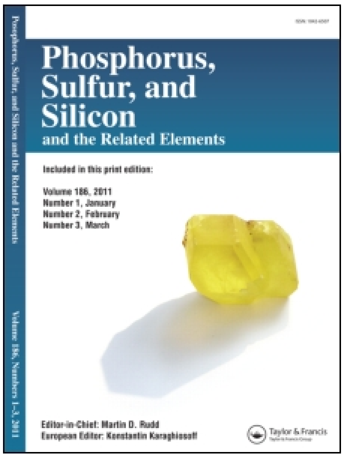

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Synthesis of Enantiomerically Enriched Mono and Bis 2,2'-Bipyridine Alkyl Sulfoxides and Their First Application as Chiral Auxiliaries[1]

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Synthesis of Enantiomerically Enriched Mono and Bis 2,2′-Bipyridine Alkyl Sulfoxides and Their First Application as Chiral Auxiliaries[1]

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The direct asymmetric oxidation of 6,6′-bis(alkylsulfanyl)-2,2′-bipyridines ***2a–e*** *to non-racemic mono sulfoxides* ***3a–e*** *and bis-sulfoxides* ***4a,c–e*** *using either Davis oxaziridine or a modified Sharples reagent is reported. The use of isolated mono- and bis-sulfoxides as chiral auxiliaries was tested in either the asymmetric addition of the diethylzinc or allyl(trichloro)silane to benzaldehyde.*

Keywords Allyl(trichloro)silane; 5,5′-bis-1,2,4-triazines; Diels–Alder/retro-Diels–Alder reaction; diethylzinc; optically active 2,2′-bipyridine sulfoxides

INTRODUCTION

Over the past two decades, a number of 2,2′-bipyridines functionalized with chiral substituents have been prepared and tested as ligands in transition metal catalysis.[2] The metal complexes of such 2,2′-bipyridines have been successfully applied as catalysts for a number of asymmetric reactions including cyclopropanations,[3] allylic substitution,[4] addition of organometallic reagents to aldehydes,[5] hydrosilylations,[6] hydrogen transfer reactions,[7] and allylic oxidations.[8] Recently, chiral 2,2′-bipyridine *bis-N*-oxides have drawn much attention, owing to their possible use as selective organocatalysts in metal-free reactions.[9] Among a variety of synthetic strategies that have been employed for the preparation of non-racemic chiral 2,2′-bipyridines, most are associated with transition metal catalyzed homo- and

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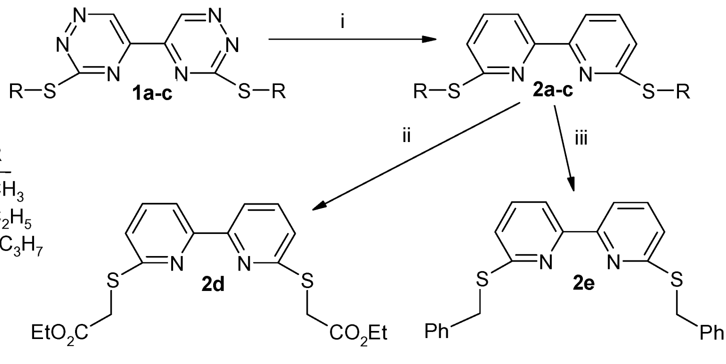
Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

Address correspondence to Andrzej Rykowski, Department of Chemistry, University of Podlasie, 3-Maja 54, 08-110 Siedlce, Poland. E-mail: rykowski@ap.siedlce.pl cross-coupling reactions of chiral pyridines[2,10] or Kröhnke-type synthesis from pyridinium salts and unsaturated ketones possessing the required chirality.[11] In contrast, the direct introduction of chirality to the prepared 2,2′-bipyridine ring system functionalized with prochiral substituents has not been widely explored.[12] The limited use of this approach for the preparation of chiral 2,2′-bipyridines may be due to the lack of efficient methods for the synthesis of suitable substrates. In previous reports, we demonstrated the use of dimeric 1,2,4-triazines as heteroaromatic azadienes for the preparation of functionalized 2,2′-bipyridines via Diels–Alder/retro-Diels–Alder reaction with inverse electron demand.[13] In a recent communication, we have described an extension of this study to the synthesis of 6,6′-bis(alkylsulfanyl)-2,2′-bipyridines and their chiral mono- and bis(sulfoxide)s via direct asymmetric oxidation.[14] Here we would like to present a full account of this work, including our recent finding on the utility of optically active, 2,2′-bipyridine sulfoxides as catalysts in an asymmetric addition of diethylzinc to benzaldehyde and allylation of benzaldehyde with allyltrichlorosilane.

RESULTS AND DISCUSSION

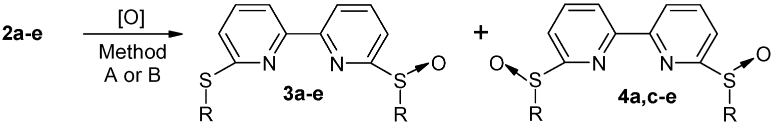
The required 6,6′-bis(alkylsulfanyl)-2,2′-bipyridines **2a–e** have been readily prepared in good yields using literature procedures, namely Diels–Alder/retro-Diels–Alder reaction of easily accessible alkyl sulfides of 5,5′-bis-1,2,4-triazines **1a–c** with norbornadiene,[15] followed by demethylation of **2a** with ethyl bromoacetate or benzyl bromide, respectively (Scheme 1).[14]



(i) norbornadiene, *p*-cymene, 160 °C, 30 h; (ii) ethyl bromoacetate, reflux, 8 h; (iii) benzyl bromide, reflux, 2 h.

SCHEME 1

Next, we have started our investigation on the direct asymmetric oxidation of the 6,6′-bis(alkylsulfanyl)-2,2′-bipyridines **2a–e** obtained. Two general approaches have been successfully applied for the synthesis of optically active 2,2′-bipyridine sulfoxides: method A—based on the use of optically active (+)-(8,8-dichlorocamphorylsulfonyl)-oxaziridine of Davis et al.,[16] and method B—based on oxidation according to the Kagan and coworker's conditions,[17] which consists in forming a complex between titanium (IV) isopropoxide, (R,R)-(+)-diethyl tartrate (DET), H_2O, and *tert*-butyl hydroperoxide (TBHP). Thus, treatment of 6,6′-bis(methylsulfanyl)-2,2′-bipyridine **2a** with 0.75 molar equivalents of (+)-(8,8-dichlorocamphorylsulfonyl)-oxaziridine at room temperature in methylene chloride solution for 24 h resulted in the formation of the expected mono sulfoxide **3a** accompanied by small amounts of bis oxidation product **4a** (see Scheme 2). Using the same reaction conditions the mono sulfoxides **3b–e** and bis sulfoxides **4a**,**c–e** were prepared in reasonable yields (Table I).

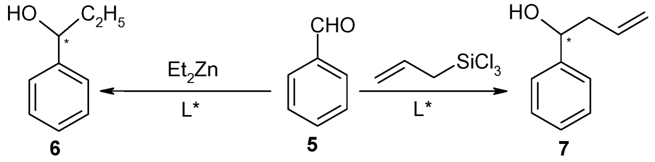


SCHEME 2

The second approach involved the reaction of 2,2′-bipyridine alkyl sulfides **2a–e** with combination of $Ti(Oi{-}Pr)_4$:(R,R)-DET:H_2O (1:2:1) in methylene chloride at −20°C for 16 h. Table I shows the results obtained in the oxidation of **2a–e** under aforementioned conditions. Although the Davis and Kagan protocols gave similar yields of optically active 2,2′-bipyridine sulfoxides, Kagan's procedure afforded better enantio-selectivites. The highest ee (99%) was obtained for bis sulfoxide **4a** (see Table I). The structures of **3a–e** and **4a**,**c–e** were fully confirmed by ^1H and ^{13}C NMR, as well as by HRMS data (see Experimental section). Moreover, the absolute configuration around both sulfinyl sulfur atoms in **4a** was confirmed by single crystal X-ray structure determination.[18]

The utility of the isolated, optically active mono and bis-sulfoxides as chiral auxiliaries was tested in the asymmetric addition of diethylzinc to benzaldehyde **5** and the allylation of the latter with allyl(trichloro)silane (Scheme 3).

A typical procedure for the addition of diethylzinc to benzaldehyde involved the use of 2.5–3% mol equiv. of optically active sulfoxides, 3 mol equiv. of diethylzinc, and 1 mol equiv. of benzaldehyde in benzene or toluene. Isolated yields and the enantiomeric excess of the resulting



SCHEME 3

1-phenyl-1-propanol (**6**) are collected in Table II; the (*S*) absolute configuration of the predominant enantiomer formed in the reaction was assigned by comparison of the sign of optical rotation with those reported in literature.[20] As can be seen from the reported data, the reactions promoted by mono sulfoxides **3a–e** afforded the corresponding alcohol **6** with poor stereocontrol. However, higher enantiomeric excesses were observed using bis-sulfoxides **4a**,**c–e**. Ligand **4d**, which had only 12% ee, provided optically active alcohol **6** with 11% ee (this corresponds to ee = 91%, for enantiomerically pure ligand). Most probably, a very high enantioselectivity observed for **4d** is due to the presence of two ethoxycarbonyl groups, next to the existing sulfinyl substituents in the ligand, which results in a better coordination of the metal ion.

The allylation of benzaldehyde with allyl(trichloro)silane was carried out in the presence of mono sulfoxides **3a**,**c–e** and bis-sulfoxides **4a**,**d–e**.

TABLE I Synthesis of Optically Active Sulfoxides 3 and 4 Based on the Davis and Kagan Protocols

Substrate	R	Product	Method	Yield [%]	ee [%]	Product	Yield [%]	ee [%]
2a	$-CH_3$	**3a**	A[a]	54	47[c]	**4a**	8	42[c]
			B[b]	40	70		13	>99[c]
2b	$-C_2H_5$	**3b**	A[a]	52	76[d]	**4b**[e]		
			B[b]	41	82[d]			
2c	$-CH(CH_3)_2$	**3c**	A[a]	36	51[c]	**4c**	11	22[d]
			B[b]	42	54[d]		9	27[d]
2d	$-CH_2CO_2C_2H_5$	**3d**	A[a]	41	5[d]	**4d**	12	17[d]
			B[b]	45	14[d]		26	12[d]
2e	$-CH_2Ph$	**3e**	A[a]	61	15[d]	**4e**	23	40[d]
			B	35	62[d]		17	5[d]

[a] Davis protocol.

[b] Kagan protocol.

[c] ee was determined by ^1H NMR using the CSA method.[19]

[d] ee was determined by HPLC analysis using a chiral stationary phase column (Chirobiotic T).

[e] Bis sulfoxide **4b** was not isolated.

TABLE II Addition of Diethylzinc to Benzaldehyde in the Presence of Optically Active Sulfoxides 3 or 4

L*	ee [%]	Amount of ligand (mol%)	Time [days]	Solvent	Yield Comp. **6** [%]	ee [%]
3a	36	3.5	3	Benzene	29	4.0 (12)[a]
3b	76	3.0	5	Benzene	37	10(13)[a]
3c	54	2.5	6	Toluene	40	14 (26)[a]
3d	14	3.0	5	Benzene	50	10 (7.5)[a]
3e	62	3.0	5	Benzene	21	9.0 (14)[a]
4a	42	3.5	2	Benzene	33	7.0 (18)[a]
4c	22	2.5	5	Benzene	41	14 (64)[a]
4d	12	3.0	5	Benzene	35	11 (91)[a]
4e	31	3.0	5	Benzene	23	8.0 (26)[a]

[a] Values calculated for enantiomerically pure ligands.

The reaction with mono-sulfoxides **3** afforded homoallylic alcohol **7** in low yields and with poor ee values. When the allylation of benzaldehyde was carried out in the presence of bis-sulfoxide **4d** (Table III), alcohol **7** was obtained in a fair ee. Thus, the enantioselectivity trend was similar to that observed for the addition of diethylzinc to benzaldehyde using the same catalysts.

In conclusion, a series of optically active mono- and bis-alkanesulfinyl -2,2′-bipyridines have been prepared and tested as chiral ligands in the addition of diethylzinc and allyl(trichloro)silane to benzaldehyde. Even if the ee values of the chiral alcohols **6** and **7** are lower then the values observed with other catalysts,[20] this work has demonstrated the possibility that optically active 2,2′-bipyridine alkyl sulfoxides can promote some enantioselective reactions with satisfactory stereocontrol.

EXPERIMENTAL

The starting sulfides were prepared according to known procedures: 6,6′-bis(methylsulfanyl)-2,2′-bipyridine **2a**,[15] 6,6′-bis(ethylsulfanyl)-2,2′-bipyridine **2b**,[14] 6,6′-bis(*i*-propylsulfanyl)-2,2′-bipyridine **2c**,[15] 6,6′-bis(ethoxycarbonylsulfanyl)-2,2′-bipyridine **2d**,[21] and 6,6′-bis(benzylsulfanyl)-2,2′-bipyridine **2e**.[22]

TABLE III Synthesis of Homoallylic Aldehyde 7

L*	ee [%]	Amount of ligand (mol%)	Time [days]	Yield [%]	ee [%]
3a	70	5	3	28	13 (19)[a]
3c	54	5	3	33	9 (16)[a]
3d	14	5	5	23	3 (24)[a]
3e	62	10	7	32	7 (11)[a]
4a	95	5	5	30	22 (23)[a]
4d	17	5	5	30	5 (31)[a]
4e	31	5	6	29	7 (22)[a]

[a] Values calculated for enantiomerically pure ligands.

Asymmetric Oxidations of Sulfides 2a–e Using (+)-(8,8-Dichlorocamphorylsulfonyl)-oxaziridine: General Procedure

Method A: To a solution of 1 mmol of the sulfide in anhydrous methylene chloride (30 mL), 0.75 mmol of oxaziridine was added and the reaction was stirred at room temperature for 24 h. Then the solvent was evaporated, and the residue was purified by flash chromatography (SiO_2:methylene chloride–acetone 10:1.5) to yield pure mono sulfoxides **3a–e** and bis sulfoxides **4a**,**c–e**.

Asymmetric Oxidation of Sulfides 2a–e Using Kagan Conditions: General Procedure

Method B: Titanium tetraisopropoxide (3 mmol, 0.9 mL) and DET (6 mmol, 0.51 mL) were introduced with a syringe to a mixture of methylene chloride (10 mL) and water (1 mL). The resulting mixture was stirred for 20 min at room temperature. Then the corresponding sulfide (1 mmol) was added, and the mixture was cooled to −20°C. Finally TBHP (0.8 mmol, 2 M solution in toluene) was added. After 16 h at this temperature, water (10 mL) was added, and stirring was continued for additional 1 h. After that time, Al_2O_3(20 mg) was added, the mixture was filtered, and the residue was washed with methylene chloride. The organic layer was stirred with 5% sodium hydroxide and brine. After decantation, the organic phase was dried (magnesium sulfate), and the solvent was evaporated. Flash chromatography of the crude product (SiO_2, methylene chloride) yielded pure mono sulfoxides **3a–e** and bis sulfoxides **4a**,**c–e**.

3a: Yellow oil. Method A: $[\alpha]_D = -99$ (*c* 1.9, CH_2Cl_2); Method B: $[\alpha]_D = +148$ (*c* 1.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.67$ (s, CH_3), 2.92 (s, CH_3), 7.24 (d, $J = 5.5$ Hz, pyridine-H), 7.63 (t, $J = 7.8$ Hz, pyridine-H), 8.01–8.14 (m, pyridine-H), 8.55 (d, $J = 6.5$ Hz, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.1$ (CH_3), 41.3 (CH_3), 116.4, 119.0, 121.7, 122.3, 136.6, 138.7, 154.0, 156.0, 159.4, 165.4. HRMS (CI): Calcd for $C_{12}H_{12}ON_2S_2$, 264.03910; Found: 264.03909.

3b: Yellow oil. Method A: $[\alpha]_D = -127.6$ (*c* 2.4, CH_2Cl_2); Method B: $[\alpha]_D = +138$ (*c* 1.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J = 7.4$ Hz, CH_3), 1.44 (t, $J = 7.4$ Hz, CH_3), 2.99 (q, $J = 7.2$ Hz, CH_2), 3.23 (q, $J = 7.2$, CH_2), 7.1 (d, $J = 8.2$, pyridine-H), 7.5 (t, $J = 7.8$ Hz, pyridine-H), 7.94–8.06 (m, pyridine-H), 8.47 (d, $J = 1.6$ Hz, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 5.4$ (CH_3), 14.5 (CH_3), 24.4 (CH_2), 47.4 (CH_2), 116.5, 120.0, 121.4, 136.6, 138.4, 154.1, 156.0, 158.9, 163.4; HRMS (CI) Calcd for $C_{12}H_{12}ON_2S_2$, 292.07041, Found 292.06918.

3c: Yellow oil. Method A: $[\alpha]_D = -179$ (*c* 0.6, CH_2Cl_2); Method B: $[\alpha]_D = +148$ (*c* 1.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.05$ (d, $J = 6.7$ Hz, CH_3), 1.46 (d, $J = 7$ Hz, CH_3), 3.24 (sept, $J = 6.9$ Hz, CH), 4.12 (sept, $J = 6.8$ Hz, CH), 7.21 (t, $J = 10.3$ Hz, pyridine-H), 7.6 (t, $J = 7.7$ Hz, pyridine-H), 7.91–8.12 (m, pyridine-H), 8.39 (d, $J = 7.51$ Hz, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.7$ (CH_3), 16.9 (CH_3), 22.9 (CH_3), 23.2 (CH_3), 42.0 (CH), 52.9 (CH), 116.5, 119.8, 120.4, 123.2, 136.6, 138.2, 154.3, 155.9, 159.2, 163.2; CI-MS $(M+1)^+$321.

3d: White oil. Method A: $[\alpha]_D = +17$ (*c* 0.61, CH_2Cl_2); Method B: $[\alpha]_D = -43.7$ (*c* 0.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J = 7.1$ Hz, CH_3), 4.00 (AB, $J = 24.2$ Hz, CH_2), 4.16 (s, CH_2), 4.06–4.36 (m, CH_2), 7.28 (d, $J = 9.4$ Hz, pyridine-H), 7.64 (t, $J = 7.1$ Hz, pyridine-H), 7.99–8.11 (m, pyridine-H), 8.52 (d, $J = 7.3$ Hz, pyridine-H), ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.5$ (CH_3), 14.1 (CH_3), 32.6 (CH_2), 58.6 (CH_2), 61.6 (CH_2), 62.0 (ester carbon atom), 117.2, 120.1, 122.3, 122.7, 137.7, 138.9, 154.0, 155.8, 164.9, 169.5; CI-MS $(M+1)^+$409.

3e: White oil. Method A: $[\alpha]_D = -129$ (*c* 1.1, CH_2Cl_2); Method B: $[\alpha]_D = +19$ (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.29$ (AB, $J = 51.7$ Hz, CH_2), 4.58 (s, CH_2), 7.00–7.18 (m, phenyl-H), 7.20–7.28 (m, arom-H), 7.32–7.49 (m, phenyl-H), 7.60–7.97 (m, pyridine-H), 11.00 (d, $J = 7.5$ Hz, pyridine-H), 8.44 (d, $J = 7.3$ Hz, pyridine-H), ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 34.4$ (CH_2), 60.1 (CH_2), 117.0, 120.4, 121.7, 122.7, 127.1, 128.1, 128.3, 128.5, 128.7, 129.3, 130.3, 136.9, 137.9, 138.4, 154.2, 155.6, 158.5, 163.2; HRMS Calcd for $C_{24}H_{20}N_2OS_2$|416.10170, Found 416.10089.

4a: White solid. mp 134°C, Method A: $[\alpha]_D = -165$ (*c* 0.3, CH_2Cl_2); Method B: $[\alpha]_D = +389$ (*c* 0.33, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$):

$\delta = 2.93$ (s, CH_3), 8.04–8.18 (m, pyridine-H), 8.42–8.51 (m, pyridine-H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 41.3$ (CH_3), 119.8, 121.9, 139.1, 154.7, 165.4; HRMS Calcd for $C_{12}H_{12}O_2N_2S_2$ 280.03402, Found 280.03399.

4c: Yellow oil. Method A: $[\alpha]_D = -323$ (*c* 1.6, CH_2Cl_2); Method B: $[\alpha]_D = +394$ (*c* 1.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.05$ (d, $J = 6.7$ Hz, CH_3), 1.47 (d, $J = 7$ Hz, CH_3), 3.25 (sept, $J = 6.8$ Hz, CH), 7.97–8.09 (m, pyridine-H), 8.43 (d, $J = 7.2$ Hz, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.7$ (CH_3), 16.0 (CH_3), 52.9 (CH), 53.0 (CH), 121.1, 121.7, 138.5, 154.6, 163.6; HRMS Calcd for $C_{16}H_{20}O_2N_2S_2$|336.09727, Found 336.09694.

4d: White oil. Method A: $[\alpha]_D = +90.1$ (*c* 0.7, CH_2Cl_2); Method B: $[\alpha]_D = -62.6$ (*c* 0.77, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.1$ Hz, CH_3), 4.05 (AB, $J = 25.4$ Hz, CH_2), 4,12 (s, CH_2), 4.22 (q, $J = 6.9$ Hz, CH_2), 8.06–8.15 (m, pyridine-H), 8.42–8.54 (m, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 58.5 (CH_2), 61.7 (CH_2), 62.1 (CH_2), 63.3 (ester carbon atom), 120.9, 122.4, 139.2, 154.6, 163.6, 164.8; HRMS Calcd for $C_{18}H_{20}O_6N_2S_2$| 424.07628, Found 424.07560.

4e: White oil. Method A: $[\alpha]_D = -277$ (*c* 0.8, CH_2Cl_2); Method B: $[\alpha]_D = +37$ (*c* 0.77, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.14$–4.58 (m, CH_2), 6.99–7.09 (m, phenyl-H), 7.00–7.18 (m, phenyl-H), 7.23–7.28 (m, arom-H), 7.67–7.85 (m, pyridine-H), 7.90–7.99 (m, pyridine-H), 8.40–8.46 (m, pyridine-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 60.3$ (CH_2), 60.4 (CH_2), 121.0, 121.1, 122.0, 128.2, 128.3, 129.1, 129.3, 130.3, 138.7, 154.3, 155.6, 163.7; HRMS Calcd for $C_{24}H_{20}N_2O_2S_2$|432.09662, Found 432.09644.

Asymmetric Addition of Diethylzinc to Benzaldehyde: General Procedure

To a solution of **3a–e**, **4a**,**c–e** (2.5%–3% mol, see Table II) in anhydrous benzene, diethylzinc (3 mmol, 1.0 M solution in hexane) was added under argon, and the reaction mixture was stirred for 10 min at room temperature. The solution was cooled at 0°C, and benzaldehyde (1 mmol) was slowly added. After being stirred for 2 h at 0°C and for 3–6 days (see Table II) at room temperature, the reaction was quenched with 1 M aqueous HCl (20 mL). The mixture was extracted with Et_2O, and the combined organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford 1-phenyl-1-propanol **6** as a colorless liquid.

Allylation of Benzaldehyde with Allyl(trichloro)silane: General Procedure

To a stirred solution of **3a**,**c–e** and **4a**,**d–e** (5–10% mol; see Table III) in methylene chloride (2 mL) under nitrogen, benzaldehyde (0.4 mmol), diisopropyl-ethylamine (0.35 mL, 2 mmol), and benzyltriethylammonium bromide 99% (130 mg, 0.47 mmol) were added. The mixture was then cooled to -50°C, and allyl(trichloro)silane (0.35 mL, 2 mmol) was added dropwise. After 2 h of stirring at this temperature and additional 5–10 days at room temperature (see Table III), the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$(1 mL). The water layer was extracted three times with EtOAc. The combined organic phases were dried over $MgSO_4$, the solvent was evaporated, and the crude 1-phenyl-3-buten-1-ol (**7**) was purified by flash chromatography with petroleum ether:ethyl acetate 10:1. The enantiomeric excess of **7** was determined by HPLC on Chiralpac AS column.

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