



# Cobalt-catalyzed selective dehydrocoupling polymerization of prochiral silanes and diols

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## ABSTRACT

As a kind of material possessing thermal stability, biocompatibility and degradability, polysilylethers (PSEs) have potential applications. Different catalytic systems have been developed for the synthesis of PSEs. However, the resulted PSEs have similar structure, which is unfavorable for adjusting its properties. We herein synthesized a series of novel PSEs with pendant Si–H groups via cobalt-catalyzed selective dehydrocoupling polymerization. Various diols and prochiral silanes are suitable for this method. This novel PSEs could also be obtained via a Co-catalyzed one-pot two-step process. Furthermore, asymmetric dehydrocoupling polymerization was studied and high- $M_n$  PSE was obtained. After the cleavage of PSE by methyl magnesium iodide, chiral silane was obtained with high yield and moderate enantioselectivity.

## 1. Introduction

Because of possessing various properties and abundant reserves of Si and O in the earth's crust [1], developing polymer containing a silicon-oxygen bond in the mainchain has been a hot topic. Until now, several polymeric materials containing Si–O bond in the mainchain have been developed and applied, including polysiloxanes, polysilylethers, polysilylestere, etc. [2]. These polymeric materials usually exhibit similar properties, such as low  $T_g$ , good thermal stability, biocompatibility, high gas permeability, degradability, etc. [3]. Among these polymers, polydimethylsiloxane (PDMS) possesses high flexibility and thermal stability, which has been successfully used as silicon oil, elastomer, adhesives, coatings, etc. [4–6].

Due to the combination of favorable properties of polycarbosilanes and polysiloxanes, polysilylethers have gradually attracted the attention in the past few decades [2]. In the early work, the synthesis of PSEs was often realized by the polycondensation of diols and dichlorosilanes or dianilinosilanes [7]. However, equivalent base or vacuum condition is required to furnish high- $M_n$  PSEs, which has negative influence on the atom-economy and further application of polymerization [8]. Afterwards, Nishikubo's group synthesized a new kind of polysilylethers with reactive pendant chloromethyl groups via TPBC catalyzed polyaddition of bis(epoxide)s and volatile dichlorosilanes [9]. In order to replace the unstable chlorosilanes, silanes were gradually applied to the synthesis of PSEs via dehydrocoupling [10] and hydrosilylation polymerization [11].

As an efficient and high atom-economic way to synthesize PSEs, dehydrocoupling polymerization has been catalyzed by the catalysts derived from precious transition metals such as palladium, platinum, rhodium, and ruthenium [12]. Various silanes and diols were used for providing PSEs with different thermal stability and degradability. In despite of these advance, drawbacks of these catalytic systems based on noble metals, such as high cost, low abundance, high catalyst loading and biological compatibility become increasingly the key problem of its development [13]. Thus, use of catalysts based on first-row transition metals like iron (Fe), manganese (Mn) and cobalt (Co) is much more sustainable for addressing the disadvantages of precious metals. Recently, the catalytic systems derived from manganese and iron have been reported [14]. However, Co-catalyzed dehydrocoupling polymerization of silanes and diols has not been developed. Moreover, another problem of the development of PSEs is that most of the PSEs reported before have similar structure and framework, which is unfavorable for adjusting its properties and expanding its applications. In 2000, Rh-catalyzed selective dehydrocoupling of prochiral silanes and diols was developed by the group of Kawakami, giving novel PSEs with pendant Si–H groups and up to 39.8% average ee of silicon atoms [15]. The reactive Si–H groups of these PSEs may react with water or divinyl compounds, which will have potential in the application as chiral column packing materials. Although the stereoselectivity of the polymerization was still not satisfactory, these results provided a new developing trend of PSEs. In the context of our continuous interest in

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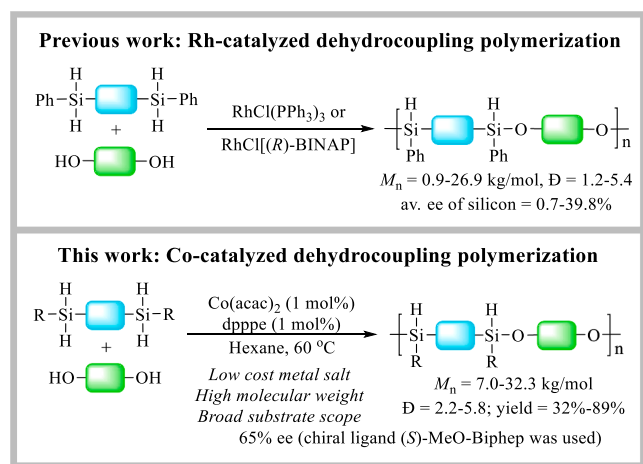
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**Scheme 1.** Transition-metal-catalyzed selective dehydrocoupling polymerization.

transition-metal-catalyzed dehydrocoupling polymerization [16], herein we reported cobalt-catalyzed selective dehydrocoupling polymerization of prochiral silanes and diols, furnishing a series of high- $M_n$  PSEs containing pendant Si-H groups. Furthermore, an asymmetric version of this transformation was also studied; moderate 65% of enantioselectivity was obtained. (Scheme 1).

## 2. Results and discussion

Original experiments employed silane **1a** and diol **2a** at 60 °C in the presence of  $\text{Co}(\text{acac})_2/\text{dppb}$  as a catalyst (Table 1). Initially, the reaction was conducted in THF, giving a polymer with moderate  $M_n$  and high yield (entry 1). When the ligand was removed, an oligomer was obtained, which indicated phosphine ligand play a vital role in the polymerization (entry 2). Then, the solvent effect was screened. It was found that high yields were also achieved in MeCN, <sup>t</sup>BuOMe and <sup>n</sup>hexane (entries 3,5,7). Among these solvents, <sup>n</sup>hexane was proved to be the best choice.

Intrigued by these promising results, the effects of ligand, reaction temperature and metal precursor were conducted (Table 2). Interestingly, for ligands with different chain length,  $M_n$  and yields of products increased first and then decreased as chain length of ligand increased (entries 1–4). Moreover, ligands with various skeleton were also screened (entries 5–6). For XantPhos, rigidity of ligand structure had adverse effect on the polymerization, giving the product with moderate molecular weight. When ligand was changed to (+/-)-BINAP, high  $M_n$  and yield were provided. In addition, the replacement of  $\text{Co}(\text{acac})_2$  with

**Table 1**

Optimization of conditions.<sup>a</sup>

Entry	Solvent	$M_n^b$	$\bar{D}^b$	Yield (%) <sup>c</sup>
1	THF	4400	1.63	86
2 <sup>d</sup>	THF	oligomer	–	53
3	<sup>t</sup> BuOMe	9100	2.74	83
4	DCM	–	–	–
5	MeCN	6300	2.19	80
6	PhMe	oligomer	–	35
7	<sup>n</sup> hexane	13,500	3.05	86

<sup>a</sup> Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol),  $\text{Co}(\text{acac})_2$  (1 mol%),  $\text{dppb}$  (1 mol%), solvent (2.0 mL), 60 °C.

<sup>b</sup> Determined by GPC with RI.

<sup>c</sup> Isolated yield.

<sup>d</sup> Without ligand.

**Table 2**

Further optimization of conditions.<sup>a</sup>

Entry	T (°C)	L	$M_n^b$	$\bar{D}^b$	Yield (%) <sup>c</sup>
1	60	dppm	–	–	–
2	60	dppb	13,500	3.05	86
3	60	dpppe	24,900	3.33	88
4	60	dpph	9800	2.17	85
5	60	XantPhos	8200	3.64	88
6	60	(+/-)-BINAP	17,700	2.12	92
7 <sup>d</sup>	60	dpppe	12,500	3.03	85
8	40	dpppe	oligomer	–	–
9	80	dpppe	28,300	2.16	40

<sup>a</sup> Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol),  $\text{Co}(\text{acac})_2$  (1 mol%), L (1 mol%), <sup>n</sup>hexane (2.0 mL).

<sup>b</sup> Determined by GPC with RI.

<sup>c</sup> Isolated yield.

<sup>d</sup>  $\text{Co}(\text{acac})_2$  was replaced with  $\text{Co}(\text{acac})_3$ .

$\text{Co}(\text{acac})_3$  resulted in PSE with lower  $M_n$ , which suggested  $\text{Co}(\text{acac})_3$  might be reduced to  $\text{Co}(\text{acac})_2$  during the polymerization (entry 7). Considering the  $M_n$ ,  $\bar{D}$  and yield of product, dpppe was proved to be beneficial for the reaction, furnishing the desired product with  $M_n$  of 24.9 kg/mol and 88% yield (entry 2). To further improve the efficiency of polymerization, the temperature was increased to 80 °C. However, yield decreased apparently, although molecular weight slightly increased (entry 9). Only oligomer was obtained by lowering temperature (entry 8). Thus, the optimized conditions were established as:  $\text{Co}(\text{acac})_2$  (1 mol%)/dpppe (1 mol%)/<sup>n</sup>hexane/60 °C.

With the optimized reaction conditions established, we next investigated the substrate scope by reacting various diols **2** with silane **1a** (Table 3). As expected, a diverse array of diols with different chain length could react smoothly under the standard conditions, giving the corresponding PSEs **3a-3e** with different  $\bar{D}$  and high molecular weight

**Table 3**

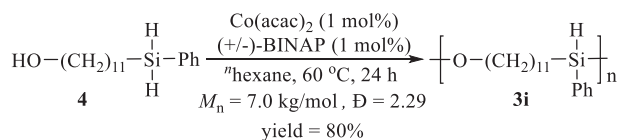
Co-catalyzed selective dehydrocoupling of AA and BB type monomers.<sup>a</sup>

Entry	Silane	Diol	$M_n^b$	$\bar{D}^b$	Yield (%) <sup>c</sup>
1	<b>1a</b>	<b>2a</b>	24,900	3.33	88 ( <b>3a</b> )
2	<b>1a</b>	<b>2b</b>	13,100	2.58	32 ( <b>3b</b> )
3	<b>1a</b>	<b>2c</b>	30,600	4.26	89 ( <b>3c</b> )
4	<b>1a</b>	<b>2d</b>	32,300	5.83	75 ( <b>3d</b> )
5	<b>1a</b>	<b>2e</b>	13,100	2.23	82 ( <b>3e</b> )
6	<b>1a</b>	<b>2f</b>	24,500	3.22	82 ( <b>3f</b> )
7	<b>1b</b>	<b>2a</b>	12,600	2.33	86 ( <b>3g</b> )
8	<b>1c</b>	<b>2a</b>	10,200	5.17	70 ( <b>3h</b> )

<sup>a</sup> Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol),  $\text{Co}(\text{acac})_2$  (1 mol%), dpppe (1 mol%), <sup>n</sup>hexane (2.0 mL), 60 °C.

<sup>b</sup> Determined by GPC with RI.

<sup>c</sup> Isolated yield.



**Scheme 2.** Co-catalyzed selective dehydrocoupling of AB type monomer.

(entries 1–5). Interestingly, when diol **2b** was applied to the polymerization, a gel with poor solubility in common organic solvents was provided, leading to low yield of polymer **3b** (entry 2). Notably, secondary alcohol **2f** could also react very well with silane **1a**, giving PSE **3f** with  $M_n$  of 24.5 kg/mol (entry 6).

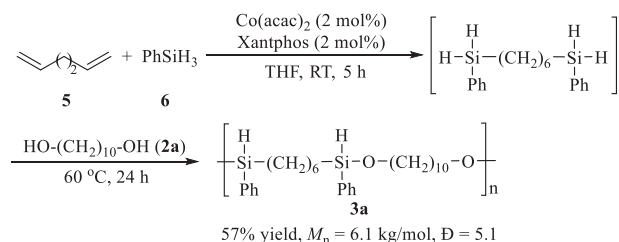
To further demonstrate the versatility of our method, the second stage of exploration of the reaction scope focused on various silanes. When the linker of silane **1a** was changed to aryl substituent, polymer **3g** was obtained with lower molecular weight (entry 7). Silane **1c** with methyl substituents on the silicon atoms could also react smoothly with diol **1a**, giving the desirable polymer **3h** with good yield and  $M_n$  of 11.8 kg/mol (entry 8).

For AB type monomer **4** derived from castor oil, low- $M_n$  polymer was obtained under the optimized conditions. However, it was found that when ligand was changed to (+/-)-BINAP, polymer **3i** was provided with good yield and  $M_n$  of 7.0 kg/mol (Scheme 2).

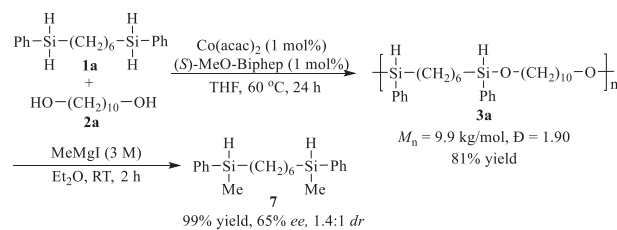
After purification by precipitation, thermal properties of polymers **3a** and **3g** were investigated under nitrogen atmosphere using TGA and DSC as shown in Figs. S25-S26 (Supporting information). Polymer **3a** showed higher  $T_5$  value than **3g**. However, the  $T_{50}$  value of **3g** was higher than **3a**. This could be attributed to the protection provided by more sterically hindered phenyl group. These two polymers exhibited indiscernible glass transition *via* DSC.

In consideration of  $\text{Co(acac)}_2/\text{XantPhos}$  act as potent tool in realizing regioselective hydrosilylation of alkenes [17], we tried Co-catalyzed one-pot two-step process (Scheme 3). In the first step, 1,5-hexadiene and phenylsilane were used as starting materials, giving the prochiral silane **1a** *via* hydrosilylation. Then, diol **2a** was added to react with in-situ prepared silane **1a** *via* Co-catalyzed dehydrocoupling polymerization. Satisfactorily, the corresponding polysilylether was obtained with moderate yield and  $M_n$ . These promising results indicated that this convenient one-pot two-step process could be applied to the synthesis of novel PSEs.

Chiral polymers have found widespread applications in the fields of chiral separation, nonlinear optics and chiral catalysis [19]. In contrast to the well-studied polymers with chirality in the side chain, the synthesis and application of polymers with chirality in the main chain are being actively explored [20]. In view of that selective dehydrocoupling polymerization could be applied to the synthesis of chiral polymer, the asymmetric version of dehydrocoupling polymerization was studied by employing cobalt catalysts in-situ generated from  $\text{Co(acac)}_2$  and chiral bisphosphine ligands (Scheme 4). After evaluating several chiral phosphine ligands, we found that asymmetric dehydrocoupling polymerization of prochiral silane **1a** and diol **2a** proceeded smoothly by employing (*S*)-MeO-Biphep, providing the chiral PSE with high yield and  $M_n$  of 9.9 kg/mol. In order to evaluate the stereoselectivity of polymers, methyl magnesium iodide in ether was used to



**Scheme 3.** Co-catalyzed one-pot two-step reaction.



**Scheme 4.** Co-catalyzed asymmetric dehydrocoupling polymerization.

react with PSE **3a**, giving the chiral silane **7** with 99% yield and 65% *ee*. This method is known to proceed with almost complete retention of the configuration of silicon atoms. Although these results are not satisfactory currently, this study exhibits a possibility of catalytic asymmetric dehydrocoupling of prochiral silanes with diols.

### 3. Conclusions

In summary, we have developed Co-catalyzed selective dehydrocoupling of prochiral silanes and diols with a catalyst generated from  $\text{Co(acac)}_2$  and *dppe*. Different types (AB type or AA and BB type) of monomers are suitable substrates for the polymerization. A series of novel PSEs with pendant Si-H groups were provided with good yields (up to 89% yield) and high molecular weight (up to 32.3 kg/mol). Moreover, the Co-catalyzed one-pot two-step process was realized. An asymmetric version of selective dehydrocoupling polymerization was also conducted, furnishing the corresponding PSE with high  $M_n$ . After the cleavage reaction, chiral silane was obtained with 99% yield and 65% *ee*. Further investigation will focus on the synthesis of chiral polymer.

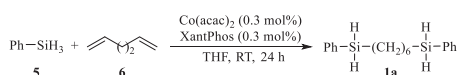
### 4. Experiments

#### 4.1. Reagents and instrumentation

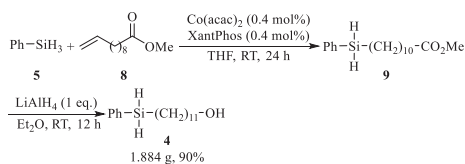
All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Diols **2a-f** were recrystallized from ethyl acetate. Other commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at room temperature in  $\text{CDCl}_3$  on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel. Infra-red spectra was recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail. Optical rotation was measured by polarimeter. GPC was performed on a Waters 1515 chromatography system equipped with Agilent PL1110 column using THF as the eluent (35 °C, 1 mL/min). Polystyrene standards were used for calibration. DSC was performed on a DSC Instruments 204 HP calorimeter (purge gas:  $\text{N}_2$ , flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: -100 to 300 °C). TGA was performed on a Setsys TGA (purge gas:  $\text{N}_2$ , flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: 40–800 °C).

#### 4.2. Synthesis of monomers

For monomers containing aromatic backbones, monomers **1b** and **1c** were conveniently prepared according to the literature method [9b,15,18]. For monomers containing aliphatic backbones, the synthesis of bis(silanes) containing four Si-H bonds could be realized by double hydrosilylation of dienes [21] and sequential double hydrosilylation of alkynes [22].



1,6-bis(phenylsilyl)hexane (**1a**) was conveniently prepared according to the modified literature method [17]. To an oven-dried 100 mL resealable Schlenk flask equipped with a magnetic stir bar was charged the Co(acac)<sub>2</sub> (15.6 mg, 0.06 mmol), xantphos (34.8 mg, 0.06 mmol) and THF (10 mL) under nitrogen. The solution was stirred at room temperature for 10 min. Then, phenylsilane (4.544 g, 42 mmol) and 1,5-hexadiene (1.574 g, 19 mmol) was added into the flask under nitrogen. The flask was stirred at room temperature for 12 h under nitrogen. Then, the resulting solution was concentrated *in vacuo*. The crude product was dissolved with hexanes, and the solution was filtered through a short pad of silica gel. The filtrate was collected and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes) to give a colorless viscous oil. To improve the polymerization performance of monomer, an anhydration process is necessary to reduce moisture content of monomer. CaH<sub>2</sub> (500 mg) was added to the monomer **1a** and the mixture was stirred overnight. The mixture was distilled under reduced pressure to obtain the anhydrous monomer **1a** (4.307 g, 76%) as a colorless liquid. Known compound [21]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74–7.54 (m, 4H), 7.51–7.31 (m, 6H), 4.32 (t, *J* = 3.7 Hz, 4H), 1.52–1.37 (m, 8H), 0.99–0.92 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.4, 132.9, 129.7, 128.1, 32.6, 25.1, 10.2.



11-(phenylsilyl)undecan-1-ol (**4**) was conveniently prepared according to the modified literature method [17]. To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged the Co(acac)<sub>2</sub> (7.7 mg, 0.03 mmol), xantphos (17.4 mg, 0.03 mmol) and THF (5 mL) under nitrogen. The solution was stirred at room temperature for 10 min. Then, phenylsilane (0.893 g, 8.3 mmol) and methyl 10-undecenoate (1.486 g, 7.5 mmol) was added into the flask under nitrogen. The flask was stirred at room temperature for 24 h under nitrogen. Then, the resulting solution was concentrated *in vacuo*. The crude product **9** was obtained by filtering through a short pad of silica gel. The solvent was removed under vacuum. To the crude product was added Et<sub>2</sub>O (30 mL). The mixture was chilled on an ice bath and LiAlH<sub>4</sub> (300 mg, 7.5 mmol) was carefully added. The reaction mixture was allowed to warm to room temperature and stirring continued for 12 h. The reaction was quenched by the addition of an aqueous solution of Rochelle salt. The mixture was stirred vigorously. Then the aqueous layer was extracted with ethyl acetate (50 mL × 2). The combined organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (50:1–10:1 hexanes:ethyl acetate) to give a colorless viscous oil. To improve the polymerization performance of monomer, an anhydration process is necessary to reduce moisture content of monomer. Toluene (20 mL) and ethanol (5 mL) were added to the monomer **4**. The azeotropic solvent was evaporated by fractional distillation, and the anhydrous monomer **4** (1.881 g, 90%) was obtained as a colorless liquid. New compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66–7.51 (m, 2H), 7.48–7.29 (m, 3H), 4.29 (t, *J* = 3.7 Hz, 2H), 3.64 (t, *J* = 6.7 Hz, 2H), 1.63–1.50 (m, 2H), 1.49–1.43 (m, 2H), 1.40–1.22 (m, 14H), 0.99–0.91 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.4, 133.0, 129.6, 128.1, 63.2, 33.0, 33.0, 29.8, 29.7, 29.7, 29.6, 29.4, 25.9, 25.2, 10.2. IR (KBr) ν 3445, 3069, 2930, 2852, 2135, 1466, 1061, 849, 699, 660 cm<sup>-1</sup>. HRMS Calculated for C<sub>17</sub>H<sub>34</sub>NOSi [M + NH<sub>4</sub>]<sup>+</sup> 296.2404; found 296.2403.

### 4.3. General procedure for the polymerization of monomers

To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged the Co(acac)<sub>2</sub> (1.0 mg, 0.004 mmol), dppe (1.8 mg, 0.004 mmol) and THF (1 mL) under nitrogen. The solution was stirred at room temperature for 5 min. The solvent was removed under reduced pressure to in-situ prepare the catalyst. Then, "hexane (2 mL), monomer (0.4 mmol) were added into the flask under nitrogen. The flask was stirred at 60 °C for 24 h under nitrogen (connected to a nitrogen Schlenk line). During the last 6 h of the reaction time, H<sub>2</sub> produced during the reaction was replaced with nitrogen every 2 h. After the polymerization, the reaction mixture was cooled to room temperature, and the content was purified by the precipitation method.

All of the polymers are soluble in dichloromethane and insoluble in methanol. So, these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of as low as possible amount of dichloromethane (1–2 mL), then, cold methanol was added portionwise (15–20 mL) until it turned to a biphasic mixture. The top layer was taken out, and the bottom viscous/solid layer was washed with MeOH two times until it gave a white/light yellow color viscous/solid polymer. The resulting polymer was dried to a constant weight and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, GPC.

**Polysilylether (3a):** 166 mg, 88% yield, colorless soft solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73–7.48 (m, 4H), 7.47–7.28 (m, 6H), 5.05–4.74 (m, 2H), 3.79–3.38 (m, 4H), 1.59–1.20 (m, 24H), 1.01–0.80 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.2, 130.1, 128.1, 65.1, 32.8, 32.6, 29.7, 29.5, 25.9, 23.0, 14.2.

**Polysilylether (3b):** 61 mg, 32% yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71–7.54 (m, 4H), 7.52–7.28 (m, 6H), 5.05–4.83 (m, 2H), 3.84–3.53 (m, 4H), 1.64–1.49 (m, 4H), 1.47–1.17 (m, 22H), 0.99–0.81 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.2, 130.1, 128.1, 65.1, 32.8, 32.6, 29.8, 29.7, 29.6, 25.9, 23.0, 14.2.

**Polysilylether (3c):** 177 mg, 89% yield, colorless soft solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82–7.49 (m, 4H), 7.49–7.26 (m, 6H), 5.08–4.78 (m, 2H), 3.92–3.33 (m, 4H), 1.65–1.10 (m, 28H), 1.02–0.80 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.2, 130.1, 128.1, 65.1, 32.8, 32.6, 29.8, 29.6, 25.9, 23.0, 14.2.

**Polysilylether (3d):** 137 mg, 75% yield, colorless soft solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70–7.47 (m, 4H), 7.47–7.26 (m, 6H), 5.02–4.80 (m, 2H), 3.81–3.47 (m, 4H), 1.66–1.14 (m, 22H), 1.00–0.80 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.2, 130.1, 128.1, 65.0, 32.8, 32.6, 29.7, 29.5, 25.9, 23.0, 14.2.

**Polysilylether (3e):** 145 mg, 82% yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68–7.50 (m, 4H), 7.49–7.27 (m, 6H), 5.04–4.79 (m, 2H), 3.79–3.49 (m, 4H), 1.66–1.16 (m, 20H), 1.00–0.74 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.2, 130.1, 128.1, 65.0, 32.8, 32.5, 29.5, 25.8, 23.0, 14.2.

**Polysilylether (3f):** 142 mg, 82% yield, light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78–7.29 (m, 10H), 5.18–4.72 (m, 2H), 3.94–3.38 (m, 2H), 2.06–1.66 (m, 4H), 1.57–1.15 (m, 12H), 0.98–0.73 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.0, 134.1, 130.1, 128.0, 72.1, 70.4, 32.8, 32.5, 32.4, 30.7, 30.5, 23.0, 14.6.

**Polysilylether (3g):** 158 mg, 85% yield, light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91–7.54 (m, 8H), 7.53–7.28 (m, 6H), 5.55–5.27 (m, 2H), 3.93–3.55 (m, 4H), 1.69–1.46 (m, 4H), 1.40–1.06 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.6, 134.8, 134.2, 134.1, 130.5, 128.2, 65.2, 32.5, 29.7, 29.5, 29.5.

**Polysilylether (3h):** 93 mg, 70% yield, colorless soft solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80–7.46 (m, 4H), 5.12–4.86 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 4H), 1.63–1.51 (m, 4H), 1.37–1.19 (m, 12H), 0.51–0.39 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.1, 133.4, 64.9, 32.6, 29.7, 29.5, 25.9, -2.6.

**Polysilylether (3i):** 88 mg, 80% yield, colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67–7.54 (m, 2H), 7.49–7.30 (m, 3H), 5.04–4.80 (m, 1H), 3.76–3.58 (m, 2H), 1.60–1.50 (m, 2H), 1.46–1.12 (m, 16H),

0.98–0.81 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.6, 134.3, 134.2, 130.1, 128.1, 65.1, 33.3, 32.6, 29.8, 29.7, 29.6, 29.5, 25.9, 23.1, 14.3.

#### 4.4. Co-catalyzed one-pot two-step reaction

To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged the  $\text{Co}(\text{acac})_2$  (2.6 mg, 0.01 mmol), XantPhos (5.8 mg, 0.01 mmol) and THF (1 mL) under nitrogen. The solution was stirred at room temperature for 5 min. Then, phenylsilane (108 mg, 1 mmol) and 1,5-hexadiene (41 mg, 0.5 mmol) was added into the flask under nitrogen. The flask was stirred at room temperature for 5 h under nitrogen, giving the prochiral silane **1a** via hydrosilylation. Then, diol **2a** (87 mg, 0.5 mmol) was added to react with in-situ prepared silane **1a** via Co-catalyzed dehydrocoupling polymerization. The flask was stirred at 60 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the content was purified by the precipitation method. PSE **3a** was obtained with moderate yield and  $M_n$  (133 mg, yield = 57%,  $M_n$  = 6100,  $\bar{D}$  = 5.05).

#### 4.5. Co-catalyzed asymmetric dehydrocoupling polymerization

To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged  $\text{Co}(\text{acac})_2$  (1.3 mg, 0.005 mmol), (*S*)-MeO-Biphep (2.9 mg, 0.005 mmol) and THF (3 mL) under nitrogen. The solution was stirred at room temperature for 5 min. Then, monomer **1a** (0.5 mmol) and **2a** (0.5 mmol) were added into the flask under nitrogen. The flask was stirred at 60 °C for 24 h under nitrogen (connected to a nitrogen Schlenk line). During the last 6 h of the reaction time,  $\text{H}_2$  produced during the reaction was replaced with nitrogen every 2 h. After the polymerization, the reaction mixture was cooled to room temperature, and the content was purified by the precipitation method. Polymer **3a** was obtained with high molecular weight (189 mg, yield = 81%,  $M_n$  = 9900,  $\bar{D}$  = 1.90).

In order to evaluate the stereoselectivity of polymers, methyl magnesium iodide in ether was used to react with PSE **3a**. Procedure for the cleavage reaction of PSE **3a**: To an oven-dried 50 mL Schlenk flask equipped with a magnetic stir bar was charged PSE **3a** (132 mg) and diethyl ether (3 mL) under nitrogen.  $\text{MeMgI}$  (3 M, 0.4 mL) in ether was added dropwise in 2 min. The flask was stirred at room temperature for 2 h under nitrogen. To the flask was added hexanes (20 mL). The product was purified by filtering through a short pad of silica gel. Chiral silane **7** (90 mg, 99% yield) was obtained as a colorless liquid.

(+)-1,6-Bis(methyl(phenyl)silyl)hexane (**7**): 90 mg, 99% yield. colorless liquid.  $[\alpha]_D^{20}$  = +3.92 (c 1.30,  $^n\text{hexane}$ ), new compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61–7.50 (m, 4H), 7.44–7.30 (m, 6H), 4.39–4.31 (m, 2H), 1.44–1.30 (m, 8H), 0.90–0.76 (m, 4H), 0.34 (d,  $J$  = 3.8 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 134.5, 129.3, 128.0, 33.0, 24.4, 13.5, –5.5. HRMS Calculated for  $\text{C}_{20}\text{H}_{34}\text{NSi}_2$   $[\text{M} + \text{NH}_4]^+$  344.2224; found 344.2243. HPLC: Chiracel OD-H column, 230 nm, 30 °C,  $^n\text{hexane}/i\text{-PrOH}$  = 100/0, flow = 0.6 mL/min, retention time 13.2 min, 15.1 min (meso) and 17.7 min (maj).

#### CRedit authorship contribution statement

**Xiao-Yong Zhai**: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **Xiao-Qing Wang**: Investigation. **Yong-Gui Zhou**: Supervision, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

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