Supporting Information

Controllable Assembly over two Co^{II}-based Coordination Polymers: Structures and Catalytic properties towards Alkene Oxyalkylation Reaction

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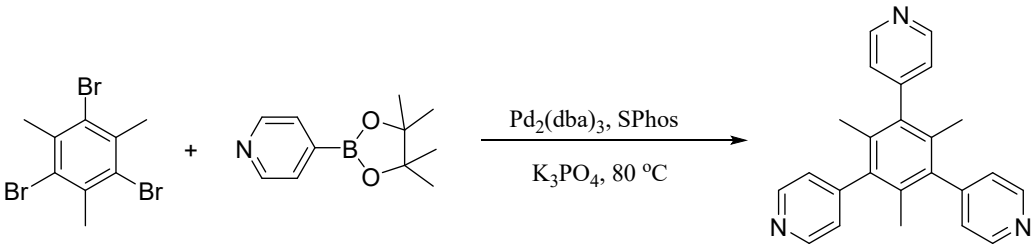
Synthesis of 4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tripyridine (4-TMTBT):



1,3,5-Tribromo-2,4,6-trimethylbenzene (357 mg, 1.0 mmol, 1 eq.), 4-Pyridineboronic acid pinacol ester (1.64 g, 8 mmol, 8 eq.), K_3PO_4 (2.55 mg, 12 mmol, 12 eq), $Pd_2(dba)_3$ (20 mg, 0.022 mmol, 0.022 eq.) and SPhos (18 mg, 0.044 mmol, 0.044 eq.) were mixed under inert atmosphere in n-butanol (50 mL). The resulting mixture was stirred at 80 °C for 3 d. After cooled down to room temperature, the reaction was filtered and washed with MeOH. The solids were suspended in water and acidified with HCl. The resulting mixture was filtered, and the filtrate was basified with NaOH until a white precipitate was obtained. The product was collected by filtration and washed with water and diethyl ether. The product 4-TMTBT was purified by column chromatography (SiO_2, EA) and obtained as a white solid (176 mg, 0.5 mmol, yield: 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71(d, 6H), 7.18 (d, 6H), 1.70 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.13, 149.34, 137.54, 132.21, 124.39, 19.05.

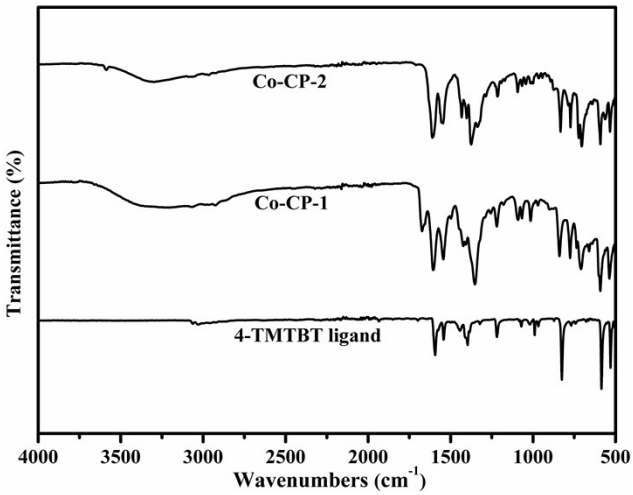


Figure S1. The FT-IR spectrum of 4-TMTBT, **Co-CP-1** and **Co-CP-2** compound.

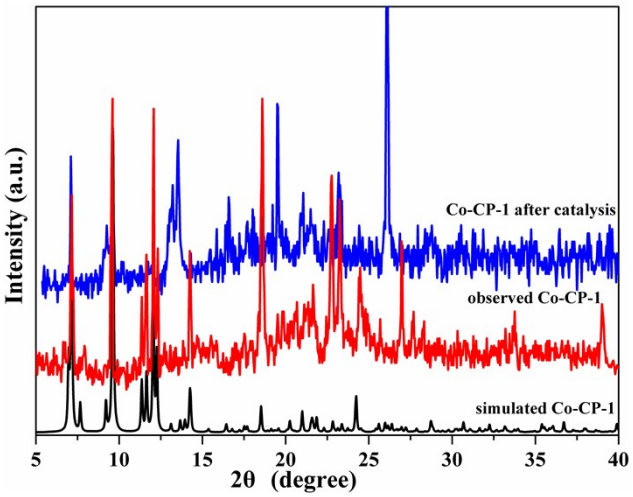


Figure S2. The PXRD curves over **Co-CP-1** before and after catalysis.

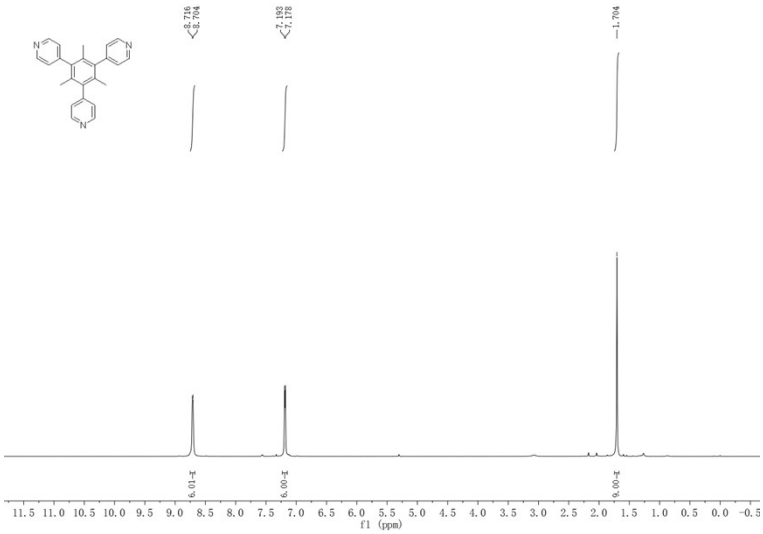


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4-TMTBT** ligand.

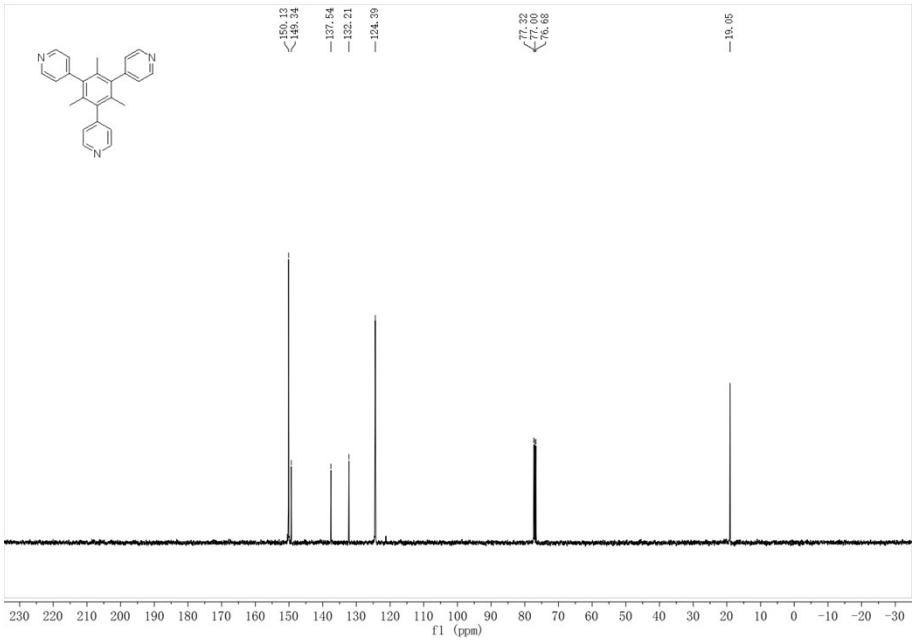


Figure S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **4-TMTBT** ligand.

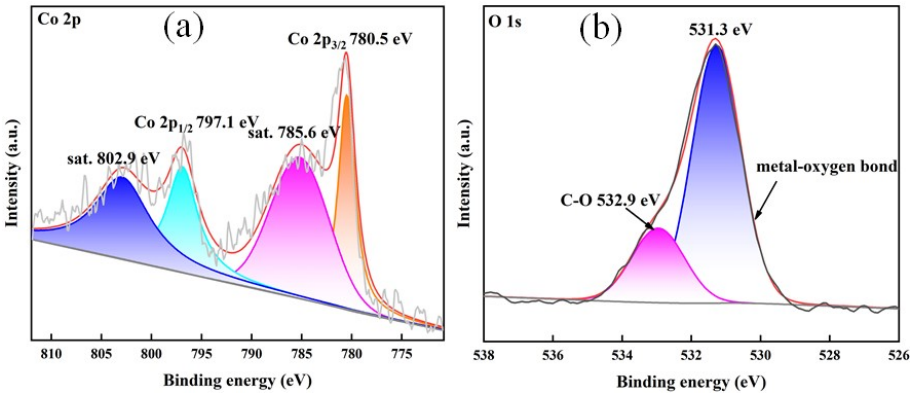
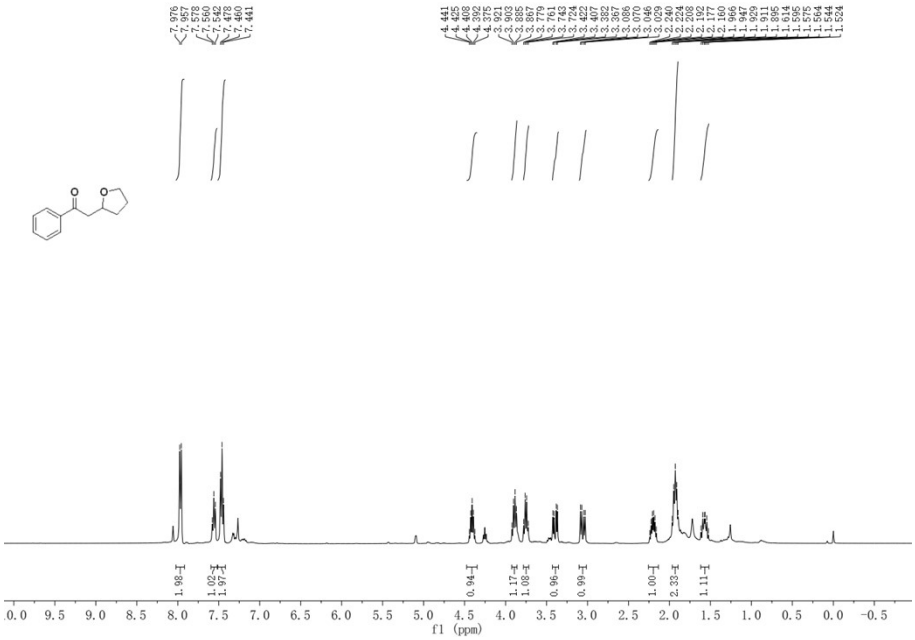
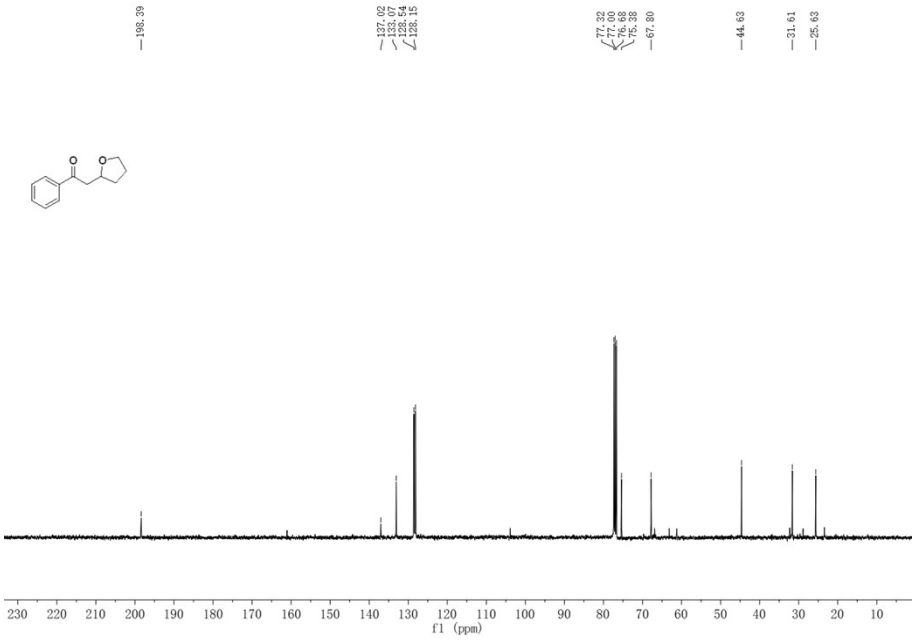


Figure S5. The high-solution Co 2p and O 1s XPS over **Co-CP-1** catalyst.

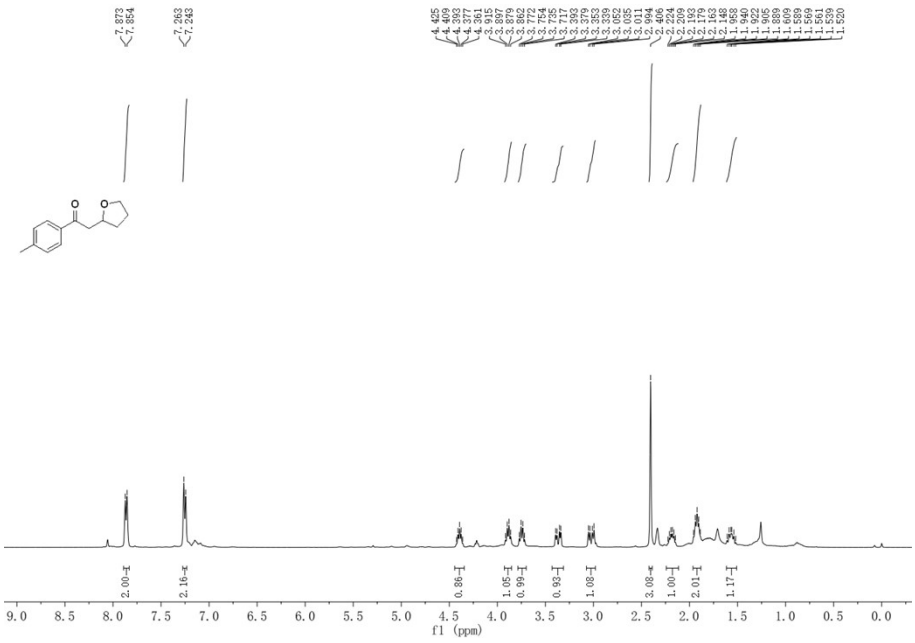
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3a.**



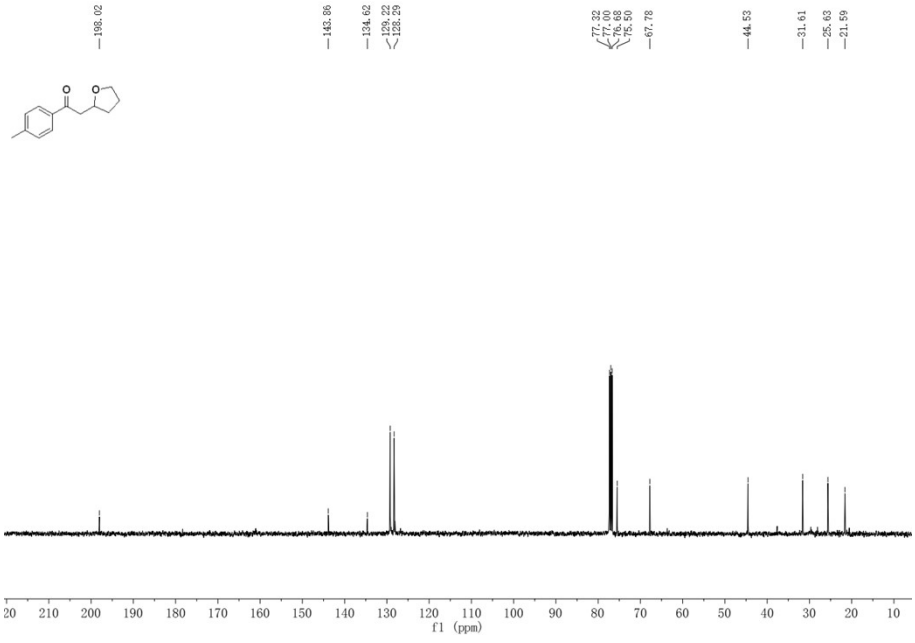
^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3a.**



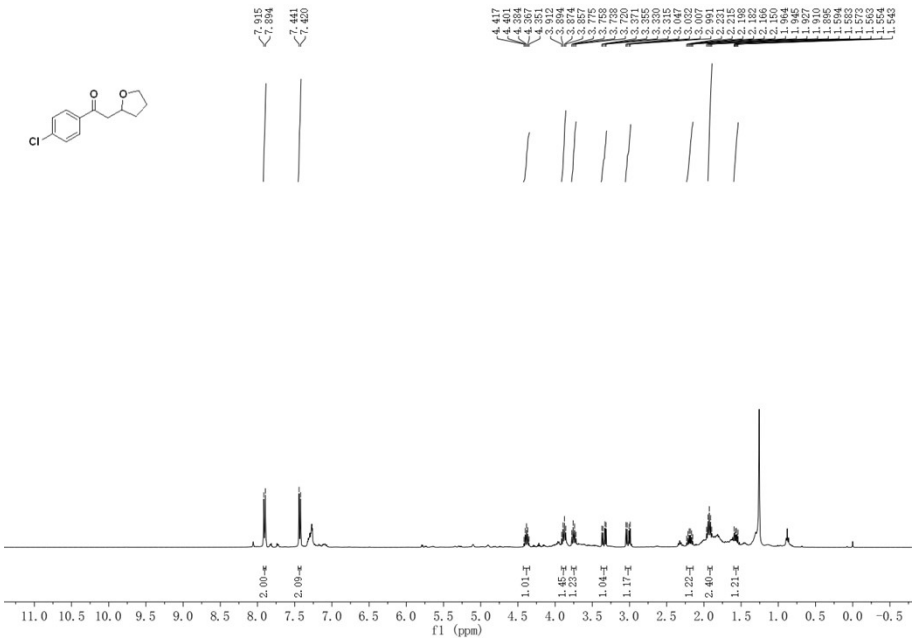
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3b.**



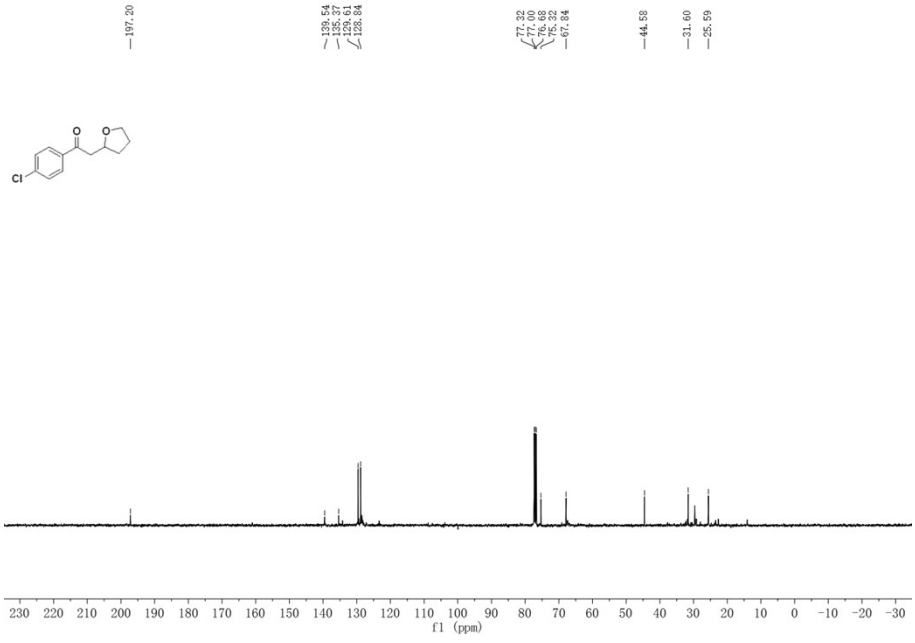
^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3b.**



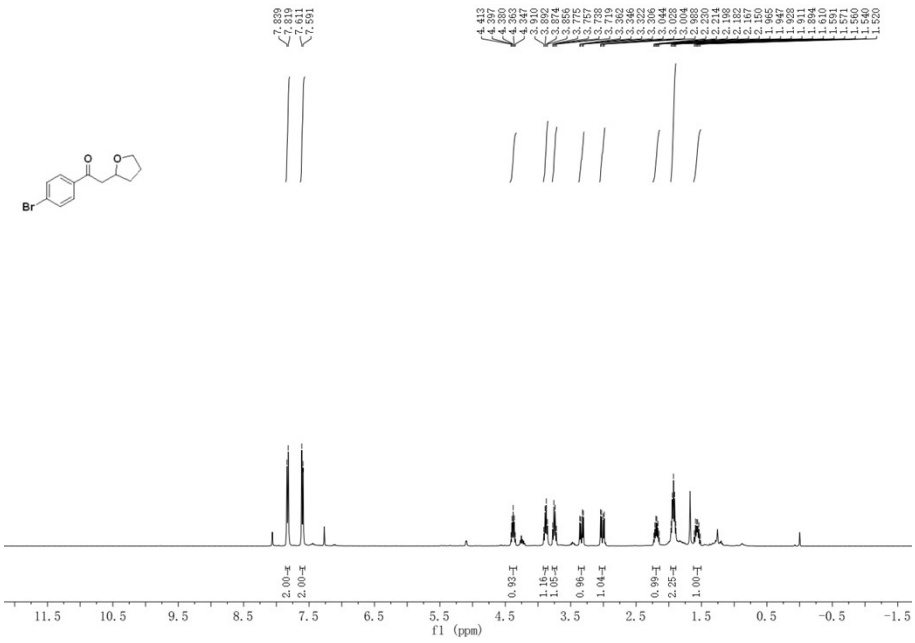
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3e.**



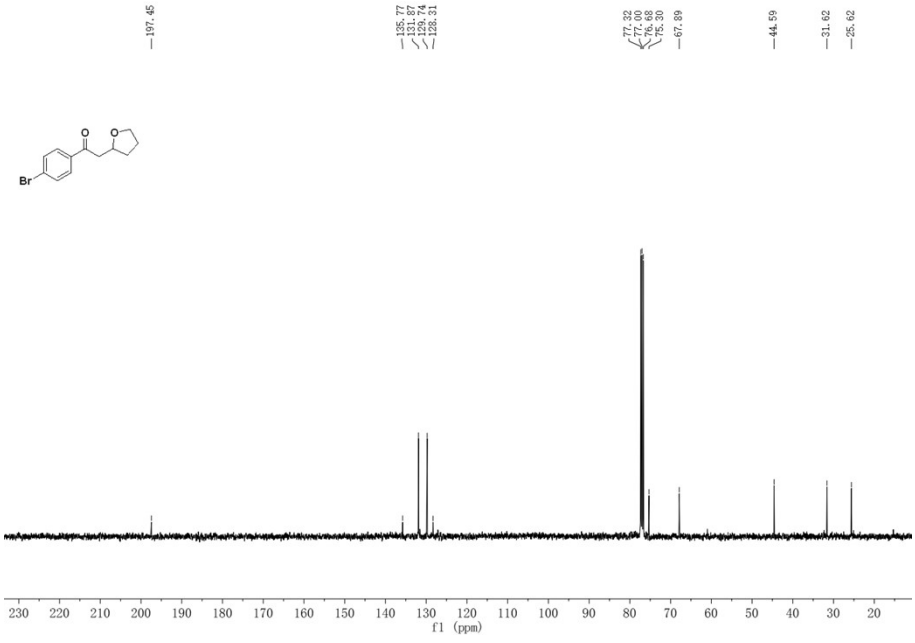
^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3e**.



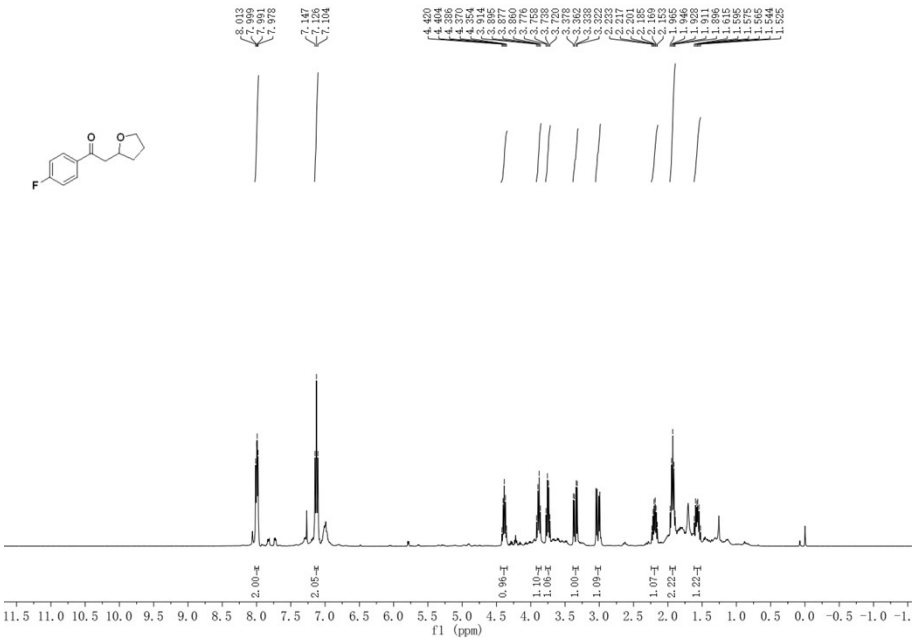
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3g.**



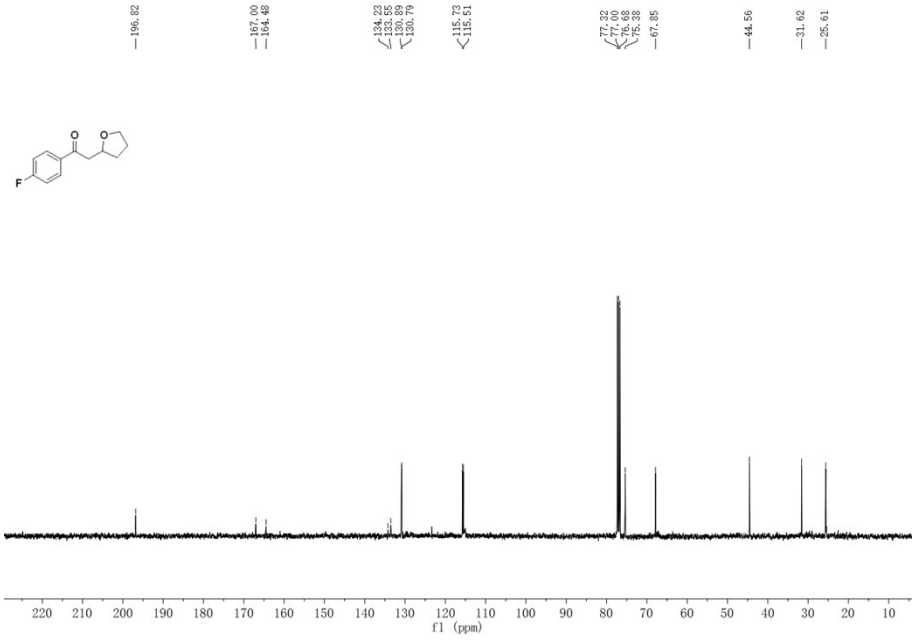
^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3g.**



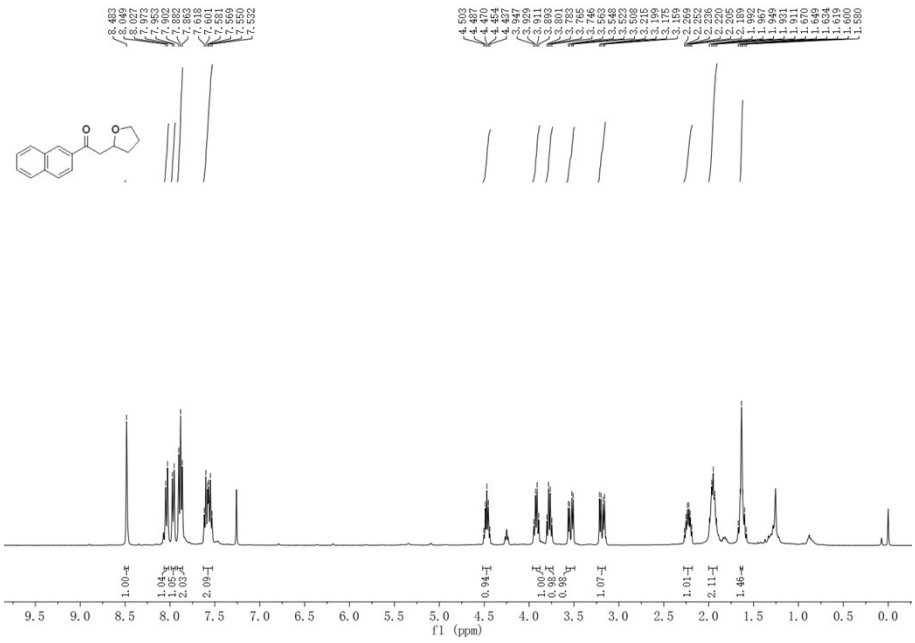
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3j.**



^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3j.**



^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3k.**



^{13}C NMR (100 MHz, $CDCl_3$) spectroscopy of **3k.**

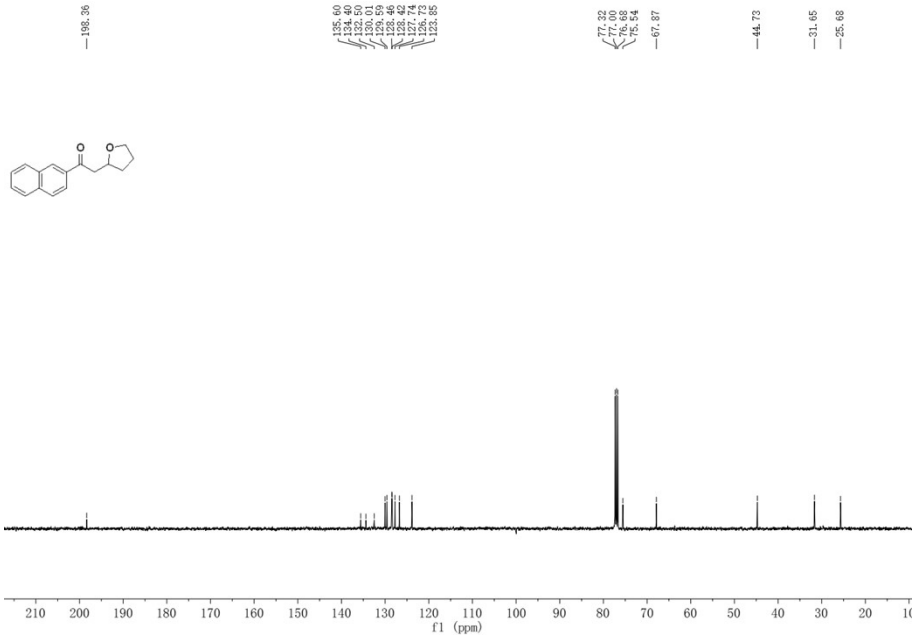


Table S1. Selected bond distances [Å] and angles [º] for **Co-CP-1 and Co-CP-2**.

Co1-O2	1.992(3)	Co1-O3#1	2.215(4)
Co1-O4#1	2.177(3)		
Co1-N1	2.153(4)	Co1-N2#2	2.196(3)
Co1-N2#3	2.196(3)		
O2- Co1-O3#1	94.75(14)	O2- Co1-O4#1	154.46(14)
O2- Co1-N1	114.70(15)	O2- Co1-N2#2	91.85(7)
O2- Co1-N2#3	91.85(7)	O3#1- Co1-O4#1	59.71(11)

O4#1- Co1-N2#2	89.62(7)	O4#1- Co1-N2#3	89.62(7)
O3#1- Co1-N1	150.56(14)	N1- Co1-O4#1	90.85(13)
N1- Co1-N2#2	86.50(7)	N1- Co1-N2#3	86.50(7)
N2#3- Co1-O3#1	92.84(8)	N2#2- Co1-O3#1	92.84(8)
N2#2- Co1-O5#1	87.12(12)	O7- Co1-O2	97.88(9)
N2#3- Co1-N2#2	172.94(14)		
Symmetry codes for **Co-CP-1**: #1 1/2+x,+y,5/2-z; #2 2-x,1-y,2-z; #3 2-x,-1/2+y,2-z.			
Co1-O1	2.062(5)	Co1-O4	2.046(4)
Co1-O5	2.066(5)	Co1-O6#1	2.106(5)
Co1-O12	2.177(5)	Co1-N1#2	2.160(6)
Co2-O2#3	2.066(5)	Co2-O4#4	2.101(4)
Co2-O7	2.068(5)	Co2-O9	2.068(5)
Co2-O10	2.068(5)	Co2-N2	2.161(6)
Co3-O3	2.106(5)	Co3-O4	2.062(5)
Co3–O8#5	2.066(5)	Co3–O11#1	2.095(6)
Co3–O13	2.165(4)	Co3–N3#6	2.143(6)
O4–Co1–O1	97.2(2)	O4–Co1–O5	92.5(2)
O1–Co1–O5	168.7(2)	O4–Co1–O6	98.50(19)
O1–Co1–O6	91.4(2)	O5–Co1–O6	92.9(2)
O4–Co1–N1	174.5(2)	O1–Co1–N1	83.0(2)
O5–Co1–N1	86.8(2)	O6–Co1–N1	87.0(2)
O4–Co1–O12	89.5(2)	O1–Co1–O12	93.1(2)
O5–Co1–O12	81.1(2)	O6–Co1–O12	170.2(2)
N1–Co1–O12	85.0(2)	O2–Co2–O10	92.2(3)
O2–Co2–O7	86.9(2)	O10–Co2–O7	173.3(2)
O2–Co2–O9	171.0(2)	O10–Co2–O9	87.8(2)
O7–Co2–O9	92.0(2)	O2–Co2–O4	100.90(18)
O10–Co2–O4	85.99(19)	O7–Co2–O4	100.7(2)
O9–Co2–O4	88.11(19)	O2–Co2–N2	89.5(2)
O10–Co2–N2	80.7(2)	O7–Co2–N2	92.7(2)
O9–Co2–N2	81.6(2)	O4–Co2–N2	163.4(2)
O4–Co3–O8	94.89(18)	O4–Co3–O11	94.29(18)
O8–Co3–O11	92.0(2)	O4–Co3–O3	95.10(18)
O8–Co3–O3	94.8(2)	O11–Co3–O3	167.87(18)
O4–Co3–N3	177.0(2)	O8–Co3–N3	86.2(2)
O11–Co3–N3	88.5(2)	O3–Co3–N3	82.0(2)
O4–Co3–O13	90.95(17)	O8–Co3–O13	172.9(2)
O11–Co3–O13	83.6(2)		
Symmetry codes for **Co-CP-2**: #1 -0.5+x, 0.5-y, -0.5+z; #2 -0.5+x, 0.5-y, 0.5+z; #3 0.5+x, 0.5+y, +z; #4 0.5+x, 0.5-y, 0.5+z; #5 +x, -y, -0.5+z; #6 -			

1.5+x, 0.5-y, -0.5+z.

The computed results of the (3,7)-connected net of **Co-CP-2** by TOPOS 4.0 are as follows:

Topology for Sc1

Atom Sc1 links by bridge ligands and has

Common vertex with					R(A-A)	
V 1	1.2598	0.8732	1.3291	(1 0 1)	9.808A	1
V 1	0.2598	0.8732	1.3291	(0 0 1)	9.866A	1
V 1	0.2598	0.8732	0.3291	(0 0 0)	9.986A	1

Topology for V1

Atom V1 links by bridge ligands and has

Common vertex with					R(A-A)	
Sc 1	-0.4044	0.8673	-0.0031	(-1 0-1)	9.808A	1
Sc 1	0.5956	0.8673	-0.0031	(0 0-1)	9.866A	1
Sc 1	0.5956	0.8673	0.9969	(0 0 0)	9.986A	1
V 1	0.7598	0.6268	0.8291	(0 1 0)	10.618A	1
V 1	-0.2402	0.6268	-0.1709	(-1 1-1)	10.618A	1
V 1	0.2598	1.1268	0.8291	(0 2 0)	10.728A	1
V 1	0.2598	1.1268	-0.1709	(0 2-1)	10.728A	1

Coordination sequences

Sc1:	1	2	3	4	5	6	7	8	9	10
Num	3	16	45	84	135	198	273	360	459	570
Cum	4	20	65	149	284	482	755	1115	1574	2144

V1:	1	2	3	4	5	6	7	8	9	10
Num	7	24	53	94	147	212	289	378	479	592
Cum	8	32	85	179	326	538	827	1205	1684	2276

TD10=2210

Vertex symbols for selected sublattice

Sc1 Point (Schlafli) symbol:{4^2.6}

V1 Point (Schlafli) symbol:{4^6.6^15}

Extended point symbol:

[4.4.4.4.4.4.6.6(2).6(2).6(2).6(2).6(3).6(3).6(4).6(4).6(5).6(5).6(7).6(7).6(7).6(7)]

Point (Schlafli) symbol for net: {4^2.6}{4^6.6^15}

3,7-c net with stoichiometry (3-c)(7-c); 2-nodal net

New topology, please, contact the authors (67300 types in 9 databases)