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Perspective Article

# Synthesis of cinchona squaramide polymers by Yamamoto coupling polymerization and their application in asymmetric Michael reaction

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ABSTRACT

Yamamoto coupling polymerization has been used for the synthesis of polymeric chiral organocatalysts. Cinchona squaramide derivatives with dibromophenyl moiety were polymerized under the Yamamoto coupling conditions to afford the corresponding chiral polymers in good yields. Using this technique, novel cinchona alkaloid polymers containing the squaramide moiety were designed and successfully synthesized. In addition to the homopolymerization of cinchona squaramide monomers with a dibromophenyl group, achiral comonomers such as dibromobenzene were copolymerized with the cinchona monomers to yield chiral copolymers. These chiral polymers were successfully utilized as polymeric catalysts in asymmetric Michael addition reactions. Good to excellent enantioselectivities were observed for different types of asymmetric Michael reactions. Using the chiral homopolymer catalyst **P4**, almost perfect diastereoselectivity (>100:1) with 99% ee was obtained for the reaction between methyl 2-oxocyclopentanecarboxylate **25** and *trans*-β-nitrostyrene **17**. The polymer catalysts developed in this study have robust structures and can be reused several times without a loss in their catalytic activities.

## 1. Introduction

Owing to the design and development of natural product-derived chiral molecular frameworks as chiral organocatalysts, asymmetric catalysis using these molecules is a popular strategy in asymmetric synthetic methodologies [1]. For the synthesis of these catalysts, significant efforts have been engrossed on the development of green and sustainable procedures. Literary survey of Szollosi reported, heterogeneous chiral catalysts obtained by the immobilization of chiral metal complexes, by anchoring chiral organocatalysts, or by modifying catalytic surfaces with optically pure compounds has been applied in asymmetric one-pot reactions, which may also integrate uncatalyzed and homogeneously catalyzed steps [2]. Cinchona alkaloid-derived organocatalysts are important examples of the catalysts used in asymmetric reactions. Owing to their several functionalities such as secondary alcohols, quinoline rings, and quinuclidine and vinyl groups, cinchona alkaloids are useful for suitable modifications to versatile catalysts in asymmetric reactions. Several types of cinchona-based chiral organocatalysts have been developed that play significant roles in asymmetric catalysis [3].

Some cinchona alkaloid derivatives with catalytic activities were attached to various types of synthetic polymers [4–7] to act as polymeric organocatalysts in asymmetric reactions [8–14]. Modified cinchona alkaloids of with different functionalities such as hydroxyl, amino, urea and thiourea on position C9 and C6′ are used in asymmetric reactions [15]. Supported bifunctional thioureas derived from cinchona alkaloids were used as catalyst in enantioselective reaction by continuous flow process reported by Rodriguez et al. [16]. Cinchona alkaloid–metal complexes were also efficient catalysts in some asymmetric reactions. Their polymeric counterparts were prepared and applied to asymmetric catalysis [17,18].

The C—C cross-coupling is one of the most powerful tools for the construction of complex organic compounds [19]. Transition metal complexes are used as catalysts for this purpose and have many advantages over the classical catalysts [20]. We have investigated several types of polymeric cinchona-derived catalysts, where the organocatalyst is incorporated into the polymer main chain as a repeating unit. Previously Mizoroki–Heck polymerization was developed for the synthesis of

*Abbreviation:* $PPh_3$, triphenyl phosphine; SEC, size exclusion chromatography; HPLC, high performance liquid chromatography; TLC, thin layer chromatography.

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cinchona-derived polymeric catalysts [10,11,21–25]. Mizoroki–Heck reaction requires two components, an olefinic double bond and an aromatic halide. In contrast, Yamamoto coupling reaction occurs between aromatic halides. The homopolymerization of aromatic dihalides is possible using this coupling reaction. Yamamoto coupling is the nickel-catalyzed coupling reaction of organic halides in the presence of neutral ligands (e.g., $PPh_3$ and bipyridine) [26,27]. The most commonly used nickel catalyst for the Yamamoto coupling reaction is bis(cyclooctadiene)nickel(0) ($Ni(COD)_2$). This coupling reaction is particularly interesting when it is applied to polymer synthesis. Yamamoto coupling polymerization proceeds through reductive elimination from a diorganonickel(II) intermediate [28–30]. Aromatic dihalides in the presence of a Ni catalyst simply react to afford π-conjugated polymers [31]. Various types of π-conjugated polymers have been synthesized via Yamamoto coupling polymerization [32]. However, to our knowledge, only one example of chiral polymer synthesis using Yamamoto coupling polymerization has been reported. Onimura et al. reported the Yamamoto coupling polymerization of chiral oxazoline monomers containing a diiodophenyl group [33]. They synthesized optically active poly(*m*-phenylene)s bearing chiral oxazoline at the side chains. The structures and chiroptical properties were characterized using spectroscopic and thermal gravimetric analyses [33]. No application of the chiral polymers to asymmetric catalysis has been reported till date.

We designed new cinchona-based chiral polymers using Yamamoto coupling polymerization. A novel type of polymeric chiral catalyst can be synthesized via this polymerization. Cinchona squaramide derivative was selected as an efficient catalyst for the Michael addition reactions. For this purpose, a dibromophenyl group or two iodophenyl groups were introduced into the cinchona alkaloids. For the polymerization reaction, the original polymerization method reported by Yamamoto was followed [34]. In addition to the chiral homopolymers, the copolymers of these cinchona squaramide monomers with an achiral aromatic dihalide were synthesized. For the linear chiral polymer synthesis, the olefinic double bond (C3-vinyl group) in cinchona alkaloid was reduced to prevent the Mizoroki–Heck-type coupling reaction. In the presence of the C3-vinyl group in the cinchona squaramide monomer, both Yamamoto coupling and Mizoroki–Heck coupling occurred simultaneously to yield hyperbranched chiral polymers, which were also used as catalysts in asymmetric reactions. In this study, the synthesis of novel chiral polymers via the Yamamoto coupling polymerization of cinchona squaramide derivatives is described. The design and synthesis of monomers suitable for Yamamoto coupling polymerization and their reaction conditions are discussed. The chiral polymers obtained by this polymerization are applied to the asymmetric catalysis of Michael addition reactions. The catalytic activities and stereoselectivities of the chiral polymers are also described.

## 2. Experimental section

### 2.1. Materials and methods

All reagents and solvents used during the investigation were purchased from Sigma–Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry (TCI) Co., Ltd. To monitor the progress of the reactions, thin layer chromatography (TLC) was performed using precoated silica gel plates (Merck TLC silica gel, 60F254). To purify the synthesized compounds, column chromatography was performed using a silica gel column (Wakogel C-200, 100–200 mesh). The $^1$H NMR spectra were recorded using JEOL JNM-ECS400 and JEOL JNM-ECX500 spectrometers operated at 400/500 MHz. The $^{13}$C NMR spectra were recorded at 100/125 MHz in $CDCl_3$ or DMSO-$d_6$ at room temperature. The chemical shifts are reported in parts per million (ppm) using tetramethyl silane (TMS) as the reference, and the *J* values are reported in Hertz (Hz). Infrared (IR) spectroscopy was performed using "KBr" pellets on a JEOL JIR-7000 FTIR spectrometer, and the wavenumbers are reported in $cm^{-1}$. High-resolution mass spectrometry (HRMS; ESI and APCI) data were recorded on a Bruker micro OTOF II HRMS instrument. High-performance liquid chromatography (HPLC) was carried out using a Jasco HPLC system composed of a DG-980-50 three-line degasser, an Intelligent HPLC pump (PU-2080), and a UV/Vis detector (UV-2075). The instrument was equipped with a chiral column (Chiralpak AS-H, Daicel) and hexane/2-propanol were used as the eluent at a flow rate of 0.7 mL/min at room temperature. HPLC was also carried out on a Jasco HPLC system composed of an HPLC pump (PU-980), a UV/Vis detector (UV-975), and a column oven CO-2065 equipped with a chiral column (Chiralcel OD-H, Chiralpak AD-H, Daicel) using hexane/2-propanol as the eluent at a flow rate of 1.0 mL/min at room temperature. Size exclusion chromatography (SEC) was performed using a Tosoh instrument with HLC 8020 UV (254 nm) or refractive index detector. Two polystyrene gel columns with a bead size of 10 μm were used, and DMF was used as the carrier solvent at a flow rate of 1.0 mL/min at 40 °C. A calibration curve was established to determine the number average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) values by comparison with the polystyrene standards. Optical rotations were recorded on a JASCO DIP-149 digital polarimeter using a 10-cm thermostatted microcell.

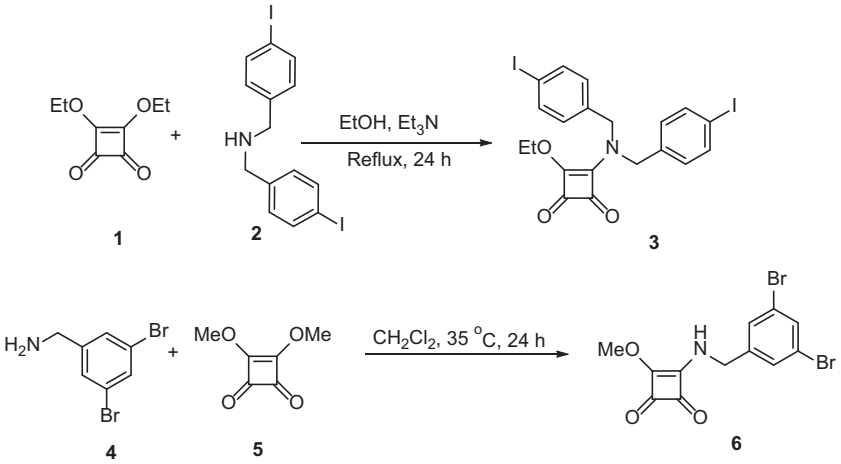
### 2.2. Synthesis of squaramides 8 and 10

First, monosquaramide **3** (410 mg, 0.71 mmol) and 10 mL of ethanol were added to a 30-mL volumetric flask. To the stirred solution, 0.86 mmol (253 mg) of 9-amino (9-deoxy)*epi* cinchonidine **7** in 10 mL ethanol was slowly added. The mixture was stirred under reflux for approximately 24 h in Ar atmosphere. A white precipitate was obtained, which was filtered, washed with ethanol, and dried to yield **8** (460 mg, 78%) as a white solid. $R_f$: 0.48 ($CH_2Cl_2$/MeOH = 9.0/1.0; mp: 229–231 °C. $^1$H NMR (400 MHz, $CDCl_3$):$\delta$ 0.90 (m, 1H), 1.29 (m, 2H), 1.61 (m, 4H), 2.27 (br,1H), 2.53–3.14 (m, 4H), 4.59 (br, 4H), 4.93 (m, 2H), 5.63 (m, 1H), 6.95(d, $J$ = 8.0 Hz, 4H), 7.72 (m, 8H), 8.14 (d, $J$ = 8.0 Hz, 1H), 8.86 (d, $J$ = 4.4 Hz, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): $\delta$ 25.9, 27.31, 27.69, 39.54, 40.77, 56.0, 94.20, 114.90, 123.57, 127.16, 129.56, 135.32, 138.41, 141.20, 149.99, 167.46, 168.0, 182.87, 183.50. IR (KBr): $\nu$ = 3324, 3065, 2933, 2862, 1788, 1667, 1561, 1484, 1343, 1285, 1182, 1088, 981, 839, 771, 649, 564 $cm^{-1}$; HRMS (APCI) *m/z* for $C_{37}H_{35}I_2N_4O_2$ [M + $H^+$] calcd. 821.0849, found 821.0844; $[\alpha]^{23.7}_D$ = −166 (*c* 0.07, DMF).

Further, monosquaramide **3** (410 mg, 0.71 mmol) was added with 10 mL of ethanol to a 30-mL volumetric flask. To the stirred solution, 9-amino (9-deoxy) 3-ethyl *epi* cinchonidine **9** (255 mg, 0.86 mmol), 10 mL of ethanol was slowly added. The mixture was stirred under reflux for approximately 24 h in Ar atmosphere. A white precipitate was obtained, which was filtered, washed with ethanol, and dried to afford **10** (480 mg, 81%) as a white solid. $R_f$: 0.48 ($CH_2Cl_2$/MeOH = 9.0/1.0; mp: 224–226 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.78 (t, $J$ = 7.6, 3H), 0.88 (m, 1H), 1.16 (m, 4H), 1.42–1.62 (m, 4H), 2.23 (br,1H), 2.52–3.14 (m, 4H), 4.59 (br, 4H), 6.95(d, $J$ = 8.0 Hz, 4H), 7.72 (m, 8H), 8.15 (d, $J$ = 7.6 Hz, 1H), 8.86 (d, $J$ = 4.4 Hz, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): $\delta$ 12.08, 24.97, 25.52, 27.60, 28.36, 37.31, 40.82, 57.69, 94.17, 123.63, 127.04, 129.46, 135.35, 138.41, 149.99, 167.82, 168.33, 182.89, 184.00. IR (KBr): $\nu$ = 3246, 2915, 2857, 1789, 1669, 1559, 1435, 1319, 1249, 1005, 839, 788, 673 $cm^{-1}$; HRMS (ESI) *m/z* for $C_{37}H_{37}I_2N_4O_2$ [M + $H^+$] calcd. 823.1006, found 823.1000; $[\alpha]^{16.7}_D$ = −190 (*c* 0.09, DMF).

### 2.3. Synthesis of squaramides 11 and 12

Monosquaramide **6** (198 mg, 0.53 mmol) and 9-amino (9-deoxy)*epi* cinchonidine **7** (171 mg, 0.58 mmol) were added to a 30-mL flask with 10 mL of MeOH and stirred at reflux temperature under Ar atmosphere for 48 h. White precipitate was obtained, which was filtered and washed with cold MeOH and finally dried in a vacuum oven to yield **11** (187 mg, 56%) as a white solid. $R_f$: 0.57 ($CH_2Cl_2$/MeOH = 1.0/1.0); mp: 296–298 °C. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 0.64 (m, 1H), 1.34 (m,




**Scheme 1.** Synthetic route to monosquaramides **3** and **6**.

2H), 1.55 (m, 4H), 2.25 (br,1H), 2.66 (m, 2H), 3.12–3.32 (m, 2H), 4.64 (br, 2H), 4.96 (m, 2H), 5.90 (m, 1H), 7.53 (s, 1H), 7.63–7.80 (m, 4H), 8.07 (d, $J = 8.5$ Hz, 2H), 8.48 (d, $J = 8.5$ Hz, 1H), 8.95 (d, $J = 4.0$ Hz, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$): $\delta$ 26.40, 27.75, 39.9, 46.15, 56.09, 59.80, 114.85, 123.18, 124.01, 126.80, 127.64, 129.97, 130.28, 130.35, 132.94, 142.70, 143.98, 148.62, 150.95, 167.5, 182.63. IR (KBr): $\nu$ = 3196, 3067, 2952, 2864, 1799, 1638, 1512, 1474, 1342, 1207, 1132, 980, 814, 766, 682 cm$^{-1}$; HRMS (APCI) *m/z* for $C_{30}H_{29}Br_2N_4O_2$ [M + H$^+$] calcd. 637.0657, found 635.0652; $[\alpha]^{17.4}_D = -43$ (*c* 0.11, DMF).

Monosquaramides **6** (198 mg, 0.53 mmol) and 9-amino (9-deoxy) 3-ethyl *epi* cinchonidine **9** (173 mg, 0.58 mmol) were added to a 30-mL flask with 10 mL of MeOH and stirred under reflux conditions with Ar gas for 48 h. White precipitate was obtained, which was filtered and washed with cold MeOH and finally dried in a vacuum oven to afford **12** (185 mg, 55%) as a white solid. $R_f$: 0.57 ($CH_2Cl_2$/MeOH = 1.0/1.0); mp: 294–296 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.61 (m, 1H), 0.78 (t, $J$ = 7.6 Hz, 3H), 1.24–1.57 (m, 8H), 2.32–2.43 (m, 1H), 2.55–2.67 (m, 1H), 3.10–3.29 (m, 3H), 4.65 (br, 2H), 7.53 (s, 1H), 7.61–7.81 (m, 4H), 8.05 (d, $J = 8.8$ Hz, 2H), 8.48 (d, $J = 8.4$ Hz, 1H), 8.94 (d, $J = 4.4$ Hz, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$): $\delta$ 12.51, 25.49, 26.20, 27.49, 28.55, 37.32, 46.13, 57.68, 59.9, 123.18, 124.03, 127.61, 129.95, 130.27, 130.45, 132.94, 144.00, 148.85, 150.96, 167.50, 182.50. IR (KBr): $\nu$ = 3196, 3066, 2955, 2861, 1799, 1638, 1563, 1420, 1342, 1276, 1101, 958, 852, 766, 681 cm$^{-1}$; HRMS (APCI) *m/z* for $C_{30}H_{31}Br_2N_4O_2$ [M + H$^+$] calcd. 637.0814, found 637.0808; $[\alpha]^{17.1}_D = -34$ (*c* 0.06, DMF).

### 2.4. Synthesis of chiral cinchona-based squaramide copolymer using Yamamoto coupling polymerization reaction

Squaramide **12** (160 mg, 0.19 mmol), 1,3-dibromo benzene **14** (22.7 μL, 0.19 mmol), 1,5-cyclooctadiene (0.21 mmol), 2,2′-bipyridyl (0.21 mmol), and Ni(COD)$_2$ (0.28 mmol) were added to a test tube with DMF (4.0 mL), and the reaction was carried out at 85 °C under $N_2$ flow. After 48 h, the polymer was precipitated in diethyl ether and washed twice with this solvent. Then, this polymer was washed with THF, HCl, and EDTA solution. After filtration, the yellowish-brown product **P2a** was dried in a vacuum oven. Yield: 158 mg (99%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.50–2.00, 4.69, 7.1–8.94; IR (KBr): $\nu$ = 3398, 3065, 2955, 2871, 1771, 1646, 1599, 1443, 1331, 1156, 1024, 969, 844, 768, 652 cm$^{-1}$; $[\alpha]^{18.8}_D = -9.0$ (*c* 0.06, DMF); $M_n$ (SEC) = 12,600; $M_w/M_n$ = 1.03.

Other chiral polymers used in this study were synthesized using this procedure.

### 2.5. Enantioselective Michael addition reaction of anthrone to trans-β-nitrostyrene

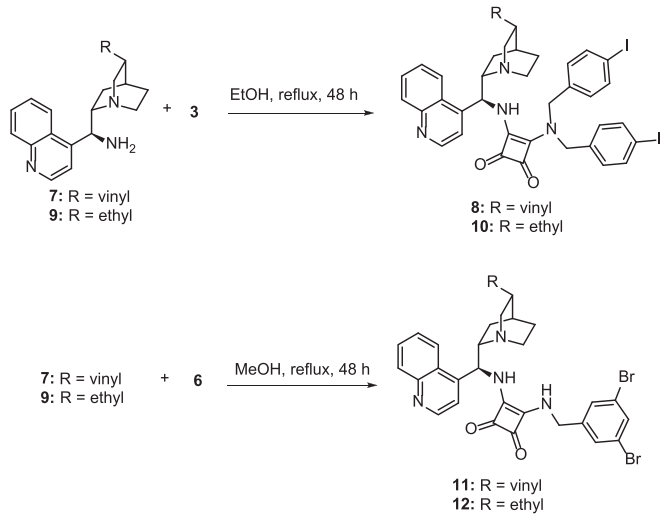
*Trans*-β-nitrostyrene **17** (29.8 mg, 0.20 mmol) and the polymeric catalyst (5.0 mol%; calculated based on the unit molecular weight of the polymer catalyst) were added to a reaction vessel with 2.0 mL of $CH_2Cl_2$. Anthrone **16** (46.6 mg, 0.24 mmol) was added to the resulting solution. The reaction was stirred at room temperature and monitored by TLC. The reaction mixture was then filtered, and the filtrate was concentrated in vacuo. The crude product was purified by silica gel (100–200 mesh) column chromatography using hexane/EtOAc (5:1) as the eluent to afford **18** as a white solid. The enantiomeric excess was determined using HPLC by employing a Chiralpak AS-H column and 5:1 hexane:2-propanol solution. Experiments to determine the effects of the solvent, substrate scope, and recyclability were performed according to this procedure. The results are summarized in Tables 2, 3, 4, and 5 (Scheme 4).

### 2.6. Enantioselective Michael addition reaction of β-ketoesters to trans-β-nitrostyrene

*Trans*-β-nitrostyrene **17** (82.1 mg, 0.55 mmol) and the polymeric catalyst (5 mol%) were added to a reaction vessel with 2.0 mL of solvent. Methyl 2-oxocyclopentanecarboxylate **25** (63 μL, 0.50 mmol) was added via a syringe into the resulting solution (Scheme 5). The reaction was stirred at room temperature, and its progress was monitored by TLC. The reaction mixture was then filtered, and the filtrate was concentrated in vacuo. The crude compound was purified by silica gel (100–200 mesh) column chromatography using hexane/EtOAc (6:1) as the eluent to afford the addition product **26** as a colorless oil. The enantioselectivity (*ee*) and diastereomeric ratio (*dr*) were determined using HPLC by employing a Chiralcel OD-H column and 4:1 hexane:2-propanol solution. The results are summarized in Table 6.

### 2.7. Enantioselective Michael addition reaction of acetylacetone to trans-β-nitrostyrene

*Trans*-β-nitrostyrene **17** (37.3 mg, 0.25 mmol) and the polymeric catalyst (5 mol%) were added to a reaction vessel with 1.0 mL of $CH_2Cl_2$. Next, acetylacetone **27** (30.6 μL, 0.275 mmol) was added to the resulting solution using a syringe (Scheme 5). The reaction was stirred at room temperature and monitored by TLC. The reaction mixture was then filtered, and the filtrate was concentrated in vacuo. The crude compound was purified by silica gel (100–200 mesh) column chromatography using hexane/EtOAc/$CH_2Cl_2$ (6:1:1) as the eluent to afford addition product **28** as a white solid. The enantiomeric excess values




**Scheme 2.** Synthetic route to cinchona squaramide monomers **8**, **10**, **11** and **12**.

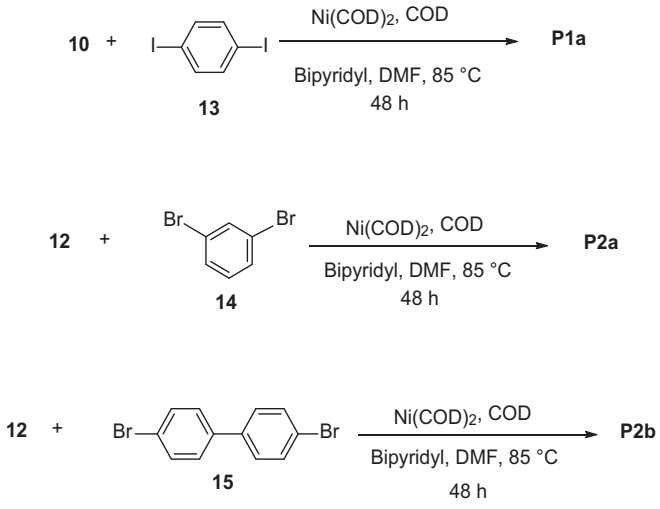
were determined using HPLC by employing a Chiralpak AD-H column and hexane:2-propanol (9:1) as the solvent. The results are summarized in Table 6.

## 3. Results and discussions

Cinchona squaramide derivatives **8**, **10**, **11**, and **12** were synthesized as monomers for the Yamamoto coupling polymerization. Scheme 1 describes the preparation of monosquaramides **3** and **6**, which contain two haloaryl moieties. These monosquaramides easily reacted with 9-amino (9-deoxy)*epi* cinchonidine **7** or 9-amino (9-deoxy) 3-ethyl epi cinchonidine **9** [25] to afford the corresponding cinchona squaramides **8**, **10**, **11**, and **12** (Scheme 2). These are chiral monomers for the Yamamoto coupling polymerization. Using these cinchona squaramide monomers (**8**, **10**, **11**, and **12**), the polymerization conditions of Yamamoto coupling polymerization were studied.

### 3.1. Preparation of chiral cinchona-based squaramide polymers using Yamamoto coupling polymerization

Since Onimura et al. reported the synthesis of chiral polymers using Yamamoto coupling polymerization [33], we used this procedure for the synthesis of cinchona squaramide polymers. First, this polymerization was applied to bis(4-iodobenzyl) derivative **10** of cinchona squaramide. Under standard conditions of Yamamoto coupling polymerization for aromatic dihalides [30], cinchona squaramide monomer **10** was polymerized to afford polymer **P1**. The results are summarized in Table 1. In the presence of $Ni(COD)_2$, monomer **10** underwent a self-polycondensation reaction at 85 °C in dimethylformamide (DMF) to provide linear polymer **P1** with a molecular weight of 7400 in quantitative yield (Table 1, entry 1). Copolymer **P1a** was also synthesized using cinchona squaramide **10** and 1,4-diiodobenzene **13** under the same Yamamoto coupling conditions (Scheme 3). Using squaramide **12** with a dibromobenzyl group, another linear polymer **P2** was synthesized. The polymerization conditions were investigated using **12** as a monomer. The polymerization of **12** in DMF at 85 °C for 24 h provided chiral polymer **P2** with a molecular weight of $M_n = 7800$ in 95% yield




**Scheme 3.** Synthesis of polymers, **P1a**, **P2a** and **P2b**.

**Table 1**
Synthesis of chiral polymers **P1**–**P4** from cinchona squaramide **8**, **10**, **11**, and **12** and their SEC data.[a]

| Entry | Monomer | Solvent | Chiral Polymers | Yield [%] | $M_n$[b] | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | **10** | DMF | **P1** | 99 | 7400 | 14,000 | 1.87 |
| 2 | **10** + **13** (1:1) | DMF | **P1a** (1:1) | 99 | 3900 | 4100 | 1.05 |
| 3 | **12** | DMF | **P2** | 99 | 8000 | 14,000 | 1.74 |
| 4 | **12** | DMSO | **P2** | 92 | 4800 | 6000 | 1.23 |
| 5 | **12** | Toluene | **P2** | 55 | 6000 | 6100 | 1.02 |
| 6[c] | **12** | DMF | **P2** | 97 | 4000 | 4600 | 1.15 |
| 7[d] | **12** | DMF | **P2** | 98 | 4300 | 5000 | 1.14 |
| 8[e] | **12** | DMF | **P2** | 95 | 7800 | 9300 | 1.20 |
| 9 | **12** + **14** (1:1) | DMF | **P2a** (1:1) | 99 | 12,600 | 13,000 | 1.03 |
| 10 | **12** + **14** (1:1.5) | DMF | **P2a** (1:1.5) | 98 | 5000 | 12,000 | 2.46 |
| 11 | **12** + **14** (1:0.7) | DMF | **P2a** (1:0.7) | 98 | 4700 | 7000 | 1.48 |
| 12 | **12** + **15** (1:1) | DMF | **P2b** (1:1) | 91 | 3600 | 3700 | 1.03 |
| 13 | **8** | DMF | **P3** | 99 | 7500 | 13,300 | 1.77 |
| 14 | **8** | DMSO | **P3** | 90 | 4900 | 6500 | 1.32 |
| 15 | **8** | Toluene | **P3** | 60 | 4400 | 5000 | 1.53 |
| 16[d] | **8** | DMF | **P3** | 98 | 8000 | 8200 | 1.02 |
| 17 | **11** | DMF | **P4** | 98 | 4400 | 5000 | 1.13 |

[a] Reaction was carried out with 0.19 mmol monomers, 0.21 mmol 2, 2′ bipyridyl, 0.21 mmol 1,5-cyclooctadiene and 4.0 mL solvent for 48 h at 85 °C.
[b] Determined by size exclusion chromatography (SEC) using DMF as the solvent at a flow rate of 1.0 mL/min at 40 °C (polystyrene standard).
[c] Reaction was carried out at 60 °C.
[d] Reaction was carried out at 110 °C.
[e] Reaction was carried out for 24 h.

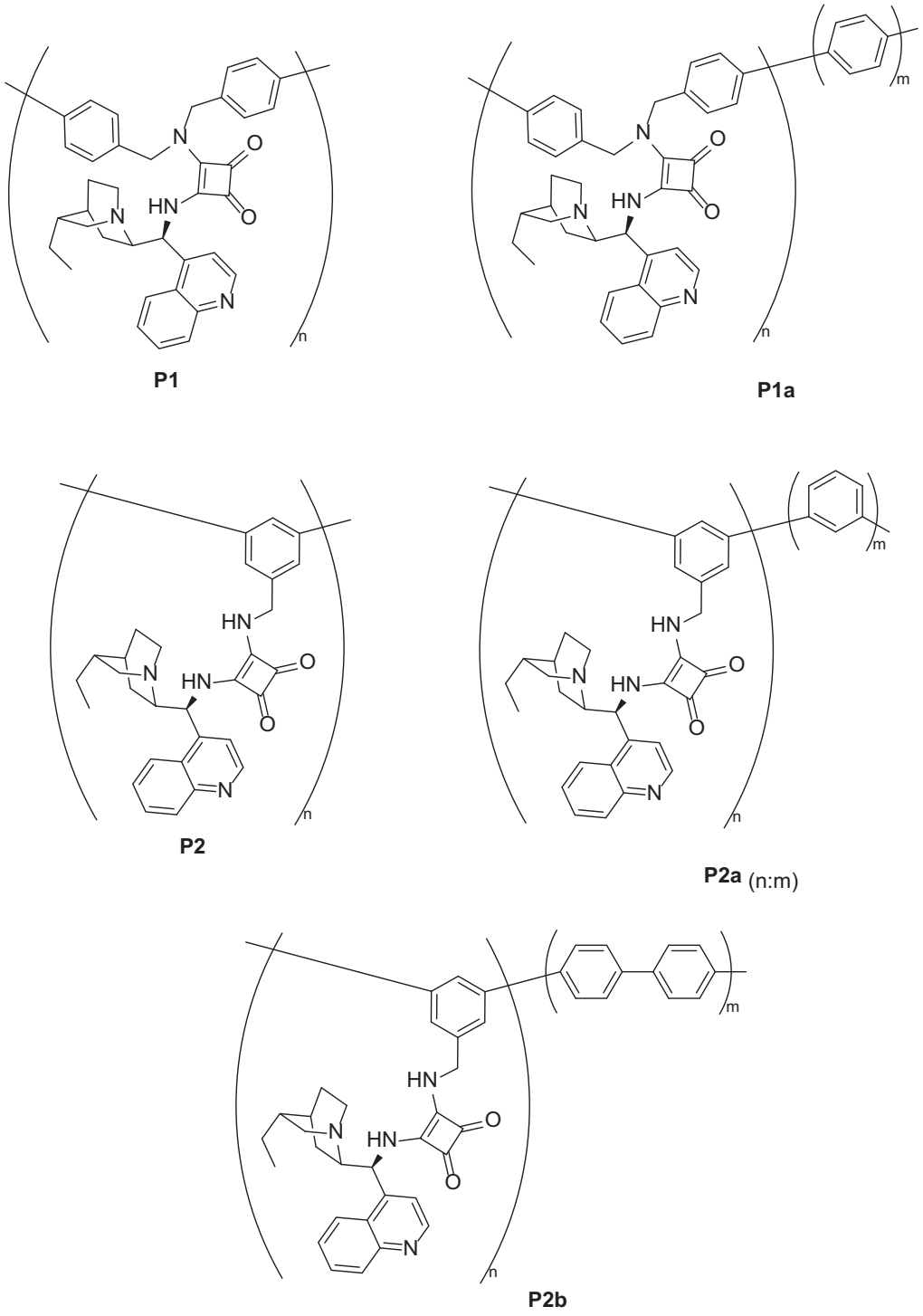



**Fig. 1.** Cinchona squaramide linear homopolymers, **P1** and **P2**, and copolymers, **P1a**, **P2a** and **P2b**.

(Table 1, entry 8). The completion of polymerization required 48 h, and **P2** with a molecular weight of $M_n = 8000$ was obtained (entry 3). Other solvents including DMSO and toluene were used for the polymerization of **12** at 85 °C for 48 h (entries 4 and 5). Low molecular weight and low yield in DMSO and toluene, respectively, were observed. At a low temperature (60 °C), polymerization occurred smoothly to afford polymer **P2** with a low molecular weight ($M_n = 4000$, entry 6). At a high temperature (110 °C), no increase in the molecular weight was observed (entry 7). We tested polymerization temperature from 60 to 110 °C (entries 6, 3, and 7). From these results, the suitable temperature for the polymerization may be 85 °C.

Under optimized conditions, copolymer **P2a** was synthesized from squaramide **12** and 1,3-dibromo benzene **14** (Fig. 1) using different ratios of **12** and **14**. An equimolar ratio of **12** to **14** afforded the copolymer **P2a** (1:1). The $^1$H nuclear magnetic resonance (NMR) spectra of **12** and polymer **P2a** (1:1) are shown in Fig. 3. By comparison the spectra of monomer and polymer, we can conclude that Yamamoto polymerization successfully occurred. Polymers **P2a** (m:n) with different ratios of **12** and **14** were prepared using the same method. For copolymerization of **12** and **14**, depending on the comonomer ratio, the

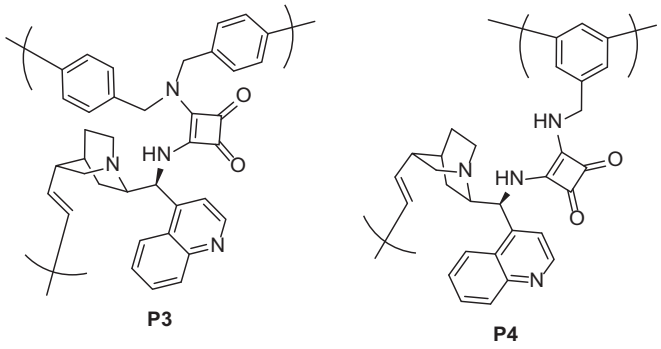



**Fig. 2.** Cinchona squaramide branched polymers, **P3** and **P4**.

molecular weights varied from 4700 to 12,600 (entries 3, 11, 9, and 10). The molecular weights were reproducible. However, no specific tendency was observed between the comonomer ratio and the molecular weight. An additional copolymer **P2b** was synthesized using **12** and 4,4′-dibromo biphenyl **15** (Fig. 1). These cinchona squaramide polymers are synthesized via the Yamamoto coupling reaction for the first time. These chiral polymers were soluble in DMF, DMSO, $CH_2Cl_2$, and $CHCl_3$ and partly soluble in other commonly used organic solvents such as MeOH, EtOAc, and THF. These were insoluble in diethyl ether and hexane, and readily precipitated in diethyl ether.

The transition-metal-catalyzed C—C coupling reaction between aryl halide and olefin is known as the Mizoroki–Heck coupling. Ni-catalyzed Mizoroki–Heck coupling is also possible [35]. In the presence of the Ni catalyst, both Yamamoto and Mizoroki–Heck coupling reactions occur simultaneously. For example, cinchona squaramide monomers **8** and **11** with a C3-vinyl group can be polymerized by either Yamamoto or Mizoroki–Heck coupling to yield hyperbranched polymers **P3** and **P4**, as shown in Fig. 2. For confirmation of that fact, under the reaction condition (in DMF, 85 °C, 48 h) established for the polymerization, we did the polymerization of dimer (only C3-vinyl group, no halide group) **29** and diiodobenzene **13**. The corresponding polymer **P5** was obtained in 96% yield which was confirmed by $^1$H NMR (Supporting Information *S1.11*).

### 3.2. Asymmetric Michael addition reaction of anthrone to trans-β-nitrostyrene

Polymeric catalysts **P1** – **P4** were studied as organocatalysts in the asymmetric Michael addition reaction of anthrone **16** and *trans*-β-nitrostyrene **17** (Scheme 4). The absolute configuration of the Michael adducts was assigned as (*S*) by comparing the reported value in the literature [36]. First, the catalytic activities of low-molecular-weight

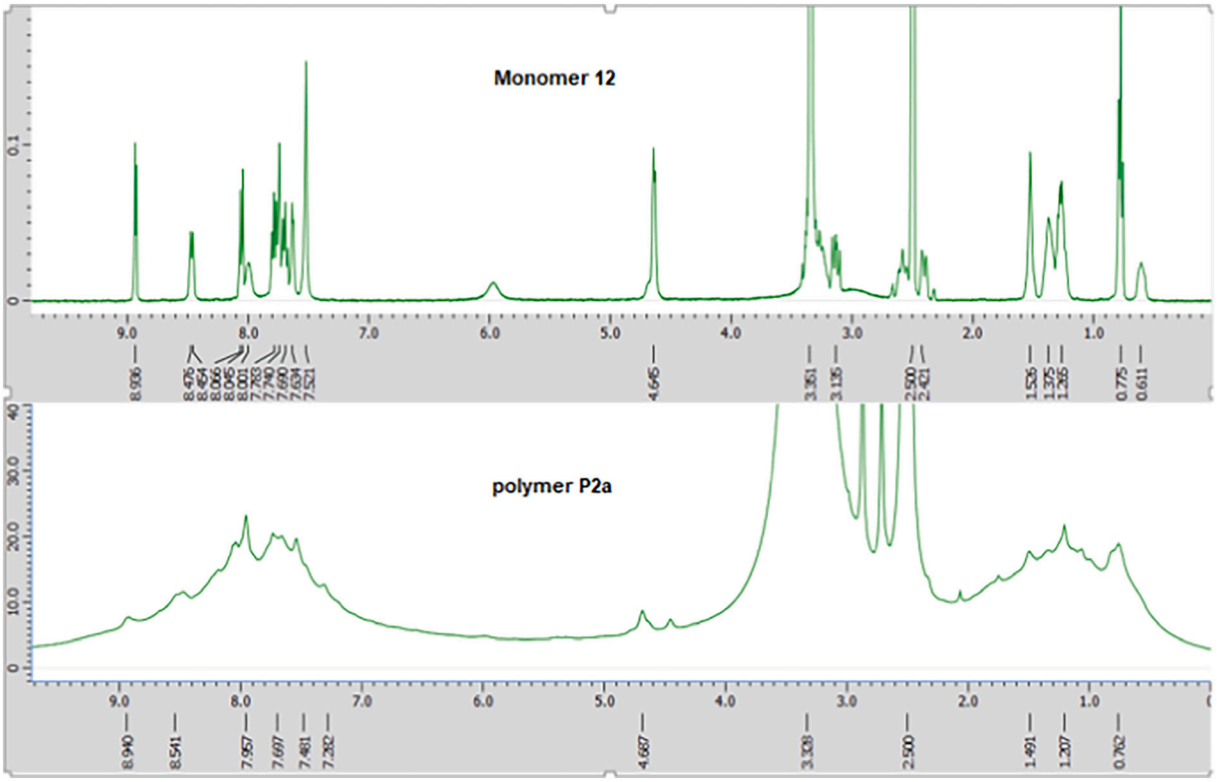
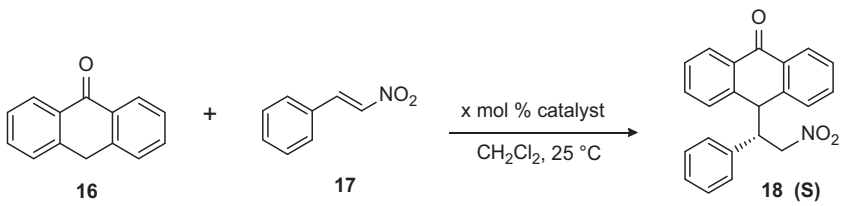



**Fig. 3.** $^1$H NMR spectra of monomer **12** and polymer **P2a**.




**Scheme 4.** Asymmetric Michael addition reaction of anthrone to *trans*-β-nitrostyrene using chiral polymeric catalysts.

**Table 2**
Reaction optimization: asymmetric Michael addition reaction of anthrone **16** to *trans*-β-nitrostyrene **14** using polymeric catalysts.[a]

| Entry | Catalyst | Catalyst loading (mol %) | Reaction time [h] | Yield[b]c [%] | *ee*[c] [%] |
|---|---|---|---|---|---|
| 1 | **10** | 5 | 7 | 93 | 58 |
| 2 | **12** | 5 | 24 | 89 | 84 |
| 3 | **P1** | 5 | 16 | 90 | 20 |
| 4 | **P1a** | 5 | 24 | 88 | 5 |
| 5 | **P2** | 5 | 12 | 90 | 66 |
| 6 | **P2a** (1:1) | 5 | 3 | 92 | 78 |
| 7 | **P2a** (1:1.5) | 5 | 6 | 91 | 61 |
| 8 | **P2a** (1:0.7) | 5 | 8 | 90 | 54 |
| 9 | **P2b** | 5 | 8 | 91 | 25 |
| 10 | **P3** | 5 | 24 | 82 | 2 |
| 11 | **P4** | 5 | 12 | 90 | 62 |
| 12 | **P2a** (1:1) | 2.5 | 3 | 92 | 75 |
| 13 | **P2a** (1:1) | 10 | 3 | 90 | 73 |
| 14 | **P2a** (1:1) | 15 | 3 | 92 | 72 |

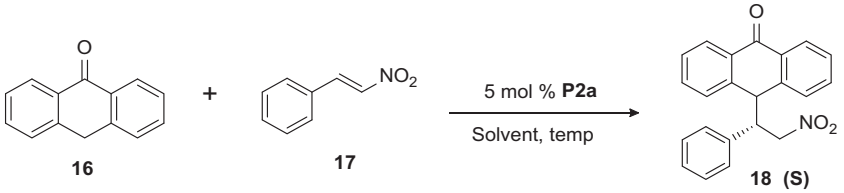
[a] Asymmetric reaction was carried out using **16** (0.24 mmol), **17** (0.2 mmol), and 5 mol% cat. in $CH_2Cl_2$ (2.0 mL) at 25 °C.
[b] Isolated yield of the product after column chromatography.
[c] Enantioselectivity (ee) was determined using HPLC (CHIRALPAK AS-H column).

cinchona squaramides **10** and **12** were examined as model catalysts. Cinchona squaramides **10** and **12** showed excellent catalytic activities in the asymmetric Michael addition reaction of anthrone and β-nitrostyrene to afford Michael adduct **18** in high yield with 58% ee and 84% ee (Table 2, entries 1 and 2). For monomeric catalyst 12, insolubility in solvent may be responsible for longer reaction time. For linear polymer **P1**, 20% enantioselectivity was observed with good yield (Table 2, entry 3). The corresponding copolymer **P1a** afforded an almost racemic product in only 5% ee with a prolonged reaction time, but the yield was good (Table 2, entry 4). Linear polymer **P2** was then used as a catalyst for the same reaction. In the presence of **P2**, the asymmetric reaction was completed within 12 h at 25 °C. Michael adduct **18** was obtained in 90% yield with 66% ee (entry 5). The enantioselectivity increased to 78% ee using copolymer **P2a** (1:1) in the same asymmetric reaction (entry 6). By employing **P2a** (1:1), the reaction was completed in three hours, which was much faster than that with the low-molecular-weight catalyst **12**, which required 24 h. The faster reaction was observed because of its high substrate accumulation efficiency in the polymer microenvironment. The chiral polymer chain of **P2a** effectively solubilized the substrate molecule for the reaction. Low-molecular-weight catalyst **12** was not soluble in the solvent and a heterogeneous reaction occurred. **P2a** could be prepared using different molar ratios of **12** and **14**. When the molar ratio was changed from 1:1 to 1:1.5 or 1:0.7, the polymeric catalysts **P2a** (1:1.5) and **P2a** (1:0.7) afforded lower enantioselectivities (entries 7 and 8). The structure of the comonomer also affected the enantioselectivity, mainly due to the change in the polymer conformation. With the use of biphenyl comonomer **15** instead of **14**, a much lower enantioselectivity (25% ee) was obtained (entry 9). Similar to the linear polymers **P1** and **P1a**, the hyperbranched polymer **P3** provided an almost racemic product, and the reaction proceeded appropriately (Table 2, entry 10). An additional hyperbranched polymer **P4** showed similar catalytic activity as **P2** (entries 5, 11).

The catalyst loading sometimes affects the catalytic performance in asymmetric reactions. Using **P2a**, different molar percentages of the catalyst were tested in the asymmetric reaction of anthrone **16** to *trans*-β-nitrostyrene **17**. Interestingly, even when the catalyst loading was decreased to 2.5 mol%, the reaction was completed in three hours (entry 12).

Solvent screening was performed using **P2a**. The results are summarized in Table 3. Various types of solvents were tested, and dichloromethane afforded the best result in the asymmetric reaction with **P2a**. The polymeric catalyst **P2a** was insoluble and shrank in hexane, requiring a long time to complete the asymmetric reaction. Relatively polar solvents such as acetonitrile, THF, acetone, methanol, and ethyl acetate resulted in low enantioselectivities (entries 5–9). The temperature effect was also examined (Table 3). At high temperature (50 °C), the reaction time decreased, and it was completed in 1.5 h, affording a slightly low enantioselectivity of 72% (Table 3, entry 11). Decreasing the temperature to −20 °C resulted in high enantioselectivity (82% ee, entry 12). Increased enantiomeric excess of 84% was obtained when the reaction was performed at −40 °C, but a long time of 48 h was needed (Table 3, entry 13).

**Table 3**
Asymmetric reaction of anthrone **16** and *trans*-β-nitrostyrene **17** using copolymer **P2a** (1:1).[a]

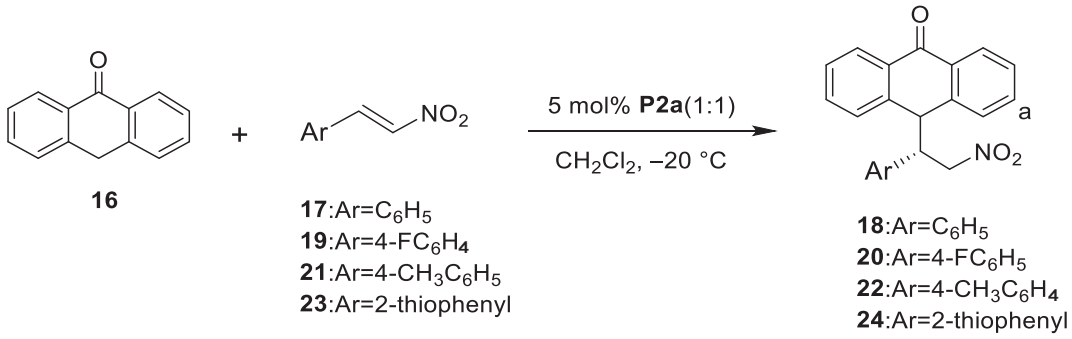



**16** **17** **18 (S)**

| Entry | Solvent | Temperature [°C] | Reaction time [h] | Yield[b] [%] | *ee*[c] [%] |
|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | 25 | 3 | 92 | 78 |
| 2 | $CHCl_3$ | 25 | 9 | 91 | 70 |
| 3 | Toluene | 25 | 10 | 89 | 63 |
| 4 | Hexane | 25 | 48 | 83 | 42 |
| 5 | Acetonitrile | 25 | 9 | 90 | 6 |
| 6 | THF | 25 | 6 | 90 | 17 |
| 7 | Acetone | 25 | 4 | 92 | 9 |
| 8 | MeOH | 25 | 8 | 87 | 17 |
| 9 | Ethyl acetate | 25 | 5 | 89 | 17 |
| 10 | Diethyl ether | 25 | 27 | 88 | 57 |
| 11 | $CH_2Cl_2$ | 50 | 1.5 | 92 | 72 |
| 12 | $CH_2Cl_2$ | −20 | 22 | 90 | 82 |
| 13 | $CH_2Cl_2$ | −40 | 48 | 89 | 84 |

[a] Asymmetric reaction was carried out using **16** (0.24 mmol), **17** (0.2 mmol), and 5 mol% **P2a** (1:1) in 2.0 mL solvent at different temperatures.
[b] Isolated yield of the product after column chromatography.
[c] Enantioselectivity (ee) was determined using HPLC (CHIRALPAK AS-H column).

**Table 4**
Substrate scope using copolymer catalyst **P2a** (1:1) in the reaction of anthrone to nitroolefins.[a]




| Entry | Michael acceptor | Product | Reaction time [h] | Yield[b] [%] | *ee*[c] [%] |
|---|---|---|---|---|---|
| 1 | **17** | **18** | 22 | 90 | 82 |
| 2 | **19** | **20** | 36 | 90 | 93 |
| 3 | **21** | **22** | 30 | 91 | 84 |
| 4 | **23** | **24** | 24 | 89 | 55 |

[a] Asymmetric reaction was carried out using **16** (0.24 mmol), nitroolefin (0.2 mmol), and 5 mol% **P2a**(1:1) in $CH_2Cl_2$ (2.0 mL) at −20 °C.
[b] Isolated yield of the product after column chromatography.
[c] Enantioselectivity (ee) was determined using HPLC (CHIRALPAK AS-H column).

**Table 5**
Recyclability test of copolymer catalyst **P2a** (1:1) in the enantioselective reaction of anthrone **16** to *trans*-β-nitrostyrene **17** in $CH_2Cl_2$ at −20 °C.[a]

| Entry | Reaction time [h] | Yield[b][%] | *ee*[c] [%] |
|---|---|---|---|
| Fresh polymer | 22 | 90 | 82 |
| Cycle 1 | 24 | 82 | 84 |
| Cycle 2 | 24 | 84 | 83 |
| Cycle 3 | 24 | 85 | 84 |
| Cycle 4 | 24 | 81 | 82 |

[a] Asymmetric reaction was carried out using **16** (0.24 mmol), **17** (0.2 mmol), and 5 mol% **P2a** (1:1) in $CH_2Cl_2$ (2.0 mL) at −20 °C.
[b] Isolated yield of the product after column chromatography.
[c] Enantioselectivity (ee) was determined using HPLC (CHIRALPAK AS-H column).

### 3.3. Substrate scope of chiral copolymer P2a (1:1)

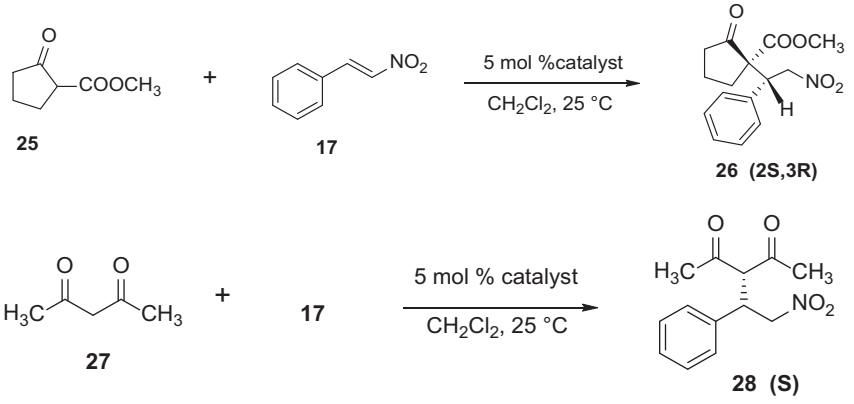
Other phenyl-substituted *trans*-β-nitrostyrene derivatives were tested in the asymmetric reaction of anthrone **16** using **P2a** (1:1) in $CH_2Cl_2$ at −20 °C (Table 4). Good (89–91%) yields were obtained in all cases. Excellent enantioselectivity of 93% was obtained with the Michael acceptor *trans*-4-fluoro-β-nitrostyrene **19** (Table 4, entry 2). The electron-withdrawing group at the para position of the benzene ring favored the enantioselectivity; 84% ee was obtained using *trans*-4-methyl-β-nitrostyrene **21** (Table 4, entry 3). Decreased enantioselectivity of 55% ee was observed for *trans*-2-thiophenyl-β-nitrostyrene **23** (Table 4, entry 4).

### 3.4. Recyclability of chiral copolymer P2a (1:1)

Chiral copolymer **P2a** (1:1) was completely soluble in $CH_2Cl_2$, and the asymmetric reaction occurred in a homogeneous system in this solvent. After completion of the reaction, the polymeric catalyst was precipitated in diethyl ether and then easily separated and recovered via simple filtration. The recovered polymeric catalyst **P2a** (1:1) was reused in the same reaction. The recyclability of **P2a** (1:1) was also examined, and in the recycling experiments, it could be used four times (Table 5); no significant differences in enantioselectivity were observed. The reaction was completed within 24 h using the reused polymeric catalyst **P2a** (1:1).

### 3.5. Michael addition reaction of other substrate combinations

An additional Michael donor, methyl 2-oxocyclopentanecarboxylate **25**, instead of anthrone was investigated. The chiral polymers **P1**–**P4** were used as organocatalysts in the reaction of **25** with **17** (Scheme 5). In all cases, the asymmetric reaction proceeded smoothly to provide chiral product **26** in good yield and excellent enantioselectivity with **P1**,




**Scheme 5.** Enantioselective Michael addition reaction using chiral polymers.

**Table 6**
Asymmetric Michael addition reaction using chiral polymeric catalysts.[a]

| Entry | Catalyst | Michael donor | Product | Reaction time [h] | Yield[c] [%] | *dr*[d] | *ee*[d] [%] |
|---|---|---|---|---|---|---|---|
| 1 | **P1** | **25** | **26** | 24 | 96 | 58:1 | 99 |
| 2 | **P1a** | **25** | **26** | 48 | 80 | 9:1 | 72 |
| 3 | **P2** | **25** | **26** | 24 | 95 | 92:1 | 98 |
| 4 | **P2a** (1:1) | **25** | **26** | 19 | 94 | >100:1 | 98 |
| 5 | **P2b** | **25** | **26** | 24 | 92 | >100:1 | 98 |
| 6 | **P3** | **25** | **26** | 48 | 85 | 6:1 | 48 |
| 7 | **P4** | **25** | **26** | 24 | 93 | >100:1 | 99 |
| 8[b] | **P2a** (1:1) | **27** | **28** | 18 | 82 | – | 78 |
| 9[b] | **P4** | **27** | **28** | 23 | 80 | – | 65 |

[a] Asymmetric reaction was carried out using **25** (0.5 mmol), **17** (0.55 mmol), and 5 mol% catalyst in $CH_2Cl_2$ (2.0 mL) at 25 °C.
[b] Asymmetric reaction was carried out using **27** (0.275 mmol), **17** (0.25 mmol), and 5 mol% catalyst in $CH_2Cl_2$ (2.0 mL) at 25 °C.
[c] Isolated yield of the product after column chromatography.
[d] Enantioselectivity (ee) and diastereomeric ratio (dr) were determined using HPLC (CHIRALCEL OD-H for entries 1–7 and CHIRALPAK AD-H for entries 8 and 9).

**P2**, and **P4** (Table 6). The absolute configuration of the Michael adducts **26** was assigned as (2*S*, 3*R*) by comparing the reported value in the literature [37,38]. Polymers **P1a** (1:1) and **P3** afforded low enantioselectivities (72% ee and 48% ee) in the prolonged reaction time of 48 h (entries 2 and 6). High diastereoselectivity (>100:1) was obtained with **P2a** (1:1), **P2b**, and **P4** catalysts (entries 4, 5, and 7). Chiral polymers **P2a** (1:1) and **P4** were also used in the asymmetric reaction of acetylacetone **27** with *trans*-β-nitrostyrene **17**. The reaction occurred smoothly with polymer **P2a** (1:1) to provide chiral Michael adduct **28** in 78% enantioselectivity with 82% yield (entry 8). With **P4** catalyst, the product was obtained in 65% ee with 80% yield (entry 9). The absolute configuration of the Michael adducts **28** was assigned as (*S*) by comparing the reported value in the literature [39]. Based on these results, a suitable microenvironment for the asymmetric reaction was created in the chiral polymer network of the polymeric catalyst **P2a** (1:1).

## 4. Conclusion

Cinchona squaramide-based chiral polymers **P1** – **P4** were successfully synthesized from monosquaramides **8**, **10**, **11** and **12** via the Yamamoto coupling reaction. Copolymers **P1a**, **P2a**, **P2b** were synthesized from **10**, **12** with achiral diiodo or dibromo aromatic compounds **13**–**15**. Chiral polymers **P1** – **P4** were applied to the asymmetric Michael addition reactions and afforded good to excellent enantioselectivities. Interestingly, polymeric catalyst **P2a** (1:1) showed a high catalytic activity in the asymmetric reaction of anthrone **16** and *trans*-β-nitrostyrene **17**. The reaction was completed within three hours in $CH_2Cl_2$ at 25 °C in the presence of only 2.5 mol% catalyst **P2a** (1:1); a suitable catalyst conformation may be formed in the case of **P2a** (1:1). Solvent screening revealed that the asymmetric reaction in $CH_2Cl_2$ afforded high enantioselectivity and high reactivity. The polymeric catalyst was used in a wide temperature range (−40–50 °C), and high enantioselectivity was obtained at low temperatures. Polymeric catalyst **P2a** (1:1) showed good performance in the asymmetric reactions for various combinations of the Michael donor and acceptor substrates. For 2-oxocyclopentanecarboxylate **25** and *trans*-β-nitrostyrene **17**, almost perfect diastereoselectivity with 98% ee was obtained with **P2a** (1:1). The polymeric catalyst was easily separated by precipitation into diethyl ether and recovered from the reaction mixture, allowing its reuse for the reaction. The recyclability of **P2a** (1:1) was determined in the asymmetric reaction of anthrone to *trans*-β-nitrostyrene for four cycles.

## Author contributions

S. A. C. and S. I. designed this study. They also contributed to writing this manuscript.

## Declaration of Competing Interest

The authors declare no conflicts of interest associated with this manuscript.

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## A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2021.104913.

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