Electronic Supplementary Material (ESI) for Dalton Transactions.

Simple and Reactive Ir(I) N-Heterocyclic Carbene Complexes for Alkyne Activation

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1. Experimental Section

1.1 General Considerations

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk or vacuum techniques,[1] or in a nitrogen-filled or argon-filled LC glove box. Reagents were purchased from Aldrich Chemical Co. Inc. or Alfa Aesar Inc. and were used as received. The metal halide salt and $IrCl_3.xH_2O$, was purchased from Precious Metals Online PMO P/L and was used without further purification. The metal precursors, $[Pd(PPh_3)_4]$,[2] $[Ir(COD)(\mu\text{-}Cl)]_2$,[3] and $NaBAr^F{}_4$,[4] were synthesised according to literature methods. The substrates 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**16a**), 2-(4-hydroxybut-1-ynyl)benzyl alcohol (**17a**),[5] 4-pentyn-1-amine (**20a**) and 5-phenyl-4-pentyn-1-amine (**21a**)[6] were synthesized following literature procedures. The products formed during the catalysed dihydroalkoxylation (**16b/c**, **17b**, **18b** and **19b**)[5, 7] and the hydroamination (**20b**, **21b** and **22b**)[6a, 8] were confirmed by comparing the ^1H NMR data with literature data. 1-phenyl-1*H*-imidazole was prepared using a modified procedure to that reported in the literature (CuI and DMF were used in place of Cu_2O and DMSO)[9], 1-(2,4,6-trimethylphenyl)1*H*-imidazole was prepared according to a previously published method.[10]. For the purposes of air sensitive manipulations and in the preparation of metal complexes, solvents were dried and distilled under an atmosphere of nitrogen or argon using standard procedures[11] and stored under nitrogen or argon in glass ampoules, each fitted with a Youngs Teflon valve prior to use. Tetrahydrofuran (THF), diethyl ether, *n*-hexane, DCM, acetonitrile and toluene were dried via LC-Technologies Solvent Purification System. Methanol (MeOH) and ethanol (EtOH) were distilled from dimethoxymagnesium and diethoxymagnesium respectively. The bulk compressed gases argon (>99.997%), nitrogen (>99.99%) and carbon monoxide (>99.5%) were obtained from BOC Australia and used as received. Nitrogen gas for Schlenk line operation came from compressed gas supplied by BOC Australia. ^1H, ^2D and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance III 300, 400, 500, and 600 spectrometers operating at 300, 400, 500, and 600 MHz (^1H), respectively, and 75, 100, 125, and 150 MHz (^{13}C), respectively. Unless otherwise stated, spectra were recorded at 25 °C and chemical shifts (δ) are quoted in ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ±0.05 Hz for ^1H and ^2D and ±0.5 Hz for ^{13}C. ^1H, ^2D and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. Air-sensitive NMR samples were prepared in an inert-gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young Teflon valve.

Infrared spectra were measured using a Nicolet 380 Avatar FTIR spectrometer as solutions in dichloromethane. Microanalyses were carried out at the Microanalytical Unit, Research School of Chemistry, Australian National University, Canberra, Australia or Macquarie University Centre for Analytical Biotechnology (MUCAB). Mass spectra were acquired using a Micromass ZQ mass spectrometer (ESI-MS). M is defined as the molecular weight of the compound of interest or cationic fragment for cationic metal complexes.

Single crystal X-ray analyses were carried out at the Mark Wainwright Analytical Centre, University of New South Wales, Sydney. Crystals were selected under the polarizing microscope (Leica M165Z), was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K using IμS Incoatec Microfocus Source with Mo-Kα radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using a cryo loop for intensity measurements, was coated with immersion oil type NVH and then quickly transferred to the cold nitrogen stream generated by an Oxford Cryostream 700 series. Symmetry related absorption corrections using the program SADABS.[12] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software.[12] The structure was solved by program SHELXT[13] (with intrinsic phasing) and the full-matrix least-square refinements were carried out using SHELXL-2018/3[14] for **5** and SHELXL-2014/7[14] for **9** through Olex2[15] suit of software. The non-hydrogen atoms were refined anisotropically.

1.2 General Procedure for the dihydroalkoxylation reactions of 16a–19a[12]

The general procedure for the catalysed dihydroalkoxylation reactions of **16a-19a** were undertaken by dissolving the substrate, catalyst (mono- 1.0 mol%, bimetallic – 0.5 mol%) and $NaBAr^F{}_4$ (1.0 mol%) in 1,1,2,2-tetrachloroethane-d_2 in an NMR tube fitted with a Teflon (Youngs) value under an inert atmosphere. The NMR tube was injected in the NMR spectrometer at 100 °C and the reactions were monitored by ^1H

NMR spectroscopy. The conversion (%) was determined by the relative integral ratios of selected ^{1}H resonances of the substrate and product(s). Turn over frequencies (TOF) were calculated at the point of 50% conversion of substrate to product(s).

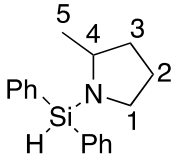
1.3 General Procedure for the hydroamination/hydrosilylation reactions of 20a and 21a

The general procedure for the catalysed hydroamination/hydrosilylation reactions of **20a** and **21a** were undertaken by dissolving the substrate, catalyst (mono- 2.0 mol%, bimetallic – 1.0 mol%) and $NaBAr^F_4$ (2.0 mol%) in toluene-d_8 in an NMR tube fitted with a Teflon (Youngs) value under an inert atmosphere. The NMR tube was injected in the NMR spectrometer at 100 °C and the reactions were monitored by ^{1}H NMR spectroscopy. Upon completion of the hydroamination step (>95% conversion), two molar equivalents of diphenylsilane (Ph_2SiH_2) relative to substrate were added to the mixture and the reaction was again heated to 100 °C in the NMR instrument. The reactions were monitored by ^{1}H NMR spectroscopy and the conversion (%) was determined by the relative integral ratios of selected ^{1}H resonances of the substrate and product(s). Turn over frequencies (TOF) were calculated at the point of 50% conversion of the substrate to product(s).

1.3.1 NMR Characterisation of 20c and 21c

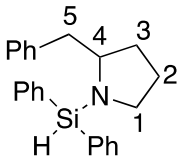
The N-silylamines **20c** and **21c** could not be isolated and purified due to their ability to hydrolyse in air. Therefore the N-silylamines were identified by diagnostic signals in the ^{1}H NMR spectra. **18c** and **19c** were hydrolysed with water, purified and confirmed by comparison of the ^{1}H NMR spectra with literature.[16]

1.3.1.1 Diagnostic signals for 20c



^{1}H NMR (500 MHz, C7D8): δ 7.60 (m, 2H, Ar**H**), 7.17 (m, 3H, Ar**H**), 5.76 (s, 1H, **H**SiPh2), 3.53 (m, 1H, H**4**), (3.04, 1.78, 1.64, 1.54, 1.27 (multiplets, 6H, belonging to H**1-3**)), 1.00 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 3H, H**5**) ppm.

1.3.1.2 Diagnostic signals for 21c

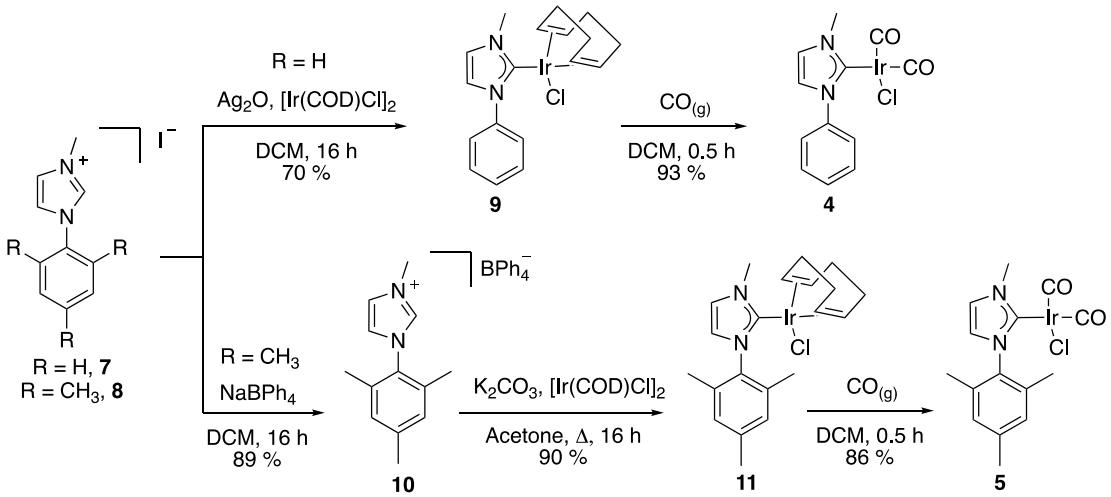


^{1}H NMR (600 MHz, C_7D_8): δ 7.60 (m, 5H, Ar**H**), 7.18 (m, 5H, Ar**H**), 7.02 (m, 2H, Ar**H**), 6.97 (m, Ar**H**), 6.87 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar**H**), 5.48 (1H, **H**SiPh$_2$), 3.69 (m, 1H, H**4**), 3.06 (t, $^3J_{H\text{-}H}$ = 6.2 Hz, 2H, H**1**), 2.79 (dd, $^2J_{H\text{-}H}$ = 13.2 Hz, $^3J_{H\text{-}H}$ = 4.7 Hz, 1H, H**5**), 2.41 (dd, $^2J_{H\text{-}H}$ = 13.2 Hz, $^3J_{H\text{-}H}$ = 9.3 Hz, 1H, H**5**), 1.65-1.49 (m, 4H, H**2** and H**3**) ppm.

1.4 General Procedure for the intermolecular hydroamination reaction of 22a with 22b

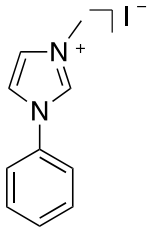
The general procedure for the catalysed intermolecular hydroaminationion reactions of **22a** with **22b** were undertaken by dissolving the substrates **22a** and **22b**, catalyst (mono- 2 mol%, bimetallic – 1 mol%) and $NaBAr^F_4$ (2 mol%) in toluene-d_8 in an NMR tube fitted with a Teflon (Youngs) value under an inert atmosphere. The NMR tube was injected in the NMR spectrometer at 80 °C and the reactions were monitored by ^{1}H NMR spectroscopy. The reactions were monitored by ^{1}H NMR spectroscopy and the conversion (%) was determined by the relative integral ratios of selected ^{1}H resonances of the substrate and product(s). Turn over frequencies (TOF) were calculated at the point of 50% conversion of the substrate to product(s).

2. Ligand Synthesis, Complex Synthesis and Characterisation Data



2.1 Synthesis of Monometallic Complexes 4 and 5

2.1.1 1-methyl-3-phenyl-1H-imidazolium iodide (7)

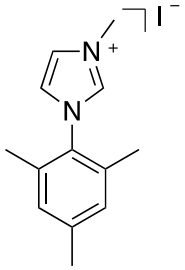


1-phenyl-1*H*-imidazole (870 mg, 6.03 mmol) and MeI (3.42 g, 24.1 mmol) were added to acetonitrile (10 mL) and the mixture was stirred in a sealed vial for 48 h. The solvent was removed *in vacuo*, the crude product was dissolved in the minimum amount of ethanol (95%) and added dropwise to a flask of stirring diethyl ether (40 mL) where a pale yellow solid precipitated. The precipitate was filtered and dried *in vacuo* yielding **4** as a pale yellow solid.

Yield: 1.63 g, 5.75 mmol, 95%.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.74 (m, 1H, NC**H**N), 8.28 (br dd, 1H, Im**H**), 7.95 (br dd, 1H, Im**H**), 7.77 (m, 2H, Ar**H**), 7.67 (m, 2H, Ar**H**), 7.59 (m, 1H, *p*-Ar**H**) 3.95 (s, 3H, ImC**H$_3$**) ppm. ^{1}H NMR data obtained agreed with known literature.[17]

2.1.2 1-methyl-3-(2,4,6-trimethylphenyl)-1*H*-imidazolium iodide (8)

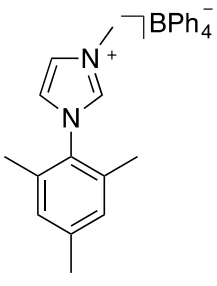


1-(2,4,6-trimethylphenyl)1*H*-imidazole (310 mg, 1.66 mmol) and MeI (944 mg, 6.65 mmol) were stirred in acetonitrile (10 mL) for 18 h. The solvent was removed *in vacuo* the crude product was dissolved in the minimum amount of ethanol (95%) and added dropwise to a flask of stirring diethyl ether (40 mL) where a pale yellow solid precipitated. The precipitate was filtered and dried *in vacuo* yielding **5** as a light brown solid.

Yield: 428 mg, 1.30 mmol, 79%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H, NC**H**N), 7.92 (t, $^3J_{H\text{-}H}$ = 1.8 Hz, 1H, Im**H**), 7.19 (t, $^3J_{H\text{-}H}$ = 1.8 Hz, 1H, Im**H**), 6.97 (s, 2H, Ar**H**), 4.33 (s, 3H, ImC**H$_3$**), 2.31 (s, 3H, ArC**H$_3$**), 2.07 (s, 6H, ArC**H$_3$**) ppm. ^{1}H NMR data obtained agreed with known literature.[18]

2.1.3 1-methyl-3-(2,4,6-trimethylphenyl)-1H-imidazolium tetraphenylborate (10)



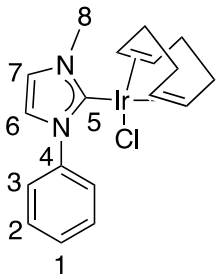
Compound **5** (268 mg, 816 µmol) and $NaBPh_4$ (282 mg, 824 µmol) were stirred in DCM (50 mL) for 18 h. The mixture was filtered through celite,the solvent reduced to *ca*. 25 mL and 20 mL of n-hexane was added to the mixture. The solvent was then completely removed *in vacuo* to yield **7** as a white solid.

Yield: 380 mg, 730 µmol , 89%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34 (m, 8H, *o*-BPh_4**H**), 7.10 (br s, 2H, MesAr**H**), 6.96 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 8H, *m*-BPh_4**H**), 6.84 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-BPh_4**H** & br t,

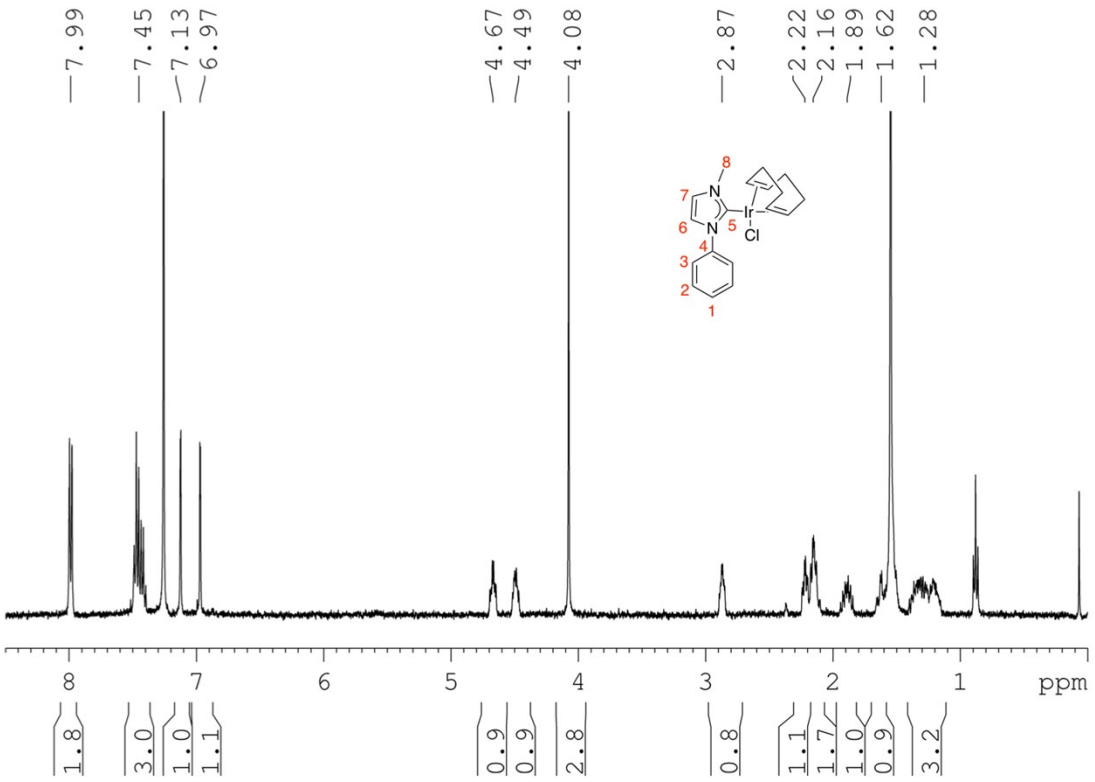
1H, Im**H**), 6.81 (t, $^{3}J_{H\text{-}H}$ = 1.7 Hz, 1H, Im**H**), 5.91 (br t, 1H, NC**H**N), 3.03 (s, 3H, ImC**H$_3$**), 2.43 (s, 3H, ArC**H$_3$**), 1.90 (s, 6H, ArC**H$_3$**) ppm.
^{1}H NMR data obtained agreed with known literature.[19]

2.1.4 [Ir(PhIMe)CODCl] (9)

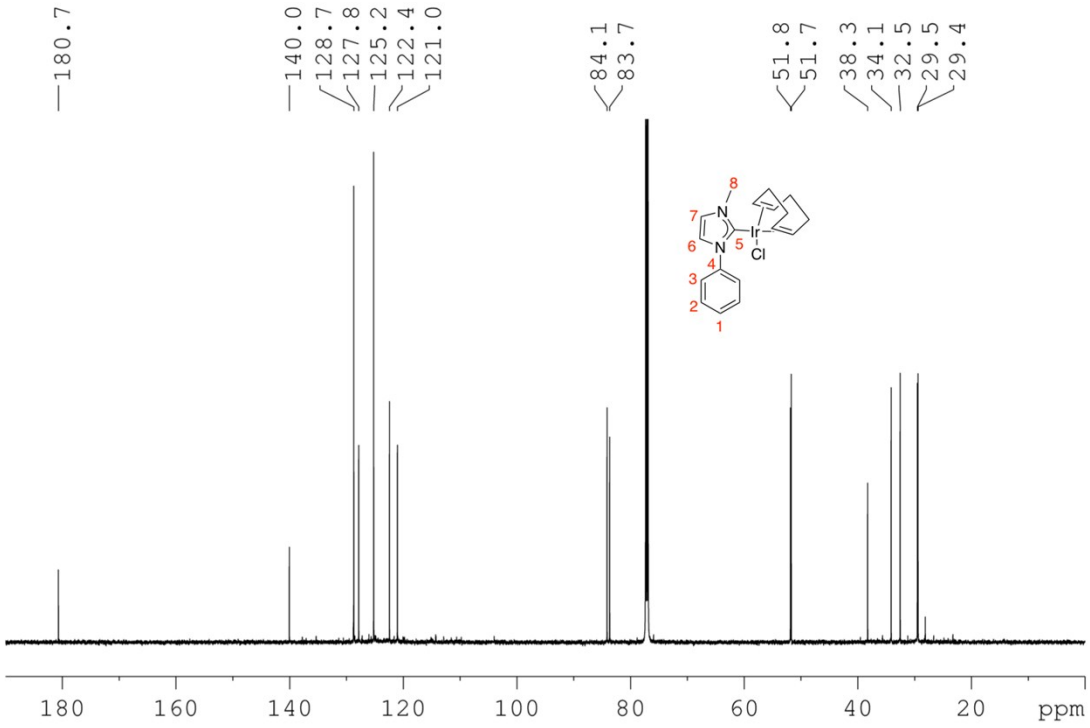


The proligand 1-methyl-3-phenyl-1H-imidazolium iodide (**7**, 304 mg, 1.07 mmol), Ag_2O (186 mg, 0.802 mmol) and $[Ir(COD)\mu\text{-}Cl]_2$ (374 mg, 0.566 mmol) were added to dichloromethane (20 mL) and the mixture was stirred for 16 h. The reaction mixture was then filtered through celite and the solvent removed from the filtrate (*in vacuo*). The complex [Ir(PhIMe)CODCl] (**9**) was recrystallised by dissolving the crude solid obtained form the filtrate in the minimum amount of dichloromethane and adding excess *n*-hexane to the mixture until a yellow precipitate was obtained. The precipitate was filtered to yield the desired complex **9** as a yellow solid.
Yield: 368 mg, 0.749 mmol, 70 %.
^{1}H NMR (400 MHz, CDCl3): δ 7.99 (m, 2H, **H**2), 7.49 (m, 2H, **H**3), 7.40 (m, 1H, **H**1), 7.13 (d, 1H, **H**6), 6.98 (d, 1H, **H**7), 4.68 (m, 1H, sp^2-COD), 4.50 (m, 1H, sp^2-COD), 4.08 (s, 3H, **H**8), 2.88 (m, 1H, sp^2-COD), 2.22 (m, 1H, sp^2-COD), 2.15 (m, 2H, sp^3-COD), 1.90 (m 1H, sp^3-COD), 1.62 (m, 1H, sp^3-COD), 1.54 (m, 2H, sp^3-COD), 1.35 (m, 1H, sp^3-COD), 1.21 (m, 1H, sp^3-COD) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 180.9 (**C**5), 140.1 (**C**4), 128.8 (**C**3), 127.9 (**C**1), 125.3 (**C**2), 122.5 (**C**7), 121.1 (**C**6), 84.2 (sp^2-COD), 83.8 (sp^2-COD), 51.9 (sp^2-COD), 51.7 (sp^2-COD), 38.3 (**C**8), 34.2 (sp^3-COD), 32.6 (sp^3-COD), 29.6 (sp^3-COD), 29.5 (sp^3-COD) ppm. Elemental Anal. found: 43.58; H, 4.55; N, 5.56 %; calculated for $C_{18}H_{22}ClIrN_2$: C, 43.76; H, 4.49; N, 5.67 %. ESI-MS (MeOH), *m/z* (%): 457.33 (95) $[M\text{-}Cl]^+$ amu.

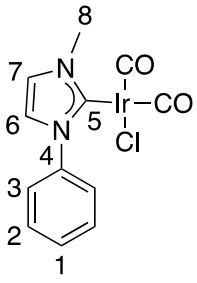
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (9)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (9)



2.1.5 [Ir(PhIMe)CO_2Cl] (4)

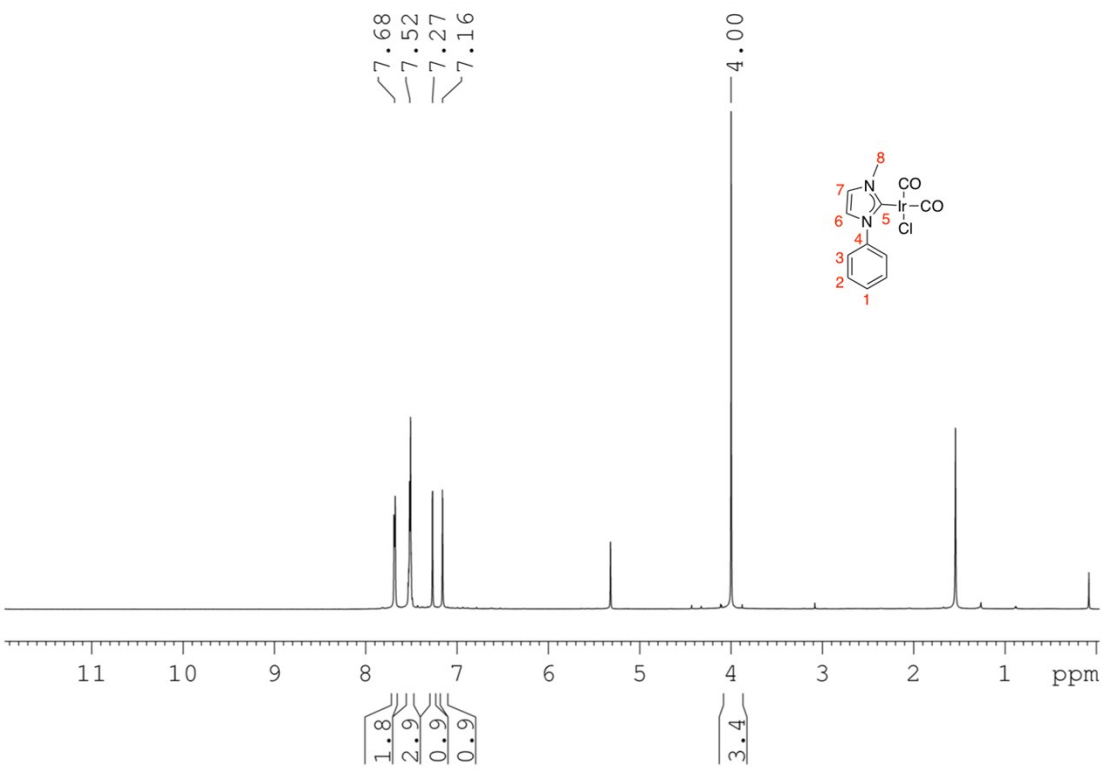


[Ir(PhIMe)CODCl] (**9**, 243 mg, 0.494 mmol) was dissolved in degassed dichloromethane (20 mL). The mixture was frozen and the headspace of the schlenk flask was evacuated. A balloon of $CO_{(g)}$ was attached to the flask and opened up to the evacuated headspace. The mixture was thawed and stirred at room temperature for 20 min. The solvent was then removed *in vacuo* and the complex (**4**) was recrystallised by dissolving the crude mixture in the minimum amount of dichloromethane and adding excess *n*-hexane until a pale yellow precipitate was obtained. The precipitate was filtered to yield the desired carbonylated complex **4** as a pale yellow solid.

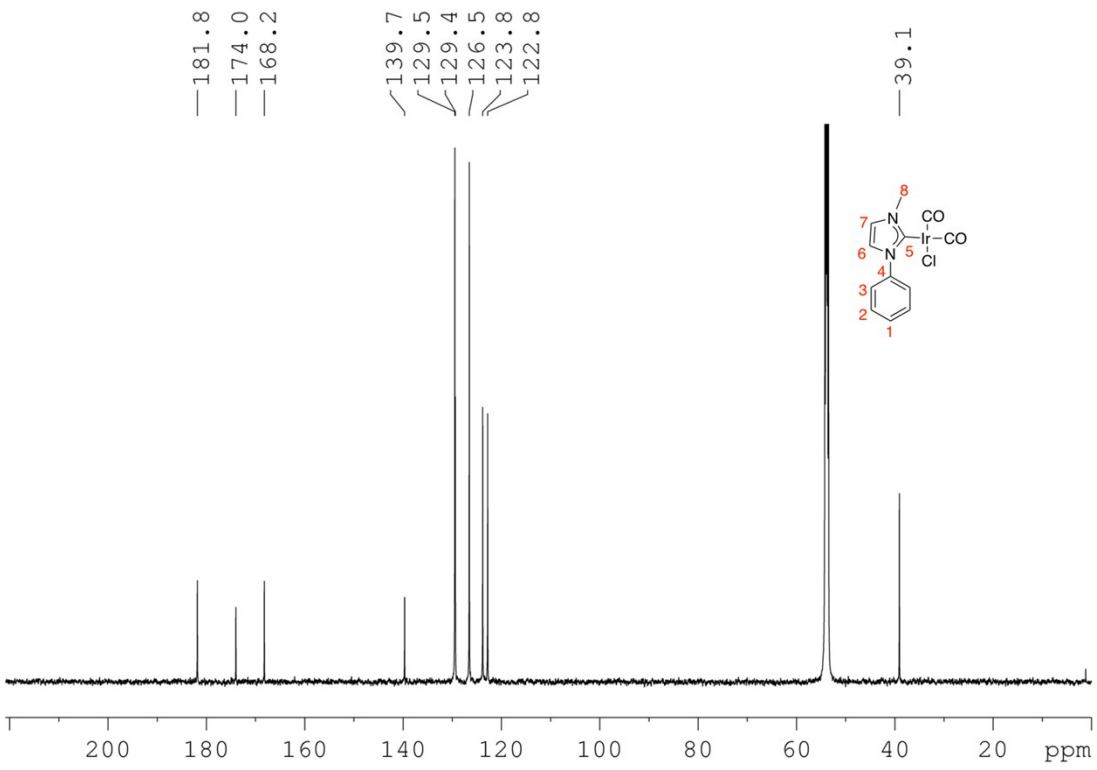
Yield: 203 mg, 0.460 mmol, 93 %.

^1H NMR (600 MHz, CD_2Cl_2): δ 7.72-7.69 (m, 2H, **H**3), 7.57-7.52 (m, 3H, H**1** and **H**3), 7.30 (d, $^3J_{H\text{-}H}$ = 1.84 Hz, 1H, **H**6), 7.19 (d, $^3J_{H\text{-}H}$ = 1.84 Hz, 1H, **H**7), 4.03 (s, 3H, **H**8) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ 181.5 (**C**O), 173.7 (**C**5), 167.9 (**C**O), 139.4 (**C**4), 192.1 & 129.0 (**C**1 and **C**2), 126.2 (**C**3), 123.5 (**C**7), 122.5 (**C**6), 38.7 (**C**8) ppm. Elemental Anal. found: C, 32.66; H, 2.41; N, 6.06 %; calculated for $C_{12}H_{10}ClIrN_2O_2$: C, 32.62; H, 2.28; N, 6.34 %. FTIR (DCM): 2066.86(s), 1984.65(s) cm^{-1}. ESI-MS (MeOH), *m/z* (%): 407.16 (100) $[M - Cl]^+$ amu.

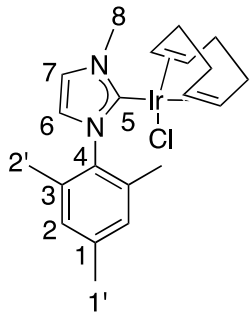
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of (4)



^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of (4)

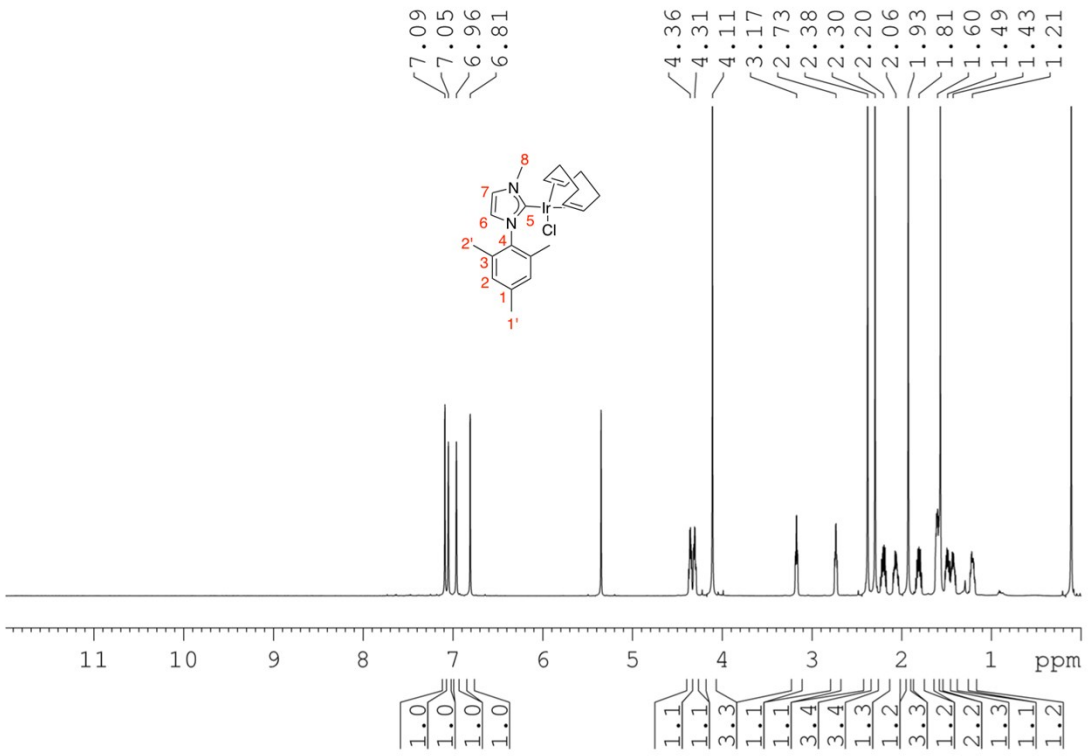


2.1.6 [Ir(MesIMe)CODCl] (11)

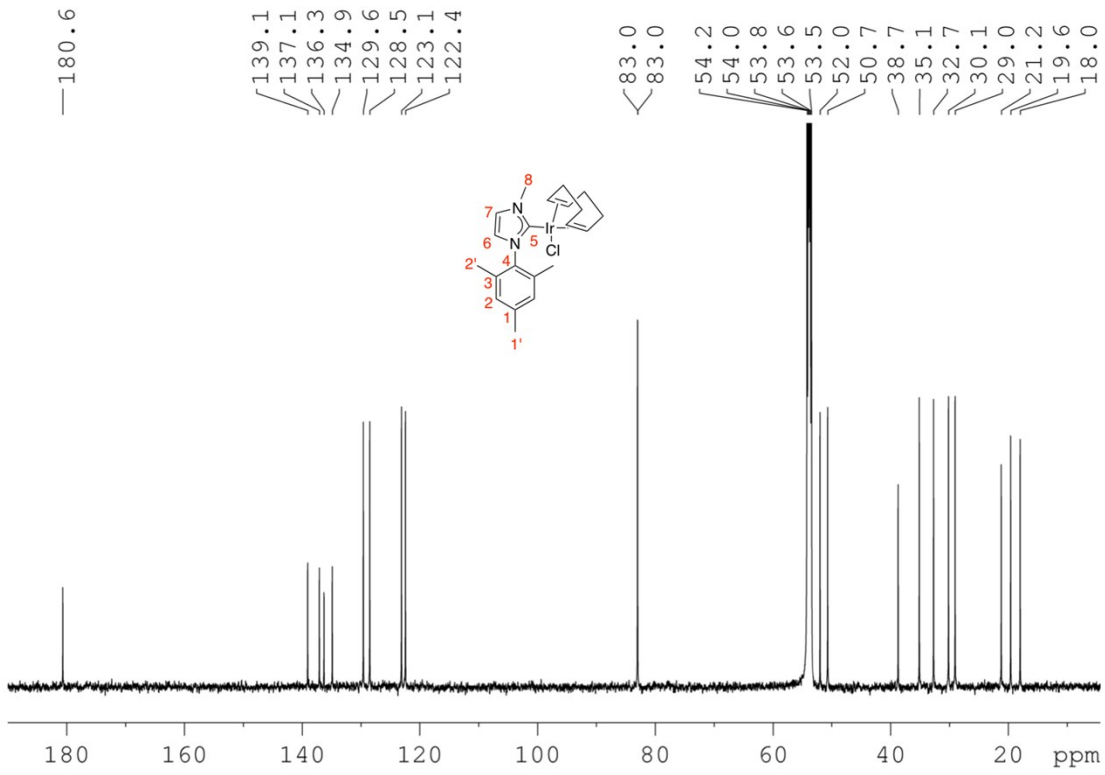


The proligand 1-methyl-3-(2,4,6-trimethylphenyl)-1H-imidazolium tetraphenylborate (**10**, 106 mg, 0.203 mmol) and K_2CO_3 (140 mg, 1.02 mmol) were added to acetone (30 mL). After 10 min of stirring the mixture [Ir(COD)μ-Cl]$_2$ (69.6 mg, 0.104 mmol) was added, the mixture turned a light orange colour and the mixture was refluxed for 4 h. The solvent was removed *in vacuo* and the crude mixture redissolved dichloromethane (20 mL) and the mixture was filtered through celite. 80 mL of *n*-hexane was added to the filtrate and the solvent was reduced to *ca*. 70 mL, heated to 60 °C and filtered through celite (while hot) to remove any traces of BPh_4 salts. The solvent was removed *in vacuo* to yield the complex [Ir(MesIMe)CODCl] (**11**) as a yellow solid. Yield: 98.1 mg, 0.183 mmol, 90%.^{1}H NMR: (600 MHz, CD_2Cl_2): δ 7.09 (d, $^3J_{H\text{-}H}$ = 1.7 Hz, 1H, **H**7), 7.05 (br d, 1H, **H**2), 6.96 (br d, 1H, **H**2*), 6.81 (d, $^3J_{H\text{-}H}$ = 1.7 Hz, 1H, **H**6), 4.39-4.28 (m, 2H, sp^2-C**H**), 4.11 (s, 3H, **H**8), 3.17 (m, 1H, sp^2-C**H**), 2.73 (m, 1H, sp^2-C**H**), 2.38 (s, 3H, **H**1'), 2.30 (s, 3H, **H**2'), 2.25-2.16 (m, 1H, sp^3-C**H**), 2.11-2.01 (m, 1H, sp^3-C**H**), 1.93 (s, 3H, **H**3'), 1.85-1.76 (m, 1H, sp^3-C**H**), 1.63-1.55 (m, 2H, sp^3-C**H**), 1.53-1.38 (m, 2H, sp^3-C**H**), 1.25-1.17 (m, 1H, sp^3-C**H**) ppm. ^{13}C{^{1}H} NMR (151MHz, CD_2Cl_2): δ 180.6 (**C**5), 139.0 (**C**1), 137.05 (**C**3), 136.3 (**C**4), 134.9 (**C**3*), 129.6 (**C**2), 128.5 (**C**2*), 123.1 (**C**6), 122.4 (**C**7), 82.99 (sp^2-**C** of COD), 83.0 (sp^2-**C** of COD), 52.0 (sp^2-**C** of COD), 50.7 (sp^2-**C** of COD), 38.7 (**C**8), 35.1 (sp^3-**C** of COD), 32.7 (sp^3-**C** of COD), 30.1 (sp^3-**C** of COD), 29.0 (sp^3-**C** of COD), 21.2 (**C**1'), 19.6 (**C**2'), 18.0 (**C**3') ppm. Elemental Anal. found: C, 45.90; H, 5.43; N, 4.87 %; calculated for $C_{21}H_{28}ClIrN_2$ + H_2O: C, 45.52; H, 5.46; N, 5.06 %. ESI-MS (MeOH), *m/z* (%): 449.19 (100) [M-Cl]$^+$, 559.17 (55) [M+Na]$^+$ amu.

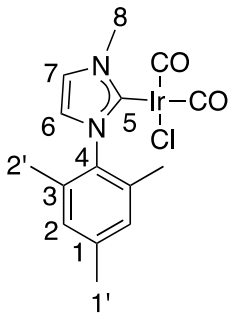
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of (11)



^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of (11)



2.1.7 [Ir(MesIMe)CO$_2$Cl] (5)

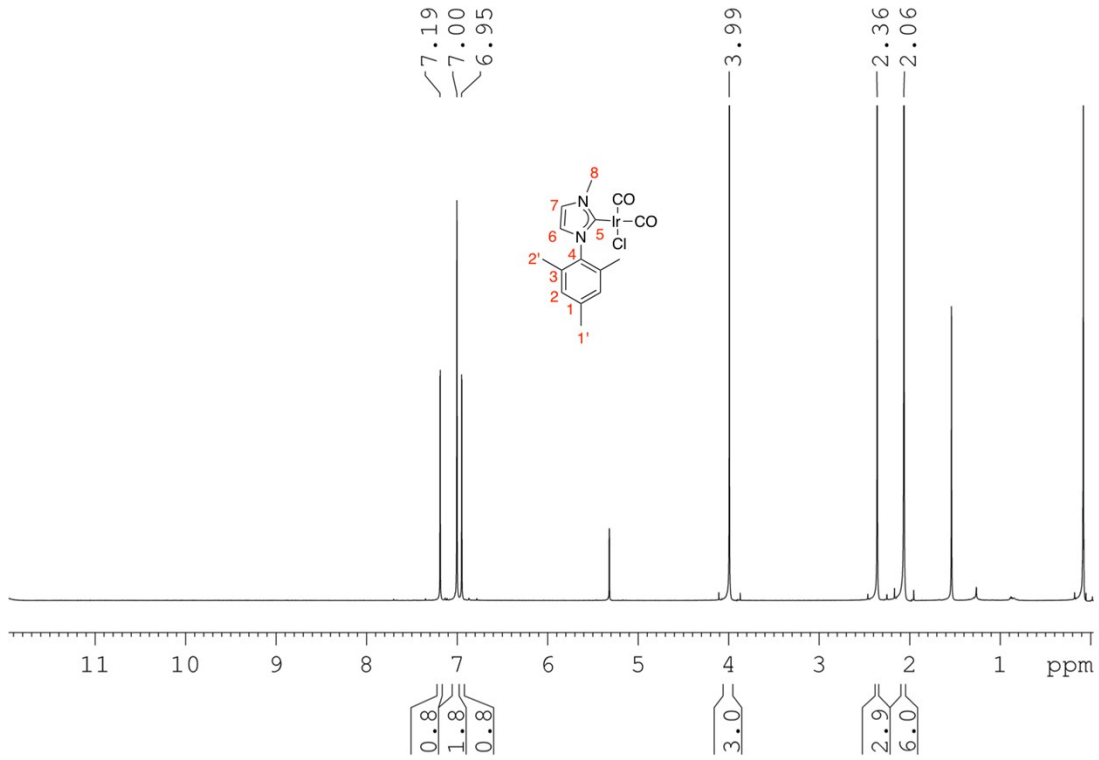


Using the same method as that used for the synthesis [Ir(PhIMe)CO$_2$Cl] (**4**), 80.0 mg (0.149 mmol) of complex **11** was carbonylated to produce complex. The product was isolated by adding 15 mL of hexane to the reaction mixture and then removing the solvent *in vacuo* to yield a lime coloured powder.

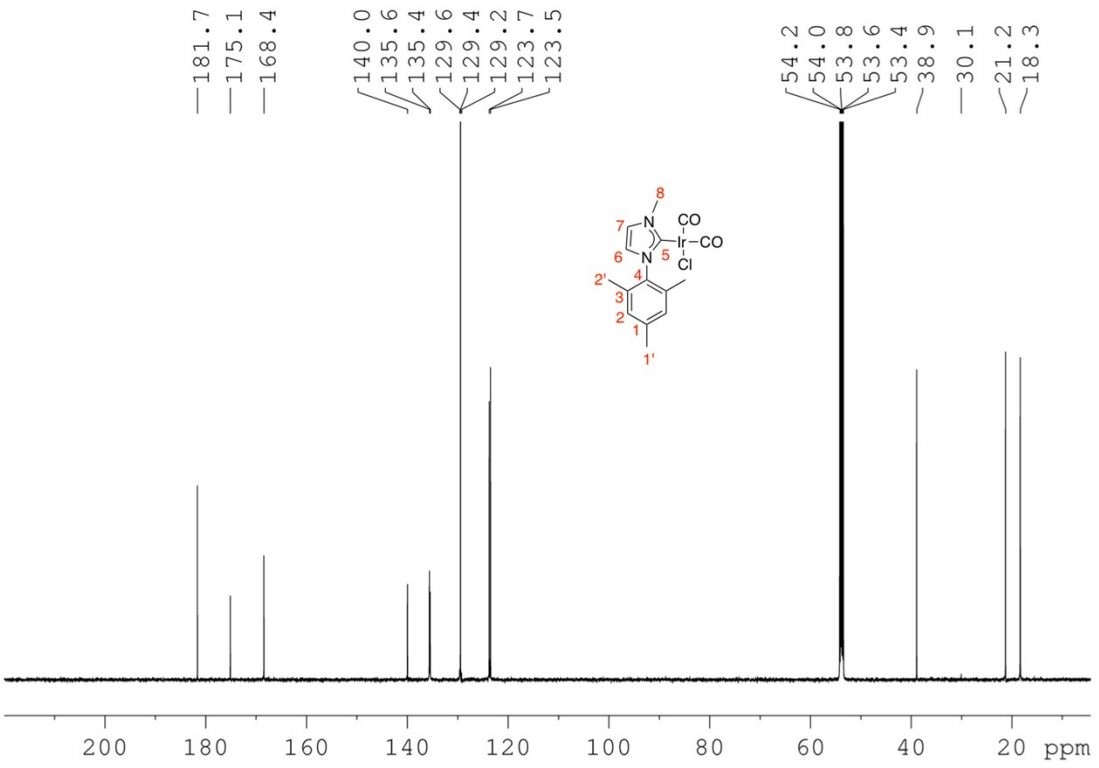
Yield: 62.1 mg, 0.128 mmol, 86 %.

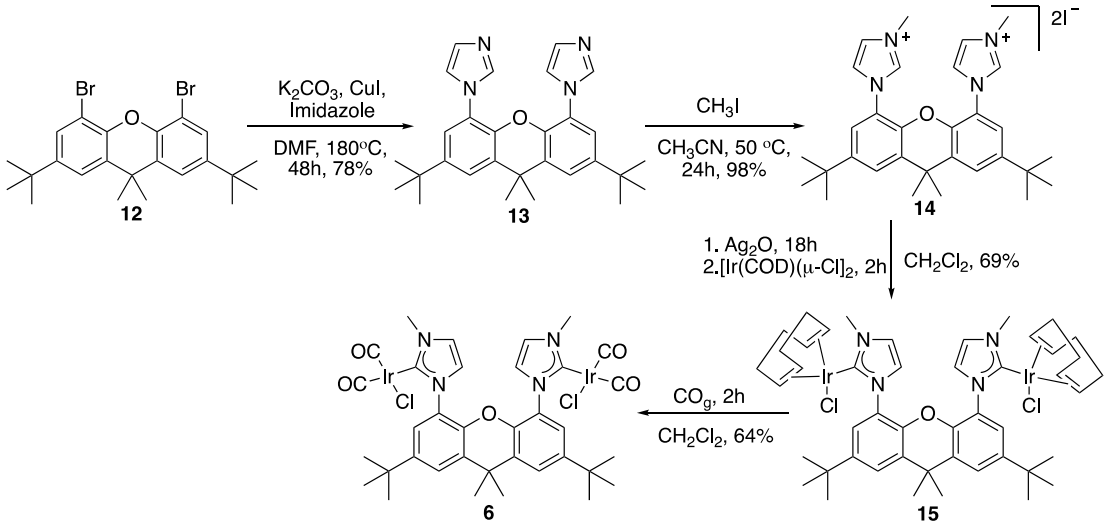
^{1}H NMR (CD_2Cl_2, 600MHz): δ 7.22 (d, $^3J_{H\text{-}H}$ = 1.7 Hz, 1H, **H**7), 7.03 (s, 2H, **H**2), 6.98 (d, $^3J_{H\text{-}H}$ = 1.7 Hz, 1H, H**6**), 4.02 (s, 3H, **H**8), 2.39 (s, 3H, **H**1'), 2.09 (s, 6H, **H**2') ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 151MHz): δ 181.6 (**C**O), 175.1 (**C**5), 168.4 (**C**O), 139.9 (**C**1), 135.6 (**C**3), 135.4 (**C**4), 129.4 (**C**2), 123.7 (**C**7), 123.5 (**C**6), 38.9 (**C**8), 21.3 (**C**1'), 18.3 (**C**2') ppm. Elemental Anal. found: C, 37.12; H, 3.58; N, 5.37 %; calculated for $C_{15}H_{16}ClIrN_2O_2$: C, 37.23; H, 3.33; N, 5.79 %. FTIR (DCM): 2054.45(s), 1974.22(s) cm^{-1}. ESI-MS (MeOH), *m/z* (%): 449.08 (100) [M-Cl]$^+$, 507.17 (93) [M+Na]$^+$ amu.

^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of (5)



^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of (5)



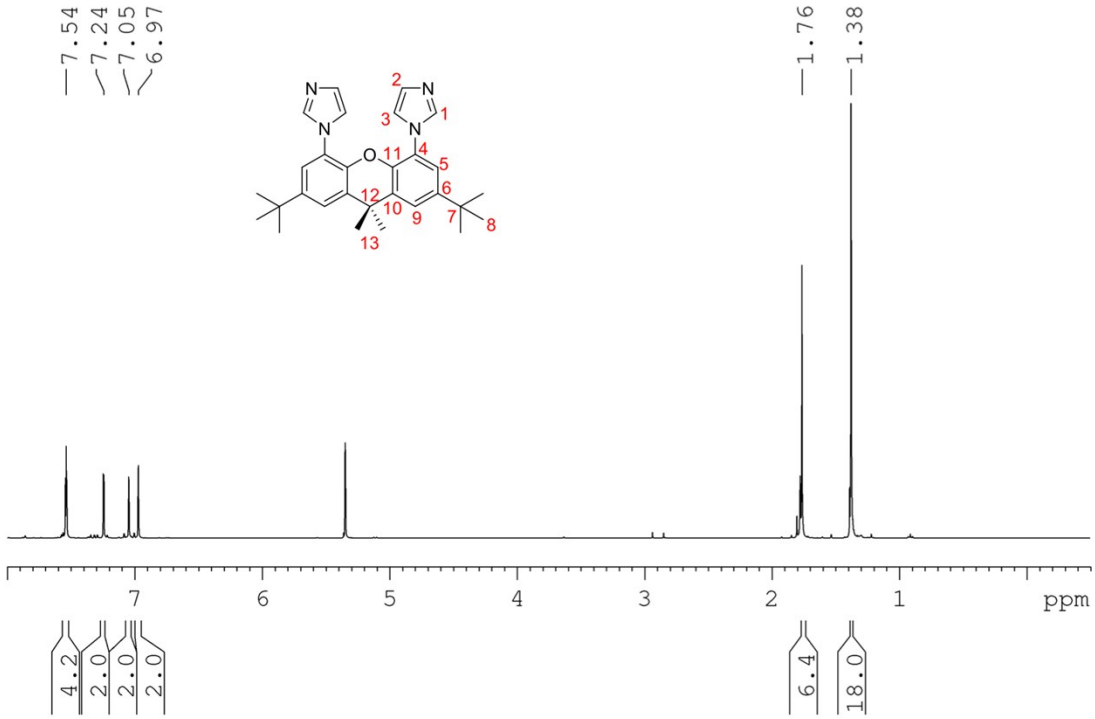


2.2 Synthesis of Bimetallic Complex 6

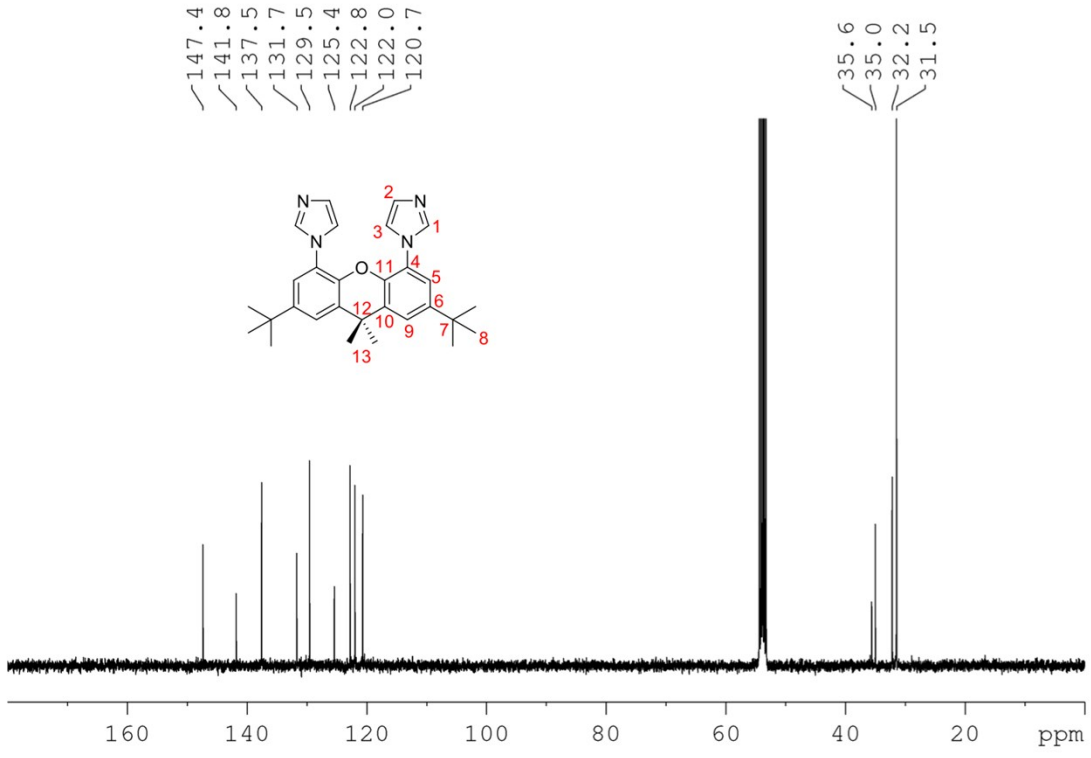
2.2.1 1,1'-(2,7-Di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (13)

A mixture of 4,5-Dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-9H-xanthene (**12**) (1.00 g, 2.09 mmol), imidazole (0.746 g, 11.0 mmol), K_2CO_3 (1.53 g, 11.1 mmol) and Copper(I) iodide (0.397 g, 2.09 mmol) in DMF (100 mL) was heated to 180 °C for 48 hours. The mixture was filtered through celite. DCM (100 mL) was added to the filtrate and stirred in a solution of ammonia (28%, 30 mL) and water (50 mL), the organic layer was extracted and washed stirred with ammonia/water a further two times. The organic layer was extracted and stirred in a saturated Na_2[EDTA] solution (100 mL) for 2 hours. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* yielding an oily yellow residue. The oily residue was precipitated from the minimum amount of DCM in hexane (100 mL) at 0 °C to yield 1,1'-(2,7-di-*tert*-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (**13**) as a beige powder.
Yield: 0.747 g (1.64 mmol), 78%.
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (m, 4H, **H**3 & **H**9), 7.24 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**5), 7.05 (t, $^4J_{H\text{-}H}$ = 1.1 Hz, 2H, **H**1), 6.97 (t, $^3J_{H\text{-}H}$ = 1.2 Hz, 2H, **H**2), 1.76 (s, 6H, **H**13), 1.38 (s, 18H, **H**8).
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 147.4 (**C**6), 141.8 (**C**11), 137.5 (**C**3), 131.7 (**C**10), 129.5 (**C**1), 125.4 (**C**4), 122.8 (**C**9), 122.0 (**C**5), 120.7 (**C**2), 35.6 (**C**12), 35.0 (**C**7), 32.2 (**C**13), 31.5 (**C**8).
Elemental Anal. Found: C, 75.26; H, 6.81; N, 12.64. Calcd. for $C_{29}H_{34}N_4O$: C, 76.60; H, 7.55; N, 12.33%.
ESI-MS (CH_3OH), *m/z* (%): 455.3 (100) $[M]^+$ amu.

^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of (13)



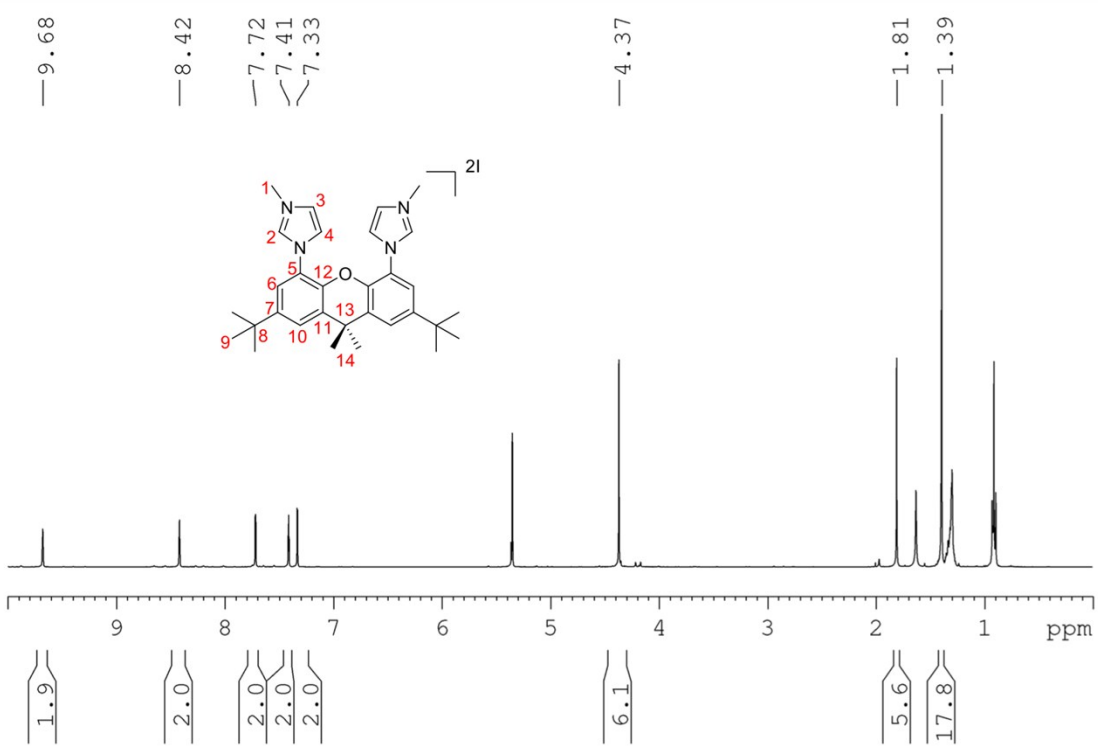
^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of (13)



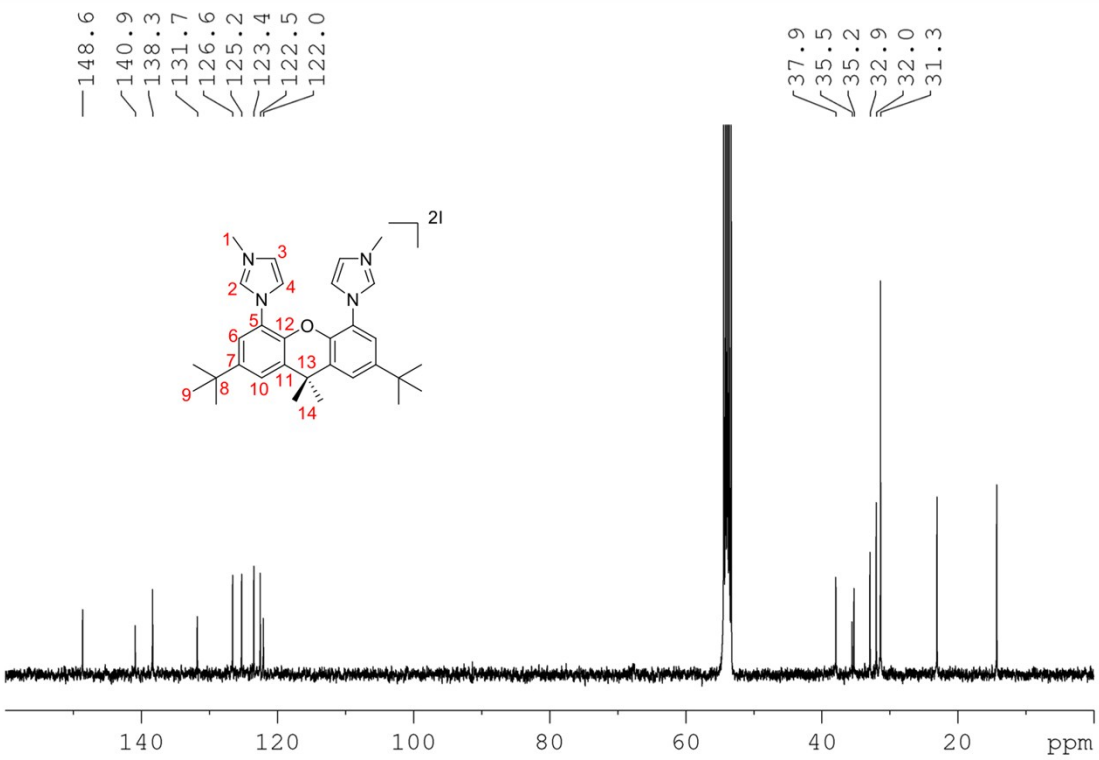
2.2.2 1,1'-(2,7-Di-*tert*-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)bis(3-methyl-1H-imidazol-3-ium) iodide [(MeNHC)2^{t}Xan]I2 (14)

1,1'-(2,7-Di-*tert*-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)*bis*(1H- imidazole) (**13**) (0.200 g, 0.439 mmol) and iodomethane (0.7 mL, 11.5 mmol) were added to acetonitrile (15 mL) in a pressure flask. The mixture was stirred at 50 °C in the absence of light for 24 hours. The mixture was allowed to cool before the solvent was removed under reduced pressure to afford an oily yellow residue. The oily residue was precipitated from the minimum amount of DCM in excess stirring hexane (50 mL) to yield 1,1'- (2,7-di-*tert*-butyl-9,9-dimethyl-9H-xanthene-4,5-diyl)*bis*(3-methyl-1H-imidazol-3-ium) iodide (**14**) as a pale yellow powder.
Yield: 0.318 g (0.431 mmol), 98%.
^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.68 (s, 2H, **H**2), 8.42 (t, $^{4}J_{H\text{-}H}$ = 1.7 Hz, 2H, **H**3), 7.72 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 2H, **H**10), 7.41 (t, $^{4}J_{H\text{-}H}$ = 1.7 Hz, 2H, **H**4), 7.33 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 2H, **H**6), 4.37 (s, 6H, **H**1), 1.81 (s, 6H, **H**14), 1.39 (s, 18H, **H**9).
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 148.6 (**C**7), 140.9 (**C**12), 138.3 (**C**2), 131.7 (**C**11), 126.6 (**C**10), 125.2 (**C**3), 123.4 (**C**4), 122.5 (**C**6), 122.0 (**C**5), 37.9 (**C**1), 35.5 (**C**13), 35.2 (**C**8), 32.0 (**C**14), 31.3 (**C**9).
ESI-MS (CH_3OH), *m/z* (%): 612.2 (100) $[M - I]^{+}$ amu.
Anal. Found: C, 51.90; H, 6.70; N, 6.61. Calcd. for $C_{31}H_{40}I_2N_4O$: C, 50.41; H, 5.47; N, 7.59%.

^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of (14)



^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of (14)



2.2.3 [Ir2((MeNHC)2^{t}Xan)(COD)2Cl2] (15)

1,1'-(2,7-Di-*tert*-butyl-9,9-dimethyl-9H-xanthene-4,5- diyl)bis(3-methyl-1H-imidazol-3-ium) iodide (**14**) (0.102 g, 0.138 mmol) and silver(I) oxide (0.044 g, 0.188 mmol) were dissolved in DCM (30 mL) and stirred at room temperature in the absence of light for 18 hours. The mixture was filtered through celite, $[Ir(COD)Cl]_2$ (0.102 g, 0.151 mmol) was added, and the mixture was stirred at room temperature for 2 hours in the absence of light. The mixture was filtered through celite and the solvent was removed under reduced pressure, resulting in a brown waxy solid. The waxy residue was precipitated from the minimum amount of DCM in excess stirring hexane to yield $[Ir_2((MeNHC)_2{}^tXan)(COD)_2Cl_2]$ (**15**) as a yellow powder.

Yield: 0.110 g (0.095 mmol), 69%.

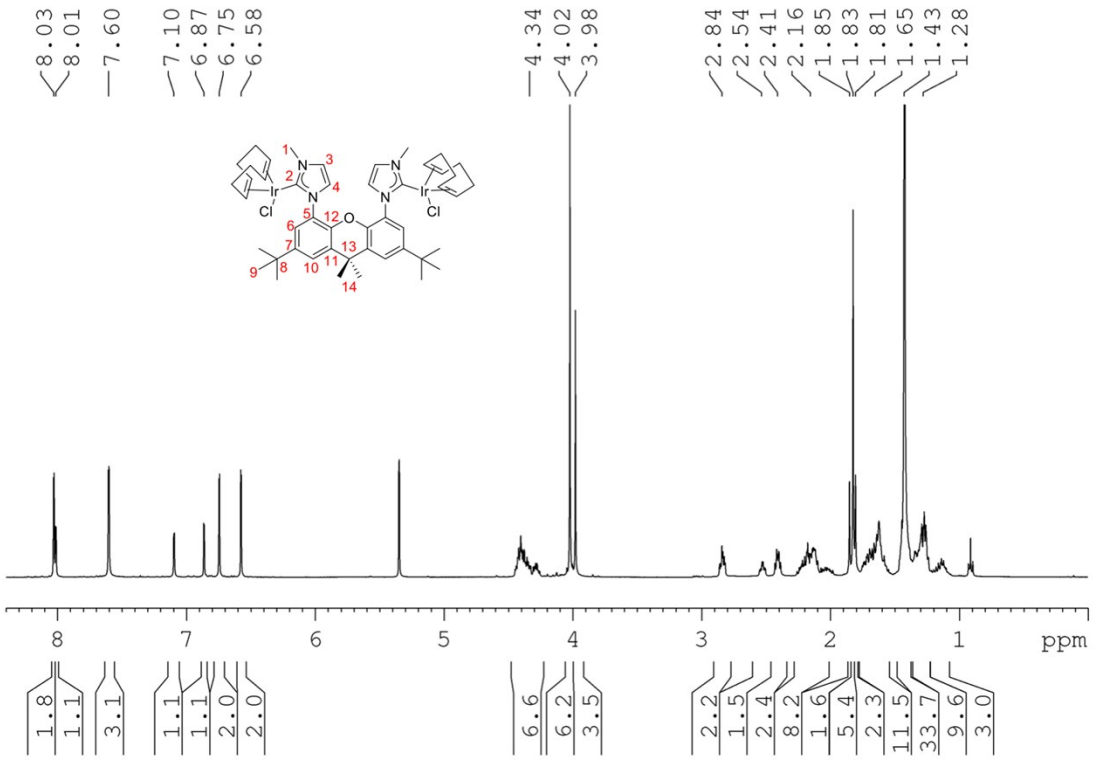
^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.03 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**6), 7.60 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**10), 6.75 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H, **H**3), 6.58 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H, **H**4), 4.02 (s, 6H, **H**1), 1.83 (s, 6H, **H**14), 1.43 (s, 18H, **H**9). **NOTE** – The ^{1}H NMR spectrum of the complex revealed two isomers of the complex in solution exisiting in a ratio of ~2:1. For simplicity only the NMR characterisation data for the major isomer has been listed. COD coligands signals while visible were not assigned due to the overlap of the COD signals from both isomers.

$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 181.6 (**C**2), 146.5 (**C**7), 140.9 (**C**12), 129.6 (**C**11), 127.5 (**C**6), 127.2 (**C**5), 123.6 (**C**10), 122.2 (**C**4), 120.9 (**C**3), 84.2 (COD-**C**H), 84.0 (COD-**C**H), 37.7 (**C**1), 35.4 (**C**13), 35.1 (**C**8), 33.6 (**C**14), 31.5 (**C**9). **NOTE** – Again in this case the majority of ^{13}C resonances belonging to the COD coligands, were not assigned due to the overlapping of the ^{1}H resonances in the ^{1}H NMR spectrum.

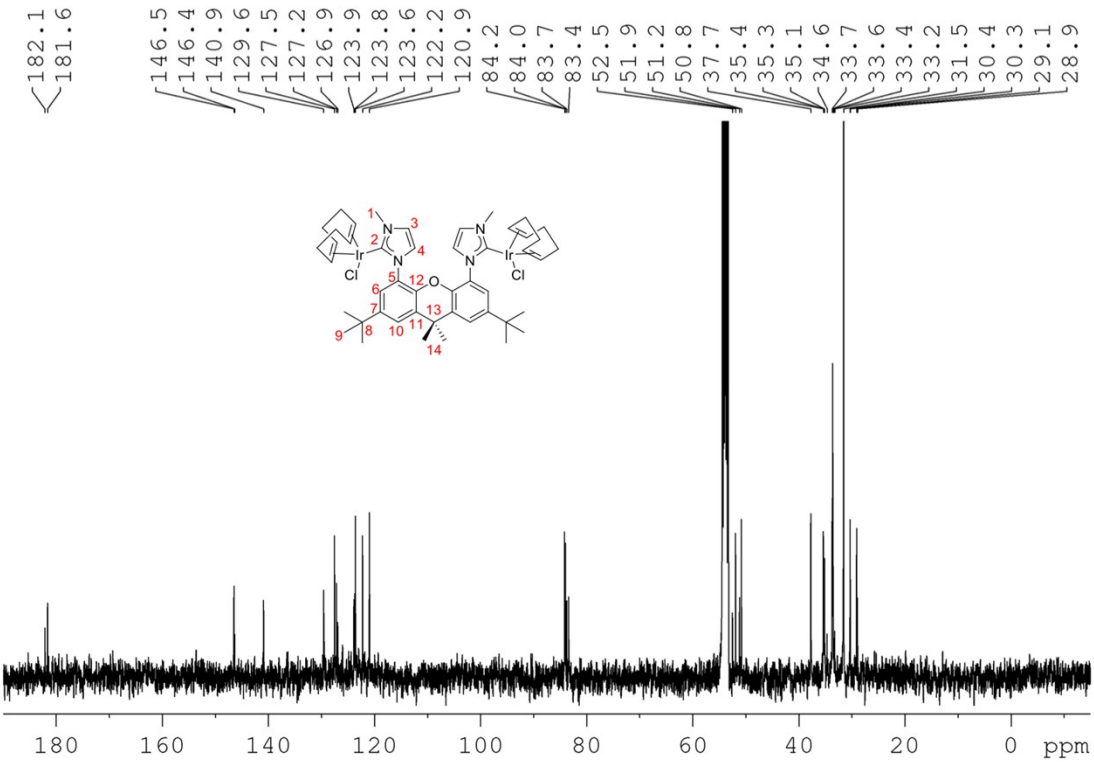
HR-ESI-MS (CH_3OH), *m/z* (%): 1177.3428 (100) $[M + Na]^+$ amu.

Anal. Found: C, 48.96; H, 5.08; N, 4.70. Calcd. for $C_{47}H_{62}Cl_2N_4OIr_2$: C, 48.89; H, 5.42; N, 4.85%.

^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of (15)



^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of (15)



2.2.4 [Ir2((MeNHC)2^{t}Xan)(CO)4Cl2] (6)

[Ir_2((MeNHC)$_2$^{t}Xan)(COD)$_2$$Cl_2$] (**15**) (49.5 mg, 0.043 mmol) was dissolved in degassed DCM (30 mL). The mixture was frozen, and the headspace of the Schleck flask was evacuated, then filled with $CO_{(g)}$ *via* a balloon. The mixture was thawed and stirred at room temperature for 2 hours. The solvent was reduced to *ca*. 10 mL in volume and then *n*-hexane was added until a precipitate appeared. The solvent was removed under reduced pressure to afford [Ir_2((MeNHC)$_2$^{t}Xan)(CO)$_4$$Cl_2$] (**6**) as a pale yellow/green solid.

Yield: 29.0 mg (0.028 mmol), 64%.

IR (solid) ν_{CO} = 2056, 1972 (s) cm^{-1}.

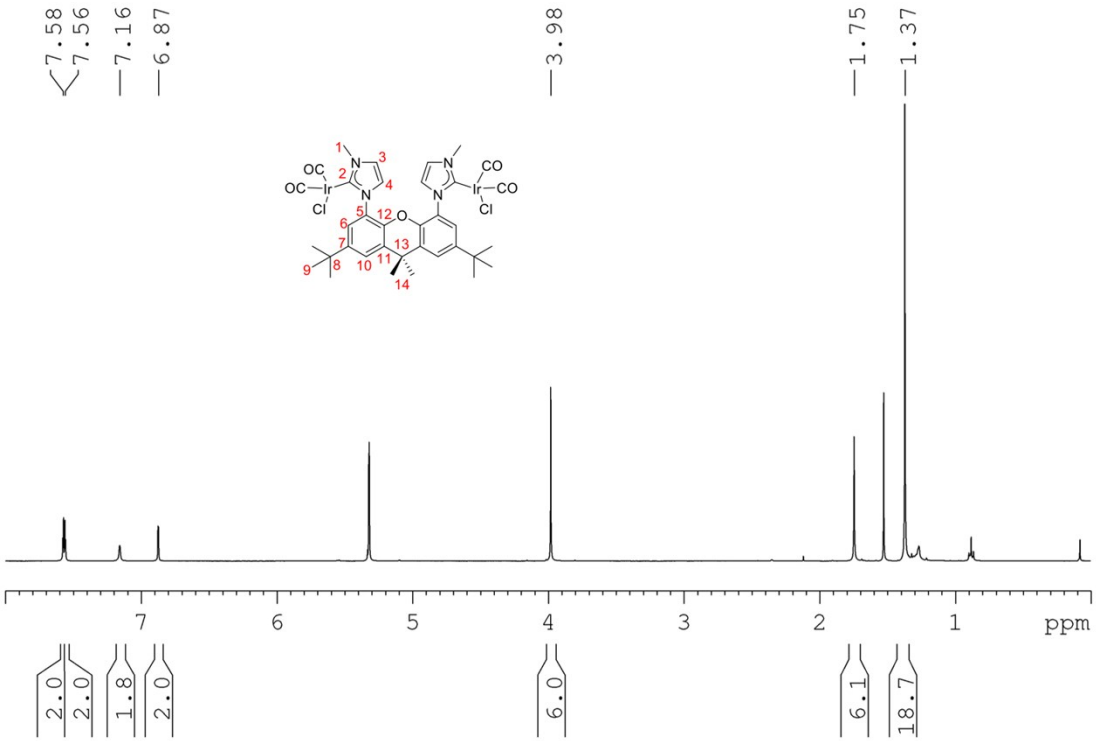
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.58 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**10), 7.56 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**6), 7.16 (s, 2H, **H**4), 6.87 (d, $^{4}J_{H\text{-}H}$ = 2.0 Hz, 2H, **H**3), 3.98 (s, 6H, **H**1), 1.75 (s, 6H, **H**14), 1.37 (s, 18H, **H**9).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 181.9 (Ir-**C**O), 174.6 (**C**2), 168.7 (Ir-**C**O), 146.5 (**C**7), 142.1 (**C**12), 130.8 (**C**11), 126.4 (**C**5), 126.0 (**C**6), 124.7 (**C**4), 124.2 (**C**10), 121.8 (**C**3), 38.6 (**C**1), 35.4 (**C**13), 35.1 (**C**8), 32.6 (**C**14), 31.4 (**C**9).

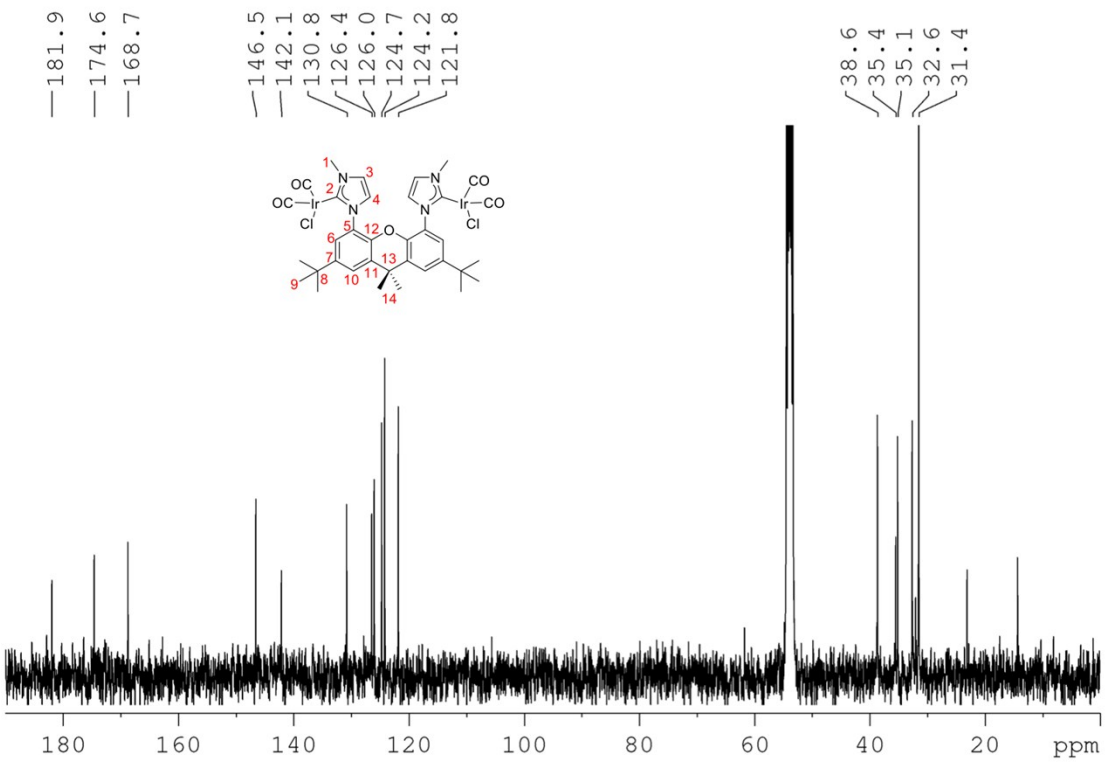
HR-ESI-MS (CH_3OH), *m/z* (%): 1073.1338 (100) $[M + Na]^{+}$ amu.

Anal. Found: C, 40.39; H, 3.33; N, 4.83. Calcd. for $C_{35}H_{38}Cl_2N_4O_5Ir_2$: C, 40.03; H, 3.65; N, 5.34%.

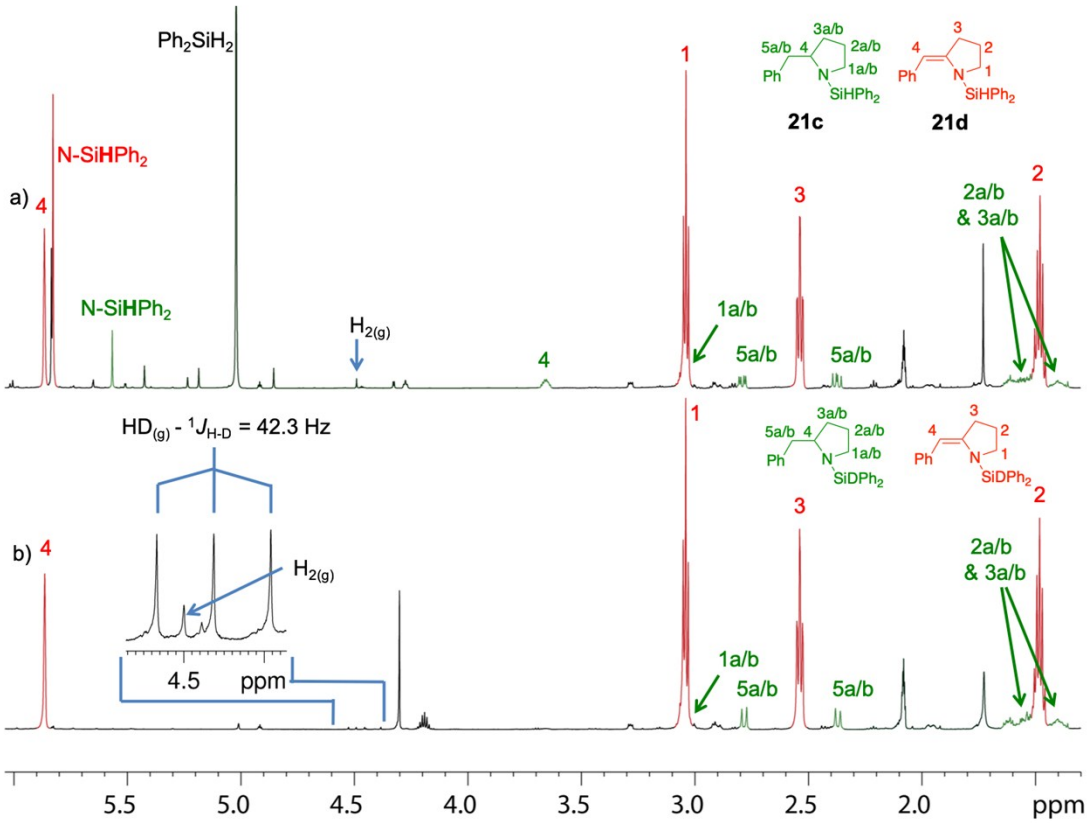
^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of (6)



^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of (6)

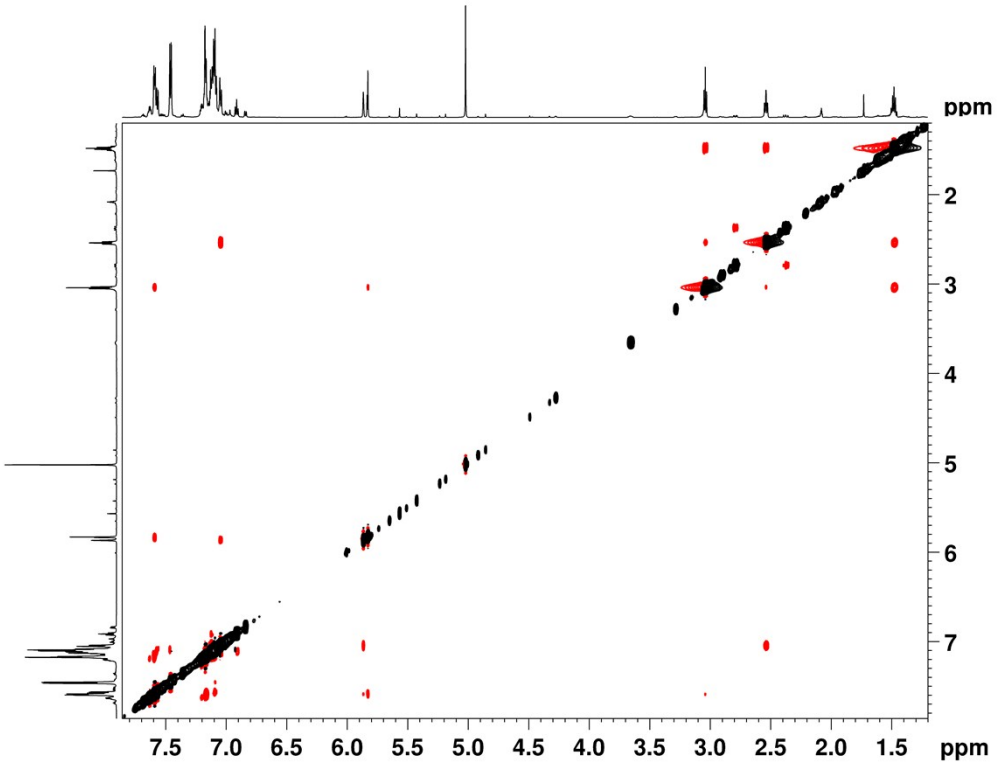


3. ^{1}H NMR Stacked Spectra for the Hydrosilylation Reaction of 21b Using Ph_2SiH_2 and Ph_2SiD_2

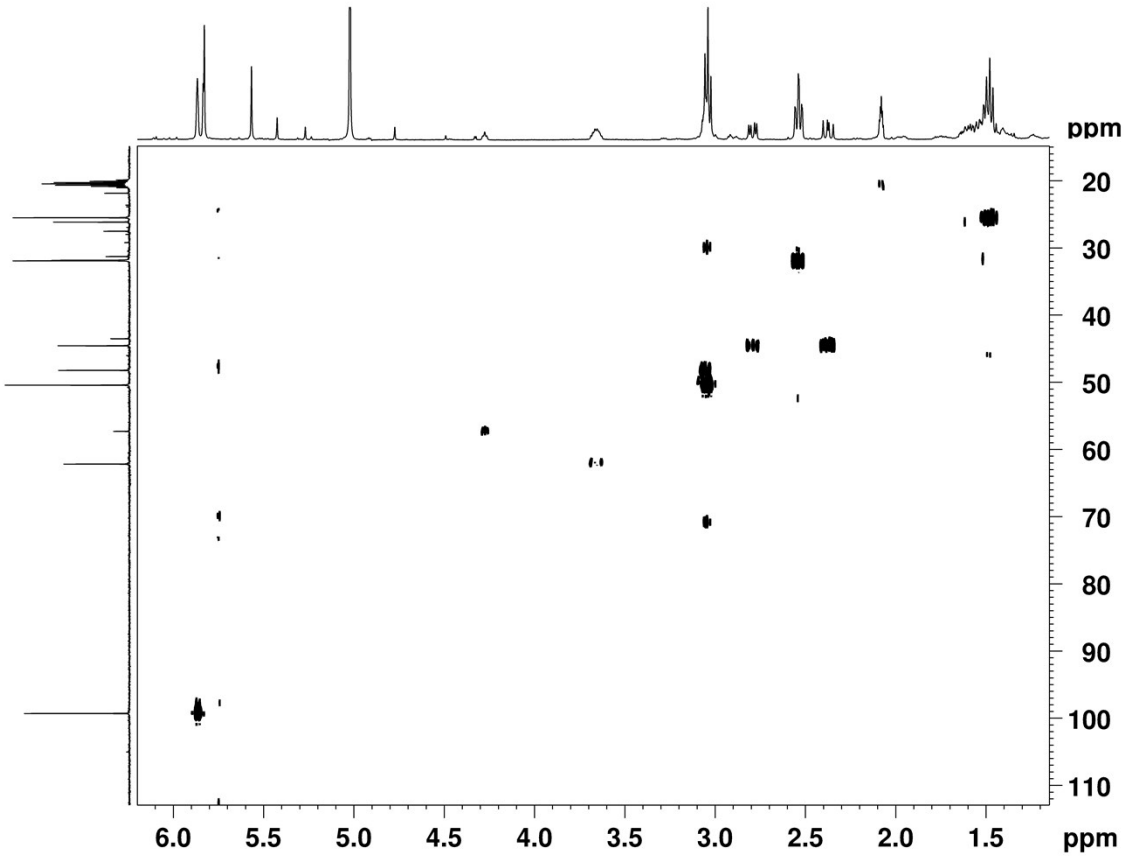


^{1}H NMR spectra of the hydrosilylation reaction of **21b** using complex **5** as the catalyst with product **21c** (green peaks) and **21d** (red peaks) using a) Ph_2SiH_2 and, b) Ph_2SiD_2 Note: The ^{1}H resonances for **21c** are chemically equivalent but magnetically inequivalent signified by a/b notation.

4. 2D NMR Spectra for 21d

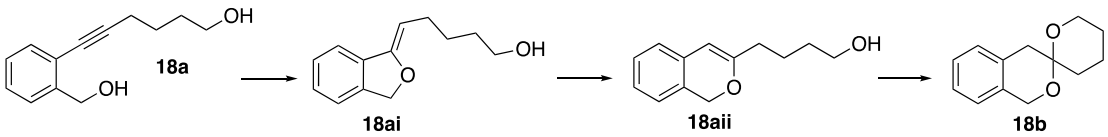


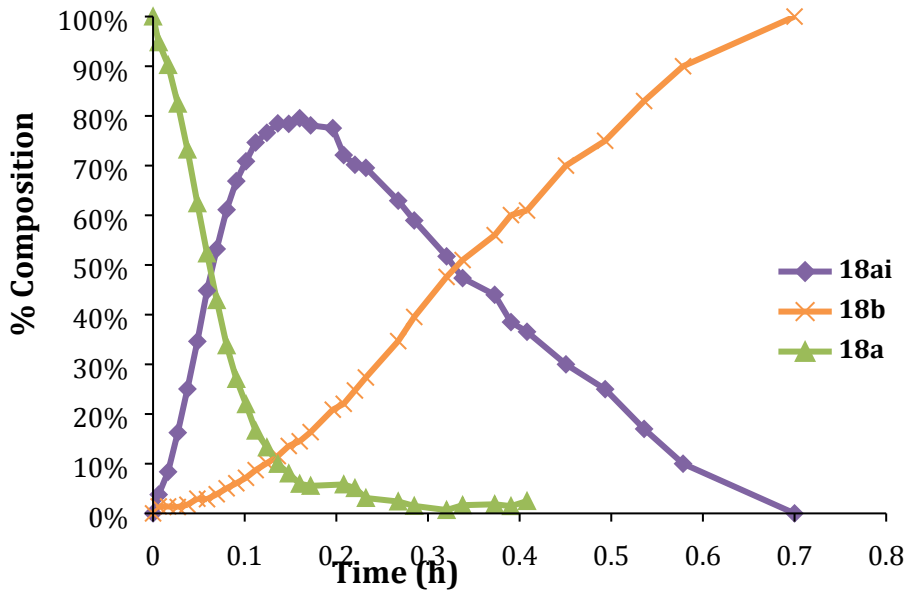
2D NOESY spectrum of **21d** clearly showing correlations between protons on the pyrroline ring (1a/b, 2a/b, 3a/b), while also exhibiting a correlation 3a/b to 4 and 4 onto the phenyl ring system.



2D ^{1}H-^{13}C HSQC spectrum of **21d**: ^{1}H resonance attributed to **4** correlates to ^{13}C resonance at ~100ppm which is the typical region where alkene carbons reside.

5. Reaction Profile of Catalysed Dihydroalkoxylation of 18a





6. Crystallographic Experimental Data Tables

	9	**5**
Chemical formula	C18H22ClIrN2	$2(C_{15}H_{16}ClIrN_2O_2)$
*M*r	494.02	967.89
Crystal system, space group	Triclinic, *P*1	Triclinic, *P*1
Temperature (K)	171	150
a, *b*, *c* (Å)	10.9491 (3), 13.1008 (4), 13.1664 (4)	8.6537 (15), 12.833 (2), 15.3914 (17)
α, β, γ (°)	c 86.173 (1), 69.332 (1), 76.042 (1)	81.863 (6), 83.238 (5), 84.662 (6)
V (Å3)	1714.54 (9)	1675.2 (4)
Z	4	2
Radiation type	Mo *K*α	Mo *K*α
μ (mm−1)	7.94	8.13
Crystal size (mm)	0.18 × 0.08 × 0.07	0.80 × 0.20 × 0.02
Data collection		
Diffractometer	Bruker *APEX*-II CCD	Bruker Kappa Apex2
Absorption correction	Multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.1530 before and 0.0369 after correction. The Ratio of minimum to maximum transmission is 0.6569. The λ/2 correction factor is 0.00150.	Multi-scan *SADABS* (Siemens, 1996)
*T*min, *T*max	0.490, 0.746	0.20, 0.85
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27293, 7486, 6783	36616, 7129, 4079
*R*int	0.027	0.136
(sin θ/λ)max (Å−1)	0.641	0.639
Refinement		
$R[F2 > 2\sigma(F2)]$, *wR*(*F*2), *S*	0.017, 0.039, 1.03	0.049, 0.117, 0.95
No. of reflections	7486	7129
No. of parameters	399	387
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρmax, Δρmin (e $Å^{-3}$)	0.90, -0.46	1.36, −1.68

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