



CuH-catalyzed consecutive hydrosilylation/dehydrocoupling polymerization of difunctional hydroxyketones with dihydrosilanes for syntheses of chiral poly(silyl ether)s

Xiao-Qing Wang^{a,b}, Bo Wu, Ph.D.^{a,*}, Yu-Qing Bai^a, Xiao-Yong Zhai^a, Yong-Gui Zhou, Ph.D.^{a,*}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

The development of structurally diverse chiral polymers via asymmetric polymerization of prochiral monomers is the frontier in polymeric chemistry. Herein, the easy-to-operate and efficient CuH-catalyzed consecutive asymmetric hydrosilylation/dehydrocoupling polymerization of difunctional hydroxyketone monomers with dihydrosilanes has been developed, providing the chiral poly(silyl ether)s. This polymerization features atom economy, low catalyst loading, broad substrate scope, mild condition, high stereoselectivity and reactivity. The results of DSC revealed poly(silyl ether)s exhibited good thermal properties.

1. Introduction

Synthesis of poly(silyl ether)s is a significant topic in polymeric chemistry [1–3] because of their importance in high-temperature elastomers, conductive materials, chiral column packing materials and degradable materials [4]. Of note, chiral poly(silyl ether)s have emerged as one of the most important class of polymers with a promising role in asymmetric catalysis and chiral stationary phases [5]. However, the efficient enantioselective methods to access poly(silyl ether)s are very finite. To date, there are only two examples [5,6]. In 2000, Kawakami's group firstly disclosed the synthesis of optically active poly(silyl ether)s by Rh-mediated cross-dehydrocoupling polymerization with moderate enantioselectivities (up to 40% a.v. ee) (Scheme 1a) [5]. Very recently, our group has successfully synthesized highly optically active poly(silyl ether)s via hydrosilylation polymerization (up to 99% ee) (Scheme 1b) [6]. The current methods to offer the chiral poly(silyl ether)s mainly focused on asymmetric dehydrocoupling polymerization and hydrosilylation polymerization. Considering the potential application of chiral poly(silyl ether)s, the evolution of a novel approach for preparation of structural diverse chiral poly(silyl ether)s remains on the chemists' wish list.

Nowadays, consecutive hydrosilylation/dehydrocoupling polymerization of difunctional hydroxyaldehyde monomers with silanes is the most atom-economic complement to access structurally diverse achiral

poly (silyl ether)s [7–9]. However, this protocol has some substantial challenges: 1) the more complex chain structure of poly(silyl ether)s, head-to-head, head-to-tail and tail-to-tail might be involved [8,9]; 2) the compatibility of catalytic systems for both hydrosilylation and dehydrocoupling. Despite of these difficulties, some efforts have been devoted to consecutive hydrosilylation/ dehydrocoupling polymerization. In 2019, Cui's group designed the monomer from the biomass to achieve consecutive hydrosilylation/dehydrocoupling polymerization through the combination of $\text{LZnH/B(C}_6\text{F}_5)_3$ as catalyst (Scheme 1c) [7]. Monomer 5-hydroxymethyl furfural, hydrosilylation of formyl group and silylation of alcohol would provide the same structural unit, which ensured the desired poly(silyl ether)s with single chain structure. Later on, Thomas and co-workers developed an elegant method for consecutive hydrosilylation/dehydrocoupling polymerization of 5-hydroxymethyl furfural using the well-defined platinum complexes (Scheme 1c) [8]. In addition, this catalyst system was also suitable for monomers of vanillin or syringaldehyde, furnishing degradable poly(silyl ether)s with Mn value up to 6000 (Scheme 1c). To achieve consecutive hydrosilylation/dehydrocoupling polymerization, the complex catalysts need to be prepared in advance and monomers are limited to the hydroxyaldehydes. To the best of our knowledge, consecutive asymmetric hydrosilylation/dehydrocoupling polymerization of readily available difunctional hydroxyketone monomers has not been reported. Hence, the development of asymmetric consecutive hydrosilylation/

* Corresponding authors at: State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China.

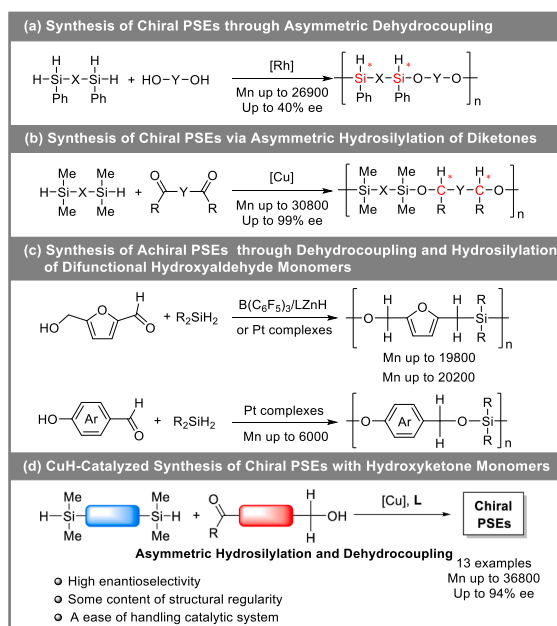
E-mail addresses: bowu@dicp.ac.cn (B. Wu), ygzhou@dicp.ac.cn (Y.-G. Zhou).

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Scheme 1. The Synthesis of Chiral Poly(silyl ether)s.

dehydrocoupling polymerization to synthesize structurally diverse chiral poly(silyl ether)s is highly in need, especially via an ease of handling catalytic system.

The concise CuH-catalyzed system shows high reactivity not only in dehydrocoupling polymerization of dihydrosilanes with diols [10], but also in asymmetric hydrosilylation polymerization of dihydrosilanes with diketones [6]. Thus, we wonder whether CuH-catalyzed system could be extended to synthesize the chiral poly(silyl ether)s using difunctional hydroxyketone monomers. Considering chiral polymers with vital performance [15,16], herein, we describe our initial development of chiral poly(silyl ether)s via CuH-catalyzed consecutive asymmetric hydrosilylation/dehydrocoupling polymerization of difunctional hydroxyketone monomers (Scheme 1d). This polymerization has merits of broad substrate scope, operational simplicity, environmental benign, good reactivity and excellent enantioselectivity (up to 95% yield and 94% ee). The poly(silyl ether)s with some content of structural regularity could be confirmed by NMR spectroscopy. The polymers containing silicon-oxygen single bond in the main chain could be selectively hydrolyzed to give the chiral diols, which could precisely characterize optical purity of poly(silyl ether)s.

2. Results and discussion

To test the viability of our proposed protocol, the study of consecutive asymmetric hydrosilylation/dehydrocoupling polymerization was initiated with model dihydrosilane monomer **1a** and difunctional hydroxyketone monomer **2a** (Table 1). Using copper cyclohexanebutyrate as metal precursor, toluene as solvent to perform the

Table 1

Optimization of Reaction Parameters.^a

Entry ^a	Solvent	[Cu]	L	Cat. (x mol%)	T (°C)	Mn ^b	PDI ^b	Yield (%) ^c	Ee (%) ^d
1	Toluene	CuR ₂ ¹	L1	2	50	7400	1.63	59	90.8
2	THF	CuR ₂ ¹	L1	2	50	4900	1.30	31	90.4
3	^t BME	CuR ₂ ¹	L1	2	50	10500	1.64	63	93.5
4	^t BME	Cu(OAc) ₂	L1	2	50	8100	1.69	66	93.2
5	^t BME	CuR ₂ ²	L1	2	50	9300	1.72	65	93.0
6	^t BME	CuR ₂ ¹	L2	2	50	7300	1.54	53	83.8
7	^t BME	CuR ₂ ¹	L3	2	50	9400	1.51	32	88.6
8	^t BME	CuR ₂ ¹	L4	2	50	7500	1.97	73	79.1
9	^t BME	CuR ₂ ¹	L5	2	50	7600	1.81	82	86.7
10	^t BME	CuR ₂ ¹	L6	2	50	8100	2.03	83	92.0
11	^t BME	CuR ₂ ¹	L7	2	50	6300	1.65	67	83.9
12	^t BME	CuR ₂ ¹	L8	2	50	10500	1.87	65	7.9
13	^t BME	CuR ₂ ¹	L6	1	50	9300	1.82	82	92.8
14	^t BME	CuR ₂ ¹	L6	0.5	50	6300	1.41	24	92.8
15	^t BME	CuR ₂ ¹	L6	1	30	5600	1.67	45	95.1
16	^t BME	CuR ₂ ¹	L6	1	60	8500	1.90	68	91.3
17	^t BME (0.75 mL)	CuR ₂ ¹	L6	1	50	14000	1.64	83	91.8

^a Reaction conditions: monomer (0.5 mmol), Cu cat. (x mol%), T °C, 24 h, solvent (1.5 mL). ^b Determined by GPC with RI. ^c isolated yield. ^d Measured by hydrolyzing the polymer and analyzing the resulting diol via HPLC. ^e CuR₂¹ = Copper(II) cyclohexanebutyrate. ^f CuR₂² = Copper(II) 2-ethyl hexanoate.

reaction at 50 °C, the polymerization took place, delivering poly(silyl ether) **3a** with moderate yield and high enantioselectivity (entry 1). Initially, solvents were evaluated (entries 1–3). A variety of solvents supported the polymerization, the best yield and enantioselectivity were obtained in *tert*-butyl methyl ether. Copper precursors had only marginal influence on the yields and stereoselectivities, giving **3a** in moderate yields (entries 4–5). Hence, the main challenge was to improve the reactivity of polymerization. Subsequently, various bisphosphine ligands were examined (entries 6–12). It was interesting to find that MeO-Biphep had a crucial influence on the reactivity (**L5–L7**), and electron-donating ligand **L6** was the best in overall terms (entry 10). **L8** gave **3a** in higher molecular weight, albeit with worse enantioselectivity (entry 12). Additionally, the molecular weight of poly(silyl ether) **3a** could be slightly improved, and the enantioselectivity was maintained when decreasing the catalyst loading to 1 mol% (entry 13). Next, the influence of temperature was explored (entries 15–16). Regardless of whether polymerization temperature was decreased or increased, the most suitable temperature was 50 °C in view of yield, molecular weight and enantioselectivity. Satisfactorily, the molecular weight of poly(silyl ether) **3a** was generally improved by increasing the monomer concentration from 0.17 to 0.34 M (entry 17). Thus, the optimized conditions of consecutive asymmetric hydrosilylation/dehydrocoupling polymerization were established: copper cyclohexanebutyrate (1 mol%)/ **L6** (1 mol%)/ *t*BME (0.75 mL)/ 50 °C.

Next, the scope of dihydrosilanes **1** was investigated under the optimized conditions (Table 2). Pleasingly, a series of commercial dihydrosilanes could efficiently polymerize with the difunctional hydroxyketone monomer **2a**, forming the target chiral poly(silyl ether)s

with good yields, high molecular weight and excellent stereoselectivities (up to 94% ee and 95% yield). However, introduction of phenyl ring link to the backbone of dihydrosilane furnished chiral poly(silyl ether) **3c** with lower molecular weight, which was attributed to the steric effect of silane. These results have suggested that consecutive asymmetric hydrosilylation/dehydrocoupling polymerization was suitable with a plethora of dihydrosilanes **1a–1e** (entries 1–5).

The generality of the protocol was further explored by evaluating various unsymmetrical monomers **2** containing mixed functional groups (Table 2). Variation of alkyl substituents of **2** had no obvious impact on the enantioselectivity and reactivity of polymerization (entries 6–7). For example, the consecutive asymmetric hydrosilylation/dehydrocoupling polymerization produced the poly(silyl ether)s **3f** and **3g** in good yields (82% and 87%) and excellent enantioselectivities (92% and 91%). For aryl substituted monomer **2d**, the polymerization proceeded smoothly with moderate molecular weight and enantioselectivity under the standard conditions (entry 8). In a similar fashion, a diverse array of monomers **2** with different chain length link were well compatible with the reaction conditions, giving the corresponding poly(silyl ether)s **3i–3j** with high enantioselectivities and molecular weight (entries 9–10). Changing the monomer to **2g**, the reactivity of polymerization was sluggish, resulting in 56% yield with **L1** as ligand after 72 h (entry 11). Chiral polymers especially those with hetero-atoms in main chain show a significant role in asymmetric catalysis [13]. To further gain insight into the utility of the consecutive asymmetric hydrosilylation/dehydrocoupling polymerization, we attempted to introduce thiophene functional group to the desired poly(silyl ether)s. To our satisfactory, the catalytic system exhibited good reactivities and enantioselectivities for

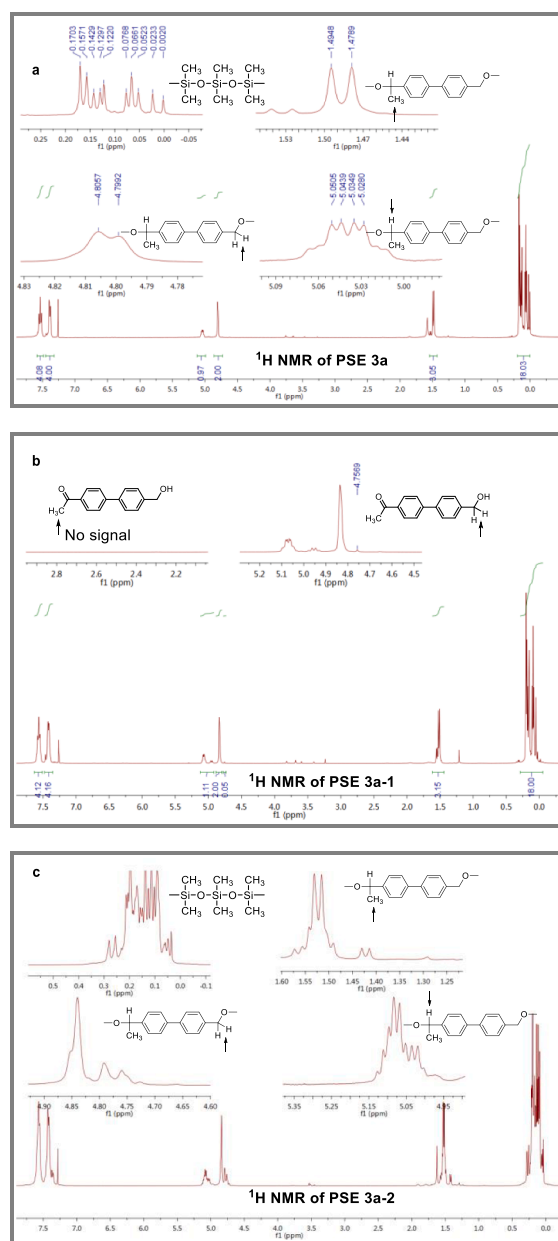
Table 2

<p style="text-align: center;">CuR₂ = Copper Cyclohexanebutyrate</p>							
Entry ^a	Dihydrosilanes 1	Hydroxyketones 2	Chiral PSEs 3	Mn ^b	PDI ^b	Yield (%) ^c	Ee (%) ^d
1	1a	2a	3a	14000	1.64	83	92
2	1b	2a	3b	9100	1.82	91	93
3	1c	2a	3c	3900	1.54	82	93
4	1d	2a	3d	36800	1.89	95	94
5	1e	2a	3e	13300	2.33	88	93
6	1a	2b	3f	8800	1.74	82	92
7	1a	2c	3g	12800	2.04	87	91
8	1a	2d	3h	6300	2.02	81	41
9	1a	2e	3i	11300	2.08	90	90
10	1a	2f	3j	13000	1.83	83	93
11 ^e	1a	2g	3k	10300	2.02	56	83
12	1a	2h	3l	11500	1.76	91	90
13	1a	2i	3m	12000	2.42	79	90

^a Reaction conditions: monomer (0.5 mmol), Cu cat. (1.0 mol %), 50 °C, 24 h, *tert*-Butyl methyl ether (0.75 mL). ^b Determined by GPC. ^c isolated yields. ^d Measured by hydrolyzing the polymer and analyzing the resulting diols via HPLC. ^e **L1** was used, 60 °C, 72 h.

the polymerization of monomers **2** containing aromatic heterocycle (entries 12–13). These enantiomerically enriched poly(silyl ether)s would expand the application in chiral separation and asymmetric catalysis.

The well-defined structure of poly(silyl ether)s were confirmed by ^1H and ^{13}C NMR spectra (Figures S21–S49 in the Supporting Information). For polymer **3a**, the aromatic protons appeared in 7.64–7.50 and 7.48–7.31 ppm. CH proton of chiral carbon in main-chain split into multiple was located at 5.12–4.99 ppm, and adjacent CH_3 protons split into doublet were situated at 1.50 ppm. CH_2 protons in main-chain were located at 4.89–4.70 ppm. And CH_3 protons adjacent to Si appeared in 0.12–0.01 ppm. For ^{13}C NMR spectra of polymer **3a** (Figure S22 in the Supporting Information), the singlets at 145.4–125.9 ppm were assigned to the aromatic carbons. The characteristic peak of chiral carbon was at 70.1 ppm and CH_2 carbon in main-chain was located at 64.1 ppm, which further supported the formation of desired poly(silyl ether) **3a**. As monomer **2a** has two different termini, it can deliver polymers with multiple connectivities in the main chain including head-to-head, head-to-tail and tail-to-tail. The new enantiopure **3a** obtained via CuH-catalyzed consecutive asymmetric hydrosilylation/dehydrocoupling polymerization revealed clearly resonances in solution ^1H NMR spectra, indicating poly(silyl ether) **3a** with some content of structural regularity (Scheme 3a) [14]. Some control experiments were achieved to further explain structural regularity of chiral poly(silyl ether) **3a** (Scheme 2, Figures S1–S5 in the Supporting Information). When employing 1.05 equiv of **2a** to polymerization, there were no protons of COCH_3 of **2a** (Scheme 2b,3b). The signal at 4.76 was attributed to the protons of ArCH_2OH of **2a**. This result indicated the rate of hydrosilylation was slightly faster than the rate of dehydrocoupling. In our previous work, we reported CuO'Bu-catalyzed dehydrocoupling polymerization [10], and envisioned using catalytic system of CuO'Bu would increase the rate of dehydrogenation coupling. The more similar rate of dehydrocoupling and hydrosilylation, the NMR spectrum of poly(silyl ether)s would be more complex. In order to verify our hypothesis, we prepared polymer **3a-2** by CuO'Bu (Scheme 2c). The NMR spectrum of polymer **3a-2** was clearly different from the poly(silyl ether) **3a** (Scheme 3c). CH_3 protons adjacent to Si became more complex. CH proton of chiral carbon in main-chain showed very broad NMR resonances. Apart from the possibility that poly(silyl ether) **3a-2** was atactic, the complexity of the NMR signals could also be caused by loss of optical purity. For the purpose of excluding the influence of optical purity on NMR, we used (*rac*)-**L1** to obtain (*rac*)-**3a-3** which had similar characteristic peaks as **3a** (Scheme 2d) (Figure S4 in the Supporting Information). In addition, low molecular weight would also increase the complexity of NMR. Compared with poly(silyl ether) **3a**, poly(silyl ether) **3a-4** also had similar characteristic



Scheme 3. NMR Spectra Analysis.

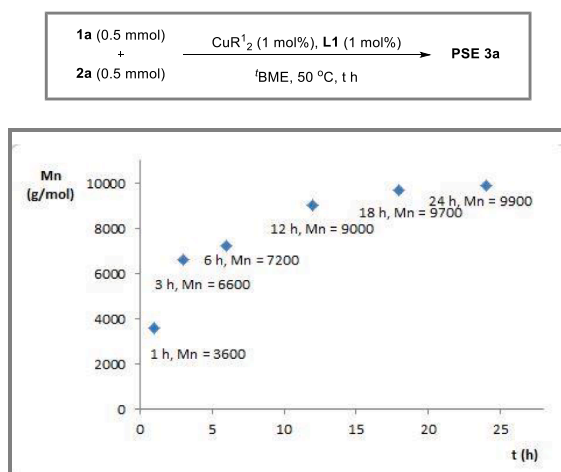
1a (0.5 mmol) + 2a (0.5 mmol)	[Cu], (<i>R</i>)- L1 , t BME, 50 $^{\circ}\text{C}$ 63% yield, Mn = 10500 PDI = 1.64, 93.5% ee	PSE 3a (a)
1a (0.5 mmol) + 2a (0.525 mmol)	[Cu], (<i>R</i>)- L1 , t BME, 50 $^{\circ}\text{C}$ 46% yield, Mn = 9300 PDI = 1.58	PSE 3a-1 (b)
1a (0.5 mmol) + 2a (0.5 mmol)	CuCl, NaO'Bu Xantphos, THF 51% yield, Mn = 6500 PDI = 2.02	PSE 3a-2 (c)
1a (0.5 mmol) + 2a (0.5 mmol)	[Cu], (<i>rac</i>)- L1 , t BME 57% yield, Mn = 9500 PDI = 1.66	PSE 3a-3 (d)
1a (0.5 mmol) + 2a (0.5 mmol)	[Cu], (<i>R</i>)- L1 , t BME, 40 $^{\circ}\text{C}$ 61% yield, Mn = 5700 PDI = 1.79, 94.8% ee	PSE 3a-4 (e)

Scheme 2. Control Experiments.

peaks as **3a** (Scheme 3e) (Figure S5 in the Supporting Information). Thus, we confirmed that the enantiopure poly(silyl ether)s with some content of structural regularity were successfully synthesized via consecutive asymmetric hydrosilylation/dehydrocoupling polymerization.

The plot of molecular weight versus time was also carried out (Scheme 4). Under the optimal polymerization temperature using **L1** as ligand, conversion of monomer **2a** reached above 80% within 10 min and molecular weight of poly(silyl ether) **3a** was unmeasured, indicating only formation of oligomer. And molecular weight of poly(silyl ether) **3a** could get 3600 within 1 h, accompanying with the complete consumption of monomer **2a**. The data showed small molecular weight species formed initially, and the molecular weight of poly(silyl ether) **3a** increased rapidly within 3 h. Then a slowly increase in molecular weight was observed, and the molecular weight reached to a steady plateau at 18 h.

Thermal properties of some representative chiral polymers (**3a**, **3f**, **3i**, **3j** and **3m**) were investigated under nitrogen atmosphere using TGA



Scheme 4. Plot of Molecular Weight versus Time.

Table 3
Thermal Analysis of Chiral PSEs ^a.

Entry	PSEs 3	T ₅ (°C) ^a	T ₅₀ (°C) ^a	T _g (°C) ^b
1	3a	385	451	−46
2	3f	312	473	−43
3	3i	386	455	−50
4	3j	390	464	−31
5	3m	329	449	−52

^a Temperature at which 5% and 50% mass loss are observed under N₂ by TGA.

^b Determined by DSC.

and DSC as shown in Table 3. All of tested chiral poly(silyl ether)s exhibited good thermal stability, T₅ values ranged from 312 to 390 °C, and T₅₀ values varied from 449 to 473 °C. For polymer **3m** containing thiophene skeleton, it had a relatively lower T₅ value. In addition, a diverse array of poly(silyl ether)s with different chain length link showed similar T₅ and T₅₀ values. All of enantiopure poly(silyl ether)s exhibited glass transition temperatures via DSC. However, the T_g value of **3j** was slightly higher than others probably due to the longer chain linker. And the glass transition temperatures of **3a**, **3f**, **3i**, **3m** could be detected at −46 °C, −43 °C, −50 °C and −52 °C, respectively.

3. Conclusions

In conclusion, we have successfully developed a facile methodology for the synthesis of chiral poly(silyl ether)s via CuH-catalyzed consecutive asymmetric hydrosilylation/dehydrocoupling polymerization of difunctional hydroxyketone monomers. A series of chiral poly(silyl ether)s with structural diversity could be conveniently prepared with good yields, high molecular weight and excellent enantioselectivities (up to 95% yield and 94% ee) under mild conditions. We expect that these new thermal stable poly(silyl ether)s with some content of structural regularity would have special material properties. Efforts are underway to expand the applications of chiral poly(silyl ether)s.

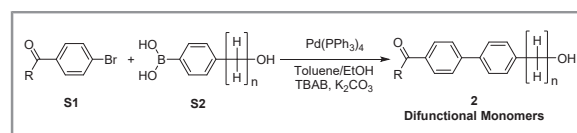
4. Experiments

4.1. Reagents and instrumentation

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Solvents were treated prior to use according to the standard methods. ¹H NMR and ¹³C NMR spectra were recorded at room temperature in CDCl₃ on 400 MHz instrument with TMS as internal standard. Flash column chromatography was performed on silica gel (200–300 mesh). The heat source for

all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. 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: nitrogen, flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: −100 to 200 °C). TGA was performed on a STA instrument 449 F3 thermogravimetric analyzer (purge gas: nitrogen, flow rate: 20 mL/min, ramp rate: 10 °C/min, temperature range: 40 to 600 °C). Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Commercially available reagents and solvents were used throughout without further purification.

4.2. Procedure for synthesis of difunctional monomers



The difunctional hydroxyketone monomers **2** could be synthesized through Miyaura-Suzuki coupling reaction from 4-bromophenylketones according to the literature method [15]. The starting materials **S1–S2** are commercially available raw materials. All difunctional monomers **2** are the unknown compounds except **2a** [16] and **2g** [17].

Typical procedure: A mixture of Pd(PPh₃)₄ (5 mol%, 452 mg), tetrabutylammonium bromide (TBAB, 1.04 mmol, 328 mg), potassium carbonate (56 mmol, 5.936 g), aryl bromides **S1b** (20 mmol, 4.260 g) and boric acids **S2b** (20 mmol, 3.040 g) in toluene/ethanol (25 mL/25 mL) were stirred at 80 °C (oil bath temperature) for 14 h. The reaction mixture was cooled to room temperature and concentrated under the reduced pressure. Water (60 mL) was added, and the mixture was extracted three times with dichloromethane (60 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under the reduced pressure. The crude residue was purified by column chromatography on silica gel using hexanes/ethyl acetate/dichloromethane (10/1/1) as eluent to afford difunctional monomer **2b**. The pure difunctional monomer **2b** could be further purified through recrystallized with hexanes/dichloromethane.

Using the above analogous experimental procedures, the difunctional monomers **2c–2f**, **2h** and **2i** could be conveniently prepared.

1-(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)propan-1-one (2b): 2.475 g, 50% yield, light yellow solid, mp 164–166 °C, new compound, R_f = 0.21 (hexanes/ethyl acetate/dichloromethane 2.5/1/1). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.3 Hz, 2H), 7.76–7.59 (m, 4H), 7.47 (d, J = 8.0 Hz, 2H), 4.76 (s, 2H), 3.04 (q, J = 7.2 Hz, 2H), 1.88 (s, 1H), 1.25 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.6, 145.3, 141.1, 139.4, 135.8, 128.7, 127.7, 127.6, 127.3, 65.1, 32.0, 8.5. HRMS Calculated for C₁₆H₁₇O₂ [M + H]⁺ 241.1223, found: 241.1195.

1-(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)butan-1-one (2c): 1.410 g, 28% yield, white solid, mp 143–145 °C, new compound, R_f = 0.30 (hexanes/ethyl acetate/dichloromethane 2.5/1/1). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.4 Hz, 2H), 7.75–7.57 (m, 4H), 7.47 (d, J = 8.1 Hz, 2H), 4.76 (s, 2H), 2.97 (t, J = 7.3 Hz, 2H), 1.95 (s, 1H), 1.86–1.73 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.3, 145.3, 141.1, 139.4, 135.9, 128.8, 127.7, 127.5, 127.2, 65.1, 40.7, 18.0, 14.1. HRMS Calculated for C₁₇H₁₉O₂ [M + H]⁺ 255.1380, found: 255.1381.

(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)(phenyl)methanone (2d): 3.293 g, 57% yield, white solid, mp 302–304 °C, new compound, R_f = 0.10 (hexanes/ethyl acetate/dichloromethane 2.5/1/1). ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.87 (m, 2H), 7.87–7.79 (m, 2H), 7.74–7.69 (m, 2H), 7.68–7.64 (m, 2H), 7.64–7.58 (m, 1H), 7.56–7.44 (m, 4H), 4.78

(s, 2H), 1.80 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.5, 145.0, 141.1, 139.4, 137.9, 136.4, 132.6, 130.9, 130.2, 128.5, 127.7, 127.6, 127.0, 65.1. HRMS Calculated for $\text{C}_{20}\text{H}_{17}\text{O}_2$ $[\text{M} + \text{H}]^+$ 289.1223, found: 289.1226.

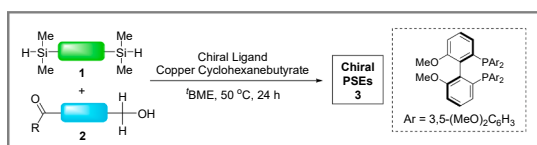
1-(4'-Hydroxy-[1,1'-biphenyl]-4-yl)butan-1-one (2e): 2.069 g, 43% yield, white solid, mp 161–163 °C, new compound, R_f = 0.40 (hexanes/ethyl acetate/dichloromethane 4/1/1). ^1H NMR (400 MHz, CD_3OD) δ 8.08–7.86 (m, 2H), 7.74–7.59 (m, 2H), 7.58–7.43 (m, 2H), 6.94–6.81 (m, 2H), 3.12–2.84 (m, 2H), 1.86–1.59 (m, 2H), 1.11–0.89 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 202.3, 159.2, 147.0, 136.1, 132.1, 129.8, 129.4, 127.3, 116.9, 41.3, 19.0, 14.2. HRMS Calculated for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M} + \text{H}]^+$ 241.1223, found: 241.1230.

1-(4'-(3-Hydroxypropyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (2f): 2.411 g, 63% yield, white solid, mp 159–161 °C, new compound, R_f = 0.27 (hexanes/ethyl acetate/dichloromethane 2/1/1). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.84–3.62 (m, 2H), 2.90–2.71 (m, 2H), 2.64 (s, 3H), 2.06–1.81 (m, 2H), 1.40 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 145.8, 142.3, 137.6, 135.8, 129.2, 129.1, 127.4, 127.1, 62.3, 34.3, 31.9, 26.8. HRMS Calculated for $\text{C}_{17}\text{H}_{19}\text{O}_2$ $[\text{M} + \text{H}]^+$ 255.1380, found: 255.1379.

1-(4-(5-(Hydroxymethyl)thiophen-2-yl)phenyl)ethan-1-one (2h): 742 mg, 32% yield, yellow solid, mp 170–172 °C, new compound, R_f = 0.20 (hexanes/ethyl acetate/dichloromethane 2/1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.65 (m, 2H), 7.65–7.63 (m, 1H), 7.47–7.39 (m, 2H), 7.35–7.29 (m, 1H), 4.74 (d, J = 5.8 Hz, 2H), 2.57 (s, 3H), 1.79 (t, J = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.8, 152.6, 143.2, 142.0, 133.6, 132.8, 127.7, 126.6, 124.0, 65.0, 26.7. HRMS Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 233.0631, found: 233.0631.

1-(5-(4-(2-Hydroxyethyl)phenyl)thiophen-2-yl)ethan-1-one (2i): 769 mg, 21% yield, yellow solid, mp 140–142 °C, new compound, R_f = 0.20 (hexanes/ethyl acetate/dichloromethane 2/1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, J = 4.0 Hz, 1H), 7.63–7.56 (m, 2H), 7.31–7.27 (m, 3H), 3.89 (t, J = 6.5 Hz, 2H), 2.90 (t, J = 6.5 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.8, 152.8, 143.0, 140.0, 133.7, 131.8, 129.9, 126.6, 123.8, 63.6, 39.0, 26.7. HRMS Calculated for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 247.0787, found: 247.0778.

4.3. Procedure for CuH-Catalyzed consecutive Hydrosilylation/dehydrocoupling polymerization



Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged copper cyclohexanebutyrate (0.005 mmol, 2.0 mg), **L6** (0.005 mmol, 4.1 mg) and *t*-butyl methyl ether (0.25 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer of dihydrosilane **1a** (0.5 mmol, 127 μL), monomer **2a** (0.5 mmol, 113.1 mg) and *t*-butyl methyl ether (0.5 mL) were added into the flask under nitrogen. The flask was heated at 50 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the poly(silyl ether) **3a** was purified by the precipitation method.

Poly(silyl ether) **3a** was 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 (1.0 mL). Then cold methanol (20 mL) was added portionwise until it turned to a biphasic mixture. The top layer was taken out, and the bottom solid layer was washed with methanol two times until it gave a white solid polymer. The resulting poly(silyl ether) **3a** was dried to a constant weight.

Using the above analogous experimental procedures, the chiral poly

(silyl ether)s **3b–3m** could be conveniently prepared and characterized by ^1H NMR, ^{13}C NMR, GPC, TG and DSC.

Poly(silyl ether) (3a): 180 mg, 83% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +39.18 (c 1.22, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.64–7.50 (m, 4H), 7.48–7.31 (m, 4H), 5.12–4.99 (m, 1H), 4.89–4.70 (m, 2H), 1.50 (d, J = 6.4 Hz, 3H), 0.20–0.01 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.38, 145.36, 140.1, 139.8, 139.7, 127.1, 127.0, 125.9, 70.1, 64.1, 26.9, 1.12, 1.08, –0.1, –0.4, –0.8.

Poly(silyl ether) (3b): 164 mg, 91% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +27.01 (c 0.52, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.62–7.50 (m, 4H), 7.49–7.31 (m, 4H), 5.15–4.94 (m, 1H), 4.90–4.69 (m, 2H), 1.63–1.43 (m, 3H), 0.22–0.01 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 140.0, 139.7, 127.3, 127.1, 126.97, 126.95, 125.9, 70.2, 70.1, 64.1, 64.0, 26.9, –0.2, –0.3, –0.4, –0.5, –0.8, –0.85, –0.87.

Poly(silyl ether) (3c): 172 mg, 82% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +17.96 (c 1.18, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.76–7.51 (m, 8H), 7.49–7.33 (m, 4H), 5.09–4.87 (m, 1H), 4.85–4.70 (m, 2H), 1.63–1.39 (m, 3H), 0.60–0.20 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 140.0, 139.9, 139.7, 139.3, 139.0, 133.5, 133.07, 133.05, 133.0, 127.3, 127.2, 127.13, 127.06, 126.9, 126.0, 71.0, 70.3, 68.6, 64.9, 27.0, 25.3, 22.3, 0.1, –0.7, –1.2, –1.6, –3.8.

Poly(silyl ether) (3d): 195 mg, 95% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +141.23 (c 1.13, THF). ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.30 (m, 18H), 5.23–4.97 (m, 1H), 4.93–4.71 (m, 2H), 1.57–1.36 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 139.7, 135.0, 132.9, 132.6, 130.5, 130.4, 128.0, 127.9, 126.8, 126.7, 125.9, 125.7, 71.1, 64.8, 64.6, 26.7.

Poly(silyl ether) (3e): 153 mg, 88% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +41.22 (c 0.90, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.63 (m, 2H), 7.59–7.27 (m, 11H), 5.17–4.96 (m, 1H), 4.93–4.59 (m, 2H), 1.61–1.38 (m, 3H), 0.54–0.27 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.3, 130.5, 130.3, 130.1, 128.14, 128.05, 128.0, 127.9, 127.2, 127.1, 127.0, 126.9, 126.0, 125.9, 70.9, 70.8, 64.7, 64.6, 26.94, 26.85, 0.2, –2.9, –3.5, –3.9.

Poly(silyl ether) (3f): 183 mg, 82% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +25.47 (c 1.06, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.49 (m, 4H), 7.42–7.33 (m, 4H), 4.85–4.78 (m, 2H), 4.79–4.70 (m, 1H), 1.85–1.68 (m, 2H), 1.00–0.85 (m, 3H), 0.23–0.00 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 140.1, 139.74, 139.71, 139.65, 127.1, 126.8, 126.5, 75.7, 75.6, 64.1, 33.4, 10.3, 1.1, 1.04, 0.95, –0.1, –0.3, –0.7.

Poly(silyl ether) (3g): 200 mg, 87% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +43.23 (c 0.99, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.50 (m, 4H), 7.50–7.33 (m, 4H), 5.04–4.64 (m, 3H), 1.87–1.64 (m, 2H), 1.55–1.28 (m, 2H), 1.06–0.81 (m, 3H), 0.30–0.08 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 140.1, 139.74, 139.71, 139.65, 127.1, 126.8, 126.4, 74.21, 74.15, 64.1, 64.0, 42.9, 19.1, 14.1, 1.1, 1.0, 0.9, –0.1, –0.3, –0.8.

Poly(silyl ether) (3h): 201 mg, 81% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +2.44 (c 0.90, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.53 (m, 4H), 7.52–7.42 (m, 5H), 7.42–7.35 (m, 3H), 7.34–7.27 (m, 1H), 6.11–5.84 (m, 1H), 4.98–4.69 (m, 2H), 0.30–0.07 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 143.7, 139.92, 139.89, 139.85, 139.80, 139.79, 128.4, 127.3, 127.1, 127.0, 126.66, 126.65, 75.9, 64.1, 64.0, 1.2, 1.1, 1.0, 0.9, –0.2, –0.75, –0.77.

Poly(silyl ether) (3i): 201 mg, 90% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +33.37 (c 0.61, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.40 (m, 4H), 7.38–7.29 (m, 2H), 7.00–6.92 (m, 2H), 4.89–4.74 (m, 1H), 1.811.59 (m, 2H), 1.46–1.25 (m, 2H), 0.96–0.84 (m, 3H), 0.27–0.06 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 143.9, 139.4, 134.6, 127.98, 127.95, 126.4, 126.3, 120.1, 74.13, 74.05, 42.8, 19.0, 14.0, 0.94, 0.87, 0.8, –0.2, –0.3, –0.4, –0.5.

Poly(silyl ether) (3j): 192 mg, 83% yield, colorless soft solid, new compound, $[\alpha]_D^{20}$ = +33.60 (c 1.00, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.45 (m, 4H), 7.44–7.32 (m, 2H), 7.27–7.24 (m, 2H), 5.05 (q, J = 6.1 Hz, 1H), 3.84–3.60 (m, 2H), 2.91–2.59 (m, 2H), 2.04–1.77 (m, 2H),

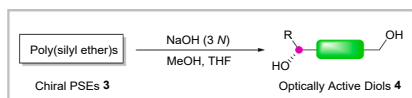
1.50 (d, $J = 6.4$ Hz, 3H), 0.22 – –0.05 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 141.2, 139.8, 138.7, 129.0, 127.1, 126.9, 125.9, 70.1, 61.7, 34.2, 31.9, 26.8, 1.14, 1.08, 1.0, –0.1, –0.4, –0.8.

Poly(silyl ether) (3k): The polymerization reaction was conducted by using monomer (0.5 mmol \times 5), affording the chiral poly(silyl ether) **3k** 498 mg, 56% yield, colorless soft solid, new compound, $[\alpha]_D^{20} = +31.06$ (c 0.46, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.21 (m, 4H), 4.99 (q, $J = 6.2$ Hz, 1H), 4.75 (s, 2H), 1.44 (d, $J = 6.4$ Hz, 3H), 0.16 – –0.02 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 139.4, 126.5, 125.4, 70.1, 64.1, 27.0, 1.1, –0.1, –0.5, –0.8.

Poly(silyl ether) (3l): 199 mg, 91% yield, colorless soft solid, new compound, $[\alpha]_D^{20} = +25.87$ (c 0.97, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.61–7.46 (m, 2H), 7.38–7.27 (m, 2H), 7.17–7.03 (m, 1H), 6.97–6.79 (m, 1H), 5.22 (q, $J = 6.2$ Hz, 1H), 4.76 (s, 2H), 1.58 (d, $J = 6.3$ Hz, 3H), 0.19–0.08 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 142.7, 139.9, 133.7, 127.1, 125.7, 123.5, 122.4, 66.6, 64.0, 26.6, 1.1, –0.1, –0.5, –0.8.

Poly(silyl ether) (3m): 180 mg, 79% yield, colorless soft solid, new compound, $[\alpha]_D^{20} = +45.98$ (c 1.02, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.38 (m, 2H), 7.23–7.14 (m, 2H), 7.13–7.02 (m, 1H), 6.89–6.77 (m, 1H), 5.21 (q, $J = 6.0$ Hz, 1H), 3.94–3.79 (m, 2H), 2.96–2.77 (m, 2H), 1.63–1.53 (m, 3H), 0.18–0.05 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 142.8, 138.2, 132.8, 129.6, 125.7, 123.4, 122.2, 66.6, 63.5, 39.1, 26.5, 1.1, –0.1, –0.5, –1.0.

4.4. Procedure for Hydrolyzation of chiral Poly(silyl ether)s



To a 25 mL flask was added the chiral poly(silyl ether)s **3** (0.15 mmol) and tetrahydrofuran (2.0 mL). After the poly(silyl ether)s **3** dissolved completely, methanol (2.0 mL) and sodium hydroxide (3 N, 2.0 mL) were added to the solution. The mixture was stirred at room temperature overnight and then extracted with dichloromethane (10 mL \times 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under the reduced pressure, and the crude residue was purified by column chromatography on silica gel using hexanes and ethyl acetate as eluent to afford optically active diols **4**.

The diol racemates **4** could be conveniently prepared through reduction of monomers **2** with sodium borohydride.

(+)-1-(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)ethan-1-ol (**4a**):

The reaction was conducted by using poly(silyl ether) **3a** (56.6 mg, 0.14 mmol), affording diol **4a** 29.5 mg, 96% yield, white solid, mp 149–151 °C, new compound, $R_f = 0.28$ (hexanes/ethyl acetate 2/1), 92% ee, $[\alpha]_D^{20} = +27.74$ (c 0.31, THF). ^1H NMR (400 MHz, CD_3OD) δ 7.67–7.55 (m, 4H), 7.50–7.33 (m, 4H), 4.89–4.83 (m, 3H), 4.64 (s, 2H), 1.47 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 146.6, 141.7, 141.2, 141.0, 128.5, 127.82, 127.78, 127.0, 70.6, 64.9, 25.6. HPLC: Chiralcel OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 13.5 min and 16.1 min (major). HRMS Calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 251.1043, found: 251.1053.

Hydrolyzation of Poly(silyl ether)s	Yield (%)	Ee (%)
PSE 3a	96	92
PSE 3b	92	93
PSE 3c	80	93
PSE 3d	61	94
PSE 3e	74	93

(+)-1-(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)propan-1-ol (**4f**):

The reaction was conducted by using poly(silyl ether) **3f** (47.0 mg, 0.11 mmol), affording diol **4f** 24.6 mg, 92 % yield, white solid, mp 93–95 °C, new compound, $R_f = 0.21$ (hexanes/ethyl acetate 2/1), 92 % ee, $[\alpha]_D^{20} =$

+22.06 (c 0.68, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.50 (m, 4H), 7.46–7.33 (m, 4H), 4.72 (s, 2H), 4.64 (t, $J = 6.6$ Hz, 1H), 2.07 (s, 2H), 1.92–1.70 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 140.3, 140.1, 140.0, 127.6, 127.3, 127.2, 126.6, 75.9, 65.2, 32.0, 10.3. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 11.5 min and 15.6 min (major). HRMS Calculated for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M} - \text{H}]^+$ 241.1234, found: 241.1235.

(+)-1-(4'-(Hydroxymethyl)-[1,1'-biphenyl]-4-yl)butan-1-ol (**4g**):

The reaction was conducted by using poly(silyl ether) **3g** (75.1 mg, 0.16 mmol), affording diol **4g** 37.1 mg, 89% yield, white solid, mp 82–84 °C, new compound, $R_f = 0.22$ (hexanes/ethyl acetate 2/1), 91% ee, $[\alpha]_D^{20} = +27.61$ (c 0.92, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.53 (m, 4H), 7.48–7.37 (m, 4H), 4.79–4.64 (m, 3H), 1.85–1.70 (m, 4H), 1.55–1.31 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 140.4, 140.1, 140.0, 127.6, 127.4, 127.2, 126.5, 74.3, 65.2, 41.4, 19.2, 14.1. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 10.9 min and 14.8 min (major). HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 279.1356, found: 279.1359.

(-)-4'-(1-Hydroxymethyl)-[1,1'-biphenyl]-4-yl (phenyl)methanol (**4h**):

The reaction was conducted by using poly(silyl ether) **3h** (59.6 mg, 0.12 mmol), affording diol **4h** 19.4 mg, 56% yield, yellow oil, new compound, $R_f = 0.15$ (hexanes/ethyl acetate 1.5/1), 41% ee, $[\alpha]_D^{20} = -1.80$ (c 0.50, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.60–7.50 (m, 4H), 7.48–7.27 (m, 9H), 5.89 (s, 1H), 4.72 (s, 2H), 2.15 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 143.1, 140.3, 140.2, 140.0, 128.7, 127.8, 127.6, 127.4, 127.3, 127.1, 126.7, 76.2, 65.2. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 22.5 min and 25.2 min (major). HRMS Calculated for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 313.1199, found: 313.1204.

(+)-4'-(1-Hydroxybutyl)-[1,1'-biphenyl]-4-ol (**4i**):

The reaction was conducted by using poly(silyl ether) **3i** (96.0 mg, 0.22 mmol), affording diol **4i** 45.9 mg, 89% yield, white solid, mp 103–105 °C, new compound, $R_f = 0.23$ (hexanes/ethyl acetate 1.5/1), 90% ee, $[\alpha]_D^{20} = +12.46$ (c 0.66, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.43 (m, 4H), 7.43–7.31 (m, 2H), 7.03–6.78 (m, 2H), 5.04 (s, 1H), 4.73 (t, $J = 6.6$ Hz, 1H), 1.90–1.70 (m, 2H), 1.51–1.30 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 143.3, 140.2, 133.7, 128.4, 126.9, 126.5, 115.8, 74.5, 41.2, 19.2, 14.1. HPLC: Chiralpak OD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 85/15, flow = 0.7 mL/min, retention time 13.2 min and 14.9 min (major). HRMS Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 265.1199, found: 265.1192.

(+)-3-(4'-(1-Hydroxyethyl)-[1,1'-biphenyl]-4-yl)propan-1-ol (**4j**):

The reaction was conducted by using poly(silyl ether) **3j** (66.9 mg, 0.15 mmol), affording diol **4j** 33.4 mg, 90% yield, white solid, mp 141–143 °C, new compound, $R_f = 0.21$ (hexanes/ethyl acetate 1.5/1), 93% ee, $[\alpha]_D^{20} = +21.52$ (c 0.92, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.60–7.54 (m, 2H), 7.54–7.49 (m, 2H), 7.48–7.41 (m, 2H), 7.30–7.26 (m, 2H), 4.95 (q, $J = 6.4$ Hz, 1H), 3.71 (t, $J = 6.4$ Hz, 2H), 2.81–2.69 (m, 2H), 1.97–1.90 (m, 2H), 1.67 (s, 2H), 1.54 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 141.1, 140.4, 138.6, 129.0, 127.24, 127.22, 126.0, 70.4, 62.4, 34.3, 31.8, 25.3. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 13.2 min and 14.2 min (major). HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 279.1356, found: 279.1334.

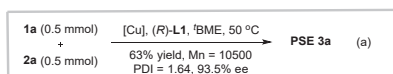
(+)-1-(4-(Hydroxymethyl)phenyl)ethan-1-ol (**4k**):

The reaction was conducted by using poly(silyl ether) **3k** (231.9 mg, 0.648 mmol), affording diol the **4k** 88.5 mg, 90% yield, white solid, the known compound [18], $R_f = 0.21$ (hexanes/ethyl acetate 2/1), 83% ee, $[\alpha]_D^{20} = +33.77$ (c 0.76, MeOH). [lit. [18]: $[\alpha]_D^{20} = -37.93$ (c 1.0, MeOH) for 97% ee for (S)-**4k**]. ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.29 (m, 4H), 4.89 (q, $J = 6.5$ Hz, 1H), 4.67 (s, 2H), 1.95 (s, 2H), 1.49 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 140.2, 127.3, 125.8, 70.3, 65.2, 25.3. HPLC: Chiralpak OJ-H column, 230 nm, 30 °C, *n*-Hexane/*i*-PrOH = 80/20, flow = 0.7 mL/min, retention time 13.1 min and 16.4 min (major).

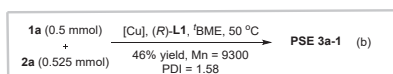
(+)-1-(5-(4-(Hydroxymethyl)phenyl)thiophen-2-yl)ethan-1-ol (4l): The reaction was conducted by using poly(silyl ether) **3l** (87.8 mg, 0.20 mmol), affording diol **4l** 35.7 mg, 76% yield, yellow oil, new compound, $R_f = 0.31$ (hexanes/ ethyl acetate 2/1), 90% ee, $[\alpha]_D^{20} = +6.56$ (c 0.64, THF). ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.56 (m, 2H), 7.38–7.35 (m, 2H), 7.18–7.15 (m, 1H), 6.95–6.93 (m, 1H), 5.12 (q, $J = 6.4$ Hz, 1H), 4.70 (s, 2H), 1.88 (s, 2H), 1.63 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 140.2, 134.0, 128.6, 127.7, 126.0, 124.3, 122.8, 66.6, 65.2, 25.3. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 18.4 min and 20.1 min (major). HRMS Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$ 257.0607, found: 257.0608.

(+)-1-(5-(4-(2-Hydroxyethyl)phenyl)thiophen-2-yl)ethan-1-ol (4m): The reaction was conducted by using poly(silyl ether) **3m** (64.2 mg, 0.14 mmol), affording diol **4m** 32.5 mg, 92% yield, white solid, mp 93–95 °C, new compound, $R_f = 0.23$ (hexanes/ethyl acetate 2/1), 90% ee, $[\alpha]_D^{20} = +7.10$ (c 0.76, THF). ^1H NMR (400 MHz, CD_3OD) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 3.6$ Hz, 1H), 6.92 (d, $J = 3.6$ Hz, 1H), 5.03 (q, $J = 6.4$ Hz, 1H), 4.88 (s, 2H), 3.76 (t, $J = 7.0$ Hz, 2H), 2.82 (t, $J = 7.0$ Hz, 2H), 1.55 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 150.8, 144.1, 139.7, 134.0, 130.6, 126.5, 125.0, 123.2, 66.8, 64.1, 39.9, 25.5. HPLC: Chiralpak OJ-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 60/40, flow = 0.7 mL/min, retention time 15.2 min and 16.2 min (major). HRMS Calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{SK}$ $[\text{M} + \text{K}]^+$ 287.0503, found: 287.0508.

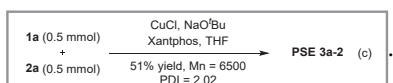
4.5. Control experiments



Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged copper cyclohexanebutyrate (0.01 mmol, 4.0 mg), (R)-L1 (0.01 mmol, 8.8 mg) and ^tBME (0.5 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer **1a** (0.5 mmol, 127 μL), monomer **2a** (0.5 mmol, 113.1 mg) and ^tBME (1.0 mL) were added into the flask under nitrogen. The flask was heated at 50 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the poly(silyl ether) **3a** was purified by the precipitation method.

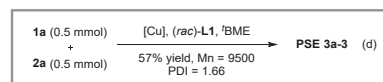


Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged copper cyclohexanebutyrate (0.01 mmol, 4.0 mg), (R)-L1 (0.01 mmol, 8.8 mg) and ^tBME (0.5 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer **1a** (0.5 mmol, 127 μL), monomer **2a** (0.525 mmol, 118.7 mg) and ^tBME (1.0 mL) were added into the flask under nitrogen. The flask was heated at 50 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the poly(silyl ether) **3a-1** was purified by the precipitation method.

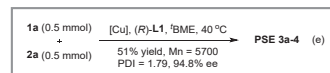


Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged CuCl (0.01 mmol, 1.0 mg), NaOtBu (0.01 mmol, 1.0 mg), XantPhos (0.01 mmol, 5.8 mg) and THF (0.5 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer **1a** (0.5 mmol, 127 μL), monomer **2a** (0.5 mmol, 113.1 mg) and THF (1.0 mL) were added into the flask under nitrogen. The flask was heated at 80 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room

temperature, and the poly(silyl ether) **3a-2** was purified by the precipitation method.



Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged copper cyclohexanebutyrate (0.01 mmol, 4.0 mg), (rac)-L1 (0.01 mmol, 8.8 mg) and ^tBME (0.5 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer **1a** (0.5 mmol, 127 μL), monomer **2a** (0.5 mmol, 113.1 mg) and ^tBME (1.0 mL) were added into the flask under nitrogen. The flask was heated at 50 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the poly(silyl ether) **3a-3** was purified by the precipitation method.



Typical procedure: To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged copper cyclohexanebutyrate (0.01 mmol, 4.0 mg), (R)-L1 (0.01 mmol, 8.8 mg) and ^tBME (0.5 mL) under nitrogen. The solution was stirred at room temperature for one hour. Then, monomer **1a** (0.5 mmol, 127 μL), monomer **2a** (0.5 mmol, 113.1 mg) and ^tBME (1.0 mL) were added into the flask under nitrogen. The flask was heated at 40 °C for 24 h under nitrogen. After the polymerization, the reaction mixture was cooled to room temperature, and the poly(silyl ether) **3a-4** was purified by the precipitation method.

CRediT authorship contribution statement

Xiao-Qing Wang: Investigation, Visualization, Writing – original draft, Writing – review & editing. **Bo Wu:** Supervision, Validation, Writing – original draft, Writing – review & editing. **Yu-Qing Bai:** Validation. **Xiao-Yong Zhai:** Investigation, Writing – original draft. **Yong-Gui Zhou:** Conceptualization, Supervision, Writing – original draft, 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2022.111474>.

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