Amination of aryl- and vinylacetylenic compounds catalyzed by rhodium(I) complexes

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New rhodium-catalyzed amination reactions of arylacetylenes and cyclohexen-1-ylacetylene in the presence of strong bases with the use of carbon dioxide as an auxiliary are described. Secondary amines attack the terminal carbon atom of the triple bond followed by protonation of the adjacent carbon atom. Alternatively, the reaction can proceed further with the addition of the second alkyne molecule. The conditions for the selective synthesis of enamines (up to 87% yield) or α-substituted propynylamines (up to 86% yield) are reported.

Key words: arylacetylenes, cyclohexen-1-ylacetylene, amination, catalysis by rhodium(I) complexes.

Amination of acetylenic compounds is an important goal of chemical research. The resulting enamines are versatile intermediates in organic synthesis.[1] However, with the exception of arylacetylenes containing electron-withdrawing groups, which react spontaneously with amines,[2] the addition of amino groups to alkynes did not give satisfactory results.[3a—c] Platinum[3b] or mercury[3c] complexes were used as catalysts for amination of acetylenic compounds. Generally, reactions catalyzed by CuCl[4] afforded adducts of amine with two alkyne molecules in substantial amounts. The intramolecular amination with the participation of palladium was also described.[5] In this work, we report a simple procedure for the rhodium-catalyzed amination of arylacetylenes, which is free from the drawbacks of procedures reported previously and proceeds selectively.

Results and Discussion

We have found that aryl- and vinylacetylenes undergo smooth amination at the terminal position of the triple bond under the action of dialkylamines or aliphatic cyclic secondary amines in the presence of rhodium(I) complexes. Aliphatic cyclic secondary amines react as dialkyl carbamates of strong bases (B) with $\log K_b \geq 23$ (such as tetramethylguanidine (TMG)), which were prepared directly in the presence of CO_2 in acetonitrile at 75 °C. The reaction does not proceed in the absence of carbon dioxide, which acts as a catalyst without being incorporated in the reaction product (Eq. (1)).

$$\underset{\mathbf{1}}{R_2NH} + \underset{\mathbf{2}}{\equiv\!\!-R'} \xrightarrow[B]{[Rh],\ CO_2} \underset{\mathbf{3}}{E\text{-}R_2NCH{=}CHR'} \xrightarrow{2} \underset{\mathbf{4}}{R_2NCH(CH_2R')C{\equiv}CR'} \quad (1)$$

1: R_2 = Et_2 (**a**), $(CH_2)_4$ (**b**), $(CH_2)_5$ (**c**), $((CH_2)_2)_2O$ (**d**), $(CH_2)_3CH(CO_2Me)$ (**e**)

2: R′ = Ph (**a**), *p*-ClC_6H_4 (**b**), *p*-MeC_6H_4 (**c**), $\underline{(CH_2)_4CH{=}C}$ (**d**)

[Rh] = $RhCl(PPh_3)_3$; B is base

Primary amines do not enter into amination reactions at the triple bond. No reaction occurs with secondary amines with too low basicity (such as aromatic secondary amines), sterically hindered amines (such as diisopropylamine and 2,2,6,6-tetramethylpiperidine), and in general, secondary amines that, although strongly basic, are not nucleophilic enough for these compounds to attack carbon dioxide. The reactions of amines **1**, which are characterized by moderately low basicity, with substituted acetylenes **2** afforded predominantly compounds **4** (rather than compounds **3** as the major product), which formally results from the addition of the second acetylenic molecule to enamines **3**.

A secondary amine : phenylacetylene molar ratio of 2 : 1 was found to give the best total yields of compounds **3** and **4**. A higher ratio, such as 4 : 1, led to better yields of enamines **3**, while a lower ratio, such as 1 : 1, resulted in a decrease in the yield of compound **3**

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Table 1. Reactions of secondary amines with terminal acetylenic derivatives in the presence of $RhCl(PPh_3)_3$ (0.093 g, 0.1 mmol), CO_2 (1 bar), and tetramethylguanidine (0.58 g, 5 mmol) in MeCN (25 mL)[a]

Run	Amine 1 ($\log K_b$)[b]	Acetylene 2 (*n*/mmol)	TMG, *n*/mmol	1 : 2	Conversion (%)[c]	Yield (%)[c]	
						3	4
1	**1a** (10.933)	**2a** (5)	5	2	95	51	25
2	**1a** (10.933)	**2a** (5)	5	4	92	59	—
3	**1a** (10.933)	**2a** (5)	5	1	96	18	42
4	**1b** (11.305)	**2a** (5)	5	2	>99	87 (73)[d]	3 (1)[d]
5	**1c** (11.123)	**2a** (5)	5	2	98	72	18
6	**1c** (11.123)	**2a** (5)	10	2	96	67	13
7	**1c** (11.123)	**2a** (5)	5	1	97	32	33
8	**1c** (11.123)	**2a** (20)	10	0.5	76	20	24
9	**1e**[e] (10.64)	**2a** (5)	5	2	96	45	39
10	**1d** (8.492)	**2a** (5)	5	2	98	9 (6)[d]	86 (70)[d]
11	**1d** (8.492)	**2a** (5)	5	4	83	13	55
12	**1b** (11.305)	**2b** (5)	5	2	97	78	1
13	**1b** (11.305)	**2c** (5)	5	2	98	81	1
14	**1b** (11.305)	**2d** (5)	5	2	39	15	—

[a] Gaseous CO_2 was slowly passed through a solution of acetonitrile, which contained amine **1** and superbase B, at −20 °C for 1 h to generate carbamate. Then acetylenic derivative **2** (0.2 mol L^{-1}) and $RhCl(PPh_3)_3$ were added. The temperature was raised to 75 °C. The reaction was carried out with stirring for 15 h.

[b] The values of $\log K_b$ (25 °C) were taken from the literature.[7]

[c] Determined by GC using an internal standard referred to the starting acetylenic substrate.

[d] The yield of the isolated product is given in parentheses.

[e] The reaction time was 20 h.

in favor of dimers or oligomers of acetylenic compounds. Rhodium(I) complexes, which were obtained by addition of different phosphine ligands (PPh_3, bis(1,2-diphenylphosphino)ethane, bis(1,3-diphenylphosphino)propane, and bis(1,4-diphenylphosphino)butane)) to μ-dichloro(tetraethylene)dirhodium(I) or to cationic complexes, such as bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate and the product of the reaction of μ-dichloro(tetraethylene)dirhodium(I) with sodium tetraphenylborate, were tested under the conditions described above. However, no significant improvement in the yield compared to that obtained in the presence of $RhCl(PPh_3)_3$ was achieved. In the absence of phosphine ligands, poor results were obtained.

Rhodium complexes can coordinate a superbase. For example, a complex was prepared by the reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with dichloro(tetraethylene)dirhodium.[6] However, this compound proved to be a poor catalyst, and it was necessary to add phosphine (2 moles per 1 mole of Rh) to attain the same result as with $RhCl(PPh_3)_3$. Association of CO_2, tetramethylguanidine, and Rh^I appears to be necessary for the reaction of catalytic amination of the title compounds to occur. Strongly activated acetylenic compounds, such as methyl prop-2-ynoate, are known to react spontaneously with secondary amines (without catalysts[1,2]), while less activated terminal or internal alkylacetylenes, such as 1-hexyne or 4-octyne, were not able to afford vinylamines in the absence of a catalyst. Alkylacetylenes did not react under the conditions reported in this work. The results obtained in the studies of catalytic amination of acetylenic compounds are given in Table 1.

It is noteworthy that the ratio of products **3** : **4** can be reversed by varying only the basicity of the amine (see Table 1, runs *4* and *10*). The secondary amine **1** : alkyne **2** molar ratio also exerts an influence on the **3** : **4** ratio, the latter decreasing as the **1** : **2** ratio decreases (see Table 1, runs *1—3* and *5—8*). This effect is less pronounced in the case of base **1d** (see Table 1, runs *10—12*).

It is noteworthy that the total yield and relative amounts of products **3** and **4** depend in a complex way on the basicity and the nature of the superbase as shown in Table 2. Thus, it has been observed that in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), the total yield of the products of the reaction of piperidine **1c** with phenylacetylene **2a** reached 97%. However, when sterically hindered superbases, such as *N*-propyltetramethylguanidine (PTMG), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), were used, the total yield of products **3** and **4** decreased although the **3** : **4** ratio increased as the superbase basicity increased. Actually, strong bases can also activate alkyne CH bonds[8] toward dimerization and polymerization to a different extent, and these side reactions would compete with the attack of alkyne at the double bond of the precursor of enamine **3** (Scheme 1).

Scheme 1

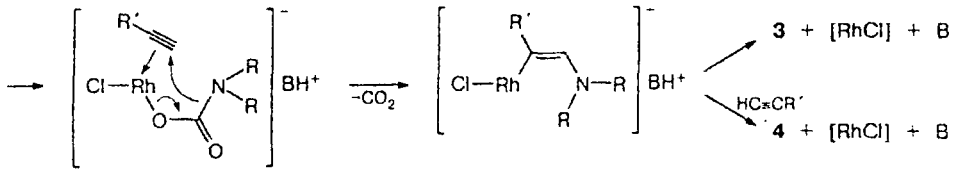

Table 2. Reaction of piperidine **1c** (0.85 g, 10 mmol) with phenylacetylene **2a** (0.51 g, 5 mmol) in the presence of $RhCl(PPh_3)_3$, CO_2, and different superbases (5 mmol)[a]

Superbase	$\log K_b$ [7]	Conversion (%)[b]	Yield (%)[b]	
			3	**4**
TMG	23.75	98	72	18
PTMG	25.00	88	18	19
TBD	25.95	>99	88	9
MTBD	25.44	89	33	16
DBU	24.33	83	51	21
BEMP	27.58	91	44	4

[a] All reactions were carried out as reported in Note "*a*" in Table 1.

[b] Determined by GC using an internal standard referred to the starting phenylacetylene.

We believe that the mechanism of the reaction involves the initial attack of carbamate on the internal carbon atom of the triple bond to form a rhodium carbamate complex followed by liberation of CO_2 (see Scheme 1). The addition of the second acetylenic molecule to form compound **4** requires rhodium and, probably, involves oxidative addition of alkyne to Rh. Coordination of other ligands to the Rh atom is not shown in Scheme 1.

The function of CO_2 is likely to be that of transferring the amino group through rhodium(I) carbamate. In this respect, its role is quite different from that which carbon dioxide plays in the corresponding reaction with ruthenium(II) in which intermediate carbamate reacts with alkyne at the oxygen atom to form vinyl carbamate.[9] Recently, we also reported that the use of superbases in the absence of metals allows the direct intramolecular insertion of CO_2 at the C≡C bond of amino-substituted acetylene at room temperature.[10] This transformation is another example of the reaction of the triple bond with the carbamate oxygen.

Experimental

ACS-grade reagents were used without further purification. Acetonitrile was dried over 3-Å molecular sieves. The complex $RhCl(PPh_3)_3$,[11a] μ-dichloro(tetraethylene)dirhodium(I),[11b] bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate,[12] and *N*-propyltetramethylguanidine[13] were prepared according to published procedures. Amines and superbases were commercially available research-grade reagents (Aldrich, Fluka, and Janssen). The melting and boiling points were not corrected.

The ^1H NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) in $CDCl_3$ with Me_4Si as the internal standard. The mass spectra were measured on a Hewlett—Packard 5971 spectrometer (70 eV) interfaced with a Hewlett—Packard 5890 Series II gas chromatograph. The Fourier transform IR spectra were recorded on a Nicolet 5PC spectrophotometer. Distillation *in vacuo* was carried out using a Buchi GRK-51 Kugelrohr oven. Elemental analysis was carried out on a Carlo Erba Model EA 1108 instrument. Gas-chromatographic analysis was performed on a Dani 3800 HR GC instrument equipped with a methylsilicone (OV-101) capillary column, and the peaks were recorded on a Hewlett—Packard 3390 A integrator. Quantitative GLC determinations were carried out with the use of the internal standard method. Silica gel 60F plates (Merck) were used for analytical TLC, and silica gel 60F 254 plates (Merck) were used for preparative TLC.

Reactions of secondary amines with terminal acetylenes in the presence of a Rh complex, CO_2, and a superbase in MeCN (general procedure). Gaseous CO_2 was passed through a solution of pyrrolidine **1b** (0.71 g, 10 mmol) and tetramethylguanidine (0.58 g, 5 mmol) in dry MeCN (25 mL), which was placed in a Schlenk tube, at atmospheric pressure at ~20 °C for 1 h. Then phenylacetylene (0.51 g, 5 mmol) and $RhCl(PPh_3)_3$ (0.093 g, 0.10 mmol) were added under a stream of CO_2, and the mixture was refluxed with stirring at 75 °C for 15 h. The solvent was removed *in vacuo*. The oily residue was diluted with ether (100 mL) and filtered off. The ethereal solution was shaken with 2 *N* HCl (50 mL). The aqueous layer was alkalized with 10 *N* NaOH and extracted with ether. The ethereal solution was dried and distilled *in vacuo* to afford compound **3** ($R_2 = (CH_2)_4$, R′ = Ph) in a yield of 73% (0.832 g, 3.65 mmol) as a pale-yellow oil along with 1% of an admixture of compound **4**.

The compounds synthesized were identified by elemental analysis, IR and ^1H NMR spectroscopy, and mass spectrometry. Product **3** ($R_2 = (CH_2)_4$, R′ = Ph)[14] was identified by comparing with the published data. The spectroscopic data for the known products **3** ($R_2 = (CH_2)_5$, R′ = Ph [15] and $R_2 = ((CH_2)_2)_2O$, R′ = Ph [16]) and **4** ($R_2 = (CH_2)_5$, R′ = Ph [6b] and $R_2 = ((CH_2)_2)_2O$, R′ = Ph [6b]) are reported below since they are lacking in the literature.

***N,N*-Diethyl-2-*E*-phenylethenylamine (3: R = Et, R′ = Ph).** Pale-yellow oil, b.p. 128—130 °C (0.5 mbar). Found (%): C, 82.19; H, 9.69; N, 7.96. $C_{12}H_{17}N$. Calculated (%): C, 82.29; H, 9.71; N, 8.00. IR (film), ν/cm^{-1}: 3002 m, 2981 s, 2942 s, 2859 s, 1625 s, 965 m. ^1H NMR, δ: 1.18 (t, 6 H, 2 Me, J = 7.1 Hz); 3.18 (q, 4 H, 2 CH_2, J = 7.1 Hz); 5.20 (d, 1 H, =CH, J = 14.0 Hz); 6.78 (d, 1 H, =CH, J = 14.0 Hz); 6.94—6.99 (m, 1 H, CH arom.); 7.16—7.24 (m,

4 H, CH arom.). MS, *m/z* (I_{rel} (%)): 175 $[M]^+$ (100), 160 (72), 146 (15), 130 (55), 117 (20), 105 (32), 91 (28), 77 (19), 56 (71).

1-[2-*E*-(4-Chlorophenyl)ethenyl]pyrrolidine (3: R_2 = $(CH_2)_4$, R′ = *p*-ClC_6H_4). Pale-yellow oil, b.p. 148—150 °C (0.3 mbar). Found (%): C, 69.32; H, 6.72; N, 6.70. $C_{12}H_{14}ClN$. Calculated (%): C, 69.40; H, 6.75; N, 6.75. IR (film), ν/cm^{-1}: 2952 m, 2854 m, 1625 s, 1450 s, 965 m. ^1H NMR, δ: 2.19—2.25 (m, 4 H, 2 CH_2); 3.50—3.55 (m, 2 H, CH_2); 3.68—3.72 (m, 2 H, CH_2); 5.44 (d, 1 H, =CH, J = 13.9 Hz); 7.28—7.43 (AA′XX′ system, 4 H, CH arom.); 7.31 (d, 1 H, =CH, J = 13.9 Hz). MS, *m/z* (I_{rel} (%)): 209 (38), 207 $[M]^+$ (75), 172 (9), 170 (12), 139 (16), 138 (25), 101 (22), 75 (29), 55 (27), 43 (100).

1-[2-*E*-(4-Methylphenyl)ethenyl]pyrrolidine (3: R_2 = $(CH_2)_4$, R′ = *p*-MeC_6H_4). Pale-yellow oil, b.p. 132—134 °C (0.3 mbar). Found (%): C, 83.36; H, 9.04; N, 7.41. $C_{13}H_{17}N$. Calculated (%): C, 83.42; H, 9.09; N, 7.49. IR (film), ν/cm^{-1}: 2932 m, 2854 m, 1625 s, 1450 s, 965 m. ^1H NMR, δ: 1.88—1.93 (m, 4 H, 2 CH_2); 2.92 (s, 3 H, Me); 3.16—3.21 (m, 2 H, CH_2); 3.25—3.29 (m, 2 H, CH_2); 5.06 (d, 1 H, =CH, J = 13.8 Hz); 7.03 (d, 1 H, =CH, J = 13.8 Hz); 7.00—7.22 (AA′XX′ system, 4 H, CH arom.). MS, *m/z* (I_{rel} (%)): 187 $[M]^+$ (100), 186 (42), 170 (6), 158 (5), 144 (7), 118 (29), 115 (10), 91 (6), 77 (4).

1-[2-*E*-(1-Cyclohexen-1-yl)ethenyl]pyrrolidine (3: R_2 = $(CH_2)_4$, R′ = *cyclo*-C_6H_{12}). Pale-yellow oil, b.p. 126—128 °C (0.5 mbar). Found (%): C, 81.28; H, 10.70; N, 7.86. $C_{12}H_{19}N$. Calculated (%): C, 81.36; H, 10.73; N, 7.91. IR (film), ν/cm^{-1}: 3002 m, 2924 m, 2854 m, 1625 s, 1450 s, 965 m. ^1H NMR, δ: 1.52—1.66 (m, 4 H, 2 CH_2); 1.89—1.94 (m, 4 H, 2 CH_2); 2.07—2.14 (m, 4 H, 2 CH_2); 3.20—3.25 (m, 4 H, 2 CH_2); 5.12 (d, 1 H, =CH, J = 13.9 Hz); 6.16—6.19 (m, 1 H, =CH); 7.03 (d, 1 H, =CH, J = 13.9 Hz). MS, *m/z* (I_{rel} (%)): 177 $[M]^+$ (52), 176 (39), 149 (38), 148 (40), 134 (55), 120 (94), 77 (50), 71 (37), 70 (82), 55 (47), 44 (92), 41 (100).

1-(2-*E*-Phenylethenyl)piperidine (3: R_2 = $(CH_2)_5$, R′ = Ph). Pale-yellow oil, b.p. 135—136 °C (0.5 mbar). Found (%): C, 83.35; H, 9.01; N, 7.39. $C_{13}H_{17}N$. Calculated (%): C, 83.42; H, 9.09; N, 7.49. IR (film), ν/cm^{-1}: 3001 m, 2922 m, 2854 m, 1630 m, 1450 s, 1025 w, 966 m. ^1H NMR, δ: 1.57—1.64 (m, 6 H, 3 CH_2); 3.01—3.05 (m, 4 H, 2 CH_2); 5.36 (d, 1 H, =CH, J = 14.1 Hz); 6.66 (d, 1 H, =CH, J = 14.1 Hz); 6.96—7.04 (m, 1 H, CH arom.); 7.18—7.21 (m, 4 H, CH arom.). MS, *m/z* (I_{rel} (%)): 187 $[M]^+$ (100), 186 (53), 130 (41), 110 (7), 104 (51), 91 (9), 83 (9), 77 (6).

4-(2-*E*-Phenylethenyl)morpholine (3: R_2 = $((CH_2)_2)_2O$, R′ = Ph). Orange solid, m.p. 74—76 °C. Found (%): C, 76.12; H, 7.89; N, 7.36. $C_{12}H_{15}NO$. Calculated (%): C, 76.19; H, 7.94; N, 7.41. IR (film), ν/cm^{-1}: 3006 m, 2965 s, 2860 s, 1628 s, 1381 s, 1350 s, 1320 s. ^1H NMR, δ: 2.95—3.07 (m, 4 H, 2 CH_2); 3.71—3.87 (m, 4 H, 2 CH_2); 6.77 (d, 1 H, =CH, J = 16.1 Hz); 7.23—7.39 (m, 5 H, CH arom.); 7.64 (d, 1 H, =CH, J = 16.1 Hz). MS, *m/z* (I_{rel} (%)): 189 $[M]^+$ (91), 158 (9), 131 (27), 130 (100), 104 (27), 91 (14), 77 (21).

Methyl ester of 1-(2-*E*-phenylethenyl)proline (3: R_2 = $(CH_2)_3CH(COOMe)$, R′ = Ph). Pale-yellow oil, b.p. 138—139 °C (0.5 mbar). Found (%): C, 72.70; H, 7.35; N, 6.00. $C_{14}H_{17}NO_2$. Calculated (%): C, 72.73; H, 7.36; N, 6.06. IR (film), ν/cm^{-1}: 3002 m, 2957 m, 2858 m, 1738 s, 1625 s, 966 m. ^1H NMR, δ: 1.66—1.73 (m, 2 H, CH_2); 1.75—1.82 (m, 1 H, CHH); 2.02—2.11 (m, 1 H, CHH); 2.82—2.88 (m, 1 H, CHH); 2.99—3.03 (m, 1 H, CHH); 3.66 (s, 3 H, OMe); 3.64—3.74 (m, 1 H, CH); 5.14 (d, 1 H, =CH, J = 14.0 Hz); 7.01 (d, 1 H, =CH, J = 14.0 Hz); 7.16—7.20 (m, 5 H, CH arom.). MS, *m/z* (I_{rel} (%)): 231 $[M]^+$ (18), 172 (100), 170 (34), 130 (9), 103 (13), 91 (12), 77 (19).

***N,N*-Diethyl(1-benzyl-3-phenylprop-2-ynyl)amine (4: R = Et, R′ = Ph).** Pale-yellow oil, b.p. 157—159 °C (0.3 mbar). Found (%): C, 86.56; H, 8.27; N, 4.98. $C_{20}H_{23}N$. Calculated (%): C, 86.64; H, 8.30; N, 5.05. IR (film), ν/cm^{-1}: 3002 m, 2962 m, 2851 m, 2212 w, 1450 m. ^1H NMR, δ: 1.10 (t, 6 H, 2 Me, J = 7.1 Hz); 2.65—2.72 (AB system, 2 d, 2 H, CH_2, J = 3.8 Hz); 3.14 (q, 4 H, 2 CH_2, J = 7.1 Hz); 3.95 (s, 1 H, CH); 7.08—7.45 (m, 10 H, CH arom.). MS, *m/z* (I_{rel} (%)): 277 $[M]^+$ (38), 262 (35), 248 (6), 232 (5), 200 (33), 182 (26), 146 (21), 115 (23), 91 (100), 77 (16), 44 (76).

1-(1-Benzyl-3-phenylprop-2-ynyl)piperidine (4: R_2 = $(CH_2)_5$, R′ = Ph). Pale-yellow oil, b.p. 165—167 °C (0.3 mbar). Found (%): C, 87.17; H, 7.94; N, 4.80. $C_{21}H_{23}N$. Calculated (%): C, 87.20; H, 7.96; N, 4.84. IR (film), ν/cm^{-1}: 3001 w, 2921 s, 2855 s, 2111 w, 1450 s. ^1H NMR, δ: 1.58—1.70 (m, 6 H, 3 CH_2); 2.65—2.76 (m, 2 H, CH_2); 2.94—3.02 (m, 4 H, 2 CH_2); 3.94 (br.s, 1 H, CH); 7.23—7.41 (m, 10 H, CH arom.). MS, *m/z* (I_{rel} (%)): 289 $[M]^+$ (46), 288 (33), 212 (54), 198 (100), 130 (29), 115 (31), 91 (78), 77 (12).

1-(1-Benzyl-3-phenylprop-2-ynyl)morpholine (4: R_2 = $((CH_2)_2)_2O$, R′ = Ph). Pale-yellow solid, m.p. 69—70 °C. Found (%): C, 82.40; H, 7.20; N, 4.76. $C_{20}H_{21}NO$. Calculated (%): C, 82.47; H, 7.22; N, 4.81. IR (film), ν/cm^{-1}: 3001 m, 2974 s, 2861 s, 2112 w, 1241 m. ^1H NMR, δ: 2.69—2.85 (m, 2 H, CH_2); 2.93—3.07 (m, 4 H, 2 CH_2); 3.37 (br.s, 1 H, CH); 3.71—3.87 (m, 4 H, 2 CH_2); 7.26—7.50 (m, 10 H, CH arom.). MS, *m/z* (I_{rel} (%)): 291 $[M]^+$ (41), 260 (12), 232 (15), 214 (16), 200 (81), 184 (68), 128 (23), 115 (57), 91 (100), 77 (27).

Methyl ester of 1-(1-benzyl-3-phenylprop-2-ynyl)proline (4: R_2 = $(CH_2)_3CH(COOMe)$, R′ = Ph). Pale-yellow solid, m.p. 86—88 °C. Found (%): C, 79.21; H, 6.88; N, 4.014. $C_{22}H_{23}NO_2$. Calculated (%): C, 79.28; H, 6.91; N, 4.20. IR (film), ν/cm^{-1}: 3002 w, 2956 m, 2851 m, 2110 w, 1739 s. ^1H NMR, δ: 1.66—1.75 (m, 2 H, CH_2); 1.77—1.83 (m, 1 H, CHH); 2.02—2.11 (m, 1 H, CHH); 2.62—2.74 (m, 2 H, CH_2); 2.84—2.97 (m, 1 H, CHH); 3.01—3.40 (m, 1 H, CHH); 3.71 (s, 3 H, OMe); 3.72—3.78 (m, 1 H, CH); 7.14—7.31 (m, 10 H, CH arom.). MS, *m/z* (I_{rel} (%)): 333 $[M]^+$ (14), 275 (19), 274 (100), 183 (17), 115 (20), 91 (31), 77 (8).

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