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Rhodium-Catalyzed Asymmetric Nitroallylation of Arylmetallics with Cyclic Nitroallyl Acetates and Applications in Organic Synthesis

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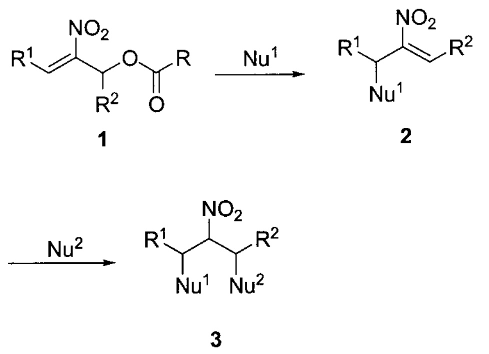
Highly enantioselective rhodium-catalyzed nitroallylations of arylboronic acids and arylzinc chlorides with cyclic nitroallyl acetates are described. Catalyst screening indicated that the rhodium complex of $[Rh(OH)(COD)]_2$ and optically pure binap is the optimal catalyst for the nitroallylation of arylboronic acids with 2-nitrocyclohex-2-enyl esters, providing good yields and high enantioselectivities of up to 99 % *ee*. The rhodium complex prepared from $Rh(acac)(C_2H_4)_2$ and (*R*)-binap efficiently catalyzed the nitroallylation of arylzinc chlorides with 2-nitrocyclohex-2-enyl acetate at 0 °C in high yields of up to 93 % and with high enantioselectivities of up to 96 % *ee*. A number of synthetically useful intermediates with high optical purity were prepared with this reaction as starting point: concise total syntheses of optically pure (+)-β-lycorane in 53 % overall yield and of (+)-γ-lycorane in 52 % overall yield were achieved by commencing with the asymmetric nitroallylation of 3,4-methylenedioxyphenylzinc chloride with 2-nitrocyclohex-2-enyl acetate.

Introduction

Organic molecules that contain multiple functionalities are always synthetically useful in organic chemistry because they can be transformed into a variety of substances through transformation of the functional groups in different organic reactions. Nitroallyl acetates **1**, as first developed by Seebach and Knochel,[1] can undergo tandem reaction sequences involving conjugated addition and ester group elimination to yield nitroolefins **2**, whilst Michael addition of further nucleophiles to the nitroolefins **2** produces nitroalkanes **3** [Equation (1)], which can be further transformed into a variety of useful compounds as the nitro group can be converted into various functionalities.[2] The utilities of these transformations involving nitroallyl acetates have been demonstrated by their applications in the organic syntheses of heterocycles and nonnatural products.[3] Despite these versatile applications, this useful transformation has not yet been operated as a catalytic asymmetric process.



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In contrast, asymmetric conjugated addition reactions of organometallics to nitroalkenes mediated by transition metal complexes have been documented.[4,5] Of those, the asymmetric addition of arylboronic acids to nitroolefins with catalysis by a rhodium complex of (*S*)-binap, recently discovered by Hayashi and co-workers,[5] has emerged as an efficient method for the preparation of optically enriched nitro-containing compounds.

Inspired by works from Seebach and Hayashi and co-workers,[1,2,5] we investigated reactions between 2-nitrocyclohex-2-enol esters **1** and arylboronic acids in the presence of chiral rhodium complexes.[6] Our preliminary results indeed indicated that the asymmetric nitroallylation of arylboronic acids with cyclic nitroallyl acetate **1a** and its structural analogues in the presence of chiral rhodium complexes proceeded smoothly, affording the chiral cyclic nitroalkenes **2** with high enantioselectivities, but in unsatisfactory yields.

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In this paper we describe highly enantioselective nitroallylations of arylboronic acids and arylzinc reagents with cyclic nitroallyl acetates **1**,[7] promoted by rhodium complexes of optically pure binap and a number of its derivatives **4**–**6** (Figure 1). The resulting nitroalkenes **2** are readily converted into a variety of optically active compounds **7** [Equation (2)], as a result of which concise syntheses of optically pure (+)-γ-lycorane (**8**)[8,9] and (+)-β-lycorane (**9**)[10] are finished in high overall yields with this reaction as starting point.

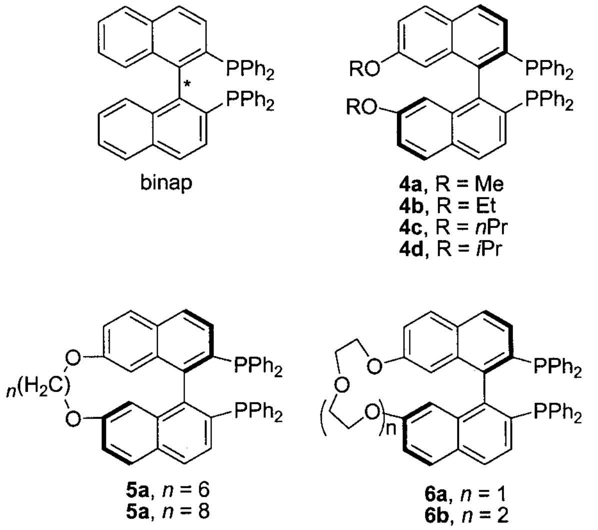
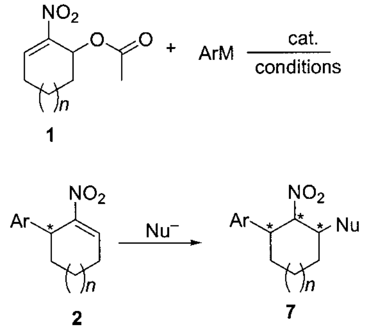


Figure 1. The chiral ligands evaluated in this study.



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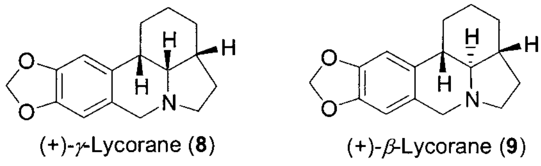


Results and Discussion

Enantioselective Nitroallylation of Arylboronic Acids and Arylzinc Chlorides with Cyclic Nitroallyl Acetates

We first investigated nitroallylation of phenylboronic acid with 2-nitrocyclohex-2-enyl acetate (**1a**)[1] with catalysis with a rhodium complex of Rh(acac)(C_2H_4)$_2$ with (*R*)-binap under the standard conditions that had been used for rhodium-catalyzed 1,4-additions of arylboronic acids to nitroalkenes.[5] We were delighted to observe that the reaction gave the desired product **2a**, the structure of which was confirmed by X-ray diffraction (Figure 2), with a high enantioselectivity of 94% *ee* (Table 1, Entry 1). The absolute configuration of the stereogenic center was determined to be *R* by correlation with a known compound **11**, which was derived from **2a** by a two-step reaction sequence involving a reduction and a functional group transformation of the nitro into a carbonyl group (Scheme 1).[5]

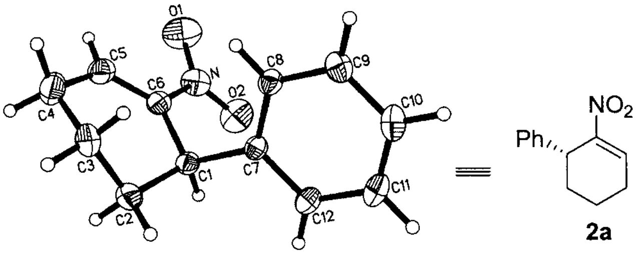
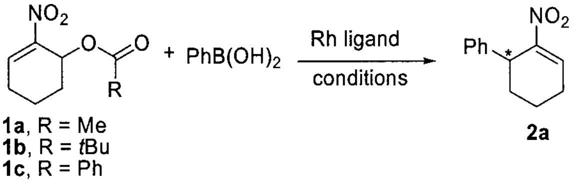


Figure 2. X-ray structure of **2a** (CCDC-289193).

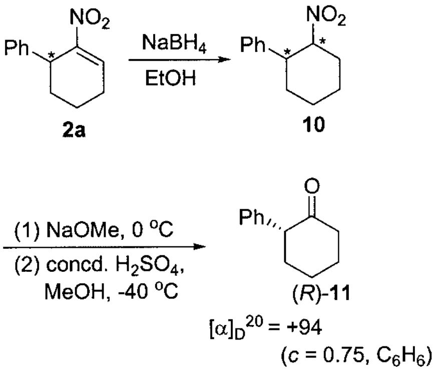
Table 1. Rhodium-catalyzed asymmetric nitroallylation of phenylboronic acid with 2-nitrocyclohex-2-enyl esters **1**.[a]



Entry	Metal	Ligand	**1**	Temp. (°C)	Time (h)	Yield (%)[b]	*ee* (%)[c]
1	Rh(acac)(C_2H_4)$_2$	(*R*)-BINAP	**1a**	100	5	30	94
2	Rh(acac)(C_2H_4)$_2$	(*R*)-BINAP	**1b**	100	5	30	95
3	Rh(acac)(C_2H_4)$_2$	(*R*)-BINAP	**1c**	100	5	48	93
4	[RhCl(COD)]$_2$	(*R*)-BINAP	**1a**	100	5	20	94
5	Rh(acac)(C_2H_4)$_2$	(*R*)-BINAP	**1a**	50	20	41	94
6	[Rh(OH)(COD)]$_2$	(*R*)-BINAP	**1a**	50	20	55	97
7	[Rh(OH)(COD)]$_2$	(*S*)-BINAP	**1a**	50	20	56	97
8	[Rh(OH)(COD)]$_2$	**4a**	**1a**	50	20	43	97
9	[Rh(OH)(COD)]$_2$	**4b**	**1a**	50	20	51	94
10	[Rh(OH)(COD)]$_2$	**4c**	**1a**	50	20	48	90
11	[Rh(OH)(COD)]$_2$	**4d**	**1a**	50	20	36	95
12	[Rh(OH)(COD)]$_2$	**5a**	**1a**	50	50	44	86
13	[Rh(OH)(COD)]$_2$	**5b**	**1a**	50	20	36	97
14	[Rh(OH)(COD)]$_2$	**6a**	**1a**	50	20	45	77
15	[Rh(OH)(COD)]$_2$	**6b**	**1a**	50	20	48	90

[a] Treatment of arylboronic acid was performed in the presence of 5 mol-% rhodium complex and 6 mol-% (*R*)-binap in a solvent mixture of dioxane/H_2O = 10:1. [b] Isolated yield. [c] The *ee* values were determined by GC.

The product **2a**, however, was isolated in only 30% yield as the starting substrate **1a** decomposed at 100 °C, so further optimization of the reaction conditions was required (Table 1). The use of 2-nitrocyclohex-2-enyl pivalate (**1b**) to replace **1a** as a substrate did not suppress the decomposi-



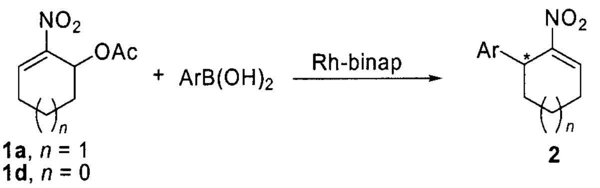
Scheme 1. The conversion of **2a** into (*R*)-2-phenylcyclohexanone (**11**) for determination of the absolute configuration of **2a**.

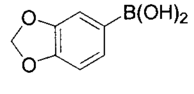
tion, and a low yield was still observed, though with the enantioselectivity maintained (Table 1, Entry 2). Although a higher yield was observed with **1c**, the enantioselectivity was decreased slightly (Entry 3), whilst the yield could be slightly improved to 41% by performing the reaction at 50 °C (Entry 4). Screening of the transition metal source revealed $[Rh(OH)(COD)]_2$[11] to be a better precatalyst (Entries 1–6), so further improvement in the yield and the enantioselectivity was achieved by using a rhodium complex generated in situ from $[Rh(OH)(COD)]_2$ and (*R*)- or (*S*)-binap, which catalyzed the reaction in good yield with 97% *ee* at 50 °C, with minimization of the decomposition of **1a** (Entries 6 and 7).

The rhodium complexes of the 7,7′-disubstituted binaps **4**–**6**, prepared starting with asymmetric oxidative coupling,[12] and $[Rh(OH)(COD)]_2$ were also examined for the model reaction (Entries 8–15), which indicated that the substitution of the ligand has a considerable influence over the stereocontrol. Of these ligands, **4a** and **5b** exhibited higher enantioselectivities than their structural analogues, though much lower enantioselectivities of 86% and 77% *ee* were observed with rhodium complexes formed from $[Rh(OH)(COD)]_2$ and **5a** and **6a**, respectively (Entries 12 and 14). The effect of the substituent on the enantioselectivity might be a function of variation of the dihedral angle.[13] Although comparable enantioselectivities was observed with **4a** and **5b**, the yields were lower than those with binap (Entries 6–8 and 13), so the rhodium complex of $[Rh(OH)(COD)]_2$ and binap can be regarded as an optimal catalyst system in terms both of catalytic activity and of enantioselectivity.

The scope of the optimal catalyst generated from $[Rh(OH)(COD)]_2$ and (*S*)-binap was then extended to catalyze the nitroallylation of a range of arylboronic acids bearing either electron-donating or electron-withdrawing substituents with cyclic nitroallyl acetates **1a** and **1d**. As shown

Table 2. Scope and limitations of the rhodium-catalyzed asymmetric nitroallylation of arylboronic acids.[a]



Entry	1	$ArB(OH)_2$	Product	Yield (%)[b]	*ee* (%)[c]
1	**1a**	$PhB(OH)_2$	**2a**	56	97
2	**1a**	$4\text{-}MeC_6H_4B(OH)_2$	**2b**	63	95
3	**1a**	$4\text{-}MeOC_6H_4B(OH)_2$	**2c**	58	96
4	**1a**	$4\text{-}ClC_6H_4B(OH)_2$	**2d**	64	99
5	**1a**	$4\text{-}FC_6H_4B(OH)_2$	**2e**	61	98
6	**1a**	4-*t*Bu-$C_6H_4B(OH)_2$	**2f**	67	90
7	**1a**	$4\text{-}CF_3C_6H_4B(OH)_2$	**2g**	52	94
8	**1a**	$3\text{-}MeOC_6H_4B(OH)_2$	**2h**	58	96
9	**1a**		**2i**	65	98
10	**1d**	$PhB(OH)_2$	**2j**	40	17

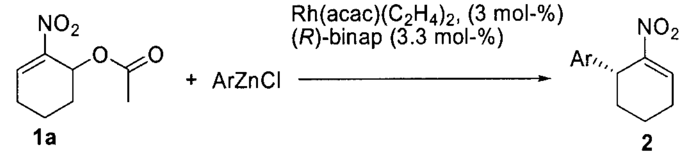
[a] The reaction of arylboronic acid was performed in the presence of 5 mol-% Rh and 6 mol-% (*S*)-binap in a solvent mixture of dioxane/H_2O = 10:1. [b] Isolated yield. [c] The *ee* values were determined by GC or HPLC.

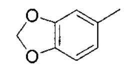
in Table 2, the reactions between 2-nitrocyclohex-2-enyl acetate (**1a**) and arylboronic acids gave the desired products in good yields and with excellent enantioselectivities ranging from 90–99% *ee* (Entries 1–9). The electronic nature of the substituents in the arylboronic acids did not significantly affect the reaction, but the enantioselectivity did to some degree depend on the steric bulkiness of the arylboronic acids: an enantioselectivity of only 90% *ee*, for example – much lower than those of its structural analogues – was observed for 4-*tert*-butylphenylboronic acid (Entry 6). The stereoselectivity of this type of reaction is also quite sensitive to the ring size of the cyclic nitroallyl acetate: much lower enantioselectivity was observed in, for example, the reaction between 2-nitrocyclopent-2-enyl acetate (**1d**) and phenylboronic acid (Entry 10).

Conducting the rhodium-catalyzed asymmetric nitroallylation at low temperature generally prevents the decomposition of the 2-nitrocyclohex-2-enyl esters, such decomposition being a possible reason for the low yield. Use of more reactive arylmetallic species to replace arylboronic acids may make the reaction proceed at a lower temperature so that the yield might be improved. Conjugated additions of arylzinc compounds to electron-deficient unsaturated olefins catalyzed by rhodium complexes have been discovered,[7a] and in this case the reaction can be carried out below room temperature. To improve the yield, asymmetric nitroallylation of **1a** with arylzinc was investigated (Table 3).

The asymmetric nitroallylation was examined in the presence of a rhodium complex of Rh(acac)(C_2H_4)$_2$ and (*R*)-binap as a catalyst and phenylzinc chloride as a nucleophilic species. The organozinc is indeed more reactive than the organoboronic acid toward the nitroallyl acetate: the nitroallylation of phenylzinc chloride with **1a** proceeded smoothly at 20 °C and even at 0 °C, giving rise to **2a** in high yields ranging from 75% to 93% (Entries 1–4). The solvent dramatically affects the enantioselectivity: use of THF as a solvent gave the highest enantioselectivity, of 85% *ee* at 20 °C (Entry 1) and improved to 93% *ee* by conducting the reaction at 0 °C (Entry 5). Asymmetric nitroallylations of some other arylzinc compounds with **1a** were also studied under these reaction conditions (Entries 6–11): the nitroallylations of arylzinc chlorides proceeded at 0 °C to generate the products in much higher yields than obtained with arylboronic acids, but the enantioselectivity had decreased by small amounts, probably due to the occurrence of the background reaction. Excellent enantioselectivities were observed, though, in the cases of 4-fluorophenyl-, phenyl-, and 3,4-methylenedioxyphenylzinc chlorides (Entries 5, 8, and 10).

Table 3. The nitroallylation of PhZnCl acetic acid with 2-nitrocyclohex-2-enyl ester **1a**.[a]

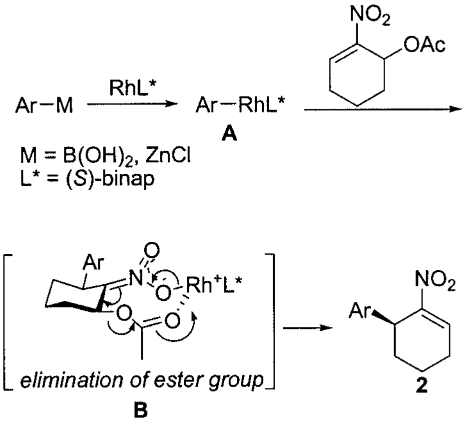


Entry	Product	Ar	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	*ee* (%)[c]
1	**2a**	Ph	THF	20	20	80	85
2	**2a**	Ph	Et_2O	20	20	75	23
3	**2a**	Ph	Toluene	20	20	89	23
4	**2a**	Ph	CH_2Cl_2	20	20	82	21
5	**2a**	Ph	THF	0	25	93	93
6	**2b**	4-MeC_6H_4	THF	0	25	90	86
7	**2c**	4-$MeOC_6H_4$	THF	0	25	79	89
8	**2e**	4-FC_6H_4	THF	0	25	91	96
9	**2h**	3-$MeOC_6H_4$	THF	0	25	83	88
10	**2i**		THF	0	25	89	96
11	**2k**	3-MeC_6H_4	THF	0	25	88	85

[a] Treatment of organozinc reagents was performed in the presence of 3 mol-% Rh(acac)(C_2H_4)$_2$ and 3.3 mol-% (*R*)-binap in THF. [b] Isolated yield. [c] The *ee* values were determined by GC or HPLC.

Mechanism Consideration

A plausible mechanism to account for the results obtained in the reaction is proposed in Scheme 2. The reaction is considered to begin with a transmetalation between the chiral rhodium complex of binap and an arylboronic acid or an arylzinc chloride to form the arylrhodium(I) species **A**,[14] and the insertion of the carbon–carbon double bond of the nitroallyl acetate into the Ar–Rh bond produces a key intermediate **B**,[5,14] which undergoes a β-elimination of the ester group to regenerate the catalyst and liberate the product **2**.[15]

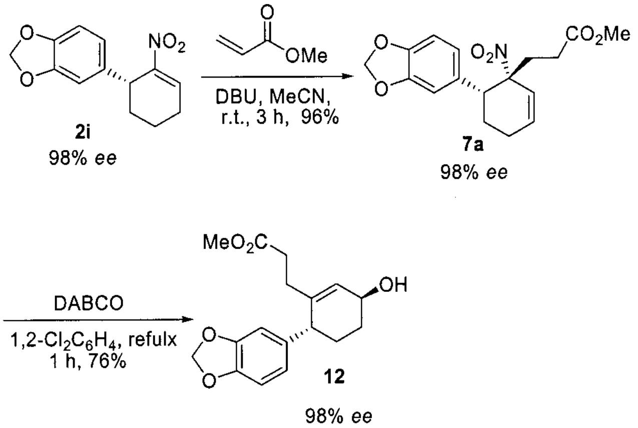


Scheme 2. A plausible mechanism for the asymmetric nitroallylation.

Application in the Synthesis of Chiral Synthetically Useful Compounds

The optically active nitroalkenes **2** obtained by the rhodium-catalyzed asymmetric addition presented here should be useful chiral building blocks since they should be readily transformable into a wide variety of optically active compounds **7** through organic reactions either at their electron-deficient carbon–carbon double bonds or at the nitro groups as mentioned in the preceding section, see Equation (2).[1,3]

To indicate the versatile utility of nitroalkenes **2**, Michael addition of enantio-enriched **2i** (98% *ee*) to methyl acrylate in the presence of DBU as a base (Scheme 3) was first tested, providing **7a** in a high yield and with a maintained enantiomeric excess (98% *ee*).[16] The relative configuration between the two contiguous stereogenic carbon atoms in **7a** was identified as *cis* by X-ray crystallographic analysis (Figure 3). Following treatment with DABCO, the com-



Scheme 3. Conversion of **2i** to methyl 3-[6-(benzo[1,3]dioxol-5-yl)-3-hydroxycyclohex-1-enyl]propionate (**12**).

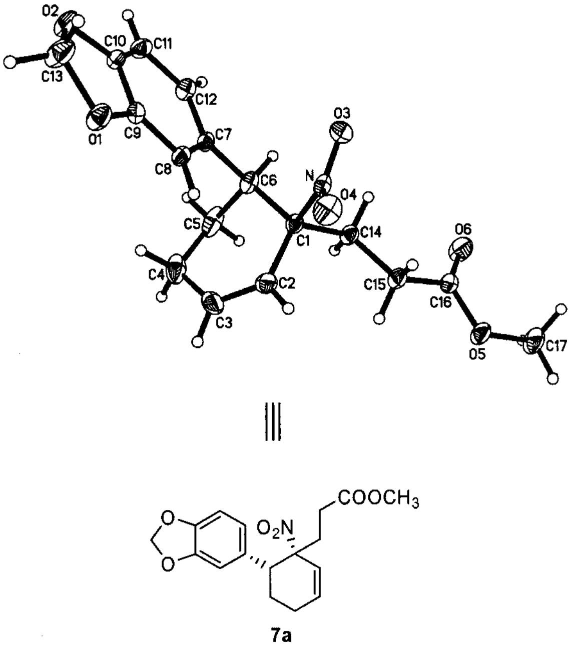
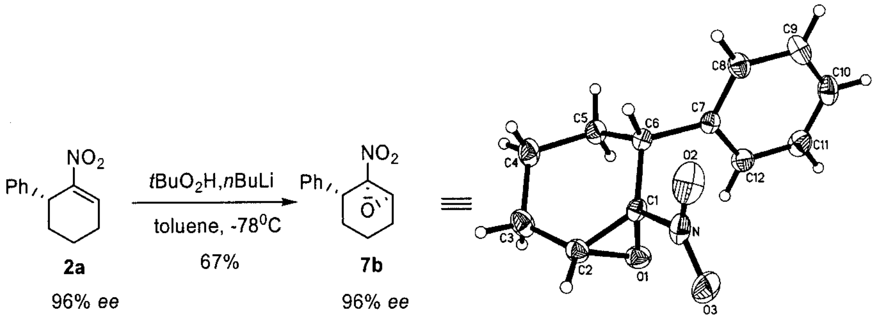


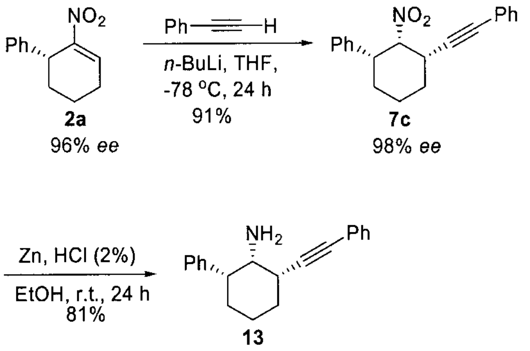
Figure 3. X-ray structure of **7a** (CCDC-605923).



Scheme 4. Diastereoselective epoxidation of **2a** to **7b** (CCDC-605922).

pound **7a** underwent a rearrangement reaction to be transformed into **12**, a promising precursor for the syntheses of enones and corresponding acetates or carbonates, in 76% yield with no loss of enantioselectivity.

Diastereoselective epoxidation of **2a** with lithium *tert*-butyl peroxide (*t*BuOOLi),[17] generated in situ from *tert*-butyl hydroperoxide and *n*-butyllithium in toluene at –78 °C, furnished **7b** as the sole diastereomer in a good yield and with a high enantioselectivity of 96% *ee* (Scheme 4). The X-ray crystal structure analysis of **7b** showed the phenyl group to be *syn* to the oxirane ring.



Scheme 5. Preparation of chiral amine **13** from **2a**.

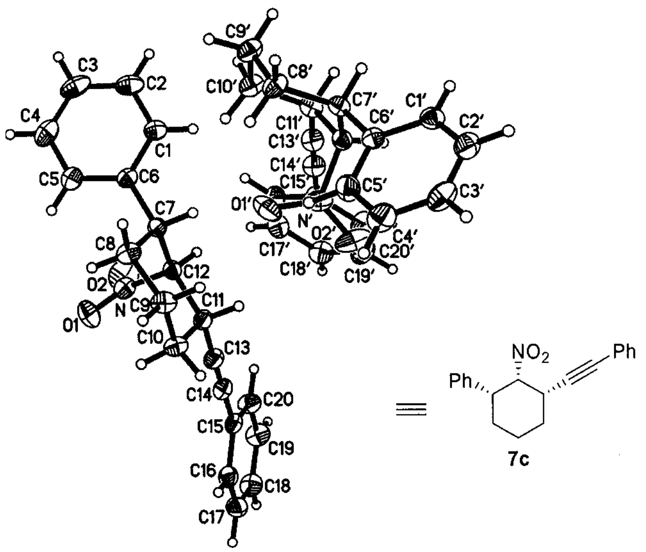


Figure 4. X-ray structure of **7c** (CCDC-605921).

Conjugated addition of phenylethynyllithium, prepared in situ from phenylacetylene and *n*-butyllithium, to **2a** in THF at –78 °C over 24 h gave **7c** as the sole diastereomer in 91% yield and with 98% *ee* (Scheme 5). The substituents at the three contiguous stereogenic centers are all *cis* on the basis of X-ray crystallographic analysis of **7c** (Figure 4). Reduction of **7c** with a combined reagent consisting of zinc powder and 2% HCl aqueous solution in ethanol at room temperature generated **13** in 81% yield.

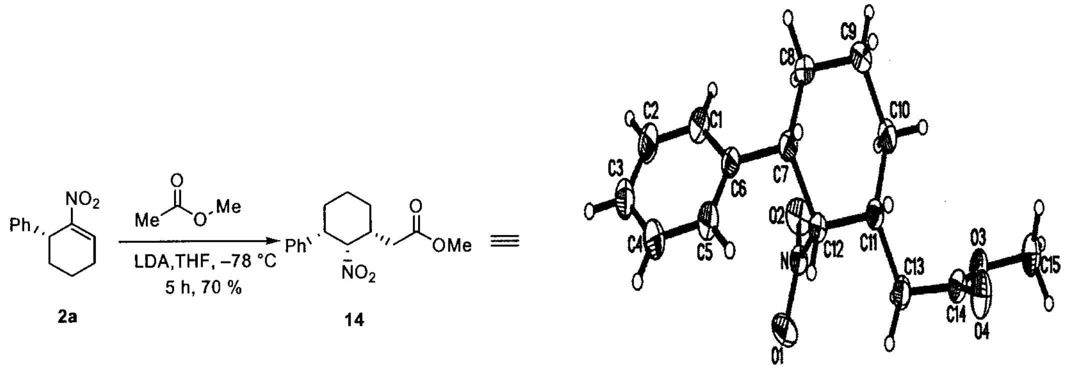
Michael addition of an enolate prepared in situ from methyl acetate and lithium diisopropylamide (LDA) at –78 °C to **2a** furnished compound **14** (CCDC-605920) in 70% yield and in a high diastereomeric ratio of 12:1 in favor of the *cis*,*cis* diastereomer, as determined by X-ray crystallographic analysis (Scheme 6).

Total Synthesis of Optically Pure (+)-γ-Lycorane and (+)-β-Lycorane

β- and γ-Lycorane are deoxygenated skeletons of Amarylliaceae alkaloids.[18] The syntheses of these molecules have received much attention from synthetic chemists because of the challenging tetracyclic galanthan skeleton and their potent biological activity.[19] Despite the apparent absence of useful pharmaceutical properties, lycorane has become a popular target for illustrating potential new strategies for the synthesis of this family of alkaloids.

All of the ring junctures in γ-lycorane are *cis*[20] and total syntheses of racemic γ-lycorane have been reported by several groups.[8] A number of efforts[9] geared towards asymmetric syntheses of optically active (+)-γ-lycorane have also been reported, but with only one example involving the asymmetric catalytic construction of the stereogenic centers (with 46% *ee*[9a]) a concise asymmetric catalytic total synthesis of optically pure (+)-γ-lycorane is of great importance.

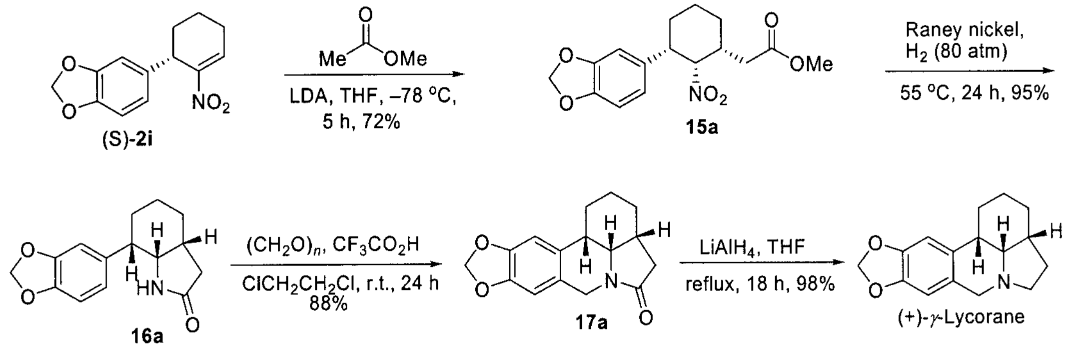
Asymmetric nitroallylation either of 3,4-methylenedioxyphenylboronic acid or of 3,4-methylenedioxyphenylzinc chloride with 2-nitrocyclohex-2-enyl acetate (**1a**) was applied to a concise asymmetric total synthesis of (+)-γ-lycorane (Scheme 7). Nitroallylation of 3,4-methylenedioxyphenylboronic acid with **1a** in the presence of 5 mol-% rhodium



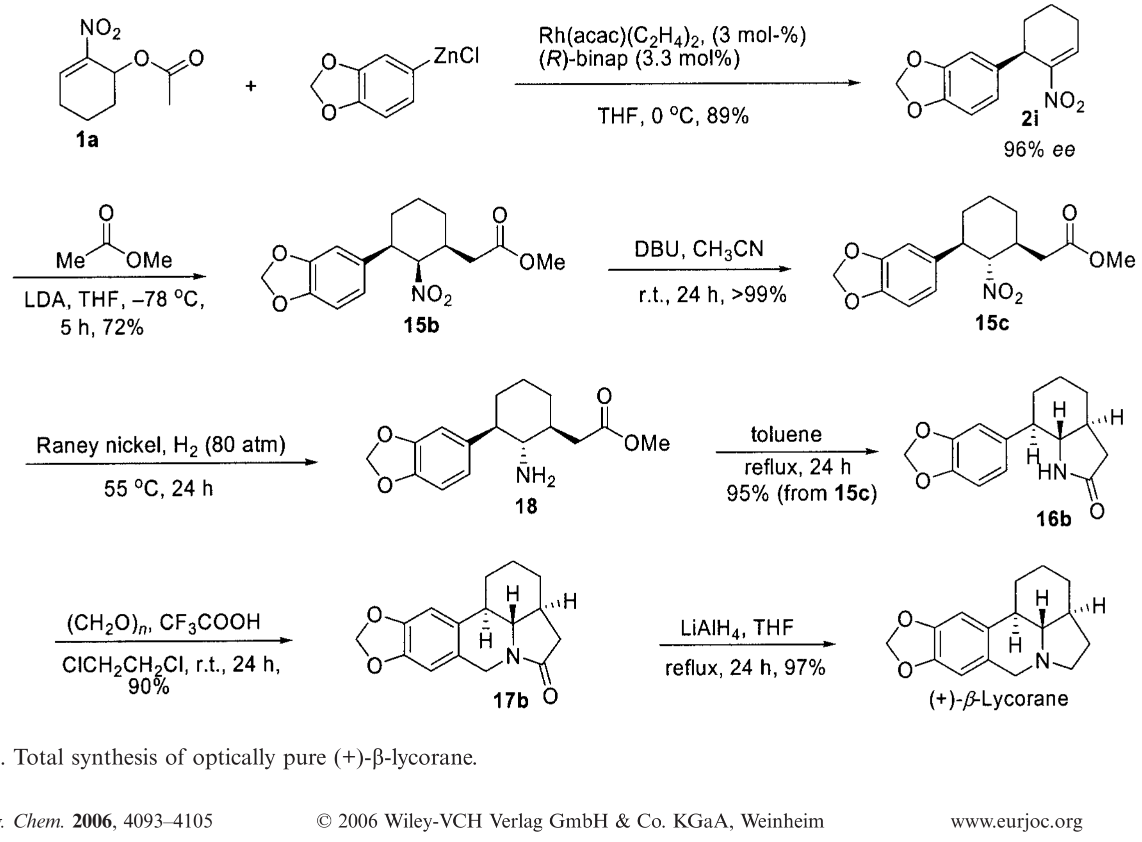
Scheme 6. Diastereoselective Michael addition of an enolate to **2a**.

complex of $[Rh(OH)(COD)]_2$ and (*S*)-binap gave the product **2i** in 65% yield and with 98% *ee* (Table 2, Entry 9), whilst the similar reaction with 3,4-methylenedioxyphenylzinc chloride catalyzed by 3 mol-% rhodium complex of $Rh(acac)(C_2H_4)_2$ and (*S*)-binap afforded the product **2i** in an improved yield of 89% yield and with an excellent enantioselectivity of 96% *ee* (Table 3, Entry 10). Treatment of **2i** with methyl acetate and lithium diisopropylamide (LDA) at –78 °C furnished compound **15a** in a high diastereomeric ratio of 7:1 in favor of the *cis,cis* diastereomer. The *cis,cis*-**15a** was subjected to Raney nickel-catalyzed hydrogenation under 80 atmosphere of hydrogen at 55 °C, which directly formed lactam **16a** in 95% yield. A modified Pictet–Spengler ring closure[21] of **16a** with paraformaldehyde and trifluoroacetic acid afforded **17a** in 88% yield, and reduction of **17a** with lithium aluminum hydride gave (+)-γ-lycorane in 98% yield with an optical rotation consistent with that of the natural product.[20] The overall yield of this concise total synthesis of optically pure (+)-γ-lycorane from the reaction between **1a** and 3,4-methylenedioxyphenylboronic acid is 38%, and was improved to 52% when the synthesis commenced with the reaction between **1a** and 3,4-methylenedioxyphenylzinc chloride.

Efforts toward the total syntheses of racemic β-lycorane have been undertaken,[10] but in contrast, no asymmetric synthesis of optically active (+)-β-lycorane has yet appeared, so such an asymmetric synthesis would be desirable. The relative configuration between the aryl and the nitro groups in β-lycorane is *trans*, whilst that between aryl and acetate is *cis*. (+)-β-Lycorane was also synthesized in the same way as (+)-γ-lycorane (Scheme 8), starting with the nitroallylation of 3,4-methylenedioxyphenylzinc chloride with **1a** in the presence of 3 mol-% rhodium complex of $Rh(acac)(C_2H_4)_2$ and (*R*)-binap to yield the product (*R*)-**2i** with 96% *ee*. Treatment of **2i** with methyl acetate and lithium diisopropylamide (LDA) at –78 °C furnished com-



Scheme 7. Highly enantioselective total synthesis of (+)-γ-lycorane.



Scheme 8. Total synthesis of optically pure (+)-β-lycorane.

pound **15b** in a high diastereomeric ratio of 7:1 in favor of the *cis*,*cis* diastereomer, treatment of **15b** with DBU in CH_3CN at room temperature for 24 h provided a thermodynamically stable diastereomer **15c** in a quantitative yield, and Raney nickel-catalyzed hydrogenation of **15c** under 80 atmospheres of hydrogen at 55 °C proceeded to generate **18**, which was converted to **16b** in an overall 95% yield by heating at reflux in toluene for 24 h. A Pictet–Spengler ring closure[21] of **16b** with paraformaldehyde and trifluoroacetic acid under conditions similar to those used for the synthesis of **17a** provided **17b** in 90% yield, and reduction of **17b** with lithium aluminum hydride in THF at reflux over 24 h gave (+)-β-lycorane in 97% yield with an optical rotation consistent with that of the natural product.[20] The overall yield of this concise total synthesis of optically pure (+)-β-lycorane from **1a** is 53% (Scheme 8). It is worth noting that this represents the first example of total synthesis of optically pure β-lycorane.

Conclusions

In conclusion, we have developed an enantioselective rhodium-catalyzed nitroallylation of arylboronic acids and organozinc reagents with nitroallyl acetates. This study demonstrates that the rhodium complex of $[Rh(OH)(COD)]_2$ and optically pure binap is an optimal catalyst, providing high enantioselectivities ranging from 90–99% *ee*s for the nitroallylation of various arylboronic acids. The rhodium complex of $Rh(acac)(C_2H_4)_2$ and (*R*)-binap shows high enantioselectivity and catalytic activity for the nitroallylation of organozinc reagents. A number of chiral synthetic intermediates have been readily prepared from the products of the asymmetric nitroallylation. Concise total syntheses of optically pure (+)-γ-lycorane in 38% overall yield by starting with nitroallylation of arylboronic acids with nitroallyl acetates and in an overall 52% yield by starting with nitroallylation of organozinc reagents with nitroallyl acetates have been accomplished and the first total synthesis of optically pure (+)-β-lycorane was completed in an overall yield of 53% commencing from the asymmetric nitroallylation of organozinc reagents with nitroallyl acetates.

Experimental Section

General Techniques: All manipulations were carried out under argon. NMR spectra were recorded with a Bruker 300-MHz spectrometer. Mass spectra were recorded with a VG 7070E instrument. Elemental analysis was recorded with a Carlo Erba 1106 instrument. HR-MS (ESI) spectra were recorded with a Bruker Bio-TOF Q instrument. THF, toluene, and dioxane were dried with sodium/benzophenone. Diethyl ether, petroleum ether (PET) and ethyl acetate for column chromatography were distilled before use. CCDC-289193 (**2a**), -605923 (**7a**), -605922 (**7b**), -605921 (**7c**), -605920 (**14**) 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.

General Procedure for the Asymmetric Nitroallylation of Arylboronic Acids with Nitroallyl Acetates Catalyzed by Chiral Rhodium Complexes: Under argon, a solution of $[Rh(OH)(COD)]_2$ (3.4 mg, 15 μmol, 5 mol-% Rh), (*S*)-binap (11.2 mg, 18 μmol, 6 mol-%) and phenylboronic acid (183 mg, 1.5 mmol, 5 equiv.) in 1,4-dioxane (1.0 mL) was stirred at 50 °C for 2 h. Then a solution of the cyclic nitroallyl acetate (0.3 mmol) in 1,4-dioxane (1.0 mL) was added to the reaction mixture, followed by addition of water (200 μL). The reaction mixture was stirred at 50 °C for another 20 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (diethyl ether/PET, 1:20).

1-Nitro-6-phenylcyclohexene (2a): Yield 34 mg, 56%; white solid, m.p. 71.3–72.0 °C. $[\alpha]_D^{20} = +92.5$ ($c = 1.07$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3456, 3023, 2946, 2920, 2867, 1663, 1510, 1491, 1451, 1413, 1333, 1077, 938 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.55–1.62 (m, 2 H), 1.89–1.92 (m, 1 H), 2.01–2.03 (m, 1 H), 2.40–2.49 (m, 2 H), 4.29 (br. s, 1 H), 7.14–7.34 (m, 5 H), 7.57 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.5, 25.0,31.5, 39.5, 126.7, 127.1, 128.5, 136.2, 141.9, 150.9 ppm. HRMS: calcd. for $C_{12}H_{13}NO_2$ 203.0940, found 203.0928. $C_{12}H_{13}NO_2$ (203.09): calcd. C 70.93, H 6.41, N 6.89; found C 70.84, H 6.44, N 6.84. Enantiomeric excess: 96%, detemined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

Crystal Data of 2a: CCDC-289193, $C_{12}H_{13}NO_2$ (203.23), orthorhombic, space group $P2_12_12_1$, a = 6.1206(5), b = 12.592(1), c = 14.007(1) Å, V = 1079.57(12) $Å^3$, T = 290(2) K, Z = 4, $D_{calcd.}$ = 1.250 mg/m^3, μ = 0.085 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 432, crystal size 0.56 × 0.50 × 0.42 mm, 1483 reflections collected, 1380 [R(int) = 0.0122]; refinement method: full-matrix least squares on F^2; goodness-of-fit on F^2 = 0.961, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0327, wR_2 = 0.0652.

6-(4-Methylphenyl)-1-nitrocyclohexene (2b): Yield 41 mg, 63%, white solid, m.p. 54.4–55.9 °C. $[\alpha]_D^{20} = +84.3$ ($c = 0.86$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3447, 3022, 2950, 2872, 1660, 1506, 1336, 809 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.57 (m, 2 H), 1.89 (m, 1 H), 2.00 (m, 1 H), 2.32 (s, 3 H), 2.39 (m, 2 H), 4.26 (br. s, 1 H), 7.04 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.55 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.4, 20.8, 24.9, 31.5, 39.0, 126.9, 129.1, 135.9, 136.2, 138.8, 151.0 ppm. HRMS: calcd. for $C_{13}H_{15}NO_2$ 217.1097, found 217.1095. Enantiomeric excess: 95%, determined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

6-(4-Methoxyphenyl)-1-nitrocyclohexene (2c): Yield 41 mg, 58%; white solid, m.p. 56.8–57.9 °C. $[\alpha]_D^{20} = +93.4$ ($c = 1.06$, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3494, 2996, 2859, 2936, 2833, 1658, 1613, 1507, 1460, 1448, 1336, 1258, 1177, 1031, 823, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.54–1.61 (m, 2 H), 1.82–1.88 (m, 1 H), 1.96–2.00 (m, 1 H), 2.39–2.47 (m, 2 H), 3.77 (s, 3 H), 4.23 (br. s, 1 H), 6.81 (d, J = 11.5 Hz, 2 H), 7.04 (d, J = 11.5 Hz, 2 H), 7.52 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.5, 25.0, 31.6, 38.7, 55.2, 113.9, 128.1, 134.0, 135.8, 151.2, 158.3 ppm. HRMS: calcd. for $C_{13}H_{15}NO_3$ 233.1046, found 233.1033. Enantiomeric excess: 95%, determined by chiral HPLC [Daicel Chiralpak OD; hexane/2-propanol, 99:1; flow 1.0 mL/min; (*R*) isomer: t_R = 12.4 min; (*S*) isomer: t_R = 14.5 min].

6-(4-Chlorophenyl)-1-nitrocyclohexene (2d): Yield 45 mg, 64%; colorless oil. $[\alpha]_D^{20} = +102.2$ ($c = 1.15$, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2943, 2867, 1662, 1517, 1488, 1336, 1091, 1013, 819. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25–1.62 (m, 2 H), 1.84–1.87 (m, 1 H), 2.03 (m, 1 H), 2.41–2.48 (m, 2 H), 4.24 (br. s, 1 H), 7.06 (d, J = 11.0 Hz, 2 H), 7.24 (d, J = 11.0 Hz, 2 H), 7.56 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.5, 24.9, 31.4, 39.0, 128.4, 128.7, 132.5, 136.6, 140.5, 150.5 ppm. HRMS calcd. for $C_{12}H_{12}ClNO_2$ 237.0551, found 237.0569. Enantiomeric excess: 99%, determined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

6-(4-Fluorophenyl)-1-nitrocyclohexene (2e): Yield 40 mg, 61%; colorless oil. $[\alpha]_D^{20}$ = +87.3 (c = 1.22, CHCl$_3$). IR (neat): $\tilde{\nu}$ = 3069, 2945, 2868, 1662, 1602, 1509, 1336, 1222, 826, 816 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.52–1.61 (m, 2 H), 1.84–1.87 (m, 1 H), 2.02 (m, 1 H), 2.39–2.48 (m, 2 H), 4.26 (br. s, 1 H), 6.95–7.01 (m, 2 H), 7.10–7.13 (m, 2 H), 7.55 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.4, 24.9, 31.5, 38.8, 115.1, 115.4, 128.5, 128.6, 136.4, 137.7, 150.8, 160.0, 163.2 ppm. HRMS: calcd. for $C_{12}H_{12}FNO_2$ 221.0846, found 221.0834. Enantiomeric excess: 98%, determined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

6-(4-*tert*-Butylphenyl)-1-nitrocyclohexene (2f): Yield 52 mg, 67%; white solid, m.p. 82.0–83.5 °C. $[\alpha]_D^{20}$ = +98.2 (c = 0.70, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2958, 2865, 1659, 1513, 1342, 1330, 1075, 1018, 823 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.28 (s, 9 H), 1.57–1.86 (m, 2 H), 1.87–2.02 (m, 2 H), 2.40–2.48 (m, 2 H), 4.25 (br. s, 1 H), 7.04 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.53 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.6, 24.9, 31.2, 31.4, 34.3, 39.0, 125.3, 126.7, 135.8, 138.7, 149.3, 149.3, 151.1 ppm. HRMS: calcd. for $C_{16}H_{21}NO_2$ 259.1567, found 259.1554. Enantiomeric excess: 90%, determined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

1-Nitro-6-(4-trifluoromethylphenyl)cyclohexene (2g): Yield 42 mg, 52%; colorless oil. $[\alpha]_D^{20}$ = +107.2 (c = 0.83, CHCl$_3$). IR (neat): $\tilde{\nu}$ = 2943, 2871, 1664, 1618, 1519, 1325, 1163, 1112, 1066, 1017 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.52–1.63 (m, 2 H), 1.87–1.90 (m, 1 H), 2.08 (m, 1 H), 2.44–2.52 (m, 2 H), 4.32 (br. s, 1 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.62 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.5, 24.9, 31.4, 39.5, 122.2, 125.5, 127.4, 128.4, 128.9, 129.3, 129.4, 137.0, 146.1, 150.2 ppm. HRMS: calcd. for $C_{13}H_{12}F_3NO_2$ 271.0814, found 271.0808. Enantiomeric excess: 94%, determined by chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

6-(3-Methoxyphenyl)-1-nitrocyclohexene (2h): Yield 41 mg, 58%; white solid, m.p. 81.7–83.6 °C. $[\alpha]_D^{20}$ = +108.5 (c = 1.29, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2942, 2866, 2835, 1662, 1600, 1583, 1515, 1487, 1330, 1285, 1263, 1042, 781 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.57–1.62 (m, 2 H), 1.88–1.93 (m, 1 H), 1.98–2.17 (m, 1 H), 2.40–2.48 (m, 2 H), 3.78 (s, 3 H), 4.24 (br. s, 1 H), 6.68 (s, 1 H), 6.72–6.78 (m, 2 H), 7.19 (m, 1 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.62 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.6, 25.0, 31.4, 39.5, 55.1, 111.6, 113.4, 119.5, 129.5, 136.2, 143.6, 150.8, 159.7 ppm. HRMS: calcd. for $C_{13}H_{15}NO_3$ 233.1046, found 233.1055. Enantiomeric excess: 96%, determined by chiral HPLC analysis [Daicel Chiralpak OD; hexane/2-propanol, 99:1; flow 1.0 mL/min; (R) isomer: t_R = 22.5 min; (S) isomer: t_R = 25.3 min].

1-Nitro-5-phenylcyclopentene (2j): Yield 23 mg, 40%, colorless oil. $[\alpha]_D^{20}$ = +7.0 (c = 0.16, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2946, 1634, 1507, 1359 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 2.06–2.11 (m, 1 H), 2.65–2.80 (m, 3 H), 4.36–4.40 (m, 1 H), 7.18–7.34 (m, 6 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 29.5, 33.3, 47.9, 126.7, 127.0, 128.8, 139.5, 142.0, 155.2 ppm. Enantiomeric excess: 17%, determined by chiral HPLC analysis [Daicel Chiralpak OD; hexane/2-propanol, 99:1; flow 1.0 mL/min; (R) isomer: t_R = 10.71 min; (S) isomer: t_R = 12.34 min].

6-(3,4-Methylenedioxyphenyl)-1-nitrocyclohexene (2i): Yield 45 mg, 65%; colorless oil. $[\alpha]_D^{20}$ = +98.2 (c = 1.40, CHCl$_3$). IR (neat): $\tilde{\nu}$ = 2942, 2897, 1661, 1607, 1513, 1486, 1439, 1333, 1249, 1231, 1037, 934, 809 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.55–1.62 (m, 2 H), 1.81–1.87 (m, 1 H), 1.95–2.00 (m, 1 H), 2.38–2.47 (m, 2 H), 4.19 (br. s, 1 H), 5.92 (s, 2 H), 6.57–6.84 (m, 3 H), 7.52 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.4, 24.9, 31.5, 39.1, 100.9, 107.7, 108.1, 120.0, 135.8, 136.1, 146.3, 147.774, 150.9 ppm. HRMS: calcd. for $C_{13}H_{13}NO_4$ 247.0839, found 247.0852. Enantiomeric excess: 98%, determined by chiral HPLC analysis [Daicel Chiralpak OD; hexane/2-propanol, 99:1; flow 1.0 mL/min; (R) isomer: t_R = 15.3 min; (S) isomer: t_R = 21.5 min].

6-(3-Methylphenyl)-1-nitrocyclohexene (2k): Yield 88%; colorless oil. $[\alpha]_D^{20}$ = –80.7 (c = 0.14, CHCl$_3$). IR (neat): $\tilde{\nu}$ = 2942, 1660, 1513, 1339 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.56–1.60 (m, 2 H), 1.85–1.90 (m, 1 H), 1.98–2.02 (m, 1 H), 2.31 (s, 3 H), 2.39–2.48 (m, 2 H), 4.25 (br. s, 1 H), 7.02–7.26 (m, 4 H), 7.53 (t, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 16.5, 20.9, 25.0, 31.6, 39.1, 127.0, 129.2, 136.0, 136.3, 138.9, 151.1 ppm. Enantiomeric excess: 85%, determined by Chiral GC analysis [CP-Cyclodextrin-2,3,6-M-19, 0.25 mm × 25 m, column temperature = 168 °C (isothermal), inject temperature 240 °C, detector temperature 260 °C, inlet pressure 10 psi].

General Procedure for the Asymmetric Nitroallylation of the Organometallic Reagent with Nitroallyl Acetates Catalyzed by Chiral Rhodium Complexes: Under argon, ArZnCl (0.30 mmol; in THF) was added dropwise to a stirred solution of Rh(acac)(C$_2$H$_4$)$_2$ (1.6 mg, 15 µmol, 3 mol-%) (R)-BINAP (4.1 mg, 18 µmol, 3.3 mol%) and substrate **1a** (37.4 mg, 0.20 mmol) in THF (1.0 mL) at 0 °C. After the mixture had been stirred at 0 °C for 20 h, the reaction was quenched with water (50 µL). After evaporation of the solvent, the residue was purified by column chromatography on silica (diethyl ether/PET, 1:20) to yield **2**.

4-[6-(3,4-Methylenedioxyphenyl)-1-nitrocyclohex-2-enyl]butan-2-one (7a): A solution of 1-nitrocyclohexene (**2i**) (110 mg, 0.44 mmol), methyl acrylate (0.08 mL, 0.88 mmol) and DBU (7.0 µL, 0.04 mmol) in acetonitrile (1.0 mL) was stirred at room temperature for 3 h. The acetonitrile was evaporated under reduced pressure. The crude product was purified by flash chromatography (PET/EA, 5:1) to give **7a** (140 mg, 96%) as a white solid; m.p. 113.4–114.5 °C. $[\alpha]_D^{20}$ = –148.6 (c = 0.64, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2947, 2891, 1739, 1535, 1489, 1441, 1352, 1265, 1203 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.68 (m, 1 H), 2.21–2.35 (m, 5 H), 2.40–2.51 (m, 2 H), 3.04 (m, 1 H), 3.66 (s, 3 H), 5.84 (d, J = 10.2 Hz, 1 H), 5.90 (s, 2 H), 6.24 (m, 1 H), 6.57 (d, J = 7.56 Hz, 1 H), 6.60 (s, 1 H), 6.69 (d, J = 7.56 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 24.2, 24.8, 28.8, 33.0, 47.6, 51.8, 91.3, 100.9, 108.0, 108.1, 121.4, 123.9, 132.6, 135.0, 146.9, 147.6, 172.5 ppm. HRMS: calcd. for $C_{17}H_{19}NNaO_6$ [M + Na]$^+$ 356.1105, found 356.1121. Enantiomeric excess: 98%, determined by chiral HPLC analysis [Daicel Chiralpak AS; hexane/2-propanol, 7:3; flow 1.0 mL/min; (R) isomer: t_R = 11.90 min; (S) isomer: t_R = 14.55 min].

Crystal Data of 7a: CCDC-605923, $C_{17}H_{19}NO_6$ (333.33), monoclinic, space group $P2(1)$, a = 9.102(2), b = 7.185(1), c = 12.243(2) Å, β = 96.02°, V = 796.22(24) Å^3, T = 296(2) K, Z = 2, $D_{\text{calcd.}}$ = 1.390 mg/m^3, μ = 0.106 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 352, crystal size: 0.52 × 0.52 × 0.26 mm, 2443 reflections collected, 2220 [R(int) = 0.0154]; refinement method: full-matrix least squares on F^2; goodness-of-fit on F^2 = 0.999, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0369, wR_2 = 0.0881.

4-[3-Hydroxy-6-(3,4-methylenedioxyphenyl)cyclohex-1-enyl]butan-2-one (12): A solution of DABCO (70 mg, 0.62 mmol) and **7a** (136 mg, 0.41 mmol) in 1,2-dichlorobenzene (2.0 mL) was refluxed for 30 min, then the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (PET/EA, 1:1) to give **12** (95 mg, 76%) as colorless oil. $[\alpha]_D^{20}$ = –65.8 (c = 0.36, CHCl$_3$). IR (neat): $\tilde{\nu}$ = 3408, 2934, 1733, 1483, 1435, 1264, 1229 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.53 (m, 1 H), 1.70–1.73 (m, 2 H), 1.90–1.91 (m, 2 H), 2.12- 2.20 (m, 2 H), 2.32–2.41 (m, 2 H), 3.21 (m, 1 H), 3.61 (s, 3 H), 4.25 (br. s, 1 H), 5.70 (br. s, 1 H), 5.91 (s, 2 H), 6.61–6.73 (m, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 28.0, 29.5, 30.2, 32.1, 43.9, 51.5, 66.3, 100.8, 108.0, 108.6, 121.3, 127.2, 137.5, 140.8, 145.9, 147.6, 173.4 ppm. HRMS: calcd. for $C_{17}H_{20}NNaO_5$ [M + Na]$^+$ 327.1203, found 327.1215. Enantiomeric excess: 98%, determined by chiral HPLC analysis [Daicel Chiralpak OD; hexane/2-propanol, 90:10; flow 1.0 mL/min; (R) isomer: t_R = 11.70 min; (S) isomer: t_R = 14.88 min].

1-Nitro-2-phenyl-7-oxabicyclo[4.1.0]heptane (7b): nBuLi (1.57 mL, 2.52 mmol, 1.6 M in hexanes) was added to a solution of tBuOOH (0.5 mL, 2.52 mmol, 5.0–6.0 M) in toluene (5.0 mL) at –78 °C. To the mixture was added dropwise a solution of **2a** (170 mg, 0.84 mmol) in toluene (1.0 mL) at –78 °C. After the mixture had been stirred for 8 h at this temperature, the reaction was quenched with an aq. saturated NH$_4$Cl solution (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with 10% aq. Na$_2$SO$_3$ solution (10 mL) and brine and dried with anhydrous sodium sulfate. After the solvent had been removed under reduced pressure, the residue was purified by flash chromatography using (PET/EA, 20:1) to give **7b** (123 mg, 67%) as a white solid; m.p. 93.7–95.1 °C. $[\alpha]_D^{20}$ = +50.0 (c = 0.80, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2944, 2929, 1538, 1493, 1362, 1270 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.60–1.68 (m, 1 H), 1.74–1.78 (m, 1 H), 1.89–1.98 (m, 2 H), 2.17–2.23 (m, 1 H), 3.61 (d, J = 4.90 Hz, 1 H), 4.07 (m, 1 H), 7.23–7.39 (m, 5 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 20.5, 23.0, 29.3, 41.7, 58.8, 89.1, 127.6, 128.1, 128.7, 138.6 ppm. HRMS: calcd. for $C_{12}H_{13}NO_3$ [M + H]$^+$ 242.0895, found 242.1172. Enantiomeric excess: 96%, determined by chiral HPLC analysis [Daicel Chiralpak AD; hexane/2-propanol, 99:1; flow 1.0 mL/min; (R) isomer: t_R = 9.86 min; (S) isomer: t_R = 11.28 min].

Crystal Data of 7b: CCDC-605922, $C_{12}H_{13}NO_3$ (219.23), monoclinic, space group $P2(1)/c$, a = 5.754(1), b = 26.725(4), c = 7.623(1) Å, β = 108.061°, V = 1079.57(12) Å^3, T = 296(2) K, Z = 4, $D_{\text{calcd.}}$ = 1.307 mg/m^3, μ = 0.094 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 464, crystal size: 0.58 × 0.40 × 0.26 mm, 2423 reflections collected, 2070 [R(int) = 0.0107]; refinement method: full-matrix least squares on F^2; goodness-of-fit on F^2 = 1.056, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0392, wR_2 = 0.1067.

[2-Nitro-3-(phenylethynyl)cyclohexyl]benzene (7c): nBuLi (0.94 mL, 1.5 mmol, 1.6 M in hexanes) was added to a solution of phenylacetylene (0.18 mL, 1.5 mmol) in THF (3.0 mL) at –78 °C, and then the mixture was stirred at 0 °C for 3 h. A solution of **2a** (101 mg, 0.5 mmol) in THF (1.0 mL) was added dropwise to the mixture at –78 °C. After the mixture had been stirred at this temperature for 24 h, the reaction was quenched with a saturated aqueous NH$_4$Cl solution (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine and dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (PET/EA, 20:1) to give **7c** (138 mg, 91%) as a white solid; m.p. 130.9–132.0 °C. $[\alpha]_D^{20}$ = –83.3 (c = 0.72, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2936, 2955, 2866, 1596, 1545, 1489, 1441, 1375, 1346, 1242 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.51 (m, 1 H), 1.82 –1.83 (m, 1 H), 2.05–2.11 (m, 1 H), 2.16- 2.17 (m, 1 H), 2.32–2.38 (m, 1 H), 2.51–2.57 (m, 1 H), 3.01–3.12 (m, 2 H), 5.10 (t, J = 4.20 Hz, 1 H), 7.19–7.36 (m, 10 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 23.4, 24.8, 26.2, 33.7, 45.6, 83.7, 86.7, 90.3, 122.5, 127.1, 127.7, 128.1, 128.2, 128.8, 131.7, 139.5 ppm. HRMS: calcd. for $C_{20}H_{19}NNaO_2$ [M + Na]$^+$ 328.1308, found 328.1319. Enantiomeric excess: 98%, determined by chiral HPLC analysis [Daicel Chiralpak AS; hexane/2-propanol, 85:15; flow 1.0 mL/min; (R) isomer: t_R = 7.48 min; (S) isomer: t_R = 8.43 min].

Crystal Data of 7c: CCDC-605921, $C_{20}H_{19}NO_2$ (205.36), triclinic, space group $P\bar{1}$, a = 10.054(2), b = 11.932(2), c = 14.177(3) Å, α = 99.36°, β = 100.40°, γ = 90.29°, V = 1649.40(47) Å^3, T = 296(2) K, Z = 4, $D_{\text{calcd.}}$ = 1.230 mg/m^3, μ = 0.079 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 648, crystal size: 0.64×0.64×0.20 mm, 6711 reflections collected, 6126 [R(int) = 0.0105]; refinement method: full-matrix least squares on F^2; goodness-of-fit on F^2 = 0.947, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0384, wR_2 = 0.0900.

2-Phenyl-6-(phenylethynyl)cyclohexylamine (13): 2% HCl (2.0 mL) and Zn powder (102 mg, 1.58 mmol) were added to a solution of **7c** (135 mg, 0.45 mmol) in EtOH (10 mL) at room temperature. After being stirred for 1 d, the mixture was filtered and concentrated. The filtrate was diluted with AcOEt (10 mL), and then washed with saturated aqueous NaHCO$_3$ (10 mL) and brine (10 mL). After removal of the solvent, the residue was purified by column chromatography on silica gel to give **13** (99.5 mg, 81% yield) as white solid; m.p. 65.8–67.8 °C. $[\alpha]_D^{20}$ = –53.6 (c = 0.39, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2929, 2854, 1596, 1488, 1440 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.11 (br. s, 2 H), 1.25 (m, 1 H), 1.42–1.47 (m, 1 H), 1.61–1.97 (m, 3 H), 2.11–2.17 (m, 1 H), 2.78–2.2.83 (m, 1 H), 2.89–2.92 (m, 1 H), 3.47 (t, J = 2.82 Hz, 1 H), 7.23–7.40 (m, 10 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 22.6, 25.6, 25.8, 36.7, 47.1, 54.0, 82.1, 92.0, 123.5, 126.3, 127.5, 127.6, 128.1, 128.3, 131.5, 143.9 ppm. HRMS: calcd. for $C_{20}H_{22}N$ [M + H]$^+$ 276.1747, found 276.1740.

Methyl 2-(2-Nitro-3-phenylcyclohex-1-yl)acetate (14): A solution of **2a** (121 mg, 0.6 mmol) in THF (3.0 mL) was added to the lithium enolate, which was prepared in situ from AcOMe (3.3 mmol), diisopropylamide (3.3 mmol), and nBuLi (3.3 mmol, 2.2 M in hexane) at –78 °C within 20 min. After stirring at –78 °C for 3 h, a solution of AcOH (0.4 mL) in THF (3.0 mL) was added, and the mixture was warmed to –40 °C within 20 min. After usual workup and purification by column chromatography on silica gel (AcOEt/PET, 1:15), compound **14** was obtained. Yield: 70%; diastereomeric ratio of 12:1 in favor of *cis,cis* derivative was determined by ^{1}H NMR spectroscopy. Physical property and characterization of the major product: m.p. 106.8–108.7 °C. IR (KBr): $\tilde{\nu}$ = 3452, 2951, 2937, 2864, 1727, 1544, 1273 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.56–1.67 (m, 2 H), 1.76–1.84 (m, 2 H), 2.06 (m, 1 H), 2.29–2.32 (m, 2 H), 2.49–2.54 (m, 2 H), 3.04–3.08 (m, 1 H), 3.68 (s, 3 H), 5.04 (t, J = 4.0 Hz, 1 H), 7.18–7.25 (m, 2 H), 7.27–7.33 (m, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 23.6, 24.9, 25.3, 36.7, 36.9, 45.7, 51.8, 90.9, 127.1, 127.4, 128.6, 139.8, 171.9 ppm. HRMS: calcd. for $C_{15}H_{19}NO_4$ 277.1308, found 277.1291.

Crystal Data of 14: CCDC-605920, $C_{15}H_{19}NO_4$ (277.31), monoclinic, space group $P2(1)/c$, a = 9.955(2), b = 10.050(2), c = 15.080(3) Å, β = 107.27°, V = 1440.61(46) Å^3, T = 293(2) K, Z = 4, $D_{calcd.}$ = 1.279 mg/m^3, μ = 0.093 mm^{-1}, λ = 0.71073 Å, F(000) = 592, crystal size: 0.58×0.38×0.38 mm, 3140 reflections collected, 2682 [R(int) = 0.0105]; refinement method: full-matrix least squares on F^2; goodness-of-fit on F^2 = 0.949, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0360, wR_2 = 0.0865.

Methyl [3-*c*-(1,3-Benzodioxol-5-yl)-2-*c*-nitrocyclohex-1-*r*-yl]acetate (15a): A solution of (*S*)-**2i** (121 mg, 0.6 mmol) in THF (3.0 mL) was added to the lithium enolate, which was prepared in situ from AcOMe (3.3 mmol), diisopropylamide (3.3 mmol), and *n*BuLi (3.3 mmol, 2.2 M in hexane) at –78 °C within 20 min. After the mixture had been stirred at –78 °C for 3 h, a solution of AcOH (0.4 mL) in THF (3.0 mL) was added and the mixture was warmed to –40 °C within 20 min. After usual workup and purification by a column chromatography on silica gel (AcOEt/PET, 1:15), compound **15a** was obtained (138 mg, 72% yield) as colorless oil. A diastereomeric ratio of 7:1 in favor of the *cis,cis* derivative was determined by ^{1}H NMR. IR (KBr): ṽ = 2939, 2864, 1733, 1543, 1504, 1440 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.48–1.78 (m, 4 H), 2.03 (m, 1 H), 2.28 (m, 2 H), 2.39- 2.45 (m, 2 H), 2.45–2.99 (m, 1 H), 3.68 (s, 3 H), 4.98 (t, J = 4.0 Hz, 1 H), 5.91 (s, 2 H), 6.63 – 6.71 (m, 2 H), 6.74 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 24.1, 24.9, 25.3, 36.7, 36.9, 45.5, 51.8, 91.1, 101.0, 107.6, 108.3, 120.4, 133.7, 146.7,147.8, 171.8 ppm. HRMS: calcd. for $C_{16}H_{19}NO_6$ 321.1207, found 321.1206.

Methyl [3-*c*-(1,3-Benzodioxol-5-yl)-2-*t*-nitrocyclohex-1-*r*-yl]acetate (15c): A solution of **15b** (96 mg, 0.3 mmol) and DBU (0.004 mL, 0.03 mmol) in acetonitrile (5.0 mL) was stirred at room temperature for 24 h. The acetonitrile was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (AcOEt/PET, 1:10) to give compound **15c** (96 mg, >99% yield) as a white solid; m.p. 93.2–94.1 °C. $[\alpha]_D^{20}$ = +60.8 (c = 0.74, CHCl$_3$). IR (KBr): ṽ = 2938, 2862, 1737, 1548, 1487, 1440, 1368, 1274 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.32 (m, 1 H), 1.51–1.62 (m, 2 H), 1.84–1.86 (m, 1 H), 1.98–2.03 (m, 2 H), 2.19–2.28 (m, 2 H), 2.34–2.40 (m, 1 H), 3.06–3.10 (m, 1 H), 3.67 (s, 3 H), 4.45 (t, J = 11.0 Hz, 1 H), 5.90 (s, 2 H), 6.59–6.71 (m, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 24.7, 30.0, 32.8, 36.8, 38.6, 48.3, 51.7, 95.3, 101.0, 107.2, 108.4, 120.5, 133.8, 146.8, 147.8, 171.3 ppm. HRMS: calcd. for $C_{16}H_{19}NNaO_6$ [M + Na]$^+$ 344.1105, found 344.1102. Enantiomeric excess: 97%, determined by chiral HPLC analysis [Daicel Chiralpak OD; hexane/2-propanol, 80:20; flow 1.0 mL/min; (R) isomer: t_R = 8.54 min; (S) isomer: t_R = 9.80 min].

(3a*R*,7*S*,7a*S*)-7-(Benzo[1,3]dioxol-5-yl)octahydroindol-2-one (16a): To a solution of **15a** (96 mg, 0.3 mmol) in absolute ethanol (1.0 mL) in an autoclave was added Raney nickel (5 mol%) previously rinsed with absolute ethanol. Hydrogen was introduced into the autoclave until the pressure reached 80 atm. The autoclave was warmed to 55 °C and maintained at that temperature for 24 h. After the autoclave was cooled to room temperature, the mixture was filtered and the filtrate was concentrated. Recrystallization from CHCl$_3$/hexane gave **16a** (74 mg, 95% yield) as a white solid; m.p. 185.9–187.2 °C. $[\alpha]_D^{20}$ = +112.3 (c = 1.30, CHCl$_3$). IR (KBr): ṽ = 3252, 2927, 2915, 2853, 1681, 1502, 1488, 1242, 1230, 1039 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.25–1.33 (m, 2 H), 1.68–1.75 (m, 3 H), 1.82 (m, 1 H), 1.96 (d, J = 16.0 Hz, 1 H), 2.47 (m, 1 H), 2.52 (m, 1 H), 2.78–2.82 (m, 1 H), 3.84 (t, J = 4.2 Hz, 1 H), 5.33 (br. s, 1 H), 5.95 (s, 2 H), 6.63 (d, J = 1.5 Hz, 1 H), 6.66 (dd, J = 1.5 Hz, 7.9 Hz, 1 H), 6.75 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 24.2, 27.5, 35.1, 40.2, 43.7, 58.8, 101.0, 107.5, 108.5, 119.7, 136.2, 146.4, 148.0, 177.9 ppm. HRMS: calcd. for $C_{15}H_{17}NO_3$ 259.1203, found 259.1203. Enantiomeric excess: 98%, determined by chiral HPLC [Daicel Chiralpak OJ-H; hexane/2-propanol, 70:30; flow 1.0 mL/min; (R) isomer: t_R = 8.1 min; (S) isomer: t_R = 13.3 min].

(3a*S*,7*R*,7a*S*)-7-(Benzo[1,3]dioxol-5-yl)octahydroindol-2-one (16b): To a solution of **15b** (96 mg, 0.3 mmol) in absolute ethanol (1.0 mL) in an autoclave was added Raney nickel (5 mol%) previously rinsed with absolute ethanol. Hydrogen was introduced into the autoclave until the pressure reached 80 atm. The autoclave was warmed to 55 °C and was maintained at the temperature for 24 h. After the autoclave was cooled to room temperature, the mixture was filtered, the filtrate was concentrated, and then refluxed in toluene (5.0 mL) for 24 h. Recrystallization from CHCl$_3$/hexane gave **16b** (74 mg, 95% yield) as a white solid; m.p. 201.7–202.5 °C. $[\alpha]_D^{20}$ = +78.6 (c = 0.70, CHCl$_3$). IR (KBr): ṽ = 3442, 3214, 2932, 2855, 1688, 1499, 1487, 1443, 1239, 1228, 1036 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.40–1.57 (m, 3 H), 1.90–1.93 (m, 3 H), 2.03–2.15 (m, 2 H), 2.33 (m, 1 H), 2.54 (m, 1 H), 3.11 (t, J = 10.0 Hz, 1 H), 5.31 (br. s, 1 H), 5.93 (s, 2 H), 6.61–6.67 (m, 2 H), 6.72–6.76 (m, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 26.0, 28.1, 32.9, 37.9, 44.8, 48.4, 65.3, 100.9, 106.9, 108.4, 119.9, 136.1, 146.4, 148.0, 177.6 ppm. HRMS: calcd. for $C_{15}H_{17}NNaO_3$ [M + Na]$^+$ 282.1101, found 282.1109.

(3a*R*,12b*S*,12c*S*)-2,3,3a,4,12b,12c-Hexahydro-1*H*,7*H*-[1,3]dioxolo-[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-5-one (17a): To a solution of **16a** (52 mg, 0.20 mmol) in anhydrous Cl(CH$_2$)$_2$Cl (5.0 mL) were added sequentially paraformaldehyde (23.1 mg, 0.77 mmol) and CF$_3$CO$_2$H (0.19 mL, 2.5 mmol) at room temperature. The mixture was stirred at room temperature for 24 h, and then the reaction was quenched with a saturated aqueous NaHCO$_3$ solution (10 mL), followed by addition of CH$_2$Cl$_2$ (40 mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine and dried with Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (AcOEt/PET, 3:1) to give **17a** (47 mg, 88% yield) as a white solid; m.p. 144.0–147.7 °C. IR (KBr): ṽ = 2927, 2854, 1676, 1503, 1483, 1440, 1418 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.12 –1.32 (m, 3 H), 1.68 (m, 3 H), 2.04 (d, J = 16.0 Hz, 1 H), 2.39 (m, 1 H), 2.51 (dd, J = 16.0 Hz, 6.8 Hz, 1 H), 2.69 (m, 1 H), 3.73 (t, J = 4.5 Hz, 1 H), 3.76 (d, J = 17.3 Hz, 1 H), 4.49 (d, J = 17.3 Hz, 1 H), 5.89 (m, 2 H), 6.57 (s, 1 H), 6.59 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 23.5, 27.8, 30.2, 32.9, 39.7, 40.2, 42.6, 55.6, 100.9, 106.6, 108.4, 123.2, 131.5, 146.5, 146.6, 175.6 ppm. HRMS:calcd. for $C_{16}H_{17}NO_3$ 271.1203, found 271.1193.

(3a*S*,12b*R*,12c*S*)-2,3,3a,4,12b,12c-Hexahydro-1*H*,7*H*-[1,3]dioxolo-[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-5-one (17b): To a solution of **16b** (52 mg, 0.20 mmol) in anhydrous Cl(CH$_2$)$_2$Cl (5.0 mL) were added sequentially paraformaldehyde (23.1 mg, 0.77 mmol) and CF$_3$CO$_2$H (0.19 mL, 2.5 mmol) at room temperature. The mixture was stirred at room temperature for 24 h, and then the reaction was quenched with a saturated aqueous NaHCO$_3$ solution (10 mL), followed by addition of CH$_2$Cl$_2$ (40 mL). The organic layer was separated, and the aqueous phase was extracted with ethyl acetate. The combined layers were washed with brine and dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (AcOEt/PET, 3:1) to give **17b** (49 mg, 90% yield) a white solid; m.p. 212.2–213.1 °C. $[\alpha]_D^{20}$ = +184.1 (c = 0.44, CHCl$_3$). IR (KBr): ṽ = 2932, 2859, 1680, 1502, 1487, 1411 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.34–1.40 (m, 2 H), 1.68 (m, 1 H), 1.92–1.99 (m, 3 H), 2.00 (m, 1 H), 2.43–2.50 (m, 3 H), 2.68 (m, 1 H), 4.37 (d, J = 3.83 Hz, 2 H), 5.92 (s, 2 H), 6.58 (s, 1 H), 6.70 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.8, 27.8, 27.8, 38.3, 40.5, 42.9, 42.9, 64.7, 101.0, 104.8, 107.3, 125.1, 130.6, 146.2, 146.7, 175.0 ppm. HRMS: calcd. for $C_{16}H_{17}NNaO_3$ $[M + Na]^+$ 294.1101, found 294.1089. Enantiomeric excess: 98%, determined by chiral HPLC analysis [Daicel Chiralcel AD; hexane/2-propanol, 85:15; flow 1.0 mL/min; (*R*) isomer: t_R = 12.35 min; (*S*) isomer: t_R = 14.45 min].

(+)-γ-Lycorane (8): A mixture of **17a** (40 mg, 0.15 mmol) and $LiAlH_4$ (17.1 mg, 0.45 mmol) in THF (5.0 mL) was stirred at reflux for 18 h, then Na_2SO_4 was added. The precipitate was removed by filtration and washed with diethyl ether (10 mL×3). The combined solutions were concentrated, and the residue was purified by flash column chromatography (Et_2O) to give (+)-γ-lycorane (37 mg, 98% yield) as colorless oil. $[\alpha]_D^{20}$ = +17.3 (c = 0.98, EtOH) {ref.[20] $[\alpha]_D^{20}$ = +17.1 (c = 0.25, EtOH)}. IR (KBr): $\tilde{\nu}$ = 2928, 2848, 1505, 1483, 1375, 1318, 1245, 1226, 1038 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25–1.35 (m, 5 H), 1.42 (m, 3 H), 1.69–2.20 (m, 3 H), 2.36 (t, J = 4.5 Hz, 1 H), 2.70 (m, 1 H), 3.18 (d, J = 14.4 Hz, 1 H), 3.23 (m, 1 H), 3.99 (d, J = 14.4 Hz, 1 H), 5.87 (m, 2 H), 6.49 (s, 1 H), 6.61 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.2, 29.2, 30.3, 31.7, 37.3, 39.4, 53.7, 57.1, 62.8, 100.6, 106.2, 108.3, 127.3, 133.1, 145.6, 146.0 ppm. HRMS: calcd. for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1489, found 258.1496. The spectroscopic data are in agreement with those reported in the literature.[20]

(+)-β-Lycorane (9): A mixture of **17b** (40 mg, 0.15 mmol) and $LiAlH_4$ (17.1 mg, 0.45 mmol) in THF (5.0 mL) was stirred at reflux for 24 h, then Na_2SO_4 was added. The precipitate was removed by filtration and washed with diethyl ether (10 mL×3). The filtrate was concentrated, and the residue was purified by flash column chromatography (Et_2O) to give (+)-β-lycorane (36 mg, 97% yield) as colorless oil. $[\alpha]_D^{20}$ = +142.5 (c = 0.17, EtOH) {ref.[20] $[\alpha]_D^{20}$ = +143.3 (c = 1.04, EtOH)}. IR (KBr): $\tilde{\nu}$ = 2928, 2845, 1724, 1483 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.13–1.17 (m, 2 H), 1.50–1.54 (m, 4 H), 1.93–1.98 (m, 2 H), 2.23- 2.34 (m, 2 H), 2.45–2.52 (m, 1 H), 3.31- 3.41 (m, 2 H), 4.04 (d, J = 14.2 Hz, 1 H), 3.23 (m, 1 H), 5.87 (dd, J = 1.41 Hz, 4.71 Hz, 2 H), 6.50 (s, 1 H), 6.71 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 26.4, 28.2, 28.8, 30.1, 41.7, 42.9, 53.8, 57.3, 71.9, 100.6, 105.3, 106.8, 128.5, 131.2, 145.6, 146.1 ppm. HRMS: calcd. for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1489, found 258.1482.

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