Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Iridium(III)-catalysed cross-linking of polysiloxanes leading to the thermally resistant luminescent silicone rubbers

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Materials and Instrumentation

Solvents, $IrCl_3 \cdot nH_2O$, 2-phenylpyridine, and isocyanides were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNSO analyzer. Mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeOH was used as the solvent. The instrument was operated at positive ion mode using *m/z* range of 50–3000. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000–400 cm^{-1}) were recorded on Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr pellets. UV-VIS spectra were measured on Shimadzu UV-2550 spectrophotometer. The luminescence spectra were recorded on a Fliorolog-3 instrument at room temperature. The complexes were dissolved in dichloromethane ($c = 1.0 \times 10^{-4}$ M), and the solutions were degassed by blowing argon for 10 minutes. The same samples were used to measure quantum yields and lifetimes of luminescence. For measurement of luminescent properties of silicone rubbers thin sheets of rubber were used. Quantum luminescence yields were determined on the same instrument with the help of direct measurement using an integrating sphere. The luminescence lifetimes were measured using the time-correlated photon counting method (TCSPC). NMR spectra were recorded on Bruker AVANCE III 400 spectrometers in $CDCl_3$ at 25 °C (at 400, and 100 MHz for ^1H and ^{13}C NMR spectra, respectively). Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$): δ 7.26 (^1H) and 77.2 (^{13}C). ^1H and ^{13}C NMR data assignment for **4** and **5** was achieved by using 2D ($^1H,^1H$-COSY, $^1H,^1H$-NOESY, $^1H,^{13}C$-HMQC/HSQC and $^1H,^{13}C$-HMBC) NMR correlation experiments.

Siloxane reagents for catalytic studies (vinyl-terminated poly(dimethylsiloxane) PDMS (the weight average molecular weight $M_w = 80000$, the number average molecular weight $M_n = 33800$, 0.5 wt% of $CH=CH_2$) and trimethylsilyl-terminated poly(dimethylsiloxane-*co*-

ethylhydrosiloxane) (EHDMS; $M_w = 8150$, $M_n = 4600$, 0.7 wt% of Si–H) were obtained from the State Institute of Synthetic Rubber (Saint Petersburg, Russian Federation).

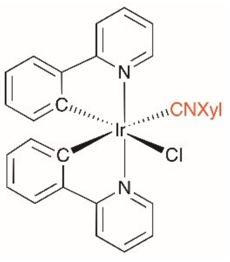
The progress of the cross-linking was monitored by DSC method using a NETZSCH DSC 204 F1 Phoenix instrument. DSC conditions are as the following: cooling from 25 to –10 °C, heating from –10 to 250 °C, and then cooling from 280 to 25 °C (10 $°C•min^{-1}$); all components were mixed before DSC studies and DSC experiments were conducted twice for each test. TG measurements were performed on a NETZSCH TG 209F1 Libra instrument. Approximately 2 mg of sample was taken in a platinum pan that was then heated from RT to 800 °C at 10 °C/min under flow of argon (50 mL/min) or in air.

All measurements were performed at Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center of Thermal Analysis and Calorimetry, Center for Optical and Laser Materials Research and Chemistry Educational Centre (all in Saint Petersburg State University).

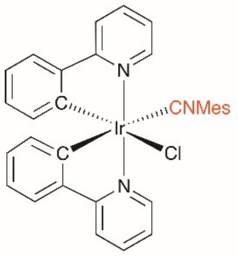
Preparation of complexes 1–6

Synthesis of [Ir(ppy)$_2$(*μ*-Cl)]$_2$ (1). Complex [Ir(ppy)$_2$(*μ*-Cl)]$_2$ (**1**, ppy = (2-phenylpyridinato-C^2,*N*)), was prepared by the method reported by Nonoyama,[1] that involves heating IrCl$_3$•*n*H$_2$O to 110 °C with 2.5 equiv of 2-phenylpyridine in a 3:1 mixture of 2-ethoxyethanol and deionized water.

Synthesis of *mono*isocyanide complexes 2 and 3. Starting [(ppy)$_2$Ir(*μ*-Cl)]$_2$ (**1**, 60 mg, 0.056 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) at RT under argon. Isocyanide CNXyl or CNMes (0.113 mmol) dissolved in CH$_2$Cl$_2$ (5 mL) was then added dropwise, and the reaction mixture was stirred at RT for 3 h. Yellow solution formed was evaporated to dryness in *vacuo* at RT, and the solid residue formed was washed with diethyl ether (2 × 5 mL) and dried in air at RT.

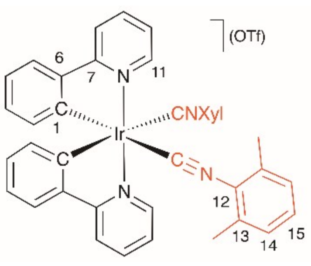


[Ir(ppy)$_2$Cl(CNXyl)] (**2**). Yield 64.3 mg (85%), pale yellow solid. Anal. Calcd. for $C_{31}H_{25}N_3ClIr$: C, 55.80; H, 3.78; N, 6.30. Found: C, 55.44; H, 3.74; N, 6.23. ESI$^+$-MS, m/z: calcd. for $C_{31}H_{25}N_3Ir^+$ 632.1678, found 632.1657 [M – Cl]$^+$. IR (KBr, selected bands, cm^{-1}): ν(C≡N) 2123 (s). ^{1}H NMR (CDCl$_3$, δ,): 2.12 (s, 6H, Me), 6.18 (d, $J_{H,H}$ = 8.5 Hz, 1H, H$_{Arom}$), 6.44 (d, $J_{H,H}$ = 8.4 Hz, $1_{H,HArom}$), 6.76–6.80 (m, 1H, H$_{Aryl}$), 6.83–6.92 (m, 3H, H$_{Aryl}$), 6.99–7.01 (m, 2H, H$_{Aryl}$), 7.08–7.17 (m, 2H, H$_{Aryl}$), 7.26–7.30 (m, 1H, H$_{Aryl}$), 7.56–7.63 (m, 2H, H$_{Aryl}$), 7.80–7.94 (m, 4H, H$_{Aryl}$), 9.28 (d, $J_{H,H}$ = 6.4 Hz, 1H, H$_{Aryl}$), 10.02 (d, $J_{H,H}$ =6.6 Hz, 1H, H$_{Aryl}$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 18.41 (Me), 118.58 (C$_{Aryl}$), 119.76 (C$_{Aryl}$),121.57 (C$_{Aryl}$), 122.14 (C$_{Aryl}$), 122.67 (C$_{Aryl}$), 122.92 (C$_{Aryl}$), 123.88 (C$_{Aryl}$), 124.11 (C$_{Aryl}$), 127.73 (C$_{Aryl}$), 128.37 (C$_{Aryl}$), 129.88 (C$_{Aryl}$), 130.01 (C$_{Aryl}$), 130.36 (C$_{Aryl}$), 131.05 (C$_{Aryl}$), 134.91 (C$_{Aryl}$), 137.01 (C$_{Aryl}$), 137.26 (C$_{Aryl}$), 143.07 (C$_{Aryl}$), 143.79 (C$_{Aryl}$), 144.25 (C$_{Aryl}$), 151.75 (C$_{Aryl}$), 153.32 (C$_{Aryl}$), 164.98 (C$_{Aryl}$), 167.58 (C$_{Aryl}$), 168.58 (C$_{ArylIr}$). Signals from C$_{isocyanide}$ and C$_{ipso}$ from Xyl were not detected.



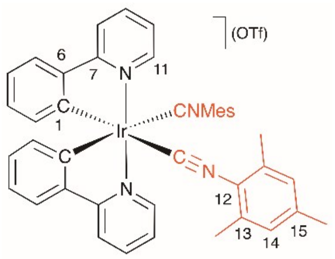
[Ir(ppy)$_2$Cl(CNMes)]•CH$_2$Cl$_2$ (**3**•CH$_2$Cl$_2$). Yield 65.2 mg (82%), pale yellow solid. Anal. Calcd. for $C_{33}H_{29}N_3Cl_3Ir$: C, 51.73; H, 3.81; N, 5.48. Found: C, 51.96; H, 3.88; N, 5.56. ESI$^+$-MS, m/z: calcd. for $C_{32}H_{27}N_3Ir^+$ 646.1834, found 646.1800 [M – Cl]$^+$. IR (KBr, selected bands, cm^{-1}): ν(C≡N) 2135 (s). 1H NMR (300.13 MHz, CDCl$_3$, δ,): 2.08 (s, 6H, *o*-Me), 2.23 (s, 3H, *p*-Me), 5.30 (s, 2H, CH$_2$Cl$_2$), 6.18 (d, $J_{H,H}$ = 7.9 Hz, 1H, H_{Aryl}), 6,44 (d, $J_{H,H}$ = 7.0 Hz, 1H, H_{Aryl}), 6.75–6.92 (m, 7H, H_{Aryl}), 7.12–7.16 (m, 1H, H_{Aryl}), 7.25–7.29 (m, 1H, H_{Aryl}), 7.57–7.63 (m, 2H, H_{Aryl}), 7.79–7.94 (m, 4H, H_{Aryl}), 9.27 (d, $J_{H,H}$ = 5.7, 1H, H_{Aryl}), 10.02 (d, $J_{H,H}$ = 5,7 Hz, 1H, H_{Aryl}). $^{13}C\{^1H\}$ NMR (75.47 MHz, CDCl$_3$, δ): 18.28 (*o*-Me), 21.13 (*p*-Me), 53.39 (CH$_2$Cl$_2$), 118.54 (C_{Aryl}), 119.72 (C_{Aryl}), 121.50 (C_{Aryl}), 122.10 (C_{Aryl}), 122.60 (C_{Aryl}), 122.88 (C_{Aryl}), 123.85 (C_{Aryl}), 124.09 (C_{Aryl}), 124.84 (C_{ipso} from Mes), 128.42 (C_{Aryl}), 129.83 (C_{Aryl}), 129.99 (C_{Aryl}), 130.38 (C_{Aryl}), 131.04 (C_{Aryl}), 134.61 (C_{Aryl}), 136.95 (C_{Aryl}), 137.20 (C_{Aryl}), 138.65 (C_{Aryl}), 143.07 (C_{Aryl}), 143.93 (C_{Aryl}), 144.25 (C_{Aryl}), 146.24 ($C_{isocyanide}$), 151.75 (C_{Aryl}), 153.34 (C_{Aryl}), 164.96 (C_{Aryl}), 167.59 (C_{Aryl}), 168.60 (C_{Aryl}).

Synthesis of *bis*isocyanide complexes 4 and 5. A mixture of the iridium complex **2** or **3** (0.03 mmol) and AgOTf (0.03 mmol, 7.7 mg) was suspended in CH$_2$Cl$_2$ (5 mL). Isocyanide CNXyl or CNMes (0.03 mmol) dissolved in CH$_2$Cl$_2$ (2 mL) was then added dropwise. The reaction mixture was stirred at RT for 24 h resulting in formation of a colourless precipitate suspended in yellow solution. Precipitate was filtered off, and the solution was evaporated to dryness in *vacuo* at RT. The solid residue formed was washed with diethyl ether (3 × 5 mL) and dried in air at RT.



[Ir(ppy)$_2$(CNXyl)$_2$](OTf) (**4**). Yield 20.3 mg (74 %), yellowish solid. Spectral data for **4** are consistent with those reported previously.[2] ESI$^+$-MS, m/z: calcd. for $C_{40}H_{34}N_4Ir^+$ 763.2413, found 763.2387 [M – CF_3SO_3]$^+$. IR (KBr, selected bands, cm^{-1}): ν(C≡N) 2151, 2177. ^{1}H

NMR (400.13 MHz, $CDCl_3$, δ): 2.11 (s, 12H, Me), 6.28 (d, $J_{H,H}$ = 7.5 Hz, 2H, H^2), 6.96 (t, $J_{H,H}$ = 7.5 Hz, 2H, H^3), 7.05 (t, $J_{H,H}$ = 7.5 Hz, 2H, H^4), 7.09 (d, $J_{H,H}$ = 7.3 Hz, 4H, H^{14}), 7.18–7.22 (m, 2H, H^{15}), 7.51 (t, $J_{H,H}$ = 6.5 Hz, H^{10}), 7.72 (d, $J_{H,H}$ = 7.5 Hz, 2H, H^5), 8.07–8.15 (m, 4H, H^8 and H^9), 9.18 (d, $J_{H,H}$ = 5.5 Hz, 2H, H^{11}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ): 18.20 (Me), 120.83 (C^8), 124.09 (C^4), 124.88 (C^5), 125.01 (C^{10}), 126.04 (C^{12}), 128.22 (C^{14}), 130.01 (C^{15}), 130.53 (C^2), 131.06 (C^3), 135.38 (C^{13}), 136.33 ($C_{isocyanide}$), 139.46 (C^9), 143.79 (C^6), 152.38 (C^1), 153.32 (C^{11}), 167.62 (C^7).



[Ir(ppy)$_2$(CNMes)$_2$](OTf) (**5**). Yield 23.2 mg (85%), yellowish solid. Anal. Calcd. For $C_{43}H_{38}N_4F_3SO_3Ir$: C, 54.94; H, 4.07; N, 5.96. Found: C, 55.20; H, 4.12; N, 6.08. ESI$^+$-MS, m/z: calcd. for $C_{42}H_{38}N_4Ir^+$ 791.2726, found 791.2726 [M – CF_3SO_3]$^+$. IR (KBr, selected bands, cm^{-1}): ν(C≡N) 2144, 2173. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 2.06 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 6.27 (d, $J_{H,H}$ = 7.5 Hz, 2H, H^2), 6.88 (s, 4H, H^{14}), 6.95 (t, $J_{H,H}$ = 7.5 Hz, 2H, H^3), 7.05 (t, $J_{H,H}$ = 7.5 Hz, 2H, H^4), 7.49 (t, $J_{H,H}$ = 6.0 Hz, 2H, H^{10}), 7.71 (d, $J_{H,H}$ =7.6 Hz, 2H, H^5), 8.06–8.13 (m, 4H, H^8 and H^9), 9.17 (d, $J_{H,H}$ = 5.8 Hz, 2H, H^{11}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ): 18.02 (*o*-Me), 21.19 (*p*-Me), 120.82 (C^8), 123.39 (C^{12}), 123.98 (C^4), 124.85 (C^5), 124.86 (C^{10}), 128.88 (C^{14}), 130.48 (C^2), 130.96 (C^3), 134.97 (C^{13}), 135.74 ($C_{isocyanide}$), 139.44 (C^9), 140.59 (C^{15}), 143.75 (C^6), 152.44 (C^1), 153.08 (C^{11}), 167.62 (C^7).

Synthesis of *tris*cyclometallated complex *fac*-[Ir(ppy)$_3$] (6). Complexes **6** was prepared via the known procedure starting from **1**.[3] Thus, a mixture of [(ppy)$_2$Ir(μ-Cl)]$_2$ (**1**, 60 mg, 0.056 mmol), phenilpyridine (22 mg, 0.14 mmol), and K_2CO_3 (77 mg, 0.56 mmol) in 10 mL of glycerol was heated at 200 °C for 24 h under argon. Resulting mixture was cooled down to RT followed by addition of 20 mL of deionized H_2O. Yellow precipitate formed was filtered off, washed with methanol (2 × 5mL), diethyl ether (5 mL) and hexanes (5 mL). Crude product was purified by flash chromatography on silica gel using dichloromethane as eluent. All fractions were combined and evaporated to dryness *in vacuo* at RT to give the title compound.

Estimate of the price for catalysts 1–6. Estimate of the catalyst cost is important for many industrial applications; for each catalyst, the overall cost depends strongly on the synthetic procedure used, amount of compound prepared, commercial availability of starting materials *etc*. In addition, one should consider not only the cost of the catalyst itself, but also the catalytic loading during selected application, stability of the catalyst over time, and applicability of the catalyst for the selected application. At this point, we believe that the rough estimate of the catalyst cost should reflect the price of the precious metal used for its preparation corrected by the metal content in the compound. In the course of the last 12 months, average platinum and iridium prices are nearly equalized (source: Johnson Matthey base price for platinum metals), with the iridium being *ca*. 10% cheaper than platinum. While platinum content in Karstedt's catalyst is *ca*. 41%, iridium content in catalysts **1**–**6** is in the 21–35% range, and 23–28% for the iridium siloxides reported by Marciniec[4] (see Figure 1). Considering that preparation of **1**–**6** from the commercially available starting materials is roughly similar in terms of complexity to the preparation of Karstedt's or iridium-siloxide species, one can speculate that the price of the catalysts from this work should be roughly similar or slightly lower than those.

Characterization of new complexes 2, 3 and 5

Complexes **2**, **3** and **5** were obtained as pale yellow (**2** and **3**) and colorless (**5**) solids. The compounds are air and moisture-stable and soluble in common polar organic solvents. Complexes **2**, **3** and **5** were characterized by elemental analyses (C, H, N), high resolution ESI$^+$-MS, IR, 1D (^{1}H, ^{13}C{^{1}H}) and ^{2}D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of **2**, **3** and **5** were elucidated by single-crystal X-ray diffraction. Spectral data for **4** were in a good agreement with those previously reported.[5]

Complexes **2**, **3** and **5** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulae. The examination of the IR spectra of **2** and **3** reveals the presence of one strong ν(C≡N) stretching vibration at 2123 cm^{-1} for **2** and at 2135 cm^{-1} for **3** that belongs to one isocyanide ligand, while complex **5** displays two overlapped ν(C≡N) bands in the interval 2144–2173 cm^{-1} indicating *cis* placement of two isocyanides in the complex. The frequency of the CN stretching vibration is only marginally increased on going from the free isocyanides (2119 cm^{-1} for CNXyl and 2114 cm^{-1} for CNMes) to the complexes **2**–**5** suggesting that the strong σ-donation from the cyclometallated 2-phenylpyridine increases electron density around metal center subsequently limiting the electron donation from the isocyanide.

Integration of the signals in ^{1}H NMR spectra for complexes **2** and **3** indicates a 2:1 ratio between ppy and CNR ligands, whereas spectra for complex **5** support a 1:1 ratio. ^{1}H NMR spectra of **5** show a single set of resonances for the ppy and CNMes ligands indicating $C2$ symmetry. For **4** and **5**, all of the ^{1}H and ^{13}C{^{1}H} NMR signals were assigned with the help of 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/HSQC, and ^{1}H,^{13}C-HMBC) NMR correlation experiments.

X-ray Structure determinations. Crystals of **2**·CH_2Cl_2, **3**·CH_2Cl_2 and **5** were obtained upon slow evaporation of solution this complexes in CH_2Cl_2 in air at RT. Single-crystal X-ray diffraction experiments were carried out on the Agilent Technologies Excalibur Eos (for **5**) and SuperNova (for **2**cʒCH_2Cl_2**,** **3**cʒCH_2Cl_2) diffractometers with monochromated MoKα or CuKα radiation, respectively. The crystals were kept at 100 K during data collection. The structures have been solved by the direct methods and refined by means of the SHELX program[6] incorporated in the OLEX2 program package[7]. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation, with Uiso(H) set to 1.5Ueq(C) and C–H 0.98 Å for the CH3 groups and Uiso(H) set to 1.2Ueq(C) and C–H 0.95 Å for the CH groups. Empirical absorption correction was applied in CrysAlisPro program complex[8] using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The crystallographic details and some parameters of refinement are summarized in **Table S1**. The plots for the structures can be found in **Figures S1** and **S2**, selected bond lengths and angles can be found in **Table S2**. CCDC numbers 1508596 (**2cʒCH_2Cl_2**), 1505628 (**3cʒCH_2Cl_2**), and 1505626 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement details for **2**·CH_2Cl_2, **3**·CH_2Cl_2 and **5**.

	2·CH_2Cl_2	**3·CH_2Cl_2**	**5**
Empirical formula	$C_{32}H_{27}Cl_3IrN_3$	$C_{33}H_{29}Cl_3IrN_3$	$C_{43}H_{38}F_3IrN_4O_3S$
Formula weight	752.12	766.14	940.03
Temperature/K	100.01(10)	100.01(10)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	16.7446(4)	17.0427(6)	9.7977(2)
b/Å	8.57762(18)	8.6872(3)	32.2237(6)
c/Å	21.5557(5)	21.3383(6)	12.8805(3)
α/°	90.00	90	90
β/°	112.277(3)	109.838(4)	110.070(3)
γ/°	90.00	90	90
Volume/$Å^3$	2864.94(12)	2971.72(17)	3819.62(17)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.744	1.712	1.635
μ/mm^{-1}	11.802	11.391	3.611
F(000)	1472.0	1504.0	1872.0
Crystal size/mm^3	0.16 × 0.12 × 0.08	0.24 × 0.16 × 0.12	0.15 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.5418)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.74 to 144.96	5.77 to 139.99	5.056 to 54.998
Index ranges	$-20 \leq h \leq 20$, $-10 \leq k \leq 10$, $-26 \leq l \leq 25$	$-20 \leq h \leq 16$, $-10 \leq k \leq 10$, $-25 \leq l \leq 26$	$-9 \leq h \leq 12$, $-41 \leq k \leq 41$, $-16 \leq l \leq 16$
Reflections collected	37122	13389	39877
Independent reflections	5634 [R_{int} = 0.0750, R_{sigma} = 0.0459]	5467 [R_{int} = 0.0505, R_{sigma} = 0.0570]	8774 [R_{int} = 0.0484, R_{sigma} = 0.0412]
Data/restraints/parameters	5634/0/354	5467/0/364	8774/0/502
Goodness-of-fit on F^2	1.096	1.070	1.124
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.1049	R_1 = 0.0334, wR_2 = 0.0738	R_1 = 0.0328, wR_2 = 0.0634
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.1114	R_1 = 0.0470, wR_2 = 0.0840	R_1 = 0.0394, wR_2 = 0.0660
Largest diff. peak/hole/e $Å^{-3}$	2.31/-1.42	1.20/-1.08	1.79/-1.99

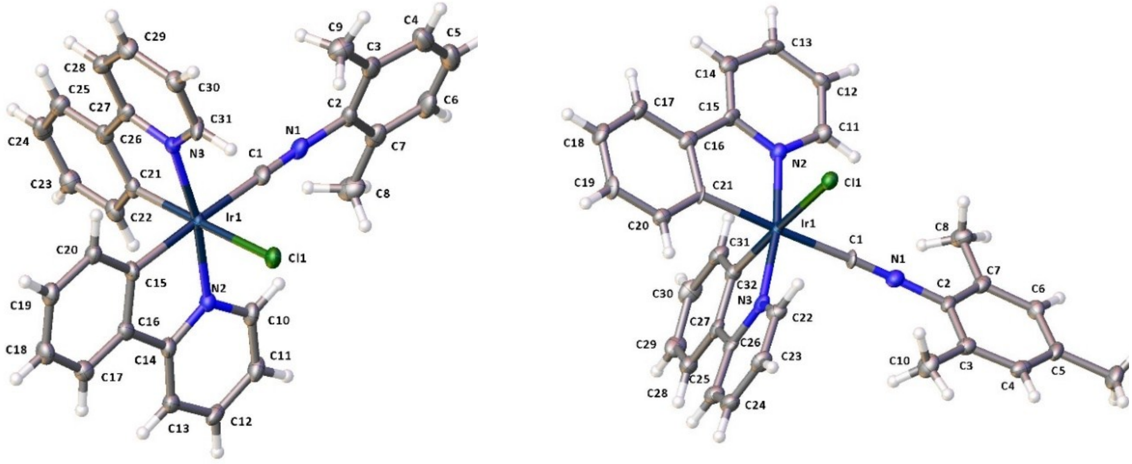


Figure S1. View of **2** (Left) and **3** (right). Thermal ellipsoids are drawn with the 50% probability level. Hydrogen labels and solvate molecules are omitted for simplicity.

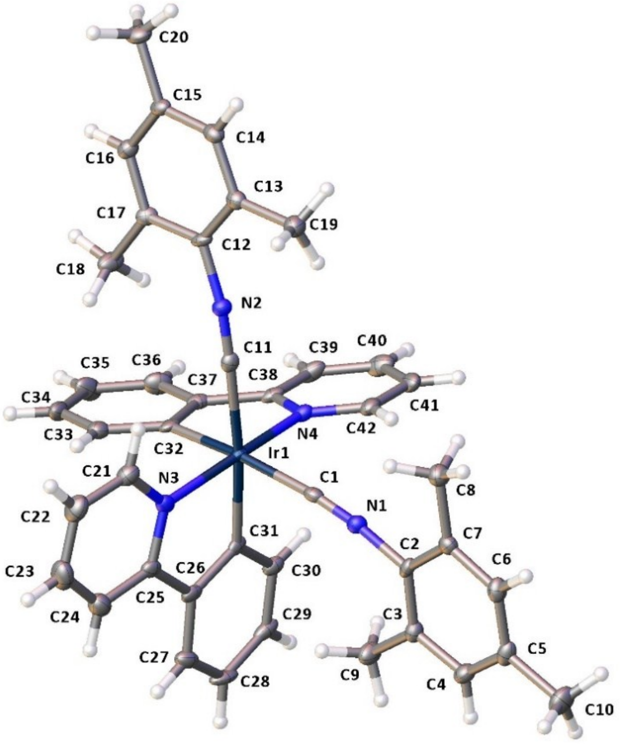


Figure S2. View of **5**. Thermal ellipsoids are drawn with the 50% probability level. Hydrogen labels and counteranion are omitted for simplicity.

Table S2. Selected bond lengths [Å] and angles [°] for **2**·CH_2Cl_2, **3**·CH_2Cl_2 and **5**.

	2·CH_2Cl_2	**3**·CH_2Cl_2	**5**
Bond lengths, Å			
Ir–$C_{isocyanide}$	1.999(6)	1.991(5)	2.023(4)
			2.025(4)
C≡N	1.146(8)	1.168(7)	1.157(4)
			1.152(4)
N−R	1.406(7)	1.392(7)	1.406(4)
			1.408(4)
Ir−C_{ppy}	2.049(5)	2.050(5)	2.051(3)
	2.027(5)	2.034(5)	2.053(4)
Ir−N_{ppy}	2.051(5)	2.050(4)	2.059(3)
	2.056(4)	2.051(5)	2.061(3)
Angles, °			
Ir−C≡N	178.4(5)	177.1(5)	171.0(3)
			172.9(3)
C≡N−R	173.5(6)	171.7(6)	171.9(4)
			167.3(4)

In all complexes, the iridium(III) center adopts a distorted octahedral coordination environment, and the two nitrogen atoms of the phenylpyridine ligands are in *trans*-position to each other. The Ir−C bonds with the isocyanides (1.991−2.025 Å) are shorter than are those with the phenylpyridine ligands (2.027−2.053 Å). The Ir−isocyanide fragments are not linear, and the angles are 171.0(3)−178.4(5)° for Ir−C≡N or 167.3(4)−173.5(6)° for C≡N−R. The Ir–$C_{isocyanide}$ bond distanced and angles measured here are similar to the reported Ir−C bond lengths of *tert*-butyl isocyanides (2.012−2.031 Å) and aryl isocyanide (1.982−2.027 Å) complexes.[5]

Catalytic cross-linking of polysiloxanes

The cross-linking was studied in a system consisting of PDMS and EHDMS as cross-linking partners and catalyst, viz. any of one **1**–**6** or Karstedt's catalyst taken for comparison, at RT or at 80 °C. A ratio [$–CH=CH_2$]:[$\equiv$Si–H] is 1:3. The standard formulation had [part A]:[part B] = 1:1 ratio; concentration of **1–6** was $1.0 \times 10^{-3} – 1.0 \times 10^{-5}$ mol•L^{-1}. [Part A]: calculated amounts of **1–6** (diluted in CH_2Cl_2) were added to PDMS, the mixture was carefully stirred and dried under vacuum at 30 °C overnight to remove the solvent. Karstedt's catalyst dissolved in vinyl-terminated polydimethylsiloxane was added to PDMS without drying in a vacuum. [Part B]: EHDMS (10 g) was added to PDMS (50 g) and this mixture was carefully stirred for homogenization.

The cross-linking process of the polysiloxanes mixture was performed in an aluminum vessel. The curing time was measured from the point of mixing equal amounts of Parts A and B at RT or from the moment of placing the aluminum vessel with equal amounts of Parts A and B mixture to a desiccator at required temperature until liquid reaction mixture getting dry cured material.

Table S3. Parameters of the catalytic cross-linking of PDMS and EHDMS.

Catalyst	$C_{catalyst}$, M	τ_{curing} at 80 °C, h	τ_{curing} at 100 °C, h	τ_{curing} at 125 °C, h	τ_{curing} at 150 °C, min	τ_{curing} at 180 °C, min
1	1.0×10^{-3}	24 (without curing)	19	3	50	15
	1.0×10^{-4}	24 (without curing)	24 (without curing)	5	100	45
	1.0×10^{-5}	24 (without curing)	24 (without curing)	6.5	130	95
2	1.0×10^{-3}	25	4	35 min	20	10
	1.0×10^{-4}	24 (without curing)	6	1 h 10 min	50	15
	1.0×10^{-5}	24 (without curing)	12	2.5	70	30
3	1.0×10^{-3}	18	3	30 min	15	10
	1.0×10^{-4}	24 (without curing)	5	1 h 10 min	45	15
	1.0×10^{-5}	24 (without curing)	11	1 h 50 min	70	30
4	1.0×10^{-3}	24 (without curing)	34 (without curing)	3.5	75	15
	1.0×10^{-4}	24 (without curing)	34 (without curing)	5	107	20
	1.0×10^{-5}	24 (without curing)	34 (without curing)	7.5	137	45
5	1.0×10^{-3}	24 (without curing)	34 (without curing)	10	147	25
	1.0×10^{-4}	24 (without curing)	34 (without curing)	10.5	147	30
	1.0×10^{-5}	24 (without curing)	34 (without curing)	11	167	50
6	1.0×10^{-3}	24 (without curing)	34 (without curing)	4.5	20	5
	1.0×10^{-4}	24 (without curing)	34 (without curing)	6.5	45	5
	1.0×10^{-5}	24 (without curing)	34 (without curing)	17	240	25

DSC curves for curing process

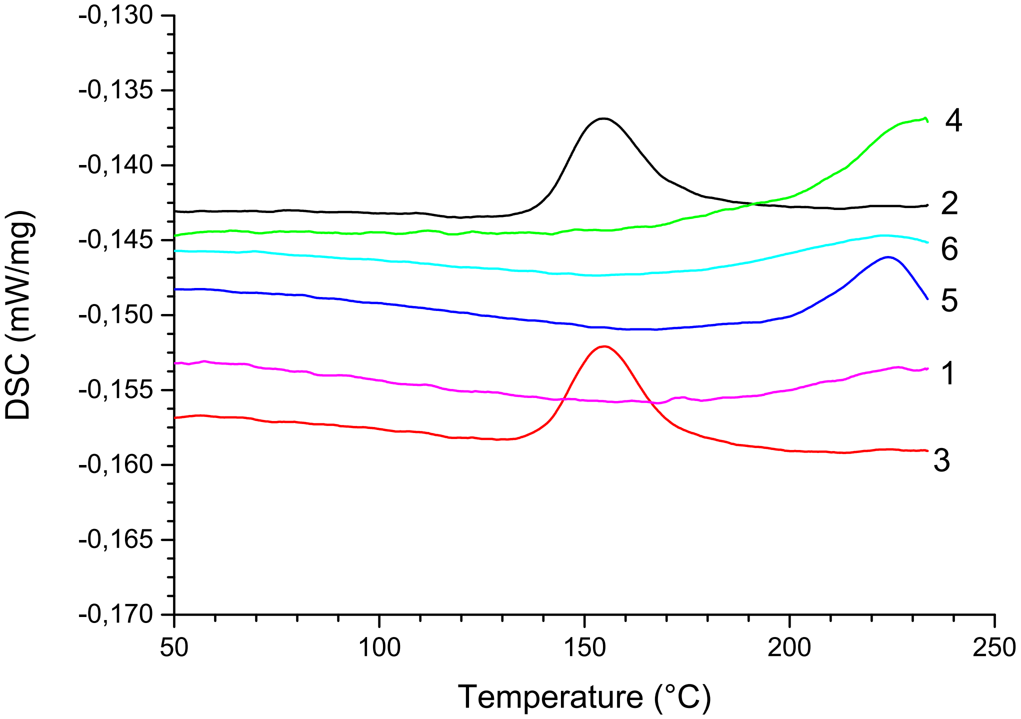


Figure S3. DSC curves of the cross-linking catalyzed by catalysts **1**–**6** ($C_{catalyst}$ = 1.0 × 10^{-4} mol•L^{-1}).

Thermogravimetric study of obtained rubbers

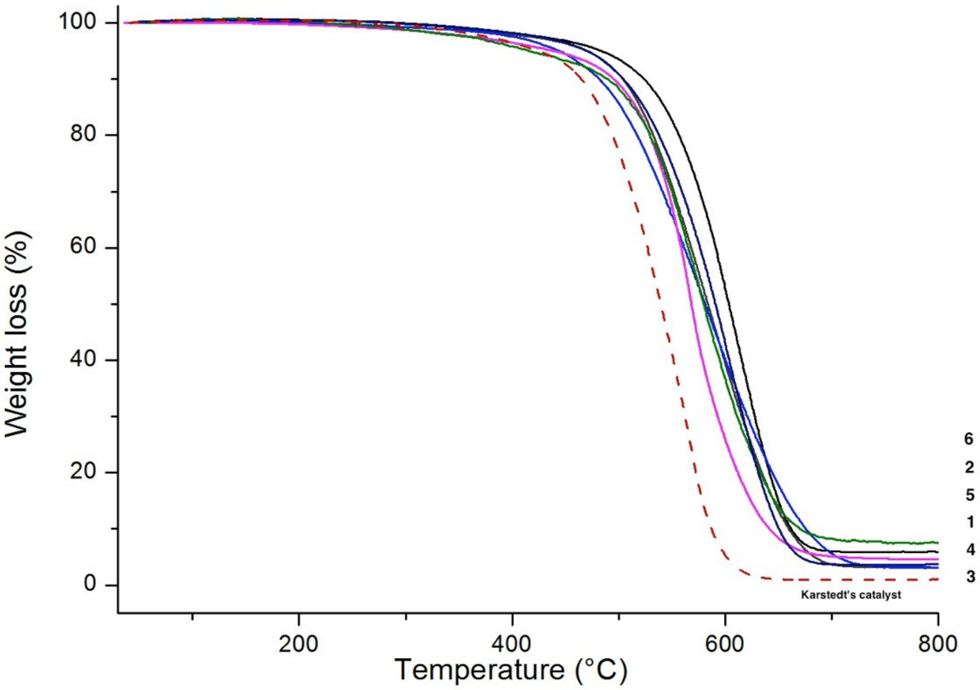


Figure S4. Effect of the nature of iridium catalyst on the thermal degradation of the PDMS–EHDMS silicone rubber in argon (cross-linking at 150 °C; $C_{catalyst} = 1.0 \times 10^{-5}$ M).

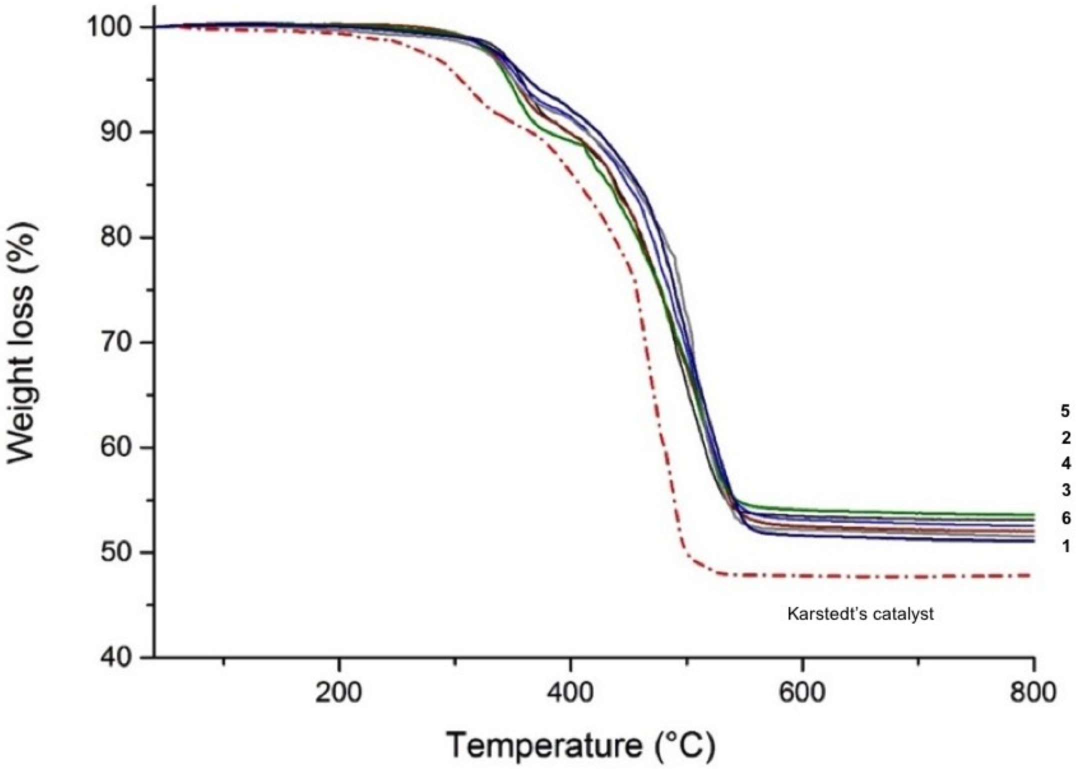


Figure S5. Effect of the nature of iridium catalyst on the thermal degradation of the PDMS–EHDMS silicone rubber in air (cross-linking at 150 °C; $C_{catalyst} = 1.0 \times 10^{-5}$ M).

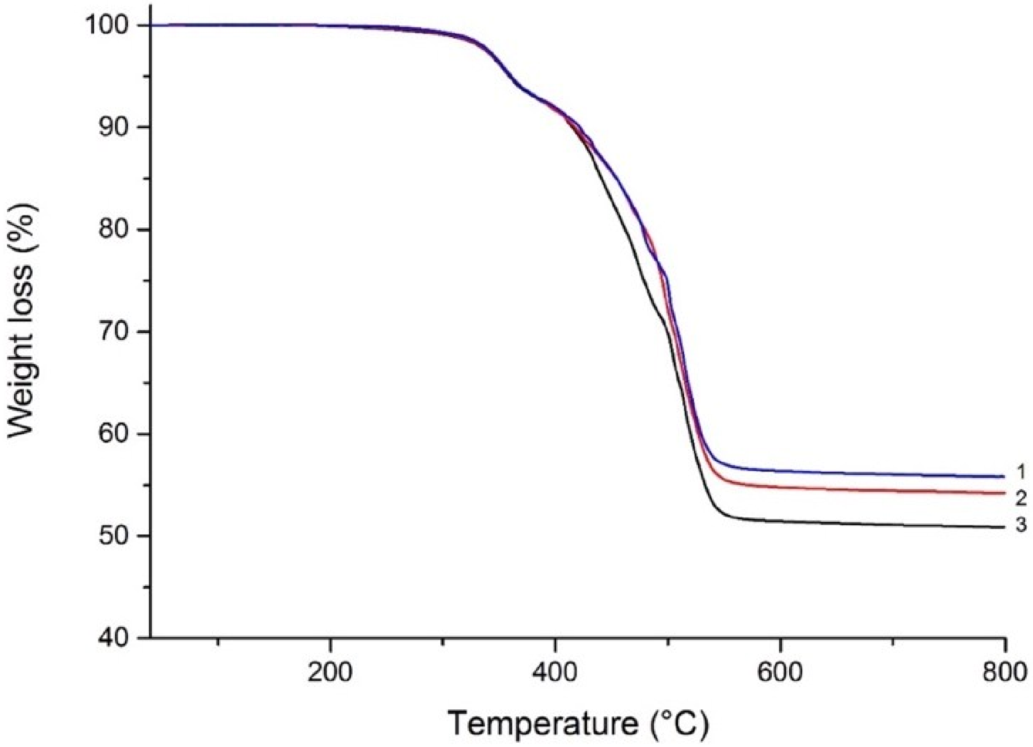


Figure S6. Effect of the cross-linking temperature on the thermal degradation of the PDMS–EHDMS silicone rubber in air (**3**; $C_{catalyst} = 1.0 \times 10^{-4}$ M). On the Figure, 1 – cross-linking at 180 °C; 2 – cross-linking at 150 °C; 3 – cross-linking at 125 °C.

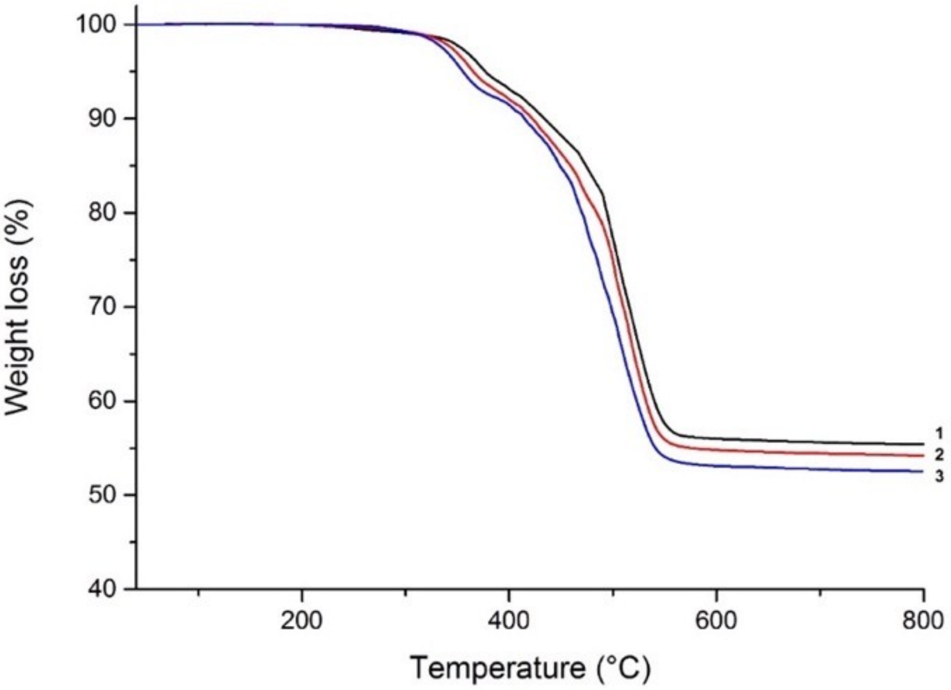


Figure S7. Effect of the concentration of iridium catalyst **3** on the thermal degradation of the PDMS–EHDMS silicone rubber in air (cross-linking at 150 °C). On the Figure: 1 – 1.0 × 10^{-3} M; 2 – 1.0 × 10^{-4} M; 3 – 1.0 × 10^{-5} M.

Table S4. Influence of concentration of **3** and cross-linking temperature on thermal stability of silicone rubber in air.

Cross-linking temperature, °C	$C_{catalyst}$, M	$T_{1\%}$, °C	$T_{5\%}$, °C	$T_{10\%}$, °C	Final residue, %
150	1.0 × 10^{-3}	310	360	420	54
	1.0 × 10^{-4}	305	355	415	53
	1.0 × 10^{-5}	300	330	390	52
180	1.0 × 10^{-4}	315	360	425	56
125	1.0 × 10^{-4}	305	360	415	51

Swelling and tensile measurements. For tensile tests, we used most active catalysts **2**, **3** and least active **5**. Silicone rubber strips were stretched until break. Elastic properties of our silicone rubbers have similar elongation at break (L) and tensile strength (σ) compared with the rubbers obtained with Karstedt's catalyst. The σ value is 2 MPa, L is 188% and 175%, Δl is 10% in the presence of **3** and **5** (1.0×10^{-4} M), respectively. In case of $[PtCl_2(PhCH_2CN)_2]$ and Karstedt's catalyst elongation at break is 235% and 170% and tensile strength is 0.25 MPa and 0.22 MPa, respectively.

For swelling measurements, a representative sample of silicone rubber prepared (0.1 g, cylindrical disk of 10 mm diameter and 1 mm thickness) was weighted for evaluating the initial dry weight (m_{unex}), swollen for one day, and then plunged in toluene (50 mL) in a sealed bottle for 2 h in the dark. A sample was then extracted, gently wiped to remove liquid solvent present on the sample surface and immediately weighted (m_s). After that, a sample was then dried overnight at RT and then at 60 °C for 2 h in *vacuo* and weighted again (m_{ex}). Soluble fraction (w_{sol}) and volume fraction of polymer in the swollen sample (υ) are calculated as follows:

$$w_{sol}(\%) = \frac{m_{unex} - m_{ex}}{m_{unex}} \times 100$$

$$v = \left[1 + \frac{m_s - m_{ex}}{m_{ex}} \times \frac{\rho_p}{\rho_s}\right]^{-1}$$

where ρ_s and ρ_p are the solvent (toluene, 0.865 g/cm^3) and polymer (PDMS, 0.965 g/cm^3) densities, respectively. Swelling experiments were carried out five times for each test.

Silicone compositions obtained with 100 poise PDMS using representative catalysts **2** and **3** (1.0×10^{-5} M) had w_{sol} of 13.3% (for **2**) and 10.7 (for **3**), and υ of 0.2 (for both). Silicone compositions obtained with catalyst **5**, possess higher w_{sol} 2.7% and υ 0.2

Photophysical studies

Table S5. Luminescent properties of iridium complexes in CH_2Cl_2 solutions. The emission spectra of complexes were recorded at λ_{exc} = 350 nm.

Sample	λ_{abs}, nm	λ_{lum}, nm	τ, μs	Φ, %
2	255,312, 348	470, 502, 530	1.5	43
3	254, 311 (sh), 344	472, 502, 535 (sh)	1.6	41
4[5]	251, 259, 305 (sh), 375	453, 484, 510, 553 (sh)	1.8	24
5	258, 302 (sh), 372	453, 484, 513, 554 (sh)	1.8	23
6[3]	244, 283, 341, 377, 405, 455, 488	510	1.9	40

Table S6. Luminescent properties of silicone rubbers obtained with iridium catalysts ($C_{catalyst}$ = 1.0×10^{-4} M). The emission spectra of complexes were recorded at λ_{exc} = 350 nm.

Sample	λ_{lum}, nm	τ, μs
2	407	0.0056(7)
3	417, 436 (sh)	0.0080(7)
5	417	0.0073(3)

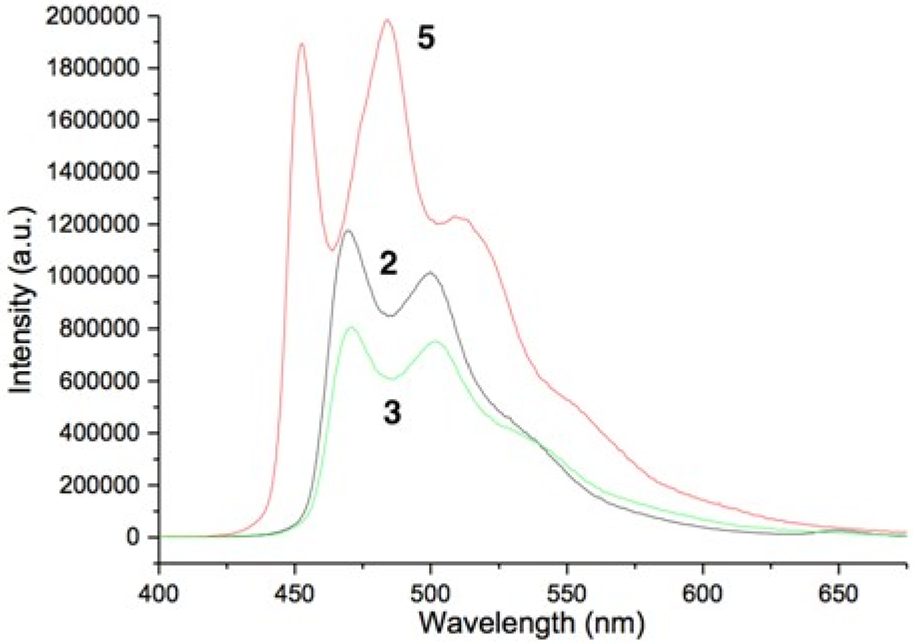


Figure S8. Emission spectra for **2**, **3**, and **5** in CH_2Cl_2 solutions (1.0×10^{-4} M).

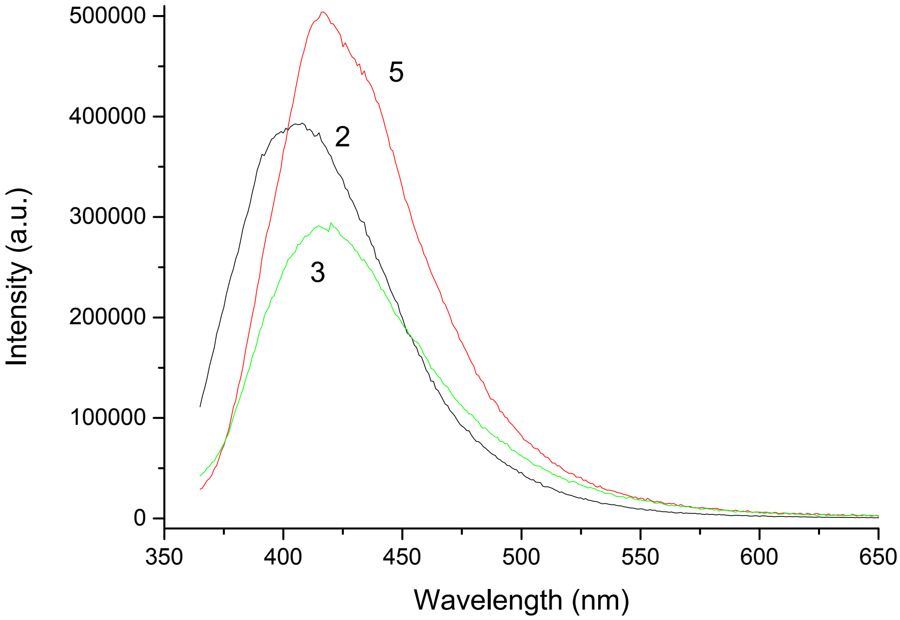


Figure S9. Emission spectra for silicone rubbers (initial concentration of catalyst was 1.0×10^{-4} M).

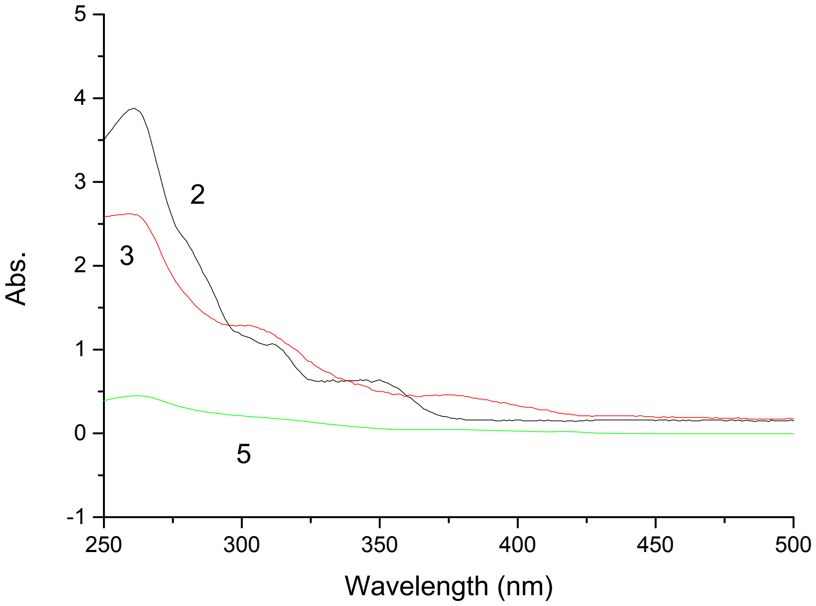


Figure S10. Absorption spectra for CH_2Cl_2 solutions of **2**, **3** and **5** (1.0×10^{-5} M).

Preparation of thin films of silicone composition. Quartz glass was covered with thin layer of cross-linking mixture and then heated to 150 °C for 20 minutes. After that, the thickness of obtained film was measured using bore micrometer and subjected to luminescence measurements. To increase thickness additional layers were deposited consequently on the same glass.

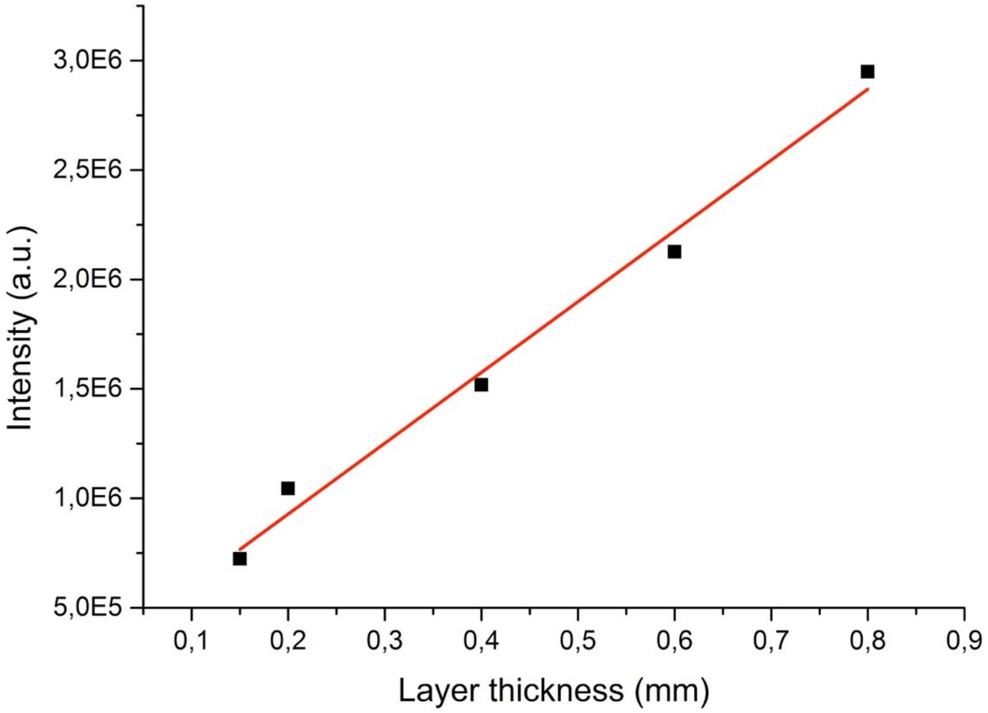


Figure S11. Plot of emission at 408 nm as a function of film thickness for a silicone composition obtained with **3** (1.0×10^{-5} M); linear fitting is used (Pearson correlation coefficient was 0.99457).

^{1}H and ^{13}C{^{1}H} NMR spectra for complexes 2–5

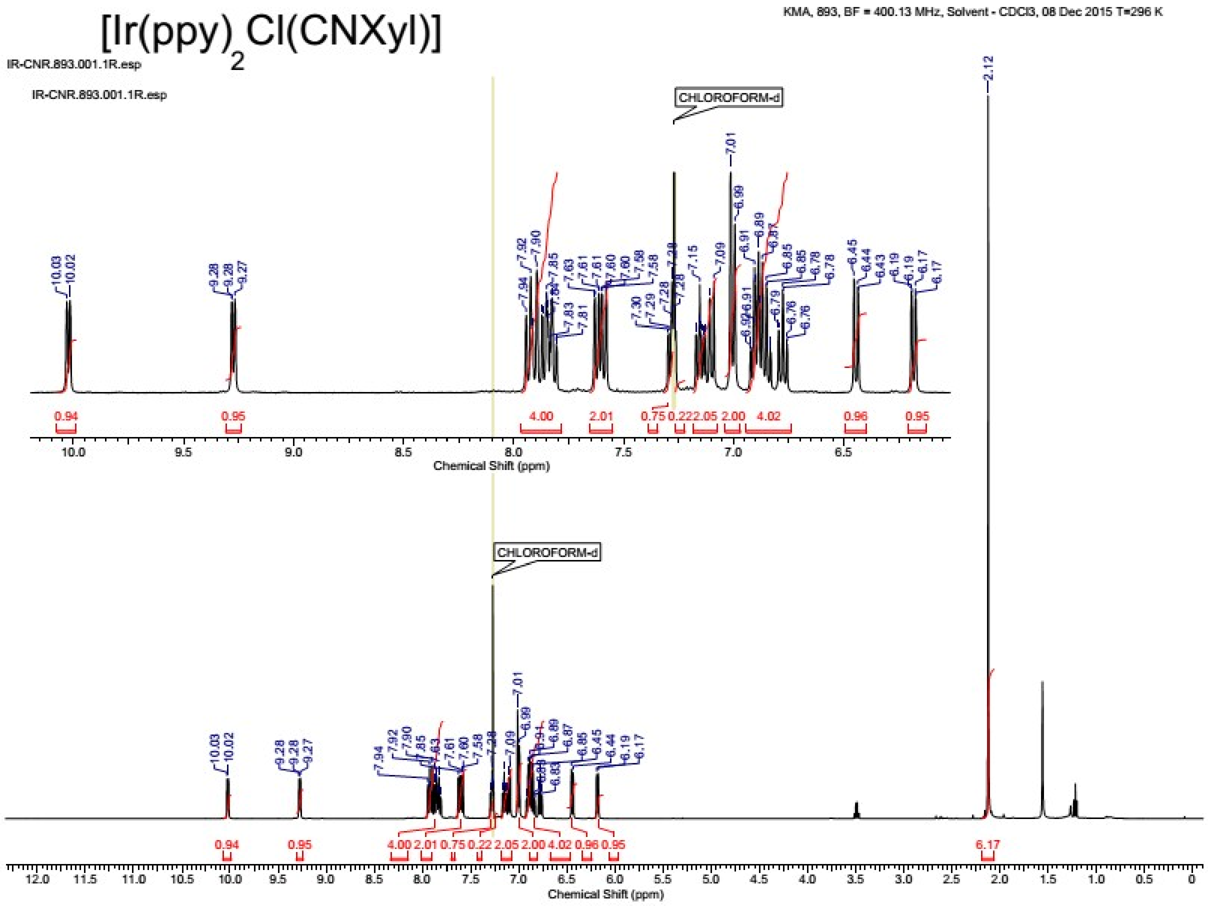


Figure S12. ^{1}H NMR spectra of **2.**

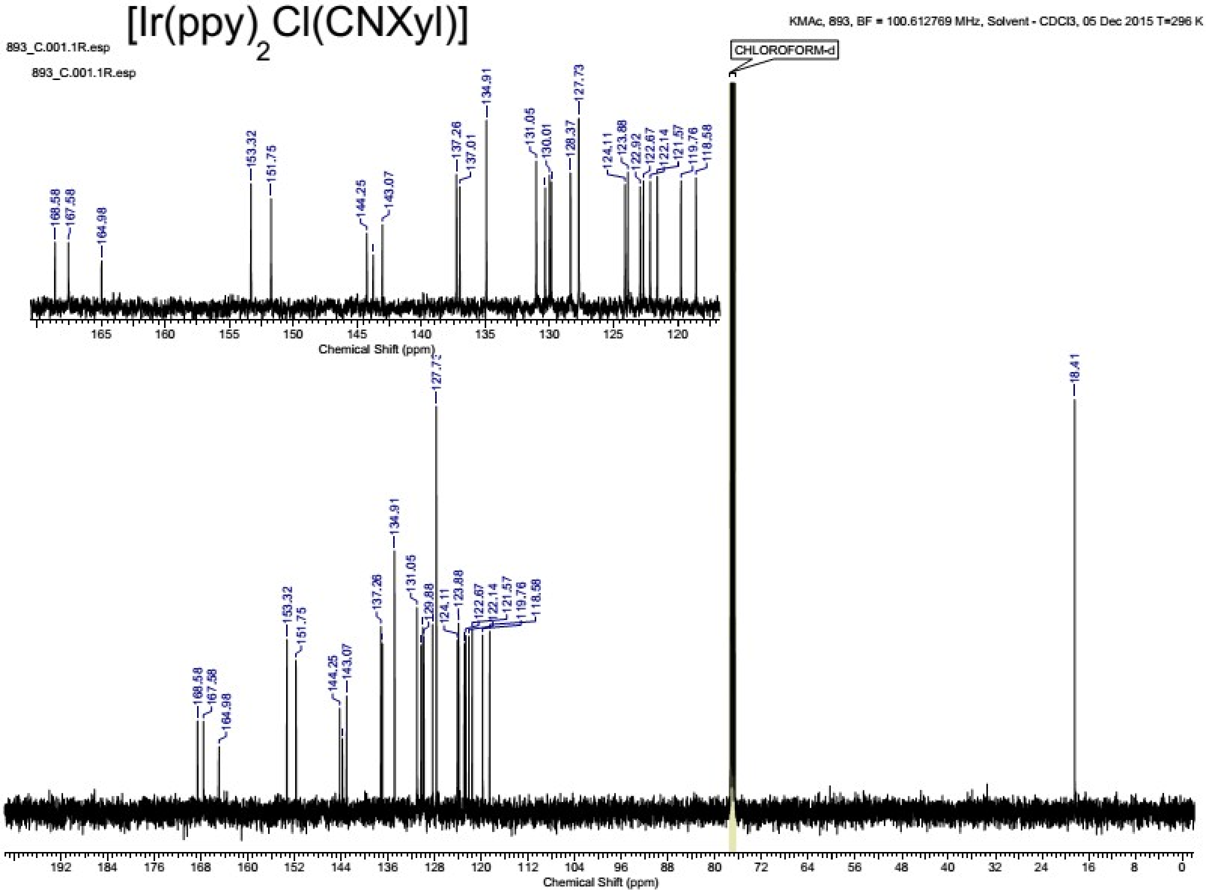


Figure S13. $^{13}C\{^{1}H\}$ NMR spectra of **2**.

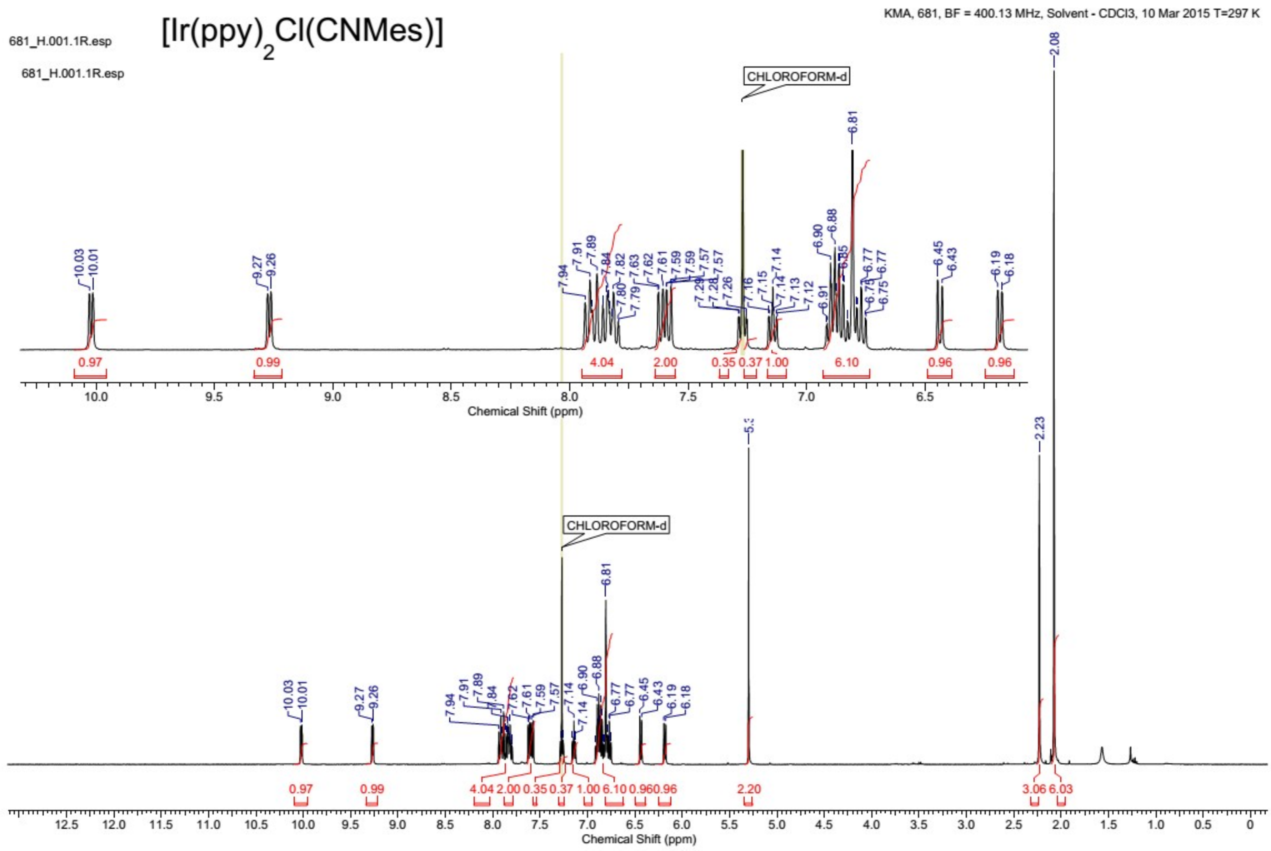


Figure S14. ^{1}H NMR spectra of **3**•CH$_2$Cl$_2$**.**

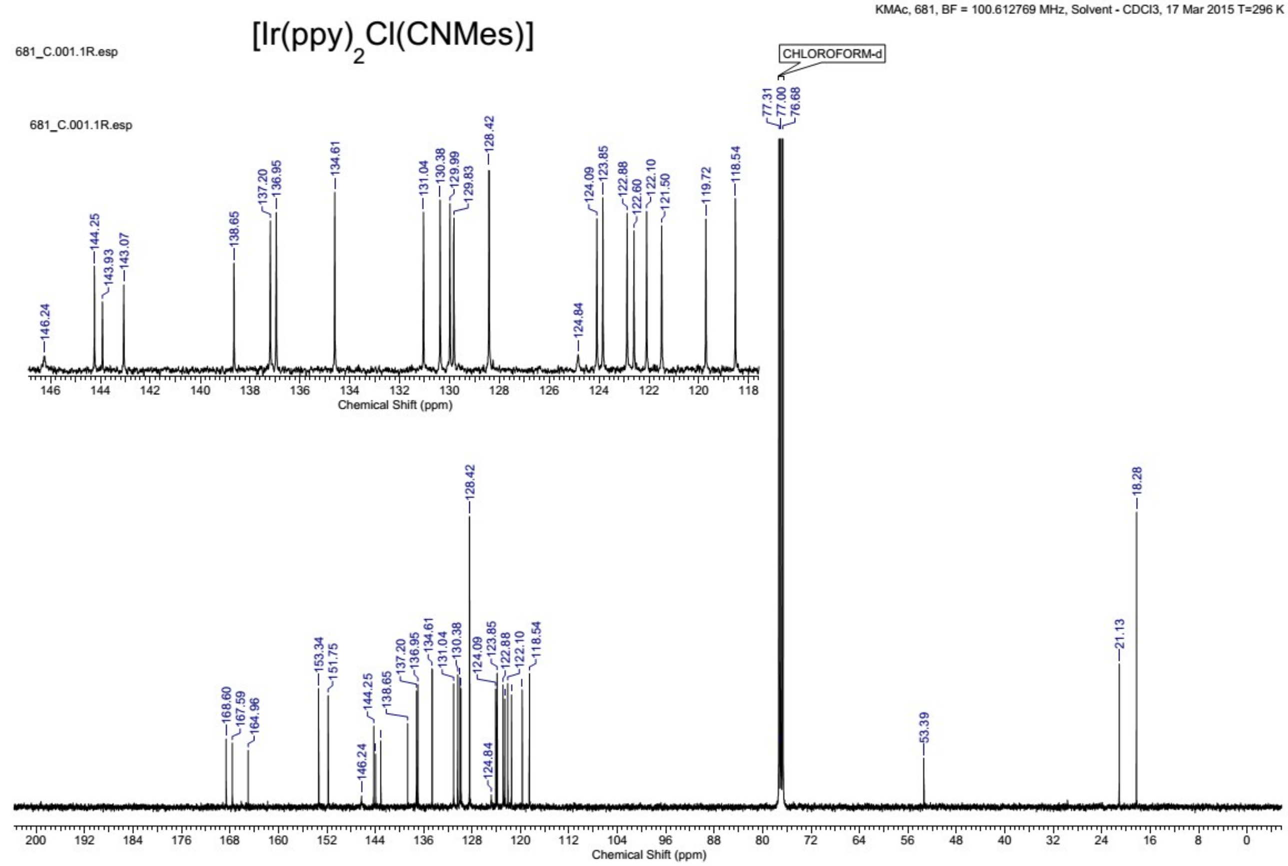


Figure S15. $^{13}C\{^{1}H\}$ NMR spectra of **3**•CH_2Cl_2.

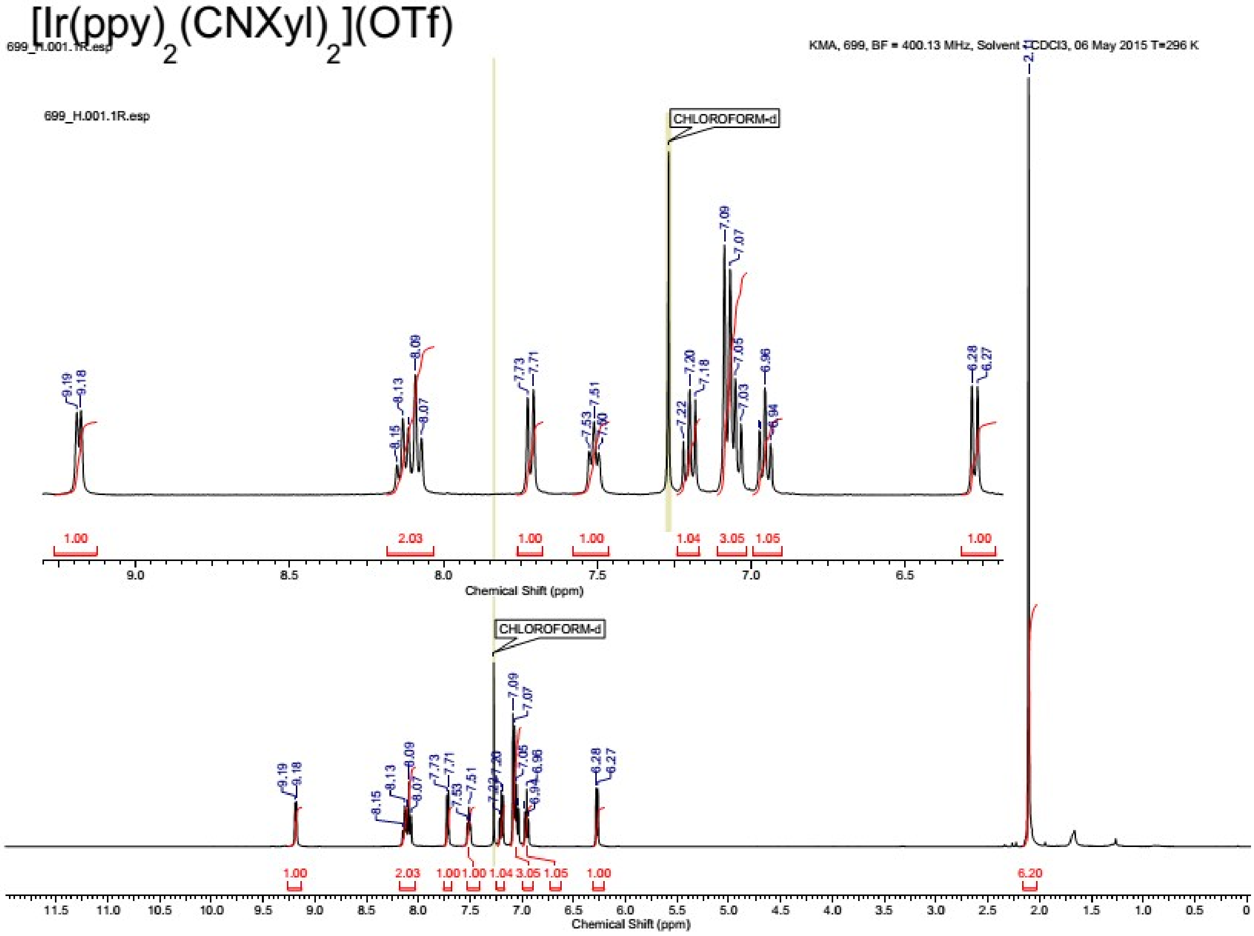


Figure S16. ^{1}H NMR spectra of **4.**

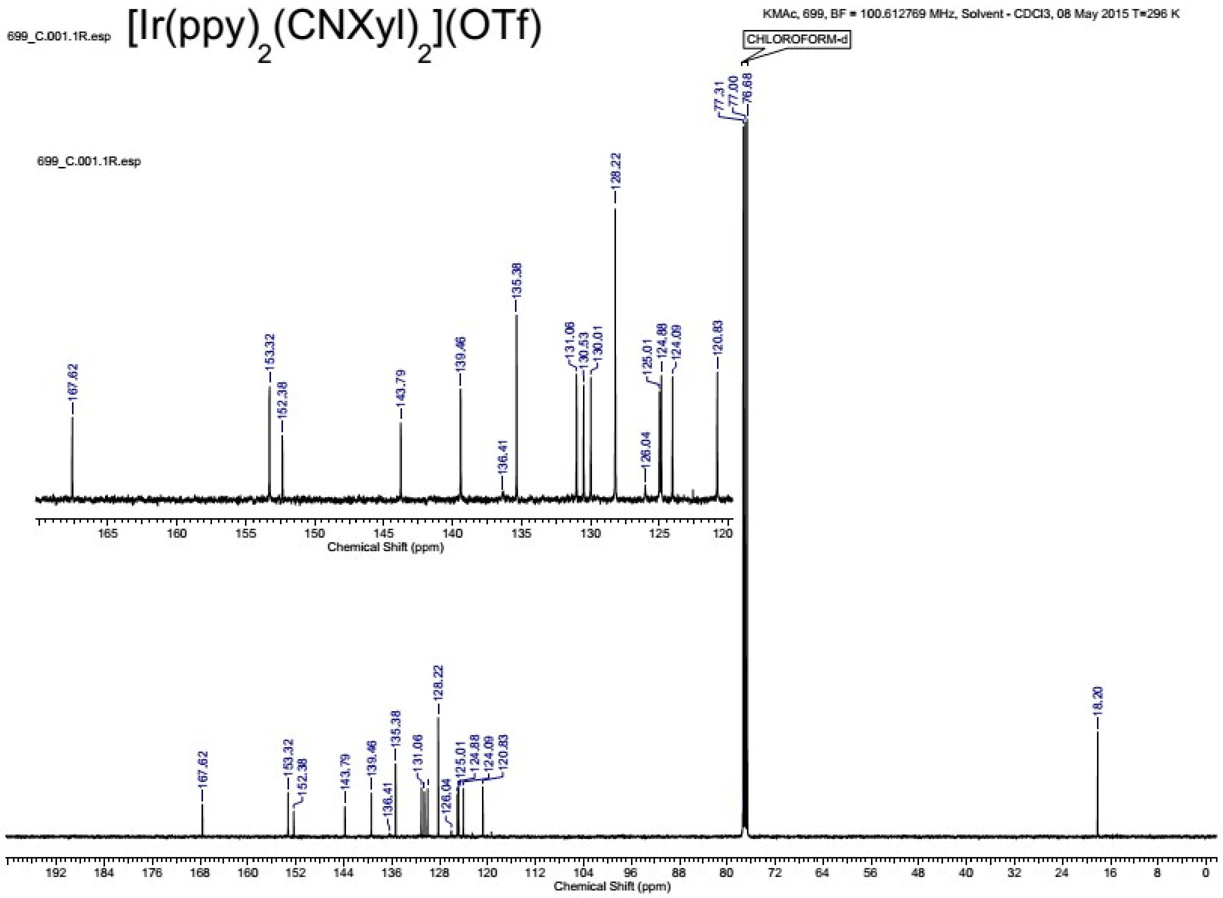


Figure S17. $^{13}C\{^1H\}$ NMR spectra of **4**.

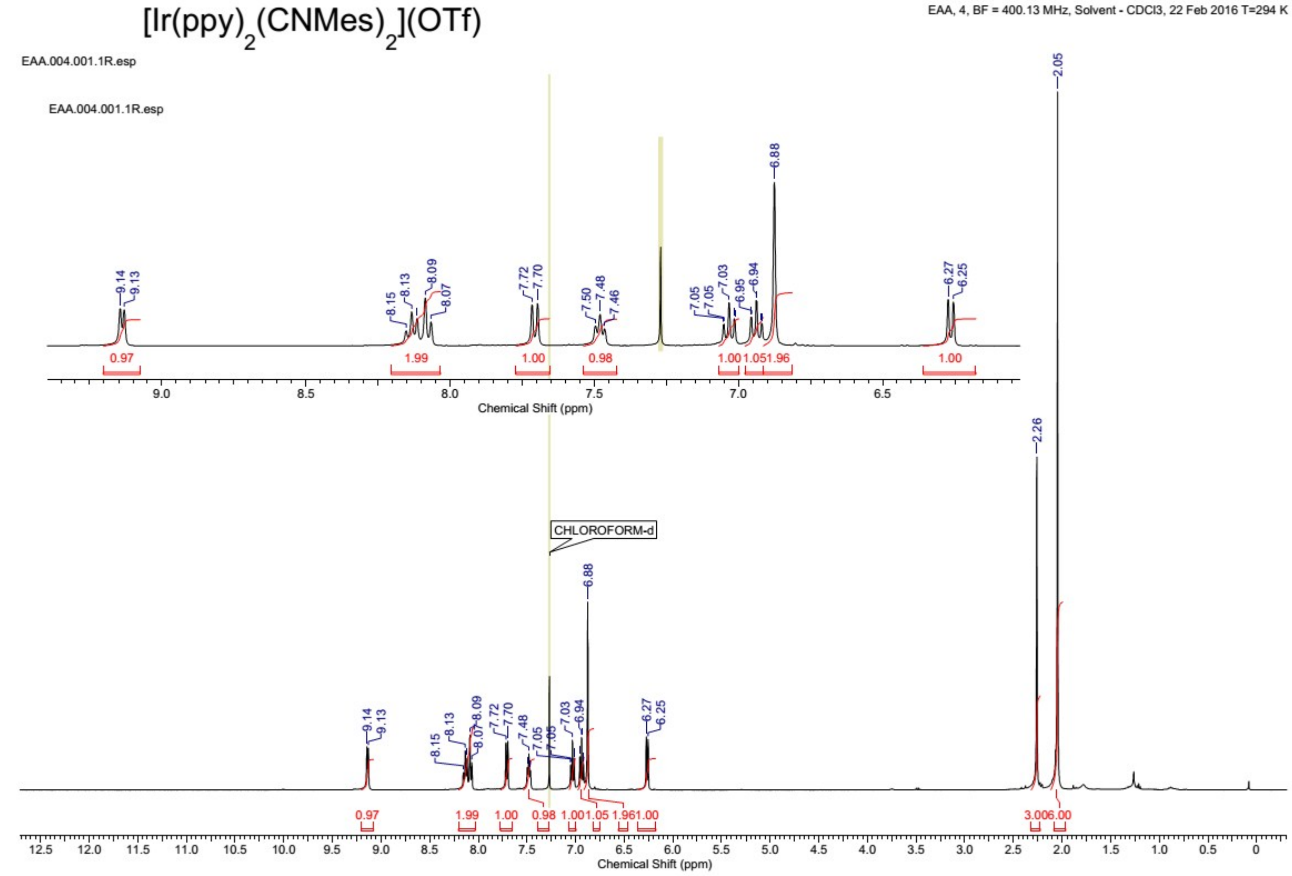


Figure S18. ^{1}H NMR spectra of **5.**

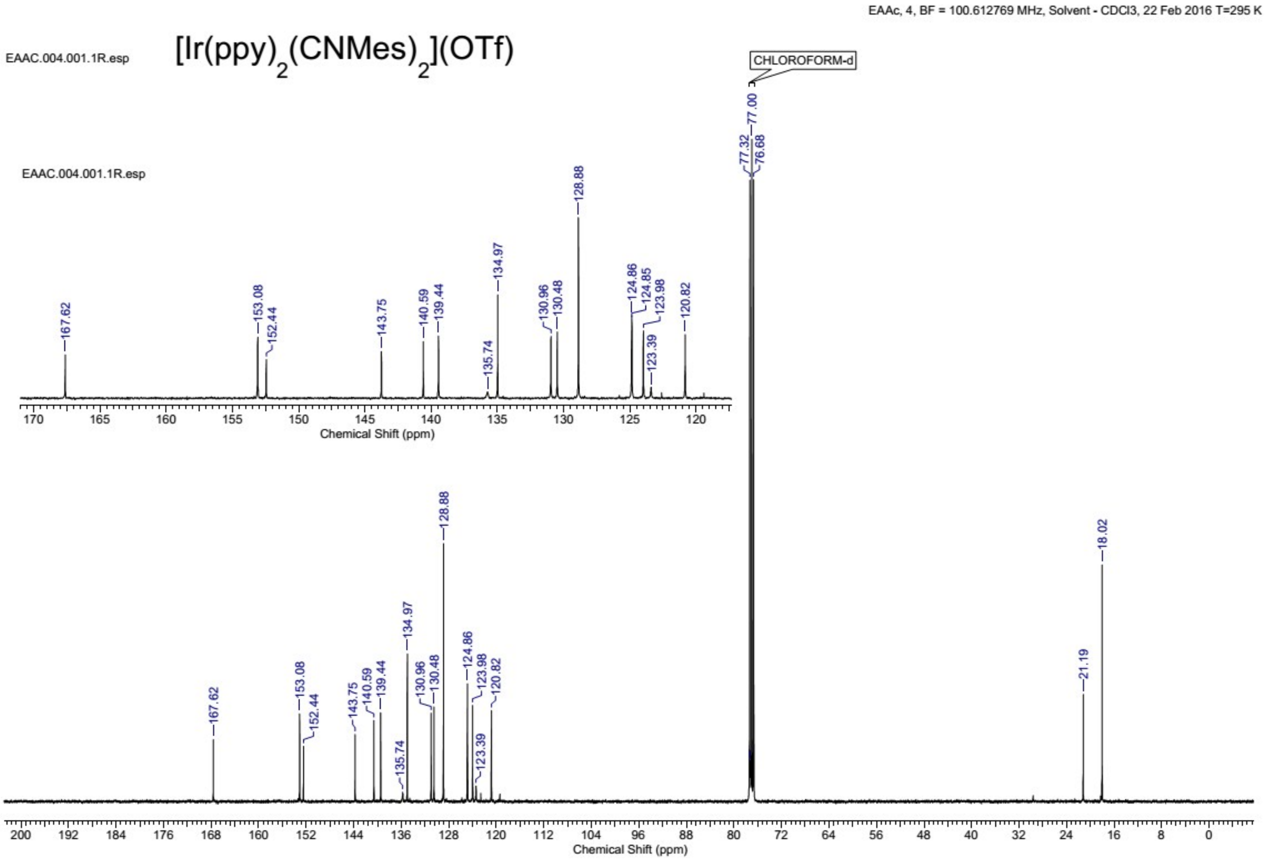


Figure S19. $^{13}C\{^{1}H\}$ NMR spectra of **5**.

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