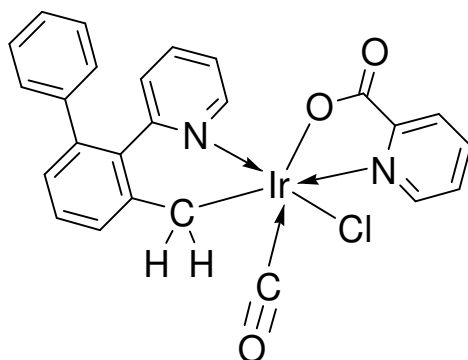


A unique six-membered chelated iridium complex

Supporting Information



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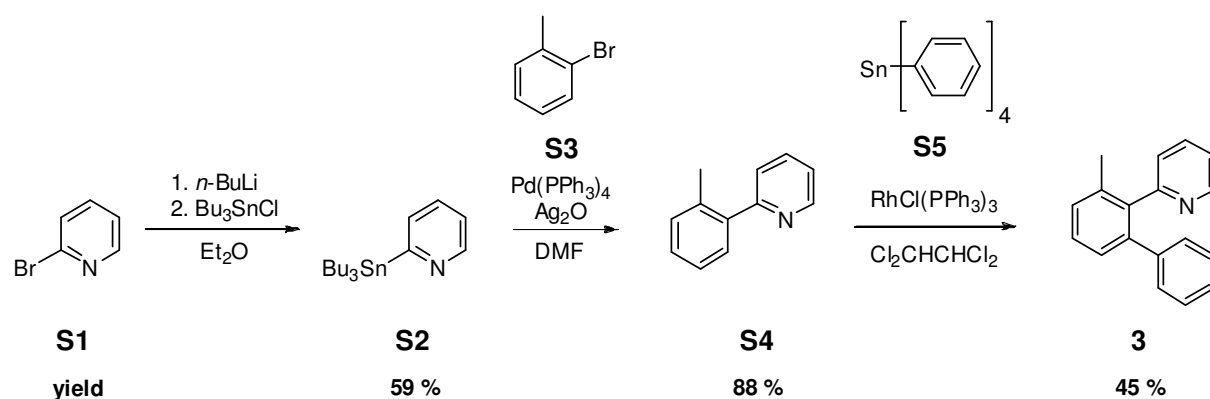
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General. Catalysts, starting materials, solvents and reagents were purchased from *ABCR* (Pd[PPh₃]₄, RhCl[PPh₃]₃) *Acros* (2-Bromotoluene, Silver(I)oxide, Silver(I)trifluoroacetic acid), *Alfa Aesar* (1,1,2,2-Tetrachlorethane), *Aldrich* (2-Bromopyridine, Tributyltin chloride, *n*-BuLi, 2-Ethoxyethanol, Tetraphenyltin), *ChemPur* (IrCl₃·*n*H₂O) and *Fluka* (DMF). For a reaction to rule out impurities in the solvent as the source of carbon 2-Ethoxyethanol was also purchased from *ABCR*. All purchased compounds were used as supplied without further purification. All reactions necessary to obtain compound **3** were carried out in flame dried glassware under an inert atmosphere of nitrogen. Reactions concerning cyclometallation (reactions to obtain compounds **2**, **5a** and **5b**) were carried out under an inert atmosphere of nitrogen.

Chromatography. TLC plates were purchased from *Macherey-Nagel GmbH & Co. KG*. Except from compound **2** mixtures of *n*-hexane and ethyl acetate were used for reaction control via TLC and purification via flash chromatography. In case of compound **2** mixtures of dichloromethane and ethyl acetate were used. Silica gel for flash chromatography was purchased from *Macherey-Nagel GmbH & Co. KG*. Complete removal of the corresponding starting material 2-*o*-tolylpyridine from compound **3** was necessary to avoid favorable side reaction with iridium. Purification was performed by reversed phase preparative HPLC. The HPLC system was purchased from *Knauer GmbH, Berlin, Germany* (K-1800 pump, K-2800 DAD detector, Eurospher 100-10-C18 precolumn, Eurospher 100-C18 column). The conditions used are described in the corresponding chapter of this supporting information.

Analytical methods. NMR experiments were recorded on a *Bruker DRX-400* and reported in parts per million (ppm). ¹H NMR spectra were obtained at 400.14 MHz and referenced relative to tetramethylsilane (TMS). ¹³C NMR spectra were obtained at 100.62 MHz and chemical shifts were recorded relative to the solvent (chloroform: 77.00 ppm). Data are reported as follows: (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad; coupling constant(s) in Hz; integration). Mass spectra (low and high resolution) were recorded on a *ThermoFinnigan MAT95*. Data are reported in relation to the base ion which is set to 100 %. UV-/Vis spectra were measured on a *Varian Cary 100 Bio*. IR spectra were recorded on a *Bruker Tensor 27* with a Diamant ATR sampling element. Data are reported as follows: (w = weak, m = middle, s = strong, vs = very strong). X-ray analysis was performed on a *Bruker SMART 1000-CCD* at a temperature of 133 K with graphite monochromated MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares calculations on F². Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced in calculated positions.

Synthesis of starting material 3^[1, 2]:



Step 1 (S2). Absolute diethylether (200 mL) and 2-bromopyridine (20.00 g, 127.0 mmol) were placed in a flame dried 3-necked flask. The mixture was cooled to $-80\text{ }^{\circ}\text{C}$ while stirring and then *n*-BuLi (88.9 mL, 139.0 mmol) was added within the next 70 min followed by a 20 min period of stirring at $-80\text{ }^{\circ}\text{C}$. Then tributyltin chloride (34.5 mL, 127.0 mmol) was added slowly under control of the temperature. After the addition was completed the brownish suspension was stirred overnight while slowly warming up to room temperature. Afterwards 40 mL of saturated aqueous NH_4Cl solution were added and the product was extracted 3 \times with diethylether, washed with water and dried over MgSO_4 . The crude product was distilled at a temperature of ca. $130 - 140\text{ }^{\circ}\text{C}$ (1 mbar) to give **S2** (59 %).

Step 2 (S4). 2-bromotoluene (13.94 g, 81.49 mmol), silver(I)oxide (6.29 g, 27.16 mmol), $\text{Pd}[\text{PPh}_3]_4$ (942 mg, 815.0 μmol) were placed together with 40 mL DMF in a 2-necked flask equipped with a condenser. The mixture was heated up to $100\text{ }^{\circ}\text{C}$ and stirred for 10 min. Then **S2** diluted in ca. 10 mL DMF was dropped to the reaction within 15 min via a septum. The darkish mixture was stirred for another 23 hours at $100\text{ }^{\circ}\text{C}$. After cooling to room temperature the crude reaction mixture was filtered over a short pad of silica gel (ca. 6 cm in height, 6.5 cm in diameter) and eluted with *n*-hexane/ethyl acetate 10:1 \rightarrow 1:1. The combined organic layer was then vigorously stirred for 45 min together with 300 mL of a aqueous KF solution (10 %) at room temperature. Afterwards an extraction with ethyl acetate and dichlormethane was performed and the combined organic layers were dried over MgSO_4 and finally purified via flash chromatography (ca. 21 cm in height, 5 cm in diameter) with *n*-hexane/ethyl acetate 10:1. Since NMR still showed large amounts of **S2** the obtained product was dissolved in ethyl acetate and stirred for 30 min with 50 mL of a aqueous KF solution (10 %) at room

temperature. Repeated extraction with ethyl acetate and drying over MgSO₄ gave 4.04 g (88 %) of a yellow oil **S4** showing diminished amounts of impurities of **S2**.

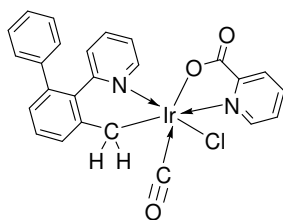
Step 3 (3). 2-*o*-tolylpyridine **S4** (3.00 g, 17.73 mmol), tetraphenyltin (7.95 g, 18.62 mmol) and Wilkinson's catalyst RhCl(PPh₃)₃ (820 mg, 886.4 μmol) are placed together with 55 mL 1,1,2,2-tetrachlorethane inside a flame dried 2-necked flask equipped with a condenser. The reddish suspension is heated to 120 °C, turns to a solution and stirred for 43 hours. The mixture was treated twice with ca. 300 mL aqueous NH₃ solution (5 %) after cooling to room temperature and extracted repeatedly with chloroform. The organic layer was washed twice with water. The combined organic layer was dried over MgSO₄ and purified via flash chromatography (ca. 25 cm in height, 7.5 cm in diameter) with *n*-hexane/ethyl acetate 6:1 → 4:1. Since NMR spectra revealed considerable amounts of **S4** which could cyclometalate to an iridium center as well and compete with **3**, we purified the product from the flash chromatography via preparative HPLC. The product was dissolved in the minimum amount of a solution of methanol/water 70:30 and chromatographed with the same ratio of solvents and a flux of 20 mL/min. The detection wavelength was 254 nm. 1.96 g (45 %) of a light yellow oil **3** were obtained showing no sign of impurities of **S4** in NMR.

Synthesis of **2**^[3, 4]:

Step 1. In a nitrogen flushed 2-necked flask equipped with a condenser $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (487 mg, 1.631 mmol) and **3** (1.00 g, 4.076 mmol) are placed together with 12 mL 2-ethoxyethanol and 4 mL water. The greenish suspension was degassed by repeated evacuation and ventilation with nitrogen and then heated under reflux for 14 hours. During the reaction a black precipitate was formed and filtered off once the reaction was cooled to room temperature. The clear filtrate was then treated with 100 mL of water whereas a precipitate was formed. The precipitate was collected and washed with portions of *n*-hexane and water and then dried at 60 °C. 523 mg of a pale yellow solid of **5a** were obtained.

Step 2. In a nitrogen flushed 2-necked flask **5a** (200 mg, 160.0 μmol), picolinic acid (43 mg, 349.0 μmol), potassium *tert*-butylate (39 mg, 349.0 μmol) and silver(I)trifluoroacetic acid (77 mg, 349.0 μmol) were placed together with dichloromethane (6.6 mL) and ethanol (2 mL). The dark green solution was stirred at room temperature in the dark for 93 hours. During the reaction the solution turned turbid. At the end of the reaction 40 mL *n*-hexane are added and the precipitate collected on a filter. The precipitate is then washed with portions of *n*-hexane, water and diethylether and then dried at 60 °C. 226 mg of a pale yellow solid are obtained following purification via flash chromatography (SiO_2 ; dichloromethane/ethyl acetate = 1:1). 27 mg (14 %) of a pale yellow solid of **2** are obtained. Single crystals for X-ray analysis were grown from slow evaporation of CHCl_3 solution.

Full spectral characterization of compound 2:



^1H NMR (400.1 MHz, CDCl_3)

δ = 8.77 (d, J = 5.1 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.10 (dt, J = 7.8, 7.7, 1.3 Hz, 1H), 7.81 (d, J = 5.9 Hz, 1H), 7.66 (ddd, J = 7.7, 5.1, 1.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6, 7.6 Hz, 1H), 7.32 (ddd, J = 8.1, 7.5, 1.5 Hz, 1H), 7.23–6.79 (m, br, 6H), 7.08 (ddd, J = 8.1, 1.6, 0.5 Hz, 1H), 6.90 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 4.21 (d, J = 10.8 Hz, 1H), 3.76 (d, J = 10.8 Hz, 1H).

^{13}C NMR (100.6 MHz, CDCl_3)

δ = 173.2 (s), 157.9 (s), 156.5 (s), 151.4 (s), 150.7 (s), 150.5 (d), 149.7 (d), 142.3 (s), 141.3 (s), 139.8 (d), 137.7 (d), 136.0 (s), 130.4 (d), 129.5 (d, br), 129.2 (d), 129.2 (d), 128.8 (d), 128.6 (d, br), 128.5 (d), 127.3 (d), 124.9 (d), 123.7 (d), 8.8 (t).

MS (EI, 70eV)

m/z (%) = 622 (37) [M^+], 594 (74), 512 (11), 433 (25), 244 (100).

UV/Vis:

λ /nm (ϵ) = 234 (29900), 307 (10100) [CH_3CN];
311 (10800) [CH_2Cl_2].

IR (FT-IR)

$\tilde{\nu}$ / cm^{-1} = 3058 (w), 2951 (w), 2021 (s, $\text{C}\equiv\text{O}$), 1733 (w), 1668 (s), 1602 (m), 1570 (m), 1478 (m), 1460 (m), 1331 (s), 1289 (m), 1238 (w), 1158 (m), 1093 (w), 1048 (w), 1025 (w), 861 (m), 798 (w), 757 (vs), 731 (s), 693 (s), 649 (w), 622 (w), 602 (m), 587 (m), 539 (m).

$\text{C}_{25}\text{H}_{18}\text{ClIrN}_2\text{O}_3 \cdot \text{CHCl}_3$ (742.5)	Calc.:	C 42.06	H 2.72	N 3.77
	Found:	C 42.07	H 2.59	N 3.29

$\text{C}_{25}\text{H}_{18}\text{ClIrN}_2\text{O}_3$

Calc.: 620.0606
Found: 620.05879 \pm 2.9 ppm

^1H NMR-spectra with magnifications of 5a

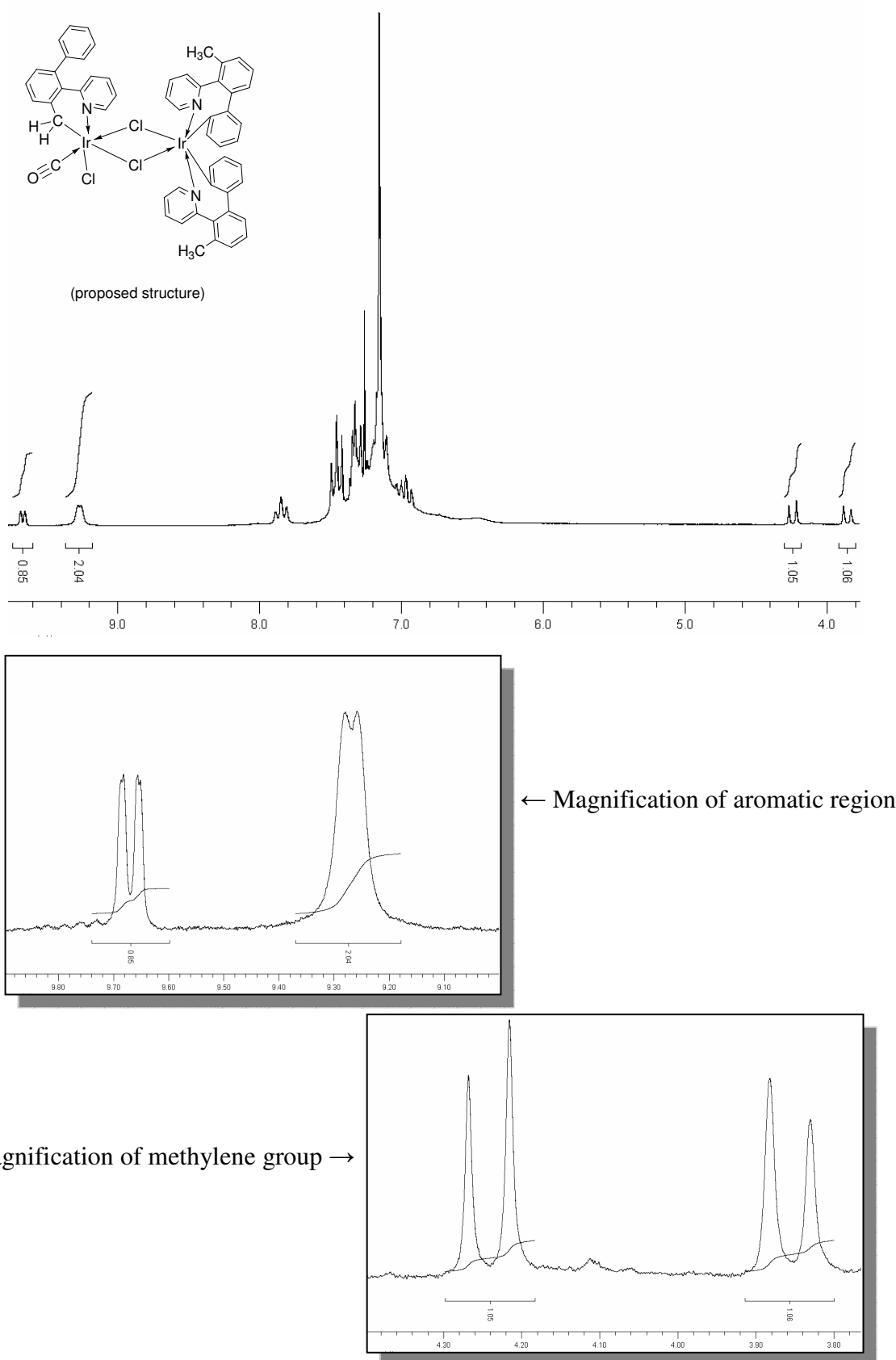


Figure S1. ^1H NMR and magnifications of 5a.

^1H and ^{13}C NMR-spectra of 2

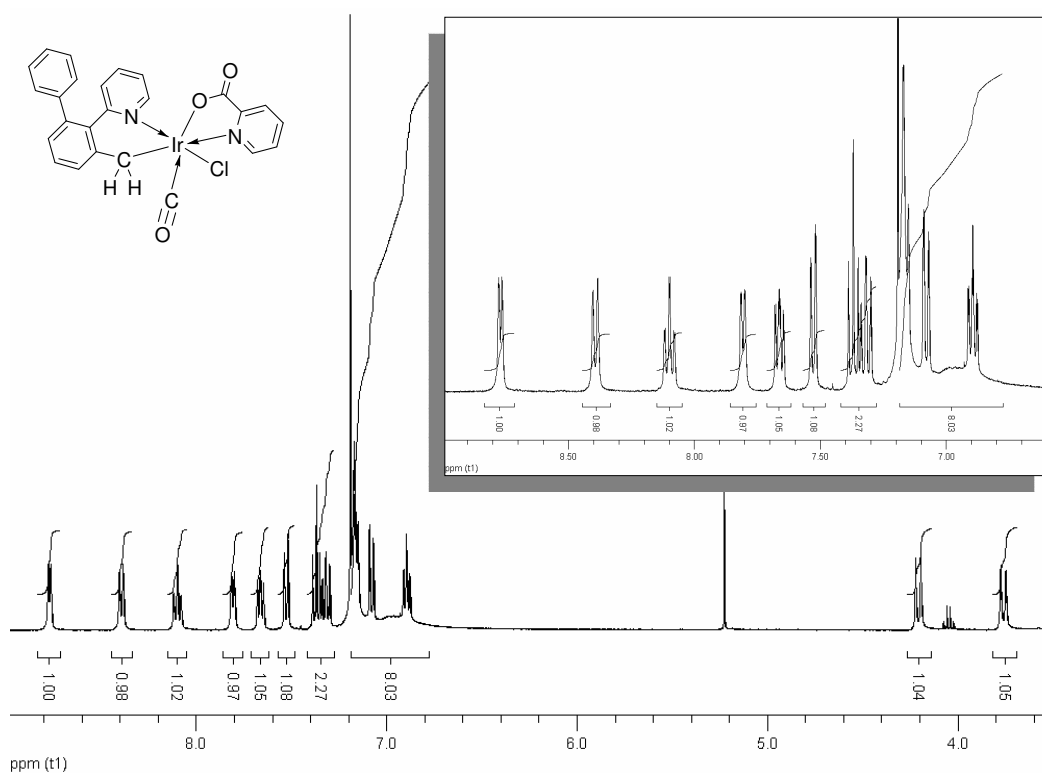


Figure S2. ^1H NMR of 2.

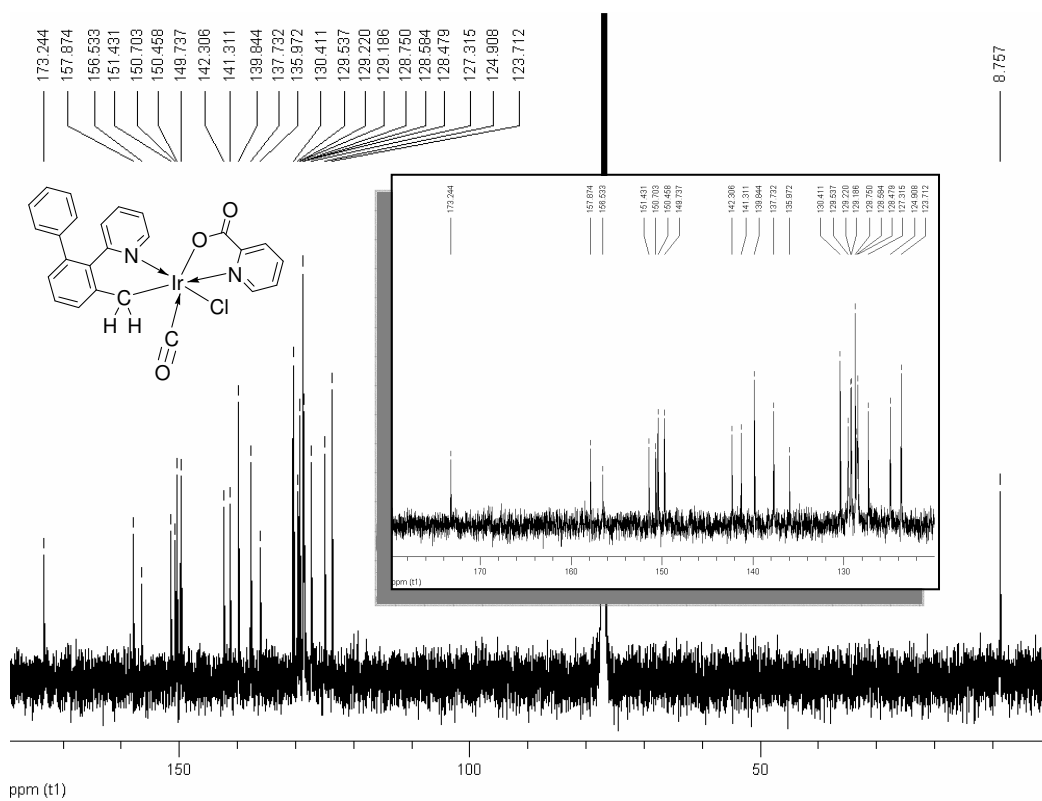


Figure S3. ^{13}C NMR of 2.

IR-spectra of 5a and 5b in comparison

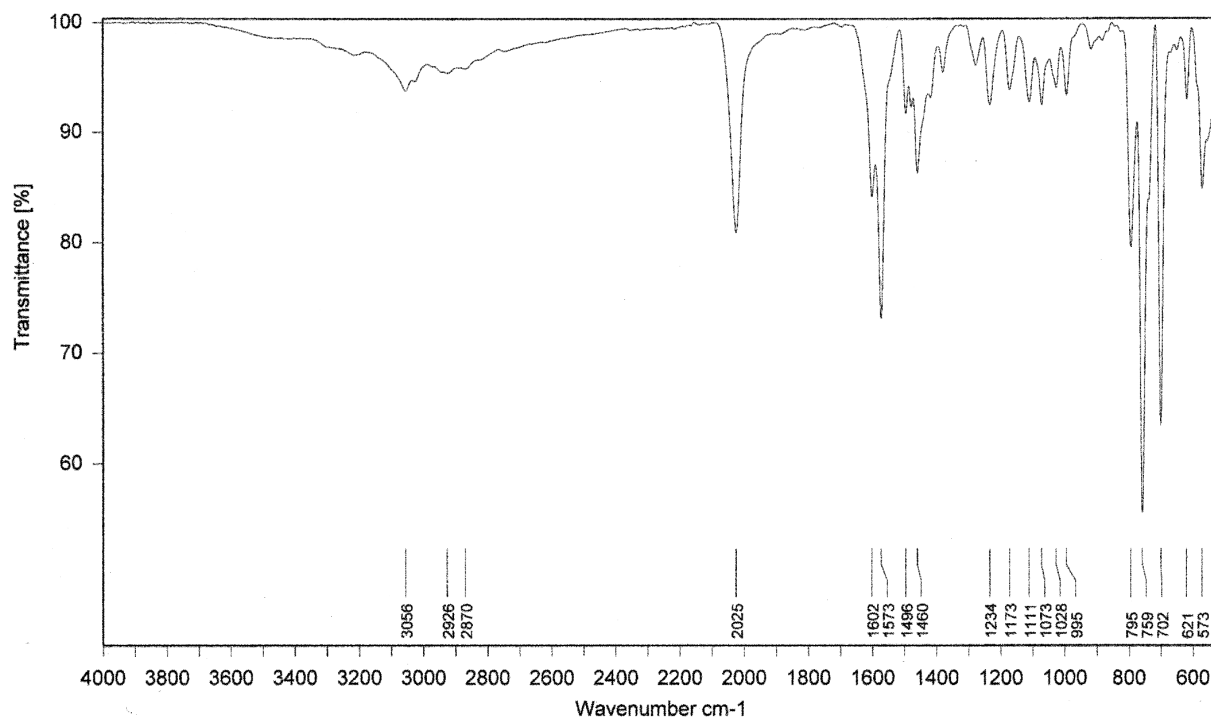


Figure S4. IR spectrum of **5a** after reaction of **3** with H₂¹⁶O: ν(CO) = 2025 cm⁻¹.

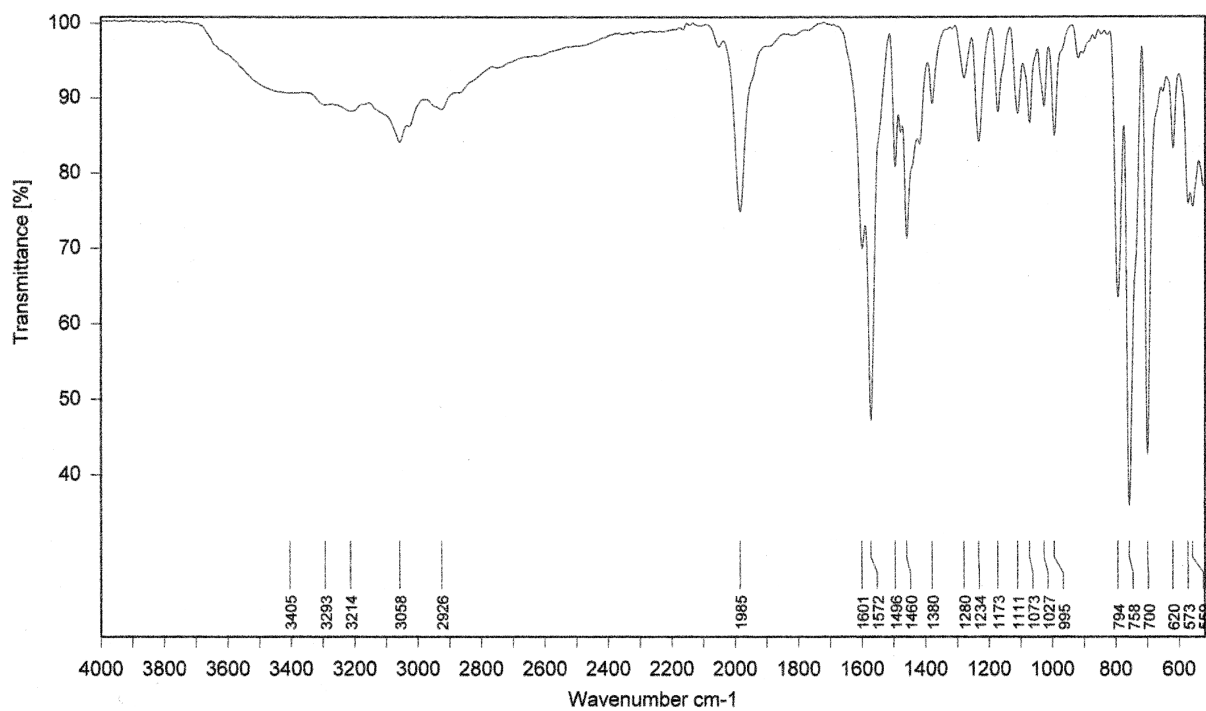


Figure S5. IR spectrum of **5b** after reaction of **3** with H₂¹⁸O: ν(CO) = 1985 cm⁻¹.

IR-spectra and GC-MS result of reactions of **3** in different solvents

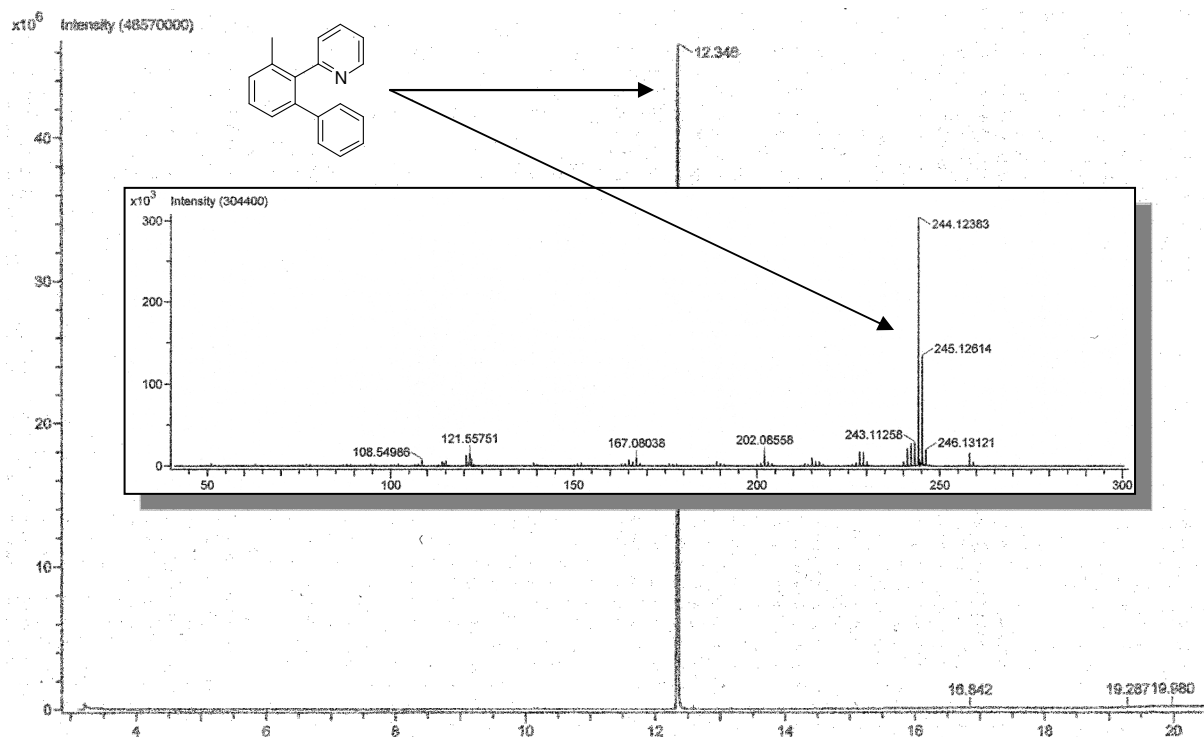


Figure S6. GC-MS result of aqueous filtrate from step 1.

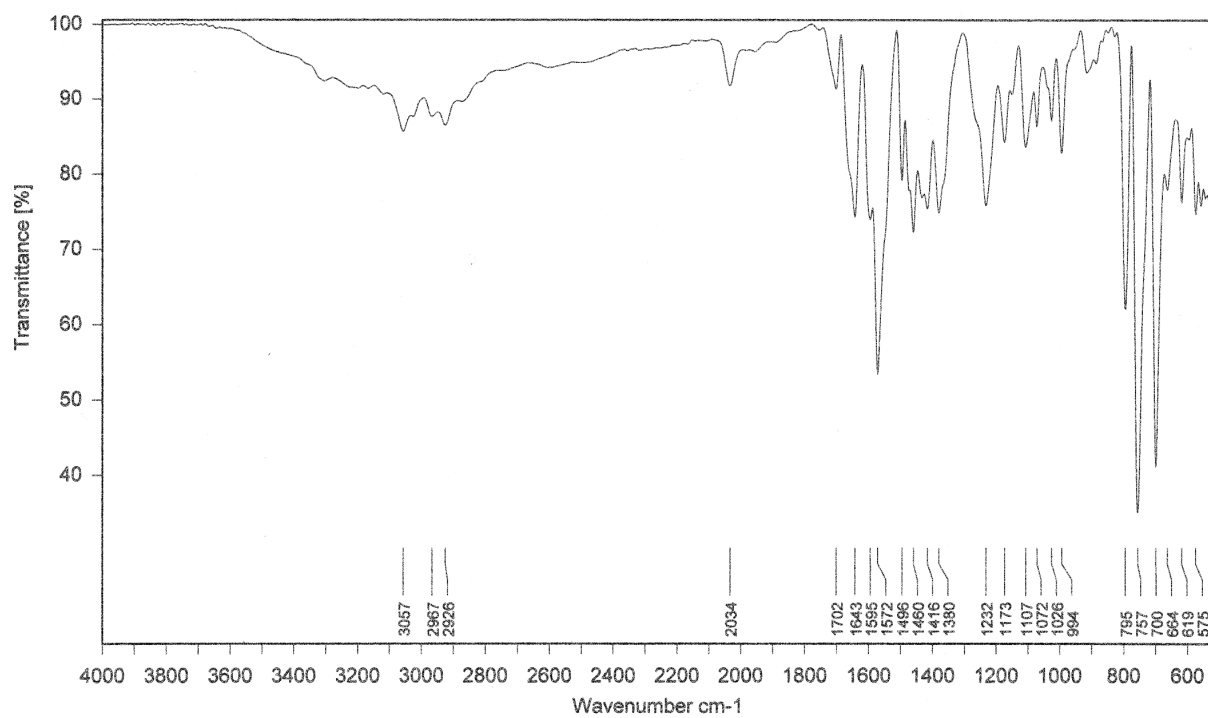


Figure S7. IR spectrum of product of reaction of **3** in phenol.

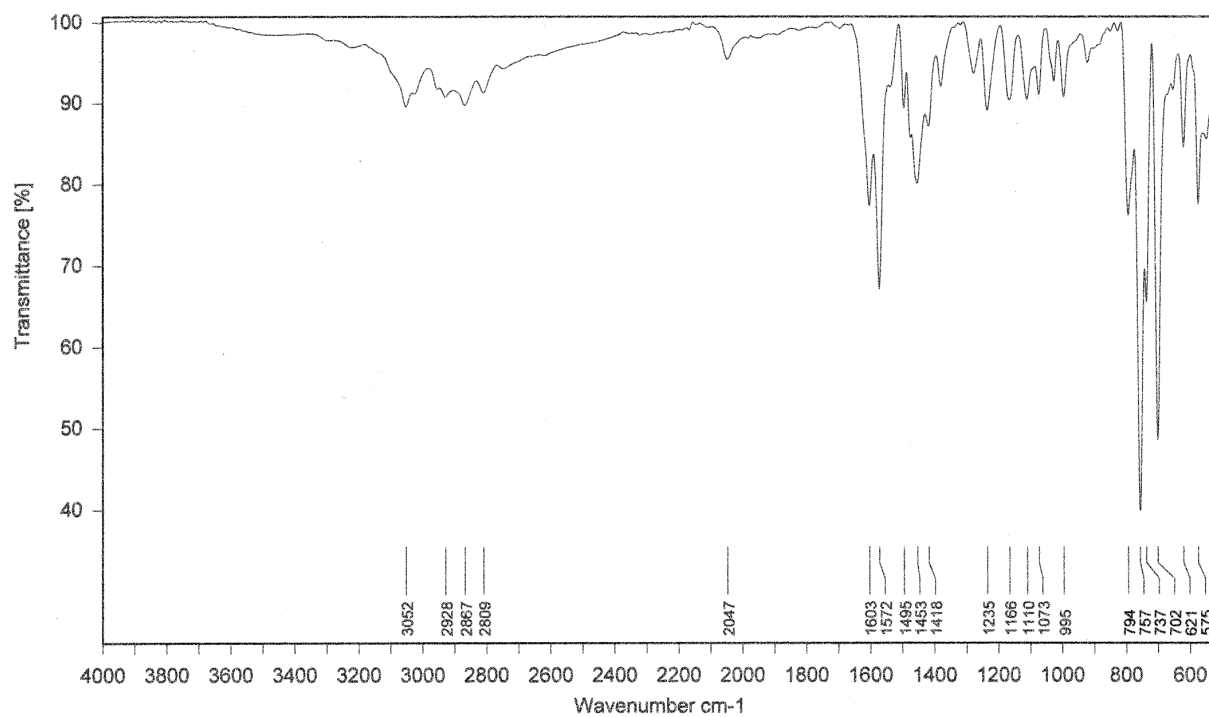


Figure S8. IR spectrum of product of reaction of **3** in di-*n*-butyl ether.

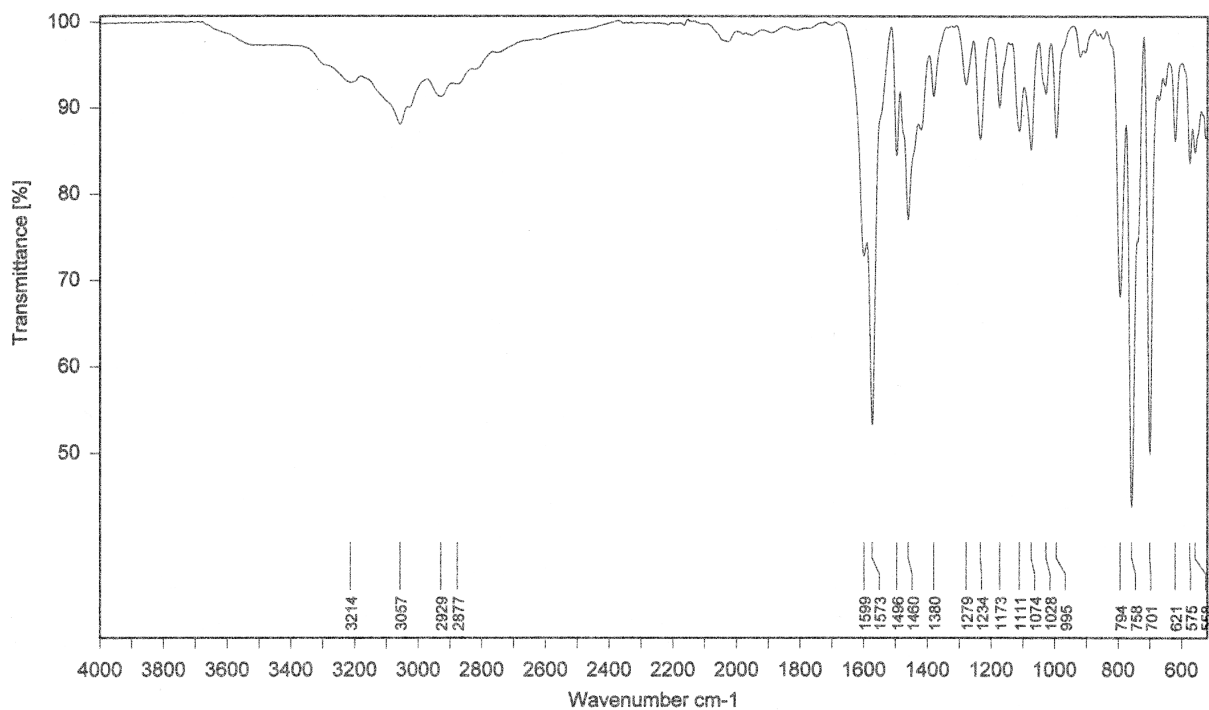


Figure S9. IR spectrum of product of reaction of **3** in diethylene glycol dimethyl ether (diglyme).

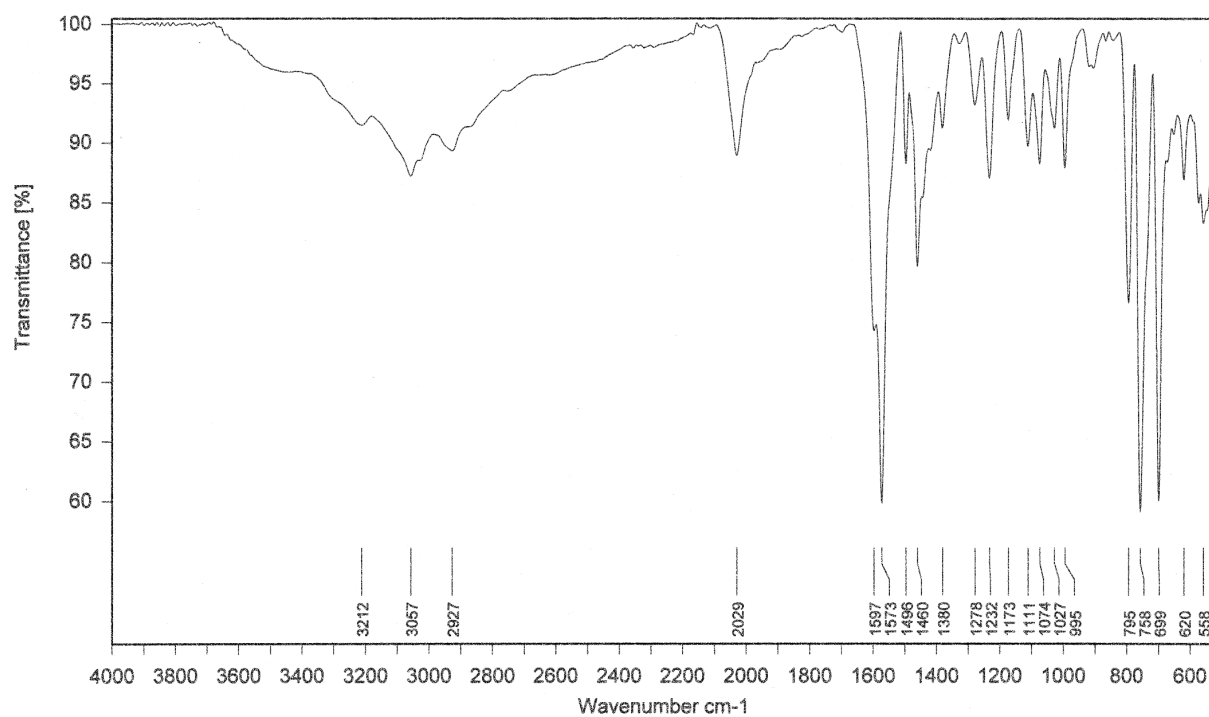


Figure S10. IR spectrum of product of reaction of **3** and IrCl₃·*n*H₂O with a ratio of 1:1 in 2-ethoxyethanol.

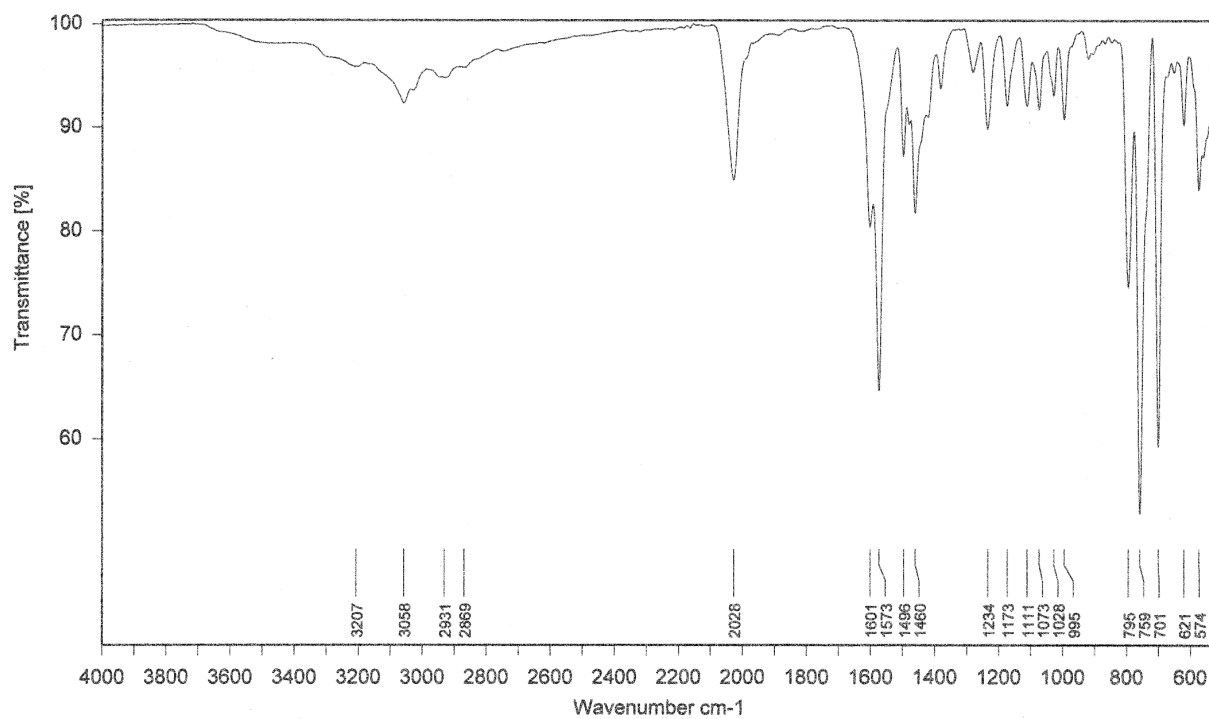


Figure S11. IR spectrum of product of reaction of **3** in 2-ethoxyethanol purchased from ABCR.

Crystallographic data of **2**^[5]

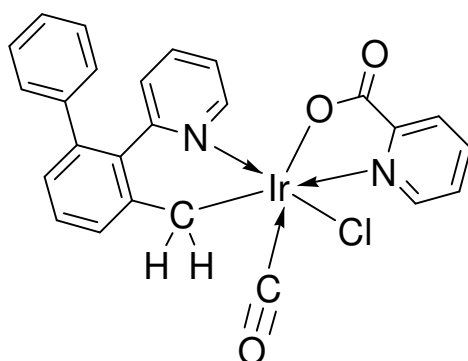


Table 1. Crystal data and structure refinement of **2**.

Empirical formula	C ₂₆ H ₁₉ Cl ₄ IrN ₂ O ₃	
Formula weight	741.43	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4605(11) Å	α = 89.693(2)°
	b = 14.1259(14) Å	β = 83.124(2)°
	c = 16.6417(16) Å	γ = 85.740(2)°
Volume	2667.3(4) Å ³	
Z	4	
Density (calculated)	1.846 Mg/m ³	
Absorption coefficient	5.438 mm ⁻¹	
F(000)	1432	
Crystal size	0.28 x 0.16 x 0.15 mm ³	
Theta range for data collection	1.23 to 30.13°	
Index ranges	-15 ≤ h ≤ 16, -19 ≤ k ≤ 19, 0 ≤ l ≤ 23	
Reflections collected	17162	
Independent reflections	17162 [R(int) = 0.0000]	
Completeness to theta = 30.00°	91.8 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4960 and 0.3442
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17162 / 908 / 667
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0425, wR2 = 0.1015
R indices (all data)	R1 = 0.0633, wR2 = 0.1083
Largest diff. peak and hole	1.732 and -1.211 e. \AA^{-3}

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