Supporting Information

Aluminum Porphyrin Complex with High Activity and Selectivity for Cyclic Carbonate Synthesis

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Contents

1. General Remarks

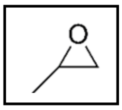
All reactions of air- and/or moisture-sensitive complexes and product manipulations were performed under inert atmosphere using standard Schlenk technique or in a glove box. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), pyrrole, propylene oxide (PO) were distilled over CaH_2 under inert atmosphere. The CO_2 gas (99.999%) was purchased and used without further purification. Bis(triphenylphosphoranylidene)ammonium bromide (PPNBr) and bis(triphenylphosphoranylidene)ammonium iodide (PPNI) were synthesized as previously reported.[1] Other chemicals were obtained from Aldrich and Acros, and used as received without further purification unless otherwise stated.

NMR Experiments Solution NMR spectra were collected at ambient temperatures using Bruker ARX-300 or Bruker AV-400 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO) with tetramethylsilane (TMS) as internal reference. Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s); DMSO-d_6, 2.50 (s). Solvent carbon shifts (ppm): $CDCl_3$, 77.16 (t); DMSO-d_6, 39.52 (m).

Mass Spectrometry Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) was performed on a Bruker atuoflex III mass spectrometer.

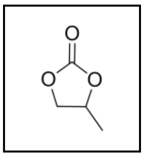
2. [1]*HNMR data for Epoxides and cyclic carbonate products*

Propylene oxide



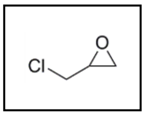
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 2.72 (m, 1H), 2.46 (m, 1H), 2.14 (m, 1H), 1.06 (m, 3H).

4-methyl-1,3-dioxolan-2-one



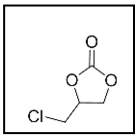
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.64 (m, 1H), 4.34 (m, 1H), 3.77 (m, 1H), 1.24 (m, 3H).

1,2-epoxy-3-chloropropane



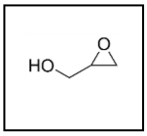
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.55 (m, 2H), 3.22 (m, 1H), 2.88 (m, 1H), 2.67 (m, 1H).

4-(chloromethyl)-1,3-dioxolan-2-one



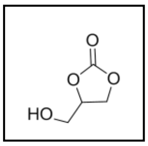
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.97 (m, 1H), 4.57 (m, 1H), 4.38 (m, 1H), 3.74 (m, 2H).

oxiran-2-ylmethanol



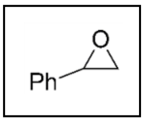
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.75 (m, 1H), 3.43 (m, 2H), 3.08 (m, 1H), 2.68 (m, 2H).

4-(hydroxymethyl)-1,3-dioxolan-2-one



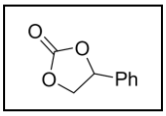
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.81 (m, 1H), 4.48 (m, 2H), 4.00 (m, 1H), 3.72 (m, 1H), 2.79 (m, 1H).

2-phenyloxirane



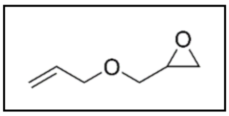
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 7.36 (m, 5H), 3.83 (m, 1H), 3.14 (m, 1H), 2.80 (m, 1H).

4-phenyl-1,3-dioxolan-2-one



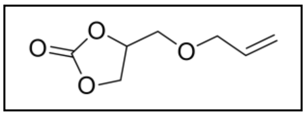
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 7.45 (m, 5H), 5.70 (m, 1H), 4.79 (m, 1H), 4.34 (m, 1H).

2-(allyloxymethyl)oxirane



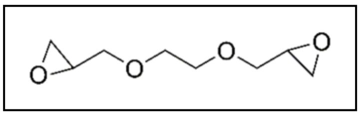
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 5.91 (m, 1H), 5.25 (m, 2H), 4.04 (m, 2H), 3.72 (m, 1H), 3.40 (m, 1H), 3.16 (m, 1H), 2.80 (m, 1H), 2.61 (m, 1H).

4-(allyloxymethyl)-1,3-dioxolan-2-one



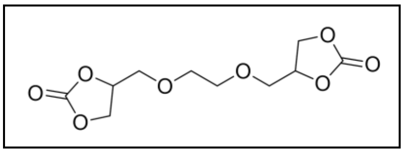
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 5.73 (m, 1H), 5.17 (m, 2H), 4.71(m, 1H), 4.40 (m, 1H), 4.25 (m, 1H), 3.90(m, 2H), 3.58 (m, 2H).

1,2-bis(oxiran-2-ylmethoxy)ethane



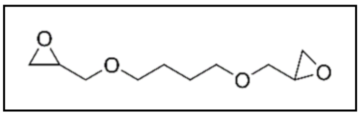
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.72(m, 2H), 3.62 (m, 4H), 3.36 (m, 2H), 3.10 (m, 2H), 2.72 (m, 2H),2.54 (m, 2H).

4-((2-((2-oxo-1,3-dioxolan-4-yl)methoxy)ethoxy)methyl)-1,3-dioxolan-2-one



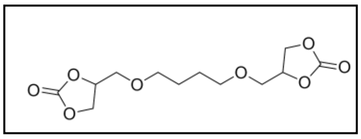
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.80(m, 2H), 4.49 (m, 2H), 4.40 (m, 2H), 3.62–3.79 (m, 8H).

2-((4-(oxiran-2-ylmethoxy)butoxy)methyl)oxirane



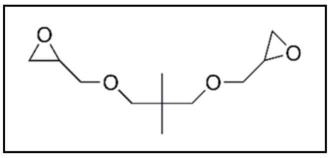
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.60(m, 2H), 3.40 (m, 4H), 3.26 (m, 2H), 3.03 (m, 2H), 2.68 (m, 2H),2.50 (m, 2H), 1.55 (m, 4H).

4-((4-((2-oxo-1,3-dioxolan-4-yl)methoxy)butoxy)methyl)-1,3-dioxolan-2-one



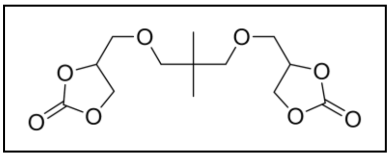
^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.76(m, 2H), 4.43 (m, 2H), 4.30 (m, 2H), 3.44–3.63 (m, 8H), 1.55(m, 4H).

1,3-bis(2,3-epoxypropoxy)-2,2-dimethylpropane



^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 3.66(m, 2H), 3.35 (m, 2H), 3.21 (m, 4H), 3.09 (m, 2H), 2.73 (m, 2H),2.56 (m, 2H), 0.86 (m, 6H).

4,4'-(((2,2-dimethylpropane-1,3-diyl)bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) [8]



^{1}H-NMR ($CDCl_3$, TMS, 300 MHz): δ (ppm) = 4.78(m, 2H), 4.42 (m, 4H), 3.62 (m, 2H), 3.52 (m, 2H), 3.18 (m, 4H),0.86 (m, 6H).

3. Additional Information for Coupling Reaction of CO_2 with Epoxide

Table S1 Effect of the Cocatalyst Concentration[a]

Entry	Catalyst	Cocatalyst	Catalyst/Cocatalyst/PO	Conversion[b] %	TOF[c] (h^{-1})
1	**4**	PPNCl	1:5:50000	34.2	34200
2	**4**	PPNCl	1:20:50000	69.4	69400
3	**4**	PPNCl	1:50:50000	88.2	88200
4	**4**	PPNCl	1:100:50000	91.7	91700
5	**4**	PPNCl	1:120:50000	96.4	96400
6	**4**	PPNCl	1:150:50000	88.6	88600

[a] Reaction Conditions: PO (20 mL, 16.6 g, 28.6 $\times 10^{-2}$ mol), Complex **4** (5.72 $\times 10^{-6}$ mol, 0.002 mol%),CO_2 (3.0 MPa), 120 ℃, 0.5 h, in a 50 mL autoclave.

[b] Determined by ^{1}H NMR

[c] Moles of propylene carbonate produced per mole of catalyst per hour.

Table S2 Effects of Reaction Pressure and Temperature[a]

Entry	T (℃)	P (MPa)	Time (h)	Cocatalyst	Catalyst/Cocatalyst/PO	Conversion[b] %	TOF[c] (h^{-1})
1	90	3	0.5	PPNCl	1:120:50000	73.5	73500
2	120	3	0.5	PPNCl	1:120:50000	96.4	96400
3	150	3	0.5	PPNCl	1:120:50000	100.0	100000
4	30	0.1	5	PPNCl	1:120:100000	18.3	3660
5	120	1	0.5	PPNCl	1:120:50000	81.9	81900
6	120	5	0.5	PPNCl	1:120:50000	90.6	90600

[a] Reaction Conditions: PO (20 mL, 16.6 g, 28.6 $\times 10^{-2}$ mol), Complex **4** (5.72 $\times 10^{-6}$ mol, 0.002 mol%), in a 50 mL autoclave.

[b] Determined by ^{1}H NMR.

[c] Moles of propylene carbonate produced per mole of catalyst per hour.

Table S3. Reusability of 4/PPNCl system[a]

Entry	Catalyst	Cocatalyst	Conversion[b] (%)	TOF[c] (h^{-1})
1	Fresh	PPNCl	74.5	149000
2	Resuse 1	PPNCl	65.5	131000
3	Resuse 2	PPNCl	58.8	117600
4	Resuse 3	PPNCl	60.0	120000
5	Resuse 4	PPNCl	61.3	122600
6[d]	Re-added PPNCl	PPNCl	71.6	143000

[a] Reaction Conditions: PO (20 mL, 16.6 g, 28.6×10^{-2} mol), Complex **4** (5.72×10^{-6} mol, 0.002 mol%),Catalyst **4**/Cocatalyst/PO = 1:120:100000, CO_2 (3.0 MPa), 120 ℃, 0.5 h, in a 50 mL autoclave.

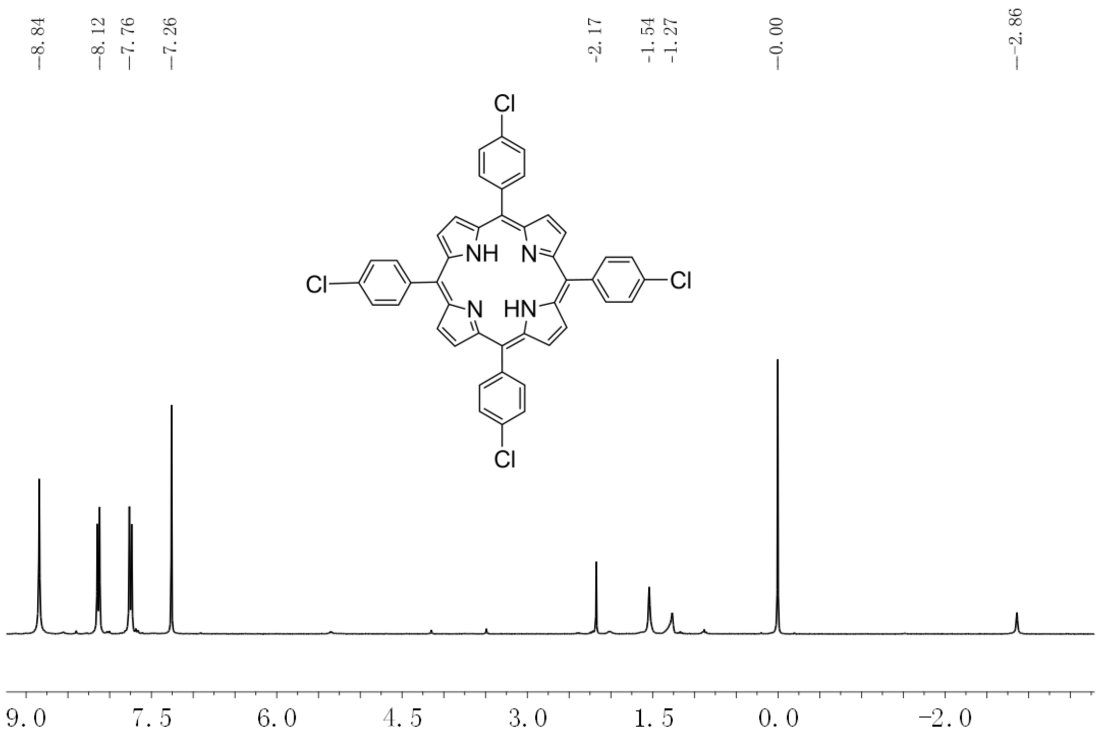
[b] Determined by ^{1}H NMR.

[c] Moles of propylene carbonate produced per mole of catalyst per hour.

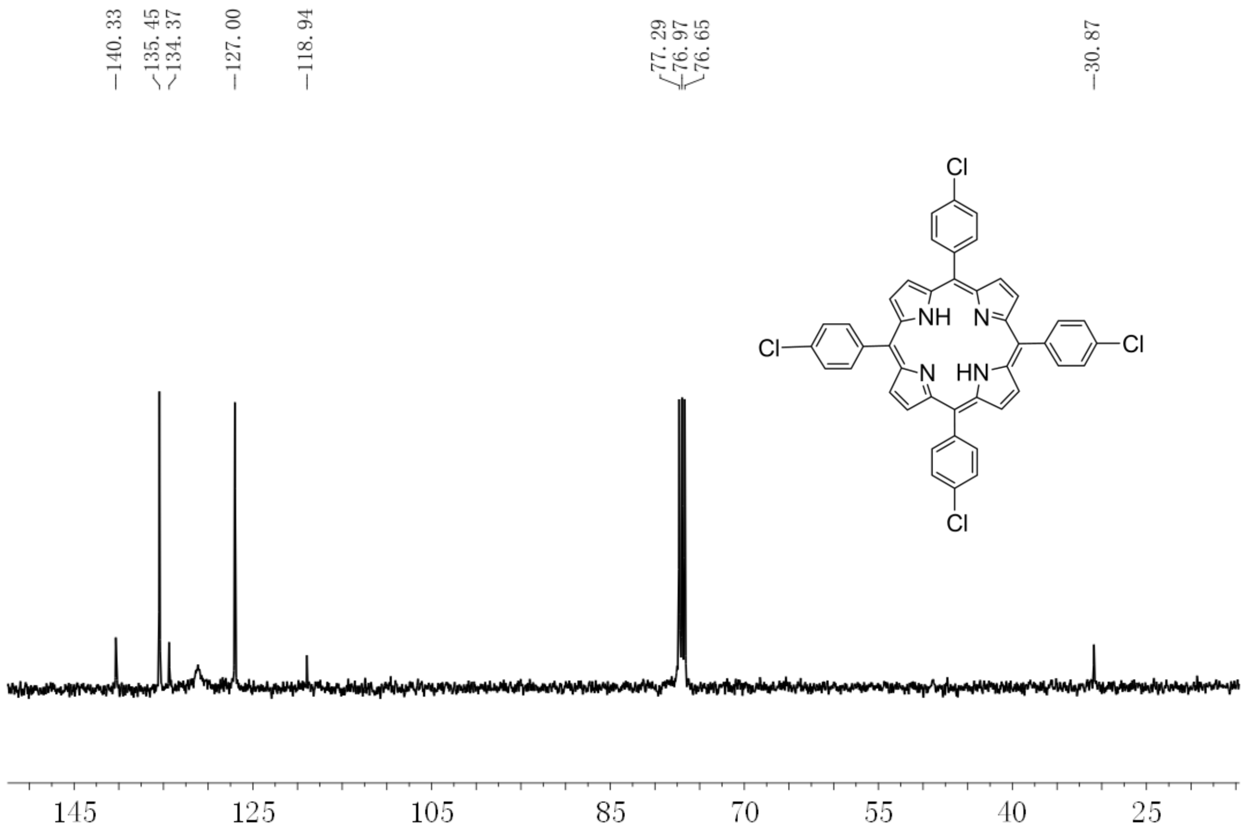
[d] The amount of the PPNCl added is the loss weight of the catalyst system.

4. ^{1}H and ^{13}C NMR Spectra

4.1 ^{1}H and ^{13}C NMR Spectra of ligand I

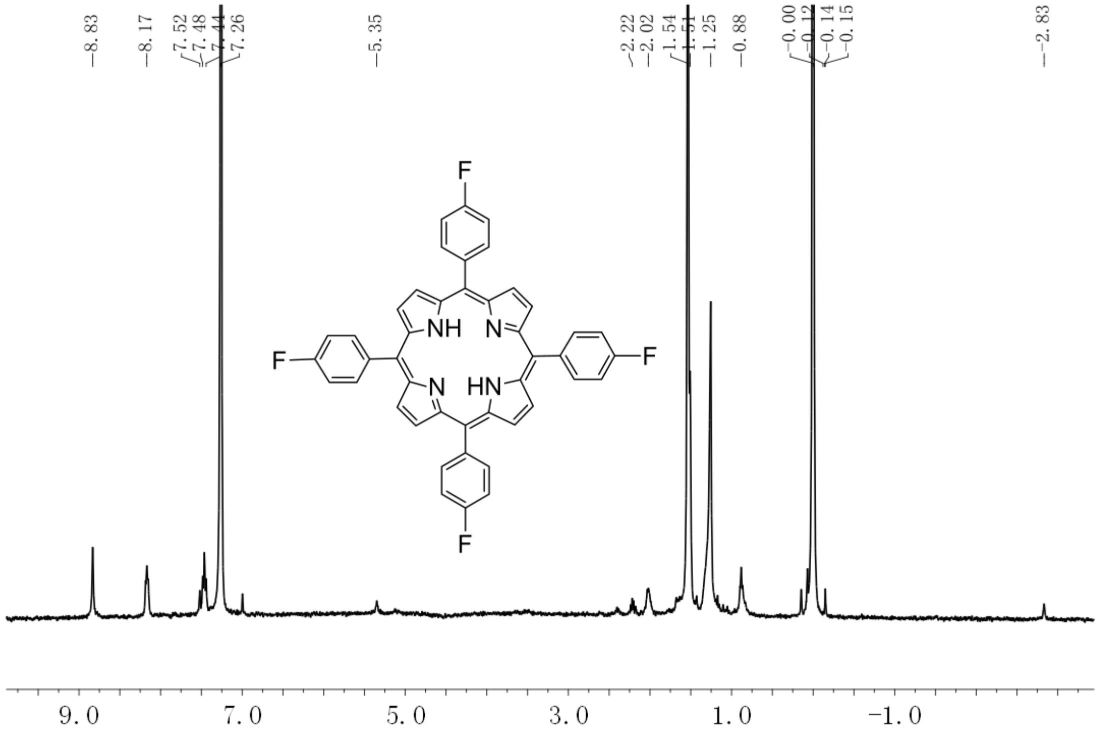


300 MHz ^{1}H NMR spectrum of **I** in $CDCl_3$

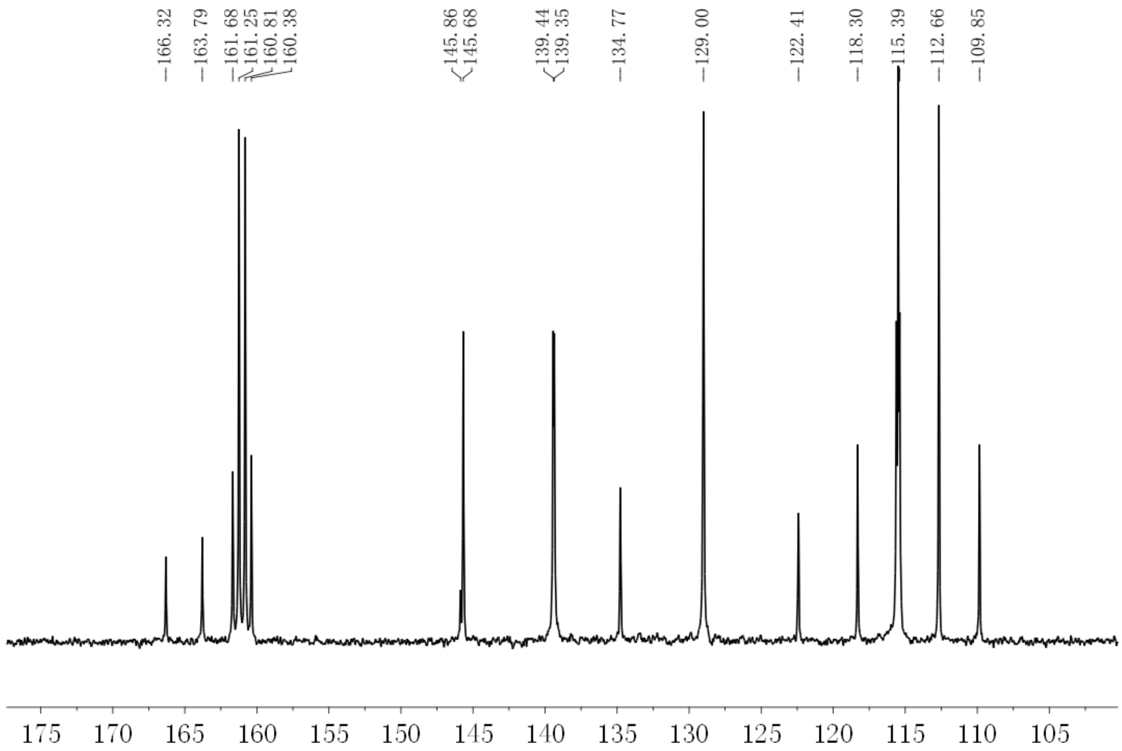


100 MHz ^{13}C NMR spectrum of **I** in $CDCl_3$.

4.2 [1]H and [13]C NMR Spectra of ligand II

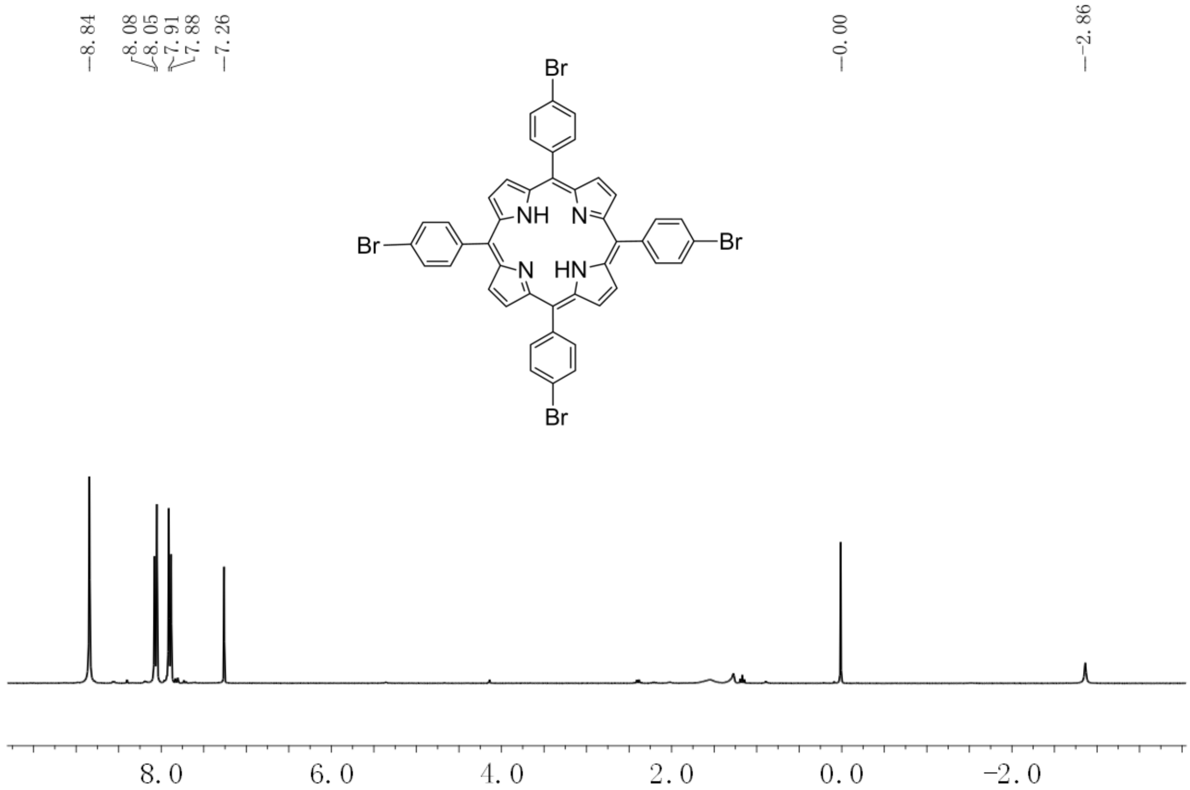


400 MHz ^{1}H NMR spectrum of **II** in $CDCl_3$

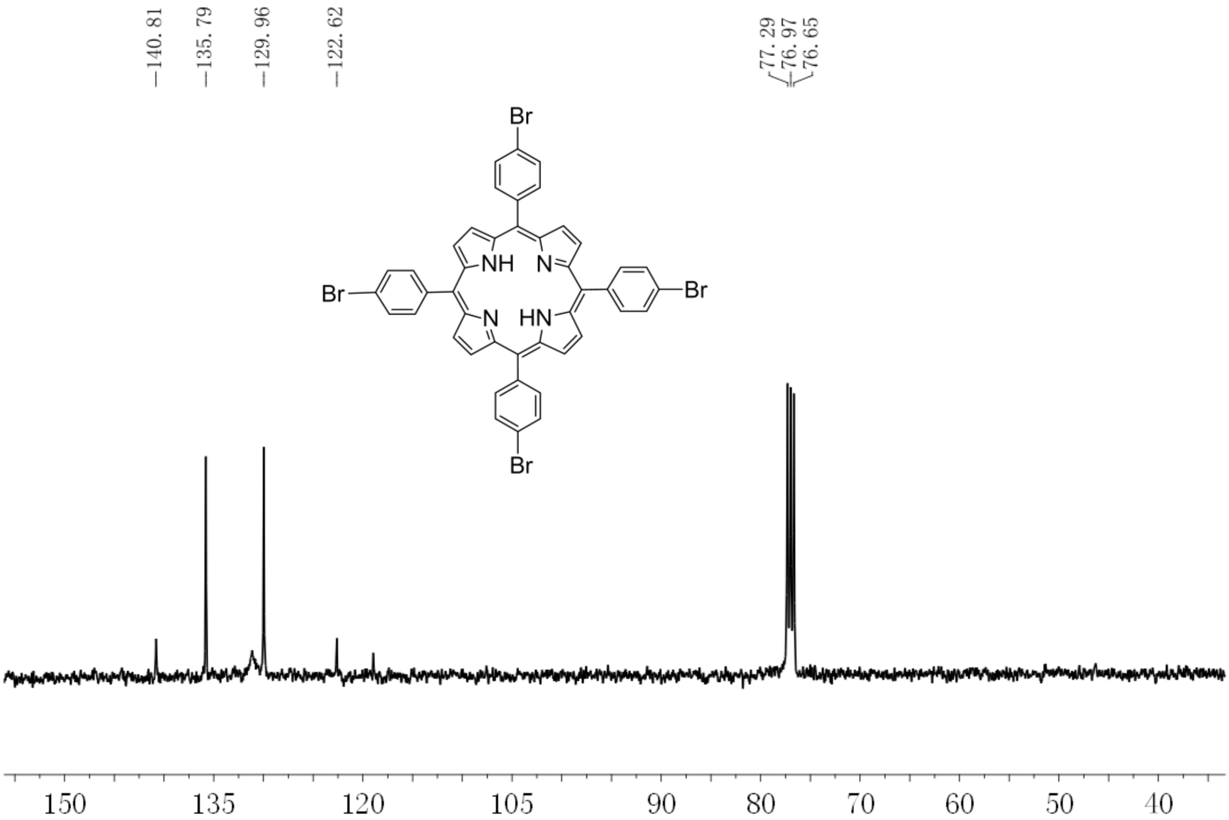


100 MHz ^{13}C NMR spectrum of **II** in TFA-D

4.3 ¹H and ¹³C NMR Spectra of ligand III

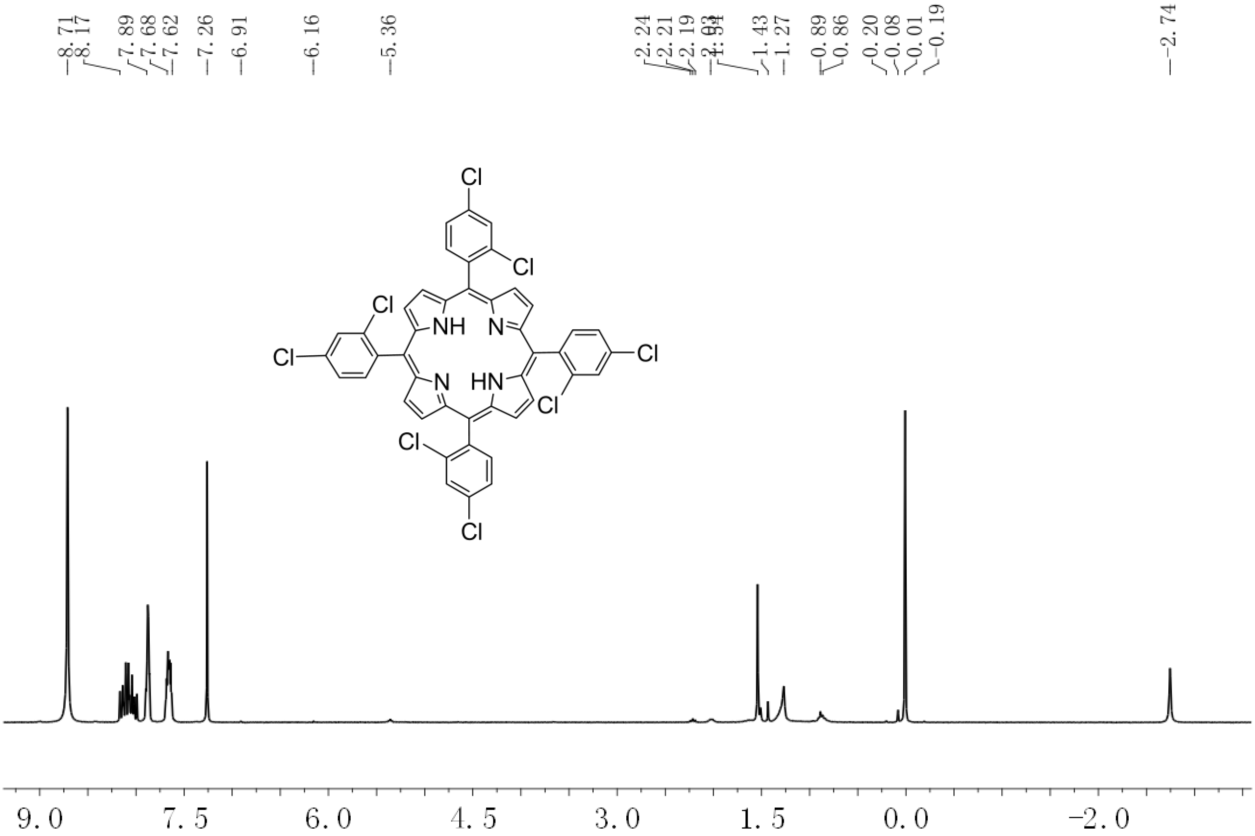


300 MHz ¹H NMR spectrum of **III** in $CDCl_3$

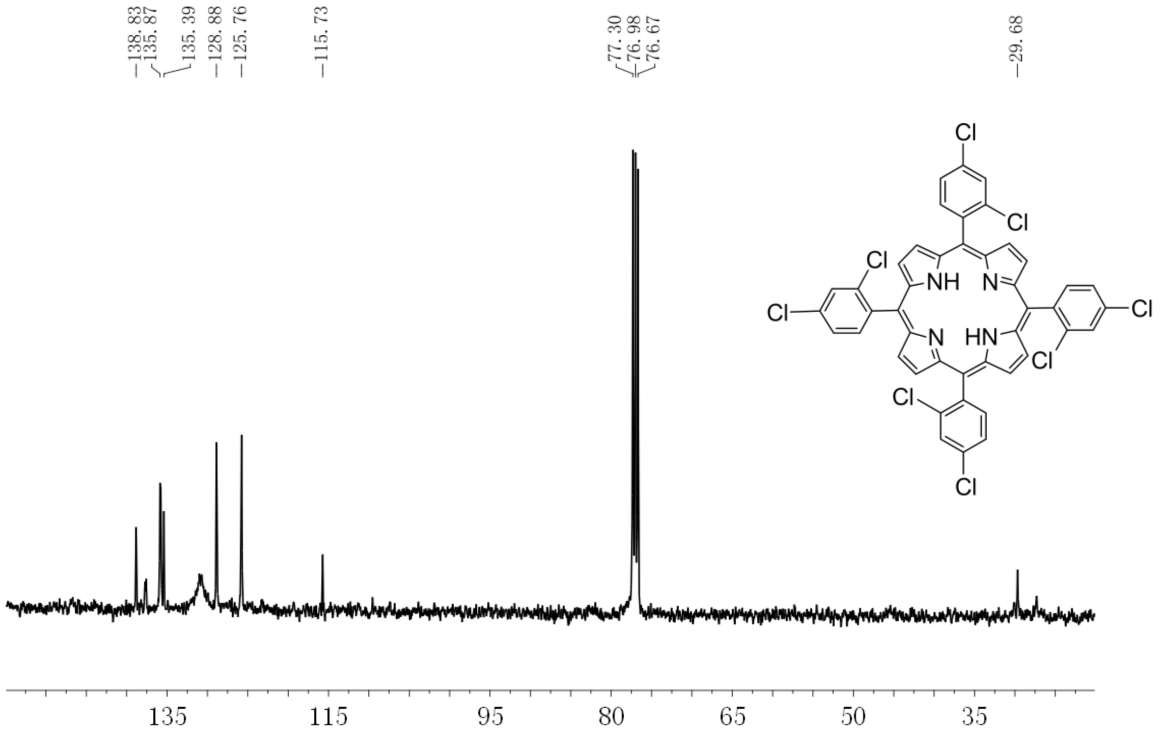


100 MHz ^{13}C NMR spectrum of **III** in $CDCl_3$.

4.4 [1]H and [13]C NMR Spectra of ligand IV

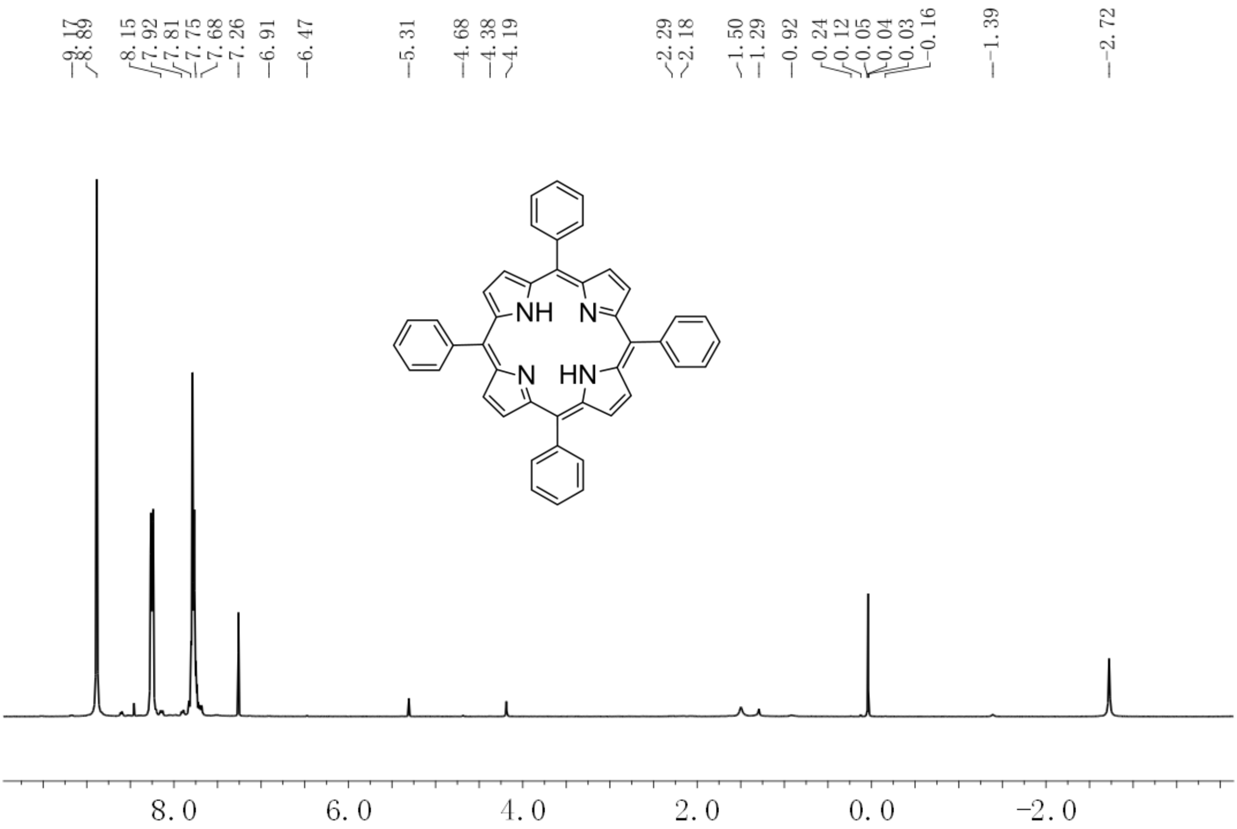


300 MHz ^{1}H NMR spectrum of **IV** in $CDCl_3$

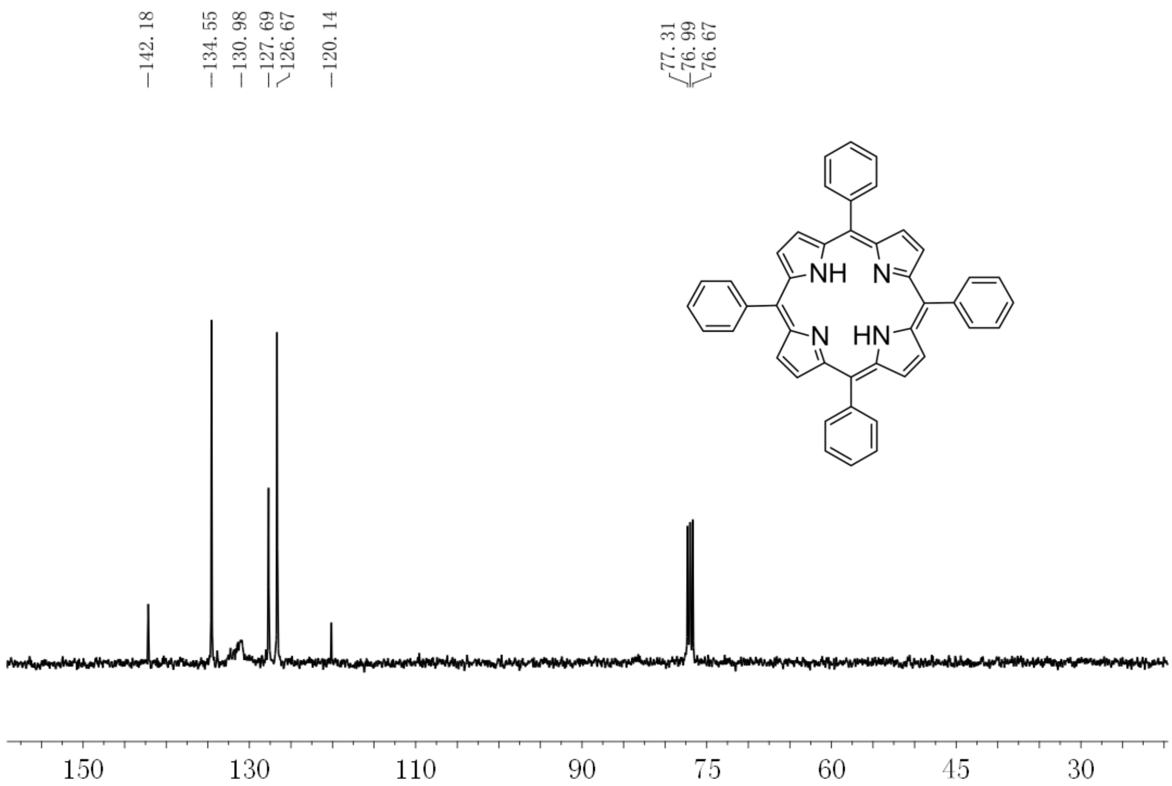


100 MHz ^{13}C NMR spectrum of **IV** in $CDCl_3$.

4.5 ^{1}H and ^{13}C NMR Spectra of ligand V

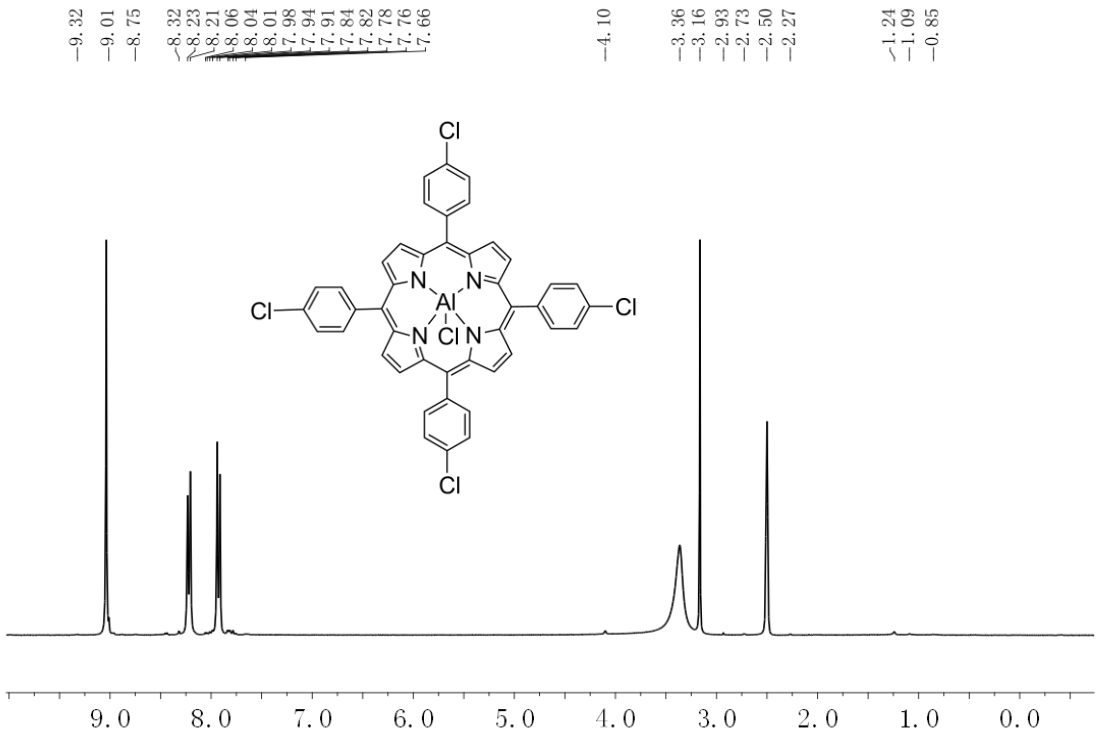


300 MHz ^{1}H NMR spectrum of **V** in $CDCl_3$

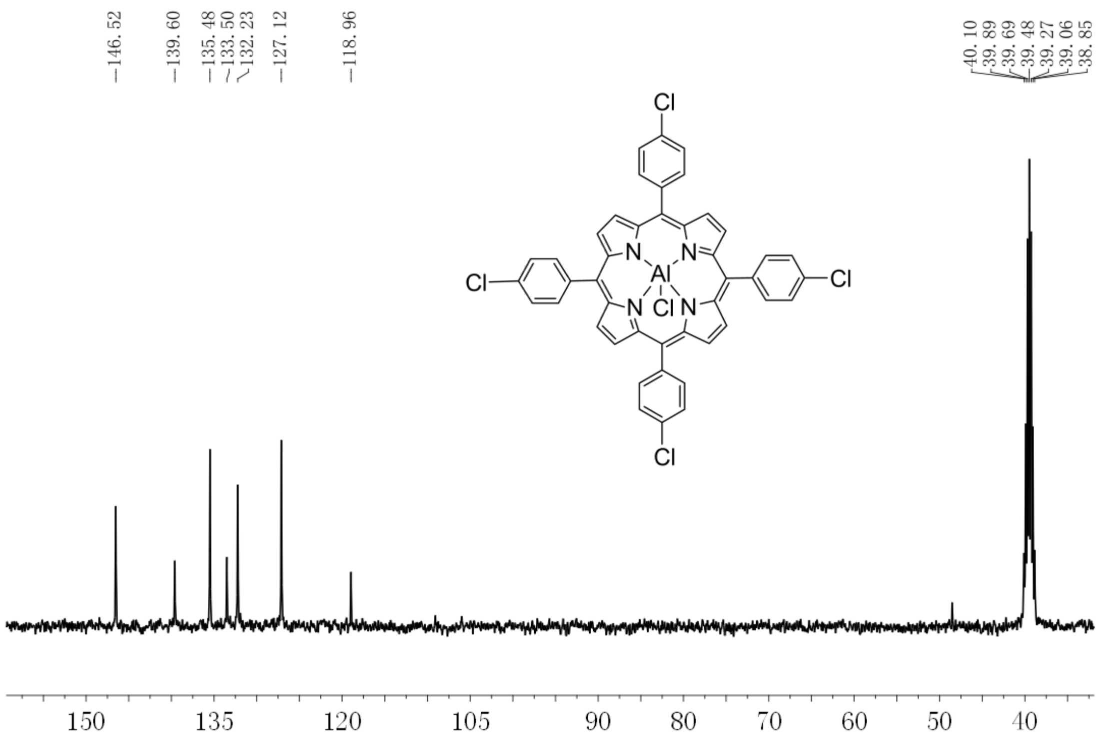


100 MHz ^{13}C NMR spectrum of **V** in $CDCl_3$.

4.6 ¹H and ¹³C NMR Spectra of complex 1

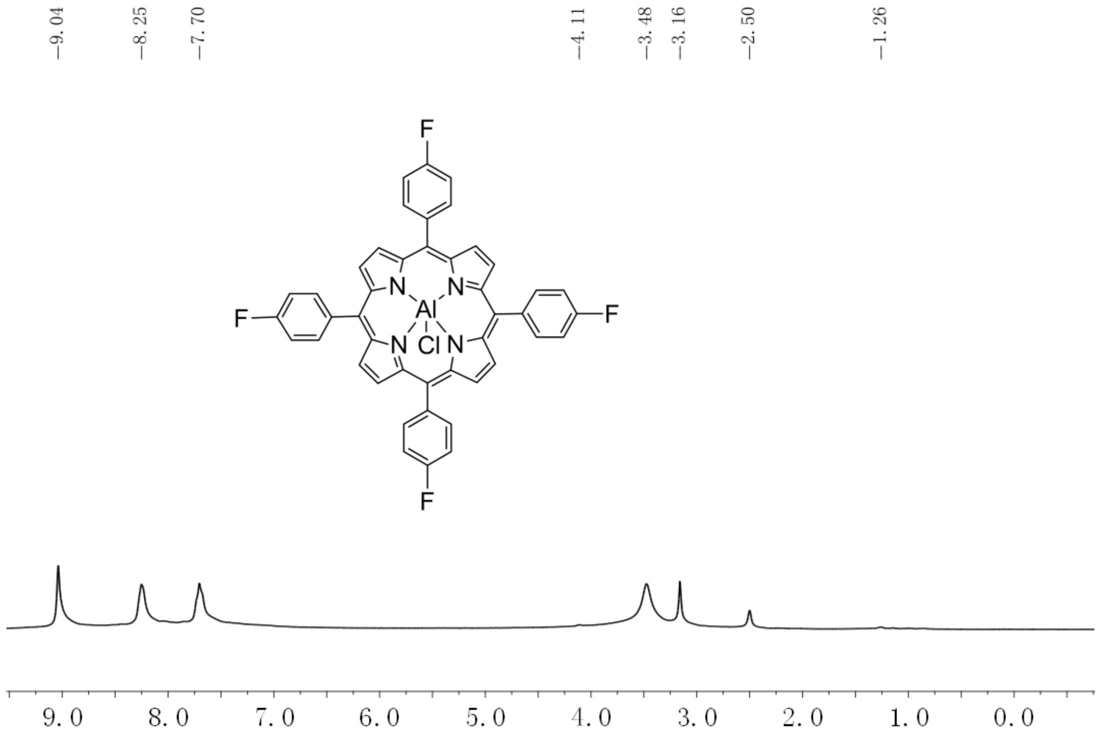


300 MHz ^{1}H NMR spectrum of **complex 1** in DMSO-d_6

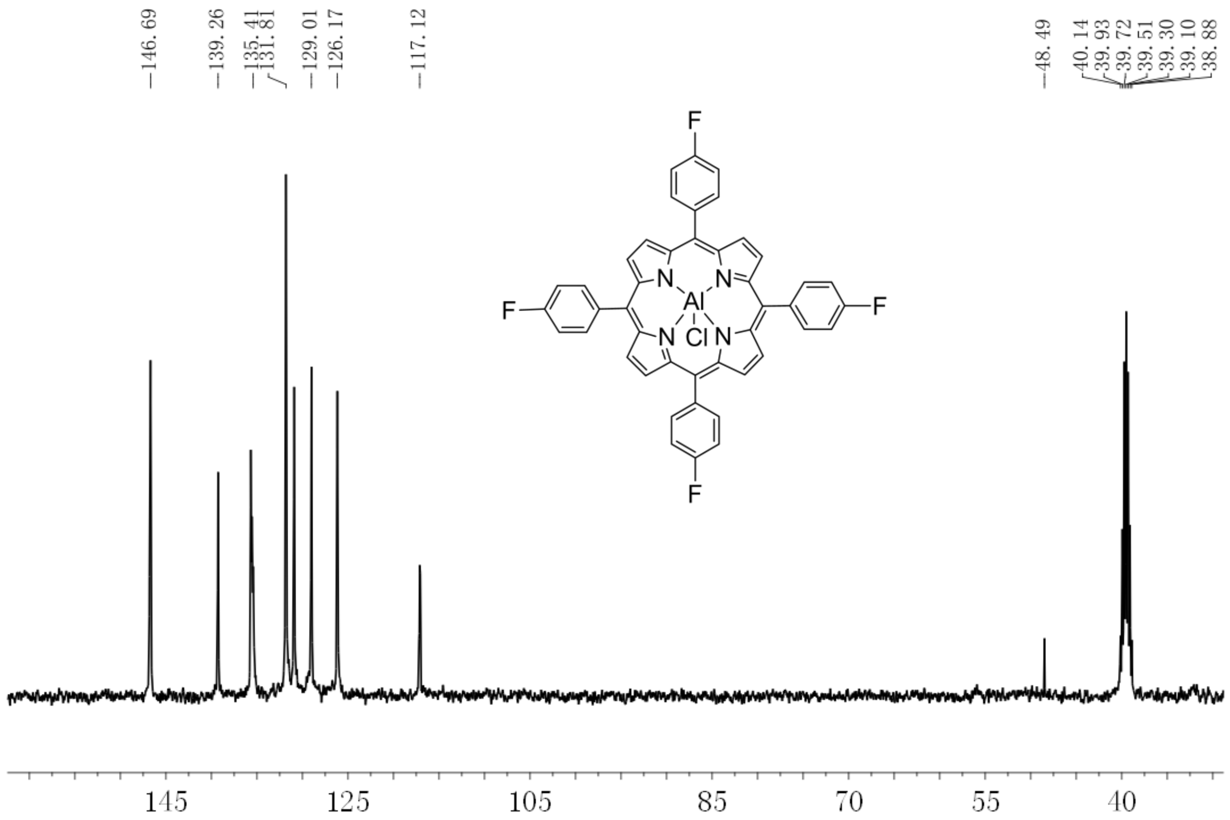


100 MHz ^{13}C NMR spectrum of **complex 1** in DMSO-d_6

4.7 ¹H and ¹³C NMR Spectra of complex 2

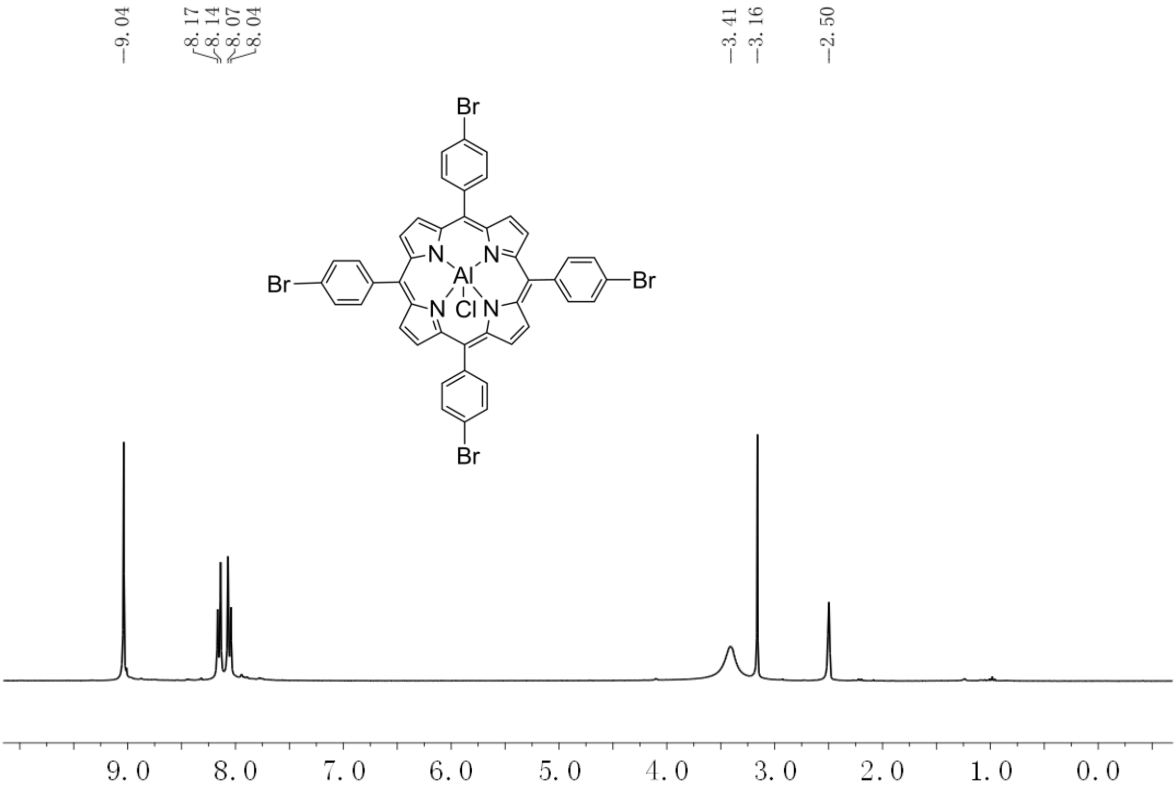


300 MHz ^{1}H NMR spectrum of **complex 2** in DMSO-d_6

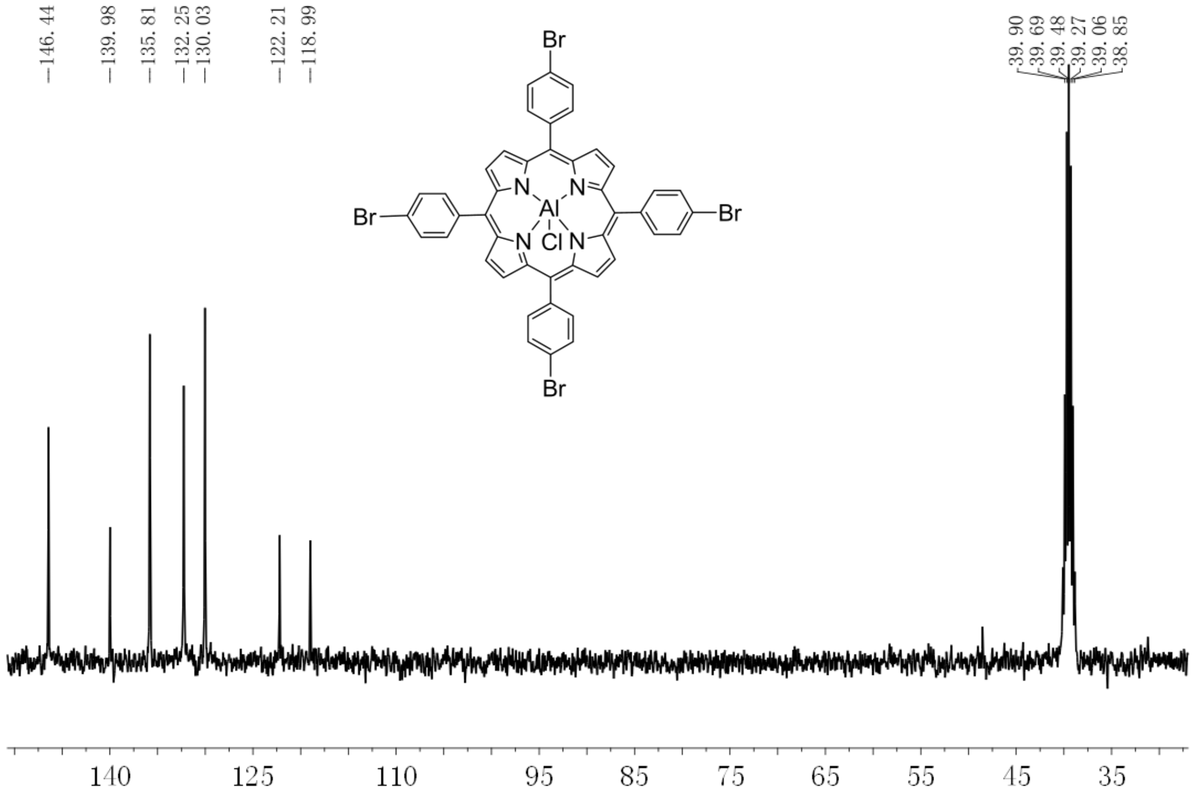


100 MHz ^{13}C NMR spectrum of **complex 2** in DMSO-d_6

4.8 ^{1}H and ^{13}C NMR Spectra of complex 3

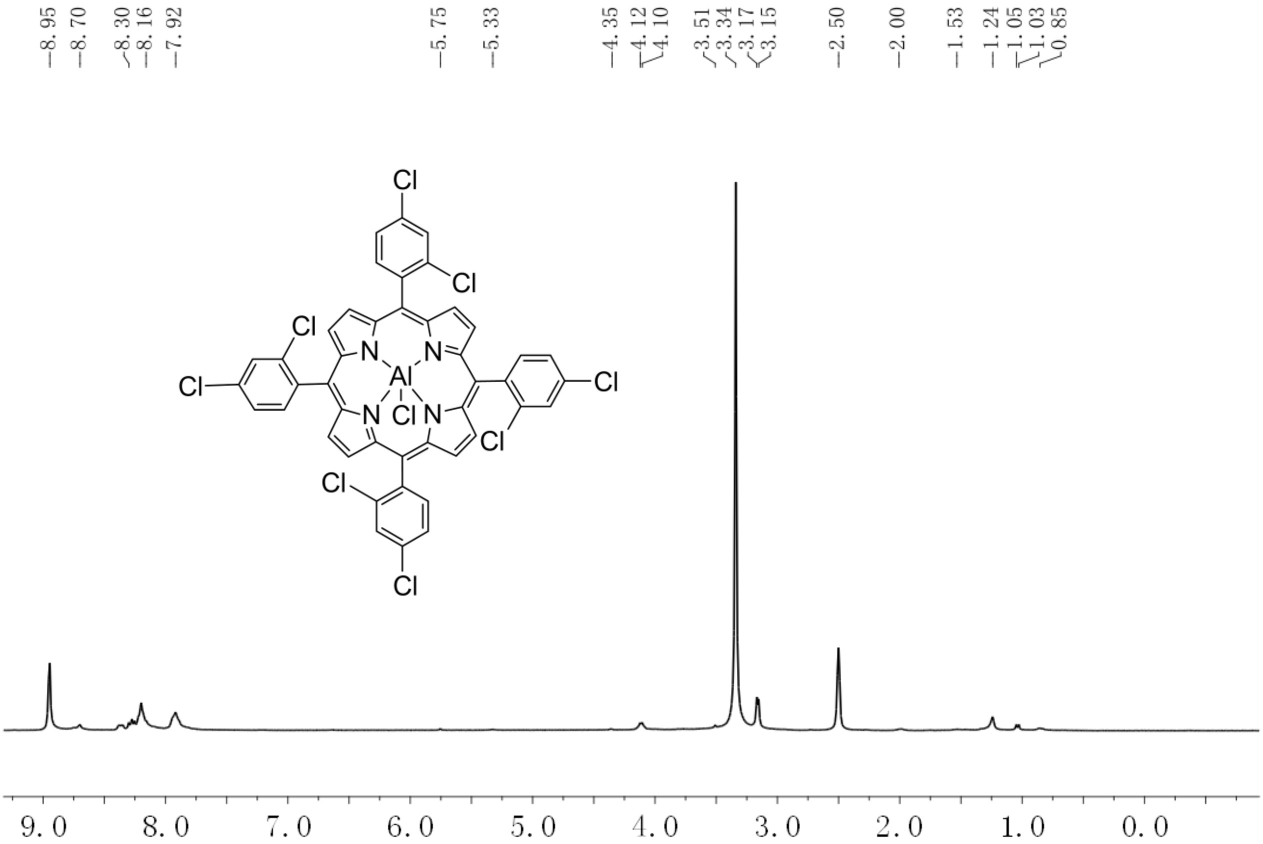


300 MHz ^{1}H NMR spectrum of **complex 3** in DMSO-d_6

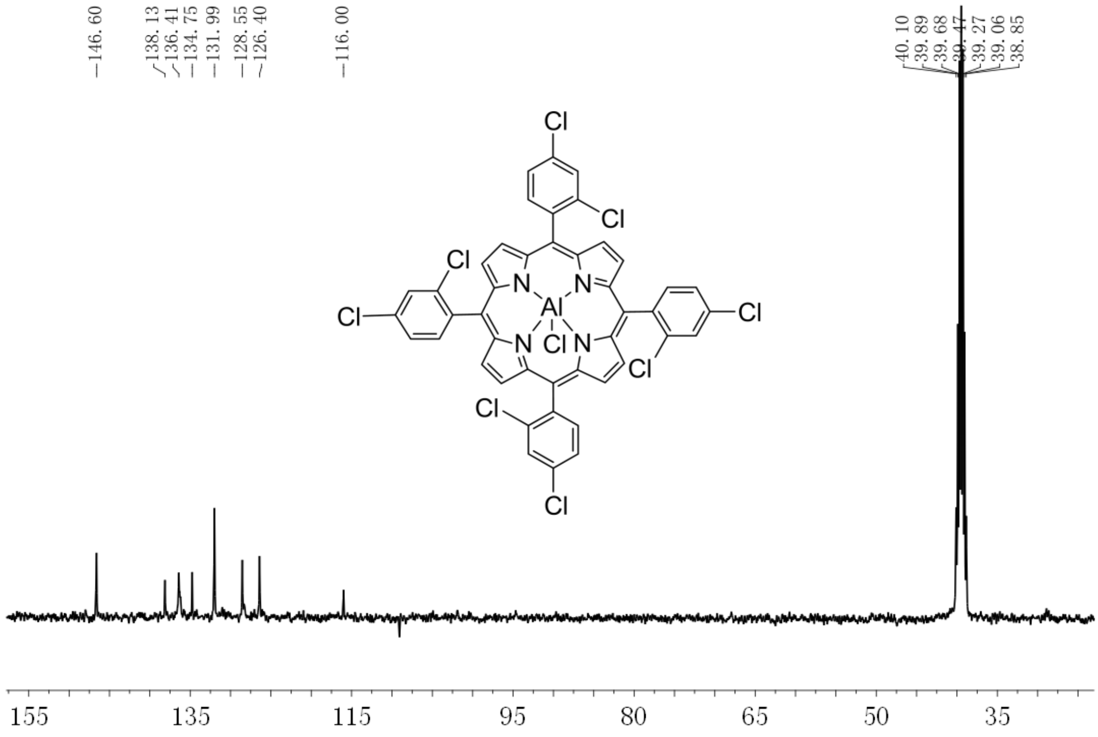


100 MHz ^{13}C NMR spectrum of **complex 3** in DMSO-d_6

4.9 ¹H and ¹³C NMR Spectra of complex 4

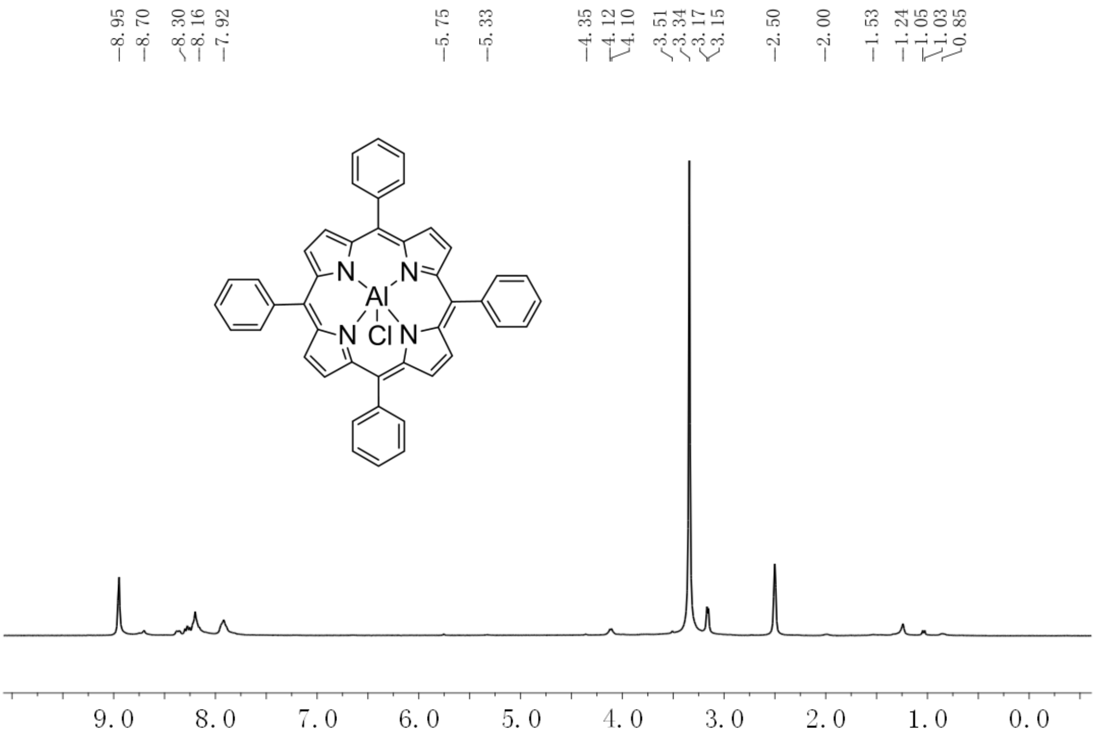


300 MHz ^{1}H NMR spectrum of **complex 4** in DMSO-d_6

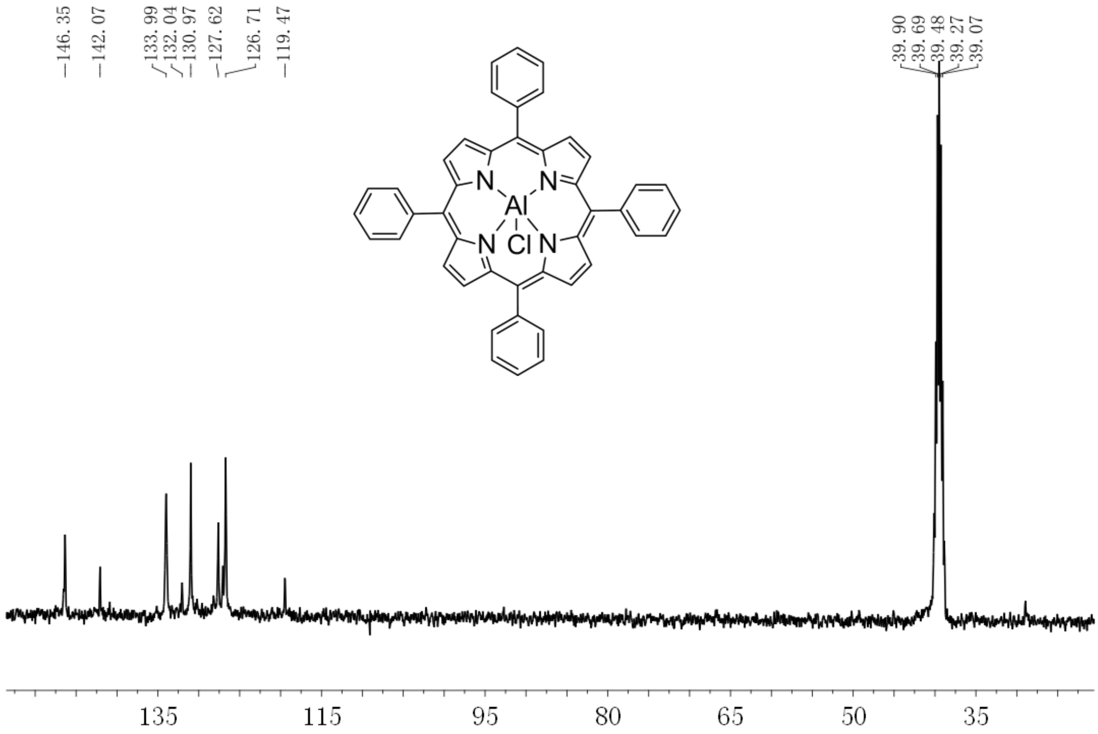


100 MHz ^{13}C NMR spectrum of **complex 4** in DMSO-d_6

4.10 ¹H and ¹³C NMR Spectra of complex 5

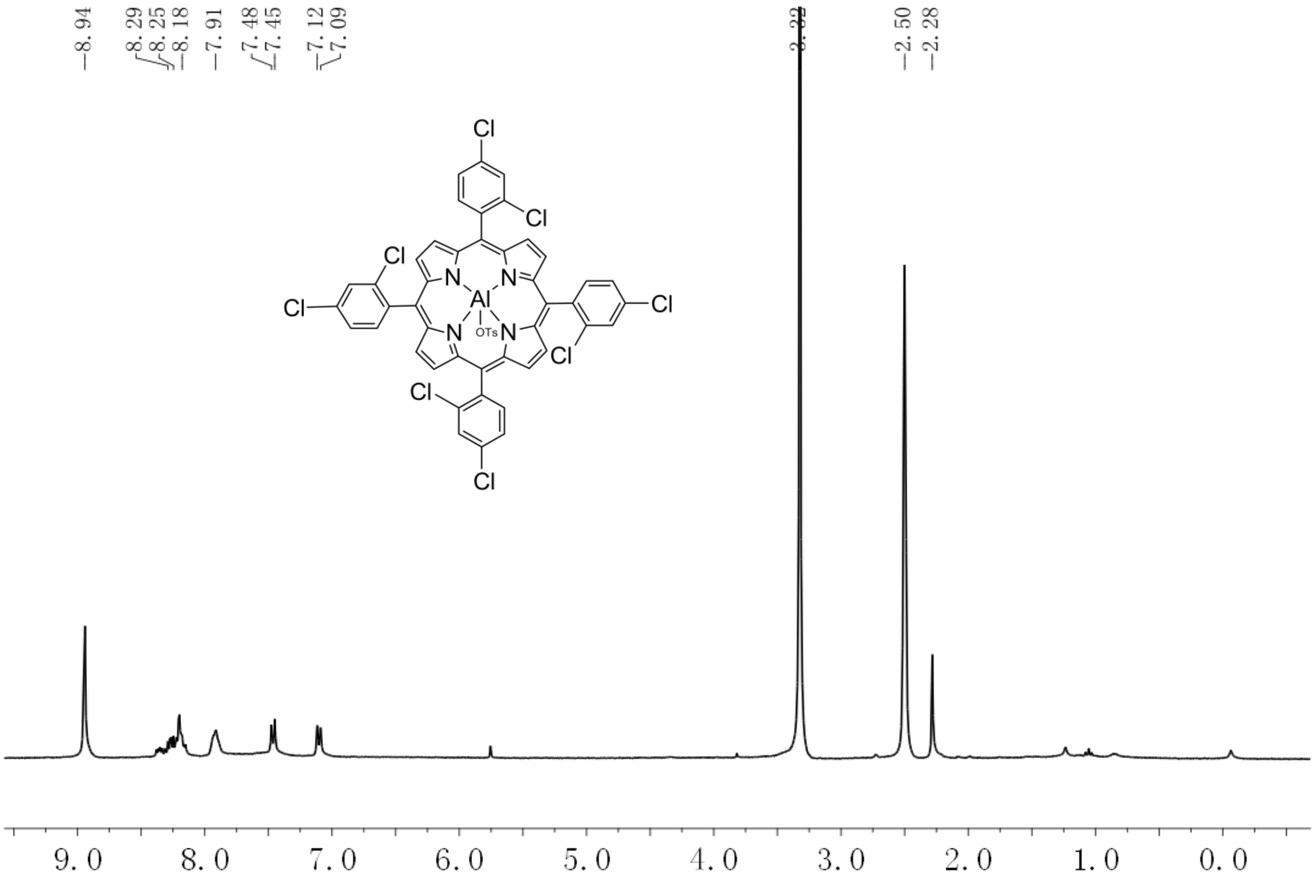


300 MHz ¹H NMR spectrum of **complex 5** in DMSO-d_6

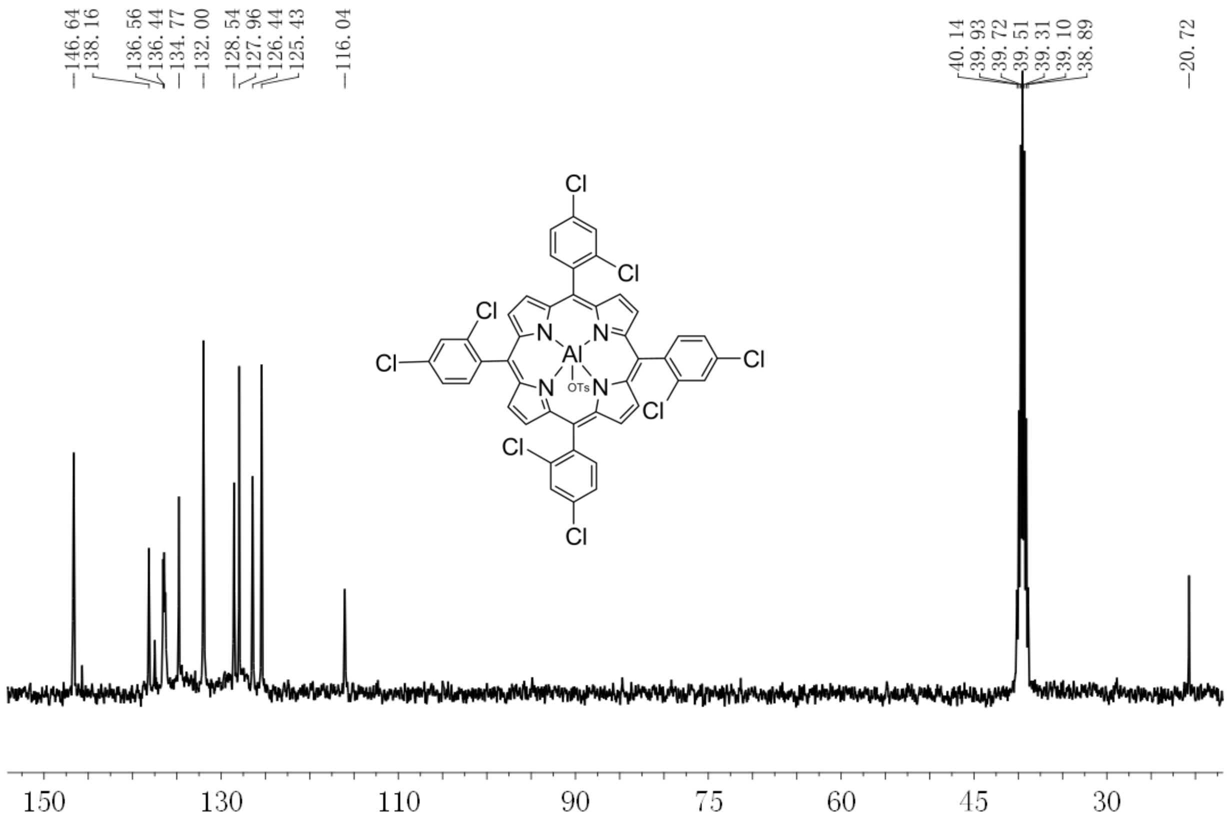


100 MHz ^{13}C NMR spectrum of **complex 5** in DMSO-d_6

4.11 ^{1}H and ^{13}C NMR Spectra of complex 6

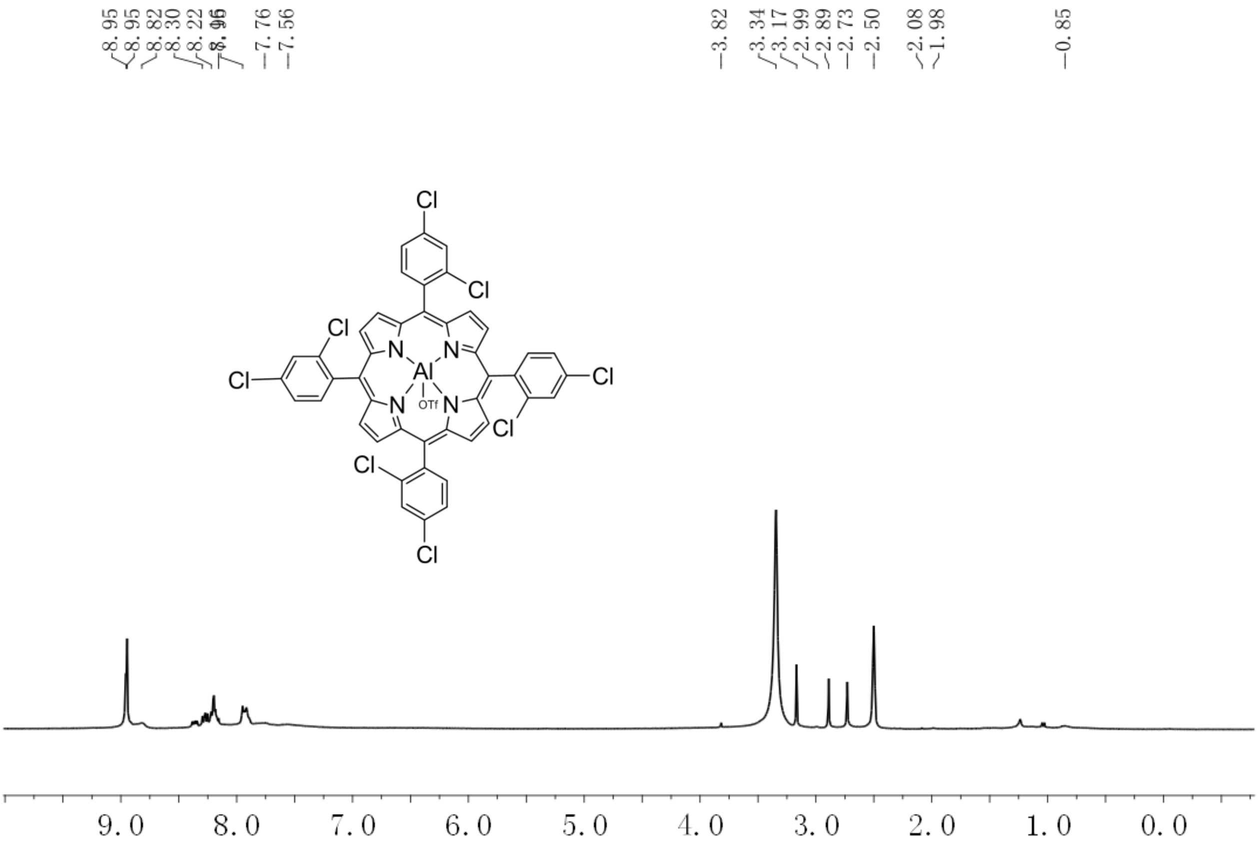


300 MHz ^{1}H NMR spectrum of **complex 6** in DMSO-d_6

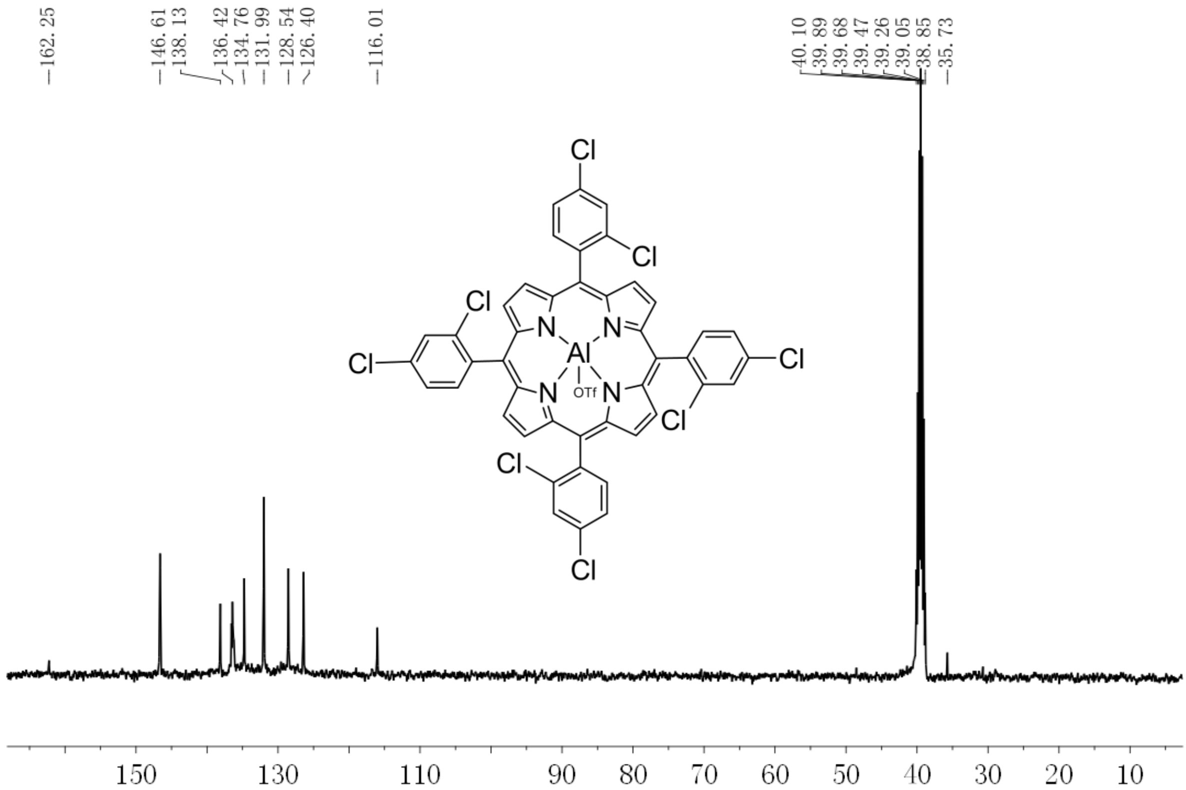


100 MHz ^{13}C NMR spectrum of **complex 6** in DMSO-d_6

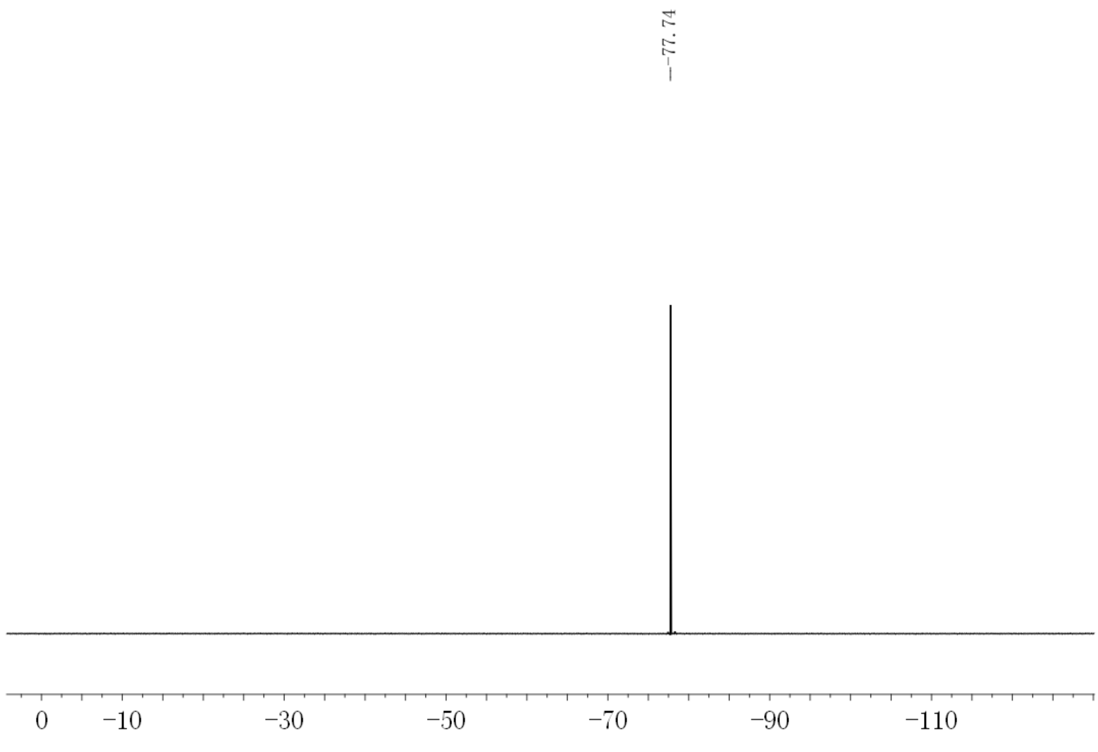
4.12 ¹H, ¹³C and ¹⁹F NMR Spectra of complex 7



300 MHz ^{1}H NMR spectrum of **complex 7** in DMSO-d_6



100 MHz ^{13}C NMR spectrum of **complex** 7 in DMSO-d_6



376 MHz ^{19}F NMR spectrum of **complex 7** in DMSO-d_6