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Synthesis of New Chiral Schiff Bases from (+)-3-Carene and Their Use in Asymmetric Oxidation of Sulfides Catalyzed by Metal Complexes

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Abstract—A number of new chiral Schiff bases were synthesized starting from accessible monoterpene (+)-3-carene, and the products were used as ligands in metal complex-catalyzed oxidation of sulfides to chiral sulfoxides. The optical purity and the sign of optical rotation of chiral sulfoxides were found to strongly depend on the oxidation temperature.

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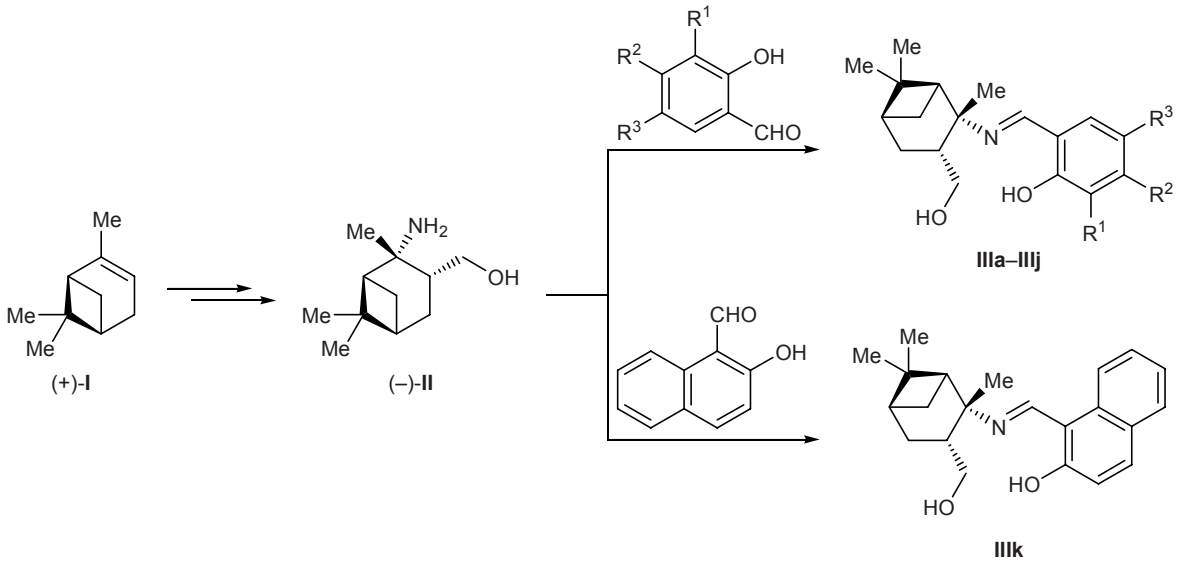
In the past few decades, asymmetric metal complex catalysis has become one of the most promising fields of fine organic synthesis. Variation of metal (Mn, Al, Co, V, Cr) and chiral ligand made it possible to obtain indispensable catalysts for asymmetric synthesis [1–4]. Chiral Schiff bases derived from substituted salicylaldehydes are widely used as chiral ligands in metal complex catalysis [5–8]. These ligands ensured successful asymmetric reactions, in particular catalytic hydrophosphorylation [7], addition of carbon dioxide to epoxypropane [5], condensation of nitromethane with aldehydes (nitroaldol reaction) [4], asymmetric sulfoxidation [2], etc.

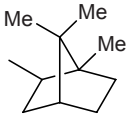
The recent interest in asymmetric metal complex-catalyzed sulfoxidation has been stimulated by wide application of optically active sulfoxides in asymmetric synthesis [9–11] and by the fact that a number of natural compounds contain a chiral sulfoxide group. Moreover, some sulfoxides with a definite configuration showed high biological activity [12–15]. Taking into account the above stated, development of effective procedures for the synthesis of chiral sulfoxides has attracted strong attention. Among known methods, one of the most convenient is asymmetric oxidation of prochiral sulfides in the presence of vanadium-containing metal complex systems [16].

As follows from numerous publications on asymmetric catalysis, the ligand structure was varied using Schiff bases derived from differently substituted salicylaldehydes [17, 18]; in almost all cases, derivatives of optically active amino acids were used as chiral auxiliaries [16, 19–21]. We recently showed [22, 23] that some terpenoids, in particular accessible (+)- and (–)-α-pinenes (**I**), can be used as source of chirality in the synthesis of optically active Schiff bases **IIIa**–**IIIk**. A number of new chiral Schiff bases **IIIa**–**IIIk** were synthesized from various substituted salicylaldehydes and amino alcohols (+)- and (–)-**II** which were prepared from the corresponding optically active pinenes according to the procedure reported in [24] (Scheme 1). Schiff bases **IIIa**–**IIIk** were successfully used as ligands in vanadium-catalyzed asymmetric oxidation of methylsulfanylbenzene [22] (which is often used as model compound) and heterocyclic sulfide **IV** which is precursor of optically active Omeprazole (**V**) [25] (Scheme 2). The *S* enantiomer of Omeprazole (Esomeprazole) is a highly efficient antiulcer drug [26].

Compound **IIIa** turned out to be the most effective ligand in the asymmetric oxidation of methylsulfanylbenzene [22], whereas the best results in the synthesis of optically active Omeprazole (**V**) were achieved using Schiff base **IIIb** [25]. These data demonstrate that there are no universal ligands equally suitable for the oxidation of any sulfide and that a broad series of ligands with different structures should be disposable

Scheme 1.



$R^1 = R^3 = t$-Bu, R^2 = H (**a**); $R^1 = R^2 = R^3$ = H (**b**); R^1 =  , R^2 = H, R^3 = Me (**c**); $R^1 = R^3 = PhC(Me)_2$, R^2 = H (**d**); R^1 = R^2 = H, $R^3 = NO_2$ (**e**); $R^1 = R^3 = NO_2$, R^2 = H (**f**); $R^1 = R^2$ = H, R^3 = OMe (**g**); R^1 = OMe, $R^2 = R^3$ = H (**h**); $R^1 = R^3$ = H, $R^2 = NEt_2$ (**i**); R^1 = Br, R^2 = H, $R^3 = NO_2$ (**j**).

to develop effective procedures for asymmetric oxidation of complex sulfides.

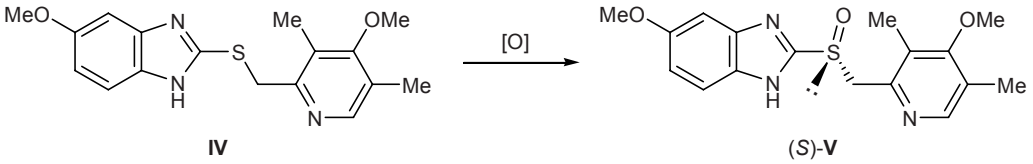
The goal of the present study was to synthesize new chiral Schiff bases on the basis of substituted salicylaldehydes and an accessible optically active monoterpene, (+)-3-carene (**VI**), and examine the efficiency of the products as ligands in metal complex-catalyzed asymmetric oxidation of methylsulfanylbenzene.

Gyónfalvi et al. [27] described a procedure for the synthesis of (+)-amino alcohol **XI** from (+)-3-carene (**VI**). In the first step, optically active monoterpene reacted with chlorosulfonyl isocyanate to give β-lactam **VII** (Scheme 3). Acid hydrolysis of compound **VII** was impossible because of its low stability in acid medium. Therefore, the NH group was activated via introduction of *tert*-butoxycarbonyl group. The subsequent methanolysis of Boc-protected lactam **VIII**, hydrolysis of **IX**, and reduction of ester **X** gave amino alcohol **XI** [27].

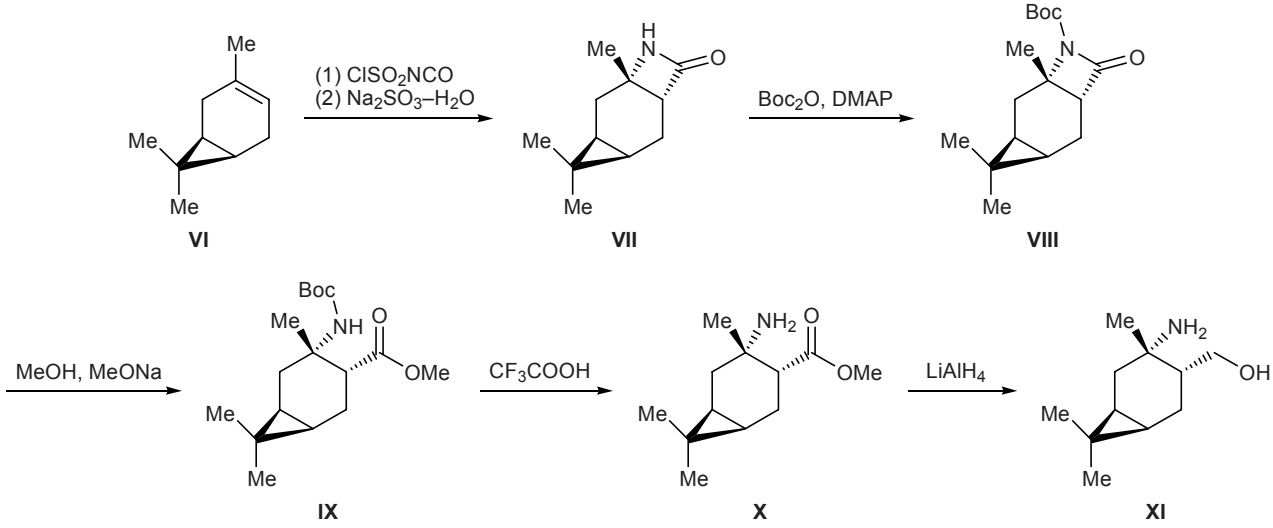
We have synthesized compound **XI** from (+)-3-carene (**VI**), following the above procedure [27]. The reaction of (+)-3-carene (**VI**) with chlorosulfonyl isocyanate was carried out in diethyl ether at room temperature. After treatment of the reaction mixture with an aqueous solution of sodium sulfite and recrystallization from hexane, we isolated compound **VII** in 50% yield. Lactam **VII** was then treated with di-*tert*-butyl dicarbonate in anhydrous tetrahydrofuran in the presence of a catalytic amount of *N*,*N*-dimethylpyridin-4-amine (DMAP), and subsequent purification by column chromatography quantitatively afforded compound **VIII** which was subjected to methanolysis in the presence of sodium methoxide; the yield of compound **IX** was 95%.

We tried to reproduce the procedure reported in [27] for removal of *tert*-butoxycarbonyl protecting group from compound **IX**. However, the reaction of **IX** with trifluoroacetic acid in methylene chloride at room temperature was accompanied by strong tarring. We

Scheme 2.



Scheme 3.

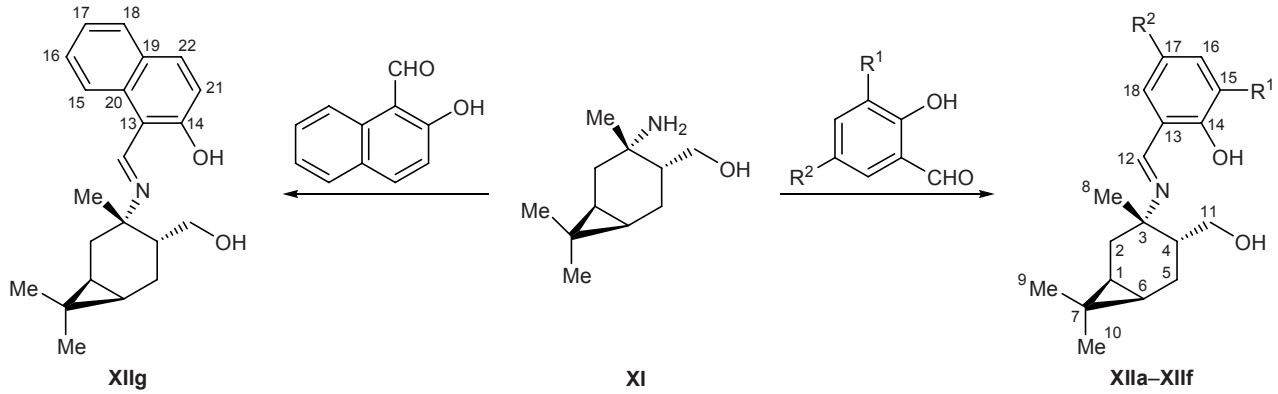


succeeded in minimizing tar formation by lowering the temperature to 0°C; by column chromatography we isolated 57% of compound **X**. Reduction of the latter with lithium tetrahydridoaluminate gave amino alcohol **XI** in 68% yield.

By condensation of amino alcohol **XI** with substituted salicylaldehydes we synthesized new chiral Schiff bases **XIIa**–**XIIg** (Scheme 4). The reaction rate and method for purification of the product strongly depended on the initial aldehyde. Schiff bases **XIIb**–**XIIf** and **XIIg** were synthesized by stirring a mixture of the reactants in anhydrous methanol at room temperature for 2.5 to 24 h, while the reaction of amino alcohol **XI** with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde required heating under reflux over a period of 7 days to obtain Schiff base **XIIa**. Compounds **XIIa** and **XIIb** were purified by column chromatography on silica gel, chiral Schiff bases **XIIc** and **XIIe**–**XIIg** were precipitated from diethyl ether with hexane, and 2-hydroxy-3,5-dinitrobenzaldehyde derivative **XIId** was recrystallized from diethyl ether.

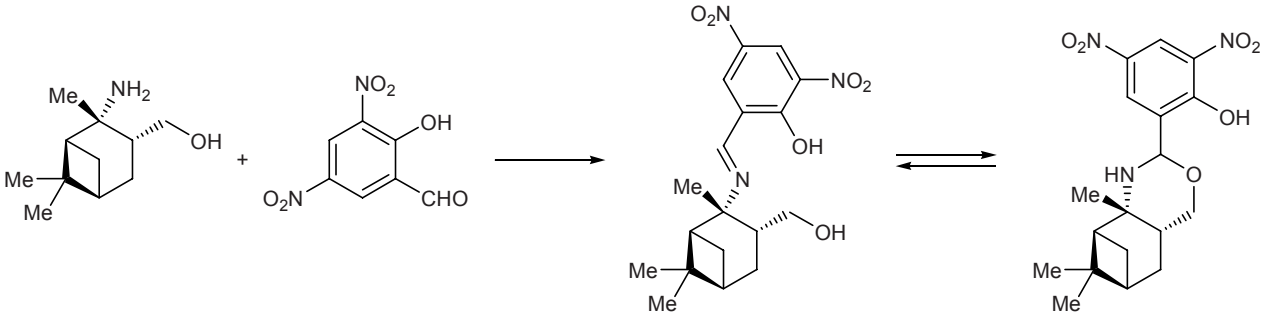
We previously found that, unlike all other aldehydes, 2-hydroxy-3,5-dinitrobenzaldehyde reacted with amino alcohol (–)-**II** to give a mixture of tricyclic compound **XIII** as the major product and expected Schiff base **IIIf** (Scheme 5); the ratio **XIII** : **IIIf** was 1 : 0.6 at 28°C [22]. However, the product obtained from (+)-3-carene (**VI**) and the same aldehyde had the structure of Schiff base **XIId**, whereas compound **XIIe** derived from 2-hydroxy-5-methoxybenzaldehyde contained an appreciable amount (~23% at 28°C) of tricyclic structure **XIV** (Scheme 6). According to the ^{1}H NMR data, closure of oxazine ring occurred to some extent (up to 10%) in the synthesis of Schiff bases **XIIc** and **XIIf**; compounds **XIIa** and **XIIb** were formed only as open-chain isomers.

Scheme 4.



$R^1 = R^2 =$ *t*-Bu (**a**), H (**b**), O_2N (**d**); $R^1 =$ H, $R^2 = O_2N$ (**c**), MeO (**e**); $R^1 =$ MeO, $R^2 =$ H (**f**).

Scheme 5.



(–)-**II** **IIIf** **XIII**

Scheme 6.

XIIe **XIV**

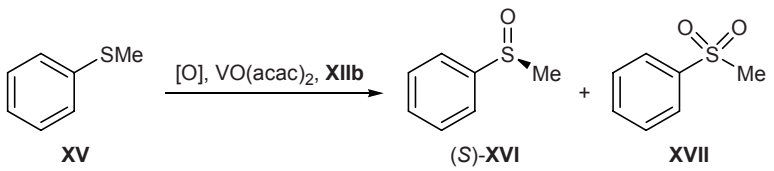
We can conclude that Schiff bases derived from amino alcohol of the pinane series and their 3-carene-based analogs display radically different relations between electronic effects of substituents in the benzene ring and the ability to form tricyclic oxazine structure. Closure of oxazine ring in compounds **IIIa**–**IIIk** requires the presence of two strongly acceptor groups, while the formation of cyclic structure from Schiff bases **XIIa**–**XIIg** is favored by donor substituents in the benzene ring.

New chiral Schiff bases **XIIa**–**XIIg** derived from accessible optically active (+)-3-carene (**VI**) were tested as ligands in vanadium-catalyzed asymmetric oxidation of methylsulfanylbenzene (**XV**). The oxidation conditions were optimized using Schiff base **XIIb** as model ligand. Under the optimal conditions ensuring the best enantioselectivity in the asymmetric oxidation of **XV** (Scheme 7) in the presence of Schiff bases derived from α-pinene (**I**) (room temperature, solvent methylene chloride, oxidant 70% hydrogen peroxide) [22] we obtained sulfoxide **XVI** with an *ee* (enantiomeric excess) value of 20% (Table 1). Both lowering the temperature to 0°C and heating to 30°C (Table 1; run nos. 2, 3) resulted in reduced enantioselectivity. Replacement of methylene chloride as solvent by chloroform led to almost complete loss of enantioselectivity.

It should be emphasized that the reaction temperature affects not only *ee* value but also configuration of the major stereoisomer. Analogous temperature dependence of enantiomeric excess was observed previously in asymmetric oxidation of aryl methyl sulfides in the presence of various metal complex systems, in particular in the oxidation of 4-methylsulfanyltoluene with Ti(OPr-*i*)$_4$–(+)-diethyl tartrate–H_2O–*t*-BuOOH [28] and of methylsulfanylbenzene (**XV**) in the presence of vanadium complex with ligand **IIIa** [22]. In these cases, both reduction and rise in temperature relative to some optimal value impaired the optical purity.

Figure shows the relation between the optical purity of sulfoxide **XVI** and reaction temperature in the oxidation catalyzed by VO(acac)$_2$–**IIIa**–H_2O_2 [22] and VO(acac)$_2$–**XIIb**–H_2O_2. Analogous relation was re-

Scheme 7.



XV (*S*)-**XVI** **XVII**

Table 1. Asymmetric oxidation of methylsulafanylbenzene (**XV**) in the presence of Schiff base **XIIb**

Run no.	Oxidant[a]	Reaction time, h	Temperature, °C	Solvent	Conversion, %	Yield,[b] %		**XVI**,[c] *ee*, %
						XVI	**XVII**	
1	70% H_2O_2	1.5	20	CH_2Cl_2	100	80	20	20 (*S*)
2	70% H_2O_2	3	0	CH_2Cl_2	100	85	15	11 (*R*)
3	70% H_2O_2	1	30	CH_2Cl_2	100	91	9	5 (*R*)
4	70% H_2O_2	2	20	$CHCl_3$	68	90	10	3 (*S*)

[a] Molar ratio $VO(acac)_2$–**XIIb**–**XV**–H_2O_2 1 : 1.5 : 106 : 132.

[b] Calculated on the reacted sulfide **XV** (according to the ^1H NMR data).

[c] The optical purity of sulfoxide **XVI** was determined by ^1H NMR spectroscopy using (*R*)-(-)-3,5-dinitro-*N*-(1-phenylethyl)benzamide as chiral shift reagent. The absolute configuration was determined by comparing the sign of optical rotation of the product with published data.

ported in [28]; presumably, the presence of a maximum on the curve given therein results from change of the oxidation mechanism.

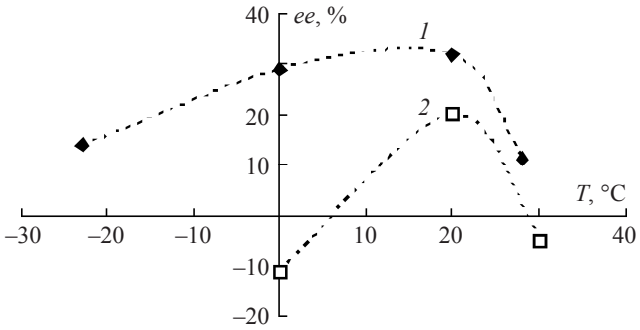
Change of the sign of optical rotation of the product was observed only in the presence of Schiff base **XIIb** as ligand. This dependence may be interpreted assuming that the oxidation process involves two concurrent pathways. One of these leads to preferential formation of the *R* isomer, and its enantioselectivity only slightly depends on the temperature. By contrast, enantioselectivity of the second process which leads to the *S* isomer strongly depends on the temperature. The final result is determined by relative contributions of the above processes, and it may show strong temperature dependence: the corresponding curve has a clearly defined maximum. Such assumption makes it possible to rationalize, at least partially, moderate enantioselectivity in the oxidation of sulfide **XV**.

With a view to elucidate the effect of the nature and size of substituents in the aromatic ring of the ligand, oxidation of compound **XV** was performed in the presence of Schiff bases **XIIa** and **XIIc**–**XIIg** under the conditions indicated in Table 1, run no. 1. Introduction of *tert*-butyl groups into the *ortho* and *para* positions with respect to the hydroxy group (compound **XIIa**) considerably reduced the optical purity of sulfoxide **XVI** (to 9%). Lower *ee* value was also obtained with the use of 2-hydroxynaphthyl derivative **XIIg** (Table 2, run no. 6). The oxidation in the presence of Schiff bases containing both electron-withdrawing (nitro group in the *para* position; Table 2, run no. 2) and electron-donating groups in the aromatic ring (methoxy group in the *para* or *ortho* position; Table 2, run nos. 4, 5) gave almost racemic sulfoxide **XVI**. The corresponding *ee* values (1–2%) approach the experimental error. As in the oxidation with ligands based on α-pinene (**I**), introduction of two nitro groups resulted in reversal of configuration of the major stereoisomer (Table 2, run no. 3).

The newly synthesized Schiff base ligands are characterized by considerably different steric hindrances created by substituents in the vicinity of the active center, as well as by different electronic factors, which makes them promising for searching optimal conditions for asymmetric oxidation of complex sulfides.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-500 and AM-400 spectrometers (500.13 and 400.13 MHz for ^1H and 125.76 and 100.61 MHz for ^{13}C, respectively) from solutions in $CDCl_3$–CCl_4 (~1 : 1, by volume) or acetone-d_6. The chemical shifts were measured relative to the solvent signals ($CHCl_3$, δ 7.24 ppm; $CDCl_3$, δ_C 76.90 ppm; acetone-d_5, δ 2.04 ppm; acetone-d_6, δ_C 29.8 ppm). The product structure was determined by analysis of the ^1H NMR



Plots of the optical purity of methyl phenyl sulfoxide **XVI** versus temperature in the oxidation of methylsulfanylbenzene with the catalytic systems (*1*) $VO(acac)_2$–**IIIa**–H_2O_2 [22] and (*2*) $VO(acac)_2$–**XIIb**–H_2O_2.

Table 2. Asymmetric oxidation of methylsulfanylbenzene (**XV**) in the presence of compounds **XIIa** and **XIIc–XIIg** as ligands[a]

Run no.	Compound no.	Reaction time, h	Conversion, %	Yield,[b] %		*ee*,[c] %
				XVI	**XVII**	
1	**XIIa**	3	78	96	4	9 (*S*)
2	**XIIc**	1.5	100	81	19	1 (*S*)
3	**XIId**	2.5	99	88	12	6 (*R*)
4	**XIIe**	1	100	82	18	0 (*S*)
5	**XIIf**	1	100	83	17	1 (*S*)
6	**XIIg**	1.5	100	86	14	4 (*S*)

[a] Molar ratio $VO(acac)_2$–ligand–**XV**–H_2O_2 1 : 1.5 : 106 : 132; temperature 20°C; solvent methylene chloride, 5 ml.

[b] Calculated on the reacted sulfide **XV** (according to the ^1H NMR data).

[c] The optical purity of sulfoxide **XVI** was determined by ^1H NMR spectroscopy using (*R*)-(-)-3,5-dinitro-*N*-(1-phenylethyl)benzamide as chiral shift reagent. The absolute configuration was determined by comparing the sign of optical rotation of the product with published data.

spectra using ^1H–^1H double resonance technique, JMOD ^{13}C NMR spectra, off-resonance ^{13}C NMR spectra, and two-dimensional ^1H–^{13}C correlation spectra (direct coupling constants, C–H COSY, $^1J_{CH}$ = 135 Hz). The high-resolution mass spectra were obtained on a Finnigan MAT-8200 instrument. The specific optical rotations $[\alpha]_{580}$ and $[\alpha]_{589}$ were measured on Polamat A and PolAAr 3005 polarimeters, respectively.

The purity of the initial compounds and reaction products was checked by GLC on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector (ZB-5 quartz capillary column, 30000× 0.25 mm; carrier gas helium, inlet pressure 1 atm).

{(1*R*,3*R*,4*S*,6*S*)-4-Amino-4,7,7-trimethylbicyclo-[4.1.0]heptan-3-yl}methanol (XI). 3-Carene (**VI**, 89%; $[\alpha]_{580}^{22}$ = +10.14°, *c* = 2.5, $CHCl_3$), 6.420 g (47 mmol), was dissolved in 50 ml of anhydrous diethyl ether, 5.3 ml (61 mmol) of chlorosulfonyl isocyanate was added dropwise under stirring and cooling with an ice bath, and additional 50 ml of anhydrous diethyl ether was added. The cooling bath was removed, and the mixture was stirred for 24 h. A solution of 10 g of Na_2SO_3 in 132 ml of water was added, and the mixture was adjusted to pH ~7–8 by adding 20% aqueous sodium hydroxide and stirred for 3 h. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The extracts were combined with the organic phase and dried over $MgSO_4$, the solvent was distilled off, and the residue was recrystallized from hexane. We thus isolated 4.223 g (50%) of (1*R*,3*R*,5*S*,7*S*)-4,4,7-trimethyl-8-azatricyclo[5.2.0.0^{3,5}]nonan-9-one (**VII**) whose ^1H NMR spectrum coincided with that reported in [27].

Compound **VII**, 3.040 g (17 mmol), was dissolved in 25 ml of anhydrous tetrahydrofuran, 0.5 ml of triethylamine, 7.270 g (33 mmol) of di-*tert*-butyl dicarbonate, and a catalytic amount of *N*,*N*-dimethylpyridin-4-amine were added, and the mixture was diluted with 25 ml of anhydrous THF, stirred for 0.5 h, and heated for 3 h under reflux. The solvent was distilled off, and the residue was purified by column chromatography on silica gel using hexane–ethyl acetate (0 to 100% of the latter, gradient elution) to isolate 1.823 g of initial compound **VII** (conversion 62%) and 1.953 g of *tert*-butyl (1*R*,3*R*,5*S*,7*S*)-4,4,7-trimethyl-9-oxo-8-azatricyclo[5.2.0.0^{3,5}]nonane-8-carboxylate (**VIII**) (quantitative yield calculated on the reacted compound **VII**). The ^1H NMR spectrum of **VIII** coincided with that reported in [27].

Compound **VIII**, 2.508 g (9 mmol), was dissolved in 10 ml of anhydrous methanol, a catalytic amount of sodium methoxide was added under stirring, and the mixture was stirred for 3 h. The solvent was distilled off, and the residue was treated with water and extracted with chloroform. The extract was dried over $MgSO_4$ and evaporated to isolate 2.664 g (95%) of methyl (1*R*,3*R*,4*S*,6*S*)-4-(*tert*-butoxycarbonylamino)-4,7,7-trimethylbicyclo[4.1.0]heptane-3-carboxylate (**IX**) whose ^1H NMR spectrum coincided with that reported in [27].

A solution of 0.430 g (1.4 mmol) of compound **IX** in 20 ml of methylene chloride was cooled in an ice bath, 1.1 ml of trifluoroacetic acid was added, and the mixture was stirred for 3 h on cooling, neutralized with a saturated aqueous solution of sodium hydrogen carbonate, and extracted with methylene chloride (2× 65 ml). The extract was dried over $MgSO_4$ and evap-

orated, and the residue was purified by column chromatography on silica gel (gradient elution with hexane–ethyl acetate, 0 to 100% of the latter) to isolate 0.170 g (57%) of methyl (1*R*,3*R*,4*S*,6*S*)-4-amino-4,7,7-trimethylbicyclo[4.1.0]heptane-3-carboxylate (**X**) whose ^{1}H NMR spectrum coincided with that reported in [27].

A solution of 0.170 g (0.81 mmol) of compound **X** in 3 ml of tetrahydrofuran was added dropwise under stirring to a suspension of 0.064 g (1.7 mmol) of $LiAlH_4$ in 4 ml of anhydrous THF on cooling with an ice bath. The cooling bath was removed, the mixture was stirred for 3.5 h and cooled again, and water was added dropwise under stirring and cooling until hydrogen no longer evolved. The precipitate was filtered off. Yield of **XI** 0.100 g (68%); its ^{1}H NMR spectrum coincided with that reported in [27].

2,4-Di-*tert*-butyl-6-[(1*S*,3*S*,4*R*,6*R*)-4-hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]phenol (XIIa). A solution of 0.098 g (0.42 mmol) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in 3 ml of anhydrous methanol was filtered and added dropwise under stirring to a solution of 0.073 g (0.40 mmol) of compound **XI** in 5 ml of anhydrous methanol, and the mixture was heated for 7 days under reflux. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the residue was purified by column chromatography on silica gel [gradient elution with hexane (containing 1% of triethylamine)–chloroform, 0 to 100% of the latter]. Yield 0.079 g (49%), orange crystals, mp 155–161°C, $[\alpha]_{580}^{22}$ = +1.5° (*c* = 1.9, MeOH). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.69 m (1-H), 0.72 m (6-H), 1.02 s (C^9H_3, $C^{10}H_3$), 1.03 s (C^8H_3), 1.32 s and 1.45 s (*t*-Bu), 1.37 m (2-H), 1.43 m (4-H), 1.63 d.d.d (5-H, ^2J = 15.0, $J_{5,4}$ = 12.5, $J_{5,6}$ = 7.0 Hz), 1.85 d.d (5′-H, ^2J = 15.0, $J_{5',4}$ = 6.5 Hz), 2.07 d.d (2′-H, ^2J = 15.0, $J_{2',1}$ = 9.0 Hz), 3.42 d.d (11-H, ^2J = 10.5, $J_{11,4}$ = 6.0 Hz), 3.78 d.d (11′-H, ^2J = 10.5, $J_{11',4}$ = 5.5 Hz), 7.12 d (18-H, $J_{18,16}$ = 2.5 Hz), 7.37 d (16-H, $J_{16,18}$ = 2.5 Hz), 8.46 s (12-H). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.87 d (C^1), 34.39 t (C^2), 58.83 s (C^3), 45.09 d (C^4), 21.23 t (C^5), 18.95 d (C^6), 17.29 s (C^7), 25.43 q (C^8), 15.19 q (C^9), 28.80 q (C^{10}), 64.90 t (C^{11}), 162.43 d (C^{12}), 117.96 s (C^{13}), 158.48 s (C^{14}), 136.70 s and 139.39 s (C^{15}, C^{17}), 126.47 d (C^{16}), 125.88 d (C^{18}), 34.97 s (C^{19}, C^{20}), 29.32 q and 31.43 q (CH_3, *t*-Bu). Found: *m*/*z* 399.31316 $[M]^+$. $C_{26}H_{41}NO_2$. Calculated: *M* 399.31371.

2-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]phenol (XIIb). A solution of 0.034 g (0.28 mmol) of 2-hydroxybenzaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.053 g (0.29 mmol) of compound **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 6 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was purified as described above for compound **XIIa**. Yield 0.042 g (53%), $[\alpha]_{580}^{22}$ = +52.6° (*c* = 0.6, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 1.00 s and 1.02 s (C^9H_3, $C^{10}H_3$), 1.32 s (C^8H_3), 0.69–0.90 m (1-H, 6-H), 1.35–1.41 m (2-H), 1.52–1.71 m (4-H, 5-H), 1.80 d.d (5′-H, ^2J = 15, $J_{5',4}$ = 7 Hz), 1.97 d.d (2′-H, ^2J = 15, $J_{2',1}$ = 9 Hz), 3.33 d.d (11-H, ^2J = 11, $J_{11,4}$ = 5.5 Hz), 3.60 d.d (11′-H, ^2J = 11, $J_{11',4}$ = 5.5 Hz), 6.78 d.d.d (17-H, $J_{17,16}$ = $J_{17,18}$ = 7.5, $J_{17,15}$ = 1.2 Hz), 6.86 br.d (15-H, $J_{15,16}$ = 8 Hz), 7.21 d.d (18-H, $J_{18,17}$ = 7.5, $J_{18,16}$ = 2 Hz), 7.24 d.d.d (16-H, $J_{16,15}$ = 8, $J_{16,17}$ = 7.5, $J_{16,18}$ = 2 Hz), 8.36 s (12-H). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.80 d (C^1), 35.45 t (C^2), 59.05 s (C^3), 45.09 d (C^4), 21.20 t (C^5), 19.03 d (C^6), 17.55 s (C^7), 24.49 q (C^8), 15.35 q (C^9), 28.83 q (C^{10}), 64.66 t (C^{11}), 161.17 d (C^{12}), 118.73 s (C^{13}), 162.67 s (C^{14}), 117.65 d (C^{15}), 132.29 d (C^{16}), 117.75 s (C^{17}), 131.42 s (C^{18}). Found: *m*/*z* 287.19030 $[M]^+$. $C_{18}H_{25}NO_2$. Calculated: *M* 287.18852.

2-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]-4-nitrophenol (XIIc). A solution of 0.047 g (0.28 mmol) of 2-hydroxy-5-nitrobenzaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.057 g (0.31 mmol) of amino alcohol **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 2.5 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was purified by reprecipitation from diethyl ether with hexane. Yield 0.097 g (96%), yellow crystals, mp 162–164°C, $[\alpha]_{580}^{22}$ = +116.7° (*c* = 0.08, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.77 d.d.d (1-H, $J_{1,2'}$ = 9.4, $J_{1,6}$ = 9.1, $J_{1,2}$ = 5.1 Hz), 0.83 d.d (6-H, $J_{6,1}$ = 9.1, $J_{6,5'}$ = 7.6 Hz), 0.96 s (C^9H_3), 1.01 s ($C^{10}H_3$), 1.33 d.d.d.d (4-H, $J_{4,5'}$ = 12.5, $J_{4,5}$ = 6.7, $J_{4,11}$ = 4.4, $J_{4,11'}$ = 4.0 Hz), 1.38 d.d (2-H, *J* = 15.4, $J_{2,1}$ = 5.1 Hz), 1.48 s (C^8H_3), 1.69 d.d (5-H, ^2J = 15.3, $J_{5,4}$ = 6.7 Hz), 1.83 d.d.d (5′-H, ^2J = 15.3, $J_{5',4}$ = 12.5, $J_{5',6}$ = 7.6 Hz), 2.21 d.d (2′-H, ^2J = 15.4, $J_{2',1}$ = 9.4 Hz), 3.48 d.d (11-H, ^2J = 11.2, $J_{11,4}$ = 4.4 Hz), 3.62 d.d (11′-H, ^2J = 11.2, $J_{11',4}$ = 4.0 Hz), 6.57 d (15-H, $J_{15,16}$ = 9.7 Hz), 7.97 d.d (16-H, $J_{16,15}$ = 9.7, $J_{16,18}$ = 2.9 Hz), 8.21 d (18-H, $J_{18,16}$ = 2.9 Hz), 8.29 br.s (12-H),

14.96 br.s (OH). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.24 d (C^1), 34.20 t (C^2), 59.59 s (C^3), 43.73 d (C^4), 20.22 t (C^5), 18.80 d (C^6), 18.06 s (C^7), 24.35 q (C^8), 15.00 q (C^9), 28.64 q (C^{10}), 62.82 t (C^{11}), 162.52 d (C^{12}), 113.71 s (C^{13}), 177.86 s (C^{14}), 122.71 d (C^{15}), 131.99 d (C^{16}), 135.02 s (C^{17}), 129.63 d (C^{18}). The ^{1}H NMR spectrum of **XIIc** indicated the presence of a small amount (~6%) of cyclic tautomer (analogous to **XIV**); it contained a singlet at δ 5.43 ppm assignable to 12-H in the cyclic structure. Found: *m*/*z* 332.1724 $[M]^+$. $C_{18}H_{24}N_2O_4$. Calculated: *M* 332.17306.

2-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]-4,6-dinitrophenol (XIId). A solution of 0.065 g (0.31 mmol) of 3,5-dinitrosalicylaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.063 g (0.34 mmol) of compound **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 4.5 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was recrystallized from diethyl ether. Yield 0.073 g (62%), orange crystals, mp 255–260°C, $[\alpha]_{580}^{22}$ = +27.1° (*c* = 0.14, $CHCl_3$). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.85–0.93 m (1-H, 6-H), 1.03 s (C^9H_3, $C^{10}H_3$), 1.50 d.d.d.d (4-H, $J_{4,5'}$ = 12.5, $J_{4,5}$ = 6.8, $J_{4,11'}$ = 4.0, $J_{4,11}$ = 3.8 Hz), 1.54 d.d (2-H, ^2J = 15.5, $J_{2,1}$ = 4.8 Hz), 1.63 s (C^8H_3), 1.80 d.d (5-H, ^2J = 15.4, $J_{5,4}$ = 6.8 Hz), 2.00 d.d.d (5′-H, ^2J = 15.4, $J_{5',4}$ = 12.5, $J_{5',6}$ = 7.6 Hz), 2.45 d.d (2′-H, ^2J = 15.5, $J_{2',1}$ = 9.4 Hz), 3.54 d.d (11-H, ^2J = 11.3, $J_{11,4}$ = 3.8 Hz), 3.78 d.d (11′-H, ^2J = 11.2, $J_{11',4}$ = 4.0 Hz), 8.67 d (18-H, $J_{18,16}$ = 3.2 Hz), 8.72 d (16-H, $J_{16,18}$ = 3.2 Hz), 8.94 br.s (12-H), 14.59 br.s (OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 17.80 d (C^1), 34.02 t (C^2), 61.38 s (C^3), 43.87 d (C^4), 20.46 t (C5), 19.47 d (C^6), 18.67 s (C^7), 24.03 q (C^8), 15.19 q (C^9), 28.92 q (C^{10}), 62.87 t (C^{11}), 165.66 d (C^{12}), 118.35 s (C^{13}), 171.11 s (C^{14}), 131.05 s (C^{15}), 127.54 d (C^{16}), 142.09 s (C^{17}), 137.52 d (C^{18}). Found: *m*/*z* 377.1578 $[M]^+$. $C_{18}H_{23}N_3O_6$. Calculated: *M* 377.1581.

2-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]-4-methoxyphenol (XIIe). A solution of 0.042 g (0.28 mmol) of 2-hydroxy-5-methoxybenzaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.057 g (0.31 mmol) of compound **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 24 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was purified by reprecipitation from diethyl ether with hexane. Yield quantitative, $[\alpha]_{580}^{22}$ = +73.9° (*c* = 0.5, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.71 d.d.d (1-H, $J_{1,6}$ = $J_{1,2'}$ = 9.4, $J_{1,2}$ = 4.8 Hz), 0.77 d.d (6-H, $J_{6,1}$ = 9.4, $J_{6,5}$ = 7.8 Hz), 1.01 s (C^9H_3), 1.02 s ($C^{10}H_3$), 1.31 s (C^8H_3), 1.36 d.d (2-H, ^2J = 15.0, $J_{2,1}$ = 4.8 Hz), 1.41 m (4-H), 1.59 d.d.d (5-H, ^2J = 14.7, $J_{5,4}$ = 11.9, $J_{5,6}$ = 7.8 Hz), 1.81 d.d (5′-H, ^2J = 14.7, $J_{5',4}$ = 6.7 Hz), 1.96 d.d (2′-H, ^2J = 15.0, $J_{2',1}$ = 9.4 Hz), 3.33 d.d (11-H, ^2J = 10.8, $J_{11,4}$ = 5.9 Hz), 3.61 d.d (11′-H, ^2J = 10.8, $J_{11',4}$ = 5.7 Hz), 3.76 s (OCH_3), 6.74 d (18-H, $J_{18,16}$ = 3.0 Hz), 6.82 d (15-H, $J_{15,16}$ = 8.9 Hz), 6.86 d.d (16-H, $J_{16,15}$ = 8.9, $J_{16,18}$ = 3.0 Hz), 8.34 s (12-H). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.89 d (C^1), 35.50 t (C^2), 59.20 s (C^3), 45.25 d (C^4), 21.26 t (C^5), 19.09 d (C^6), 17.53 s (C^7), 24.56 q (C^8), 15.35 q (C^9), 28.85 q (C^{10}), 64.85 t (C^{11}), 160.82 d (C^{12}), 118.49 s (C^{13}), 156.01 s (C^{14}), 118.01 d (C^{15}), 119.37 d (C^{16}), 151.74 s (C^{17}), 114.78 d (C^{18}), 55.76 q (C^{19}).

Tautomer **XIV**. ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.52 d.d.d (1-H, $J_{1,2'}$ = 9.5, $J_{1,6}$ = 9.2, $J_{1,2}$ = 5.0 Hz), 0.68 d.d.d (6-H, $J_{6,1}$ = 9.2, $J_{6,5'}$ = 8.8, $J_{6,5}$ = 1.2 Hz), 0.86 s (C^9H_3), 0.99 s ($C^{10}H_3$), 1.14 d.d (2-H, ^2J = 15.4, $J_{2,1}$ = 5.0 Hz), 1.36 s (C^8H_3), 1.64 d.d.d (5-H, ^2J = 15.3, $J_{5,4}$ = 8.5, $J_{5,6}$ = 1.2 Hz), 1.90 d.d (2′-H, ^2J = 15.4, $J_{2',1}$ = 9.5 Hz), 2.27 d.d.d (5′-H, ^2J = 15.3, $J_{5',6}$ = 8.8, $J_{5',4}$ = 8.8 Hz), 3.61 s (OCH_3), 4.21 d.d (11-H, ^2J = 11.5, $J_{11,4}$ = 2.1 Hz), 5.42 s (12-H), 6.71 d (18-H, *J* = 3.0 Hz); signals from the other protons were overlapped by those of the major isomer. ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 15.13 d (C^1), 33.97 t (C^2), 48.53 s (C^3), 34.44 d (C^4), 18.58 t (C^5), 17.74 d (C^6), 17.15 s (C^7), 24.76 q (C^8), 15.41 q (C^9), 28.13 q (C^{10}), 67.94 t (C^{11}), 80.59 d (C^{12}), 125.00 s (C^{13}), 152.73 s (C^{14}), 115.29 and 117.04 d (C^{15}, C^{16}), 149.10 s (C^{17}), 111.16 d (C^{18}), 55.65 q (C^{19}). Found: *m*/*z* 317.1981 $[M]^+$. $C_{19}H_{27}NO_3$. Calculated: *M* 317.19855.

2-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]-6-methoxyphenol (XIIf). A solution of 0.044 g (0.29 mmol) of 2-hydroxy-3-methoxybenzaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.059 g (0.32 mmol) of compound **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 24 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was purified by reprecipitation from diethyl ether with hexane. Yield quantitative, yellow crystals, mp 133–135°C, $[\alpha]_{580}^{22}$ = +55.7° (*c* = 0.13, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.72 d.d.d (1-H, $J_{1,2'}$ = 10.0, $J_{1,6}$ = 9.5, $J_{1,2}$ = 5.0 Hz), 0.87 d.d (6-H, $J_{6,1}$ = 9.5, $J_{6,5}$ = 8.80 Hz), 0.98 s

(C^9H_3), 1.00 s ($C^{10}H_3$), 1.34 s (C^8H_3), 1.35 d.d (2-H, ^2J = 15.0, $J_{2,1}$ = 5.0 Hz), 1.38 m (4-H), 1.63 d.d.d (5-H, ^2J = 14.8, $J_{5,4}$ = 11.8, $J_{5,6}$ = 8.0 Hz), 1.77 d.d (5′-H, ^2J = 14.8, $J_{5',4}$ = 6.9 Hz), 1.96 d.d (2′-H, ^2J = 15.0, $J_{2',1}$ = 10.0 Hz), 3.32 d.d (11-H, ^2J = 10.8, $J_{11,4}$ = 5.5 Hz), 3.56 d.d (11′-H, ^2J = 10.8, $J_{11',4}$ = 5.9 Hz), 3.86 s (OCH_3), 6.64 t (17-H, J = 7.9 Hz), 6.78–6.82 m (16-H, 18-H), 8.27 s (12-H). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.59 d (C^1), 35.61 t (C^2), 58.79 s (C^3), 45.00 d (C^4), 20.98 t (C^5), 18.86 d (C^6), 17.59 s (C^7), 24.26 q (C^8), 15.33 q (C^9), 28.65 q (C^{10}), 64.56 t (C^{11}), 161.02 d (C^{12}), 117.80 s (C^{13}), 149.38 s (C^{14}), 155.75 s (C^{15}), 113.23 d C^{16}), 116.27 d (C^{17}), 123.15 d (C^{18}), 55.72 q (C^{19}). The ^{1}H NMR spectrum of **XIIf** also contained a singlet at δ 5.42 ppm, which may be assigned (by analogy with compound **XIV**) to 12-H of the cyclic tautomer (~9%). Found: *m*/*z* 317.1987 $[M]^+$. $C_{19}H_{27}NO_3$. Calculated: *M* 317.19855.

1-[(1*S*,3*S*,4*R*,6*R*)-4-Hydroxymethyl-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yliminomethyl]naphthalen-2-ol (XIIg). A solution of 0.046 g (0.27 mmol) of 2-hydroxy-1-naphthaldehyde in 5 ml of anhydrous methanol was added dropwise under stirring to a solution of 0.056 g (0.31 mmol) of amino alcohol **XI** in 4 ml of anhydrous methanol, and the mixture was stirred for 3.5 h. When the reaction was complete (TLC, hexane–ethyl acetate, 3:4), the solvent was distilled off, and the product was purified by reprecipitation from diethyl ether with hexane. Yield 0.041 g (45%), green–yellow crystals, mp 172–175°C, $[\alpha]_{580}^{22}$ = +157.9° (*c* = 0.4, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm: 0.83 d.d.d (1-H, $J_{1,2'}$ = $J_{1,6}$ = 9.6, $J_{1,2}$ = 5.0 Hz), 0.95 d.d.d (6-H, $J_{6,1}$ = 9.6, $J_{6,5'}$ = 7.0, $J_{6,5}$ = 1.8 Hz), 0.99 s (C^9H_3), 1.05 s ($C^{10}H_3$), 1.38 d.d (2-H, ^2J = 15.0, $J_{2,1}$ = 5.0 Hz), 1.38 m (4-H), 1.51 s (C^8H_3), 1.70–1.84 m (2H, 5-H), 2.17 d.d (2′-H, ^2J = 15.0, $J_{2',1}$ = 9.6 Hz), 3.49 d.d (11-H, ^2J = 10.8, $J_{11,4}$ = 5.0 Hz), 3.60 d.d (11′-H, ^2J = 10.8, $J_{11',4}$ = 5.6 Hz), 6.82 d (15-H, $J_{15,16}$ = 9.4 Hz), 7.14 d.d.d (18-H, $J_{18,17}$ = 7.8, $J_{18,19}$ = 7.0, $J_{18,20}$ = 1.0 Hz), 7.34 d.d.d (19-H, $J_{19,20}$ = 8.2, $J_{19,18}$ = 7.0, $J_{19,17}$ = 1.4 Hz), 7.52 d.d (17-H, $J_{17,18}$ = 7.8, $J_{17,19}$ = 1.4 Hz), 7.59 d (16-H, $J_{16,15}$ = 9.4 Hz), 7.74 br.d (20-H, $J_{20,19}$ = 8.2 Hz), 8.72 br.s (12-H), 14.72 br.s (OH). ^{13}C NMR spectrum ($CDCl_3$–CCl_4), δ_C, ppm: 17.29 d (C^1), 35.14 t (C^2), 57.11 s (C^3), 44.44 d (C^4), 20.51 t (C^5), 18.77 d (C^6), 17.99 s (C^7), 24.74 q (C^8), 15.24 q (C^9), 28.66 q (C^{10}), 63.84 t (C^{11}), 153.49 d (C^{12}), 106.07 s (C^{13}), 178.84 s (C^{14}), 126.13 d (C^{15}), 137.63 d (C^{16}), 129.25 d (C^{17}), 122.24 d (C^{18}), 127.83 d (C^{19}), 117.21 d (C^{20}), 134.40 s (C^{21}), 125.84 s (C^{22}). Found: *m*/*z* 337.2034 $[M]^+$. $C_{22}H_{27}NO_2$. Calculated: *M* 337.2036.

Asymmetric oxidation of methylsulfanylbenzene (XV). A mixture of 2 mg (8 μmol) of $VO(acac)_2$ and 12 μmol of the corresponding ligand in 2 ml of anhydrous solvent was stirred until it became homogeneous (~20 min), a solution of 0.105 g (847 μmol) of sulfide **XV** in 3 ml of the same solvent was added, and the mixture was cooled if necessary. The corresponding oxidant, 1060 μmol, was then added, and the progress of the reaction was monitored by GLC. When the reaction was complete, 10 ml of distilled water was added to the mixture, the organic layer was separated, and the aqueous phase was extracted with appropriate solvent (2×5 ml). The extracts were combined with the organic phase, washed with water (2×10 ml), and dried over $MgSO_4$, the drying agent was filtered off, and the solvent was distilled off on a rotary evaporator. The substrate conversion and product ratio were determined by ^{1}H NMR spectroscopy. The enantiomeric excess was determined from the ^{1}H NMR spectrum (CCl_4–$CDCl_3$) recorded in the presence of an equal amount of (*R*)-(–)-3,5-dinitro-*N*-(1-phenylethyl)benzamide.

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