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Asymmetric Electrophilic Amination of Various Carbon Nucleophiles with Enantiomerically Pure Chiral *N*-H Oxaziridines Derived from Camphor and Fenchone

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The first two stable enantiomerically pure chiral *N*-H oxaziridines, derived from camphor and fenchone, are shown to act as electrophilic sources of nitrogen upon reaction with various carbon nucleophiles. Nitrogen is transferred, together with the camphor/fenchone unit, when deprotonated esters, malonates, and nitriles are used as nucleophiles. One of the ester or nitrile units in the substrate usually undergoes hydrolysis; a cyclic mechanism is proposed to account for this observation.

Introduction

The synthesis and chemistry of oxaziridines has been widely studied.[1−3] It has been established that the attack of a nucleophile occurs at either the oxygen or the nitrogen atoms of the ring, depending upon the nature of the nucleophile and the substituents on the oxaziridine, especially at the nitrogen atom. For example, oxaziridines bearing electron-withdrawing substituents on the nitrogen atom or on both the nitrogen and the carbon atoms of the three-membered ring have been developed for their ability to transfer oxygen atoms to nucleophiles. In particular, *N*-fluoroalkyloxaziridines,[4] *N*-phosphinoyloxaziridines,[5] and *N*-sulfonyloxaziridines[6] have proved to be efficient reagents for the oxidation of sulfides to sulfoxides, the asymmetric hydroxylation of enolates, and the stereoselective epoxidation of olefins. Oxygen transfer may also be performed with hindered oxaziridines and hindered nucleophiles,[7] and may be promoted by acid, forming an *N*-protonated oxaziridine that is believed to be the active oxidizing species.[8]

Nitrogen transfer has also been performed, mainly using *N*-H, *N*-alkyl-, *N*-aryl-, *N*-acyl-, *N*-carboxamido-, or *N*-alkoxycarbonyloxaziridines, with sulfur, nitrogen, phosphorus, and carbon nucleophiles.[7,9−14] However, none of these electrophilic aminations have been carried out with enantiomerically pure chiral *N*-substituted oxaziridines. To date, only one report of an enantiomerically pure chiral *N*-acyloxaziridine has been published.[15] Although the first *N*-H oxaziridine was reported in the 1960s,[16,17] due to their general instability, only a few *N*-H oxaziridines have been prepared and utilized for their ability to transfer an amino group to various nucleophiles.[18−21] The preparation and derivatization of the first stable enantiomerically pure chiral *N*-H oxaziridines has recently been accomplished in our laboratories.[22] We report

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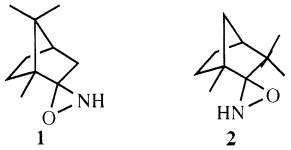
here the first use of these *N*-H oxaziridines, derived from (1*R*)-(+)-camphor and (1*R*)-(−)-fenchone, as asymmetric sources of electrophilic nitrogen for the amination of various ester- and nitrile-containing carbon nucleophiles. This approach is a potential alternative to the more usual asymmetric electrophilic amination accomplished by the use of chiral auxiliary chemistry.[23,24]

Results and Discussion

Crystalline *N*-H oxaziridine **1**, derived from (1*R*)-(+)-camphor, was prepared as previously described by oxidation of the corresponding imine with *m*-CPBA in 94% yield.[22] It is remarkable for its stability: It can be kept in its pure form for months at 5 °C, heated under reflux in THF solution, or submitted to column chromatography on silica gel without any noticeable decomposition. Similar oxidation of (1*R*)-fenchone imine provided, in 86% yield, the corresponding (1*R*)-(−)-fenchyl oxaziridine **2** as an oily liquid stable under reflux in THF or toluene solutions. It has been proven, by chemical derivatization coupled with NMR spectroscopy, that **1** and **2** each consist



of a pair of diastereoisomers in a ratio of about 60:40, isomeric at the pyramidal nitrogen atom.[22] An unusual feature of nitrogen-containing three-membered heterocycles is that there is a rather high barrier to inversion at nitrogen.[25]

We have tested these *N*-H oxaziridines as asymmetric nitrogen transfer agents in reactions with a range of

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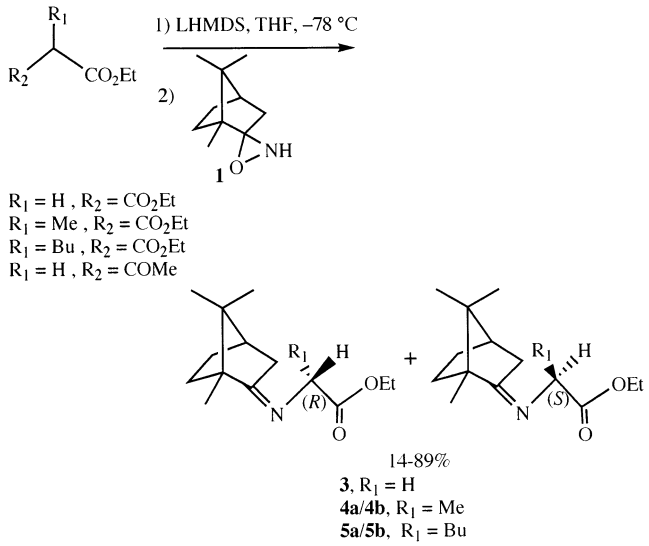

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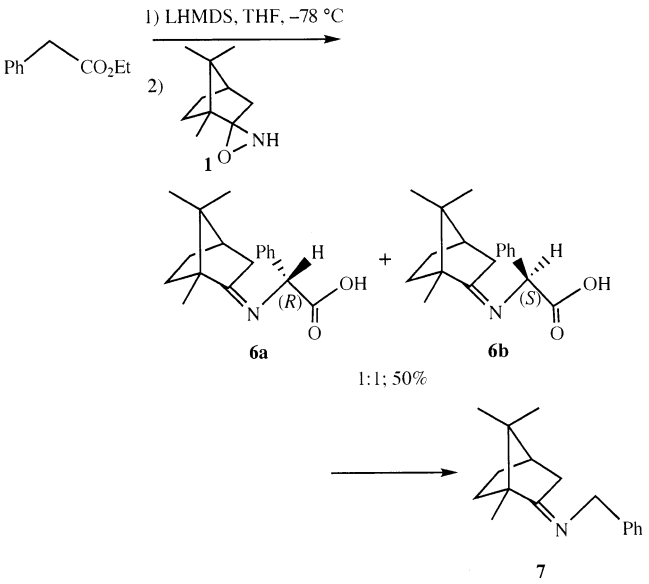

enolates, initially using ester enolates as potential precursors of α-amino acids (Schemes 1 and 2). The relatively stable and unreactive enolate of an unsubstituted malonate, diethyl malonate, was investigated first. Under thermodynamic conditions, using a mixture of sodium ethoxide and the camphor-derived *N*-H oxaziridine **1** in ethanolic solution at room temperature, addition of diethyl malonate provided the (*R*)-camphor imine of ethyl glycinate **3** [26] in 68% yield after 3 h at room temperature (Table 1, entry 1). One ester group has thus been lost during the reaction process. Two geometrical isomers of **3** are possible at the imine double bond. The ^{1}H NMR spectrum of the product was however consistent with the presence of only one isomer, believed to be that with *E* configuration. It has been previously reported that the *Z* isomer is highly destabilized by a steric interaction with the C-10 methyl group of the camphor unit.[26] When an α-substituted malonate, diethyl methylmalonate, was treated with base and **1** under the same conditions, diastereoisomeric imines **4a**/**4b** were formed as a 1:1 mixture of isomers (^{1}H NMR) in 89% yield after a 4 h

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TABLE 1. Reactions between (+)-Camphoryloxaziridine 1 and Esters[a]

entry	substrate	base	time (h)	products	yield (%)[b]
1	$EtOCOCH_2CO_2Et$	NaOEt[c]	3	**3**	68
2	$EtOCOCH_2CO_2Et$	LHMDS	6	**3**	50
3	$EtOCOCH(Me)CO_2Et$	NaOEt[c]	4	**4a**/**4b**	89
4	$EtOCOCH(Me)CO_2Et$	LHMDS	56	**4a**/**4b**	20
5	$EtOCOCH(Ph)CO_2Et$	LHMDS	60		0[d]
6	$EtOCOCH(Bu)CO_2Et$	LHMDS	49	**5a**/**5b**	14
7	CH_3CO_2Et	LHMDS	7.5		0[d]
8	$CH_3(CH_2)_2CO_2Et$	LHMDS	5.5		0[d]
9	$PhCH_2CO_2Et$	LHMDS	29	**6a**/**6b**	50
10	$MeCOCH_2CO_2Et$	LHMDS	48	**3**	43

[a] All reactions run at −78 °C, then allowed to reach room temperature after addition of **1** unless otherwise noted. [b] Yields of isolated products after chromatography on silica gel. [c] Reaction run at room temperature. [d] Only starting materials detected by TLC and ^{1}H NMR analysis of the crude reaction mixtures.

reaction time (entry 3). We were surprised to find that decarboxylation always occurs under these conditions.

We next investigated the reactivity of camphoryl oxaziridine **1** toward malonate anions under kinetic conditions. Reactions were typically carried out by formation of the enolates at −78 °C with LHMDS in THF solution, followed by addition of a solution of 1 equiv of **1** in THF. The reaction mixtures were stirred at −78 °C for the times indicated (Table 1), then allowed to reach room temperature and quenched with aqueous ammonium chloride.

Not only were the reaction times much longer than for the ethoxide/ethanol conditions, even in the case of the unsubstituted diethyl malonate (entry 2), but the yields were also lower: 50% and 20% for diethyl malonate and diethyl methylmalonate respectively (entries 2 and 4). More bulky α-substituents seemed to hinder the progress of the reaction; for example, no reaction was observed after 60 h under these kinetic conditions with diethyl phenylmalonate as substrate, and only starting materials were detected by ^{1}H NMR spectroscopy of the crude reaction mixture (entry 5). Further, when diethyl butylmalonate was used as substrate, the yield of the corresponding imine was very low (14%) even after a very long reaction time (entry 6). For this particular substrate, we also investigated a different experimental procedure whereby the malonate was added to a solution of **1** in THF at −78 °C prior to slow addition of the solution of LHMDS. No improvement was observed, and after 48 h the yield was only 13%.

Monoesters, the enolates of which are less stabilized and more reactive than those of malonates, were next investigated, again under kinetic conditions. Neither ethyl acetate nor ethyl butyrate gave any reaction, and only starting materials, together with decomposition products, were present in the reaction mixture after several hours (entries 7 and 8). In contrast, ethyl phenylacetate afforded surprising results: A 1:1 mixture of the corresponding acids **6a** and **6b** could be isolated in a 50% yield after 29 h (entry 9). These acids proved to be unstable even when kept at −30 °C and, like malonates, undergo decarboxylation to provide the stable (*R*)-camphor imine of benzylamine **7** (Scheme 2). [27] The fact that no reaction took place with ethyl acetate or butyrate may suggest that the transformation is most successful with stabilized carbanions.

Other stabilized enolates were therefore investigated. For example, when ethyl acetoacetate was treated with LHMDS followed by (+)-camphoryloxaziridine **1**, the reaction did not reach completion even after 48 h, a much slower process than that with diethyl malonate as substrate. We were surprised to find that the only product isolated was the (*R*)-camphor imine of ethyl glycinate **3** [26] in a 43% yield, corresponding to loss of acetyl, decarboxylation of the ester not occurring in this case (Table 1, entry 10). β-Keto esters have, however, been shown to undergo scission under various conditions to form decarboxylated compounds, products of retro-Claisen condensation reactions, or mixtures of both types of product. In general, under acidic conditions, decarboxylation of the free acid form of acetoacetate derivatives has been shown to be the predominant pathway, whereas under basic conditions, products of retro-Claisen reaction or mixtures of products are commonly formed.[28]

As the initial products of decarboxylation are presumably enolates, then any diastereoisomeric excesses observed in the final products would necessarily arise from diastereoselective protonation of these enolates induced by the chiral camphor moiety, or from equilibration following reaction, and not by an initial enantioselective amination of the nucleophiles. No diastereoisomeric excess was observed, however, by ^{1}H NMR spectroscopy of the imine products derived from any of these reactions with esters: 1:1 mixtures of the two inseparable diastereoisomers **4a**/**4b**, **5a**/**5b**, and **6a**/**6b** were obtained (entries 4, 6, and 9, respectively).

Nitrile derivatives were next investigated, using both camphoryl oxaziridine **1** and fenchyl oxaziridine **2** (Tables 2 and 3). In a typical experimental procedure, benzyl cyanide was treated with 1.1 equiv of LHMDS in THF at −78 °C for 1 h, then 1 equiv of (+)-camphoryl oxaziridine **1** was added and the reaction mixture was allowed to reach room temperature. After completion, washing with saturated aqueous NH_4Cl, and subsequent chromatographic purification on silica gel, the two diastereoisomers **8a** and **8b**, in which the nitrile groups have been hydrolyzed to primary amide, were isolated in a 78% yield and with a 25% de (Table 2, entry 1). Single-crystal X-ray diffraction was carried out on both isomers, and proved the major one, **8b**, to have the imine bond in an *E* configuration and to have the *S* configuration at the newly created asymmetric carbon atom. The minor product **8a** was shown to be the (*E*, *R*) product.

Similarly, when other aromatic nitriles, including naphthyl derivatives and 4-chloro- and 4-methoxybenzyl cyanides (Scheme 3), were treated with 1.1 equiv of LHMDS followed by (+)-camphoryl oxaziridine **1** in THF at −78 °C, the corresponding α-imino ethanamides **9**−**12** were isolated in excellent yields (73−80%) but moderate de values (5−33%), as indicated in Table 2 (entries 3 to 6).

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TABLE 2. Reactions between (+)-Camphoryl Oxaziridine 1 and Nitriles[a]

entry	substrate	base	time (h)	products	yield (%)[b]	de (%)[c]
1	$PhCH_2CN$	LHMDS	4.5	**8a**/**8b**	78	25
2	$PhCH_2CN$	LDA[d]	3.5	**8a**/**8b**	62	5
3	2-naphthylacetonitrile	LHMDS	4.5	**9a**/**9b**	73	33
4	1-naphthylacetonitrile	LHMDS	4.5	**10a**/**10b**	80	33
5	$4\text{-}ClC_6H_4CH_2CN$	LHMDS	5	**11a**/**11b**	80	16
6	$4\text{-}MeOC_6H_4CH_2CN$	LHMDS	9	**12a**/**12b**	75	5
7	$4\text{-}O_2NC_6H_4CH_2CN$	LHMDS	6	**13**	21	
8	CH_3CH_2CN	LHMDS	4.5	**13**	36	
9	$CH_3CH_2CH_2CN$	LHMDS	6.5	**13**, **14**	83,[e] 17[f]	
10	$NCCH_2CN$	LHMDS	6	**15a**/**15b**	82	0
11	$CH_2{=}CHCH_2CN$	LHMDS	26.5	**16**	45	
12	$EtOCOCH_2CN$	LHMDS	5.5	**17a**/**17b**	11	0
13	EtOCOCH(Ph)CN	LHMDS	31	**18a**/**18b**	68[g]	0

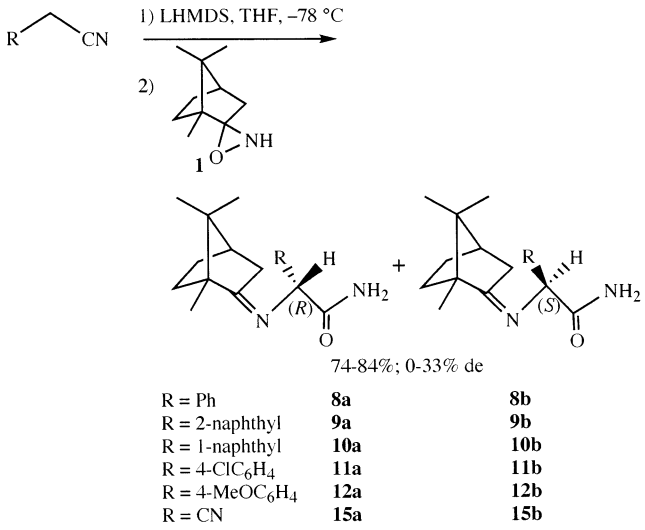
[a] All reactions run at −78 °C, then allowed to reach room temperature after addition of **1**. [b] Yields of isolated products after chromatography on silica gel. [c] Based on ^1H NMR spectroscopy of the crude product mixture. Compound **8b** was the major isomer in entries 1 and 2. [d] With HMPA (1.1 equiv.). [e] Yield of α-campholenic amide **13**.[29,20] [f] Yield of 1,8,8-trimethyl-2-azabicyclo[3.2.1]octan-3-one (**14**).[29,31] [g] 9% of a mixture of **8a**/**8b** and 23% of the starting material were also isolated.

TABLE 3. Reactions between (−)-Fenchyl Oxaziridine 2 and Nitriles[a]

entry	substrate	base	time (h)	products	yield (%)[b]	de (%)[c]
1	$PhCH_2CN$	LHMDS	5	**19a**/**19b**	55	50
2	2-naphthylacetonitrile	LHMDS	9	**20a**/**20b**	31	52
3	1-naphthylacetonitrile	LHMDS	4	**21a**/**21b**	48	33
4	$NCCH_2CN$	LHMDS	7	**22a**/**22b**	57	23

[a] All reactions run at −78 °C, then allowed to reach room temperature after addition of **2**. [b] Yields of isolated products after chromatography on silica gel. [c] Based on ^1H NMR spectroscopy of the crude product mixture.

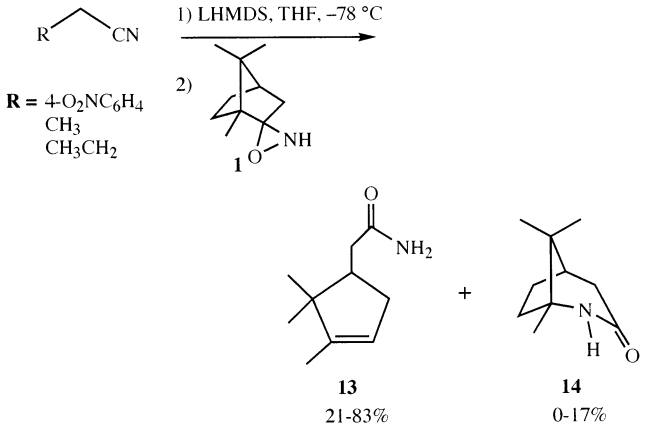
SCHEME 3



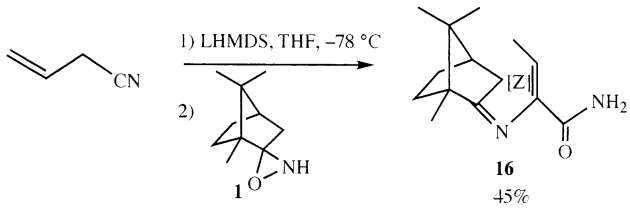
Surprisingly, reaction of 4-nitrophenylacetonitrile proved to be inefficient (entry 7), perhaps due to a stabilizing effect of the nitro group reducing the reactivity of the anion. α-Campholenic amide **13**[29,30] was the only product isolated, in a 21% yield, presumably through rearrangement induced under the reaction conditions (Scheme 4). Amide **13** is also the product formed by Beckman or photochemical rearrangements of camphor oxime.[29]

Amide **13** was also isolated as the major product when aliphatic nitriles such as propionitrile or butyronitrile were submitted to the reaction conditions (entries 8 and 9). Indeed, in the latter case, α-campholenic amide **13** and 1,8,8-trimethyl-2-azabicyclo[3.2.1]octan-3-one **14** [29,31] were isolated in 83% and 17% yields, respectively (Scheme 6), as the only products, corresponding to the complete rearrangement of camphoryl oxaziridine **1** (entry 9).

SCHEME 4

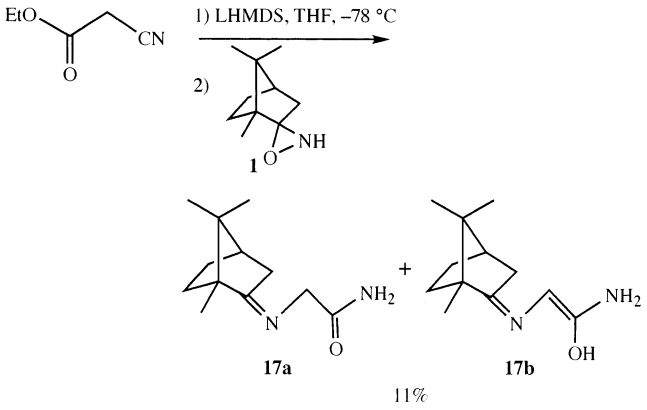


SCHEME 5

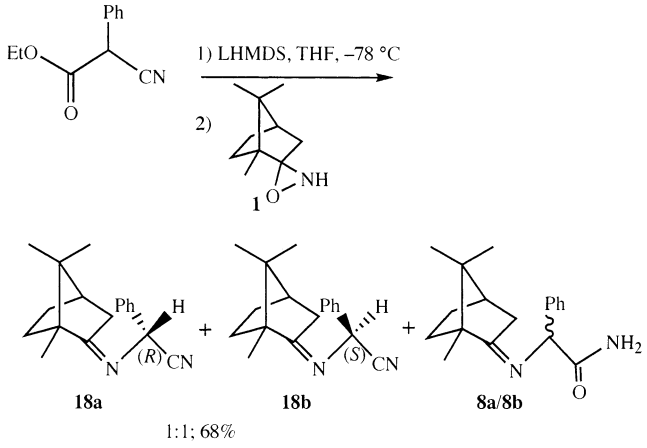


When malonitrile was treated similarly (Scheme 3), hydrolysis to primary amide of only one nitrile group was observed, and a 1:1 mixture of the two diastereoisomers **15a** and **15b** was isolated in 82% yield (entry 10). Allyl cyanide was observed to be less reactive, 26.5 h being necessary for the complete consumption of **1** (entry 11). Enamide **16** was the only product isolated, in a moderate yield of 45%, in which isomerization of the terminal double bond to the more stable cross-conjugated position has occurred (Scheme 5). The *Z* configuration of the

SCHEME 6



SCHEME 7



olefinic double bond was proved by single-crystal X-ray diffraction.

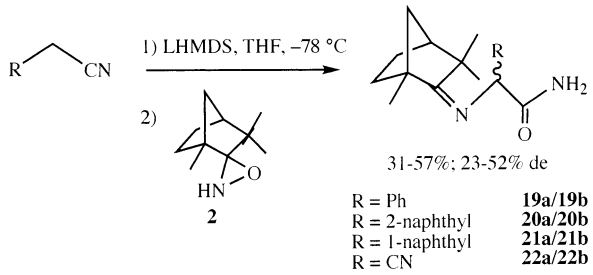
Reaction between ethyl cyanoacetate and (+)-camphoryl oxaziridine **1** (Scheme 6) under the same conditions gave a mixture of the decarboxylated amido compound **17a** with its enol tautomer **17b** in a poor yield of 11% (entry 12).

In the nitrile series, the most successful substrates thus appear to be those containing an aromatic substituent located α to the nitrile group. Consistent with this interpretation is the observation that when ethyl phenylcyanoacetate was treated with LHMDS followed by (+)-camphoryl oxaziridine **1**, a long reaction time of 31 h was necessary for complete consumption of **1**, but a good yield of the two decarboxylated diastereoisomers **18a** and **18b** was obtained (68%) together with 9% of a mixture of the corresponding primary amides **8a** and **8b** (entry 13) (Scheme 7). Ethyl phenylcyanoacetate was also recovered, in 23% yield.

In an attempt to improve the diastereoisomeric excesses in our reactions, we investigated the reactivity of (−)-fenchyl oxaziridine **2** toward nitrile anions as nucleophiles on the basis that a better diastereoselective induction might be expected from a higher degree of steric approach control induced by the presence of the *endo*-methyl group adjacent to the carbon atom bearing the oxaziridine ring (Scheme 8 and Table 3).

When benzyl cyanide was treated with LHMDS followed by **2**, the yield of imine products **19a**/**19b** was lower (55%) than that obtained with camphoryl oxaziridine **1**;

SCHEME 8



however, a 50% de was observed, determined by ^{1}H NMR spectroscopy of the reaction mixture (Table 3, entry 1). When 2-naphthylacetonitrile was used as the substrate, the yield of imino compounds **20a**/**20b** was only 31%, but a 52% de was obtained (entry 2). With 1-naphthylacetonitrile, the yield was slightly better (48%) but with a lower de (33%) (entry 3). Finally, when malonitrile was investigated, a 23% de was observed (entry 4), while 0% de was obtained when **1** was used as the chiral aminating agent.

Although the yields obtained with (−)-fenchyl oxaziridine **2** are more moderate than those with **1**, possibly a result of a lower reactivity of this oxaziridine compared with **1** due to the steric hindrance generated by the *endo*-methyl group, the diastereoisomeric ratios observed are promising.

The mechanism involved in reaction at the oxaziridine unit may be a stepwise process, as is already suggested in the literature for the oxidation of nucleophilic reagents with sulfonyloxaziridines.[32] In this case, the first step may be nucleophilic attack of the anion at the nitrogen atom of the oxaziridine ring, causing N−O bond cleavage and giving a hemiaminal oxyanion as the intermediate (Scheme 9). Although mild conditions were used for these reactions, hydrolysis of an ester or nitrile group normally occurred. This may be rationalized by a mechanism in which cyclization occurs next by attack of the oxyanion on an ester or nitrile moiety to give a heterocyclic intermediate[20] which in turn breaks down to generate a species containing imine and a carboxylate or derivative. Decarboxylation or simple protonation on workup, for example to give primary amide, may then occur, dependent upon the nature of any other substituents.

Presumably as a result of steric factors, the imine bond in all the products is particularly stable. The best method found for the generation of the free amino ester from this type of imines is transimination with hydroxylamine.[26,33]

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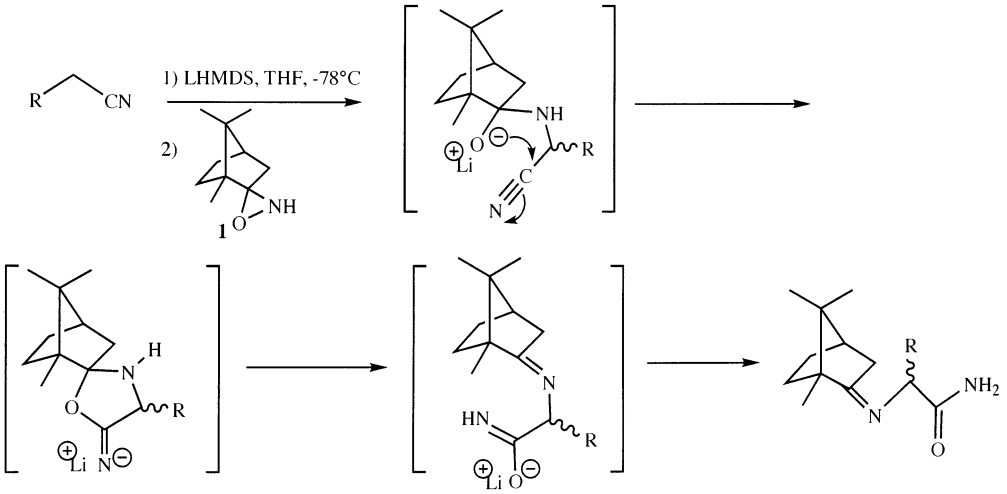
SCHEME 9



Conclusion

The first stable enantiomerically pure chiral *N*-H oxaziridines derived from (1*R*)-(+)-camphor **1** and (1*R*)-(−)-fenchone **2** were investigated in the amination of various carbon nucleophiles such as esters and nitriles. Yields were moderate to good, especially when **1** was used with nitriles, but the observed diastereoselectivities were improved when **2** was employed as chiral electrophilic aminating reagent. The ready access to these compounds from the inexpensive commercially available parent ketones, coupled with their remarkable stability, suggests that members of this group of compounds may prove to be effective reagents for asymmetric nitrogen transfer.

Experimental Section

General. Thin-layer chromatography was carried out on aluminum-backed plates coated with silica gel and visualized by spraying with potassium permanganate solution followed by heating. Flash column chromatography was performed with use of 230−400 mesh silica gel. Melting points were determined with use of an electronic melting point apparatus and are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ at 250 and 400 MHz and at 62.9 and 100.6 MHz, respectively, with TMS as internal standard. In the description of ^{1}H NMR spectra, the letter A refers to the first isomer eluted (major) and B to the minor one. Infrared spectra were recorded from thin films. Mass spectra were obtained by using the electron impact (EI) ionization technique. Optical rotations were measured at $\lambda = 589$ nm corresponding to the sodium (D) line at the temperature indicated.

General Amination Procedures. Procedure A: Sodium (100 mg, 4.35 mmol) was added to dry ethanol (5 mL) and the solution was stirred until the effervescence had ceased and all of the sodium had reacted. After allowing the solution to cool to room temperature, a solution of (+)-camphoryloxaziridine **1** (250 mg, 1.50 mmol) in ethanol (1 mL) was added followed by the corresponding malonate (1.50 mmol). The reaction mixture was then stirred at room temperature for the time indicated. When the reaction was complete (TLC), the reaction mixture was added to saturated aqueous ammonium chloride (40 mL). The mixture was extracted with dichloromethane (3 × 40 mL), the combined organic extracts were dried over $MgSO_4$, and the solvent was removed in vacuo to give a pale yellow oil that was purified by column chromatography on silica gel with ethyl acetate/light petroleum as eluent.

Procedure B: A solution of ester or nitrile (1.50 mmol) in THF (1 mL) was added dropwise to a cooled (−78 °C), stirred solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 1.60 mL, 1.60 mmol) in dry THF (5 mL). After 1 h at −78 °C, a solution of dry (+)-camphoryloxaziridine **1** or (−)-fenchyloxaziridine **2** (250 mg, 1.50 mmol) in THF (1 mL) was added dropwise and the reaction was allowed to reach room temperature over a period of 2 h. The reaction mixture was stirred at room temperature for the additional time indicated until completion (TLC). Aqueous ammonium chloride (20 mL) was added and the reaction mixture was extracted with dichloromethane (3 × 35 mL). The combined organic solution was dried over $MgSO_4$ and the solvent was removed in vacuo to give an oil that was purified by column chromatography on silica gel with ethyl acetate/light petroleum as eluent.

Ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanoate (3).[26] **Reaction between diethyl malonate and (+)-camphoryloxaziridine 1:.** Diethyl malonate (230 μL, 243 mg, 1.50 mmol) was treated with **1** according to procedure A and the reaction mixture was stirred for 3 h. After purification, compound **3** was isolated as a colorless oil (242 mg, 68%).

When procedure B was applied with diethyl malonate as the substrate, the reaction was quenched after 6 h and gave product **3** (178 mg, 50%).

Reaction between ethyl acetoacetate and (+)-camphoryloxaziridine 1: Ethyl acetoacetate (191 μL, 195 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was quenched after 48 h. Upon purification, the starting materials ethyl acetoacetate and (+)-camphoryloxaziridine **1** (85 mg) were first eluted followed by the title product **3** isolated as a colorless oil (132 mg, 43%).

$[\alpha]^{25}_D$ +3° (*c* 0.62, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 1743, 1686; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.18 (q, $J = 7.2$ Hz, 2 H), 4.09 (br s, 2 H), 2.38−2.28 (m, 1 H), 1.97 (t, $J = 4.3$ Hz, 1 H), 1.93−1.79 (m, 2 H), 1.70 (dt, $J = 11.2$, 3.6 Hz, 1 H), 1.48−1.38 (m, 1 H), 1.27 (t, $J = 7.1$ Hz, 3 H), 1.23−1.17 (m, 1 H), 1.03 (s, 3 H), 0.94 (s, 3 H), 0.81 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.0 (C_{quat}), 170.3 (C_{quat}), 60.8 (CH_2), 54.4 (C_{quat}), 53.9 (CH_2), 47.4 (C_{quat}), 43.8 (CH), 35.8 (CH_2), 32.0 (CH_2), 27.4 (CH_2), 19.6 (CH_3), 18.9 (CH_3), 11.2 (CH_3), 9.3 (CH_3); MS *m*/*z* 238 (MH^+), 237 (M^+), 222, 208, 194, 180, 164, 150, 135, 129, 122, 108, 99, 95, 83, 75, 67, 59, 56, 41; HRMS calcd for $C_{14}H_{23}NO_2$ (M^+) 237.17288, found 237.1726.

(2*R*)-Ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}propanoate (4a) and (2*S*)-Ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}propanoate (4b). Diethyl methylmalonate (258 μL, 261 mg, 1.50 mmol) was treated with **1** according to procedure A and the reaction mixture was stirred at room temperature

for 4 h. After purification, imines **4a**/**4b** were isolated (335 mg, 89%). The products **4a**/**4b** were found to be present in a 1:1 ratio by ^{1}H NMR spectroscopy.

When procedure B was applied, the reaction was quenched after an additional 54 h of stirring at room temperature and gave **4a**/**4b** (75.3 mg, 20%).

4a/**4b**: IR ν_{max} (neat)/cm^{-1} 1740, 1683; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.27−3.99 (m, 2 H_{A+B}), 4.04 (q, J = 6.8 Hz, 1 H_A), 4.03 (q, J = 6.8 Hz, 1 H_B), 2.47−2.29 (m, 1 H_{A+B}), 1.97−1.80 (m, 2 H_{A+B}), 1.68 (dt, J = 12.5, 3.8 Hz, 1 H_{A+B}), 1.41 (d, J = 6.6 Hz, 3 H_A), 1.40 (d, J = 6.8 Hz, 3 H_B), 1.31−1.16 (m, 3 H_{A+B}), 1.00 (s, 6 H_{A+B}), 0.93 (s, 6 H_{A+B}), 0.81 (s, 3 H_A), 0.76 (s, 3 H_B); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 184.3, 184.2, 172.89, 172.86, 60.6, 59.34, 59.27, 53.8, 47.2, 46.8, 43.7, 35.6, 35.5, 35.3, 35.2, 31.9, 31.8, 31.7, 27.4, 27.3, 27.2, 19.4, 18.9, 18.8, 18.6, 18.5, 18.4, 14.0, 13.9, 11.3; MS *m*/*z* 252 (MH^+), 251 (M^+), 236, 222, 179, 178, 162, 152, 150, 135, 122, 109, 95, 83, 70, 55; HRMS calcd for $C_{15}H_{25}NO_2$ (M^+) 251.18853, found 251.18836.

(2*R*)-Ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}hexanoate (5a) and (2*S*)-Ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}hexanoate (5b). Diethyl butylmalonate (330 μL, 324 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred at room temperature for 47 h. After purification, (2*R*)-ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}hexanoate (**5a**) and (2*S*)-ethyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-hexanoate (**5b**), a mixture of inseparable diastereoisomers in a 1:1 ratio, were isolated as a colorless oil (62 mg, 14%). The starting materials diethyl butylmalonate (259 mg, 1.197 mmol) and (+)-camphoryloxaziridine **1** (150 mg, 0.898 mmol) were also isolated.

5a/**5b**: IR ν_{max} (neat)/cm^{-1} 1741, 1684; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.17−4.11 (m, 2 H_{A+B}), 3.88 (dd, J = 8.8, 5.3 Hz, 1 H_A), 3.86 (dd, J = 8.8, 5.1 Hz, 1 H_B), 2.46−2.32 (m, 1 H_A), 2.38−2.26 (m, 1 H_B), 1.98−1.13 (m, 15 H_{A+B}), 1.00 (s, 6 H_{A+B}), 0.94 (s, 3 H_A), 0.93 (s, 3 H_B), 0.79 (s, 3 H_A), 0.75 (s, 3 H_B); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 184.8 (2 C_{quat}), 172.64 (C_{quat}), 172.60 (C_{quat}), 64.5 (CH), 64.4 (CH), 60.6 (2 CH_2), 54.2 (C_{quat}), 54.1 (C_{quat}), 47.4 (C_{quat}), 46.7 (C_{quat}), 44.0 (CH), 43.9 (CH), 36.2 (CH_2), 35.9 (CH_2), 32.7 (2 CH_2), 32.4 (CH_2), 31.9 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 22.4 (CH_2), 19.6 (CH_3), 19.5 (CH_3), 19.1 (CH_3), 18.9 (CH_3), 14.2 (2 CH_3), 14.0 (2 CH_3), 11.5 (CH_3), 11.4 (CH_3); MS *m*/*z* 294 (MH^+), 293 (M^+), 278, 265, 250, 237, 220, 208, 192, 178, 163, 150, 135, 112, 95, 83, 73, 69, 55, 41; HRMS calcd for $C_{18}H_{31}NO_2$ (M^+) 293.23548, found 293.23568.

(2*R*)-2-Phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanoic Acid (6a) and (2*S*)-2-Phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanoic Acid (6b). Ethyl phenylacetate (239 μL, 246 mg, 1.50 mmol) was treated with **1** according to procedure B. After addition of (+)-camphoryloxaziridine **1**, the reaction mixture was stirred for 29 h then quenched and purified as described. (2*R*)-2-Phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanoic acid (**6a**) and (2*S*)-2-phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanoic acid (**6b**) were isolated as a mixture of diastereoisomers in a 1:1 ratio (210 mg, 50%). These acids were not stable and decarboxylated after a few hours even when kept at −30 °C to give the imine *N*-[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]phenylmethanamide (**7**).[26]

6a: colorless oil; IR ν_{max} (neat)/cm^{-1} 2958, 1771, 1683; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.07 (br s, 1H), 7.36−7.28 (m, 5 H), 4.93 (s, 1 H), 2.52−2.42 (m, 1 H), 1.96 (t, J = 4.2 Hz, 1 H), 1.93−1.83 (m, 1 H), 1.82−1.68 (m, 1 H), 1.56 (d, J = 17.9 Hz, 1 H), 1.48−1.32 (m, 1 H), 1.11 (s, 3 H), 0.97 (m, 1 H), 0.95 (s, 3 H), 0.78 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 184.0 (C_{quat}), 172.2 (C_{quat}), 137.5 (C_{quat}), 128.8 (CH), 128.1 (CH), 127.4 (CH), 127.2 (CH), 124.8 (CH), 67.3 (CH), 55.4 (C_{quat}), 48.0 (C_{quat}), 43.9 (CH), 37.2 (CH_2), 31.8 (CH_2), 27.0 (CH_2), 19.6 (CH_3), 19.3 (CH_3), 11.1 (CH_3).

6b: colorless oil; IR ν_{max} (neat)/cm^{-1} 2958, 1771, 1683; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.08 (br s, 1 H), 7.35−7.23 (m, 5 H), 4.89 (s, 1 H), 2.00−1.71 (m, 5 H), 1.48−1.36 (m, 1 H), 1.30−1.20 (m, 1 H), 1.09 (s, 3 H), 0.92 (s, 3 H), 0.50 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 184.0 (C_{quat}), 172.2 (C_{quat}), 137.0 (C_{quat}), 128.7 (CH), 128.3 (CH), 128.0 (CH), 127.3 (CH), 126.4 (CH), 66.4 (CH), 54.1 (C_{quat}), 47.2 (C_{quat}), 43.8 (CH), 35.9 (CH_2), 32.2 (CH_2), 27.5 (CH_2), 19.5 (CH_3), 18.9 (CH_3), 11.4 (CH_3).

7:[26] colorless oil; IR ν_{max} (neat)/cm^{-1} 1685; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.34−7.17 (m, 5 H), 4.47 (q_{ab}, J = 15.2 Hz, 2 H), 2.41 (dt, J = 16.6, 3.5 Hz, 1 H), 1.96 (t, J = 4.4 Hz, 1 H), 1.92 (d, J = 17.3 Hz, 1 H), 1.86−1.80 (m, 1 H), 1.70 (dt, J = 16.2, 3.6 Hz, 1 H), 1.48−1.37 (m, 1 H), 1.26−1.16 (m, 1 H), 1.04 (s, 3 H), 0.95 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 183.5 (C_{quat}), 140.6 (C_{quat}), 128.3 (2 CH), 127.4 (2 CH), 126.4 (CH), 55.6 (CH_2), 54.0 (C_{quat}), 47.1 (C_{quat}), 43.9 (CH), 35.8 (CH_2), 32.3 (CH_2), 27.5 (CH_2), 19.8 (CH_3), 19.2 (CH_3), 11.5 (CH_3); HRMS calcd for $C_{17}H_{23}N$ (M^+) 241.18305, found 241.18286.

(2*R*)-2-Phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (8a) and (2*S*)-2-Phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (8b). Benzyl cyanide (174 μL, 176 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 2.5 h. Upon purification, (2*R*)-2-phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**8a**, 137 mg, 32%) was first eluted followed by (2*S*)-2-phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo-[2.2.1]hept-2-yliden]amino}ethanamide (**8b**, 196 mg, 46%).

8a: colorless needles, mp 131−133 °C; $[\alpha]^{25}_D$ −87° (*c* 0.85, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3438, 3170, 1696, 1651; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (br s, 1 H), 7.43−7.20 (m, 5 H), 6.26 (br s, 1 H), 4.78 (br s, 1 H), 2.42 (d, J = 17.3 Hz, 1 H), 1.91 (t, J = 4.4 Hz, 1 H), 1.81−1.71 (m, 1 H), 1.65 (dt, J = 12.1, 3.9 Hz, 1 H), 1.56 (d, J = 17.3 Hz, 1 H), 1.27−1.21 (m, 1 H), 1.04 (s, 3 H), 0.98−0.89 (m, 1 H), 0.93 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 185.5 (C_{quat}), 176.0 (C_{quat}), 139.9 (C_{quat}), 128.8 (CH), 128.7 (CH), 127.8 (CH), 127.6 (CH), 126.6 (CH), 68.3 (CH), 54.9 (C_{quat}), 47.5 (C_{quat}), 44.2 (CH), 36.3 (CH_2), 32.1 (CH_2), 27.5 (CH_2), 19.9 (CH_3), 19.3 (CH_3), 11.6 (CH_3); MS *m*/*z* 285 (MH^+), 241, 224, 212, 198, 184, 172, 135, 118, 106, 91, 79, 69, 55, 41; HRMS calcd for $C_{18}H_{24}N_2O$ (M^+) 284.18942, found 284.18987. Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85. Found: C, 76.02; H, 8.48; N, 9.60.

8b: colorless crystals, mp 173−177 °C; $[\alpha]^{25}_D$ +111° (*c* 1.03, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3435, 3200, 1700, 1654; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (br s, 1 H), 7.43−7.37 (m, 2 H), 7.30−7.18 (m, 3 H), 6.30 (br s, 1 H), 4.80 (br s, 1 H), 2.00 (dt, J = 17.4, 3.4 Hz, 1 H), 1.93−1.83 (m, 3 H), 1.74−1.70 (m, 1 H), 1.36−1.32 (m, 1 H), 1.26−1.21 (m, 1 H), 1.04 (s, 3 H), 0.90 (s, 3 H), 0.50 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 185.4 (C_{quat}), 175.5 (C_{quat}), 139.2 (C_{quat}), 128.4 (CH), 128.3 (CH), 127.6 (CH), 127.4 (CH), 127.2 (CH), 68.5 (CH), 54.3 (C_{quat}), 47.7 (C_{quat}), 43.7 (CH), 36.2 (CH_2), 31.9 (CH_2), 27.2 (CH_2), 19.2 (CH_3), 18.9 (CH_3), 11.3 (CH_3); MS *m*/*z* 284 (M^+), 241, 224, 211, 198, 184, 172, 135, 118, 106, 91, 79, 69, 55, 41; HRMS calcd for $C_{18}H_{24}N_2O$ (M^+) 284.18942, found 284.18917. Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85. Found: C, 75.71; H, 8.45; N, 9.72.

(2*R*)-2-Naphthalen-2-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (9a) and (2*S*)-2-Naphthalen-2-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo-[2.2.1]hept-2-yliden]amino}ethanamide (9b). 2-Naphthylacetonitrile (251 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 2.5 h. Upon purification, (2*R*)-2-naphthalen-2-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-ethanamide (**9a**, 135 mg, 27%) was first eluted followed by (2*S*)-2-naphthalen-2-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (**9b**, 234 mg, 47%).

9a: colorless solid, mp 159−162 °C; $[\alpha]^{25}_D$ −91° (*c* 0.92, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3428, 1692, 1652; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.83−7.76 (m, 4 H), 7.58−7.54 (m, 2 H), 7.45−

7.42 (m, 2 H), 6.18 (br s, 1 H), 4.93 (br s, 1 H), 2.51−2.42 (m, 1 H), 1.89 (t, J = 4.2 Hz, 1 H), 1.76−1.71 (m, 1 H), 1.67 (dd, J = 12.1, 3.1 Hz, 1 H), 1.56 (d, J = 17.5 Hz, 1 H), 1.28−1.18 (m, 1 H), 1.07 (s, 3 H), 0.92 (s, 3 H), 0.92−0.88 (m, 1 H), 0.77 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 186.1 (C_{quat}), 176.0 (C_{quat}), 136.9 (C_{quat}), 133.3 (C_{quat}), 133.0 (C_{quat}), 128.3 (CH), 128.1 (CH), 127.7 (CH), 126.4 (CH), 126.1 (CH), 126.0 (CH), 125.2 (CH), 68.1 (CH), 54.5 (C_{quat}), 47.2 (C_{quat}), 43.9 (CH), 36.0 (CH_2), 31.8 (CH_2), 27.2 (CH_2), 19.7 (CH_3), 19.0 (CH_3), 11.4 (CH_3); MS m/z 334 (M^+), 305, 291, 290, 265, 222, 199, 185, 172, 155, 141, 127, 108, 95, 81, 69, 55, 43; HRMS calcd for $C_{22}H_{26}N_2O$ (M^+) 334.20451, found 334.20367.

9b: colorless solid, mp 145−150 °C; $[\alpha]^{25}_D$ +115° (c 1.01, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3429, 1694, 1651; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.86−7.75 (m, 4 H), 7.62 (br s, 1 H), 7.56 (dd, J = 8.7, 1.7 Hz, 1 H), 7.48−7.40 (m, 2 H), 5.68 (br s, 1 H), 4.96 (br s, 1 H), 2.04−1.65 (m, 5 H), 1.44−1.34 (m, 1 H), 1.29−1.19 (m, 1 H), 1.09 (s, 3 H), 0.89 (s, 3 H), 0.47 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 186.1 (C_{quat}), 175.9 (C_{quat}), 136.5 (C_{quat}), 133.4 (C_{quat}), 133.0 (C_{quat}), 128.3 (CH), 128.1 (CH), 127.7 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 125.1 (CH), 68.7 (CH), 54.5 (C_{quat}), 47.9 (C_{quat}), 43.9 (CH), 36.0 (CH_2), 32.1 (CH_2), 27.4 (CH_2), 19.4 (CH_3), 19.1 (CH_3), 11.6 (CH_3); MS m/z 335 (MH^+), 334 (M^+), 291, 274, 261, 246, 234, 222, 206, 193, 185, 168, 156, 141, 128, 109, 95, 81, 69, 55, 41; HRMS calcd for $C_{22}H_{26}N_2O$ (M^+) 334.20451, found 334.20384. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.01; H, 7.84; N, 8.38. Found: C, 79.12; H, 7.85; N, 8.36.

(2*R*)-2-Naphthalen-1-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (10a) and (2*S*)-2-Naphthalen-1-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (10b). 1-Naphthylacetonitrile (251 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 2.5 h. Upon purification, (2*R*)-2-naphthalen-1-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-ethanamide (**10a**, 154 mg, 31%) was first eluted followed by (2*S*)-2-naphthalen-1-yl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (**10b**, 266 mg, 53%).

10a: colorless powder, mp 156−158 °C; $[\alpha]^{25}_D$ −127° (c 1.04, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3420, 1696, 1653; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 1 H), 7.83−7.72 (m, 2 H), 7.63 (br s, 1 H), 7.56−7.36 (m, 4 H), 6.39 (br s, 1 H), 5.45 (s, 1 H), 2.46−2.37 (m, 1 H), 1.81 (t, J = 4.4 Hz, 1 H), 1.73−1.62 (m, 1 H), 1.55 (dt, J = 11.5, 3.7 Hz, 1 H), 1.33 (d, J = 17.3 Hz, 1 H), 1.20−1.08 (m, 1 H), 1.05 (s, 3 H), 0.89 (s, 3 H), 0.77 (s, 3 H), 0.76−0.70 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 185.3 (C_{quat}), 175.6 (C_{quat}), 136.5 (C_{quat}), 134.1 (C_{quat}), 131.6 (C_{quat}), 128.7 (CH), 128.2 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 125.3 (CH), 125.0 (CH), 65.2 (CH), 54.6 (C_{quat}), 47.1 (C_{quat}), 43.9 (CH), 36.1 (CH_2), 31.4 (CH_2), 27.0 (CH_2), 19.6 (CH_3), 18.9 (CH_3), 11.4 (CH_3); MS m/z 334 (M^+), 290, 222, 185, 172, 155, 141, 127, 115, 95, 69, 55, 41; HRMS calcd for $C_{22}H_{26}N_2O$ (M^+) 334.20451, found 334.20483. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.01; H, 7.84; N, 8.38. Found: C, 78.94; H, 7.89; N, 8.39.

10b: colorless powder, mp 190−191.5 °C; $[\alpha]^{25}_D$ +133° (c 1.01, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3429, 3196, 1697, 1651; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 1 H), 7.82−7.71 (m, 3 H), 7.56−7.34 (m, 4 H), 6.26 (br s, 1 H), 5.46 (s, 1 H), 1.92−1.63 (m, 5 H), 1.40 (dt, J = 12.5, 3.9 Hz, 1 H), 1.26−1.15 (m, 1 H), 1.04 (s, 3 H), 0.83 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 186.1 (C_{quat}), 175.8 (C_{quat}), 136.4 (C_{quat}), 134.2 (C_{quat}), 131.8 (C_{quat}), 128.9 (CH), 128.4 (CH), 126.5 (CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 125.3 (CH), 65.9 (CH), 54.7 (C_{quat}), 48.2 (C_{quat}), 44.1 (CH), 37.0 (CH_2), 32.3 (CH_2), 27.6 (CH_2), 19.4 (CH_3), 19.3 (CH_3), 11.8 (CH_3); MS m/z 335 (MH^+), 334 (M^+), 291, 262, 234, 222, 206, 185, 168, 156, 141, 129, 109, 95, 81, 69, 55, 41; HRMS calcd for $C_{22}H_{26}N_2O$ (M^+) 334.20451, found 334.20420. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.01; H, 7.84; N, 8.38. Found: C, 78.64; H, 7.80; N, 8.40.

(2*R*)-2-(4-Chlorophenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (11a) and (2*S*)-2-(4-Chlorophenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (11b). 4-Chlorobenzyl cyanide (178 μL, 228 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 3 h. Upon purification, (2*R*)-2-(4-chlorophenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-ethanamide (**11a**, 165 mg, 34%) was first eluted followed by (2*S*)-2-(4-chlorophenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (**11b**, 218 mg, 46%).

11a: pale yellow oil; $[\alpha]^{25}_D$ −113° (c 1.02, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3429, 3200, 1694; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.46 (br s, 1 H), 7.38−7.32 (m, 2 H), 7.29−7.25 (m, 2 H), 6.13 (br s, 1 H), 4.73 (s, 1 H), 2.47−2.35 (m, 1 H), 1.92 (t, J = 4.3 Hz, 1 H), 1.87−1.61 (m, 2 H), 1.52 (d, J = 17.2 Hz, 1 H), 1.29−1.14 (m, 1 H), 1.04 (s, 3 H), 0.93 (s, 3 H), 0.96−0.84 (m, 1 H), 0.75 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 185.3 (C_{quat}), 174.9 (C_{quat}), 137.1 (C_{quat}), 133.2 (C_{quat}), 128.5 (2 CH), 128.4 (2 CH), 67.1 (CH), 54.5 (C_{quat}), 47.0 (C_{quat}), 43.7 (CH), 35.9 (CH_2), 31.6 (CH_2), 27.0 (CH_2), 19.4 (CH_3), 18.8 (CH_3), 11.1 (CH_3).

11b: colorless needles, mp 145−146 °C; $[\alpha]^{25}_D$ +146° (c 1.04, $CHCl_3$); IR ν_{max} (neat)/cm^{-1} 3430, 3200, 1694; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.53 (br s, 1 H), 7.37−7.34 (m, 2 H), 7.29−7.23 (m, 2 H), 5.61 (br s, 1 H), 4.76 (br s, 1 H), 2.00−1.85 (m, 3 H), 1.84−1.67 (m, 2 H), 1.41−1.30 (m, 1 H), 1.29−1.16 (m, 1 H), 1.04 (s, 3 H), 0.91 (s, 3 H), 0.51 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 185.4 (C_{quat}), 173.2 (C_{quat}), 135.9 (C_{quat}), 131.2 (C_{quat}), 128.43 (2 CH), 128.40 (2 CH), 67.7 (CH), 54.2 (C_{quat}), 47.6 (C_{quat}), 43.7 (CH), 36.2 (CH_2), 31.8 (CH_2), 27.2 (CH_2), 19.3 (CH_3), 18.9 (CH_3), 11.3 (CH_3); MS m/z 318 (M^+), 303, 277, 260, 239, 232, 218, 206, 192, 171, 169, 152, 140, 133, 125, 109, 95, 89, 83, 77, 69, 55, 43, 41; HRMS calcd for $C_{18}H_{23}N_2OCl$ (M^+) 318.14987, found 318.15068. Anal. Calcd for $C_{18}H_{23}N_2OCl$: C, 67.81; H, 7.27; N, 8.79. Found: C, 67.86; H, 7.19; N, 8.75.

(2*R*)-2-(4-Methoxyphenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (12a) and (2*S*)-2-(4-Methoxyphenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (12b). 4-Methoxybenzyl cyanide (203 μL, 221 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 7 h. Upon purification, (2*R*)-2-(4-methoxyphenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**12a**) and (2*S*)-2-(4-methoxyphenyl)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-ethanamide (**12b**) were isolated by column chromatography on silica gel as an oily mixture of inseparable diastereoisomers in a 1:1 ratio (355 mg, 75%).

Mixture of **12a**/**12b**: IR ν_{max} (neat)/cm^{-1} 3430, 3269, 1686, 1654; MS m/z 314 (M^+), 271, 227, 214, 202, 175, 164, 148, 136, 121, 109, 93, 91, 81, 77, 69, 67, 55; HRMS calcd for $C_{19}H_{26}N_2O_2$ (M^+) 314.19940, found 314.19907.

12a: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.51 (br s, 1 H), 7.34−7.30 (m, 2 H), 6.86−6.82 (m, 2 H), 6.09 (br s, 1 H), 4.71 (s, 1 H), 3.78 (s, 3 H), 2.45−2.35 (m, 1 H), 1.91 (t, J = 4.3 Hz, 1 H), 1.80−1.63 (m, 2 H), 1.55 (d, J = 17.2 Hz, 1 H), 1.25−1.15 (m, 1 H), 1.03 (s, 3 H), 0.98−0.93 (m, 1 H), 0.93 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 184.9 (C_{quat}), 175.9 (C_{quat}), 158.9 (C_{quat}), 131.8 (C_{quat}), 128.1 (2 CH), 113.9 (2 CH), 67.3 (CH), 55.4 (CH_3), 54.2 (C_{quat}), 47.0 (C_{quat}), 43.9 (CH), 35.8 (CH_2), 31.7 (CH_2), 27.3 (CH_2), 19.5 (CH_3), 19.0 (CH_3), 11.2 (CH_3).

12b: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.52 (br s, 1 H), 7.34−7.29 (m, 2 H), 6.86−6.79 (m, 2 H), 6.65 (br s, 1 H), 4.71 (s, 1 H), 3.75 (s, 3 H), 2.00−1.95 (m, 1 H), 1.92−1.59 (m, 4 H), 1.38−1.14 (m, 2 H), 1.01 (s, 3 H), 0.89 (s, 3 H), 0.49 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 184.8 (C_{quat}), 176.0 (C_{quat}), 158.6 (C_{quat}), 131.4 (C_{quat}), 128.1 (2 CH), 113.7 (2 CH), 67.8 (CH), 55.2 (CH_3), 54.7 (C_{quat}), 47.9 (C_{quat}), 43.7 (CH), 36.2 (CH_2), 31.6 (CH_2), 27.1 (CH_2), 19.3 (CH_3), 18.8 (CH_3), 11.4 (CH_3).

Trimethylcyclopent-3-enyl)ethanamide (α-Campholenic Amide) (13)[31,32] and 1,8,8-Trimethyl-2-azabicyclo[3.2.1]-octan-3-one (14).[31,33] Reaction between 4-nitrophenylacetonitrile and (+)-camphoryloxaziridine 1: 4-Nitrophenylacetonitrile (245 mg, 1.513 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 4 h at

room temperature until complete disappearance of the camphoryloxaziridine was observed by TLC analysis. 2-(2,2,3-Trimethylcyclopent-3-enyl)ethanamide (α-campholenic amide) (**13**) was isolated as a colorless solid (52 mg, 21%).

Reaction between propionitrile and (+)-camphoryloxaziridine 1: Propionitrile (83.3 mg, 108 μL, 1.513 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 2 h at room temperature until complete disappearance of the camphoryloxaziridine was observed by TLC analysis. 2-(2,2,3-Trimethylcyclopent-3-enyl)ethanamide (**13**) was isolated as a colorless solid (91 mg, 36%).

Reaction between butyronitrile and (+)-camphoryloxaziridine 1: Butyronitrile (104.6 mg, 132 μL, 1.513 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 4 h at room temperature until complete disappearance of the camphoryloxaziridine was observed by TLC analysis. 2-(2,2,3-Trimethylcyclopent-3-enyl)ethanamide (**13**) was first eluted as a colorless solid (210 mg, 83%) followed by 1,8,8-trimethyl-2-azabicyclo[3.2.1]octan-3-one (**14**, 43 mg, 17%).

13:[29,30] colorless crystals, mp 130 °C (lit.[30a] mp 127−128 °C; lit.[30b] mp 124 °C; lit.[29] mp 130.5−131 °C); IR ν_{max} (neat)/cm^{-1} 3373, 3196, 1662, and 1628; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.20 (br s, 1 H), 5.78 (br s, 1 H), 5.23 (br s, 1 H), 2.44−2.07 (m, 4 H), 1.97−1.86 (m, 1 H), 1.61 (q, J = 1.5 Hz, 3 H), 1.01 (s, 3 H), 0.78 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.2 (C_{quat}), 148.0 (C_{quat}), 121.7 (CH), 47.0 (C_{quat}), 46.8 (CH), 37.0 (CH_2), 35.3 (CH_2), 25.5 (CH_3), 19.9 (CH_3), 12.6 (CH_3); MS m/z 167 (M^+), 152, 134, 108, 93, 79, 67, 41; HRMS calcd for $C_{10}H_{17}NO$ (M^+) 167.13101, found 167.13112.

14:[29,31] colorless crystals (ethyl acetate, light petroleum); mp 184−187 °C (lit.[29] mp 197−198 °C in a sealed tube; lit.[31a] mp 156−160 °C; lit.[31b,c] mp 133−136 °C); IR ν_{max} (neat)/cm^{-1} 3318, 1652; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.59 (br s, 1 H), 2.60 (ddd, J = 18.0, 4.5, 2.6 Hz, 1 H), 2.17 (dd, J = 18.0, 1.6 Hz, 1 H), 2.10−1.89 (m, 4 H), 1.56−1.45 (m, 1 H), 1.13 (s, 3 H), 1.02 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 172.8 (C_{quat}), 63.6 (C_{quat}), 43.4 (C_{quat}), 42.9 (CH), 40.1 (CH_2), 39.5 (CH_2), 27.8 (CH_2), 23.4 (CH_3), 18.3 (CH_3), 18.0 (CH_3); HRMS calcd for $C_{10}H_{17}NO$ (M^+) 167.13101, found 167.13087.

(2*R*)-2-Cyano-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (15a) and (2*S*)-2-Cyano-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (15b). Malonitrile (94 μL, 99 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 4 h. Upon purification, (2*R*)-2-cyano-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (**15a**) and (2*S*)-2-cyano-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**15b**) were isolated by column chromatography on silica gel as an oily mixture of inseparable diastereoisomers in a 1:1 ratio (288 mg, 82%).

15a/**15b**: colorless solid, mp 139−140 °C; IR ν_{max} (neat)/cm^{-1} 3413, 3165, 2254, 1704, 1675; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50 (br s, 1 H_{A+B}), 6.11 (br s, 1 H_{A+B}), 4.65 (s, 1 H_A), 4.64 (s, 1 H_B), 2.82−2.70 (m, 1 H_A), 2.47−2.36 (m, 1 H_B), 2.17 (d, J = 18.0 Hz, 1 H_B), 2.10 (t, J = 4.3 Hz, 1 H_{A+B}), 1.99−1.85 (m, 1 H_{A+B} and 1 H_A), 1.84−1.70 (m, 1 H_{A+B}), 1.47−1.21 (m, 2 H_{A+B}), 1.01 (s, 3 H_{A+B}), 0.98 (s, 3 H_{A+B}), 0.82 (s, 3 H_A), 0.74 (s, 3 H_B); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 193.5 (C_{quat}), 193.1 (C_{quat}), 167.2 (2 C_{quat}), 115.1 (C_{quat}), 114.6 (C_{quat}), 55.7 (C_{quat}), 55.6 (C_{quat}), 53.8 (CH), 53.7 (CH), 48.8 (C_{quat}), 47.6 (C_{quat}), 44.0 (2 CH), 37.1 (CH_2), 36.5 (CH_2), 31.9 (CH_2), 31.4 (CH_2), 27.1 (2 CH_2), 19.6 (CH_3), 19.5 (CH_3), 19.0 (CH_3), 18.9 (CH_3), 11.2 (CH_3), 11.0 (CH_3); MS m/z 234 (MH^+), 233 (M^+), 218, 207, 189, 175, 162, 150, 133, 121, 108, 95, 77, 69, 55, 41; HRMS calcd for $C_{13}H_{19}N_3O$ (M^+) 233.15281, found 233.15326. Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.91; H, 8.13; N, 17.82.

(*Z*)-2-{[(1*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yliden]amino}but-2-enamide (16). Allyl cyanide (121 μL, 101 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 24.5 h. Upon purification, (*Z*)-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}but-2-enamide (**16**) was isolated as pale yellow crystals (157 mg, 45%). The *Z* configuration of the double bond of the lateral chain was proved by single-crystal X-ray diffraction.

16: mp 115.5−116.5 °C; IR ν_{max} (neat)/cm^{-1} 3466, 3315, 2957, 1676, 1630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (br s, 1H), 6.14 (q, J = 7.2 Hz, 1 H), 6.04 (br s, 1 H), 2.27−2.16 (m, 1 H), 1.97 (t, J = 4.0 Hz, 1 H), 1.94−1.78 (m, 2 H), 1.74 (d, J = 18.0 Hz, 1 H), 1.56 (d, J = 7.2 Hz, 3 H), 1.48−1.36 (m, 1 H), 1.29−1.18 (m, 1 H), 1.07 (s, 3 H), 0.97 (s, 3 H), 0.81 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 189.0 (C_{quat}), 167.1 (C_{quat}), 141.7 (C_{quat}), 116.6 (CH), 54.8 (C_{quat}), 47.6 (C_{quat}), 43.7 (CH), 38.1 (CH_2), 32.5 (CH_2), 27.2 (CH_2), 19.9 (CH_3), 19.0 (CH_3), 12.5 (CH_3), 11.1 (CH_3); MS m/z 234 (M^+), 219, 206, 189, 174, 152, 146, 135, 124, 108, 93, 81, 77, 67, 59, 55, 41; HRMS calcd for $C_{18}H_{24}N_2O$ (M^+) 234.17321, found 234.17307.

2-{[(1*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (17a) and 1-Amino-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}eth-1-en-1-ol (17b). Ethyl cyanoacetate (161 μL, 171 mg, 1.51 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 2.5 h. Upon purification, 2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}-ethanamide (**17a**) and 1-amino-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}eth-1-en-1-ol (**17b**) were isolated as an inseparable mixture of isomers (35 mg, 11%).

17a/**17b**: colorless solid, mp 159−166 °C; IR ν_{max} (neat)/cm^{-1} 3627, 3418, 1668, 1652, 1645, 1634; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (br s, 1 H_A), 5.56 (br s, 1 H_A), 4.96 (s, 1 H_B), 2.75−2.65 (m, 1 H_B), 2.31−2.21 (m, 1 H_A), 2.13 (d, J = 16.9 Hz, 1 H_A), 1.95 (t, J = 4.3 Hz, 1 H_{A+B}), 1.90−1.78 (m, 1 H_{A+B} and 1 H_B), 1.75−1.61 (m, 1 H_{A+B}), 1.45−1.12 (m, 2 H_{A+B}, 2 H_A, 3 H_B), 1.00 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H), 0.82 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 197.5 (C_{quat}), 186.7 (C_{quat}), 186.6 (C_{quat}), 173.5 (C_{quat}), 78.3 (CH), 54.5 (2 C_{quat}), 47.5 (C_{quat}), 47.1 (C_{quat}), 44.04 (CH), 43.96 (CH), 37.0 (CH_2), 36.4 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 27.6 (CH_2), 27.2 (CH_2), 19.6 (CH_3), 19.5 (CH_3), 19.01 (CH_3), 18.96 (CH_3), 11.5 (CH_3), 11.4 (CH_3); MS m/z 208 (M^+), 207, 191, 162, 152, 136, 123, 108, 95, 81, 69, 55, 41; HRMS calcd for $C_{12}H_{20}N_2O$ (M^+) 208.15756, found 208.15709.

(*R*)-1-Phenyl-1-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}methyl Cyanide (18a) and (*S*)-1-Phenyl-1-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}methyl Cyanide (18b). Ethyl phenylcyanoacetate (260 μL, 284 mg, 1.50 mmol) was treated with **1** according to procedure B and the reaction mixture was stirred for 29 h. Upon purification, (*R*)-1-phenyl-1-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}methyl cyanide (**18a**) and (*S*)-1-phenyl-1-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}methyl cyanide (**18b**) were isolated as an inseparable mixture of diastereoisomers in a 1:1 ratio (271 mg, 68%). The starting material, ethyl phenylcyanoacetate (64 mg, 0.338 mmol), and a mixture of the diastereoisomers (2*R*)-2-phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (**8a**) and (2*S*)-2-phenyl-2-{[(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**8b**, 38 mg, 0.134 mmol) were also isolated in 23% and 9% yields, respectively.

18a/**18b**: colorless oil; IR ν_{max} (neat)/cm^{-1} 2239, 1674; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49−7.31 (m, 10 H), 5.29 (s, 1 H_A), 5.28 (s, 1 H_B), 2.69−2.59 (m, 1 H_A), 2.41−2.32 (m, 1 H_B), 2.13−1.98 (m, 1 H_A and 1 H_B), 1.94−1.64 (m, 1 H_{A+B}, 1 H_A and 2 H_B), 1.53−1.40 (m, 1 H_A), 1.40−1.08 (m, 1 H_{A+B} and 1 H_B), 1.04 (s, 3 H), 1.02 (s, 3 H), 0.96 (s, 3 H), 0.94 (s, 3 H), 0.93−0.88 (m, 1 H_A), 0.83 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 189.6 (C_{quat}), 189.2 (C_{quat}), 135.8 (2 C_{quat}), 129.0 (2 CH), 128.9 (2 CH), 128.6 (2 CH), 127.2 (2 CH), 127.1 (2 CH), 118.8 (C_{quat}), 118.5 (C_{quat}), 55.1 (C_{quat}), 55.0 (C_{quat}), 54.8 (CH), 54.6 (CH), 47.9 (C_{quat}), 47.4 (C_{quat}), 44.0 (2 CH), 36.3 (CH_2),

36.1 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 27.3 (CH_2), 27.2 (CH_2), 19.54 (CH_3), 19.49 (CH_3), 19.0 (CH_3), 18.9 (CH_3), 11.19 (CH_3), 11.15 (CH_3); MS *m*/*z* 267 (MH^+), 266 (M^+), 240, 209, 150, 123, 117, 109, 91, 89, 81, 77, 67, 55, 41; HRMS calcd for $C_{18}H_{22}N_2$ (M^+) 266.17830, found 266.17851.

(2*R*)-2-Phenyl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide and (2*S*)-2-Phenyl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (19a/19b). Benzyl cyanide (174 μL, 176 mg, 1.50 mmol) was treated with **2** according to procedure B and the reaction mixture was stirred for 3 h. Upon purification, (2*R*)-2-phenyl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-phenyl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**19a**/**19b**, 234 mg, 55%) were isolated as a mixture of 50% de. The first diastereoisomer eluted was the major one and could be purified by recrystallization, allowing the assignment of the NMR spectra for both diastereoisomers.

Mixture of **19a**/**19b**: colorless solid, mp 162−170 °C; IR ν_{max} (neat)/cm^{-1} 3431, 3284, 1693; MS *m*/*z* 285 (MH^+), 240, 152, 134, 106; HRMS calcd for $C_{18}H_{25}N_2O$ (MH^+) 285.19725, found 285.19755.

19a: major diastereoisomer; colorless crystals, mp 170−178 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.52−7.47 (m, 2 H), 7.34−7.23 (m, 3 H), 7.18 (br s, 1 H), 5.78 (br s, 1 H), 5.32 (s, 1 H), 1.84 (br s, 1 H), 1.78−1.53 (m, 5 H), 1.43 (dd, J = 10.4, 1.6 Hz, 1 H), 1.30 (s, 3 H), 1.25 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.2 (C_{quat}), 175.9 (C_{quat}), 140.7 (C_{quat}), 129.1 (CH), 128.7 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 67.2 (CH), 53.5 (C_{quat}), 50.1 (CH), 44.9 (C_{quat}), 42.5 (CH_2), 34.0 (CH_2), 25.43 (CH_2), 25.41 (CH_3), 24.6 (CH_3), 17.9 (CH_3). Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85. Found: C, 76.00; H, 8.51; N, 9.83.

19b: minor diastereoisomer; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.55−7.50 (m, 2 H), 7.34−7.23 (m, 3 H), 6.96 (br s, 1 H), 5.78 (br s, 1 H), 5.33 (s, 1 H), 1.79 (br s, 1 H), 1.78−1.53 (m, 5 H), 1.43−1.38 (m, 1 H), 1.31 (s, 3 H), 1.29 (s, 3 H), 0.96 (s, 3 H); 13C NMR (100.6 MHz, $CDCl_3$) δ 187.4 (C_{quat}), 175.6 (C_{quat}), 140.9 (C_{quat}), 128.73 (CH), 128.67 (CH), 127.8 (CH), 126.9 (2 CH), 67.3 (CH), 53.7 (C_{quat}), 50.0 (CH), 45.0 (C_{quat}), 42.6 (CH_2), 33.9 (CH_2), 25.7 (CH_2), 25.4 (CH_3), 24.6 (CH_3), 18.2 (CH_3).

(2*R*)-2-Naphthalen-2-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-Naphthalen-2-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino} ethanamide (20a/20b). 2-Naphthylacetonitrile (253 mg, 1.513 mmol) was treated with **2** according to procedure B and the reaction mixture was stirred for 7 h. Upon purification, (2*R*)-2-naphthalen-2-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-naphthalen-2-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (**20a**/**20b**) were isolated as an inseparable mixture (141 mg, 31%) of 52% de.

20a/**20b**: pale yellow solid, mp 175−182 °C; IR ν_{max} (neat)/cm^{-1} 3433, 1690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1 H_A), 7.92 (s, 1 H_B), 7.83−7.79 (m, 3 H_{A+B}), 7.73−7.67 (m, 1 H_{A+B}), 7.48−7.41 (m, 2 H_{A+B}), 7.26 (br s, 1 H_A), 7.03 (br s, 1 H_B), 6.01 (br s, 1 H_{A+B}), 5.51 (s, 1 H_A), 5.48 (s, 1 H_B), 1.95−1.75 (m, 2 H_{A+B}), 1.68−1.51 (m, 3 H_{A+B}), 1.47−1.40 (m, 1 H_{A+B}), 1.35 (s, 3 H_A), 1.34 (s, 3 H_{A+B}), 1.29 (s, 3 H_B), 1.27−1.16 (m, 1 H_{A+B}), 1.01 (s, 3 H_B), 0.97 (s, 3 H_A); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.8 (C_{quat}), 187.6 (C_{quat}), 175.8 (C_{quat}), 175.5 (C_{quat}), 138.4 (C_{quat}), 138.2 (C_{quat}), 133.72 (C_{quat}), 133.70 (C_{quat}), 133.34 (C_{quat}), 133.28 (C_{quat}), 128.48 (CH), 128.46 (CH), 128.43 (CH), 128.36 (CH), 128.0 (2 CH), 126.30 (CH), 126.29 (CH), 126.13 (2 CH), 125.9 (CH), 125.7 (CH), 125.2 (2 CH), 67.4 (CH), 67.3 (CH), 53.8 (C_{quat}), 53.6 (C_{quat}), 50.1 (CH), 50.0 (CH), 45.0 (2 C_{quat}), 42.7 (CH_2), 42.5 (CH_2), 34.1 (CH_2), 33.9 (CH_2), 25.7 (CH_2), 25.5 (CH_3), 25.42 (CH_2), 25.36 (CH_3), 24.7 (CH_3), 24.6 (CH_3), 18.3 (CH_3), 18.0 (CH_3); MS *m*/*z* 335 (MH^+), 291, 290, 246, 208, 185, 184, 156, 141, 129, 107; HRMS calcd for $C_{22}H_{27}N_2O$ (MH^+) 335.21234, found 335.21228. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.01; H, 7.84; N, 8.38. Found: C, 78.37; H, 7.76; N, 8.22.

(2*R*)-2-Naphthalen-1-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-Naphthalen-1-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (21a/21b). 1-Naphthylacetonitrile (253 mg, 1.513 mmol) was treated with **2** according to procedure B and the reaction mixture was stirred for 2 h. Upon purification, (2*R*)-2-naphthalen-1-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-naphthalen-1-yl-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide (**21a**/**21b**) were isolated as an inseparable mixture (218 mg, 48%) of 33% de.

21a/**21b**: pale yellow solid, mp 136−140 °C; IR ν_{max} (neat)/cm^{-1} 3433, 1690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.4 Hz, 1 H_A), 8.58 (d, J = 8.4 Hz, 1 H_B), 7.84 (d, J = 7.9, 1 H_{A+B}), 7.75 (d, J = 7.7, 2 H_{A+B}), 7.61−7.57 (m, 1 H_{A+B}), 7.50−7.41 (m, 2 H_{A+B}), 7.28 (br s, 1 H_A), 7.03 (br s, 1 H_B), 6.20 (s, 1 H_B), 6.11 (s, 1 H_A), 5.98 (br s, 1 H_B), 5.94 (br s, 1 H_A), 1.82−1.76 (m, 2 H_{A+B}), 1.57−1.51 (m, 2 H_{A+B}), 1.45−1.42 (m, 1 H_{A+B}), 1.36 (s, 3 H_{A+B}), 1.35 (s, 3 H_A), 1.34 (s, 3 H_B), 1.29−1.25 (m, 1 H_{A+B}), 1.19−1.16 (m, 1 H_{A+B}), 0.80 (s, 3 H_A), 0.77 (s, 3 H_B); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.3 (C_{quat}), 187.0 (C_{quat}), 175.7 (C_{quat}), 175.4 (C_{quat}), 137.8 (C_{quat}), 137.7 (C_{quat}), 134.39 (C_{quat}), 134.35 (C_{quat}), 131.5 (C_{quat}), 131.4 (C_{quat}), 129.0 (CH), 128.9 (CH), 128.33 (CH), 128.25 (CH), 126.7 (CH), 126.6 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 125.1 (CH), 125.0 (CH), 124.5 (CH), 63.34 (CH), 63.27 (CH), 53.8 (C_{quat}), 53.6 (C_{quat}), 50.2 (CH), 50.1 (CH), 44.93 (C_{quat}), 44.85 (C_{quat}), 42.53 (CH_2), 42.46 (CH_2), 34.0 (CH_2), 33.8 (CH_2), 25.7 (CH_2), 25.5 (CH_3), 25.4 (CH_2), 25.1 (CH_3), 24.0 (2 CH_3), 18.2 (CH_3), 18.0 (CH_3); MS *m*/*z* 334 (M^+), 185, 156, 141, 129, 115, 91, 84, 69, 47; HRMS calcd for $C_{22}H_{26}N_2O$ (M^+) 334.20451, found 334.20466.

(2*R*)-2-Cyano-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]-hept-2-yliden]amino}ethanamide and (2*S*)-2-Cyano-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]-amino}ethanamide (22a/22b). Malonitrile (94 μL, 99 mg, 1.50 mmol) was treated with **2** according to procedure B and the reaction mixture was stirred for 5 h. Upon purification, (2*R*)-2-cyano-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide and (2*S*)-2-cyano-2-{[(1*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-yliden]amino}ethanamide (**22a**/**22b**) were isolated by column chromatography on silica gel as an inseparable oily mixture of diastereoisomers (200 mg, 57%) of 23% de.

22a/**22b**: colorless solid, mp 130−131 °C; IR ν_{max} (neat)/cm^{-1} 3432, 3239, 2257, 1712, 1671; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (br s, 1 H_A), 6.96 (br s, 1 H_B), 6.73 (br s, 1 H_B), 6.70 (br s, 1 H_A), 5.14 (s, 1 H_B), 5.08 (s, 1 H_A), 2.02 (br s, 1 H_B), 1.93 (br s, 1 H_A), 1.84−1.41 (m, 6 H_{A+B}), 1.36 (s, 3 H_A), 1.29 (s, 3 H_B), 1.24 (s, 3 H_B), 1.20 (s, 3 H_A), 1.19 (s, 3 H_A), 1.09 (s, 3 H_B); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 195.8 (C_{quat}), 195.7 (C_{quat}), 167.4 (C_{quat}), 167.2 (C_{quat}), 116.4 (C_{quat}), 116.0 (C_{quat}), 54.52 (C_{quat}), 54.50 (C_{quat}), 54.3 (2 CH), 50.2 (CH), 50.1 (CH), 45.9 (C_{quat}), 45.8 (C_{quat}), 42.5 (CH_2), 42.4 (CH_2), 33.9 (CH_2), 33.8 (CH_2), 25.42 (CH_2), 25.38 (CH_2), 24.6 (CH_3), 24.5 (2 CH_3), 24.1 (CH_3), 17.7 (CH_3), 17.4 (CH_3); MS *m*/*z* 234 (MH^+), 207, 189, 176, 154, 136, 123, 107; HRMS calcd for $C_{13}H_{20}N_3O$ (MH^+) 234.16064, found 234.16061.

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