Stereoselective Hydrocoupling of Optically Active 3-*trans*-Cinnamoyloxazolidinones by Electroreduction

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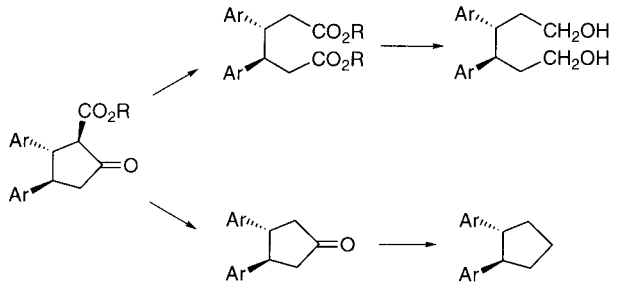
Reductive hydrocoupling of chiral 3-*trans*-cinnamoyloxazolidinones was studied by an electrochemical method. The electroreduction was performed conveniently at a constant current using an undivided cell. The stereoselectivity of the hydrodimers was strongly affected by the electrolyte employed. Electroreduction of (*S*)-4-isobutyl-3-*trans*-cinnamoyloxazolidinone **1a** in 0.3 M Et_4NOTs/AN gave a mixture of two diastereomers of all-trans cyclized hydrodimer **2a**, and the selectivity was R,S,R/S,R,S = 85:15. On the other hand, the reduction of **1a** in 1.7 M $LiClO_4$/THF afforded a diastereomeric mixture of hydrodimers in a selectivity of R,R/S,S/R,S = 5:52:43. The stereoselectivities were explained by considering stable conformations of intermediate anion radicals, that is, syn-Z type for naked anion radicals and anti-Z type for lithiated anion radicals. Semiempirical calculations also supported this hypothesis. Electroreductions of (*S*)-4-isobutyl-3-*cis*-cinnamoyloxazolidinone and (*S*)-4-isobutyl-3-phenylpropioloyloxazolidinone gave **2a** in the same stereoselectivity as electroreduction of **1a** did. The electroreductive hydrocoupling was not inhibited by para and meta substitution on the aryl group of 3-*trans*-cinnamoyloxazolidinones. An ortho substitution, however, hindered the hydrocoupling and lowered the stereoselectivity of the hydrodimers. Electroreduction of 3-*trans*-cinnamoyloxazolidinethione and thiazolidinethione gave *trans*-3,4-diphenylcyclopentanone as a product, and the stereoselectivities were similar to that obtained from the corresponding oxazolidinone.

Electroreductive hydrocoupling of α,β-unsaturated compounds in aqueous solution is well-known as a practical method for the synthesis of adipic acid derivatives.[1] The electroreductive hydrocoupling of β-substituted α,β-unsaturated compounds is, however, usually nondiastereoselective. On the other hand, it has been reported that the electroreduction of cinnamic acid esters in an aprotic solvent gave cyclized products of hydrodimers[2] and they were obtained as all-trans isomers stereospecifically (eq 1).[2a−c] These results prompt us to investigate enantioselective hydrocoupling of cinnamic acid derivatives, because the obtained hydrodimers are able to be converted into a variety of C_2-symmetric compounds (Scheme 1). We have started the study using easily available chiral auxiliaries (X) such as optically active alcohols, oxazolines,[3] and oxazolidinones.[3b,4] Among them, we have found that optically active oxazolidinones were most effective as the chiral auxiliary for the stereoselective hydrocoupling (eq 2).[5,6] In this paper, we report the results of further study on the stereoselective hydrocoupling of optically active 3-*trans*-cinnamoyloxazolidinones

Scheme 1



1 by electroreduction. We found that the electroreductive hydrocoupling of **1** was achieved under constant current conditions more conveniently than under constant potential conditions. We also found that the stereoselectivity was strongly influenced by the supporting electrolyte. Use of a tetraalkylammonium salt as an electrolyte was essential for high stereoselectivity. The observed stereoselectivities were interpreted by regarding the reaction mechanism as homocoupling of stable conforma-

(1) (a) Baizer, M. M. *J. Electrochem. Soc.* **1964**, *111*, 215−222. (b) Baizer, M. M.; Anderson, J. D. *J. Electrochem. Soc.* **1964**, *111*, 223−226. (c) Rifi, M. R. In *Technique of Electroorganic Synthesis, Part II*; Weinberg, N. L., Ed.; Wiley: New York, 1975; pp 192−215.

(2) (a) Klemm, L. H.; Olson, D. R. *J. Org. Chem.* **1973**, *58*, 3390−3394. (b) Kanetsuna, H.; Nonaka, T. *Denki Kagakuoyobi Kogyo Butsuri Kagaku* **1981**, *49*, 526−531. (c) Smith, C. Z.; Utley, H. P. *J. Chem. Soc., Chem. Commun.* **1981**, 492−494. (d) Nishiguchi, I.; Hirashima, T. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 52−53.

(3) (a) Lutomski, K. A.; Meyers, A. I. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. III, pp 213−274. (b) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835−875.

(4) (a) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. III, pp 87−90. (b) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. III, pp 184−188.

(5) Kise, N.; Echigo, M.; Shono, T. *Tetrahedron Lett.* **1994**, *35*, 1897−1900.

(6) Electroreduction of *trans*-cinnamates derived from optically active alcohols such as (−)-menthol, (−)-8-phenylmenthol, and (−)-*endo*-borneol gave the corresponding *dl*-hydrodimers in modest selectivities (10−20% ee). Oxazolines derived from *trans*-cinnamic acid yielded only simply reduced products. After our report,[5] electroreductive hydrodimerization of chiral cinnamates was presented by Utley et al.[7] They reported >95% *dl*-selectivity using (−)-*endo*-bornyl *trans*-cinnamate on the basis of ^{1}H NMR and HPLC analyses of the cyclized hydrodimer. We therefore re-examined the reduction of (−)-*endo*-bornyl ester under their and our conditions. However, we could not reproduce such high selectivity. In all the cases, only modest selectivities (10−20% ee) were obtained by ^{1}H NMR with $Eu(hfc)_3$ and chiral HPLC analyses of 3,4-diphenyl adipate and 3,4-diphenylcyclopentanone derived from the hydrodimers.

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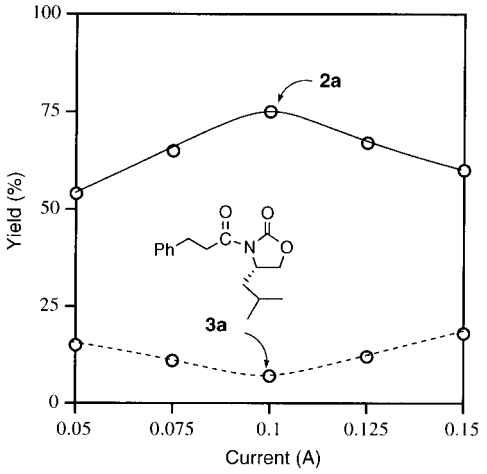
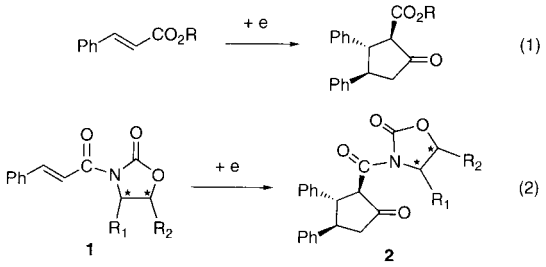


Figure 1. Correlation between yields of the products and currents in the electrolysis of **1a** in 0.3 M Et_4NOTs/AN.

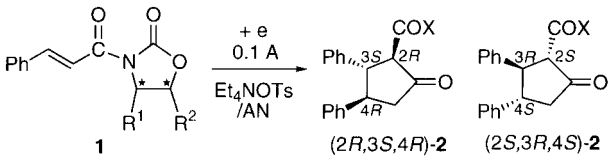
tions of anion radical intermediates. A semiempirical calculation of anion radicals also supported this mechanism. The result obtained from the cis isomer of **1** was identical to that from **1**. Aryl-substituted **1** gave the similar results under the same conditions, except for ortho-substituted **1**. Electroreduction of 3-*trans*-cinnamoyloxazolidinethione and thiazolidinethione resulted in similar stereoselectivities, although the hydrocoupling product was obtained as *trans*-3,4-diphenylcyclopentanone. Furthermore, other reductive methods employing metal reducing agents were investigated. However, electroreduction was most effective for the reductive hydrocoupling of **1**.



Results and Discussion

Constant Current Electrolysis. In our preliminary study,[5] the electroreduction of 3-*trans*-cinnamoyloxazolidinones **1** was carried out at a constant potential of −1.8 V versus SCE in acetonitrile (AN) containing Et_4NOTs as a supporting electrolyte. From a standpoint of synthetic chemistry, a constant current electorolysis is much more convenient than constant potential one. Therefore, we employed constant current electorolysis for the electroreduction of (*S*)-4-isobutyl-3-*trans*-cinnamoyloxazolidinone **1a** in 0.3 M Et_4NOTs/AN using an undivided cell and a Pb cathode. Figure 1 shows the correlation between yields of cyclized hydrodimer **2a** and simply reduced product **3a** and currents. At 0.1 A of current, the best yield of **2a** (75%) was obtained and the stereoselectivity was the same as that in constant potential electorolysis (R,S,R/S,R,S = 85:15 by ^{1}H NMR). This result shows that constant current electorolysis is also effective for the hydrocoupling of **1**. Table 1 summarizes the results of constant current (0.1 A) electrolysis of several 3-*trans*-cinnamoyloxazolidinones **1a**−**e**.

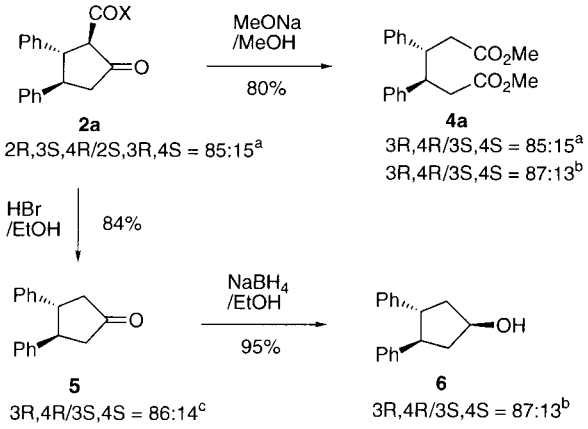
Table 1. Electroreduction of 1 at a Constant Current of 0.1 A



1	R^1	R^2	% yield of **2**[a] (2R,3S,4R/2S,3R,4S)[b]
1a	i-Bu (*S*)	H	75 (85:15)
1b	i-Pr (*S*)	H	76 (83:17)
1c	Bn (*S*)	H	68 (70:30)
1d	Ph (*R*)	H	70 (30:70)
1e	Me (*S*)	Ph (*R*)	72 (75:25)

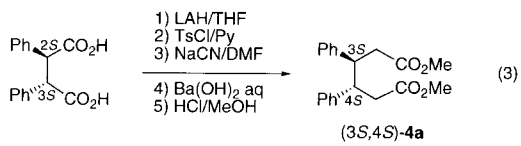
[a] Isolated yields. [b] Diastereomeric ratios determined by ^{1}H NMR spectra.

Scheme 2



[a] By ^{1}H NMR. [b] By chiral HPLC. [c] By optical rotation.

Determination of Stereoselectivity. The diastereoselectivites of **2a**−**e** were measured by their ^{1}H NMR spectra. The absolute configurations of **2a**−**e** were assigned by their conversion to dimethyl 3,4-diphenyladipate **4a** and comparison with authentic sample of (*S*,*S*)-**4a** prepared from (2*S*,3*S*)-2,3-diphenylsuccinic acid[8] (eq 3). The enantioselectivity of **4a** was determined by ^{1}H NMR with $Eu(hfc)_3$ and chiral HPLC analysis. Cyclized hydrodimer **2a** was also transformed to 3,4-diphenylcyclopentanone **5** by acid hydrolysis. The selectivity of **5** was measured by its optical rotation[7] and further confirmed by transformation to 3,4-diphenylcyclopenntanol **6** and its chiral HPLC analysis. As shown in Scheme 2, all the measurements of stereoselectivity gave similar values.

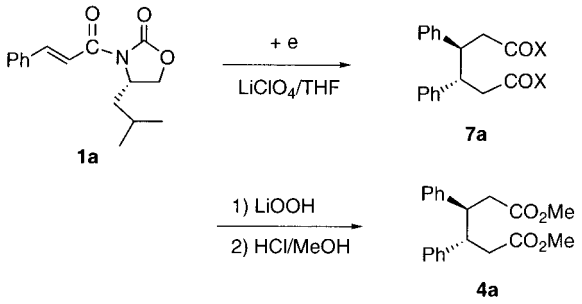


Effects of Supporting Electrolyte. The effect of the supporting electolyte on the hydrocoupling of **1a** was

(7) Utley, J. H. P.; Güllü, M.; Motevalli, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1961−1970.

(8) (a) Wren, H.; Still, C. J. *J. Chem. Soc.* **1915**, 444−451. (b) Buchan, R.; Watson, M. B. *J. Chem. Soc. C* **1968**, 2465−2467. (c) Kise, N.; Kumada, K.; Terao, Y.; Ueda, N. *Tetrahedron* **1998**, *54*, 2697−2708.

Table 2. Electroreduction of 1a with LiClO4 as an Electrolyte in THF



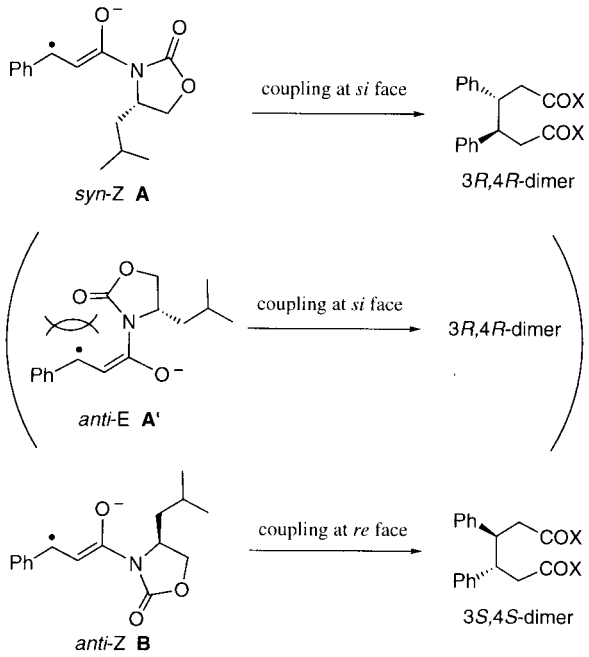
concn of $LiClO_4$ (M)	yield of **4a** (%)[a]	*dl*/meso of **4a**[b]	3R,4R/3S,4S of *dl*-**4a**[c]
0.3	63	50:50	46:54
1.1	45	50:50	24:76
1.7	44	48:52	11:89

[a] Isolated yields. [b] Determined by isolation. [c] Determined by ^{1}H NMR spectra using Eu(hfc)$_3$.

investigated. Use of tetrabutylammonium perchlolate (0.3 M in AN) gave **2a** in 50% yield, and the stereoselectivity (R,S,R/S,R,S = 87:13) was similar to that obtained with Et_4NOTs. Use of $LiClO_4$ in AN caused deposition of Li metal on the cathode surface, and the starting **1a** was recovered, whereas electroreduction in THF with $LiClO_4$ gave hydrodimer **7a** in place of cyclized dimer **2a**. The diastereomeric mixture of **7a** was transformed to dimethyl 3,4-diphenyladipate **4a**, and its stereoselectivity was confirmed by ^{1}H NMR (Table 2). It is noted that *S,S*-selectivity increased with an increase in the concentration of $LiClO_4$. However, significant amounts of meso-isomer were also formed. These results show that the stereoselectivities in the electroreductive hydrocoupling of chiral 3-*trans*-cinnamoyloxazolidinones are strongly influenced by the supporting electrolyte. On the other hand, stereoselectivities in the hydrocoupling of chiral cinnamic acid esters were little affected by the supporting electrolyte. For example, similar selectivities were obtained in the electroreduction of (−)-*endo*-bornyl *trans*-cinnamate using Et_4NOTs (R,S,R/S,R,S = 55:45) and $LiClO_4$ (R,S,R/S,R,S = 60:40) as a supporting electrolyte. The large effect of the supporting electrolyte on the stereoselectivity is characteristic of the hydrocoupling of 3-cinnamoyloxazolidinones.

Reaction Mechanism. The reaction mechanism of the hydrocoupling of **1** can be speculated to be similar to that reported previously for cinnamic acid esters.[2a,b,9] Namely, the cyclized hydrodimers **2** are formed by coupling of two anion radicals produced by one-electron transfer to **1** and a subsequent Dieckmann condensation. Complete diastereoselectivity (dl/meso = ∼100:0) in the cyclized hydrodimer obtained by electroreduction of cinnamic acid esters has been interpreted by interaction between anion radicals and the cathode surface[2a,b] or by templating between two anion radicals and water.[9] Stereoselectivity in the formation of **2** can be explained by steric interaction between the substituents on oxazolidinone rings. In our previous report,[5] we have supposed an *E*-enolate type anion radical (**A′** in Scheme 3) as the most plausible intermediate for the electroreductive hydrocoupling of **1** to elucidate the observed stereoselectivity. However, it is well-known that *E*-enolates of

Scheme 3



3-acyloxazolidinones are much more unstable than *Z*-enolates owing to steric repulsion. The intermediate is therefore either of two conformers of the *Z*-enolate-type anion radicals **A** and **B** (Scheme 3). The results from electroreduction using a tetraalkylammonium salt as a supporting electrolyte suggest that the reaction occurs from conformation **A** by coupling at the less hindered Si face (*β*-side) to give *R,R*-dimer selectively. In the electroreduction with $LiClO_4$ as a supporting electrolyte, on the contrary, conformation **B** couples each other at the less hindered *Re* face (α-side) to afford the *S,S*-dimer preferentially. According to our knowledge about enolate anions of 3-acyloxazolidinones, conformation **A** seems less stable than **B** for the naked anion radical due to electronic repulsion between two oxygen atoms, while the Li-chelated anion radical (lithiated **A**) seems more favorable than the nonchelated one (lithiated **B**). Therefore, we carried out semiempirical calculations of the anion radicals to evaluate their stable conformations. The geometrry optimizations using the PM3 and AM1 methods[10] gave two conformations **C** and **D** for naked anion radicals of 3-*trans*-cinnamoyloxazolidinones (Scheme 4, Table 3). In the gas phase, conformation **D** is more stable than **C**, whereas calculations with the COSMO method[11] revealed conformation **C** is more stable than **D** in AN or THF. These results show conformation **C** is more likely in a polar solvent. On the other hand, PM3 calculations of lithiated anion radicals indicated conformation **E** is more stable than **F** in the gas phase, but conformation **F** is more stable than **E** in a polar solvent (Scheme 4, Table 3). These results from semiempirical calculations are consistent with the above-mentioned mechanism for the electroreduction of **1a** (Scheme 3); that is, the naked anion radical of **1a** favors conformation **A** and the lithiated one prefers conformation **B**.

(9) Fussing, I.; Güllü, M.; Hammerich, O.; Hussain, A.; Nielsen, M. F.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 649−658.

(10) All calculations were made by MOPAC 93 incorporated in CS MOPAC Pro v.3.5 (KembrigeSoft Corporation, 1996). The optimizations were carried on until GNORM < 0.1 (in gas phase) or 0.3 (in solution, EPS = 36.0 for AN and 7.58 for THF) using EF.

(11) Klamt, A.; Schüürman, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799−805.

Scheme 4

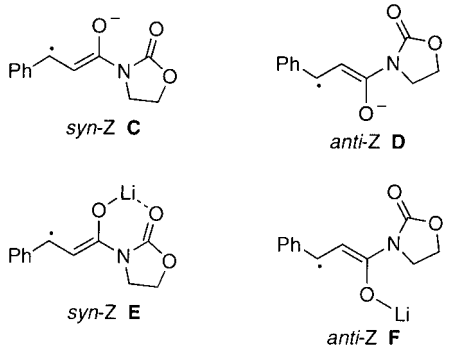
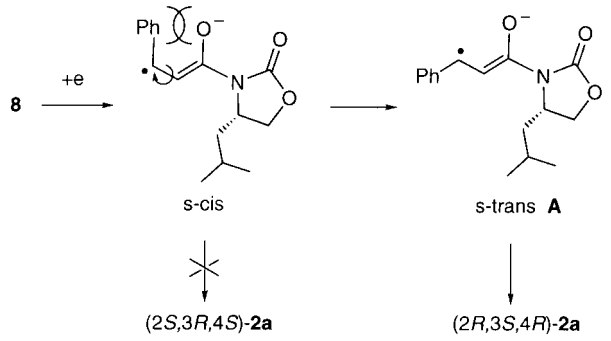


Table 3. Semiempirical Calculations of Anion Radicals

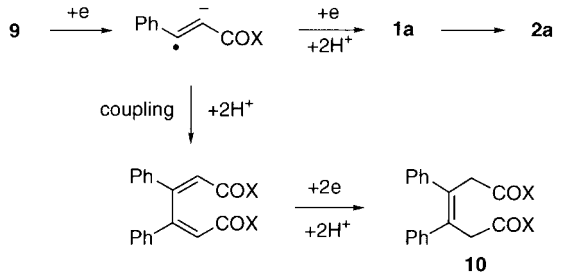
		heats of formation (kcal/mol)[a]			
method	phase	**C**	**D**	**E**	**F**
PM3	gas	−112.31	**−113.37**	**−79.03**	−69.24
	in AN[b]	**−182.67**	−181.46	−94.44	**−96.78**
	in THF[b]	**−171.17**	−170.01	−100.57	**−103.50**
AM1	gas	−92.49	**−93.93**		
	in AN[b]	**−164.50**	−163.92		

[a] Boldfaced values show more stable conformations. [b] Using the COSMO method (EPS = 36.0 for AN and 7.58 for THF).

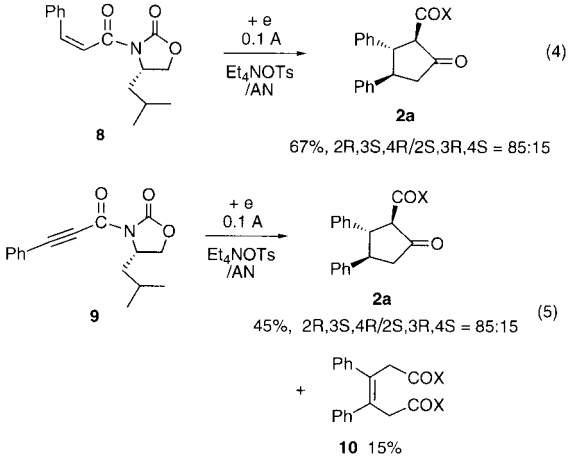
Scheme 5



Scheme 6

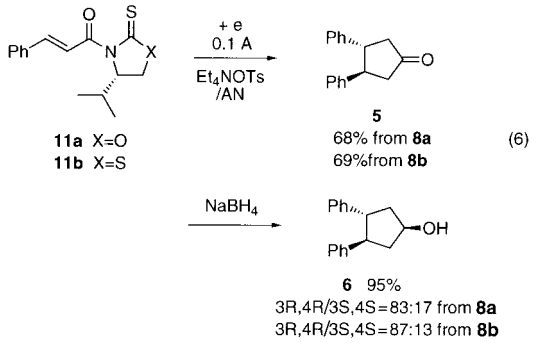


Electroreductive Hydrocoupling of 3-*cis*-Cinnamoyl- and 3-Phenylpropioloyloxazolidinones. Electroreduction of the cis analogue of **1a** (**8**) was examined, since inversion of the stereoselectivity was expected (eq 4). The stereoselectivity was however the same as that obtained from **1a**. This result shows that the sterically hindered s-cis anion radical isomerized quickly to the s-trans one (**A**),[12] which couples to give the *R,R*-dimer preferentially (Scheme 5). Electroreduction of 3-phenylpropioloyloxazolidinone **9** also gave cyclized dimer **2a** in the same stereoselectivity as above (eq 5). In this case, noncyclized dimer **10** was yielded together with **2a**. These results show that the cyclized dimer **2a** was formed from **1a**, which was produced in situ by electroreduction of **9** (Scheme 6).



Electroreductive Hydrocoupling of Ar-Substituted 1. Several aryl-substituted 3-*trans*-cinnamoyloxazolidinones **1** were electrochemically reduced under the constant current conditions described above. As shown in Table 4, para and metasubstitution did not inhibit the hydrocoupling, whereas orthosubstitution hindered it considerably. In addition, orthosubstitution lowered the stereoselectivity, especially in the case of the α-naphthyl derivative **1j**. Although the absolute stereoconfigurations of **4f**−**j** could not be confirmed, their major isomers were assumed to be R,R from ^{1}H NMR correlation of **2f**−**j** with **2a**.

Electroreductive Hydrocoupling of 3-*trans*-Cinnamoyloxazolidinethiones and Thiazolidinethiones. Electroreduction of 3-*trans*-cinnamoyloxazolidinethione **11a** and thiazolidinethione **11b** gave *trans*-3,4-diphenylcyclopentanone **5** as the sole product (eq 6). In these cases, cyclized hydrodimers such as **2a** are hydrolyzed and then decarboxylated under the conditions of electroreduction. The stereoselectivitiy of **5** was determined by conversion to alcohol **6** and its chiral HPLC analysis. The stereoselectivities were similar to that observed in the hydrocoupling of the corresponding oxazolidinone **1b**.

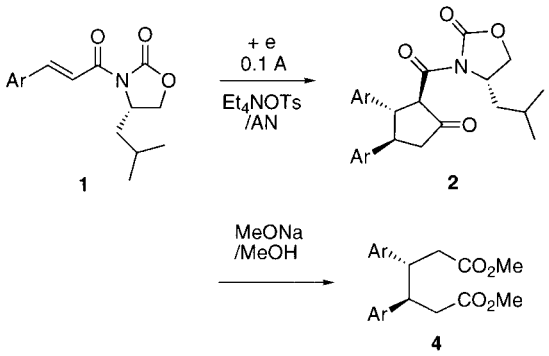


Reduction of 1a with Metal Reducing Agents. Since reductive hydrocoupling of α,β-unsaturated carbonyl compounds has been reported with Na,[13] SmI_2,[14] and

(12) The isomerization of a cis-radical anion to a trans one has been reported: Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 2783−2799.

(13) (a) Totton, E. L.; Freeman, R, C.; Powell, H.; Yarboro, T. L. *J. Org. Chem.* **1961**, *26*, 343−346. (b) House, H. O.; Giese, R, W.; Kronberger, K.; Kaplan, J. P.; Simeone, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 2800−2810.

Table 4. Electroreductive Coupling of Aryl Substituted 1



Ar		%yield[a] 2 (dr)[b]	4	3R,4R/3S,4S of 4[c]
Ph	**1a**	75 (85:15)	80	85:15
p-FC_6H_4	**1f**	78 (75:25)	63	77:23
o-$MeOC_6H_4$	**1g**	31 (65:35)	65	69:31
m-$MeOC_6H_4$	**1h**	64 (70:30)	80	72:28
p-$MeOC_6H_4$	**1i**	73 (80:20)	78	83:17
1-Naphthyl	**1j**	50 (60:40)	60	56:44

[a] Isolated yields. [b] Diastereomeric ratios determined by ^1H NMR spectra. [c] Determined by ^1H NMR spectra with $Eu(hfc)_3$.

$TiCl_4$−Zn[15] as a reducing agent, these nonelectrochemical methods were employed for the reduction of **1a**. However, the reactions of **1a** with Na in Et_2O or THF and with SmI_2 in THF−HMPA under the reported conditions gave complex mixtures, and no hydrodimer was detected. Only when the reaction was carried out with $TiCl_4$−Zn in THF according to the reported method was the cyclized hydrodimer **2a** obtained in 35% yield and R,S,R/S,R,S = 70:30 selectivity.

Experimental Section

Starting Materials. Optically active 3-acyl-2-oxazolidinones **1** were prepared by treatment of optically active 2-oxazolidinones with *n*-BuLi/hexane and acyl chlorides successively in THF at −30 °C according to the reported method.[16] In a similar manner, 3-*trans*-cinnamoyl-2-oxazolidinethione **11a** and 2-thiazolidinethione **11b** were synthesized from (*S*)-4-isopropyl-2-oxazolidinethione and (*S*)-4-isopropyl-2-thiazolidinethione,[17] respectively. All the starting materials were purified by column chromatography on silica gel or recrystallization from hexane−ethyl acetate.

(*S*)-3-*trans*-Cinnamoyl-4-isobutyl-2-oxazolidinone (1a). R_f = 0.45 (hexane−ethyl acetate, 5:1). mp 65−66 °C. $[\alpha]^{20}_D$ +87.1 (*c* 1.54, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.99 (d, 3 H, *J* = 6.4 Hz), 1.01 (d, 3 H, *J* = 6.4 Hz), 1.40−1.78 (m, 2 H), 1.78−1.98 (m, 1 H), 4.16 (dd, 1 H, *J* = 2.8, 8.6 Hz), 4.43 (t, 1 H, *J* = 8.6 Hz), 4.54−4.70 (m, 1 H), 7.36−7.49 (m, 3 H), 7.57−7.70 (m, 2 H), 7.83 (d, 1 H, *J* = 15.7 Hz), 7.90 (d, 1 H, *J* = 15.7 Hz).

(*S*)-3-*trans*-Cinnamoyl-4-isopropyl-2-oxazolidinone (1b). R_f = 0.3 (hexane−ethyl acetate, 5:1). $[\alpha]^{20}_D$ +89.9 (*c* 2.07, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.92 (d, 3 H, *J* = 7.0 Hz), 0.95 (d, 3 H, *J* = 7.0 Hz), 2.33−2.59 (m, 1 H), 4.19−4.40 (m, 2 H), 4.50−4.62 (m, 1 H), 7.32−7.48 (m, 3 H), 7.56−7.69 (m, 2 H), 7.85 (d, 1 H, *J* = 15.8 Hz), 7.96 (d, 1 H, *J* = 15.8 Hz).

(*S*)-4-Benzyl-3-*trans*-cinnamoyl-2-oxazolidinone (1c). mp 122−123 °C. $[\alpha]^{20}_D$ +56.3 (*c* 1.82, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 2.86 (dd, 1 H, *J* = 9.5, 13.4 Hz), 3.39 (dd, 1 H, *J* = 3.3, 13.4 Hz), 4.16−4.37 (m, 2 H), 4.73−4.90 (m, 1 H), 7.20−7.52 (m, 8 H), 7.59−7.75 (m, 2 H), 7.94 (s, 2 H).

(*R*)-3-*trans*-Cinnamoyl-4-phenyl-2-oxazolidinone (1d). mp 172−173 °C. $[\alpha]^{20}_D$ −5.2 (*c* 2.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 4.33 (dd, 1 H, *J* = 3.7, 8.8 Hz), 4.75 (t, 1 H, *J* = 8.8 Hz), 5.57 (dd, 1 H, *J* = 3.7, 8.8 Hz), 7.30−7.50 (m, 3 H), 7.54−7.68 (m, 2 H), 7.79 (d, 1 H, *J* = 15.8 Hz), 7.95 (d, 1 H, *J* = 15.8 Hz).

(4*S*,5*R*)-3-*trans*-Cinnamoyl-4-methyl-5-phenyl-2-oxazolidinone (1e). mp 118 °C. $[\alpha]^{20}_D$ −85.0 (*c* 1.55, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.98 (d, 3 H, *J* = 6.6 Hz), 4.80−4.98 (m, 1 H), 5.73 (d, 1 H, *J* = 7.3 Hz), 7.29−7.52 (m, 8 H), 7.58−7.71 (m, 2H), 7.87 (d, 1 H, *J* = 15.8 Hz), 7.96 (d, 1 H, *J* = 15.8 Hz).

(*S*)-3-(*trans*-4-Fluorocinnamoyl)-4-isobutyl-2-oxazolidinone (1f). R_f = 0.8 (hexane−ethyl acetate, 2:1). mp 77−78 °C. $[\alpha]^{20}_D$ +90.9 (*c* 1.39, $CHCl_3$). IR (KBr) 1736, 1605, 1510, 837, 756 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.99 (d, 3 H, *J* = 6.5 Hz), 1.00 (d, 3 H, *J* = 6.5 Hz), 1.49−1.68 (m, 2 H), 1.79−1.90 (m, 1 H), 4.15 (dd, 1 H, *J* = 2.7, 8.4 Hz), 4.43 (t, 1 H, *J* = 8.4 Hz), 4.57−4.64 (m, 1 H), 7.04−7.11 (m, 2 H), 7.57−7.62 (m, 2 H), 7.77 (d, 1 H, *J* = 15.9 Hz), 7.83 (d, 1 H, *J* = 16.2 Hz). ^{13}C NMR ($CDCl_3$) δ 21.48 (q), 23.19 (q), 24.61 (d), 41.36 (t), 53.01 (d), 67.55 (t), 115.78 (d, J_{CCF} = 19.8 Hz), 116.76 (d), 130.27 (d, J_{CCCF} = 6.6 Hz), 130.66 (s), 144.32 (d), 153.53 (s), 163.83 (s, J_{CF} = 247.9 Hz), 164.64 (s). Anal. Calcd for $C_{16}H_{18}NO_3F$: C, 65.97; H, 6.23; N, 4.81. Found: C, 65.96; H, 6.27; N, 4.74.

(*S*)-3-(*trans*-2-Methoxycinnamoyl)-4-isobutyl-2-oxazolidinone (1g). R_f = 0.3 (hexane−ethyl acetate, 5:1). mp 82−83 °C. $[\alpha]^{20}_D$ +92.9 (*c* 1.58, $CHCl_3$). IR (KBr) 1760, 1670, 1590, 750 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.98 (d, 3 H, *J* = 6.5 Hz), 1.00 (d, 3 H, *J* = 6.5 Hz), 1.48−1.68 (m, 2 H), 1.83−1.92 (m, 1 H), 3.89 (s, 3 H), 4.13 (dd, 1 H, *J* = 2.8, 8.6 Hz), 4.41 (t, 1 H, *J* = 8.6 Hz), 4.45−4.65 (m, 1 H), 6.90−6.99 (m, 2 H), 7.27−7.39 (m, 1 H), 7.62 (dd, 1 H, *J* = 1.8, 7.7 Hz), 7.95 (d, 1 H, *J* = 15.9 Hz), 8.20 (d, 1 H, *J* = 15.9 Hz). ^{13}C NMR ($CDCl_3$) δ 21.58 (q), 23.34 (q), 24.81 (d), 41.55 (t), 53.20 (d), 55.41 (q), 67.60 (t), 111.08 (d), 117.35 (d), 120.63 (d), 123.56 (s), 129.15 (d), 131.79 (d), 141.29 (d), 153.68 (s), 158.57 (s), 165.43 (s). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.25; H, 6.99; N, 4.58.

(*S*)-3-(*trans*-3-Methoxycinnamoyl)-4-isobutyl-2-oxazolidinone (1h). R_f = 0.3 (hexane−ethyl acetate, 5:1). $[\alpha]^{20}_D$ +80.9 (*c* 3.54, $CHCl_3$). IR (neat) 1774, 1678, 1620, 1580, 704, 679 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.99 (d, 3 H, *J* = 6.5 Hz), 1.00 (d, 3 H, *J* = 6.5 Hz), 1.48−1.71 (m, 2 H), 1.83−1.92 (m, 1 H), 3.83 (s, 3 H), 4.10−4.16 (m, 1 H), 4.42 (t, 1 H, *J* = 8.1 Hz), 4.56−4.65 (m, 1 H), 6.93−6.96 (m, 1 H), 7.11−7.33 (m, 3 H), 7.76−7.90 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 21.58 (q), 23.29 (q), 24.81 (d), 41.55 (t), 53.20 (d), 55.21 (q), 67.65 (t), 113.33 (d), 116.46 (d), 117.49 (d), 121.16 (d), 129.73 (d), 135.90 (s), 145.84 (d), 153.63 (s), 159.84 (s), 164.89 (s). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.18; H, 7.11; N, 4.53.

(*S*)-3-(*trans*-4-Methoxycinnamoyl)-4-isobutyl-2-oxazolidinone (1i). R_f = 0.65 (hexane−ethyl acetate, 2:1). mp 84−85 °C. $[\alpha]^{20}_D$ +82.2 (c 1.28, $CHCl_3$). IR (KBr) 1765, 1667, 1590, 1510, 995, 830 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.98 (d, 3 H, *J* = 6.5 Hz), 1.00 (d, 3 H, *J* = 6.5 Hz) 1.48−1.70 (m, 2 H), 1.82−1.90 (m, 1 H), 3.83 (s, 3 H), 4.13 (dd, 1 H, *J* = 2.8, 8.6 Hz), 4.41 (t, 1 H, *J* = 8.6 Hz), 4.55−4.63 (m, 1 H), 6.88−6.92 (m, 2 H), 7.54−7.57 (m, 2 H), 7.78 (d, 2 H, *J* = 4.3 Hz). ^{13}C NMR ($CDCl_3$) δ 21.53 (q), 23.29 (q), 24.76 (d), 41.50 (t), 53.11 (d), 55.21 (q), 67.55 (t), 114.16 (d), 114.51 (d), 127.28 (s), 130.22 (d), 145.65 (d), 153.68 (s), 161.56 (s), 165.68 (s). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.26; H, 7.01; N, 4.54.

(*S*)-3-[*trans*-3-(1-Naphthyl)propenoyl]-4-isobutyl-2-oxazolidinone (1j). R_f = 0.35 (hexane−ethyl acetate, 5:1). mp 65−66 °C. $[\alpha]^{20}_D$ +95.9 (c 1.09, $CHCl_3$). IR (KBr) 1770, 1660, 1605, 760 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.00 (d, 3 H, *J* = 6.2 Hz), 1.02 (d, 3 H, *J* = 6.5 Hz), 1.51−1.75 (m, 2 H), 1.87−1.96 (m, 1

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H), 4.15 (dd, 1 H, J = 3.1, 8.3 Hz), 4.43 (t, 1 H, J = 8.3 Hz), 4.60−4.67 (m, 1 H), 7.46−7.59 (m, 3 H), 7.85−8.01 (m, 4 H), 8.23 (d, 1 H, J = 8.4 Hz), 8.70 (d, 1 H, J = 15.4 Hz). ^{13}C NMR ($CDCl_3$) δ 21.58 (q), 23.34 (q), 24.86 (d), 41.60 (t), 53.25 (d), 67.75 (t), 119.60 (d), 123.22 (d), 125.42 (d), 125.57 (d), 126.06 (d), 126.84 (d), 128.66 (d), 130.81 (d), 131.54 (s), 131.69 (s), 133.65 (s), 142.66 (d), 153.68 (s), 164.99 (s). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.24; H, 6.57; N, 4.28.

(*S*)-3-*cis*-Cinnamoyl-4-isobutyl-2-oxazolidinone (8). R_f = 0.35 (hexane−ethyl acetate, 5:1). mp 68−69 °C. $[\alpha]^{20}_D$ +124 (*c* 1.10, $CHCl_3$). IR (KBr) 1745, 1685, 1608, 980, 795, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 6 H, J = 6.8 Hz), 1.45−1.66 (m, 2 H), 1.81−1.89 (m, 1 H), 4.12 (dd, 1 H, J = 3.0, 8.5 Hz), 4.38 (t, 1 H, J = 8.5 Hz), 4.50−4.59 (m, 1 H), 6.83 (d, 1 H, J = 12.7 Hz), 7.00 (d, 1 H, J = 12.7 Hz), 7.30−7.40 (m, 3 H), 7.50−7.55 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 21.48 (q), 23.29 (q), 24.66 (d), 41.11 (t), 52.81 (d), 67.50 (t), 120.19 (d), 128.02 (d), 128.95 (d), 129.34 (d), 134.87 (s), 142.32 (d), 153.33 (s), 164.69 (s). Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.32; H, 7.05; N, 5.08.

(*S*)-3-Phenylpropioloyl-4-isobutyl-2-oxazolidinone (9). R_f = 0.35 (hexane−ethyl acetate, 5:1). $[\alpha]^{20}_D$ +54.4 (*c* 2.15, $CHCl_3$). IR (neat) 1780, 1650, 990, 750, 725, 685 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.99 (d, 6 H, J = 6.2 Hz), 1.49−1.71 (m, 2 H), 1.83−1.93 (m, 1 H), 4.15 (dd, 1 H, J = 2.7, 8.2 Hz), 4.42 (t, 1 H, J = 8.2 Hz), 4.51−4.60 (m, 1 H), 7.35−7.50 (m, 3 H), 7.64−7.70 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 21.58 (q), 23.19 (q), 24.66 (d), 41.21 (t), 52.96 (d), 67.50 (t), 81.16 (s), 93.99 (s), 119.70 (s), 128.46 (d), 130.81 (d), 133.11 (d), 150.49 (s), 152.06 (s). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.36; N, 5.16. Found: C, 70.64; H, 6.46; N, 5.00.

(*S*)-3-*trans*-Cinnamoyl-4-isobutyl-2-oxazolidinethione (11a). R_f = 0.35 (hexane−ethyl acetate, 2:1). mp 53−54 °C. $[\alpha]^{20}_D$ +166 (*c* 2.24, $CHCl_3$). IR (KBr) 1677, 1612, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.92 (d, 3 H, J = 6.8 Hz), 0.96 (d, 3 H, J = 7.0 Hz), 2.44−2.50 (m, 1 H), 4.43−4.50 (m, 2 H), 4.76−4.82 (m, 1 H), 7.39−7.42 (m, 3 H), 7.59−7.63 (m, 2 H), 7.75 (d, 1 H, J = 15.7 Hz), 8.44 (d, 1 H, J = 15.7 Hz). ^{13}C NMR ($CDCl_3$) δ 14.82 (q), 18.10 (q), 28.82 (d), 63.34 (d), 67.89 (t), 118.81 (d), 128.41 (d), 128.75 (d), 130.47 (d), 134.53 (s), 145.01 (d), 166.26 (s), 186.33 (s). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.50; H, 6.29; N, 5.01.

(*S*)-3-*trans*-Cinnamoyl-4-isobutyl-2-thiazolidinethione (11b). R_f = 0.5 (hexane−ethyl acetate, 5:1). $[\alpha]^{20}_D$ +222 (*c* 3.37 $CHCl_3$). IR (neat) 1674, 1614, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 3 H, J = 6.5 Hz), 1.07 (d, 3 H, J = 7.0 Hz), 2.47−2.55 (m, 1 H), 3.13 (dd, 1 H, J = 2.7, 11.3 Hz), 3.56 (dd, 1 H, J = 8.2, 11.3 Hz), 5.06−5.12 (m, 1 H), 7.37−7.39 (m, 4 H), 7.53−7.56 (m, 1 H), 7.66 (d, 1 H, J = 15.6 Hz), 7.93 (d, 1 H, J = 15.6 Hz). ^{13}C NMR ($CDCl_3$) δ 16.92 (q), 18.69 (q), 30.37 (d), 30.55 (t), 71.68 (d), 119.91 (d), 128.04 (d), 128.65 (d), 129.99 (d), 134.39 (s), 143.19 (d), 166.36 (s), 202.23 (s). Anal. Calcd for $C_{15}H_{17}NOS_2$: C, 61.82; H, 5.88; N, 4.81. Found: C, 61.96; H, 5.93; N, 4.65.

General Procedure for Constant Current Electrolysis. A solution of **1** (1 mmol) and Et_4NOTs (1.5 g, 5 mmol) in dry acetonitrile (16.5 mL) was put into a 40 mL beaker (3 cm diameter, 6 cm height) equipped with a lead cathode (5 × 5 cm^2) and a platinum anode (2 × 2 cm^2). Electricity was passed at a constant current of 0.1 A at room temperature until almost all of **1** was consumed (ca. 250 c). The mixture was poured into water (50 mL) and extracted with ether. The cyclized hydrodimers **2** were isolated as diastereomeric mixtures by column chromatography on silica gel. Diastereomers of **2b** and **2d** could be separated by column chromatography and further purified by recrystallization from hexane−ethyl acetate.

2a (85:15 mixture of two diastereomers). R_f = 0.22 (hexane−ethyl acetate, 5:1). IR (neat) 1778, 1747, 1693,764, 733, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.84 (d, 0.45 H, J = 6.5 Hz), 0.87 (d, 0.45 H, J = 6.2 Hz), 0.94 (d, 2.55 H, J = 5.9 Hz), 0.96 (d, 2.55 H, J = 5.9 Hz), 1.48−1.67 (m, 2 H), 1.72−1.88 (m, 1 H), 2.60−2.77 (m, 1 H), 2.93−3.07 (m, 1 H), 3.46−3.62 (m, 1 H), 4.00−4.12 (m, 2 H), 4.27 (t, 0.85 H, J = 8.3 Hz), 4.35−4.53 (m, 1.15 H), 5.50 (d, 1 H, J = 10.9 Hz), 7.10−7.32 (m, 10 H). Anal. Calcd for $C_{25}H_{27}NO_4$: C, 71.24; H, 6.45; N, 3.32. Found: C, 71.16; H, 6.52; N, 3.14.

(*R,S,R*)-2b (Major). R_f = 0.55 (hexane−ethyl acetate, 2:1). mp 159−161 °C. $[\alpha]^{20}_D$ −59.0 (*c* 0.50, $CHCl_3$). IR (KBr) 1770, 1750, 1680, 750, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 3 H, J = 7.0 Hz), 1.01 (d, 3 H, J = 6.7 Hz), 2.25−2.48 (m, 1 H), 2.68 (dd, 1 H, J = 11.7, 19.7 Hz), 3.04 (dd, 1 H, J = 7.7, 19.7 Hz), 3.47−3.68 (m, 1 H), 4.06 (t, 1 H, J = 11.9 Hz), 4.21 (d, 2 H, J = 5.2 Hz), 4.34−4.48 (m, 1 H), 5.52 (d, 1 H, J = 11.9 Hz), 7.10−7.32 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 13.99 (q), 17.46 (q), 27.78 (d), 46.22 (t), 47.28 (d), 51.83 (d), 58.26 (d), 62.33 (d), 62.93 (t), 126.95 (d), 127.12 (d), 127.41 (d), 127.67 (d), 128.51 (d), 138.96 (s), 139.96 (s), 153.85 (s), 167.47 (s), 207.75 (s). Anal. Calcd for $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.60; H, 6.45; N, 3.53.

(*S,R,S*)-2b (Minor). R_f = 0.50 (hexane−ethyl acetate, 2:1). mp 188−190 °C. $[\alpha]^{20}_D$ +194 (*c* 0.50, $CHCl_3$). IR (KBr) 1770, 1750, 1680, 770, 750, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.53 (d, 3 H, J = 6.2 Hz), 0.79 (d, 3 H, J = 7.1 Hz), 2.02−2.25 (m, 1 H), 2.69 (dd, 1 H, J = 10.2, 20.2 Hz), 3.03 (dd, 1 H, J = 8.1, 20.2 Hz), 3.48−3.70 (m, 1 H), 4.04 (t, 1 H, J = 12.0 Hz), 4.17 (dd, 1 H, J = 2.5, 8.2 Hz), 4.32 (t, 1 H, J = 8.2 Hz), 4.39−4.50 (m, 1 H), 5.57 (d, 1 H, J = 12.0 Hz), 7.04−7.48 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 13.96 (q), 17.37 (q), 28.16 (d), 46.24 (t), 47.45 (d), 53.13 (d), 58.69 (d), 62.12 (d), 63.27 (t), 127.05 (d), 127.22 (d), 127.44 (d), 128.50 (d), 128.57 (d), 138.36 (s), 139.88 (s), 154.08 (s), 167.92 (s), 208.32 (s). Anal. Calcd for $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.58; H, 6.42; N, 3.54.

2c (70:30 Mixture of Two Diastereomers). R_f = 0.46, 0.59 (hexane−ethyl acetate, 2:1). IR (KBr) 1780, 1740, 1680, 750, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.60−3.17 (m, 3 H), 3.25−3.43 (m, 1 H), 3.46−3.70 (m, 1 H), 4.00−4.20 (m, 2.7 H), 4.30 (t, 0.3 H, J = 8.1 Hz), 4.53−4.80 (m, 1 H), 5.52 (d, 1 H, J = 11.0 Hz), 6.78−6.92 (m, 0.6 H), 6.95−7.40 (m, 14.4 H).

(*S,R,S*)-2d (Major). R_f = 0.53 (hexane−ethyl acetate, 2:1). mp 186−188 °C. $[\alpha]^{20}_D$ −37.0 (*c* 1.00, $CHCl_3$). IR (KBr) 1770, 1740, 1690, 760, 745, 710, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.60 (dd, 1 H, J = 12.1, 18.8 Hz), 3.01 (dd, 1 H, J = 8.0, 18.8 Hz), 3.45−3.67 (m, 1 H), 4.00 (t, 1 H, J = 12.1 Hz), 4.21 (dd, 1 H, J = 5.2, 8.8 Hz), 4.63 (t, 1 H, J = 8.8 Hz), 5.33 (dd, 1 H, J = 5.2, 8.8 Hz), 5.50 (d, 1 H, J = 12.1 Hz), 7.02−7.50 (m, 15 H). ^{13}C NMR ($CDCl_3$) δ 46.39 (t), 47.47 (d), 51.54 (d), 57.90 (d), 62.49 (d), 69.81 (t), 125.95 (d), 127.08 (d), 127.26 (d), 127.46 (d), 127.78 (d), 128.63 (d), 129.23 (d), 138.,40 (s), 139.02 (s), 139.87 (s), 153.78 (s), 166.90 (s), 207.24 (s). Anal. Calcd for $C_{27}H_{23}NO_4$: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.16; H, 5.48; N, 3.24.

(*R,S,R*)-2d (Minor). R_f = 0.44 (hexane−ethyl acetate, 2:1). mp 168−170 °C. $[\alpha]^{20}_D$ −184 (c 1.00, $CHCl_3$). IR (KBr) 1750, 1690, 1660, 760, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.61 (dd, 1 H, J = 12.1, 19.1 Hz), 2.95 (dd, 1 H, J = 8.1, 19.1 Hz), 3.42−3.64 (m, 1 H), 3.88 (t, 1 H, J = 11.8 Hz), 4.07 (dd, 1 H, J = 3.4, 8.8 Hz), 4.62 (t, 1 H, J = 8.8 Hz), 5.38 (dd, 1 H, J = 3.4, 8.8 Hz), 5.60−5.30 (m, 1 H), 6.67−7.23 (m, 15 H). ^{13}C NMR ($CDCl_3$) δ 46.59 (t), 47.50 (d), 53.52 (d), 57.64 (d), 62.38 (d), 69.87 (t), 125.37 (d), 127.19 (d), 127.34 (d), 127.55 (d), 127.66 (d), 128.53 (d), 128.70 (d), 129.19 (d), 138.33 (s), 138.43 (s), 139.93 (s), 153.84 (s), 168.07 (s), 208.68 (s). Anal. Calcd for $C_{27}H_{23}NO_4$: C, 76.22; H, 5.45; N, 3.29. Found: C, 76.10; H, 5.38; N, 3.19.

2e (75:25 Mixture of Two Diastereomers). R_f = 0.54, 0.59 (hexane−ethyl acetate, 2:1). IR (KBr) 1760, 1680, 760, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.77 (d, 0.75 H, J = 6.6 Hz), 0.93 (d, 2.25 H, J = 6.5 Hz), 2.60−2.80 (m, 1 H), 3.05 (dd, 1 H, J = 8.0, 19.0 Hz), 3.50−3.69 (m, 1 H), 4.00−4.17 (m, 1 H), 4.67−4.83 (m, 1 H), 5.50 (d, 1 H, J = 12.8 Hz), 5.57 (d, 0.75 H, J = 7.7 Hz), 5.77 (d, 0.25 H, J = 7.2 Hz), 7.10−7.50 (m, 15 H).

2f (75:25 Mixture of Two Diastereomers). R_f = 0.20, 0.28 (hexane−ethyl acetate, 5:1). IR (KBr) 1770, 1750, 1685, 830 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 0.75 H, J = 6.5 Hz), 0.88 (d, 0.75 H, J = 6.5 Hz), 0.94 (d, 2.25 H, J = 6.2 Hz), 0.96 (d, 2.25 H, J = 5.1 Hz), 1.30−1.90 (m, 3 H), 2.54−2.78 (m 1 H), 2.86−3.06 (m, 1 H,), 3.37−3.58 (m, 1 H), 3.90−4.03 (m, 1 H), 4.05−4.17 (m, 1 H), 4.27−4.51 (m, 2 H), 5.32−5.55 (m, 1 H), 6.86−6.98 (m, 4 H), 7.04−7.17 (m, 4 H).

2g (65:35 Mixture of Two Diastereomers). R_f = 0.60 (hexane−ethyl acetate, 2:1). IR (neat) 1770, 1740, 1685, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.84 (d, 1.05 H, J = 6.5 Hz), 0.88 (d, 1.05 H, J = 6.2 Hz), 0.93 (d, 1.95 H, J = 5.9 Hz), 0.95 (d, 1.95 H, J = 6.5 Hz), 1.25−1.85 (m, 3 H), 2.58−2.73 (m, 1 H), 2.87−3.01 (m, 1 H), 3.66 (s, 1.95 H), 3.67 (s, 1.05 H), 3.75 (s, 3 H), 3.57−3.87 (m, 1 H), 4.00−4.30 (m, 2 H), 4.34−4.53 (m, 2 H), 5.56−6.00 (m, 1 H), 6.72−6.88 (m, 4 H), 7.07−7.28 (m, 4 H).

2h (70:30 Mixture of Two Diastereomers). R_f = 0.60 (hexane−ethyl acetate, 2:1). IR (neat) 1780, 1747, 1693, 735, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 0.9 H, J = 6.2 Hz), 0.88 (d, 0.9 H, J = 6.5 Hz), 0.94 (d, 2.1 H, J = 6.2 Hz), 0.96 (d, 2.1 H, J = 5.9 Hz), 1.25−1.80 (m, 3 H), 2.57−2.75 (m, 1 H), 2.92−3.06 (m, 1 H), 3.42−3.60 (m, 1 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 3.95−4.13 (m, 2 H), 4.30 (t, 0.7 H, J = 8.2 Hz), 4.37−4.55 (m, 1.3 H), 5.30−5.56 (m, 1 H), 6.62−6.81 (m, 6 H), 7.06−7.20 (m, 2 H).

2i (80:20 Mixture of Two Diastereomers). R_f = 0.56 (hexane−ethyl acetate, 2:1). IR (neat) 1770, 1740, 1680, 1605, 825, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 0.6 H, J = 6.5 Hz), 0.88 (d, 0.6 H, J = 6.2 Hz), 0.93 (d, 2.4 H, J = 5.9 Hz), 0.95 (d, 2.4 H, J = 5.9 Hz), 1.40−1.87 (m, 3 H), 2.52−2.71 (m, 1 H), 2.87−3.03 (m, 1 H), 3.37−3.52 (m, 1 H), 3.71 (s, 2.4 H), 3.72 (s, 0.6 H), 3.73 (s, 3 H), 3.87−4.16 (m, 2 H), 4.28 (t, 0.8 H, J = 8.2 Hz), 4.36−4.51 (m, 1.2 H), 5.30−5.53 (m, 1 H), 6.70−6.81 (m, 4 H), 7.00−7.12 (m, 4 H).

2j (60:40 Mixture of Two Diastereomers). R_f = 0.60 (hexane−ethyl acetate, 2:1). IR (KBr) 1770, 1740, 1680, 790, 770 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.65 (d, 1.2 H, J = 5.7 Hz), 0.73 (d, 1.2 H, J = 6.2 Hz), 0.80−1.05 (m, 3.6 H), 1.35−1.85 (m, 3 H), 2.55−2.98 (m, 1 H), 3.10−3.47 (m, 1 H), 3.70−4.83 (m, 4 H), 5.53−5.84 (m, 1 H), 7.22−8.30 (m, 14 H).

10. R_f = 0.33 (hexane−ethyl acetate, 2:1). mp 185−186 °C. $[\alpha]^{20}_D$ +33.8 (*c* 0.37, $CHCl_3$). IR (KBr) 1763, 1697, 755, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.90 (d, 6 H, J = 6.2 Hz), 0.91 (d, 6 H, J = 6.5 Hz), 1.20−1.32 (m, 2 H), 1.35−1.63 (m, 4 H), 3.82−4.00 (m, 6 H), 4.16 (t, 2 H, J = 8.4 Hz), 4.28−4.33 (m, 2 H), 7.22−7.40 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 21.72 (q), 23.29 (q), 24.61 (d), 41.16 (t), 42.29 (t), 52.91 (d), 67.35 (t), 127.24 (d), 127.63 (d), 128.61 (d), 134.97 (s), 141.24 (s), 170.42 (s). Anal. Calcd for $C_{32}H_{38}N_2O_6$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.16; H, 7.10; N, 4.98.

General Procedure for Methanolysis of Cyclized Hydrodimers 2. To a solution of sodium methoxide (2.2 mmol) in MeOH (20 mL) was added a solution of **2** (1 mmol) in MeOH (5 mL) at 0 °C, and the temperature was allowed to equilibrate to room temperature. After being stirred for 8 h, the mixture was neutralized with *1* N HCl, diluted with sat. NaCl (aq), and then extracted with ether. Dimethyl esters **4** were isolated by column chromatography on silica gel (hexane−ethyl acetate). Enantioselectivity in **4** was determined by ^{1}H NMR analysis with Eu(hfc)$_3$. The enantiomeric excess of **4a** was alternatively measured by chiral HPLC analysis: column, Chiralpak OT (Daicel Chemical Ind., Ltd); eluent, methanol; flow rate, 0.50 L/min; column temperature, 0 °C; detection, 284 nm; retention times, 15.3 min for (*S*,*S*)-**4a** and 18.2 min for (*R*,*R*)-**4a**. Optically pure enantiomers of **4a** were obtained from the separated diastereomers of **2b** and **2d**.

(*R*,*R*)-4a (>98% ee). R_f = 0.30 (hexane−ethyl acetate, 5:1). $[\alpha]^{20}_D$ +17.4 (*c* 2.10, $CHCl_3$). IR (neat) 1725, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.54−2.81 (m, 4 H), 3.42−3.58 (m, 2 H), 3.55 (s, 6 H), 6.82−6.96 (m, 4 H), 7.10−7.24 (m, 6 H). ^{13}C NMR ($CDCl_3$) δ 37.47 (t), 46.14 (d), 51.52 (q), 126.86 (d), 127.98 (d), 128.90 (d), 140.19 (s), 172.76 (s). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.55; H, 7.78.

(*S*,*S*)-4a (>98% ee). $[\alpha]^{20}_D$ −17.3 (*c* 1.00, $CHCl_3$).

4f (54% ee). R_f = 0.62 (hexane−ethyl acetate, 2:1). $[\alpha]^{20}_D$ +7.1 (*c* 2.0, $CHCl_3$). IR (neat) 1750, 1732, 837 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.52−2.63 (m, 2 H), 2.68−2.79 (m, 2 H), 3.38−3.49 (m, 2 H), 3.56 (s, 6 H), 6.76−7.12 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 38.12 (t), 45.62 (d), 51.59 (q), 114.70 (d, J_{CCF} = 19.8 Hz), 130.03 (d, J_{CCCF} = 6.6 Hz), 135.56 (s), 161.56 (s, J_{CF} = 244.6 Hz), 172.09 (s). Anal. Calcd for $C_{20}H_{20}O_4F_2$: C, 66.29; H, 5.56. Found: C, 66.36; H, 5.59.

4g (38% ee). R_f = 0.57 (hexane−ethyl acetate, 2:1); $[\alpha]^{20}_D$ +13.4 (*c* 1.78, $CHCl_3$). IR (neat) 1739, 1732, 754 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.61−2.77 (m, 4 H), 3.51 (s, 6 H), 3.75 (s, 6 H), 4.01−4.13 (m, 2 H), 6.65−6.75 (m, 6 H), 7.03−7.10 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 37.05 (t), 39.01 (d), 51.25 (q), 55.11 (q), 110.15 (d), 119.60 (d), 127.28 (d), 129.39 (s), 129.59 (d), 157.35 (s), 173.02 (s). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.55; H, 6.90.

4h (44% ee). R_f = 0.58 (hexane−ethyl acetate, 2:1). $[\alpha]^{20}_D$ −9.7 (*c* 5.4, $CHCl_3$). IR (neat) 1750, 1732, 785, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.55−2.78 (m, 4 H), 3.42−3.53 (m, 2 H), 3.57 (s, 6 H), 3.68 (s, 6 H), 6.41 (t, 2 H, J = 1.9 Hz), 6.53 (d, 2 H, J = 7.8 Hz), 6.67−6.74 (m, 2 H), 7.10 (t, 2 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ 37.34 (t), 46.01 (d), 51.44 (q), 54.87 (q), 112.30 (d), 114.31 (d), 121.07 (d), 128.66 (d), 141.58 (s), 158.96 (s), 172.28 (s). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.49; H, 6.83.

4i (67% ee). R_f = 0.53 (hexane−ethyl acetate, 2:1). $[\alpha]^{20}_D$ +33.5 (*c* 1.60, $CHCl_3$). IR (neat) 1750, 1732, 1717, 814 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.48−2.60 (m, 2 H), 2.63−2.75 (m, 2 H), 3.35−3.47 (m, 2 H), 3.55 (s, 6 H), 3.75 (s, 6 H), 6.69−6.80 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 37.93 (t), 45.42 (d), 51.39 (q), 54.97 (q), 113.13 (d), 129.73 (d), 131.89 (s), 158.23 (s), 172.48(s). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.44; H, 6.80.

4j (12% ee). R_f = 0.61 (hexane−ethyl acetate, 2:1). mp 123−124 °C. $[\alpha]^{20}_D$ −9.5 (*c* 2.1, $CHCl_3$). IR (KBr) 1730, 780 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.75−3.00 (m, 4 H), 3.35 (s, 6 H), 4.52−4.76 (m, 2 H), 7.18−7.76 (m, 12 H), 8.31 (d, 2 H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ 37.68 (t), 39.69 (d), 51.39 (q), 123.27 (d), 124.74 (d), 125.33 (d), 125.86 (d), 127.28 (d), 128.80 (d), 131.84 (s), 133.89 (s), 137.91 (s), 172.43 (s). Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 78.67; H, 6.21.

Synthesis of Authentic Sample of (*S*,*S*)-4a. To an ice-cooled solution of (2*S*,3*S*)-diphenylsuccinic acid (1.0 g, 3.7 mmol), prepared by our method (>98% ee),[8c] in THF (15 mL) was added LAH (0.42 g, 11 mmol) and the suspension was stirred at room temperature for 24 h. After the usual workup, the crude diol (0.75 g) was treated with TsCl (1.7 g, 8.9 mmol) in pyridine (10 mL) at 5 °C for 3 h. The mixture was diluted with 1 M HCl (50 mL) and extracted with ether. The crude ditosylate (1.3 g) was stirred with NaCN (0.49 g, 10 mmol) in dry DMF (20 mL) at room temperature for 24 h. The mixtures were diluted with sat. NaCl(aq)(60 mL) and extracted with ether. The crude dinitrile (0.31 g) was refluxed with $Ba(OH)_2$ (1.0 g) in water (20 mL) for 12 h. After filtration, the aqueous solution was acidfied with concentrated HCl and extracted with CH_2Cl_2. The crude diacid (0.25 g) was dissolved in sat. HCl−MeOH, and the solution was stirred for 12 h at room temperature. After removal of the solvent, (*S*,*S*)-**4a** was isolated by column chromatography on silica gel (0.16 g, 13% total yield): $[\alpha]^{20}_D$ −17.1 (*c* 1.05, $CHCl_3$).

Hydrolysis of 2a. A 85:15 diastereomeric mixture of **2a** (406 mg, 1 mmol) was refluxed in 48% HBr (4 mL) and EtOH (5 mL) for 6 h. After cooling, the mixture was diluted with NaCl(aq)(30 mL) and extracted with ether. A 199 mg amount of *trans*-3,4-diphenylcyclopentanone **5** was isolated by column chromatography on silica gel (84% yield). The enantiomeric excess of **5** was determined on the basis of the reported value of the optical rotation for the enantiomer of **5** (lit.[7] 219).

(*R*,*R*)-5 (72% ee). R_f = 0.45 (hexane−ethyl acetate, 5:1). mp 162−165 °C. $[\alpha]^{20}_D$ −156 (*c* 2.06, $CHCl_3$). IR (KBr) 1735, 760, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.48−2.67 (m, 2 H), 2.79−2.96 (m, 2 H), 3.40−3.56 (m, 2 H), 7.08−7.28 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 47.17 (t), 50.11 (d), 126.84 (d), 127.19 (d), 128.56 (d), 140.85 (s), 215.74 (s). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.32; H, 6.85.

Reduction of 5. To a solution of **5** (118 mg, 0.5 mmol) in EtOH (5 mL) was added $NaBH_4$ (57 mg, 1.5 mmol) at room temperature. After being stirred for 30 min, the mixture was diluted with NaCl(aq)(30 mL) and extracted with ether. A 113 mg amount of 3,4-diphenylcyclopentanol **6** was isolated by column chromatography on silica gel (95% yield). The enantiomeric excess of **6** was measured by chiral HPLC analysis: column, Chiralpak OT (Daicel Chemical Ind., Ltd); eluent,

methanol; flow rate, 0.50 L/min; column temperature, 0 °C; detection, 284 nm; retention times, 9.3 min for (*S*,*S*)-**6** and 10.6 min for (*R*,*R*)-**6**.

***(R,R)*-6 (74% ee).** R_f = 0.50 (hexane−ethyl acetate, 2:1). mp 65−66 °C. $[\alpha]^{20}_D$ −112 (*c* 5.07, $CHCl_3$). IR (KBr) 3250, 750, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.72 (brs, 1 H), 1.84−1.96 (m, 1 H), 2.06−2.27 (m, 2 H), 2.62−2.76 (m, 1 H), 3.11 (dd, 1 H, J = 9.2, 19.7 Hz), 3.40−3.55 (m, 1 H), 4.55−4.63 (m, 1 H), 7.06−7.25 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 44.78 (t), 51.34 (d), 52.52 (d), 71.81 (d), 125.96 (d), 127.24 (d), 127.53 (d), 128.22 (d), 143.00 (s), 143.59 (s). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.64; H, 7.61.

Electroreduction of 1a in $LiClO_4$−THF. A solution of **1a** (272 mg, 1 mmol) and $LiClO_4$ (3.0 g, 28 mmol) in dry THF (16.5 mL) was put into a 40 mL beaker (3 cm diameter, 6 cm height) equipped with a lead cathode (5 × 5 cm^2) and a platinum anode (2 × 2 cm^2). Electricity was passed at a constant current of 0.1 A at room temperature until almost all of **1** was consumed (ca. 300 *c*). The mixture was poured into water (50 mL) and extracted with ether. The product **7a** was isolated as a diastereomeric mixture by column chromatography on silica gel (145 mg). R_f = 0.40−0.65 (hexane−ethyl acetate, 2:1). ^1H NMR ($CDCl_3$) δ 0.7−1.2 (m, 12 H), 1.2−2.1 (m, 6 H), 2.6−4.7 (m, 12 H), 6.6−7.8 (m, 10 H). Although the isolated **7a** was contaminated by small amounts of impurities, it was subjected to hydrolysis without further purification.

Hydrolysis of 7a. To an ice-cooled solution of a diastereomeric mixture of **7a** (145 mg) in THF (4 mL) and distilled water (3 mL) was added $LiOH \cdot H_2O$ (0.21 g, 5 mmol) and 30% H_2O_2 (1 mL) successively. The mixture was stirred for 24 h at room temperature and then quenched with 1.5 M Na_2SO_3 (4 mL) at 0 °C. After the addition of 1 M HCl (10 mL), the mixture was extracted with CH_2Cl_2. The crude diacid was dissolved in sat. HCl−MeOH, and the solution was stirred for 12 h at room temperature. After removal of the solvent, *dl*- and *meso*-**4a** were isolated by column chromatography on silica gel (38 and 34 mg, respectively, 44% total yield from **1a**). The enantiomeric excess of *dl*-**4a** was measured by ^1H NMR analysis with $Eu(hfc)_3$.

***meso*-4a.** R_f = 0.40 (hexane−ethyl acetate, 5:1). mp 174−177 °C (lit.[12b] 175−177 °C). IR (KBr) 1725, 705 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.30−2.54 (m, 4 H), 3.22−3.40 (m, 2 H), 3.36 (s, 6 H), 7.02−7.46 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 39.60 (t), 47.59 (d), 51.20 (q), 127.23 (d), 128.25 (d), 128.80 (d), 141.86 (s), 172.65 (s).

Supporting Information Available: Optimized conformations of anion radicals **C**−**F** obtained by semiempirical calculations (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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