New Journal of Chemistry

Zinc Complexes Formed by 2,2'-Bipyridine and 1,10-Phenanthroline Moieties Combined with 2-Azanorbornane: Modular Chiral Catalysts for Aldol Reaction

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Robert Wieczorek. and Jacek Wojaczyński

Electronic Supplementary Information

Contents

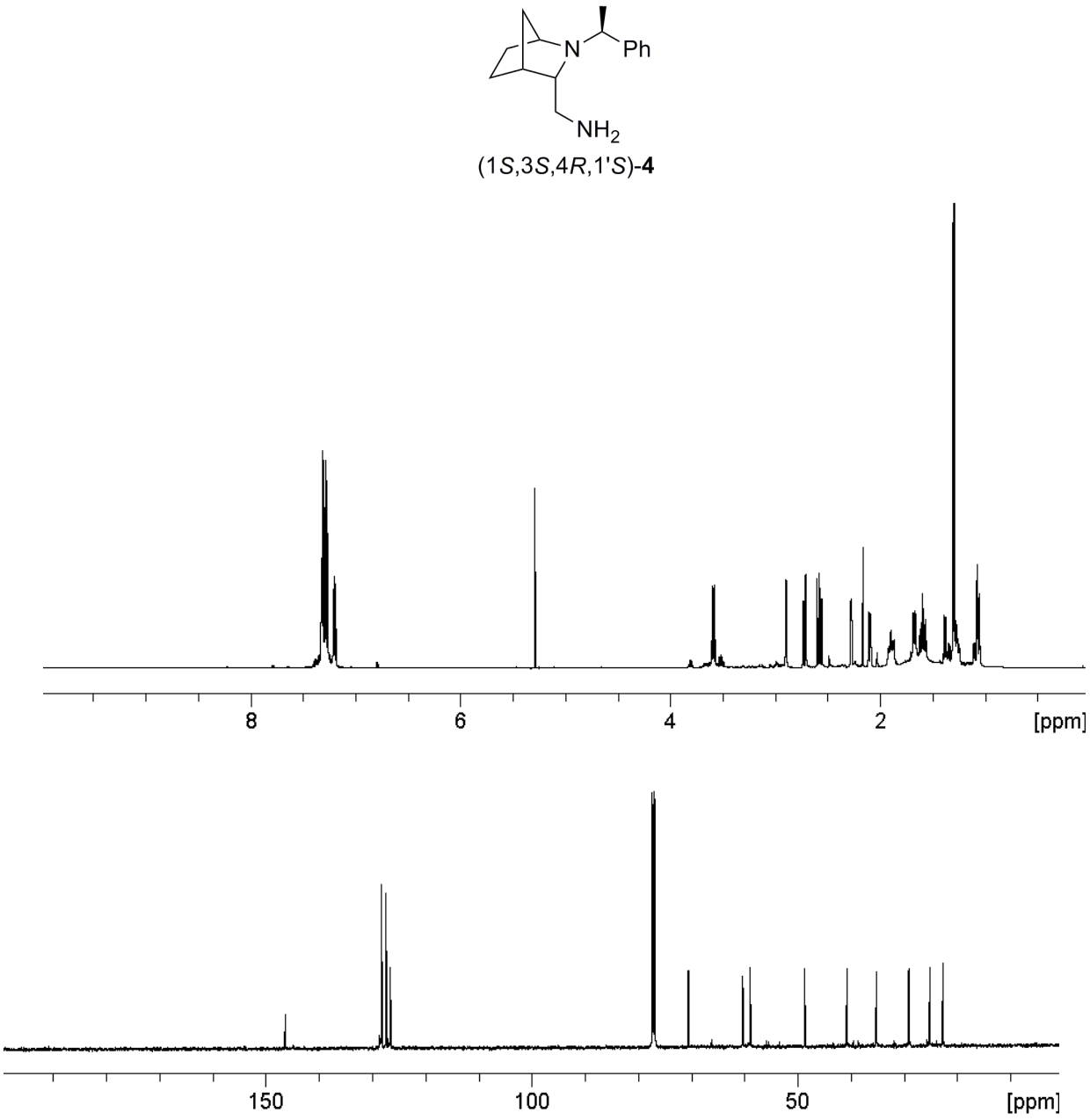


Figure S1. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **4**

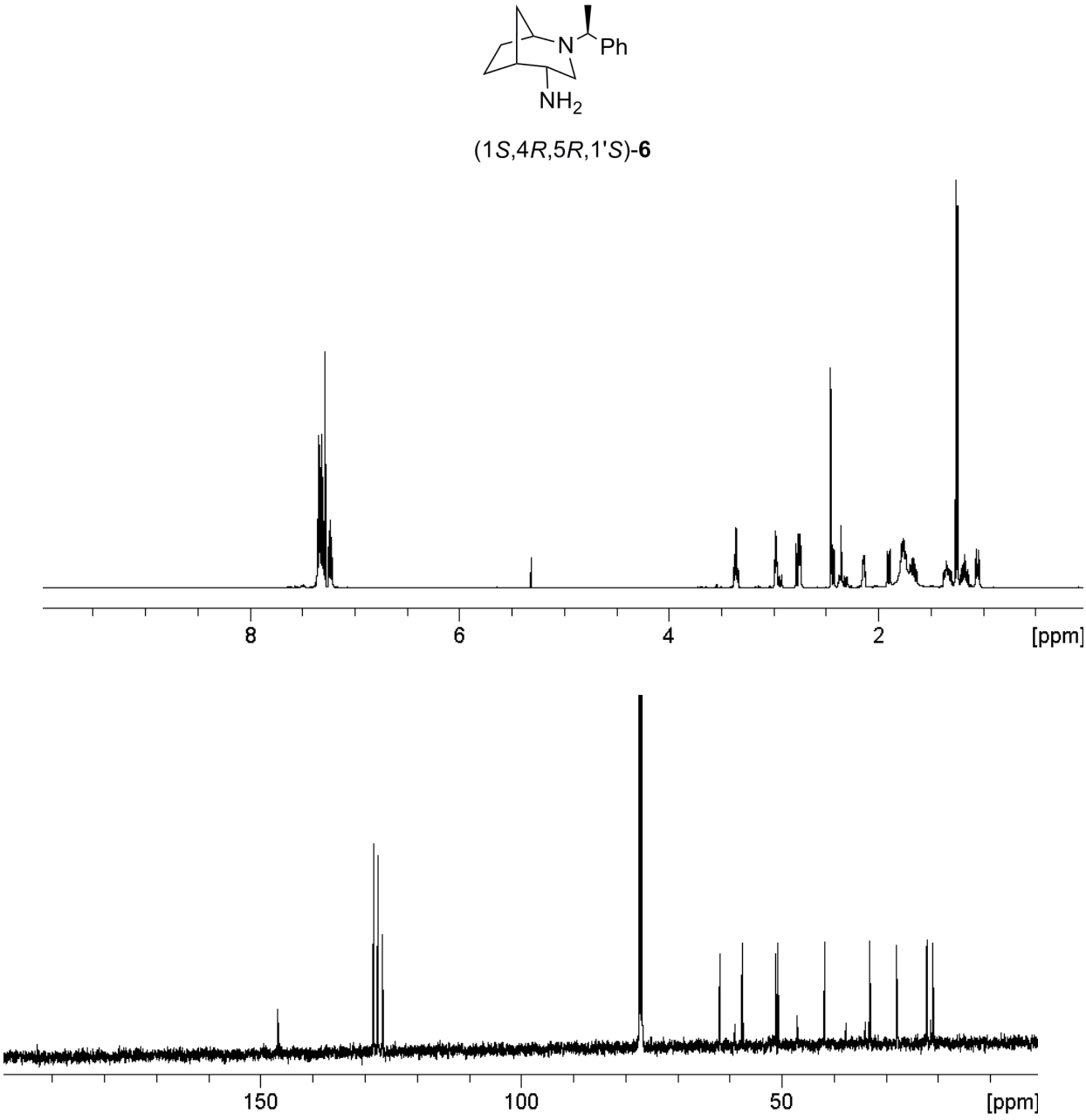


Figure S2. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **6**

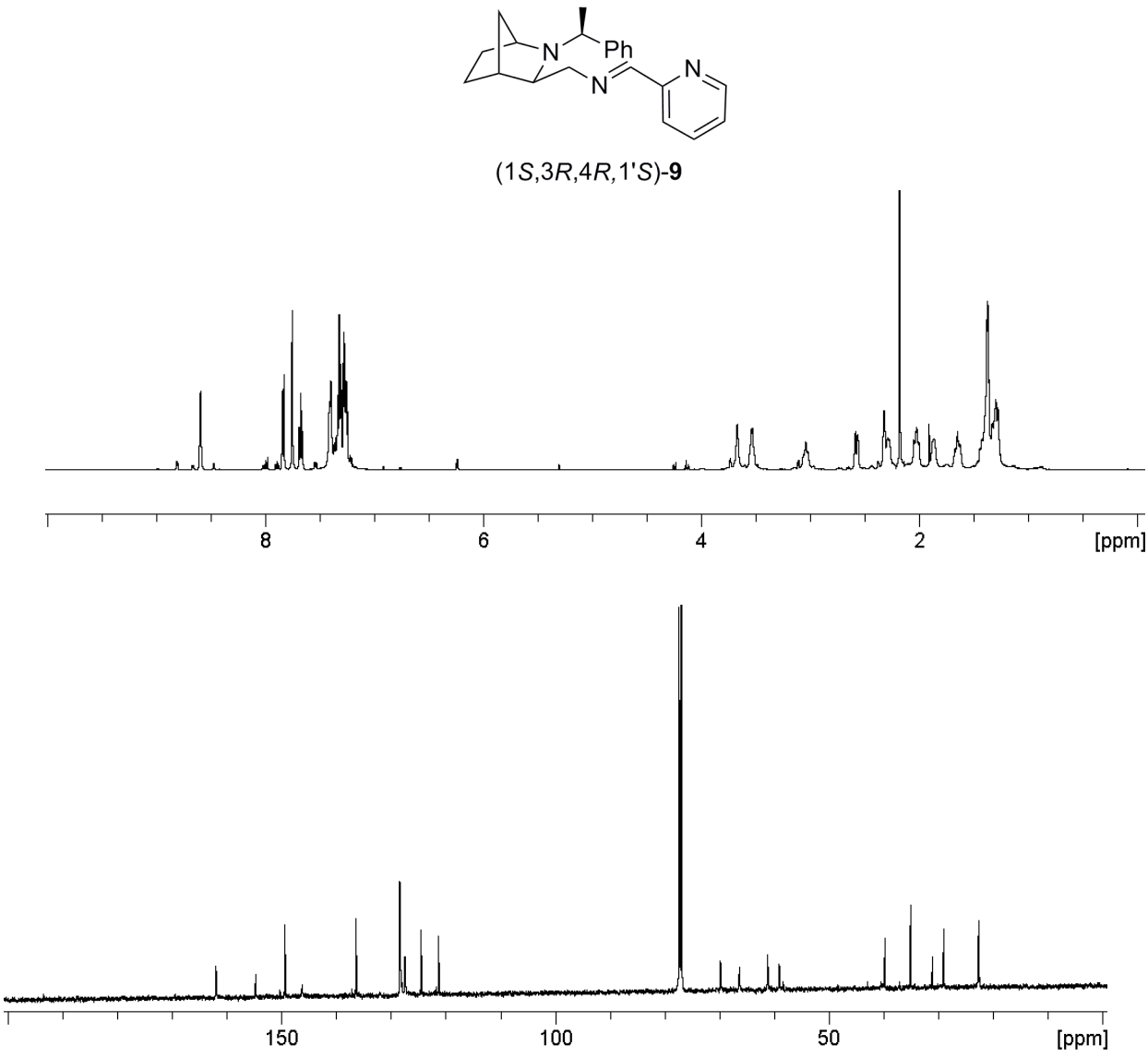


Figure S3. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **9**

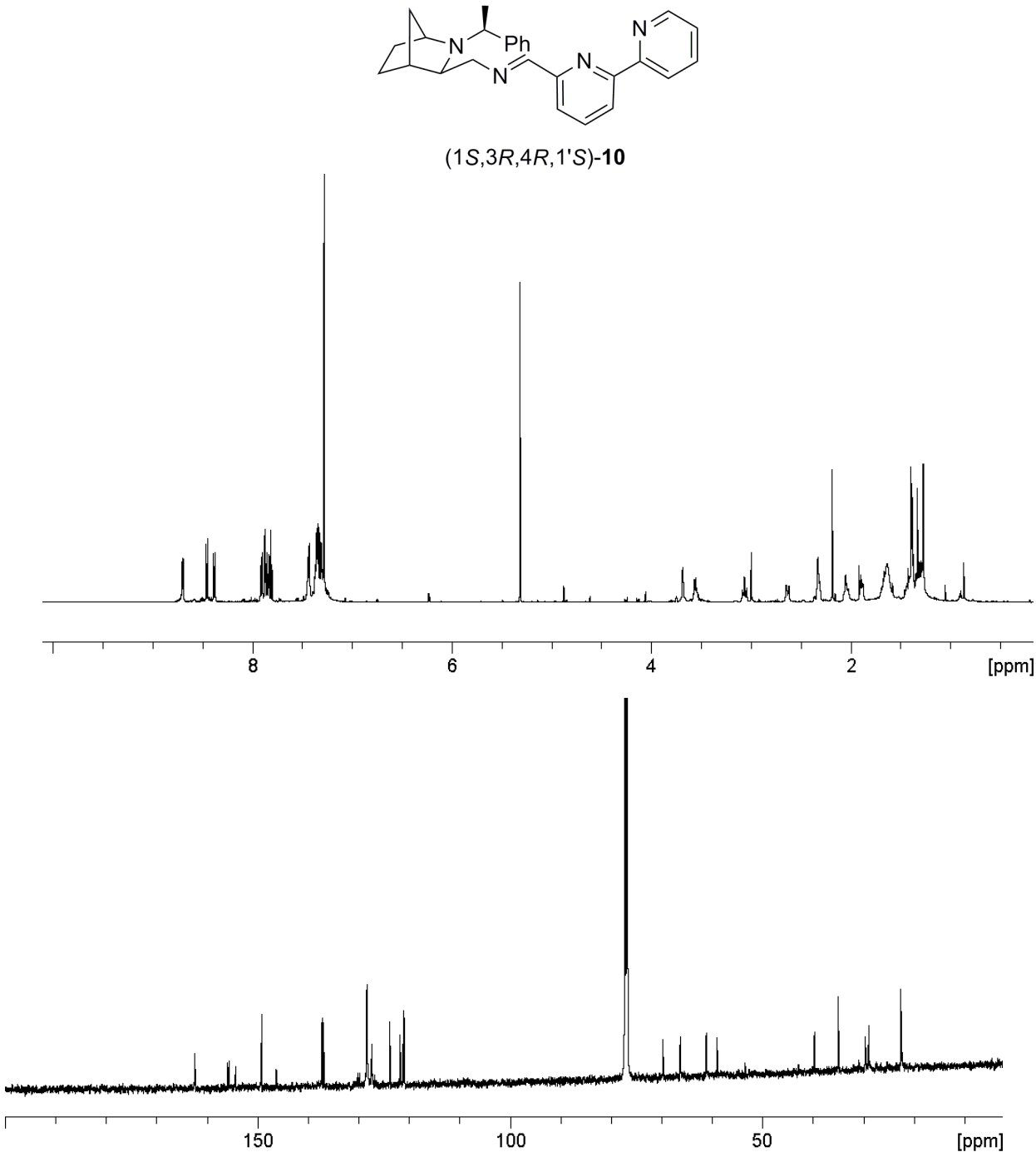


Figure S4. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **10**

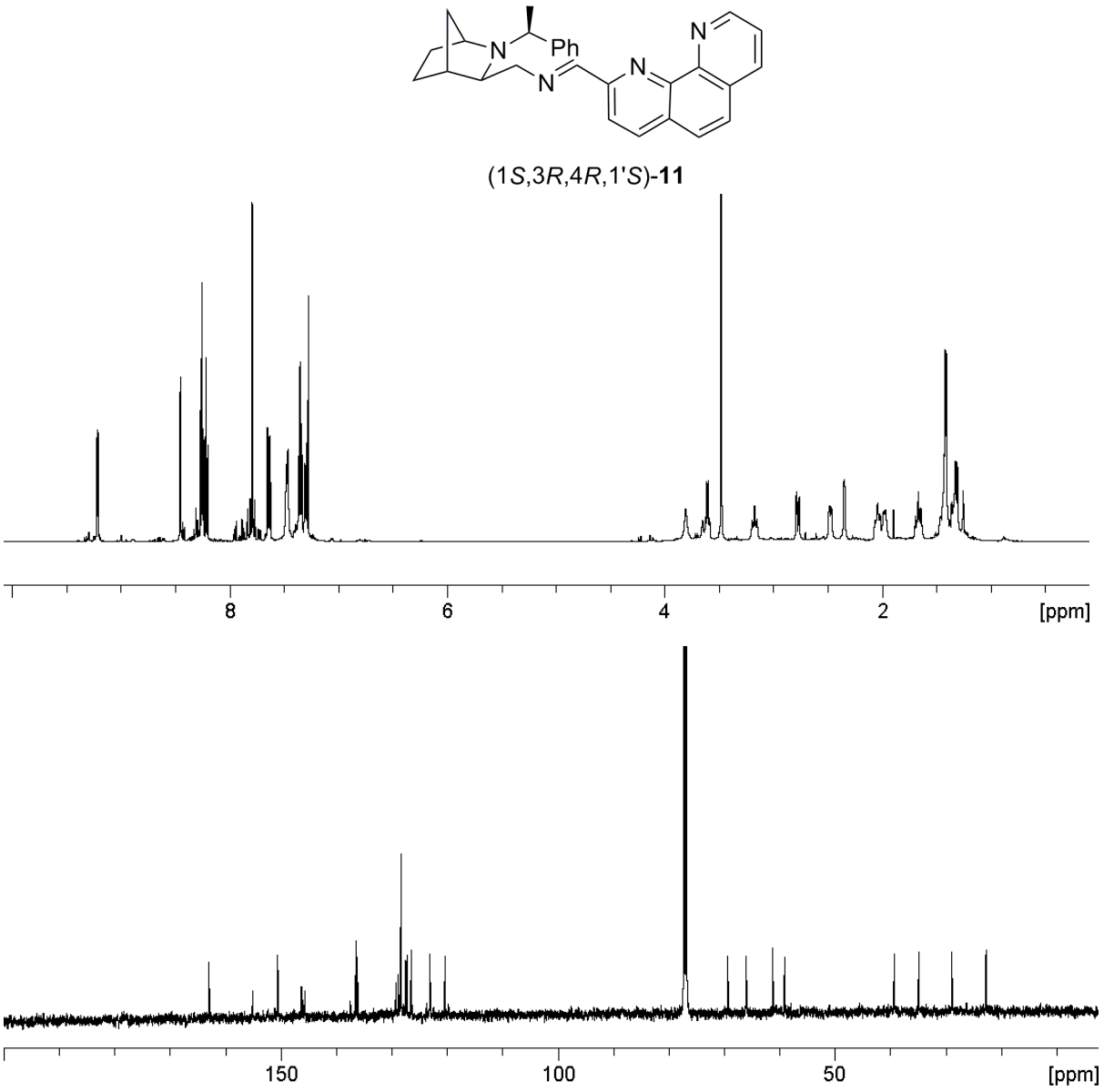
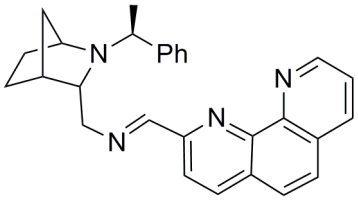


Figure S5. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **11**



(1*S*,3*S*,4*R*,1'*S*)-**12**

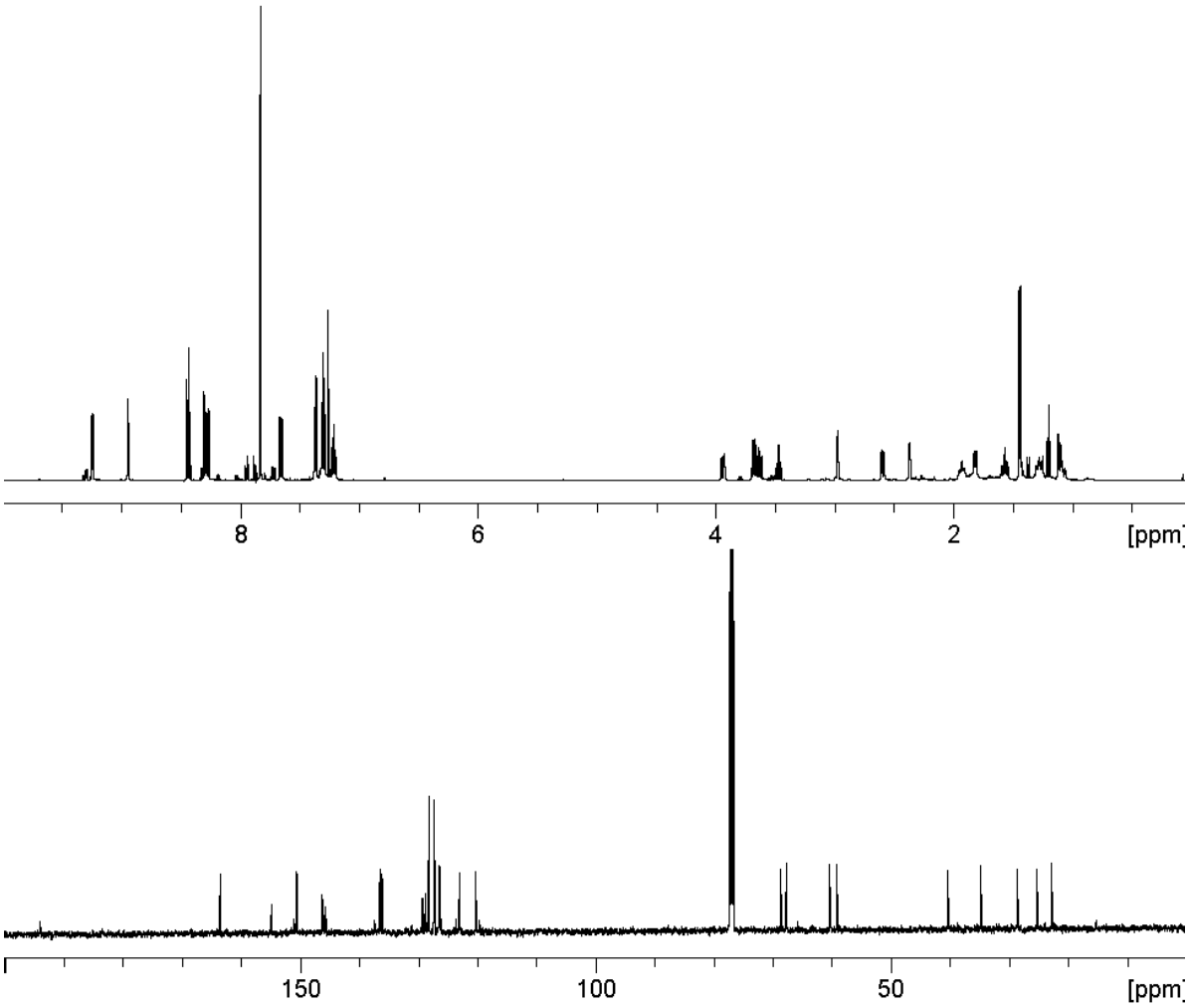


Figure S6. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **12**

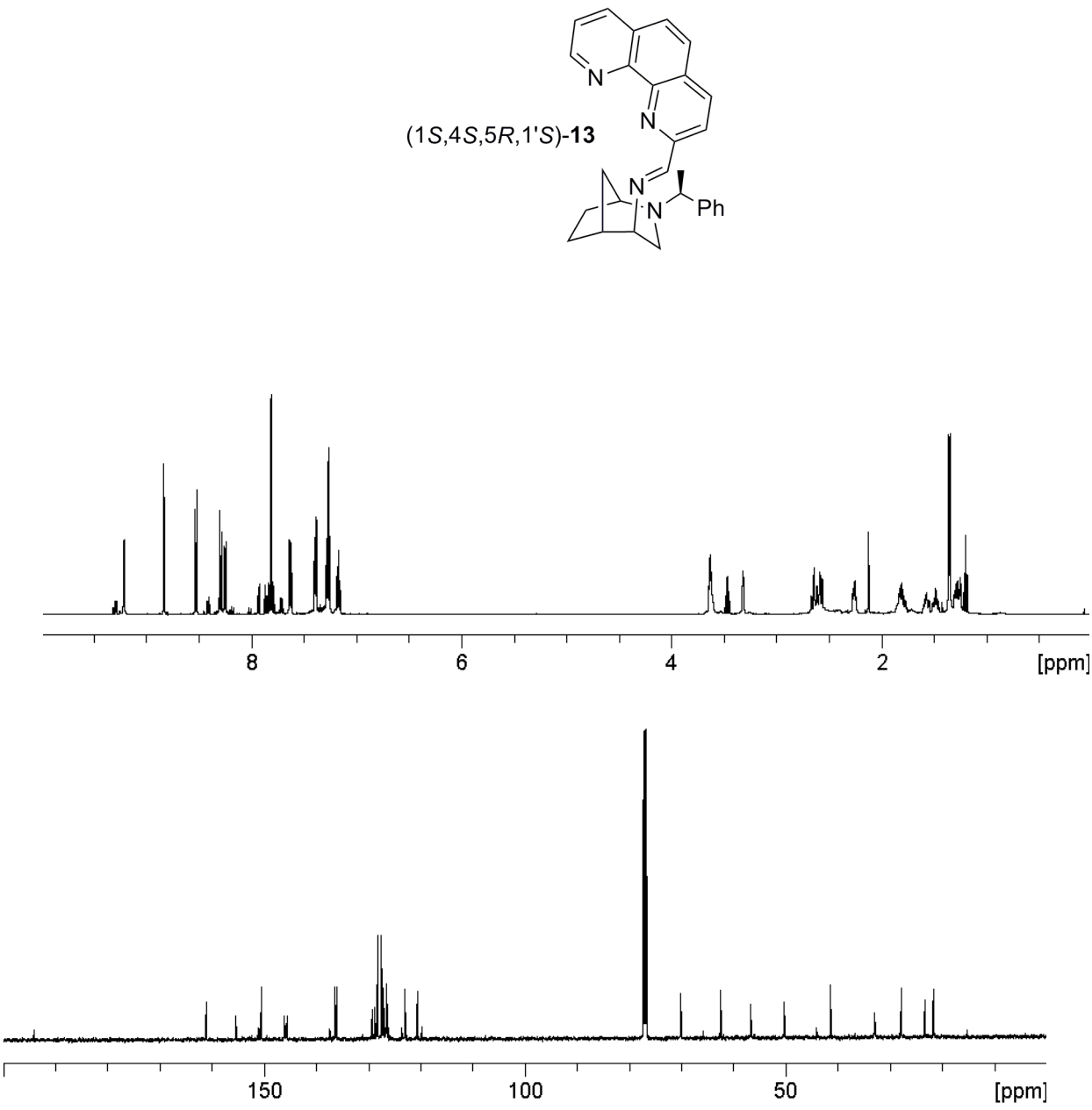


Figure S7. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **13**

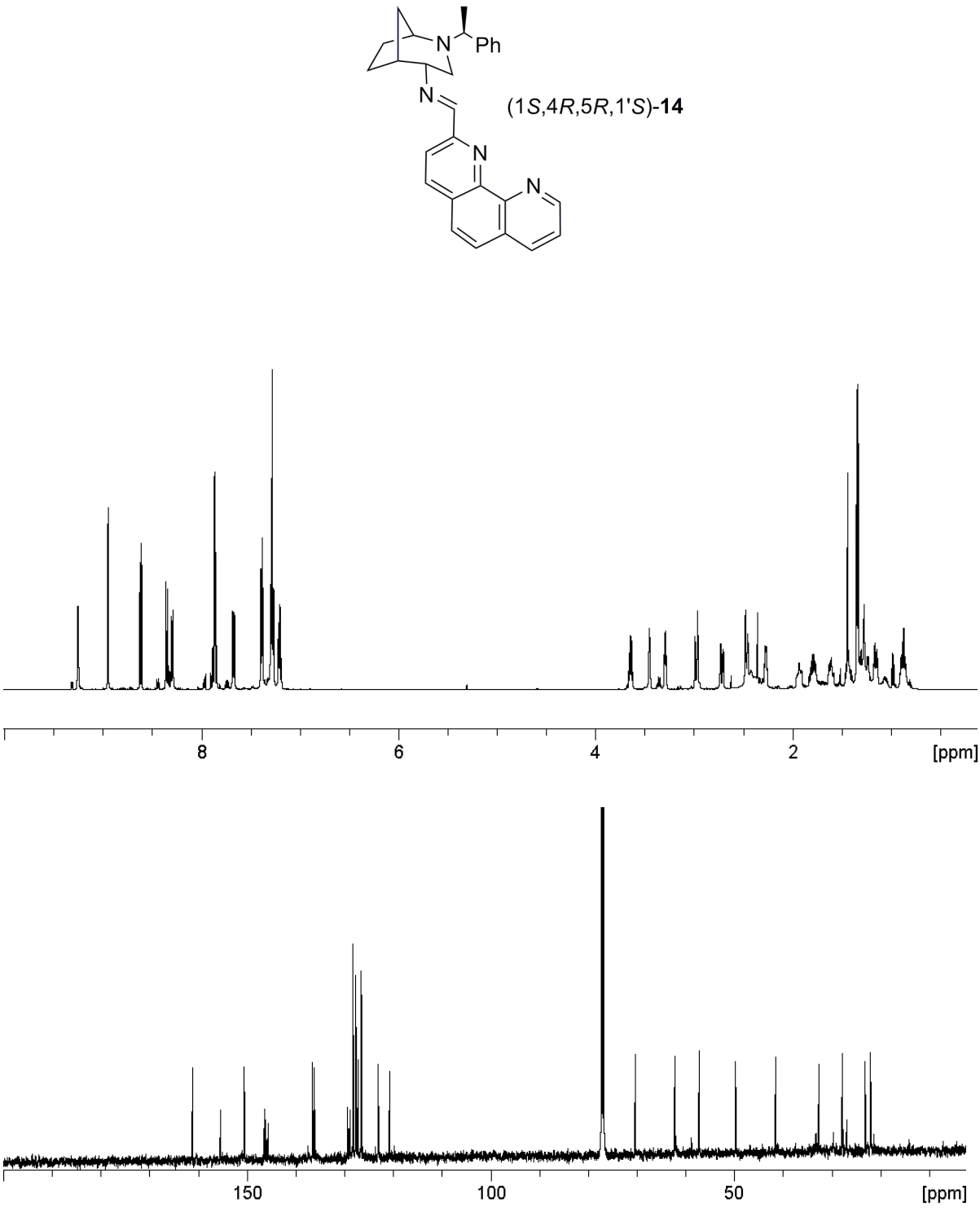


Figure S8. ^{1}H NMR and ^{13}C NMR spectra (chloroform-*d*, 300 K) of **14**

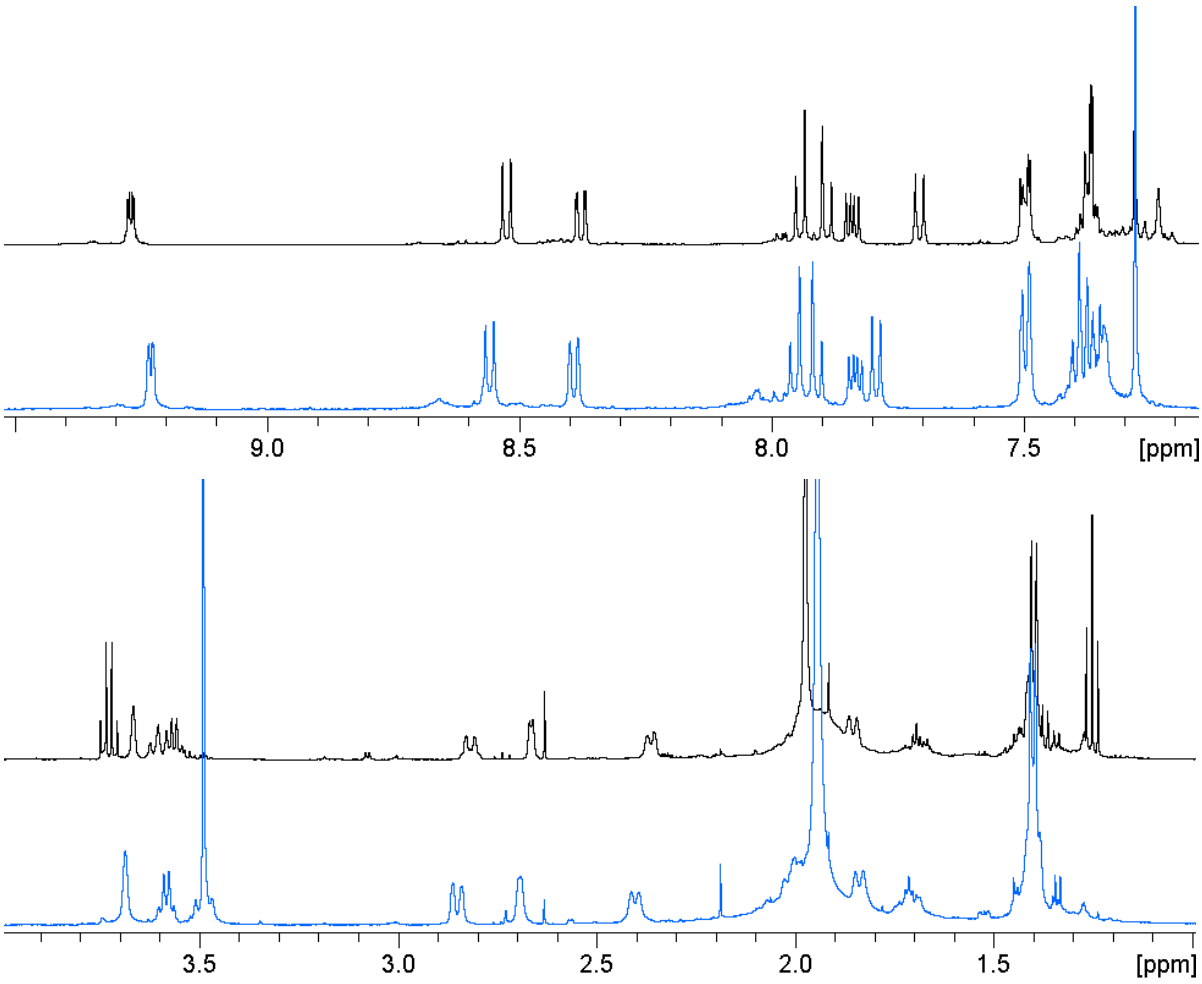
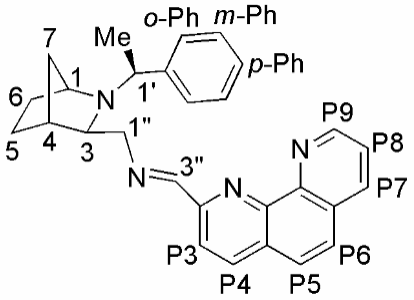


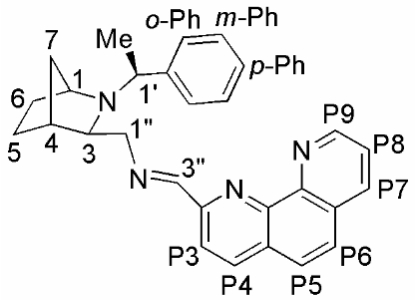
Figure S9. Comparison of ^{1}H NMR spectra of monomeric Zn(II) (blue line) and Cd(II) (black line) complexes of ligand **11** (chloroform-*d*, 300 K)

Table S1 ^{1}H NMR chemical shifts of ligand **11** and its zinc complexes (methanol-d_4, 300 K; L = ligand **11**, X = OAc^-). Numbering scheme for ligand **11** is shown. Entries 4 and 5 show the chemical shift changes with the most pronounced differences (≥ 0.2 ppm) listed in bold.



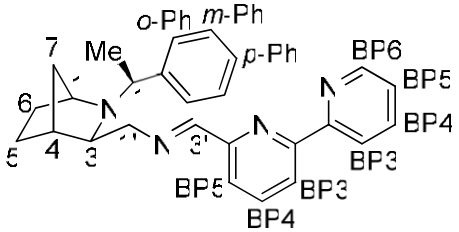
Entry	Species	1	3	4	5	6	7	1’	1’-Me	*o*-Ph	*m*-Ph	*p*-Ph	1”	3”	P3	P4	P5	P6	P7	P8	P9
1	Ligand **11**	3.72	2.49	2.31	1.38 1.71	1.48 2.13	1.39 1.92	3.66	1.40	7.49	7.38	7.31	3.11	8.27	8.23	8.42	7.97	7.97	8.47	7.79	9.10
2	$[ZnL_2]^{2+}$	3.36	1.06	0.86	-1.46 0.25	1.30 1.40	0.90 1.61	2.65	0.99	6.89	7.44	7.43	2.50 3.04	8.84	8.88	9.45	8.45	8.31	8.65	7.63	7.63
3	$[ZnLX_n]^{(2-n)+}$	3.73	2.57	2.45	1.41 1.69	1.49 2.10	1.39 1.84	3.66	1.40	7.51	7.41	7.39	2.89 3.45	7.78	8.12	8.91	8.15	8.15	8.68	7.99	9.08
4	Difference 3-1	0.01	0.08	0.14	0.03 -0.02	0.01 -0.03	0.00 -0.08	0.00	0.00	0.01	0.03	0.08	0.18 **0.34**	**-0.49**	-0.11	**0.49**	0.18	0.18	**0.21**	**0.20**	-0.02
5	Difference 2-3	**-0.37**	**-1.51**	**-1.59**	**-2.87** **-1.44**	-0.19 **-0.70**	**-0.49** **-0.23**	**-1.01**	**-0.41**	**-0.62**	0.03	0.04	**-0.39** **-0.41**	**1.06**	**0.76**	**0.54**	**0.30**	0.16	-0.03	**-0.36**	**-1.45**

Table S2. ^{13}C NMR chemical shifts of ligand **11** and its zinc complexes (methanol-d_4. 300 K; L = ligand **11**, X = OAc^-). Quaternary carbons not included. Numbering scheme for ligand **11** is shown.



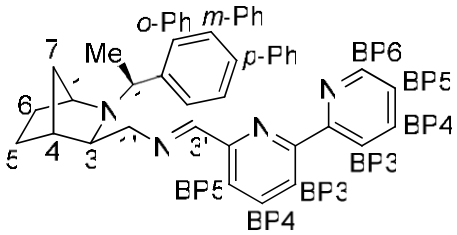
Entry	Species	1	3	4	5	6	7	1’	1’-Me	*o*-Ph	*m*-Ph	*p*-Ph	1”	3”	P3	P4	P5, P6	P7	P8	P9
1	Ligand **11**	59.2	69.3	39.4	28.4	21.7	34.3	61.0	21.0	128	128	128	65.2	163.0	119.8	136.8	126.3 127.4	136.8	123.3	149.7
2	$[ZnL_2]^{2+}$	58.2	67.2	38.2	26.3	21.9	33.0	61.1	22.8	127.5	128.4	128.3	63.7	162.0	126.4	143.7	126.5 129.6	139.6	126.8	148.6
3	$[ZnLX_n]^{2-n}$	59.0	68.7	40.5	28.3	21.9	34.4	61.1	21.3	128.5	128.4	127.2	64.4	159.4	124.8	141.2	125.8 128.5	138.5	125.9	149.6

Table S3 ^{1}H NMR chemical shifts of ligand **10** and its zinc complexes (methanol-d_4, 300 K; L = ligand **10**, X = OAc^{-}). Numbering scheme for ligand **10** is shown. Entries 4 and 5 show the chemical shift changes with the most pronounced differences listed in bold.



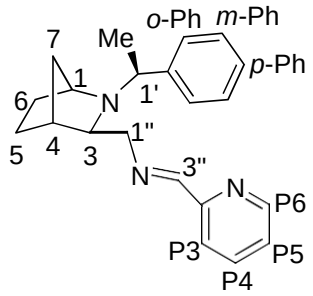
Entry	Species	1	3	4	5	6	7	1’	1’-Me	*o*-Ph	*m*-Ph	*p*-Ph	1”	3”	BP3	BP4	BP5	BP3’	BP4’	BP5’	BP6’
1	Ligand **10**	3.71	2.37	2.31	1.34	1.49	1.37	3.63	1.41	7.48	7.38	7.34	2.60	7.78	8.48	7.95	7.86	8.36	7.98	7.45	8.66
					1.72	2.13	1.88						3.10								
2	$[ZnL_2]^{2+}$	3.48	1.26	0.92	-0.26	1.12	1.02	2.93	1.08	6.97	7.42	7.42	2.43	8.56	9.02	8.89	8.57	8.67	8.18	7.46	7.29
					0.77	1.60	1.66						2.91								
3	$[ZnLX_n]^{2-n}$	3.73	2.52	2.43	1.38	1.48	1.43	3.66	1.43	7.51	7.41	7.35	2.85	7.59	8.63	8.41	7.87	8.51	8.21	7.74	8.76
					1.70	2.10	1.83						3.37								
4	Difference 3-1	0.02	0.15	0.12	0.04	-0.01	0.06	0.03	0.02	0.03	0.03	0.01	**0.25**	-0.19	0.15	**0.46**	0.01	0.15	**0.23**	**0.29**	0.10
					-0.02	-0.03	-0.05						**0.27**								
5	Difference 2-3	**-0.25**	**-1.26**	**-1.51**	**-1.64**	**-0.36**	**-0.41**	**-0.73**	**-0.35**	**-0.54**	0.01	0.07	**-0.42**	**0.97**	**0.39**	**0.48**	**0.70**	0.16	-0.03	**-0.28**	**-1.47**
					-2.47	**-0.50**	-0.17						**-0.46**								

Table S4. ^{13}C NMR chemical shifts of ligand **10** and its zinc complexes (methanol-d_4. 300 K; L = ligand **10**, X = OAc^-). Quaternary carbons not included. Numbering scheme for ligand **10** is shown.



Entry	Species	1	3	4	5	6	7	1’	1’-Me	*o*-Ph	*m*-Ph	*p*-Ph	1”	3”	BP3	BP4	BP5	BP3’	BP4’	BP5’	BP6’
1	Ligand **10**	59.0	69.5	39.6	28.2	21.6	34.3	61.1	21.1	128.3	128.1	127.3	65.5	163.2	121.4	137.7	120.9	121.8	137.2	124.0	148.7
2	$[ZnL_2]^{2+}$	58.4	66.9	38.2	27.5	21.8	33.0	61.3	22.8	127.4	128.3	128.3	63.3	162.1	125.6	145.2	128.8	123.6	141.1	127.8	147.2
3	$[ZnLX_n]^{2-n}$	59.0	68.5	40.5	28.4	21.6	34.1	60.9	21.1	128.3	128.0	128.0	63.9	159.7	123.6	142.8	126.5	121.9	140.2	126.6	148.7

Table S5. ^{1}H and ^{13}C NMR chemical shifts of ligand **9** and its zinc complex (methanol-d_4. 300 K; L = ligand **9,** X = OAc^{-}). Quaternary carbons not included. Numbering scheme for ligand **9** is shown.



Entry	Species	1	3	4	5	6	7	1’	1’-Me	*o*	*m*	*p*	1”	3”	P3	P4	P5	P6
1	Ligand **9**	3.71	2.34	2.30	1.35	1.48	1.39	3.63	1.40	7.45	7.36	7.31	2.55	7.70	7.86	7.86	7.44	8.57
					1.71	2.12	1.87						3.05					
		59.0	69.7	39,7	28.4	21.7	34.4	60.9	20.9	128.3	128.2	127.2	65.4	161.9	121.4	137.2	125.2	148.8
2	$[ZnLX_n]^{2-n}$	3.72	2.45	2.44	1.38	1.49	1.41	3.66	1.42	7.50	7.40	7.36	2.76	7.41	7.79	8.26	7.84	8.74
					1.68	2.08	1.80						3.43					
		58.8	69.2	40.2	27.6	21.7	34.5	60.8	20.9	128.4	128.2	127.4	62.6	162.6	127.1	141.3	128.5	149.4

Table S6. DFT calculated energies (in hartree, differences given in kcal/mol)

Ligand 10	
Compact conformation	-1225.982791
Open conformation	-1225.988750
	-3.74 kcal/mol
Ligand 11	
Compact conformation	-1302.180957
Open conformation	-1302.173447
	-4.71 kcal/mol
$[ZnL]^{2+}$ complexes	
Ligand **10**, (N2) coordination	-3004.956221
Ligand **10**, (N4) coordination	-3004.987887
	-19.87 kcal/mol
Ligand **11**, (N2) coordination	-3081.149052
Ligand **11**, (N4) coordination	-3081.174177
	-15.77 kcal/mol
$[ZnL_2]^{2+}$ complexes	
Ligand **10**, (N4) coordination	-4231.030063
Ligand **10**, (N6) coordination	-4231.075199
	-28.32 kcal/mol
Ligand **11**, (N4) coordination	-4383.415267
Ligand **11**, (N6) coordination	-4383.452777
	-23.54 kcal/mol

Ligand 10 – a compact conformation

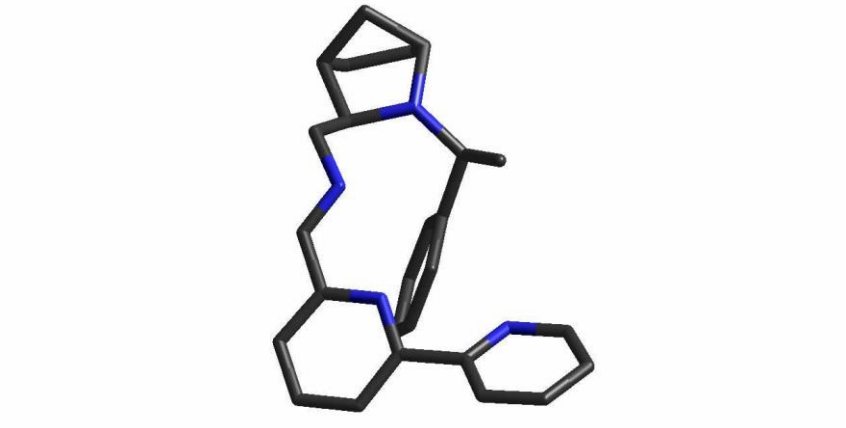


Table S7. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
BP6’	9.22	8.66	0.56
H3”	8.55	7.78	0.77
BP4	8.52	7.95	0.57
BP4’	8.36	7.98	0.38
BP3’	8.26	8.36	-0.10
BP3	8.22	8.48	-0.26
ortho-H	8.02	7.48	0.54
BP5	7.70	7.76	-0.06
BP5’	7.62	7.45	0.17
para-H	7.03	7.34	-0.31
meta-H	6.66	7.38	-0.72
H1”	4.00	3.10	0.90
H1’	3.94	3.63	0.31
H1	3.30	3.71	-0.41
H1”	3.04	2.60	0.44
H6	2.15	2.13	0.02
H4	1.88	2.31	-0.43
H7	1.86	1.88	-0.02
1’-Me	1.76	1.41	0.35
H5	1.69	1.72	-0.03
H6	1.61	1.49	0.12
H7	1.34	1.37	-0.03
H3	1.24	2.37	-1.13
H5	1.14	1.34	-0.20

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

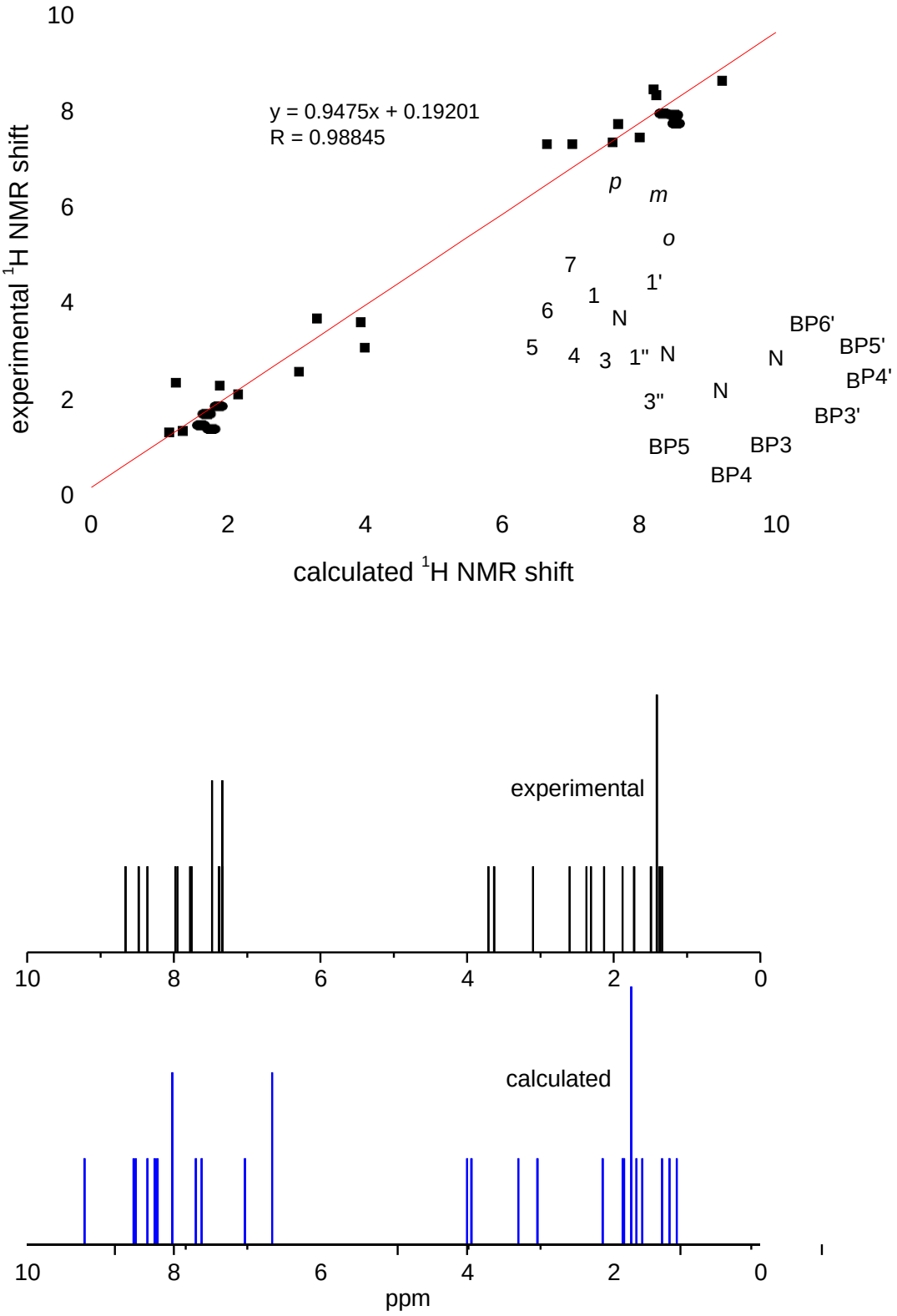


Figure S10. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of ligand **10** (compact conformation) and the correlation of shift values for particular positions.

Ligand 10 – an open conformation

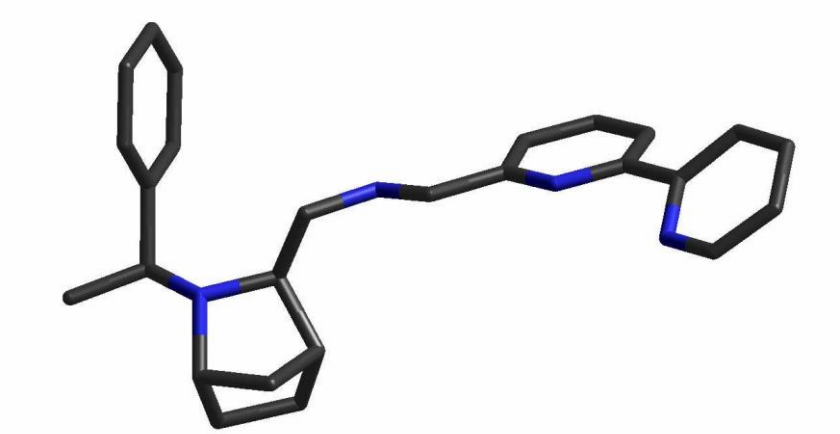


Table S8. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
BP6’	9.15	8.66	0.49
H3”	8.66	7.78	0.88
BP4’	8.29	7.98	0.31
BP5	8.19	7.86	0.33
BP4	8.18	7.95	0.23
BP3’	8.07	8.36	-0.29
BP3	7.96	8.48	-0.52
ortho-H	7.80	7.48	0.32
meta-H	7.72	7.38	0.34
BP5’	7.71	7.45	0.26
para-H	7.65	7.34	0.31
H1’	3.60	3.63	-0.03
H1	3.47	3.71	-0.24
H1”	2.93	3.10	-0.17
H1”	2.78	2.60	0.18
H3	2.40	2.37	0.03
H6	2.11	2.13	-0.02
H7	1.76	1.88	-0.12
H4	1.56	2.31	-0.75
H5	1.46	1.72	-0.26
H6	1.41	1.49	-0.08
1’-Me	1.32	1.41	-0.09
H7	1.21	1.37	-0.16
H5	1.06	1.34	-0.28

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

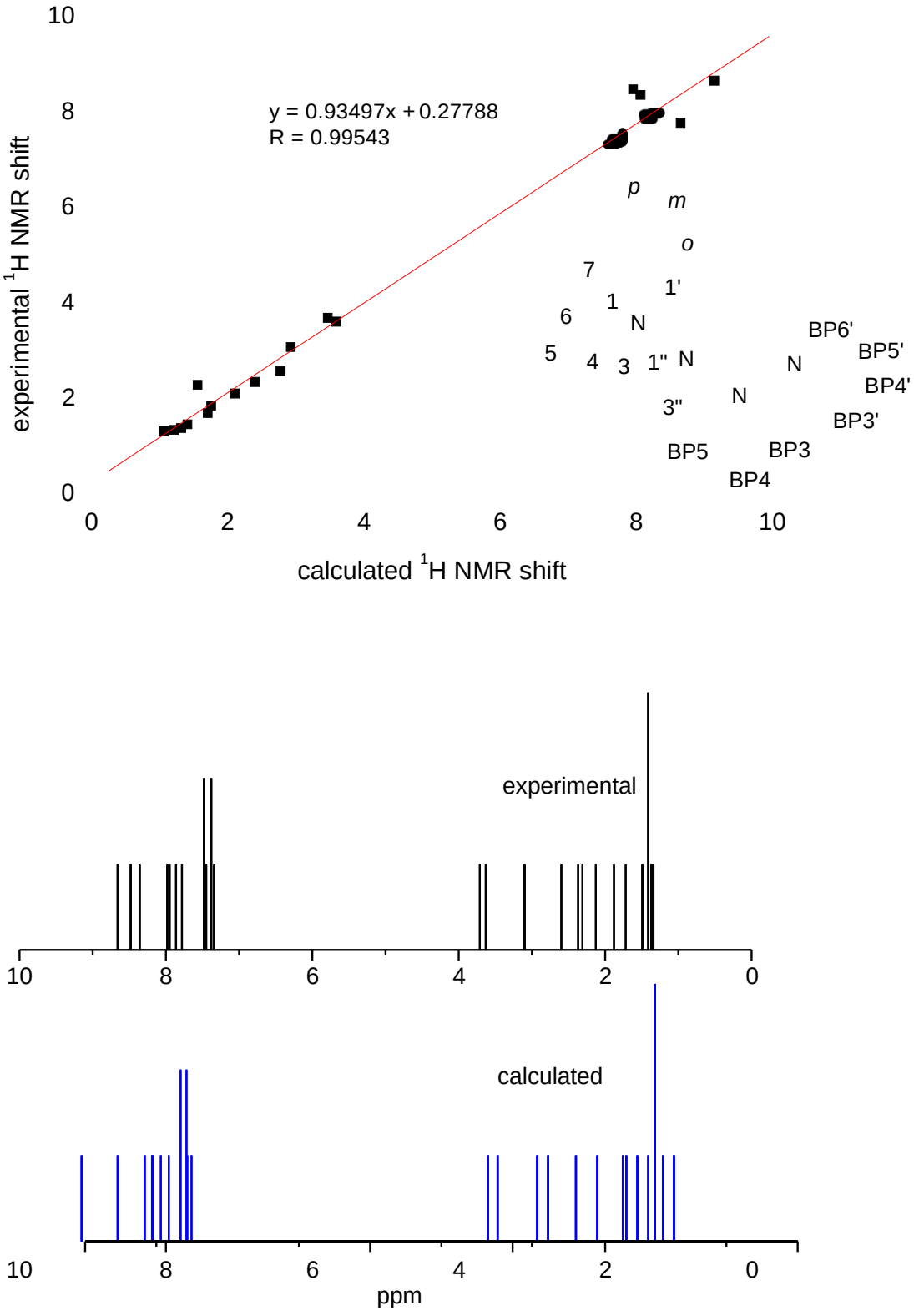


Figure S11. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of ligand **10** (open conformation) and the correlation of shift values for particular positions.

Ligand **11** - a compact conformation

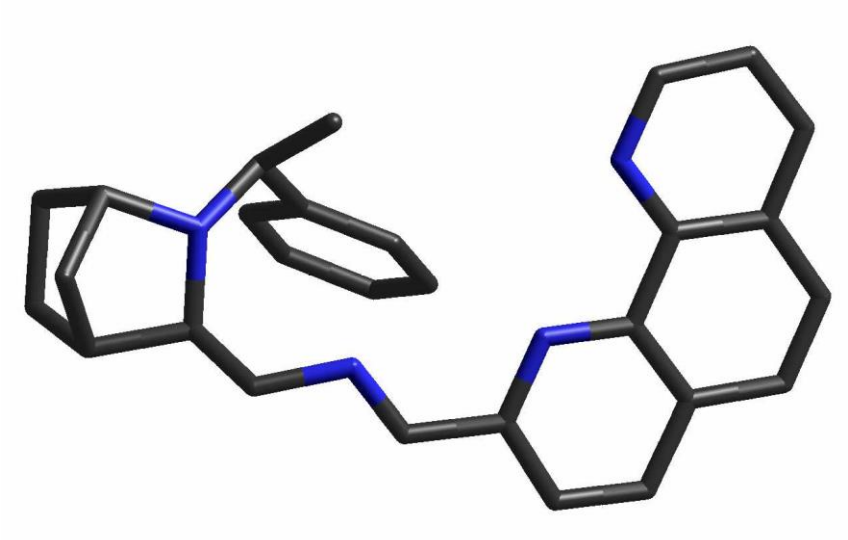


Table S9. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
P9	9.61	9.50	0.11
P4	8.90	8.42	0.48
H3”	8.86	8.27	0.59
P7	8.75	8.47	0.28
P5	8.41	7.97	0.44
P6	8.39	7.97	0.42
P3	8.13	8.23	-0.10
P8	7.99	7.79	0.20
ortho-H	7.98	7.49	0.49
para-H	6.89	7.31	-0.42
meta-H	6.40	7.38	-0.98
H1”	4.14	3.11	1.03
H1’	3.90	3.66	0.24
H1	3.36	3.72	-0.36
H1”	3.22	2.71	0.51
H6	2.11	2.13	-0.02
H7	1.99	1.92	-0.07
H4	1.96	2.31	-0.35
H5	1.67	1.71	-0.04
H6	1.65	1.48	0.17
1’-Me	1.93	1.40	0.53
H7	1.38	1.39	-0.01
H3	1.20	2.49	-1.29
H5	1.05	1.38	-0.33

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

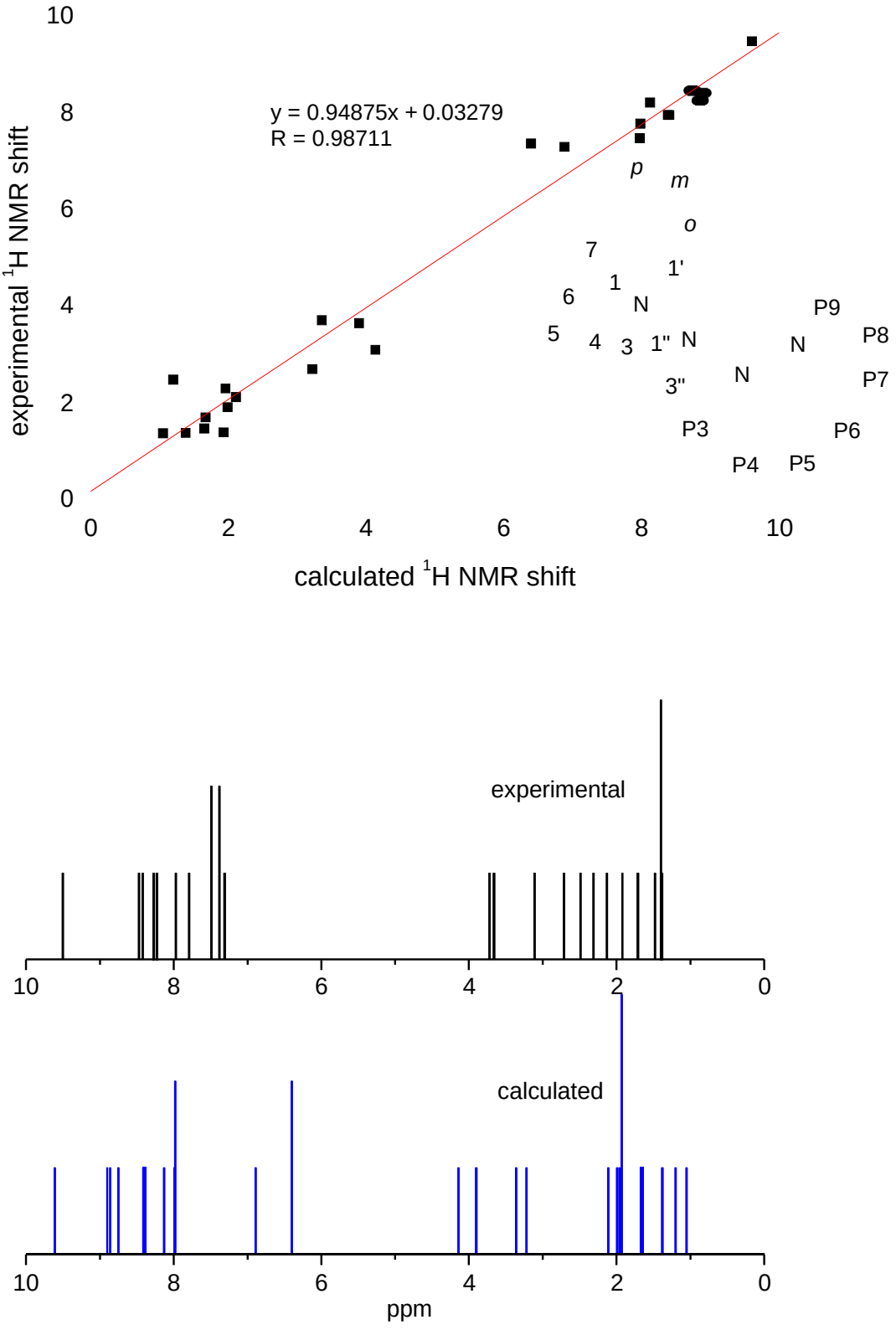


Figure S12. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of ligand **11** (compact conformation) and the correlation of shift values for particular positions.

Ligand 11 – an open conformation.

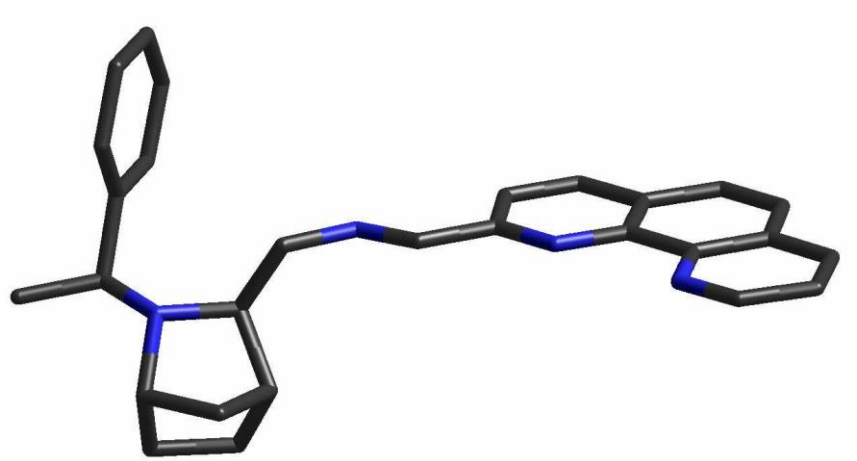


Table S10. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
P9	9.69	9.10	0.59
H3”	8.93	8.27	0.66
P4	8.76	8.42	0.34
P3	8.62	8.23	0.39
P7	8.50	8.47	0.03
P5	8.18	7.97	0.21
P6	8.09	7.97	0.12
ortho-H	7.92	7.49	0.43
P8	7.80	7.79	0.01
meta-H	7.78	7.38	0.40
para-H	7.74	7.31	0.43
H1’	3.65	3.66	-0.01
H1	3.49	3.72	-0.23
H1”	2.96	3.11	-0.15
H1”	2.76	2.71	0.05
H3	2.46	2.49	-0.03
H6	2.12	2.13	-0.05
H7	1.72	1.92	-0.20
H4	1.60	2.31	-0.71
H5	1.51	1.71	-0.20
H6	1.41	1.48	-0.07
1’-Me	1.38	1.40	-0.02
H7	1.28	1.39	-0.11
H5	1.16	1.38	-0.22

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

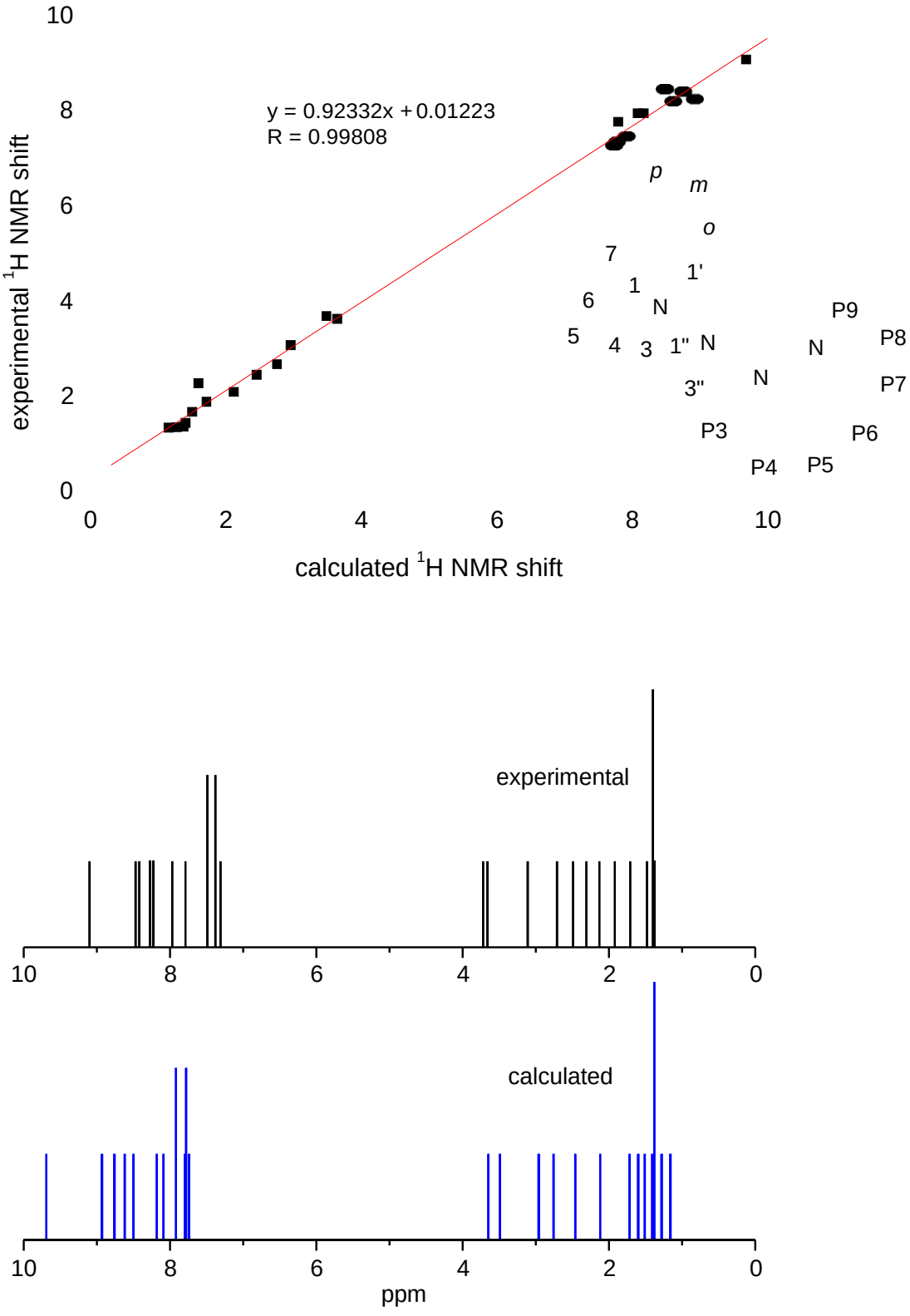


Figure S13. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of ligand **11** (open conformation) and the correlation of shift values for particular positions.

Compound 10, $[ZnL]^{2+}$ complex. (N2) coordination

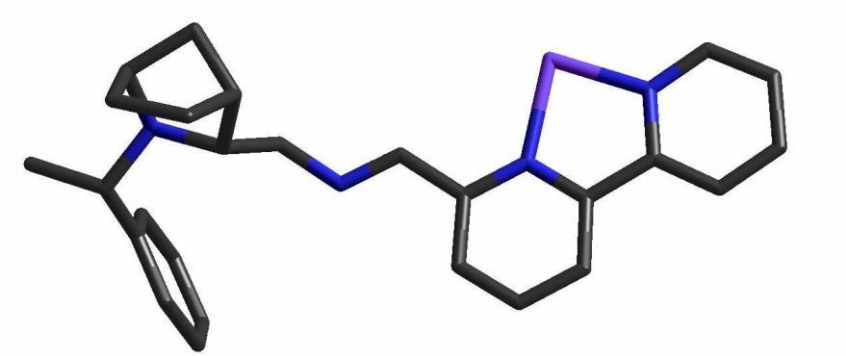


Table S11. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
BP3’	8.82	8.51	0.55
BP6’	9.03	8.76	0.22
BP4’	8.67	8.21	0.73
BP3	9.08	8.63	0.24
BP5	8.81	7.87	0.98
BP4	8.81	8.41	0.26
H3”	8.44	7.59	0.83
BP5’	7.98	7.74	0.49
ortho-H	7.92	7.51	0.23
meta-H	7.78	7.41	0.27
para-H	7.66	7.35	0.23
H1’	3.61	3.66	0.50
H1	3.59	3.73	-0.27
H1”	2.93	3.37	0.05
H3	2.53	2.52	0.75
H1”	2.75	2.85	-0.04
H6	2.10	2.10	-0.16
1’-Me	1.55	1.43	0.29
H7	1.54	1.83	-0.15
H5	1.63	1.70	-0.09
H6	1.27	1.48	0.04
H4	1.45	2.43	-1.04
H5	1.23	1.38	-0.05

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

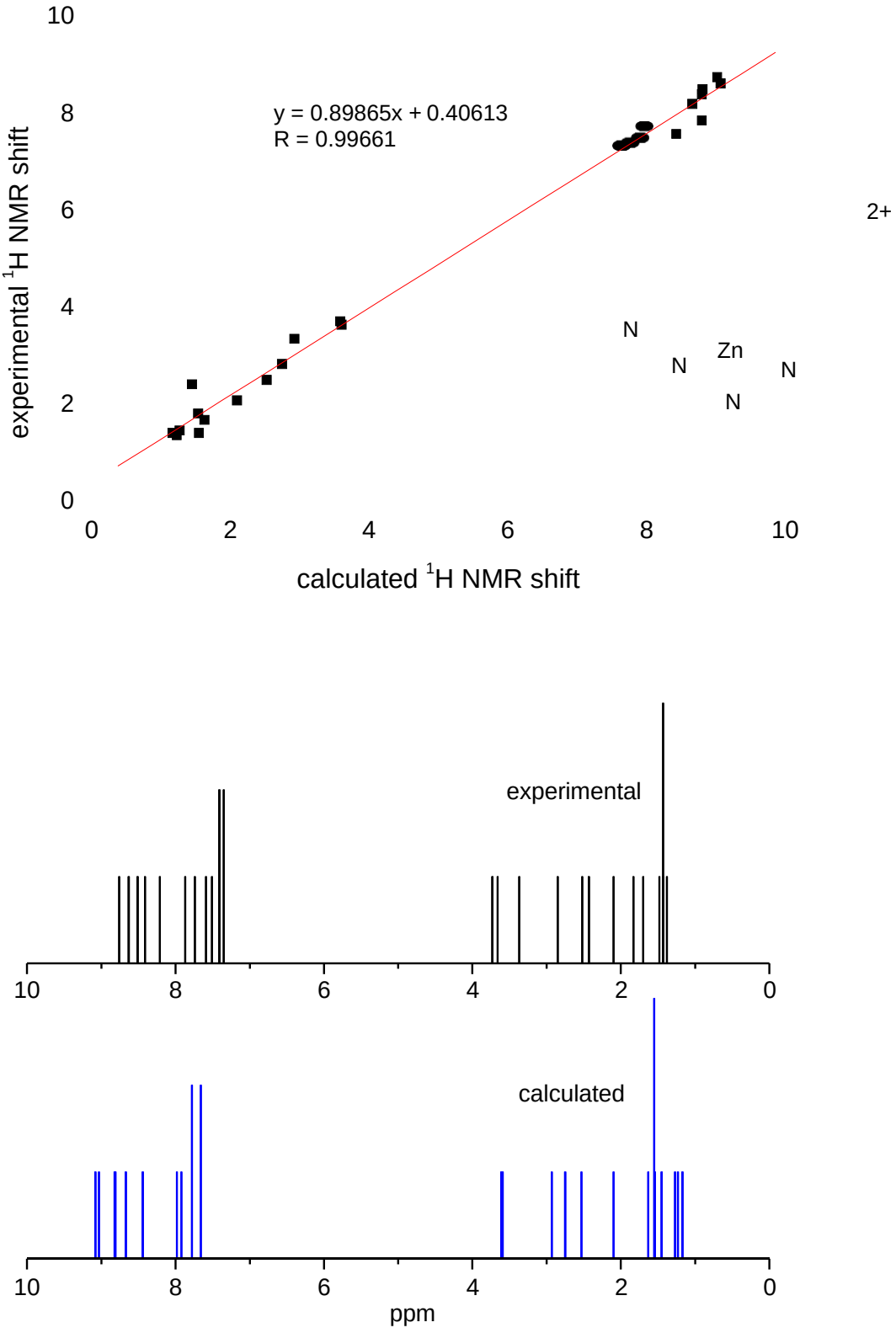


Figure S14. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 2N-coordinated $[ZnL]^{2+}$ complex of ligand **10** and the correlation of shift values for particular positions.

Compound 10, $[ZnL]^{2+}$ complex. (N4) coordination

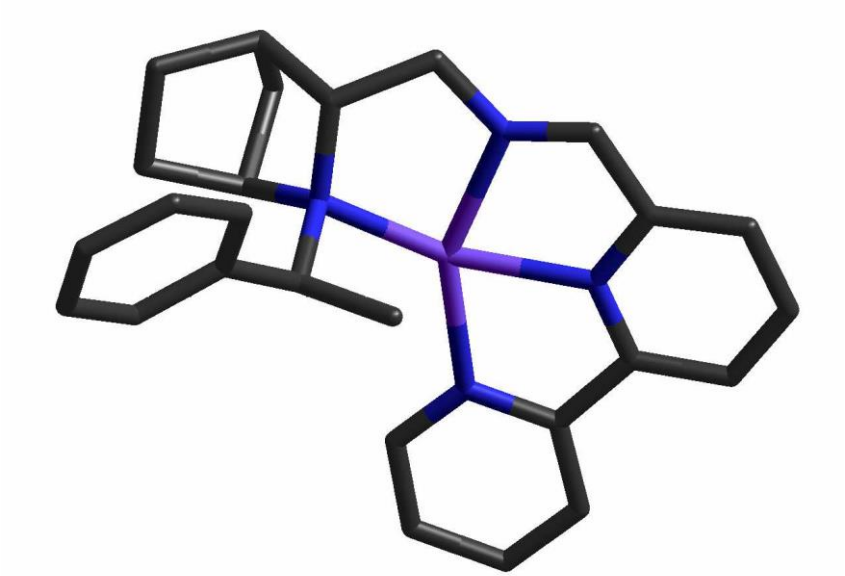


Table S12. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated	Experimental	Difference
BP6’	9.34	8.76	0.58
H3”	9.20	7.59	1.61
BP3	8.90	8.63	0.27
BP4	8.90	8.41	0.49
BP4’	8.87	8.21	0.66
BP3’	8.87	8.51	0.36
BP5’	8.27	7.74	0.53
BP5	8.27	7.87	0.40
meta-H	7.82	7.41	0.41
para-H	7.82	7.35	0.47
ortho-H	7.75	7.51	0.24
H1’	4.67	3.66	1.01
H1”	4.56	3.37	1.19
H1	4.23	3.73	0.50
H3	3.93	2.52	1.41
H1”	3.78	2.85	0.93
H6	2.42	2.10	0.32
H4	2.01	2.43	0.42
H7	1.80	1.83	-0.03
H7	1.50	1.43	0.07
H5	1.34	1.70	-0.26
1’-Me	1.31	1.43	-0.12
H6	1.30	1.48	-0.18
H5	-0.04	1.38	-1.42

*Average values of calculated chemical shifts for *ortho*-H, *meta*-H and 1’-Me were given.

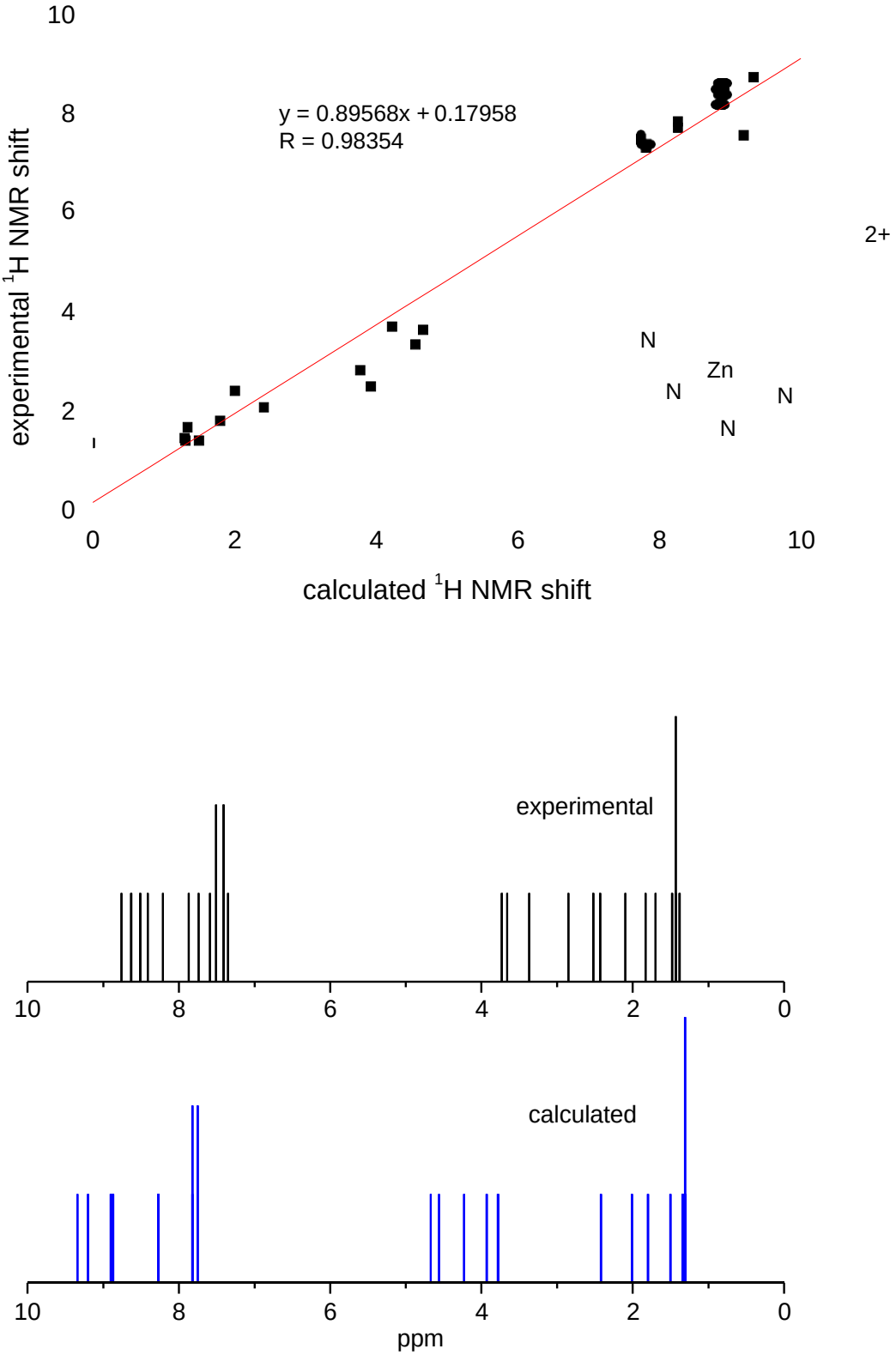


Figure S15. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 4N-coordinated $[ZnL]^{2+}$ complex of ligand **10** and the correlation of shift values for particular positions.

Compound 10. $[ZnL_2]^{2+}$ complex. (N4) coordination

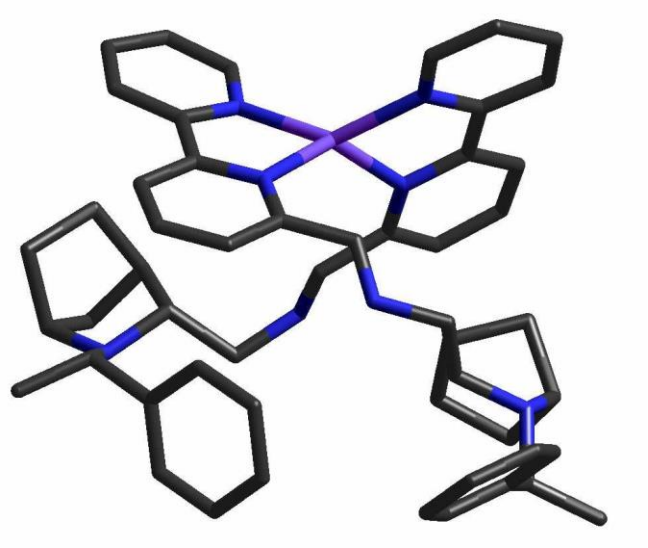


Table S13. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated (average)	Experimental	Difference
BP3	9.08	9.02	0.06
BP4	8.84	8.89	-0.05
BP3’	9.08	8.67	0.41
BP5	8.51	8.57	-0.06
H3”	8.46	8.56	-0.10
BP4’	8.87	8.18	0.69
BP5’	8.14	7.46	0.68
para-H	7.65	7.42	0.23
meta-H	7.57	7.42	0.15
BP6’	8.66	7.29	1.37
ortho-H	6.96	6.97	-0.01
H1	3.26	3.48	-0.22
H1’	3.16	2.93	0.23
H1”	2.69	2.43	0.26
H1”	2.06	1.91	0.15
H7	1.07	1.66	-0.59
H6	1.59	1.60	-0.01
H3	1.72	1.26	0.46
H6	0.89	1.12	-0.23
1’-Me	1.22	1.08	0.14
H7	0.08	1.02	-0.94
H4	0.82	0.92	-0.10
H5	0.47	0.77	-0.30
H5	-0.56	-0.26	-0.30

*Average values of calculated chemical shifts for the two subunits were given.

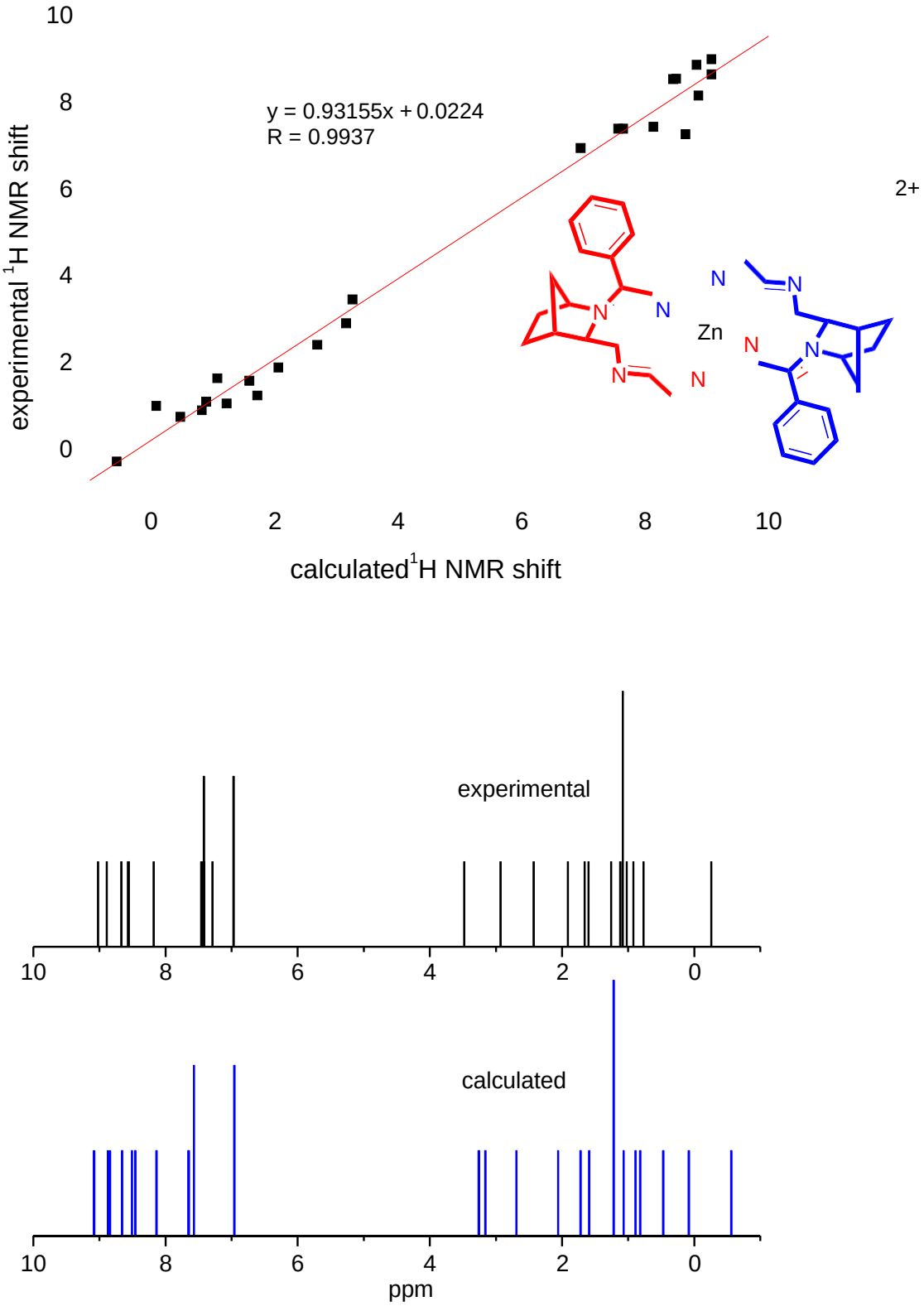


Figure S16. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 4N-coordinated $[ZnL_2]^{2+}$ complex of ligand **10** and the correlation of shift values for particular positions.

Compound 10. $[ZnL_2]^{2+}$ complex. (N6) coordination

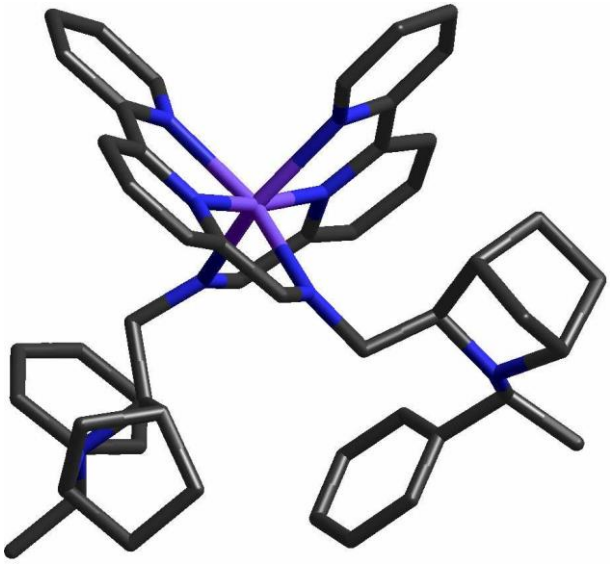


Table S14. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated (average)	Experimental	Difference
BP3	9.00	9.02	-0.02
BP4	9.04	8.89	0.15
BP3’	8.65	8.67	-0.02
BP5	8.40	8.57	-0.17
H3”	8.18	8.56	-0.38
BP4’	8.28	8.18	0.10
BP5’	7.52	7.46	0.06
para-H	7.93	7.42	0.51
meta-H	7.90	7.42	0.48
BP6’	7.38	7.29	0.09
ortho-H	7.65	6.97	0.68
H1	3.22	3.48	-0.26
H1’	3.16	2.93	0.23
H1”	2.46	2.43	0.03
H1”	2.06	1.91	0.15
H7	1.05	1.66	-0.61
H6	1.76	1.60	0.16
H3	0.68	1.26	-0.58
H6	1.20	1.12	0.08
1’-Me	1.22	1.08	0.14
H7	0.68	1.02	-0.34
H4	0.38	0.92	-0.54
H5	0.83	0.77	0.06
H5	0.50	-0.26	0.76

*Average values of calculated chemical shifts for the two subunits were given.

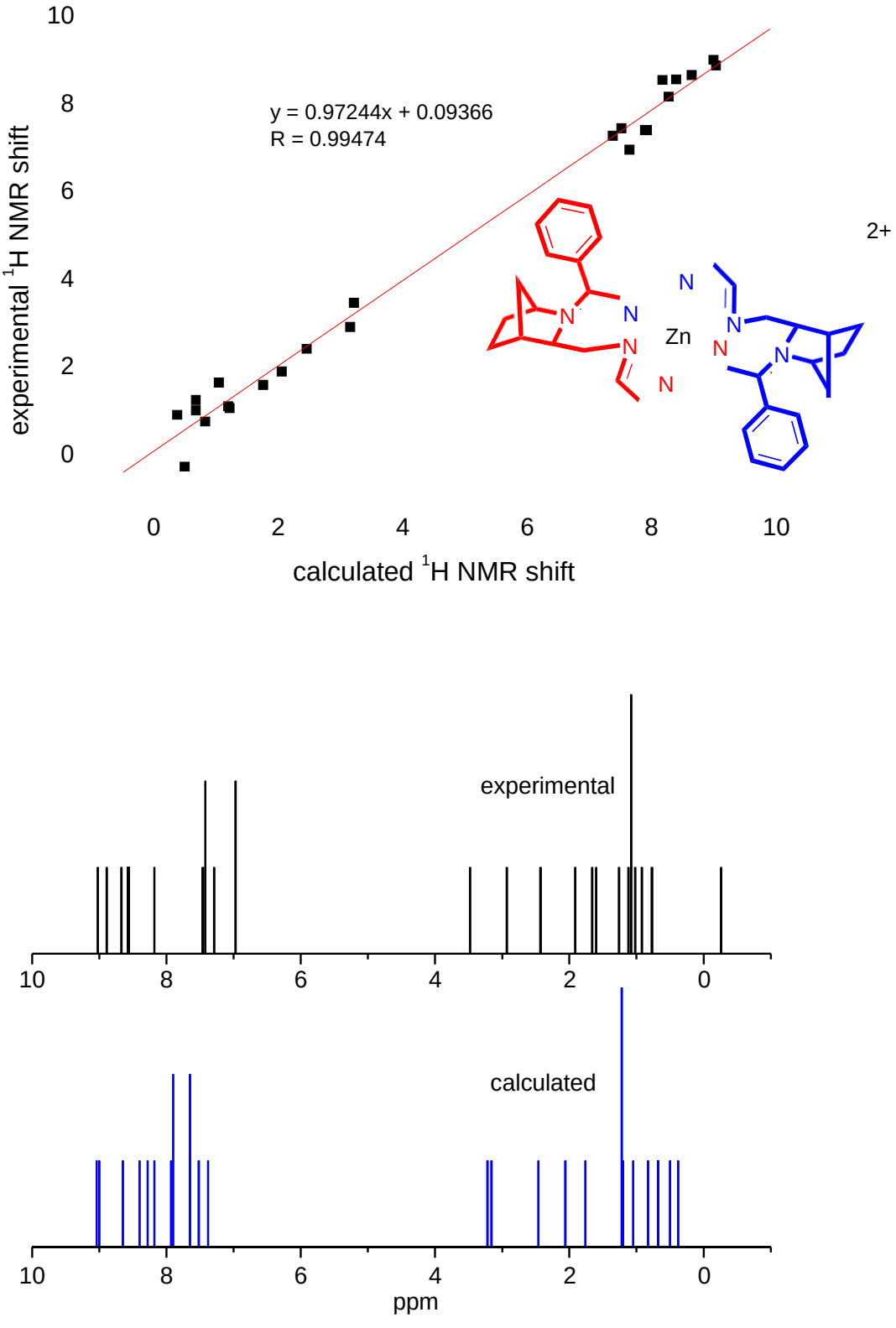
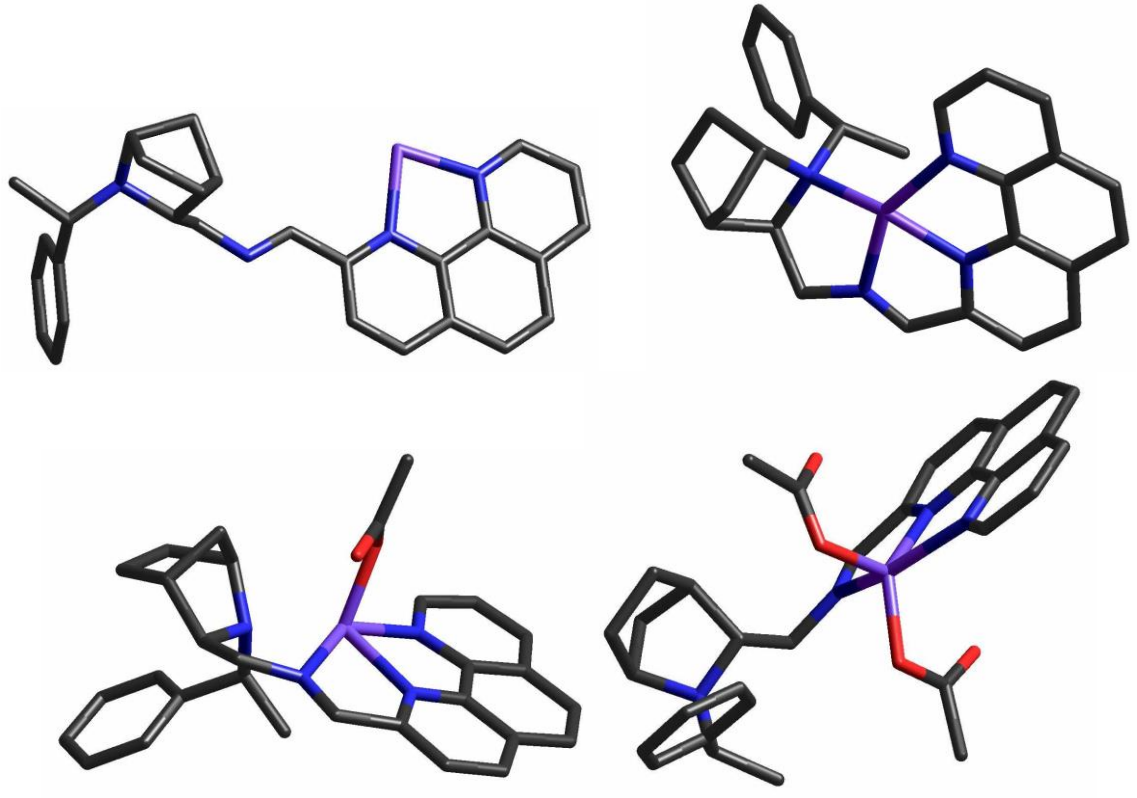


Figure S17. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 6N-coordinated $[ZnL_2]^{2+}$ complex of ligand **10** and the correlation of shift values for particular positions.

Compound 11, Zn(II) complexes of 1:1 stoichiometry

Table S15. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)

Position	Calculated ^{1}H NMR chemical shift				Experimental ^{1}H NMR chemical shift
	$[ZnL]^{2+}$ (2N)	$[ZnL]^{2+}$ (4N)	$[ZnL(OAc)]^{+}$	$[ZnL(OAc)_2]$	
P9	9.38	9.54	9.77	9.60	9.08
P4	9.05	9.36	9.25	9.08	8.91
P7	9.50	9.30	9.07	8.90	8.68
P6	8.83	8.67	8.53	8.46	8.15
P5	8.61	8.64	8.52	8.40	8.15
P3	9.09	8.58	8.50	8.36	8.12
P8	8.60	8.43	8.46	8.30	7.99
H3”	8.67	9.26	9.12	9.06	7.78
ortho-H	7.81	7.64	7.72	8.30	7.51
meta-H	7.69	7.76	7.73	7.80	7.41
para-H	7.57	7.81	7.75	7.69	7.39
H1	3.49	4.25	4.26	3.10	3.73
H1’	4.26	4.54	4.58	4.02	3.66
H1”	3.44	4.51	4.41	4.31	3.45
H1”	2.97	3.86	4.11	3.58	2.89
H3	3.17	3.91	3.99	3.84	2.57
H4	1.33	2.14	2.04	1.35	2.45
H6	1.99	2.45	2.39	0.80	2.10
H7	1.71	1.92	2.35	1.52	1.84
H5	1.55	1.43	1.39	0.87	1.69
H6	1.51	1.35	1.31	0.64	1.49
H5	1.23	-0.03	0.00	0.65	1.41
1’-Me	1.75	1.06	1.12	1.73	1.40
H7	1.06	1.63	1.40	0.92	1.39



Compound 11, $[ZnL]^{2+}$ complex. (N2) coordination

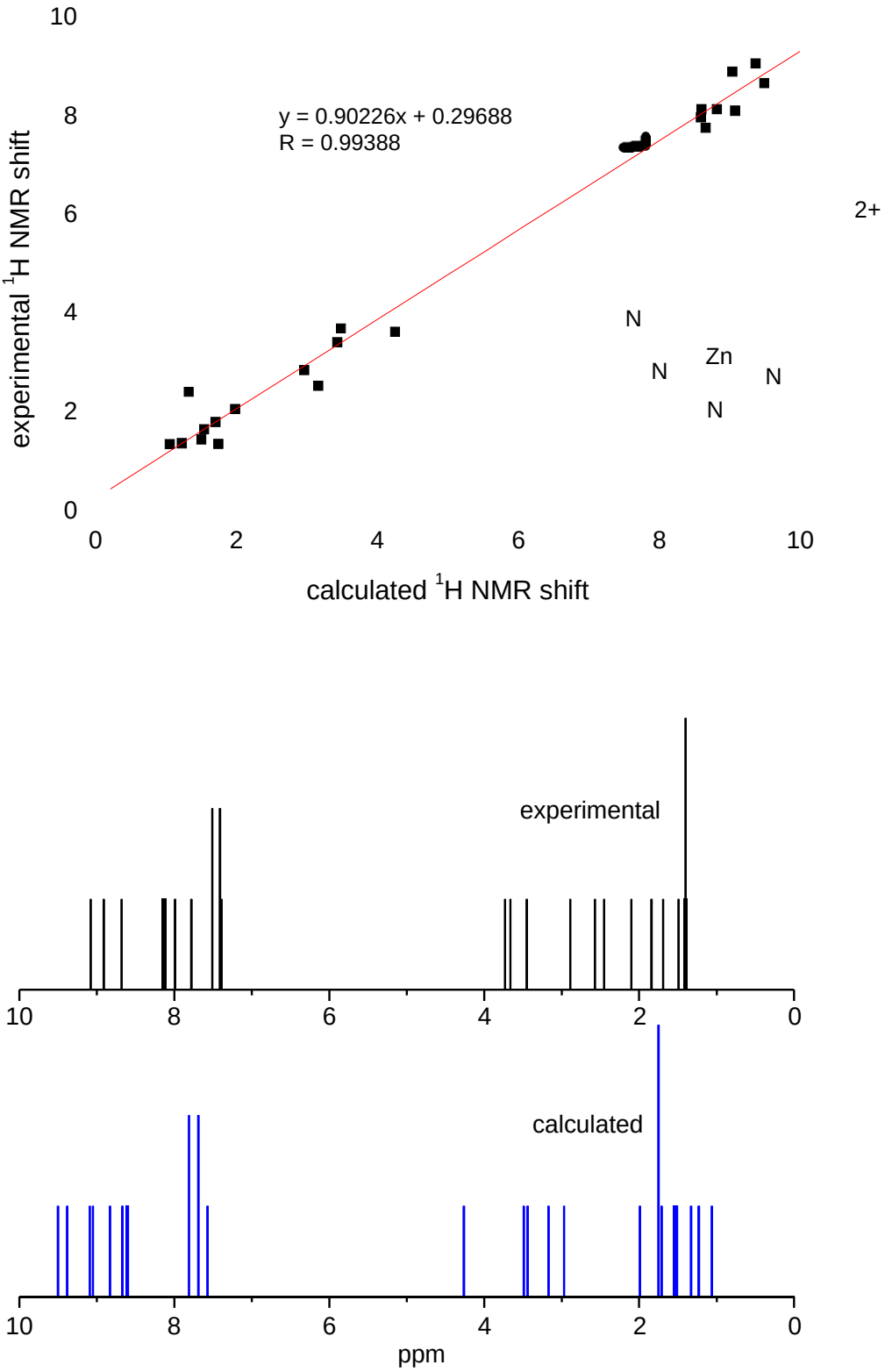


Figure S18. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 2N-coordinated $[ZnL]^{2+}$ complex of ligand **11** and the correlation of shift values for particular positions.

Compound 11, $[ZnL]^{2+}$ complex. (N4) coordination

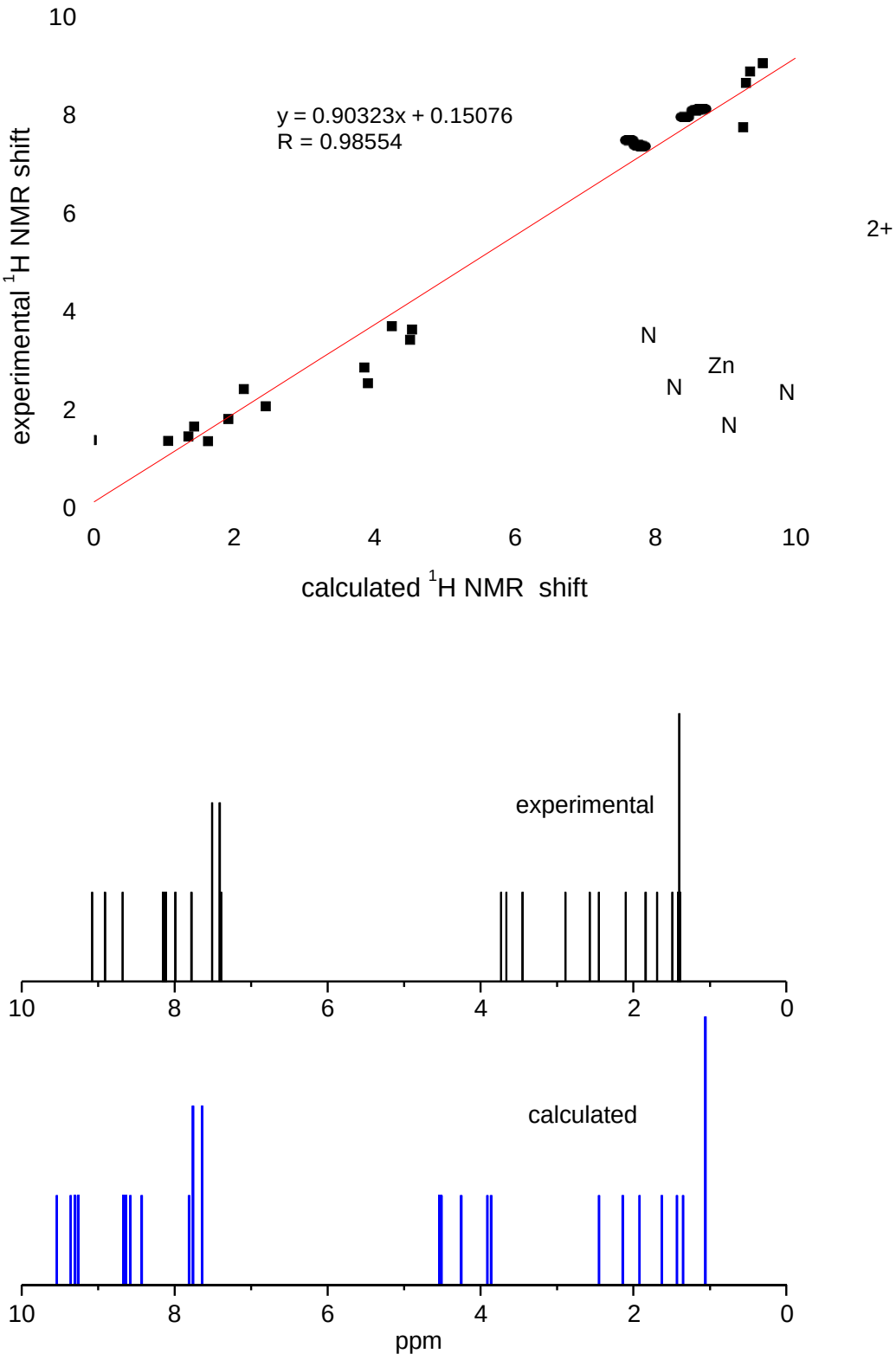


Figure S19. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 4N-coordinated $[ZnL]^{2+}$ complex of ligand **11** and the correlation of shift values for particular positions.

Ligand 11, $[ZnL(OAc)]^+$ complex

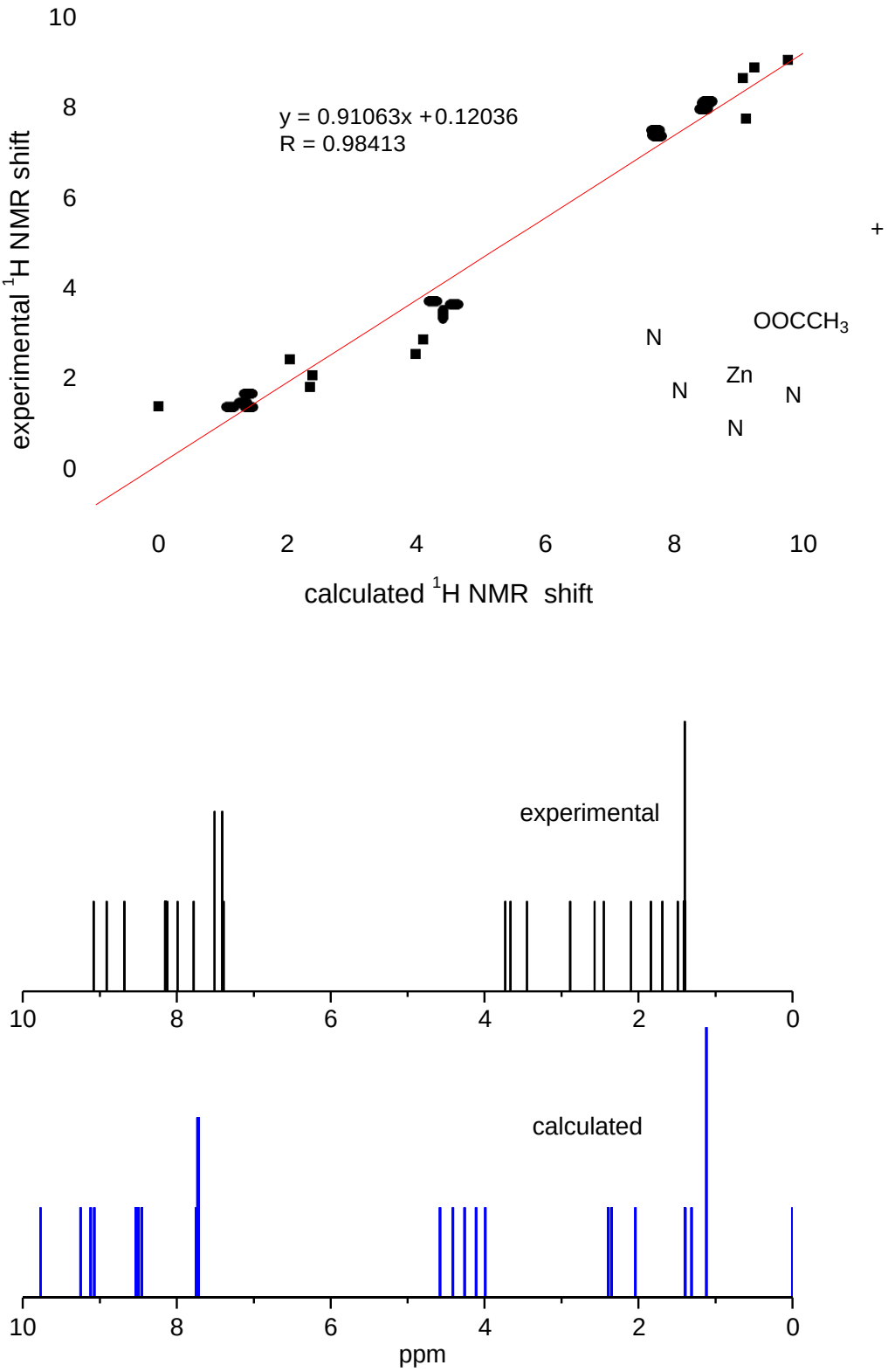


Figure S20. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of $[ZnL(OAc)]^+$ complex of ligand **11** and the correlation of shift values for particular positions.

Compound 11, [ZnL(OAc)$_2$] complex

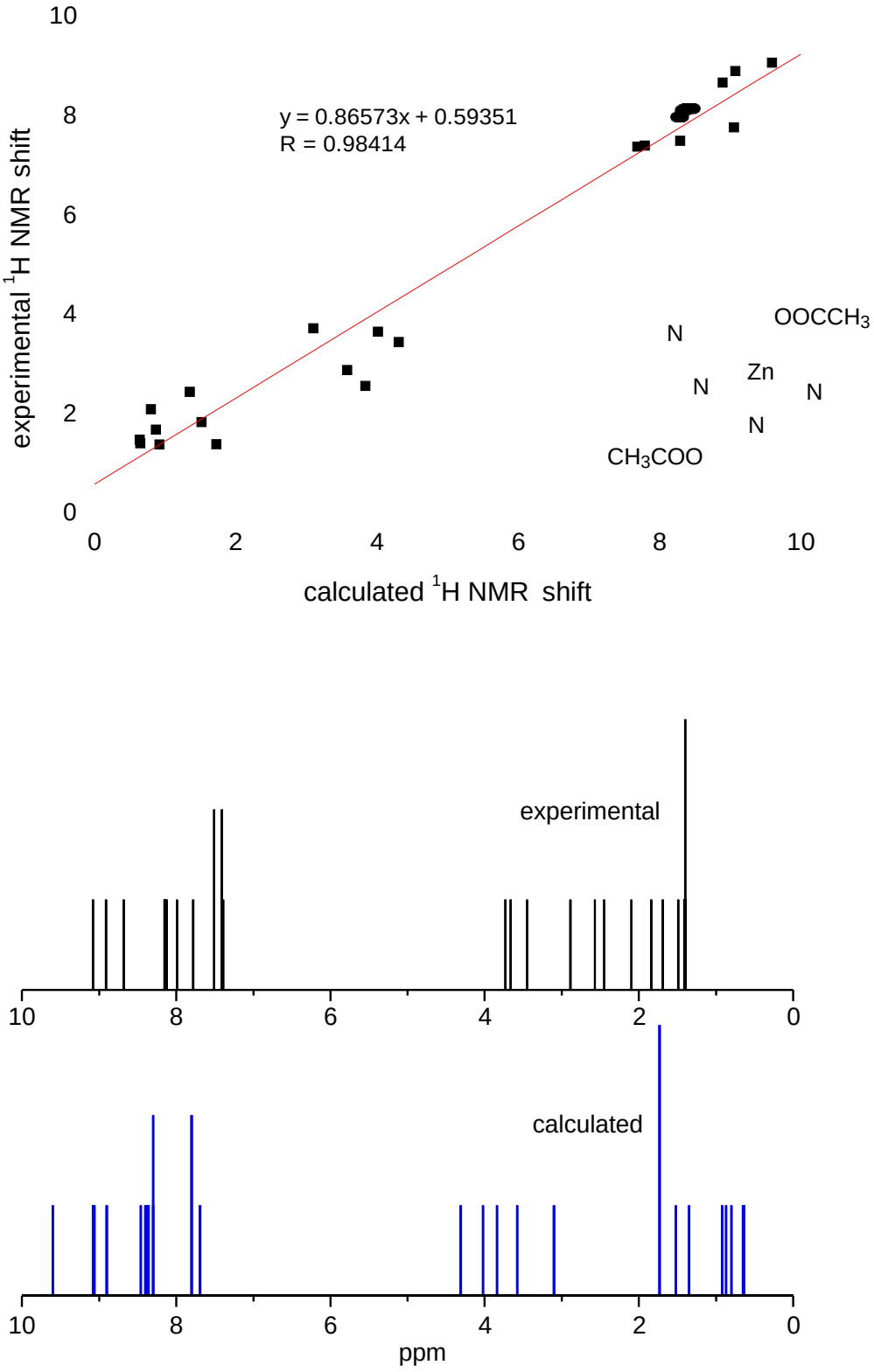


Figure S21. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of [ZnL(OAc)$_2$] complex of ligand **11** and the correlation of shift values for particular positions.

Compound 11. $[ZnL_2]^{2+}$ complex. (N4) coordination

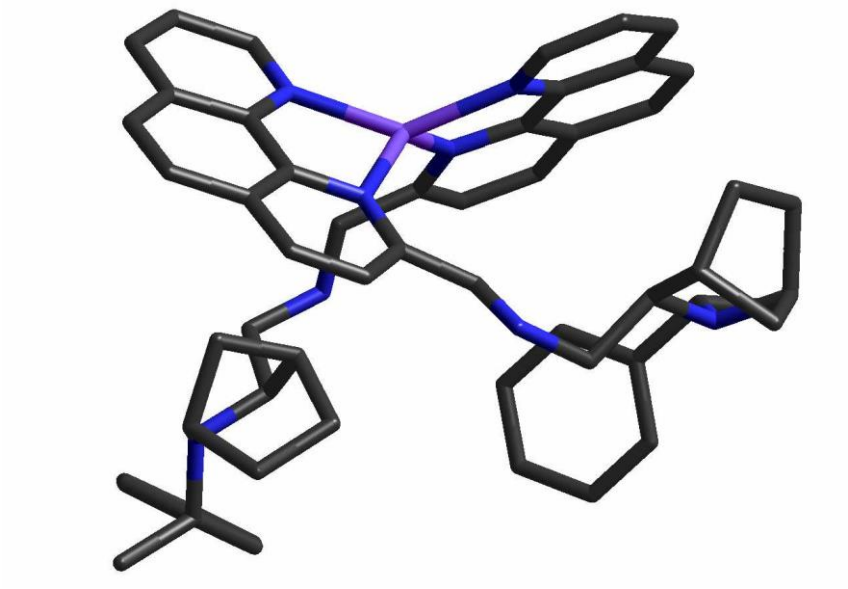


Table S16. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated (average)	Experimental	Difference
P4	9.18	9.45	-0.27
P3	8.78	8.88	-0.10
H3”	8.73	8.84	-0.11
P7	9.42	8.65	0.77
P5	8.70	8.45	0.25
P6	8.86	8.31	0.55
P9	9.26	7.63	1.63
P8	8.50	7.63	0.87
meta-H	7.33	7.44	-0.11
para-H	7.49	7.43	0.06
ortho-H	6.73	6.89	-0.16
H1	2.98	3.36	-0.38
H1”	2.76	3.04	-0.28
H1’	2.03	2.65	-0.62
H1”	2.08	2.50	-0.42
H7	0.66	1.61	-0.95
H6	0.84	1.40	-0.56
H6	1.14	1.30	-0.16
H3	1.10	1.06	0.04
1’-Me	0.96	0.99	-0.03
H7	-0.46	0.90	-1.36
H4	1.14	0.86	0.28
H5	0.58	0.25	0.33
H5	0.28	-1.46	1.74

*Average values of calculated chemical shifts for the two subunits were given.

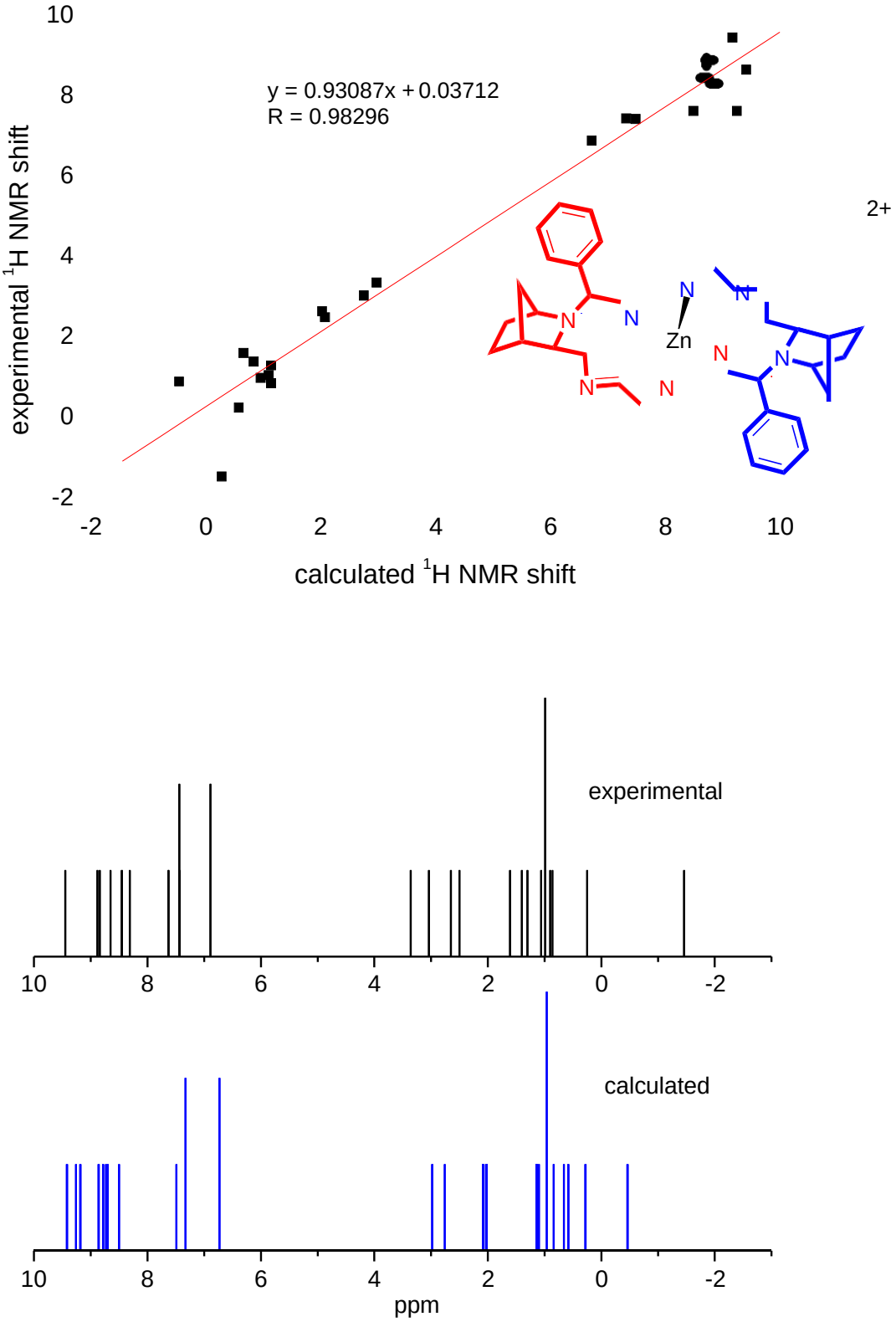


Figure S22. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 4N-coordinated $[ZnL_2]^{2+}$ complex of ligand **11** and the correlation of shift values for particular positions.

Compound 11. $[ZnL_2]^{2+}$ complex. (N6) coordination

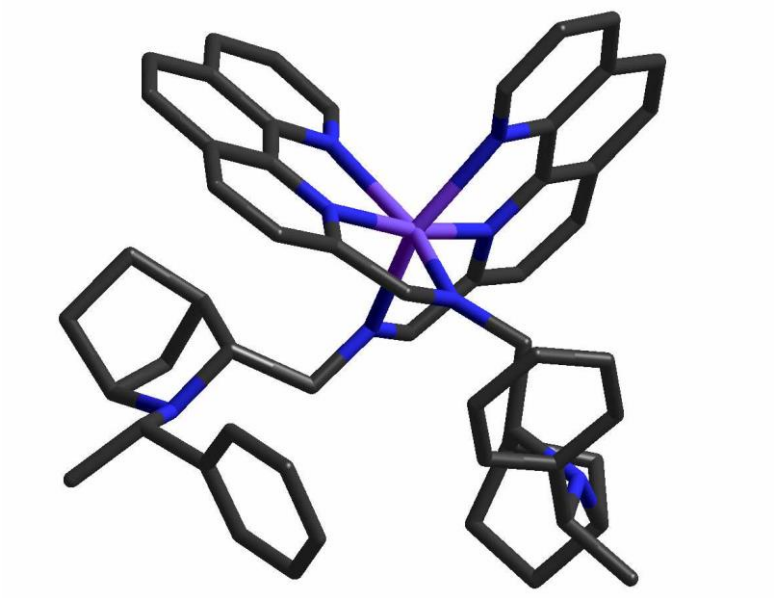


Table S17. Comparison of DFT calculated and experimental ^{1}H NMR chemical shifts (methanol-d_4, all values in ppm)*

Position	Calculated (average)	Experimental	Difference
P4	9.57	9.45	0.12
P3	8.84	8.88	0.04
H3”	8.54	8.84	-0.30
P7	8.80	8.65	0.15
P5	8.66	8.45	0.21
P6	8.57	8.31	0.26
P8	7.76	7.63	0.13
P9	7.58	7.63	-0.05
meta-H	7.93	7.44	0.49
para-H	7.98	7.43	0.55
ortho-H	7.60	6.89	0.71
H1	3.13	3.36	-0.23
H1”	2.58	3.04	-0.46
H1’	3.06	2.65	0.41
H1”	2.18	2.50	-0.32
H7	1.03	1.61	-0.58
H6	1.47	1.40	0.07
H6	0.98	1.30	-0.32
H3	0.72	1.06	-0.34
1’-Me	1.14	0.99	0.15
H7	0.54	0.90	-0.36
H4	0.39	0.86	-0.47
H5	0.70	0.25	0.45
H5	-0.68	-1.46	0.78

*Average values of calculated chemical shifts for the two subunits were given.

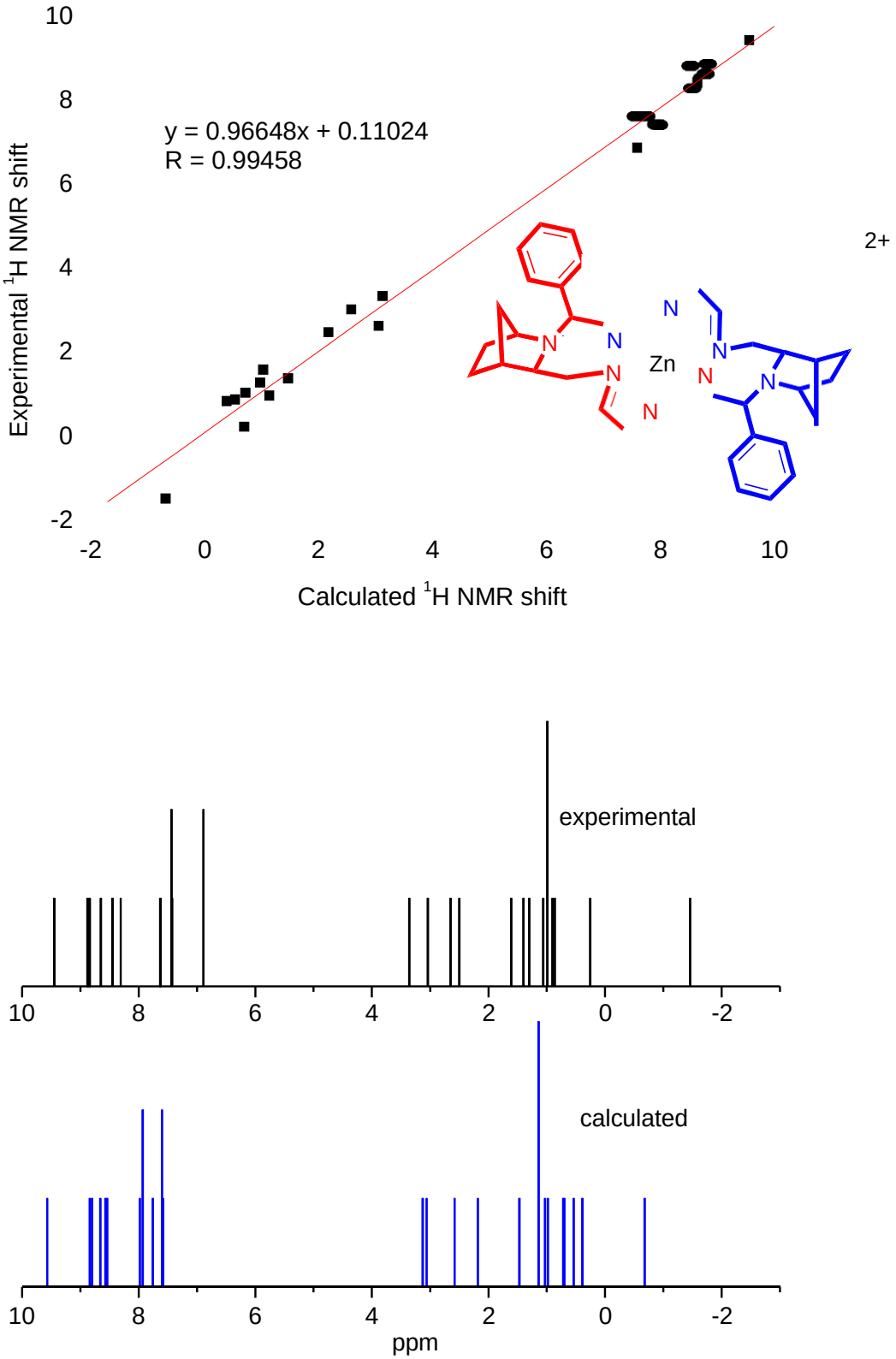


Figure S23. Comparison of experimental and DFT calculated averaged chemical ^{1}H NMR shift patterns of 6N-coordinated $[ZnL_2]^{2+}$ complex of ligand **11** and the correlation of shift values for particular positions.