Electronic supplementary materials *Mendeleev Commun.*, 2015, **25**, 377−379

Reaction of α,β-alkynylketones with β-amino alcohols: pseudoephedrine-assisted cleavage of triple bond *via* formal internal redox process

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General information

Melting points were determined with a Kofler apparatus. Combustion analysis was performed with CHN-analyzer. IR spectra were recorded in KBr pellets on a Vector 22 instrument. NMR spectra were recorded on Bruker AV-300, AV-400 and AV-600 spectrometer at 300.13 (^{1}H) and 75.47 MHz (^{13}C), 400.13 (^{1}H) and 100.61 MHz (^{13}C), 600.30 (^{1}H) and 150.95 MHz (^{13}C) in $CDCl_3$, DMSO-d_6 and CD_2Cl_2. Chemical shifts δ were given in ppm relative to the signals for $CDCl_3$ (δ_H 7.24 ppm and δ_C 77.23 ppm), DMSO-d_6 (δ_H 2.50 ppm and δ_C 39.50 ppm) and CD_2Cl_2 (δ_H 5.32 ppm). Mass spectra (HRMS) were measured on a “Thermo Scientific DFS (Double Focusing Sector Mass Spectrometer) Thermo Electron Corporation”, 70 eV. Column chromatography was performed on SiO_2 (Merck 60 (0.063-0.2 mm)). Analytical TLC was performed with Merck silica gel 60 F_{254} plates. 1,4-Dioxane, pyridine, CuCl, 2-aminoethanol, 2-(*N*-methylamino)ethanol and (1*S*,2*S*)-2-(*N*-methylamino)-1-phenylpropan-1-ol (Aldrich) were commercially available reactants. The initial ynones **1a-c** were prepared and described earlier.[1]

General Procedure. Synthesis of 2a,b.

A mixture of appropriate ynone (**1a,b**) (1.0 mmol) and ethanolamine (2.0 mmol) in 1,4-dioxane (10 mL) was refluxed for 3-10 h. The volatiles were evaporated *in vacuo*, the residues were recrystallized from benzene or ethanol to give **2a,b**.

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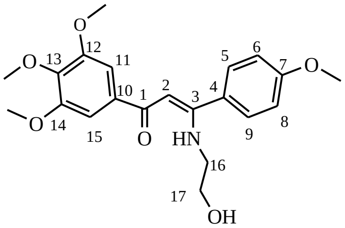
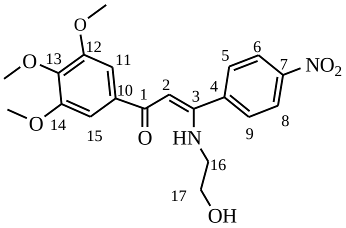
[1] S. Roy, M. P. Davydova, R. Pal, K. Gilmore, G. A. Tolstikov, S. F. Vasilevsky and I. V Alabugin, *J. Org. Chem.*, 2011, **76** (18), 7482.

(*Z*)-3-(2-Hydroxyethylamino)-3-(4-methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (2a).



Yield 365 mg (94%), mp 140-142 °C (benzene). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.40 (dt, 2H, *J* 5.4, 5.6, C^{16}H$_2$), 3.72 (t, 2H, *J* 5.4, C^{17}H$_2$), 3.84 (s, 3H, 7-OCH$_3$), 3.86 (s, 3H, 13-OCH$_3$), 3.87 (s, 6H, 12,14-OCH$_3$), 5.70 (s, 1H, C^{2}H), 6.95 (m, 2H, C^{6}H and C^{8}H), 7.12 (s, 2H, C^{11}H and C^{15}H), 7.36 (m, 2H, C^{5}H and C^{9}H), 11.43 (br.t, 1H, *J* 5.6, NH). ^{13}C NMR (100 MHz, CDCl$_3$): δ 46.17 (C^{16}), 54.66 (7-O$\underline{C}$H$_3$), 55.46 (12,14-O$\underline{C}$H$_3$), 60.13 (13-O$\underline{C}$H$_3$), 61.34 (C^{17}), 92.81 (C^2), 103.56 (C^{11} and C^{15}), 113.25 (C^6 and C^8), 126.95 (C^4), 128.62 (C^5 and C^9), 135.03 (C^{10}), 139.71 (C^{13}), 152.14 (C^{12} and C^{14}), 159.89 (C^7), 166.37 (C^3), 186.68 (C^1). IR (KBr, cm^{-1}): 1606 (C=O), 3437 (OH). HRMS calculated for $C_{21}H_{25}NO_6$ [M]$^+$ 387.1676, found 387.1671.

(*Z*)-3-(2-Hydroxyethylamino)-3-(4-nitrophenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (2b).

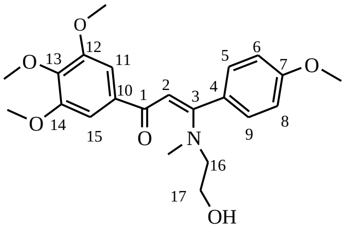


Yield 340 mg (85%), mp 198-199 °C (ethanol). ^{1}H NMR (400 MHz, CDCl3): δ 2.28 (br. t, 1H, *J* 5.3, OH), 3.30 (dt, 2H, *J* 5.2, 5.7, C^{16}H$_2$), 3.72 (dt, 2H, *J* 5.2, 5.3, C^{17}H$_2$), 3.87 (s, 9H, 12,13,14-OCH$_3$), 5.66 (s, 1H, C^{2}H), 7.10 (s, 2H, C^{11}H and C^{15}H), 7.61 (m, 2H, C^{5}H and C^{9}H), 8.30 (m, 2H, C^{6}H and C^{8}H), 11.30 (br. t, 1H, *J* 5.7, NH). ^{13}C NMR (100 MHz, CDCl$_3$) δ 47.07 (C^{16}), 56.46 (12,14-O$\underline{C}$H$_3$), 61.15 (13-O$\underline{C}$H$_3$), 62.17 (C^{17}), 93.94 (C^2), 104.68 (C^{11} and C^{15}), 124.16 (C^6 and C^8), 129.42 (C^5 and C^9), 135.26 (C^{10}), 141.19 (C^{13}), 141.93 (C^4), 148.64 (C^7), 153.22 (C^{12} and C^{14}), 164.43 (C^3), 188.42 (C^1). IR (KBr, cm^{-1}) 1605 (C=O), 3440 (NH). HRMS calculated for $C_{20}H_{22}N_2O_7$ [M]$^+$ 402.1417, found 402.1422 [M]$^+$.

General Procedure. Synthesis of 3a-c.

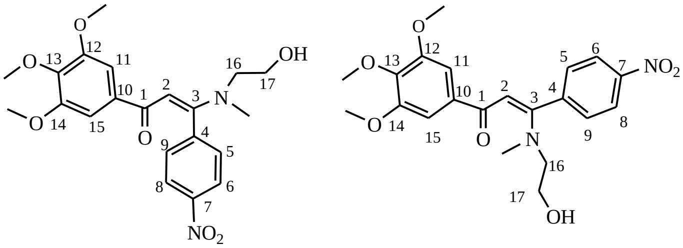
A mixture of appropriate ynone (**1a-c**) (1.0 mmol) and 2-(*N*-methylamino)ethanol (2.0 mmol) in 1,4-dioxane (10 mL) was refluxed for 3-5 h. The volatiles were evaporated *in vacuo*, the residues were recrystallized from benzene to give **3a-c**. Additionally amino enone **3b** was purified by column chromatography (toluene-ethyl acetate 1:1, ethyl acetate) to give **3b** and **4**.

(*Z*)-3-[*N*-(2-Hydroxyethyl)-*N*-methylamino]-3-(4-methoxyphenyl)-1-(3,4,5-trimethoxy-phenyl)prop-2-en-1-one (3a).



Yield 320 mg (80%), mp 85-88 °C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (s, 3H, NCH_3), 3.39 (m, 2H, *J* 4.4, 5.5 Hz, $C^{16}H_2$), 3.58 (m, 2H, *J* 4.2, 5.8 Hz, $C^{17}H_2$), 3.83 (s, 3H, 7-OCH_3), 3.87 (s, 9H, 12,13,14-OCH_3), 5.83 (s, 1H, C^2H), 6.91 (m, 2H, *J* 0.4, 2.1, 8.5Hz, C^6H and C^8H), 7.18 (s, 2H, $C^{11}H$ and $C^{15}H$), 7.47 (m, 2H, *J* 0.4, 1.8, 8.5 Hz, C^5H and C^9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.1 ($N\underline{C}H_3$), 55.66 (C^{16}), 56.37 (C^{17}), 57.57 (7-$O\underline{C}H_3$), 57.66 (12,13-$O\underline{C}H_3$), 61.12 (14-$O\underline{C}H_3$), 99.45 (C^2), 105.57 (C^{11}, C^{15}), 114.18 (C^6, C^8), 130.12 (C^4), 132.19 (C^5, C^9), 141.01 (C^{10}), 136.02 (C^{13}), 153.06 (C^{12}, C^{14}), 162.12 (C^7), 168.29 (C^3), 185.88 (C^1). IR (KBr, cm^{-1}) 1608 (C=O), 3419 (OH). HRMS calculated for $C_{22}H_{27}NO_6$ $[M]^+$ 401.1833, found 401.1827 $[M]^+$.

(*E,Z*)-3-[*N*-(2-Hydroxyethyl)-*N*-methylamino]-3-(4-nitrophenyl)-1-(3,4,5-trimethoxy-phenyl)prop-2-en-1-one (3b).



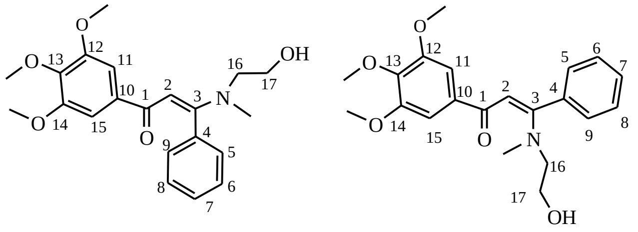
Yield 180 mg (43%), mp 152-154 °C (benzene)**.** <u>*E*-isomer (58%).</u> ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.11 (br.s, 3H, NCH_3), 3.28 (m, 2H, *J* 4.4, 5.5 Hz, $C^{16}H_2$), 3.72 (m, 2H, *J* 4.2, 5.8 Hz,

$C^{17}H_2$), 3.85 (s, 9H, 12,13,14-OCH_3), 5.95 (s, 1H, C^2H), 7.08 (s, 2H, $C^{11}H$ and $C^{15}H$), 7.42 (m, 2H, *J* 0.4, 1.8, 8.4 Hz, C^5H and C^9H), 8.27 (m, 2H, *J* 0.4, 2.1, 8.4 Hz, C^6H and C^8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.38 ($N\underline{C}H_3$), 54.22 (C^{16}), 56.50 (12,13-$O\underline{C}H_3$), 60.64 (C^{17}), 61.13 (14-$O\underline{C}H_3$), 94.71 (C^2), 105.39 (C^{11} and C^{15}), 124.00 (C^6 and C^8), 129.62 (C^5 and C^9), 136.60 (C^{13}), 141.10 (C^{10}), 144.33 (C^4), 153.00 (C^{12} and C^{14}), 162.35 (C^7), 186.62 (C^1).

Z-isomer (42%). ^1H NMR (400 MHz, $CDCl_3$) δ 3.07 (br.s, 3H, NCH_3), 3.28 (m, 2H, *J* 4.4, 5.5 Hz, $C^{16}H_2$), 3.62 (m, 2H, *J* 4.2, 5.8 Hz, $C^{17}H_2$), 3.88 (s, 9H, 12,13,14-OCH_3), 5.86 (s, 1H, C^2H), 7.18 (s, 2H, $C^{11}H$ and $C^{15}H$), 7.72 (m, 2H, *J* 0.4, 1.8, 8.4 Hz, C^5H and C^9H), 8.26 (m, 2H, *J* 0.4, 2.1, 8.4 Hz, C^6H and C^8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.33 ($N\underline{C}H_3$), 57.36 (C^{16}), 57.79 (C^{17}), 56.46 (12,13-$O\underline{C}H_3$), 61.13 (14-$O\underline{C}H_3$), 101.60 (C^2), 105.89 (C^{11} and C^{15}), 124.00 (C^6 and C^8), 131.38 (C^5 and C^9), 135.04 (C^{13}), 141.40 (C^{10}), 144.64 (C^4), 153.23 (C^{12} and C^{14}), 164.90 (C^7), 186.86 (C^1). IR (KBr, cm^{-1}) 1606 (C=O), 3321 (OH). HRMS calculated for $C_{21}H_{24}N_2O_7$ $[M]^+$ 416.1572, found 416.1578 $[M]^+$.

(*Z*)-3-Hydroxy-3-(4-nitrophenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (4). Yield 75 mg (20%), mp 203-205 °C (benzene). ^1H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H, OCH_3), 3.95 (s, 6H, $2OCH_3$), 6.78 (s, 1H), 7.23 (s, 2H), 8.11 (d, 2H, *J* 8.8 Hz), 8.32 (d, 2H, *J* 8.8 Hz), 16.74 (br. s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.33, 60.95, 93.97, 104.89, 123.77, 127.85, 130.41, 140.70, 142.69, 149.71, 153.22, 180.19, 187.98. IR (KBr, cm^{-1}) 1591 (C=O), 3425 (OH). HRMS calculated for $C_{18}H_{17}NO_7$ $[M]^+$ 359.0999, found 359.1000 $[M]^+$.

(*E*,*Z*)-3-[*N*-(2-hydroxyethyl)-*N*-methylamino]-3-phenyl-1-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one (3c).



Yield 350 mg (94%), mp 77-80 °C (benzene). *E*-isomer (19%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 3H, NCH_3), 3.08 (m, 2H, $C^{16}H_2$), 3.93 (m, 2H, $C^{17}H_2$), 3.84 (s, 3H, 13-OCH_3), 3.84 (s, 6H, 12,14-OCH_3), 5.89 (s, 1H, C^2H), 7.09 (s, 2H, $C^{11}H$ and $C^{15}H$), 7.22 (m, 2H, C^5H and C^9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.90 ($N\underline{C}H_3$), 52.40 (C^{16}), 56.41 (12,14-$O\underline{C}H_3$), 57.57

(C^{17}), 61.07 (13-O<u>C</u>H_3), 94.61 (C^2), 105.46 (C^{11}, C^{15}), 128.34 (C^5 and C^9), 137.47 (C^{10}), 140.78 (C^{13}), 152.88 (C^{12} and C^{14}), 165.10 (C^3), 187.00 (C^1).

<u>*Z*-isomer (81%).</u> ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (br.s, 3H, NCH_3), 3.37 (m, 2H, $C^{16}H_2$), 3.59 (m, 2H, $C^{17}H_2$), 3.87 (s, 3H, 13-OCH_3), 3.88 (s, 6H, 12,14-OCH_3), 5.86 (s, 1H, C^2H), 7.19 (s, 2H, C^{11}H and C^{15}H), 7.41 (m, 2H, *J* 0.4, 1.3, 7.5, 7.9 Hz, C^6H and C^8H), 7.47 (m, 1H, *J* 1.2, 7.5 Hz, C^7H), 7.53 (m, 2H, *J* 0.4, 2.2, 7.9 Hz, C^5H and C^9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.40 (N<u>C</u>H_3), 56.41 (12,14-O<u>C</u>H_3), 57.46 (C^{16}), 57.80 (C^{17}), 61.17 (13-O<u>C</u>H_3), 100.22 (C^2), 105.74 (C^{11} and C^{15}), 128.82 (C^6 and C^8), 130.60 (C^5 and C^9), 131.03 (C^7), 135.80 (C^{10}), 138.20 (C^4), 141.24 (C^{13}), 153.14 (C^{12} and C^{14}), 168.50 (C^3), 186.30 (C^1). IR (KBr, cm^{-1}) 1606 (C=O), 3442 (OH). HRMS calculated for $C_{21}H_{25}NO_5$ $[M]^+$ 371.1727, found 371.1731 $[M]^+$.

General procedure. Synthesis of 5a, 6 and 7b,c.

A mixture of appropriate ynone (**1a-c**) (1.0 mmol) and (+)-pseudoephedrine (2.0 mmol) in 1,4-dioxane (7 mL) was refluxed for 12-50 h. The solvent was removed *in vacuo* and the residues were purified by column chromatography (hexane–toluene 1:1, toluene, toluene-ethyl acetate 1:1, ethyl acetate) to give **5a, 6** and **7 b,c**.

(*E*)-3-{[*N*-(1*S*,2*S*)-1-Hydroxy-1-phenylprop-2-yl]-*N*-methylamino}-3-(4-methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (5a). Yield 350 mg (71%) mp 183-185 °C (benzene). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (d, 3H, *J* 6.7 Hz, CH_3), 3.10 (s, 3H, NCH_3), 3.82 (m, 1H, CH), 3.85 (s, 3H, OCH_3), 3.87 (s, 9H, 3OCH_3), 4.5 (m, 1H, CH), 5.82 (s, 1H, CH), 6.09 (br.s, 1H, OH), 6.93 (d, 2H, *J* 8.9 Hz, CH_{Ar}), 7.10 (m, 2H, CH_{Ar}), 7.2 (m, 4H, CH_{Ar}), 7.34 (s, 1H, CH_{Ar}), 7.48 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.55, 35.10, 54.98, 55.75, 60.45, 73.77, 98.61, 105.09, 113.58, 126.70, 126.97, 127.17, 127.77, 127.87, 128.03, 130.62, 135.29, 137.30, 140.65, 161.33, 169.17, 185.00. IR (KBr, cm^{-1}) 1602 (C=O), 3253 (OH). HRMS calculated for $C_{29}H_{33}NO_6$ $[M]^+$ 491.2302, found 473.2190 $[M-H_2O]^+$, calculated for $C_{29}H_{31}NO_5$ $[M]^+$ 473.2197.

1-(3,4,5-Trimethoxyphenyl)ethanone (6). From **1b** yield 70 mg (42%), mp 78-80 °C; From **1c** yield 150 mg (70%), mp 77-79 °C, lit. mp 78-79 °C.[2]

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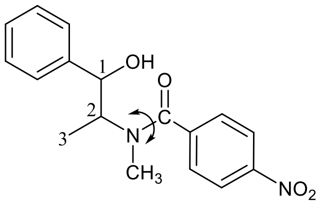
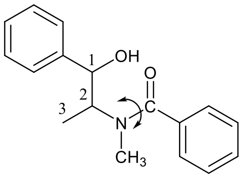
[2] V. J. Harding, *J. Chem. Soc. Trans.*, 1914, **105**, 2790.

N-(1-Hydroxy-1-phenylprop-2-yl)-*N*-methyl-4-nitrobenzamide (7b).



Yield 110 mg (44%), mp 170-175 °C, lit. mp 170 °C.[3] *cis*-Rotamer (75% at room temperature). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 0.91 (d, $^3J_{3H\text{-}2H}$ 6.8 Hz, 3H, C^{3}H$_3$), 2.99 (s, 3H, NCH$_3$), 3.54 (dq, 1H, $^3J_{3H\text{-}2H}$ 6.8 Hz, $^3J_{2H\text{-}1H}$ 8.3 Hz, C^{2}H), 4.52 (d, 1H, $^3J_{1H\text{-}2H}$ 8.3 Hz, C^{1}H), 5.71 (br.s, 1H, OH), 7.10 (d, 2H, *J* 6.6 Hz, CH$_{Ar}$), 7.20-7.30 (m, 5H, CH$_{Ar}$), 8.26-8.30 (m, 2H, CH$_{Ar}$). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 14.91 (C^{3}H$_3$), 26.93 ($N\underline{C}H_3$), 59.54 (C^{2}H), 73.47 (C^{1}H), 123.59 (C$_{Ar}$), 126.74 (C$_{Ar}$), 127.51 (C$_{Ar}$), 128.14 (C$_{Ar}$), 128.23 (C$_{Ar}$), 143.09 (C$_{Ar}$), 143.98 (C$_{Ar}$), 147.33 (C$_{Ar}$), 169.57 (CO). *trans*-Rotamer (25 % at room temperature). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 0.99 (d, 3H, $^3J_{3H\text{-}2H}$ 6.7 Hz, C^{3}H$_3$), 2.75 (s, 3H, NCH$_3$), 3.54 (dq, 1H, $^3J_{3H\text{-}2H}$ 6.7 Hz, $^3J_{2H\text{-}1H}$ 7.2 Hz, C^{2}H), 4.69 (d, 1H, $^3J_{1H\text{-}2H}$ 7.2 Hz, C^{1}H), 5.57 (br.s, 1H, OH), 7.49-7.54 (m, 9H, CH$_{Ar}$). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 13.88 (C^{3}H$_3$), 32.09 ($N\underline{C}H_3$), 54.03 (C^{2}H), 73.58 (C^{1}H) 123.78 (C$_{Ar}$), 126.87 (C$_{Ar}$), 127.35 (C$_{Ar}$), 127.84 (C$_{Ar}$), 128.07 (C$_{Ar}$), 143.34 (C$_{Ar}$), 143.82 (C$_{Ar}$), 147.48 (C$_{Ar}$), 168.81 (CO). IR (KBr, cm^{-1}) 1602 (C=O), 3282 (OH). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91; found: C, 64.93; H, 5.71; N, 8.55.

N-(1-Hydroxy-1-phenylprop-2-yl)-*N*-methylbenzamide (7c).



Yield 180 mg (61%), mp 137-139°C, lit. mp 122-124 °C.[4]

cis-Rotamer (70% in DMSO-d$_6$ and 45% in CD$_2$Cl$_2$ at room temperature) ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 0.88 (d, 3H, $^3J_{3H\text{-}2H}$ 6.7 Hz, C^{3}H$_3$), 2.96 (s, 3H, NCH$_3$), 3.72 (dq, 1H, $^3J_{2H\text{-}3H}$ 6.7 Hz, $^3J_{1H\text{-}2H}$ 8.3 Hz, C^{2}H), 4.51 (dd, 1H, $^3J_{1H\text{-}2H}$ 8.3 Hz, $^3J_{1H\text{-}OH}$ 3.6 Hz, C^{1}H), 5.60 (d, 1H,

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[3] S. Ikuma, *Yakugaku Zasshi*, 1952, **72**, 951.

[4] S. Guizzetti, M. Benaglia, F. Cozzi and R. Annunziata, *Tetrahedron*, 2009, **65** (32), 6354.

$^3J_{\text{OH-1H}}$ 3.6 Hz, OH), 7.23-7.29 (m, 7H, CH_{Ar}), 7.38-7.40 (m, 3H, CH_{Ar}). ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.01 (C^3H_3), 26.77 (N$\underline{C}H_3$), 59.20 (C^2H), 73.57 (C^1H), 126.67 (C_{Ar}), 126.68 (C_{Ar}), 127.34 (C_{Ar}), 128.08 (C_{Ar}), 128.09 (C_{Ar}), 128.62 (C_{Ar}), 137.66 (C_{Ar}), 143.40 (C_{Ar}), 171.38 (CO). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.92 (d, 3H, $^3J_{\text{3H-2H}}$ 6.7 Hz, C^3H_3), 3.03 (s, 3H, NCH_3), 3.93 (m broad, 1H, C^2H), 4.70 (s broad, 2H, C^1H, OH), 7.23-7.29 (m, 7H, CH_{Ar}), 7.23-7.4 (m, CH_{Ar}).

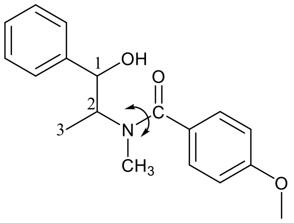
trans-Rotamer (30% in DMSO-d_6 and 45% in CD_2Cl_2 at room temperature). ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.99 (d, 3H, $^3J_{\text{3H-2H}}$ 6.6 Hz, C^3H_3), 2.75 (s, 3H, NCH_3), 4.76 (dq, 1H, $^3J_{\text{3H-2H}}$ 6.6 Hz, $^3J_{\text{3H-1H}}$ 7.4 Hz, C^2H), 4.69 (dd, 1H, $^3J_{\text{1H-2H}}$ 7.4 Hz, $^3J_{\text{1H-OH}}$ 4.3 Hz, ^{1}CH), 5.53 (d, 1H, $^3J_{\text{OH-1H}}$ 4.3 Hz, OH), 7.23-7.29 (m, 7H, CH_{Ar}), 7.38-7.40 (m, 3H, CH_{Ar}). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.85 (C^3H_3), 32.29 (N$\underline{C}H_3$), 53.81 (C^2H), 73.68 (C^1H), 126.46 (C_{Ar}), 126.79 (C_{Ar}), 127.17 (C_{Ar}), 127.96 (C_{Ar}), 128.22 (C_{Ar}), 128.94 (C_{Ar}), 137.56 (C_{Ar}), 143.50 (C_{Ar}), 170.56 (CO). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.22 (d, 3H, $^3J_{\text{3H-2H}}$ 6.6 Hz, C^3H_3), 2.74 (s, 3H, NCH_3), 4.51 (broad, 2H, ^{2}CH, ^{1}CH), 3.09 (broad, 1H, OH), 7.23-7.4 (m, CH_{Ar}). IR (KBr, cm^{-1}) 1606 (C=O), 3249 (OH). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20; found: C, 75.93; H, 7.08; N, 5.31.

Synthesis of 6 and 7a from acetylenic ketone 1a.

Method A. The solution of 652 mg ynone **1a** (2 mmol), 330 mg (+)-pseudoephedrine (2 mmol) and 15 mg CuCl in mixture of 1,4-dioxane (10 mL) and pyridine (1 mL) was refluxed for 29 h. Then solvents were removed *in vacuo* and the residue was purified by column chromatography (hexane-toluene (1:1), toluene, toluene-ethyl acetate (1:1), ethyl acetate) to afford:

1-(3,4,5-Trimethoxyphenyl)ethanone (6). Yield 120 mg (28%), mp 76-78 °C.

***N*-(1-Hydroxy-1-phenylprop-2-yl)-4-methoxy-*N*-methylbenzamide (7a).**



Yield 135 mg (22%), mp 140-143°C. *cis*-Rotamer (70% at room temperature).^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 (d, 3H, $^3J_{\text{3H-2H}}$ 6.5 Hz, C^3H_3), 2.92 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 3.82 (m, 1H, C^2H), 4.51(d, 1H, $^3J_{\text{1H-2H}}$ 7.3 Hz, C^1H), 5.59 (br.s, 1H, OH), 6.93 (d, 2H, J

8.8 Hz, CH_{Ar}), 7.24-7.31 (m, 7H, CH_{Ar}). ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.18 (C^3H_3), 27.01 (NCH_3), 55.22 (OCH_3), 59.37 (C^2H), 73.70 (C^1H), 113.43 (C_{Ar}), 126.80 (C_{Ar}), 127.41 (C_{Ar}), 128.18 (C_{Ar}), 128.68 (C_{Ar}), 129.71 (C_{Ar}), 143.48 (C_{Ar}), 159.51 (C_{Ar}), 171.43 (CO). *trans*-Rotamer (30 % at room temperature). ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.96 (br.s, 3H, C^3H_3), 2.79 (s, 3H, NCH_3), 3.78 (s, 3H, $O\underline{C}H_3$), 4.7 (br.s, 1H, C^2H), 4.68 (br.s, 1H, C^1H), 5.52 (br.s, 1H, OH), 6.93 (d, 2H, *J* 8.8 Hz, CH_{Ar}), 7.24-7.31 (m, 7H, CH_{Ar}). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.87 (C^3H_3), 32.52 ($N\underline{C}H_3$), 55.22 ($O\underline{C}H_3$), 54.21 (C^2H), 73.79 (C^1H), 113.42 (C_{Ar}), 126.83 (C_{Ar}), 127.26 (C_{Ar}), 128.06 (C_{Ar}), 128.67 (C_{Ar}), 129.55 (C_{Ar}), 143.57 (C_{Ar}), 159.82 (C_{Ar}), 170.58 (CO). IR (KBr, cm^{-1}) 1609 (C=O), 3251 (OH). Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68; found: C, 72.10; H, 6.95; N, 4.68.

Method B.

The solution of 140 mg amino enone **5a** (0.3 mmol) and 15 mg CuCl in mixture of 1,4-dioxane (5 mL) and pyridine (1 mL) was refluxed for 24 h. Then solvents were removed *in vacuo* and a residue was purified by column chromatography (hexane-toluene (1:1), toluene, toluene-ethyl acetate (1:1), ethyl acetate) to afford:

1-(3,4,5-Trimethoxyphenyl)ethanone (6). Yield 20 mg (31%), mp 77-79 °C.

***N*-(1-Hydroxy-1-phenylprop-2-yl)-4-methoxy-*N*-methylbenzamide (7a).** Yield 50 mg (55%), mp 142-146°C. For its spectral characteristics, see above.