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Chiral phosphine oxide aziridinyl phosphonate as a Lewis base catalyst for enantioselective allylsilane addition to aldehydes

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Dedicated to the memory of Professor Dr Tugmac Sayrac

ABSTRACT

A series of chiral Lewis bases, phosphine oxide ferrocenyl aziridinyl methanol **1**–**4**, phosphinyl aziridinyl phosphonates **5** and **6**, and phosphine oxide aziridinyl phosphonates **7** and **8** were screened for allylsilane additions to aldehydes. Among the Lewis bases, **8** was found to catalyze the reaction by forming the product in up to 94% yield and with 77% ee.

1. Introduction

Chiral Lewis base catalyzed asymmetric synthesis has gained much attention and become a popular strategy for the enantioselective synthesis of organic compounds. Silicon has found many applications in organocatalytic reactions.[1] Tetra-coordinated silicon compounds and chiral Lewis bases can form five- or six-coordinated hypervalent silicon species in situ and promote catalytic enantioselective reactions in good yields and enantioselectivities.[2] Phosphoramides,[3] formamides,[4] sulfoxides,[5] and pyridine *N*-oxides[6] have been used as Lewis bases with silicon for the enantioselective synthesis of organic compounds. Chiral Lewis bases with phosphine oxide bonds are highly nucleophilic due to the polarization of the P–O bond. As a result, when used with trichlorosilyl compounds, they are able to form hypervalent silicates as intermediates to provide high enantioselectivity.[7] One important use of these bases with silicon is the enantioselective allylsilane addition to aldehydes. This is an important carbon–carbon bond formation reaction which produces chiral homoallylic alcohols. Nakajima et al. reported the use of BINAPO as the Lewis base catalyst for the enantioselective addition of allyltrichlorosilanes to aldehydes.[8] Kocovsky et al. reported the bromoallyltrichlorosilane addition to aldehydes catalyzed by BINAPO and other phosphine dioxide Lewis bases.[9] Scettri et al. reported chiral imino- and amino-sulfoxides as activators of allyltrichlorosilane in the asymmetric allylation of aldehydes.[10] Ishimaru et al. used C_2-symmetrical chiral bisformamides for asymmetric allylation reactions of aromatic aldehydes with allyltrichlorosilane in the presence of potassium carbonate and potassium phosphate.[11] We have recently reported the use of phosphine oxide ferrocenyl aziridinyl methanols **1**–**4** as chiral ligands for the metal catalyzed enantioselective synthesis of organic compounds[12] and phosphine oxide aziridinyl phosphonates **7** and **8** as chiral Lewis bases for the Abramov-type phosphonylation of aldehydes.[13] Herein we report the results of these compounds **1**–**8** as chiral Lewis base catalysts for the enantioselective allylsilane addition to aldehydes.

2. Results and discussion

The first series of chiral Lewis bases **1**–**4** were synthesized via a Gabriel–Cromwell reaction starting from acryloyl ferrocene.[12a] The second series of chiral Lewis bases **5**–**8** were also synthesized by the same reaction starting from vinyl phosphonate or its α-tosylated derivative Figure 1.[13] After preparing the chiral Lewis bases, their performance was tested for the allylsilane addition reaction to aldehydes and the results are summarized in Table 1. As can be seen from these results, the first series of Lewis bases showed no enantioselectivity (entries 1–7). Therefore Lewis base screening studies were continued with the second series **5**–**8**. In this series, the results were not satisfactory for Lewis bases **5**–**7**; the products were isolated in low yields and with poor enantioselectivities (entries 8–15). Fortunately, Lewis base **8** showed a promising result in the first trial (entry 16) therefore further optimization was continued with this Lewis base. Repeating the reactions with this Lewis base at different temperatures, concentrations, solvents, and with different additives, the highest yield and ee obtained were 55% and 61%, respectively, (entries 17–27).

After obtaining the product in reasonable yield and enantioselectivity, the catalytic effect of Lewis base **8** on different aldehydes was studied, and the results are summarized in Table 2. The effect of the electron withdrawing nitro group was very small on the ee,

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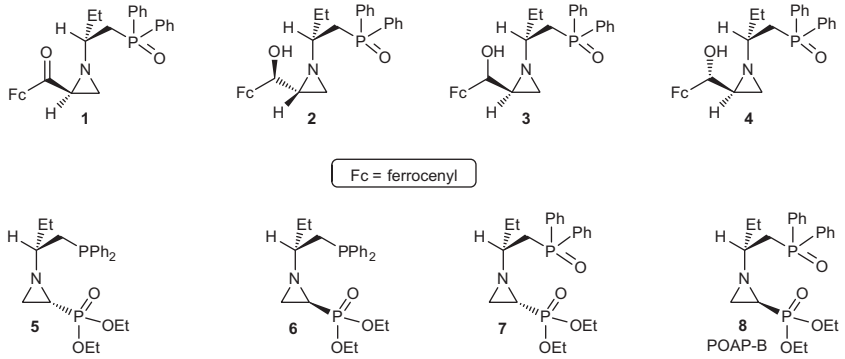
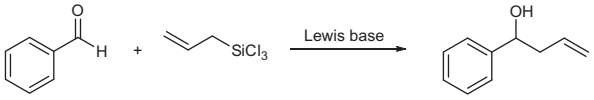


Figure 1. Structures of Lewis bases.

Table 1
Lewis base screening and optimization studies[a]



Entry	Lewis base	Concn (M)	Additive	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	ee[c] (%)	Confign.[d]
1	**1**	0.40	—	CH_3CN	0	48	nd	nd	
2	**2**	0.25	—	CH_3CN	0	48	nd	nd	
3	**3**	0.40	—	CH_3CN	0	48	nd	nd	
4	**4**	0.40	—	CH_3CN	0	24	83	*rac*	
5	**3**	0.40	Bu_4NI	CH_3CN	0	48	9	nd	
6	**1**	0.40	Bu_4NI	CH_3CN	0	48	70	*rac*	
7	**1**	0.40	DMF	DCM	0	24	nd	nd	
8	**5**	0.30	DIPEA	CH_3CN	0	24	34	17	(*S*)
9	**5**	0.30	DIPEA	DCM	0	24	34	12	(*S*)
10	**6**	0.30	DIPEA	CH_3CN	0	24	34	15	(*R*)
11	**6**	0.30	DIPEA	CH_3CN	−20	24	34	5	(*R*)
12	**6**	0.30	DIPEA	DCM	−20	24	34	5	(*R*)
13	**7**	0.40	DIPEA	CH_3CN	0	24	72	10	(*S*)
14	**7**	0.15	DIPEA	DCM	−78	24	25	10	(*R*)
15	**7**	0.15	DIPEA	DCM	Rt	24	42	10	(*R*)
16	**8**	0.40	DIPEA	CH_3CN	Rt	24	45	35	(*R*)
17	**8**	0.40	DIPEA	CH_3CN	−78	24	22	10	(*R*)
18	**8**	0.40	—	CH_3CN	Rt	24	78	33	(*R*)
19	**8**	0.40	—	Toluene	Rt	24	23	17	(*S*)
20	**8**	0.40	Bu_4NI	CH_3CN	Rt	24	25	7	(*R*)
21	**8**	0.50	Et_3N	CH_3CN	Rt	24	40	27	(*S*)
22	**8**	0.50	Et_3N	DCM	Rt	24	45	45	(*S*)
23	**8**	0.50	DABCO	DCM	Rt	24	45	*rac*	
24	**8**	0.50	TMEDA	DCM	Rt	48	nd	nd	
25	**8**	0.50	DIPEA	DCM	Rt	24	34	58	(*S*)
26[e]	**8**	0.50	DIPEA	DCM	Rt	24	56	61	(*S*)
27[e]	**8**	0.50	DIPEA	DCM	Rt	24	58	21	(*S*)

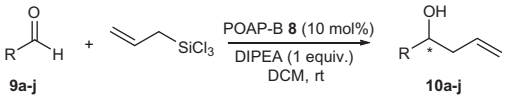
[a] Conditions: benzaldehyde (0.30 mmol), allyltrichlorosilane (0.36 mmol), Lewis base (0.03 mmol), and additive (0.30 mmol). Reaction was stirred at room temperature for 24 h.
[b] Isolated yields.
[c] Determined by chiral HPLC.
[d] The absolute configurations were assigned by comparison of the chiral HPLC data reported in the literature.[3d]
[e] DIPEA was used in 0.5 equiv.

but significantly changed the yield depending on the position on the aromatic ring (entries 2–4). While the electron donating methyl group at the *ortho*-position of the aldehyde formed the product in highest yield and with acceptable ee (entry 5), electron donors at the *para*-position of the aldehyde formed the products in acceptable yield but with low enantioselectivities (entries 7 and 8). The highest ee was obtained with *m*-bromobenzaldehyde (entry 6). For the naphthaldehydes, the yield and ee were good for 2-naphthaldehyde but the ee was relatively low for 1-naphthaldeyde (entries 9 and 10). This result may be attributed to the steric effects.

3. Conclusion

A series of chiral Lewis bases were screened for catalytic enantioselective allylsilane additions to aromatic aldehydes. Lewis bases with a phosphine oxide group and a ferrocenyl substituent on the aziridine ring **1**–**4** did not show catalytic activity for this reaction. Lewis bases **5** and **6** with a phosphinyl group and a phosphonate unit on their structure showed small catalytic activity. Lewis bases **7** and **8** with a phosphine oxide and phosphonate units in their structures showed acceptable catalytic activity. Aldehyde screening studies with the most active Lewis base **8**

Table 2
Aldehyde screening studies[a]



9a-j 10a-j

Entry	R	Substrate	Yield[b] (%)	ee[c] (%)	Confign.[d]
1	Ph	**9a**	56	61	(*S*)
2	*p*-$NO_2C_6H_4$	**9b**	60	60	(*S*)
3	*m*-$NO_2C_6H_4$	**9c**	21	57	(*S*)
4	*o*-$NO_2C_6H_4$	**9d**	73	61	(*S*)
5	*o*-MeC_6H_4	**9e**	94	61	(*S*)
6	*m*-BrC_6H_4	**9f**	73	77	(*S*)
7	*p*-$MeOC_6H_4$	**9g**	62	24	(*S*)
8	*p*-MeC_6H_4	**9h**	61	32	(*S*)
9	2-Naphthyl	**9i**	81	67	(*S*)
10	1-Naphthyl	**9j**	67	18	(*R*)

[a] Conditions: arylaldehyde (0.30 mmol), allyltrichlorosilane (0.36 mmol), **8** (0.03 mmol), $^{i}Pr_2NEt$ (0.30 mmol), and DCM (0.6 mL). Reaction was stirred at room temperature for 24 h.
[b] Isolated yields.
[c] Determined by chiral HPLC.
[d] The absolute configurations were assigned by comparison of the sign of the specific rotations with the ones reported in the literature. For compound **10d**, assignment was based on the chiral HPLC data.[5f]

formed homoallylic alcohols in reasonable yields and enantioselectivities. These results warrant further development of phosphine oxide aziridinyl phosphonates as organocatalysts for catalytic asymmetric transformations.

4. Experimental

4.1. General

All asymmetric reactions were performed under an inert atmosphere in dry glassware. DCM was dried and distilled from calcium hydride prior to use. Diisopropylethylamine was distilled from calcium hydride. Products were purified by flash column chromatography on Silica Gel 60 (Merck, 230–400 mesh ASTM). TLC analyses were performed on 250 μm Silica Gel 60 F254 plates. Enantiomeric excess (ee) was determined by chiral HPLC. IR spectra are reported in reciprocal centimeters (cm^{-1}). ^1H and ^{13}C NMR spectra were reported on a Brucker spectrospin Avance DPX-400 Ultra shield instrument at 400 MHz and 100 MHz respectively relative to TMS. A Rudolph Research Analytical Autopol III Polarimeter was used to measure optical rotations.

4.2. General procedure for asymmetric allyl trichlorosilane additions to aldehydes

Chiral Lewis base **8** (13 mg, 0.03 mmol), dry DCM (0.6 mL), benzaldehyde (30 μL, 0.30 mmol), $^{i}Pr_2NEt$ (52 μL, 0.30 mmol), and allyltrichlorosilane (51 μL, 0.36 mmol) were added respectively to a dried Schlenk tube under a nitrogen atmosphere. The resulting mixture was then stirred at room temperature for 24 h, after which the reaction mixture was hydrolyzed by adding saturated $NaHCO_3$ (5 mL), then extracted with EtOAc (3 × 5 mL). The combined organic phase was dried over $MgSO_4$. The concentrated crude product was purified by flash column chromatography using silica gel (hexane/acetone 2:1) to give homoallylic alcohol in 56% yield (25 mg, 0.17 mmol). Enantioselectivity was determined by chiral HPLC.

4.2.1. (*S*)-1-Phenyl-3-buten-1-ol 10a

R_f = 0.12, hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −17.1 (*c* 0.2, CH_2Cl_2) for 61% ee (*S*). Lit.[3d] $[\alpha]_D^{26}$ = +31.7 (*c* 3.5, benzene) for 61% ee (*R*); ^1H NMR δ 7.31–7.19 (m, 5H), 5.83–5.75 (m, 1H), 5.16–5.03 (m, 2H), 4.70–4.65 (m, 1H), 2.51–2.39 (m, 2H), 1.95 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR δ 41.4, 71.3, 116.1, 123.4, 125.1, 126.4, 132.1; HPLC: Chiralcel OD column, UV detection at 220 nm, eluent: hexane/2-propanol 95:5, flow 1.0 mL min^{-1}, t_R = 21.7 min (*R*, minor), 28.5 min (*S*, major).

4.2.2. (*S*)-1-(4-Nitrophenyl)-3-buten-1-ol 10b

R_f = 0.12 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −30.9 (*c* 3.3, CH_2Cl_2) for 60% ee (*S*). Lit.[3d] $[\alpha]_D^{27}$ = +31.7 (*c* 3.5, benzene) for 21% ee (*R*); ^1H NMR δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 5.91–5.63 (m, 1H), 5.27–5.12 (m, 2H), 4.87 (dd, *J* = 7.8, 4.7 Hz, 1H), 2.69–2.52 (m, 1H), 2.50–2.44 (m, 1H), 2.24 (br s, 1H); ^{13}C NMR δ 43.8, 72.2, 96.1, 119.9, 123.8, 126.7, 133.0, 151.1; HPLC: Chiralcel AS-H column, UV detection at 210 nm, eluent: hexane/2-propanol 98:2, flow 0.7 mL min^{-1}, t_R = 81.4 min (*R*, minor), 88.7 min (*S*, major).

4.2.3. (*S*)-1-(3-Nitrophenyl)-3-buten-1-ol 10c

R_f = 0.12 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −19.8 (*c* 0.4, CH_2Cl_2) for 57% ee (*S*). Lit.[6f] $[\alpha]_D^{25}$ = +47 (*c* 1.0, $CHCl_3$) for 72% ee (*R*); ^1H NMR δ 8.15 (s, 1H), 8.05 (m, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 5.72 (m, 1H), 5.12 (m, 2H), 4.77 (dd, *J* = 8.1, 4.6 1H), 2.50 (m, 1H), 2.40 (m, 1H), 2.17 (br s, 1H); ^{13}C NMR δ 42.9, 71.1, 118.7, 119.9, 121.5, 128.3, 130.9, 132.2, 144.9; HPLC: Chiralcel OD column, UV detection at 220 nm, eluent: hexane/2-propanol 150:1, flow 1 mL min^{-1}, t_R = 62.3 min (*R*, minor), 69.4 min (*S*, major).

4.2.4. (*S*)-1-(2-Nitrophenyl)-3-buten-1-ol 10d

R_f = 0.21 hexane/ethyl acetate 10:1; ^1H NMR δ 8.15 (s, 1H), 8.05 (m, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 5.72 (m, 1H), 5.14–5.09 (m, 2H), 4.77 (dd, *J* = 8.1, 4.6 Hz, 1H), 2.54–2.47 (m, 1H), 2.43–2.36 (m, 1H), 2.17 (br s, 1H); ^{13}C NMR δ 42.9, 68.5, 118.6, 124.4, 128.2, 133.3, 134.0, 139.3, 147.8; HPLC: Chiralcel OD column, UV detection at 210 nm, eluent: hexane/2-propanol 99:1, flow 0.5 mL min^{-1}, t_R = 50.2 min (*R*, minor), 66.2 min (*S* major) for 61% ee. Lit.[5f] HPLC: Chiralcel OD column, eluent: hexane/2-propanol 99:1, flow 0.5 mL min^{-1}, t_R = 72.5 min (*R* minor), 77.7 min (*S* major).

4.2.5. (*S*)-1-(2-Methylphenyl)-3-buten-1-ol 10e

R_f = 0.32 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −44.3 (*c* 1.2, CH_2Cl_2) for 61% ee (*S*). Lit.[14a] $[\alpha]_D^{24}$ = +68.8 (*c* 1.1, benzene) for 93% ee (*R*); ^1H NMR δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.21–7.00 (m, 3H), 5.86–5.74 (m, 1H), 5.11 (dd, *J* = 20.7, 5.2 Hz, 2H), 4.90 (dd, *J* = 7.6, 3.1 Hz, 1H), 2.50–2.30 (m, 2H), 2.26 (s, 3H), 1.85 (br s, 1H); ^{13}C NMR δ 19.1, 42.6, 69.8, 125.1, 126.2, 127.3, 130.4, 134.4, 134.8; HPLC: Chiralcel AD-H column, UV detection at 210 nm, eluent: hexane/2-propanol 90:10, flow 1 mL min^{-1}, t_R = 7.1 min (*R*, minor), 8.1 min (*S* major).

4.2.6. (*S*)-1-(3-Bromophenyl)-3-buten-1-ol 10f

R_f = 0.30 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −41.6 (*c* 1.3, CH_2Cl_2) for 77% ee (*S*). Lit.[14b] $[\alpha]_D^{20}$ = −39.5 (*c* 0.6, $CHCl_3$) for 90% ee (*S*); ^1H NMR δ 7.53 (s, 1H), 7.42–7.39 (m, 1H), 7.27–7.22 (m, 2H), 5.82–5.78 (m, 1H), 5.21–5.17 (m, 2H), 4.72 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.52–2.48 (m, 2H), 2.17 (br s, 1H); ^{13}C NMR δ 43.8, 72.5, 96.1, 119.0, 122.7, 124.4, 128.9, 130.6, 133.9, 146.1; HPLC: Chiralcel OD column, UV detection at 210 nm, eluent: hexane/2-propanol 150:1, flow 1 mL min^{-1}, t_R = 35.4 min (*S*, major), 43.2 min (*R* minor).

4.2.7. (*S*)-1-(4-Methoxyylphenyl)-3-buten-1-ol 10g

R_f = 0.18 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −6.8 (*c* 1.1, CH_2Cl_2) for 24% ee (*S*). Lit.[3d] $[\alpha]_D^{27}$ = +20.0 (*c* 4.0, benzene) for 21% ee (*R*); ^1H NMR δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.82–

5.61 (m, 1H), 5.15–4.98 (m, 2H), 4.61 (t, J = 6.5 Hz, 1H), 3.73 (s, 3H), 2.42 (t, J = 6.9 Hz, 2H), 1.91 (br s, 1H); ^{13}C NMR δ 43.8, 55.3, 73.0, 96.1, 113.8, 118.2, 127.1, 134.6; HPLC: Chiralcel OD column, UV detection at 210 nm, eluent: hexane/2-propanol 98:2, flow 1 mL min^{-1}, t_R = 19.9 min (R, minor), 24.5 min (S major).

4.2.8. (*S*)-1-(4-Methylphenyl)-3-buten-1-ol 10h

R_f = 0.27 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = +5.0 (c 0.3, CH_2Cl_2) for 32% ee (S). Lit.[5e] $[\alpha]_D^{25}$ = −31.5 (c 1.0, $CHCl_3$) for 79% ee (S); ^{1}H NMR δ 7.17 (d, J = 6.8 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 5.80–5.65 (m, 1H), 5.15–5.02 (m, 2H), 4.68–4.60 (m, 1H), 2.50–2.39 (m, 2H), 2.25 (s, 3H), 1.90 (br s, 1H); ^{13}C NMR δ 21.2, 43.6, 73.2, 118.1, 125.7, 129.2, 134.5, 137.3, 140.3; HPLC: Chiralcel AD column, UV detection at 210 nm, eluent: hexane/2-propanol 98:2, flow 1 mL min^{-1}, t_R = 15.6 min (R, minor), 17.3 min (S major).

4.2.9. (*S*)-1-(2-Naphthyl)-3-buten-1-ol 10i

R_f = 0.33 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = −23.6 (c 1.03, CH_2Cl_2) for 67% ee (R). Lit.[6f] $[\alpha]_D^{25}$ = +58.0 (c 1.0, $CHCl_3$) for 83% ee (R); ^{1}H NMR δ 7.73 (m, 4H), 7.45–7.32 (m, 3H), 5.76–5.72 (m, 1H), 5.16–5.00 (m, 2H), 4.80 (dd, J = 7.1, 5.7 Hz, 1H), 2.62–2.41 (m, 2H), 2.20 (br s, 1H); ^{13}C NMR δ 42.7, 72.4, 117.5, 123.0, 123.5, 124.8, 125.1, 126.6, 126.9, 127.2, 131.9, 132.2, 133.3, 140.2; HPLC: Chiralcel OD-H column, UV detection at 210 nm, eluent: hexane/2-propanol 95:5, flow 0.7 mL min^{-1}, t_R = 35.5 min (R, major), 38.9 min (S minor).

4.2.10. (*R*)-1-(1-Naphthyl)-3-buten-1-ol 10j

R_f = 0.27 hexane/ethyl acetate 10:1; $[\alpha]_D^{25}$ = +7.1 (c 1.1, CH_2Cl_2) for 18% ee (R); Lit.[6f] $[\alpha]_D^{27}$ = +84 (c 1.0, $CHCl_3$) for 84% ee (R); ^{1}H NMR δ 8.08 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 6.9 Hz, 1H), 7.55–7.42 (m, 3H), 5.93 (m, 1H), 5.53 (d, J = 4.7 Hz, 1H), 5.28–5.10 (m, 2H), 2.77 (m, 1H), 2.68–2.53 (m, 1H), 2.17 (br s, 1H); ^{13}C NMR δ 42.9, 70.0, 118.4, 122.9, 123.0, 125.4, 125.5, 126.1, 128.0, 129.0, 133.8, 134.8, 139.4; HPLC: Chiralcel OD-H column, UV detection at 210 nm, eluent: hexane/2-propanol 95:5, flow 0.5 mL min^{-1}, t_R = 33.9 min (S minor), 37.5 min (R, major).

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