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DIASTEREOSELECTIVE NUCLEOPHILIC CYCLOPROPANATION OF 1,2-DIKETONES AND α-KETOIMINES WITH BIS(IODOZINCIO)METHANE

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This paper is dedicated to Professor Dr. Ryoji Noyori as we celebrate his 70th birthday.

Abstract – A reaction of 1,2-diketones and α-ketoimines with bis(iodozincio)methane gave cyclopropan-1,2-diol and 2-aminocyclopropanol respectively via nucleophilic [2+1]cycloaddition. The reaction proceeded via a sequential nucleophilic attack of the dizinc reagent to vicinal two carbonyl group. The reaction showed high diastereoselectivity to give *cis*-isomer via a face-to-face coordination between the substrate and bis(iodozincio)methane.

INTRODUCTION

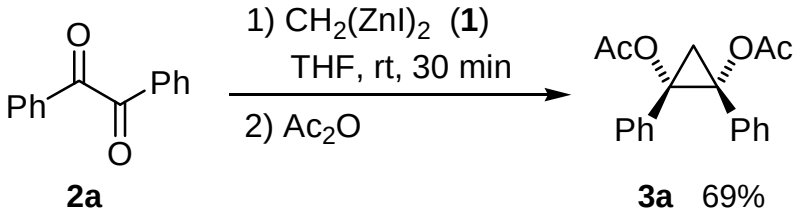
Cyclopropane-skeletons have been found in many natural products, and also used as versatile synthetic intermediates.[1] The most famous cyclopropanation is Simmons-Smith reaction: Zinc carbenoid reacts with alkenes electrophilically to give a three-membered ring.[2] The zinc carbenoid can be prepared easily from diiodomethane and zinc-copper couple in diethyl ether. Meanwhile, when diiodomethane was treated with zinc in the presence of catalytic amount of lead in THF, the Simmons-Smith reagent is not obtained. In this condition, the further reduction of the reagent proceeds to give bis(iodozincio)methane (**1**).[3] This dizinc reagent, which possess a couple of zinc atoms on a carbon, works as a dianion equivalent.[4,5] The reagent has an ability to form a couple of C-C bond on the same carbon, so treatment of this reagent with the substrate, carrying two electrophilic group vicinally,

such as 1,2-diketones may arise [2+1]cycloaddition. This nucleophilic cycloaddition would afford cyclopropan-1,2-diol.

In fact, treatment of benzil (**2a**) with bis(iodozincio)methane (**1**) gave *cis*-1,2-diphenyl-cyclopropane-1,2-diol in good yield.[6] It is notable that treatment of a simple ketone with the reagent did not proceed satisfactorily. For example, treatment of acetophenone with the dizinc at room temperature resulted in the complete recovery of the starting material.[7] The reason why the reaction with benzil proceed smoothly is that a double coordination with the substrate enhances the reactivity of the dizinc reagent. Such activation was also observed in the reaction of Grignard reagent and α-alkoxyketones via Cram's chelation.[8] The reaction of benzil and dizinc proceeded with high diastereoselectivity. We investigated the scope and limitation of this nucleophilic [2+1]cycloaddition.

RESULTS AND DISCUSSION

Benzil (**2a**) was treated with bis(iodozincio)methane (**1**) at 25 °C in THF for 0.5 h. Acetic anhydride was added to the reaction mixture to convert the formed diol to the stable diacetate, and the whole was stirred for another 30 min at 25 °C. After aqueous work-up followed by purification with silica-gel column chromatography, 1,2-diphenylcyclpropan-1,2-diol diacetate (**3a**) was obtained in 69% yield diastereoselectively (Scheme 1).



2a **3a** 69%

Scheme 1. Nucleophilic [2+1] cyclopropanation of bis(iodozincio)methane (**1**) with benzil (**2a**)

The stereochemistry of the product was confirmed by X-ray crystallographic analysis. The ORTEP figure of **3a** was shown in Figure 1. The figure shows that the product has *cis*-configuration. This, however, seems to be sterically unfavored.

By ab initio calculation, we had shown the reason why the reaction affords a sterically unfavored *cis*-configuration.[9] The study suggested that the reaction of bis(iodozincio)methane (**1**) with 1,2-diketone **2** proceeds via a double coordination, that is face-to-face coordination, to afford the *cis*-isomer **3** (Scheme 2).

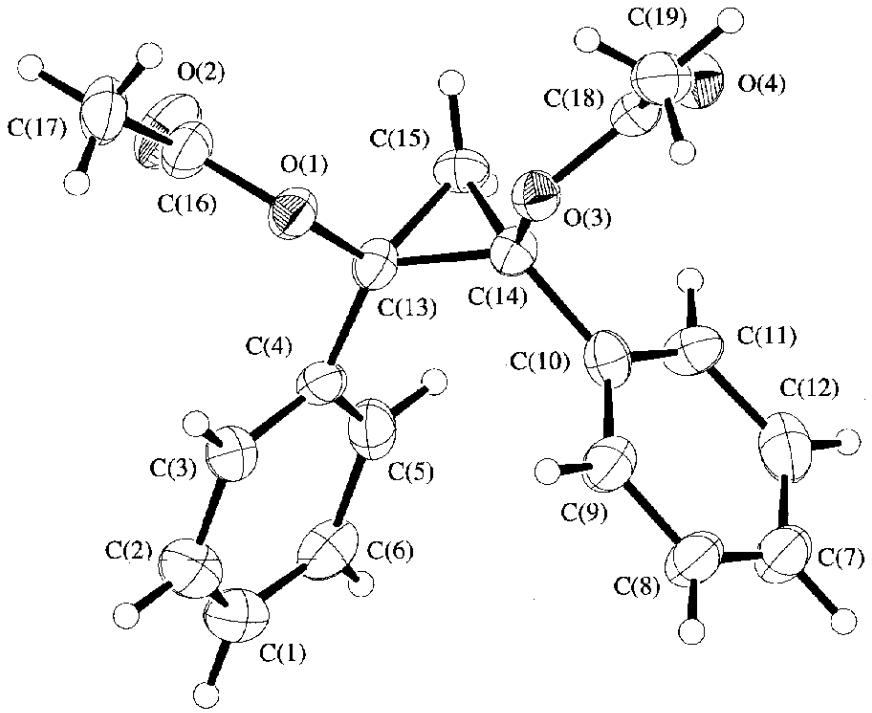
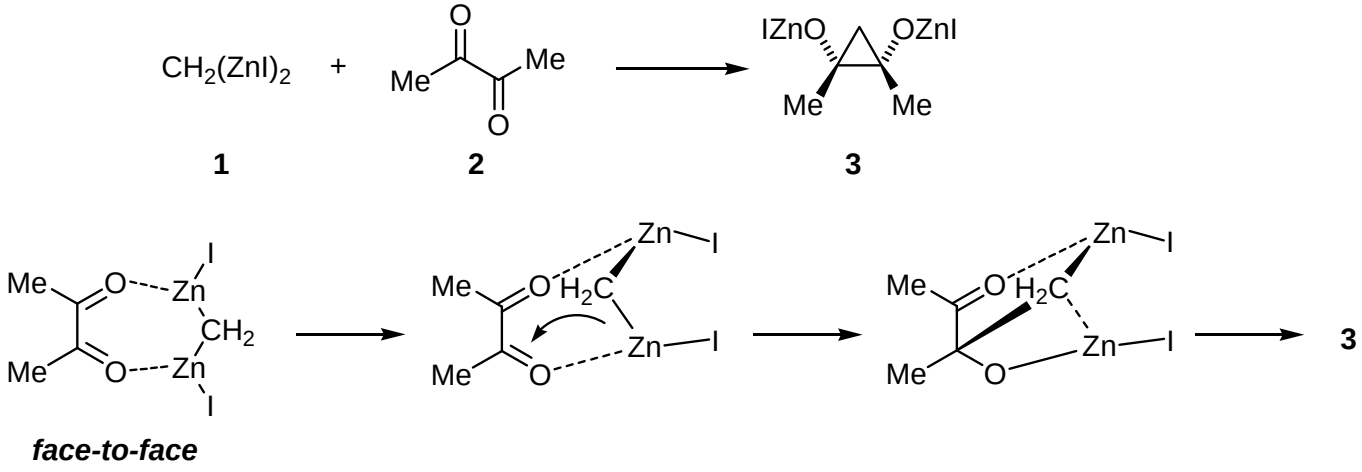
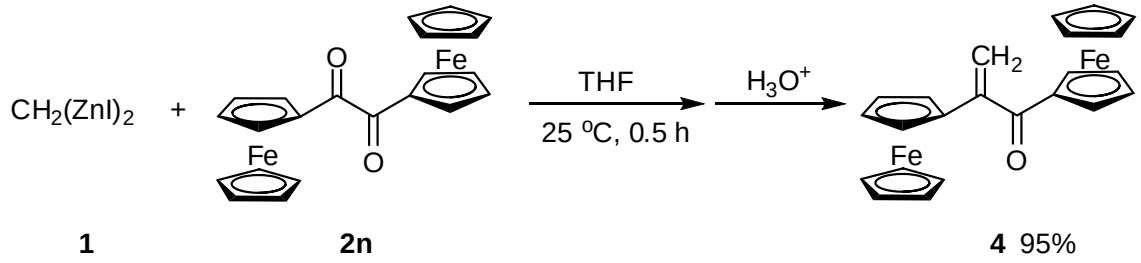


Figure 1. X-Ray analysis of *cis*-1,2-Diacetoxy-1,2-diphenylcyclopropane (**3a**). Crystal data: M = 310.35, Monoclinic, C2/c, a = 43.816(9), b = 5.922(2), c = 38.178(8) Å, β = 100.53°, V = 9739(3) Å^3, Z = 24, ρ_{cacl} = 1.270 g / cm^3, λ (Mo$_{k\alpha}$) = 0.71069 Å, *F(000)* = 3936.00, μ (Mo$_{k\alpha}$) = 0.88 cm^{-1}, T = 296 K, $2\theta_{max}$ = 54.0°, R = 0.130 for 4583 reflections ($I > 2\sigma(I)$).



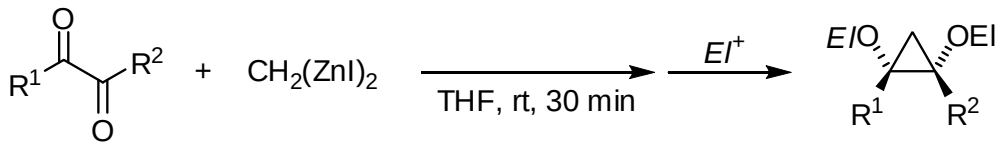
Scheme 2. Coordination pattern of bis(iodozincio)methane (**1**) with 2,3-butanedione (**2**)

Other examples are summarized in Table 1. In all cases, the reaction proceeded to give *cis*-diol derivatives diastereoselectively. Instead of acetylation, an addition of chlorotrimethylsilane to the reaction mixture gave the silyl ether (entries 1 and 4). Depending on the substrate, the formed cyclopropan-1,2-diol possesses reasonable stability that enables isolation by silica-gel column chromatography (entry 2). In the case of **2b** (entries 3, 4 and 5), this substrate tends to form a conjugated enolate. The dizinc reagent may work not only as nucleophile but also as base,[10] and the cyclopropanation proceeds prior to the enolization of 1,2-diketones. This fact was also explained by the ab initio calculation.[9] The calculation suggested that the dihedral angle formed by two carbonyl groups of 1,2-diketone in face-to-face initial complex is 47.7°. As the two carbonyl groups are not placed in the same plane, the carbonyl group at C-1 position can not contribute to facilitate a deprotonation at C-3 position via conjugation in 1-phenylpropan-1,2-diol (**2b**). The reaction of α-ketoaldehyde accompanied methylenation to some extent (entry 6). The diketone which has either electron donating group or electron withdrawing group was also examined (entries 7-9). The reaction of basic nitrogen atom containing substrates, such as 4,4'-bis(*N*,*N*-dimethylamino)benzyl (**2h**) and 1,2-di(2-quinolinyl)ethanedione (**2i**), did not afford the cyclopropane adducts (entries 10 and 11). The coordination of basic nitrogen atom to dizinc **1** prevents the interaction of **1** with diketone. Meanwhile, the reaction of oxygen or sulfur atom containing substrates, 2,2'-furil (**2j**) and 1,2-di(2-thiophenyl)ethan-1,2-dione (**2k**), afforded the desired cycloadducts without any interruption of oxygen or sulfur atom (entries 12 and 13). 1,2-Di(*o*-tolyl)ethan-1,2-dione (**2l**) and 1,2-di(2-naphthyl)ethan-1,2-dione (**2m**) were also converted into sterically unfavored *cis*-cyclopropan-1,2-diol derivatives in good yields with high diastereoselectivity (entries 14 and 15). While the reaction with 1,2-diferrocenylethan-1,2-dione (**2n**) resulted in methylenation to give α,β-enone (**4**) (Scheme 4). It may be explained that **2n** is difficult to take the face-to-face coordination because of the steric hindrance of two ferrocenyl groups (Scheme 3).

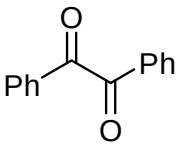
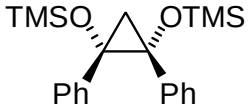
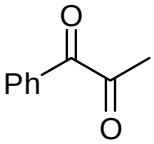
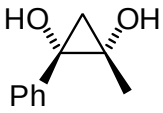
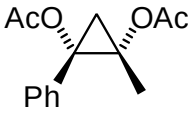
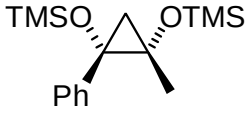
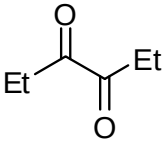
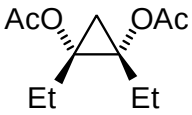
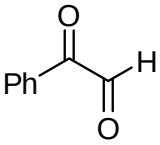
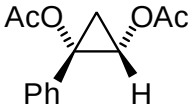
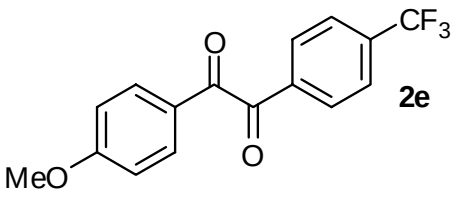
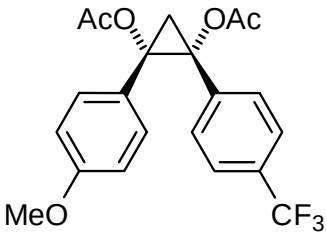
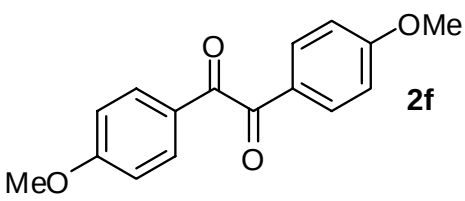
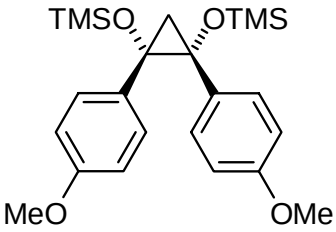


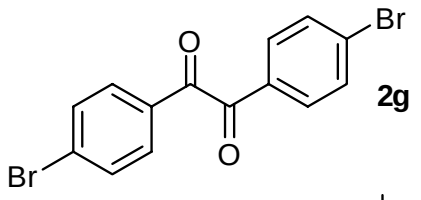
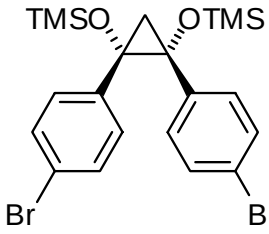
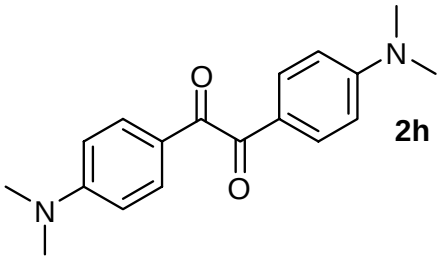
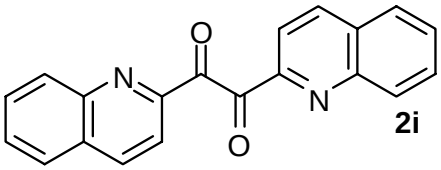
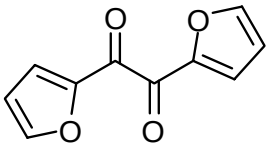
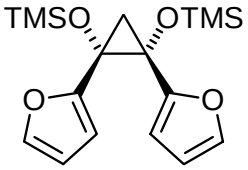
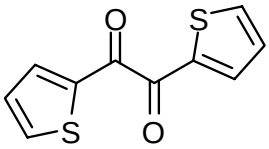
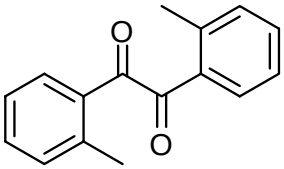
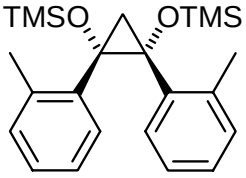
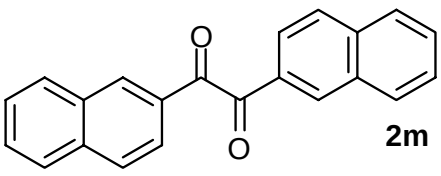
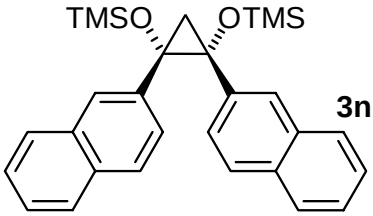
Scheme 3. Reaction of bis(iodozincio)methane (**1**) with 1,2-diferrocenyl-1,2-ethandione (**2n**)

Table 1. [2+1] Reaction of bis(iodozincio)methane (**1**) with 1,2-dicarbonyl compounds[a]



2 **1** **3**

entry	substrate **2**		*El*$^+$	product **3**		yield(%)[b]
1		**2a**	TMSCl		**3b**	78
2		**2b**	H_3O^+		**3c**	80
3		**2b**	Ac_2O		**3d**	98
4		**2b**	TMSCl		**3e**	97
5		**2c**	Ac_2O		**3f**	59
6		**2d**	Ac_2O		**3g**	58[c]
7		**2e**	Ac_2O		**3h**	94
8		**2f**	TMSCl		**3i**	93

9	 **2g**	TMSCl		**3j**	80
10	 **2h**	TMSCl	—		0[d]
11	 **2i**	TMSCl	—		0[e]
12	 **2j**	TMSCl		**3k**	96
13	 **2k**	TMSCl		**3l**	77
14	 **2l**	TMSCl		**3m**	82
15	 **2m**	TMSCl		**3n**	89

[a] 1,2-diketone (**2**, 1.0 mmol), *gem*-dizinc **1** (1.2 mmol) and El^+ (2.4 mmol) were used.

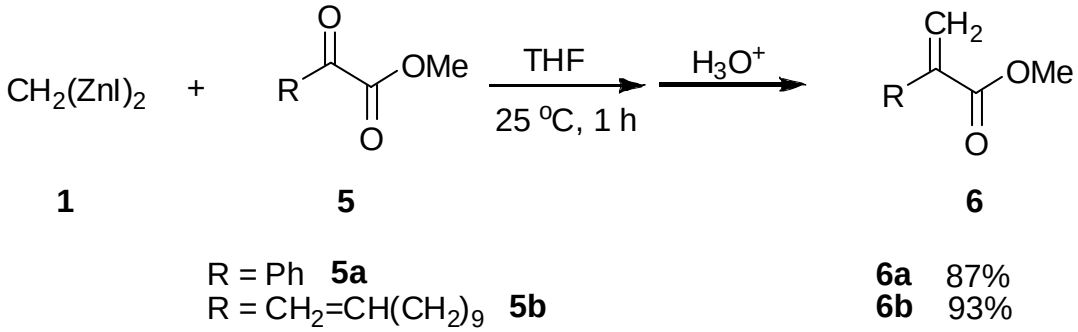
[b] Isolated yields. In each entry, only *cis*-isomer was obtained diastereoselectively.

[c] The methylenated product (1-phenyl-2-propenone) was also isolated in 17% yield.

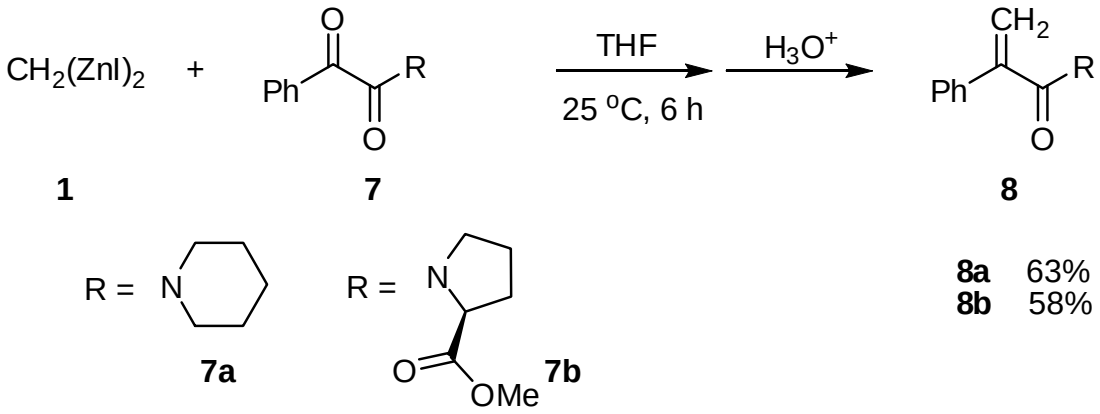
[d] Starting material (**2h**) was recovered.

[e] Complex mixture was obtained.

Treatment of α-ketoester **5** and α-ketoamides **7** with the dizinc **1** gave the methylenation products **6** and **8** without forming the cyclopropan-1,2-diols (Scheme 4 and 5). The zinc reagent is not nucleophilic enough to attack ester or amide group.



Scheme 4. Reaction of bis(iodozincio)methane (**1**) with α-ketoester (**5**)

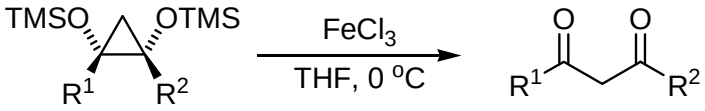


Scheme 5. Reaction of bis(iodozincio)methane (**1**) with α-ketoamide (**7**)

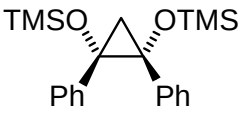
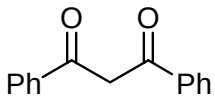
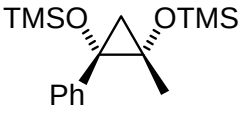
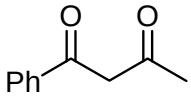
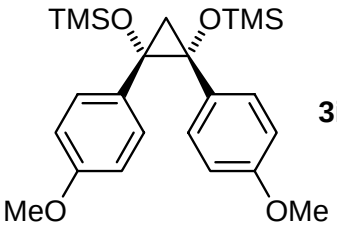
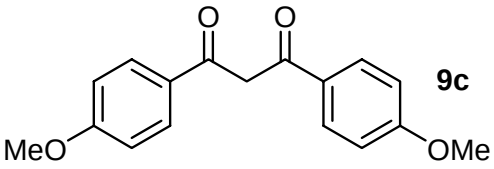
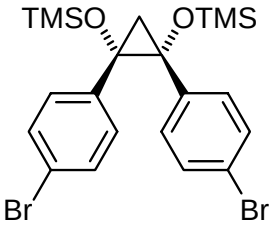
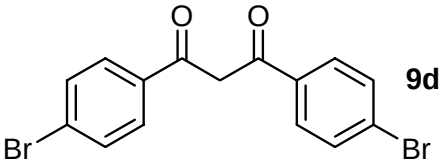
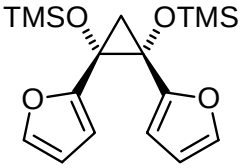
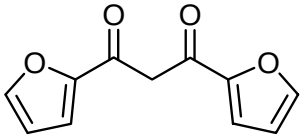
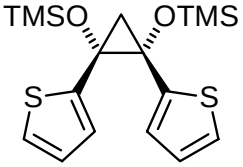
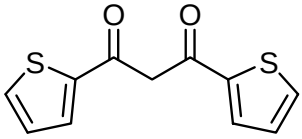
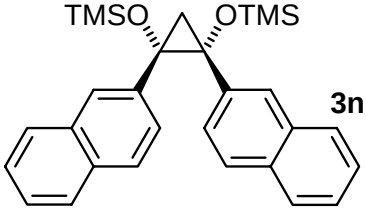
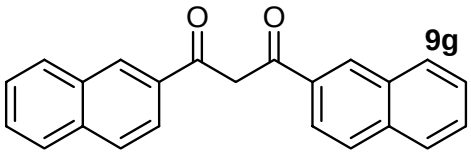
We also tried to perform a ring-opening reaction of the obtained silyl ethers of cyclopropan-1,2-diols with Lewis acid which has oxidizing ability.[11] As shown in Table 2, trimethylsilyl ethers of cyclopropanediols were converted into 1,3-diketone in good to excellent yields with iron(Ⅲ) chloride in THF. Considering cyclopropanation of 1,2-diketones, the net transformation can be regarded as methylene insertion to 1,2-diketone compounds.[12]

Instead of 1,2-diketone, monotosylimide of benzil **10a** , which was prepared following the reported procedure,[13] was treated with dizinc **1**. At the end of the reaction, addition of acetic anhydride to the reaction mixture gave *cis*-2-aminocyclopropanol acetate **11a** diastereoselectively in 95% yield (Scheme 6).

Table 2. Ring opening isomerization into 1,3-diketones (**3**)[a]

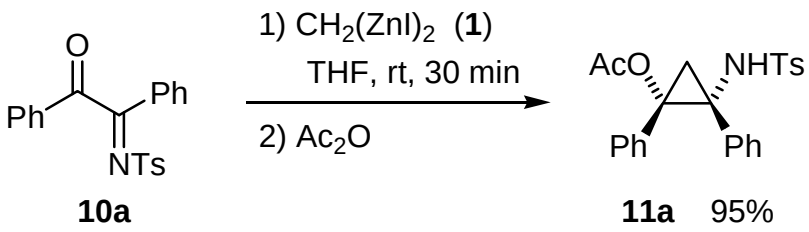


3 **9**

entry	substrate		product		yield(%)[b]
1		**3b**		**9a**	96
2		**3e**		**9b**	83
3		**3i**		**9c**	85
4		**3j**		**9d**	89
5		**3k**		**9e**	97
6		**3l**		**9f**	99
7		**3n**		**9g**	72

[a] 1,2-bis(trimethylsiloxy)cyclopropane (**3**, 0.5 mmol), $FeCl_3$ (0.75 mmol) were used.

[b] Isolated yields.



10a **11a** 95%

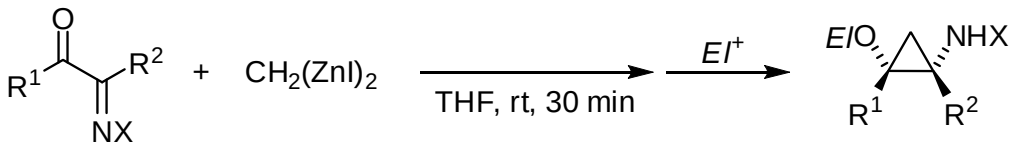
Scheme 6. Reaction of bis(iodozincio)methane (**1**) with α-ketoimine (**10a**)

The stereochemistry of **11a** was confirmed by X-ray analysis (Figure 2). The product was only *cis*-isomer. This result indicates that the reaction with α-ketoimine also proceeds via the face-to-face coordination.

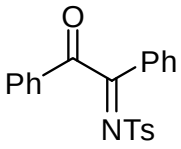
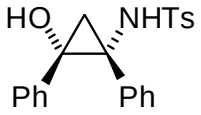
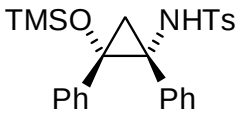
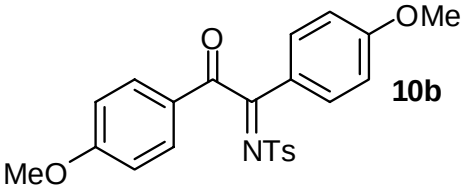
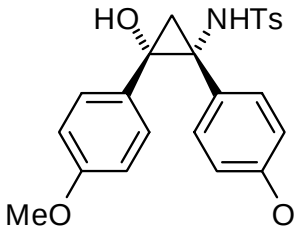
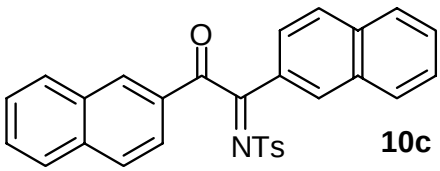
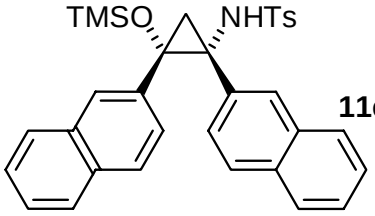
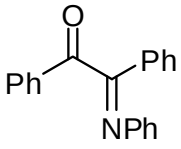
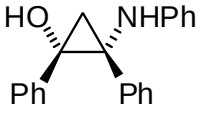
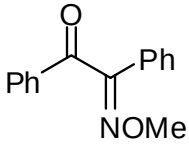
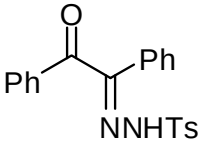
Figure 2 X-Ray analysis of *cis*-1,2-Diacetoxy-1,2-diphenylcyclopropane (**11a**). Crystal data: M = 421.49, Monoclinic, C2/c, a = 12.7365(13), b = 10.8102(11), c = 16.3267(17) Å, β = 105.936°, V = 2161.5(4) Å^3, Z = 4, ρ_{cacl} = 1.295 g / cm^3, λ ($Mo_{k\alpha}$) = 0.71073 Å, T = 296 K, $2\theta_{max}$ = 54.0°, R = 0.049 for 4711 reflections ($I > 2\sigma(I)$).

Other examples are summarized in Table 3. An acidic aqueous work-up and quenching with chlorotrimethylsilane gave the corresponding products (entries 1 and 2). Electron-donating group, methoxy, on benzene ring did not disturb the cyclopropanation reaction (entry 3). Tosylimine of 1,2-di(2-naphthyl)ethan-1,2-dione **10c** was also converted into *cis*-2-aminocyclopropanol derivative **11e** in 92% yield with high diastereoselectivity (entry 4). An attempt to isolate the corresponding 2-aminocyclopropanol without a protection with trimethylsilyl group was failed. The ring opening product, β-hydroxyimide, was isolated quantitatively. Instead of tosylimine, phenylimine was examined for the cyclopropanation reaction. Treatment of **10d** with dizinc **1** followed by aqueous work-up afforded *cis*-2-aminocyclopropanol **11f** quantitatively (entry 5). In the case of *O*-methyl oxime **10e** or tosylhydrazone **10f**, the reaction resulted in the complete recovery of the starting materials (entries 6 and 7).

Table 3. Nucleophilic [2+1]cycloaddition of bis(iodozincio)methane (**1**) with 1,2-ketoimines (**10**)[a]



10 **1** **11**

entry	substrate		El^+	product		yield(%)[b]
1		**10a**	H_3O^+		**11a**	97
2		**10a**	TMSCl		**11c**	>99
3		**10b**	H_3O^+		**11d**	>99
4		**10c**	TMSCl		**11e**	92
5		**10d**	H_3O^+		**11f**	>99
6		**10e**	H_3O^+	—		0[c]
7		**10f**	H_3O^+	—		0[c]

[a] α-keto imine (**10**, 1.0 mmol), *gem*-dizinc **1** (2.0 mmol) and El^+ (2.4 mmol) were used.

[b] Isolated yields. In each entry, only *cis*-isomer was formed diastereoselectively.

[c] Starting material was recovered.

CONCLUSION

We showed the scope of the nucleophilic [2+1]cycloaddition of bis(iodozincio)methane and 1,2-diketones or α-ketoimines. Various substrates, which can coordinate with dizinc **1** as the face-to-face manner, were converted into *cis*-cyclopropan-1,2-diol derivatives diastereoselectively. These products have potential to apply for effective ligands of organometallic chemistry, pharmaceutical applications and functionalized materials.

EXPERIMENTAL

All solvents except tetrahydrofuran were used as obtained from commercial suppliers. Tetrahydrofuran was distilled over benzophenone–ketyl. Zinc powder was used after washing with 10% HCl according to the reported procedure.[14] Chromatographic purification of products was accomplished using forced-flow chromatography on Kanto Chemical Co., INC. Silica gel 60 N (spherical, neutral).

^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini-2000 (300 MHz and 75 MHz, respectively) instrument and are internally referenced to residual protio solvent signals. Data for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported as chemical shift.

For the X-ray diffraction, a crystal was mounted on a glass fiber coated with epoxy resin. Measurements were made on a Rigaku Mercury charge-coupled device (CCD) system with graphite monochromated Mo kα radiation.

Bis(iodozincio)methane (1): A mixture of Zn (25 mmol), diiodomethane (1.0 mmol), and $PbCl_2$ (0.01 mmol) in THF (2.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. To the mixture, diiodomethane (10 mmol) in THF (20 mL) was added dropwise over 15 min at 0 ° C with vigorous stirring. The mixture was stirred for 2 h at 0 ° C. After the stirring was stopped, the reaction vessel was stood undisturbed for several hours. Excess zinc was separated by sedimentation. ^{1}H NMR spectra of the obtained supernatant showed a broad singlet at -1.2 ppm at 0 ° C, which corresponded to the methylene proton of **1**. The supernatant was used for the further reaction as a solution of **1** in THF (0.5–0.6 M). Bis(Iodozincio)methane in THF can be kept unchanged at least for a month in the sealed reaction vessel.

General Procedure for the preparation of 1,2 -cyclopropanediol: To a solution of 1,2-diketone (1.0 mmol) in THF (3 mL), dizinc **1** (1.2 mmol) was added dropwise at 25 °C. The mixture was stirred 30

min. Quenching reagent (2.4 mmol, water, acetic anhydride, and chlorotrimethylsilane) was added dropwise and the resulting mixture was stirred for another 30 min. The mixture was poured into sat. NH_4Cl aq and extracted with Et_2O. The combined ethereal phases were washed with brine and dried over Na_2SO_4. Purification on a neutral silica-gel column chromatography gave the corresponding 1,2-cyclopropanediol derivative.

***cis*-1,2-Diacetoxy-1,2-diphenylcyclopropane (3a)**: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.28-7.20 (m, 4H), 7.18-7.10 (m, 6H), 2.51 (d, *J* = 9.0 Hz, 1H), 2.11 (s, 6H), 1,83 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ 170.1, 135.3, 128.8, 127.8, 64.9, 23.8, 21.1. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.25; H, 5.95.

***cis*-1,2-Bis(trimethylsiloxy)-1,2-diphenylcyclopropane (3b)**: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.17-6.90 (m, 10H), 2.18 (d, *J* = 7.5 Hz, 1H), 1,48 (d, *J* = 7.5 Hz, 1H), 0.08 (s, 18H); ^{13}C NMR (75MHz, $CDCl_3$) δ 140.0, 127.9, 127.5, 126.5, 64.8, 23.1, 0.90. Anal. Calcd for $C_{21}H_{30}O_2Si_2$: C, 68.05; H, 8.16. Found: C, 67.80; H, 7.93.

***cis*-1,2-Dihydroxy-1-methyl-2-phenylcyclopropane (3c)**: ^{1}H NMR (500MHz, $CDCl_3$) δ 7.60-7.20 (m, 5H), 3.85 (bs, 2H), 1.27 (d, *J* = 7.5 Hz, 1H), 1.13 (s, 3H), 0.98 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125MHz, C_6D_6) δ 140.1, 128.4, 128.3, 127.3, 62.0, 58.8, 24.5, 20.5. HRMS calcd for $C_{10}H_{12}O_2$ M^+: 164.0837, found 164.0834.

***cis*-1,2-Diacetoxy-1-methyl-2-phenylcyclopropane (3d)**: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.65-7.56 (m, 2H), 7.38 – 7.20 (m, 3H), 2.09 (s, 3H), 1.92 (s, 3H), 1.68 (d, *J* = 9.0 Hz, 1H), 1,39 (d, *J* = 9.0 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ 170.6, 170.2, 135.6, 129.6, 128.3, 128.2, 125.9, 63.5, 60.5, 22.8, 21.0, 20.7, 18.3. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.84; H, 6.59.

***cis*-1,2-Bis(trimethylsiloxy)-1-methyl-2-phenylcyclopropane (3e)** : ^{1}H NMR (300MHz, $CDCl_3$) δ 7.41-7.15 (m, 5H), 1.34 (d, *J* = 6.9 Hz, 1H), 1,06 (d, *J* = 6.9 Hz, 1H), 1.05 (s, 3H), 0.23 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (75MHz, $CDCl_3$) δ 141.1, 128.0, 127.9, 126.9, 63.7, 59.7, 24.1, 22.2, 1.24, 0.82. Anal. Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.28; H, 9.15. Found: C, 61.98; H, 9.27.

***cis*-1,2-Diacetoxy-1,2-diethylcyclopropane (3f)**: ^{1}H NMR (300MHz, $CDCl_3$) δ 1.98 (s, 6H), 1.84 (ddq, *J* = 15.0, 7.5, 0.9 Hz, 2H), 1.74 (dq, *J* = 15.0, 7.5 Hz, 2H), 1.07 (dt, *J* = 8.4, 0.9 Hz, 1H), 1.00 (t, *J* = 7.5

Hz, 6H), 0.87 (d, *J* = 8,4 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ 170.4, 64.1, 24.2, 23.1, 20.9, 9.4. HRMS calcd for $C_{11}H_{19}O_4$ $[M + H]^+$: 215.1283, found 215.1289.

***cis*-1,2-Diacetoxy-1-phenylcyclopropane (3g)** : ^{1}H NMR (300MHz, $CDCl_3$) δ 7.51-7.40 (m, 2H), 7.41-7.28 (m, 3H), 4.26 (dd, *J* = 8.1, 4.8 Hz, 1H), 2.13 (s, 3H), 2.04 (s, 3H), 1.80 (dd, *J* = 8.4, 8.4 Hz, 1H), 1,49 (dd, *J* = 8.4, 4.8 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ 171.2, 170.2, 137.5, 128.4, 128.1, 127.7, 59.9, 55.0, 20.8, 20.4, 18.8. HRMS calcd for $C_{13}H_{15}O_4$ $[M + H]^+$: 235.0970, found 235.0963.

***cis*-1,2-Diacetoxy-1-(4-anisyl)-2-(4-trifluoromethylphenyl)cyclopropane (3h):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.25-7.22 (m, 2H), 6.70-6.67 (m, 2H), 3.72 (s, 3H), 2.43 (d, *J* = 9.0 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 1.85 (d, J = 9 Hz, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 170.2, 170.0, 159.4, 140.0, 131.3, 129.5 (q, *J* = 32.5 Hz), 128.0, 126.4, 124.8 (q, *J* = 3.9 Hz), 123.9 (q, J = 270.6 Hz), 113.4, 65.2, 64.0, 55.1, 24.3, 21.13, 21.07. HRMS calcd for $C_{21}H_{19}O_5F_3$ M^+: 408.1185, found 408.1193.

***cis*-1,2-Bis(trimethylsiloxy)-1,2-di(4-anisyl)cyclopropane (3i):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.04-7.01 (m, 4H), 6.62-6.59 (m, 4H), 3.69 (s, 6H), 2.02 (d, *J* = 7.5 Hz, 1H), 1.37 (d, *J* = 7.5 Hz, 1H), 0.05 (s, 18H); ^{13}C NMR (125MHz, $CDCl_3$) δ 158.0, 132.4, 129.1, 112.8, 64.4, 55.0, 24.0, 1.08. Anal. Calcd for $C_{23}H_{34}O_4Si_2$: C, 64.14; H, 7.96. Found: C, 64.27; H, 7.97. HRMS calcd for $C_{23}H_{34}O_4Si_2$ M^+: 430.1996, found 430.1993.

***cis*-1,2-Bis(trimethylsiloxy)-1,2-di(4-bromophenyl)cyclopropane (3j):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 4H), 6.96 (d, *J* = 8.5 Hz, 4H), 2.08 (d, *J* = 7.5 Hz, 1H), 1.47 (d, *J* = 7.5 Hz, 1H), 0.06 (s, 18H); ^{13}C NMR (125MHz, $CDCl_3$) δ 138.9, 130.9, 129.4, 120.8, 64.3, 23.8, 1.07. Anal. Calcd for $C_{21}H_{28}O_2Br_2Si_2$: C, 47.73; H, 5.34. Found: C, 47.64; H, 5.24. HRMS calcd for $C_{21}H_{28}O_2Br_2Si_2$ M^+: 525.9995, found 525.9988.

***cis*-1,2-Di(2-furyl)-1,2-bis(trimethylsilyloxy)cyclopropane (3k):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.22 (dd, *J* = 1.5, 1.0 Hz, 2H), 6.16 (dd, *J* = 3.5, 1.5 Hz, 2H), 5.92 (dd, *J* = 3.5, 1.0 Hz, 2H), 1.88 (d, *J* = 6.5 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 1H), 0.10 (s, 18H); ^{13}C NMR (125MHz, $CDCl_3$) δ 153.4, 141.4, 110.1, 107.6, 58.7, 25.1, 0.54. Anal. Calcd for $C_{17}H_{26}O_4Si_2$: C, 58.25; H, 7.48. Found: C, 58.04; H, 7.41. HRMS calcd for $C_{17}H_{26}O_4Si_2$ M^+: 350.1370, found 350.1369.

***cis*-1,2-Di(thiophen-2-yl)-1,2-bis(trimethylsilyloxy)cyclopropane (3l):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.07 (dd, *J* = 5.0, 1.0 Hz, 2H), 6.73 (dd, *J* = 5.0, 3.5 Hz, 2H), 6.59 (dd, *J* = 3.5, 1.0 Hz, 2H), 2.01 (d, *J* = 7.5 Hz, 1H), 1.66 (d, *J* = 7.5 Hz, 1H), 0.13 (s, 18H); ^{13}C NMR (125MHz, $CDCl_3$) δ 145.2, 125.8, 125.2, 125.0, 62.0, 28.9, 0.93. HRMS calcd for $C_{17}H_{26}O_2S_2Si_2$ M^+: 382.0913, found 382.0915.

***cis*-1,2-Bis(trimethylsiloxy)-1,2-di(2-tolyl)cyclopropane (3m):** ^{1}H NMR (300MHz, $CDCl_3$) δ 7.05-6.95 (m, 4H), 6.82-6.77 (m, 4H), 2.57 (s, 6H), 2.01 (d, *J* = 7.2 Hz, 1H), 1.41 (d, *J* = 7.2 Hz, 1H), -0.01 (s, 18H); ^{13}C NMR (75Hz, $CDCl_3$) δ 138.9, 138.2, 130.7, 127.7, 126.9, 124.5, 65.1, 25.8, 21.3, 1.38. Anal. Calcd for $C_{23}H_{34}O_2Si_2$: C, 69.29; H, 8.60. Found: C, 69.02; H, 8.44. HRMS calcd for $C_{23}H_{34}O_2Si_2$ M^+: 398.2097, found 398.2094.

***cis*-1,2-Bis(trimethylsiloxy)-1,2-di(2-naphtyl)cyclopropane (3n):** ^{1}H NMR (500MHz, $CDCl_3$) δ 7.63-7.59 (m, 6H), 7.47 (d, *J* = 9.0Hz, 2H), 7.35-7.29 (m, 6H), 2.48 (d, *J* = 7.5 Hz, 1H), 1.62 (d, *J* = 7.5 Hz, 1H), 0.09 (s, 18H); ^{13}C NMR (125MHz, $CDCl_3$) δ 137.5, 132.6, 132.2, 127.8, 127.4, 127.3, 126.5, 126.2, 125.6, 125.5, 65.2, 24.0, 1.14. Anal. Calcd for $C_{29}H_{34}O_2Si_2$: C, 73.99; H, 7.28. Found: C, 73.93; H, 7.32. HRMS calcd for $C_{29}H_{34}O_2Si_2$ M^+: 470.2097, found 470.2101.

1,2-Diferrocenylpropenone (4): ^{1}H NMR (500MHz, $CDCl_3$) δ 5.77 (s, 1H), 5.68 (s, 1H), 4.84 (t, *J* = 2.0 Hz, 2H), 4.54 (t, *J* = 2.0 Hz, 2H), 4.52 (s, 2H), 4.29 (s, 2H), 4.23 (s, 5H), 4.14 (s, 5H); ^{13}C NMR (125MHz, $CDCl_3$) δ 200.3, 147.4, 114.4, 80.8, 78.4, 72.3, 71.0, 70.0, 69.7, 69.0, 67.1. Anal. Calcd for $C_{23}H_{20}OFe_2$: C, 65.14; H, 4.75. Found: C, 64.86; H, 4.78. HRMS calcd for $C_{23}H_{20}OFe_2$ M^+: 424.0213, found 424.0209.

Methyl 2-methylene-2-phenylacetate (6a): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.43-7.32 (m, 5H), 6.37 (d, *J* = 1.0 Hz, 1H), 5.90 (d, *J* = 1.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 167.3, 141.3, 136.7, 128.3, 128.2, 128.1, 126.9, 52.2. HRMS calcd for $C_{10}H_{10}O_2$ M^+: 162.0681, found 162.0680.

Methyl 2-methylene-12-tridecenoate (6b): ^{1}H NMR (500MHz, $CDCl_3$) δ 6.12 (dt, *J* = 1.5, 0.5 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.0, 6.5 Hz, 1H), (dt, *J* = 1.5, 1.5 Hz, 1H), 4.99 (ddt, *J* = 17.0, 2.0, 1.5 Hz, 1H), 4.93 (ddt, *J* = 10.0, 2.0, 1.5 Hz, 1H), 3.75 (s, 3H), 2.29 (ddt, *J* = 7.5, 1.0, 0.5 Hz, 2H), 2.06-2.01 (m, 2H), 1.45 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.37 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.34-1.25 (m, 10H) ; ^{13}C NMR (125MHz, $CDCl_3$) δ 167.8, 140.8, 139.2, 124.4, 114.1, 51.7, 33.8, 31.9, 29.5, 29.43, 29.37, 29.2, 29.1, 28.9, 28.3. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.49; H, 10.71. HRMS calcd for $C_{15}H_{26}O_2$ M^+:

238.1933, found 238.1935.

2-Phenyl-1-piperidin-1-ylpropenone (8a): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.37-7.28 (m, 3H), 5.71 (s, 1H), 5.33 (s, 1H), 3.71-3.65 (m, 2H), 3.32-3.30 (m, 2H), 1.63-1.60 (m, 4H), 1.40-1.33 (m, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 169.1, 145.2, 135.7, 128.7, 128.5, 125.7, 113.3, 48.0, 42.4, 26.3, 25.6, 24.5. HRMS calcd for $C_{14}H_{17}NO$ M^+: 215.1310, found 215.1306.

(S)-Methyl 1-(2-phenylacryloyl)pyrrolidine-2-carboxylate (8b): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.42-7.29 (m, 3H), 5.76 (s, 0.80H), 5.68 (s, 0.20H), 5.49 (s, 0.80H), 5.34 (s, 0.20H), 4.62 (dd, *J* = 8.0, 5.0 Hz, 0.80H), 4.24 (dd, *J* = 6.0, 2.5 Hz), 3.79 (s, 2.4H), 3.49 (s, 0.6H), 3.39-3.31 (m, 1.6H), 2.29-2.21 (m, 0.8H), 2.18-2.07 (m, 0.2H), 2.02-1.91 (m, 2H), 1.88-1.80 (m, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 172.60, 172.58, 169.4, 169.3, 145.5, 145.4, 135.3, 135.1, 128.8, 128.7, 128.6, 128.5, 126.1, 125.9, 115.25, 115.17, 60.4, 58.4, 52.3, 52.1, 48.5, 46.0, 31.2, 29.4, 24.9, 22.6. HRMS calcd for $C_{15}H_{17}NO_3$ M^+: 259.1208, found 259.1205.

General Procedure for the p reparation of 1,3-diketone : To a solution of *cis*-1,2-bis(trimethylsiloxy)-1,2-dialkylcyclopropane (0.5 mmol) in THF (1 mL), $FeCl_3$ (0.75 mmol) was added at 0 °C. The mixture was stirred for 30 min. The mixture was poured into 1NHClaq and extracted with EtOAc. The combined organic phases were washed with brine and dried over Na_2SO_4. Purification on a neutral silica-gel column chromatography gave the corresponding 1,3-diketone.

1,3-Diphenyl-1,3-propanedione (9a): ^{1}H NMR (300MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 4H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.50 (dd, *J* = 7.0, 7.0 Hz, 4H), 6.87 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ 185.7, 135.5, 132.4, 128.7, 127.1, 93.1. HRMS calcd for $C_{15}H_{12}O_2$ M^+: 224.0837, found 224.0836.

1-Methyl-3-phenyl-1,3-propanedione (9b): ^{1}H NMR (300MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 7.0 Hz, 2H), 6.18 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ 193.8, 183.3, 134.8, 132.3, 128.6, 127.0, 96.7, 25.8. HRMS calcd for $C_{10}H_{10}O_2$ M^+: 162.0681, found 162.0679.

1,3-Di(4-anisyl)-1,3-propanedione (9c): ^{1}HNMR (500MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 6.74 (s, 1H), 3.89 (s, 6H); ^{13}CNMR (125MHz, $CDCl_3$) δ 184.6, 163.0, 129.1, 128.2, 113.9, 91.5, 55.5. HRMS calcd for $C_{17}H_{16}O_4$ M^+: 284.1049, found 284.1048.

1,3-Di(4-bromophenyl)-1,3-propanedione (9d): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 4H), 7.63 (d, *J* = 8.5 Hz, 4H), 6.77 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 184.7, 134.2, 132.0, 128.7, 127.5, 92.9. HRMS calcd for $C_{15}H_{10}O_2{}^{79}Br_2$ M^+: 379.9048, found 379.9044.

1,3-Di(2-furyl)-1,3-propanedione (9e): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.61 (dd, *J* = 1.5, 1.0 Hz, 2H), 7.20 (dd, *J* = 3.5, 1.0 Hz, 2H), 6.65 (s, 1H), 6.58 (dd, *J* = 3.5, 1.5 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 174.7, 150.3, 146.1, 115.5, 112.6, 92.1. HRMS calcd for $C_{11}H_8O_4$ M^+: 204.0423, found 204.0421.

1,3-Di(2-thiophenyl)-1,3-propanedione (9f): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.78 (dd, *J* = 4.0, 1.0 Hz, 2H), 7.62 (dd, *J* = 5.0, 1.0 Hz, 2H), 7.17 (dd, *J* = 5.0, 4.0 Hz, 2H), 6.54 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$) δ 178.8, 140.6, 132.0, 130.0, 128.3, 92.6. HRMS calcd for $C_{11}H_8O_2S_2$ M^+: 235.9966, found 235.9971.

1,3-Di(2-naphtyl)-1,3-propanedione (9g): ^{1}HNMR (500MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.5 Hz, 2H), 8.08 (d, *J* = 8.5, 2.0 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.63-7.56 (m, 4H), 7.16 (s, 1H); ^{13}CNMR (125MHz, $CDCl_3$) δ 185.6, 135.3, 132.8, 132.8, 129.4, 128.5, 128.4, 128.2, 127.8, 126.8, 123.3, 93.8. HRMS calcd for $C_{23}H_{16}O_2$ M^+: 324.1150, found 324.1152.

General Procedure for the preparation of 2-aminocyclopropanol: To a solution of α-keto imine (1.0 mmol) in THF (4 mL), dizinc **1** (2.0 mmol) was added dropwise at 25 °C. The mixture was stirred for 30 min. Quenching reagent (2.4 mmol, water, acetic anhydride, and chlorotrimethylsilane) was added dropwise and the resulting mixture was stirred for another 30 min. The mixture was poured into sat. NH_4Claq, then sat. $NaHCO_3$ aq was added to neutralize and extracted with Et_2O. The combined ethereal phases were washed with brine and dried over Na_2SO_4. Purification on a neutral silica-gel column chromatography gave the corresponding 2-aminocyclopropanol derivative.

***cis*-*N*-(2-Acetoxy-1,2-diphenylcyclopropyl)-4-methylbenzenesulfonamide (11a):** ^{1}HNMR (300MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.07-6.98 (m, 7H), 6.90-6.83 (m, 5H), 5.83 (s, 1H), 2.39 (d, *J* = 8.4 Hz, 1H), 2.30 (s, 3H), 2.18 (d, *J* = 8.4 Hz, 1H), 2.13 (s, 3H); ^{13}CNMR (75MHz, $CDCl_3$) δ 171.0, 143.1, 137.9, 135.9, 134.9, 129.3, 129.0, 128.5, 128.0, 127.93, 127.87, 127.4, 127.1, 66.2, 46.7, 22.4, 21.8, 21.7. HRMS calcd for $C_{24}H_{23}NO_4S$ M^+: 421.1348, found 421.1357.

***cis*-*N*-(2-Hydroxy-1,2-diphenylcyclopropyl)-4-methylbenzenesulfonamide (11b):** ^{1}HNMR (300MHz,

$CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.06-7.02 (m, 7H), 6.89-6.83 (m, 5H), 6.04 (s, 1H), 3.39 (bs, 1H), 2.32 (s, 3H), 2.23 (d, *J* = 7.8Hz, 1H), 1.77 (d, *J* = 7.8 Hz, 1H); ^{13}CNMR (75MHz, $CDCl_3$) δ 143.2, 137.8, 137.7, 136.3, 129.3, 129.2, 128.0, 127.7, 127.5, 127.48, 127.3, 126.9, 63.4, 47.5, 23.8, 21.8. HRMS calcd for $C_{22}H_{21}NO_3S$ M^+: 379.1242, found 379.1241.

***cis*-*N*-(2-Trimethylsiloxy-1,2-diphenylcyclopropyl)-4-methylbenzenesulfonamide (11c):** ^{1}HNMR (500MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.10-7.07 (m, 2H), 7.04-6.98 (m, 5H), 6.95-6.92 (m, 2H), 6.90-6.86 (m, 3H), 5.91 (s, 1H), 2.34 (s, 3H), 2.31 (d, *J* = 8.0 Hz, 1H), 1.42 (d, *J* = 8.0 Hz, 1H), -0.01 (s, 9H); ^{13}CNMR (125MHz, $CDCl_3$) δ 142.8, 138.3, 137.5, 136.6, 129.1, 128.8, 127.8, 127.6, 127.31, 127.29, 127.28, 126.4, 64.0, 45.2, 21.8, 21.4, 0.72. HRMS calcd for $C_{25}H_{29}NO_3SSi$ M^+: 451.1637, found 451.1634.

***cis*-*N*-(2-Hydroxy-1,2-di-4-anisylcyclopropyl)-4-methylbenzenesulfonamide (11d):** ^{1}HNMR (300MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.40 (d, *J* = 8.7 Hz, 2H), 3.67 (s, 3H), 3.63 (s, 3H), 2.33(s, 3H), 2.07 (d, *J* = 7.5 Hz, 1H), 1.61 (d, *J* = 7.5 Hz, 1H); ^{13}CNMR (75MHz, $CDCl_3$) δ 157.4, 157.1, 139.0, 130.7, 129.2, 128.9, 128.4, 127.8, 127.5, 127.2, 126.9, 126.2, 111.5, 111.4, 61.1, 53.3, 45.7, 22.4. HRMS calcd for $C_{24}H_{25}NO_5S$ M^+: 439.1453, found 439.1453.

***cis*-*N*-(2-Trimethylsiloxy-1,2-di-2-naphthylcyclopropyl)-4-methylbenzenesulfonamide (11e):** ^{1}HNMR (300MHz, C_6D_6) δ 7.60-6.94 (m, 16H), 6.39-6.36 (m, 2H), 6.20 (s, 1H), 2.60 (d, *J* = 8.1 Hz, 1H), 2.15 (d, *J* = 8.1 Hz, 1H), 1.63 (s, 3H), 0.05 (s, 9H); ^{13}CNMR (75MHz, C_6D_6) δ 142.0, 139.3, 135.8, 134.4, 132.8, 132.73, 132.66, 132.3, 128.6, 127.7, 127.6, 127.4, 127.3, 127.0, 126.5, 126.1, 126.0, 125.8, 125.6, 125.5, 64.8, 46.3, 23.6, 20.8, 0.9. HRMS calcd for $C_{33}H_{33}O_3NSSi$ M^+: 551.1950, found 551.1950.

1,2-Diphenyl-2-(phenylamino)cyclopropanol (11f): ^{1}HNMR (300MHz, C_6D_6) δ 7.15-6.67 (m, 15H), 2.02 (d, *J* = 7.2 Hz, 1H), 1.08 (d, *J* = 7.2 Hz, 1H); ^{13}CNMR (300MHz, C_6D_6) δ 147.2, 139.7, 138.6, 129.2, 128.8, 128.4, 128.0, 127.4, 126.1, 120.0, 118.5, 115.2, 66.5, 47.0, 25.0. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35. Found: C, 83.39; H, 6.16.; HRMS calcd for $C_{21}H_{19}NO$ M^+: 301.1463, found 301.1459.

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