7-Mesityl-2,2-dimethylindan-1-ol: a novel alcohol which serves as both a chiral auxiliary and a protective group for carboxy functions

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A novel chiral indanol **11** is conveniently synthesized by using a stepwise displacement of the methoxy groups of 2,6-dimethoxybenzoic ester **1** by a vinyl and then an aryl Grignard reagent as the key step. The racemic indanol **11** is optically resolved as the diastereomeric (S_a)-2′-methoxy-1,1′-binaphthyl-2-carboxylic esters **12** by column chromatography. The absolute stereochemistry of the indanol (+)-**11** is established to be *S* by an X-ray crystallographic analysis of the ester (S_a,*S*)-**12**. Performance of the indanol **11** as a chiral auxiliary, and as a protective group for the carboxy function, is examined in the atrolactic acid synthesis from phenylglyoxylic ester **13** and methylmagnesium iodide and in the biphenyl coupling reaction of 2,3-dimethoxybenzoic ester **15** with 2-methoxy-4,6-dimethylphenylmagnesium bromide, resulting in quantitative formations of atrolactic ester **14** with up to 83% de and biphenyl **16** with 72% de, respectively.

Introduction

In the last three decades, diastereoselective asymmetric syntheses have enjoyed much success, a large part of which resulted from the continuing efforts to develop novel chiral auxiliaries.[1] Among such entities, cyclohexanol-based chiral auxiliaries,[2] especially those bearing an aryl substituent, such as Corey's 8-phenylmenthol[2b] and Whitesell's *trans*-2-phenylcyclohexanol,[2c] fulfil big roles because of their high stereoselectivity and wide applicability.[1,3] These auxiliaries were designed, when used to derivatize a carboxylic acid such as an α-keto acid or an α,β-unsaturated acid, to prevent nucleophiles from attacking from one side of the diastereotopic faces of the resulting ester by virtue of the aryl substituent as schematically visualized in Fig. 1(**a**).The auxiliaries, however, will not always be applicable

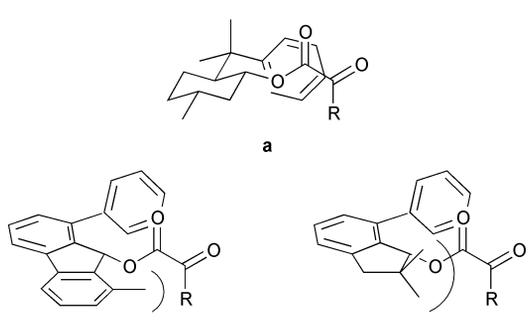

Fig. 1 Schematic views of α-keto esters of 8-phenylmenthol **a**, 1-methyl-8-phenylfluoren-9-ol **b** and 2,2-dimethyl-7-phenylindan-1-ol **c**.

to the system where the nucleophiles are so highly reactive as to attack the ester carbonyl group, because they are not designed to work as a protective group for the carboxy function.[4] To address this limitation, we recently designed fluoren-9-ols bearing an alkyl and an aryl substituent at the 1- and 8-position, respectively, which provide a steric environment quite similar to those offered by the arylcyclohexanols and may protect the carboxy group with the 1- and 8-substituent (**b**).[5] Although they showed intrinsically high chiral induction ability, their esters were found to readily racemize *via* the cyclopentadienyl anions under basic conditions. We assumed that a 2,2-dialkyl-7-arylindan-1-ol skeleton would embody similar structural features to the fluorenols but resist racemization (**c**). Here, we report a convenient synthesis of such an indanol **11** and its optical resolution. Also reported are the performances of the indanol **11** as a chiral auxiliary, as well as a protective group for the carboxy function.

Results and discussion

Synthesis of indanol 11

In previous papers,[6,7] we reported that an ester function substantially activates an *ortho* alkoxy group for nucleophilic aromatic substitution (S_NAr) reaction by various nucleophiles, providing a convenient substitute for the oxazoline-mediated *ortho*-alkoxy displacement from aryloxazolines (the Meyers reaction).[8] The reaction was advantageously utilized for the synthesis of the indanol **11** (Scheme 1). Thus, the 2,6-di-*tert*-butyl-4-methoxyphenyl ester (BHA ester) of 2,6-dimethoxybenzoic acid, ester **1**, was allowed to react with 1.4 equiv. of prop-1-enylmagnesium bromide at room temperature to give the vinyl benzene **2** in good yield. It has been shown that control of steric bulk of the ester alkoxy moiety corresponding to the bulkiness of the Grignard reagents is crucial to obtaining good results in the ester-mediated S_NAr reaction.[9] For example, the BHA ester of 2-methoxybenzoic acid reacted readily with phenylmagnesium bromide to afford the corresponding biphenyl in almost quantitative yield, but the ester did not react with bulkier mesitylmagnesium bromide at all. Thus, the BHA moiety of the ester **2** was replaced with a 2,6-diisopropylphenyl (DIPP) group to give ester **4** *via* a transesterification–hydrolysis sequence[9a,10] to acid **3**, followed by its esterification with 2,6-diisopropylphenol. The S_NAr reaction of the DIPP ester **4** with the mesityl Grignard reagent gave the biphenyl **5**, which was

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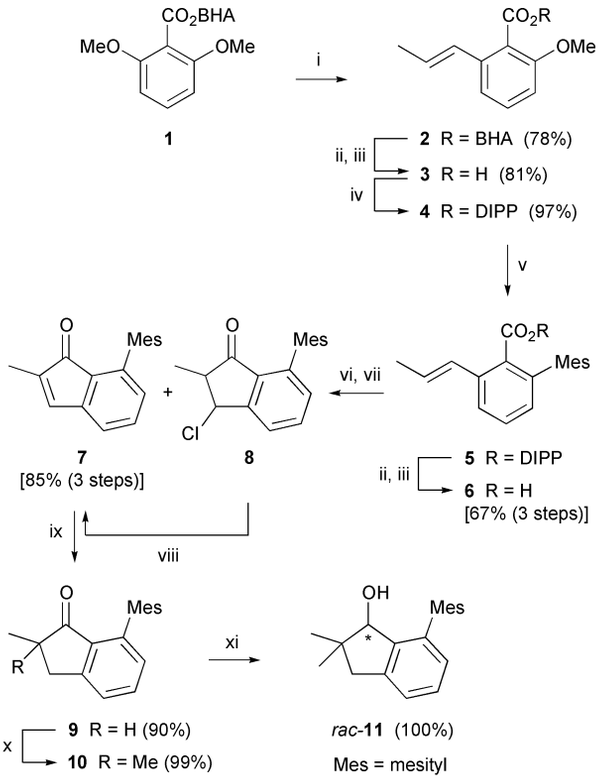
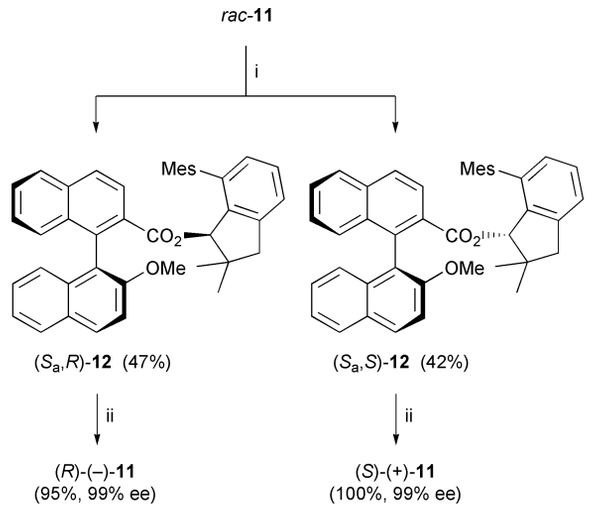


Scheme 1 *Reagents*: i, prop-1-enylmagnesium bromide, THF–PhH; ii, NaOMe, PhMe–HMPA; iii, water; iv, DIPPOH, TFAA, PhH; v, mesitylmagnesium bromide, Et_2O–PhH; vi, $SOCl_2$; vii, $SnCl_4$, PhH; viii, Et_3N, PhH; ix, SiH_2Ph_2, $Pd(PPh_3)_4$, $ZnCl_2$, $CHCl_3$; x, NaH, MeI, PhH; xi, LAH, THF.

hydrolyzed without purification to give acid **6** in good yield. It should be noted that an alternative route to the biphenyl **5**, that is, first, mesitylation of the DIPP ester of 2,6-dimethoxybenzoic acid and then vinylation of the resulting biphenyl, resulted in failure because of preferential attack of the prop-1-enyl Grignard reagent on the ester carbonyl moiety of the biphenyl during the latter transformation. The vinyl acid **6** was then subjected to an intramolecular Friedel–Crafts acylation[11] after conversion into the acyl chloride. The reaction gave a mixture of the indenone **7** and its hydrochloric acid adduct **8**; the latter could be converted into the former by treatment of the mixture with triethylamine. The indenone **7** was then reduced to the indanone **9** *via* a palladium-catalyzed hydrosilylation by using $ZnCl_2$ as the Lewis acid co-catalyst.[12] Methylation of the indanone **9**, followed by LAH reduction of the resulting dimethylindanone **10**, gave the desired racemic indanol **11** in 31% yield based on the starting benzoic ester **1**.

Optical resolution of the indanol 11 and determination of the absolute configuration

Recently, we and others have shown that axially chiral 2′-methoxy-1,1′-binaphthyl-2-carboxylic acid is very useful as a chiral auxiliary for enantiomeric resolution of alcohols and amines, as well as for determination of their absolute stereochemistry by HPLC, ^{1}H NMR or X-ray crystallographic analysis.[5,13] The acid was adopted as a chiral resolving agent for the indanol **11** (Scheme 2). Thus, racemic indanol **11** was treated with (S_a)-2′-methoxy-1,1′-binaphthyl-2-carbonyl chloride to afford a diastereomeric mixture of esters **12**, which could be separated well by column chromatography on silica gel. The first-eluted fraction was evaporated to give the ester of indanol (−)-**11** [(S_a,*R*)-**12**] in 47% yield, while the second gave the ester of (+)-**11** [(S_a,*S*)-**12**] in 42% yield. The diastereomerically pure esters **12** could not be hydrolyzed by treatment with potassium hydroxide in aqueous ethanol at room temperature but were reductively cleaved with LAH to give the corresponding enantiomers **11**, the optical purities of which were determined to be 99% ee by chiral HPLC analyses. On the other hand, the absolute stereochemistry of indanol **11** was determined to be *S*-(+) by an X-ray crystallographic analysis of the ester of indanol (+)-**11** [(S_a,*S*)-**12**] (Fig. 2).



Scheme 2 *Reagents*: i, (S_a)-2′-methoxy-1,1′-binaphthyl-2-carbonyl chloride, 4-pyrrolidinopyridine, PhMe–pyridine, ii, LAH, THF.

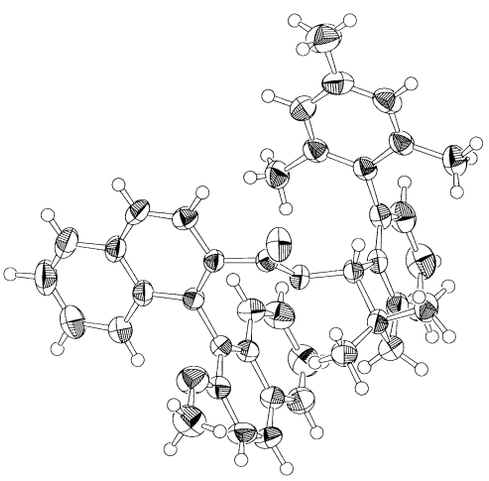


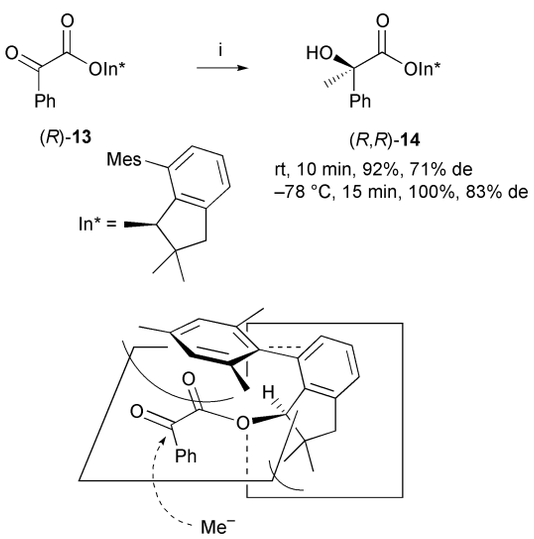
Fig. 2 ORTEP drawing of ester (S_a,*S*)-**12**.

The ORTEP[14] drawing of ester (S_a,*S*)-**12** shows that the carbinyl C–H bond and the carbonyl moiety adopt an almost eclipsed conformation, the torsion angle being 26.7°. As a result, the 7-mesityl group and the 2,2-dimethyl groups are positioned on opposite sides of the carbonyl plane to each other so as to prevent nucleophilic attack at the carbonyl carbon. In addition, the mesityl group seems to be substantially bulkier than the dimethyl groups, which allows high diastereoselectivity in the auxiliary-based asymmetric reactions to be achieved.

Utilization of the indanol 11 as a chiral auxiliary

Atrolactic acid synthesis. Diastereoselective 1,2-addition of organometallics to α-keto acid derivatives with the aid of a chiral auxiliary provides an easy access to chiral α,α-disubstituted α-hydroxy acid derivatives, which are important intermediates for the synthesis of biologically active natural products.[15] Therefore, a considerable number of studies have been made to clarify the relationship between the structure of the auxiliary employed and the diastereoselectivity in the reaction, and the reaction has sometimes been used to estimate the intrinsic asymmetric induction ability of an alcohol as a

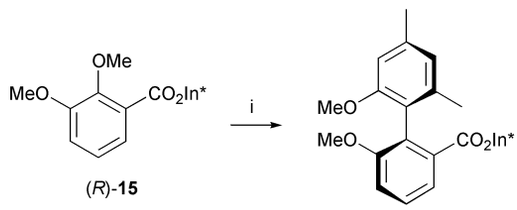
chiral auxiliary.[2] Phenylglyoxylic ester (*R*)-**13** derived from indanol (*R*)-**11** was treated with methylmagnesium iodide in diethyl ether–toluene at room temperature to give atrolactic ester **14**, the optical purity of which was determined to be 71% de by ^{1}H NMR analysis (Scheme 3). The de value increased



Scheme 3 *Reagents*: i, MeMgI, Et_2O–PhMe.

to 83% when the reaction was carried out at −78 °C. The *R* absolute stereochemistry of the induced quaternary carbon center was established by comparison of the sign of the specific rotation with that reported in the literature after hydrolysis of the ester **14**. The auxiliary **11** was recovered from the ester **14** without loss of chiral integrity by hydrolysis. The stereochemical course of the reaction can be rationalized by a steric model depicted in Scheme 3. The crystal structure of ester **12** (Fig. 2) suggests that the O=C–O–C–H bonds of the ester **13** lie in the same plane, where the carbinyl hydrogen is oriented *syn* to the carbonyl group. The two carbonyl groups will adopt a *syn*-coplanar conformation due to formation of a magnesium chelate[16] and/or a stabilizing interaction between the mesityl HOMO and the glyoxyl LUMO,[17,18] as suggested in the related reactions of 8-phenylmenthyl esters.[19] Accordingly, the Grignard reagent will attack the keto carbonyl group from the opposite face to the mesityl substituent to avoid steric repulsion, leading to the preferential formation of atrolactic ester (*R,R*)-**14**.

Biphenyl coupling reaction. It has been reported that in the ester-mediated biaryl coupling reaction, axial chirality of the biaryl unit can be efficiently induced by central chirality of the leaving alkoxy[20] or sulfinyl[21] group, as well as by planar chirality of the substrate, such as cyclophanes[22] or arene–chromium complexes.[23] However, only poor to moderate asymmetric induction (up to 56% de) has been achieved by using a chiral ester group,[20a,24] due to the remote location of the chiral center from the reaction site. In addition, the known cyclohexanol-based auxiliaries could scarcely be applied to the asymmetric synthesis of biphenyls, because these alkoxy moieties cannot protect the ester carbonyl function from attack by the aryl Grignard reagents (*vide supra*). To our pleasure, the reaction of the mesityldimethylindanyl ester of 2,3-dimethoxybenzoic acid, ester **15**, with phenylmagnesium bromide proceeded smoothly in diethyl ether–benzene at room temperature to give the corresponding biphenyl in 95% yield, while a control reaction of isopropyl 2,3-dimethoxybenzoate gave the S_NAr product in only 13% yield, accompanied by formation of the carbonyl addition product, (2,3-dimethoxyphenyl)diphenylmethanol, in 31% yield. Asymmetric coupling of the indanyl ester (*R*)-**15** with 2-methoxy-4,6-dimethylphenylmagnesium bromide was conducted in diethyl ether–toluene at lower temperature to give the biphenyl **16** in 91% yield with fairly good diastereoselectivity (72% de) (Scheme 4). The



Scheme 4 *Reagents and conditions*: i, 2-methoxy-4,6-dimethylphenylmagnesium bromide, Et_2O–PhMe, −10 ⟶ 0 °C.

induced axis was assigned to be R_a by chemical correlation to the corresponding carboxylic acid.[20c] In order to gain insight into the mechanism of the asymmetric induction, a binaphthyl coupling reaction was carried out. Thus, the 1-methoxy-2-naphthoic ester derived from the indanol (*R*)-**11** was allowed to react with 2-methoxy-1-naphthylmagnesium bromide in diethyl ether–benzene at room temperature to give the binaphthyl **12** in 85% yield with 49% de. The direction of the preferentially induced binaphthyl axis was determined to be S_a by ^{1}H NMR analysis. This agrees with the previous result that (*S*)-1-phenylethyl 1-methoxy-2-naphthoate induced an R_a axis in the binaphthyl coupling reaction.[20a] Therefore, it may be concluded that an identical mechanism operates in both cases.[20a]

In conclusion, we have shown here a convenient method for the synthesis of the novel indanol **11** by using the ester-mediated S_NAr reaction as the key step. Optical resolution of the racemic indanol could be achieved by column chromatography after conversion into the diastereomeric esters of 2′-methoxy-1,1′-binaphthyl-2-carboxylic acid. The indanol showed good performance as a chiral auxiliary, as well as a protective group, in diastereoselective asymmetric reactions.

Experimental

Mps were taken using a Mitamura Riken MP-P apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-100 polarimeter and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Microanalyses were carried out in the Microanalytical Laboratory of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DPX-400 or DRX-500 spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. *J*-Values are given in Hz. X-ray data† were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation and a rotating anode generator, and the structure was solved by direct methods (SIR92[25]) and expanded using Fourier techniques (DIRDIF-94[26]). Merck silica gel 60GF_{254} was used for analytical and preparative TLC (PLC). Silica gel columns were prepared by use of Merck silica gel 60 (63–200 μm). Water- and air-sensitive reactions were routinely carried out under nitrogen. Diethyl ether, THF, benzene and toluene were distilled from sodium diphenyl ketyl just before use. Other solvents for experiments requiring anhydrous conditions were purified by usual methods. Grignard reactions were performed by a similar procedure to that described in the previous papers.[10,20a]

† CCDC reference number(s) 172909. See http://www.rsc.org/suppdata/p1/b1/b109396g/ for crystallographic files in .cif or other electronic format.

Synthesis of the indanol 11

Vinylation of ester 1 to the vinylbenzene 2. To a solution of ester **1**[5] (24.4 g, 60.9 mmol) in benzene (200 cm^3) was added a solution of prop-1-enylmagnesium bromide, which had been prepared from 1-bromopropene (10.3 g, 85.1 mmol) and magnesium turnings (3.32 g) in THF (200 cm^3) and diluted with benzene (200 cm^3). The mixture was stirred at room temperature for 12 h. After usual work-up, the crude product was chromatographed on a silica gel column with hexane–ethyl acetate (40 : 1) as eluent to give the vinylbenzene **2** (19.6 g, 78%) as colorless crystals, mp 110–111 °C (Found: C, 76.15; H, 8.2. Calc. for $C_{26}H_{34}O_4$: C, 76.1; H, 8.4%); ν_{max} (KBr)/cm^{-1} 1713; δ_H(400 MHz) 1.35 (18 H, s, $Bu^t \times 2$), 1.79 (3 H, dd, *J* 6.6 and 1.8, CH=CH*Me*), 3.81 (3 H, s, OMe), 3.91 (3 H, s, OMe), 6.03 (1 H, dq, *J* 15.5 and 6.6, CH=C*H*Me), 6.90 (2 H, s, ArH), 6.92 (1 H, dd, *J* 7.9 and 0.8, ArH), 7.04 (1 H, dq, *J* 15.5 and 1.8, C*H*=CHMe), 7.13 (1 H, dd, *J* 7.9 and 0.8, ArH) and 7.40 (1 H, t, *J* 7.9, ArH).

Hydrolysis of the vinylbenzene 2 to acid 3. Vinylbenzene derivative **2** (18.5 g, 45.1 mmol) was added to a solution of 10 equiv. of sodium methoxide in toluene (60 cm^3)–dry HMPA (20 cm^3) and the mixture was refluxed for 1 day. To the mixture was added water (5.0 cm^3) and the resulting mixture was refluxed for a further 2 h. After cooling, the mixture was diluted with water, washed with diethyl ether, and acidified by the addition of conc. HCl to liberate the free acid, which was extracted with diethyl ether and the extract was washed successively with 2 M HCl and water, dried ($MgSO_4$), and evaporated. The residue was recrystallized from hexane–dichloromethane to give acid **3** (7.02 g, 81%) as colorless crystals, mp 107–108 °C (Found: C, 68.4; H, 6.3. Calc. for $C_{11}H_{12}O_3$: C, 68.7; H, 6.3%); ν_{max}(KBr)/cm^{-1} 1647 and 2839; δ_H(400 MHz) 1.90 (3 H, d, *J* 6.6, CH=CH*Me*), 3.90 (3 H, s, OMe), 6.25 (1 H, dq, *J* 15.3 and 6.6, CH=C*H*Me), 6.67 (1 H, d, *J* 15.3, C*H*=CHMe), 6.83 (1 H, d, *J* 8.0, ArH), 7.14 (1 H, d, *J* 8.0, ArH) and 7.33 (1 H, t, *J* 8.0, ArH).

Esterification of acid 3 to ester 4. This compound was prepared by the same procedure as used for the preparation of similar esters before.[10] A mixture of acid **3** (7.02 g, 36.5 mmol), 2,6-diisopropylphenol (6.52 g, 36.6 mmol), TFAA (10 cm^3) and benzene (25 cm^3) was stirred at room temperature for 1 day. After work-up, the crude product was purified by column chromatography on silica gel and elution with hexane–ethyl acetate (9 : 1) to give ester **4** (12.5 g, 97%) as colorless crystals, mp 73.5–74.5 °C (Found: C, 78.5; H, 8.0. Calc. for $C_{23}H_{28}O_3$: C, 78.4; H, 8.0%); ν_{max}(KBr)/cm^{-1} 1736; δ_H(400 MHz) 1.23 (12 H, br, $CHMe_2 \times 2$), 1.90 (3 H, d, *J* 6.6, CH=CH*Me*), 3.39 (2 H, sept, *J* 6.6, C*H*$Me_2 \times 2$), 3.90 (3 H, s, OMe), 6.28 (1 H, dq, *J* 15.4 and 6.6, CH=C*H*Me), 6.73 (1 H, d, *J* 15.4, C*H*=CHMe), 6.87 (1 H, d, *J* 8.1, ArH), 7.17 (1 H, d, *J* 8.1, ArH), 7.17 (1 H, d, *J* 7.9, ArH), 7.21–7.28 (2 H, m, ArH) and 7.35 (1 H, t, *J* 8.1, ArH).

Conversion of ester 4 into acid 6. To a solution of ester **4** (12.5 g, 35.5 mmol) in benzene (125 cm^3) was added a solution of mesitylmagnesium bromide, which had been prepared from 2-bromomesitylene (12.9 g, 64.8 mmol) and magnesium turnings (2.51 g) in diethyl ether (125 cm^3) and diluted with benzene (125 cm^3). The mixture was refluxed for 1 day. Work-up gave the biphenyl **5**, which was hydrolyzed without further purification by the same procedure as mentioned for ester **2**. Column chromatography of the crude product on silica gel with hexane–ethyl acetate (2 : 1) as eluent gave acid **6** (6.69 g, 67%) as colorless crystals. The sample sublimed at around 145 °C (Found: C, 81.3; H, 7.2. Calc. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2%); ν_{max}(KBr)/cm^{-1} 1693 and 2916; δ_H(500 MHz) 1.90 (3 H, dd, *J* 6.6 and 1.5, CH=CH*Me*), 1.96 (6 H, s, Ar*Me* × 2), 2.30 (3 H, s, Ar*Me*), 6.30 (1 H, dq, *J* 15.6 and 6.6, CH=C*H*Me), 6.55 (1 H, dd, *J* 15.6 and 1.5, C*H*=CHMe), 6.87 (2 H, s, ArH), 6.97 (1 H, d, *J* 7.6, ArH), 7.40 (1 H, t, *J* 7.6, ArH) and 7.52 (1 H, d, *J* 7.6, ArH).

Cyclization of acid 6 to the indenone 7. Acid **6** (6.60 g, 23.5 mmol) was refluxed for 2 h in thionyl dichloride (15 cm^3) in the presence of several drops of DMF and volatiles were removed under reduced pressure to give the acid chloride, which was dissolved in benzene (30 cm^3). To the ice-cold solution was added dropwise $SnCl_4$ (12.2 g, 46.8 mmol) and the mixture was stirred at 0 °C for 20 min. The reaction was quenched by successive additions of water (30 cm^3) and 2 M HCl (30 cm^3) and the two layers were separated. The water layer was extracted with diethyl ether and the combined organic layer was washed successively with 2 M HCl, 1 M NaOH and water, dried ($MgSO_4$), and evaporated to give a mixture of the indenone **7** and its hydrochloric acid adduct **8**. To a solution of the mixture in benzene (40 cm^3) was added triethylamine (2.90 g, 28.7 mmol) and the mixture was refluxed for 3 h. After cooling, the mixture was poured into 2 M HCl (20 cm^3) and the resulting mixture was extracted with diethyl ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (6 : 1) as eluent to give the indenone **7** (5.27 g, 85%) as pale yellow crystals, mp 76.9–78.3 °C (Found: C, 87.2; H, 6.9. Calc. for $C_{19}H_{18}O$: C, 87.0; H, 6.9%); ν_{max}(KBr)/cm^{-1} 1701; δ_H(500 MHz) 1.79 (3 H, d, *J* 1.8, Me), 1.95 (6 H, s, Ar*Me* × 2), 2.32 (3 H, s, Ar*Me*), 6.84 (1 H, d, *J* 7.6, ArH), 6.92 (2 H, s, ArH), 6.92 (1 H, d, *J* 7.6, ArH), 7.14 (1 H, q, *J* 1.8, ArCH) and 7.29 (1 H, t, *J* 7.6, ArH).

Reduction of the indenone 7 to the indanone 9. A mixture of the indenone **7** (5.19 g, 19.8 mmol), diphenylsilane (8.75 g, 47.5 mmol), $ZnCl_2$ (2.08 g, 15.3 mmol), $Pd(PPh_3)_4$ (32.0 mg, 27.7 μmol) and chloroform (120 cm^3) was stirred at room temperature for 4 h. Precipitates were filtered off on a silica gel plug and the filtrate was evaporated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (30 : 1) as eluent to give the indanone **9** (4.71 g, 90%) as an amorphous solid (Found: C, 86.5; H, 7.7. Calc. for $C_{19}H_{20}O$: C, 86.3; H, 7.6%); ν_{max}(KBr)/cm^{-1} 1707; δ_H(500 MHz) 1.24 (3 H, d, *J* 6.7, Me), 1.87 (3 H, s, Ar*Me*), 1.88 (3 H, s, Ar*Me*), 2.33 (3 H, s, Ar*Me*), 2.64 (1 H, dqd, *J* 8.1, 6.7 and 4.4, C*H*Me), 2.75 (1 H, dd, *J* 17.0 and 4.4, ArCH_2), 3.41 (1 H, dd, *J* 17.0 and 8.1, ArCH_2), 6.92 (1 H, s, ArH), 6.93 (1 H, s, ArH), 7.06 (1 H, dd, *J* 7.5 and 0.9, ArH), 7.42 (1 H, dd, *J* 7.5 and 0.9, ArH) and 7.59 (1 H, t, *J* 7.5, ArH).

Methylation of the indanone 9 to the dimethylindanone 10. A mixture of the indanone **9** (4.47 g, 16.9 mmol), NaH (1.14 g, 47.5 mmol), iodomethane (11.2 g, 78.9 mmol) and benzene (50 cm^3) was refluxed for 2 days. The cooled mixture was poured into 2 M HCl and extracted with diethyl ether. The extract was washed successively with 1 M $NaHSO_3$ and water, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel with hexane–ethyl acetate (10 : 1) as eluent to give the dimethylindanone **10** (4.67 g, 99%) as pale yellow crystals, mp 82.3–84.1 °C (Found: C, 86.5; H, 7.7. Calc. for $C_{20}H_{22}O$: C, 86.3; H, 8.0%); ν_{max}(KBr)/cm^{-1} 1710; δ_H(400 MHz) 1.17 (6 H, s, Me × 2), 1.87 (6 H, s, Ar*Me* × 2), 2.32 (3 H, s, Ar*Me*), 3.01 (2 H, s, ArCH_2), 6.92 (2 H, s, ArH), 7.08 (1 H, d, *J* 7.5, ArH), 7.40 (1 H, d, *J* 7.5, ArH) and 7.60 (1 H, t, *J* 7.5, ArH).

Reduction of the dimethylindanone 10 to the indanol *rac*-11. To a cooled solution of the dimethylindanone **10** (1.90 g, 6.83 mmol) in THF (50 cm^3) was added LAH (1.30 g, 34.3 mmol) portionwise at 0 °C and the mixture was stirred at this temperature for 2 h. The reaction was quenched by successive

additions of ethanol (5.0 cm^3), water (5.0 cm^3) and 1 M HCl (20 cm^3), and the two layers was separated. The water layer was extracted with diethyl ether and the organic layer was washed successively with 1 M Na_2CO_3 and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (10 : 1) as eluent to give the indanol **11** (1.91 g, 100%) as colorless crystals, mp 47.7–49.0 °C (Found: C, 85.8; H, 8.5. Calc. for $C_{20}H_{24}O$: C, 85.7; H, 8.6%); ν_{max}(KBr)/cm^{-1} 2954 and 3384; δ_H(400 MHz) 1.04 (3 H, s, Me), 1.10 (3 H, s, Me), 1.30 (1 H, s, OH), 1.93 (3 H, s, Ar*Me*), 2.01 (3 H, s, Ar*Me*), 2.32 (3 H, s, Ar*Me*), 2.63 (1 H, d, *J* 15.6, ArCH_2), 2.94 (1 H, d, *J* 15.6, ArCH_2), 4.26 (1 H, s, C*H*OH), 6.90 (1 H, dd, *J* 7.5 and 0.8, ArH), 6.93 (2 H, s, ArH), 7.18 (1 H, dd, *J* 7.5 and 0.8, ArH) and 7.28 (1 H, t, *J* 7.5, ArH).

Optical resolution of indanol 11

Esterification of the indanol 11 to esters 12 and their chromatographic separation. Enantiomerically pure (S_a)-2′-methoxy-1,1′-binaphthyl-2-carboxylic acid[20a] (1.50 g, 4.57 mmol) was refluxed for 2 h in thionyl dichloride (5.0 cm^3) in the presence of several drops of DMF and volatiles were removed under reduced pressure to give the acid chloride, which was dissolved in toluene (10 cm^3) along with the racemic indanol **11** (802 mg, 2.86 mmol), 4-pyrrolidinopyridine (848 mg, 5.72 mmol) and dry pyridine (2.0 cm^3). The mixture was refluxed for 12 h. The cooled mixture was poured into 1 M HCl and extracted with diethyl ether. The extract was washed successively with 1 M HCl, 1 M Na_2CO_3 and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (30 : 1) as eluent to give the diastereomerically pure esters **12**.

*Ester (S_a,R)-(−)-**12***. As the first-eluted fraction; yield 794 mg, 47%; $[\alpha]_D^{28}$ −46.1 (*c* 1.40, $CHCl_3$) (Found: C, 85.4; H, 6.6. Calc. for $C_{42}H_{38}O_3$: C, 85.4; H, 6.5%); ν_{max}(KBr)/cm^{-1} 1705 and 2959; δ_H(400 MHz) 0.15 (3 H, s, Me), 0.82 (3 H, s, Me), 1.64 (3 H, s, Me), 1.79 (3 H, s, Me), 2.24 (3 H, s, Me), 2.29 (1 H, d, *J* 15.6, ArCH_2), 2.36 (1 H, d, *J* 15.6, ArCH_2), 3.26 (3 H, s, OMe), 5.34 (1 H, s, ArC*H*) and 6.66–7.95 (17 H, m, ArH).

*Ester (S_a,S)-(−)-**12***. As the second-eluted fraction; yield 710 mg, 42%; $[\alpha]_D^{30}$ −30.4 (*c* 1.01, $CHCl_3$) (Found: C, 85.35; H, 6.7. Calc. for $C_{42}H_{38}O_3$: C, 85.4; H, 6.5%); ν_{max}(KBr)/cm^{-1} 1703 and 2993; δ_H(500 MHz) 0.37 (3 H, s, Me), 0.77 (3 H, s, Me), 1.73 (3 H, s, Me), 1.82 (3 H, s, Me), 1.96 (1 H, d, *J* 15.5, ArCH_2), 2.18 (1 H, d, *J* 15.5, ArCH_2), 2.29 (3 H, s, Me), 3.63 (3 H, s, OMe), 5.37 (1 H, s, ArC*H*) and 6.78–7.95 (17 H, m, ArH). The absolute stereochemistry was established by an X-ray crystallographic analysis (*vide infra*).

Reduction of esters 12 to the indanols 11. To a solution of the diastereomerically pure ester (S_a,*R*)-**12** (506 mg, 0.857 mmol) in THF (8.5 cm^3) was added LAH (326 mg, 8.59 mmol) portionwise at 0 °C and the mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. After being stirred for 30 h, the mixture was cooled to 0 °C and quenched by successive additions of ethanol (1.0 cm^3), water (1.0 cm^3) and 1 M HCl (10 cm^3). The resulting mixture was extracted with diethyl ether and the extract was washed successively with 1 M Na_2CO_3 and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel and eluted with benzene to give the indanol (*R*)-(−)-**11** (228 mg, 95%) as colorless crystals; $[\alpha]_D^{25}$ −4.27 (*c* 1.04, $CHCl_3$). The spectral data of the sample were identical with those of racemic **11** (*vide supra*). Optical purity of the sample was determined to be 99% ee by an HPLC analysis on a Daicel Chiralcel OD-H with 0.3% propan-2-ol in hexane as the eluent.

The dextrorotatory counterpart of the indanol **11** was obtained from the diastereomerically pure ester (S_a,*S*)-**12** by a similar procedure. Ester (S_a,*S*)-**12** (498 mg, 0.843 mmol) was treated with LAH (320 mg, 8.43 mmol) in THF (8.5 cm^3) at room temperature for 2 h. After work-up, the crude product was purified by column chromatography with hexane–ethyl acetate (10 : 1) as eluent to give the indanol (*S*)-(+)-**11** of 99% ee (236 mg, 100%) as colorless crystals; $[\alpha]_D^{25}$ +4.29 (*c* 1.02, $CHCl_3$).

Determination of the absolute configuration of ester 12

The slower-running counterpart of the diastereomeric indanyl esters **12** on a silica gel column (*vide supra*) was crystallized from ethyl acetate to give prismatic crystals, one of which was subjected to X-ray crystallographic analysis. The absolute stereochemistry of the indanyl moiety was assigned to be *S* by using the (S_a)-binaphthyl axis as an internal reference. See Fig. 2 for the ORTEP drawing.

Crystal data. $C_{42}H_{38}O_3$, *M* = 590.76, orthorhombic, *a* = 15.260(2), *b* = 16.228(2), *c* = 13.263(2) Å, *V* = 3284.6(7) $Å^3$, *T* = 22 °C, space group $P2_12_12_1$ (no. 19), *Z* = 4, μ (Mo-Kα) = 0.73 cm^{-1}, 4223 unique reflections, *R*(*F*) = 0.0329 [*wR*(*F*) = 0.029].

Atrolactic acid synthesis

Preparation of phenylglyoxylic ester 13. Phenylglyoxylic acid (182 mg, 1.21 mmol) was treated with oxalyl dichloride (290 mg, 2.28 mmol) in the presence of several drops of DMF in dry dichloromethane (1.0 cm^3) at room temperature for 2 h and volatiles were removed under reduced pressure to give the acid chloride, which was dissolved in dry pyridine (5.0 cm^3). To the solution was added the indanol (*R*)-(−)-**11** (170 mg, 0.606 mmol) and the mixture was stirred at room temperature for 12 h. The reaction was quenched with 1 M HCl (30 cm^3) and the mixture was extracted with diethyl ether. The extract was washed successively with 1 M HCl, saturated aq. Na_2CO_3 and brine, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel with hexane–ethyl acetate (25 : 1) as eluent to give phenylglyoxylic ester (*R*)-**13** (230 mg, 92%) as an oil, $[\alpha]_D^{26}$ −7.41 (*c* 0.940, $CHCl_3$) (Found: C, 81.65; H, 6.6. Calc. for $C_{28}H_{28}O_3$: C, 81.5; H, 6.8%); ν_{max}(neat)/cm^{-1} 1686, 1724 and 2960; δ_H(400 MHz) 1.17 (3 H, s, Me), 1.22 (3 H, s, Me), 1.72 (3 H, s, Ar*Me*), 1.99 (3 H, s, Ar*Me*), 2.28 (3 H, s, Ar*Me*), 2.73 (1 H, d, *J* 15.8, ArCH_2), 3.13 (1 H, d, *J* 15.8, ArCH_2), 5.72 (1 H, s, ArC*H*), 6.69 (1 H, s, ArH), 6.93 (1 H, d, *J* 7.5, ArH), 6.96 (1 H, s, ArH), 7.22 (1 H, d, *J* 7.5, ArH), 7.35 (1 H, t, *J* 7.5, ArH), 7.44–7.49 (2 H, m, ArH), 7.62–7.66 (1 H, s, ArH) and 7.73–7.76 (2 H, m, ArH).

Typical procedure for the Grignard reaction of ester 13. Methylmagnesium iodide was prepared from iodomethane (233 mg, 1.64 mmol) and magnesium turnings (65 mg) in diethyl ether (7.0 cm^3). One-fifth portion of the Grignard reagent was added dropwise to a cooled solution of ester (*R*)-**13** (113 mg, 0.274 mmol) in toluene (2.7 cm^3) over a period of 10 min at −78 °C and the mixture was stirred at this temperature for 5 min before being quenched with saturated aq. NH_4Cl (10 cm^3). After warming to room temperature, the mixture was extracted with diethyl ether and the extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC with hexane–ethyl acetate (20 : 1) as the developer to give atrolactic ester **14** (117 mg, 100%) as an oil (Found: C, 81.5; H, 7.2. Calc. for $C_{29}H_{32}O_3$: C, 81.3; H, 7.5%); δ_H(400 MHz) 0.55, 0.77 [3 H: s, Me (minor); s, Me (major)], 0.96, 0.98 [3 H: s, Me (minor); s, Me (major)], 1.52, 1.53 [3 H: s, Me (minor); s, Me (major)], 1.71, 1.84 [3 H: s, Me (major); s, Me (minor)], 1.94, 1.95 [3 H: s, Me (minor); s, Me (major)], 2.29, 2.32 [3 H: s, Me (minor); s, Me (major)], 2.55, 2.64 [1 H: d, *J* 15.7, ArCH_2 (minor); d, *J* 15.7, ArCH_2 (major)], 2.84, 2.91 [1 H: d, *J* 15.7, ArCH_2 (minor); d, *J* 15.7, ArCH_2 (major)], 2.95, 3.68 [1 H: s, OH (major); s, OH (minor)], 5.59, 5.69 [3 H: s, ArC*H* (minor);

s, ArC*H* (major)] and 6.73–7.44 (10 H, m, ArH). ^{1}H NMR analysis of the sample easily differentiated the methyl signal resonating at the highest magnetic field, between the diastereomers, which determined the optical purity to be 83% de.

The ester **14** (116 mg, 0.271 mmol) was boiled with KOH (400 mg) in aq. ethanol (10 cm^3) for 1 day. After usual work-up, the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (1 : 2) as eluent to give atrolactic acid (39.3 mg, 87%), $[\alpha]_D^{30}$ −29.5 (*c* 1.75, EtOH) {lit.,[27] $[\alpha]_D^{25}$ +36.3 (*c* 2.7, EtOH) for (*S*)-enantiomer}. This determined the absolute stereochemistry of the ester **14** to be *R,R*. The chiral auxiliary **11** (73.1 mg, 96%) was recovered from the ester **14** by hydrolysis without loss of chiral integrity (99% ee).

Biphenyl coupling reaction

Preparation of ester 15. This compound was prepared by a similar procedure to that employed for the preparation of ester **12**. The acyl chloride prepared from 2,3-dimethoxybenzoic acid (590 mg, 3.24 mmol) was allowed to react with the indanol (*R*)-**11** (227 mg, 0.810 mmol) in dry pyridine (4.0 cm^3) at 90 °C for 1 day. After work-up, the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (40 : 1 to 20 : 1) to give ester (*R*)-**15** (306 mg, 85%) as an amorphous solid (Found: C, 78.15; H, 7.0. Calc. for $C_{29}H_{32}O_4$: C, 78.4; H, 7.3%); δ_H(400 MHz) 1.16 (3 H, s, Me), 1.19 (3 H, s, Me), 1.69 (3 H, s, Ar*Me*), 1.96 (3 H, s, Ar*Me*), 2.24 (3 H, s, Ar*Me*), 2.73 (1 H, d, *J* 15.7, ArCH_2), 3.09 (1 H, d, *J* 15.7, ArCH_2), 3.68 (3 H, s, OMe), 3.85 (3 H, s, OMe), 5.77 (1 H, s, ArC*H*), 6.64 (1 H, s, ArH), 6.90 (1 H, s, ArH), 6.92 (1 H, d, *J* 7.5, ArH), 6.98–7.03 (3 H, m, ArH), 7.22 (1 H, d, *J* 7.5, ArH) and 7.33 (1 H, t, *J* 7.5, ArH).

Typical procedure for the Grignard reaction of ester 15. The Grignard reagent was prepared from 1-bromo-2-methoxy-4,6-dimethylbenzene (374 mg, 1.74 mmol) and magnesium turnings (68 mg) in diethyl ether (3.0 cm^3), dissolution being achieved by the addition of toluene (3.0 cm^3). A half portion of the Grignard solution was added to a solution of the ester (*R*)-**15** (194 mg, 0.436 mmol) in toluene (1.5 cm^3) at −10 °C and the mixture was stirred at this temperature for 7 h and then at 0 °C for 1 h. After work-up, the reaction mixture was subjected to ^{1}H NMR analysis. A methoxy signal of the diastereomers was differentiated well (*vide infra*), which determined the diastereoselectivity of the reaction to be 72%. The crude product was chromatographed on a silica gel column with hexane–ethyl acetate (20 : 1) as eluent to give the diastereomerically pure esters **16**.

*Ester (R$_a$,R)-(+)-**16**.* As the major isomer; yield 186 mg, 78%; $[\alpha]_D^{30}$ +28.7 (*c* 0.685, $CHCl_3$) (Found: C, 81.2; H, 7.2. Calc. for $C_{37}H_{40}O_4$: C, 81.0; H, 7.4%); δ_H(400 MHz) 0.69 (3 H, s, Me), 0.95 (3 H, s, Me), 1.70 (3 H, s, Me), 1.77 (3 H, s, Me), 1.84 (3 H, s, Me), 2.26 (3 H, s, Me), 2.34 (3 H, s, Me), 2.44 (1 H, d, *J* 15.6, ArCH_2), 2.66 (1 H, d, *J* 15.6, ArCH_2), 3.23 (3 H, s, OMe), 3.66 (3 H, s, OMe), 5.41 (1 H, s, ArC*H*), 6.45 (1 H, s, ArH), 6.63 (1 H, s, ArH), 6.71 (1 H, s, ArH), 6.84 (1 H, s, ArH), 6.89 (1 H, d, *J* 7.4, ArH), 7.05 (1 H, dd, *J* 8.0 and 1.3, ArH), 7.17 (1 H, d, *J* 7.4, ArH), 7.22 (1 H, dd, *J* 8.0 and 1.3, ArH), 7.28 (1 H, t, *J* 8.0, ArH) and 7.29 (1 H, t, *J* 7.4, ArH).

*Ester (S$_a$,R)-(−)-**16**.* As the minor isomer; yield 31.0 mg, 13%; $[\alpha]_D^{28}$ −13.4 (*c* 1.41, $CHCl_3$); δ_H(400 MHz) 0.60 (3 H, s, Me), 0.92 (3 H, s, Me), 1.64 (3 H, s, Me), 1.67 (3 H, s, Me), 1.86 (3 H, s, Me), 2.28 (3 H, s, Me), 2.33 (3 H, s, Me), 2.41 (1 H, d, *J* 15.6, ArCH_2), 2.68 (1 H, d, *J* 15.6, ArCH_2), 3.55 (3 H, s, OMe), 3.66 (3 H, s, OMe), 5.42 (1 H, s, ArC*H*), 6.55 (1 H, s, ArH), 6.63 (1 H, s, ArH), 6.74 (1 H, s, ArH), 6.85 (1 H, s, ArH), 6.86 (1 H, d, *J* 7.5, ArH), 7.03 (1 H, dd, *J* 8.0 and 1.1, ArH), 7.13 (1 H, dd, *J* 8.0 and 1.1, ArH), 7.17 (1 H, d, *J* 7.5, ArH), 7.28 (1 H, t, *J* 8.0, ArH) and 7.29 (1 H, t, *J* 7.5, ArH).

The major isomer (+)-**16** was hydrolyzed by a similar procedure to that used for the preparation of acid **3**. Thus, the ester (+)-**16** (135 mg, 0.246 mmol) was heated at 120 °C with 10 equiv. of sodium methoxide in toluene (2.0 cm^3)–dry HMPA (1.0 cm^3) for 12 h. To this mixture was added water (1.0 cm^3) and the resulting mixture was heated at 110 °C for 2 h. After work-up, the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (2 : 1) as eluent to give (+)-2′,6-dimethoxy-4′,6′-dimethylbiphenyl-2-carboxylic acid (63.4 mg, 90%), $[\alpha]_D^{27}$ +98.6 (*c* 1.34, $CHCl_3$) {lit.,[20c] $[\alpha]_D^{22}$ +66.9 (*c* 1.02, $CHCl_3$) for (R_a)-isomer of 79% ee}. This determined the absolute stereochemistry of the acid to be R_a. Thus, the R_a,*R* absolute configuration of the ester (+)-**16** was established. The chiral auxiliary **11** (63.0 mg, 91%) was recovered from the ester **16** by hydrolysis without appreciable loss of chiral integrity (98% ee).

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