Supporting Information for

Aldoximes Enable Proton-Relayed NMR Hyperpolarisation

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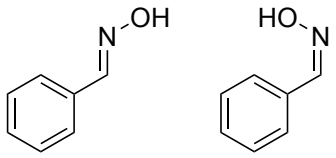
Appendix S1. Experimental methods and characterisation

1.1 General experimental

All reagents and solvents were used directly from commercial sources unless otherwise stated. Petroleum here refers to the fraction of petroleum spirits boiling between 40-60 °C, and silica refers to Chemsupply silica gel 60 (0.04-0.06 mm, 230-400 mesh). Thin layer chromatography (TLC) used Merck F_{254} aluminium-backed silica plates, which were visualized under UV light (254 and 365 nm), or using ethanolic anisaldehyde or potassium permanganate stains. High-field NMR spectra (400 MHz for ^{1}H and 100 MHz for ^{13}C with broadband decoupling) were acquired on a Bruker AVANCE 400 spectrometer, while low-field NMR spectra (60 MHz for ^{1}H) were acquired on an Nanalysis 60e benchtop spectrometer. Chemical shifts are represented in parts per million (ppm) and calibrated to the solvent residual ^{1}H signal or ^{13}C signal.[1] Scalar coupling constants (*J*) are given in Hertz (Hz).

1.2 Synthesis of oximes

Benzaldehyde oxime (1)



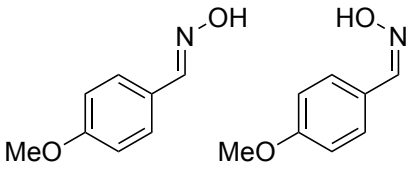
***E*-1** ***Z*-1**

To a solution of benzaldehyde dimethyl acetal (1.0 mL, 6.7 mmol) in THF (100 mL) and H_2O (10 mL) was added hydroxylamine hydrochloride (510 mg, 7.3 mmol, 1.1 eq.), and the reaction mixture was stirred at room temperature overnight. Diluted with brine (100 mL) and extracted with CH_2Cl_2 (3 x 100 mL), washed with further brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purified by flash column chromatography on silica, eluting with 10% EtOAc/petroleum, to give:

***E*-1** (457 mg, 56%) as a colourless oil; **^{1}H NMR** (400 MHz, d_6-DMSO) 11.25 (s, 1H), 8.14 (s, 1H), 7.60-7.58 (m, 2H), 7.41-7.36 (m, 3H); **^{13}C NMR** (101 MHz, d_6-DMSO) 148.2 (CH), 133.1 (C), 129.3 (CH), 128.8 (2 CH), 126.5 (2 CH), and

***Z*-1** (35 mg, 4%) as a colourless solid; **^{1}H NMR** (400 MHz, d_6-DMSO) 11.63 (s, 1H), 7.96 (dd, J = 7.9, 1.8 Hz, 2H), 7.45-7.39 (m, 3H); **^{13}C NMR** (101 MHz, d_6-DMSO) 144.9 (CH), 131.2 (C), 130.4 (2 CH), 129.6 (CH), 128.5 (2 CH).

p-Methoxybenzaldehyde oxime (2)



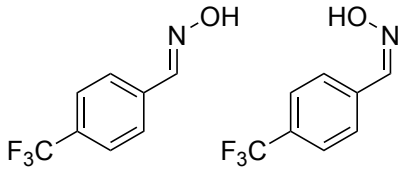
***E*-2** ***Z*-2**

To a solution of anisaldehyde dimethyl acetal (0.90 mL, 5.3 mmol) in THF (50 mL) and H_2O (5 mL) was added hydroxylamine hydrochloride (630 mg, 9.1 mmol, 1.7 eq.), and the reaction mixture was stirred at room temperature overnight. Diluted with brine (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL), washed with further brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purified by flash column chromatography on silica, eluting with 20% EtOAc/petroleum, to give:

***E*-2** (468 mg, 58%) as a colourless solid; **^{1}H NMR** (400 MHz, d_6-DMSO) 11.01 (s, 1H), 8.08 (s, 1H), 7.54-7.52 (m, 2H), 6.94-6.92 (m, 2H), 3.75 (s, 3H); **^{13}C NMR** (101 MHz, d_6-DMSO) 160.4 (C), 148.0 (CH), 128.1 (2 CH), 125.8 (C), 114.3 (2 CH), 55.3 (CH_3), and

***Z*-2** (66 mg, 8%) as a colourless solid; **^{1}H NMR** (400 MHz, d_6-DMSO) 11.40 (s, 1H), 7.95-7.93 (m, 2H), 7.31 (s, 1H), 6.98-6.96 (m, 2H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, d_6-DMSO) 159.9 (C), 144.4 (CH), 132.4 (2 CH), 124.3 (C), 113.8 (2 CH), 52.3 (CH_3).

p-Trifluoromethylbenzaldehyde oxime (3)[2]



***E*-3** ***Z*-3**

p-(Trifluoromethyl)benzaldehyde (680 µL, 5.0 mmol) was added to a solution of hydroxylamine hydrochloride (380 mg, 5.5 mmol, 1.1 eq.) in THF/EtOH/H_2O (2:5:1, 8 mL), and the reaction mixture was stirred at room temperature overnight. The volatiles were removed under reduced pressure and the residue extracted with Et_2O (3 x 20 mL). The organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purified by flash column chromatography on silica, eluting with 10% EtOAc/petroleum, to give:

***E*-3** (682 mg, 72%) as a colourless solid; **^{1}H NMR** (400 MHz, d_6-DMSO) 11.61 (s, 1H), 8.25 (s, 1H), 7.81-7.79 (m, 2H), 7.75-7.73 (m, 2H); **^{13}C NMR** (101 MHz, d_6-DMSO) 147.1 (s, CH), 137.1 (s, C), 129.2 (q, $^2J_{CF}$ = 32.2 Hz, C), 127.0 (s, 2 CH), 125.6 (q, $^3J_{CF}$ = 3.9 Hz, 2 CH), 124.1 (q, $^1J_{CF}$ = 272 Hz, CF_3); **^{19}F NMR** (376 MHz, d_6-DMSO) -61.2 (s), and

***Z*-3** (24 mg, 3%) as a colourless solid; **^{1}H NMR** (400 MHz, d_6-DMSO) 12.0 (s, 1H), 8.18-8.16 (m, 2H), 7.82-7.80 (m, 2H), 7.58 (s, 1H); **^{13}C NMR** (101 MHz, d_6-DMSO) 143.5 (s, CH), 134.4 (s, C), 130.9 (s, 2 CH), 129.2 (q, $^2J_{CF}$ = 31.4 Hz, C), 125.3 (q, $^3J_{CF}$ = 3.8 Hz, 2 CH), 124.0 (q, $^1J_{CF}$ = 272 Hz, CF_3); **^{19}F NMR** (376 MHz, d_6-DMSO) -61.3 (s).

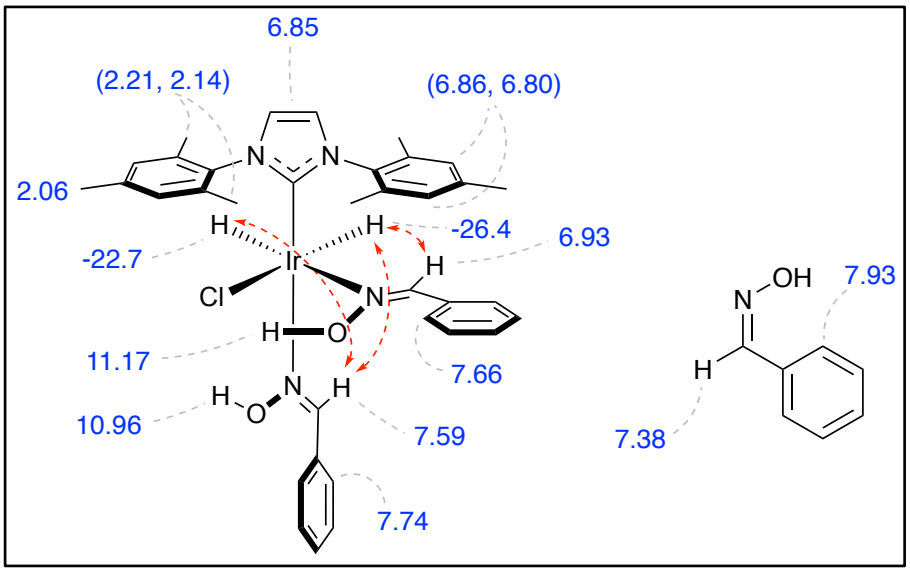
1.3 General procedure for SABRE experiments

[IrCl(COD)(IMes)] was produced from $[Ir(COD)Cl]_2$ and IMes.HCl according to established procedures.[3] Hydrogen gas (>99.999% purity) was generated from a Domnick Hunter 60H and fed through a coaxial parahydrogen generator (HyperSpin Scientific UG) submerged in liquid nitrogen to achieve a conversion temperature of 77 K, to produce p-H_2 with approximately 50% enrichment level. Samples containing [IrCl(COD)(IMes)] (10 mM) and oxime (30 mM) in CD_2Cl_2 (0.6 mL) were prepared in a Norrell S-5-300-JY-7 NMR tube (5 mm diameter, fitted with a J Young's tap), and degassed using the freeze-pump-thaw method. The sample tube was pressurised to 2 bar (gauge) with p-H_2, sealed, and shaken for 10 seconds at 65 G in a handheld

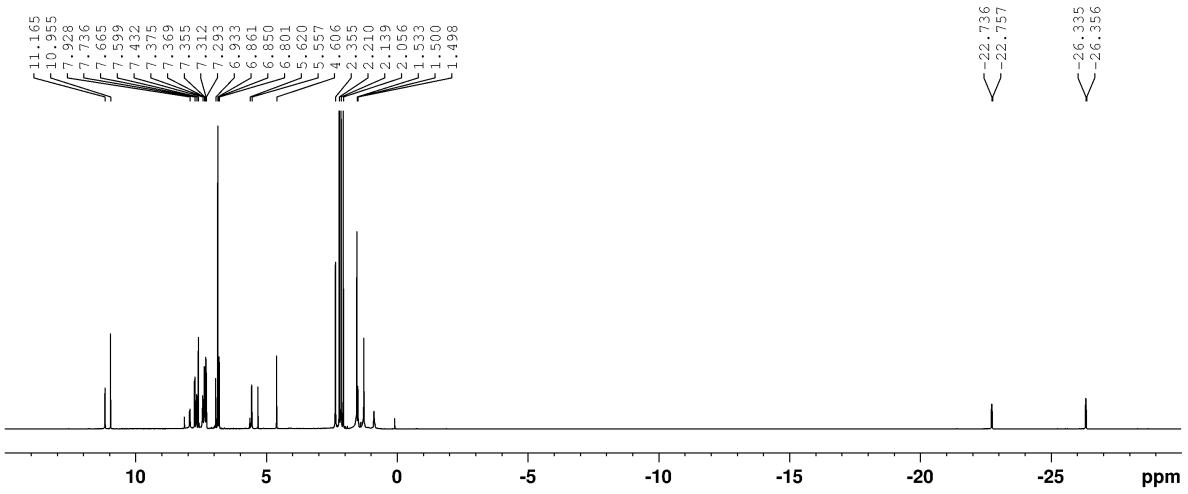
shaker[4] then transferred to a NMR spectrometer operating at 60 MHz or 400 MHz described above. A single 90° pulse was immediately applied to measure each hyperpolarised ^{1}H spectrum, and the sample headspace evacuated and refilled with fresh p-H_2 before each acquisition (typically 4 replicates). A thermally polarised reference spectrum using identical parameters was acquired after allowing the hyperpolarised signal to relax to thermal equilibrium. Enhancement factors were calculated as the ratio of hyperpolarised to thermally polarised integrals.

1.4 NMR assignment of [IrCl(H)$_2$(IMes)(*Z*-1)$_2$]

Prepared *in situ* from the mixture of compound ***Z*-1** (30 mM, 3 equiv.) and [IrCl(COD)(IMes)] (10 mM) in CD_2Cl_2, under H_2 (2 bar) for 1 h. Some diagnostic NOEs depicted in red.

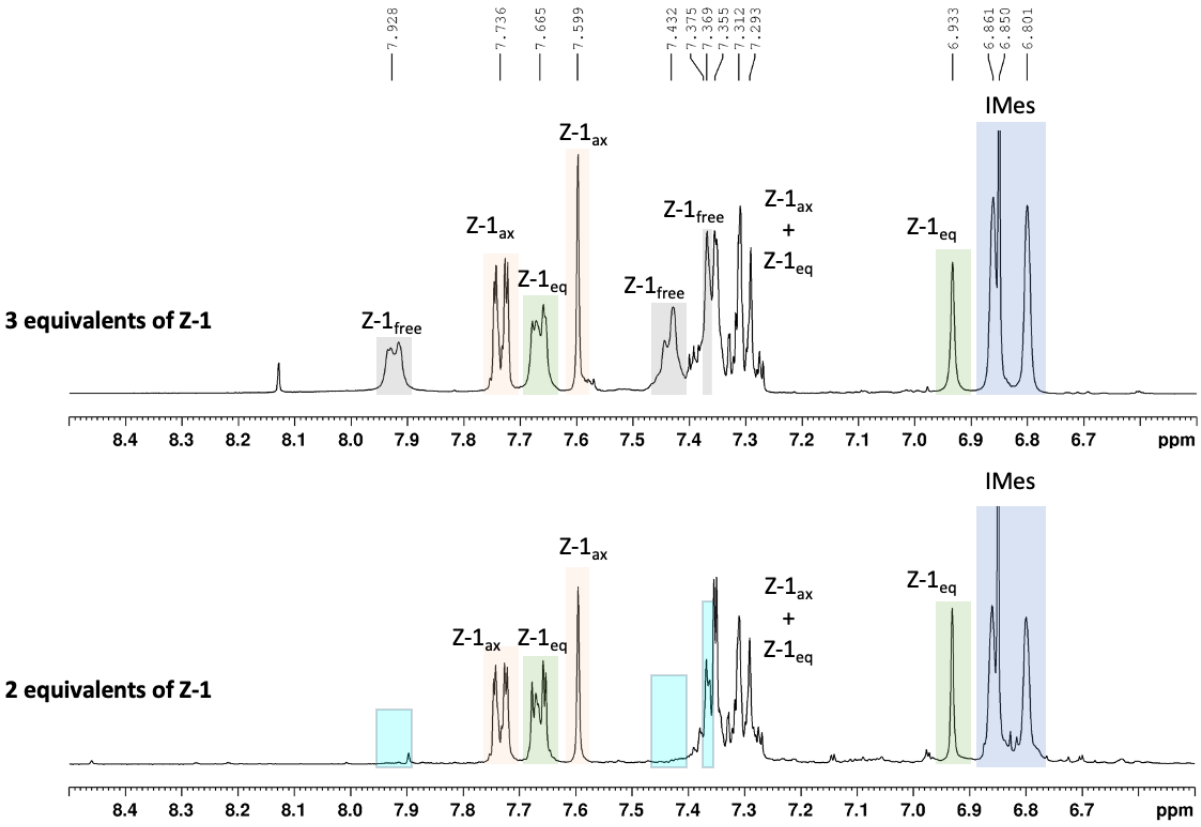


1D ^{1}H spectrum: 400 MHz, CD_2Cl_2

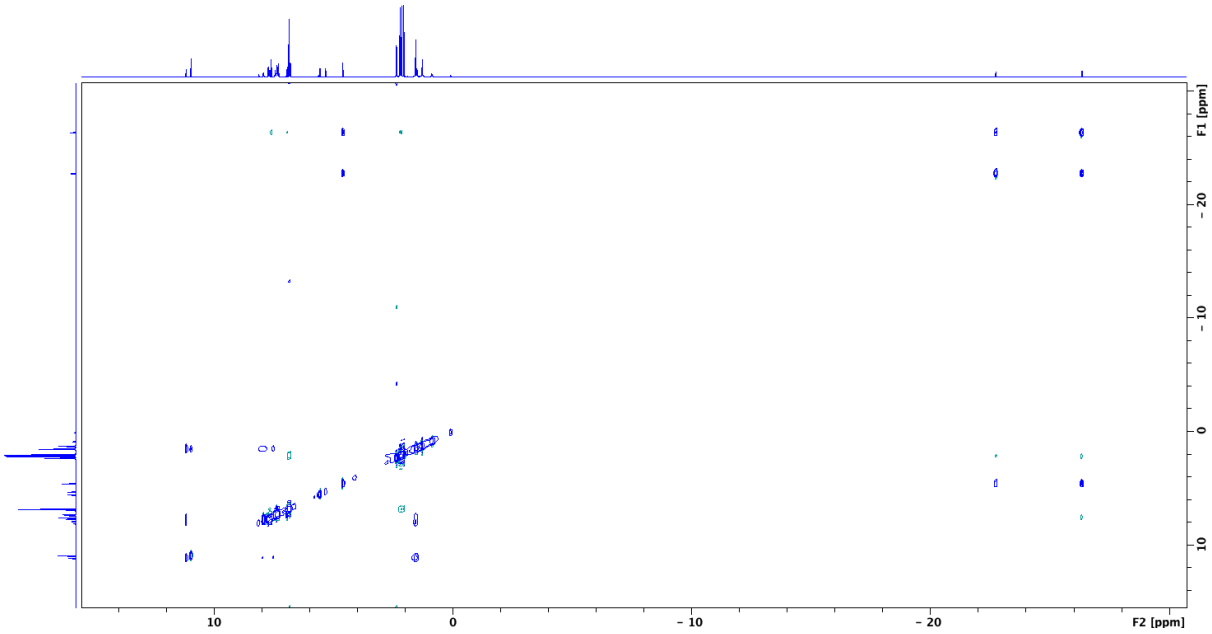


Inset between 8.5 – 6.5 ppm: 400 MHz, CD_2Cl_2

Identical formation of $[IrCl(H)_2(IMes)(Z\text{-}1)_2]$ from only **2 eq. of Z-1**; free peaks are absent.



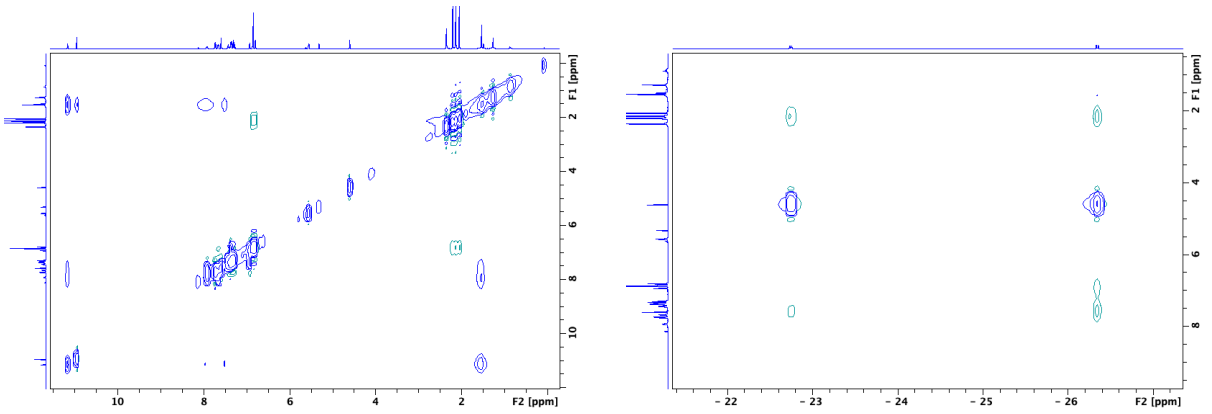
2D Spectrum - NOESY:



Inset:

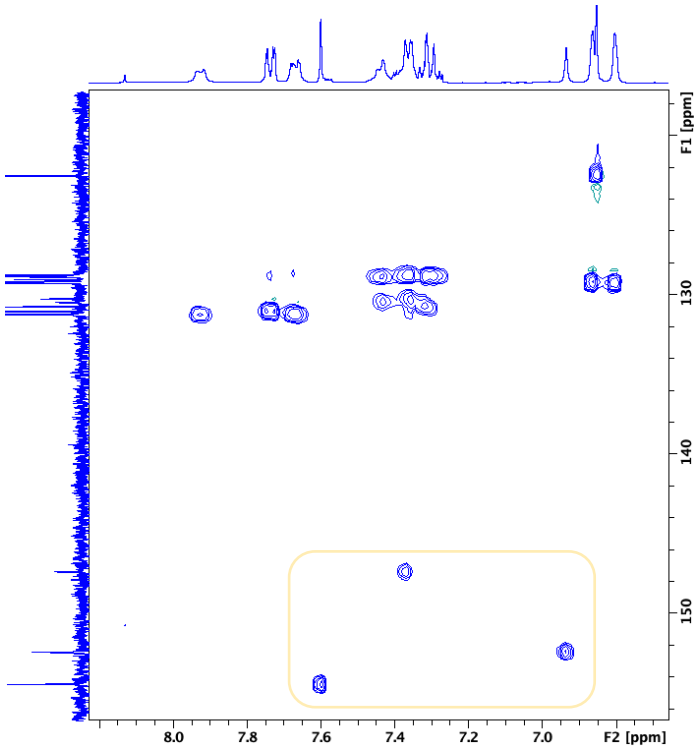
Left, **exchange** between **oxime OH** (x2 at ~11 ppm bound, ~7.5 ppm free) and **H_2O** (1.5 ppm).

Right, **NOEs** between bound **oxime HC=N** (6.9 & 7.6 ppm) and **Ir-H** (-22.7 & -26.4 ppm).



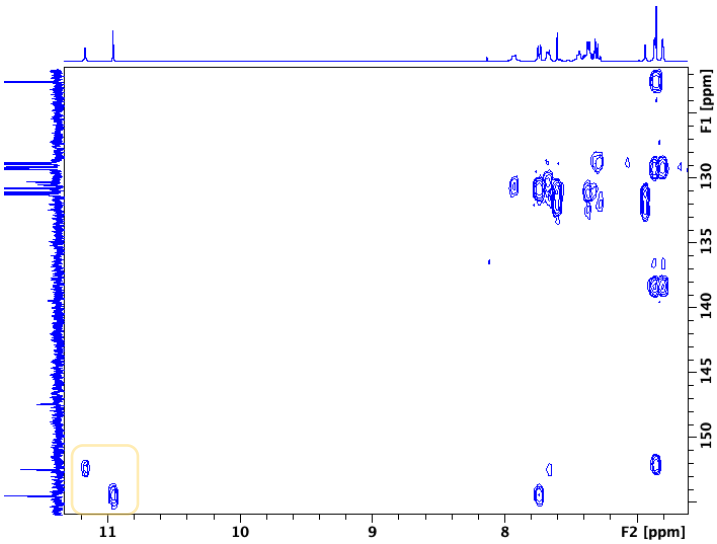
2D Spectrum - HSQC:

Highlighting correlations at the HC=N sites for **Z-1$_{free}$**, **Z-1$_{ax}$** and **Z-1$_{eq}$**.

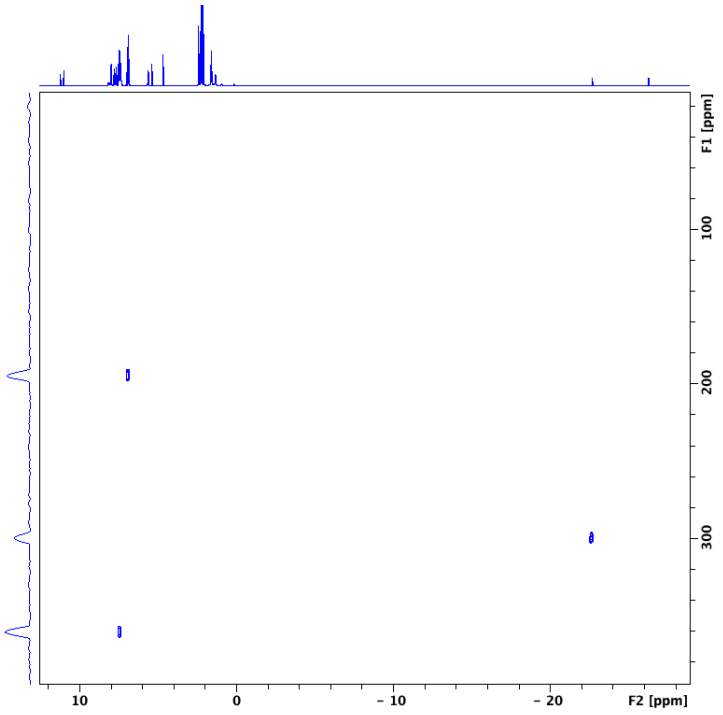


2D Spectrum – ^{1}H-^{13}C HMBC:

Highlighting correlations with bound OH sites for **Z-1$_{ax}$** and **Z-1$_{eq}$**.

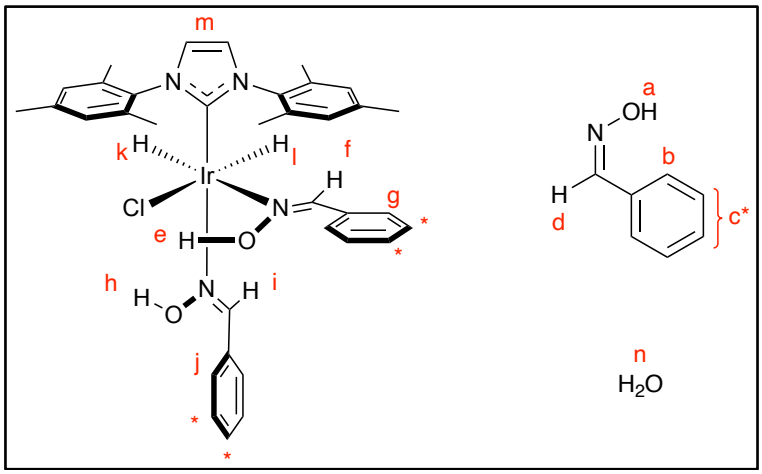


2D Spectrum – ^{1}H-^{15}N HMBC:



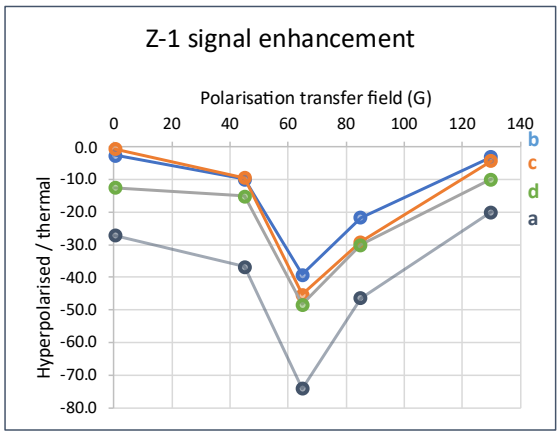
Appendix S2. Hyperpolarised ^{1}H spectra – 400 MHz

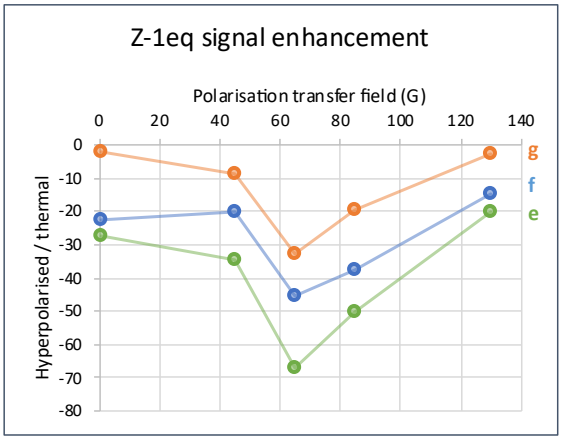
2.1 ^{1}H enhancement factors for Z-1, [IrCl(H)$_2$(IMes)(Z-1)$_2$], and H_2O as a function of polarisation transfer field

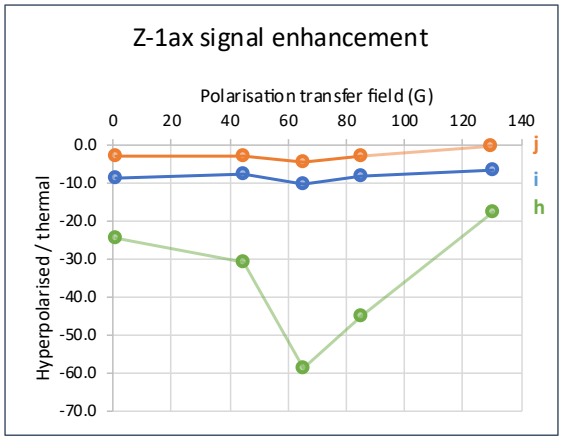


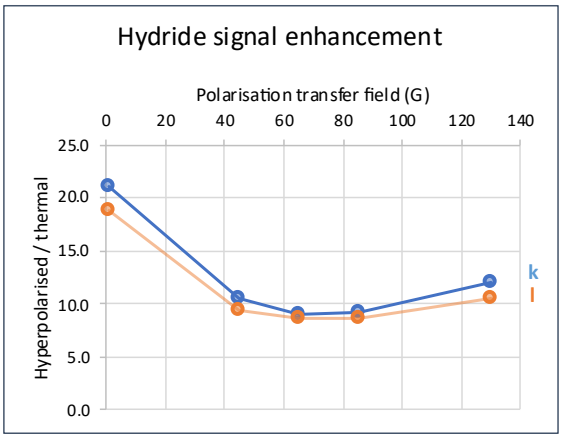
** Hyperpolarised enhancements combined or not determined due to spectral overlap*

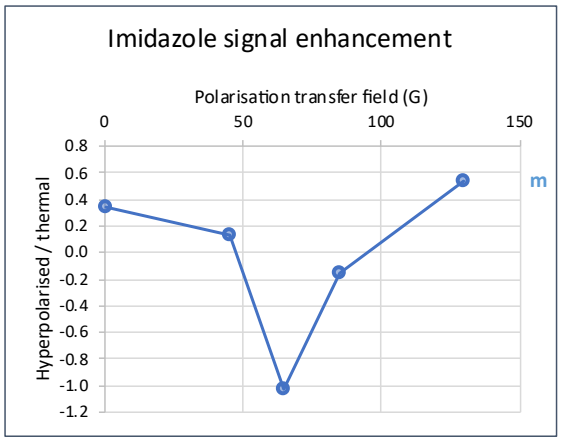
Position label	Position description	Chemical shift (δ)	Polarisation transfer field (PTF)				
			0.5 G	45 G	65 G	85 G	130 G
a	***Z*-1** (free)	8.10 ppm	-27.1	-36.7	-74.0	-46.3	-19.9
b	***Z*-1** (free)	7.93 ppm	-2.5	-9.9	-39.2	-21.6	-3.0
c	***Z*-1** (free)	7.44 ppm	-0.5	-9.4	-45.3	-29.1	-4.2
d	***Z*-1** (free)	7.38 ppm	-12.4	-15.0	-48.3	-30.0	-9.9
e	***Z*-1** (eq)	11.17 ppm	-27.5	-34.6	-67.3	-50.5	-19.9
f	***Z*-1** (eq)	6.93 ppm	-22.3	-20.2	-45.7	-37.7	-14.9
g	***Z*-1** (eq)	7.66 ppm	-2.4	-8.9	-32.7	-19.8	-2.8
h	***Z*-1** (ax)	10.96 ppm	-24.3	-30.7	-58.8	-44.8	-17.5
i	***Z*-1** (ax)	7.59 ppm	-8.6	-7.5	-10.3	-8.4	-6.7
j	***Z*-1** (ax)	7.74 ppm	-2.7	-3.0	-4.5	-3.1	-0.5
k	Ir-H	-22.7 ppm	21.2	10.6	9.0	9.1	12.1
l	Ir-H	-26.4 ppm	18.9	9.4	8.7	8.7	10.6
m	IMes	6.85 ppm	0.3	0.1	-1.0	-0.1	0.5
n	H_2O	1.57 ppm	-24.5	-30.4	-67.5	-40.8	-16.5

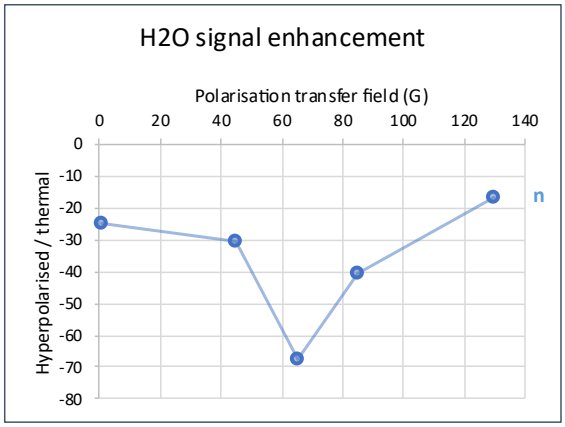





Z-1ax signal enhancement
Polarisation transfer field (G)
0
20
40
60
80
100
120
140
0.0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
Hyperpolarised / thermal
j
i
h

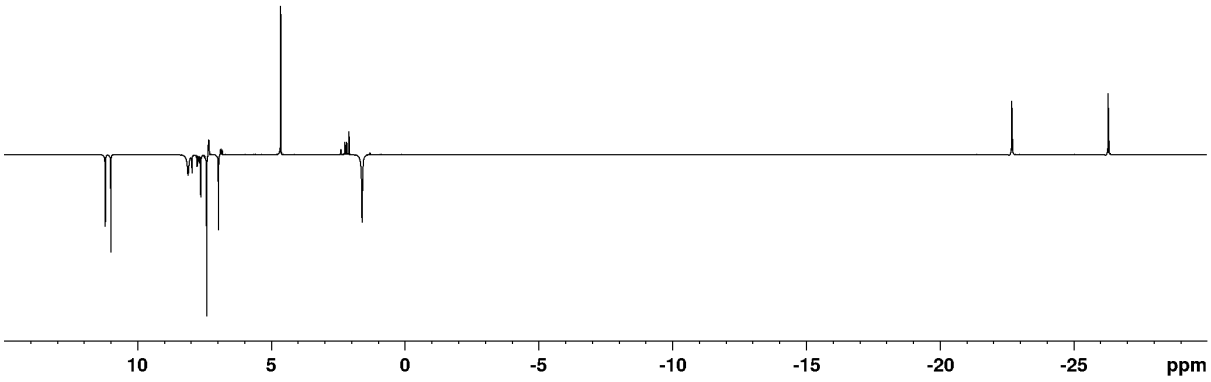

Hydride signal enhancement
Polarisation transfer field (G)
0
20
40
60
80
100
120
140
25.0
20.0
15.0
10.0
5.0
0.0
Hyperpolarised / thermal
k
l


Imidazole signal enhancement
Polarisation transfer field (G)
0
50
100
150
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
Hyperpolarised / thermal
m


H2O signal enhancement
Polarisation transfer field (G)
0
20
40
60
80
100
120
140
0
-10
-20
-30
-40
-50
-60
-70
-80
Hyperpolarised / thermal
n

2.2 ^{1}H SABRE spectra as a function of polarisation transfer field

PTF = 0.5 G



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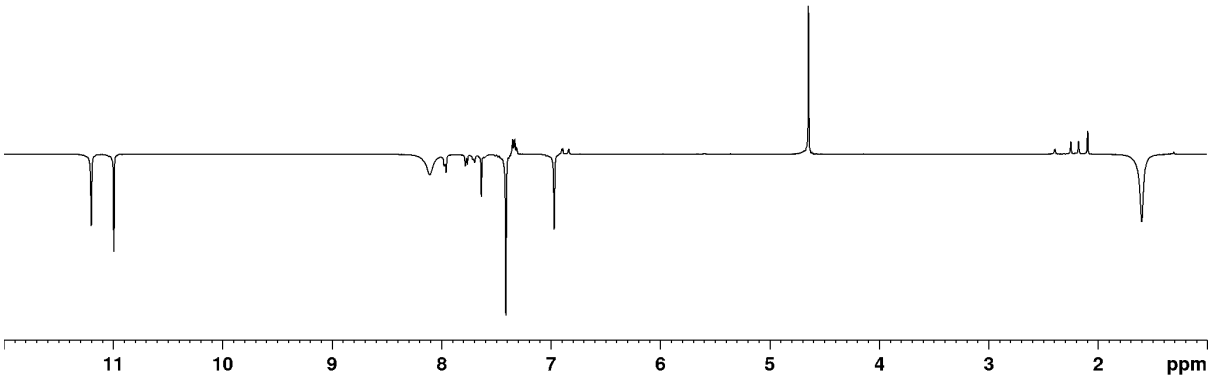
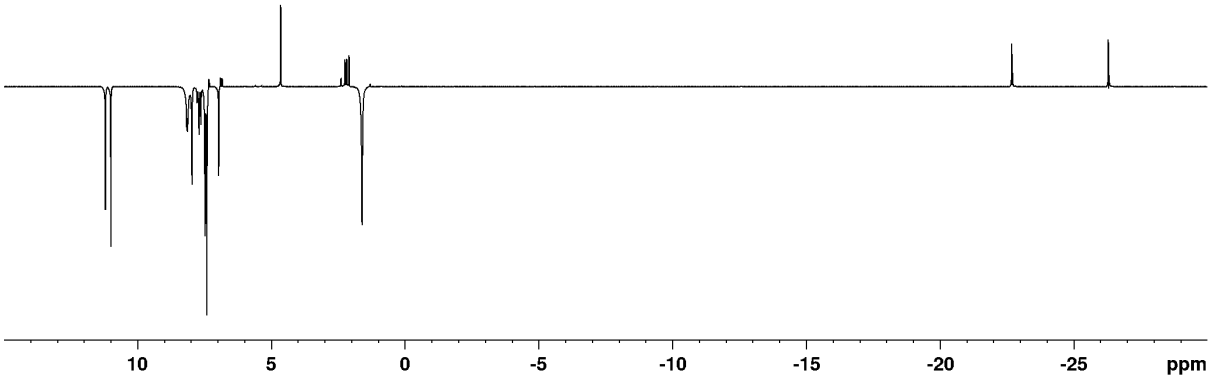


PTF = 45 G



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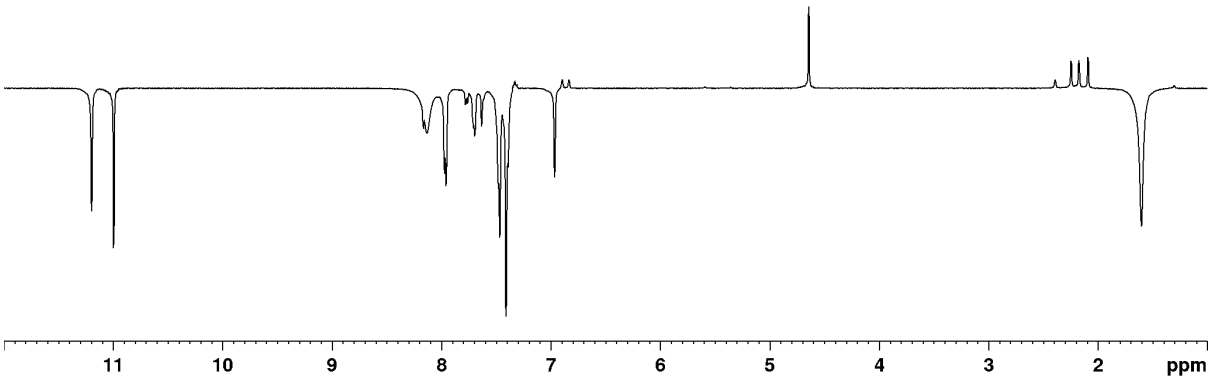
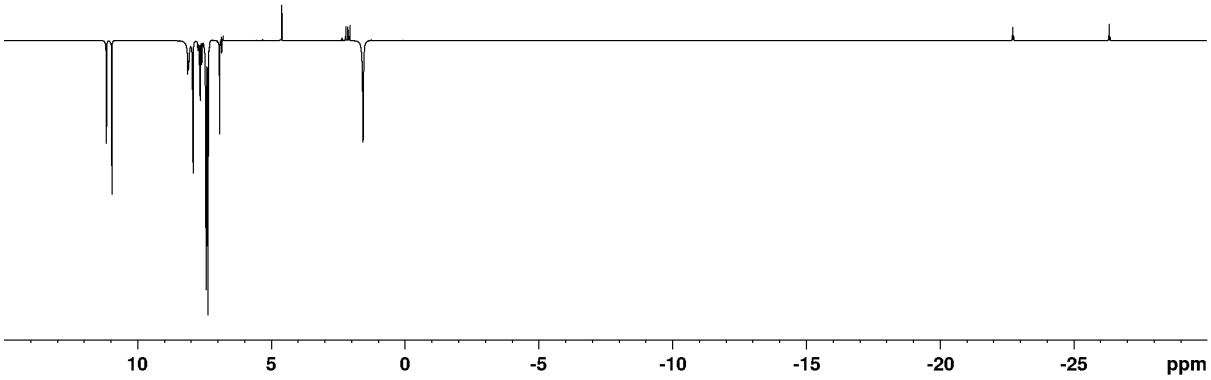


PTF = 65 G



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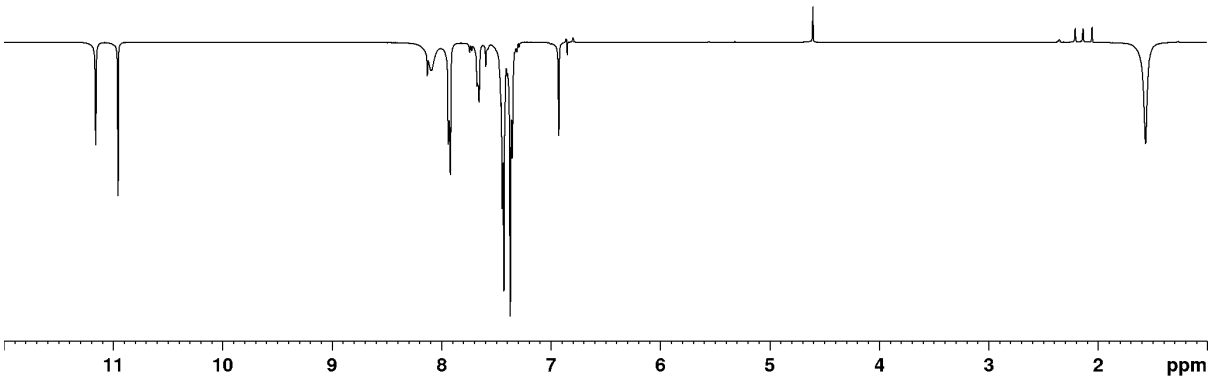
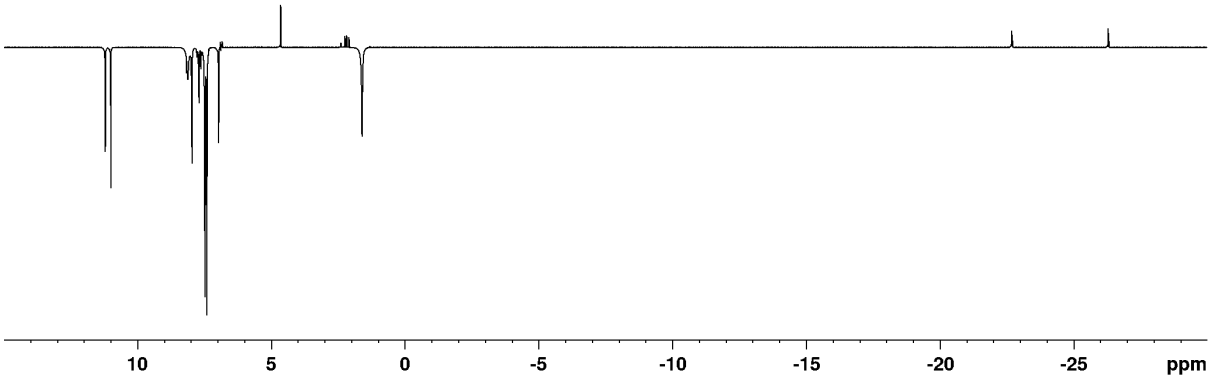


PTF = 85 G



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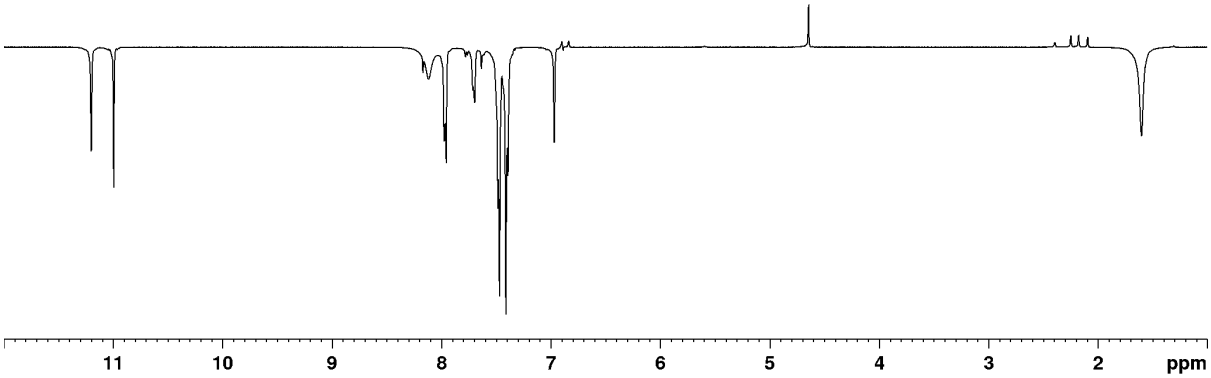
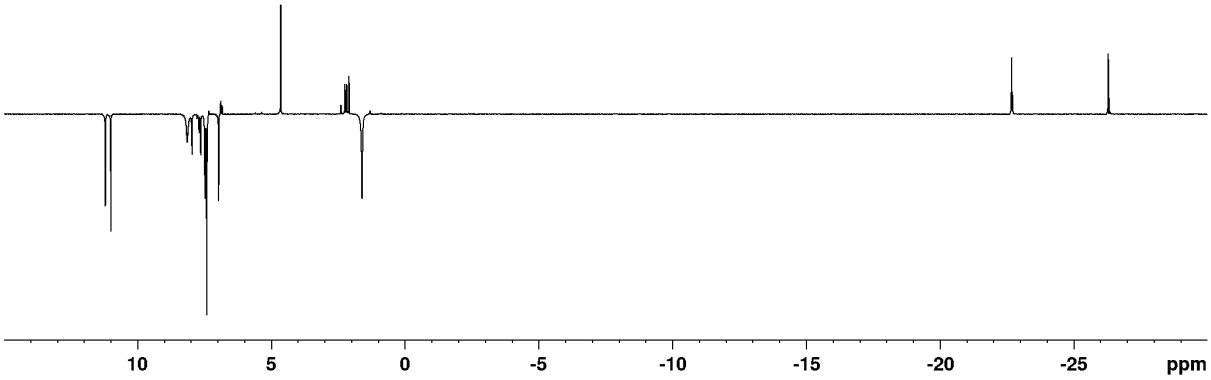


PTF = 130 G



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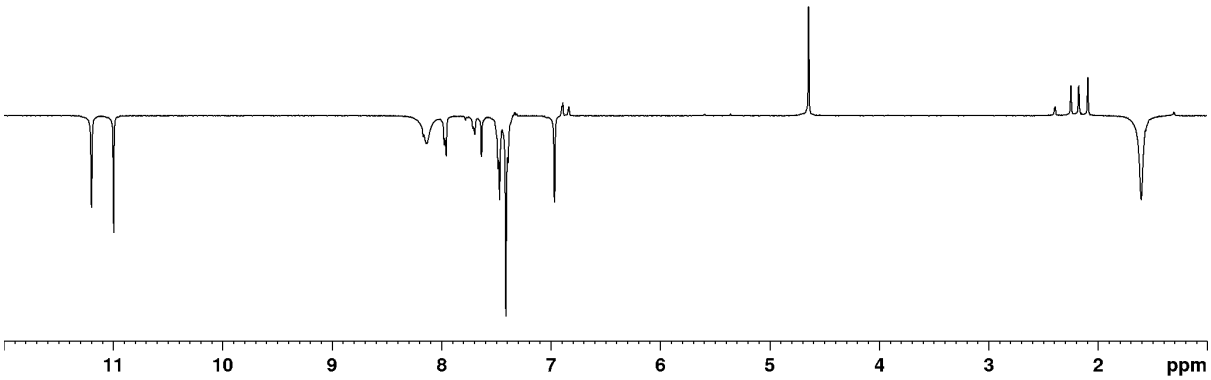
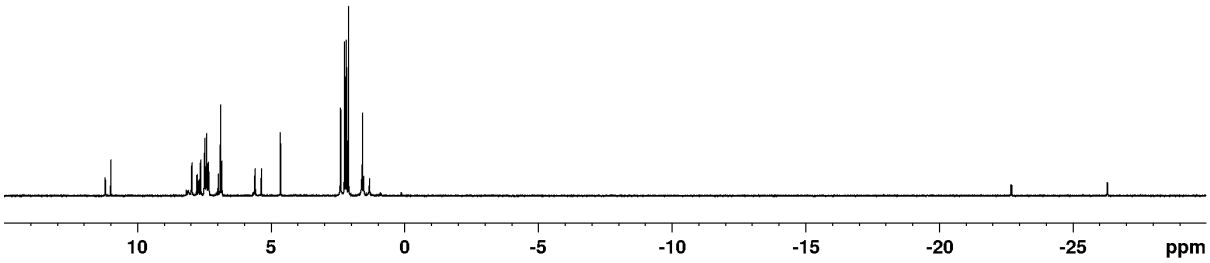


Thermally polarised spectrum:



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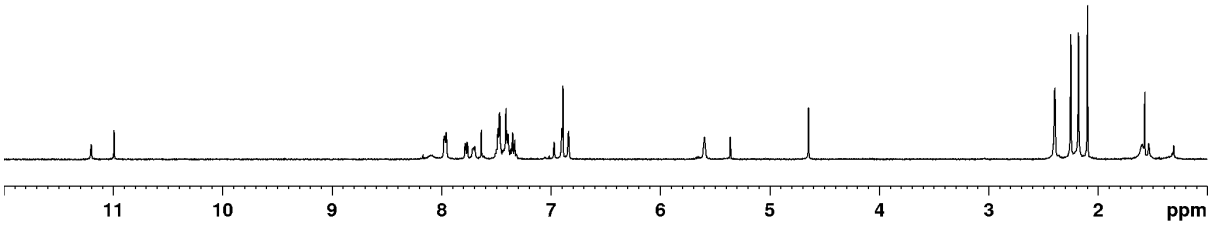
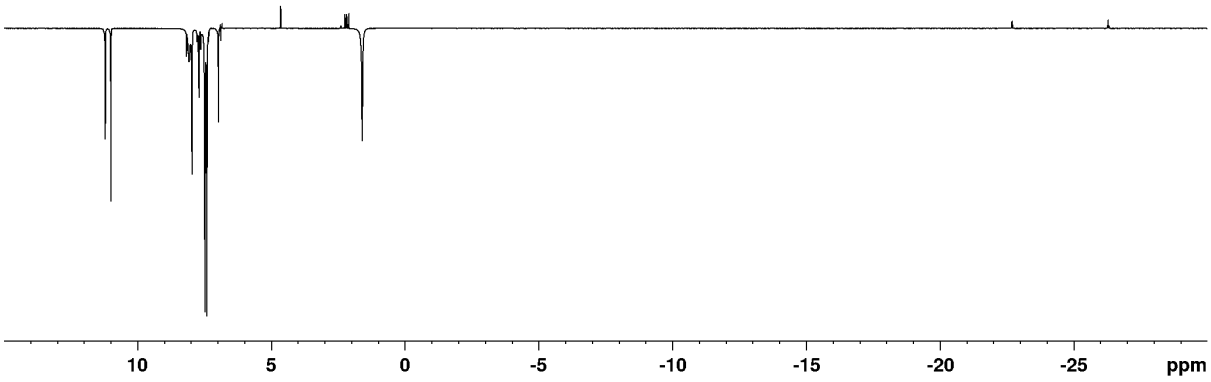


2.3 Polarisation transfer at increased temperature

Polarisation transfer at 40 °C (PTF = 65 G).



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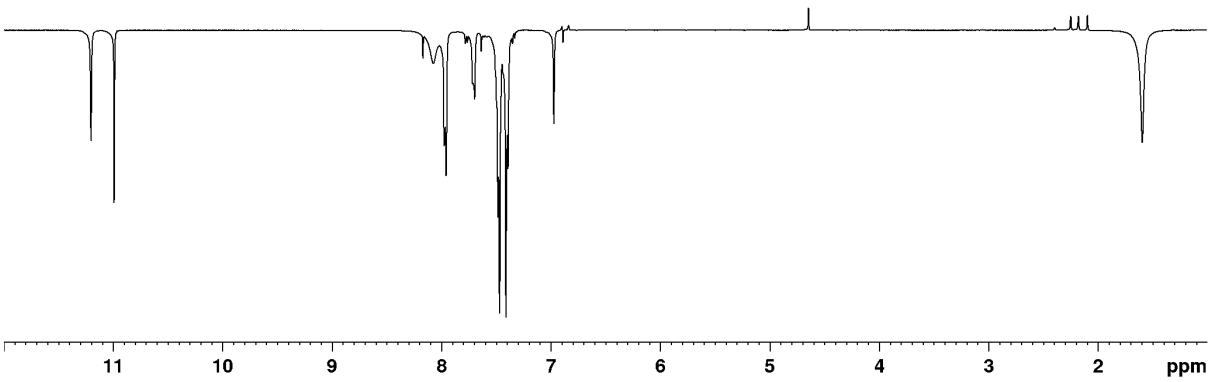
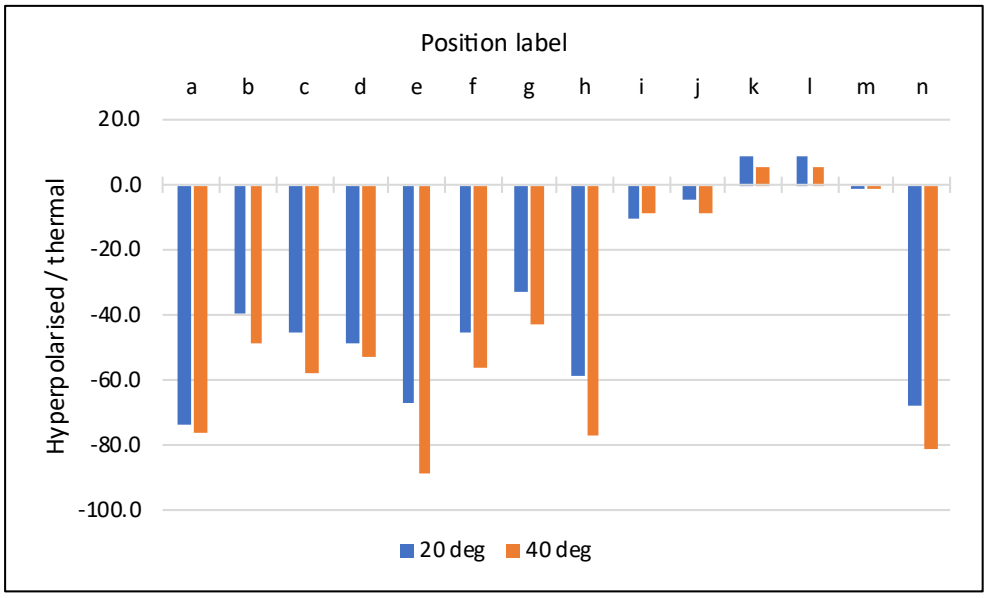
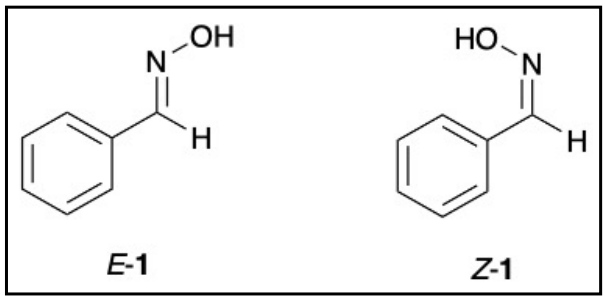


Position label	Position description	Chemical shift (δ)	Polarisation transfer temperature (°C)		enhancement change (%) 20°C → 40°C
			20	40	
a	***Z*-1** (free)	8.10 ppm	-74.0	-76.3	+3%
b	***Z*-1** (free)	7.93 ppm	-39.2	-48.8	+25%
c	***Z*-1** (free)	7.44 ppm	-45.3	-58.0	+28%
d	***Z*-1** (free)	7.38 ppm	-48.3	-52.8	+9%
e	***Z*-1** (eq)	11.17 ppm	-67.3	-88.9	+32%
f	***Z*-1** (eq)	6.93 ppm	-45.7	-55.8	+22%
g	***Z*-1** (eq)	7.66 ppm	-32.7	-43.1	+32%
h	***Z*-1** (ax)	10.96 ppm	-58.8	-77.2	+31%
i	***Z*-1** (ax)	7.59 ppm	-10.3	-8.9	-14%
j	***Z*-1** (ax)	7.74 ppm	-4.5	-8.4	+87%
k	Ir-H	-22.7 ppm	9.0	5.7	-37%
l	Ir-H	-26.4 ppm	8.7	6.0	-31%
m	IMes	6.85 ppm	-1.0	-1.4	+38%
n	H_2O	1.57 ppm	-67.5	-81.2	+20%

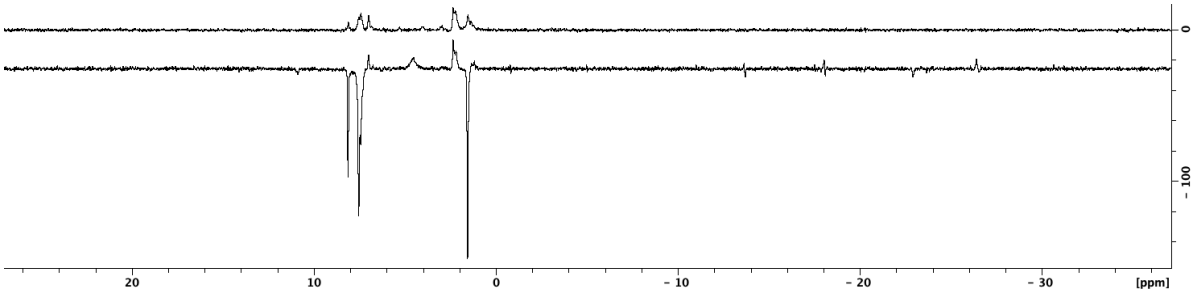


Appendix S3. Hyperpolarised ^{1}H spectra – 60 MHz



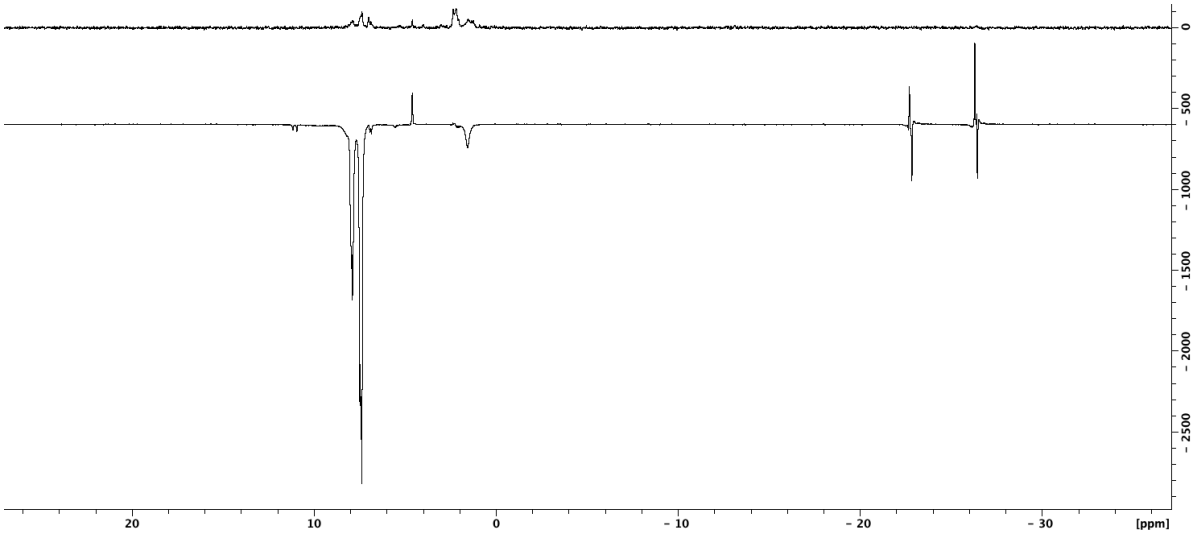
3.1 Compound *E*-1

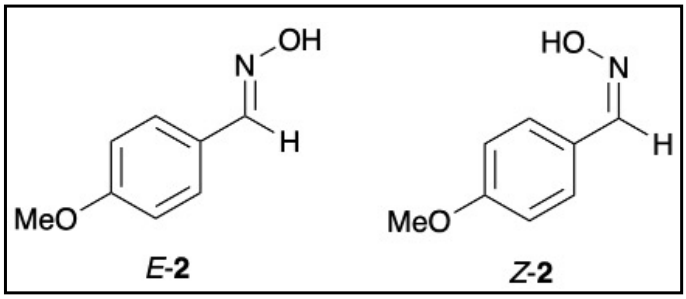
Top: thermal spectrum. *Bottom*: hyperpolarised spectrum. 60 MHz



3.2 Compound *Z*-1

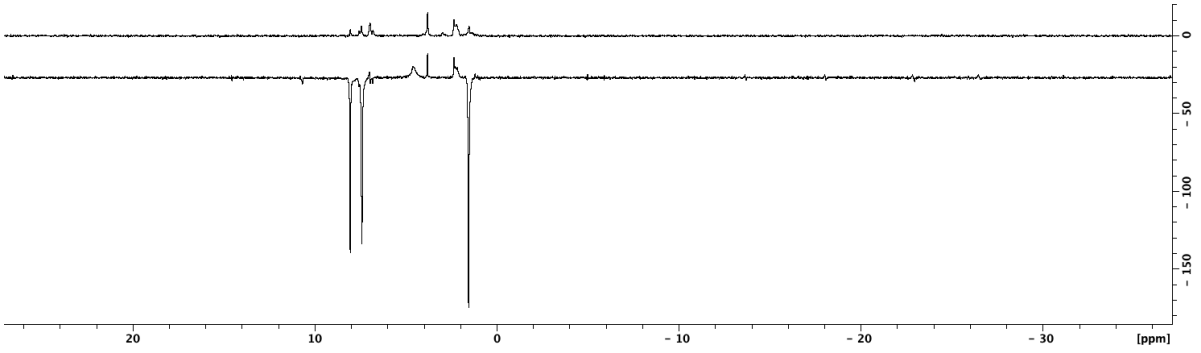
Top: thermal spectrum (vertically expanded x8). *Bottom*: hyperpolarised spectrum. 60 MHz





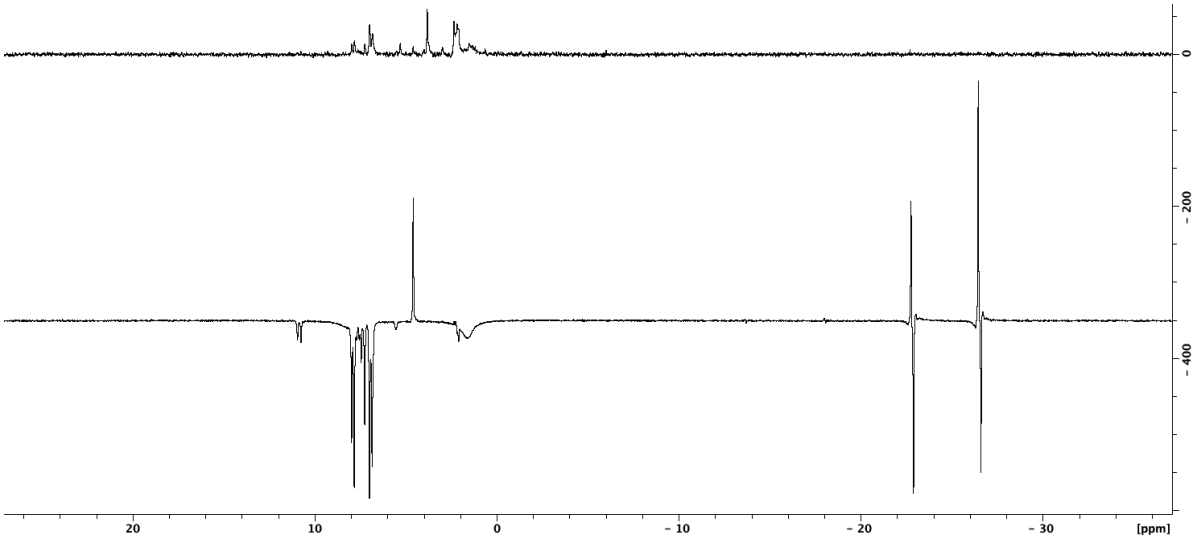
3.3 Compound *E*-2

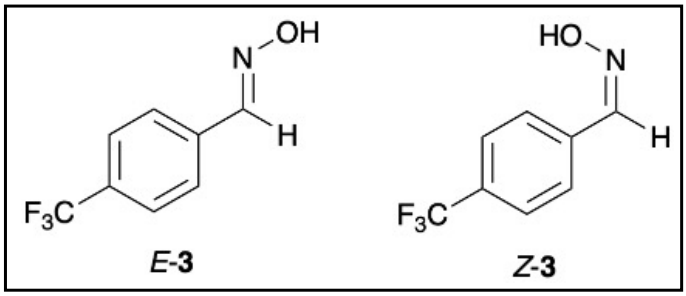
Top: thermal spectrum. *Bottom*: hyperpolarised spectrum. 60 MHz



3.4 Compound *Z*-2

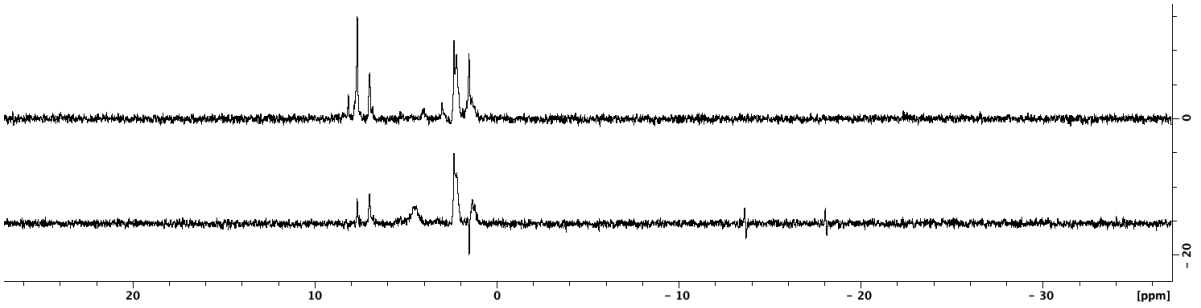
Top: thermal spectrum (vertically expanded x4). *Bottom*: hyperpolarised spectrum. 60 MHz





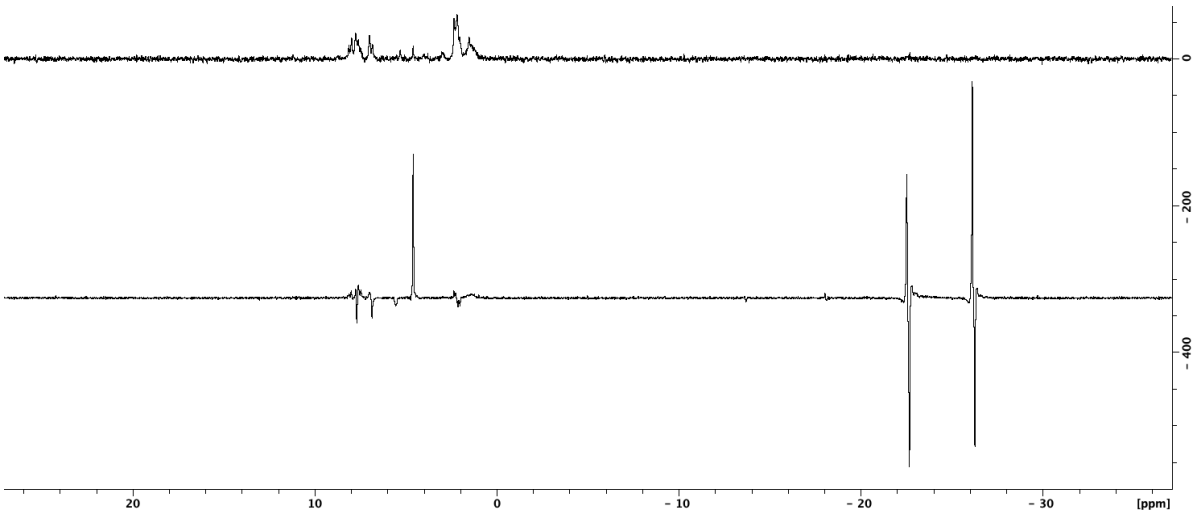
3.5 Compound *E*-3

Top: thermal spectrum. *Bottom*: hyperpolarised spectrum. 60 MHz



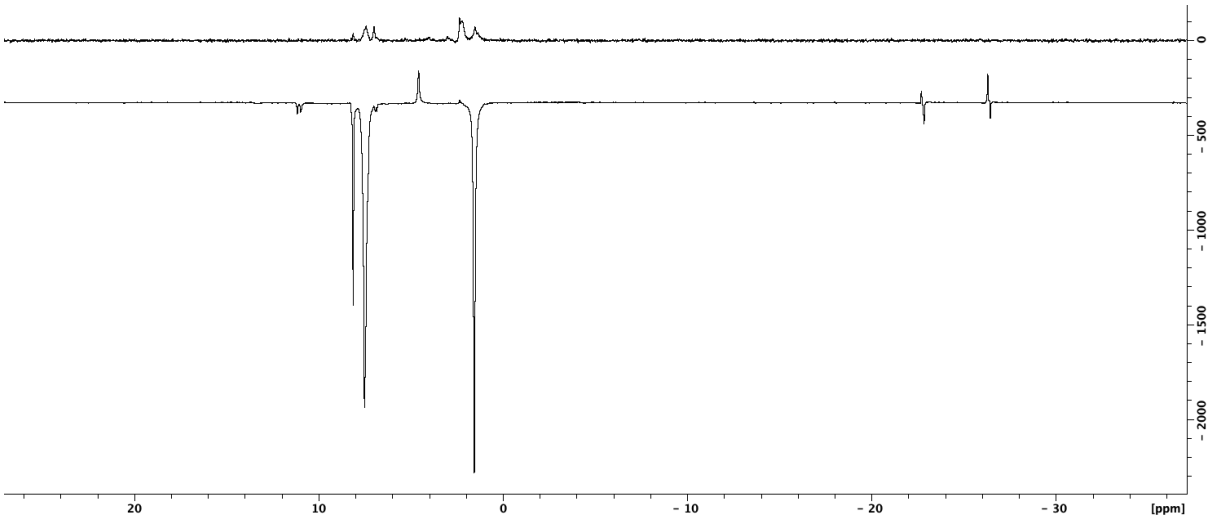
3.6 Compound *Z*-3

Top: thermal spectrum (vertically expanded x4). *Bottom*: hyperpolarised spectrum. 60 MHz



3.7 Compound (*E*:*Z*)-1 (14:1 mixture)

Top: thermal spectrum (vertically expanded x8). *Bottom*: hyperpolarised spectrum. 60 MHz



3.8 Summary of oxime enhancements

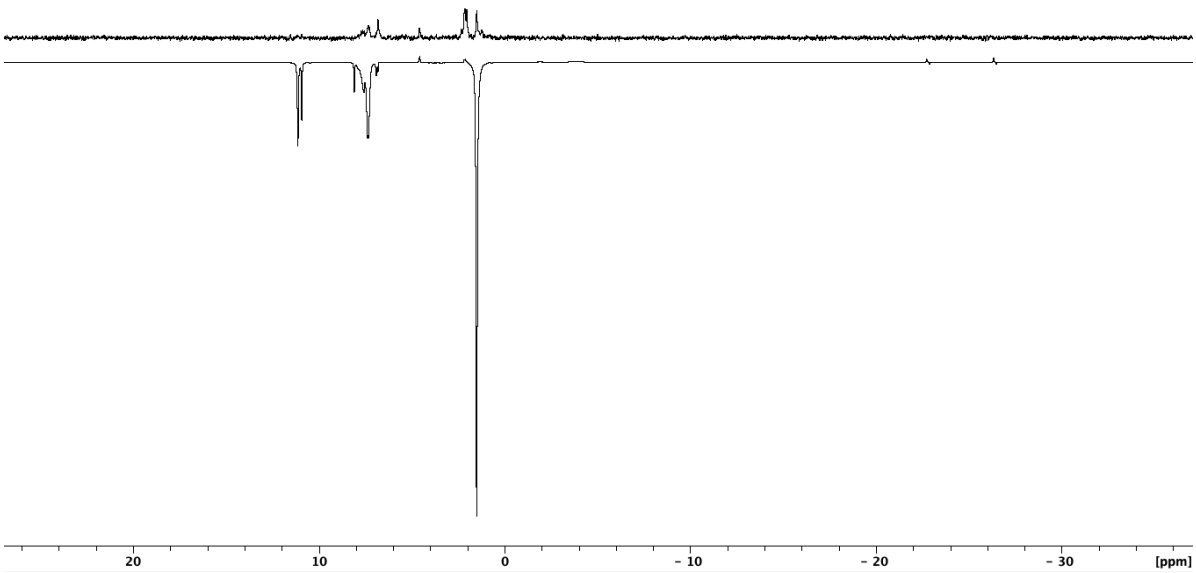
Enhancement factor $= \frac{\text{Signal(hyperpolarised)}}{\text{Signal(thermal)}}$, determined for the range corresponding to combined oxime CH resonances.

	Range (ppm)	Enhancement factor
***E*-1**	8.3-7.1	**-6.3**
***Z*-1**	8.7-6.7	**-113.0**
(14:1 mix) ***E*:*Z*-1**	8.5-6.7	**-108.4**
***E*-2**	8.2-7.1	-15.0
***Z*-2**	8.7-6.6	-28.4
***E*-3**	8.3-7.4	0.1
***Z*-3**	8.3-6.7	0.3

3.9 SABRE-Relay: H_2O hyperpolarisation after extended reaction times

In order to exclude the possibility of an overlapping PHIP response from production of cyclooctane (~1.5 ppm) from cyclooctadiene, a sample of **Z-1** and [IrCl(COD)(IMes)] in CD_2Cl_2 prepared according to the procedure in Section 1.3 was left for 3 days under H_2 (2 bar) to consume any residual cyclooctadiene or cyclooctane, then refilled with fresh p-H_2 for analysis of SABRE as before.

Z-1: *Top*: thermal spectrum (vertically expanded x64). *Bottom*: hyperpolarised spectrum. 60 MHz

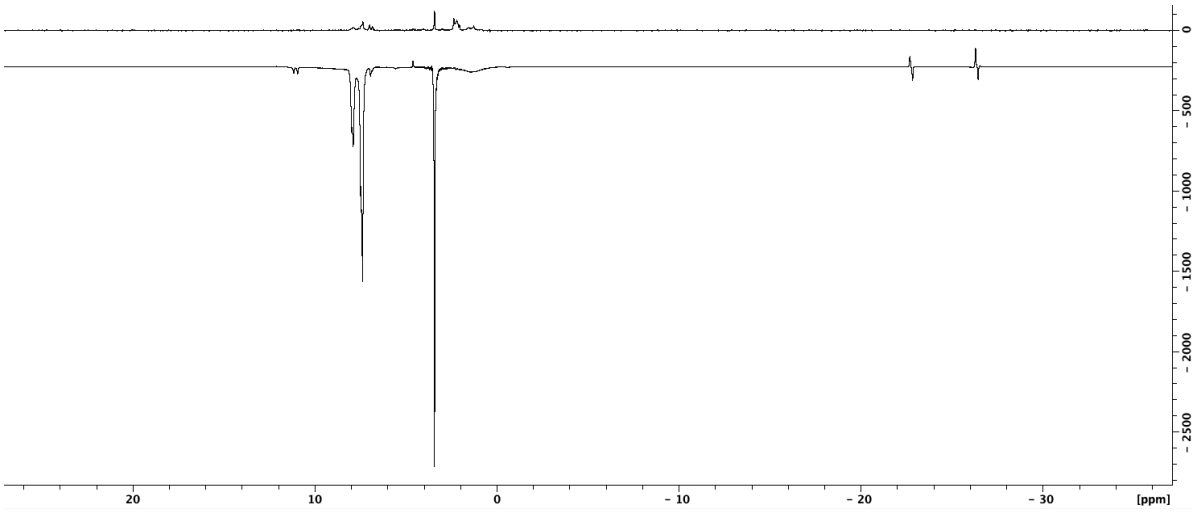


	Range (ppm)	Enhancement factor
Oxime CH	8.3-6.7	**-272.0**
H_2O	2.0-0.9	**-660.6**

3.10 SABRE-Relay: MeOH hyperpolarisation in dried CD_2Cl_2

Z-1 (30 mM), **MeOH** (20 mM), [IrCl(COD)(IMes)] (10 mM) in CD_2Cl_2 (dried over CaH_2 and 4A MS), under H_2 (2 bar), hyperpolarised according to the procedure in Section 1.3.

Top: thermal spectrum (vertically expanded x8). *Bottom*: hyperpolarised spectrum. 60 MHz



	Range (ppm)	Enhancement factor
Oxime CH	8.3-6.7	**-132.1**
C<u>H</u>$_3$OH	3.6-3.1	**-173.1**

Appendix S4. Computational details

4.1 General details and summary of energies

All calculations were performed using the Gaussian 16 program package.[5] Geometry optimisations were conducted at the SMD[6]-(DCM)-ωB97X-D[7]/def2-SVP[8] level of theory, with frequency calculations run at the same level of theory to confirm the resulting structures as energy minima with no imaginary frequencies and to obtain ZPVE and thermal corrections. No wavefunction instabilities were found. Subsequent single point calculations were performed at the SMD[6]-(DCM)-ωB97X-D[7]/def2-TZVPP[8] level of theory to obtain a refined electronic energy.

	SCF Energy (Ha)	Thermal correction to Gibbs Free Energy (Ha)
[IrCl(H)$_2$(IMes)(*Z*-1)$_2$]	-2292.080995	0.602034
[Ir(H$_2$O)(H)$_2$(IMes)(*Z*-1)$_2$]$^+$	-1908.131533	0.628443
[IrCl(H)$_2$(IMes)(*E*-1)$_2$]	-2292.077068	0.602454
[IrCl(H)$_2$(IMes)(*Z*-1$_{ax}$)(*E*-1$_{eq}$)]	-2292.077379	0.601473
***Z*-1**	-400.900292	0.096417
***E*-1**	-400.903636	0.095408
H$_2$O	-76.448441	0.003801
Cl$^-$	-460.369284	-0.015023

4.2 Cartesian coordinates for optimised geometries

[IrCl(H)$_2$(IMes)(*Z*-1)$_2$]

0 1

C	-3.157704	-3.033399	0.618079
C	-1.962258	-3.659891	0.645711
N	-1.000084	-2.684573	0.438324
C	-1.558417	-1.450932	0.274034
N	-2.900093	-1.690628	0.393184
C	-3.962416	-0.728766	0.343349
C	-4.665258	-0.558973	-0.856722
C	-5.708812	0.370121	-0.873764
C	-6.059963	1.106915	0.261755
C	-5.351256	0.883087	1.446320
C	-4.300809	-0.035258	1.513340
C	-4.302891	-1.349264	-2.083043
C	-3.534374	-0.248811	2.788330
C	-7.160449	2.132662	0.202167
C	0.396502	-2.996469	0.441330
C	1.006046	-3.374407	-0.762072

C	2.362338	-3.699125	-0.729044
C	3.099560	-3.662281	0.459596
C	2.448357	-3.290390	1.638516
C	1.092504	-2.950792	1.653795
C	0.411917	-2.508377	2.919294
C	0.221283	-3.394424	-2.043350
C	4.570397	-3.976557	0.449503
Ir	-0.665091	0.315741	-0.049547
H	-2.064519	0.933413	0.297305
H	-0.354837	0.395426	1.487936
Cl	-1.078273	0.293026	-2.644612
N	1.460896	-0.301166	-0.623935
N	0.166871	2.287887	-0.338912
O	1.746049	-0.453509	-1.937264
C	2.458026	-0.291297	0.182730
C	3.900447	-0.415829	-0.060246
O	-0.031939	2.889748	-1.533577
C	0.843833	2.948375	0.531808
C	1.475991	4.269724	0.456730
C	4.506498	-0.601793	-1.315472
C	5.892807	-0.713408	-1.413212
C	6.694954	-0.646425	-0.274290
C	6.103638	-0.466944	0.977356
C	4.721534	-0.353074	1.080511
C	1.419178	5.150080	-0.639899
C	2.075015	6.378277	-0.584470
C	2.793478	6.751637	0.551142
C	2.855339	5.888081	1.645876
C	2.202100	4.661661	1.597681
H	-4.169860	-3.408941	0.738500
H	-1.696825	-4.702659	0.794804
H	-6.263401	0.521503	-1.804415
H	-5.623280	1.439286	2.348100
H	-3.261610	-1.149145	-2.378279
H	-4.956118	-1.083989	-2.925487
H	-4.396417	-2.432491	-1.906734
H	-4.045450	0.223356	3.638202
H	-2.526791	0.189395	2.706067
H	-3.404043	-1.318786	3.011706
H	-7.949691	1.836321	-0.504185
H	-6.764940	3.104194	-0.137526
H	-7.618731	2.290800	1.189101
H	2.862323	-3.977802	-1.661149
H	3.013614	-3.251954	2.574190
H	1.077877	-2.623052	3.785161
H	-0.506488	-3.084238	3.111967
H	0.116677	-1.449132	2.849454
H	-0.595360	-4.132924	-2.001937
H	0.867108	-3.646647	-2.895037
H	-0.241306	-2.415248	-2.239841

H	4.771713	-4.931100	-0.060639
H	4.979519	-4.035938	1.467839
H	5.125504	-3.194373	-0.093386
H	0.881206	-0.314450	-2.386659
H	2.155723	-0.166893	1.225027
H	-0.459993	2.196775	-2.086184
H	0.961394	2.410813	1.475003
H	3.891513	-0.660741	-2.209585
H	6.350090	-0.856443	-2.395005
H	7.780239	-0.737019	-0.360933
H	6.722271	-0.417183	1.876217
H	4.260679	-0.216589	2.062450
H	0.862029	4.872350	-1.530686
H	2.022429	7.051886	-1.442861
H	3.304935	7.716483	0.584032
H	3.414432	6.171731	2.540284
H	2.252180	3.987593	2.456646

[Ir(H$_2$O)(H)$_2$(IMes)(*Z*-1)$_2$]$^+$

1 1

C	1.449243	-1.511838	-0.369793
N	2.730036	-1.807748	-0.015836
C	2.971966	-3.170815	-0.069053
C	1.815908	-3.749351	-0.461755
N	0.895986	-2.727087	-0.636064
C	3.681830	-0.857912	0.468144
C	-0.479125	-2.978659	-0.950631
C	-1.350226	-3.282954	0.102336
C	-2.690338	-3.527621	-0.210486
C	-3.161069	-3.465381	-1.523846
C	-2.250070	-3.178377	-2.548188
C	-0.897744	-2.946987	-2.288311
C	4.566185	-0.246755	-0.427452
C	5.453814	0.704626	0.085771
C	5.481289	1.034081	1.443488
C	4.596963	0.376816	2.310299
C	3.694229	-0.584061	1.845401
Ir	0.628025	0.315541	-0.584373
H	1.805949	0.603399	-1.627149
H	-0.161726	-0.310623	-1.755599
N	-0.177356	2.259109	-1.007043
N	-0.994930	0.007196	0.860921
O	1.565702	1.455034	1.328914
C	2.745036	-1.286995	2.778637
C	4.560297	-0.610095	-1.885253
C	6.462851	2.042075	1.975965
C	0.081615	-2.681683	-3.398110
C	-4.612368	-3.709492	-1.839818
C	-0.863385	-3.322831	1.524636

H	1.547998	2.416499	1.201057
H	2.489662	1.230431	1.537415
O	0.254726	2.822106	-2.167504
O	-0.705404	0.216935	2.176604
C	-1.013974	2.948096	-0.314473
C	-1.601905	4.269333	-0.544677
C	-2.201518	-0.327461	0.579447
C	-3.365866	-0.547571	1.439923
C	-3.349683	-0.582426	2.846048
C	-4.524462	-0.841803	3.549137
C	-5.723333	-1.064996	2.872063
C	-5.750344	-1.032140	1.476645
C	-4.580873	-0.780259	0.768935
C	-2.502675	4.710777	0.443761
C	-1.340338	5.107030	-1.645307
C	-1.965774	6.347876	-1.739561
C	-2.854690	6.773526	-0.752309
C	-3.123530	5.950374	0.342105
H	3.941658	-3.591932	0.180826
H	1.552967	-4.789529	-0.632061
H	-3.387936	-3.751119	0.601119
H	-2.601976	-3.141782	-3.583277
H	6.145205	1.201771	-0.600105
H	4.614436	0.613064	3.377975
H	2.848544	-0.905632	3.802880
H	2.937211	-2.371175	2.794771
H	1.697369	-1.156415	2.466587
H	3.567327	-0.445281	-2.329681
H	4.806196	-1.674415	-2.025868
H	5.294417	-0.012472	-2.441635
H	6.816747	2.717144	1.184211
H	7.344877	1.533648	2.398617
H	6.019644	2.647444	2.780062
H	-0.415426	-2.718816	-4.376619
H	0.891715	-3.427938	-3.396245
H	0.553671	-1.693402	-3.288023
H	-5.221378	-3.754992	-0.926103
H	-4.741868	-4.661770	-2.378986
H	-5.016677	-2.915541	-2.486250
H	-0.342171	-2.392114	1.796024
H	-0.150952	-4.148569	1.680896
H	-1.701197	-3.462067	2.220926
H	0.901518	2.179961	-2.502964
H	0.173782	0.645137	2.158610
H	-1.328167	2.443801	0.602172
H	-2.357407	-0.470156	-0.492902
H	-2.420933	-0.415386	3.385945
H	-4.500747	-0.870763	4.640786
H	-6.638807	-1.267917	3.432610
H	-6.684613	-1.208925	0.939461

H	-4.598054	-0.768978	-0.323812
H	-2.716684	4.066488	1.300518
H	-0.651878	4.788612	-2.423613
H	-1.754692	6.989662	-2.597732
H	-3.340168	7.748490	-0.836705
H	-3.819340	6.275730	1.118283

[IrCl(H)$_2$(IMes)(*E*-1)$_2$]

0 1

N	-0.372789	-2.020267	1.308628
C	-1.153788	-1.077089	0.699467
N	-2.416943	-1.398257	1.106105
C	-2.420039	-2.512239	1.930178
C	-1.134842	-2.903604	2.057560
C	-3.627967	-0.702037	0.788747
C	1.057485	-2.121168	1.289963
C	1.657373	-3.036803	0.415103
C	3.047609	-3.168828	0.459381
C	3.830028	-2.434903	1.354775
C	3.188642	-1.554658	2.230856
C	1.801763	-1.386249	2.225154
C	-4.411115	-1.171939	-0.271572
C	-5.604176	-0.501766	-0.548476
C	-6.017498	0.603321	0.200971
C	-5.218982	1.020853	1.271001
C	-4.022454	0.375343	1.593085
C	1.133705	-0.449462	3.193379
C	0.828439	-3.874064	-0.519736
C	5.324854	-2.609144	1.388287
C	-3.973198	-2.361390	-1.079381
C	-7.279920	1.344368	-0.151197
C	-3.197646	0.807972	2.774238
Ir	-0.546467	0.469414	-0.417831
N	0.557427	-0.849935	-1.972043
H	-1.396162	1.379964	0.536980
Cl	-2.442474	0.487648	-2.297638
N	0.209860	2.212629	-1.519489
H	-3.340239	-2.912553	2.346071
H	-0.681975	-3.720665	2.611825
H	3.532514	-3.865862	-0.230254
H	3.785082	-0.977086	2.942928
H	-6.222441	-0.847039	-1.382079
H	-5.539997	1.870118	1.881178
H	1.839804	-0.115723	3.965595
H	0.275095	-0.926398	3.690688
H	0.750102	0.441727	2.673245
H	0.083453	-3.272957	-1.059016
H	0.280627	-4.653698	0.034664
H	1.465179	-4.377563	-1.260435

H	5.728633	-2.784946	0.380715
H	5.602710	-3.476728	2.009894
H	5.823742	-1.725708	1.811583
H	-2.930009	-2.250134	-1.406625
H	-4.601638	-2.482405	-1.971988
H	-4.037268	-3.290058	-0.489189
H	-8.023174	0.678674	-0.613617
H	-7.065283	2.149330	-0.873555
H	-7.734778	1.811414	0.734506
H	-3.716461	1.586127	3.350162
H	-2.225539	1.210274	2.450892
H	-2.988998	-0.037637	3.448351
H	0.591620	0.592906	0.625679
C	1.042172	3.142266	-1.220106
C	1.631144	3.409800	0.099724
O	-0.122910	2.243738	-2.841632
C	0.941201	3.249097	1.309803
C	1.574607	3.521664	2.519645
C	2.898038	3.965199	2.539098
C	3.581192	4.160274	1.338321
C	2.947918	3.894667	0.126550
O	-0.349793	-1.590287	-2.686646
C	1.754006	-1.115347	-2.346971
C	3.013704	-0.586484	-1.817023
C	3.123347	0.300419	-0.738649
C	4.375006	0.715434	-0.294433
C	5.535629	0.258593	-0.919277
C	5.439403	-0.622081	-1.997493
C	4.188564	-1.042194	-2.440166
H	1.368420	3.782186	-2.049517
H	-0.926222	1.672688	-2.898687
H	-0.095799	2.916565	1.297916
H	1.026555	3.391337	3.455585
H	3.392219	4.173863	3.490935
H	4.611990	4.521588	1.344286
H	3.484592	4.047079	-0.813316
H	-1.187734	-1.074946	-2.618294
H	1.849017	-1.837667	-3.168162
H	2.222256	0.645279	-0.234514
H	4.439755	1.397938	0.555443
H	6.515649	0.585387	-0.563672
H	6.342004	-0.986467	-2.493135
H	4.116229	-1.736815	-3.281219

[IrCl(H)$_2$(IMes)(*Z*-1$_{ax}$)(*E*-1$_{eq}$)]

0 1

N	1.762406	2.357750	0.336667
C	1.873719	1.000888	0.234235
N	3.182711	0.765942	0.553890

C	3.855869	1.943505	0.838579
C	2.961734	2.946045	0.701656
C	3.830442	-0.508428	0.662086
C	0.562849	3.114779	0.153839
C	0.291609	3.660738	-1.103242
C	-0.901378	4.373024	-1.257182
C	-1.795418	4.546595	-0.198520
C	-1.458645	4.024139	1.057004
C	-0.278378	3.310725	1.259143
C	4.599905	-0.972611	-0.412857
C	5.232509	-2.210681	-0.273344
C	5.119739	-2.969968	0.895511
C	4.365129	-2.455063	1.954205
C	3.715172	-1.221829	1.863144
C	0.096583	2.774640	2.613912
C	1.249751	3.472319	-2.245720
C	-3.106856	5.260263	-0.391778
C	4.734420	-0.163231	-1.672416
C	5.777274	-4.320264	1.001053
C	2.891134	-0.691169	3.002675
Ir	0.468312	-0.354057	-0.233648
N	-1.293058	0.950814	-1.213542
H	1.513885	-1.401885	0.246023
Cl	1.262443	-0.591623	-2.731921
N	-0.993789	-1.877635	-0.677173
H	4.906579	1.949071	1.114042
H	3.057235	4.020512	0.830131
H	-1.145732	4.784564	-2.240280
H	-2.142379	4.166942	1.898805
H	5.831845	-2.591999	-1.105144
H	4.279804	-3.028682	2.881718
H	-0.723515	2.910849	3.331671
H	0.984555	3.293947	3.009472
H	0.347366	1.703735	2.570161
H	1.543176	2.418158	-2.355326
H	2.174515	4.050245	-2.084963
H	0.801886	3.804871	-3.191514
H	-3.169332	5.732774	-1.382153
H	-3.255012	6.038815	0.372252
H	-3.948044	4.553850	-0.300337
H	3.747544	0.007380	-2.128839
H	5.366832	-0.683123	-2.404946
H	5.184078	0.822147	-1.472279
H	6.712835	-4.358742	0.424165
H	5.113642	-5.105121	0.601943
H	6.001869	-4.579301	2.045825
H	3.073786	-1.265391	3.921008
H	1.817819	-0.759286	2.762972
H	3.111071	0.367988	3.206178
H	-0.007465	-0.293955	1.255819

C	-1.923668	-2.266228	0.120123
C	-3.076404	-3.143096	-0.107365
O	-1.022388	-2.386762	-1.930728
C	-4.032911	-3.161401	0.925323
C	-5.186703	-3.929939	0.818689
C	-5.401174	-4.706148	-0.321336
C	-4.456493	-4.705050	-1.347710
C	-3.302134	-3.930374	-1.251190
O	-1.007887	1.338166	-2.490042
C	-2.520125	1.190950	-0.932496
C	-3.224487	0.899299	0.322908
C	-2.604825	0.787512	1.574013
C	-3.353352	0.494707	2.710163
C	-4.734641	0.311720	2.616691
C	-5.365029	0.433788	1.378382
C	-4.616731	0.735277	0.242587
H	-1.847133	-1.821194	1.113357
H	-0.275277	-1.940899	-2.391898
H	-3.866527	-2.550414	1.816530
H	-5.920349	-3.924418	1.627892
H	-6.304870	-5.313901	-0.408929
H	-4.619174	-5.314496	-2.239652
H	-2.573927	-3.936858	-2.058430
H	-0.178202	0.862310	-2.715055
H	-3.130150	1.615222	-1.741075
H	-1.529423	0.923400	1.649952
H	-2.852569	0.411087	3.677544
H	-5.319441	0.079428	3.509826
H	-6.445328	0.295868	1.295181
H	-5.114649	0.834513	-0.725432

***Z*-1**

0 1

C	-1.507616	1.423802	-0.000021
C	-0.186926	0.977526	-0.000074
C	0.095260	-0.401282	-0.000037
C	-0.983394	-1.305359	0.000101
C	-2.299478	-0.854634	0.000164
C	-2.565779	0.515422	0.000100
C	1.444478	-0.995856	-0.000074
N	2.615190	-0.478852	-0.000096
O	2.652760	0.885155	-0.000051
H	1.474920	-2.091325	-0.000124
H	0.628843	1.696220	-0.000161
H	-1.710001	2.497463	-0.000069
H	-3.597714	0.874254	0.000152
H	-3.120992	-1.574724	0.000260
H	-0.779475	-2.379550	0.000146
H	3.596741	1.090673	-0.000071

***E*-1**

0 1

C	-2.765655	0.266923	-0.000000
C	-1.863564	1.334894	0.000000
C	-0.493325	1.096181	0.000000
C	-0.003704	-0.220411	0.000000
C	-0.914706	-1.285159	0.000000
C	-2.288146	-1.042820	-0.000000
C	1.437976	-0.515829	0.000000
N	2.306941	0.417483	-0.000000
O	3.587752	-0.056518	-0.000000
H	-3.841229	0.458843	-0.000000
H	-2.234104	2.362716	0.000000
H	0.213161	1.928835	0.000000
H	-0.541797	-2.312897	0.000000
H	-2.987454	-1.882151	-0.000000
H	1.754443	-1.569432	0.000001
H	4.133122	0.741174	-0.000001

H_2O

0 1

O	0.000000	0.000000	0.120145
H	-0.000000	-0.754362	-0.480579
H	-0.000000	0.754362	-0.480579

Cl^-

-1 1

Cl	0.000000	0.000000	0.000000

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