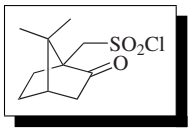
10-Camphorsulfonyl Chloride[1]



(1*R*)
[21286-54-4] $C_{10}H_{15}ClO_3S$ (MW 250.75)
InChI = 1/C10H15ClO3S/c1-9(2)7-3-4-10(9,8(12)5-7)6-15(11,13)14/h7H,3-6H2,1-2H3/t7-,10-/m0/s1
InChIKey = BGABKEVTHIJBIW-XVKPBYJWBY
(1*S*)
[39262-22-1]
InChI = 1/C10H15ClO3S/c1-9(2)7-3-4-10(9,8(12)5-7)6-15(11,13)14/h7H,3-6H2,1-2H3/t7-,10-/m1/s1
InChIKey = BGABKEVTHIJBIW-GMSGAONNBT
(±)
[6994-93-0]
InChI = 1/C10H15ClO3S/c1-9(2)7-3-4-10(9,8(12)5-7)6-15(11,13)14/h7H,3-6H2,1-2H3
InChIKey = BGABKEVTHIJBIW-UHFFFAOYAQ

(enantiomeric excess determination;[2] chemical resolution;[3] synthesis of chiral auxiliaries;[4] chiral precursor for natural product synthesis;[1] synthesis of chiral reagents[5])

Physical Data: mp 65–67 °C; (1*S*)-(+): $[\alpha]_D + 32.1°$ (*c* 1, $CHCl_3$).

Solubility: sol CH_2Cl_2; slightly sol ether; insol H_2O.

Form Supplied in: both enantiomers and the racemic sulfonyl chloride are commercially available.

Preparative Methods: can be prepared from ***10-Camphorsulfonic Acid*** upon treatment with ***Phosphorus(V) Chloride*** or ***Thionyl Chloride***.[6]

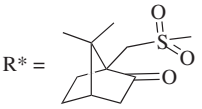
Purification: crystallized from hexane or from MeOH.

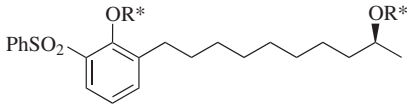
Handling, Storage, and Precautions: corrosive and moisture-sensitive. This reagent should be handled in a fume hood.

Original Commentary

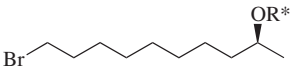
André B. Charette
Université de Montréal, Québec, Canada

Reagent for Determination of Enantiomeric Excesses and for Chemical Resolution of Alcohols and Amines. 10-Camphorsulfonyl chloride has been widely used as a chiral derivatizing agent for the assay of enantiomeric purity of alcohols and amines by NMR techniques.[2] A typical procedure for the preparation of the sulfonate ester or sulfonamide involves mixing a solution of the alcohol or amine in CH_2Cl_2 with camphorsulfonyl chloride in the presence of an amine base (Et_3N, py, or DMAP). This reagent has been particularly valuable for determining the enantiomeric purity of secondary alcohols (**1**, **2**) and β-hydroxy esters (**3**).[7]

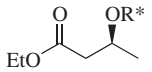




(1)

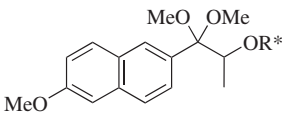


(2)



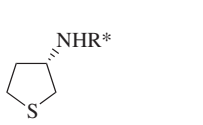
(3)

In some cases (**3**), the addition of a chiral shift reagent ($Eu(hfc)_3$) is necessary to obtain baseline separation of the signals corresponding to the β-proton of both diastereomers by ^1H NMR. Diastereomeric mixtures derived from secondary alcohols have also been analyzed by HPLC.[8] The resolution of a secondary alcohol (**4**) could be achieved by a selective crystallization of one of the two diastereomeric camphorsulfonate esters.[3]

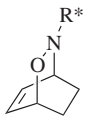


(4)

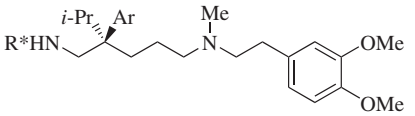
The enantiomeric purities of primary and secondary amines have also been established by ^1H NMR spectroscopy by their conversion into the corresponding sulfonamide. These derivatives often produce crystalline compounds that are suitable for X-ray crystallographic studies. For example, the enantiomeric purities of amines (**5**),[9] (**6**),[10] and (**7**)[11] were determined by ^1H NMR spectroscopy and the absolute stereochemistry of (**7**) was unequivocally established by X-ray crystallography.



(5)

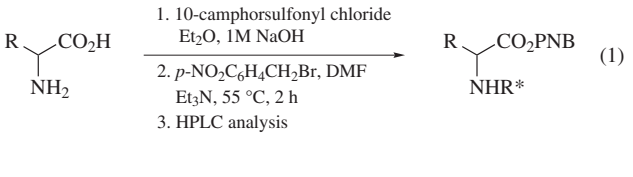


(7)

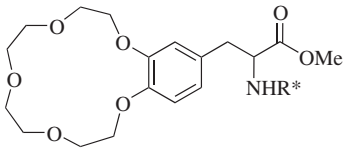


(6) Ar = 3,4-$(OMe)_2C_6H_3$

A general protocol for the HPLC separation of diastereomeric camphorsulfonamides[12] derived from racemic α-amino acids has been developed (eq 1).[13] More complex amino acids, such as (**8**), were successfully analyzed by this procedure.[14]

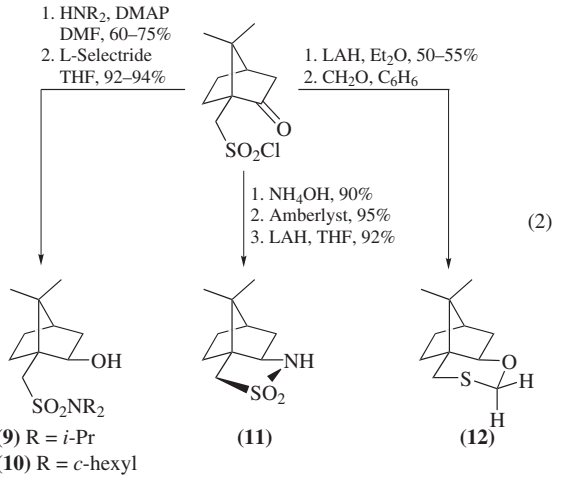


(1)



(8)

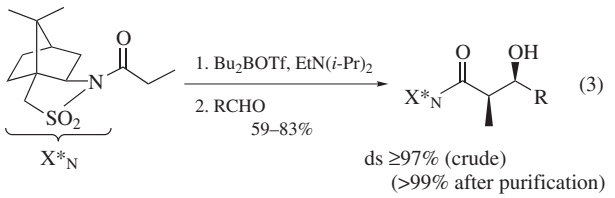
Synthesis of Chiral Auxiliaries. Their availability and crystalline nature has made camphor derivatives the precursors of choice for the design and synthesis of chiral auxiliaries.[4] 10-Camphorsulfonyl chloride is the starting material for the synthesis of chiral auxiliaries (**9**)–(**12**) (eq 2). Sulfonamides (**9**) and (**10**)[15] have been used as chiral auxiliaries in a number of reactions, e.g. the Lewis acid-catalyzed Diels–Alder reaction, the [3 + 2] cycloaddition of a nitrile oxide to an acrylate, and the stereoselective conjugate addition reaction of organocopper reagents to α,β-unsaturated esters.[4]



(2)

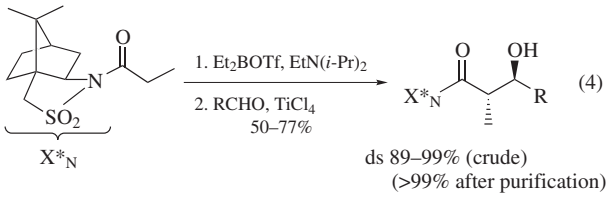
(9) R = *i*-Pr
(10) R = *c*-hexyl
(11)
(12)

In addition to being an efficient chiral controller in a number of stereoselective transformations of chiral acrylates, (i.e. the Diels–Alder reaction,[4] the conjugate reduction,[16] the asymmetric dihydroxylation,[17] and the nitrile oxide cycloaddition[18]) the bornanesultam (**11**)[19] has been shown to be an exceptionally efficient chiral auxiliary for stereoselective aldol condensations (eqs 3 and 4). Depending upon the reaction conditions, *N*-propionylsultam can produce either the *syn* or *anti* aldol product with an excellent diastereoselectivity.[20] Furthermore, good diastereoselectivities are also observed for the corresponding acetate aldol reaction (eq 5).[21]



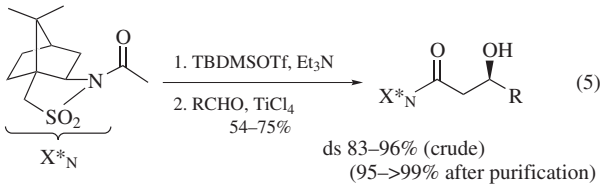
(3)

ds ≥97% (crude)
(>99% after purification)



(4)

ds 89–99% (crude)
(>99% after purification)



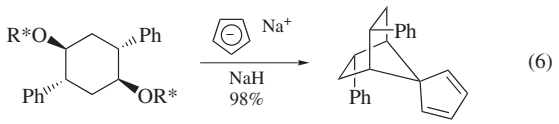
(5)

ds 83–96% (crude)
(95–>99% after purification)

Oxathiane (**12**) has been shown to be an efficient chiral auxiliary in the nucleophilic addition to carbonyl compounds.[22]

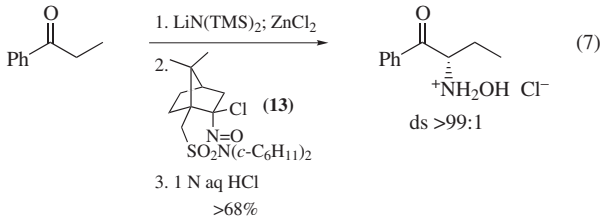
10-Camphorsulfonyl chloride has also been widely used as a useful precursor to chiral dienophiles in hetero-Diels–Alder reactions.[23]

An elegant use of the chirality and the leaving group ability of the camphorsulfonate ester has been reported in the synthesis of a chiral C_2 symmetric cyclopentadienyl ligand (eq 6).[24]



(6)

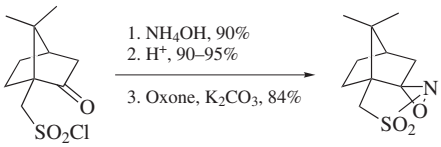
Synthesis of Chiral Reagents. An efficient chiral α-chloro-α-nitroso reagent derived from 10-camphorsulfonyl chloride (1. Cy_2NH; 2. NH_2OH; 3. *t*-BuOCl; 70–78%) has been developed for the asymmetric α-amination of ketone enolates (eq 7).[25] The resulting β-keto *N*-hydroxylamine can be converted to the *anti*-1,2-hydroxyamine under reducing conditions ($NaBH_4$; Zn, HCl, AcOH).



(7)

ds >99:1

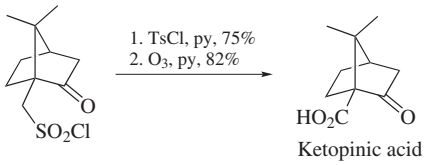
Several oxaziridines related to (**14**)[5] (eq 8) have been used, most notably in the enantioselective oxidation of sulfides to sulfoxides,[26] of selenides to selenoxides,[27] and of alkenes to oxiranes.[28] It is also the reagent of choice for the hydroxylation of lithium and Grignard reagents[29] and for the asymmetric oxidation of enolates to give α-hydroxy carbonyl compounds.[5,30] A similar chiral fluorinating reagent has also been developed.[31]



(8)

(14)

Chiral Precursor for Natural Product Synthesis. 10-Camphorsulfonyl chloride has been used as a chiral starting material for the synthesis of a number of products[1] such as ketopinic acid[32] (eq 9), which has been used to resolve alcohols[33] and hemiacetals.[34]



(9)

First Update

Qingwei Yao
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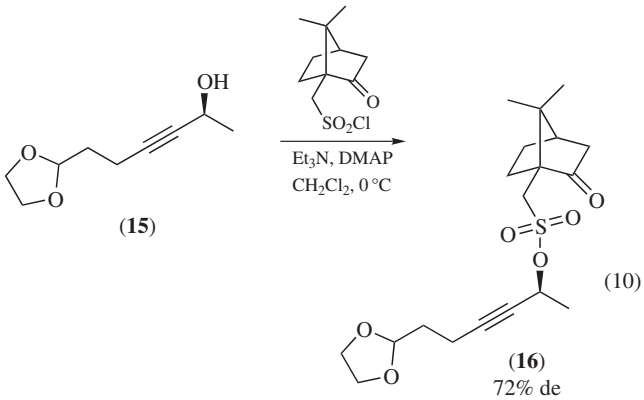
Determination of Enantiomeric Excesses of Chiral Alcohols, Amines, and Related Compounds.[35–39] 10-Camphor sulfonyl chloride continues to be used extensively as a convenient derivatizing agent for chiral alcohols, amines, and related compounds for determination of their enantiomeric access or verification of their optical purity. For example, the secondary propargyl alcohol **15** was converted to the (*S*)-10-camphorsulfonate ester **16** (eq 10) and the de determined by NMR spectroscopy.[35]



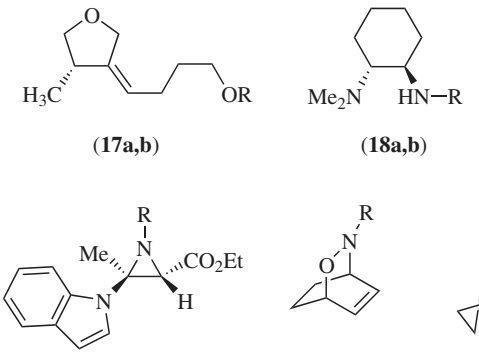
(**15**)

(**16**)
72% de

(10)

Other examples of compounds whose ee's were determined using (*S*)-(+)-10-camphorsulfonyl chloride as the chiral derivatizing reagent include alcohol **17a**,[36] amine **18a**,[37] aziridine **19a**,[38] and the cyclic hydroxylamines **20a** and **21a**.[39]

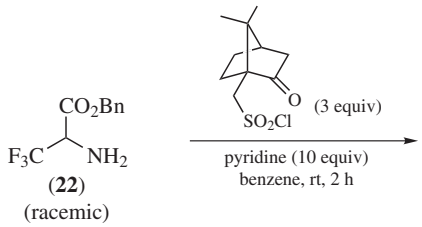
Resolution and Determination of Absolute Configuration of Chiral Amines, Alcohols, and Related Compounds.[40–51] Camphorsulfonyl chloride can be used as a resolving reagent for chiral amines, alcohols, and binaphthols. Derivatives of camphorsulfonates and camphorsulfonamides are generally crystalline compounds and frequently form crystals suitable for X-ray analysis. For example, racemic 3,3,3-trifluoroalanine derivative **22** was resolved into optically pure sulfonamides **23a** and **23b** by derivatization with (1*S*)-camphorsulfonyl chloride followed by HPLC separation (eq 11).[40] Upon recrystallization from ethyl acetate–hexane (1:5), isomer **23a** forms white needles and X-ray analysis established its configuration as (*R*,*S*).



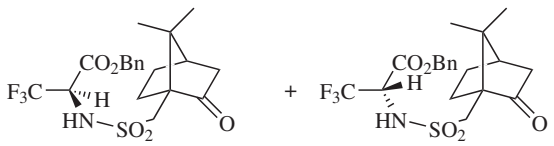
(**17a,b**) (**18a,b**)

(**19a,b**) (**20a,b**) (**21a,b**)

a: R = H
b: R = (*S*)-camphorsulfonyl



(**22**)
(racemic)

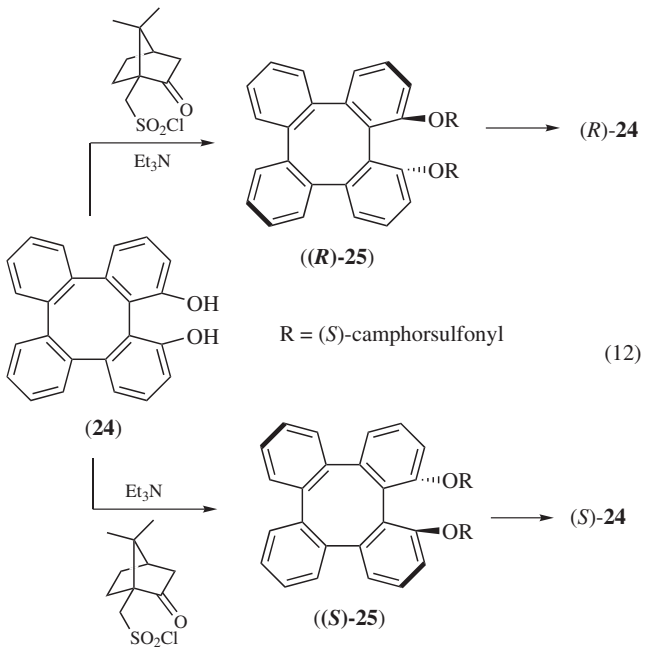


(**23a**)
(*R*,*S*)
(white crystal)

(**23b**)
(*S*,*S*)
(oily)

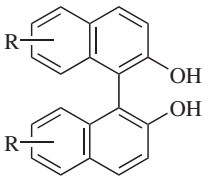
(11)

Camphorsulfonyl chloride has proved to be quite a general resolving agent for analogs of binaphthol as exemplified by the resolution of 1,16-dihydroxytetraphenylene **24** (eq 12).[41]

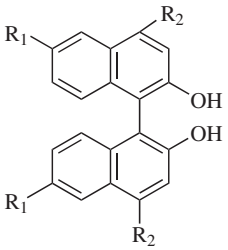


(12)

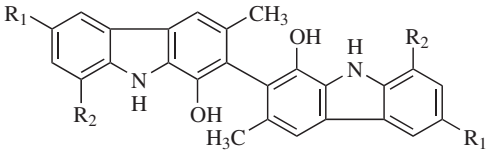
Other axially chiral molecules that were resolved with camphorsulfonyl chloride include binaphthols **26** and **27**, the dihydroxylbiscarbazoles **28**, biflavone **29**, 2-diarylphosphino-20-methoxy-1,10-binaphthalenes **30**, phenol **31** and alcohol **32** with axial chirality about a C–N bond, and the amino[2.2]paracyclophane **33**.[42–48]



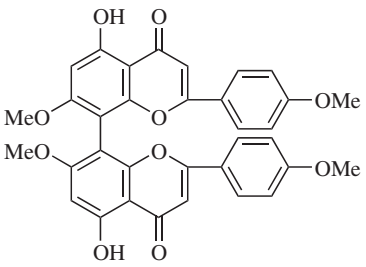
(**26a**), R = H; (**26b**), R = 3-Br
(**26c**), R = 4-Br; (**26d**), R = 6-OMe
(**26e**), R = 7-OMe



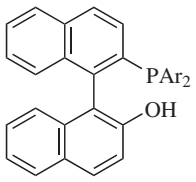
(**27a**), R_1 = H; R_2 = C_4H_9
(**27b**), R_1 = C_4H_9; R_2 = C_4H_9
(**27c**), R_1 = C_8H_{17}; R_2 = C_8H_{17}



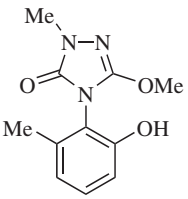
(**28a**), R_1 = R_2 = H
(**28b**), R_1 = OMe; R_2 = H
(**28c**), R_1 = R_2 = OMe



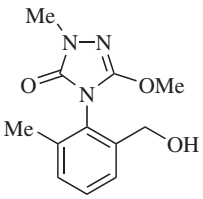
(**29**)



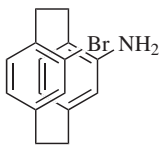
(**30a**), Ar = Ph
(**30b**), Ar = p-C_6H_5



(**31**)



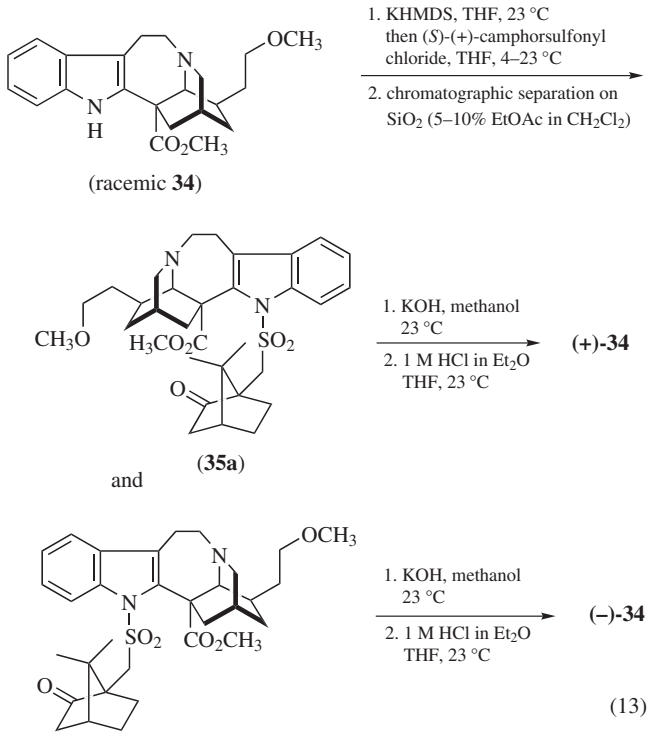
(**32**)



(**33**)

Chemical resolution of racemic 18-methoxycoronaridine (18-MC) **34** was achieved by the formation and chromatographic separation of the diastereomeric sulfonamides **35** (eq 13).[49] The key to the formation of the sulfonamides was the use of potassium bis(trimethylsilyl)amide as the base in this reaction.

The naturally occurring azedaralide **36** was obtained by total synthesis and resolution of its racemate through the formation of enol camphorsulfonate esters. The absolute stereochemistry of the (+)-enantiomer was confirmed by X-ray crystal structure analysis of its (1*S*)-10-camphorsulfonate ester **37**.[50]



(racemic **34**)

1. KHMDS, THF, 23 °C
then (*S*)-(+)-camphorsulfonyl chloride, THF, 4–23 °C
2. chromatographic separation on SiO_2 (5–10% EtOAc in CH_2Cl_2)

(**35a**)

and

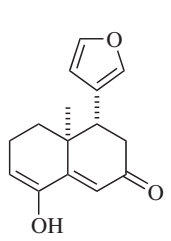
(**35b**)

1. KOH, methanol 23 °C
2. 1 M HCl in Et_2O THF, 23 °C

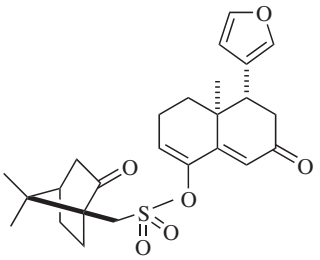
(+)-34

(–)-34

(13)

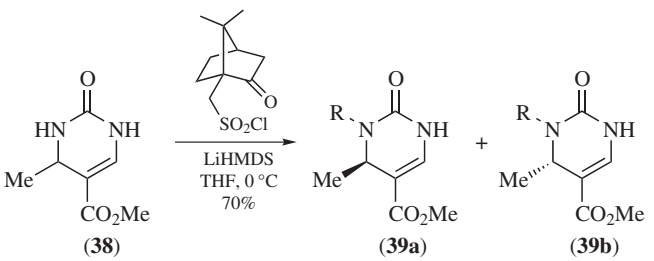


(**36**)
(+)-azedaralide



(**37**)

Amides such as the 3,4-dihydropyrimidin-2(1*H*)-one **38** can also be resolved in the form of their camphorsulfonamides (eq 14).[51] Regioselective sulfonylation of the dianion of **38** with (*S*)-camphorsulfonyl chloride furnished a mixture of sulfonamides **39a** and **39b**. The diastereoisomers were then resolved by column chromatography, and the absolute configuration of **39a** was verified by X-ray crystallography of a subsequent derivative.



(**38**)

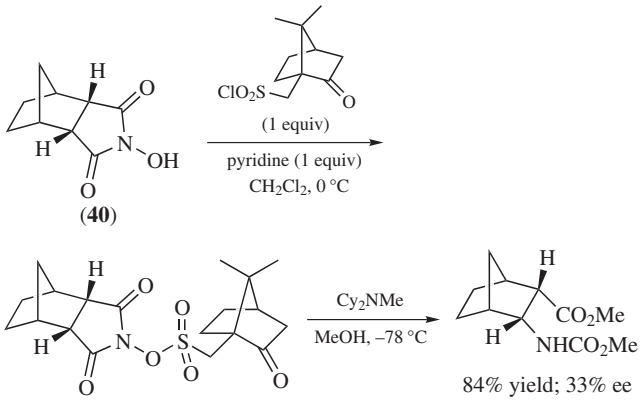
LiHMDS
THF, 0 °C
70%

(**39a**) + (**39b**)

R = (*S*)-camphorsulfonyl

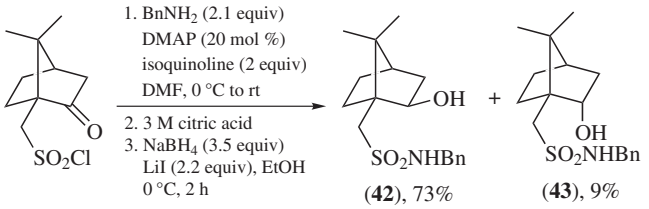
(14)

Synthesis of Chiral Auxiliaries for Diastereoselective Synthesis.[52–56] (1*S*)-(+)-10-Camphorsulfonyl chloride and its enantiomer continue to serve as building blocks for a number of useful chiral auxiliaries.[52–56] For example, in an effort to develop a chiral version of Lossen reaction[55] as a vehicle to desymmetrize *meso*-hydroxamic acids, the camphorsulfornyl group was introduced as both an activator and a chiral director. Methanolysis of camphorsulfonate ester **41** derived from the norbornene-fused *N*-hydroxamic acid **40** led to the formation of the carbamate product in 84% yield and modest ee (33%) (eq 15).[56]

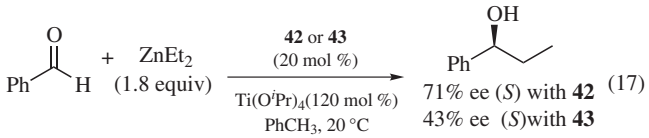


(15)

Synthesis of Chiral Ligands for Titanium Alkoxide-promoted Addition of Dialkylzinc to Aldehydes and Ketones. Camphorsulfonyl-derived sulfonamides have been synthesized and screened as ligands for titanium alkoxide-promoted addition of dialkylzinc to aldehydes and ketones. The first example involved the conversion of (*S*)-(+)-camphorsulfonyl chloride to its *N*-benzyl sulfonamide, which was reduced by $NaBH_4$ to afford the diastereomeric hydroxysulfonamides **42** and **43** (eq 16).[57] These ligands were tested in the titanium-catalyzed diethylzinc addition to benzaldehyde.[58–60] Only the exo-epimer **42** turned out to give high levels of stereoselectivity (eq 17).

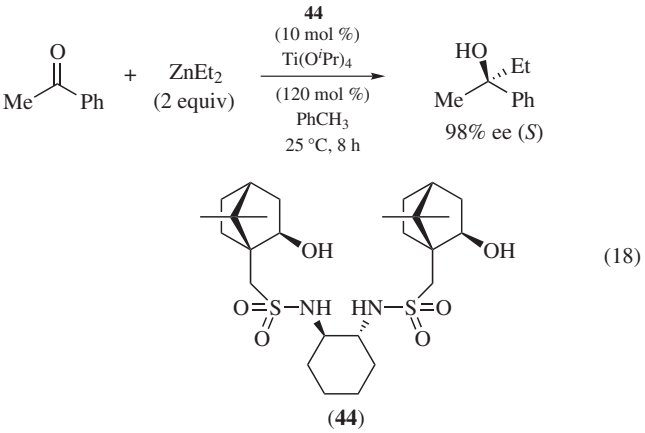


(16)



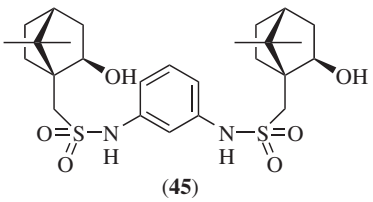
(17)

Most of the efforts in this area centered on the synthesis of bis-camphorsulfonamides from either a chiral or an achiral diamine scaffold.[61,62] The optimum derivative was found to be **44**, which proved to be an excellent ligand for the $Ti(O^iPr)_4$-catalyzed addition of Et_2Zn to ketones (eq 18).[63]

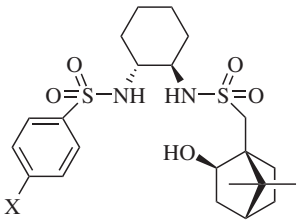


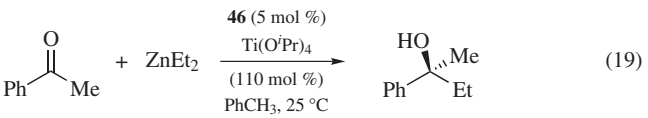
(18)

Similar ligands have been synthesized from aromatic diamines. For example, ligand **45** can be readily assembled from 1,3-benzenediamine, (*S*)-(+)-camphorsulfonyl chloride, and a reducing reagent.[64,65] Good enantioselectivity for the addition of Et_2Zn to benzaldehyde[64] and excellent enantioselectivity for the addition of Me_2Zn to ethyl phenyl ketone[65] were observed with this reagent.

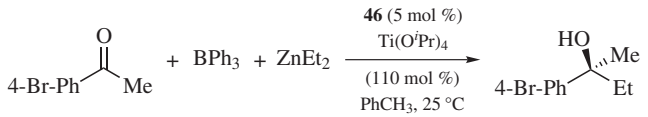


Mixed bis-sulfonamide ligands of the type **46** were also prepared and shown to be highly effective for the addition of organozinc reagents to ketones (eqs 19 and 20).[66,67]





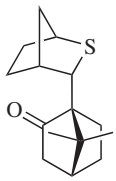
(19)



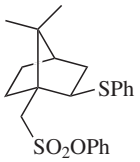
(20)

As Precursor for the Synthesis of Chiral Organosulfur and Organoselenium Catalysts or Reagents. The increasing pop-

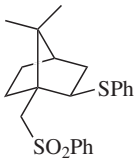
ularity of chiral organosulfur and organoselenium reagents in organic chemistry has prompted a tremendous amount of effort in the synthesis of new organosulfur and organoselenium compounds. The usefulness of 10-camphorsulfonyl chloride as a starting material for the preparation of such molecules is shown by the synthesis of chiral sulfides **47**–**49** and chiral selenides **50**–**52**.[68,69] Compounds **48**–**52** were all prepared from the common intermediate (*S*)-camphorsulfonate **53** derived (*S*)-camphorsulfonyl chloride.[69]



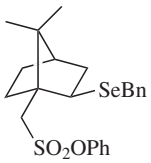
(**47**)



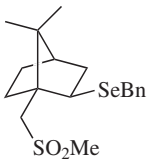
(**48**)



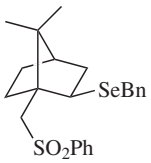
(**49**)



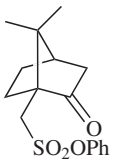
(**50**)



(**51**)

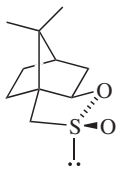


(**52**)

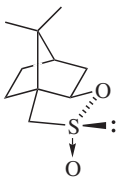


(**53**)

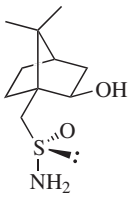
A number of enantiopure sulfinic acid derivatives, including sultines **54** and **55**, sulfinamides **56**–**59**, sulfinimines **60** and **61**, and the chiral sulfoxide **62**, were synthesized from (1*S*)-camphorsulfinic acid that was formed by reduction of (1*S*)-camphorsulfonyl chloride with sodium borohydride.[70]



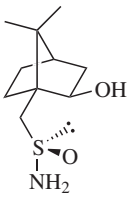
(**54**)



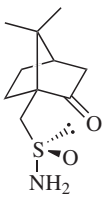
(**55**)



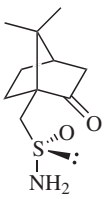
(**56**)



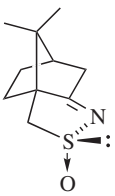
(**57**)



(**58**)

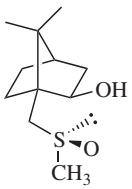


(**59**)



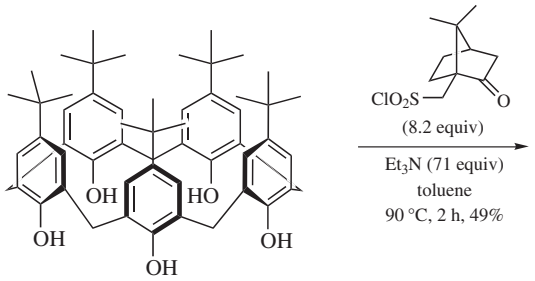
(**60**)

(**61**)



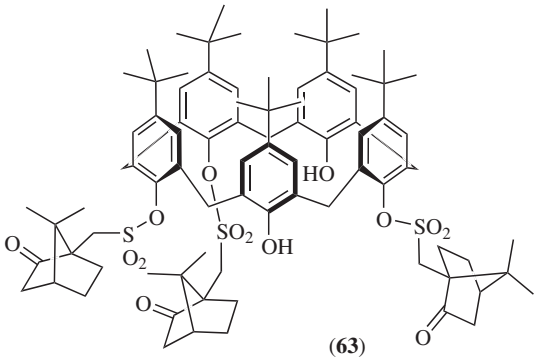
(**62**)

Synthesis of Chirally Modified Calixarenes and Resorcinarenes. (1*S*)-Camphorsulfonyl chloride was used to introduce camphorsulfonate groups to form the chirally modified calixarene **63** (eq 21)[71] and the diastereomeric tetraalkoxyresorcin[4]arenes **65** from racemic **64** (eq 22).[72] Diastereomers **65a** and **65b** can be separated chromatographically. This allowed **64** to be resolved into chiral nonracemic (*P*,*S*)-(+)-**64** and (*M*,*R*)-(−)-**64** after cleavage of the sulfonate ester groups. The absolute stereochemistry of (*P*,*S*)-(+)-**64** and (*M*,*R*)-(−)-**64** was obtained from an X-ray structure analysis of **65a**.

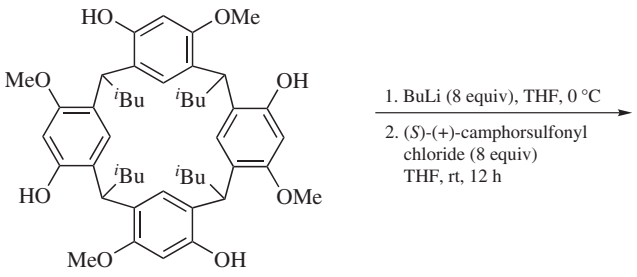


(8.2 equiv)
Et_3N (71 equiv)
toluene
90 °C, 2 h, 49%

(21)

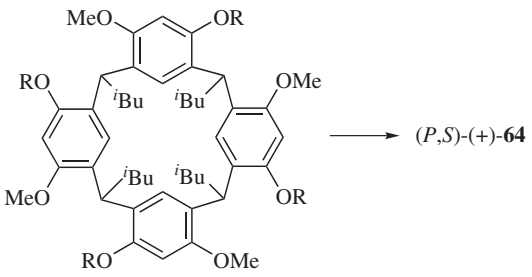


(**63**)



1. BuLi (8 equiv), THF, 0 °C
2. (*S*)-(+)-camphorsulfonyl chloride (8 equiv)
THF, rt, 12 h

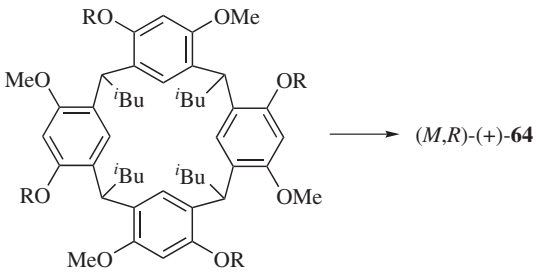
(racemic **64**)



(*P*,*S*)-(+)-**64**

(**65a**)

and



(*M*,*R*)-(+)-**64**

(**65b**)

R = (*S*)-camphorsulfonyl (22)

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