Supplemental Information

Parahydrogen-induced hyperpolarization of a Zn(II) complex using NMR signal amplification by reversible exchange (SABRE)

Experimental section

General NMR procedure

TPA and $ZnCl_2$ were purchased from Sigma Aldrich and used without further purification. Methanol-d_4 (CD_3OD, 99.8 atom% D, Eurisotop) was used as received. ^{1}H NMR hyperpolarized signals were recorded with a Bruker Avance III NMR spectrometer operating at 300 MHz and referenced to the residual CH_3 peak of CD_3OD ($\delta = 3.31$ ppm). A custom-built instrument was used to generate *para*hydrogen from hydrogen gas (Hanmi gas, >99.9%). A mixture of the spin isomer forms—*ortho*hydrogen and *para*hydrogen—was passed through a heat exchanger packed with an FeO(OH) catalyst (Sigma Aldrich). This structure was filled with liquid nitrogen in a Dewar flask and produced approximately 50% *para*hydrogen. In each experiment, *para*hydrogen was passed continuously into each sample at a rate of 6 mL/min at 23 °C and 1 atm.

A GPS-1850D power supply (bench power supply, linear DC) with a Helmholtz coil was used to obtain the external magnetic fields. This system consists of two coils of insulated copper wire, one inside the other, resulting in a uniform magnetic field over a space measuring 200 mm in diameter and 190 mm in height. The magnetic field through the shielded coil was regulated by setting the current at 0–5 A. The magnetic field for each controlled current was measured using a Lakeshore Gaussmeter.

Different ratios of $ZnCl_2$ and TPA (0, 5, 10, 50, 80, and 100%, corresponding to 0.43, 0.87, 4.34, 6.95 and 8.68 mg, respectively) were prepared using a fixed concentration of TPA (0.0624 mmol), and the optimized concentration of the Ir catalyst (5%, ([Ir(IMes)(COD)Cl], 2 mg, 3.1×10^{-3} mmol)) was added to the sample. The samples with different $ZnCl_2$ concentrations and a fixed concentration of TPA (0.0624 mmol) in 600 μL of deuterated methanol were added to the NMR tube. Deuterated methanol (300 μL) was added to dissolve the Ir catalyst. *Para*hydrogen (ca. 50%) was bubbled through the solution for 20 min to cause activation. The samples were then moved to an NMR spectrometer and spectra were acquired in varying magnetic fields (1 min at ambient, 30, 50, 70, 90, 110, and 130 G) after polarization of the substrate. Each measurement was performed thrice, and the average enhancement factor and standard deviation were computed. The samples were allowed to fully relax in an ambient magnetic field for 3 min between measurements.

Single crystals of Zn(II)-TPA, suitable for X-ray diffraction analysis, were obtained using a concentrated methanol solution containing $ZnCl_2$ and TPA. A clear, light, colorless cubic-shaped crystal of Zn(II)-TPA ($0.5 \times 0.5 \times 0.4$ mm^3) was coated with Paratone-N oil, and the diffraction data were measured at 100 K using synchrotron radiation on the 2D beamline at the Pohang Accelerator Laboratory, Korea. Using the Olex2 software, the structure was solved by the ShelXT structure solution programusing intrinsic phasing and refined using the ShelXL refinement package[4] with least squares minimization. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were added at their ideal positions. A solvent mask was used to exclude disorders. CCDC 2245001 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Zn(II)-TPA complex

Tris(2-pyridylmethyl)amine) (10 mg) and $ZnCl_2$ (1 equiv) were dissolved in 1 mL of methanol at room temperature. The mixture was mixed for 10 min. Crystals of zinc complexes were formed after several days.

Crystallographic Analyses

Empirical formula	$C_{108}H_{108}Cl_6N_{24}Zn_6$
Formula weight	2347.10
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	15.458(3)
b/Å	19.827(4)
c/Å	22.137(4)
α/°	97.02(3)
β/°	106.20(3)
γ/°	99.82(3)
Volume/Å^3	6315(2)
Z	2
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	1.299
F(000)	2412.0
Crystal size/mm^3	0.5 × 0.5 × 0.5
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.948 to 60.8
Index ranges	$-21 \leq h \leq 21$, $-28 \leq k \leq 28$, $-31 \leq l \leq 31$
Reflections collected	61057
Independent reflections	34700 [R_{int} = 0.0431, R_{sigma} = 0.0671]
Data/restraints/parameters	34700/0/1297
Goodness-of-fit on F^2	1.179
Final R indexes [I>=2σ (I)]	R_1 = 0.0614, wR_2 = 0.1897
Final R indexes [all data]	R_1 = 0.0916, wR_2 = 0.2047
Largest diff. peak/hole / e Å^{-3}	0.99/-1.73

Table S1. Crystal data and structure Zn(II)-TPA complex.

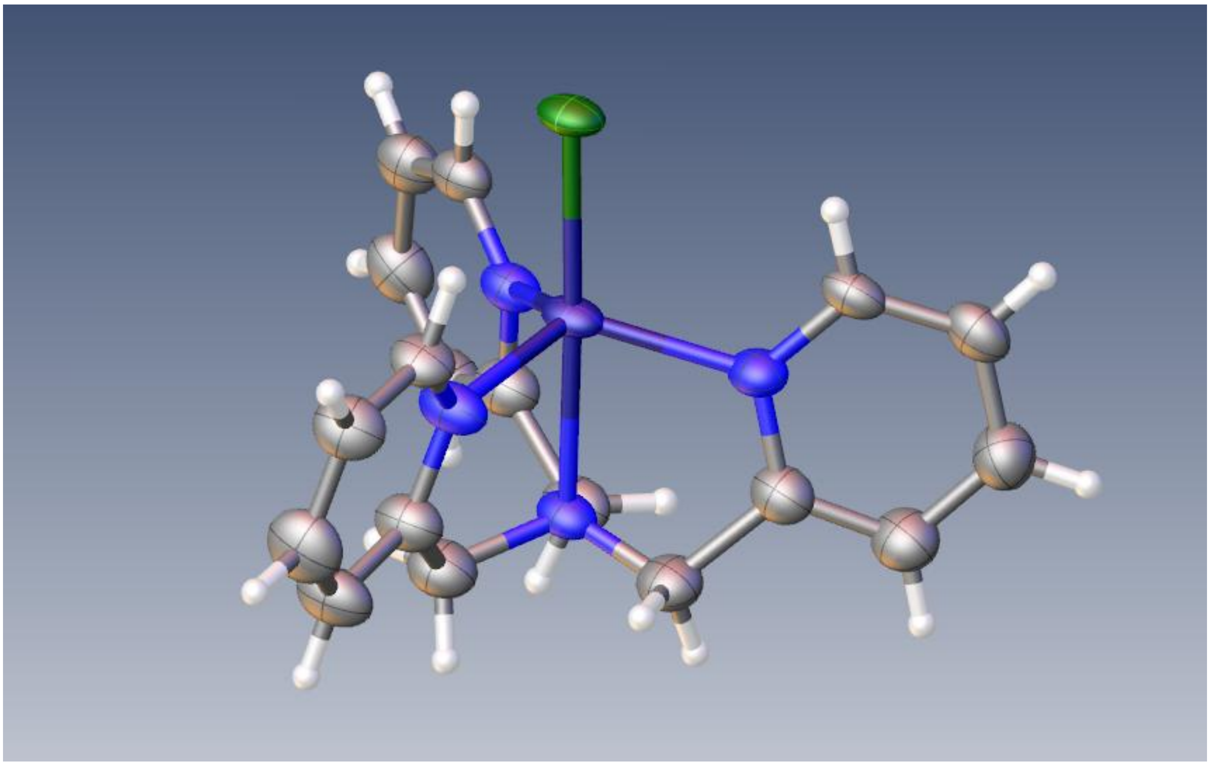
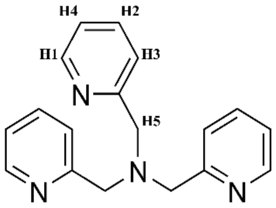


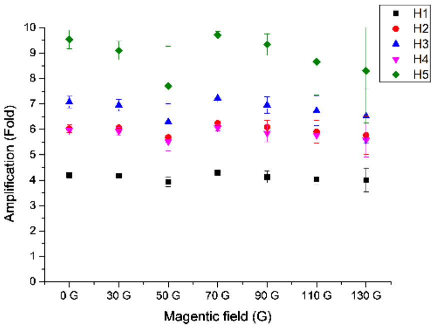
Figure S1. Crystal structure of Zn(II)-TPA complex.

Zn(II)-TPA complex Calculation

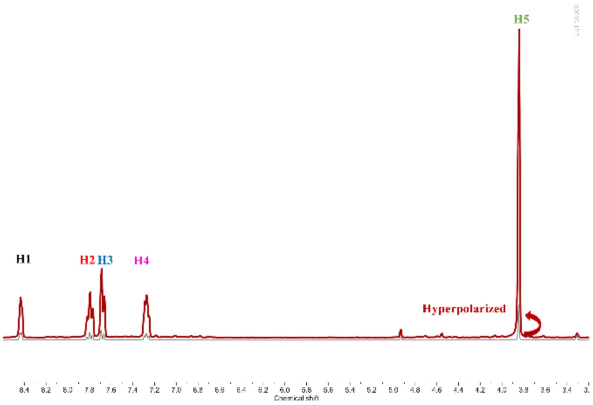
All geometry optimizations and frequency calculations were carried out using the M06 functional. A mixed basis set was employed: the 6-31G(d,p) basis set was used for all main group elements (C, H, N, O, etc.), while the LANL2DZ basis set and effective core potential (ECP) were applied to the Zn atom. All calculations were performed without symmetry constraints.

SABRE experiment





a)



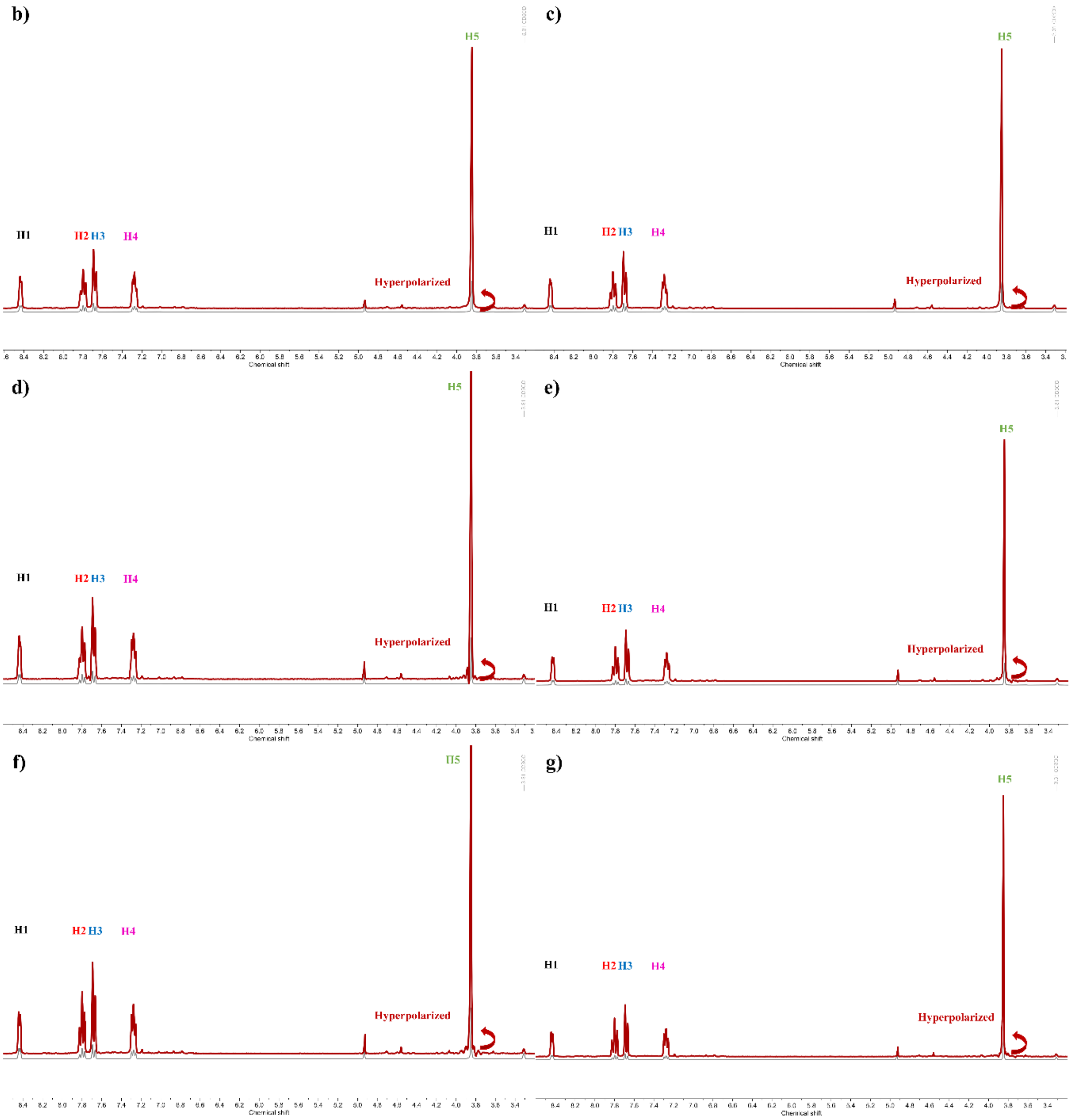
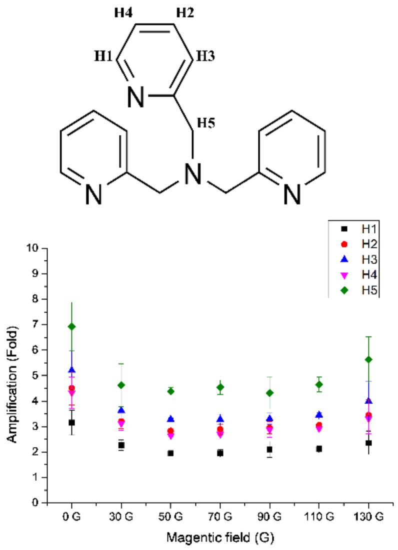
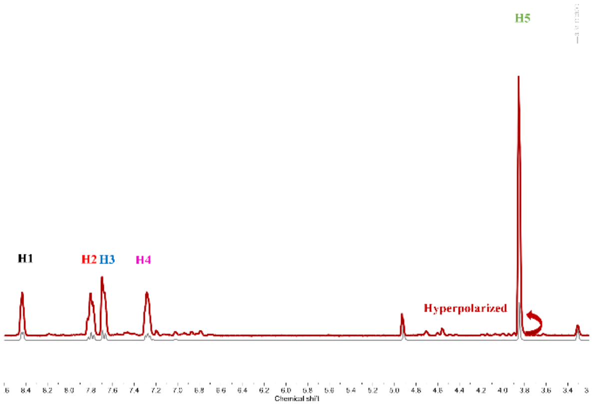


Figure S2. NMR amplification number of each labeled proton of TPA (0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


H4
H2
H1
H3
N
H5
N
N
N
H1
H2
H3
H4
H5
Amplification (Fold)
0
1
2
3
4
5
6
7
8
9
10
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)

a)


H5
H1
H2
H3
H4
Hyperpolarized
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
Chemical shift

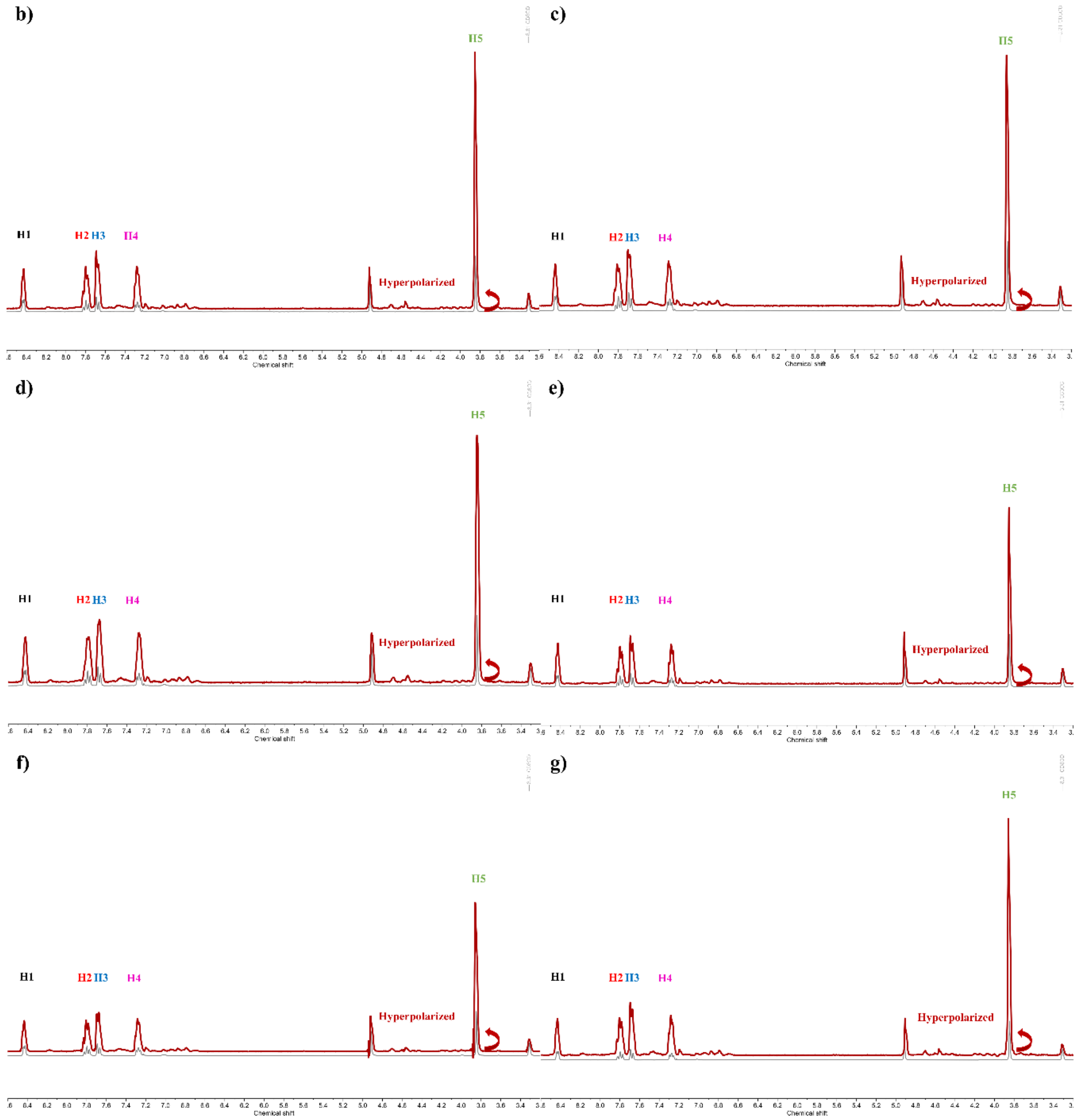
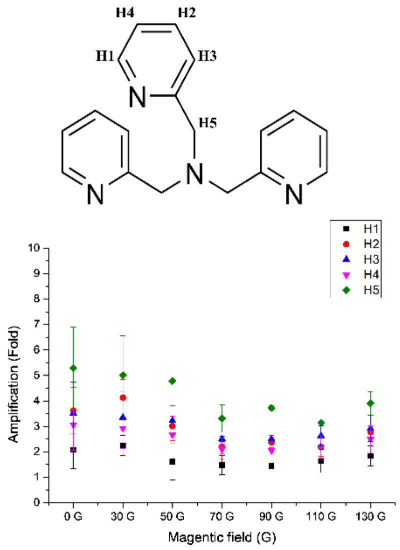
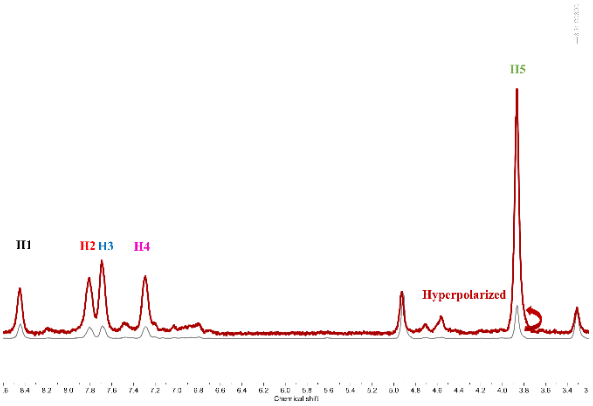


Figure S3. NMR amplification number of each labeled proton of TPA (0.0314 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of TPA in the different magnetic fields. A) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


H4
H2
H1
H3
N
H5
N
N
N
H1
H2
H3
H4
H5
Amplification (Fold)
10
9
8
7
6
5
4
3
2
1
0
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)

a)


H5
H1
H2
H3
H4
Hyperpolarized
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
Chemical shift

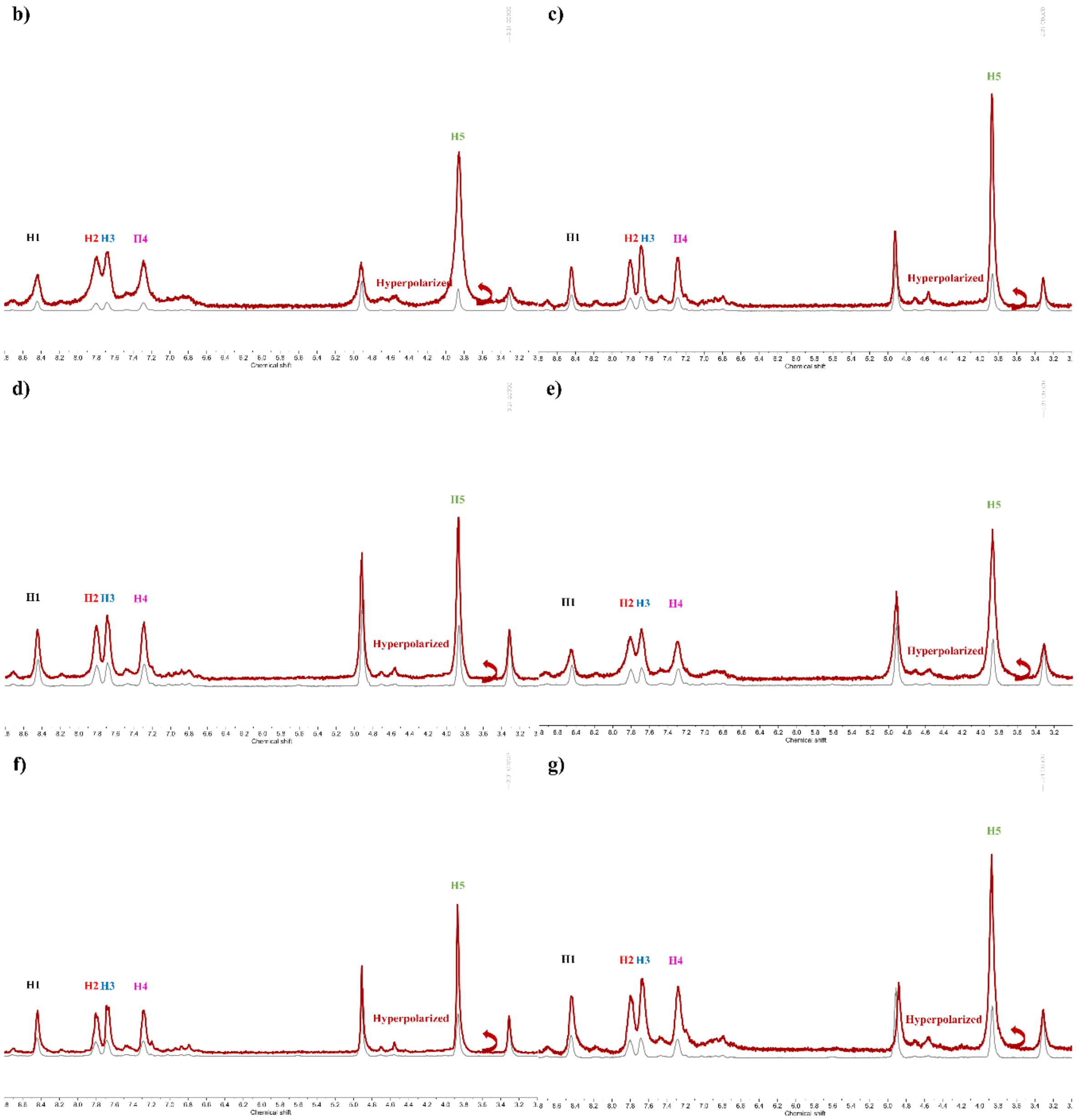
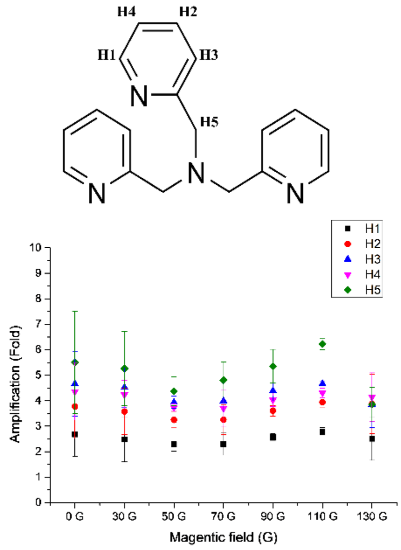
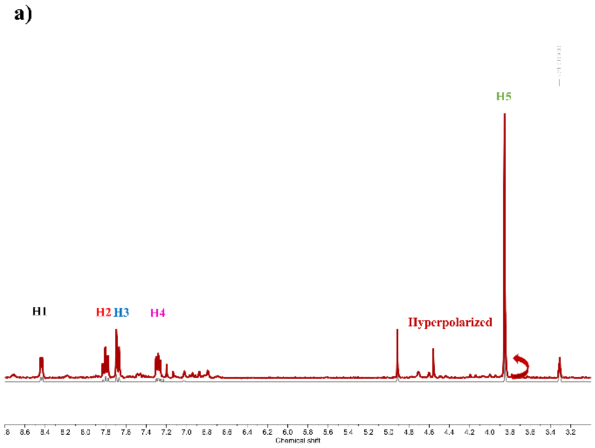


Figure S4. NMR amplification number of each labeled proton of TPA (0.0156 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of TPA in the different magnetic fields. A) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


H4
H2
H1
H3
N
H5
N
N
N
H1
H2
H3
H4
H5
Amplification (Fold)
10
9
8
7
6
5
4
3
2
1
0
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)


a)
H5
H1
H2
H3
H4
Hyperpolarized
8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
Chemical shift

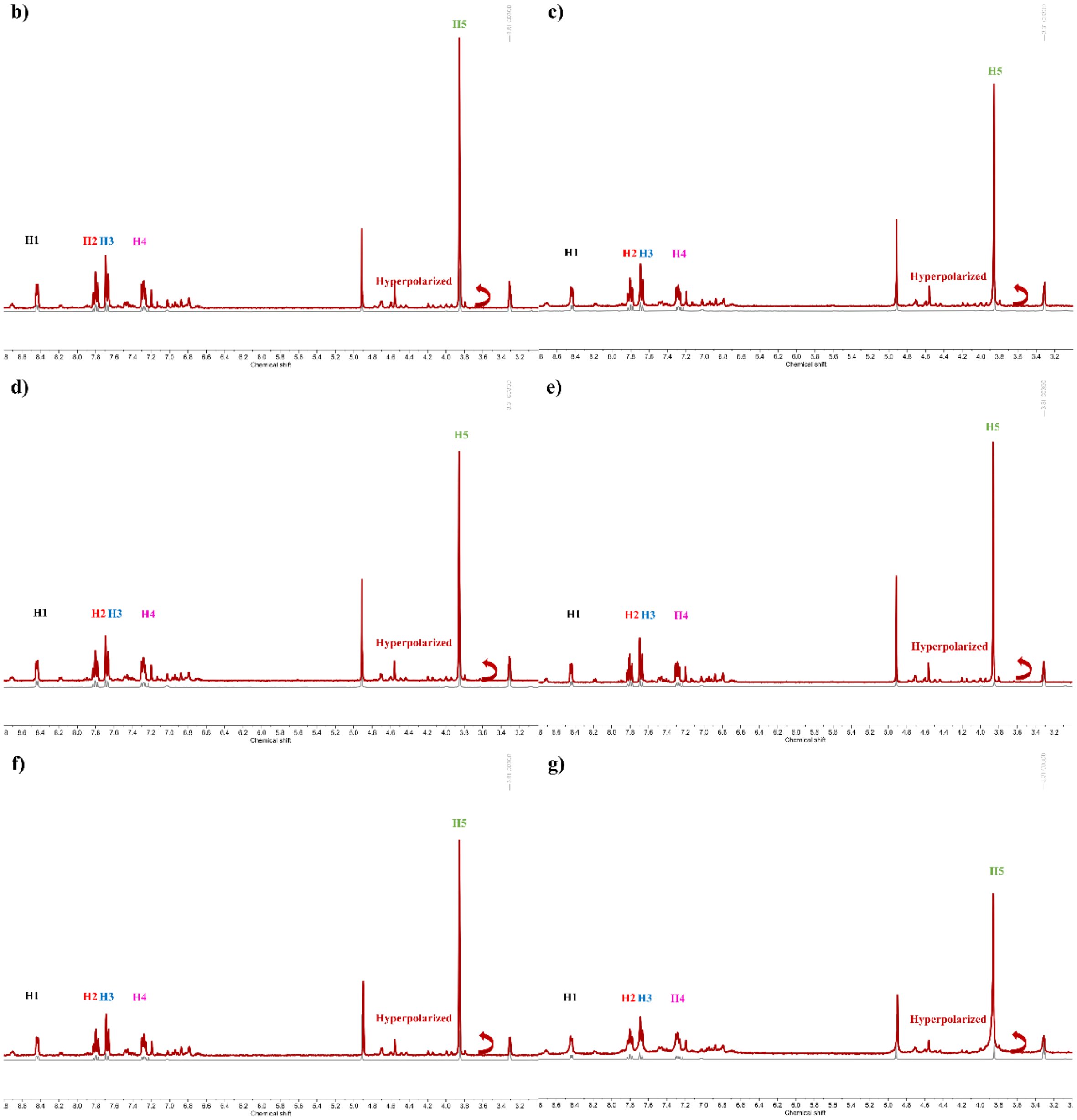


Figure S5. NMR amplification number of each labeled proton of TPA (0.0105 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of TPA in the different magnetic fields. A) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.

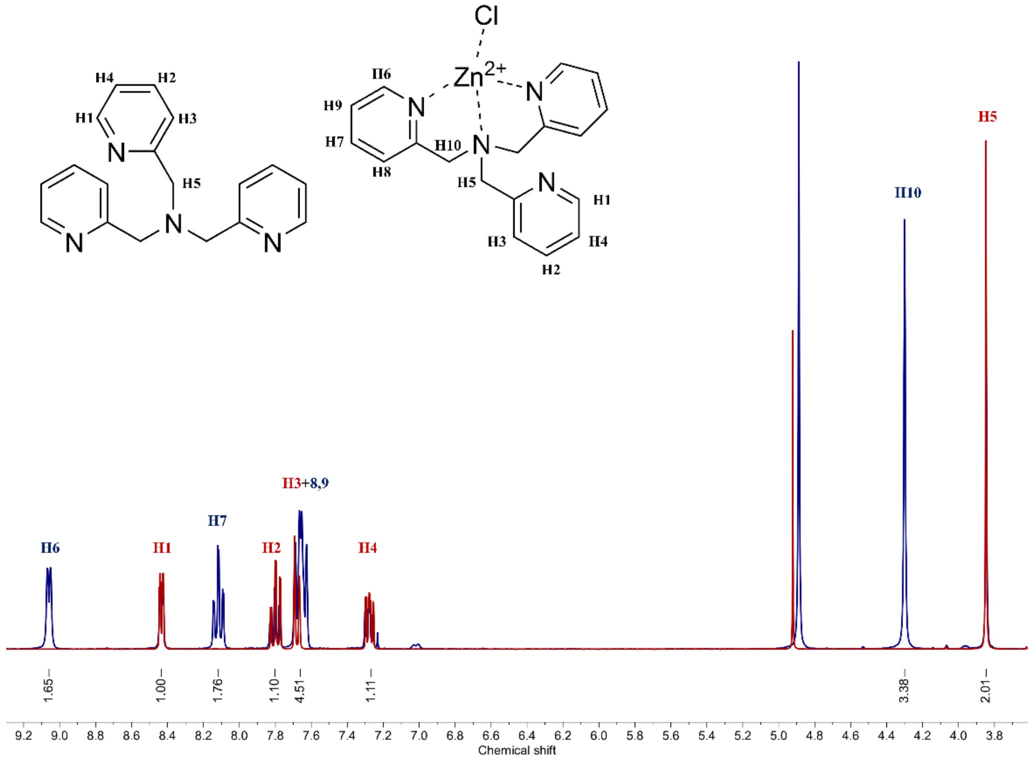


Figure S6. Stacked ^{1}H NMR spectrum of TPA (Red) and Zn(II)-TPA (Blue) structure.

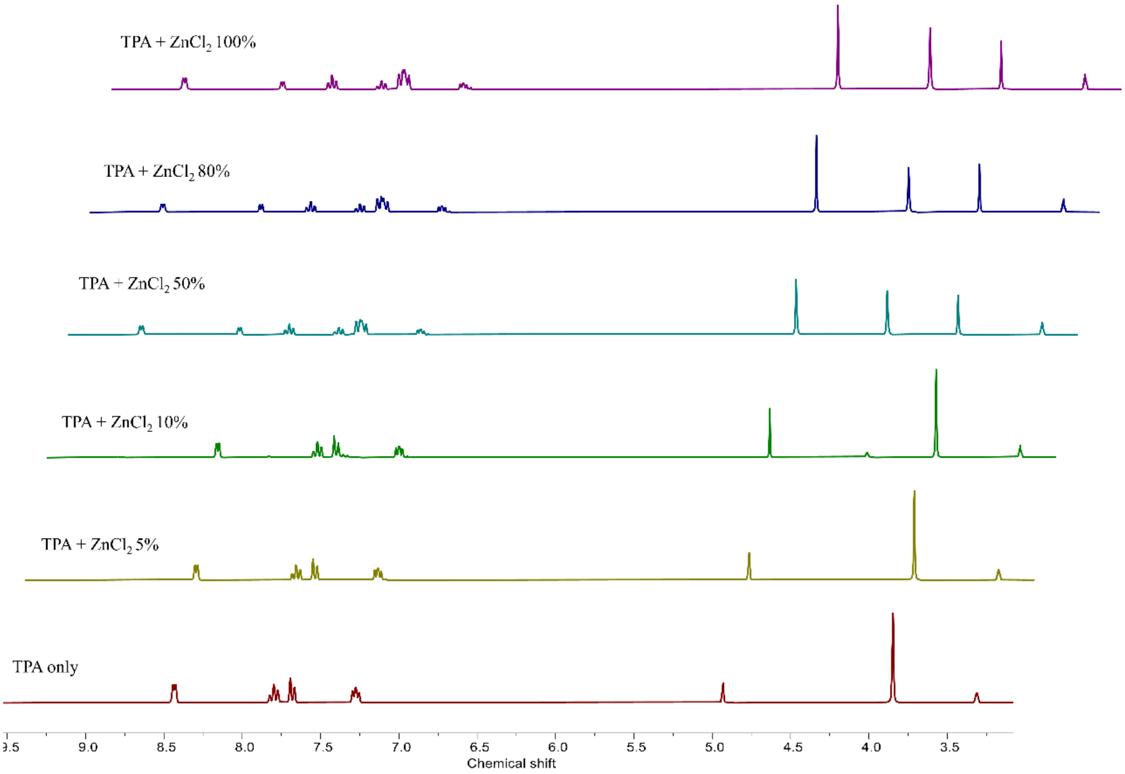
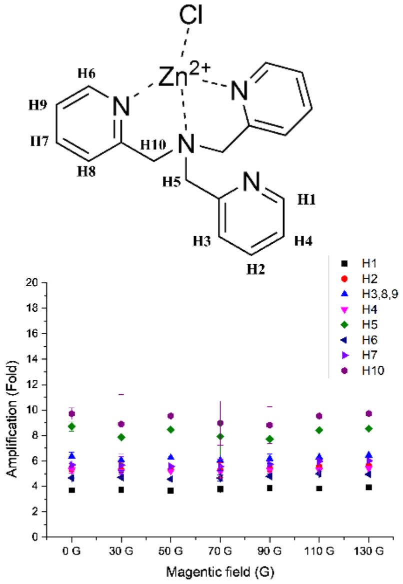
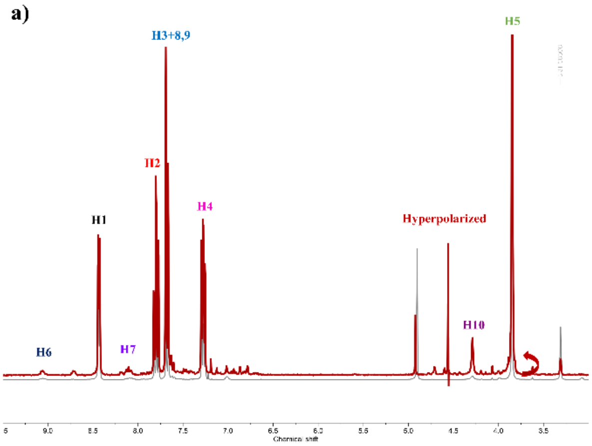


Figure S7. Stacked ^{1}H NMR spectrum of different concentrations of TPA and Zn(II)-TPA.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H10
H8
H5
H1
H3
H4
H2
H1
H2
H3,8,9
H4
H5
H6
H7
H10
Amplification (Fold)
0
2
4
6
8
10
12
14
16
18
20
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)

a)


H5
H3+8,9
H2
H1
H4
Hyperpolarized
H10
H6
H7
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical shift

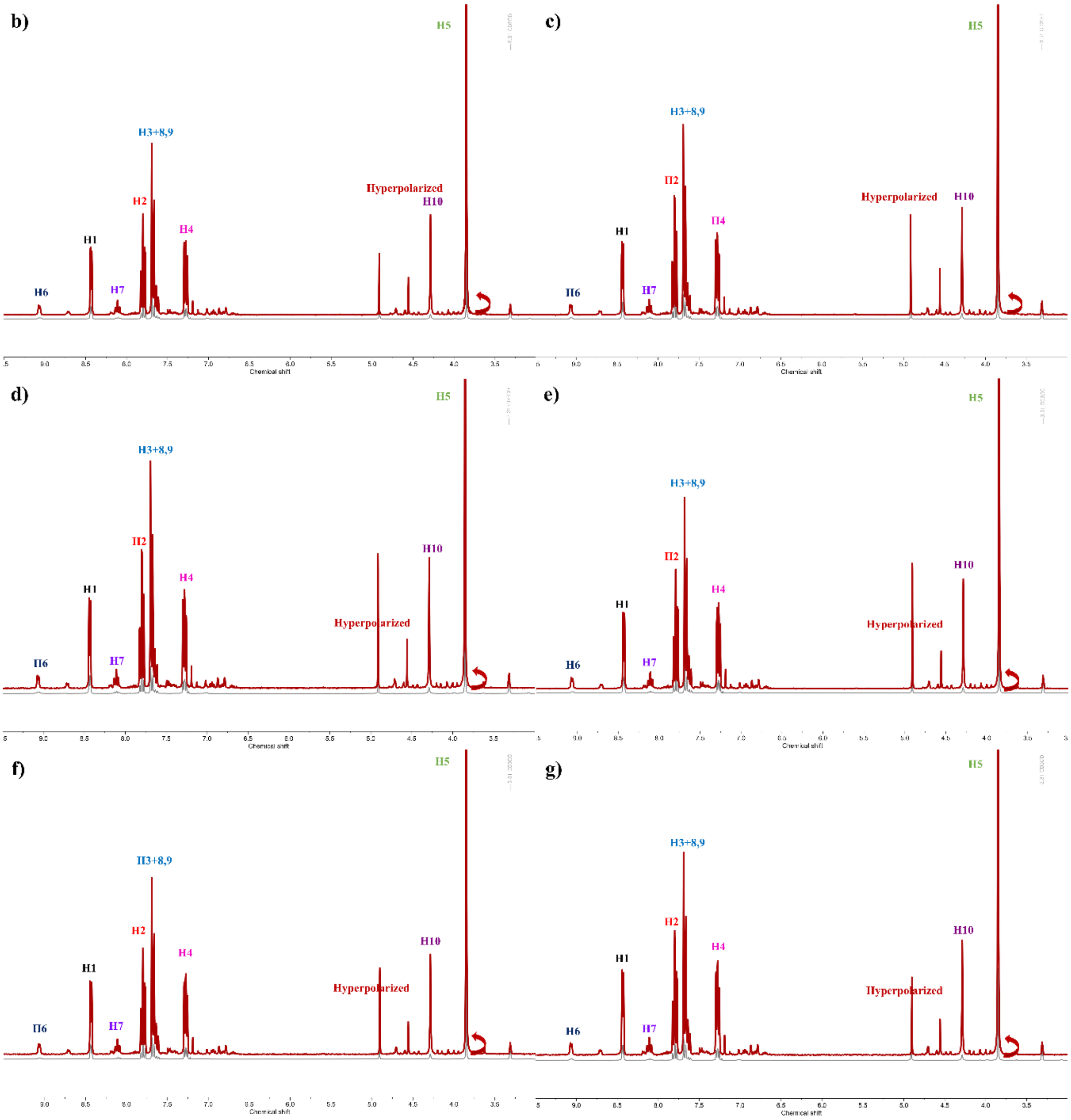
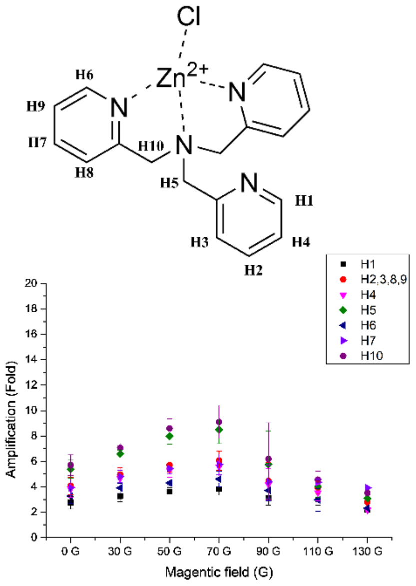
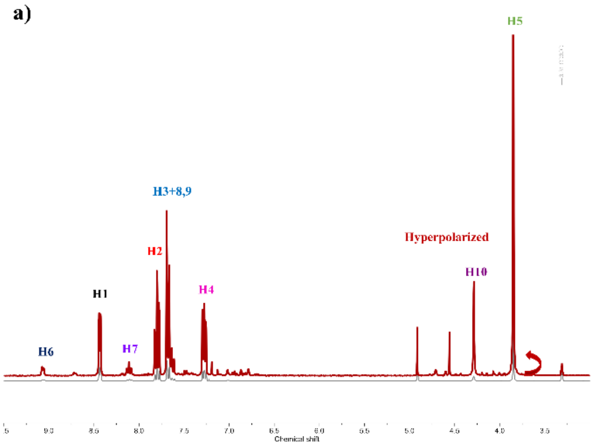


Figure S8. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.00312 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. A) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H10
H8
H5
H1
H3
H4
H2
H1
H2,3,8,9
H4
H5
H6
H7
H10
20
18
16
14
12
10
8
6
4
2
0
Amplification (Fold)
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)

a)


H5
H3+8,9
Hyperpolarized
H2
H10
H1
H4
H6
H7
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical shift

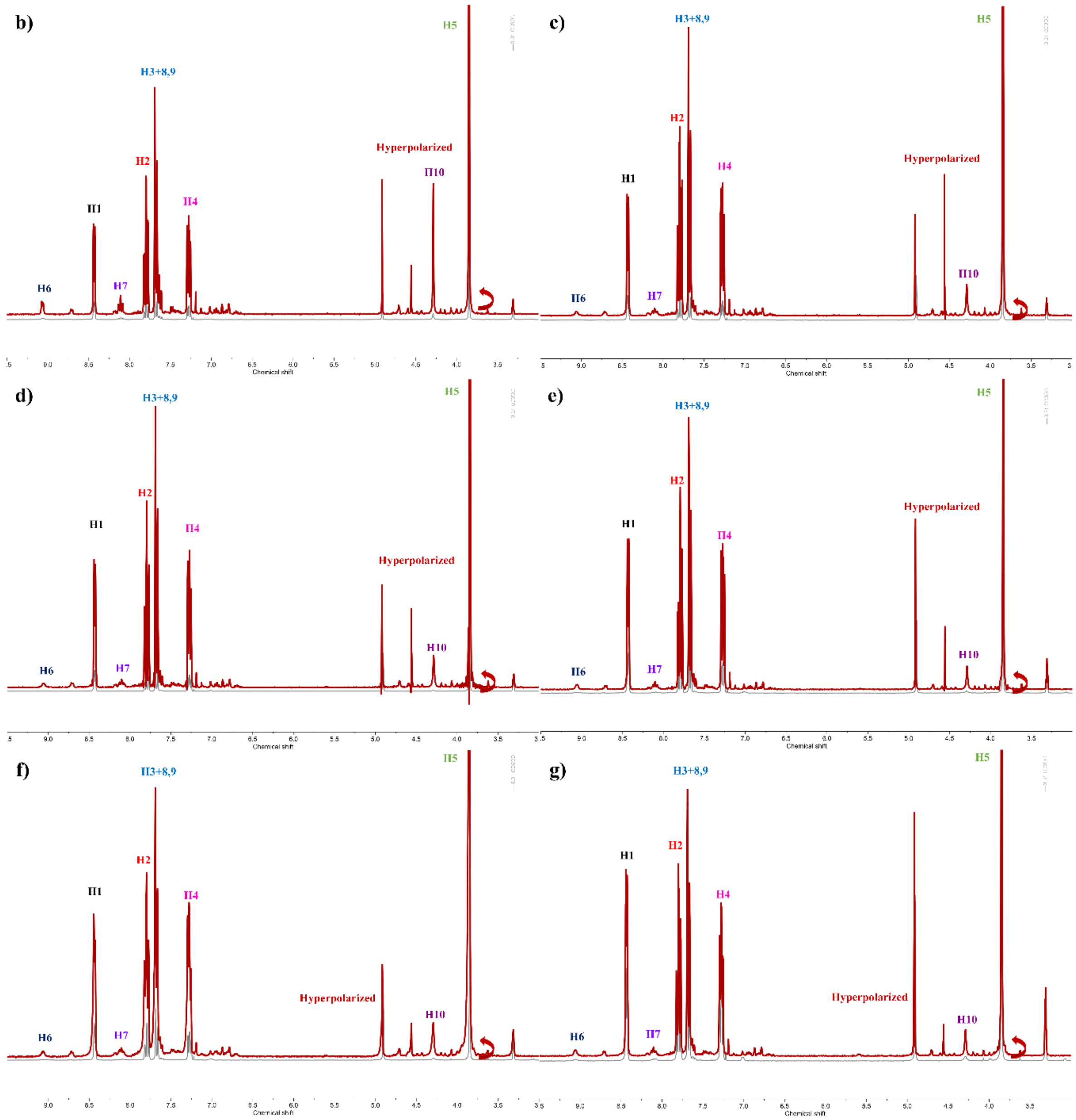
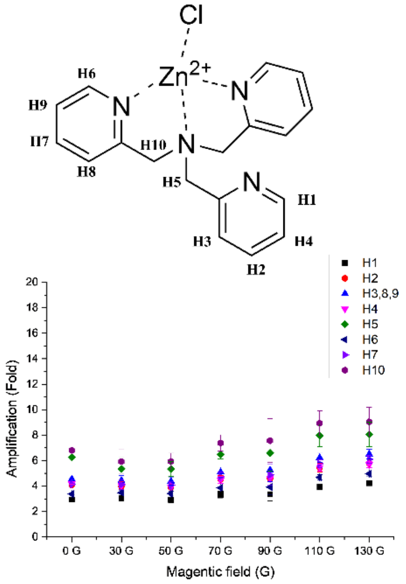
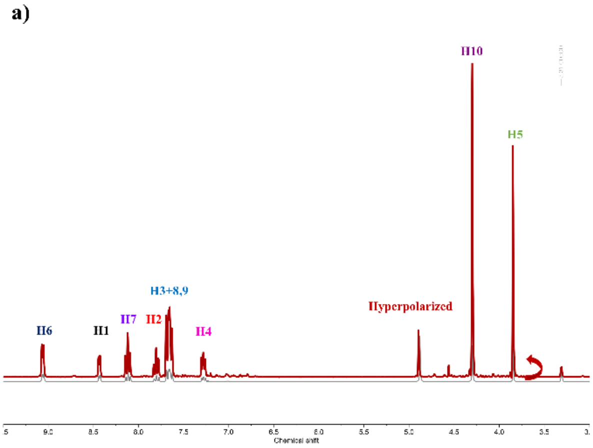


Figure S9. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.00624 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H10
H8
H5
H1
H3
H4
H2
H1
H2
H3,8,9
H4
H5
H6
H7
H10
Amplification (Fold)
0
2
4
6
8
10
12
14
16
18
20
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)


a)
H10
H5
H3+8,9
Hyperpolarized
H6
H1
H7
H2
H4
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.
Chemical shift

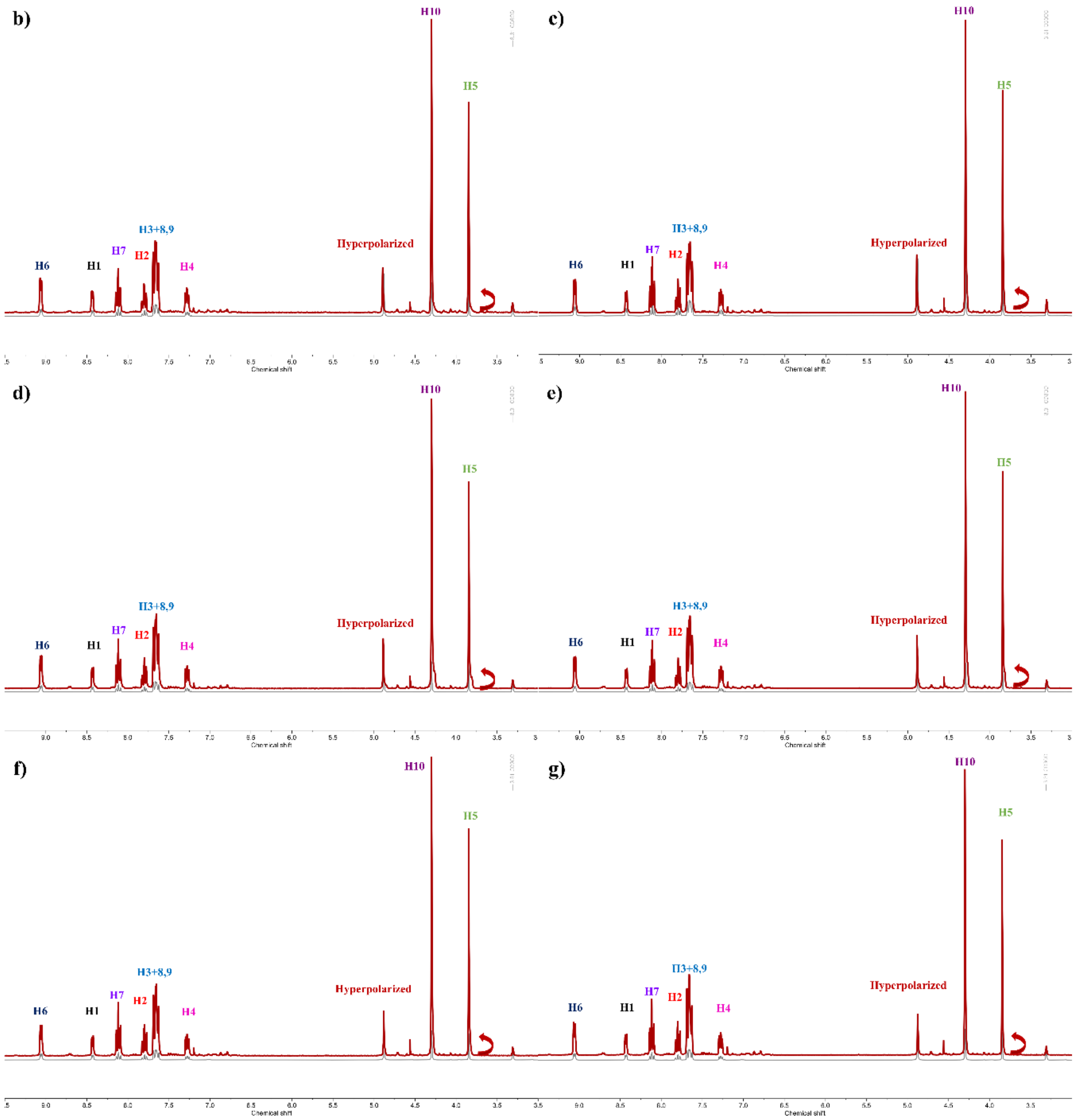
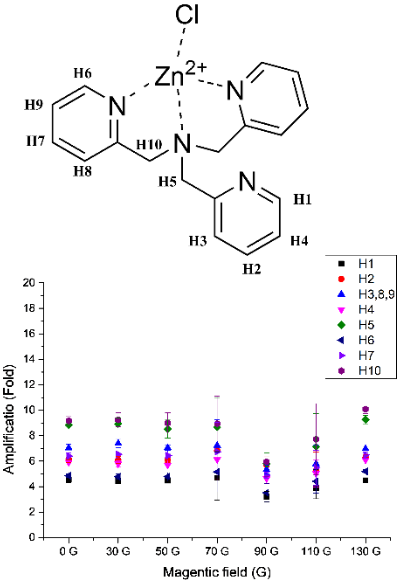
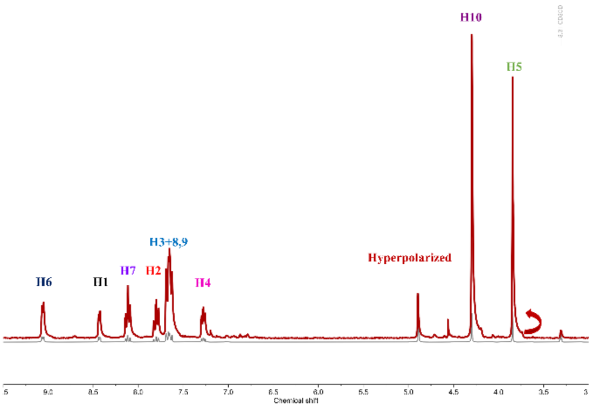


Figure 10. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.0312 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H8
H10
H5
H1
H3
H4
H2
Amplificatio (Fold)
Magentic field (G)
0 G
30 G
50 G
70 G
90 G
110 G
130 G
0
2
4
6
8
10
12
14
16
18
20
H1
H2
H3,8,9
H4
H5
H6
H7
H10

a)


H10
H5
3.3 CD3OD
H3+8,9
H6
H1
H7
H2
H4
Hyperpolarized
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3
Chemical shift

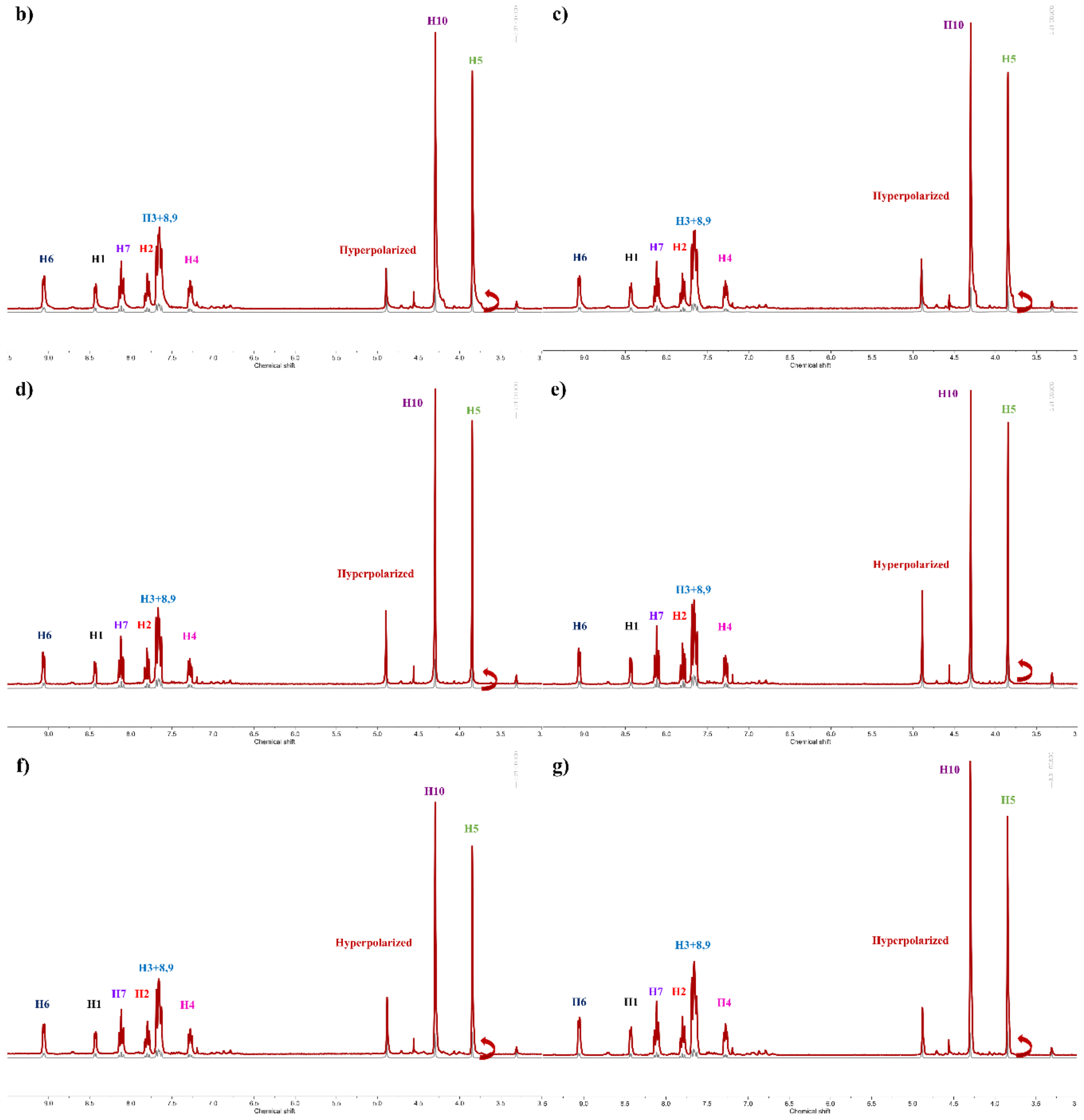
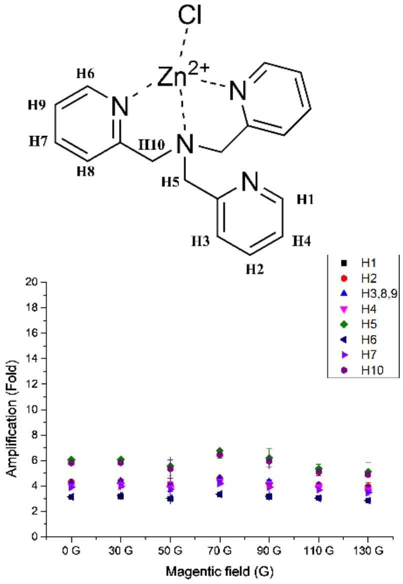
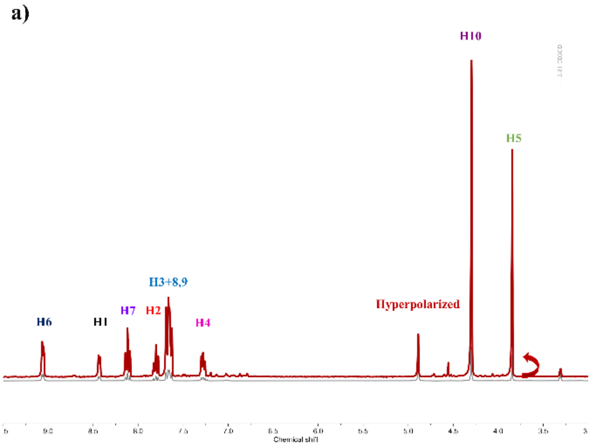


Figure S11. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.0499 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H8
H10
H5
H1
H3
H4
H2
Amplification (Fold)
0
2
4
6
8
10
12
14
16
18
20
0 G
30 G
50 G
70 G
90 G
110 G
130 G
Magentic field (G)
H1
H2
H3,8,9
H4
H5
H6
H7
H10


a)
H10
H5
H3+8,9
H6
H1
H7
H2
H4
Hyperpolarized
5
9.0
8.5
8.0
7.5
7.0
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5.5
5.0
4.5
4.0
3.5
3
Chemical shift

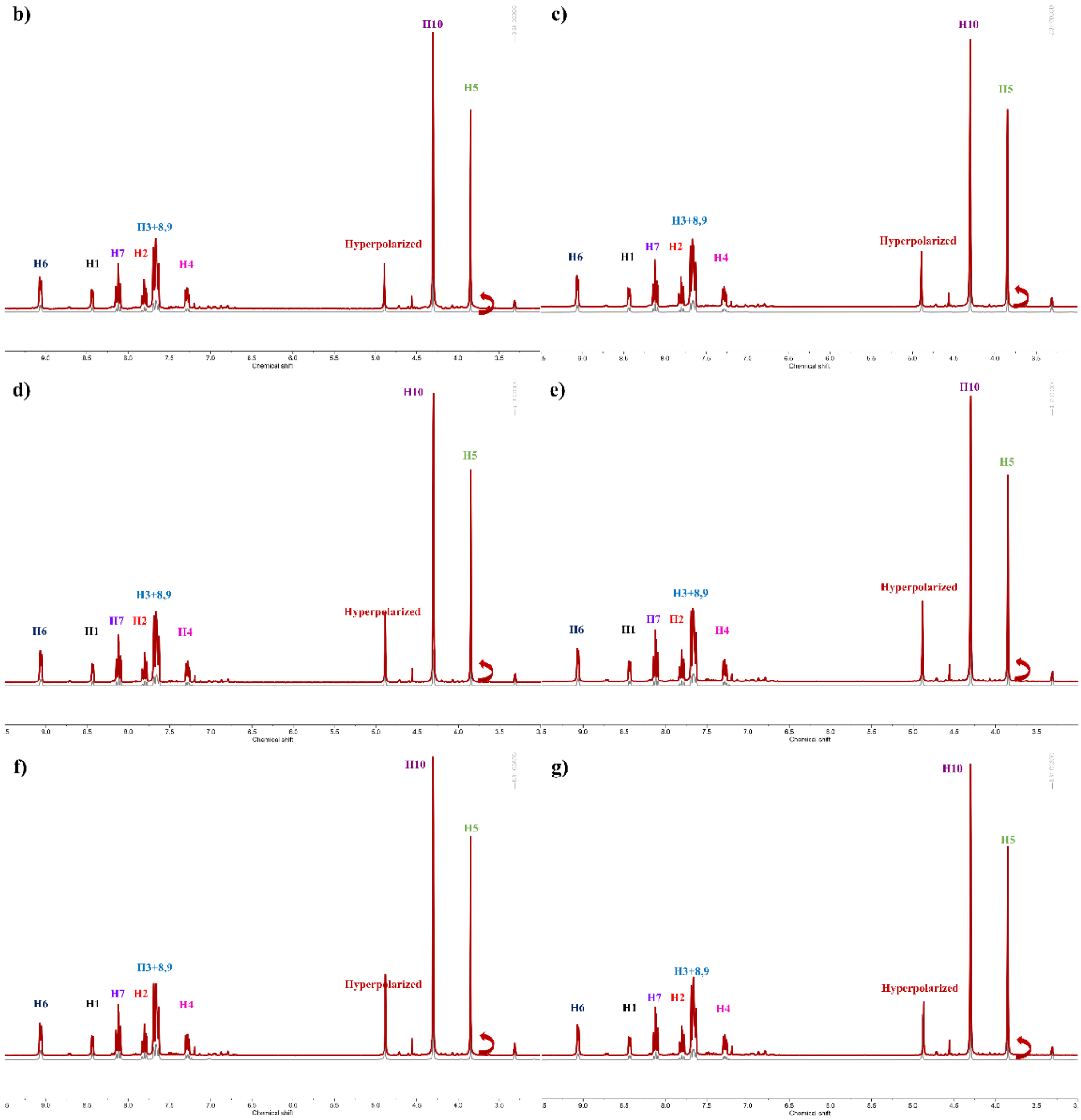


Figure S12. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.0624 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G, g) 130 G.

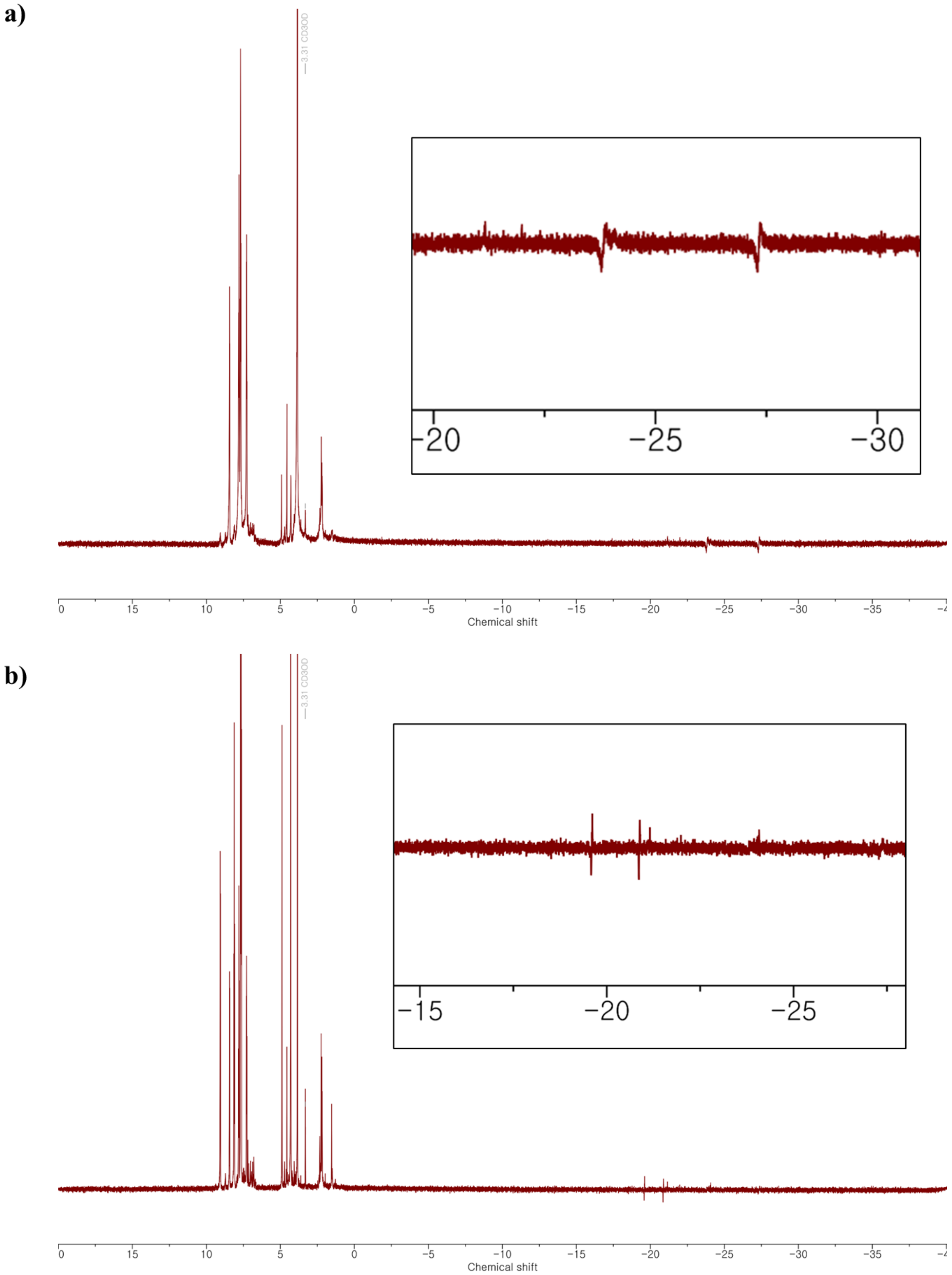
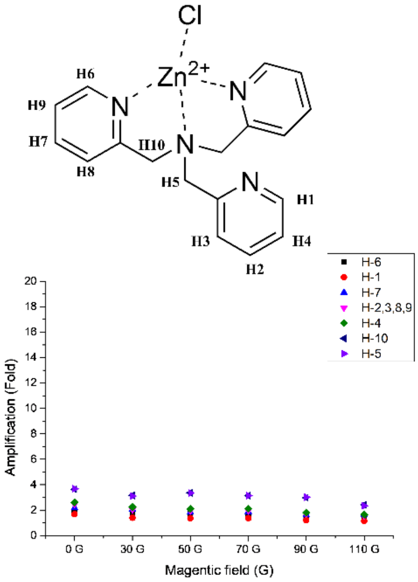
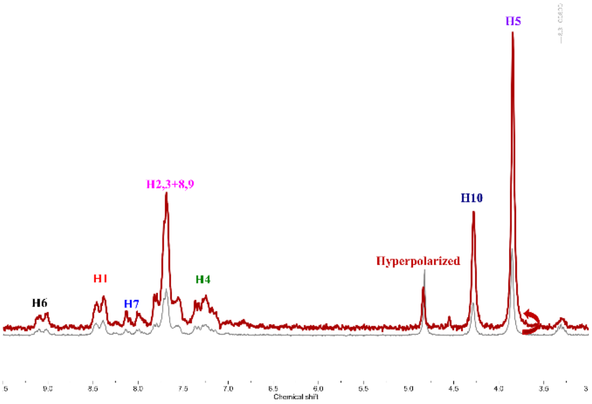


Figure S13. Full 1H spectrum of hyperpolarized Zn(II)-TPA in different concentrations of Zn(II) at Earth Field. a) Zn(II) : TPA = 0.00312 mmol : 0.0624 mmol (Same main hydride signals from TPA only) b) Zn(II) : TPA = 0.0624 mmol : 0.0624 mmol. The hydride region (δ -15 to -25 ppm) shows characteristic signals of the active SABRE catalyst species. Note the distinct patterns between the low Zn(II) concentration (a) and equimolar (b) samples, indicating different iridium species formation dependent on Zn(II) coordination state.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H8
H10
H5
H1
H3
H4
H2
H-6
H-1
H-7
H-2,3,8,9
H-4
H-10
H-5
20
18
18
14
12
10
8
6
4
2
0
Amplification (Fold)
0 G
30 G
50 G
70 G
90 G
110 G
Magentic field (G)

a)


H5
H10
H2,3+8,9
H1
H7
H6
H4
Hyperpolarized
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3
Chemical shift

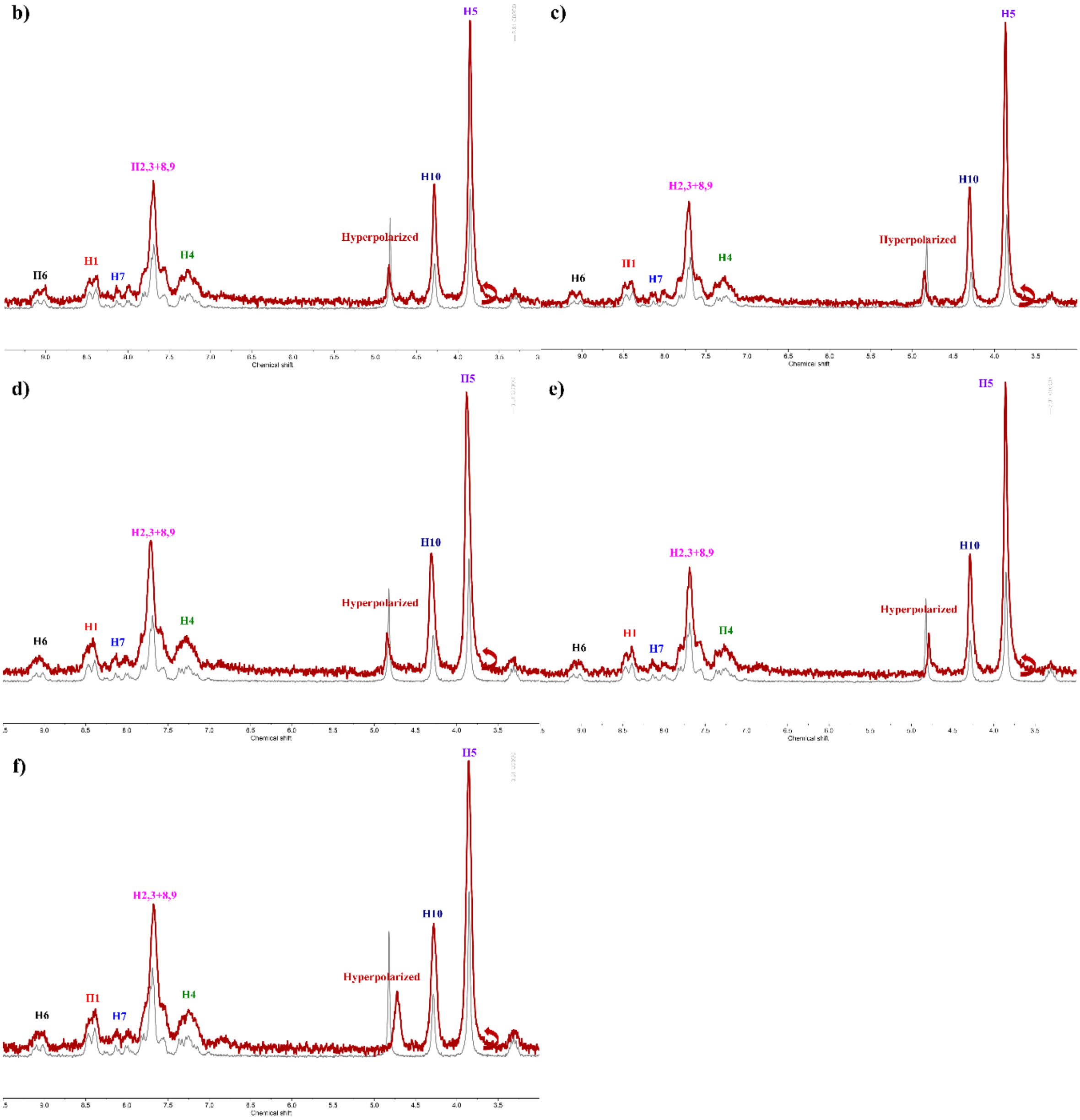
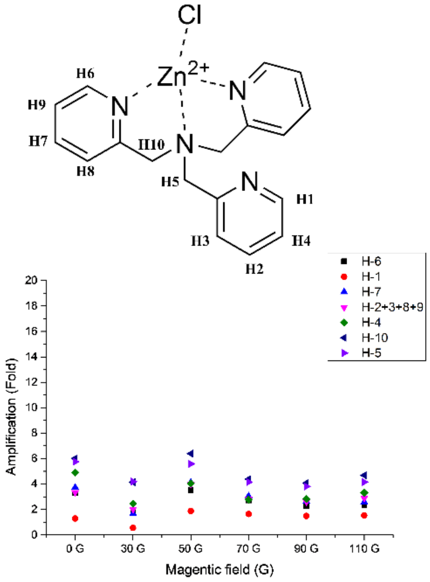
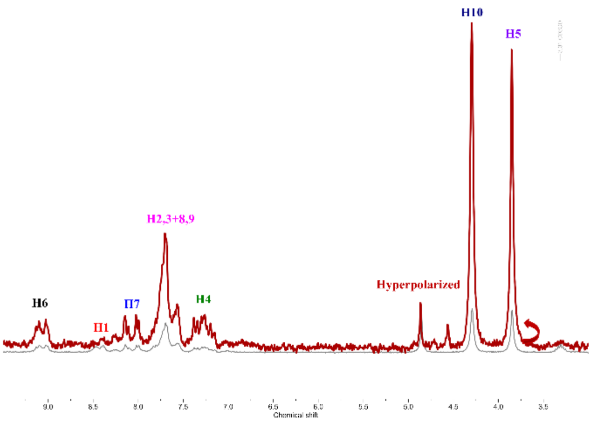


Figure S14. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.0187 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization measured at 1.4 T. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G.


Cl
Zn2+
N
N
N
N
H6
H9
H7
H8
H10
H5
H1
H4
H3
H2
Amplification (Fold)
Magentic field (G)
0 G
30 G
50 G
70 G
90 G
110 G
0
2
4
6
8
10
12
14
16
18
20
H-6
H-1
H-7
H-2+3+8+9
H-4
H-10
H-5

a)


H10
H5
H2,3+8,9
H6
H1
H7
H4
Hyperpolarized
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical shift

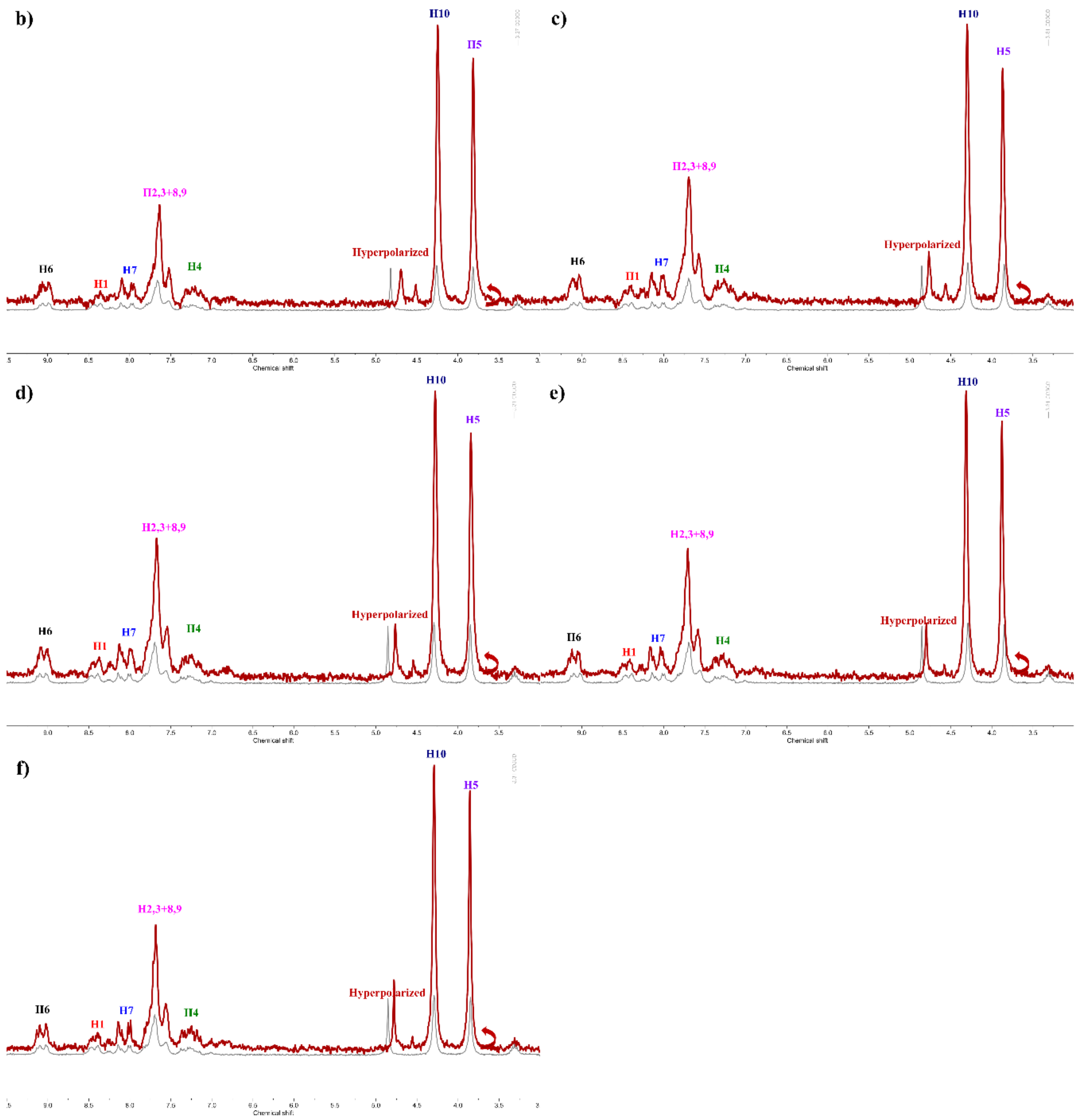


Figure S15. NMR amplification number of each labeled proton Zn(II)-TPA(Zn(II) : TPA = 0.0312 mmol : 0.0624 mmol) versus the utilized magnetic field for hyperpolarization measured at 1.4 T. Comparison between the normal (grey) and hyperpolarized (red) ^{1}H spectra of Zn(II)-TPA in the different magnetic fields. a) Earth field, b) 30 G, c) 50 G, d) 70 G, e) 90 G, f) 110 G.

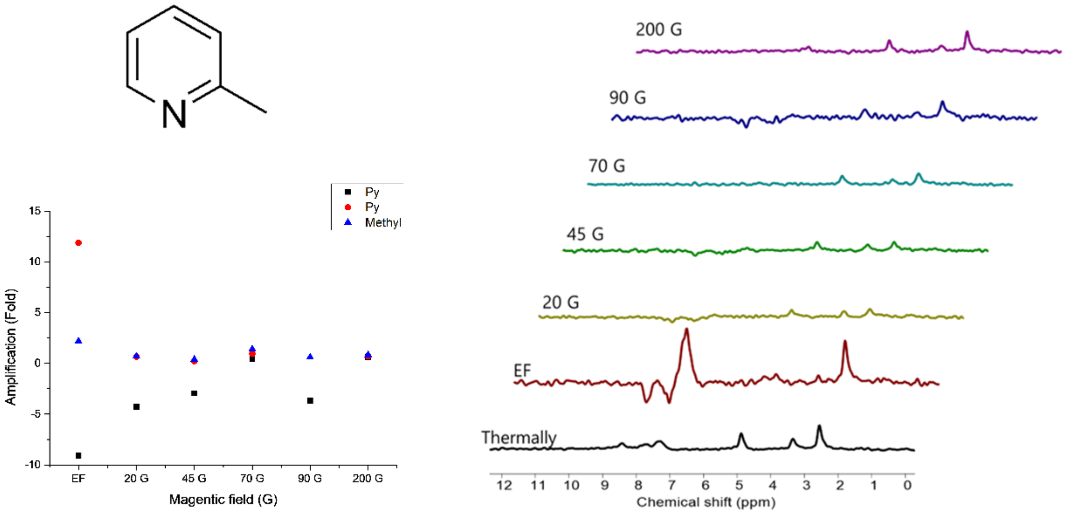


Figure S16. NMR amplification number of each labeled proton 2-methylpyridine versus the utilized magnetic field for hyperpolarization measured at 1.4 T. Stacked ^{1}H NMR spectrum of the hyperpolarized region of 2-methylpyridine in the different magnetic fields.

T_1 relaxation time

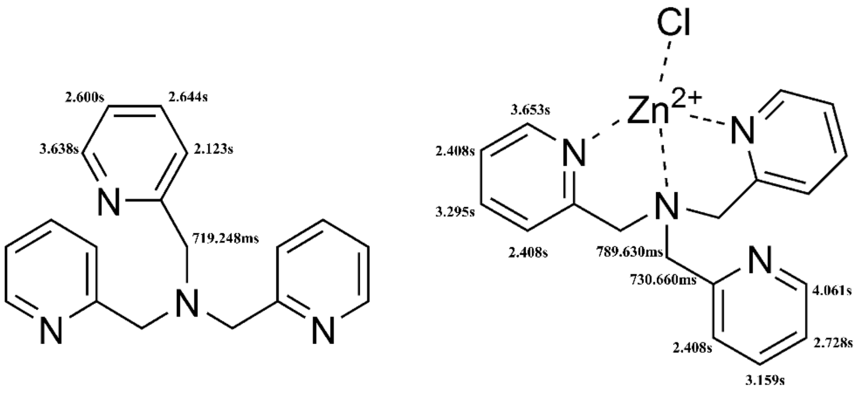


Figure S17. T_1 relaxation time at 298 K measured at 7.0 T.

Optimized structure of Zn(II)-TPA in Methanol

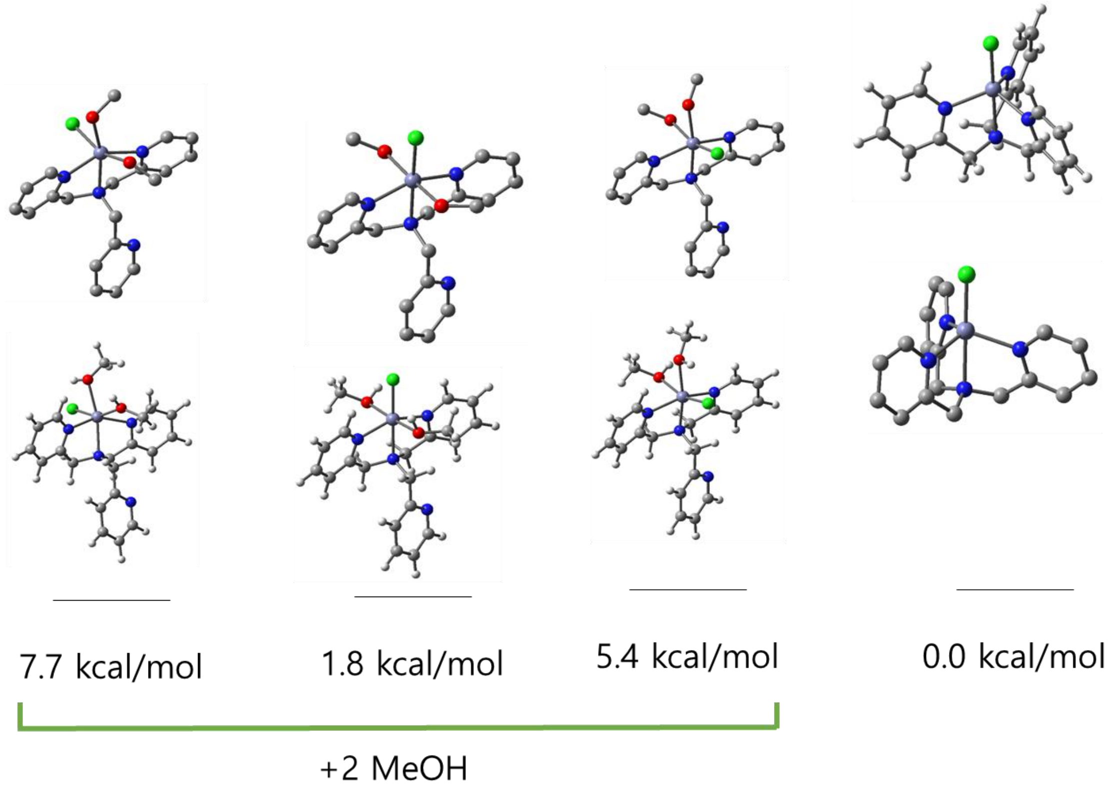


Figure S18. DFT-optimized structures of Zn(II)-TPA complex in methanol environment showing energetically favorable coordination geometries.

Optimized structure of Zn(II)-TPA in water

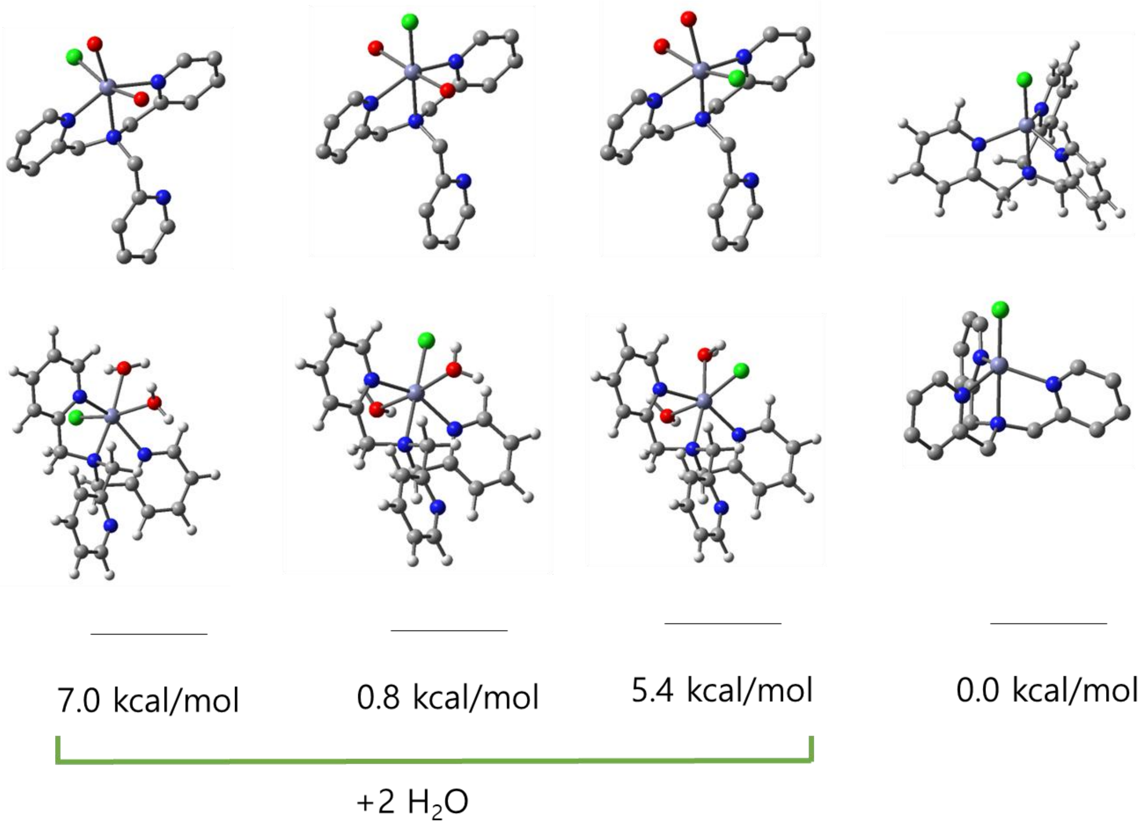


Figure S19. DFT-optimized structures of Zn(II)-TPA complex in water environment showing energetically favorable coordination geometries.

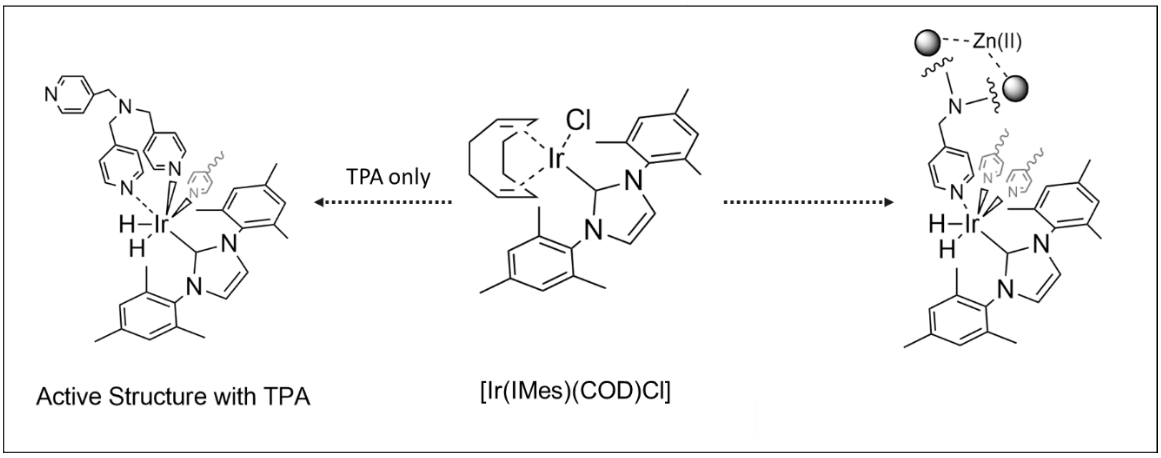


Figure S20. Active catalyst structures formed with both TPA and Zn(II)-TPA