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On the Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerization Reaction. Electronic and Torsional Ligand Control of Absolute Stereoselection.†

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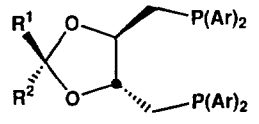
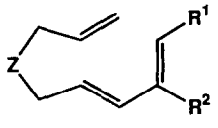
Abstract: **The use of bisphosphine ligands related to DIOP as chiral modifiers in the Rh(I) catalyzed [4+2] cycloisomerization reaction results in moderate to good levels of enantioselection. The mode of absolute stereoinduction is subject to electronic and torsional modification of the chelating ligand.**

Enantioselective transformations catalyzed by homochiral transition metal complexes have assumed a position of increasing significance in molecular synthesis.[2] Central to the design of new catalyst types will be a detailed understanding of the features intrinsic to the controller ligand that regulate asymmetric induction. Our interests in Rh(I) templated carbocyclizations[3] led us to examine the influence that certain homochiral bisphosphines might exert on the stereochemical outcome of this catalytic reaction.[4,5] Based on our knowledge that optimum cyclization efficiencies in the Rh(I) catalyzed [4+2] cycloaddition reaction[6] are given by bisphosphines which chelate to give 7-membered ligation ensembles, a series of ligands **1a-f** related to (+)-DIOP was chosen for *initial* study. Further impetus for the selection of this family of bisphosphines was provided by the following considerations: (1) the *absolute* stereochemical integrity for this homogeneous series of ligands [derived from (2*R*,3*R*)-(+)-tartaric acid][7] was guaranteed; (2) the resident steric *and electronic* properties of the ligating phosphorus centers within these compounds were subject to facile modification; and (3) the dihedral "bite" associated with ligation was susceptible to alteration by modifying the torsional bias of the 1,3-dioxolane ring via substitution at the 2-position.



1a: $R^1 = R^2 = CH_3$, Ar = Ph
1b: $R^1 = CH_3$, R^2 = Ph, Ar = Ph
1c: R^1 = H, R^2 = *t*-Bu, Ar = Ph
1d: $R^1 = R^2 = CH_3$, Ar = 3,5-$(CF_3)_2C_6H_3$
1e: $R^1 = R^2 = CH_3$, Ar = 2-$(CH_3)C_6H_4$
1f : $R^1 = R^2 = CH_3$, Ar = 2-$(CF_3)C_6H_4$

Cyclization Studies: Representative asymmetric Rh(I) catalyzed ene-diene and diene-yne cyclizations were conducted in CF_3CH_2OH (TFE) under reaction conditions analogous to those reported previously.[3] Enantiomeric excesses were determined by conversion of the product bicycles **3a,b** and **6** to the corresponding Mosher's esters[8] **8a,b** and **9** via hydroboration / oxidation (a) BMS, b) H_2O_2 - OH^-) followed by esterification. In the case of bicycle **3c**, catalytic bis-hydroxylation (OsO_4 / NMO) followed by *selective* esterification of the *equatorial* hydroxyl of the resulting diol was used to prepare the requisite Mosher derivative **8c**. For each of the examples **2a-c** and **5** studied, the corresponding racemic Rh(I) catalyzed cyclizations were performed by using $(i\text{-}C_3F_6HO)_3P$ as an achiral ligand so that accurate product spectroscopic analyses and ee determinations could be made. In every instance, the critical ^{1}H-NMR resonances for the ester methine signals of interest within the diastereomeric Mosher's derivatives were cleanly resolved.[9] The results obtained for the enantioselective Rh(I) catalyzed cyclizations of the substrates **2a-c** and **5** using the stereochemically homogeneous but structurally differentiated phosphines **1a-f** are summarized in **Table I.**[10]



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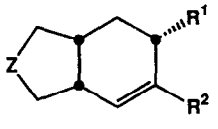

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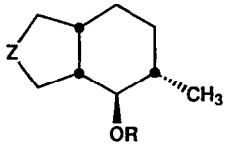
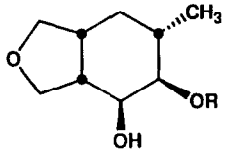
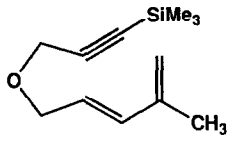


4a,b (R = H)
8a,b (R = MTP) (*R*)



4c (R = H)
8c (R = MTP) (*R*)

a: R^1= H, R^2= CH_3, Z = O
b: R^1= H, R^2= CH_3, Z = $C(CH_2OCH_3)_2$
c: R^1= CH_3, R^2= H, Z = O



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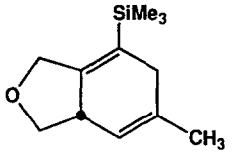

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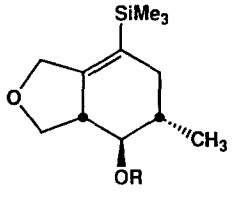

7 (R = H)
9 (R = MTP) (*R*)

Table I. Asymmetric Rh(I) Catalyzed [4+2] Cycloadditions Mediated by Homochiral Bisphosphines.

Entry	Cycloadduct[a]	Ligand	Isolated Yield (%)	Ester	de[a,b]
1	**3a**	**1a**	86	**8a**	7 (*R*)
2	**3a**	**1b**	79	**8a**	20 (*S*)
3	**3a**	**1d**	85	**8a**	2 (*R*)
4	**3a**	**1e**	72	**8a**	42 (*S*)
5	**3a**	**1f**	79	**8a**	62 (*R*)
6	**3b**	**1a**	83	**8b**	10 (*R*)
7	**3b**	**1e**	69	**8b**	67 (*S*)
8	**3b**	**1f**	83	**8b**	28 (*R*)
9	**3c**	**1a**	84	**8c**	73 (*R*)
10	**3c**	**1b**	73	**8c**	47 (*S*)
11	**3c**	**1c**	72	**8c**	54 (*S*)
12	**3c**	**1e**	N. R.	—	—
13	**3c**	**1f**	N. R.	—	—
14	**6**	**1a**	89	**9**	52 (*R*)
15	**6**	**1b**	76	**9**	87 (*S*)
16	**6**	**1e**	81	**9**	37 (*S*)
17	**6**	**1f**	99	**9**	42 (*S*)

[a]Ester de = cycloadduct ee. [b]*R* or *S* refers to the stereochemistry of the carbon bearing the MTPO group in the esters **8a-c** and **9**.

An examination of the experimental results presented in **Table I** reveals that not only the magnitude, but also the absolute sense of asymmetric induction can be influenced by torsional alteration of the *4,5-bis(diphenylphosphinomethyl)*-1,3-dioxolane dihedral angle as well as electronic/steric perturbations at phosphorus.[11] Sterically derived conformational biasing of the 1,3-dioxolane ring[12] has been suggested to result in a perturbation of the "edge-face"[13] presentation of the phenyl groups adjacent to the site of metal binding in a series of tartrate derived ligands related to **1a-c**.[5a] The observed reversal in the absolute sense of asymmetric induction when ligands **1b** and **c** were employed relative to **1a** (entries 2, 10, 11 and 15) may well derive from this type of conformational alteration during Rh catalyzed bond formation.

That "simple" electronic effects alone may *not* result in significant deviations in asymmetric induction can be ascertained by comparing entries 1 and 3. By way of contrast, substantial variations in ee's were observed when the controller ligands **1e** and **f** [bearing 2-(methyl)phenyl and 2-(trifluoro-

methyl)phenyl phosphine substituents respectively] were employed as chiral modifiers (entries 4-5 and 7-8). For the *roughly* isosteric pair of ligands **1e** and **f**, the aryl substituents were expected to induce a greater degree of steric pseudochirality at phosphorus when compared to the phosphines **1a** and **d**. In the case of **1f**, however, the existence of a lone CF_3 group at the 2-position of the respective phenyl rings on phosphorus was anticipated to exert strong dipole-dipole interactions that might substantially alter the "edge-face"[13] arraying of these substituents. In all likelihood, the manifestation of the above features contributed to the observed variations in the ee's obtained in the foregoing cyclizations. The relatively high enantioselectivity observed in the cyclization of **2c** using DIOP (**1a**) (73% ee, entry 9) is noteworthy when compared to the lower values obtained with this ligand for the substrates **2a** and **b** (entries 1 and 6). In all likelihood, the enhanced enantiocontrol obtained in the case of **2c** is a consequence of increased steric differention resulting from the use of a *terminally substituted* diene as a cycloaddition component. In consonance with this rationale, **2c** failed to undergo cyclization in the presence of Rh(I) catalysts derived from the more sterically hindered ligands **1e** and **1f**. The results obtained with ligands **1e** and **f** for the acetylenic substrate **5** (entries 16 and 17) reveal further that the asymmetric mode selectivity of cyclization may also be substrate dependent.

Although product antipodal inversions resulting from substituent *conformational* reorientation within bisphosphines of a common stereochemical origin have been described previously for asymmetric hydrogenations,[14] the preceding examples constitute the first instances of this phenomenon in carbocyclizations. Further studies in these laboratories will hopefully reveal the full extent to which this, as well as other *less subtle* factors, can influence absolute stereoinduction in Rh(I) catalyzed cycloaddition reactions.

Acknowledgements: Generous financial support in the form of grants from the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation is gratefully acknowledged. The authors thank the Johnson Matthey Corporation for providing a discounted sample of $RhCl_3 \cdot 3H_2O$ on the "Precious metals on loan" program.

EXPERIMENTAL SECTION

General experimental details: Tetrahydrofuran (THF) and 1,2-dimethoxyethane (1,2-DME) were distilled from K. Diethyl ether (Et_2O) was distilled from Na–benzophenone. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), benzene, toluene and 2,2,2-trifluoroethanol (TFE) were distilled from CaH_2. The molarities indicated for organolithium reagents were established by titration with 2-butanol. ^1H NMR and ^{13}C NMR were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. ^{31}P NMR were measured at 202 MHz with a Bruker AM-500 spectrometer. ^1H NMR chemical shifts are reported as δ values in ppm relative to TMS. ^{31}P NMR chemical shifts are reported as δ values in ppm relative to the ^{31}P resonance of H_3PO_4 (85%) (0.0) or triphenylphosphine (−6.0). ^1H NMR and ^{31}P NMR coupling constants are reported in Hz and refer to

apparent multiplicities and not true coupling constants. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); sx (sextet); br (broad); m (multiplet); app d (apparent doublet); app t (apparent triplet); dd (doublet of doublets); etc. High resolution mass spectra were measured on a VG Analytical 7070E spectrometer by Dr. L. J. Sears. Infrared spectra were recorded with either a Perkin-Elmer 1800 FTIR or 237B grating IR. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. Elemental Analyses were performed by Desert Analytics, Tucson, Arizona. TLC and column chromatography were done with E. Merck silica gel. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried vessels. Concentrations were performed under reduced pressure with a Büchi rotary evaporator.

Typical Substrate Synthesis: **1,3,3aβ,6,7,7aβ-hexahydro-5-methylisobenzofuran (3a).** A flame-dried test tube (25 x 150 mm) equipped with a stirring flea was charged with $[(C_8H_{14})_2RhCl]_2$ (35.88 mg, 0.0500 mmol) and flushed with argon. The Rh dimer was then dissolved by the addition of CH_2Cl_2 (0.5 mL). A smaller flame-dried test tube (12 x 75 mm) was charged with **1f** (92.5 mg, 0.120 mmol), and flushed with argon. The ligand was then dissolved by the addition of CH_2Cl_2 (1.5 mL) and the resulting solution was transferred to the $[(C_8H_{14})_2RhCl]_2$ solution via syringe. To the resulting red-orange solution was added 2,2,2-trifluoroethanol (6.0 mL), followed by **2a** (276.5 mg, 2.00 mmol). The reaction mixture was then heated at 55 °C for 2.5 h. Upon completion of cyclization, the solution was transferred to a 25 mL round-bottomed flask and solvent was evaporated under reduced pressure. The residue was then dissolved in CH_2Cl_2 (15 mL) and the solution was concentrated again. This process was repeated 3 more times. Bulb-to-bulb distillation of the resulting residue gave 218.4 mg (79%) of **3a** as a colorless oil. ^1H NMR ($CDCl_3$) δ 5.33 (s, fine struct., 1H, C=C*H*), 3.94 (dd, J = 1.8, 7.2 Hz, 1H, OC*H*), 3.90 (dd, J =1.8, 7.7 Hz, 1H, OC*H*), 3.58 (dd, J = 4.7, 7.6 Hz, 1H, OC*H*), 3.43 (dd, J = 7.3, 7.6 Hz, 1H, OC*H*), 2.65 (m, 1H, C*H*), 2.30 (m, 1H, C*H*), 1.92 (t, J = 5.8 Hz, 2H, CH_2), 1.68 (s, 3H, CH_3), 1.65 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 135.5, 120.3, 73.0, 72.5, 53.2, 39.3, 36.1, 27.6, 23.7; IR (film) 2972, 2944, 2920, 2856, 1442, 1356, 1108, 1084, 1046, 1030, 970, 894, 734, 670, 638 cm^{-1}. High resolution mass spectrum calcd. for $C_9H_{14}O$: 138.1045. Found: 138.1045.

1,3,3aβ,4α,5β,6,7,7aβ-octahydro-4-hydroxy-5-methylisobenzofuran (4a). A flame-dried test tube (12 x 125 mm) equipped with a stirring flea was charged with **3a** (138 mg, 1.00 mmol) and THF (1.0 mL). The vessel was then flushed with nitrogen and cooled to −5 °C. $BH_3{\cdot}S(CH_3)_2$ (121 μL of a 10.1 M solution, 1.21 mmol) was added dropwise over 5 min. The reaction was then warmed to 25 °C and stirred for 4 h. After cooling to −5 °C, absolute ethanol (0.50 mL) was added, followed by NaOH (0.41 mL of a 3N solution, 1.22 mmol) and H_2O_2 (30% aq) (0.45 mL, 3.99 mmol). The mixture was stirred vigorously for 2 h. Ice water (5.0 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic phases were

dried ($MgSO_4$), concentrated and the resulting residue was subjected to flash chromatography on silica gel (hexanes-EtOAc 1:9 for elution) to give 135 mg (87%) of **4a** as a viscous beige oil. ^1H NMR ($CDCl_3$) δ 4.04 (app d, J = 8.5 Hz, 1H, HOC*H*), 3.81 (dd, J = 8.4, 8.8 Hz, 1H, OC*H*), 3.74 (dd, J = 4.5, 8.4 Hz, 1H, OC*H*), 3.49 (dd, J = 7.9, 10.9 Hz, 1H, OC*H*), 3.09 (dd, J = 10.0, 10.9 Hz, 1H, OC*H*), 2.56 (m, 1H, C*H*), 1.90 (m, 1H, C*H*), 1.85 (br, 1H, O*H*), 1.60 (m, 2H, CH_2), 1.36 (m, 1H, C*H*), 1.15 (m, 2H, CH_2), 1.00 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 74.5, 71.9, 69.1, 47.3, 38.7, 38.2, 28.4, 22.6, 18.2; IR (film) 3406, 2926, 2870, 1716, 1456, 1062, 1042, 984, 884 cm^{-1}. Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.12; H, 10.22.

Preparation of Esters of (*R*)-α-Methoxy-α-trifluoromethylphenylacetic Acid. The following procedure was used to prepare all MTPA derivatives for NMR studies. (*S*)-(+)-MTPA-Cl was prepared from (*R*)-(+)-MTPA and distilled.[8] A flame-dried test tube (12 x 125 mm) equipped with a stirring flea was charged with 4-dimethylaminopyridine (DMAP) (51 mg, 0.42 mmol) and CH_2Cl_2 (0.50 mL). The solution was cooled to 0 °C and the test tube was flushed with nitrogen. (*S*)-(+)-MTPA-Cl (99 mg, 0.39 mmol) was then added by syringe, followed by a solution of **4a** (40 mg, 0.26 mmol) in CH_2Cl_2 (0.50 mL). The reaction mixture was stirred and then allowed to stand at 25 °C for an additional 15 h. The mixture was diluted with Et_2O (3.0 mL) and added to cold 5% HCl (2.0 mL) contained in a separatory funnel. The organic layer was separated, washed with cold satd. Na_2CO_3 (3.0 mL) and extracted with cold 5% $CuSO_4$ (3.0 mL). The organic layer was then washed with cold water until the remaining $CuSO_4$ was removed, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was dissolved in CH_2Cl_2 (2.0 mL) and the solution was concentrated again. This process was repeated 3 more times to give 94 mg (97%) of the two diastereomeric MTPA-esters (corresponding to **8a**), as a beige solid. All compounds gave ^1H NMR spectra consistent with their assigned structures. In all cases the nonequivalence of the diagnostic diastereotopic substituents was clearly discernable. Purification of the final product and ee determination can be accomplished by preparative GLC. Care, however, must be taken that both isomers are completely collected.

Typical ligand synthesis: **Bis(2-trifluoromethylphenyl)phosphine Oxide.**[15] An oven-dried, three-necked round-bottomed flask was fitted with a pressure equalizing addition funnel, condenser, and magnetic stirring bar. The vessel was charged with Mg powder (–50 mesh, 99+%) (4.86 g, 0.200 mol) and purged with nitrogen. THF (20 mL) was then added followed by 2-bromobenzotrifluoride (4.13 g, 0.0180 mol) by syringe. The reaction mixture was gently heated in order to initiate the Grignard reaction. The remainder of the 2-bromobenzotrifluoride (41.4 g, 0.184 mol) was dissolved in THF (60 mL) and added to the activated Mg mixture over a period of 1 h.

Subsequently, the reaction mixture was refluxed for an additional 2 h. Meanwhile, an oven-dried, round-bottomed flask was charged with NaH (60% oil dispersion, 4.00 g, 0.100 mol) and the oil was removed by trituration with pentane (3 x 15 mL). THF (75 mL) was then added and the flask was purged with nitrogen. The mixture was cooled to 0 °C and freshly distilled diethyl phosphite (13.8 g, 0.100 mol) was added dropwise over a period of 15 min. The grey slurry was then warmed to 25 °C and stirred for an additional 1 h. The resulting solution of sodium diethyl phosphite was added *via* cannula to the 2-trifluoromethylphenylmagnesium bromide mixture at 0 °C over a period of 1 h. Subsequently, the reaction mixture was refluxed for 8 h. After cooling to 0 °C, conc. HCl (40 mL) in cold water (80 mL) was added slowly whereupon a small quantity of tan ppt. formed in the red solution. This mixture was poured into a separatory funnel containing Et_2O (200 mL) and water (100 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 x 20 mL). The organic layers were combined, washed with water (2 x 10 mL), brine (20 mL), dried ($MgSO_4$) and the solvents were removed *in vacuo*. The resulting tan solid was purified by bulb-to-bulb sublimation (160 °C, 25 μtorr) to yield 24.4 g (72%) of the phosphine oxide as a yellow crystalline material: mp 124.2-126.8 °C; ^{1}H NMR ($CDCl_3$) δ 8.54 (d sept., J = 2.8, J^{P-H} = 537 Hz, 1H, P-*H*), 7.96 (m, 1H, Ar-*H*), 7.92 (m, 1H, Ar-*H*), 7.77 (m, 2H, Ar-*H*), 7.70 (m, 4H, Ar-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5 (CH), 134.4 (CH), 132.7 (CH), 132.0 (CH), 131.9 (CH), 130.0 (C), 127.0 (CH), 125.5 (C), 121.7 (C); ^{31}P NMR ($CDCl_3$) δ 9.0 (d, J^{H-P} = 538 Hz); IR (KBr) 1314, 1170, 1118, 1036, 940, 770, 700, 516 cm^{-1}.

Bis(2-trifluoromethylphenyl)phosphine.[15] An oven-dried, round-bottomed flask was fitted with a rubber septum and a magnetic stirring bar. The vessel was charged with bis(2-trifluoromethyl-phenyl)phosphine oxide (1.50 g, 4.66 mol) and purged with argon. Diphenylsilane (903 mg, 4.89 mmol) was then added by syringe at 25 °C. The reaction mixture was heated and stirred at 140 °C for 30 min whereupon it became homogeneous. The solution was then stirred at 210 °C for 2.5 h. Subsequently, the phosphine was distilled directly from the reaction mixture (40 °C, 10 μtorr) to provide 1.4 g (93%) of a clear viscous oil.

***(R,R)-trans*-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (1f).** The following procedure is a modification of one described by Hobbs and Knowles.[7] An oven-dried, round-bottomed flask was fitted with a rubber septum and a magnetic stirring bar. The vessel was charged with deoiled KH *vide infra* (88.6 mg, 2.21 mmol) and purged with argon. After cooling to −78 °C, a solution of bis(2-trifluoromethylphenyl)phosphine (677 mg, 2.10 mmol) in THF (1.75 mL) was added dropwise over a period of 10 min. The dark red solution was stirred at −78 °C for an additional 15 min, then warmed to 25 °C. After stirring at 25 °C for 5 min, the

reaction mixture was re-cooled to −78 °C and a solution of (*S,S*)-*trans*-4,5-bis[(*p*-tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane[16] (470 mg, 1.00 mmol) in THF (3.0 mL) was slowly added. The resulting mixture was warmed to 25 °C and stirred for an additional 12 h. The THF was evaporated under reduced pressure and the residue was dissolved in degassed Et_2O (10 mL). The resulting solution was washed with degassed water (3 x 5 mL). The organic layer was separated, dried ($MgSO_4$) and solvent was evaporated under reduced pressure to give a light yellow solid material. Purification by crystallization under argon from abs. ethanol afforded 670 mg (87%) of the title compound as a white crystalline solid: mp 140.6-142.9 °C; $[\alpha]^{25}$-27.0 (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.67 (m, 4H, Ar-*H*), 7.51 (m, 8H, Ar-*H*), 7.43 (m, 4H, Ar-*H*), 4.00 (m, 2H, OC*H*), 2.40 (dd, J = 5.1, 15.9 Hz, 2H, P-CH_2), 2.25 (dd, J = 5.1, 15.9 Hz, 2H, P-CH_2), 1.26 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 134.0 (CH), 133.6 (CH), 131.6 (CH), 131.5 (CH), 128.9 (CH), 126.7 (C), 121.2 (C), 109.3 (C), 79.1 (CH), 79.0 (CH), 32.8 (CH_2), 32.5 (CH_2), 26.9 (CH_3); ^{31}P NMR ($CDCl_3$) δ −33.6 (septet, J = 50 Hz); IR (KBr) 3075, 2984, 2929, 2893, 1594, 1573, 1308, 1262, 1112, 1033, 764 cm^{-1}. Anal Calcd. for $C_{35}H_{28}F_{12}O_2P_2$: C, 54.56; H, 3.66; F, 29.59; P, 8.04. Found C, 54.55; H, 3.58; F, 29.38; P, 8.0 (min).

REFERENCES AND NOTES

† This article is dedicated to the memory of Professor Paul G. Gassman.

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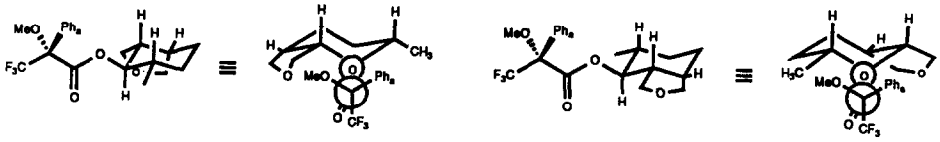
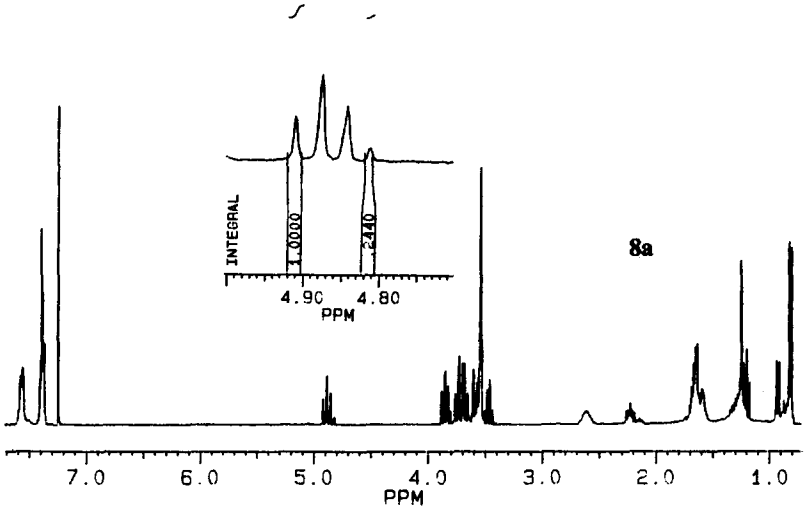
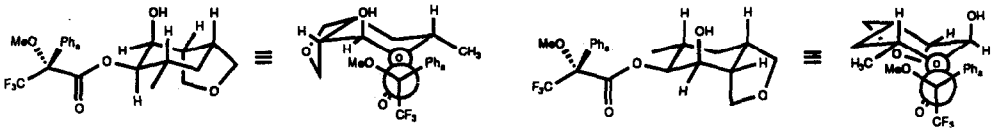
9. The absolute stereochemistry of the cycloadducts was assigned by using the method first described by Mosher.[8] As shown in the Newman projections below, the methyl group syn to the phenyl ring is further upfield in **8a**(*R*) due to through-space interaction with the phenyl moiety (Ph_a) on the MTPA ester.



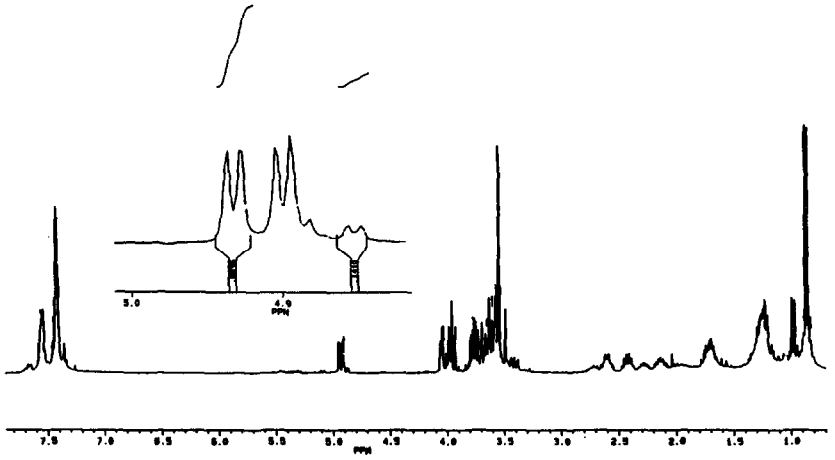
8a *(R)* **8a** *(S)*

The ratios of diastereomers for **8a-c** and **9** were measured by integration of the ester methine proton resonances, which were well resolved at 300 MHz, at 4.81 and 4.91 ppm for **8a**, at 4.85 and 4.95 ppm for **8c** and at 4.82 and 4.92 ppm for **9**. The ester methine proton resonances for the two diastereomeric esters of **8b** were resolved at 500 MHz at 4.82 and 4.86 ppm. Absolute stereochemical assignments for the Mosher's esters **8b,c** and **9** were made in a similar fashion.





8c *(R)* **8c** *(S)*



10. All new compounds were fully characterized by IR, MS, ^{1}H and ^{13}C NMR and possessed satisfactory combustion analyses or exact mass.
11. Impressive ligand induced control in the asymmetric alkene hydrocyanation reaction has recently been reported: a) Nugent, W. A.; RajanBabu, T. V.; Burk, M. J. *Science* **1993**, *259*, 479. b) RajanBabu. T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265.
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15. The procedure for preparation of phosphine oxides is a modification of an unpublished procedure provided by C. F. Hobbs of the Monsanto Corporation, through personal communication.
16. Prepared according to the literature procedure (ref. 7).

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