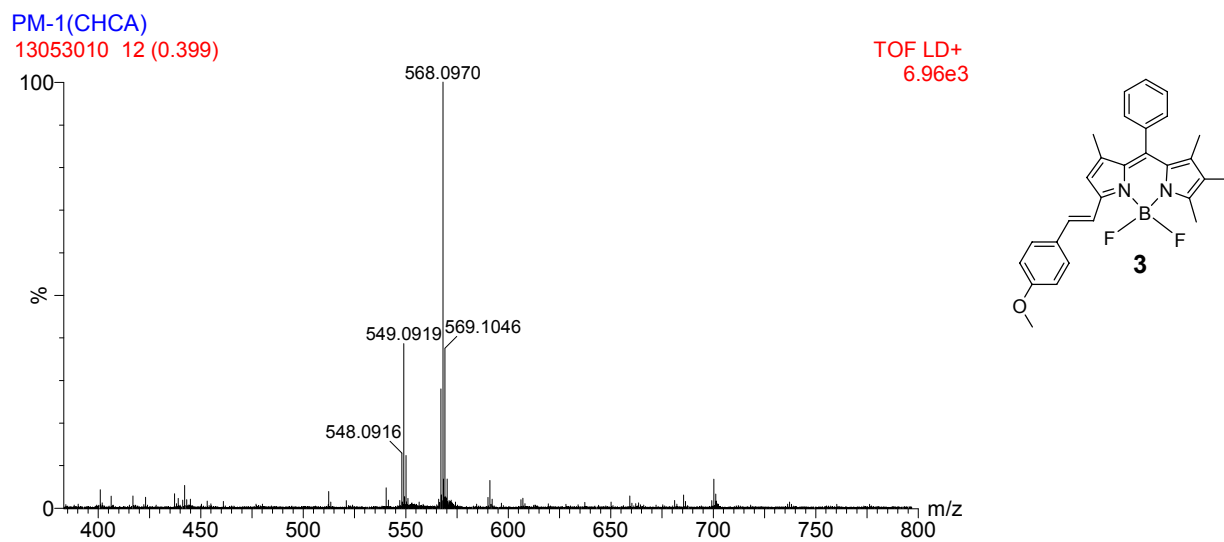


Fig. S8. TOF MALDI-HRMS of compound **3**

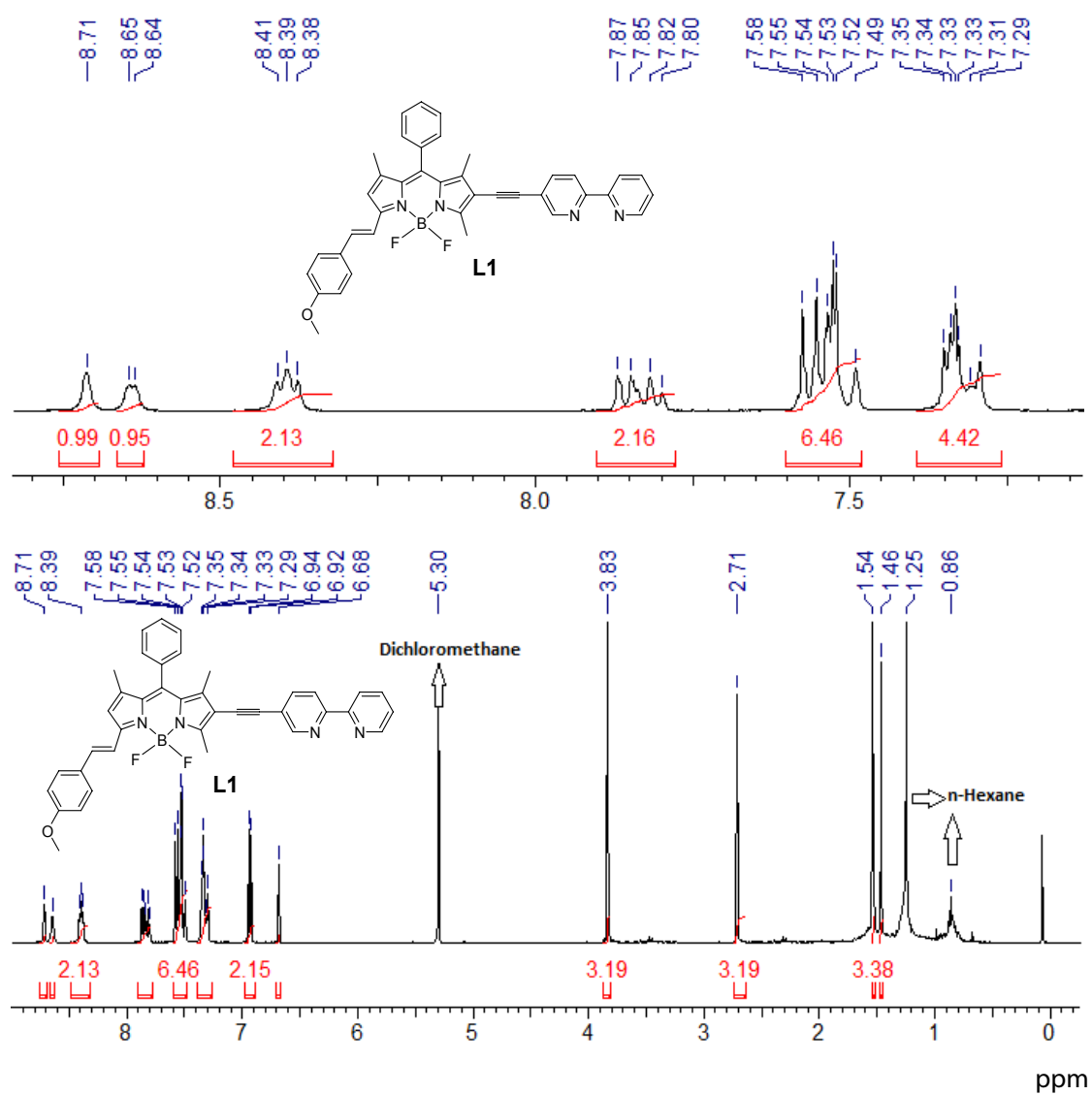


Fig. S9. ^1H NMR spectrum of Compound **L1** (400 MHz, CD_2Cl_2).

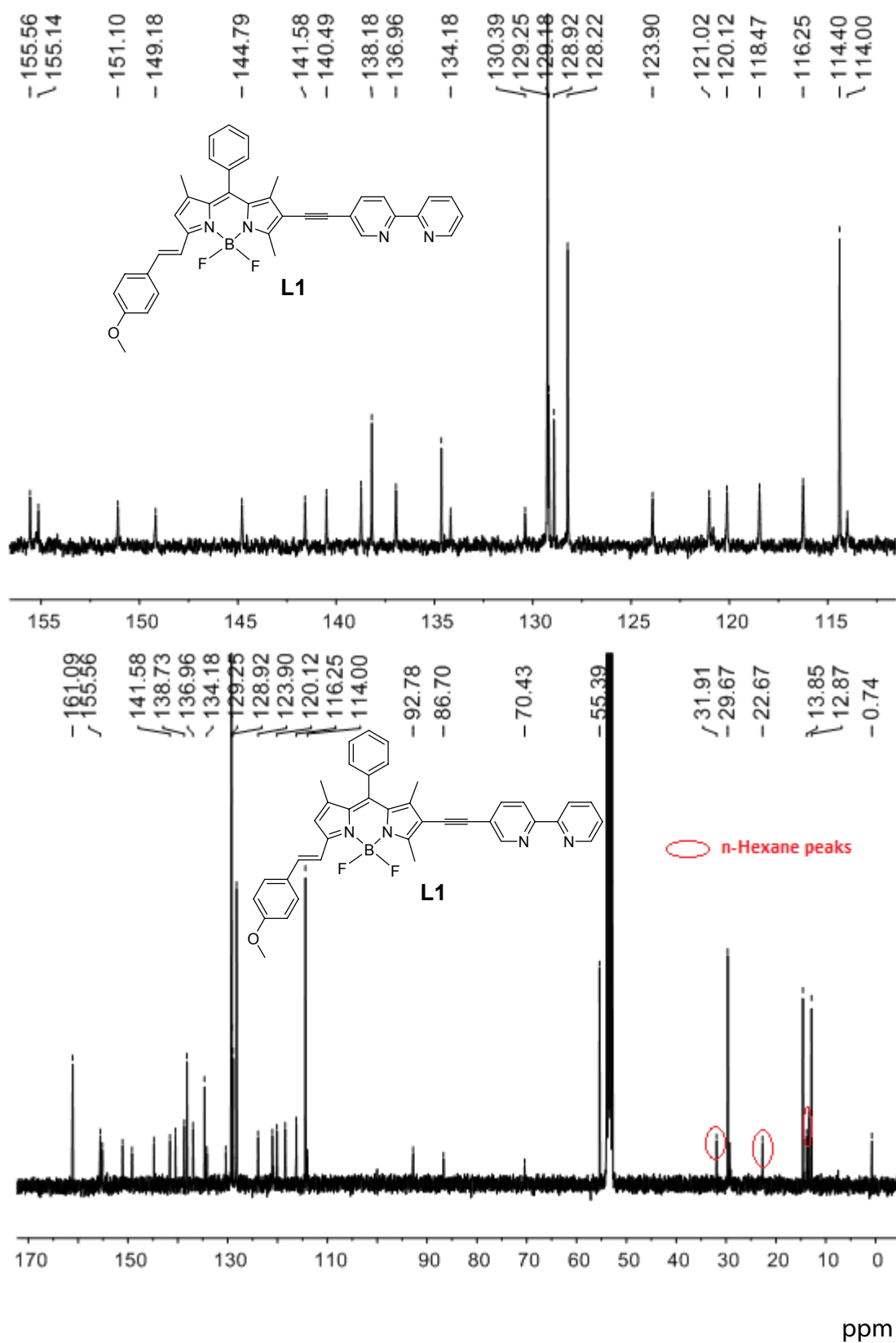


Fig. S10. ^{13}C NMR spectrum of Compound **L1** (100 MHz, CD_2Cl_2).

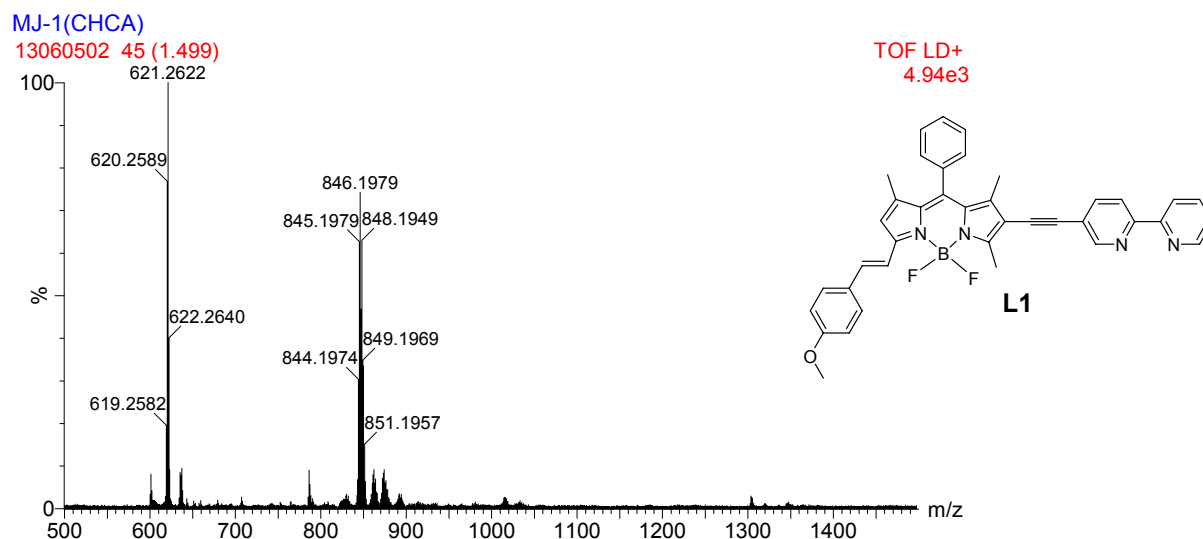


Fig. S11. TOF MALDI-HRMS of compound **L1**

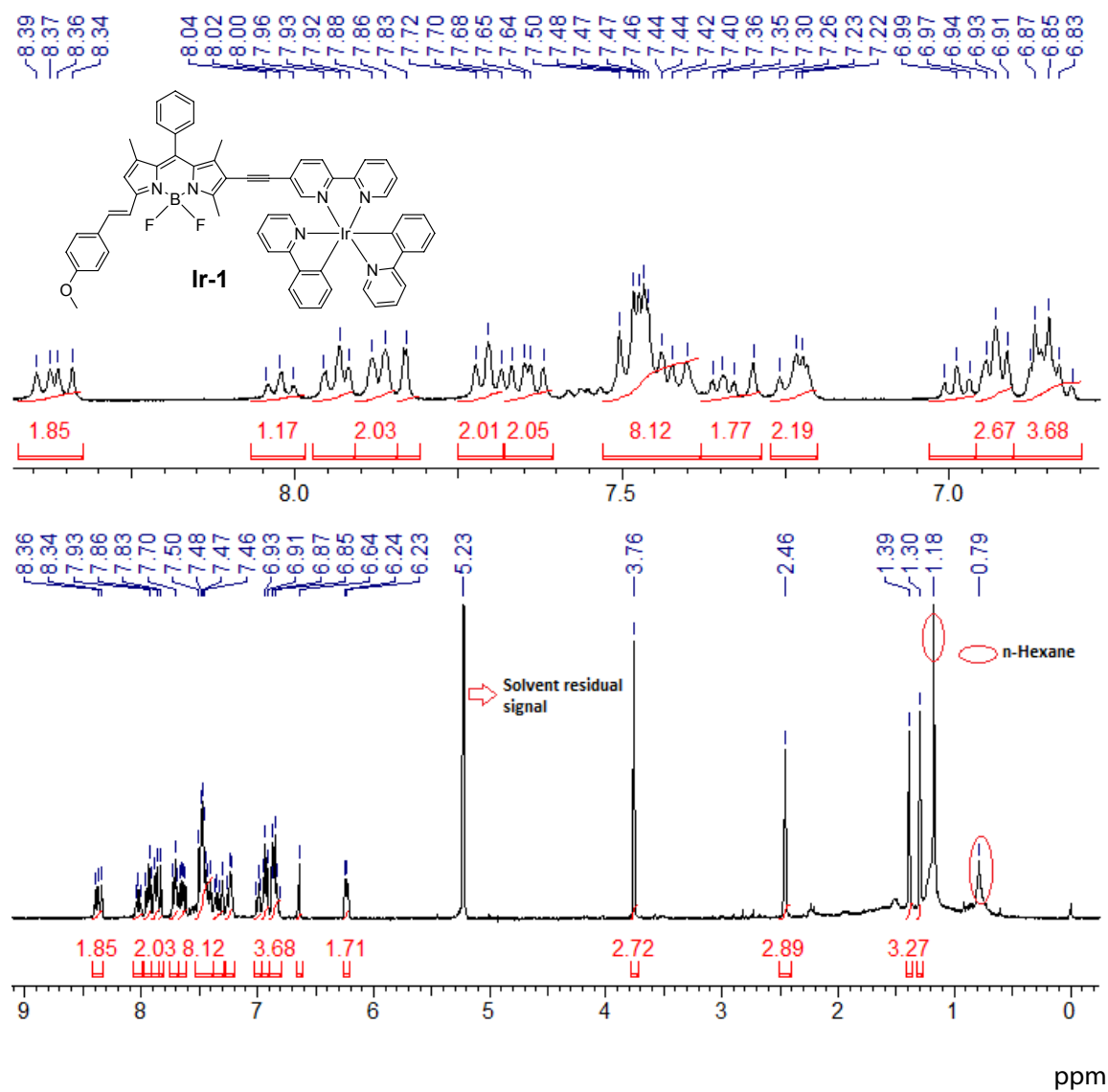


Fig. S12. ^1H NMR spectrum of Compound **Ir-1** (400 MHz, CD_2Cl_2).

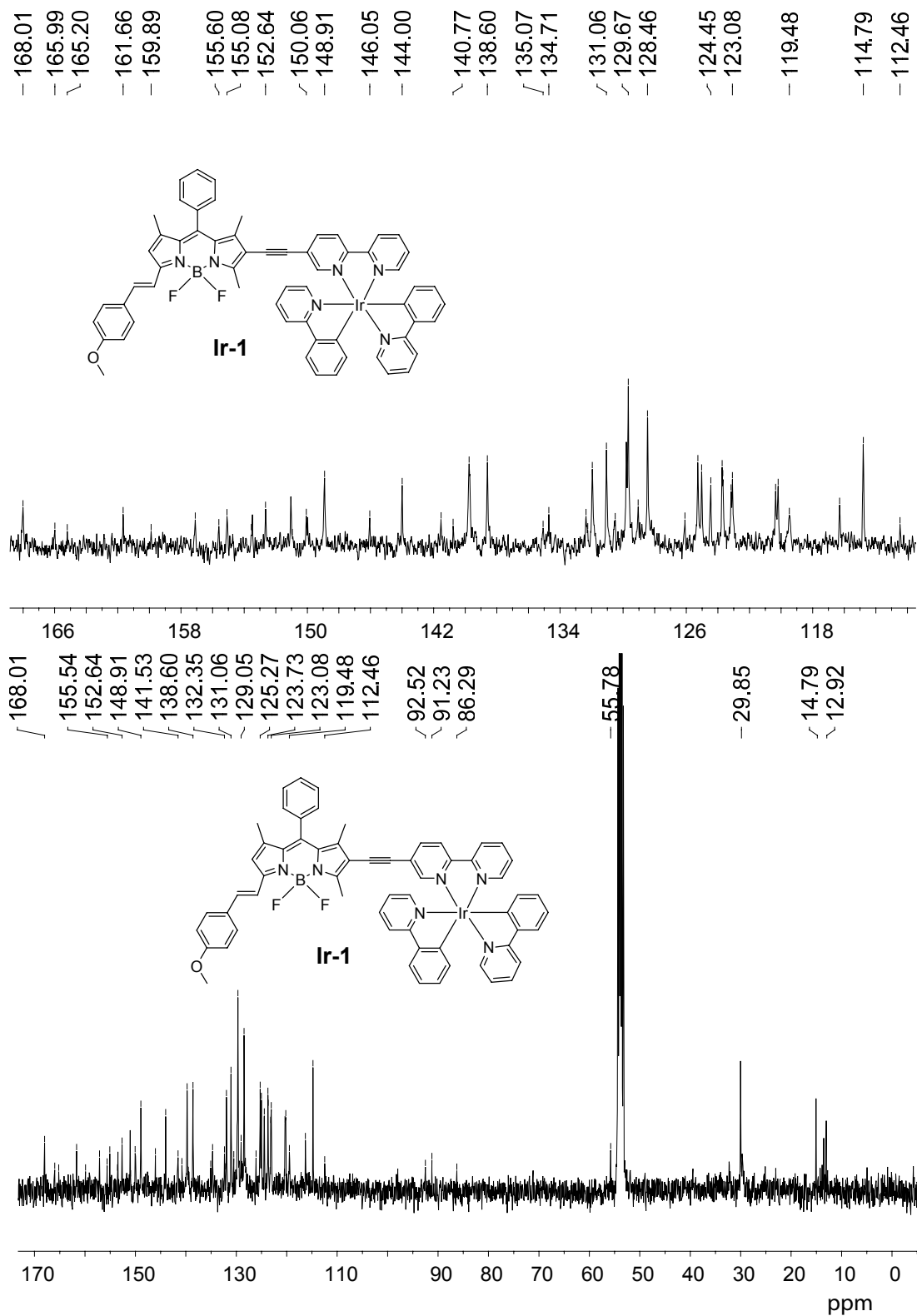


Fig. S13. ^{13}C NMR spectrum of Compound **Ir-1** (100 MHz, CD_2Cl_2).

MJ-5(CHCA)
13060506 14 (0.467)

TOF LD+
4.92e3

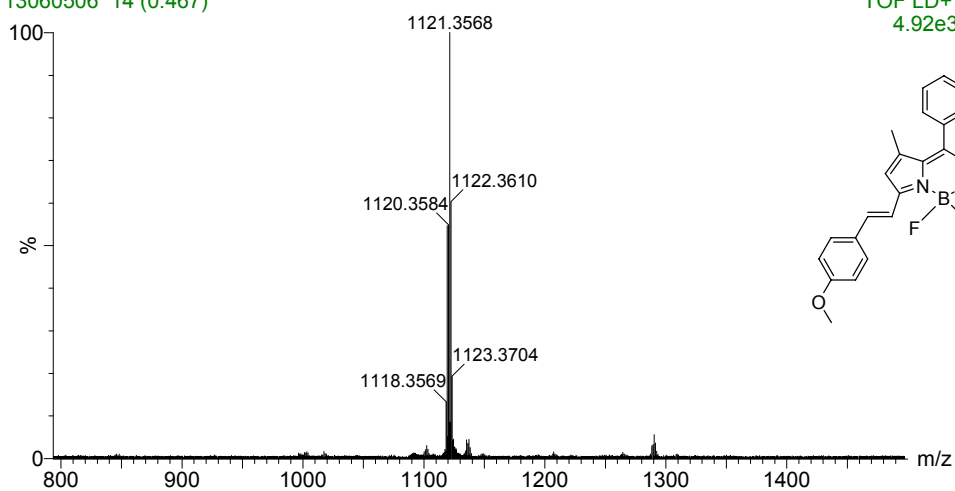


Fig. S14. TOF MALDI-HRMS of compound **Ir-1**

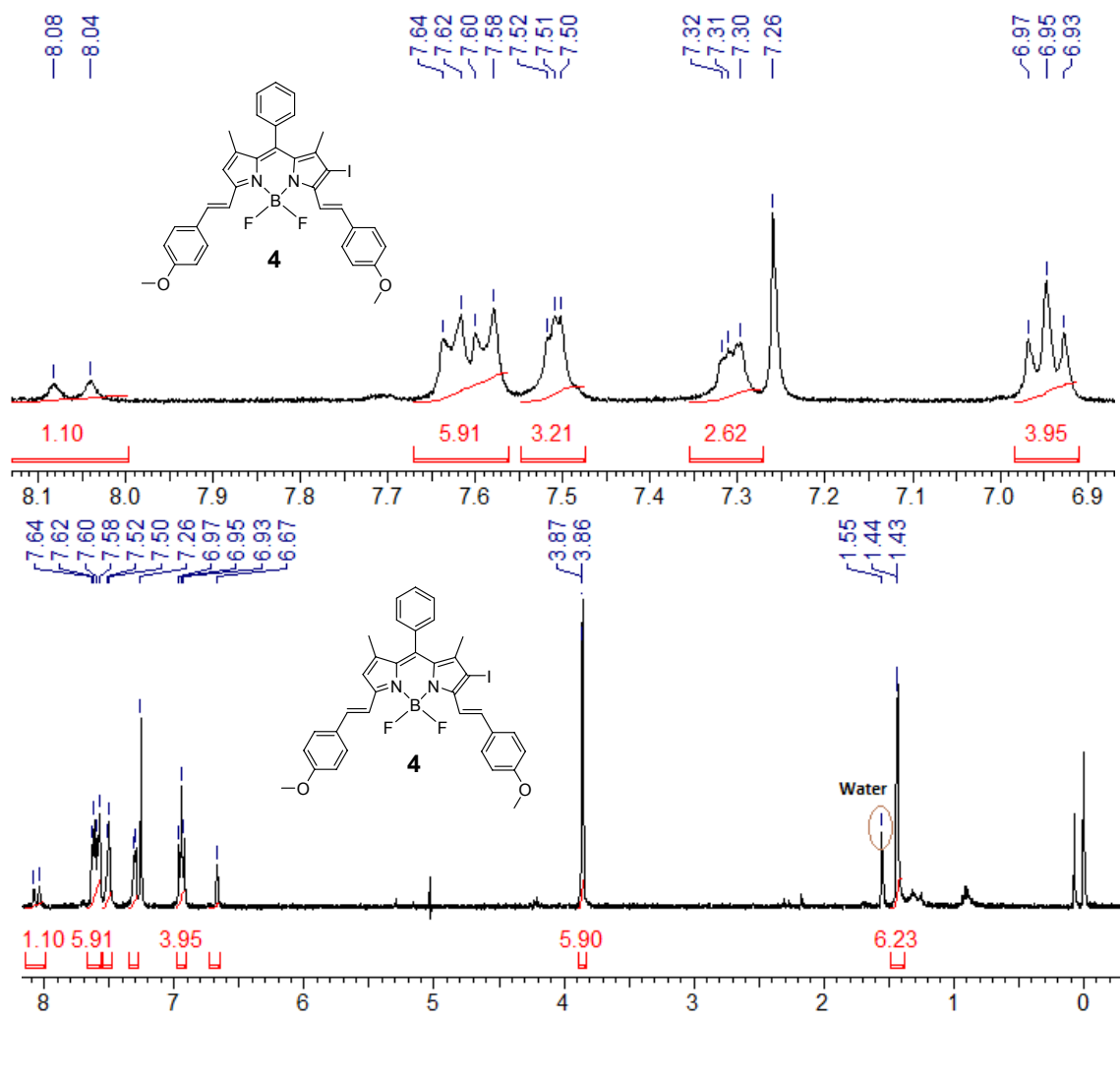


Fig. S15. ^1H NMR spectrum of Compound **4** (400 MHz, CDCl_3).



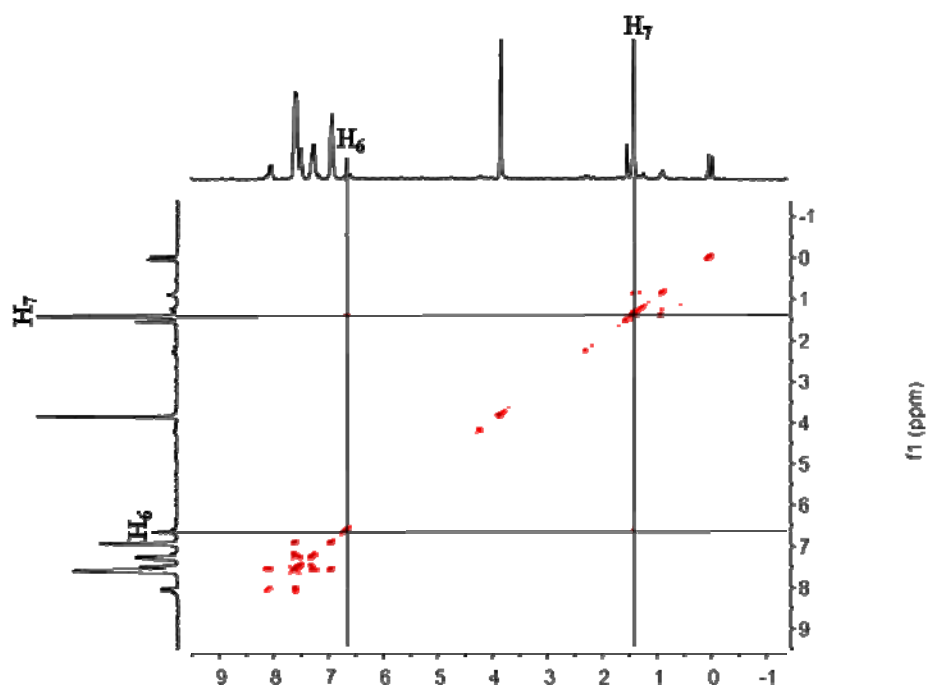


Fig. S17. ^1H - ^1H 2D g-COSY NMR of compound **4** (400 MHz, CDCl_3).

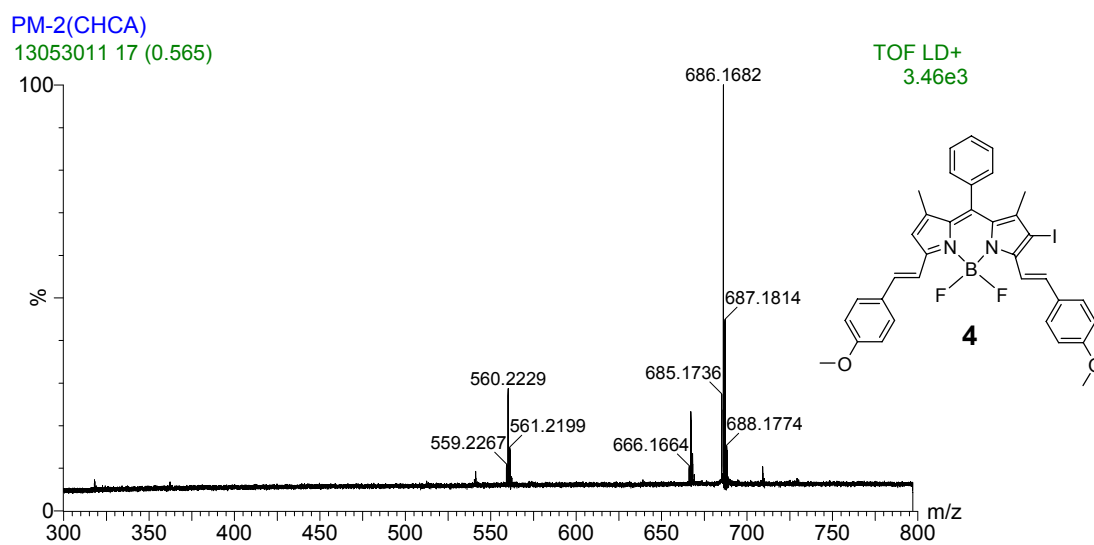


Fig. S18. TOF MALDI-HRMS of compound **4**.

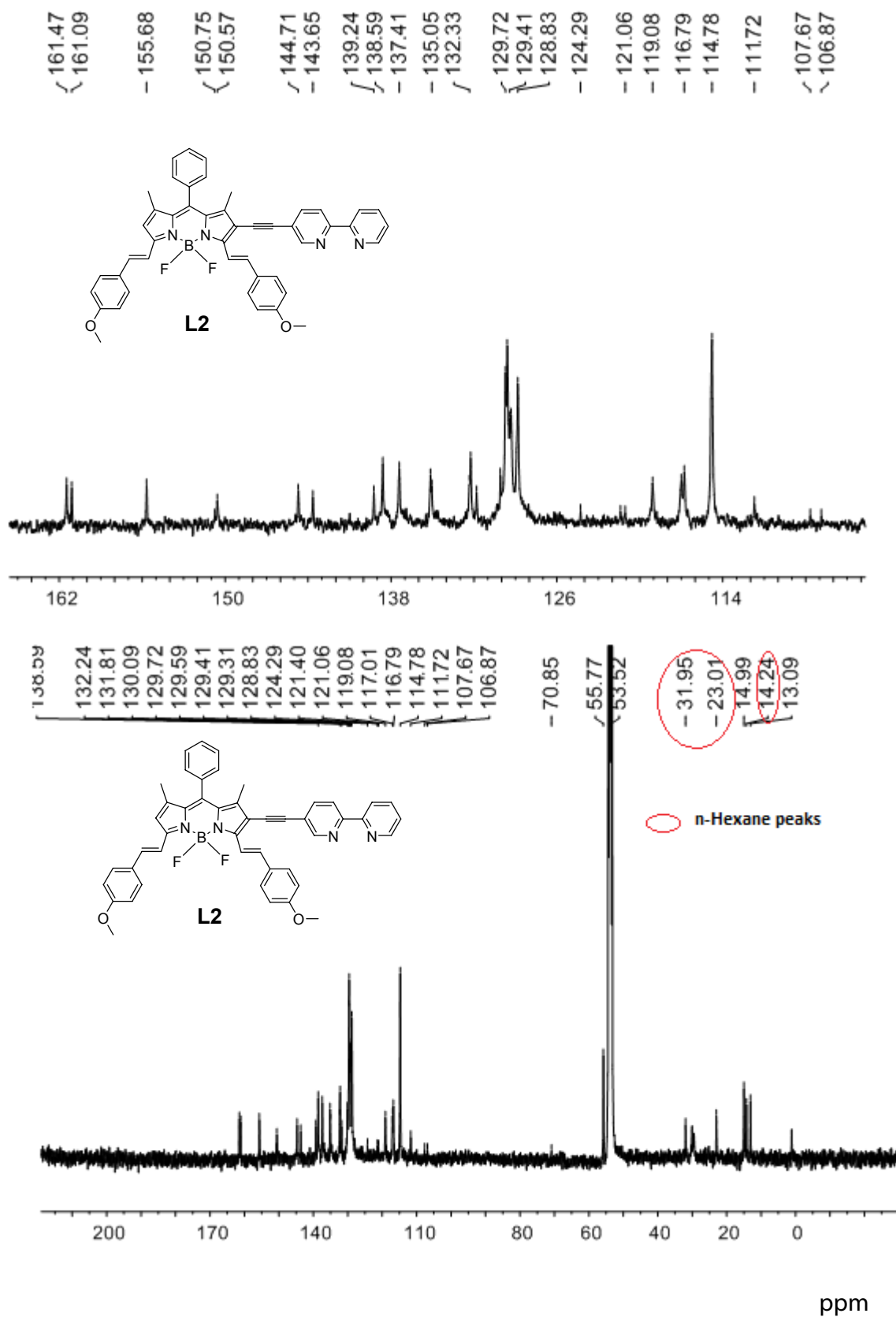


Fig. S20. ^{13}C NMR spectrum of Compound **L2** (100 MHz, CD_2Cl_2).

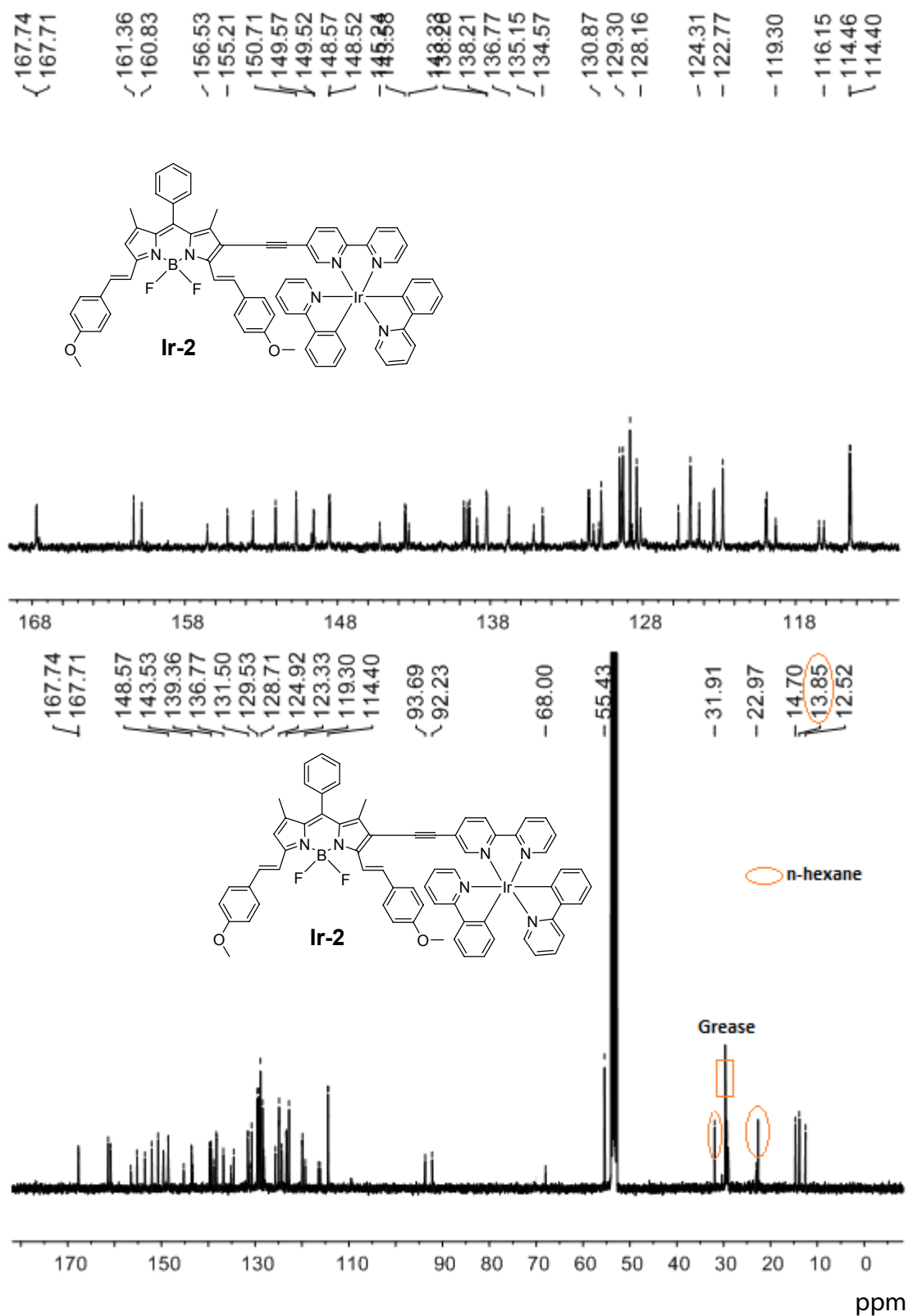


Fig. S23. ¹³C NMR spectrum of Compound **Ir-2** (100 MHz, CD₂Cl₂).

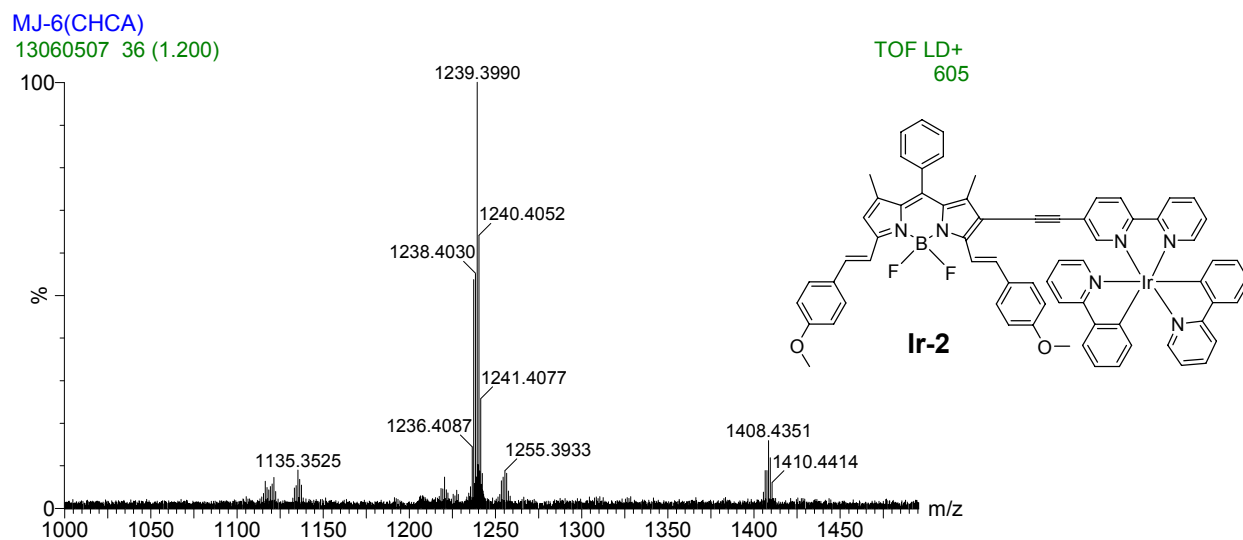


Fig. S24. TOF MALDI HRMS of compound Ir-2

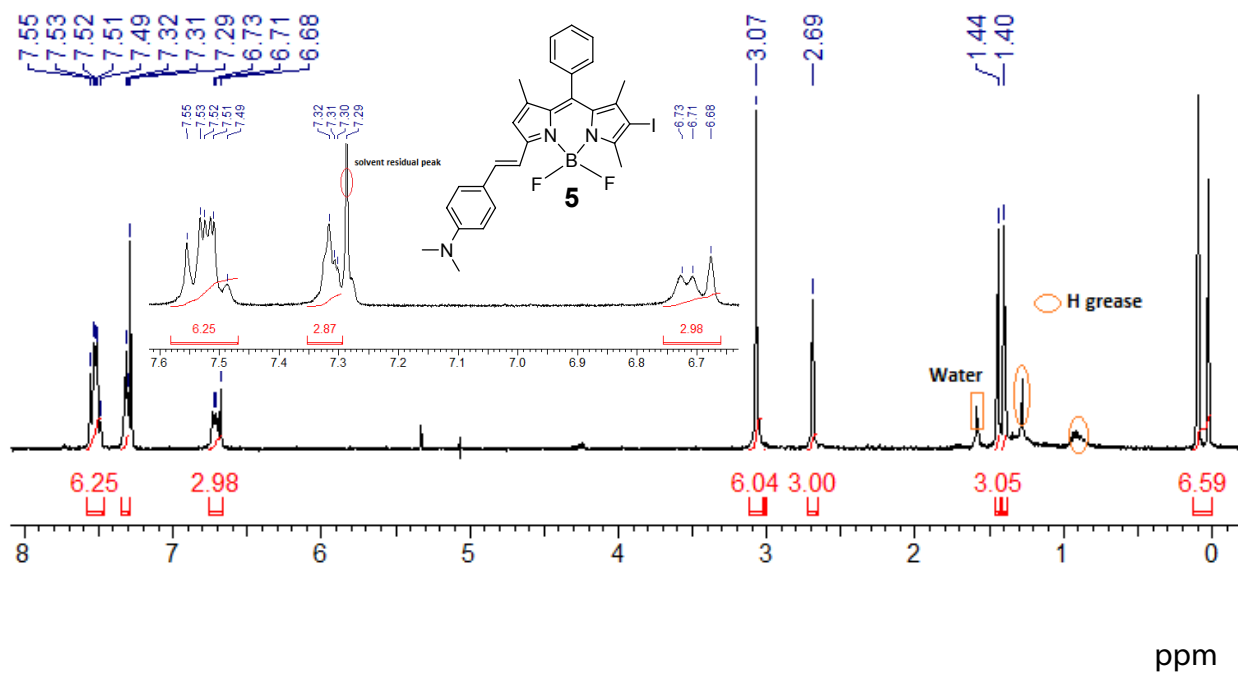


Fig. S25. ^1H NMR spectrum of Compound 5 (400 MHz, CDCl_3).

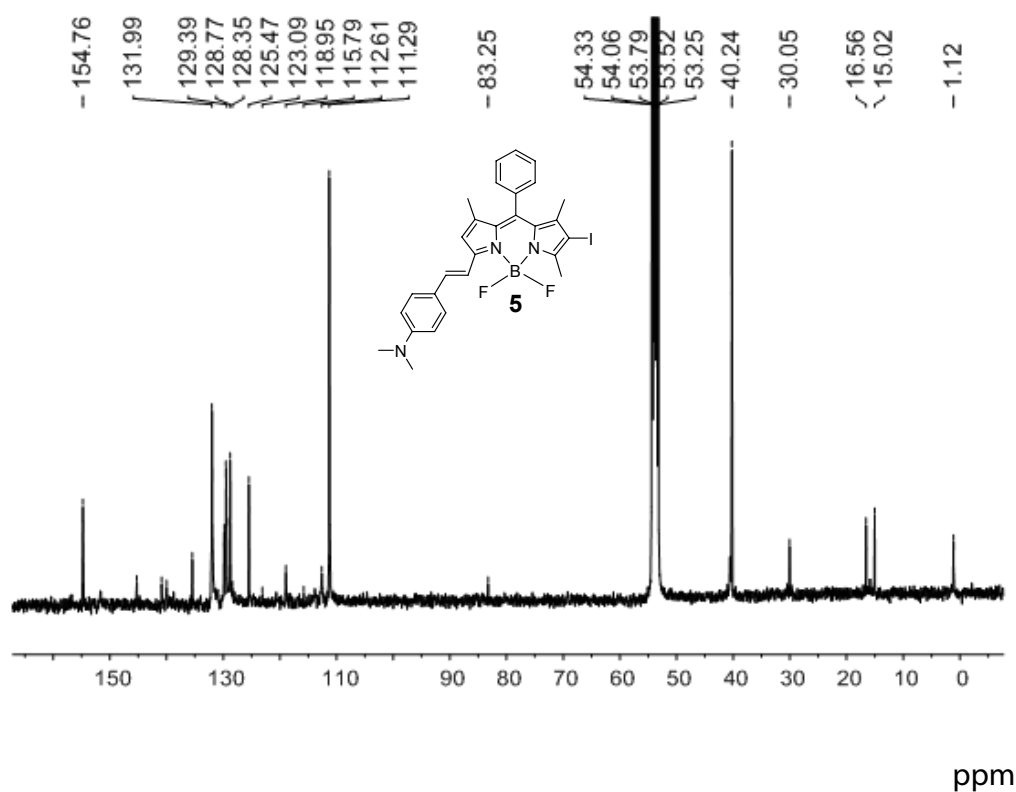


Fig. S26. ^{13}C NMR spectrum of Compound **5** (100 MHz, CDCl_3).

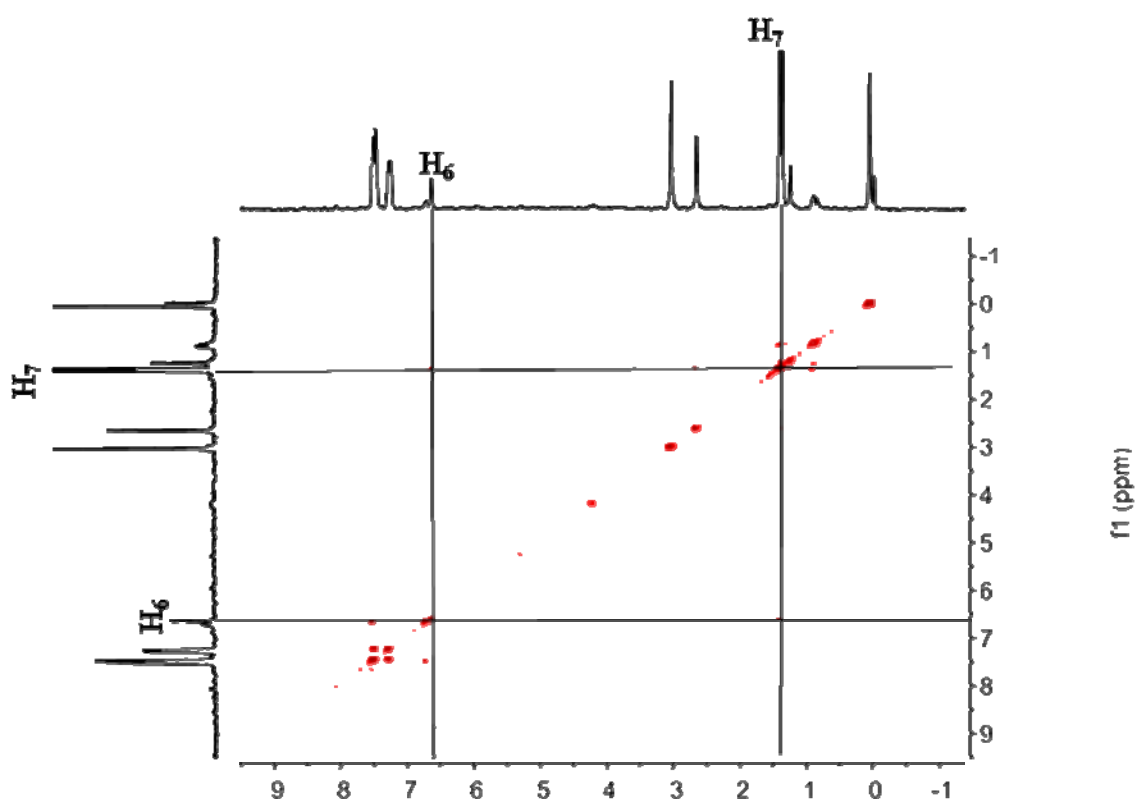


Fig. 27. ^1H - ^1H 2D g-COSY NMR of compound **5** (400 MHz, CDCl_3).

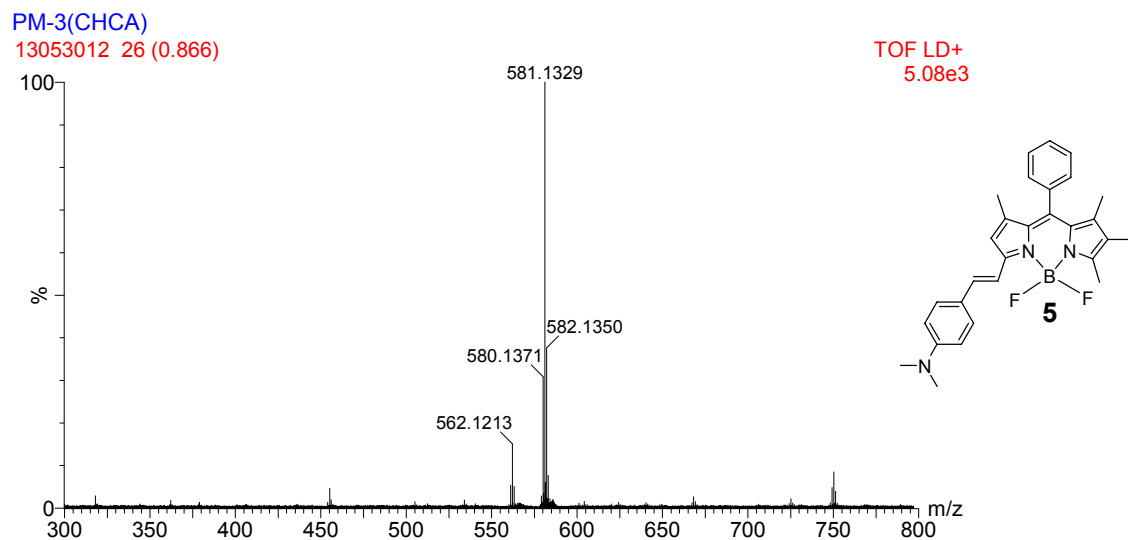


Fig. S28. TOF MALDI-HRMS of compound **5**

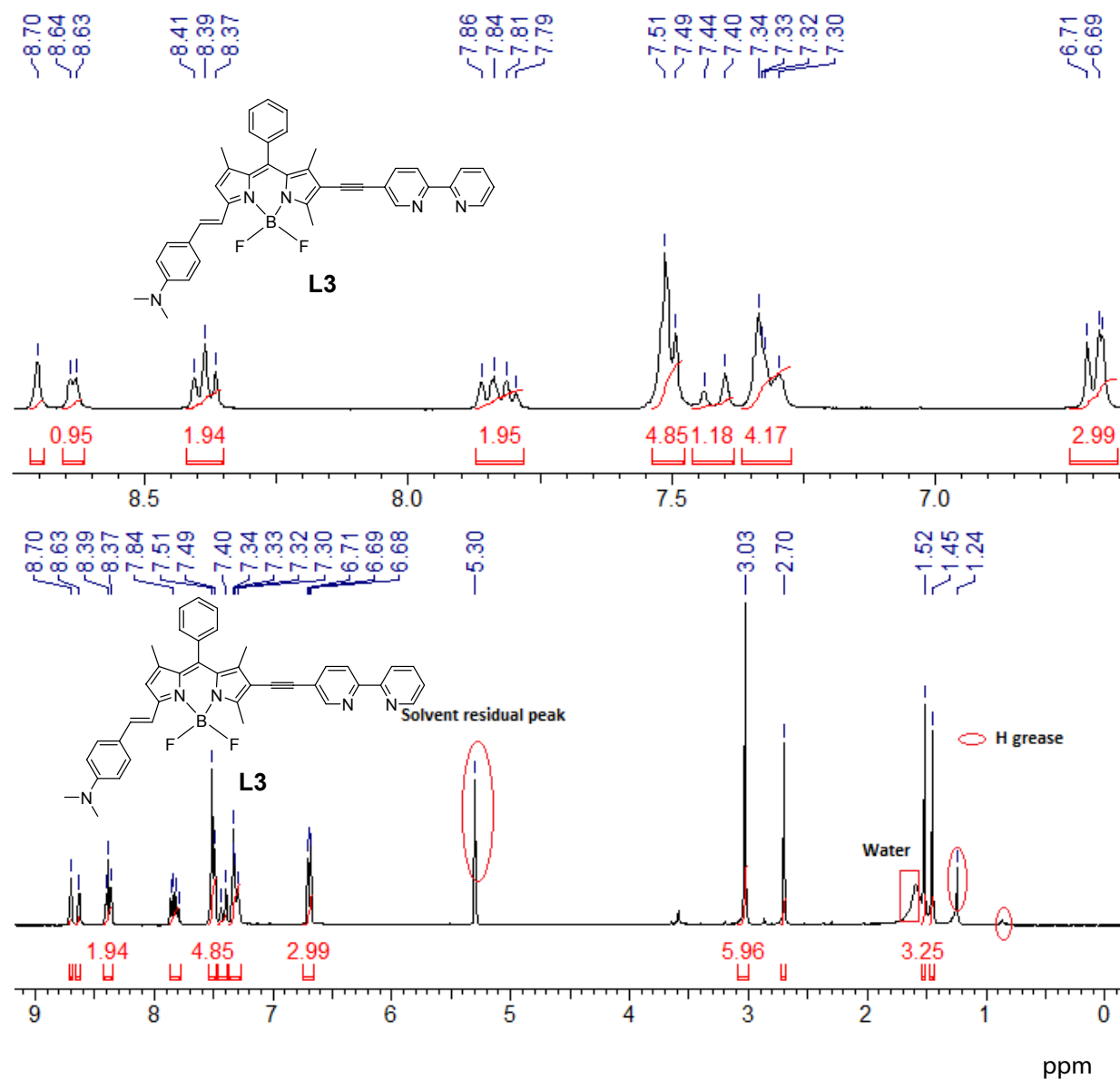


Fig. S29. ^1H NMR spectrum of Compound **L3** (400 MHz, CD_2Cl_2).

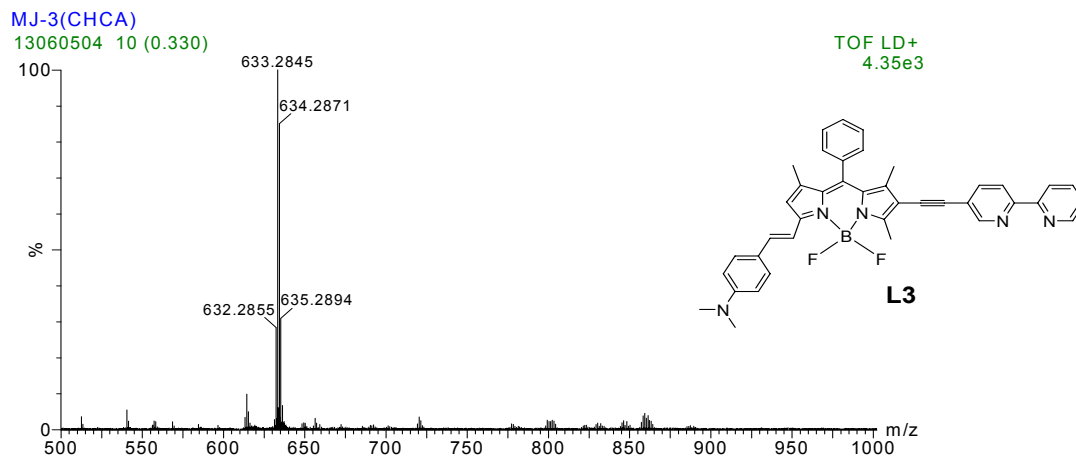


Fig. S30. TOF MALDI-HRMS of compound **L3**

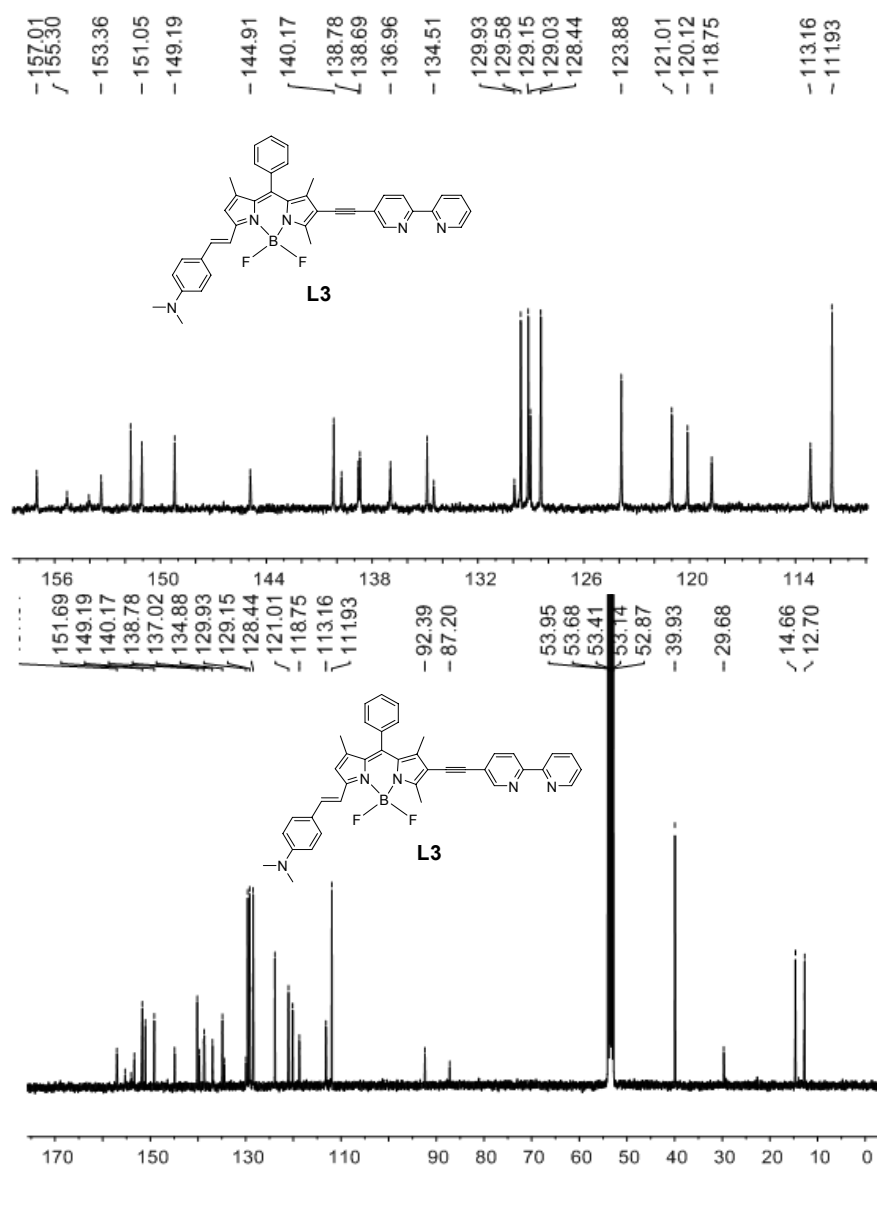
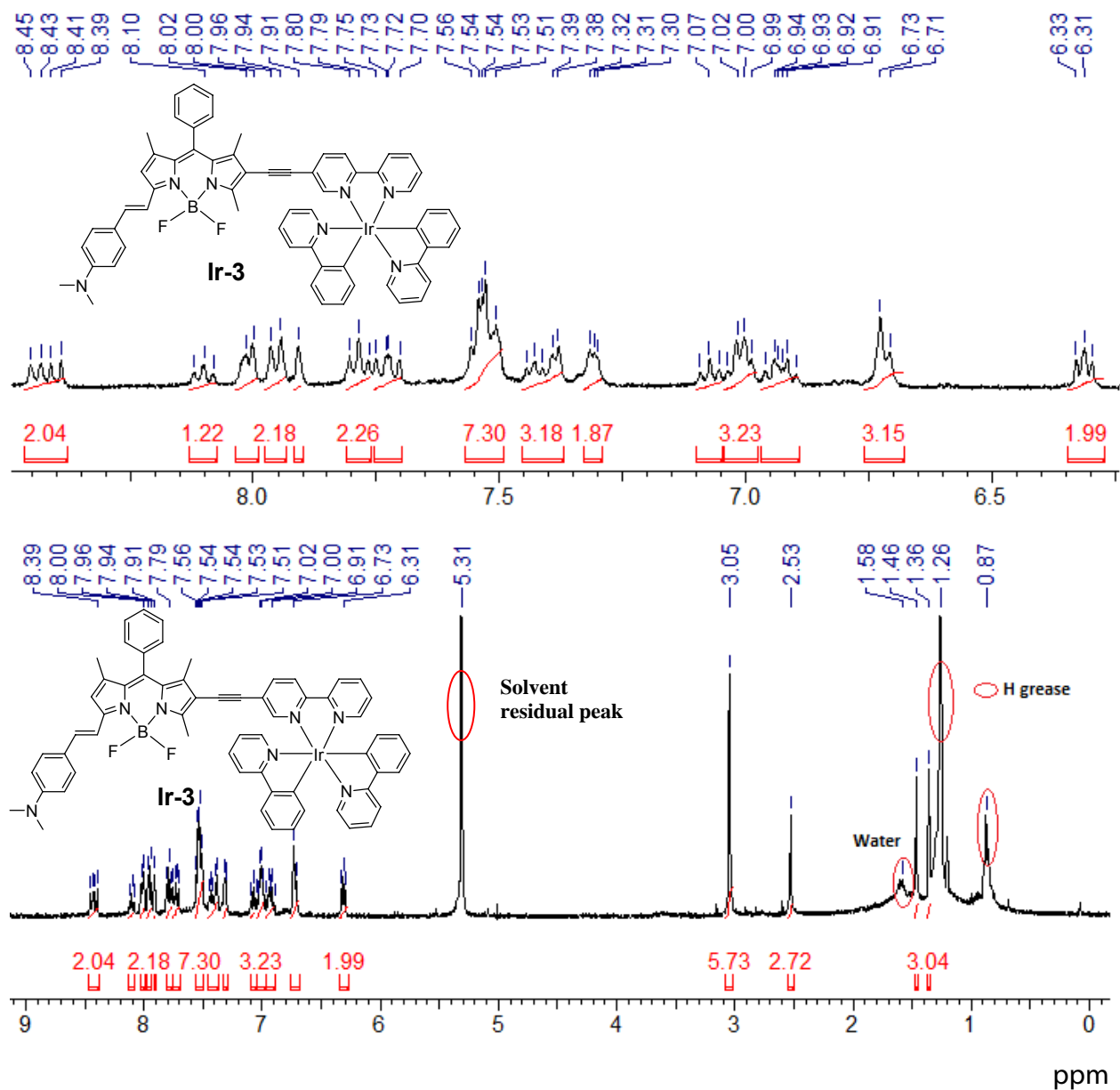


Fig. S31. ^{13}C NMR spectrum of Compound **L3** (100 MHz, CD_2Cl_2).



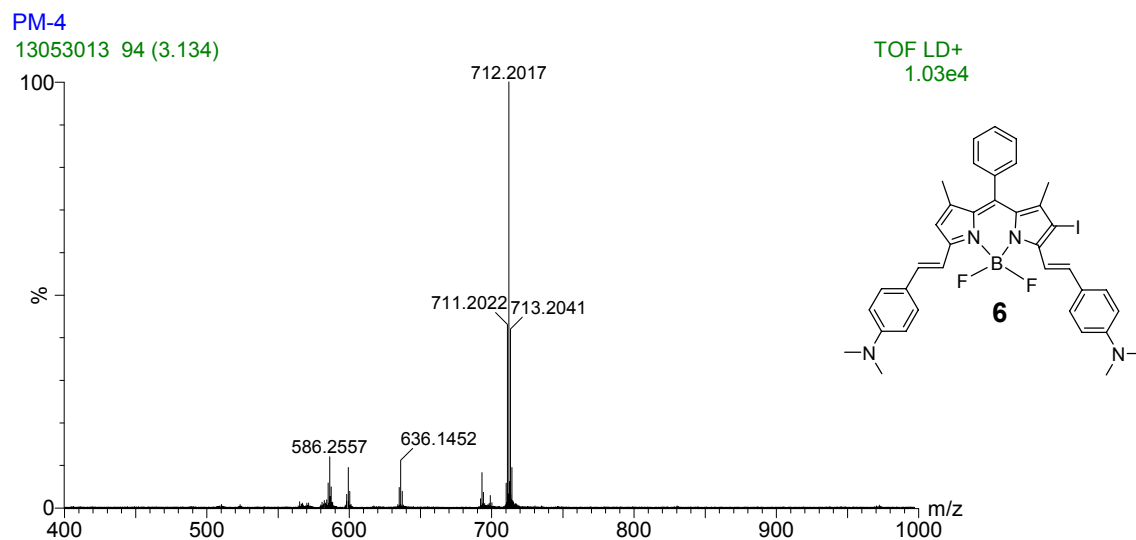


Fig. S35. TOF MALDI-HRMS of compound **6**

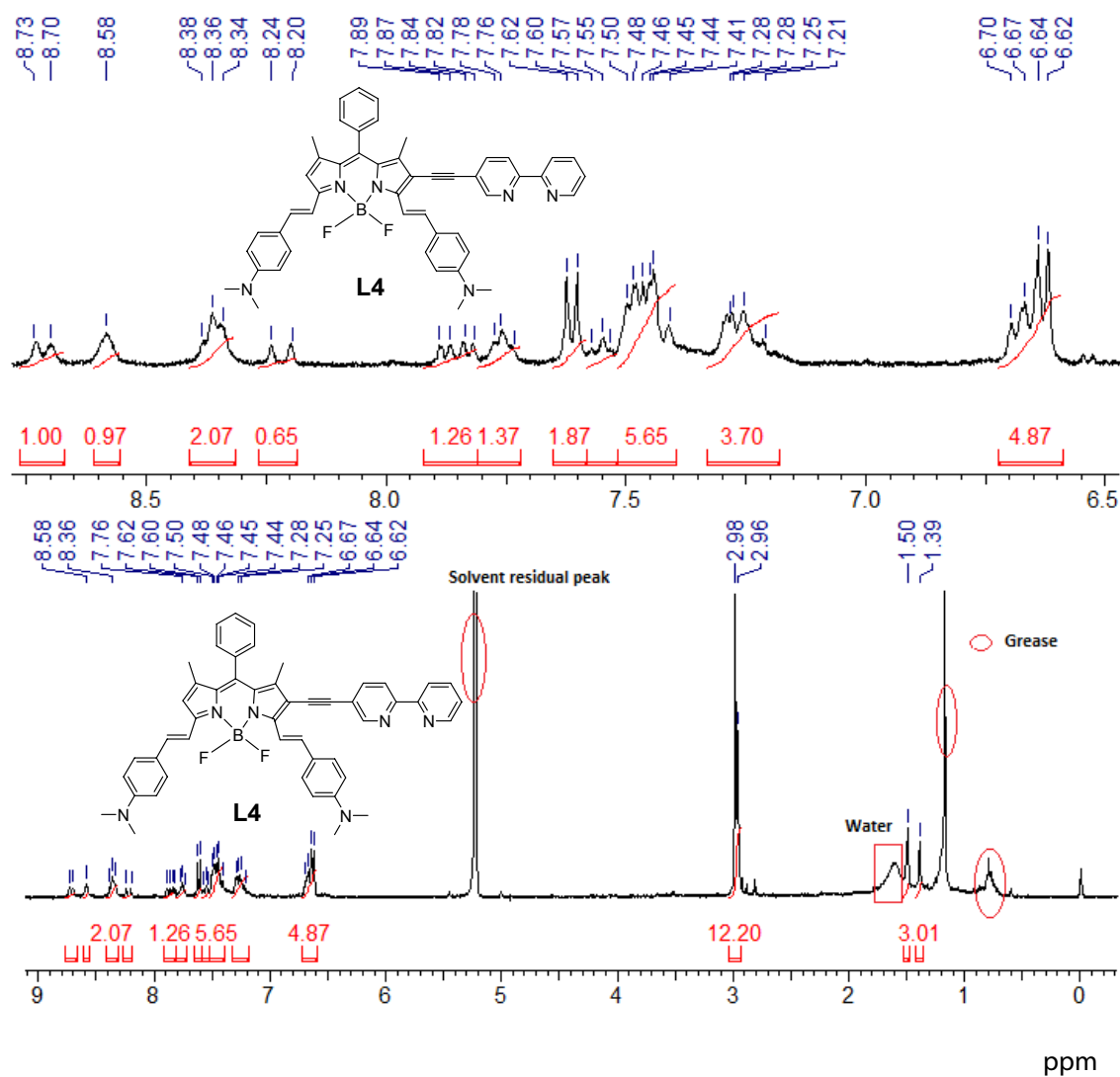


Fig. S36. ^1H NMR spectrum of Compound **L4** (400 MHz, CD_2Cl_2).

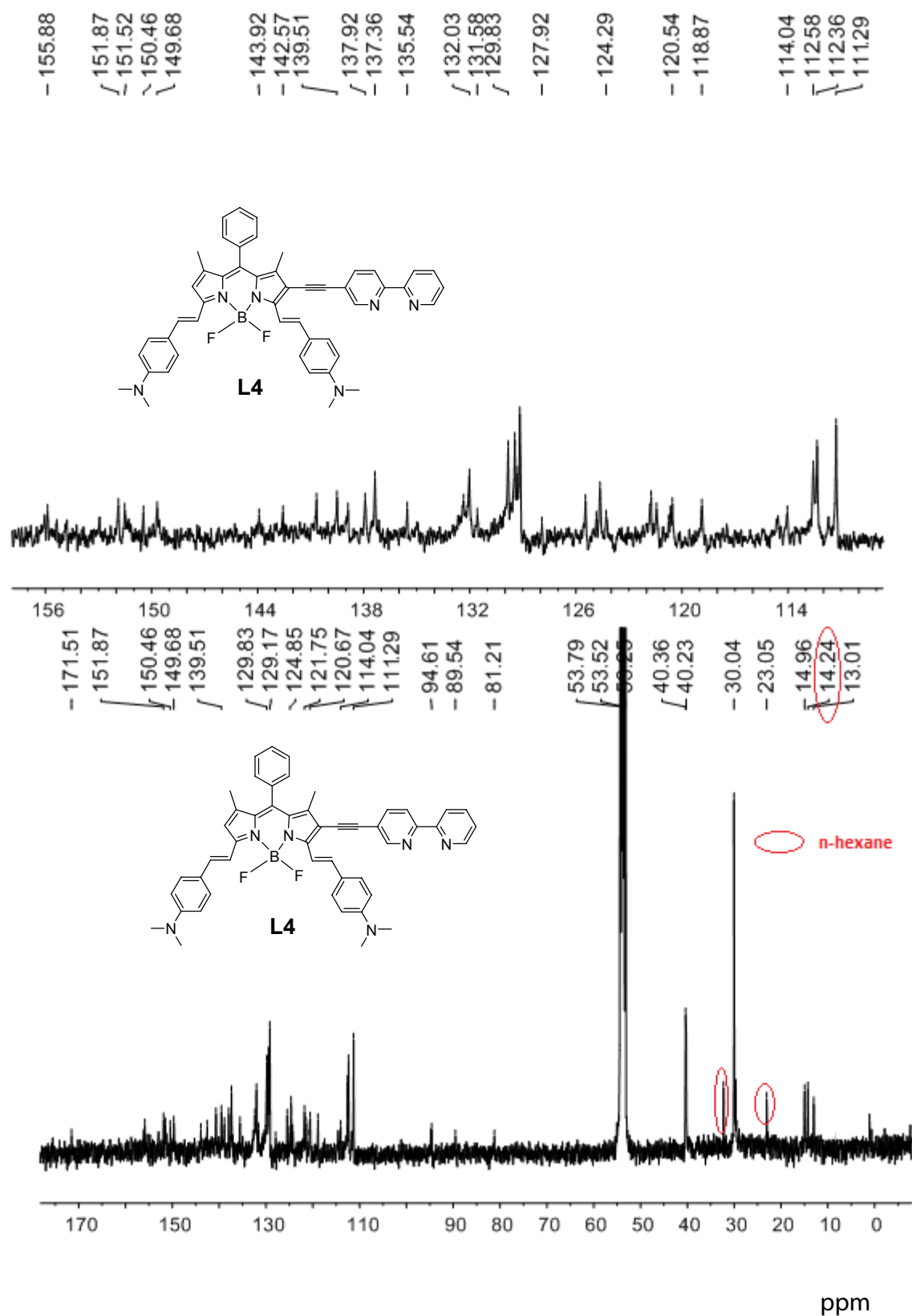


Fig. S37. ^{13}C NMR spectrum of Compound **L4** (100 MHz, CD_2Cl_2).

MJ-4(CHCA)
13060505 30 (0.999)

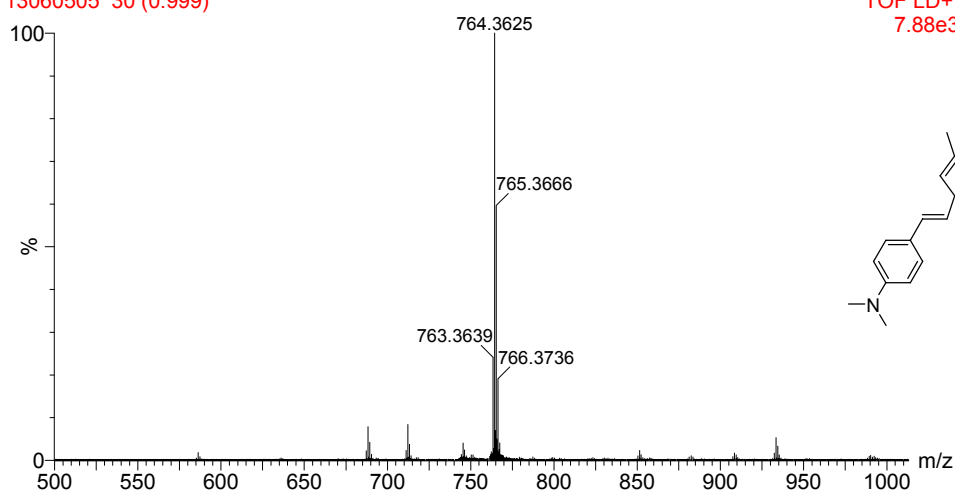


Fig. S38. TOF MALDI-HRMS of compound **L4**

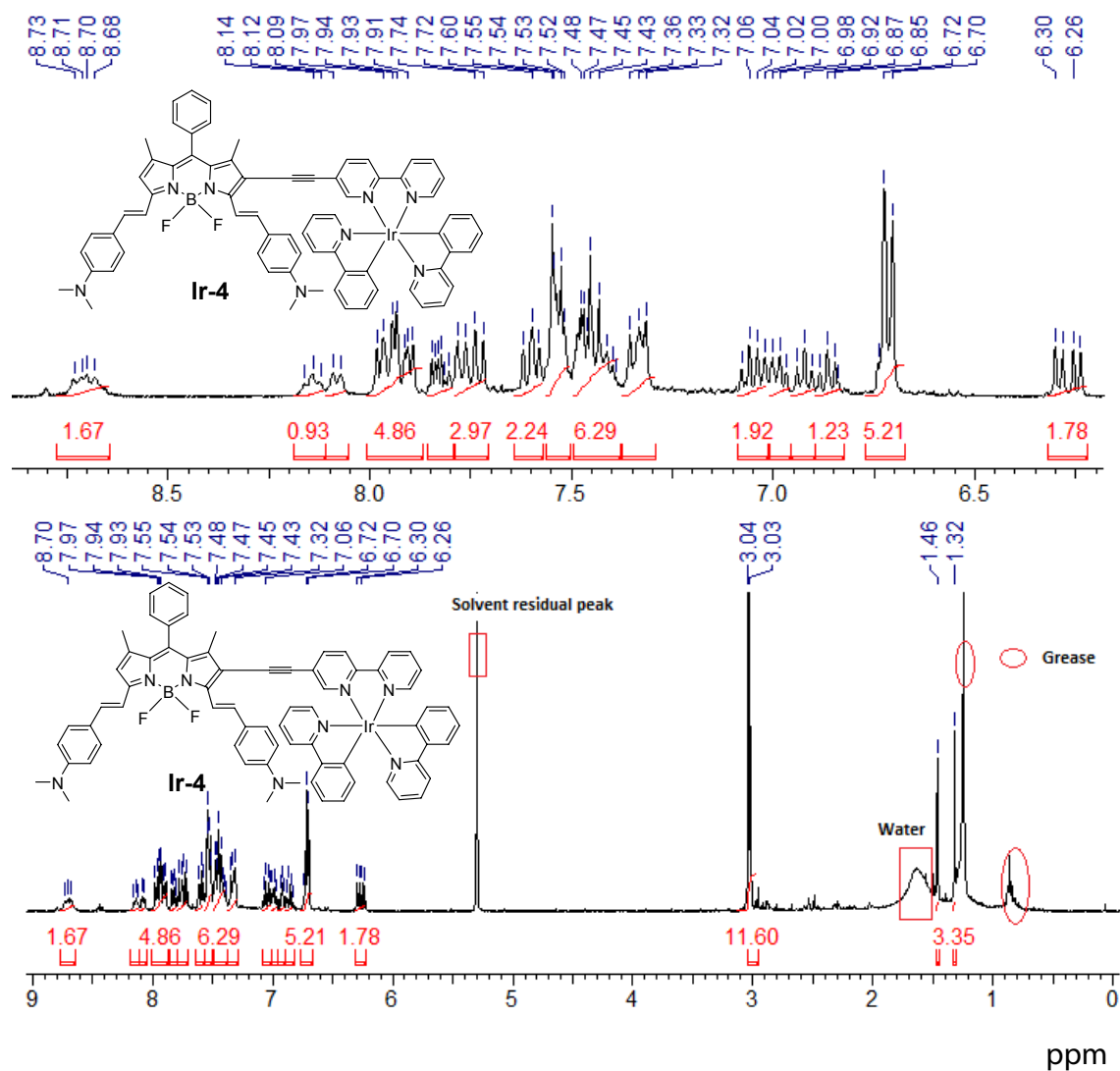


Fig. S39. ^1H NMR spectrum of Compound **Ir-4** (400 MHz, CD_2Cl_2).

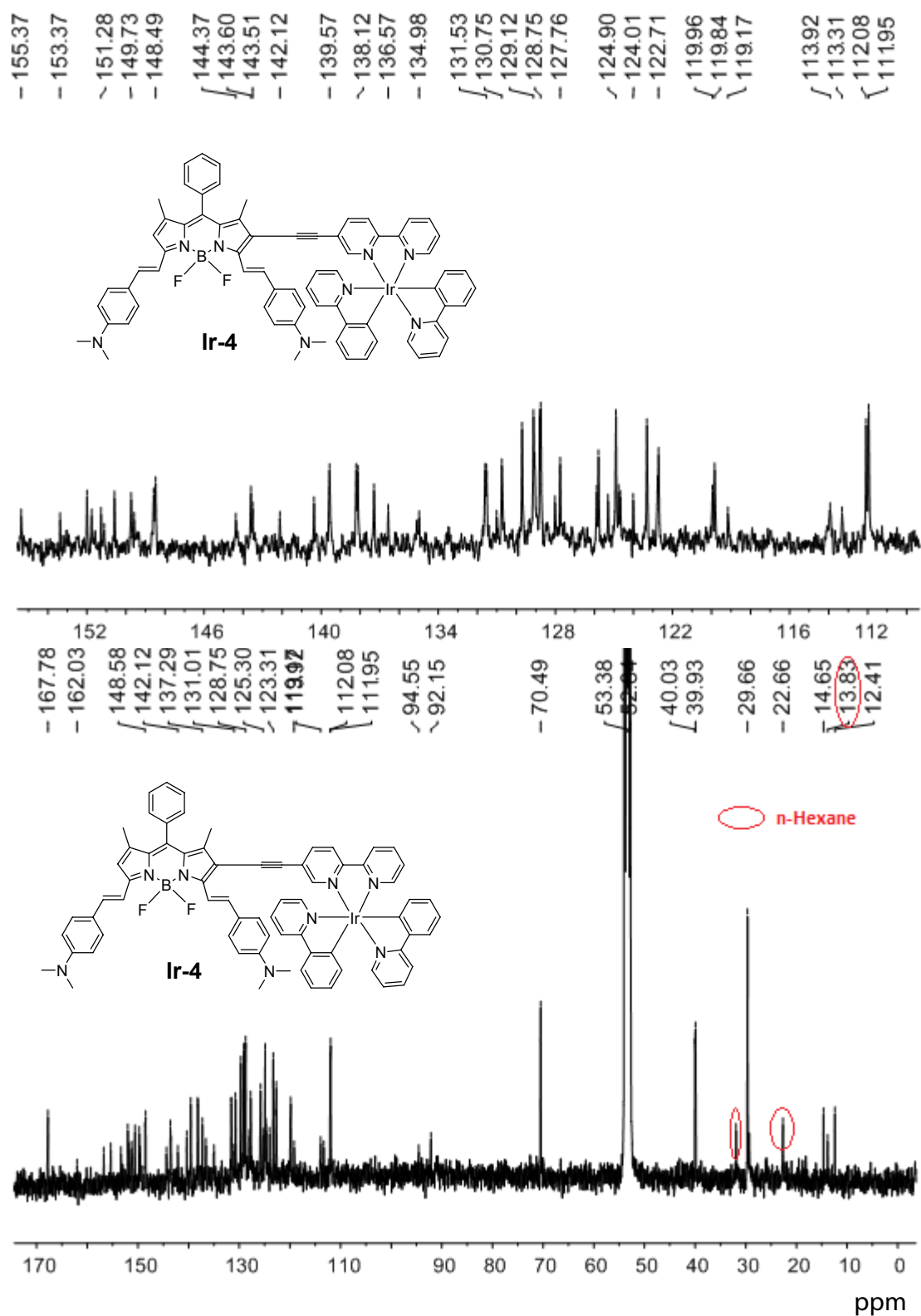


Fig. S40. ¹³C NMR spectrum of Compound **Ir-4** (100 MHz, CD₂Cl₂).

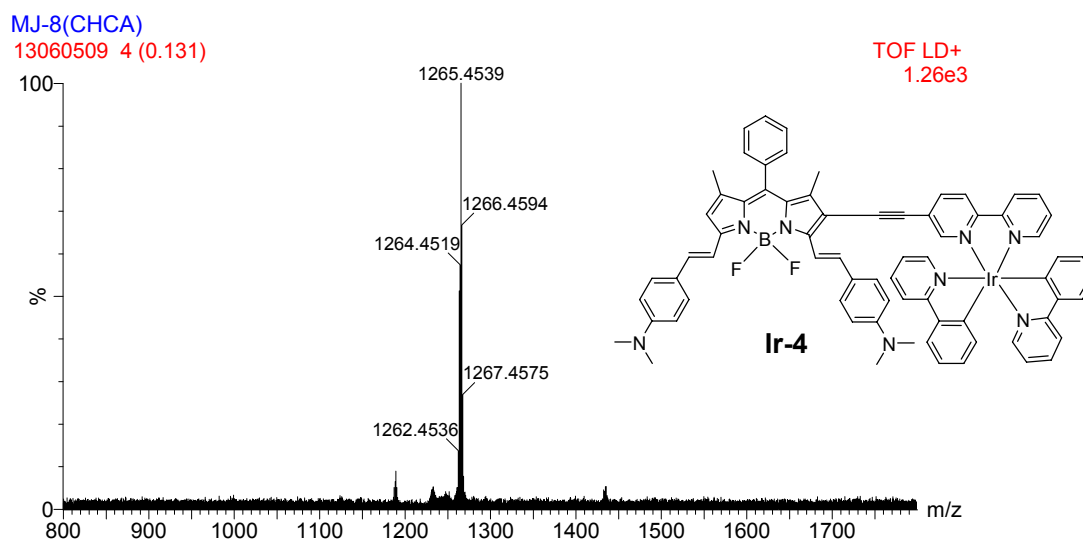


Fig. S41. TOF MALDI-HRMS of compound **Ir-4**

3.0. Absorption and Emission Spectra of the ligands and complexes

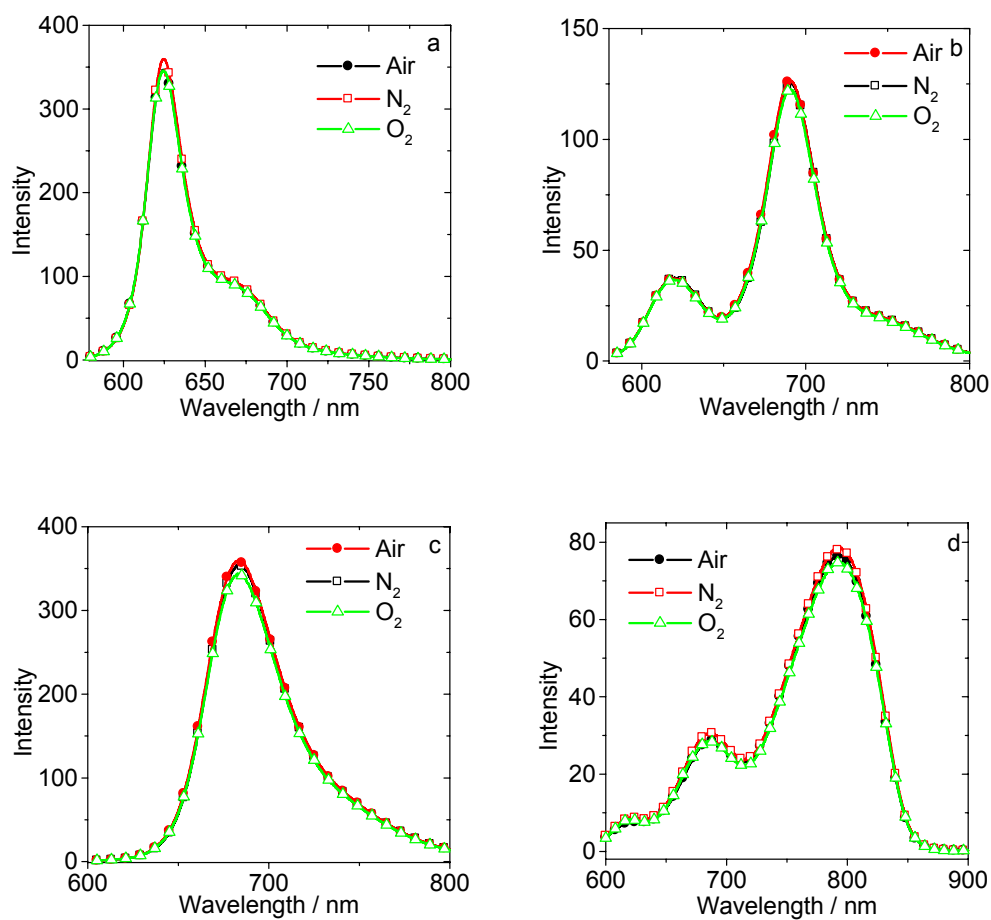


Fig. S42. Emission spectra of the complexes (a) **Ir-1** ($\lambda_{\text{ex}} = 570 \text{ nm}$), (b) **Ir-2** ($\lambda_{\text{ex}} = 580 \text{ nm}$), (c) **Ir-3** ($\lambda_{\text{ex}} = 595 \text{ nm}$), and (d) **Ir-4** ($\lambda_{\text{ex}} = 580 \text{ nm}$) at different atmosphere of air, N_2 , and O_2 . $c = 1.0 \times 10^{-5} \text{ M}$ in toluene.

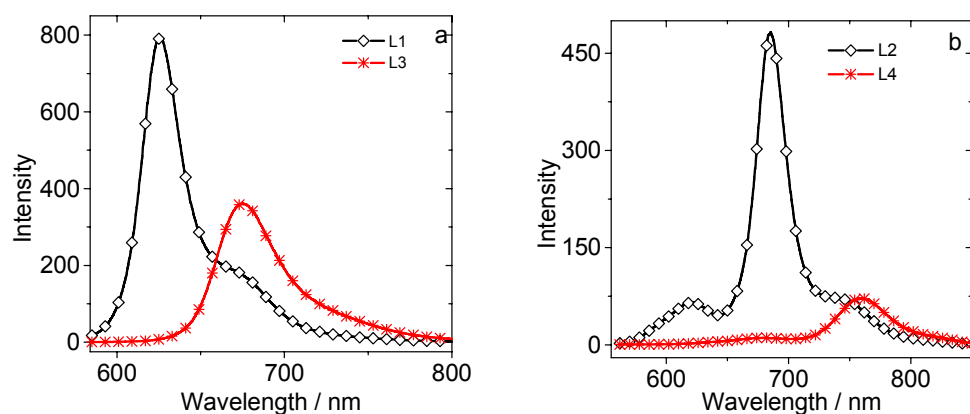


Fig. S43. Comparison of the emission intensities of the ligands and complexes: (a) **L1** and **L3**, $\lambda_{\text{ex}} = 580 \text{ nm}$; (b) **L2** and **L4**, $\lambda_{\text{ex}} = 552 \text{ nm}$. $c = 1.0 \times 10^{-5} \text{ M}$ in toluene.

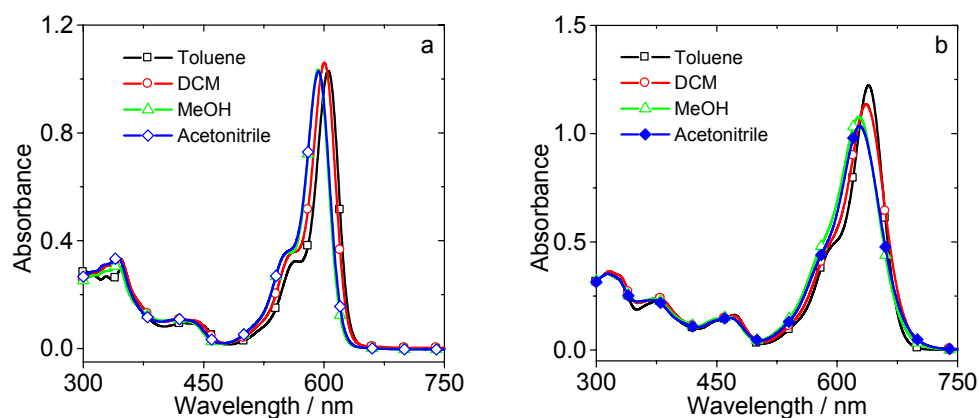


Fig. S44. Solvent-polarity-dependence of the absorption of the ligands ($c = 1.0 \times 10^{-5} \text{ M}$): (a) **L1**, (c) **L3**.

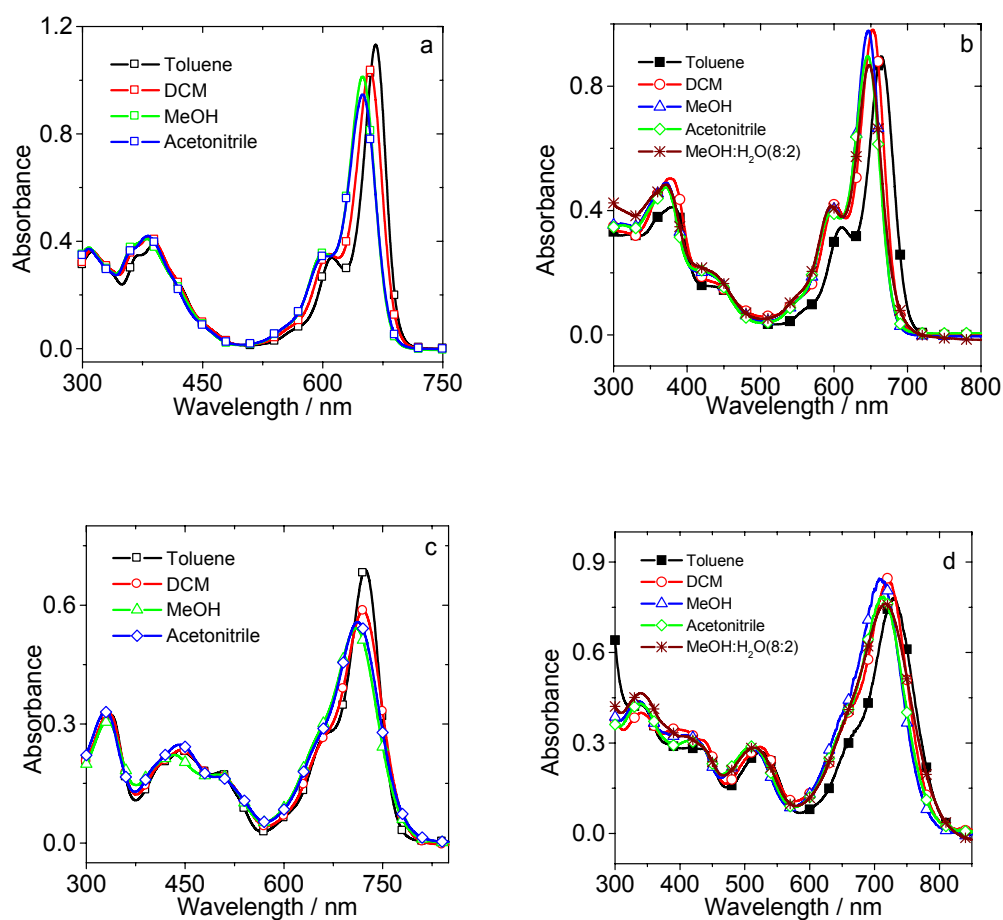


Fig. S45 Solvent-polarity-dependence of the absorption of the ligands and complexes ($c = 1.0 \times 10^{-5}$ M): (a) **L2**, (b) **Ir-2**, (c) **L4**, (d) **Ir-4**.

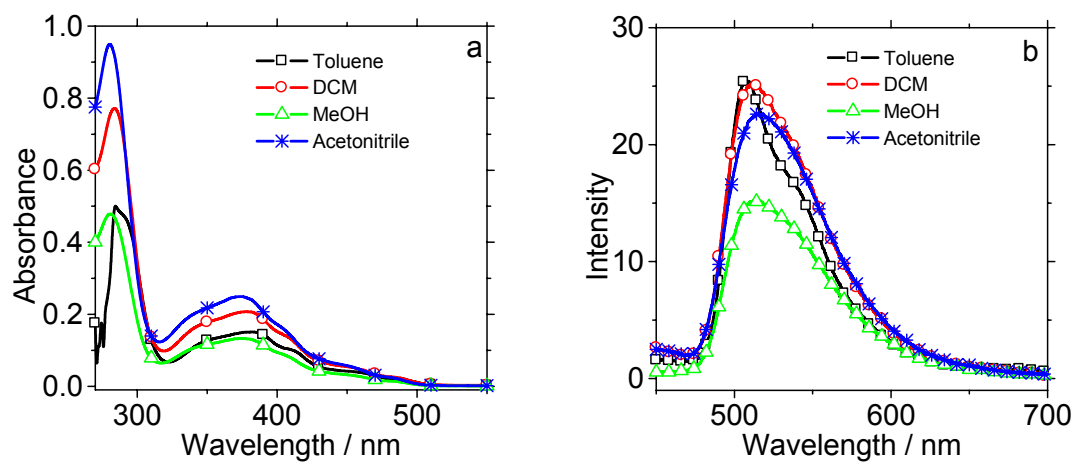


Fig. S46 (a) Solvent-polarity-dependence of the absorption of the complex **Ir-0**; (b) Solvent-polarity-dependence of the emission of the complex **Ir-0** ($\lambda_{\text{ex}} = 370$ nm). ($c = 1.0 \times 10^{-5}$ M).

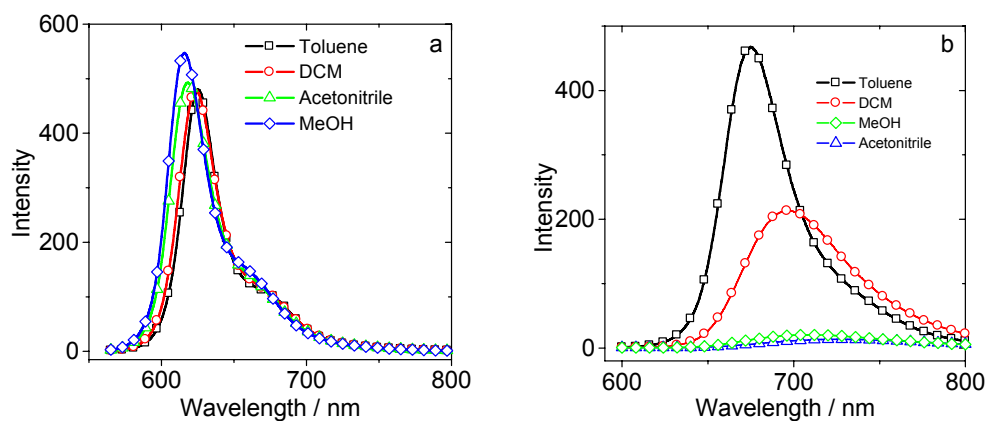


Fig. S47. Solvent-polarity-dependence of the emission of the ligands ($c = 1.0 \times 10^{-5}$ M): (a) **L1**, $\lambda_{\text{ex}} = 560$ nm; (c) **L3**, $\lambda_{\text{ex}} = 580$ nm.

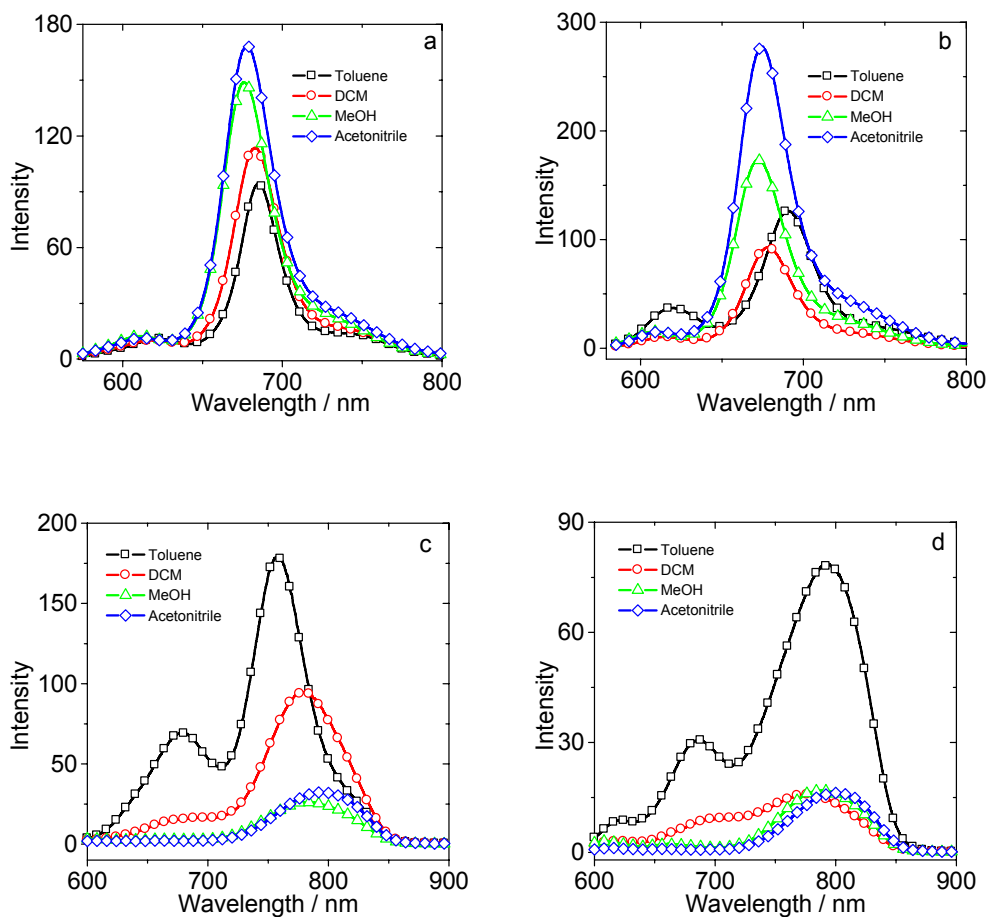


Fig. S48. Solvent-polarity-dependence of the emission of the ligands and complexes ($c = 1.0 \times 10^{-5}$ M): (a) **L-2**, $\lambda_{\text{ex}} = 570$ nm; (b) **Ir-2**, $\lambda_{\text{ex}} = 580$ nm; (c) **L-4**, $\lambda_{\text{ex}} = 580$ nm; (d) **Ir-4**, $\lambda_{\text{ex}} = 580$ nm.

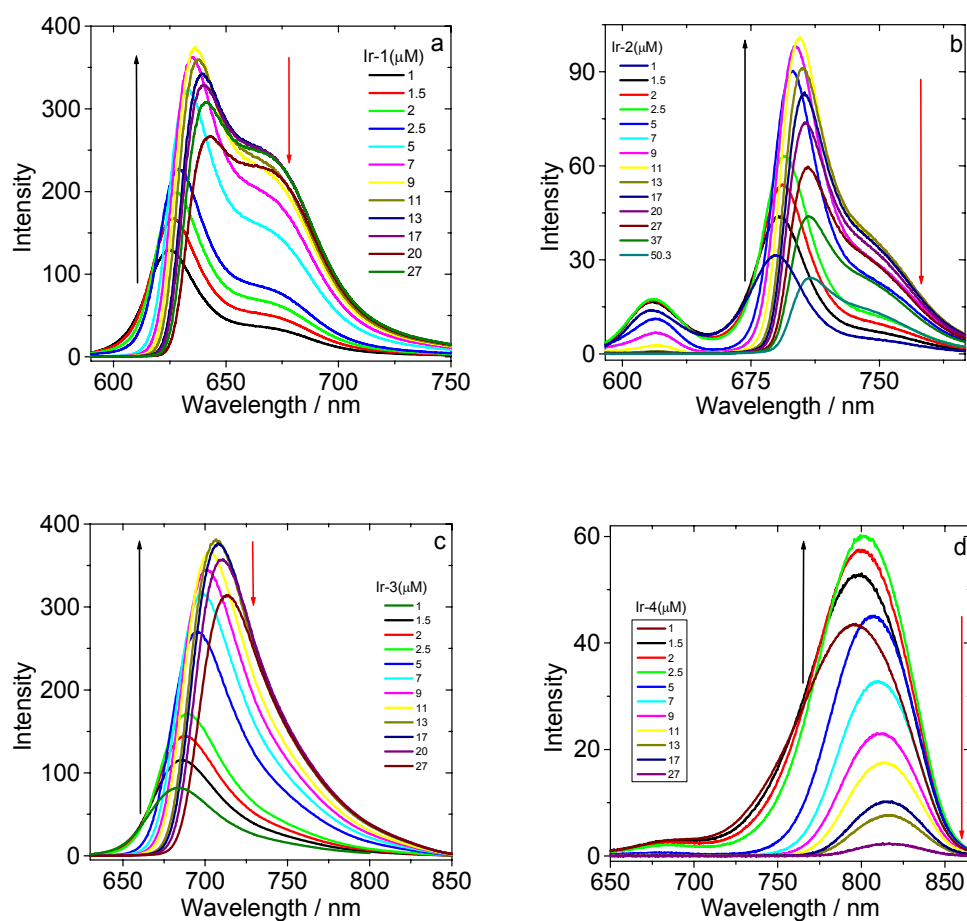


Fig. S49. Fluorescence spectral changes of complexes with increasing concentration in toluene: (a) **Ir-1** ($\lambda_{\text{ex}} = 496 \text{ nm}$), (b) **Ir-2** ($\lambda_{\text{ex}} = 546 \text{ nm}$), (c) **Ir-3** ($\lambda_{\text{ex}} = 496 \text{ nm}$) and (d) **Ir-4** ($\lambda_{\text{ex}} = 546 \text{ nm}$).

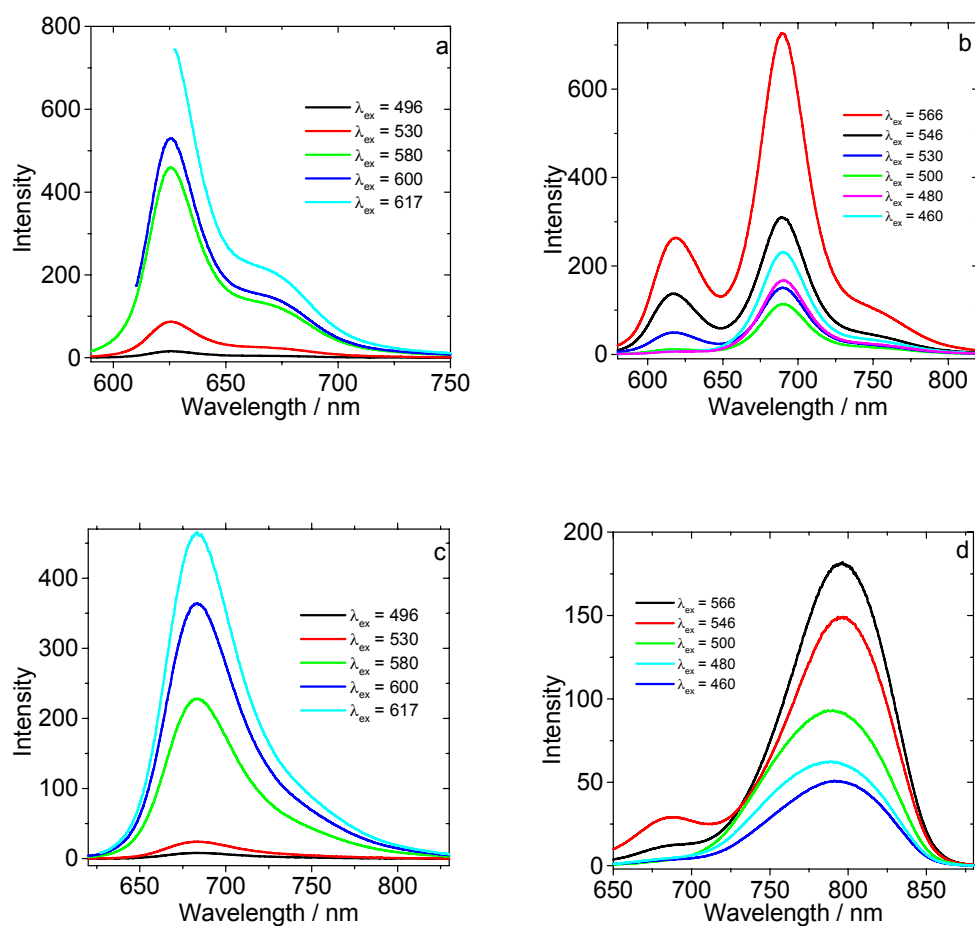


Fig. S50. Fluorescence dependence of the complexes on excitation energy ($c = 1.0 \times 10^{-5}$ M in toluene): (a) **Ir-1**, (b) **Ir-2**, (c) **Ir-3** and (d) **Ir-4**.

4.0. Nanosecond time-resolved transient difference absorption spectra of the complexes

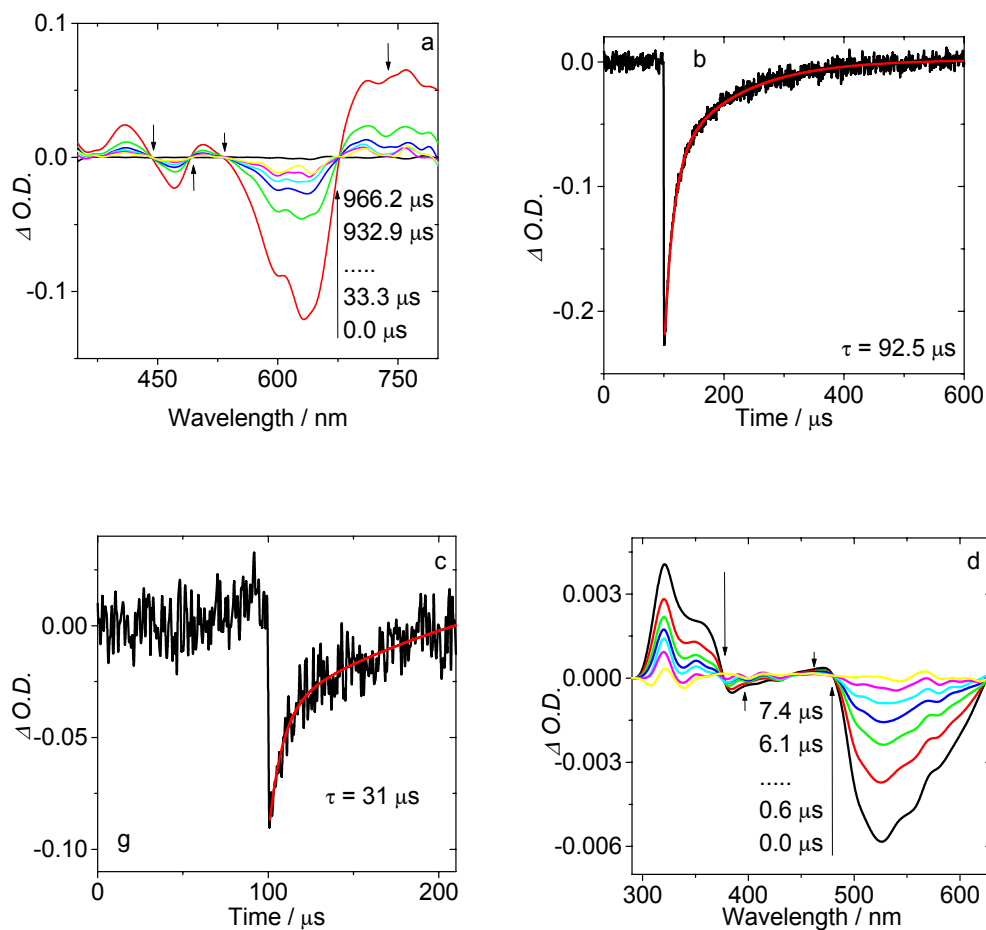


Fig. S51. Nanosecond time-resolved transient difference absorption spectra after pulsed excitation: (a) **Ir-3** and (d) **Ir-0**; decay traces of (b) **Ir-3** and (c) **Ir-4**. ($\lambda_{\text{ex}} = 532 \text{ nm}$ for **Ir-3** and **Ir-4**; $\lambda_{\text{ex}} = 355 \text{ nm}$ for **Ir-0**; $c = 1.0 \times 10^{-5} \text{ M}$ in toluene).

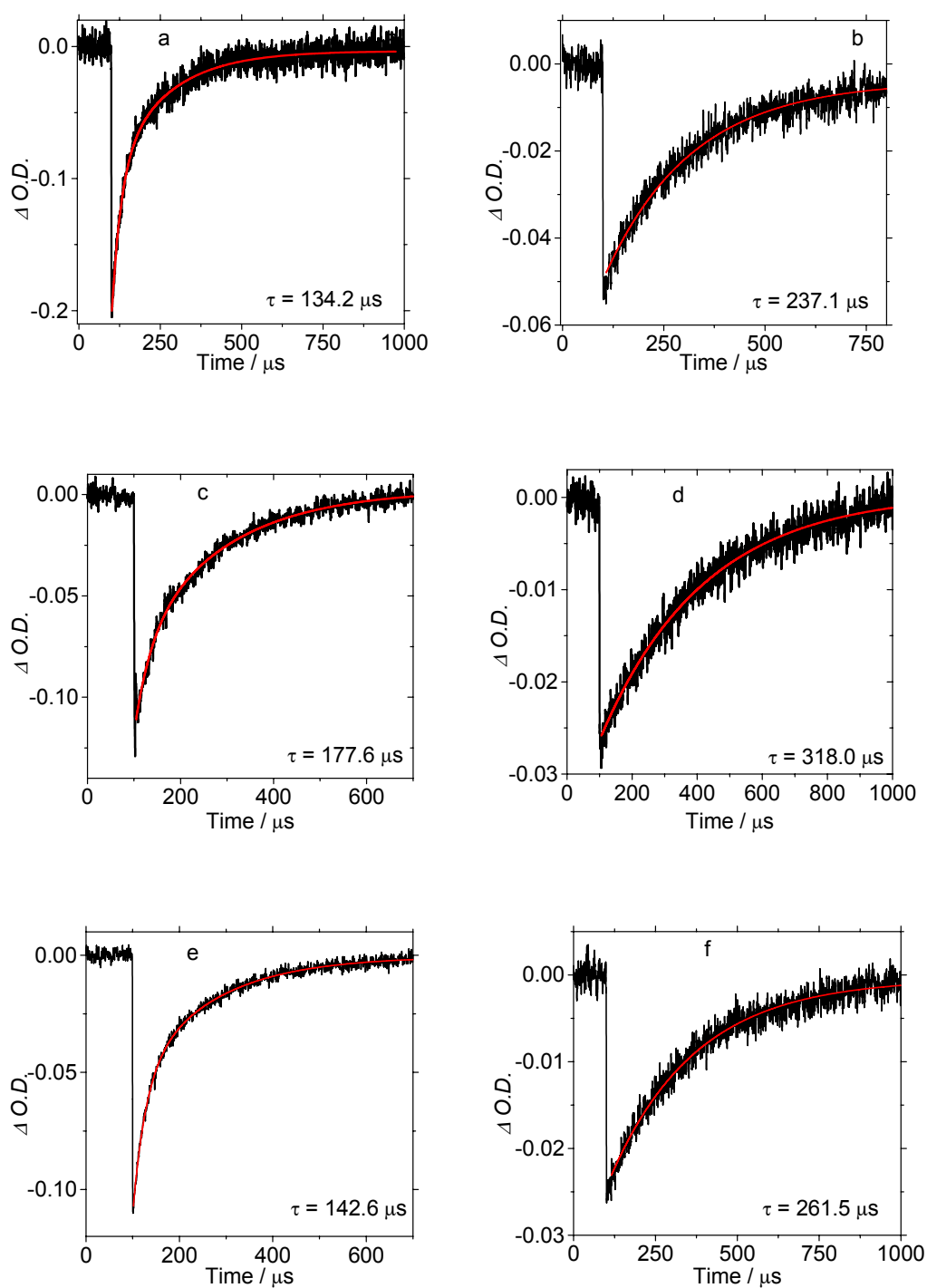


Fig. S52. Decay traces of complexes in: $c = 5.0 \times 10^{-6} M$ in toluene - (a) **Ir-1**, (c) **Ir-2**, (e) **Ir-3**; in $c = 1.0 \times 10^{-6} M$ in toluene - (b) **Ir-1**, (d) **Ir-2**, (f) **Ir-3**. ($\lambda_{ex} = 532 \text{ nm}$).

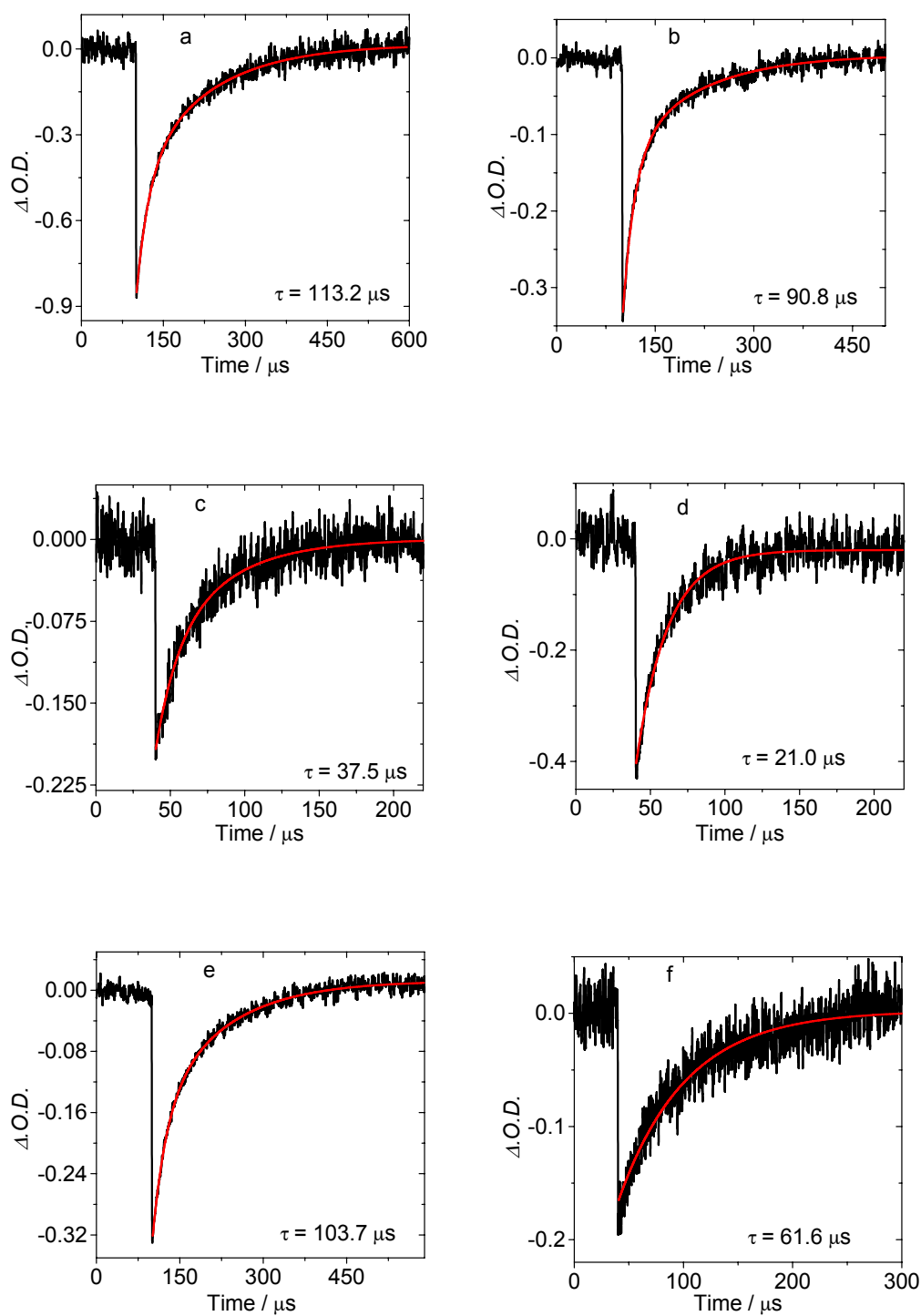


Fig. S53. Decay traces of (a) **Ir-1**, (b) **Ir-2**, (c) **Ir-3** in $c = 1.0 \times 10^{-5}$ M in methanol; (d) **Ir-1**, (e) **Ir-2**, (f) **Ir-3** in $c = 1.0 \times 10^{-5}$ M in acetonitrile. ($\lambda_{ex} = 532$ nm).

Table S1. Pseudo-first-order kinetics parameters, $^1\text{O}_2$ generation quantum efficiencies and yields of Juglone for the photo-oxidations of DHN using complexes **Ir-1**, **Ir-2**, **Ir-3**, **Ir-4**, **MB** and **TPP** as sensitizers

	τ_T^a [μs]	τ_T^b [μs]	k_{obs}^c	ν_i^d	Φ_{Δ}^e	Φ_{Δ}^j	Φ_{Δ}^o	Yield ^f [%]
Ir-1	106.6	113.2	51.1	1.022	0.53 ^f	0.92 ^k	0.70 ^p	72.3
Ir-2	156.5	90.8	48.4	0.968	0.81 ^g	0.39 ^l	0.35 ^q	91.2
Ir-3	92.5	37.5	9.1	0.182	0.06 ^h	0.00 ^m	0.00 ^r	58.4
Ir-4	31.4	- ^u	0	0	0.02 ⁱ	0.00 ⁿ	0.00 ^s	41.0
Ir-0	1.34	- ^u	5.2	0.104	- ^u	- ^u	- ^u	48.7
MB	83.3	- ^u	49.1	0.982	0.57	- ^u	- ^u	86.2
TPP	82.5	- ^u	68.9	1.378	0.65	- ^u	- ^u	99.9

Triplet excited state lifetimes, measured by nanosecond time-resolved transient absorptions ^a ($c = 1.0 \times 10^{-5}$ M in toluene) and ^b ($c = 1.0 \times 10^{-5}$ M in MeOH). ^cPseudo-first-order rate constant, $\ln(C_t/C_0) = -k_{\text{obs}}t$. In 10^{-3} min^{-1} . ^dInitial consumption rate of DHN, $\nu_i = k_{\text{obs}}[\text{DHN}]$. In 10^{-5} min^{-1} . Singlet Oxygen ($^1\text{O}_2$) generation quantum yield measured using Methylene Blue as a reference: ^e($\Phi_{\Delta} = 0.57$ in CH_2Cl_2), ^j(Φ_{Δ} in MeOH), and ^o(Φ_{Δ} in a mixture of MeOH:H₂O(8:2)). ^f $\lambda_{\text{ex}} = 611 \text{ nm}$; ^g $\lambda_{\text{ex}} = 652 \text{ nm}$; ^h $\lambda_{\text{ex}} = 642 \text{ nm}$; ⁱ $\lambda_{\text{ex}} = 664 \text{ nm}$. ^k $\lambda_{\text{ex}} = 607 \text{ nm}$; ^l $\lambda_{\text{ex}} = 602 \text{ nm}$; ^m $\lambda_{\text{ex}} = 639 \text{ nm}$; ⁿ $\lambda_{\text{ex}} = 673 \text{ nm}$. ^p $\lambda_{\text{ex}} = 606 \text{ nm}$; ^q $\lambda_{\text{ex}} = 602 \text{ nm}$; ^r $\lambda_{\text{ex}} = 637 \text{ nm}$; ^s $\lambda_{\text{ex}} = 675 \text{ nm}$. ^tYield of juglone after photoreaction for 40 min. ^uNot applicable

5.0. DFT calculations

Table S2. Electronic excitation energies (eV) and corresponding oscillator strengths (f), main configurations and CI coefficients of the low-lying electronic excited states of the complex **Ir-3** calculated by TDDFT// M062X/ GENECP based on the DFT// M062X / GENECP optimized ground state geometries

TDDFT// M062X / GENECP						
	Electronic transition	Energy [eV/nm] ^a	f^b	Composition ^c	CI ^d	Character
Singlet	$S_0 \rightarrow S_1$	2.16/ 573	2.1565	H $\rightarrow$ L	0.53149	ILCT
	$S_0 \rightarrow S_2$	2.92/424	0.2536	H $\rightarrow$ L+2	0.52803	ILCT/LLCT
	$S_0 \rightarrow S_3$	3.20/388	0.4112	H-1 $\rightarrow$ L	0.50807	ILCT
	$S_0 \rightarrow S_5$	3.58/346	0.3640	H-3 $\rightarrow$ L	0.40224	ILCT/LLCT
				H-1 $\rightarrow$ L+1	0.39268	ILCT
Triplet	$S_0 \rightarrow T_1$	1.14 eV 1090.22 nm	0.0000 ^e	H $\rightarrow$ L+1	0.54843	ILCT
				H $\rightarrow$ L	0.40863	ILCT

^aOnly the selected low-lying excited states are presented. ^bOscillator strengths. ^cOnly the main configurations are presented. ^dThe CI coefficients are in absolute values. ^eNo spin-orbital coupling effect was considered, thus the f values are zero.

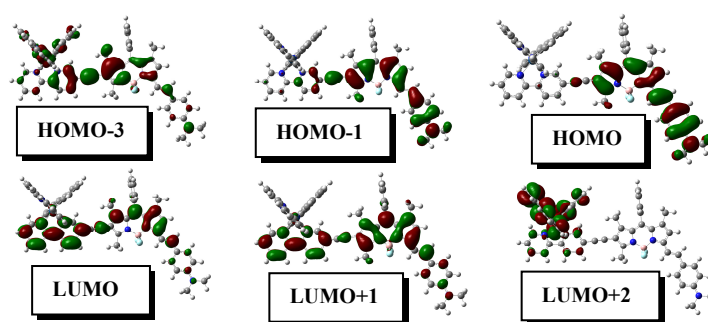


Fig. S54. Electron density maps of the frontier molecular orbital of the complex **Ir-3**. Based on ground state optimized geometry by the DFT calculations at the M06X2/GENECP level with Gaussian 09W.

Table S3. Electronic excitation energies (eV) and corresponding oscillator strengths (f), main configurations and CI coefficients of the low-lying electronic excited states of the complex **Ir-4** calculated by TDDFT//M062X/ GENECP based on the DFT// M062X / GENECP optimized ground state geometries

TDDFT//M062X / GENECP						
	Electronic transition	Energy [eV/nm] ^a	f^b	Composition ^c	CI ^d	Character
Singlet	$S_0 \rightarrow S_1$	1.95/636	1.7355	H $\rightarrow$ L	0.49915	ILCT
	$S_0 \rightarrow S_2$	2.38/521	0.2514	H $\rightarrow$ L+1	0.48343	ILCT
	$S_0 \rightarrow S_3$	2.90/428	1.0433	H-1 $\rightarrow$ L	0.49554	ILCT
	$S_0 \rightarrow S_8$	3.59/345	0.3221	H-2 $\rightarrow$ L+1	0.33722	ILCT
	$S_0 \rightarrow S_{11}$	3.77/328	0.3782	H-1 $\rightarrow$ L+2	0.38960	LLCT/MLCT
	$S_0 \rightarrow S_{18}$	4.13/299	0.1719	H-5 $\rightarrow$ L+2	0.37867	LLCT/MLCT
				H-5 $\rightarrow$ L+3	0.35606	LLCT/MLCT
Triplet	$S_0 \rightarrow T_1$	1.02/1219	0.0000 ^e	H $\rightarrow$ L+1	0.56190	ILCT
				H $\rightarrow$ L	0.38995	ILCT

^aOnly the selected low-lying excited states are presented. ^bOscillator strengths. ^cOnly the main configurations are presented. ^dThe CI coefficients are in absolute values. ^eNo spin-orbital coupling effect was considered, thus the f values are zero.

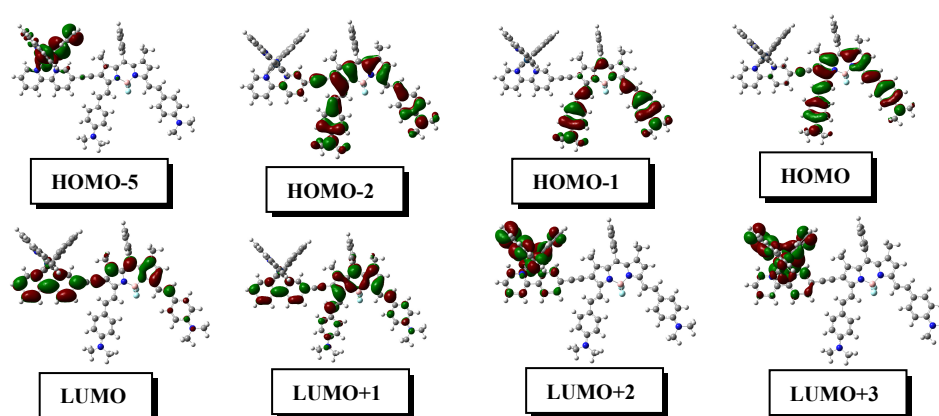


Fig. S55. Electron density maps of the frontier molecular orbital of the complex **Ir-4**. Based on ground state optimized geometry by the DFT calculations at the M06X2/GENECP level with Gaussian 09W.

Table S4. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Ir-0** Calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized Ground State Geometries.

TDDFT//B3LYP/ GENECP						
	Electronic transition	Energy [eV/nm] ^a	f^b	Compositio n ^c	CI ^d	Character
Singlet	$S_0 \rightarrow S_1$	2.90 eV /428 nm	0.006	H→L	0.6963	LLCT/MLCT
	$S_0 \rightarrow S_5$	3.11 eV/398 nm	0.0225	H-2→L	0.6482	MLCT/LLCT
				H-2→L+2	0.1521	LLCT
				H-1→L+1	0.1607	LLCT/MLCT
	$S_0 \rightarrow S_8$	3.20 eV/387 nm	0.0540	H-2→L+1	0.4371	LLCT/MLCT
				H-1→L	0.2384	LLCT
				H-1→L+1	0.1517	LLCT/MLCT
				H-1→L+2	0.4369	LLCT/MLCT
	$S_0 \rightarrow S_{10}$	3.43 eV/361 nm	0.0478	H-2→L+2	0.3343	LLCT
				H-1→L+1	0.3316	LLCT/MLCT
Triplet	$S_0 \rightarrow T_1$	2.64eV/470 nm	0.0000 ^e	H-2→L+1	0.1519	LLCT/MLCT
				H-1→L+1	0.1803	LLCT/MLCT
				H-1→L+2	0.1598	LLCT/MLCT
				H→L	0.5557	LLCT/MLCT

^aOnly the selected low-lying excited states are presented. ^bOscillator strengths. ^cOnly the main configurations are presented. ^dThe CI coefficients are in absolute values. ^eNo spin-orbital coupling effect was considered, thus the f values are zero.

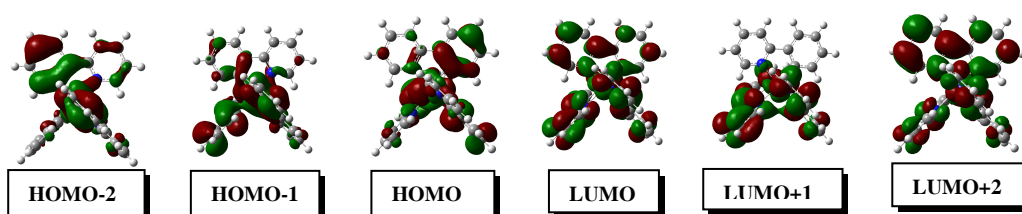


Fig. S56. Electron density maps of the frontier molecular orbital of the complex **Ir-0**. Based on ground state optimized geometry by the DFT calculations at the B3LYP/ GENECP level with Gaussian 09W.

6.0. Photooxidation

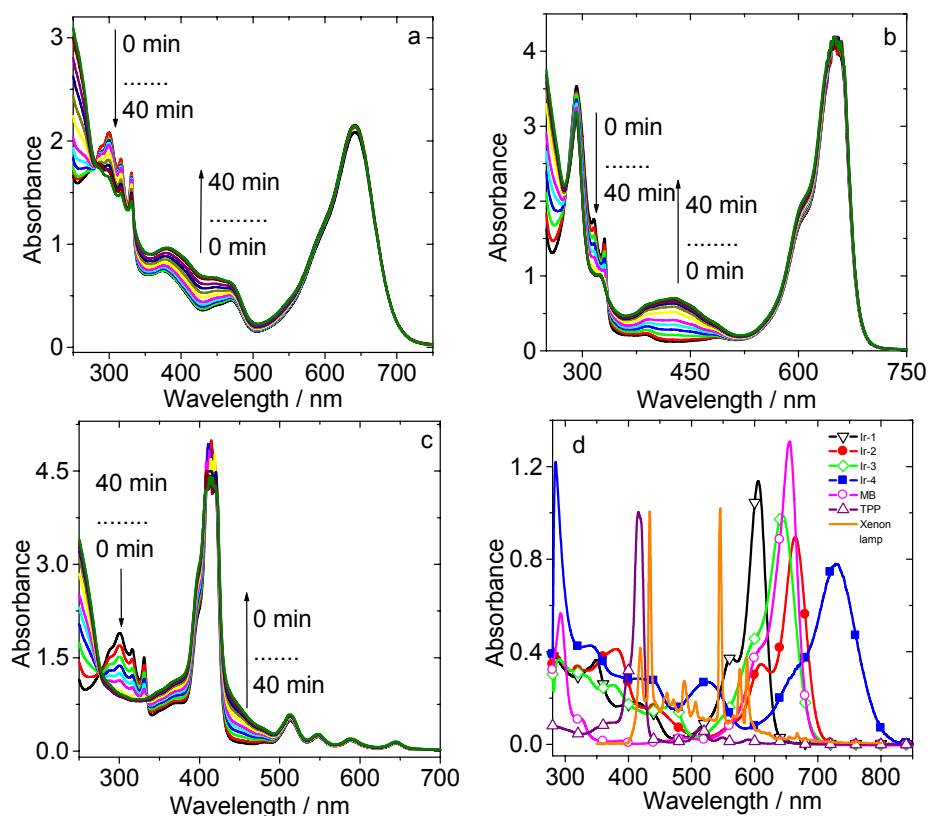


Fig. S57 UV-Vis absorption spectral change for DHN using complex (a) **Ir-3**, (b) **MB**, (c) **TPP** as photosensitizers. (Irradiated with a 35 W xenon lamp (20 mW cm^{-2} in the photoreactor; the UV light with a wavelength shorter than 385 nm was blocked by 0.72 M NaNO_2 solution). In CH_2Cl_2 – CH_3OH (9:1, v/v); $c[\text{DHN}] = 2.0 \times 10^{-4} \text{ M}$; $c[\text{photosensitizer}] = 2.0 \times 10^{-5} \text{ M}$; 20°C). (d) Comparison of the UV-Vis absorption spectra of complexes **Ir-1**, **Ir-2**, **Ir-3**, **Ir-4**, **MB**, **TPP** and the emission spectra of the 35 W xenon lamp (measured with spectrofluorometer). The excitation of xenon lamp with wavelength shorter than 387 nm was blocked by 0.72 M NaNO_2 solution.

7.0. Fluorescent Imaging and effects on Cell Growth/Viability

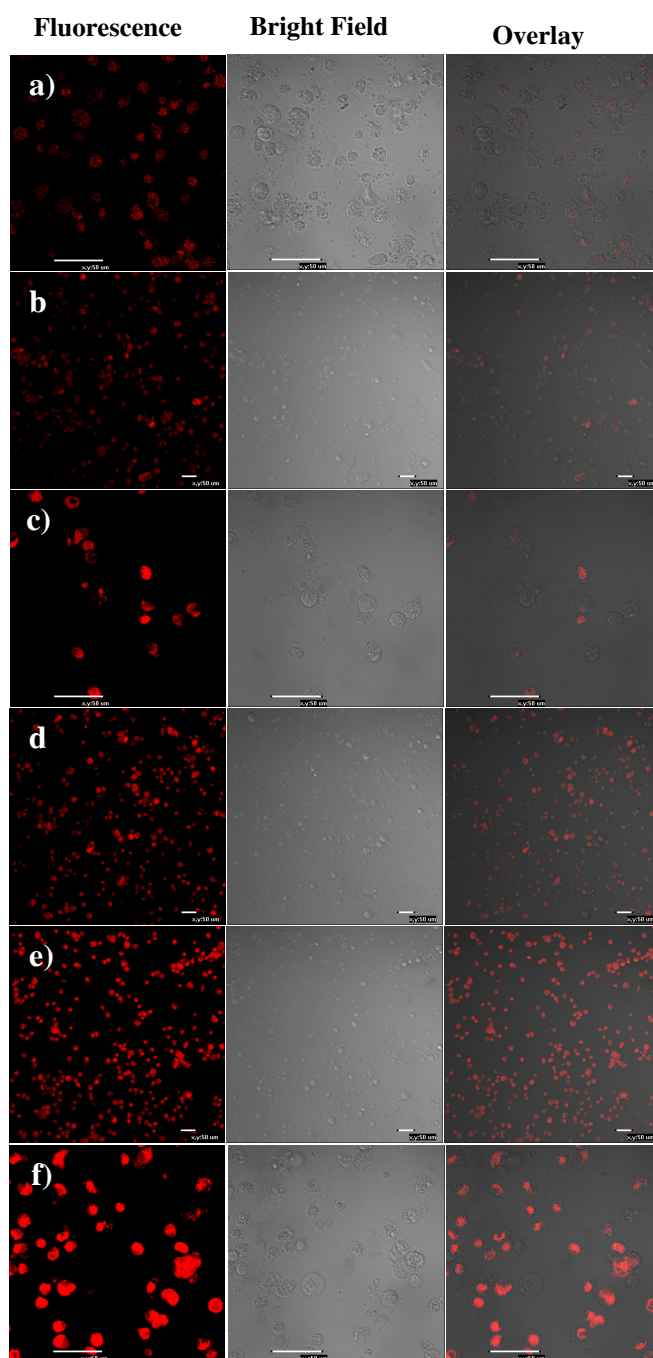


Fig. S58 Confocal fluorescence images in LLC cells: **Ir-1** treated cells in the dark for 24 h (a) 1 μ M, (c) 10 μ M, (e) 20 μ M; Ir-1 treated cells on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h (b) 1 μ M, (d) 10 μ M, (f) 20 μ M.

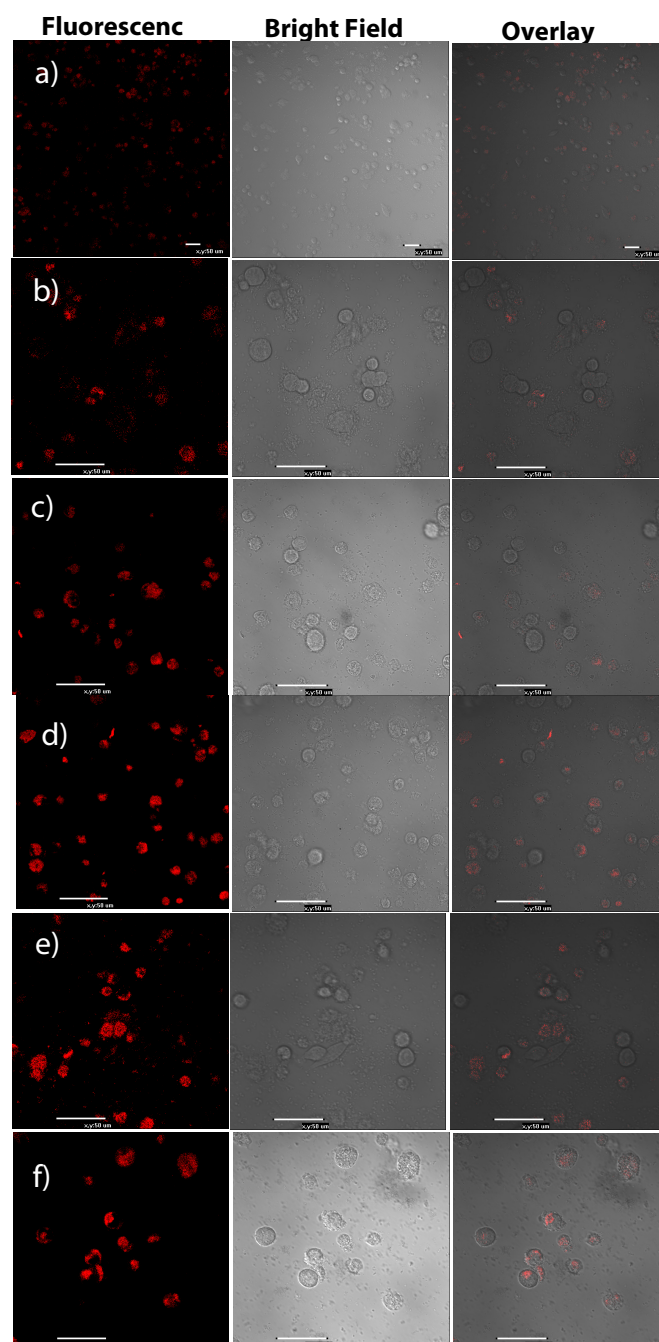


Fig. S59 Confocal fluorescence images in LLC cells: **Ir-2** treated cells in the dark for 24 h (a) 1 μ M, (c) 10 μ M, (e) 20 μ M; **Ir-2** treated cells on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h (b) 1 μ M, (d) 10 μ M, (f) 20 μ M.

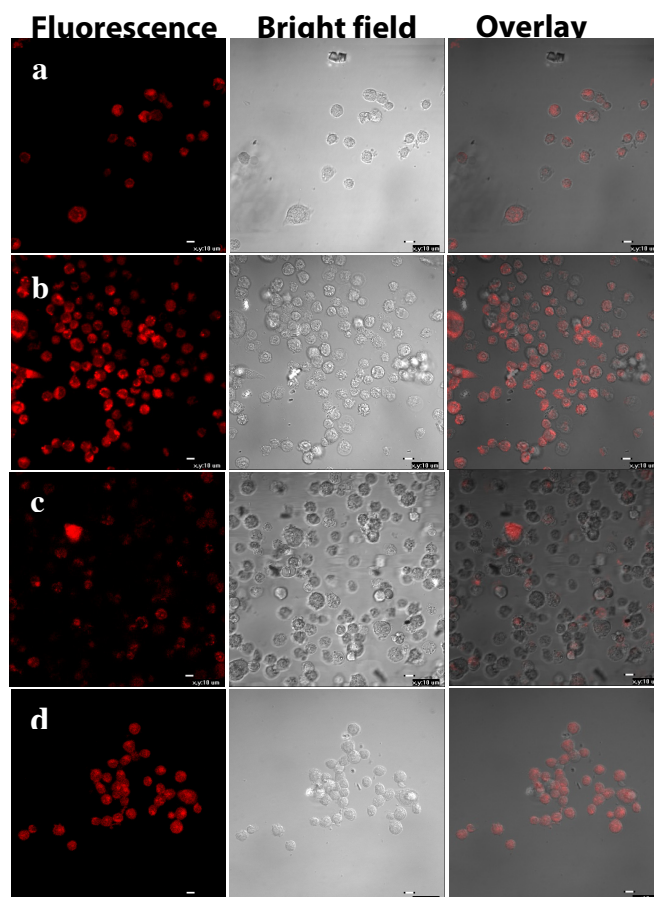


Fig. S60 Confocal fluorescence images in LLC cells . (a) **Ir-3** (10 μ M) treated cells in the dark for 24 h; (b) **Ir-3** (10 μ M) treated cells on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h. (c) **Ir-4** (10 μ M) treated cells in the dark for 24 h; (d) **Ir-4** (10 μ M) treated cells on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h.

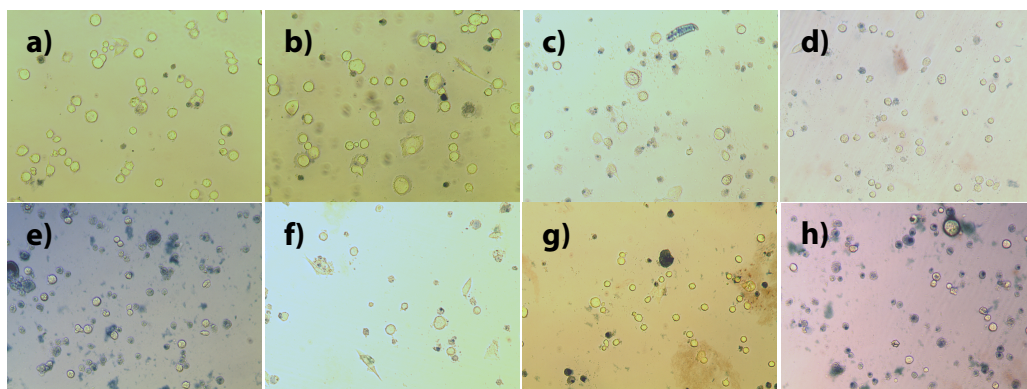


Fig. S61 Trypan blue staining images of LLC cells treated with (a) in absence of LED and photosensitizers; (b) in presence of 635 nm LED and absence of photosensitizers; in absence of LED and **Ir-1** (c) 1 μ M, (d) 10 μ M, (e) 20 μ M; and in absence of LED and **Ir-2** (f) 1 μ M, (g) 10 μ M, (h) 20 μ M.

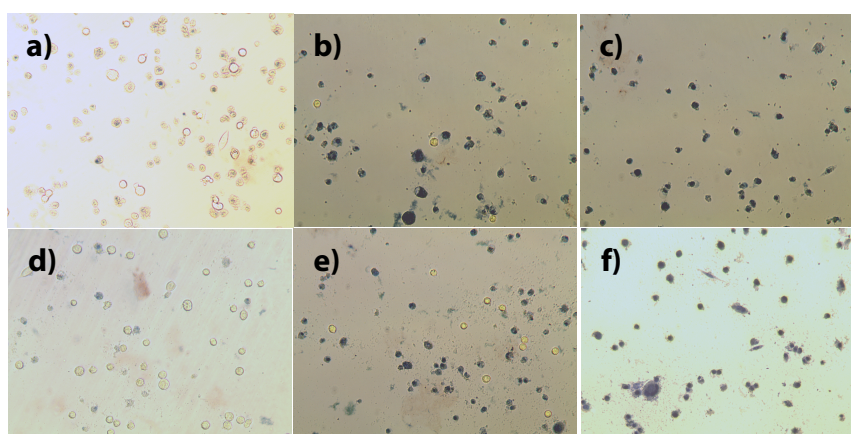


Fig. S62 Trypan blue staining images of LLC cells treated with **Ir-1** on 4 hr illumination of 635 nm LED (a) 1 μ M, (b) 10 μ M, (c) 20 μ M; **Ir-2** on 4 hr illumination of 635 nm LED (d) 1 μ M, (e) 10 μ M, (f) 20 μ M.

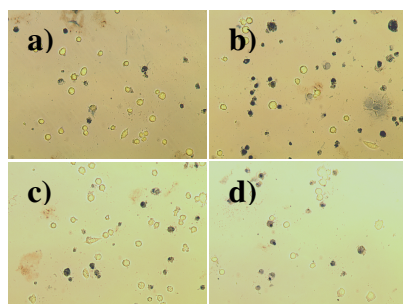


Fig. S63 Trypan blue staining images of LLC cells treated with **Ir-1**(10 μM) on illumination of 635 nm LED (a) 1 hr (b) 3 hr; **Ir-2**(10 μM) on illumination of 635 nm LED (c) 1 hr, (d) 3 hr.

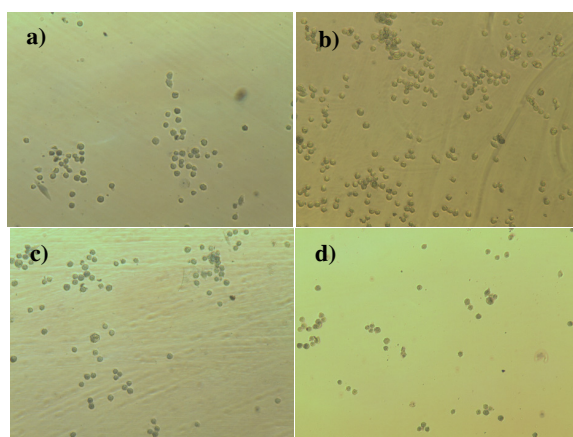


Fig. S64 Trypan blue staining images of LLC cells treated with **Ir-3**(10 μM) (a) in absence of LED, (b) on 4 hr illumination of 635 nm LED; **Ir-4**(10 μM) (c) in absence of LED, (d) on 4 hr illumination of 635 nm LED;

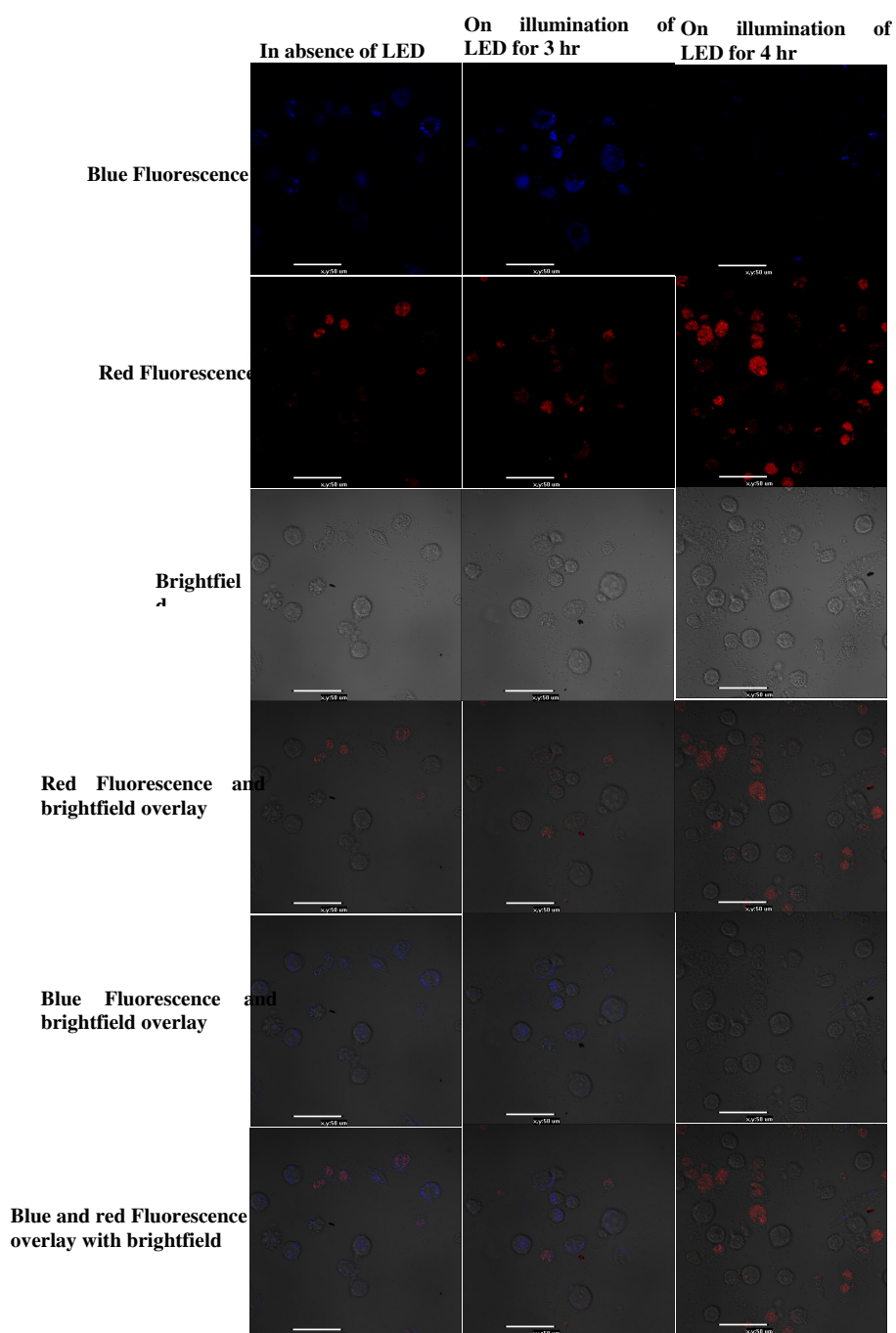


Fig. S65 Confocal fluorescence images of TPP(10 μm) treated LLC cells in absence of LED and on irradiation for 4 h and 3 h by a 635 nm LED followed by further incubation in the dark for 24 h.

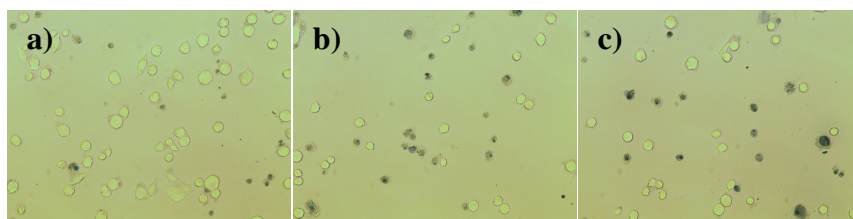


Fig. S66 Trypan blue staining images of LLC cells treated with **TPP** (10 μm) as photosensitizers (a) in absence of LED; on illumination of 635 nm LED for (b) 3 hr, (c) 4 hr.

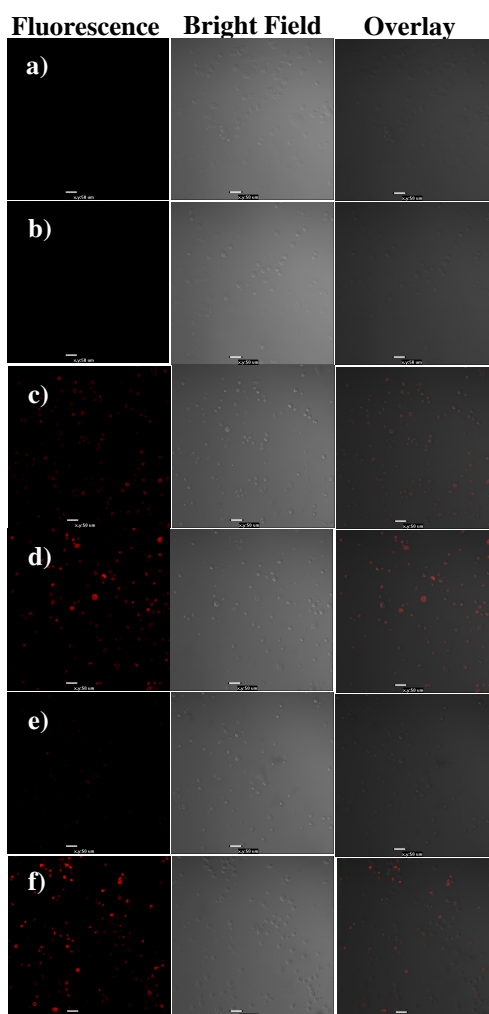


Fig. S67 Confocal fluorescence images in LLC cells . (a) Cells in control on incubation in the dark for 24 h; (b) Cells in control on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h; (c) **Ir-2** (10 μ M) treated cells in the dark for 24 h; (d) **Ir-2** (10 μ M) treated cells on irradiation for 4 hour by a 635 nm LED followed by further incubation in the dark for 24 h.

Initially, the cells were treated with the 1 μ M ,10 μ M and 20 μ M Ir(III) complexes as photosensitizers and were kept either in the dark or were illuminated with a 635 nm LED. Since, porphyrin derivatives are clinically approved photosensitizers, herein TPP is used as reference compound. To ascertain the cellular uptake of the photosensitizers by LLC cells, incubated cells were imaged using confocal fluorescence microscopy (Fig. 14, Fig. S58, Fig. S59 and Fig. S60). The **Ir-1** (Fig. S58) and **Ir-2** (Fig. S59) exhibits a strong red fluorescence signal(λ_{ex} = 543 nm) for 10 μ M and 20 μ M in comparison to 1 μ M. The overlay of fluorescence and bright field images, confirm the good cellular permeability of the photosensitizers, **Ir-1** and **Ir-2** for 10 μ M and 20 μ M concentrations, both in absence and presence of the LED. Good cellular permeability was also observed for **Ir-3** (10 μ M), in contrast, cellular uptake of **Ir-4** was poor in absence of light (Fig. S60). As a control the cells were incubated in absence of light and also in presence of light and sensitizers. No fluorescence was observed in the respective controls. On the other hand, when the cells were treated with **TPP** (Fig. S65) as sensitizers, the fluorescence was found to be weaker than Ir(III) complexes.

The effect of Ir(III) complexes for cell viability was investigated both in presence and absence of light using trypan blue staining. Trypan Blue is one of the dye exclusion procedures for viable cell counting. This method is based on the principle that live (viable) cells do not take up certain dyes, whereas dead (nonviable) cells do. Since cells are very selective to the compound that penetrates through the cell membrane in a viable cell,

Trypan blue is not absorbed and hence, live cells with undamaged cell membranes are not colored. However, it traverses the membrane of the dead cell and binds to several intracellular proteins, staining the cell blue. Therefore, dead cells are shown to be a distinctive dark black colour at the center of the cell under a light microscope, and living cells are excluded from staining. Trypan blue staining is used only to determine the dead cells in a population and not the apoptotic cells.

The cytotoxicity of Ir(III) complexes was assessed, and found, its presence inhibits cell viability and growth. Cytotoxicity studies reveal that although **Ir-1** (IC_{50} in dark = 8.16 μ M) and **Ir-2** (IC_{50} in dark = 15.63 μ M) at different concentrations, is essentially noncytotoxic in the absence of light, it exhibits high photocytotoxicity (IC_{50} for **Ir-1** on photoirradiation = 6.81 μ M and IC_{50} for **Ir-2** on photoirradiation = 9.80 μ M). Dark black spots were observed mostly in the LED treated regions, which demonstrated that most of irradiated cells were severely damaged or destroyed. **Ir-1** was found to reduce the viability of these LLC cells by approximately 80-90% for 10 μ M concentration and by 90-100% for 20 μ M concentration in the light (on 4 h illumination) (Fig. S62) whereas the negligible effect was found in the dark indicating (Fig. S61) a light-dependent cytotoxic death effect. No dead cells was observed in the control i.e incubated cells in absence of light and sensitizers. No significant change was also observed in case of **Ir-2** when the cells were kept in the dark (Fig. S61), whereas it was found to reduce the viability of the LLC cells by 60-70% for 10 μ M concentration and by 90-100% for 20 μ M concentration (Fig. S62) in a light dependent cytotoxic death effect. In contrast, almost all of the cells were found to be viable both in presence and absence of light in case of **Ir-3** (10 μ M), **Ir-4** (10 μ M) (Fig. S64) and **TPP** (10 μ M) (Fig. S66). Further, the viability of the LLC cell was also studied on decreasing the illumination time for **Ir-1** (10 μ M) and **Ir-2** (10 μ M) to distinguish the effect of optical doses (Fig. 14 and Fig. S63). On irradiation of **Ir-1** (10 μ M) treated LLC cells for one hour, no significant change was observed whereas on illumination for 3 h 50-60% reduced viability of the LLC cells was observed (Fig. S63a and Fig. 63b). The cells treated with **Ir-2** (10 μ M) on illumination of 635 nm LED for 1 h and 3 h, exhibited negligible effect (Fig. S63c and Fig. 63d). These results demonstrated the phototoxicity of the Ir(III) complexes were in accordance with 1O_2 generation and cellular uptake data and there is a clear potential for the development of **Ir-1** and **Ir-2** into new PDT agents. Since, **Ir-1** have higher molar absorption coefficients in 606 nm, high singlet oxygen quantum yield and low toxicity in the absence of light, it has a significant potential to deliver PDT agents that could be individually modify for an exact therapeutic requirement.

8.0. The x-y-z coordinates of the triplet optimized geometries of complexes

Ir-1 ground state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	6.02969840	0.01601910	-0.74480020
C	5.47454819	-2.32123267	-0.87633435
H	5.75915157	1.06155962	-0.68048471
C	6.83106676	-2.59072713	-0.91955532
H	4.74910132	-3.12663768	-0.91142699
C	7.76741660	-1.54975159	-0.87943775
H	7.16520425	-3.61894691	-0.98994437
C	9.22084227	-1.75663019	-0.96137466
C	9.82420648	-3.01313809	-1.11247262
C	11.31497612	-0.72281944	-0.99751683
C	11.20860683	-3.10469097	-1.20492556
H	9.22022720	-3.91077942	-1.16580216
C	11.97303242	-1.93795327	-1.14960777
H	11.85738872	0.21541789	-0.95596595
H	11.68344351	-4.07345599	-1.32490454
H	13.05447466	-1.96311118	-1.22687072
N	9.97900622	-0.63061971	-0.89701201
C	5.03346716	-0.98238548	-0.79595470
C	8.17150572	0.89838005	-3.70072396
C	9.41558022	2.05777176	-5.43524042
C	8.95213667	1.48396597	-2.69256229
H	7.36663024	0.21654253	-3.43920328
C	10.20687128	2.65400991	-4.46055158
H	9.58831860	2.27372952	-6.48524721
C	9.98120332	2.37404300	-3.10141271
H	10.99561389	3.33718559	-4.76365072
C	10.76128113	2.96808639	-2.01815840
C	11.81063634	3.88833090	-2.16569604
C	11.03669911	3.04813875	0.31875153
C	12.47212552	4.38373171	-1.05106053
H	12.09706120	4.21338683	-3.15886594
C	12.07923607	3.95661892	0.22096025
H	10.68382567	2.68938538	1.27737106
H	13.28174724	5.09769724	-1.16873982
H	12.56255069	4.32190969	1.12023658
N	10.39744346	2.55812498	-0.76301126
C	8.39686128	1.17909837	-5.05050964
H	7.77368197	0.71175589	-5.80909078
C	7.01807922	3.65341640	-1.28498702
C	5.87146988	4.92722383	0.43283283
C	7.57953269	2.78747508	-0.33252916
H	7.23850308	3.50515790	-2.33725777
C	6.41030612	4.08823288	1.40077846
H	5.22167396	5.74738515	0.72353077
C	7.25617684	3.02521169	1.03413983
H	6.16810225	4.26779439	2.44434792
C	7.83393026	2.10908608	2.02686587
C	7.60481139	2.16140853	3.41268999
C	9.22180125	0.24246954	2.33670428
C	8.20219292	1.23364588	4.25521084
H	6.95687758	2.92595108	3.82411443

C	9.03079399	0.24748457	3.71140679
H	9.85400691	-0.49878170	1.85836271
H	8.02339456	1.27563134	5.32560094
H	9.51524103	-0.49765944	4.33287690
N	8.64944455	1.14246163	1.51714149
C	6.17710750	4.70511244	-0.91317939
H	5.76086122	5.35684170	-1.67747908
Ir	8.81935995	1.21075559	-0.68802413
C	3.66901217	-0.63721340	-0.77270533
N	7.34102022	-0.25311157	-0.78013673
C	0.06178694	-1.01599776	-0.75321643
C	0.51706994	1.23631235	-0.80880403
C	-0.88034323	1.01419393	-0.80928989
C	-1.97771222	1.91502385	-0.84519177
C	-3.28932782	1.44810276	-0.83853230
C	-4.55831519	2.14204286	-0.87406100
C	-4.89122255	-0.10717281	-0.79890233
N	-1.10934780	-0.37044585	-0.77229528
N	-3.56117681	0.07053583	-0.79322055
B	-2.50693937	-1.07425255	-0.74689629
F	-2.63862296	-1.89315416	-1.86148186
F	-2.64097615	-1.80376901	0.42813687
C	1.29449561	2.51726479	-0.83942971
H	1.09093291	3.09901746	-1.74459446
H	1.05246850	3.16411855	0.00999830
H	2.36612054	2.30017778	-0.80879611
C	-4.83511553	3.61444184	-0.92878717
H	-4.39776487	4.08228567	-1.81705519
H	-5.91524054	3.78619450	-0.95089336
H	-4.42427231	4.14225095	-0.06173044
C	0.17730429	-2.50304404	-0.71274538
H	-0.32646710	-2.94830708	-1.57677580
H	1.22757861	-2.80291952	-0.70904997
H	-0.31766916	-2.89961189	0.17989957
C	-1.71149124	3.38521056	-0.89905267
C	-1.60502591	4.13168623	0.28248165
C	-1.56718645	4.03108076	-2.13466709
C	-1.35999959	5.50528084	0.22739333
C	-1.32274572	5.40473332	-2.18682087
H	-1.65060569	3.45581306	-3.05283517
H	-1.28370170	6.07565564	1.14896551
H	-1.21697965	5.89642829	-3.14984768
C	-1.21895777	6.14421235	-1.00648593
H	-1.03210491	7.21350191	-1.04820371
H	-1.71854459	3.63511635	1.24245650
C	-5.52924532	1.15812989	-0.84824509
H	-6.60044342	1.31162989	-0.86326675
C	1.11104909	-0.05184444	-0.77449329
C	2.47947708	-0.35707323	-0.77095722
C	-5.54732682	-1.49982352	-0.75826753
H	-4.93521786	-2.37676737	-0.72374063
C	-6.89729942	-1.61848203	-0.76608859
H	-7.51461159	-0.74519007	-0.80053930
C	-7.54511468	-3.01500193	-0.72525273
C	-8.93465520	-3.13984263	-0.73321301
C	-6.74274261	-4.15506211	-0.68042010
C	-9.52161067	-4.40447507	-0.69566544
H	-9.56695834	-2.24082134	-0.76778544
C	-7.32971150	-5.42018670	-0.64385264
H	-5.64754973	-4.05685637	-0.67431975

C	-8.71891560	-5.54505891	-0.65132962
H	-10.61685975	-4.50293409	-0.70130346
H	-6.69682071	-6.31890990	-0.60892291
O	-9.32101596	-6.84155401	-0.61291593
C	-10.74442787	-6.70791886	-0.64357838
H	-11.19436318	-7.67844214	-0.62028062
H	-11.06813162	-6.14422208	0.20634034
H	-11.03585882	-6.20109964	-1.53973812

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 2 4 2.0 5 1.0 18 1.5
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 6 8 1.0 61 1.5
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Ir-1 lowest-lying triplet state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 3

```

1 3
C      2.39108300 -1.11332200 -0.07029700
C      1.44013300 -3.32145600 -0.14178900
H      2.30263400 -0.03559900 -0.04781200
C      2.73037200 -3.82376400 -0.13722700
H      0.58727100 -3.99053700 -0.17080700
C      3.83133500 -2.95972200 -0.09821200
H      2.88211000 -4.89570700 -0.16270800
C      5.22876600 -3.42032300 -0.09855500
C      5.60604600 -4.76742700 -0.17630800
C      7.47079800 -2.76983600 -0.02661400
C      6.95600800 -5.10295200 -0.17606900
H      4.85729200 -5.54712500 -0.24206900
C      7.90989100 -4.08714000 -0.10028000
H      8.16838000 -1.94162200  0.02860500
H      7.25771600 -6.14360500 -0.23785900
H      8.97225800 -4.30401500 -0.10168900
N      6.16841500 -2.44204900 -0.02093900
C      1.24001700 -1.92577600 -0.10953900
C      4.79939400 -0.77886000 -2.99455200
C      6.31438700  0.04495200 -4.70568400
C      5.62447100 -0.28995900 -1.96931800
H      3.87290000 -1.29077000 -2.74905300
C      7.15424400  0.54056800 -3.71414500
H      6.57360800  0.17067900 -5.75277300
C      6.81677300  0.37814300 -2.35913400
H      8.06748100  1.05441700 -4.00133000
C      7.64112600  0.88016400 -1.26010700
C      8.84959700  1.58026300 -1.39025300
C      7.81513100  1.03359100  1.08234100
C      9.53891500  2.00510400 -0.26259000
H      9.24067000  1.78974300 -2.37874000
C      9.01358700  1.72669300  1.00245100
H      7.36086800  0.79462600  2.03538800
H      10.47302500  2.54856700 -0.36618800
H      9.51495800  2.04114300  1.91081000
N      7.14551300  0.61588300 -0.01138700
C      5.13533900 -0.61523100 -4.34106100
H      4.47383900 -1.00307200 -5.11209100
C      4.03961400  2.26287200 -0.78854100
C      3.03891000  3.80907000  0.79103700
C      4.39278400  1.36988800  0.23707300
H      4.28554900  2.01828800 -1.81707300
  
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C	3.37672000	2.94940000	1.83059500
H	2.52261100	4.74122500	1.00125700
C	4.04561000	1.73971900	1.56811500
H	3.11466200	3.22746100	2.84731400
C	4.40559300	0.79734600	2.63813700
C	4.12507400	0.97245100	4.00331800
C	5.43038000	-1.25827700	3.11784100
C	4.51193500	0.00711900	4.92408800
H	3.60336000	1.86039700	4.33922200
C	5.17971200	-1.13687200	4.47799300
H	5.94551200	-2.12434600	2.71580200
H	4.29427100	0.14333000	5.97914900
H	5.49824700	-1.91545600	5.16220600
N	5.06068500	-0.32388300	2.22347800
C	3.37212400	3.46107300	-0.52166700
H	3.11244000	4.12698400	-1.34114500
Ir	5.34709300	-0.41919900	0.03533300
C	-0.04341200	-1.33969300	-0.11143700
N	3.63661300	-1.60619100	-0.06111100
C	-3.65685000	-0.95616700	-0.04552700
C	-2.73092700	1.14434000	-0.13401400
C	-4.14224800	1.23096100	-0.10434100
C	-5.02146400	2.34658300	-0.13429500
C	-6.40274900	2.16654700	-0.13703300
C	-7.49031700	3.12310000	-0.18886700
C	-8.31756400	0.99858600	-0.14399100
N	-4.66522600	-0.07060600	-0.05226000
N	-6.96640200	0.88442000	-0.11111500
B	-6.17264100	-0.43833700	0.08594600
F	-6.52396200	-1.36590900	-0.89701300
F	-6.41481700	-0.96745800	1.35264100
C	-1.69503600	2.22605100	-0.19684900
H	-1.78698300	2.82954400	-1.10605600
H	-1.77049400	2.91663700	0.64940300
H	-0.69565500	1.78155000	-0.18539300
C	-7.43358100	4.62081100	-0.24196800
H	-6.90943500	4.97931500	-1.13391100
H	-8.44912000	5.02749500	-0.25666100
H	-6.90915500	5.04089500	0.62235800
C	-3.85646200	-2.43365900	0.02058800
H	-4.40925000	-2.79027500	-0.85446800
H	-2.89115800	-2.94262700	0.06779000
H	-4.44768800	-2.70213500	0.90269700
C	-4.44468000	3.72563800	-0.16965500
C	-4.16499600	4.40529000	1.02438000
C	-4.17199800	4.35102400	-1.39451700
C	-3.62358900	5.69220500	0.99266100
C	-3.62998200	5.63771300	-1.42377800
H	-4.38714500	3.82871800	-2.32271200
H	-3.41387300	6.21099500	1.92394800
H	-3.42482400	6.11364600	-2.37863900
C	-3.35503800	6.31064000	-0.23087800
H	-2.93566900	7.31250200	-0.25465000
H	-4.37472400	3.92480800	1.97608000
C	-8.65220000	2.38620800	-0.19220400
H	-9.65481400	2.78843900	-0.24201800
C	-2.42887100	-0.24225100	-0.09866000
C	-1.15287600	-0.82979700	-0.10767200
C	-9.19492700	-0.13952200	-0.14318700
H	-8.72037100	-1.11068900	-0.21855800

C	-10.54843400	-0.03700900	-0.06542300
H	-10.98757900	0.95700500	0.00425400
C	-11.51165000	-1.12354600	-0.05809400
C	-12.88429100	-0.81736300	0.00443100
C	-11.15102000	-2.49160600	-0.10817500
C	-13.86382600	-1.80720700	0.01458800
H	-13.19177300	0.22478500	0.04510600
C	-12.11169600	-3.48523200	-0.09788200
H	-10.10458600	-2.77678600	-0.15235800
C	-13.48039200	-3.15494100	-0.03683000
H	-14.90857600	-1.52394400	0.06278400
H	-11.83463300	-4.53406100	-0.13479100
O	-14.33833700	-4.20480000	-0.03136800
C	-15.73810700	-3.94257400	0.03311400
H	-16.22334400	-4.91932500	0.02595400
H	-16.00113300	-3.41048700	0.95520200
H	-16.07426700	-3.36107900	-0.83368400

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Ir-2 ground state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	6.02969840	0.01601910	-0.74480020
C	5.47454819	-2.32123267	-0.87633435
H	5.75915157	1.06155962	-0.68048471
C	6.83106676	-2.59072713	-0.91955532
H	4.74910132	-3.12663768	-0.91142699
C	7.76741660	-1.54975159	-0.87943775
H	7.16520425	-3.61894691	-0.98994437
C	9.22084227	-1.75663019	-0.96137466
C	9.82420648	-3.01313809	-1.11247262
C	11.31497612	-0.72281944	-0.99751683
C	11.20860683	-3.10469097	-1.20492556
H	9.22022720	-3.91077942	-1.16580216
C	11.97303242	-1.93795327	-1.14960777
H	11.85738872	0.21541789	-0.95596595
H	11.68344351	-4.07345599	-1.32490454
H	13.05447466	-1.96311118	-1.22687072
N	9.97900622	-0.63061971	-0.89701201
C	5.03346716	-0.98238548	-0.79595470
C	8.17150572	0.89838005	-3.70072396
C	9.41558022	2.05777176	-5.43524042
C	8.95213667	1.48396597	-2.69256229
H	7.36663024	0.21654253	-3.43920328
C	10.20687128	2.65400991	-4.46055158
H	9.58831860	2.27372952	-6.48524721
C	9.98120332	2.37404300	-3.10141271
H	10.99561389	3.33718559	-4.76365072
C	10.76128113	2.96808639	-2.01815840
C	11.81063634	3.88833090	-2.16569604
C	11.03669911	3.04813875	0.31875153
C	12.47212552	4.38373171	-1.05106053
H	12.09706120	4.21338683	-3.15886594
C	12.07923607	3.95661892	0.22096025
H	10.68382567	2.68938538	1.27737106
H	13.28174724	5.09769724	-1.16873982

H	12.56255069	4.32190969	1.12023658
N	10.39744346	2.55812498	-0.76301126
C	8.39686128	1.17909837	-5.05050964
H	7.77368197	0.71175589	-5.80909078
C	7.01807922	3.65341640	-1.28498702
C	5.87146988	4.92722383	0.43283283
C	7.57953269	2.78747508	-0.33252916
H	7.23850308	3.50515790	-2.33725777
C	6.41030612	4.08823288	1.40077846
H	5.22167396	5.74738515	0.72353077
C	7.25617684	3.02521169	1.03413983
H	6.16810225	4.26779439	2.44434792
C	7.83393026	2.10908608	2.02686587
C	7.60481139	2.16140853	3.41268999
C	9.22180125	0.24246954	2.33670428
C	8.20219292	1.23364588	4.25521084
H	6.95687758	2.92595108	3.82411443
C	9.03079399	0.24748457	3.71140679
H	9.85400691	-0.49878170	1.85836271
H	8.02339456	1.27563134	5.32560094
H	9.51524103	-0.49765944	4.33287690
N	8.64944455	1.14246163	1.51714149
C	6.17710750	4.70511244	-0.91317939
H	5.76086122	5.35684170	-1.67747908
Ir	8.81935995	1.21075559	-0.68802413
C	3.66901217	-0.63721340	-0.77270533
N	7.34102022	-0.25311157	-0.78013673
C	0.06178694	-1.01599776	-0.75321643
C	0.51706994	1.23631235	-0.80880403
C	-0.88034323	1.01419393	-0.80928989
C	-1.97771222	1.91502385	-0.84519177
C	-3.28932782	1.44810276	-0.83853230
C	-4.55831519	2.14204286	-0.87406100
C	-4.89122255	-0.10717281	-0.79890233
N	-1.10934780	-0.37044585	-0.77229528
N	-3.56117681	0.07053583	-0.79322055
B	-2.50693937	-1.07425255	-0.74689629
F	-2.63862296	-1.89315416	-1.86148186
F	-2.64097615	-1.80376901	0.42813687
C	1.29449561	2.51726479	-0.83942971
H	1.09093291	3.09901746	-1.74459446
H	1.05246850	3.16411855	0.00999830
H	2.36612054	2.30017778	-0.80879611
C	-4.83511553	3.61444184	-0.92878717
H	-4.39776487	4.08228567	-1.81705519
H	-5.91524054	3.78619450	-0.95089336
H	-4.42427231	4.14225095	-0.06173044
C	-1.71149124	3.38521056	-0.89905267
C	-1.60502591	4.13168623	0.28248165
C	-1.56718645	4.03108076	-2.13466709
C	-1.35999959	5.50528084	0.22739333
C	-1.32274572	5.40473332	-2.18682087
H	-1.65060569	3.45581306	-3.05283517
H	-1.28370170	6.07565564	1.14896551
H	-1.21697965	5.89642829	-3.14984768
C	-1.21895777	6.14421235	-1.00648593
H	-1.03210491	7.21350191	-1.04820371
H	-1.71854459	3.63511635	1.24245650
C	-5.52924532	1.15812989	-0.84824509
H	-6.60044342	1.31162989	-0.86326675

C	1.11104909	-0.05184444	-0.77449329
C	2.47947708	-0.35707323	-0.77095722
C	-5.54732682	-1.49982352	-0.75826753
H	-4.93521786	-2.37676737	-0.72374063
C	-6.89729942	-1.61848203	-0.76608859
H	-7.51461159	-0.74519007	-0.80053930
C	-7.54511468	-3.01500193	-0.72525273
C	-8.93465520	-3.13984263	-0.73321301
C	-6.74274261	-4.15506211	-0.68042010
C	-9.52161067	-4.40447507	-0.69566544
H	-9.56695834	-2.24082134	-0.76778544
C	-7.32971150	-5.42018670	-0.64385264
H	-5.64754973	-4.05685637	-0.67431975
C	-8.71891560	-5.54505891	-0.65132962
H	-10.61685975	-4.50293409	-0.70130346
H	-6.69682071	-6.31890990	-0.60892291
C	-10.74442787	-6.70791886	-0.64357838
H	-11.19436318	-7.67844214	-0.62028062
H	-11.06813162	-6.14422208	0.20634034
H	-11.03585882	-6.20109964	-1.53973812
C	0.18101465	-2.55080718	-0.71144547
H	-0.70262709	-3.15400478	-0.69628215
C	1.40126319	-3.14008648	-0.69382609
H	2.28847429	-2.54214754	-0.70884203
C	1.51136650	-4.67557726	-0.65204895
C	2.76642088	-5.28465737	-0.63384587
C	0.35642239	-5.45740978	-0.63229678
C	2.86641457	-6.67528109	-0.59658076
H	3.67676619	-4.66801676	-0.65020291
C	0.45627249	-6.84844360	-0.59402459
H	-0.63283670	-4.97751928	-0.64645945
C	1.71099218	-7.45746038	-0.57630290
H	3.85562787	-7.15545339	-0.58286481
H	-0.45452327	-7.46461718	-0.57804285
C	1.14186517	-9.43094730	0.66621170
H	0.08222573	-9.34943924	0.54203169
H	1.40545295	-10.45698621	0.81676283
H	1.44669851	-8.85605548	1.51560915
O	-9.32101596	-6.84155401	-0.61291593
O	1.81671684	-8.92312523	-0.53694746

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Ir-2 lowest-lying triplet state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 3

C	-2.73313400	0.65243400	-0.17597000
C	-1.68090600	2.76954400	-0.62168500
H	-2.69538600	-0.40683400	0.03948500
C	-2.94682000	3.31966700	-0.73001100
H	-0.79811500	3.38473600	-0.75711800
C	-4.08671900	2.52412000	-0.56103100
H	-3.04874300	4.37498400	-0.95087600
C	-5.46152600	3.03394300	-0.68333000
C	-5.77501300	4.36158500	-1.00289100
C	-7.73176000	2.49586400	-0.57880600
C	-7.10782900	4.74610800	-1.10678500
H	-4.98973400	5.08742300	-1.17417900
C	-8.10857000	3.79726600	-0.89239700
H	-8.46776400	1.71854700	-0.40648300
H	-7.36014100	5.77192800	-1.35546100
H	-9.15961300	4.05268400	-0.96818500
N	-6.44639800	2.12208100	-0.47135800
C	-1.54588600	1.39373900	-0.34029600
C	-5.07079300	-0.11097500	-3.04016100
C	-6.56833500	-1.18527900	-4.62290800
C	-5.94093900	-0.37915800	-1.97127200
H	-4.13349400	0.40925800	-2.86124200
C	-7.45281800	-1.46458800	-3.58659600
H	-6.80348500	-1.49197400	-5.63782300
C	-7.14694300	-1.06778000	-2.27305700
H	-8.37680700	-1.99227500	-3.80627100
C	-8.02199000	-1.32826700	-1.13037800
C	-9.25271900	-2.00018300	-1.17129500
C	-8.26843000	-1.03702700	1.19246700
C	-9.98977400	-2.18438800	-0.00940900
H	-9.62312500	-2.37794400	-2.11684600
C	-9.48999900	-1.69330400	1.20005400
H	-7.83039800	-0.64254500	2.10022800
H	-10.94095600	-2.70665100	-0.04324000
H	-10.02833800	-1.81786100	2.13283500
N	-7.55341000	-0.85080600	0.06422100
C	-5.37633000	-0.50642300	-4.34510500
H	-4.68075900	-0.28607300	-5.15141700
C	-4.49112000	-2.71842400	-0.26587100
C	-3.59012500	-3.96062800	1.61349700
C	-4.83847000	-1.63363600	0.55669500
H	-4.69871500	-2.66869900	-1.33017500
C	-3.92268200	-2.90585200	2.45650800
H	-3.11381800	-4.84988200	2.01598800
C	-4.54058100	-1.74996400	1.94494700
H	-3.69670700	-2.98949500	3.51558700
C	-4.89945100	-0.61059100	2.80299500
C	-4.66727700	-0.52934100	4.18592800
C	-5.88026400	1.52051100	2.84765600
C	-5.05551200	0.60171400	4.89274900
H	-4.18315800	-1.34910500	4.70270600
C	-5.67761400	1.65377000	4.21468100
H	-6.36053300	2.30300600	2.26989800
H	-4.87532600	0.66367600	5.96174700
H	-5.99760000	2.55389700	4.72770300
N	-5.50631000	0.42677400	2.16009900
C	-3.87632600	-3.86313900	0.24831600
H	-3.62033000	-4.68281900	-0.41876400

Ir	-5.71608600	0.11254700	-0.01722000
C	-0.29049200	0.76011800	-0.22539000
N	-3.95478600	1.19234300	-0.27766300
C	3.34589700	0.18368600	-0.04295200
C	2.21991200	-1.82731100	-0.03500100
C	3.61944400	-2.05078000	-0.03002200
C	4.36940500	-3.25690800	-0.03683900
C	5.76290100	-3.22896200	-0.07160900
C	6.73940100	-4.29643000	-0.13912000
C	7.78945400	-2.27153600	-0.14372900
N	4.26791700	-0.81221500	-0.04129700
N	6.45729700	-2.01469400	-0.07959200
B	5.80673800	-0.61996100	0.13913000
F	6.29195300	0.27963500	-0.81909300
F	6.08050400	-0.15010500	1.41956100
C	1.08846000	-2.81054200	-0.04861300
H	1.08492500	-3.41677300	-0.96070500
H	1.14277500	-3.50746500	0.79327200
H	0.13460700	-2.27871000	0.00777000
C	6.52375500	-5.78030700	-0.17511300
H	5.93179700	-6.08761000	-1.04347300
H	7.48999700	-6.29134300	-0.22335900
H	5.99171500	-6.13892700	0.71200200
C	3.65175900	-4.56848900	-0.01862800
C	3.35910900	-5.19860500	1.19926100
C	3.26539500	-5.18341800	-1.21785600
C	2.68995000	-6.42444700	1.21610200
C	2.59761600	-6.40979000	-1.19910300
H	3.49075000	-4.69967000	-2.16440900
H	2.46971400	-6.90437000	2.16564500
H	2.30538000	-6.87804100	-2.13491500
C	2.30862700	-7.03253100	0.01754700
H	1.79015900	-7.98710600	0.03160600
H	3.65725700	-4.72696900	2.13161100
C	7.97263100	-3.68654000	-0.18387600
H	8.92504800	-4.19375200	-0.25580000
C	2.04561700	-0.42446500	-0.05186000
C	0.80667200	0.23088100	-0.13670000
C	8.78574400	-1.23626800	-0.17446000
H	8.41790800	-0.21923800	-0.23452800
C	10.12233500	-1.48427800	-0.14428000
H	10.45543600	-2.51943000	-0.08736800
C	11.19533900	-0.50572100	-0.17686700
C	12.52941100	-0.95391500	-0.14715600
C	10.97945700	0.89215700	-0.23695700
C	13.60751800	-0.07255500	-0.17723200
H	12.72660600	-2.02213800	-0.09971100
C	12.03913100	1.77914500	-0.26726500
H	9.96790800	1.28511700	-0.25781200
C	13.36654800	1.30727000	-0.23808000
H	14.61770600	-0.46378300	-0.15318800
H	11.87300000	2.85085500	-0.31267400
C	15.69553500	1.85317300	-0.24159800
H	16.28106100	2.77273200	-0.27601600
H	15.92714900	1.30656300	0.68044000
H	15.94365000	1.22921200	-1.10860700
C	3.72473000	1.57479000	-0.04775600
H	4.75943000	1.76462100	-0.30762400
C	2.90357500	2.60857200	0.26611500
H	1.88499800	2.38860600	0.57426400

C	3.24634700	4.02480400	0.25988700
C	2.29266300	4.96137700	0.71754500
C	4.48517600	4.52986400	-0.18050100
C	2.55869200	6.32126100	0.73999800
H	1.32783200	4.60373200	1.07009700
C	4.76784300	5.89212100	-0.16430700
H	5.24722200	3.84985700	-0.54863500
C	3.80295600	6.80177700	0.29898700
H	1.82252200	7.03475200	1.09701700
H	5.73413900	6.23636700	-0.51382400
C	5.22048900	8.69647700	-0.06211500
H	5.41509000	8.48334200	-1.12023900
H	5.13374900	9.77446200	0.08048300
H	6.04926300	8.31363700	0.54554500
O	14.33026500	2.26133000	-0.27169900
O	3.97383700	8.14830500	0.35720700

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Ir-3 ground state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	6.02969840	0.01601910	-0.74480020
C	5.47454819	-2.32123267	-0.87633435
H	5.75915157	1.06155962	-0.68048471
C	6.83106676	-2.59072713	-0.91955532
H	4.74910132	-3.12663768	-0.91142699
C	7.76741660	-1.54975159	-0.87943775
H	7.16520425	-3.61894691	-0.98994437
C	9.22084227	-1.75663019	-0.96137466
C	9.82420648	-3.01313809	-1.11247262
C	11.31497612	-0.72281944	-0.99751683
C	11.20860683	-3.10469097	-1.20492556
H	9.22022720	-3.91077942	-1.16580216
C	11.97303242	-1.93795327	-1.14960777
H	11.85738872	0.21541789	-0.95596595
H	11.68344351	-4.07345599	-1.32490454
H	13.05447466	-1.96311118	-1.22687072
N	9.97900622	-0.63061971	-0.89701201
C	5.03346716	-0.98238548	-0.79595470
C	8.17150572	0.89838005	-3.70072396
C	9.41558022	2.05777176	-5.43524042
C	8.95213667	1.48396597	-2.69256229
H	7.36663024	0.21654253	-3.43920328
C	10.20687128	2.65400991	-4.46055158
H	9.58831860	2.27372952	-6.48524721
C	9.98120332	2.37404300	-3.10141271
H	10.99561389	3.33718559	-4.76365072

C	10.76128113	2.96808639	-2.01815840
C	11.81063634	3.88833090	-2.16569604
C	11.03669911	3.04813875	0.31875153
C	12.47212552	4.38373171	-1.05106053
H	12.09706120	4.21338683	-3.15886594
C	12.07923607	3.95661892	0.22096025
H	10.68382567	2.68938538	1.27737106
H	13.28174724	5.09769724	-1.16873982
H	12.56255069	4.32190969	1.12023658
N	10.39744346	2.55812498	-0.76301126
C	8.39686128	1.17909837	-5.05050964
H	7.77368197	0.71175589	-5.80909078
C	7.01807922	3.65341640	-1.28498702
C	5.87146988	4.92722383	0.43283283
C	7.57953269	2.78747508	-0.33252916
H	7.23850308	3.50515790	-2.33725777
C	6.41030612	4.08823288	1.40077846
H	5.22167396	5.74738515	0.72353077
C	7.25617684	3.02521169	1.03413983
H	6.16810225	4.26779439	2.44434792
C	7.83393026	2.10908608	2.02686587
C	7.60481139	2.16140853	3.41268999
C	9.22180125	0.24246954	2.33670428
C	8.20219292	1.23364588	4.25521084
H	6.95687758	2.92595108	3.82411443
C	9.03079399	0.24748457	3.71140679
H	9.85400691	-0.49878170	1.85836271
H	8.02339456	1.27563134	5.32560094
H	9.51524103	-0.49765944	4.33287690
N	8.64944455	1.14246163	1.51714149
C	6.17710750	4.70511244	-0.91317939
H	5.76086122	5.35684170	-1.67747908
Ir	8.81935995	1.21075559	-0.68802413
C	3.66901217	-0.63721340	-0.77270533
N	7.34102022	-0.25311157	-0.78013673
C	0.06178694	-1.01599776	-0.75321643
C	0.51706994	1.23631235	-0.80880403
C	-0.88034323	1.01419393	-0.80928989
C	-1.97771222	1.91502385	-0.84519177
C	-3.28932782	1.44810276	-0.83853230
C	-4.55831519	2.14204286	-0.87406100
C	-4.89122255	-0.10717281	-0.79890233
N	-1.10934780	-0.37044585	-0.77229528
N	-3.56117681	0.07053583	-0.79322055
B	-2.50693937	-1.07425255	-0.74689629
F	-2.63862296	-1.89315416	-1.86148186
F	-2.64097615	-1.80376901	0.42813687
C	1.29449561	2.51726479	-0.83942971
H	1.09093291	3.09901746	-1.74459446
H	1.05246850	3.16411855	0.00999830
H	2.36612054	2.30017778	-0.80879611
C	-4.83511553	3.61444184	-0.92878717
H	-4.39776487	4.08228567	-1.81705519
H	-5.91524054	3.78619450	-0.95089336
H	-4.42427231	4.14225095	-0.06173044
C	0.17730429	-2.50304404	-0.71274538
H	-0.32646710	-2.94830708	-1.57677580
H	1.22757861	-2.80291952	-0.70904997
H	-0.31766916	-2.89961189	0.17989957
C	-1.71149124	3.38521056	-0.89905267

C	-1.60502591	4.13168623	0.28248165
C	-1.56718645	4.03108076	-2.13466709
C	-1.35999959	5.50528084	0.22739333
C	-1.32274572	5.40473332	-2.18682087
H	-1.65060569	3.45581306	-3.05283517
H	-1.28370170	6.07565564	1.14896551
H	-1.21697965	5.89642829	-3.14984768
C	-1.21895777	6.14421235	-1.00648593
H	-1.03210491	7.21350191	-1.04820371
H	-1.71854459	3.63511635	1.24245650
C	-5.52924532	1.15812989	-0.84824509
H	-6.60044342	1.31162989	-0.86326675
C	1.11104909	-0.05184444	-0.77449329
C	2.47947708	-0.35707323	-0.77095722
C	-5.54732682	-1.49982352	-0.75826753
H	-4.93521786	-2.37676737	-0.72374063
C	-6.89729942	-1.61848203	-0.76608859
H	-7.51461159	-0.74519007	-0.80053930
C	-7.54511468	-3.01500193	-0.72525273
C	-8.93465520	-3.13984263	-0.73321301
C	-6.74274261	-4.15506211	-0.68042010
C	-9.52161067	-4.40447507	-0.69566544
H	-9.56695834	-2.24082134	-0.76778544
C	-7.32971150	-5.42018670	-0.64385264
H	-5.64754973	-4.05685637	-0.67431975
C	-8.71891560	-5.54505891	-0.65132962
H	-10.61685975	-4.50293409	-0.70130346
H	-6.69682071	-6.31890990	-0.60892291
C	-10.74442787	-6.70791886	-0.64357838
H	-11.19436318	-7.67844214	-0.62028062
H	-11.06813162	-6.14422208	0.20634034
H	-11.03585882	-6.20109964	-1.53973812
N	-9.32101596	-6.84155401	-0.61291593
C	-9.20699389	-6.90403118	0.85132298
H	-9.38794569	-5.93391299	1.26487726
H	-9.92709624	-7.59570360	1.23595513
H	-8.22294409	-7.22795354	1.11894265

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60 100 3.0
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62 69 1.5 82 1.0 99 1.5
63 64 1.5 74 1.0 99 1.5
64 65 1.5 69 1.5
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Ir-3 lowest-lying triplet state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 3

C	-2.56919700	-1.08910600	-0.17011500
C	-1.56440200	-3.25093400	-0.49102100
H	-2.50807300	-0.01928100	-0.02314300
C	-2.84118300	-3.78519900	-0.52101500
H	-0.69566400	-3.88998300	-0.60409800
C	-3.96300600	-2.96019000	-0.37369100
H	-2.96629200	-4.85213100	-0.65844600
C	-5.34704900	-3.45839800	-0.37770700
C	-5.68879700	-4.81027800	-0.51667600
C	-7.60306400	-2.88046200	-0.19957900
C	-7.02792900	-5.18535700	-0.49475600
H	-4.92005000	-5.56370000	-0.63602000

C	-8.00705800	-4.20440400	-0.33119500
H	-8.32161500	-2.07971500	-0.06530400
H	-7.30188200	-6.23021200	-0.59990600
H	-9.06193900	-4.45354700	-0.30234700
N	-6.31156400	-2.51294000	-0.22790800
C	-1.39806100	-1.86171100	-0.30999100
C	-4.77348700	-1.31743100	2.88629000
C	-6.18085500	-0.83319700	4.80639200
C	-5.67648100	-0.68970400	2.01342500
H	-3.85698100	-1.75396400	2.49847600
C	-7.09609300	-0.20463800	3.96883000
H	-6.36902400	-0.89021600	5.87444800
C	-6.85066500	-0.13054000	2.58655200
H	-7.99652600	0.22734400	4.39685200
C	-7.75916900	0.52048100	1.64291500
C	-8.96793800	1.15435200	1.96673500
C	-8.09990400	1.05001700	-0.62541000
C	-9.74252600	1.73674800	0.97273600
H	-9.29157400	1.18916300	3.00017100
C	-9.30239600	1.68471200	-0.35292600
H	-7.70803400	0.98451700	-1.63229300
H	-10.67678100	2.22822600	1.22627600
H	-9.87189000	2.12890200	-1.16149200
N	-7.34830100	0.47843100	0.33747100
C	-5.01838200	-1.38924700	4.26011800
H	-4.29819100	-1.87993200	4.91054800
C	-4.23124900	2.07236200	1.16354100
C	-3.35245500	3.87247700	-0.20562000
C	-4.63231200	1.34339800	0.03142500
H	-4.40865200	1.66205200	2.15264900
C	-3.74000800	3.17920400	-1.34712700
H	-2.86377100	4.83833900	-0.29478000
C	-4.37432700	1.92771600	-1.24188500
H	-3.54451500	3.61976700	-2.32048800
C	-4.79225300	1.16084600	-2.42513300
C	-4.60330400	1.55740300	-3.75932400
C	-5.83387400	-0.80774400	-3.16330100
C	-5.04435800	0.74608200	-4.79698200
H	-4.11064300	2.49653000	-3.98029400
C	-5.67563700	-0.46489400	-4.49928400
H	-6.31768000	-1.73401400	-2.87252200
H	-4.89765100	1.05344200	-5.82804400
H	-6.03580200	-1.12777500	-5.27817900
N	-5.40946200	-0.02434400	-2.15581300
C	-3.60034700	3.31412400	1.05223300
H	-3.30160500	3.84885500	1.95067800
Ir	-5.53791300	-0.48101900	0.00148100
C	-0.13064200	-1.24564300	-0.26486400
N	-3.80153900	-1.61271900	-0.20088200
C	3.47196900	-0.78008000	-0.22563800
C	2.49818700	1.29504100	-0.06327200
C	3.90513800	1.41258600	-0.05023200
C	4.76025900	2.54675100	0.05098400
C	6.14163900	2.39359900	0.09562700
C	7.20816300	3.37059600	0.21556800
C	8.08221300	1.26364900	0.13794900
N	4.45930700	0.12669600	-0.14536700
N	6.73425300	1.12440600	0.04952500
B	5.97890400	-0.20391300	-0.23072100
F	6.30671300	-1.16232200	0.73201300

F	6.28764300	-0.68236000	-1.50412700
C	1.43579800	2.34982100	0.02344800
H	1.50698500	2.92930500	0.94984700
H	1.49888300	3.06625800	-0.80241300
H	0.44724300	1.88227600	-0.00805300
C	7.11633500	4.86464900	0.30877000
H	6.56316900	5.18663400	1.19717000
H	8.12176200	5.29319800	0.35962900
H	6.60306200	5.29720600	-0.55614800
C	3.70843900	-2.24826400	-0.35474700
H	4.24141700	-2.63475500	0.51996600
H	2.75722300	-2.77546000	-0.45739100
H	4.33350100	-2.46117200	-1.22869100
C	4.15102700	3.91091500	0.11094700
C	3.87429600	4.61276300	-1.07100100
C	3.84331300	4.50104300	1.34497800
C	3.30286500	5.88596400	-1.01861300
C	3.27054400	5.77376500	1.39548900
H	4.05473700	3.96123600	2.26401300
H	3.09679100	6.42202900	-1.94094500
H	3.03817700	6.22170900	2.35768800
C	2.99991400	6.46884200	0.21435600
H	2.55699400	7.46004200	0.25457200
H	4.11077600	4.15987800	-2.02995800
C	8.38313900	2.65911400	0.23981000
H	9.37415700	3.08079800	0.33808700
C	2.22812800	-0.09657900	-0.17392800
C	0.96703300	-0.71133000	-0.22239200
C	8.98359300	0.15133500	0.14084300
H	8.53367800	-0.83414800	0.15956800
C	10.34117000	0.28991400	0.13480600
H	10.75276300	1.29822100	0.11822700
C	11.33046500	-0.76143900	0.14309600
C	12.70200000	-0.42270500	0.14122300
C	11.01854500	-2.14127000	0.15283000
C	13.70129700	-1.37975900	0.15088500
H	12.98420400	0.62776400	0.13263000
C	12.00191500	-3.11159300	0.16242200
H	9.98065900	-2.46084600	0.15113400
C	13.38206600	-2.76340300	0.16253300
H	14.73490200	-1.05615000	0.14955800
H	11.70366700	-4.15288600	0.16877000
C	15.76523900	-3.33925400	0.16569900
H	16.38289400	-4.23764300	0.17385100
H	16.02084500	-2.75793800	-0.73020300
H	16.02453800	-2.73947800	1.04822900
N	14.36043500	-3.72472600	0.17282200
C	14.00394000	-5.13735200	0.18356100
H	13.42473900	-5.41640000	-0.70669400
H	14.91535100	-5.73566700	0.19500800
H	13.41413900	-5.39910200	1.07192500

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Ir-4 ground state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	6.02969840	0.01601910	-0.74480020
C	5.47454819	-2.32123267	-0.87633435
H	5.75915157	1.06155962	-0.68048471
C	6.83106676	-2.59072713	-0.91955532
H	4.74910132	-3.12663768	-0.91142699
C	7.76741660	-1.54975159	-0.87943775
H	7.16520425	-3.61894691	-0.98994437
C	9.22084227	-1.75663019	-0.96137466
C	9.82420648	-3.01313809	-1.11247262
C	11.31497612	-0.72281944	-0.99751683
C	11.20860683	-3.10469097	-1.20492556
H	9.22022720	-3.91077942	-1.16580216
C	11.97303242	-1.93795327	-1.14960777
H	11.85738872	0.21541789	-0.95596595
H	11.68344351	-4.07345599	-1.32490454
H	13.05447466	-1.96311118	-1.22687072
N	9.97900622	-0.63061971	-0.89701201
C	5.03346716	-0.98238548	-0.79595470
C	8.17150572	0.89838005	-3.70072396
C	9.41558022	2.05777176	-5.43524042
C	8.95213667	1.48396597	-2.69256229
H	7.36663024	0.21654253	-3.43920328
C	10.20687128	2.65400991	-4.46055158
H	9.58831860	2.27372952	-6.48524721
C	9.98120332	2.37404300	-3.10141271
H	10.99561389	3.33718559	-4.76365072
C	10.76128113	2.96808639	-2.01815840
C	11.81063634	3.88833090	-2.16569604
C	11.03669911	3.04813875	0.31875153
C	12.47212552	4.38373171	-1.05106053
H	12.09706120	4.21338683	-3.15886594
C	12.07923607	3.95661892	0.22096025
H	10.68382567	2.68938538	1.27737106
H	13.28174724	5.09769724	-1.16873982
H	12.56255069	4.32190969	1.12023658
N	10.39744346	2.55812498	-0.76301126
C	8.39686128	1.17909837	-5.05050964
H	7.77368197	0.71175589	-5.80909078
C	7.01807922	3.65341640	-1.28498702
C	5.87146988	4.92722383	0.43283283
C	7.57953269	2.78747508	-0.33252916
H	7.23850308	3.50515790	-2.33725777
C	6.41030612	4.08823288	1.40077846
H	5.22167396	5.74738515	0.72353077
C	7.25617684	3.02521169	1.03413983
H	6.16810225	4.26779439	2.44434792
C	7.83393026	2.10908608	2.02686587
C	7.60481139	2.16140853	3.41268999
C	9.22180125	0.24246954	2.33670428
C	8.20219292	1.23364588	4.25521084
H	6.95687758	2.92595108	3.82411443
C	9.03079399	0.24748457	3.71140679
H	9.85400691	-0.49878170	1.85836271
H	8.02339456	1.27563134	5.32560094
H	9.51524103	-0.49765944	4.33287690
N	8.64944455	1.14246163	1.51714149

C	6.17710750	4.70511244	-0.91317939
H	5.76086122	5.35684170	-1.67747908
Ir	8.81935995	1.21075559	-0.68802413
C	3.66901217	-0.63721340	-0.77270533
N	7.34102022	-0.25311157	-0.78013673
C	0.06178694	-1.01599776	-0.75321643
C	0.51706994	1.23631235	-0.80880403
C	-0.88034323	1.01419393	-0.80928989
C	-1.97771222	1.91502385	-0.84519177
C	-3.28932782	1.44810276	-0.83853230
C	-4.55831519	2.14204286	-0.87406100
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C	1.29449561	2.51726479	-0.83942971
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Ir-4 lowest-lying triplet state configuration (B3LYP/6-31G/LANL2DZ)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 3

C	-2.94197800	0.60270300	-0.19144700
C	-1.85197200	2.70139000	-0.63586100
H	-2.92232400	-0.45696600	0.02434200
C	-3.10788300	3.27289300	-0.74571600
H	-0.95835300	3.30110700	-0.76996500
C	-4.26251300	2.49785100	-0.57747300
H	-3.19136400	4.32988000	-0.96674900
C	-5.62738000	3.03080400	-0.69973200

C	-5.91837500	4.36336700	-1.02213300
C	-7.90727800	2.53359700	-0.59222400
C	-7.24400300	4.77102800	-1.12565500
H	-5.12043400	5.07460300	-1.19621900
C	-8.26152500	3.84053500	-0.90821700
H	-8.65693400	1.76990800	-0.41782500
H	-7.47840600	5.80056800	-1.37663000
H	-9.30796400	4.11426600	-0.98371600
N	-6.62860900	2.13704900	-0.48489900
C	-1.74019100	1.32272900	-0.35416100
C	-5.29902000	-0.12195300	-3.05363900
C	-6.81850000	-1.17209800	-4.63176600
C	-6.17117900	-0.37408700	-1.98243500
H	-4.35274900	0.38253300	-2.87714100
C	-7.70536300	-1.43494000	-3.59321800
H	-7.06112000	-1.47586500	-5.64582300
C	-7.38965500	-1.04212800	-2.28076900
H	-8.63880400	-1.94690200	-3.81020900
C	-8.26609300	-1.28683000	-1.13572300
C	-9.50780000	-1.93853200	-1.17281400
C	-8.50123000	-0.99044800	1.18760600
C	-10.24453300	-2.10998200	-0.00879300
H	-9.88695400	-2.31082400	-2.11707600
C	-9.73336000	-1.62664100	1.19903000
H	-8.05391700	-0.60292200	2.09386700
H	-11.20425500	-2.61659300	-0.03969000
H	-10.27097700	-1.74206000	2.13340900
N	-7.78651000	-0.81636000	0.05727000
C	-5.61428200	-0.51356700	-4.35738000
H	-4.91680300	-0.30624200	-5.16550800
C	-4.76060900	-2.73770400	-0.27706900
C	-3.87664100	-3.99284800	1.60183400
C	-5.08582800	-1.64537600	0.54457800
H	-4.97008500	-2.68593900	-1.34091600
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C	-4.78600000	-1.76482200	1.93214100
H	-3.96006000	-3.01677000	3.50251800
C	-5.12107300	-0.61749900	2.78911100
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H	-6.53172700	2.32070100	2.25530300
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C	2.82884800	-5.40608200	-1.16005000
C	2.22340300	-6.60283800	1.28815700
C	2.11744200	-6.60738800	-1.12629100
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