Supporting Information

Probing the hydrogenation of vinyl sulfoxides using *para*-hydrogen

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S1. General remarks

All NMR measurements were carried out on a 400 MHz Bruker Avance III spectrometer at 298 K unless otherwise stated. *Para*-hydrogen (*p*-H_2) was produced by passing hydrogen gas over a spin-exchange catalyst (Fe_2O_3) at 28 K and used for all hyperpolarization experiments. This method produces constant *p*-H_2 with ca. 93% purity. ^{1}H (400 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded with an internal deuterium lock. Chemical shifts are quoted as parts per million and referenced to methanol. ^{13}C NMR spectra were recorded with broadband proton decoupling. Coupling constants (*J*) are quoted in Hertz. All starting compounds were purchased from Sigma Aldrich, Fluorochem or Alfa-Aesar and used as supplied without further purification.
The shake & drop method was employed for recording hyperpolarized SABRE NMR spectra.[1] Samples were prepared in a 5 mm NMR tube that was fitted with a J. Young's tap. The iridium precatalyst used was [IrCl(COD)(IMes)] (where IMes = 1,3-bis(2,4,6-trimethyl-phenyl)imidazole-2-ylidene and COD = cis,cis-1,5-cyclooctadiene) and was synthesized in our laboratory according to a literature procedure.[2] The NMR samples were subsequently degassed by two freeze-pump-thaw cycles before filling the tube with *p*-H_2 at 3 bar pressure. Once filled with *p*-H_2, the NMR tubes were shaken vigorously for 10 seconds in the 65 Gauss fringe field of a 9.4 T Bruker spectrometer. Immediately after that, the NMR tubes were put inside the spectrometer for NMR detection.

S2. Characterization of products

S2.1. Characterization of phenylvinyl sulfoxide, A

A sample containing 0.1 mL phenylvinylsulfoxide, **A**, and 0.5 mL methanol-d_4 was characterized using NMR spectroscopy at 298 K.

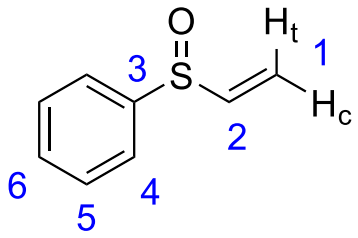

*Figure S1: Structure of the starting phenylvinylsulfoxide, **A**, where the labels refer to the resonance numbers of Table S1.*

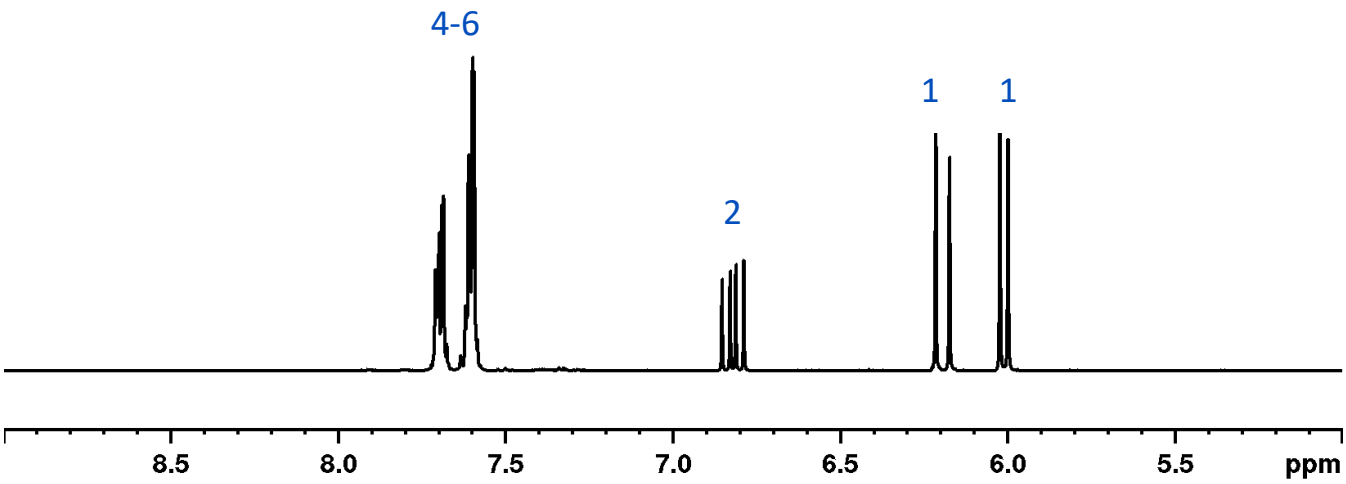

Figure S2: Partial ^{1}H NMR spectrum of a solution containing 0.1 mL phenylvinylsulfoxide and 0.5 mL methanol-d_4 at 298 K where the labels reflect the resonances shown in Figure S1.

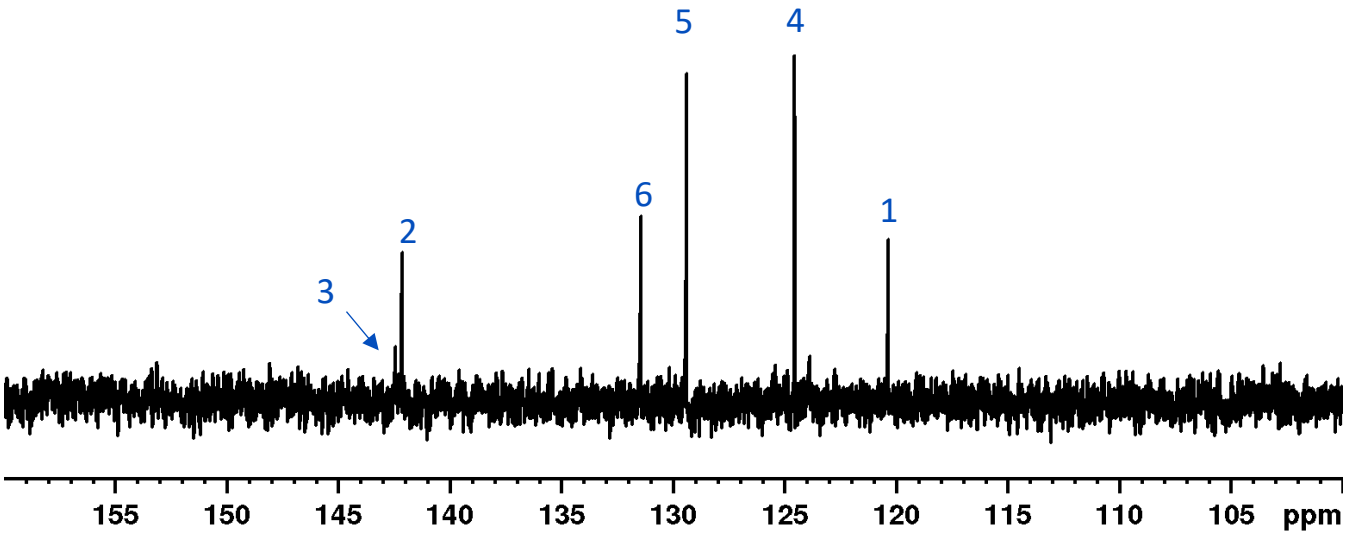

Figure S3: Partial ^{13}C NMR spectrum of a solution containing 0.1 mL phenylvinylsulfoxide and 0.5 mL methanol-d_4 at 298 K where the labels reflect the resonances shown in Figure S1.

*Table S1: NMR characterisation data of the starting phenylvinylsulfoxide, **A**, of Figure S1 at 298 K.*

Resonance	^{1}H	^{13}C
1	$^{1}H_t$ 6.18 d ($^{3}J_{trans}$ = 16.5 Hz)	120.43
	$^{1}H_c$ 5.97 d ($^{3}J_{cis}$ = 9.5 Hz)	
2	6.79 dd ($^{3}J_{trans}$ = 16.5 Hz, $^{3}J_{cis}$ = 9.5 Hz)	142.31
3	-	142.61
4	7.5-7.6 (overlap)	124.61
5	7.5-7.6 (overlap)	129.50
6	7.5-7.6 (overlap)	131.49

S2.2. Characterization of phenylethyl sulfoxide, B

A sample containing 2 mg [IrCl(COD)(IMes) and 2 µL phenylvinylsulfoxide, **A**, in 0.6 mL methanol-d_4 were hydrogenated with 3 bar H_2 for 800 minutes at 298 K. The resultant solution was characterized using NMR spectroscopy at 298 K. An aliquot of this 0.6 mL NMR tube solution was taken for mass spectral analysis. Electrospray high resolution mass spectra were recorded on a Bruker Daltronics microOTOF spectrometer. The presence of the phenylethyl sulfoxde was confirmed.

$[C_8H_{10}OS + H]^+$ calc. 155.0531 found 155.0522

$[C_8H_{10}OS + Na]^+$ calc. 177.0350 found 177.0343

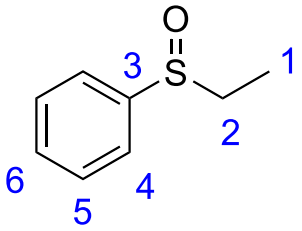

*Figure S4: Structure of the hydrogenated product phenylethylsulfoxide, **B** where the labels refer to the resonance numbers of Table S2.*

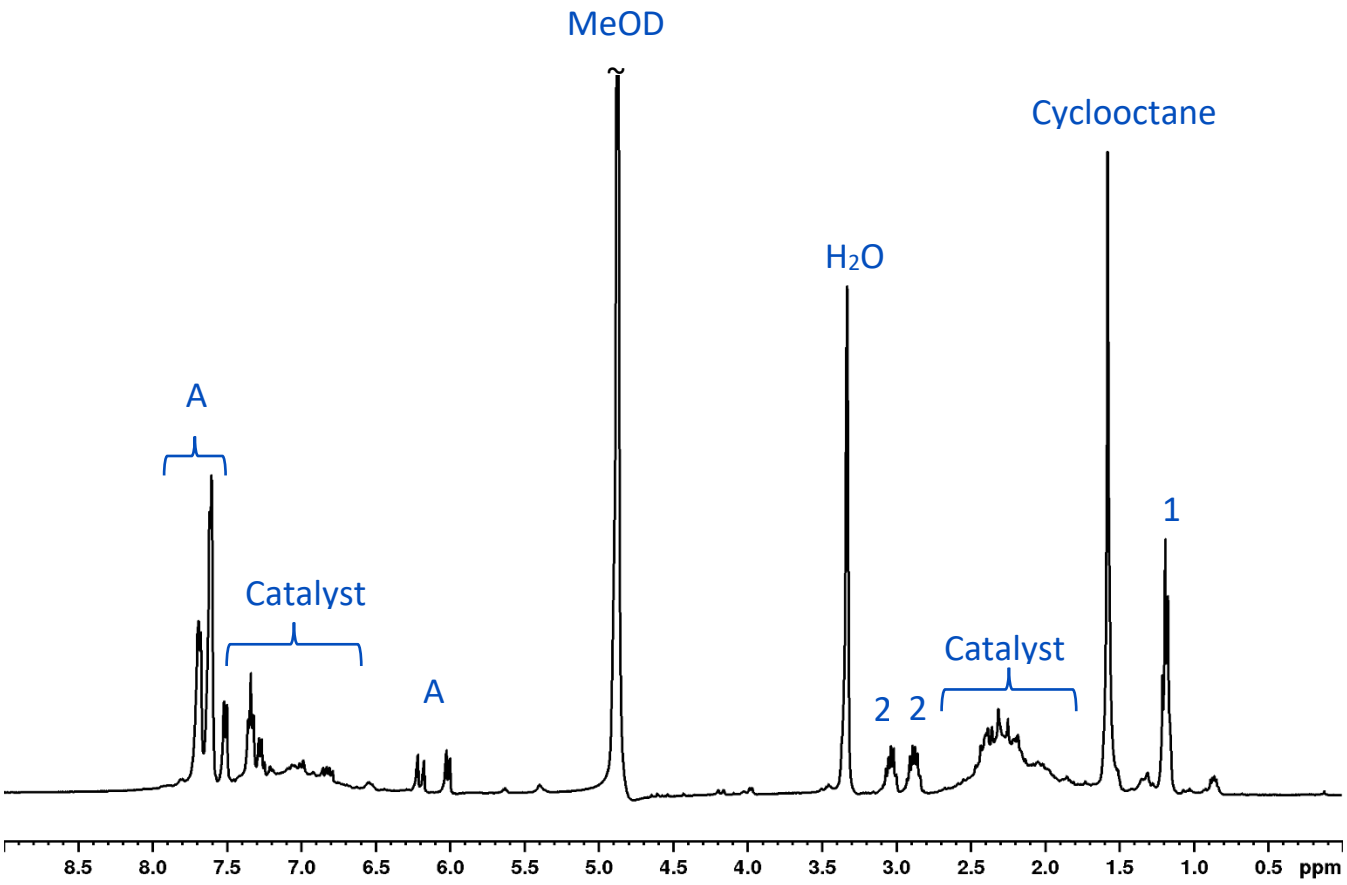

*Figure S5: Partial ^{1}H NMR spectrum after a solution containing 2 mg [IrCl(COD)(IMes)] and 2 µL phenylvinylsulfoxide, **A**, in 0.6 mL methanol-d_4 were hydrogenated with 3 bar H_2 for 800 minutes at 298 K where the numerical labels reflect the resonances shown in Figure S4.*

*Table S2: NMR characterisation data of the hydrogenated product phenylethylsulfoxide, **B** of Figure S2 at 298 K.*

Resonance	^{1}H	^{13}C
1	1.19 t (^{3}J = 7 Hz)	4.79
2	2.89 (m), 3.09 (m)	49.6
3	-	141.66
4	7.71	123.73
5	7.64 (overlap)	129.17
6	7.64 (overlap)	131.18

S2.3: Characterization of [IrCl(H)$_2$(dibenzyl sulfoxide)$_2$(IMes)], 3

A sample containing 2 mg [IrCl(COD)(IMes)] and 4 eq. dibenzyl sulfoxide, **C** in 0.6 mL methanol-d_4 were left under 3 bar H_2 for 1 hour at 298 K before 2D NMR characterization was performed at 245 K. An aliquot of this 0.6 mL NMR tube solution was taken for mass spectral analysis.

$[C_{14}H_{14}NaOS + Na]^+$ calc. 253.0663 found 253.0656 (**C**)

$[C_{49}H_{54}ClIrN_2O_2S_2 - C_{14}H_{16}ClOS]^+$ calc. 727.2334 found 727.2338 (**3** fragment)

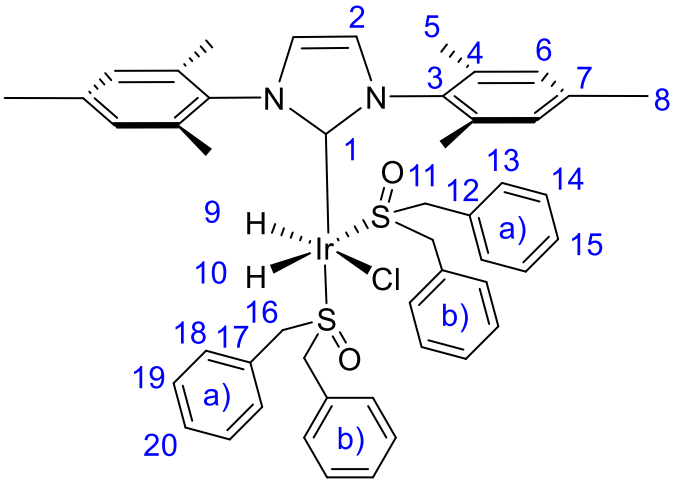

*Figure S6: Structure of [IrCl(H)$_2$(**C**)$_2$(IMes)], **3** where the labels refer to the resonance numbers of Table S3.*

*Table S3: NMR characterisation data of [IrCl(H)$_2$(**C**)$_2$(IMes)], **3** of Figure S3 at 245 K.*

Resonance	^{1}H	^{13}C
1	-	-
2	~ 7 (overlap)	~ 128 (overlap)
3	-	~ 135 (overlap)
4	-	135.45
5	2.21	17.89
6	7.06	~ 128 (overlap)
7	-	131.40
8	2.42	20.16
9	−15.78 ($^2J_{HH}$ = 6 Hz)	-
10	−20.89 ($^2J_{HH}$ = 6 Hz)	-
11	a) 2.47, 3.13 ($^2J_{HH}$ = 14 Hz) b) 3.71, 4.95 ($^2J_{HH}$ = 12 Hz)	a) 65.99 b) 64.02
12	-	~ 132 (overlap)
13	a) 6.91 b) 6.83	a) 131.23 b) 132.55
14	a) 7.32 b) 7.18	a) 128.03 b) 128.41
15	a) 7.43 b) 7.62	~ 128 (overlap)
16	a) 4.98, 5.35 ($^2J_{HH}$ = 11 Hz) b) 3.78, 5.44 ($^2J_{HH}$ = 13 Hz)	a) 61.1 b) 50.91
17	-	~ 133 (overlap)
18	a) ~ 7 (overlap) b) 6.23	a) ~ 132 (overlap) b) 132.90
19	a) ~ 7 (overlap) b) 6.99	a) ~ 128 (overlap) b) 126.67
20	a) ~ 7 (overlap) b) 7.09	~ 128 (overlap)

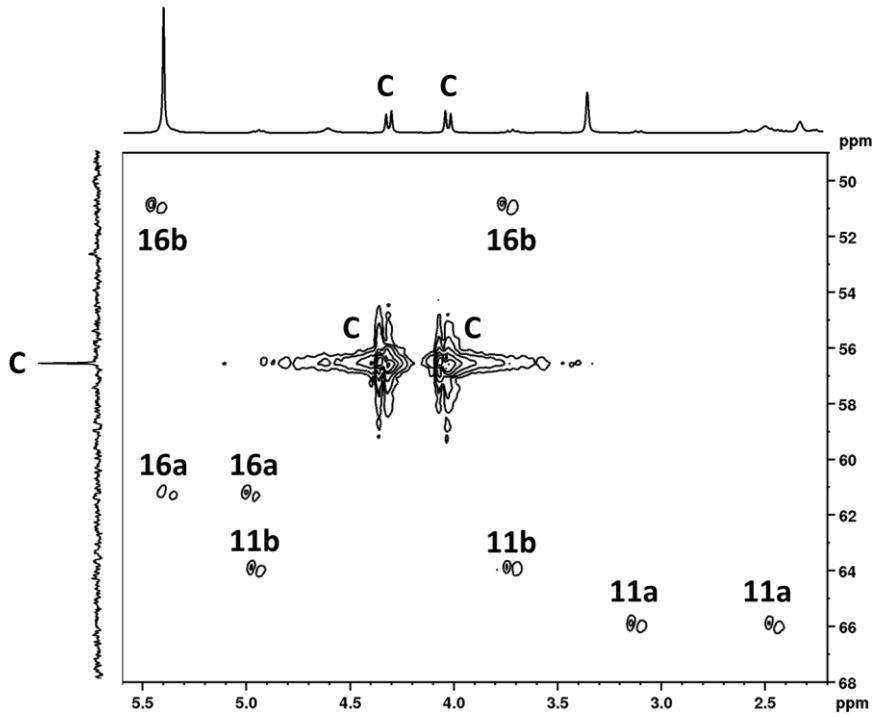

*Figure S7: In a short range HMQC at 245 K [IrCl(H)$_2$(**C**)$_2$(IMes)] exhibits four pairs of diastereotopic CH$_2$ protons corresponding to the two bound **C** ligands.*

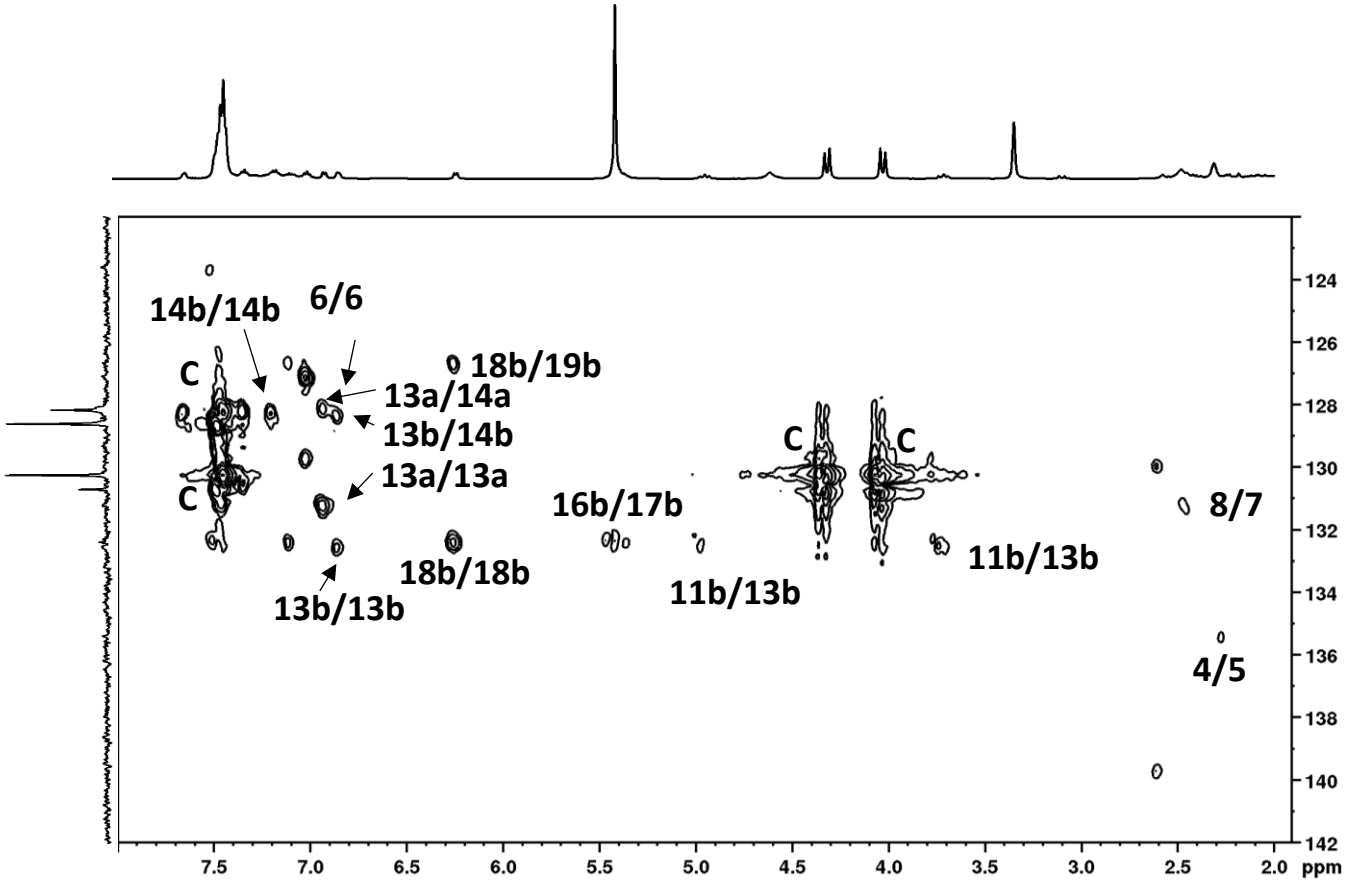

*Figure S8: A partial long range ^{1}H-^{13}C HMQC at 245 K of a solution of [IrCl(H)$_2$(**C**)$_2$(IMes)] in methanol-d$_4$ with (^{1}H/^{13}C) resonance labels corresponding to those in Figure S6 and Table S3.*

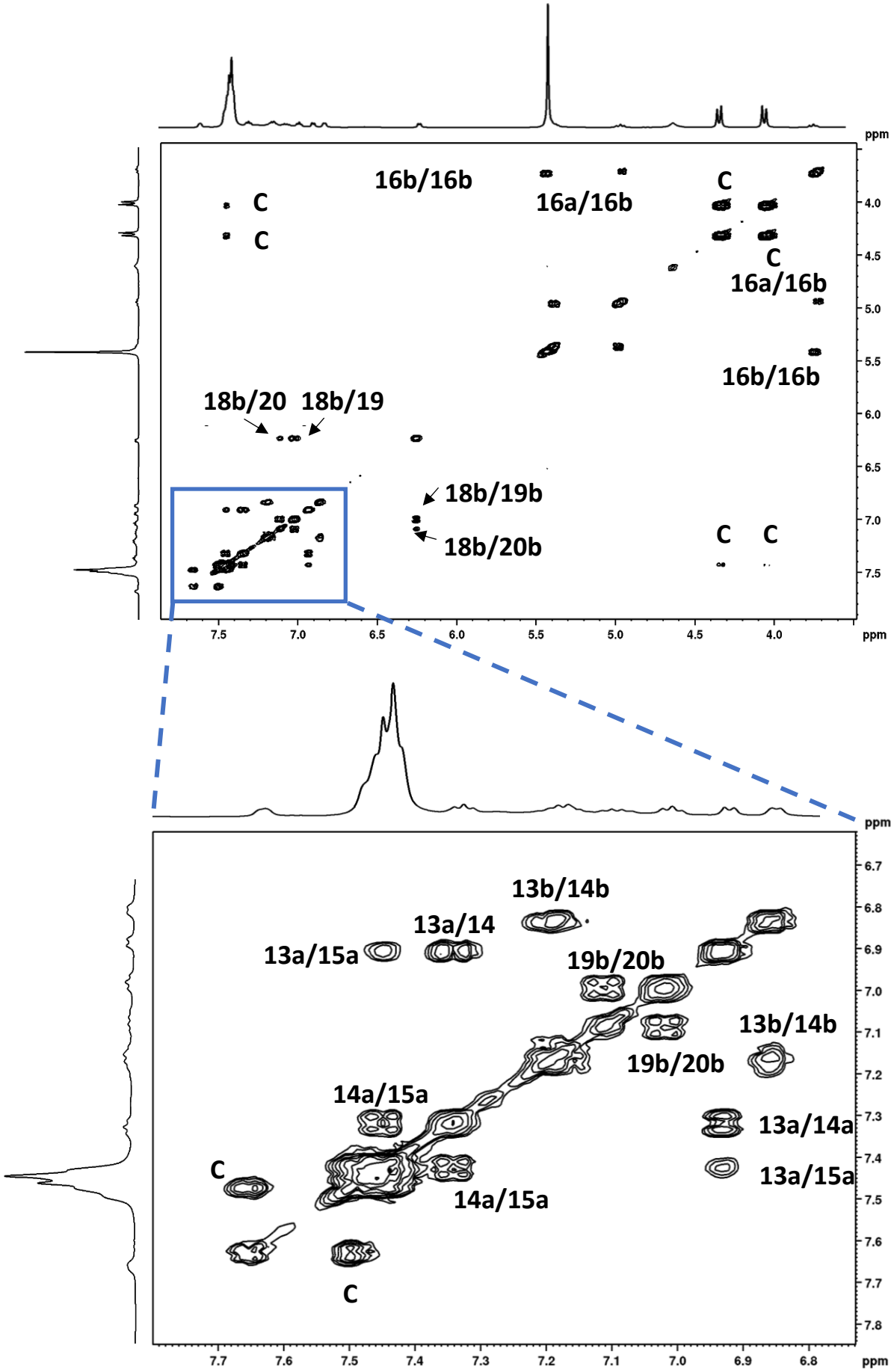

*Figure S9: A partial ^{1}H-^{1}H COSY at 245 K of a solution of [IrCl(H)$_2$(**C**)$_2$(IMes)] in methanol-d$_4$ with resonance labels corresponding to those in Figure S6 and Table S3.*

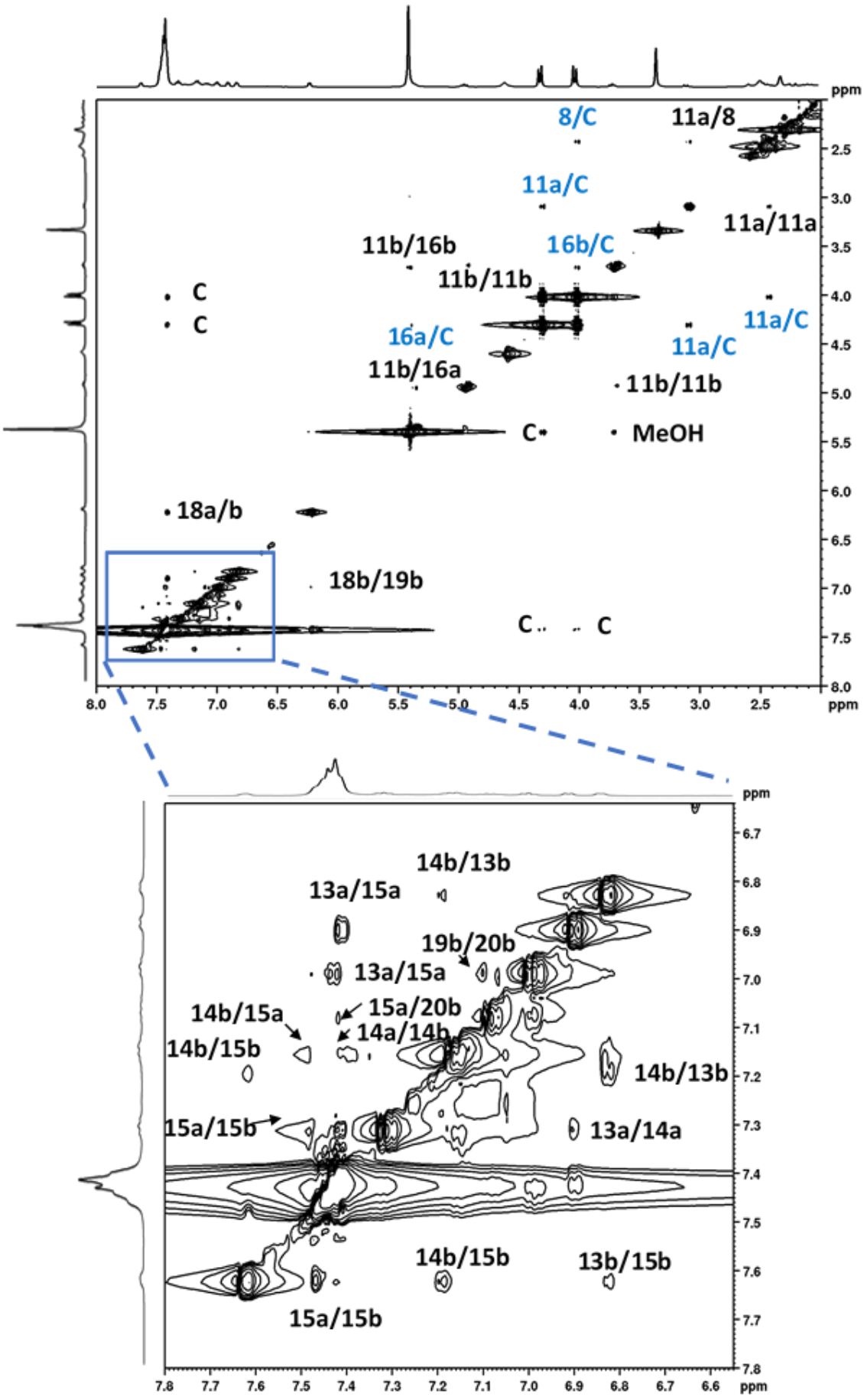

*Figure S10: A partial ^{1}H-^{1}H NOESY at 245 K of a solution of [IrCl(H)$_2$(**C**)$_2$(IMes)] in methanol-d_4 with resonance labels corresponding to those in Figure S6 and Table S3. Those resonance labels in blue reflect exchange peaks while those in black reflect NOE interactions.*

S2.4: Characterization of $[Ir_2(H)_3(\kappa^2\text{-}H)(\kappa^2\text{-}SPh)_2(IMes)_2(S(O)(Et)(Ph))]$, 4 and $[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$, 5

$[Ir_2(H)_3(\kappa^2\text{-}H)(\kappa^2\text{-}SPh)_2(IMes)_2(S(O)(Et)(Ph))]$, **4** and $[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$, **5** were prepared by leaving a solution of [IrCl(COD)(IMes)] (5 mM), sodium-1,2-pyruvate-[$^{13}C_2$] (5 eq.) and phenylvinylsulfoxide (4 eq.) with 3-bar H_2 in methanol-d_4 at 278 K for a period of several weeks.

For X-ray diffraction studies, a suitable crystal was selected and mounted on an Oxford Diffraction SuperNova- X-ray diffractometer. The crystal was kept at 110 K during data collection. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "CrysAlisPro".[3] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2,[4] the structure was solved with the ShelXT[5] structure solution program using Intrinsic Phasing and refined with the ShelXL[6] refinement package using Least Squares minimisation.

Table S4: Crystal data and structure refinement for the crystal structure of $[Ir_2(H)_3(\kappa^2\text{-}H)(\kappa^2\text{-}SPh)_2(IMes)_2(S(O)(Et)(Ph))]$, ***4*** *and $[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$,* ***5****.*

Compound	$[Ir_2(H)_3(\kappa^2\text{-}H)(\kappa^2\text{-}SPh)_2(IMes)_2(S(O)(Et)(Ph))]$	$[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$
Empirical formula	$C_{63}H_{76}Ir_2N_4O_2S_3$	$C_{70}H_{80}Ir_2N_4O_2S_3$
Formula weight	1401.85	1489.96
Temperature/K	110.05(10)	110.10(14)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	11.9397(4)	19.8526(2)
b/Å	12.7147(4)	15.10020(10)
c/Å	20.2094(6)	21.9966(2)
α/°	91.573(3)	90
β/°	92.120(3)	105.3940(10)
γ/°	101.839(3)	90
Volume/Å^3	2998.74(16)	6357.53(10)
Z	2	4
ρ_{calc}g/cm^3	1.553	1.557
μ/mm^{-1}	4.583	4.328
F(000)	1400.0	2984.0
Crystal size/mm^3	0.147 × 0.125 × 0.067	0.199 × 0.165 × 0.121
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.758 to 56.55	6.64 to 52.744
Index ranges	-15 ≤ h ≤ 14, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26	-14 ≤ h ≤ 24, -17 ≤ k ≤ 18, -27 ≤ l ≤ 21
Reflections collected	24647	26164
Independent reflections	13472 [R_{int} = 0.0297, R_{sigma} = 0.0517]	12962 [R_{int} = 0.0259, R_{sigma} = 0.0408]
Data/restraints/parameters	13472/7/719	12962/0/758
Goodness-of-fit on F^2	1.102	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0786	R_1 = 0.0260, wR_2 = 0.0535
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.0861	R_1 = 0.0353, wR_2 = 0.0576
Largest diff. peak/hole / e Å^{-3}	2.44/-1.41	1.15/-0.94

For characterisation by NMR a sample of $[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$, **5** was prepared by leaving a solution of [IrCl(COD)(IMes)] (5 mM), sodium-1,2-pyruvate-[$^{13}C_2$] (5 eq.) and phenylvinylsulfoxide (4 eq.) with 3-bar H_2 in methanol-d_4 at 278 K for a period of several weeks. The solid precipitate that formed was redissolved in DCM-d_2 and a ^{1}H NMR spectrum was recorded at 245 K. The hydride region of these spectra showed the presence of **3** at δ – 15.68 and δ – 22.38 in addition to a hydride resonance at δ – 18.49 which is expected to correspond to **5**. **3** and **5** are present in a 8:1 ratio which makes full 2D NMR characterisation of **5** challenging due to its low concentration, peak overlap and the inability to seperate them in this mixture. Unfortunately, we were unable to observe NOE peaks from the hydride resonance of **5** to other sites.

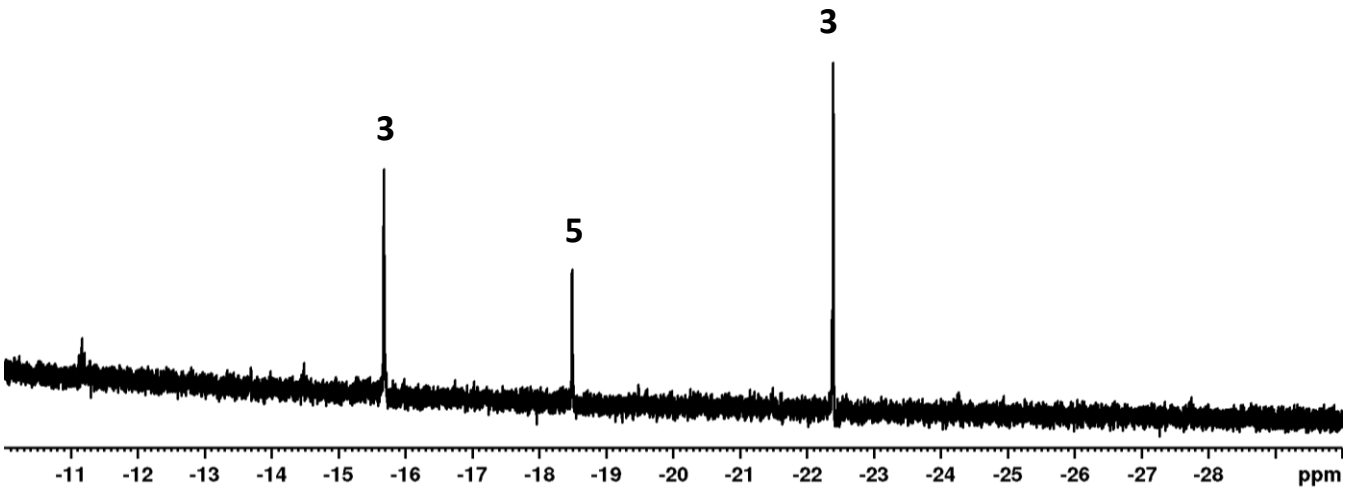

*Figure S11: A partial ^{1}H NMR spectra recorded at 245 K after a solid precipitate of **3** and **5** were dissolved in DCM-d_2.*

For analysis by high resolution mass spectrometry, a solid sample ocontaining $[Ir_2(H)_3(\kappa^2\text{-}H)(\kappa^2\text{-}SPh)_2(IMes)_2(S(O)(Et)(Ph))]$, **4** was prepared. This involved adding 3 bar H_2 to a solution of [IrCl(COD)(IMes) (5 mM) and 4 eq. phenylvinylsulfoxide in methanol and leaving for several days beforeby removing the solvent.

$[C_8H_{10}NaOS + Na]^+$ calc. 177.0350 found 177.0343 (**B**)

$[C_{62}H_{72}Ir_2N_4OS_3 – C_{27}H_{35}IrN_2S + Na]^+$ calc. 781.1874 found 781.1898 (**4** fragment)

Crystals of $[Ir_2(H)_4(\kappa^2\text{-}S)(IMes)_2(S(O)(CH_2Ph)_2)_2]$, **5** were prepared as described above and submitted for mass spectral analysis

$[C_{70}H_{80}Ir_2N_4O_2S_3 – C_{21}H_{27}N_2S]^+$ calc. 1151.2807 found 1151.2761 (**5** fragment)

S3. Monitoring formation of products

S3.1. Formation of phenylethylsulfoxide, B

The formation of phenylethylsulfoxide at 298 K was monitored by recording a series of one scan hyperpolarised ^{1}H NMR spectra with 90^o pulse angles after 3 bar H_2 addition to a solution of 2 mM **1** (2 mg) and 4 eq. vinyl sulfoxide (1.5 µL) in methanol-d_4.

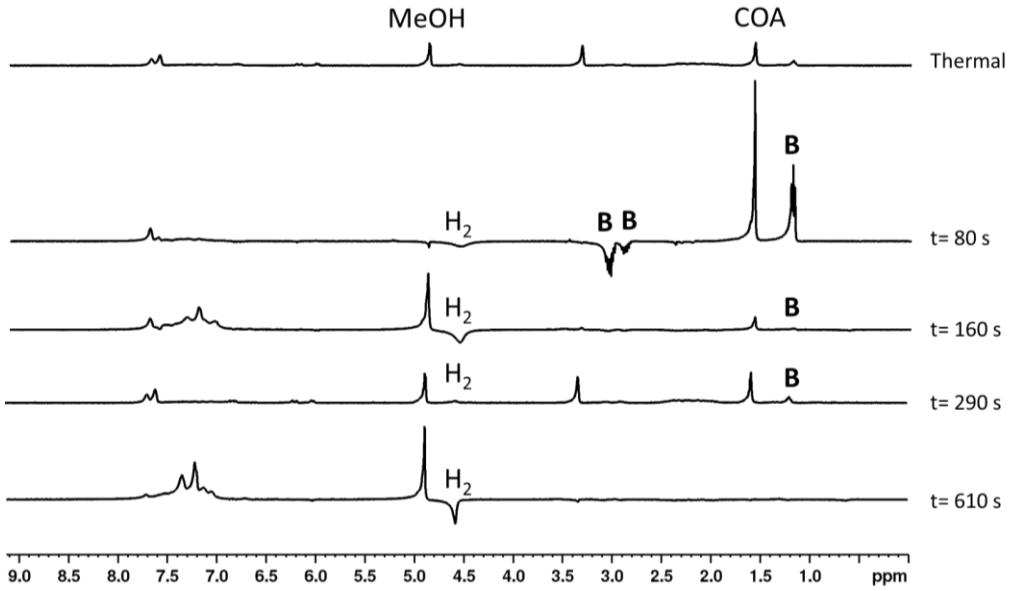

*Figure S12: A series of single scan ^{1}H NMR spectra recorded with 90^o pulses at various times (t) after 3 bar H_2 addition to a solution of 5 mM **1** and 4 eq. **A** at 298 K. COA corresponds to cyclcoctane.*

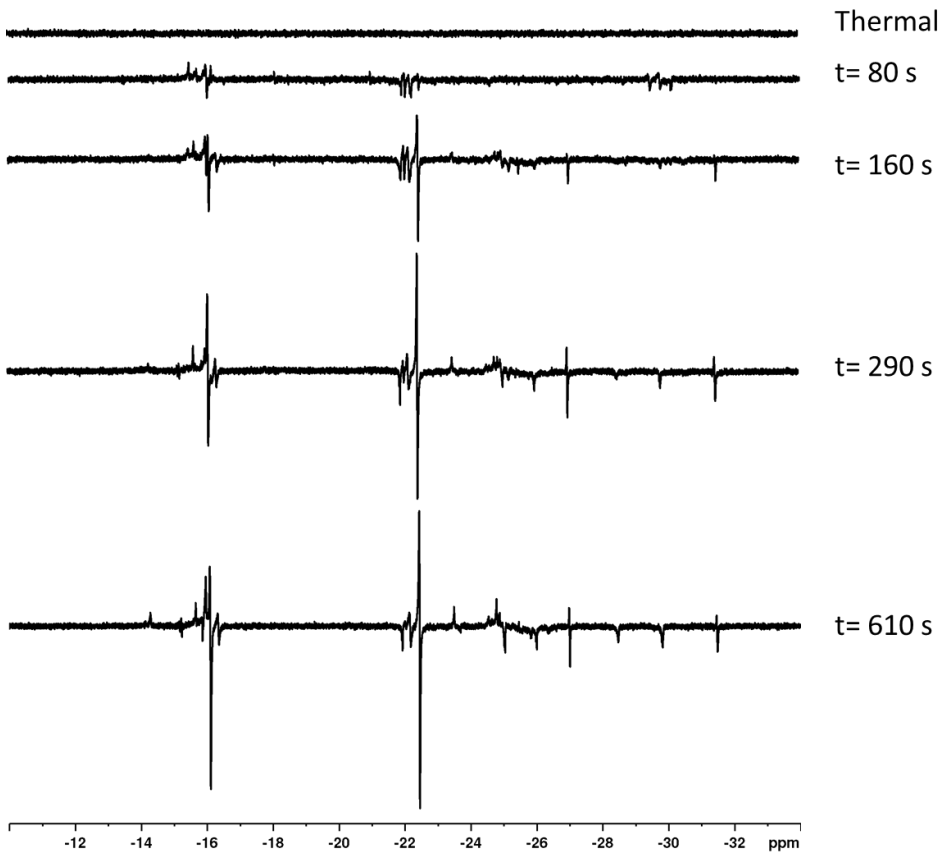

*Figure S13: The hydride region of a series of single scan ^{1}H NMR spectra recorded with 90^o pulses at various times (t) after 3 bar H_2 addition to a solution of 5 mM **1** and 4 eq. **A** at 298 K. This plot is scaled vertically by a factor of 16 relative to Figure S12.*

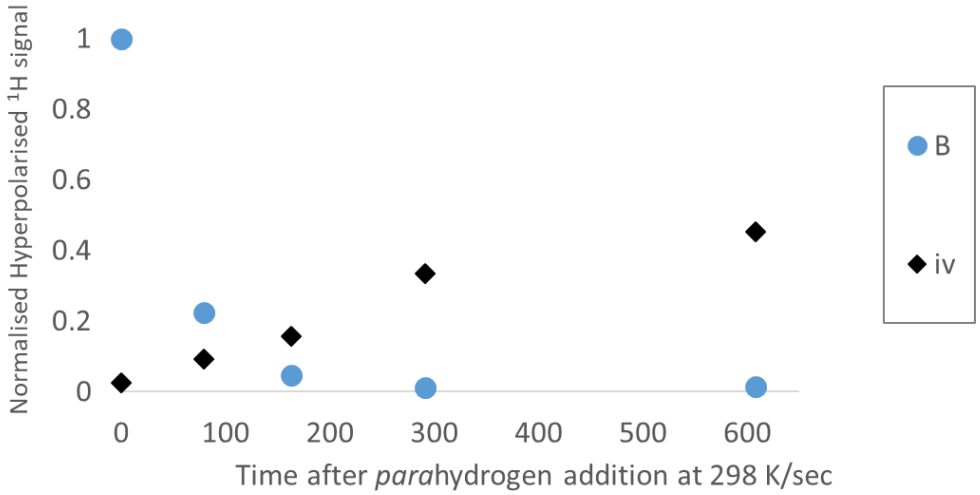

*Figure S14: The evolution of the hyperpolarised signals of phenylethylsulfoxide, **B** and the major hyperpolarised hydride signal (iv) at δ −16.20 and δ −12.37 can be monitored over time at 298 K.*

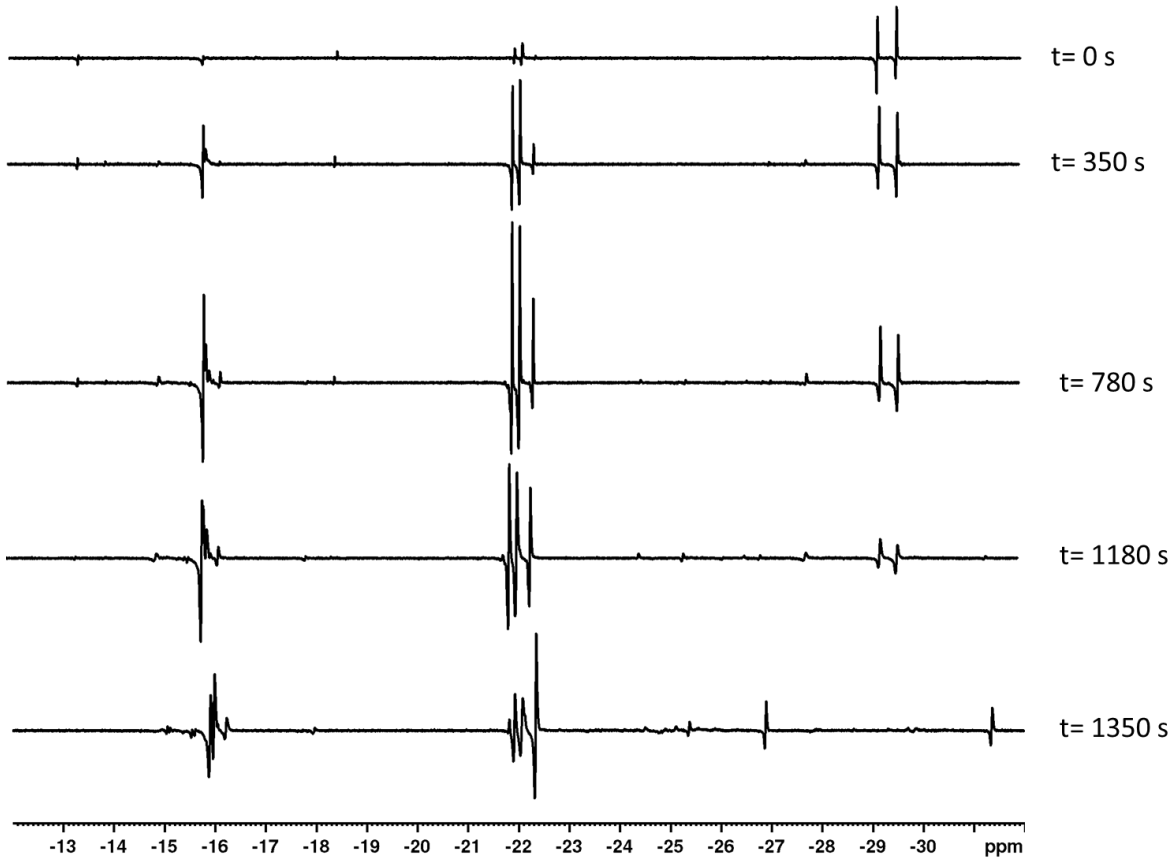

*Figure S15: Hydride region of a series of single scan ^{1}H NMR spectra recorded with 45° pulses at various times (t) after 3 bar H_2 addition to a solution of 5 mM **1** and 4 eq. **A** at 263 K.*

The formation of phenylethylsulfoxide at 298 K was also monitored using thermally polarised methods by recording a series of ^{1}H NMR spectra after 3 bar H_2 addition to solutions of **1** and phenylvinyl sulfoxide in 0.6 mL methanol-d_4. The proportion of each species in solution was determined from diagnostic alkene resonances of phenylvinyl sulfoxide at δ 5.97, δ 6.18 and δ 6.79 and phenylethyl sulfoxide resoannces at δ 1.19, δ 2.89 and δ 3.09.

These conversions have been measured under four conditions: i) [IrCl(COD)(IMes)] (1.94 mg) and phenylvinyl sulfoxide (1.5 µL, 4 eq.) ii) phenylvinyl sulfoxide (1.5 µL, 4 eq.) added to a solution of [IrCl(COD)(IMes)] (1.92 mg) and dibenzyl sulfoxide (3 mg) preactivated with 3-bar H_2 for 90 mins iii) [IrCl(COD)(IMes)] (0.3 mg) and phenylvinyl sulfoxide (1.5 µL, 25 eq.) and iv)

[IrCl(COD)(IMes)] (1.99 mg) and phenylvinyl sulfoxide (1 mL, 2400 eq.) and are shown in Figure S9. The turnovers for each condition are given in Table S5.

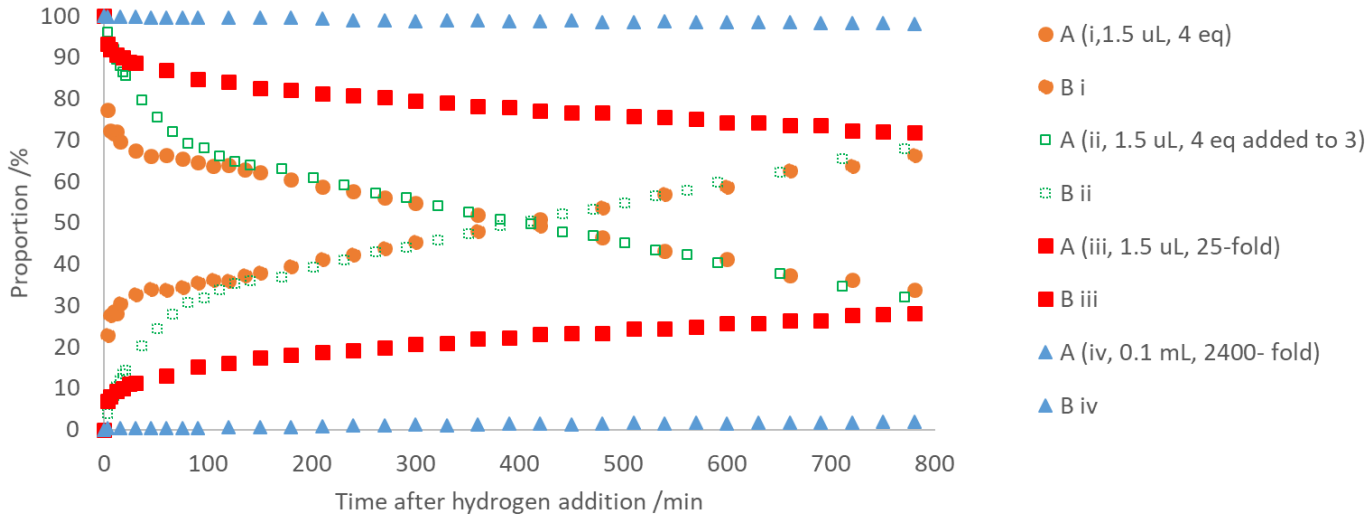

*Figure S16: Results from monitoring the hydrogenation of vinyl sulfoxide in 0.6 mL methanol-d_4 at 298 K after 3 bar H_2 addition to solutions of **1** and **A** according to conditions i-iv.*

*Table S5: Catalytic turnovers for the hydrogenation of **A** by **1** in the first 15, 30, 60 and 720 minutes according to conditions i-iv.*

Conditions	Turnover /s^{-1}				Turnover number
	First 15 mins	First 30 mins	First 1 hour	First 12 hours	
i	1.3×10^{-3}	6.7×10^{-4}	3.5×10^{-4}	5.5×10^{-5}	3
ii	5.0×10^{-4}	3.7×10^{-4}	2.6×10^{-4}	5.8×10^{-5}	3
iii	2.5×10^{-3}	1.5×10^{-3}	8.7×10^{-4}	1.5×10^{-4}	9
iv	7.8×10^{-4}	3.2×10^{-4}	2.8×10^{-4}	9.5×10^{-5}	48

S3.2. Formation of $[IrCl(H)_2(C)_2(IMes)]$, 3

The formation of **3** at 245 K can be monitored by recording a series of ^1H NMR spectra after 3 bar H_2 addition to a solution of 5 mM **1** and 4 eq. **C** in methanol-d_4. The proportion of each species in solution was determined from diagnostic IMes resonances of **1**, bound CH_2 sulfoxide resonances of **3**, and CH_2 resonances of **C**.

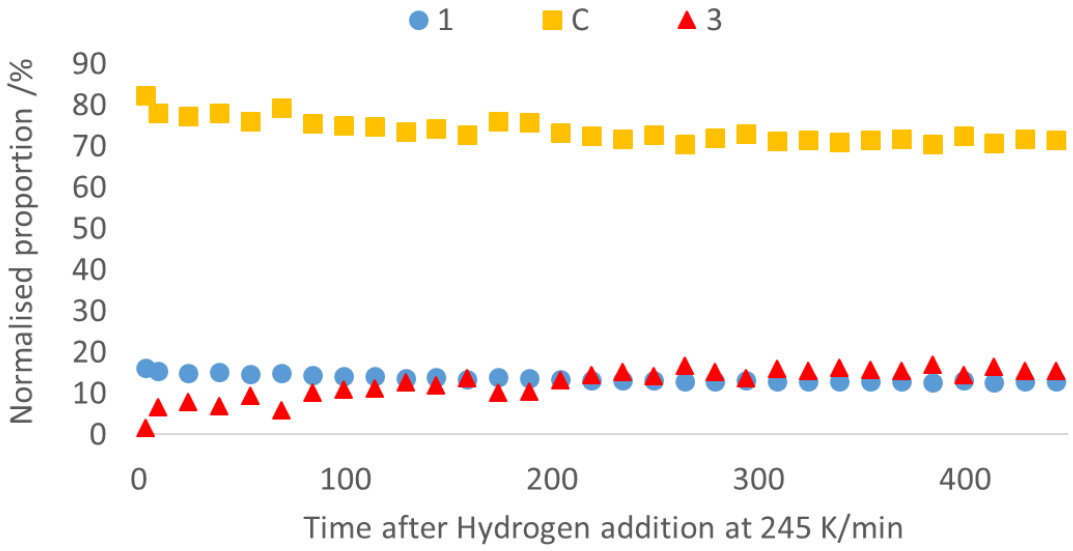

*Figure S17: Results from monitoring the formation of $[IrCl(H)_2(\mathbf{C})_2(IMes)]$ in methanol-d_4 at 245 K after 3 bar H_2 addition to a solution of 5 mM **1** and 4 eq. **C**.*

S4. References

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5. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crys. Sec. A.* **2015,** *71* (1), 3-8.
6. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crys. Sec. C.* **2015,** *71* (1), 3-8.