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Catalytic Performance of Tridentate Versus Bidentate Co(II) Complexes Supported by Schiff Base Ligands in Vinyl Addition Polymerization of Norbornene

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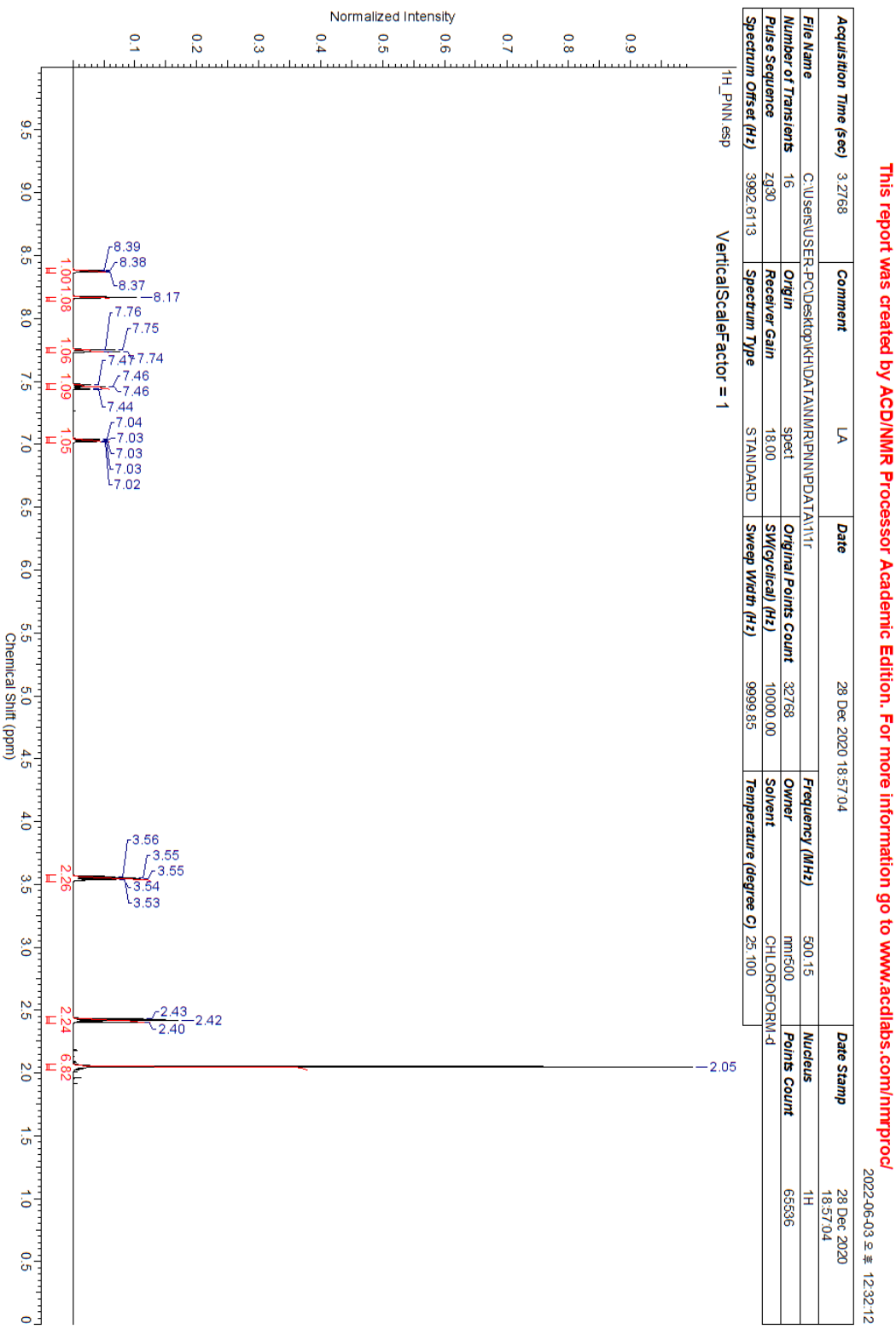

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Figure S2. ^{13}C NMR spectra of (*E*)-N^1,N^1-dimethyl-N^2-(pyridin-2-ylmethylene)ethane-1,2-diamine (L_A).

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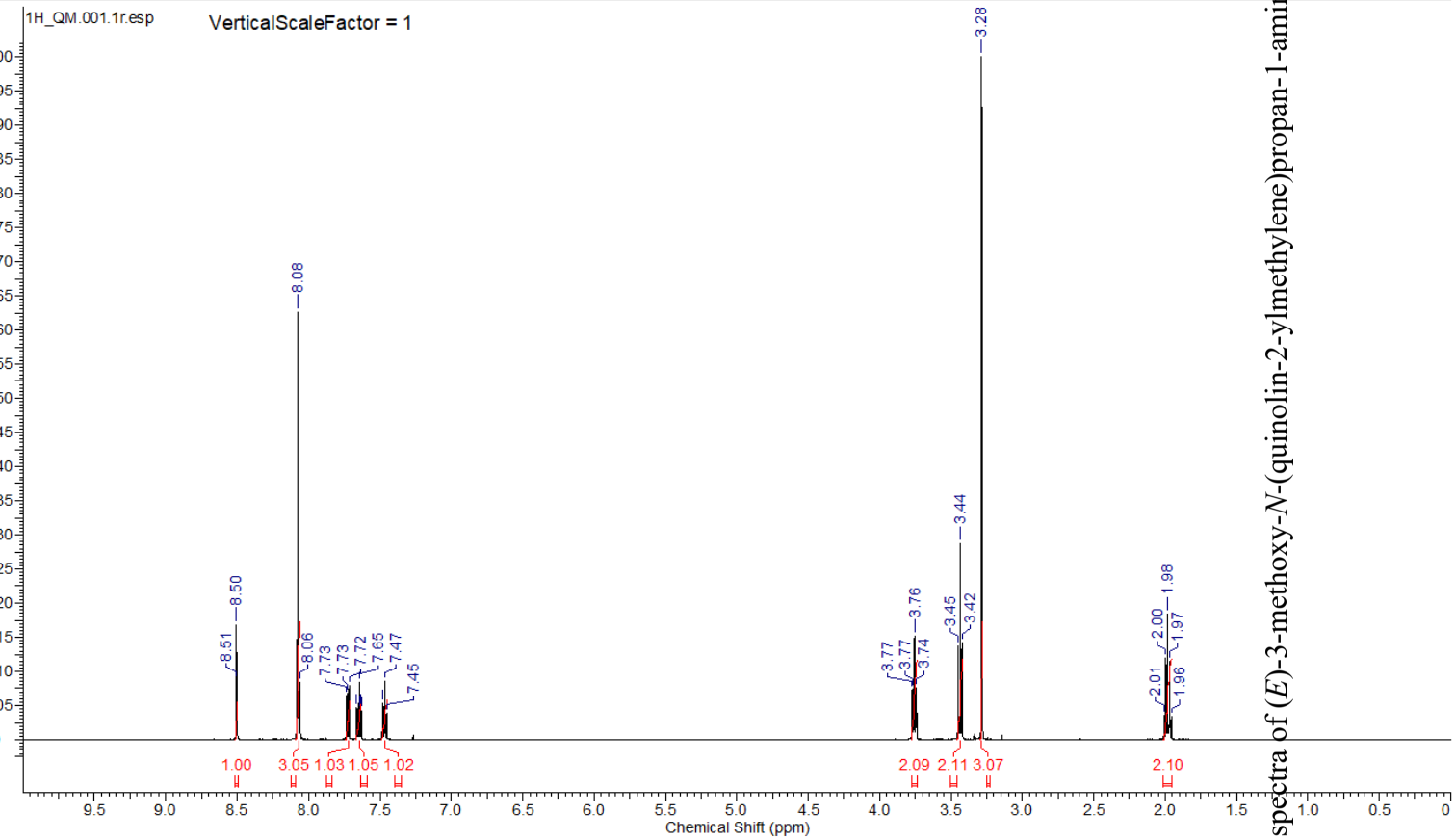

Figure S3. ^{1}H NMR spectra of (*E*)-3-methoxy-*N*-(quinolin-2-ylmethylene)propan-1-amine (L_B).

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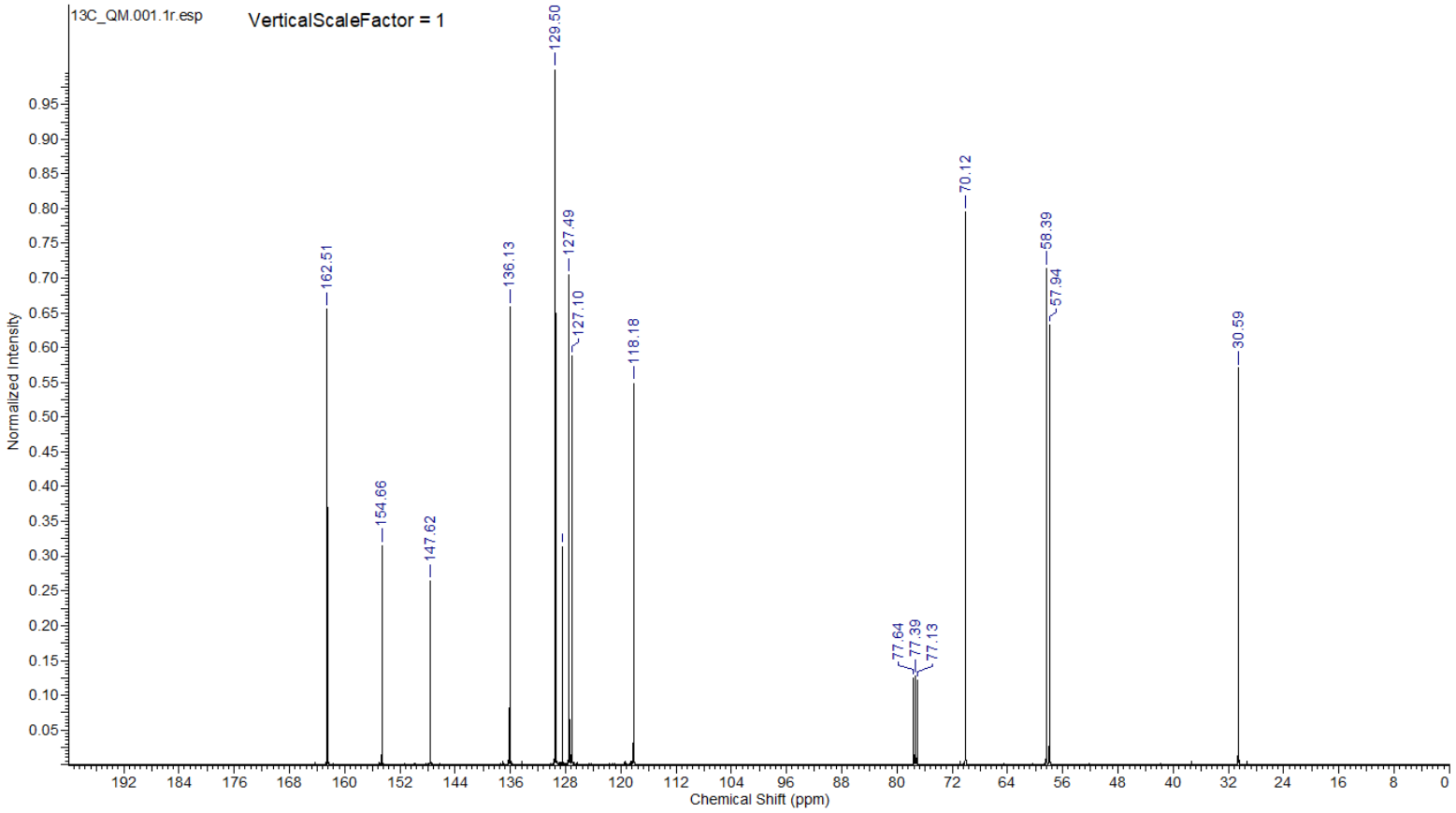

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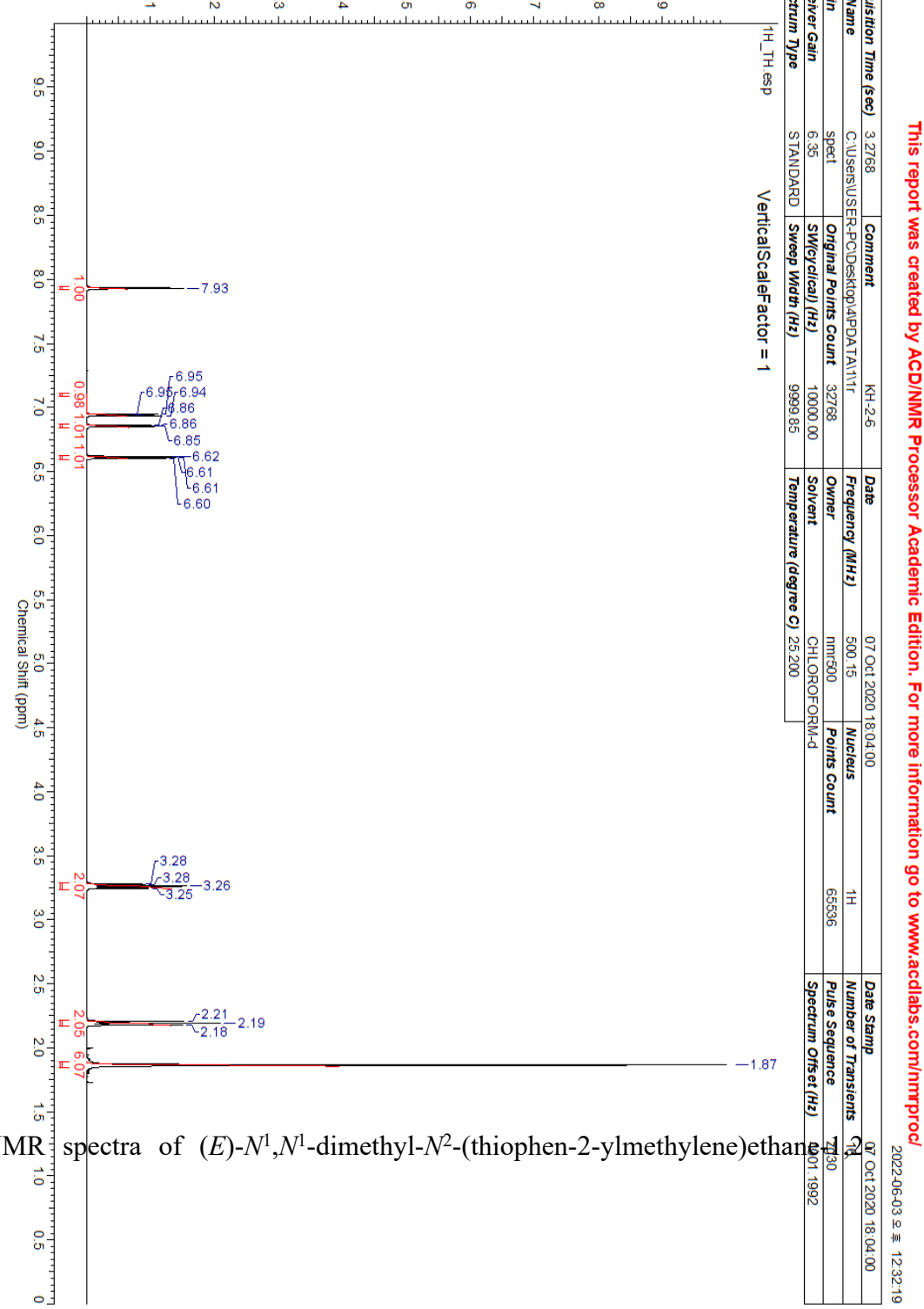

Figure S5. ^{1}H NMR spectra of (*E*)-N^1,N^1-dimethyl-N^2-(thiophen-2-ylmethylene)ethane-1,2-diamine (L_C).

Figure S6. ^{13}C NMR spectra of (*E*)-N^1,N^1-dimethyl-N^2-(thiophen-2-ylmethylene)ethane-1,2-diamine (L_C).

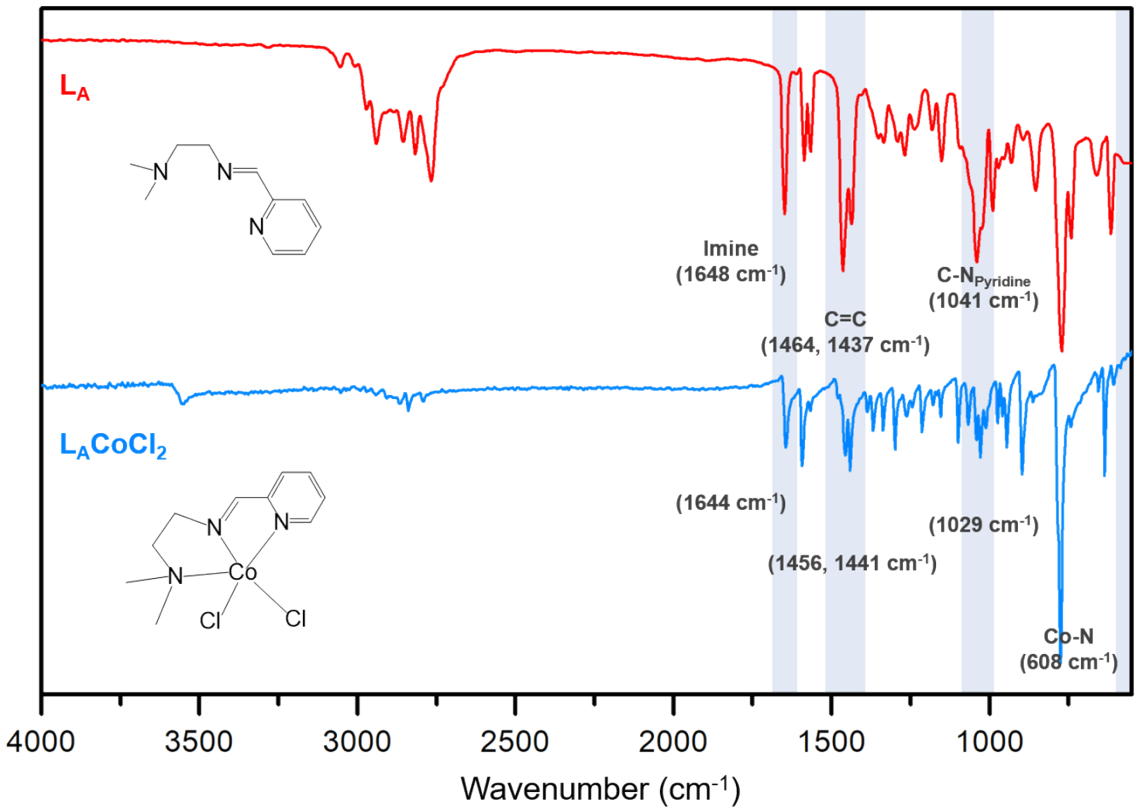

Figure S7. FT-IR spectrum of L_A (top) and [L_ACoCl_2] (bottom).

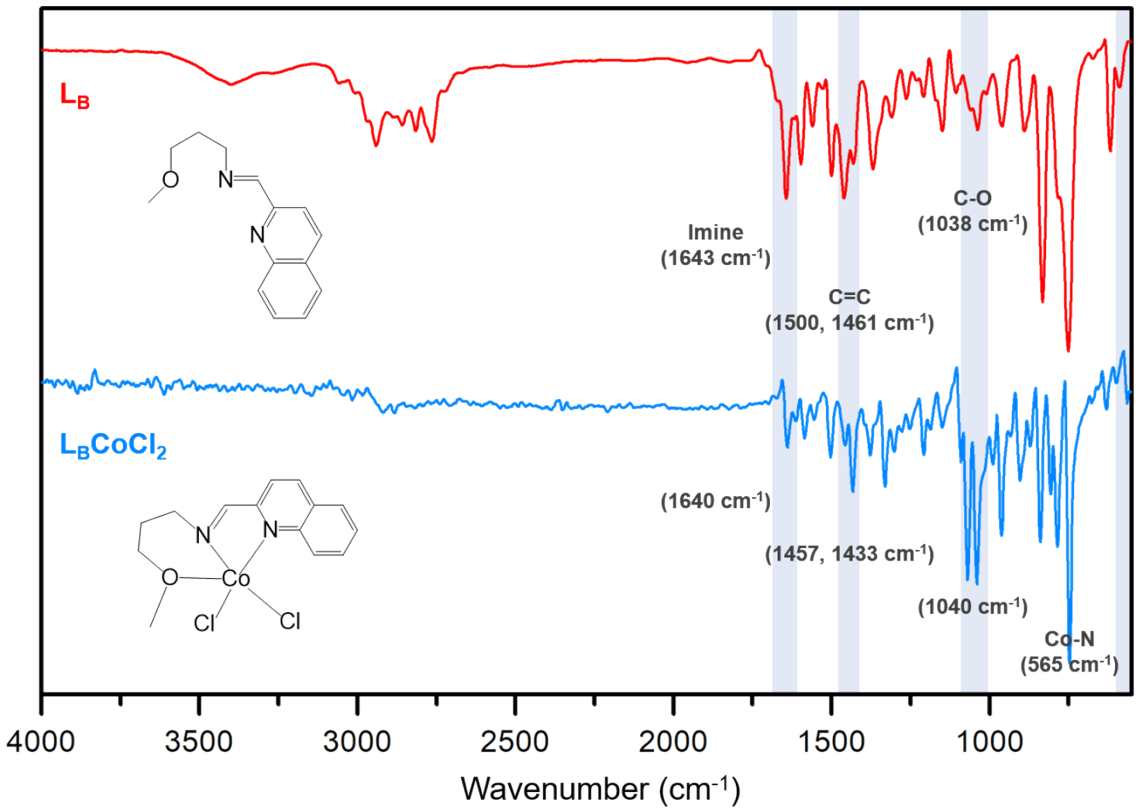

Figure S8. FT-IR spectrum of L_B (top) and [L_BCoCl_2] (bottom).

(A) **[$L_B CoCl_2$]**

(B) **[$L_C CoCl_2$]**

Figure S9. Elemental analysis of the synthesized (A) [$L_B CoCl_2$] and (B) [$L_C CoCl_2$].

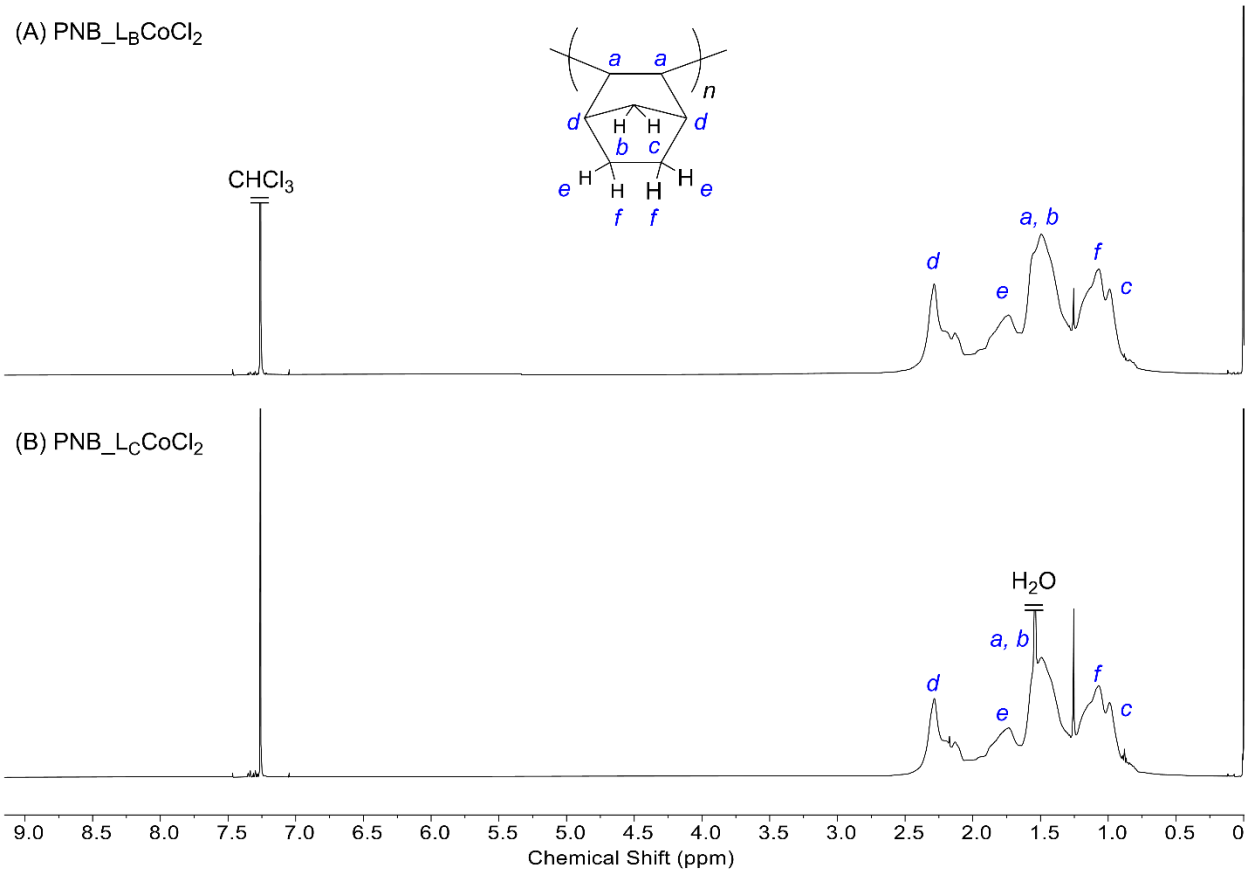

Figure S10. ^{1}H NMR spectra of polynorbornenes (PNBs) using (A) [L_BCoCl_2] and (B) [L_CCoCl_2] in $CDCl_3$.

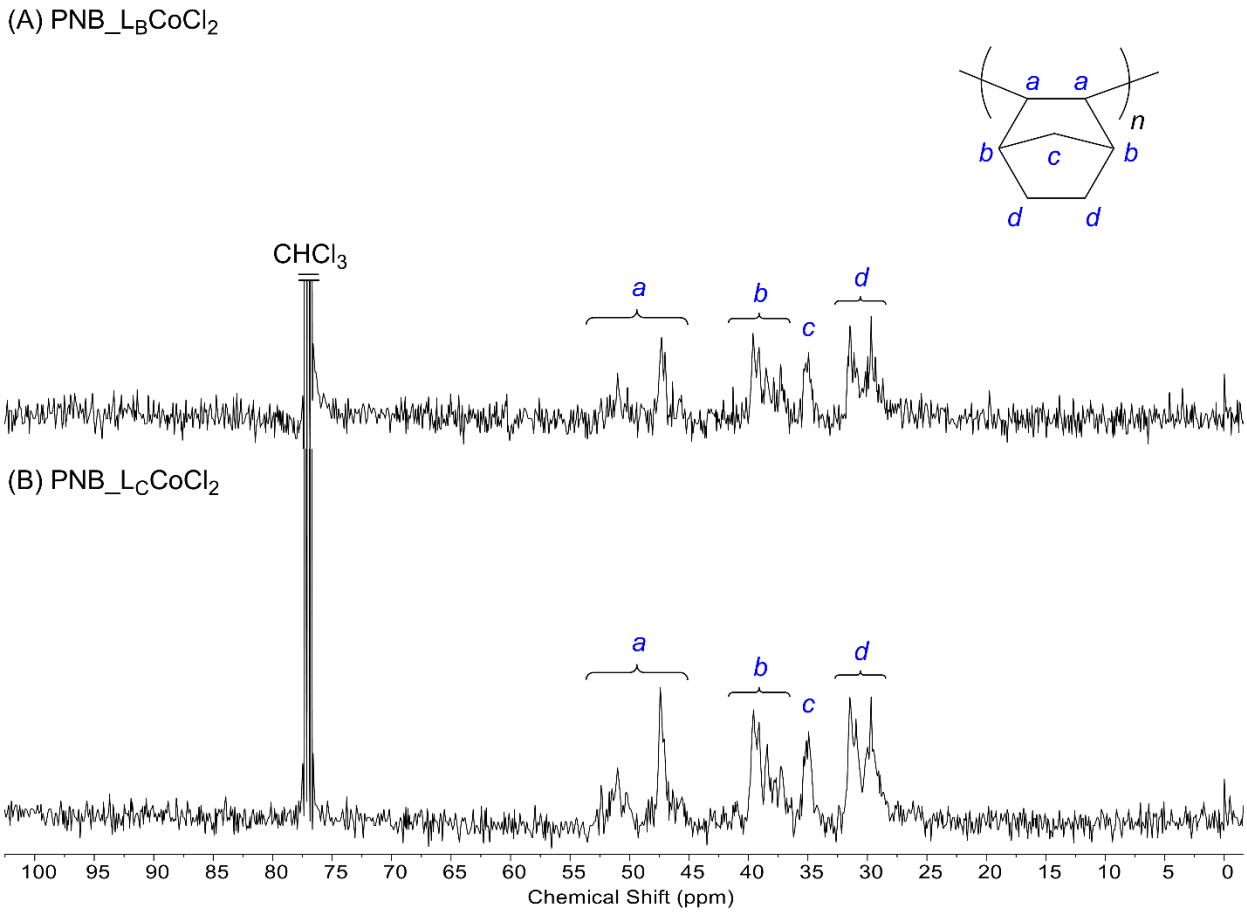

Figure S11. ^{13}C NMR spectra of polynorbornenes (PNBs) using (A) [L_BCoCl_2] and (B) [L_CCoCl_2] in $CDCl_3$.

Figure S12. FT-IR spectra of polynorbornene (PNB) using [L_BCoCl_2].

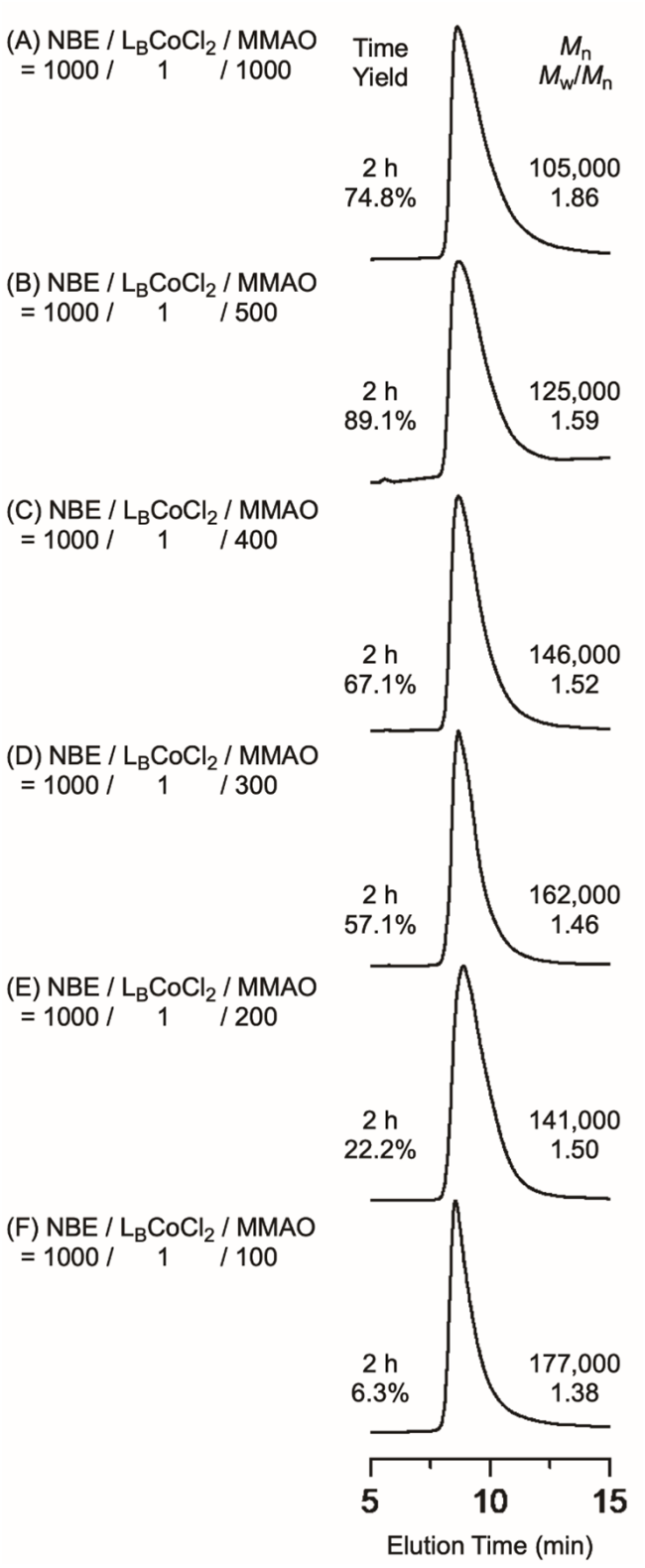

Figure S13. Screening of conditions for [L_BCoCl_2] catalyzed addition polymerization of norbornene depending on amount of MMAO cocatalyst.

Table S1. Crystal data and structure refinements of $[L_BCoCl_2]$ and $[L_CCoCl_2]$.

	$[L_BCoCl_2]$	**$[L_CCoCl_2]$**
Empirical formula	**$C_{14}H_{16}Cl_2CoN_2O$**	**$C_9H_{14}Cl_2CoN_2S$**
Formula weight	358.12	321.11
Temperature (K)	293(2)	220(2)
Wavelength (Å)	0.650	0.630
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.3140(17)	9.7710(19)
b (Å)	11.697(2)	11.046(2)
c (Å)	15.790(3)	12.622(3)
α (°)	90	90
β (°)	98.79(3)	108.05(3)
γ (°)	90	90
Volume (Å^3), Z	1517.5(5), 4	1295.3(5), 4
Density (calculated) (Mg m^{-3})	1.567	1.601
Absorption coefficient (mm^{-1})	1.146	1.324
F(000)	732	636
Crystal size (mm^3)	0.08 × 0.05 × 0.02	0.03 x 0.03 x 0.02
Theta range for data collection (°)	2.387 to 29.506	1.943 to 33.447
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-23 \le l \le 23$	$-15 \le h \le 15$, $-19 \le k \le 19$, $-21 \le l \le 21$
Reflections collected	19291	20842
Independent reflections	5283 [R(int) = 0.0453]	6206 [R(int) = 0.0801]
Completeness to theta	97.6 %	100.0 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5283 / 0 / 182	6206 / 0 / 138
Goodness-of-fit on F^2	0.765	10.1213
Final R indices [I>2sigma(I)]	R_1 = 0.3990	R_1 = 0.0672
	wR_2 = 0.1101	wR_2 = 0.2077
R indices (all data)	R_1 = 0.0407	R_1 = 0.0898
	wR_2 = 0.1121	wR_2 = 0.2205
Largest diff. peak and hole (e. Å^{-3})	0.775 and -1.208	1.788 and -1.762

Table S2. Selected bond lengths (Å) and angles (°) of [L_BCoCl_2] and [L_CCoCl_2].

[L_BCoCl_2]		**[L_CCoCl_2]**	
Bond lengths (Å)			
Co(1)-N(2)	2.0509(12)	Co(1)-N(1)	2.040(2)
Co(1)-N(1)	2.1827(12)	Co(1)-N(2)	2.078(2)
Co(1)-Cl(2)	2.2767(6)	Co(1)-Cl(2)	2.2428(9)
Co(1)-Cl(1)	2.333(2)	Co(1)-Cl(1)	2.2365(10)
Co(1)-O(1)	2.212(12)	N(1)-C(5)	1.278(3)
O(1)-C(13)	1.4406(19)	N(1)-C(6)	1.487(4)
N(2)-C(10)	1.2798(17)	S(1)-C(1)	1.663(4)
Bond angles (°)			
N(2)-Co(1)-N(1)	107.14(4)	N(1)-Co(1)-N(2)	85.14(9)
N(2)-Co(1)-O(1)	118.68(3)	N(1)-Co(1)-Cl(1)	111.57(7)
N(1)-Co(1)-O(1)	124.14(3)	N(1)-Co(1)-Cl(2)	112.84(8)
N(2)-Co(1)-Cl(1)	101.12(3)	Cl(1)-Co(1)-Cl(2)	106.76(7)
N(1)-Co(1)-Cl(1)	95.62(3)	C(5)-N(1)-C(6)	114.7(2)
O(1)-Co(1)-Cl(1)	104.57(2)	C(5)-N(1)-Co(1)	135.25(19)
N(2)-Co(1)-Cl(2)	105.75(9)	C(6)-N(1)-Co(1)	109.55(16)
N(1)-Co(1)-Cl(2)	130.62(8)	C(1)-S(1)-C(4)	93.03(17)
O(1)-Co(1)-Cl(2)	121.72(8)	C(2)-C(1)-S(1)	113.9(3)
Cl(1)-Co(1)-Cl(2)	111.11(1)	C(9)-N(2)-C(7)	109.3(2)

Table S3. The polymerization of norbornene by [L_BCoCl_2] in the presence of various [Al]/[Co] ratios.

Entry	Catalyst[a]	Ratio[b]	Yield.[c] (%)	Activity[d] (g/mol Cat·h)×10^4	M_n[e] (g/mol) ×10^5 (GPC)	PDI
1	**[L_BCoCl_2]**	1:100:1000	6.3	0.30	1.77	1.38
2	**[L_BCoCl_2]**	1:200:1000	52.2	2.70	1.41	1.50
3	**[L_BCoCl_2]**	1:300:1000	57.1	2.96	1.62	1.46
4	**[L_BCoCl_2]**	1:400:1000	67.1	3.48	1.46	1.52
5	**[L_BCoCl_2]**	1:500:1000	89.1	4.22	1.25	1.59
6	**[L_BCoCl_2]**	1:1000:1000	74.8	3.54	1.05	1.86

[a][Co(II) catalyst]0 = 15 μmol, $[norbornene]_0/[MMAO]_0$ = 65 mM, polymerization solvent, 20 mL of chlorobenzene; polymerization temperature = 25 °C; polymerization time = 2 h . [b]Yield is defined as a mass of dried polymer recovered/mass of monomer used. [c]Activity is calculated as (gPNB mol cat^{-1} h^{-1}). [d]M_n refers to the number average molecular weights of PNB and determined by GPC eluted with chloroform at room temperature, related to PS standard.

Table S4. The polymerization of norbornene by [L_CCoCl_2] in the presence of MMAO with increasing reaction time.

Entry[a]	Catalyst[a]	Time (min)	Yield[b] (%)	Activity[c] (g/mol Cat·h)×10^4	M_n[d] (g/mol)×10^5	PDI
1	**[L_CCoCl_2]**	5	56.4	64.1	1.51	1.43
2	**[L_CCoCl_2]**	10	60.2	34.2	1.35	1.55
3	**[L_CCoCl_2]**	20	64.4	18.3	1.34	1.54
4	**[L_CCoCl_2]**	30	66.7	12.6	1.34	1.55
5	**[L_CCoCl_2]**	60	76.9	7.28	0.89	1.85
6	**[L_CCoCl_2]**	90	80.1	5.06	1.48	1.43
7	**[L_CCoCl_2]**	120	98.9	4.69	2.40	1.13

[a][Co(II) catalyst]0 = 15 μmol, $[norbornene]_0/[MMAO]_0/[Co(II)\ catalyst]_0$ = 1000:500:1, polymerization solvent, 20 mL of chlorobenzene; polymerisation temperature = 25 °C. [b]Yield is defined as a mass of dried polymer recovered/mass of monomer used. [c]Activity is calculated as (gPNB mol cat^{-1} h^{-1}). [d]M_n refers to the number average molecular weights of PNB and determined by GPC eluted with chloroform at room temperature, related to PS standard.

Table S5. The polymerization of norbornene catalyzed by $[L_nCoCl_2]$/MMAO (L_n = L_A–L_C) system in various solvents.

Entry	Catalyst[a]	Solvent	Temp. (℃)	Yield[b] (%)
1	**$[L_ACoCl_2]$**	chlorobenzene	25	72.7
2	**$[L_ACoCl_2]$**	dichloroethane	25	>10.0
3	**$[L_ACoCl_2]$**	Toluene	80	69.3
4	**$[L_BCoCl_2]$**	chlorobenzene	25	89.1
5	**$[L_BCoCl_2]$**	dichloroethane	25	60.1
6	**$[L_BCoCl_2]$**	Toluene	80	68.0
7	**$[L_CCoCl_2]$**	chlorobenzene	25	98.9
8	**$[L_CCoCl_2]$**	dichloroethane	25	20.9
9	**$[L_CCoCl_2]$**	Toluene	80	64.5

[a]$[\text{Co(II) catalyst}]_0$ = 15 μmol, $[\text{norbornene}]_0/[\text{MMAO}]_0/[\text{Co(II) catalyst}]_0$ = 1000:500:1, polymerization solvent, 20 mL of chlorobenzene or dichloroethane or toluene; polymerization time = 2 h. [b]Yield is defined as a mass of dried polymer recovered/mass of monomer used. [c]Activity is calculated as (gPNB mol cat^{-1} h^{-1}).