Supplementary Information

Utilisation of water soluble iridium catalysts for Signal Amplification by Reversible Exchange (SABRE)

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PASADENA and ALTADENA[1]

*Para*hydrogen incorporation into a sample at high field has been given the name *Para*hydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignment (PASADENA). Under these conditions in the corresponding ^{1}H NMR spectrum we obtain characteristic out of phase signals. The incorporation of *para*hydrogen can also occur at low magnetic field. This variation was named Adiabatic Longitudinal Transport After Dissociation Engenders Net Alignment (ALTADENA) due to the adiabatic transfer into a magnetic field after the addition of *para*hydrogen. The result of this change is that only the lower energy βα or αβ spin state is populated (Figure S1). Under PASADENA conditions, the resulting NMR signals appear as two equal intense pairs. An individual resonance therefore features one line in absorption, pointing upwards and a second in emission, pointing downwards (antiphase doublets). Under ALTADENA conditions only two components are observed for each resonance, with different phase.

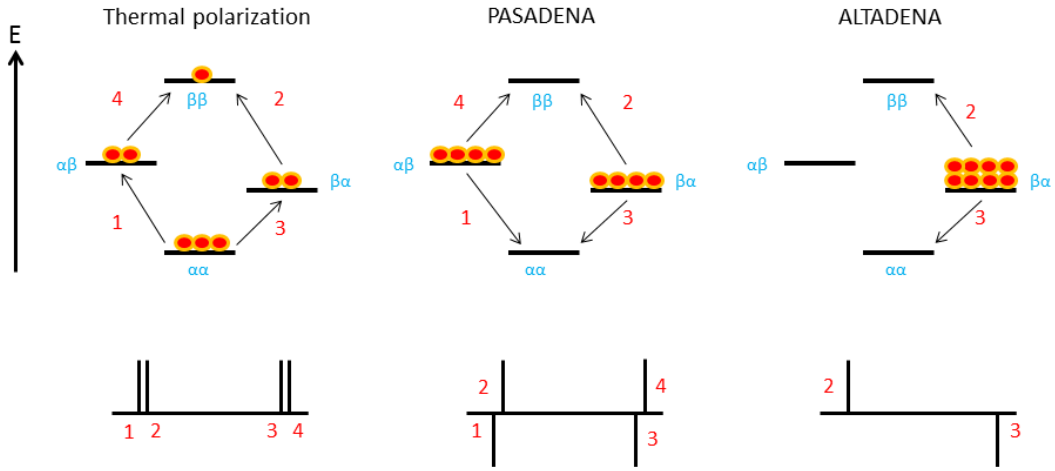


Figure S1: Schematic representation of the NMR characteristics of reaction products that form from natural abundant hydrogen addition (left) and *para*hydrogen addition under PASADENA (middle) and ALTADENA (right). The pictures reflect spin configurations while the lower traces correspond to the predicted NMR spectra.

Instrumentation and procedures

All NMR measurements were recorded on Bruker Avance III series 400 MHz or 500 MHz systems. NMR samples were prepared in 5 mm NMR tubes that were fitted with a Young`s valve. In order to complete the field dependent polarisation transfer studies a flow system was designed to enable a solution containing the catalyst (in our case complexes **1** and **3**) and the ligand (pyridine or acetonitrile) to be polarised using *para*hydrogen within a reaction chamber outside of the main NMR magnet. This solution was then transferred into the Bruker Avance III series 400 MHz spectrometer for interrogation in a NMR flow probe. Once interrogated, the solution could be returned to a polarising chamber and this process repeated as required. A coil surrounded the reaction chamber such that a magnetic field could be generated in the z direction. This coil was designed to produce static DC fields in the range of 0 to 150 G.

General experimental conditions

All experimental procedures were carried out under dinitrogen by using standard Schlenk techniques or in a MBraun Unilab glovebox. General solvents for synthetic chemistry were dried using an Innovative Technology anhydrous solvent engineering system or were distilled from an appropriate drying agent under N_2 as necessary.

Sample preparation

Samples for substrate polarization were prepared in a glove box. The complex was dissolved in a solvent (deuterated or protic or in mixture of them) to get around 9 mM solution. Pyridine (5-10 fold) was then added by eppendorf. For the SABRE – shake method experiments, the resulting solutions were then taken up by syringe and transferred into a Young`s tap capped NMR tube. The sample was then degassed on a high-vacuum line via three `cool`-pump-thaw cycles (the sample was cooled to -78 ºC using of acetone-dry ice bath). This NMR tube was filled with 3 bar *para*hydrogen. For the SABRE – flow method experiments the complexes were dissolved in 3 mL of methanol-d_4 (5 mM) and pyridine (20 or 5 fold) was added by Eppendorf. This solution was then transferred in to a sample vial in a flow probe.

Polarization step

1. R. Bowers and D. P. Weitekamp, Phys. Rev. Lett., 1986, 57, 2645-2648. C. R. Bowers and D. P. Weitekamp, J. Am. Chem. Soc., 1987, 109, 5541-5542.

The sample was shaken (to replenish the *p*-H_2 in solution) for approximately 10 seconds in a magnetic field of about 65 G, and then rapidly (within 5 seconds) inserted into the NMR spectrometer, after which NMR spectra were immediately acquired.

Calculations of enhancement factors

For calculation of the signal enhancement of the ^{1}H NMR signals the following formula was used:

$$E = \frac{S_{pol}}{S_{unpol}}$$

E = enhancement
S_{pol} = signal of polarized sample
S_{unpol} = signal of unpolarized (reference) sample
Experimentally the reference spectra were acquired on the same sample that was used for the hyperpolarized measurements after it had fully relaxed (typical 5-10 minutes at high magnetic field). Reference and polarized spectra were collected using identical acquisition parameters, particularly the receiver gain. The raw integrals of the relevant resonances in the polarized and unpolarized spectra were then used to determine the enhancement level.

Kinetics of hydride and ligand exchange

The ligand exchange studies were completed using the EXSY protocol[2]. A selected resonance was probed and the magnetisation flow was followed as a function of the reaction time between zero and 1 second, in steps typically of 0.1 seconds. The intensity data was then simulated using a differential model, bases on a least-mean squares fit to experiment, in order to extract the associated experimental site-exchange rate constants.

Table S1. Experimentally determined observed ligand exchange rate constants for **2** in methanol-d_4 solution in the 290 - 310 K temperature range.

Temp (K)	complex	H_2 loss (s^{-1})	Hydride exchange (s^{-1})	Pyridine exchange (s^{-1})	MeCN exchange (s^{-1})
290	**2c**	0.0138	-	0.025	0.214
295	**2c**	0.0286	-	0.050	0.353
	2d		-	0.018	0.150
	2a		-	0.009	0.106
298	**2b**		0.240	0.022	0.711
	2c	0.0449	0.057	0.073	0.466
300	**2c**	0.0565	0.116	0.097	0.559
	2d		0.225	0.040	0.218
	2a		0.034	0.014	0.195
305	**2c**	0.1038	0.235	0.182	0.921
	2d		0.580	0.103	0.342
	2a		0.101	0.029	0.388
310	**2b**		1.380	0.111	2.52
	2d		1.011	0.118	0.606
	2a		0.230	0.059	0.717

2. K.D. Atkinson, M.J. Cowley, P.I.P. Elliott, S.B. Duckett, G.G.R. Green, J. Lopez-Serrano, A.C.J. Whitwood, *J. Am. Chem. Soc.*, **2009**, *131*, 13362-13368.

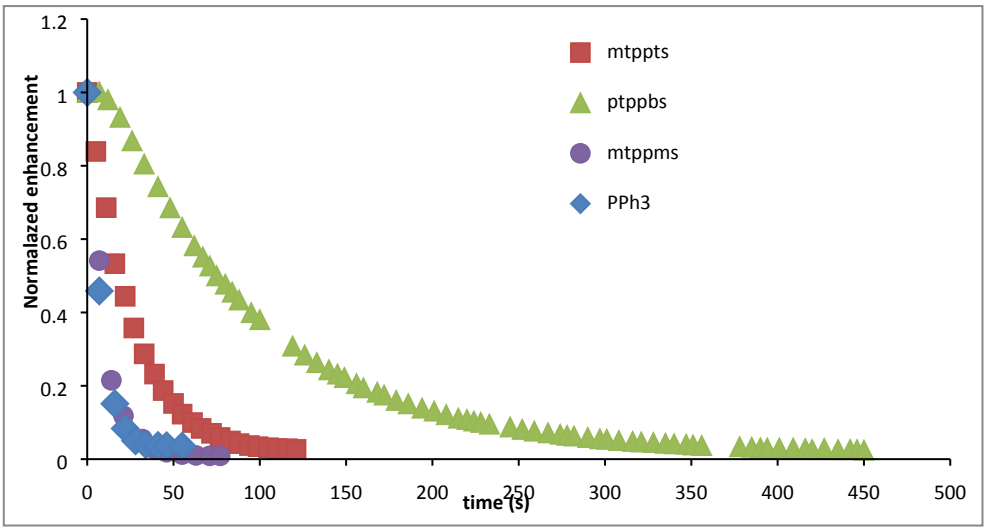


Figure S1. Plot of hydride signal enhancement versus time for 2

Table S2. Experimentally determined observed ligand exchange rate constants at 300 K for **2** and **4** in methanol-d_4

Complex	Hydride exchange (s^{-1})	Pyridine exchange (s^{-1})	MeCN exchange (s^{-1})
2a	0.507 ± 0.008	0.039 ± 0.004	0.966 ± 0.009
2b	0.034 ± 0.001	0.0143 ± 0.0004	0.195 ± 0.003
2c	0.064 ± 0.001	0.097 ± 0.001	0.559 ± 0.006
2d	0.360 ± 0.005	0.040 ± 0.005	0.218 ± 0.001
4a		1.23 ± 0.08	
4b		0.171± 0.004	

Experiments with ^{15}N labelled pyridine

When using ^{15}N labelled pyridine instead of normal pyridine we could observe an additional splitting of 19.0 Hz on the hydride NMR signal for the ligand which lies *trans* to the pyridine molecule, as shown in Figure S2.

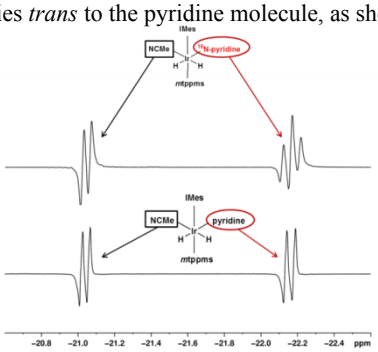


Figure S2. Hydride signals of complex **2c** in the corresponding ^{1}H NMR spectra using normal (lower) and ^{15}N labelled pyridine (upper).

Field dependent polarisation transfer studies

The reaction chamber contained a solution comprising the Ir-complex (5 mM), the ligand for polarization (5 - 20 fold excess) and 3 mL of the specified deuterated solution. *Para*hydrogen, prepared by cooling hydrogen gas over charcoal in a copper block at 30 K, was then bubbled through the solution at the pressure of 3 bar for the range of times which was present. The solution was then allowed to settle for 1 s before a single scan ^{1}H NMR spectrum was collected.

The polarization transfer field profile of the absolute values of the total signal enhancement for pyridine in methanol-d_4 solution, catalyzed by the highlighted complex, is shown in Figure S3.

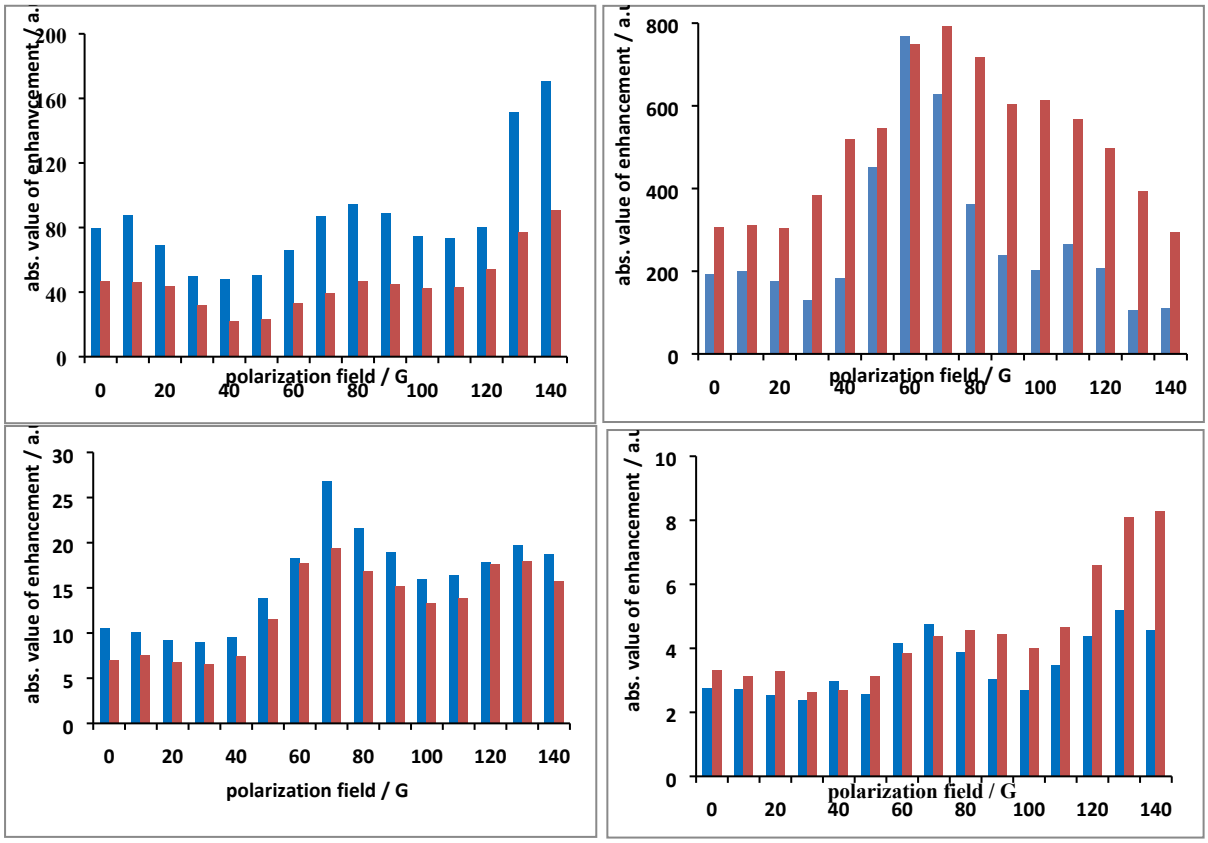


Figure S3. Absolute values of the total signal enhancement of pyridine in methanol-d_4 solution using **2c** (upper left), **4a** (upper right**)**, **4b** (lower left), **4c** (lower right**)** complex with 2 (blue) and 34 (red) fold excesses of pyridine respectively as a function of polarization transfer field.

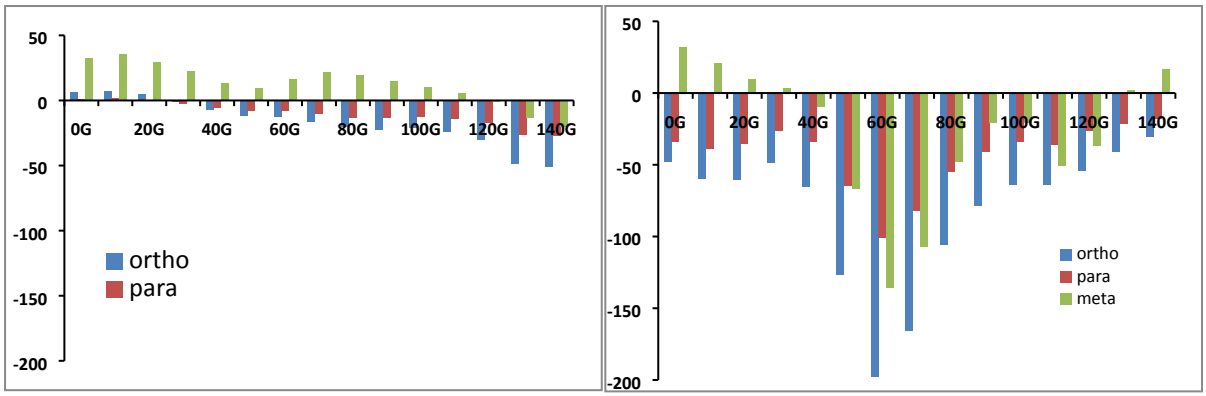


Figure S4: Polarisation transfer field profiles for the pyridine ^{1}H NMR signal enhancement in the methanol-d_4 solution using **2c** (left) and **4a** (right), when a 2-fold excess of acetonitrile is present.

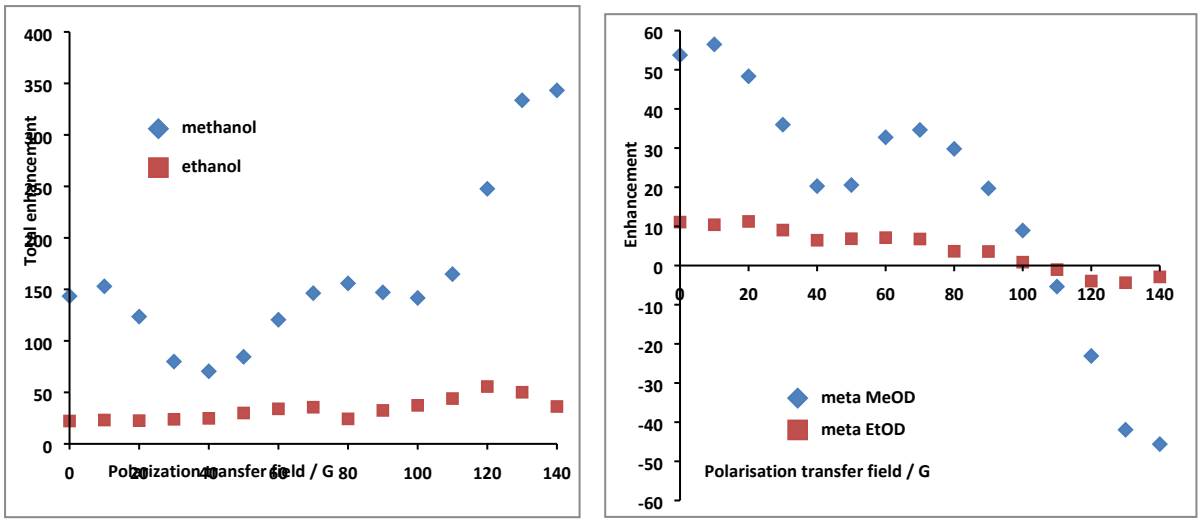


Figure S5: (left) Polarisation transfer field profiles for the pyridine total ^{1}H NMR signal enhancement (fold) in the methanol-d_4 and ethanol-d_6 solution. (right) PTF profile of the *meta* proton signal enhancement in the methanol-d_4 and ethanol-d_6 solution using [**2a**] = 5.5 mM, 20 fold pyridine, 2 fold NCMe, 3 mL solvent **.**

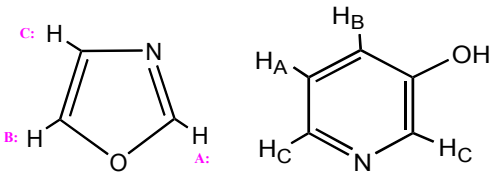


Figure S6: Structure of oxazole and 3-hydroxypyridine**.**

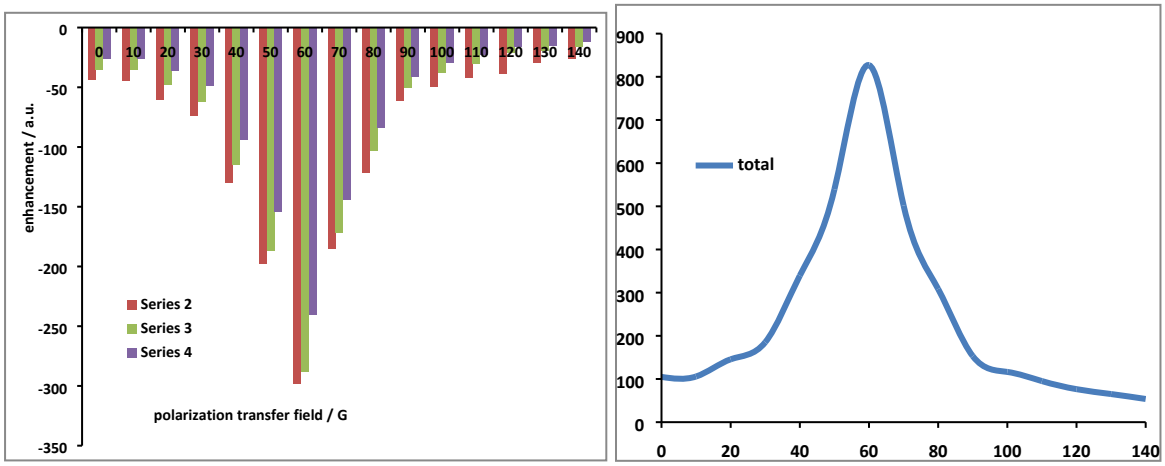


Figure S7: Left: Polarisation transfer field profile under SABRE of oxazole ^{1}H NMR signal enhancement in methanol-d_4 solution using **2c** as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe. **red**: H_A, **green**: H_B and **blue**: H_C. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.

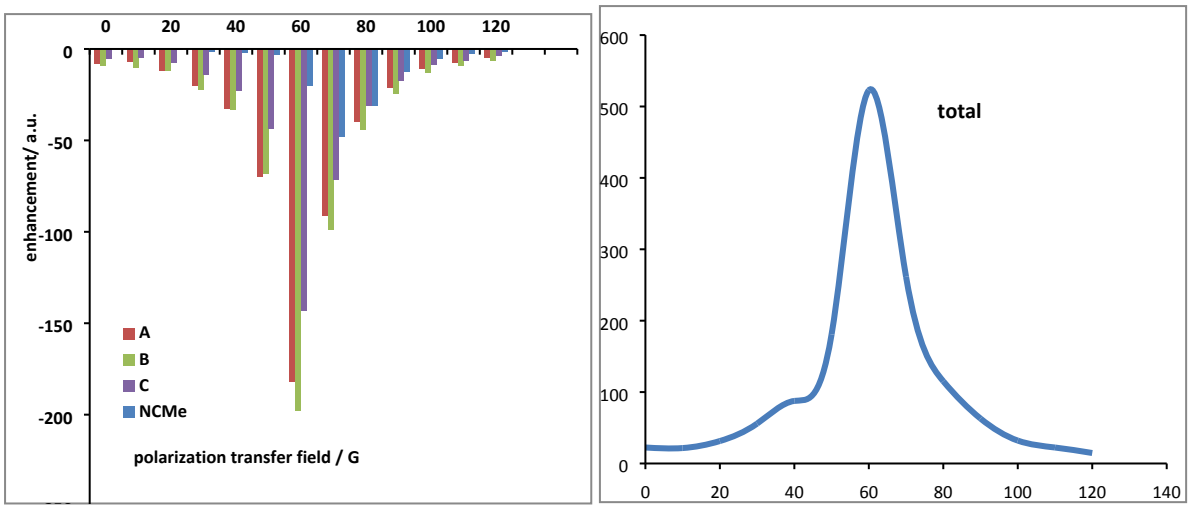


Figure S8: Left: Polarisation transfer field profile under SABRE of oxazole ^{1}H NMR signal enhancement in ethanol-d_6 solution using **2c** as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe. **red**: H_A, **green**: H_B and **blue**: H_C. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.

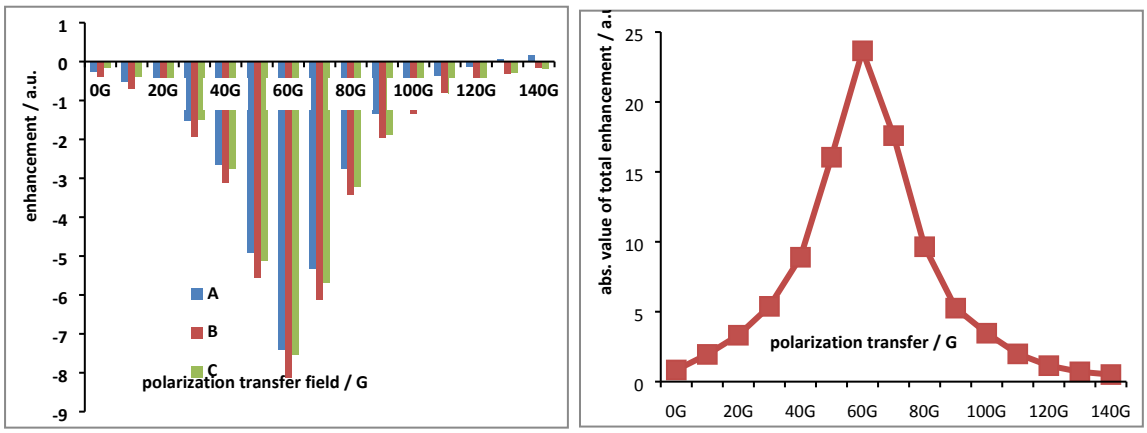


Figure S9: Left: Polarisation transfer field profile under SABRE of the oxazole ^{1}H NMR signal enhancement in methanol-d_4 solution using **4a** as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe **. blue**: H_A, **red**: H_B and : **green** H_C. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.

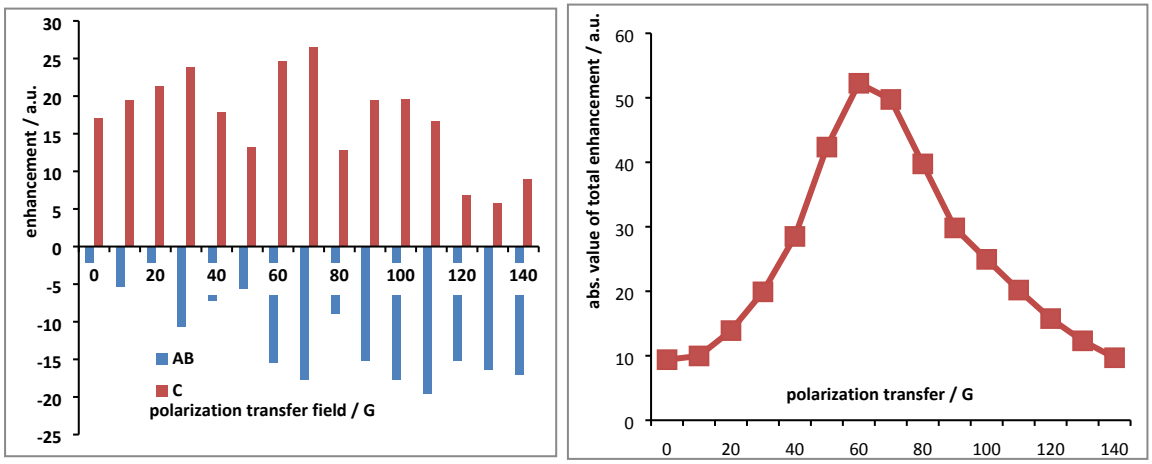


Figure S10: Left: Polarisation transfer field profile under SABRE of 3-hydroxypyridine ^{1}H NMR signal enhancement in methanol-d_4 solution using **2c** as the catalyst with a 5 fold excess of 3-hydroxypyridine. **blue**: H_A and H_B and : **red** H_C. Right: Absolute value plot of the total proton signal enhancement of 3-hydroxypyridine versus polarization transfer field under SABRE.

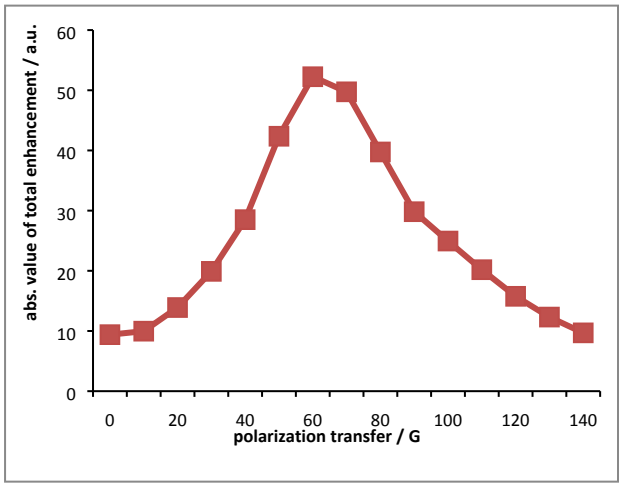


Figure S11: Polarisation transfer field profile of 3-hydroxypyridine proton signal enhancement in the methanol-d_4 solution using **4a** as the catalyst with a 5 fold excess of 3-hydroxypyridine.

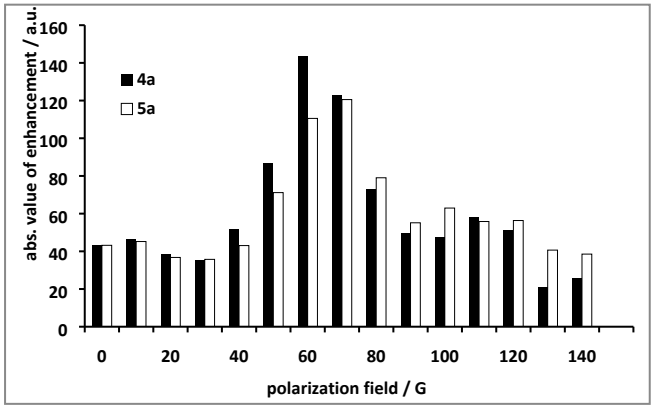
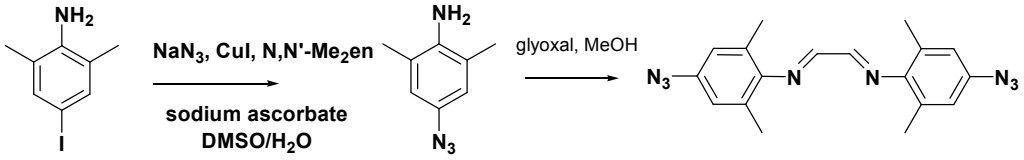


Figure S12: Absolute values of the total ^{1}H NMR signal enhancement of pyridine in methanol-d_4 solution using **4a** (black) and **5a** (white), when a 19-fold excess of pyridine is present.

Synthesis and characterisation

Preparation of the diimine precursor:



4-azidoaniline: 4-iodo-2,6-dimethylaniline[3] (24.4 g, 98.9 mmol, 1.0 eq.), NaN_3 (12.9 g, 197.9 mmol, 2.0 eq.) and N,N′-dimethylethylenediamine (1.60 mL, 14.9 mmol, 15 mol%) were dissolved in dmso/water (180 mL/45 mL). Ascorbic acid (1.70 g, 9.9 mmol, 10 mol%) and NaOH (400 mg, 9.9 mmol, 10 mol%) were added and the mixture degassed by argon bubbling for 20 min at 50 °C. CuI (1.90 g, 9.9 mmol, 10 mol%) was then added and the resulting mixture stirred at 50 °C for 4 hr. Brine (200 mL) was added and the aqueous layer extracted with 3 × 100 mL of diethyl ether, then dried over $MgSO_4$ and evaporated under reduced pressure to afford 12.6 g of a brownish oil (77.7 mmol, 79 %). ^{1}H NMR (400 MHz, dmso-d_6, 298 K): δ 2.07 (s, 6H, Me), 4.59 (s, 2H, NH_2), 6.59 (s, 2H,HAr). $^{13}C\{^1H\}$ NMR (101 MHz, dmso-d_6, 298 K): δ 17.8 (CH_3), 118.2 (Carom), 122.3 (Carom-N_3), 125.8 (Caro-CH_3),142.2 (Caro-NH_2).

N,N′-bis(4-azido-2,6-dimethylphenyl)1,4-diazabuta-1,3-diene: 4-azido-2,6-dimethylaniline (12.6 g, 77.9 mmol, 1.0 eq.) was dissolved in 44 mL of methanol at 50 °C. Glyoxal (30% w/w in water, 5.7 mL, 35 mmol, 0.45 eq.) and acetic acid (0.4 mL, 6.2 mmol, 0.21 eq.) added. The resulting mixture was stirred at room temperature for 4 h. A yellow solid separated. It was filtered and washed with cold methanol to afford, after drying under vacuum, 10.69 g of a yellow powder (30.9 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.11 (s, 12H, Me), 7.19 (s, 4H, HAr), 8.02 (s, 2H, Himine) . $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ 18.5 (CH_3), 118.8 (CHarom), 128.7 (Carom-N_3), 136.3 (Carom-CH_3), 146.8 (Carom-N), 163.7 (Cimine).

***N,N′*-bis{2,6-dimethyl-4-[4-(*N,N,N*-trimethyl)ammonio methyl]-1,2,3-1H-triazol-1-yl]phenyl}ethane-1,2-diamine dichloride hydrochloride**: *N,N′*-bis(4-azido-2,6-dimethylphenyl)-ethane-1,2-diamine (5.78 g, 16.50 mmol, 1 eq.), *N,N,N*-triimethylprop-2-yn-1-aminium chloride[4] (5.50 g, 41.2 mmol, 2.5 eq.) and [CuCl(SIMes)(4,7-Cl_2-phen)] catalyst (108 mg, 0.28 mmol, 1 mol%) were dissolved in 55 mL methanol. The mixture was stirred at room temperature overnight. The solvent was evaporated to yield brownish oil. An ethanolic solution of HCl (prepared by dropwise addition over 10 minutes with stirring of 4 mL (5 eq.) of acetyl chloride to 35 mL anhydrous ethanol) was added on the crude mixture which was vigorously stirred until a beige solid was obtained. The product was recovered by filtration and washed with 2x100mL Et_2O and dried in vacuum to give 11.12 g of a beige powder (16.1 mmol, 98%). ^{1}H NMR (400 MHz, dmso-d_6, 298 K): δ 2.54 (s, 12H, CH_3). 3.54 (s, 18H, CH_3), 4.80 (s, 4H, NH_2) 5.01 (s, 4H, Ctriazole-CH_2), 7.72 (s, 4H, -CH=), 9.12 (s, 2H, -CHtriazole). $^{13}C\{^1H\}$ NMR: (101 MHz, dmso-d_6, 298 K): δ 18.7 (CH_3), 46.8 (NH-CH_2-CH_2-NH), 52.1 (CH_3-N), 59.1 (CH_2-N^+), 121.1 (-CH, arom), 126.4 (-CH=, triazole), [132.7, 133.0, 136.4, 139.6 (=C-)]. HRMS (ESI+): calcd. for $C_{30}H_{46}N_{10}^{2+}$ [M-2HCl-2Cl]$^{2+}$: 273.1948. Found: 273.1923.

***N,N′*-bis{2,6-dimethyl-4-[4-(*N,N,N*-tri-(methyl) ammonio methyl]-1,2,3-1H-triazol-1-yl]phenyl} imidazolinium chloride (SIMesTrimet.HCl$_3$, s3b)** : 1.20 g (1.74 mmol) of *N,N′*-bis{2,6-dimethyl-4-[4-(*N,N,N*-trimethyl) ammoniomethyl]-1,2,3-1H-triazol-1-yl]phenyl}ethane-1,2-diamine dichloride hydrochloride was dissolved in 24 mL of anhydrous methanol. 12 mL of trimethyl orthoformate and 3 drops of formic acid were then added. The resulting suspension was refluxed overnight prior to the solvent being removed on a rotary evaporator. The crude salt was then taken up into 170 mL of water and the resulting solution heated to boiling in an open flask for 2.5 h. Activated charcoal was added until a colourless supernatant was obtained. Charcoal was then removed by vacuum filtration over a silica plug and the water was rotary evaporated. Finally, the resulting white solid was dissolved in 15 mL of methanol, and the product precipitated, under stirring, by dropwise addition of 70 mL of acetone. The resulting white solid was recovered by filtration (996 mg, 1.50 mmol, 86%). ^{1}H NMR (400 MHz, dmso-d_6, 298 K): δ 2.56 (s, 12H, CH_3), 3.15 (s, 18H, N^+-CH_3), 4.60 (s, 4H, N-CH_2-CH_2-N), 4.82 (s, 4H, Ctriazole-CH_2), 7.98 (s, 4H, CH=arom) 9.25 (s, 2H, -CH=triazole), 9.40 (s, 1H, NCHN) $^{13}C\{^1H\}$ NMR (101 MHz, dmso-d_6, 298 K): δ 17.7 (CH_3) 51.0 (CH_2Im), 52.0 (CH_3-N), 60.0 (CH_2-N^+), 120.5 (-CH=Ar), 126.8 (-CH= triazole), [133.6, 136.8(2C), 138.3 (=C-)], 160.8 (NCHN). HRMS(ESI+): calcd. for $C_{31}H_{45}N_{10}^{3+}$ [M-3Cl]$^{3+}$: 185.7937. Found: 185.7887.

***N,N′*-bis(4-(4-hydroxymethyl–1,2,3-^{1}H-triazolyl)-2,6-dimethylphenyl)-1,4-diazabuta-1,3-diene**: *N,N′*-bis(4-azido-2,6-dimethylphenyl)-1,4-diazabuta-1,3-diene (2.60 g, 7.50 mmol, 1 eq.) and propargyl alcohol (1.0 mL, 975 mg, 17.4 mmol, 2.3 eq.) as well as [CuCl(SIMes)(4,7-Cl_2-phen)][5] (24 mg, 0.5 mol–%) were added to a mixture of methanol (8 mL) and ethyl acetate (35 mL). The resulting solution was stirred at 60°C for 2 days after which time a yellow precipitate was observed. The desired compound was recovered by filtration and washing successively with

3. H. Ibrahim, C. Gibard, A. Hospital, C. Gaulier, N. Hewitt, A. Gautier and F. Cisnetti, *Protocol Exchange*, 2012, doi: 10.1038/protex.2012.058.
4. C. Gaillard, P. Adumeau, J.-L. Canet, A. Gautier, D. Boyer, C. Beaudoin, C. Hesling, L. Morel and R. Mahiou, J. Mater. Chem (B). 2013, 1, 4306-4312.
5. M.-L. Teyssot, L. Nauton, J.-L. Canet, F. Cisnetti, A. Chevry and A. Gautier, Eur. J. Org. Chem., 2010, 2010, 3507-03515.
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cold ethyl acetate, and cold diethyl ether/acetone v/v 1:1. 3.160 g of a yellow powder (6.89 mmol, 92%) was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 298 K): δ 2.23 (s, 12H, Me), 4.61 (d, 4H, J =5.3 Hz, CH_2), 5.53 (t, 2H, J =5.3 Hz, OH), 7.70 (s, 4H, H_{Ar}), 8.28 (s, 2H, H_{imine}), 8.63 (s, 2H, $H_{triazole}$). ^{13}C NMR (^{13}C-^{1}H HSQC, dmso-d_6, 298 K): 17.7 (CH_3), 54.6 (CH_2), 119.8 (CH=arom), 127.5 (-CH= triazole). Very poor solubility in common NMR solvents prevented the recording of a standard ^{13}C NMR spectrum. HRMS(ESI$^+$): calcd. for $C_{24}H_{26}N_8O_2^+$ $[M^+H]^+$: 459.2252. Found: 459.2233.

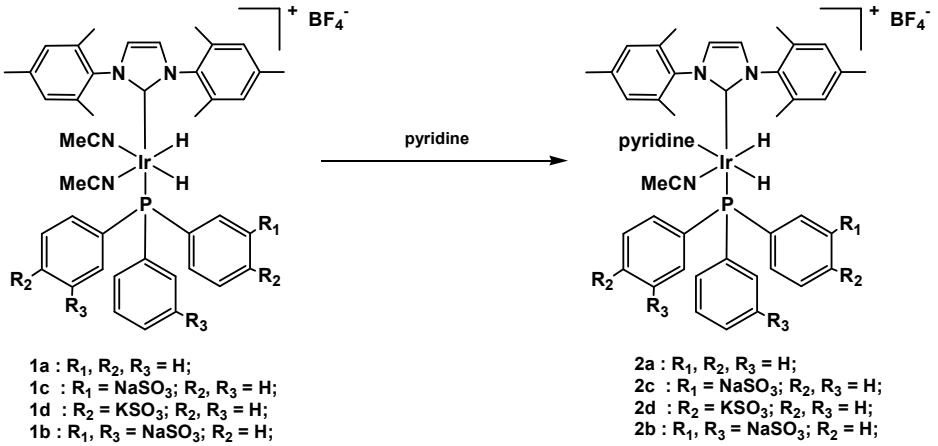
***N*,*N*′-bis(4-(4-hydroxymethyl–1,2,3-1H-triazolyl)-2,6-dimethylphenyl)imidazolium chloride (IMesOH.HCl, s3c)** : *N*,*N*′-bis(4-(4-hydroxymethyl–1,2,3-triazolyl)-2,6-dimethylphenyl)1,4-diazabuta-1,3-diene (ESI) (900 mg, 1.96 mmol, 1 eq.) was added to 15 mL of freshly distilled dmso in a flask under argon. Pivaloyloxymethyl chloride (430 µL, 449 mg, 2.98 mmol, 1.52 eq) was added dropwise to the reaction medium. The reaction was allowed to proceed at 50° overnight. After cooling to room temperature, the resulting dark solution was added to 100 mL acetone. After 30 minutes of vigorous stirring, a brownish solid was recovered by filtration (661 mg, 1.30 mmol, 66%). ^{1}H NMR (400 MHz, dmso-d_6, 298 K): δ 2.32 (s, 12H, Me), 4.65 (s, 4H, CH_2), 8.07 (s, 4H, HAr), 8.48 (s, 2H, NCHCHN), 8.85 (s, 2H, Htriazole), 10.04 (s, 1H, NCHN), . OH not detected due to exchange with traces of water. ^{13}C{^{1}H} NMR: δ 17.3 (CH_3), 54.9 (CH_2), 119.7 (-CH=arom), 121.2 (-CH=Im), 124.8 (-CH=triazole), [139.1, 137.8, 137.1, 132.9, (-C=)], 149.67 (NCHN). HRMS (ESI$^+$): calcd. for $C_{25}H_{27}N_8O_2^+$ [M-Cl]$^+$: 471.2252. Found: 471.2249.

Characterization of iridium complexes

NMR data for [Ir(H)$_2$(NCMe)(py)(IMes)(*m*tppts)]BF$_4$ (2b): ^{1}H NMR (400 MHz, methanol-d$_4$, 298 K): δ -21.97 (dd, 1H, J_{HP} = 18.4 Hz, J_{HH} = 7.2 Hz), δ -21.07 (dd, 1H, J_{HP} = 16.6 Hz, J_{HH} = 6.7 Hz) 1.73 (s, 3H, NCCH_3), 1.94 (s, 6H, -CH_3 of IMes), 2.09 (s, 6H, -CH_3 of IMes), 2.37 (s, 6H, -CH_3 of IMes), (s, 4H, -C*H*=), 6.76 (t, 2H, *meta* proton of pyridine), 7.01 (s, 2H, -C=, IMes), 7.08 (s, 2H, -CH=), 7.13 (t, 4H, *m*tppts), 7.25 (t, 4H, *m*tppts), 7.34 (t, 2H, *meta* proton of pyridine), 7.51 (s, 2H, -CH=, IMes), 7.62 (s, 2H, -CH=, IMes), 7.66 (t, 1H, *para* proton of pyridine), 7.75 (t, 4H, *m*tppts), 7.97 (d, 2H, *ortho* proton of pyridine). **^{31}P{^{1}H} NMR** (162 MHz, MeOD, 298 K): δ 24.3 ppm.

NMR data for [Ir(H)$_2$(NCCH$_3$)(py)(IMes)(*m*tppms)]BF$_4$ (2c): ^{1}H NMR (400 MHz, methanol-d$_4$, 298 K): δ -22.17 (dd, 1H, J_{HP} = 18.5 Hz), δ -21.05 (dd, 1H, J_{HP} = 16.3 Hz), 1.61 (s, 3H, NCCH_3), 1.89 (s, 6H, -CH_3 of IMes), 2.11 (s, 6H, -CH_3 of IMes), 2.39 (s, 6H, -CH_3 of IMes), (s, 4H, -C*H*=), 6.76 (t, 2H, *meta* proton of pyridine), 6.95 (s, 2H, -C=, IMes), 7.07 (t, 4H, mtppms)), 7.10 (s, 2H, -CH=, IMes), 7.16 (t, 4H, *m*tppms), 7.25 (s, 2H, IMes), 7.30 (m, 6H, mtppms), 7.51 (t, 1H, *para* proton of pyridine), 7.67 (t, 2H, *m*tppts), 7.77 (d, 2H, *ortho* proton of pyridine). **^{31}P{^{1}H} NMR** (162 MHz, methanol-d$_4$, 298 K): δ 18.27 ppm.

NMR data for [Ir(H)$_2$(NCCH$_3$)(py)(IMes)(*p*tppbs)]BF$_4$ (2d): ^{1}H NMR (400 MHz, methanol-d$_4$, 298 K): δ -22.23 (dd, 1H, J_{HP} = 19.1 Hz), δ -21.08 (dd, 1H, J_{HP} = 16.2 Hz), 1.61 (s, 3H, NCCH_3), 1.89 (s, 6H, -CH_3 of IMes), 2.11 (s, 6H, -CH_3 of IMes), 2.39 (s, 6H, -CH_3 of IMes), (s, 4H, -C*H*=), 6.78 (t, 2H, *meta* proton of pyridine), 6.83 (t, 1H, *p*tppbs), 6.95 (s, 2H, -C=, IMes), 7.10 (s, 2H, -CH=, IMes), 7.19 (t, 4H, *p*tppbs), 7.26 (s, 2H, IMes), 7.30 (m, 6H, *p*tppbs), 7.51 (t, 1H, *para* proton of pyridine), 7.55 (d, 1H, *p*tppbs), 7.62 (d, 1H, *p*tppbs), 7.71 (d, 2H, *ortho* proton of pyridine). **^{31}P{^{1}H} NMR** (162 MHz, methanol-d$_4$, 298 K): δ 19.82 ppm.



Scheme S1. Ligand variation in **1** and **2**

NMR data for [Ir(H)$_2$(pyridine)$_3$(SIMesCh)]$^+$ (4a) : ^{1}H NMR (400 MHz, methanol-d$_4$, 298 K): δ -22.54 (2H, hydrides), 2.57-2.53 (br, 24H, CH(CH_3)$_2$), 2.70 (m, 4H, CH(CH_3)$_2$), 4.89 (d, J_{HH} = 5.95 Hz), 5.29 (br, 2H, OH), 7.14 (t, 1H, *para* proton, py$_{ax}$), 7.65 (t, 2H, *meta* proton py$_{ax}$), 7.74 (t, 1H, *para* py$_{eq}$) 7.77 (s, 2H, H_{Ar}), 7.83 (s, 2H, H_{Ar}), 7.95 (s, 2H, NCH-

CHN), 8.17 (t, 1H, *para* proton py_{ax}), 8.40 (d, 2H, *ortho* proton py_{eq}), 8.70 (d, 2H, *ortho* proton py_{ax}), 8.98 (s, 1H, $H_{triazole}$), 9.03 (s, 1H, $H_{triazole}$).

NMR data for $[Ir(H)_2(pyridine)_3(SIMesTrimet)]^+$ (4b) : ^{1}H NMR (400 MHz, methanol-d_4, 298 K): δ -22.72 (2H, hydrides), 2.65 (s, 12H, $CH(CH_3)_2$), 3.29 (12H, $(CH_3)_2$-N^+), 4.16 (4H, -CH_2-imid), 4.74 (s, 4H, N^+-CH_2-$C_{triazol}$), 6.71 (t, 2H, *meta* proton py_{eq}), 7.71 (t, 1H, *para* proton py_{eq}), 7.96 (s, 2H, -C*H*=, $H_{Ar,}$), 8.20 (d, 2H, *ortho* proton py_{eq}), 8.751 (d, 2H, *ortho* proton py_{ax}), 8.80 (s, 2H, $H_{triazole}$), 9.06 (s, 1H, $H_{triazole}$).

NMR data for $[Ir(H)_2(pyridine)_3(IMesOH)]^+$ (4c) : ^{1}H NMR (400 MHz, methanol-d_4, 298 K): δ -22.66 (2H, hydrides), 8.78 (d, 2H, *ortho* proton py_{ax}), 8.35 (d, 2H, *ortho* proton py_{eq}), 8.49 (s, 2H, -C*H*=, imid), 8.31 (t, 1H, *para* proton py_{ax}), 8.09 (t, 2H, *meta* proton py_{ax} and 2H, -C*H*=, triazol), 7.80 (s, 2H, -C*H*=, $H_{Ar,}$), 7.67 (t, 1H, *para* proton py_{eq}), 7.25 (t, 2H, *meta* proton py_{eq}), 4.85 (s, 4H, -CH_2-$C_{triazol}$), 2.84 (4H, -CH_2-imid),2.30 (s, 12H, $CH(CH_3)_2$).

NMR data for $[Ir(H)_2(NCMe)(pyridine)_2(SIMesCh)]^+$ (5a) : ^{1}H NMR (400 MHz, methanol-d_4, 298 K) δ -21.15 (d, J_{HH} = 5 Hz, *trans* to NCMe) and -22.26 (d, J_{HH} = 5 Hz, *trans* to pyridine).

NMR data for $[Ir(H)_2(NCMe)(pyridine)_2(SIMesTrimet)]^+$ (5b) : ^{1}H NMR (400 MHz, methanol-d_4, 298 K) δ -21.24 (d, J_{HH} = 5 Hz, *trans* to NCMe) and -22.38 (d, J_{HH} = 5 Hz, *trans* to pyridine).

NMR data for $[Ir(H)_2(NCMe)(pyridine)_2(IMesOH)]^+$ (5c) : ^{1}H NMR (400 MHz, methanol-d_4, 298 K) δ -21.06 (d, J_{HH} = 5 Hz, *trans* to NCMe) and -22.17 (d, J_{HH} = 5 Hz, *trans* to pyridine).