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Tetrahedron 62 (2006) 3380–3388
Tetrahedron

# Catalytic enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one by chiral copper catalyst

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Received 10 November 2005; accepted 16 January 2006

Available online 13 February 2006

**Abstract**—A new catalytic system for enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one with thioacetylene derivatives is described. The use of a catalytic amount (20–30 mol%) of copper(II) salt with chiral bis-pyridine ligand was found to be effective in promoting the [2+2]-cycloaddition reaction, furnishing the corresponding bicyclic compound in good yield and good enantioselectivity.


## 1. Introduction

[2+2]-Cycloaddition reaction has been recognized as a powerful tool for the construction of a functionalized four-membered ring system.[1] The reaction usually proceeds under photo-irradiation or Lewis acid (also Brønsted acid)-catalyzed conditions.[1b] Among them, the Lewis acid-catalyzed condition is an attractive method, because the reaction proceeds under mild conditions with high siteselectivity.[2–4] Chiral Lewis acid-catalyzed enantioselective [2+2]-cycloaddition reaction is a useful tool for the synthesis of a poly-functionalized four-membered ring system as an optically active form. Narasaka et al. reported a Ti–TADDOL complex catalyzed enantioselective [2+2]-cycloaddition reaction of acryloyl oxazolidinone derivatives and the reaction provided excellent enantioselectivity (Eq. 1).[5,6] On the other hand, the enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one (**1**), which can be useful for preparation of a chiral bicyclic system, has not yet been reported (Eq. 2). The preparation of a bicyclic system containing a four-membered ring as optically active form is important for the synthesis of natural and biologically active compounds. Although asymmetric 1,4-addition of a nucleophile such as ketene silyl acetal to 2-methoxycarbonyl-2-cyclopenten-1-one (**1**) have been reported by several groups, the yield and enantio- or diastereoselectivity were moderate.[7–10] We tried to develop a chiral catalytic system (Scheme 1) for the addition of a nucleophile to 2-methoxycarbonyl-2-cyclopenten-1-one (**1**) and report herein a catalytic enantioselective [2+2]-cycloaddition of 2-alkoxycarbonyl-2-cycloalken-1-one with thioacetylene derivatives for the construction of a chiral bicyclic system.[11]

## 2. Results and discussion

### 2.1. The [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one catalyzed by Lewis acid

The Lewis acid catalyst for the [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one (**1**) was examined. The substrates **1** and **2** were prepared according to the literature procedure.[12,13] Substrate **1** was used for [2+2]-cycloaddition reaction without purification due to instability (>90% from $^1$H NMR). The result of the [2+2]-cycloaddition reaction is shown in Table 1. In the presence of 30 mol% of titanium chloride or zirconium chloride, the reaction proceeded to give cycloaddition product **3** along with a significant amount of by-product **4** and other by-products (entries 1 and 2). Another halogenated metal-catalyzed reaction also gave by-product **4**. Only under zinc bromide-catalyzed conditions, the reaction smoothly proceeded to provide the desired product **3** in 59% yield without a halogenated by-product (entry 5). The best result was obtained by employing 10 mol% of zinc bromide as a catalyst to prevent the decomposition of the product **3** (entry 6).

A plausible mechanism for the formation of **4** is shown in Scheme 2. The 1,4-addition of phenylthioacetylene (**2**) to

*Keywords*: [2+2]-Cycloaddition reaction; Ligand; Copper salt.
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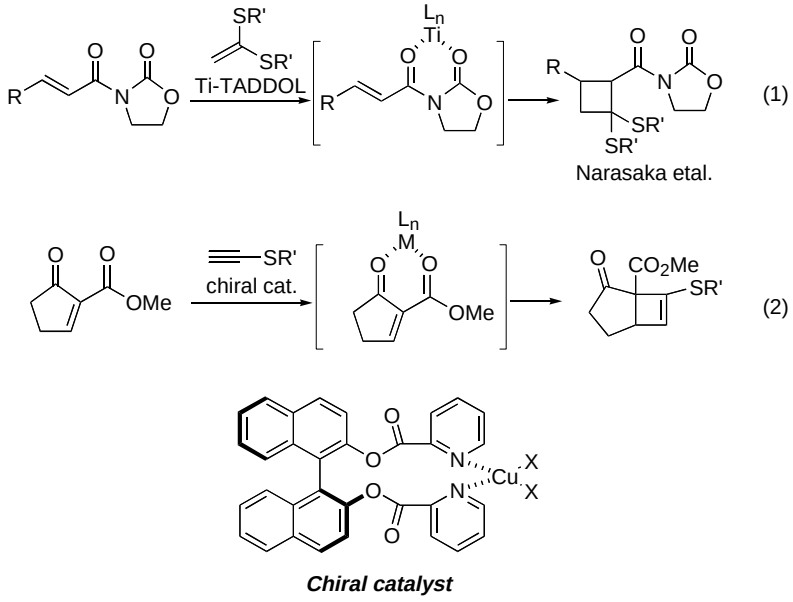
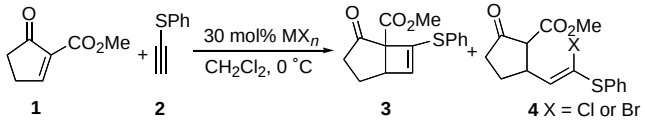
doi:10.1016/j.tet.2006.01.050



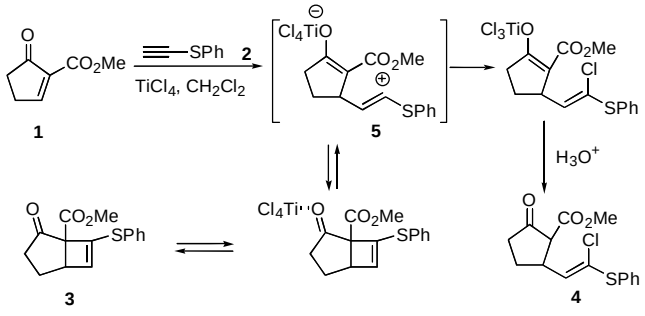

**Scheme 1.**

**Table 1**. Survey of metal salt catalysts for the [2+2]-cycloaddition reaction




| Entry | $MX_n$ | Time (h) | **3**:**4**[a] | Yield of **3** (%)[b] |
|---|---|---|---|---|
| 1 | $TiCl_4$ | 0.5 | 1:1.1 | 32 |
| 2 | $ZrCl_4$ | 0.5 | 1:1.9 | 26 |
| 3 | $MgBr_2 \cdot OEt_2$ | 1 | 1:0.9 | 16 |
| 4 | $CuCl_2$ | 48 | 1:0.8 | 33 |
| 5 | $ZnBr_2$ | 0.5 | 1:0 | 59 |
| 6[c] | $ZnBr_2$ | 2 | 1:0 | 84 |
| 7 | $Sc(OTf)_3$ | 0.5 | 1:0 | 42 |
| 8[c] | $Sc(OTf)_3$ | 0.5 | 1:0 | 65 |
| 9 | $Yb(OTf)_3$ | 0.5 | 1:0 | 57 |
| 10[c] | $Yb(OTf)_3$ | 1.3 | 1:0 | 75 |
| 11 | $Cu(OTf)_2$ | 0.5 | 1:0 | 51 |
| 12[c] | $Cu(OTf)_2$ | 0.5 | 1:0 | 80 |

[a] Ratio was determined by $^1$H NMR analysis.
[b] Isolated yield.
[c] Catalyst (10 mol%) was employed.




**Scheme 2.**

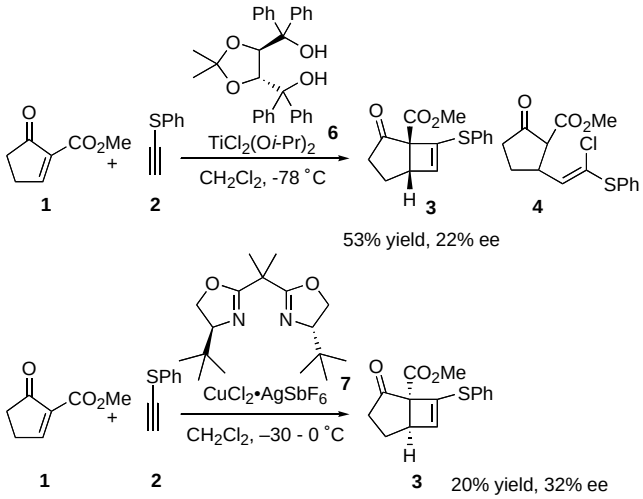
the substrate **1** gave intermediate **5**. The intramolecular reaction of the resulting titanium enolate to the carbocation on the carbon bearing the thiophenyl group gave the desired [2+2]-cycloadduct **3**. During this pathway, the reaction of the chloride anion to the carbocation in the intermediate **5** proceeded competitively to give by-product **4**. Another plausible route for the formation of **4** is as follows. After the formation of cycloadduct **3**, the decomposition of **3** proceeded based on the coordination of Lewis acid to the carbonyl group on the cyclopentane ring. Actually, compound **4** was obtained by the treatment of **3** with titanium chloride (vide infra).

To prevent the side-reaction, metal triflate catalyst was examined due to the low nucleophilicity of triflate anion and the results are shown in Table 1 (entries 7–12). Under the metal triflate-catalyzed conditions, the uncyclized compound such as **4** was not detected. Most of the examined triflates worked nicely, and the reaction in the presence of 10 mol% of copper triflate at 0 °C gave the best result (entry 12).

## 2.2. Enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one by reported chiral catalyst

Based on the result of the examination of Lewis acid catalysts, several reported chiral Lewis acid catalysts were examined for the asymmetric [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one (**1**) with phenylthioacethylene (**2**) prior to the development of a novel catalyst. The result is shown in Scheme 3.

As mentioned above, the Ti–TADDOL catalyst was effective for the [2+2]-cycloaddition reaction of acryloyloxazolidinone derivatives with thioacetylenes or ketene dithioacetals.[5] Therefore, this catalytic system was examined at first. Although moderate yield (53% yield) along with by-product **4** was obtained under 30 mol% of Ti–TADDOL complex **6**-catalyzed conditions, the enantiomeric excess of the product was not satisfactory (22% ee). We also examined the reaction catalyzed by a chiral copper catalyst.[9d,14] Under the presence of 20 mol% of a copper-BOX complex **7**, the reaction proceeded to give cycloadduct



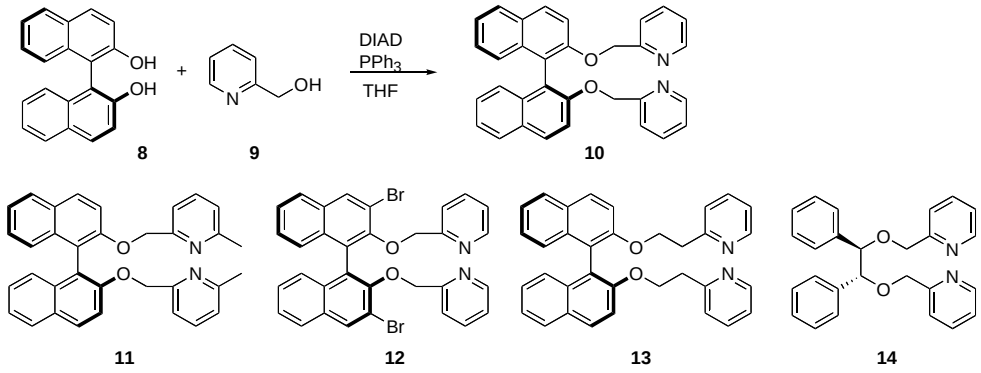

**Scheme 3.**

**3** in moderate enantiomeric excess (32% ee), but the yield was very low (20% yield). The titanium–BINOL catalyst[15] was also examined. Although good enantioselectivity was observed (79% ee), the yield was quite low (8% yield).

### 2.3. Enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one by novel copper catalyst

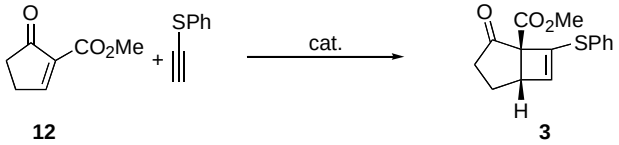
Based on the examination of the reported chiral catalyst as shown in Scheme 3, the development of a novel catalyst was examined. We employed copper(II) salt as Lewis acid and a novel and simple $C_2$-symmetric ligand having a binaphthyl moiety as a chiral source and two pyridine moieties as a coordination site to copper salt with appropriate binding affinity.

Novel chiral ligand **10** having two pyridine moieties was prepared from (*S*)-binaphthol (**8**) with 2-pyridinemethanol (**9**) by Mitsunobu reaction[16] (Scheme 4). Other modified chiral ligands **11**–**13** were also prepared in the same manner. The results of the enantioselective [2+2]-cycloaddition reaction of compound **1** with phenylthioacetylene (**2**) are shown in Table 2. In the case of a catalyst prepared from ligand **10** with copper triflate, the reaction proceeded at 0 °C and moderate ee was obtained but the yield was unsatisfactory (entry 1). The use of toluene or THF as a solvent instead of $CH_2Cl_2$ significantly decreased both the yield and ee (entries 2 and 3). In these cases, the low yield



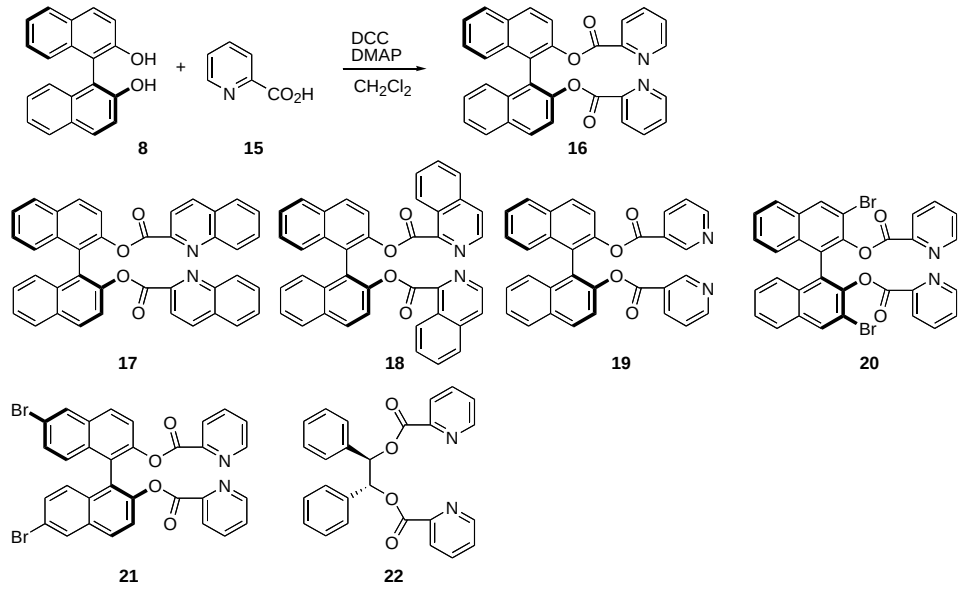

**Scheme 4.**

**Table 2**. Chiral copper-catalyzed [2+2]-cycloaddition reaction




| Entry | Ligand | Copper salt | Mol% | Solvent | Temperature (°C) | Time (h) | Yield (%)[a] | ee (%)[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | **10** | $Cu(OTf)_2$ | 30 | $CH_2Cl_2$ | −78 to 0 | 13 | 13 | 44 |
| 2 | **10** | $Cu(OTf)_2$ | 30 | Toluene | −78 to 0 | 17 | 7 | 20 |
| 3 | **10** | $Cu(OTf)_2$ | 30 | THF | −78 to 0 | 17 | NR | — |
| 4 | **10** | $Sc(OTf)_2$ | 30 | $CH_2Cl_2$ | 0 | 17 | 13 | 11 |
| 5 | **10** | $CuCl_2+AgSbF_6$ | 30 | $CH_2Cl_2$ | −78 to −30 | 14 | 56 | 41 |
| 6 | **10** | $CuCl_2+AgSbF_6$ | 50 | $CH_2Cl_2$ | −78 to −30 | 14 | 69 | 40 |
| 7 | **10** | $CuCl_2+AgSbF_6$ | 100 | $CH_2Cl_2$ | −30 | 19 | 65 | 39 |
| 8 | **11** | $Cu(OTf)_2$ | 30 | $CH_2Cl_2$ | −30 to 0 | 13 | 6 | 16 |
| 9 | **11** | $CuCl_2+AgSbF_6$ | 30 | $CH_2Cl_2$ | −30 to 0 | 19 | <5 | — |
| 10 | **12** | $CuCl_2+AgSbF_6$ | 30 | $CH_2Cl_2$ | 0 | 12 | 24 | 30 |
| 11 | **13** | $CuCl_2+AgSbF_6$ | 30 | $CH_2Cl_2$ | 0 | 5 | 18 | 29 |
| 12 | **14** | $CuCl_2+AgSbF_6$ | 30 | $CH_2Cl_2$ | −30 | 10 | 50 | 25 |

[a] Isolated yield.
[b] Ratio was determined by chiral HPLC analysis.



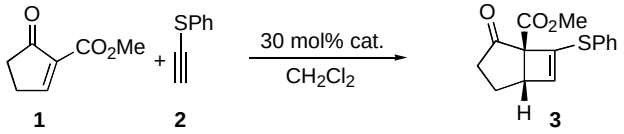

**Scheme 5.**

was observed due to the decomposition of substrate **1** during the long reaction time at 0 °C. To improve the ee and yield, other metal salts were examined and the best results were obtained with the use of hexafluoroantimonate as a counter anion of copper[9] (entries 5–7). With the increase of the Lewis acidity, the reaction proceeded even at −30 °C and the yield was significantly improved due to avoid the decomposition of substrate **1**. In the presence of 50 mol% of catalyst, best yield was obtained (69%, entry 6). The use of other modified ligands **11**–**14** decreased both the yield and ee (entries 8–12). These results indicated that the catalytic activity is not enough in the present catalysts due to the strong Lewis basicity of the nitrogen atom on the ligand. Therefore, novel ligands having a picolinate moiety to decrease the Lewis basicity of the coordination site to the metal center were designed.

The ligand **16** was prepared from (*S*)-binaphthol (**8**) with picolinic acid (**15**) by a condensation reaction using dicyclohexylcarbodiimide in 94% yield (Scheme 5). Other modified ligands **17**–**22** were prepared in the same manner.

The reaction of compound **1** with **2** catalyzed by the picolinate catalyst prepared from ligand **16** with copper triflate proceeded at 0 °C to give the [2+2]-adduct **3** in 31% yield with 24% ee (Table 3). This result showed significant improvement of the yield compared with the result of the 30 mol% of catalyst prepared from ligand **10** with copper triflate. The use of hexafluoroantimonate as a counter anion of copper instead of triflate increased the catalytic activity and the reaction proceeded at low temperature and the product **3** was obtained at −30 °C in 62% yield with 53% ee (entry 2). The reaction also proceeded at −78 °C and 64% ee was obtained (entry 3). The catalytic activities of the modified chiral ligands **17**–**22** were also examined. The ligand **17** and **18**, which is larger than pyridine ring, were prepared to increase the steric repulsion between catalyst and substrate and the reaction

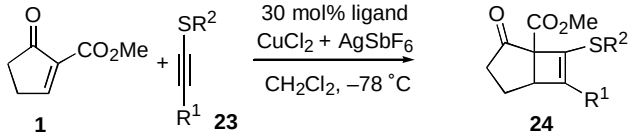
**Table 3**. Chiral copper catalyst catalyzed [2+2]-cycloaddition reaction




| Entry | Ligand | Copper salt | Temperature (°C) | Time (h) | Yield (%)[a] | ee (%)[b,c] |
|---|---|---|---|---|---|---|
| 1 | **16** | $Cu(OTf)_2$ | 0 | 2.5 | 31 | 24 |
| 2 | **16** | $CuCl_2+AgSbF_6$ | −30 | 0.6 | 62 | 53 |
| 3 | **16** | $CuCl_2+AgSbF_6$ | −78 | 3 | 48 | 64 |
| 4 | **17** | $Cu(OTf)_2$ | −30 | 2 | 35 | 23 |
| 5 | **17** | $CuCl_2+AgSbF_6$ | −30 | 3 | 38 | 24 |
| 6 | **18** | $Cu(OTf)_2$ | −30 to 0 | 1.5 | 14 | 12 |
| 7 | **18** | $CuCl_2+AgSbF_6$ | −30 | 0.8 | 45 | 19 |
| 8 | **19** | $CuCl_2+AgSbF_6$ | −30 | 12 | 7 | 13 |
| 9 | **20** | $CuCl_2+AgSbF_6$ | −30 | 3 | 35 | 0 |
| 10 | **21** | $CuCl_2+AgSbF_6$ | −78 | 1.5 | 13 | 73 |
| 11 | **22** | $CuCl_2+AgSbF_6$ | −30 | 4 | 41 | 13 |

[a] Isolated yield.
[b] Ratio was determined by chiral HPLC analysis.
[c] The absolute configurations of the major enatiomer were (1*R*,5*S*) except for entry 11.

**Table 4**. Chiral copper-catalyzed [2+2]-cycloaddition reaction of substituted thioacetylene derivatives



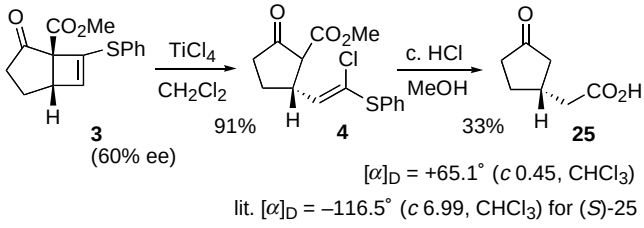

| Entry | 23 | Ligand | Time (h) | Product | Yield (%)[a] | ee (%)[b] |
|---|---|---|---|---|---|---|
| 1 | $R^1$=*n*Bu, $R^2$=Ph (**23a**) | **10** | 16 | **24a** | 9 | 45 |
| 2 | $R^1$=*n*Bu, $R^2$=Ph (**23a**) | **16** | 16 | **24a** | 75 | 32 |
| 3 | $R^1$=TMS, $R^2$=Ph (**23b**) | **16** | 16 | — | NR | — |
| 4 | $R^1$=TMS, $R^2$=Me (**23c**) | **10** | 16 | **24c** | 3 | 73 |
| 5 | $R^1$=*n*Bu, $R^2$=Me (**23c**) | **16** | 2 | **24c** | 51 | 15 |

[a] Isolated yield.
[b] Ratio was determined by chiral HPLC analysis.

gave product **3** but the ee was decreased in both cases (entries 4–7). The ligand **19** having a nicotinate moiety instead of picolinate was also examined and the product **3** was obtained with low yield and ee (entry 8). To increase the steric bulkiness of the naphthalene ring, modification of the BINOL moiety was also examined. The reaction of the ligand **20** prepared from 3,3′-dibromobinaphthol gave racemate **3**. In the case of ligand **21** derived from 6,6′-dibromobinaphthol, the reaction proceeded at −78 °C and the product **3** was obtained in 13% yield with 73% ee (entry 10).

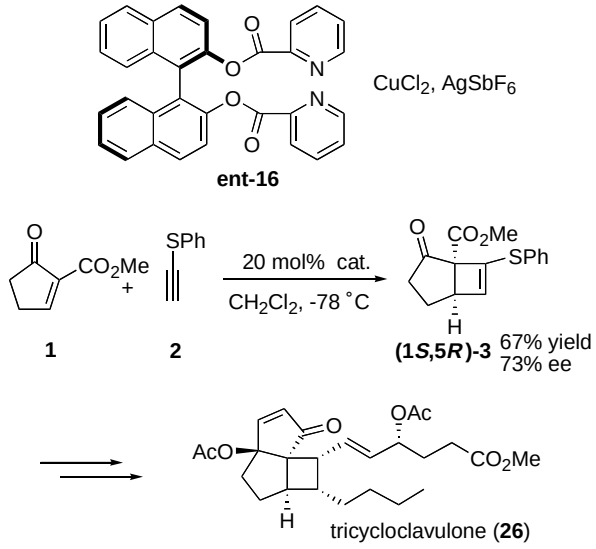
The [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one (**1**) with thioacetylene derivatives **23**[17] was also examined and the results are shown in Table 4. In the case of compound **23a**, good enantiomeric excess was found by using both ligand **10** and **16** (entries 1 and 2). As mentioned above, the use of ligand **10** decreased the yield of the cycloaddition product (entries 1 and 4). Although the yield was low, high enantiomeric excess was achieved in the case of TMS-substituted substrate **23c** (entry 4).

The absolute stereochemistry of the product was determined by comparison of the $[\alpha]_D$ value after conversion of compound **3** to known compound **25**[18] as shown in Scheme 6. Compound **3** (60% ee) prepared by the use of ligand **16** derived from (*S*)-binaphthol was treated with titanium chloride to cleave the four-membered ring to give chlorinated compound **4** (vide supra). The acid hydrolysis and decarboxylation of compound **4** with concentrated HCl in MeOH gave known compound **25**. A comparison of the optical rotation value with that of (*S*)-**25** suggested that the absolute configuration of the chiral center of compound **25** was *R* configuration. According to the above-mentioned conversion, the absolute configuration of the major enantiomer of the [2+2]-adduct **3** could be determined as (1*R*,5*S*) configuration.




**Scheme 6.**

The present enantioselective [2+2]-cycloaddition reaction was applied to the first step of an enantioselective total synthesis of (+)-tricycloclavulone (**26**) as shown in Scheme 7.[11] For the synthesis of tricycloclavulone as a natural form, the ligand **ent-16** derived from (*R*)-binaphthol was employed. In a 20 mmol scale reaction under the presence of 20 mol% of the catalyst, the reaction proceeded and the best enantioselectivity was achieved (73% ee). One cause of the improvement of the enantioselectivity is that both substrates were prepared just before use.




**Scheme 7.**

## 3. Conclusion

We have shown our efforts for the development of a catalytic system for [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one with thioacetylene derivatives. Among the survey of Lewis acid catalysts to accelerate the cycloaddition reaction, zinc bromide and copper triflate worked efficiently to give a four-membered ring product. Based on this result, we prepared a simple chiral ligand from BINOL and picolinic acid having the coordination ability to copper salt. The presented chiral

catalyst worked to give [2+2]-cycloadduct in good yield and enantiomeric excess. This catalytic system was applied to the enantioselective total synthesis of marine prostanoid tricycloclavulone.

## 4. Experimental

### 4.1. General procedure for the preparation of ligand 10–13

**4.1.1. 2,2′-Bis(2-pyridylmethoxy)-(1*S*)-1,1′-binaphthalene (10).** To a solution of (*S*)-BINOL (1.0 g, 3.49 mmol) in THF (30 mL) was added triphenylphosphine (2.0 g, 7.68 mmol), 2-(hydroxymethyl)pyridine (0.70 mL, 7.68 mmol) and a solution of diisopropyl azodicarboxylate (1.5 mL, 7.68 mmol) in THF (2 mL) at room temperature. After being stirred for 15 h, the reaction mixture was concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/AcOEt, 1:1–1:3 and $CHCl_3$/AcOEt, 2:1) to afford compound **10** (1.31 g, 2.80 mmol, 80% yield). White amorphous solid. $[\alpha]_D^{28}$ −63.6 (*c* 0.53, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1685, 1654, 1636, 1618, 749. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 5.22 (4H, s), 6.72 (2H, d, $J$=7.9 Hz), 7.04 (2H, dd, $J$=5.2, 7.2 Hz), 7.23–7.28 (6H, m), 7.35 (2H, m), 7.46 (2H, d, $J$=9.0 Hz), 7.90 (2H, d, $J$=8.2 Hz), 7.98 (2H, d, $J$=9.0 Hz), 8.45 (2H, d, $J$=4.5 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 71.4, 115.0, 120.1, 120.7, 122.1, 123.8, 125.4, 126.5, 127.9, 129.5, 134.1, 136.4, 148.6, 153.6, 157.7, 162.3. HRESIMS calcd for $C_{32}H_{25}N_2O_2$: 469.1916 $(M+H)^+$, found: 469.1911. Anal. Calcd for $C_{32}H_{24}N_2O_2$: C, 82.03; H, 5.16; N, 5.98. Found: C, 81.85; H, 5.21; N, 5.97.

**4.1.2. 2,2′-Bis[6-methyl(2-pyridylmethoxy)]-(1*S*)-1,1′-binaphthalene (11).** Colorless crystals. Mp 130–132 °C (from hexane–AcOEt). $[\alpha]_D^{28}$ −56.0 (*c* 0.53, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1618, 1593, 806, 775. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 2.47 (6H, s), 5.18 (4H, s), 6.53 (2H, d, $J$=7.7 Hz), 6.88 (2H, d, $J$=7.6 Hz), 7.15 (2H, t, $J$=7.7 Hz), 7.24–7.26 (4H, m), 7.30–7.37 (2H, m), 7.44 (2H, d, $J$=4.0 Hz), 7.88 (2H, d, $J$=8.1 Hz), 7.96 (2H, d, $J$=9.0 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 24.2, 71.4, 114.9, 117.5, 120.0, 121.6, 123.7, 125.4, 126.4, 127.9, 129.3, 129.5, 134.1, 136.7, 153.7, 157.0, 157.2. HRESIMS calcd for $C_{34}H_{29}N_2O_2$: 497.2229 $(M+H)^+$, found: 497.2225.

**4.1.3. 2,2′-Bis(2-pyridylmethoxy)-(1*S*)-[3,3′-dibromo-1,1′-binaphthalene] (12).** Colorless crystals. Mp 138–140 °C (from ether). $[\alpha]_D^{27}$ +40.0 (*c* 0.87, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1595, 1572, 760. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 4.71 (2H, d, $J$=13.1 Hz), 5.12 (2H, d, $J$=13.1 Hz), 6.89 (2H, d, $J$=7.9 Hz), 7.01 (2H, t, $J$=8.4 Hz), 7.42 (4H, q, $J$=8.1, 15.9 Hz), 7.75 (2H, d, $J$=8.1 Hz), 8.12 (2H, s), 8.31 (2H, br d, $J$=4.3 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 75.5, 117.3, 120.6, 122.0, 125.8, 126.1, 126.7, 127.0, 127.2, 131.5, 132.9, 133.0, 136.4, 148.3, 151.8, 157.0. HRESIMS calcd for $C_{32}H_{23}N_2O_2Br_2$: 625.0126 $(M+H)^+$, found: 625.0132.

**4.1.4. 2,2′-Bis(2-pyridylethoxy)-(1*S*)-1,1′-binaphthalene (13).** Colorless oil. $[\alpha]_D^{22}$ −43.2 (*c* 0.75, $CHCl_3$). IR (neat) $\nu$ $cm^{-1}$; 1591, 1508, 809, 748. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 2.81 (4H, td, $J$=6.3, 1.7 Hz), 4.24 (4H, t, $J$=6.3 Hz), 6.26 (2H, d, $J$=7.8 Hz), 6.89 (2H, ddd, $J$=1.0, 4.9, 7.4 Hz), 6.99–7.21 (6H, m), 7.30 (2H, ddd, $J$=1.5, 6.5, 8.0 Hz), 7.38 (2H, d, $J$=9.0 Hz), 7.86 (2H, d, $J$=8.2 Hz), 7.93 (2H, d, $J$=9.0 Hz), 8.33 (2H, dt, $J$=0.9, 4.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 38.2, 68.3, 114.9, 120.1, 120.9, 123.4, 123.7, 125.3, 126.0, 127.6, 129.0, 129.1, 134.0, 135.6, 148.6, 153.9, 158.3. HRESIMS calcd for $C_{34}H_{29}N_2O_2$: 497.2229 $(M+H)^+$, found: 497.2201. Anal. Calcd for $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64. Found: C, 82.17; H, 5.74; N, 5.45.

**4.1.5. (*R*,*R*)-1,2-Diphenyl-1,2-bis(2-pyridylethoxy)ethane (14).** Colorless crystals. Mp 78–80 °C (from hexane–AcOEt). $[\alpha]_D^{28}$ −59.1 (*c* 0.65, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1597, 1589, 760, 698. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 4.57 (2H, d, $J$=14.0 Hz), 4.70 (2H, s), 4.70 (2H, d, $J$=14.0 Hz), 7.08–7.26 (12H, m), 7.48 (2H, d, $J$=7.8 Hz), 7.61 (2H, dt, $J$=1.8, 7.7 Hz), 8.47 (2H, d, $J$=4.8 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 72.1, 85.8, 121.2, 122.0, 127.7, 127.8, 127.9, 136.5, 138.1, 148.8, 159.0. HRESIMS calcd for $C_{26}H_{25}N_2O_2$: 397.1916 $(M+H)^+$, found: 397.1915. Anal. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.66; H, 6.01; N, 6.94.

### 4.2. General procedure for the preparation of ligand 16–22

**4.2.1. 2,2′-Bis(picolinyloxy)-(1*S*)-1,1′-binaphthalene (16).** To a solution of (*S*)-BINOL (1.0 g, 3.49 mmol), picolinic acid (946 mg, 7.68 mmol) and 4-dimethylaminopyridine in $CH_2Cl_2$ (10 mL) was added a solution of dicyclohexylcarbodiimide (1.66 g, 8.03 mmol) in $CH_2Cl_2$ (5 mL) at room temperature. After being stirred for 15 h, the mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt, 1:5) to afford compound **16** (1.63 g, 3.28 mmol) in 94% yield. White amorphous solid. $[\alpha]_D^{28}$ −84.9 (*c* 0.59, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1752, 1685, 1654, 1582, 745. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 7.31–7.48 (14H, m), 7.56–7.61 (4H, m), 7.90 (2H, d, $J$=8.1 Hz), 8.00 (2H, d, $J$=8.9 Hz), 8.63 (2H, d, $J$=4.6 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 121.5, 123.5, 125.4, 125.9, 126.1, 126.9, 127.1, 127.9, 129.8, 131.6, 133.3, 136.9, 146.8, 147.0, 150.0, 162.8. HRESIMS calcd for $C_{32}H_{21}N_2O_4$: 497.1501 $(M+H)^+$, found: 497.1496. Anal. Calcd for $C_{32}H_{20}N_2O_4$: C, 77.41; H, 4.06; N, 5.64. Found: C, 77.20; H, 4.15; N, 5.58.

**4.2.2. 2,2′-Bis(2-quinolinecarbonyloxy)-(1*S*)-1,1′-binaphthalene (17).** Colorless crystals. Mp 193–195 °C (from hexane–AcOEt). $[\alpha]_D^{28}$ +53.7 (*c* 0.51, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1768, 1744, 1654, 839, 777. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 7.34–7.79 (16H, m), 7.91 (2H, d, $J$=8.0 Hz), 8.02 (2H, d, $J$=8.9 Hz), 8.06 (2H, d, $J$=8.6 Hz), 8.18 (2H, d, $J$=8.3 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 121.5, 122.0, 123.9, 126.3, 126.6, 127.6, 127.8, 128.4, 129.0, 129.6, 130.2, 130.5, 131.0, 131.2, 133.7, 137.6, 147.4, 147.5, 148.1, 163.4. HRESIMS calcd for $C_{40}H_{25}N_2O_4$: 597.1814 $(M+H)^+$, found: 597.1768. Anal. Calcd for $C_{40}H_{24}N_2O_4$: C, 80.52; H, 4.05; N, 4.70. Found: C, 80.43; H, 4.04; N, 4.71.

**4.2.3. 2,2′-Bis(2-isoquinolinecarbonyloxy)-(1*S*)-1,1′-binaphthalene (18).** Colorless crystals. Mp 209–211 °C (from hexane–AcOEt). $[\alpha]_D^{28}$ +6.4 (*c* 0.5, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1735, 1701, 1654, 1560, 801. $^1H$ NMR $\delta$; (300 MHz, $CDCl_3$) 712–7.22 (4H, m), 7.39–7.44 (2H, m), 7.49–7.59 (6H, m), 7.63 (2H, d, *J*=8.9 Hz), 7.65–7.75 (4H, m), 7.98 (2H, d, *J*=8.9 Hz), 8.04 (2H, d, *J*=8.9 Hz), 8.49 (2H, d, *J*=5.6 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 121.9, 123.7, 124.0, 125.7, 126.0, 126.1, 126.6, 126.7, 127.1, 128.0, 128.2, 130.1, 130.4, 132.0, 133.5, 136.4, 141.4, 147.4, 148.9, 164.6. HRESIMS calcd for $C_{40}H_{25}N_2O_4$: 597.1814 $(M+H)^+$, found: 597.1768. Anal. Calcd for $C_{40}H_{24}N_2O_4$: C, 80.52; H, 4.05; N, 4.70. Found: C, 80.31; H, 4.28; N, 4.67.

**4.2.4. 2,2′-Bis(nicotinyloxy)-(1*S*)-1,1′-binaphthalene (19).** White amorphous solid. $[\alpha]_D^{28}$ −74.1 (*c* 0.56, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1741, 1589, 1508, 1420, 730. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 7.20 (2H, ddd, *J*=0.8, 4.9, 8.0 Hz), 7.32–7.42 (4H, m), 7.49 (2H, ddd, *J*=2.3, 5.8, 8.3 Hz), 7.55 (2H, d, *J*=8.9 Hz), 7.86 (2H, td, *J*=2.0, 8.0 Hz), 7.93 (2H, d, *J*=8.2 Hz), 8.01 (2H, d, *J*=8.9 Hz), 8.65 (2H, dd, *J*=1.7, 4.9 Hz), 8.75 (2H, dd, *J*=0.8, 2.2 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 121.4, 123.2, 123.5, 125.1, 125.9, 126.1, 127.1, 128.2, 129.9, 131.6, 133.2, 146.5, 151.0, 153.6, 163.4. HRESIMS calcd for $C_{32}H_{21}N_2O_4$: 497.1510 $(M+H)^+$, found: 497.1496. Anal. Calcd for $C_{32}H_{21}N_2O_4$: C, 77.41; H, 4.06; N, 5.64. Found: C, 77.07; H, 4.21; N, 5.61.

**4.2.5. 2,2′-Bis(picolinyloxy)-(1*S*)-[3,3′-dibromo-1,1′-binaphthalene] (20).** Colorless crystals. Mp 156–158 °C (from acetone). $[\alpha]_D^{24}$ −2.7 (*c* 0.75, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1764, 1578, 745. $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$; 7.23 (2H, d, *J*=8.3 Hz), 7.41 (2H, t, *J*=7.6 Hz), 7.47–7.61 (4H, m), 7.83–8.09 (6H, m), 8.43 (2H, s), 8.61 (2H, br d, *J*=4.5 Hz). $^{13}C$ NMR (75 MHz, acetone-$d_6$) $\delta$; 115.6, 125.9, 126.3, 126.5, 127.5, 127.8, 127.9, 128.0, 132.4, 133.6, 137.5, 144.9, 146.9, 150.5, 162.1. HRESIMS calcd for $C_{32}H_{19}N_2O_4Br_2$: 652.9712 $(M+H)^+$, found: 652.9655.

**4.2.6. 2,2′-Bis(picolinyloxy) -(1*S*)-[6,6′-dibromo-1,1′-binaphthalene] (21).** Colorless crystals. Mp 78–80 °C (from ether–hexane). $[\alpha]_D^{24}$ −80.1 (*c* 0.71, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1756, 1584, 744. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 7.21 (2H, d, *J*=9.0 Hz), 7.36 (2H, d, *J*=6.1 Hz), 7.41 (2H, dd, *J*=1.3, 9.2 Hz), 7.54–7.69 (6H, m), 7.90 (2H, d, *J*=9.0 Hz), 8.06 (2H, s), 8.65 (2H, br d, *J*=4.7 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 122.0, 122.7, 123.2, 125.4, 127.1, 127.6, 129.1, 130.0, 130.1, 131.6, 132.6, 137.0, 146.6, 147.1. HRESIMS calcd for $C_{32}H_{19}N_2O_4Br_2$: 652.9712 $(M+H)^+$, found: 652.9692. Anal. Calcd for $C_{32}H_{18}N_2O_4Br_2$: C, 58.74; H, 2.77; N, 4.28. Found: C, 58.53; H, 2.85; N, 4.05.

**4.2.7. (*R*,*R*)-1,2-Diphenyl-1,2-bis(picolinyloxy)ethane (22).** White amorphous solid. $[\alpha]_D^{28}$ +72.4 (*c* 0.51, $CHCl_3$). IR (KBr) $\nu$ $cm^{-1}$; 1733, 1582, 697. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 6.58 (2H, s), 7.20–7.35 (10H, m), 7.41 (2H, ddd, *J*=0.9, 4.6, 7.6 Hz), 7.78 (2H, dt, *J*=1.7, 7.7 Hz), 8.11 (2H, d, *J*=7.8 Hz), 8.71 (2H, d, *J*=4.6 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 78.5, 125.2, 126.8, 127.9, 128.3, 128.7, 135.5, 137.0, 147.7, 150.1, 163.7. HRESIMS calcd for $C_{26}H_{21}N_2O_4$: 425.1501 $(M+H)^+$, found: 425.1536.

### 4.3. General procedure for the enantioselective [2+2]-cycloaddition reaction of 2-methoxycarbonyl-2-cyclopenten-1-one (1) with thioacetylene derivatives

**4.3.1. (1*S*,5*R*)-1-Methoxycarbonyl-2-oxo-7-(phenylthio)-bicyclo[3.2.0]hept-6-ene (3).** To a suspension of copper(II) chloride (1.3 g, 9.7 mmol) and ligand **ent-16** (5.76 g, 11.6 mmol) in $CH_2Cl_2$ (110 mL) was stirred at ambient temperature for 30 min and silver hexafluoroantimonate (7.0 g, 20.4 mmol) was added to the resulting mixture in the dark. After being stirred for 1 h at ambient temperature, a solution of 2-methoxycarbonyl-2-cyclohexen-1-one (**1**) (6.40 g, 45.7 mmol) and phenylthioacetylene (**2**) (7.24 g, 54.8 mmol) in $CH_2Cl_2$ (130 mL) was added to the mixture at −78 °C. After being stirred for 1.5 h at the same temperature, phosphate buffer (pH 6.86, 150 mL) was added to the mixture and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$. Filtration and concentration of the mixture under reduced pressure gave crude material, which was purified by silica gel column chromatography (hexane/AcOEt, 7:1) to afford compound **3** (8.44 g, 30.8 mmol) in 67% yield. 73% ee (Chiralcel OJ-H, hexane/IPA=95:5). Pale yellow oil. $[\alpha]_D^{22}$ +499 (*c* 1.33, $CHCl_3$). IR (neat) $\nu$ $cm^{-1}$; 1746, 1731, 1294, 747. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 1.89 (1H, bdd, *J*=9.1, 13.5 Hz), 2.13 (1H, dddd, *J*=6.9, 8.7, 11.9, 13.5 Hz), 2.39 (1H, ddd, *J*=1.0, 8.7, 18.3 Hz), 3.02 (1H, ddd, *J*=9.1, 11.9, 18.3 Hz), 3.67 (1H, d, *J*=6.9 Hz), 3.75 (3H, s), 5.88 (1H, s), 7.26–7.38 (3H, m), 7.49–7.53 (2H, m). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 22.4 ($CH_2$), 34.9 ($CH_2$), 48.3 (CH), 52.3 ($CH_3$), 66.2 (C), 128.8 (CH), 129.4 (CH), 129.7 (C), 133.0 (CH), 133.8 (CH), 140.5 (C), 167.6 (C), 208.4 (C). EI-MS *m*/*z*: 274 ($M^+$). Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.55; H, 5.11.

**4.3.2. 1-Methoxycarbonyl-2-oxo-6-butyl-7-(phenylthio)-bicyclo[3.2.0]hept-6-ene (24a).** Pale yellow oil. $[\alpha]_D^{26}$ −148 (32% ee, *c* 0.71, $CHCl_3$). IR (neat) $\nu$ $cm^{-1}$; 1743, 1734, 1730. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 0.88 (3H, t, *J*=7.3 Hz), 1.19–1.50 (4H, m), 1.88–2.25 (4H, m), 2.34 (1H, ddd, *J*=1.3, 8.6, 18.3 Hz), 2.84 (1H, ddd, *J*=9.3, 11.9, 18.3 Hz), 3.53 (3H, s), 3.64 (1H, d, *J*=7.0 Hz), 7.20–7.33 (3H, m), 7.36–7.45 (2H, m). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 13.4, 20.3, 22.6, 27.5, 28.4, 35.0, 49.4, 51.9, 65.3, 127.5, 128.8, 129.5, 132.1, 132.4, 160.0, 168.1, 207.7. HRESIMS calcd for $C_{19}H_{23}O_3S$: 331.1368 $(M+H)^+$, found: 331.1384.

**4.3.3. 1-Methoxycarbonyl-2-oxo-6-trimethylsilyl-7-(methylthio)bicyclo[3.2.0]hept-6-ene (24c).** Pale yellow oil. $[\alpha]_D^{26}$ −383 (73% ee, *c* 0.35, $CHCl_3$). IR (neat) $\nu$ $cm^{-1}$; 1747, 1732. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 0.16 (9H, s), 1.89 (1H, dd, *J*=9.0, 13.5 Hz HH), 2.06–2.13 (1H, m), 2.33 (3H, s), 2.29–2.41 (1H, m), 2.96 (1H, ddd, *J*=9.0, 12.2, 18.2 Hz), 3.54 (1H, d, *J*=6.8 Hz), 3.74 (3H, s). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; −1.7, 13.9, 22.9, 35.1, 49.9, 52.2, 68.5, 149.0, 151.4, 168.4, 210.0. HRESIMS

calcd for $C_{13}H_{20}O_3NaSiS$: 307.0800 $(M+Na)^+$, found: 307.0808.

**4.3.4. 2-(Methoxycarbonyl)-3-(2-chloro-2-phenylthioethenyl)cyclopentan-1-one (4).** To a solution of **3** (60% ee) (135 mg, 0.429 mmol) in $CH_2Cl_2$ (2 mL) was added titanium tetrachloride (53 μL, 0.428 mmol) at 0 °C. After being stirred for 30 min at same temperature, neutral phosphate buffer solution (pH 6.86, 1 mL) was added to the reaction mixture. The resulting mixture was extracted with AcOEt and the organic layer was dried over $MgSO_4$ and consentrated under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt, 5:1) to afford compound 4 (140 mg, 0.45 mmol) in 91% yield. $[\alpha]_D^{28}$ +267 (*c* 0.51, $CHCl_3$). IR (neat) $\nu\,cm^{-1}$; 1760, 1730, 1584. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 1.68–1.79 (1H, m), 2.25–2.23 (3H, m), 3.08 (1H, d, $J=11.3$ Hz), 3.73 (3H, s), 3.88–3.98 (1H, m), 6.15 (1H, d, $J=9.5$ Hz), 7.30–7.39 (5H, m). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 27.5, 37.8, 42.8, 52.6, 60.6, 127.8, 129.2, 129.5, 130.5, 132.1, 139.1, 168.4, 209.3. HRESIMS calcd for $C_{15}H_{15}O_3NaSCl$: 333.0328 $(M+Na)^+$, found: 333.0302.

**4.3.5. 3-(Hydroxycarbonylmethyl)cyclopentan-1-one (25).** The mixture of compound **4** (60 mg, 0.193 mmol) and concentrated HCl (0.1 mL) in MeOH (1 mL) was heated at 60 °C. After being stirred for 12 h at same temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/isopropanol, 1:5) to afford compound **25**[18] (9 mg, 0.063 mmol) in 33% yield. $[\alpha]_D^{28}$ +65.1 (*c* 0.45, $CHCl_3$). IR (neat) $\nu\,cm^{-1}$; 1737. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$; 1.20–1.25 (1H, m), 1.53–1.70 (1H, m), 1.86–1.96 (1H, m), 2.14–2.39 (3H, m), 2.48–2.68 (3H, m). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$; 29.1, 33.1, 38.3, 39.3, 44.5, 177.7, 218.3.

## Acknowledgements

We thank the Uehara Memorial Foundation for financial support.

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