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Complete Asymmetric Induction in [1, 2]-Wittig Rearrangement of a System Involving a Binaphthol Moiety

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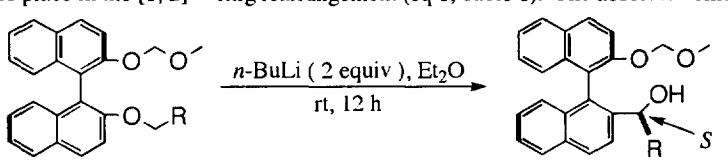
Abstract: The benzyl and allyl ethers of mono-methoxymethyl binaphthol undergo [1, 2]-Wittig rearrangement with complete control of asymmetric induction to afford a novel chiral binaphthyl auxiliary.

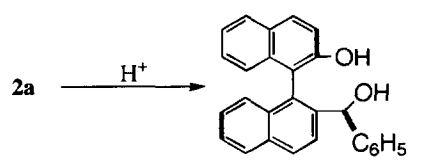
In the field of asymmetric synthesis, the efficiency of the chiral binaphthyl structure has been widely recognized.[1] Regarding chiral ester enolates, however, utilization of such a binaphthyl moiety is not known except a few special cases.[2] The reason why binaphthol has not been used as an alcohol function in chiral esters is attributed to the serious unstability of the metal enolate derived from the ester.[3] It is essential to reduce the leaving ability of the alcohol moiety for the development of chiral ester enolates involving binaphthyl. The compound **2** introducing an aliphatic alcohol function into the binaphthyl moiety might resolve the confronted problem. The [1, 2]-Wittig rearrangement of **1** is expected to provide an effective route to **2**.

When the benzyl ether of mono-methoxymethyl binaphthol ((*R*)-**1a**) was treated with *n*-BuLi (2 equiv) in ether at room temperature for 12 h, a single [1, 2]-Wittig rearrangement product (**2a**) was obtained in 57% yield, without any detection of the counter diastereomer. From this result it is inferred that a complete asymmetric induction takes place in the [1, 2]-Wittig rearrangement (eq 1, Table 1). The absolute configuration at the newly



(*R*)-**1** **2** (1)

created chiral center of **2a** was determined to be *S* by comparing the ^{19}F-NMR chemical shifts of its (*R*)- and (*S*)-MTPA derivatives (Table 2).[5] As shown in Table 1, the reaction using (*S*)-**1** (**1a***) gave the corresponding **2a*** with the reverse stereochemistry (entry 2) and in the case of allyl and methallyl ethers, similar results were observed (entries 5 and 6). After deprotection of **2a** with 10% HCl in THF, a novel chiral diol **3** was obtained in 97% yield ($[\alpha]^{18}_{D}$ -214° (*c* 0.45, $CHCl_3$)) (eq 2).



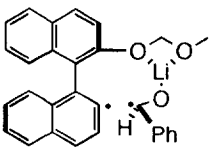
3 (2)

It is recognized from the mechanism of the [1, 2]-Wittig rearrangement of α-lithioethers that the 1, 2-migration proceeds via a radical dissociation-recombination (not in a concerted mode) with inversion of the configuration at the carbanion C atom.[6] Furthermore, when the lithium cation is coordinated to the neighboring oxygen groups (chelation), it has been reported that the radical coupling proceeds via a favorable comformation of the lithium template with a minimum of non-bonded interactions.[7] Such a chelation control (like **4**) allows to

Table 1. [1, 2]-Wittig Rearrangement of Binaphthol Derivatives 1[a]

Entry	Substrate (R)		Product (yield, %)[b]			$[\alpha]^{25}_D$ ($CHCl_3$)
1	**1a**	C_6H_5	**2a**	(57)	*R-S*[c]	-213.8 (*c* 1.08)
2	**1a***[d]	C_6H_5	**2a***[d]	(52)	*S-R*[c]	+212.3 (*c* 1.09)
3	**1b**	p-Me-C_6H_4	**2b**	(48)	*R-S*[c]	-184.5 (*c* 1.03)
4	**1c**	p-Cl-C_6H_4	**2c**	(48)	*R-S*[c]	-232.5 (*c* 1.60)
5	**1d**		**2d**	(39)	*R-S*[c]	-54.4 (*c* 1.38)
6	**1e**		**2e**	(50)	*R-S*[c]	-97.2 (*c* 1.20)

[a] Unless otherwise noted, all reactions were conducted in ether solution with *n*-BuLi (2.0 equiv) at room temperture for 12 h. [b] Isolated yield of the single isomers, ***the counter diastereomers were not found***. In the reactions (entries 1-4) starting ethers were recovered, while deallylation products from starting ethers also were obtained in the reactions (entries 5 and 6). [c] *R-S* sign represents a combination of (*R*)-binaphthyl and (*S*)-alcohol. [d] Asterisks indicate the substrates derived from (*S*)-binaphthol.



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account for the excellent stereoselectivity on stereochemistry at the newly created chiral center in our reaction system.

Applications of the novel chiral auxiliary to asymmetric reactions are now underway and will be reported elsewhere.

References and Notes

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3. Heathcock, C. H. ; Kiyooka, S. -i. unpublished results in the postdoctral research works (S. -i. K.) at Berkeley, **1982** ; The lithium enolates prepared from the acetate and propionate rapidly decomposed before the following aldol condensation.
4. The ^{13}C-NMR spectra (22.6 MHz, $CDCl_3$) ; **2a** δ 56.08, 72.98, 96.12, 117.73, 123.71, 124.66, 125.51, 125.84, 126.06, 126.15, 126.67, 127.83, 127.95, 128.65, 130.02, 130.08, 132.10, 132.80, 132.98,134.17, 141.09, 142.78, 152.34. **2d** δ 55.81, 71.73, 96.06, 114.08, 117.98, 123.65, 124.50, 124.75, 125.75, 126.06, 126.24, 125.52, 127.80, 128.50, 129.87, 131.67, 132.77, 132.95, 134.08, 138.83, 139.47, 152.19.
5. **Table 2.** ^{19}F- and ^{1}H-NMR Chemical Shift Data of MTPA Esters

	^{19}F-NMR / δ (ppm)[a]	^{1}H-NMR[b] / δ (ppm)
(*S*)-MTPA ester from **2a**	4.94	—
(*R*)-MTPA ester from **2a**	4.67	—
(*S*)-MTPA ester from **2d**	4.93	5.67
(*R*)-MTPA ester from **2d**	4.58	5.77

[a] Internal TFA. [b] Olefinic α-proton.

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