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Syntheses of 2-Substituted Indoles and Fused Indoles by Photostimulated Reactions of *o*-Iodoanilines with Carbanions by the $S_{RN}1$ Mechanism

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2-Substituted indoles (**5a**,**b** and **7**) and fused indoles (**9a**−**c**, **11a**,**b**, and **12**) have been obtained by the $S_{RN}1$ mechanism from photostimulated reactions of *o*-iodoaniline (**1**) and 1-halo-2-naphthalen-2-ylamines (**3a**,**b**) with enolate ions of acyclic (acetophenone (**6**), 2- (**4a**) and 4-acetylpyridine (**4b**)) and cyclic ketones (1- (**8a**) and 2-indanone (**10a**), 1- (**8b**) and 2-tetralone (**10b**) and 1-benzosuberone (**8c**)) in DMSO and liquid ammonia as solvents. The carbanions derived from **4a**,**b**, **8a**, and **10b** are novel nucleophiles that form new C−C bonds by the $S_{RN}1$ mechanism.

Introduction

Indoles are probably the most widely distributed heterocyclic compounds in nature. The indole ring belongs to an important class of compounds due to their pharmacological activity.[1−3]

There are several reported procedures to obtain indoles. The most used method is the Fischer synthesis, which involves the reaction of *N*-arylhydrazones in acid media or in the presence of $ZnCl_2$.[4] Most often, the indole is obtained directly form the ketone and phenylhydrazine without isolation of the intermediate. Recently, the synthesis of *N*-arylhydrazones has been improved by using palladium catalysis.[5] Another approach utilized in acidic media is the Bischler synthesis, which has been modified in the last years by Moody.[6]

Indoles can be obtained from *o*-alkynylanilines by palladium-catalyzed cyclization under acid[7] or basic conditions[8] or from *o*-alkenylbenzonitriles by radical cyclization.[9] Another procedure is the preparation of indoles from *o*-haloanilines by the palladium cross-coupling reaction followed by Rh-catalyzed hydroformylation of the Heck adducts.[10] Recently, a method for indole synthesis using a palladium-catalyzed annulation between *o*-iodoaniline and ketones has been described.[11] The development of a new method for the regioselective synthesis of functionalized indoles through the benzyne mechanism has also been reported.[12]

The $S_{RN}1$ mechanism is an important route to achieve the formation of a new C−C bond by the reaction of aromatic substrates with carbanions.[13] Good yields of substitution are usually obtained in the reactions of aliphatic and aromatic ketones enolate ions. These anions react with aromatic halides under photostimulation in liquid ammonia or in DMSO as solvents.

The $S_{RN}1$ mechanism is a chain process. The initiation step (eq 1) is an electron transfer (ET) from the nucleophile to the substrate to afford a radical anion. In some of these systems the ET step is spontaneous but in others light is required to catalyze the reaction. Electrons (from dissolution of alkali metals in liquid ammonia, or from a cathode) and inorganic salts (Fe^{2+}, SmI_2) can initiate the reaction as well. The propagation steps consist of the fragmentation of the radical anion to afford a radical and the nucleofugal group (eq 2) and coupling of the radical

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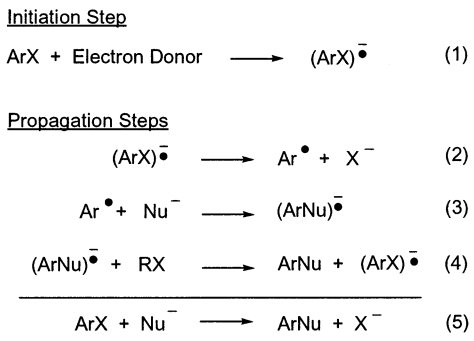
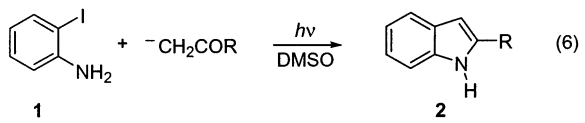
with the nucleophile to afford a radical anion (eq 3), which by ET to the substrate (eq 4) forms the intermediate necessary to continue the propagation cycle. Overall, eqs 2−4 depict a nucleophilic substitution (eq 5) in which radicals and radical anions are intermediates.



One of the most widely studied approaches to ring closure reactions is the $S_{RN}1$ substitution of aromatic compounds that have an appropriate substituent ortho to the leaving group.[14] An important example of substitution followed by spontaneous ring closure in the reaction media is the synthesis of indoles by the photostimulated reaction of *o*-iodoaniline (**1**) with carbanions derived from aliphatic ketones in liquid ammonia to give 2-substituted indoles **2** (eq 6).[15,16]



Unsubstituted and substituted *o*-bromo- and *o*-chloroanilines are adequate substrates for obtaining indoles with functionalities such as Me, Ph, or MeO groups in 50−90% yield.[17]

Under electrochemical initiation, the reactions of **1** with the enolate ions of acetone, isopropyl methyl ketone, and acetaldehyde afford the respective indoles in 75−93% yields.[18]

The syntheses of benzo[*e*]- and benzo[*g*]indoles have been performed by reaction of 2-amino-1-bromo- and 1-amino-2-bromonaphthalene with the anion of pinacolone, respectively.[19]

The reactions of **1** with the enolate anions of aromatic ketones (viz. acetophenone, 2-naphthyl-methyl ketone, 2-acetyl-*N*-methylpyrrole, and 2-acetylthiophene) furnish the corresponding 2-substituted indoles **2** in good yields in DMSO as solvent.[20] Depending on the ketone enolate ion involved, the reactions can occur under light or Fe^{2+} initiation.

TABLE 1. Reactions of 1 with Ketone Enolate Ions[a]

expt	nucleophile	conditions	X^- [b] (%)	product (%)	aniline (%)
1	**4a**	DMSO, dark, 3 h	<1		
2	**4a**	DMSO, *hν*, 3 h	95	**5a** (63)	23
3	**4a**	DMSO, *hν*, 3 h[c]	64	**5a** (39)	*d*
4	**4b**	DMSO, dark, 3 h	<2		
5	**4b**	DMSO, *hν*, 3 h	101	**5b** (74)	17
6	**4b**	DMSO, *hν*, 3 h[c]	41	**5b** (30)	*d*
7[e]	**6**	DMSO, *hν*, 3 h	84	**7** (46)	18
8[f]	**6**	DMSO, *hν*, 3 h	90	**7** (48)	37
9[g]	**8a**	DMSO, dark, 3 h	18	**9a** (14)	*d*
10[g]	**8a**	DMSO, *hν*, 3 h	101	**9a** (71)	31
11	**8a**	NH_3, *hν*, 2 h	91	**9a** (65)	14
12	**8b**	DMSO, dark, 3 h	<2		
13	**8b**	DMSO, *hν*, 3 h	98	**9b** (58)	34
14	**8b**	DMSO, *hν*, 3 h[c]	88	**9b** (48)	*d*
15	**8b**	NH_3, *hν*, 2 h	91	**9b** (54)	13
16	**8c**	DMSO, *hν*, 3 h	108	**9c** (58)	32
17	**8c**	NH_3, *hν*, 2 h	92	**9c** (71)[h]	*d*
18	**10a**	DMSO, *hν*, 3 h	100	**11a** (54)	48
19	**10a**	NH_3, *hν*, 2 h	97	**11a** (50)	11
20	**10b**	DMSO, *hν*, 3 h	101	**11b** (47)	18
21	**10b**	DMSO, *hν*, 3 h[i]	100	**11b** (56)	*d*
22	**10b**	NH_3, *hν*, 2 h	92	**11b** (73)	*d*
23[j]	**8b**	DMSO, *hν*, 3 h	96	**12** (36)	50
24[k]	**8b**	DMSO, *hν*, 3 h	82	**12** (23)	23
25[l]	**8b**	DMSO, *hν*, 3 h	82	**12** (36)	51

[a] Reactions carried out under N_2 at 40 °C in 20 mL of DMSO (**1** (0.50 mmol), ketone (2.50 mmol), and *t*-BuOK (2.55 mmol)) or in 150 mL of liquid ammonia (**1** (0.50 mmol), ketone (1.50 mmol) and *t*-BuOK (2.0 mmol)) unless otherwise indicated. [b] Determined potentiometrically. [c] *p*-DNB (20 mol %) was added. [d] Not quantified. [e] The substrate was **3a** (0.40 mmol), **6** (2.00 mmol), and *t*-BuOK (2.20 mmol) in 10 mL of DMSO. Aniline is 2-naphthylamine. [f] The substrate was **3b** (0.26 mmol), **6** (1.30 mmol) and *t*-BuOK (1.31 mmol) in 10 mL of DMSO. Aniline is 2-naphthylamine. [g] *t*-BuOK (2.75 mmol) was used. [h] Isolated yield. [i] Reaction carried out under N_2 at 40 °C in 20 mL of DMSO: **1** (0.50 mmol), ketone (5.0 mmol), and *t*-BuOK (5.05 mmol). [j] The substrate was **3a** (0.40 mmol), **8b** (2.00 mmol), and *t*-BuOK (2.20 mmol) in 10 mL of DMSO. Aniline is 2-naphthylamine. [k] The substrate was **3a** (0.40 mmol), **8b** (2.00 mmol), pinacolone (2.00 mmol), and *t*-BuOK (4.40 mmol) in 10 mL of DMSO. Aniline is 2-naphthylamine. [l] The substrate was **3b** (0.35 mmol), **8b** (1.60 mmol), and *t*-BuOK (1.62 mmol) in 10 mL of DMSO. Aniline is 2-naphthylamine.

We hereby report the syntheses of 2-pyridin-2-yl-1*H*-indole, 2-pyridin-4-yl-1*H*-indole, and 2-phenyl-3*H*-benz(*e*)indole. Fused indoles are important molecules because of their pharmaceutical applications, and they can also be precursors to other planar molecules. In the present study, we undertake the syntheses of these indoles, starting from cyclic ketones and **1**, and 1-halonaphthalen-2-ylamines (**3**) under irradiation in DMSO and in liquid ammonia.

Results and Discussion

To study the scope and limitations of the syntheses of 2-substituted indoles and benzoindoles by the $S_{RN}1$ mechanism, we made use of several aromatic ketones on reaction with both **1** and **3** as substrates.

The enolate ion of 2-acetylpyridine (**4a**) reacts under photostimulation with **1** to afford the 2-substituted indole (**5a**) in 64% yield (eq 7). This reaction does not occur in the dark, and it is inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions[13] (Table 1, experiments 1−3). The enolate ion of the 4-acetylpyridine

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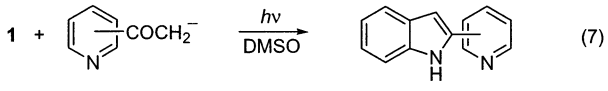
(**4b**) reacts under photostimulation with **1** to give the 2-pyridin-4-yl-1*H*-indole (**5b**) in 74% yield (eq 7). This reaction does not occur in the dark, and it is inhibited by *p*-DNB (Table 1, experiments 4−6). The dark reactions of **1** with enolate ion **4** in the presence of $FeBr_2$ afford indoles **5** in low yield (36%).

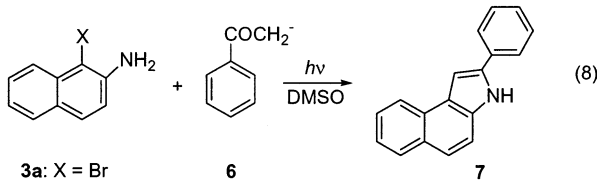


(7)

4a, 2-acetyl
4b, 4-acetyl

5a, 2-pyridyl
5b, 4-pyridyl

The photostimulated reaction of 1-bromo-2-naphthalen-2-ylamine (**3a**) with acetophenone enolate ion (**6**) in DMSO furnishes 2-phenyl-3*H*-benzo(*e*)indole (**7**) in 46% yield, together with the reduced product 2-naphthylamine (18%) (eq 8). To asses the dependence of product yield on substrate leaving group nature, we studied the iodo analogue **3b**. However, indole **7** was obtained in 48% yield, and the reduced product increased in yield up to 37% (Table 1, experiments 7 and 8).



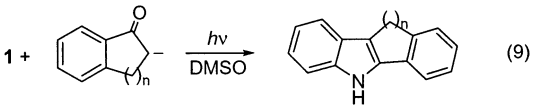
(8)

3a: X = Br
3b: X = I

6

7

Substrate **1** reacts sluggishly in the dark in DMSO with the enolate anion of 1-indanone (**8a**) to afford 5,10-dihydroindeno[1,2-*b*]indole (**9a**) in 14% yield, which upon irradiation increases to 71% yield (eq 9, $n = 1$). A similar yield of **9a** is obtained by a photostimulated reaction in liquid ammonia as solvent (Table 1, experiments 9−11).



(9)

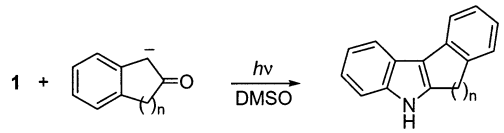
8a, n = 1
8b, n = 2
8c, n = 3

9a, n = 1
9b, n = 2
9c, n = 3

The enolate ions of 1-tetralone (**8b**) have been arylated by the $S_{RN}1$ mechanism in DMSO and in liquid ammonia to afford products in variables yields (35−80%).[21] There is no reaction of **1** with **8b** in the dark in DMSO; however, upon photostimulation, 5,11-dihydro-6*H*-benzo[*a*]carbazole (**9b**) is obtained in 58% yield (eq 9, $n = 2$). This reaction is partially inhibited by *p*-DNB. Similar yields of **9b** are obtained in liquid ammonia (Table 1, experiments 12−15).

The enolate ions of 6,7,8,9-tetrahydrobenzocyclohepten-5-one (1-benzosuberone) (**8c**) react with **1** under photostimulation in DMSO to afford the indole 5,6,7,12-tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]indole (**9c**) in 58% yield (eq 9, $n = 3$). The dark reaction catalyzed by $FeBr_2$ renders indole **9c** in poor yield. However, the photostimulated reaction of **1** with **8c** in liquid ammonia affords indole **9c** in 71% isolated yield (Table 1, experiments 16−17).

5,6-Dihydroindeno[2,1-*b*]indole (**11a**) is obtained by a photostimulated reaction of **1** with the enolate anion of 2-indanone (**10a**) in 54% yield in DMSO and in 50% yield in liquid ammonia (eq 10, $n = 1$) (Table 1, experiments 18 and 19).



(10)

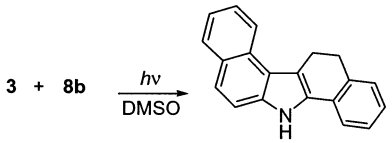
10a, n = 1
10b, n = 2

11a, n = 1
11b, n = 2

The anion derived from 2-tetralone (**10b**) fails to react with alkyl halides to obtain 1-substituted-2-tetralones. Syntheses of these compounds are carried out in good yields by different methods.[22,23] On the other hand, **10b** reacts under irradiation with iodobenzene and 1-iodonaphthalene in DMSO to render the substitution products by $S_{RN}1$ reactions in good yields.[24]

In the photostimulated reaction of **1** with **10b**, 5,7-dihydro-6*H*-benzo[*c*]carbazole (**11b**) is obtained in 47% yield. When the concentrations of **10b** and *t*-BuOK are increased, the yield of **11b** is enhanced up to 56% in DMSO. However, the yield of **11b** is 73% upon photostimulation in liquid ammonia (Table 1, experiments 20−22) (eq 10, $n = 2$). Enolate ions **10a** and **10b** do not react with **1** in the presence of 1 equiv of $FeBr_2$ and 1 equiv of acetone enolate ions.

The photostimulated reactions of **3a** and **3b** in DMSO as solvent with **8b** furnish 36% yield of indole **12**. The yield does not improve in the presence of pinacolone enolate ion (Table 1, experiments 23−25).



(11)

12

Conclusions

We have found that carbanions derived from 1-indanone (**8a**), 2-tetralone (**8b**), and 2- and 4-acetylpyridines (**4a** and **4b**) are novel nucleophiles that form new C−C bonds by the $S_{RN}1$ mechanism in fairly good yields.

The photostimulated reactions of several cyclic and acyclic ketone enolate ions with substrate **1** in DMSO and liquid ammonia afford 2-substituted indoles and fused indoles in acceptable yields by the $S_{RN}1$ mechanism (50−74%) (comparable to the Fisher indole synthesis), together with the reduced product aniline. An exception in favor of our methodology is to be found with 2-indanone enolate ion (**10a**) that affords 54% of product **11a**

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by the $S_{RN}1$ mechanism and only 8% yield by the Fisher indole synthesis.[25]

Although we found that $FeBr_2$ induced the reaction of ketone enolate ions to form indoles in high yields by the $S_{RN}1$ mechanism,[20] the ketone enolate ions studied in the present investigation cannot be induced to react by the inorganic salt intermediacy. The role of Fe^{2+} ion in the reaction still remains intriguing. Its presence is required from catalytic to equimolecular amounts, which depends on the leaving group and the nucleophile used.

In the photostimulated reactions of substrate **3** and the ketone enolate ions **6** (46−48% yields of indole **7**), and **8b** (36% of the fused indole **12**), the product yields are lower than those with substrate **1**. However, considering the availability/simplicity of the starting materials, and the readiness of the procedure, this reaction becomes a valid alternative to the synthesis of indoles.

Experimental Section

General Methods. ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.32 MHz) spectra were conducted in $CDCl_3$ or acetone-d_6 as solvents. Coupling constants (J) are given in Hz. The internal standard method was used for quantitative GC analysis using authentic samples, the column employed was an HP1 column (0.53 mm × 5m) with an HP data system. Liquid chromatographic analyses were performed with a gradient pump with a variable-wavelength monitor (programmable detector, covering the 190 nm to 600 nm UV range) using a Spherisorb ODS 2 column (4.0 mm × 250 mm). The purification of the products was done with radial TLC using silica gel 60 PF-254 with calcium sulfate as binder. Irradiation was conducted in a photochemical reactor equipped with two 400-W Hg lamps emitting maximally at 350 nm (air and water refrigerated). Potentiometric titration of halide ions was performed in a pHmeter using a Ag/Ag^+ electrode. Melting points were uncorrected.

Materials. *t*-BuOK was commercially available and used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å). *o*-Iodoaniline, 2-acetylpyridine, 4-acetypyridine, 1-tetralone, 2-tetralone, 1-indanone, 2-indanone, acetophenone, and 1-benzosuberone were commercially available and distilled under reduced pressure. 1-Bromo-2-naphthylamine[19] and 1-iodo-2-naphthylamine[26,27] were prepared as previously reported.

Photostimulated Reaction of 1-Tetralone Enolate Ions (8b) with *o*-Iodoaniline (1) in DMSO. The following procedure is representative of all these reactions. They were carried out in a 50 mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 20 mL of dry and deoxygenated DMSO under nitrogen was added 2.55 mmol (0.286 g) of *t*-BuOK and 2.50 mmol (0.365 g) of 1-tetralone. After 15 min, **1** (0.50 mmol, 0.110 g) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate and water. The mixture was extracted with methylene chloride, and the organic extract was washed with water, dried over anhydrous Na_2SO_4, and then quantified by GLC using the internal standard method. The iodide ions in the aqueous solution were determined potentiometrically.

Alternatively, in other runs the solvent was removed under reduced pressure and the residue obtained was purified by radial TLC (eluted with petroleum ether (60−80 °C): acetone).

Photostimulated Reaction of 1-Tetralone Enolate Ions (8b) with 1 in Liquid Ammonia. The following procedure is representative of all these reactions. Into a three-necked, 250 mL, round-bottomed flask equipped with a coldfinger condenser charged with dry ice−ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 150 mL of ammonia previously dried with sodium metal under nitrogen. The *t*-BuOK (2.0 mmol) and 1-tetralone (1.5 mmol) were added. To this solution was added 0.5 mmol of **1**, and the mixture was irradiated for 120 min. The reaction was quenched by addition of ammonium nitrate in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with methylene chloride, and the organic extract was washed with water and dried over anhydrous Na_2SO_4. The iodide ions in the aqueous solution were determined potentiometrically. The product was quantified by GLC using the internal standard method. In other runs, the solvent was removed under reduced pressure and the residue obtained was purified by radial TLC (eluted with petroleum ether (60−80 °C): acetone).

Isolation and Identification of Products. 2-Pyridin-2-yl-1*H*-indole (5a). Compound **5a** was purified by radial TLC (eluent: gradient 98−90% petroleum ether:acetone); light yellow crystals were obtained. Mp: 150−152 °C (lit.[28] mp 154−155 °C). ^{1}H NMR ($CDCl_3$) δ_H: 9.91 (1H, br s); 8.56 (1H, ddd, J = 4.8, 1.8, 1.1); 7.79 (1H, td, J = 8.0, 1.1); 7.68 (1H, td, J = 8.0, 1.8); 7.64 (1H, dt, J = 8.0); 7.35 (1H, br d, J = 8.0); 7.23−7.05 (3H, cplx m); 7.01 (1H, dd, J = 2.2, 0.7). ^{13}C NMR ($CDCl_3$) δ_C: 150.44; 149.07; 136.72; 136.59; 129.10; 123.11; 121.93; 121.12; 120.09; 119.88; 111.36; 100.58. GC/MS EI, *m*/*z*: 195 (13); 194 (100); 193 (34); 167 (8); 166 (8); 97 (10); 89 (10); 83 (6); 78 (7); 63 (6).

2-Pyridin-4-yl-1*H*-indole (5b). Compound **5b** was purified by radial TLC (eluent: gradient 100−70% petroleum ether/acetone); white crystals were obtained. Recrystallization from ethanol produces needlelike white crystals. Mp: 204−206 °C (lit.[29] mp 208−209 °C). ^{1}H NMR (CD_3COCD_3) δ_H: 10.91 (2 H, br s); 8.61 (2 H, dd, J = 4.4, 1.5); 7.78 (1H, dd, J = 4.4, 1.8); 7.63 (1H, br d, J = 7.9); 7.45 (1H, dd, J = 7.9, 0.74); 7.22−7.03 (3H, cplx.m). ^{13}C NMR (CD_3COCD_3) δ_C: 151.30; 140.32; 138.91; 135.89; 129.80; 123.97; 121.81; 120.98; 119.91; 112.43; 102.79. GC/MS EI, *m*/*z*: 195 (14); 194 (100); 193 (20); 167 (7); 166 (9); 140 (6); 139 (8); 97 (11); 90 (10); 89 (12); 83 (6); 70 (9).

2-Phenyl-3*H*-benzo(*e*)indole (7). Compound **7** was purified by radial TLC (eluent: hexanes); white crystals were obtained. Mp: 135−136 °C (lit.[30] mp 132 °C). ^{1}H NMR ($CDCl_3$) δ_H: 8.62 (1H, br s); 8.26 (1H, br d, J = 8.0); 7.89 (1H, br d, J = 8.0); 7.72−7.68 (2H, cplx m); 7.62−7.24 (8H, cplx m). ^{13}C NMR ($CDCl_3$) δ_C: 136.11; 133.25; 132.47; 129.37; 129.07; 128.61; 128.07; 127.35; 125.84; 124.84; 124.30; 123.52; 123.33; 122.95; 112.50; 99.32. GC/MS EI, *m*/*z*: 244 (21); 243 (100); 242 (13); 215 (8); 140 (9); 139 (17); 122 (30); 121 (15); 106 (5); 94 (8). Compound **7** was quantified by HPLC with $MeOH/H_2O$ (75:25) as eluent.

5,10-Dihydroindeno[1,2-*b*]indole (9a). Compound **9a** was purified by radial TLC (eluent: petroleum ether); light yellow crystals were obtained. Mp: 208−210 °C dec (lit.[31] mp 226−227 °C, lit.[32] mp 235 °C dec, lit.[33] mp 249−255 °C dec). ^{1}H NMR (CD_3COCD_3) δ_H: 10.63 (1H, br s); 7.61−7.44 (4H, cplx m); 7.32 (1H, br t, J = 7.4); 7.19 (1H, td, J = 7.4, 1.1); 7.12−7.02 (2H, 10 lines); 3.71 (2H, br s). ^{13}C NMR ($CDCl_3$) δ_C: 147.83; 143.36; 140.69; 135.03; 130.88; 128.80; 126.57; 125.51; 124.79; 121.74;

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120.26; 118.99; 117.29; 112.06; 30.34. GC/MS EI, *m*/*z*: 206 (14); 205 (100); 204 (80); 176 (9); 102 (40); 89 (6); 88 (17).

5,11-Dihydro-6*H*-benzo[*a*]carbazole (9b). Compound **9b** was purified by radial TLC (eluent: petroleum ether/acetone 95:5). It was recrystallized from *n*-hexane to give needlelike white crystals. Mp: 160−161 °C (lit.[34] mp 164−165 °C). ^{1}H NMR ($CDCl_3$) δ_H: 8.16 (1H, br s); 7.55 (1H, cplx d, J = 8.0); 7.40−7.07 (7H, cplx m); 3.02 (4H, cplx m). ^{13}C NMR ($CDCl_3$) δ_C: 137.13; 136.67; 133.17; 129.02; 128.61; 127.59; 126.83; 126.75; 122.47; 120.01, 119.93, 118.91; 112.82; 111.25; 29.64; 19.80. GC/MS EI, *m*/*z*: 220 (10); 219 (66); 218 (100); 217 (46); 189 (6); 109 (48); 108 (10); 96 (11); 94 (15).

5,6,7,12-Tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]indole (9c). Compound **9c** was purified by radial TLC (eluent: petroleum ether/acetone 99:1); white crystals were obtained. Mp: 95−96 °C (lit.[35] mp 98−99 °C). ^{1}H NMR ($CDCl_3$) δ_H: 8.05 (1H, br s); 7.62−7.56 (2H, cplx m); 7.42−7.13 (6H, cplx m); 3.14 (2H, t, J = 6.8); 2.94 (2H, m); 2.20 (2H, q, J = 6.8). ^{13}C NMR ($CDCl_3$) δ_C: 142.33; 136.27; 132.68; 131.77; 130.04; 129.75; 127.00; 126.46; 125.13; 122.79; 119.50; 118.64; 114.68; 110.58; 35.28; 26.76; 26.00. GC/MS EI, *m*/*z*: 234 (12); 233 (80); 232 (100); 230 (18); 217 (28); 115 (17); 109 (36); 102 (12).

5,6-Dihydroindeno[2,1-*b*]indole (11a). Compound **11a** was purified by radial TLC (eluent: petroleum ether/acetone 98:2). It was recrystallized from chloroform to give colorless needles. Mp: 205−207 °C dec (lit.[25] mp 205 °C dec). ^{1}H NMR ($CDCl_3$) δ_H: 8.24 (1H, br s); 7.87−7.83 (1H, cplx m); 7.64 (1H, br d, J = 7.3); 7.42−7.05 (6H, cplx m); 3.70 (2H, s s). ^{13}C NMR ($CDCl_3$) δ_C: 146.00; 142.49; 140.61; 139.99; 127.56; 127.02; 124.68; 122.55; 122.20; 121.50; 120.39; 119.23; 118.42; 111.77; 31.19. GC/MS EI, *m*/*z*: 206 (15); 205 (100); 204 (69); 176 (13); 102 (32); 89 (9); 88 (22); 76 (7); 75 (8).

5,7-Dihydro-6*H*-benzo[*c*]carbazole (11b). Compound **11b** was purified by radial TLC (eluent: petroleum ether); white needles were obtained. Mp: 99−101 °C (lit.[34] mp 102−103 °C). ^{1}H NMR ($CDCl_3$) δ_H: 8.04−7.98 (1H, cplx m); 7.88 (br NH, overlapped); 7.84 (1H, br d, J = 7.7); 7.33−7.15 (5H, cplx m); 7.07 (1H, td, J = 7.3, 1.5); 2.96 (4H, cplx m). ^{13}C NMR ($CDCl_3$) δ_C: 137.16; 136.16; 133.82; 133.25; 127.94; 126.89; 124.92; 124.27; 122.25; 121.39; 120.53; 119.45; 111.07; 110.69; 29.46; 22.45. GC/MS EI, *m*/*z*: 220 (19); 219 (100); 218 (93); 217 (86); 110 (12); 109 (39); 95 (14); 94 (13); 82 (7); 44 (8).

12,13-Dihydro-7*H*-dibenzo[*a*,*g*]carbazole (12). Compound **12** was purified by radial TLC (eluent: petroleum ether/dichloromethane 99:1); white crystals were obtained. Mp: 191−193 °C (lit.[36] mp 197 °C). ^{1}H NMR ($CDCl_3$) δ_H: 8.53 (1H, br s); 8.40 (1H, br d, J = 8.4); 7.90 (1H, dd, J = 8.0, 1.5); 7.59−7.11 (8H, cplx m); 3.45 (2H, cplx m, J = 8.0); 3.14 (2H, br t, J = 8.0). ^{13}C NMR ($CDCl_3$) δ_C: 135.54; 133.44; 131.42, 129.93; 129.23; 128.94; 128.80; 128.37; 126.70; 126.43; 125.59; 123.60; 123.44; 123.11; 120.90; 119.45; 114.79; 112.79; 29.67; 22.53. GC/MS EI, *m*/*z*: 271 (22); 270 (92); 269 (100); 268 (78); 134 (38); 133 (25); 132 (9); 121 (7); 120 (8); 119 (6). Compound **12** was quantified by HPL with MeOH/H_2O (85:15) as eluent.

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