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Supporting information for

Controllable assembly of rectangular macrocycles bearing different numbers of unsaturated sites based on half-sandwich iridium fragments

Li-Long Dang, Yue-Jian Lin and Guo-Xin Jin*

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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1. General

The starting materials [Cp*IrCl(μ-Cl)]$_2$ (**1**), [Cp*$_2$Ir$_2$(μ–η^4-C_2O_4)]Cl$_2$ (**2**) and [Cp*$_2$Ir$_2$(μ–CA)]Cl$_2$ (**3**) were prepared according to literature methods. All reagents and solvents including proligands diamine $H_4\boldsymbol{L_1}$ and dihydroxy $H_2\boldsymbol{L_2}$ were obtained commercially and used without further purification. Both $H_4\boldsymbol{L_1}$ and $H_2\boldsymbol{L_2}$ possess two identical "soft" N-monodentate sites. However, an obvious difference exists in their chelating sites: $H_4\boldsymbol{L_1}$ bears the "soft" N,N' site while $H_2\boldsymbol{L_2}$ bears the "hard" O,O' site, and these sites were found to play crucial roles in the formation of complexes. NMR spectra were recorded on Bruker AVANCE I 400 spectrometers at room temperature and referenced to the residual protonated solvent. Elemental analyses were performed on an Elementar III Vario EI analyzer. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} are measured on a Nicolet Avatar-360 spectrophotometer.

Table S1 Crystallographic data and structure refinement parameters for complexes **4**, **5a** and **5b**.

	4	**5a**	**5b**
formula	$C_{35}H_{51}Cl_6Ir_3N_4$	$C_{76}H_{98}F_{12}Ir_6N_8O_{20}S_4$ 2CH_3OH 2H_2O	$C_{84}H_{98}Cl_4F_{12}Ir_6N_8O_{20}S_4$ 6CH_3OH 1H_2O
Mr	1317.09	3053.17	3198.26
crystal system	Triclinic	Monoclinic	Monoclinic
space group	*P*-1	*P*2$_1$/n	*P*2$_1$/c
a [Å]	11.7964(10)	17.2426(10)	14.020(2)
b [Å]	14.234(2)	12.2074(7)	24.957(4)
c [Å]	14.7093(12)	24.9090(14)	16.397(2)
α [º]	106.465(2)	90	90
β [º]	111.0350(10)	100.386(2)	98.073(2)
γ [º]	104.122(2)	90	90
V [Å^3]	2039.1(4)	5157.1 (5)	5680.3(14)
T [K]	203(2)	173(2)	203(2)
Z	2	2	2
ρ_{calcd} [g cm^{-3}]	2.145	1.966	1.989
μ [mm^{-1}]	10.189	10.694	7.260
F(000)	1244	2920	3276
independent reflections	0.0256	0.0550	0.0697
data/restraints/parameters	7849/108/421	10906/131/678	13024/272/728
R_1/wR_2 [I>2σ(*I*)][a]	0.0431/0.1559	0.0430/0.1100	0.0539/0.1430
R_1/wR_2 (all data)[a]	0.0567/0.2022	0.0541/0.1177	0.1148/0.1918
goodness-of-fit	1.100	1.039	0.932
largest residuals [e Å^{-3}]	2.808/-2.172	3.071/-1.414	4.258/-3.284

[a] $R_1 = \Sigma||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$); $wR_2 = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2F0^2 + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$

Table S2 Crystallographic data and structure refinement parameters for complexes **6a**, **6b** and **7**.

	6a	**6b**	**7**
formula	$C_{86}H_{106}F_{12}Ir_6N_4O_{26}S_4$ $2CH_3OH$ $4H_2O$ $4CH_3OH$	$C_{90}H_{98}Cl_6F_6Ir_6N_4O_{18}S_2$ $4CH_3OH$	$C_{87}H_{125}F_{12}Ir_6N_7O_{29}S_4$
Mr	3321.41	1597.95	3242.37
crystal system	Monoclinic	Monoclinic	Triclinic
space group	*C2/c*	$P2_1/c$	*P*-1
a [Å]	16.9993(7)	14.2389(11)	17.8224(19)
b [Å]	22.0621(10)	20.1647(16)	21.279(2)
c [Å]	28.645(3)	19.0241(15)	29.878(3)
α [º]	90	90	71.018(2)
β [º]	91.725(2)	103.2420(10)	84.763(2)
γ [º]	90	90	88.326(2)
V [Å^3]	10744.1(8)	5317.0(7)	10670(2)
T [K]	173(2)	173(2)	203(2)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	2.053	1.996	2.018
μ [mm^{-1}]	10.348	7.748	7.629
F(000)	6416	3064	6248
independent reflections	0.0668	0.0364	0.0488
data/restraints/parameters	10576/259/710	12098/18/638	41428/722/2519
R_1/wR_2 [I>2σ(*I*)][a]	0.0625/0.1760	0.0323/0.0926	0.0721/0.2016
R_1/wR_2 (all data)[a]	0.0757/0.1879	0.0466/0.1074	0.1207/0.2637
goodness-of-fit	1.084	0.942	1.029
largest residuals [e Å^{-3}]	2.217/-1.964	1.860/-1.068	9.187/-4.723

[a] $R_1 = \Sigma||F_o| - |F_c||$ (based on reflections with $Fo^2 > 2\sigma F^2$); $wR_2 = \{\Sigma[\omega(Fo^2 - Fc^2)^2]/\Sigma[\omega(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2F0^2 + (0.095P)^2]$; $P = [\max(Fo^2, 0) + 2Fc^2]/3$ (also with $Fo^2 > 2\sigma F^2$

Table S3 Selected bond lengths (Å) for **4**, **5a**, **5b** the free ligand H_4L_1.

H_4L_1		**4**		**5a**		**5b**	
N(3)-C(1)	1.266	N(3)-C(1)	1.293(18)	N(3)-C(3)	1.325(8)	N(3)-C(7)	1.346(14)
N(4)-C(2)	1.266	N(4)-C(2)	1.336(16)	N(4)-C(4)	1.319(8)	N(4)-C(8)	1.298(15)
C(1)-C(2)	1.385	C(1)-C(2)	1.463(17)	C(3)-C(4)	1.442(9)	C(7)-C(8)	1.454(15)
N(1)-C(4)	1.353	N(1)-C(4)	1.321(19)	N(1)-C(3)	1.340(8)	N(1)-C(7)	1.34(4)
N(1)-C(1)	1.353	N(1)-C(1)	1.38(2)	N(1)-C(6)	1.374(8)	N(1)-C(10)	1.32(3)
N(2)-C(2)	1.353	N(2)-C(2)	1.311(17)	N(2)-C(4)	1.348(8)	N(2)-C(8)	1.365(15)
N(2)-C(3)	1.353	N(2)-C(3)	1.366(19)	N(2)-C(5)	1.381(8)	N(2)-C(9)	1.349(16)
C(3)-C(4)	1.385	C(3)-C(4)	1.36(2)	C(5)-C(6)	1.360(9)	C(9)-C(10)	1.363(16)
		Ir(3)-N(4)	2.004(11)	Ir(3)-N(3)	2.008(5)	Ir(3)-N(4)	1.983(9)
		Ir(3)-N(3)	2.005(10)	Ir(3)-N(4)	2.004(5)	Ir(3)-N(3)	1.984(10)

Table S4 Selected bond lengths (Å) for **6a**, **6b**, **7** and the free ligand H_2L_2.

H_2L_2		**6a**		**6b**		**7**	
O(7)-C(6)	1.355	O(5)-C(3)	1.295(11)	O(5)-C(7)	1.280(7)	N(11)-C(91)	1.34 (2)
O(8)-C(5)	1.355	O(6)-C(4)	1.289(10)	O(6)-C(8)	1.274(7)	N(12)-C(92)	1.339(18)
C(5)-C(6)	1.380	C(3)-C(4)	1.437(14)	C(7)-C(8)	1.480(8)	C(91)-C(92)	1.46(2)
N(1)-C(6)	1.350	N(1)-C(3)	1.353(12)	N(1)-C(7)	1.315(8)	N(9)-C(91)	1.31(2)
N(2)-C(5)	1.350	N(1)-C(10)	1.410(11)	N(1)-C(14)	1.404(8)	N(9)-C(94)	1.36(2)
N(1)-C(2)	1.348	N(2)-C(4)	1.330(12)	N(2)-C(8)	1.327(8)	N(10)-C(92)	1.301(19)
C(2)-C(3)	1.418	N(2)-C(5)	1.404(11)	N(2)-C(9)	1.399(8)	N(10)-C(93)	1.415(17)
		C(5)-C(10)	1.435(12)	C(9)-C(14)	1.435(9)	C(93)-C(94)	1.35(2)
		Ir(3)-O(5)	2.097(7)	Ir(3)-O(5)	2.113(4)	Ir(12)-N(11)	1.996(13)
		Ir(3)-O(6)	2.116(8)	Ir(3)-O(6)	2.110(4)	Ir(12)-N(12)	1.994(14)
						O(19)-C(83)	1.310(18)
						O(20)-C(84)	1.290(19)
						C(83)-C(84)	1.492(19)
						N(7)-C(83)	1.298(19)
						N(7)-C(90)	1.41(2)
						N(8)-C(84)	1.31(2)
						N(8)-C(85)	1.42(2)
						C(85)-C(90)	1.39(2)

3. NMR Spectra

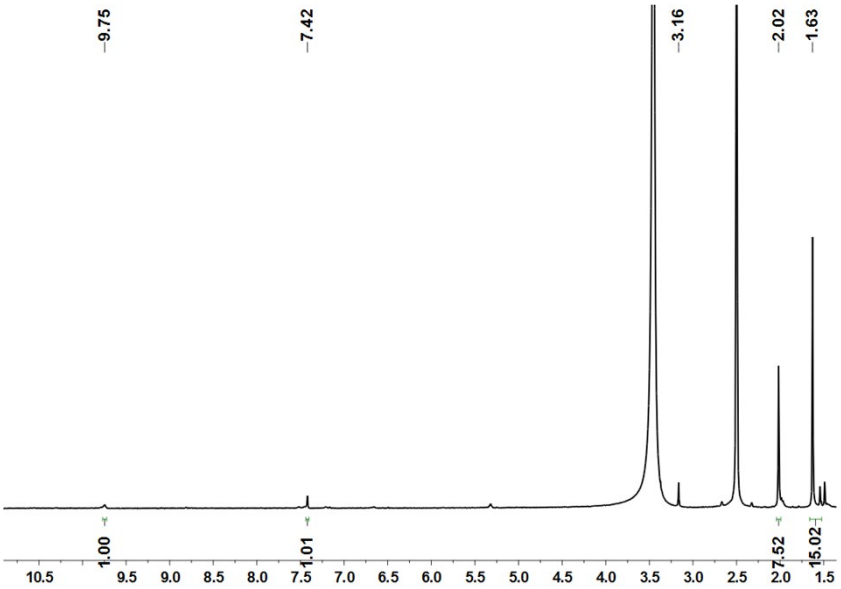

Figure. S1 The ^{1}H NMR spectra of complex **4** in DMSO-D6 solution.

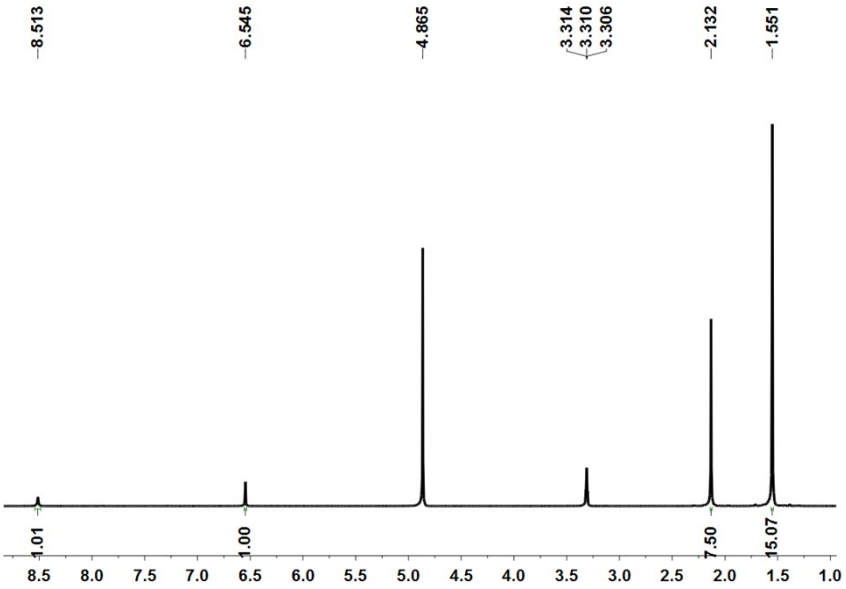

Figure. S2 The ^{1}H NMR spectra of complex **5a** in CD_3OD solution.

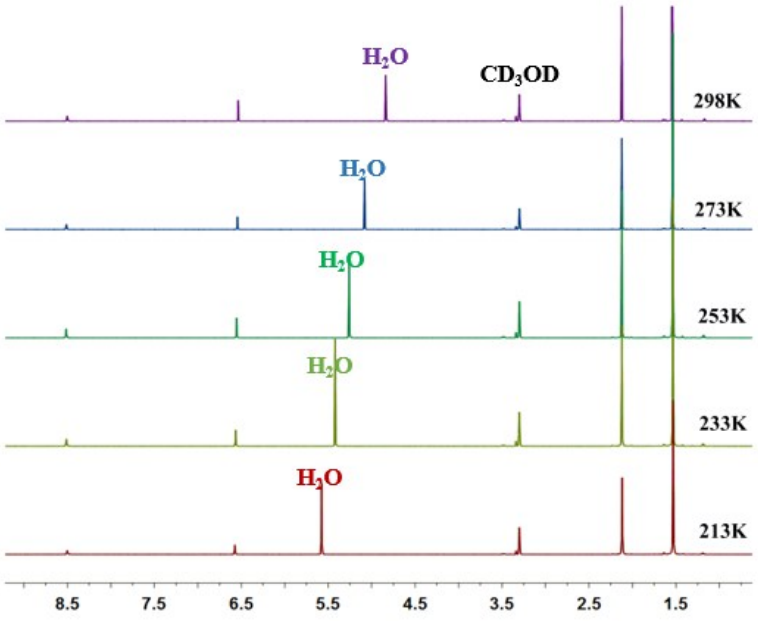

Figure. S3 Variable-temperature ^{1}H NMR studies of complex **5a** in CD_3OD solution.

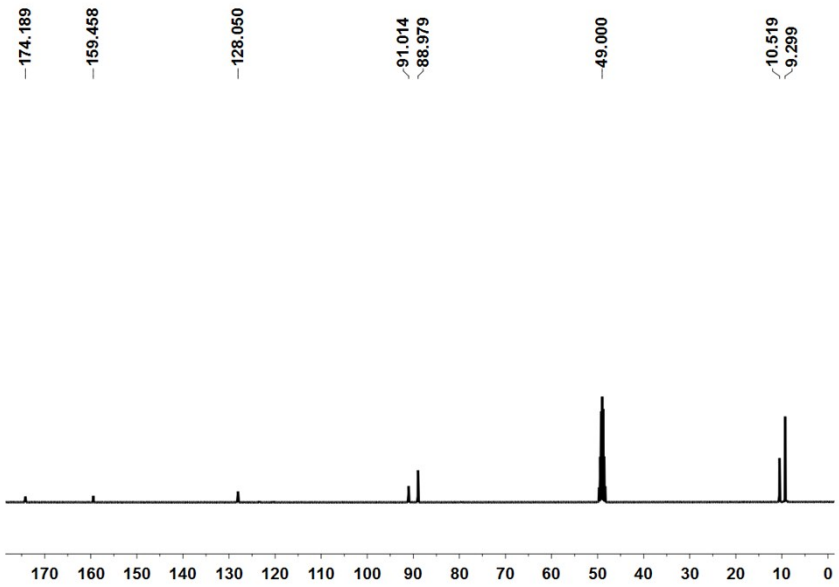

Figure. S4 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for complex **5a**.

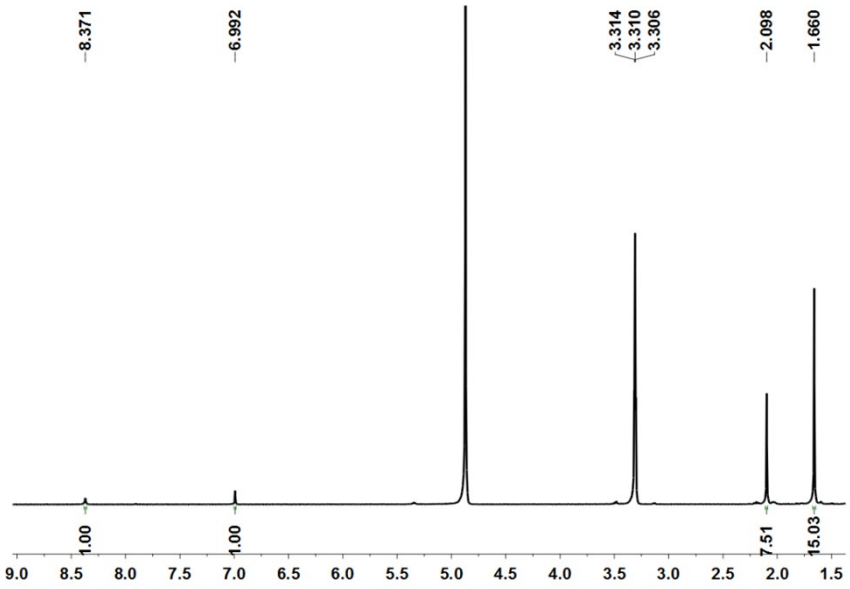

Figure. S5 The ^{1}H NMR spectra of complex **5b** in CD_3OD solution.

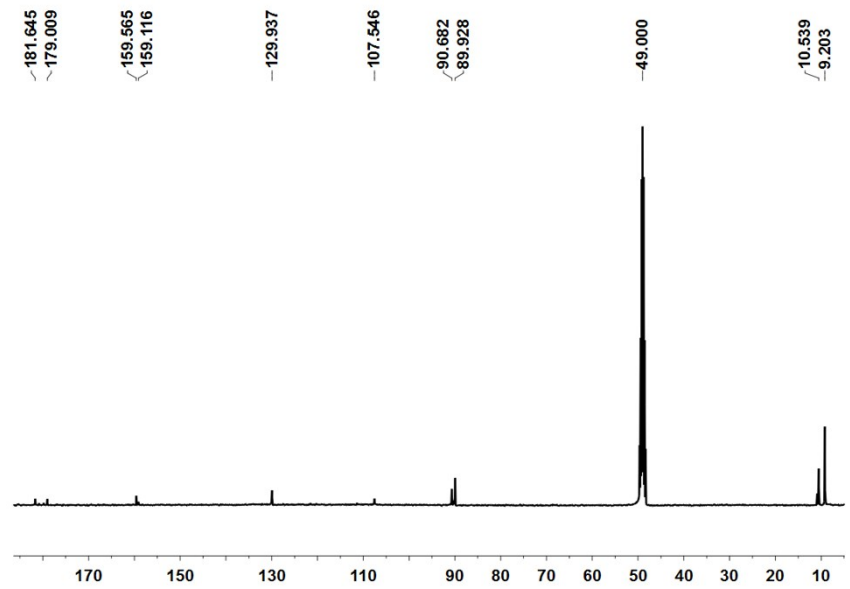

Figure. S6 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for complex **5b**.

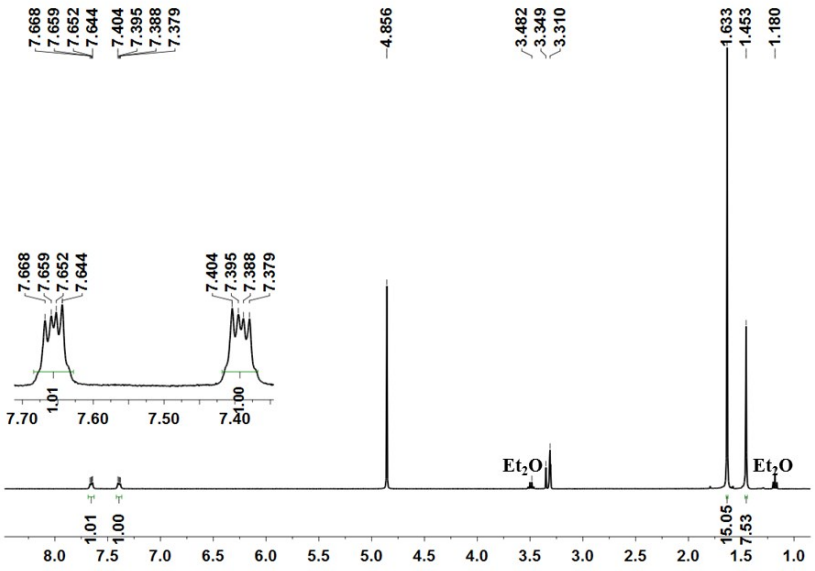

Figure. S7 The ^{1}H NMR spectra of complex **6a** in CD_3OD solution.

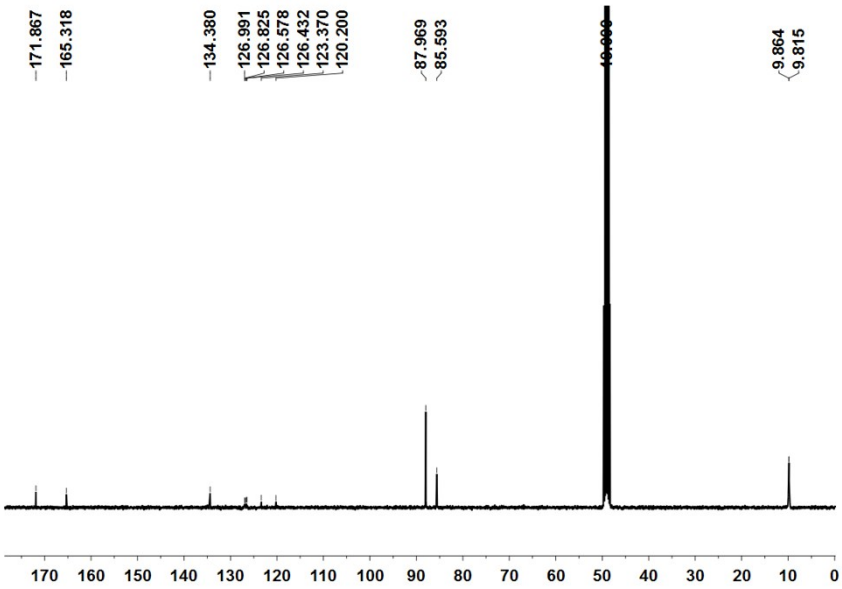

Figure. S8 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for complex **6a**.

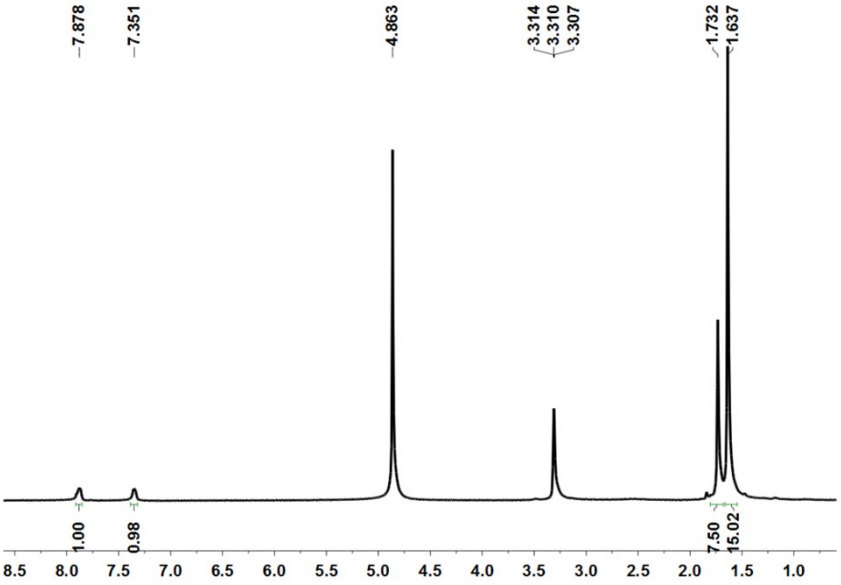

Figure. S9 The ^{1}H NMR spectra of complex **6b** in CD_3OD solution.

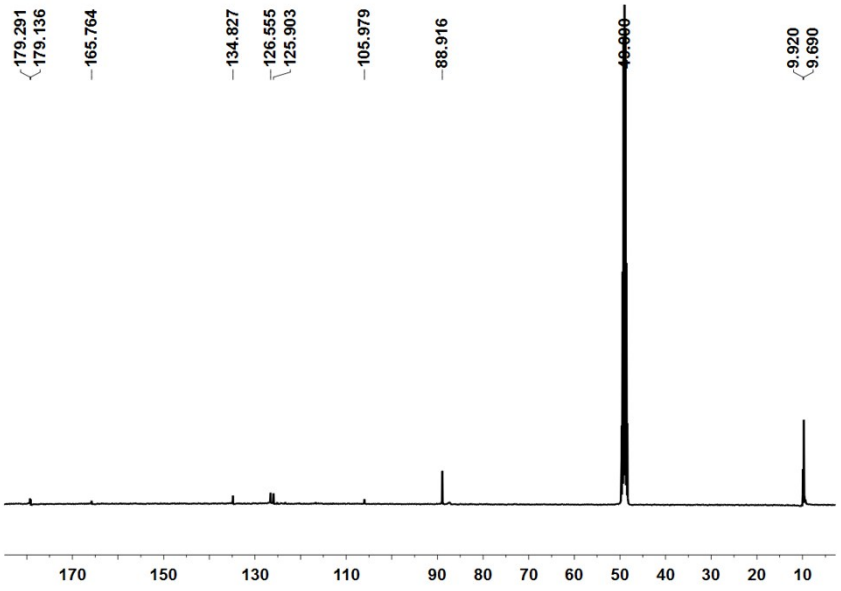

Figure. S10 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for complex **6b**.

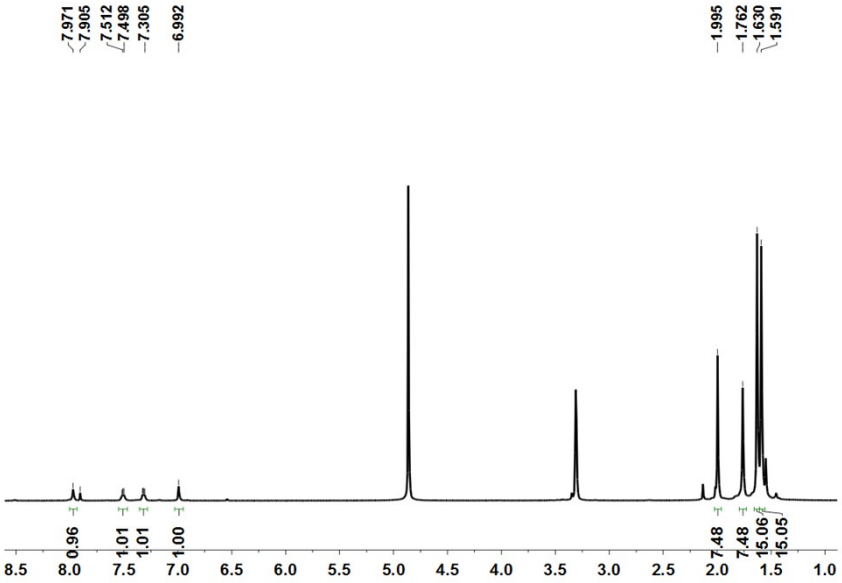

Figure. S11 The ^{1}H NMR spectra of complex **7** in CD_3OD solution.

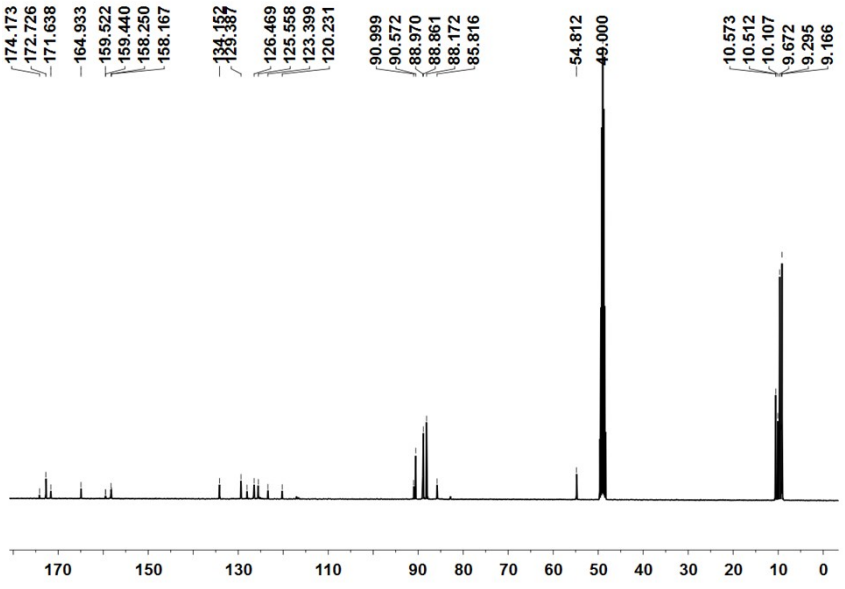

Figure. S12 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for complex **7**.

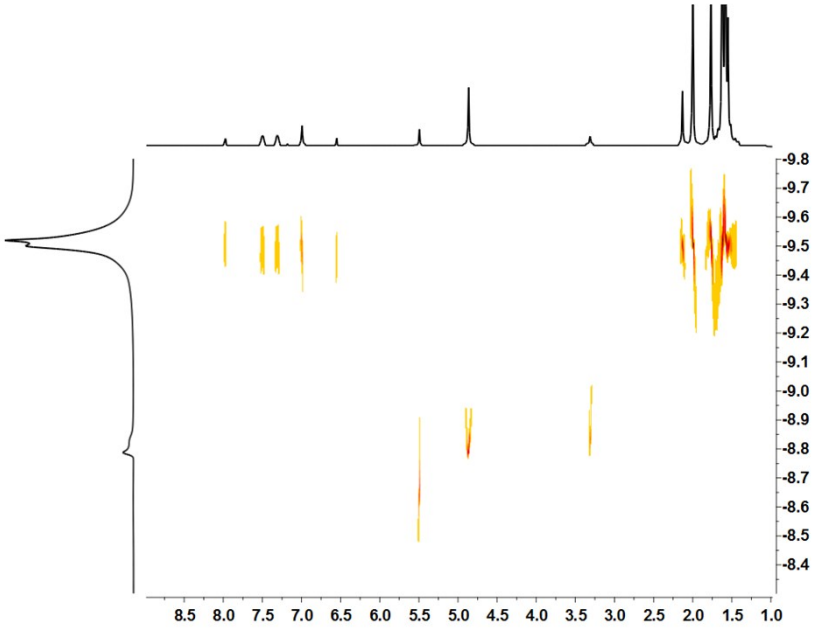

Figure. S13 ^{1}H DOSY NMR (400 MHz, CD_3OD, ppm) for complex **7**.

4. X-ray Crystallography Details.

Single-crystal XRD data of these compounds were collected on a Bruker APEX DUO diffractometer. Complexes **4**, **5b**, **6b** and **7** were collected with Mo-Kα radiation (λ = 0.71073 Å) at 203, 203, 173, 203K, respectively. Complexes **5a** and **6a** were collected with Ga-Kα radiation (λ = 0.71073 Å) at 173K. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All calculations were carried out with the SHELXTL program. In these data, the disordered solvent molecules that could not be restrained properly were removed using the SQUEEZE method.

In asymmetric unit of **4**, there was one disordered dichloromethane molecule which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. 18 ISOR instructions were used to restrain ligand and Cp* fragments so that there were 108 restraints in the data.

In asymmetric unit of **5a**, one triflate anion was disordered and it was divided into two parts (68:32). C39 was refined isotropically and other non-hydrogen atoms were refined anisotropically. 17 ISOR, 1 SIMU and 17 DFIX instructions were used to restrain anions and solvents so that there were 131 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **5b**, there were disordered solvents (one methanol and half of a diethyl ether molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One triflate anion was disordered and it was divided into two parts (63:37). 19 ISOR, 2 SIMU and 26 DFIX instructions were used to restrain anions and Cp* fragments so that there were 272 restraints in the data. Hydrogen of water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **6a**, there were disordered solvents (two methanol and two water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One triflate anion was disordered and it was divided into two parts (57:43). 38 ISOR, 2 SIMU, 1 DELU and 12 DFIX instructions were used to restrain anions and Cp* fragments so that there were 259 restraints in the data. Hydrogen of methanol molecule could not be found and others were put in calculated positions.

In asymmetric unit of **6b**, there was one disordered methanol molecule which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. One triflate anion and one methanol molecule were disordered and they were divided into two parts (59:41). 3 ISOR instructions were used to restrain anion so that there were 18 restraints in the data. Hydrogen of methanol molecule could not be found and others were put in calculated positions.

In asymmetric unit of **7**, there were disordered solvents (nine methanol and three water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One pentamethylcyclopentadienyl ligand (Cp* for short) was disordered and it was divided into two parts (60:40). 110 ISOR, 1 SIMU and 26 DFIX instructions were used to restrain anions, ligands and Cp* fragments so that there were 722 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated positions.