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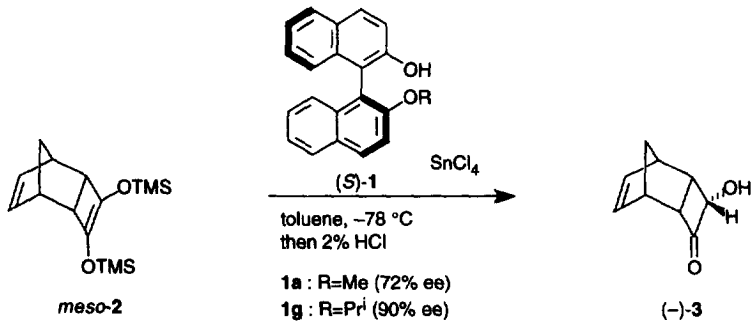
An expedient route to some monoalkyl ethers of enantiomerically pure bi-β-naphthol

Michiyasu Takahashi and Kunio Ogasawara *
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980-77, Japan

Abstract: An expedient route to a series of monoalkyl ethers of optically active bi-β-naphthol has been established by use of the Mitsunobu reaction. © 1997 Elsevier Science Ltd

Recently, Yamamoto and co-workers[1] have found that a complex generated from optically active bi-β-naphthol monomethyl ether (BINOL-Me) **1a** and tin tetrachloride serves as an effective chiral proton source for enantioselective protonation of prochiral silyl enol ethers and ketene bistrimethylsilyl acetals to give chiral 2-substituted ketones and chiral 2-substituted carboxylic acids in high degrees of enantioselectivity after acid work up. Quite recently, we found[2] that the same complex may be used for the enantioselective protonation of the tricyclic *meso* 1,2-enediol bis-silyl ethers **2** which furnished the enantiomerically enriched tricyclic acyloins **3** in moderate enantiomeric excesses (~72%) in the presence of stoichiometric amounts of the complex. Moreover, we found that enantiomeric excess of the *meso* asymmetrization was improved to 90% when (*S*)-BINOL monoisopropyl ether (BINOL-Pr^i) **1g** in place of (*S*)-BINOL-Me **1a** was used under the same stoichiometric conditions[2] (Scheme 1).

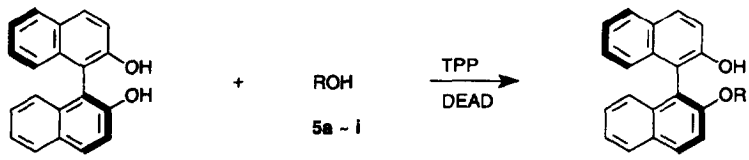


Scheme 1.

In relation to these findings as well as in relation to the preparation of the monodentate BINOL monoether phosphine ligands used for a variety of asymmetric reactions,[3,4] we examined the preparation of a series of BINOL monoethers (BINOL-*R*) **1a–j** starting from BINOL **4** and appropriate alcohols **5a–j** by use of the Mitsunobu reaction.[5] Rather surprisingly, the Mitsunobu reaction has not been employed so far in the preparation of BINOL-*R* **1** or BINOL bisethers except one recent example where the etherification of racemic bi-β-naphthol (BINOL) **4** with optically active 2*R*,4*R*-2,4-pentanediol **6** was carried out to give a diastereomeric mixture of the nine-membered BINOL bisethers in 21% yield and some other products including monoether products for structure determination.[6] In this report, we describe the synthesis of a series of BINOL monoethers[7] **1a–j** in one step by the reaction between BINOL **4** and appropriate alcohols **5a–j** under the standard Mitsunobu conditions in the presence of triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD) in THF.

* Corresponding author. Fax: +81-22-217-6845; Email: konol@mail.cc.tohoku.ac.jp

Table 1. The Mitsunobu reaction between BINOL **4** and alcohols **5**



(*S*)-**4** **1a ~ i**

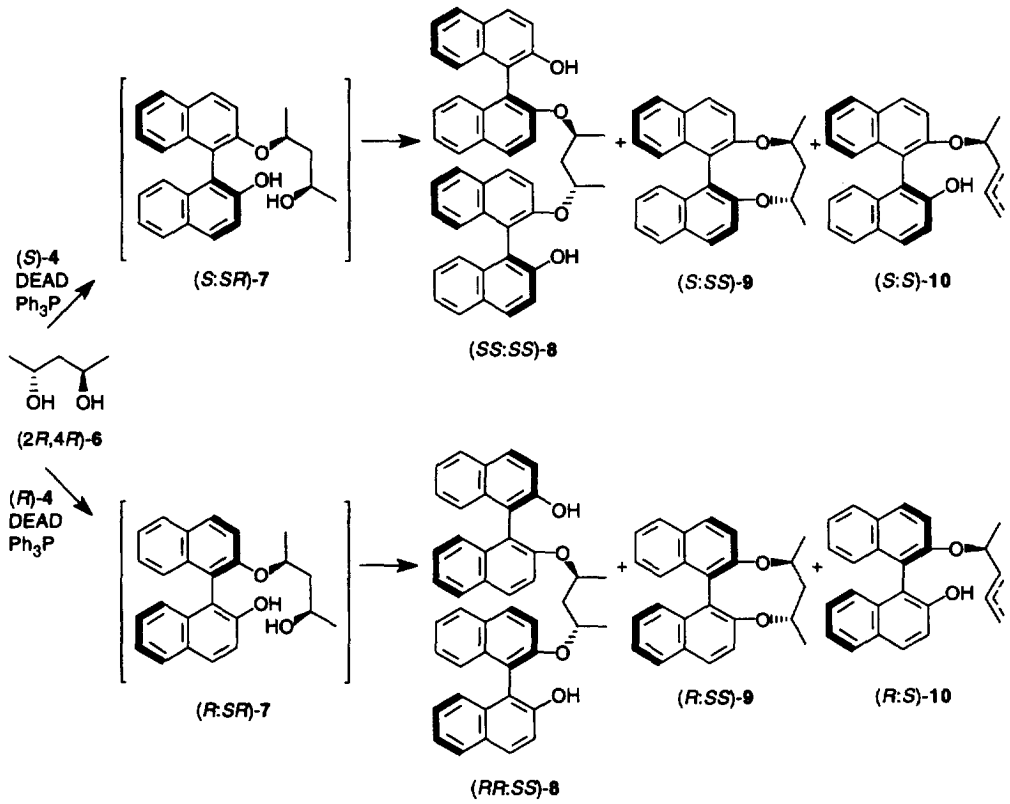
Entry	BINOL **4** config.	Alcohol **5** ROH		BINOL-*R* **1** (%)		**4** (recovery:%)
1	*S*	a:	MeOH	(*S*)-**a**	82	13[a]
2	*S*	b:	EtOH	(*S*)-**b**	82	18
3	*R/S*	b:	EtOH	(*R/S*)-**b**	85	13
4	*S*	c:	$BnO(CH_2)_2OH$	(*S*)-**c**	85	14
5	*R/S*	c:	$BnO(CH_2)_2OH$	(*R/S*)-**c**	84	15
6	*S*	d:	$BnO(CH_2)_3OH$	(*S*)-**d**	83	16
7	*R/S*	d:	$BnO(CH_2)_3OH$	(*R/S*)-**d**	83	15
8	*S*	e:	BnOH	(*S*)-**e**	84	15
9	*R/S*	e:	BnOH	(*R/S*)-**e**	81	10
10	*R*	f:	nerol	(*R*)-**f**	72	22[b]
11	*R/S*	f:	nerol	(*R/S*)-**f**	81	10[b]
12	*S*	g:	Pr^iOH	(*S*)-**g**	82	16
13	*R/S*	g:	Pr^iOH	(*R/S*)-**g**	72	19
14	*S*	h:	Ph_2CHOH	(*S*)-**h**	61	34
15	*R/S*	h:	Ph_2CHOH	(*R/S*)-**h**	57	39
16	*R/S*	i:	$Pr^i{}_2CHOH$	(*R/S*)-**i**	6	91
17	*S*	j:	*tert*-BuOH	(*S*)-**j**	17	75
18	*R/S*	j:	*tert*-BuOH	(*R/S*)-**j**	11	87

a. The bisether was obtained in 5% yield only in this case. b. The S_N2' product was obtained in ~5% yield.

We examined the etherification reaction of both racemic and enantiomerically pure BINOLs **4** with alcohols **5a–j** having a primary, a secondary or a tertiary hydroxy group. With the primary alcohols **5a–f**, the reaction proceeded in a satisfactory way to give good yields (~85%) of the desired BINOL monoethers **1a–f** with recovery of the unreacted BINOL **4** (~20%) regardless of the stereochemistry of **4** when equimolar amounts of TPP and DEAD were used (Table 1, entries 1–11). Of the secondary alcohols **5g–i**, although the reaction proceeded at a much slower rate with **5g** and **h** than the primary alcohols **5a–f**, the monoethers **1g** and **h** were obtained in satisfactory yields with recovery of some starting BINOL **4** (Table 1, entries 12–15). However, the etherification took place very slowly with the secondary alcohol 2,4-dimethyl-3-pentanol **5i** to give the BINOL-*R* **1i** in less than 10% yield, which may be due to the steric interference of four methyl groups at the two neopentyl positions (Table 1, entry 16). Similarly, the reaction between **4** and *tert*-butanol **5j** proceeded slowly to give the mono-*tert*-butyl ether **1j** in 11% yield with 87% recovery of BINOL **4** (Table 1, entries 17, 18). In general, the formation of BINOL bisethers was found to be negligible provided that excess amounts of TPP and DEAD were not used even if an excess amount of an alcohol was present in the reaction medium (Table 1).

When an enantiomerically pure C_2-symmetric 2,4-diol (2*R*,4*R*)-pentane-2,4-diol[6] **6** was reacted with 2.2 equiv. of enantiomerically pure (*S*)- and (*R*)-BINOLs **4**, respectively, in the presence of 2.2 equiv. of

TPP and 2.2 equiv. of DEAD, the stereochemical profile of the reaction was found to be dependent on the stereochemistry of BINOL **4** used. Thus, under these conditions, (*S*)-BINOL **4** afforded a mixture of four compounds consisting of 67% of the bismonoether **8**, 3% of the nine membered bisether **9**, and 15% of an inseparable mixture of two monoether olefins **10** besides 25% of the unreacted (*S*)-BINOL **4**. (*R*)-BINOL **4** afforded a mixture of four compounds consisting of 24% of the bismonoether **8**, 36% of the nine membered bisether **9**, and 18% of an inseparable mixture of two monoether olefins **10** with 39% recovery of the unreacted (*R*)-BINOL **4** under the same conditions. In both cases, neither the monoethers **7** nor the unreacted 2*R*,4*R*-**6** were detected in the reactions. The observed large differences in the formation of the nine-membered bisethers **8** and the bimolecular bismonoethers **9** between (*S*)- and (*R*)-BINOLs **4** may be due to the stereochemical environment of the monoether intermediates **7** in which the second reaction occurred so as to minimize steric interactions. Namely, (*S*:*SR*)-**7** reacted intermolecularly to give the bismonoether (*SS*:*SS*)-**8**, while (*R*:*SR*)-**7** reacted intramolecularly to yield the nine-membered bisether (*R*:*SS*)-**9**, as the major products, respectively (Scheme 2).



Scheme 2.

In summary, we have developed an expedient route to monoalkyl ethers (BINOL-*R*) of enantiomerically pure bi-β-naphthol, some of which are useful as chiral catalysts as well as chiral ligands, by employing the Mitsunobu reaction of enantiomerically pure BINOL with appropriate alcohols having a primary, a secondary, or a tertiary hydroxy group.

Experimental

Melting points were determined on a Yanagimoto hotstage instrument and are uncorrected. IR spectra were recorded on a JASCO-IR 700 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-2000 (300 MHz) spectrometer. Optical rotations were measured with a JASCO-DIP-370 digital

polarimeter. Optical purities were determined on a Gilson Model-307 instrument equipped with a chiral column.

Typical procedure exemplified by the synthesis of (S)-BINOL monomethyl ether ***1a***

To a stirred solution of (*S*)-BINOL **4** (99% ee, 1.43 g, 5 mmol), triphenylphosphine (1.32 g, 5 mmol) and methanol (**5a**, 1.0 ml, 24.7 mmol) in THF (50 ml) was added DEAD (40% in toluene, 2.2 ml, 5 mmol) dropwise at room temperature. After stirring for 24 h at the same temperature, the mixture was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (80 g) to give (*S*)-BINOL monomethyl ether **1a** (1.23 g, 82%) from a hexane–AcOEt (8:1) eluent and the unreacted (*S*)-BINOL **4** (179 mg, 12.5%) from a hexane–AcOEt (4:1) eluent.

Physical data of the racemic and the optically active monoethers ***1a–j*** *and the bisethers* ***8*** *and* ***9***

1a: optically active, mp 89–91°C (toluene–hexane) (lit.[7c] mp 85–87°C), $[\alpha]_D^{27}$ −38.9 (*c* 0.68, THF), $[\alpha]_D^{28}$ +44.8 (*c* 1.4, $CHCl_3$), 99.3% ee (CHIRALCEL OD, 5% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 25.12 min; for the (*S*)-enantiomer, 35.47 min) {lit.[7c] $[\alpha]_D^{22}$ −39.4 (*c* 0.7, THF)}. IR (Nujol): ν=3478 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=8.06 (1H, d, *J*=9.1 Hz), 7.90 (2H, d, *J*=8.5 Hz), 7.86 (1H, br d, *J*=8.0 Hz), 7.49 (1H, d, *J*=9.3 Hz), 7.40–7.14 (6H, m), 7.04 (1H, br d, *J*=7.7 Hz), 4.91 (1H, s, exchangeable with D_2O), 3.81 (3H, s). MS *m/z*=300 (M^+, 100%).

1b: racemic, mp 139–140°C (toluene–hexane) (lit.[7a] mp 139–140°C).

1b: optically active, mp 79–82°C (toluene–hexane), $[\alpha]_D^{27}$ +43.7 (*c* 1.2, $CHCl_3$), 99.2% ee (CHIRALCEL OD, 5% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 21.36 min; for the (*S*)-enantiomer, 27.19 min). IR (Nujol): ν=3540 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=8.02 (1H, d, *J*=9.1 Hz), 7.92–7.83 (3H, m), 7.46 (1H, d, *J*=9.1 Hz), 7.40–7.14 (6H, m), 7.06 (1H, br d, *J*=8.2 Hz), 4.96 (1H, s, exchangeable with D_2O), 4.16–3.99 (2H, m), 1.11 (3H, t, *J*=7.1 Hz). MS: *m/z*=314 (M^+, 100%).

1c: optically active, $[\alpha]_D^{29}$ +12.0 (*c* 0.8, $CHCl_3$), 98.5% ee (CHIRALCEL OD, 5% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 46.51 min; for the (*S*)-enantiomer, 54.15 min). IR (film): ν=3510 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=8.03 (1H, d, *J*=9.1 Hz), 7.93–7.82 (3H, m), 7.49 (1H, d, *J*=9.1 Hz), 7.42–7.16 (9H, m), 7.07 (1H, br d, *J*=8.5 Hz), 7.01–6.95 (2H, m), 5.15 (1H, s, exchangeable with D_2O), 4.30–4.10 (4H, m), 3.55 (2H, t, *J*=4.9 Hz). MS: *m/z*=420 (M^+, 100%). HRMS: calcd for $C_{29}H_{24}O_3$: 420.1725. Found: 420.1732.

1d: optically active, $[\alpha]_D^{27}$ +20.3 (*c* 1.9, $CHCl_3$), 98.7% ee (CHIRALCEL OD, 10% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 18.20 min; for the (*S*)-enantiomer, 21.45 min). IR (film): ν=3508 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=8.03 (1H, d, *J*=8.8 Hz), 7.92–7.83 (3H, m), 7.48 (1H, d, *J*=9.1 Hz), 7.41–7.15 (11H, m), 7.05 (1H, br d, *J*=8.5 Hz), 4.96 (1H, s, exchangeable with D_2O), 4.21–4.04 (4H, m), 3.20–3.03 (2H, m), 1.84–1.68 (2H, m). MS: *m/z*=434 (M^+, 100%). HRMS: calcd for $C_{30}H_{26}O_3$: 434.1882. Found: 434.1904.

1e: racemic, mp 103–106°C (toluene–hexane).

1e: optically active, mp 120.5–121.5°C (toluene–hexane), $[\alpha]_D^{30}$ +2.8 (*c* 1.2, $CHCl_3$), 99.1% ee (CHIRALCEL OD, 5% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 30.00 min; for the (*S*)-enantiomer, 37.01 min). IR (film): ν=3516 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.98 (1H, d, *J*=9.1 Hz), 7.92 (1H, d, *J*=8.8 Hz), 7.88 (2H, br d, *J*=8.0 Hz), 7.46 (1H, d, *J*=9.1 Hz), 7.42–7.14 (10H, m), 7.11–7.00 (2H, m), 5.11 (1H, d, *J*=12.6 Hz), 5.07 (1H, d, *J*=12.6 Hz), 4.93 (1H, s, exchangeable with D_2O). MS: *m/z*=376 (M^+), 285 (100%). HRMS: calcd for $C_{27}H_{20}O_2$: 376.1463. Found: 376.1469.

1f: optically active, $[\alpha]_D^{27}$ +39.5 (*c* 1.0, THF), 98.8% ee (CHIRALCEL OD, 1% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 28.86 min; for the (*S*)-enantiomer, 37.39 min) {lit.[7b] $[\alpha]_D^{20}$ +39.4 (*c* 0.8, THF)}. IR (film): ν=3536 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=8.00 (1H, d, *J*=8.8 Hz), 7.92–7.82 (3H, m), 7.45 (1H, d, *J*=9.1 Hz), 7.40–7.13 (6H, m), 7.05 (1H, br d, *J*=8.8 Hz), 5.16 (1H, td, *J*=6.6, 1.4 Hz), 5.00–4.92 (1H, m), 4.97 (1H, s, exchangeable with D_2O), 4.60–4.45 (2H, m),

1.96–1.88 (4H, m), 1.64 (3H, br s), 1.60 (3H, d, *J*=1.4 Hz), 1.54 (6H, s). MS: *m/z*=422 (M^+), 286 (100%).

1g: racemic, mp 153–154°C (toluene–hexane) (lit.[7a] mp 153–155°C).

1g: optically active, $[\alpha]_D^{27}$ +81.8 (*c* 0.9, $CHCl_3$), 98.5% ee (CHIRALCEL OD, 2% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 21.32 min; for the (*S*)-enantiomer, 24.60 min). IR (Nujol): ν=3534 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.99 (1H, d, *J*=9.1 Hz), 7.92–7.83 (3H, m), 7.44 (1H, d, *J*=9.1 Hz), 7.40–7.13 (6H, m), 7.06 (1H, br d, *J*=8.2 Hz), 5.06 (1H, s, exchangeable with D_2O), 4.43 (1H, heptet, *J*=6.0 Hz), 1.12 (3H, d, *J*=6.0 Hz), 0.98 (3H, d, *J*=6.0 Hz). MS: *m/z*=328 (M^+), 286 (100%).

1h: racemic, mp 67–70°C (toluene–hexane).

1h: optically active, $[\alpha]_D^{27}$ +13.1 (*c* 1.0, $CHCl_3$), 98.3% ee (CHIRALCEL OD-H, 2% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 34.25 min; for the (*S*)-enantiomer, 39.98 min). IR (film): ν=3532 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.93 (1H, d, *J*=9.1 Hz), 7.89 (2H, d, *J*=9.1 Hz), 7.84 (1H, d, *J*=8.2 Hz), 7.42 (1H, d, *J*=9.1 Hz), 7.39–6.99 (15H, m), 6.96–6.90 (2H, m), 6.24 (1H, s), 4.93 (1H, s, exchangeable with D_2O). MS: *m/z*=452 (M^+), 167 (100%). HRMS: calcd for $C_{33}H_{24}O_2$: 452.1776. Found: 452.1781.

1i: racemic, IR (film): ν=3534 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.98 (1H, d, *J*=9.1 Hz), 7.90–7.82 (3H, m), 7.47 (1H, d, *J*=9.3 Hz), 7.37–7.16 (6H, m), 7.10 (1H, br d, *J*=8.5 Hz), 5.02 (1H, s, exchangeable with D_2O), 4.06 (1H, t, *J*=5.5 Hz), 1.90–1.75 (1H, m), 1.73–1.57 (1H, m), 0.84 (3H, d, *J*=6.9 Hz), 0.69 (3H, d, *J*=6.9 Hz), 0.67 (3H, d, *J*=7.1 Hz), 0.44 (3H, d, *J*=6.9 Hz). MS: *m/z*=384 (M^+), 286 (100%). HRMS: calcd for $C_{27}H_{28}O_2$: 384.2089. Found: 384.2076.

1j: racemic, mp 157–159°C (toluene–hexane).

1j: optically active, $[\alpha]_D^{26}$ +249.5 (*c* 0.3, $CHCl_3$), 98.0% ee (CHIRALCEL OD-H, 0.5% Pr^iOH–hexane, retention time for the (*R*)-enantiomer, 30.63 min; for the (*S*)-enantiomer, 26.42 min). IR (film): ν=3540 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.93 (1H, d, *J*=8.8 Hz), 7.91–7.82 (3H, m), 7.48 (1H, d, *J*=9.1 Hz), 7.43–7.16 (6H, m), 7.08 (1H, br d, *J*=8.5 Hz), 5.64 (1H, s, exchangeable with D_2O), 1.07 (9H, s). MS: *m/z*=342 (M^+), 286 (100%). HRMS: calcd for $C_{24}H_{22}O_2$: 342.1620. Found: 342.1624.

(*SS*:*SS*)-**8**: mp 156–158°C (toluene–hexane), $[\alpha]_D^{29}$ +278.7 (*c* 0.5, $CHCl_3$). IR (film): ν=3512 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.91–7.80 (8H, m), 7.40–7.21 (10H, m), 7.14 (2H, br d, *J*=8.5 Hz), 7.03 (2H, br d, *J*=8.5 Hz), 6.98 (2H, d, *J*=9.1 Hz), 4.86 (2H, s, exchangeable with D_2O), 4.01 (2H, sextet, *J*=6.0 Hz), 1.23 (2H, br t, *J*=6.3 Hz), 0.76 (6H, d, *J*=6.0 Hz). MS: *m/z*=640 (M^+), 286 (100%). HRMS: calcd for $C_{45}H_{36}O_4$: 640.2614. Found: 640.2597.

(*S*:*SS*)-**9**: $[\alpha]_D^{27}$ +37.6 (*c* 0.1, $CHCl_3$) {lit.[6] $[\alpha]_D^{20}$ +33.9 (*c* 0.1, $CHCl_3$)}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.84 (4H, br t, *J*=8.8 Hz), 7.34–7.27 (4H, m), 7.14 (2H, ddd, *J*=8.5, 6.9, 1.4 Hz), 6.87 (2H, br d, *J*=8.5 Hz), 4.85–4.70 (2H, m), 1.82 (2H, dd, *J*=7.4, 5.5 Hz), 1.11 (6H, d, *J*=6.0 Hz).

(*RR*:*SS*)-**8**: mp 114–117°C (benzene–hexane), $[\alpha]_D^{27}$ +220.4 (*c* 0.5, $CHCl_3$). IR (film): ν=3530 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.94 (2H, d, *J*=9.1 Hz), 7.90–7.81 (6H, m), 7.38–7.10 (14H, m), 7.00 (2H, br d, *J*=8.5 Hz), 4.96 (2H, s, exchangeable with D_2O), 4.49 (2H, sextet, *J*=6.3 Hz), 1.34 (2H, br t, *J*=6.3 Hz), 0.85 (6H, d, *J*=6.0 Hz). MS: *m/z*=640 (M^+), 286 (100%). HRMS: calcd for $C_{45}H_{36}O_4$: 640.2614. Found: 640.2626.

(*R*:*SS*)-**9**: mp >230°C (toluene–hexane) [lit.[6] mp >230°C (sublimed)], $[\alpha]_D^{26}$ −347.9 (*c* 0.4, $CHCl_3$) {lit.[6] $[\alpha]_D^{20}$ −308 (*c* 0.2, $CHCl_3$)}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.93 (2H, d, *J*=8.8 Hz), 7.87 (2H, d, *J*=8.2 Hz), 7.45 (2H, d, *J*=8.8 Hz), 7.35 (2H, ddd, *J*=8.0, 5.8, 2.2 Hz), 7.23 (4H, dd, *J*=5.8, 1.1 Hz), 4.74–4.63 (2H, m), 1.87 (2H, t, *J*=3.8 Hz), 1.35 (6H, d, *J*=6.6 Hz).

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