Supporting Information

"Mechanistic Insights into Transfer Hydrogenation Catalysis by [Ir(cod)(NHC)$_2$]$^+$ Complexes with Functionalized *N*-Heterocyclic Carbene ligands"

M. Victoria Jiménez,* Javier Fernández-Tornos, Jesús J. Pérez-Torrente,* Francisco J. Modrego, Pilar García-Orduña, and Luis A. Oro

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain.

Figures S1, S2: NMR spectra for [Ir(cod){MeIm(2-methoxybenzyl)}$_2$]PF$_6$ (**4·PF$_6$**).

Figures S3, S4: NMR spectra for [Ir(cod){MeIm(pyridine-2-ylmethyl)}$_2$]PF$_6$ (**5·PF$_6$**).

Figures S5, S6: NMR spectra for [Ir(cod)(MeIm{MeIm(quinolin-8-ylmethyl)}$_2$]PF$_6$ (**6·PF$_6$**).

Figures S7, S8, S9: NMR spectra for [IrH$_2${MeIm(pyridine-2-ylmethyl)}$_2$]PF$_6$ (**7·PF$_6$**).

2D EXSY spectra Figures: Methyl groups exchange analysis for 5a$^+$ and 5b$^+$ diasteromers of [Ir(cod){MeIm(pyridin-2-ylmethyl)}$_2$] PF$_6$ (**5·PF$_6$**) at different temperatures.

Estimation of the kinetic parameters for the equilibrium 5a$^+$ ⇆ 5b$^+$.

Estimation of the thermodynamic parameters for the equilibrium 5a$^+$ ⇆ 5b$^+$.

Figure S10. Energy profiles for all the proposed catalytic cycles: via hydride (involving hydrido species), and via MPV mechanism. The "**a**" numbered series refer to the catalyst bearing a pyridin-2-ylmethyl functionalized NHC ligand while the "**b**" series are those referred to the catalyst having a NHC with a 2-methoxybenzyl wingtip.

Table S1. Calculated electronic and free energies

[Ir(cod)(MeIm(2-methoxybenzyl))$_2$]PF$_6$ (**4·PF$_6$**)
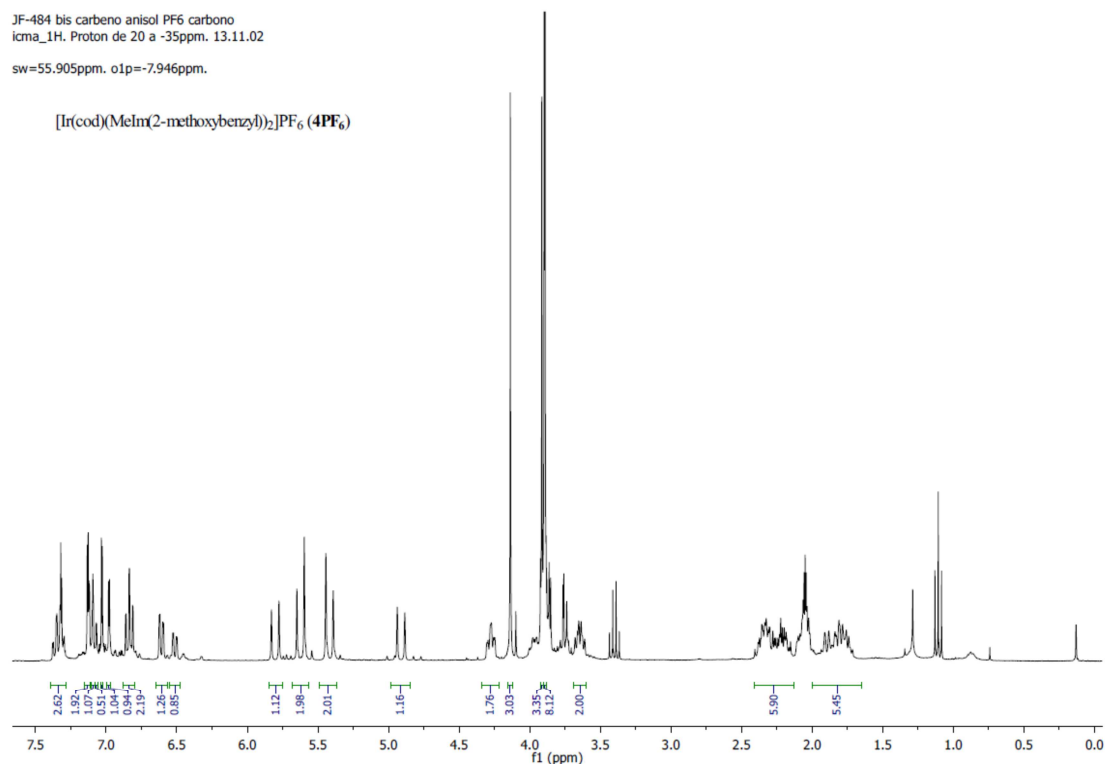
Figure S1. ^{1}H (acetone-d_6, 298 K) NMR spectrum of [Ir(cod){MeIm(2-methoxybenzyl)}$_2$]PF$_6$ (**4·PF$_6$**).

[Ir(cod)(MeIm(2-methoxybenzyl))$_2$]PF$_6$ (**4·PF$_6$**)
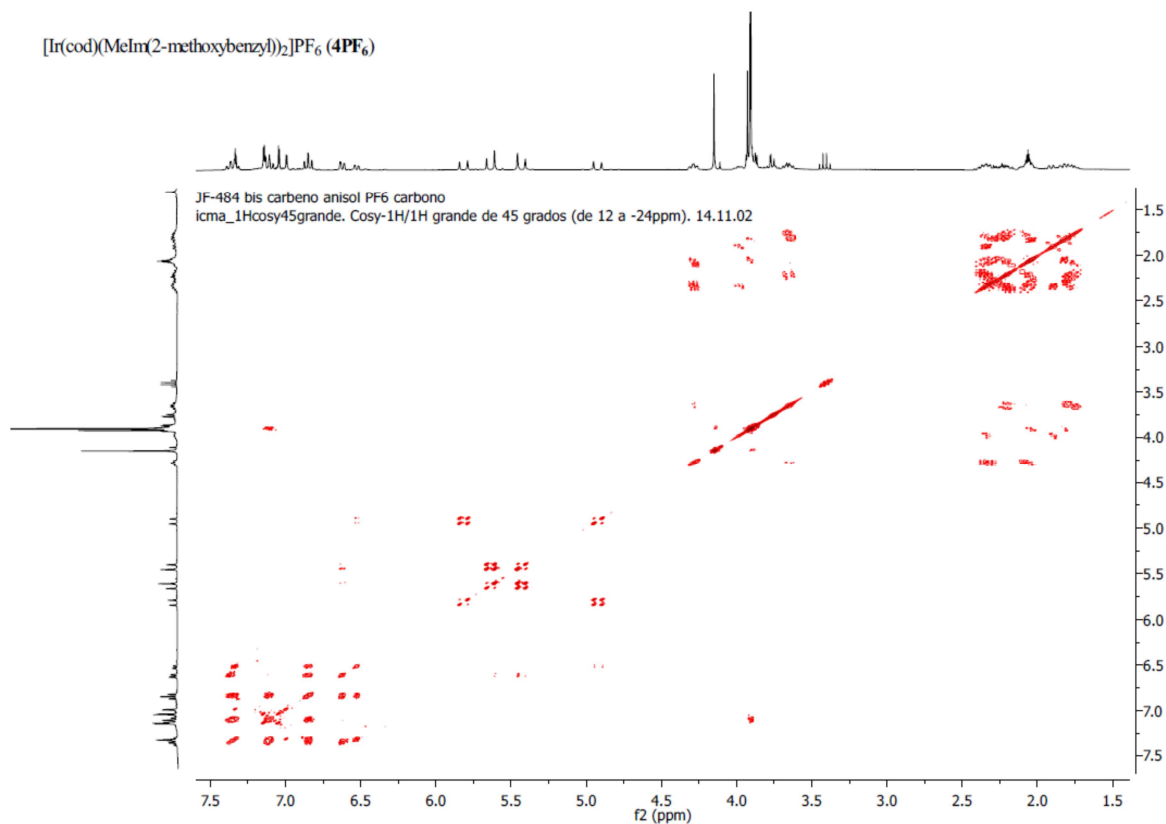
Figure S2. ^{1}H-^{1}H-cosy (acetone-d_6, 298 K) NMR spectrum of [Ir(cod){MeIm(2-methoxybenzyl)}$_2$]PF$_6$ (**4·PF$_6$**)..

[Ir(cod)(MeIm((pyridin-2-ylmethyl)))₂]PF₆ (5PF₆)
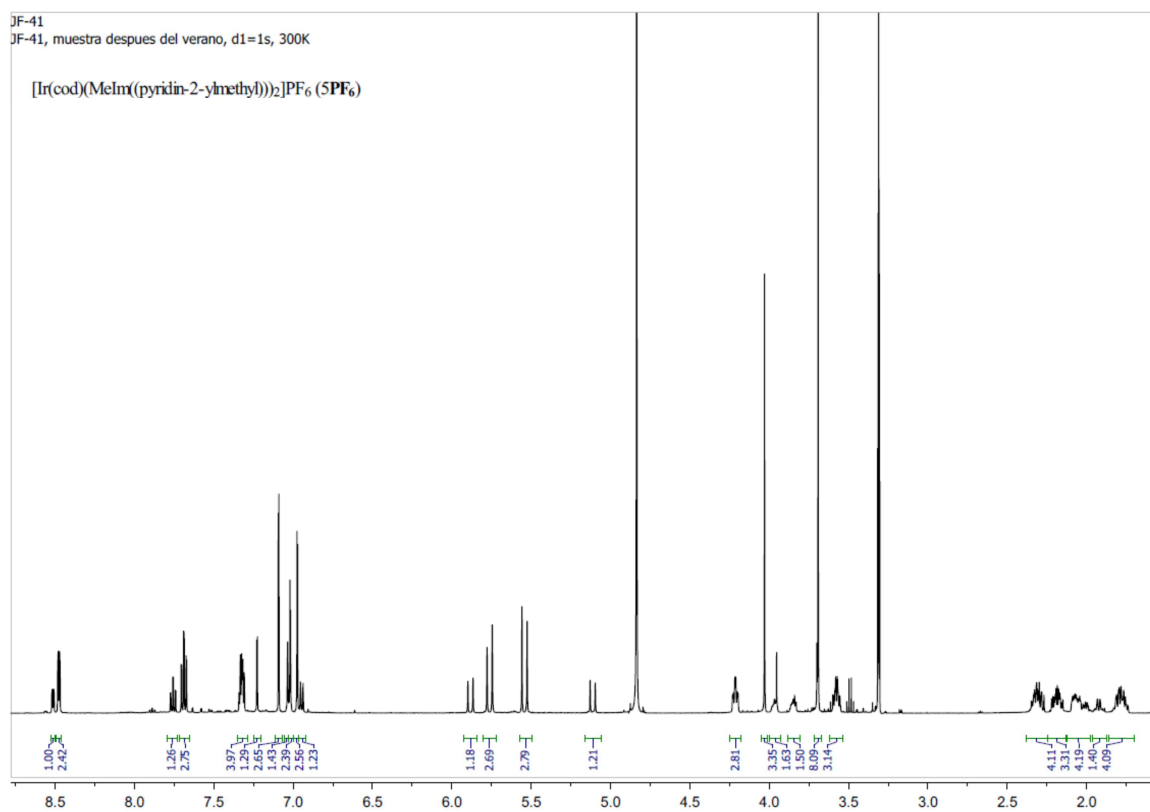
Figure S3. ^{1}H (MeOD, 298 K) NMR spectrum of [Ir(cod){MeIm(pyridine-2-ylmethyl)}₂]PF₆ (**5·PF₆**).

^{1}H -1H-noesy(cd2cl2, 300 K) [Ir(cod)(MeIm(pyridin-2-ylmethyl))₂]PF₆ (5PF₆).
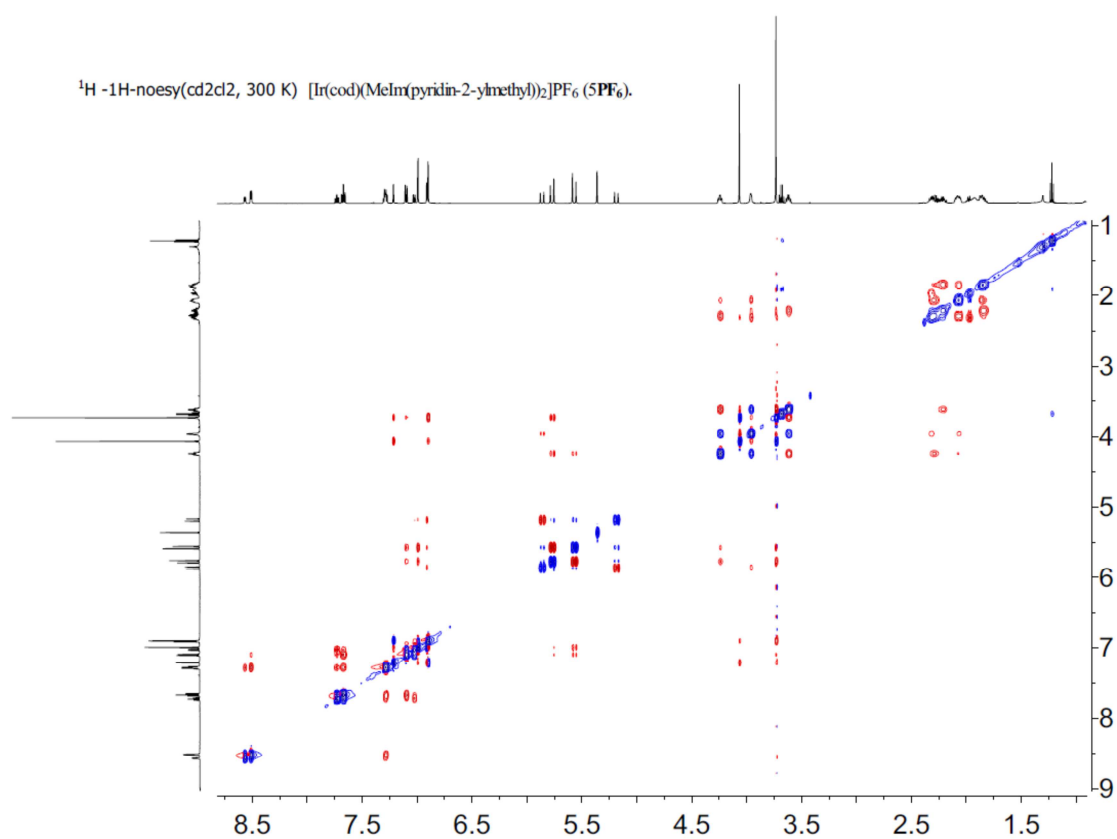

Figure S4. ^{1}H-^{1}H-noesy (cd2cl2, 298 K) NMR spectrum of [Ir(cod){MeIm(pyridine-2-ylmethyl)}₂]PF₆ (**5·PF₆**).
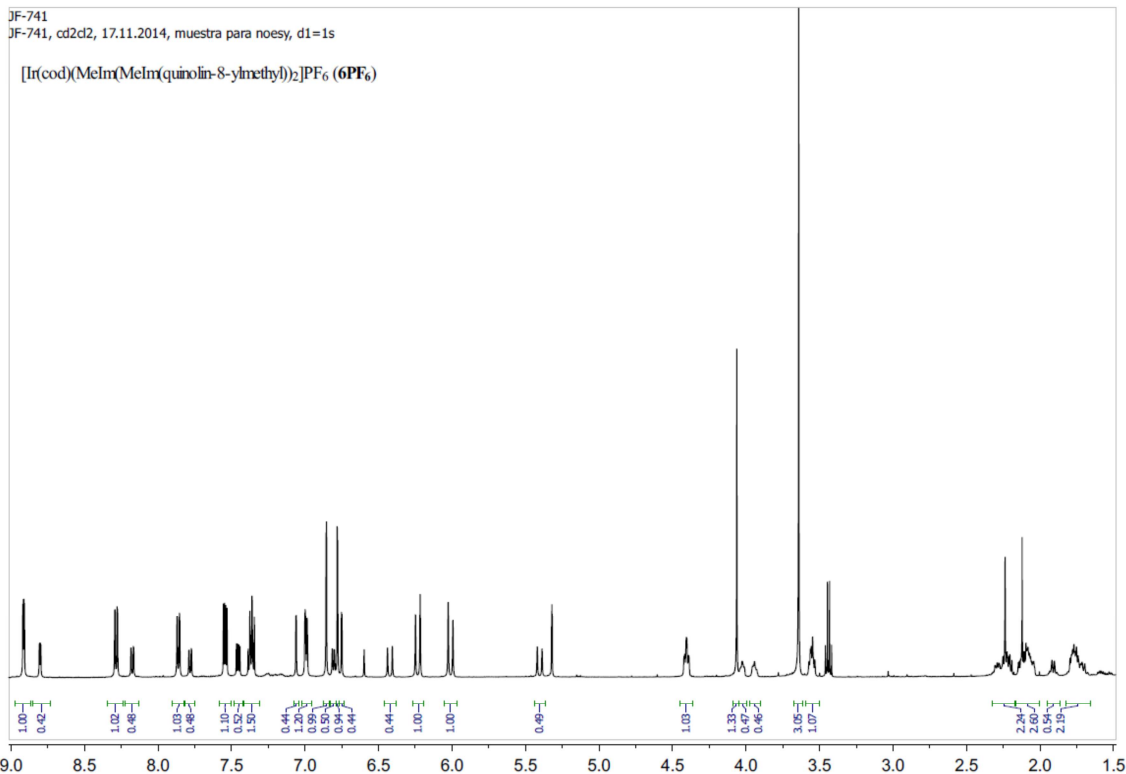
Figure S5. ^{1}H (CD$_2$Cl$_2$, 298 K) NMR spectrum of [Ir(cod){MeIm(MeIm(quinolin-8-ylmethyl)}$_2$]PF$_6$ (**6·PF$_6$**).
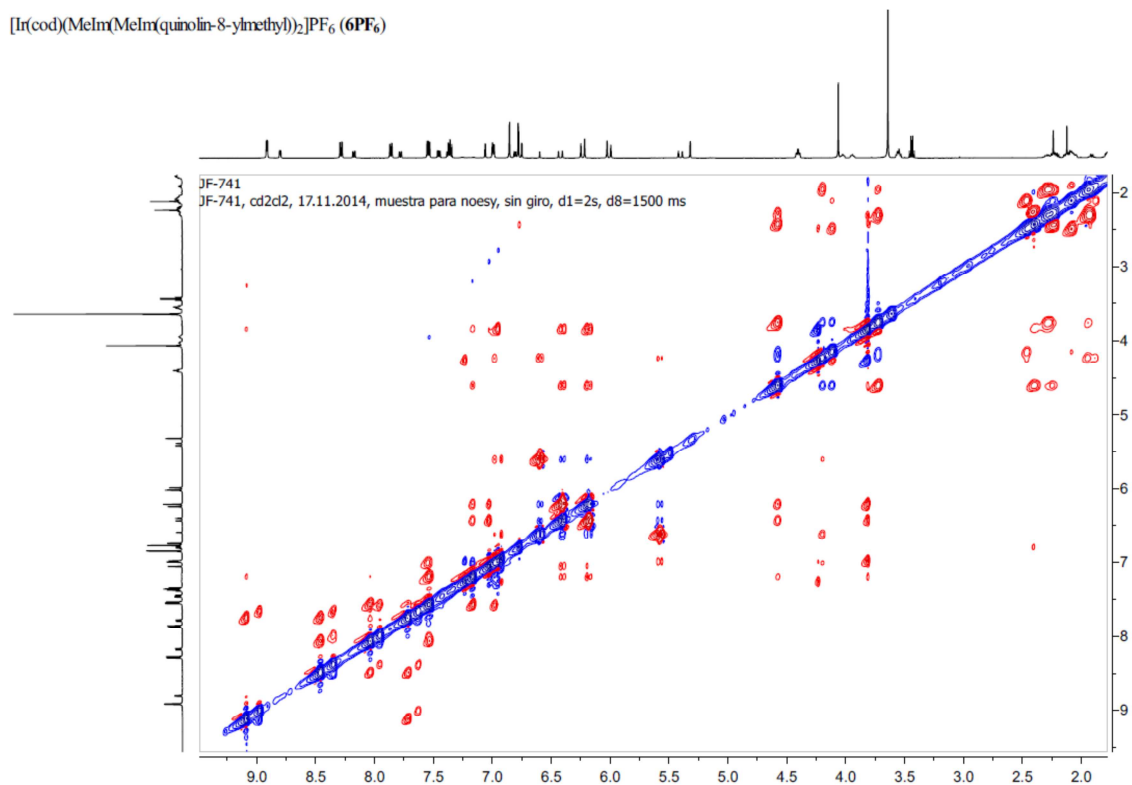

Figure S6. [1]H-1H-NOESY (CD$_2$Cl$_2$, 298 K) NMR spectrum of [Ir(cod)(MeIm{MeIm(quinolin-8-ylmethyl)}$_2$]PF$_6$ (**6·PF$_6$**).
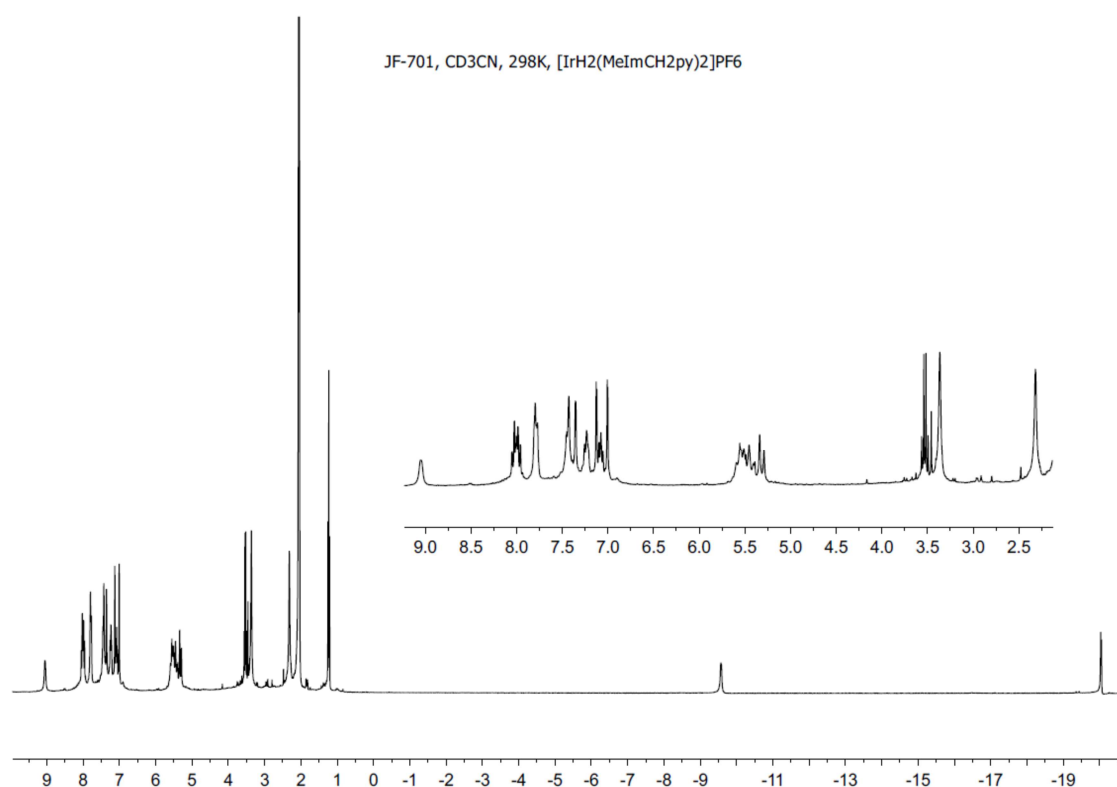
Figure S7. ^{1}H (CD3CN, 298 K) NMR spectrum of [IrH$_2${MeIm(pyridine-2-ylmethyl)}$_2$]PF$_6$ (**7·PF$_6$**).
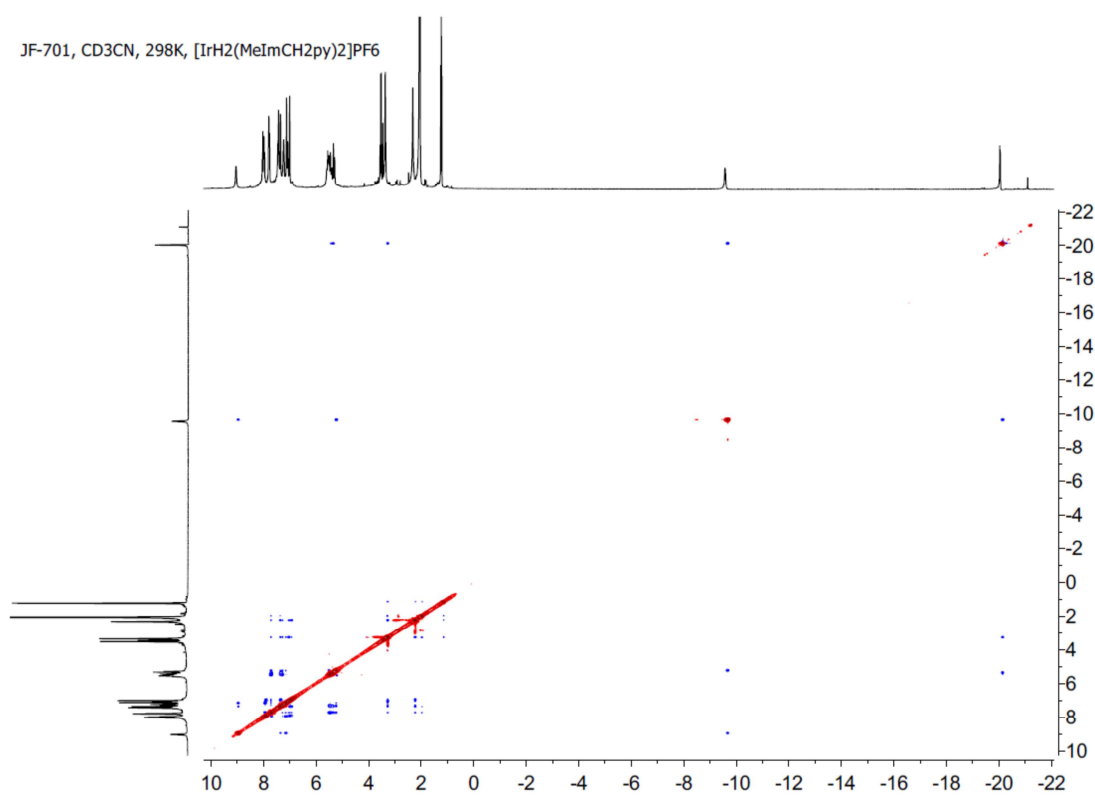
Figure S8. ^{1}H-1H-NOESY (CD3CN, 298 K) NMR spectrum of [IrH$_2${MeIm(pyridine-2-ylmethyl)}$_2$]PF$_6$ (**7·PF$_6$**).
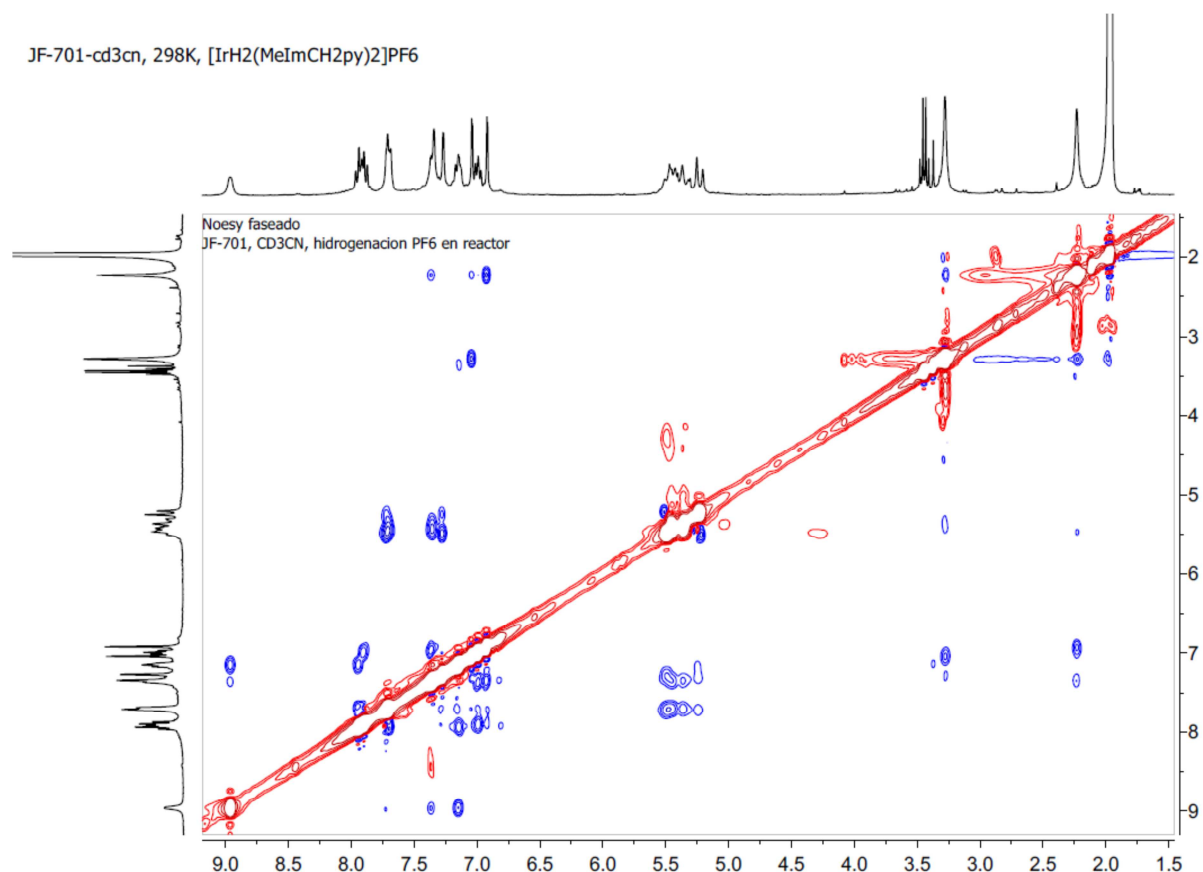
Figure S9. 9.0-1.0 ppm ^{1}H-^{1}H-NOESY (CD3CN, 298 K) expanded NMR spectrum of [IrH$_2$\{MeIm(pyridine-2-ylmethyl)\}$_2$]PF$_6$ (**7·PF$_6$**).

Experimental procedure for the determination of the kinetic parameters by 2D-EXSY spectroscopy.

Rate constants (k_1 and k_{-1}/s^{-1}) for the equilibrium **5a$^+$** ⇆ **5b$^+$** in compound **5·PF$_6$** were obtained from the 2D EXSY spectra by using a gradient-selected NOESY program from Bruker (noesygpph). All spectra were recorded at 500.13 MHz at 500ms as mixing time (t_m) optimised for 300 K. The spectra were recorded with a sweep of 11 ppm, 2048 data points in

the *F*2 direction, 512 increments in the *F*1, eight transients per increment, acquisition time (t_{ac}) of 75 ms, and relaxation delay (d_1) optimised by using the equation:

$$3T_1 = t_{ac} + t_m + d_1$$

The spectra were apodised with a qsine function and zero filled. They were phased to give negative signals along the diagonal. The baseline in *F*1 and *F*2 was corrected and then, all spectra were phased using the phase-sensitive method from Bruker. The basis of the calculation of the kinetic data (k_1 and k_{-1}/s^{-1}) from the EXSY experiments was the integration of the cross-peak amplitudes of the 2D EXSY spectra performed by using MestReC software [1] The methyl resonances of the 3-methyl-1-(pyridin-2-ylmethyl)-imidazol-2-ylidene ligands involved in the exchange process are conveniently separated from the others in the NMR spectrum, which allows the application of the MestReC approach. Two different 2D EXSY NMR spectra were acquired and processed under identical conditions (temperature, number of scans, etc.) for each sample. The first spectrum was an EXSY experiment acquired at the optimised mixing time (t_m) and the second was an EXSY experiment acquired at 0 or very short mixing times (reference experiment). The amplitudes (intensities) of the signals in exchange, A_{ij}, were quantified for both spectra, both diagonal and cross-peaks in the first spectrum and only the diagonal peaks, A(0), in the reference spectrum, since there are no cross-peaks due to the absence of magnetization exchange. The longitudinal relaxation times, T_1, were measured by using the inversion-recovery method with the appropriate pulse sequence. For a system with two exchange sites, i and j, of equal relaxation time, T_1, the optimum value of the mixing time (t_m) to maximise the cross-peaks intensities can be calculated using the following equation, in which k_{ij} and k_{ji} are the exchange rate constants between them.[2,3]

$$t_m = \left(1/k_{ij} + k_{ji}\right)\left[\ln\left(1 + \left(k_{ij} + k_{ji}\right)T_1\right)\right]$$

An adequate approximation for the optimum mixing time (t_m) derived from a statistical analysis is given by the following equation.[4]

$$t_m \approx 1 / \left[T_1^{-1} + k_{ij} + k_{ji} \right]$$

The activation energies, $\Delta G_1^{\#}$ and $\Delta G_{-1}^{\#}$ (kJ·mol^{-1}) were calculated from the chemical exchange-rate constants obtained from ESXYCalc, k_1 and k_{-1}, using the Eyring equation.

$$k = (k_B T / h) \exp(-\Delta G^{\#} / RT)$$

The activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, were calculated from a linear least-squares fit of $\ln(k/T)$ vs $1/T$.

$$\ln(k/T) = \ln(k_b/h) + \Delta S^{\#}/R - \Delta H^{\#}/RT$$

The uncertainties in $\Delta H^{\#}$ and $\Delta S^{\#}$ were computed from the error propagation formulas derived from the Eyring equation by Girolami and co-workers.[5] The total uncertainty in the determination of k was assumed to be 5%. The estimated uncertainty in the temperature measurements was 1K.
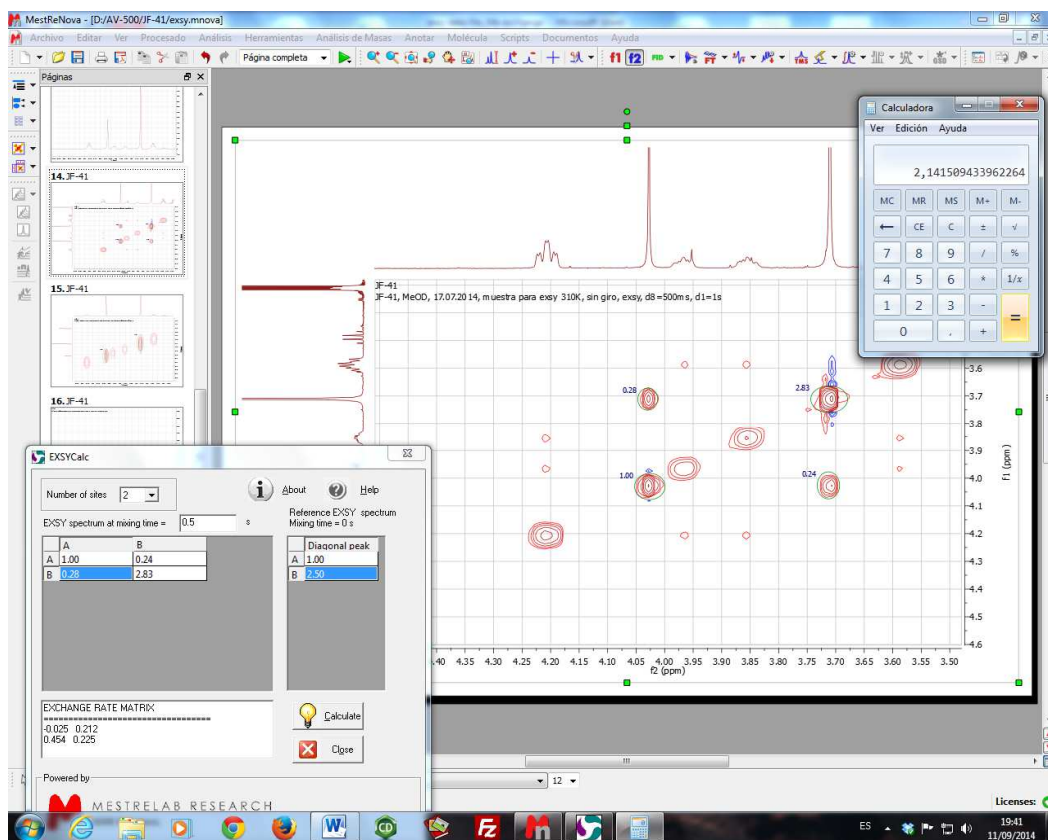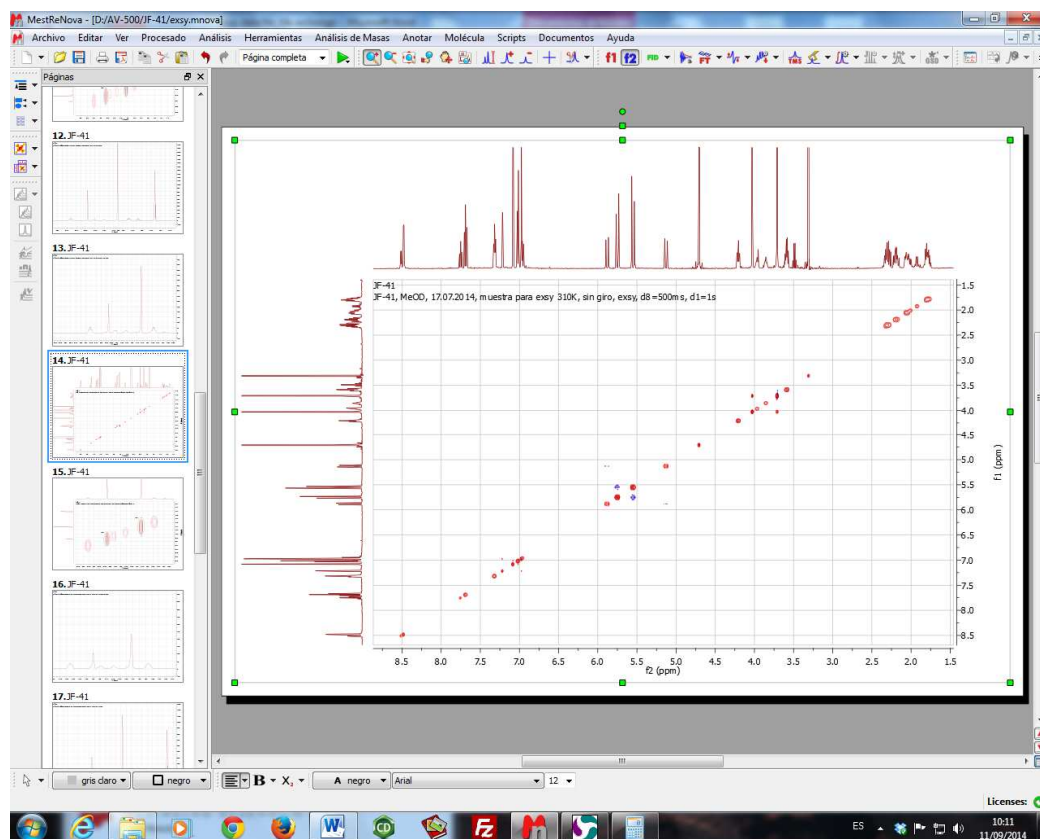
Methyl groups exchange analysis for 5a$^+$ and 5b$^+$ diasteromers of [Ir(cod){MeIm(pyridin-2-ylmethyl)}$_2$] PF$_6$ (5·PF$_6$) at different temperatures.
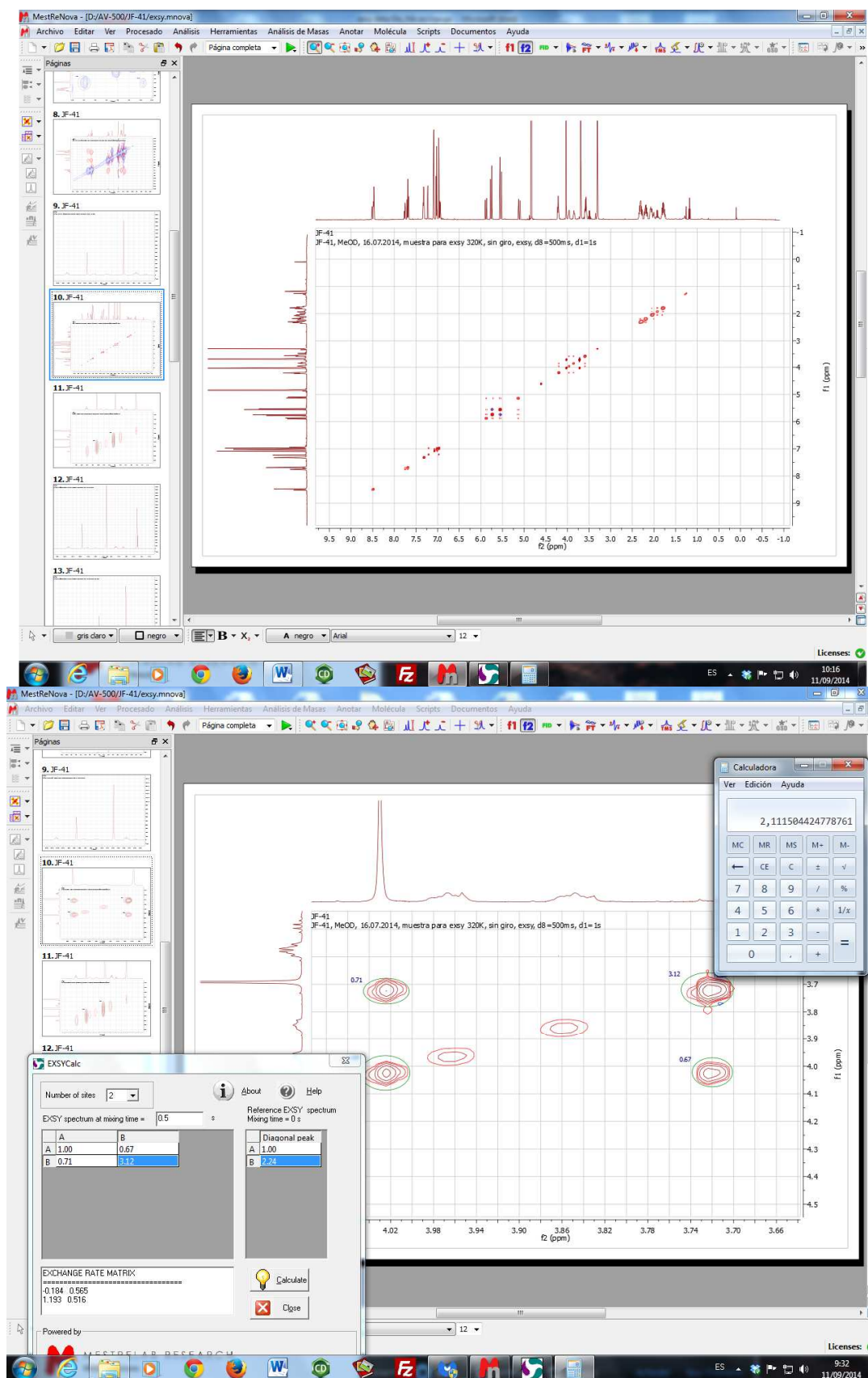
- **300 K**
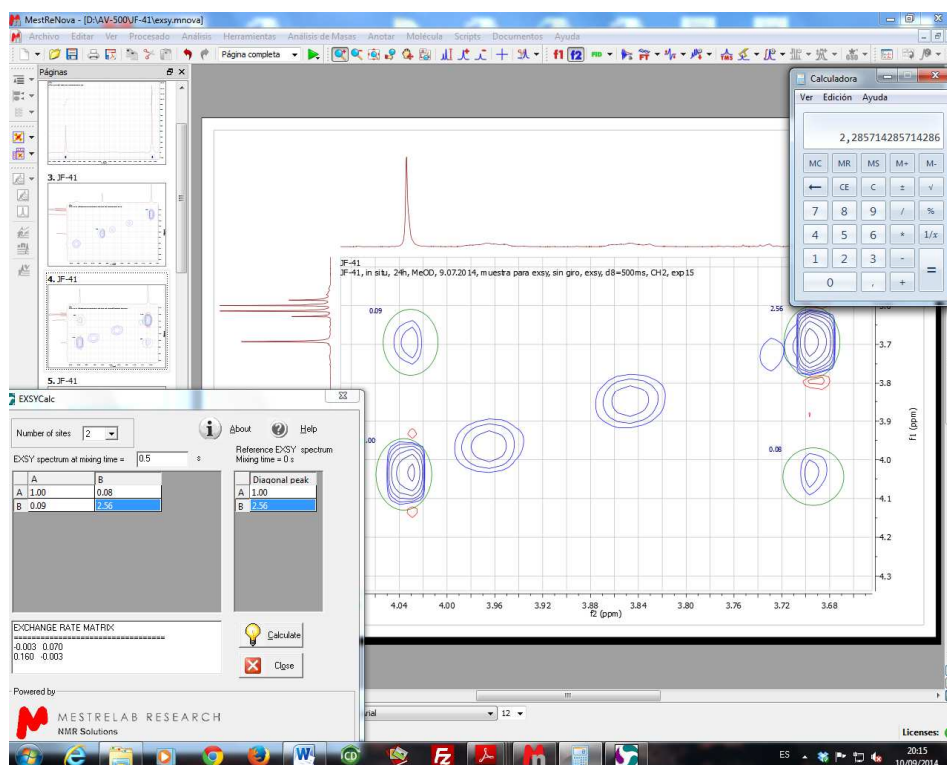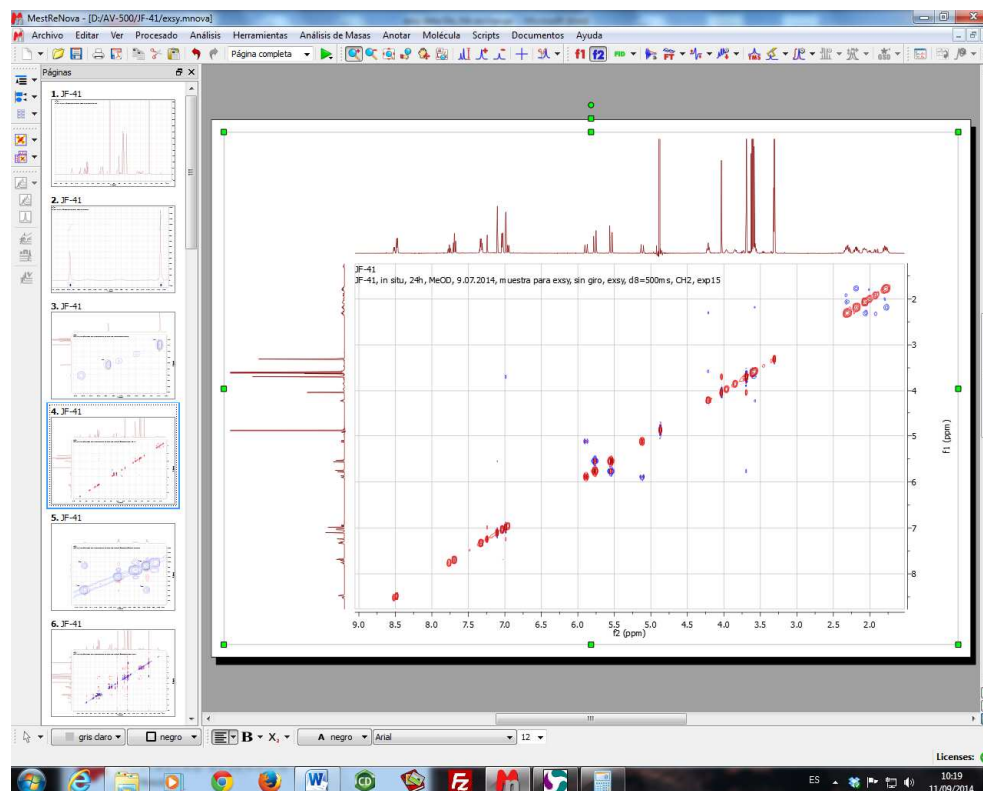
t_m = 500 ms; **Integral ratio: 2.36 / 1 = 2.36**; $K = k_1 / k_{-1} = 0.160 / 0.070 = 2.28$
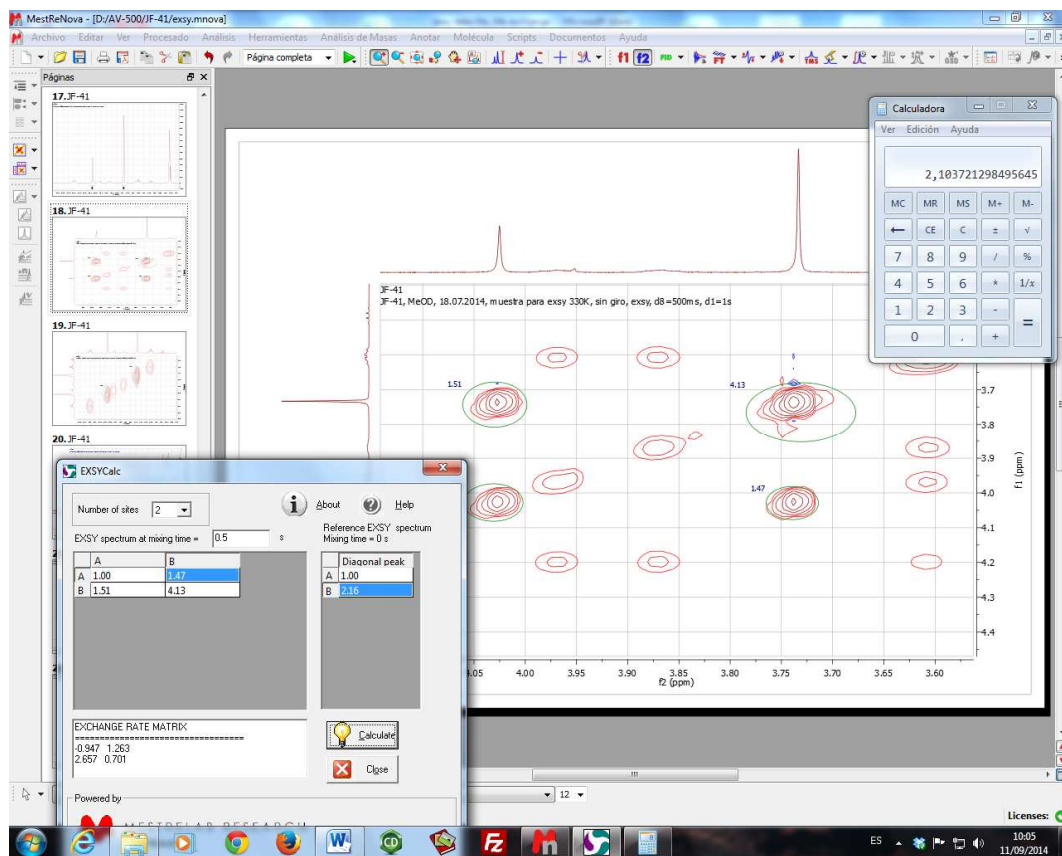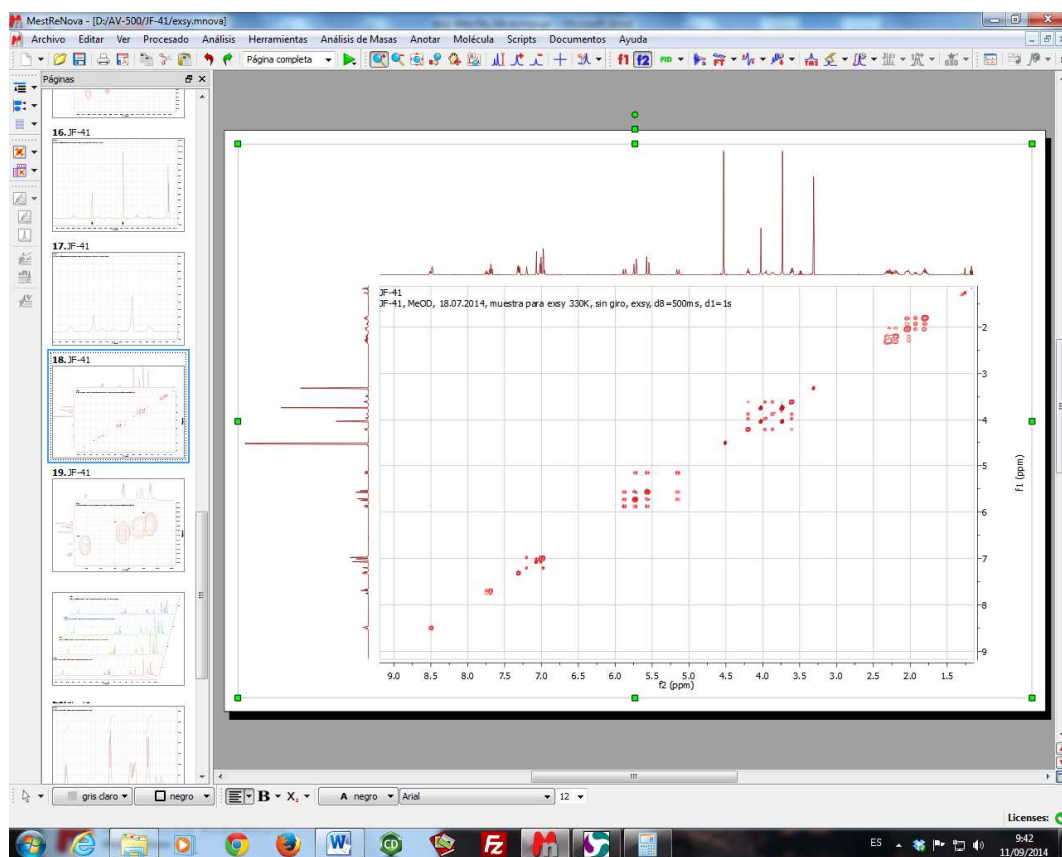
- **310 K**

t_m = 500 ms; **Integral ratio: 2.29 / 1 = 2.29**; $K = k_1 / k_{-1} = 0.454 / 0.212 = 2.14$

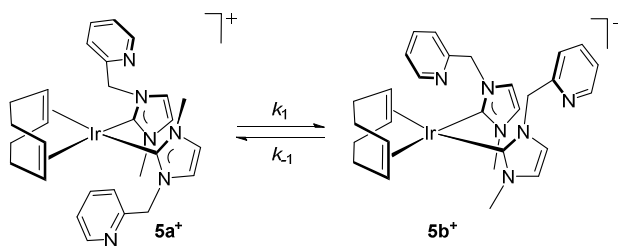- **320 K**

$t_m = 500\text{ms}$; **Integral ratio: 2.19 / 1 = 2.19**; $K = k_1 / k_{-1} = 1.193 / 0.565 = 2.11$

- **330 K**

t_m = 500 ms; **Integral ratio: 2.09 / 1 = 2.09**; $K = k_1 / k_{-1}$ = 2.657 / 1.263 = 2.10

Estimation of the kinetic parameters for the equilibrium 5a$^+$ ⇆ 5b$^+$.

T (K)	k_1 (s^{-1})	k_{-1} (s^{-1})	$K = k_1/k_{-1}$
300	1,60E-01	7,00E-02	2,29E+00
310	4,54E-01	2,12E-01	2,14E+00
320	1,19E+00	5,65E-01	2,11E+00
330	2,66E+00	1,26E+00	2,10E+00

$$\ln\left(k/T\right) = \ln\left(k_b/h\right) + \Delta S^{\#}/R - \Delta H^{\#}/RT$$

Eyring Plot (k$_1$)

y = -8996,6x + 22,478
R² = 0,999
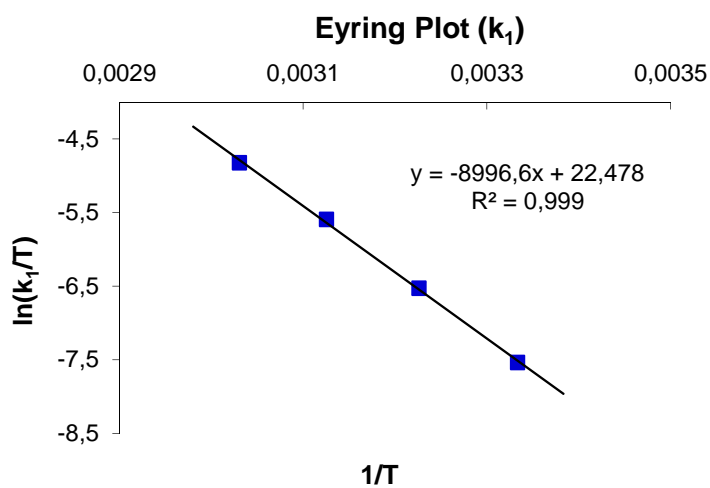
$\Delta H_1^{\#} = 74.8 \pm 4.1$ kJmol^{-1}

$\Delta S_1^{\#} = $ -11 $\pm$ 13 JK^{-1}mol^{-1}

$\Delta G_1^{\#} = 78 \pm 8$ kJmol^{-1} (298.15 K)

Eyring Plot (k₋₁)

$y = -9260{,}7x + 22{,}547$
$R^2 = 0{,}9981$
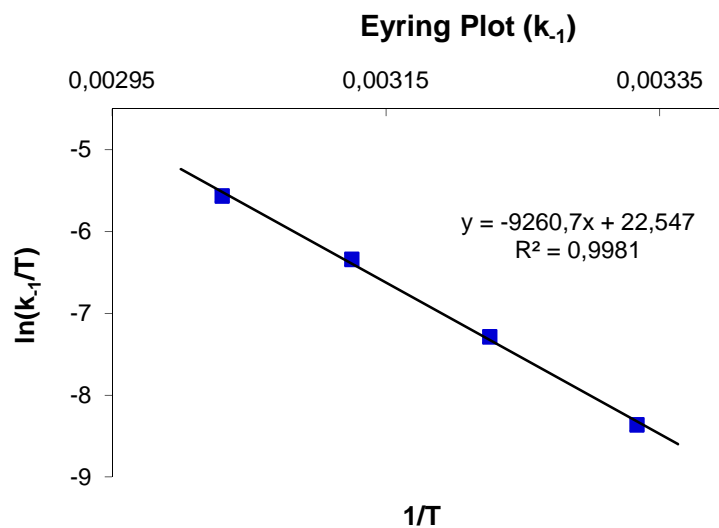
$$\Delta H_{-1}^{\#} = 77.0 \pm 4.2 \text{ kJmol}^{-1}$$

$$\Delta S_{-1}^{\#} = -11 \pm 13 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta G_{-1}^{\#} = 80 \pm 8 \text{ kJmol}^{-1} \text{ (298.15 K)}$$

Estimation of the thermodynamic parameters for the equilibrium 5a⁺ ⇆ 5b⁺.

T (K)	K	ln$K$	1/T
300	2,360E+00	0,85866	3,333E-03
310	2,290E+00	0,82855	3,226E-03
320	2,190E+00	0,78390	3,125E-03
330	2,090E+00	0,73716	3,030E-03

$$\ln K = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R}$$
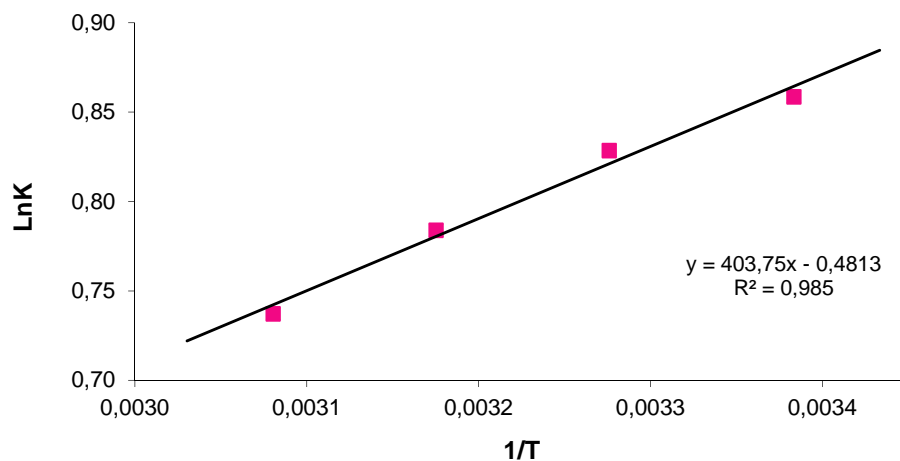
$\Delta H^{\mathrm{o}} = -3.4$ kJmol^{-1} and $\Delta S^{\mathrm{o}} = -4.0$ Jmol^{-1}

Figure S10. Energy profiles for all the proposed catalytic cycles: via hydride (involving hydrido species), and via MPV mechanism. The "**a**" numbered series refer to the catalyst bearing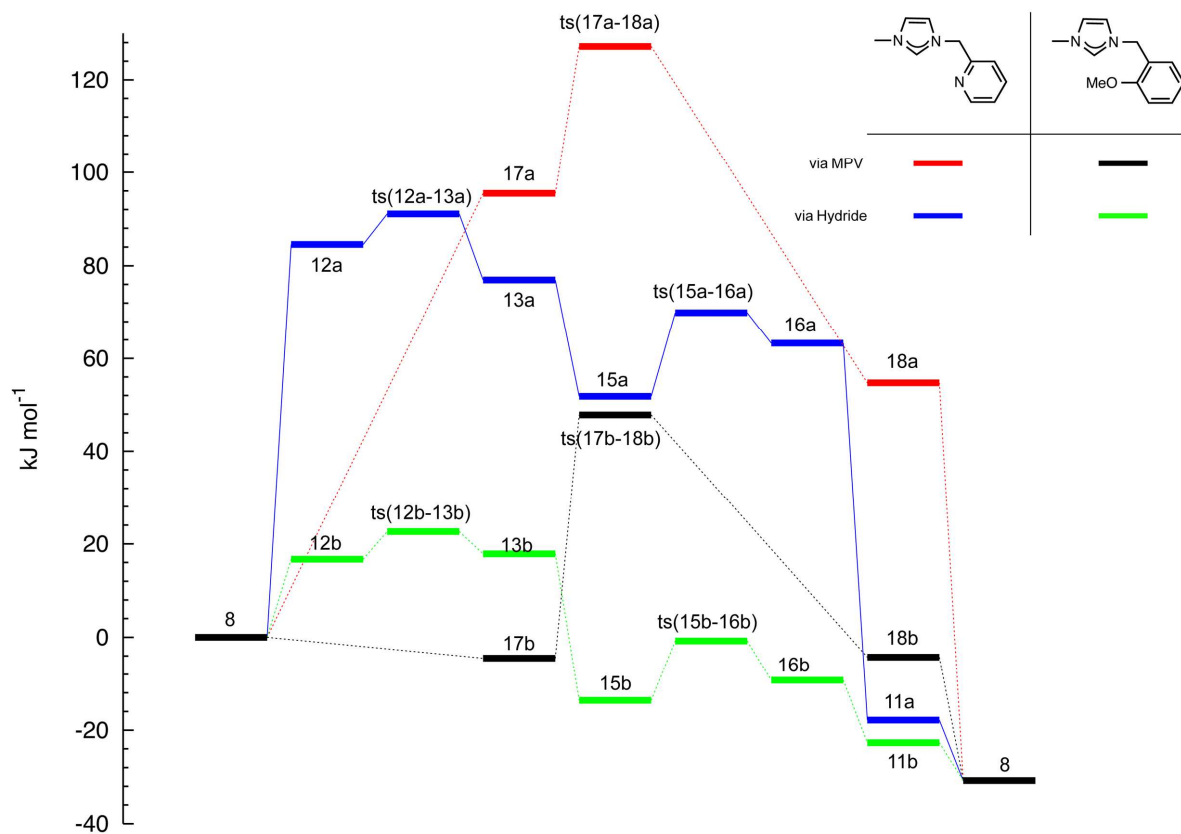 a pyridin-2-ylmethyl functionalized NHC ligand while the "**b**" series are those referred to the catalyst having a NHC with a 2-methoxybenzyl wingtip.

Table S1. Calculated electronic and free energies

Compound	E (RB3PW91, Hartree)	G (Sum of electronic and free energies, Hartree)
Cyclohexanoxide	-310.35389342	-310.22506700
Ciclohexanone	-309.78209865	-309.66183700
Isopropoxide	-193.65466127	-193.58945900
Acetone	-193.08744760	-193.03264100
Isopropanol	-194.29197494	-194.21120600
Cyclohexanol	-310.99701728	-310.85212100
7a	-961.85284359	-961.56820300
8a	-1154.97465775	-1154.60307200
TS 8a-9a	-1154.91950844	-1154.55223900
9a	-1154.93839928	-1154.56663500
10a	-1271.63980892	-1271.20368500
TS 10a_11a	-1271.62057558	-1271.18924000
11a	-1271.67519176	-1271.23906800
11a	-1271.67519176	-1271.23906800
12a	-1154.93553327	-1154.57087800
TS 12a-13a	-1154.93026773	-1154.56838000
13a	-1154.93668983	-1154.57376000
15a	-1271.63867869	-1271.21252200
TS 15a-16a	-1271.63168563	-1271.20564200
16a	-1271.63746773	-1271.20815700
17a	-1464.73810721	-1464.22854400
TS 17a-18a	-1464.72627787	-1464.21646200
18a	-1464.75246090	-1464.24406700
7b	-1060.26961651	-1059.94420800
8b	-1253.39381999	-1252.98210300
11b	-1370.09683585	-1369.61994400
12b	-1253.38238670	-1252.97574300
TS 12b-13b	-1253.37660217	-1252.97348400
13b	-1253.37466800	-1252.97529700
15b	-1370.08667415	-1369.61648300
TS 15b-16b	-1370.07891265	-1369.61160200
16b	-1370.08487390	-1369.61483100
17b	-1563.19646232	-1562.64564300
TS 17b-18b	-1563.17769617	-1562.62572700
18b	-1563.19683420	-1562.64555800

(1) Cross peaks were integrated and processed with the EXSYCalc software distributed by

Mestrelab Research (http://mestrelab.com/).

(2) (a) Perrin, C. L.; Dwyer, T. J. Chem. Rev. 1990, 90, 935–967. (b) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Šik, V.; Stephenson, D. J. Magn. Reson. 1986, 70, 34–53; (c) Ernst, R. R.; Bodenhausen, G.; Wokau, A. Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Oxford University Press, Oxford, 1983.

(3) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. J. Chem. Phys. 1979, 71, 4546–4553.

(4) Perrin, C. J. Magn. Resn. 1989, 82, 619–621.

(5) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. Organometallics 1994, 13, 1646–1655.