One Pot Synthesis of Substituted Dihydroindeno[1,2-*b*]indoles and Dihydrobenzo[*a*]carbazoles by Photostimulated Reactions of *o*-Iodoaniline with Carbanions by the $S_{RN}1$ Mechanism

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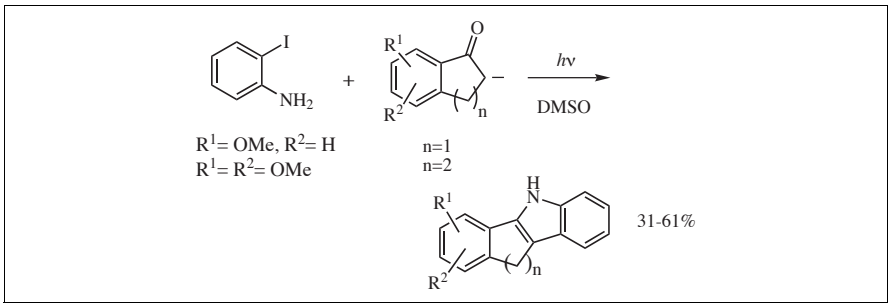

The photostimulated reaction of enolate anions of cyclic aromatic ketones such as substituted indan-1-ones and 3,4-dihydro-2*H*-naphthalen-1-one with *o*-iodoaniline in DMSO affords 1-, 2-, 3-, and 4-methoxy-5,10-dihydroindeno[1,2-*b*]indoles (34-40%), 1,2-, 1,4-, and 2,3-dimethoxy-5,10-dihydroindeno[1,2-*b*]-indoles (31-43%), and 1-, 2-, and 3-methoxy-5,11-dihydro-6*H*-benzo[*a*]carbazoles (42-61%) by the $S_{RN}1$ mechanism in one pot reactions.

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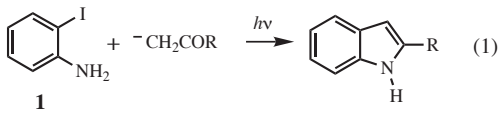
Introduction.

The indole nucleus is present in a family of compounds known to be pharmacologically active as well as in a broad number of other bioactive molecules [1]. This fact accounts for the continued interest in developing new, efficient, and selective synthetic pathways toward these compounds [2].

Classical approaches to indole synthesis include the Fischer method [3]. Within this methodology, the preparation of the *N*-arylhydrazones used as substrates has recently been improved by means of palladium catalysis [4]. Another approach utilized in acidic media is the Bischler synthesis, which has been modified in the last years by Moody [5]. More recently, a new pathway toward the regioselective synthesis of functionalized indoles and six-membered benzo-fused N-, O-, and S- heterocycles has been proposed. The key step of this procedure involves the generation of a benzyne-tethered vinyl or aryllithium compound that undergoes a subsequent intramolecular anionic cyclization to afford indoles and tetrahydrocarbazoles, among other heterocycles [6].

In the indole synthesis area, as in others of organic synthesis, the contribution of transition-metal chemistry has been very important. Thus, transition-metal-based reactions and particularly palladium-catalyzed protocols [7] have been widely employed providing increased functional group tolerance and improved yields. In this field, the preparation of 2-aryl and 2-heteroaryl indoles from 1-alkynes and *o*-iodotrifluoroacetanilide by a copper-catalyzed coupling-cyclization process has been reported more recently [8].

The radical nucleophilic substitution mechanism ($S_{RN}1$) is another interesting methodology through which different indoles have been obtained. Within this approach, one of the most widely studied pathways to ring closure reactions is the $S_{RN}1$ substitution of aromatic compounds that have an appropriate substituent *ortho*- to the leaving group [9]. Following this methodology, the indole synthesis is based on the electron transfer catalyzed nucleophilic substitution of an aromatic halide that bears an amino group *ortho*- to the leaving halide. The substitution product obtained by reaction of this type of substrates with carbanions from acyclic aliphatic and aromatic ketones spontaneously cyclizes to furnish 2-substituted indoles in good yields, as indicated for *o*-iodoaniline (**1**) in equation 1 [10,11].

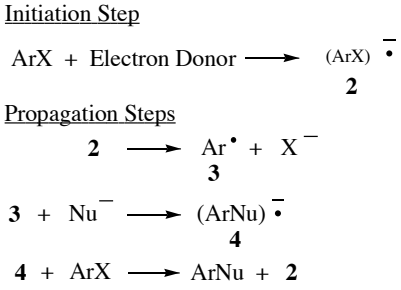


1 (1)

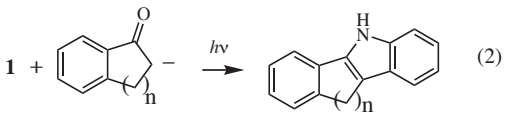
The scope of the $S_{RN}1$ mechanism in ring closure reactions is based on the excellent yields of new C-C bond formation usually achieved by reaction of unactivated aromatic and heteroaromatic substrates (halides being the most widely used leaving groups) with carbanions [12,13], where the reactions are usually performed under photo-initiation in liquid ammonia or in DMSO as solvents.

The mechanism is a chain process depicted in Scheme 1. The initiation step is an electron transfer from the nucleophile to the substrate to afford a radical anion (**2**). In some systems the electron transfer step is spontaneous, but in others light is required to induce the reaction. The propagation steps consist of the fragmentation of the radical anion **2** to afford an aromatic radical **3** and the nucleofugal group. The radical **3** then couples with the nucleophile to afford a radical anion **4**, which by electron transfer to the substrate forms the intermediate necessary to continue the propagation cycle. Overall, Scheme 1 depicts a nucleophilic substitution in which radicals and radical anions are intermediates.

Scheme 1



Fused indoles are important molecules due to their pharmaceutical applications. Besides, they can also be precursors to other planar molecules. Within this subject we have previously informed about the $S_{RN}1$ synthesis, with good yields, of 5,10-dihydroindeno[1,2-*b*]indole (**6a**) and 5,11-dihydro-6*H*-benzo[*a*]carbazole (**6b**) by photostimulated reaction of enolate ions of 1-indanone (**5a**) and 1-tetralone (**5b**) respectively, with **1** in DMSO or in liquid ammonia (equation 2) [14].



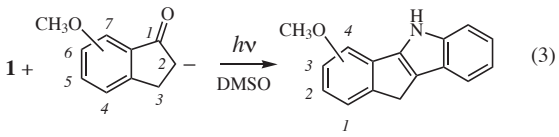
5a, n=1 **6a**, n=1
5b, n=2 **6b**, n=2

We now report an extension of our methodology to the synthesis of methoxy substituted dihydroindeno[1,2-*b*]-indoles and dihydrobenzo[*a*]carbazoles. A wide range of different mono and disubstitution positions is being report. The value of this approach is based on the fact that methoxy functionalized tetracyclic indoles can be easily prepared under mild conditions in one-pot reaction from readily accessible starting materials. Besides, the presence of methoxy-substituents on indole or carbazole nucleus might change their biological activity. For instances, some methoxy indole alkaloids exhibit strong effects on the nervous system [15]. Extensive studies on indole bioisosteres of melatonin have demonstrated that suitable spaced methoxy moieties are important for binding and activation of the melatonin receptors [16].

Results and Discussion.

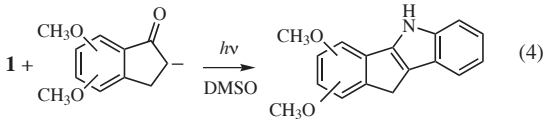
Following the $S_{RN}1$ approach, substrate **1** was reacted under irradiation with the enolate anion of methoxyindan-1-ones (**7a-d**) to give methoxy-5,10-dihydroindeno-[1,2-*b*]indoles (**8a-d**) in 34-40% yield (experiments 1-4, Table 1) (equation 3).

Unfortunately, in addition to the desired product, we also observed aniline. A plausible route to this compound is the reduction of the radicals by hydrogen abstraction from ammonia [17].



7a, 4-methoxy **8a**, 1-methoxy
7b, 5-methoxy **8b**, 2-methoxy
7c, 6-methoxy **8c**, 3-methoxy
7d, 7-methoxy **8d**, 4-methoxy

Similar yields are observed when the dimethoxy derivatives of the indan-1-ones are employed as nucleophiles. The 4,5-, 4,7-, and 5,6-dimethoxy derivatives **9a-c** were inspected. The photostimulated reaction of these nucleophiles with **1** gives dimethoxy-5,10-dihydro[1,2-*b*]indoles (**10a-c**) in 31-43% yields (experiments 5-7, Table 1) (equation 4).



9a, 4,5-dimethoxy **10a**, 1,2-dimethoxy
9b, 4,7-dimethoxy **10b**, 1,4-dimethoxy
9c, 5,6-dimethoxy **10c**, 2,3-dimethoxy

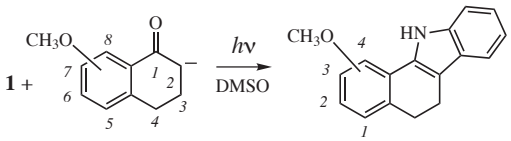
The preparation of methoxy carbazoles was also achieved. The photostimulated reaction of **1** with methoxy-3,4-dihydro-2*H*-naphthalen-1-one enolate ions (**11a-c**) in DMSO affords methoxy-5,11-dihydro-6*H*-benzo[*a*]carbazoles (**12a-c**) in 42-61% yields (experiments 8-10, Table 1) (equation 5).

Table 1

Photostimulated Reaction of **1** with Ketone Enolate Ions [a]

Expt.	**1** (mmol)	Nucleophile (mmol)	X^- (%)[b]	Indole (%)[c]	Aniline (%)[c]
1	0.50	**7a** (2.00)	98	**8a** (34)	37
2	0.75	**7b** (3.00)	87	**8b** (40)	37
3	0.75	**7c** (3.00)	93	**8c** (35) [d]	34
4	0.50	**7d** (2.00)	100	**8d** (34)	49
5	0.62	**9a** (2.50)	99	**10a** (43)	37
6	0.62	**9b** (2.50)	92	**10b** (31)	46
7	0.55	**9c** (2.20)	93	**10c** (43)	41
8	0.50	**11a** (2.00)	94	**12a** (61)	40
9	0.50	**11b** (2.00)	93	**12b** (42)	45
10	0.50	**11c** (2.00)	93	**12c** (49)	36

[a] Photostimulated reactions carried out under N_2 at 40°C in 10 mL of DMSO. [b] Determined potentiometrically. [c] Determined by GC by the internal standard method. [d] Isolated yield.



(5)

11a, 5-methoxy
11b, 6-methoxy
11c, 7-methoxy

12a, 1-methoxy
12b, 2-methoxy
12c, 3-methoxy

Conclusions.

The photostimulated reactions of several mono- and di-substituted cyclic ketone enolate ions derived from 1-tetralone and 1-indanone with substrate **1** in DMSO afford fused indoles in acceptable yields by the $S_{RN}1$ mechanism (34-61%) together with the reduced product aniline. Considering the availability/simplicity of the starting materials, and the readiness of the procedure, this reaction becomes a valid alternative to the synthesis of tetracyclic indoles.

The wide range of mono- and dimethoxy substitution positions covered makes the system of special interest in the field of biological assays and in synthetic organic chemistry.

EXPERIMENTAL

^{1}H nmr (200.13 MHz) and ^{13}C nmr (50.32 MHz) spectra were recorded on a Bruker AC 200 nuclear magnetic resonance spectrometer with $CDCl_3$, CD_3COCD_3 or DMSO-d_6 as solvent. Coupling constants (J) are given in Hz units. Mass spectra were obtained with a GC/MS Shimadzu QP5050A. Melting points were recorded on Büchi 510 and were uncorrected. Gas chromatographic analyses were performed with a Hewlett Packard 5890 series II with a flame ionization detector using a HP1 column (0.53 mm x 5m) and a HP data system. The purification of the products was done with radial tlc using silica gel 60 PF-254 with calcium sulfate (Merck). The distillation at reduced pressure was performed in a Kügelrohr. Irradiation was performed in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (Philips Model HPT, air and water refrigerated). Potentiometric titration of halide ions was performed in a pH meter using an Ag/Ag+ electrode.

t-BuOK was commercially available and used as received. DMSO was distilled under vacuum and stored over molecular sieves (4Å). *o*-Iodoaniline, 5-methoxy-3,4-dihydro-2*H*-naphthalen-1(2*H*)-one (**11a**), 6-methoxy-3,4-dihydro-2*H*-naphthalen-1(2*H*)-one (**11b**), and 7-methoxy-3,4-dihydro-2*H*-naphthalen-1(2*H*)-one (**11c**) were commercially available and distilled under reduced pressure in the Kügelrohr. The substituted 1-indanones **7a-d**, and **9a-c**, were prepared according to well established methods [18-24].

4-Methoxyindan-1-one (**7a**). mp 102° (lit [18] mp 103-104°); ^{1}H nmr ($CDCl_3$): δ 7.33 (m, 2H), 7.01 (m, 1H), 3.89 (s, 3H), 3.02 (t, 2H), 2.64 (t, 2H).

5-Methoxyindan-1-one (**7b**). mp 101° (lit [19] mp 108-110.5°); ^{1}H nmr ($CDCl_3$): δ 7.67 (m, 2H), 6.88 (m, 1H), 3.86 (s, 3H), 3.07 (t, 2H), 2.66 (t, 2H).

6-Methoxyindan-1-one (**7c**). mp 105-107° (lit [19] mp 108-108.5°, lit [20] 107-109°); ^{1}H nmr ($CDCl_3$): δ 7.35 (dd, 3H, J = 8.2, 2.5 Hz), 7.17 (d, 1H, J = 2.5 Hz), 7.15 (d, 1H, J = 8.2 Hz), 3.76 (s, 3H), 3.05 (t, 2H), 2.70 (t, 2H).

7-Methoxyindan-1-one (**7d**). mp 104° (lit [21] mp 108°); ^{1}H nmr (CD_3COCD_3): δ 7,49 (t, 1H, J = 7.7, 7.9 Hz), 6.99 (1H, d, J = 7.4 Hz), 6.79 (d, 1 H, J = 8.2 Hz), 3.93 (s, 3H), 3.06 (t, 2H), 2.65 (t, 2H).

4,5-Dimethoxyindan-1-one (**9a**). mp 78-79° (lit [22] 82°, lit [23] mp 74-75°); ^{1}H nmr ($CDCl_3$): δ 7.15 (d, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 3.00 (t, 2H), 2.63 (t, 2H).

4,7–Dimethoxyindan-1-one (**9b**). mp 122-124° (lit [24] mp 124-125°); ^{1}H mnr (CD_3COCD_3): δ 6.98 (d, 1H), 6.72 (d, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.96 (t, 2H), 2.65 (t, 2H).

5,6-Dimethoxyindan-1-one (**9c**). mp 117-120° (lit [19] mp 118.8-119.5°, lit [23] 117-119°); ^{1}H nmr ($CDCl_3$): δ 7.15 (s, 1H), 6.86 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.02 (t, 2H), 2.64 (t, 2H).

General Procedure for the Photostimulated Reaction of Ketone Enolate Ions **7a-d**, **9a-c**, and **11a-c** with *o*-Iodoaniline (**1**).

The following procedure is representative of all these reactions. They were carried out in a 20 mL three-neck round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer. To 10 mL of dry and degassed DMSO under nitrogen was added 2.02 mmol (0.227 g) of *t*-BuOK and 2.0 mmol (0.352 g) of 3,4-dihydro-1-methoxy-2*H*-naphthalen-1-one (**11a**). After 15 minutes **1** (0.50 mmol, 0.109 g) was added and the reaction mixture was irradiated for 180 minutes. The reaction was quenched with an excess of ammonium nitrate and water (60 mL). The mixture was extracted three times with methylene chloride (20 mL each), the organic extract was washed twice with water, dried over Na_2SO_4, and quantified by gc using the internal standard method. The iodide ions in the aqueous solution were determined potentiometrically. In other experiments, the solvent was removed under reduced pressure. From the remaining residue product purification was accomplished by radial tlc (eluted with petroleum ether (60-80°C):acetone).

1-Methoxy-5,10-dihydroindeno[1,2-*b*]indole (**8a**).

Compound **8a** was purified by radial tlc. It was recrystallized from benzene. White needles, mp 156-157°; ^{1}H nmr ($CDCl_3$): δ

8.23 (s, 1H), 7.66-7.62 (m, 1H), 7.42-7.07 (m, 5H), 6.79 (d, 1H, J = 8.0 Hz), 3.93 (s, 3H), 3.67 (s, 2H); ^{13}C nmr ($CDCl_3$): δ 156.05, 143.22, 140.69, 136.46, 134.22, 128.26, 124.76, 121.93, 121.63, 120.18, 118.96, 112.04, 110.74, 107.86, 55.36, 27.51; ms: m/z 236 (17), 235 (100), 234 (18), 220 (19), 205 (11), 204 (63), 192 (16), 191 (25), 190 (12), 118 (15), 102 (17), 96 (13).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.52; H, 5.58; N, 5.77.

2-Methoxy-5,10-dihydroindeno[1,2-*b*]indole (**8b**).

Compound **8b** was purified by radial tlc. It was recrystallized from ethyl alcohol, white crystals, mp 225-226° dec; ^{1}H nmr (DMSO-d_6): δ 11.43 (s, 1H), 7.52-7.39 (m, 3H), 7.18 (s, 1H), 7.08-6.97 (m, 2H), 6.92 (dd, 1H, J = 8.0, 2.2 Hz), 3.8 (s, 3H), 3.65 (s, 2H); ^{13}C nmr (DMSO-d_6): δ 157.54, 149.59, 143.42, 140.21, 128.19, 124.36, 120.30, 119.19, 118.11, 118.06, 112.29, 112.21, 112.16, 111.94, 55.31, 30.03; ms: m/z 236 (17), 235 (100), 234 (12), 221 (15), 220 (91), 192 (24), 191 (38), 190 (19), 118 (12), 96 (16). HRMS: (EI) *Anal.* Calcd for $C_{16}H_{13}NO$: 235.0997. Found: 235.1032.

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.44; H, 5.48; N, 5.69.

3-Methoxy-5,10-dihydroindeno[1,2-*b*]indole (**8c**).

Compound **8c** was purified by radial tlc. Recrystallization from benzene produces a white needle crystals, mp 206-207° dec; ^{1}H NMR ($CDCl_3$): δ 8.24 (s, 1H), 7.64-7.59 (m, 1H), 7.41-7.35 (m, 2H), 7.22-7.10 (m, 2H), 7.01 (d, 1H, J = 2.6 Hz), 6.75 (dd, 1H, J = 8.0, 2.6 Hz), 3.86 (s, 3H), 3.64 (s, 2H); ^{13}C nmr ($CDCl_3$): δ 158.99, 143.06, 140.66, 139.88, 136.16, 125.73, 124.76, 123.22, 121.79, 120.23, 118.99, 112.06, 109.94, 103.84, 55.57, 29.54; ms: m/z 236 (18), 235 (100), 234 (16), 220 (40), 219 (11), 204 (47), 192 (25), 191 (36), 190 (18), 118 (14), 96 (16). HRMS: (EI) Calcd for $C_{16}H_{13}NO$: 235.0997. Found: 235.1009.

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.76; H, 5.60; N, 5.71.

4-Methoxy-5,10-dihydroindeno[1,2-*b*]indole (**8d**).

Compound **8d** was purified by radial TLC. It was recrystallized from ethyl alcohol. White needles, mp 177-178°; ^{1}H mnr ($CDCl_3$): δ 8.57 (s, 1H), 7.63-7.57 (m, 1H), 7.47-7.39 (m, 1H), 7.17-7.12 (m, 4H), 6.89-6.81 (m, 1H), 3.97 (s, 3H), 3.72 (s, 2H); ^{13}C nmr ($CDCl_3$): δ 152.25, 149.47, 142.39, 140.47, 126.05, 124.57, 124.19, 120.99, 119.96, 119.31, 118.59, 118.50, 111.98, 108.67, 55.44, 30.67; ms: m/z 236 (18), 235 (100), 234 (13), 221 (12), 220 (74), 204 (23), 192 (31), 191 (32), 190 (17), 118 (17), 102 (12), 96 (27). HRMS: (EI) Anal. Calcd for $C_{16}H_{13}NO$: 235.0997. Found: 235.1002.

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.65; H, 5.33; N, 5.97.

1,2-Dimethoxy-5,10-dihydro[1,2-*b*]indole (**10a**).

Compound **10a** was purified by radial tlc. It was recrystallized from benzene. White needles, mp 184-186°; ^{1}H nmr ($CDCl_3$): δ 8.22 (s, 1H), 7.58 (dd, 1H, J = 5.8, 2.9 Hz), 7.42-7.34 (m, 1H), 7.18-7.12 (m, 2H), 7.09 (d, 1H, J = 8.0 Hz), 6.86 (d, 1H, J = 8.0 Hz), 3.99 (s, 3H), 3.90 (s, 3H), 3.76 (s, 2H); ^{13}C nmr ($CDCl_3$): δ 150.82, 146.35, 142.95, 140.53, 139.91, 129.42, 124.92, 121.26, 120.55, 120.20, 118.59, 112.58, 111.93, 111.15, 60.34, 56.30, 27.81; ms: m/z 266 (19), 265 (100), 264 (14), 263 (46), 252 (48), 250 (91), 235 (42), 234 (22), 233 (15), 220 (34), 219 (21), 190 (14), 178 (14), 177 (14), 89 (18), 76 (22), 75 (16). HRMS: (EI) Anal. Calcd for $C_{17}H_{15}NO_2$: 265.1103. Found: 265.0978.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.85; H, 5.71; N, 5.24.

1,4-Dimethoxy-5,10-dihydro-[1,2-*b*]indole (**10b**).

Compound **10b** was purified by radial tlc. It was recrystallized from benzene. Light yellow needles, mp 136-137°; ^{1}H nmr (DMSO-d_6): δ 11.25 (s, 1H), 7.53 (dd, 1H, J = 6.4, 3.3 Hz), 7.49 (dd, 1H, J = 6.6, 2.9 Hz), 7.11-6.98 (m, 2H), 6.93 (d, 1H, J = 9.0 Hz), 6.8 (d, 1H, J = 9.0 Hz), 3.91 (s, 3H), 3.83 (s, 3H), 3.59 (s, 2H); ^{13}C nmr (DMSO-d_6): δ 150.18, 146.68, 141.64, 140.99, 134.63, 125.07, 123.72, 120.40, 119.11, 118.27, 118.14, 112.64, 110.43, 108.65, 55.93, 55.50, 27.39; ms: m/z 266 (19), 265 (100), 250 (49), 235 (20), 234 (32), 222 (28), 207 (30), 191 (13), 179 (10), 178 (13), 133 (10), 76 (10).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.77; H, 5.84; N, 5.30.

2,3-Dimethoxy-5,10-dihydro-[1,2-*b*]indole (**10c**).

Compound **10c** was purified by chromatography on silica gel. Recrystallization from hexane:1,2-dichloroethane produces light yellow crystals, mp 234-235° dec; ^{1}H nmr (DMSO-d_6): δ 11.38 (s, 1H), 7.51-7.40 (m, 2H), 7.24 (s, 1H), 7.23 (s, 1H), 7.07-6.97 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.59 (s, 2H); ^{13}C nmr (DMSO-d_6): δ 148.06, 146.90, 143.99, 140.19, 139.83, 127.84, 124.39, 120.05, 119.14, 118.65, 117.90, 112.18, 110.67, 102.48, 55.91, 55.72, 29.65; ms: m/z 266 (18), 265 (100), 250 (53), 222 (36), 221 (35), 220 (21), 204 (17), 191 (14), 179 (13), 178 (15), 132 (19), 110 (10), 102 (10), 96 (14), 89 (11), 76 (22). HRMS: (EI) Anal. Calcd for $C_{17}H_{15}NO_2$: 265.1103. Found: 265.1115.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.81; H, 5.80; N, 5.27.

1-Methoxy-5,11-dihydro-6*H*-benzo[*a*]carbazole (**12a**).

Compound **12a** was purified by radial tlc. It was recrystallized from benzene as white crystals, mp: 141-142°; ^{1}H nmr ($CDCl_3$): δ 8.13 (s, 1H), 7.55 (d, 1H, J = 7.0 Hz), 7.37-7.33 (m, 1H), 7.25-7.07 (m, 3H), 6.96 (d, 1H, J = 7.7 Hz), 6.79 (d, 1H, J = 8.0 Hz), 3.86 (s, 3H), 3.12-2.90 (m, 4H); ^{13}C nmr ($CDCl_3$): δ 157.05, 137.00, 132.95, 129.91, 127.48, 127.02, 124.22, 122.30, 119.83, 118.80, 112.77, 112.58, 111.04, 109.53, 55.57, 21.37, 19.05; ms: m/z 250 (18), 249 (100), 248 (97), 247 (13), 233 (25), 218 (11), 217 (17), 205 (16), 204 (40), 117 (28), 108 (19), 102 (27), 88 (11).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.98; H, 6.06; N, 5.53

2-Methoxy-5,11-dihydro-6*H*-benzo[*a*]carbazole (**12b**).

Compound **12b** was purified by radial tlc. It was recrystallized from benzene. White crystals, mp 168-169° (lit [25] mp 169°); ^{1}H nmr ($CDCl_3$): δ 8.05 (br.s, 1H); 7.53-7.49 (cplx.m, 1H); 7.35-7.30 (cplx.m, 1H); 7.22-7.06 (cplx.m, 3H); 6.84 (d, 1H, J = 2.6); 6.74 (dd, 1H, J s= 8.4, 2.6); 3.8 (s, 3H); 3.07-2.89 (m, 4H); ^{13}C nmr ($CDCl_3$): δ 158.67, 138.53, 136.78, 133.17, 127.62, 122.09, 121.77, 120.88, 119.80, 118.37, 114.92, 111.34, 110.93, 110.80, 55.30, 29.99, 19.67; ms: m/z 250(18), 249 (100), 248 (83), 247 (27), 234 (20), 233 (20), 217 (12), 205 (18), 204 (47), 124 (12), 117 (26), 108 (21), 102 (34), 88 (12).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.19; H, 6.00; N, 5.65.

3-Methoxy-5,11-dihydro-6*H*-enzo[*a*]carbazole (**12c**).

Compound **12c** was purified by radial tlc. It was recrystallized from benzene. White crystals, mp 126-127° (lit [26] mp 131-133°); ^{1}H nmr ($CDCl_3$): δ 8.12 (s, 1H), 7.54 (d, 1H, J = 7.5 Hz), 7.33 (d, 1H, J = 7.0 Hz), 7.20-7.07 (m, 3H), 6.86 (d, 1H, J = 2.6 Hz), 6.69 (dd, 1H, J = 8.0, 2.6 Hz), 3.82 (s, 3H), 2.94 (s, 2H); ^{13}C nmr ($CDCl_3$): δ 158.50, 137.00, 132.98, 129.80, 129.13, 128.72, 127.43, 122.39, 119.83, 118.80, 113.25, 111.18, 111.09, 106.49, 55.38, 28.62, 19.91; ms: m/z 250 (18), 249 (100), 248 (100), 247 (30), 234 (11), 233 (19), 217 (21), 205 (25), 204 (51), 117 (12), 109 (12), 108 (11), 102 (26), 88 (11).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.12; H, 5.79; N, 5.48.

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