Supporting Information

Exploring the hyperpolarisation of EGTA-based ligands using SABRE

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S1. Formation of SABRE active complexes with agents $S_{1\text{-}3}$

Samples were prepared containing [IrCl(COD)(IMes)] (2.5 mM) and **$S_{1\text{-}3}$** (4 equiv.) in 0.6 mL methanol-d_4. 3 bar H_2 was added and left at room temperature for several hours before ^{1}H NMR spectra were recorded. These spectra are shown in Figure S1.

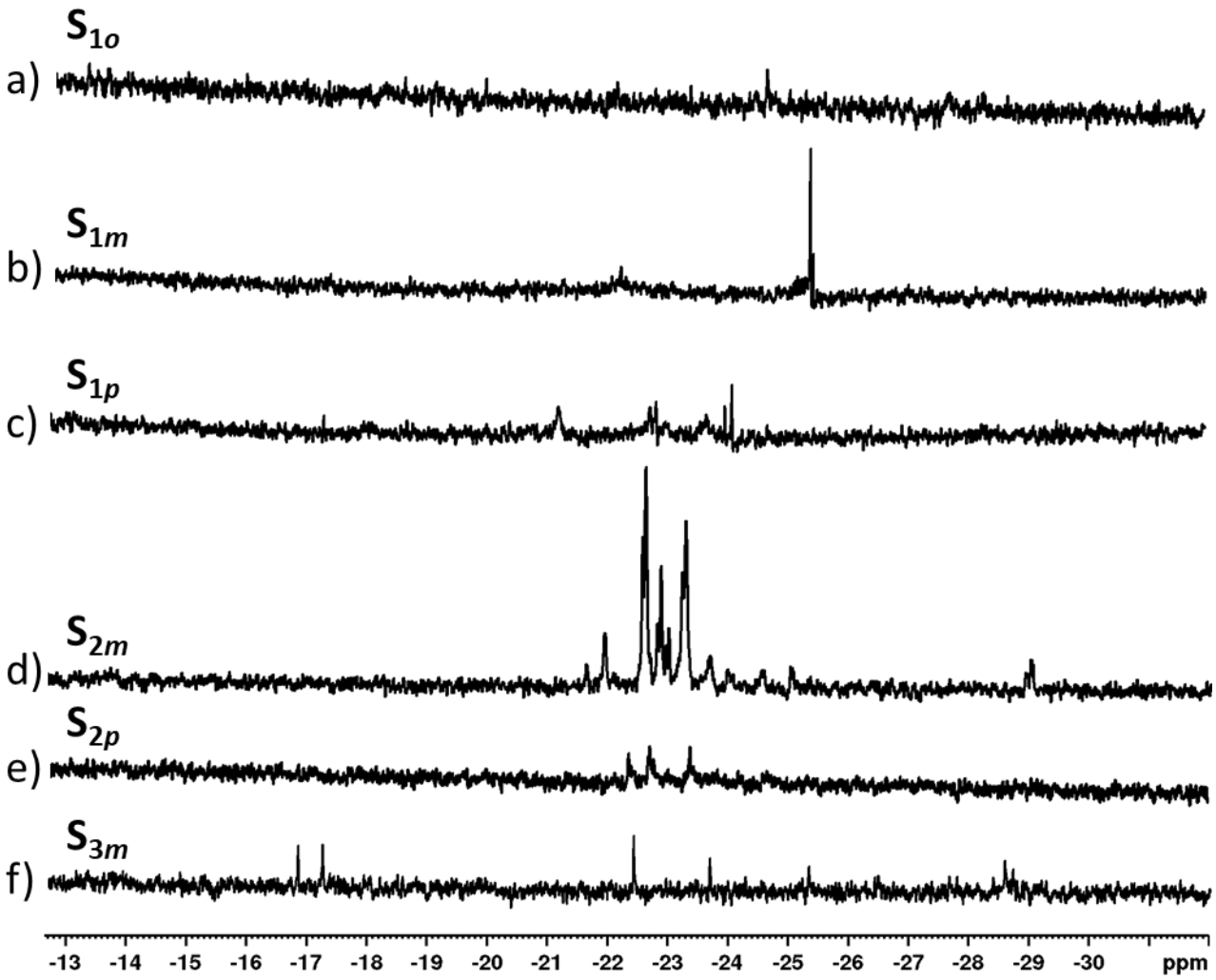

Figure S1: Partial ^{1}H NMR spectra (128 scans) recorded several hours after the addition of 3 bar H_2 to [IrCl(COD)(IMes)] (2.5 mM) and 4 equiv a) S_{1o} b) S_{1m} c) S_{1p} d) S_{2m} e) S_{2p} and e) S_{3m} in 0.6 mL methanol-d_4.

Samples were then shaken with 3 bar pH_2 for 10 seconds at 65 G to observe any hyperpolarised ^{1}H NMR resonances for $\mathbf{S_{1\text{-}3}}$. Under these conditions, only $\mathbf{S_{2m}}$ was shown to exhibit enhanced resonances (Figure S2). ^{1}H NMR signal enhancements at different temperatures are given in Table S1.

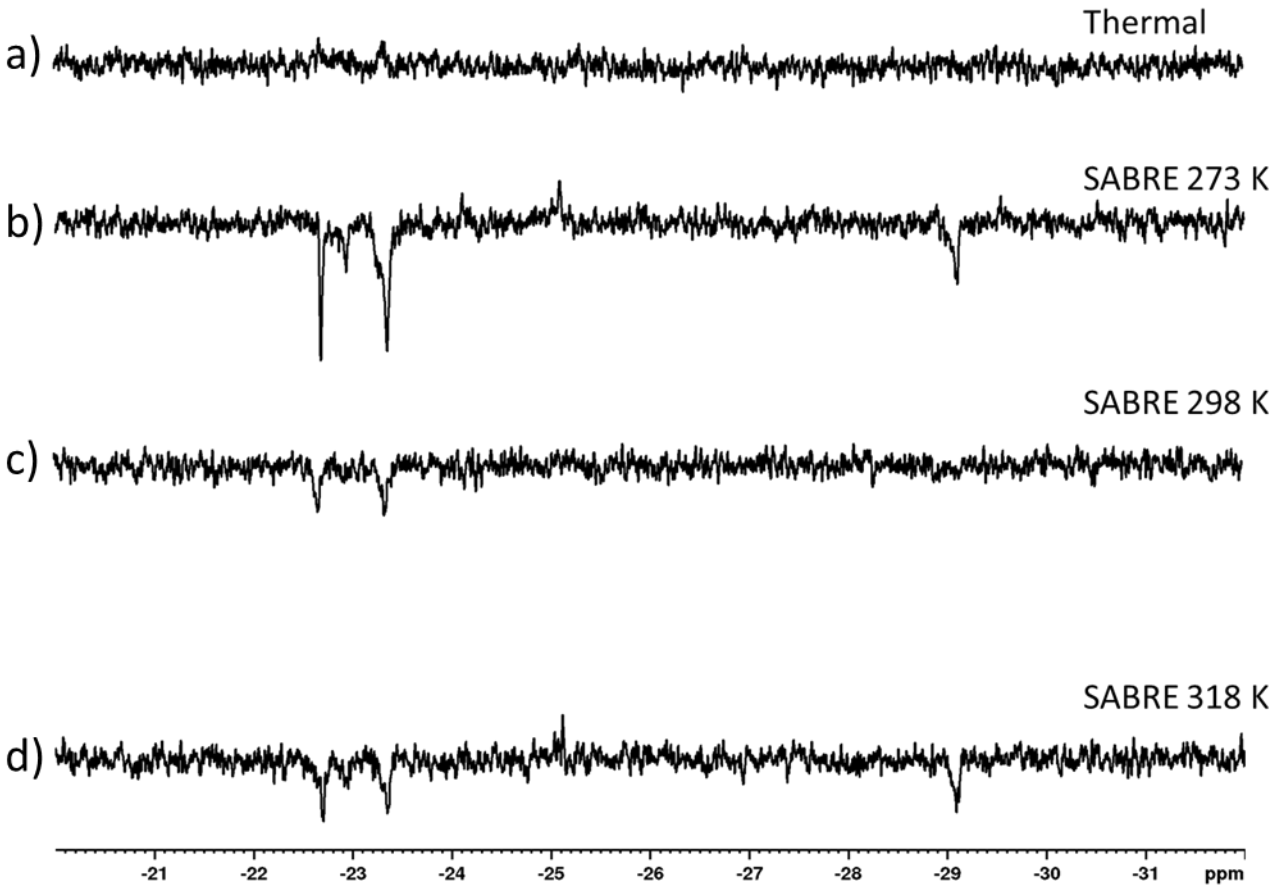

Figure S2: a) Partial single scan ^{1}H NMR spectrum of the hydride region when a sample containing [IrCl(COD)(IMes)] (2.5 mM) and S_{2m} (4 equiv.) in 0.6 mL methanol-d_4 is recorded under Boltzmann conditions b)-d) SABRE hyperpolarized spectra when the sample described in a) was shaken with 3 bar pH_2 at 65 G for 10 seconds after being left in a thermostatically controlled water bath at b) 273 K c) 298 K and d) 318 K for 60 seconds prior to pH_2 shaking.

Table S1: ^{1}H NMR signal enhancements when a sample containing [IrCl(COD)(IMes)] (2.5 mM) and S_{2m} (4 equiv.) in 0.6 mL methanol-d_4 is shaken with 3 bar pH_2 at 65 G for 10 seconds at the indicated temperature.

T /K	^{1}H NMR Signal Enhancements /fold				
	b	***o***	***m***	***p***	**Total free S_{2m} (per proton)**
273	15 ± 1	17 ± 1	5 ± 1	9 ± 1	9 ± 1
298	16 ± 1	13 ± 1	9 ± 1	12 ± 1	12 ± 1
318	32 ± 3	37 ± 3	12 ± 1	21 ± 2	23 ± 2

S2. Use of coligands to form stable SABRE active complexes.

S2.1 Formation of [IrH_2(IMes)($NCCH_3$)(κ^2-*N*,*N*-S_{1m})]Cl

Samples were prepared containing the indicated agent (3 equiv.), [IrCl(COD)(IMes)] (4 mM) and acetonitrile (2 equiv.) with 3 bar H_2 in 0.6 mL methanol-d_4. After leaving at room temperature for 3-4 hours the samples were shaken with 3 bar pH_2 for 10 seconds at 65 G and single scan ^{1}H NMR spectra were immediately collected.

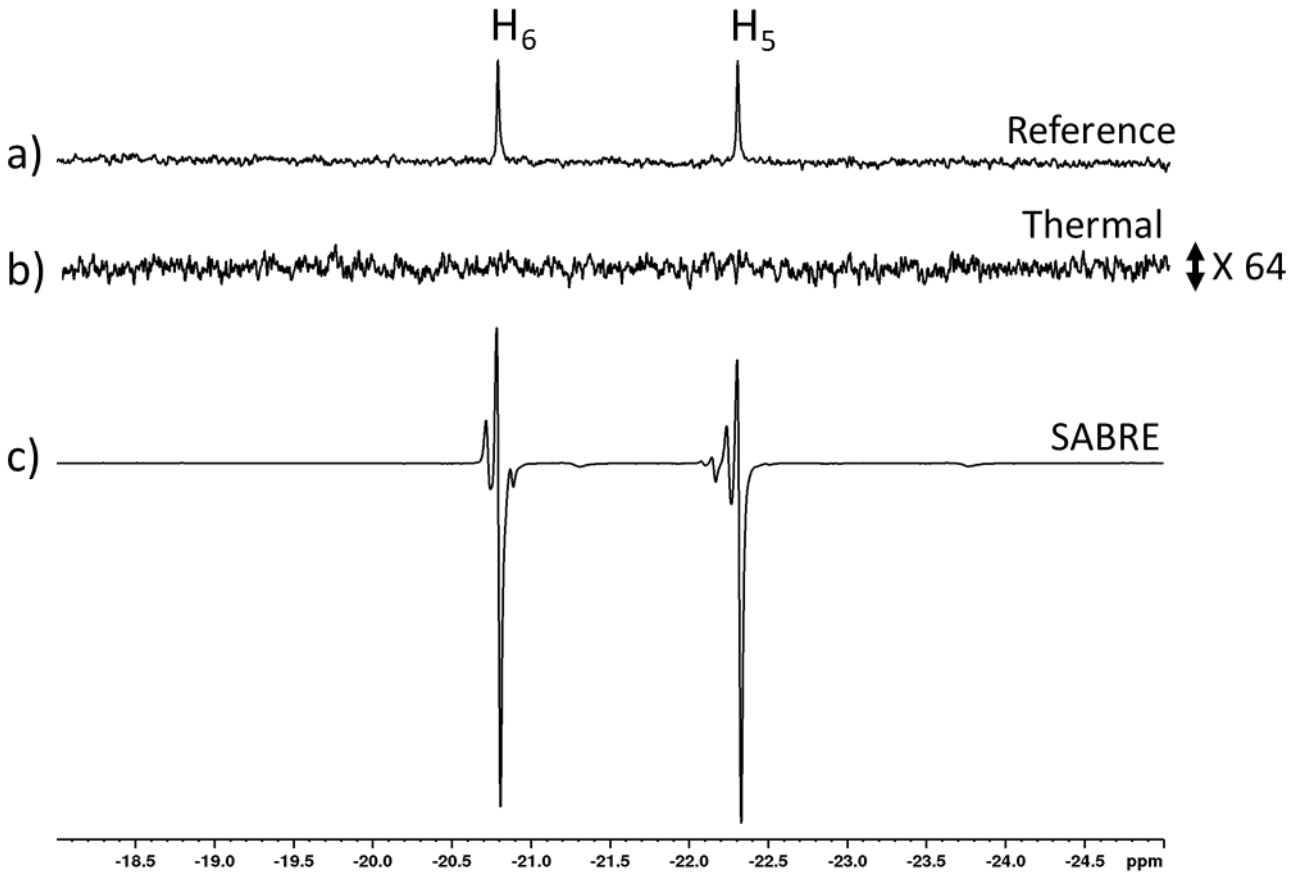

Figure S3: Partial ^{1}H NMR spectra of the hydride region when a sample containing [IrCl(COD)(IMes)] (4 mM), S_{1m} (3 equiv.) and acetonitrile (2 equiv.) in 0.6 mL methanol-d_4 is examined by a) a 128 scan ^{1}H NMR measuremnet (30^o flip angle) b) a single scan thermal measurement (90^o flip angle) and c) a single scan hyperpolarised measurement (90^o flip angle) recorded immediately after shaking the sample with pH_2 for 10 seconds at 65 G and 298 K. Note that b) has been expanded vertically by a factor of 64 relative to b) while a) is not to scale. Resonance labels in a) correspond to the positions denoted in Figure S5.

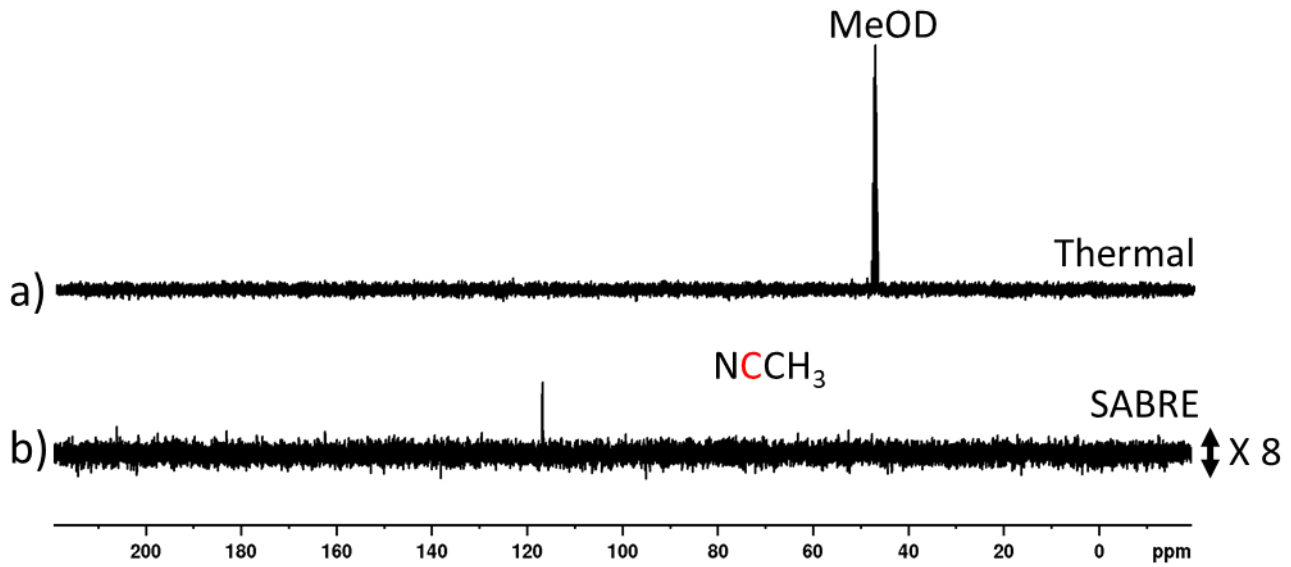

Figure S4: Single scan ^{13}C NMR spectra of a sample containing [IrCl(COD)(IMes)] (4 mM), S_{1m} (3 equiv.) and acetonitrile (2 equiv.) in 0.6 mL methanol-d_4 a) recorded under Boltzmann conditions b) recorded under SABRE hyperpolarized conditions by shaking with pH_2 for 10 seconds in a mu metal shield at 298 K. Note that b) has been expanded vertically by a factor of 8 relative to a).

2D NMR characterisation of this solution was then performed to identify the species giving rise to these hyperpoalrised signals shown in Fiugre S3. The structure of the complex formed in this mixture is shown in Figure S4 and its NMR resonances are detailed in Table S2.

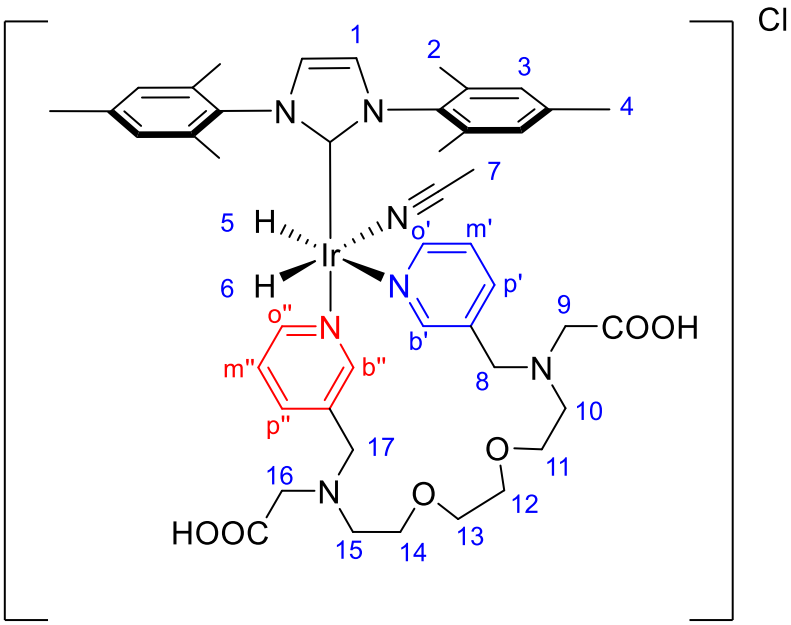

Figure S5: Structure of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-N,N-S$_{1m}$)]Cl determined from the NMR data given in Table S2.

Table S2: ^{1}H NMR resonances of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-N,N-S$_{1m}$)]Cl collected at 9.4 T and 298 K in methanol-d$_4$ with the resonance positions corresponding to those shown in Figure S5.

Resonance Position	^{1}H Chemical Shift
1	7.09
2	2.19
3	6.84, 7.05
4	2.34
5	− 22.28
6	−20.77
7	1.91
8, 17	4.1-4.5 (overlap)
9-16	3.5-3.9 (overlap)
o’	8.45, d, *J* = 5 Hz
m’	7.25, t, *J* = 6 Hz
p’	7.95, d, *J* = 7.5 Hz
b’	8.43, s
o’’	8.72, d, *J* = 5 Hz
m’’	7.15, d, *J* = 6.5 Hz
p’’	7.85, d, *J* = 7.5 Hz
b’’	8.38, s

A ^{1}H NMR spectrum of this species synthesised from a sample containing [IrCl(COD)(IMes)] (4 mM), **S$_{1m}$** (0.9 equiv.) and acetonitrile (3 equiv.) in 0.6 mL methanol-d_4 was recorded and is shown in Figure S6. The similarity of the chemical shifts/signal profile confirms the formation of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-*N*,*N*-**S$_{1m}$**)]Cl in which **S$_{1m}$** acts as a bidentate ligand rather than complexes of the form [IrH$_2$(IMes)(NCCH$_3$)(κ^1-*N*-**S$_{1m}$**)$_2$]Cl containing two molecules of **S$_{1m}$** with each acting as a monodentate ligand.

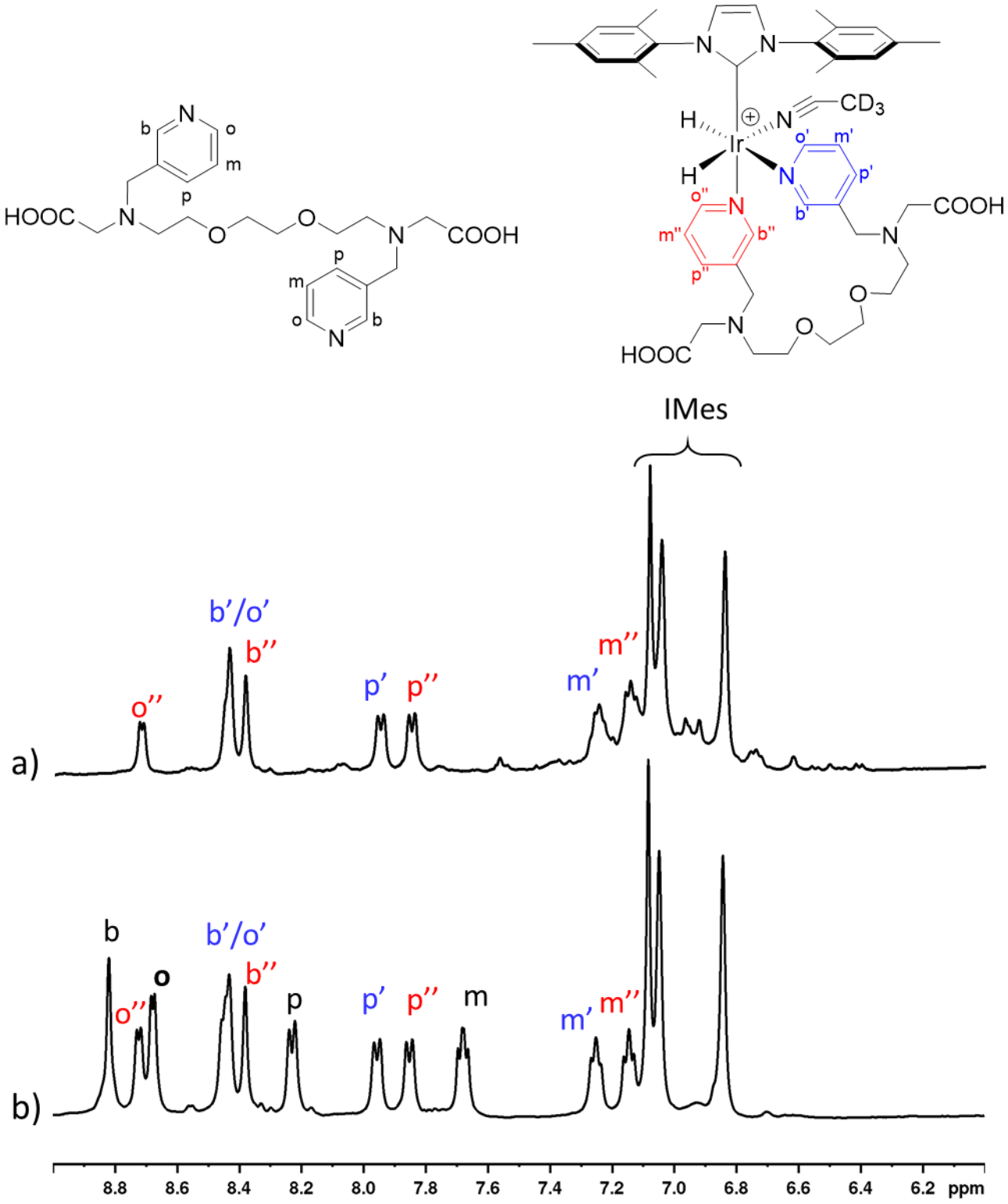

Figure S6: ^{1}H NMR spectra of samples containing [IrCl(COD)(IMes)] (4 mM) with a) S$_{1m}$ (0.9 equiv.) and acetonitrile (3 equiv.) and b) S$_{1m}$ (3 equiv.) and acetonitrile (2 equiv.) in 0.6 mL methanol-d$_4$ with 3 bar H$_2$ at 298 K (not to the same vertical scale).

S2.2 Formation of [IrH$_2$(IMes)(NCCD$_3$)(κ^2-*N*,*N*-S$_{2m}$)]Cl

A sample was prepared containing [IrCl(COD)(IMes)] (4 mM), **S$_{2m}$** (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4. 3 bar H_2 was added and left at room temperature for 5-6 hours before ^{1}H NMR spectra were recorded, an example is shown in Figure S7.

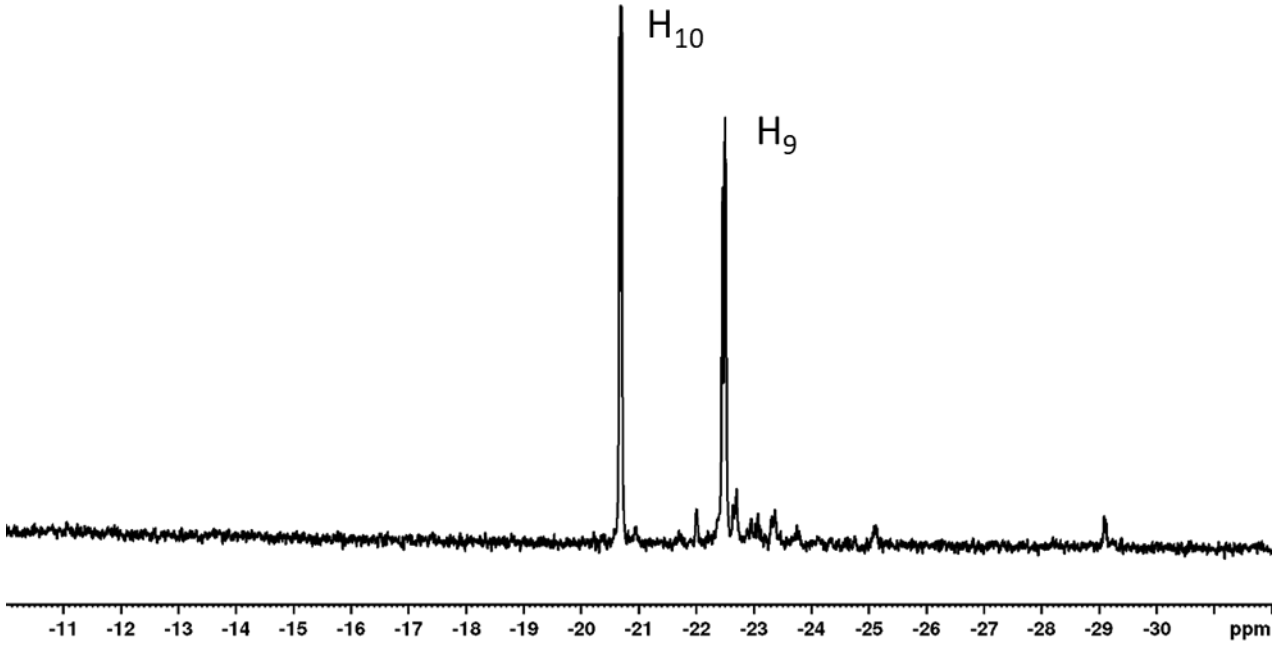

Figure S7: Partial ^{1}H NMR spectra (64 scans) recorded several hours after the addition of 3 bar H_2 to [IrCl(COD)(IMes)] (2.5 mM), S_{2m} (4 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4. Resonance labels correspond to those shown in Figure S10.

When this sample was shaken with 3 bar pH_2 at 65 G for 10 seconds enhanced resonances for **S$_{2m}$** were observed. This is shown in the hyperpolarised spectra presented in Figure S8. The corrresponding NMR signal enhancements are given in Table S3. The PHIP enhanced hydride region is also shown in Figure S9.

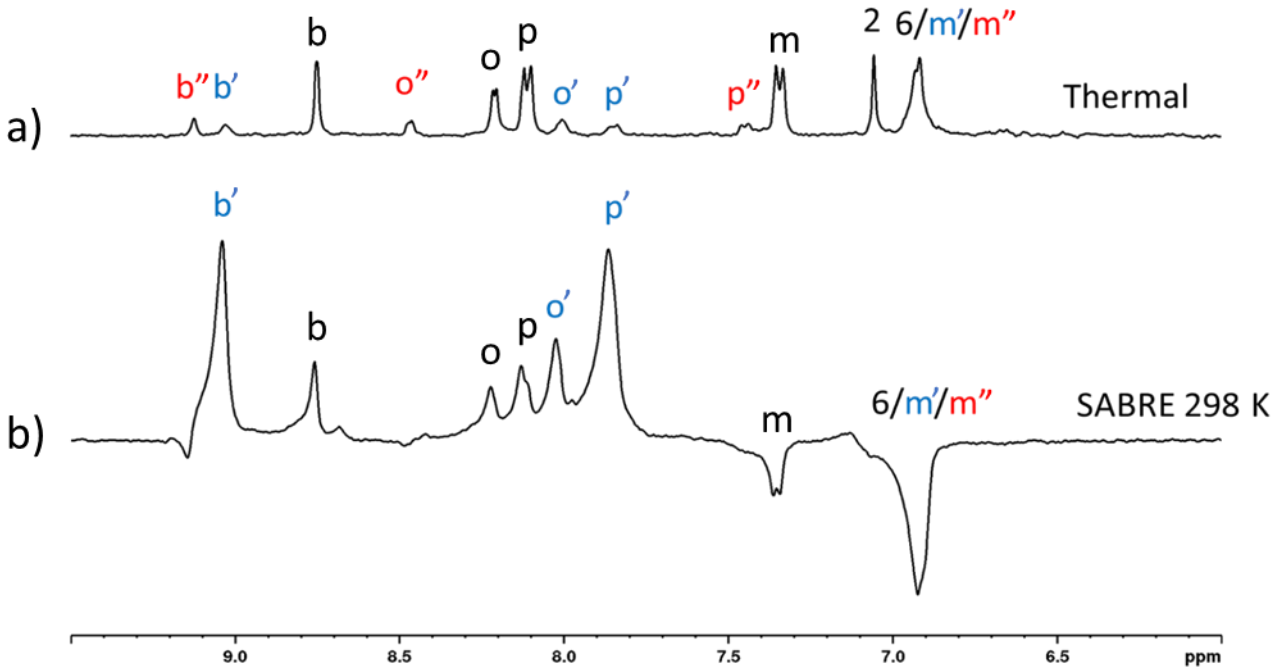

Figure S8: Partial single scan ^{1}H NMR spectra of the aromatic region of a sample containing [IrCl(COD)(IMes)] (2.5 mM), S_{2m} (4 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 recorded a) under Boltzmann conditions and b) SABRE hyperpolarised conditions by shaking with

3 bar pH_2 at 65 G for 10 seconds. Resonance positions are labelled according to Figure S10. Resonances o, b, m and p correspond to those of the free material.

Table S3: ^{1}H NMR signal enhancements when a sample containing [IrCl(COD)(IMes)] (2.5 mM), S_{2m} (4 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 is shaken with 3 bar pH_2 at 65 G for 10 seconds. Note the meta resonances of the pyridyl rings of the bound agent are not included as these overlap with those of the catalyst (as shown in Figure S9).

T /K	^{1}H Signal Enhancements /fold								
	b'	*b*	*o*	*p*	*o'*	*p'*	*m*	Total free S_{2m} (per proton)	Total bound S_{2m} (per proton)
273	19 ± 2	1 ± 1	2 ± 1	1 ± 1	4 ± 1	2 ± 1	6 ± 1	1 ± 0	19 ± 1
298	18 ± 2	2 ± 1	2 ± 1	2 ± 1	4 ± 1	3 ± 1	6 ± 1	2 ± 0	18 ± 2
318	16 ± 2	4 ± 1	6 ± 1	3 ± 1	5 ± 1	5 ± 1	7 ± 1	3 ± 1	17 ± 2

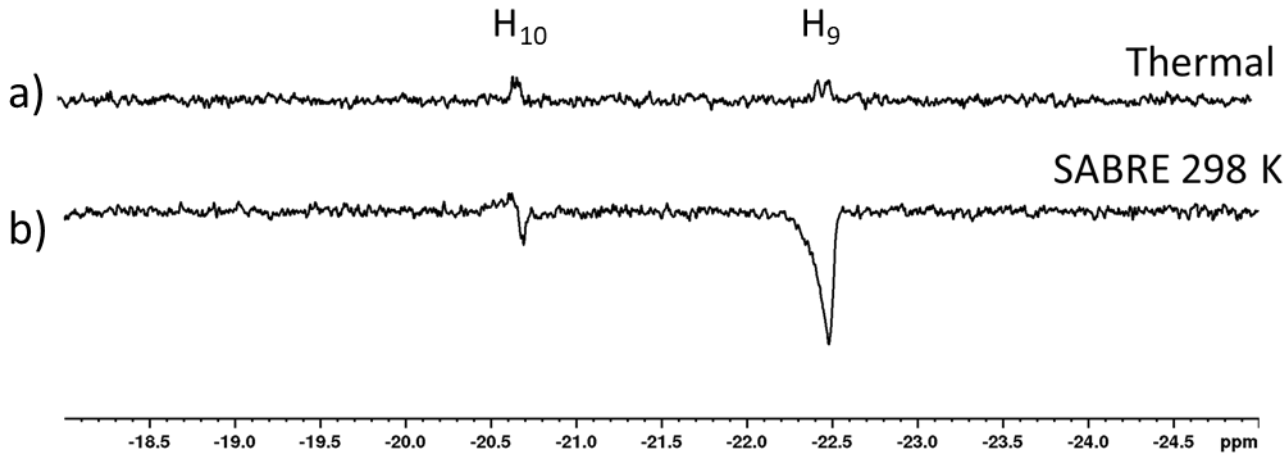

Figure S9: Partial single scan ^{1}H NMR spectra of the hydride region when a sample containing [IrCl(COD)(IMes)] (2.5 mM), S_{2m} (4 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 is shaken with 3 bar pH_2 at 65 G for 10 seconds. Resonance positions are labelled according to Figure S10.

2D NMR characterisation was performed at 298 K to confirm the identity of the active SABRE polarisation transfer catalyst. The structure of this species is shown in Figure S9 and its NMR resonances are detailed in Table S4. NOE measurements showed both hydrides close in space to a phenyl resoanance at δ 8.47 (o'') and the IMes ligand at δ 2.05 (averaged, H_4). The hydride at δ −20.70 (H_{10}) was close in space to a phenyl resonance at δ 8.02 (o'). This gives the orientation of the phenyl rings in the complex and the remaining phenyl ^{1}H resonances were found using a COSY (example shown in Figure S11) with ^{13}C resonances found using a HMQC (not shown).

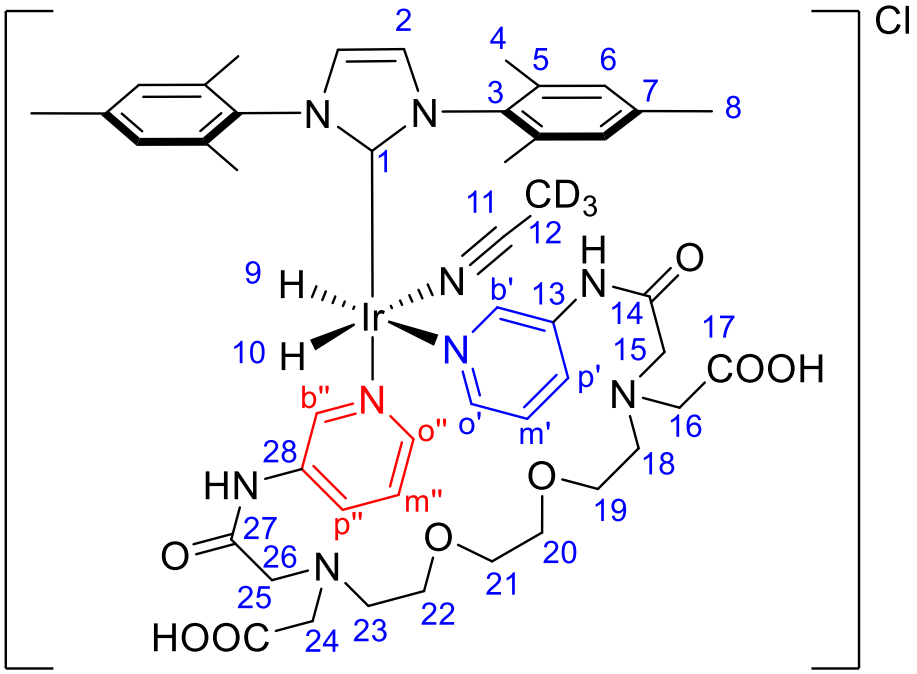

Figure S10: Structure of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-N,N-S$_{2m}$)]Cl determined from the NMR data shown in Table S4.

Table S4: ^{1}H and ^{13}C NMR resonances of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-N,N-S$_{2m}$)]Cl collected at 9.4 T and 298 K in methanol-d$_4$ with the resonance positions corresponding to those shown in Figure S10.

Resonance Position	^{1}H Chemical Shift	^{13}C Chemical Shift
1	-	150.10
2	7.07	121.86
3	-	135.88
4	2.03, 2.08	17.00, 17.05
5	-	137.72
6	6.94	128.32
7	-	138.41
8	2.33	19.90
9	−22.51 d ($^2J_{HH}$ = 6.5 Hz)	-
10	−20.70 d ($^2J_{HH}$ = 6.5 Hz)	-
13-28	N/A	N/A
o'	8.02	151.57
m'	6.91	124.71
p'	7.86	125.75
b'	9.03	143.81
o''	8.47	154.71
m''	6.96	123.86
p''	7.45	125.28
b''	9.13	142.77

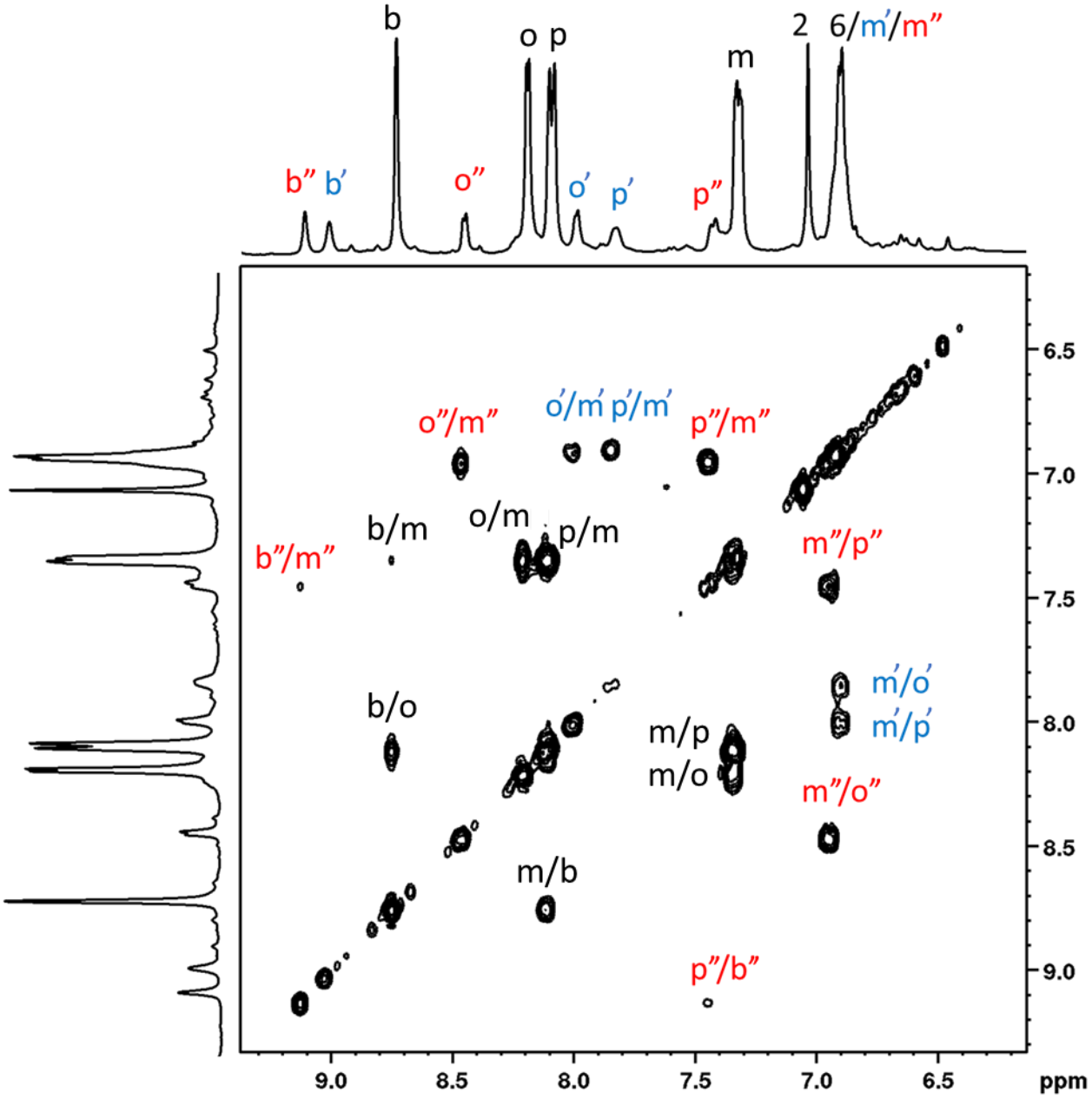

Figure S11: *^{1}H-^{1}H COSY of [IrH$_2$(IMes)(NCCH$_3$)(κ^2-N,N-S2$_m$)]Cl collected at 9.4 T and 298 K in methanol-d$_4$ with the resonance positions corresponding to those shown in Figure S10. Resoannces labelled O, M, P and B correspond to those of the free material.*

S2.3 Use of benzylamine as a coligand

A sample was prepared containing [IrCl(COD)(IMes)] (**A**, 4 mM), **S_{1m}** (3 equiv.), and benzylamine in methanol-d_4 (0.6 mL) and activated for several hours at room temperature with 3 bar H_2. After this point thermal and hyperpolarised ^{1}H NMR spectra were collected. These are shown in Figures S12 and S13.

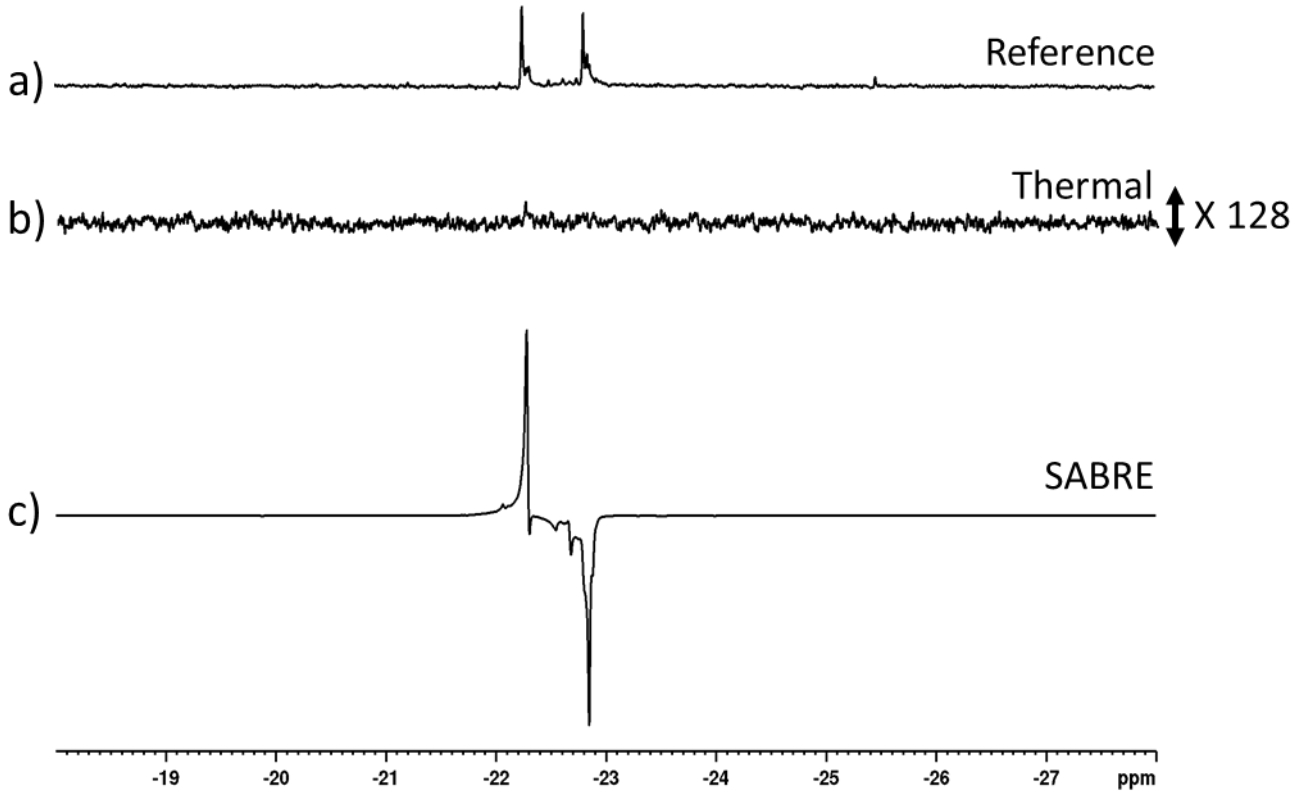

Figure S12: Partial single scan ^{1}H NMR spectra recorded at 9.4 T and 298 K after a sample containing [IrCl(COD)(IMes)] (4 mM), S_{1m} (3 equiv.) and benzylamine (2 equiv.) in 0.6 mL methanol-d_4 is recorded a) under Boltzmann conditions and b) under SABRE hyperpolarized conditions by shaking with 3 bar pH_2 for 10 seconds at 65 G.

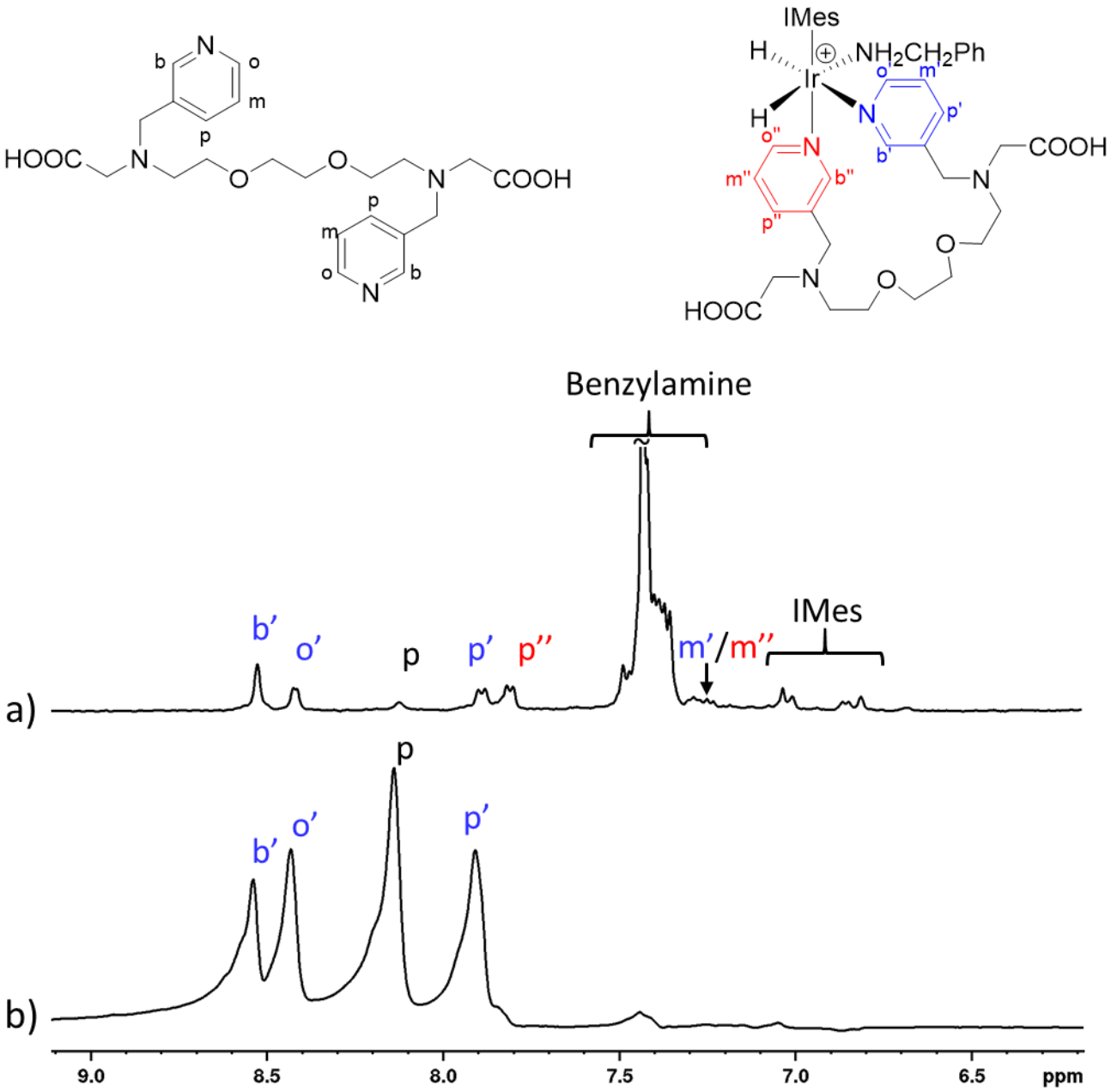

Figure S13: Partial single scan ^{1}H NMR spectra of the aromatic region of a sample containing [IrCl(COD)(IMes)] (4 mM), S_{1m} (3 equiv.) and benzylamine (2 equiv.) in 0.6 mL methanol-d_4 recorded under a) Boltzmann conditions with multiple scans (90^o flip angle) and b) SABRE hyperpolarised conditions immediately after shaking the sample with pH_2 for 10 seconds at 65 G and 298 K.

S2.4 Formation of [IrH$_2$(SIMes)(NCCH$_3$)(κ^2-*N*,*N*-S$_{1m}$)]Cl

A sample was prepared containing [IrCl(COD)(SIMes)] (4 mM), acetonitrile (2 eq) and **S$_{1m}$** (3 equiv.) in 0.6 mL methanol-d_4 and activated with 3 bar H_2 for several hours at room temperature. This sample was prepared for NMR characterisation purposes. The structure of the [IrH$_2$(SIMes)(NCCH$_3$)(κ^2-*N*,*N*-**S$_{1m}$**)]Cl species that formed is shown in Figure S14 and its NMR resonances are detailed in Table S5. A representative COSY spectrum used to assist these assignemnts is shown in Figure S15.

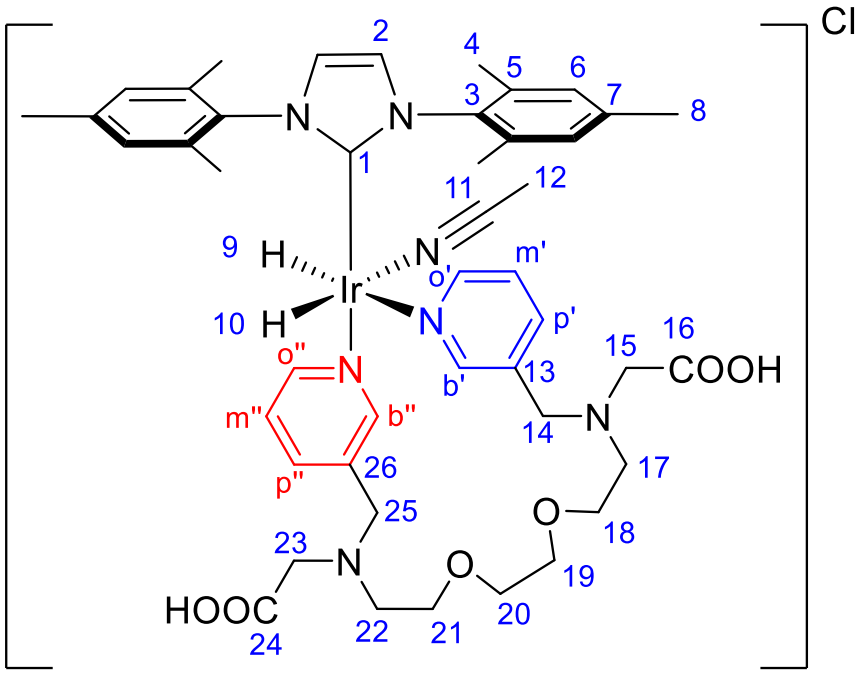

Figure S14: Structure of [IrH$_2$(SIMes)(NCCH$_3$)(κ^2-N,N-S$_{1m}$)]Cl determined from the NMR data presented in Table S5.

Table S5: ^{1}H NMR resonances of [IrH$_2$(SIMes)(NCCH$_3$)(κ^2-N,N-S$_{1m}$)]Cl collected at 9.4 T and 298 K in methanol-d_4 with the resonance positions corresponding to those shown in Figure S14.

Resonance Position	^{1}H Chemical Shift	^{13}C Chemical Shift
1	-	N/A
2	N/A	N/A
3	-	N/A
4	2.09, 2.30	17.18, 17.42
5	-	137.30, 137.92
6	6.75, 7.02	128.78
7	-	136.78
8	2.42	19.85
9	−22.10 d ($^2J_{NHtrans}$ = 20.0 Hz)	-
10	−20.55 d ($^2J_{NHtrans}$ = 21.5 Hz)	-
11	-	N/A
12	2.04	N/A
13, 26	-	N/A
14, 25	3.86	N/A
15, 23	4.03	53.04
16, 24	-	168.09, 168.90
17, 22	4.36	N/A
18-21	N/A	N/A
o’	~8.33 (overlap)	N/A
m’	7.25	N/A
p’	8.00	N/A
b’	~8.33 (overlap)	N/A
o’’	8.64	N/A
m’’	7.16	N/A
p’’	7.92	N/A
b’’	~8.33 (overlap)	N/A

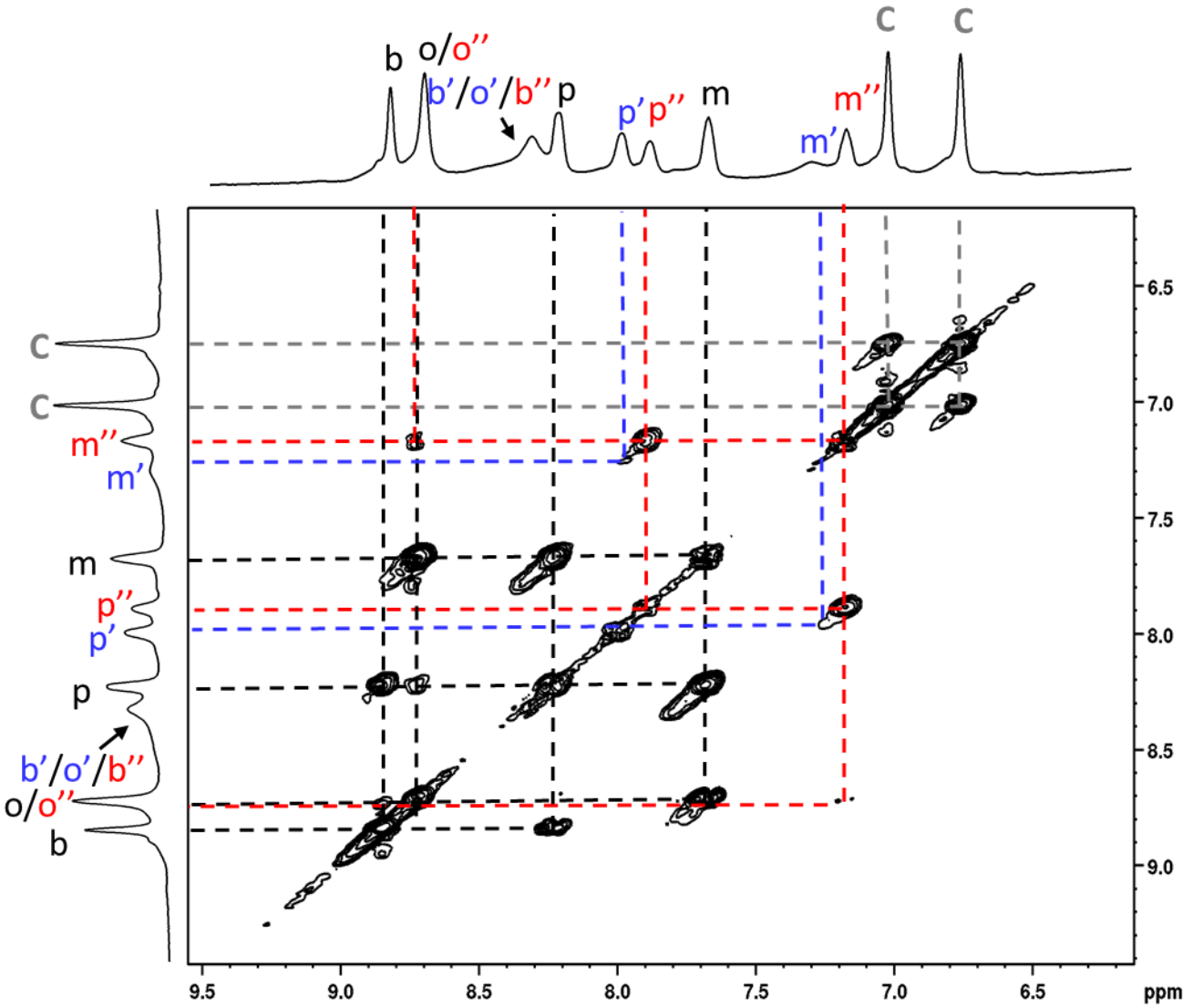

Figure S15: Partial ^{1}H COSY of a sample containing [IrCl(COD)(SIMes)] (4 mM), $S1_m$ (3 equiv.) and acptonitrile (2 equiv.) in 0.6 mL methanol-d_4 where the resonance labels correspond to those of Figure S13. Note the resonances labelled o, m, b and P coorrespond to the free materialwhereas those labelled C correspond to the carbene ligand of catalyst C.

S3. Optimization of SABRE performance

S3.1 Effect of precatalyst on SABRE enhancement of S1*m*

Samples were prepared containing **B** or **C** (4 mM), acetonitrile-d_3 (2 eq) and **S1*m*** (3 equiv.) in 0.6 mL methanol-d_4. These samples were activated with 3 bar H_2 for several hours at room temperature. After this, these mixtures were shaken with 3 bar pH_2 for 10 seconds at 65 G and hyperpolarised ^{1}H NMR spectra were recorded immediately after insertion into the 9.4 T spectrometer. Example spectra are shown in Figures S16 and S17. The corresponding ^{1}H NMR signal enhancements are given in Table S6.

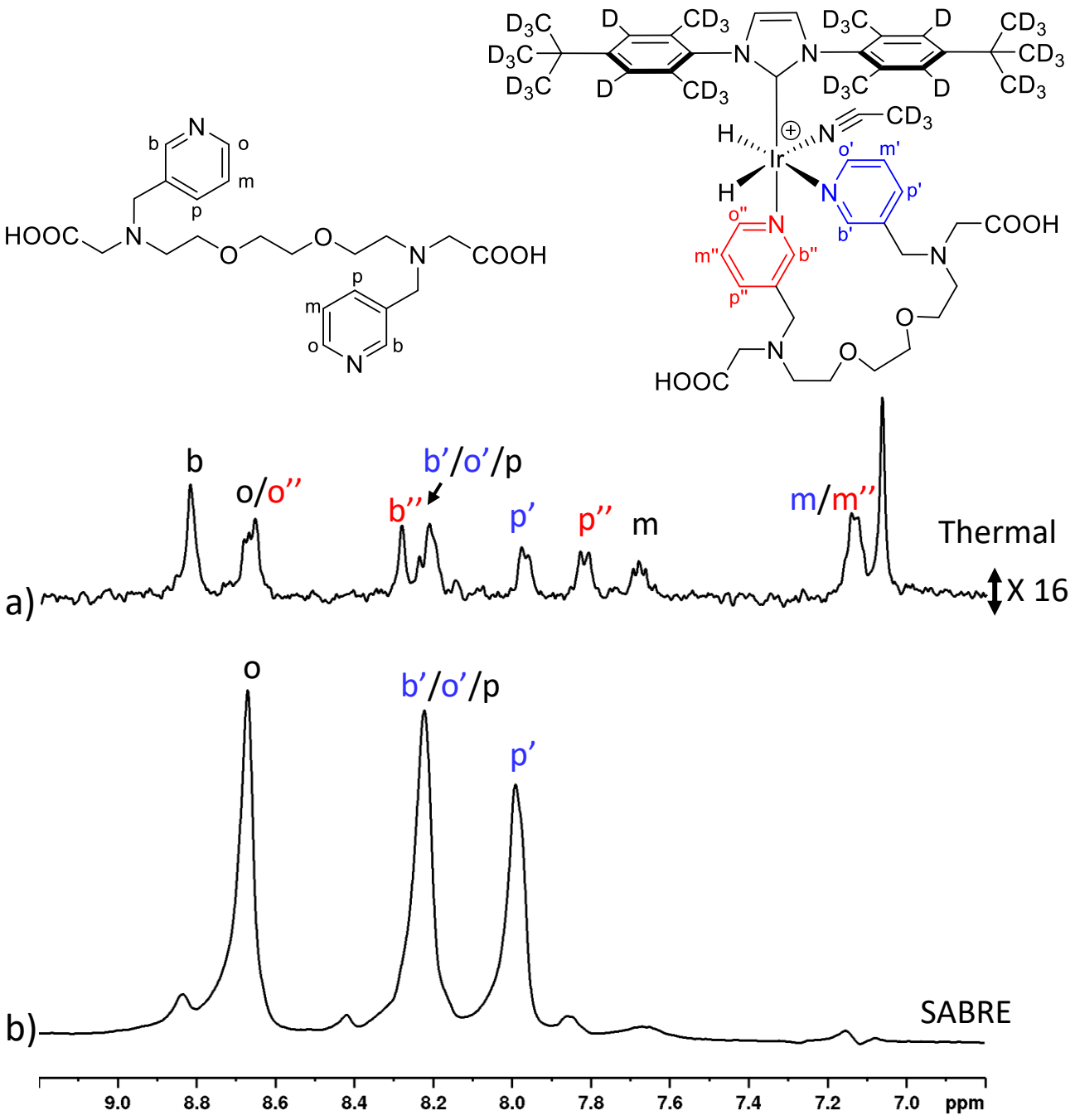

Figure S16: Partial single scan ^{1}H NMR spectra recorded at 9.4 T and 298 K after a sample containing B (4 mM), S_{1m} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 under a) Boltzmann conditions and b) SABRE hyperpolarised conditions following shaking with 3 bar pH_2 for 10 seconds at 65 G. Note that a) has been expanded vertically by a factor of 16 relative to b).

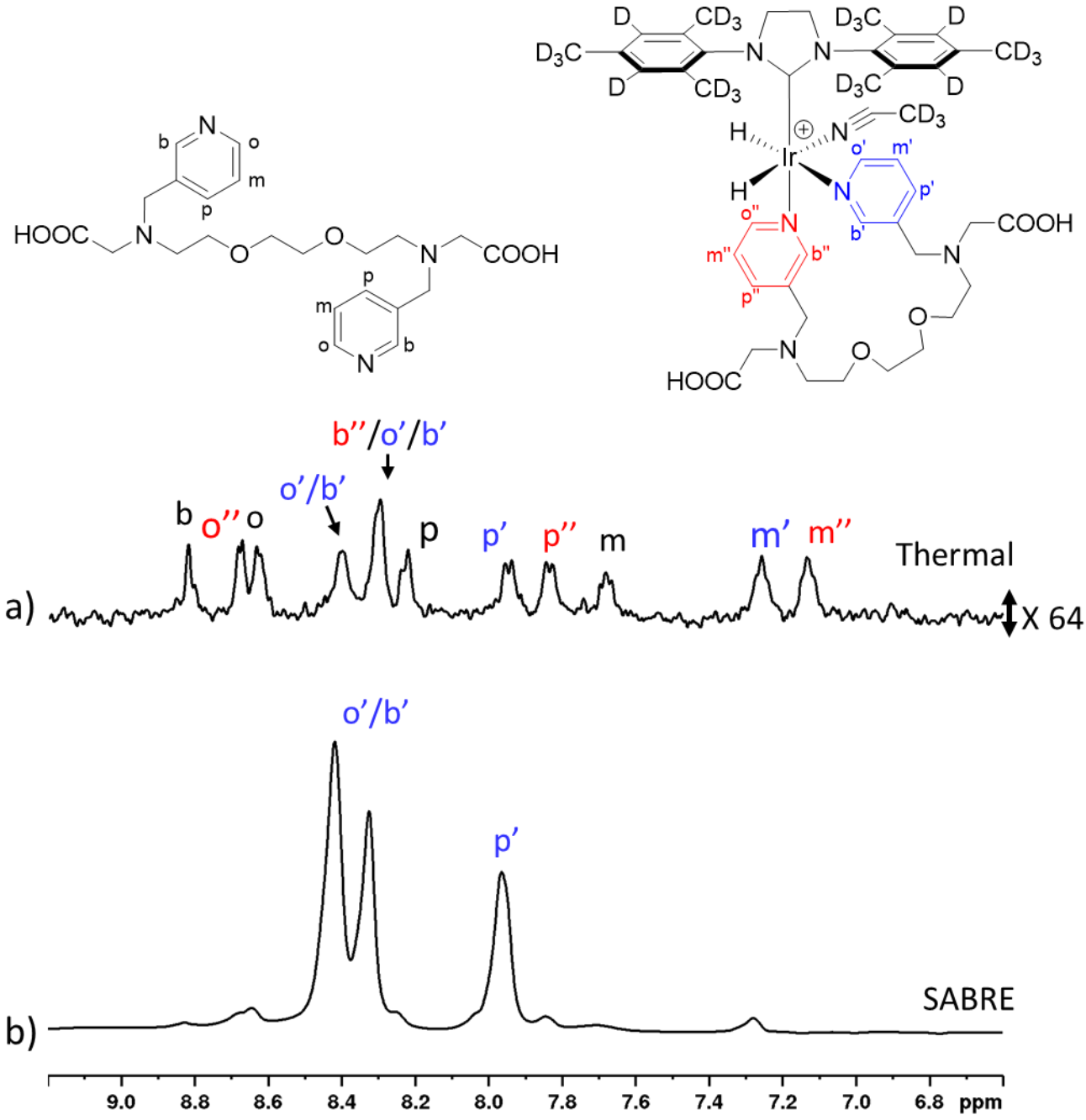

Figure S17: Partial single scan ^{1}H NMR spectra recorded at 9.4 T and 298 K of a sample containing C (4 mM), S_{1m} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 under a) Boltzmann conditions and b) SABRE hyperpolarized condition following shaking with 3 bar pH_2 for 10 seconds at 65 G. Note that a) has been expanded vertically by a factor of 64 relative to b).

S3.2 Table of NMR signal enhancements for S_{1m}

Table S6: SABRE ^1H signal enhancements for S_{1m} when 4 mM precatalyst, S_{1m} (3 equiv.) and coligand (2 equiv.) in 0.6 mL methanol-d_4 are shaken with 3 bar pH_2 for 10 seconds at 65 G. For measurements recorded at 273 K and 318 K the samples were placed in a thermostatically controlled water bath for 60 seconds prior to pH_2 shaking and detection at 298 K.

Agent	Conditions			^1H Signal Enhancements /fold													
	Coligand	Catalyst	T /K	*b*	*o*	*o''*	*b'*	*o'*	*b''*	*p*	*p'*	*p''*	*m*	*m'*	*m''*	Total free signal enhancement (per proton) [+]	Total bound signal enhancement (per proton) [+]
S_{1m}	CH_3CN	A	298	0	0	7 ± 1	63 ± 5*	63 ± 5*	7 ± 1	3 ± 1	53 ± 5	8 ± 1	0	3 ± 1	0	3 ± 0	26 ± 2
			318	0	0	12 ± 3	107 ±7*	107 ±7*	7 ± 2	10 ± 4	86 ± 5	9 ± 1	0	2 ± 1	0	10 ± 4	42 ± 4
S_{1m}	$PhCH_2NH_2$	A	298	0	0	0	13 ± 2	16 ± 2	0	52 ± 2	18 ± 2	0	0	0	0	52 ± 2	15 ± 2
			318	0	0	0	15 ± 1	18 ± 2	0	42 ± 4	19 ± 2	0	0	0	0	42 ± 4	17 ± 1
S_{1m}	CD_3CN	B	273	17 ± 1	44 ± 5	0	39 ± 5*	39 ± 5*	0	39 ± 5*	75 ± 5	11 ± 1	6 ± 1	2 ± 1[&]	2 ± 1[&]	21 ± 10	18 ± 9
			298	17 ± 2	72 ± 3	0	64 ± 3*	64 ± 3*	0	64 ± 3*	111 ± 6	14 ± 1	9 ± 1	2 ± 1[&]	2 ± 1[&]	49 ± 3	43 ± 3
			318	15 ± 3	72 ± 10	0	65 ± 9*	65 ± 9*	0	65 ± 9*	106 ± 13	12 ± 2	9 ± 2	5 ± 1[&]	5 ± 1[&]	48 ± 7	44 ± 6
S_{1m}	CD_3CN	C	273	17 ± 1	32 ± 1*	32 ± 1*	333 ± 13[%]	121 ± 4[%]	0	18 ± 1	203 ± 6	26 ± 1	15 ± 1	24 ± 3	3 ± 1	17 ± 1	110 ± 4
			298	20 ± 1	30 ± 1*	30 ± 1*	350 ± 21[%]	138 ± 5[%]	0	21 ± 1	211 ± 13	26 ± 1	15 ± 1	16 ± 2	5 ± 1	19 ± 1	117 ± 6
			318	23 ± 1	28 ± 1*	28 ± 1*	306 ± 15[%]	114 ± 5[%]	0	19 ± 1	183 ± 8	24 ± 1	11 ± 1	18 ± 3	5 ± 1	18 ± 1	101 ± 5

[&]signals can not be distinguished due to resonance overlap, this signal enhancement is average signal gain for each of the overlapping sites*

[+]Total signal enhancements have been calculated by diving the sum of all pyridyl resonances in a hyperpolarised measurement by their intensity in a corresponding thermal measurement

[%]Signals gains are attributed to either o' or b'

S4. Optimization of SABRE performance

Samples were prepared containing the indicated substrate (3 equiv.) with **C** (4 mM) and acetonitrile-d_3 (2 eq) in 0.6 mL methanol-d_4. These samples were activated with 3 bar H_2 for several hours at room temperature. In the case of $\mathbf{S_{2m}}$ an anologous sample was prepared without the addition of acetonitrile. After this, these mixtures were shaken with 3 bar pH_2 for 10 seconds at 65 G and hyperpolarised ^{1}H NMR spectra were recorded immediately after insertion into the 9.4 T spectrometer. Example spectra are shown in Figures S18-S21. The corresponding ^{1}H NMR signal enhancements are given in Tables S7-10.

S4.1 SABRE performance of S_{1o}

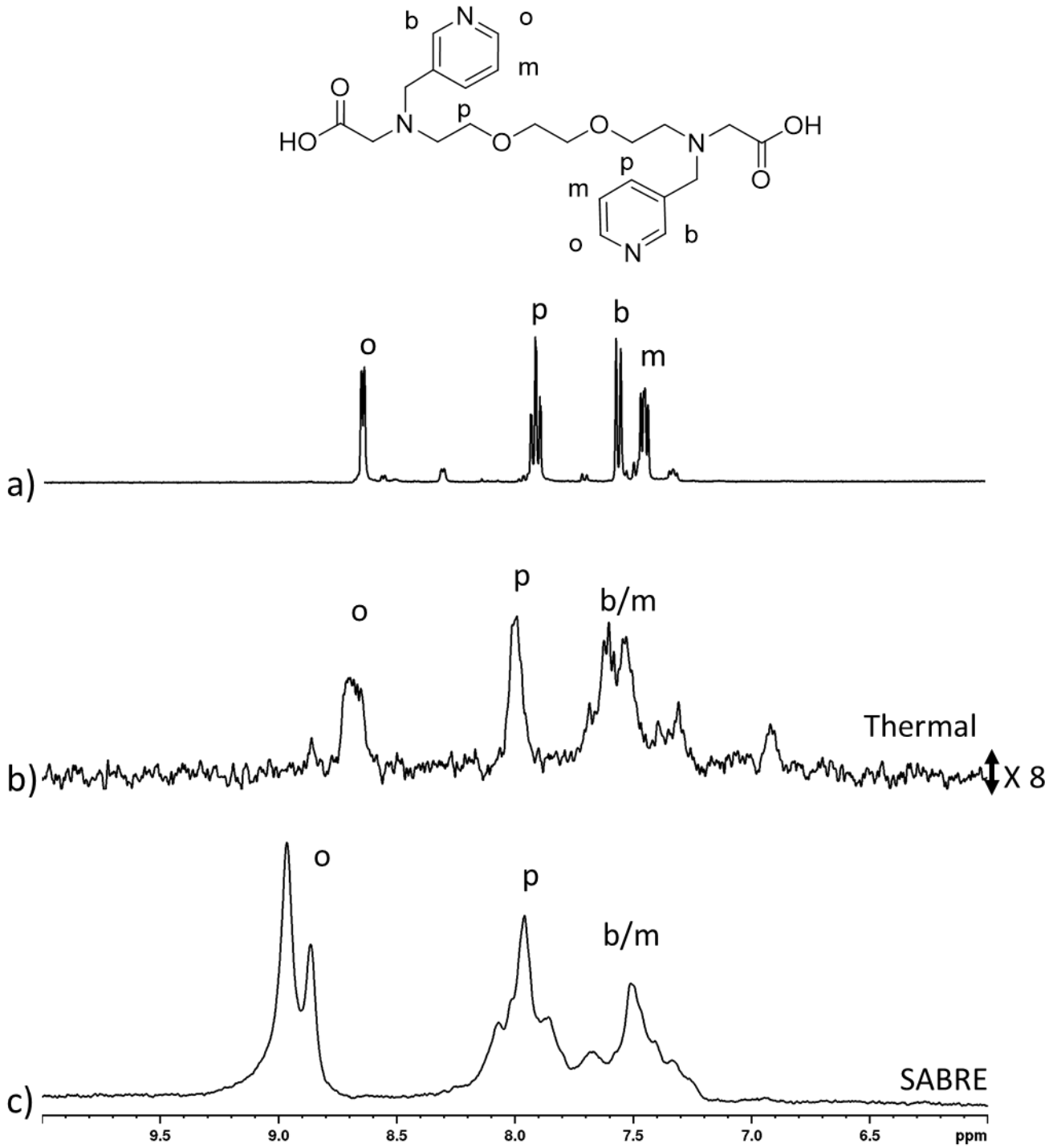

Figure S18: a) ^{1}H NMR spectrum of S_{1o} in 0.6 mL methanol-d_4 recorded at 9.4 T and 298 K b)-c) partial single scan ^{1}H NMR spectra recorded at 9.4 T and 298 K for a sample containing C (4 mM), S_{1o} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 b) in a single scan under Boltzmann conditions and c) after shaking with 3 bar pH_2 for 10 seconds at 65 G. Note that a) is not to scale and b) is expanded vertically by a factor of 8 relative to c).

Table S7: SABRE ^1H signal enhancements for S_{1o} when 4 mM precatalyst C (4 mM), S_{1o} (3 equiv.) acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 are shaken with 3 bar pH_2 for 10 seconds at 65 G. For measurements recorded at 273 K and 318 K the samples were placed in a thermostatically controlled water bath for 60 seconds prior to pH_2 shaking and detection at 298 K.

Agent	Conditions			^1H Signal Enhancements /fold			
	Coligand	Precatalyst	T /K	o	p	b/m *	Total free S_{1o} (per proton) +
S_{1o}	CD_3CN	**C**	273	26 ± 1	18 ± 1	6 ± 1	19 ± 1
			298	25 ± 1	19 ± 1	7 ± 1	20 ± 1
			318	30 ± 2	24 ± 2	10 ± 2	25 ± 3

*Signals can not be distinguished due to resonance overlap, this signal enhancement is average signal gain for each of the overlapping sites
+Total signal enhancements have been calculated by diving the sum of all pyridyl resonances in a hyperpolarised measurement by their intensity in a corresponding thermal measurement

S4.2 SABRE performance of S_{1p}

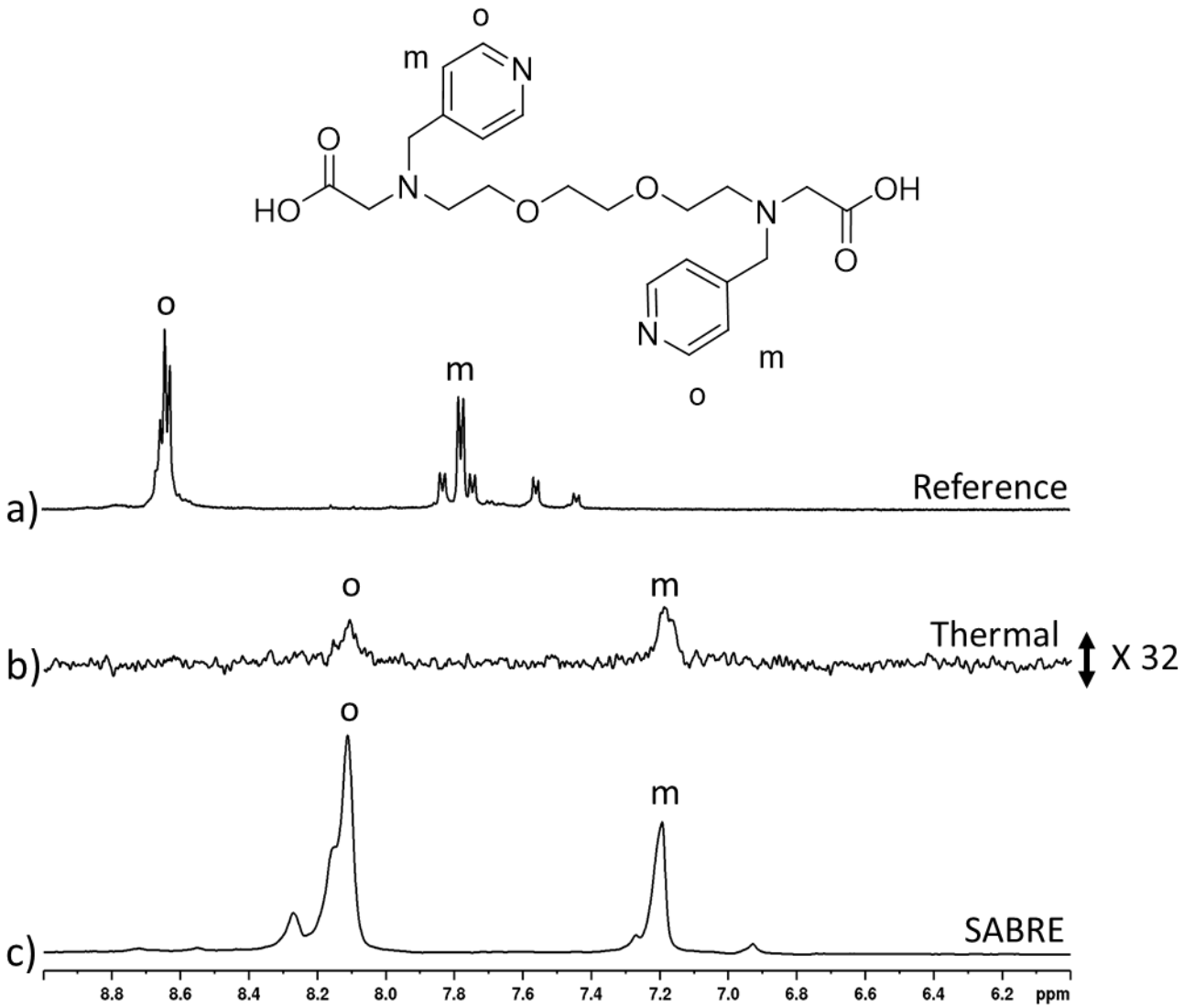

Figure S19: a) ^1H NMR spectrum of S_{1p} in 0.6 mL methanol-d_4 recorded at 9.4 T and 298 K b)-c) partial single scan ^1H NMR spectra recorded at 9.4 T and 298 K for a sample containing C (4 mM), S_{1p} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 a) under Boltzmann conditions using multiple scans b) under Boltzmann conditions in a single scan and c) after shaking with 3 bar pH_2 for 10 seconds at 65 G. Note that a) is not to scale and b) is expanded vertically by a factor of 32 relative to c).

Table S8: SABRE ^{1}H signal enhancements for S_{1p} when C (4 mM), $S1_p$ (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 are shaken with 3 bar pH_2 for 10 seconds at 65 G. For measurements recorded at 273 K and 318 K the samples were placed in a thermostatically controlled water bath for 60 seconds prior to pH_2 shaking and detection at 298 K.

Agent	Conditions			^{1}H Signal Enhancements /fold		
	Coligand	Precatalyst	T /K	*o*	*m*	Total free S_{1p} (per proton) [+]
S_{1p}	CD_3CN	**C**	273	159 ± 20	92 ± 17	127 ± 19
			298	138 ± 12	68 ± 9	104 ± 10
			318	102 ± 2	57 ± 2	81 ± 2

[+]Total signal enhancements have been calculated by diving the sum of all pyridyl resonances in a hyperpolarised measurement by their intensity in a corresponding thermal measurement

S4.3 SABRE performance of S_{2m}

Table S9: Signal enhancements when a sample containing C (4 mM) and S_{2m} (3 equiv.) (no coligand) in 0.6 mL methanol-d_4 is shaken with 3 bar pH_2 at 65 G for 10 seconds. For measurements recorded at 273 K and 318 K the samples were placed in a thermostatically controlled water bath for 60 seconds prior to pH_2 shaking and detection at 298 K.

T /K	^{1}H Signal Enhancements /fold				
	b	*o*	*m*	*p*	Total free S_{2m} (per proton)
273	24 ± 1	20 ± 1	20 ± 1	12 ± 1	18 ± 1
298	39 ± 5	29 ± 3	29 ± 3	22 ± 2	29 ± 3
318	45 ± 8	35 ± 5	35 ± 5	20 ± 3	33 ± 5

S4.4 SABRE performance of S_{2p}

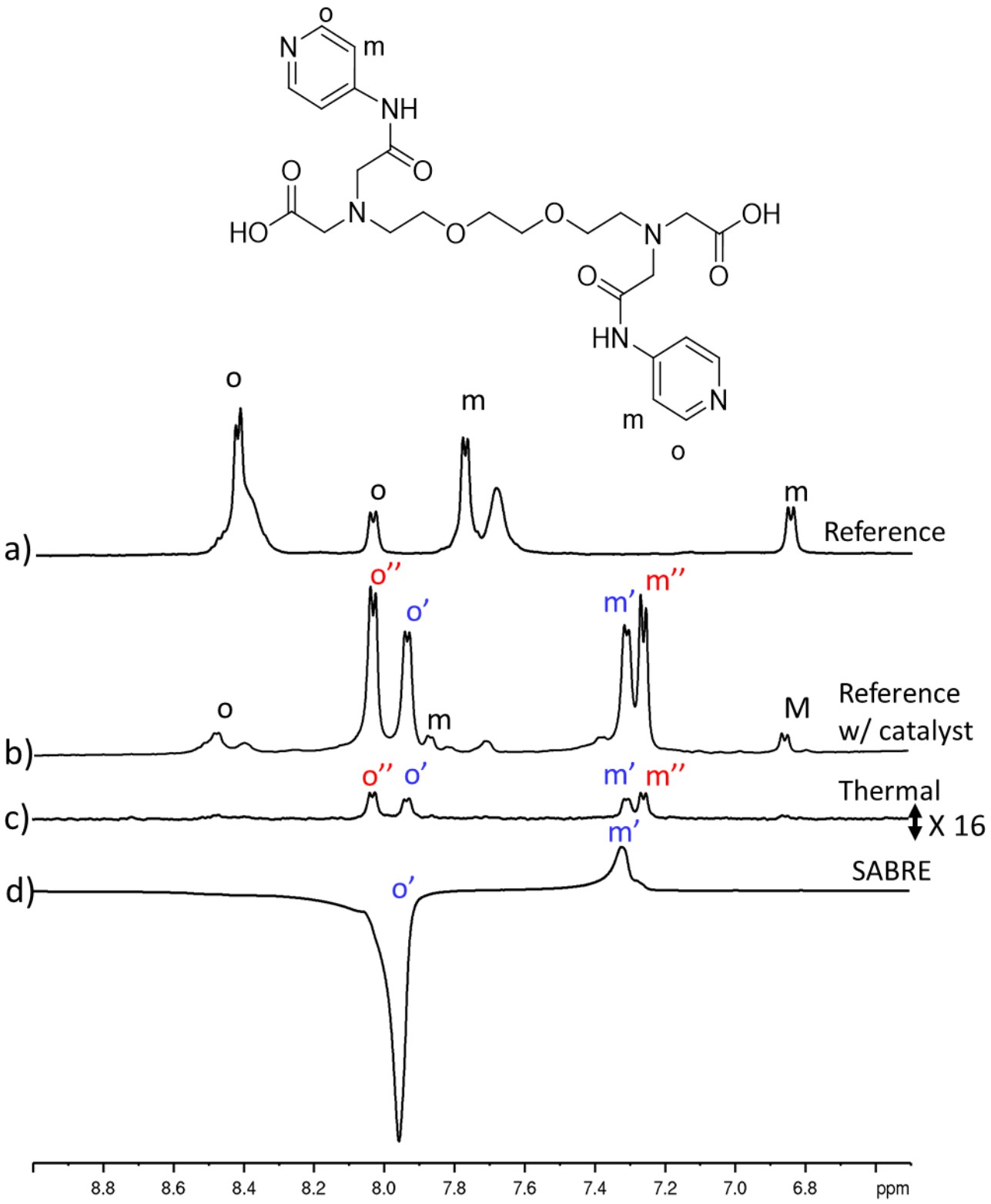

Figure S20: a) ^{1}H NMR spectrum of S_{2p} in 0.6 mL methanol-d_4 recorded at 9.4 T and 298 K b)-d) partial ^{1}H NMR spectra recorded at 9.4 T and 298 K of a sample containing C (4 mM), S_{2p} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 b) using multiple scans under Boltzmann conditions c) using a single scan under Boltzmann conditions and d) after shaking with 3 bar pH_2 for 10 seconds at 65 G. Note that a) and b) are not to scale and c) is expanded vertically by a factor of 32 relative to d). Signals labelled as o', m', o'' and m'' are suggested to arise from ortho (o) and meta (m) sites of S_{2p} bound trans and cis to hydrides respectively.

Table S10: SABRE ^{1}H signal enhancements for substrate S_{2p} when C (4 mM), S_{2p} (3 equiv.) and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 are shaken with 3 bar pH_2 for 10 seconds at 65 G. For measurements recorded at 273 K and 318 K the samples were placed in a thermostatically controlled water bath for 60 seconds prior to pH_2 shaking and detection at 298 K.

Agent	Conditions			^{1}H Signal Enhancements /fold			
	Coligand	Precatalyst	T /K	o	o'	m'	Total bound S_{2p} (per proton) [+]
S_{2p}	CD_3CN	**C**	273	9 ± 1	106 ± 11	26 ± 1	70 ± 6
			298	5 ± 1	124 ± 6	19 ± 5	77 ± 3
			318	9 ± 2	112 ± 8	18 ± 2	70 ± 5

[+]Total signal enhancements have been calculated by diving the sum of all pyridyl resonances in a hyperpolarised measurement by their intensity in a corresponding thermal measurement

We confirm that differences in SABRE efficiency of $\mathbf{S_{1o}}$, $\mathbf{S_{1m}}$, $\mathbf{S_{1p}}$ and $\mathbf{S_{2p}}$ is not due to differences in the identity of the polarisation transfer catalyst (Figure S21).

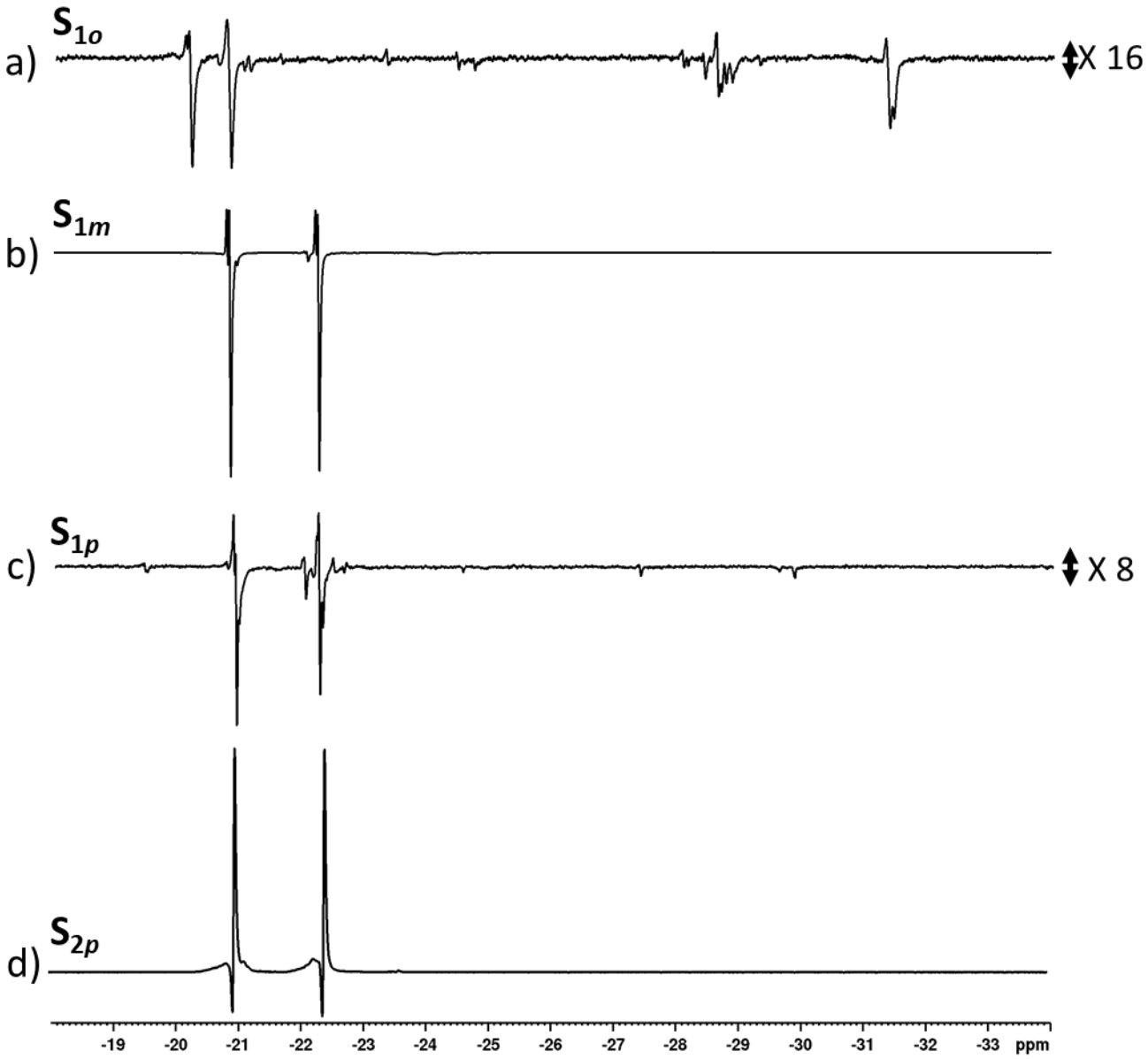

Figure S21: Partial single scan ^{1}H NMR spectra of the hydride region recorded at 9.4 T and 298 K after samples containing a) S_{1o}, b) S_{1m} c) S_{1p} and d) S_{2p} (3 equiv.), C (4 mM), and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 were shaken with 3 bar pH_2 for 10 seconds at 65 G.

S4.5 SABRE performance of S_{3m}

In this case no signal enhancemnts for **S_{3m}** are observed. No PHIP enhanced hydride complexes are observed, as shown in Figure S22.

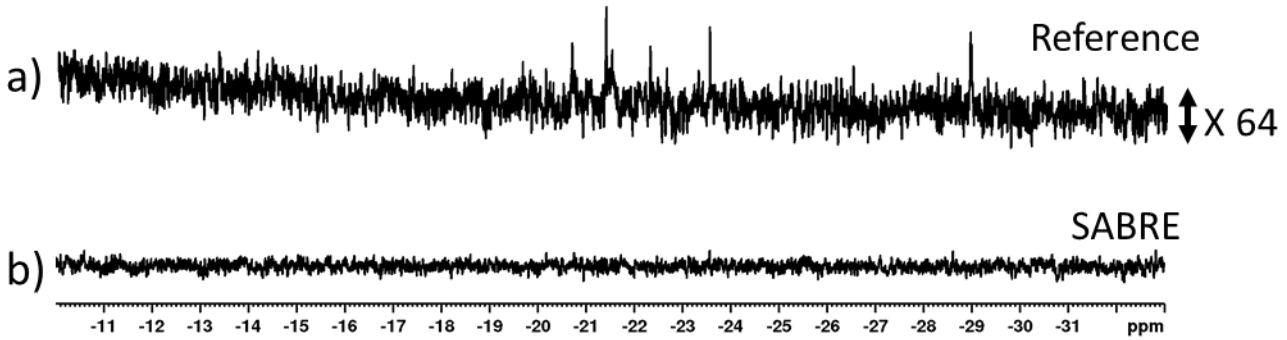

Figure S22: Partial single scan ^{1}H NMR spectra of the hydride region recorded at 9.4 T and 298 K for a sample containing S_{3m} (3 equiv.), C (4 mM), and acetonitrile-d_3 (2 equiv.) in 0.6 mL methanol-d_4 a) under Boltzmann conditions using 64 scans and b) immediately after shaking with 3 bar pH_2 for 10 seconds at 65 G. Note these spectra recorded using different spectral acquisition parameters.