Full Articles

Azomethine ylides derived from dichlorocarbene and *O*-acylsalicylaldehyde anils in the synthesis of 2,5-epoxy-2,3,4,5-tetrahydro-1,4-benzoxazepin-2-ones and 2-aminoethanols*

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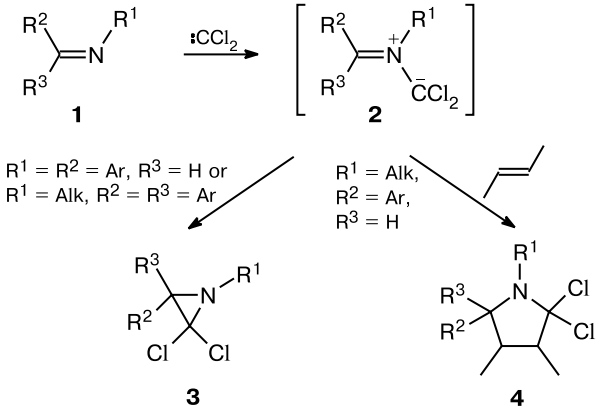
Iminiodichloromethanides generated by the reaction of *O*-acylsalicylaldehyde anils with dichlorocarbene undergo regioselective intramolecular 1,3-dipolar cycloaddition to the ester carbonyl group to give 2,5-epoxy-2,3,4,5-tetrahydro-1,4-benzoxazepin-2-ones. These compounds are expedient precursors for the synthesis of *N*-(2-hydroxybenzyl)ethanolamines.

Key words: dihalocarbenes, azomethine ylides, cycloaddition, aminoethanols.

The reaction of dichlorocarbene with Schiff bases **1** is known as a procedure for the generation of unstable azomethine ylides, *viz.*, iminiodichloromethanides **2**.[1—3] These reactive intermediates are of interest from the synthetic standpoint because they can undergo cyclization to form aziridines **3**, which are useful intermediates for the synthesis of α-chloroimidoyl chlorides, α-chloroamides, ketene imines, and some other compounds, and can also be involved in 1,3-dipolar cycloaddition with electron-deficient alkenes to form pyrrolidine derivatives **4** (Scheme 1).[4—6]

Scheme 1



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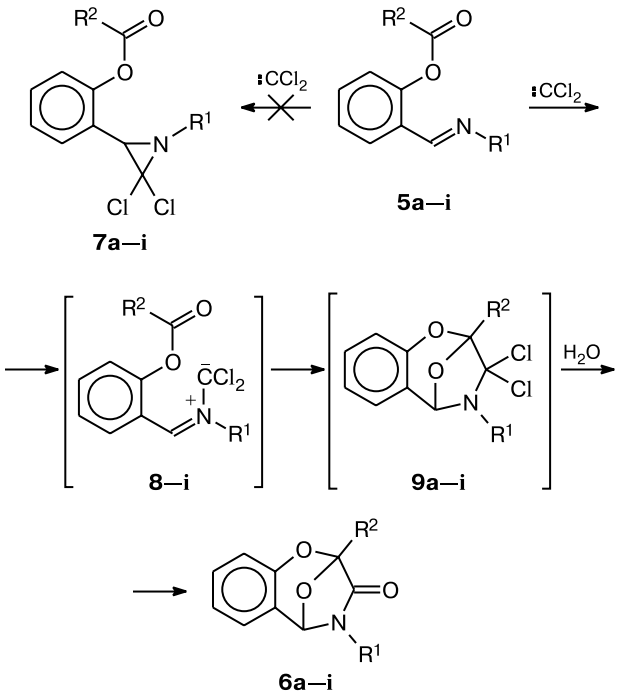
The transformation pathway of iminiodichloromethanides depends primarily on the nature of substituents in the ylide fragment (see Scheme 1). Ylides generated by the reaction of dichlorocarbene with benzaldehyde *N*-alkylimines are readily involved in intermolecular 1,3-dipolar cycloaddition, whereas azomethine ylides generated from *N*-benzylideneanilines or benzophenone *N*-alkyl- and *N*-arylimines undergo predominantly 1,3-cyclization to give aziridines. For example, the reaction of *N*-benzylideneaniline with dichlorocarbene in the presence of one of the most highly reactive dipolarophiles, *viz.*, dimethyl acetylenedicarboxylate, afforded the 1,3-dipolar cycloaddition product, *viz.*, the pyrrole derivative, as an impurity (2%), whereas the 1,3-cyclization product, *viz.*, dichloroaziridine, was obtained as the major product (69%).[3] In spite of this fact, *N*-aryl-substituted iminiodichloromethanides can be subjected to intramolecular 1,3-dipolar cycloaddition. Recently,[7] we have demonstrated that the ester carbonyl group can serve as an efficient intramolecular trap for *gem*-difluoro-substituted azomethine ylides. In the present study, we studied intramolecular 1,3-dipolar cycloaddition of *N*-aryl-substituted iminiodichloromethanides to ester carbonyl and demonstrated that the products of this reaction can be used in the synthesis of 2-aminoethanols containing the phenol fragments.

Although *N*-benzylideneanilines, including *ortho*-substituted derivatives,[8] generally react with dichlorocarbene to form aziridines, the reactions of *ortho*-acyloxy-substituted benzaldehyde anils **5a—g** under conditions of generation of dichlorocarbene give 2,5-epoxy-1,4-benzoxazepin-3-ones **6a—g** in good yields (Scheme 2). The method for generating dichlorocarbene has no effect on the reaction pathway and influences only slightly the yields of the final products. Neither decomposition of chloroform under alkaline conditions ($CHCl_3$/KOH/$BnEt_3NCl$) nor thermocatalytic decomposition of sodium trichloroacetate (Cl_3CCO_2Na/$BnEt_3NCl$/$CHCl_3$) afforded even traces of *gem*-dichloroaziridines **7a—g**. The yields of compounds **6a—g** and the reaction conditions are given in Table 1.

The sequence of transformations (see Scheme 2) giving rise to 2,5-epoxybenzoxazepinones **6a—g** involves the generation of iminiodichloromethanides **8a—g** and intramolecular 1,3-dipolar cycloaddition at the C=O bond of the ester group to form dichlorides **9a—g** followed by their hydrolysis. Cycloaddition of the ylide fragment at the C=O group occurs regioselectively to give exclusively the bridged cycloadduct.

Under alkaline conditions of generation of dichlorocarbene, dichloride **9** is hydrolyzed, apparently, directly under the action of KOH, whereas in the case of thermal generation of $:CCl_2$ from Cl_3CCO_2Na, the resulting dichloride is hydrolyzed in the course of chromatography. In no case was dichloride **9** isolated or detected.

Scheme 2



	R^1	R^2		R^1	R^2
a	Ph	4-$MeOC_6H_4$	**e**	4-BrC_6H_4	Ph
b	4-BrC_6H_4	4-$MeOC_6H_4$	**f**	4-BrC_6H_4	4-NCC_6H_4
c	Ph	*trans*-PhCH=CPh	**g**	Ph	2-furyl
d	Ph	2,4-$Cl_2C_6H_3$	**i**	CH_2SiMe_3	Ph

The compositions and structures of compounds **6a—g** were established based on the data from elemental analysis and the results of ^1H and ^{13}C NMR and IR spectroscopy. The IR spectra of compounds **6a—g** have an absorption band at 1740—1750 cm^{-1} characteristic of stretching vibrations of the carbonyl group of the oxazolidin-4-one fragment.[9] The ^1H NMR spectra show

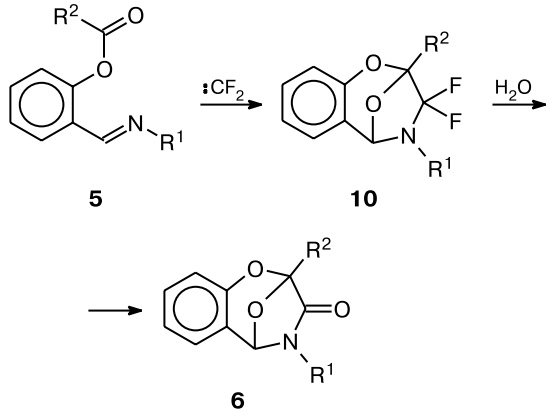
Table 1. Conditions and yields of the products of the reaction of dichlorocarbene with imines **5a—g**

Imine	R^1	R^2	Method*	Product	Yield (%)
5a	Ph	4-$MeOC_6H_4$	*A*	**6a**	82
5a	Ph	4-$MeOC_6H_4$	*B*	**6a**	92
5b	4-BrC_6H_4	4-$MeOC_6H_4$	*A*	**6b**	97
5c	Ph	*trans*-PhCH=CPh	*A*	**6c**	100
5d	Ph	2,4-$Cl_2C_6H_3$	*A*	**6d**	56
5e	4-BrC_6H_4	Ph	*B*	**6e**	60
5f	4-BrC_6H_4	4-NCC_6H_4	*B*	**6f**	74
5g	Ph	2-furyl	*B*	**6g**	47

* The method of generation of CCl_2, method *A*: $CHCl_3$/KOH/$BnEt_3NCl$/20 °C; method *B*: Cl_3CCO_2Na/$BnEt_3NCl$/$CHCl_3$/60 °C.

a singlet at δ 6.3—6.5 corresponding to the H(5) proton. The presence of the acetal and hemiaminal C atoms of the bicyclic fragment in molecules **6a—g** is confirmed by the fact that the ^{13}C NMR spectra show two signals at δ 98—100 and 83—87. The spectroscopic data for compounds **6a—g** are consistent with the characteristics of the only known compound of this series, *viz.*, **6i**, which we have synthesized earlier[7] by the reaction of *O*-benzoylsalicylaldehyde *N*-trimethylsilylmethylimine with difluorocarbene. Anils **5** react with difluorocarbene to give stable difluoro derivatives **10**, which are hydrolyzed upon prolonged storage on silica gel to give oxo derivatives **6** (Scheme 3). However, this hydrolysis of difluorides **10** not always proceeds unambiguously and can lead to destruction of the bicyclic system.[7]

Scheme 3



Taking into account that the reactions with difluorocarbene are more laborious than the reactions with $:CCl_2$ and require more expensive reagents, the above-described procedure for the synthesis of epoxybenzoxazepinones **6a—g** (see Scheme 2) is a method of choice.

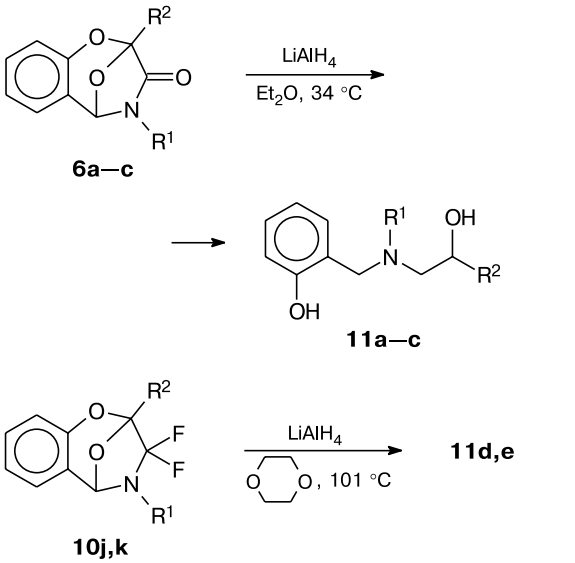
Compounds **6** may also be of interest as intermediates for the synthesis of biologically active compounds. Reduction of epoxybenzoxazepinones **6a—c** with lithium aluminum hydride in diethyl ether affords the corresponding amino alcohols **11a—c** (Scheme 4). We also examined an alternative procedure for the preparation of compounds **11** by reduction of difluorides **10**, which gave compounds **11** under much more drastic conditions, for example, under the action of $LiAlH_4$ in refluxing dioxane (see Scheme 4, Table 2).

Table 2. Yields of products of reduction of compounds **6** and **10** with $LiAlH_4$

Compound	Product	R^1	R^2	Yield (%)
6a	**11a**	Ph	4-$MeOC_6H_4$	77
6b	**11b**	4-BrC_6H_4	4-$MeOC_6H_4$	47*
6c	**11c**	Ph	*trans*-PhCH=CPh	68
10j	**11d**	Ph	Ph	65
10k	**11e**	$(4\text{-}ClC_6H_4)_2CH$	Ph	70

* The conversion of imine **6b** was 75%.

Scheme 4



6	R^1	R^2	**10**, **11**	R^1	R^2
a	Ph	4-$MeOC_6H_4$	**10j**, **11d**	Ph	Ph
b	4-BrC_6H_4	4-$MeOC_6H_4$	**10k**, **11e**	$(4\text{-}ClC_6H_4)_2CH$	Ph
c	Ph	*trans*-PhCH=CPh			

The structures of ethanolamines **11a—e** were established by spectroscopy. The IR spectra show two characteristic absorption bands at 3600 and 3300 cm^{-1}, which confirm the presence of two different hydroxy groups in the molecules. The ethanolamine fragment is characterized by a three-spin ABX system at δ 4.25—3.43 and 5.87—5.02. The mass spectra of compounds **11a,b,e** have molecular ion peaks.

To summarize, 1,3-cyclization of azomethine ylides generated from *O*-acylsalicylaldehyde anils and dichlorocarbene is completely suppressed by intramolecular 1,3-dipolar cycloaddition to the ester carbonyl group. The cycloaddition occurs regioselectively to form the bridged regioisomer. 2,5-Epoxy-2,3,4,5-tetrahydro-1,4-benzoxazepin-2-ones synthesized in the present study are convenient intermediates for the synthesis of ethanolamines containing the phenol fragments.

Experimental

The IR spectra were recorded on a UR-20 (Carl Zeiss) instrument in $CHCl_3$; the thickness of the absorbing layer was 400 μm. The ^1H and ^{13}C NMR spectra were measured on a

Bruker DPX-300 instrument (300 MHz for ^{1}H and 75 MHz for ^{13}C). The mass spectra were obtained on an HP-59970C instrument (EI, 70 eV). Elemental analysis was carried out on an HP-185B C,H,N-analyzer. The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. The course of the reactions was monitored by TLC on Silufol-254 plates. The reaction mixtures were separated by column chromatography on LS 5/40 silica gel (Chemapol).

O-Acylsalicylaldehydes were synthesized by acylation of salicylaldehyde with the corresponding acid chlorides in dry DMF in the presence of anhydrous K_2CO_3. Imines were prepared by condensation of aldehydes with amines in ethanol.[10] Sodium trichloroacetate was dried over P_2O_5 for one week. The reactions were carried out with the use of chloroform, which was purified from the stabilizer and distilled over P_2O_5.

Reactions of imines with dichlorocarbene (general procedure). ***A.*** Powdered KOH (1.1—1.7 g, 20—30 mmol) was added portionwise with vigorous stirring to the reaction mixture containing imine (1.4 mmol) and benzyltriethylammonium chloride (0.16 g, 0.7 mmol) in dry $CHCl_3$ (40 mL) at 20 °C for 1—2 h, the composition of the reaction mixture being monitored by TLC. Then hexane (10 mL) was added to the reaction mixture, the mixture was filtered through a layer of silica gel (5 mm), the solvent was removed *in vacuo*, and the residue was recrystallized.

B. Sodium trichloroacetate (3.5 g, 20 mmol) was added portionwise with stirring and refluxing to the reaction mixture containing imine (1.4 mmol) and benzyltriethylammonium chloride (0.16 g, 0.7 mmol) in dry $CHCl_3$ (40 mL) for 1 h. The reaction mixture was refluxed for ~1 h, the composition of the reaction mixture being monitored by TLC. Then the mixture was cooled and filtered. The solvent was distilled off *in vacuo* and the residue was purified by column chromatography (a hexane—ethyl acetate mixture as the eluent) followed by recrystallization of the product.

2,5-Epoxy-2-(4-methoxyphenyl)-4-phenyl-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6a). M.p. 164—165 °C (from hexane—AcOEt). Found (%): C, 73.64; H, 4.72; N, 3.86. $C_{22}H_{17}NO_4$. Calculated (%): C, 73.53; H, 4.77; N, 3.90. IR, ν/cm^{-1}: 1740 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, OMe); 6.46 (s, 1 H, H(5)); 6.93—7.87 (m, 13 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 55.0 (OMe); 86.4 (C(5)); 101.0 (C(2)); 113.5, 117.0, 119.6, 120.4, 121.7, 124.0, 124.7, 125.5, 127.7, 129.1, 130.7, 134.9, 151.3, 160.7 (Ar); 164.6 (C=O).

4-(4-Bromophenyl)-2,5-epoxy-2-(4-methoxyphenyl)-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6b). M.p. 171—172 °C (from hexane—AcOEt). Found (%): C, 60.24; H, 3.78; N, 3.08. $C_{22}H_{16}BrNO_4$. Calculated (%): C, 60.29; H, 3.68; N, 3.20. IR, ν/cm^{-1}: 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, OMe); 6.42 (s, 1 H, H(5)); 6.93—7.84 (m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 55.0 (OMe); 86.2 (C(5)); 100.8 (C(2)); 113.5, 117.1, 118.6, 120.46, 121.0, 121.3, 123.9, 124.4, 127.6, 130.9, 132.1, 133.9, 151.2, 160.8 (Ar); 164.6 (C=O).

(*E*)-2-(1,2-Diphenylvinyl)-2,5-epoxy-4-phenyl-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6c). M.p. 204—205 °C (from hexane—AcOEt). Found (%): C, 80.78; H, 5.00; N, 3.27. $C_{29}H_{21}NO_3$. Calculated (%): C, 80.72; H, 4.91; N, 3.25. IR, ν/cm^{-1}: 1740 (C=O). ^{1}H NMR ($CDCl_3$), δ: 6.31 (s, 1 H, H(5)); 6.91—7.52 (m, 20 H, Ar); 7.67 (s, 1 H, PhCH=). ^{13}C NMR (DMSO-d_6), δ: 82.9 (C(5)); 99.0 (C(2)); 114.4, 116.7, 118.8, 120.0, 122.9, 123.3, 125.8, 125.9, 126.4, 127.1, 127.3, 127.8, 128.8, 130.6, 130.8, 132.3, 132.4, 132.8, 148.4 (Ar, C_{vinyl}); 161.6 (C=O).

2-(2,4-Dichlorophenyl)-2,5-epoxy-4-phenyl-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6d). M.p. 220—222 °C (from hexane—AcOEt). Found (%): C, 63.34; H, 3.36; N, 3.44. $C_{21}H_{13}Cl_2NO_3$. Calculated (%): C, 63.34; H, 3.29; N, 3.52. IR, ν/cm^{-1}: 1750 (C=O). ^{1}H NMR ($CDCl_3$), δ: 6.48 (s, 1 H, H(5)); 6.98—8.18 (m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 83.8 (C(5)); 98.0 (C(2)), 114.7, 117.0, 119.4, 120.4, 122.9, 123.6, 125.4, 126.9, 127.4, 128.3, 128.7, 129.1, 131.5, 132.7, 134.4, 148.0 (Ar); 161.2 (C=O).

4-(4-Bromophenyl)-2,5-epoxy-2-phenyl-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6e). M.p. 186—188 °C (from hexane—AcOEt). Found (%): C, 61.83; H, 3.45; N, 3.34. $C_{21}H_{14}BrNO_3$. Calculated (%): C, 61.78; H, 3.46; N, 3.43. IR, ν/cm^{-1}: 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 6.45 (s, 1 H, H(5)); 6.94—7.93 (m, 13 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 86.3 (C(5)); 100.8 (C(2)); 117.1, 118.7, 120.7, 121.0, 121.4, 123.9, 126.1, 128.1, 130.0, 130.9, 132.1, 132.2, 133.9, 151.1 (Ar); 164.4 (C=O).

4-(4-Bromophenyl)-2-(4-cyanophenyl)-2,5-epoxy-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6f). M.p. 227—228 °C (from hexane—AcOEt). Found (%): C, 61.16; H, 3.09; N, 6.56. $C_{22}H_{13}BrN_2O_3$. Calculated (%): C, 60.99; H, 3.02; N, 6.47. IR, ν/cm^{-1}: 1745 (C=O); 2240 (C≡N). ^{1}H NMR ($CDCl_3$), δ: 6.49 (s, 1 H, H(5)); 6.97—8.03 (m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 86.6 (C(5)); 100.0 (C(2)); 113.9, 117.1, 117.9, 119.1, 121.15, 121.17, 124.1, 127.1, 131.2, 131.9, 132.3, 133.5, 136.9, 150.7 (Ar, C=N); 163.7 (C=O).

2,5-Epoxy-2-(2-furyl)-4-phenyl-2,3,4,5-tetrahydro-1,4-benzoxazepin-3-one (6g). M.p. 179—181 °C (from EtOH). Found (%): C, 71.42; H, 4.12; N, 4.21. $C_{19}H_{13}NO_4$. Calculated (%): C, 71.47; H, 4.10; N, 4.39. IR, ν/cm^{-1}: 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 6.43 (s, 1 H, H(5)); 6.55—6.57 (m, 1 H, H_{furyl}); 6.94—7.09 (m, 3 H, Ar); 7.23—7.27 (m, 1 H, H_{furyl}); 7.32—7.63 (m, 6 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 86.6 (C(5)); 97.6 (C(2)); 110.3, 112.1 (Ar); 117.0 ($C(3)_{furyl}$); 119.8 ($C(4)_{furyl}$); 120.8, 121.7, 124.1, 125.8, 129.1, 130.8, 134.6 (Ar); 144.3 ($C(5)_{furyl}$); 144.9 (Ar); 150.9 ($C(2)_{furyl}$); 162.8 (C=O).

Amino alcohols 11a—c (general procedure). Lithium aluminum hydride (0.038 g, 1 mmol) was added to a solution of compound **6a—c** (0.3 mmol) in anhydrous Et_2O (30 mL). The reaction mixture was refluxed for 2 h and cooled. Water (0.04 mL), a 15% NaOH solution (0.04 mL), and water (0.12 mL) were successively added to the reaction mixture. The precipitate that formed was filtered off. The filtrate was dried with $MgSO_4$, Et_2O was removed *in vacuo*, and the residue was recrystallized from a hexane—diethyl ether mixture.

2-{*N*-[2-Hydroxy-2-(4-methoxyphenyl)ethyl]anilinomethyl}phenol (11a). M.p. 133—135 °C (from hexane—diethyl ether). Found (%): C, 75.99; H, 6.61; N, 3.86. $C_{22}H_{23}NO_3$. Calculated (%): C, 75.62; H, 6.63; N, 4.01. IR, ν/cm^{-1}: 3300 br (OH); 3590 (OH). ^{1}H NMR ($CDCl_3$), δ: 3.39, 3.47, and 4.94 (ABX system, 3 H, CH_2, C<u>H</u>OH, J_{AB} = 14.5 Hz, J_{AX} = 10.7 Hz, J_{BX} = 4.9 Hz); 3.82 (s, 3 H, OMe); 4.47 and 4.56 (both m, AB system, 2 H, CH_2, J = 14.5 Hz); 6.78—7.33 (m, 13 H, Ar); 8.79 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 55.0 (OMe); 55.6 and 61.6 (both CH_2); 71.4 (CHOH); 113.7, 116.1, 119.1, 119.6, 121.6, 122.3, 126.9, 128.5, 128.8, 128.9, 133.8, 148.9, 156.1, 159.1 (Ar). MS, m/z (I_{rel} (%)): 349 $[M]^+$ (2), 243 (9), 212 (40), 137 (11), 107 $[HOC_6H_4CH_2]^+$ (44), 106 (100), 77 $[Ph]^+$ (17).

2-{4-Bromo-*N*-[2-hydroxy-2-(4-methoxyphenyl)ethyl]anilinomethyl}phenol (11b). M.p. 135—137 °C (from hexane—diethyl ether). IR, ν/cm^{-1}: 3320 br (OH); 3600 (OH). ^{1}H NMR ($CDCl_3$), δ: 3.38, 3.46, and 4.95 (ABX system, 3 H, CH_2, CHOH, J_{AB} = 14.6 Hz, J_{AX} = 9.9 Hz, J_{BX} = 4.7 Hz); 3.82 (s, 3 H, MeO); 4.45 and 4.54 (AB system, 2 H, CH_2, J = 15.4 Hz); 6.75—7.37 (m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 54.6 (CH_2); 55.0 (MeO); 61.6 (CH_2); 71.4 (CHOH); 113.3, 113.8, 116.1, 119.8, 119.9, 122.1, 126.9, 128.6, 128.8, 131.7, 133.5, 148.0, 155.6, 159.2 (Ar). MS, m/z (I_{rel} (%)): 429 (7), 427 $[M]^+$ (7), 321 (15), 292 (38), 246 (2), 212 (11), 184 (96), 137 (83), 107 $[HOC_6H_4CH_2]^+$ (100), 77 (46), 51 (11).

(*Z*)-2-{*N*-[2-Hydroxy-2-(1,2-diphenylvinyl)ethyl]anilinomethyl}phenol (11c). M.p. 156—158 °C (from hexane—diethyl ether). Found (%): C, 82.16; H, 6.50; N, 3.30. $C_{29}H_{27}NO_2$. Calculated (%): C, 82.63; H, 6.46; N, 3.32. IR, ν/cm^{-1}: 3300 br (OH); 3590 (OH). ^{1}H NMR ($CDCl_3$), δ: 3.25, 3.42, and 4.87 (ABX system, 3 H, CH_2, CHOH, J_{AB} = 12.5 Hz, J_{AX} = 9.1 Hz, J_{BX} = 0 Hz); 4.47 and 4.53 (AB system, 2 H, CH_2, J = 14.6 Hz); 6.81—7.34 (m, 20 H, Ar, H_{vinyl}). ^{13}C NMR ($CDCl_3$), δ: 55.6 and 59.2 (both CH_2); 74.2 (CHOH); 116.1, 118.9, 119.6, 121.4, 122.4, 126.5, 126.6, 127.3, 127.6, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 135.9, 137.8, 142.3, 148.8, 156.0 (Ar, C_{vinyl}).

Amino alcohols 11d,e (general procedure). Lithium aluminum hydride (0.038 g, 1 mmol) was added to a solution of difluoride **10j,k** [7] (0.3 mmol) in anhydrous dioxane (30 mL). The reaction mixture was refluxed for 2 h and cooled. Then diethyl ether (30 mL), water (0.04 mL), a 15% NaOH solution (0.04 mL), and water (0.12 mL) were successively added. The precipitate that formed was filtered off and the filtrate was dried with $MgSO_4$. After evaporation of the solvent, the dry residue was recrystallized from a hexane—diethyl ether mixture.

2-[*N*-(2-Hydroxy-2-phenylethyl)anilinomethyl]phenol (11d). M.p. 102—103 °C (from hexane—diethyl ether). Found (%): C, 79.04; H, 6.70; N, 4.65. $C_{21}H_{21}NO_2$. Calculated (%): C, 78.97; H, 6.63; N, 4.39. IR, ν/cm^{-1}: 3300 br (OH); 3600 (OH). ^{1}H NMR ($CDCl_3$), δ: 3.43, 3.48, and 4.99 (ABX system, 3 H, CH_2, CHOH, J_{AB} = 14.5 Hz, J_{AX} = 12.0 Hz, J_{BX} = 8.0 Hz); 4.48 and 4.58 (AB system, 2 H, CH_2, J = 14.5 Hz); 6.77—7.39 (m, 15 H, Ar), 8.84 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 55.4 and 61.7 (both CH_2); 71.8 (CHOH); 116.0, 119.0, 119.6, 121.6, 122.3, 125.6, 127.7, 128.3, 128.4, 128.8, 128.9, 141.6, 148.9, 155.9 (Ar).

2-{*N*-[Bis(4-chlorophenyl)methyl]-*N*-(2-hydroxy-2-phenylethyl)aminomethyl}phenol (11e). M.p. 149—151 °C (from hexane—diethyl ether). Found (%): C, 70.76; H, 5.65; N, 2.77. $C_{28}H_{25}ClNO_2$. Calculated (%): C, 70.30; H, 5.27; N, 2.93. IR, ν/cm^{-1}: 3300 br (OH); 3600 (OH). ^{1}H NMR ($CDCl_3$), δ: 2.52 (dd, 1 H, J = 13.1 and 2.9 Hz); 3.05 (dd, 1 H, CH_2, J = 13.1 and J = 10.2 Hz); 3.71 and 4.20 (both d, 1 H each, CH_2, J = 13.8 Hz); 5.02 (dd, 1 H, CHOH, J = 10.2 and J = 2.9 Hz); 5.09 (s, 1 H, $CHAr_2$); 6.77—7.34 (m, 17 H, Ar); 10.2 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 53.7 and 56.9 (both CH_2); 66.0 (CHOH); 71.5 ($CHAr_2$); 116.1, 119.3, 121.6, 125.6, 127.8, 128.2, 128.3, 128.4, 128.8, 129.1, 130.0, 130.8, 132.8, 133.4, 136.0, 137.6, 142.1, 157.0 (Ar). MS, m/z (I_{rel} (%)): 481 (2), 479 (18), 477 $[M]^+$ (21), 370 (17), 264 (10), 239 (10), 237 (65), 235 $[(4\text{-}ClC_6H_4)_2CH]^+$ (100), 201 (19), 165 (39), 107 $[HOC_6H_4CH_2]^+$ (15), 79 (9).

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