Electronic Supporting Information

Vinyl Acetate Living Radical Polymerization Mediated by Cobalt Porphyrins: Kinetic-Mechanistic Studies

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I. Data of LRP mediated by Co^{II}(TMP)

Table SI1. PVAc mediated by Co^{II}(TMP) in THF at 60 ºC. The condition was listed in Table 1 entry 1.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	120	3.9	3,900	4,200	1.31
2	150	16.7	4,300	15,200	1.46
3	180	23.7	4,300	21,200	1.48
4	200	29.1	4,200	25,900	1.50
5	215	32.0	4,300	28,400	1.49
6	230	35.1	4,200	31,000	1.51
7	245	38.3	4,500	33,800	1.44

Table SI2. PVAc mediated by Co^{II}(TMP) in EA at 60 ºC. The condition was listed in Table 1 entry 2.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	420	4.8	4,000	4,900	1.08
2	460	11.5	12,700	10,700	1.16
3	490	21.3	16,900	19,100	1.29
4	520	28.6	21,000	25,400	1.34
5	550	35.5	22,700	31,400	1.43
6	580	41.5	24,400	36,600	1.49
7	620	46.2	24,800	40,600	1.69
8	670	53.1	25,600	46,500	1.75
9	720	58.0	27,000	50,700	1.75

Table SI3. PVAc mediated by Co^{II}(TMP) in acetone at 60 ºC. The condition was listed in Table 1 entry 3.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	440	7.4	8,100	7,200	1.14
2	470	18.0	9,900	49,720	1.32
3	500	23.1	10,200	20,700	1.52
4	530	27.5	11,200	24,500	1.57
5	560	34.2	10,600	30,300	1.73
6	620	41.9	11,800	36,900	1.67
7	680	49.0	11,600	43,000	1.72
8	775	58.3	11,100	51,100	1.80

Table SI4. PVAc mediated by Co^{II}(TMP) in DCM at 60 ºC. The condition was listed in Table 1 entry 4.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	410	2.9	1,700	3,300	1.05
2	450	6.5	3,700	6,500	1.11
3	480	12.1	7,500	12,300	1.32
4	510	19.4	9,500	17,500	1.52
5	540	25.4	10,000	22,700	1.71
6	570	31.5	10,600	28,000	1.78
7	600	35.1	10,600	31,000	1.84
8	640	40.1	11,200	35,400	1.85
9	690	44.1	11,100	38,800	1.91
10	750	50.5	11,200	44,300	1.92
11	820	55.0	11,700	48,100	1.89

Table SI5. PVAc mediated by Co^{II}(TMP) in benzene at 60 ºC. The condition was listed in Table 1 entry 5.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	480	1.9	2,800	2,500	1.07
2	525	2.9	4,500	3,300	1.11
3	570	5.7	6,500	5,700	1.12
4	615	7.4	7,700	7,200	1.14
5	660	9.1	9,400	8,700	1.18
6	750	13.0	12,500	12,100	1.28
7	840	17.4	15,300	15,800	1.36
8	930	21.9	16,800	19,700	1.45
9	1020	25.4	18,200	22,700	1.50
10	1140	29.1	18,500	25,900	1.61
11	1260	34.2	19,000	30,300	1.69
12	1400	37.5	19,700	33,100	1.72

Table SI6. PVAc mediated by Co^{II}(TMP) in bulk at 60 ºC. The condition was listed in Table 1 entry 6.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	390	5.7	6,200	5,700	1.08
2	410	19.4	21,300	17,500	1.08
3	430	31.0	31,900	27,600	1.12
4	450	40.8	40,300	36,000	1.16
5	470	49.0	44,900	43,000	1.19
6	490	62.3	55,400	54,400	1.25
7	510	70.0	67,100	61,100	1.34

Table SI7. PVAc mediated by Co^{II}(TMP) in bulk at 60 ºC. The condition was listed in Table 1 entry 7.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	400	5.7	12,000	8,100	1.07
2	430	23.1	36,700	30,600	1.10
3	460	35.1	56,000	46,100	1.15
4	470	39.4	57,000	51,700	1.18
5	480	46.0	63,200	60,100	1.19
6	490	51.9	64,700	67,800	1.20
7	500	55.2	71,800	72,000	1.27

Table SI8. PVAc mediated by Co^{II}(TMP) in bulk at 60 ºC. The condition was listed in Table 1 entry 8.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	420	1.0	6,300	2,600	1.09
2	435	5.7	15,100	10,600	1.11
3	450	11.5	29,300	20,600	1.13
4	465	18.0	39,900	31,900	1.16
5	480	24.8	51,400	43,600	1.19
6	500	32.0	61,700	55,900	1.24
7	520	34.6	69,200	60,500	1.24
8	550	43.8	92,400	76,300	1.28

Table SI9. Polymerization of vinyl acetate mediated by Co^{II}(TMP) in coordinating solvents [a].

Entry	[VAc]/[Co^{II}]	[additives]/[Co^{II}]	Time(min)	Conv.(%) [d]	M_n(g mol^{-1})	$M_{n,th}$(g mol^{-1}) [e]	PDI
1[b]	1000	1	465	49.8	42,700	43,700	1.29
2[b]	1000	25	406	59.4	79,800	51,900	1.37
3[b]	1000	50	280	62.6	75,800	54,700	1.52
4[c]	1000	1	470	49.5	42,200	43,400	1.33
5[c]	1000	25	480	63.0	70,400	55,000	1.51
6[c]	1000	50	470	32.9	43,400	29,200	1.78

[a] General condition: $[Co^{II}(TMP)]_o$/ $[AIBN]_o$ = 1/ 8, $[VAc]_o$ = 10.74 M in bulk, reaction temperature = 333 K. With [b] THF and [c] pyridine as an additive. [d] Conversion was determined by ^{1}H NMR. [e] $M_{n,\,th} = [VAc]_o/[Co^{II}(TMP)]_o \times$ conversion × M. W. of VAc.

Table SI10. PVAc mediated by Co^{II}(TMP) in bulk with THF as additives at 60 ºC. The condition was listed in Table SI9 entry 1.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	390	12.3	14,900	11,400	1.07
2	405	18.0	22,300	16,400	1.08
3	420	27.5	29,300	24,500	1.12
4	435	37.1	32,400	32,800	1.15
5	450	42.5	35,900	37,500	1.20
6	465	49.8	42,700	43,700	1.29

Table SI11. PVAc mediated by Co^{II}(TMP) in bulk with THF as additives at 60 ºC. The condition was listed in Table SI9 entry 2.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	300	3.9	6,200	4,200	1.08
2	320	12.3	21,900	11,400	1.09
3	340	26.0	40,400	23,200	1.12
4	350	30.6	44,200	27,100	1.18
5	360	36.7	48,600	32,400	1.20
6	370	40.1	56,300	35,400	1.23
7	382	46.5	64,500	40,900	1.24
8	392	51.0	70,400	44,700	1.35
9	406	59.4	79,800	51,900	1.37

Table SI12. PVAc mediated by Co^{II}(TMP) in bulk with THF as additives at 60 ºC. The condition was listed in Table SI9 entry 3.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	180	2.0	6,300	2,500	1.12
2	220	21.3	39,700	19,100	1.15
3	230	30.1	50,600	26,700	1.20
4	240	37.1	52,800	32,800	1.25
5	250	41.5	54,900	36,600	1.27
6	260	44.4	57,500	39,100	1.32
7	270	58.9	63,500	51,500	1.46
8	280	62.6	75,800	54,700	1.52

Table SI13. PVAc mediated by Co^{II}(TMP) in bulk with pyridine as additives at 60 ºC. The condition was listed in Table SI9 entry 4.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	390	5.7	5,200	5,700	1.12
2	400	9.9	89,00	9,400	1.13
3	420	19.4	17,400	17,500	1.15
4	440	27.0	25,200	24,100	1.18
5	460	42.9	33,600	37,700	1.23
6	470	49.5	42,200	43,400	1.33

Table SI14. PVAc mediated by Co^{II}(TMP) in bulk with pyridine as additives at 60 ºC. The condition was listed in Table SI9 entry 5.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	300	2.0	8,600	1,700	1.68
2	330	7.4	13,100	6,400	1.76
3	360	15.3	19,800	12,900	1.63
4	390	18.0	26,100	15,500	1.55
5	420	24.8	31,200	20,600	1.50
6	450	32.4	36,500	27,500	1.52
7	480	35.1	42,700	30,100	1.46

Table SI15. PVAc mediated by Co^{II}(TMP) in bulk with pyridine as additives at 60 ºC. The condition was listed in Table SI9 entry 6.

Entry	Time (min)	Conversion (%)	M_n	$M_{n,th}$	M_n/M_w
1	180	1.0	28,000	1,700	1.69
2	200	2.9	31,000	3,300	1.65
3	230	8.3	34,100	8,000	1.71
4	260	12.3	35,500	11,400	1.73
5	290	15.3	40,900	13,400	1.64
6	320	19.4	41,300	17,500	1.69
7	350	21.3	41,400	19,100	1.70
8	380	24.2	41,600	21,700	1.78
9	410	26.5	42,600	23,600	1.79
10	440	30.1	42,900	26,700	1.79
11	470	32.9	43,400	29,200	1.78

II. GPC traces

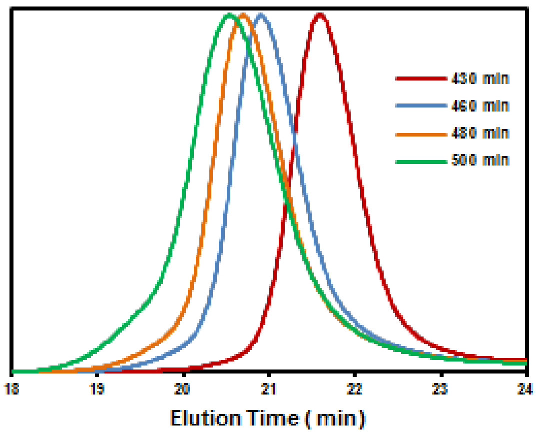

Fig. SI1 The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 1500/ 8/ 1, $[VAc]_0$ = 10.74 M.

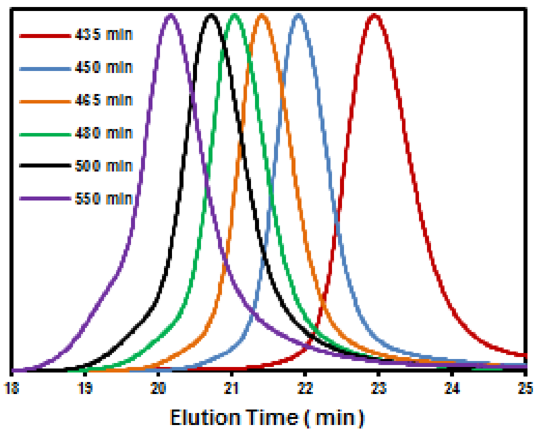

Fig. SI2 The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 2000/ 8/ 1, $[VAc]_0$ = 10.74 M.

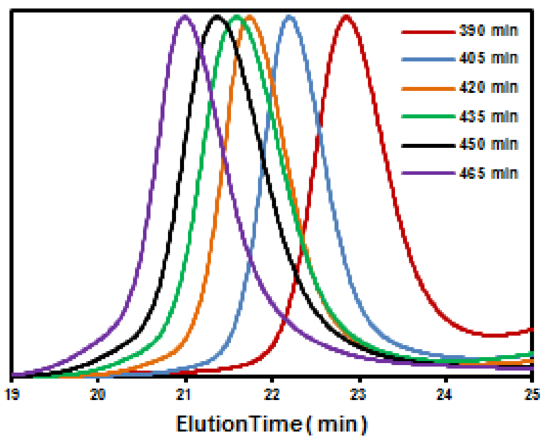

Fig. SI3 The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[THF]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 1000/ 1/ 8/ 1, $[VAc]_0$ = 10.74 M.

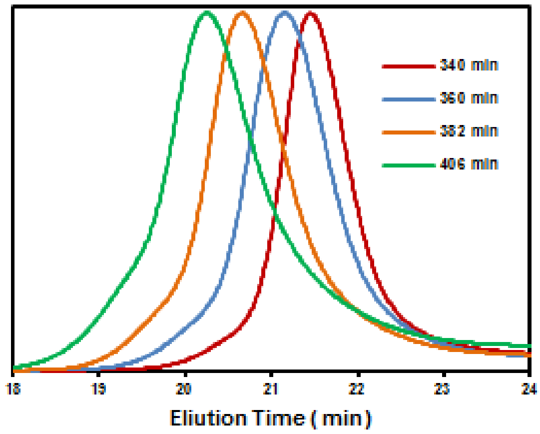

Fig. SI4. The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[THF]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 1000/ 25/ 8/ 1, $[VAc]_0$ = 10.74 M.

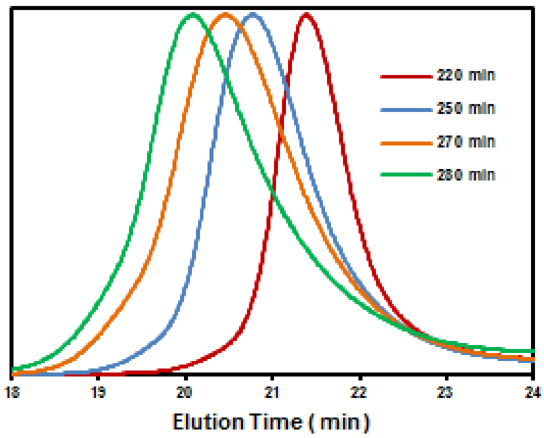

Fig. SI5. The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[THF]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 1000/ 50/ 8/ 1, $[VAc]_0$ = 10.74 M.

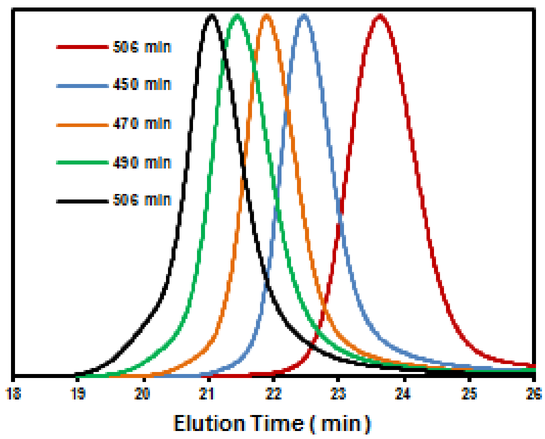

Fig. SI6. The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0$/ $[Py]_0$/ $[AIBN]_0$/ $[Co^{II}(TMP)]_0$ = 1000/ 1/ 8/ 1, $[VAc]_0$ = 10.74 M.

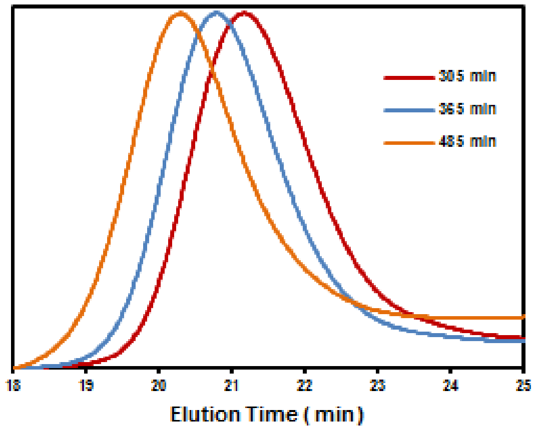

Fig. SI7. The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0/ [Py]_0/ [AIBN]_0/ [Co^{II}(TMP)]_0$ = 1000/ 25/ 8/ 1, $[VAc]_0$ = 10.74 M.

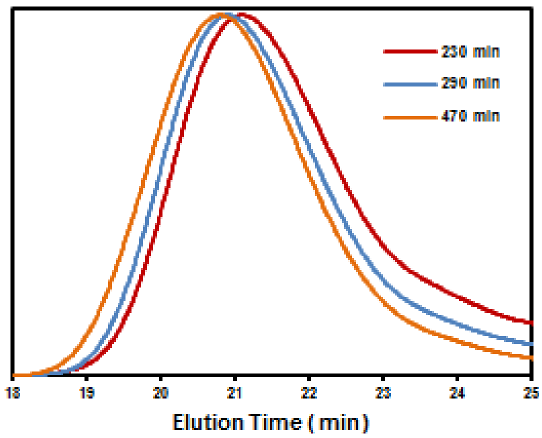

Fig. SI8. The GPC traces for polymerization of VAc in bulk at 333K under the condition of $[VAc]_0/ [Py]_0/ [AIBN]_0/ [Co^{II}(TMP)]_0$ = 1000/ 50/ 8/ 1, $[VAc]_0$ = 10.74 M.

III. Full ^{1}H spectrum of model reaction

1. Model reaction of Co(TMP) without additive.

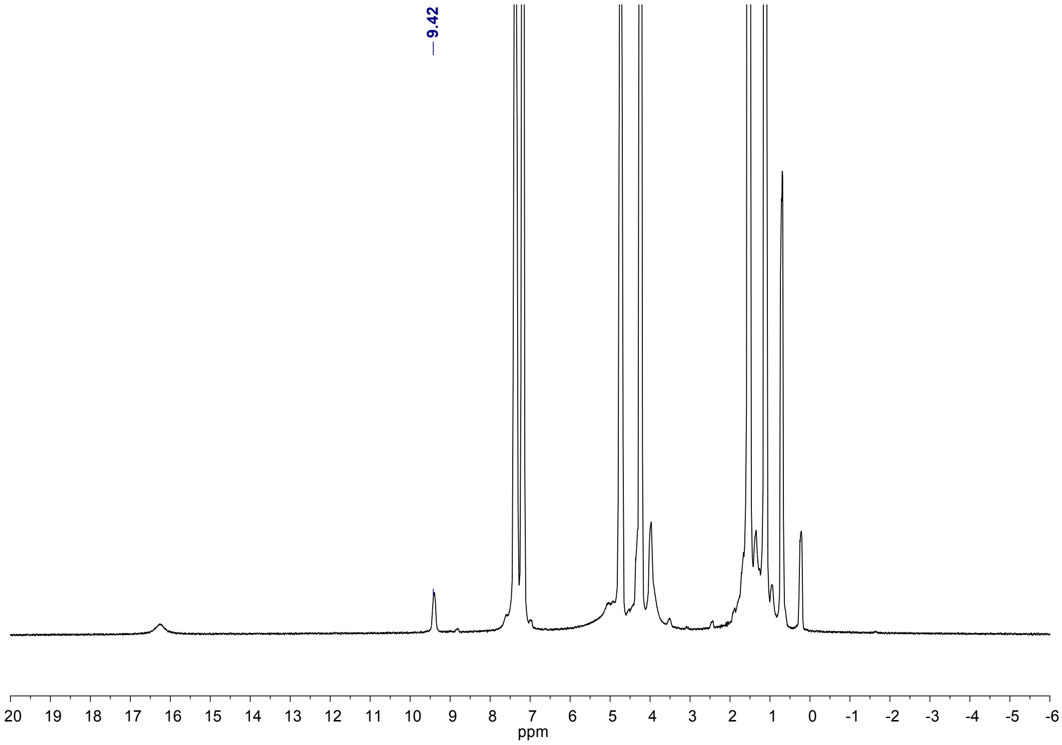

Fig. SI9 ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 0 minute.

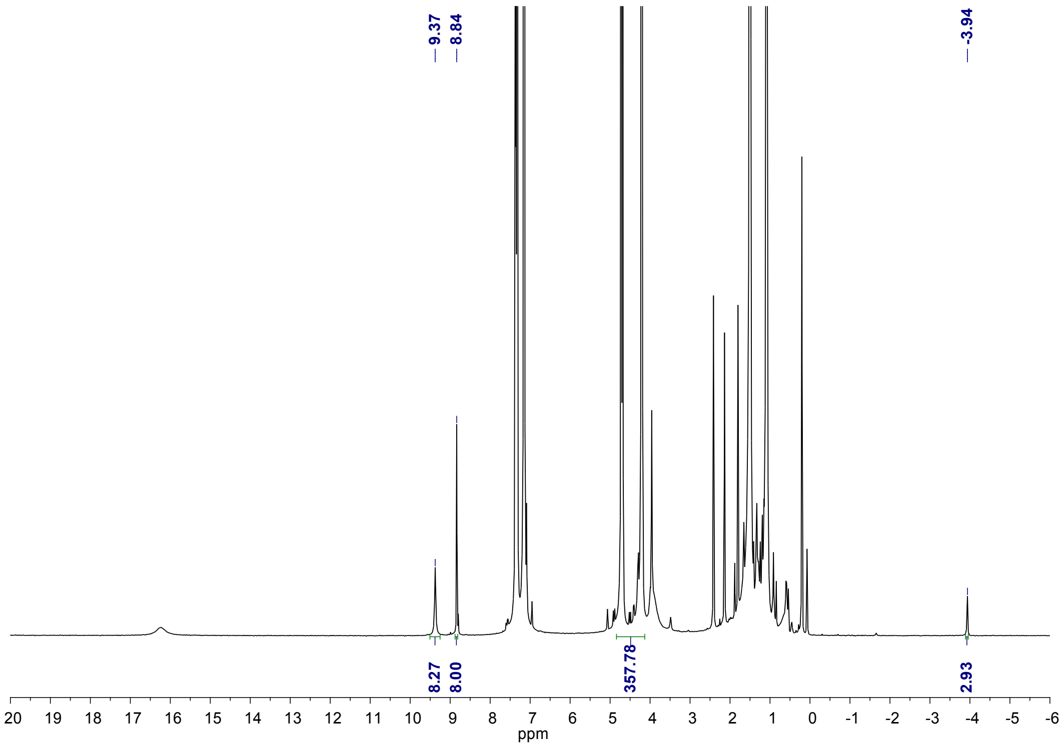

Fig. SI10 ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 60 minutes.

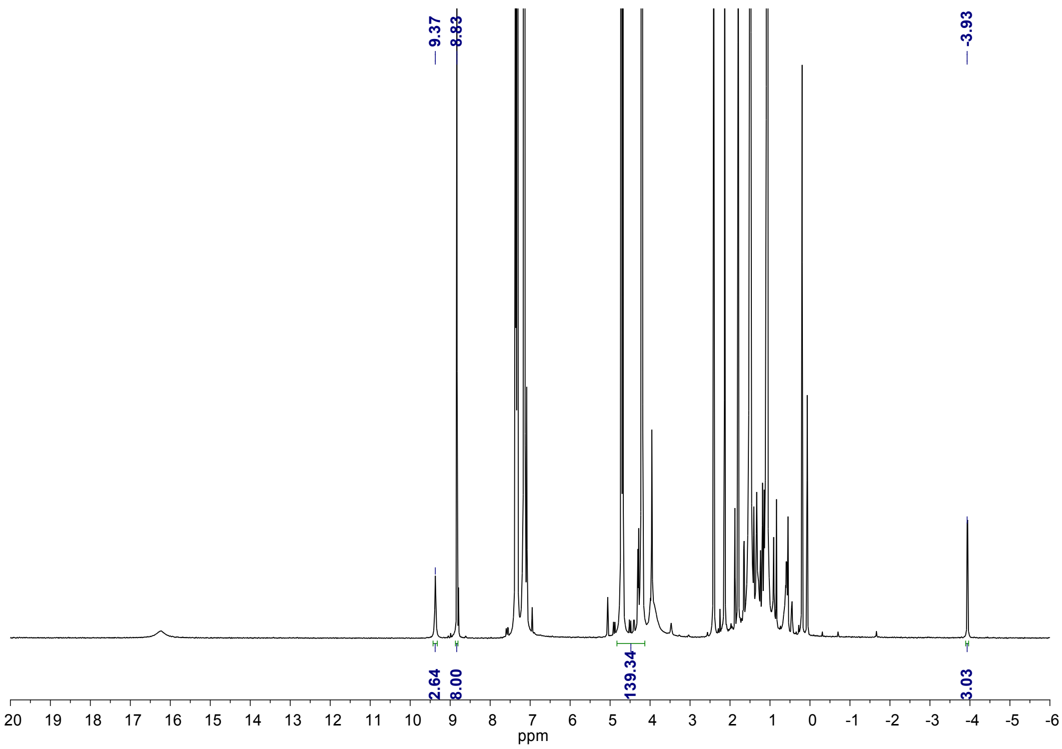

Fig. SI11 ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 120 minutes.

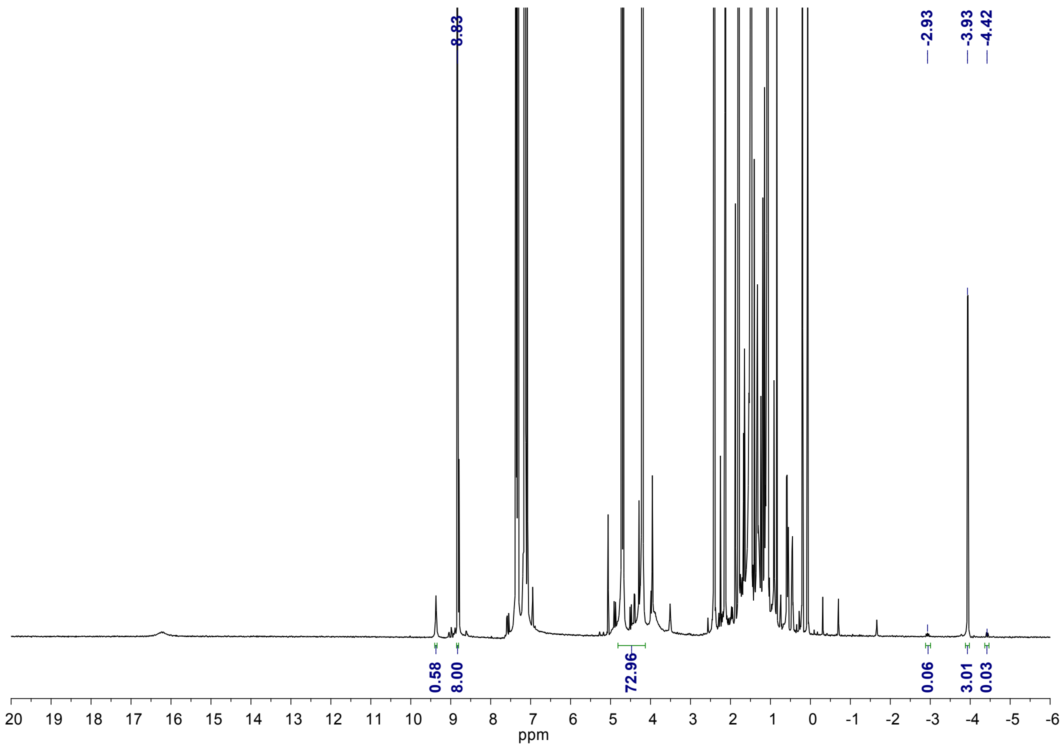

Fig. SI12. ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 180 minutes.

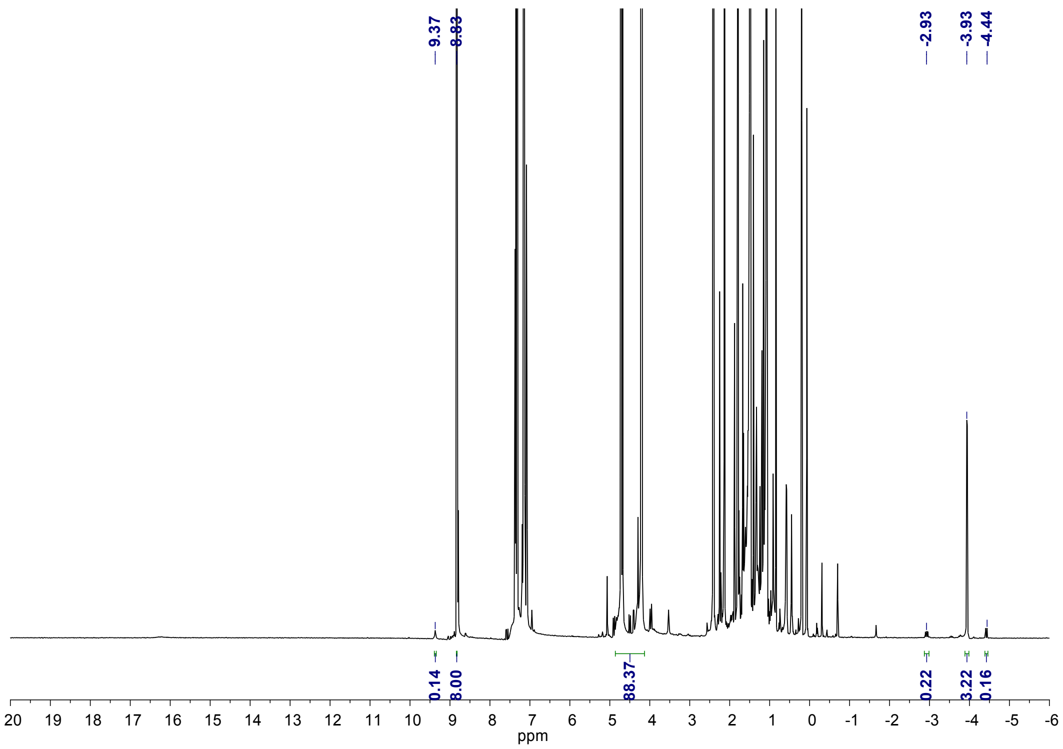

Fig. SI13. ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 300 minutes.

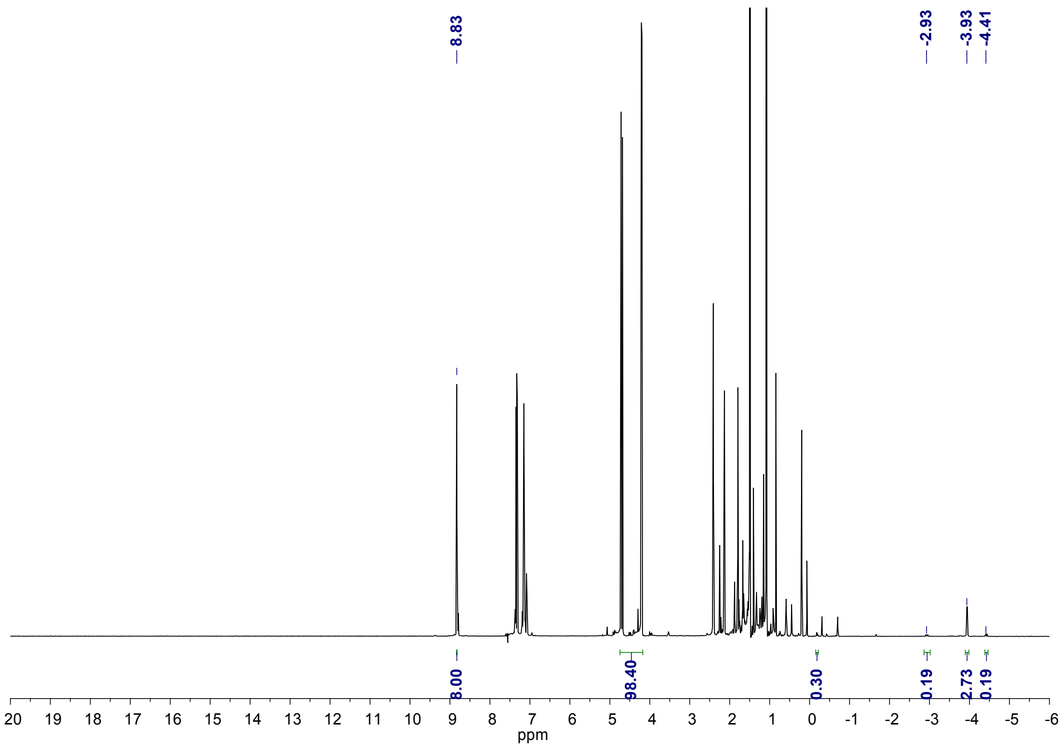

Fig. SI14. ^{1}H NMR LRP of VAc mediated by Co^{II}(TMP) in C_6D_6 at 420 minutes.

2. Model reaction of Co(TMP) with THF.

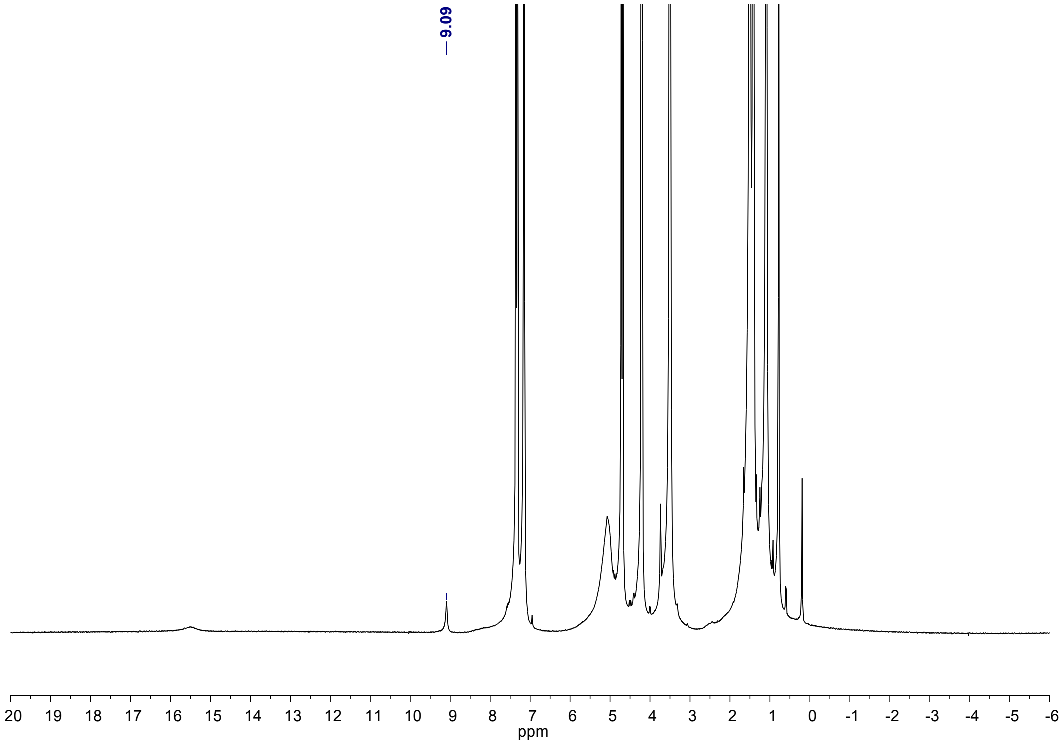

Fig. SI15 ^{1}H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 0 minutes.

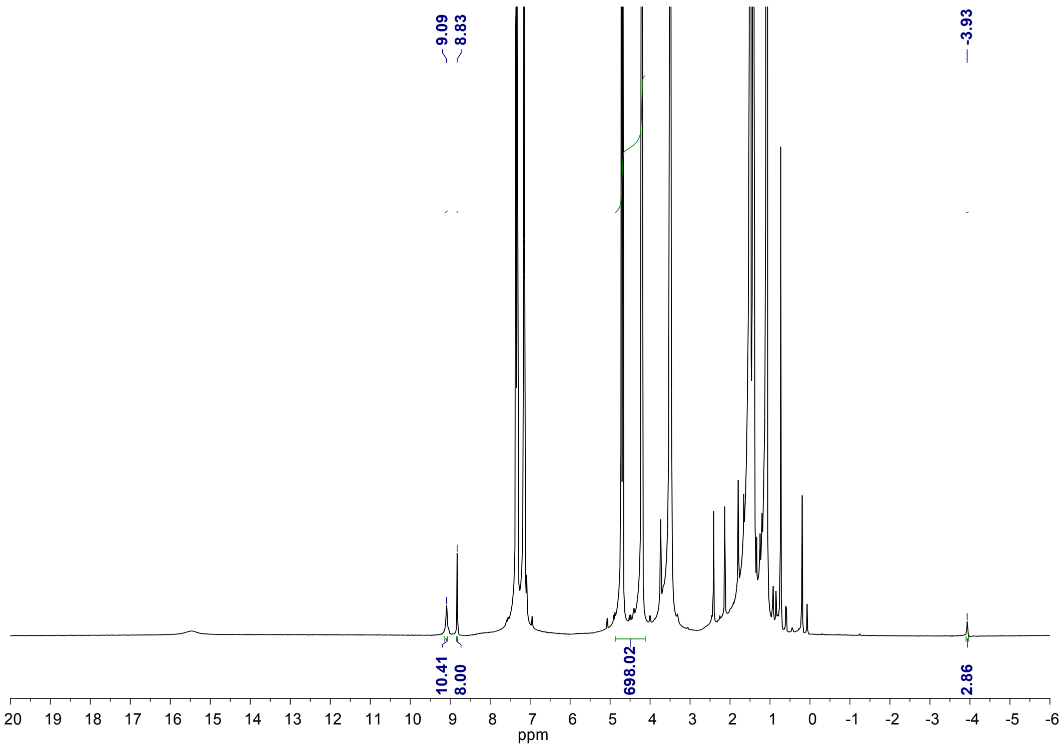

Fig. SI16 ^{1}H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 40 minutes.

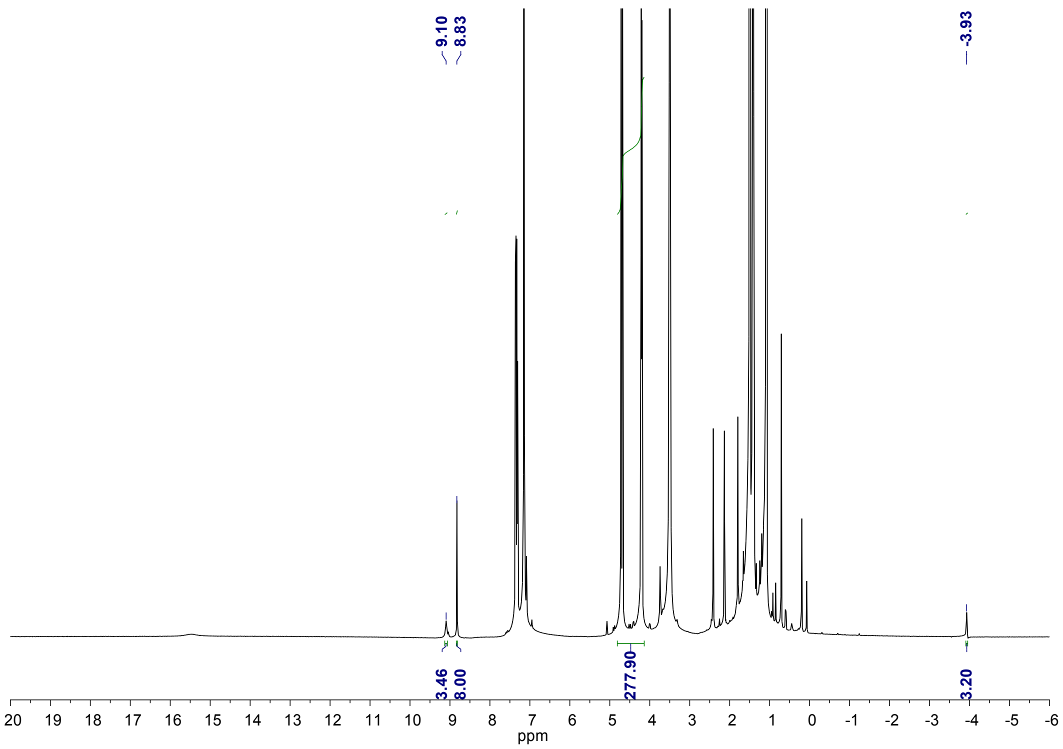

Fig. SI17 [1]H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 80 minutes.

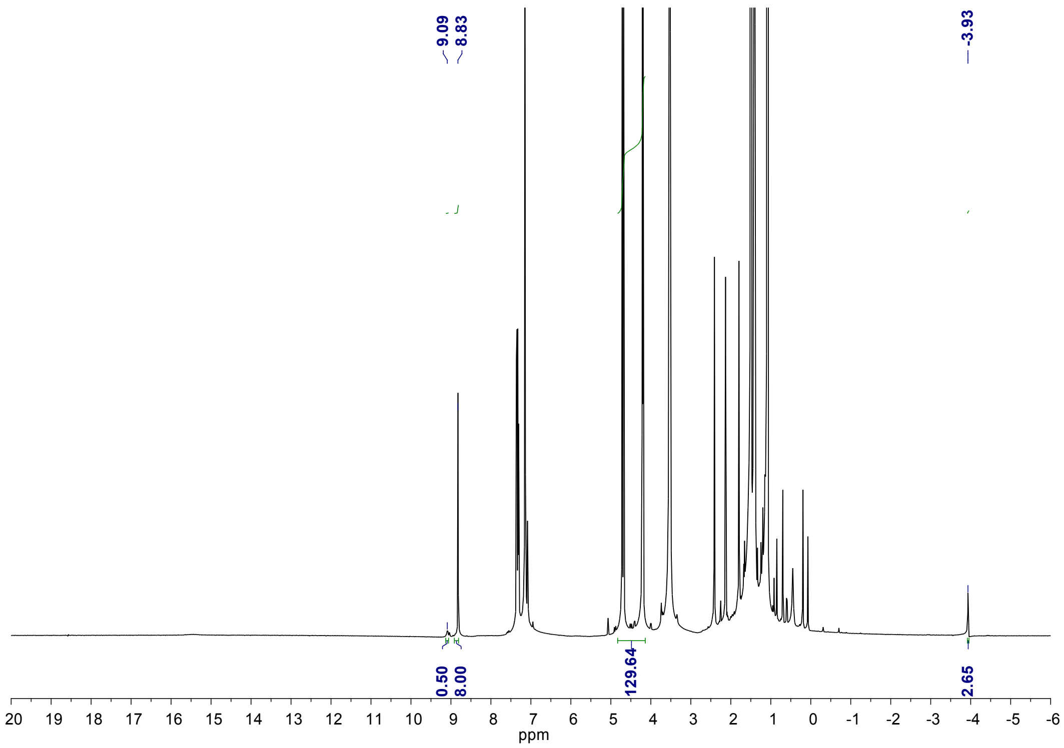

Fig. SI18 [1]H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 120 minutes.

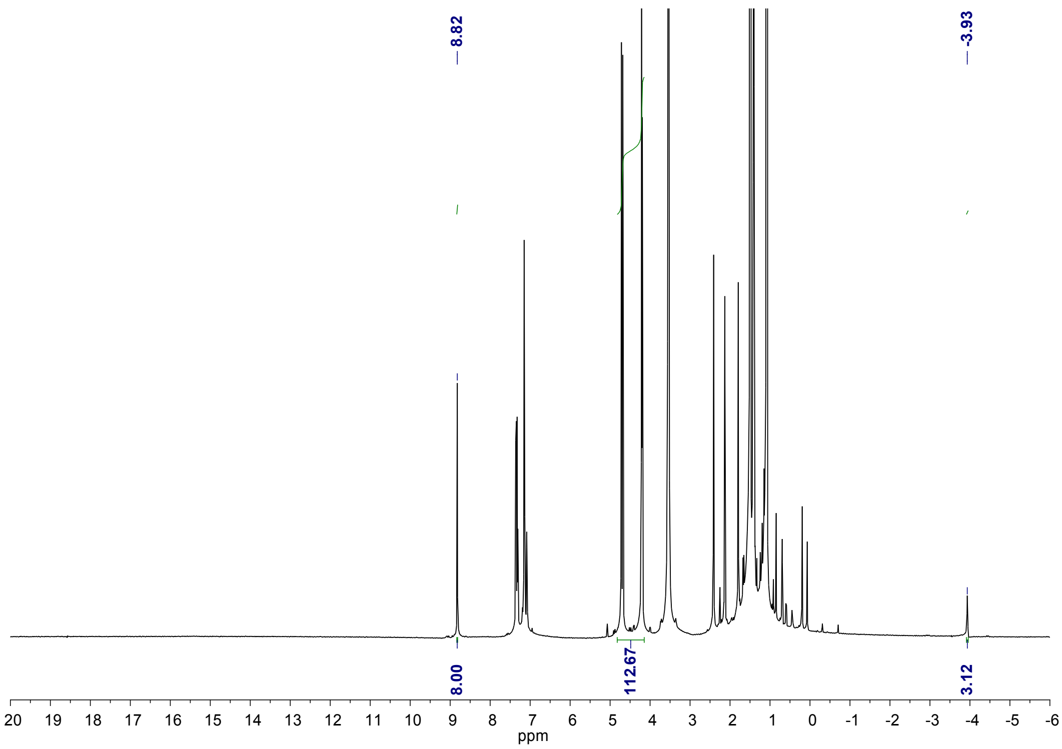

Fig. SI19 ^{1}H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 160 minutes.

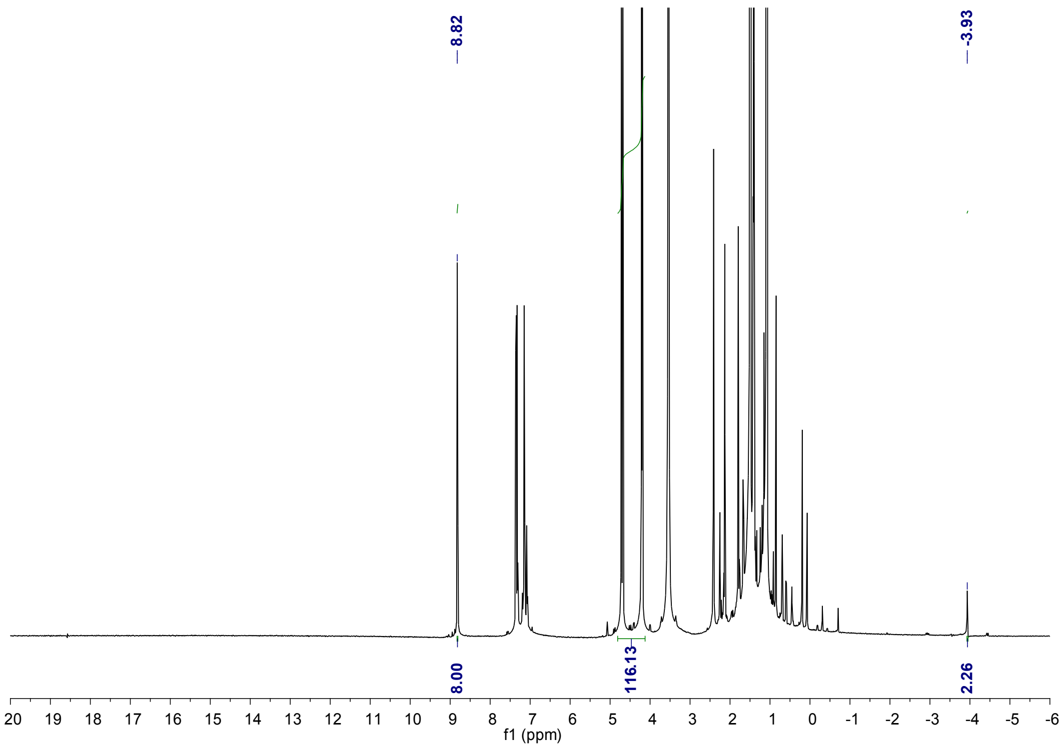

Fig. SI20 ^{1}H NMR of $Co^{II}(TMP)$ with THF in C_6D_6 at 240 minutes.

3. Model reaction of Co(TMP) with pyridine..

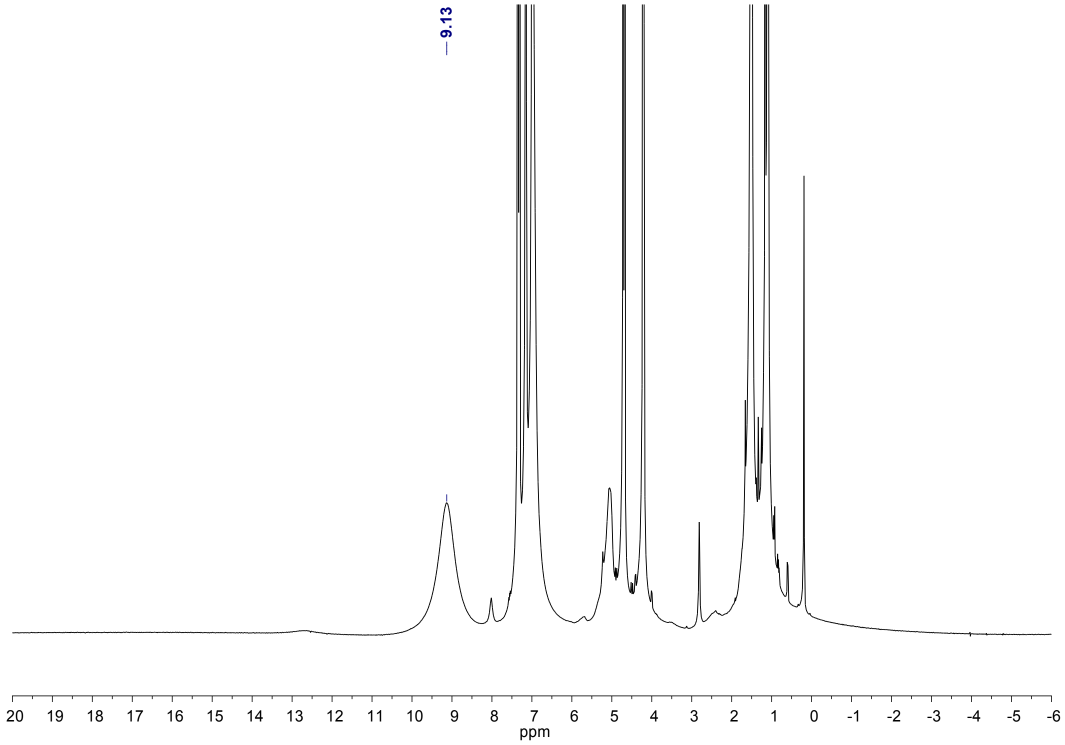

Fig. SI21 ^{1}H NMR of $Co^{II}(TMP)$ with pyridine in C_6D_6 at 0 minutes.

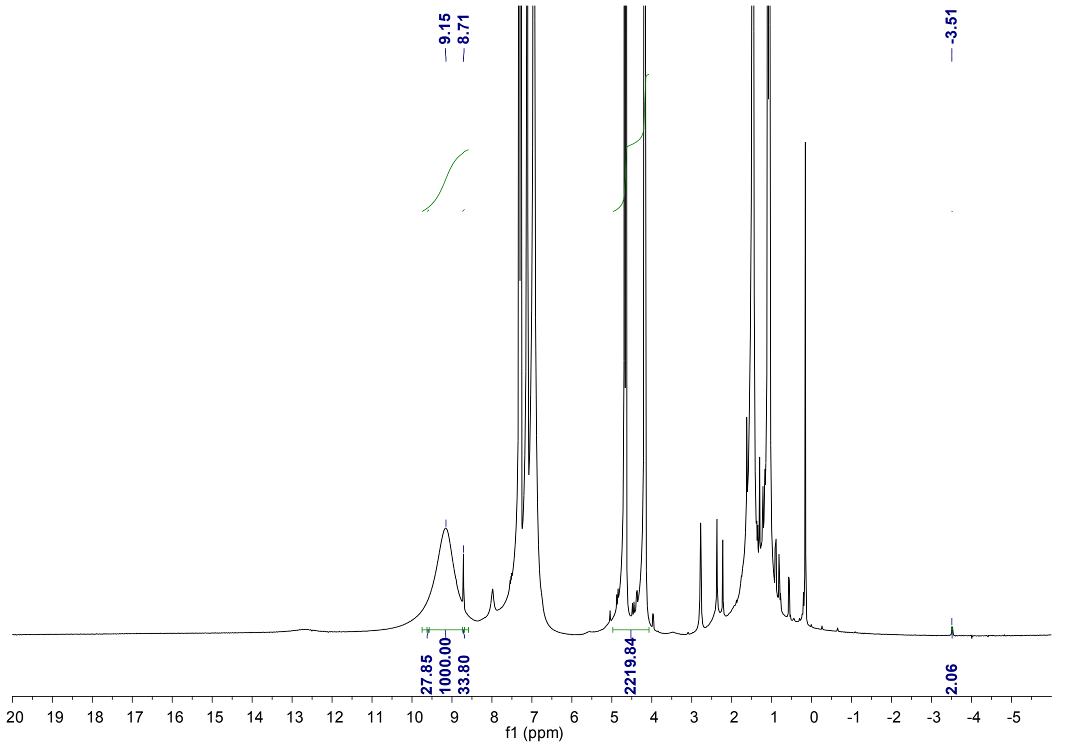

Fig. SI22 ^{1}H NMR of $Co^{II}(TMP)$ with pyridine in C_6D_6 at 40 minutes.

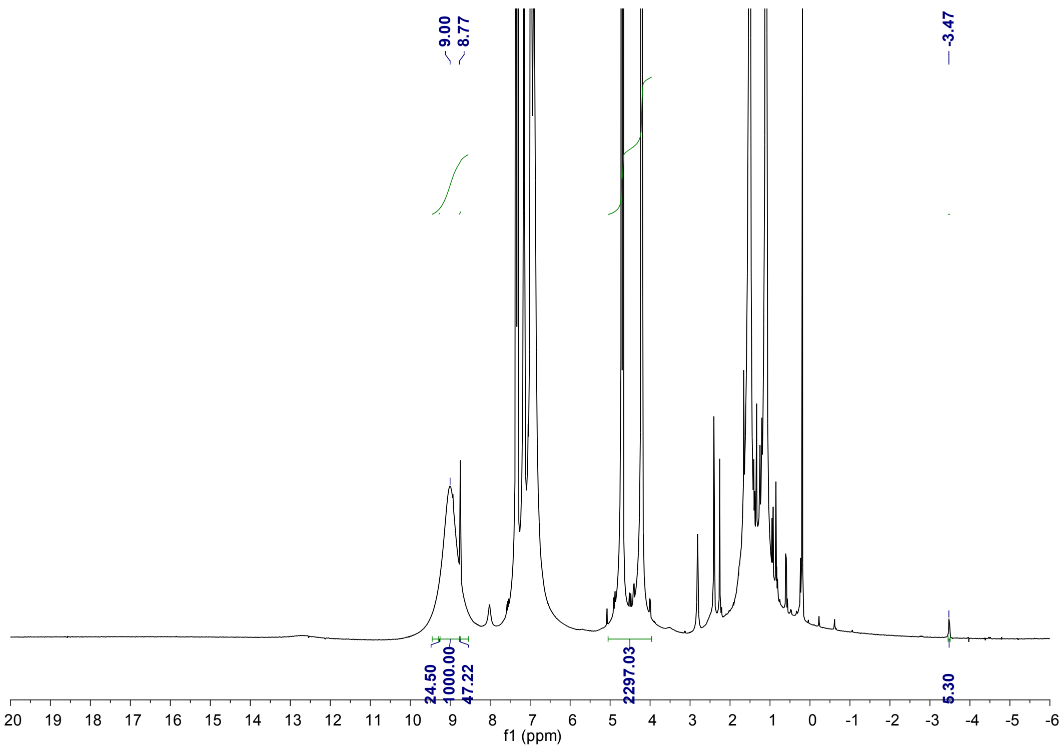

Fig. SI23 [1]H NMR of Co^{II}(TMP) with pyridine in C_6D_6 at 80 minutes.

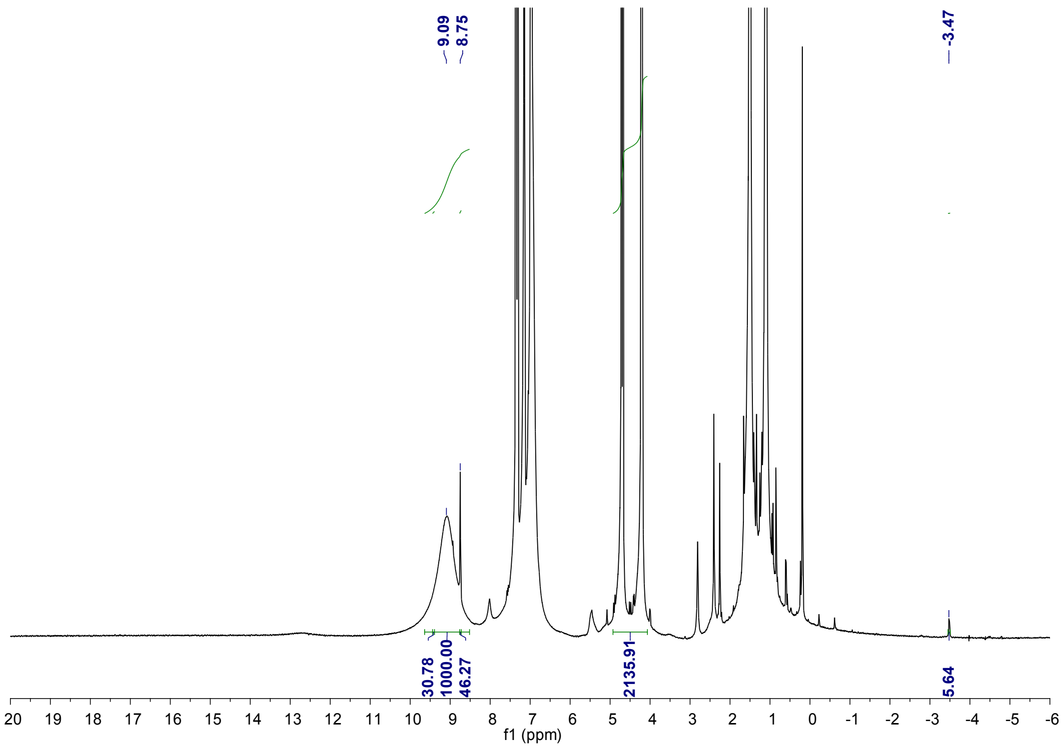

Fig SI24 [1]H NMR of Co^{II}(TMP) with pyridine in C_6D_6 at 120 minutes.

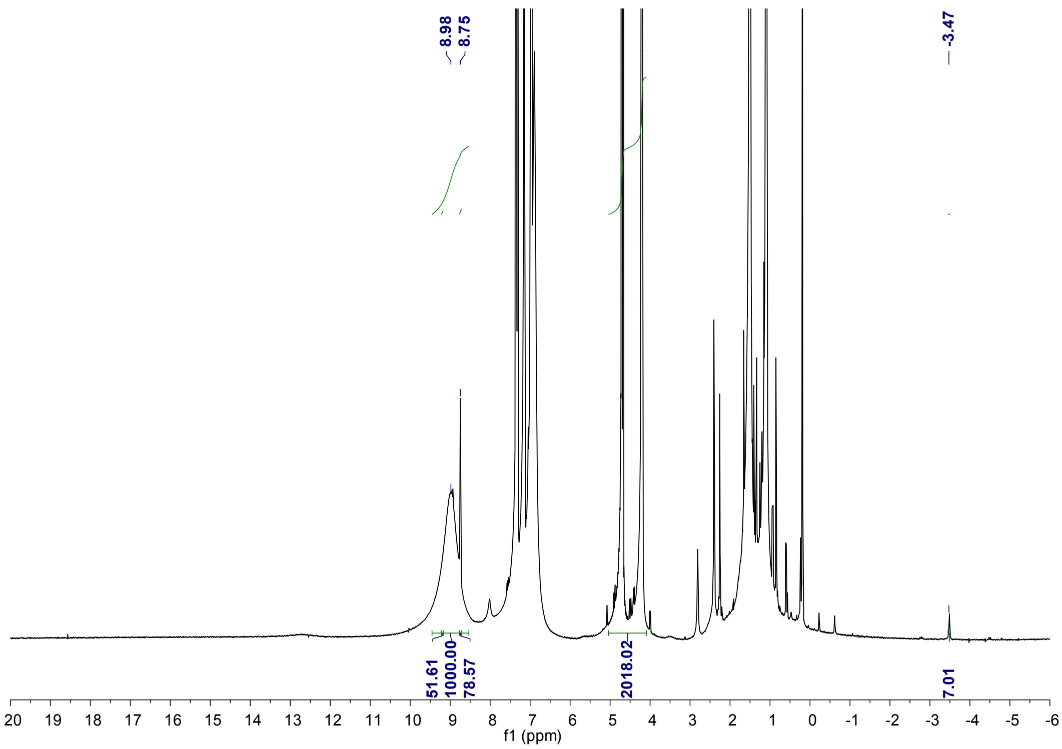

Fig. SI25 ^{1}H NMR of Co^{II}(TMP) with pyridine in C_6D_6 at 160 minutes.

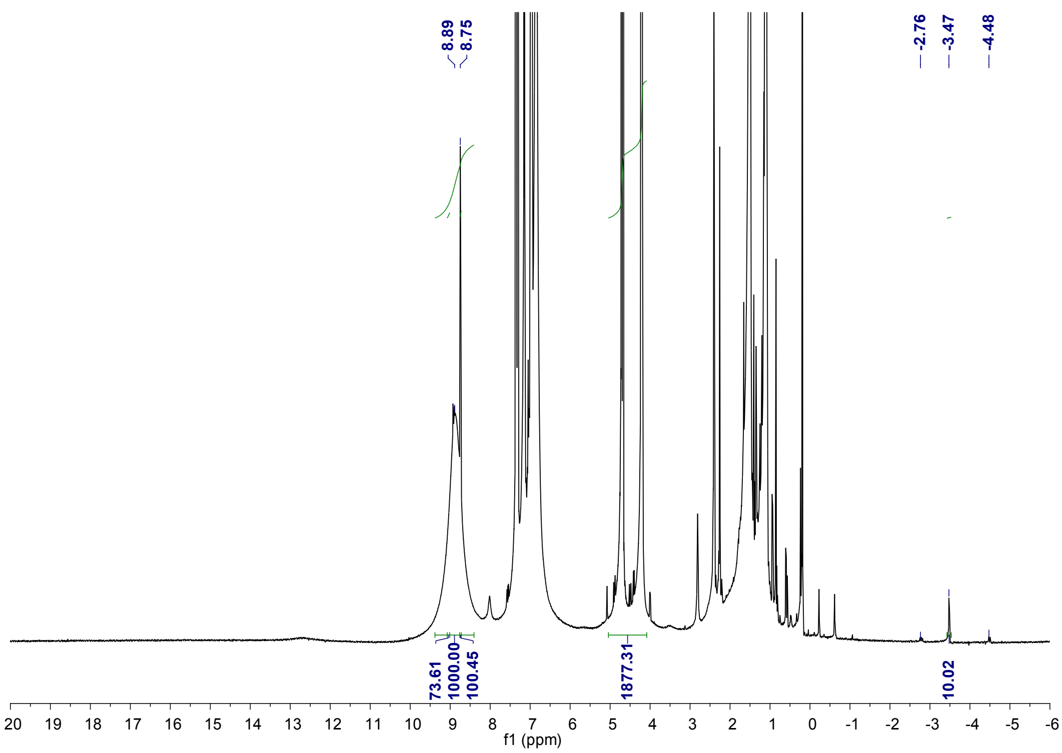

Fig. SI26 ^{1}H NMR of Co^{II}(TMP) with pyridine in C_6D_6 at 240 minutes.

IV. UV-vis of Co^{II} and Co^{III} with pyridine

UV (in CH_2Cl_2)	Co^{II}	Co^{II}-py	Co^{III}	Co^{III}-py
λ_{max}	411	411	408	434
ε	289,000	281,000	161,000	271,000

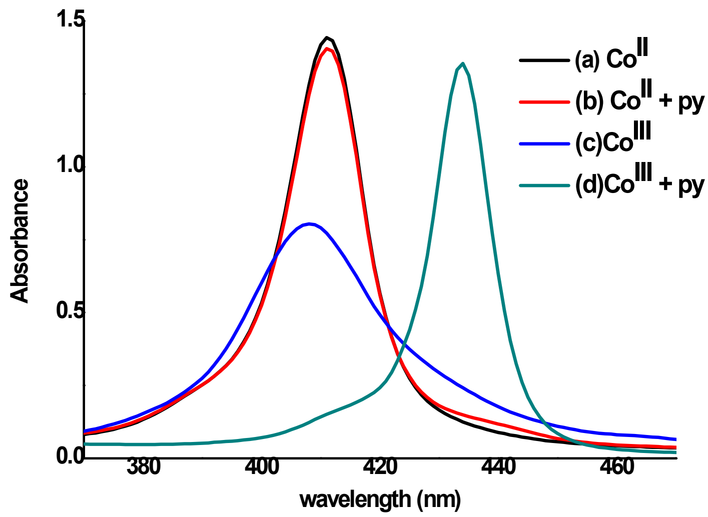

Fig. SI27 UV-vis spectra of (a) Co^{II} (b)Co^{II} + py (c) Co^{III} (d) Co^{III} + py.