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Asymmetric Allylation with Chiral Formamide Catalysts

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Abstract: The successful example of chiral formamides that function as asymmetric catalysts is described. (*S,S*)-*N,N*-Bis(α-methylbenzyl)formamide mediates the enantioselective addition of allyl- and crotyltrichlorosilanes to aliphatic aldehydes with the assistance of hexamethylphosphoramide (HMPA) to afford the corresponding homoallylic alcohols in up to 98% enantiomeric excess.

Keywords: Aldehydes; Allylation; Asymmetric synthesis; Catalysts.

INTRODUCTION

Denmark *et al.* and we have independently developed the asymmetric allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes mediated by chiral phosphoramides.[1-3] Chiral Lewis base catalysts including these phosphoramides have the advantage of stereoselectively producing the *syn* and *anti* homoallylic alcohols, respectively, from (*Z*)- and (*E*)-crotyltrichlorosilanes,[4,5] while chiral Lewis acids provide the optically active *syn* homoallylic alcohols from either stereoisomer of crotyltrialkylsilanes and -stannanes.[6-9] However, the chiral Lewis bases are useless for aliphatic aldehydes.

N,N-Dimethylformamide (DMF) was found to be an effective Lewis base that catalyzes several useful reactions such as allylation[10-14] and hydrosilylation[15] of carbonyl compounds.[16] We became interested in using chiral formamides for developing a new class of asymmetric catalyses and began our studies with the design and preparation of such catalysts and their application to asymmetric allylation. We recently reported the (*S,S*)-*N,N*-bis(α-methylbenzyl)formamide (**1**) efficiency for the reaction of aliphatic aldehydes[17] and the details are described in this paper.

RESULTS AND DISCUSSION

Allylation in the presence of stoichiometric amounts of chiral formamides. Several C_2-symmetric formamides **1-6** were prepared by formylation of the corresponding chiral amines with acetic formic anhydride.[18-20] Their capability as asymmetric catalysts was then assessed for the allylation of cyclohexanecarboxaldehyde (**7**) with allyltrichlorosilane (**8**), a model substrate. The reaction was carried out using a stoichiometric amount of the chiral formamides and ten equivalents of **8** in dichloromethane at -78°C for 96 h. After the obtained trichlorosilyl ether was hydrolyzed with aqueous $NaHCO_3$, the corresponding homoallylic alcohol **9** was

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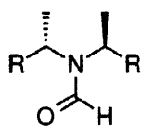
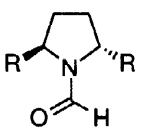
isolated by flash chromatography and its optical yield was determined by HPLC analysis of the corresponding 3,5-dinitrobenzoate using a chiral column. These results are summarized in Table 1. The formamide **1** gave the optically active alcohol **9** with 73% ee in 70 % yield (entry 1). The absolute configuration of the major enantiomer was determined to be *R* by comparison of the $[\alpha]_D$ value with the reported data.[21] The attachment of methyl groups at the *p*-position of the benzene rings in **1** slightly decreased the enantioselectivity (entry 2), while the introduction of trifluoromethyl groups into the same positions dramatically suppressed the optical yields (entry 3). The 1-naphthyl and cyclohexyl analogs, **4** and **5**, afforded the (*S*)-riched homoallylic alcohol **9**, though the optical yields were modest (entries 4 and 5). The *N*-formylpyrrolidine analog **6** was not suitable for the allylation (entry 6).

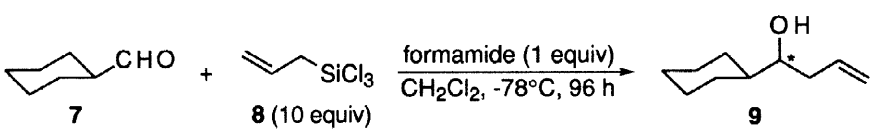


1: R = Ph
2: R = 4-$CH_3C_6H_4$
3: R = 4-$CF_3C_6H_4$
4: R = 1-naphthyl
5: R = cyclohexyl



6: R = Ph

Table 1. Asymmetric Allylation of Cyclohexanecarboxaldehyde (**7**) with Allyltrichlorosilane (**8**) in the Presence of Stoichiometric Amounts of Chiral Formamides **1-6**



7 **8** (10 equiv) **9**

Entry	Formamide	Product **9**	Yield (%)[a]	Ee (%)[b]	
1	**1**		70	73	(*R*)
2	**2**		73	63	(*R*)
3	**3**		40	5	(*R*)
4	**4**		12	35	(*S*)
5	**5**		18	15	(*S*)
6	**6**		30	13	(*R*)

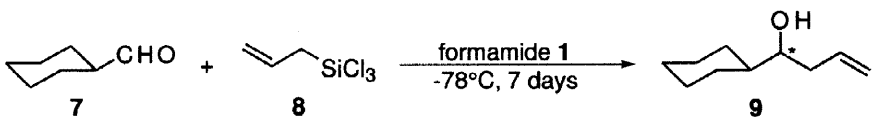
a) Isolated yield; b) HPLC analysis of the corresponding 3,5-dinitrobenzoate using a Daicel Chiralcel OD-H column.

Allylation of aldehyde 7 using a substoichiometric amount of formamide 1. We next examined the allylation of aldehyde **7** in the presence of a catalytic amount of formamide **1** (Table 2). Contrary to our expectation, the reaction was not catalytic (entries 1-4). Furthermore, a decrease in the amount of **1** dramatically suppressed the enantioselectivity (entries 2-4), and it is interesting that the use of 10 and 25 mol% reversed the enantioface selection to afford the (*S*)-rich alcohol **9** with 30 and 32% enantiomeric excesses, respectively (entries 3 and 4). To overcome these drawbacks, we began by using additives which may accelerate the catalytic cycle and envisioned that HMPA would dissociate formamide **1** from the reaction product, the trichlorosilyl ether of **9**, to facilitate the catalyst regeneration and enhance the reaction rate. The allylation of aliphatic aldehydes with allylsilane **8** is scarcely catalyzed by HMPA which effectively mediates the reaction of benzaldehyde.[1] The addition of 100 mol% HMPA was found to remarkably improve the chemical yields.

Very surprisingly, excellent optical yields were obtained at all concentrations of catalyst **1** (entries 5-7). For example, the reaction with 50 mol% formamide **1**, 100 mol% HMPA and 10 equivalents of allylsilane **8** was carried out in dichloromethane at -78°C for 7 days to provide the (*R*)-rich alcohol **9** in 79% yield and with 94% ee (entry 6).

Entries 7-10 show the effects of reaction media during the allylation of **7** with 25 mol% formamide **1**, 100 mol% HMPA and 10 equivalents of allylsilane **8** at -78°C for 7 days. Dichloromethane, nitroethane, propionitrile and acetone gave almost similar chemical yields and excellent optical yields. The highest enantioselectivity (98% ee) was obtained with acetone (entry 10). The reactions in other solvents such as tetrahydrofuran (THF), diethyl ether, ethyl acetate and toluene were very sluggish. After extensive optimization, the best ratio of **1** to HMPA and the optimized amount of **8** were found to be 1:5 and 1.5 equivalents to the aldehyde, respectively, for the chemical and optical yields. The use of 20 mol% formamide **1**, 100 mol% HMPA and 1.5 equivalents of allylsilane **8** at -78°C for 14 days provided the (*R*)-rich alcohol **9** in 80% yield and with 98% ee (entry 11). However, elevating the reaction temperature to -20°C dramatically decreased the enantioselectivity (entry 13). The chiral catalyst **1** can be recovered without racemization in >95% yield by column chromatography.

Table 2. Asymmetric Allylation of Aldehyde **7** with Allylsilane **8** in the Presence of Substoichiometric Amounts of Chiral Formamide **1**



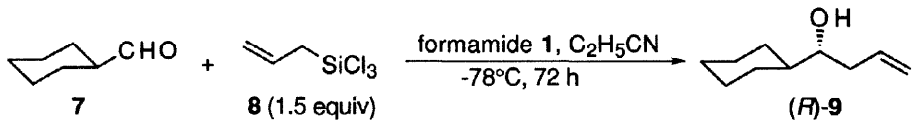
Entry	Formamide **1** (mol%)	HMPA (mol%)	Allylsilane **8** (equiv)	Solvent	Yield[a] (%)	Ee[b] (%)	
1	100	0	10	CH_2Cl_2	81	68	(*R*)
2	50	0	10	CH_2Cl_2	45	44	(*R*)
3	25	0	10	CH_2Cl_2	20	30	(*S*)
4	10	0	10	CH_2Cl_2	12	32	(*S*)
5	100	100	10	CH_2Cl_2	89	96	(*R*)
6	50	100	10	CH_2Cl_2	79	94	(*R*)
7	25	100	10	CH_2Cl_2	33	94	(*R*)
8	25	100	10	$C_2H_5NO_2$	27	92	(*R*)
9	25	100	10	C_2H_5CN	30	97	(*R*)
10	25	100	10	Acetone	27	98	(*R*)
11[c]	20	100	1.5	C_2H_5CN	80	98	(*R*)
12	20	0	1.5	C_2H_5CN	50	71	(*R*)
13[d]	20	100	1.5	C_2H_5CN	62	4	(*R*)

a) Isolated yield; b) HPLC analysis of the corresponding 3,5-dinitrobenzoate using a Daicel Chiralcel OD-H column; c) 14 days; d) The reaction was carried out at -20°C for 2 days.

Influences of several additives on the chemical and optical yields. Encouraged by the effect of HMPA, we undertook the asymmetric allylation using various organic bases to enhance the chemical and optical yields. The reaction was carried out using aldehyde **7**, allylsilane **8**, formamide **1** and an additive in propionitrile at -78°C. DMF,[22] dimethyl sulfoxide (DMSO), trimethylphosphate, triphenylphosphate and THF gave lower chemical and optical yields compared to HMPA and could not improve the enantioselectivity given in the

absence of additives (entries 1-6 and 9). Two amine bases, triethylamine and Hünig's base, provided excellent optical yields (entries 7 and 8). However, the former amine made the reaction very sluggish. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) and *N*-methyl-2-pyrrolidinone (NMP) significantly suppressed the reaction.

Table 3. Effects of Additives on the Chemical and Optical Yields in the Allylation of Aldehyde **7** with Allylsilane **8** Catalyzed by Chiral Formamide **1**



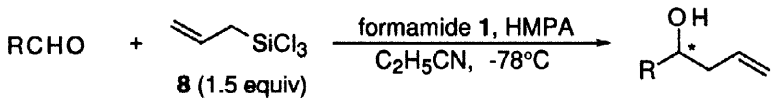
7 **8** (1.5 equiv) (*R*)-**9**

Entry	Additive (mol%)	Formamide **1** (mol%)	Yield (%)[a]	Ee (%)[b]
1	HMPA (200)	50	52	97
2	DMF (200)	50	27	63
3	DMSO (200)	50	26	70
4	$(MeO)_3PO$ (200)	50	38	71
5	$(PhO)_3PO$ (200)	50	28	59
6	THF (200)	50	40	69
7[c]	Et_3N (100)	20	63	98
8[d]	*i*-Pr_2NEt (100)	20	65	92
9[d]	none	20	50	71

a) Isolated yield; b) HPLC analysis of the corresponding 3,5-dinitrobenzoate using a Daicel Chiralcel OD-H column; c) 14 days; d) 7 days.

Asymmetric allylations of various aldehydes catalyzed by formamide 1. We next examined the utility of formamide **1** as an asymmetric catalyst for the allylation of various aldehydes. The reaction was carried out using five equivalents of HMPA to **1** in propionitrile or acetone at -78°C. These results are summarized in Table 4. Cyclopentanecarboxaldehyde (**10**) reacted with allylsilane **8** in the presence of 20 mol% formamide **1** and 100 mol% HMPA in propionitrile at -78°C for 14 days to afford the corresponding homoallylic alcohol **11** with 91% ee in 72% yield (entry 1). The three-week reaction of hydrocinnamaldehyde (**12**) in acetone gave the homoallylic alcohol **13** with 95% ee in 84% yield, and the absolute configuration of the major enantiomer was determined to be *S* by comparison of the $[\alpha]_D$ value with previously reported data (entry 2).[23] Branched-chain aldehydes, 2-ethylbutanal (**14**) and 2,2-dimethylpropanal (**16**), provided the corresponding alcohols **15** and **17** with 93% and 98% enantiomeric excesses, respectively, (entries 3 and 4), while a straight-chain aldehyde, *n*-heptanal (**18**), gave relatively low enantioselectivity (entry 5). The straight-chain aldehydes bearing an unsaturated bond, 4-pentenal (**20**) and 4-pentynal (**22**), afforded higher optical yields compared to the aldehyde **18** (entries 6 and 7). Acetone is more effective than propionitrile for the enantioselectivity with straight-chain substrates although the reaction rate in acetone is rather low compared with that in propionitrile. An α,β-unsaturated aldehyde, (*E*)-2-octenal (**24**), showed low enantioselectivity (entry 8). A typical aromatic aldehyde, benzaldehyde (**26**), gave the corresponding homoallylic alcohol **27** in good chemical yield but a very low enantiomeric excess (entry 9). This result may be ascribed to the allylation of the aldehyde catalyzed by HMPA itself or the mismatch between formamide **1** and the aldehyde.

Table 4. Catalytic Enantioselective Allylations of Various Aldehydes Mediated by Formamide **1**

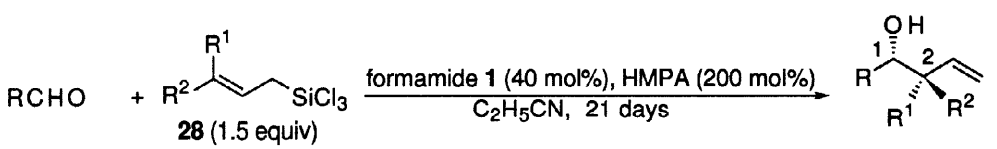


Entry	R	Formamide **1** (mol%)	HMPA (mol%)	Time (d)	Yield[a] (%)	Ee[b] (%)	
1	*c*-C_5H_9 (**10**)	20	100	14	72	91	(**11**)
2	$PhCH_2CH_2$ (**12**)[c]	20	100	21	84	95 (*S*)	(**13**)
3	$(C_2H_5)_2CH$ (**14**)	20	100	21	74	93	(**15**)
4	$(CH_3)_3C$ (**16**)	40	200	28	61	98	(**17**)
5	$CH_3(CH_2)_5$ (**18**)[c]	40	200	28	53	68	(**19**)
6	$CH_2{=}CHCH_2CH_2$ (**20**)[c,d]	20	100	21	56[e]	86	(**21**)
7	$CH{\equiv}CCH_2CH_2$ (**22**)[c]	40	200	21	51[e]	88	(**23**)
8	(*E*)-$CH_3(CH_2)_4CH{=}CH$ (**24**)	40	200	7	91	22	(**25**)
9	Ph (**26**)	20	100	7	94	8[f] (*R*)	(**27**)

a) Isolated yield; b) HPLC analysis of the corresponding 3,5-dinitrobenzoate using a Daicel Chiralcel OD-H column; c) Carried out in acetone; d) Ten equivalents of **8** was used; e) Because homoallylic alcohols are volatile, values reported are those for the corresponding 3,5-dinitrobenzoates; f) Determined by HPLC using a Daicel Chiralcel OD-H column.

Asymmetric crotylations catalyzed by formamide 1. Finally, the crotylation of aldehydes was also examined using 1.5 equivalents of (*E*)- or (*Z*)-crotyltrichlorosilane **28** in the presence of the catalyst **1** (40 mol%) and HMPA (200 mol%). As shown in Table 5, cyclohexanecarboxaldehyde (**7**) and hydrocinnamaldehyde (**12**) highly diastereo- and enantioselectively reacted with (*E*)-**28** in propionitrile at -78°C for 3 weeks to provide the corresponding optically active *anti* alcohols **29** and **30** with 98% and 94% enantiomeric excesses, respectively. In both cases, an extremely high *anti* stereoselectivity (*anti*/*syn* = >99/1) was obtained (entries 1 and 2). The major enantiomer of the *anti*-alcohol **29** was found to have the (1*S*,2*R*)-configuration by comparison to literature values.[24]

Table 5. Asymmetric Crotylations Catalyzed by Formamide **1**



(*E*)-**28**: R^1 = H, R^2 = Me (*E*/*Z* = 97/3)
(*Z*)-**28**: R^1 = Me, R^2 = H (*E*/*Z* = 1/99)

anti: R^1 = H, R^2 = Me
syn: R^1 = Me, R^2 = H

Entry	R	Crotylsilane	Temp. (°C)	Yield[a] (%)	*anti*/*syn*[b]	Ee[c] (%)	
1	*c*-C_6H_{11} (**7**)	(*E*)-**28**	-78	92	>99/1	98 (*anti*)	(**29**)
2	$PhCH_2CH_2$ (**12**)	(*E*)-**28**	-78	97	>99/1	94 (*anti*)	(**30**)
3	*c*-C_6H_{11} (**7**)	(*Z*)-**28**	-78	19	60/40	98 (*anti*)	(**29**)
4	*c*-C_6H_{11} (**7**)	(*Z*)-**28**	-20	34	5/95	3 (*syn*)	(**29**)

a) Isolated yield; b) Determined by GC analysis; c) HPLC analysis of the corresponding 3,5-dinitrobenzoate using a Daicel Chiralcel OD-H column.

However, the reaction of aldehyde **7** with (*Z*)-**28** at -78°C was extremely sluggish and the homoallylic alcohol **29** was obtained in only 19% yield after 21 days (entry 3). Furthermore, the reaction was not diastereoselective and the *anti*/*syn* ratio was 60:40, although the obtained *anti*-**29** showed 98% ee [(1*S*,2*R*)-**29**]. Elevating the reaction temperature to -20°C provided the highly *syn*-rich alcohol **29** in 34% yield (entry 4). However, the enantiomeric excess of the *syn*-isomer (*syn*-**29**) was only 3%. These unsatisfactory results from the (*Z*)-silane **28** could be caused by the mismatch between the catalyst **1** and (*Z*)-**28**.

Mechanism. An asymmetric amplifying phenomenon was observed during allylation catalyzed by formamide **1**.[25-27] The reaction of aldehyde **7** with 1.5 equivalents of allylsilane **8** was carried out using 40 mol% of the catalyst in 20-100% ee and 200 mol% of HMPA in propionitrile at -78°C for 7 days. When (-)-**1** of 40% ee was used, (*R*)-**9** was produced in 70% ee and 84% yield. The mediation by (-)-**1** of 80% ee gave (*R*)-**9** with 92% ee (89% yield). This enantiomeric excess is close to the value of 96% obtained using enantiomerically pure formamide **1**. The nonlinear effect is clear in Figure 1.

The reason why HMPA enhances not only the chemical yield but also the enantioselectivity remains unclear. However, the stereochemical outcome of the crotylation with (*E*)-**28** has been shown to consist of a common cyclic chair-like transition state.[10,28-31] We propose a possible transition structure **31** involving a hexavalent silicate which coordinates with the oxygen atoms of the aldehyde, the catalyst **1** and HMPA (Figure 2). The above-mentioned poor results from (*Z*)-**28** can also explained by assessing the steric repulsion between the methyl group (R^1) and the HMPA.

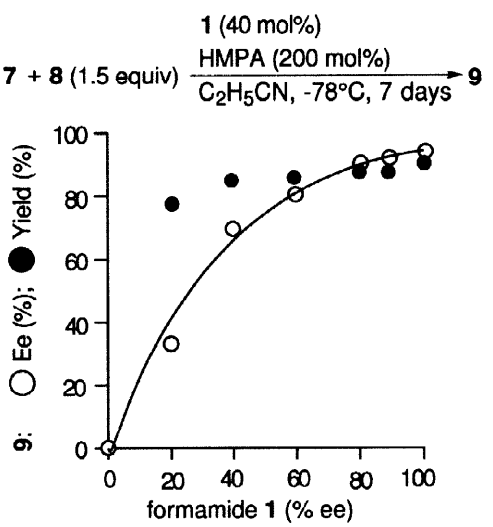
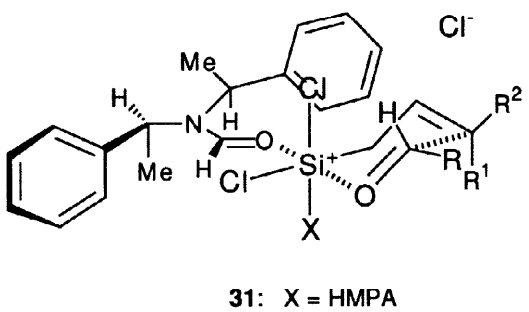


Fig. 1. Nonlinear effect in the allylation catalyzed by formamide **1**



31: X = HMPA

Fig. 2. Cyclic chair-like transition structure

CONCLUSION

We have succeeded in developing (*S*,*S*)-*N*,*N*-bis(α-methylbenzyl)formamide (**1**) as an efficient Lewis base catalyst for the enantioselective addition of allylic trichlorosilanes to aliphatic aldehydes, wherein the use of HMPA as an additive has proven to increase the enantioselectivity and accelerate the catalytic cycle.

Studies on the mechanism as well as the design of new chiral formamides for enhancing the chemical and optical yields are presently in progress.

EXPERIMENTAL

General. All reactions were carried out under an argon atmosphere with magnetic stirring in oven-dried glassware. Dichloromethane and propionitrile were distilled from CaH_2 immediately before use. Acetone was distilled from K_2CO_3. Other solvents and reagents were used as supplied or purified. Anhydrous $MgSO_4$ was used as the drying agent. TLC was carried out with pre-coated Kieselgel $60F_{254}$ plates (Merck). Silica gel 60 (Merck, 230-400 mesh) was used for column chromatography. GLC analyses were carried out on a Shimadzu GC-17A instrument using a J&W Scientific (30-m x 0.25-mm) DB-1 capillary column whose film thickness was 0.25 μm. Liquid chromatographic analyses were performed on a Shimadzu LC-10A at 254 nm using a Daicel Chiralcel OD-H column. Optical rotations were measured at 589 nm using a 1.0-dm cell with a total volume of 1 mL on a JASCO DIP-370 polarimeter. Melting points were measured on a Yanaco MP-500D micro-melting point apparatus and are uncorrected. Infrared spectra were taken either neat or as KBr pellets on a Perkin-Elmer 1600 FT-IR. Absorption was expressed in reciprocal centimeters (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz, respectively, on a Varian Gemini-200 instrument. ^1H NMR signals were expressed in parts per million (ppm) downfield from TMS as the internal standard (δ). ^{13}C NMR spectra were given with $CHCl_3$ (77.0 ppm) as the internal standard. Coupling constants are in hertz. $CDCl_3$ served as the solvent for the ^1H and ^{13}C NMRs. Low- and high-resolution mass spectral analyses were performed at 70 eV electron-impact (EI) using a Kratos CONCEPT-1H double-focusing magnetic sector spectrometer. Elemental analyses were carried out at the Toray Research Center, Inc., Tokyo.

Materials. (*S,S*)-Bis(α-methylbenzyl)amine was purchased from AZmax Co. Ltd., Chiba, Japan. Acetic formic anhydride was prepared according to reported procedures.[20] Allyltrichlorosilane (**8**) was purchased from Aldrich Chemical Company, Inc. and distilled before use. (*E*)- and (*Z*)-Crotyltrichlorosilanes (**28**) were prepared according to the literature.[3,28,32-34]

Preparation of (S,S)-N,N-bis(α-methylbenzyl)formamide (1). To a solution of (*S,S*)-bis(α-methylbenzyl)amine (5 g, 22.2 mmol) in dichloromethane (50 mL) was added dropwise acetic formic anhydride (96% purity, 5.1 g, 55.6 mmol) at room temperature. After stirring for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous phase extracted with dichloromethane (2 x 50 mL). The combined extracts were washed with brine and dried. After evaporation of the solvent, the residue was purified by flash chromatography (SiO_2, EtOAc:*n*-hexane 1:3) and recrystallized from Et_2O-*n*-hexane to give **1** (5.5 g, 98% yield) as colorless needles: m.p. 80.2-81.8°C; $[\alpha]_D^{25}$ -214.1 (*c* 1.02, $CHCl_3$); IR (KBr): 2976, 1645, 1248, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.67 (d, *J* = 7.2 Hz, 3H), 1.71 (d, *J* = 7.2 Hz, 3H), 4.50 (q, *J* = 7.2 Hz, 1H), 5.69 (q, *J* = 7.2 Hz, 1H), 6.78-7.30 (m, 10H), 8.33 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 17.1, 22.4, 50.7, 52.9, 126.7, 127.4, 127.7, 128.1, 128.3, 139.8, 141.0, 162.6; MS: *m/z* 253 [M^+], 148, 120, 105; Anal. Calcd for $C_{17}H_{19}NO$: C, 80.6; H, 7.6; N, 5.5. Found: C, 80.6; H, 7.5; N, 5.5.

(S,S)-N,N-Bis(α,4-dimethylbenzyl)formamide (2). Formamide **2** was obtained using the same procedure as **1**: colorless needles; m.p. 51.3-52.0°C (Et_2O-*n*-hexane); $[\alpha]_D^{24}$ -246.8 (*c* 1.03, $CHCl_3$); IR (KBr): 2976, 1661, 1410, 1157, 821 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.64 (d, *J* = 7.2 Hz, 3H), 1.67 (d, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 2.31 (s, 3H), 4.44 (q, *J* = 7.2 Hz, 1H), 5.63 (q, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 17.1, 20.8, 21.0, 22.3, 50.5, 52.5, 126.8, 128.5, 129.1, 137.0, 137.2, 137.4, 138.2, 162.8; MS: *m/z* 281 [M^+], 162, 134, 119, 91; HRMS Calcd for $C_{19}H_{23}NO$ [M^+]: 281.1780. Found: 281.1788.

(S,S)-N,N-Bis[α-methyl-4-(trifluoromethyl)benzyl]formamide (3). Formamide **3** was obtained using the same procedure as **1**: a colorless oil; $[\alpha]_D^{24}$ +8.2 (*c* 0.70, $CHCl_3$); IR (neat): 2982, 1662, 1417, 1124, 848 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.71 (d, *J* = 7.2 Hz, 3H), 1.74 (d, *J* = 7.2 Hz, 3H), 4.54 (q, *J* = 7.2 Hz, 1H), 5.60 (q, *J* = 7.2 Hz, 1H), 6.90-7.43 (m, 8H), 8.47 (s, 1H); MS: *m/z* 389 [M^+], 216, 188, 173, 145; HRMS Calcd for $C_{19}H_{17}F_6NO$ [M^+]: 389.1214. Found: 389.1221.

(S,S)-N,N-Bis[1-(1-naphthyl)ethyl]formamide (4). Formamide **4** was obtained using the same procedure as **1**: colorless needles; m.p. 149.6-151.3°C (Et_2O); $[\alpha]_D^{24}$ +213.8 (*c* 1.10, $CHCl_3$); IR (KBr): 2979, 1646, 1271, 774 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.70 (d, *J* = 7.0 Hz, 3H), 1.79 (d, *J* = 7.0 Hz, 3H), 5.23 (q, *J* = 7.0 Hz, 1H), 6.65 (q, *J* = 7.0 Hz, 1H), 6.70-8.05 (m, 14H), 8.70 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 17.4, 23.4, 47.1, 49.7, 121.9, 123.1, 123.8, 124.3, 124.4, 125.0, 125.1, 125.5, 125.7, 126.4, 127.3, 128.3, 128.7, 129.4, 132.2, 133.1, 134.4, 136.5; MS: *m/z* 353 [M^+], 198, 155, 129; HRMS Calcd for $C_{25}H_{23}NO$ [M^+]: 353.1780. Found: 353.1773.

(S,S)-N,N-Bis(1-cyclohexylethyl)formamide (5). Formamide **5** was obtained using the same procedure as **1**: a colorless oil; $[\alpha]_D^{27}$ +16.3 (*c* 1.09, $CHCl_3$); IR (neat): 2924, 1656, 1449, 757 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.75-1.05 (m, 4H), 1.08-1.50 (m, 6H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.55-1.90 (m, 12H), 2.98-3.08 (m, 1H), 3.30-3.37 (m, 1H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 16.3, 17.9, 26.0, 26.1, 26.2, 26.3, 26.3, 28.3, 30.6, 31.1, 31.1, 40.6, 42.5, 58.4, 59.5, 162.5; MS: *m/z* 265 [M^+], 182, 156, 111, 72; HRMS Calcd for $C_{17}H_{31}NO$ [M^+]: 265.2406. Found: 265.2412.

(R,R)-1-Formyl-2,5-diphenylpyrrolidine (6). Formamide **6** was obtained using the same procedure as **1**: colorless needles; m.p. 117.0-117.5°C (Et_2O-EtOAc); $[\alpha]_D^{26}$ +230.3 (*c* 1.04, $CHCl_3$); IR (KBr): 2970, 1655, 1452, 1376, 702 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.80-2.02 (m, 2H), 2.35-2.60 (m, 2H), 5.18 (dd, *J* = 7.2, 3.2 Hz, 1H), 5.40 (dd, *J* = 7.5, 2.6 Hz, 1H), 7.15-7.46 (m, 10H), 8.20 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 32.0, 33.2, 60.2, 62.4, 125.5, 126.4, 126.4, 127.0, 127.9, 128.6, 129.0, 129.0, 129.0, 142.0, 142.7, 162.9; MS: *m/z* 251 [M^+], 194, 147, 104; HRMS Calcd for $C_{17}H_{17}NO$ [M^+]: 251.1310. Found: 251.1311.

General procedure for the preparation of 3,5-dinitrobenzoate derivatives. To a solution of an optically active homoallylic alcohol (65 μmol) in CH_2Cl_2 (2 mL) were added triethylamine (0.5 mL, 3.59 mmol), 3,5-dinitrobenzoyl chloride (77 mg, 0.33 mmol), and a catalytic amount of 4-dimethylaminopyridine at room temperature. The reaction mixture was stirred for 18 h, poured into ice water and extracted with Et_2O. The combined extracts were washed with 0.5 N HCl, saturated aqueous $NaHCO_3$ and brine, dried and filtered. After evaporation of the solvent, a solution of the residue in CH_2Cl_2 was passed through a short silica gel column. The 3,5-dinitrobenzoate was completely recovered completely by elution with CH_2Cl_2 and the combined fractions were concentrated *in vacuo*. The obtained residue was analyzed by HPLC using a Daicel Chiralcel OD-H column to determine the enantiomeric excess.

Typical procedure for allylation with allyltrichlorosilane (8). (R)-1-Cyclohexyl-3-buten-1-ol (9). To a solution of aldehyde **7** (112 mg, 1.0 mmol), catalyst **1** (50.7 mg, 0.2 mmol) and HMPA (175 μL, 1.0 mmol) in C_2H_5CN (2 mL) was added dropwise allylsilane **8** (263 mg, 1.5 mmol) at -78°C within 2 min under argon. After stirring at -78°C for 14 days, the reaction mixture was poured into an ice-cooled mixture of Et_2O (30 mL) and saturated aqueous $NaHCO_3$ (30 mL) and stirred for 15 min. The organic layer was separated and the aqueous phase extracted with Et_2O (2 x 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The oily residue was purified by flash chromatography (SiO_2, EtOAc:*n*-hexane 1:20) to afford **9** (123 mg, 80% yield) as a colorless oil. $[\alpha]_D^{24}$ +9.7° (*c* 1.00, ethanol) (98% ee);.^1H NMR ($CDCl_3$): δ 0.80-2.40 (m, 12H), 2.04-2.42 (m, 2H), 3.34-3.46 (m, 1H), 5.08-5.20 (m, 2H), 5.74-5.95 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 26.1, 26.2, 26.5, 28.1, 29.0, 38.8, 43.0, 74.7, 118.0, 135.5; IR (neat): 3384, 2925, 1640, 1450, 986,

910 cm^{-1}; MS: *m/z* 113 [M^+-41], 95, 67, 55. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (retention time) (major), 14.3 min (99.0%); t_R (minor), 15.9 min (1.0%) (Chiralcel OD-H, *n*-hexane/EtOH 50/1, 1.0 mL/min). Elution with *n*-hexane-EtOAc (3:1) recovered the chiral formamide **1** (49.4 mg) without racemization.

1-Cyclopentyl-3-buten-1-ol (11). Compound **11** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{25}$ -17.1° (*c* 0.90, $CHCl_3$) (91% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.18-2.22 (m, 11H), 2.29-2.45 (m, 1H), 3.38-3.54 (m, 1H), 5.07-5.21 (m, 2H), 5.75-5.98 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 25.9, 26.0, 29.1, 29.4, 41.1, 46.1, 75.1, 118.4, 135.7; IR (neat): 3382, 2952, 1641, 1451, 912 cm^{-1}; MS: *m/z* 139 [M^+-1], 99, 81; HRMS calcd for $C_9H_{15}O$ [M^+-H]: 139.1123. Found: 139.1125. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 28.0 min (95.4%); t_R (minor), 30.0 min (4.6%) (Chiralcel OD-H, *n*-hexane/EtOH 50/1, 0.5 mL/min).

(S)-1-Phenyl-5-hexen-3-ol (13). Compound **13** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{25}$ -21.6° (*c* 1.19, $CHCl_3$) (95% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.58 (bs, 1H), 1.74-1.86 (m, 2H), 2.10-2.41 (m, 2H), 2.62-2.90 (m, 2H), 3.60-3.74 (m, 1H), 5.08-5.22 (m, 2H), 5.72-5.93 (m, 1H), 7.13-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 32.0, 38.4, 42.0, 69.9, 118.4, 125.9, 128.5, 134.7, 142.1; IR (neat): 3384, 2930, 1640, 1603, 1455, 916, 700 cm^{-1}; MS: *m/z* 176 [M^+], 135, 117, 91. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 16.3 min (97.3%); t_R (minor), 19.1 min (2.7%) (Chiralcel OD-H, *n*-hexane/EtOH 9/1, 1.0 mL/min).

5-Ethyl-1-hepten-4-ol (15). Compound **15** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{25}$ -2.9° (*c* 0.72, $CHCl_3$) (93% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 0.91 (t, *J* = 7.1 Hz, 6H), 1.18-1.58 (m, 6H), 2.06-2.40 (m, 2H), 3.60-3.70 (m, 1H), 5.08-5.22 (m, 2H), 5.76-5.97 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 11.6, 21.2, 21.9, 38.7, 46.1, 71.8, 117.9, 135.8; IR (neat): 3384, 2934, 1640, 1459, 995, 912 cm^{-1}; MS: *m/z* 141 [M^+-1], 101, 83, 71, 59; HRMS calcd for $C_9H_{17}O$ [M^+-H]: 141.1279. Found: 141.1278. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 12.2 min (96.7%); t_R (minor), 13.7 min (3.3%) (Chiralcel OD-H, *n*-hexane/EtOH 50/1, 1.0 mL/min).

2,2-Dimethyl-5-hexen-3-ol (17). Compound **17** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{24}$ +10.4° (*c* 0.11, benzene) (98% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 0.93 (s, 9H), 1.59 (bs, 1H), 1.90-2.08 (m, 1H), 2.30-2.45 (m, 1H), 3.26 (dd, *J* = 10.5, 2.2 Hz, 1H), 5.08-5.21 (m, 2H), 5.77-5.98 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 26.0, 34.6, 34.8, 72.0, 118.4, 135.8; IR (neat): 3422, 2956, 1640, 1480, 991, 910 cm^{-1}; MS: *m/z* 113 [M^+-15], 95, 83, 67. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (minor), 8.9 min (1.0%); t_R (major), 13.8 min (99.0%) (Chiralcel AD, *n*-hexane/EtOH 50/1, 1.0 mL/min).

1-Decen-4-ol (19). Compound **19** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{25}$ -8.6° (*c* 0.54, CCl_4) (68% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 0.81-1.56 (m, 14H), 2.05-2.40 (m, 2H), 3.58-3.72 (m, 1H), 5.08-5.20 (m, 2H), 5.73-5.94 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 25.6, 29.3, 31.8, 36.8, 41.9, 70.7, 118.1, 135.0; IR (neat): 3356, 2929, 1641, 1466, 994, 913 cm^{-1}; MS: *m/z* 115 [M^+-41], 97, 55. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 7.6 min (83.9%); t_R (minor), 9.5 min (16.1%) (Chiralcel AD, *n*-hexane/EtOH 9/1, 1.0 mL/min).

1,7-Octadien-4-yl 3,5-dinitrobenzoate (3,5-dinitrobenzoate of 21). Compound **21** was obtained using the same procedure as **9**. 3,5-Dinitrobenzoate of **21**: a brown solid; $[\alpha]_D^{25}$ -7.7° (*c* 0.73, $CHCl_3$) (86% ee); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.82-1.98 (m, 2H), 2.13-2.22 (m, 2H), 2.45-2.58 (m, 2H), 4.98-5.18 (m, 4H), 5.26-5.35 (m, 1H), 5.75-5.86 (m, 2H), 9.13 (d, *J* = 2.2 Hz, 2H), 9.22 (t, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ

29.6, 32.6, 38.6, 76.0, 115.6, 118.7, 122.3, 129.4, 132.9, 134.3, 137.2, 148.7, 162.2; IR (KBr): 3102, 1729, 1545, 1346, 1279, 722 cm^{-1}; MS: *m/z* 320 [M^+], 279, 195, 179, 149, 67; HRMS calcd for $C_{15}H_{16}N_2O_6$ [M^+]: 320.1008. Found: 320.1001. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 11.0 min (92.9%); t_R (minor), 14.7 min (7.1%) (Chiralcel AD, *n*-hexane/EtOH 9/1, 1.0 mL/min).

Oct-1-en-7-yn-4-yl 3,5-dinitrobenzoate (3,5-dinitrobenzoate of 23). Compound **23** was obtained using the same procedure as **9**. 3,5-Dinitrobenzoate of **23**: a brown solid; $[\alpha]_D^{25}$ -33.5° (*c* 0.47, $CHCl_3$) (88% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.94-2.10 (m, 3H), 2.28-2.40 (m, 2H), 2.49-2.60 (m, 2H), 5.05-5.22 (m, 2H), 5.34-5.49 (m, 1H), 5.69-5.92 (m, 1H), 9.16 (d, *J* = 2.1 Hz, 2H), 9.24 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.9, 29.6, 32.1, 38.4, 69.4, 75.4, 82.8, 119.1, 122.4, 129.5, 132.5, 148.8, 162.2; IR (KBr): 3293, 1720, 1546, 1346, 720 cm^{-1}; MS: *m/z* 277 [M^+-41], 195, 149, 91, 75; HRMS calcd for $C_{15}H_{14}N_2O_6$ [M^+]: 318.0852. Found: 318.0844. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 22.7 min (94.2%); t_R (minor), 32.7 min (5.8%) (Chiralcel AD, *n*-hexane/EtOH 9/1, 1.0 mL/min).

Undeca-1,5-dien-4-ol (25). Compound **25** was obtained using the same procedure as **9**: a colorless oil; $[\alpha]_D^{25}$ +2.6° (*c* 1.05, $CHCl_3$) (22% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.20-1.45 (m, 6H), 1.59 (bs, 1H), 1.98-2.38 (m, 4H), 4.07-4.18 (m, 1H), 5.08-5.21 (m, 2H), 5.41-5.93 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.4, 28.8, 31.3, 32.1, 42.0, 71.9, 118.1, 132.0, 132.5, 134.5; IR (neat): 3377, 2927, 1711, 1641, 971 cm^{-1}; MS: *m/z* 150 [M^+-18], 127, 109, 83, 67; HRMS calcd for $C_{11}H_{18}$ [M^+-H_2O]: 150.1409. Found: 150.1402. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 8.0 min (61.1%); t_R (minor), 11.4 min (38.9%) (Chiralcel AD, *n*-hexane/EtOH 9/1, 1.0 mL/min).

Typical procedure for crotylation with (E)-crotyltrichlorosilane [(E)-28]. (1S,2R)-1-Cyclohexyl-2-methyl-3-buten-1-ol (anti-29). To a solution of aldehyde **7** (112 mg, 1.0 mmol), catalyst **1** (101.4 mg, 0.4 mmol) and HMPA (350 μL, 2.0 mmol) in C_2H_5CN (2 mL) was added dropwise (*E*)-crotylsilane **28** (237 μL, 1.5 mmol) at -78°C within 2 min under argon. After stirring at -78°C for 3 weeks, the reaction mixture was poured into an ice-cooled mixture of Et_2O (30 mL) and saturated aqueous $NaHCO_3$ (30 mL) and stirred for 15 min. The organic layer was separated and the aqueous phase extracted with Et_2O (2 x 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The oily residue was purified by flash chromatography (SiO_2, EtOAc:*n*-hexane 1:20) to afford *anti*-**29** (155 mg, 92% yield) as a colorless oil. $[\alpha]_D^{23}$ +18.4° (*c* 1.29, $CHCl_3$) (98% ee);.^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.03 (d, *J* = 6.9 Hz, 3H), 1.03-1.81 (m, 12H), 2.34-2.43 (m, 1H), 3.10 (dd, *J* = 5.9, 5.9 Hz, 1H), 5.08-5.13 (m, 2H), 5.73-5.83 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 16.9, 26.1, 26.4, 26.5, 27.0, 30.0, 40.3, 40.5, 78.9, 116.2, 140.5; IR (neat): 3384, 2924, 1637, 1450, 1002, 910 cm^{-1}; MS: *m/z* 168 [M^+], 151, 113, 95, 83. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 8.1 min (99.0%); t_R (minor), 9.1 min (1.0%) (Chiralcel AD, *n*-hexane/EtOH 50/1, 1.0 mL/min). Elution with *n*-hexane-EtOAc (3:1) recovered the chiral formamide **1** (98.3 mg) without racemization.

anti-4-Methyl-1-phenyl-5-hexen-3-ol (anti-30). Compound *anti*-**30** was obtained using the same procedure as *anti*-**29**. a colorless oil; $[\alpha]_D^{25}$ -14.4° (*c* 1.79, $CHCl_3$) (94% ee); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 1.03 (d, *J* = 6.9 Hz, 3H), 1.52 (bs, 1H), 1.66-1.91 (m, 2H), 2.19-2.28 (m, 1H), 2.63-2.88 (m, 2H), 3.39-3.44 (m, 1H), 5.05-5.16 (m, 2H), 5.71-5.79 (m, 1H), 7.14-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 16.2, 32.1, 36.1, 44.3, 74.0, 116.6, 125.8, 128.3, 128.4, 128.5, 140.3, 142.4, 169.0; IR (neat): 3385, 2930, 1638, 1603, 1454, 914, 700 cm^{-1}; MS: *m/z* 190 [M^+], 172, 134, 117, 105, 91, 78. HPLC analysis of the corresponding 3,5-dinitrobenzoate: t_R (major), 9.8 min (97.0%); t_R (minor), 12.9 min (3.0%) (Chiralcel OD-H, *n*-hexane/EtOH 20/1, 1.0 mL/min).

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