

## *Supporting information*

# Isospecific ring-opening polymerization of *rac*-lactide initiated by achiral heteroscorpionate zwitterionic zinc complexes

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## Contents

1. Experimental section .....	S2
2. NMR spectra of heteroscorpionate zinc complexes 1–9.....	S10
3. X-ray molecular structures. ....	S24
4. Homonuclear decoupled <sup>1</sup> H NMR and <sup>13</sup> C{ <sup>1</sup> H} NMR spectra of representative resulting PLAs.....	S26
5. <sup>1</sup> H NMR and MALDI-TOF mass spectra of oligomers. ....	S29
6. The results of polymerization kinetics and optical activities. ....	S31
7. DSC measurement of polymers.....	S32
8. References .....	S33

## 1. Experimental section

**General procedures.** All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box filled with dry nitrogen. Hexane and toluene were purified using an SPS Braun system. THF and benzene were dried by distillation over sodium with benzophenone as indicator under a nitrogen atmosphere and was stored over freshly cut sodium in a glove box. Bis(3,5-dimethylpyrazolyl)methane was synthesized according to the literature from 3,5-dimethylpyrazole and dichloromethane catalyzed by  $n\text{Bu}_4\text{NBr}$ . Anhydrous  $\text{ZnCl}_2$  was purchased from Aldrich and used as received.  $\text{KN}(\text{SiHMe}_2)_2$  and  $\text{KOBn}$  were prepared from  $\text{HN}(\text{SiHMe}_2)_2$  and  $\text{BnOH}$  with  $\text{KH}$ , respectively.  $\text{KN}(\text{SiMe}_3)_2$  was purchased from shanghai Darui finechemical company. The molecular weight and molecular weight distribution of the polymers were measured using a TOSOH HLC 8220 GPC instrument at 40 °C with THF as eluent against polystyrene standards. Organometallic samples for NMR spectroscopic analysis were prepared in a glove box by the use of NMR spectroscopy tubes and then sealed by paraffin film.  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AV400 spectrometer. MALDI-TOF mass spectrum was obtained with a Bruker Daltonic MicroFlex LT at the National Analytic Research Center of the Changchun Institute of Applied Chemistry (CIAC).

**Differential scanning calorimeter measurement.** Samples weighted (typically in a 5–10 mg range) and sealed in hermetic aluminum pans using a DSC press, were first heated from 25 °C to 180 °C at 10 °C/min, equilibrated at this temperature for 3 min, then cooled to 25 °C at 10 °C/min, held at this temperature for 3 min and finally reheated to 180 °C at 10 °C/min.  $T_g$  and  $T_m$  values were obtained from the second scan after removing the thermal history.

**X-ray crystallographic studies.** Crystals for X-ray analysis were obtained as described in the following preparations. The crystals were manipulated in a glove box. Data collection was performed at -86.5 °C using a Bruker SMART APEX diffractometer with a CCD area detector and graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The determination of crystal class and unit-cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program.

**ROP of *rac*-LA.** Polymerizations of *rac*-LA were carried out in a 15 mL flask under a N<sub>2</sub> atmosphere. A typical procedure in THF was described as follows: A solution of complex **1** (11.5 mg, 20  $\mu$ mol, [LA]/[Zn] = 200:1) in THF (2 mL) was injected to a stirred solution of *rac*-LA (0.576 g, 4 mmol) in THF (3 mL) in an oil bath (at a certain temperature). It was stirred for 10 h and then quenched by adding several drops acidified ethanol, and a small sample of the viscous solution was separated for the measurement of conversion by <sup>1</sup>H NMR spectroscopy. Then polymers were precipitated with abundant ethanol, collected and dried at 40 °C for 24 h *in vacuo*. The molecular weight and polydispersity index of the resulting polymers were determined by GPC. The tacticity of the PLA was calculated according to the homonuclear decoupled <sup>1</sup>H NMR spectrum of methine region.

A typical procedure in toluene or benzene was described as follows: *rac*-LA (0.576 g, 4 mmol) and 3 mL was added into a flask in glove-box, and then dipped in an oil bath at 30 °C. 5 min later, a solution of complex **5** (20  $\mu$ mol) in toluene was injected forming a heterogeneous mixture. The mixture was stirred for a certain time to form a viscous clear solution, along with the monomer being consumed and dissolving, then quenched by adding several drops acidified ethanol, and a small

sample of the viscous solution was separated for the measurement of conversion by  $^1\text{H}$  NMR spectroscopy. Then polymers were precipitated with abundant ethanol, collected and dried at 40 °C for 24 h *in vacuo*. The molecular weight and polydispersity index of the resulting polymers were determined by GPC. The tacticity of the PLA was calculated according to the homonuclear decoupled  $^1\text{H}$  NMR spectrum of methine region.

### Synthesis of heteroscorpionate zinc complexes 1–9.

*Synthesis of complex 1.* (3,5-Me<sub>2</sub>pz)<sub>2</sub>CHP(Ph)<sub>2</sub>NPh (0.336 g, 0.70 mmol) dissolved in dry THF (5 mL) was added dropwise to a solution of ZnEt<sub>2</sub> in hexane (0.7 mL, 1.0 M in hexane) at room temperature. After 5 h later, the volatiles were evaporated to dryness under reduced pressure to afford a white powder. The powder was dissolved in approximate 1.0 mL THF and allowed to stand at room temperature for several days to give complex **1** as white crystals. Yield: 0.329 g, 82%. Anal. Calcd for C<sub>31</sub>H<sub>34</sub>N<sub>5</sub>PZn: C, 64.98; H, 5.98; N, 12.22; for C<sub>31</sub>H<sub>34</sub>N<sub>5</sub>PZn(C<sub>4</sub>H<sub>8</sub>O): C, 65.16; H, 6.56; N, 10.86. Found: C, 65.10; H, 6.51; N, 10.83.  $^1\text{H}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.72-7.66 (m, 4H; Ph-*H*), 7.27 (d,  $J$  = 8 Hz, 2H; Ph-*H*), 7.04 (t,  $J$  = 8 Hz, 2H; Ph-*H*), 6.99-6.94 (m, 2H; Ph-*H*), 6.93-6.88 (m, 4H; Ph-*H*), 6.66 (t,  $J$  = 8 Hz, 1H; Ph-*H*), 5.30 (s, 2H; Pz-*H*), 2.20 (s, 6H; Pz-CH<sub>3</sub>), 2.09 (t,  $J$  = 8 Hz, 3H; Zn-CH<sub>2</sub>CH<sub>3</sub>), 1.90 (s, 6H; Pz-CH<sub>3</sub>), 1.30 ppm (q,  $J$  = 8 Hz, 2H; Zn-CH<sub>2</sub>CH<sub>3</sub>);  $^{31}\text{P}$  NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 34.13 ppm;  $^{13}\text{C}$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 151.32, 151.20 (C<sup>3</sup> or C<sup>5</sup>), 144.89, 144.82 (C<sup>3</sup> or C<sup>5</sup>), 147.77, 133.19, 133.11, 131.21, 131.19, 129.42, 128.99, 128.42, 128.13, 122.43, 122.28, 118.47 (*Ph*), 103.97 (C<sup>4</sup>), 63.67 (d,  $J$  = 92 Hz; P-C), 14.20 (Zn-CH<sub>2</sub>CH<sub>3</sub>), 13.26 (Pz-CH<sub>3</sub>), 11.64 (Pz-CH<sub>3</sub>), 0.87 ppm (Zn-CH<sub>2</sub>CH<sub>3</sub>).

*Synthesis of complex 2.* The synthesis of **2** was carried out in an identical manner to **1** and extending the reaction time to 10 h. (3,5-Me<sub>2</sub>Pz)<sub>2</sub>CP(Cy)<sub>2</sub>NPh (0.246 g, 0.50 mmol), ZnEt<sub>2</sub> (0.5 mL, 1.0 M in

hexane). Yield: 0.231 g, 79%. Anal. Calcd for  $C_{31}H_{46}N_5PZn$ : C, 63.64; H, 7.92; N, 11.97. Found: C, 63.67; H, 7.84; N, 11.95.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  = 7.33-7.26 (m, 4H; Ph-*H*), 6.88-6.85 (m, 1H; Ph-*H*), 5.52 (s, 2H; Pz-*H*), 2.30 (s, 6H; Pz- $CH_3$ ), 2.19 (s, 6H; Pz- $CH_3$ ), 1.90 (t,  $J$  = 8 Hz, 3H; Zn- $CH_2CH_3$ ), 1.04 (q,  $J$  = 8 Hz, 2H; Zn- $CH_2CH_3$ ), 2.04-2.01 (m, 2H; Cy-*H*), 1.61-1.42 (m, 11H; Cy-*H*), 1.08-0.82 (m, 7H; Cy-*H*), 0.62-0.53 ppm (m, 2H; Cy-*H*),  $^{31}P$  NMR (162 MHz,  $C_6D_6$ ):  $\delta$  = 48.94 ppm;  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ):  $\delta$  = 152.17, 152.06 ( $C^3$  or  $C^5$ ), 144.90, 144.82 ( $C^3$  or  $C^5$ ), 148.06, 129.76, 124.23, 124.12, 119.72 (*Ph*), 105.09 ( $C^4$ ), 61.34 (d,  $J$  = 75.1 Hz, P-*C*), 38.81 (d,  $J$  = 63.7 Hz, P-*CH*), 28.66, 28.54, 28.15, 28.05, 27.26 (*Cy*), 14.76 (Zn- $CH_2CH_3$ ), 13.80 (Pz- $CH_3$ ), 12.79 (Pz- $CH_3$ ), 0.31 ppm (Zn- $CH_2CH_3$ ).

*Synthesis of complex 3.* A solution of  $LiCH_2SiMe_3$  (0.70 mmol, 0.066 g) in THF (5 mL) was added to a cooled (-30 °C), stirred suspension of  $(3,5-Me_2pz)_2CHP(Ph)_2NPh$  (0.70 mmol, 0.336 g) in THF (8 mL). The mixture was allowed to warm to 15 °C and stirred for 30 min, which resulted in a yellow transparent solution. The solution was added dropwise to a suspension of  $ZnCl_2$  (0.70 mmol, 0.095 g) in THF (5 mL). The mixture was heated to 40 °C and stirred for 1 h. The solvent was removed under reduced pressure. The product was extracted with toluene (15 mL), and the insoluble lithium salt was removed by filtration. The filtrate was evaporated under reduced pressure and the resulting white solid was recrystallized from THF (3 mL) at room temperature to give the complex **3** as white crystals. Yield: 0.28 g, 69%. Anal. Calcd for  $C_{29}H_{29}ClN_5PZn$ : C, 60.12; H, 5.04; N, 12.09; for  $C_{29}H_{29}ClN_5PZn(C_4H_8O)$ : C, 60.84; H, 5.72; N, 10.75. Found: C, 60.78; H, 5.69; N, 10.72.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  = 7.67-7.62 (m, 4H; Ph-*H*), 7.58 (d,  $J$  = 8 Hz, 2H; Ph-*H*), 7.00 (t,  $J$  = 8 Hz, 2H; Ph-*H*), 6.97-6.87 (m, 6H; Ph-*H*), 6.64 (t,  $J$  = 8 Hz, 1H; Ph-*H*), 5.19 (s, 2H; Pz-*H*), 2.31 (s, 6H; Pz- $CH_3$ ), 1.79 (s, 6H; Pz- $CH_3$ );  $^{31}P$  NMR (162 MHz,  $C_6D_6$ ):  $\delta$  = 36.36 ppm;  $^{13}C$  NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  = 149.31, 149.21, (*C*<sup>3</sup> or *C*<sup>5</sup>), 145.59, 145.51 (*C*<sup>3</sup> or *C*<sup>5</sup>), 148.77, 132.76, 132.67, 131.74, 131.72, 128.59, 128.45, 128.34, 127.66, 126.64, 121.70, 121.56, 118.43 (*Ph*), 104.21 (*C*<sup>4</sup>), 63.74 (d, *J* = 94 Hz), P-C), 13.15 (Pz-CH<sub>3</sub>), 11.56 ppm (Pz-CH<sub>3</sub>).

*Synthesis of complex 4.* Compound **4** was synthesized in a one-pot reaction. A solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (0.70 mmol, 0.066 g) in THF (5 mL) was added to a cooled (-30 °C), stirred suspension of (3,5-Me<sub>2</sub>pz)<sub>2</sub>CHP(R)<sub>2</sub>NPh (0.70 mmol, 0.336 g) in THF (8 mL). The mixture was allowed to warm to 15 °C and stirred for 30 min, which resulted in a yellow transparent solution. The solution was added dropwise to a suspension of ZnCl<sub>2</sub> (0.70 mmol, 0.095 g) in THF (5 mL). The mixture was heated to 40 °C and stirred for 1 h, after that the mixture was cooled to room temperature and a solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (0.70 mmol, 0.066 g) was added, then stirred for another 2 h at this temperature. The solvent was removed under reduced pressure and the residue was extracted with toluene (8 mL), and the insoluble lithium salt was removed by filtration. The filtrate was evaporated under reduced pressure and the resulting white solid was recrystallized from THF (2 mL) at room temperature to give the complex **4** as white crystals. Yield: 0.38 g, 86%. Anal. Calcd for C<sub>33</sub>H<sub>40</sub>N<sub>5</sub>PSiZn: C, 62.80; H, 6.39; N, 11.10; for C<sub>33</sub>H<sub>40</sub>N<sub>5</sub>PSiZn(C<sub>4</sub>H<sub>8</sub>O): C, 63.19; H, 6.88; N, 9.96. Found: C, 63.15; H, 6.84; N, 9.91. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.70-7.64 (m, 4H; Ph-*H*), 7.22 (d, *J* = 8 Hz, 2H; Ph-*H*), 7.03 (t, *J* = 8 Hz, 2H; Ph-*H*), 6.98-6.90 (m, 6H; Ph-*H*), 6.66 (t, *J* = 8 Hz, 1H; Ph-*H*), 5.32 (s, 2H; Pz-*H*), 2.21 (s, 6H; Pz-CH<sub>3</sub>), 1.90 (s, 6H; Pz-CH<sub>3</sub>), 0.52 (s, 9H; CH<sub>2</sub>SiCMe<sub>3</sub>), 0.08 ppm (s, 2H; Zn-CH<sub>2</sub>SiMe<sub>3</sub>), <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 35.59 ppm; <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 150.87, 150.76 (*C*<sup>3</sup> or *C*<sup>5</sup>), 144.89, 144.81 (*C*<sup>3</sup> or *C*<sup>5</sup>), 147.88, 133.11, 133.03, 131.21, 131.19, 129.58, 128.86, 128.58, 128.14, 127.94, 123.34, 123.21, 119.02 (*Ph*), 104.05 (*C*<sup>4</sup>), 63.63 (d, *J* = 93.9 Hz, P-C), 13.62 (Pz-CH<sub>3</sub>), 11.66 (Pz-CH<sub>3</sub>), 4.46 (Zn-CH<sub>2</sub>SiMe<sub>3</sub>), -8.25 ppm (Zn-CH<sub>2</sub>SiMe<sub>3</sub>).

*Synthesis of complex 5.* Compound **5** was synthesized in a one-pot reaction. A solution of  $\text{LiCH}_2\text{SiMe}_3$  (0.70 mmol, 0.066 g) in THF (5 mL) was added to a cooled ( $-30\text{ }^\circ\text{C}$ ), stirred suspension of  $(3,5\text{-Me}_2\text{pz})_2\text{CHP(Ph)}_2\text{NPh}$  (0.70 mmol, 0.336 g) in THF (8 mL). The mixture was allowed to warm to  $15\text{ }^\circ\text{C}$  and stirred for 30 min, which resulted in a yellow transparent solution. The solution was added dropwise to a suspension of  $\text{ZnCl}_2$  (0.70 mmol, 0.095 g) in THF (5 mL). The mixture was heated to  $40\text{ }^\circ\text{C}$  and stirred for 30 min, after that the mixture was cooled to room temperature and a solution of  $\text{K}[\text{N}(\text{SiHMe}_2)_2]$  (0.70 mmol, 0.120 g) was added, then stirred for another 2 h at this temperature. The solvent was removed under reduced pressure and the residue was extracted with toluene (8 mL), and the insoluble lithium salt was removed by filtration. The filtrate was evaporated under reduced pressure and the resulting white solid was recrystallized from THF (2 mL) at room temperature to give the complex **5** as white crystals. Yield: 0.388 g, 82%. Anal. Calcd for  $\text{C}_{33}\text{H}_{43}\text{N}_6\text{PSi}_2\text{Zn}$ : C, 58.61; H, 6.41; N, 12.43; for  $\text{C}_{33}\text{H}_{43}\text{N}_6\text{PSi}_2\text{Zn}(\text{C}_4\text{H}_8\text{O})$ : C, 59.38; H, 6.87; N, 11.23. Found: C, 59.36; H, 6.82; N, 11.20.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.59\text{-}7.53$  (m, 4H; Ph-*H*), 7.19 (d,  $J = 8$  Hz, 2H; Ph-*H*), 7.01 (t,  $J = 8$  Hz, 2H; Ph-*H*), 6.93 (m, 6H; Ph-*H*), 6.65 (t,  $J = 8$  Hz, 1H; Ph-*H*), 5.52 (sept,  $J = 2.8$  Hz, 2H; Si-*H*), 5.33 (s, 2H; Pz-*H*), 2.43 (s, 6H; Pz- $\text{CH}_3$ ), 1.84 (s, 6H; Pz- $\text{CH}_3$ ), 0.63 ppm (d,  $J = 2.8$  Hz, 12H, SiH- $\text{Me}_2$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 39.11$  ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 149.88, 149.77$  ( $\text{C}^3$  or  $\text{C}^5$ ), 145.47, 145.39 ( $\text{C}^3$  or  $\text{C}^5$ ), 148.71, 133.07, 132.98, 131.40, 131.37, 128.90, 128.18, 127.95, 124.00, 123.88, 119.54 (*Ph*), 104.58 ( $\text{C}^4$ ), 63.50 (d,  $J = 95.7$  Hz, P-*C*), 13.99 (Pz- $\text{CH}_3$ ), 11.71 (Pz- $\text{CH}_3$ ), 4.04 ppm (SiH- $\text{Me}_2$ ).

*Synthesis of complex 6.* Compound **6** was synthesized in a one-pot reaction. A solution of  $\text{LiCH}_2\text{SiMe}_3$  (0.70 mmol, 0.066 g) in THF (5 mL) was added to a cooled ( $-30\text{ }^\circ\text{C}$ ), stirred suspension of  $(3,5\text{-Me}_2\text{pz})_2\text{CHP(Ph)}_2\text{NPh}$  (0.70 mmol, 0.336 g) in THF (8 mL). The mixture was allowed to

warm to 15 °C and stirred for 30 min, which resulted in a yellow transparent solution. The solution was added dropwise to a suspension of ZnCl<sub>2</sub> (0.70 mmol, 0.095 g) in THF (5 mL). The mixture was heated to 40 °C and stirred for 30 min, after that the mixture was cooled to room temperature and a solution of K[N(SiMe<sub>3</sub>)<sub>2</sub>] (0.70 mL, 1.0 M) in hexane was added, then stirred for 2 h at this temperature. The solvent was removed under reduced pressure and the residue was extracted with toluene (8 mL), and the insoluble lithium salt was removed by filtration. The filtrate was evaporated under reduced pressure and the resulting white solid was recrystallized from THF (2 mL) at room temperature to give the complex **6** as white crystals. Yield: 0.394 g, 80%. Anal. Calcd for C<sub>35</sub>H<sub>47</sub>N<sub>6</sub>PSi<sub>2</sub>Zn: C, 59.68; H, 6.73; N, 11.93. Found: C, 59.62; H, 6.70; N, 11.88. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.56-7.51 (m, 4H; Ph-H), 7.18 (d, *J* = 8 Hz, 2H; Ph-H), 7.02 (t, *J* = 8 Hz, 2H; Ph-H), 6.94 (m, 6H; Ph-H), 6.66 (t, *J* = 8 Hz, 1H; Ph-H), 5.35 (s, 2H; Pz-H), 2.42 (s, 6H; Pz-CH<sub>3</sub>), 1.84 (s, 6H; Pz-CH<sub>3</sub>), 0.57 ppm (s, 18H, Si-Me<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 27.34 ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 150.06, 149.95 (C<sup>3</sup> or C<sup>5</sup>), 145.53, 145.46 (C<sup>3</sup> or C<sup>5</sup>), 148.71, 133.16, 133.07, 131.37, 131.35, 129.08, 128.90, 128.22, 128.11, 124.41, 124.29, 119.66 (*Ph*), 104.72 (C<sup>4</sup>), 63.30 (d, *J* = 95.7 Hz, P-C), 14.36 (Pz-CH<sub>3</sub>), 11.79 (Pz-CH<sub>3</sub>), 6.75 ppm (Si-Me<sub>3</sub>).

*Synthesis of complex 7.* Complex **7** was synthesized using a similar procedure as **5**. Yield: 71%. Anal. Calcd for C<sub>33</sub>H<sub>55</sub>N<sub>6</sub>PSi<sub>2</sub>Zn: C, 57.58; H, 8.05; N, 12.21. Found: C, 57.55; H, 7.99; N, 12.19. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.26 (t, *J* = 7.2 Hz, 2H; Ph-H), 7.21 (d, *J* = 7.2 Hz, 2H; Ph-H), 6.90 (t, *J* = 8 Hz, 1H; Ph-H), 5.53 (s, 2H; Pz-H), 5.30 (sept, *J* = Hz, 2H; Si-H), 2.43 (s, 6H; Pz-CH<sub>3</sub>), 2.23 (s, 6H; Pz-CH<sub>3</sub>), 2.04, 1.58, 1.51, 0.94, 0.54 (m, 22H; Cy-H), 0.46 ppm (d, *J* = 3.2 Hz, 12H, SiH-Me<sub>2</sub>). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 51.32 ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 150.23, 150.12 (C<sup>3</sup> or C<sup>5</sup>), 144.88, 144.80 (C<sup>3</sup> or C<sup>5</sup>), 148.36, 129.24, 125.73, 125.64, 120.60, 105.11 (C<sup>4</sup>), 60.54 (d, *J* =



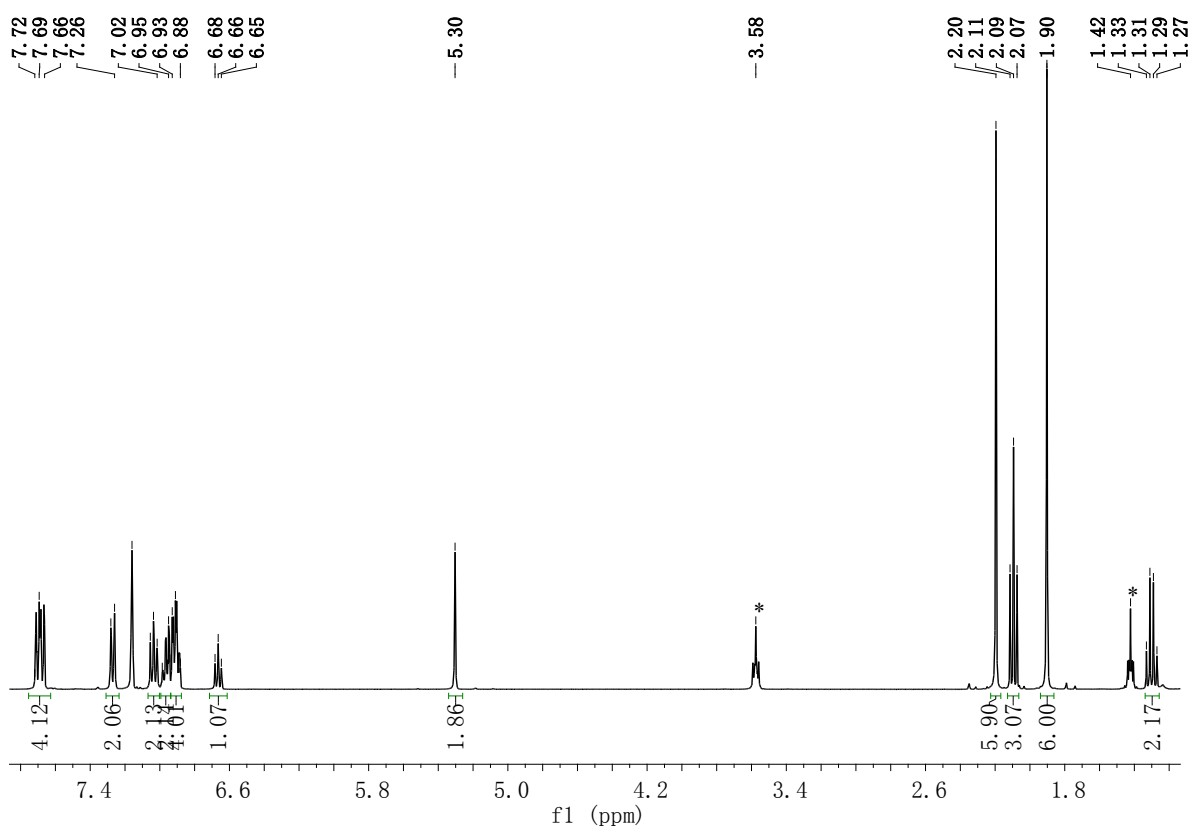
77.5 Hz, P-C), 38.42 (d,  $J = 64.3$  Hz, P-CH), 28.02, 27.90, 27.79, 27.76, 27.49, 27.38, 26.67, 26.51, 26.47 (Cy), 14.05 (Pz-CH<sub>3</sub>), 12.30 (Pz-CH<sub>3</sub>), 4.02 ppm (SiH-Me<sub>2</sub>).

*Synthesis of complex 8.* Complex **8** was synthesized using a similar procedure as **6**. Yield: 75%. Anal. Calcd for C<sub>35</sub>H<sub>59</sub>N<sub>6</sub>PSi<sub>2</sub>Zn: C, 58.68; H, 8.30; N, 11.73. Found: C, 58.65; H, 8.22; N, 11.68. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.25$  (t,  $J = 7.2$  Hz, 2H; Ph-H), 7.19 (d,  $J = 7.2$  Hz, 2H; Ph-H), 6.91 (t,  $J = 8$  Hz, 1H; Ph-H), 5.58 (s, 2H; Pz-H), 2.44 (s, 6H; Pz-CH<sub>3</sub>), 2.23 (s, 6H; Pz-CH<sub>3</sub>), 2.02, 1.55, 1.43, 0.94, 0.52 (m, 22H; Cy-H), 0.40 ppm (s, 18H, Si-Me<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 52.13$  ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 150.34$ , 150.23 (C<sup>3</sup> or C<sup>5</sup>), 144.93, 144.85 (C<sup>3</sup> or C<sup>5</sup>), 148.30, 129.19, 126.38, 126.30, 120.86 (C<sup>4</sup>), 60.35 (d,  $J = 87.3$  Hz, P-C), 38.41 (d,  $J = 64.4$  Hz, P-CH), 28.04, 27.92, 27.79, 27.76, 27.52, 27.41, 26.68, 26.56, 26.53 (Cy), 14.39 (Pz-CH<sub>3</sub>), 12.35 (Pz-CH<sub>3</sub>), 6.64 ppm (Si-Me<sub>3</sub>).

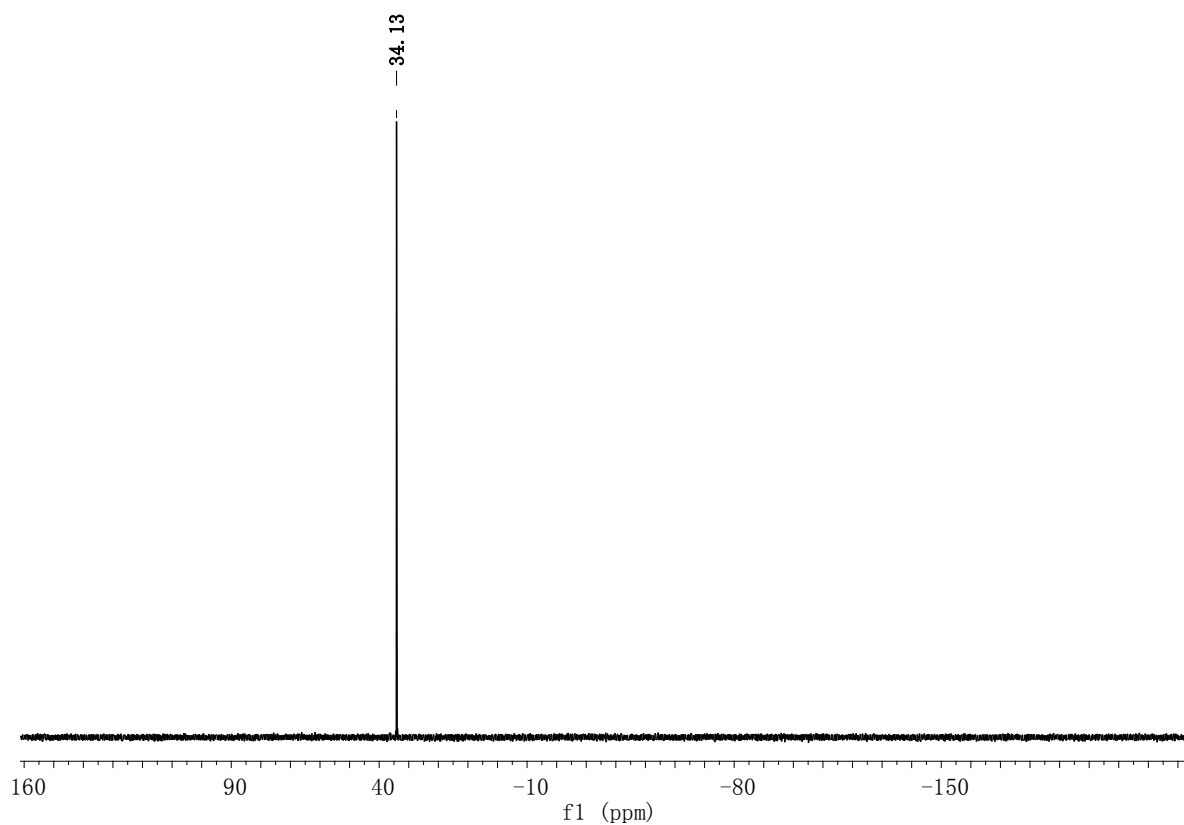
*Synthesis of complex 9.* Compound **9** was synthesized in a one-pot reaction. KH (0.80 mmol, 0.032 g) was added to a stirred suspension of (3,5-Me<sub>2</sub>pz)<sub>2</sub>CHP(Ph)<sub>2</sub>NPh (0.80 mmol, 0.384 g) in THF (10 mL). The mixture was stirred for 5 h, which resulted in a yellow transparent solution. The solution was added dropwise to a suspension of ZnCl<sub>2</sub> (0.80 mmol, 0.109 g) in THF (5 mL). The mixture was stirred for another 5 h, then KOBn (0.80 mmol, 0.117 g) was added, after that the mixture was heated to 45 °C and stirred for additional 2 h. The insoluble potassium salt was removed by filtration. The filtrate was evaporated under reduced pressure and the resulting white solid was recrystallized from THF/hexane at -30 °C to give the complex **9** as white solids. Yield: 0.312 g, 60%. Anal. Calcd for C<sub>36</sub>H<sub>36</sub>N<sub>5</sub>OPZn: C, 66.41; H, 5.57; N, 10.76. Found: C, 66.38; H, 5.52; N, 10.74. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 8.09$  (d,  $J = 7.24$  Hz, 2H; Ph-H), 7.69-7.65 (m, 4H; Ph-H), 7.56 (d,  $J = 8.02$  Hz, 2H; Ph-H), 7.44 (t,  $J = 7.51$  Hz, 2H; Ph-H), 7.23 (t,  $J = 7.36$  Hz, 1H; Ph-H), 7.02 (t,  $J = 7.80$  Hz, 2H; Ph-H),

6.97-6.95 (m, 2H; Ph-*H*), 6.92-6.88 (m, 4H; Ph-*H*), 6.66 (t,  $J = 7.29$  Hz, 1H; Ph-*H*), 5.99 (s, 2H; Ph- $\text{CH}_2\text{-O}$ ), 5.23 (s, 2H; Pz-*H*), 2.17 (s, 6H; Pz- $\text{CH}_3$ ), 1.83 ppm (s, 6H; Pz- $\text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 35.50$  ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 150.24, 150.13$  ( $\text{C}^3$  or  $\text{C}^5$ ), 145.46, 145.38 ( $\text{C}^3$  or  $\text{C}^5$ ), 148.60, 133.15, 133.07, 131.57, 131.55, 129.22, 128.43, 126.58, 125.82, 122.42, 122.28 (*Ph*), 104.19 ( $\text{C}^4$ ), 70.66 (Ph- $\text{CH}_2\text{-O}$ ), 63.83 (d,  $J = 94.57$  Hz, P-*C*), 13.18 (Pz- $\text{CH}_3$ ), 11.60 ppm (Pz- $\text{CH}_3$ ).

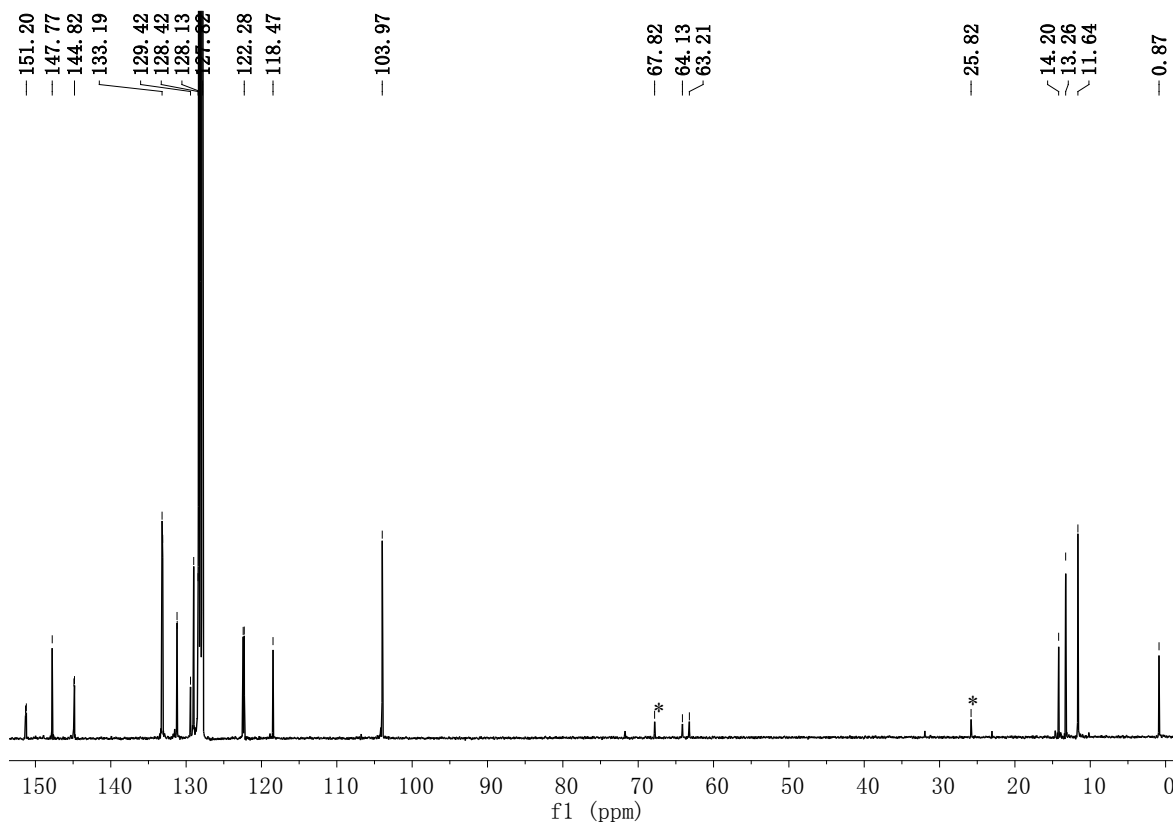
## 2. NMR spectra of heterosorption zinc complexes 1–9.



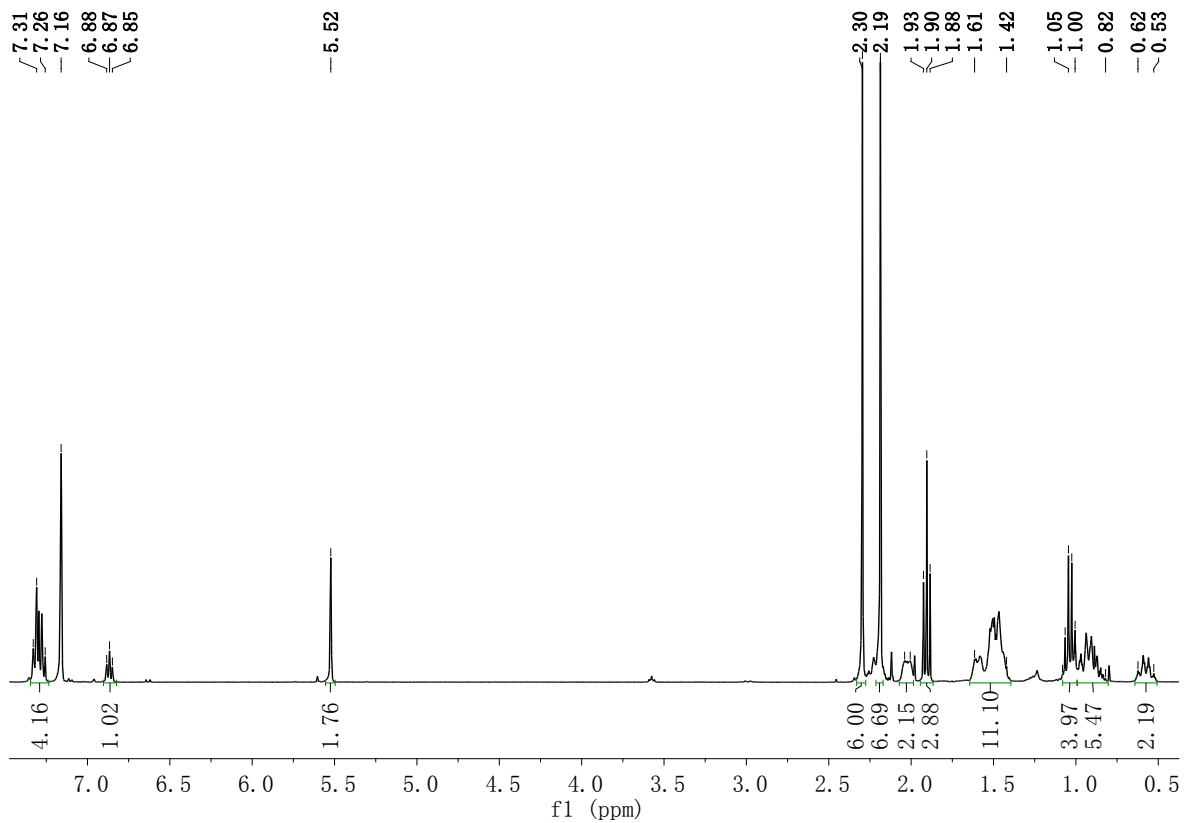
**Figure S1.**  $^1\text{H}$  NMR spectrum of complex 1 ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).



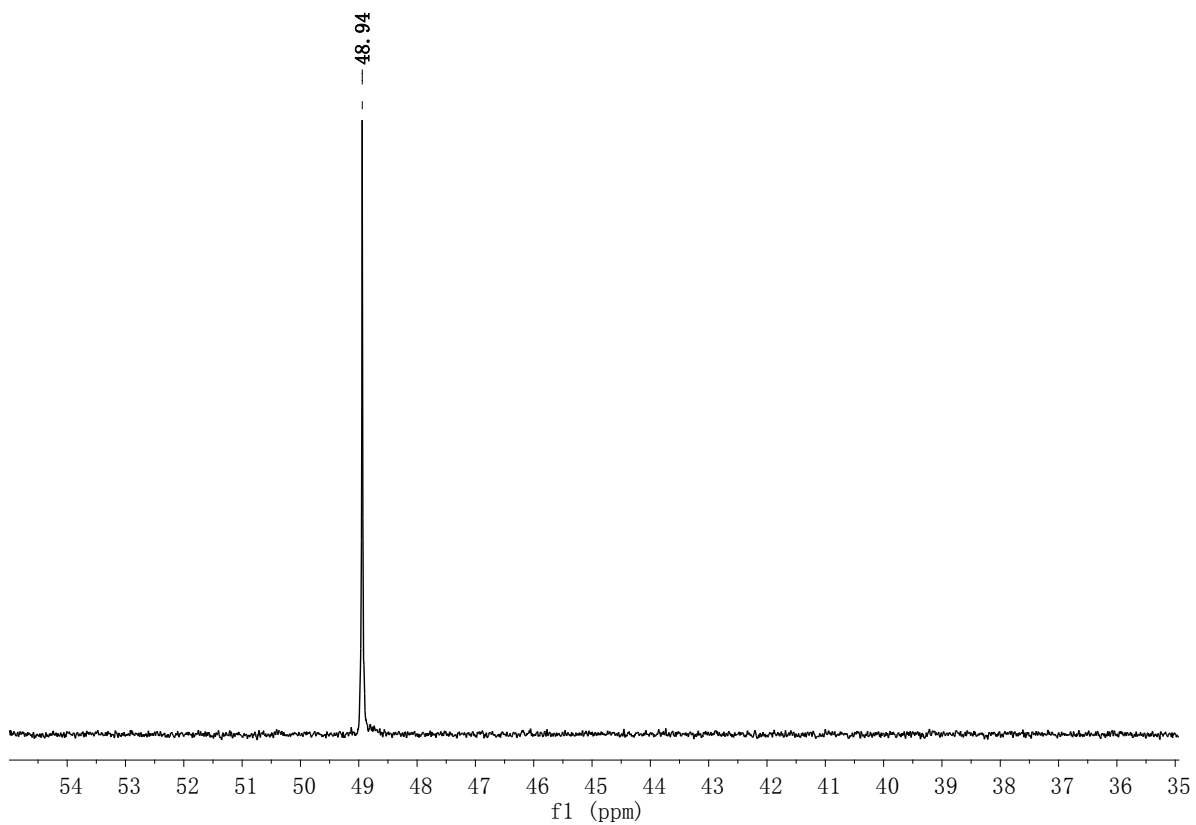
**Figure S2.** <sup>31</sup>P NMR spectrum of complex 1 (C<sub>6</sub>D<sub>6</sub>).



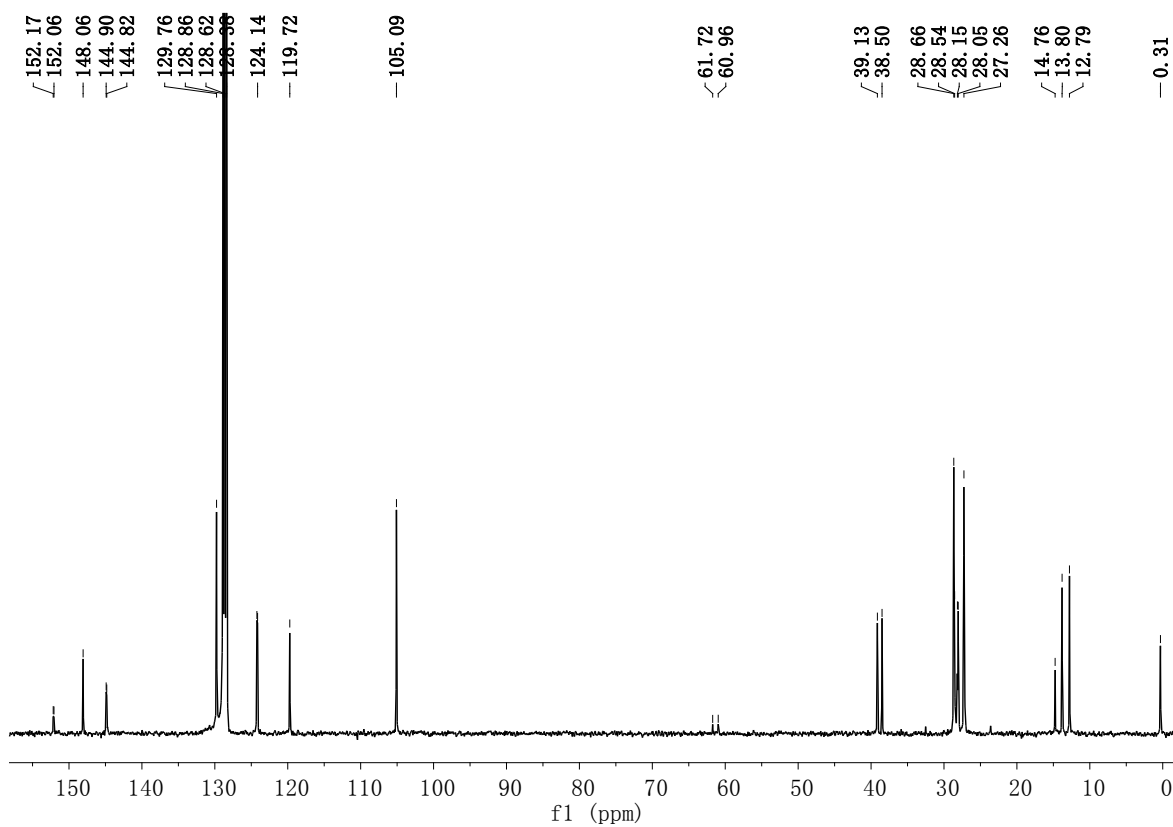
**Figure S3.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex 1 (C<sub>6</sub>D<sub>6</sub>) (\*, residual THF signals).



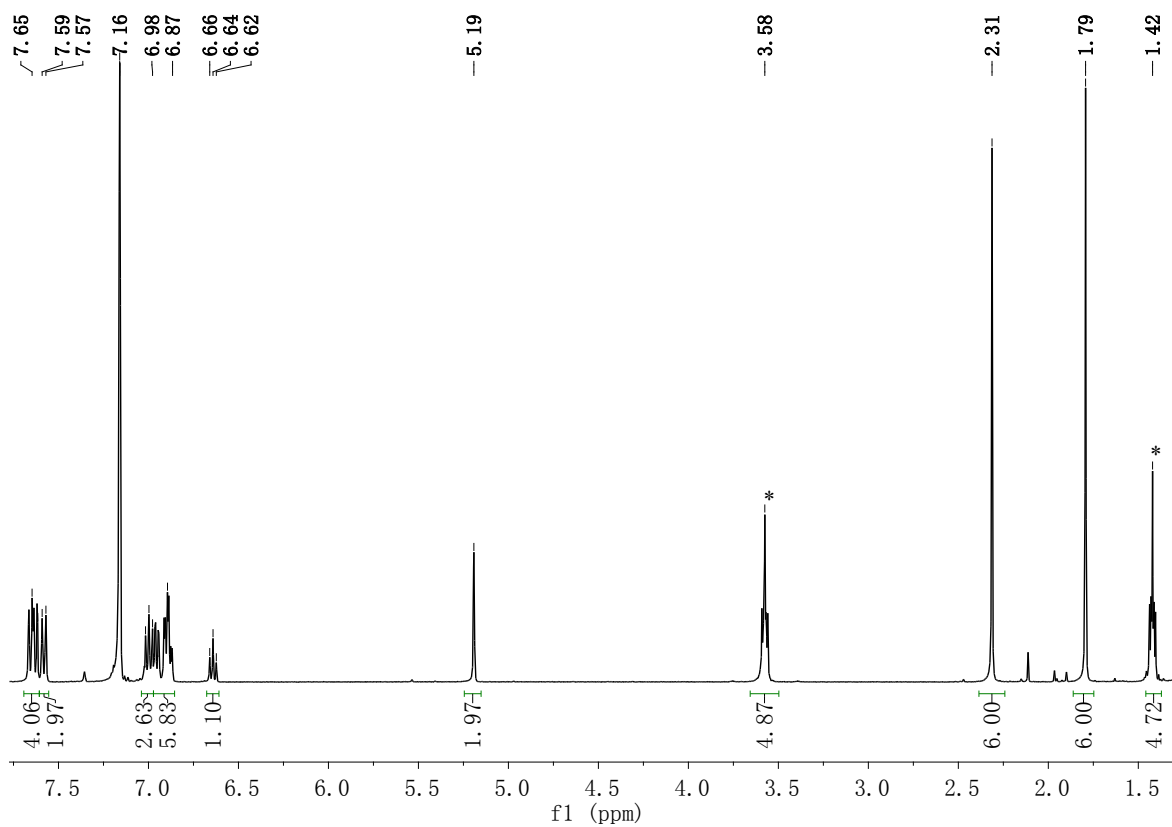
**Figure S4.**  $^1\text{H}$  NMR spectrum of complex **2** ( $\text{C}_6\text{D}_6$ ).



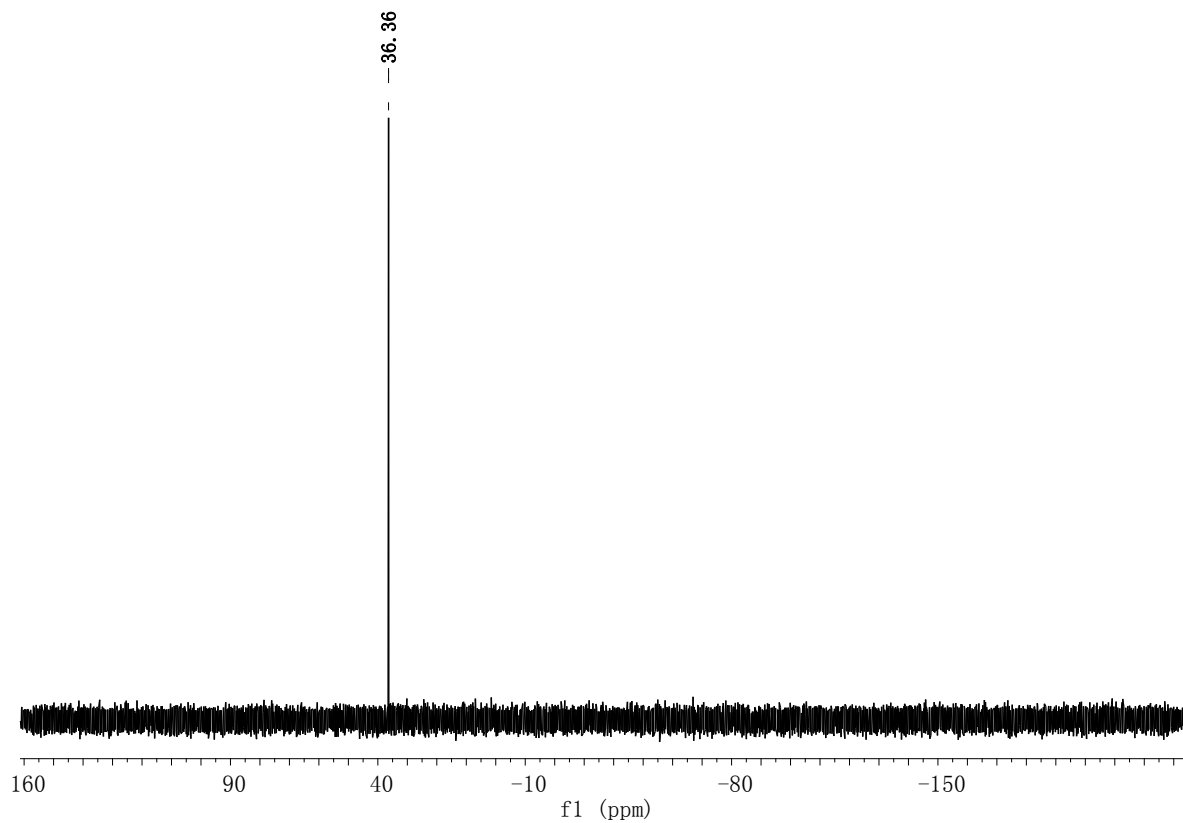
**Figure S5.**  $^{31}\text{P}$  NMR spectrum of complex **2** ( $\text{C}_6\text{D}_6$ ).



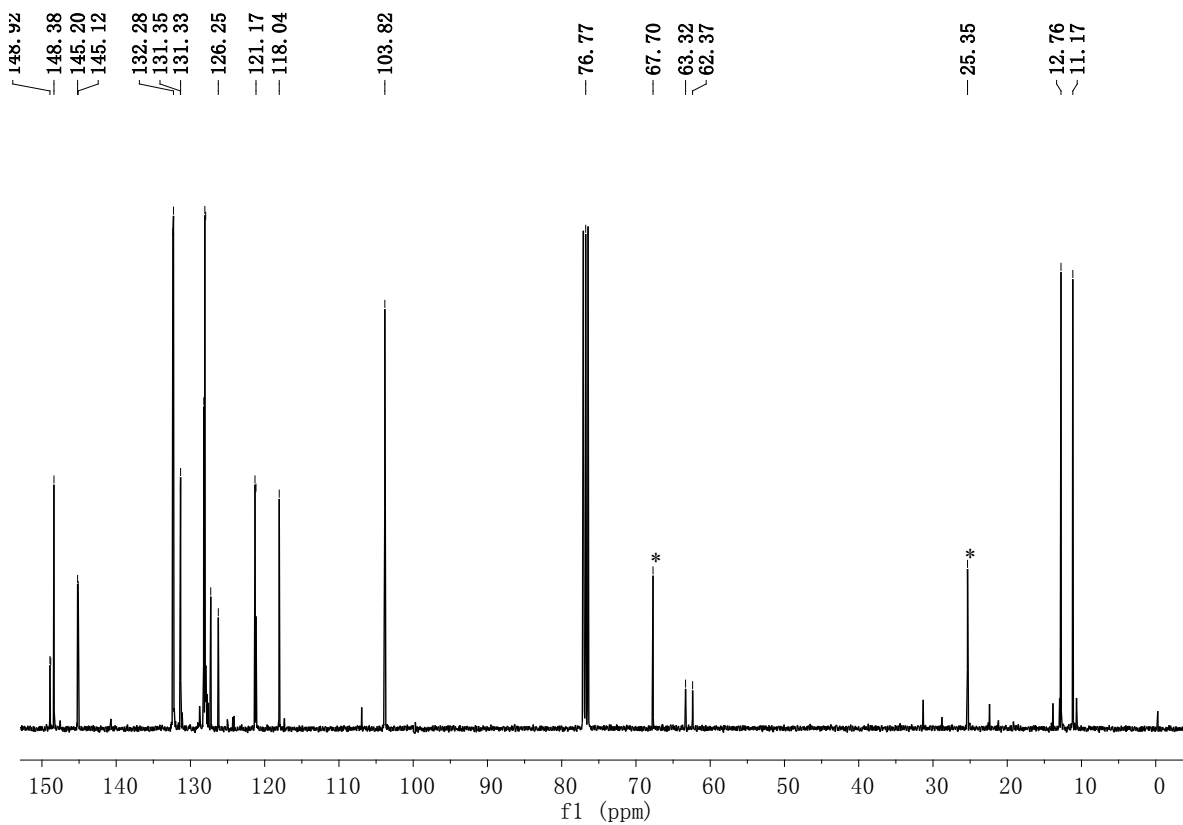
**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **2** ( $\text{C}_6\text{D}_6$ ).



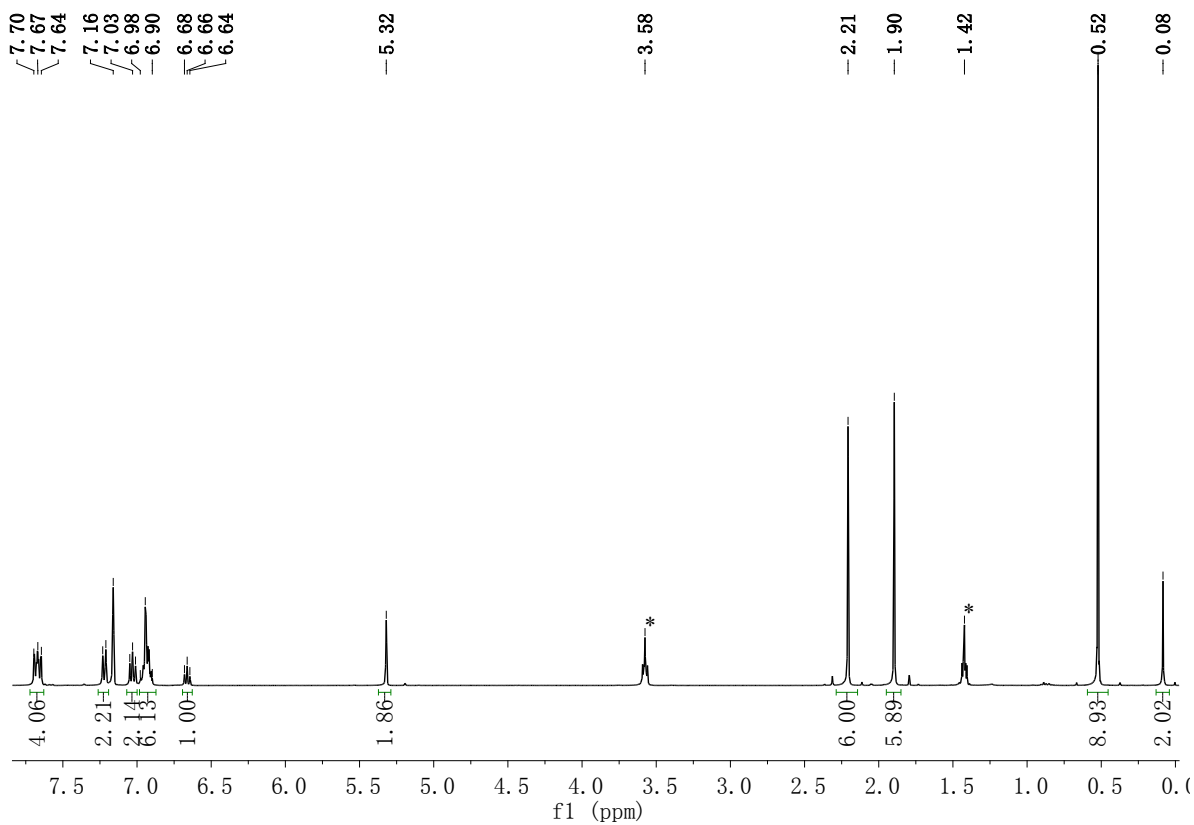
**Figure S7.**  $^1\text{H}$  NMR spectrum of complex **3** ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).



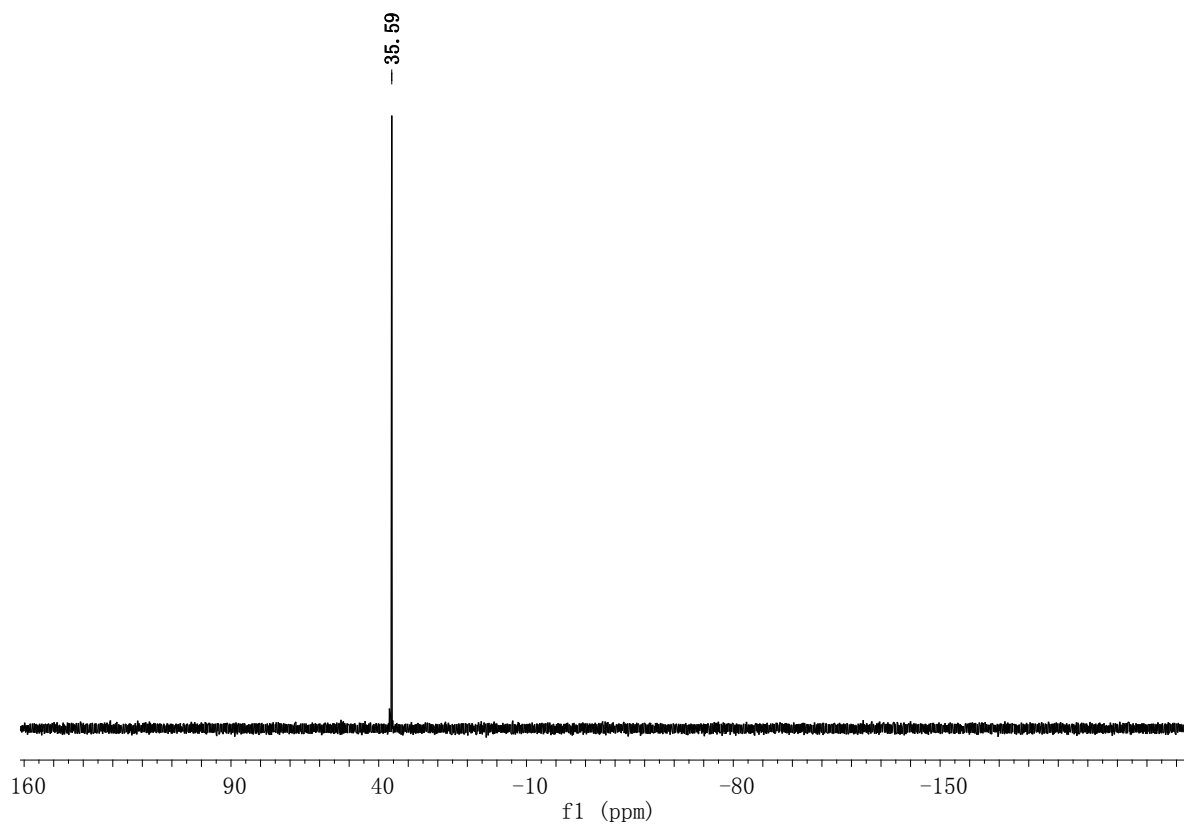
**Figure S8.**  $^{31}\text{P}$  NMR spectrum of complex **3** ( $\text{C}_6\text{D}_6$ ).



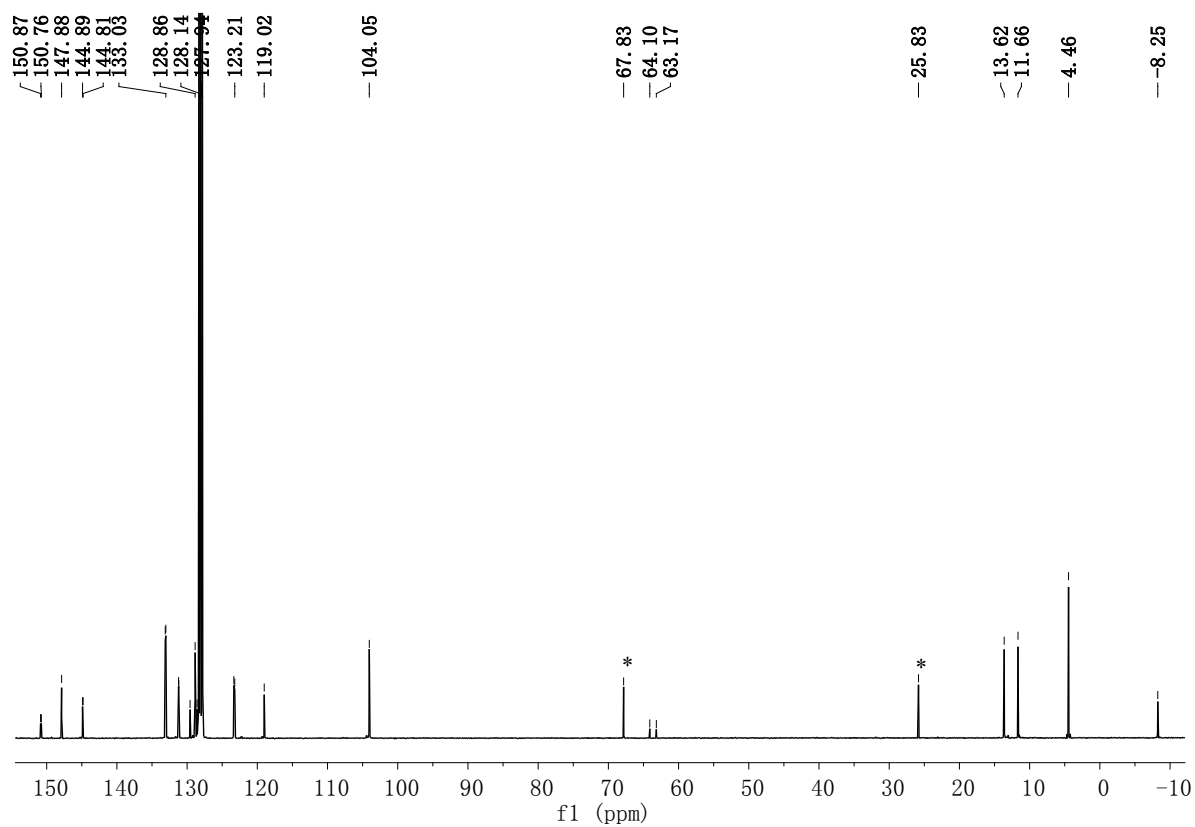
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **3** ( $\text{CDCl}_3$ ) (\*, residual THF signals).



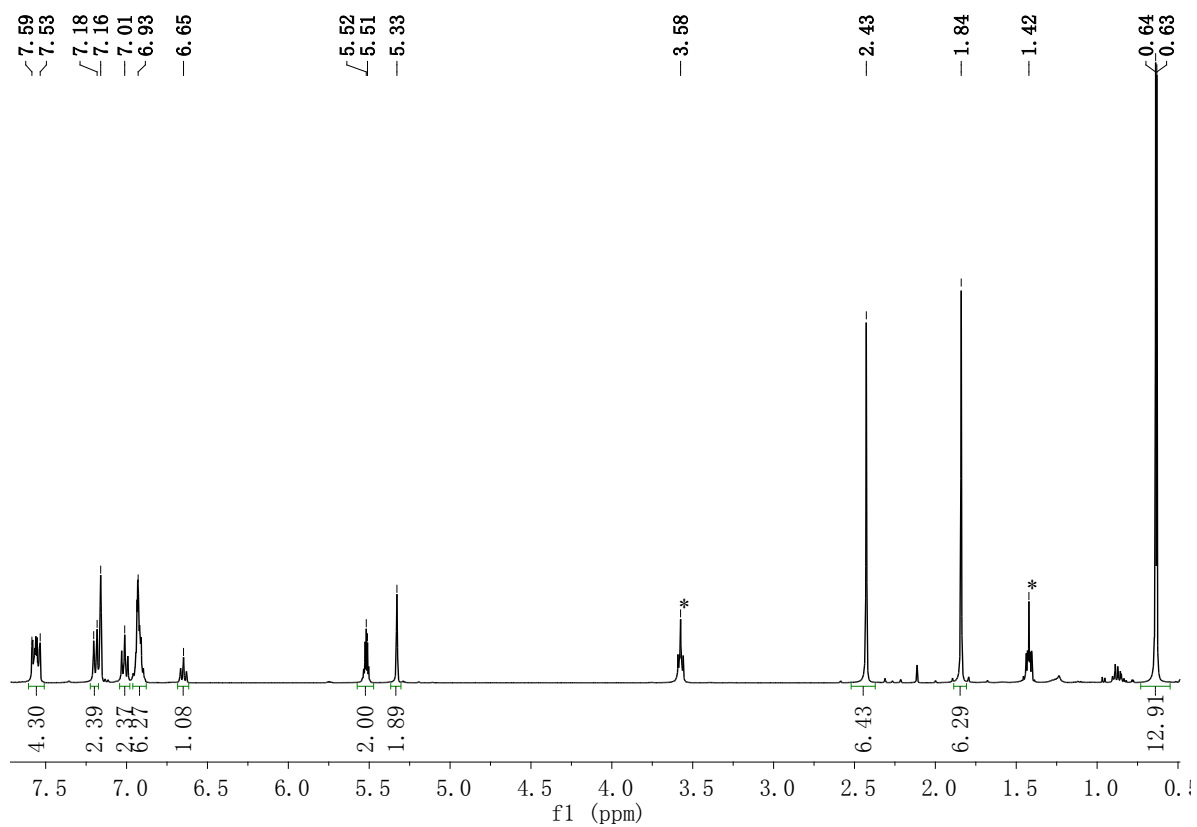
**Figure S10.**  $^1\text{H}$  NMR spectrum of complex **4** ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).



**Figure S11.**  $^{31}\text{P}$  NMR spectrum of complex **4** ( $\text{C}_6\text{D}_6$ ).

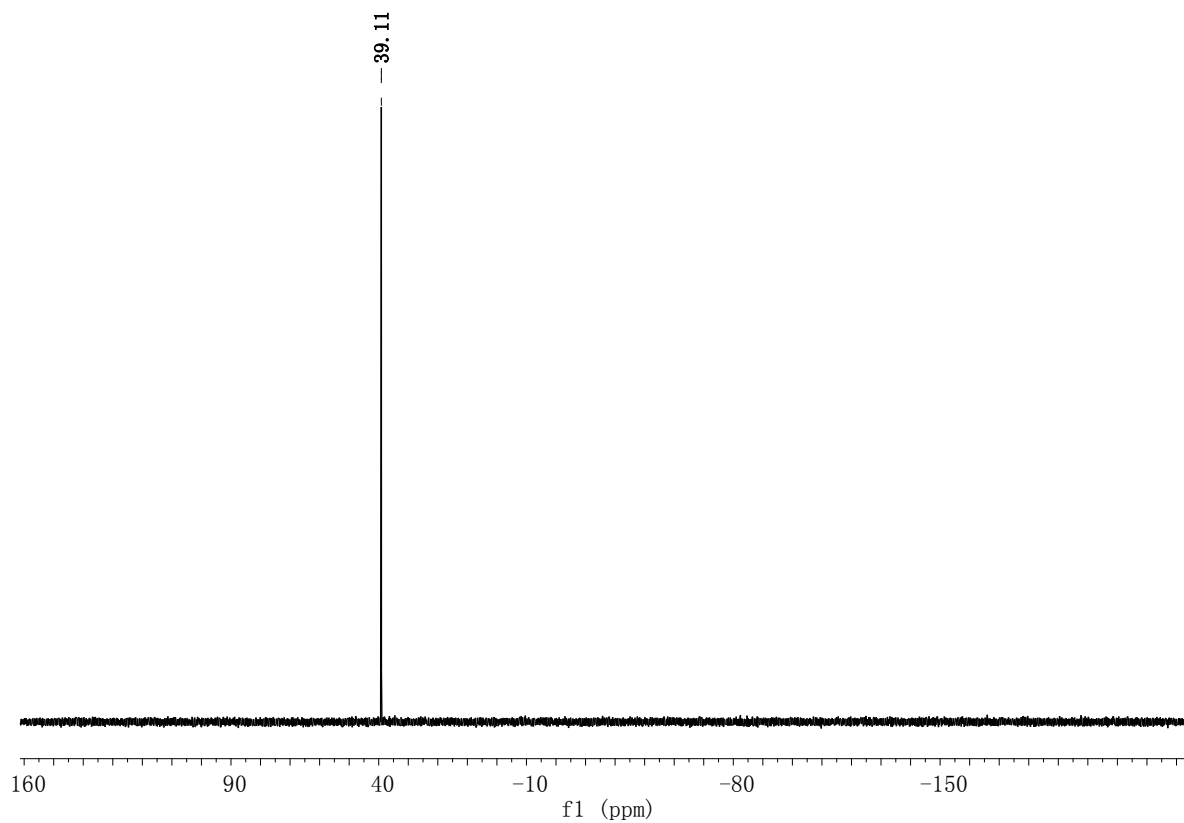


**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **4** ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).

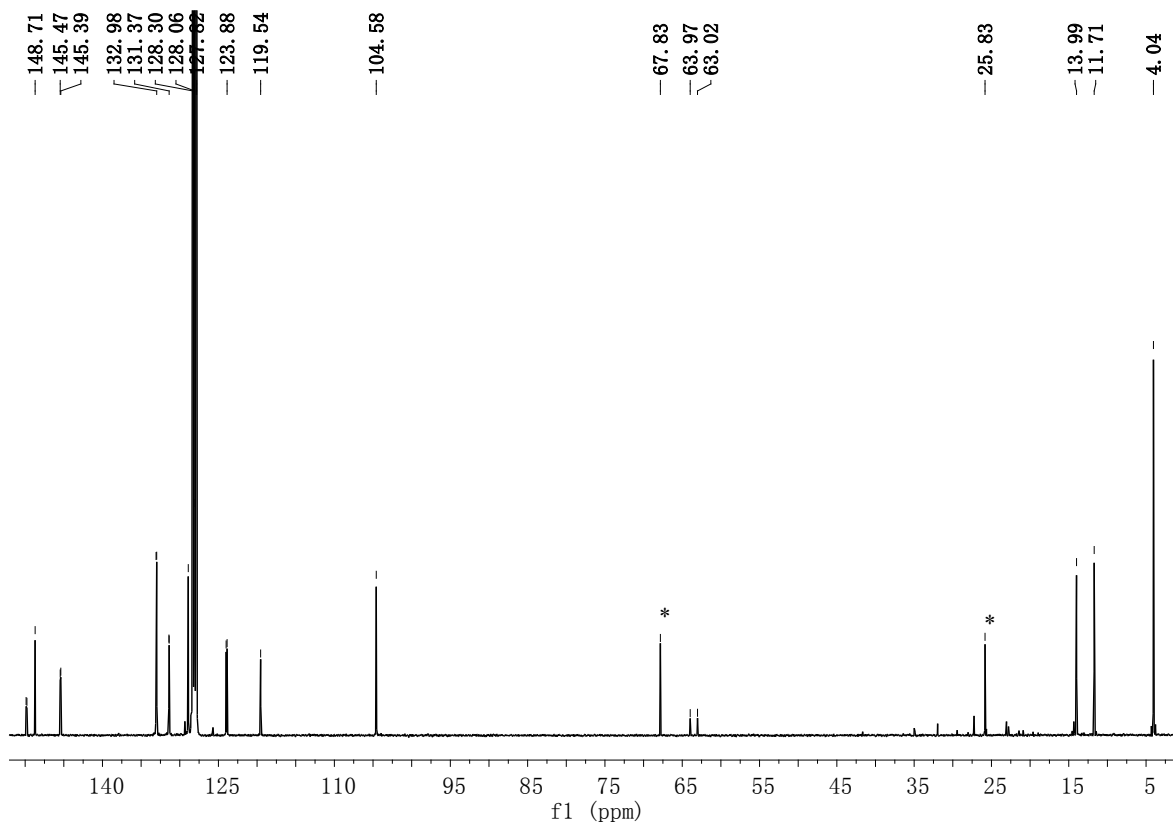




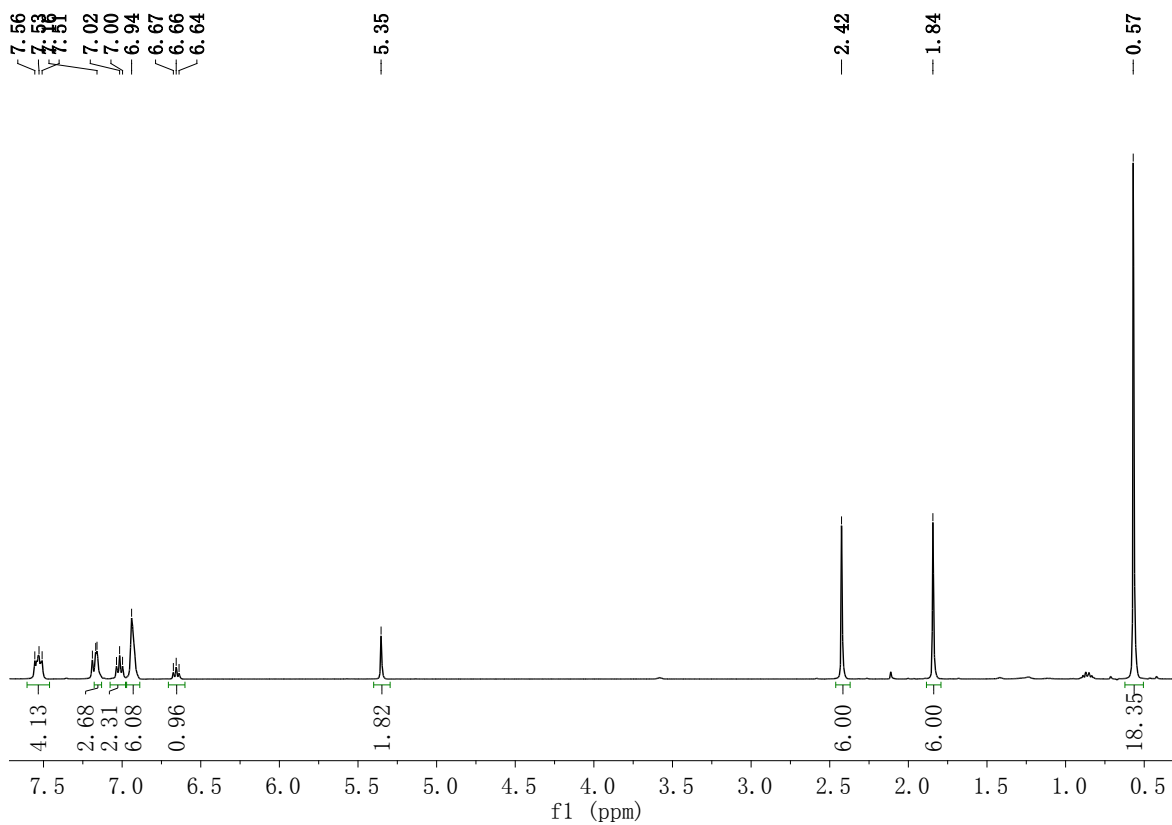
**Figure S13.**  $^1\text{H}$  NMR spectrum of complex **5** ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).



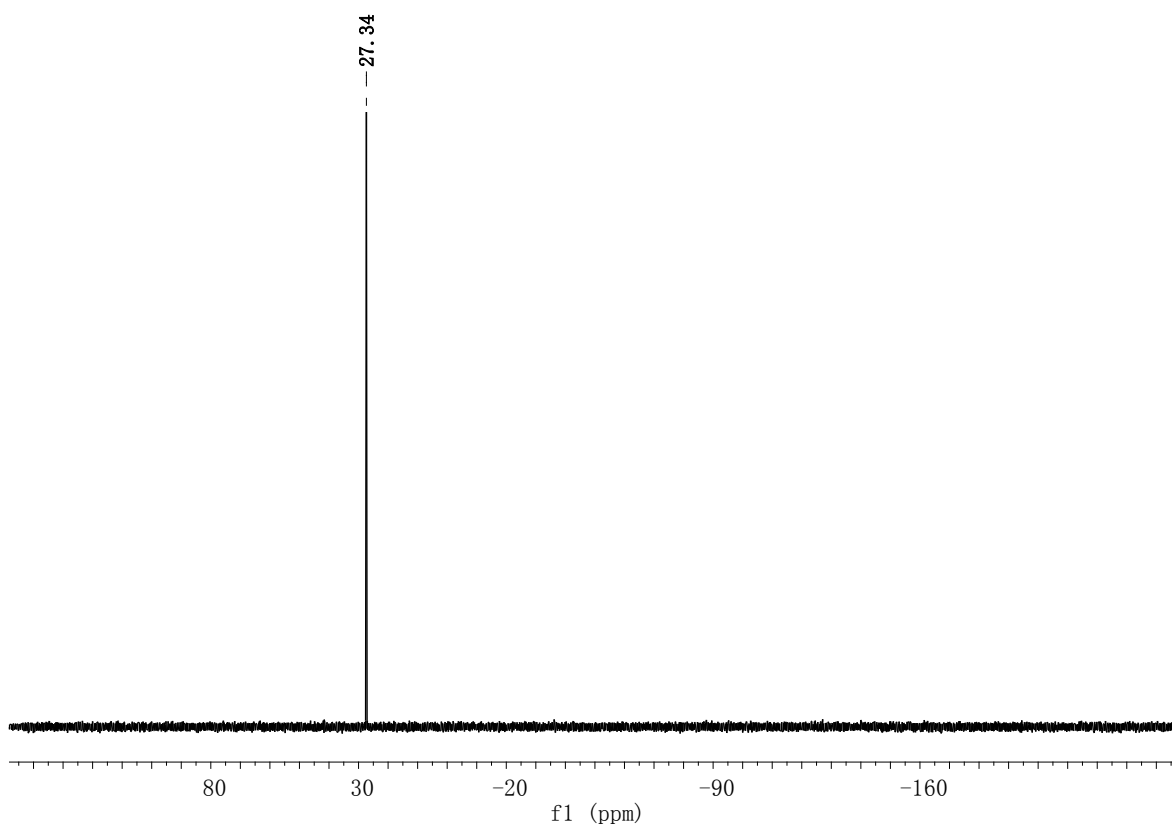
**Figure S14.**  $^{31}\text{P}$  NMR spectrum of complex **5** ( $\text{C}_6\text{D}_6$ ).



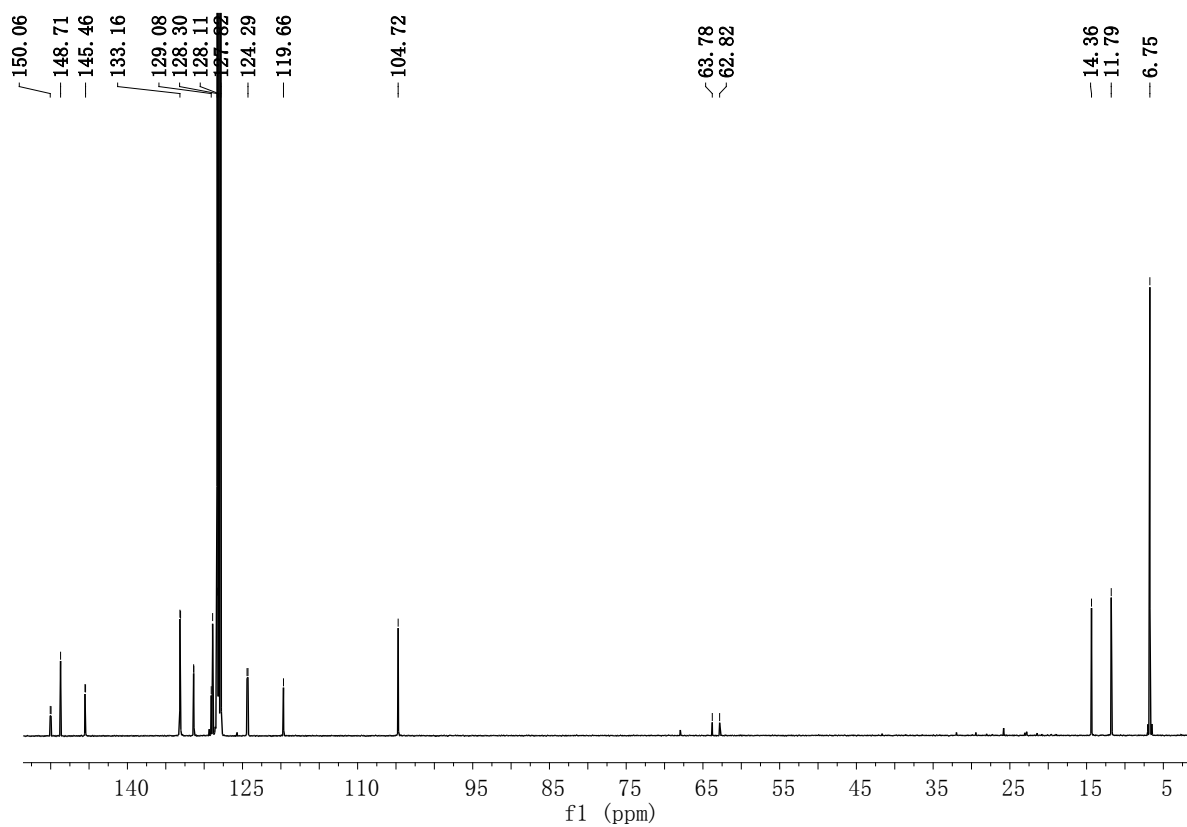
**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **5** ( $\text{C}_6\text{D}_6$ ) (\*, residual THF signals).



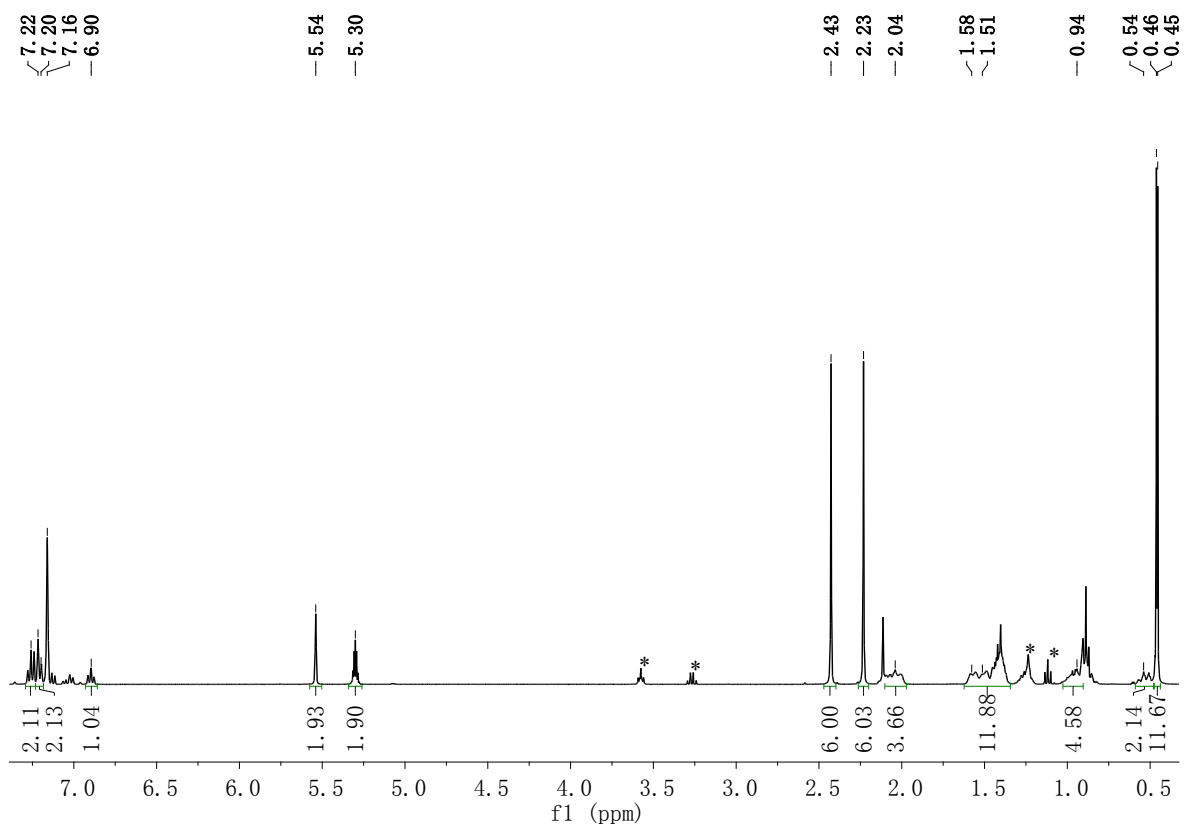
**Figure S16.**  $^1\text{H}$  NMR spectrum of complex **6** ( $\text{C}_6\text{D}_6$ ).



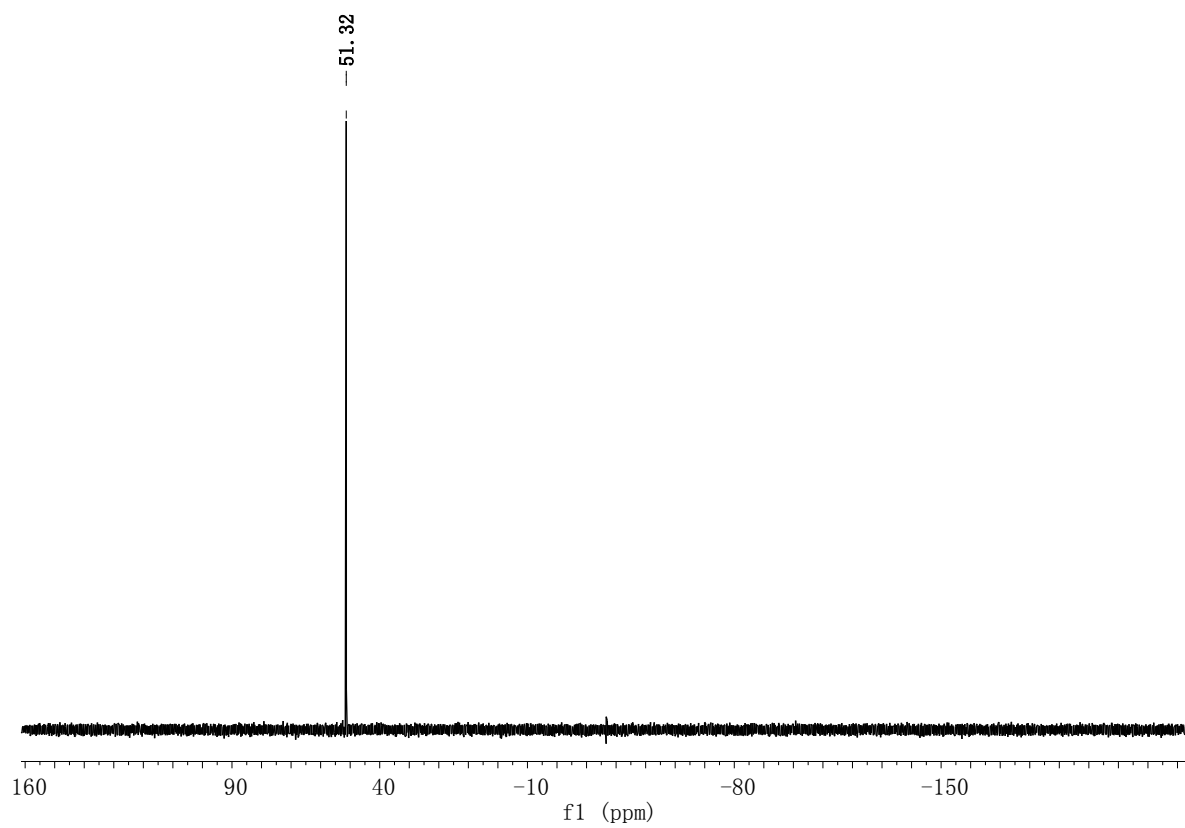
**Figure S17.**  $^{31}\text{P}$  NMR spectrum of complex **6** ( $\text{C}_6\text{D}_6$ ).



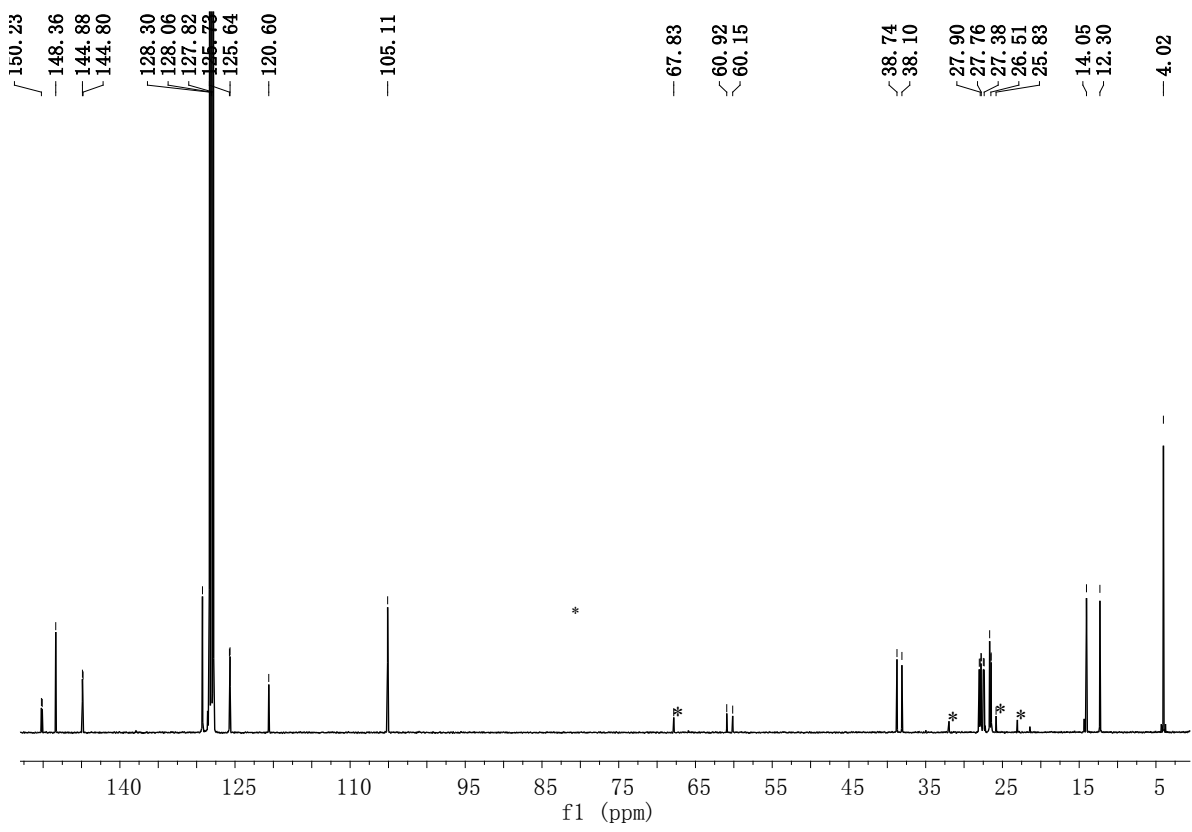
**Figure S18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **6** ( $\text{C}_6\text{D}_6$ ).



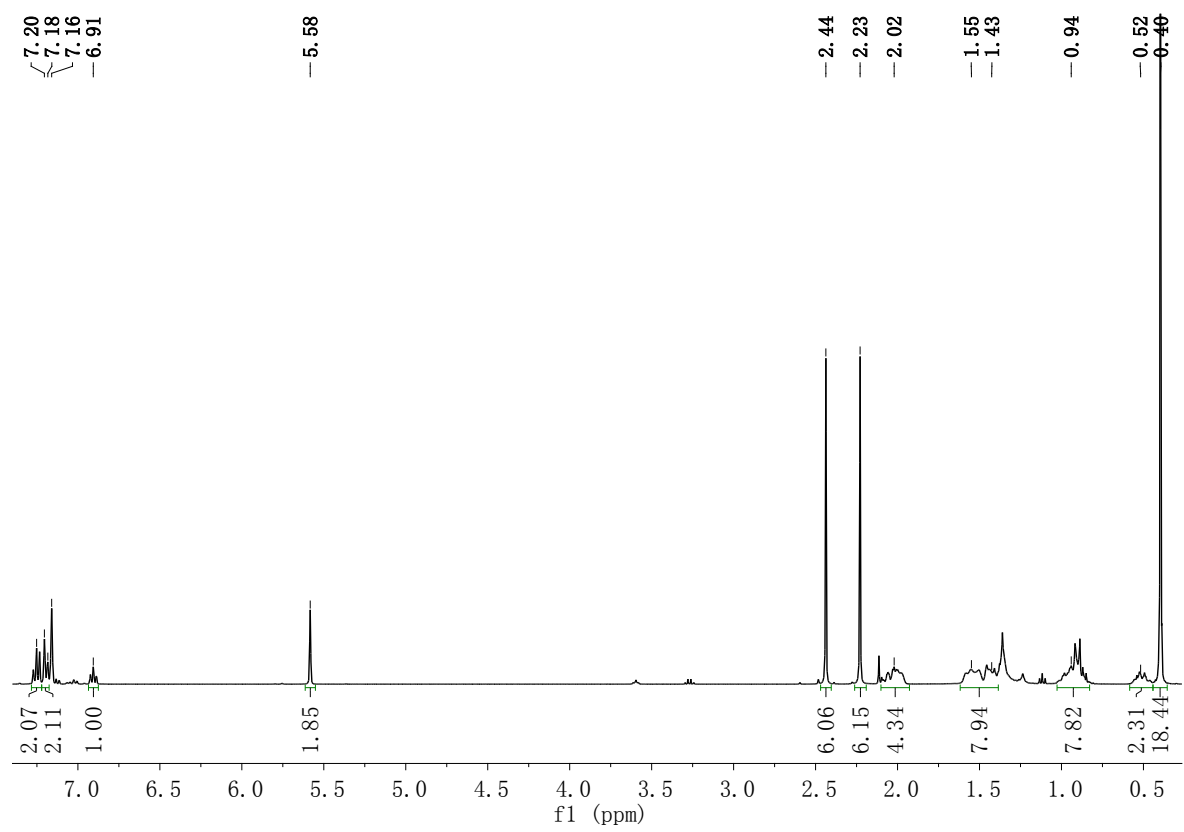
**Figure S19.**  $^1\text{H}$  NMR spectrum of complex **7** ( $\text{C}_6\text{D}_6$ ) (\*, residual solvents signals).



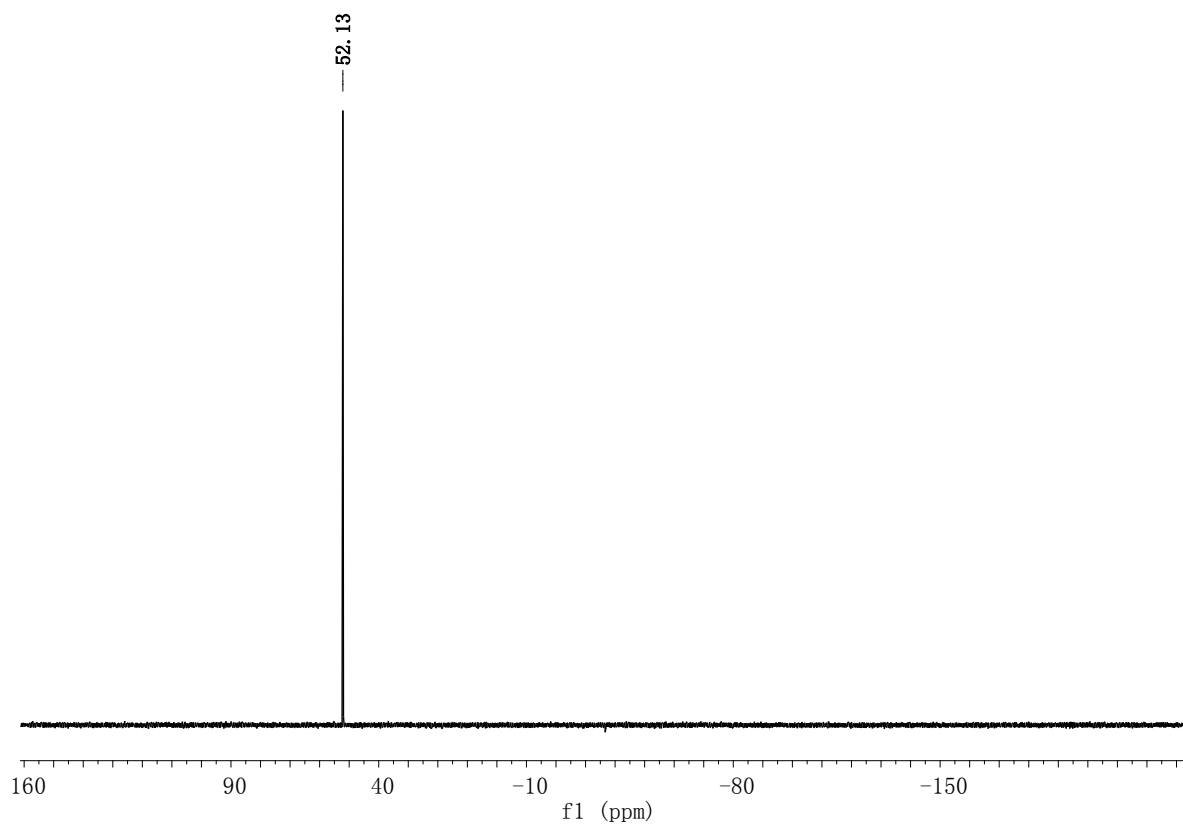
**Figure S20.**  $^{31}\text{P}$  NMR spectrum of complex **7** ( $\text{C}_6\text{D}_6$ ).



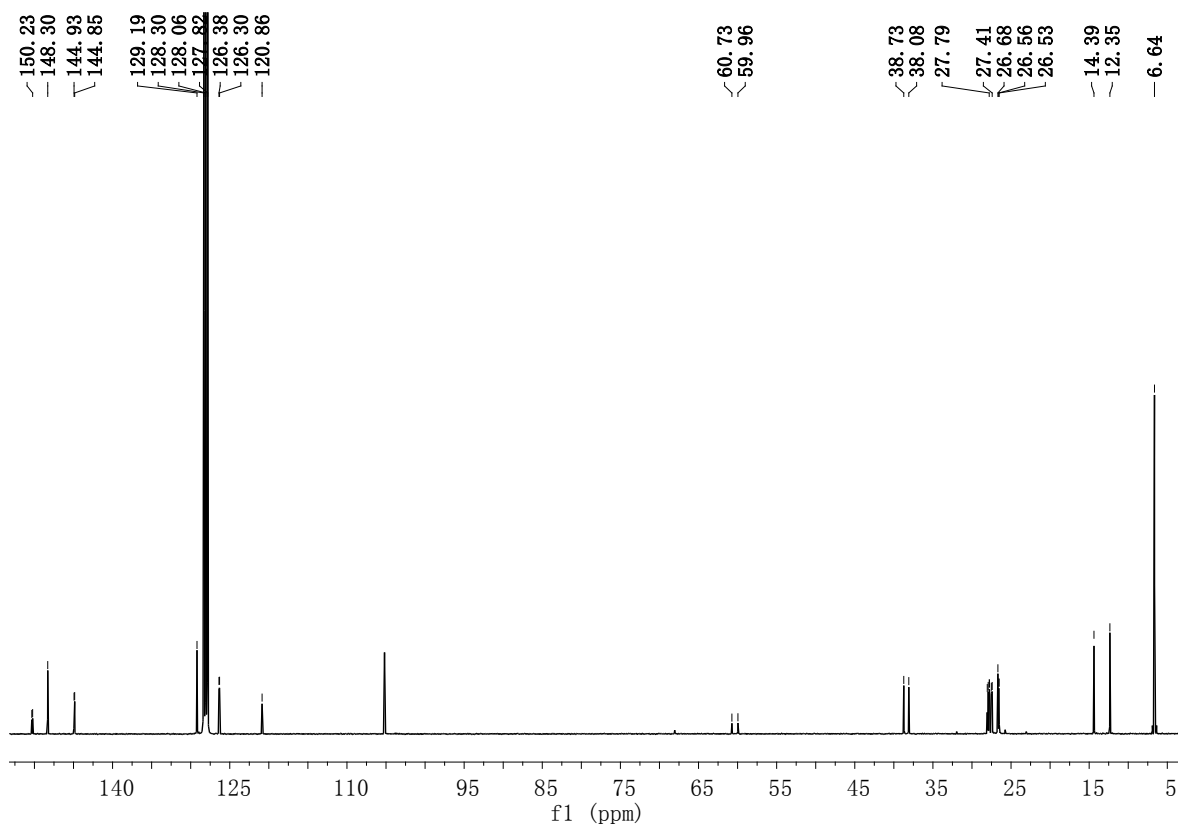
**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **7** ( $\text{C}_6\text{D}_6$ ) (\*, residual solvents signals).



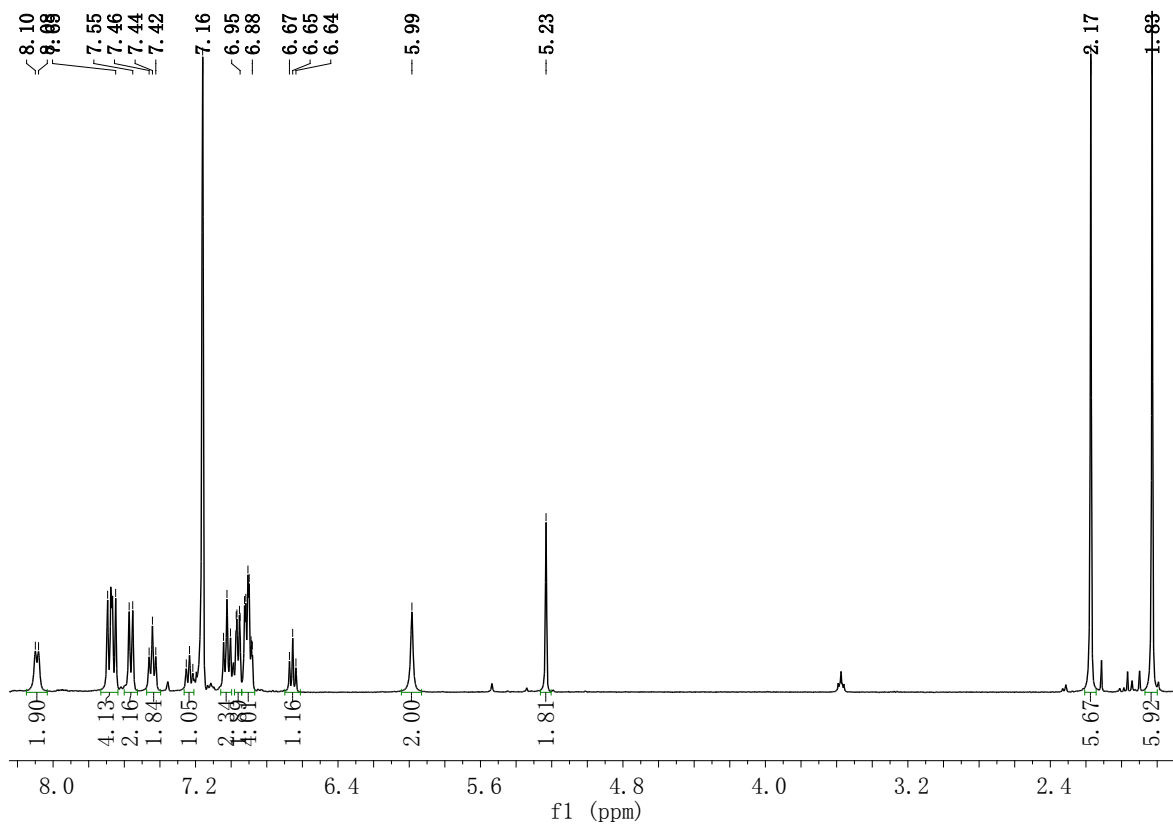
**Figure S22.**  $^1\text{H}$  NMR spectrum of complex **8** ( $\text{C}_6\text{D}_6$ ).



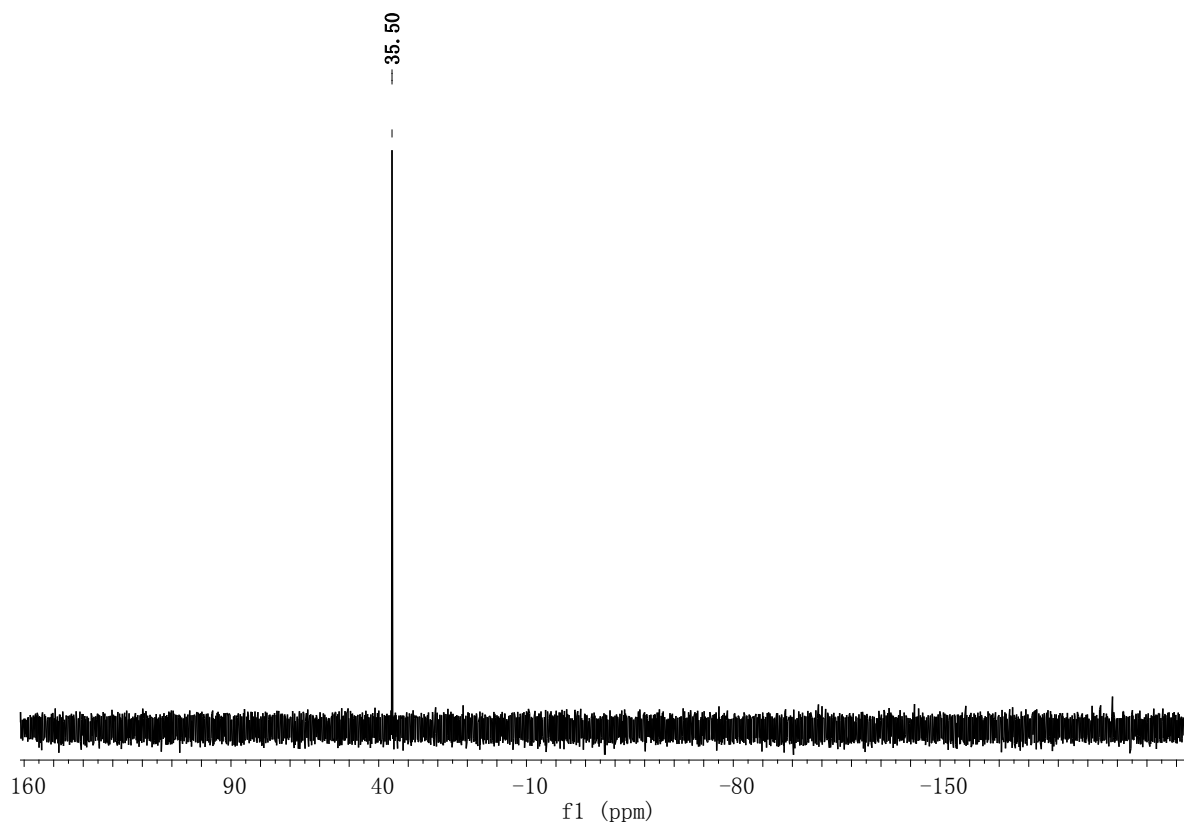
**Figure S23.**  $^{31}\text{P}$  NMR spectrum of complex **8** ( $\text{C}_6\text{D}_6$ ).



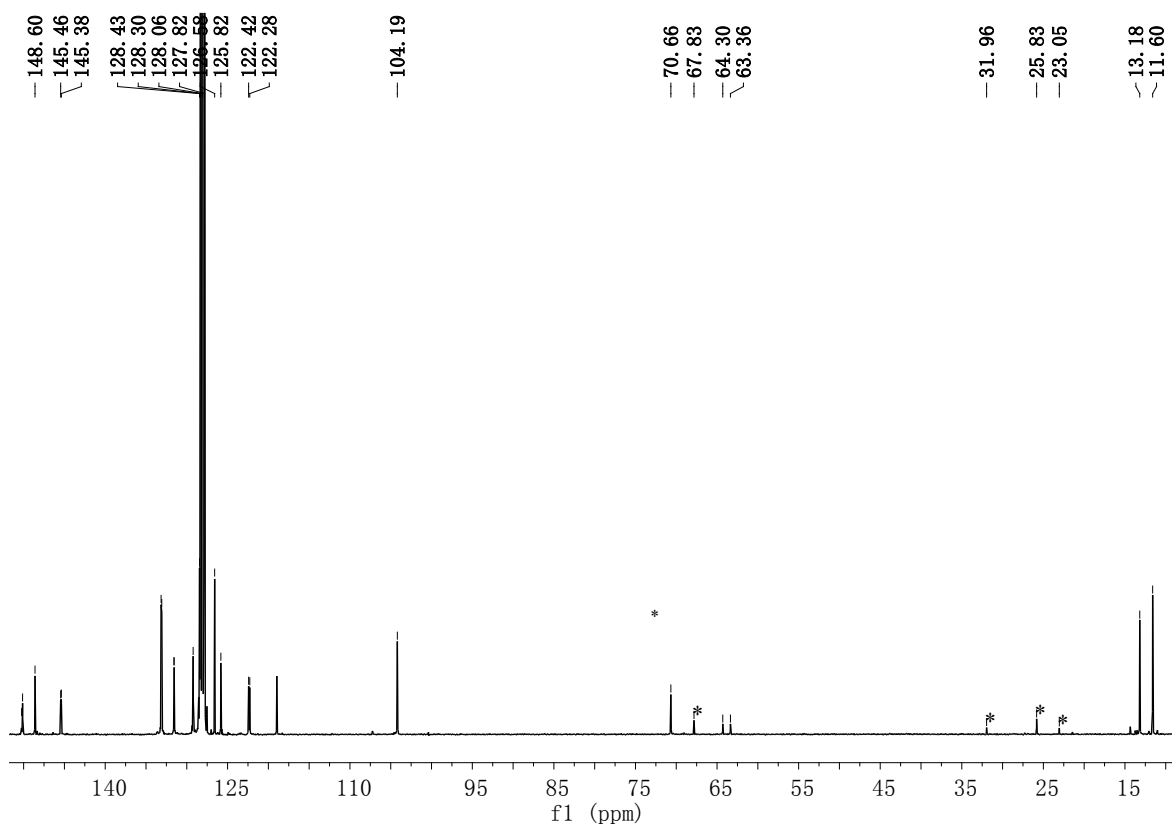
**Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **8** ( $\text{C}_6\text{D}_6$ ).



**Figure S25.**  $^1\text{H}$  NMR spectrum of complex **9** ( $\text{C}_6\text{D}_6$ ).

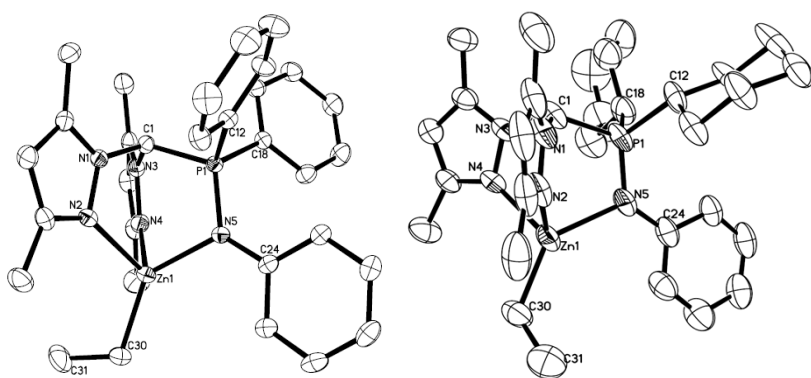


**Figure S26.**  $^{31}\text{P}$  NMR spectrum of complex **9** ( $\text{C}_6\text{D}_6$ ).

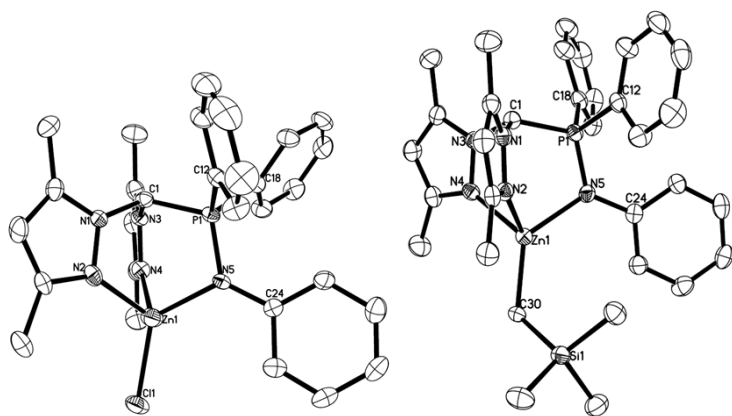


**Figure S27.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **9** ( $\text{C}_6\text{D}_6$ ) (\*, residual solvents signals).

### 3. X-ray molecular structures.







**Figure S28.** Molecular structures of complexes **1-4** with 35% probability of thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

**Table S1.** Selected bond lengths (Å) and angles (°) for complexes **1-4** and **6**.

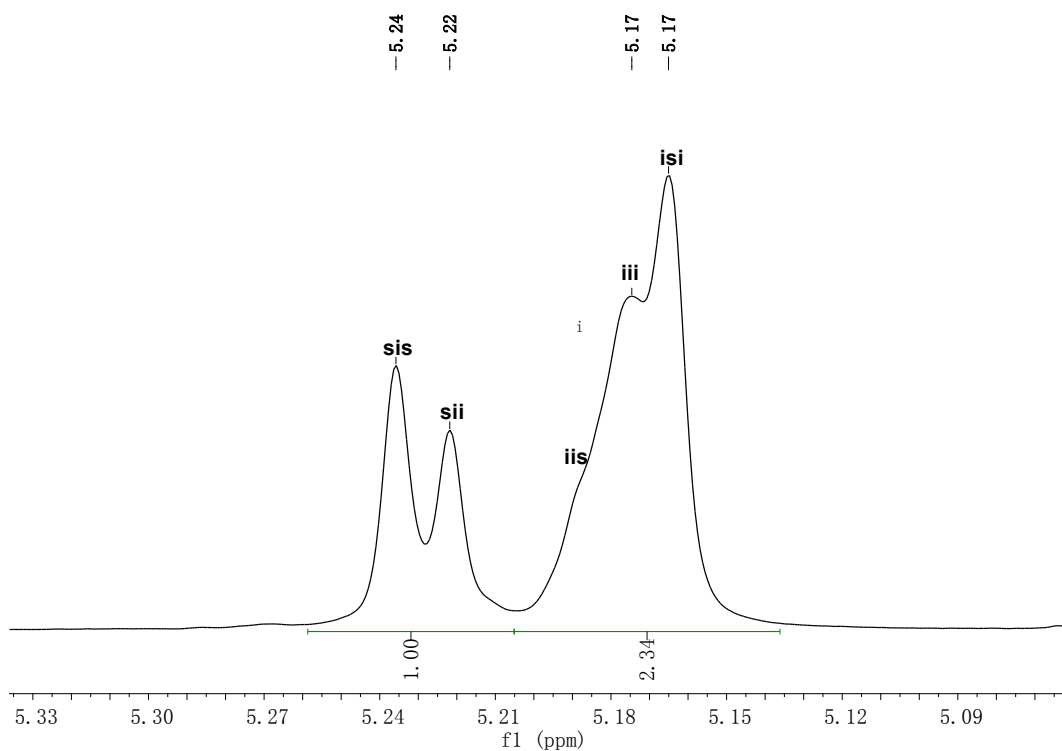
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>6</b>
N(2)–Zn(1)	2.1207(18)	2.104(4)	2.045(2)	2.124(3)	2.153(2)
N(4)–Zn(1)	2.1036(19)	2.137(3)	2.067(2)	2.110(3)	2.081(2)
N(5)–Zn(1)	2.0512(18)	2.056(3)	2.018(2)	2.079(3)	2.049(2)
N(5)–P(1)	1.6321(17)	1.635(4)	1.637(2)	1.629(3)	1.628(2)
C(1)–P(1)	1.751(2)	1.745(4)	1.744(3)	1.731(3)	1.737(3)
Cl(1)–Zn(1)			2.1915(8)		
N(6)–Zn(1)					1.939(2)
C(30)–Zn(1)	1.994(2)	1.993(4)		1.992(3)	
N(5)–Zn(1)–N(2)	93.07(7)	95.26(12)	100.65(9)	98.05(10)	90.85(8)
N(5)–Zn(1)–N(4)	95.17(7)	94.94(12)	98.34(9)	94.38(11)	101.05(9)
N(2)–Zn(1)–N(4)	91.07(7)	88.39(13)	92.70(9)	88.46(11)	89.86(8)
N(5)–Zn(1)–Cl(1)			128.15(7)		
N(5)–Zn(1)–N(6)					126.53(9)
N(5)–Zn(1)–C(30)	134.51(10)	134.18(18)		127.66(14)	
P(1)–N(5)–Zn(1)	109.37(10)	110.41(17)	106.47(12)	108.26(14)	108.75(11)
N(3)–C(1)–N(1)	112.44(17)	109.7(3)	111.6(2)	112.2(3)	112.2(2)
N(3)–C(1)–P(1)	111.94(14)	112.8(2)	111.68(18)	113.7(2)	114.48(18)
N(1)–C(1)–P(1)	110.87(14)	113.8(3)	114.57(19)	111.9(2)	110.46(17)

**Table S2.** Crystallographic data and structure refinement details for complexes **1-4** and **6**.

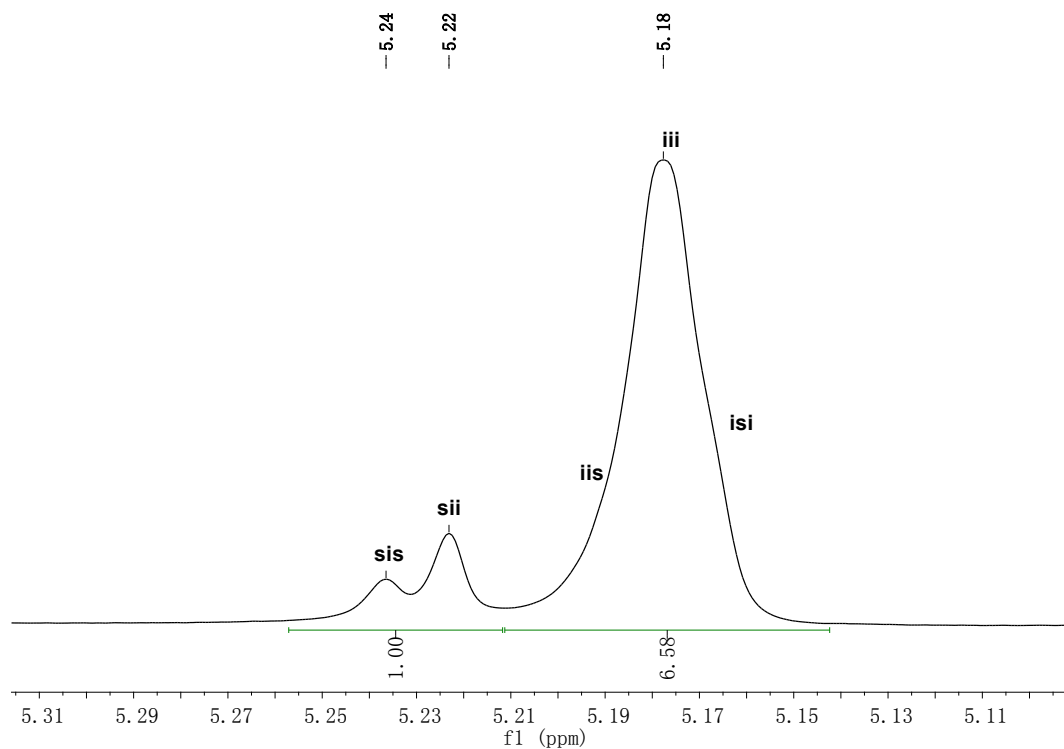
Parameter	<b>1·THF</b>	<b>2</b>	<b>3·THF</b>	<b>4·THF</b>	<b>6</b>
Empirical formula	C <sub>35</sub> H <sub>42</sub> N <sub>5</sub> OPZn	C <sub>31</sub> H <sub>46</sub> N <sub>5</sub> PZn	C <sub>33</sub> H <sub>37</sub> ClN <sub>5</sub> OPZn	C <sub>37</sub> H <sub>48</sub> N <sub>5</sub> OPSiZn	C <sub>35</sub> H <sub>47</sub> N <sub>6</sub> PSi <sub>2</sub> Zn
Formula weight	645.08	585.07	651.47	703.23	704.31
Temperature/K	273(2)	195(2)	273(2)	273(2)	273(2)
Wavelength/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic

space group	P2(1)/c	P2(1)/n	P2(1)/n	P-1	P2(1)/c
<i>a</i> (Å)	10.6521(6)	13.0170(9)	14.4797(9)	9.9691(5)	18.0474(12)
<i>b</i> (Å)	14.2354(8)	17.0162(11)	10.8889(6)	11.3621(6)	12.0098(7)
<i>c</i> (Å)	21.9063(12)	14.0147(9)	20.9293(13)	17.9387(10)	17.5841(11)
$\alpha$ (deg)	90	90	90	102.2200(10)	90
$\beta$ (deg)	95.8750(10)	90.0910(10)	100.0880(10)	98.4140(10)	102.7680(10)
$\gamma$ (deg)	90	90	90	109.4780(10)	90
<i>V</i> (Å <sup>3</sup> )	3304.4(3)	3104.3(4)	3248.9(3)	1819.61(17)	3717.0(4)
<i>Z</i>	4	4	4	2	4
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.297	1.252	1.332	1.284	1.259
$\mu$ [mm <sup>-1</sup> ]	0.827	0.870	0.921	0.788	0.801
<i>F</i> [000]	1360	1248	1360	744	1488
$2\theta_{\max}$ [deg]	52.02	52.10	52.08	52.10	52.08
Reflections collected	20746	19594	19839	10037	22288
Independent reflections	6493 [R(int)=0.0252]	6127 [R(int)=0.0382]	6403 [R(int) = 0.0437]	7034 [R(int) = 0.0226]	7301 [R(int)=0.0418]
GOF	1.057	1.017	1.028	1.020	1.024
Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0382 wR <sub>2</sub> = 0.1031	R <sub>1</sub> = 0.0565 wR <sub>2</sub> = 0.1390	R <sub>1</sub> = 0.0459 wR <sub>2</sub> = 0.1035	R <sub>1</sub> = 0.0545 wR <sub>2</sub> = 0.1282	R <sub>1</sub> = 0.0449 wR <sub>2</sub> = 0.1011

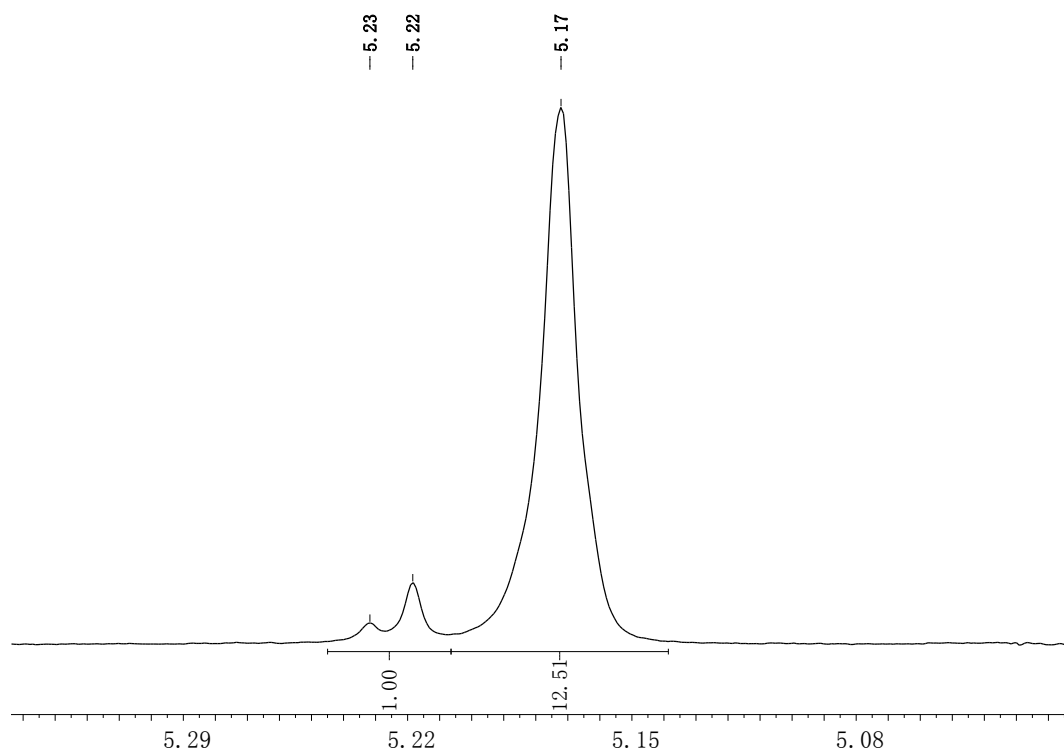
#### 4. Homonuclear decoupled $^1\text{H}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of representative resulting PLAs.



**Figure S29.** Homonuclear decoupled  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of atactic PLA produced from *rac*-LA using complex **2** (Table 1, run 3). The tacticity of the polymer was assigned using the methine signals as described by Hillmyer and co-workers.<sup>1</sup>

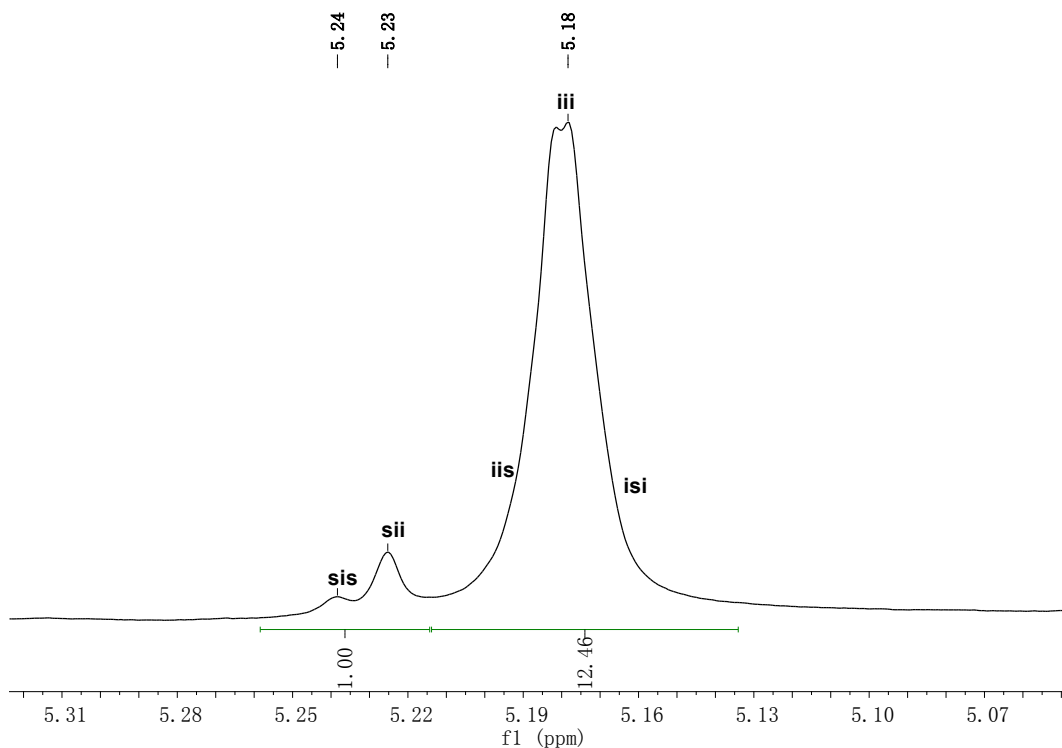


**Figure S30.** Homonuclear decoupled  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) showing moderate isotactic bias in PLA produced from *rac*-LA using complex **5** (Table 1, run 7). The three peaks (iis, iii, isi) partially overlap.<sup>2</sup>

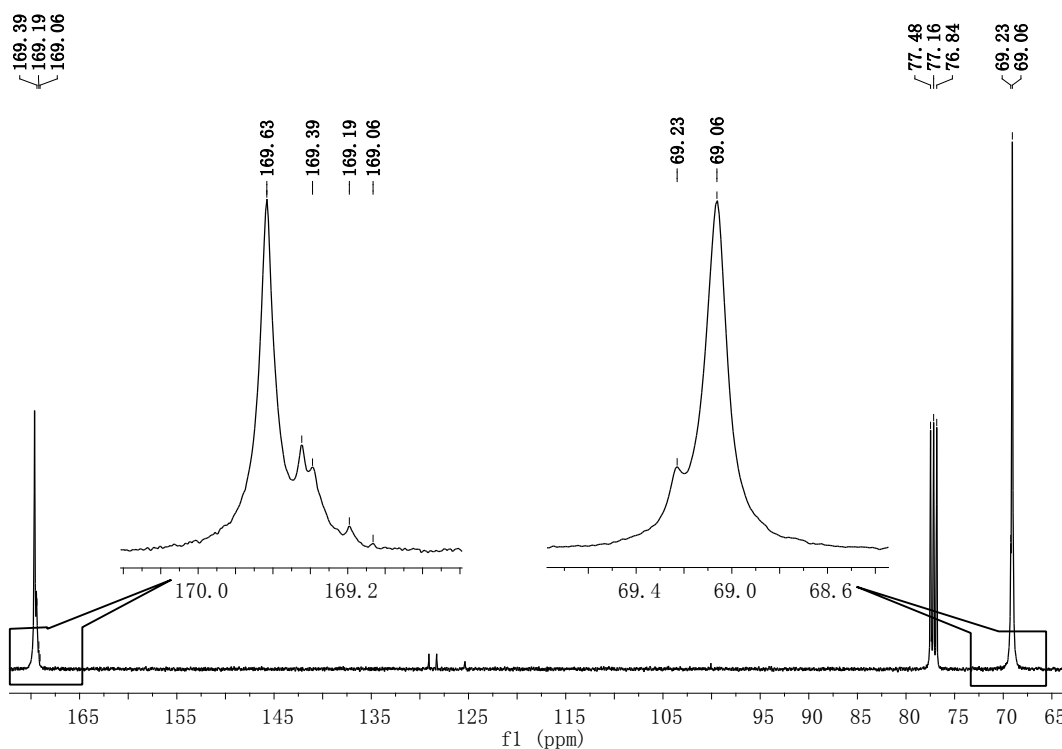


**Figure S31.** Homonuclear decoupled  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) showing highly isotactic

bias in PLA produced from *rac*-LA using complex **5** (Table 1, run 14).



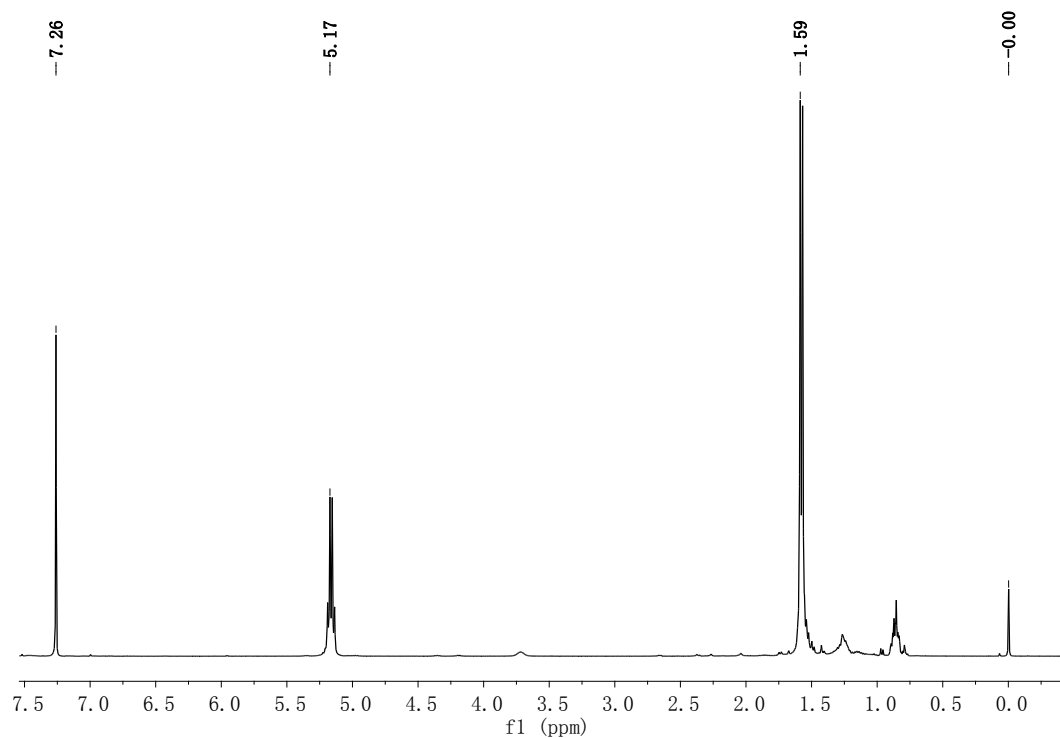
**Figure S32.** Homonuclear decoupled  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) showing highly isotactic bias in PLA produced from *rac*-LA using complex **5** (Table 1, run 15).



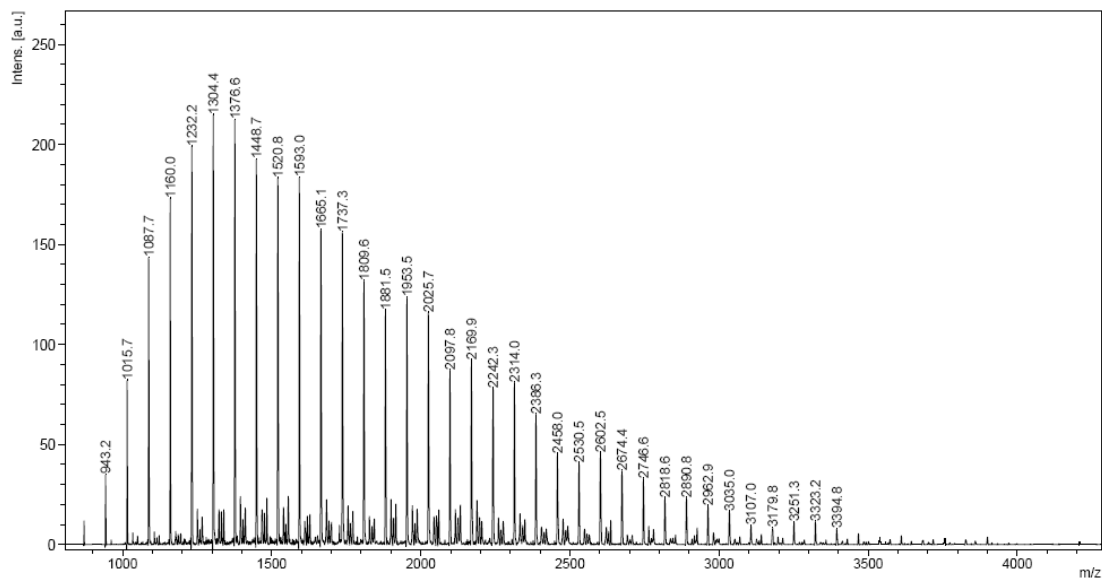
**Figure S33.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) showing highly isotactic bias in PLA

produced from *rac*-LA using complex **5** (Table 1, run 15).

## 5. $^1\text{H}$ NMR and MALDI-TOF mass spectra of oligomers.



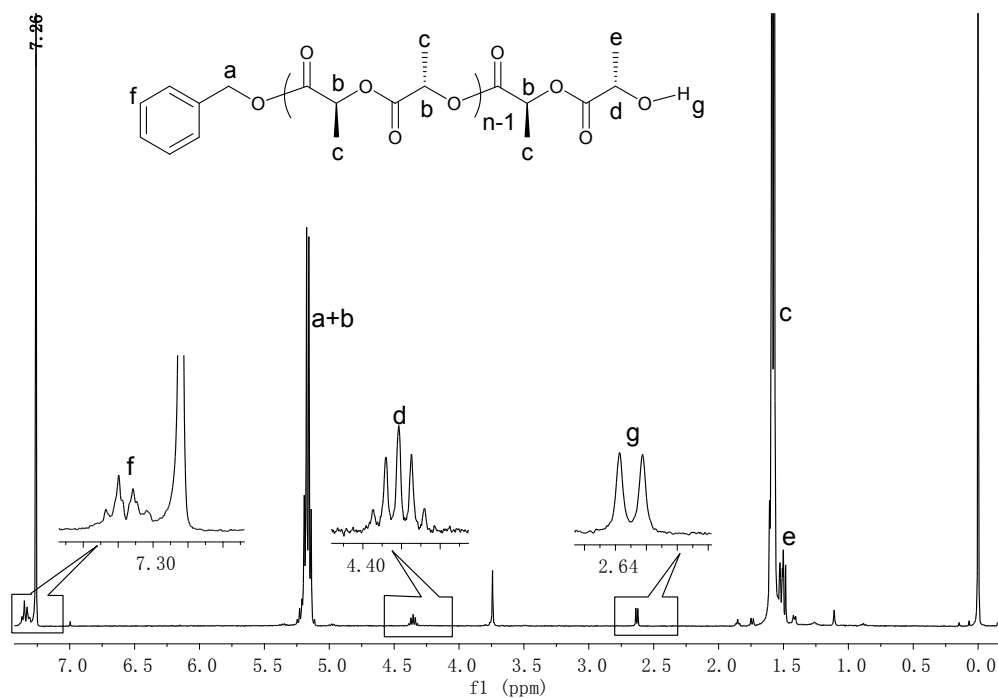
**Figure S34.**  $^1\text{H}$  NMR spectrum for an oligomeric PLLA obtained using complex **1**.



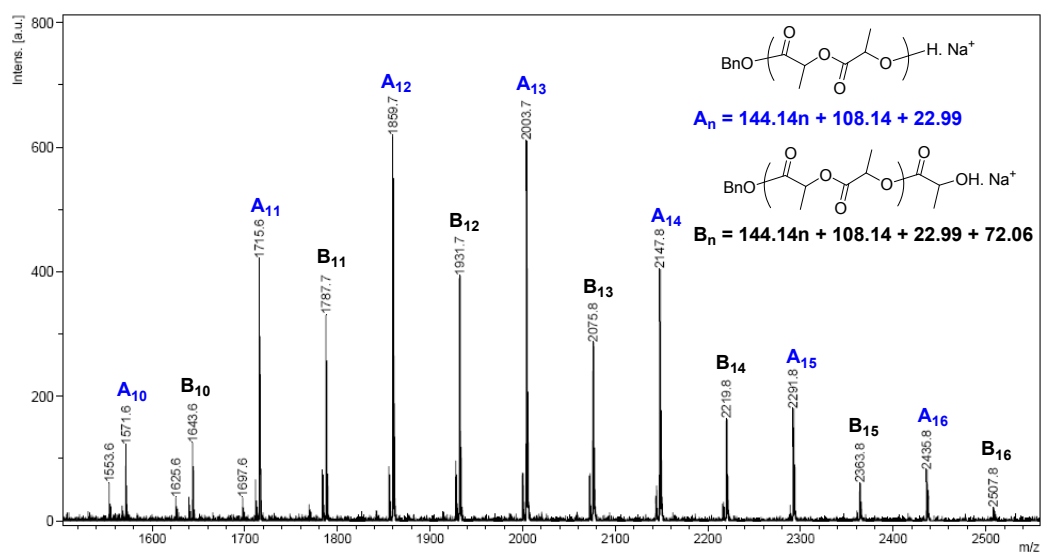
Bruker Daltonics flexAnalysis

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**Figure S35.** MALDI-TOF mass spectrum for an oligomeric PLLA obtained using complex **1**.



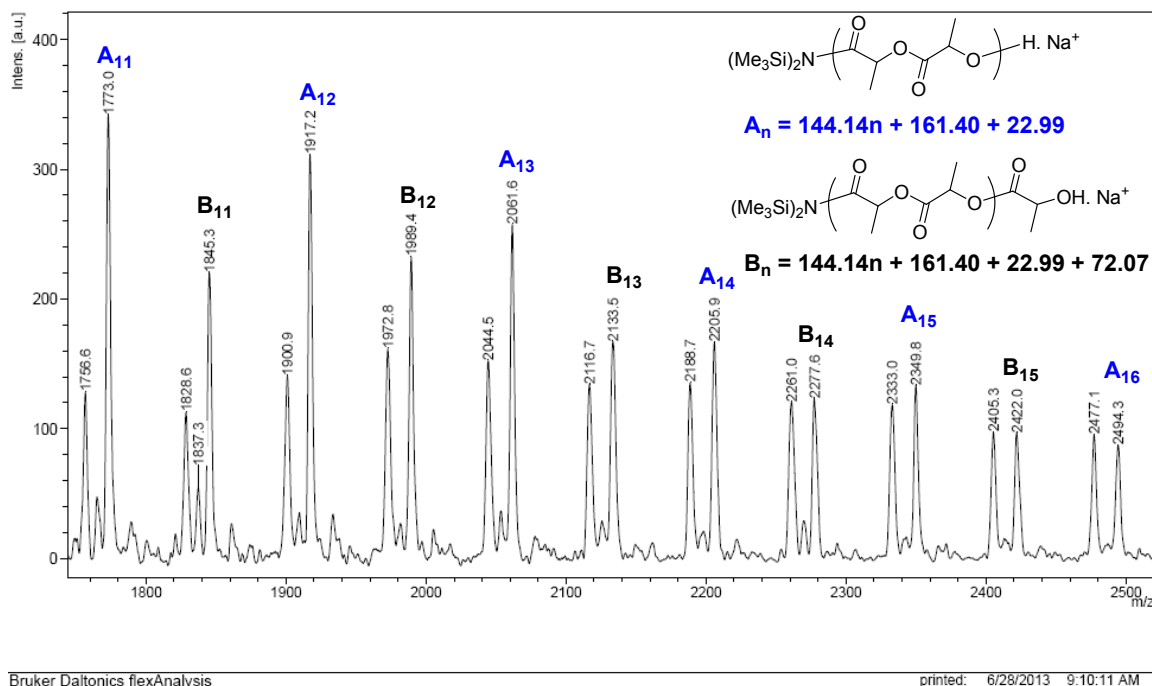
**Figure S36.**  $^1\text{H}$  NMR spectrum of oligomeric PLLA obtained by complex **9** after quenched with methanol ( $[\text{L-LA}]_0 / [\text{Zn}]_0 = 20$ ).



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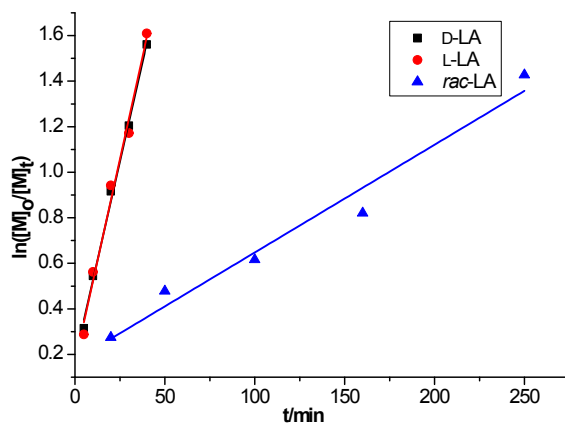
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**Figure S37.** MALDI-TOF mass spectrum of oligomeric PLLA obtained with complex **9**.



**Figure S38.** MARDI-TOF mass spectrum for an oligomeric PLLA obtained using complex **6**.

## 6. The results of polymerization kinetics and optical activities.



**Figure S39.** Semilogarithmic plots of lactide conversion versus time mediated by complex **9**: D-LA (black squares,  $k_{\text{app}} = 3.48 \times 10^{-2} \text{ min}^{-1}$ ,  $R^2 = 0.995$ ); L-LA (red circles,  $k_{\text{app}} = 3.58 \times 10^{-2} \text{ min}^{-1}$ ,  $R^2 = 0.984$ ); rac-LA (blue triangles,  $k_{\text{app}} = 4.73 \times 10^{-3} \text{ min}^{-1}$ ,  $R^2 = 0.961$ ). Conditions:  $T = 20 \text{ }^\circ\text{C}$ ;  $[\text{M}]/\text{cat.} = 200$ ;  $[\text{M}]_0 = 0.8 \text{ M}$ , THF as solvent.

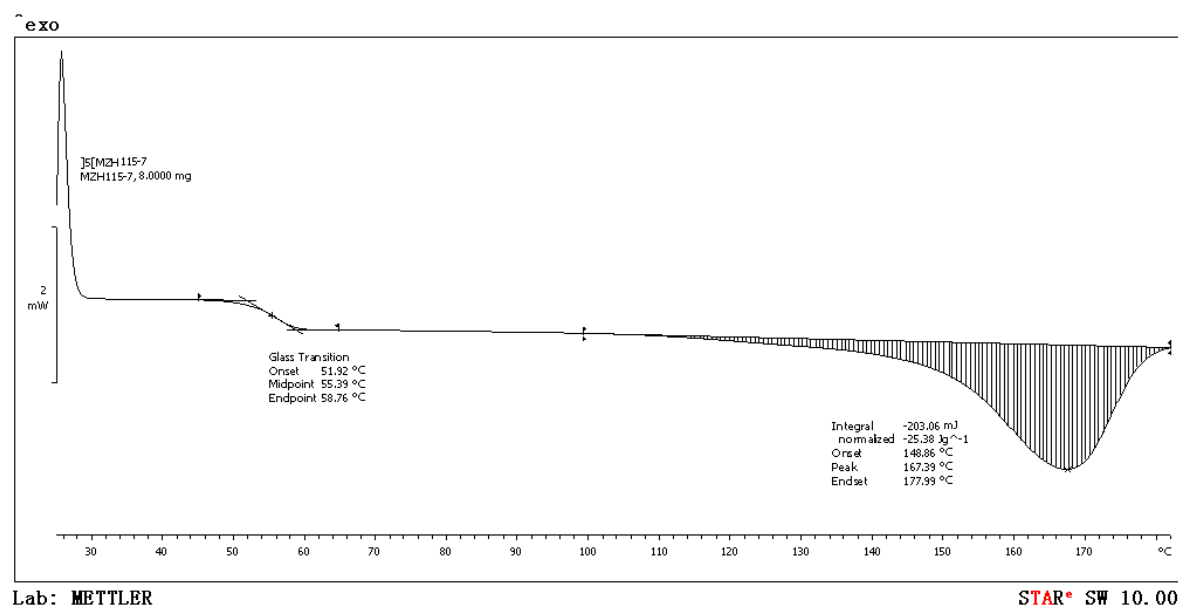


**Table S3. Polymerization of *rac*-lactide at different conversions with complex 9.<sup>a</sup>**

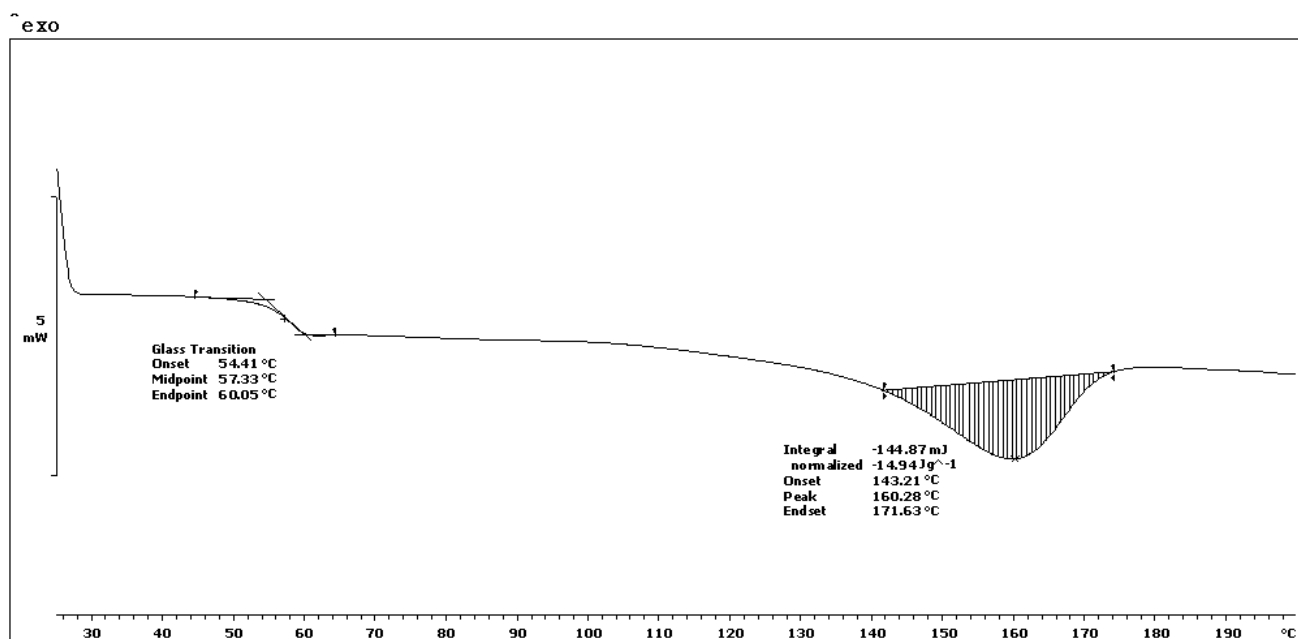
Run	Time (min)	Conv. <sup>b</sup> (%)	$M_{n,calcd}^c$ (10 <sup>4</sup> )	$M_{n,exp}^d$ (10 <sup>4</sup> )	$M_w/M_n^d$	$P_1^e$	$[\alpha]_{Df}^{20}$
1	20	24	0.69	0.97	1.06	0.77	-0.2
2	50	38	1.09	1.49	1.07	0.78	-0.2
3	100	46	1.32	1.64	1.09	0.77	+0.2
4	160	56	1.61	1.98	1.10	0.76	+0.2
5	250	76	2.19	2.42	1.19	0.77	+0.3

<sup>a</sup> Conditions:  $T = 20\text{ }^\circ\text{C}$ ;  $[M]/cat. = 200$ ;  $cat., 20\text{ }\mu\text{mol}$ ; solvent: THF (5 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>  $M_{n,calcd} = [M]/cat. \times 144 \times conv. (\%)$ . <sup>d</sup> Determined by GPC against polystyrene standard. <sup>e</sup> Determined from the relative intensity of the tetrad signals of the methine region in the homonuclear decoupled <sup>1</sup>H NMR spectra.  $P_1 = (I_2 - I_1)/(I_2 + I_1)$ , with  $I_1 = \delta 5.20\sim 5.23\text{ ppm}$  (sis, sii) and  $I_2 = \delta 5.13\sim 5.20\text{ ppm}$  (iis, iii, isi).<sup>3</sup> <sup>f</sup>In CHCl<sub>3</sub>,  $c = 1.0\text{ g/mL}$ .

## 7. DSC measurement of polymers.



**Figure S40.** Thermal analysis of highly isotactic PLA obtained from *rac*-LA with complex 5 (Table 1, run 14). The curve shows a glass transition temperature of 55.39 °C, and a melting point of 167.39 °C.



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**Figure S41.** Thermal analysis of highly isotactic PLA obtained from *rac*-LA with complex **5** (Table 1, run 15). The curve shows a glass transition temperature of 57.33 °C, and a melting point of 160.28 °C.

## 8. References

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2. D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun.*, 2013, **49**, 4295.
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