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Development of new methods toward efficient immobilization of chiral catalysts

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Abstract—BINOL moieties are efficiently immobilized onto the surface of a micelle-derived spherical polymer and a monolayer-protected Au cluster (Au-MPC). Ti-BINOLate complexes generated from the BINOL immobilized polymer and Au-MPC are found to promote catalytic asymmetric alkylation of benzaldehyde with Et_2Zn to afford the adduct in up to 84% ee and 86% ee, respectively. Au-MPC-supported multicomponent asymmetric catalyst was prepared and used in the Michael reaction of 2-cyclohexen-1-one with dibenzyl malonate affording the adduct in up to 67% yield and 98% ee.

1. Introduction

Development of new supports for chiral catalysts with selectivities comparable to those of non-immobilized homogenous catalysts is a task of great importance. The simplest and most often used method for immobilization relies on introducing chiral ligands to commercially available polymers (e.g., polystyrene).[1] In such a system, the catalytic site remains deep inside the polymer backbone, giving less access to reaction partners, and resulting in substantial decreases in activity and selectivity as compared with the parent non-immobilized catalysts. An efficient immobilization depends mainly on placement of catalyst and its easy access to the reaction partners. Recently, nanoparticles such as dendrimers[2] and metal clusters[3] of nanometer size have emerged as efficient supports for chiral catalyst. Nanoparticles with appropriate surface coating are readily dispersible in organic solvents. Owing to their small sizes, nanoparticles tend to have very high surface areas and thus can be used as novel supports to prepare 'supported' asymmetric catalysts that are more accessible to reactants. Dendrimers are a type of regular and highly branched spherical nanomaterial and provide appropriate placement of functional groups. Dendrimer-supported chiral catalysts exhibit levels of selectivity comparable to those of homogenous counterparts, when the chiral ligands are placed at the periphery.[2i] However, the synthesis of dendrimers by either the convergent or divergent route involves multisteps and often results in low overall yield. Thus, in order to realize the advantages of dendrimer-supported catalysts, there must be developed new, innovative methods to prepare dendrimer-like architectures via short and simple routes.

Herein we describe synthesis of micelle-derived spherical polymers[4a] and monolayer-protected Au clusters (Au-MPC)[4b] as efficient supports for chiral catalysts. As a representative example, BINOL moieties are immobilized on micelle-derived polymers and Au-MPC surfaces as depicted in Figure 1.

2. Result and discussion

2.1. Micelle-derived polymer supports

The process of micelle formation is well known and has been studied extensively.[5] Surfactants possessing hydrophilic (polar) 'heads' and hydrophobic (non-polar) 'tails' form micelles upon addition to polar solvents such as water. Upon dissolution, like regions align and an aggregate is formed where the hydrocarbon tails are directed inward and the polar head groups face outward toward the aqueous environment. A non-polar 'pocket' is created on the inside of the micelle, due to the hydrocarbon ends of the molecules. Micelles possess unique characters and spherical shapes. We envisaged that surfactants possessing a functionalized chiral or achiral head group and an olefin unit at the terminal of hydrophobic non-polar tail on polymerization would produce spherical nanoparticles, with a functionalized hydrophilic region at the periphery.[5d]

Keywords: Micelle-derived polymer; Immobilization; MPC; Enantioselective reactions.
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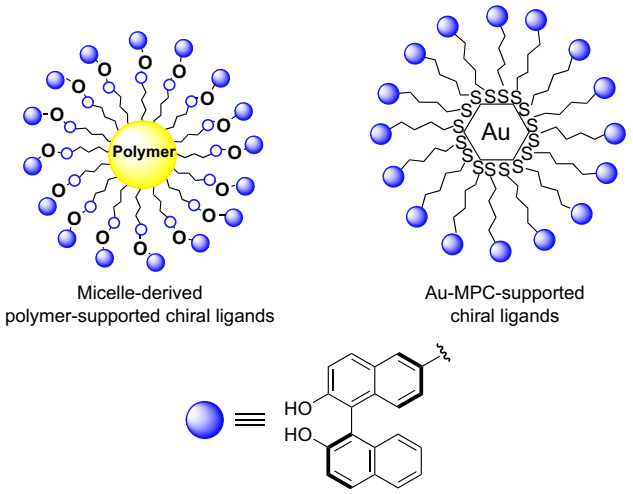
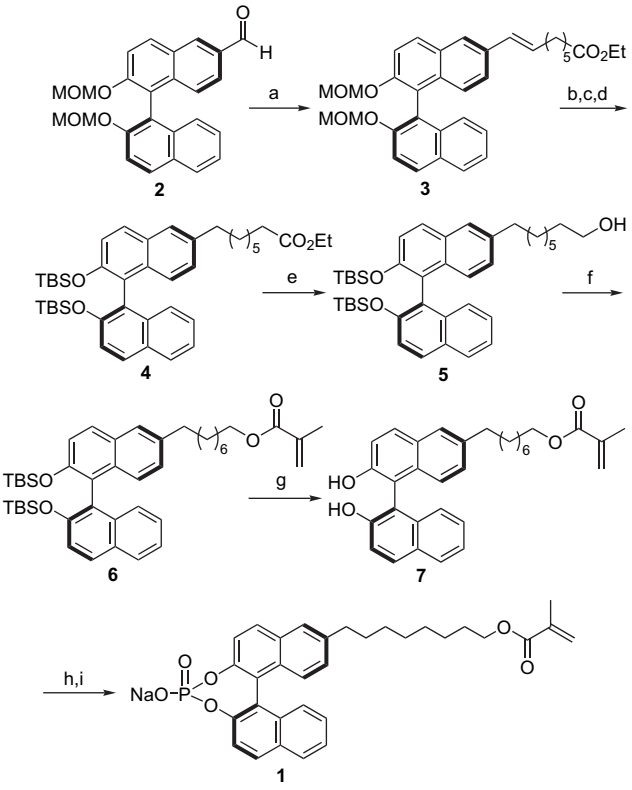


Figure 1. Micelle-derived polymer and Au-MPC-supported BINOL.

We explored two different synthetic strategies toward developing a new immobilization method for chiral catalysts. Method A involves direct polymerization of surfactant monomers bearing chiral hydrophilic regions, whereas method B relies on stepwise synthesis of micelle-derived polymer and immobilization of chiral catalysts. Figure 2 shows a schematic diagram for the synthesis of micelle-derived chiral nanoparticles (method A).

The chiral surfactant **1** was designed as a suitable monomer for conversion to a chiral catalyst after polymerization and removal of phosphate functionality. Sodium phosphate substituted 1,1′-binaphthyl moiety was chosen as the hydrophilic region in surfactant monomer **1**, in consideration of tremendous applications of (*R*)-BINOL in enantioselective catalysis.[6] The hydrophobic region includes an olefin unit for polymerization attached to the chiral hydrophilic region through a C_8 alkyl chain, which also serves as an appropriate spacer for the catalyst after polymerization. As depicted in Scheme 1, the synthesis of chiral surfactant monomer was commenced from a known compound (*R*)-6-formyl-2,2′-bis(methoxymethyloxy)-1,1′-binaphthyl[7] (**2**). Thus, Wittig reaction of **2** with $BrPPh_3(CH_2)_6CO_2Et$ produced **3**, which was converted to alcohol **5** in four simple steps. Then the olefin unit required for polymerization was introduced by reaction of alcohol **5** with methacrolyl chloride to give **6**, which upon deprotection with TBAF produced 1,1′-bi-2-naphthol (BINOL) derivative **7**. The hydrophilic region, sodium phosphate moiety was then introduced on BINOL derivative **7** in excellent yield to produce desired chiral surfactant monomer **1**. The synthesis of chiral surfactant monomer **1** was achieved in 56% overall yield after eight simple steps starting from **2**.



Scheme 1. Preparation of surfactant monomer **1**. *Reagents and conditions*: (a) 1.5 equiv $BrPPh_3(CH_2)_6CO_2Et$, 1.5 equiv NaOEt, DMF; (b) Pd–C/H_2, EtOH; (c) TsOH, CH_2Cl_2; (d) TBSCl, imidazole, DMF; (e) LAH, THF; (f) methacryloyl chloride, Et_3N, CH_2Cl_2; (g) TBAF, THF; (h) $POCl_3$, Et_3N, CH_2Cl_2; and (i) THF-15% NaOH.

The critical micelle concentration (cmc) of the chiral surfactant monomer **1** was determined in water using UV band

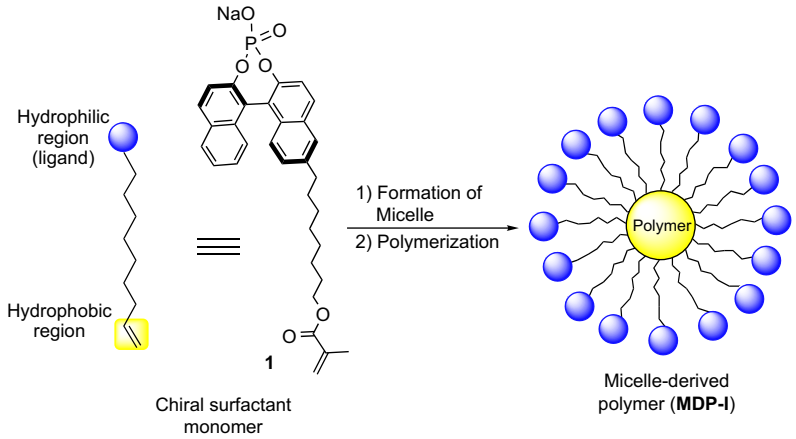


Figure 2. Polymerization of chiral surfactant monomer under micellar system (method A).

intensity variations in pinacyanol chloride monomer absorbance (9.0 mM at 25 °C).[8] Next, the polymerization of chiral surfactant monomer **1** was attempted in water by means of various radical initiators and concentrations. The use of known radical initiators such as benzoyl peroxide, Cu-bipyridyl complex, 2,2-6,6-tetramethylpiperidine-1-oxyl (TEMPO), and 4,4′-azobis-(4-cyano-valeric acid) (AVA) was less effective in polymerization of surfactant monomer **1**. Effective polymerization was achieved by means of 10 mol % of Et_3B as a radical initiator and maintaining concentration higher (100 mM) than cmc of monomer **1** at 0 °C under Ar for 8 h. Apparent molecular weight (M_w= 1.88×10^5, PDI (polydispersity index)=1.81) and diameter (6.7 nm) of micelle-derived polymer **MDP-I** were determined at 25 °C by size-exclusion chromatography connected to a UV detector and multiangle light scattering instrument (SEC-MALS).

Further, the spherical shape of polymer **MDP-I** was confirmed by scanning tunneling microscopy (STM), which also revealed spherical nanoparticles 5 nm in diameter along with aggregates of 9–20 nm in diameter (Fig. 3).[9] These results suggest that the shape of micelle was retained throughout the polymerization.

Although method A afforded chiral spherical nanoparticles,[10] a more general method is desirable to introduce a variety of chiral catalysts onto the surface of micelle-derived dendrimer-like nanoparticles. Toward this, method B was envisioned, in which an achiral surfactant monomer on polymerization under a micellar system provides spherical nanoparticles possessing immobilization sites at the periphery (Fig. 4).

The monomer selected for method B was achiral surfactant monomer **8**.[11,12] The monomer **8** possesses polyethyleneglycol as the hydrophilic region, and on polymerization provides free hydroxyl groups at the periphery for the immobilization of chiral ligands. The polymerization reaction of monomer **8** in water under several conditions and by means of various radical initiators and concentrations was attempted. However, the polymerization afforded rod-shaped polymers with low molecular weights. We reasoned that the monomer **8** has a long hydrophilic region and a short hydrophobic region (styrene unit), consequently monomer may easily escape from the micelle core, causing polymerization to occur in the aqueous phase rather than in the micelle core. To address this problem, we adopted a copolymerization method; thus, polymerization of monomer **8** was carried out by use of styrene (1 equiv) in the presence of photopolymerization initiator 2,2′-dimethoxy-2-phenylacetophenone. Indeed, this method produced spherical polymer **MDP-II** (M_w=2.84×10^4, PDI=2.85, diameter=3.2 nm as determined by SEC-MALS and STM analyses) consisting of **8** and styrene in 1:1 ratio, as confirmed by ^{1}H NMR.

After the successful synthesis of micelle-derived spherical polymer, BINOL moieties were immobilized on the surface

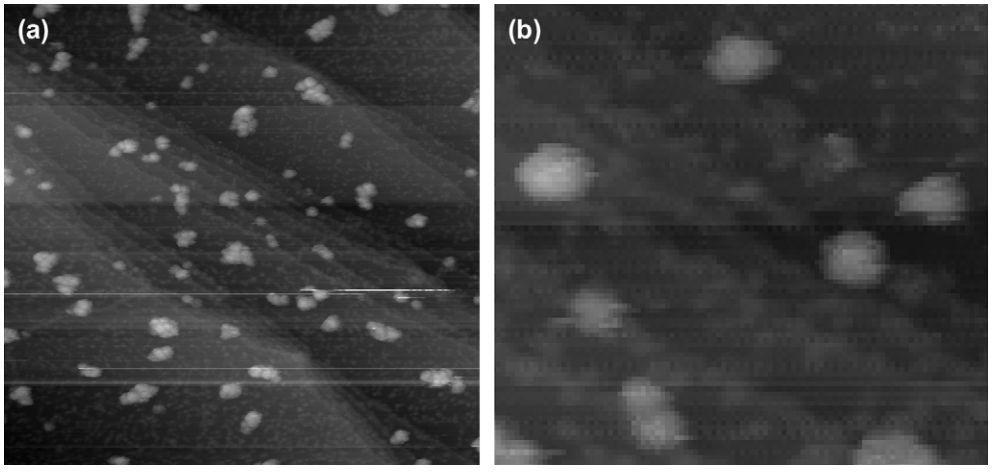


Figure 3. STM images of **MDP-I**: (a) 200×200 nm and (b) 30×30 nm.

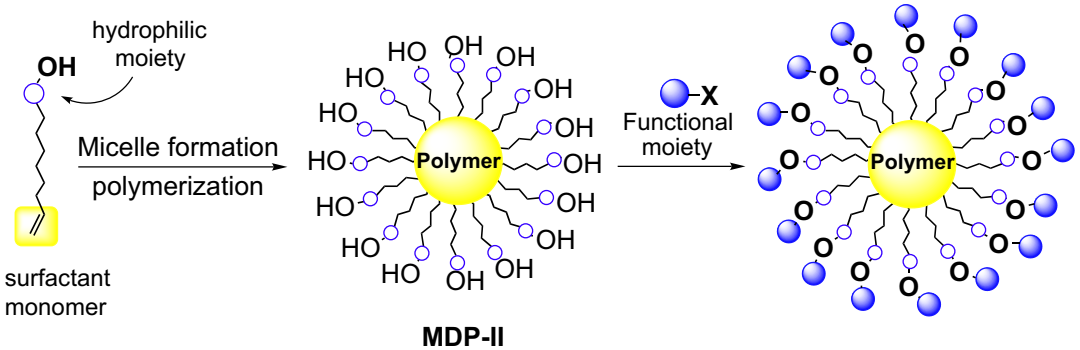


Figure 4. Schematic diagram for the synthesis of functionalized nanoparticles (method B).

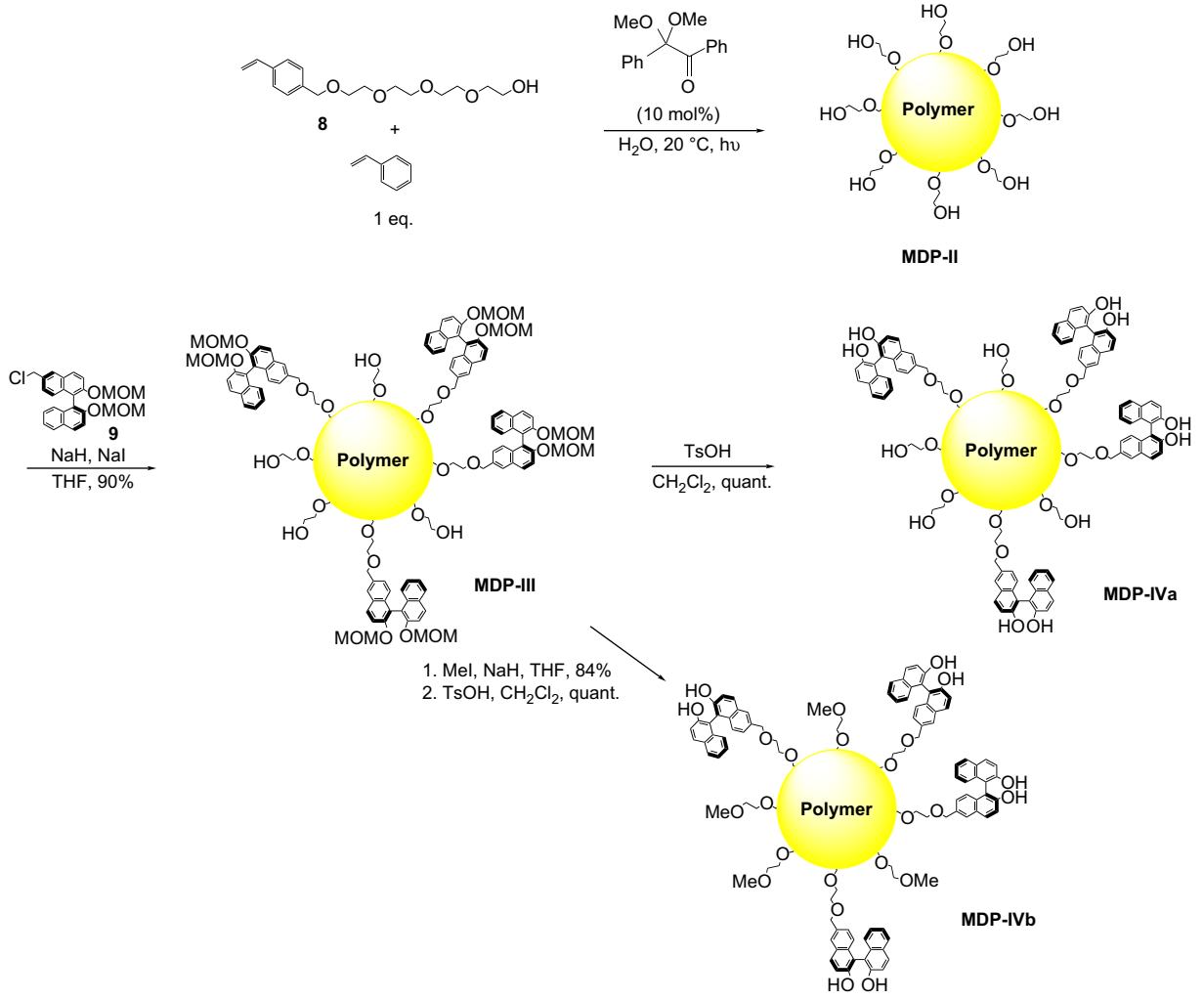
of **MDP-II** (Scheme 2). Immobilization of BINOL moieties was achieved by coupling reaction of **MDP-II** and BINOL derivative **9** in the presence of NaH and NaI to afford soluble polymer **MDP-III**. It is worthy to mention that, ^{1}H NMR studies revealed 90% of **9** was successfully immobilized onto the surface of **MDP-II**. The remaining free hydroxyl groups were capped with methyl group by treatment with methyl iodide, in consideration of the hydroxyl group interference in further asymmetric reactions. The removal of MOM group produced corresponding polymers **MDP-IVb** having free BINOL moieties at the periphery. The polymer **MDP-IVa** was also synthesized by deprotection of **MDP-III** to compare catalytic efficiency with that of capped polymer **MDP-IVb**.

In order to evaluate the catalytic efficiency of micelle-derived polymer supported catalysts, a linear polymer **LP** was synthesized by copolymerization of monomer **8** and styrene (1 equiv) in THF (M_w=1.10×10^4, PDI=2.56 by SEC). The polymer **LP** was then used for immobilization of BINOL moieties (Scheme 3).

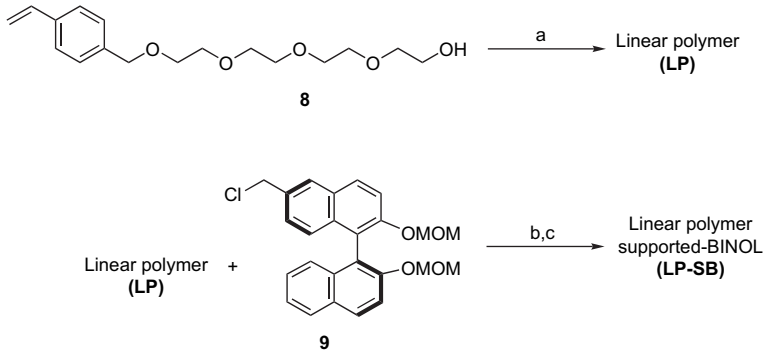
Thus, the treatment of **LP** with BINOL derivative **9** in the presence of NaH and NaI followed by removal of MOM group produced linear polymer-supported BINOL (**LP-SB**). The catalyst loading of linear polymer-supported BINOL (**LP-SB**) was low (0.025 mmol g^{-1}) as compared with the high catalyst loadings observed for the spherical micelle-derived polymer-supported BINOL **MDP-IVa** (1.32 mmol g^{-1}) and **MDP-IVb** (1.31 mmol g^{-1}), as confirmed by ^{1}H NMR analysis. The high catalyst loading obtained using micelle-derived polymer **MDP-II** as compared with the linear polymer **LP** is considered to reflect the exposed nature of hydroxyl groups located at the periphery in the former polymer.

To demonstrate the catalytic activity of spherical polymers **MDP-IVa** and **MDP-IVb**, catalytic asymmetric alkylation of benzaldehyde with Et_2Zn was performed (Table 1).[13] The heterogenous Ti-BINOLate complexes[14] were formed by addition of Ti(O-*i*-Pr)$_4$ to capped polymer **MDP-IVb** and uncapped polymer **MDP-IVa**.

The alkylation of benzaldehyde with Et_2Zn (2 equiv) and 1 equiv of Ti(O-*i*-Pr)$_4$ using polymer **MDP-IVa** (9 mol %) proceeded smoothly to produce product (*S*)-**10** in moderate yield and enantioselectivity (entry 1). As expected, the capped polymer **MDP-IVb** showed slight enhancement in the catalytic activity as compared with the uncapped polymer **MDP-IVa** (entry 2). Further, increasing the amount of

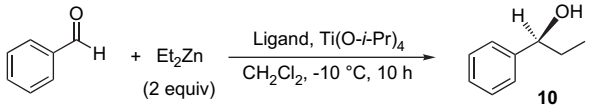


Scheme 2. Method B: copolymerization of achiral surfactant monomer **8** and immobilization of BINOL moieties.



Scheme 3. Linear polymer-supported BINOL. *Reagents and conditions*: (a) AIBN (10 mol %), styrene (1 equiv), THF, 60 °C; (b) NaH, NaI, THF, rt, 24 h; and (c) $TsOH \cdot H_2O$, CH_2Cl_2, rt, 2 h.

Table 1. Catalytic asymmetric alkylation over micelle-derived spherical polymer-supported Ti-BINOLate complex



Entry	Ligand	$Ti(O\text{-}i\text{-}Pr)_4$ (equiv)	Yield[b] (%)	ee[c] (%)
1	**MDP-IVa** (9 mol %)[a]	1.0	51	76
2	**MDP-IVb** (9 mol %)[a]	1.0	60	81
3	**MDP-IVb** (18 mol %)[a]	1.0	Quant	79
4	**MDP-IVb** (18 mol %)[a]	2.0	96	84
5	**LP-SB** (18 mol %)[a]	1.0	50	25
6	BINOL (9 mol %)	1.0	Quant	89

[a] As a monomeric ligand.
[b] Determined by ^1H NMR.
[c] Determined by HPLC (Diacel Chiralcel OD-H, hexane/*i*-PrOH=19/1).

polymer **MDP-IVb** (18 mol %) afforded product (*S*)-**10** in quantitative yield and 79% ee (entry 3). Moreover, the use of 2 equiv $Ti(O\text{-}i\text{-}Pr)_4$ further improved the level of enantioselectivity up to 84% ee (entry 4).[15] Notably, linear polymer-supported BINOL (**LP-SB**) under the present conditions afforded product (*S*)-**10** with low yield and enantioselectivity (50% yield, ee 25%, entry 5). The catalytic efficiency of micelle-derived polymer **MDP-IVb** is comparable to that of homogenous catalysis using BINOL (entry 4 vs entry 6).[16]

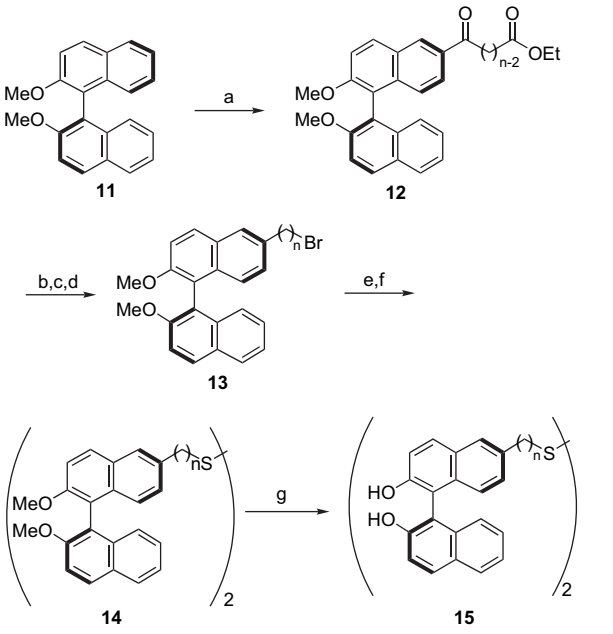
Thus a new, short, and efficient method for the synthesis of chiral or achiral spherical nanoparticles has been developed. This method has numerous advantages over traditional linear polymers in terms of both catalyst loading and catalytic efficiency.

2.2. Monolayer-protected Au cluster (Au-MPC)-supported chiral catalysts

A monolayer-protected metal cluster of nanometer size provides another efficient method for the immobilization of catalysts.[3d] The design and synthesis of structurally well-defined Au clusters is relatively simple and provides most of the advantages offered by spherical dendrimer-like nanoparticles. Similar to micelle-derived polymers, MPCs prepared with thiols/disulfides containing a chiral ligand moiety position chiral ligands on the surface of a metal cluster. Therefore, the catalyst generated from Au-MPC-supported ligands is expected to show high catalyst activity.

To prepare MPCs bearing chiral BINOL moieties on the Au surface for their applications to asymmetric reactions, disulfides with varying lengths of alkyl chain possessing BINOL units at terminal end were designed.

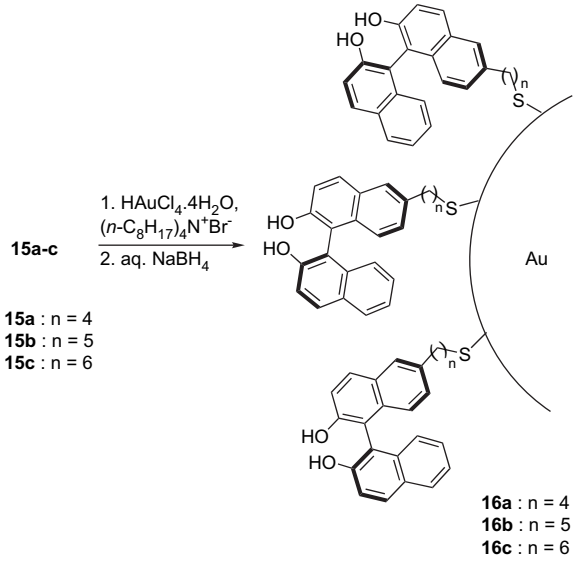
The synthetic route used for the preparation of various disulfides is described in Scheme 4. Alkyl chains with varying chain lengths were successfully introduced at the 6-position of BINOL by means of a series of simple chemical transformations. Thus Friedel–Craft's acylation[17] of 2,2′-dimethoxy-1,1′-binaphthalene (**11**) with varying chain lengths of acid chlorides produced compound **12**. The reduction of ketone[17] and ester followed by bromination of resulting alcohol afforded corresponding bromide **13**. The conversion of bromide to desired disulfide **14** was achieved by reacting bromide with thiourea and subsequent treatment with iodine in aq NaOH. Finally, removal of Me groups on the BINOL moiety with BBr_3 afforded free BINOL-terminated disulfide **15**. Preparation of disulfides **15a–c** with various lengths of



Scheme 4. Preparation of disulfide **15**. *Reagents and conditions*: (a) 1.5 equiv $CH_3OCOC_6H_{12}COCl$, 1.5 equiv $AlCl_3$, CH_2Cl_2; (b) Et_3SiH, TFA, CH_2Cl_2; (c) LAH, THF; (d) PPh_3, CBr_4, THF; (e) $(NH_2)_2C{=}S$, DMSO; (f) I_2, aq NaOH; and (g) BBr_3, CH_2Cl_2.

alkyl chain as spacers (n=4, 5, and 6) has been achieved in overall yield of 31–34% in seven simple steps.

The obtained disulfides **15a–c** with various spacer lengths were then used to synthesize BINOL functionalized Au-MPCs (Scheme 5). The disulfide **15** consisting of two (*R*)-BINOL moieties was added to a toluene solution of $AuCl_4^-(n\text{-}C_8H_{17})_4N^+$ generated in situ by treatment of aqueous solution of $HAuCl_4$ with tetraoctylammonium bromide.[18] Subsequently, the reaction mixture was treated with $NaBH_4$ to obtain BINOL functionalized Au-MPCs **16a–c** quantitatively. The amounts of disulfide immobilized onto Au-MPCs and loading of BINOL (**16a**: 1.30 mmol g^{-1}; **16b**: 1.28 mmol g^{-1}; **16c**: 1.26 mmol g^{-1}) were determined by elemental analysis.



Scheme 5. Au-MPC-supported BINOL moieties.

The size of representative Au-MPC **16b** was analyzed by transmission electron microscopy (TEM), and the TEM image revealed formation of MPC with a diameter less than 5 nm for the Au core (Fig. 5).[19]

Further, the catalytic efficiency of BINOL-functionalized Au-MPCs **16a–c** was screened in the asymmetric alkylation of benzaldehyde with Et_2Zn.[13] Similar to the case of micelle-derived polymers, addition of Ti(O-*i*-Pr)$_4$ to Au-MPCs **16a–c** resulted in heterogenous Ti-BINOlate complexes.[14] As described in Table 2, all Au-MPC-supported catalysts showed excellent reactivity, producing corresponding product (*R*)-**10** in high yield, and good enantioselectivity.

Thus, reaction of benzaldehyde with 2 equiv of Et_2Zn and 1 equiv of Ti(O-*i*-Pr)$_4$ was promoted by 10 mol % of Au-MPC **16a** to give adduct (*R*)-**10** in 92% yield with 80% ee (entry 1). The use of Au-MPC **16b**, having spacer length n=5, improved enantioselectivity up to 86% ee (entry 2). However, further increase in spacer length (n=6), employing Au-MPC **16c** lowered enantioselectivity (entry 3). The catalyst amount could be decreased to 5 mol % with a slight decrease in enantioselectivity (entry 4). Moreover, the reaction using 3 equiv of Et_2Zn afforded product (*R*)-**10** in high enantiomeric excess (entry 6). Notably, the activity of heterogenous

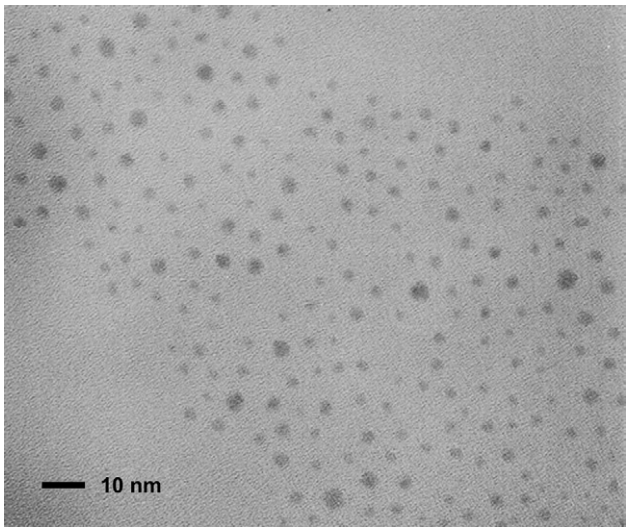
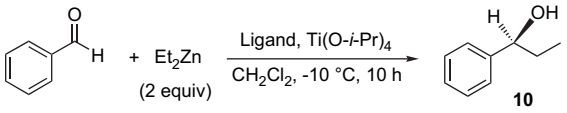


Figure 5. TEM image of MPC **16b**.

Table 2. Catalytic asymmetric alkylation over Au-MPC-supported Ti-BINOLate complex



Entry	MPC[a] (mol %)	n[b]	Et_2Zn (equiv)	Time (h)	Yield[c] (%)	ee (%)
1	**16a** (10)	4	2	7	92	80
2	**16b** (10)	5	2	7	98[d]	86
3	**16c** (10)	6	2	7	95	72
4	**16b** (5)	5	2	7	95	80
5	**16b** (10)	5	1	16	33	73
6	**16b** (10)	5	3	1	95	84

[a] As a monomeric ligand.
[b] Lengths of alkyl chains as spacers.
[c] Determined by ^{1}H NMR.
[d] Isolated yield.

Au-MPC catalyst[20] was comparable to those of homogenous parent Ti-BINOLate complexes. The high loading of BINOL on Au surface, the TEM image, and the excellent catalytic activity of MPC suggest the naked character of BINOL moieties on the surface of Au-MPC.

2.3. Au-MPC-supported BINOL ligands for the immobilization of multicomponent asymmetric catalysts

Previously, we have reported a series of multicomponent asymmetric catalysts that consist of two or three BINOL moieties and two kinds of metals for a range of asymmetric transformations.[6d,21] Analogous to enzymatic reactions, the synergistic cooperation between two or more functional groups and metals is important for realizing high reactivity and stereoselectivity.

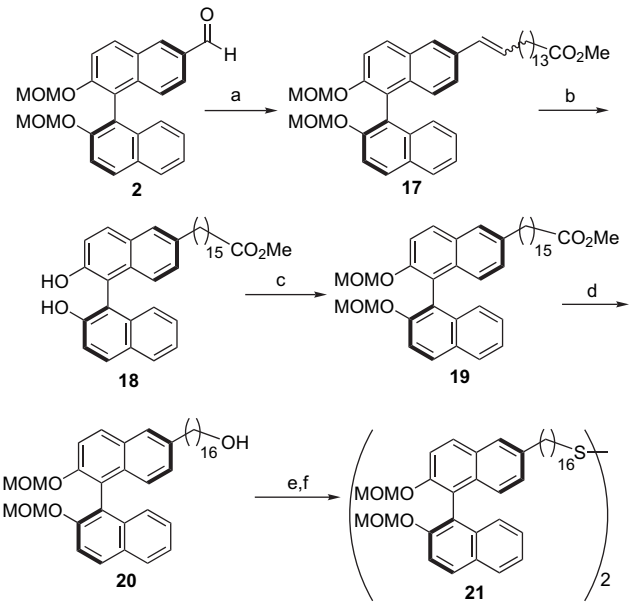
Immobilization of multicomponent asymmetric catalyst is a challenging task, as specific organization of ligands on a support is crucial for obtaining products with high yield and enantioselectivity. The random orientation of ligands as observed in BINOL immobilized on polystyrene resin resulted in producing product with low yield and low

enantiomeric excess. We have developed several new methods for the efficient immobilization of multicomponent asymmetric catalyst, such as Al–Li-bis(binaphthoxide) complex (ALB) and Ga–Na-bis(binaphthoxide) complex (GaSB).[2i,22]

Having been encouraged by the results obtained in asymmetric alkylation of benzaldehyde using Au-MPC-supported BINOL moieties, we focused our attention toward immobilization of multicomponent asymmetric catalysts.[23] The general schematic representation for the Au-MPC-supported multicomponent asymmetric catalyst is depicted in Figure 6.

Initial results obtained using the ALB complex prepared from Au-MPC **16b** were disappointing in the asymmetric Michael reaction of 2-cyclohexe-1-one with dibenzyl malonate, affording Michael adduct in 7% yield and 7% ee. In Au-MPC **16b**, due to shorter spacer, the BINOL moieties are arranged on the Au surface in close proximity and with limited flexibility, and thus hamper synergistic cooperation between two BINOL ligands required to generate catalytically active ALB complex. In order to obtain efficient synergistic cooperation between two BINOL ligands, orientation of BINOL units on the Au surface is crucial. We envisaged the use of long alkyl spacers, which would give enough flexibility to BINOL moieties to adopt favorable orientations. After screening several BINOL-terminated disulfides with spacers of varying alkyl chain lengths, disulfide **21** (n=16) was chosen to prepare BINOL immobilized Au-MPC. The synthetic route for the preparation of disulfide **21** is shown in Scheme 6.

The Wittig reaction of (*R*)-6-formyl-2,2′-bis(methoxymethyloxy)-1,1′-binaphthyl (**2**) with $IPPh_3(CH_2)_{14}CO_2Me$ afforded **17**. A surprising subsequent reduction of olefin **17** was problematic, and under most of the conditions produced products in low yields. Fortunately, **17** was smoothly reduced using $Pd(OH)_2/H_2$/AcOH in quantitative yield along with undesired cleavage of MOM group. Next, a series of simple chemical transformations involving reduction of



Scheme 6. Synthesis of disulfide **21**. *Reagents and conditions*: (a) $IPPh_3(CH_2)_{14}CO_2Me$, MeONa, DMF, 0 °C; (b) $Pd(OH)_2$, H_2, AcOH, CH_2Cl_2, 45 °C; (c) MOMCl, NaH, THF, 0 °C; (d) $LiAlH_4$, THF, rt; (e) PPh_3, CBr_4, THF, 0 °C; and (f) $(NH_2)_2CS$, DMSO, 35 °C.

ester, conversion of alcohol to bromide, and treatment with thiourea produced protected BINOL-terminated disulfide **21** in good yield. Disulfide **21** was then used to prepare Au-MPC **22**, which upon deprotection of MOM group produced Au-MPC **23** (Scheme 7).

The loading of BINOL unit was determined by elemental analysis (1.09 mmol g^{-1}), and the size of Au-MPC **23** was 5 nm as analyzed by transmission electron microscopy (TEM).

To demonstrate the catalytic activity of Au-MPC **23** in asymmetric Michael reaction, GaSB catalyst, which is less sensitive to moisture as compared with ALB catalyst was

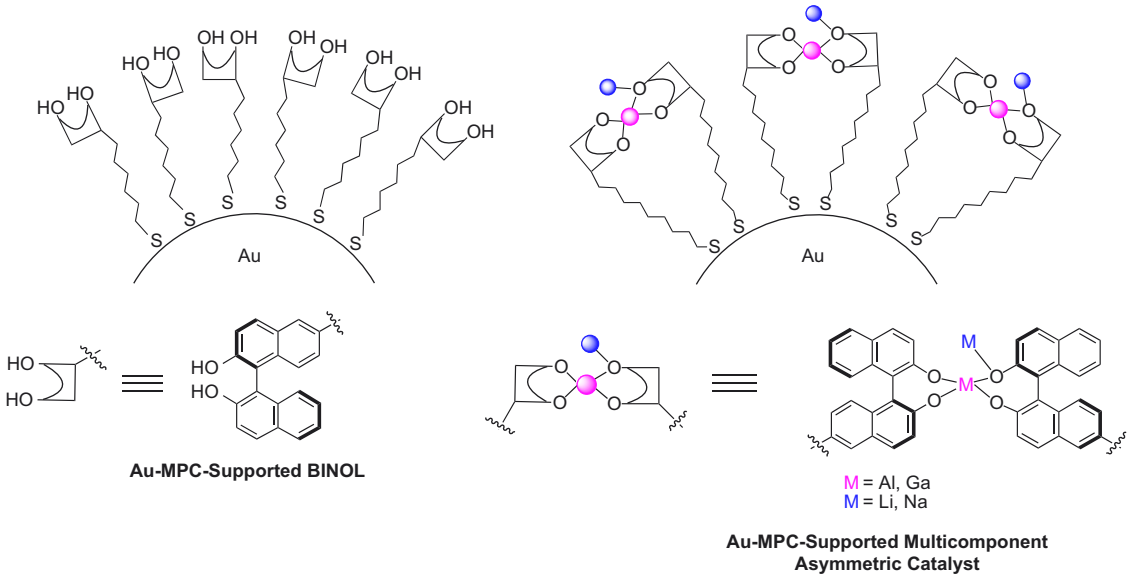
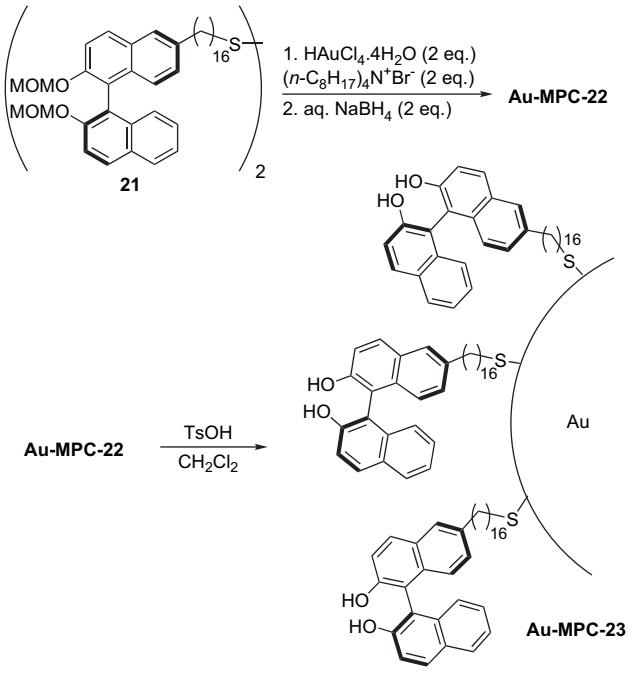


Figure 6. Au-MPC-supported multicomponent asymmetric catalysts.

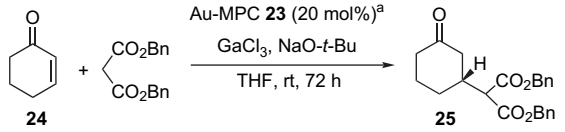


Scheme 7. Synthesis of Au-MPC **23**.

prepared from Au-MPC **23**. Table 3 summarizes the results obtained in Michael reaction of 2-cyclohexen-1-one (**24**) with dibenzyl malonate promoted by 20 mol % of Au-MPC **23** with varying amounts of $GaCl_3$ and NaO-*t*-Bu.

The GaSB catalyst prepared from Au-MPC **23** (20 mol %), $GaCl_3$ (15 mol %), and NaO-*t*-Bu (65 mol %) afforded Michael adduct **25** in 44% yield and 85% ee (entry 1). Interestingly, increasing the amount of NaO-*t*-Bu improved enantioselectivity up to 97% ee with a slight increase in the yield (entry 2). These results are in good agreement with our previous studies using BINOL, where activated GaSB with base[21b] generated by addition of 0.9 equiv of NaO-*t*-Bu to initially-prepared GaSB catalyst improved yield and enantioselectivity of Michael adduct **25**. After screening several reaction parameters, we were pleased to find optimum conditions using NaO-*t*-Bu (85 mol %) and $GaCl_3$ (20 mol %) to produce Michael adduct in 67% yield with 98% ee (entry 4). Although yield of Michael adduct using

Table 3. Michael reaction using Au-MPC-supported GaSB catalyst



Entry	$GaCl_3$ (mol %)	NaO-*t*-Bu (mol %)	Yield[b] (%)	ee[c] (%)
1	15	65	44	85
2	15	75	58	97
3	15	85	67	88
4	20	85	67	98
5	20	95	89	69
6	25	95	87	70

[a] As a monomeric ligand.
[b] Isolated yield.
[c] Determined by HPLC (Chiralpak AS, hexane/*i*-PrOH=4/1).

Au-MPC **23**-supported GaSB catalyst was slightly lower than that using the parent homogenous catalyst prepared from BINOL, a comparable level of enantioselectivity was observed. To the best of the authors' knowledge, this is the first report on Au-MPC-supported asymmetric multicomponent catalyst.

3. Conclusion

Micelle-derived polymers and Au-MPCs serve as novel supports for chiral catalysts. A new method has been developed for the preparation of spherical nanoparticles from a micellar system. BINOL moieties were immobilized on the spherical surfaces of micelle-derived polymer and Au-MPCs. The catalytic efficiency of chiral catalysts generated from micelle-derived polymers and Au-MPC-supported BINOL moieties was demonstrated in the asymmetric alkylation of benzaldehyde. A suitable organization of BINOL moieties required to generate asymmetric multicomponent catalyst was achieved by using Au-MPC-supported BINOL moieties. The catalytic efficiency of Au-MPC-supported asymmetric multicomponent catalyst has been demonstrated in the asymmetric Michael reaction.

4. Experimental section

4.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX270 FT NMR (^{1}H NMR 270 MHz, ^{13}C NMR 67.7 MHz). All signals are expressed as parts per million down field from tetramethylsilane used as an internal standard. FTIR spectra were recorded on a SHIMADZU FTIR-8300. Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU-980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as an eluent. Mass spectra were obtained on JEOL JMS-700 (for FABMS). Elemental analysis was performed on Perkin–Elmer 2400. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using Shodex GPC KF 803L and a KF806M column. Dynamic light scattering (DLS) was measured with Microtrac version 10.0.4-J005 by Nikkiso Co., Ltd. Transmission electron microscopy (TEM) was performed with JEM-3000F. Column chromatography on SiO_2 was performed with Kanto silica gel 60 (40–100 μm). Commercially available organic and inorganic compounds were used without further purification, except for the solvent, which was distilled by a known method before use.

4.1.1. (*S*)-Ethyl 8-[2,2′-bis(methoxymethyloxy)-1,1′-binaphth-6-yl]oct-7-enoate (3). To the phosphonium salt $BrPPh_3(CH_2)_6CO_2Et$ (freshly prepared by treatment of $Br(CH_2)_6CO_2Et$ (3 mL, 16 mmol) with PPh_3 (3.9 g, 15 mmol)) dissolved in DMF (100 mL), NaOEt (1.2 g, 18 mmol) was added under an argon atmosphere, and the resulting solution was stirred at room temperature for 2 h. To this solution, (*S*)-6-formyl-2,2′-bis(methoxymethyloxy)-1,1′-binaphthyl (**2**) (3.8 g, 9.5 mmol) in DMF (15 mL) was added, and stirring continued at room temperature for an

additional 2 h. After completion of reaction, the reaction mixture was quenched with 10% HCl (100 mL), followed by extraction with EtOAc (100 mL×3). The combined organic layers were further washed with water (50 mL) and brine (50 mL) and then dried over Na_2SO_4. Evaporation of solvent and purification by column chromatography using hexane/EtOAc (1/1) as an eluent afforded compound (*S*)-**3** (4.1 g, 82% yield). ^{1}H NMR ($CDCl_3$): δ 1.18–1.64 (m, 13H), 2.03 (s, 2H), 2.27–2.39 (m, 4H), 3.12–3.15 (m, 6H), 4.04–4.14 (m, 4H), 4.96–4.98 (m, 2H), 5.03–5.07 (m, 2H), 5.62–6.30 (m, 1H), 6.46–6.52 (m, 1H), 7.09–7.32 (m, 5H), 7.52–7.57 (m, 2H), 7.72 (s, 1H), 7.72–7.88 (m, 2H), 7.92 (d, J=12.6 Hz, 1H). FABHRMS. Calcd for $C_{34}H_{38}O_6$ [M$^+$]: 542.2668. Found: 542.2650.

4.1.2. (*S*)-Ethyl 8-[2,2′-bis(methoxymethloxy)-1,1′-binaphth-6-yl]octanoate. To a stirred solution of compound (*S*)-**3** (4.1 g, 7.6 mmol) in EtOH (10 mL)/MeOH (10 mL), Pd–C (750 mg) was added, and the resulting mixture was subjected to hydrogenation under 1 atm pressure at 40 °C for 24 h. The reaction mixture was then filtered through Celite® and solvent was evaporated under reduced pressure to give (*S*)-ethyl 8-[2,2′-bis(methoxymethyloxy-1,1′-binaphth-6-yl]octanoate (4.1 g, quantitative yield). IR (neat): ν_{max} 3055, 2932, 2856, 1730, 1595, 1506, 1265, 1240, 1196, 1150, 1069, 1015, 1013, 921, 893, 810, 731,72 cm^{-1}. $[\alpha]_D^{20}$ −35.9 (*c* 5.64, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.31–1.35 (m, 2H), 1.57–1.66 (m, 6H), 2.24–2.36 (m, 4H), 2.67 (t, J=7.8 Hz, 2H), 3.70 (s, 3H), 3.72 (s, 3H), 3.74 (s, 3H), 7.00–7.31 (m, 5H), 7.88 (d, J=8.9 Hz, 1H), 7.94 (d, J=8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.2, 24.9, 29.0, 29.1, 31.1, 34.3, 35.7, 55.6, 55.7, 60.0, 95.0, 95.1, 117.1, 117.1, 121.0, 121.3, 123.8, 125.2, 126.0, 127.6, 127.6, 128.6, 129.6, 129.8, 132.2, 133.8, 138.1, 151.8, 152.3, 173.5. FABHRMS. Calcd for $C_{34}H_{40}O_6$ [M$^+$]: 544.2824. Found: 544.2834.

4.1.3. (*S*)-Ethyl 8-(2,2′-dihydroxy-1,1′-binaphth-6-yl)-octanoate. *p*-Toluenesulfonic acid monohydrate (1.22 g, 6.40 mmol) was added to a stirred solution of (*S*)-ethyl 8-[2,2′bis(methoxymethoxy)-1,1′-binaphth-6-yl)]octanoate (1.7 g, 3.1 mmol) in CH_2Cl_2 (100 mL) at 0 °C under an argon atmosphere. The solution was stirred at room temperature for 12 h and then neutralized with saturated aq Na_2CO_3. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL×2). The combined organic layers were washed with water (50 mL) and brine (50 mL) and then dried over Na_2SO_4. The CH_2Cl_2 was evaporated and residue was purified by column chromatography using hexane/EtOAc (4/1) to afford (*S*)-ethyl 8-(2,2′-dihydroxy-1,1′-binaphth-6-yl)-octanoate (1.4 g, quantitative yield). IR (neat): ν_{max} 3393, 3044, 2928, 2855, 1716, 1597, 1506, 1464, 1379, 1340, 1275, 1242, 1178, 1144, 1124, 1094, 1069, 1013, 907, 862, 816, 781, 727 cm^{-1}. $[\alpha]_D^{20}$ +26.1 (*c* 7.89, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.21–1.30, 1.45–1.75 (each m, 13H), 2.04 (s, 1H), 2.25–2.29 (m, 2H), 2.69–2.74 (m, 2H), 4.07–4.17 (m, 2H), 5.00 (s, 1H), 5.13 (s, 1H), 7.00–7.18 (m, 3H), 7.27–7.43 (m, 5H), 7.66 (s, 1H), 7.89–8.00 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 14.2, 24.9, 29.0, 29.1, 31.2, 34.2, 35.7, 60.1, 110.8, 111.2, 117.5, 117.6, 123.7, 124.0, 124.1, 126.6, 127.1, 128.1, 128.7, 129.1, 129.3, 130.4, 130.9, 131.6, 133.3, 138.1, 151.9, 152.5, 173.6. FABHRMS. Calcd for $C_{30}H_{32}O_4$ [M$^+$]: 456.2301. Found: 456.2314.

4.1.4. (*S*)-Ethyl 8-[2,2′-bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]octanoate (4). To a solution of (*S*)-ethyl 8-(2,2′-dihydroxy-1,1′-binaphth-6-yl)octanoate (817 mg, 1.8 mmol) in CH_2Cl_2 (20 mL) under an argon atmosphere, imidazole (500 mg, 7.8 mmol) was added at 0 °C. After stirring for 10 min, *tert*-butyl dimethyl silyl chloride (TBSCl) (810 mg, 5.4 mmol) was added to the above mixture. The mixture was stirred at room temperature for 18 h, and after completion of reaction the mixture was quenched with water (50 mL), followed by extraction with CH_2Cl_2 (50 mL×2). The combined organic layers were washed with brine and dried over Na_2SO_4, and after removal of solvent, subjected to column chromatography on SiO_2 with EtOAc/hexane (1/9) as the eluent to give compound (*S*)-**4** (1.13 g, 93% yield). IR (neat): ν_{max} 3055, 2932, 2856, 1506, 1472, 1263, 1217, 1080, 1032, 999, 939, 895, 839, 814, 733, 702 cm^{-1}. $[\alpha]_D^{20}$ −10.8 (*c* 0.26, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.19 (d, J=3.8 Hz, 6H), −0.02 (d, J=4.9 Hz, 6H), 0.45 (s, 18H), 1.20–1.31, 1.57–1.62 (each m, 13H), 2.26 (t, J=7.8 Hz, 2H), 2.67 (t, J=7.8 Hz, 2H), 4.10 (q, J=7.3 Hz, 2H), 7.00–7.28 (m, 6H), 7.55 (s, 1H), 7.69–7.80 (m, 3H). ^{13}C NMR ($CDCl_3$): δ −5.1, −4.5, −4.3, −4.1, 14.3, 17.6, 25.0, 25.1, 26.0, 29.0, 29.1, 29.1, 29.2, 29.7, 31.3, 34.4, 35.8, 60.1, 120.3, 121.1, 121.8, 122.9, 123.0, 125.0, 125.1, 125.6, 125.7, 125.9, 127.0, 127.2, 127.4, 127.8, 127.9, 128.2, 128.4, 129.0, 129.2, 129.5, 132.8, 133.7, 134.4, 137.3, 150.2, 150.8, 173.6. FABHRMS. Calcd for $C_{42}H_{60}O_4Si_2$ [M$^+$]: 684.4030. Found: 684.4014.

4.1.5. (*S*)-8-[2,2′-Bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]octan-1-ol (5). To a solution of compound (*S*)-**4** (1.2 g, 1.6 mmol) in THF (50 mL) under an argon atmosphere, $LiAlH_4$ (60 mg, 1.6 mmol) was added at 0 °C. The mixture was stirred for an additional 1 h at the same temperature. After completion of reaction, the reaction mixture was quenched with water (10 mL) in an ice bath and extracted with EtOAc (50 mL×3). The organic layer was washed with 1 N HCl (10 mL) and brine (20 mL), then dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/4) as an eluent. Compound (*S*)-**5** (1.0 g, 93% yield) was obtained as colorless oil. ^{1}H NMR ($CDCl_3$): δ −0.19 (d, J=4.9 Hz, 6H), −0.02 (d, J=4.6 Hz, 6H), 0.45 (s, 18H), 1.18–1.34, 1.52–1.78 (each m, 12H), 2.67, 4.19 (each m, 4H), 6.90–7.30 (m, 5H), 9.54 (s, 1H), 7.68–7.82 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −4.3 (2), −4.1 (2), 9.2, 25.1 (6), 25.5, 29.0, 29.1 (2), 29.3, 31.3, 35.7, 37.4, 70.1, 120.3 (2), 121.8, 122.1, 123.1, 125.6, 125.7, 125.9 (2), 127.2, 127.4, 127.9, 128.4, 129.0, 129.2, 132.8, 134.4, 137.3, 150.3, 150.8. FABHRMS. Calcd for $C_{40}H_{58}O_3Si_2$ [M$^+$]: 642.3924. Found: 642.3917.

4.1.6. (*S*)-2-Methyl-acrylic acid-8-[2,2′-bis(*tert*-butyldimethylsilyloxy)-1,1′-binaphth-6-yl]octylester (6). To a mixture of compound (*S*)-**5** (930 mg, 1.7 mmol) and Et_3N (0.5 mL, 3.5 mmol) in CH_2Cl_2 (30 mL), methyl-methacryloyl chloride (0.3 mL, 3.0 mmol) was added at 0 °C under an argon atmosphere. The resulting reaction mixture was allowed to stirred at room temperature for 5 h and then quenched with 1 N HCl (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL×2). The combined organic layers were washed with water (20 mL) and brine (20 mL) and then dried over

Na_2SO_4. The solvent was evaporated to dryness, and the residue was purified by column chromatography using hexane/EtOAc (4/1) to give (*S*)-**6** (980 mg, 98% yield). IR (neat): ν_{max} 3057, 2930, 2856, 1713, 1593, 1500, 1472, 1464, 1358, 1340, 1323, 1263, 1250, 1169, 1080, 999, 941, 895, 839, 812, 781, 733, 704 cm^{-1}. $[\alpha]_D^{20}$ −20.0 (*c* 7.91 $CHCl_3$). ^1H NMR ($CDCl_3$): δ −0.17 (d, *J*=3.5 Hz, 6H), −0.12 (d, *J*=3.8 Hz, 6H), 0.51 (s, 18H), 1.20–1.50, 1.62–1.75 (each m, 12H), 1.99 (s, 3H), 2.74 (t, *J*=7.5 Hz, 2H), 4.18 (t, *J*=6.7 Hz, 2H), 5.58 (s, 1H), 6.14 (s, 1H), 7.06–7.38 (m, 7H), 7.61 (s, 1H), 7.72–7.90 (m, 3H). ^{13}C NMR ($CDCl_3$): δ −4.3 (2), −4.1, −4.1, 17.6, 18.4, 25.1 (6), 26.0, 28.8, 29.2, 29.3, 29.4, 31.4, 35.8, 38.8, 66.0, 120.3, 120.3, 121.8, 122.1, 123.0, 125.0, 125.6, 125.7, 125.9 (2), 127.3, 127.4, 127.9, 128.4, 129.0, 129.2, 132.8, 134.4, 136.4, 137.3, 150.2, 150.8, 167.3. FABHRMS. Calcd for $C_{44}H_{62}O_4Si_2$ [M^+]: 710.4186. Found: 710.4214.

4.1.7. (*S*)-2-Methyl-acrylic acid-8-(2,2′-dihydroxy-1,1′-binaphth-6-yl)octylester (7). Tetrabutylammonium fluoride (1.3 mL, 1 M THF solution) was added to a solution of (*S*)-**6** (700 mg, 1.2 mmol) in THF (25 mL) at 0 °C under an argon atmosphere. After stirring for 1 h at room temperature, the reaction mixture was quenched by addition of 1 N HCl (5 mL), followed by extraction with EtOAc (50 mL×2). The organic layer was washed with water (20 mL) and brine (20 mL) and then dried over Na_2SO_4. Purification by column chromatography using hexane/EtOAc (4/1) afforded (*S*)-**7** (427 mg, 90% yield). IR (neat): ν_{max} 3525, 2930, 1706, 1596, 1506, 1465, 1298, 1180, 1145, 904, 817, 725 cm^{-1}. $[\alpha]_D^{20}$ +22.5 (*c* 1.93, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.17–1.31, 1.47–1.63 (each m, 12H), 2.05 (s, 3H), 2.61 (t, *J*=7.5 Hz, 2H), 4.00 (t, *J*=6.7 Hz, 2H), 4.96 (s, 1H), 5.06 (s, 1H), 5.42 (s, 1H), 5.97 (s, 1H), 6.95 (d, *J*=8.4 Hz, 1H), 7.04 (d, *J*=12.4 Hz, 2H), 7.17–7.33 (m, 4H), 7.54 (s, 1H), 7.77 (d, *J*=6.5 Hz, 1H), 7.78 (d, *J*=9.2 Hz, 1H), 7.84 (d, *J*=8.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 18.4, 25.9, 28.6, 29.2, 29.2 (2), 29.4, 30.9, 31.3, 35.7, 64.8, 110.6, 111.0, 123.8, 124.0, 124.1, 125.0, 126.7, 127.2, 128.2, 128.8, 129.2, 129.4, 130.6, 131.1, 131.6, 133.3, 136.3, 138.3, 151.9, 152.5, 178.3. FABHRMS. Calcd for $C_{32}H_{34}O_4$ [M^+]: 482.2457. Found: 456.2455.

4.2. Surfactant monomer (*S*)-1

Phosphorous oxychloride (0.1 mL, 1.1 mmol) was added dropwise to a solution of (*S*)-**7** (500 mg, 1.0 mmol) and Et_3N (0.3 mL, 2.1 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred for an additional 30 min and then CH_2Cl_2 was evaporated under reduced pressure. The obtained residue was dissolved in THF (20 mL) and cooled to 0 °C, followed by addition of 15% NaOH aq solution (5 mL). The reaction mixture was then stirred at room temperature for 15 min and then extracted with EtOAc (20 mL×3). The organic layer was dried over Na_2SO_4 and evaporated to dryness under reduced pressure to afford chiral surfactant monomer (*S*)-**1** (534 mg, 91% yield). IR (neat): ν_{max} 2926, 2855, 1717, 1506, 1240, 1211, 1159, 1101, 1070, 995, 962, 845, 814, 748, 698, 664 cm^{-1}. $[\alpha]_D^{20}$ −33.8 (*c* 0.51, MeOH). ^1H NMR (CD_3OD): δ 1.25–1.45 (m, 8H), 1.55–1.75 (m, 4H), 1.98 (s, 3H), 2.72 (t, *J*=7.5 Hz, 2H), 4.11 (t, *J*=6.6 Hz, 2H), 5.55 (s, 1H), 6.04 (s, 1H), 7.11 (dd, *J*=1.6, 8.9 Hz, 1H), 7.19 (d, *J*=8.9 Hz, 1H), 7.26 (dd, *J*=1.4, 6.2 Hz, 1H), 7.30 (d, *J*=8.4 Hz, 1H), 7.41 (dt, *J*=1.4, 6.5 Hz, 1H), 7.48–7.55 (m, 2H), 7.72 (s, 1H), 7.92–8.02 (m, 3H). ^{13}C NMR (CD_3OD): δ 18.4, 27.0, 29.6, 30.2, 30.2, 30.4, 32.3, 36.7, 65.8, 122.6, 122.6, 122.9, 123.0, 123.3, 123.3, 125.7, 126.9, 127.6, 127.7, 128.5, 129.2, 130.7, 131.1, 132.0, 132.5, 132.7, 133.6, 137.6, 140.4, 149.7, 150.2, 175.0. ESIHRMS. Calcd for $C_{32}H_{32}Na_2O_6P$ ($M+Na^+$): 589.1732. Found: 589.1686.

*Polymerization of chiral surfactant monomer **1***: To a solution of surfactant monomer **1** (15 mg, 0.027 mmol) in water (2.7 mL), Et_3B (2.7 μL, 1 M in hexane solution, 0.0027 mmol) was added under an argon atmosphere at 0 °C. Stirring was continued at the same temperature for 8 h. The polymerization was then quenched by addition of MeOH (5 mL) to the reaction mixture. After evaporation of solvents under reduced pressure the residue was precipitated by means of hexane. The obtained white solid was centrifuged and dried under reduced pressure to give **MDP-I** (14 mg).

MDP-I: Average molecular weight (M_w)=1.88×10^5, and PDI (polydispersity index)=1.81 were determined at 25 °C by size-exclusion chromatography. The polymer was analyzed by STM analysis to measure diameter=5 nm (along with aggregates of 9–20 nm in diameter).

4.3. Synthesis of MDP-II (photoradical polymerization of monomer 8)

A solution of surfactant monomer **8** (435 mg, 1.4 mmol) and styrene (160 μL, 1.4 mmol) in water (30 mL) was stirred at 20 °C for 1 h under an argon atmosphere, resulting in the formation of a white emulsion. 2,2′-Dimethoxy-2-phenylacetophenone (36 mg, 0.14 mmol) was then added, and the solution was deoxygenated by argon bubbling. The resulting solution was irradiated for 8 h by means of a UV lamp assembled with a jacket containing saturated aq copper sulfate solution. The polymerization was quenched by adding MeOH to the reaction mixture. After the removal of solvents in vacuo, the residue was precipitated using hexane/EtOAc (150/1). The resulting white solid was centrifuged and dried under reduced pressure to obtain **MDP-II** (278 mg).

MDP-II: Average molecular weight (M_w)=2.84×10^4, PDI=2.85, and diameter=3.2 nm were obtained by SEC-MALS and STM analyses.

4.4. Immobilization of BINOL moieties onto the surface of MDP-II

4.4.1. Synthesis of MDP-III. A solution of (*S*)-6-chloromethyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalenyl (**9**) (80 mg, 0.19 mmol) in THF (1 mL) and NaI (34 mg, 0.23 mmol) was stirred at room temperature for 18 h under an argon atmosphere. The resulting reaction mixture was added slowly at 0 °C to a solution of **MDP-II** (64 mg, 0.16 mmol, monomer **8**: styrene=1:1, monomeric M_w= 414.54) and 60% NaH (26 mg, 0.65 mmol) in THF (5 mL). After stirring at room temperature for 24 h, the reaction mixture was quenched with ice and 1 N HCl (3 mL) in an ice bath. The reaction mixture was then centrifuged to obtain insoluble material, which was separated and washed

with MeOH, followed by drying under reduced pressure to afford **MDP-III** (120 mg).

4.4.2. Synthesis of MDP-IVa. *p*-Toluenesulfonic acid monohydrate (30 mg, 0.16 mmol) was added to a stirred solution of **MDP-III** (58 mg) in CH_2Cl_2 (5 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 2 h, followed by addition of MeOH (5 mL). The resulting mixture was centrifuged to obtain polymer, which was precipitated by use of THF/MeOH. The obtained solid was dried under reduced pressure to give **MDP-IVa** (40 mg).

4.4.3. Synthesis of MDP-IVb. NaH 60% (48 mg, 1.2 mmol) was added to a stirred solution of **MDP-III** (240 mg) in THF (10 mL) at 0 °C under an argon atmosphere. MeI (50 μL, 1.08 mmol) was then added to the above mixture and allowed to stir at room temperature for 24 h. The reaction mixture was quenched with ice and 1 N HCl (3 mL) in an ice bath. The insoluble solid was separated and precipitated by use of THF/MeOH. The white solid was then centrifuged and dried under reduced pressure to give Me capped polymer, which, upon deprotection of MOM group as described above for **MDP-IVa**, afforded **MDP-IVb**.

4.5. General procedure for compound 12

To a solution of chiral 2,2′-dimethoxy-1,1′-binaphthyl (**11**) (29 mmol) in CH_2Cl_2 (250 mL) under an argon atmosphere, $AlCl_3$ (35 mmol) was added as a powder at 0 °C. After stirring for 10 min, corresponding acid chloride mono ethyl ester (32 mmol) was added dropwise to the above mixture. The reaction mixture was then stirred at room temperature until consumption of **11** by TLC (16–24 h). The reaction was quenched with water at 0 °C. The mixture was extracted with EtOAc (50 mL×3) and then washed with 1 N HCl (50 mL) and brine (50 mL), then dried over Na_2SO_4, filtered, and concentrated. To the crude mixture, a small amount of acetone was added. Compound **11**, which was unreacted, was precipitated and removed by Celite® filtration, and the filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/9). Compound **12** was obtained as a yellow oil.

4.5.1. (*R*)-Ethyl 4-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-4-oxobutanoate (12a)[17] (*n*=4). Yield 75%.

4.5.2. (*R*)-Ethyl-5-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-5-oxopentanoate (12b) (*n*=5). Yield 62%. IR (neat): ν_{max} 3059, 2978, 2941, 2905, 2837, 1728, 1676, 1616, 1593, 1508, 1479, 1466, 1443, 1375, 1246, 1173, 1148, 1094, 1065, 1045, 1020, 955, 907, 808, 750, 687, 596 cm^{-1}. $[\alpha]_D^{20}$ +4.5 (*c* 1.13, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.24 (t, *J*=7.0 Hz, 3H), 1.97 (quin, *J*=7.3 Hz, 2H), 2.09 (t, *J*=7.3 Hz, 2H), 2.40 (t, *J*=7.3 Hz, 2H), 3.74 (s, 3H), 3.77 (s, 3H), 4.12 (q, *J*=7.0 Hz, 2H), 7.02–7.32 (m, 4H), 7.44 (d, *J*=9.0 Hz, 1H), 7.49 (d, *J*=9.0 Hz, 1H), 7.74 (dd, *J*=9.0, 1.8 Hz, 1H), 7.85 (d, *J*=8.1 Hz, 1H), 7.97 (d, *J*=9.0 Hz, 1H), 8.08 (d, *J*=9.0 Hz, 1H), 8.50 (d, *J*=1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.2, 19.7, 33.5, 37.3, 56.5, 56.7, 60.3, 113.9, 114.3, 118.5, 119.4, 123.4, 124.1, 124.7, 125.5, 126.3, 127.8, 127.9, 129.0, 129.5, 130.0, 131.2, 131.8, 133.6, 136.2, 154.7, 156.9, 173.1, 198.9. FABHRMS. Calcd for $C_{29}H_{28}O_5$ [M^+]: 456.1937. Found: 456.1934.

4.5.3. (*S*)-Ethyl 6-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-6-oxohexanoate (12c) (*n*=6). Yield 69%. IR (neat): ν_{max} 2978, 2941, 2866, 1730, 1707, 1622, 1456, 1373, 1267, 1248, 1178, 1148, 1096, 1067, 1030, 910, 808, 752 cm^{-1}. $[\alpha]_D^{25}$ −2.0 (*c* 1.94, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.23 (t, *J*=7.0 Hz, 3H), 1.60–1.78 (m, 6H), 2.30 (t, *J*=7.6 Hz, 2H), 3.06 (t, *J*=7.3 Hz, 2H), 3.74 (s, 3H), 3.78 (s, 3H), 4.11 (q, *J*=7.0 Hz, 2H), 7.00–7.31 (m, 4H), 7.43 (d, *J*=9.2 Hz, 1H), 7.49 (d, *J*=9.2 Hz, 1H), 7.72 (dd, *J*=9.2, 2.2 Hz, 1H), 7.85 (d, *J*=9.2 Hz, 1H), 7.97 (d, *J*=9.2 Hz, 1H), 8.08 (d, *J*=9.2 Hz, 1H), 8.48 (d, *J*=2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 24.1, 24.3, 33.6, 38.0, 56.6, 56.8, 60.3, 113.9, 114.4, 123.4, 124.2, 124.7, 125.5, 126.1, 126.3, 127.8, 127.9, 129.0, 129.6, 129.9, 131.2, 131.9, 156.9, 173.1, 173.3, 198.9. FABMS (*m*/*z*): 470 [M^+]. Anal. Calcd for $C_{30}H_{30}O_5 \cdot 19/3H_2O$: C, 61.63; H, 7.36. Found: C, 61.63; H, 7.45.

4.6. General procedure for reduction of 12a–c

To a solution of compound **12** (18 mmol) in CH_2Cl_2 (10 mL) under an argon atmosphere, trifluoroacetic acid (21 mL) and triethylsilane (7.2 mL) were added dropwise at 0 °C. The mixture was stirred at ambient temperature until the reaction reached completion as determined by monitoring with TLC analysis. The reaction was quenched with water (5 mL) in an ice bath and then neutralized with saturated aq Na_2CO_3 (10 mL), washed with brine (10 mL), and dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/9) to afford the product as a yellow oil.

4.6.1. (*R*)-Ethyl 4-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-butanoate.[17] Yield 89%.

4.6.2. (*R*)-Ethyl 5-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-pentanoate. Yield 72%. IR (neat): ν_{max} 3059, 2934, 2837, 1730, 1620, 1593, 1505, 1481, 1462, 1433, 1371, 1352, 1331, 1246, 1177, 1148, 1134, 1094, 1067, 1047, 1020, 889, 806, 748, 689, 665, 592 cm^{-1}. $[\alpha]_D^{25}$ +12.2 (*c* 1.94, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.24 (t, *J*=7.0 Hz, 3H), 1.68–1.76 (m, 4H), 2.29–2.36 (m, 2H), 2.70–2.76 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.11 (q, *J*=7.0 Hz, 2H), 7.00–7.33 (m, 5H), 7.41 (d, *J*=6.5 Hz, 1H), 7.45 (d, *J*=6.5 Hz, 1H), 7.63 (s, 1H), 7.86 (d, *J*=9.2 Hz, 1H), 7.90 (d, *J*=9.2 Hz, 1H), 7.96 (d, *J*=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 24.7, 30.7, 34.2, 35.4, 56.9, 56.9, 60.2, 114.1, 114.3, 119.4, 119.6, 123.3, 125.1, 126.2, 127.6, 127.7, 128.6, 129.0, 129.1, 129.2, 132.3, 132.8, 137.0, 154.3, 154.7, 173.4. FABHRMS. Calcd for $C_{29}H_{30}O_4$ [M^+]: 442.2144. Found: 442.2143.

4.6.3. (*S*)-Ethyl 6-(2,2′-dimethoxy-1,1′-binaphth-6-yl)-hexanoate. Yield 80%. IR (neat): ν_{max} 3059, 2934, 2853, 2837, 1732, 1622, 1593, 1558, 1541, 1508, 1464, 1373, 1352, 1333, 1265, 1178, 1148, 1134, 1096, 1067, 1018, 889, 808, 748, 590 cm^{-1}. $[\alpha]_D^{25}$ −13.7 (*c* 1.27, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.23 (t, *J*=7.0 Hz, 3H), 1.36–1.44 (m, 2H), 1.68–1.76 (m, 4H), 2.29–2.36 (m, 2H), 2.70–2.76 (m,

2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.11 (q, J=7.0 Hz, 2H), 7.00–7.33 (m, 5H), 7.41 (d, J=6.5 Hz, 1H), 7.44 (d, J=6.5 Hz, 1H), 7.62 (s, 1H), 7.85 (d, J=9.2 Hz, 1H), 7.89 (d, J=9.2 Hz, 1H), 7.95 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 24.9, 28.8, 30.9, 30.9, 34.3, 35.6, 56.8, 56.9, 60.1, 114.1, 114.2, 119.4, 119.6, 123.3, 125.0, 125.1, 126.1, 126.1, 127.7, 128.6, 129.0, 129.1, 129.2, 132.3, 133.8, 137.3, 154.2, 154.7, 173.5. FABHRMS. Calcd for $C_{30}H_{32}O_4$ [M$^+$]: 456.2301. Found: 456.2292.

4.7. General procedure for $LiAlH_4$ reduction

To a solution of the above obtained ester (20 mmol) in THF (150 mL) under an argon atmosphere, $LiAlH_4$ (20 mmol) was added, followed by stirring at 0 °C. The mixture was stirred until the reaction reached completion as determined by monitoring with TLC analysis. The reaction was quenched with water in an ice bath and extracted with EtOAc (100 mL×3). The organic layer was washed with 1 N HCl (50 mL) and brine (50 mL), then dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/4). The corresponding alcohol was obtained in quantitative yield as colorless oil.

4.7.1. (*R*)-4-(2,2′-Dimethoxy-1,1′-binaphth-6-yl)butan-1-ol (*n*=4). IR (neat): ν_{max} 3393, 3059, 3007, 2934, 2837, 1620, 1594, 1505, 1480, 1460, 1351, 1330, 1263, 1178, 1148, 1092, 1067, 1047, 1018, 889, 808, 748, 689, 660 cm^{-1}. $[\alpha]_D^{25}$ +14.5 (*c* 1.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, OH), 1.59–1.79 (m, 4H), 2.73 (t, J=7.6 Hz, 2H), 3.64 (t, J=6.3 Hz, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 6.99–7.32 (m, 5H), 7.41 (d, J=7.0 Hz, 1H), 7.44 (d, J=7.0 Hz, 1H), 7.62 (s, 1H), 7.85 (d, J=9.2 Hz, 1H), 7.88 (d, J=9.2 Hz, 1H), 7.95 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 27.3, 32.4, 35.5, 56.9, 57.0, 62.8, 114.1, 114.2, 119.4, 119.5, 123.3, 125.1, 126.1, 126.2, 127.7, 127.7, 128.7, 129.0, 129.2, 132.3, 133.8, 137.1, 154.3, 154.7. FABMS (*m*/*z*): 386 [M$^+$]. Anal. Calcd for $C_{26}H_{26}O_3\cdot 2/3H_2O$: C, 78.36; H, 6.91. Found: C, 78.18; H, 6.72.

4.7.2. (*S*)-5-(2,2′-Dimethoxy-1,1′-binaphth-6-yl)pentan-1-ol (*n*=5). IR (neat): ν_{max} 3377, 3058, 2999, 2932, 2837, 1622, 1593, 1506, 1481, 1460, 1352, 1331, 1256, 1178, 1148, 1134, 1094, 1065, 1047, 1018, 885, 806, 748, 689, 660 cm^{-1}. $[\alpha]_D^{25}$ −16.1 (*c* 1.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.36–1.47 (m, 2H), 1.54–1.75 (m, 4H), 2.71 (t, J=7.6 Hz, 2H), 3.61 (t, J=6.5 Hz, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 7.00–7.33 (m, 5H), 7.41 (d, J=7.2 Hz, 1H), 7.44 (d, J=7.2 Hz, 1H), 7.62 (s, 1H), 7.85 (d, J=9.2 Hz, 1H), 7.88 (d, J=9.2 Hz, 1H), 7.95 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.5, 31.1, 32.7, 35.8, 56.9, 57.0, 62.9, 114.1, 114.3, 119.4, 119.6, 123.3, 125.1, 125.1, 126.1, 126.2, 127.7, 128.6, 129.0, 129.2, 129.2, 132.3, 133.9, 137.4, 154.3, 154.7. FABMS (*m*/*z*): 400 [M$^+$]. Anal. Calcd for $C_{27}H_{28}O_3\cdot 1/3H_2O$: C, 79.77; H, 7.11. Found: C, 79.74; H, 7.11.

4.7.3. (*S*)-6-(2,2′-Dimethoxy-1,1′-binaphth-6-yl)hexan-1-ol (*n*=6). IR (neat): ν_{max} 3356, 3059, 2999, 2930, 2853, 1622, 1593, 1506, 1481, 1460, 1352, 1330, 1254, 1178, 1148, 1134, 1094, 1065, 1047, 1020, 889, 806, 748, 689, 664, 592 cm^{-1}. $[\alpha]_D^{25}$ −14.0 (*c* 0.56, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.36–1.41 (m, 4H), 1.55 (t, J=6.7 Hz, 2H), 1.65–1.71 (m, 2H), 2.71 (t, J=7.8 Hz, 2H), 3.60 (t, J=6.5 Hz, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 7.00–7.33 (m, 5H), 7.41 (d, J=7.2 Hz, 1H), 7.44 (d, J=7.2 Hz, 1H), 7.62 (s, 1H), 7.85 (d, J=9.2 Hz, 1H), 7.88 (d, J=9.2 Hz, 1H), 7.96 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.6, 29.1, 31.2, 32.7, 35.7, 56.9, 56.9, 62.9, 114.1, 114.2, 119.4, 119.6, 123.3, 125.0, 125.1, 126.1, 127.7, 127.8, 128.6, 129.0, 129.1, 129.2, 132.3, 133.8, 137.5, 154.2, 154.7. FABHRMS. Calcd for $C_{28}H_{30}O_3$ [M$^+$]: 414.2195. Found: 414.2188.

4.8. General procedure for conversion of alcohol to bromide

To a mixture of the above obtained alcohol (12 mmol) and PPh_3 (24 mmol) in THF (150 mL) under an argon atmosphere, CBr_4 (24 mmol) was added at 0 °C. The mixture was stirred until the reaction had reached completion as determined by monitoring with TLC analysis. The reaction mixture was diluted with hexane, and PPh_3O was precipitated and filtered through Celite®. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/10) to afford the corresponding bromide as a yellow oil.

4.8.1. (*S*)-6-(4-Bromobutyl)-2,2′-dimethoxy-1,1′-binaphthalenyl (13a) (*n*=4). Yield 70%. IR (neat): ν_{max} 3060, 2998, 2933, 2837, 1623, 1593, 1507, 1481, 1462, 1351, 1328, 1263, 1178, 1147, 1134, 1092, 1067, 1047, 1018, 889, 808, 748, 689 cm^{-1}. $[\alpha]_D^{25}$ −14.5 (*c* 1.12, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.76–1.97 (m, 4H), 2.74 (t, J=7.0 Hz, 2H), 3.42 (t, J=6.5 Hz, 2H), 3.75 (s, 3H), 3.76 (s, 3H), 7.00–7.34 (m, 5H), 7.42 (d, J=5.4 Hz, 1H), 7.45 (d, J=5.4 Hz, 1H), 7.63 (s, 1H), 7.86 (d, J=9.2 Hz, 1H), 7.90 (d, J=9.2 Hz, 1H), 7.97 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 29.6, 32.3, 33.8, 34.8, 56.9, 56.9, 114.0, 114.3, 119.5, 123.3, 125.1, 125.2, 126.1, 126.3, 127.6, 127.7, 128.7, 129.0, 129.2, 132.4, 133.8, 136.6, 154.3, 154.7. FABMS (*m*/*z*): 448 [M$^+$]. Anal. Calcd for $C_{26}H_{25}BrO_2\cdot 3/7H_2O$: C, 68.32; H, 5.70; Br, 17.48. Found: C, 68.05; H, 5.73; Br, 17.56.

4.8.2. (*S*)-6-(5-Bromopentyl)-2,2′-dimethoxy-1,1′-binaphthalenyl (13b) (*n*=5). Quantitative yield. IR (neat): ν_{max} 3058, 2999, 2933, 2837, 1622, 1593, 1508, 1480, 1460, 1352, 1329, 1263, 1178, 1148, 1134, 1092, 1067, 1047, 1018, 889, 804, 748, 689 cm^{-1}. $[\alpha]_D^{25}$ −14.7 (*c* 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.45–1.57 (m, 2H), 1.65–1.77 (m, 2H), 1.85–1.96 (m, 2H), 2.74 (t, J=7.3 Hz, 2H), 3.40 (t, J=6.9 Hz, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 7.00–7.35 (m, 5H), 7.43 (d, J=5.9 Hz, 1H), 7.46 (d, J=5.9 Hz, 1H), 7.65 (s, 1H), 7.88 (d, J=9.2 Hz, 1H), 7.92 (d, J=9.2 Hz, 1H), 7.98 (d, J=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 27.9, 30.4, 32.7, 33.8, 35.6, 56.8, 56.9, 114.1, 114.2, 119.4, 119.5, 123.3, 125.1, 126.1, 126.2, 127.6, 127.7, 128.6, 129.0, 129.2, 132.3, 133.8, 137.1, 154.3, 154.7. FABHRMS. Calcd for $C_{27}H_{27}BrO_2$ [M$^+$]: 462.1194. Found: 462.1194.

4.8.3. (*S*)-6-(6-Bromohexyl)-2,2′-dimethoxy-1,1′-binaphthalenyl (13c) (*n*=6). Yield 90%. IR (neat): ν_{max} 3058,

2999, 2934, 2853, 1623, 1592, 1508, 1481, 1460, 1352, 1329, 1263, 1178, 1148, 1134, 1092, 1067, 1047, 1018, 889, 808, 748, 689 cm^{-1}. $[\alpha]_D^{25}$ −13.8 (*c* 1.58, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.34–1.50 (m, 4H), 1.65–1.73 (m, 2H), 1.79–1.90 (m, 2H), 2.71 (t, *J*=7.5 Hz, 2H), 3.36 (t, *J*=6.7 Hz, 2H), 3.73 (s, 3H), 3.77 (s, 3H), 7.00–7.33 (m, 5H), 7.42 (d, *J*=5.9 Hz, 1H), 7.45 (d, *J*=5.9 Hz, 1H), 7.62 (s, 1H), 7.88 (d, *J*=9.2 Hz, 1H), 7.90 (d, *J*=9.2 Hz, 1H), 7.96 (d, *J*=9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 28.0, 28.4, 31.0, 32.7, 33.9, 35.6, 56.8, 56.9, 114.1, 114.3, 119.4, 119.6, 123.3, 125.1, 125.1, 126.1, 126.1, 127.7, 128.6, 129.0, 129.1, 129.2, 132.3, 133.9, 137.3, 154.3, 154.7. FABMS (*m/z*): 477 [M^+]. Anal. Calcd for $C_{28}H_{29}BrO_2 \cdot 3/10H_2O$: C,69.65; H, 6.18; Br, 16.55. Found: C, 69.35; H, 6.23; Br, 16.84.

4.9. General procedure for preparation of disulfide 14

To a solution of the above obtained bromide **13** (12 mmol) in DMSO (100 mL) under an argon atmosphere, thiourea (24 mmol) was added, followed by stirring at 35 °C. The mixture was stirred until bromide was consumed completely as determined by monitoring with TLC analysis. Aq NaOH 20% was added to adjust to pH 11. After 3 h, the reaction mixture was acidified with 5 N HCl to pH 3, and extracted with EtOAc (50 mL×3). The organic layer was washed with brine (20 mL) and dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/4). A mixture of disulfide **14** and corresponding thiol was obtained as a colorless oil. The mixture was treated with iodine (6 mmol) in NaOH aq (12 mmol) to afford a red oil, which was purified through column chromatography on SiO_2 with EtOAc/hexane (1/4) to give disulfide **14** as a colorless oil.

4.9.1. (*S*)-Disulfide 14a (*n*=4). Yield 71%. IR (neat): ν_{max} 3050, 3000, 2933, 2830, 1622, 1594, 1503, 1482, 1461, 1431, 1355, 1331, 1263, 1216, 1175, 1148, 1134, 1092, 1067, 1047, 1018, 889, 806, 748, 664, 592 cm^{-1}. $[\alpha]_D^{25}$ −15.5 (*c* 1.13, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.59–1.82 (m, 8H), 2.61–2.74 (m, 8H), 3.74 (s, 6H), 3.76 (s, 6H), 7.00–7.33 (m, 10H), 7.38–7.45 (m, 4H), 7.62 (s, 2H), 7.83–7.90 (m, 4H), 7.95 (d, *J*=8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.9, 30.0, 35.3, 39.0, 56.9, 56.9, 114.1, 114.3, 119.5, 119.6, 123.3, 125.1, 126.1, 126.2, 127.6, 127.7, 128.7, 129.0, 129.2, 129.2, 132.4, 133.9, 136.9, 154.3, 154.8. FABHRMS. Calcd for $C_{52}H_{50}O_4S_2$ [M^+]: 802.3150. Found: 802.3145.

4.9.2. (*R*)-Disulfide 14b (*n*=5). Yield 75%. IR (neat): ν_{max} 3051, 3001, 2929, 2835, 1620, 1593, 1503, 1481, 1460, 1431, 1354, 1331, 1246, 1215, 1176, 1148, 1134, 1092, 1065, 1047, 1018, 889, 806, 748, 665, 592 cm^{-1}. $[\alpha]_D^{25}$ +15.5 (*c* 1.06, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.40–1.51 (m, 4H), 1.57–1.74 (m, 8H), 2.61 (t, *J*=7.3 Hz, 4H), 2.70 (t, *J*=7.6 Hz, 4H), 3.74 (s, 6H), 3.75 (s, 6H), 7.00–7.33 (m, 10H), 7.42 (d, *J*=8.6 Hz, 2H), 7.44 (d, *J*=8.6 Hz, 2H), 7.62 (s, 2H), 7.86 (d, *J*=8.9 Hz, 2H), 7.88 (d, *J*=8.9 Hz, 2H), 7.95 (d, *J*=8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.6, 28.9, 30.7, 30.8, 30.9, 35.4, 35.6, 56.8, 56.9, 114.0, 114.2, 119.3, 119.5, 123.3, 125.0, 125.1, 126.1, 126.1, 127.7, 128.6, 129.0, 129.1, 129.2, 132.2, 133.8, 137.3, 154.2, 154.7. FABHRMS. Calcd for $C_{54}H_{54}O_4S_2$ [M^+]: 830.3463. Found: 830.3449.

4.9.3. (*S*)-Disulfide 14c (*n*=6). Yield 69%. IR (neat): ν_{max} 3056, 3000, 2934, 2853, 1622, 1592, 1504, 1480, 1459, 1431, 1354, 1331, 1263, 1216, 1178, 1148, 1134, 1092, 1067, 1047, 1022, 889, 808, 748, 665, 592 cm^{-1}. $[\alpha]_D^{25}$ −14.2 (*c* 1.14, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.36–1.41 (m, 4H), 1.64–1.69 (m, 4H), 2.62–2.71 (m, 4H), 3.74 (s, 6H), 3.75 (s, 6H), 7.02–7.32 (m, 10H), 7.42 (d, *J*=8.6 Hz, 2H), 7.43 (d, *J*=8.6 Hz, 2H), 7.61 (s, 2H), 7.84 (d, *J*=8.9 Hz, 2H), 7.87 (d, *J*=8.9 Hz, 2H), 7.95 (d, *J*=8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.4, 29.0, 29.1, 31.1, 35.7, 39.1, 56.9, 57.0, 114.2, 114.3, 119.5, 119.7, 123.3, 125.0, 125.2, 126.1, 127.7, 128.7, 129.1, 129.2, 129.3, 132.3, 133.9, 137.5, 154.3, 154.8. FABHRMS. Calcd for $C_{56}H_{58}O_4S_2$ [M^+]: 858.3776. Found: 858.3751.

4.10. General procedure for preparation of disulfide 15

To a solution of compound **14** (8 mmol) in CH_2Cl_2 (80 mL) under an argon atmosphere, 1 M BBr_3 solution in CH_2Cl_2 (24 mL, 24 mmol) was added at 0 °C. The mixture was stirred until the reaction reached completion as determined by monitoring with TLC analysis. The reaction was quenched with ice, and the aqueous layer was separated and extracted with CH_2Cl_2 (50 mL×2). The combined organic layers were washed with 1 N HCl (50 mL) and brine (50 mL), then dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/2). Compound **15** was obtained in quantitative yield as a yellow powder.

4.10.1. (*R*)-Disulfide 15a (*n*=4). Mp 103–105 °C (EtOAc/hexane). IR (neat): ν_{max} 3497, 3393, 3059, 3014, 2930, 2853, 1618, 1597, 1508, 1463, 1433, 1380, 1340, 1271, 1256, 1215, 1178, 1146, 1126, 1070, 1026, 982, 949, 818, 750, 667 cm^{-1}. $[\alpha]_D^{25}$ −44.8 (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.57–1.79 (m, 8H), 2.59–2.74 (m, 8H), 5.04 (br, OH), 7.02–7.14 (m, 6H), 7.27–7.37 (m, 8H), 7.63 (s, 2H), 7.85–7.88 (m, 4H), 7.95 (d, *J*=8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.5, 28.8, 29.9, 30.0, 30.8, 31.0, 35.2, 38.9, 110.6, 110.8, 117.6, 123.8, 124.1, 126.8, 127.3, 128.2, 128.7, 129.2, 129.2, 129.4, 130.7, 131.1, 131.6, 133.2, 137.7, 151.9, 152.5. FABHRMS. Calcd for $C_{48}H_{42}O_4S_2$ [M^+]: 746.2524. Found: 746.2502.

4.10.2. (*R*)-Disulfide 15b (*n*=5). Mp 74–75 °C (EtOAc/hexane). IR (neat): ν_{max} 3504, 3422, 3059, 3014, 2926, 2853, 1618, 1597, 1508, 1463, 1433, 1381, 1340, 1315, 1271, 1256, 1215, 1178, 1146, 1126, 1070, 1026, 982, 949, 818, 750, 671 cm^{-1}. $[\alpha]_D^{25}$ −49.0 (*c* 0.52, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.40–1.49 (m, 4H), 1.54–1.72 (m, 8H), 2.58 (t, *J*=7.3 Hz, 4H), 2.70 (t, *J*=7.6 Hz, 4H), 5.05 (br, OH), 7.03–7.15 (m, 6H), 7.24–7.38 (m, 8H), 7.63 (s, 2H), 7.85–7.88 (m, 4H), 7.94 (d, *J*=9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.5, 28.9, 30.7, 30.9, 35.4, 35.6, 110.5, 110.9, 117.6, 123.8, 124.0, 124.1, 126.8, 127.3, 128.2, 128.8, 129.2, 129.4, 130.7, 131.2, 131.6, 133.2, 138.0, 151.9, 152.5. FABHRMS. Calcd for $C_{50}H_{46}O_4S_2$ [M^+]: 774.2837. Found: 774.2839.

4.10.3. (*R*)-Disulfide 15c (*n*=6). Mp 77–78 °C (EtOAc/hexane). IR (neat): ν_{max} 3489, 3420, 3059, 3007, 2926, 2853,

1618, 1597, 1506, 1464, 1437, 1379, 1344, 1313, 1271, 1256, 1213, 1178, 1144, 1124, 1070, 1026, 981, 947, 887, 862, 818, 748, 667 cm^{-1}. $[\alpha]_D^{25}$ −46.5 (*c* 0.78, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.30–1.40 (m, 8H), 1.62–1.66 (m, 8H), 2.57–2.72 (m, 8H), 5.02 (br, OH), 7.00–7.15 (m, 6H), 7.24–7.38 (m, 8H), 7.63 (s, 2H), 7.82–7.88 (m, 4H), 7.94 (d, J=9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.3, 28.7, 28.9, 29.0, 29.1, 30.8, 31.2, 35.6, 39.1, 110.6, 111.0, 117.6, 123.8, 124.0, 124.1, 127.3, 128.2, 128.8, 129.3, 129.5, 130.7, 131.1, 131.6, 133.3, 138.2, 151.9, 152.5. FABHRMS. Calcd for $C_{52}H_{50}O_4S_2$ [M^+]: 802.3150. Found: 802.3170.

4.11. General procedure for the synthesis of MPC 16

To a solution of tetraoctylammonium bromide (2.8 mmol) in toluene (120 mL), $HAuCl_4 \cdot 4H_2O$ (1.4 mmol) was added in deionized water (50 mL). The yellow $HAuCl_4 \cdot 4H_2O$ aq solution quickly cleared, and the toluene phase became orange-brown as the $AuCl_4^-$ was transferred into it. The organic layer was isolated, disulfide **15** (0.7 mmol) was added, and the resulting solution was stirred for 10 min at room temperature. The reaction solution was then vigorously stirred, followed by addition of $NaBH_4$ (14 mmol) in deionized water (50 mL). The black organic phase was further stirred for another 12 h. The aqueous phase was removed, and the solvent was concentrated. The black residue was washed with EtOH, redissolved in toluene (10 mL), and precipitated from EtOH to afford the corresponding MPC **16** in quantitative yield.

*Characterization of MPC **16a–c***: MPCs **16a–c** were dried under reduced pressure at 50 °C for 24 h and characterized by elemental analysis. Furthermore, a suspension of MPC **16b** in THF was sonicated for 5 min. The resulting suspension of MPC **16b** was measured by DLS instrument and TEM instrument.

*Au-MPC **16a*** (n=4): Anal. C, 40.63; H, 5.42; S, 2.84; Au, 45.96, loading of BINOL units on the Au cluster 1.30 mmol g^{-1}.

*Au-MPC **16b** (n=5)*: Anal. C, 40.71; H, 4.52; S, 3.11; Au, 46.68, loading of BINOL units on the Au cluster 1.28 mmol g^{-1}.

*Au-MPC **16c** (n=6)*: Anal. C, 40.25; H, 4.75; S, 3.61; Au, 46.13, loading of BINOL units on the Au cluster 1.26 mmol g^{-1}.

4.11.1. (*S*)-Methyl 16-[2,2′-bis(methoxymethoxy)-1,1′-binaphth-6-yl]hexadec-15-enoate (17). The procedure is similar to that of (*S*)-**3**, using $IPPh_3(CH_2)_{14}CO_2Me$ (14.2 g, 22.0 mmol), MeONa (1.40 g, 25.0 mmol), and (*S*)-6-formyl-2,2′-bis(methoxymethyloxy)-1,1′-binaphthyl (**2**) (3.6 g, 9.0 mmol) to give compound (*S*)-**17** (5.60 g). $[\alpha]_D^{20}$ −14.0 (*c* 0.53, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.24–1.28 (m, 20H), 1.43–1.45 (m, 2H), 1.56–1.64 (m, 2H), 2.27–2.39 (m, 4H), 3.15 (d, J=7.4 Hz, 6H), 3.66 (s, 3H), 4.95–4.99 (m, 2H), 5.05–5.09 (m, 2H), 5.62–6.30 (m, 1H), 6.46–6.52 (m, 1H), 7.08–7.37 (m, 5H), 7.51–7.58 (m, 2H), 7.75 (s, 1H), 7.85–7.89 (m, 2H), 7.94 (d, J=12.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.0, 28.8, 29.1, 29.3, 29.4, 29.6, 30.0, 30.9, 33.1, 34.1, 51.3, 55.7, 95.1, 117.1, 121.0, 121.1, 121.2, 123.9, 125.1, 125.4, 125.6, 127.3, 127.5, 127.7, 128.2, 128.4, 129.1, 129.2, 129.6, 129.7, 129.9, 131.3, 132.0, 132.2, 133.0, 133.4, 133.5, 133.8, 152.4, 174.0. FABHRMS. Calcd for $C_{41}H_{53}O_6$ [$(M+H)^+$]: 641.3764. Found: 641.3732.

4.11.2. (*S*)-Methyl 16-[2,2′-dihydroxy-1,1′-binaphth-6-yl]hexadecanoate (18). To a stirred solution of (*S*)-**17** (5.45 g, 8.50 mmol) in EtOH (10 mL)/MeOH (10 mL) and AcOH (10 mL), $Pd(OH)_2$–C (750 mg) was added, and the resulting mixture was subjected to hydrogenation under 1 atm pressure at 40 °C for 24 h. The reaction mixture was then filtered through Celite® and solvent was evaporated under reduced pressure to give (*S*)-**18** (4.72 g). ^1H NMR ($CDCl_3$): δ 1.23–1.30 (m, 22H), 1.58–1.66 (m, 4H), 2.27 (t, J=10.4 Hz, 2H), 2.71 (t, J=10.4 Hz, 2H), 3.66 (s, 3H), 5.01 (s, 1H), 5.11 (s, 1H), 7.05–7.33 (m, 5H), 7.37 (t, J=12.2 Hz, 2H), 7.66 (s, 1H), 7.88–7.92 (m, 2H), 7.97 (d, J=12.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.1, 25.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.9, 31.5, 34.1, 35.8, 51.5, 60.4, 110.8, 111.2, 117.6, 117.7, 123.8, 124.0, 124.2, 126.7, 127.2, 128.2, 128.8, 129.3, 129.6, 130.7, 131.1, 131.7, 133.4, 138.4, 151.9, 152.5, 174.2.

4.11.3. (*S*)-Methyl 16-[2,2′-bis(methoxymethoxy)-1,1′-binaphth-6-yl]hexadecanoate (19). Compound (*S*)-**18** (1.40 g, 2.5 mmol) in THF (12 mL) was added slowly to a solution of 60% NaH (211 mg, 8.8 mmol) in THF (3 mL) at 0 °C under an argon atmosphere. Stirring was continued for 30 min, followed by addition of MOMCl (0.60 mL, 7.5 mmol). The reaction mixture was then allowed to stir at room temperature for 8 h. After completion of reaction, the mixture was quenched with water (10 mL) in an ice bath and extracted with EtOAc (50 mL×3). The organic layer was washed with brine (50 mL) and evaporated under reduced pressure. The residue was subjected to column chromatography with an eluent EtOAc/hexane (1/4) to afford (*S*)-**19** (1.61 g). ^1H NMR ($CDCl_3$): δ 0.83–0.90 (m, 2H), 1.25–1.26 (m, 20H), 1.59–1.68 (m, 4H), 2.30 (t, J=10.4 Hz, 2H), 2.70 (t, J=10.4 Hz, 2H), 3.13 (d, J=6.3 Hz, 6H), 3.65 (s, 3H), 4.93–4.98 (m, 2H), 5.04–5.08 (m, 2H), 7.07–7.36 (m, 5H), 7.55 (t, J=12.2 Hz, 2H), 7.63 (s, 1H), 7.85–7.88 (m, 2H), 7.93 (d, J=12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.0, 29.2, 29.3, 29.5, 29.6, 29.7, 29.8, 31.4, 34.2, 35.9, 51.4, 53.4, 55.7, 55.8, 95.1, 95.2, 95.3, 117.2, 117.3, 121.1, 121.4, 123.9, 125.3, 125.4, 125.5, 126.0, 126.1, 126.2, 127.7, 129.2, 129.3, 129.7, 130.0, 132.3, 133.9, 138.4, 151.9, 152.5, 174.1.

4.11.4. (*S*)-16-[2,2′-Bis(methoxymethoxy)-1,1′-binaphth-6-yl]-hexadecan-1-ol (20). $LiAlH_4$ (161 mg, 4.25 mmol) was added to a solution of (*S*)-**19** (1.61 g, 2.5 mmol) in THF (30 mL) at 0 °C under argon. The reaction mixture was stirred at room temperature for 17 h and then quenched with 10% HCl (100 mL), followed by extraction with EtOAc (50 mL×3). The organic layer was washed with water (50 mL) and brine (50 mL) and then dried over Na_2SO_4. Evaporation of solvent in vacuo and purification by column chromatography using eluent EtOAc/hexane (1/2) produced alcohol (*S*)-**20** (1.00 g). ^1H NMR ($CDCl_3$): δ 1.18–1.25 (m, 24H), 1.48–1.53 (m, 2H), 1.62–1.66 (m, 2H), 2.68 (t, J=10.4 Hz, 2H), 3.10 (d, J=8.9 Hz, 6H), 3.54 (t, J=8.9 Hz, 2H), 4.90–4.95 (m, 2H), 5.01–5.05 (m, 2H), 7.06–7.30 (m,

5H), 7.56 (t, J=11.8 Hz, 2H), 7.61 (s, 1H), 7.81–7.86 (m, 2H), 7.90 (d, J=11.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.7, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7, 29.8, 31.3, 32.6, 35.8, 55.5, 55.6, 62.7, 94.9, 95.0, 117.0, 120.9, 121.2, 123.8, 125.2, 125.3, 126.0, 126.2, 127.6, 127.7, 128.6, 129.0, 129.6, 129.8, 132.1, 133.7, 138.3, 151.7, 152.3.

4.11.5. (*S*)-6-(16-Bromohexadecyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalenyl. To a mixture of compound (*S*)-**20** (1 g, 1.63 mmol) and PPh_3 (853 mg, 3.20 mmol) in THF (20 mL), CBr_4 (1.06 g, 3.20 mmol) was added at 0 °C under an argon atmosphere. The mixture was stirred for 16 h at room temperature. The reaction mixture was then diluted with hexane, and precipitated PPh_3O was filtered off through Celite®. The filtrate was concentrated under vacuum to give oil, which was subjected to column chromatography on SiO_2 with EtOAc/hexane (1/4) to afford corresponding bromide (1.10 g) as yellow oil. $[\alpha]_D^{20}$ −21.6 (*c* 0.51, $CHCl_3$). IR (neat): ν_{max} 3059, 2920, 2851, 1506, 1271, 1254, 1215, 1180, 1144, 1124, 962, 948, 885, 862, 816, 779, 748, 721 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.12–1.34 (m, 24H), 1.53–1.58 (m, 2H), 1.71–1.77 (m, 2H), 2.60 (t, J=11.1 Hz, 2H), 3.04 (d, J=8.9 Hz, 6H), 3.01–3.06 (m, 5H), 4.82–4.88 (m, 2H), 4.93–4.97 (m, 2H), 6.97–7.25 (m, 5H), 7.44 (t, J=12.2 Hz, 2H), 7.53 (s, 1H), 7.74–7.78 (m, 2H), 7.83 (d, J=12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 28.2, 28.8, 29.4, 29.5, 29.6, 29.7, 29.8, 30.0, 31.3, 32.6, 32.8, 35.8, 53.4, 55.7, 55.8, 95.0, 95.1, 117.1, 121.0, 121.3, 123.9, 124.5, 125.2, 125.4, 126.1, 127.7, 127.8, 127.9, 128.6, 129.1, 129.6, 129.9, 132.2, 133.8, 138.3, 151.8, 152.4. FABMS (*m*/*z*): 678 $[M+H]^+$.

4.11.6. (*S*)-Disulfide 21. The procedure is similar to those of disulfides (*R*)-**15a–c**. Thus the above obtained bromide (12.2 g, 18 mmol) and thiourea (4.11 g, 54 mmol) produced disulfide (*S*)-**21** (8.86 g). $[\alpha]_D^{20}$ −35.9 (*c* 0.57, $CHCl_3$). IR (neat): ν_{max} 3059, 2920, 2851, 1506, 1456, 1238, 1196, 1148, 1082, 1069, 1015, 921, 889, 862, 810, 779, 746, 719 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28–1.34 (m, 48H), 1.68–1.70 (m, 8H), 2.70–2.76 (m, 8H), 3.16 (d, J=8.1 Hz, 12H), 4.96 (t, J=9.3 Hz, 4H), 5.07–5.11 (m, 4H), 7.10–7.38 (m, 10H), 7.58 (t, J=13.0 Hz, 4H), 7.66 (s, 2H), 7.87–7.91 (m, 4H), 7.96 (d, J=12.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 22.8, 28.6, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.4, 35.9, 38.8, 39.2, 53.4, 55.7, 55.8, 95.1, 95.2, 117.2, 121.1, 121.4, 123.6, 125.3, 125.5, 126.0, 126.1, 127.7, 127.8, 128.7, 129.1, 129.7, 129.9, 132.2, 133.8, 138.4, 151.8, 152.4. FABMS (*m*/*z*): 1261 $[M+H]^+$.

4.12. Preparation of MPC 22

MPC **22** was prepared by the method described for the preparation of MPC **16a–c**. MPC **22** was then directly used for the synthesis of MPC **23**.

4.13. Preparation of MPC 23

p-Toluenesulfonic acid monohydrate (610 mg, 3.20 mmol) was added to a stirred solution of MPC **22** (800 mg, 0.800 mmol, in consideration of BINOL loading 1.0 mmol g^{-1} on Au cluster surface) in CH_2Cl_2 (20 mL) at 0 °C under an argon atmosphere. The solution was stirred at room temperature for 12 h and then neutralized with saturated aq Na_2CO_3 (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL×2). The combined organic layers were washed with water (50 mL) and brine (50 mL), and then dried over Na_2SO_4. The CH_2Cl_2 was evaporated and the black residue was washed with EtOH, dissolved in toluene (10 mL) and precipitated from EtOH to afford the corresponding MPC **23** in quantitative yield.

*MPC **23** (n=16)*: Anal. C, 38.98; H, 4.04; S, 3.50; Au, 49.31, loading of BINOL units on the Au cluster 1.09 mmol g^{-1}.

4.14. Typical procedures for catalytic asymmetric alkylation of benzaldehyde

A suspension of polymer or MPC **16a–c** and Ti(O-*i*-Pr)$_4$ (0.25 mmol) in 0.5 mL of CH_2Cl_2 was stirred at room temperature for 30 min. To the suspension, benzaldehyde (0.25 mmol) was added, and the apparatus was cooled to −10 °C. After stirring for 30 min at this temperature, diethyl zinc solution (1.0 M in hexane) was added dropwise to the stirred mixture and the entire mixture was stirred for the indicated reaction time. After the addition of 1 N HCl, the crude mixture was extracted with Et_2O (10 mL×3). The solvent was evaporated under reduced pressure, followed by purification using column chromatography on SiO_2 to give compound **10**. Optical purity was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OD-H, *i*-PrOH/hexane=1/19, 1.0 mL min^{-1}, 254 nm).

4.15. Typical procedure for catalytic asymmetric Michael reaction

MPC **23** (27.5 mg, 0.03 mmol as a BINOL unit) was dissolved in dry THF (0.45 mL) and stirred at room temperature for 15 min. NaO-*t*-Bu (0.6 mL, 0.06 mmol, 0.1 M in THF) was then added in one portion and stirred for an additional 30 min. To the resulting reaction mixture, $GaCl_3$ (0.15 mL, 0.015 mmol, 0.1 M in Et_2O) was added, and stirring continued for an additional 24 h. Additional NaO-*t*-Bu (0.07 mL, 0.007 mmol, 0.1 M in THF) was then added, and the reaction mixture was further stirred at room temperature for 1 h. To the resulting MPC-supported GaSB catalyst, dibenzyl malonate (38 μL, 0.15 mmol) was added, and after stirring for 30 min, 2-cyclohexen-1-one (**24**) (16 μL, 0.165 mmol) was added. After completion of reaction, the mixture was quenched with saturated NH_4Cl and extracted with Et_2O (10 mL×3). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Concentration and purification by flash chromatography with hexane/acetone (15/1) gave Michael adduct **25**. The enantiomeric purity of **25** was determined by chiral HPLC analysis (Diacel Chiralpak AS, *i*-PrOH/hexane=1/4, 1.0 mL min^{-1}, 254 nm).

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10. Although the phosphate moiety was removed from the BINOL unit of **MDP-I** to check the catalytic activity of the resulting polymer (**MDP-Ia**), removal of the phosphate moiety using LAH (1 equiv, 15 h) was not successful and IR studies of **MDP-Ia** revealed the persistence of the phosphate group. Other reaction conditions, including extended reaction periods and the use of excess amounts of LAH, resulted in the cleavage of the BINOL moieties due to reduction of the ester units of **MDP-I** and **MDP-Ia**.
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20. In a preliminary attempt to reuse Au-MPC **16b**, after completion of first cycle the reaction was terminated using 1 N HCl and Au-**16b** was easily recovered by simple precipitation from EtOH. The recovered Au-MPC **16b** was then reused for asymmetric alkylation of benzaldyheyde with Ti(O-*i*-Pr)$_4$ to afford product (*R*)-**10** in 92% yield and 68% ee.
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