Enamides *via* Long-Distance Migration of Double Bonds

by **Sergey A. Sergeyev** and **Manfred Hesse***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
(phone: 41-1-6354281; fax: 41-1-6356812; e-mail: mtbohley@oci.unizh.ch)

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 $[Fe(CO)_5]$ 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.

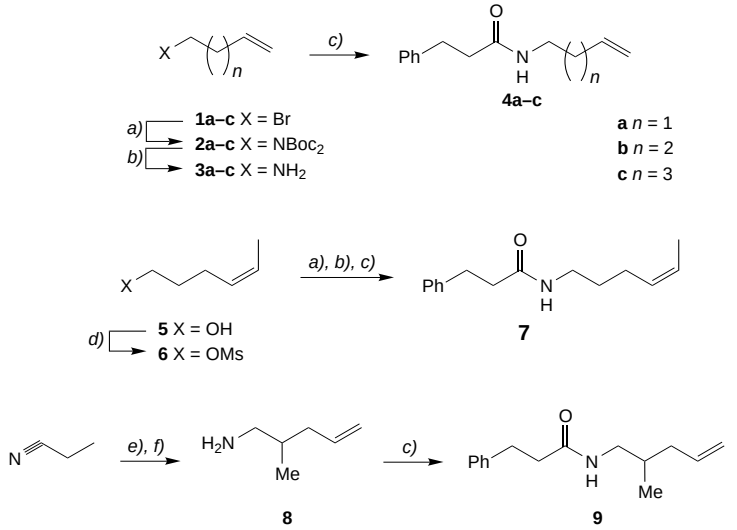
Introduction. – Enamides (*N*-(alken-1-yl) amides) are interesting substrates for various synthetic transformations [1]. Several methods have been employed for the preparation of simple enamides, but they are often structurally limited or suffer from low yields [2]. Discovery of natural enamides, which 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 $[Fe(CO)_5]$ [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 $(Boc)_2NH$ [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

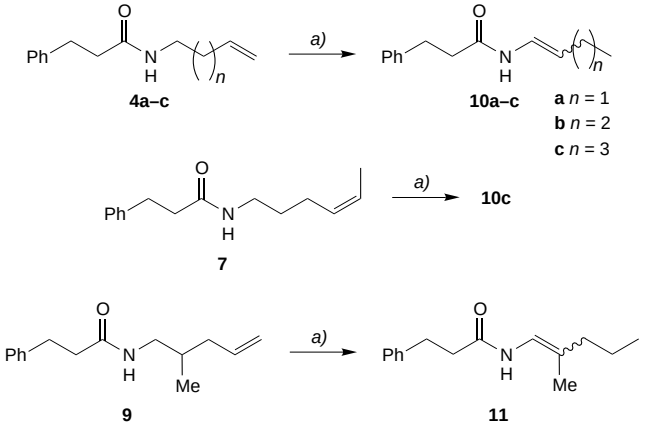


a) $(Boc)_2NH$, Cs_2CO_3, DMF, 70°. *b*) TFA, CH_2Cl_2, r.t. *c*) $PhCH_2CH_2COCl$, Et_3N, CH_2Cl_2, 0°. *d*) MsCl, Et_3N, CH_2Cl_2, −10°. *e*) 1. LDA, THF, −80°; 2. $CH_2{=}CHCH_2Br$, −80°. *f*) $LiAlH_4$, Et_2O, reflux.

The isomerization of the unsaturated amides **4a**–**4c**, **7**, and **9** was performed in the presence of 1 equiv. of $[Fe(CO)_5]$ 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 C*H*=CHN in ^{1}H-NMR spectra of the mixture of isomers. The configuration of the C=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 *Me*C=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' C=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



a) $Fe(CO)_5$, 120°, *without solvent.*

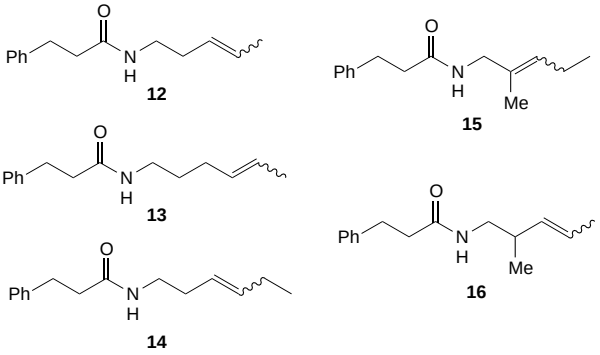
Table. *Isomerization of the Amides* **4a**–**4c**, **7**, **9** *in the Presence of [Fe(CO)$_5$]*

Starting amide	Enamide (yield [%])	(*E*)/(*Z*) 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.

[$Fe(CO)_5$] 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].

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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): SiO_2, *Merck 60* (40–63 μm). TLC: precoated SiO_2 plates, *Merck 60* F_{254}; detection by UV at 254 nm or by spraying with $KMnO_4$ soln. M.p.: *Mettler FP-5*. ^{1}H-NMR: *Bruker ARX-300* (300 MHz); chemical shifts δ in ppm relative to Me_4Si as internal standard; *J* values in Hz. ^{13}C-NMR: *Bruker ARX-300* (75 MHz); chemical shifts δ in ppm relative to Me_4Si as internal standard; signals multiplicity determined from DEPT experiments. CI-MS (NH_3 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), Cs_2CO_3 (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 CH_2Cl_2 (50 ml) and H_2O (50 ml), the org. phase was separated and washed with H_2O (2 × 50 ml), dried ($MgSO_4$), and concentrated to afford crude bis(Boc) derivative **2**, which was dissolved in CH_2Cl_2 (20 ml) and treated with CF_3COOH (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 CH_2Cl_2 (30 ml) and Et_3N (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 H_2O (25 ml), 10% aq. citric acid (25 ml), again H_2O (2 × 25 ml), and dried ($MgSO_4$). 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 N_2. Content of the trap was treated with 5% soln. of $FeCl_3$ in EtOH to destroy toxic $[Fe(CO)_5]$. The residue in the reaction flask was dissolved in CH_2Cl_2/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 (CH_2Cl_2/AcOEt 4:1), **4a** (1.58 g, 86%). Colorless oil. R_f (CH_2Cl_2/AcOEt 10:1) 0.38. ^{1}H-NMR ($CDCl_3$): 2.18 (*q*-like *m*, CH_2CH); 2.45 (*t*, *J* = 7.7, CH_2CO); 2.95 (*t*, *J* = 7.7, PhCH_2); 3.24–3.32 (*m*, CH_2N); 4.97–5.05 (*m*, CH=CH_2); 5.44 (br. *s*, NH); 5.68 (*ddt*, *J* = 16.7, 10.7, 6.8, C*H*=CH$_2$); 7.17–7.30 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 31.6 (*t*, Ph*C*H$_2$); 33.5 (t, *C*H$_2$CH=); 38.3, 38.4 (2*t*, *C*H$_2$N, *C*H$_2$CO); 117.0 (*t*, CH=*C*H$_2$); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 135.1 (*d*, *C*H=CH$_2$); 140.7 (*s*, arom. C); 172.0 (*s*, C=O). CI-MS: 221 (18, $[M+NH_4]^+$), 126 (100, $[M+1]^+$).

N-*(Pent-4-enyl)-3-phenylpropanamide* (**4b**). According to *GP 1*, *5-bromopent-1-ene* (**1b**) afforded, after CC (CH_2Cl_2/AcOEt 5:1), **4b** (1.64 g, 84%). Colorless oil. R_f (CH_2Cl_2/AcOEt 10:1) 0.39. ^{1}H-NMR ($CDCl_3$): 1.52 (*quint.*-like *m*, CH_2CH$_2$N); 1.95–2.04 (*m*, CH_2CH=CH$_2$); 2.45 (*t*, *J* = 7.6, CH_2CO); 2.95 (*t*, *J* = 7.6, PhCH_2); 3.17–3.25 (*m*, CH_2N); 5.08–5.18 (*m*, CH=CH_2); 5.40 (br. *s*, NH); 5.75 (*ddt*, *J* = 17.0, 10.3, 6.6, C*H*=CH$_2$); 7.16–7.31 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 28.6 (*t*, *C*H$_2$CH$_2$N); 30.9, 31.7 (2*t*, Ph*C*H$_2$, *C*H$_2$CH=CH$_2$); 38.5, 38.9 (2*t*, CH_2N, *C*H$_2$CO); 115.0 (*t*, CH=*C*H$_2$); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 137.6 (*d*, *C*H=CH$_2$); 140.8 (*s*, arom. C); 171.9 (*s*, C=O). CI-MS: 235 (6, $[M+NH_4]^+$), 218 (100, $[M+1]^+$).

N-*(Hex-5-enyl)-3-phenylpropanamide* (**4c**). According to *GP 1*, *6-bromohex-1-ene* (**1c**) afforded, after CC (CH_2Cl_2/AcOEt 5:1), **4c** (1.72 g, 83%). Colorless oil. R_f (CH_2Cl_2/AcOEt 10:1) 0.43. ^{1}H-NMR ($CDCl_3$): 1.25–1.49 (*m*, CH_2CH_2CH$_2$N); 1.99–2.07 (*m*, CH_2CH=CH$_2$); 2.45 (*t*, *J* = 7.7, CH_2CO); 2.96 (*t*, *J* = 7.7, PhCH_2); 3.17–3.24 (*m*, CH_2N); 4.92–5.03 (*m*, CH=CH_2); 5.29 (br. *s*, NH); 5.76 (*ddt*, *J* = 17.0, 10.3, 6.7, C*H*=CH$_2$); 7.16–7.31 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 25.9, 28.8 (2*t*, *C*H$_2$C*H*$_2$CH$_2$N); 31.7 (*t*, Ph*C*H$_2$); 33.2 (*t*, *C*H$_2$CH=CH$_2$); 38.5, 39.2

(2*t*, *C*H$_2$CO, CH$_2$N); 114.6 (*t*, CH=*C*H$_2$); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 138.3 (*d*, *C*H=CH$_2$); 140.8 (*s*, arom. C); 171.8 (*s*, C=O). CI-MS: 249 (7, $[M+NH_4]^+$), 232 (100, $[M+1]^+$).

N-*[(Z)-Hex-4-enyl]-3-phenylpropanamide* (**7**). A mixture of **6** (1.78 g, 10 mmol), (Boc)$_2$NH (2.60 g, 12 mmol), Cs_2CO_3 (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 CH_2Cl_2 (50 ml) and H_2O (50 ml), the org. phase was separated, washed with H_2O (2 × 50 ml), dried ($MgSO_4$), 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 (CH_2Cl_2/AcOEt 5:1), **7** (1.85 g, 89%). Colorless oil. R_f (CH_2Cl_2/AcOEt 10:1) 0.40. ^{1}H-NMR ($CDCl_3$): 1.49 (*quint*-like *m*, C*H*$_2$CH$_2$N); 1.58 (*d*-like *m*, Me); 1.96–2.04 (*m*, C*H*$_2$CH=CH$_2$); 2.45 (*t*, *J* = 7.7, CH$_2$CO); 2.95 (*t*, *J* = 7.7, PhC*H*$_2$); 3.18–3.25 (*m*, CH$_2$N); 5.28–5.52 (*m*, CH=CH, NH); 7.16–7.31 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 12.62 (*q*, Me); 24.1 (*t*, *C*H$_2$CH=CH$_2$); 29.2 (*t*, *C*H$_2$CH$_2$N); 31.7 (*t*, PhCH$_2$); 38.5, 39.1 (2*t*, *C*H$_2$CO, CH$_2$N); 124.6 (*d*, MeCH=); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 129.3 (*d*, CH$_2$CH=); 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 Et$_3$N (0.70 ml, 5 mmol) in Et$_2$O (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 H_2O (25 ml), 10% aq. citric acid (25 ml), again H_2O (2 × 25 ml), and dried ($MgSO_4$). Evaporation of the solvent *in vacuo* and CC (CH_2Cl_2/AcOEt 10:1) gave **9** (0.88 g, 95%). Colorless oil. R_f (CH_2Cl_2/AcOEt 10:1) 0.44. ^{1}H-NMR ($CDCl_3$): 0.82 (*d*, *J* = 6.7, Me); 1.65 (*oct.*-like *m*, MeC*H*); 1.78–1.89, 1.96–2.06 (2*m*, C*H*$_2$CH=); 2.48 (*t*, *J* = 7.6, CH$_2$CO); 2.96 (*t*, *J* = 7.6, PhC*H*$_2$); 3.00–3.19 (*m*, CH$_2$N); 4.95–5.03 (*m*, CH=CH$_2$); 5.52 (br. *s*, NH); 5.65–5.79 (*m*, C*H*=CH$_2$); 7.16–7.31 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 17.3 (*q*, Me); 31.7 (*t*, *C*H$_2$Ph); 33.0 (*d*, Me*C*H); 38.4, 38.7 (2*t*, *C*H$_2$CO, *C*H$_2$CH=); 45.0 (*t*, CH$_2$N); 116.2 (*t*, CH=*C*H$_2$); 126.1 (*d*, arom. CH); 128.2, 128.4 (2*d*, 2 × 2 arom. CH); 136.4 (*d*, *C*H=CH$_2$); 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 (CH_2Cl_2/AcOEt 10:1) 0.45. Spectral data of the mixture. ^{1}H-NMR ($CDCl_3$): (*E*)-**10a**: 0.99 (*t*, *J* = 7.4, Me); 1.96–2.05 (*m*, Me*C*H$_2$); 2.49 (*t*, *J* = 7.8, CH$_2$CO); 2.90–2.98 (*m*, PhC*H*$_2$); 5.12 (*dt*, *J* = 14.2, 6.7, *C*H=CHN); 6.73–6.79 (*m*, CH=C*H*N); 7.15–7.31 (*m*, Ph, NH); (*Z*)-**10a**: 0.94 (*t*, *J* = 7.5, Me); 1.82–1.90 (*m*, Me*C*H$_2$); 2.57 (*t*, *J* = 7.6, CH$_2$CO); 4.66 (*dt*, *J* = 8.8, 7.3, C*H*=CHN); 6.59–6.66 (*m*, CH=C*H*N). Other signals overlapped with those of (*E*)-**10a**. ^{13}C-NMR ($CDCl_3$): (*E*)-**10a**: 14.1 (*q*, Me); 22.8 (*t*, Me*C*H$_2$); 31.4 (*t*, PhCH$_2$); 38.2 (*t*, *C*H$_2$CO); 114.9 (*d*, *C*H=CHN); 121.7 (*d*, CH=*C*HN); 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*, Me*C*H$_2$); 113.1 (*d*, *C*H=CHN); 120.0 (*d*, CH=*C*HN); 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, $[M+NH_4]^+$), 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 (CH_2Cl_2/AcOEt 10:1) 0.48. Spectral data of the mixture: ^{1}H-NMR ($CDCl_3$): (*E*)-**10b**: 0.86 (*t*, *J* = 7.4, Me); 1.28–1.41 (*m*, Me*C*H$_2$); 1.91–2.01 (*m*, C*H*$_2$CH=); 2.50 (*t*, *J* = 7.8, CH$_2$CO); 2.91–2.98 (*m*, PhC*H*$_2$); 5.13 (*dt*, *J* = 14.2, 7.2, C*H*=CHN); 6.68–6.76 (*m*, CH=C*H*N); 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*, C*H*$_2$CHC=); 2.58 (*t*, *J* = 7.6, CH$_2$CO); 4.67 (*dt*, *J* = 8.9, 7.4, C*H*=CHN); 6.62–6.68 (*m*, CH=C*H*N); 7.36 (br. *d*, NH). Other signals overlapped with those of (*E*)-**10b**. ^{13}C-NMR ($CDCl_3$): (*E*)-**10b**: 13.4 (*q*, Me); 22.9 (*t*, Me*C*H$_2$); 31.4 (*t*, PhCH$_2$); 31.7 (*t*, *C*H$_2$CH=); 38.1 (*t*, *C*H$_2$CO); 113.2 (*d*, *C*H=CHN); 122.5 (*d*, CH=*C*HN); 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*, Me*C*H$_2$); 27.6 (*t*, *C*H$_2$CH=); 111.6 (*d*, *C*H=CHN); 120.7 (*d*, CH=*C*HN); 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 (CH_2Cl_2/AcOEt 10:1) 0.50. Spectral data of the mixture. ^{1}H-NMR ($CDCl_3$): (*E*)-**10c**: 0.84–0.90 (*m*, Me); 1.22–1.36 (*m*, C*H*$_2$C*H*$_2$Me); 1.94–2.01 (*m*, C*H*$_2$CH=); 2.47 (*t*, *J* = 7.7, CH$_2$CO); 2.90–2.99 (*m*, PhC*H*$_2$); 5.10 (*dt*, *J* = 14.2, 7.1, C*H*=CHN); 6.68–6.76 (*m*, CH=C*H*N); 7.15–7.32 (*m*, Ph); 7.53 (br. *d*, NH). (*Z*)-**10c**: 1.82–1.89 (*m*, C*H*$_2$CH=); 2.57 (*m*, CH$_2$CO); 4.67 (*dt*, *J* = 8.8, 7.4, C*H*=CHN); 6.61–6.68 (*m*, CH=C*H*N) 7.36 (br. *d*, NH). Other signals overlapped with those of (*E*)-**10c**. ^{13}C-NMR ($CDCl_3$): (*E*)-**10c**: 13.8 (*q*, Me); 22.0 (*t*, Me*C*H$_2$); 29.2, 31.4, 31.9 (3*t*, *C*H$_2$*C*H$_2$CH=, *C*H$_2$Ph); 38.1 (*t*, *C*H$_2$CO); 113.3 (*d*, *C*H=CHN); 122.3 (*d*, CH=*C*HN); 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*, Me*C*H$_2$); 25.2 (*t*, *C*H$_2$CH=); 111.6 (*d*,

*C*H=CHN); 120.5 (*d*, CH=*C*HN); 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 (CH_2Cl_2/AcOEt 10 : 1) 0.51. ^{1}H-NMR ($CDCl_3$): (*E*)-**11** 0.85 (*t*, *J* = 7.2, $MeCH_2$); 1.29 – 1.42 (*m*, $MeCH_2$); 1.49 (*s*, MeC=); 1.94 (*t*, *J* = 7.4, CH_2C=); 2.56 (*m*, CH_2CO); 2.96 (*m*, $PhCH_2$); 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, CH_2C=). Other signals overlapped with those of (*E*)-**11**. ^{13}C-NMR ($CDCl_3$): (*E*)-**11**: 13.5, 14.4 (2*q*, 2 Me); 20.8 (*t*, $MeCH_2$); 31.5 (*t*, $PhCH_2$); 38.1 (*t*, CH_2CO), 38.6 (*t*, CH_2C=); 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*, $MeCH_2$); 32.5 (*t*, CH_2C=); 119.4 (*s*, C=). Other signals overlapped with those of (*E*)-**11**. CI-MS: 232 ([*M* + 1]$^+$).

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