Supporting information

From Isoselectivity to Syndioselectivity: Lewis Base Regulates Stereochemistry in 2-Vinylpyridine Polymerization

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1 Experimental Section

1.1 Materials, Reagents, and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon-filled glovebox. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen, degassed and stored over fresh Na chips. 2-vinylpyridine (2VP), pyridine (Py), 2-Me-pyridine, 2,6-Me_2-pyridine, 2,6-Ph_2-pyridine, and n-hexane were dried over CaH_2 while stirring for 48 h and distilled before use, and then degassed and stored over 4 Å sieves. C_6D_6 was dried over sodium. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2, and then degassed and stored over 4 Å sieves. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C), or a Varian Inova 400 MHz spectrometer, or a Varian Inova 500 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were referred to $SiMe_4$ (TMS). The molecular weight and molecular weight distribution of the polymers were measured by Agilent Technologies 1260 Infinity GPC (Column: PL gel 5μm MIXED-C) at 30 ℃ using DMF as an eluent (the flowing rate is 1.0 mL/min) against poly(2-vinylpyridine) (P2VP) standards.

Literature procedures were employed or modified for the preparation of the following complexes: $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$, $(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$, $(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(THF)$.[1]

1.2 Typical polymerization procedure

1.2.1 Subtituted pyridine as Lewis base

In the glove box, a toluene solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (10 mg, 10 μmol) was added to a toluene solution (1 mL) of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (5 mg, 10 μmol) in a 20-mL flask. The mixture was stirred at room temperature for a few minutes, and 10 μmol of 2-Me-pyridine was added under vigorous stirring. The mixture was stirred at room temperature for a few minutes, and 2 mmol of 2VP was added under vigorous stirring. After the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 2- mL vial containing 0.5 mL of undried “wet” $CDCl_3$ stabilized by 250 ppm of BHT; the quenched aliquots were analyzed by ^1H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched, after the removal of the aliquot, by addition of 5 mL wet n-hexane. The quenched mixture was precipitated into 100 mL of n-hexane, stirred for 1 h, filtered, washed with n-hexane, and dried in a vacuum oven at 25 ℃ overnight to a constant weight.

1.2.2 Styrene as Lewis base

In the glove box, a toluene solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (10 mg, 10 μmol) was added to a toluene solution (1 mL) of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (5 mg, 10 μmol) in a 20-mL flask. The mixture was stirred at room temperature for a few minutes, and a mixture of 2 mmol of styrene and 2 mmol of 2VP was added under vigorous stirring. After the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 2- mL vial containing 0.5 mL of undried “wet” $CDCl_3$ stabilized by 250 ppm of BHT; the quenched aliquots were analyzed by ^1H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched, after the removal of the aliquot, by addition of 5 mL wet n-hexane. The quenched mixture was precipitated into 100 mL of n-hexane, stirred for 1 h, filtered, washed with n-hexane, and dried in a vacuum oven at 25 ℃ overnight to a constant weight.

1.3 Polymer characterizations

Polymer number (M_n) and weight (M_w) average molecular weights and polydispersity index (= M_w/M_n) were measured by gel permeation chromatography (GPC) analyses carried out at 30 ℃ and a flow rate of 1.0 mL/min with DMF as the eluent, on an Agilent 1260 GPC instrument equipped with four PLgel 5 μm mixed-C columns (Polymer Laboratories; linear range of molecular weight = 200 ‒ 2,000,000). The instrument was calibrated with 10 P(2-VP) standards.

1.4 Wide Angle X-ray Diffraction (WAXD)

Powder X-ray diffraction data were collected on an EMPYREAN diffractometer with Cu KR radiation (λ = 1.54056 Å) over the 2θ range of 5 – 40° with a scan speed of 0.3333°/s and a step size of 0.01° at room temperature.

1.5 Differential Scanning Calorimetry (DSC)

DSC was carried out with a NETZSCH DSC 206 thermal analyzer and the samples are analyzed with a heating rate of 10 K/min and a cooling rate of 10 K/min. Due to the slow recrystallization of the melted P2VP, only one heating and cooling cycle was performed.

Therefore, the melting point (T_m) and glass transition temperature (T_g) were taken from the first heat. The middle point of raw data was taken as T_g.

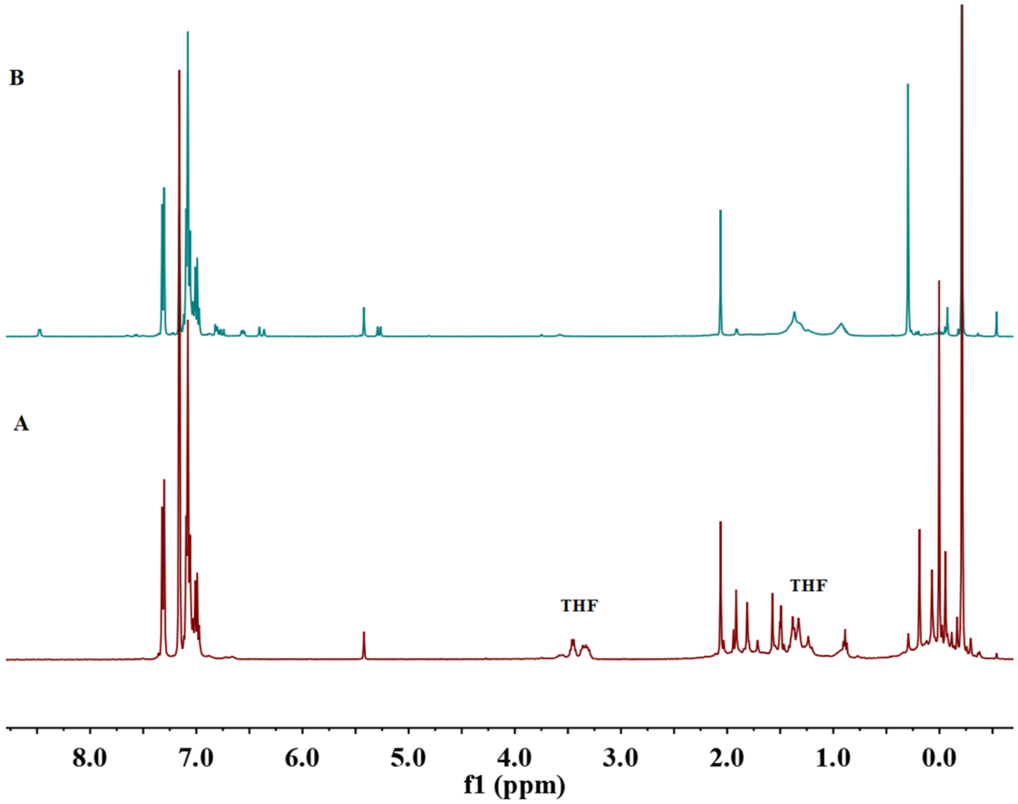

Figure **S1**. ^{1}H NMR spectrum of a mixture of 10 μmol of catalyst 1 and 10 μmol of $[Ph_3C][B(C_6F_5)_4]$ (A); a mixture after adding 100 μmol of 2VP and removing volatile substance (B).

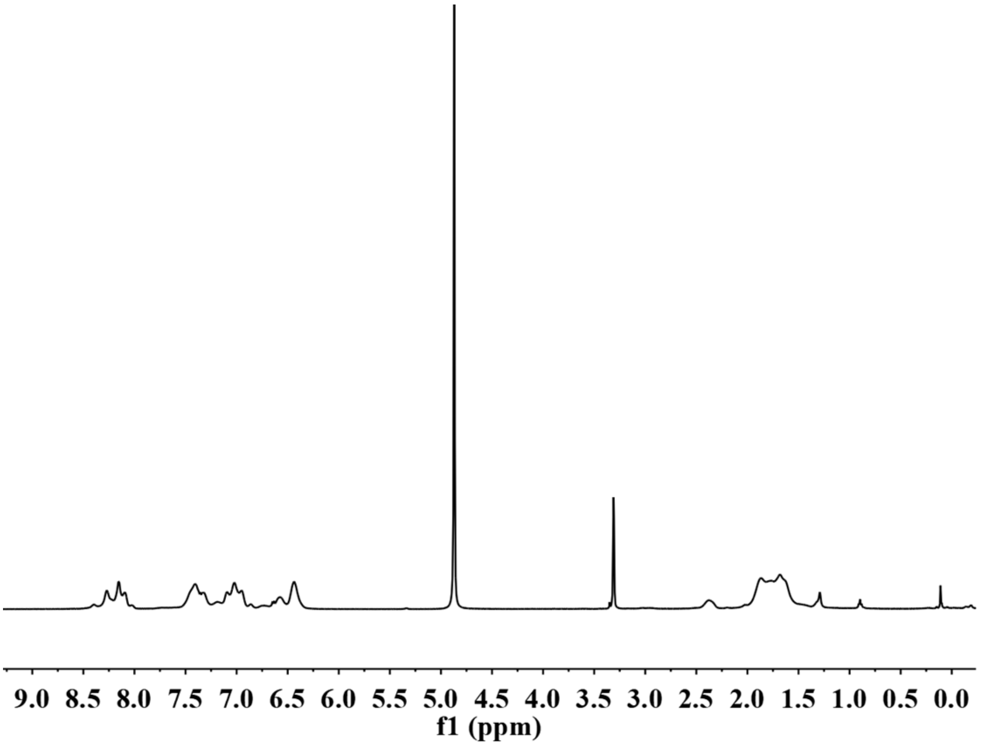

Figure **S2**. ^{1}H NMR spectrum of P2VP oligomer produced by catalyst 1.

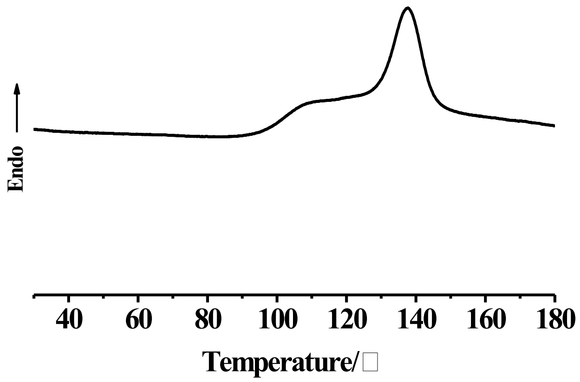

Figure **S3**. DSC profile of P2VP produced by catalyst 1 (run 17, Table 1).

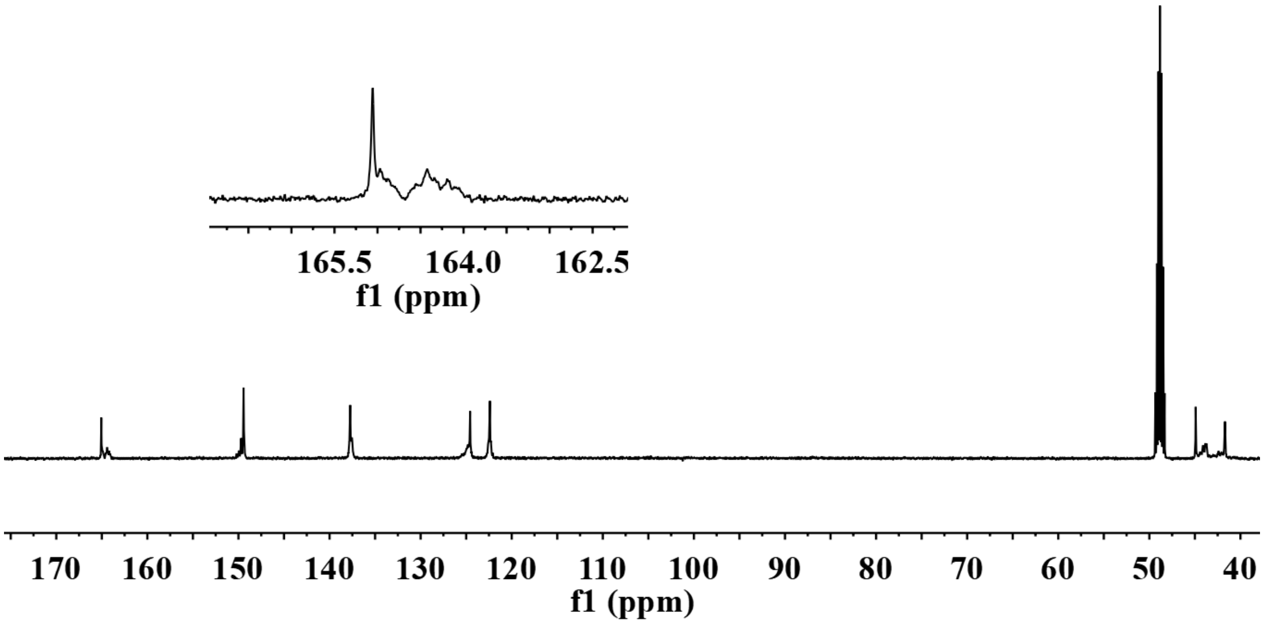

Figure S4. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 ℃ in CD_3OD (run 2, Table 1).

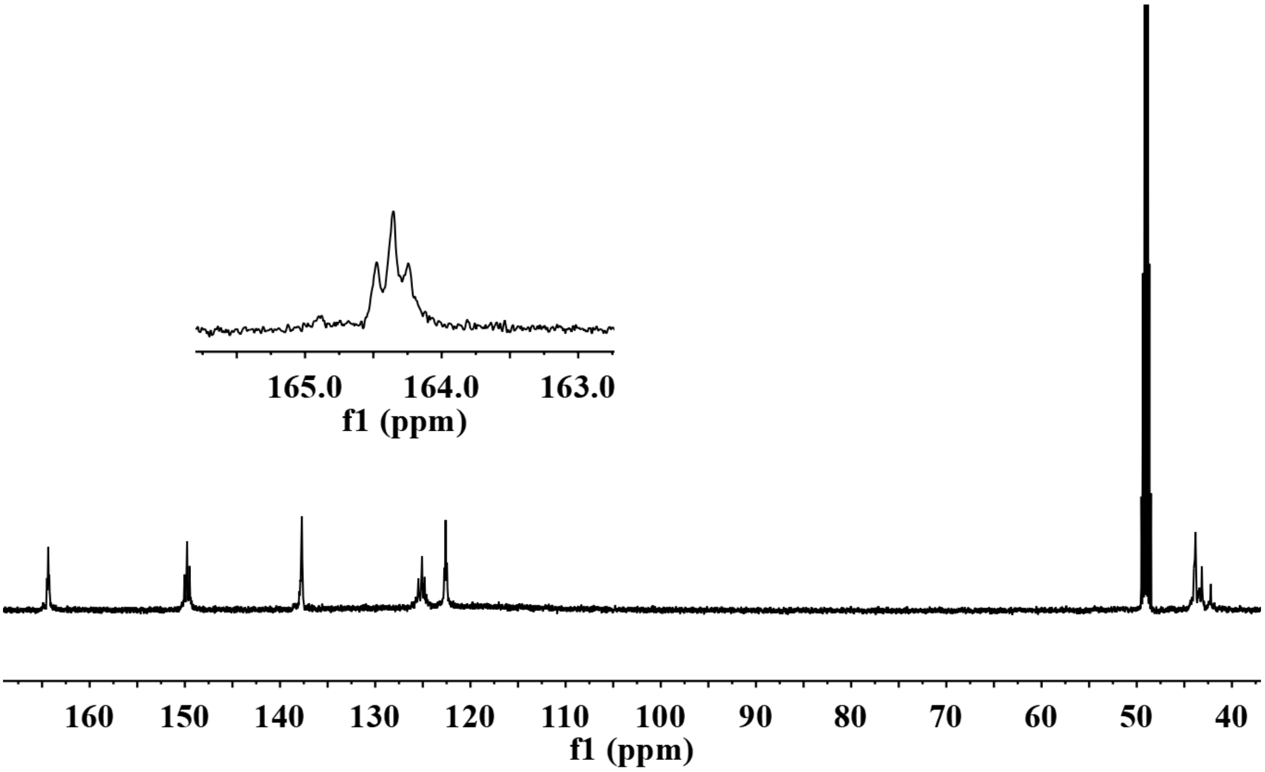

Figure S5. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 ℃ in CD_3OD (run 9, Table 1).

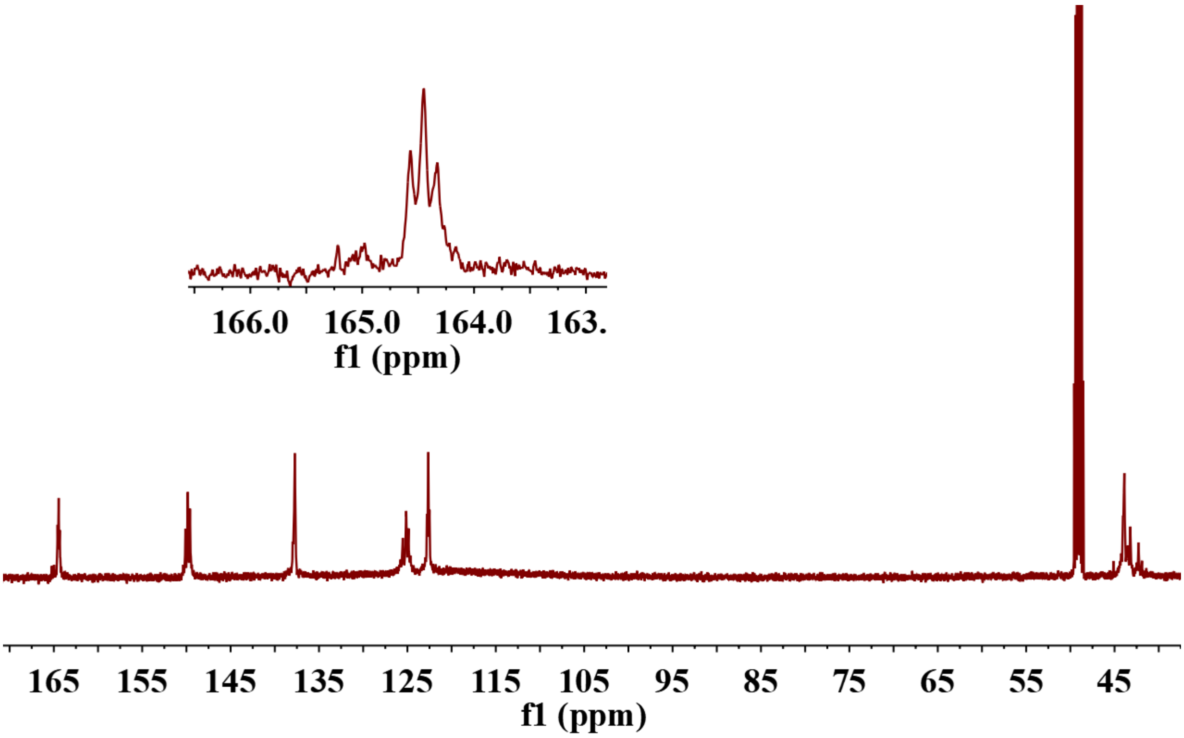

Figure S6. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 °C in CD_3OD (run 11, Table 1).

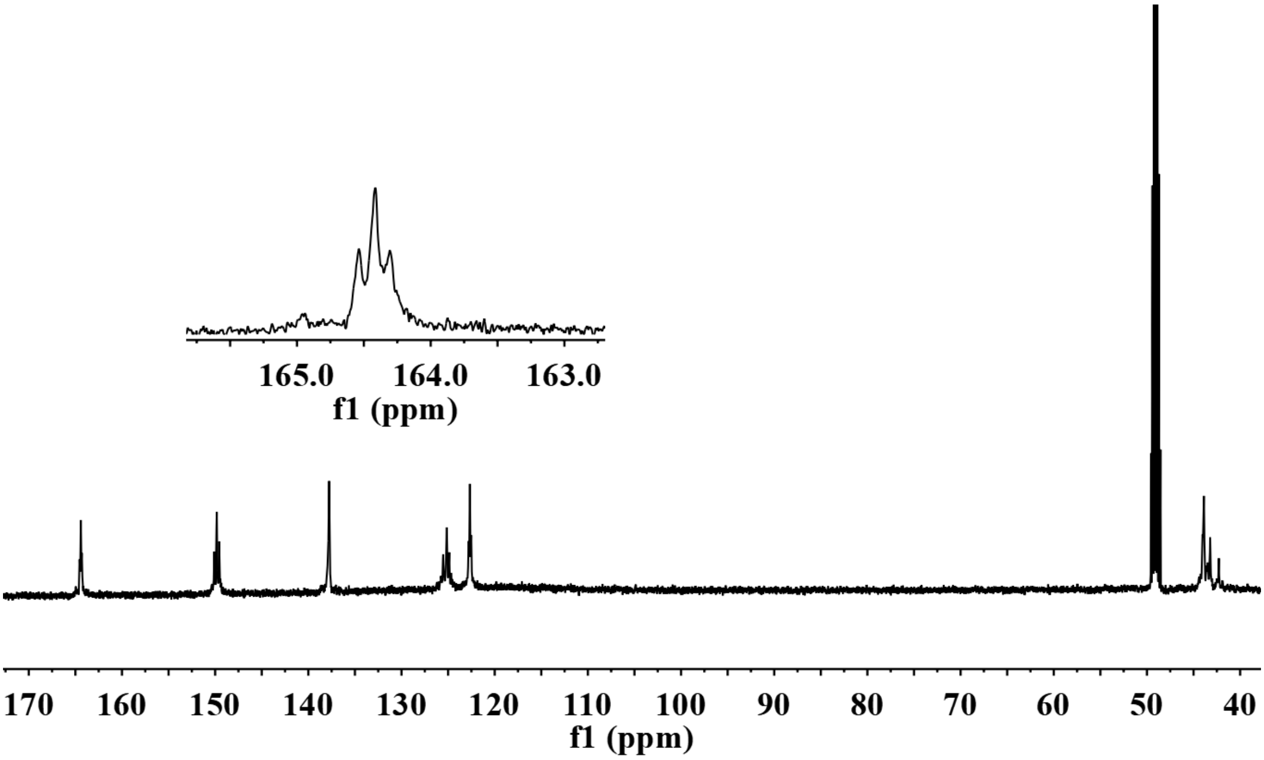

Figure S7. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst 1 in toluene at 25 °C in CD_3OD (run 12, Table 1).

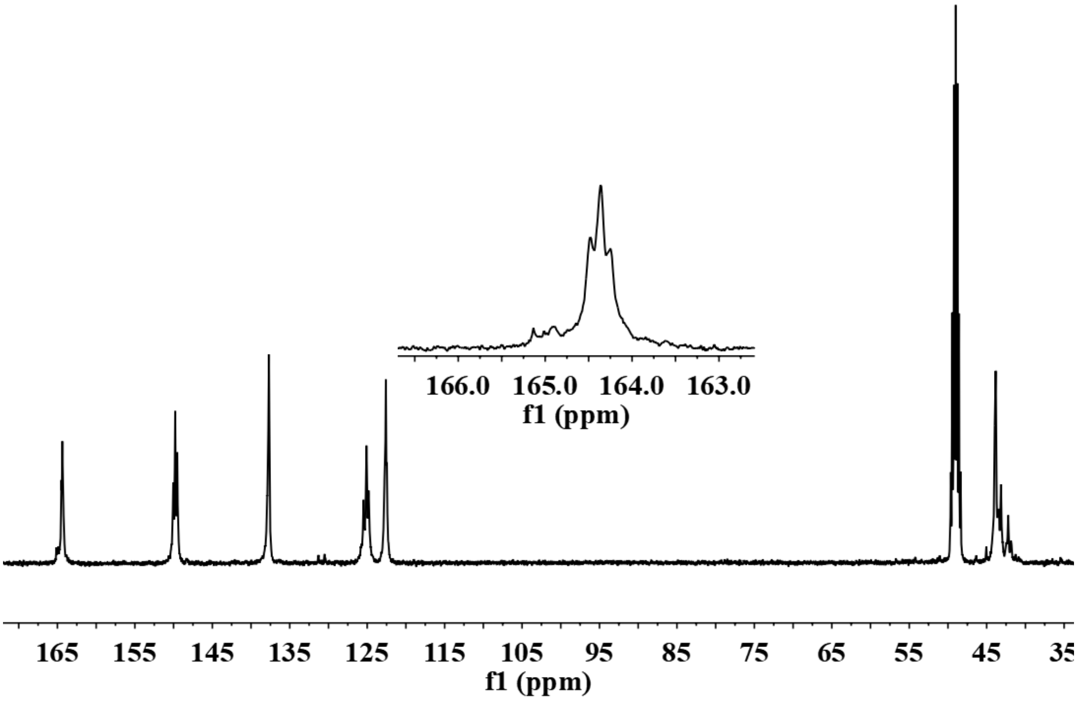

Figure S8. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 ℃ in CD_3OD (run 13, Table 1).

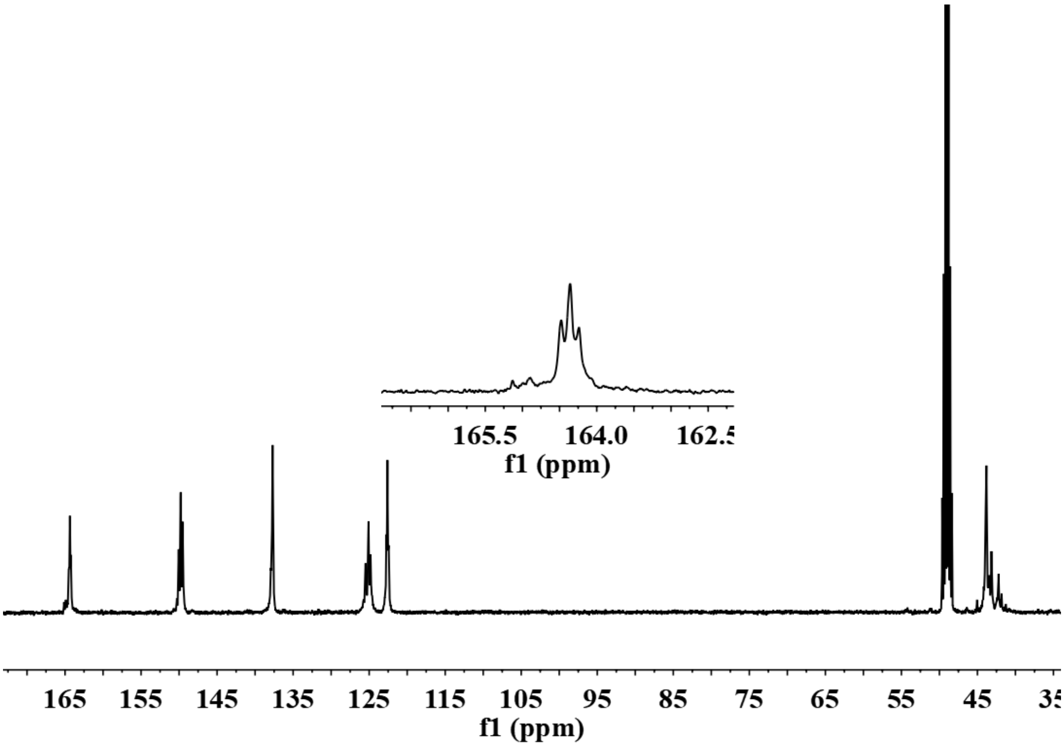

Figure S9. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 ℃ in CD_3OD (run 14, Table 1).

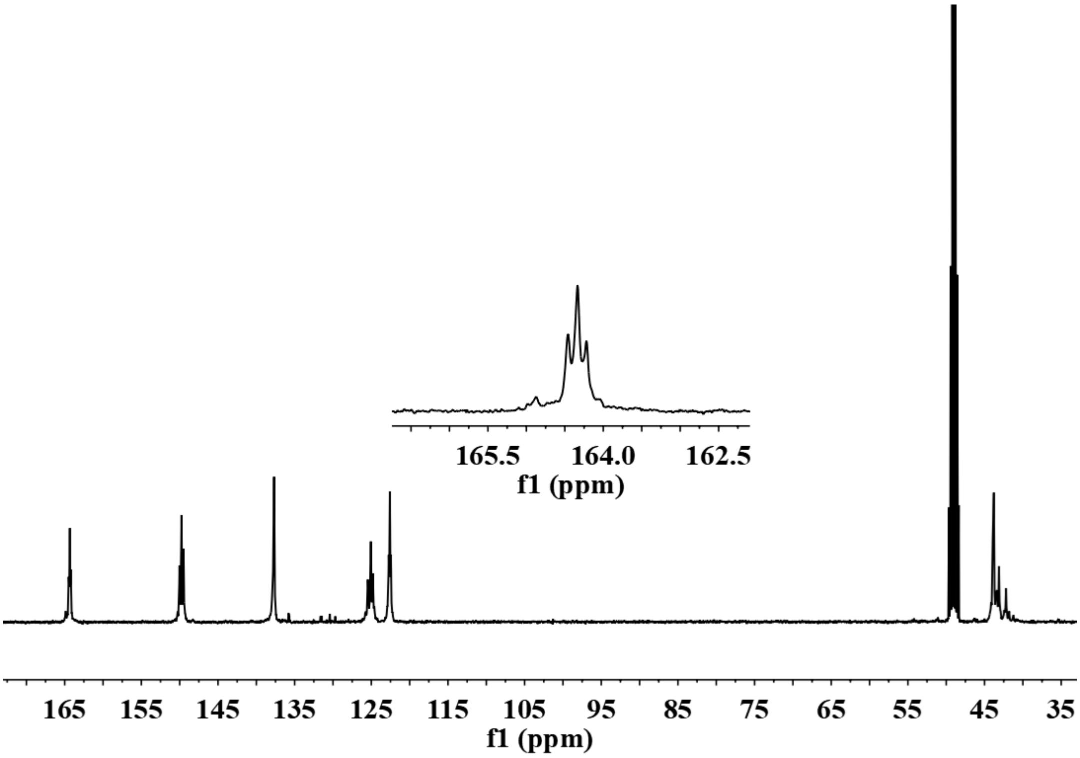

Figure S10. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 °C in CD$_3$OD (run 15, Table 1).

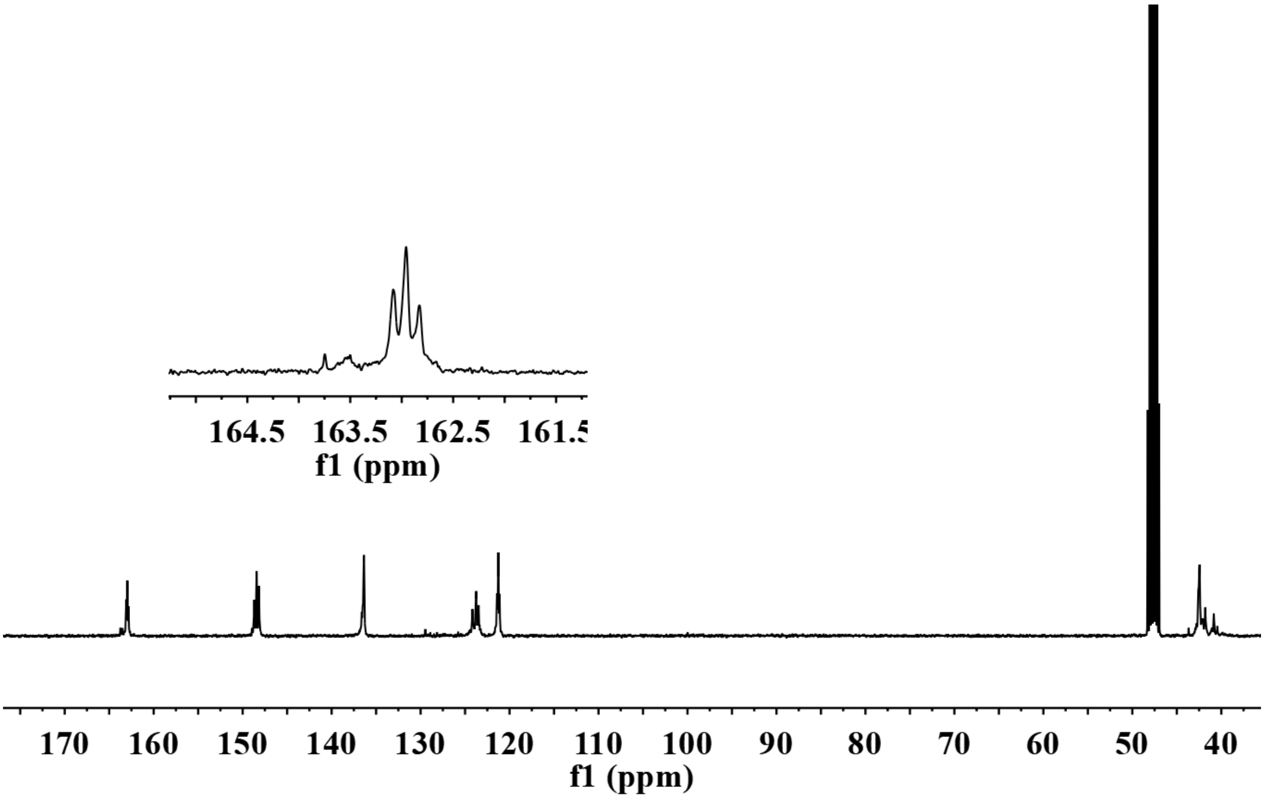

Figure S11. The ^{13}C NMR spectrum of P2VP obtained from 2VP by using catalyst **1** in toluene at 25 °C in CD$_3$OD (run 18, Table 1).

REFERENCES

[1] Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910-13911.