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Synthesis and evaluation of a chiral menthol functionalized silsesquioxane: application to diastereoselective [2+2] photocycloaddition

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Abstract A novel chiral menthol derivative supported on silsesquioxane was easily synthesized by hydrosilylation of the corresponding arylmenthyl olefin with commercially available silsesquioxane-type hydrosilane. We evaluated the applicability of the silsesquioxane-based compound to diastereoselective [2+2] photocycloaddition reaction. The newly synthesized silsesquioxane-based chiral menthol derivative **9** indicated similar diastereoselectivity to the corresponding *p*-methoxyphenyl menthol derivative.

Keywords Menthol auxiliary · Silsesquioxane · Organic–inorganic hybrid material · Diastereoselectivity · Photocycloaddition

Introduction

Silsesquioxane is the general term for an organosilicon polymer with the general formula $(RSiO_{3/2})_n$. These polymers have one organic substituent group on the Si atom. In general, silsesquioxanes are soluble in organic solvent and have high thermal and chemical stability, and their physical properties are well defined for the introduction of substituent groups [1, 2]. Silsesquioxanes have been widely used in the electronics industry as resistors, interlayer insulators, optical materials, resins, and rubbers. Silsesquioxanes have a similar structure to the active sites assumed in solid catalysts such as zeolites and silica-supported catalysts, and therefore have

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been studied as molecular model compounds of silica-supported catalysts or precursors of heterogeneous catalysts [3]. The structures of silsesquioxanes have been characterized using the following terms, as illustrated in Fig. 1 cage-type (T_8), partial cage-type, random type, and ladder type.

In particular, the cage structure (T_8) is a molecular model for silica-grafted compounds in heterogeneous materials. Furthermore, there is substantial interest in cage-type octafunctional silsesquioxanes, where all the side groups (*R*) on the silicon atoms are identical and reactive. Although a large number of possible side groups can be introduced, ranging from alkyls, alcohols, amides, and carboxylates to halides, nitrates, and phosphanes [4–19], there are few reports regarding silsesquioxanes containing chiral groups [20].

Thus far, we have systematically investigated asymmetric [2+2] photocycloadditions, and clarified the utility of menthol derivatives as a chiral auxiliary on these reactions [21–23]. Chiral menthyl auxiliaries have been widely applied not only to photoreactions but also to various thermal reactions [24, 25], such as Michael additions [26], radical reactions [27], Diels–Alder reactions [28], and Friedel–Crafts reactions [29].

From these viewpoints, we focused on the combination of silsesquioxane and chiral menthyl. A novel cage-type silsesquioxane, functionalized with chiral menthyl, was synthesized and characterized. Moreover, diastereoselective [2+2] photocycloadditions of ethylene to cyclohexenones modified with the chiral silsesquioxane were carried out in order to evaluate the nature of the asymmetric introduction.

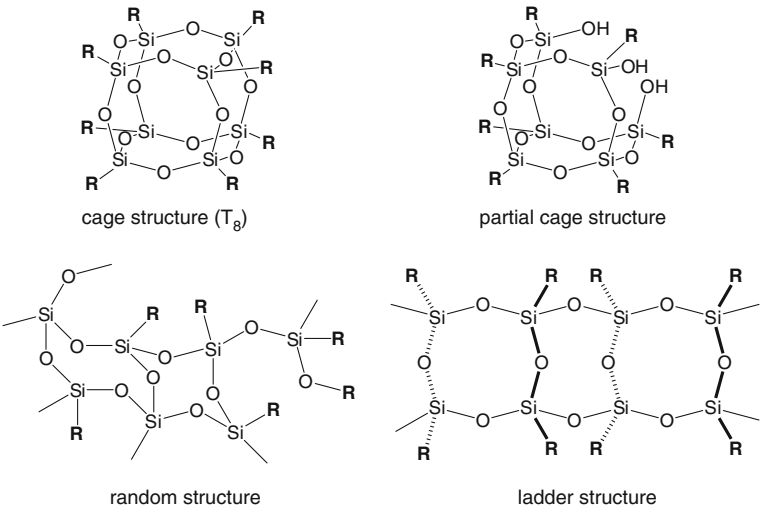


Fig. 1 Structures of silsesquioxanes

Experimental

General methods

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. Reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL LNM-ECP500, and a JEOL JNM-ECP600NK. ^{1}H NMR spectra are reported as a chemical shift in ppm based on the peak of TMS ($\delta = 0.0$ ppm), integration, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublets, m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra are reported as chemical shifts in ppm based on the middle peak of $CDCl_3$ ($\delta = 77.0$ ppm). TOF–MS spectra were performed with a Bruker Daltonics Autoflex II. Infrared spectra were obtained on a JASCO FTIR-420 spectrometer; absorption peaks are reported in reciprocal centimeters. Optical rotation was obtained on a JASCO DIP-1000. UV/Vis and CD spectra were measured in a quartz cell (10 mm thickness) on a JASCO V-630 and a JASCO J-725, respectively.

Syntheses of materials

(–)-8-[(*p*-Methoxy)phenyl]menthol **1** was prepared from (*R*)-(+)-pulegone according to the modified Corey's procedure [30]. After the protection of the secondary alcohol, demethylation was carried out with boron tribromide to produce (–)-8-[(*p*-(hydroxy)phenyl]menthyl acetate **2** [22].

*Synthesis of chiral menthyl acetate derivative **4***

Menthyl acetate **2** (435 mg, 1.5 mmol), Cs_2CO_3 (1,950 mg, 6.0 mmol), and 11-bromo-1-undecene **3** (0.7 mL, 3.0 mmol) were added to *N*, *N*-dimethylformamide (DMF, 20.0 mL). The mixture was stirred for 3 h at 80 °C. After addition of water, the mixture was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by flash column chromatography on silica gel using ethyl acetate–hexane as an eluent (90 %). Colorless oil; ^{1}H NMR ($CDCl_3$, ppm) δ 7.17 (2H, d, $J = 8.6$ Hz), 6.81 (2H, d, $J = 8.6$ Hz), 5.85–5.77 (1H, m), 4.99 (1H, dd, $J = 17.4$, 1.5 Hz), 4.93 (1H, dd, $J = 9.8$, 1.5 Hz), 4.78 (1H, ddd, $J = 10.5$, 10.5, 4.7 Hz), 3.92 (2H, t, $J = 6.4$ Hz), 2.05–2.03 (2H, m), 1.94–1.91 (1H, m), 1.87–1.85 (1H, m), 1.76–1.74 (2H, m), 1.67–1.64 (2H, m), 1.62 (3H, s), 1.43–1.38 (7H, m), 1.29 (9H, m), 1.19 (3H, s), 1.09–1.04 (1H, m), 0.96–0.93 (1H, m), 0.86 (3H, d, $J = 6.7$ Hz), 0.83–0.80 (1H, m); ^{13}C NMR ($CDCl_3$, ppm) δ 143.49, 139.22, 126.29 (2C), 114.12, 113.80 (2C), 74.18, 67.93, 50.42, 41.78, 39.08, 34.54, 34.41, 33.80, 31.27, 29.51, 29.41, 29.38, 29.36, 29.34, 29.10, 28.91, 27.81, 26.60, 26.05, 25.43, 21.79, 21.32.

*Synthesis of chiral menthol derivative **5***

Menthyl acetate derivative **4** (1.72 g, 3.9 mmol) and NaOH (0.78 g, 19.5 mmol) were added to *i*-PrOH (80 mL). The mixture was stirred for 5 h at 80 °C. After

addition of 1 N HCl, the mixture was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by flash column chromatography on silica gel using ethyl acetate–hexane as an eluent (95 %). Colorless oil;^{1}H NMR ($CDCl_3$, ppm) δ 7.30 (2H, d, $J = 8.6$ Hz), 6.85 (2H, d, $J = 8.6$ Hz), 5.86–5.78 (1H, m), 4.99 (1H, dd, $J = 17.0$, 2.3 Hz), 4.93 (1H, dd, $J = 10.5$, 2.3 Hz), 3.92 (2H, t, $J = 6.4$ Hz), 3.52 (1H, ddd, $J = 10.1$, 10.1, 4.3 Hz), 2.05–2.03 (2H, m), 1.84–1.83 (1H, m), 1.77–1.74 (3H, m), 1.68–1.65 (2H, m), 1.56 (1H, brs), 1.44–1.41 (3H, m), 1.38 (3H, s), 1.36–1.28 (9H, m), 1.26 (3H, s), 1.05–1.03 (2H, m), 0.96–0.86 (1H, m), 0.88 (3H, d, $J = 6.7$ Hz), 0.86–0.80 (1H, m); ^{13}C NMR ($CDCl_3$, ppm) δ 146.87, 139.24, 126.74 (2C), 114.36 (2C), 112.05, 72.92, 67.88, 54.12, 45.15, 39.01, 35.18, 34.91, 33.80, 31.44, 29.51, 29.45, 29.42, 29.37, 29.31, 29.11, 28.91, 26.48, 26.39, 26.06, 22.01; $[\alpha]_D^{24} = -7.4$ ($c = 0.9$, MeOH).

Synthesis of silsesquioxane-based chiral menthol derivative ***7***

Octakis(dimethylsilyloxy)silsesquioxane **6** (100 mg, 0.1 mmol), olefin 5 (400 mg, 1.0 mmol), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt(dvs)) (74 μL, 0.005 mmol) were added to toluene (10 mL). The mixture was stirred for 24 h at room temperature. The mixture was filtered using Florisil. The product was purified by HPLC ($CHCl_3$) (73 %). Colorless oil; IR (neat, cm^{-1}) 3551, 2921, 1511, 1455, 1250, 1183, 1097, 831, 558; ^{1}H NMR ($CDCl_3$, ppm) δ 7.29 (16H, d, $J = 8.6$ Hz), 6.84 (16H, d, $J = 8.6$ Hz), 3.90 (16H, t, $J = 6.7$ Hz), 3.51 (8H, ddd, $J = 10.2$, 10.2, 4.6 Hz), 1.88–1.79 (8H, m), 1.79–1.70 (24H, m), 1.70–1.58 (16H, m), 1.39–1.24 (192H, m), 1.05–1.00 (8H, m), 0.90–0.85 (40H, m), 0.59 (16H, t, $J = 7.6$ Hz), 0.12 (48H, m); ^{13}C NMR ($CDCl_3$, ppm) δ 157.13 (8C), 142.80 (8C), 126.71 (16C), 114.30 (16C), 72.87 (8C), 67.85 (8C), 54.06 (8C), 45.16 (8C), 39.00 (8C), 34.89 (8C), 33.50 (8C), 31.43 (8C), 29.73 (8C), 29.71 (8C), 29.66 (8C), 29.49 (8C), 29.44 (8C), 29.35 (8C), 26.39 (8C), 26.11 (8C), 23.91 (8C), 22.97 (8C), 22.00 (8C), 17.69 (8C), −0.03 (8C), −0.34 (16C); MALDI–TOF MS (*m*/*z*): 4243.3 $(M + Na)^+$; Anal. Calcd for $C_{232}H_{408}O_{36}Si_{16}$: C, 65.98; H, 9.74. Found: C, 64.79; H, 9.69.

Synthesis of silsesquioxane-based chiral menthyl cyclohexenecarboxylate derivative ***9***

Silsesquioxane-based chiral menthol derivative **7** (41 mg, 0.01 mmol), cyclohexen-3-one-1-carboxylic acid **8** (14.0 mg, 0.10 mmol), diisopropylcarbodiimide (DIPC, 371 mg, 0.24 mmol), and *N*, *N*-dimethyl-4-aminopyridine (DMAP, 9 mg, 0.064 mmol) were added to CH_2Cl_2 (5 mL). The mixture was stirred for 12 h at room temperature, and filtered using Florisil. The product was purified by HPLC ($CHCl_3$) (74 %). Colorless oil; IR (neat, cm^{-1}) 2923, 2853, 1711, 1685, 1512, 1456, 1252, 1225, 1184, 1093, 830, 788, 556; ^{1}H NMR ($CDCl_3$, ppm) δ 7.12 (16H, d, $J = 8.6$ Hz), 6.71 (16H, d, $J = 8.6$ Hz), 6.23 (8H, s), 4.98 (8H, ddd, $J = 10.5$, 10.5, 4.5 Hz), 3.81 (16H, t, $J = 6.7$ Hz), 2.38–2.20 (24H, m), 2.14–2.13 (8H, m), 2.06–2.01 (8H, m), 1.89–1.84 (32H, m), 1.72–1.70 (24H, m), 1.47–1.12 (192H, m),

1.01–0.95 (16H, m), 0.88 (24H, d, $J = 6.7$ Hz), 0.59 (16H, t, $J = 7.6$ Hz), 0.12 (48H, s); ^{13}C NMR ($CDCl_3$, ppm) δ 200.15 (8C), 165.29 (8C), 156.58 (8C), 148.77 (8C), 143.36 (8C), 132.32 (8C), 126.14 (16C), 113.64 (16C), 74.94 (8C), 67.65 (8C), 50.43 (8C), 41.74 (8C), 38.81 (8C), 37.50 (8C), 34.41 (8C), 33.51 (8C), 31.28 (8C), 29.77 (8C), 29.74 (8C), 29.70 (8C), 29.65 (8C), 29.57 (8C), 29.47 (8C), 26.32 (8C), 26.19 (8C), 24.35 (8C), 23.54 (8C), 23.00 (8C), 21.90 (8C), 21.76 (8C), 17.70 (8C), −0.02 (8C), −0.34 (16C); MALDI–TOF MS (*m*/*z*): 5223.5 $(M + Na)^+$, Anal. Calcd for $C_{288}H_{456}O_{52}Si_{16}$: C, 66.52; H, 8.84. Found: C, 66.45; H, 8.77; $[\alpha]_D^{22} = -286.2$ ($c = 0.9$, MeOH).

Diastereoselective [2+2] photocycloaddition

Photoreaction of **9** with ethylene: Irradiations (>280 nm) were carried out in a Pyrex flask installed in a water-cooled quartz immersion apparatus, using a HALOS 500-W high-pressure Hg lamp as the light source (Scheme 3). A 0.006 M solution of **9** (0.008 mmol) was purged with ethylene for 5 min at 25 °C and irradiated at a given temperature under ethylene until the enone was almost completely consumed. The amount of dissolved ethylene was estimated to be large excess over that of **9** [32, 33]. The reaction was monitored by TLC on silica gel. After the solvent was evaporated, the residue was purified chromatographically to produce a photoadduct. The diastereomeric excess (de) value of **10** was determined by ^{1}H NMR spectroscopy. Colorless oil; ^{1}H NMR ($CDCl_3$, ppm) δ 7.04 (16H, d, $J = 8.5$ Hz), 6.99 (5H, d, $J = 8.5$ Hz), 6.66 (16H, d, $J = 8.5$ Hz), 6.59 (5H, d, $J = 8.5$ Hz), 4.90 (8H, m), 3.76 (16H, m), 3.69 (5H, m), 2.95 (8H, m), 2.82 (3H, m), 2.39 (8H, m), 2.24 (16H, m), 2.11 (16H, m), 2.02–1.81 (48H, m), 1.78–1.72 (16H, m) 1.69–1.65 (8H, m), 1.57 (16H, m), 1.43 (24H, s), 1.32 (144H, m), 1.19 (24H, s) 1.00 (16H, m), 0.84 (32H, m), 0.59 (16H, m), 0.12 (48H, s); ^{13}C NMR ($CDCl_3$, ppm) δ 175.38, 175.05, 157.04, 156.92, 143.37, 138.18, 129.35, 128.54, 126.68, 126.49, 125.61, 114.12, 113.98, 75.64, 68.17, 50.77, 50.42, 48.77, 46.24, 46.12, 42.09, 42.05, 39.69, 39.22, 34.79, 33.86, 31.62, 30.68, 30.09, 29.83, 28.77, 28.55, 27.74, 27.27, 26.97, 26.49, 23.33, 22.12, 21.69, 21.45, 21.19, 21.05, 18.04, 0.32 (These NMR spectra were measured as mixture product of major isomer and minor isomer.); MALDI–TOF MS (*m*/*z*): 5446.6 $(M + Na)^+$.

Results and discussion

Synthesis and characterization of chiral menthol functionalized silsesquioxane

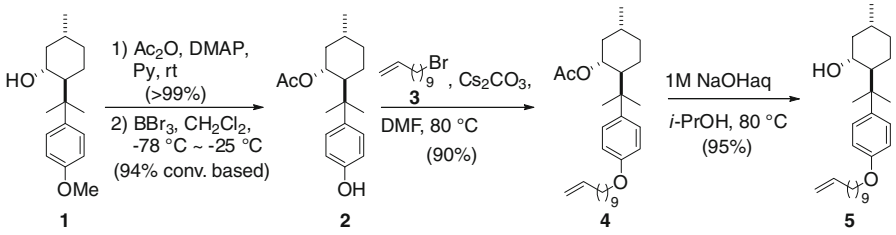
One versatile method of introducing organic functional groups onto the silsesquioxane molecule is based on platinum-catalyzed hydrosilylation of a Si–H to an unsaturated compound such as alkene or alkyne [34]. We initially prepared the menthol auxiliary containing an alkenyl group such as **5** (Scheme 1). The synthesis of **5** was carried out according to our previous method for the preparation of similar compounds [22]. First, (–)-8-[(*p*-methoxy)phenyl]menthol **1** was synthesized from (*R*)-(+)-pulegone according to the reported procedure [21]. The protection of the

secondary alcohol **1**, followed by demethylation with boron tribromide produced the known compound **2** [22]. The undecenyl group was introduced into **2**, then removal of the acetyl protecting group produced the desired product **5**.

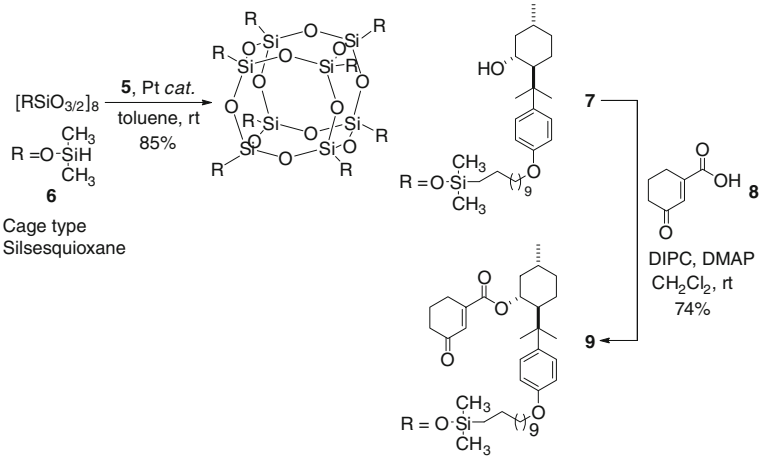
We synthesized a novel chiral menthol derivative supported on a cage-type silsesquioxane, as shown in Scheme 2. Introduction of a chiral menthol group to silsesquioxane was carried out by platinum-catalyzed hydrosilylation reaction of the menthol **5** with octakis(dimethylsilyloxy)silsesquioxane **6**. In the ^{1}H NMR spectrum of **7**, a peak of the methine proton (C*H*OH) of menthol groups appeared at δ 3.51 ppm. The MALDI–TOF MS of **7** indicated that eight menthol groups were attached to a silsesquioxane core. The elemental analysis also showed the expected composition. The condensation reaction of the silsesquioxane-functionalized octamenthol **7** with **8** proceeded to produce **9** in a good yield (74 %) (Scheme 2).

Diastereoselective [2+2] photocycloaddition of **9** with ethylene

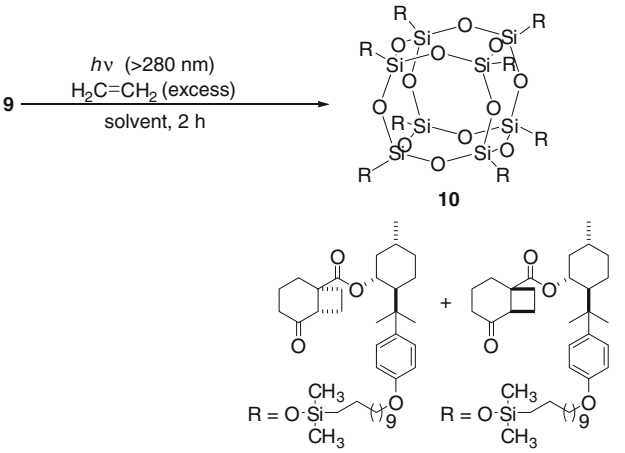
We experimentally evaluated the performance of the menthol-silsesquioxane molecule by asymmetric [2+2] photocycloaddition (Table 1). In this reaction,



Scheme 1 Synthesis of a novel chiral menthol derivative **5**

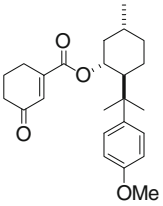


Scheme 2 Synthesis of a novel silsesquioxane-based chiral menthyl cyclohexenecarboxylate derivative **9**



Scheme 3 Diastereoselective [2+2] photocycloaddition

Table 1 Comparison between **9** and **11** of the diastereoselectivity for [2+2] photocycloaddition

Entry	Enone (Conc./M)	Solvent	Temp (°C)	Yield (%)[a]	De (%)[b]
1		Methylcyclohexane	−78	83	71
2		CH_2Cl_2	−78	85	54
3	9 (0.006)	Toluene	−78	84	80
4			−60	88	77
5			−40	85	63
6			−20	90	49
7[c]		Methylcyclohexane	−78	96	81
8[c]	 **11** (0.05)	CH_2Cl_2	−78	95	50
9		Toluene	−78	99	75
10			−60	92	69
11			−40	98	60
12			−20	99	47

Excess amount of ethylene were dissolved. See Refs. [31, 32]

[a] Isolated yield

[b] Determined by ^{1}H NMR

[c] Ref. [23]

diastereoselectivity was induced by shielding the attack of an ethylene molecule from one side due to the phenyl ring of the auxiliary, and it was dependent on the conformation of the substrate [23]. To enhance the electrostatic and/or dipole–dipole interactions between the C=O moiety of cyclohexenone and the aromatic ring, less polar solvent produced good selectivity (entries 1–3). Toluene was the best solvent for selectivity, due to the π–π stacking interaction between toluene and the aromatic ring (entry 3). Lower temperature was better for selectivity because of the thermodynamic stability of the substrate (entries 3–6). This result showed a similar tendency to the corresponding *p*-methoxyphenylmenthol derivative as a chiral auxiliary **11** (entries 7–12). Less polar solvent produced good selectivity (entries 7–9), which was enhanced at lower temperature (entries 9–12).

Moreover, we confirmed the conformation of **9** together with those of **11** (Fig. 2). Previously, we showed from the CD spectra of **11** that its stacked conformations

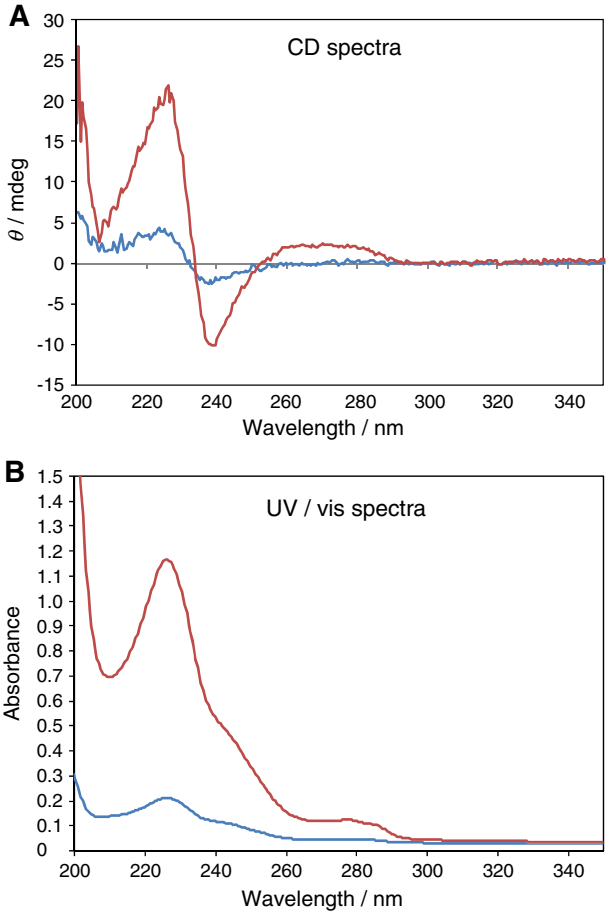


Fig. 2 CD Spectra **a** and UV/Vis spectra, **b** of **9** (1.0×10^{-5} M; *red line*) and **11** (1.0×10^{-5} M; *blue line*) in methylcyclohexane at room temperature. (Color figure online)

were essential for high diastereoselectivity [23]. The CD spectra of **9** showed almost the same Cotton effect as that of **11** except for the peak intensity. These results suggest that the phenylmenthyl cyclohexenonecarboxylate moiety on silsesquioxane **9** adopts the stacked conformation in solution similar to that of **11**, leading to high diastereoselectivity.

Conclusions

We successfully prepared a novel silsesquioxane-based chiral menthol derivative and examined the performance of the chiral silsesquioxane as a chiral auxiliary for [2+2] photocycloaddition. The diastereoselectivity was similar to the corresponding *p*-methoxyphenyl menthol derivative. The cage structures (T_8) were model compounds of silica, so we planned for the immobilization of menthols to silica.

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