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Asymmetric Catalysis of Intramolecular Cyclopropanation of 5-Aryl-1-diazo-1-mesitylsulfonyl-5-hexen-2-ones

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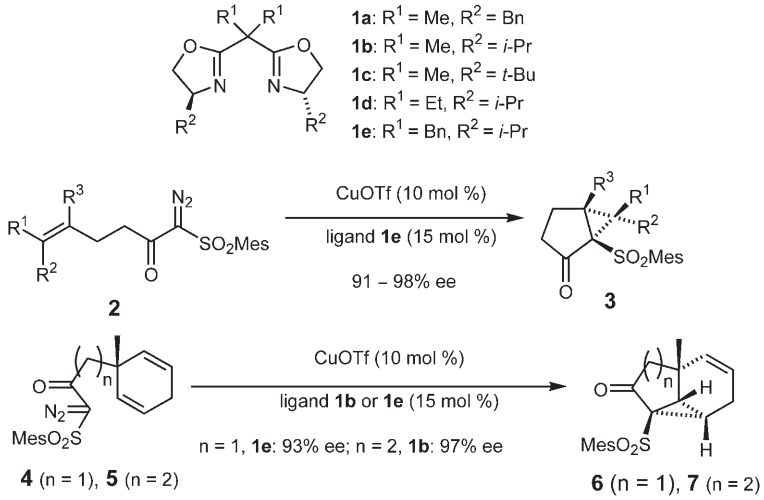
Abstract: We have examined the catalytic asymmetric intramolecular cyclopropanation (IMCP) reactions of 5-aryl-1-diazo-1-mesitylsulfonyl-5-hexen-2-ones, and found that the substituent of the 5-aryl group dramatically changes the enantioselectivity. That is, no enantioselectivity was observed when the substituent was a methoxy group; however, enantioselectivity was moderate when the substituent was a methylenedioxy group or a *tert*-butyldimethylsilyloxy group, and it dramatically increased when the substituent was lacking (96% ee) or a benzoyloxy group (93% ee).

Keywords: asymmetric catalysis; cyclization; cyclopropanes; diazo compounds; enantioselectivity

Since the pioneering work of Nozaki et al.,[1] asymmetric catalysis in cyclopropanations using diazo compounds has been extensively studied,[2] and many catalytic asymmetric intramolecular cyclopropanation (IMCP) reactions of α-diazo ketones, α-diazoacetates, and α-diazoacetamidates have been reported.[2,3]

We have reported the highly enantioselective catalytic asymmetric IMCP reactions of α-diazo-β-keto sulfones (Scheme 1).[4] In these reactions, **2**, **4**, and **5** are transformed to **3**, **6**, and **7**, respectively, with ees ranging from 91 to 98%. Since these products are highly crystalline and easily purified by a single recrystallization, this catalytic asymmetric IMCP reaction is useful to prepare new chiral building blocks for the efficient total synthesis of natural products. Actually, we have succeeded in the first asymmetric total synthesis of (−)-allocyathin B_2 using the new chiral building block prepared by this IMCP reaction,[5] proving the usefulness of this asymmetric catalysis.

Some natural products possess a stereogenic quaternary carbon at the benzylic position. For example, a *Sceletium* alkaloid, (−)-mesembrine (Figure 1),[6] has a stereogenic quaternary carbon bearing a 3,4-dimethoxyphenyl group. This interesting stereostructure has



Scheme 1. Catalytic asymmetric IMCP reaction of **2**, **4**, and **5**.

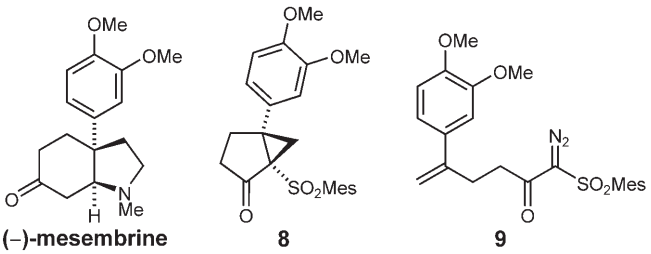


Figure 1. Structure of (−)-mesembrine, a proposed key intermediate **8**, and its precursor **9**.

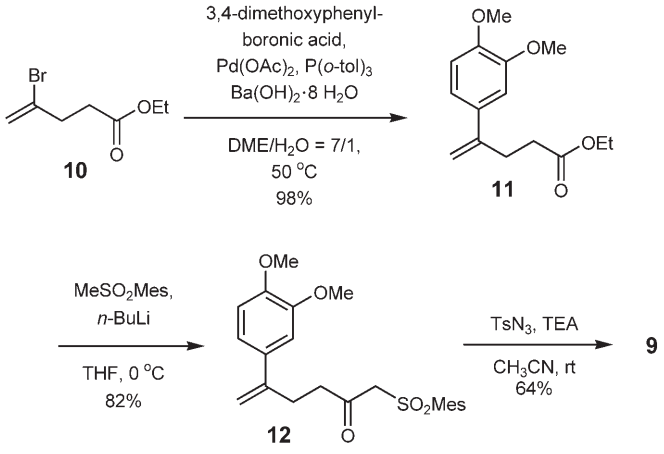
made (−)-mesembrine an attractive synthetic target, and a number of studies has been carried out.[7–9,10]

We envisaged that cyclopropane **3** ($R^1 = R^2 = H$; $R^3 =$ Ar) would be a potential chiral building block for a new synthesis of the compound possessing a stereogenic quaternary carbon at its benzylic position. For instance, cyclopropane **8** could be a key intermediate for the synthesis of (−)-mesembrine, because the cyclopropane ring could open to afford the product with a stereogenic quaternary carbon at the benzylic position. Hence, we started to examine the catalytic asymmetric IMCP reaction of α-diazo-β-keto sulfone **9** (Figure 1).

The preparation of **9** is shown in Scheme 2. A Suzuki–Miyaura coupling reaction of 3,4-dimethoxyphenylboronic acid[11] with ethyl 4-bromo-4-pentenoate **10**[4a] cleanly afforded **11** in a 98% yield. Reaction of the dianion of mesityl methyl sulfone with **11** produced **12**, and the subsequent treatment with *p*-toluenesulfonyl azide furnished α-diazo-β-keto sulfone **9**.

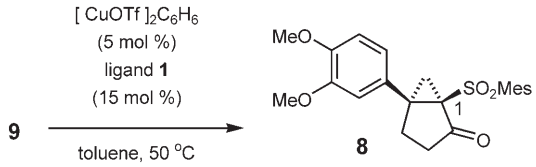
The IMCP reaction of **9** was examined using ligands **1b**, **1d**, and **1e** under the same conditions as employed in Scheme 1; however, only a racemic product was obtained in all the cases as shown in Table 1.

An interesting preliminary observation was that there was no enantioselectivity in this IMCP reaction. Therefore, next we examined the IMCP reaction of a simplified substrate **13** to compare the difference of enantioselectivity. α-Diazo-β-keto sulfone **13** was successfully prepared according to the same procedure as for **9** using phenylboronic acid instead of 3,4-dimethoxyphenylboronic acid.



Scheme 2. Preparation of **9**.

Table 1. Catalytic asymmetric IMCP reactions of **9**.



Entry	Ligand	Time [h]	Yield[a] [%]	ee[b] [%]
1	**1b**	1.5	44	0
2	**1d**	0.5	86	0
3	**1e**	12	55	0

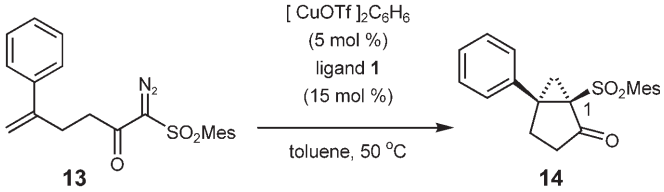
[a] Yields of isolated products.
[b] ee determined by HPLC. For HPLC conditions, see Supporting Information.

As shown in Table 2, the IMCP reaction of **13** with ligands **1a**–**e** under the same conditions as for **9** generated the corresponding product **14** with moderate to high ee, and ligand **1e** was found to be the most effective to afford the maximum enantioselectivity (Table 2, entry 5, 96% ee).

An X-ray crystallographic analysis of **14** proved that the absolute configuration of **14** is 1*R* as shown in Figure 2.[12] This result is well explained by the proposed model[4a] which rationalized the outcome of enantioselectivity of the IMCP reaction.

The IMCP reactions of **13** clearly indicated that the unusual lack of enantioselectivity in the reactions of **9** arose from the two methoxy substituents on the 5-phenyl group. Hence, we decided to investigate the IMCP reactions of substrates with different protections of the two hydroxy groups.

Table 2. Catalytic asymmetric IMCP reactions of **13**.



Entry	Ligand	Time [h]	Yield[a] [%]	ee[b] [%]
1	**1a**	1.0	quant	71 (1*R*)
2	**1b**	1.5	quant	82 (1*R*)
3	**1c**	8.5	61	68 (1*R*)
4	**1d**	7.0	quant	87 (1*R*)
5	**1e**	2.5	95	96 (1*R*)

[a] Yields of isolated products.
[b] ee determined by HPLC. For HPLC conditions, see Supporting Information.

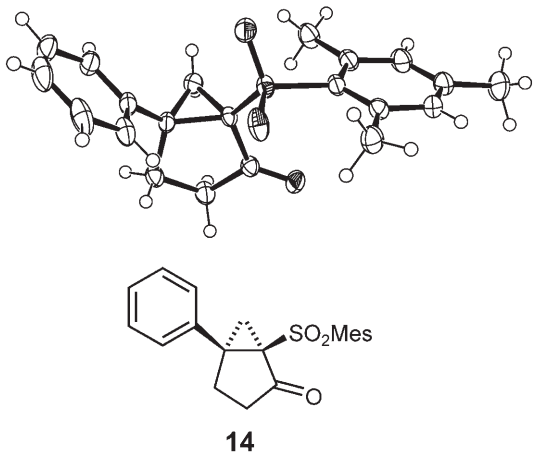
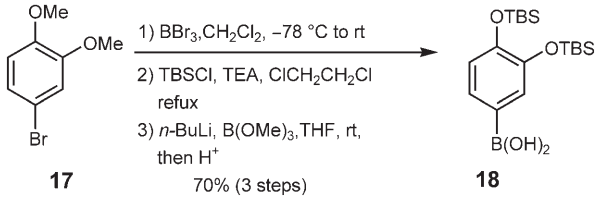


Figure 2. X-ray crystal structure of **14**.[12]

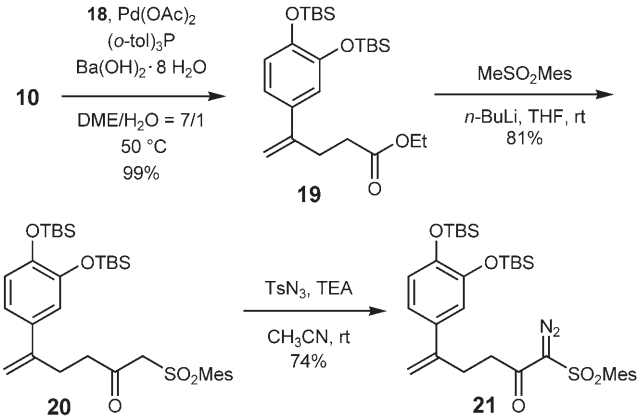
Since we surmised that the two methoxy groups had worked as a bidentate ligand coordinating with CuOTf and liberated the chiral bisoxazoline ligand to result in the lack of enantioselectivity, then we examined the α-diazo-β-keto sulfone **15** possessing a methylenedioxy group instead of the two methoxy groups. Substrate **15** was successfully prepared according to the same procedure as for **9** using 3,4-methylenedioxyphenylboronic acid, again.[13]

The results of the IMCP reactions of **15** are shown in Table 3, indicating the enantioselectivities are lower than those of **13** but are moderate except for entry 1. That is, the change of the protective group for the two hydroxy groups was found to affect the enantioselectivity.

The IMCP reaction of **21** was next examined because the hydroxy groups of **21** are protected with bulky and electron-donating TBS groups that were surmised to prevent coordination of the hydroxy oxygen with CuOTf.



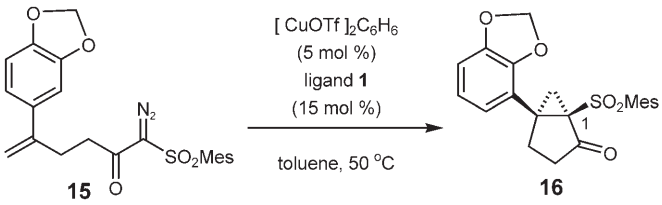
Scheme 3. Preparation of **18**.



Scheme 4. Preparation of **21**.

The new boronic acid **18** was prepared from **17** (Scheme 3), and the synthesis of **21** is shown in Scheme 4. That is, **17** was demethylated with BBr_3, and the resulting alcohol was protected with TBS groups, followed by a halogen-lithium exchange reaction, and the subsequent reaction with $B(OMe)_3$ afforded **18** in 70% overall yield. Substrate **21** was prepared according to the same procedure as for **11** starting from **10** and **18**.

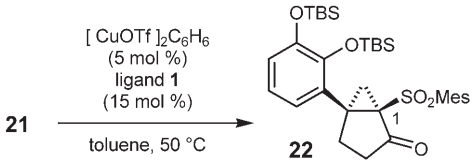
Table 3. Catalytic asymmetric IMCP reaction of **15**.



Entry	Ligand	Time [h]	Yield[a] [%]	ee[b] [%]
1	**1a**	1.0	73	0
2	**1b**	2.0	79	38
3	**1c**	1.0	77	20
4	**1d**	2.0	83	67
5	**1e**	5.0	86	55

[a] Yields of isolated products.
[b] ee determined by HPLC. For HPLC conditions, see Supporting Information.

Table 4. Catalytic asymmetric IMCP reaction of **21**.



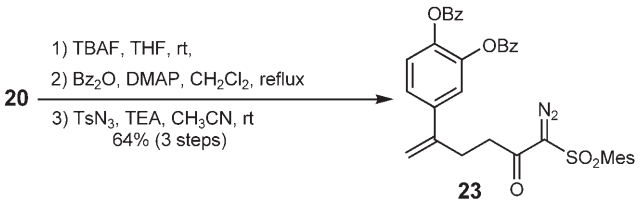
Entry	Ligand	Time [h]	Yield[a] [%]	ee[b] [%]
1	**1a**	0.5	66	9
2	**1b**	0.5	80	30
3	**1c**	1.0, 3.0[c]	61	51
4	**1d**	1.0	73	64
5	**1e**	0.5	77	55

[a] Yields of isolated products.
[b] ee determined by HPLC. For HPLC conditions, see Supporting Information.
[c] Reaction was carried out at 50 °C for 1.0 h and 70 °C for 3.0 h, respectively.

As shown in Table 4, the IMCP reactions of **21** gave almost the same results as those obtained in the reactions of **15**, implying that a factor other than the coordination would decrease the enantioselectivity in the reactions of **15** and **21**.

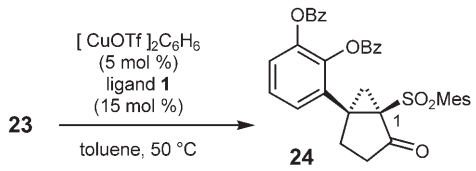
Since all the protective groups examined so far, methyl groups, a methylenedioxy group, and TBS groups, were electron-donating groups, the IMCP reaction of **23** possessing electron-withdrawing benzoyl groups as the protective groups was next examined. As shown in Scheme 5, preparation of **23** started from **22**; thus, removal of the TBS groups of **20** with TBAF, benzoylation of the resultant 1,2-diol, and introduction of the diazo group generated **23**.

The IMCP reactions of **23** with ligands **1a**–**e** afforded **24** with moderate to excellent enantioselectivity, as shown in Table 5, and the highest ee (93% ee) was gratifyingly achieved by ligand **1e** (Table 5, entry 5). The obtained **24** was surmised to have the 1*R* configuration, which was proposed by our model,[4a] but unfortunately the absolute configuration has not been determined because the obtained crystal was not suitable for X-ray crystallographic analysis; hence, we are now trying to prepare another crystalline derivative to determine the absolute configuration.



Scheme 5. Preparation of **23**.

Table 5. Catalytic asymmetric IMCP reaction of **23**.



Entry	Ligand	Time [h]	Yield[a] [%]	ee[b] [%]
1	**1a**	2.5	74	36
2	**1b**	1.0	75	69
3	**1c**	2.0, 1.5[c]	56	54
4	**1d**	1.0	55	80
5	**1e**	1.5	96	93

[a] Yields of isolated products.
[b] ee determined by HPLC. For HPLC conditions, see Supporting Information.
[c] Reaction was carried out at 50 °C for 2.0 h and 70 °C for 1.5 h, respectively.

The IMCP reactions of **9**, **13**, **15**, **21**, and **23** revealed that the protective groups of the two hydroxy groups on the phenyl group are crucial for the enantioselectivity. There is no evidence that the two methoxy groups acted as a bidentate ligand coordinating with CuOTf; however, as mentioned above, comparison of the obtained results cannot rule out that the lack of enantioselectivity of the IMCP reaction of **11** arose from the coordination of the substrate with CuOTf at the oxygen atom attaching to the phenyl group, because the difference of the data between **9** and **15** cannot be explained by only the electronic factors of the substituents.

Although there is no evidence, the low ee may be alternatively attributed to the ylide intermediate formed between the carbene and the oxygen atom attaching to the phenyl group; that is, the ylide thus formed may dissociate from the metal, reacting with the alkene intramolecularly to result in the low enantioselectivity.[14]

The results in Table 5 strongly suggest that the benzoyl groups affected the enantioselectivity of the IMCP reaction of **23**, disclosing that electron-withdrawing protective groups for the hydroxy groups on the 5-phenyl group of 5-aryl-1-diazo-1-mesitylsulfonyl-5-hexen-2-ones would give high ee in the IMCP reactions. At the same time, the results in Table 5 contrasted with the results in Table s1, 3, and 4, suggesting electron-donating protective groups for the hydroxy groups on the 5-phenyl group would give low ee in the IMCP reactions.

In the intermolecular cyclopropanation reaction of the substituted styrene with a diazoacetate[3 l, m] or its derivative, the substituent effect on the enantioselectivity has been reported;[14] that is, the ee decreases when the substituent on the phenyl group is an electron-donating methoxy group in place of an electron-withdrawing halogen. To the best of our knowledge, however, the result described above is a first example of the substituent effect arising from the nature of the protecting group for the hydroxy group on the phenyl group.

The reason for the lack of enantioselectivity in the reaction of **11** and the moderate selectivity in the reactions of **15** and **20** cannot be explained precisely at this time; however, a certain interaction between the substrate possessing the electron-donating protective group and the asymmetric catalyst could occur, resulting in the low the enantioselectivity.

In summary, examination of the catalytic asymmetric IMCP reactions of 5-aryl-1-diazo-1-mesitylsulfonyl-5-hexen-2-ones revealed that the substituent of the 5-aryl group dramatically changes the enantioselectivity. That is, no enantioselectivity was observed when the substituent was a methoxy group; however, enantioselectivity was moderate when the substituent was a methylenedioxy group or a *tert*-butyldimethylsilyloxy group, and it dramatically increased to 96 or 93% ee when the substituent was lacking or a benzoyloxy group, respectively. Although the rationale of this substituent effect arising from the nature of the protective group is now

under investigation, the findings of the substituent effect made in this study inform us that the enantioselectivity in the cyclopropanation of the styrene type substrates could be changed by the protective group for the hydroxy group on the phenyl group. The chiral building blocks prepared through this study are now being converted to natural products, and the related synthetic studies will be reported in due course.

Experimental Section

(1*R*,5*R*)-2-Oxo-5-phenyl-1-(2,4,6-trimethylphenylsulfonyl)bicyclo[3.1.0]hexane (14)

$[CuOTf]_2 \cdot C_6H_6$ (1.2 mg, 0.00238 mmol, 10 mol % as CuOTf) was placed in a dried flask (10 mL) under an argon atmosphere and to this flask was added a solution of ligand **1e** (1.9 mg, 0.00714 mmol, 15 mol %) in toluene (0.5 mL × 2) via a cannula. The mixture was stirred at room temperature for 0.5 h and then to the light blue solution was added a solution of **13** (18.2 mg, 0.0476 mmol) in toluene (0.5 mL × 2) via a cannula. The reaction mixture was stirred at room temperature for 2.5 h, quenched with NH_4OH aqueous solution (2 mL), extracted with ether (5 mL) and CH_2Cl_2 (5 mL × 2). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and evaporated. The residue was purified by preparative TLC (benzene/ethyl acetate = 10/1) to afford **14** as a white solid; yield: 16.0 mg (96% ee, 95%). The absolute configuration was determined by X-ray crystallographic analysis of the recrystallized **14**. The ee was determined by HPLC [(254 nm, Daicel Chiral Cell AS-H 0.46 cm ϕ × 25 cm; hexane/2-propanol = 3/1; flow rate = 0.5 mL/min); retention time: 18.0 min for *ent*-**14**, 25.0 min for **14**; $R_f = 0.48$ (hexane/ethyl acetate = 2/1)]; mp 162–163 °C (hexane/CH_2Cl_2); $[\alpha]_D^{19}$: −181 (*c* 0.45, $CHCl_3$, 100% ee); IR (KBr): ν = 2984, 1728, 1604, 1450, 1316, 1300, 1266, 1204, 1146, 1058, 1034, 764, 698, 668, 608, 516 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 7.1, 7.8 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 6.94 (s, 2H), 3.05 (d, 5.4 Hz, 1H), 2.65 (s, 6H), 2.70–2.20 (m, 4H), 2.08 (d, *J* = 5.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 203.9, 142.9, 140.6, 136.4, 135.2, 132.0, 129.7, 128.3, 59.4, 48.2, 34.1, 30.5, 26.8, 23.5, 21.1; HR-MS (FAB): *m/z* = 355.1339; calcd. for $C_{21}H_{22}O_3SH^+$: 355.1368.

Acknowledgements

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