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

Hyperpolarization through reversible interactions with *para*hydrogen

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Supplementary Information

1. General

All experimental procedures were performed under an atmosphere of either dinitrogen or argon, using standard Schlenk line techniques or an MBraun Unilab glovebox, unless otherwise stated. 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. Materials were purchased from commercial suppliers unless stated otherwise and were used as supplied. Hyperpolarisation NMR measurements were made on a Bruker Avance III series 400 MHz NMR spectrometer (^{1}H at 400.13 MHz, ^{13}C at 100 MHz). Characterisation of **1-NHC** and **3-NHC** complexes were made using Bruker Avance 400, 500 and 600 MHz NMR spectrometers. NMR samples were made up in Young's tap equipped 5 mm NMR tubes. *Para*hydrogen was prepared by cooling hydrogen gas over Fe_2O_3 at 30 K.

2. Synthesis

Synthesis of **1-NHC**[1]

NHC.hydrochloride (1.8 eq.) and potassium *tert*-butoxide (1.8 eq.) were added to a Schlenk flask. Dry THF was added to the flask and the mixture was stirred for 30 min. $[IrCl(COD)]_2$ (1 eq.) was dissolved in a minimum volume of dry THF, the resulting solution then added to the first Schlenk by cannula transfer and stirred for 1 hour. The solvent was then removed under vacuum and the resulting solid was purified by column chromatography with an eluent of DCM:Acetone (19:1) resulting in a yellow/orange powder (64 % **1-IMes**, 77 % **1-SIMes**, 12 % **1-ICy**, 37 % **1-IPr**, 41 % **1-SiPr**, 63 % **1-IMe** and 75 % **1-ImMe$_2$*N*Pr$^i_2$**).

Abbreviations for the various NHCs are:

IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene

SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene

ICy = 1,3-bis(cyclohexyl)-imidazole

IPr = 1,3-bis(2,6-diisopropyl)-imidazol-2-ylidene

SiPr = 1,3-bis(2,6-diisopropyl)-4,5-dihydroimidazol-2-ylidene

IMe = 1,3-bis(methyl)-imidazol-2-ylidene

$ImMe_2NPr^i_2$ = 1,3-bis(isopropyl)-imidazol-4,5-diemthyl-2-ylidene

Synthesis of ICy.HCl

Cyclohexylamine (4.96 g, 50 mmol) was added to toluene (50 ml) in a 250 ml round bottomed flask. Under N_2 and with intense stirring, paraformaldehyde (1.5 g, 50 mmol) was added. This was stirred vigorously for 30 min at room temperature and then cooled to 0 °C. A further portion of cyclohexylamine (4.96 g, 50 mmol) was added and the solution stirred at 0 °C for a further 10 min. 3.3 M HCl (15 ml, 50 mmol) was then added drop-wise over 10 min and the solution allowed to warm up to room temperature. 40 % aqueous glyoxal (72.5 ml, 50 mmol) was added slowly and stirred at 50 °C for 12 hr. It was then allowed to cool. Diethyl ether (50 ml) was added followed by saturated sodium carbonate solution (25 ml). The organic layer was collected and the aqueous layer was washed further with diethyl ether (3 x 50 ml). The combined organic fractions were concentrated *in vacuo*. The residue was taken up in dichloromethane (75 ml), dried with magnesium sulphate, filtered and solvent removed *in vacuo* to afford ICy.HCl as a light brown solid. Yield = 1.35 g (12 %). It was immediately stored under N_2.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): 10.97 (s, 1H, N-CH-N), 7.31 (s, 2H, N-CH-CH-N), 4.59 (tt, J = 12.0, 3.8 Hz, 2H, CH^{cy}), 2.24 (d, J = 11.5 Hz, 4H, CH_2^{cy}), 1.93 (dm, J = 13.9 Hz, 4H, CH_2^{cy}), 1.76 (m, 4H, CH_2^{cy}), 1.52 (qt, J = 13.2, 3.2 Hz, 4H, CH_2^{cy}), 1.28 (qt, J = 13.1, 3.7 Hz, 4H, CH_2^{cy}).

^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 298 K): 136.6 (N-CH-N), 119.1 (N-CH-CH-N), 59.7 (CH^{cy}), 33.53 (CH_2^{cy}), 24.8 (CH_2^{cy}), 24.6 (CH_2^{cy}).

MS (ESI) *m/z*: 234 (ICy–Cl), 233 (ICy–Cl–H)

Synthesis of $ImMe_2NPr^i_2$[2,3]

Step1

Diisopropylthiourea (16.03 g, 100 mmol), 3-hydroxybutanone (9.69 g, 110 mmol) and pentan-1-ol (65 ml) were added to a round bottom flask equipped with a magnetic stirrer, dean stark trap and reflux condenser. The resulting solution was heated in an oil bath for 48 hours at 142 °C, at which point no more water was produced indicating complete conversion. The mixture was allowed to cool overnight. The solution was then filtered under vacuum and washed several times with cold methanol (-20 °C).The product was further dried in a Schlenk

tube for 48 hours. Yield =13.0 g (61 %). Other than mass spectrometry data (ESI m/z= 213), no other spectroscopic data was collected.

Step 2

To the product obtained in step 1 (1.06 g, 5 mmol) was added DME (30 ml) under a dinitrogen atmosphere. The reaction vessel was bathed in dry ice prior to the addition of potassium (0.5 g, 12.79 mmol) in small quantities. Once potassium addition was complete, the mixture was refluxed for 4 hours at 88 °C and then allowed to cool overnight. The mixture was filtered through a cannula to a clean Schlenk tube and evaporated to dryness to afford an orange/brown powder. Dry hexane (45 ml) was added to the powder and stirred for 1.5 hours. The solution was then pipetted off and evaporated to dryness. This process afforded yellow crystals of $ImMe_2iPr_2$, which was immediately transferred to a glove box for storage. Yield = 0.81 g (90 %).

^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): 4.95 (sept, 2H, N(1,3)-CH(CH_3)$_2$, ^{3}J= 6.74), 2.40 (s, 6H, C(4,5)-CH_3), 1.61 (d, 12H, N(1,3)-CH(CH_3)$_2$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, 298 K): δ=209.27 (C(2)), 126.6 (C(4,5)), 50.40 (N(1,3)-CH(CH_3))$_2$), 22.03 (N(1,3)-CH(CH_3)$_2$), 7.72 [C(4,5) – CH_3].

3. Characterisation of active complexes in the presence of pyridine

a. [Ir(IMes)(py)$_3$(H)$_2$]Cl, 3-IMes

[Ir(IMes)(COD)Cl] (2.0 mg, 0.0031 mmol) and pyridine (5 μL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (CD_3OD, 500 MHz, 243 K): 8.34 (d, J = 4.98 Hz, 4H, orthoH, py *trans* to hydride), 8.09 (d, J= 5.43 Hz, 2H, orthoH, py *cis* to hydride), 7.79 (tt, J = 7.53, 1.46 Hz, 2H, paraH, py *trans* to hydride), 7.69 (t, J = 7.67 Hz, 1H, paraH, py *cis* to hydride), 7.18 (s, 2H, N-CH-CH-N), 7.14 (m, 4H, metaH, py *trans* to hydride), 6.99 (m, 2H, metaH, py *cis* to hydride), 6.67 (s, 4H, CH^{mes}), 2.20 (s, 6H, *p*CH_3^{mes}), 2.06 (s, 12 H, *o*CH_3^{mes}), −22.52 (s, 2H, hydrides)

^{13}C{^{1}H} NMR (MeOD, 151 MHz, 243 K): 194.0 (NCN), 167.5 (N-Cmes), 155.3 (orthoC, py *cis* to hydride), 154.3 (orthoC, py *trans* to hydride), 138.2 (Car), 136.3 (paraC, py *cis* to hydride), 135.8 (paraC, py *trans* to hydride), 135.1 (Car), 128.4 (CHar), 125.3 (metaC, py *cis*

to hydride), 125.2 (metaC, py *trans* to hydride), 122.4 (NCHCHN), 19.7 (paraCH_3mes), 17.7 (orthoCH_3mes).

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 194.5 (Carbene N), 255.6 (py *trans* to Hydride), 239.1 (py *cis* to hydride).

b. [Ir(SIMes)(py)$_3$(H)$_2$]Cl, 3-SIMes

[Ir(SIMes)(COD)Cl] (2.0 mg, 0.0031 mmol) and pyridine (5 µL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (MeOD, 600 MHz, 298 K): 8.32 (broad, 4H, orthoH, py *trans* to hydride), 7.97 (d, J = 4.39 Hz, 2H, orthoH, py *cis* to hydride), 7.76 (broad, 2H, paraH, py *trans* to hydride), 7.66 (tt, J = 7.56, 1.64 Hz, 1H, paraH, py *cis* to hydride), 7.12 (broad, 4H, metaH, py *trans* to hydride), 6.97 (t, J = 6.72 Hz, 2H, metaH, py *cis* to hydride), 6.63 (s, 4H, $CH^{Ar,\ mes}$), 3.90 (s, 4H, N-CH_2-CH_2-N), 2.27 (s, 12H, orthoCH_3^{mes}), 2.16 (s, 6H, paraCH_3^{mes}), -22.69 (s, 2H, hydrides).

^{13}C{^{1}H} NMR (MeOD, 126 MHz, 298 K): 208.6 (N-C-N), 179.7 (N-Cmes), 154.8 (orthoC, py *trans* to hydride), 154.0 (orthoC, py *cis* to hydride), 148.6 (orthoC, free py), 138.4 (paraC, py *trans* to hydride), 137.1 (paraC, free py), 136.4 (C^{ar}), 135.9 (paraC, py *cis* to hydride), 128.7 (CH^{ar}), 128.4 (C^{ar}), 125.1 (metaC, py *cis* to hydride), 124.9 (metaC, py *trans* to hydride), 50.4 (N-CH_2-CH_2-N), 19.4 (paraCH_3^{mes}), 17.4 (orthoCH_3^{mes}).

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 208.6 (Carbene N), 254.7 (N, pyridine *trans* to hydride), 240.1 (N, pyridine *cis* to hydride).

c. [Ir(IPr)(py)$_3$(H)$_2$]Cl, 3-IPr

[Ir(IPr)(COD)Cl] (2.3 mg, 0.0031 mmol) and pyridine (5 µL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (CD_3OD, 500 MHz): 8.22 (4H, orthoH bound *trans,* Py), 7.91 (d, 2H, orthoH bound *cis,* Py), 7.75 (2H, paraH bound *trans*, Py), 7.71 (1H, t, paraH bound *cis,* Py), 7.34 (d, 2H, CH^{Ar}), 7.16 (4H metaH bound *trans,* Py), 7.14 (4H, CH^{Ar}), 7.00 (2H metaH bound *cis,* Py)

6.98 (t, 2H, NCH=CHN), 2.94 (m, 4H, CH), 1.20 (d, J_{HH} = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.15 (d, J_{HH} = 6.8 Hz, 12H, $CH(CH_3)_2$), -22.60 (2H, bound H).

$^{13}C\{^1H\}$ NMR (MeOD, 151 MHz): 155.17 (C, C^{Ar}), 153.74 (C, C^{Ar}), 145.78 (CH, CH^{Ar}), 129.64 (CH, CH^{Ar}), 123.55 (CH, NCH=CHN), 29.28 (CH, $CH(CH_3)_2$), 28.77 (CH_3, $CH(CH_3)_2$) 26.34 (CH, $CH(CH_3)_2$) 24.99 (CH_3, $CH(CH_3)_2$) 20.90 (CH_3, $CH(CH_3)_2$)

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 255.15 (N, pyridine *trans* to hydride), 238.92 (N, pyridine *cis* to hydride), 194.42 (N, Ir-C-$(NR)_2$).

d. [Ir(SiPr)$(py)_3(H)_2$]Cl, 3-SiPr

[Ir(SiPr)(COD)Cl] (2.3 mg, 0.0031 mmol) and pyridine (5 μL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^1H NMR (MeOD, 500 MHz, 253 K): 8.20 (q, J=4.9 Hz, 4H, orthoH bound *trans,* py), 7.83 (d, J=5.36 Hz, 2H, orthoH bound *cis,* Py), 7.79 (t, J=6.3 Hz, 2H, paraH bound *trans*, Py), 7.71 (t, J=7.6 Hz, 1H, t, paraH bound *cis,* Py), 7.22 (m, 2H, CH^{Ar}), 7.21 (m, 4H, metaH bound *trans,* Py), 7.08 (d, J=7.72 Hz, 4H, CH^{Ar}), 7.02 (m, 2H, metaH bound *cis,* Py), 4.11 (s, 4H, NCH_2=CH_2N), 3.44 (sep, J=6.8 Hz, 4H, CH^{iPr}), 1.26 (d, J = 6.79 Hz, 12H, C**H**$_3^{iPr}$), 1.19 (m, 12H, C**H**$_3^{iPr}$), -22.24 (s, 2H, hydride).

$^{13}C\{^1H\}$ NMR (MeOD, 126 MHz, 253 K): 182.91 (carbene carbon), 153.56 (orthoC bound *trans,* py), 154.72 (orthoC bound *cis,* Py), 146.3 ($iPrC^{Ar}$), 139.41 (NC^{Ar}), 136.88 (paraC bound *cis,* Py), 136.42 (paraC bound *trans*, Py), 128.63 (CH^{Ar}), 125.81 (metaC bound *trans,* Py), 124.06 (CH^{Ar}), 125.28 (metaC bound *cis,* Py), 53.8 (NCH_2=CH_2N), 28.59 (CH^{iPr}), 25.4 (CH_3^{iPr}), 21.5 (CH_3^{iPr}).

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 254.5 (N, pyridine *trans* to hydride), 239.17 (N, pyridine *cis* to hydride), 138.9 (N, Ir-C-$(NR)_2$).

e. [Ir(ICy)$(py)_3(H)_2$]Cl, 3-ICy

[Ir(ICy)(COD)Cl] (1.8 mg, 0.0031 mmol) and pyridine (5 μL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (MeOD, 400 MHz, 280 K): 8.75 (d, J = 4.82 Hz, 4H, orthoH, py *trans* to hydride), 8.31 (d, J = 5.04 Hz, 2H, orthoH, py *cis* to hydride), 8.00 (tt, J = 7.69, 1.54 Hz, 2H, paraH, py *trans* to hydride), 7.94 (tt, J = 7.69, 1.54 Hz, 1H, paraH, py *cis* to hydride), 7.47 (under free py signal, correlation observed in COSY, metaH, py *trans* to hydride), 7.27 (m, 2H, metaH, py *cis* to hydride), 7.22 (s, 2H, N-CH-CH-N), 4.30 (m, 2H, CH^{Cy}), 2.25-0.6 (m, 20H, CH_2^{Cy}), -22.49 (s, 2H, hydrides).

^{13}C{^{1}H} NMR (MeOD, 101 MHz, 280 K): 197.6 (N-C-N), 156.4 (orthoC, py *cis* to hydride), 154.7 (orthoC, py *trans* to hydride), 137.39 (paraC, py *trans* to hydride), 136.8 (paraC, py *cis* to hydride), 126.3 (metaC, py *trans* to hydride), 125.9 (metaC, py *cis* to hydride), 117.7 (N-CH-CH-N), 59.2 (CH^{Cy}), 33.0 (CH_2^{Cy}), 25.6 (CH_2^{Cy}), 24.8 (CH_2^{Cy}).

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 254.0 (N, pyridine *trans* to hydride), 236.3 (N, pyridine *cis* to hydride), 202.4 (N, Ir-C-$(NR)_2$).

f. [Ir(IMe)(py)$_3$(H)$_2$]Cl, 3-IMe

[Ir(IMe)(COD)Cl] (1.3 mg, 0.0031 mmol) and pyridine (5 µL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (MeOD, 400 MHz, 280 K): 8.67 (m, 4H, orthoH, py *trans* to hydride), 8.44 (m, 2H, orthoH, py *cis* to hydride), 8.01 (m, 2H, paraH, py *trans* to hydride), 7.99 (m, 1H, paraH, py *cis* to hydride), 7.45 (m, 4H, metaH, py *trans* to hydride), 7.33 (m, 2H, metaH, py *cis* to hydride), 7.15 (s, 2H, N-CH-CH-N), 3.16 (s, 6H, CH_3), -21.98 (s, 2H, hydrides).

^{13}C{^{1}H} NMR (MeOD, 101 MHz, 280 K): 221.5 (NCN), 156.3 (orthoC, py *cis* to hydride), 154.2 (orthoC, py *trans* to hydride), 137.3 (paraC, py *trans* to hydride), 136.9 (paraC, py *cis* to hydride), 126.1 (metaC, py *trans* to hydride), 125.9 (metaC, py *cis* to hydride), 121.7 (N-CH-CH-N), 37.5 (s, 6H, CH_3).

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 251.6 (N, pyridine *trans* to hydride), 236.7 (N, pyridine *cis* to hydride), 177.9 (N, Ir-C-$(NR)_2$).

g. [Ir(ImMe$_2$*N*Pr$^{i}_2$)(py)$_3$(H)$_2$]Cl, 3- ImMe$_2$*N*Pr$^{i}_2$

[Ir(ImMe$_2$*N*Pr$^{i}_2$)(COD)Cl] (1.8 mg, 0.0031 mmol) and pyridine (5 µL, 0.062 mmol) were dissolved in 0.6 mL methanol in a Young's tap NMR tube and degassed using three freeze-

thaw cycles. Hydrogen was added at a pressure of 3 bar and the sample shaken to dissolve the hydrogen into solution.

^{1}H NMR (CD_3OD, 500 MHz, 298 K): 8.78 (d, J=4.26 Hz, 2H, orthoH, axial pyridine), 8.27 (d, J=4.26 Hz, 2H, orthoH, pyridine *trans* to H), 8.01 (m, 1H, paraH, axial pyridine), 7.92 (m, 1H, paraH, pyridine *trans* to H), 7.50 (m, 2H, metaH, axial pyridine), 7.25 (m, 2H, metaH, pyridine *trans* to H), 6.05 (sept, J=7.2 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.22 (s, 6H, NC(C<u>H$_3$</u>)C(C<u>H$_3$</u>)N), 1.72 (d, J=6.93 Hz, 6H, CH(C<u>H$_3$</u>)$_2$), 1.44 (d, J=6.93 Hz, 6H, CH(C<u>H$_3$</u>)$_2$), −22.77 (s, 2H, Hydrides)

^{13}C{^{1}H} NMR (MeOD, 151 MHz, 298 K): 176.3 (NCN), 155.93 (Ar-CH), 155.1 (Ar-CH), 138.2 (Ar-CH), 137.3 (Ar-CH), 126.3 (Ar-CH), 125.8 (Ar-CH), 125.7 (NCCN), 54. (CH), 20.1 (CH_3), 19.5 (CH_3), 9.68 (CH_3)

^{15}N NMR (MeOD, 50.6 MHz, 253 K): 198.8 (Carbene N), 242.67 (axial pyridine N), 253.75 (equatorial pyridine N)

4. Polarisation transfer experiment data

The polarisation transfer experiments reported were conducted via either an NMR tube equipped with a Young's Tap (Method A) or an automated polarizer (Method B).

Method A

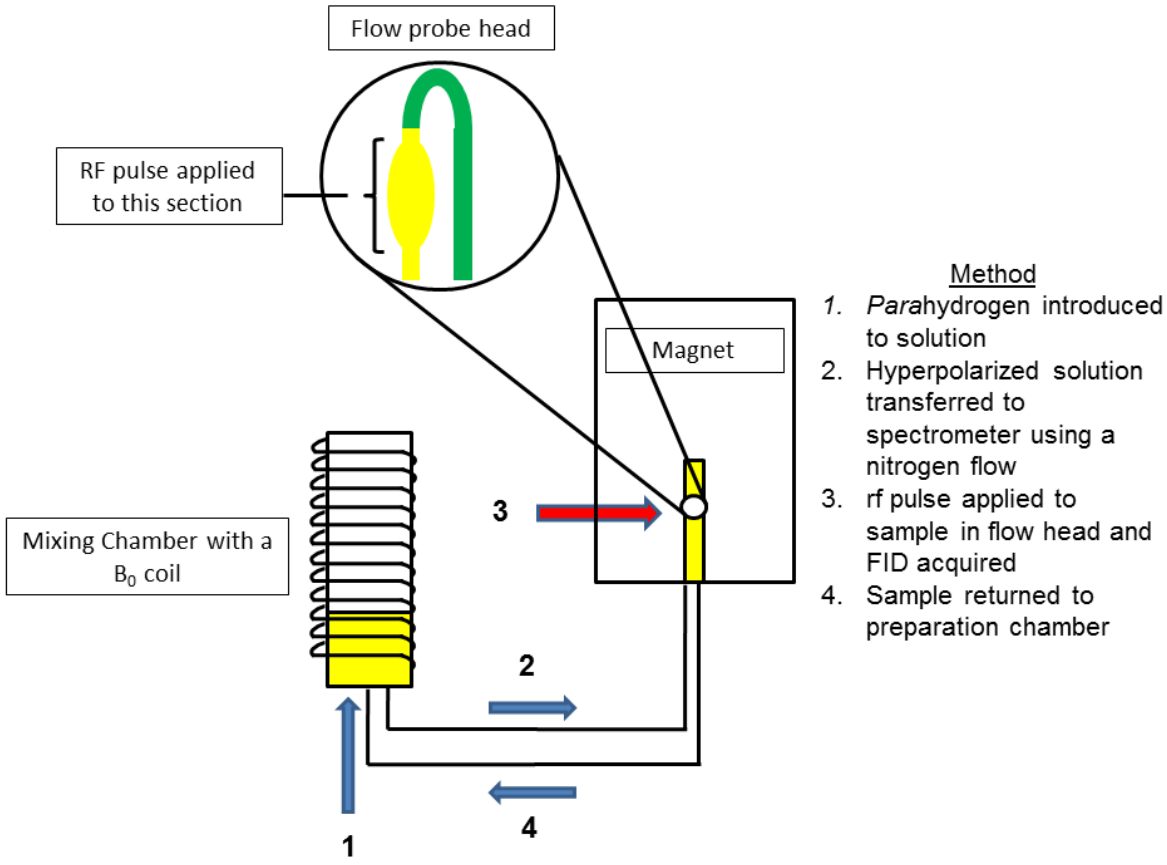
Samples for these polarization transfer experiments were conducted using a solution of **1** and pyridine in methanol-d_4 (0.6 ml). The samples were degassed prior to the introduction of *para*hydrogen at a pressure of 3 bar. Samples were then shaken for 8 s in the fringe field of a NMR spectrometer before being rapidly transported to the magnet for interrogation by NMR spectroscopy.

Method B

For automated polarizer measurements, samples consisted of **1-NHC** and pyridine in a methanol-d_4 solution (3ml).

A schematic representation of the Polarizer used for flow measurements is shown in sScheme 1. The Mixing Chamber (MC) is housed within a tunable copper coil (0 to ±150 G). The coil was situated in a magnetic field which has the components x 4.9 – 5.1 G, y 3.3 – 3.6 G and z 1.5 – 2.1 G. All magnitudes of the magnetic fields in which polarization transfer occurs (PTF) are stated without correction for this local field. The MC houses the solvent, catalyst and substrate. Liquid and gas flow is computer-controlled via the pulse program. As such, the system is entirely automated.

*Para*hydrogen is introduced into the MC first to activate the catalyst. Nitrogen gas is used to shuttle the hyperpolarized solution from the MC to the NMR probehead for measurement. The transportation time was calibrated to 2.9 s. A further delay of 0.5 s was allowed for settling of the sample prior to signal acquisition (1 s).



Scheme 1 Schematic of the Polarizer, the hyperpolarization process and its subsequent NMR analysis.

5. Calculation of ^{1}H NMR enhancement factors

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

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

E = enhancement

S_{pol} = signal of polarized sample measured by integral

S_{unpol} = signal of unpolarized (reference) sample measured by integral

Experimentally, reference spectra were acquired with the same sample that was used for the hyperpolarised measurement after it had fully relaxed (typically 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 thermal spectra were used to determine the enhancement level using the equation above.

6. Effect of temperature on polarisation transfer

The total enhancement in the following tables has been calculated by taking the modulus of the enhancements, and adding 2×ortho, 2×meta and 1×para, to consider the total on all five observed protons.

	T / °C	*Ortho*	*Meta*	*Para*	Total
SIMes	21	-93.2	31.0	-78.3	326.7
	-10	9	92.9	-172.5	389.7
	-20	-53.8	109.8	-196.7	523.9
	-30	10.6	120.2	-201.4	479.8
	-40	15.9	111.1	-201.7	493.3

	T / °C	*Ortho*	*Meta*	*Para*	Total
ICy	50	-12.9	10.0	-13.7	59.6
	40	-10.9	9.4	-11.3	51.8
	30	-9.3	7.6	-9.7	43.5
	20	-5.7	5.5	-6.2	28.6
	0	-2.6	2.3	-2.6	12.3

	T / °C	*Ortho*	*Meta*	*Para*	Total
IPr	30	-27.6	17.0	-28.5	117.7
	20	-43.4	32.2	-45.2	196.4
	10	-96.1	72.0	-100.7	436.9
	-4	-131.2	103.6	-137.1	606.7
	-20	-147.4	101.0	-127.8	624.6
	-44	-132.5	81.5	-97.2	525.2

	T / °C	*Ortho*	*Meta*	*Para*	Total
SIPr	20	-1.5	0.7	-1.3	5.7
	8	-3.5	1.9	-3.2	14.0
	-2	-9.1	5.3	-8.0	36.8
	-16	-14.3	8.7	-11.4	57.4
	-50	-21.7	11.5	-15.4	81.8
	-85	-22.8	11.7	-14.6	83.6

	T / °C	*Ortho*	*Meta*	*Para*	Total
$ImMe_2NPri_2$	60	-32.1	22.6	-29.8	51.2
	40	-35.9	16.0	-34.0	75.6
	21	-20.3	9.1	-16.8	137.7
	0	-13.6	5.7	-12.6	139.3

	T / °C	*Ortho*	*Meta*	*Para*	Total
IMes	37	-91	67	-54	370
	32	-143	34	-65	419
	28	-136	39	-67	417
	17	-246	72	-110	746
	1	-212	114	-97	749
	-20	-183	82	-95	625

	T / °C	*Ortho*	*Meta*	*Para*	Total
IMe	50	-35.2	17.8	-45.4	151.4
	40	-21.9	13.1	-28.7	98.6
	30	-16.6	11.9	-22.8	79.9
	20	-16.2	11.0	-21.4	75.7

7. Effect of magnetic field on polarisation transfer

a. [Ir(IMes)(py)$_3$(H)$_2$]Cl, 3-IMes

This data has been reported previously.[4]

b. [Ir(SIMes)(py)$_3$(H)$_2$]Cl, 3-SIMes

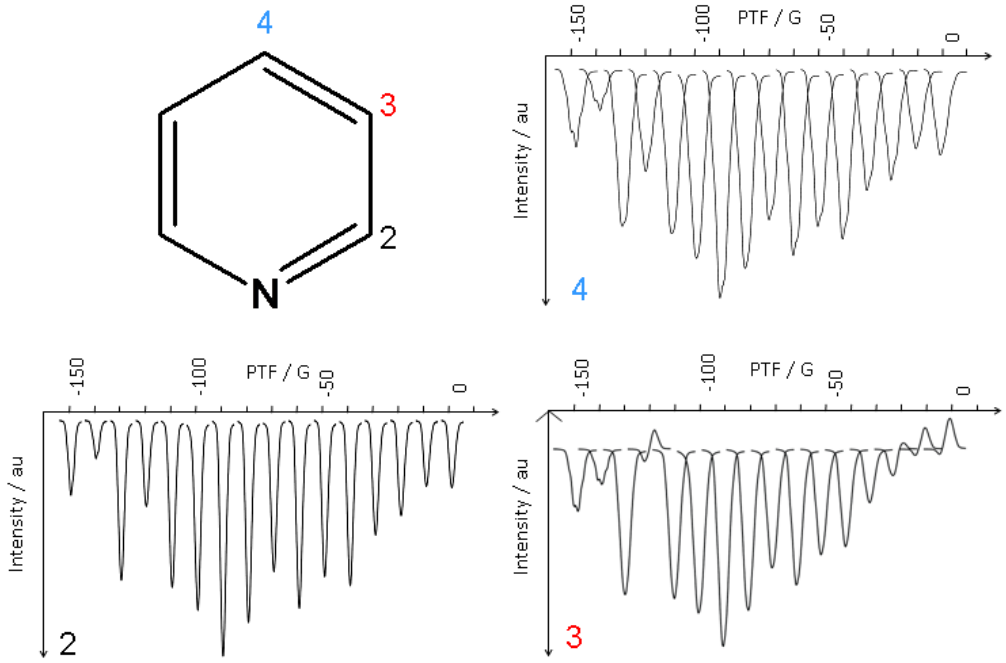


Figure 1 Effect of changing the PTF on the observed enhancement of pyridine using **3-SIMes**.

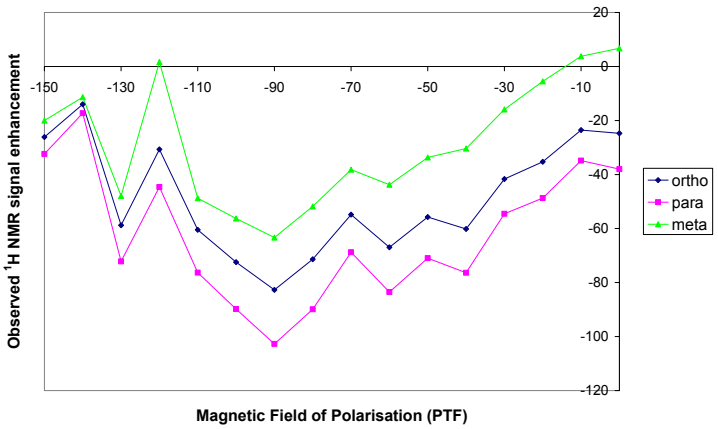


Figure 2 Graphical representation of the effect of changing the PTF on the observed enhancement of pyridine using **3-SIMes**.

c. [Ir(IPr)(py)$_3$(H)$_2$]Cl, 3-IPr

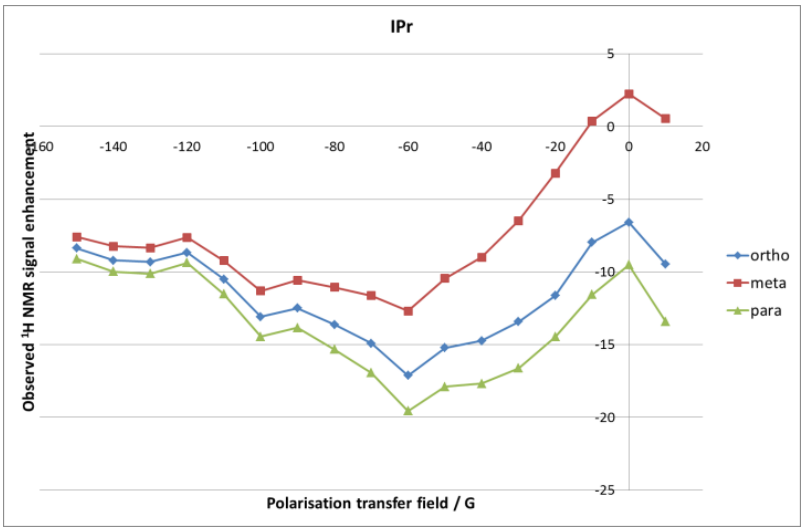


Figure 3 Graphical representation of the effect of changing the PTF on the observed enhancement of pyridine using **3-IPr**

d. [Ir(SiPr)(py)$_3$(H)$_2$]Cl, 3-SiPr

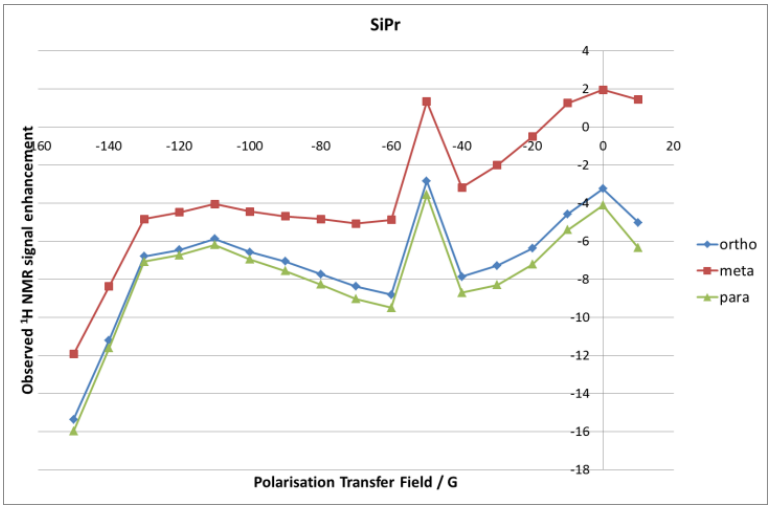


Figure 4 Graphical representation of the effect of changing the PTF on the observed enhancement of pyridine using **3-SiPr**

e. [Ir(ICy)(py)$_3$(H)$_2$]Cl, 3-ICy

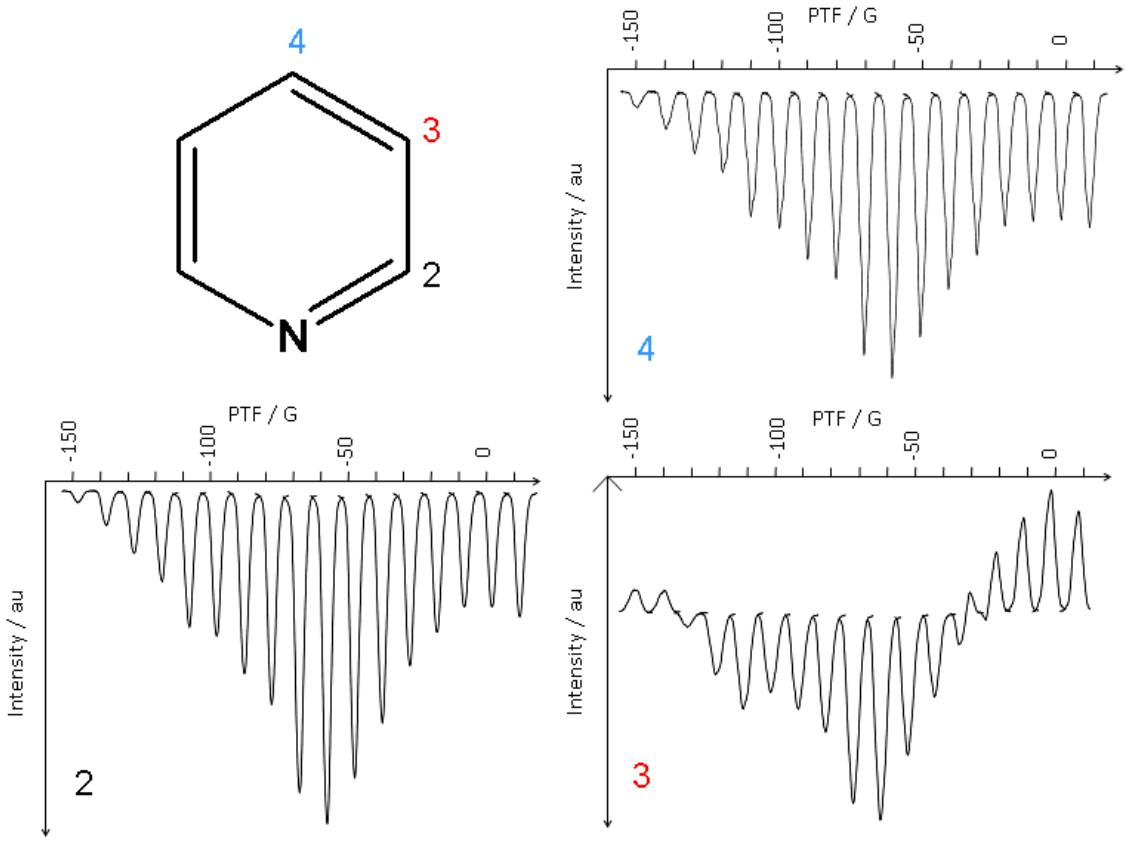


Figure 5 Effect of changing the PTF on the observed enhancement of pyridine using **3-ICy**.

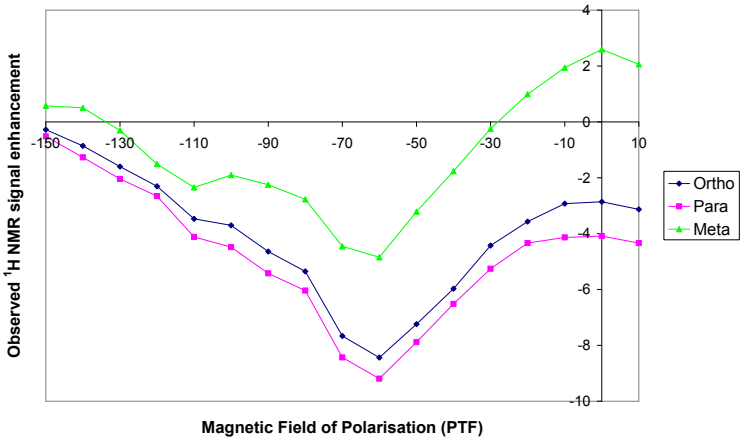


Figure 6 Graphical representation of changing the PTF on the observed enhancement of pyridine using **3-ICy**.

f. [Ir(ImMe$_2$*N*Pr$^i_2$)(py)$_3$(H)$_2$]Cl, 3- ImMe$_2$*N*Pr$^i_2$

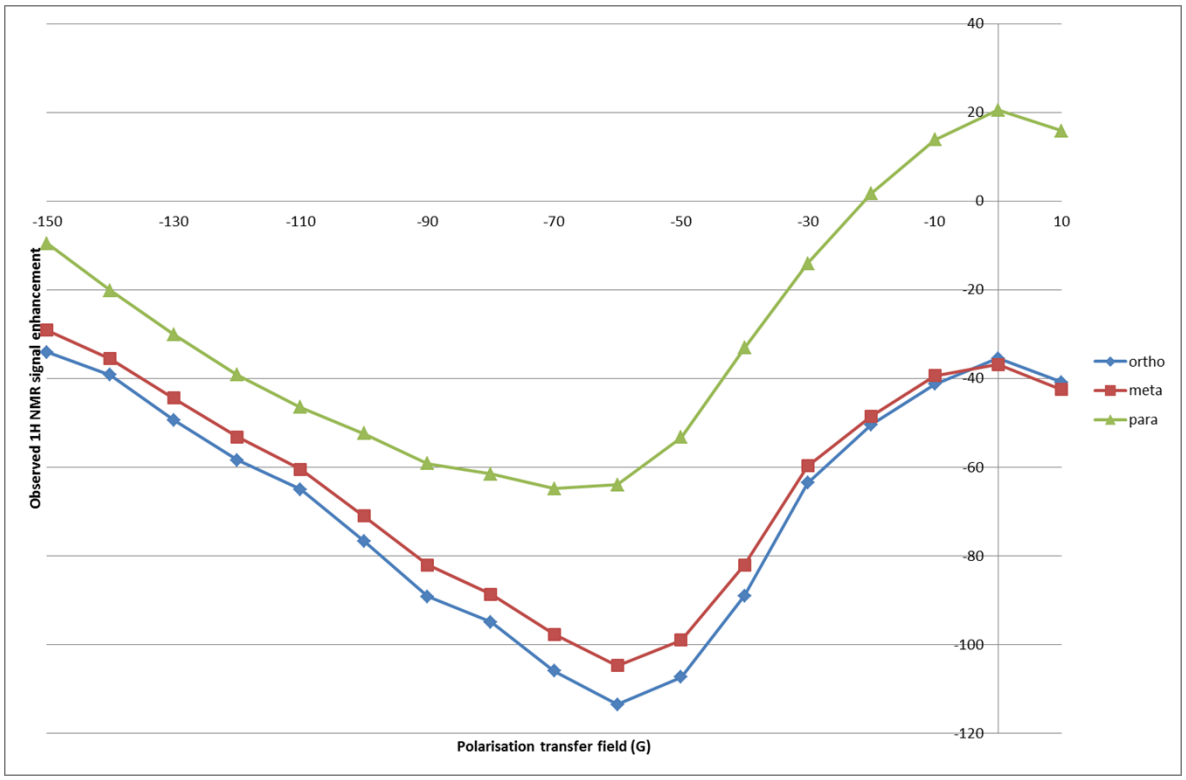


Figure 7 Graphical representation of changing the PTF on the observed enhancement of pyridine using **3-ImMe$_2$*N*Pr$^i_2$**.

8. Effect of changing the excess of pyridine on polarisation transfer

Constant catalyst concentration (5 mM) in a PTF of 65 G.

IMes Pyridine (mM)	Eq. to **1-NHC**	Excess to **3-NHC**	Enhancement			Magnitude enhancement			
			Ortho	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
1000	200	197	-7.1	4.6	-6.5	7.1	4.6	6.5	18.2
500	100	97	-16.2	10.5	-14.1	16.2	10.5	14.1	40.8
250	50	47	103.3	-93	-75.7	103.3	93	75.7	272
100	20	17	392.3	-191.7	-322.5	392.3	191.7	322.5	906.5
75	15	12	520.5	197.3	-501.7	520.5	197.3	501.7	1219.5
50	10	7	-504	-675	-651.8	504	675	651.8	1830.8
40	8	5	-513.5	-746	-721.3	513.5	746	721.3	1980.8
30	6	3	-1034.7	-764	-752.7	1034.7	764	752.7	2551.4
20	4	1	-2397.3	-1472	-1628.7	2397.3	1472	1628.7	5498

IPr Pyridine (mM)	Eq. to **1-NHC**	Excess to **3-NHC**	Enhancement			Magnitude enhancement			
			Ortho	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
250	50	47	-65	-67	-111	65	67	111	243
75	15	12	-155	-71	-111	155	71	11	237
50	10	7	-146	-69	-108	146	69	108	323
40	8	5	-254	-117	-190	254	117	190	561
30	6	3	-263	-137	-205	263	137	205	605
20	4	1	-327	-176	-248	327	176	248	751

SIMes	Eq. to	Excess	Enhancement			Magnitude enhancement			
Pyridine (mM)	**1-NHC**	to **3-NHC**	*Ortho*	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
1000	200	197	-5.2	1.0	-4.4	5.2	1.0	4.4	10.6
500	100	97	-12.2	1.6	-10.8	12.2	1.6	10.8	24.6
250	50	47	87.5	-112	-72	87.5	112	72	271.5
100	20	17	-432.5	-324.8	-203.5	432.5	324.8	203.5	960.8
75	15	12	-418.4	-359	-215.7	418.4	359	215.7	993.1
50	10	7	-598.8	-442.8	-272	598.8	442.8	272	1313.5
40	8	5	-539	-407	-257	539	407	257	1203
30	6	3	-484.3	-380.3	-245.5	484.3	380.3	245.5	1110
20	4	1	-585.7	-431	-300.7	585.7	431	300.7	1317.3

9. Effect of concentration on polarisation transfer

Ratio of catalyst to pyridine (1:4) kept constant with concentration of catalyst changed in a PTF of 65 G.

1-IMes	Enhancement			Magnitude enhancement			
Conc. (mM)	*Ortho*	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
15	-882.6	-457.6	-457.6	882.6	457.6	457.6	1797.8
10	-961.4	-482.8	-511.8	961.4	482.8	511.8	1956
5	-2397.3	-1472.0	-1628.7	2397.3	1472.0	1628.7	5498
2.5	-1785.8	-982.4	-965.2	1785.8	982.4	965.2	3733.4
0.5	-475.5	-288.0	-238.3	475.5	288.0	238.3	1001.8

1-IPr	Enhancement			Magnitude enhancement			
Conc. (mM)	*Ortho*	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
15	-213	-122	-160	213	122	160	495
10	-449	-250	-324	449	250	324	1023
5	-327	-176	-248	327	176	-248	751
2.5	-107	-53	-85	107	53	85	245
0.5	-99	-48	-78	99	48	127.8	225

1-SIMes	Enhancement			Magnitude enhancement			
Conc. (mM)	*Ortho*	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	Total
15	-273.7	-192.7	-201.1	273.7	192.7	201.1	667.5
10	-331	-228	-234	331	228	234	793
5	-506	-300.7	-386.7	506	300.7	386.7	1193.4
2.5	-329.5	-255.6	-172	329.5	255.6	172	757.1
0.5	-133.7	-80.7	-103	133.7	80.7	103	317.4

10. Polarisation transfer experiments utilising d_5-pyridine

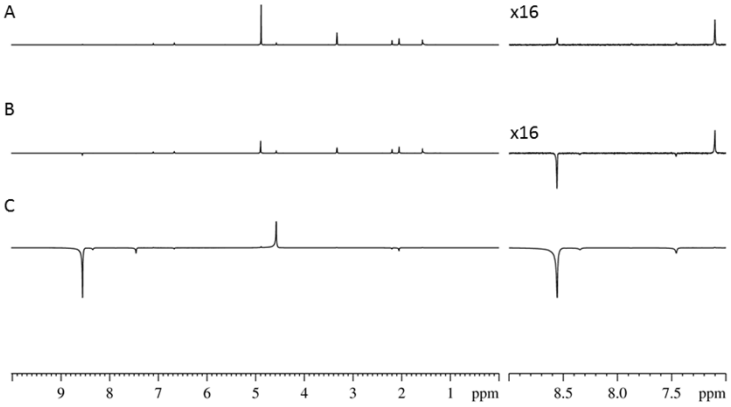


Figure 8 ^{1}H NMR spectra of a sample consisting of **1-IPr** (2 mg) and d_5-pyridine (5 μL) in MeOD (0.6 ml) acquired using a π/2 pulse to interrogate magnetisation; A) at thermal Boltzmann equilibrium; B) 2 minutes after introduction of *para*hydrogen to the tube and subsequent transfer to the measurement field; C) immediately after introduction of *para*hydrogen and the sample being shaken in a PTF of 65 G.

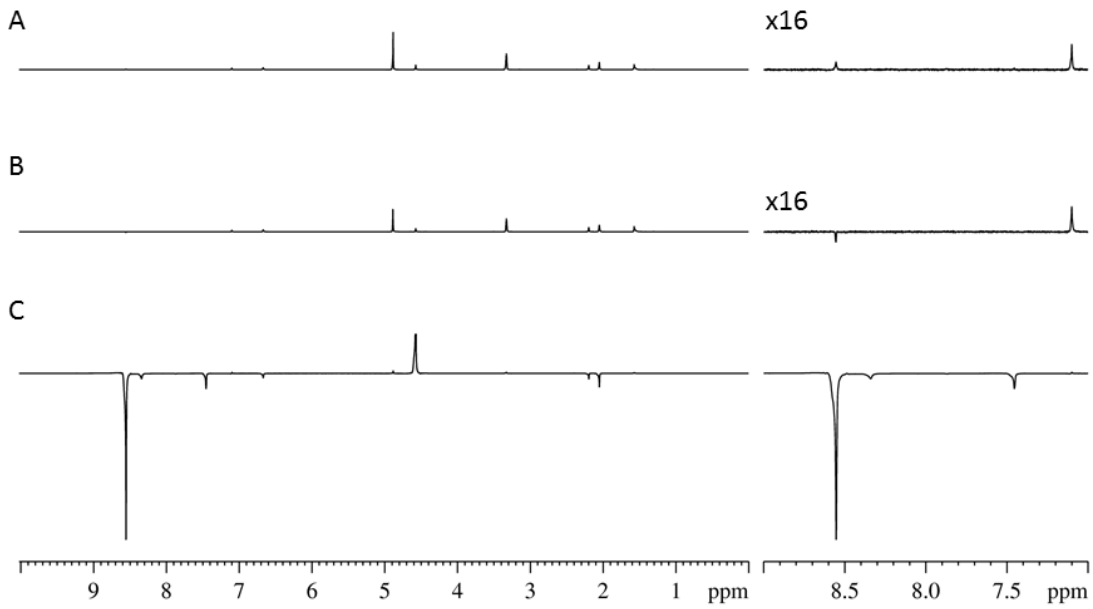


Figure 9 ^{1}H NMR spectra of a sample consisting of **1-IMes** (2 mg) and d_5-pyridine (5 μL) in MeOD (0.6 ml) acquired using a π/2 pulse to interrogate magnetisation; A) at thermal Boltzmann equilibrium; B) 2 minutes after introduction of *para*hydrogen to the tube and subsequent transfer to the measurement field; C) immediately after introduction of *para*hydrogen and the sample being shaken in a PTF of 65 G.

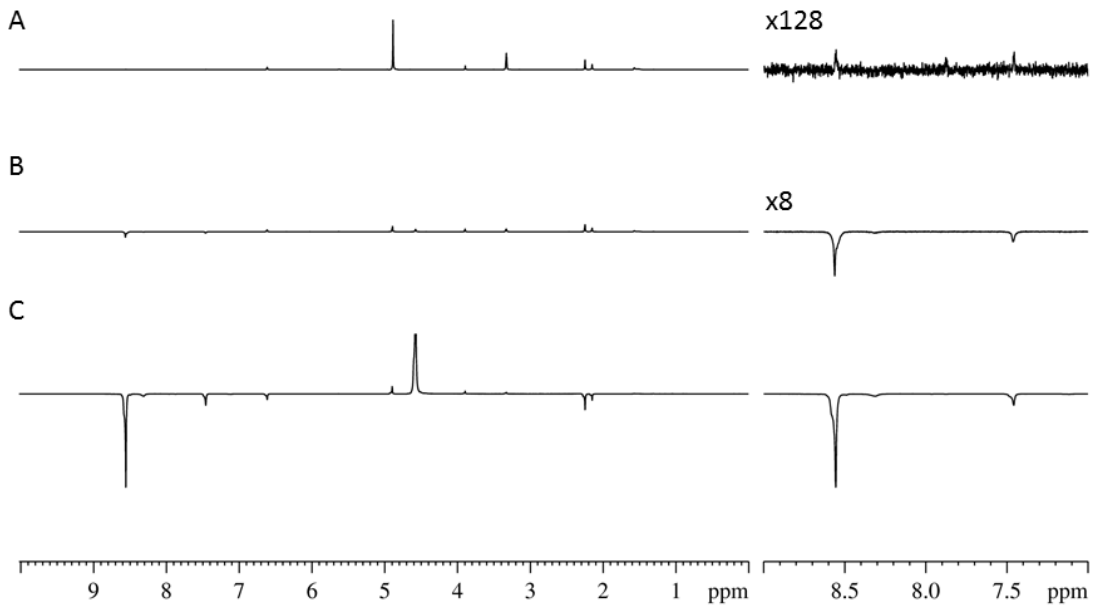


Figure 10 ^{1}H NMR spectra of a sample consisting of **1-SIMes** (2 mg) and d_5-pyridine (5 μL) in MeOD (0.6 ml) acquired using a π/2 pulse to interrogate magnetisation; A) at thermal Boltzmann equilibrium; B) 2 minutes after introduction of *para*hydrogen to the tube and subsequent transfer to the measurement field; C) immediately after introduction of *para*hydrogen and the sample being shaken in a PTF of 65 G.

11. Effect of H_2 pressure on the hydride exchange rate at 258 K

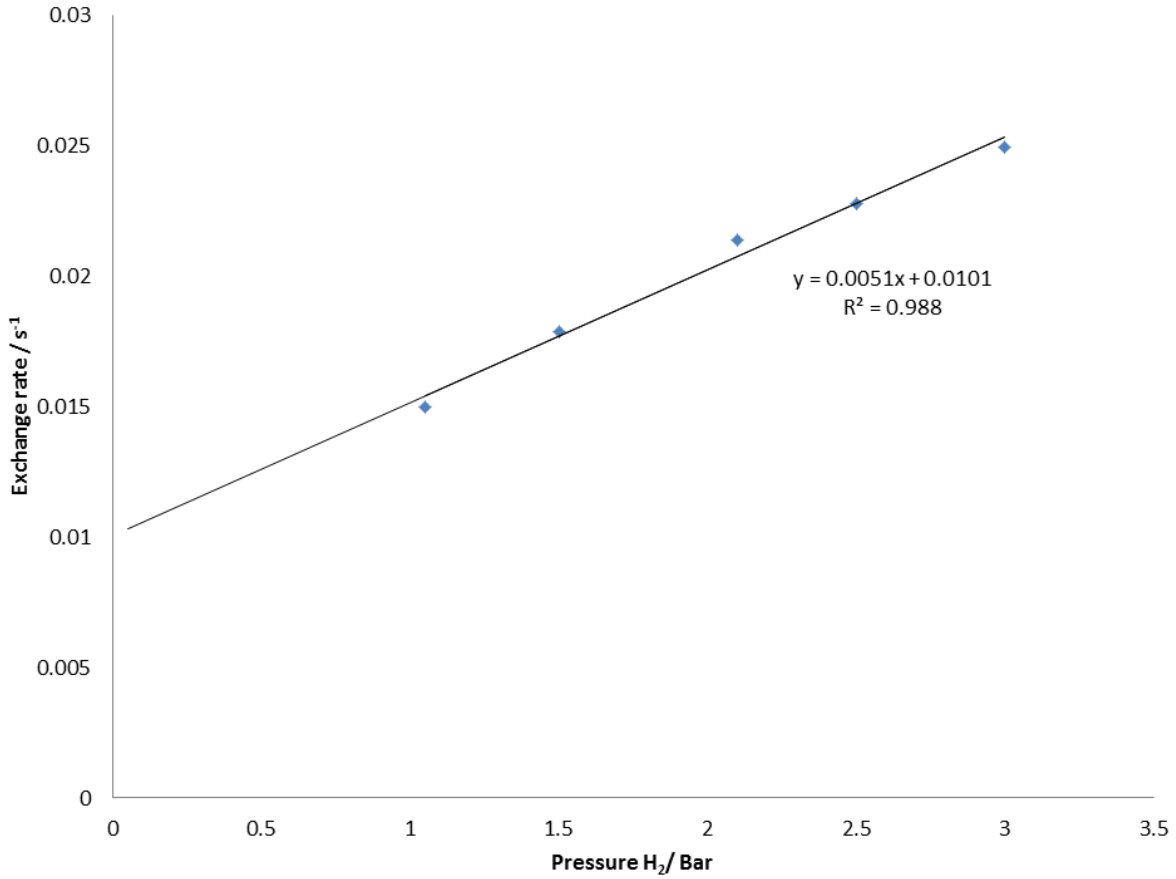


Figure 11 Effect of H_2 pressure on the hydride exchange rate over the pressures of 1 – 3 Bar for a solution containing **1-IMes** (10 mg) and pyridine (4 equiv) at 258 K.

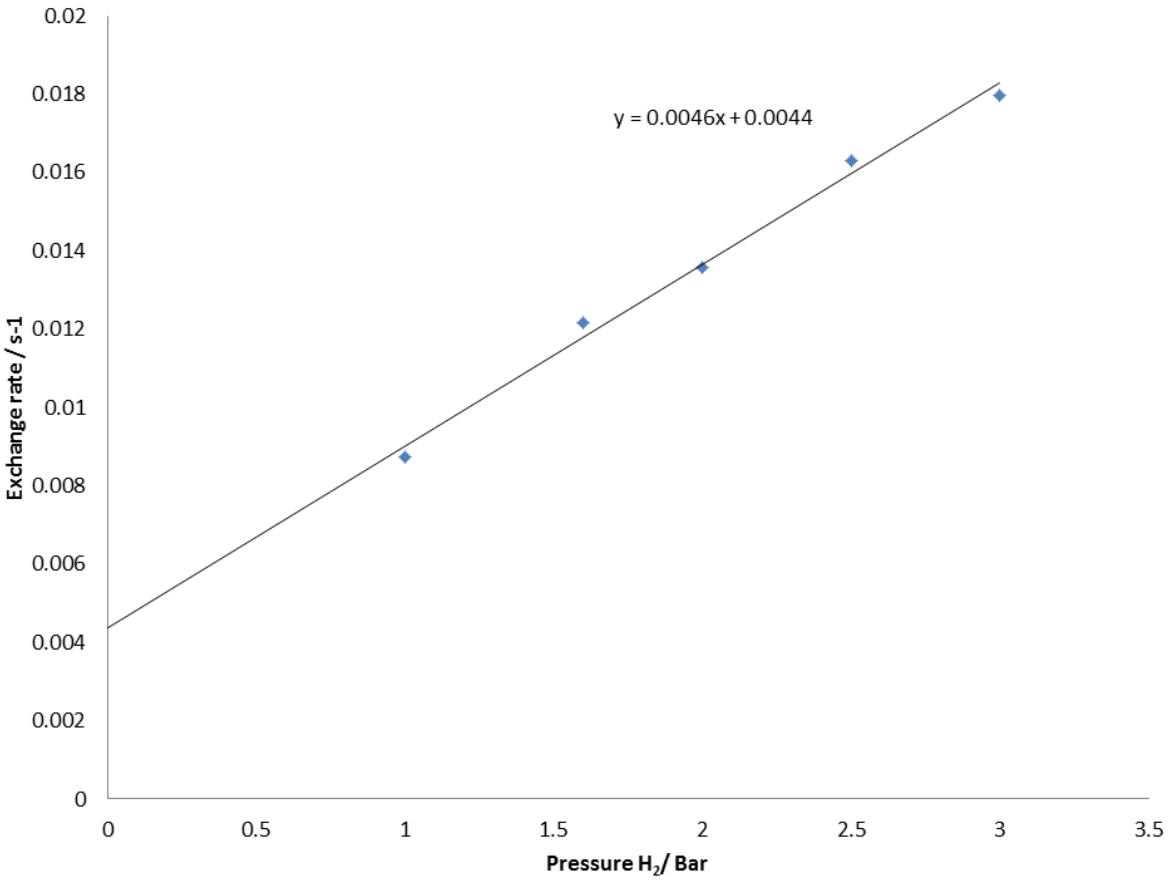


Figure 12 Effect of H_2 pressure on the hydride exchange rate over the pressures of 1 – 3 Bar for a solution containing **1-ImMe$_2$NPri$_2$** (10 mg) and pyridine (4 equiv) at 258 K.

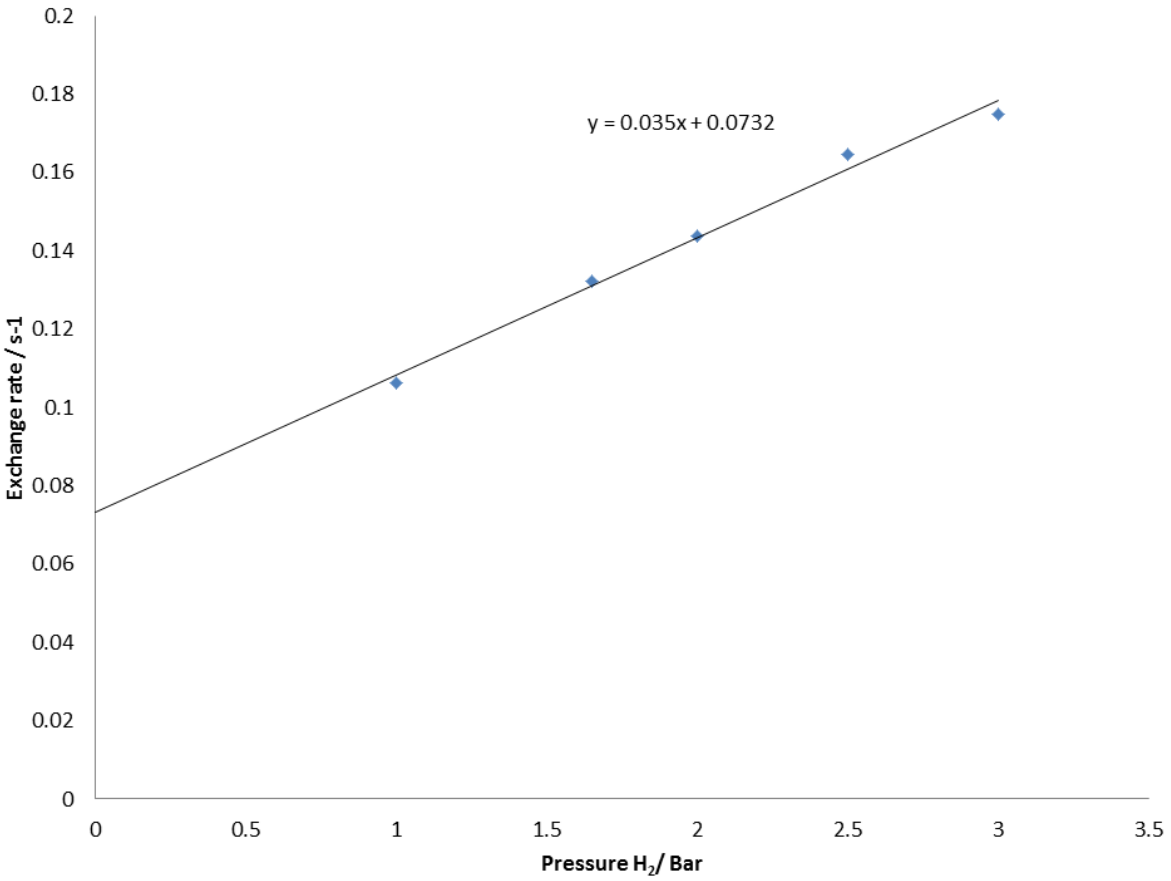


Figure 13 Effect of H_2 pressure on the hydride exchange rate over the pressures of 1 – 3 Bar for a solution containing **1-SIMes** (10 mg) and pyridine (4 equiv) at 258 K.

12. References

(1) S. Wolf; H. Plenio *J. Organomet. Chem.* **2009**, *694*, 1487-1492.

(2) N. Kuhn; T. Kratz *Synthesis* **1993**, *1993*, 561-562.

(3) R. A. Kunetskiy; I. Císařová; D. Šaman; I. M. Lyapkalo *Chem.Eur. J.* **2009**, *15*, 9477-9485.

(4) M. J. Cowley; R. W. Adams; K. D. Atkinson; M. C. R. Cockett; S. B. Duckett; G. G. R. Green; J. A. B. Lohman; R. Kerssebaum; D. Kilgour; R. E. Mewis *J. Am. Chem. Soc.* **2011**, *133*, 6134-6137.