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A Novel Binaphthylamine Auxiliary for Asymmetric Imidate Claisen Rearrangement

Benno Hungerhoff and Peter Metz*

Institut für Organische Chemie, Technische Universität Dresden, Mommsenstr. 13, D-01062 Dresden, Germany

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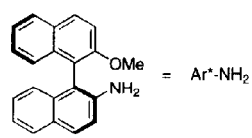
Dedicated to Professor *Achim Mehlhorn* on the occasion of his 60th birthday.

Abstract: The enantiomerically pure methyl substituted binaphthylamine **7** has been prepared *via* a regioselective directed *ortho*-metallation of the methoxy substituted binaphthyl carboxylic acid **5** as the key step and used as an auxiliary for asymmetric imidate Claisen rearrangement. Excellent auxiliary induction as well as simple (*anti/syn*) diastereoselection was achieved. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Metallation, Rearrangements, Imidic acids and derivatives, Enantiocontrol

INTRODUCTION

We have recently described an auxiliary induced, highly enantioselective method for the Claisen rearrangement of imidates derived from prochiral primary allylic alcohols.[1,2] As auxiliary, we used the axially chiral binaphthylamine (*S*)-**1**[3] (Figure 1).



(*S*)-**1**

Fig. 1

Allyl imidates **2** were readily prepared from (*S*)-**1**, and the azaenolates **3** obtained from **2** upon deprotonation with lithium diethylamide (LDEA) already rearranged at 0 °C to give the γ,δ-unsaturated amides **4** with extremely high simple (*anti/syn*) selectivity as well as excellent auxiliary control over the absolute configuration at C-2 and C-3 (Scheme 1). In order to rationalize the stereochemical outcome, we proposed a $(Z)_{CC}/(E)_{CN}$ configuration of the azaenolate **3** and, furthermore, a chelation of the lithium atom with participation of the methoxy group. The naphthyl hydrogen *ortho* to the nitrogen atom in the depicted reactive conformation of **3** would sterically shield the bottom face of the azaenolate and thus, C-C coupling would proceed by preferential *re* attack on the azaenolate double bond, as was observed experimentally. This model suggested replacing of the crucial C-3 hydrogen atom with a larger group in order to achieve a further increase in selectivity. Here we report our first studies on such a modification.

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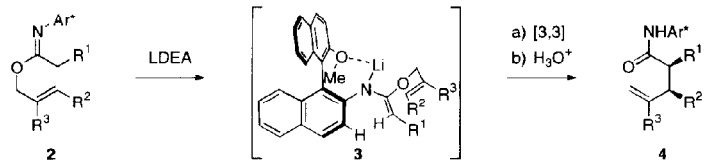
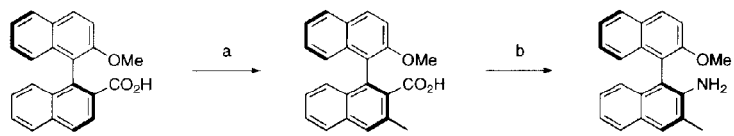


2 3 4

Scheme 1. Asymmetric imidate Claisen rearrangement

RESULTS AND DISCUSSION

The introduction of a methyl group at C-3 of (*S*)-**1** was easily achieved *via* a highly regioselective directed *ortho*-metallation[4] of carboxylic acid **5**[5] and subsequent alkylation to give **6**. Using freshly prepared salt-free *s*-butyllithium, only traces (ca. 3 %) of a dimethylated product were detected by GC/MS next to **6**, while ketone formation was not observed at all. Carboxylic acid **6** was efficiently transformed to binaphthylamine **7** by Curtius degradation[3,6] (Scheme 2).



5 6 7

Scheme 2. Preparation of binaphthylamine **7**. a: (i) *s*-BuLi, TMEDA, –105 °C – –90 °C, THF, (ii) MeI, –78 °C, 60 %; b: (i) $SOCl_2$, cat. DMF, reflux, (ii) NaN_3, acetone, H_2O, r.t., (iii) benzene, reflux, (iv) 50 % aq. KOH, reflux, 90 % from **6**
(TMEDA = *N,N,N',N'*-tetramethylethylenediamine)

In order to investigate the influence of the methyl substituent in **7** on the auxiliary induction for asymmetric imidate Claisen rearrangement, binaphthylamine **7** was converted to crotyl imidate **9** by acylation with propionyl chloride followed by activation of amide **8** to an imido chloride[7] and coupling of this intermediate with lithium (*E*)-2-buten-1-oxide (Scheme 3). An X-ray diffraction analysis of **9** unequivocally proved the attachment of the methyl group to C-3.[8] Upon deprotonation of imidate **9** with LDEA, the resultant azaenolate rearranged at low temperature to give the desired γ,δ-unsaturated amide **10** (Table 1).

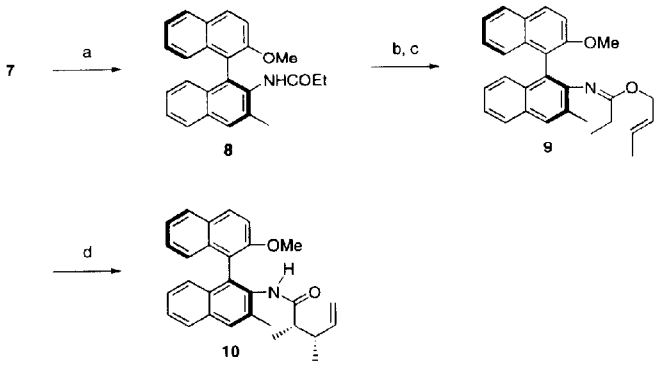
Table 1. Claisen Rearrangement of Imidate **9** to Amide **10**.

rearrangement temp. (°C)	equiv. LDEA	rearrangement time (h)	yield **10** (%)[a]	*ds* **10** (%)[b]
0	2	6	23	98
0	4	6	54	98
–10	4	10	48	>98
–20	4	24	43	>98

[a] Yield after chromatographic purification. [b] Diastereoselectivity determined by ^{1}H NMR integration.

Whereas our original protocol[1] developed for imidates **2** (2 equiv. of LDEA, 0 °C) led to a low yield for rearrangement of **9**, using 4 equiv. of base significantly increased the efficiency of this process. According to ^{1}H NMR integration, amide **10** was formed with excellent auxiliary control as well as simple (*anti/syn*) diastereoselectivity. Next to isomer **10**, the configuration of which was assigned in analogy with the one

determined for **4**,[1] only traces of one additional diastereomer [δ 0.32 (d, J = 6.9 Hz, 3 H, CH-C<u>H</u>$_3$), 0.76 (d, J = 6.8 Hz, 3 H, CH-C<u>H</u>$_3$)] were observed by ^{1}H NMR analysis of the crude product obtained after rearrangement at 0 °C. Upon further decreasing the temperature for the rearrangement step to –10 °C or –20 °C, only signals for amide **10** were detected.



Scheme 3. Preparation and asymmetric Claisen rearrangement of imidate **9**. a: (i) EtCOCl, pyridine, cat. DMAP, CH_2Cl_2, r.t., 95 %; b: $COCl_2$, cat. DMF, benzene, toluene, r.t.; c: (*E*)-Me-CH=CH-CH_2OLi, THF, r.t., 46 % from **8**; d: (i) LDEA, THF, –78 °C, (ii) 0 °C, (iii) aq. NH_4Cl, 54 % from **9**
(DMAP = 4-dimethylaminopyridine; LDEA = lithium diethylamide)

While these results indicate that the methyl group present in **7** indeed further enhances the auxiliary induction for asymmetric imidate Claisen rearrangement, this novel binaphthylamine might as well be a useful addition to the arsenal of enantiopure 2,2'-*N,O*-substituted binaphthyls for asymmetric synthesis[9] in general.

EXPERIMENTAL

General Experimental Information

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. 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_c = 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 Varian MAT CH-7 + data system Varian SS 200. Microanalyses were performed by the analytical laboratory of the Organisch-Chemisches Institut, Universität Münster.

(S)-2'-Methoxy-3-methyl-[1,1']binaphthalene-2-carboxylic Acid (**6**)

To a solution of TMEDA (1.39 g, 12 mmol) in dry THF (10 mL) cooled to –40 °C is slowly added *s*-BuLi (12 mmol, 1.5 M salt-free solution in pentane). After stirring for 10 min, the mixture is cooled to –105 °C, and a solution of carboxylic acid **5** (656 mg, 2 mmol) in dry THF (10 mL) is slowly added. The resultant orange mixture is stirred for 1 h at –90 °C, and methyl iodide (5.11 g, 36 mmol) is added dropwise at –78 °C with vigorous stirring. Stirring is continued for 30 min at –78 °C, the mixture is treated with water, and the resultant suspension is allowed to warm to room temperature. The solvent is removed in vacuo, and the residue is taken up in dichloromethane. After washing with 1 N HCl (2x) and brine (1x), drying over $MgSO_4$, and evaporation of the solvent in vacuo, the residue is recrystallized from EtOH to give **6** (2.05 g, 60 %). Mp 189 °C; $[\alpha]^{20}_D$ = –95.6 (*c* 1.0, THF); IR (neat): 3460 (s, br, CO_2H), 3050 (w), 3000 (w), 2925 (w), 2838 (w), 1699 (s, C=O), 1622 (s), 1594 (s), 1510 (s), 1473 (m), 1463 (m), 1432 (s), 1294 (m), 1267 (s), 1250 (s), 1148 (m), 1086 (m), 1067 (m), 1020 (m), 886 (m), 813 (s), 805 (s), 779 (s), 747 (s) cm^{-1}; ^1H NMR (acetone-d_6): δ 2.59 (s, 3 H, CH_3), 3.74 (s, 3 H, OCH_3), 7.00 (br d, *J* = 8.7 Hz, 1 H, 1 H_{ar}), 7.08 (br d, *J* = 8.3 Hz, 1 H, 1 H_{ar}), 7.15 - 7.27 (m, 3 H, 3 H_{ar}), 7.42 - 7.56 (m, 2 H, 2 H_{ar}), 7.84 - 7.95 (m, 3 H, 3 H_{ar}), 8.03 (br d, *J* = 9.1 Hz, 1 H, 1 H_{ar}); ^{13}C NMR ($CDCl_3$): δ 20.5 (q, CH_3), 56.9 (q, OCH_3), 115.1 (d, CH_{ar}), 121.6 (s, C_{ar}), 124.4 (d, CH_{ar}), 126.5 (d, CH_{ar}), 126.7 (d, CH_{ar}), 127.1 (d, CH_{ar}), 127.3 (d, CH_{ar}), 127.6 (d, CH_{ar}), 128.5 (d, CH_{ar}), 128.7 (d, CH_{ar}), 129.0 (d, CH_{ar}), 130.0 (s, C_{ar}), 130.9 (d, CH_{ar}), 132.2 (s, C_{ar}), 132.6 (s, C_{ar}), 134.9 (s, C_{ar}), 135.2 (s, C_{ar}), 155.6 (s, $\underline{C}_{ar}$-OCH_3), 170.5 (s, $\underline{C}_{ar}$-CO_2H), 206.5 (s, CO_2H); MS (GC/MS; methyl ester) *m/z* (relative intensity): 356 (100) [M^+], 323 (65) [$M^+ - CH_3 - H_2O$], 309 (7), 293 (20), 282 (21), 252 (10), 213 (41); HRMS (CI, NH_4^+) Calcd for ($C_{23}H_{18}O_3 + NH_4^+$) [$M^+ + NH_4^+$]: 360.159. Found: 360.162. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found C, 80.96; H, 5.03.

(S)-2'-Methoxy-3-methyl-[1,1']binaphthalen-2-ylamine (**7**)

A mixture of carboxylic acid **6** (3.42 g, 10 mmol), freshly distilled thionyl chloride (27 mL), and dimethylformamide (10 drops) is heated to reflux for 1 h under argon. After distilling off most of the excess thionyl chloride in vacuo, remaining traces of thionyl chloride are carefully removed by addition of dry benzene (10 mL) and subsequent concentration in vacuo (3x). The residue is dissolved in warm acetone (90 mL), and a solution of sodium azide (850 mg, 13 mmol) in water (1.8 mL) is added. The resultant mixture is stirred for 30 min at room temperature, cooled to 0 °C, and treated with water (30 mL). After extraction with benzene (3x 10 mL), the combined organic layers are washed with ice-cold water and ice-cold brine, dried over $MgSO_4$, and filtered. The filtrate is heated to reflux for 2 h under argon, 50 % aqueous KOH (50 mL) is added, and the mixture is heated to reflux for 1 h. After cooling to room temperature, the aqueous layer is removed, and the organic layer is washed with sat. aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. Purification by HPLC (petroleum ether/diethyl ether, 1:1) gives **7** (2.82 g, 90 % from **6**). Mp 145 °C; R_f 0.44 (petroleum ether/diethyl ether, 1:1); $[\alpha]^{20}_D$ = –116.3 (*c* 1.0, THF); IR (neat): 3457 (m, NH_2), 3374 (m, NH_2), 3048 (w), 2929 (w), 2837 (w), 1626 (s, NH), 1591 (s), 1504 (s), 1461 (m), 1429 (s), 1360 (m), 1331 (m), 1266 (s), 1019 (m), 901 (m), 813 (m), 782 (w), 748 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.41 (s, 3 H, CH_3), 3.58 (br s, 2 H, NH_2), 3.73 (s, 3 H, OCH_3), 6.90 (d, *J* = 8.3 Hz, 1 H, 1 H_{ar}), 7.05 - 7.25 (m, 4 H, 4 H_{ar}), 7.32 (m_c, 1 H, 1 H_{ar}), 7.45 (d, *J* = 9.1 Hz, 1 H, 1 H_{ar}), 7.63 - 7.54 (m, 2 H, 2 H_{ar}), 7.85 (d, *J* = 8.1 Hz, 1 H, 1 H_{ar}), 7.97 (d, *J* = 9.1 Hz, 1 H, 1 H_{ar}); ^{13}C NMR ($CDCl_3$): δ 18.4 (q, CH_3), 56.9 (q, OCH_3), 113.8 (s, C_{ar}), 114.4 (d, CH_{ar}), 119.3 (s, C_{ar}), 122.1 (d, CH_{ar}), 123.9 (d, CH_{ar}), 124.1 (d, CH_{ar}), 125.0 (s, C_{ar}), 125.1 (d, CH_{ar}), 125.3 (d, CH_{ar}), 126.9 (d, CH_{ar}), 127.2 (d, CH_{ar}), 128.0 (d, CH_{ar}), 128.1 (s, C_{ar}), 128.6 (d, CH_{ar}), 129.6 (s, C_{ar}), 129.9 (d, CH_{ar}), 133.0 (s, C_{ar}), 133.7 (s, C_{ar}), 141.2 (s, C_{ar}-NH_2), 155.5 (s, $\underline{C}_{ar}$-OCH_3); MS (GC/MS) *m/z* (relative intensity): 313 (100) [M^+], 298 (8) [$M^+ - CH_3$], 281 (26) [$M^+ - CH_3OH$], 267 (13), 170 (45), 141 (11); HRMS Calcd for ($C_{22}H_{19}NO^+$) [M^+]: 313.147. Found 313.148. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found C, 84.12; H, 6.31; N, 4.59.

(S)-N-(2'-Methoxy-3-methyl-[1,1']binaphthalen-2-yl)propionamide (**8**)

To a solution of amine **7** (3.13 g, 10 mmol) in dry dichloromethane (10 mL) is added dry pyridine (0.89 mL, 11 mmol) and a small amount of DMAP. The mixture is cooled to 0 °C, and propionyl chloride (10.5 mmol) is added dropwise. After stirring for 16 h at room temperature, the mixture is washed successively with water (3x), sat. aqueous $NaHCO_3$ (1x), brine (1x), and dried over $MgSO_4$. Removal of the solvent in vacuo provides a colorless residue that crystallizes upon treatment with diethyl ether to give **8** (3.51 g, 95 %). Mp 112 °C; R_f 0.40 (diethyl ether); $[\alpha]^{20}_D$ = –47.2 (*c* 0.25, THF); IR (neat): 3227 (br, m, NH), 3058 (w), 2954 (w), 2837 (w), 1654 (s, C=O), 1620 (m), 1592 (m), 1514 (m), 1491 (m), 1456 (m), 1431 (s), 1352 (m), 1336 (m), 1266 (s), 1249 (m), 1214 (m), 1178 (w), 1148 (m), 1085 (s), 1048 (m), 1019 (m), 941 (m), 903 (m), 892 (m), 857 (m), 808 (s), 747 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.63 (t, *J* = 7.6 Hz, 3 H CH_2-C$\underline{H}_3$), 1.89 (m_c, 2 H, C$\underline{H}$H'-CH_3), 2.52 (br s, 3 H, CH_3), 3.73 (s, 3 H, OCH_3), 6.66 (br s, 1 H, NH), 7.02 - 7.46 (m, 7 H, 7 H_{ar}), 7.78 - 7.89 (m, 3 H, 3 H_{ar}), 7.98 (d, *J* = 9.1 Hz, 1 H, 1 H_{ar}); ^{13}C NMR ($CDCl_3$): δ 9.7 (q, CH_2-$\underline{C}H_3$), 19.3 (q, CH_3), 29.8 (t, CH_2), 56.8 (q, OCH_3), 113.6 (d, CH_{ar}), 119.6 (s, C_{ar}), 124.0 (d, CH_{ar}), 125.3 (d, intense, 2x CH_{ar}), 125.7 (d, CH_{ar}), 126.1 (d, CH_{ar}), 127.1 (d, CH_{ar}), 127.3 (d, CH_{ar}), 127.8 (d, CH_{ar}), 129.1 (d, CH_{ar}), 129.2 (s, C_{ar}), 129.8 (s, C_{ar}), 130.1 (d, CH_{ar}), 131.7 (s, C_{ar}), 132.8 (s, C_{ar}), 133.6 (s, C_{ar}), 133.8 (s, C_{ar}), 134.5 (s, C_{ar}), 154.8 (s, $\underline{C}_{ar}$-OCH_3), 172.4 (s, C=O); MS (GC/MS) *m/z* (relative intensity): 369 (55) [M^+], 313 (100) [M^+ - C_2H_4CO], 295 (10), 281 (53) [M^+ - C_2H_4CO - CH_3OH], 265 (14), 252 (7), 226 (74), 170 (48), 57 (23) [$C_2H_5CO^+$]. HRMS Calcd for ($C_{25}H_{23}NO_2^+$) [M^+]: 369.173. Found 369.172. Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found C, 81.05; H, 6.44; N, 3.95.

(E)-2-Buten-1-yl (S)-N-(2'-Methoxy-3-methyl-[1,1']binaphthalen-2-yl]propanimidate (**9**)

To a solution of amide **8** (10 mmol) in dry benzene (20 mL) is added phosgene (14 mmol, 2 M solution in toluene) at 5 °C. Three drops of dimethylformamide are added, and the mixture is stirred for 6 h at room temperature. Excess phosgene and most of the solvent are distilled off in vacuo (rotary evaporator, 40 °C bath temperature). After refilling with argon, the residue is diluted with dry THF (10 mL) and added dropwise to a solution of lithium (*E*)-2-buten-1-oxide in THF at 0 °C [the lithium alkoxide is prepared by addition of 1 equivalent of *n*-butyllithium in *n*-hexane to a solution of (*E*)-2-buten-1-ol (14 mmol) in dry THF (10 mL) at 0 °C and stirring at this temperature for 30 min]. The resulting mixture is stirred for 20 h at room temperature. After evaporation of the solvent, the residue is 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 yield pure **9** (1.95 g, 46 % from **8**). R_f 0.58 (petroleum ether/diethyl ether, 3:2); $[\alpha]^{20}_D$ = –216.7 (*c* 1.5, THF); IR (neat): 3056 (w), 2962 (w), 2936 (m), 2837 (w), 1674 (s, C=N), 1621 (m), 1593 (m), 1508 (w), 1499 (w), 1462 (m), 1294 (m), 1265 (s), 1248 (m), 1178 (s), 1085 (m), 1008 (w), 967 (w), 807 (w), 749 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 2 isomers (3:1) visible, major isomer: δ 0.83 (t, *J* = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.49 (br d, *J* = 6.4 Hz, 3 H, =CH-C$\underline{H}_3$), 1.75 - 2.15 (m, 2 H, C$\underline{H}$H'-CH_3), 2.30 (br s, 3 H, CH_3), 3.68 (s, 3 H, OCH_3), 3.82 - 4.08 (m, 2 H, C$\underline{H}$H'O), 4.96 (m_c, 1 H, =CH), 5.34 (m_c, 1 H, =CH), 7.05 - 7.38 (m, 7 H, 7 H_{ar}), 7.70 - 7.82 (m, 3 H, 3 H_{ar}), 7.86 (d, *J* = 9.1 Hz, 1 H, 1 H_{ar}), minor isomer: δ 0.42 (t, *J* = 7.6 Hz, 3 H, CH_2-C$\underline{H}_3$), 1.50 - 1.90 (m, 2 H, C$\underline{H}$H'-CH_3), 1.64 (br d, *J* = 6.4 Hz, 3 H, =CH-C$\underline{H}_3$), 2.28 (br s, 3 H, CH_3), 3.74 (s, 3 H, OCH_3), 3.25 - 4.43 (m, 2 H, C$\underline{H}$H'O), 5.36 (m_c, 1 H, =CH), 5.58 (m_c, 1 H, =CH), 7.05 - 7.38 (m, 7 H, 7 H_{ar}), 7.70 - 7.82 (m, 3 H, 3 H_{ar}), 7.86 (d, *J* = 9.1 Hz, 1 H, 1 H_{ar}); ^{13}C NMR ($CDCl_3$) 2 isomers visible, major isomer: δ 10.1 (q, CH_3), 17.5 (q, CH_3), 19.2 (q, CH_3), 23.5 (t, CH_2), 55.7 (q, OCH_3), 65.7 (t, OCH_2), 112.6 (d, CH), 120.8 (s, C_{ar}), 121.1 (s, C_{ar}), 123.4 (d, CH), 123.6 (d, CH), 125.0 (d, CH), 125.5 (d, CH), 126.1 (d, CH), 126.2 (d, CH), 127.2 (d, CH), 127.5 (d, CH), 128.1 (d, CH), 129.0 (d, CH), 129.1 (d, CH), 129.3 (d, CH), 130.3 (s, C_{ar}), 132.5 (s, C_{ar}), 132.9 (s, C_{ar}), 144.8 (s, $\underline{C}_{ar}$-N=C), 154.7 (s, $\underline{C}_{ar}$-OCH_3), 161.9 (s, C=N), minor isomer: δ 9.5 (q, CH_3), 17.7 (q, CH_3), 19.2 (q, CH_3), 24.0 (t, CH_2), 57.1 (q, OCH_3), 65.7 (t, OCH_2), 114.8 (d, CH), 123.2 (d, CH), 125.2 (d, CH), 125.7 (d, CH), 125.9 (d, CH), 126.3 (d, CH), 126.5 (d, CH), 128.0 (d, CH), 128.2 (d, CH), 129.2 (d, CH) – the missing signals for both isomers are overlapped by the signals listed above. MS (GC/MS) *m/z* (relative intensity): 423 (15) [M^+], 408 (7) [M^+ - CH_3], 394 (12) [M^+ -

CH_2CH_3], 392 (70) [M^+ - CH_3OH], 366 (25), 352 (24) [M^+ - $OCH_2CH{=}CHCH_3$], 313 (35) [Ar(Me)-NH_2^+], 296 (15), 281 (72), 265 (13), 226 (21), 55 (100) [$CH_3CH{=}CHCH_2^+$]. Anal. Calcd for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.31. Found C, 81.95; H, 7.14; N, 3.48.

(2S,3S)-2,3-Dimethyl-4-pentenoic Acid (S)-N-(2'-Methoxy-3-methyl-[1,1']binaphthalen-2-yl)amide (**10**)

To a solution of dry diethylamine (4.0 mmol, 0.41 mL) in dry THF (3 mL) is added *n*-butyllithium (4.0 mmol, hexane solution) at 0 °C. After 10 min at 0 °C, the resulting solution of lithium diethylamide is cooled to –78 °C and a solution of imidate **9** (1.0 mmol) in dry THF (0.5 mL) is added dropwise. After stirring for 1 h at this temperature, the mixture is kept at 0 °C for 6 h. The solution is diluted with diethyl ether (20 mL), washed with sat. aqueous NH_4Cl, brine, and dried over $MgSO_4$. After evaporation of the solvent, flash chromatography (petroleum ether/diethyl ether, 3:2) affords pure amide **10** (228 mg, 54 %). IR (neat): 3409 (m, NH), 3059 (w), 2970 (m), 2933 (w), 2875 (w), 2839 (w), 1691 (s, C=O), 1621 (m), 1596 (s), 1499 (s), 1457 (m), 1428 (m), 1376 (w), 1333 (w), 1269 (s), 1181 (w), 1148 (w), 1084 (s), 1056 (m), 1021 (w), 998 (w), 914 (m), 864 (w), 814 (s), 775 (w), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.44 (d, J = 6.9 Hz, 3 H, CH-C$\underline{H}_3$), 0.70 (d, J = 6.7 Hz, 3 H, CH-C$\underline{H}_3$), 1.70 (m_c, 1 H, O=C-C$\underline{H}$-CH-CH_3), 2.06 (m_c, 1 H, =CH-C$\underline{H}$-CH_3), 2.53 (s, 3 H, CH_3), 3.73 (s, 3 H, OCH_3), 4.73 - 4.85 (m, 2 H, CH=C$\underline{H}\underline{H}'$), 5.29 (ddd, J = 8.1 Hz, J = 10.0 Hz, J = 17.2 Hz, 1 H, CH-C$\underline{H}$=CH_2), 7.04 - 7.44 (m, 7 H, 7 H_{ar}), 7.83 (m_c, 3 H, 3 H_{ar}), 7.97 (d, J = 9.1 Hz, 1 H, 1 H_{ar}); ^{13}C NMR ($CDCl_3$): δ 15.4 (q, CH_3), 18.2 (q, CH_3), 19.5 (q, CH_3), 40.9 (d, CH), 46.9 (d, CH), 56.8 (q, OCH_3), 113.6 (d, CH_{ar}), 114.6 (t, CH=$\underline{C}H_2$), 117.6 (s, C_{ar}), 119.8 (s, C_{ar}), 124.1 (d, CH_{ar}), 125.3 (d, intense, 2x CH_{ar}), 125.7 (d, CH_{ar}), 126.1 (d, CH_{ar}), 127.1 (d, CH_{ar}), 127.3 (d, CH_{ar}), 127.7 (d, CH_{ar}), 129.0 (d, CH_{ar}), 129.3 (s, C_{ar}), 130.0 (d, CH_{ar}), 131.8 (s, C_{ar}), 132.8 (s, C_{ar}), 133.7 (s, C_{ar}), 133.8 (s, C_{ar}), 134.6 (s, C_{ar}), 141.3 (d, CH_2=$\underline{C}H$), 154.3 (s, $\underline{C}_{ar}$-OCH_3), 174.0 (s, C=O); MS (GC/MS) *m/z* (relative intensity): 423 (31) [M^+], 408 (9) [M^+ - CH_3], 367 (2) [M^+ - $CH_3CH{=}CHCH_3$], 340 (7) [M^+ - $CH_3CHCH(CH_3)CH{=}CH_2$], 313 (100) [Ar(Me)-NH_2^+], 280 (48), 265 (8), 170 (25), 83 (10) [$CH_3CHCH(CH_3)CH{=}CH_2^+$], 55 (56) [$CH_2{=}CHCHCH_3^+$]. Anal. Calcd for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.31. Found C, 81.90; H, 7.22; N, 3.24.

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