

Electronic Supplementary Information

Stable iridium(IV) complexes supported by tetradentate salen ligands. Synthesis, structures and reactivity

Chi Lun Lee,^a Liangliang Wu,^a Jie-Sheng Huang^{*a} and Chi-Ming Che^{*ab}

^a State Key Laboratory of Synthetic Chemistry and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

^b HKU Shenzhen Institute of Research & Innovation, Shenzhen, China

E-mail: cmche@hku.hk; jshuang@hku.hk

Table of Contents

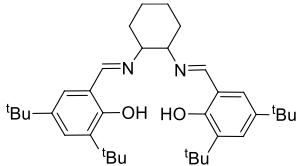
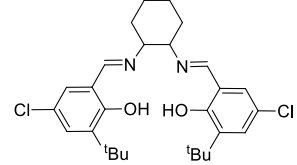
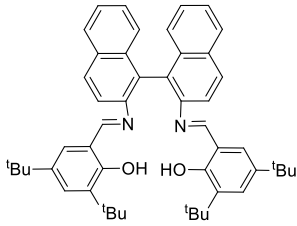
Experimental Section	
Preparation of H ₂ salen ligands	S3
Preparation and characterization of complexes 1 , 2 , [Ir ^{III} (L ³)(Cl)(CO)] and 3	S4
Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by iridium-salen complexes under reflux conditions	S6
Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by dichloroiridium(IV)-salen complex 1 under irradiation with an incandescent lamp (150 W)	S6
Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by iridium-salen complexes under microwave-assisted conditions	S6
Computational details	S8
References	S9
Fig. S1 UV-vis spectrum of complex 1 in CH ₂ Cl ₂	S10
Fig. S2 UV-Vis spectrum of complex 2 in CH ₂ Cl ₂	S11
Fig. S3 UV-Vis spectrum of complex [Ir ^{III} (L ³)(Cl)(CO)] in CH ₂ Cl ₂	S12
Fig. S4 UV-Vis spectrum of complex 3 in CH ₂ Cl ₂	S13
Fig. S5 Experimental and simulated EPR spectrum of complex 1 in CH ₂ Cl ₂ at 10 K	S14
Fig. S6 Experimental and simulated EPR spectrum of complex 2 in CH ₂ Cl ₂ at 10 K	S15
Fig. S7 Experimental and simulated EPR spectrum of complex 3 in CH ₂ Cl ₂ at 10 K	S16
Fig. S8 Variable temperature ¹ H NMR spectra of [Ir ^{III} (L ³)(Cl)(CO)] in CDCl ₃	S17
Fig. S9 ESI-MS spectrum of complex 1 with one equivalent of azide 4c in degassed DCE under reflux conditions	S18
Table S1 Crystallographic data of complex 1	S19
Table S2 Crystallographic data of complex 2	S20
Table S3 Crystallographic data of complex [Ir ^{III} (L ³)(Cl)(CO)]	S21
Table S4 Crystallographic data of complex 3	S22
Table S5 Redox potentials and peak separations for complexes 1–3 and [Ir ^{III} (L ³)(Cl)(CO)]	S23
Table S6 Solvent effect of dihydroquinazolinone and/or quinazolinone formation catalyzed by complex 1	S24
Table S7 Quinazolinone formation catalyzed by complex 1 under irradiation with an incandescent lamp (150 W)	S25
Scheme S1 Synthesis of complex 1 using NaCl as a secondary source of Cl	S5
Scheme S2 Synthesis of complex 3 using strongly oxidizing chlorine source PhICl ₂	S6
Scheme S3 Treatment of 5a with complexes 1 , 3 and [Ir ^{III} (L ³)(Cl)(CO)]	S26
Cartesian coordinates for the DFT optimized structure of complex 1	S27

Experimental Section

General. Chemicals purchased from commercial sources were used without further purification. Unless otherwise stated, all reactions were performed in dried glassware under a dry argon atmosphere. DCE was freshly distilled from CaH_2 under an argon atmosphere. Merck silica gel 60 was used for flash column chromatography. NMR spectra were recorded on a Bruker AV-400 or DPX-300 spectrometer; chemical shifts were expressed in ppm and were determined with tetramethylsilane as internal reference. UV-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer or on a Perkin-Lambda 19 UV-vis spectrophotometer. Cyclic voltammetry was conducted on a Princeton Applied Research Model 273A Potentiostat/galvanostat coulometer and Model 270/250 universal programmer equipped with PowerSuit 2.12.1 program. The working electrode was glassy carbon; the reference electrode was an Ag/AgNO_3 (0.1 M in MeCN) electrode; the counter electrode was a platinum wire/coil. X-band EPR spectra were recorded with a Bruker EMX EPR spectrometer equipped with a variable-temperature helium flow cryostat system (Oxford Instruments), using dichloromethane as the solvent. Positive-ion-mode FAB mass spectra and EI mass spectra were recorded on a Thermo Scientific DFS high-resolution magnetic sector MS. X-ray diffraction data of single crystals were collected on a MAR PSD diffractometer with a 300 mm image plate detector or Bruker X8 Proteum diffractometer.

General procedure for the preparation of H_2salen ligands. The H_2salen ligands were prepared according to the literature procedures.¹⁻³ To a solution of diamine (1 mmol) in EtOH (10 mL) was added the corresponding salicylaldehyde (2 mmol), and the mixture was stirred at reflux overnight. After cooling to room temperature, the resulting light yellow H_2salen ligand was precipitated, separated from the solution by filtration and dried under vacuum.

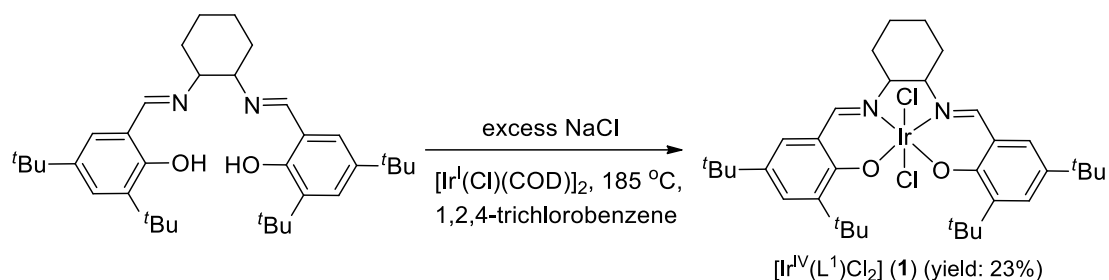
Literature references of H₂salen ligands

	Ref. 1
	Ref. 3
	Ref. 2

General procedure for the preparation of dichloroiridium(IV)-salen complexes **1 and **2**.** To a single-neck 50-mL round bottom flask were added bis(1,5-cyclooctadiene)diiridium(I) dichloride [Ir(Cl)(COD)]₂ (0.15 mmol) and the corresponding H₂salen ligand (0.2 mmol), followed by addition of 1,2,4-trichlorobenzene (10 mL). The mixture was stirred in open atmosphere at 185 °C for 40 min before cooling to room temperature. The mixture was then subjected to flash chromatography on a silica gel column with *n*-hexane/dichloromethane (15:1 to 2:1 v/v) as eluent. The product was obtained by removing the solvent under vacuum. Diffraction-quality crystals of **1** and **2** were obtained by carefully layering *n*-hexane on the top of the CH₂Cl₂ solutions of **1** and **2** using the samples of the two complexes prepared from enantiopure H₂L¹ and H₂L² ligands, respectively. A similar preparation of **1** in the presence of a secondary source of Cl (NaCl) is depicted in Scheme S1.

1: Yield (28%); paramagnetic; FAB-MS *m/z* 807 [M]⁺. Elemental analysis Calcd for C₃₆H₅₂Cl₂IrN₂O₂: C, 53.52; H, 6.49; N, 3.47. Found: C, 53.60; H, 6.71; N, 3.38.

2: Yield (20%); paramagnetic; FAB-MS *m/z* 764 [M]⁺. Elemental analysis Calcd for C₂₈H₃₄Cl₄IrN₂O₂: C, 43.98; H, 4.48; N, 3.66. Found: C, 43.91; H, 4.51; N, 3.63.



Scheme S1 Synthesis of complex **1** using NaCl as a secondary source of Cl.

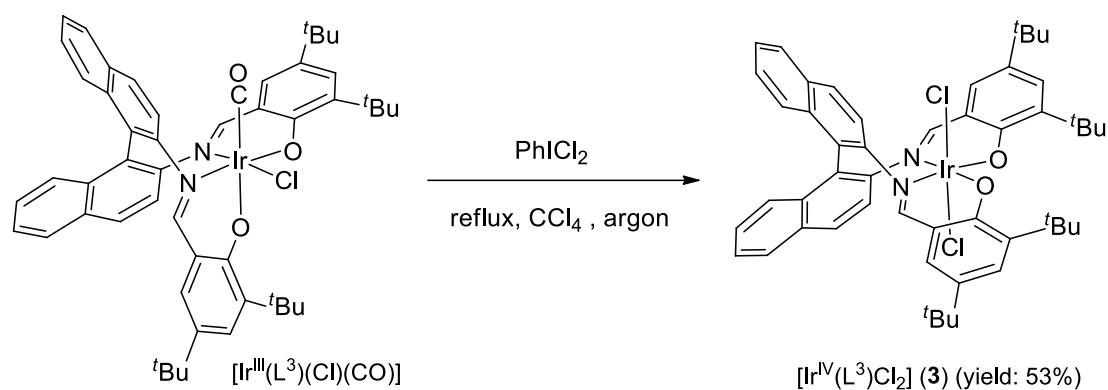
Procedure for the preparation of iridium(III)-salen complex [Ir^{III}(L³)(Cl)(CO)].

To a 50-mL round bottom flask were added bis(1,5-cyclooctadiene)diiridium(I) dichloride [Ir(Cl)(COD)]₂ (0.15 mmol) and the salen ligand H₂L³ (0.2 mmol) in open atmosphere, followed by the addition of 1,2,4-trichlorobenzene (10 mL). The mixture was stirred at 185 °C for 2 h before cooling to room temperature. The mixture was then subjected to flash chromatography on a silica gel column with *n*-hexane/dichloromethane (20:1 to 1:1 v/v) as eluent, which afforded the product. A diffraction-quality crystal of [Ir^{III}(L³)(Cl)(CO)] was obtained by carefully layering *n*-hexane on the top of a solution of the complex in CH₂Cl₂.

[Ir^{III}(L³)(Cl)(CO)]: yield (31%); ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.20 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.97 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.57-7.45 (m, 3H), 7.43 (s, 1H), 7.42-7.35 (m, 2H), 7.27-7.23 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H), 1.25 (s, 9H), 1.18 (s, 9H); IR 2059 cm⁻¹ (ν(CO)); FAB-MS *m/z* 970 [M]⁺. Elemental analysis Calcd for C₅₁H₅₄ClIrN₂O₃: C, 63.11; H, 5.61; N, 2.89. Found: C, 63.02; H, 5.66; N, 2.83.

Procedure for the preparation of dichloroiridium(IV)-salen complex 3. To a two-neck 50-mL round bottom flask was added *cis*-β-[Ir^{III}(L₃)(Cl)(CO)] (0.1 mmol), followed by addition of carbon tetrachloride (20 mL). The mixture was refluxed under argon for 2 days before cooling to room temperature. The mixture was then subjected to flash chromatography on a silica gel column with *n*-hexane/dichloromethane (15:1 to 5:1 v/v) as eluent. The product was obtained by removing the solvent under vacuum. A diffraction-quality crystal of **3** was obtained by carefully layering *n*-hexane on the top of a solution of **3** in CH₂Cl₂. For similar preparation of **3** using a strongly oxidizing chlorine source (PhICl₂), see Scheme S2.

3: yield (46%); paramagnetic; FAB-MS *m/z* 978 [M]⁺. Elemental analysis Calcd for C₅₀H₅₄Cl₂IrN₂O₂: C, 61.40; H, 5.56; N, 2.86. Found: C, 61.48; H, 5.60; N, 2.81.



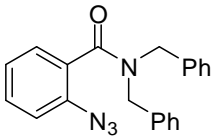
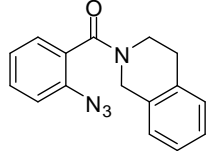
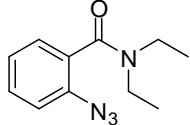
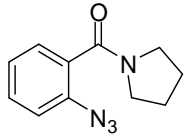
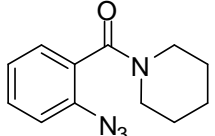
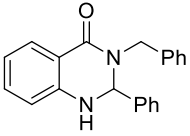
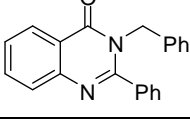
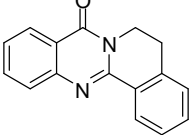
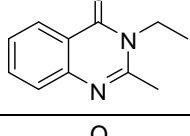
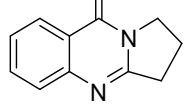
Scheme S2 Synthesis of complex **3** using strongly oxidizing chlorine source PhICl_2 .

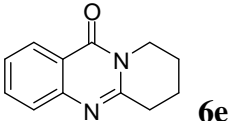
Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by iridium-salen complexes under reflux conditions. A mixture of aryl azide (0.1 mmol) and the Ir(IV)-salen complex **1** (5 mol%) was refluxed in DCE under N_2 for 18 h before cooling to room temperature. The solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR spectroscopy and then purified by flash chromatography (*n*-hexane/ CH_2Cl_2) to afford the corresponding product.

Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by dichloroiridium(IV)-salen complex 1 under irradiation with an incandescent lamp (150 W). A mixture of aryl azide (0.1 mmol) and complex **1** (5 mol%) was stirred under irradiation using an incandescent lamp (150 W) in DCE under N_2 for 12 h before cooling to room temperature. The solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR spectroscopy and then purified by flash chromatography (*n*-hexane/ CH_2Cl_2) to afford the corresponding product.

Typical procedure for the intramolecular C–N bond formation from aryl azides catalyzed by iridium-salen complexes under microwave-assisted conditions. A mixture of aryl azide (0.1 mmol) and complex **1** (5 mol%) was stirred for 1 h at 120 °C in open atmosphere under microwave irradiation (200 W) in DCE before cooling to room temperature. The solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR spectroscopy and then purified by flash chromatography (*n*-hexane/ CH_2Cl_2) to afford the corresponding product.

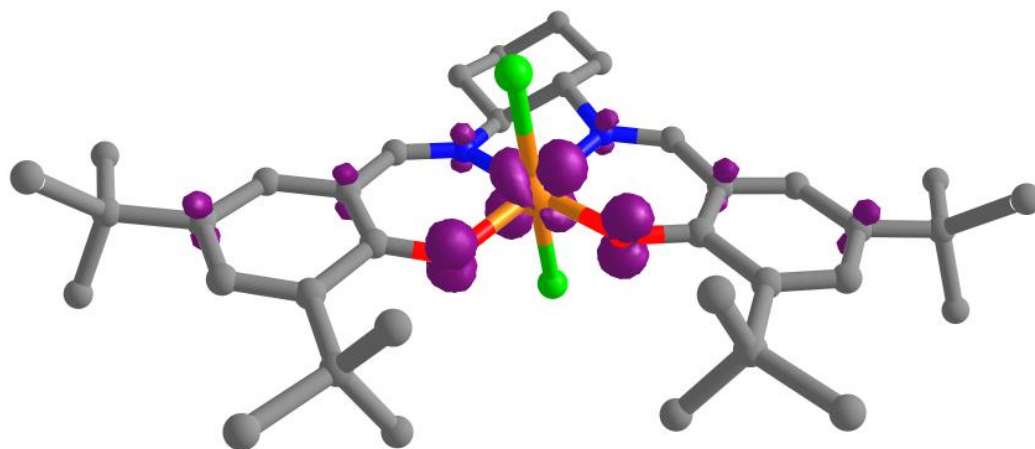
Literature references of the known substrates and products

 <p>4a</p>	
 <p>4b</p>	
 <p>4c</p>	Ref. 4
 <p>4d</p>	
 <p>4e</p>	
 <p>5a</p>	Ref. 4
 <p>6a</p>	Ref. 5
 <p>6b</p>	Ref. 6
 <p>6c</p>	Ref. 7
 <p>6d</p>	Ref. 8

	Ref. 6
---	--------

Computational details

DFT calculations on the Ir(IV)-salen complexes were performed using complex **1** as example. The hybrid density functional, PBE0,⁹ was employed for all calculations using the program package G09.¹⁰ The 6-31G* basis set¹¹ was used for all atoms except Ir, which is described by the Stuttgart relativistic pseudopotential and its accompanying basis set (ECP60MWB).¹² Geometry optimizations of the ground state were carried out without symmetry constraints. Frequency calculations were performed on the optimized structures to ensure that they are minimum energy structures by the absence of imaginary frequency (i.e. NImag = 0). The computed spin density distribution was based on the modified Mulliken atom population defined by Ros and Schuit (SCPA);¹³ the spin density plot is depicted below:



Spin density plot (contour value: 0.01) for complex **1**. Hydrogen atoms are not shown for clarity.

References

- 1 L. Deng and E. N. Jacobsen, *J. Org. Chem.*, 1992, **57**, 4320.
- 2 N. Takenaka, Y. Huang and V. H. Rawal, *Tetrahedron*, 2002, **58**, 8299.
- 3 A. M. DiCiccio, J. M. Longo, G. G. Rodriguez-Calero and G. W. Coates, *J. Am. Chem. Soc.*, 2016, **138**, 7107.
- 4 Y. Liu, J. Wei and C.-M. Che, *Chem. Commun.*, 2010, **46**, 6926.
- 5 M. Carpintero, M. Cifuentes, R. Ferritto, R. Haro and M. A. Toledo, *J. Comb. Chem.*, 2007, **9**, 818.
- 6 W. R. Bowman, M. R. J. Elsegood, T. Stein and G. W. Weaver, *Org. Biomol. Chem.*, 2007, **5**, 103.
- 7 M. Dabiri, P. Salehi, A. A. Mohammadi and M. Baghbanzadeh, *Synth. Commun.*, 2005, **35**, 279.
- 8 C. Zhang, C. K. De, R. Mal and D. Seidel, *J. Am. Chem. Soc.*, **2008**, 130, 416.
- 9 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
- 10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision D.01*, Gaussian Inc., Wallingford CT, 2013.
- 11 (a) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople. *J. Chem. Phys.*, 1982, **77**, 3654.
- 12 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123.
- 13 P. Ros and G. C. A. Schuit, *Theor. Chim. Acta*, 1966, **4**, 1.

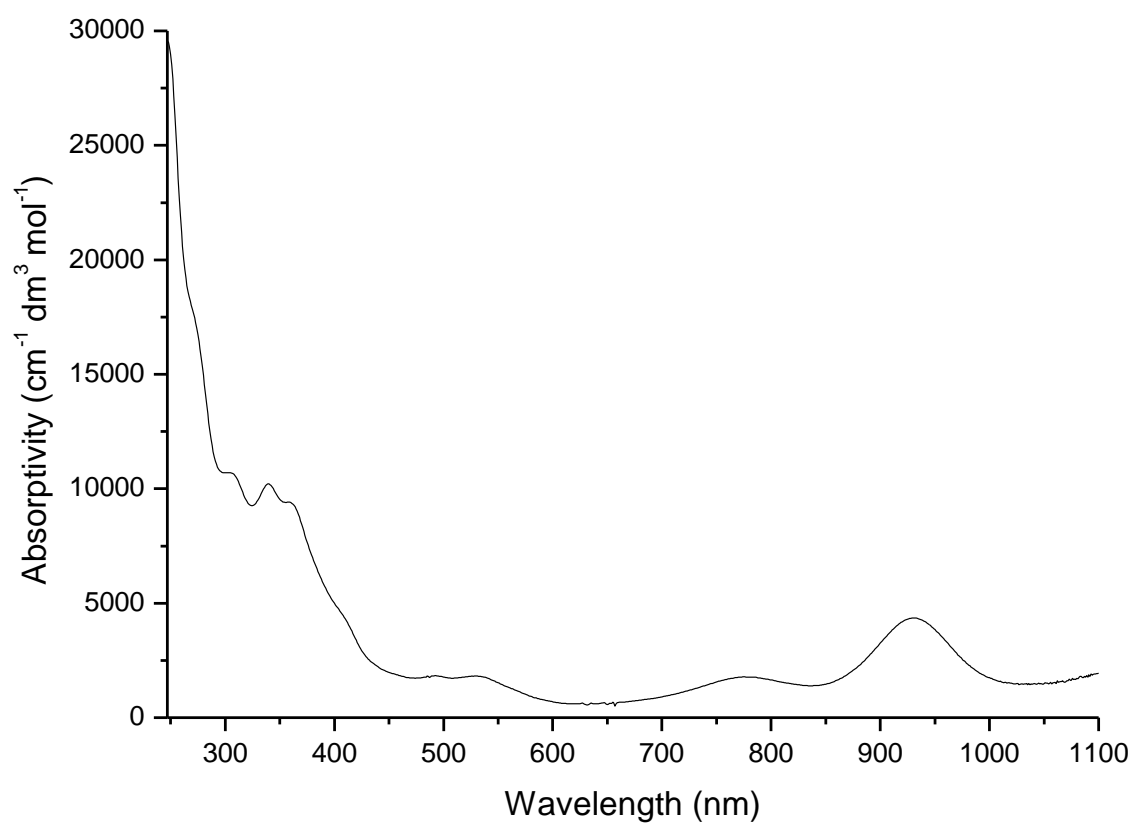


Fig. S1 UV-vis spectrum of complex **1** in CH₂Cl₂ (concentration $\sim 2 \times 10^{-5}$ M).

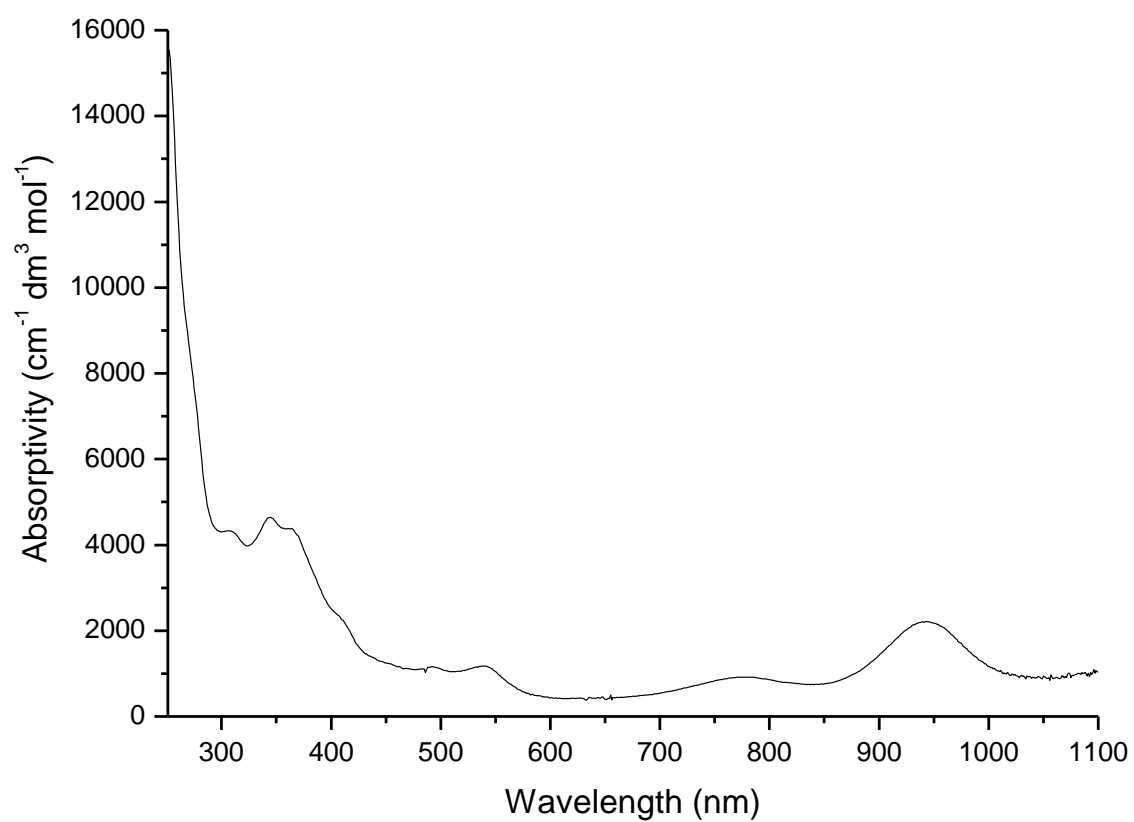


Fig. S2 UV-vis spectrum of complex **2** in CH₂Cl₂ (concentration $\sim 2 \times 10^{-5}$ M).

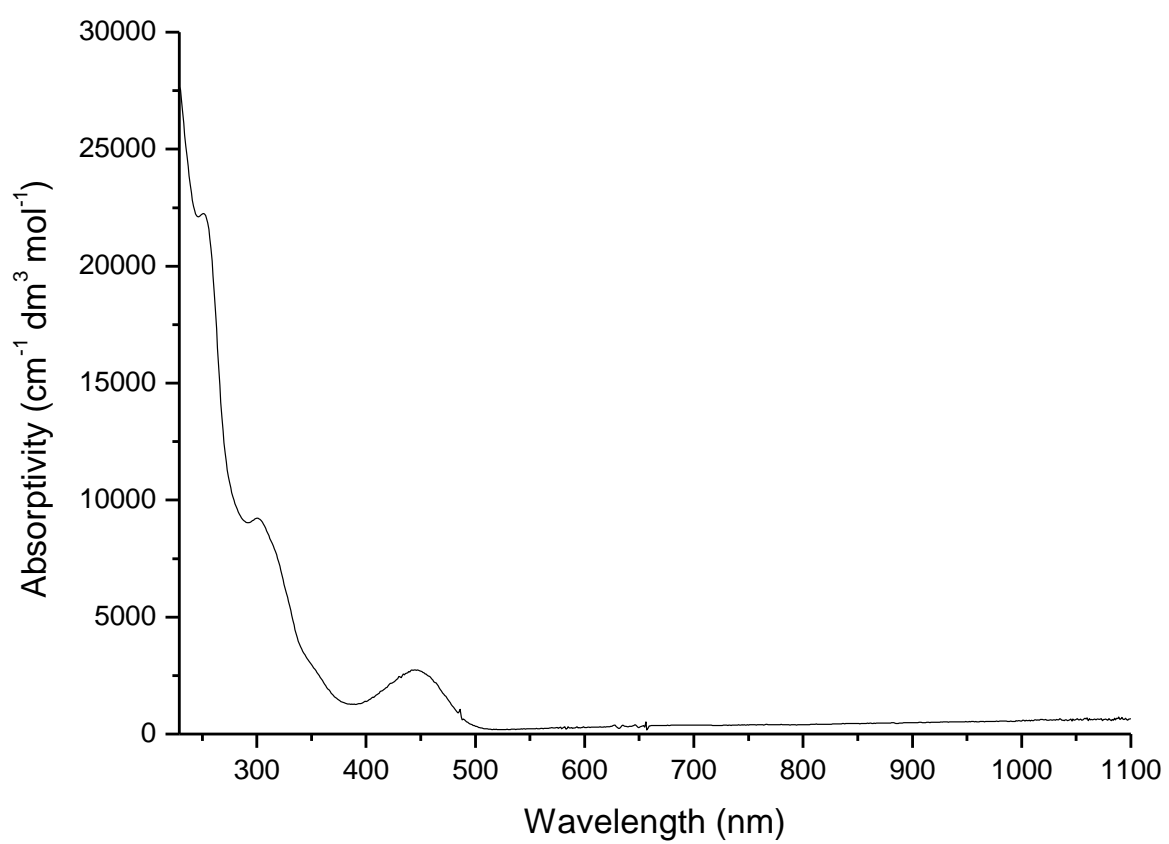


Fig. S3 UV-vis spectrum of complex $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$ in CH_2Cl_2 (concentration $\sim 2 \times 10^{-5} \text{ M}$).

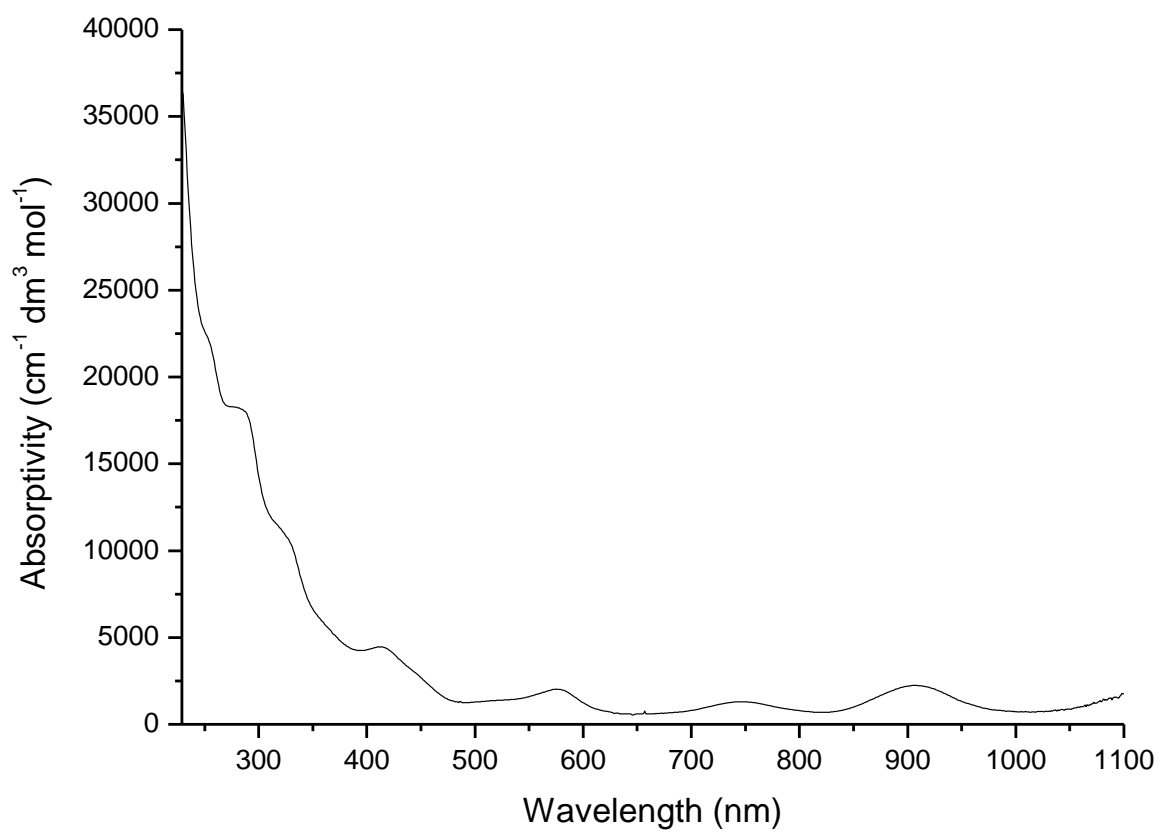


Fig. S4 UV-vis spectrum of complex **3** in CH₂Cl₂ (concentration $\sim 2 \times 10^{-5}$ M).

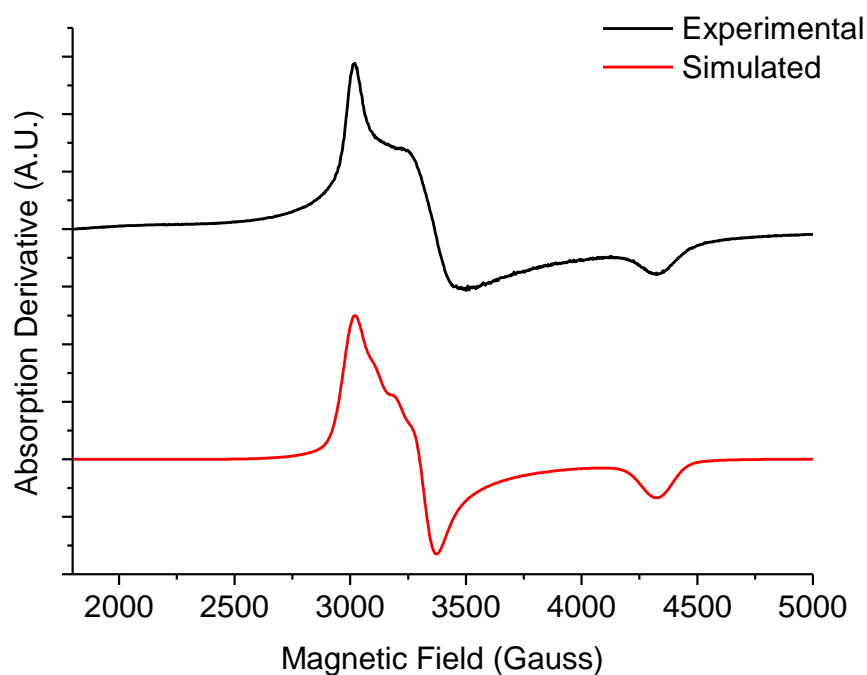


Fig. S5 Experimental and simulated EPR spectrum of complex **1** in CH_2Cl_2 at 10 K. Experimental conditions: frequency, 9.37 GHz; microwave power, 2.00 mW; modulation frequency, 100.0 kHz; modulation amplitude, 5.0 G. Simulation parameters: $g_x = 2.11$, $g_y = 2.10$, $g_z = 1.55$, $A_{xx} = 92.8$ Gauss, $A_{yy} = 35.7$ Gauss, $A_{zz} = 35$ Gauss.

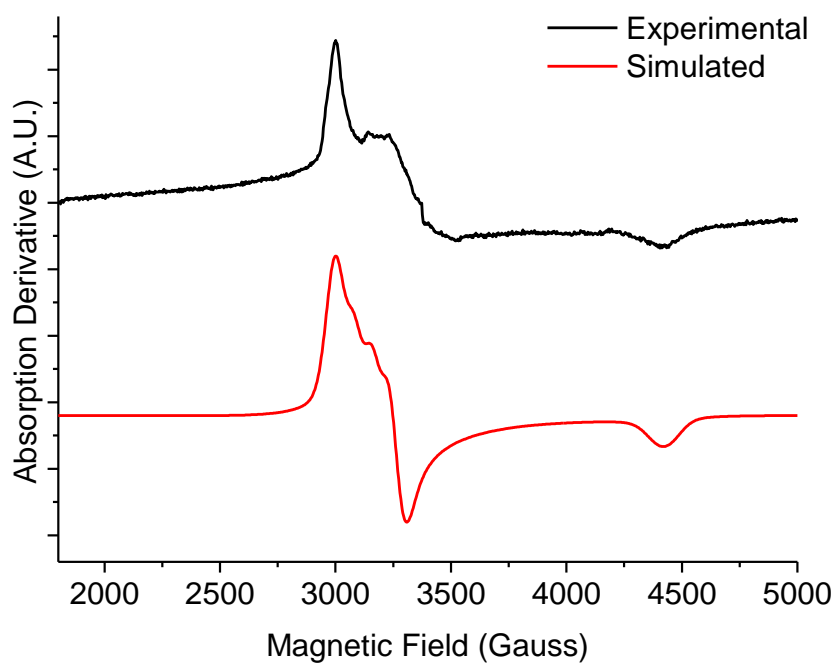


Fig. S6 Experimental and simulated EPR spectrum of complex **2** in CH₂Cl₂ at 10 K. Experimental conditions: frequency, 9.37 GHz; microwave power, 2.00 mW; modulation frequency, 100.0 kHz; modulation amplitude, 5.0 G. Simulation parameters: $g_x = 2.14$, $g_y = 2.12$, $g_z = 1.51$, $A_{xx} = 77$ Gauss, $A_{yy} = 74$ Gauss, $A_{zz} = 30$ Gauss.

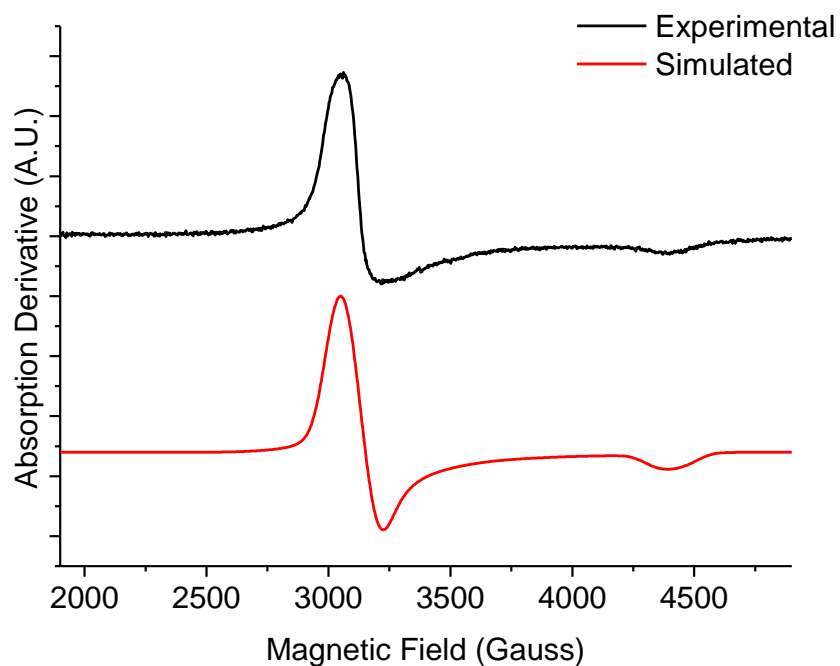


Fig. S7 Experimental and simulated EPR spectrum of complex **3** in CH_2Cl_2 at 10 K. Experimental conditions: frequency, 9.37 GHz; microwave power, 2.00 mW; modulation frequency, 100.0 kHz; modulation amplitude, 5.0 G. Simulation parameters: $g_x \sim g_y = 2.17$, $g_z = 1.52$, $A_{xx} \sim A_{yy} = 38$ Gauss, $A_{zz} = 26$ Gauss.

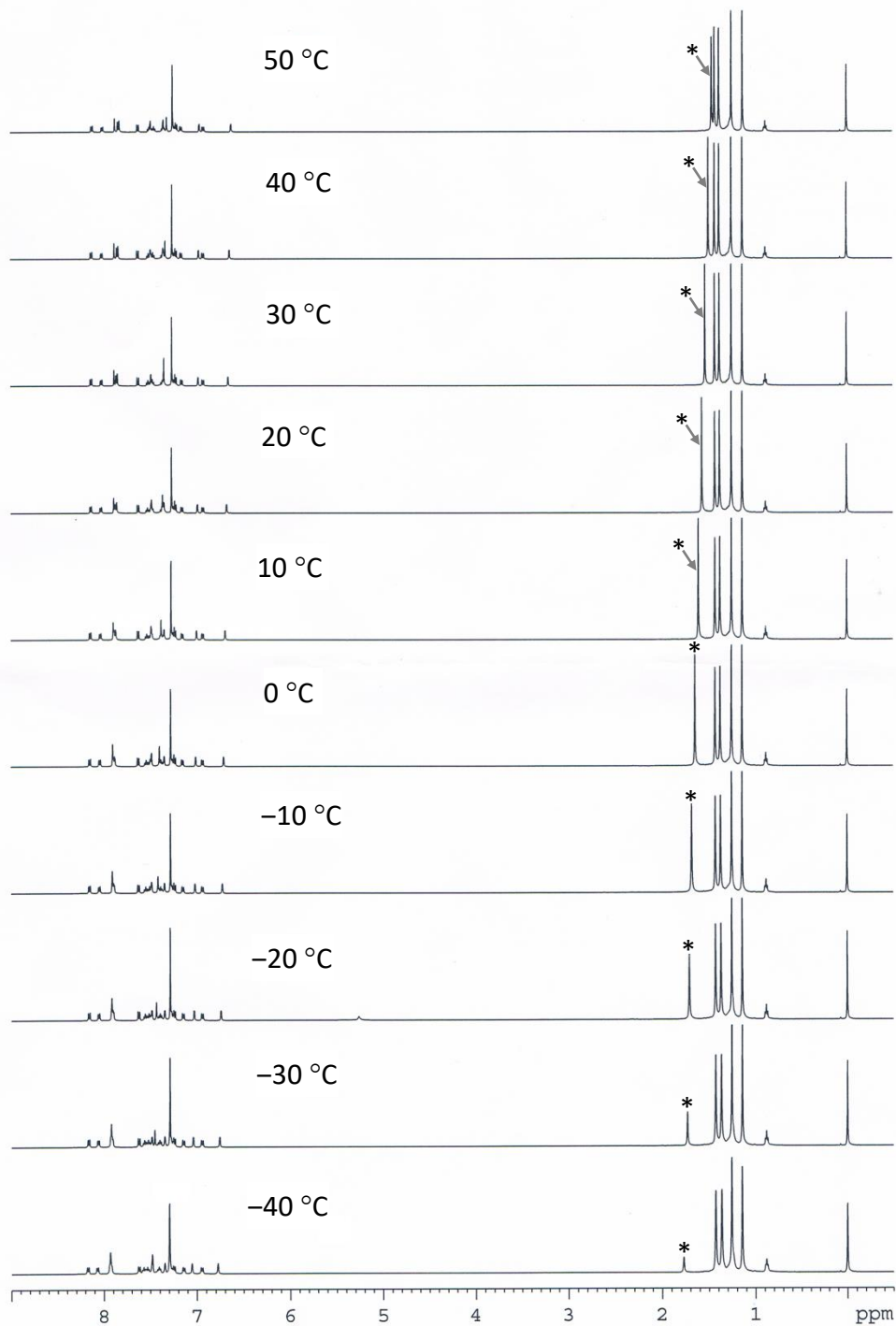


Fig. S8 Variable temperature ^1H NMR spectra of $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$ in CDCl_3 ($-40\text{ }^\circ\text{C}$ to $50\text{ }^\circ\text{C}$). The peak marked with an asterisk came from water.

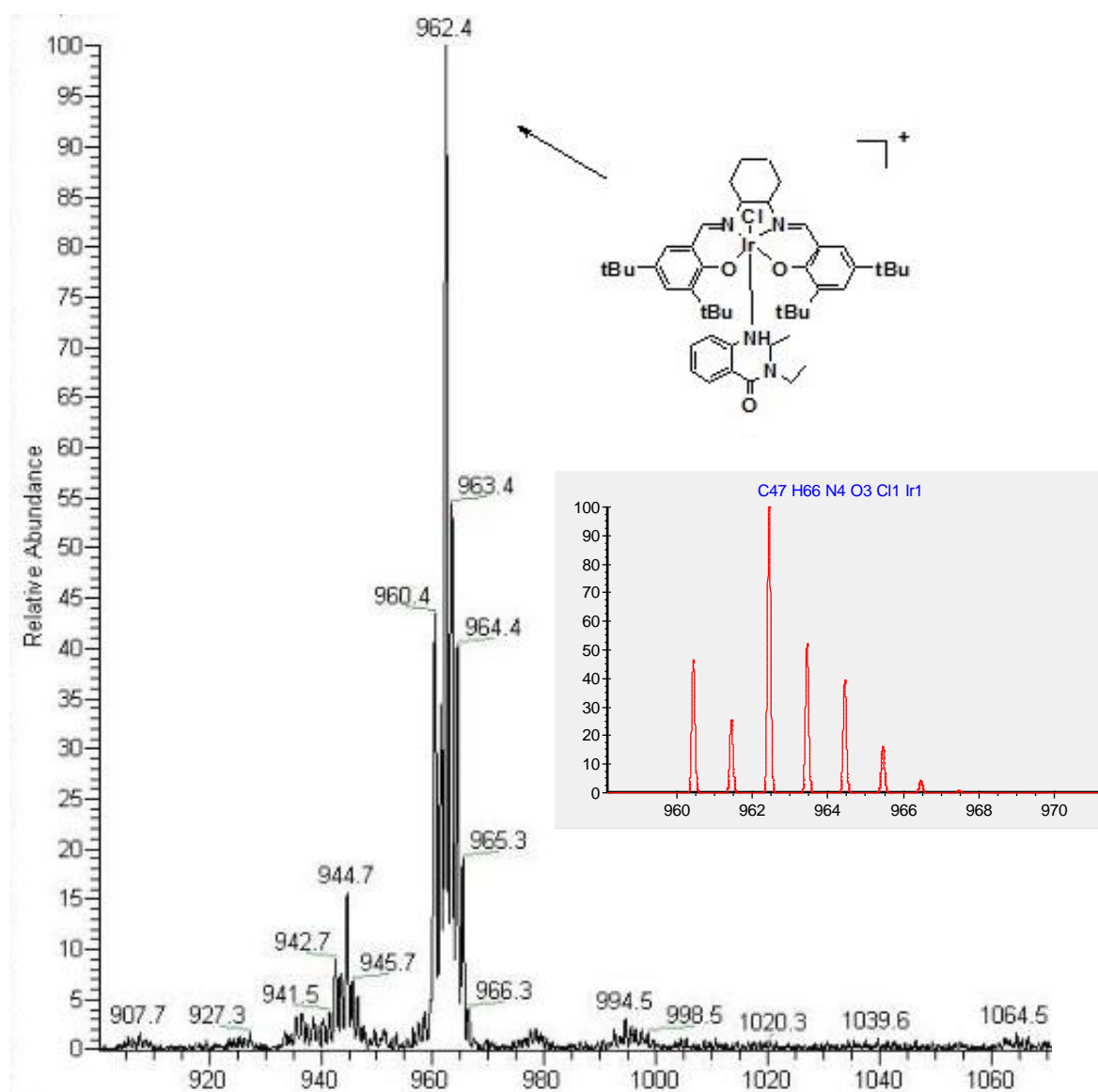


Fig. S9 ESI-MS spectrum of complex **1** with one equivalent of azide **4c** in degassed DCE under reflux conditions for 30 min and simulated spectrum of the target species showing the isotopic distribution pattern.

Table S1 Crystallographic data of complex **1**·2CH₂Cl₂

Empirical formula	C ₃₈ H ₅₆ Cl ₆ IrN ₂ O ₂
Formula weight	977.74
Temperature/K	100
Crystal system	triclinic
Space group	P1
a/Å	12.6783(7)
b/Å	12.9154(7)
c/Å	14.6274(8)
α/°	81.8890(10)
β/°	73.0200(10)
γ/°	65.1680(10)
Volume/Å ³	2078.5(2)
Z	2
ρ _{calc} /cm ³	1.562
μ/mm ⁻¹	10.031
F(000)	986
Crystal size/mm ³	0.3 × 0.06 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.32 to 135.28
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -14 ≤ l ≤ 16
Reflections collected	37568
Independent reflections	13132 [R _{int} = 0.0513, R _{sigma} = 0.0516]
Data/restraints/parameters	13132/3/907
Goodness-of-fit on F ²	1.025
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0331, wR ₂ = 0.0900
Final R indexes [all data]	R ₁ = 0.0333, wR ₂ = 0.0904
Largest diff. peak/hole / e Å ⁻³	1.37/-0.73
Flack parameter	-0.035(5)

Table S2 Crystallographic data of complex **2**

Empirical formula	C ₂₈ H ₃₄ Cl ₄ IrN ₂ O ₂
Formula weight	764.57
Temperature/K	100
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2
a/Å	11.8989(4)
b/Å	12.7089(4)
c/Å	23.2281(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3512.60(19)
Z	4
ρ _{calc} /cm ³	1.446
μ/mm ⁻¹	10.346
F(000)	1508
Crystal size/mm ³	0.25 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	3.804 to 135.306
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -27 ≤ l ≤ 27
Reflections collected	30388
Independent reflections	6301 [R _{int} = 0.0445, R _{sigma} = 0.0297]
Data/restraints/parameters	6301/0/341
Goodness-of-fit on F ²	1.046
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0251, wR ₂ = 0.0661
Final R indexes [all data]	R ₁ = 0.0265, wR ₂ = 0.0677
Largest diff. peak/hole / e Å ⁻³	1.03/-0.44
Flack parameter	0.007(4)

Table S3 Crystallographic data of complex [Ir^{III}(L³)(Cl)(CO)]·CH₂Cl₂

Empirical formula	C ₅₂ H ₅₆ Cl ₃ IrN ₂ O ₃
Formula weight	1055.54
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.1578 (11)
b/Å	14.0956 (12)
c/Å	15.0289 (13)
α/°	71.647 (1)
β/°	85.234 (1)
γ/°	70.951 (1)
Volume/Å ³	2500.1 (4)
Z	2
ρ _{calc} /cm ³	1.402
μ/mm ⁻¹	2.872
F(000)	1068
Crystal size/mm ³	0.40 × 0.27 × 0.25
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.26 to 50.06
Index ranges	-15 ≤ h ≤ 12, -16 ≤ k ≤ 16, -17 ≤ l ≤ 16
Reflections collected	14009
Independent reflections	8640 [R _{int} = 0.0124, R _{sigma} = N/A]
Data/restraints/parameters	8640/ 54 / 581
Goodness-of-fit on F ²	1.05
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0244, wR ₂ = 0.0645
Final R indexes [all data]	R ₁ = 0.0287, wR ₂ = 0.0673
Largest diff. peak/hole / e Å ⁻³	0.94/-0.67

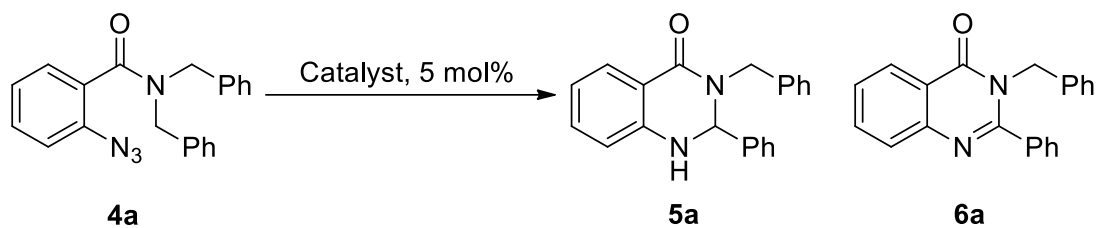
Table S4 Crystallographic data of complex **3**·2.41CHCl₃

Empirical formula	C _{52.41} H _{56.41} Cl _{9.23} IrN ₂ O ₂
Formula weight	1265.58
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	24.7754(14)
b/Å	14.4960(8)
c/Å	16.5663(9)
α/°	90
β/°	98.226(2)
γ/°	90
Volume/Å ³	5888.5(6)
Z	4
ρ _{calc} /cm ³	1.428
μ/mm ⁻¹	8.537
F(000)	2539
Crystal size/mm ³	0.3 × 0.06 × 0.06
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	3.604 to 134.482
Index ranges	-29 ≤ h ≤ 28, -12 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	83040
Independent reflections	10085 [R _{int} = 0.0983, R _{sigma} = 0.0502]
Data/restraints/parameters	10085/9/635
Goodness-of-fit on F ²	1.136
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0468, wR ₂ = 0.1259
Final R indexes [all data]	R ₁ = 0.0493, wR ₂ = 0.1274
Largest diff. peak/hole / e Å ⁻³	2.17/-0.99

Table S5 Redox potentials ($E_{1/2}$) and peak separations ($\Delta E_{1/2}$) for complexes **1–3** and $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$ (E vs Ag/AgNO_3 (0.1 M in MeCN))

Complex	Reduction		Oxidation I		Oxidation II	
	$E_{1/2}$ (V)	$\Delta E_{1/2}$ (mV)	$E_{1/2}$ (V)	$\Delta E_{1/2}$ (mV)	$E_{1/2}$ (V)	$\Delta E_{1/2}$ (mV)
1	-0.17	124	0.75	136	-	-
2	0.08	90	0.99	84	-	-
3	-0.11	102	0.80	109	-	-
$[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$	-	-	0.89	177	1.27	183

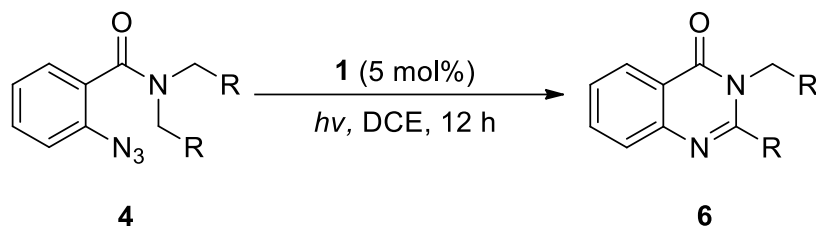
Table S6 Solvent effect of dihydroquinazolinone and quinazolinone formation catalyzed by complex **1**^a



Entry	Solvent	Time (h)	5a Yield (%) ^b	6a Yield (%) ^b
1	benzene	18	9	89
2	acetonitrile	18	—	—
3	dichloromethane	18	—	—
4	DCE	18	—	95

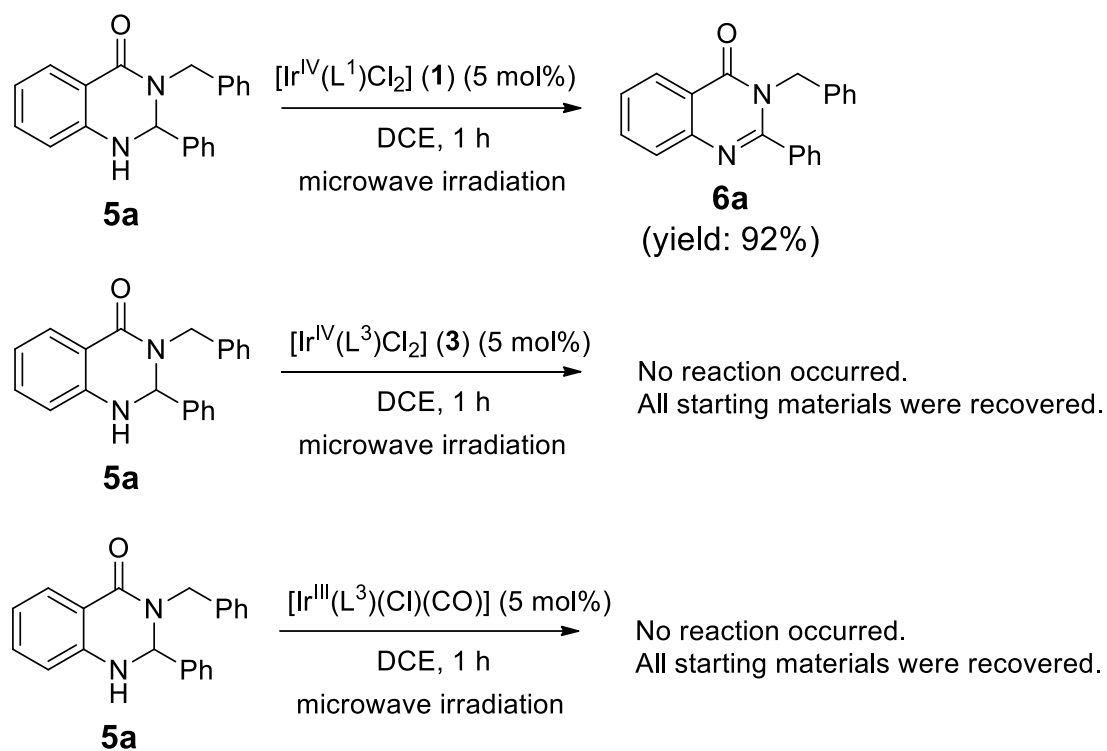
^a Reaction conditions: A mixture of substrate **4a** (0.1 mmol) and complex **1** (5 mol%) was refluxed in degassed solvent under N₂. ^b Isolated yield.

Table S7 Quinazolinone formation catalyzed by complex **1** under irradiation with an incandescent lamp (150 W)^a



Entry	Substrate	6 (Yield %) ^b
1	<p style="text-align: center;">4a</p>	<p style="text-align: center;">6a (95)</p>
2	<p style="text-align: center;">4b</p>	<p style="text-align: center;">6b (91)</p>
3	<p style="text-align: center;">4c</p>	<p style="text-align: center;">6c (65)</p>
4	<p style="text-align: center;">4d</p>	<p style="text-align: center;">6d (69)</p>
5	<p style="text-align: center;">4e</p>	<p style="text-align: center;">6e (61)</p>

^a Reaction conditions: A mixture of substrate (0.1 mmol) and **1** (5 mol%) was stirred under irradiation with an incandescent lamp (150 W) in DCE under N₂. ^b Isolated yield.



Scheme S3 Treatment of **5a** with complexes **1**, **3** and $[\text{Ir}^{\text{III}}(\text{L}^3)(\text{Cl})(\text{CO})]$.

Cartesian coordinates for the DFT optimized structure of complex 1

Ir	18.907557930	9.639566165	5.385728546
Cl	18.439359204	11.962090397	5.540985922
Cl	19.380474906	7.319264107	5.210084710
O	17.454026880	9.421545720	3.999265516
O	20.248706284	10.036110005	3.925755392
N	17.671657903	9.262111653	6.876027201
N	20.257056066	9.834086800	6.810458224
C	16.306537554	8.851701411	4.198960922
C	15.472967444	8.592681054	3.052476441
C	14.252496427	7.984541564	3.267333607
H	13.629181932	7.778750088	2.404620446
C	13.747550098	7.609894761	4.536823937
C	14.541803714	7.884928233	5.628277678
H	14.204299016	7.637991268	6.630312001
C	15.811284165	8.490827716	5.500422952
C	16.484062445	8.765019638	6.735362998
H	15.920336801	8.543104660	7.640085699
C	18.262391219	9.632598488	8.172104312
H	18.172678107	10.727697890	8.229705256
C	17.627145894	9.008893090	9.407269788
H	16.573991197	9.301474291	9.482983834
H	17.662622095	7.913579477	9.327131820
C	18.369218453	9.468600849	10.663763171
H	17.924881811	8.988598454	11.542560208
H	18.228069312	10.550945492	10.790179012
C	19.859624690	9.155063488	10.586129217
H	20.004497387	8.066080316	10.568099513
H	20.373559147	9.526354725	11.479474025
C	20.502291779	9.768729018	9.340942976
H	20.468417873	10.865416110	9.400205695
H	21.556063073	9.472252066	9.294904556
C	19.766751913	9.302145870	8.092177063
H	19.853704784	8.208767934	8.003607132
C	21.433333004	10.348175883	6.640527185
H	22.066300433	10.459169858	7.519550763
C	22.011250812	10.772667955	5.400220858
C	23.292503816	11.358048431	5.504647638
H	23.706834732	11.479366708	6.501033205
C	24.005688324	11.764049198	4.398296208
C	23.403410900	11.546613071	3.134750073
H	23.962414431	11.854013034	2.258291909
C	22.163738634	10.971095664	2.940173170
C	21.414593303	10.575357814	4.105948676
C	15.938076622	8.975220271	1.642703809
C	16.157740638	10.496570201	1.554750502
H	16.916033855	10.835587024	2.263046593

H	15.223922396	11.034105487	1.758770584
H	16.485567849	10.762602527	0.542271412
C	17.239411056	8.231488160	1.291857356
H	17.084960463	7.146283790	1.323701672
H	18.047996962	8.487191634	1.978836420
H	17.552025426	8.497633835	0.274538195
C	14.899484724	8.602656098	0.577961639
H	15.279917340	8.899669159	-0.405621317
H	13.944915061	9.120157634	0.730676198
H	14.709246191	7.523322898	0.544467905
C	12.377411827	6.943809250	4.637232182
C	11.998671891	6.621209252	6.084686917
H	12.711685580	5.928901422	6.547330870
H	11.012800811	6.143847664	6.106544848
H	11.942293823	7.525020128	6.702463890
C	12.390931617	5.630207958	3.837162702
H	13.137561715	4.935526810	4.238307193
H	12.619150948	5.797599211	2.778966264
H	11.408387158	5.146537392	3.893695189
C	11.308151885	7.884110972	4.055540479
H	10.320914999	7.410189194	4.112213113
H	11.501500710	8.124716860	3.004566431
H	11.268037498	8.825118986	4.615872445
C	25.386970010	12.409721749	4.476436817
C	25.867255462	12.569092421	5.920889043
H	25.193283464	13.205262324	6.506255179
H	26.856051040	13.040839121	5.926515044
H	25.958973733	11.601754187	6.428248420
C	25.335512973	13.803408038	3.827836466
H	25.034708569	13.754820835	2.775780786
H	26.325409557	14.273455656	3.870062360
H	24.625979947	14.453244208	4.352544750
C	26.402995462	11.533898847	3.723650319
H	26.468246773	10.536552612	4.173199807
H	27.397818791	11.993354876	3.765237115
H	26.136825973	11.412207447	2.668149452
C	21.593450662	10.762654386	1.532489291
C	20.283790471	11.554344298	1.367463683
H	20.461042942	12.627434477	1.507556861
H	19.524828268	11.232945162	2.082737473
H	19.889478595	11.407433792	0.354321395
C	22.560019314	11.250451403	0.446622678
H	23.514466948	10.711145067	0.468595028
H	22.764598180	12.324738105	0.525800627
H	22.106325971	11.074565268	-0.534983472
C	21.344442868	9.264184387	1.281729200
H	20.948994425	9.120865831	0.268625963
H	20.628607552	8.849623703	1.993761891
H	22.281317003	8.699603699	1.360100144