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CATALYTIC ASYMMETRIC INTRAMOLECULAR CYCLOPROPANATION OF α-DIAZO-α-PHOSPHORYL ACETATE

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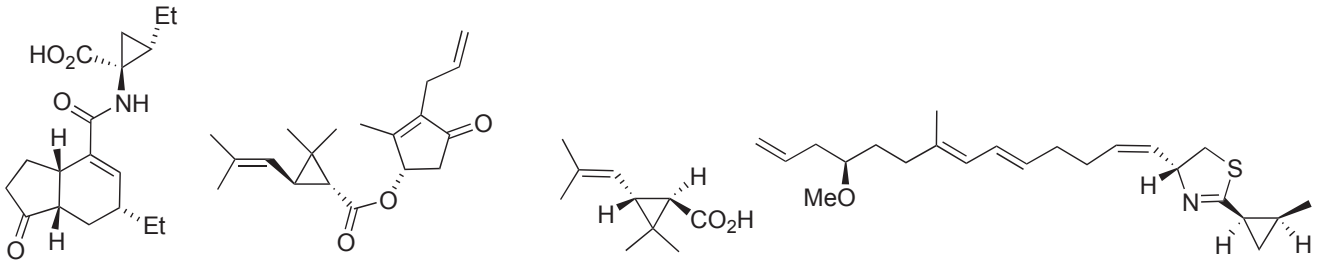
Abstract – The catalytic asymmetric intramolecular cyclopropanation (CAIMCP) of α-diazo-α-diphenylphosphoryl acetate has been investigated. The maximum *ee* of the CAIMCP was 91% and the absolute configuration of the two products was successfully determined. Our previously reported model to explain the enantiofacial selectivity of the reacting alkene was successfully applied to rationalize the enantioselectivity of the CAIMCP.

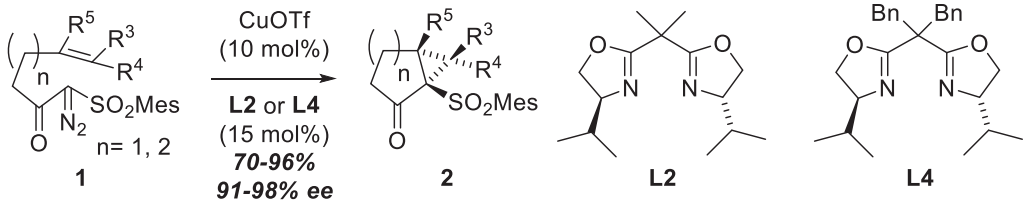
Bioactive compounds incorporating a chiral cyclopropane have been isolated. For example, coronatine, bioallethrin, *trans*-chrysanthemic acid, and curacin A have been reported as a phytotoxin, an ectoparasiticide, an insecticide, and an antimitotic agent, respectively (Figure 1).[1] Cyclopropane is a highly strained molecule and easily undergoes ring-opening reactions, which allow a variety of transformations and bond-forming reactions. Therefore, cyclopropanes have been used as key intermediates in the synthesis of many compounds, indicating that the development of synthesis methods for chiral cyclopropanes is important.



(+)-coronatine *phytotoxin* | bioallethrin *ectoparasiticide* | (+)-*trans*-chrysanthemic acid *insecticide* | (+)-curacin A *antimitotic agent*

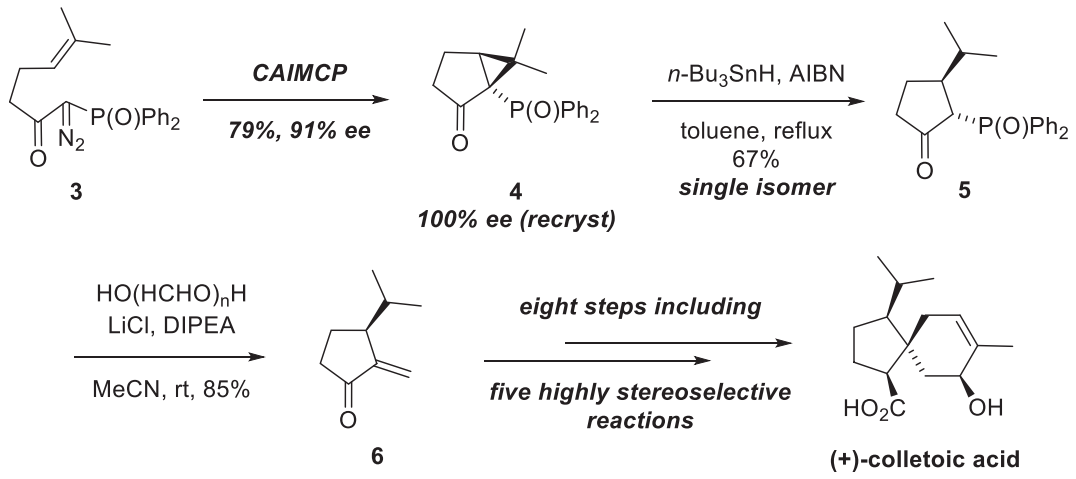
Figure 1. Structures of bioactive natural products including cyclopropane

We have been pursuing the research on the catalytic asymmetric intramolecular cyclopropanation (CAIMCP) and have revealed that a substrate bearing a bulky substituent at the α-position of the diazo group that goes through this reaction affords a product with high enantiomeric excess (*ee*).[2] Indeed, the CAIMCP of α-diazo-β-keto sulfone **1** with Cu(I)-bisoxazoline ligand **L2** or **L4** affords product **2** with excellent yield and enantioselectivity (Scheme 1).[2a-d] This catalytic asymmetric reaction has been widely applied to prepare a variety of chiral cyclopropanes, which have been successfully used as chiral building blocks for the enantioselective total syntheses of bioactive natural products in our laboratory.



Scheme 1. CAIMCP of α-diazo-β-keto sulfone

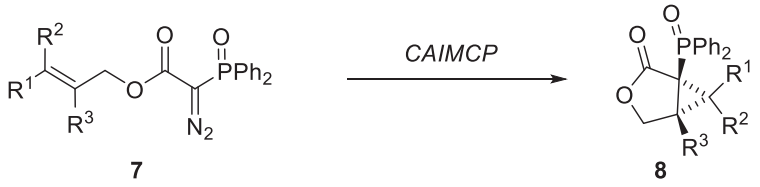
We previously reported the first CAIMCP of α-diazo-β-ketophosphine oxide **3** that proceeded with excellent yield and enantioselectivity (Scheme 2).[2g] Then, the prepared chiral cyclopropane **4** was converted to the corresponding β-ketophosphine oxide **5** by the reductive opening reaction of the cyclopropane, and subsequent transformations involving nine highly stereoselective reactions successfully led to the first total synthesis of (+)-colletoic acid.[2g]



Scheme 2. First total synthesis of (+)-colletoic acid via the CAIMCP of α-diazo-β-ketophosphine oxide **3**

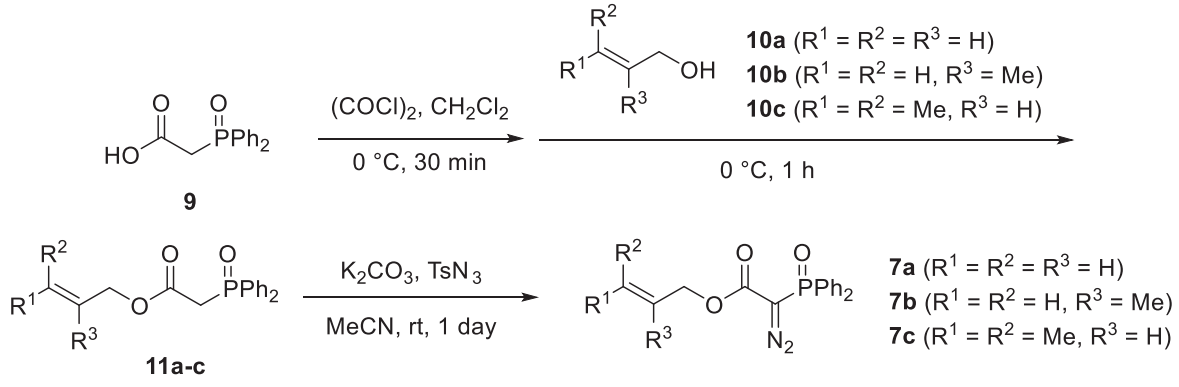
As described above, the CAIMCP of α-diazo-β-ketophosphine oxide **3** features high yield and enantioselectivity, as well as the utility of chiral cyclopropane **4**. The ring-opening reaction of **4** affords

β-ketophosphine oxide **5**, which undergoes Horner-Wittig reaction to afford enone **6** at the more hindered α-position of the carbonyl group. Moreover, phosphine oxides are generally crystalline, and hence, the products could be enantioenriched by recrystallization. However, despite its promising utility, the CAIMCP of α-diazo-β-ketophosphine oxide has been limited to only one reported example, that of ours. Hence, we have studied the CAIMCP of α-diazo-α-diphenylphosphoryl acetate **7** that afford oxabicyclo[3.2.1]hexane derivative **8** (Scheme 3) and herein report the successful results.



Scheme 3. CAIMCP of α-diazo-α-diphenylphosphoryl acetate **7**

Preparation of α-diazo-α-diphenylphosphoryl acetates **7** for the CAIMCP was commenced with the reaction of known carboxylic acid **9**[3] (Scheme 4). Carboxylic acid **9** was converted to the corresponding acid chloride using oxalyl chloride, and subsequent reactions with allylic alcohols **10a-c** afforded the corresponding esters **11a-c**. Finally, α-diazo-α-diphenylphosphoryl acetates **7a-c** were successfully prepared by the diazo-transfer reaction using TsN_3 and K_2CO_3 in acetonitrile.

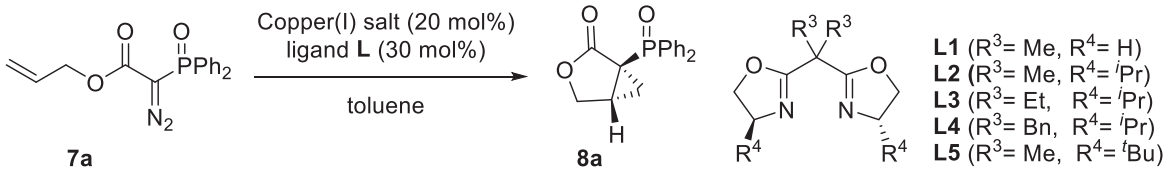


Scheme 4. Preparation of α-diazo-α-diphenylphosphoryl acetates **7a-c**

With α-diazo-α-diphenylphosphoryl acetates **7a-c** in hand, their CAIMCPs were examined. First, the reaction of allyl ester **7a** using CuOTf (10 mol%) and achiral ligand **L1** (15 mol%) was carried out in toluene to prepare the standard sample for HPLC analysis using a chiral column (entry 1, Table 1). The reaction proceeded at 60 °C and afforded the desired product within 4 h, but the yield was low because the reaction was slow owing to the low solubility of the complex formed by and ligand **L1**. Then, the

CAIMCP of **7a** was carried out using CuOTf (10 mol%) and chiral ligand **L2** (15 mol%) (entry 2) to afford the product with 6% *ee* and 63% yield. The *ee* was 10% when the reaction was carried out with CuOTf (10 mol%) and **L3** (15 mol%) (entry 3). The *ee* was improved to 37% by using ligand **L4** (entry 4), but the yield decreased to 34%. The enantioselectivity improved when the R^4 group of the ligand was larger; hence, the next CAIMCP was examined using ligand **L5**, but the *ee* decreased to 17% (entry 5). The yield was low, too, owing to the formation of unidentified products. The effect of the counter anion of Cu(I) was surveyed as well. The reaction using $Cu(MeCN)_4BF_4$ and **L4** increased the yield and the *ee* to 75% and 52%, respectively (entry 6), and the *ee* was further improved to 74% when $Cu(MeCN)_4PF_6$ and **L4** were used (entry 7).

Table 1. CAIMCP of **7a**

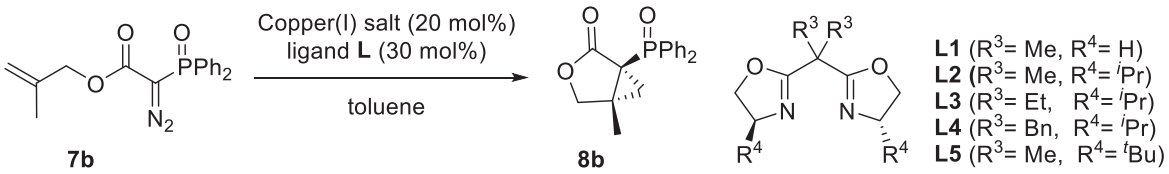


entry	Cu(I) salt	ligand	temp (°C)	time (h)	yield (%)[a]	*ee* (%)[b]
1	$(CuOTf)_2$·PhMe	**L1**	60	4	21	-
2	$(CuOTf)_2$·PhMe	**L2**	60	4	63	6
3	$(CuOTf)_2$·PhMe	**L3**	60	4	53	11
4	$(CuOTf)_2$·PhMe	**L4**	60	4	34	37
5	$(CuOTf)_2$·PhMe	**L5**	90	4	27	17
6	$Cu(MeCN)_4BF_4$	**L4**	80	1	75	52
7	$Cu(MeCN)_4PF_6$	**L4**	60	6	72	74

[a]Isolated yield. [b]*Ee* determined by HPLC. For conditions, see Experimental part.

Next, the CAIMCP of methallyl ester **7b** was examined (Table 2). The reaction of **7b** using 20 mol% of CuOTf and 15 mol% of achiral ligand **L1** afforded **8a** with 90% yield (entry 1). The effect of chiral ligands **L2-5** was surveyed (entries 2-5) and low enantioselectivity was observed in all cases. Interestingly, the reaction using the most bulky ligand **L5** almost afforded the **8a** racemate, though it required heating to 100 °C. Because the use of **L4** produced **8b** with 33% *ee*, the effect of the counter anion of Cu(I) was examined (entries 6 and 7). However, the reaction with $Cu(MeCN)_4BF_4$ decreased the *ee*, while the use of $Cu(MeCN)_4PF_6$ slightly increased it to 37%. The yield was low except for entries 1 and 2, which suggests that the reactions using the relatively bulky ligands **L3-5** suffered from severe steric interaction between the reacting alkene and the ligand.

Table 2. CAIMCP of **7b**

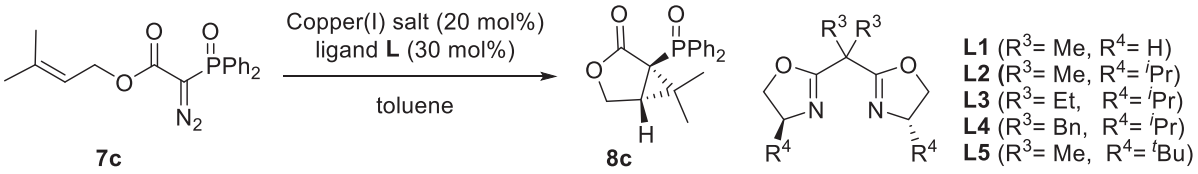


entry	Cu(I) salt	ligand	temp (°C)	time (h)	yield (%)[a]	*ee* (%)[b]
1	$(CuOTf)_2$·PhMe	**L1**	60	2	90	-
2	$(CuOTf)_2$·PhMe	**L2**	60	2	92	25
3	$(CuOTf)_2$·PhMe	**L3**	60	5	11	13
4	$(CuOTf)_2$·PhMe	**L4**	60	48	29	33
5	$(CuOTf)_2$·PhMe	**L5**	100	2	33	3
6	$Cu(MeCN)_4BF_4$	**L4**	80	4	30	21
7	$Cu(MeCN)_4PF_6$	**L4**	80	4	48	37

[a]Isolated yield. [b]*Ee* determined by HPLC. For conditions, see Experimental part.

Finally, the CAIMCP of **7c** was carried out (Table 3). After the preparation of **8c** as a racemic mixture using 20 mol% of CuOTf and 15 mol% of achiral ligand **L1** (entry 1), the CAIMCP of **7c** using **L2-5** was examined (entries 2-5). As a result, the *ee* increased depending on the bulkiness of the R^3 group of the ligand; i.e., when R^3 was changed from methyl to ethyl, the *ee* increased from 56% to 75%, and 89% *ee* was observed when R^3 was a benzyl. The reaction using **L5** afforded **8c** with low *ee* again; hence, the CAIMCPs using **L4** and other Cu(I) salts were examined (entries 6 and 7). Although the reaction with $Cu(MeCN)_4BF_4$ slightly decreased the *ee*, $Cu(MeCN)_4PF_6$ successfully improved the *ee* to 91%.

Table 3. CAIMCP of **7c**

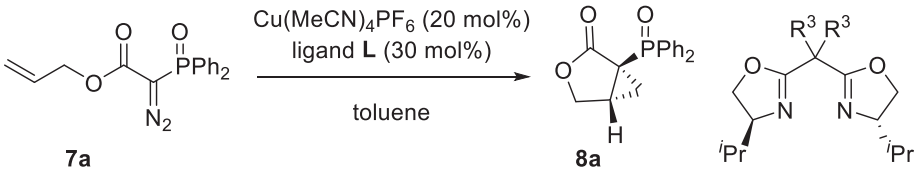


entry	Cu(I) salt	ligand	temp (°C)	time (h)	yield (%)[a]	*ee* (%)[b]
1	$(CuOTf)_2$·PhMe	**L1**	60	2.5	64	-
2	$(CuOTf)_2$·PhMe	**L2**	60	2.5	84	56
3	$(CuOTf)_2$·PhMe	**L3**	60	2.5	90	75
4	$(CuOTf)_2$·PhMe	**L4**	60	2.5	75	89
5	$(CuOTf)_2$·PhMe	**L5**	60	2.5	51	23
6	$Cu(MeCN)_4BF_4$	**L4**	80	1	86	85
7	$Cu(MeCN)_4PF_6$	**L4**	80	1	83	91

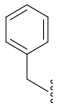
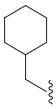
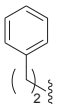
[a]Isolated yield. [b]*Ee* determined by HPLC. For conditions, see Experimental part.

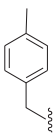
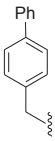
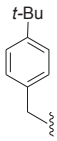
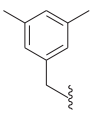
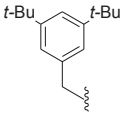
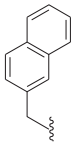
In the case of the CAIMCP of α-diazo-β-keto sulfone **1**, we reported that the enantioselectivity was increased by using the ligand with a large R^3 substituent. In all the CAIMCPs of **7a-c**, the use of the ligand bearing a large R^3 substituent also increased the *ee*. Hence, further studies on the CAIMCP using the ligand with a bulkier R^3 substituent are expected to improve the reaction's enantioselectivity.

Table 4. CAIMCP of **7a** using a variety of ligands



7a **8a**

	L4	**L6**	**L7**	**L8**	**L9**	**L10**
R^3						
temp (°C)	60	60, 80[a]	60	60	60	60
time (h)	6	72, 24[a]	5	24	4	4
yield (%)[b]	72	15	6	24	18	22
ee (%)[c]	74	76	37	32	80	79

	L11	**L12**	**L13**	**L14**	**L15**	**L16**
R^3						
temp (°C)	60	60	60	100	60	60, 80[a]
time (h)	4	4	4	12	7	20, 11[a]
yield (%)[b]	32	11	90	43	37	48
ee (%)[c]	80	76	85	58	50	56

[a]Reaction was carried out at the indicated temperatures for the indicated times, respectively. [b]Isolated yields. [a]*Ee* determined by HPLC. For HPLC conditions, see Experimental part.

Accordingly, the CAIMCP of **7a** was further examined using ligands **L6-16**[2a,4] (Table 4). The CAIMCP using **L6** proceeded sluggishly and product **8a** was obtained with a low yield, but the *ee* was almost

unchanged, suggesting that factors other than the steric interaction, such as π-π interactions, would be negligible to explain the observed enantioselectivity. **L7** and **L8** decreased the *ee*, but all the ligands bearing mono-substituted benzyl groups, **L9-13**, increased it, although the ligands bearing di-substituted benzyl groups, **L14** and **L15**, and the naphthyl group, **L16**, decreased it.

Interestingly, all the yields observed using **L6-16**, except **L13**, were low. These results could be attributed to the increased steric hindrance in the transition states, which was derived from the ligands bearing bulky R^3 substituents. As described above, the *ee* of **8a** was successfully increased to 85% by using **L13**, again indicating that steric tuning of the ligand, especially the substituent at the oxazoline junction, is effective to improve the enantioselectivity of the CAIMCP as observed in the case of the CAIMCP of α-diazo-β-keto sulfone.

Compounds **8a** and **8c** were successfully recrystallized to afford enantiomerically pure compounds, which were suitable for X-ray crystallographic analysis.[5] The crystal structures are shown in Figure 2.

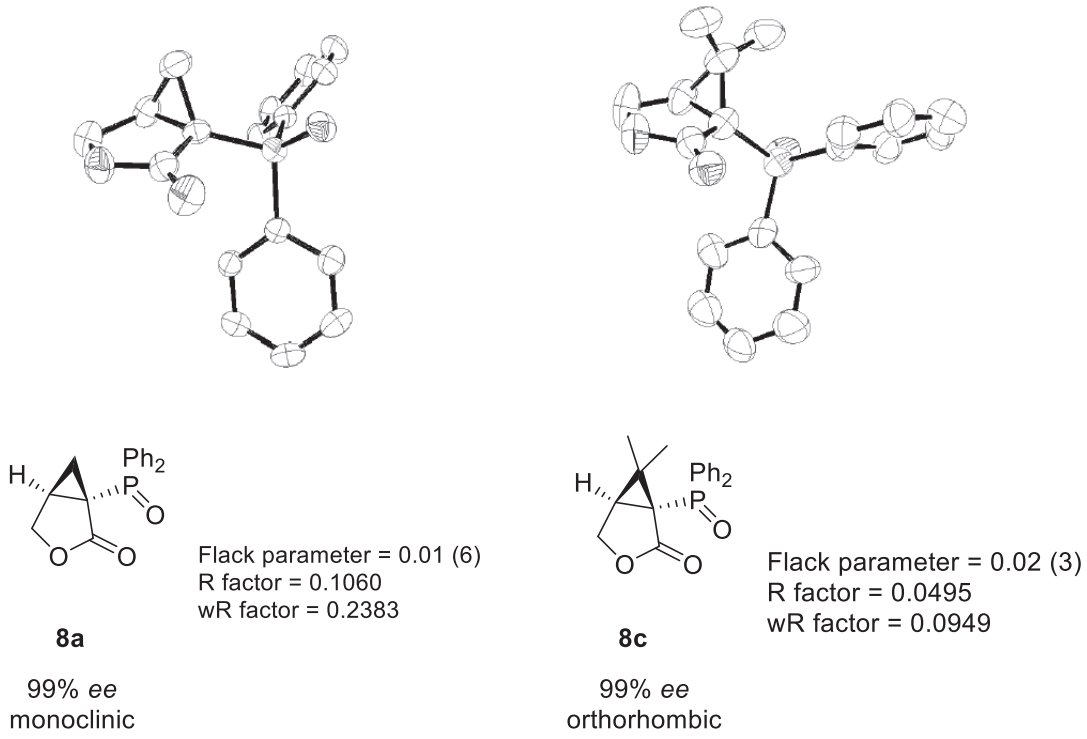


Figure 2. X-Ray crystal structures of **8a** and **8c**

On the basis of the absolute configuration of products **8a** and **8c**, the outcome of the CAIMCPs of **7a** and **7c** could be explained via the *Re*-face attack model in Figure 3, which was previously proposed for the CAIMCPs of α-diazo-β-keto sulfones by us. That is, the CAIMCPs favorably take place at the *Re*-face (defined by the Cu=C−C arrangement) of the chiral catalyst-carbene complexes to circumvent the steric interaction that would be encountered during the reactions at the *Si*-face. That is, if the alkene approaches

from the *Si*-face, the resultant pyramidal conformation of the carbene carbon atom in the transition state causes unfavorable steric interactions between the diphenylphosphoryl group with the isopropyl (repulsion B) of the ligand. As a result, the reaction at the *Si*-face will be unfavorable. In contrast, the reaction at the *Re*-face would be favorable because the steric interaction derived from the diphenylphosphoryl group would be negligible in the transition state and the steric interactions between the isopropyl group and the carbonyl group (repulsion A) are small. As shown in Figure 3, the diphenylphosphoryl group plays a crucial role in the enantioface selectivity.

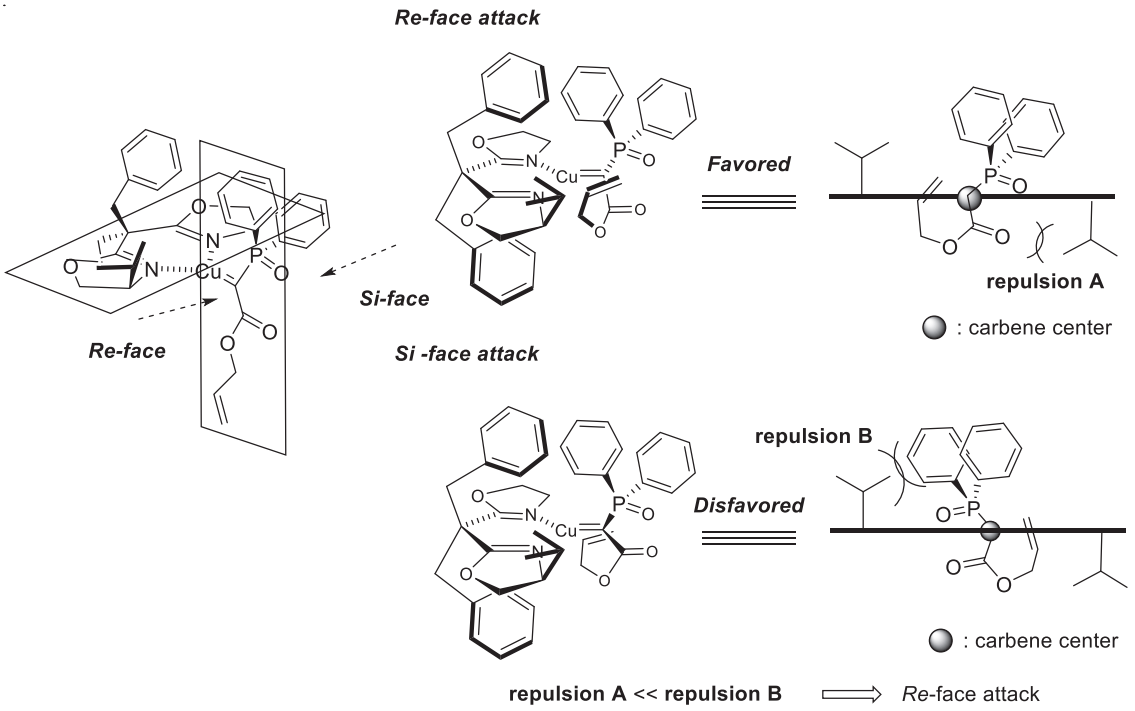


Figure 3. Proposed models for the *Re*- and *Si*-face attacks in the CAIMCP of **7a**

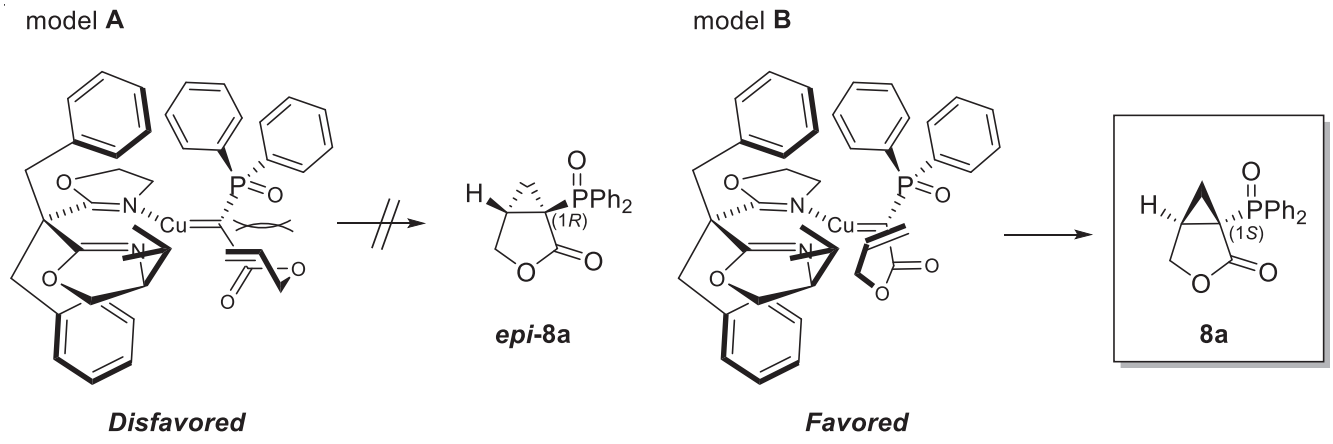


Figure 4. Proposed models **A** and **B** for the preferential formation of **8a**

As we reported earlier, two models of reaction are possible for the *Re*-face attack, as shown in Figure 4. Thus, the reaction via model **A** affords ***epi*-8a**, while the reaction via model **B** affords **8a**. In the reactions of **7a** and **7c**, formation of **8a** and **8c** was observed. Model **A** would be energetically unfavorable because of the steric interactions between the olefin and the diphenylphosphoryl group, which emerges during the reaction. Model **B** would be energetically more favorable owing to less steric interaction. This explanation is well supported by the result of the reaction of **7c** bearing two methyl groups at the terminal position, which afforded **8c** with a higher *ee* when compared with the reaction of **7a**.

In the case of **7b**, the *ee* was lower than that with **7a** and **7c**. Although the quantitative analysis is yet to be supported by theoretical calculation to explain the difference, the results could indicate that the energy level between models **A** and **B** is not as large probably because the methallyl group does not fit both models.

In summary, the CAIMCP of α-diazo-α-diphenylphosphoryl acetate was found to proceed with high yields and enatioselectivities. The maximum *ee* observed was 91% and the absolute configuration of the two products was successfully determined. Our previously reported model was successfully used to explain the enantiofacial selectivity of the reacting alkene. Because the products can be converted to the corresponding β-oxo diphenylphosphine oxides, which undergo Horner-Wittig reactions, the unique and highly enantioselective CAIMCP of α-diazo-α-diphenylphosphoryl acetate would be a promising method for natural product synthesis; hence, further studies on the CAIMCP of α-diazo-α-diphenylphosphoryl acetate, as well as its applications, are underway.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer or a JEOL ECZ500R spectrometer. Chemical shifts are reported in ppm with the residual solvent resonance as internal standard ($CDCl_3$ 1H, δ = 7.26 ppm, 13C, δ = 77.16 ppm). The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; sep, septet; br, broad. IR spectra were recorded on a JASCO FT/IR-8300. Optical rotations were measured using a 2 mL cell with a 1 dm path length on a JASCO DIP-1000. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Melting point (mp) is uncorrected, recorded on a Yamato capillary melting point apparatus. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970 detector. Chiral gas chromatography analysis was performed on capillary column RT-γ-DEXsm, SUPELCO, 30 m × 0.25 mm × 0.25 μm at 150 °C constant, pressure: 138 kPa, column flow amount: 2.50 mL/min, line speed: 53.9 *m/s*, ratio of sprit: 40.0, total flow amount: 106 mL/min, SPRIT, and career gas was He. All reactions were monitored by

thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Kanto Chemical Silica Gel 60N (spherical, neutral, 63-210 μm or 40-50 μm partial size) was used for flash chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254). TLC Rfs of purified compounds were included. THF and Et_2O were distilled from sodium/benzophenone ketyl, and CH_2Cl_2, benzene, and hexane from calcium hydride. DMF and DMSO were distilled from calcium hydride under reduced pressure. Toluene and EtOH were distilled from sodium. MeOH was distilled from magnesium and I_2. All reagents were purchased from Aldrich, TCI, Merck, or Kanto Chemical Co., Ltd.

Allyl 2-diazo-2-diphenylphosphorylacetate (7a). General Procedure for the preparation of α-diazo α-diphenylphosphoryl acetate: ***Procedure A.*** To a stirred solution of 2-diphenylphosphorylacetic acid **9**[3] (1.13 g, 4.34 mmol) in CH_2Cl_2 (43.4 mL) at 0 °C was added oxalyl chloride (0.44 mL, 5.20 mmol). After 30 min, allyl alcohol **10a** (0.52 mL, 5.20 mmol) was added at 0 °C and the resultant mixture was stirred for 1 h. The mixture was quenched with aqueous $NaHCO_3$ solution (5 mL), extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and evaporated. The residue was roughly purified by short silica gel column chromatography to afford allyl 2-diphenylphosphorylacetate **11a**, which was used for the next reaction without further purification.

To a stirred solution of the crude **11a** in MeCN (12.1 mL) was added K_2CO_3 (1.2 g, 8.76 mmol) at room temperature, and then a solution of *p*-toluenesulfonyl azide (1.33 g, 8.76 mmol) in MeCN (5 mL × 2) via a cannula. The reaction mixture was stirred at room temperature for 1 day. The light yellow reaction mixture was quenched with 3M KOH aqueous solution (20 mL), extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography (hexane/EtOAc = 1/1) to afford **7a** (888 mg, 63%) as a yellow solid: R_f = 0.74 (hexane/EtOAc = 1/1); mp 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.82 (4H, m), 7.62-7.58 (2H, m), 7.50 (4H, m), 5.79-5.69 (1H, ddt, *J* = 17.1, 10.7, 5.6 Hz), 5.17 (1H, d, *J* = 17.1 Hz), 5.16 (1H, d, *J* = 10.7 Hz), 4.57 (2H, d, *J* = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 12.1 Hz), 132.8 (d, *J* = 2.4 Hz), 131.9 (d, *J* = 10.9 Hz), 131.39, 130.0 (d, *J* = 102.6 Hz), 128.7 (d, *J* = 13.3 Hz), 118.9, 66.1; IR(ATR) ν_{max} 2115, 1697, 1438, 1362, 1270, 1202, 1120, 939, 742, 725, 701, 573, 562, 551 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd for $C_{17}H_{15}N_2O_3NaP$: 349.0718, found: 349.0712.

(1*S*,5*R*)-1-Diphenylphosphoryl-3-oxabicyclo[3.1.0]hexan-2-one (8a). General Procedure for the catalytic asymmetric intramolecular cyclopropanation of α-diazo-α-diphenylphosphoryl acetate: ***Procedure B.*** Tetrakis(acetonitrile)copper(I)hexafluorophosphate (6.1 mg, 0.0165 mmol) and ligand **L13** (13.1 mg, 0.0247 mmol) was placed in a dried flask (8.2 mL) under Ar atmosphere and the mixture was stirred at room temperature for 1 h. To the light green solution, **7a** (26.9 mg, 0.0824 mmol) in toluene

(0.5 mL × 3) was added via a cannula. The reaction mixture was stirred at 60 °C for 4 h, then cooled to room temperature, quenched with aqueous NH_4OH solution (5 mL), and extracted with EtOAc (2 mL × 3). The combined organic layer was washed with brine (5 mL), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography (EtOAc) to afford **8a** (22.0 mg, 90%, 85% *ee*) as a white solid. R_f = 0.11 (benzene/EtOAc = 1/1). Recrystallization (hexane/CH_2Cl_2) afforded **8a** with >99% *ee*. *Ee* was determined by HPLC (254 nm); Daicel Chiral Cell IA-3 0.46 cm φ × 25 cm; hexane/isopropanol = 2/1; flow rate = 0.5 mL/min); retention time: 12.5 min for ***ent*-8a**, 15.0 min for **8a**; R_f = 0.20 (benzene/EtOAc = 1/1); mp 159-161 °C; $[\alpha]_D^{23}$ –52.4 (c 0.38, $CHCl_3$, >99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.99 (2H, m), 7.82-7.72 (2H, m), 7.63-7.46 (6H, m), 4.33 (2H, m), 2.99 (1H, m), 2.11 (1H, m), 1.44 (1H, m); ^{13}CNMR (100 MHz, $CDCl_3$) δ 172.9 (d, *J* = 10.9 Hz), 132.7, 132.6, 132.1 (d, *J* = 10.9 Hz), 131.7 (d, *J* = 10.9 Hz,), 131.3 (d, *J* = 64.0 Hz), 130.4 (d, *J* = 64.0 Hz), 128.8 (d, *J* = 12.1 Hz), 128.7 (d, *J* = 12.1 Hz), 68.0, 26.7 (d, *J* = 102.6 Hz), 24.7, 17.5; IR(ATR) ν_{max} 1765, 1437, 1189, 1122, 1051, 993, 703, 540, 530 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd for $C_{17}H_{15}O_3NaP$: 321.0657, found: 321.0650.

2-Diazo-2-methylallyl 2-diphenylphosphorylacetate (7b). 7b was prepared from **9** according to ***Procedure A*** and was purified by flash chromatography (hexane/EtOAc = 1/1) to afford **7b** (67%) as a yellow solid; R_f = 0.7 (hexane/EtOAc = 1/1); mp 64-66 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.92-7.73 (4H, m), 7.54-7.48 (6H, m), 4.83 (1H, s), 4.79 (1H, s), 4.50 (2H, s), 1.57 (3H, s); ^{13}CNMR (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 12.1 Hz), 132.7 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 10.9 Hz), 131.3, 129.7 (d, *J* = 73.2 Hz), 128.7 (d, *J* = 13.3 Hz), 113.6, 68.8, 19.2; IR(ATR) ν_{max} 3062, 2117, 1699, 1659, 1438, 1271, 1200, 1161, 1120, 741, 725, 701, 574, 561 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd for $C_{18}H_{17}O_3N_2NaP$: 363.0874, found: 363.0867.

(1*S*,5*R*)-1-Diphenylphosphoryl-5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (8b). 8b was prepared from **7b** according to ***Procedure B*** and was purified by flash chromatography (EtOAc) to afford **8b** (16.5 mg, 57%, 37% *ee*) as a white solid.; *Ee* was determined by HPLC (254 nm); Daicel Chiral Cell IA-3 0.46 cm φ × 25 cm; hexane/2-propanol = 2/1; flow rate = 0.5 mL/min); retention time: 12.5 min for ***ent*-8b**, 14.9 min for **8b**; R_f = 0.19 (benzene/EtOAc = 1/1); mp 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.75 (4H, m), 7.61-7.48 (6H, m), 4.28 (1H, d, *J* = 9.8 Hz), 4.04 (1H, d, *J* = 9.8 Hz), 1.68 (3H, s), 1.52 (1H, d, *J* = 4.1 Hz), 1.51 (1H, d, *J* = 4.1 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 173.7 (d, *J* = 10.9 Hz), 132.5, 132.4 (d, *J* = 2.4 Hz), 132.0 (d, *J* = 10.9 Hz), 131.8, 131.7 (d, *J* = 10.9 Hz), 131.0, 128.8 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 13.3 Hz), 72.4, 34.8, 28.5 (d, *J* = 102.0 Hz), 23.1, 14.6; IR(ATR) ν_{max} 1761, 1437, 1305, 1210, 1193, 1122, 1068, 794, 727, 704, 694, 605, 538 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd for $C_{18}H_{17}NaO_3P$: 335.0813, found: 335.0803.

2-Diazo-3-methylbut-2-enyl 2-diphenylphosphorylacetate (7c). 7c was prepared from **9** according to ***Procedure A*** and was puried by flash chromatography (hexane/EtOAc = 1/1) to afford **7c** (686 mg, 32%)

as a yellow solid; R_f = 0.41 (hexane/EtOAc = 1/1); mp 65-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (4H, m), 7.62-7.46 (6H, m), 5.13 (1H, t, *J* = 7.1 Hz), 4.57 (2H, d, *J*= 7.1 Hz), 1.70 (3H, s), 1.59 (3H, s); ^{13}CNMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 12.1 Hz), 134.2 (d, *J* = 2.4 Hz), 131.0 (d, *J* = 10.5 Hz), 130.7, 129.9 (d, *J* = 102.5 Hz), 128.8 (d, *J* = 13.3 Hz), 118.6, 68.7, 24.6, 19.1; IR(ATR) ν_{max} 2972, 2103, 1684, 1386, 1342, 1233, 1172, 995, 739 cm^{-1}. HRMS (ESI) $[M+Na]^+$ calcd for $C_{19}H_{19}N_2O_3P$: 354.1133, found: 354.1126.

(1*R*,5*R*)-1-Diphenylphosphoryl-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (8c). 8c was prepared from **7c** according to ***Procedure B*** and was purified by flash chromatography (EtOAc) to afford **8c** (25.2 mg, 83%, 91% *ee*) as a white solid. **8c** was recrystallized with hexane and CH_2Cl_2 (99% *ee*); R_f = 0.19 (benzene/EtOAc = 1/1); mp 166-168 °C; *Ee* was determined by HPLC (254 nm); Daicel Chiral Cell IA-3 0.46 cm φ × 25 cm; hexane/2-propanol = 4/1; flow rate = 0.5 mL/min); retention time: 18.0 min for ***ent*-8c**, 24.4 min for **8c**; $[\alpha]_D^{23}$ –155 (*c* 0.64, $CHCl_3$, 99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.07 (2H, m), 7.65-7.35 (8H, m), 4.43 (1H, dd, *J* = 10.0, 5.5 Hz), 4.25 (1H, d, *J* = 10.0 Hz), 3.01 (1H, dd, *J* = 10.0, 5.5 Hz), 1.36 (3H, s), 1.30 (3H, s); ^{13}CNMR (100 MHz, $CDCl_3$) δ 172.4 (d, *J* = 10.9 Hz), 133.1, 132.2, 131.9, 131.6 (d, *J* = 10.9 Hz,), 131.3 (d, *J* = 10.9 Hz), 130.2, 128.5 (d, *J* = 13.3 Hz), 128.2 (d, *J* = 12.1 Hz), 65.52, 37.37 (d, *J* = 97.8 Hz), 34.87, 31.27, 20.7, 16.90; IR(ATR) ν_{max} 1754, 1460, 1437, 1250, 1178, 1120, 1101, 988, 725, 702, 694 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd for $C_{19}H_{19}O_3NaP$: 349.0970, found: 349.0963.

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5. CCDC 1528227 (**8a**) and CCDC 1528228 (**8c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.