Synthesis, Photophysics and Tunable Reverse Saturable Absorption of Bis-tridentate Iridium(III) Complexes *via* Modification on Diimine Ligand

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1. Experimental section

Materials

All reagents were purchased from Sinopharm Chemical Reagent Co. Ltd and used as received unless otherwise mentioned. All the high-performance liquid chromatography (HPLC)-grade solvents used for spectroscopic study were without any further purification. Ultrapure water was used in the experiments and silica column chromatography was carried out on silica gel (200-300 mesh).

Measurements

The ligands and complexes characterized by mass spectra and ^{1}H NMR. High resolution-mass (HR-MS) spectra were measured on an AB Sciex X-500B QTOF-mass spectrometer, and ^{1}H NMR spectra of the ligands and complexes in $CDCl_3$ or DMSO-d_6 solvent were measured on a Bruker Avance instrument, with tetramethylsilane for ^{1}H NMR spectra as an internal standard.

UV-vis spectra were acquired on Persee-TU-1900 UV spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F4600 fluorescence spectrophotometer. Quantum yields were obtained on an Edinburgh FS-5 fluorescence spectrometer. The nanosecond time-resolved transient difference absorption spectra were detected by Edinburgh analytical instruments (LP980, Edinburgh Instruments,

(U.K.). The emission lifetimes were collected using an Edinburgh ns-lifetime instrument with a 355 nm laser as the excited source. Before each measurement, the sample solutions were degassed with N_2 for 30 min.

The nonlinear transmission experiments for Ir(III) complexes were carried out in CH_3CN solution in a 2 mm cuvette using 4.1 ns laser pulses. A Quantal Brilliant ns laser with a repetition rate of 10 Hz was used as the light source. The experimental setup and details have been described previously. An f = 10 cm planoconvex lens was used to focus the beam to the sample cuvette. The radius of beam waist at the focal point is approximately 0.101 mm, measured by a knife edge. The linear transmission of the solution was adjusted to 80%, at 532 nm in the 2 mm cuvette.

Preparation of ligands

Ligands **L1-L5** are presented in **Scheme S1**.

6-phenyl-2,2'-bipyridine (**L1**). 6-bromo-2,2'-bipyridine (234 mg, 1 mmol), phenylboronic acid (122 mg, 1 mmol), Na_2CO_3 (0.423 g, 4 mmol), toluene (30 mL) and water (10 mL) were added to a 100 mL round-bottom flask under nitrogen. The mixture was refluxed (95 ^oC) with stirred for 24 h, then cooled to room temperature. The residue was taken into H_2O, extracted with ethyl acetate for three times. The remnant was dried over anhydrous Na_2SO_4, and concentrated. The mixture was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (1:2, v/v) as the eluent to give white solid (255 mg, yield 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, J = 4.9, 1.8, 0.9 Hz, 3H), 7.72 (td, J = 7.7, 1.8 Hz, 3H), 7.50 - 7.41 (m, 5H), 7.22 (ddd, J = 7.5, 4.8, 1.1 Hz, 5H).

2-phenyl-1,10-phenanthroline (**L2**). 2-chloro-1,10-phenanthroline (180 mg, 1 mmol), phenylboronic acid (122 mg, 1 mmol), Na_2CO_3 (0.423 g, 4 mmol), toluene (30mL) and water (10 mL) were added to a 100 mL round-bottom flask under nitrogen. The mixture was refluxed (95 ^oC) with stirred for 24 h, then cooled to room temperature. The residue was taken into H_2O, extracted with ethyl acetate for three times. The remnant was dried over anhydrous Na_2SO_4, and concentrated. The mixture was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (1:2,

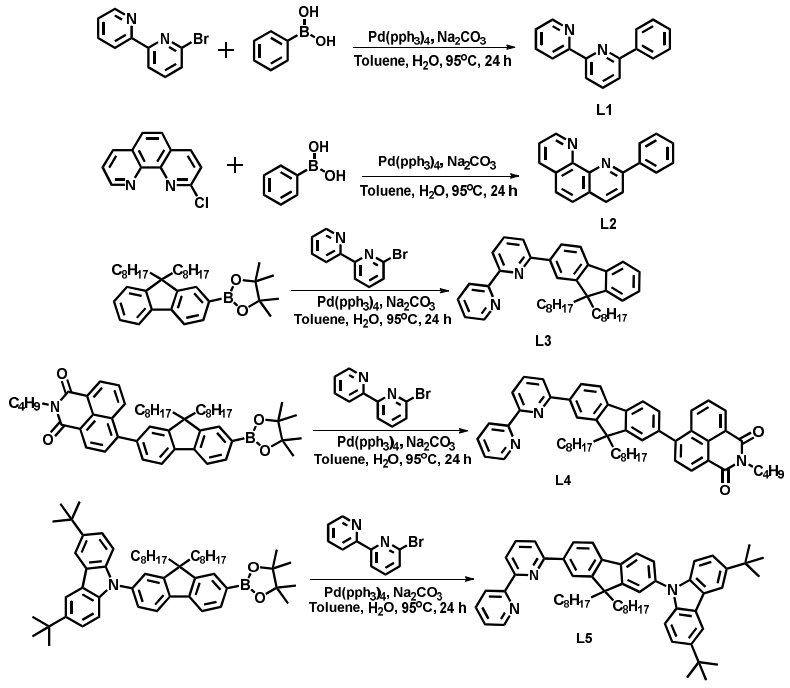
v/v) as the eluent to give white solid (205 mg, yield 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 4.3, 1.5 Hz, 1H), 8.35 (dd, *J* = 5.2, 3.3 Hz, 2H), 8.32 - 8.20 (m, 2H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.78 (q, *J* = 8.8 Hz, 2H), 7.63 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.51 - 7.42 (m, 1H).

6-(9,9-dioctyl-9H-fluoren-2-yl)-2,2'-bipyridine (**L3**). 2-(9,9-dioctyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (516 mg, 1 mmol), 6-bromo-2,2'-bipyridine (234mg, 1 mmol), Na_2CO_3 (0.423g, 4 mmol), toluene (30 mL) and water (10 mL) were added to a 100 mL round-bottom flask under nitrogen. The mixture was refluxed (95 ^{o}C) with stirred for 24 h, then cooled to room temperature. The residue was taken into H_2O, extracted with ethyl acetate for three times. The remnant was dried over anhydrous Na_2SO_4, and concentrated. The mixture was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (4:1, v/v) as the eluent to give yellow liquid (535 mg, yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 - 8.64 (m, 2H), 8.37 (d, *J* = 7.7 Hz, 1H), 8.20 - 8.07 (m, 2H), 7.93 - 7.83 (m, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.38 - 7.28 (m, 3H), 2.18 - 1.97 (m, 4H), 0.92 - 0.50 (m, 30H).

6-(7-([2,2'-bipyridin]-6-yl)-9,9-dioctyl-9H-fluoren-2-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**L4**). 2-butyl-6-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (692 mg, 1 mmol), 6-bromo-2,2'-bipyridine (234 mg, 1 mmol), Na_2CO_3 (0.423 g, 4 mmol) , toluene (30 mL) and water (10 mL) were added to a 100 mL round-bottom flask under nitrogen. The mixture was refluxed (95 ^{o}C) with stirred for 24 h, then cooled to room temperature. The residue was taken into H_2O, extracted with ethyl acetate for three times. The remnant was dried over anhydrous Na_2SO_4, and concentrated. The mixture was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (4:1, v/v) as the eluent to give yellow liquid (788 mg, yield 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 - 8.63 (m, 4H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.32 (dd, *J* = 13.6, 4.7 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 5.4 Hz, 1H), 7.96 - 7.90 (m, 3H), 7.86 (dd, *J* = 13.5, 7.6 Hz, 2H), 7.75 - 7.66 (m, 2H), 7.53 (t, *J* = 4.6 Hz, 1H), 7.49 (dd, *J* = 7.7, 4.2 Hz, 1H), 7.39 - 7.33 (m, 1H), 4.32 - 4.18 (m, 2H),

2.25 - 2.03 (m, 4H), 1.82 - 1.71 (m, 2H), 1.49 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.00 (dd, *J* = 15.5, 8.1 Hz, 3H), 0.91 - 0.51 (m, 30H).

9-(7-([2,2'-bipyridin]-6-yl)-9,9-dioctyl-9H-fluoren-2-yl)-3,6-di-tert-butyl-9H-carbazole (**L5**). 3,6-di-tert-butyl-9-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)-9H-carbazole (792 mg, 1 mmol), 6-bromo-2,2'-bipyridine (234 mg, 1 mmol) , Na_2CO_3 (0.423 g, 4 mmol) , toluene (30 mL) and water (10 mL) were added to a 100 mL round-bottom flask under nitrogen. The mixture was refluxed (95°C) with stirred for 24 h, then cooled to room temperature. The residue was taken into H_2O, extracted with ethyl acetate for three times. The remnant was dried over anhydrous Na_2SO_4, and concentrated. The mixture was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (4:1, v/v) as the eluent to give white solid (771 mg, yield 65%). ^{1}H NMR (400 MHz, CDCl3) δ 9.29 (d, *J* = 23.5 Hz), 8.85 - 8.74 (m, 1H), 8.40 - 8.28 (m, 2H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.17 (t, *J* = 2.4 Hz, 2H), 8.10 (t, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.83 - 7.76 (m, 1H), 7.67 (dd, *J* = 5.9, 4.7 Hz, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.53 (d, *J* = 6.4, 2H), 7.50 - 7.43 (m, 2H), 7.39 - 7.30 (m, 2H), 2.20 (d, *J* = 15.2, 5.0 Hz, 2H), 2.09 - 1.98 (m, 2H), 1.48 (s, 18H), 1.02 - 0.50 (m, 30H).



Scheme S1. The molecular structures and synthetic route to ligands **L1-L5**

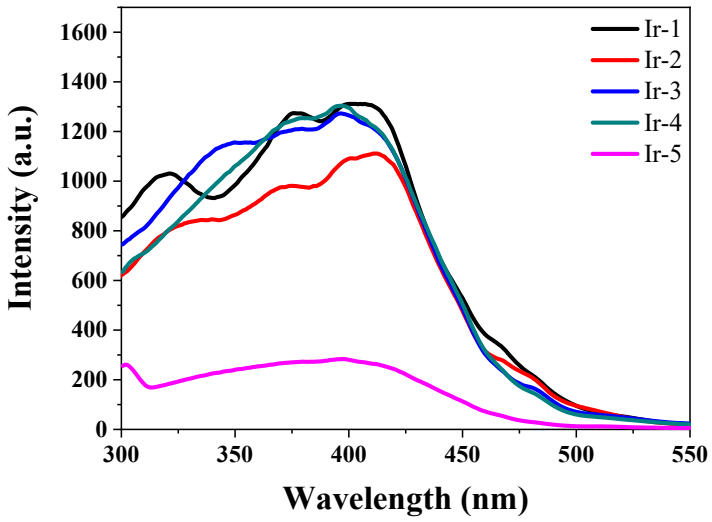
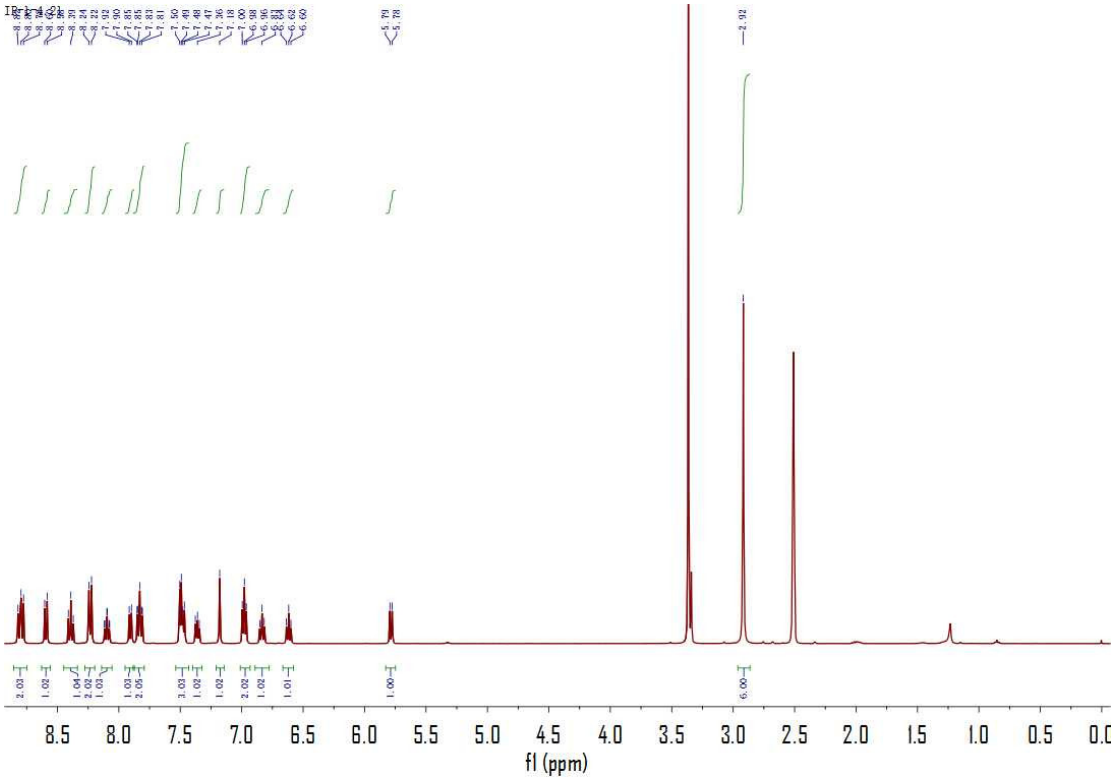


Figure S1. The excitation spectra of complexes Ir-1-Ir-5 in CH_3CN.

Table S1. Contribution of fragments in Ir complexes.

		Contribution (%)	
	Fragment	HOMO	LUMO
Ir-1	Ir	31.9	3.51
	Bipyrdine	3.69	90.4
	Benzene	3.56	0.72
	N^C^N ligand	60.8	5.37
Ir-2	Ir	30.8	3.54
	Phenanthroline	3.52	94.5
	Benzene	3.51	1.14
	N^C^N ligand	62.17	0.82
Ir-3	Ir	6.04	3.47
	Bipyrdine	9.60	94.9
	Fluorene	80.0	0.75
	N^C^N ligand	4.36	0.88
Ir-4	Ir	0.64	3.50
	Bipyrdine	3.01	94.81
	Fluorene	31.1	0.78
	Naphthalimide	65.0	0.01
	N^C^N ligand	0.25	0.90
Ir-5	Ir	0.05	3.47
	Bipyrdine	1.00	94.9
	Fluorene	12.9	0.76
	Carbazole	84.7	0.01
	N^C^N ligand	1.34	0.86

^{1}H NMR spectra and mass spectrometry



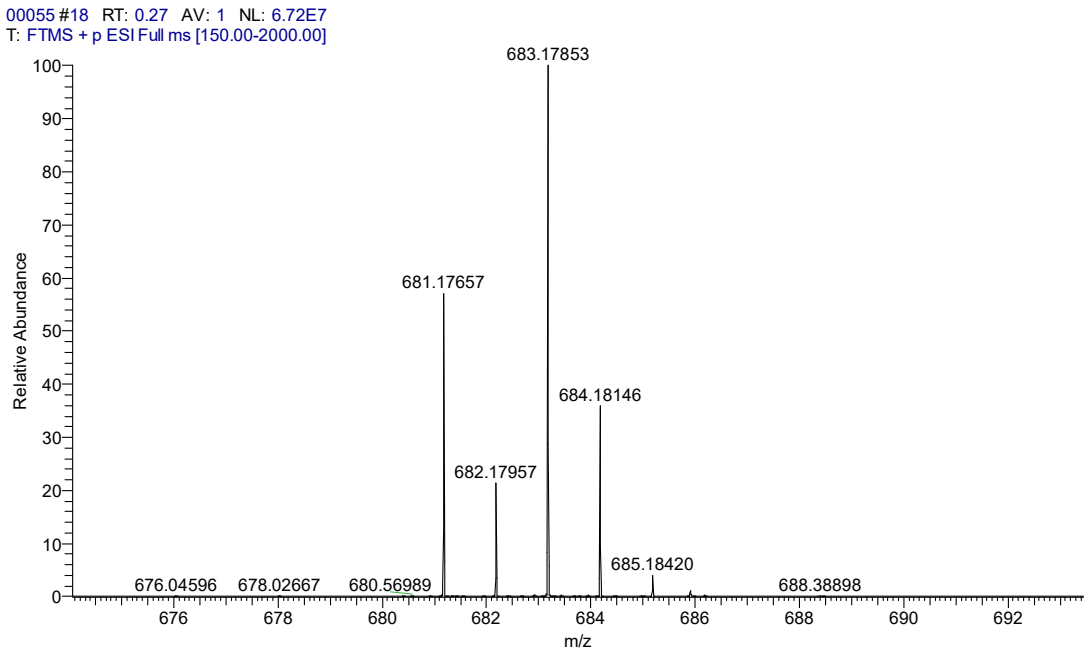
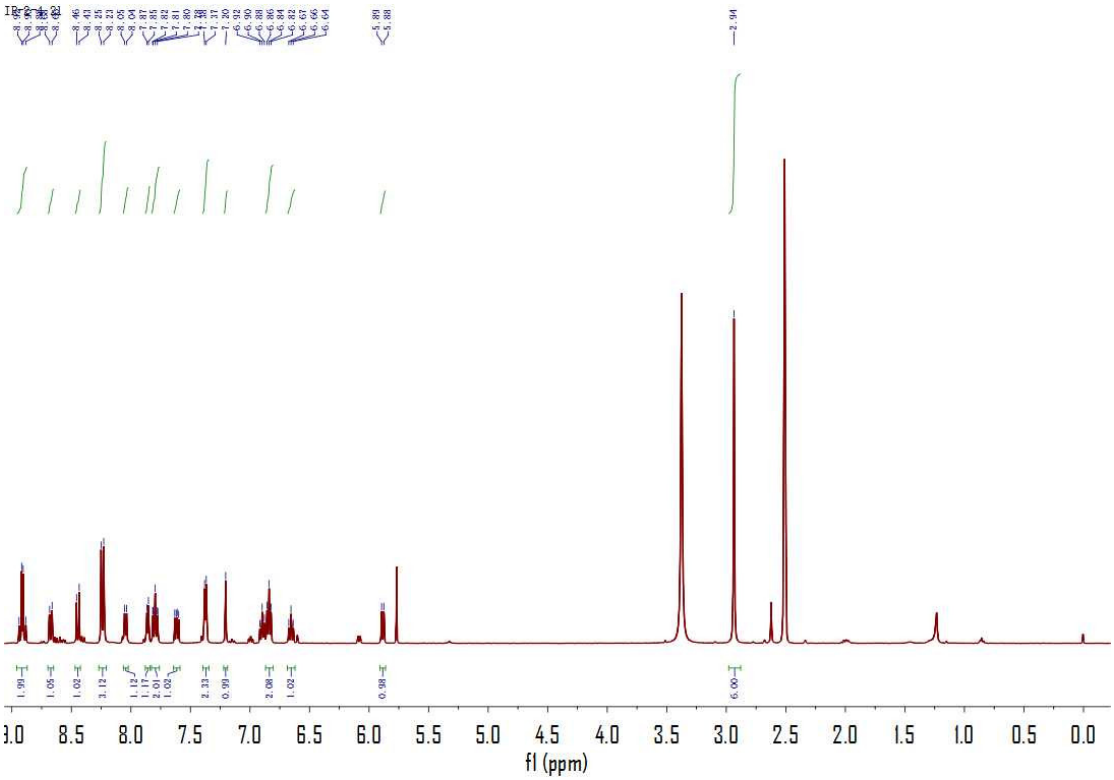


Figure. S2 ^{1}H NMR spectra (up) and mass spectrometry (down) of **Ir-1**



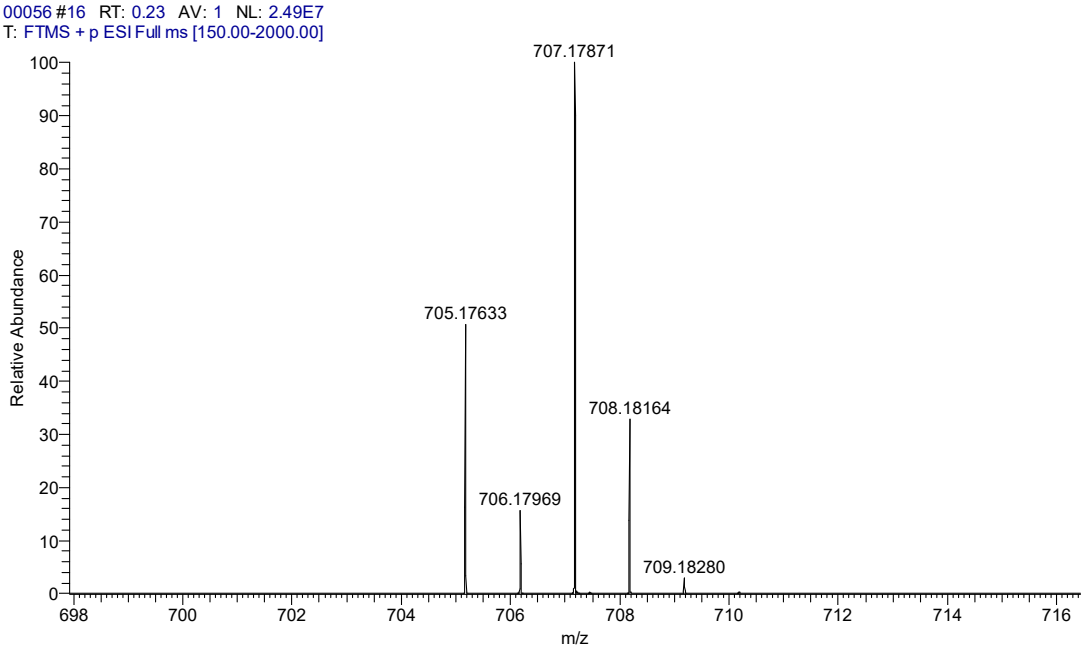
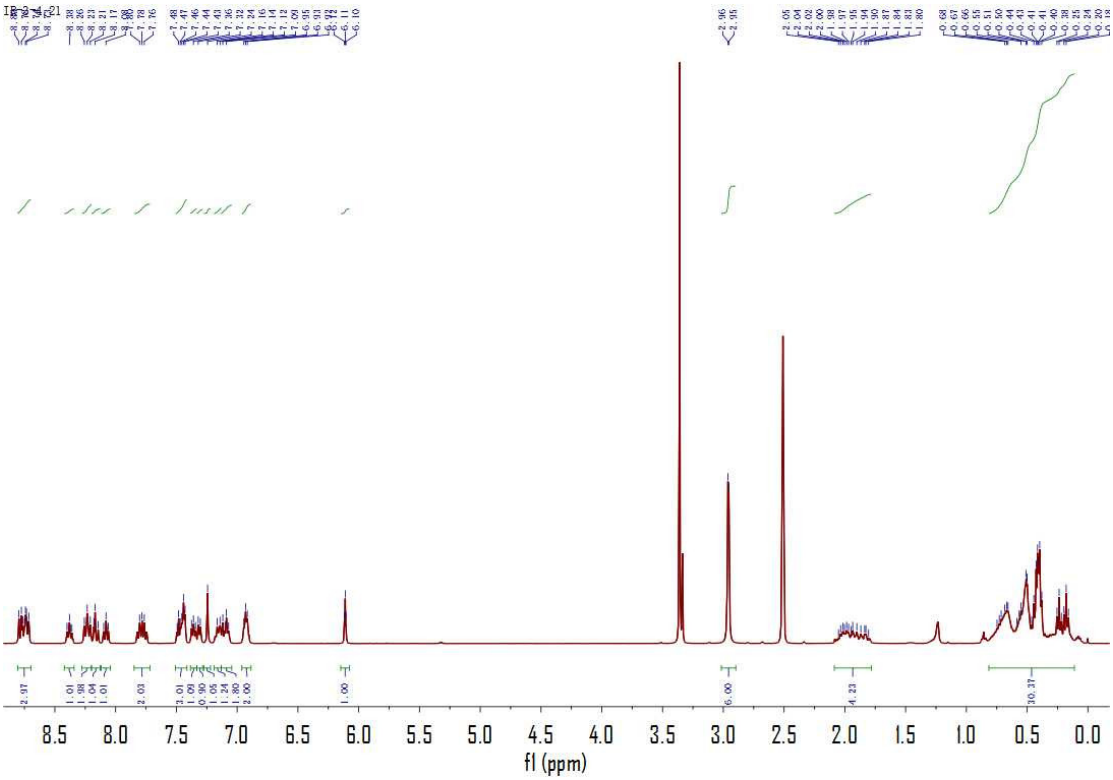


Figure. S3 ^{1}H NMR spectra (up) and mass spectrometry (down) of **Ir-2**



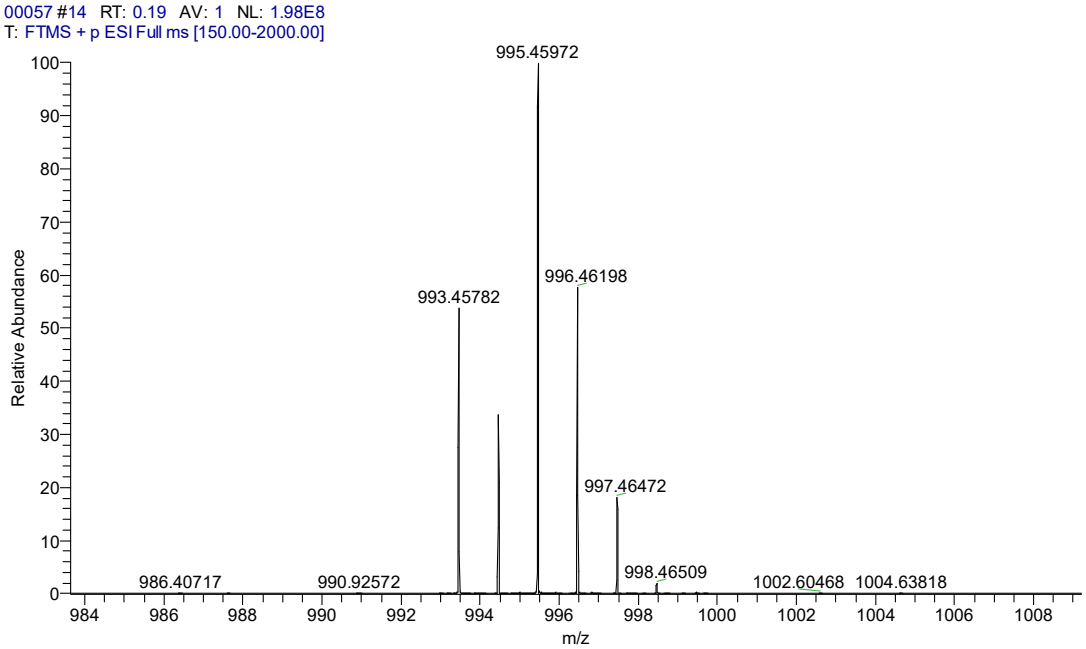
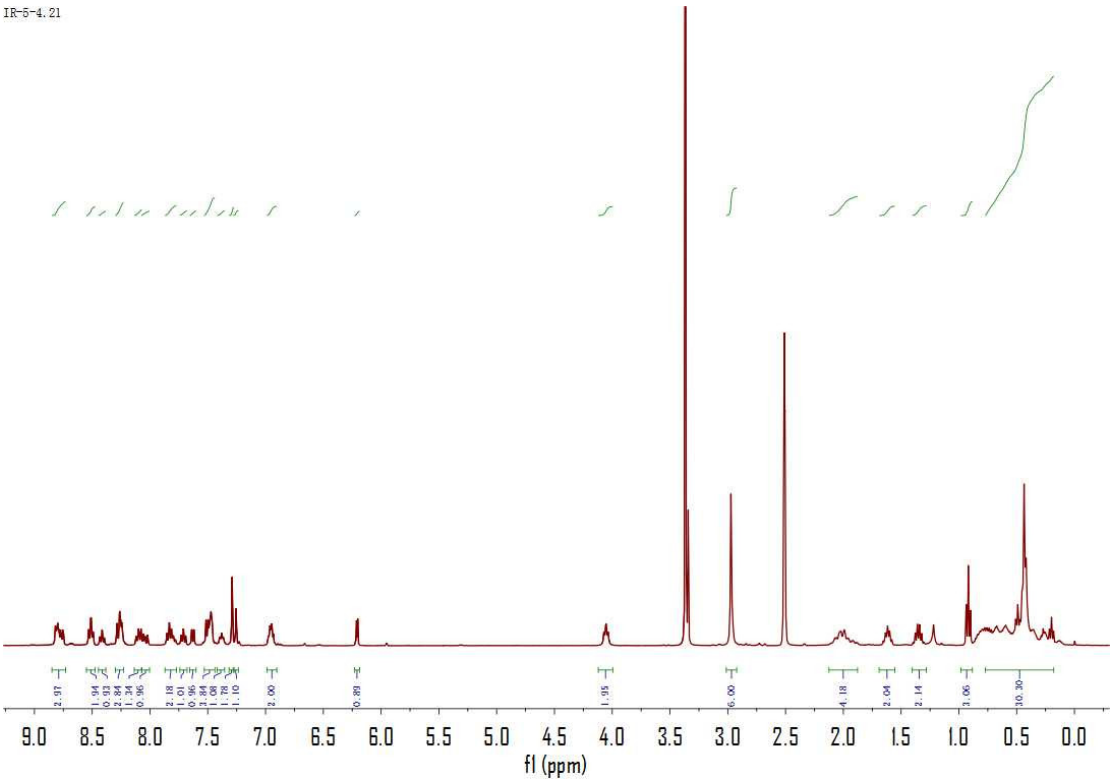


Figure. S4 ^{1}H NMR spectra (up) and mass spectrometry (down) of **Ir-3**



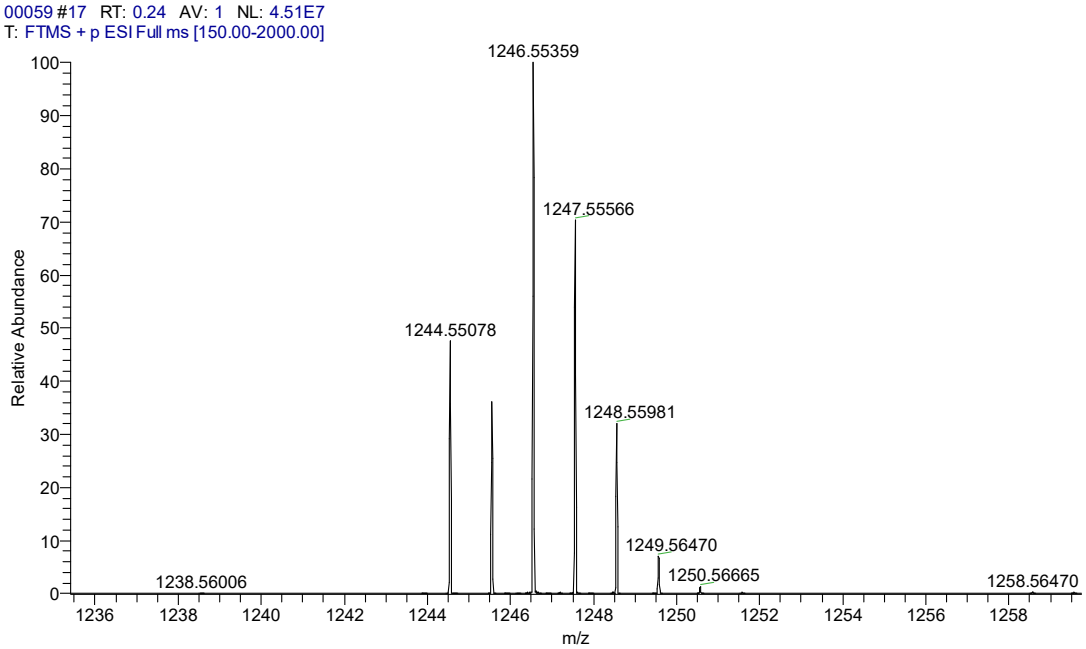
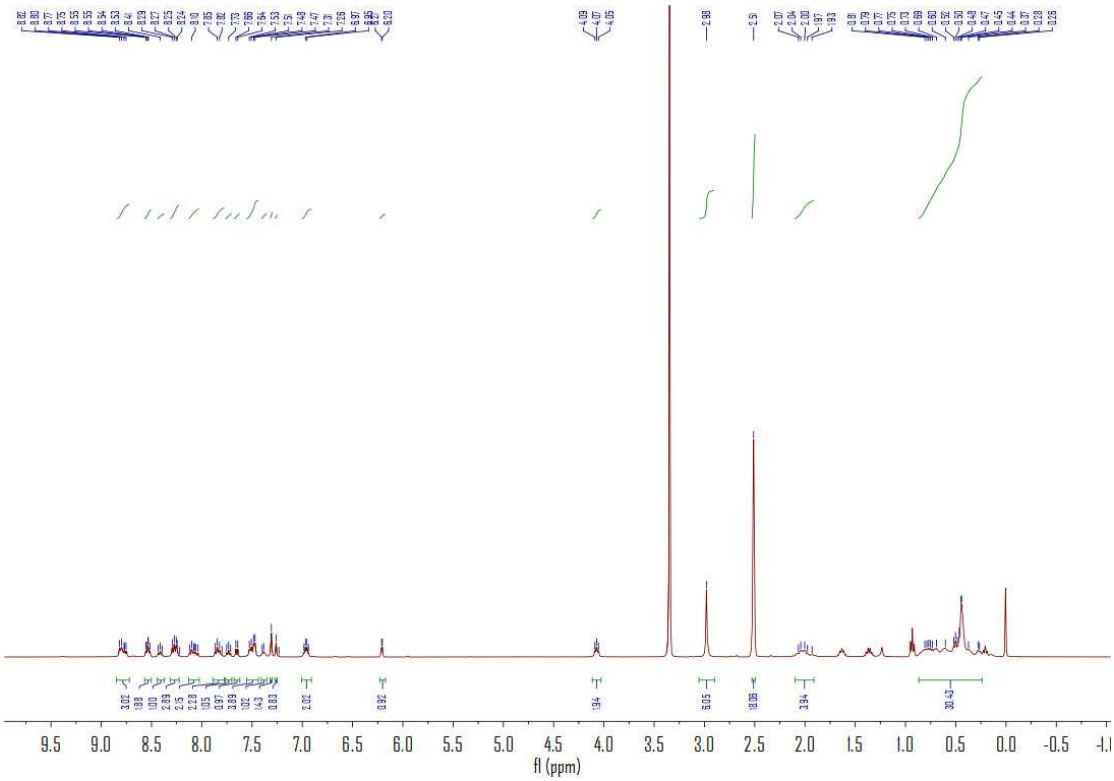


Figure. S5 ^{1}H NMR spectra (up) and mass spectrometry (down) of **Ir-4**



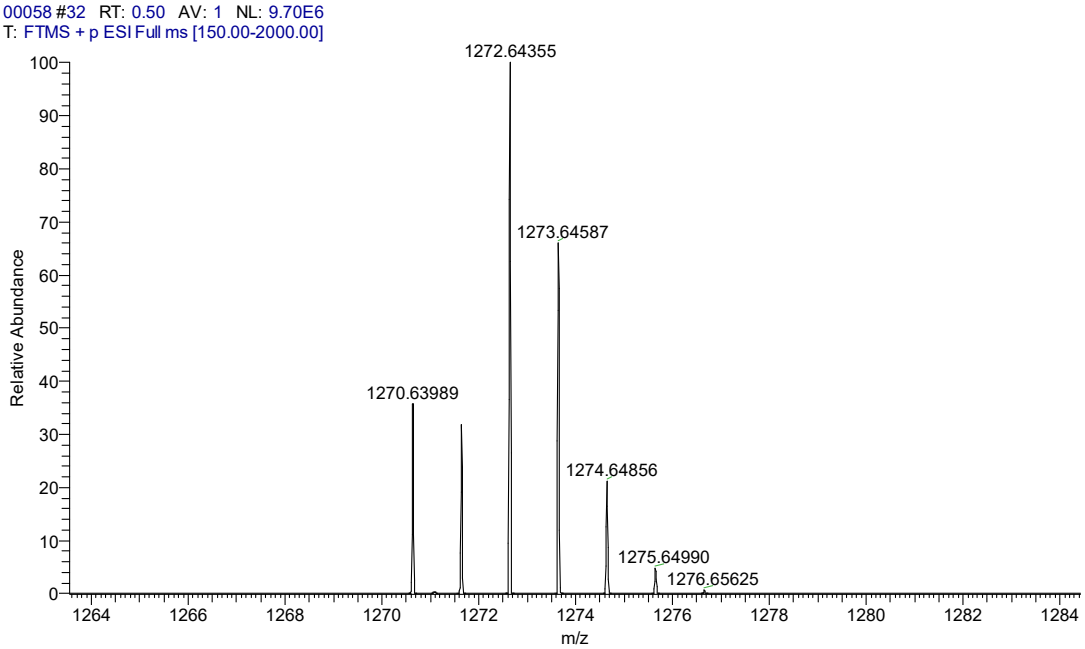


Figure. S6 ^{1}H NMR spectra (up) and mass spectrometry (down) of **Ir-5**