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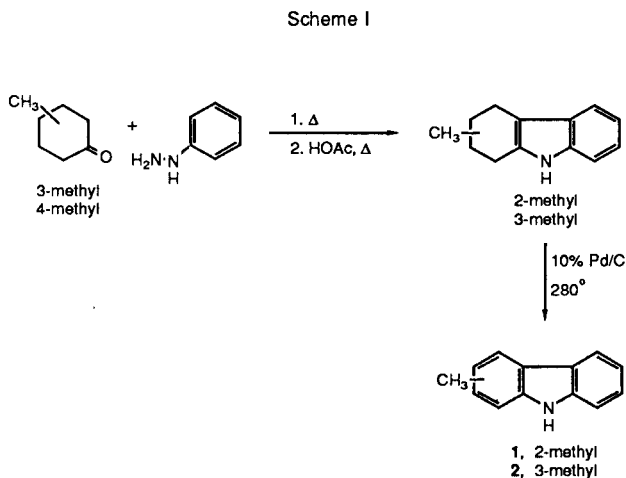
Dedicated to Professor Ernest Campaigne on the occasion of his 75th birthday

The synthesis of naphthylethylcarbazole derivatives is described.

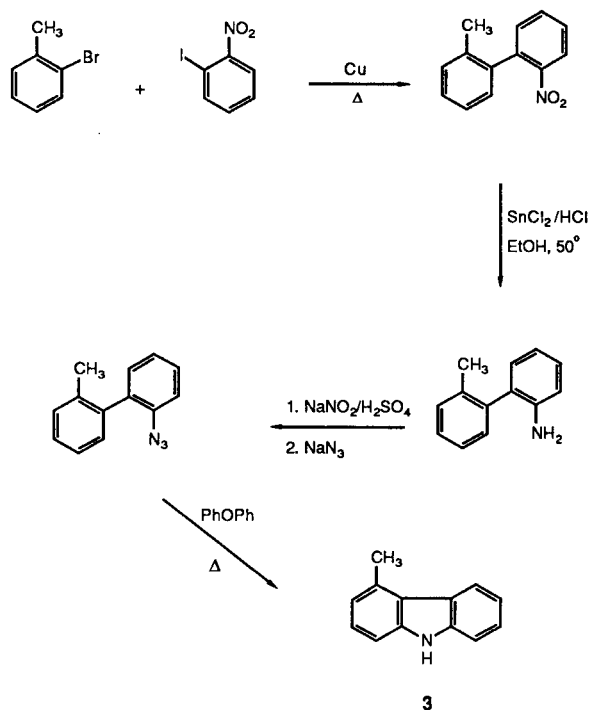
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In our continuing study of the components of coal-derived products we have turned our attention to the synthesis of nitrogen heterocycles which are coupled to a naphthalene ring system with a $-\text{CH}_2\text{CH}_2-$ bridge. In this paper we report the synthesis of naphthylethylcarbazoles since it has long been known that carbazole derivatives are present in coal-derived products [1] [2].

The key intermediates in this investigation are carbazolecarboxaldehydes. In a search of the literature, Plant *et al* [3] demonstrated that all four carbazolecarboxaldehydes could be obtained by decomposition of the corresponding *p*-toluenesulfonylhydrazidocarbonylcarbazoles in 7.5 to 67% yields, which made the synthesis of the 2- and 3-carbazolecarboxaldehydes impractical. In view of the photobromination of 3-methyl-9-benzenesulfonylcarbazole [4], a mixture of 80% of 3-bromomethyl- and 10% of 3-dibromomethyl-9-benzenesulfonylcarbazole was obtained although a 1:1 ratio of protected carbazole and bromine in carbon tetrachloride was applied. This suggests to us that the bromination with a 1:2 ratio of protected carbazoles and *N*-bromosuccinimide (NBS) would readily provide the dibromomethyl derivatives, which upon hydrolysis would form the required key intermediates, *e.g.*, carbazolecar-



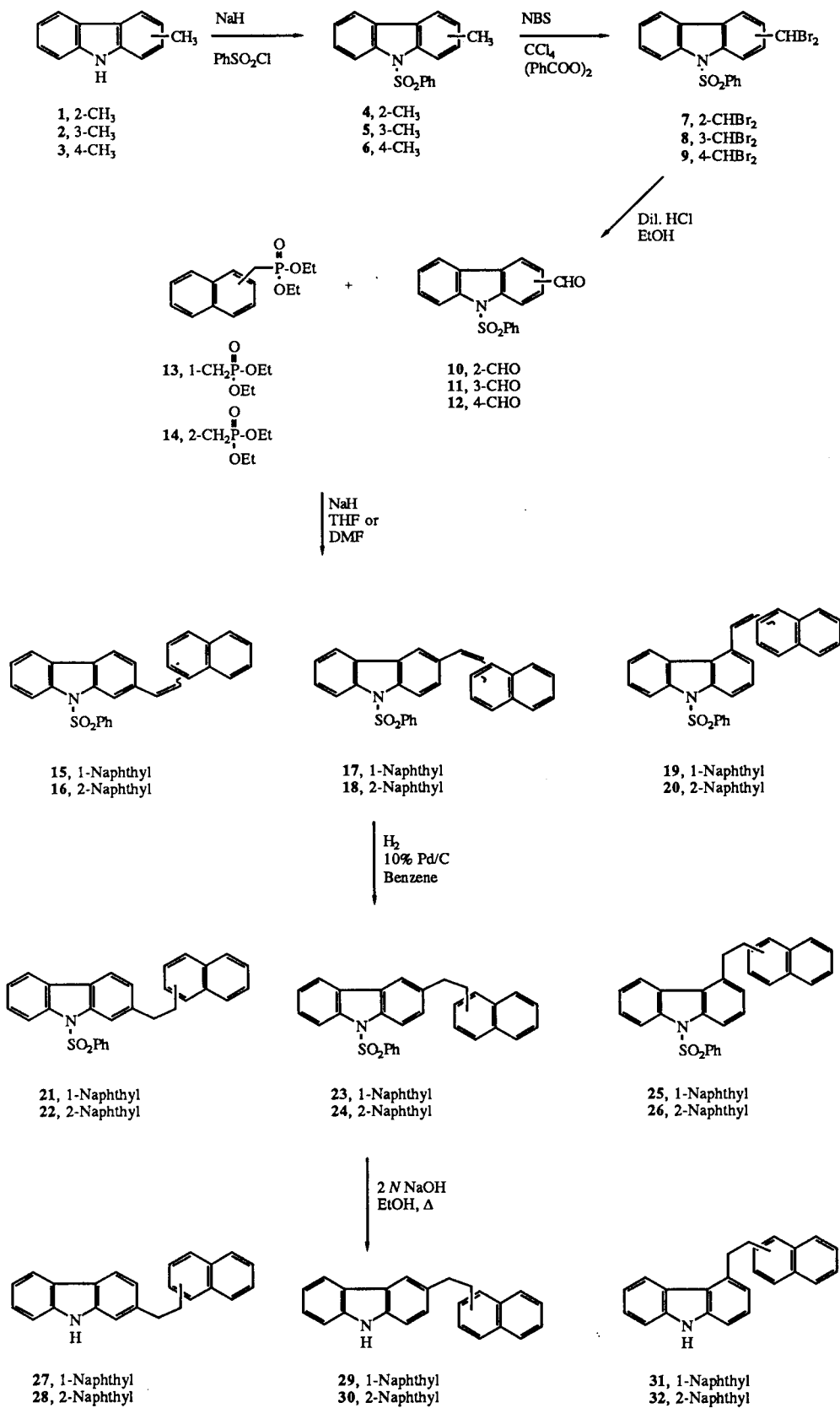
Scheme II



boxaldehydes.

Thus, the 2- and 3-methylcarbazoles (1) and (2) were obtained in excellent yields *via* a process analogous to the Fischer indole synthesis [5], followed by a dehydrogenation of the tetrahydrocarbazoles by fusion at $270\text{--}290^\circ$ in the presence of 10% Pd-C as the catalyst, which is illustrated in Scheme I. On the other hand, the thermal decomposition of *o*-azidobiphenyl and its substituted derivatives proved to be a convenient synthesis of carbazole and its corresponding derivatives [6] [7]. Therefore, 4-methylcarbazole (3) [8] was synthesized by the pyrolysis of 2-azido-2'-methylbiphenyl as shown in Scheme II. By modifying Goetz's method [4], 2-, 3- and 4-methylcarbazole (1), (2) and (3) were converted to the corresponding 9-benzenesulfonyl derivatives 4, 5 and 6 in 91, 94 and 87%

Scheme III



yields, respectively, by reacting the methylcarbazoles with benzenesulfonyl chloride using sodium hydride as the condensing agent (Scheme III). Dibromination of **4**, **5** and **6** with 2 moles of NBS in carbon tetrachloride in the presence of benzoyl peroxide as the initiator, the corresponding dibromoethylcarbazoles **7**, **8** and **9** were isolated in 85, 82 and 89% yields, respectively. Hydrolysis of compounds **7**, **8** and **9** with dilute hydrochloric acid and ethanol provided the key intermediates, 9-benzenesulfonyl-2-, 3-, and 4-carbazolecarboxaldehydes **10**, **11** and **12** in excellent yields. Condensations of **10**, **11** and **12** with diethyl 1- and 2-naphthylmethylphosphonates **13** and **14** respectively, under Wadsworth-Emmons conditions resulted in 40-75% yields of ethenes **15-20**, which upon catalytic hydrogenation in the presence of 10% Pd-C under atmospheric pressure gave the corresponding 1,2-diarylethanes **21-26** in 58-90% yields. Deprotection of **21-26** with dilute sodium hydroxide solution and ethanol under reflux provided naphthylethylcarbazoles **27-32** in 68-85% yields. It is worthwhile to note that compounds **21**, **23**, **26**, **27**, **29** and **32** exhibited a complex splitting pattern centered at δ 3.3 for the ethyl linkage in their $^1\text{H-nmr}$ spectra, whereas **22**, **24**, **25**, **28**, **30** and **31** showed only a singlet attributed to the relatively symmetrical structures for the latter (Figure 1).

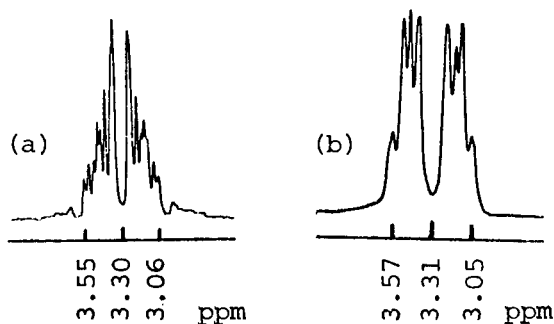


Figure 1. The characteristic ^1H nmr splitting patterns of the ethylene linkage in: (a) compounds **21**, **23** and **26**; (b) compounds **27**, **29** and **32**.

The naphthylethylcarbazoles will be used as standards in order to search for these types of compounds in coal-derived products by gc-ms techniques and these results will be published elsewhere.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The ir spectra were recorded on a Beckman FT 1100 spectrometer as potassium bromide pellets and frequencies are expressed in cm^{-1} . The $^1\text{H-nmr}$ spectra were obtained on a JEOL FX-90R spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values are in Hz. The mass spectra were carried out on a Hewlett-Packard 5980A mass spectrometer.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. For column chromatography, silica gel (Aldrich grade 12, 28-200 mesh) was used.

2-Methylcarbazole (1).

A mixture of 5.0 g (27 mmoles) of 2-methyl-1,2,3,4-tetrahydrocarbazole [**5**] and 0.7 g of 10% Pd-C was heated to 250-270° under nitrogen until effervescence was no longer vigorous (about 20 minutes). Upon cooling the mixture was extracted with boiling 95% ethanol and the catalyst was removed by filtration. The filtrate was cooled to room temperature and the precipitate was collected by filtration to give 4.14 g (85%) of **1** as colorless plates, mp 260-262° (lit mp 259° [**5**], [**9**], 261-262° [**10**]); ir: 3394 cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): 2.47 (s, 3H, CH_3), 6.92-7.51 (m, 5H, ArH), 7.91-8.19 (m, 2H, ArH), 11.06 (br s, 1H, NH).

3-Methylcarbazole (2).

A mixture of 25 g (0.135 mole) of 3-methyl-1,2,3,4-tetrahydrocarbazole [**5**] and 3.36 g of 10% Pd-C was heated to 270-280° under nitrogen until effervescence was no longer vigorous (about 30 minutes). Upon cooling the mixture was extracted with boiling 95% ethanol and the catalyst was removed by filtration. The filtrate was cooled to room temperature and the precipitate was collected by filtration to give 22.25 g (91%) of **2** as colorless plates, mp 205-206° (lit mp 203° [**5**], 206.5-207.5° [**10**]); ir: 3404 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 2.52 (s, 3H, CH_3), 7.10-7.42 (m, 4H, ArH), 7.86-8.07 (m, 3H, ArH).

2-Methyl-9-benzenesulfonylcarbazole (4).

To a mixture of 1.98 g (82.5 mmoles) of 99% sodium hydroxide in 60 ml of anhydrous tetrahydrofuran (THF) was added dropwise to a solution of 11.5 g (63.5 mmoles) of 2-methylcarbazole (**1**) in 80 ml of anhydrous THF. The solution was refluxed for 30 minutes after the addition was completed, then cooled to room temperature. To the above solution 12.32 g (69.8 mmoles) of benzenesulfonyl chloride was added dropwise and stirred overnight at ambient temperature. The solution was evaporated to dryness and 100 ml of water was added. The undissolved solid was collected by filtration and recrystallized from 95% ethanol to give 18.5 g (91%) of **4** as colorless needles, mp 151-152°; ir: 1368, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 2.55 (s, 3H, CH_3), 7.12-7.46 (m, 6H, ArH), 7.72-7.89 (m, 4H, ArH), 8.14-8.33 (m, 2H, ArH); ms: m/z (relative abundance) 323 ($\text{M}^+ + 2$, 3%), 322 ($\text{M}^+ + 1$, 8%), 321 (M^+ , 44%), 181 ($\text{M}^+ - \text{PhSO}_2$, 100%), 77 (5%).

Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{S}$: C, 71.00; H, 4.71; N, 4.36; S, 9.98. Found: C, 70.83; H, 4.70; N, 4.32; S, 10.12.

3-Methyl-9-benzenesulfonylcarbazole (5).

To a mixture of 1.09 g (45.5 mmoles) of 99% sodium hydride in 50 ml of anhydrous THF was added dropwise a solution of 6.33 g (34.9 mmoles) of 3-methylcarbazole (**2**) in 45 ml of anhydrous THF. After the addition was completed, the solution was refluxed for 30 minutes then cooled to room temperature. To the above solution, 6.78 g (38.4 mmoles) of benzenesulfonyl chloride was added dropwise and stirred overnight at ambient temperature. The solution was evaporated to dryness *in vacuo* and 80 ml of water was added to the solid residue. The undissolved solid was collected by filtration and recrystallized from 95% ethanol to give 10.5 g (94%) of **5** as colorless prisms, mp 145-146° (lit [**4**] mp 147°); ir: 1360, 1172 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 2.44 (s, 3H, CH_3), 7.20-7.46 (m, 6H, ArH), 7.63 (m, 4H, ArH), 8.14-8.33 (m, 2H, ArH).

4-Methyl-9-benzenesulfonylcarbazole (6).

To a solution of 8.07 g (44.5 mmoles) of 4-methylcarbazole (3) [6] in 100 ml of anhydrous THF was added 1.35 g (5.63 mmoles) of 99% sodium hydride. The solution was refluxed for 30 minutes before 8.25 g (46.7 mmoles) of benzenesulfonyl chloride was added dropwise. The solution was refluxed for 1 hour after the addition of benzenesulfonyl chloride was completed. After cooling the solution was evaporated to dryness *in vacuo* and 80 ml of water was added. The solid was collected by filtration and was recrystallized from 95% ethanol to afford 12.44 g (87%) of 6 as colorless prisms, mp 176-178°; ir: 1368, 1185 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 2.74 (s, 3H, CH_3), 7.08-8.46 (m, 12H, ArH); ms: m/z (relative abundance) 323 ($\text{M}^+ + 2$, 4%), 322 ($\text{M}^+ + 1$, 10%), 321 (M^+ , 46%), 181 (15%), 180 ($\text{M}^+ - \text{PhSO}_2$, 100%), 152 (8%), 77 (3%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}$: C, 71.00; H, 4.71; N, 4.36; S, 9.98. Found: C, 70.81; H, 4.83; N, 4.31; S, 9.79.

2-Dibromomethyl-9-benzenesulfonylcarbazole (7).

A mixture of 14.93 g (4.64 mmoles) of 2-methyl-9-benzenesulfonylcarbazole (4) and 16.52 g (92.8 mmoles) of NBS and 0.2 g of benzoyl peroxide in 350 ml of carbon tetrachloride was refluxed overnight. The solvent was removed by evaporation *in vacuo*. The solid residue was dissolved in 600 ml of methylene chloride and washed with 10% sodium bicarbonate solution (300 ml x 3) and water (300 ml x 1). The organic solution was dried over anhydrous magnesium sulfate. After filtration the filtrate was evaporated to dryness and the solid was recrystallized from carbon tetrachloride to afford 19.0 g (85%) of 7 as yellow prisms, mp 168-169°; ir: 1368, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 6.84 (s, 1H, CHBr_2), 7.19-7.90 (m, 10H, ArH), 8.27-8.54 (m, 2H, ArH); ms: m/z (relative abundance) 479 (M^+ , 7%), 477 (2%), 402 (8%), 401 (21%), 400 ($\text{M}^+ - ^{79}\text{Br}$, 94%), 398 ($\text{M}^+ - ^{81}\text{Br}$, 100%), 259 (69%), 257 (74%), 177 (29%), 151 (28%), 77 (10%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{NO}_2\text{S}$: C, 47.62; H, 2.93; N, 2.92; S, 6.69. Found: C, 47.47; H, 2.96; N, 2.79; S, 6.46.

3-Dibromomethyl-9-benzenesulfonylcarbazole (8).

A mixture of 25.0 g (77.8 mmoles) of 3-methyl-9-benzenesulfonylcarbazole (5), 27.69 g (155.6 mmoles) of NBS and 0.2 g of benzoyl peroxide in 500 ml of carbon tetrachloride was refluxed for 24 hours. After cooling the solution was evaporated to dryness *in vacuo*. The solid residue was dissolved in 1000 ml of methylene chloride and extracted with saturated sodium bicarbonate solution (300 ml x 2) and washed with water (300 ml), dried over anhydrous magnesium sulfate. After filtration, the organic solution was evaporated to dryness *in vacuo* and the residue was recrystallized from toluene to afford 30.5 g (82%) of 8 as colorless crystals, mp 226-228° dec; ir: 1373, 1167 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 6.81 (s, 1H, $-\text{CHBr}_2$), 7.19-8.36 (m, 12H); ms: m/z (relative abundance) 479 (M^+ , 6%), 402 (7%), 401 (23%), 400 ($\text{M}^+ - ^{79}\text{Br}$, 100%), 398 ($\text{M}^+ - ^{81}\text{Br}$, 96%), 259 (61%), 257 (62%), 177 (15%), 151 (16%), 91 (20%), 77 (8%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{NO}_2\text{S}$: C, 47.62; H, 2.73; Br, 33.35; N, 2.92; S, 6.69. Found: C, 47.84; H, 2.87; Br, 33.41; N, 2.89; S, 6.59.

4-Dibromomethyl-9-benzenesulfonylcarbazole (9).

A mixture of 11.90 g (37.0 mmoles) of 4-methyl-9-benzenesulfonylcarbazole (6), 13.18 g (74.0 mmoles) of NBS and 0.2 g of benzoyl peroxide in 400 ml of carbon tetrachloride was refluxed for

20 hours. After cooling, the solution was evaporated to dryness *in vacuo* and the solid residue was dissolved in 300 ml of methylene chloride and extracted with 10% sodium bicarbonate solution (150 ml x 2) and washed with water (150 ml). The organic solution was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The solid was recrystallized from cyclohexane to 15.82 g (89%) of 9 as yellow prisms, mp 170-171°; ir: 1371, 1178 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.22-8.07 (m, 11H, ArH and $-\text{CHBr}_2$), 8.36-8.50 (m, 2H, ArH); ms: m/z (relative abundance) 479 (M^+ , 12%), 477 (6%), 402 (7%), 401 (22%), 400 ($\text{M}^+ - ^{79}\text{Br}$, 100%), 398 ($\text{M}^+ - ^{81}\text{Br}$, 94%), 259 (41%), 257 (42%), 178 (24%), 177 (16%), 151 (18%), 77 (6%), 56 (16%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{NO}_2\text{S}$: C, 47.62; H, 2.73; Br, 33.35; N, 2.92; S, 6.69. Found: C, 47.82; H, 3.00; Br, 33.48; N, 2.82; S, 6.42.

9-Benzenesulfonyl-2-carbazolecarboxaldehyde (10).

A mixture of 18.0 g (37.6 mmoles) of 2-dibromomethyl-9-benzenesulfonylcarbazole (7) in 150 ml of 0.5 *N* hydrochloric acid and 450 ml of ethanol was refluxed for 5 hours. The solution was evaporated to dryness *in vacuo* and 200 ml of water was added. The solid was collected by filtration and recrystallized from 95% ethanol to yield 11.10 g (88%) of 10 as yellowish needles, mp 221-223°; ir: 2828, 2726, 1697, 1368, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.26-8.08 (m, 10H, ArH), 8.35 (d, 1H, J = 8.3 Hz, H-3), 8.81 (s, 1H, H-1), 10.16 (s, 1H, CHO); ms: m/z (relative abundance) 337 ($\text{M}^+ + 2$, 6%), 336 ($\text{M}^+ + 1$, 17%), 335 (M^+ , 73%), 194 ($\text{M}^+ - \text{PhSO}_2$, 100%), 166 (20%), 77 (11%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$: C, 68.04; H, 3.91; N, 4.18; S, 9.56. Found: C, 68.17; H, 3.96; N, 4.19; S, 9.48.

9-benzenesulfonyl-3-carbazolecarboxaldehyde (11).

A mixture of 30.5 g (63.7 mmoles) of 3-dibromomethyl-9-benzenesulfonylcarbazole (8) in 125 ml of 1 *N* hydrochloric acid and 500 ml of ethanol was refluxed for 24 hours. The solution was evaporated to dryness *in vacuo* and then 400 ml of water was added. The solid, collected by filtration, was recrystallized from benzene-ethanol to give 19.70 g (92%) of 11 as colorless prisms, mp 218-220°; ir: 2852, 2759, 1687, 1368, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform + 2 drops of DMSO-d_6): 7.34-8.51 (m, 12H, ArH), 10.12 (s, 1H, CHO); ms: m/z (relative abundance) 337 ($\text{M}^+ + 2$, 7%), 336 ($\text{M}^+ + 1$, 23%), 335 (M^+ , 100%), 194 ($\text{M}^+ - \text{PhSO}_2$, 98%), 166 (60%), 77 (16%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$: C, 68.04; H, 3.91; N, 4.18; S, 9.56. Found: C, 67.87; H, 4.07; N, 4.11; S, 9.37.

9-Benzenesulfonyl-4-carbazolecarboxaldehyde (12).

A mixture of 15.79 g (32.9 mmoles) of 4-dibromomethyl-9-benzenesulfonylcarbazole (9) in 130 ml of 0.5 *N* hydrochloric acid and 400 ml of ethanol was refluxed for 5 hours. After cooling, the solution was evaporated to dryness *in vacuo* and 200 ml of water was added with stirring. The solid, collected by filtration, was recrystallized from 95% ethanol to yield 10.38 g (94%) of 12 as yellow prisms, mp 173-174°; ir: 2900, 2782, 1692, 1373, 1167; cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.20-7.95 (m, 9H, ArH), 8.38-8.98 (m, 3H, ArH), 10.43 (s, 1H, CHO); ms: m/z (relative abundance) 338 ($\text{M}^+ + 3$, 1%), 337 ($\text{M}^+ + 2$, 5%), 336 ($\text{M}^+ + 1$, 11%), 335 (M^+ , 49%), 195 (15%), 194 ($\text{M}^+ - \text{PhSO}_2$, 100%), 166 (31%), 140 (8%), 139 (8%), 77 (7%), 51 (2%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$: C, 68.04; H, 3.91; N, 4.18; S, 9.56. Found: C, 67.82; H, 4.08; N, 4.05; S, 9.66.

9-Benzenesulfonyl-2-(1-naphthylethenyl)carbazole (**15**).

To a mixture of 0.079 g (3.3 mmoles) of 99% sodium hydride in 15 ml of anhydrous THF was added 0.84 g (3.0 mmoles) of diethyl 1-naphthylmethylphosphonate (**13**) in 10 ml of anhydrous tetrahydrofuran with stirring under a nitrogen atmosphere at room temperature for 1 hour. A solution of 1.01 g (3.0 mmoles) of 9-benzenesulfonyl-2-carbazolecarboxaldehyde (**10**) in 20 ml of anhydrous THF was added dropwise to the above solution. The mixture was stirred at room temperature for 4 hours. The orange solution was poured into 250 ml of ice-water. The solution was then extracted with ethyl acetate (80 ml x 3), dried over anhydrous magnesium sulfate. After filtration and evaporation, the residue was triturated with petroleum ether. The solid, collected by filtration, was recrystallized from cyclohexane to afford 1.0 g (73%) of **15** as a creamy powder, mp 141-143°; ir: 1368, 1178 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.33-8.38 (m, 20H, ArH), 8.54 (s, 1H, H-1); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 3%), 461 ($\text{M}^+ + 2$, 12%), 460 ($\text{M}^+ + 1$, 34%), 459 (M^+ , 100%), 318 ($\text{M}^+ - \text{PhSO}_2$, 99%), 317 (62%), 158 (9%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.46; H, 4.88; N, 3.08; S, 7.18.

9-Benzenesulfonyl-2-(2-naphthylethenyl)carbazole (**16**).

To a mixture of 0.13 g (5.4 mmoles) of 99% sodium hydroxide in 20 ml of anhydrous dimethylformamide (DMF) was added 1.24 g (4.5 mmoles) of diethyl 2-naphthylmethylphosphonate (**14**) in 10 ml of anhydrous DMF with stirring under a nitrogen atmosphere at room temperature for 2 hours. A solution of 1.50 g (4.5 mmoles) of 9-benzenesulfonyl-2-carbazolecarboxaldehyde (**10**) in 20 ml of anhydrous DMF was added to the above solution over a 5 minute period. The mixture was stirred at room temperature for 30 minutes, then the temperature was raised to 80° for 2 hours. After cooling, the solution was poured into 250 ml of ice-water. The precipitate, collected by filtration, was recrystallized from benzene to give 1.50 g (73%) of **16** as yellow crystals, mp 224-226°; ir: 1373, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.31-8.37 (m, 20H, ArH), 8.52 (d, 1H, J = 0.74 Hz, H-1); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 3%), 461 ($\text{M}^+ + 2$, 11%), 460 ($\text{M}^+ + 1$, 35%), 459 (M^+ , 100%), 318 ($\text{M}^+ - \text{PhSO}_2$, 90%), 158 (8%), 77 (3%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.14; H, 4.80; N, 2.86; S, 6.71.

9-Benzenesulfonyl-3-(1-naphthylethenyl)carbazole (**17**).

To a mixture of 0.168 g (7.0 mmoles) of 99% sodium hydride in 20 ml of anhydrous DMF was added 1.84 g (6.6 mmoles) of diethyl 1-naphthylmethylphosphonate (**13**) in 10 ml of anhydrous DMF with stirring under a nitrogen atmosphere at room temperature for 1 hour. A solution of 2.014 g (6.0 mmoles) of 9-benzenesulfonyl-3-carbazolecarboxaldehyde (**11**) in 35 ml of anhydrous DMF was then added dropwise to the above solution and stirred at 80° for 2 hours. After cooling, the solution was poured into 200 ml of ice-water and stirred for 30 minutes. The solid, collected by filtration, was recrystallized from a cyclohexane-benzene mixture to give 2.068 g (75%) of **17** as a cream powder, mp 182-184°; ir: 1371, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.15-8.13 (m, 19H), 8.20-8.39 (m, 2H); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 1%), 461 ($\text{M}^+ + 2$, 6%), 460 ($\text{M}^+ + 1$, 18%), 459 (M^+ , 55%), 319 (26%), 318 ($\text{M}^+ - \text{PhSO}_2$, 100%), 317 (42%), 316 (17%), 159 (4%), 77 (2%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.39; H, 4.75; N, 3.07; S, 6.77.

9-Benzenesulfonyl-3-(2-naphthylethenyl)carbazole (**18**).

To a mixture of 0.168 g (7.0 mmoles) of anhydrous DMF was added 1.84 g (6.6 mmoles) of diethyl 2-naphthylmethylphosphonate (**14**) in 10 ml of anhydrous DMF with stirring under a nitrogen atmosphere at room temperature for 1 hour. A solution of 2.014 g (6.0 mmoles) of 9-benzenesulfonyl-3-carbazolecarboxaldehyde (**11**) in 35 ml of anhydrous DMF was then added dropwise to the above solution and stirred at 80° for 2 hours. After cooling, the solution was poured into 200 ml of ice-water and stirred for 30 minutes. The solid, collected by filtration, was recrystallized from a cyclohexane-benzene mixture to afford 1.68 g (56%) of **18** as yellowish crystals, mp 177-178°; ir: 1368, 1180 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.21-8.03 (m, 19H), 8.27-8.37 (m, 2H); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 1%), 461 ($\text{M}^+ + 2$, 6%), 460 ($\text{M}^+ + 1$, 18%), 459 (M^+ , 50%), 319 (31%), 318 ($\text{M}^+ - \text{PhSO}_2$, 100%), 317 (42%), 316 (15%), 159 (8%), 78 (28%), 77 (8%), 52 (8%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.39; H, 4.55; N, 2.90; S, 6.96.

9-Benzenesulfonyl-4-(1-naphthylethenyl)carbazole (**19**).

To a mixture of 0.135 g (5.5 mmoles) of 99% sodium hydride in 20 ml of anhydrous DMF was added dropwise 1.50 g (5.4 mmoles) of diethyl 1-naphthylmethylphosphonate (**13**) in 10 ml of anhydrous DMF with stirring under a nitrogen atmosphere at room temperature for 2 hours. A solution of 1.50 g (4.47 mmoles) of 9-benzenesulfonyl-4-carboxaldehyde (**12**) in 35 ml of anhydrous DMF was added dropwise to the above solution and stirred at 80° for 2 hours. After cooling the solution was poured into 200 ml of ice-water and stirred for 30 minutes. The solution was extracted with ether (150 ml x 3), dried over anhydrous magnesium sulfate and the organic solution was evaporated to dryness *in vacuo*. The gummy residue was triturated with petroleum ether. The solid, collected by filtration, was recrystallized from a benzene-cyclohexane mixture to obtain 0.82 g (40%) of **19** as a yellow powder, mp 178-180°; ir: 3055, 1373, 1185 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.23-8.46 (m); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 2%), 461 ($\text{M}^+ + 2$, 8%), 460 ($\text{M}^+ + 1$, 27%), 459 (M^+ , 84%), 319 (27%), 318 ($\text{M}^+ - \text{PhSO}_2$, 100%), 317 (56%), 316 (20%), 289 (3%), 159 (5%), 77 (2%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.19; H, 4.81; N, 2.92; S, 6.78.

9-Benzenesulfonyl-4-(2-naphthylethenyl)carbazole (**20**).

To a mixture of 0.135 g (5.5 mmoles) of 99% sodium hydride in 20 ml of anhydrous DMF was added dropwise 1.50 g (5.36 mmoles) of diethyl 2-naphthylmethylphosphonate (**14**) in 10 ml of anhydrous DMF with stirring under a nitrogen atmosphere at room temperature for 2 hours. A solution of 1.5 g (4.47 mmoles) of 9-benzenesulfonyl-4-carbazolecarboxaldehyde (**12**) in 30 ml of anhydrous DMF was added dropwise to the above mixture and stirred at 80° for 2 hours. After cooling, the solution was poured into 200 ml of ice-water and stirred for 30 minutes. The solid was collected by filtration and recrystallized from cyclohexane to yield 1.50 g (73%) of **20** as a creamy powder, mp 139-141°; ir: 3052, 1368, 1185 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 7.17-8.48 (m); ms: m/z (relative abundance) 462 ($\text{M}^+ + 3$, 2%), 461 ($\text{M}^+ + 2$,

8%), 460 ($M^+ + 1$, 27%), 459 (M^+ , 78%), 319 (26%), 318 ($M^+ - \text{PhSO}_2$, 100%), 317 (54%), 280 (12%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.40; H, 4.61; N, 3.05; S, 6.98. Found: C, 78.55; H, 4.73; N, 2.83; S, 6.75.

9-Benzenesulfonyl-2-(1-naphthylethyl)carbazole (21).

To a solution of 0.86 g (1.85 mmoles) of 9-benzenesulfonyl-2-(1-naphthylethenyl)carbazole (15) in 100 ml of benzene was added 0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the hydrogen up-take had ceased. After filtration the filtrate was evaporated to dryness. The residue was dissolved in 3 ml of chloroform and subjected to column chromatography (silica gel, 28-200 mesh) eluted with hexane/methylene chloride (2:1 ratio by volume). The fractions containing the desired product were pooled and evaporated to dryness. The solid, thus obtained, was recrystallized from cyclohexane to afford 0.5 g (58%) of 21 as silky needles, mp 130.0-131.5°; ir: 3060, 2934, 2870, 1368, 1175 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.20-3.40 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 6.98-8.36 (m, 19H, ArH); ms: m/z (relative abundance) 463 ($M^+ + 2$, 3%), 462 ($M^+ + 1$, 10%), 461 (M^+ , 31%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (44%), 141 (15%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.30; S, 6.95. Found: C, 78.20; H, 5.20; N, 2.80; S, 6.71.

9-Benzenesulfonyl-2-(2-naphthylethyl)carbazole (22).

To a solution of 0.8 g (1.74 mmoles) of 9-benzenesulfonyl-2-(2-naphthylethenyl)carbazole (16) in 100 ml of benzene was added 0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the up-take of hydrogen ceased. The catalyst was filtered and washed with 20 ml of benzene. The combined filtrate was evaporated to dryness. The residue was triturated with petroleum ether. The solid, collected by filtration, was recrystallized from a cyclohexane-benzene mixture to yield 0.72 g (90%) of 22 as colorless prisms, mp 152-154°; ir: 3062, 2924, 2854, 1368, 1180 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.21 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 7.02-8.34 (m, 19H, ArH); ms: m/z (relative abundance) 463 ($M^+ + 2$, 4%), ($M^+ + 1$, 11%), 461 (M^+ , 34%), 321 (22%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (39%), 141 (15%), 115 (3%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.30; S, 6.95. Found: C, 77.84; H, 5.20; N, 2.78; S, 6.76.

9-Benzenesulfonyl-3-(1-naphthylethyl)carbazole (23).

To a solution of 0.3 g (0.65 mmole) of 9-benzenesulfonyl-3-(1-naphthylethenyl)carbazole (17) in 80 ml of benzene was added 0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the up-take of hydrogen had ceased. The catalyst was filtered and washed with 20 ml of benzene. The combined filtrate was evaporated to dryness and the solid was recrystallized from cyclohexane to afford 0.2 g (66%) of 23 as colorless crystals, mp 161-163°; ir: 3057, 3044, 2926, 2849, 1368, 1180 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.09-3.51 (m, $-\text{CH}_2\text{CH}_2-$), 7.18-8.37 (m, 19H, ArH); ms: m/z (relative abundance) 463 ($M^+ + 2$, 3%), 462 ($M^+ + 1$, 7%), 461 (M^+ , 22%), 337 (9%), 321 (24%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (37%), 168 (10%), 141 (9%), 84 (8%), 56 (9%), 41 (18%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.03; S, 6.96. Found: C, 77.94; H, 5.17; N, 2.86; S, 6.85.

9-Benzenesulfonyl-3-(2-naphthylethyl)carbazole (24).

To a solution of 0.6 g (1.3 mmoles) of 9-benzenesulfonyl-3-(2-naphthylethenyl)carbazole (18) in 100 ml of benzene was added

0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the up-take of hydrogen had ceased. The combined filtrate was evaporated to dryness *in vacuo* and the solid residue was recrystallized from cyclohexane to give 0.53 g (88%) of 24 as colorless crystals, mp 118-119°; ir: 3050, 3019, 2926, 2859, 1363, 1183 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.13 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 7.17-8.36 (m, 19H); ms: m/z (relative abundance) 463 ($M^+ + 2$, 3%), 462 ($M^+ + 1$, 10%), 460 (M^+ , 25%), 321 (21%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (42%), 141 (40%), 115 (4%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.05; S, 6.95. Found: C, 78.20; H, 4.94; N, 3.09; S, 6.81.

9-Benzenesulfonyl-4-(1-naphthylethyl)carbazole (25).

To a solution of 0.773 g (1.68 mmoles) of 9-benzenesulfonyl-4-(1-naphthylethenyl)carbazole (19) in 100 ml of benzene was added 0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the up-take of hydrogen ceased. The catalyst was filtered and washed with 20 ml of benzene. The combined filtrate was evaporated to dryness *in vacuo*. The solid residue was recrystallized from a benzene-cyclohexane mixture to afford 0.53 g (69%) of 25 as colorless crystals, mp 177-179°; ir: 3057, 2939, 2872, 1376, 1183 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.52 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 6.99-8.48 (m, 19H, ArH); ms: m/z (relative abundance) 463 ($M^+ + 2$, 6%), 462 ($M^+ + 1$, 17%), 461 (M^+ , 49%), 321 (23%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (27%), 141 (36%), 115 (4%), 77 (2%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.03; S, 6.95. Found: C, 77.92; H, 4.98; N, 2.99; S, 6.98.

9-Benzenesulfonyl-4-(2-naphthylethyl)carbazole (26).

To a solution of 0.9 g (1.96 mmoles) of 9-benzenesulfonyl-4-(2-naphthylethenyl)carbazole (20) in 120 ml of benzene was added 0.1 g of 10% Pd-C. The mixture was hydrogenated at room temperature under atmospheric pressure until the up-take of hydrogen had ceased. The catalyst was filtered and washed with 30 ml of benzene. The combined filtrate was evaporated to dryness *in vacuo*. The solid residue was recrystallized from a benzene-cyclohexane mixture to yield 0.74 g (82%) of 26 as colorless crystals, mp 186-187°; ir: 3055, 2926, 2849, 1368, 1183 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): 3.10-3.59 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 7.03-8.49 (m, 19H, ArH); ms: m/z (relative abundance) 463 ($M^+ + 2$, 6%), 462 ($M^+ + 1$, 18%), 461 (M^+ , 49%), 321 (23%), 320 ($M^+ - \text{PhSO}_2$, 100%), 179 (29%), 141 (44%), 115 (5%), 77 (2%).

Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{NO}_2\text{S}$: C, 78.06; H, 5.02; N, 3.03; S, 6.95. Found: C, 78.21; H, 5.17; N, 2.94; S, 6.77.

2-(1-Naphthylethyl)carbazole (27).

A mixture of 0.48 g (1.03 mmoles) of 9-benzenesulfonyl-2-(1-naphthylethyl)carbazole (21) in 8.5 ml of 2 *N* sodium hydroxide solution and 40 ml of ethanol was refluxed for 3 days. After cooling, the solution was evaporated to dryness *in vacuo* and 30 ml of water was added and stirred for 30 minutes. The solid, collected by filtration, was recrystallized from ethanol to yield 0.28 g (85%) of 27 as a colorless powder, mp 185-187°; ir: 3407, 3060, 3042, 2929, 2864 cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): 3.10-3.66 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 7.02-8.22 (m, 14H, ArH); ms: m/z (relative abundance) 323 ($M^+ + 2$, 1%), 322 ($M^+ + 1$, 8%), 321 (M^+ , 28%), 181 (15%), 180 (100%), 179 (5%), 152 (5%), 141 (5%), 115 (1%).

Anal. Calcd. for $\text{C}_{24}\text{H}_{19}\text{N}$: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.83; H, 6.09; N, 4.39.

2-(2-Naphthylethyl)carbazole (28).

A mixture of 0.28 g (0.607 mmole) of 9-benzenesulfonyl-2-(2-naphthylethyl)carbazole (**22**) in 5 ml of 2 *N* sodium hydroxide and 15 ml of ethanol was refluxed for 3 days. After cooling the solution was evaporated to dryness *in vacuo* and then 10 ml of water was added with stirring. The solid, collected by filtration, was recrystallized from an ethanol-benzene mixture to afford 0.14 g (71%) of **28** as colorless crystals, mp 262-265° dec; ir: 3404, 3044, 3019, 2926, 2911, 2846 cm⁻¹; ¹H-nmr (DMSO-d₆): 3.18 (s, 4H, -CH₂CH₂-), 7.02-8.06 (m, 14H, ArH); ms: m/z (relative abundance) 323 (M⁺ + 2, 1%), 322 (M⁺ + 1, 7%), (M⁺, 26%), 181 (15%), 180 (100%), 179 (5%), 141 (6%), 115 (2%).

Anal. Calcd. for C₂₄H₁₉N: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.85; H, 6.03; N, 4.20.

3-(1-Naphthylethyl)carbazole (29).

A mixture of 0.55 g (1.2 mmoles) of 9-benzenesulfonyl-3-(1-naphthylethyl)carbazole (**23**) in 10 ml of 2 *N* sodium hydroxide and 50 ml of ethanol was refluxed for 2 days. After cooling, the solution was evaporated to dryness *in vacuo* and 40 ml of water was added with stirring for 30 minutes. The solid, collected by filtration, was recrystallized from an ethanol-water mixture to yield 0.263 g (68%) of **29** as colorless crystals, mp 168-170°; ir: 3415, 3050, 3034, 2926, 2862 cm⁻¹; ¹H-nmr (DMSO-d₆): 3.11-3.52 (m, 4H, -CH₂CH₂-), 7.11-8.30 (m, 14H, ArH); ms: m/z (relative abundance) 323 (M⁺ + 2, 1%), 322, (M⁺ + 1, 5%), 321 (M⁺, 20%), 181 (15%), 180 (100%), 179 (6%), 141 (5%).

Anal. Calcd. for C₂₄H₁₉N: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.49; H, 6.10; N, 4.32.

3-(2-Naphthylethyl)carbazole (30).

A mixture of 0.473 g (1.02 mmoles) of 9-benzenesulfonyl-3-(2-naphthylethyl)carbazole (**24**) in 10 ml of 2 *N* sodium hydroxide solution and 60 ml of ethanol was refluxed for 2 days. After cooling the solution was evaporated to dryness *in vacuo* and 40 ml of water was added and stirred for 30 minutes. The solid collected by filtration was recrystallized from an ethanol-benzene mixture to give 0.258 g (79%), of **30** as colorless crystals, mp 260-261° dec; ir: 3410, 3052, 2921, 2857 cm⁻¹; ¹H-nmr (deuteriochloroform): 3.17 (s, 4H, -CH₂CH₂-), 7.03-8.08 (m, 14H); ms: m/z (relative abundance) 323 (M⁺ + 2, 1%), 322 (M⁺ + 1, 7%), 321 (M⁺, 22%), 181 (15%), 180 (100%), 179 (6%), 152 (5%), 141 (5%), 115 (2%).

Anal. Calcd. for C₂₄H₁₉N: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.52; H, 6.00; N, 4.28.

4-(1-Naphthylethyl)carbazole (31).

A mixture of 0.414 g (0.9 mmole) of 9-benzenesulfonyl-4-(1-

naphthylethyl)carbazole (**25**) in 8 ml of 2 *N* sodium hydroxide solution and 40 ml of ethanol was heated under reflux for 2 days. After cooling, the solution was evaporated to dryness and water (30 ml) was added and stirred for 30 minutes. The solid, collected by filtration, was recrystallized from ethanol to give 0.22 g (76%) of **31** as colorless crystals, mp 189-191°; ir: 3394, 3055, 3034, 2942, 2872 cm⁻¹; ¹H-nmr (DMSO-d₆): 3.42 (s, 4H, -CH₂CH₂-), 6.95-8.19 (m, 14H, ArH); ms: m/z (relative abundance) 323 (M⁺ + 2, 1%), 322 (M⁺ + 1, 8%), 321 (M⁺, 30%), 181 (14%), 180 (100%), 141 (13%), 115 (3%).

Anal. Calcd. for C₂₄H₁₉N: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.76; H, 6.03; N, 4.34.

4-(2-Naphthylethyl)carbazole (32).

A mixture of 0.57 g (1.24 mmoles) of 9-benzenesulfonyl-4-(2-naphthylethyl)carbazole (**26**) in 10 ml of 2 *N* sodium hydroxide solution and 45 ml of ethanol was heated under reflux for 2 days. After cooling, the solution was evaporated, water added and stirred for 30 minutes. The solid, collected by filtration, was recrystallized from a benzene-ethanol mixture to yield 0.29 g (72%) of **32** as colorless needles, mp 180-181°; ir: 3386, 3052, 2929, 2867 cm⁻¹; ¹H-nmr (DMSO-d₆): 3.15-3.67 (m, 4H, -CH₂CH₂-), 6.91-8.21 (m, 14H, ArH); ms: m/z (relative abundance) 323 (M⁺ + 2, 1%), 322 (M⁺ + 1, 9%), 321 (M⁺, 31%), 181 (15%), 180 (100%), 141 (11%), 115 (3%).

Anal. Calcd. for C₂₄H₁₉N: C, 89.68; H, 5.96; N, 4.36. Found: C, 89.65; H, 5.93; N, 4.27.

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