Highly Enantioselective Claisen Rearrangement of Imidates Derived from Primary Allyl Alcohols†

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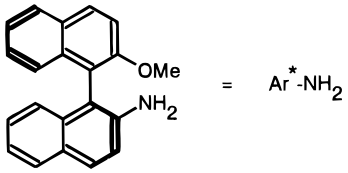
A highly enantioselective and diastereoselective Claisen rearrangement of *N*-arylimidates derived from an axially chiral binaphthylamine auxiliary is reported. Upon deprotonation of the imidates with lithium diethylamide, the resultant azaenolates rearrange at 0 °C to give anti α,*β*-disubstituted, *γ*,*δ*-unsaturated *N*-binaphthyl amides. A iodolactonization/zinc reduction sequence readily converts these amides into the corresponding carboxylic acids of 91−95% ee and allows an efficient recovery of the chiral auxiliary.

Introduction

The aliphatic Claisen rearrangement provides a facile access to synthetically valuable *γ*,*δ*-unsaturated carbonyl compounds with the option of simultaneously generating two new stereogenic centers α and *β* to the carbonyl group.[1] In the course of our studies on rearrangement reactions of allyl imidates,[2] we have recently achieved a highly diastereoselective conversion of prochiral allyl *N*-phenylimidates derived from primary allylic alcohols to racemic α,*β*-disubstituted, *γ*,*δ*-unsaturated anilides via [3,3] sigmatropic rearrangement of *N*-silyl ketene *N*,*O*-acetals.[2b,d] Here we give a full account on our observation[2a] that the transition from *N*-phenyl- to *N*-arylimidates easily available from binaphthylamine (*S*)-**1**[3] as a chiral auxiliary allows a highly enantioselective Claisen rearrangement with excellent simple diastereoselectivity.[4,5]

Results and Discussion

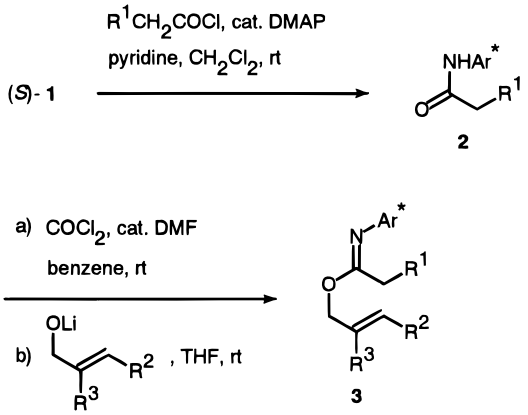
For the preparation of chirally modified imidates **3**, binaphthylamine (*S*)-**1** was acylated to give amides **2** (**2a**: R^1 = Me, 97% yield; **2b**: R^1 = Et, 97% yield), which



(*S*)- **1**

Figure 1.

Scheme 1



in turn were smoothly activated to imido chlorides with phosgene.[6] After coupling of the crude imido chlorides with the requisite lithium alkoxides (1.1−1.4 equiv), imidates **3** were isolated in good overall yield (Scheme 1, Table 1).

Surprisingly, no Claisen rearrangement occurred at room temperature after deprotonation/silylation of imidates **3** under our standard conditions.[2b,d] In order to test the deprotonation step separately, imidates **3d** and **3f** were treated with lithium diethylamide, and a subsequent intermolecular alkylation[7] using ethyl or methyl iodide was performed. Gratifying, a clean formation of epimers **4** and **5**, respectively, with pronounced asymmetric induction was noticed (Scheme 2). The stereochemical assignment for **4** and **5** follows from hydrolysis of **4** to a (2*S*)-methylbutyric amide identical to an authentic sample prepared by acylation of (*S*)-**1** with (2*S*)-

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† Dedicated to Professor H. J. Schäfer on the occasion of his 60th birthday.

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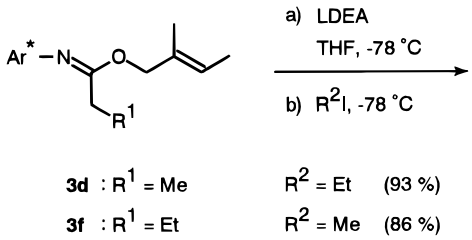
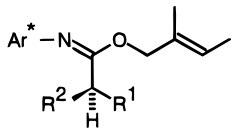
Table 1. Preparation of Imidates 3 and Enantioselective Claisen Rearrangement via Lithium Azaenolates 6

3, 7	R^1	R^2	R^3	yield of 3 (%)[a]	yield of 7 (%)[a]	time (h)[c]	7 anti(1):anti(2)[d]
a	Me	Me	H	72	78	5	97:3
b	Me	Et	H	72	60	8	97:3
c	Et	Me	H	69.	59	10	97:3
d	Me	Me	Me	62	56	23	96:4
e	Me	Et	Me	68	45	40	96:4
f	Et	Me	Me	73	47	48	>91:9

[a] Isolated yield after chromatographic purification. [b] Isolated yield of major diastereomer **7** [anti(1)] including minor diastereomers after chromatographic purification. [c] Rearrangement time (0 °C) after deprotonation of **3**. [d] Determined by ^{1}H NMR integration. The anti:syn ratio is ≥97:3 for all entries. Due to partly overlapping signals, only a lower limit for the ratio of the two anti diastereomers is listed for entry **f**.

Scheme 2

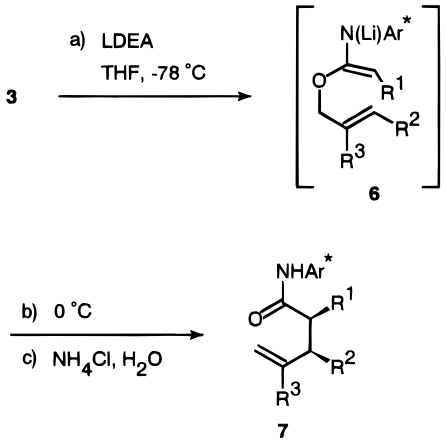




4 (*dr* = 84 : 16)

5 (*dr* = 94 : 6)

Scheme 3



methylbutyric anhydride. Encouraged by this result, we studied the [3,3] sigmatropic rearrangement of the intermediate lithium azaenolates as well.

To our delight, the lithiated species **6** already rearranged at 0 °C to give the desired γ,δ-unsaturated amides **7** (Scheme 3, Table 1). The reaction rate strongly depends on the substitution pattern. Whereas substrates with R^3 = Me (entries **d**–**f**) required 1–2 days for the rearrangement step, the sterically less encumbered azaenolates with R^3 = H (entries **a**–**c**) reacted within a few hours. All amides **7** were produced with extremely high anti selectivity, which can be rationalized by a $(Z)_{CC}$ configuration of the azaenolate fragment in **6** and a preferred chairlike transition state geometry for the

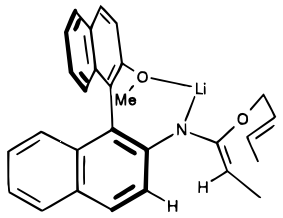
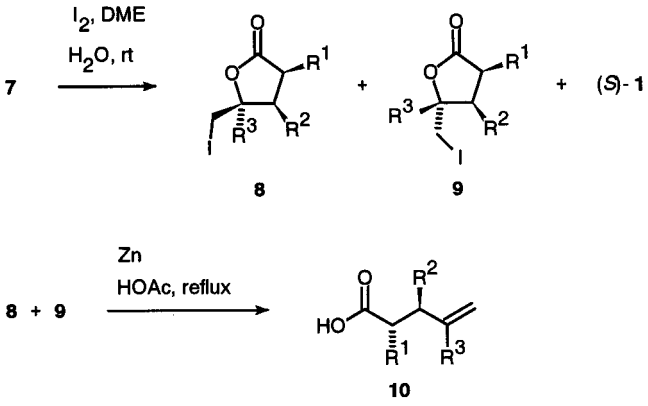


Figure 2.

Scheme 4



Claisen rearrangement.[2b,d] More importantly, the auxiliary control (anti(1):anti(2) in Table 1) turned out to be exceptional, too. Indeed, the ^{13}C NMR spectra of amides **7** recorded without prior separation of diastereomers showed only one set of signals for the major stereoisomer.[8] This implies an enhanced communication between the axially chiral auxiliary and the prostereogenic moiety of the substrate through chelation of the lithium atom in **6** with participation of the methoxy group. A transition state model based on this assumption and on an $(E)_{CN}$ configuration[2b,7] of the azaenolate is depicted in Figure 2 for the Claisen rearrangement of **6a** to amide **7a**. The stereochemical outcome can then be rationalized by a steric shielding of the *si* face of the prostereogenic azaenolate carbon by the naphthyl hydrogen β to the nitrogen atom. It is noteworthy that both the intermolecular α-alkylation and the intramolecular α-allylation involve a preferential *re* attack on the azaenolate double bond.

Our iodolactonization/reduction sequence developed for the mild hydrolysis of γ,δ-unsaturated anilides[9] was easily adapted to the conversion of *N*-binaphthyl amides **7** into carboxylic acids **10** without epimerization α to the carbonyl group (Scheme 4, Table 2). After iodolactonization of **7**, which proceeded with a diastereoselectivity resembling the corresponding transformation of related anilides,[9] the auxiliary (*S*)-**1** was recovered almost quantitatively. Subjecting the resultant mixture of iodolactones **8** and **9** to a zinc reduction led to the highly enantioenriched carboxylic acids **10**. Gratifyingly, capillary GC analysis of the methyl esters derived from **10** not only established an anti:syn ratio ≥99:1 for all entries but also allowed a precise determination of the enantiomeric excess and thus, a more accurate measurement of

(8) In order to rapidly prepare all four diastereomeric Claisen rearrangement products for analytical reasons, we also subjected imidates **3** to a thermal isomerization (see ref 2e) in refluxing decalin. As anticipated, these reactions proceeded cleanly and syn selectively but without significant auxiliary induction.

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Table 2. Iodolactonization/Reduction of Amides 7

7−10	yield of 8 + 9 (%)[a]	ratio 8:9[b]	yield of 10 (%)[a]	ee 10 (%)[c]
a	92	65:35	84	95
b	87	14:86	82	95
c	86	74:26	79	91
d	90	84:16	80	94
e	91	36:64	87	92
f	89	82:18	85	93

[a] Isolated yield after chromatographic purification. [b] Determined by GC analysis of the crude product. Racemic **8a/9a** and **8d/9d** are known compounds, see ref 9, while the relative configuration for entries **b**, **c**, **e**, **f** was assigned by comparison of ^{1}H and ^{13}C NMR shift data with **8a/9a** and **8d/9d**. [c] Determined by GC analysis of the corresponding methyl esters (CH_2N_2) on chiral cyclodextrin columns. The absolute configuration for entries **a**, **c** follows from the sign of optical rotation for the known acid **10a**, see ref 10, or the known benzyl esters of acids *ent*-**10a** and *ent*-**10c**, respectively, see ref 11. All other absolute configurations were assigned by analogy with entries **a** and **c**. In all cases, crude acids **10** contained only traces (≤1%) of the syn isomer.

the auxiliary control than ^{1}H NMR integration at the stage of **7**.[12]

Conclusion

In view of the high simple and auxiliary induced stereoselectivity as well as the relatively short times for rearrangement, this protocol for enantioselective Claisen rearrangement compares very favorably to published alternative procedures.[4,5] Moreover, we have not yet utilized a further enhancement in the relative proportion of the major diastereomer **7** by recrystallization or chromatographic separation of the solid mixture of rearrangement products obtained. This option and other aspects of this new method are currently under investigation.

Experimental Section

All reactions requiring exclusion of moisture were run under argon using flame-dried glassware. Solvents were dried by distillation from potassium (THF) or else CaH_2. Flash chromatography was performed on Merck silica gel 60 (40−63 μm). Capillary GC analyses were performed with a Shimadzu GC-14APFsc, a Shimadzu C-R6A integrator, a SE 54 CB column, 25 m length, 0.25 mm i.d., 0.25 μm film. Chiral capillary GC analyses of the carboxylic acids **10** were performed after esterification (CH_2N_2) on the following modified cyclodextrin columns. For **10a**, **10b**: Macherey and Nagel Lipodex E (70 % 2,6-pentyl-3-butyryl-γ-cyclodextrin, 30 % OV 17 01), 25 m length, 0.25 mm i.d., column temperature 45 °C; for **10c**: Supelco Beta-Dex 120, 30 m length, 0.25 mm i.d., 0.25 μm film, column temperature 55 °C; for **10d**: Supelco Beta-Dex 120, 30 m length, 0.25 mm i.d., 0.25 μm film, column temperature 65 °C; for **10e**: Macherey and Nagel Lipodex E (50% 6-methyl-2,3-pentyl-β-cyclodextrin, 50% OV 17 01), 25 m length, 0.25 mm i.d., column temperature 50 °C; for **10f**: Supelco Beta-Dex 120, 30 m length, 0.25 mm i.d., 0.25 μm film, column temperature 75 °C. HPLC separations were performed with a Knauer 64 pump, a Knauer 42.00 recorder, a Rheodyne injector, and a Knauer Polygosil 60 (5 μm) column, 250 mm length, 32 mm i.d. Melting points were determined on a Kofler microscope desk. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.47 MHz) were obtained on a Bruker WM 300; m = multiplet centered at, br = broad. ^{13}C multiplicities were determined using INEPT or DEPT pulse sequences. FT-IR spectra were obtained on a Bruker IFS 28, w = weak, s = strong, m = medium, br = broad. Mass spectra (70 eV) were recorded with a Varian MAT CH-7A + data system Finnigan MAT 200 (GC/MS), a Finnigan MAT 8230 + data system Finnigan SS 300 (GC/MS), and a Variant MAT CH-7 + data system Varian SS 200. Microanalyses were performed by the analytical laboratory of the Organisch-Chemisches Institut, Universität Münster.

Amides 2. General Procedure. To a solution of amine (*S*)-**1** (2.99 g, 10 mmol) in dry dichloromethane (10 mL) were added dry pyridine (0.89 mL, 11 mmol) and a small amount of DMAP. The mixture was cooled to 0 °C, and the requisite acid chloride (10.5 mmol) was added dropwise. After stirring for 16 h at rt, the mixture was washed successively with water (3×), sat. aqueous $NaHCO_3$ (1×), and brine (1×) and dried over $MgSO_4$. Removal of the solvent in vacuo provided a colorless residue that crystallized upon treatment with diethyl ether.

(*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)propionamide (2a). Yield 97%; mp 124 °C; R_f 0.38 (petroleum ether/ethyl acetate, 3:5); $[\alpha]^{20}_D = -13.6$ (*c* 1.3, THF); IR (KBr): 3395 (m), 3284 (m), 1681 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.82 (t, *J* = 7.5 Hz, 3 H), 2.02 (br q, *J* = 7.5 Hz, 2 H), 3.77 (s, 3 H), 6.90 (br s, 1 H), 7.04−7.09 (m, 2 H), 7.12−7.27 (m, 2 H), 7.33−7.40 (m, 2 H), 7.48 (d, *J* = 8.9 Hz, 1 H), 7.86−8.07 (m, 4 H), 8.59 (br d, *J* = 8.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 9.3 (q), 30.3 (t), 56.5 (q), 113.5 (d), 117.1 (s), 120.8 (d), 120.9 (s), 121.3 (s), 124.1 (d), 124.6 (d), 124.7 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.6 (d), 129.2 (s), 130.8 (d), 132.9 (s), 133.5 (s), 134.4 (s), 155.1 (s), 171.7 (s); MS *m*/*z* (relative intensity): 355 (83) [M$^+$], 299 (100). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96. Found: C, 81.19; H, 5.98.

(*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)butyramide (2b). Yield: 97%; mp 110 °C; R_f 0.40 (petroleum ether/diethyl ether, 1:4); $[\alpha]^{20}_D = -14.8$ (*c* 1.0, THF); IR (KBr): 3410 (m), 3310 (m), 1672 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.66 (t, *J* = 7.4 Hz, 3 H), 1.32 (tq, $J_t = J_q = 7.4$ Hz, 2 H), 1.96 (br t, *J* = 7.4 Hz, 2 H), 3.76 (s, 3 H), 6.90 (br s, 1 H), 7.04−7.09 (m, 2 H), 7.12−7.27 (m, 2 H), 7.33−7.40 (m, 2 H), 7.48 (d, *J* = 8.9 Hz, 1 H), 7.86−8.07 (m, 4 H), 8.59 (br d, *J* = 8.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 13.2 (q), 18.6 (t), 39.5 (t), 56.5 (q), 113.5 (d), 117.1 (s), 120.8 (d), 120.9 (s), 121.3 (s), 124.1 (d), 124.6 (d), 124.7 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.6 (d), 129.2 (s), 130.8 (d), 132.9 (s), 133.5 (s), 134.4 (s), 155.0 (s), 171.0 (s); MS *m*/*z* (relative intensity): 369 (83) [M$^+$], 299 (100). Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 80.90; H, 6.35; N, 4.08.

Imidates 3. General Procedure. To a solution of amide **2** (10 mmol) in dry benzene (20 mL) was added phosgene (14 mmol, 2 M solution in toluene) at 5 °C. After addition of three drops of dimethylformamide, the reaction started with evolution of HCl/CO_2. A white precipitate was produced that dissolved later on. After 6 h at rt, excess phosgene and most of the solvent were distilled off in vacuo (rotary evaporator, 40 °C bath temperature). After refilling with argon, the slightly red oil was diluted with dry THF (10 mL) and added dropwise to a solution of the corresponding lithium allyl alkoxide in THF at 0 °C [the lithium alkoxide was prepared by addition of 1 equiv of *n*-butyllithium in *n*-hexane to a solution of the allyl alcohol (14 mmol) in dry THF (10 mL) at 0 °C and stirring at this temperature for 30 min]. The resulting mixture was stirred for 20 h at rt. After evaporation of the solvent, the residue was dissolved in diethyl ether (30 mL), washed with sat. aqueous NH_4Cl, and dried over $MgSO_4$. Flash chromatography (column: 5 cm length, 5 cm i.d.; basic alumina, activity III, elution with ethyl acetate/petroleum ether, 1:18, including 1 vol % triethylamine) and subsequent removal of the solvent in vacuo yielded pure **3** as low-melting colorless crystals or slightly yellow oil in the yield listed in Table 1.

(*E*)-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)propanimidate (3a). Mp 45 °C; R_f 0.26 (petroleum/ethyl acetate, 18:1, 1 vol % triethylamine); $[\alpha]^{20}_D = -197.1$ (*c* 1.0, THF); IR (film): 1672 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.92 (t, *J* = 7.6 Hz, 3 H), 1.56 (dd, $J_d = 1.2$ Hz, $J_d = 6.4$ Hz, 3 H), 2.13

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(11) Corey, E. J.; Lee, D.-H. *J. Am. Chem. Soc.* **1991**, *113*, 4026−4028 and Supporting Information.

(12) As reference substances, racemic acids **10** prepared by Ireland−Claisen rearrangement were used, see: Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868−2877.

(q, J = 7.6 Hz, 1 H), 2.15 (q, J = 7.6 Hz, 1 H), 3.75 (s, 3 H), 4.09−4.13 (m, 2 H), 5.09 (m_c, 1 H), 5.43 (m_c, 1 H), 7.13 (d, J = 8.8 Hz, 1 H), 7.20−7.41 (m, 6 H), 7.82−7.94 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 10.7 (q), 17.5 (q), 23.6 (t), 56.2 (q), 65.8 (t), 113.4 (d), 120.8 (s), 122.2 (d), 122.6 (s), 123.3 (d), 123.7 (d), 125.6 (d), 125.7 (d), 126.0 (d), 126.1 (d), 126.2 (d), 127.7 (d), 127.9 (d), 128.4 (d), 129.0 (s), 129.1 (d), 129.4 (d), 130.3 (s), 133.4 (s), 133.9 (s), 145.1 (s), 154.7 (s), 162.7 (s); MS m/z (relative intensity): 409 (3) [M$^+$], 378 (100). Anal. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 81.84; H, 6.62; N, 3.36.

***(E)*-2-Penten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)propanimidate (3b).** Oil; R_f 0.26 (petroleum ether/ethyl acetate, 18:1, 1 vol % triethylamine); $[\alpha]^{20}_D$ = −179.9 (*c* 0.97, THF); IR (film): 1671 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.93 (t, J = 7.6 Hz, 3 H), 0.95 (t, 3 H, J = 7.4 Hz), 1.93 (m_c, 2 H), 2.14 (ddq, J_d = 1.2 Hz, J_d = 6.2 Hz, J_q = 7.4 Hz, 2 H), 3.78 (s, 3 H), 4.17 (m_c, 2 H), 5.10 (ttd, J_t = 1.7 Hz, J_t = 6.5 Hz, J_d = 15.5 Hz, 1 H), 5.48 (ttd, J_t = 1.2 Hz, J_t = 6.2 Hz, J_d = 15.5 Hz, 1 H), 7.14 (d, J = 8.6 Hz, 1 H), 7.23−7.45 (m, 6 H), 7.83−7.98 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 10.7 (q), 13.3 (q), 23.6 (t), 25.1 (t), 56.3 (q), 65.9 (t), 113.4 (d), 120.8 (s), 122.2 (d), 122.6 (s), 123.3 (d), 123.7 (d), 124.0 (d), 125.6 (d), 125.7 (d), 126.0 (d), 126.1 (d), 127.7 (d), 127.9 (d), 128.4 (d), 129.1 (s), 129.2 (d), 130.3 (s), 133.4 (s), 133.9 (s), 136.3 (d), 145.1 (s), 154.7 (s), 162.8 (s); MS m/z (relative intensity): 423 (42) [M$^+$], 392 (100). Anal. Calcd for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.31. Found: C, 81.99; H, 7.29; N, 2.99.

***(E)*-2-Buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)butanimidate (3c).** Oil; R_f 0.26 (petroleum ether/ethyl acetate, 18:1, 1 vol % triethylamine); $[\alpha]^{20}_D$ = −207.5 (*c* 1.06, THF); IR (film): 1671 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.79 (t, J = 7.4 Hz, 3 H), 1.41 (m_c, 2 H), 1.56 (br dd, J_d = 1.4 Hz, J_d = 6.7 Hz, 3 H), 2.08 (m_c, 2 H), 3.75 (s, 3 H), 4.10 (m_c, 2 H), 5.08 (qtd, J_q = 1.4 Hz, J_t = 6.2 Hz, J_d = 15.3 Hz, 1 H), 5.42 (tqd, J_t = 0.8 Hz, J_q = 6.7 Hz, J_d = 15.3 Hz, 1 H), 7.15 (d, J = 8.5 Hz, 1 H), 7.19−7.43 (m, 6 H), 7.81−7.96 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 13.7 (q), 17.5 (q), 19.4 (t), 32.1 (t), 56.1 (q), 65.8 (t), 113.4 (d), 120.8 (s), 122.3 (d), 122.5 (s), 123.4 (d), 123.7 (d), 125.6 (d), 125.8 (d), 126.0 (d, very intense), 126.2 (d), 127.7 (d), 127.9 (d), 128.4 (d), 129.0 (s), 129.1 (d), 129.5 (d), 130.3 (s), 133.4 (s), 133.9 (s), 145.0 (s), 154.7 (s), 161.7 (s). MS m/z (relative intensity): 423 (6) [M$^+$], 392 (100); HRMS Calcd for $C_{29}H_{29}NO_2$ [M$^+$]: 423.219. Found: 423.219.

***(E)*-2-Methyl-2-buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)propanimidate (3d).** Oil; R_f 0.26 (petroleum ether/ethyl acetate, 18:1, 1 vol % triethylamine); $[\alpha]^{20}_D$ = −140.8 (*c* 1.09, THF); IR (film): 1672 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J = 7.6 Hz, 3 H), 1.27 (br s, 3 H), 1.50 (br d, J = 6.9 Hz, 3 H), 2.09 (m_c, 1 H), 2.10 (m_c, 1 H), 3.78 (s, 3 H), 3.90 (d, J = 11.9 Hz, 1 H), 4.10 (d, J = 11.9 Hz, 1 H), 5.20 (br q, J = 6.9 Hz, 1 H), 7.09 (d, J = 8.7 Hz, 1 H), 7.21−7.39 (m, 6 H), 7.81−7.92 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 10.6 (q), 13.0 (q), 13.1 (q), 23.7 (t), 56.1 (q), 70.5 (t), 113.1 (d), 120.5 (d), 122.0 (d), 122.1 (d), 122.4 (s), 123.1 (d), 123.5 (d), 123.7 (s), 125.5 (d), 125.6 (d), 125.9 (s), 126.7 (s), 127.5 (s), 127.7 (s), 128.2 (d), 128.9 (d), 130.1 (d), 131.8 (d), 133.2 (d), 133.7 (s), 144.9 (s), 154.5 (s), 162.9 (s); MS m/z (relative intensity): 423 (6) [M$^+$], 355 (100); HRMS Calcd for $C_{29}H_{29}NO_2$ [M$^+$]: 423.219. Found: 423.219.

***(E)*-2-Methyl-2-penten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)propanimidate (3e).** Oil; R_f 0.26 (petroleum ether/ethyl acetate, 18:1, vol % triethylamine); $[\alpha]^{20}_D$ = −163.9 (*c* 0.83, THF); IR (film): 1672 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J = 7.5 Hz, 3 H), 0.94 (t, J = 7.5 Hz, 3 H), 1.29 (s, 3 H), 1.96 (dq, J_d = 7.5 Hz, J_q = 7.5 Hz, 2 H), 2.07 (m_c, 1 H), 2.08 (m, 1 H) 3.77 (s, 3 H), 3.95 (d, J = 11.9 Hz, 1 H), 4.05 (d, J = 11.9 Hz, 1 H), 5.17 (br t, J = 7.5 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 7.20−7.44 (m, 6 H), 7.83−7.96 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 10.5 (q), 13.2 (q), 13.7 (q), 20.8 (t), 23.6 (t), 56.2 (q), 70.7 (t), 113.3 (d), 120.7 (s), 122.2 (d), 122.4 (s), 123.2 (d), 123.6 (d), 124.1 (s), 125.6 (d), 125.7 (d), 125.9 (d), 127.5 (d), 127.6 (d), 127.9 (d), 128.3 (d), 129.0 (d), 129.8 (d), 130.2 (s), 130.5 (s), 133.4 (s), 133.8 (s), 145.0 (s), 154.6 (s), 163.0 (s); MS m/z (relative intensity): 437 (15) [M$^+$], 55 (100); HRMS Calcd for $C_{30}H_{31}NO_2$ [M$^+$]: 437.235. Found: 437.234.

***(E)*-2-Methyl-2-buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)butanimidate (3f).** Oil; R_f 0.26 (petroleum ether/ethyl acetate, 18:1, 1 vol % triethylamine); $[\alpha]^{20}_D$ = −169.0 (c 0.94, THF); IR (film): 1666 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (t, J = 7.4 Hz, 3 H), 1.30 (br s, 3 H), 1.39 (m_c, 2 H), 1.51 (br d, J = 6.7 Hz, 3 H), 2.06 (m_c, 2 H), 3.75 (s, 3 H), 3.93 (d, J = 11.9 Hz, 1 H), 4.07 (d, J = 11.9 Hz, 1 H), 5.20 (br q, J = 6.7 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 7.19−7.39 (m, 6 H), 7.81−7.92 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 13.0 (q), 13.2 (q), 13.7 (q), 19.4 (t), 32.2 (t), 56.1 (q), 70.7 (t), 113.3 (d), 120.7 (d), 122.2 (d), 122.3 (d), 122.4 (s), 123.3 (d), 123.7 (d), 123.8 (s), 125.7 (d), 125.8 (d), 126.0 (s), 126.9 (s), 127.6 (s), 127.9 (s), 128.4 (d), 129.1 (d), 130.3 (d), 131.9 (d), 133.4 (d), 133.9 (s), 145.0 (s), 154.7 (s), 162.1 (s); MS m/z (relative intensity): 437 (15) [M$^+$], 41 (100). Anal. Calcd for $C_{30}H_{31}NO_2$: C, 82.35; H, 7.14; N, 3.20. Found: C, 82.01; H, 7.24; N, 3.12.

Diastereoselective Alkylation of 3d,f. General Procedure. To a solution of dry diethylamine (2.05 mL, 20 mmol) in dry THF (15 mL) was added dropwise *n*-butyllithium (20 mmol, 1.60 M solution in hexane) at 0 °C. After stirring for 10 min at this temperature, the resulting solution of lithium diethylamide (LDEA) was cooled to −78 °C, and a solution of imidate **3** (10 mmol) in dry THF (5 mL) was slowly added. The mixture was stirred for 1 h at this temperature and then treated with the requisite alkyl iodide (20 mmol). After 3 h at −78 °C, the mixture was allowed to warm to rt, treated with sat. aqueous NH_4Cl, and extracted twice with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent yielded a mixture of diastereomeric imidates **4**, **5** (for ratios, see Scheme 2) as colorless oil in analytically pure form.

***(E)*-2-Methyl-2-buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)-(2*S*)-methylbutanimidate (4).** From ethylation of **3d**. Total yield 93%; ^{1}H NMR ($CDCl_3$): δ 0.71 (t, J = 7.6 Hz, 3 H), 0.78 (d, J = 6.7 Hz, 3 H), 1.24 (br s, 3 H), 1.25 (m_c, 2 H), 1.51 (br d, J = 6.7 Hz, 3 H), 2.46 (m_c, 1 H), 3.75 (s, 3 H), 3.85 (d, J = 12.2 Hz, 1 H), 4.03 (d, J = 12.2 Hz, 1 H), 5.18 (br q, J = 6.7 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 7.19−7.40 (m, 6 H), 7.81−7.92 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 11.7 (q), 13.0 (q), 13.0 (q), 17.1 (q), 27.1 (t), 36.4 (d), 56.0 (q), 70.4 (t), 113.0 (d), 120.4 (d), 122.2 (d), 122.3 (d), 122.4 (s), 123.3 (d), 123.7 (d), 123.8 (s), 125.7 (d), 125.8 (d), 126.0 (s), 126.9 (s), 127.6 (s), 127.9 (s), 128.4 (d), 129.1 (d), 130.3 (d), 131.9 (d), 133.4 (d), 133.9 (s), 144.7 (s), 154.7 (s), 164.4 (s); MS m/z (relative intensity): 451 (7) [M$^+$], 41 (100).

***(E)*-2-Methyl-2-buten-1-yl (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)-(2*R*)-methylbutanimidate (5).** From methylation of **3f**. Total yield 86%; ^{1}H NMR ($CDCl_3$): δ 0.57 (d, J = 6.9 Hz, 3 H), 0.69 (t, J = 7.4 Hz, 3 H), 1.30 (br s, 3 H), 1.30 (m_c, 2 H), 1.51 (br d, J = 6.7 Hz, 3 H), 2.39 (m_c, 1 H), 3.74 (s, 3 H), 4.00 (d, J = 12.2 Hz, 1 H), 4.09 (d, J = 12.2 Hz, 1 H), 5.21 (br q, J = 6.7 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 1 H), 7.19−7.40 (m, 6 H), 7.80−7.93 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 11.6 (q), 13.0 (q), 13.2 (q), 17.0 (q), 26.8 (t), 36.4 (d), 56.2 (q), 70.4 (t), 113.4 (d), 120.7 (d), 122.2 (d), 122.3 (d), 122.4 (s), 123.3 (d), 123.7 (d), 123.8 (s), 125.7 (d), 125.8 (d), 126.0 (s), 126.9 (s), 127.6 (s), 127.9 (s), 128.4 (d), 129.1 (d), 130.3 (d), 131.9 (d), 133.4 (d), 133.9 (s), 144.7 (s), 154.7 (s), 164.4 (s); MS m/z (relative intensity): 451 (7) [M$^+$], 41 (100).

Acidic Hydrolysis of 4. The 84:16 mixture of imidates **4** and **5** (1 mmol) obtained upon ethylation of **3d** was dissolved in THF (10 mL), treated with 0.1 N HCl (3 mL), and stirred for 1 h at rt. After evaporation in vacuo, the residue was dissolved in dichloromethane (10 mL), washed with brine, and dried over $MgSO_4$. The solvent was removed in vacuo to give a crude product (containing 57% amine (*S*)-**1** according to GC) that was purified by flash chromatography (petroleum ether/diethyl ether, 1:1) to give two diastereomeric amides in a 83:17 ratio (38% total yield). The major diastereomer was identical to an authentic sample prepared from amine (*S*)-**1** and (2*S*)-methylbutyric anhydride in 83% yield according to the general procedure of amide synthesis as described above.

***(S)*-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)-(2*S*)-methylbutyramide (major diastereomer).** ^{1}H NMR ($CDCl_3$): δ 0.67 (t, J = 7.4 Hz, 3 H), 0.81 (d, J = 6.9 Hz, 3 H), 1.04−1.43 (m, 2 H), 1.86 (m_c, 1 H), 3.75 (s, 3 H), 6.91 (br s, 1 H), 7.04−

7.15 (m, 2 H), 7.15−7.29 (m, 2 H), 7.32−7.42 (m, 2 H), 7.49 (d, J = 8.9 Hz, 1 H), 7.86−8.07 (m, 4 H), 8.61 (br d, J = 8.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.4 (q), 17.0 (q), 27.1 (t), 43.9 (d), 56.5 (q), 113.5 (d), 117.1 (s), 120.8 (d), 120.9 (s), 121.3 (s), 124.1 (d), 124.6 (d), 124.7 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.6 (d), 129.2 (s), 130.8 (d), 132.9 (s), 133.5 (s), 134.5 (s), 155.1 (s), 174.4 (s); MS m/z (relative intensity): 383 (100) [M^+].

Claisen Rearrangement to 7 via Deprotonation of 3. General Procedure. To a solution of dry diethylamine (20 mmol, 2.05 mL) in dry THF (15 mL) was added *n*-butyllithium (20 mmol, hexane solution) at 0 °C. After 10 min at 0 °C, the resulting solution of lithium diethylamide was cooled to −78 °C, and a solution of imidate **3** (10 mmol) in dry THF (5 mL) was added dropwise. After stirring for 1 h at this temperature, the mixture was kept at 0 °C for the indicated period of time (Table 1). The red solution was diluted with diethyl ether (100 mL), washed with sat. aqueous NH_4Cl and brine, and dried over $MgSO_4$. After evaporation of the solvent, flash chromatography (petroleum ether/diethyl ether, 3:2); afforded pure amide **7** in the yield listed in Table 1. Data of major diastereomers:

(2*S*,3*S*)-2,3-Dimethyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7a). R_f 0.25 (petroleum ether/diethyl ether, 3:2); IR (film): 3409 (m), 1691 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.76 (d, J = 6.6 Hz, 3 H), 0.80 (d, J = 6.6 Hz, 3 H), 1.74 (m_c, 1 H), 2.07 (m_c, 1 H), 3.75 (s, 3 H), 4.72 (dd, J_d = 1.8 Hz, J_d = 10.0 Hz, 1 H), 4.78 (ddd, J_d = J_d = 1.8 Hz, J_d = 17.2 Hz, 1 H), 5.32 (ddd, J_d = 8.1 Hz, J_d = 10.0 Hz, J_d = 17.2 Hz, 1 H), 6.90 (br s, 1 H), 7.02−7.11 (m, 2 H), 7.17−7.27 (m, 2 H), 7.31−7.41 (m, 2 H), 7.47 (d, J = 9.1 Hz, 1 H), 7.83−7.92 (m, 2 H), 7.97 (d, J = 9.1 Hz, 1 H), 8.06 (d, J = 9.1 Hz, 1 H), 8.57 (d, J = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 15.2 (q), 18.0 (q), 41.3 (d), 47.8 (d), 56.4 (q), 113.4 (d), 115.0 (t), 117.1 (s), 120.9 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.7 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.8 (d), 130.9 (s), 132.9 (s), 133.5 (s), 134.3 (s), 140.8 (d), 155.1 (s), 173.6 (s); MS m/z (relative intensity): 409 (30) [M^+], 299 (100); HRMS (CI, H^+) Calcd for ($C_{28}H_{27}NO_2$ + H^+) [M + H^+]: 410.212. Found: 410.215.

(2*S*,3*S*)-3-Ethyl-2-methyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7b). R_f 0.28 (petroleum ether/diethyl ether, 3:2); IR (film): 3407 (w), 1688 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.62 (t, J = 7.3 Hz, 3 H), 0.77 (d, J = 7.2 Hz, 3 H), 0.95 (m_c, 1 H), 1.30 (m_c, 1 H), 1.80 (m_c, 2 H), 3.74 (s, 3 H), 4.75 (m_c, 1 H), 4.79 (m_c, 1 H), 5.13 (ddd, J_d = 8.6 Hz, J_d = 10.2 Hz, J_d = 17.2 Hz, 1 H), 6.91 (br s, 1 H), 7.02−7.11 (m, 2 H), 7.16−7.27 (m, 2 H), 7.30−7.40 (m, 2 H), 7.48 (d, J = 9.1 Hz, 1 H), 7.85−7.92 (m, 2 H), 7.97 (d, J = 9.1 Hz, 1 H), 8.07 (d, J = 9.1 Hz, 1 H), 8.58 (d, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.7 (q), 15.1 (q), 25.1 (t), 46.6 (d), 49.3 (d), 56.5 (q), 113.4 (d), 117.0 (t), 117.2 (s), 120.9 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.8 (d), 130.9 (s), 132.9 (s), 133.5 (s), 134.3 (s), 138.7 (d), 155.1 (s), 173.8 (s); MS m/z (relative intensity): 423 (22) [M^+], 299 (100). Anal. Calcd for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.31. Found: C, 81.87; H, 7.00; N, 3.49. HRMS (CI, H^+) Calcd for ($C_{29}H_{29}NO_2$ + H^+) [M + H^+]: 424.228. Found: 424.229.

(2*S*,3*S*)-2-Ethyl-3-methyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7c). R_f 0.28 (petroleum ether/diethyl ether, 3:2); IR (film): 3418 (m), 1697 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.49 (t, J = 7.4 Hz, 3 H), 0.84 (d, J = 6.7 Hz, 3 H), 1.28 (m_c, 2 H), 1.49 (m_c, 1 H), 2.09 (m_c, 1 H), 3.75 (s, 3 H), 4.79 (dd, J_d = 1.7 Hz, J_d = 10.2 Hz, 1 H), 4.84 (dd, J_d = 1.9 Hz, J_d = 17.1 Hz, 1 H), 5.40 (ddd, J_d = 8.6 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 1 H), 6.91 (br s, 1 H), 7.02−7.13 (m, 2 H), 7.19−7.28 (m, 2 H), 7.32−7.42 (m, 2 H), 7.49 (d, J = 9.1 Hz, 1 H), 7.85−7.94 (m, 2 H), 8.00 (d, J = 9.1 Hz, 1 H), 8.08 (d, J = 9.1 Hz, 1 H), 8.59 (d, J = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.4 (q), 18.3 (q), 23.7 (t), 40.8 (d), 56.0 (d), 56.4 (q), 113.4 (d), 114.6 (t), 117.2 (s), 120.9 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.8 (d), 131.0 (s), 132.9 (s), 133.5 (s), 134.3 (s), 141.3 (d), 155.0 (s), 172.8 (s); MS m/z (relative intensity): 423 (22) [M^+], 299 (100); HRMS (CI, H^+) Calcd for ($C_{29}H_{29}NO_2$ + H^+) [M + H^+]: 424.228. Found: 424.228.

(2*S*,3*R*)-2,3,4-Trimethyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7d). R_f 0.29 (petroleum ether/diethyl ether, 3:2); IR (film): 3408 (w), 1691 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.72 (d, J = 6.7 Hz, 3 H), 0.77 (d, J = 6.7 Hz, 3 H), 1.40 (s, 3 H), 1.77 (m_c, 1 H), 1.92 (m_c, 1 H), 3.76 (s, 3 H), 4.51 (br s, 1 H), 4.59 (br s, 1 H), 6.87 (br s, 1 H), 7.02−7.12 (m, 2 H), 7.17−7.28 (m, 2 H), 7.31−7.41 (m, 2 H), 7.48 (d, J = 9.1 Hz, 1 H), 7.83−7.92 (m, 2 H), 7.98 (d, J = 9.1 Hz, 1 H), 8.07 (d, J = 9.1 Hz, 1 H), 8.57 (d, J = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 16.3 (q), 17.6 (q), 18.2 (q), 45.1 (d), 46.4 (d), 56.4 (q), 112.0 (t), 113.4 (d), 117.1 (s), 121.0 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.8 (d), 130.9 (s), 133.0 (s), 133.5 (s), 134.3 (s), 146.7 (s), 155.1 (s), 174.0 (s); MS m/z (relative intensity): 423 (23) [M^+], 299 (100); HRMS (CI, H^+) Calcd for ($C_{29}H_{29}NO_2$ + H^+) [M + H^+]: 424.228. Found: 424.228.

(2*S*,3*R*)-3-Ethyl-2,4-dimethyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7e). R_f 0.32 (petroleum ether/diethyl ether, 3:2); IR (film): 3418 (m), 1697 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.50 (t, J = 7.2 Hz, 3 H), 0.72 (d, J = 6.7 Hz, 3 H), 0.97 (m_c, 1 H), 1.25 (m_c, 1 H), 1.35 (s, 3 H), 1.65 (m_c, 1 H), 1.78 (m_c, 1 H), 3.74 (s, 3 H), 4.50 (br s, 1 H), 4.69 (br s, 1 H), 6.90 (br s, 1 H), 7.02−7.11 (m, 2 H), 7.16−7.27 (m, 2 H), 7.30−7.40 (m, 2 H), 7.48 (d, J = 9.1 Hz, 1 H), 7.85−7.92 (m, 2 H), 7.97 (d, J = 9.1 Hz, 1 H), 8.07 (d, J = 9.1 Hz, 1 H), 8.58 (d, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.8 (q), 16.5 (q), 17.7 (q), 23.6 (t), 45.9 (d), 52.9 (d), 56.5 (q), 114.3 (t), 113.3 (d), 117.0 (s), 120.9 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.7 (s), 130.8 (d), 132.9 (s), 133.5 (s), 134.3 (s), 143.5 (s), 155.1 (s), 174.3 (s); MS m/z (relative intensity): 437 (28) [M^+], 299 (100); HRMS (CI, H^+) Calcd for ($C_{30}H_{31}NO_2$ + H^+) [M + H^+]: 438.243. Found: 438.244.

(2*S*,3*R*)-2-Ethyl-3,4-dimethyl-4-pentenoic Acid (*S*)-*N*-(2′-Methoxy-[1,1′]binaphthalen-2-yl)amide (7f). R_f 0.32 (petroleum ether/diethyl ether, 3:2); IR (film): 3409 (w), 1687 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.43 (t, J = 7.4 Hz, 3 H), 0.77 (d, J = 6.7 Hz, 3 H), 1.13 (m_c, 2 H), 1.41 (s, 3 H), 1.53 (td, J_t = 6.9 Hz, J_d = 10.2 Hz, 1 H), 1.95 (m_c, 1 H), 3.77 (s, 3 H), 6.89 (br s, 1 H), 7.02−7.13 (m, 2 H), 7.17−7.28 (m, 2 H), 7.31−7.41 (m, 2 H), 7.48 (d, J = 9.1 Hz, 1 H), 7.89 (2 × d, J = 8.4 Hz, 2 H), 7.98 (d, J = 9.1 Hz, 1 H), 8.07 (d, J = 9.1 Hz, 1 H), 8.55 (d, J = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.4 (q), 17.8 (q), 18.2 (q), 24.3 (t), 44.3 (d), 54.5 (d), 56.5 (q), 111.8 (t), 113.5 (d), 117.0 (s), 120.9 (d), 121.5 (s), 124.1 (d), 124.5 (d), 124.6 (d), 125.6 (d), 126.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.2 (s), 130.8 (d), 131.0 (s), 132.9 (s), 133.5 (s), 134.3 (s), 147.0 (s), 155.0 (s), 173.1 (s); MS m/z (relative intensity): 437 (18) [M^+], 299 (100); HRMS (CI, H^+) Calcd for ($C_{30}H_{31}NO_2$ + H^+) [M + H^+]: 438.243. Found: 438.241.

Iodolactones 8, 9. General Procedure. Iodine (2.5 mmol) was added to a solution of amide **7** (1 mmol) in 1,2-dimethoxyethane (1.2 mL)/water (0.2 mL) at rt, and the resultant mixture was stirred at rt for 16 h with exclusion of light. After dilution with diethyl ether (50 mL), the mixture was washed successively with 10% aqueous $Na_2S_2O_3 \times 5H_2O$ (10 mL) and brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by HPLC (petroleum ether/diethyl ether, 3:2) afforded pure auxiliary (*S*)-**1** (ca. 90%) and the mixture of diastereomeric iodolactones **8**, **9** in the yield and ratio listed in Table 2.

(2*S*,3*R*,4*S*)-4-(Iodomethyl)-2,3-dimethyl-γ-butyrolactone (8a). R_f 0.33 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 0.88 (d, J = 7.2 Hz, 3 H), 1.19 (d, J = 7.3 Hz, 3 H), 2.73 (m_c, 1 H), 2.87 (dq, J_d = 7.2 Hz, J_q = 7.3 Hz, 1 H), 3.09 (dd, J_d = 10.2 Hz, J_d = 10.0 Hz, 1 H), 3.44 (dd, J_d = 5.7 Hz, J_d = 10.0 Hz, 1 H), 4.58 (ddd, J_d = 4.6 Hz, J_d = 5.7 Hz, J_d = 10.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 0.1 (t), 7.0 (q), 9.9 (q), 37.2 (d), 41.1 (d), 80.4 (d), 178.2 (s); MS m/z (relative intensity): 254 (23) [M^+], 43 (100).

(2*S*,3*R*,4*R*)-4-(Iodomethyl)-2,3-dimethyl-γ-butyrolactone (9a). R_f 0.24 (petroleum ether/diethyl ether, 2:1); ^{1}H

NMR ($CDCl_3$): δ 1.08 (d, J = 7.1 Hz, 3 H), 1.19 (d, J = 7.3 Hz, 3 H), 2.55 (m_c, 1 H), 2.83 (dq, J_d = 8.5 Hz, J_q = 7.3 Hz, 1 H), 3.34 (m_c, 2 H), 4.13 (ddd, J_d = 4.6 Hz, J_d = 5.9 Hz, J_d = 5.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 5.1 (t), 10.3 (q), 13.9 (q), 37.8 (d), 38.3 (d), 83.6 (d), 178.1 (s); MS m/z (relative intensity): 254 (17) [M^+], 43 (100).

(2*S*,3*R*,4*S*)-3-Ethyl-4-(iodomethyl)-2-methyl-γ-butyrolactone (8b). R_f 0.24 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.4 Hz, 3 H), 1.27 (d, J = 7.4 Hz, 3 H), 1.37 (m_c, 1 H), 1.52 (m_c, 1 H), 2.58 (m_c, 1 H), 2.83 (dq, J_d = 7.4 Hz, J_q = 7.4 Hz, 1 H), 3.28 (dd, J_d = 7.4 Hz, J_d = 10.4 Hz, 1 H), 3.40 (dd, J_d = 7.4 Hz, J_d = 10.4 Hz, 1 H), 4.64 (ddd, J_d = 5.7 Hz, J_d = 7.4 Hz, J_d = 7.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 1.0 (t), 10.9 (q), 12.3 (q), 16.6 (t), 40.0 (d), 43.2 (d), 81.7 (d), 178.0 (s); MS m/z (relative intensity): 268 (23) [M^+], 141 (100).

(2*S*,3*R*,4*R*)-3-Ethyl-4-(iodomethyl)-2-methyl-γ-butyrolactone (9b). R_f 0.24 (petroleum ether/diethyl ether, 2:1); IR (film): 1775 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.0 (t, J = 7.4 Hz, 3 H), 1.20 (d, J = 7.6 Hz, 3 H), 1.37 (m_c, 1 H), 1.54 (m_c, 1 H), 2.31 (m_c, 1 H), 2.87 (dq, J_d = 7.4 Hz, J_q = 7.6 Hz, 1 H), 3.33 (dd, J_d = 5.0 Hz, J_d = 10.6 Hz, 1 H), 3.39 (dd, J_d = 6.0 Hz, J_d = 10.6 Hz, 1 H), 4.20 (ddd, J_d = 5.0 Hz, J_d = 5.2 Hz, J_d = 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 6.0 (t), 10.3 (q), 11.6 (q), 20.5 (t), 37.1 (d), 45.1 (d), 81.0 (d), 178.0 (s); MS m/z (relative intensity): 268 (28) [M^+], 141 (100).

(2*S*,3*R*,4*S*)-2-Ethyl-4-(iodomethyl)-3-methyl-γ-butyrolactone (8c). R_f 0.37 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 0.86 (d, J = 7.1 Hz, 3 H), 1.03 (dd, J_d = 7.6 Hz, J_d = 7.4 Hz, 3 H), 1.45 (m_c, 1 H), 1.87 (m_c, 1 H), 2.61 (m_c, 1 H), 2.77 (m_c, 1 H), 3.09 (dd, J_d = 10.0 Hz, J_d = 10.0 Hz, 1 H), 3.43 (dd, J_d = 5.5 Hz, J_d = 10.0 Hz, 1 H), 4.54 (ddd, J_d = 4.3 Hz, J_d = 5.5 Hz, J_d = 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 0.1 (t), 6.5 (q), 12.0 (q), 18.2 (t), 35.7 (d), 48.2 (d), 80.5 (d), 177.3 (s); MS m/z (relative intensity): 268 (19) [M^+], 55 (100).

(2*S*,3*R*,4*R*)-2-Ethyl-4-(iodomethyl)-3-methyl-γ-butyrolactone (9c). R_f 0.33 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.02 (d, J = 6.7 Hz, 3 H), 1.08 (dd, J_d = 6.7 Hz, J_d = 6.7 Hz, 3 H), 1.55 (m_c, 1 H), 1.76 (m_c, 1 H), 2.60 (m_c, 2 H, 2-H), 3.31 (m_c, 2 H), 4.15 (m_c, 1 H); ^{13}C NMR ($CDCl_3$): δ 4.8 (t), 12.2 (q), 13.9 (q), 18.9 (t), 37.4 (d), 44.1 (d), 83.8 (d), 177.3 (s); MS m/z (relative intensity): 268 (10) [M^+], 55 (100); HRMS (CI, NH_4^+) Calcd for ($C_8H_{13}O_2I$ + NH_4^+) [M + NH_4^+]: 286.030. Found: 286.034.

(2*S*,3*R*,4*S*)-4-(Iodomethyl)-2,3,4-trimethyl-γ-butyrolactone (8d). R_f 0.27 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.02 (d, J = 6.7 Hz, 3 H), 1.18 (d, J = 7.3 Hz, 3 H), 1.64 (s, 3 H), 2.46 (dq, J_d = 7.4 Hz, J_q = 6.7 Hz, 1 H), 3.08 (dq, J_d = 7.4 Hz, J_q = 7.3 Hz, 1 H), 3.22 (d, J = 10.2 Hz, 1 H), 3.40 (d, J = 10.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 9.6 (t), 10.0 (q), 10.5 (q), 25.7 (q), 39.2 (d), 41.1 (d), 83.7 (s), 178.3 (s); MS m/z (relative intensity): 268 (7) [M^+], 127 (100).

(2*S*,3*R*,4*R*)-4-(Iodomethyl)-2,3,4-trimethyl-γ-butyrolactone (9d). R_f 0.27 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.00 (d, J = 6.8 Hz, 3 H), 1.20 (d, J = 7.3 Hz, 3 H), 1.53 (s, 3 H), 2.74 (dq, J_q = 8.7 Hz, J_q = 6.8 Hz, 1 H), 2.94 (dq, J_d = 8.7 Hz, J_q = 7.3 Hz, 1 H), 3.38 (m_c, 2 H); ^{13}C NMR ($CDCl_3$): δ 11.1 (q), 11.4 (q), 13.5 (t), 22.4 (q), 38.8 (d), no more signals detectable in the diastereomeric mixture; MS m/z (relative intensity): 268 (6) [M^+], 127 (100).

(2*S*,3*R*,4*S*)-3-Ethyl-4-(iodomethyl)-2,4-dimethyl-γ-butyrolactone (8e). R_f 0.23 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.02 (t, J = 7.4 Hz, 3 H), 1.29 (d, J = 7.3 Hz, 3 H), 1.53 (m_c, 2 H), 1.60 (s, 3 H), 2.46 (m_c, 1 H), 2.87 (dq, J_d = 8.1 Hz, J_q = 7.3 Hz, 1 H), 3.30 (d, J = 11.0 Hz, 1 H), 3.38 (d, J = 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.7 (t), 12.3 (q), 13.0 (q), 18.5 (t), 28.1 (q), 38.3 (d), 48.4 (d), 84.4 (s), 178.3 (s); MS m/z (relative intensity): 282 (3) [M^+], 141 (100).

(2*S*,3*R*,4*R*)-3-Ethyl-4-(iodomethyl)-2,4-dimethyl-γ-butyrolactone (9e). R_f 0.23 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.4 Hz, 3 H), 1.28 (d, J = 7.3 Hz, 3 H), 1.51 (s, 3 H), 1.53 (m_c, 2 H), 2.48 (m_c, 1 H), 2.87 (dq, J_d = 8.1 Hz, J_q = 7.4 Hz, 1 H), 3.39 (d, J = 11.0 Hz, 1 H), 3.49 (d, J = 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 12.3 (q), 12.8 (q), 16.0 (t), 19.0 (t), 22.5 (q), 38.3 (d), 46.9 (d), 84.4 (s), 178.2 (s); MS m/z (relative intensity): 282 (3) [M^+], 141 (100).

(2*S*,3*R*,4*S*)-2-Ethyl-4-(iodomethyl)-3,4-dimethyl-γ-butyrolactone (8f). R_f 0.46 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 0.96−1.08 (m, 6 H), 1.46 (m_c, 1 H), 1.64 (s, 3 H), 1.84 (m_c, 1 H), 2.47 (dq, J_d = 7.2 Hz, J_q = 7.2 Hz, 1 H), 2.82 (ddd, J_d = 7.2 Hz, J_d = 7.4 Hz, J_d = 7.6 Hz, 1 H), 3.32 (d, J = 10.2 Hz, 1 H), 3.40 (d, J = 10.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 9.5 (q), 9.6 (t), 12.2 (q), 18.7 (t), 25.3 (q), 39.9 (d), 46.3 (d), 83.5 (s), 178.2 (s); MS m/z (relative intensity): 282 (7) [M^+], 141 (100).

(2*S*,3*R*,4*R*)-2-Ethyl-4-(iodomethyl)-3,4-dimethyl-γ-butyrolactone (9f). R_f 0.46 (petroleum ether/diethyl ether, 2:1); ^{1}H NMR ($CDCl_3$): δ 0.96−1.08 (m, 6 H), 1.46 (m_c, 1 H), 1.53 (s, 3 H), 1.84 (m_c, 1 H), 2.70 (dq, J_d = 8.5 Hz, J_q = 7.0 Hz, 1 H), 2.76 (m_c, 1 H), 3.38 (m_c, 2 H); ^{13}C NMR ($CDCl_3$): δ 11.0 (q), 12.4 (q), 12.8 (t), 19.1 (t), 22.4 (q), 38.4 (d), 45.7 (d), 84.2 (s), 178.1 (s); MS m/z (relative intensity): 282 (7) [M^+], 141 (100); HRMS (CI, NH_4^+) Calcd for ($C_9H_{15}O_2I$ + NH_4^+) [M + NH_4^+]: 300.046. Found: 300.043.

Acids 10. General Procedure. The iodolactones **8**, **9** (1 mmol) were dissolved in glacial acetic acid (2 mL) and treated with zinc dust (10 mmol). The mixture was heated at 65 °C for 1.5 h (complete conversion of **8**, **9**) and cooled to rt, and 1 N HCl (20 mL) was added. After extraction with diethyl ether (7 × 20 mL) and drying over $MgSO_4$, the solvent was removed in vacuo (rotary evaporator, 5 min at 40 °C bath temperature). Filtration of the crude product through a short column filled with silica gel (2 cm length, 2 cm i.d.) using diethyl ether (20 mL) as the eluent and subsequent evaporation of the solvent in vacuo (rotary evaporator, 10 min at 35 °C bath temperature) gave the pure acids **10** as colorless oils in the yield and enantiomeric excess listed in Table 2.

(2*S*,3*S*)-2,3-Dimethyl-4-pentenoic Acid (10a). $[\alpha]^{20}_D$ = −37.6 (*c* 1.24, $CHCl_3$); IR (film): 3250−2400 (br), 1710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J = 6.6 Hz, 3 H), 1.13 (d, J = 6.9 Hz, 3 H), 2.36 (m_c, 1 H), 2.46 (m_c, 1 H), 5.04 (br d, J = 10.2 Hz, 1 H), 5.06 (br d, J = 17.1 Hz, 1 H), 5.66 (ddd, J_d = 8.2 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 14.3 (q), 18.3 (q), 40.8 (d), 44.9 (d), 115.3 (t), 140.5 (d), 182.6 (s); MS m/z (relative intensity, methyl ester): 142 (8) [M^+], 55 (100).

(2*S*,3*S*)-3-Ethyl-2-methyl-4-pentenoic Acid (10b). $[\alpha]^{20}_D$ = −19.0 (*c* 0.60, THF); IR (film): 3250−2400 (br), 1708 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 7.4 Hz, 3 H), 1.11 (d, J = 6.9 Hz, 3 H), 1.32 (m_c, 1 H), 1.49 (m_c, 1 H), 2.22 (m_c, 1 H), 2.43 (dq, J_d = 7.3 Hz, J_q = 6.9 Hz, 1 H), 5.05 (dd, J_d = 2.1 Hz, J_d = 16.9 Hz, 1 H), 5.10 (dd, J_d = 1.9 Hz, J_d = 10.3 Hz, 1 H), 5.66 (ddd, J_d = 9.3 Hz, J_d = 10.3 Hz, J_d = 16.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.8 (q), 14.0 (q), 25.5 (t), 43.6 (d), 48.6 (d), 117.3 (t), 138.6 (d), 182.9 (s); MS m/z (relative intensity, methyl ester): 156 (2) [M^+], 41 (100). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.60; H, 9.88.

(2*S*,3*S*)-2-Ethyl-3-methyl-4-pentenoic Acid (10c). $[\alpha]^{20}_D$ = −35.3 (*c* 0.62, THF); IR (film): 3250−2400 (br), 1707 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.92 (t, J = 7.4 Hz, 3 H), 1.06 (d, J = 6.9 Hz, 3 H), 1.59 (m_c, 2 H), 2.14 (m_c, 1 H), 2.41 (m_c, 1 H), 5.01 (dd, J_d = 1.7 Hz, J_d = 10.2 Hz, 1 H), 5.05 (dd, J_d = 1.7 Hz, J_d = 17.2 Hz, 1 H), 5.65 (ddd, J_d = 8.6 Hz, J_d = 10.2 Hz, J_d = 17.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 11.9 (q), 18.6 (q), 23.4 (t), 40.4 (d), 53.0 (d), 115.0 (t), 141.2 (d), 181.9 (s); MS m/z (relative intensity, methyl ester): 156 (2) [M^+], 55 (100).

(2*S*,3*R*)-2,3,4-Trimethyl-4-pentenoic Acid (10d). $[\alpha]^{20}_D$ = −29.5 (*c* 0.59, THF); IR (film): 3250−2400 (br), 1706 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J = 6.6 Hz, 3 H), 1.11 (d, J = 6.5 Hz, 3 H), 1.64 (br s, 3 H), 2.30−2.50 (m, 2 H), 4.79 (br s, 2 H); ^{13}C NMR ($CDCl_3$): δ 16.1 (q), 18.2 (q, very intense), 43.6 (d), 44.6 (d), 112.5 (t), 146.5 (s), 183.2 (s); MS m/z (relative intensity, methyl ester): 156 (22) [M^+], 69 (100).

(2*S*,3*R*)-3-Ethyl-2,4-dimethyl-4-pentenoic Acid (10e). $[\alpha]^{20}_D$ = −28.8 (*c* 0.64, THF); IR (film): 3250−2400 (br), 1709 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.80 (t, J = 7.4 Hz, 3 H), 1.09 (d, J = 6.9 Hz, 3 H), 1.23−1.50 (m, 2 H), 1.46 (br s, 3 H), 2.15 (m_c, 1 H), 2.37 (m_c, 1 H), 4.79 (br s, 1 H), 4.89 (br s, 1 H); ^{13}C NMR ($CDCl_3$): δ 12.0 (q), 16.2 (q), 17.6 (q), 24.0 (t), 42.9 (d), 52.2 (d), 114.9 (t), 143.2 (s), 183.6 (s); MS m/z (relative intensity, methyl ester): 170 (3) [M^+], 55 (100); Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.15; H, 10.48.

(2*S*,3*R*)-2-Ethyl-3,4-dimethyl-4-pentenoic Acid (10f). $[\alpha]^{20}_D = -29.3$ (*c* 0.55, THF); IR (film): 3500−2400 (br), 1704 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.92 (t, $J = 7.4$ Hz, 3 H), 1.50 (m_c, 2 H), 1.64 (br s), 2.20−2.49 (m, 2 H), 4.79 (br s, 2 H); ^{13}C NMR ($CDCl_3$): δ 11.9 (q), 18.1 (q, very intense), 24.2 (t), 43.8 (d), 51.4 (d), 112.3 (t), 146.8 (s), 182.7 (s); MS *m*/*z* (relative intensity, methyl ester): 170 (3) [M^+], 41 (100). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.13; H, 10.20.

Benzyl Esters of Acids 10a,c. For elucidation of the absolute configuration, the acids **10a,c** (1 mmol) were converted to their benzyl esters according to the procedure described by Corey.[11]

Benzyl (2*S*,3*S*)-2,3-Dimethyl-4-pentenoate. Yield 81%; $[\alpha]^{20}_D = -12.1$ (*c* 0.26, $CHCl_3$); IR (film): 1735 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.00 (d, $J = 6.6$ Hz, 3 H), 1.12 (d, $J = 6.7$ Hz, 3 H), 2.40 (m_c, 2 H), 4.75 (m_c, 1 H), 5.02 (m_c, 1 H), 5.12 (s, 1 H), 5.13 (s, 1 H), 5.64 (m_c, 1 H), 7.28−7.42 (m_c, 5 H).

Benzyl (2*S*,3*S*)-2-Ethyl-3-methyl-4-pentenoate. Yield 80%; $[\alpha]^{20}_D = -23.2$ (*c* 0.34, $CHCl_3$); IR (film): 1734 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.84 (t, $J = 7.4$ Hz, 3 H), 0.98 (d, $J = 6.7$ Hz, 3 H), 1.57 (m_c, 2 H), 2.19 (m_c, 1 H), 2.41 (m_c, 1 H), 5.04 (m_c, 2 H), 5.13 (s, 2 H), 5.63 (m_c, 1 H), 7.28−7.42 (m_c, 5 H).

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Supporting Information Available: ^1H NMR spectra of **3c**−**e**, **4**, **5**, (*S*)-*N*-(2′-methoxy-[1,1′]binaphthalen-2-yl)-(2*S*)-methylbutyramide (from hydrolysis of **4** and from (*S*)-**1**), **7a**, **7c**−**f**, **8a/9a**−**8f/9f**, and ^{13}C NMR spectra of **10a,c,d** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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