

Synthesis and Odor Evaluation of Stereoisomers of Imine Derivatives in Roasted Spotted Shrimp

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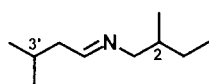
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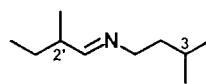
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All possible stereoisomers of imine derivatives **1–4**, which have the characteristic roast odor of seafood, were synthesized. As a result of odor evaluation of all isomers, we found that each isomer has a different and characteristic odor of roasted seafood.

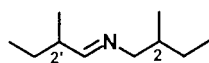
Introduction. – Imine derivatives **1–4** have the characteristic roast odor of seafood.



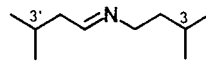
2-Methyl-*N*-(3'-methylbutylidene)butanamine (**1**)



3-Methyl-*N*-(2'-methylbutylidene)butanamine (**2**)



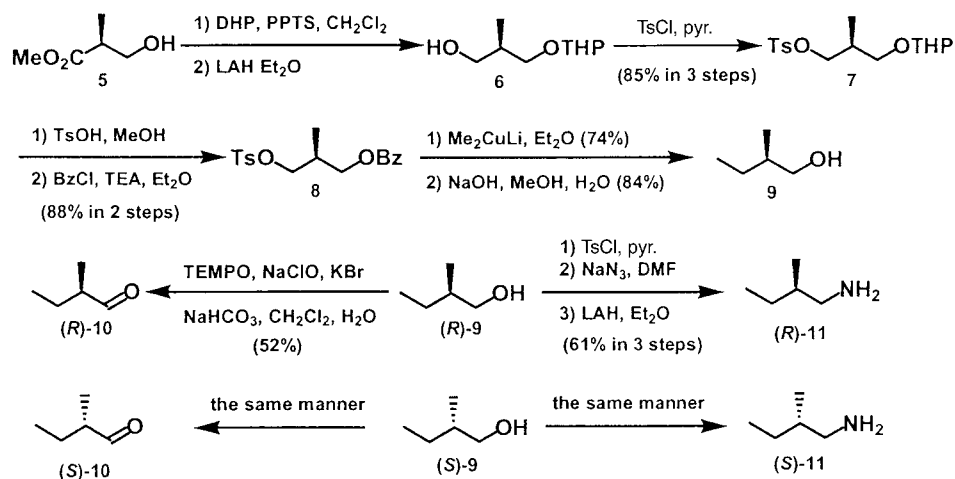
2-Methyl-*N*-(2'-methylbutylidene)butanamine (**3**)



3-Methyl-*N*-(3'-methylbutylidene)butanamine (**4**)

In 1974, *Lien* and *Nawar* found that thermolysis of leucine gave imine **4**, while thermolysis of isoleucine gave imine **3** [1]. Imines **2**, **3**, and **4** were detected from hydrolyzed corn protein by *Flath* and co-workers in 1989 [2]. Imines **2** and **4** were detected in dried squid as volatile compounds by *Kawai* and co-workers in 1991 [3], and, recently, we also found them in roasted spotted shrimp. There is, however, no report on odor evaluation of those stereoisomers. We were interested in the relationship of the configuration and the odor of the stereoisomers. Therefore, we synthesized all possible stereoisomers and evaluated their odors.

Results and Discussion. – The synthesis of both enantiomers of 2-methylbutanal (**10**) and 2-methylbutanamine (**11**), key intermediates of imine derivatives, is shown in *Scheme 1*.

Scheme 1. Synthesis of Both Enantiomers of 2-Methylbutanal (**10**) and 2-Methylbutanamine (**11**)

DHP = 3,4-Dihydro-2*H*-pyran, LAH = LiAlH₄, PPTS = pyridinium *p*-toluenesulfonate, TEA = Et₃N, TEMPO = 2,2,6,6-tetramethylpiperidin-1-yl-oxyl, THP = tetrahydro-2*H*-pyran-2-yl.

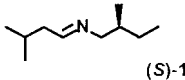
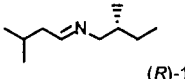
Commercially available methyl (*S*)-3-hydroxy-2-methylpropionate (**5**) was employed as the starting material. Tosylate **7** was obtained from **5** in three steps by a known route [4]. Exchange of the protecting group THP with a Bz group in two steps gave benzoate **8** for easy purification at a later step. The replacement of the TsO group with a Me group with Me₂CuLi and then deprotection of the Bz group under hydrolytic conditions gave (*R*)-2-methylbutan-1-ol (**9**). The conversion of **9** to (*R*)-2-methylbutanal (**10**) was achieved by TEMPO oxidation [5], while the conversion to (*R*)-2-methylbutylamine **11** was achieved in three steps: tosylation, azidation, and reduction. (*S*)-2-methylbutanal (**10**) and (*S*)-2-methylbutanamine were prepared in the same manner from commercially available (*S*)-2-methylbutan-1-ol (**9**).

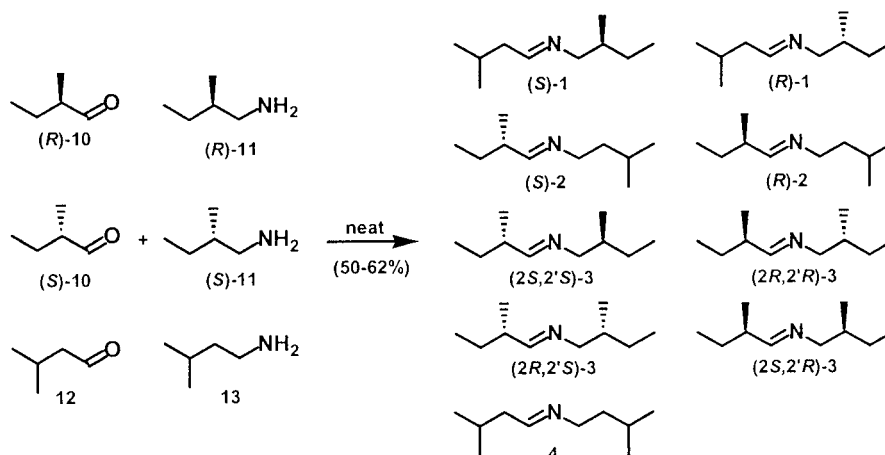
All stereoisomers of imine **1–3** and **4** were synthesized from combinations of aldehydes and amines under neat conditions (Scheme 2).

Odor Evaluation. The odors of all synthesized stereoisomers of **1–3** and **4** were evaluated by special panelists. The results of the odor evaluations are shown in Tables 1–4.

In the case of the enantiomers of **1**, we found that (*S*)-**1** has amine- and butter-like odor, while (*R*)-**1** has esteric and fruity odor (Table 1).

Table 1. Odor Evaluation of Both Enantiomers of 2-Methyl-N-(3'-methylbutylidene)butanamine (**1**)

	Amine, internal organs of shrimp, cocoa-like element with sweet butter-like odor.
	Heavier esteric odor than (<i>S</i>)- 1 . Fruity, cereal-like with slightly fishy scent.

Scheme 2. Synthesis of all Stereoisomers of Imine Derivatives **1–3** and **4**

In the case of the enantiomers of **2**, we found that both have a heavy, strong seafood element, but **(S)-2** has stronger odor than **(R)-2**. Also, we found that **(S)-2** has a fruity element along with the seafood element, while **(R)-2** has a sweet butter element along with the seafood element (*Table 2*).

Table 2. Odor Evaluation of Both Enantiomers of 3-Methyl-N-(2'-methylbutylidene)butanamine (**2**)

	Light and strong seafood element with fruity element including apple, pineapple, chinese quince, pear.
	Heavy and strong seafood element. Image of seaweed (wakame), laver with sweet butter-like odor.

In the case of four stereoisomers of **3**, it was found that the **(2S)**-isomer has a metallic element, while **(2R)**-isomer has a phenolic element. All stereoisomers had a fruity element (*Table 3*).

Odor evaluation of **4** is presented in *Table 4*.

As a result of odor evaluation, we found that all imine derivatives can be used not only as seafood flavors, but also as fruit flavors, for instance, mango flavor.

The mechanism of generation of these odor compounds is thought to be as follows. When spotted shrimp is roasted, leucine and isoleucine are thermolyzed to give the corresponding aldehydes *via* decarboxylation, dehydrogenation, and then hydrolysis. On the other hand, amines were generated by decarboxylation of these amino acids. Condensation of these aldehydes and amines afford imine derivatives **1–4** [6]. Therefore, we predict that the absolute configuration of all these natural imines must

Table 3. Odor Evaluation of Both Enantiomers of 2-Methyl-N-(2'-methylbutylidene)butanamine (**3**)

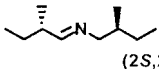
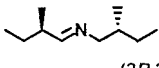
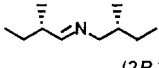
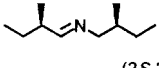
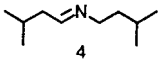
 (2 <i>S</i> ,2' <i>S</i>)-3	Light, metallic, oily character. Seafood (internal organs of shrimp) with sweet butter-like and esteric scent.
 (2 <i>R</i> ,2' <i>R</i>)-3	Mild, sweet, fruity, slightly phenolic element, including the peel of mango, apple, citrus.
 (2 <i>R</i> ,2' <i>S</i>)-3	Seafood, including fish odor with phenolic, esteric, fruity element.
 (2 <i>S</i> ,2' <i>R</i>)-3	Metallic, slightly heavy, cocoa-like odor with esteric, fruity element. Sweeter odor than (2 <i>S</i> ,2' <i>S</i>)-3. Image of burned fish, shrimp.

Table 4. Odor Evaluation of Both Enantiomers of 3-Methyl-N-(3'-methylbutylidene)butanamine (**4**)

 4	Oily element with aldehyde-like stimulus scent. Slightly sweet atmosphere. Image of crab, internal organs of shrimp, burned fish, fish guts pickled in salt. Bacon-like element with sweet chocolate, cocoa, jam.
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be (*S*). To prove this hypothesis, separation of racemic imines **1–3** by GLC analysis with proper chiral stationary phase is now being investigated.

In conclusion, we have succeeded in the stereoselective synthesis of imine derivatives found in spotted shrimp that have the characteristic roast odor of seafood. By odor evaluation, it was revealed that each stereoisomer has a different and characteristic odor.

We thank *Mitsubishi Rayon Co., Ltd.* for the generous gift of methyl (*S*)-3-hydroxy-2-methylpropionate (**5**).

Experimental Part

General. M.p.: *Yazawa BY-2*. Optical rotations: *HORIBA SEPA-200*. Neutral column chromatography (CC): *Kanto Chemical silica gel 60N* (spherical, neutral). GC: *HP5890* gas chromatograph; ee values were determined on a 50% heptakis(2,3-di-*O*-acetyl-6-*O*-TBDMS)- β -CD (*OV-1701*) column (0.25 mm I.D. \times 30 ml) with the following temp. program 40° to 140° (0.7°/min); analysis of (*R*)-2-methylbutanal ((*R*)-**10**): t_R 33.4 min, analysis of (*S*)-2-methylbutanal ((*S*)-**10**): t_R 34.9 min. IR Spectra: *Jasco FT/IR-300E* spectrometer, in $\tilde{\nu}$ [cm⁻¹]. ¹H- and ¹³C-NMR spectra: *Jeol JNM-LA400* spectrometer (400 and 100 MHz). HR-MS: *Hitachi M-80B* mass spectrometer.

(*R*)-2-Methyl-3-[(4-methylphenylsulfonyl)oxy]propyl Benzoate (**8**). To a soln. of 2-methyl-3-[(tetrahydro-2H-pyran-2-yl)oxy]propyl 4-methylbenzenesulfonate (**7**; 41.5 g, 126.4 mmol) in MeOH (250 ml) was added cat. amount of TsOH \cdot H₂O (2.0 g) at r.t. The mixture was stirred for 1 h at r.t. Na₂CO₃ (2 g), was added to the mixture and the mixture was concentrated. The residue was added to sat. Na₂CO₃ soln. and extracted with Et₂O. The extract was washed with brine, dried (MgSO₄), and concentrated *in vacuo* to give crude oil (32.96 g), which was employed in the next step without further purification.

To a soln. of this crude alcohol (32.9 g) and Et₃N (17.7 g, 175 mmol) in Et₂O (350 ml) was added BzCl (20.8 g, 148 mmol) over 10 min at 0°. The mixture was stirred for 3 h at r.t. The mixture was added to H₂O. The Et₂O layer was separated, washed with sat. NaHCO₃ soln. and brine, dried (MgSO₄), and concentrated *in vacuo*. The residue was obtained as a white solid. Recrystallization from hexane gave **8** (38.7 g; 88% from **7**). Colorless

needles. M.p. 59–60°. $[\alpha]_D^{20} = +4.22$ ($c = 0.99$, CHCl_3). IR (KBr): 2927, 1717, 1455, 1351, 1278, 1174, 1116, 939, 841, 810, 720, 668, 592, 556. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.05 ($d, J = 6.8, 3 \text{ H}$); 2.33 ($s, 3 \text{ H}$); 4.06 ($d, J = 5.9, 2 \text{ H}$); 4.14 ($dd, J = 6.8, 11.2, 1 \text{ H}$); 4.22 ($dd, J = 5.0, 11.2, 1 \text{ H}$); 7.24–7.26 ($m, 2 \text{ H}$); 7.40–7.44 ($m, 2 \text{ H}$); 7.54–7.58 ($m, 1 \text{ H}$); 7.77 ($d, J = 8.3, 2 \text{ H}$); 7.91 ($d, J = 7.1, 2 \text{ H}$). HR-MS: 348.1065 (M^+ , $\text{C}_{18}\text{H}_{20}\text{O}_5$; calc. 348.1031).

(*R*)-2-Methylbutan-1-ol (**9**). To a suspension of CuI (19.8 g, 104 mmol) in dry Et_2O (200 ml) was added 1.04M MeLi (200 ml, 208 mmol) over 30 min under Ar at -30° , and the mixture was stirred for 2 h at 0° . To the mixture was added a soln. of **8** (30.3 g, 87 mmol) in dry Et_2O (50 ml) over 20 min at -10° , and the mixture was stirred for 2 h at 0° . The mixture was added to sat. NH_4Cl soln., filtered, and separated. The Et_2O layer was washed with sat. NaHCO_3 soln. and brine, dried (MgSO_4), and concentrated *in vacuo*. The oily residue was purified by distillation (b.p. $95^\circ/0.4 \text{ kPa}$) to give 12.4 g (74%) of (*R*)-2-methylbutyl benzoate. $[\alpha]_D^{20} = -4.95^\circ$ ($c = 1.29$, CHCl_3). IR (film): 2963, 2877, 1720, 1451, 1314, 1273, 1113, 711. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.96 ($t, J = 7.2, 3 \text{ H}$); 1.02 ($d, J = 6.8, 3 \text{ H}$); 1.26–1.32 ($m, 1 \text{ H}$); 1.51–1.57 ($m, 1 \text{ H}$); 1.84–1.89 ($m, 1 \text{ H}$); 4.13 ($dd, J = 6.8, 10.8, 1 \text{ H}$); 4.21 ($dd, J = 6.0, 10.8, 1 \text{ H}$); 7.42–7.46 ($m, 2 \text{ H}$); 7.53–7.58 ($m, 1 \text{ H}$); 8.04–8.06 ($m, 2 \text{ H}$). HR-MS: 192.1103 (M^+ , $\text{C}_{12}\text{H}_{16}\text{O}_2$; calc. 192.1150).

To a soln. of NaOH (2.67 g, 66.8 mmol) in H_2O (20 ml) and MeOH (5 ml) was added (*R*)-2-methylbutyl benzoate (10.7 g, 55.7 mmol) at r.t. The mixture was stirred for 2 h at reflux temp. The mixture was added to NaCl and extracted with Et_2O . The extract was washed with brine, dried (MgSO_4), and concentrated *in vacuo*. The oily residue was purified by distillation (b.p. $82^\circ/15.7 \text{ kPa}$) to give 4.1 g (84%) of **9**. $[\alpha]_D^{20} = +5.85$ ($c = 0.90$, MeOH). IR (film): 3339, 2961, 2876, 1463, 1380, 1046, 1015, 648. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.91 ($t, J = 7.3, 3 \text{ H}$); 0.91 ($d, J = 6.8, 3 \text{ H}$); 1.05–1.20 ($m, 1 \text{ H}$); 1.38–1.59 ($m, 2 \text{ H}$); 1.70 ($s, 1 \text{ H}$); 3.42 ($dd, J = 6.6, 10.5, 1 \text{ H}$); 3.51 ($dd, J = 5.8, 10.5, 1 \text{ H}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 11.5; 16.2; 25.9; 37.5; 68.2. HR-MS: 88.0917 (M^+ , $\text{C}_5\text{H}_{12}\text{O}$; calc. 88.0888).

(*R*)-2-Methylbutanal (**10**). To a soln. of **9** (2.0 g, 22.7 mmol) in CH_2Cl_2 (28 ml) were added TEMPO (36 mg, 0.23 mmol) in CH_2Cl_2 (28 ml) and KBr (270 mg, 2.3 mmol) in H_2O (4.8 ml) at 0° . The mixture was added to a mixture of NaClO (43 ml), H_2O (55.44 ml), and NaHCO_3 (4.92 g) at 0° . The mixture was stirred for 15 min at 0° . The mixture was separated, and the org. layer was washed with brine, dried (MgSO_4), and concentrated at low temperature *in vacuo*. The oily residue was purified by CC (neutral silica gel (50 g); hexane/10:1) furnishing pure **10** as an oil (1.0 g, 52%; 98% ee). $[\alpha]_D^{20} = -35.8^\circ$ ($c = 1.21$, MeOH). IR (film): 2971, 2935, 2878, 1713, 1463, 1191, 1103, 970. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.95 ($t, J = 7.6, 3 \text{ H}$); 1.09 ($d, J = 7.1, 3 \text{ H}$); 1.39–1.50 ($m, 1 \text{ H}$); 1.70–1.81 ($m, 1 \text{ H}$); 2.23–2.32 ($m, 1 \text{ H}$); 9.63 ($d, J = 1.7, 1 \text{ H}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 11.3; 12.7; 23.4; 47.6; 205.2. HR-MS: 86.0742 (M^+ , $\text{C}_5\text{H}_{10}\text{O}$; calc. 86.0732).

(*R*)-2-Methylbutanamine (**11**). To a soln. of **9** (2.0 g, 22.7 mmol) in pyridine (10 ml) was added TsCl (5.2 g, 27.3 mmol) at 0° , and the mixture was allowed to stand overnight. The mixture was poured into ice-water and extracted with Et_2O . The Et_2O soln. was washed with H_2O , CuSO_4 soln., NaHCO_3 soln., and brine, dried (MgSO_4), and concentrated *in vacuo* to give 5.5 g of tosylate as oil. This was employed in the next step without further purification.

To a soln. of crude tosylate (5.5 g) in DMF (25 ml) was added NaN_3 (3.0 g, 45.4 mmol) at r.t. The mixture was stirred for 3 h at 100° . The mixture was poured into H_2O and extracted with Et_2O . The Et_2O soln. was washed with brine, dried (MgSO_4), and concentrated *in vacuo* to give 2.2 g of azide as oil. This was employed in the next step without further purification.

A soln. of crude azide (2.2 g) in dry Et_2O (10 ml) was added dropwise to a stirred suspension of LiAlH_4 (1.5 g, 40 mmol) in dry Et_2O (50 ml) at 0° . The mixture was stirred for 4 h at r.t. The excess LiAlH_4 was decomposed by the successive addition of H_2O (1.5 ml), 15% aq. NaOH (1.5 ml), and H_2O (4.5 ml). The mixture was filtered, and the solid was washed with Et_2O . The combined filtrate and washings were dried (MgSO_4) and concentrated *in vacuo*. The oily residue was purified by distillation (b.p. $42-44^\circ/1.6 \text{ kPa}$) to give 1.2 g (61% from **9**) of **11**. $[\alpha]_D^{20} = +5.9$ ($c = 1.05$, MeOH). IR (film): 3373, 3298, 2960, 2926, 2874, 1603, 1462, 1379, 923, 840. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.90 ($t, J = 7.4, 3 \text{ H}$); 0.90 ($d, J = 6.4, 3 \text{ H}$); 1.10–1.17 ($m, 1 \text{ H}$); 1.34–1.44 ($m, 2 \text{ H}$); 1.61 ($s, 2 \text{ H}$); 2.49 ($dd, J = 6.8, 12.4, 1 \text{ H}$); 2.63 ($dd, J = 5.4, 12.4, 1 \text{ H}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 11.3; 17.0; 26.8; 37.8; 48.0. HR-MS: 87.0987 (M^+ , $\text{C}_5\text{H}_{13}\text{N}$; calc. 87.1048).

Imine Derivatives **1–4**. A soln. of aldehyde (1.0 equiv.) and amine (1.0 equiv.) was stirred for 3 h at r.t. The mixture was diluted with Et_2O and was washed with sat. NaHCO_3 soln. and brine, dried (MgSO_4), and concentrated *in vacuo*. The oily residue was purified by distillation to give the corresponding imine.

(*S*)-2-Methyl-N-(3'-methylbutylidene)butanamine ((*S*)-**1**): yield 59%. B.p. $62^\circ/2.0 \text{ kPa}$. $[\alpha]_D^{20} = -7.10$ ($c = 0.17$, MeOH). IR (film): 1167, 1380, 1463, 1670, 2826, 2873, 2929, 2957. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.86 ($d, J = 6.8, 3 \text{ H}$); 0.90 ($t, J = 5.1, 3 \text{ H}$); 0.96 ($d, J = 6.6, 6 \text{ H}$); 1.09–1.19 ($m, 1 \text{ H}$); 1.35–1.45 ($m, 1 \text{ H}$); 1.66–1.74 ($m, 1 \text{ H}$); 1.90–1.97 ($m, 1 \text{ H}$); 2.15 ($dd, J = 5.6, 12.2, 2 \text{ H}$); 3.12 ($dd, J = 7.3, 10.8, 1 \text{ H}$); 3.34 ($dd, J = 5.8, 10.8, 1 \text{ H}$);

7.61 (*tt*, $J = 1.2, 5.4, 1 \text{ H}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.3; 17.6; 22.5; 26.4; 27.4; 35.6; 44.7; 67.8; 164.6. GC/MS: 154 ($[M - 1]^+$), 140, 126, 113, 98, 84, 70, 56, 42, 39, 29. HR-MS: 155.1596 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

Compound (R)-1: yield 62%. $[\alpha]_{\text{D}}^{20} = 7.12$ ($c = 0.15$, MeOH). HR-MS: 155.1726 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

(S)-3-Methyl-N-(2'-methylbutylidene)butanamine ((S)-2): yield: 56%. $79^\circ/3.3 \text{ kPa}$. $[\alpha]_{\text{D}}^{20} = 17.7$ ($c = 0.19$, MeOH). IR (film): 1383, 1462, 1670, 2871, 2928, 2959. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.90 (*d*, $J = 6.6, 6 \text{ H}$); 0.91 (*t*, $J = 5.1, 3 \text{ H}$); 1.04 (*d*, $J = 6.8, 3 \text{ H}$); 1.31–1.66 (*m*, 5 H); 2.14–2.26 (*m*, 1 H); 3.36 (*t*, $J = 7.3, 2 \text{ H}$); 7.45 (*d*, $J = 5.8, 1 \text{ H}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.5; 17.0; 22.4; 22.5; 25.7; 27.0; 39.9; 40.9; 59.4; 168.9. GC/MS: 154 ($[M - 1]^+$), 140, 127, 113, 98, 84, 71, 56, 43, 39, 29. HR-MS: 155.1671 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

Compound (R)-2: yield: 58%. $[\alpha]_{\text{D}}^{20} = -17.5$ ($c = 0.18$, MeOH). HR-MS: 155.1709 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

(2S,2'S)-2-Methyl-N-(2'-methylbutylidene)butanamine ((2S,2'S)-3): yield: 51%. B.p. $59^\circ/2.0 \text{ kPa}$. $[\alpha]_{\text{D}}^{20} = -4.61$ ($c = 0.13$, MeOH). IR (film): 1379, 1460, 1671, 2821, 2875, 2929, 2962. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.85 (*dd*, $J = 1.7, 4.6, 3 \text{ H}$); 0.90 (*d*, $J = 5.1, 3 \text{ H}$); 0.90 (*dd*, $J = 5.1, 11.0, 3 \text{ H}$); 1.05 (*d*, $J = 6.8, 3 \text{ H}$); 1.08–1.73 (*m*, 5 H); 2.18–2.28 (*m*, 1 H); 3.10 (*dd*, $J = 7.3, 11.0, 1 \text{ H}$); 3.34 (*dd*, $J = 5.8, 11.0, 1 \text{ H}$); 7.41 (*d*, $J = 5.9, 1 \text{ H}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.3; 11.6; 17.1; 17.4; 27.1; 27.3; 35.5; 40.9; 67.6; 169.4. GC/MS: 154 ($[M - 1]^+$), 140, 127, 112, 98, 84, 70, 56, 43, 39, 29. HR-MS: calc. for $\text{C}_{10}\text{H}_{21}\text{N}$, 155.1674, found 155.1776.

Compound (2R,2'R)-3: yield: 50%. $[\alpha]_{\text{D}}^{20} = 5.17$ ($c = 0.12$, MeOH). HR-MS: 155.1683 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

Compound (2R,2'S)-3: yield: 55%. B.p. $58^\circ/2.0 \text{ kPa}$. $[\alpha]_{\text{D}}^{20} = 3.63$ ($c = 0.11$, MeOH). IR (film): 1379, 1460, 1671, 2821, 2875, 2929, 2962. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.85 (*dd*, $J = 1.5, 6.6, 3 \text{ H}$); 0.90 (*d*, $J = 4.9, 3 \text{ H}$); 0.90 (*dd*, $J = 5.1, 11.0, 3 \text{ H}$); 1.05 (*d*, $J = 6.8, 3 \text{ H}$); 1.08–1.73 (*m*, 5 H); 2.18–2.28 (*m*, 1 H); 3.10 (*dd*, $J = 7.3, 11.0, 1 \text{ H}$); 3.34 (*dd*, $J = 5.8, 11.0, 1 \text{ H}$); 7.41 (*d*, $J = 5.9, 1 \text{ H}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.3; 11.6; 17.1; 17.4; 27.1; 27.3; 35.5; 40.9; 67.6; 169.4. GC/MS: 154 ($[M - 1]^+$), 140, 127, 112, 98, 84, 70, 56, 43, 39, 29. HR-MS: 155.1617 (M^+ ; $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

Compound (2S,2'R)-3: yield: 53%. $[\alpha]_{\text{D}}^{20} = -3.84$ ($c = 0.10$, MeOH). HR-MS: 155.1614 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

3-Methyl-N-(3'-methylbutylidene)butanamine (4): yield: 58%. B.p. $66^\circ/2.0 \text{ kPa}$. IR (film): 1366, 1467, 1670, 2869, 2955. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.89 (*d*, $J = 6.3, 6 \text{ H}$); 0.94 (*d*, $J = 6.6, 6 \text{ H}$); 1.31–1.89 (*m*, 4 H); 2.11 (*t*, $J = 6.2, 2 \text{ H}$); 3.37 (*t*, $J = 7.2, 2 \text{ H}$); 7.64 (*t*, $J = 5.3, 1 \text{ H}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 22.5; 26.2; 26.4; 39.9; 44.7; 59.5; 164.2. GC/MS: 154 ($[M - 1]^+$), 140, 126, 113, 98, 84, 70, 57, 43, 39, 27. HR-MS: 155.1679 (M^+ , $\text{C}_{10}\text{H}_{21}\text{N}$; calc. 155.1674).

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Received July 18, 2002