Supporting Information

Stereochemistry of a $[Zn(L)_2]^{2+}$ complex: Structural determination by solution-state NMR spectroscopy, X-ray crystallography and DFT calculations.

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Contents

Possible isomers of [M(A-B-C)$_2$] complexes

Enumeration of different isomers of [M(A-B-C)$_2$] complexes start from three isomers of [M(A-B-A)$_2$] complexes [Ref. 3 in manuscript]. The *cis-fac* isomer can exist in two enantiomeric configurations Δ and Λ:

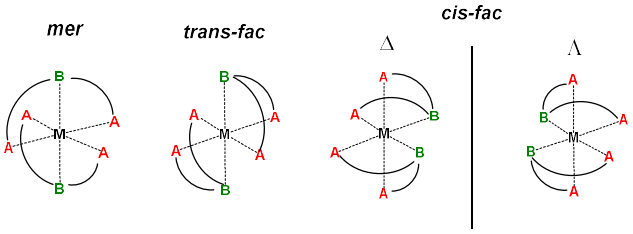


Figure S1. Different isomers of [M(A-B-A)$_2$] complexes.

One A coordinating atom on each of two coordination ligands can be replaced with C coordinating atom leading to four modifications for each [M(A-B-A)$_2$] isomer. It is sufficient to consider only one enantiomer of the *cis-fac* [M(A-B-A)$_2$] isomer; the other modificated enantiomers are obtained by mirror symmetry of the considered modificated enantiomers.

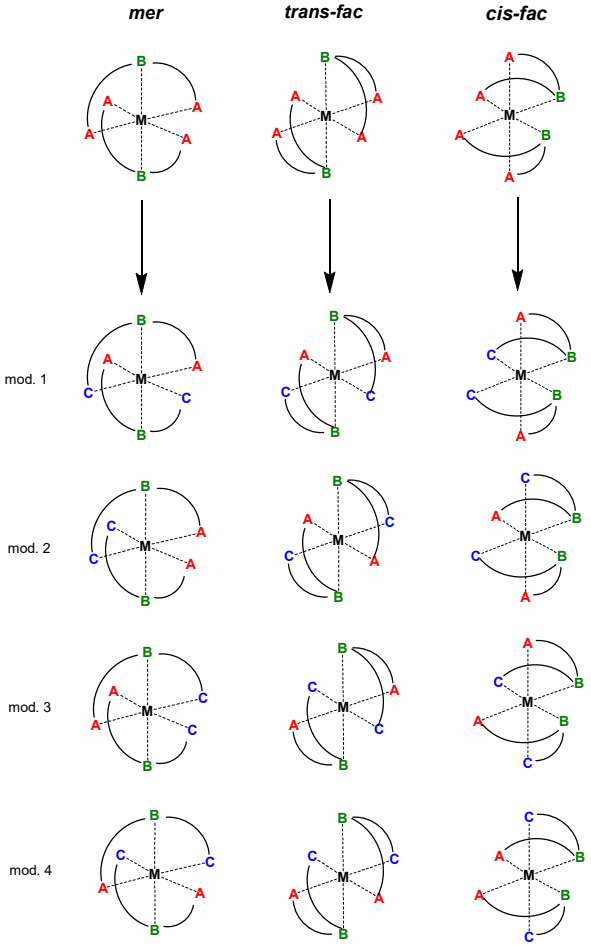


Figure S2. Modifications of [M(A-B-A)$_2$] complexes obtained by replacing one A coordinating atom on each ligand by C coordinating atom as all possible forms of the [M(A-B-C)$_2$] complexes

There are several equalities among 12 modifications given in Figure S2. Identical structures, i.e. those that can be converted one into another by proper rotations are given in Figure S3:

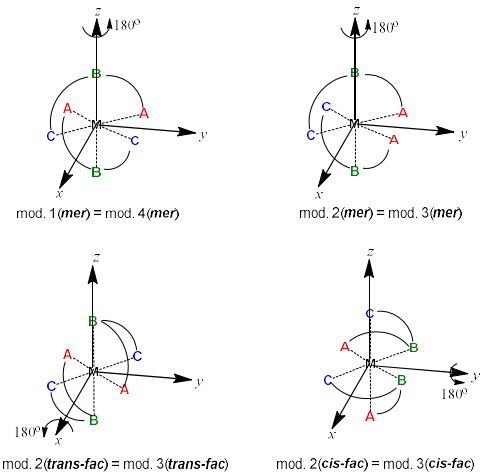


Figure S3. Rotations around *z*, *x* or *y* axes which show equalities of several modifications given in Figure S2.

Modification 2 (or 3) of *trans-fac* isomer (Figure S2) is centrosymmetric. Modification 2 of *mer* isomer is an opposite enantiomer of modification 1 of *mer* isomer; modification 4 of *trans-fac* isomer is an opposite enantiomer of modification 1 of *trans-fac* isomer. Mirror symmetry conversions are shown in Figure S4.

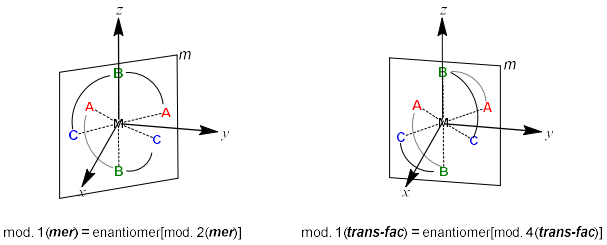


Figure S4. Mirror symmetries (*m*) between modifications of *mer* and *trans-fac* isomers converting modificated structures into their enantiomer forms. In the case of *mer* isomer, mirror plane is the plane of the "upper" ligand, in the case of *trans-fac* isomer, mirror plane is the *yz* plane.

Taking equalities given in Figures S3 and S4, the $[M(A\text{-}B\text{-}C)_2]$ modifications of $[M(A\text{-}B\text{-}A)_2]$ isomers can be grouped in six groups shown in Figure S5. Δ and Λ enantiomers of three *cis-fac* types are generated from Δ and Λ enantiomers of *cis-fac* isomer of the $[M(A\text{-}B\text{-}A)_2]$ complex (Figure S1)].

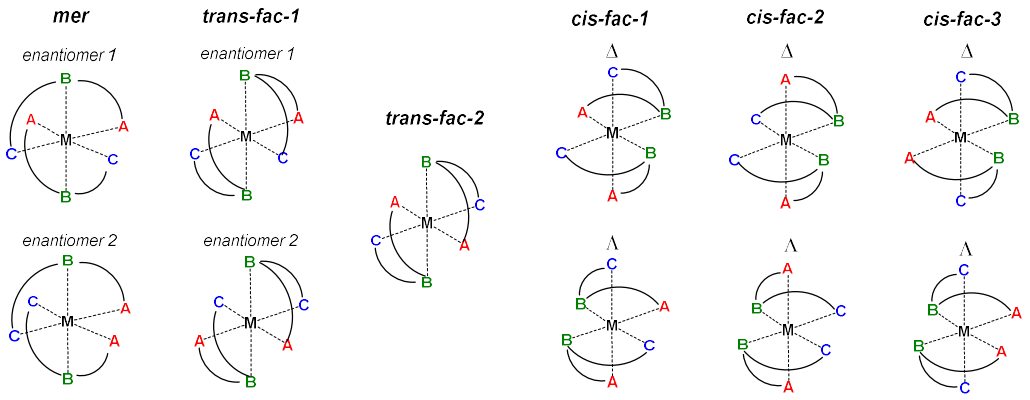


Figure S5. Six groups of structural different $[M(A\text{-}B\text{-}C)_2]$ isomers generated from modifications of $[M(A\text{-}B\text{-}A)_2]$ isomers. One enantiomer from each group is given in **Scheme 2** of the manuscript.

NMR spectroscopy

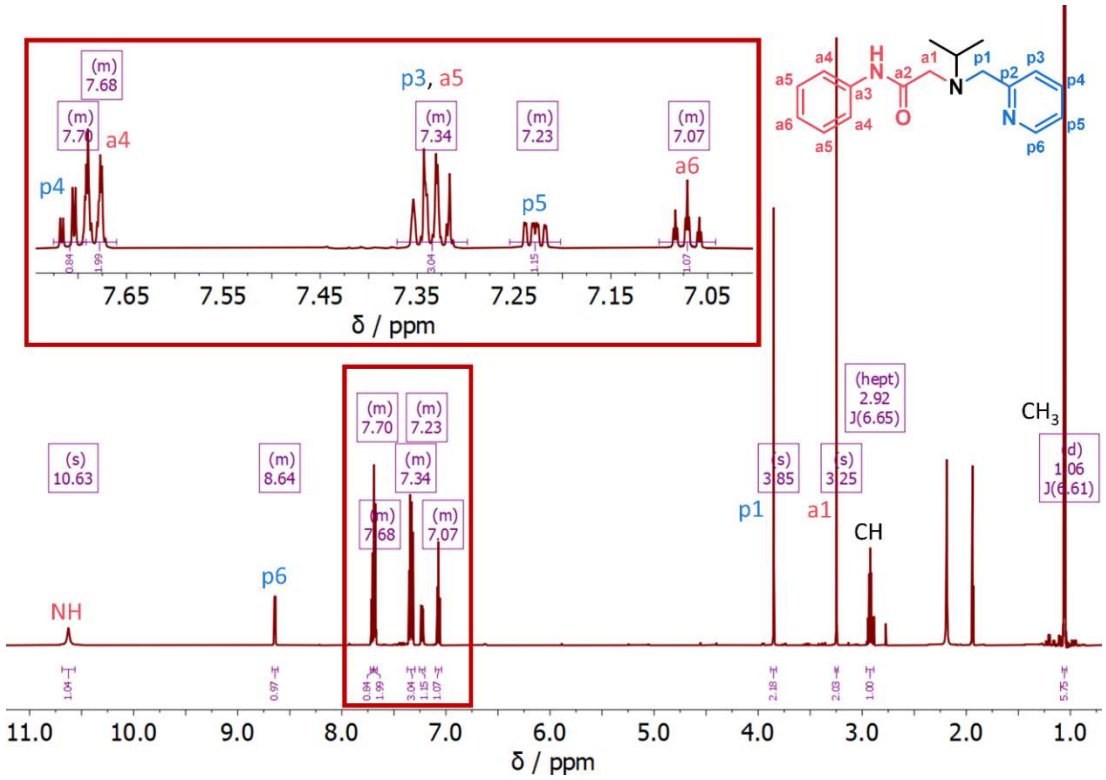


Figure S6. ^{1}H NMR (CD_3CN) of ligand **L**

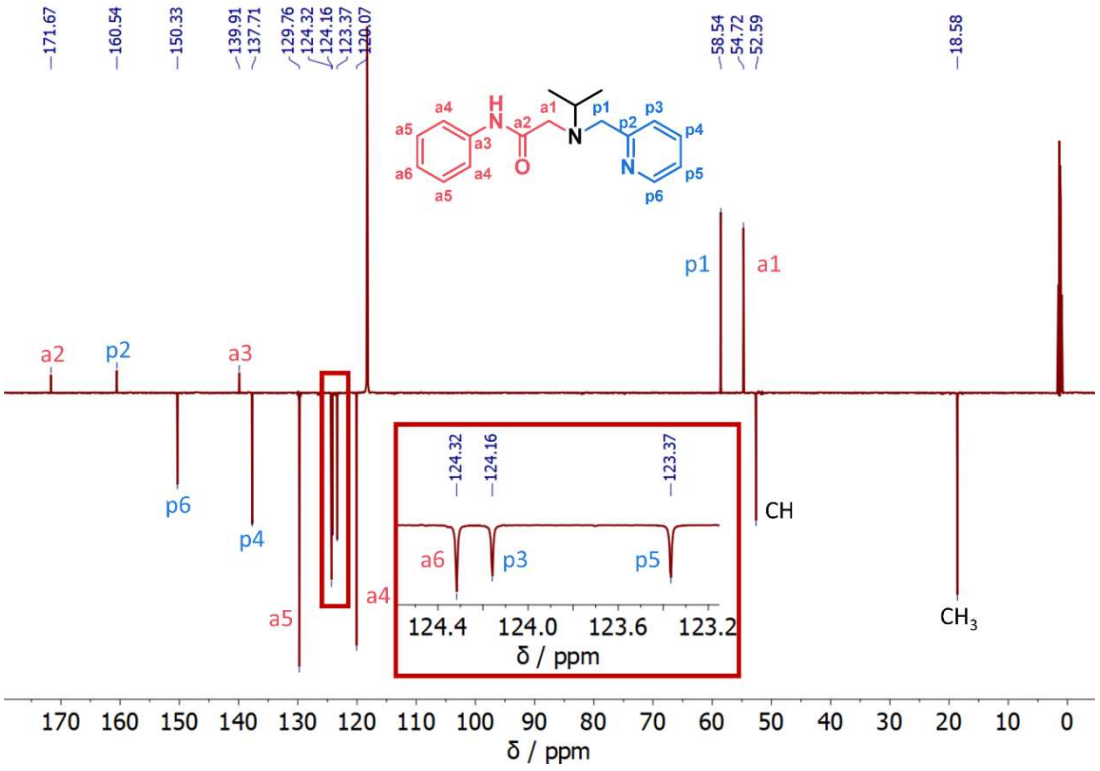


Figure S7. ^{13}C APT NMR (CD_3CN) of ligand **L**

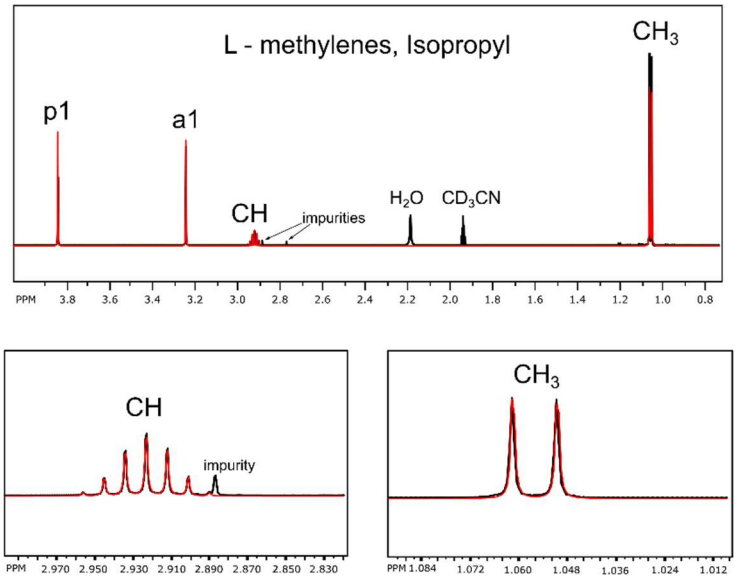


Figure S8. Comparison of the ^{1}H NMR experimental spectra of **L** in aliphatic region (black) and simulations (red) for Isopropyl and methylene spin systems, with parameters given in Table 2 of manuscript as the observed NMR parameters. Multiplets are shown enlarged in separate frames to emphasize the quality of the fit.

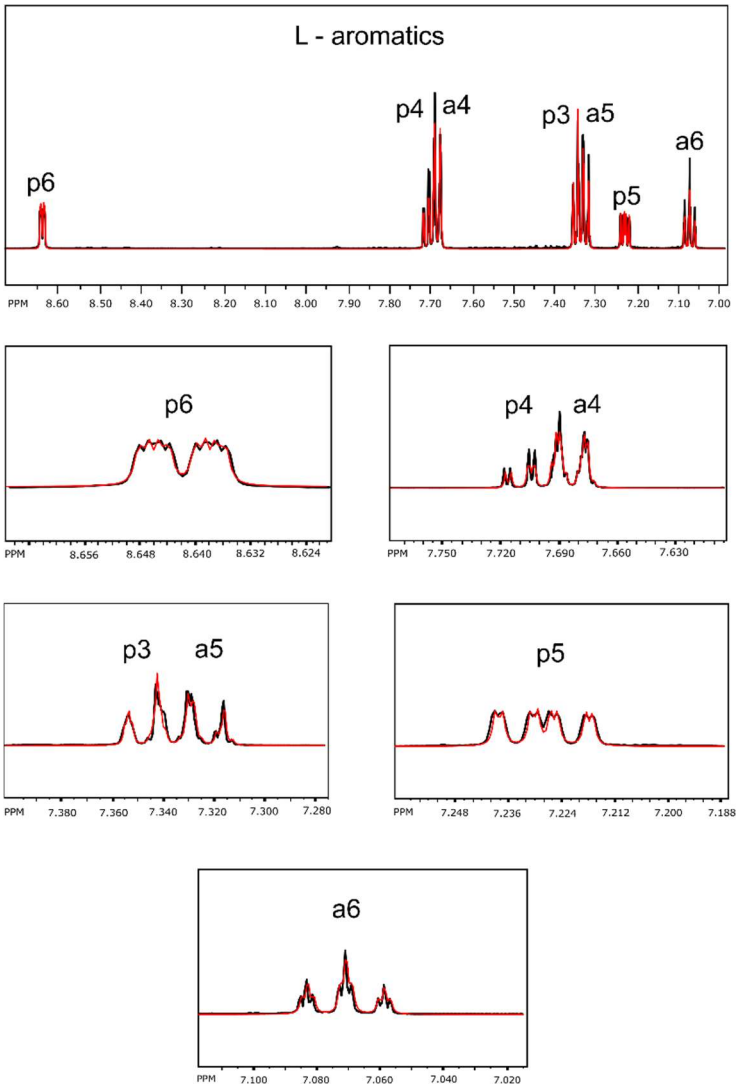


Figure S9. Comparison of the ^{1}H NMR experimental spectra of **L** in aromatic region (black) and simulations (red) for Pyridyl and Phenyl spin systems with parameters given in Table 2 of manuscript as the observed NMR parameters. Multiplets are shown enlarged in separate frames to emphasize the quality of the fit.

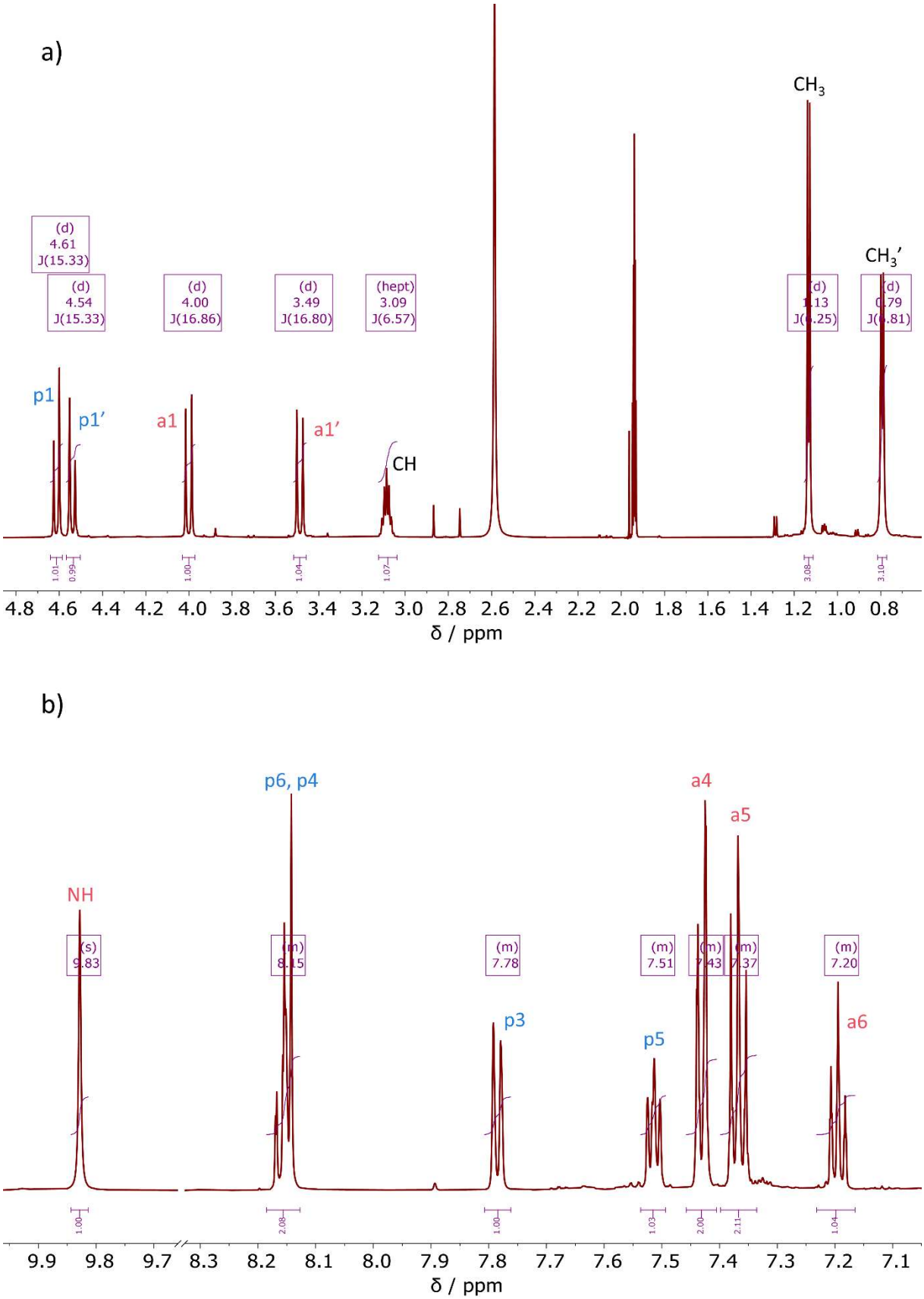


Figure S10. ^{1}H NMR (CD_3CN, -40 °C) of $[Zn(L)_2](CF_3SO_3)_2$, aliphatic (a) and aromatic (b) region.

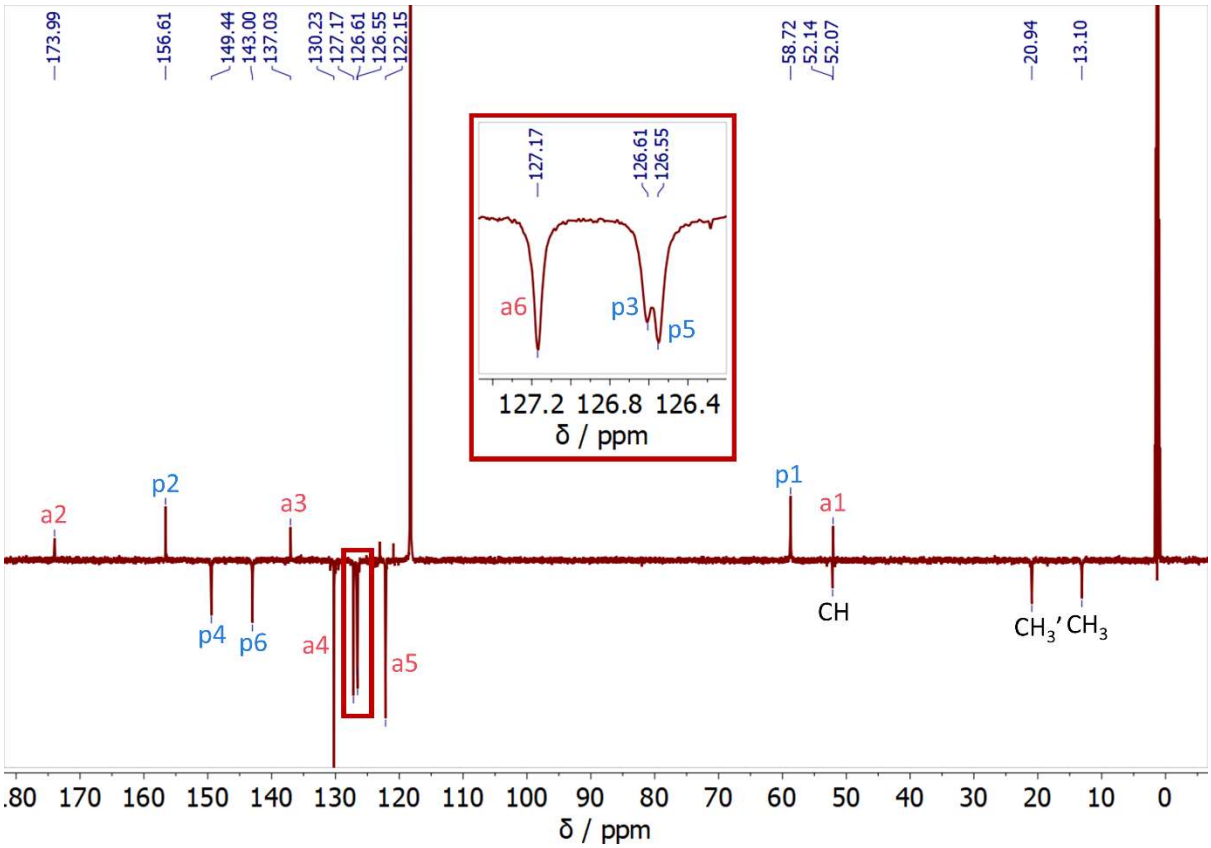


Figure S11. ^{13}C APT NMR (CD_3CN) of $[Zn(L)_2](CF_3SO_3)_2$

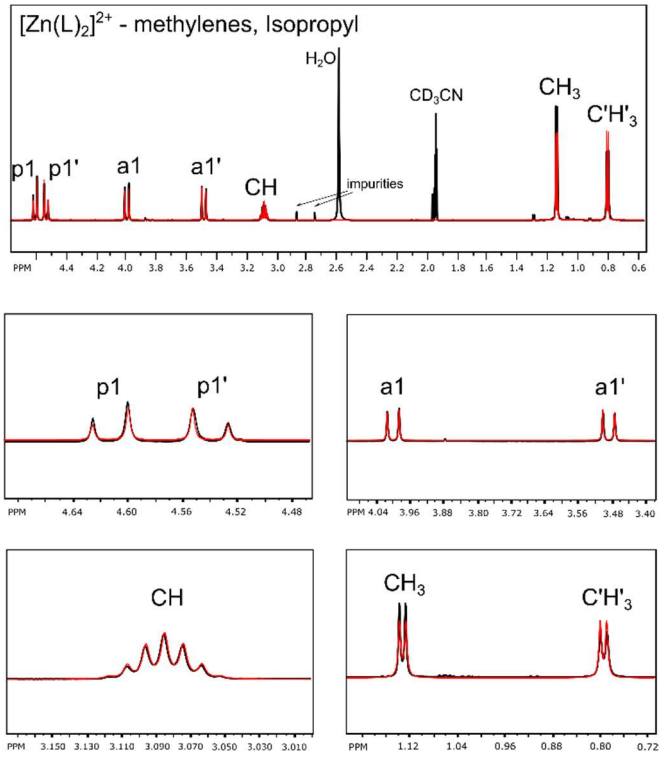


Figure S12. Comparison of the ^1H NMR experimental spectra (-40 °C) for **$[Zn(L)_2]^{2+}$** in aliphatic region (black) and simulations (red) for Isopropyl and for methylene spin systems, with parameters given in Table 2 of manuscript as the observed NMR parameters. Multiplets are shown enlarged in separate frames to emphasize the quality of the fit.

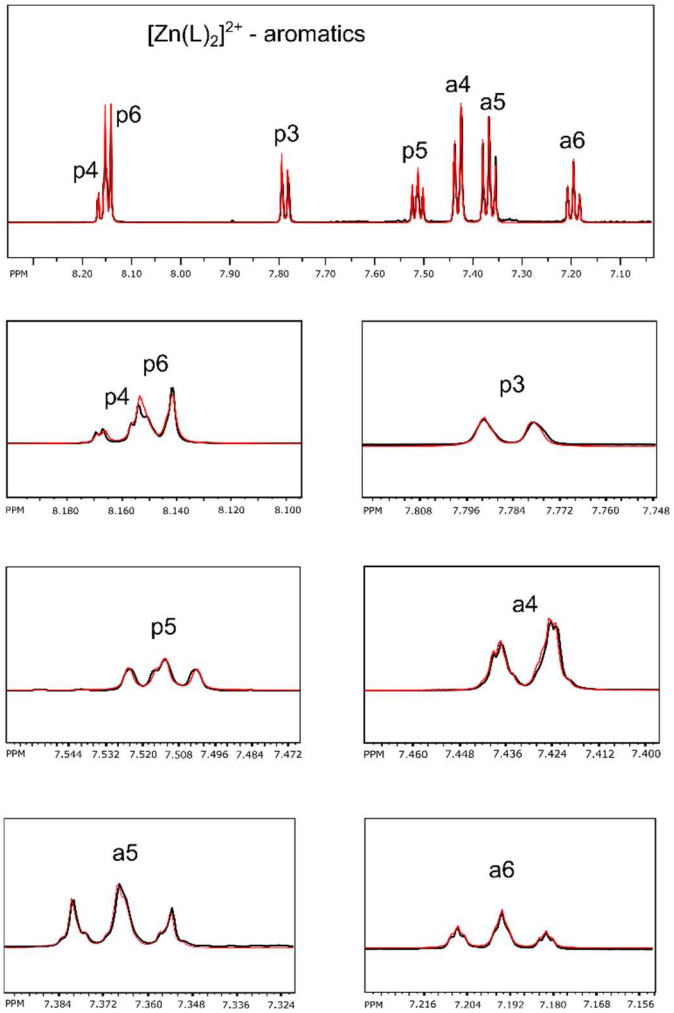


Figure S13. Comparison of the ^{1}H NMR experimental spectra (-40 ^{o}C) for **$[Zn(L)_2]^{2+}$** in aromatic region (black) and simulations (red) for Pyridyl and Phenyl spin systems with parameters given in Table 2 of manuscript as the observed NMR parameters. Multiplets are shown enlarged in separate frames to emphasize the quality of the fit.

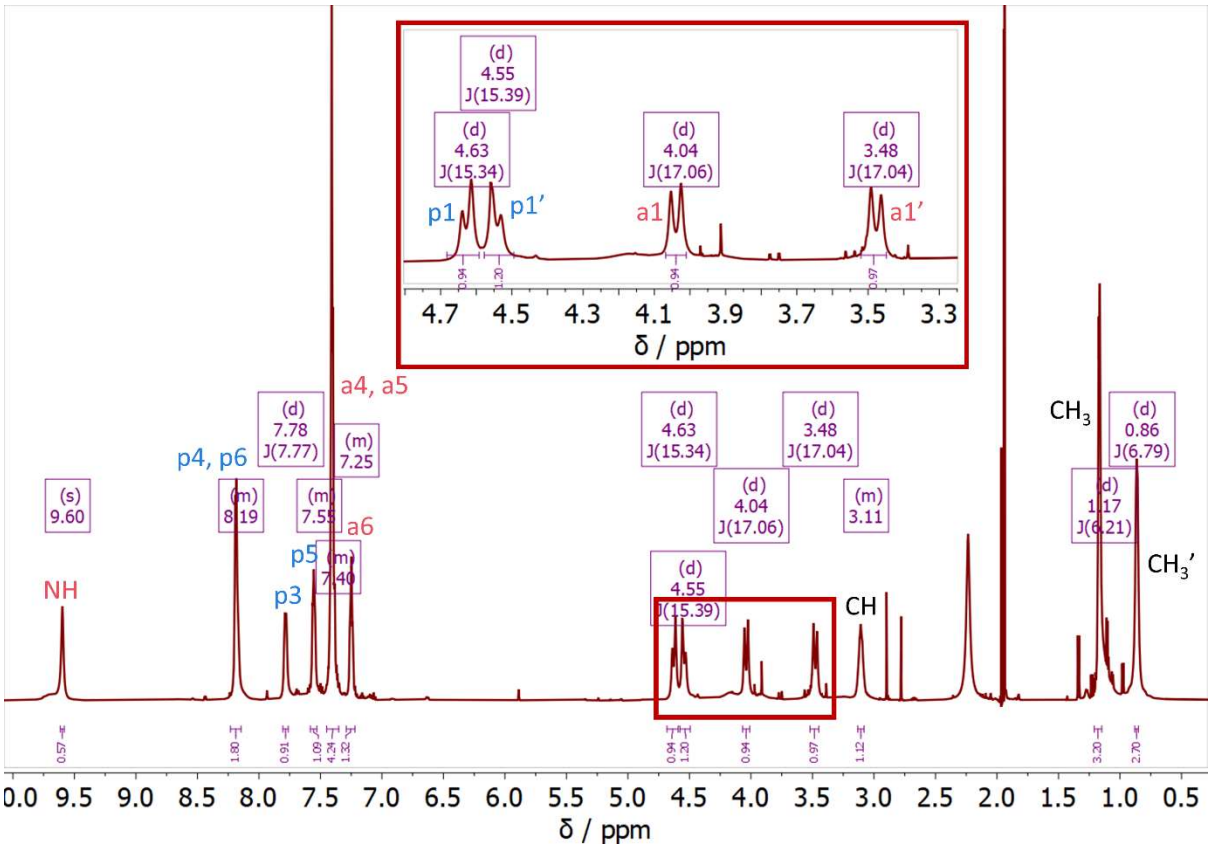


Figure S14. ^{1}H NMR (CD_3CN) of $[Zn(L)_2](CF_3SO_3)_2$ (room temperature)

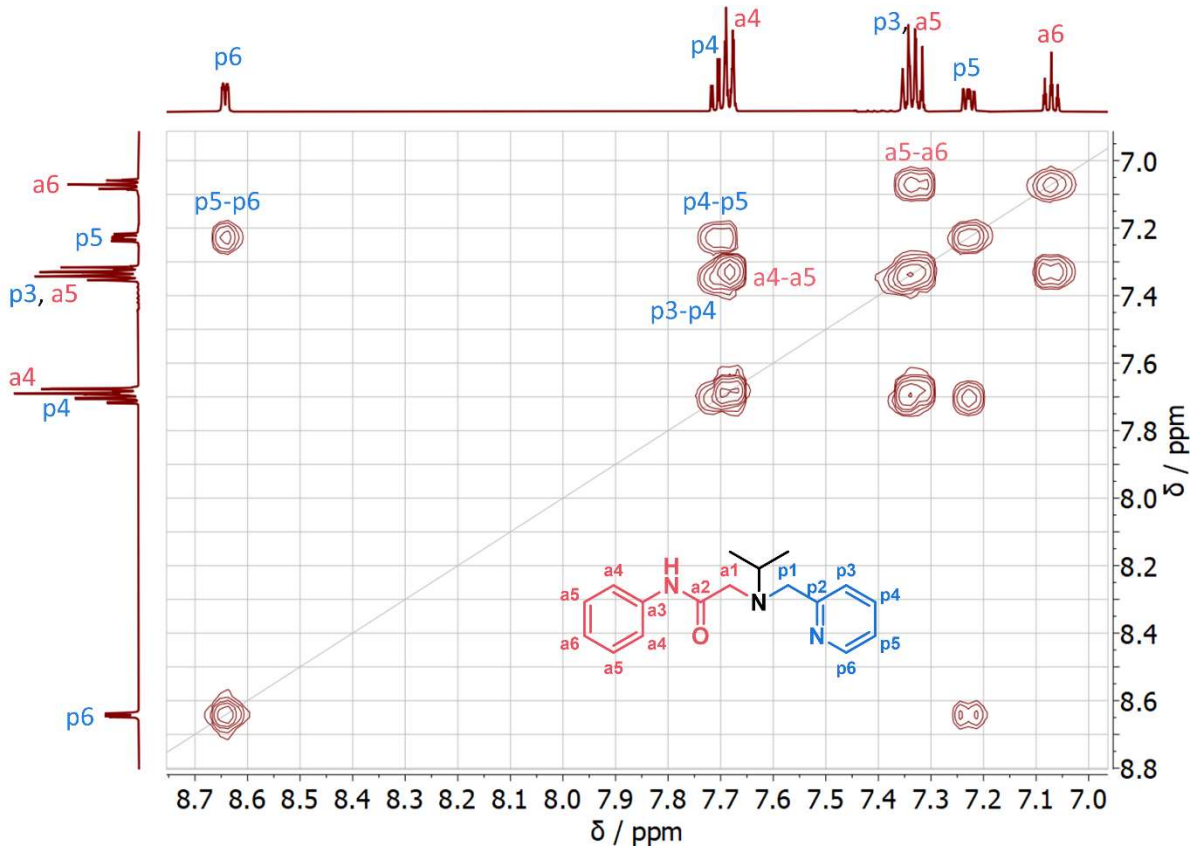


Figure S15. ^{1}H-^{1}H COSY NMR (CD_3CN, aromatic region) of ligand L

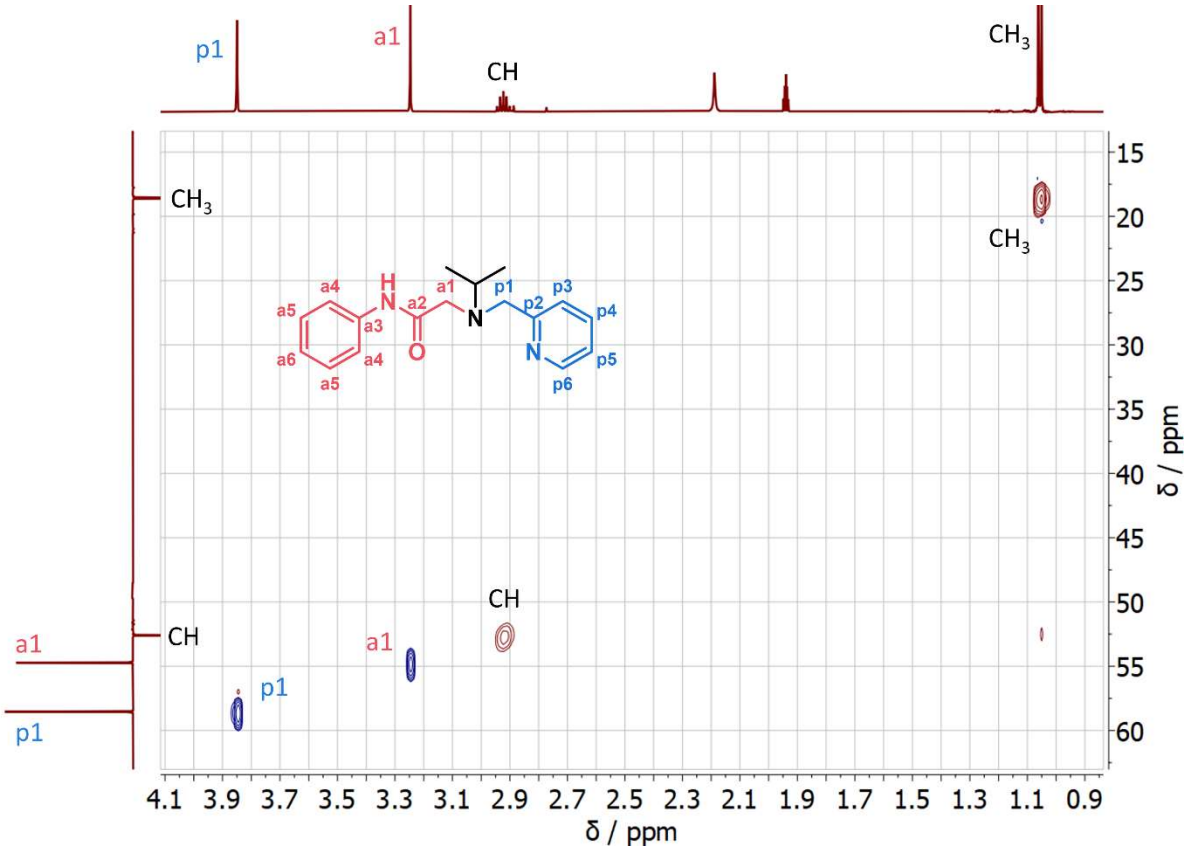


Figure S16 ^{1}H-^{13}C HSQC NMR (CD_3CN, aliphatic region) of ligand L

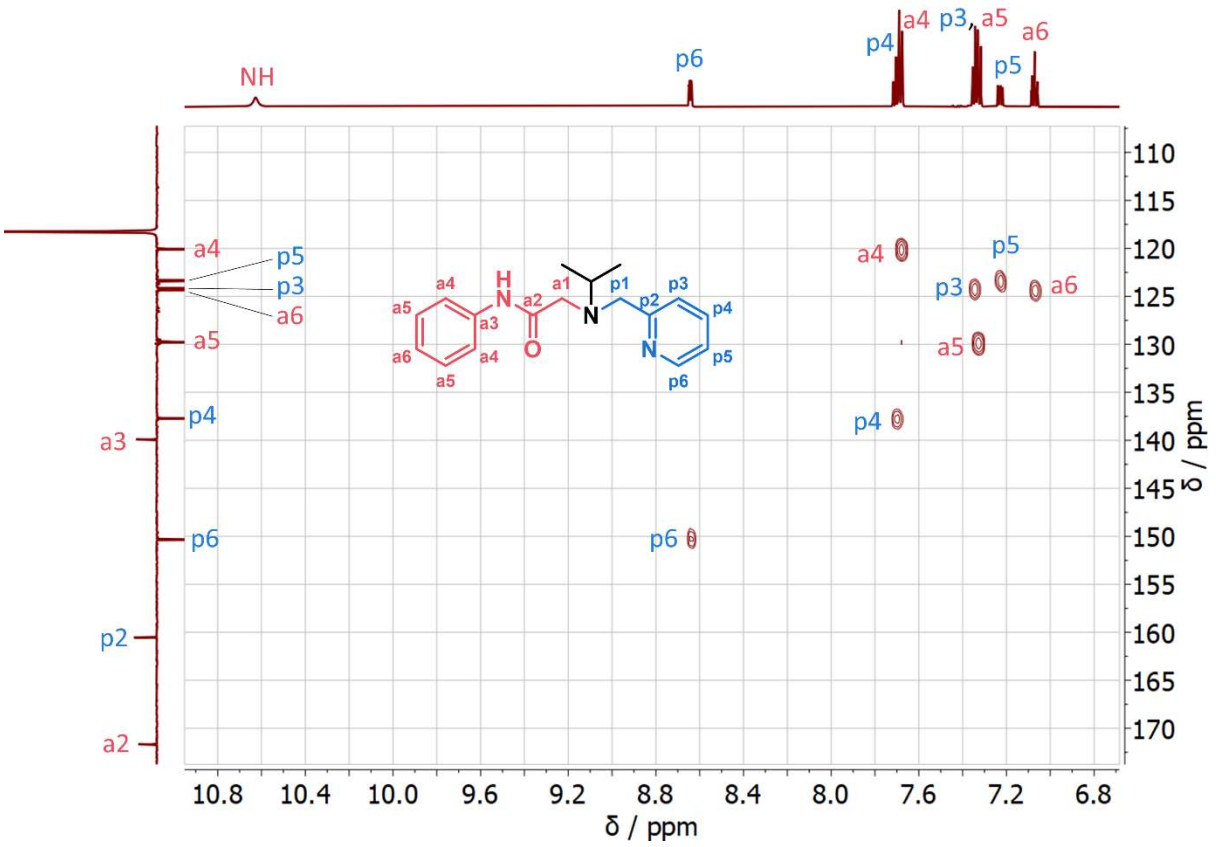


Figure S17. ^{1}H-^{13}C HSQC NMR (CD_3CN, aromatic region) of ligand L

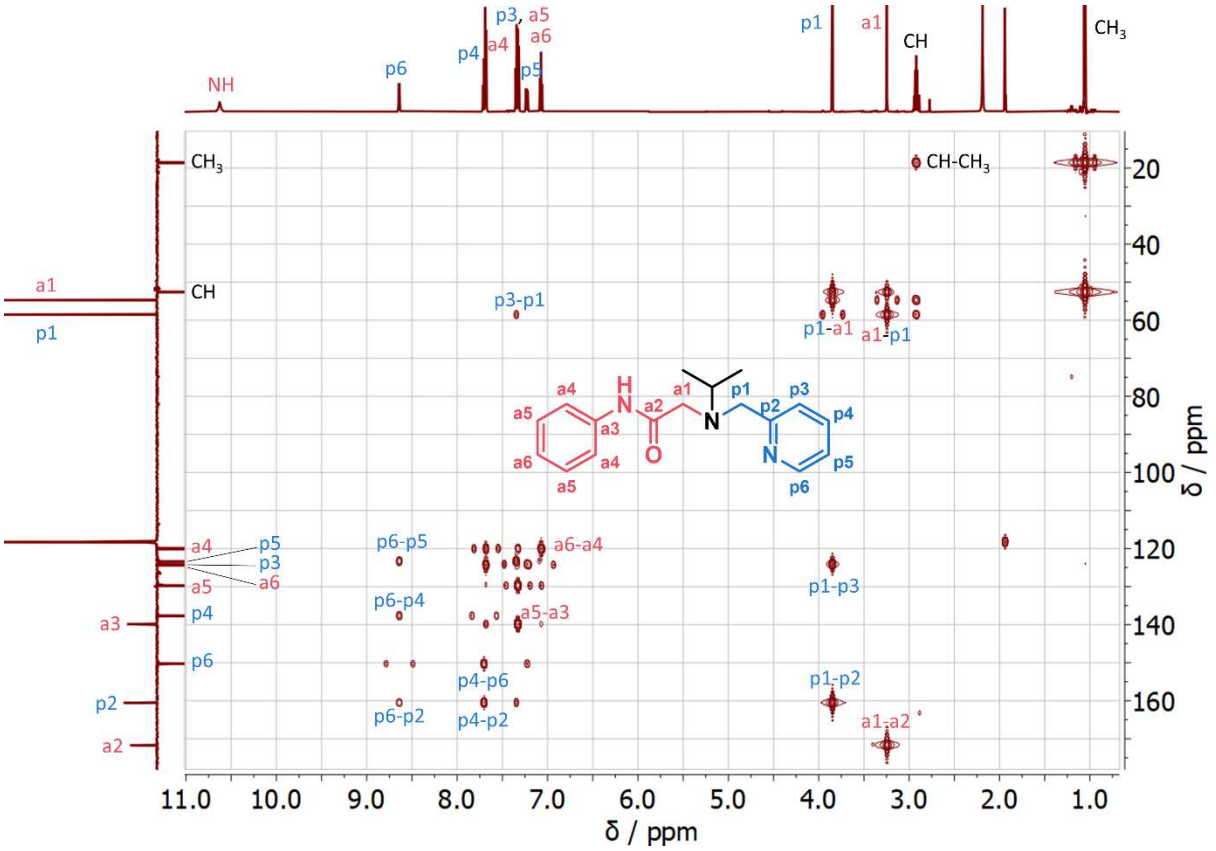


Figure S18. ^{1}H-^{13}C HMBC NMR (CD_3CN) of ligand L

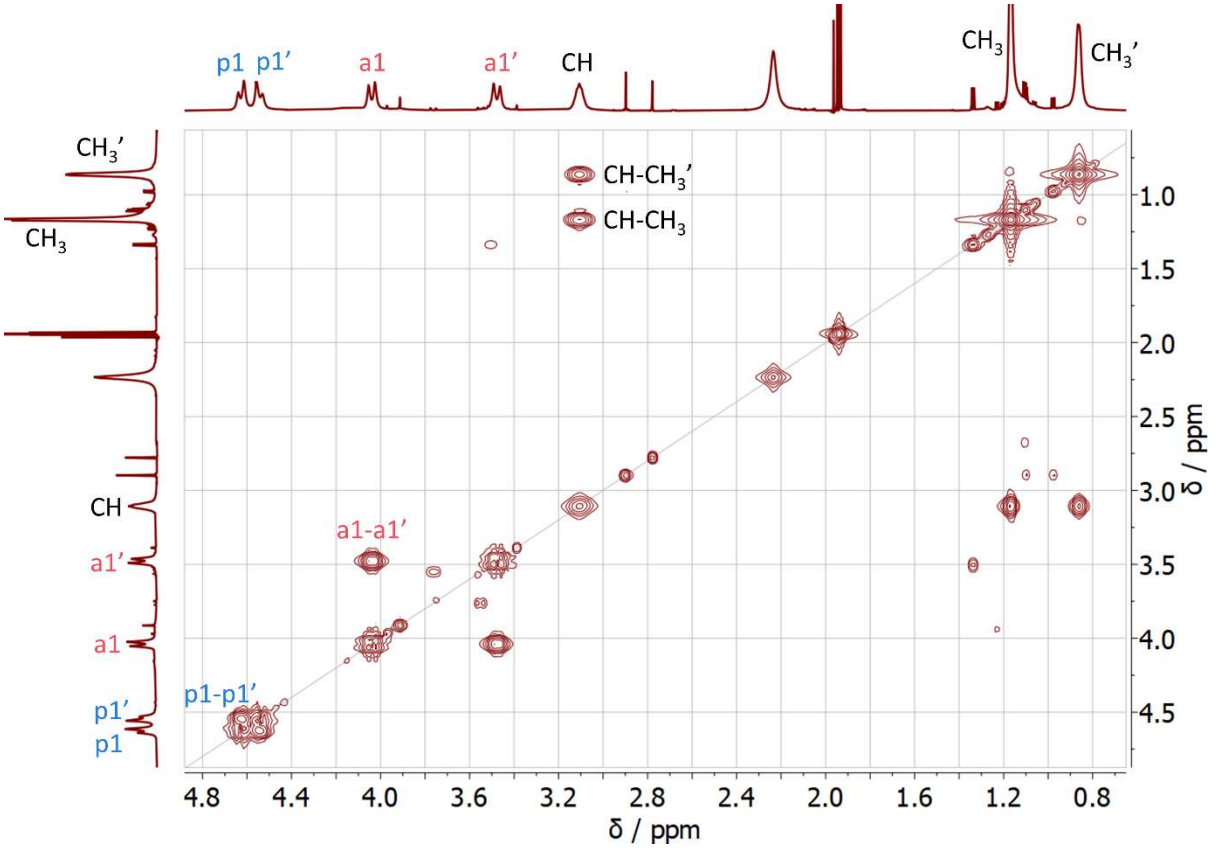


Figure S19. ^{1}H-^{1}H COSY NMR (room temperature, CD_3CN, aliphatic region) of $[Zn(L)_2](CF_3SO_3)_2$

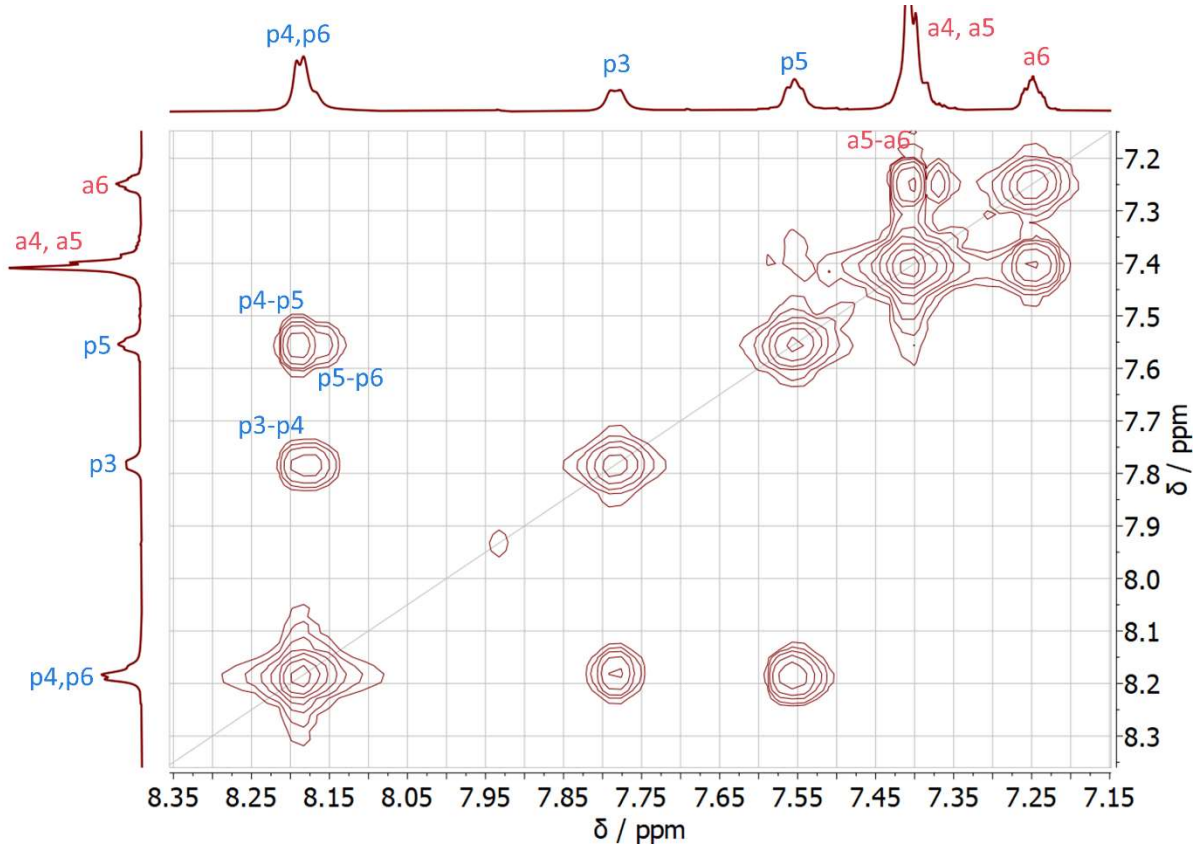


Figure S20. ^{1}H-^{1}H COSY NMR (room temperature, CD_3CN, aromatic region) of $[Zn(L)_2](CF_3SO_3)_2$

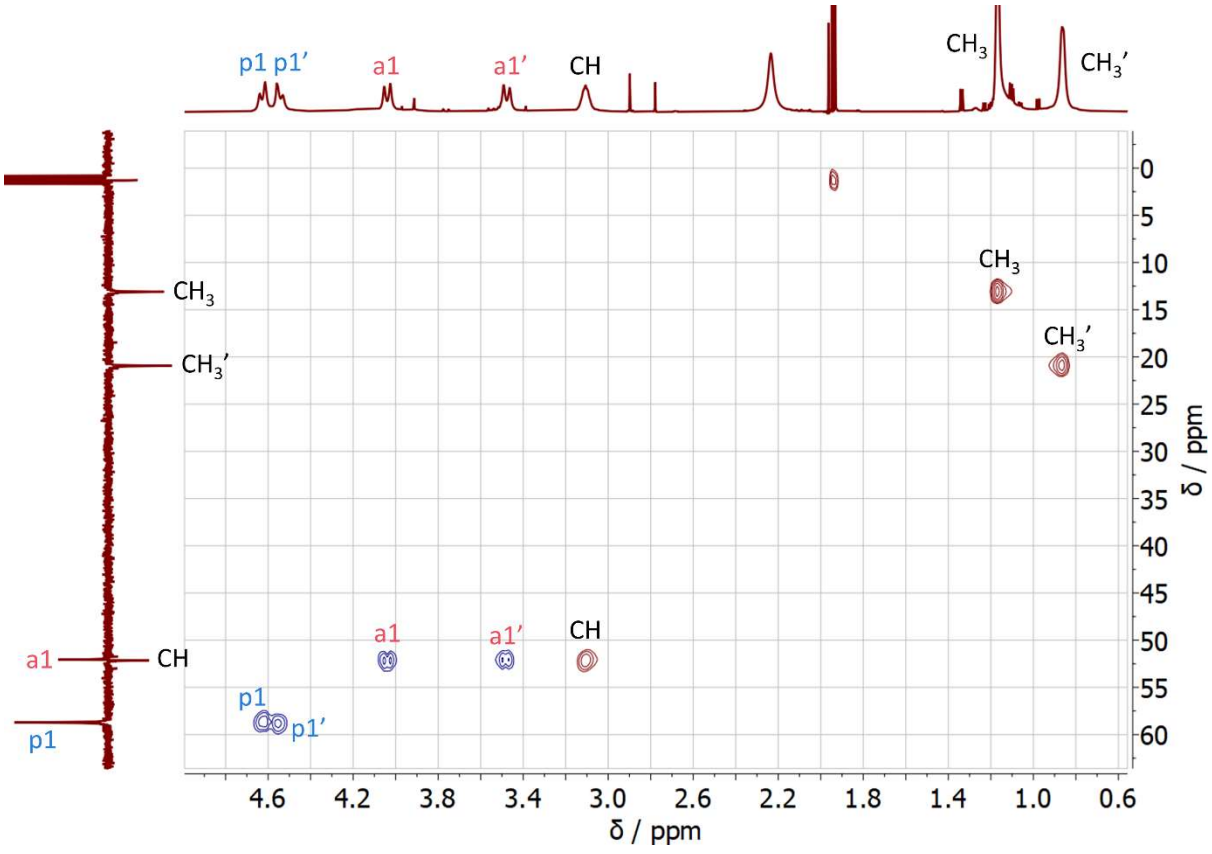


Figure S21. ^{1}H-^{13}C HSQC NMR (room temperature, CD_3CN, aliphatic region) of $[Zn(L)_2](CF_3SO_3)_2$

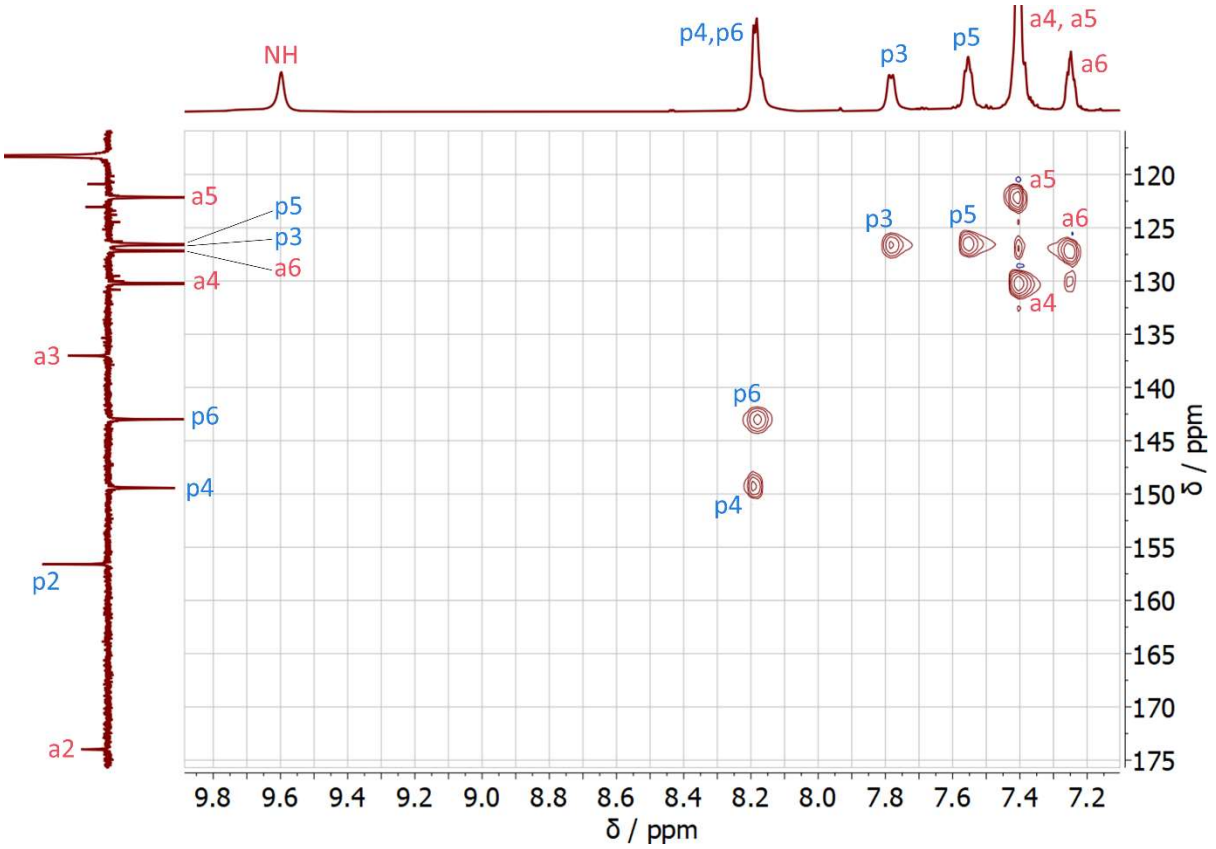


Figure S22. ^{1}H-^{13}C HSQC NMR (room temperature, CD_3CN, aromatic region) of $[Zn(L)_2](CF_3SO_3)_2$

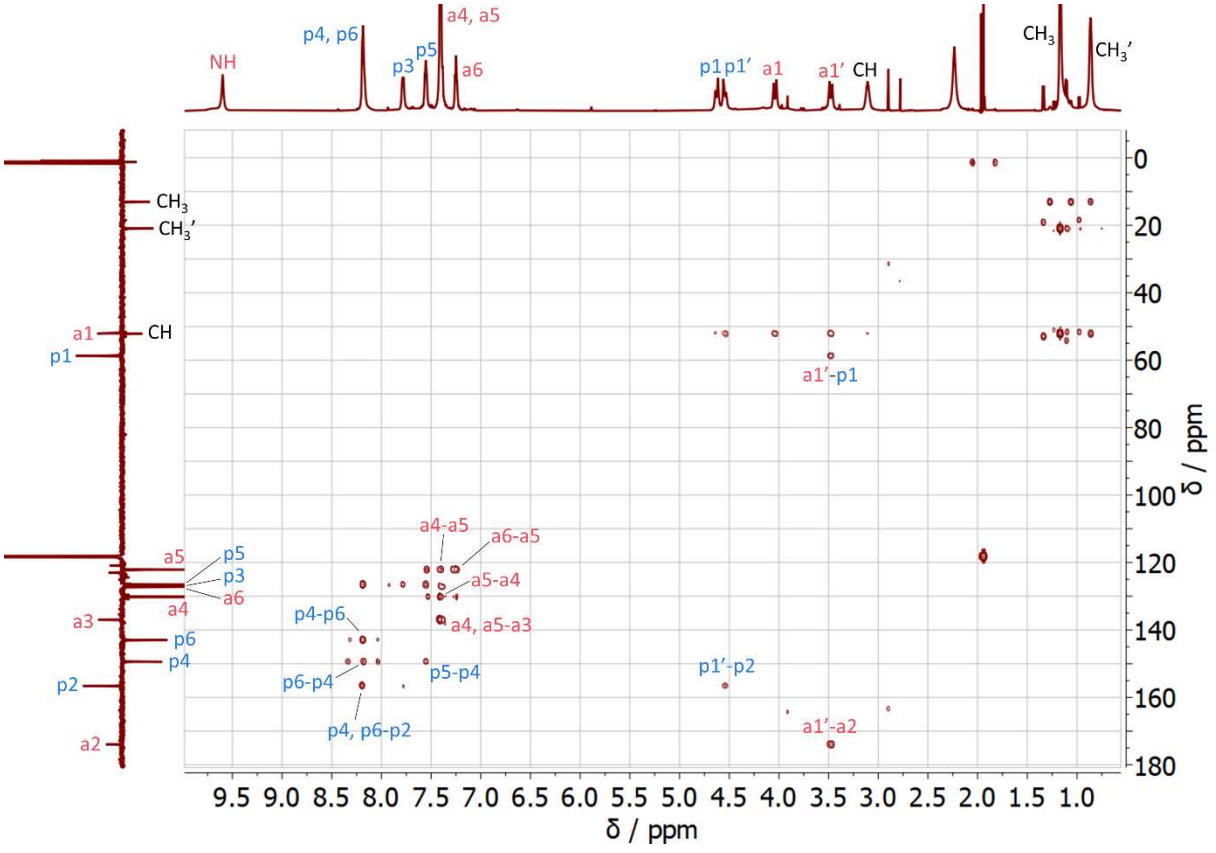


Figure S23. ^{1}H-^{13}C HMBC NMR (room temperature, CD_3CN) of $[Zn(L)_2](CF_3SO_3)_2$

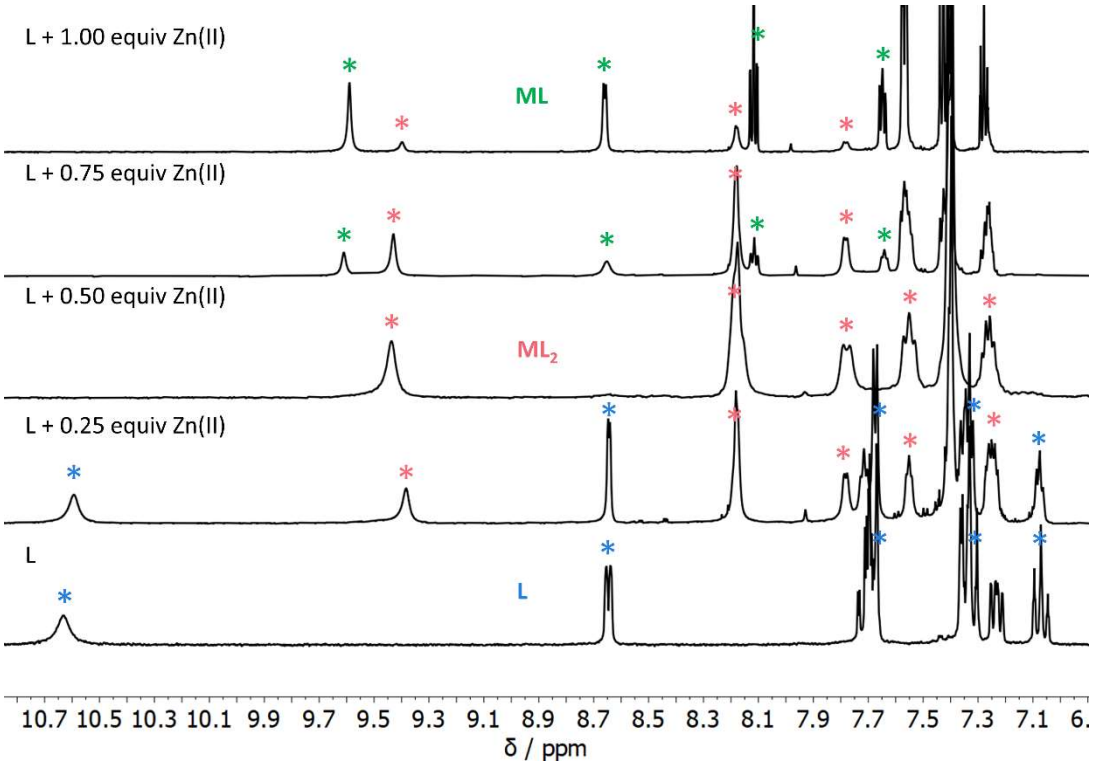


Figure S24. ^{1}H NMR (CD_3CN) spectra (aromatic region) of L with different additions of $Zn(CF_3SO_3)_2$

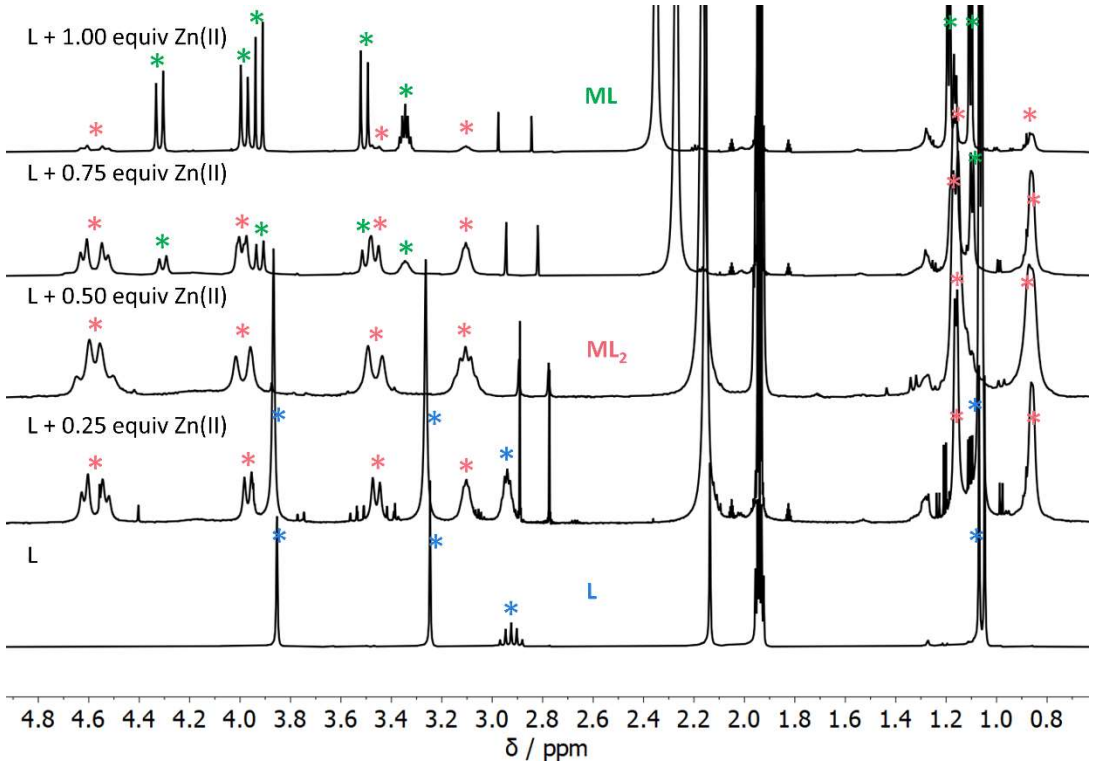


Figure S25. ^{1}H NMR (CD_3CN) spectra (aliphatic region) of L with different additions of $Zn(CF_3SO_3)_2$

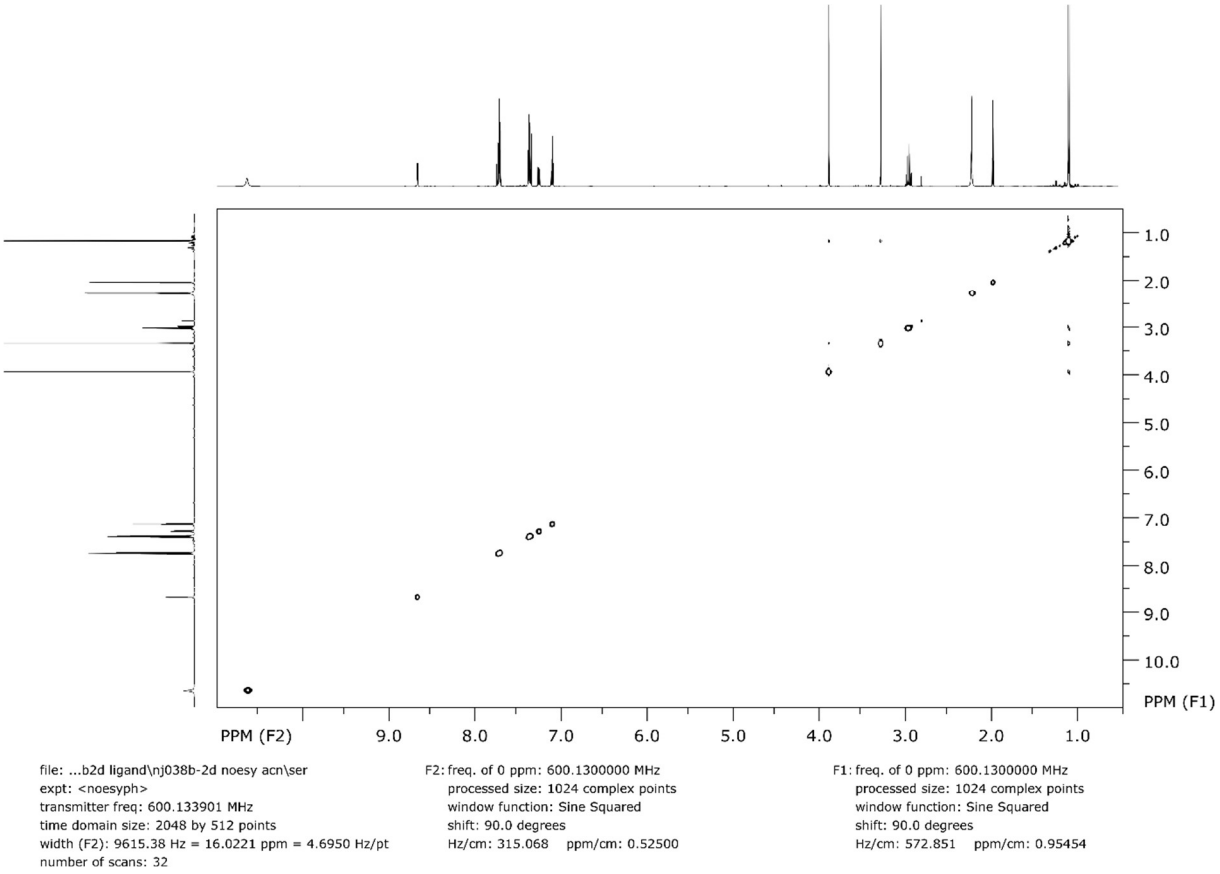
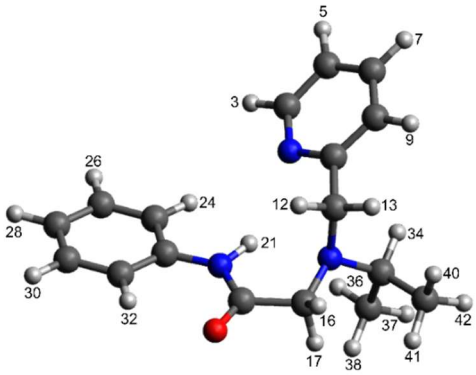
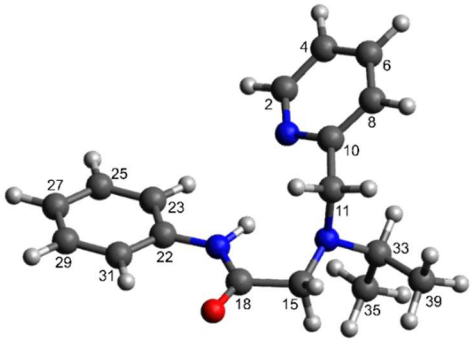


Figure S26. ^{1}H NOESY spectrum of **L** with parameters of measurement. The same parameters are used for NOESY spectra of **$[Zn(L)_2]^{2+}$** (Figure 5b of the manuscript).

DFT-NMR calculations and correlations with experiment





NMR assignation (^{1}H)	label
p6	3
p5	5
p4	7
p3	9
p1	12
p1	13
a1	16
a1	17
NH	21
a4	24
a5	26
a6	28
a5	30
a4	32
CH	34
CH_3	36
CH_3	37
CH_3	38
CH_3	40
CH_3	41
CH_3	42

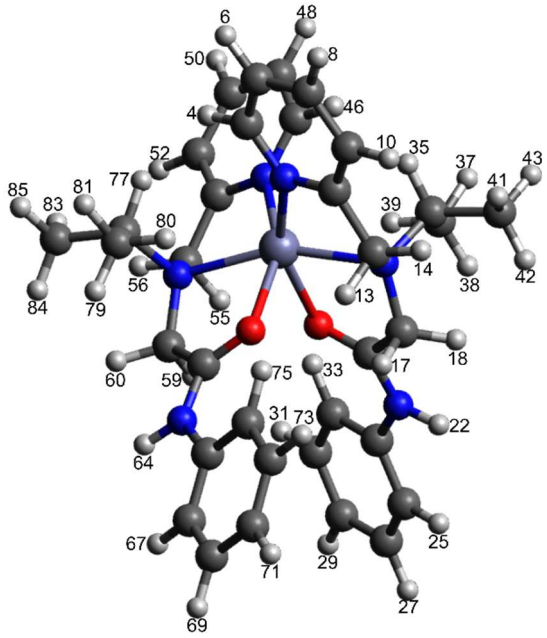
NMR assignation (^{13}C)	label
p6	2
p5	4
p4	6
p3	8
p2	10
p1	11
a1	15
a2	18
a3	22
a4	23
a5	25
a6	27
a5	29
a4	31
CH	33
CH_3	35
CH_3	39

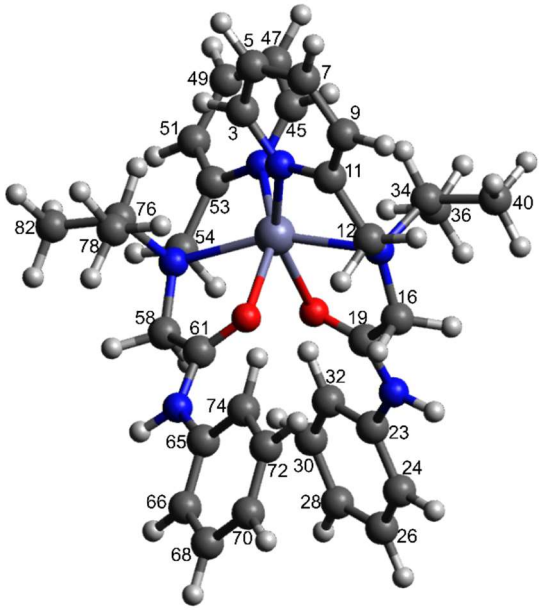
$^{1H}\sigma(p3)=\sigma(9)$ $^{1H}\sigma(p4)=\sigma(7)$ $^{1H}\sigma(p5)=\sigma(5)$ $^{1H}\sigma(p6)=\sigma(3)$
$^{1H}\sigma(p1)=[\sigma(12)+\sigma(13)]/2$
$^{1H}\sigma(a1)=[\sigma(16)+\sigma(17)]/2$
$^{1H}\sigma(a4)=[\sigma(24)+\sigma(32)]/2$ $^{1H}\sigma(a5)=[\sigma(26)+\sigma(30)]/2$ $^{1H}\sigma(a6)=\sigma(28)$
$^{1H}\sigma(CH)=\sigma(34)$ $^{1H}\sigma(CH_3)=[\sigma(36)+\sigma(37)+\sigma(38)+\sigma(40)+\sigma(41)+\sigma(42)]/6$

$^{3}J(p3,p4)=J(7,9)$ $^{3}J(p4,p5)=J(5,7)$ $^{3}J(p5,p6)=J(3,5)$ $^{4}J(p4,p6)=J(3,7)$ $^{4}J(p3,p5)=J(5,9)$ $^{5}J(p3,p6)=J(3,9)$
$^{3}J(a4,a5)=[J(24,26)+J(30,32)]/2$ $^{3}J(a5,a6)=[J(26,28)+J(28,30)]/2$ $^{4}J(a4,a4)=J(24,32)$ $^{4}J(a5,a5)=J(26,30)$
$^{5}J(a4,a5)=[J(24,30)+J(26,32)]/2$ $^{4}J(a4,a6)=[J(24,28)+J(28,32)]/2$
$^{3}J(CH,CH_3)=[J(34,36)+J(34,37)+J(34,38)+J(34,40)+J(34,41)+J(34,42)]/6$

$^{13C}\sigma(p2)=\sigma(10)$ $^{13C}\sigma(p3)=\sigma(8)$ $^{13C}\sigma(p4)=\sigma(6)$ $^{13C}\sigma(p5)=\sigma(4)$ $^{13C}\sigma(p6)=\sigma(2)$
$^{13C}\sigma(p1)=\sigma(11)$
$^{13C}\sigma(a1)=\sigma(15)$
$^{13C}\sigma(a2)=\sigma(18)$
$^{13C}\sigma(a3)=\sigma(22)$ $^{13C}\sigma(a4)=[\sigma(23)+\sigma(31)]/2$ $^{13C}\sigma(a5)=[\sigma(25)+\sigma(29)]/2$ $^{13C}\sigma(a6)=\sigma(27)$
$^{13C}\sigma(CH)=\sigma(33)$ $^{13C}\sigma(CH_3)=[\sigma(35)+\sigma(39)]/2$

Figure S27. Atom labels used in DFT calculations for **L** (left - H atoms, right - C atoms) shown on the structural model of second conformer (Figure S30) with table of assignations used in the interpretation of the NMR spectra. Formulas are definitions for averaged ^{1}H shieldings ($^{1H}\sigma$) used in ^{1}H correlation calculations (Figures S29-S38) and for averaged *J* couplings used in *J* coupling correlation diagrams (Figures S42-S51) and in spin systems of Table 2 of the manuscript (spin systems for **L**). Definitions for averaged ^{13}C shieldings ($^{13C}\sigma$) used in ^{13}C correlation calculations are also specified (Figures S29-S38).





NMR assignation (^{1}H)	label (first ligand)	label (second ligand)
p6	4	46
p5	6	48
p4	8	50
p3	10	52
p1	13	55
p1’	14	56
a1’	17	59
a1	18	60
NH	22	64
a4	25	67
a5	27	69
a6	29	71
a5	31	73
a4	33	75
CH	35	77
C’H’$_3$	37	79
C’H’$_3$	38	80
C’H’$_3$	39	81
CH_3	41	83
CH_3	42	84
CH_3	43	85

NMR assignation (^{13}C)	label (first ligand)	label (second ligand)
p6	3	45
p5	5	47
p4	7	49
p3	9	51
p2	11	53
p1	12	54
a1	16	58
a2	19	61
a3	23	65
a4	24	66
a5	26	68
a6	28	70
a5	30	72
a4	32	74
CH	34	76
C’H’$_3$	36	78
CH_3	40	82

(A)

$^{1H}\sigma(p3)=[\sigma(10)+\sigma(52)]/2$ $^{1H}\sigma(p4)=[\sigma(8)+\sigma(50)]/2$ $^{1H}\sigma(p5)=[\sigma(6)+\sigma(48)]/2$ $^{1H}\sigma(p6)=[\sigma(4)+\sigma(46)]/2$

$^{1H}\sigma(p1)=[\sigma(13)+\sigma(55)]/2$

$^{1H}\sigma(p1')=[\sigma(14)+\sigma(56)]/2$

$^{1H}\sigma(a1')=[\sigma(17)+\sigma(59)]/2$

$^{1H}\sigma(a1)=[\sigma(18)+\sigma(60)]/2$

$^{1H}\sigma(a4)=[\sigma(25)+\sigma(33)+\sigma(67)+\sigma(75)]/4$ $^{1H}\sigma(a5)=[\sigma(27)+\sigma(31)+\sigma(69)+\sigma(73)]/4$ $^{1H}\sigma(a6)=[\sigma(29)+\sigma(71)]/2$

$^{1H}\sigma(CH)=[\sigma(35)+\sigma(77)]/2$ $^{1H}\sigma(C'H'_3)=[\sigma(37)+\sigma(38)+\sigma(39)+\sigma(79)+\sigma(80)+\sigma(81)]/6$

$^{1H}\sigma(CH_3)=[\sigma(41)+\sigma(42)+\sigma(43)+\sigma(83)+\sigma(84)+\sigma(85)]/6$

$^{3}J(p3,p4)=[J(8,10)+J(50,52)]/2$ $^{3}J(p4,p5)=[J(6,8)+J(48,50)]/2$ $^{3}J(p5,p6)=[J(4,6)+J(46,48)]/2$ $^{4}J(p4,p6)=[J(4,8)+J(46,50)]/2$

$^{4}J(p3,p5)=[J(6,10)+J(48,52)]/2$ $^{5}J(p3,p6)=[J(4,10)+J(46,52)]/2$

$^{2}J(p1,p1')=[J(13,14)+J(55,56)]/2$

$^{2}J(a1,a1')=[J(17,18)+J(59,60)]/2$

$^{3}J(a4,a5)=[J(25,27)+J(31,33)+J(67,69)+J(73,75)]/4$ $^{3}J(a5,a6)=[J(27,29)+J(29,31)+J(69,71)+J(71,73)]/4$

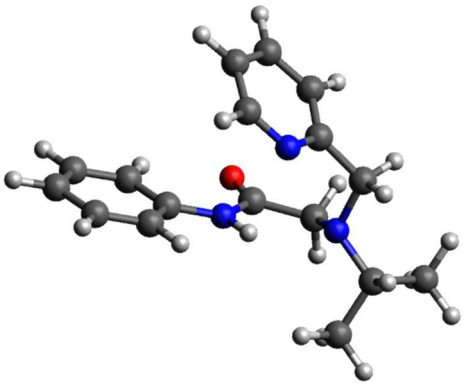
^{4}J(a4,a4)=[J(25,33)+J(67,75)]/2 ^{4}J(a5,a5)=[J(27,31)+J(69,73)]/2
^{5}J(a4,a5)=[J(25,31)+J(27,33)+J(67,73)+J(69,75)]/4 ^{4}J(a4,a6)=[J(25,29)+J(29,33)+J(67,71)+J(71,75)]/4
^{3}J(CH,C'H'$_3$)=[J(35,37)+J(35,38)+J(35,39)+J(77,79)+J(77,80)+J(77,81)]/6
^{3}J(CH,CH$_3$)=[J(35,41)+J(35,42)+J(35,43)+J(77,83)+J(77,84)+J(77,85)]/6
^{4}J(CH$_3$,C'H'$_3$)=[J(37,41)+J(37,42)+J(37,43)+J(38,41)+J(38,42)+J(38,43)+J(39,41)+J(39,42)+J(39,43)+
J(79,83)+J(79,84)+J(79,85)+J(80,83)+J(80,84)+J(80,85)+J(81,83)+J(81,84)+J(81,85)]/18

$^{13C}\sigma$(p2)=[σ(11)+σ(53)]/2 $^{13C}\sigma$(p3)=[σ(9)+σ(51)]/2 $^{13C}\sigma$(p4)=[σ(7)+σ(49)]/2 $^{13C}\sigma$(p5)=[σ(5)+σ(47)]/2
$^{13C}\sigma$(p6)=[σ(3)+σ(45)]/2
$^{13C}\sigma$(p1)=[σ(12)+σ(54)]/2
$^{13C}\sigma$(a1)=[σ(16)+σ(58)]/2
$^{13C}\sigma$(a2)=[σ(19)+σ(61)]/2
$^{13C}\sigma$(a3)=[σ(23)+σ(65)]/2 $^{13C}\sigma$(a4)=[σ(24)+σ(32)+σ(66)+σ(74)]/4 $^{13C}\sigma$(a5)=[σ(26)+σ(30)+σ(68)+σ(72)]/4
$^{13C}\sigma$(a6)=[σ(28)+σ(70)]/2
$^{13C}\sigma$(CH)=[σ(34)+σ(76)]/2
$^{13C}\sigma$(CH$_3$)=[σ(36)+σ(78)]/2
$^{13C}\sigma$(CH$_3$)=[σ(40)+σ(82)]/2

(B)

Figure S28 (A). Atom labels used in DFT calculations for **[Zn(L)$_2$]$^{2+}$** (left - H atoms, right - C atoms) shown on the structural model of first conformer (Figure S39) with table of associated assignations used in the interpretation of the NMR spectra. (B). Definitions for averaged ^{1}H shieldings ($^{1H}\sigma$) used in ^{1}H correlation calculations (Figures S39-S41) and averaged *J* couplings used in *J* coupling correlation diagrams (Figures S52-S54) and in spin systems of Table 2 of the manuscript (spin systems for **[Zn(L)$_2$]$^{2+}$**). Definitions for averaged ^{13}C shieldings ($^{13C}\sigma$) used in ^{13}C correlation calculations are also specified (Figures S39-S41).

L - Conformer 1

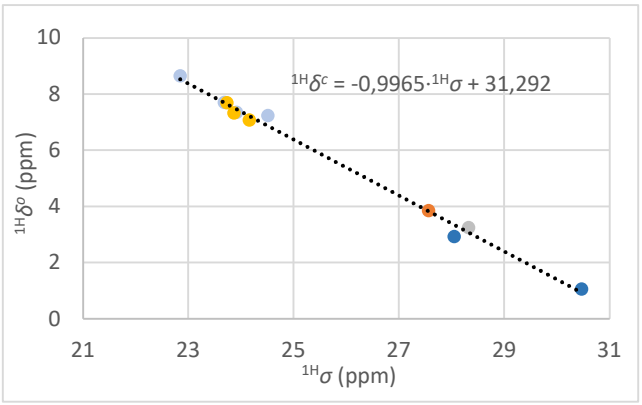


Free Energy (G) [kcal/mol]	population [%] 293 K
0	0.211

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,846	8,642	8,525961
p5	24,51	7,228	6,867785
p4	23,683	7,704	7,691891
p3	23,919	7,348	7,456717
p1	27,5645	3,85	3,823976
a1	28,3225	3,247	3,068629
a4	23,734	7,683	7,641069
a5	23,8695	7,329	7,506043
a6	24,162	7,071	7,214567
CH	28,048	2,923	3,342168
CH3	30,46783	1,056	0,930804

MAE = 0,15531

^{1}H correlation



assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	28,495	150,33	152,4071
p5	60,078	123,37	121,7242
p4	43,585	137,71	137,7472
p3	57,346	124,16	124,3784
p2	18,83	160,54	161,7967
p1	119,212	58,54	64,27554
a1	132,061	54,72	51,79274
a2	8,163	171,67	172,1596
a3	42,077	139,91	139,2122
a4	65,6375	120,07	116,3232
a5	52,3525	129,76	129,2295
a6	60,029	124,32	121,7718
CH	125,832	52,59	57,84421
CH3	169,326	18,58	15,58979

MAE = 2,15394

^{13}C correlation

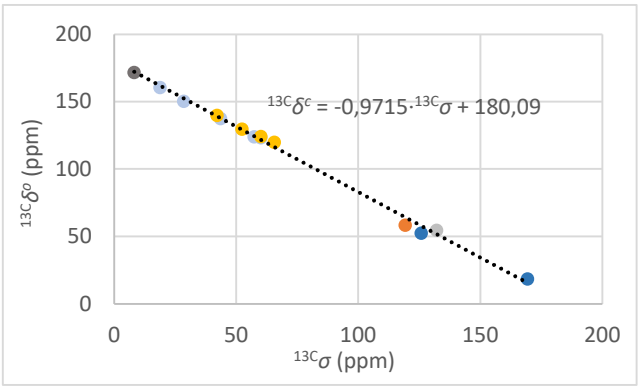
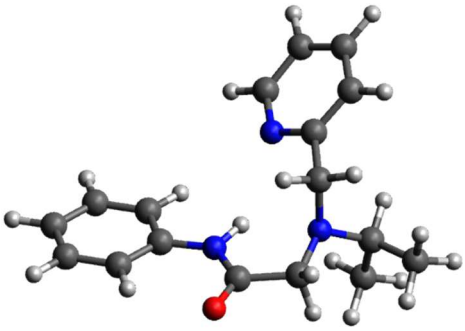


Figure S29. Lowest energy conformer of **L** (G=0), with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 2

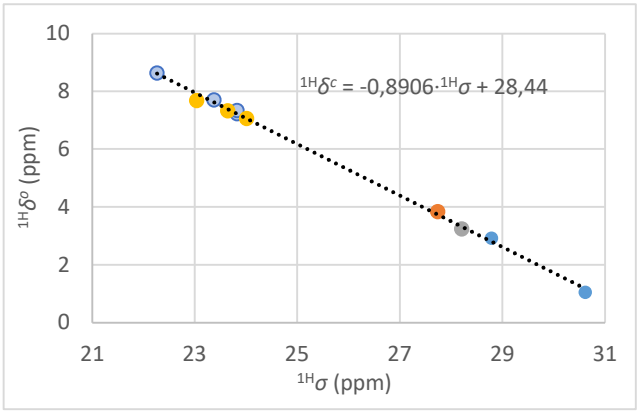


Free Energy (G) [kcal/mol]	population [%] 293 K
0.002	0.210

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,264	8,642	8,611682
p5	23,827	7,228	7,219674
p4	23,375	7,704	7,622225
p3	23,823	7,348	7,223236
p1	27,7365	3,85	3,737873
a1	28,2035	3,247	3,321963
a4	23,04	7,683	7,920576
a5	23,6405	7,329	7,385771
a6	24,013	7,071	7,054022
CH	28,784	2,923	2,80497
CH3	30,61533	1,056	1,173984

MAE = 0,08906

^{1}H correlation



assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	29,907	150,33	150,6613
p5	59,486	123,37	122,9102
p4	43,546	137,71	137,8651
p3	57,474	124,16	124,7979
p2	17,513	160,54	162,2893
p1	126,658	58,54	59,88946
a1	132,662	54,72	54,25651
a2	8,021	171,67	171,1947
a3	40,906	139,91	140,342
a4	64,5425	120,07	118,1662
a5	51,969	129,76	129,9627
a6	59,779	124,32	122,6353
CH	134,818	52,59	52,23375
CH3	170,185	18,58	19,05243

MAE = 0,76239

^{13}C correlation

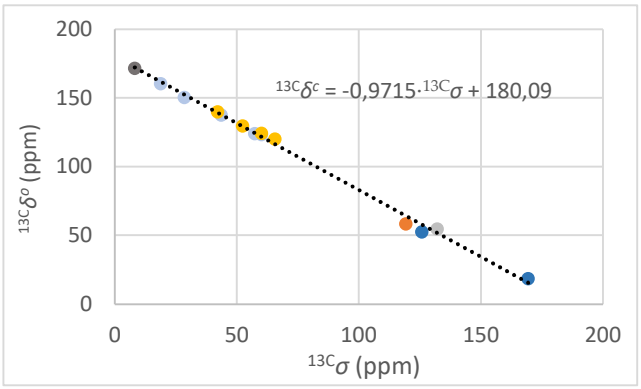
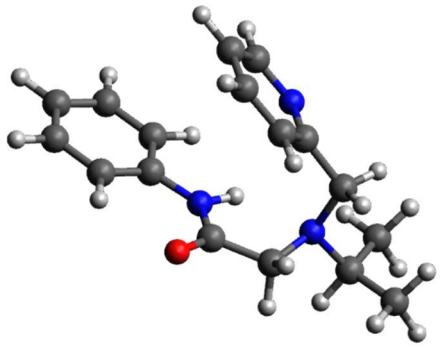


Figure S30. 2nd conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 3

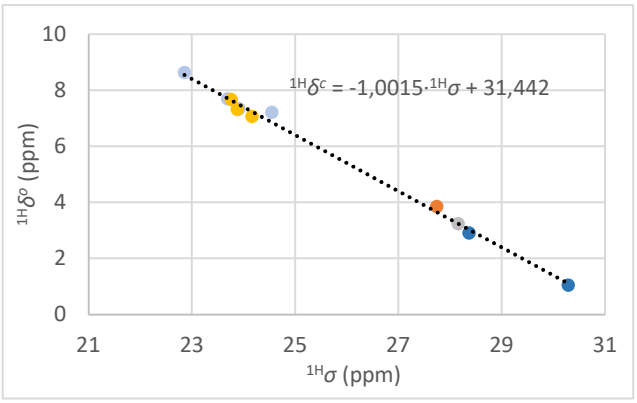


Free Energy (G) [kcal/mol]	population [%] 293 K
0.282	0.130

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,856	8,642	8,55171
p5	24,548	7,228	6,85717
p4	23,696	7,704	7,71045
p3	23,909	7,348	7,497136
p1	27,7415	3,85	3,6588877
a1	28,154	3,247	3,24576
a4	23,76	7,683	7,6463
a5	23,8795	7,329	7,5266807
a6	24,163	7,071	7,242755
CH	28,367	2,923	3,032449
CH3	30,28617	1,056	1,11040408

MAE = 0,12536



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	28,273	150,33	152,7259698
p5	60,315	123,37	121,408119
p4	43,621	137,71	137,7248346
p3	57,04	124,16	124,609104
p2	18,264	160,54	162,5087664
p1	129,152	58,54	54,1268352
a1	121,786	54,72	61,3263636
a2	8,941	171,67	171,6210666
a3	42,156	139,91	139,1567256
a4	65,6255	120,07	116,2176363
a5	52,4005	129,76	129,1437513
a6	60,021	124,32	121,6954746
CH	124,892	52,59	58,2905592
CH3	168,4675	18,58	15,6998655

MAE = 2,44901

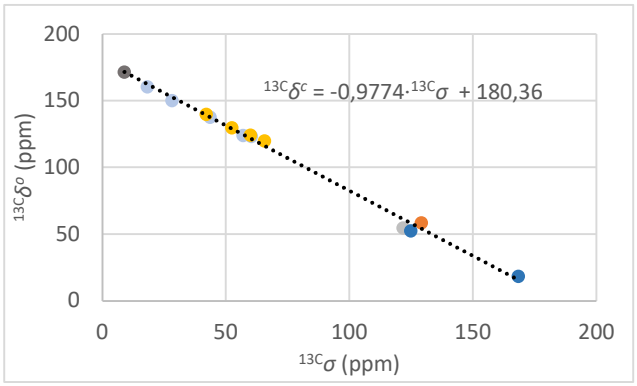
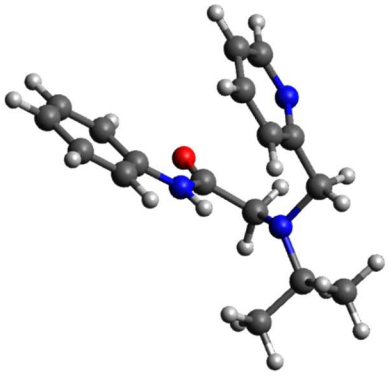


Figure S31. 3rd conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 4

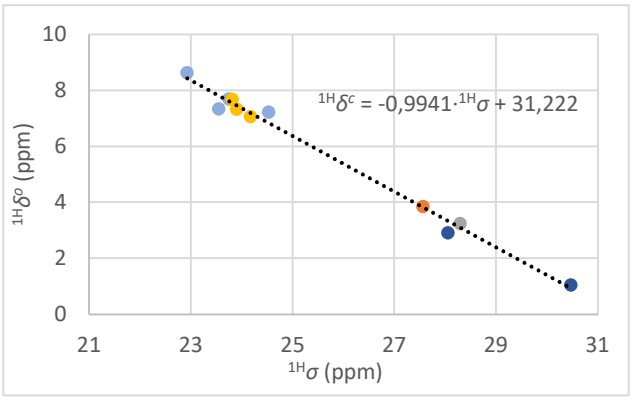


Free Energy (G) [kcal/mol]	population [%] 293 K
0.348	0.116

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,928	8,642	8,429275
p5	24,533	7,228	6,833745
p4	23,754	7,704	7,608149
p3	23,548	7,348	7,812933
p1	27,562	3,85	3,822616
a1	28,291	3,247	3,097917
a4	23,8135	7,683	7,549
a5	23,901	7,329	7,462016
a6	24,174	7,071	7,190627
CH	28,052	2,923	3,335507
CH3	30,47183	1,056	0,92995

MAE = 0,206312



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	30,883	150,33	150,1054
p5	60,086	123,37	121,6763
p4	42,926	137,71	138,3815
p3	55,665	124,16	125,9801
p2	18,165	160,54	162,4864
p1	119,072	58,54	64,25341
a1	132,065	54,72	51,60472
a2	8,093	171,67	172,2915
a3	42,266	139,91	139,024
a4	65,816	120,07	116,0981
a5	52,449	129,76	129,1109
a6	60,097	124,32	121,6656
CH	125,402	52,59	58,09115
CH3	169,2305	18,58	15,42411

MAE = 2,330351

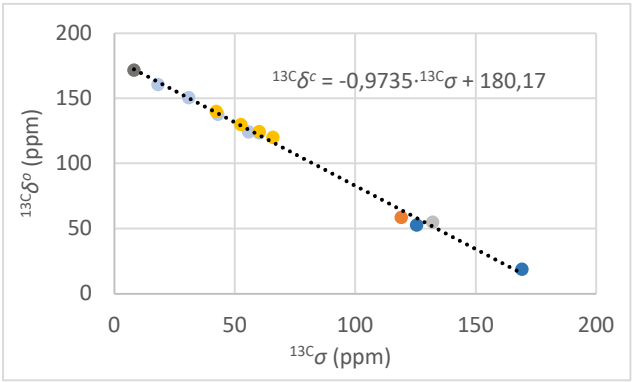
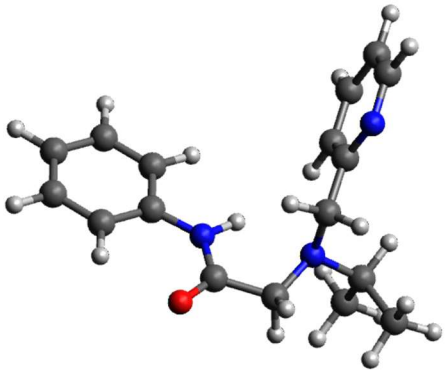


Figure S32. 4th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 5

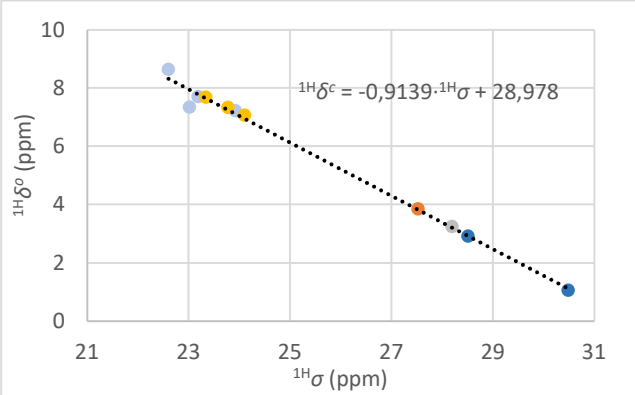


Free Energy (G) [kcal/mol]	population [%] 293 K
0.409	0.104

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,603	8,642	8,321118
p5	23,921	7,228	7,116598
p4	23,191	7,704	7,783745
p3	23,02	7,348	7,940022
p1	27,5245	3,85	3,823359
a1	28,1955	3,247	3,210133
a4	23,3395	7,683	7,648031
a5	23,779	7,329	7,246372
a6	24,106	7,071	6,947527
CH	28,51	2,923	2,922711
CH3	30,48417	1,056	1,11852

MAE = 0,133767



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	30,202	150,33	150,8533
p5	60,566	123,37	122,1836
p4	43,221	137,71	138,5607
p3	61,142	124,16	121,6397
p2	16,972	160,54	163,345
p1	125,352	58,54	61,01264
a1	132,006	54,72	54,72993
a2	8,506	171,67	171,3386
a3	41,341	139,91	140,3358
a4	65,194	120,07	117,8138
a5	51,9665	129,76	130,3032
a6	59,713	124,32	122,989
CH	134,218	52,59	52,64136
CH3	170,353	18,58	18,5227

MAE = 1,097471

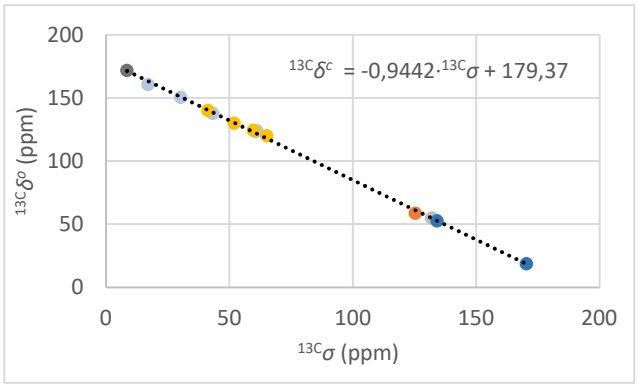
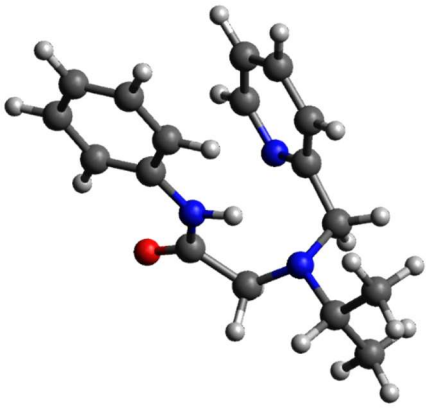


Figure S33. 5th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 6

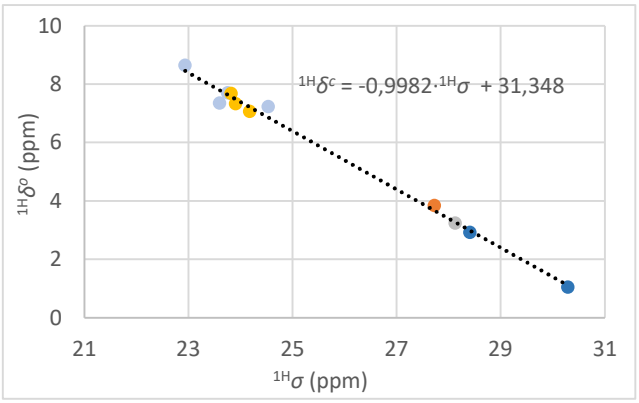


Free Energy (G) [kcal/mol]	population [%] 293 K
0.642	0.070

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,935	8,642	8,454283
p5	24,535	7,228	6,857163
p4	23,749	7,704	7,641748
p3	23,595	7,348	7,795471
p1	27,7265	3,85	3,671408
a1	28,127	3,247	3,271629
a4	23,8175	7,683	7,573372
a5	23,905	7,329	7,486029
a6	24,175	7,071	7,216515
CH	28,405	2,923	2,994129
CH3	30,286	1,056	1,116515

MAE = 0,165029



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	30,819	150,33	150,3413
p5	60,199	123,37	121,5812
p4	43,001	137,71	138,4163
p3	56,029	124,16	125,6632
p2	17,761	160,54	163,1238
p1	129,258	58,54	53,97934
a1	121,945	54,72	61,13804
a2	8,866	171,67	171,8311
a3	42,246	139,91	139,1554
a4	65,8345	120,07	116,0646
a5	52,4305	129,76	129,1858
a6	60,069	124,32	121,7085
CH	124,731	52,59	58,41082
CH3	168,3995	18,58	15,66373

MAE = 1,097471

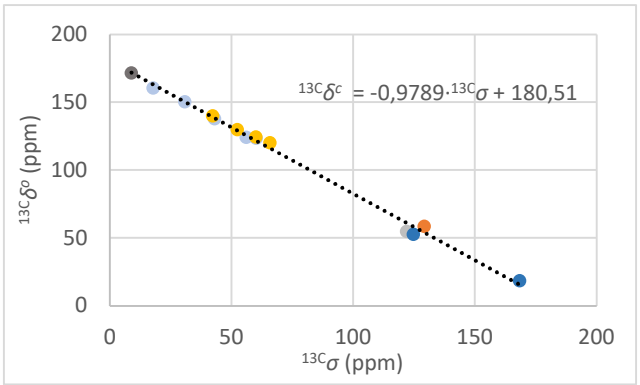
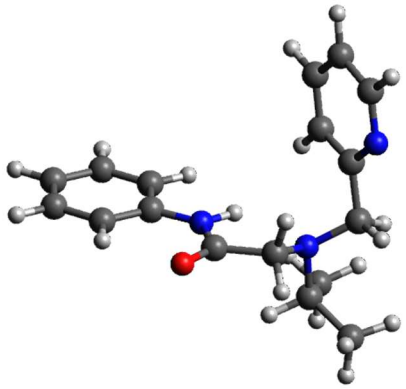


Figure S34. 6th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 7

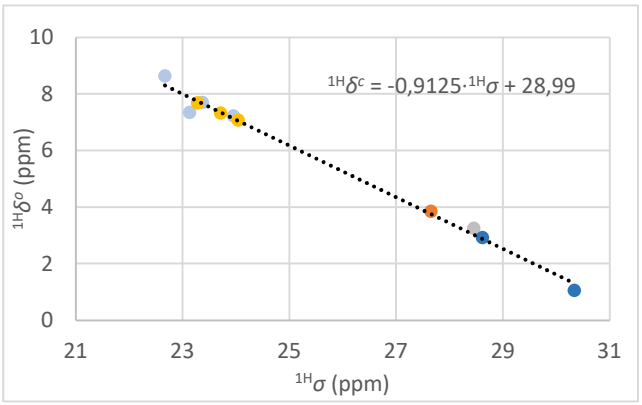


Free Energy (G) [kcal/mol]	population [%] 293 K
0.811	0.052

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,67	8,642	8,303625
p5	23,956	7,228	7,13015
p4	23,373	7,704	7,662138
p3	23,132	7,348	7,88205
p1	27,652	3,85	3,75755
a1	28,456	3,247	3,0239
a4	23,2845	7,683	7,742894
a5	23,7165	7,329	7,348694
a6	24,042	7,071	7,051675
CH	28,619	2,923	2,875163
CH3	30,3375	1,056	1,307031

MAE = 0,15686



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	31,166	150,33	149,7014
p5	59,807	123,37	122,5927
p4	43,906	137,71	137,643
p3	57,507	124,16	124,7696
p2	15,904	160,54	164,1469
p1	131,457	58,54	54,77595
a1	128,492	54,72	57,58232
a2	8,823	171,67	170,849
a3	41,184	139,91	140,2193
a4	65,386	120,07	117,3122
a5	51,966	129,76	130,0142
a6	59,658	124,32	122,7337
CH	130,634	52,59	55,55492
CH3	169,823	18,58	18,46253

MAE = 1,50906

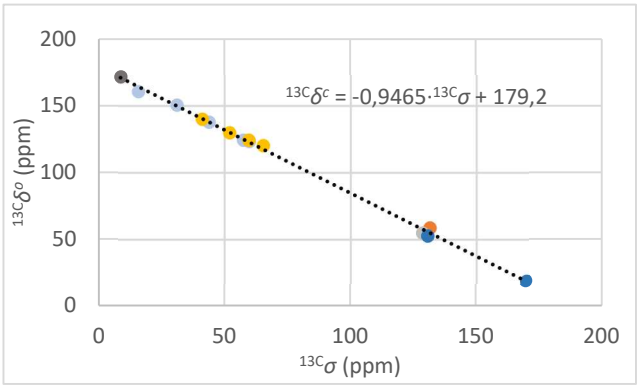
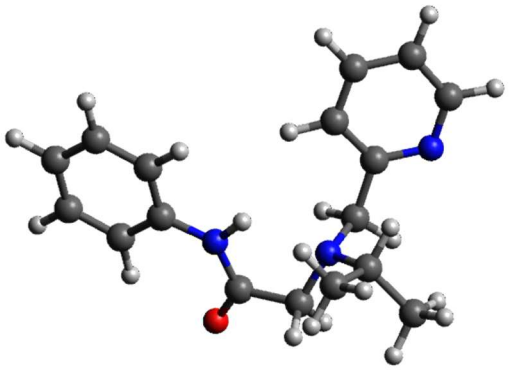


Figure S35. 7th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 8

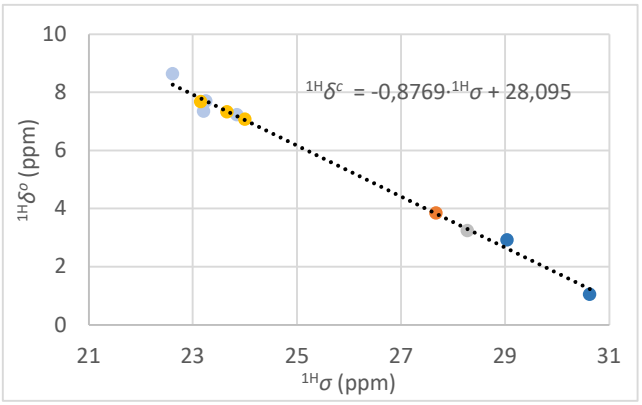


Free Energy (G) [kcal/mol]	population [%] 293 K
0.912	0.044

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,613	8,642	8,26566
p5	23,848	7,228	7,182689
p4	23,25	7,704	7,707075
p3	23,21	7,348	7,742151
p1	27,6745	3,85	3,827231
a1	28,274	3,247	3,301529
a4	23,154	7,683	7,791257
a5	23,6535	7,329	7,353246
a6	24,001	7,071	7,048523
CH	29,035	2,923	2,634209
CH3	30,62717	1,056	1,238038

MAE = 0,13836

^{1}H correlation



assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	31,166	150,33	149,7014
p5	59,807	123,37	122,5927
p4	43,906	137,71	137,643
p3	57,507	124,16	124,7696
p2	15,904	160,54	164,1469
p1	131,457	58,54	54,77595
a1	128,492	54,72	57,58232
a2	8,823	171,67	170,849
a3	41,184	139,91	140,2193
a4	65,386	120,07	117,3122
a5	51,966	129,76	130,0142
a6	59,658	124,32	122,7337
CH	130,634	52,59	55,55492
CH3	169,823	18,58	18,46253

MAE = 1,509062

^{13}C correlation

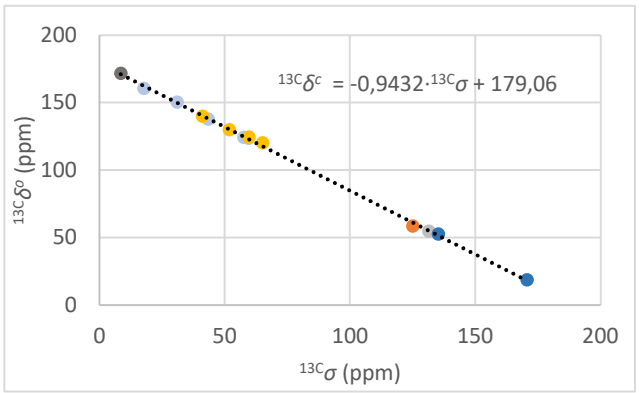
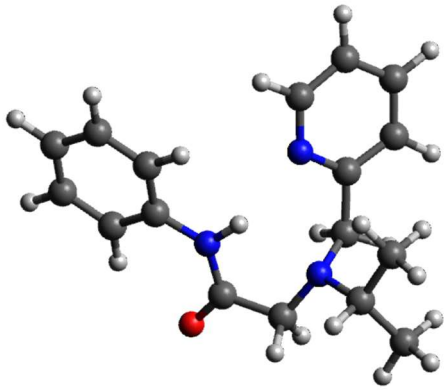


Figure S36. 8th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 9

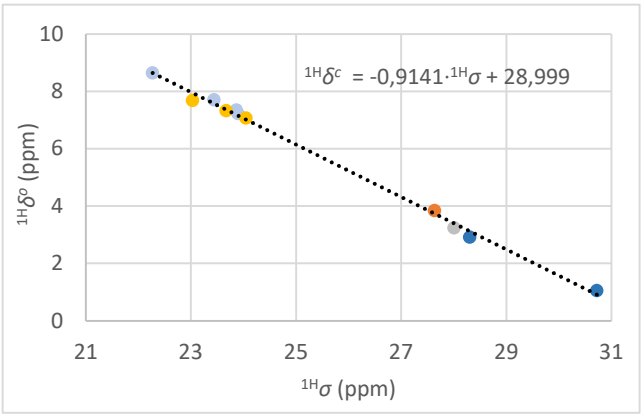


Free Energy (G) [kcal/mol]	population [%] 293 K
1.013	0.037

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,269	8,642	8,642907
p5	23,894	7,228	7,157495
p4	23,435	7,704	7,577067
p3	23,862	7,348	7,186746
p1	27,6335	3,85	3,739218
a1	28,0025	3,247	3,401915
a4	23,0305	7,683	7,94682
a5	23,6675	7,329	7,364538
a6	24,045	7,071	7,019466
CH	28,3	2,923	3,12997
CH3	30,721	1,056	0,916934

MAE = 0,120202

^{1}H correlation



assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	31,08	150,33	149,5539
p5	60,112	123,37	121,6744
p4	43,164	137,71	137,9496
p3	59,456	124,16	122,3044
p2	14,692	160,54	165,2913
p1	131,568	58,54	53,05525
a1	122,688	54,72	61,58271
a2	8,745	171,67	171,0022
a3	40,876	139,91	140,1468
a4	63,8125	120,07	118,1209
a5	52,187	129,76	129,2848
a6	59,724	124,32	122,047
CH	127,048	52,59	57,39581
CH3	169,286	18,58	16,83465

MAE = 2,41562

^{13}C correlation

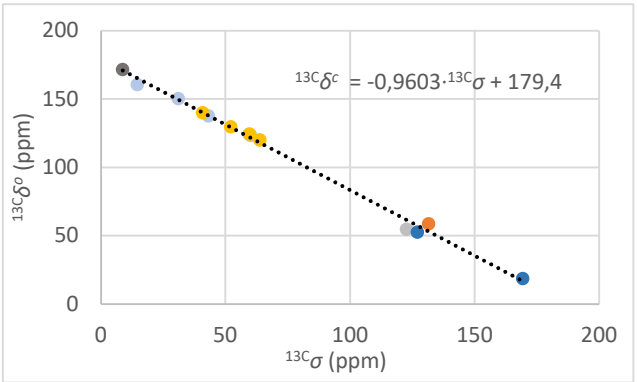
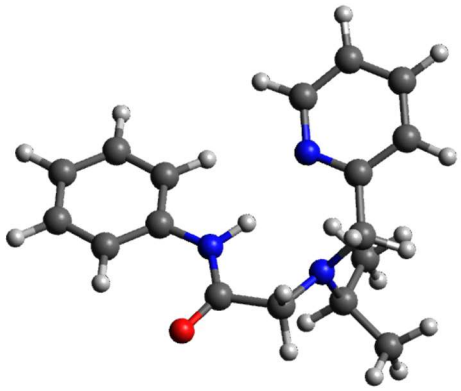


Figure S37. 9th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

L - Conformer 10

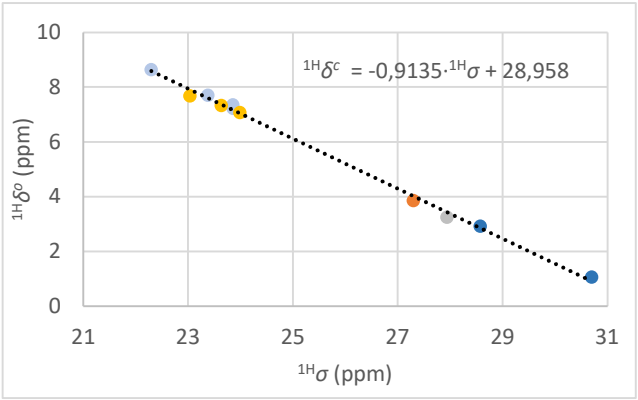


Free Energy (G) [kcal/mol]	population [%] 293 K
1.215	0.026

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,299	8,642	8,587864
p5	23,859	7,228	7,162804
p4	23,379	7,704	7,601284
p3	23,853	7,348	7,168285
p1	27,3015	3,85	4,01808
a1	27,938	3,247	3,436637
a4	23,0385	7,683	7,91233
a5	23,633	7,329	7,369255
a6	23,987	7,071	7,045876
CH	28,578	2,923	2,851997
CH3	30,69967	1,056	0,913854

MAE = 0,115213

^{1}H correlation



assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	30,541	150,33	149,4049
p5	60,206	123,37	121,2706
p4	43,193	137,71	137,4058
p3	60,939	124,16	120,5755
p2	12,715	160,54	166,3111
p1	128,96	58,54	56,06434
a1	121,672	54,72	62,97628
a2	5,754	171,67	172,9129
a3	40,47	139,91	139,9883
a4	64,4335	120,07	117,2613
a5	52,004	129,76	129,0494
a6	59,972	124,32	121,4926
CH	131,053	52,59	54,07933
CH3	169,6675	18,58	17,45734

MAE = 2,406871

^{13}C correlation

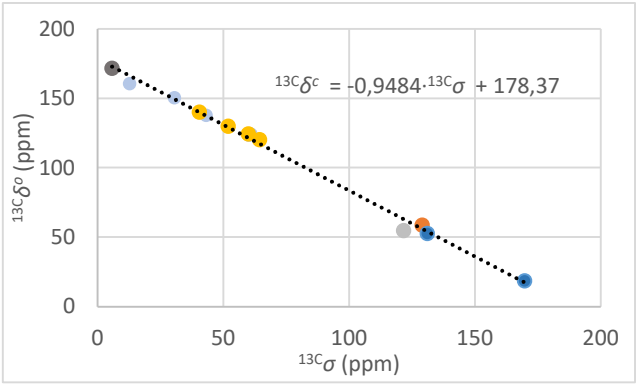
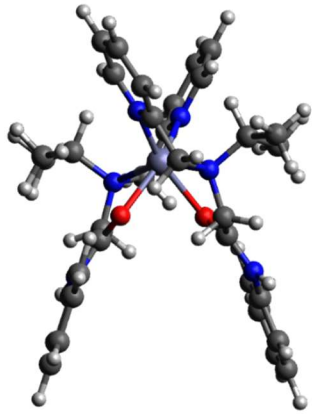


Figure S38. 10th conformer in free energy scale for **L**, with its calculated population at 293 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

$[Zn(L)_2]^{2+}$ - Conformer 1

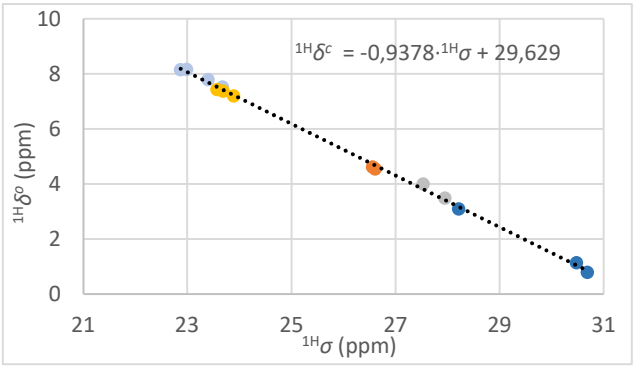


Free Energy (G) [kcal/mol]	population [%]	
	293 K	295 K
0	0.828	0.869

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,87	8,147	8,181514
p5	23,6715	7,514	7,429867
p4	22,9845	8,155	8,074136
p3	23,395	7,786	7,689169
p1	26,559	4,610	4,72197
p1'	26,6095	4,542	4,674611
a1'	27,947	3,488	3,420303
a1	27,5315	4,001	3,809959
a4	23,5705	7,431	7,524585
a5	23,68975	7,368	7,412752
a6	23,8915	7,195	7,223551
CH	28,2115	3,085	3,172255
C'H'3	30,6875	0,794	0,850262
CH3	30,4745	1,133	1,050014

MAE = 0,085218



^{13}C correlation

assign.	$^{13C}\sigma$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	30,641	149,44	150,2714
p5	57,031	126,55	125,1323
p4	38,3285	143	142,9483
p3	56,433	126,61	125,7019
p2	21,642	156,61	158,8438
p1	126,3545	58,72	59,0947
a1	132,788	52,07	52,96615
a2	6,0705	173,99	173,6772
a3	43,711	137,03	137,8209
a4	62,11775	122,15	120,2866
a5	51,66925	130,23	130,2399
a6	56,276	127,17	125,8515
CH	131,881	52,14	53,83016
C'H'3	165,8365	20,94	21,48415
CH3	176,192	13,1	11,6195

MAE = 0,98158875

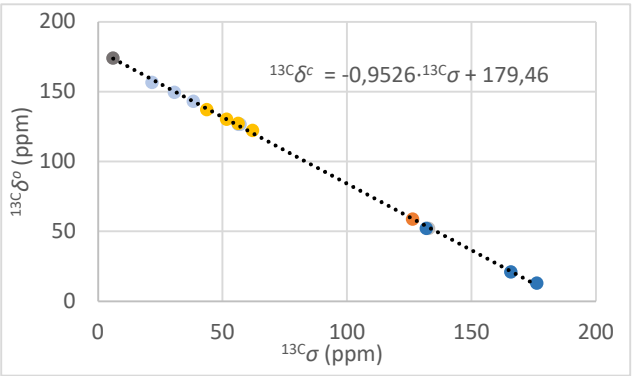
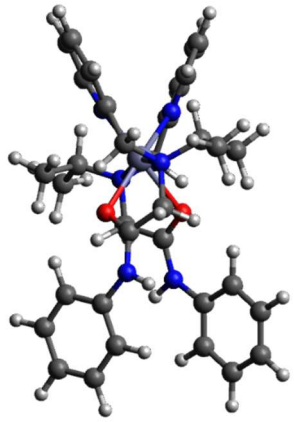


Figure S39. Lowest energy conformer of $[Zn(L)_2]^{2+}$ (G=0), with its calculated populations at 293 and 253 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

$[Zn(L)_2]^{2+}$ - Conformer 2

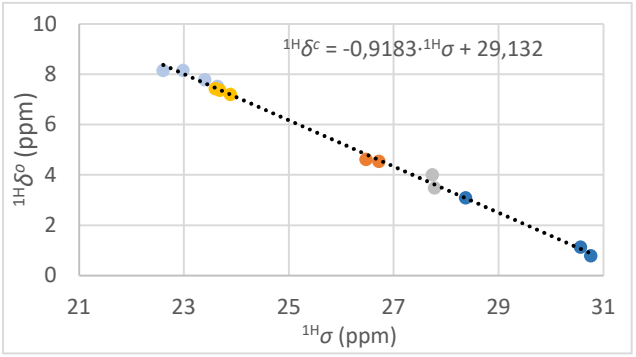


Free Energy (G) [kcal/mol]	population [%]	
	293 K	295 K
1.029	0.141	0.112

^{1}H correlation

assign.	$^{1H}\sigma$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	22,6055	8,147	8,373369
p5	23,643	7,514	7,420633
p4	22,9805	8,155	8,029007
p3	23,3955	7,786	7,647912
p1	26,474	4,61	4,820926
p1'	26,716	4,542	4,598697
a1'	27,782	3,488	3,619789
a1	27,736	4,001	3,662031
a4	23,6005	7,431	7,459661
a5	23,68475	7,368	7,382294
a6	23,886	7,195	7,197486
CH	28,3685	3,085	3,081206
C'H'3	30,75767	0,794	0,887235
CH3	30,56317	1,133	1,065844

MAE = 0,109416



^{13}C correlation

assign.	$^{13C}\sigma^{c}$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	31,1925	149,44	149,8035
p5	57,5585	126,55	123,8567
p4	38,352	143	142,7578
p3	56,672	126,61	124,7291
p2	20,011	156,61	160,8072
p1	123,9785	58,72	58,49276
a1	126,9895	52,07	55,52963
a2	6,041	173,99	174,5551
a3	43,7625	137,03	137,4333
a4	62,0905	122,15	119,3967
a5	51,67225	130,23	129,6493
a6	56,2355	127,17	125,1586
CH	125,764	52,14	56,73565
C'H'3	165,2275	20,94	17,89962
CH3	170,1535	13,1	13,05194

MAE = 1,804113

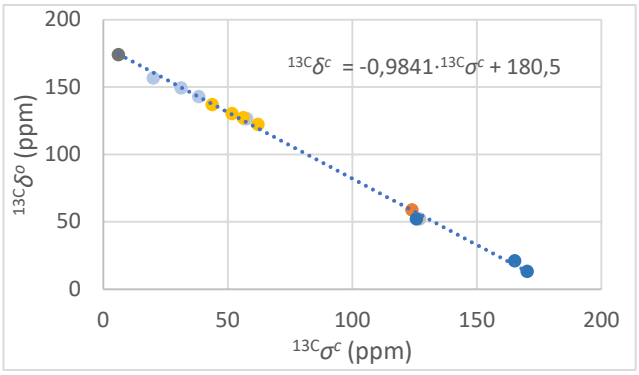
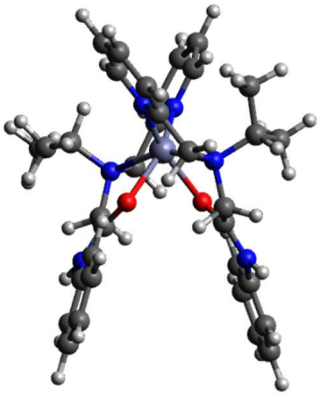


Figure S40. 2nd conformer in free energy scale for **$[Zn(L)_2]^{2+}$**, with its calculated populations at 293 and 253 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

$[Zn(L)_2]^{2+}$ - Conformer 3

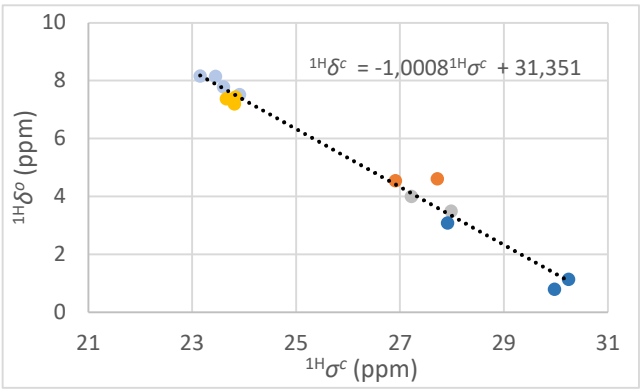


Free Energy (G) [kcal/mol]	population [%]	
	293 K	295 K
1.913	0.031	0.019

^{1}H correlation

assign.	$^{1H}\sigma^{c}$	$^{1H}\delta^{o}$	$^{1H}\delta^{c}$
p6	23,4465	8,147	7,716928
p5	23,911	7,514	7,248712
p4	23,152	8,155	8,013784
p3	23,6015	7,786	7,560688
p1	27,7205	4,61	3,408736
p1'	26,913	4,542	4,222696
a1'	27,984	3,488	3,143128
a1	27,2205	4,001	3,912736
a4	23,83325	7,431	7,327084
a5	23,6565	7,368	7,505248
a6	23,814	7,195	7,346488
CH	27,917	3,085	3,210664
C'H'3	29,972	0,794	1,139224
CH3	30,24467	1,133	0,864376

MAE = 0,29626829



^{13}C correlation

assign.	$^{13C}\sigma^{c}$	$^{13C}\delta^{o}$	$^{13C}\delta^{c}$
p6	31,334	149,44	149,9169
p5	56,7165	126,55	125,3695
p4	38,9635	143	142,5384
p3	57,2265	126,61	124,8763
p2	21,969	156,61	158,9738
p1	126,7185	58,72	57,67054
a1	132,4965	52,07	52,08263
a2	5,0095	173,99	175,3753
a3	44,1305	137,03	137,5414
a4	62,354	122,15	119,9174
a5	51,7425	130,23	130,1798
a6	56,3765	127,17	125,6983
CH	128,974	52,14	55,48924
C'H'3	164,7095	20,94	20,92944
CH3	172,7255	13,1	13,17717

MAE = 1,091117

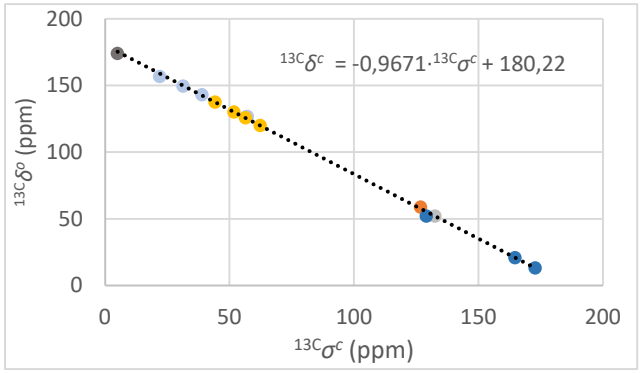


Figure S41. 3rd conformer in free energy scale for **$[Zn(L)_2]^{2+}$**, with its calculated populations at 293 and 253 K. In tables are data for the DFT calculated shieldings ($^{1H}\sigma$ or $^{13C}\sigma$) and observed chemical shifts ($^{1H}\delta^{o}$ or $^{13C}\delta^{o}$) and in diagrams are linear regression equations used for evaluation of the calculated chemical shits ($^{1H}\delta^{c}$ or $^{13C}\delta^{c}$) with Mean Absolute Error (MAE) for this conformer.

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,692	6,84
^{3}J(p4,p5)	6,64	7,5
^{3}J(p5,p6)	4,199	4,8
^{4}J(p4,p6)	1,386	1,73
^{4}J(p3,p5)	0,829	0,95
^{5}J(p3,p6)	1,023	0,83
^{3}J(a4,a5)	7,184	8,16
^{3}J(a5,a6)	6,3935	7,31
^{4}J(a4,a4)	2	2,27
^{4}J(a5,a5)	1,206	1,53
^{5}J(a4,a5)	0,6545	0,47
^{4}J(a4,a6)	0,829	1,13
^{3}J(CH,CH$_3$)	6,023833	6,62

MAE = 0,4489

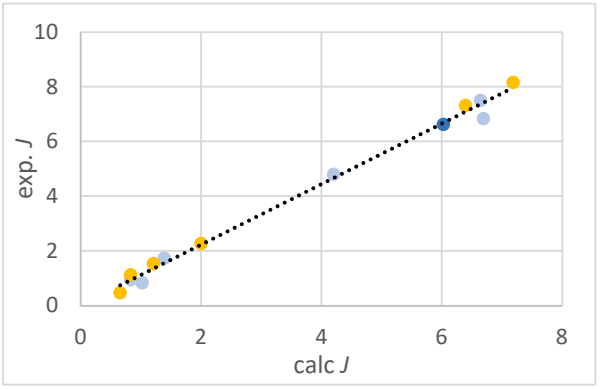


Figure S42. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 1 of **L**.

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,69	6,84
^{3}J(p4,p5)	6,637	7,5
^{3}J(p5,p6)	4,164	4,8
^{4}J(p4,p6)	1,378	1,73
^{4}J(p3,p5)	0,833	0,95
^{5}J(p3,p6)	1,025	0,83
^{3}J(a4,a5)	7,19	8,16
^{3}J(a5,a6)	6,3825	7,31
^{4}J(a4,a4)	2,015	2,27
^{4}J(a5,a5)	1,238	1,53
^{5}J(a4,a5)	0,6645	0,47
^{4}J(a4,a6)	0,8445	1,13
^{3}J(CH,CH$_3$)	5,993167	6,62

MAE = 0,45115

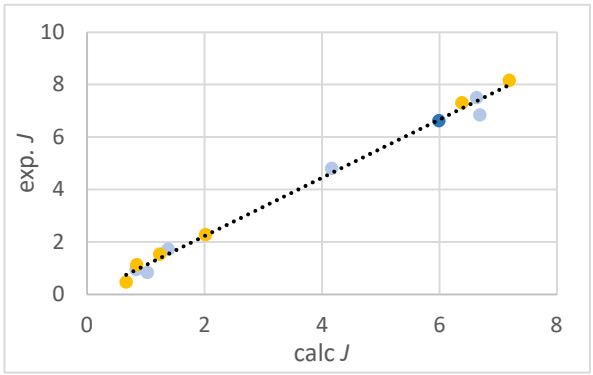


Figure S43. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 2 of **L**-

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,715	6,84
^{3}J(p4,p5)	6,633	7,5
^{3}J(p5,p6)	4,209	4,8
^{4}J(p4,p6)	1,383	1,73
^{4}J(p3,p5)	0,836	0,95
^{5}J(p3,p6)	1,022	0,83
^{3}J(a4,a5)	7,1795	8,16
^{3}J(a5,a6)	6,395	7,31
^{4}J(a4,a4)	2,002	2,27
^{4}J(a5,a5)	1,212	1,53
^{5}J(a4,a5)	0,6595	0,47
^{4}J(a4,a6)	0,837	1,13
^{3}J(CH,CH$_3$)	6,015833	6,62

MAE = 0,4465

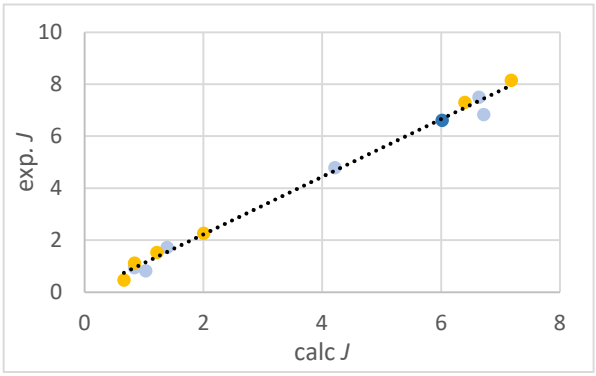


Figure S44. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 3 of **L**.

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,845	6,84
^{3}J(p4,p5)	6,522	7,5
^{3}J(p5,p6)	4,344	4,8
^{4}J(p4,p6)	1,365	1,73
^{4}J(p3,p5)	0,813	0,95
^{5}J(p3,p6)	1,068	0,83
^{3}J(a4,a5)	7,1805	8,16
^{3}J(a5,a6)	6,3955	7,31
^{4}J(a4,a4)	2,01	2,27
^{4}J(a5,a5)	1,21	1,53
^{5}J(a4,a5)	0,6505	0,47
^{4}J(a4,a6)	0,8265	1,13
^{3}J(CH,CH$_3$)	6,017333	6,62

MAE = 0,44151

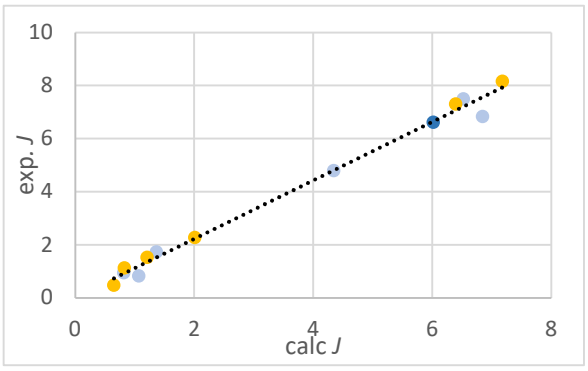


Figure S45. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 4 of **L**.

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	7,001	6,84
^{3}J(p4,p5)	6,524	7,5
^{3}J(p5,p6)	4,204	4,8
^{4}J(p4,p6)	1,395	1,73
^{4}J(p3,p5)	0,843	0,95
^{5}J(p3,p6)	1,062	0,83
^{3}J(a4,a5)	7,1745	8,16
^{3}J(a5,a6)	6,396	7,31
^{4}J(a4,a4)	2,039	2,27
^{4}J(a5,a5)	1,227	1,53
^{5}J(a4,a5)	0,664	0,47
^{4}J(a4,a6)	0,833	1,13
^{3}J(CH,CH$_3$)	5,999167	6,62

MAE = 0,45787

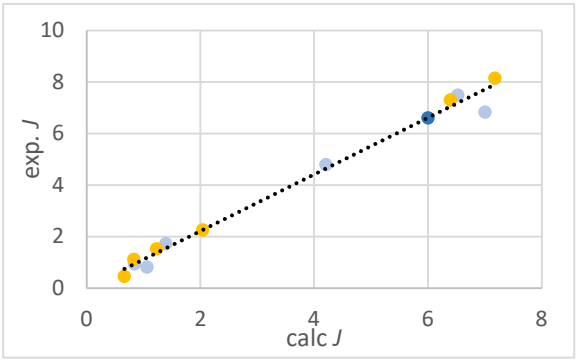


Figure S46. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 5 of **L.**

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,857	6,84
^{3}J(p4,p5)	6,522	7,5
^{3}J(p5,p6)	4,337	4,8
^{4}J(p4,p6)	1,37	1,73
^{4}J(p3,p5)	0,829	0,95
^{5}J(p3,p6)	1,07	0,83
^{3}J(a4,a5)	7,163	8,16
^{3}J(a5,a6)	6,4035	7,31
^{4}J(a4,a4)	2,014	2,27
^{4}J(a5,a5)	1,213	1,53
^{5}J(a4,a5)	0,6525	0,47
^{4}J(a4,a6)	0,8305	1,13
^{3}J(CH,CH$_3$)	6,0235	6,62

MAE = 0,44108

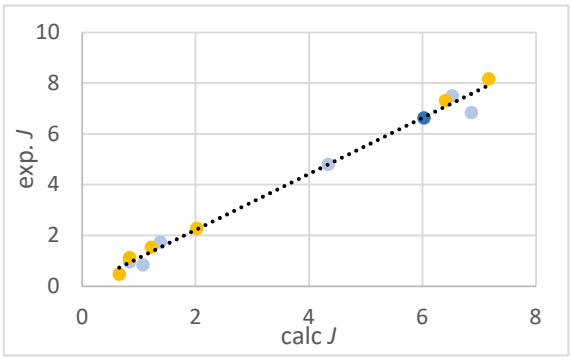


Figure S47. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 6 of **L.**

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,952	6,84
^{3}J(p4,p5)	6,436	7,5
^{3}J(p5,p6)	4,365	4,8
^{4}J(p4,p6)	1,36	1,73
^{4}J(p3,p5)	0,849	0,95
^{5}J(p3,p6)	1,078	0,83
^{3}J(a4,a5)	7,1745	8,16
^{3}J(a5,a6)	6,3985	7,31
^{4}J(a4,a4)	2,022	2,27
^{4}J(a5,a5)	1,22	1,53
^{5}J(a4,a5)	0,666	0,47
^{4}J(a4,a6)	0,8325	1,13
^{3}J(CH,CH$_3$)	6,004167	6,62

MAE = 0,45341

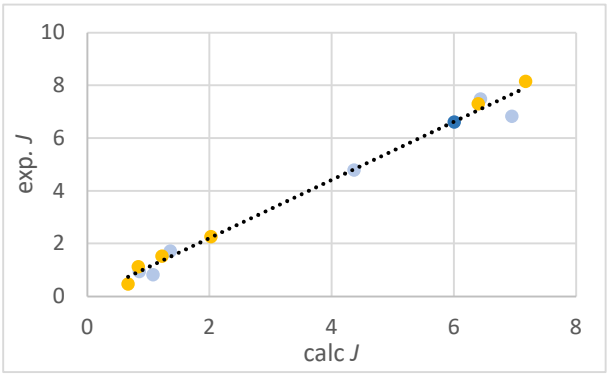


Figure S48. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 7 of **L.**

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,907	6,84
^{3}J(p4,p5)	6,509	7,5
^{3}J(p5,p6)	4,338	4,8
^{4}J(p4,p6)	1,364	1,73
^{4}J(p3,p5)	0,818	0,95
^{5}J(p3,p6)	1,076	0,83
^{3}J(a4,a5)	7,1785	8,16
^{3}J(a5,a6)	6,398	7,31
^{4}J(a4,a4)	2,017	2,27
^{4}J(a5,a5)	1,211	1,53
^{5}J(a4,a5)	0,6585	0,47
^{4}J(a4,a6)	0,824	1,13
^{3}J(CH,CH$_3$)	6,021167	6,62

MAE = 0,44791

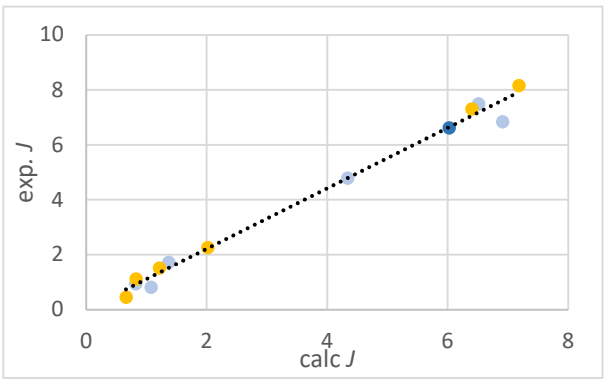


Figure S49. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 8 of **L.**

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,81	6,84
^{3}J(p4,p5)	6,529	7,5
^{3}J(p5,p6)	4,251	4,8
^{4}J(p4,p6)	1,374	1,73
^{4}J(p3,p5)	0,819	0,95
^{5}J(p3,p6)	1,047	0,83
^{3}J(a4,a5)	7,2055	8,16
^{3}J(a5,a6)	6,3805	7,31
^{4}J(a4,a4)	2,007	2,27
^{4}J(a5,a5)	1,247	1,53
^{5}J(a4,a5)	0,671	0,47
^{4}J(a4,a6)	0,8525	1,13
^{3}J(CH,CH$_3$)	6,031667	6,62

MAE = 0,44237

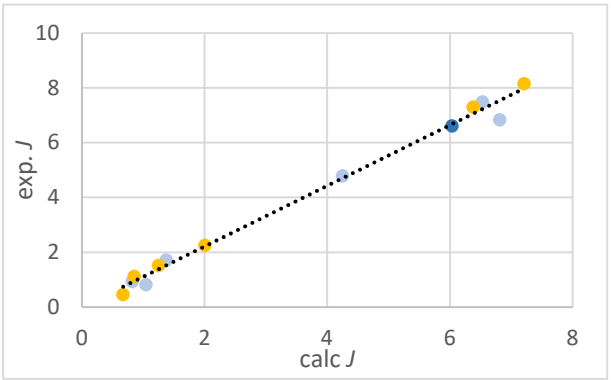


Figure S50. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 9 of **L.**

assign.	calc. *J* (Hz)	exp. *J* (Hz)
^{3}J(p3,p4)	6,823	6,84
^{3}J(p4,p5)	6,479	7,5
^{3}J(p5,p6)	4,273	4,8
^{4}J(p4,p6)	1,361	1,73
^{4}J(p3,p5)	0,807	0,95
^{5}J(p3,p6)	1,059	0,83
^{3}J(a4,a5)	7,177	8,16
^{3}J(a5,a6)	6,387	7,31
^{4}J(a4,a4)	1,99	2,27
^{4}J(a5,a5)	1,239	1,53
^{5}J(a4,a5)	0,662	0,47
^{4}J(a4,a6)	0,852	1,13
^{3}J(CH,CH_3)	5,969833	6,62
	MAE = 0,45409	

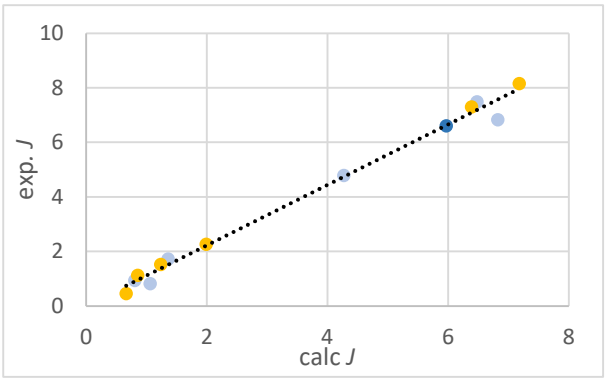


Figure S51. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 10 of **L.**

assign.	calc. *J* (Hz) (-40 ºC)	exp. *J* (Hz) (-40 ºC)
^{2}J(p1,p1')	-15,2135	-15,56
^{2}J(a1,a1')	-17,502	-16,96
^{3}J(p3,p4)	6,8695	7,66
^{3}J(p4,p5)	6,6765	7,57
^{3}J(p5,p6)	4,7215	5,71
^{4}J(p4,p6)	1,2315	1,72
^{4}J(p3,p5)	0,905	0,78
^{5}J(p3,p6)	0,995	0,70
^{3}J(a4,a5)	7,23025	8,10
^{3}J(a5,a6)	6,46825	7,43
^{4}J(a4,a4)	2,097	2,38
^{4}J(a5,a5)	1,185	1,40
^{5}J(a4,a5)	0,6625	0,44
^{4}J(a4,a6)	0,77725	0,97
^{3}J(CH,C'H'$_3$)	6,139667	6,56
^{3}J(CH,CH_3)	5,736167	6,47
^{4}J(CH_3,C'H'$_3$)	0,350111	0,22
	MAE = 0,499913	

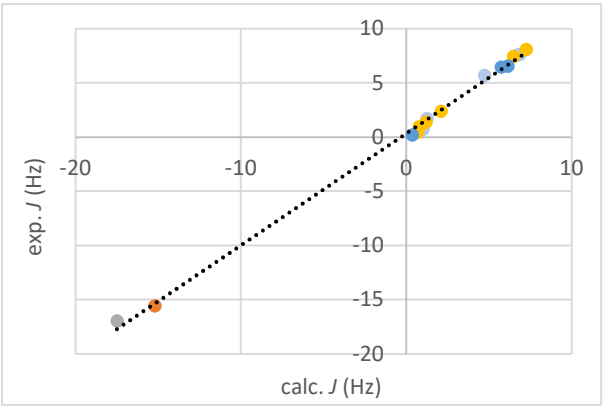


Figure S52. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 1 of **[Zn(L)$_2$]$^{2+}$**.

assign.	calc. *J* (Hz) (-40 °C)	exp. *J* (Hz) (-40 °C)
^{2}J(p1,p1')	-16,085	-15,56
^{2}J(a1,a1')	-17,6035	-16,96
^{3}J(p3,p4)	6,896	7,66
^{3}J(p4,p5)	6,6235	7,57
^{3}J(p5,p6)	4,829	5,71
^{4}J(p4,p6)	1,2305	1,72
^{4}J(p3,p5)	0,9195	0,78
^{5}J(p3,p6)	0,982	0,70
^{3}J(a4,a5)	7,24325	8,10
^{3}J(a5,a6)	6,46475	7,43
^{4}J(a4,a4)	2,1015	2,38
^{4}J(a5,a5)	1,194	1,40
^{5}J(a4,a5)	0,66125	0,44
^{4}J(a4,a6)	0,78175	0,97
^{3}J(CH,C'H'$_3$)	6,055167	6,56
^{3}J(CH,CH$_3$)	5,728167	6,47
^{4}J(CH$_3$,C'H'$_3$)	0,400056	0,22
	MAE = 0,518454	

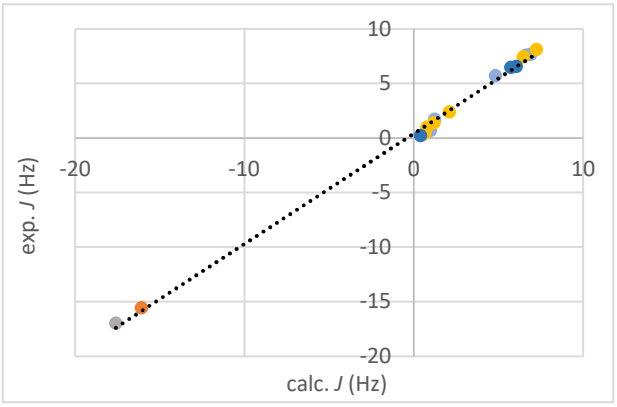


Figure S53. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 2 of **[Zn(L)$_2$]$^{2+}$**.

assign.	calc. *J* (Hz) (-40 °C)	exp. *J* (Hz) (-40 °C)
^{2}J(p1,p1')	-15,957	-15,56
^{2}J(a1,a1')	-17,265	-16,96
^{3}J(p3,p4)	6,928	7,66
^{3}J(p4,p5)	6,63	7,57
^{3}J(p5,p6)	4,7755	5,71
^{4}J(p4,p6)	1,225	1,72
^{4}J(p3,p5)	0,9155	0,78
^{5}J(p3,p6)	0,9985	0,70
^{3}J(a4,a5)	7,20575	8,10
^{3}J(a5,a6)	6,46575	7,43
^{4}J(a4,a4)	2,096	2,38
^{4}J(a5,a5)	1,184	1,40
^{5}J(a4,a5)	0,66325	0,44
^{4}J(a4,a6)	0,779	0,97
^{3}J(CH,C'H'$_3$)	6,134	6,56
^{3}J(CH,CH$_3$)	5,806	6,47
^{4}J(CH$_3$,C'H'$_3$)	0,345333	0,22
	MAE = 0,483858	

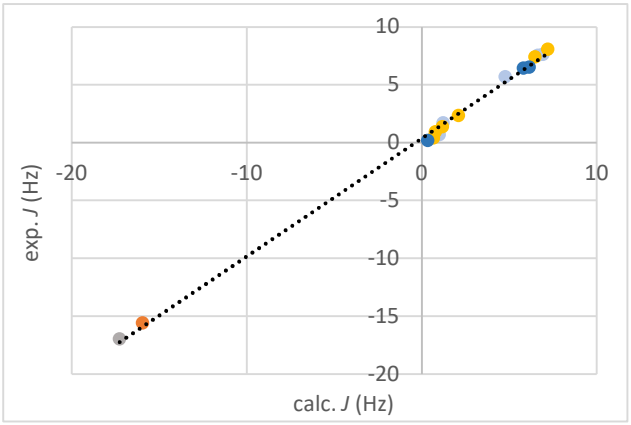


Figure S54. Correlation diagram between observed and calculated ^{1}H-^{1}H *J* couplings for conformer 3 of **[Zn(L)$_2$]$^{2+}$**.

X-ray crystallography

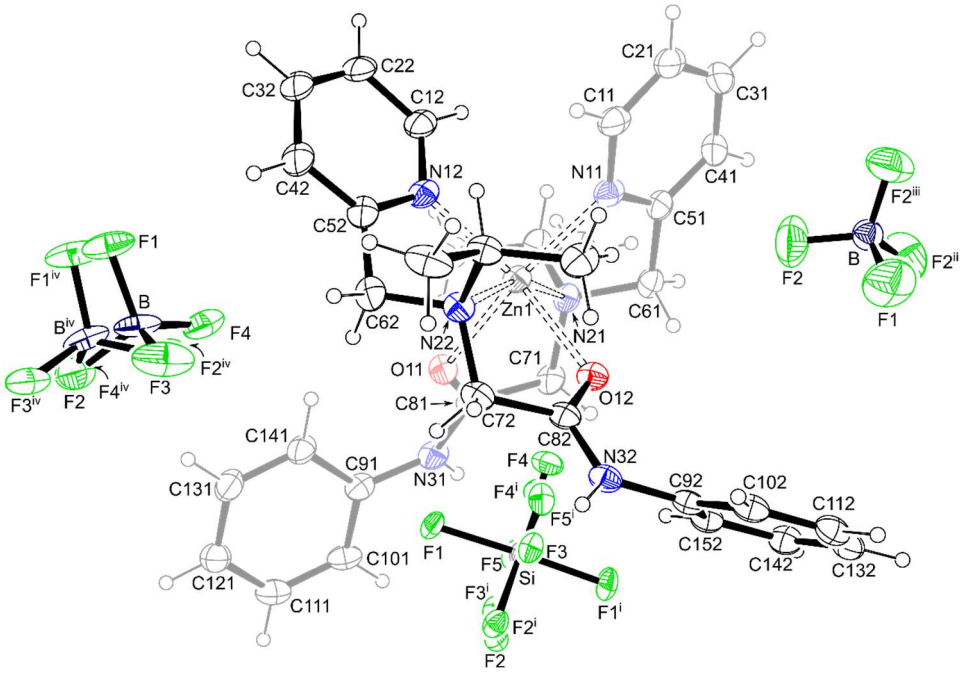


Figure S55. The ORTEP-III [ref. 32 in manuscript] diagram of the **$[Zn(L)_2]_2[SiF_6][BF_4]_2$** with complete atom labbeling scheme. Symmetry codes: (i) 1/2-*y*, 1/2-*x*, 1/2-*z*; (ii) 1/2-*z*, 1/2-*x*, *z*; (iii) 1/2-*y*, *z*, 1/2-*x*; (iv) 3/2-*x*, *y*, 1/2-*z*.

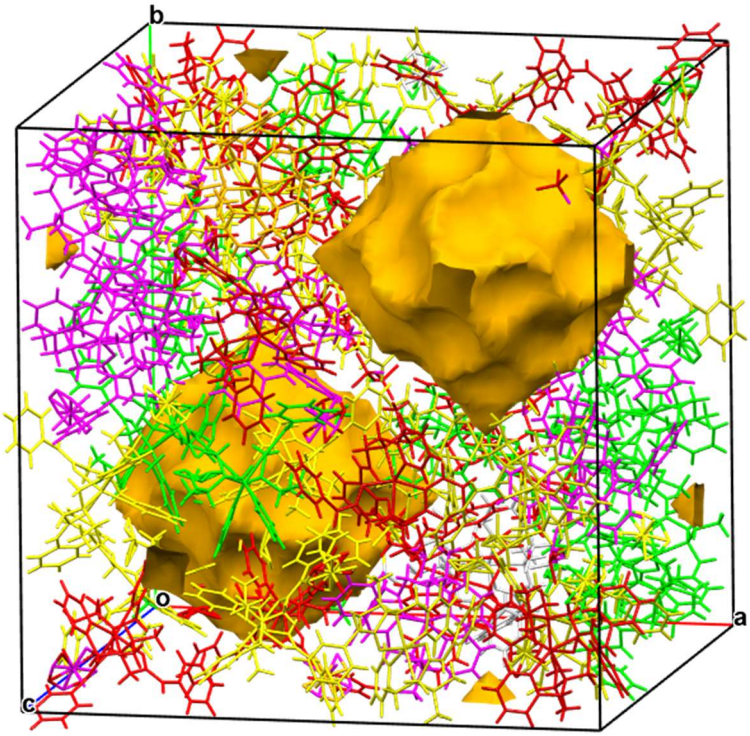


Figure S56. Crystal packing of cations and anions in solid-state structure of **$[Zn(L)_2]_2[SiF_6][BF_4]_2$** with representation of solvent accessible areas in unit cell. Cations and anions are shown in different colours.

Table S1. Comparison of bonds and selected angles for the most stable *mer* - **[Zn(L$_2$)]$^{2+}$** cation obtained from DFT-NMR analysis (Figure S39) and the *mer*- **[Zn(L$_2$)]$^{2+}$** cation obtained from the single-crystal X-ray diffraction.

parameter [1]		**[Zn(L$_2$)]$^{2+}$ from DFT/NMR** (C_2 symmetry)	**[Zn(L$_2$)]$^{2+}$ from X-ray diffraction**	
bonds				
L1	**L2**		**L1**	**L2**
Zn-N11	Zn-N12	2.120	2.101(3)	2.107(2)
Zn-N21	Zn-N22	2.241	2.250(2)	2.228(2)
Zn-O11	Zn-O12	2.178	2.140(2)	2.153(2)
N11-C51	N12-C52	1.344	1.347(4)	1.358(4)
N11-C11	N12-C12	1.342	1.350(4)	1.339(4)
C11-C21	C12-C22	1.386	1.364(5)	1.384(4)
C21-C31	C22-C32	1.391	1.376(6)	1.388(6)
C31-C41	C32-C42	1.389	1.387(6)	1.381(6)
C41-C51	C42-C52	1.389	1.382(5)	1.378(4)
C51-C61	C52-C62	1.506	1.501(4)	1.492(5)
C61-N21	C62-N22	1.481	1.481(4)	1.489(4)
N21-C71	N22-C72	1.468	1.471(4)	1.473(4)
C71-C81	C72-C82	1.522	1.520(4)	1.523(4)
C81-O11	C82-O22	1.244	1.242(3)	1.246(3)
C81-N31	C82-N32	1.342	1.333(4)	1.331(4)
N31-C91	N32-C92	1.414	1.413(4)	1.427(4)
C91-C101	C92-C102	1.399	1.387(4)	1.387(4)
C91-C141	C92-C142	1.388	1.394(4)	1.394(4)
C101-C111	C102-C112	1.394	1.389(5)	1.382(4)
C111-C121	C112-C122	1.392	1.389(5)	1.391(4)
C121-C131	C122-C132	1.392	1.382(4)	1.382(4)
C131-C141	C132-C142	1.398	1.381(5)	1.384(4)
N21-C151	N22-C152	1.512	1.509(4)	1.514(3)
C151-C161	C152-C162	1.530	1.537(5)	1.529(4)
C151-C171	C152-C172	1.524	1.515(4)	1.521(5)
selected angles [2]				
N11-Zn-N21	N12-Zn-N22	78.2	78.54(9)	78.08(9)N
N21-Zn-O11	N22-Zn-O12	76.6	76.42(8)	77.52(8)
N11-Zn-O11	N12-Zn-O12	154.8	154.84(9)	155.56(8)
N11-Zn-N22	N12-Zn-N21	117.1	117.57(9)	114.53(9)
N11-Zn-O12	N12-Zn-O11	94.8	95.50(8)	93.77(9)
N21-Zn-O12	N22-Zn-O11	87.4	89.36(8)	87.41(8)
N11-Zn-N12		96.2	94.40(10)	
N21-Zn-N22		158.3	159.80(9)	
O11-Zn-O12		84.6	86.63(8)	
Zn-N11-C51	Zn-N12-C52	113.2	113.42(19)	112.9(2)
N11-C51-C61	N12-C52-C62	116.1	115.0(3)	115.6(2)
C51-C61-N21	C52-C62-N22	110.2	109.4(2)	109.1(2)
Zn-N21-C61	Zn-N22-C62	100.6	99.34(16)	100.06(16)
Zn-N21-C71	Zn-N22-C72	106.5	104.67(16)	105.64(15)
N21-C71-C81	N22-C72-C82	110.5	109.5(2)	109.8(2)
C71-C81-O11	C72-C82-O12	121.0	119.5(2)	120.4(3)
Zn-O11-C81	Zn-O12-C82	114.5	115.74(18)	114.53(18)
Zn-N21-C151	Zn-N22-C152	112.3	116.07(17)	115.18(17)
N21-C151-C161	N22-C152-C162	114.0	113.8(3)	113.0(2)
N21-C151-C171	N22-C152-C172	111.4	112.1(3)	111.3(2)
C161-C151-C171	C162-C152-C172	110.2	109.7(3)	111.3(3)

[1] Labels are according to crystal structure, Figure S55

[2] Angles at metal atom, angles in chelating rings and angles in isopropyl groups.

Table S2. Comparison of selected torsion angles for the most stable *mer* - **[Zn(L$_2$)]$^{2+}$** cation obtained from DFT-NMR analysis (Figure S39) and the *mer* - **[Zn(L$_2$)]$^{2+}$** cation obtained from the single-crystal X-ray diffraction.

torsion angle [1]		**[Zn(L$_2$)]$^{2+}$ from DFT-NMR** (C_2 symmetry)	**[Zn(L$_2$)]$^{2+}$ from X-ray diffraction**	
L1	**L2**		**L1**	**L2**
O12-Zn-N11-C51	O11-Zn-N12-C52	67.7	73.2(2)	67.4(2)
Zn-N11-C51-C61	Zn-N12-C52-C62	-4.2	-10.6(3)	-5.2(3)
N11-C51-C61-N21	N12-C52-C62-N22	38.8	45.4(3)	41.1(3)
C51-C61-N21-C71	C52-C62-N22-C72	-161.3	-161.6(2)	-162.7(2)
C61-N21-C71-C81	C62-N22-C72-C82	143.2	146.2(2)	144.6(2)
N21-C71-C81-N31	N22-C72-C82-N32	159.4	150.5(2)	151.6(2)
N21-C71-C81-O11	N22-C72-C82-O12	-23.1	-30.4(4)	-29.8(4)
C71-C81-O11-Zn	C72-C82-O12-Zn	-2.5	2.3(3)	4.5(3)
C81-O11-Zn-N21	C82-O12-Zn-N22	17.1	16.17(19)	13.35(19)
C71-C81-N31-C91	C72-C82-N32-C92	174.0	177.9(3)	-176.9(2)
C81-N31-C91-C101	C82-N32-C92-C102	160.9	-158.0(3)	125.6(3)
O11-Zn-N21-C151	O12-Zn-N22-C152	97.0	94.40(19)	97.29(19)
Zn-N21-C151-C161	Zn-N22-C152-C162	168.8	173.2(2)	169.4(2)
Zn-N21-C151-C171	Zn-N22-C152-C172	-65.8	-61.6(3)	-64.5(3)

[1] Labels are according to the crystal structure, Figure S55

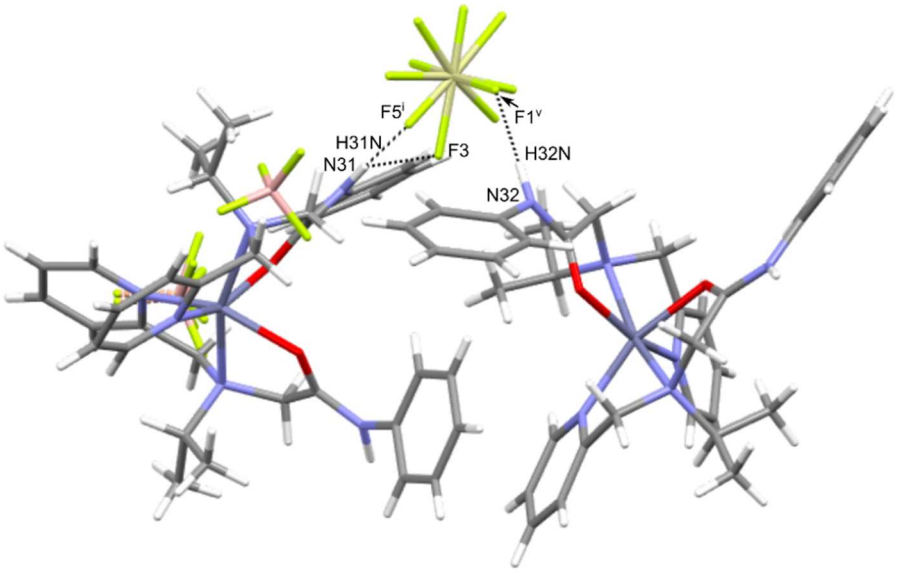


Figure S57. Hydrogen bonds between amide N-H groups of coordinated ligands to Zn^{2+} and fluorine acceptors from the $[SiF_6]^{2-}$ anions in vicinity listed in Table 3. The phenyl groups from neighbouring **[Zn(L$_2$)]$^{2+}$** cations form a specific contact arrangement.

Table S3. Table of Hydrogen bond parameters in crystal structure of **[Zn(L)$_2$]$_2$[SiF$_6$][BF$_4$]$_2$**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	H···A (Å)	D-H···A (°)
N31-H31N···F3	0.83(4)	1.97(4)	2.710(4)	148(4)
N31-H31N···F5^{i}	0.83(4)	2.08(4)	2.881(4)	162(4)
N32-H32N···F1^{v}	0.99(4)	1.82(4)	2.791(3)	165(3)

Symmetry codes: (i) 1/2-*y*, 1/2-*x*, 1/2-*z*; (v) 1-*z*, -*y*, -1/2+*x*

Additional characterization

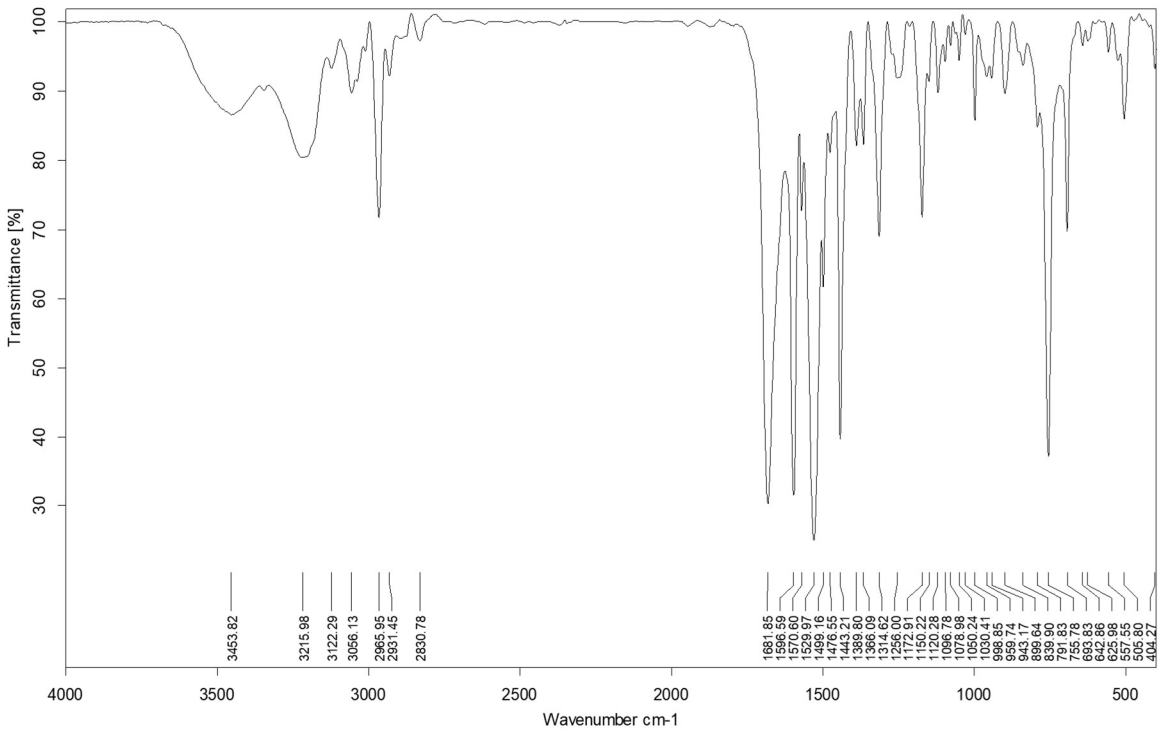


Figure S58. IR (KBr) spectrum of **L**

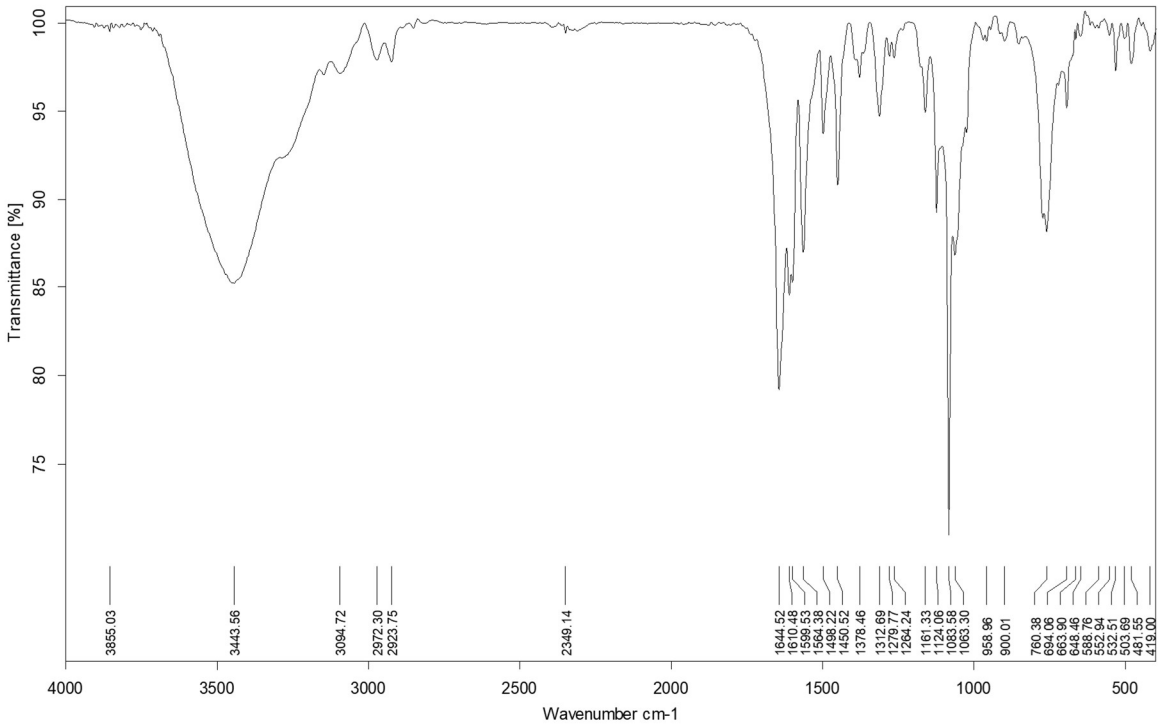


Figure S59. IR (KBr) spectrum of **$[Zn(L)_2]_2[SiF_6][BF_4]$**

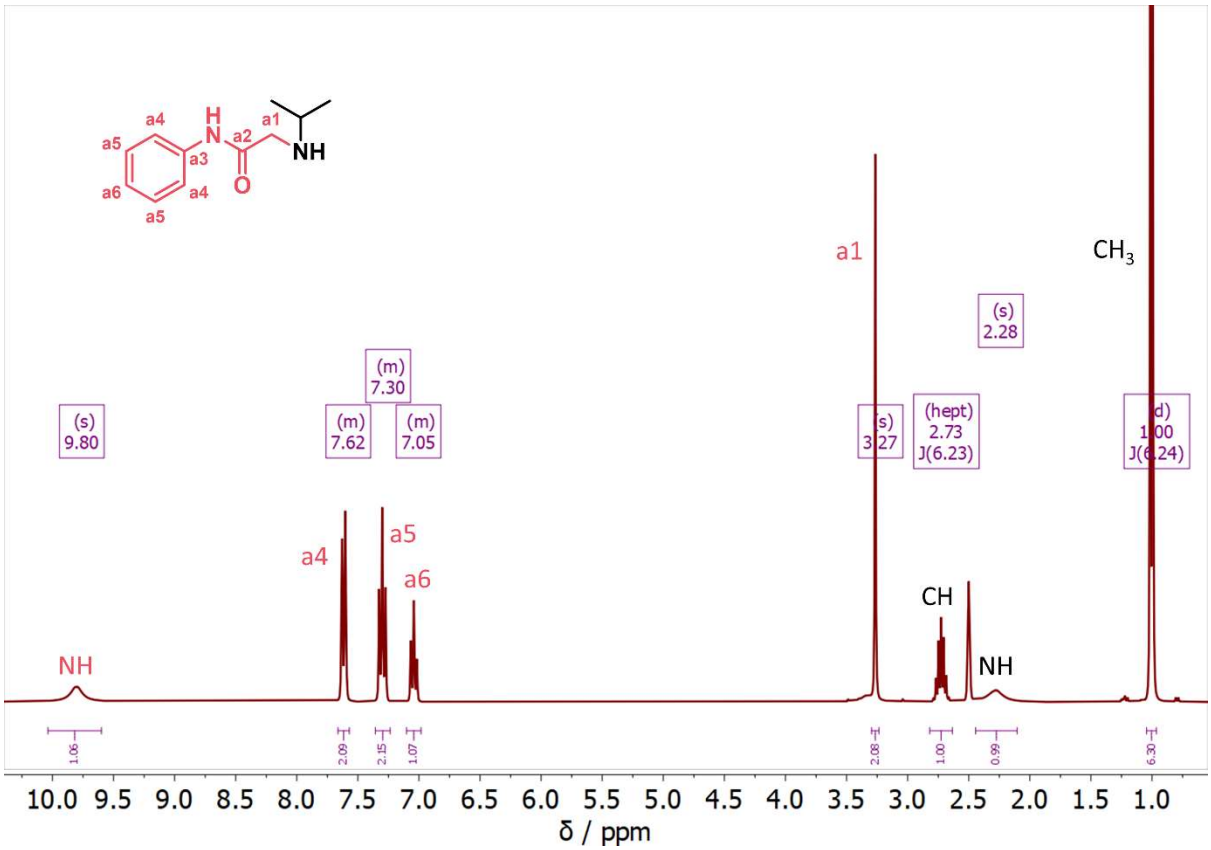


Figure S60. ^{1}H NMR ($(CD_3)_2SO$) of **P2**

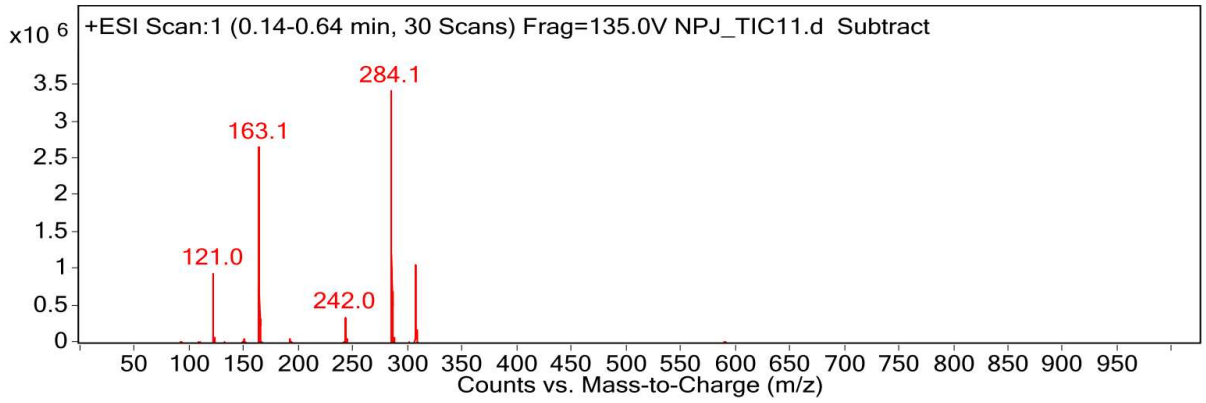


Figure S61. ESI-MS of **L**