

Electronic Supplementary Information

Polystyrenes with Chiral Phosphoramidate Substituents as Lewis-base Catalysts for Asymmetric Addition of Allyltrichlorosilane: Enhancement of Catalytic Performance by Polymer Effect

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Experimental

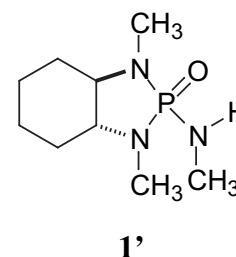
General. ¹H-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz) in CDCl₃ by the use of tetramethylsilane as an internal standard. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer. High performance liquid chromatographic analyses (HPLC) by using 2-propanol / *n*-hexane = 1 / 20 (v/v) as an eluent were carried out on a Shimadzu LC-6A with SPD-6AV UV spectrophotometer (Daicel CHIRALCEL[®] OD-H chiral column, eluting rate 500 μL / min). Optical rotations were measured with a Horiba SEPA-200 polarimeter by using chloroform as a solvent.

Unless otherwise noted, the materials were obtained from commercial sources. (*R,R*)-*N,N'*-Dimethylcyclohexane-1,2-diamine was prepared according to the literature [1]. 4-Vinylbenzylpiperazine was synthesised by a modified procedure of the literature [2]. Dichloromethane, chlorobenzene and triethylamine were distilled under nitrogen from CaH₂. THF and toluene were distilled from sodium diphenylketyl.

Synthesis of (*R,R*)-1. In a 300 mL four-necked flask equipped with mechanical stirrer, reflux condenser and dropping funnel were placed (*R,R*)-*N,N'*-dimethylcyclohexane-1,2-diamine (1.8 g, 13 mmol), triethylamine (7.3 mL, 52 mmol), a small amount of inhibitor and chlorobenzene (30 mL). Phosphoryl chloride (1.2 mL, 13 mmol) was added dropwise to the solution at 0 °C and the system was refluxed for 4 hours. 4-Vinylbenzylpiperazine (2.6 g, 13 mmol) in 70 mL of chlorobenzene was added dropwise to the mixture and reflux was kept for further 24 hours. The resulting mixture was cooled to ambient temperature and filtered. The filtrate was concentrated with rotary evaporator and extracted with dichloromethane-0.5 N NaOHaq. The organic layer was dried with anhydrous MgSO₄, filtered and evaporated to give crude (*R,R*)-1. Recrystallisation from hexane afforded (*R,R*)-1 in 58 % yield (3.0 g). ¹H-NMR(δ, ppm) 1.27 (m, 4H), 1.8 – 2.0 (m, 4H), 2.37 (t, *J* = 4.6 Hz, 4H), 2.47 (-CH₃, t, *J* = 9.2 Hz, 6H), 2.5 – 2.7 (m, 2H), 3.15 (m, 4H), 3.49 (N-CH₂-Ar, s, 2H), 5.21 (dd, *J* = 10.9, 0.81 Hz, 1H), 5.72 (dd, *J* = 17.7, 1.1 Hz, 1H), 6.71 (dd, *J* = 17.8, 11.3 Hz, 1H), 7.30 (Ar-H, m, 4H). $[\alpha]_{\text{D}}^{20} = -65.5^{\circ}$ (*c* = 1.0, CHCl₃).

Synthesis of (*R,R*)-2. Into a 300 mL four-necked flask equipped with mechanical stirrer, reflux condenser and dropping funnel were added (*R,R*)-*N,N'*-dimethylcyclohexane-1,2-diamine (8.4 g, 60 mmol), triethylamine (20 mL, 150 mmol) and toluene (120 mL). Phosphoryl chloride (5.5 mL, 60 mmol) was added dropwise to the solution at 0 °C and the system was refluxed for 4 hours. The system was cooled to -78 °C and methylamine (30 g, 0.95 mol) in toluene (50 mL) was added dropwise. The temperature was gradually raised to 80 °C and the mixture was stirred for 24 hours. The resulting precipitate was filtered off, and the filtrate was concentrated with rotary evaporator and extracted with dichloromethane-0.5N NaOHaq. The organic layer was

dried with anhydrous MgSO₄, filtered and evaporated to give crude (*R,R*)-**1'**. Recrystallisation from hexane afforded (*R,R*)-**1'** in 94 % yield (12.0 g).



NaH (0.40 g, 17 mmol), a small amount of inhibitor and toluene (8.0 mL) were placed in a 100 mL four-necked flask equipped with mechanical stirrer, reflux condenser and dropping funnel. To the mixture was added dropwise (*R,R*)-**1'** (3.1 g, 14 mmol) in 10 mL of toluene. After the system was heated to 50 °C, 4-chloromethylstyrene (3.0 mL, 21 mmol) was added and the mixture was stirred for 12 hours. 10 mL of water was poured into the reaction system and the resulting mixture was extracted with dichloromethane. The organic layer was dried with anhydrous MgSO₄, filtered and evaporated to give crude (*R,R*)-**2**. Purification by column chromatography on silica gel (chloroform : methanol = 9 : 1) afforded (*R,R*)-**2** in 77% yield (3.7 g). ¹H-NMR(δ, ppm) 1.30 (m, 4H), 1.8 – 2.0 (m, 4H), 2.52 (-CH₃, m, 9H), 2.5 – 2.8 (m, 2H), 4.22 (N-CH₂-Ar, m, 2H), 5.24 (d, *J* = 11.9 Hz, 1H), 5.76 (d, *J* = 17.1 Hz, 1H), 6.70 (dd, *J* = 17.6, 11.1 Hz, 1H), 7.34 (Ar-H, m, 4H). [α]_D²⁰ = -62.7° (*c* = 1.0, CHCl₃).

Polymerisation. Radical polymerisations of chiral phosphoramidate monomers (*R,R*)-**1** and (*R,R*)-**2** were carried out in chlorobenzene (*ca.* 2.0 M) at 80 °C for 24 hours in the presence of 5 mol% of AIBN. The resulting solution was poured into diethyl ether (poly**1**) or hexane (poly**2**) and the polymer collected by suction filtration was dried *in vacuo* at 60 °C for 24 hours. Copolymerisations of chiral monomers with styrene were also conducted by similar procedures. Yield, reduced viscosity and specific rotation of the obtained polymers are shown in Table 1. ¹H-NMR spectra of the homopolymers and the representative copolymers (poly**1**(47)-St and poly**2**(71)-St) are shown in Figures S1

– S4. No peak assigned to the protons of the vinyl group was observed in all the ^1H -NMR spectra of the homo- and copolymers.

Asymmetric allylation. In a 30 mL three-necked flask equipped with mechanical stirrer were placed polymeric catalyst poly**2** (98.4 mg, 0.295 mmol of phosphoramidate unit), ethyldiisopropylamine (2.6 mL, 15 mmol) and dichloromethane (10 mL) and the solution was cooled to $-78\text{ }^\circ\text{C}$. Allyltrichlorosilane (0.621 g, 3.54 mmol) was added dropwise to the solution. After being stirred for 10 minutes, benzaldehyde (0.313 g, 2.95 mmol) was added and the mixture was stirred at $-78\text{ }^\circ\text{C}$ for 6 hours. The resulting mixture was poured into an ice-cold mixed solution of saturated NaHCO_3 (10 mL) and saturated KF (10 mL) with vigorous stirring. The mixture was stirred at room temperature for 2 hours. The precipitate was filtered off and the filtrate was extracted by dichloromethane (4 times). The combined organic layer was dried over MgSO_4 and concentrated under reduced pressure. The obtained liquid was added dropwise to a large amount of hexane. After overnight stirring, the supernatant was recovered and evaporated to give the crude product. Purification by silica gel chromatography (dichloromethane : hexane = 3 : 1) afforded 1-phenyl-3-buten-1-ol in 84% yield (0.37 g). Enantiomeric excess of the product was 63% ee (*R*).

References

- [1] Alexandre, A.; Mutti, S.; Mangeney, P. *J. Org. Chem.* **1992**, *57*, 1224.
- [2] Craig, J. C.; Young, R. J. *Org. Synth.* **1973**, *Coll. Vol. 5*, 88.

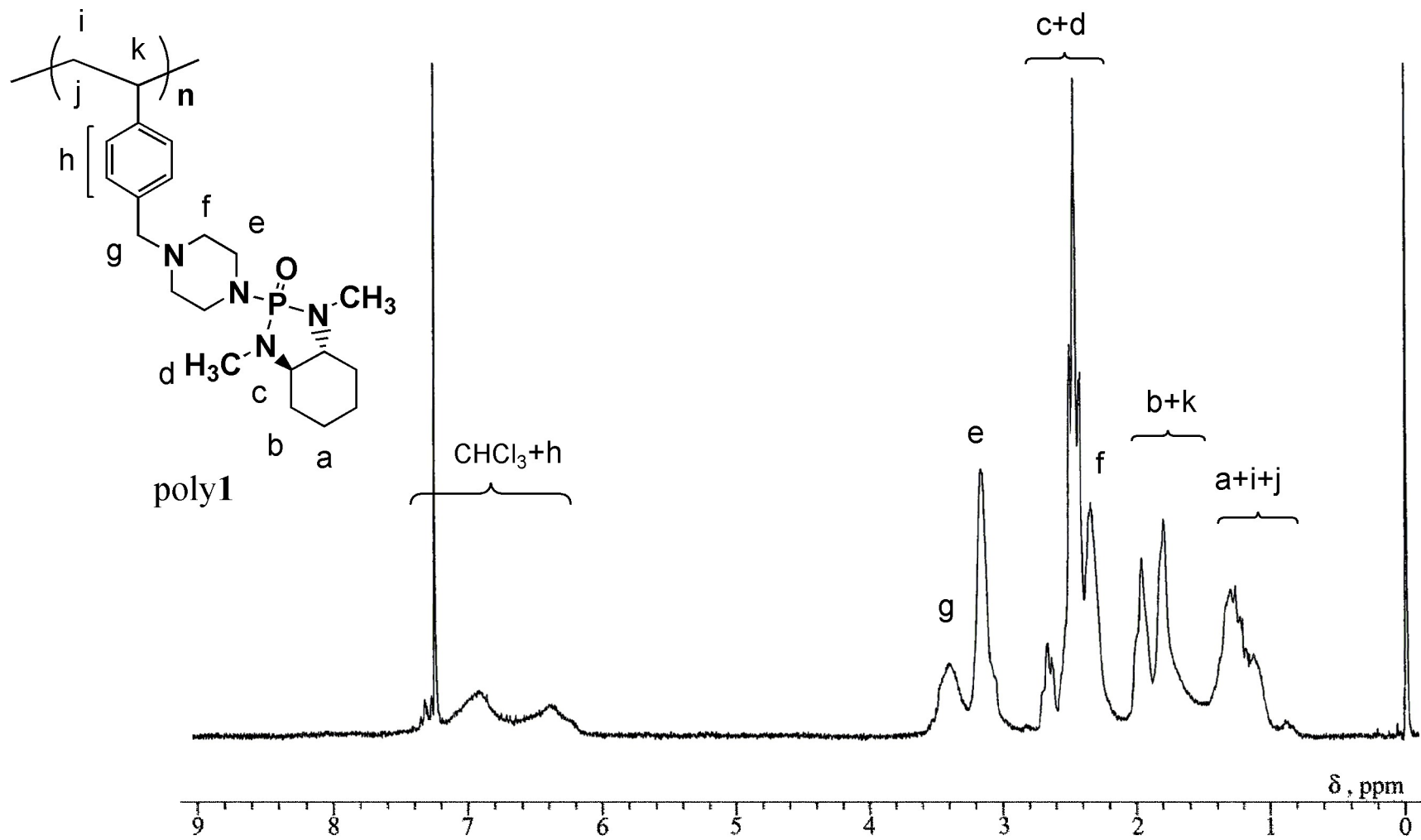


Figure S1 ¹H-NMR spectrum of poly1 (CDCl₃, 60°C)

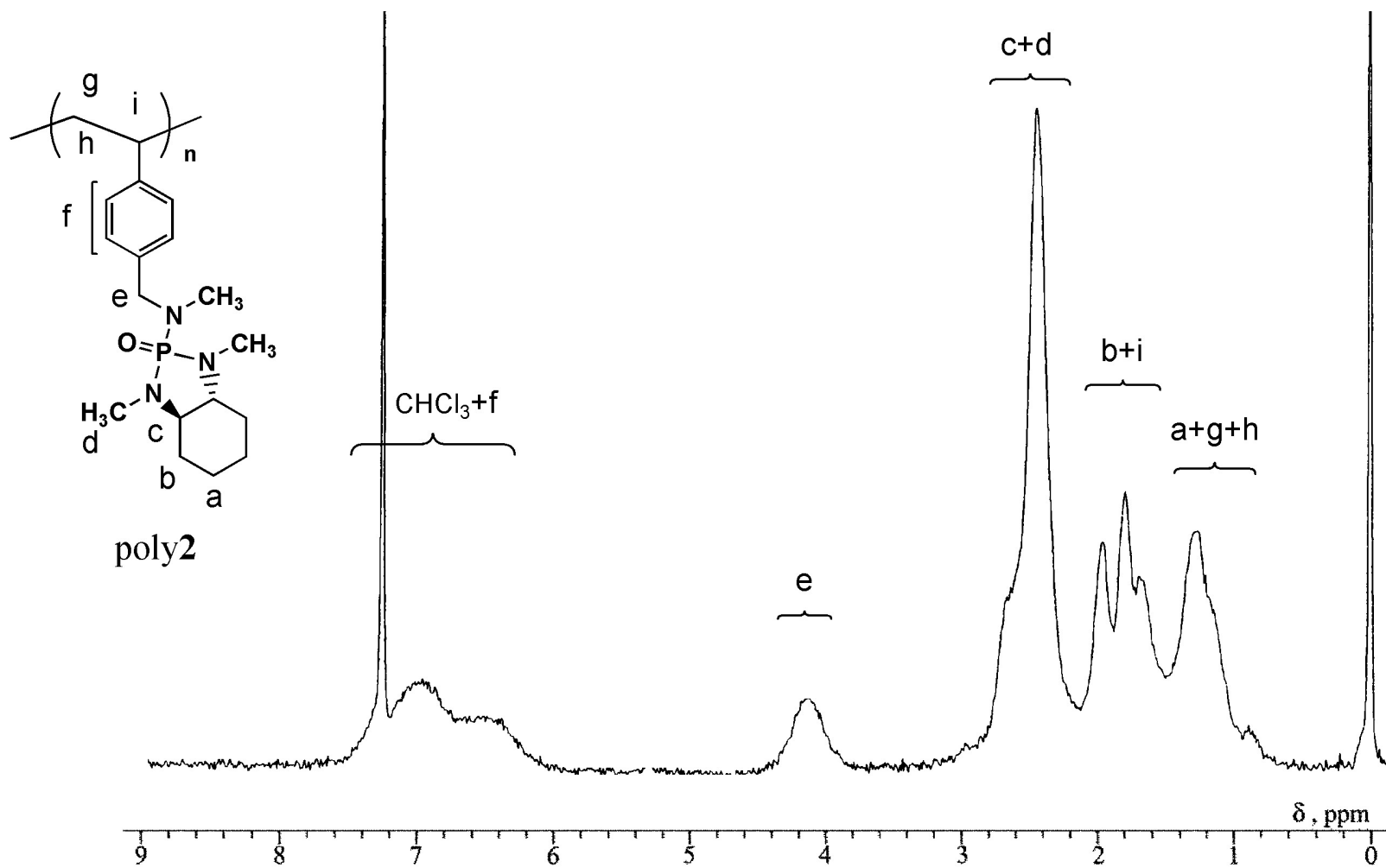


Figure S2 $^1\text{H-NMR}$ spectrum of poly2 (CDCl_3 , 60°C)

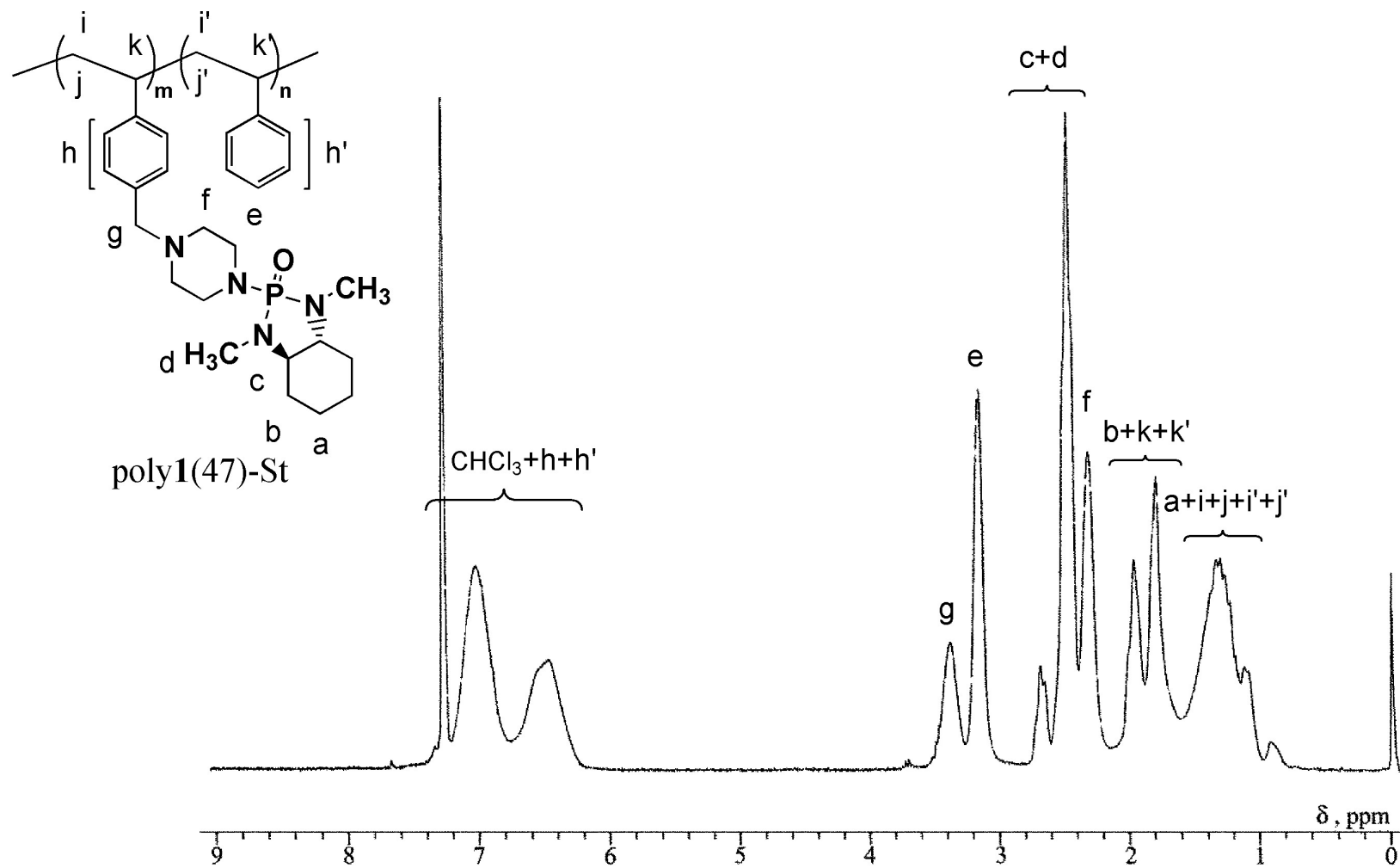


Figure S3 ¹H-NMR spectrum of poly1(47)-St (CDCl₃, 60°C)

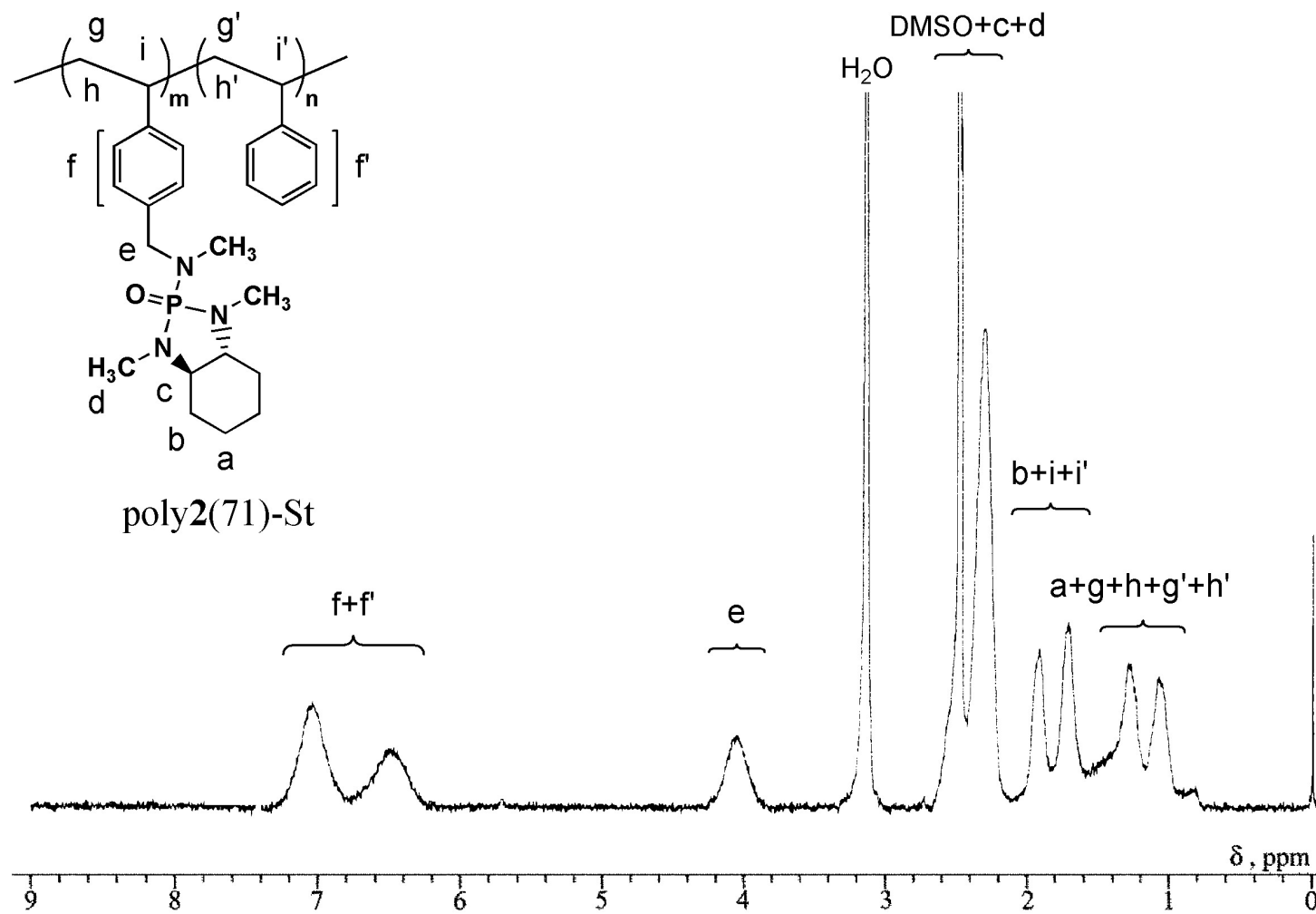


Figure S4 $^1\text{H-NMR}$ spectrum of poly2(71)-St (DMSO- d_6 , 60°C)