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General Procedure for the Synthesis of *ortho*-Vinylbenzyl-Substituted Amines, Ethers, and Sulfides

N. M. Shcheglova, V. D. Kolesnik, and R. V. Ashirov

NIOST Ltd., ul. Kuzovlevskii trakt 2/270, Tomsk, 634067 Russia e-mail: schnm@niost.ru

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Abstract—A convenient procedure has been proposed for the synthesis *ortho*-vinylbenzyl-substituted ethers, amines, and sulfides via reaction of *o*-(2-bromoethyl)benzyl bromide with various nucleophiles.

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In recent time, substituted styrenes having an electron-donating group in the *ortho* position have attracted much interest as chelating ligands for carbene ruthenium complexes [1] which catalyze metathesis reactions. Therefore, development of a general procedure for the synthesis of styrenes with donor substituents is an important problem.

We now propose a general method for the preparation of *ortho*-vinylbenzyl-substituted amines, ethers, and sulfides using o-(2-bromoethyl)benzyl bromide (I) [2] as the key intermediate product. o-(2-Bromoethyl)- benzyl bromide can be synthesized from isochroman which is readily available from 2-phenylethanol [3] (Scheme 1). The known procedure for the synthesis of dibromide I by treatment of isochroman with 40% HBr in acetic acid [4] is very sensitive to moisture and is complicated due to formation of acetates.

We have found that passing of gaseous HBr through isochroman yields a mixture of dibromide I with 2-(2-bromomethylphenyl)ethanol; treatment of this mixture with bromine in the presence of red phosphorus gives target product I in an overall yield of 63%.



 $R = R' = Et(a); RR' = (CH_2)_5(b), (CH_2CH_2)_2O(c); R = R' = cyclo-C_6H_{11}(d), HOCH_2CH_2(e).$





 $R = Et(a), i-Pr(b), Ph(c), 4-t-BuC_6H_4(d).$

The reactions of dibromide I with excess secondary amines led to the formation of tetrahydroisoquinolinium bromides IIa–IIe (Scheme 1). Microwave activation considerably accelerated the process and increased its selectivity. Ammonium salts IIa–IIe can readily be converted into the corresponding aminostyrenes IIIa–IIIe by the action of potassium *tert*butoxide in *tert*-butyl alcohol or via Hofmann elimination.

The reaction of dibromide I with *N*-methylaniline under microwave irradiation gave no expected tetrahydroisoquinolinium salt, while the isolated product was *N*-phenyltetrahydroisoquinoline. With a view to obtain salt **IIf** dibromide I was treated with lithium *N*-methylanilide without microwave irradiation (Scheme 1).

The described approach is also applicable to the synthesis of bis-amines (Scheme 1). For example, treatment of hexane-1,6-diamine with 2 equiv of dibromide I afforded 2,2'-hexamethylenediisoquinoline (IV) whose alkylation with methyl iodide, followed by treatment with a base, led to the formation of N,N'-bis-(2-vinylbenzyl)-N,N'-dimethylhexane-1,6-diamine (V).

The reactions of **I** with oxygen-centered nucleophiles (alcohols and phenols) produced *ortho*-vinylbenzyl-substituted ethers **VIa**–**VId** in one step (Scheme 2). Dibromide **I** reacted with sodium sulfide in methanol to give thioisochroman (**VII**), and the subsequent alkylation of **VII** with methyl iodide and treatment with a base afforded 2-(methylsulfanylmethyl)styrene (VIII). Dibromide I is readily converted into 2-bromomethylstyrene (IX) by the action of potassium *tert*-butoxide under mild conditions. The reactions of bromide IX with nucleophiles also gave targeted *ortho*-substituted styrenes X and XI (Scheme 2).

Thus we have proposed a general and convenient procedure for the synthesis of a wide series of *ortho*-substituted styrenes with the use of readily accessible *o*-(2-bromoethyl)benzyl bromide as key intermediate product.

EXPERIMENTAL

Microwave-assisted reactions were carried out in a CEM MARS 5 chemical microwave furnace at an irradiation power of 400 W. The ¹H and ¹³C NMR spectra were measured at 25°C on a Bruker Avance III 400 spectrometer operating at 400.1 and 100.6 MHz, respectively; CDCl₃ and DMSO- d_6 [for 2-(phenoxymethyl)styrene] were used as solvents, and tetramethylsilane, as internal reference. The mass spectra were obtained on an Agilent 7890A–5975S GC/MS system (HP-5MS column, 30 m×0.25 mm; electron impact, 70 eV). The high-resolution mass spectra were recorded on an Agilent 1200-6210 mass spectrometer (electrospray ionization, time-of-flight detector).

2-(2-Bromoethyl)benzyl bromide (I). Anhydrous hydrogen bromide [5] was passed over a period of 2 h

through 5.00 g (37.31 mmol) of isochroman [3] heated to 70°C. A mixture of dibromide I and 2-(2-bromomethylphenyl)ethanol at a ratio of 5:2 was formed. The mixture was cooled, 15 ml of methylene chloride and 0.32 g (10.20 mmol) of red phosphorus were added, and a solution of 2.46 g (15 mmol) of bromine in methylene chloride was added dropwise under stirring. The mixture was stirred for 1 h, poured into ice water, and extracted with petroleum ether. The extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Yield 63%, light brown oily substance which solidified on storage. ¹H NMR spectrum, δ , ppm: 3.28 t (2H, CH₂CH₂Br, *J* = 8.0 Hz), 3.62 t (2H, CH₂CH₂Br, *J* = 8.0 Hz), 4.53 s (2H, CH₂), 7.18–7.38 m (4H, H_{arom}) [6].

Aminomethylstyrenes IIIa–IIId (general procedure). A solution of 2 g (7.2 mmol) of dibromide I and 21.6 mmol of the corresponding secondary amine in 15 ml of dioxane was heated for 1 h at 120–130°C under microwave irradiation. The mixture was cooled and evaporated, the residue was treated with diethyl ether, and the precipitate was filtered off and dried on a filter. The yellow powder thus isolated was dissolved in 40 ml of *tert*-butyl alcohol, 2.50 g (22 mmol) of potassium *tert*-butoxide was added, and the mixture was heated for 1 h under reflux, cooled, and evaporated under reduced pressure. The residue was treated with water and extracted with diethyl ether, and the extract was dried over anhydrous sodium sulfate, filtered, and evaporated.

N-(2-Ethenylbenzyl)-N-ethylethanamine (IIIa) was isolated by vacuum distillation. Yield 52%, colorless transparent oily substance, bp 90–95°C (3 mm) [2]. ¹H NMR spectrum, δ , ppm: 1.00 t (6H, CH₂CH₃, J = 7.2 Hz), 2.49 q (4H, CH₂CH₃, J = 7.2 Hz), 3.55 s $(2H, ArCH_2), 5.24 \text{ d.d} (1H, =CH_2, J = 10.8, 1.6 \text{ Hz}),$ 5.60 d.d (1H, =CH₂, J = 17.6, 1.6 Hz), 7.12–7.25 m (3H, H_{arom}, CH=), 7.30–7.34 m (1H, H_{arom}), 7.4–7.51 m (1H, H_{arom}). ¹³C NMR spectrum, δ_C , ppm: 11.6 (CH₃), 46.7 (CH₂CH₃), 55.5 (CH₂), 114.9 (=CH₂), 125.5 (C⁶), 127.0 (C⁵), 127.3 (C⁴), 130.1 (C³), 134.9 (C²), 137.0 (CH=), 137.6 (C¹). Mass spectrum, m/z (I_{rel} , %): 189 (16.7) $[M]^+$, 188 (21.2), 175 (7.6), 174 (51.5), 161 (8.3), 160 (18.2), 118 (15.2), 117 (100), 116 (13.6), 115 (49.2), 91 (14.40), 86 (9.1). Found: m/z 190.15892 $[M + H]^+$. C₁₃H₁₉N. Calculated: $[M + H]^+$ 190.15957.

1-(2-Ethenylbenzyl)piperidine (IIIb) was isolated by chromatography on silica gel using ethyl acetate– petroleum ether (1:10) as eluent. Yield 65%, colorless transparent oily substance. ¹H NMR spectrum, δ , ppm: 1.39 m (2H, 4'-H), 1.58 m (4H, 3'-H, 5'-H), 2.41 m (4H, 2'-H, 6'-H), 3.5 s (2H, ArCH₂), 5.23 d.d (1H, =CH₂, J = 10.8, 1.6 Hz), 5.60 d.d (1H, =CH₂, J = 19.2, 1.6 Hz), 7.21–7.29 m (4H, H_{arom}, CH=), 7.55 m (1H, H_{arom}). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 24.5 (C^{4'}), 26.1 (C^{3'}, C^{5'}), 54.6 (C^{2'}, C^{6'}), 61.3 (ArCH₂), 115.0 (=CH₂), 125.6 (C⁶), 127.1 (C⁵), 127.3 (C⁴), 130.3 (C²), 135.0 (C³), 136.0 (CH=), 137.8 (C¹). Mass spectrum, m/z ($I_{\rm rel}$, %): 202 (7.9) [M + H]⁺, 201 (59.1) [M]⁺, 200 (89.0), 187 (14.2), 186 (97.6), 172 (18.9), 158 (15.0), 145 (9.4), 144 (13.4), 130 (8.7), 119 (7.9), 118 (55.9), 117 (100), 116 (26.0), 115 (71.7), 98 (26.8), 91 (23.6), 84 (27.6). Found: m/z 202.15952 [M + H]⁺. C₁₄H₁₉N. Calculated: [M + H]⁺ 202.15957.

4-(2-Ethenylbenzyl)morpholine (IIIc) was isolated by chromatography on silica gel using ethyl acetate-petroleum ether (1:9) as eluent. Yield 45%, colorless transparent liquid. ¹H NMR spectrum, δ, ppm: 2.47 t (4H, NCH₂CH₂O, J = 4.3 Hz), 3.54 s (2H, ArCH₂), 3.71 m (4H, OCH₂), 5.33 d.d (1H, =CH₂, J = 12.4, 1.6 Hz), 5.68 d.d (1H, =CH₂, J = 17.6, 1.6 Hz), 7.19-7.30 m (4H, H_{arom}, CH=), 7.55 m (1H, H_{arom}). ¹³C NMR spectrum, δ_{C} , ppm: 53.6 (NCH₂CH₂O), 61.1 (ArCH₂), 67.1 (CH₂O), 115.3 (=CH₂), 125.7 (C⁶), 127.3 (C⁵), 127.5 (C⁴), 130.5 (C²), 134.8 (C³), 136.8 (CH=), 137.9 (C¹). Mass spectrum, m/z (I_{rel} , %): 203 (24.5) $[M]^+$, 202 (26.5), 188 (26.1), 174 (7.9), 172 (11.1), 159 (9.5), 158 (23.3), 146 (21.7), 145 (22.1), 144 (33.2), 131 (7.9), 130 (11.1), 129 (7.9), 119 (6.3), 118 (49.8), 117 (100), 116 (36.4), 115 (77.5), 100 (11.1), 91 (26.1), 86 (11.9), 56 (14.2). Found: m/z 204.13877 $[M + H]^+$. C₁₃H₁₇NO. Calculated: $[M + H]^+$ 204.13883.

N-Cyclohexyl-N-(2-ethenylbenzyl)cyclohexanamine (IIId) was isolated by chromatography on silica gel using chloroform-petroleum ether (1:10) as eluent. Yield 42%, light yellow oily substance. ¹H NMR spectrum, δ, ppm: 0.85–1.35 m (8H, Cy), 1.61 m (4H, Cy), 1.78 m (8H, Cy), 2.56 m (2H, NCH), 3.83 s (2H, $ArCH_2$), 5.26 d.d (1H, = CH_2 , J = 16.0, 1.6 Hz), 5.59 d.d (1H, CH=CH₂, J = 20.0, 1.6 Hz), 7.18–7.29 m (3H, H_{arom}, CH=), 7.46 m (1H, H_{arom}), 7.58 m (1H, H_{arom}). ¹³C NMR spectrum, δ_{C} , ppm: 26.3 (C^{4'}), 26.5 $(C^{3'}, C^{5'})$, 31.8 $(C^{2'}, C^{6'})$, 47.5 (ArCH₂), 57.7 $(C^{1'})$, 114.8 (=CH₂), 125.4 (C⁶), 126.2 (C⁵), 127.4 (C⁴), 129.0 (C²), 135.0 (C³), 136.8 (CH=), 139.7 (C¹). Mass spectrum, m/z ($I_{\rm rel}$, %): 297 (11.4) [M]⁺, 254 (12.6), 215 (6.7), 214 (26.8), 213 (92.1), 212 (100), 172 (9.4), 144 (5.9), 130 (9.8), 118 (9.4), 117 (64.2), 116 (11.0), 115 (35.0), 91 (11.4), 55 (15.7), 41 (8.7). Found: m/z 298.25333 $[M + H]^+$. C₂₁H₃₁N. Calculated: $[M + H]^+$ 298.25347.

2,2'-[(2-Ethenylbenzyl)imino]diethanol (IIIe). A solution of 2.00 g (7.20 mmol) of dibromide I and 2.27 g (21.60 mmol) of diethanolamine in 15 ml of dioxane was heated for 1 h at 120-130°C under microwave irradiation. The mixture was cooled and evaporated, the residue was washed with THF, and the precipitate was filtered off and dried on a filter. The product was dissolved in 40 ml of 50% isopropyl alcohol, and the solution was applied to a column charged with AV-17-8 anion exchanger (OH form). The column was eluted with 50% ethanol until neutral eluate, the eluate was evaporated, and the residue was kept for 3 h at 100–180°C (4 mbar) and purified by chromatography on silica gel using ethyl acetate as eluent. Yield 46%, colorless oily substance. ¹H NMR spectrum, δ , ppm: 2.71 t (4H, CH₂CH₂OH, J = 4.4 Hz), 3.59 t (4H, CH₂CH₂OH, J = 4.4 Hz), 3.80 s $(2H, ArCH_2), 5.37 \text{ d.d} (1H, =CH_2, J = 13.4, 1.6 \text{ Hz}),$ 5.68 d.d (1H, =CH₂, J = 16.8, 1.6 Hz), 7.16 d.d (1H, CH=, J = 13.4, 16.8 Hz), 7.20–7.40 m (3H, H_{arom}), 7.52 d (1H, H_{arom}, J = 7.2 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 56.0 (CH₂CH₂OH), 58.2 (ArCH₂), 59.8 (CH₂OH), 115.7 (=CH₂), 126.5 (C⁶), 127.8 (C⁵), 128.0 (C^4) , 130.6 (C^2) , 135.1 (C^3) , 135.7 (CH=), 137.6 (C^1) . Mass spectrum, m/z (Irel, %): 191 (8.0), 190 (59.3), 118 (11.4), 117 (100), 116 (10.3), 115 (41.1), 91 (13.3). Found: m/z 222.14911 $[M + H]^+$. C₁₃H₁₉NO₂. Calculated: $[M + H]^+$ 222.14939.

N-Methyl-N-(2-ethenylbenzyl)aniline (IIIf). A solution of 1.00 g (9.40 mmol) of N-methylaniline in 10 ml of THF was cooled to 0°C, 6.20 ml (9.92 mmol) of 1.60 M n-butyllithium was added, and the mixture was stirred for 30 min. A solution of 2.62 g (9.42 mmol) of dibromide I in 10 ml of THF was then added dropwise at 0°C, and the mixture was stirred for 15 min, treated with a saturated solution of ammonium chloride, diluted with water, and extracted with diethyl ether. The extract was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure. The residue was a yellow powder which was dissolved in 20 ml of tert-butyl alcohol, 1.74 g (15.60 mmol) of potassium tert-butoxide was added, and the mixture was heated for 1 h under reflux. The mixture was cooled and evaporated, 50 ml of water was added to the residue, and the mixture was extracted with diethyl ether. The extract was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure. Yield 50%, light yellow transparent oily substance. ¹H NMR spectrum, δ, ppm: 2.99 s (3H, Me), 4.55 s (2H, $ArCH_2$), 5.32 d.d (1H, = CH_2 , J = 11.2, 1.2 Hz), 5.65 d.d (1H, = CH_2 , J = 18.4, 1.2 Hz), 6.69 m (3H,

H_{arom}), 6.95 d.d (1H, CH=, J = 11.2, 18.4 Hz), 7.19 m (5H, H_{arom}), 7.50 d (1H, H_{arom}, J = 7.2 Hz). ¹³C NMR spectrum, δ_C, ppm: 38.3 (Me), 54.5 (ArCH₂), 112.2 (=CH₂), 116.3 (2C, C_{arom}), 116.8 (C_{arom}), 126.1 (C⁶), 126.7 (C⁵), 127.0 (C⁴), 127.9 (C²), 129.2 (2C, C_{arom}), 133.7 (C³), 135.3 (CH=), 136.4 (C¹), 149.6 (C_{arom}). Mass spectrum, m/z (I_{rel} , %): 224 (15.3) [M + 1]⁺, 223 (90.8) [M]⁺, 222 (50.0), 209 (7.6), 208 (46.9), 194 (13.7), 193 (19.8), 192 (38.5), 191 (7.6), 180 (6.1), 179 (13.0), 132 (6.9), 120 (30.5), 118 (21.4), 117 (100), 116 (26.0), 115 (90.8), 107 (26.7), 106 (16.0), 105 (7.6), 104 (13.0), 91 (36.6), 89 (6.1), 78 (6.1), 77 (29.0), 65 (8.4), 51 (9.9), 39 (6.0). Found: m/z 224.14056 [M + H]⁺. C₁₆H₁₇N. Calculated: [M + H]⁺ 224.14392.

N,N'-Bis(2-ethenylbenzyl)-N,N'-dimethylhexane-1,6-diamine (V). A solution of 0.23 g (2 mmol) of hexane-1,6-diamine in 5 ml of dioxane was added to a solution of 1.11 g (4 mmol) of dibromide I in 10 ml of dioxane. The mixture was stirred for 1 h, 3.50 ml of 40% aqueous potassium carbonate was added, and the mixture was heated for 1 h at 70°C and left to stand for 42 h. The mixture was then filtered, the filtrate was added to 28.38 g (200 mmol) of methyl iodide, the mixture was stirred for 24 h at room temperature, the solvent was distilled off, the light yellow residue was dissolved in 35 ml of *tert*-butyl alcohol, 0.68 g (6.10 mmol) of potassium tert-butoxide was added, and the mixture was heated for 1 h under reflux. After cooling, the solvent was distilled off, the residue was treated with 50 ml of water and extracted with diethyl ether, the extract was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure, and the residue was purified by chromatography on silica gel using toluene-methanol-aqueous ammonia (10:0.08:0.05) as eluent. Yield 20%, light yellow oily substance. ¹H NMR spectrum, δ, ppm: 1.25 m (4H, 3'-H, 4'-H), 1.46 m (4H, 2'-H, 5'-H), 2.13 s (6H, Me), 2.32 m (4H, 1'-H, 6'-H), 3.45 s (4H, ArCH₂), 5.23 d.d $(2H_2 = CH_2, J = 11.0, 1.2 Hz), 5.60 d.d (2H_2 = CH_2, J = 11.0)$ 17.5, 1.2 Hz), 7.1-7.3 m (7H, H_{arom}, CH=), 7.47 m (2H, H_{arom}). ¹³C NMR spectrum, δ_C , ppm: 27.3 (C^{3'}, C^{4'}), 27.4 (C^{2'}, C^{5'}), 42.1 (Me), 57.7 (C^{1'}, C^{6'}), 60.6 (ArCH₂), 114.9 (=CH₂), 125.6 (C⁶), 127.2 (C⁵), 127.3 (C^4) , 130.4 (C^2) , 135.0 (C^3) , 136.4 (CH=), 137.8 (C^1) . Mass spectrum, *m/z* (*I*_{rel}, %): 260 (7.0), 259 (35.2), 161 (5.1), 160 (42.5), 146 (6.6), 144 (5.5), 118 (11.0), 117 (100), 116 (10.6), 115 (35.2), 112 (10.6), 91 (12.5). Found: m/z 377.29603 $[M + H]^+$. C₂₆H₃₆N₂. Calculated: $[M + H]^+$ 377.29513.

2-(Ethoxymethyl)styrene (VIa). Dibromide I, 5.0 g (18 mmol), was added to a solution of 0.99 g (43 mmol) of metallic sodium in 70 ml of ethanol. The mixture was heated for 1 h under reflux, the solvent was removed under reduced pressure, and the residue was treated with 250 ml of water and extracted with ethyl acetate. The extract was dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure, and the residue was distilled in a vacuum. Yield 54%, colorless transparent viscous liquid, bp 70–90°C (4 mm). ¹H NMR spectrum, δ , ppm: 1.30 t (3H, Me, J = 7.0 Hz), 3.60 g (2H, CH₂CH₃, J = 7.0 Hz), 4.60 s (2H, ArCH₂), 5.37 d.d (1H, =CH₂, J = 11.2, 1.6 Hz), 5.72 d.d (1H, =CH₂, J = 17.6, 1.6 Hz), 7.05–7.13 d.d (1H, CH=, J = 17.6, 11.2 Hz), 7.28-7.32 m (2H, 2H) H_{arom}), 7.40 d (1H, H_{arom} , J = 7.2 Hz), 7.59 d (1H, H_{arom} , J = 7.2 Hz). ¹³C NMR spectrum, δ_C , ppm: 15.3 (Me), 65.8 (CH₂CH₃), 70.8 (ArCH₂), 115.9 (=CH₂), 125.8 (C^6), 127.6 (C^5), 128.0 (C^4), 129.1 (C^2), 134.2 (C³), 135.8 (CH=), 137.1 (C¹). Mass spectrum, m/z $(I_{\rm rel}, \%)$: 162 (22.6) $[M]^+$, 134 (13.5), 133 (100), 119 (7.1), 118 (55.5), 117 (72.7), 116 (41.6), 115 (89.5), 106 (6.2), 105 (65.0), 103 (17.4), 102 (5.3), 91 (30.9), 89 (8.3), 79 (18.6), 78 (6.7), 77 (22.6), 65 (7.1), 63 (7.1), 51 (7.1). Found: m/z 163.11252 $[M + H]^+$. $C_{11}H_{14}O$. Calculated: $[M + H]^+$ 163.11229.

2-(Isopropoxymethyl)styrene (VIb) was synthesized in a similar way from propan-2-ol. Yield 85%, colorless viscous liquid, bp 100–110°C (7 mm). The spectral parameters of **VIb** were identical to those reported previously [7].

2-(Phenoxymethyl)styrene (VIc). A solution of 7.20 mmol of phenol in 5 ml of THF was added to a suspension of 0.32 g (7.90 mmol) of sodium hydride (60 wt %) in 20 ml of THF. The mixture was stirred for 5 min, a solution of 1.00 g (3.60 mmol) of dibromide I in 5 ml of THF was added, the mixture was stirred for 3 h at 50°C, 0.96 g (8.60 mmol) of potassium tertbutoxide was added, and the mixture was heated for 2 h under reflux. The mixture was cooled, poured into 100 ml of brine, and extracted with diethyl ether. The extract was washed with 10% aqueous sodium hydroxide, dried over anhydrous Na₂SO₄, filtered, and evaporated, and the residue was purified by chromatography on silica gel using chloroform–petroleum ether (1:20) as eluent. Yield 72%, light yellow transparent oily substance. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 5.13 s (2H, CH₂), 5.34 d.d (1H, =CH₂, *J* = 11.2, 1.6 Hz), 5.78 d.d (1H, =CH₂, J = 17.6, 1.6 Hz), 6.93-6.98 m (1H, H_{arom}), 6.99-7.06 m (4H, H_{arom}, CH=), 7.25-7.34 m (2H, H_{arom}), 7.37 t (1H, H_{arom} , J = 7.6 Hz),

7.45 d (1H, H_{arom}, J = 7.6 Hz), 7.63 d (1H, H_{arom}, J = 7.6 Hz). ¹³C NMR spectrum (DMSO- d_6), δ_C , ppm: 67.3 (ArCH₂), 114.6 (2C, C_{arom}), 116.4 (=CH₂), 120.7 (C_{arom}), 125.4 (C³), 127.7 (C⁶), 128.4 (C⁵), 129.4 (2C, C_{arom}), 129.4 (C⁴), 133.4 (C¹), 133.7 (CH=), 136.5 (C²), 158.2 (C_{arom}). Mass spectrum, m/z (I_{rel} , %): 210 (9.5) $[M]^+$, 118 (9.9), 117 (100.0), 116 (27.5), 115 (56.4), 91 (17.6), 65 (8.4), 39 (5.3). Found: m/z 211.12362 $[M + H]^+$. C₁₅H₁₄O. Calculated: $[M + H]^+$ 211.11229.

2-(4-tert-Butylphenoxymethyl)styrene (VId) was synthesized in a similar way from 4-tert-butylphenol. Yield 78%, light yellow transparent oily substance. ¹H NMR spectrum, δ , ppm: 1.32 s (9H, *t*-Bu), 5.08 s $(2H, CH_2), 5.34 \text{ d.d} (1H, =CH_2, J = 10.8, 1.6 \text{ Hz}),$ 5.71 d.d (1H, =CH₂, J = 17.2, 1.6 Hz), 6.95 m (2H, H_{arom}), 7.01 d.d (1H, CH=, J = 10.8, 17.2 Hz), 7.27– 7.38 m (4H, H_{arom}), 7.44 d (1H, H_{arom} , J = 7.2 Hz), 7.58 d (1H, H_{arom}, J = 7.2 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 31.5 (Me), 34.1 [C(CH₃)₃], 68.2 (ArCH₂), 114.2 (2C, C_{arom}), 116.6 (=CH₂), 125.9 (C⁶), 126.2 (2C, Carom), 127.9 (C⁵), 128.6 (C⁴), 129.2 (C³), 133.6 (C_{arom}), 133.7 (CH=), 137.1 (C¹), 143.8 (C²), 156.5 (C_{arom}). Mass spectrum, m/z (I_{rel} , %): 266 (15.4) $[M]^+$, 150 (6.6), 135 (27.8), 118 (10.3), 117 (100.0), 116 (23.8), 115 (39.6), 91 (16.8). Found: m/z 267.12143 $[M + H]^+$. C₁₉H₂₂O. Calculated: $[M + H]^+$ 267.12020.

2-(Methylsulfanylmethyl)styrene (VIII). Methyl iodide, 22.79 g (160.55 mmol), was added to 1.95 g (13.00 mmol) of isothiochroman (VII) [8], and the mixture was kept for 24 h. The precipitate was filtered off, washed with diethyl ether, and dried over Na₂SO₄, 40 ml of tert-butyl alcohol and 2.45 g (21.80 mmol) of potassium tert-butoxide were added, and the mixture was heated for 1 h under reflux. The mixture was cooled and evaporated under reduced pressure, the residue was treated with 150 ml of water and extracted with diethyl ether, the extract was dried over anhydrous Na₂SO₄, filtered, and evaporated, and the residue was purified by chromatography on silica gel using ethyl acetate-petroleum ether (1:5) as eluent. Yield 70%, light brown transparent oily substance. ¹H NMR spectrum, δ, ppm: 2.00 s (3H, Me), 3.70 s (2H, CH₂), 5.31 d.d (1H, = CH_2 , J = 12.0, 1.2 Hz), 5.64 d.d (1H, =CH₂, J = 20.0, 1.2 Hz), 7.02–7.10 d.d (1H, CH=, J = 12.0, 20.0 Hz), 7.10-7.30 m (3H, H_{arom}), 7.47 d (1H, H_{arom} , J = 8.0 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 15.2 (Me), 35.9 (CH₂S), 116.0 (=CH₂), 126.3 (C⁴), 127.5 $(C^{6}), 127.6 (C^{5}), 130.2 (C^{3}), 134.3 (CH=), 134.9 (C^{1}),$ 137.1 (C²). Mass spectrum, m/z (I_{rel} , %): 164 (43.7) [M]⁺, 149 (35.5), 134 (4.9), 118 (9.4), 117 (78.8), 116 (40.9), 115 (100.0), 91 (23.6), 89 (7.4), 65 (6.1), 63 (6.9). Found: m/z 165.07484 $[M + H]^+$. C₁₀H₁₂S. Calculated: $[M + H]^+$ 165.07325.

2-(Butylsulfanylmethyl)styrene (X). Potassium tert-butoxide, 1.61 g (14.40 mmol), was added to a solution of 4.00 g (14.40 mmol) of dibromide I in 120 ml of THF, and the mixture was stirred for 2.5 h at 35°C. Compound IX was formed; its structure was confirmed by mass spectrometry [9]. Butane-1-thiol, 2.21 g (24.50 mmol), and potassium carbonate, 3.38 g (24.50 mmol), were added, and the mixture was stirred for 24 h, poured into 50 ml of water, and 100 ml of brine was added. The organic phase was separated, the aqueous phase was extracted with ethyl acetate, the extract was combined with the organic phase, dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure, and the residue was purified by chromatography on silica gel using ethyl acetatepetroleum ether (1:5) as eluent. Yield 42%, light brown transparent oily substance. ¹H NMR spectrum, δ, ppm: 0.97 t (3H, Me, J = 7.3 Hz), 1.46 m (2H, CH₂CH₃), 1.62 m (2H, SCH₂CH₂), 2.51 t (2H, SCH₂, J = 7.3 Hz), 3.80 s (2H, ArCH₂), 5.39 d.d (1H, =CH₂) J = 11.0, 1.2 Hz), 5.73 d.d (1H, =CH₂, J = 17.4, 1.2 Hz), 7.1-7.3 m (4H, H_{arom}, CH=), 7.56 d (1H, H_{arom} , J = 7.0 Hz). ¹³C NMR spectrum, δ_C , ppm: 13.7 (Me), 22.1 (CH₂CH₃), 31.5 (SCH₂CH₂), 31.6 (SCH₂), 34.0 (ArCH₂), 116.0 (=CH₂), 126.2 (C⁴), 127.4 (C⁶), 127.6 (C⁵), 130.1 (C³), 134.2 (CH=), 135.5 (C¹), 136.9 (C²). Mass spectrum, m/z (I_{rel} , %): 206 (22.6) [M]⁺, 151 (5.1), 149 (62.0), 135 (19.7), 134 (6.6), 118 (23.4), 117 (100), 116 (42.0), 115 (97.4), 91 (24.5), 89 (6.9), 65 (6.6), 39 (6.2). Found: m/z 207.11959 $[M + H]^+$. $C_{13}H_{18}S$. Calculated: $[M + H]^+$ 207.12020.

N,*N*-Bis(2-ethenylbenzyl)methanamine (XI). A solution of 1.67 g (24.90 mmol) of potassium hydroxide in 50 ml of water was added to a mixture of 1.98 g (28.60 mmol) of methylamine hydrochloride and 50 ml of isopropyl alcohol, the mixture was stirred for 1 h, 1.0 g (3.6 mmol) of compound IX was added, and the mixture was stirred for 24 h at room temperature and for 24 h at 50°C. The solvent was distilled off, and the residue was purified by chromatography on

silica gel using methylene chloride-petroleum ether (1:15) as eluent. Yield 57%, light yellow transparent oily substance. ¹H NMR spectrum, δ , ppm: 2.13 s (3H, Me), 3.53 s (4H, ArCH₂), 5.19 d.d (2H, =CH₂, J =11.0, 1.4 Hz), 5.60 d.d (2H, =CH₂, J = 17.5, 1.4 Hz), 7.03–7.13 d.d (2H, CH=, J = 11.0, 17.5 Hz), 7.51 m (2H, H_{arom}), 7.16–7.28 m (6H, H_{arom}). ¹³C NMR spectrum, δ_C, ppm: 42.1 (Me), 60.2 (ArCH₂), 114.8 (=CH₂), 125.5 (C⁶), 127.4 (C⁵), 127.5 (C⁴), 130.8 (C²), 134.9 (C^3), 136.1 (CH=), 137.8 (C^1). Mass spectrum, m/z ($I_{\rm rel}$, %): 263 (5.3) [M]⁺, 262 (14.7), 248 (13.9), 220 (7.7), 160 (7.3), 159 (6.6), 158 (53.5), 148 (7.7), 147 (8.8), 146 (59.3), 145 (19.0), 144 (65.2), 132 (11.7), 131 (21.2), 130 (11.0), 119 (13.2), 118 (25.6), 117 (100.0), 116 (35.9), 115 (83.5), 105 (7.0), 103 (5.5), 91 (33.3), 89 (5.3), 77 (7.0), 65 (6.2), 42 (7.3), 39 (5.1). Found: m/z 264.17148 $[M + H]^+$. C₁₉H₂₁N. Calculated: $[M + H]^+$ 264.17522.

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