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# Catalytic hydrogenolysis of enantioenriched donor-acceptor cyclopropanes using $H_2$ and Palladium on charcoal

Yoshitomo Sone, Yumi Kimura, Ryotaro Ota, Takehito Mochizuki, Junki Ito and Yoshinori Nishii*[a]

This paper is dedicated to Prof. Dennis P. Curran in celebration of his recovery and 64th birthday.

**Abstract:** The hydrogenolysis of enantioenriched donor-acceptor (D-A) cyclopropanes using $H_2$ (1 atm) and a catalytic amount of Palladium on charcoal afforded *trans*-α-alkoxycarbonyl-β-benzyl lactones or γ-aryl-β-substituted diesters with high enantiomeric excess. The present reaction was also successfully employed as a key step in the asymmetric total synthesis of yatein with high ee and excellent dr, thus demonstrating the utility of this new protocol for the asymmetric synthesis of *trans*-α,β-disubstituted γ-butyrolactones. D-A cyclopropanes containing electron-withdrawing groups at the β-position were not susceptible to hydrogenolysis under these conditions. The reductive ring-opening of a D-A cyclopropane using $D_2$ instead of $H_2$ generated the corresponding mono-deuterated product.

## Introduction

Cyclopropanes represent an important class of organic compounds due to their synthetic utility and their widespread occurrence in nature.[1,2] In addition, the rigid conformation of cyclopropanes as the smallest conceivable [$C_3$] ring compound can be exploited in stereo-controlled syntheses. Especially donor–acceptor (D–A) cyclopropanes have attracted considerable attention due to recent synthetic developments.[2d-h,3] During our synthetic studies on the transformation of cyclopropanes,[4] we have recently reported a Cu-catalyzed oxy-homo-Michael reaction,[4h] and a Cu-catalyzed 1,5-addition[4i] of Grignard reagents to enantioenriched donor-acceptor (D-A) cyclopropanes. According to the Walsh model[5] for cyclopropanes, their single bonds resemble π-bonds. Although the hydrogenolysis of several types of cyclopropanes using $H_2$ (1 atm) in combination with heterogeneous Pd or Ni catalysts has been studied,[6] the background information for the hydrogenolysis of cyclopropanes present in the scientific literature is not sufficient to establish comprehensive guidelines for the regioselectivity of the bond cleavage (Fig. 1). For example, phenyl-substituted acceptor-less cyclopropanes were cleaved at bond *a* (eq. 1).[6c] In the case of D-A cyclopropanes such as arylcycanocyclopropanes, the ring-opening if the cyclopropanes occurs at bond *a*, i.e., the bond between the donor and the acceptor group (eq. 2 and 3).[6d,f] However, bond *a* between the donor and acceptor group was not cleaved during the hydrogenolysis of alkyl- and acetyl-substituted D-A cyclopropanes (eq. 4).[6e] To the best of our knowledge, even the hydrogenolysis of representative D-A cyclopropanes of the type 2-arylcyclopropane-1,1-dicarboxylic diester has not yet been reported. Herein, we report the hydrogenolysis of D–A cyclopropanes, including enantioenriched bicyclic lactones **1** and arylcyclopropanedicarboxylic diesters **3**, using $H_2$ (1 atm) and a catalytic amount of Palladium on charcoal (Pd-C).

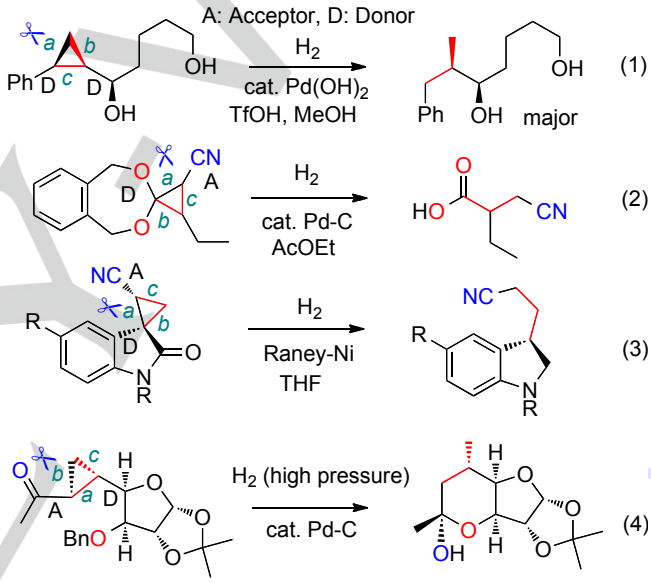
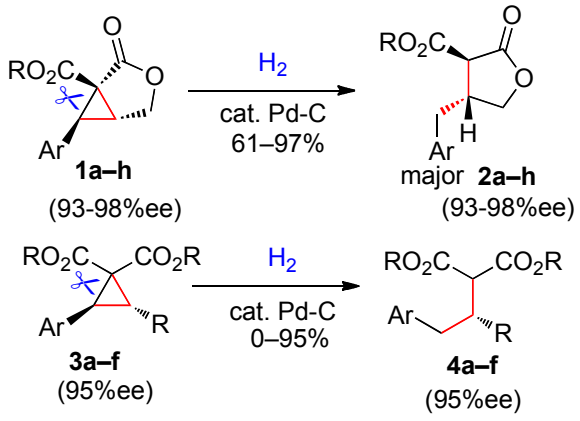



**Fig. 1.** Examples for the hydrogenolysis of cyclopropanes that contain donor (D) and/or acceptor (A) groups.




**Scheme 1**. Hydrogenolysis of D–A cyclopropanes **1** and **3** using $H_2$/Pd-C.

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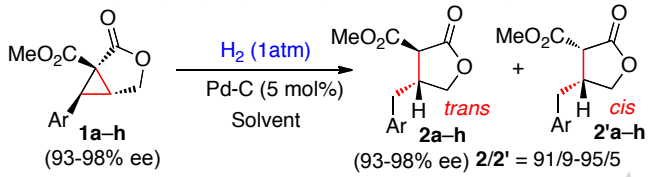
## Results and Discussion

Following our previous study,[4h] we initially prepared bicyclic lactones **1**. Treatment of bicyclic lactone **1a** with $H_2$ from a balloon (1 atm) in the presence of Pd-C in THF at room temperature resulted in reductive ring-opening and afforded optically active *trans*-α,β-disubstituted lactone **2a** as the major isomer (61%), whereby the inseparable *cis*-α,β-disubstituted lactone **2'a** was obtained as the minor product (Table 1, entry 1). Similar reactions in AcOEt also immediately furnished a 91:9 mixture of **2a** and **2'a** in good yield (entries 2 an 3), and the yield of **2a** and **2'a** was slightly increased at $T$ = 0 °C (entry 3). In methanol, the yield of the mixture of **2a** and **2'a** was also increased (entry 4). The scope of aryl groups on the substrates was investigated under mild reaction conditions (AcOEt; $T$ = 0 °C). The hydrogenolysis of **1a**–**1d**, which contain electron-donating aryl groups such as alkoxyphenyl groups, afforded the corresponding ring-opened lactones **2b**–**2d** and **2'b**–**2'd** in high yield (entries 5–7).

**Table 1.** Catalytic hydrogenolysis of bicyclolactone **1a**–**h** using $H_2$/Pd-C.




| Entry | 1[a] | Ar | Solvent | $T$ (°C) | 2 + 2' | Yield (%)[b] | dr[c] 2/2' |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | Ph | THF | rt | **2a** + **2'a** | 61 | 91/9 |
| 2 | | | AcOEt | rt | | 65 | 91/9 |
| 3 | | | | 0 | | 78 | 91/9 |
| 4 | | | MeOH | rt | | 78 | 91/9 |
| 5 | **1b** | DMP | AcOEt | 0 | **2b** + **2'b** | 93 | 93/7 |
| 6 | **1c** | TMP | AcOEt | 0 | **2c** + **2'c** | 87 | 93/7 |
| 7 | **1d** | MDP | AcOEt | 0 | **2d** + **2'd** | 94 | 92/8 |
| 8 | **1e** | BMP | AcOEt | 0 | **2e** + **2'e** | 90 | 93/7 |
| 9 | | | | rt | **2ee** + **2'ee**[d] | 80 | 91/9 |
| 10 | **1f** | FP | AcOEt | 0 | **2f** + **2'f** | 96 | 92/8 |
| 11 | **1g** | MCP | AcOEt | 0 | **2g** + **2'g** | 97 | 95/5 |
| 12 | **1h** | NP | AcOEt | 0 | **2h** + **2'h** | 75 | 92/8 |
| 13 | | | MeOH | rt | **2hh** + **2'hh** | 94 | 92/8 |

[a] Enantioenriched substrates **1a**–**c** (95% ee), **1d** (93% ee), **1e**–**f** (94% ee), and **1h** (94% ee) were used; [b] isolated yield; [c] determined by $^1$H-NMR spectroscopy; [d] $T$ = rt, $t$ = 23 h; debenzylation of OBn afford a phenolic OH group together with the ring-opening.

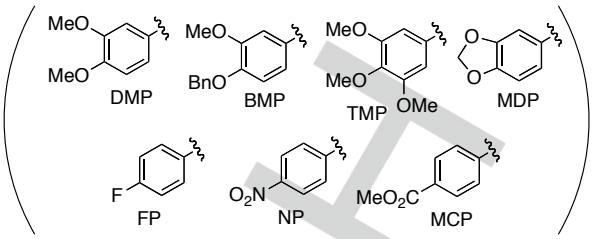


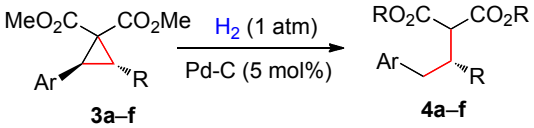

**Fig. 2**. Abbreviations for the aryl groups in Tables 1 and 2, as well as in Schemes 2 and 3.

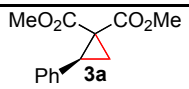
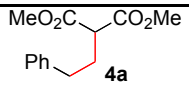
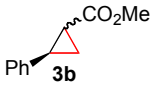
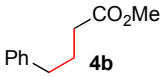
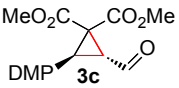
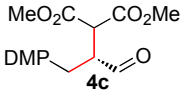
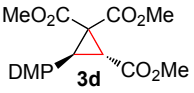
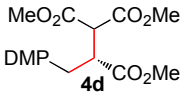
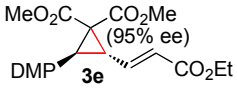
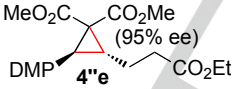
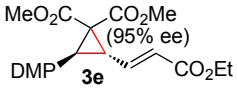
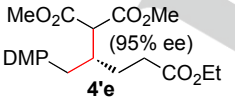
The relative stereostructure of the major product **2c** (*trans*-isomer) was determined by a comparison of its spectra with previously reported data.[7] In a similar fashion, **2a**, **2b**, and **2d**–**2h** were also assigned as the *trans*-isomers after comparison of their NMR spectra with that of **2c**. It should be noted that **1e**, which contains a benzyloxy methoxy phenyl (BMP) group, was selectively hydrolyzed at 0 °C in 1 h, whereby the benzyl group of BMP remained intact, to furnish a 95:5 mixture of **2e** and **2'e** in high yield (entry 8). However, when the same reaction was carried out at room temperature for 12 h, a debenzylation of BMP occurred together with the ring-opening, which afforded a 95:5 mixture of **2ee** and **2'ee** in high yield (entry 9). The hydrogenolysis of **1f**–**h**, which bear electron-withdrawing aryl groups, also furnished the corresponding ring-opened lactones **2f**–**h** and **2'f**–**h** in good to high yields (entries 10–12). Notably, the reductive ring-opening of 4-fluorophenyl-substituted **1f** and 4-methoxycarbonylphenyl substrate **1g** proceeded in very high yield (entries 10 and 11). The hydrogenolysis of 4-nitrophenyl-substituted **1h** induced a ring-opening in 75% yield, whereby a reduction of the nitro group was not observed (entry 12). When the same reaction was carried out at room temperature in MeOH for 18 h, a reduction of the nitro group occurred in addition to the ring-opening, which afforded **4hh** in high yield (entry 13).

Subsequently, we examined the catalytic hydrogenolysis of monocyclic D–A cyclopropanes **3** using $H_2$/Pd-C (Table 2). The hydrogenolysis of the simple D–A cyclopropyldicarboxylic diester **3a** at 0 °C in AcOEt provided the corresponding acyclic product (**4a**) in 95% yield after 0.5 h (entry 1), whereas cyclopropylcarboxylic monoester **3b** afforded **4b** in low yield under similar conditions (entry 2). This result suggests that the presence of two geminal carbonyl substituents accelerates the hydrogenolysis of the cyclopropyl ring. However, prolonging the reaction time ($t$ = 1.5 h) increased the yield of **3b** to 90%. D–A cyclopropanes **3c** and **3d**, which bear electron-withdrawing formyl or ester groups at the β-position and an electron-donating 3,4-dimethoxyphenyl group at the β'-position, were not susceptible to ring scission and 90% of **3c** and **3d** were recovered (entries 3 and 4). Therefore, the electron-withdrawing groups at the β-position should eliminate the reactivity toward hydrogenolysis. Especially electron-withdrawing groups at the β-position lead to a depletion of electron density in the HOMO of the Walsh orbitals, which contains an antibonding component at

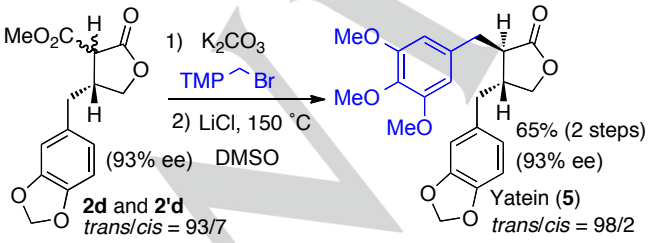
the bond to be opened. D–A cyclopropane **3e**, which contains an electron-deficient olefin, underwent hydrogenation of the olefin moiety prior to the ring-opening of the cyclopropane under similar conditions (entry 5). Increasing the reaction time ($t$ = 18 h) resulted in a ring-opening hydrogenolysis and a hydrogenation of the olefin moiety to afford **4'e** in 85% yield (entry 6).

**Table 2.** Catalytic hydrogenolysis of D-A cyclopropanes **3a–d** using $H_2$/Pd-C.



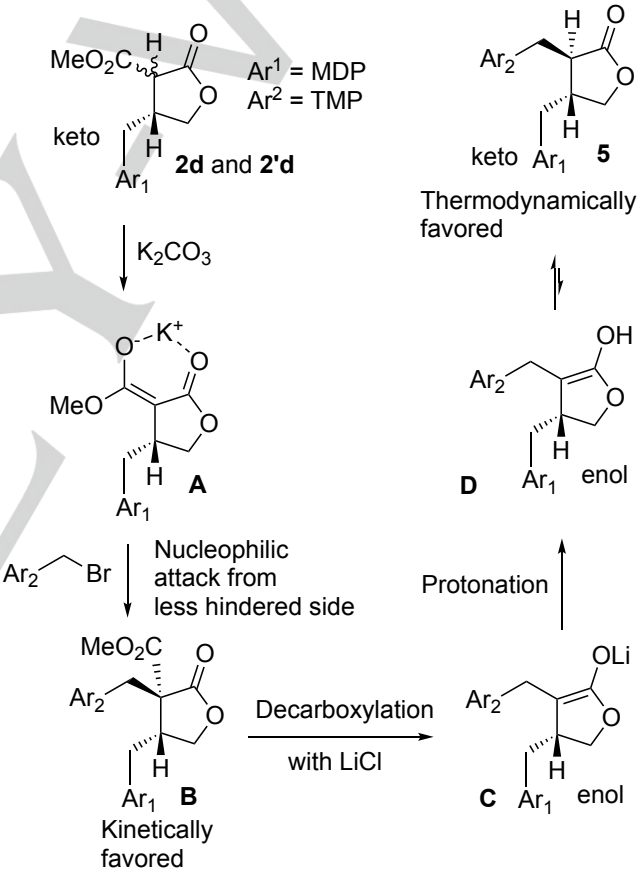

| Entry | Substrates | Products | Yield [a] (%) |
|---|---|---|---|
| 1 |  **3a** |  **4a** | 95[c] |
| 2 |  **3b** |  **4b** | 13[c] 90[d] |
| 3 |  **3c** |  **4c** | 0[d] 0[b,d] |
| 4 |  **3d** |  **4d** | 0[d] |
| 5 |  **3e** |  **4"e** | 33[c,e] |
| 6 |  **3e** |  **4'e** | 85[f] |

[a] Isolated yield; [b] $Pd(OH)_2$-C was used instead of Pd-C; [c] $t$ = 0.5 h; [d] $t$ = 1.5 h; [e] 62% of **3e** was recovered; [f] $t$ = 18 h.

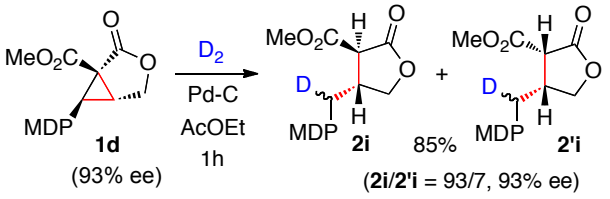



**Scheme 2**. Total synthesis of yatein (**5c**).

The utility of this hydrogenolysis in total synthesis was demonstrated by the asymmetric total synthesis of yatein (**5**) from lactones **2d** and **2'd**, which proceeded in 93% ee (Scheme 2). Specifically, the benzylation of a 93:7 mixture of **2d** and **2'd** under basic conditions, followed by decarboxylation using LiCl in DMSO at 150 °C, furnished (-)-yatein (**5**) in 65% yield (over 2 steps) with 93% ee and excellent *trans*-selectivity (98:2). The spectral data of **5** were in good accordance with those reported previously.[8] We assumed that the tautomerization from the enol- (**E**) to the keto-form (**5**) furnished the thermodynamically favored *trans*-product **5** with excellent dr (Scheme 3). In the literature, a similar decarboxylation using LiCl in DMF generated similar lignan lactones as a 85:15 mixture of the *trans*- and *cis*-isomers.[7] Therefore, Bouyssi and Balme *et. al*. treated the mixture of *trans* and *cis* isomers with DBU in $CH_2Cl_2$ to enrich the *trans*-isomer (19:1).[7a] In our case, the decarboxylation at 150 °C in DMSO provided the *trans*-product with excellent *trans*-selectivity (98:2).




**Scheme 3**. Highly *trans*-selective synthetic pathway to yatein (**5**).




**Scheme 4.** Ring-opening deuteration of bicyclic lactone **1d**.

Treatment of bicyclolactone **1d** with $D_2$ in the presence of a catalytic amount of Pd-C in AcOEt afforded deuterated lactone **2i** in 85% yield (Scheme 4). The deuteration occurred only at the benzylic position, and afforded a 93:7 mixture of **2i** and **2'i**, even though trace amounts of deuteration at the α-position of the ester were also observed.[9a] The hydrogen at the α-position of **2i** and **2'i** might stem from $H_2O$ present in the charcoal of Pd-C and/or the solvents.[9] At this point, the reaction mechanism remains ambiguous.

## Conclusions

In conclusion, we established a synthetic protocol for the highly regioselective reductive ring-opening of enantioenriched D–A cyclopropanedicarboxylic diesters using $H_2$ (1 atm) and a catalytic amount of Pd-C, which afforded the ring-opened products in high ee. The synthetic utility of the present reaction was demonstrated by the asymmetric total synthesis of yatein with high ee (93% ee) and excellent dr (98:2). The present reaction can also be used as a new protocol for the asymmetric synthesis of γ-substituted diesters and *trans*-α,β-disubstituted γ-butyrolactones. In addition, a reaction of a D-A cyclopropane with $D_2$ in the presence of a catalytic amount of Pd-C afforded the mono-deuterated ring-opened product. Mechanistic studies are currently in progress in our laboratory. The results of the present study thus provide insight into the reactivity and regioselectivity of the reductive bond cleavage in D-A cyclopropanes.

## Experimental Section

A summary of the preparative procedures, hydrolyses, asymmetric total synthesis of yatein, and the determination of ee values is shown in Scheme **5**, and details are described in the ESI.

**Preparation of bicyclic D–A cyclopropanes 1a-h.**

Bicyclolactones **1a**-**1h** were prepared according to previous reports.[4f,h,i] For the details of the synthesis of **1a**, **1c**, **1d**, and **1f**, as well as their characterization, see the Supporting Information of these reports.

**Typical procedure for the catalytic hydrogenolysis of 1a to afford a 91:9 mixture of 2a and 2'a**.

Pd-C (12 mg, 5 mol%) was added to a solution of ester **1a** (50 mg, 0.22 mmol) in AcOEt (1.1 mL) at 0 ˚C, followed by stirring at the same temperature for 1 h under an atmosphere of $H_2$ (1 atm, balloon). After filtration, the filtrate was concentrated under reduced pressure, and the thus obtained crude oil was purified by column chromatography ($SiO_2$, hexane/AcOEt = 2/1, v/v) to give a 91:9 mixture of **2a** and **2'a** (39 mg, 78%). **2a**: colorless liquid; $[\alpha]^{26}_D$ = 34.4° (*c* 1.00, chloroform, l = 589 nm); $^1$H NMR (400 MHz, $CDCl_3$) δ 2.79-2.89 (m, 2H), 3.35-3.25 (m, 2H), 3.69 (s, 3H), 4.01 (dd, *J* = 8.0, 9.1 Hz, 1H), 4.43 (dd, *J* = 7.0, 9.1 Hz, 1H), 7.14-7.34 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 38.2, 42.0, 52.2, 53.4, 71.8, 127.5, 129.2, 129.3, 137.3, 168.1, 172.1; IR (NaCl, neat) 2953, 1778, 1738, 1437, 1250, 1207, 1146, 1018, 702 cm$^{-1}$, HRMS (APCI) calcd for $C_{13}H_{14}O_4$ $(M+H)^+$ 233.0808 , found 233.0805 ; HPLC analysis: 95% ee [Daicel CHIRALPAK IC (25 cm) at 25 ˚C, flow rate = 1.0 mL/min, solvent: hexane/ethanol = 2/1 (v/v), $t_R$(racemic) = 10.2 min and 13.7 min, $t_R$(**2a**) = 9.6 min for the major and 12.9 min for the minor product]. Selected data for **2'a** (minor product): $^1$H NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 9.7, 13.9 Hz, 0.1H), 2.97 (dd, *J* = 6.1, 13.9 Hz, 0.1H), 3.07-3.20 (m, 0.1H), 3.61 (d, *J* = 8.7 Hz, 0.1H), 3.81 (s, 0.3H), 4.22-4.29 (m, 0.2H). As the absolute configuration at the β-position does not change during the hydrogenolysis, the ee values of **2a** and **2'a** were assigned on the basis of the ee value of **1a** (95% ee), which was obtained from the HPLC analysis (see ESI).

**(α*S*,β*R*)-α-Methoxycarbonyl-β-(3,4-methylenedioxyphenyl)methyl-γ-butyrolactone (2d) and (α*R*,β*R*)-α-Methoxycarbonyl-β-(3,4-methylenedioxyphenyl)methyl-γ-butyrolactone (2'd)**

Following the procedure for the hydrogenolysis of **1a** using AcOEt as the solvent at 0 ˚C, the reaction of **1d** (60 mg, 0.22 mmol) afforded a 92:8 mixture of **2d** and **2'd** (57 mg, 94%). **2d**: colorless liquid; $[\alpha]^{26}_D$ = 8.5° (*c* 1.00, chloroform, l = 589 nm); $^1$H NMR (400 MHz, $CDCl_3$) δ 2.68-2.82 (m, 2H), 3.23 (m, 1H), 3.32 (d, *J* = 8.7 Hz, 1H), 3.74 (s, 3H), 3.99 (dd, *J* = 9.0, 7.7 Hz, 1H), 4.42 (dd, *J* = 9.0, 7.2 Hz, 1H), 5.95 (s, 2H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.64 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 37.9, 42.1, 52.1, 71.8, 101.5, 108.9, 109.4, 122.3, 131.0, 147.1, 148.4, 168.1, 172.0; IR (NaCl, neat) 2955, 2909, 1778, 1738, 1504, 1491, 1445, 1242, 1148, 1038, 1018, 928, 812 cm$^{-1}$; HRMS (APCI) calcd for $C_{14}H_{14}O_6$ $(M+H)^+$ 277.0707, found 277.0715; HPLC analysis: 93% ee [Daicel CHIRALPAK IC (25 cm) at 25 ˚C, flow rate = 0.8 mL/min, solvent: hexane/ethanol = 2/1 (v/v), $t_R$(**2d**) = 14.4 min for the minor and 19.9 min for major product]. Selected data for **2'd** (minor product): $^1$H NMR (400 MHz, $CDCl_3$) δ 2.55 (dd, *J* = 9.8, 14.0 Hz, 0.09H), 2.88 (dd, *J* = 6.2, 14.0 Hz, 0.09H), 3.00-3.12, (m, 0.09H), 3.59 (d, *J* = 8.7 Hz, 0.09H), 3.81 (s, 0.27H), 4.20-4.30 (m, 0.18H). As the absolute configuration at the β -position does not change during the hydrogenolysis, the ee values of **2d** and **2'd** were assigned on the basis of the ee value of **1d** (93% ee), which was obtained from the HPLC analysis (see ESI).

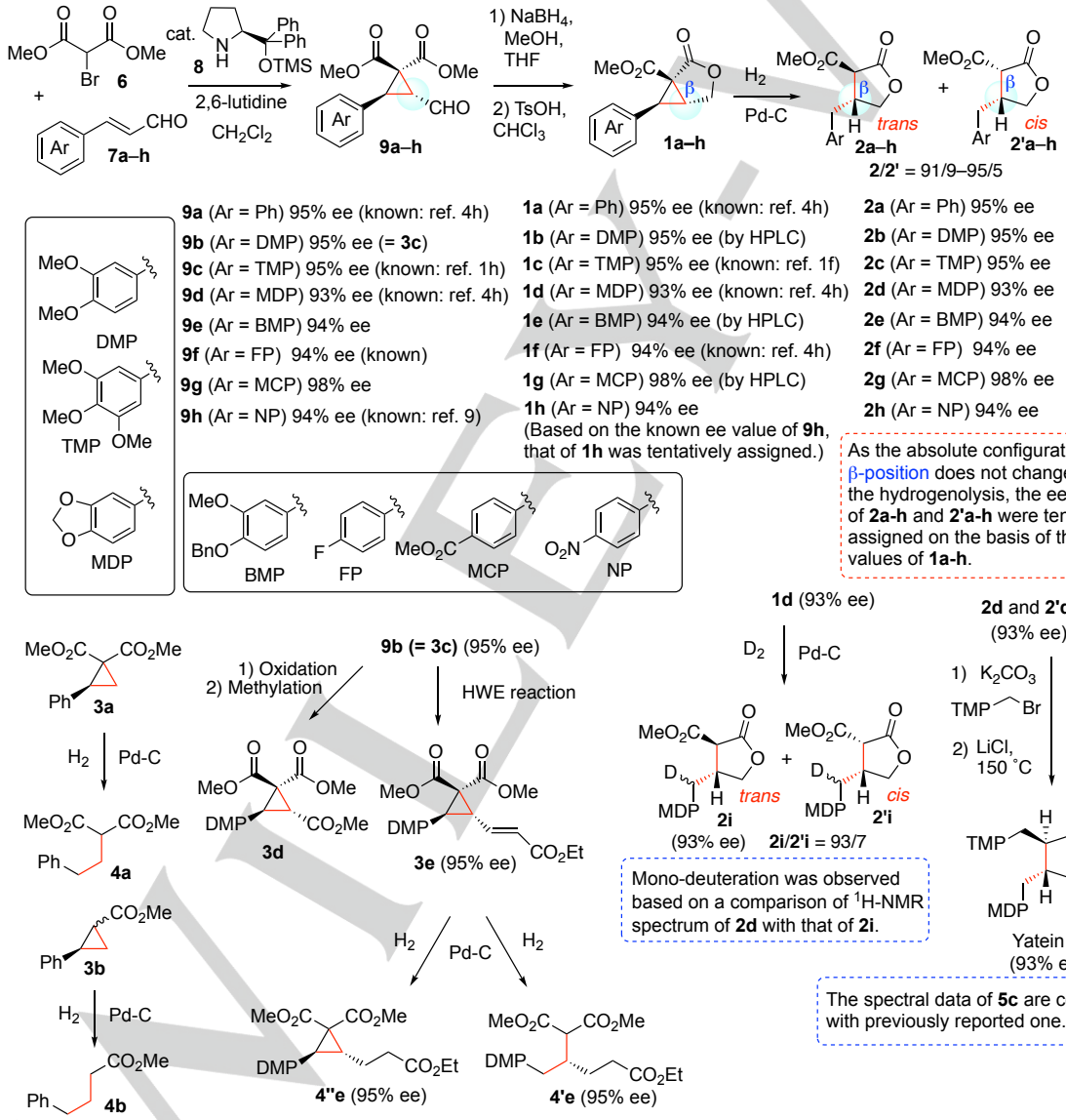
**Total synthesis of yatein from a 92:8 mixture of 2d and 2'd.**

A DMF (1 mL) solution of **2d** was added to a suspension of $K_2CO_3$ in DMF (1.0 mL) at 0 ˚C. Subsequently, a DMF solution of 3,4,5-trimethoxybenzyl bromide (394 mg, 1.5 mmol) was added at 0 ˚C, and stirring at room temperature was continued for 3 h. Aqueous HCl (1 M, 10 mL) was added to the reaction mixture, which was then extracted with AcOEt (ca. 5 x 10 mL). The organic phase was separated, washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The thus obtained crude oil was purified by column chromatography ($SiO_2$, hexane/AcOEt = 2/1, v/v) to give the product **pre-5** (422 mg, 91%). Then, LiCl (39 mg, 0.92 mmol) was added to a solution of **pre-5** (422 mg, 0.92mmol) in DMSO (0.92 mL). This mixture was

stirred for 1 h at 150 ˚C, before water (20 mL) was added. Then, the mixture was extracted with AcOEt (ca. 3 x 10 mL), the organic phase was washed with brine, dried over, $Na_2SO_4$, filtered, and concentrated under reduced pressure. The thus obtained crude oil was purified by column chromatography ($SiO_2$, hexane/AcOEt = 3/2, v/v) to furnish (-)-yatein (**5**) (262 mg, 72%). **5**: colorless liquid; $[\alpha]^{21}_D$ = -24.7° (*c* 1.00, chloroform, l = 589 nm); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.43-2.66 (m, 4H), 2.85-2.97 (m, 2H), 3.83 (s, 3H), 3.83 (s, 6H), 3.85-3.91 (m, 1H), 4.18 (dd, *J* = 7.2, 9.1 Hz, 1H), 5.92-5.95 (m, 2H), 6.36 (s, 2H), 6.45-6.49 (m, 2H), 6.70 (d, *J* = 7.5 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 178.9, 153.7, 148.3, 146.8, 137.3, 133.8, 132.0, 121.9, 109.2, 108.7, 106.7, 101.5, 71.6, 61.3, 56.5, 46.9, 41.4, 38.7, 35.7; IR (NaCl, neat) 2938, 1778, 1771, 1591, 1504, 1489, 1456, 1346, 1128, 1038, 1011, 926, 733 cm$^{-1}$; HRMS (APCI) calcd for $C_{22}H_{24}O_7$ $(M+H)^+$ 401.1595, found 401.1593. As the absolute configuration at the $\beta$ -position does not change during the transformations from **2d** to **5d**, the ee values of **5d** were assigned on the basis of the ee value of **2d** (93% ee). The spectral data of **5d** were in good accordance with reported data.[8]

**Pd-catalyzed deuteration of bicyclolactone 1d.**

Following the procedure for the hydrogenolysis of **1a** at 0 ˚C in AcOEt, the reaction of **1d** (20 mg, 72 µmol) under an atmosphere of $D_2$ instead of $H_2$ afforded a 93:7 mixture of **2i** and **2'i** (17 mg, 85%). **2i**: colorless liquid; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.76 (d, *J* = 6.9 Hz, 1H), 3.17-3.27 (m, 1H), 3.32 (d, *J* = 8.8 Hz, 1H), 3.74 (s, 3H), 3.99 (dd, *J* = 7.8, 9.0 Hz, 1H), 4.42 (dd, *J* = 7.4, 9.0 Hz, 1H), 5.95 (s, 2H), 6.60 (dd, *J* = 1.7, 7.9 Hz, 1H), 6.64 (d, *J* = 1.7, 1H), 6.75 (d, *J* = 7.9 Hz, 1H); (APCI) calcd for $C_{14}H_{13}DO_6$ $(M+H)^+$ 280.0926, found 280.0914. Selected data for **2'i** (minor product): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.86 (d, *J* = 6.2 Hz, 0.09H), 3.00-3.10, (m, 0.09H), 3.59 (d, *J* = 8.8 Hz, 0.09H), 3.81 (s, 0.27H), 4.20-4.30 (m, 0.18H). Mono-deuteration was observed based on a comparison of the $^1$H-NMR spectra of **2d** and **2i**. As the absolute configuration at the $\beta$ -position does not change during the hydrogenolysis, the ee value of **2i** was tentatively assigned based on that of **3e** (93% ee).



**Scheme 5**. Summary of the experimental work of this study including typical procedures (for details, see ESI).

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**Keywords:** hydrogenolysis • deuteration • donor-acceptor cyclopropane • cyclopropane ring opening • enantiomeric excess

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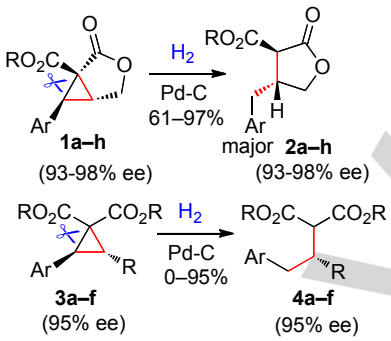
**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

## FULL PAPER

The hydrogenolysis of enantioenriched donor-acceptor (D-A) cyclopropanes **1** or **3** using 1 atm of $H_2$ and a catalytic amount of Palladium on charcoal afforded *trans*-α-alkoxycarbonyl-β-benzyl lactones **2** or γ-aryl-β-substituted-α,α-diesters **4** with high enantiomeric excess. This reaction was also successfully employed as a key step in the asymmetric total synthesis of yatein.




**Key Topic* Hydrogenolysis of cyclopropanes, Asymmetric synthesis**

*Yoshitomo Sone, Yumi Kimura, Ryotaro Ota, Takehito Mochizuki, Junki Ito and Yoshinori Nishii**

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**Catalytic hydrogenolysis of enantioenriched donor-acceptor cyclopropanes using $H_2$ and Palladium on charcoal**

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