

Enamides *via* Long-Distance Migration of Double Bonds

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A new method for preparation of enamides (*N*-(alken-1-yl) amides) by means of the ‘long-distance’ migration of the double bond in unsaturated amides in the presence of $[\text{Fe}(\text{CO})_5]$ is described. The method is shown to be particularly useful for the isomerization of *N*-(but-3-enyl)amides, while, in the case of *N*-(pent-4-enyl) and *N*-(hex-5-enyl) amides the mixture of products was formed and the yield of the enamide was relatively low.

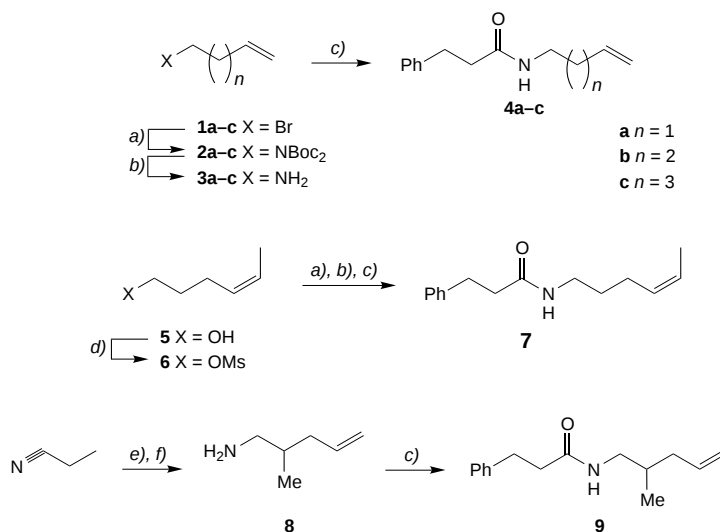
Introduction. – Enamides (*N*-(alken-1-yl) amides) are interesting substrates for various synthetic transformations [1]. Several methods have been employed for the preparation of simple enamides, but they are often structurally limited or suffer from low yields [2]. Discovery of natural enamides, which possess a wide spectrum of biological activity [3], stimulated research in the enamide synthesis in recent years [4].

Among other methods, isomerization of *N*-allyl amides to enamides is particularly attractive since *N*-allyl amides are readily available [5]. *Stille* and *Becker* [6] reported isomerization of several simple *N*-allyl amides to (*Z*)/(*E*)-enamide mixtures in moderate-to-high yields in the presence of hydridorhodium or -ruthenium complexes. Recently, we have found that various enamides can be smoothly prepared from the *N*-allyl amides in the presence of $[\text{Fe}(\text{CO})_5]$ [7]. The main advantage of the method is the availability of both starting materials and the catalyst. The procedure is compatible with various functional groups, and the yields are generally high. Later, we have successfully applied this procedure to the synthesis of macrocyclic enamide alkaloid neoperiphylline [8]. We are interested in the extension of this method to other unsaturated amides. In the present paper, we report successful preparation of enamides by the ‘long-distance’ migration of a C=C bond and discuss the limitations of this method.

Results and Discussion. – The unsaturated amides **4a–4c**, containing two to four CH_2 units between the amido group and the C=C bond, were prepared similarly to the method published recently [7] starting from commercially available bromides **1a–1c** (*Scheme 1*). Alkylation of $(\text{Boc})_2\text{NH}$ [9] with **1a–1c** in the presence of Cs_2CO_3 as phase-transfer catalyst afforded the *N,N*-bis(Boc) derivatives **2a–2c**, which were smoothly and quantitatively hydrolyzed with CF_3COOH (TFA) to the corresponding amines **3a–3c**. Acylation of the latter with 3-phenylpropanoyl chloride in the presence of Et_3N led to the unsaturated amides **4a–4c**. (*Z*)-*N*-(Hex-4-enyl)-3-phenylpropanamide (**7**) was prepared similarly from commercially available (*Z*)-hex-3-en-1-ol (**5**), which was first converted to the methanesulfonate **6** according to a published

procedure [10]. The unsaturated amine **8** with an additional side chain was prepared by alkylation of propanenitrile with allyl bromide, followed by reduction with LiAlH_4 as described by Tamaru *et al.* [11]. Subsequent acylation with 3-phenylpropanoyl chloride gave amide **9** (Scheme 1).

Scheme 1

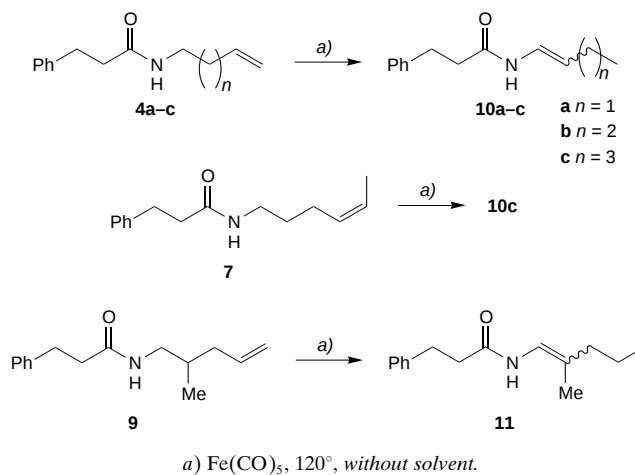


a) $(\text{Boc})_2\text{NH}$, Cs_2CO_3 , DMF, 70° . b) TFA, CH_2Cl_2 , r.t. c) $\text{PhCH}_2\text{CH}_2\text{COCl}$, Et_3N , CH_2Cl_2 , 0° . d) MsCl , Et_3N , CH_2Cl_2 , -10° . e) 1. LDA, THF, -80° ; 2. $\text{CH}_2=\text{CHCH}_2\text{Br}$, -80° . f) LiAlH_4 , Et_2O , reflux.

The isomerization of the unsaturated amides **4a–4c**, **7**, and **9** was performed in the presence of 1 equiv. of $[\text{Fe}(\text{CO})_5]$ at 120° without solvent (*cf.* [7]). In all cases, both (*E*)- and (*Z*)-isomers of enamides (Scheme 2), which were very difficult to separate by column chromatography, were obtained. Therefore, the (*E*)/(*Z*) ratio was determined from the intensities of the signals of $\text{CH}=\text{CHN}$ in $^1\text{H-NMR}$ spectra of the mixture of isomers. The configuration of the $\text{C}=\text{C}$ bond in **10a–10c** was assigned on the basis of the coupling constants (typically *ca.* 14 Hz for (*E*)- and *ca.* 9 Hz for (*Z*)-enamides; *cf.* [7]). For the enamide **11**, the (*E*)/(*Z*) ratio was determined from the integral intensities of the signals of $\text{MeC}=\text{CH}$ (see *Exper. Part*).

For the *N*-but-3-enyl amide **4a**, we observed complete conversion of the starting material to the enamide **10a**, which was obtained in almost the same yield as by the isomerization of *N*-(but-2-enyl)-3-phenylpropanamide [7][12]. Unfortunately, in the case of *N*-pent-4-enyl- or *N*-hex-5-enyl amides (**4b** and **4c**, resp.) the yields of the enamides were relatively low, and a considerable amount of side-product resulting from the ‘incomplete’ $\text{C}=\text{C}$ bond shift, was isolated (Table). All attempts to increase the yield of the enamides with higher temperatures or prolonged reaction times remained unsuccessful and resulted even in lower yields of the enamides because of decomposition. However, the enamides can be easily separated from the other products by column chromatography. Moreover, when *N*-(pent-2-enyl)-3-phenylpropanamide (**12**), the side product from the isomerization of **4b**, was treated with

Scheme 2

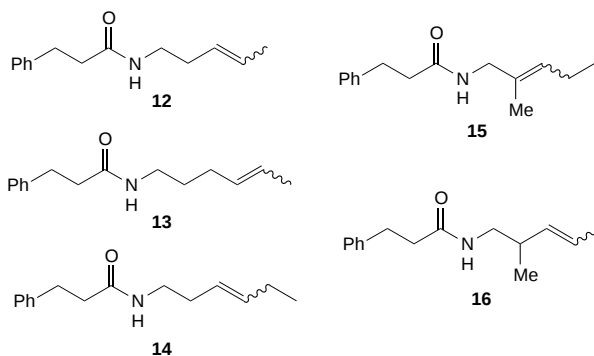
Table. Isomerization of the Amides **4a–4c**, **7**, **9** in the Presence of $[\text{Fe}(\text{CO})_5]$

Starting amide	Enamide (yield [%])	(<i>E</i>)/(<i>Z</i>) Ratio	Side products (yield [%])
4a	10a (56)	75 : 25	Not detected
4b	10b (32)	70 : 30	12 (55)
4c	10c (23)	71 : 29	13 , 14 (49) ^a)
7	10c (23)	66 : 34	13 , 14 (60) ^a)
9	11 (31)	62 : 38	15 , 16 (55) ^a)

^a) Total yield of all isolated side products.

$[\text{Fe}(\text{CO})_5]$ under the same conditions, an additional amount of the enamide **10b** (33% with respect to **12**) was isolated, and the total yield of **10b** from this two-run experiment was increased to 48% based on starting **4b**.

From (*Z*)-*N*-(hex-4-enyl)-3-phenylpropanamide (**7**), the enamide **10c** was obtained in the same yield as its isomer **4c** with the terminal C=C bond. Amide **9** with a



branched *N*-substituent also afforded enamide **11** in 31% yield, together with the side products **15** and **16**. Interestingly, only in this case were we able to detect remarkable amounts of amide **15** with allylic position of the C=C bond. It is consistent with the observation that additional substituents in the allylic moiety dramatically decreased the rate of isomerization of *N*-allyl amides to enamides [7][12].

We thank the *Swiss National Science Foundation* for financial support.

Experimental Part

General. All chemicals and solvents were obtained from commercial sources (*Fluka*, *Aldrich*, and *Merck*) and used without further purification unless stated otherwise. Technical-grade solvents were distilled before use. *[(Z)-Hex-4-enyl]methanesulfonate* (**6**) [10] and *2-methylpent-4-ene-1-amine* (**8**) [11] were prepared according to published procedures. Column chromatography (CC): SiO₂, *Merck 60* (40–63 µm). TLC: precoated SiO₂ plates, *Merck 60 F₂₅₄*; detection by UV at 254 nm or by spraying with KMnO₄ soln. M.p.: *Mettler FP-5*. ¹H-NMR: *Bruker ARX-300* (300 MHz); chemical shifts δ in ppm relative to Me₄Si as internal standard; *J* values in Hz. ¹³C-NMR: *Bruker ARX-300* (75 MHz); chemical shifts δ in ppm relative to Me₄Si as internal standard; signals multiplicity determined from DEPT experiments. CI-MS (NH₃ as reactant gas): *Finnigan MAT 90*, *m/z* and relative intensities (% of base peak) are given.

General Procedure 1 (GP 1) for the Preparation of Unsaturated Amides. A mixture of bromide **1** (15 mmol), (Boc)₂NH (2.17 g, 10 mmol), Cs₂CO₃ (3.26 g, 10 mmol), and DMF (10 ml) was stirred for 12 h at 70°, then the volatile materials were removed *in vacuo*. The residue was partitioned between CH₂Cl₂ (50 ml) and H₂O (50 ml), the org. phase was separated and washed with H₂O (2 × 50 ml), dried (MgSO₄), and concentrated to afford crude bis(Boc) derivative **2**, which was dissolved in CH₂Cl₂ (20 ml) and treated with CF₃COOH (TFA; 3 ml, ca. 40 mmol) in one portion. After 4 h stirring at r.t., the mixture was concentrated, and the residue was dried *in vacuo* to give crude amine **3** as TFA salt. It was dissolved in a mixture of CH₂Cl₂ (30 ml) and Et₃N (4.15 ml, 30 mmol), and treated dropwise at 0° with 3-phenylpropanoyl chloride (1.33 ml, 9 mmol). The mixture was stirred for 1 h at 0°, then allowed to reach r.t., washed with H₂O (25 ml), 10% aq. citric acid (25 ml), again H₂O (2 × 25 ml), and dried (MgSO₄). Evaporation of the solvent *in vacuo* and CC of the residue afforded **4**.

General Procedure 2 (GP 2) for the Isomerization of Unsaturated Amides. A mixture of unsaturated amide (**2** mmol) and [Fe(CO)₅] (0.2 ml, 1 mmol) was stirred under Ar for 16 h at 120°. The mixture was allowed to reach r.t., then the catalyst was removed *in vacuo* and collected in a trap cooled by liquid N₂. Content of the trap was treated with 5% soln. of FeCl₃ in EtOH to destroy toxic [Fe(CO)₅]. The residue in the reaction flask was dissolved in CH₂Cl₂/hexane 1:1 and filtered through *Celite*. The solvent was evaporated *in vacuo*, and the residue was purified by CC.

N-(But-3-enyl)-3-phenylpropanamide (4a). According to GP 1, 4-bromobut-1-ene (**1a**) afforded, after CC (CH₂Cl₂/AcOEt 4:1), **4a** (1.58 g, 86%). Colorless oil. *R_f* (CH₂Cl₂/AcOEt 10:1) 0.38. ¹H-NMR (CDCl₃): 2.18 (*q*-like *m*, CH₂CH); 2.45 (*t*, *J* = 7.7, CH₂CO); 2.95 (*t*, *J* = 7.7, PhCH₂); 3.24–3.32 (*m*, CH₂N); 4.97–5.05 (*m*, CH=CH₂); 5.44 (br. *s*, NH); 5.68 (*ddt*, *J* = 16.7, 10.7, 6.8, CH=CH₂); 7.17–7.30 (*m*, Ph). ¹³C-NMR (CDCl₃): 31.6 (*t*, PhCH₂); 33.5 (*t*, CH₂CH=); 38.3, 38.4 (*2t*, CH₂N, CH₂CO); 117.0 (*t*, CH=CH₂); 126.1 (*d*, arom. CH); 128.2, 128.4 (*2d*, 2 × 2 arom. CH); 135.1 (*d*, CH=CH₂); 140.7 (*s*, arom. C); 172.0 (*s*, C=O). CI-MS: 221 (18, [*M* + NH₄]⁺), 126 (100, [*M* + 1]⁺).

N-(Pent-4-enyl)-3-phenylpropanamide (4b). According to GP 1, 5-bromopent-1-ene (**1b**) afforded, after CC (CH₂Cl₂/AcOEt 5:1), **4b** (1.64 g, 84%). Colorless oil. *R_f* (CH₂Cl₂/AcOEt 10:1) 0.39. ¹H-NMR (CDCl₃): 1.52 (*quint*-like *m*, CH₂CH₂N); 1.95–2.04 (*m*, CH₂CH=CH₂); 2.45 (*t*, *J* = 7.6, CH₂CO); 2.95 (*t*, *J* = 7.6, PhCH₂); 3.17–3.25 (*m*, CH₂N); 5.08–5.18 (*m*, CH=CH₂); 5.40 (br. *s*, NH); 5.75 (*ddt*, *J* = 17.0, 10.3, 6.6, CH=CH₂); 7.16–7.31 (*m*, Ph). ¹³C-NMR (CDCl₃): 28.6 (*t*, CH₂CH₂N); 30.9, 31.7 (*2t*, PhCH₂, CH₂CH=CH₂); 38.5, 38.9 (*2t*, CH₂N, CH₂CO); 115.0 (*t*, CH=CH₂); 126.1 (*d*, arom. CH); 128.2, 128.4 (*2d*, 2 × 2 arom. CH); 137.6 (*d*, CH=CH₂); 140.8 (*s*, arom. C); 171.9 (*s*, C=O). CI-MS: 235 (6, [*M* + NH₄]⁺), 218 (100, [*M* + 1]⁺).

N-(Hex-5-enyl)-3-phenylpropanamide (4c). According to GP 1, 6-bromohex-1-ene (**1c**) afforded, after CC (CH₂Cl₂/AcOEt 5:1), **4c** (1.72 g, 83%). Colorless oil. *R_f* (CH₂Cl₂/AcOEt 10:1) 0.43. ¹H-NMR (CDCl₃): 1.25–1.49 (*m*, CH₂CH₂CH₂N); 1.99–2.07 (*m*, CH₂CH=CH₂); 2.45 (*t*, *J* = 7.7, CH₂CO); 2.96 (*t*, *J* = 7.7, PhCH₂); 3.17–3.24 (*m*, CH₂N); 4.92–5.03 (*m*, CH=CH₂); 5.29 (br. *s*, NH); 5.76 (*ddt*, *J* = 17.0, 10.3, 6.7, CH=CH₂); 7.16–7.31 (*m*, Ph). ¹³C-NMR (CDCl₃): 25.9, 28.8 (*2t*, CH₂CH₂CH₂N); 31.7 (*t*, PhCH₂); 33.2 (*t*, CH₂CH=CH₂); 38.5, 39.2

(2*t*, CH₂CO, CH₂N); 114.6 (*t*, CH=CH₂); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 138.3 (*d*, CH=CH₂); 140.8 (*s*, arom. C); 171.8 (*s*, C=O). CI-MS: 249 (7, [M + NH₄]⁺), 232 (100, [M + 1]⁺).

N-[(*Z*)-Hex-4-enyl]-3-phenylpropanamide (**7**). A mixture of **6** (1.78 g, 10 mmol), (Boc)₂NH (2.60 g, 12 mmol), Cs₂CO₃ (3.26 g, 10 mmol), and DMF (10 ml) was stirred for 12 h at 70°, then DMF was removed *in vacuo*. The residue was partitioned between CH₂Cl₂ (50 ml) and H₂O (50 ml), the org. phase was separated, washed with H₂O (2 × 50 ml), dried (MgSO₄), and concentrated. The intermediate *N,N*-bis-Boc derivative was isolated by CC (hexane/AcOEt 2:1). Subsequent transformation as described in GP 1 gave, after CC (CH₂Cl₂/AcOEt 5:1), **7** (1.85 g, 89%). Colorless oil. *R*_f (CH₂Cl₂/AcOEt 10:1) 0.40. ¹H-NMR (CDCl₃): 1.49 (*quint*-like *m*, CH₂CH₂N); 1.58 (*d*-like *m*, Me); 1.96–2.04 (*m*, CH₂CH=CH₂); 2.45 (*t*, *J* = 7.7, CH₂CO); 2.95 (*t*, *J* = 7.7, PhCH₂); 3.18–3.25 (*m*, CH₂N); 5.28–5.52 (*m*, CH=CH, NH); 7.16–7.31 (*m*, Ph). ¹³C-NMR (CDCl₃): 12.62 (*q*, Me); 24.1 (*t*, CH₂CH=CH₂); 29.2 (*t*, CH₂CH₂N); 31.7 (*t*, PhCH₂); 38.5, 39.1 (2*t*, CH₂CO, CH₂N); 124.6 (*d*, MeCH=); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 129.3 (*d*, CH₂CH=); 140.8 (*s*, arom. C); 171.8 (*s*, C=O). CI-MS: 232 ([M + 1]⁺).

N-(2-Methylpent-4-enyl)-3-phenylpropanamide (**9**). A soln. of **8** (4 mmol) and Et₃N (0.70 ml, 5 mmol) in Et₂O (20 ml) was treated dropwise at 0° with 3-phenylpropanoyl chloride (0.76 ml, 4 mmol). The mixture was stirred for 30 min at 0°, then allowed to reach r.t., washed with H₂O (25 ml), 10% aq. citric acid (25 ml), again H₂O (2 × 25 ml), and dried (MgSO₄). Evaporation of the solvent *in vacuo* and CC (CH₂Cl₂/AcOEt 10:1) gave **9** (0.88 g, 95%). Colorless oil. *R*_f (CH₂Cl₂/AcOEt 10:1) 0.44. ¹H-NMR (CDCl₃): 0.82 (*d*, *J* = 6.7, Me); 1.65 (*oct*-like *m*, MeCH); 1.78–1.89, 1.96–2.06 (2*m*, CH₂CH=); 2.48 (*t*, *J* = 7.6, CH₂CO); 2.96 (*t*, *J* = 7.6, PhCH₂); 3.00–3.19 (*m*, CH₂N); 4.95–5.03 (*m*, CH=CH₂); 5.52 (*br. s*, NH); 5.65–5.79 (*m*, CH=CH₂); 7.16–7.31 (*m*, Ph). ¹³C-NMR (CDCl₃): 17.3 (*q*, Me); 31.7 (*t*, CH₂Ph); 33.0 (*d*, MeCH); 38.4, 38.7 (2*t*, CH₂CO, CH₂CH=); 45.0 (*t*, CH₂N); 116.2 (*t*, CH=CH₂); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 136.4 (*d*, CH=CH₂); 140.7 (*s*, arom. C); 172.0 (*s*, C=O). CI-MS: 232 ([M + 1]⁺).

N-(*But*-1-enyl)-3-phenylpropanamide (**10a**). According to GP 2, **4a** (2 mmol, 406 mg) afforded, after CC, **10a** (227 mg, 56%) as a mixture of (*E*)- and (*Z*)-isomers. Colorless solid. *R*_f (CH₂Cl₂/AcOEt 10:1) 0.45. Spectral data of the mixture. ¹H-NMR (CDCl₃): (*E*)-**10a**: 0.99 (*t*, *J* = 7.4, Me); 1.96–2.05 (*m*, MeCH₂); 2.49 (*t*, *J* = 7.8, CH₂CO); 2.90–2.98 (*m*, PhCH₂); 5.12 (*dt*, *J* = 14.2, 6.7, CH=CHN); 6.73–6.79 (*m*, CH=CHN); 7.15–7.31 (*m*, Ph, NH); (*Z*)-**10a**: 0.94 (*t*, *J* = 7.5, Me); 1.82–1.90 (*m*, MeCH₂); 2.57 (*t*, *J* = 7.6, CH₂CO); 4.66 (*dt*, *J* = 8.8, 7.3, CH=CHN); 6.59–6.66 (*m*, CH=CHN). Other signals overlapped with those of (*E*)-**10a**. ¹³C-NMR (CDCl₃): (*E*)-**10a**: 14.1 (*q*, Me); 22.8 (*t*, MeCH₂); 31.4 (*t*, PhCH₂); 38.2 (*t*, CH₂CO); 114.9 (*d*, CH=CHN); 121.7 (*d*, CH=CHN); 126.2 (*d*, arom. CH); 128.2, 128.5 (2*d*, 2 × 2 arom. CH); 140.6 (*s*, arom. C); 169.3 (*s*, C=O); (*Z*)-**10a**: 13.8 (*q*, Me); 18.8 (*t*, MeCH₂); 113.1 (*d*, CH=CHN); 120.0 (*d*, CH=CHN); 126.3 (*d*, arom. CH); 169.4 (*s*, C=O). Other signals overlapped with those of (*E*)-**10a**. CI-MS: 407 (7, [2M + 1]⁺), 221 (37, [M + NH₄]⁺), 204 (100, [M + 1]⁺).

N-(*Pent*-1-enyl)-3-phenylpropanamide (**10b**). According to GP 2, **4b** (2 mmol, 434 mg) afforded, after CC, **10b** (140 mg, 32%) as a mixture of (*E*)- and (*Z*)-isomers. Colorless solid. *R*_f (CH₂Cl₂/AcOEt 10:1) 0.48. Spectral data of the mixture: ¹H-NMR (CDCl₃): (*E*)-**10b**: 0.86 (*t*, *J* = 7.4, Me); 1.28–1.41 (*m*, MeCH₂); 1.91–2.01 (*m*, CH₂CH=); 2.50 (*t*, *J* = 7.8, CH₂CO); 2.91–2.98 (*m*, PhCH₂); 5.13 (*dt*, *J* = 14.2, 7.2, CH=CHN); 6.68–6.76 (*m*, CH=CHN); 7.13–7.28 (*m*, Ph); 7.91 (*br. d*, NH). (*Z*)-**10b**: 0.87 (partially overlapped *t*, *J* = 7.3, Me); 1.82–1.91 (*m*, CH₂CH=); 2.58 (*t*, *J* = 7.6, CH₂CO); 4.67 (*dt*, *J* = 8.9, 7.4, CH=CHN); 6.62–6.68 (*m*, CH=CHN); 7.36 (*br. d*, NH). Other signals overlapped with those of (*E*)-**10b**. ¹³C-NMR (CDCl₃): (*E*)-**10b**: 13.4 (*q*, Me); 22.9 (*t*, MeCH₂); 31.4 (*t*, PhCH₂); 31.7 (*t*, CH₂CH=); 38.1 (*t*, CH₂CO); 113.2 (*d*, CH=CHN); 122.5 (*d*, CH=CHN); 126.1 (*d*, arom. CH); 128.2, 128.5 (2*d*, 2 × 2 arom. CH); 140.7 (*s*, arom. C); 169.5 (*s*, C=O); (*Z*)-**10b**: 13.8 (*q*, Me); 22.4 (*t*, MeCH₂); 27.6 (*t*, CH₂CH=); 111.6 (*d*, CH=CHN); 120.7 (*d*, CH=CHN); 126.3 (*d*, arom. CH); 169.8 (*s*, C=O). Other signals overlapped with those of (*E*)-**10b**. CI-MS: 435 (6, [2M + 1]⁺); 218 (100, [M + 1]⁺).

N-(*Hex*-1-enyl)-3-phenylpropanamide (**10c**). a). According to GP 2, **4c** (2 mmol, 462 mg) afforded, after CC, **10c** (106 mg, 23%) as a mixture of (*E*)- and (*Z*)-isomers. b). According to GP 2, **7** (2 mmol, 462 mg) afforded, after CC **10c** (108 mg, 23%). Colorless solid. *R*_f (CH₂Cl₂/AcOEt 10:1) 0.50. Spectral data of the mixture. ¹H-NMR (CDCl₃): (*E*)-**10c**: 0.84–0.90 (*m*, Me); 1.22–1.36 (*m*, CH₂CH₂Me); 1.94–2.01 (*m*, CH₂CH=); 2.47 (*t*, *J* = 7.7, CH₂CO); 2.90–2.99 (*m*, PhCH₂); 5.10 (*dt*, *J* = 14.2, 7.1, CH=CHN); 6.68–6.76 (*m*, CH=CHN); 7.15–7.32 (*m*, Ph); 7.53 (*br. d*, NH). (*Z*)-**10c**: 1.82–1.89 (*m*, CH₂CH=); 2.57 (*m*, CH₂CO); 4.67 (*dt*, *J* = 8.8, 7.4, CH=CHN); 6.61–6.68 (*m*, CH=CHN) 7.36 (*br. d*, NH). Other signals overlapped with those of (*E*)-**10c**. ¹³C-NMR (CDCl₃): (*E*)-**10c**: 13.8 (*q*, Me); 22.0 (*t*, MeCH₂); 29.2, 31.4, 31.9 (3*t*, CH₂CH₂CH=, CH₂Ph); 38.1 (*t*, CH₂CO); 113.3 (*d*, CH=CHN); 122.3 (*d*, CH=CHN); 126.1 (*d*, arom. CH); 128.2, 128.5 (2*d*, 2 × 2 arom. CH); 140.6 (*s*, arom. C); 169.3 (*s*, C=O). (*Z*)-**10c**: 22.2 (*t*, MeCH₂); 25.2 (*t*, CH₂CH=); 111.6 (*d*,

CH=CHN); 120.5 (*d*, CH=CHN); 126.3 (*d*, arom. CH); 140.4 (*s*, arom. C); 169.5 (*s*, C=O). Other signals overlapped with those of (*E*)-**10c**. CI-MS: 232 ($[M+1]^+$).

N-(2-Methylpent-1-enyl)-3-phenylpropanamide (**11**). According to GP 2, **9** (2 mmol, 462 mg) afforded, after CC, **11** (143 mg, 31%) as a mixture of (*E*)- and (*Z*)-isomers. Colorless solid. R_f (CH₂Cl₂/AcOEt 10:1) 0.51. ¹H-NMR (CDCl₃): (*E*)-**11** 0.85 (*t*, *J* = 7.2, MeCH₂); 1.29–1.42 (*m*, MeCH₂); 1.49 (*s*, MeC=); 1.94 (*t*, *J* = 7.4, CH₂C=); 2.56 (*m*, CH₂CO); 2.96 (*m*, PhCH₂); 6.52 (*d*-like *m*, CH=); 7.16–7.31 (*m*, Ph, NH). (*Z*)-**11**: 1.63 (*s*, MeC=); 1.84 (*t*, *J* = 7.5, CH₂C=). Other signals overlapped with those of (*E*)-**11**. ¹³C-NMR (CDCl₃): (*E*)-**11**: 13.5, 14.4 (2*q*, 2 Me); 20.8 (*t*, MeCH₂); 31.5 (*t*, PhCH₂); 38.1 (*t*, CH₂CO), 38.6 (*t*, CH₂C=); 116.9 (*d*, CH=); 118.9 (*s*, C=); 126.2 (*d*, arom. CH); 128.2, 128.5 (2*d*, 2 × 2 arom. CH); 140.6 (*s*, arom. C); 169.3 (*s*, C=O). (*Z*)-**11**: 13.8, 20.0 (2*q*, 2 Me); 20.2 (*t*, MeCH₂); 32.5 (*t*, CH₂C=); 119.4 (*s*, C=). Other signals overlapped with those of (*E*)-**11**. CI-MS: 232 ($[M+1]^+$).

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