o-Tosylaminobenzaldehyde aminals in the synthesis of 1,3-disubstituted propargylamines, derivatives of 3*H*-2-vinylidene-3-aminoindoline and quinoline

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o-Tosylaminobenzaldehyde aminals react with propargyl alcohol and its phenyl ether on heating in acetonitrile in the presence of CuI to yield 3*H*-2-vinylidene-3-aminoindoline derivatives. Analogous reactions with phenylacetylene and dimethylethynylcarbinol result in 1,3-disubstituted propargylamines. The possibility of using the latter compounds in synthesis of quinoline derivatives was shown: cyclization of 1-(*o*-tosylaminophenyl)-1-morpholino-3-phenylprop-2-yne in the presence of H_2SO_4 and KOH gave 2-phenylquinoline and 2-phenyl-4-morpholinoquinoline, respectively. 3*H*-2-Phenoxymethylvinylidene-3-morpholinoindoline was studied by X-ray diffraction spectroscopy.

Key words: *o*-tosylaminobenzaldehyde aminals, 3*H*-2-vinylidene-3-aminoindoline derivatives, 1,3-disubstituted propargylamines, quinoline derivatives, X-ray diffraction study.

Previously[1] we showed that aminals of aromatic *o*-hydroxyaldehydes react with terminal acetylenes to give 1,3-disubstituted propargylamines or derivatives of 3*H*-2-vinylidene-3-amino-2,3-dihydrobenzofuran. The purpose of the present study was to use this reaction for synthesizing nitrogen-containing heterocycles. It was found that *o*-tosylaminobenzaldehyde aminals (**1**) react with propargyl alcohol and its phenyl ether (**2**) in boiling acetonitrile in the presence of CuI to give 3*H*-1-tosyl-2-vinylidene-3-aminoindolines (**3**) (Scheme 1).

As in the case of 3*H*-2-vinylidene-3-amino-2,3-dihydrobenzofuran derivatives,[1] the IR spectra of compounds **3** contain characteristic medium-intensity bands in the region around 1690 cm^{-1}, which we attributed to vibrations of the exocyclic double bond.

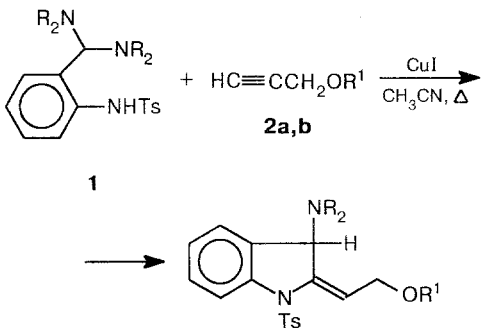
The reaction with phenylacetylene (**4**) under the same conditions gives propargylamines (**5**) (Scheme 2).

The reaction of tosylaminobenzaldehyde morpholinal (**1a**) with dimethylethynylcarbinol (**2c**), which was previously shown[1] to react with *o*-hydroxyaldehyde aminals to give cyclic products, also afforded propargylamine (**5d**) (Scheme 3).

In this case, reaction termination after the formation of propargylamine is probably caused by steric factors.

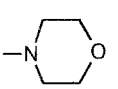
Propargylamines (**5**) have spectral features that we reported previously for analogous *o*-hydroxyaldehydes[1]: their IR spectra do not contain stretching vibration bands corresponding to triple bonds and NH groups.

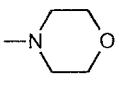
Scheme 1

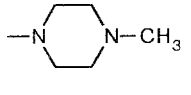


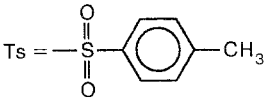
2a: R^1 = H

2b: R^1 = Ph

3a: R^1 = H; $-NR_2$ = 

3b: R^1 = Ph; $-NR_2$ = 

3c: R^1 = Ph; $-NR_2$ = 

Ts = 

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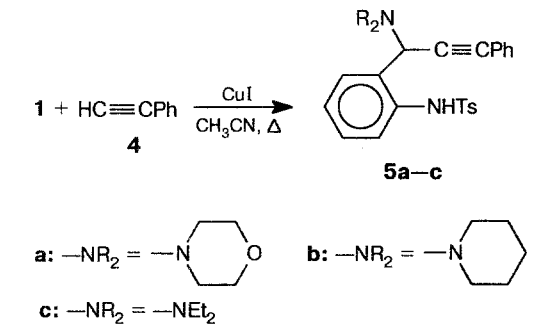
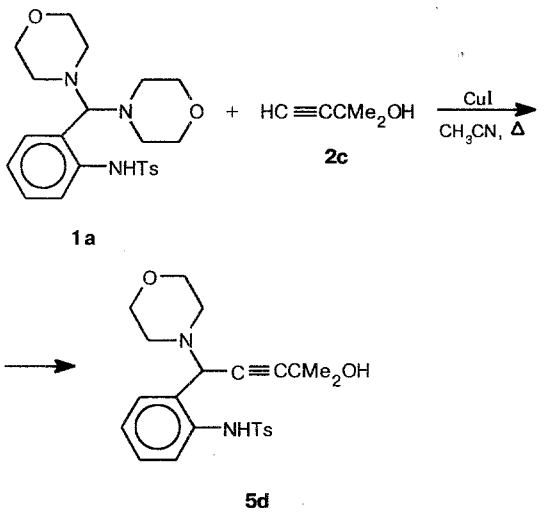
Scheme 2

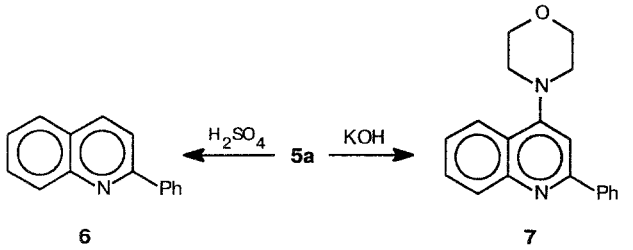


Scheme 3



When propargylamine **5a** is treated with concentrated sulfuric acid, its cyclization into 2-phenylquinoline (**6**) occurs, while its refluxing in butyl cellosolve with KOH affords 2-phenyl-4-morpholinoquinoline (**7**) (Scheme 4).

Scheme 4



Although reactions with preliminarily isolated aminals usually occur more selectively and in higher yields, the use of aminals *in situ* is sometimes preferable because they are hygroscopic or difficult to obtain in the crystalline form. In particular, compound **5c** was obtained by this method as we did not manage to isolate *o*-tosylaminobenzaldehyde diethylaminal in the crystalline form.

Compounds **3** are isostructural to Fisher bases. However, unlike the latter, they are enesulfonylamides rather than enamines, which makes them less reactive and absolutely stable in air under ambient conditions.

The structures of compounds **3** were independently confirmed by an X-ray diffraction study of 3*H*-2-phenoxymethylvinylidene-3-morpholinoindoline (**3b**). The geometric parameters of the molecule are presented in Tables 1 and 2, and its general view is shown in Fig. 1.

Table 1. Bond lengths *d* (Å) in molecule **3b**

Bond	*d*	Bond	*d*
S(1)—O(1)	1.419(5)	C(5)—C(6)	1.378(8)
S(1)—O(2)	1.411(5)	C(6)—C(7)	1.380(7)
S(1)—N(1)	1.682(5)	C(7)—C(7a)	1.366(7)
S(1)—C(8)	1.757(6)	C(8)—C(9)	1.373(8)
O(3)—C(16)	1.443(7)	C(8)—C(13)	1.369(8)
O(3)—C(17)	1.370(5)	C(9)—C(10)	1.373(7)
O(4)—C(24)	1.417(7)	C(10)—C(11)	1.37(1)
O(4)—C(25)	1.427(6)	C(11)—C(12)	1.375(8)
N(1)—C(2)	1.445(7)	C(11)—C(14)	1.504(8)
N(1)—C(7a)	1.435(6)	C(12)—C(13)	1.383(7)
N(2)—C(3)	1.461(7)	C(15)—C(16)	1.488(7)
N(2)—C(23)	1.470(5)	C(17)—C(18)	1.38(1)
N(2)—C(26)	1.462(6)	C(17)—C(22)	1.352(8)
C(2)—C(3)	1.522(6)	C(18)—C(19)	1.389(8)
C(2)—C(15)	1.304(7)	C(19)—C(20)	1.33(1)
C(3)—C(3a)	1.509(7)	C(20)—C(21)	1.35(1)
C(3a)—C(4)	1.380(6)	C(21)—C(22)	1.388(7)
C(3a)—C(7a)	1.385(6)	C(23)—C(24)	1.505(9)
C(4)—C(5)	1.373(8)	C(25)—C(26)	1.50(1)

Table 2. Bond angles ω (deg) in molecule **3b**

Angle	ω	Angle	ω
O(1)—S(1)—O(2)	120.6(2)	N(1)—C(7a)—C(3a)	110.7(4)
O(1)—S(1)—N(1)	105.2(2)	N(1)—C(7a)—C(7)	127.4(4)
O(2)—S(1)—N(1)	106.9(2)	C(3a)—C(7a)—C(7)	121.9(4)
O(1)—S(1)—C(8)	108.1(3)	S(1)—C(8)—C(9)	118.1(4)
O(2)—S(1)—C(8)	108.3(2)	S(1)—C(8)—C(13)	121.2(3)
N(1)—S(1)—C(8)	107.0(2)	C(9)—C(8)—C(13)	120.6(4)
C(16)—O(3)—C(17)	116.9(4)	C(8)—C(9)—C(10)	118.8(5)
C(24)—O(4)—C(25)	110.0(4)	C(9)—C(10)—C(11)	122.4(5)
S(1)—N(1)—C(2)	119.6(2)	C(10)—C(11)—C(12)	117.5(5)
S(1)—N(1)—C(7a)	117.2(3)	C(10)—C(11)—C(14)	121.6(5)
C(2)—N(1)—C(7a)	106.7(3)	C(12)—C(11)—C(14)	121.0(6)
C(3)—N(2)—C(23)	114.2(3)	C(11)—C(12)—C(13)	121.5(6)
C(3)—N(2)—C(26)	114.5(4)	C(8)—C(13)—C(12)	119.3(4)
C(23)—N(2)—C(26)	109.9(3)	C(2)—C(15)—C(16)	128.8(5)
N(1)—C(2)—C(3)	108.2(4)	O(3)—C(16)—C(15)	109.4(4)
N(1)—C(2)—C(15)	124.7(4)	O(3)—C(17)—C(18)	115.7(5)
C(3)—C(2)—C(15)	126.4(4)	O(3)—C(17)—C(22)	125.1(5)
N(2)—C(3)—C(2)	111.2(4)	C(18)—C(17)—C(22)	119.2(4)
N(2)—C(3)—C(3a)	119.5(3)	C(17)—C(18)—C(19)	119.8(7)
C(2)—C(3)—C(3a)	101.7(3)	C(18)—C(19)—C(20)	121.0(7)
C(3)—C(3a)—C(4)	130.9(4)	C(19)—C(20)—C(21)	119.0(5)
C(3)—C(3a)—C(7a)	109.7(4)	C(20)—C(21)—C(22)	121.7(6)
C(4)—C(3a)—C(7a)	119.4(4)	C(17)—C(22)—C(21)	119.3(6)
C(3a)—C(4)—C(5)	119.3(4)	N(2)—C(23)—C(24)	108.9(4)
C(4)—C(5)—C(6)	120.4(4)	O(4)—C(24)—C(23)	111.7(5)
C(5)—C(6)—C(7)	120.9(5)	O(4)—C(25)—C(26)	111.4(4)
C(6)—C(7)—C(7a)	118.1(4)	N(2)—C(26)—C(25)	108.9(4)

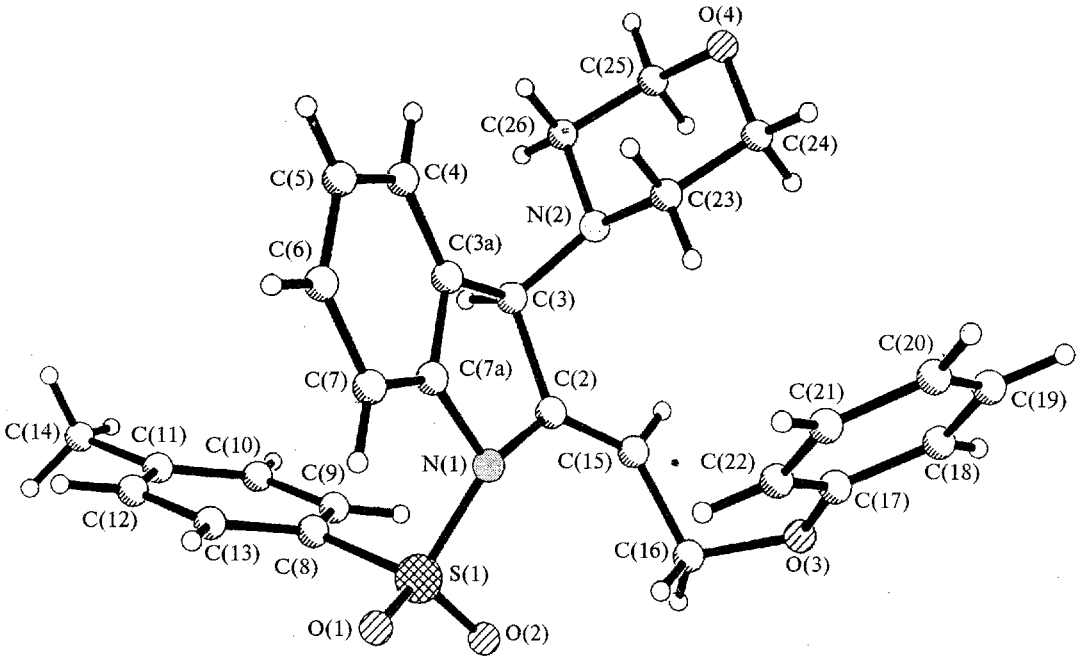


Fig. 1. General view of the 3*H*-2-phenoxymethylvinylidene-3-morpholinoindoline (**3b**) molecule.

In a crystal, the C(2)=C(15) bond in molecule **3b** has a *Z* configuration. The pyrroline ring has a strongly distorted envelope conformation (the C(2) and N(1) atoms deviate from the plane of the remaining ring atoms by 0.302(6) and 0.049(6) Å, respectively), although, according to data from the Cambridge structure database,[2] the pyrroline ring in structures incorporating a dihydroindole moiety generally has a planar conformation. Evidently, the pyrroline ring in the molecule studied does not have a planar conformation because of steric hindrance between bulky substituents at positions 1, 2, and 3. The same steric hindrance explains the pyramidal configuration of the N(1) atom (the sum of the bond angles is 343.6(8)°). The polyhedron of the morpholine substituent is an almost ideal chair (the modules of torsion angles range within 57.7—58.8(6°). Some deviation of the torsion angle C(3a)—C(3)—N(2)—C(23), which is 45.5(5)°, from the expected value of 60° (in the ideal twisted conformation) is probably due to steric factors. The N(2) atom has a typical pyramidal configuration (the sum of bond angles is 338.6(9)°). The coordination polyhedron of the sulfur atom is a distorted tetrahedron: the bond angle O(1)=S=O(2) is 120.6(2)°, which is more than the other angles (105.2(2)—108.3(2)°, see Table 3) because of repulsion between electron orbitals of the S=O double bonds and unshared electron pairs of the O(1) and O(2) atoms. The C(2)=C(15) double bond is almost not twisted (the torsion angle N(1)—C(2)—C(15)—C(16) is 2.1(5)°). The bond angles belonging to the C(2)=C(15) double bond are greater than 120°, as is the case for the majority of organic compounds, due to predominating repulsion between the σ,π-electron orbitals of the C(2)=C(15) double bond and the σ-orbitals of single

Table 3. Coordinates of non-hydrogen atoms (×10⁴) in structure **3b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S(1)	3438(1)	1553(1)	5577(1)	C(6)	3423(5)	6135(4)	3723(4)	C(17)	4150(5)	1164(5)	1546(4)
O(1)	4733(3)	2254(3)	5438(2)	C(7)	3789(4)	4830(4)	4026(3)	C(18)	4094(6)	1180(7)	511(5)
O(2)	3387(3)	193(3)	5715(2)	C(7a)	2848(4)	3855(4)	4112(3)	C(19)	4724(7)	2309(9)	−536(5)
O(3)	3503(4)	7(3)	2532(3)	C(8)	2052(4)	1652(4)	6763(3)	C(20)	5409(7)	3372(7)	−561(5)
O(4)	−1093(4)	3929(4)	1389(3)	C(9)	788(5)	800(5)	7226(4)	C(21)	5488(6)	3342(6)	453(5)
N(1)	3041(3)	2460(3)	4358(3)	C(10)	−291(5)	843(5)	8172(4)	C(22)	4852(5)	2242(5)	1519(4)
N(2)	83(3)	2921(3)	3222(3)	C(11)	−142(5)	1690(5)	8686(4)	C(23)	1011(4)	3681(4)	1994(3)
C(2)	1903(4)	1912(4)	4127(3)	C(12)	1138(6)	2528(5)	8205(4)	C(24)	299(6)	3490(5)	1205(4)
C(3)	744(4)	2869(4)	4082(3)	C(13)	2239(5)	2519(5)	7244(4)	C(25)	−1989(5)	3195(5)	2582(5)
C(3a)	1548(4)	4141(4)	3921(3)	C(14)	−1329(5)	1706(6)	9733(4)	C(26)	−1349(4)	3382(5)	3412(4)
C(4)	1194(4)	5449(4)	3625(3)	C(15)	1979(4)	885(4)	3840(3)				
C(5)	2141(5)	6443(4)	3519(4)	C(16)	3208(5)	81(4)	3648(4)				

bonds at substituted atoms. This, *e.g.*, explains the increase in the C(2)=C(15)—C(16) bond angle to 128.8(5)°. The phenoxymethylene moiety has a usual flattened conformation (the C(22)—C(17)—O(3)—C(16) torsion angle is 17.5(6)°).

The molecules of indolines **1**—**3** contain asymmetric carbon atoms and hence should exist as two enantiomers. As a result, the ^{1}H NMR signals of diastereotopic methylene protons in prochiral substituents ($CH_2OC_6H_5$, CH_2OH) manifest themselves as an AB-spectrum. The presence of a substituted vinylidene moiety enables geometric isomerism, which is detected from the presence of two different chemical shifts in the ^{1}H NMR spectra of both methylene and vinylidene protons. The spin system of the protons in CH_2CH can be regarded as ABX. The corresponding coupling constants are presented in Experimental.

Experimental

IR spectra were recorded on a Specord IR-75 spectrophotometer in Vaseline oil. The ^{1}H NMR spectra of compounds **3a,b,c** and **5a,c,d** and the ^{13}C NMR spectrum of compound **5a** were recorded on a UNITY 300 radio-frequency spectrometer; ^{1}H NMR spectra of compounds **5b** and **7** were obtained on a Tesla BS-487C spectrometer using HMDS as the internal standard.

X-Ray diffraction analysis of compound 3b. The crystals of compound **3b** are monoclinic, space group $P\bar{1}$; at 20 °C a = 9.83(1), b = 10.83(2), c = 13.21(1) Å, α = 66.48(1), β = 71.36(1), γ = 88.71(1)°, V = 1212(1) Å^3, M = 490.60, Z = 2, d_{calc} = 1.344 g cm^{-3}, μ(MoKα) = 0.17 mm^{-1}.

The parameters of the unit cell and reflection intensities were measured on a Siemens P3/PC automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$-scanning, θ_{max} = 28°). The structure was solved by a direct method (MULTAN program) and refined by full-matrix least-squares method in an anisotropic approximation for non-hydrogen atoms; corrections for absorption were not made. The initial positions of hydrogen atoms were calculated and refined by the riding model with fixed U_{iso} = 0.08 Å. The final discrepancy factors were R = 0.052 and R_w = 0.054 for 2690 independent reflections with $I \geq 3\sigma(I)$. All calculations were performed on IBM PC/AT-286 using the SHELXTL PLUS programs.[4] The coordinates of non-hydrogen atoms are presented in Table 3.

***o*-Tosylaminobenzaldehyde morpholinal (1a). a.** A mixture of *o*-tosylaminobenzaldehyde (8.2 g, 0.03 mol), morpholine (17.4 g, 0.2 mol), and 2-propanol (20 mL) was refluxed for 2 h and cooled with ice. The precipitate was filtered off, washed with 2-propanol and hexane, and dried. The yield was 11 g (85 %).

b. The reagents were mixed in the same ratio. The mixture was brought to boiling and left for 12 h. The resulting precipitate was filtered off, washed with 2-propanol and hexane, and dried. The yield was 12 g (93 %). Colorless needles with m.p. 181—183 °C (from 2-propanol). Found (%): C, 61.00; H, 6.84; N, 10.01; S, 7.34. $C_{22}H_{29}N_3O_4S$. Calculated (%): C, 61.25; H, 6.73; N, 9.74; S, 7.42.

***o*-Tosylaminobenzaldehyde piperidinal (1b).** A mixture of *o*-tosylaminobenzaldehyde (5.5 g, 0.02 mol) and piperidine (4.25 g, 0.05 mol) was heated until complete homogenization and kept for 12 h. The mixture, which began to crystallize, was triturated with hexane (30 mL). The precipitate was filtered off, washed with hexane on the filter, and dried. Yield 8.0 g (93.8 %). Colorless crystals with m.p. 128—130 °C (from ethyl acetate). Found (%): C, 67.50; H, 8.01; N, 9.68; S, 6.53. $C_{24}H_{33}N_3O_2S$. Calculated (%): C, 67.45; H, 7.73; N, 9.84; S, 7.49.

***o*-Tosylaminobenzaldehyde *N*-methylpiperazinal (1c).** *o*-Tosylaminobenzaldehyde (2.75 g, 0.01 mol) was dissolved with heating in 2-propanol (20 mL), and then *N*-methylpiperazine (3 mL, 0.025 mol) was added. The mixture was heated to boiling and poured into a Petri dish. The solvent was evaporated, and the oil that formed was crystallized on trituration with petroleum ether. The precipitate was transferred on a filter, washed with petroleum ether, and dried. Yield 4.6 g (quantitative). M.p. 222—225 °C (from a 2-propanol—octane mixture, 1 : 10). Found (%): C, 63.58; H, 7.09; N, 14.97; S, 6.73. $C_{24}H_{35}N_5O_2S$. Calculated (%): C, 63.02; H, 7.66; N, 15.32; S, 7.00.

3*H*-1-Tosyl-2-hydroxymethylvinylidene-3-morpholinoindoline (3a). A mixture of *o*-tosylaminobenzaldehyde morpholinal **1a** (2.16 g, 0.005 mol), CuI (1 g, 0.005 mol), and propargyl alcohol (0.3 g, 0.0054 mol) in dry acetonitrile (8 mL) was refluxed for 30 min and cooled. Water (25 mL) and concentrated NH_4OH (25 mL) were added; the mixture was extracted with $CHCl_3$ (20 mL), and the extract was passed through a column with Al_2O_3. A small head portion was thrown off. The solvent was evaporated from the next fraction to give 1.7 g (85 %) of a practically pure product as a yellowish powder. M.p. 196—198 °C (from 2-propanol). Found (%): C, 63.75; H, 6.39; N, 7.08; S, 7.44. $C_{21}H_{24}N_2O_4S$. Calculated (%): C, 63.00; H, 6.00; N, 7.00; S, 8.00. IR, ν/cm^{-1}: 3560 (OH), 1687 (C=C), 1600 (arom.), 1361, 1167 (SO_2), 1114 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, CH_3), 2.41—2.60 (m, 5 H, CH_2N, OH), 3.47—3.59 (m, 4 H, CH_2O), 3.78 (s, 1 H, CH), 4.40—4.60 (m, 2 H, CH_2, $^3J_{CH_2,CH}$ = 7.6 Hz), 5.92—5.98 (m, 1 H, =CH, $^3J_{CH,CH_2}$ = 7.61 Hz), 7.08—7.20 (m, 4 H, H arom.), 7.26—7.38 (m, 3 H, H arom.), 7.72 (d, 1 H, H arom.).

3*H*-1-Tosyl-2-phenoxymethylvinylidene-3-morpholinoindoline (3b). A mixture of *o*-tosylaminobenzaldehyde morpholinal **1a** (2.16 g, 0.005 g), phenylpropargyl ether (0.8 mL, 0.005 mol), and CuI (0.95 g, 0.005 mol) in dry acetonitrile (10 mL) was refluxed for 45 min with stirring and was then cooled, and concentrated NH_4OH (20 mL) and water (40 mL) were added. The resulting precipitate was filtered off and recrystallized from a 2-propanol-hexane mixture (1 : 1). Yield 1.52 g (63.6 %). Colorless crystals with m.p. 136—138 °C (from 2-propanol). Found (%): C, 67.78; H, 6.28; N, 5.86; S, 6.69. $C_{27}H_{28}N_2O_4S$. Calculated (%): C, 68.07; H, 5.88; N, 5.88; S, 6.72. IR, ν/cm^{-1}: 1694 (C=C), 1594, 1587 (arom.), 1367, 1167 (SO_2), 1127, 1107 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, CH_3), 2.35 (m, 2 H, CH_2N), 2.45 (m, 2 H, CH_2N), 3.40 (m, 4 H, CH_2O), 3.87 (s, 1 H, CH), 4.97—5.04 (m, 1 H, CH_2, $^3J_{BX}$ = 4.1 Hz), 5.17—5.25 (m, 1 H, CH_2, $^3J_{AX}$ = 7.61 Hz), 5.92 (m, 1 H, =CH, $^2J_{AB}$ = 14.3 Hz), 6.68—6.95 (m, 3 H, H arom.), 7.08—7.48 (m, 9 H, H arom.), 7.77 (d, 1 H, H arom.).

3*H*-1-Tosyl-2-phenoxymethylvinylidene-3-(*N*-methylpiperazino)indoline (3c). A mixture of *o*-tosylaminobenzaldehyde *N*-methylpiperazinal **1c** (2.3 g, 0.005 mol), phenylpropargyl ether (0.8 mL, 0.005 mol), CuI (0.95 g, 0.005 mol), and acetonitrile (10 mL) was refluxed for 0.5 h with stirring, filtered off, and cooled. Concentrated NH_4OH (10 mL) and water (50 mL) were added to the filtrate. The precipitate was filtered off, washed with water, and dried. The yield of the crude product was 2 g (83 %). To obtain an analytically pure

product, it was passed through a column with Al_2O_3 ($CHCl_3$ as the eluent) and recrystallized from a 2-propanol—octane mixture (1 : 1). Colorless crystals with m.p. 178 °C. Found (%): C, 68.60; H, 6.68; N, 8.10; S, 5.98. $C_{28}H_{31}N_3O_3S$. Calculated (%): C, 68.71; H, 6.34; N, 8.59; S, 6.54. IR, ν/cm^{-1}: 1700 (C=C), 1600, 1580 (arom.), 1360, 1166 (SO_2). ^{1}H NMR ($CDCl_3$), δ: 2.18 (m, 4 H, CH_2N), 2.19 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.39 (m, 2 H, CH_2N), 2.54 (m, 2 H, CH_2N), 3.91 (s, 1 H, CH), 4.95—5.02 (m, 1 H, CH_2, $^3J_{BX}$ = 3.8 Hz), 5.17—5.25 (m, 1 H, CH_2, $^3J_{AX}$ = 8.2 Hz), 5.91—5.96 (m, 1 H, =CH, $^3J_{AB}$ = 14.1 Hz), 6.85—7.73 (m, 12 H, H arom.), 7.77 (d, 1 H, H arom.).

1-Morpholino-1-(2-tosylamino)phenyl-3-phenylpropyne-2 (5a). A mixture of *o*-tosylaminobenzaldehyde morpholinal **1a** (2.16 g, 0.005 mol), phenylacetylene (0.5 g, 0.005 mol), and CuI (0.95 g, 0.005 mol) was refluxed for 30 min with dry acetonitrile (7 mL) and cooled, and concentrated NH_4OH (10 mL) and water (40 mL) were then added. The oil that formed was extracted with chloroform (2 × 10 mL) and passed through a column with Al_2O_3 (d = 2.5 cm, h = 5 cm, dry packing), collecting the head colorless or weakly colored fraction. The solvent was distilled off to give 2.1 g (94.4 %) of colorless crystals with m.p. 143—145 °C (from MeOH). Found (%): C, 69.64; H, 6.03; N, 6.97, S, 6.61. $C_{26}H_{26}N_2O_3S$. Calculated (%): C, 69.95; H, 5.83; N, 6.28; S, 7.17. IR, ν/cm^{-1}: 3180 (NH), 1594, 1581 (arom.), 1341, 1167 (SO_2), 1114 (C—O—C), 761, 687 (C_6H_5). ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, CH_3), 2.62 (t, 4 H, CH_2N), 3.78 (t, 4 H, CH_2O), 4.46 (s, 1 H, CH), 7.00—7.75 (m, 13 H, H arom.), 10.64 (s, 1 H, NH). ^{13}C NMR, $CDCl_3$, δ: 21.39 (CH_3), 48.98, 60.22, 66.76 (CH, CH_2), 81.55, 90.45 (C≡C), 120.86, 122.08, 123.95, 125.49, 126.69, 128.32, 128.66, 129.20, 129.39, 129.63, 131.70, 137.11, 137.74, 143.55 (arom.).

1-Piperidino-1-(2-tosylamino)phenyl-3-phenylpropyne-2 (5b). A mixture of *o*-tosylaminobenzaldehyde piperidinal **1b** (2.14 g, 0.005 mol), phenylacetylene (0.5 g, 0.005 mol), and CuI (0.95 g, 0.005 mol) was refluxed for 30 min with dry acetonitrile (7 mL) and cooled, and concentrated NH_4OH (10 mL) and water (20 mL) were then added. The resulting precipitate was filtered off, washed with water, and dissolved in $CHCl_3$ (15 mL). The solution was passed through a column with Al_2O_3. The solvent was distilled off, and the oil that formed was crystallized on trituration with hexane. Yield 2.1 g (94.6 %). Colorless crystals with m.p. 149—150 °C (from 1-propanol). Found (%): C, 73.37; H, 6.98; N, 6.08; S, 7.31. $C_{27}H_{28}N_2O_2S$. Calculated (%): C, 792.97; H, 6.31; N, 6.31; S, 7.21. ^{1}H NMR ($CDCl_3$), δ: 1.33—1.80 (m, 6 H, CH_2), 2.26 (s, 3 H, CH_3), 2.50 (t, 4 H, CH_2N), 4.40 (s, 1 H, CH), 7.00—7.70 (m, 13 H, H arom.).

1-Diethylamino-1-(2-tosylamino)phenyl-3-phenylpropyne-2 (5c). A solution of *o*-tosylaminobenzaldehyde (0.7 g, 0.0025 mol) and diethylamine (0.75 mL, 0.0073 mol) in acetonitrile (10 mL) was heated to boiling and kept for 30 min. Phenylacetylene (0.3 mL, 0.0025 mol) and CuI (0.47 g, 0.0025 mol) were then added, and the mixture was refluxed for 30 min. Concentrated NH_4OH (5 mL) and water (30 mL) were added to the cooled reaction mixture, and the oil that formed was separated and triturated with acetonitrile with cooling by ice. The resulting crystals were dried, dissolved in $CHCl_3$, and passed through a column with Al_2O_3. The solvent was evaporated, and the light oil was triturated with acetonitrile with a seed crystal of compound **5c**. After rapid crystallization of the whole bulk, the compound was transferred on a filter, and dried to give colorless crystals with m.p. 119—121 °C (from CH_3CN). Yield of the raw product 0.97 g (88 %). Found (%): C, 72.40; H, 6.62; N, 6.33; S, 6.70. $C_{26}H_{28}N_2O_2S$. Calculated (%): C, 72.06; H, 6.70; N, 6.47; S, 7.39. IR, ν/cm^{-1}: 1607, 1601, 1587 (arom.), 1341, 1167 (SO_2), 754, 700 (monosubstituted benzene ring). ^{1}H NMR ($CDCl_3$), δ: 1.15 (s, 3 H, CH_3, J = 7 Hz), 2.38 (s, 3 H, CH_3), 2.50—2.70 (m, 4 H, CH_2), 4.81 (s, 1 H, CH), 7.00—7.71 (m, 13 H, H arom.), 11.14 (s, 1 H, NH).

1-Morpholino-1-(2-tosylamino)phenyl-3,3-dimethylpropyne-2-ol-3 (5d). A solution of *o*-tosylaminobenzaldehyde morpholinal **1a** (1.08 g, 0.0025 mol), dimethylethylcarbinol (0.3 mL, 0.003 mol), and CuI (0.45 g, 0.0025 mol) in 8 mL of dry acetonitrile was refluxed for 30 min with stirring, then the mixture was cooled, and 10 mL of concentrated NH_4OH and 40 mL of H_2O were added. The solution was extracted with chloroform, the solvent was evaporated, and the solid residue was extracted several times with boiling octane. The mixture was cooled with ice and the crystalline precipitate formed was filtered off to afford 0.33 g (31 %) of **5d** as colorless crystals with m.p. 173 °C (from aqueous MeOH). Found (%): C, 64.32; H, 6.65; N, 6.72; S, 7.35. $C_{23}H_{28}N_2O_4S$. Calculated (%): C, 64.48; H, 6.54; N, 6.54. S, 7.48. IR, ν/cm^{-1}: 3527, 3447 (OH), 1607, 1594, (arom.), 1341, 1161 (SO_2), 1121, 1114 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 1.60 (s, 6 H, CH_3), 2.39 (s, 3 H, CH_3), 2.52 (m, 4 H, CH_2N), 3.76 (m, 4 H, CH_2O), 4.27 (s, 1 H, CH), 7.00—7.71 (m, 8 H, H arom.), 10.52 (s, 1 H, NH).

2-Phenylquinoline (6). A solution of propargylamine **5a** (0.89 g, 0.002 mol) in conc. H_2SO_4 (5 mL) was kept for 2 h at ~20 °C and then poured into cold water (20 mL) and neutralized with $NaHCO_3$. The yellowish precipitate was filtered off, yield 0.4 g (95 %). Recrystallization from 2-propanol gave colorless needles with m.p. 83—84 °C (*cf.* Ref. 3: m.p. 82—83 °C). Found (%): C, 87.47; H, 5.35; N, 7.13. $C_{15}H_{11}N$. Calculated (%): C, 87.80; H, 5.37; N, 6.83.

2-Phenyl-4-(*N*-morpholino)quinoline (7). A solution of propargylamine **5a** (0.67 g, 0.0015 mmol) and KOH (0.11 g, 0.002 mol) in butyl cellosolve (5 mL) was refluxed for 3 h and cooled, and water (25 mL) was added. The oil that formed crystallized on trituration to give colorless needles with m.p. 135—136 °C (from 2-propanol). Yield 0.4 g (91 %). Found (%): C, 78.82; H, 6.28; N, 10.03. $C_{19}H_{18}N_2O$. Calculated (%): C, 78.62; H, 6.27; N, 9.66. IR, ν/cm^{-1}: 1594, 1554, 1514, 1495 (C=C and C=N), 1114 (C—O—C), 774, 701 (C_6H_5). ^{1}H NMR ($CDCl_3$), δ: 3.12 (t, 4 H, CH_2N), 3.85 (t, 4 H, CH_2O), 7.15—8.10 (m, 10 H, H arom.).

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