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Synthesis of Carbazoles by Intramolecular Arylation of Diarylamide Anions

María E. Budén, Victoria A. Vaillard, Sandra E. Martin,* and Roberto A. Rossi*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

rossi@fcq.unc.edu.ar

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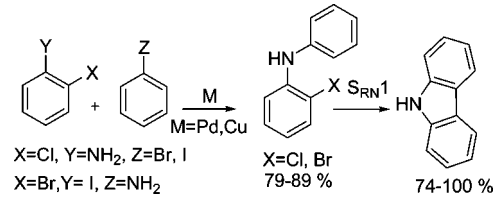

The synthesis of a series of substituted 9*H*-carbazoles by the photostimulated $S_{RN}1$ substitution reaction with diarylamines as starting substrate was performed. The diarylamines were obtained by two approaches, the Pd-catalyzed reactions (Buchwald−Hartwig) or Cu-catalyzed reactions of 2-haloanilines with aryl halides, or 2-bromoiodobenzene with anilines, with moderate to very good isolated yields (45−89%). Through an intramolecular C−C bond formation of diarylamines by the $S_{RN}1$ mechanism, carbazoles were achieved. These reactions proceeded synthetically in very good to excellent yields (81−99%) in liquid ammonia and DMSO. The reaction of *N*-(2-bromophenyl)-2-phenylbenzenamine gave 1-phenyl-9*H*-carbazole (38%) and the isomer 9*H*-tribenz[*b*,*d*,*f*]azepine (58%). By using this methodology, 9*H*-carbazoles, substituted 9*H*-carbazoles, benzocarbazoles, and even 3,3′-bi(9*H*-carbazole) were obtained by a double $S_{RN}1$ reaction with benzidine.

Introduction

Condensed heterocyclic compounds are playing increasingly important roles as synthetic building blocks and pharmacophores.[1] Carbazoles are heteroaromatic compounds which display a wide variety of biological activity and hence are attractive synthetic targets.[2] Their particularly interesting pharmacological properties related to the planarity of the system and consequently to its DNA-chain intercalating ability make them suitable for antineoplastic or mutagenic applications.[3]

Recently, new synthetic methods of carbazoles carbazomycin B, rimcazole, and ellipticine were development (Figure 1).[4] Furthermore, the anti-inflammatory properties of carbazomycin B,[5] antipsychotic properties of rimcazole,[6] and the antitumor properties of ellipticine derivatives[7] were reported. Carbazoles are also widely used as building blocks for potential organic

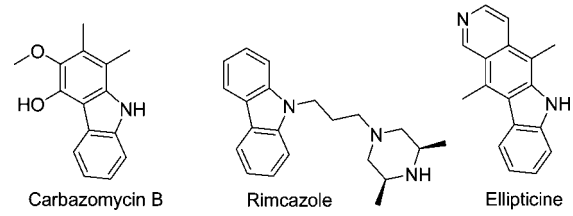

FIGURE 1. Therapeutically valuable carbazole alkaloids.

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semiconductors,[8] organic light-emitting diodes,[9] and electroluminescent materials.[10]

Considerable effort has been directed to the improvement of efficient methods for the construction of these ring systems.[2,11] Intramolecular direct arylation reactions have been extensively utilized in organic synthesis as a route to numerous complex polycyclic ring systems as carbazoles.[12] Fagnou et al. developed new conditions employing electron-rich *N*-heterocyclic carbene (NHC) ligands to promote direct arylation of a broad range of aryl chlorides to form six- and five-membered ring biaryls.[13] In addition, the synthesis of Mukonine (carbazole natural product) was carried out in three steps with very good yield by a direct intramolecular arylation process.[14] Very recently, for instance, Jordan-Hore et al. reported a new Pd(II)-catalyzed intramolecular C−H bond amination to synthesize carbazoles in good to excellent yields.[15]

Although a number of useful synthetic procedures to prepare these compounds have been developed,[11] several limitations still need to be overcome. Most of these procedures have involved several steps, and the overall yields were in general not very good. Moreover, the starting materials were often not readily available. One simple, efficient, and general method to synthesize carbazole would be desirable because of the growing interest of these particular heterocycles.[16]

On the other hand, the unimolecular radical nucleophilic substitution, or $S_{RN}1$ reaction, is an alternative process by which an aromatic nucleophilic substitution is achieved. It involves a chain process with radical and radical anions as intermediates. Since the scope of this reaction has increased considerably over the last decades, nowadays it serves as an important synthetic strategy.[17] The initiation step is an electron transfer (ET) from a suitable donor (i.e., the nucleophile or the base) to the substrate to afford a radical anion. In some systems, the ET step is spontaneous; however, in others light, electrons from dissolved alkali metals in liquid ammonia or from a cathode or inorganic salts (i.e., Fe^{2+} or SmI_2) can initiate the reaction.

Several nucleophiles such as carbanions and heteroatom anions can be used for $S_{RN}1$ reactions to form new C−C or C−heteroatom bonds in good yields. An exception to this is the reaction of aromatic amide ions with aromatic substrates. In these cases, both C−N and C−C bond formations are achieved instead. For instance, the *intermolecular* reaction of phenylamide anion with iodobenzene initiated by K metal in liquid ammonia afforded diphenylamine (19%), and 2- (11%) and 4-biphenylamines (11%).[18] When 2-naphthylamide ions reacted by the photostimulated $S_{RN}1$ reaction with iodoarenes, 1-aryl-2-naphthylamines were regioselectively formed in 45−63% yields, with only 3−6% of *N*-arylation.[19] Additionally, the anion of azaheterocycles such as pyrrole and 4-methylimidazole gave only C−C bond formation.[20,21]

Furthermore, a synthetic strategy using the $S_{RN}1$ reaction as a main tool to obtain heterocyclic compounds was developed. When a substrate has both the leaving group and the nucleophilic center, the *intramolecular* reaction affords a cyclic product.[22] This method has been recently applied to the synthesis of 1-phenyl-1-oxazolino-indan derivatives and related compounds,[23] and to the synthesis of aporphine and homoaporphine alkaloids by ortho-arylation of phenoxide ions.[24]

Although the syntheses of phenanthridines and benzophenanthridines by intramolecular ortho-arylation of benzyl amide ions with aryl halides are known,[25] so far there has been no instance of the intramolecular arylation of the anion of diarylamines with a suitable leaving group in a pendant aryl moiety to obtain carbazoles.

Herein, we report our results on the synthesis of substituted 9*H*-carbazoles by the photostimulated $S_{RN}1$ substitution reaction using diarylamines as starting substrates. The synthesis of diarylamines by two different methods is also reported.

Results and Discussion

A Pd-catalyzed reaction of anilines with aryl halides or Buchwald−Hartwig procedure was described as a synthetic

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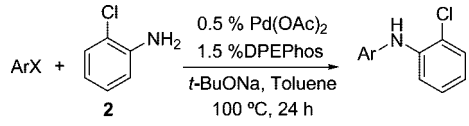
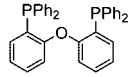
SCHEME 1



ArX = Iodobenzene (**1a**)	**3a** (85%)
4-Iodobiphenyl (**1b**)	**3b** (80%)
1-Bromo-4-*t*-butybenzene (**1c**)	**3c** (83%)
2-Bromonaphthalene (**1d**)	**3d** (79%)
9-Bromophenantrene(**1e**)	**3e** (80%)
4-Bromobenzophenone(**1f**)	**3f** (66%)



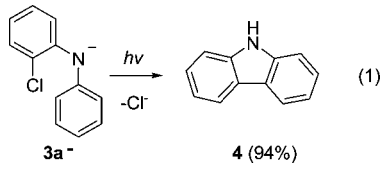
DPEPhos

method to obtain diarylamines.[26] When we carried out the Pd-catalyzed reaction of PhI (**1a**) with 2-chloroaniline (**2**) using DPEPhos as ligand and *t*-BuONa as base in toluene at 100 °C,[27] 2-chloro-*N*-phenylbenzenamine (**3a**) was formed in 85% isolated yield (Scheme 1).

With use of the same procedure as described above, the Pd-catalyzed reaction of aniline **2** with different aryl halides (**1b**−**f**) afforded the corresponding diarylamines (**3b**−**e**) with 66−83% isolated yield (Scheme 1).

Alternatively, our aim to pursue an inexpensive, convenient, and greener procedure for the synthesis of *o*-halodiarylamines led us to explore the viability of employing Cu(I)-catalyzed reactions. Recently, Buchwald et al. developed a new Cu(I)-catalyzed monoarylation of anilines with iodides and bromides, which gave diarylamines in moderate to good yields.[28] In our case, the reaction was carried out with CuI as catalyst, K_3PO_4 as base, and pyrrole 2-carboxylic acid (L) as ligand in DMSO at 100 °C during 20 h. When 2 equiv of **2** reacted with 1 equiv of PhI under these conditions, diarylamine **3a** was obtained in 60% isolated yield.

When diarylamine **3a** was treated with 2 equiv of *t*-BuOK in liquid ammonia, anion **3a**$^-$ was formed. After 60 min of irradiation, a 94% yield of 9*H*-carbazole (**4**) was obtained (eq 1) (entry 1, Table 1).



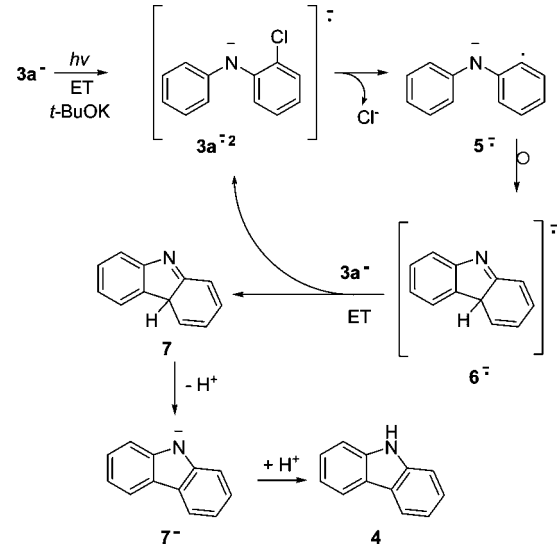
The same result was obtained with 30 min of irradiation, and even with 10 min of irradiation **4** was formed in 80% yield (entries 4 and 5, Table 1). There was no reaction in 60 min in dark conditions (entry 2, Table 1), and inhibition was observed when anion **3a**$^-$ was irradiated in the presence of 1,4-dinitrobenzene, a well-known inhibitor of $S_{RN}1$ reactions (entries 3 and 6, Table 1).

It is important to notice that the acidic hydrogen of carbazole **4** should be more acidic than that of diarylamine **3a**. Even though we do not know the pK_a of carbazole **4** and diarylamine **3a** in liquid ammonia, the pK_a of **4** is 19.9 in DMSO,[29] and as a model of the amine **3a**, the diphenylamine has a pK_a of 25.0 in the same solvent.[29] Moreover, when the reaction was carried out with only 1 equiv of *t*-BuOK, only 52% of **4** was formed, indicating that **4** is deprotonated by anion **3a**$^-$ (entry 7, Table 1).

The photostimulated reaction of anion **3a**$^-$ was also carried out in THF as solvent, and carbazole **4** was obtained with 81% yield (entry 8, Table 1). In this reaction the reduction product diphenylamine increased up to 11% yield. Alternatively, DMSO proved to be an appropriate solvent for this photostimulated reaction (entry 9, Table 1).

The lack of formation of products in dark conditions or the inhibition of the reaction when irradiated in the presence of 1,4-dinitrobenzene indicated that product **4** could be formed by the $S_{RN}1$ mechanism. The reaction of **3a** with *t*-BuOK in excess afforded amide anion **3a**$^-$. The initiation step is the photoinduced ET to yielding radical dianion **3**$^{\bullet 2-}$.[30] Fragmentation of the C−Cl bond of **3**$^{\bullet 2-}$ gave the distonic radical anion **5**$^{\bullet -}$ and Cl$^-$ anion. The intermediate radical anion **5**$^{\bullet -}$, via an intramolecular C−C arylation, yielded the conjugated radical anion **6**$^{\bullet -}$.[31] An ET from **6**$^{\bullet -}$ to **3a**$^-$ afforded intermediate **7** and radical dianion **3**$^{\bullet 2-}$, propagating the reaction. Intermediate **7** gave anion **7**$^-$ under these basic reaction conditions. Upon acidification of the reaction media, product **4** was formed (Scheme 2).

SCHEME 2



The acid−base reaction of **3b**−**c** with *t*-BuOK in excess in DMSO gave amide anions **3b**$^-$ and **3c**$^-$. After 60 min of irradiation 3-phenyl-9*H*-carbazole (**8**) and 3-*tert*-butyl-9*H*-carbazole (**9**) were obtained in 94% and 99% yields, respectively (entries 10 and 12, Table 1).

Alternatively, the photostimulated reaction of anions **3b**$^-$ and **3c**$^-$ was carried out in NH_3 liquid as solvent, and both carbazoles **8** and **9** were obtained with 96% yield (entries 11 and 13, Table 1).

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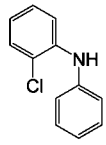
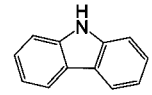
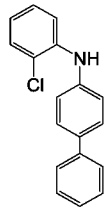
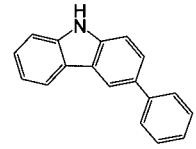
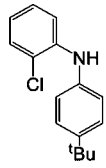
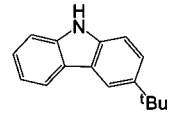
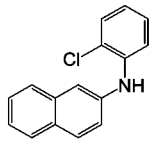
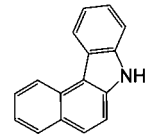
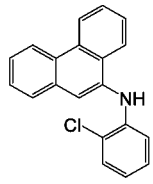
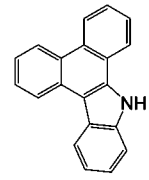
(30) The possibility of an intramolecular ET from the amide ion to the chloroarene cannot be ruled out. The fact that the reaction is inhibited by 1,4-DNB indicates that radical anions are intermediates. Probably *t*-BuO$^-$ ion (pK_a of *t*-BuOH is 32.2 in DMSO) is a better electron donor than diphenylamide ion of lower pK_a, see ref 29.

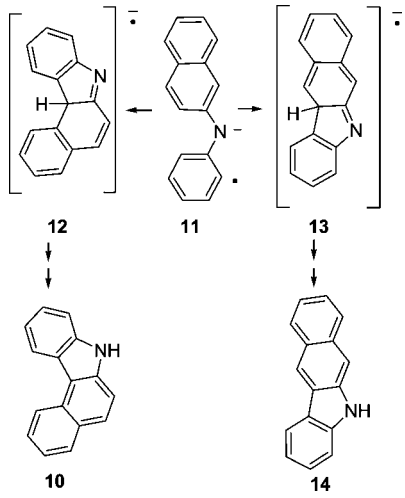
(31) The conjugated radical anion **6** is ca. 27 kcal/mol more stable than the distonic radical anion **5** (AM1/UHF method), this being the driving force of the coupling reaction.

TABLE 1. Intramolecular Photostimulated Reactions of Chloro Diarylamines[a]

Entry	Substrate	Solvent	Substrate recovered %[b]	Conditions	Product	Yield %[b]	Cl^- %[c]
1	 **3a**	NH_3	-	*hv*, 60 min	 **4**	94 (93)	98
2		NH_3	97	dark, 60 min		-	< 7
3[d]		NH_3	22	*hv*, 60 min		75	78
4		NH_3	-	*hv*, 30 min		94	99
5		NH_3	15	*hv*, 10 min		80	82
6[d]		NH_3	36	*hv*, 10 min		63	65
7[e]		NH_3	20	*hv*, 60 min		52[f]	76
8		THF	-	*hv*, 120 min		81[g]	93
9		DMSO	-	*hv*, 60 min		87	88
10	 **3b**	DMSO	-	*hv*, 60 min	 **8**	94 (86)	100
11		NH_3	-	*hv*, 60 min		96	98
12	 **3c**	DMSO	-	*hv*, 60 min	 **9**	99 (94)	100
13		NH_3		*hv*, 60 min		96	100
14[h]	 **3d**	DMSO	-	*hv*, 60 min	 **10**	85	100
15[h]		NH_3		*hv*, 60 min		97	100
16	 **3e**	DMSO	-	*hv*, 30 min	 **15**	98 (95)	97
17		NH_3	-	*hv*, 30 min		99 (90)	100

[a] The reactions were performed in 150 mL of liquid ammonia (or in 6 mL of DMSO), with 1 equiv of **3** and 2 equiv of *t*-BuOK, and irradiated for 60 min with two 400-W lamps emitting maximally at 350 nm (refrigerated with air and water) unless otherwise indicated. [b] Yields were determined by GC (internal standard method). Isolated yields in parentheses. [c] Chlorine anions were determined potentiometrically. [d] 30 mol % of 1,4-dinitrobenzene was added. [e] The reaction with 1 equiv of **3a** and 1 equiv of *t*-BuOK. [f] The reduction product diphenylamine was formed in 16% yield. [g] Diphenylamine was formed in 11% yield. [h] 5*H*-benzo[*b*]carbazole **14** was detected by GC-MS.

SCHEME 3

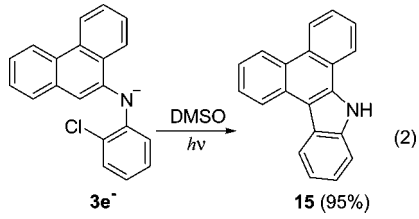


In the photostimulated reaction of anion $\mathbf{3d}^-$ in DMSO, prepared from **3d** and *t*-BuOK in excess, and after 60 min of irradiation, 7*H*-benzo[*c*]carbazole (**10**) was achieved in 85% yield (entry 14, Table 1).

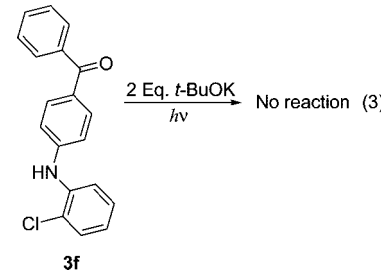
In this reaction, after the ET to $\mathbf{3d}^-$ and fragmentation of the C−Cl bond of the resulting radical dianion, the distonic radical anion intermediate $\mathbf{11}^{\bullet-}$ is formed. The radical anion $\mathbf{11}^{\bullet-}$ has two possibilities of coupling in the naphthyl moiety to give the conjugated radical anions, in position one to afford **12**, which ultimately yields carbazole **10**, and in position three to afford **13**, and finally 5*H*-benzo[*b*]carbazole **14** (Scheme 3). It is known that position one is more reactive toward radicals than position three.[25]

By GC-MS we found a small amount of a compound with the same molecular weight as **10**, which could be **14**. We performed the same reaction in liquid ammonia as solvent, so as to have more selectivity due to temperature difference (about 60 °C), and in this photostimulated reaction we found 97% of product **10**, and only a trace of this impurity (entry 15, Table 1).

Furthermore, in the photoinitiated reaction of anion $\mathbf{3e}^-$ in DMSO as a solvent (30 min) 13*H*-13-aza-indeno[1,2-*l*]phenanthrene (**15**) was formed in 95% isolated yield (entry 16, Table 1) (eq 2). This reaction provides an access to the pentacyclic system **15** in very good yields. Product **15** was obtained in liquid ammonia in 90% isolated yield (entry 17, Table 1).



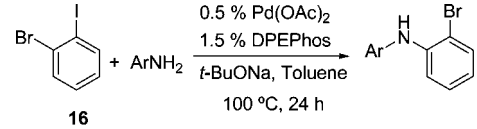
On the other hand, in the acid−base reaction of **3f** with *t*-BuOK in excess, amide anion $\mathbf{3f}^-$ was formed, and there was no reaction at all after 90 min of irradiation in liquid ammonia, and substrate **3f** was quantitatively recovered (eq 3).



This absence of reaction may suggest that when anion $\mathbf{3f}^-$ received an electron, radical dianion $\mathbf{3f}^{\bullet 2-}$ was formed, but the C−Cl bond in this intermediate did not fragment. It was reported that stabilized radical anions with Ar-CO moiety holding a pendant aryl moiety with halogens as substituent did not fragment. This was discussed in terms of the energetic of the intramolecular ET from π-ArCO radical anion to σ-C−X bond.[32]

Another approach to the synthesis of diarylamines by the Pd-catalyzed reaction could be through the reaction of 2-bromoiodobenzene (**16**) with arylamines.[26,27] To test the scope of this method we prepared bromo diarylanilines (**18a**−**f**) from the corresponding anilines (**17a**−**f**) and **16** (Scheme 4). In the reaction of **16** with aniline, 2-bromo-*N*-phenylbenzenamine (**18a**) was isolated in 80% yield. Furthermore, the new bromo diarylamines **18b**−**f** were obtained in excellent isolated yields (84−89%).

SCHEME 4



$ArNH_2$ =		
	Aniline (**17a**)	**18a** (80%)
	4-Methoxyaniline (**17b**)	**18b** (85%)
	1-Naphthylamine (**17c**)	**18c** (84%)
	2-Pyrrolylaniline (**17d**)	**18d** (89%)
	2-Phenylaniline (**17e**)	**18e** (89%)
	Bencidine (**17f**)	**18f** (45%)

With the objective of comparing this reaction with the Cu-catalyzed one, the same product was synthesized by using the last reaction with K_3PO_4 as base and pyrrole-2-carboxylic acid (L) as ligand. In this case, 56% of **18a** was isolated. Like the previous approach, the Pd-catalyzed amination gave better yields than the Cu-catalyzed one.

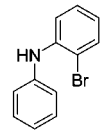
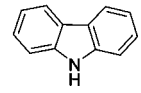
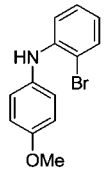
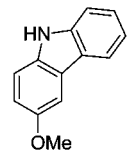
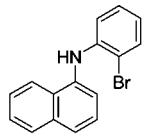
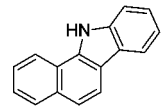
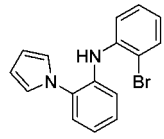
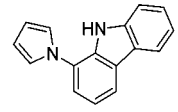
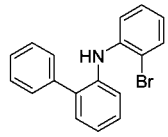
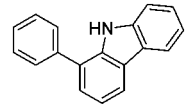
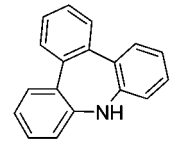
After that, bromo diarylamines were used as substrates in the photoinduced $S_{RN}1$ intramolecular reactions to obtain the corresponding carbazoles. The results are shown in Table 2.

When substrate **18a** was treated with 2 equiv of *t*-BuOK in liquid ammonia, anion $\mathbf{18a}^-$ was formed. When the reaction mixture was irradiated for 120 min, 9*H*-carbazole **4** was obtained in 99% yield (entry 1, Table 2). Moreover, the photostimulated reactions of diarylamines anions $\mathbf{18b}-\mathbf{d}^-$ afforded the expected carbazoles **19**, **20** and the novel carbazole **21** in very good yields (entries 2−4, Table 2).

However, when anion $\mathbf{18e}^-$ reacted in liquid ammonia and was irradiated for 60 min, carbazole **22** and the isomeric product **23** were obtained in 38% and 58% isolated yield, respectively (entry 5, Table 2). In this case, after ET to $\mathbf{18e}^-$ and

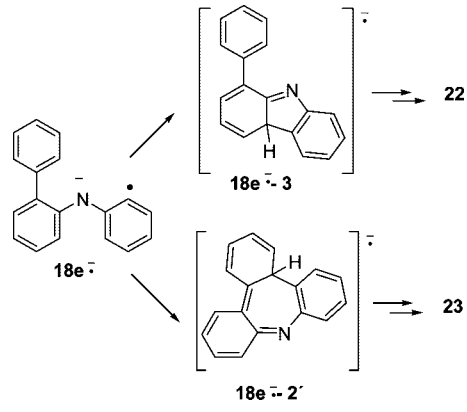
(32) Baumgartner, M. T.; Jimenez, L. B.; Pierini, A. B.; Rossi, R. A. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 1092–1097.
(33) AM1/UHF method.

TABLE 2. Synthesis of Bromo Diarylamines by Pd-Catalyzed Reaction and Carbazoles by the Photostimulated $S_{RN}1$ Reaction[a]

Entry	Diarylaniline	Solvent	Carbazole	Yield %[b]	Br^- %[c]
1	 **18a**	NH_3	 **4**	99	96
2	 **18b**	NH_3	 **19**	86	96
		DMSO		83[d] (80)	88
3	 **18c**	NH_3[e]	 **20**	68	72
		NH_3		87 (85)	96
		DMSO		74	97
4	 **18d**	NH_3	 **21**	99 (91)	100
5	 **18e**	NH_3	 **22**	38 (32)	100
			 **23**	58(52)	

[a] The reactions were performed in 150 mL of liquid ammonia (or 6 mL of DMSO) with 1 equiv of substrate and 2 equiv of *t*-BuOK irradiated for 60 min with two 400-W lamps emitting maximally at 350 nm (refrigerated with air and water). [b] Yields were determined by GC (internal standard method). Isolated yields in parentheses. [c] Bromide anions were determined potentiometrically. [d] The reduction product was formed in 6% yield. [e] The irradiation time was 30 min and the substrate was recovered in 27% yield.

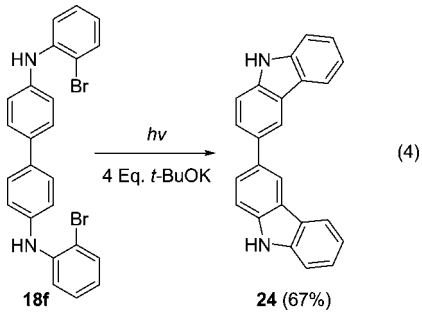
SCHEME 5



fragmentation of the C−Br bond of the radical dianion intermediate, the distonic radical anion intermediate **18e**$^{\bullet-}$ was formed. This intermediate has two possibilities of coupling in the phenyl moiety to give the conjugated radical anions, in position 3 to give **18e**$^{\bullet-}$**−3** and ultimately 1-phenyl-9*H*-carbazole (**22**), and in position 2′ to give **18e**$^{\bullet-}$**−2′** and finally 9*H*-tribenz[*b*,*d*,*f*]azepine (**23**) (Scheme 5).

Two isomers are formed with this substrate due to the fact that, in the coupling reaction, both positions are favorable. The coupling reaction in position 3 is exothermic by about 37 kcal/mol and in position 2′ is exothermic by 42 kcal/mol. Moreover, radical anion **18e**$^{\bullet-}$**−2′** is about 5 kcal/mol more stable than radical anion **18e**$^{\bullet-}$**−3**.[33]

To extend the application of the methodology developed to obtain carbazoles, we evaluated the reactivity of an aryldiamine in this system. In the photostimulated reaction of **18f** with 4 equiv of *t*-BuOK in DMSO for 90 min, 3,3′-bi(9*H*-carbazole) (**24**) was achieved in 67% isolated yield (eq 4).



18f **24** (67%) (4)

Conclusions

In this work we present a simple and readily available method for the synthesis of 9*H*-carbazoles, substituted 9*H*-carbazoles, benzo-9*H*-carbazoles, 13*H*-13-aza-indeno[1,2-*l*]phenanthrene, and 3,3′-bi(9*H*-carbazole) using diarylamines as starting materials. The synthetic strategy involves a first step of arylation of amines followed by an $S_{RN}1$ substitution reaction in DMSO, NH_3, or THF as solvent under photoinitiation. Particularly, 3,3′-bi(9*H*-carbazole) is achieved by a double reaction of a benzidine.

The synthesis of diarylanilines can be done by two approaches, the reaction of 2-chloroaniline with aryl halides or 2-bromoiodobenzene with anilines, by Pd- or Cu-catalyzed reactions.

The $S_{RN}1$ mechanism accounts for the substitution reactions and the products are obtained in very good to excellent yields. Although many substituents can be compatible with $S_{RN}1$ reactions,[17] in this case only *t*-Bu, OCH_3, and pyrrolyl were utilized as substituents for carbazole synthesis.

Considering the availability and/or simplicity of the starting materials, and the readiness and mild conditions of the procedure involved, we have demonstrated that this can be a general methodology for the synthesis of this family of compounds.

Experimental Section

Representative Procedure for Buchwald−Hartwig Reactions. An oven-dried Schlenk tube was charged with *o*-chloroaniline (2.4 mmol), $Pd(OAc)_2$ (0.010 mmol), and DPEphos (0.015 mmol), evacuated, and filled with nitrogen. Iodobenzene (2 mmol) was added to the flask via syringe, followed by toluene (4 mL). The resulting mixture was stirred for 5 min at room temperature, affording a clear yellow solution. The flask was opened, solid *t*-BuONa (2.8 mmol) was added in one portion, and the solution turned a deep red. The reaction tube was purged for 3 min with nitrogen, and the mixture was heated with stirring to 100 °C until the aryl halide was consumed as judged by GC analysis. The mixture was then cooled to room temperature and taken up in methylene chloride. The resulting solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by chromatography on silica gel affording the product.

General Procedure for the Cu-Catalyzed Cross-Coupling of Anilines with Aryl Halides.[28] An oven-dried Schlenk was charged with K_3PO_4 (424 mg, 2.0 mmol). The tube was sealed and the base was flame-dried under vacuum and cooled under a purge of N_2. CuI (19 mg, 0.10 mmol), pyrrole 2-carboxylic acid (22 mg, 0.20 mmol), and a magnetic stir bar were added to the cooled vessel. The tube was then evacuated and backfilled with nitrogen. The evacuation/backfill sequence was repeated two further times. Aryl halide (1.0 mmol), amine (2.0 mmol), and DMSO (0.50 mL) were then added by syringe. The vessel was immersed in a preheated oil bath and the reaction mixture was stirred vigorously until TLC and/or GC analysis of the crude reaction mixture indicated that the aryl halide had been completely consumed.

2-Chloro-*N*-phenylbenzenamine (3a). The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (100:0 → 80:20). Colorless oil was isolated in 85% yield (346.0 mg, 1.70 mmol). ^{1}H NMR (CCl_3D) δ 6.14 (1H, s), 6.84 (1H, m), 7.07 (1H, m), 7.17 (3H, m), 7.31 (1H, dd, J = 8.2, 1.2 Hz), 7.37 (3H, m). ^{13}C NMR (CCl_3D) δ 115.50, 120.13, 120.32, 121.44, 122.60, 127.38, 129.41, 129.70, 140.23, 141.45. GC-MS (*m*/*z*) 205 (M^+ + 2, 23), 203 (M^+, 68), 169 (12), 168 (100), 167 (78), 166 (11), 84 (36), 77 (13), 51 (16).[34]

***N*-(2-Chlorophenyl)biphenyl-4-amine (3b).** The product was purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10 → 60:40). White crystals were isolated in 80% yield (446.5 mg, 1.60 mmol). ^{1}H NMR (CCl_3D) δ 6.15 (1H, s), 6.82 (1H, m), 7.15 (1H, m), 7.22 (2H, m), 7.37 (3H, m), 7.43 (2H, m), 7.57 (4H, m). ^{13}C NMR (CCl_3D) δ 115.93, 120.09, 120.59, 121.74, 126.66, 126.85, 127.45, 128.05, 128.76, 129.78, 135.38, 140.04, 140.65, 140.91. GC-MS (*m*/*z*) 281 (M^+ + 2, 34), 280 (19), 279 (M^+, 100), 244 (48), 243 (26), 242 (12), 241 (10), 167 (11). Mp 76.4−77.9 °C. HR MS (EI) calcd for $C_{18}H_{14}ClN$ 279.0815, found 279.0820.

***N*-(4-*tert*-Butylphenyl)-2-chlorobenzenamine (3c).** The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (95:5 → 70:30). White crystals were isolated in 83% yield (432.9 mg, 1.67 mmol). ^{1}H NMR (CCl_3D) δ 1.33 (9H, s), 6.05 (1H, s), 6.75 (1H, m), 7.09 (3H, m), 7.22 (1H, m), 7.33 (3H, m). ^{13}C NMR (CCl_3D) δ 31.40, 34.26, 115.01, 119.74, 120.43, 120.90, 126.21, 127.34, 129.59, 138.68, 140.77, 145.85. GC-MS (*m*/*z*) 262 (2), 261 (M^+ + 2, 11), 260 (6), 259 (M^+, 34), 246 (34), 245 (16), 244 (100), 90 (22). Mp 47.0−49.0 °C. HR MS (EI) calcd for $C_{16}H_{18}ClN$ 259.1128, found 259.1133.

***N*-(2-Chlorophenyl)naphthalen-2-amine (3d).** The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (90:10 → 70:30). White crystals were isolated in 79% yield (400.5 mg, 1.58 mmol). ^{1}H NMR (CCl_3D) δ 6.29 (1H, s), 6.87 (1H, td, ^1J = 7.7 Hz, ^2J = 1.5 Hz), 7.18 (1H, td, ^1J = 7.6 Hz, ^2J = 1.5 Hz), 7.33 (1H, dd, ^1J = 8.7 Hz, ^2J = 2.3 Hz), 7.40 (3H, m), 7.46 (1H, m), 7.56 (1H, d, J = 2.3 Hz), 7.72 (1H, J = 8.3 Hz), 7.81 (2H, t, J = 8.6 Hz). ^{13}C NMR (CCl_3D) δ 114.90, 116.00, 120.72, 121.28, 121.84, 124.22, 126.52, 126.75, 127.47, 127.66, 129.28, 129.80, 129.93, 134.39, 139.15, 140.14. GC-MS (*m*/*z*) 255 (M^+ + 2, 22), 254 (12), 253 (M^+, 65), 219 (17), 218 (100), 217 (71), 216 (16), 115 (11), 109 (38). Mp 87.3−88.4 °C. HR MS (EI) calcd for $C_{16}H_{12}ClN$ 253.0658, found 253.0663.

***N*-(2-Chlorophenyl)phenanthren-9-amine (3e).** The product was purified by column chromatography on silica gel eluting with petroleum ether/acetone (90:10). Yellow crystals were isolated in 80% yield (482.5 mg, 1.60 mmol). ^{1}H NMR (CCl_3D) δ 6.41 (1H, s br), 6.82 (1H, ddd, ^1J = 7.9 Hz, ^2J = 7.4 Hz, ^3J = 1.5 Hz), 6.94 (1H, dd, ^1J = 8.2 Hz, ^2J = 1.5 Hz), 7.08 (1H, m), 7.45 (1H, dd, ^1J = 7.9 Hz, ^2J = 1.5 Hz), 7.62 (3H, m), 7.69 (1H, s), 7.73 (1H, m), 7.80 (1H, m), 8.15 (1H, dd, ^1J = 8.2 Hz, ^2J = 1.0 Hz), 8.69 (1H, d br, J = 8.2 Hz), 8.77 (1H, d br, J = 8.2 Hz). ^{13}C NMR (CCl_3D) δ 115.86, 119.08, 119.77, 120.77, 122.53, 122.89, 123.21, 125.83, 126.86, 126.93, 127.02, 127.52, 127.83, 128.56, 128.88, 129.52, 131.52, 132.14, 135.40, 141.99. GC-MS (*m*/*z*) 305 (M^+ + 2, 24), 304 (M^+ + 1, 14), 303 (M^+, 67), 269 (19), 268 (100), 267 (80), 266 (17), 165 (15), 134 (60), 134 (22), 119 (14). Mp 118.9−120.3 °C. HR MS (EI) calcd for $C_{20}H_{14}ClN$ 303.0815, found 303.0820.

(4-(2-Chlorophenylamino)phenyl)(phenyl)methanone (3f). The product was purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10 → 70:30). White crystals were isolated in 66% yield (406.5 mg, 1.32 mmol). ^{1}H NMR (CCl_3D) δ 6.38 (1H, s), 6.99 (1H, td, ^1J = 7.8 Hz, ^2J = 1.4 Hz), 7.14 (2H, m), 7.25 (1H, m), 7.44 (1H, dd, ^1J = 7.9 Hz, ^2J = 1.4 Hz), 7.50 (3H, m), 7.59 (1H, m), 7.82 (4H, m). ^{13}C NMR (CCl_3D) δ 115.97, 119.07, 122.98, 124.15, 127.50, 128.15, 129.64,

(34) This compound is commercial. CAS registry no.: 1205-40-9.

130.00, 130.09, 131.75, 132.51, 137.82, 138.37, 146.52, 195.17. GC-MS (*m*/*z*) 310 (5), 309 ($M^+ + 2$, 23), 308 (17), 307 (M^+, 47), 232 (34), 231 (16), 230 (100), 167 (43), 166 (14), 105 (15), 77 (24). Mp 123.3−124.3 °C (lit.[35] mp 123−125 °C).

2-Bromo-*N*-phenylbenzenamine (18a).[36] The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (90:10). Colorless oil was isolated in 80% yield (395.2 mg, 1.60 mmol). ^{1}H NMR (CCl_3D) δ 6.12 (1H, s), 6.78 (1H, t, $J = 7.6$ Hz), 7.08 (1H, t, $J = 7.4$ Hz), 7.20 (3H, m), 7.29 (1H, d, $J = 7.7$ Hz), 7.36 (2H, t, $J = 7.7$ Hz), 7.56 (1H, d, $J = 8.0$ Hz). ^{13}C NMR (CCl_3D) δ 112.22, 115.83, 120.31, 120.93, 122.74, 128.13, 129.49, 133.01, 141.47, 141.63. GC-MS (*m*/*z*) 250 (6), 249 ($M^+ + 2$, 47), 247 (M^+, 49), 169 (14), 168 (100), 167 (97), 166 (18), 139 (12), 84 (57), 77 (11), 71 (11), 51 (16).

2-Bromo-*N*-(4-methoxyphenyl)benzenamine (18b). The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (60:40). Colorless oil was isolated in 85% yield (436.6 mg, 1.58 mmol). ^{1}H NMR (CCl_3D) δ 3.84 (3H, s), 5.97 (1H, s), 6.67 (1H, td, $^1J = 7.8$ Hz, $^2J = 1.5$ Hz), 6.94 (3H, m), 7.13 (3H, m), 7.50 (1H, dd, $^1J = 7.9$ Hz, $^2J = 1.5$ Hz). ^{13}C NMR (CCl_3D) δ 55.50, 110.51, 113.96, 114.71, 119.53, 124.65, 128.10, 132.72, 134.08, 143.22, 156.37. GC-MS (*m*/*z*) 280 (11), 279 ($M^+ + 2$, 78), 277 (M^+, 77), 265 (12), 264 (97), 263 (12), 262 (100), 183 (10), 182 (22), 155 (48), 154 (49), 128 (15), 127 (13), 99 (15), 77 (15), 64 (10), 63 (13). HR MS (EI) calcd for $C_{13}H_{12}BrNO$ 277.0102, found 277.0096.

***N*-(2-Bromophenyl)naphthalen-1-amine (18c).** The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (100:0 → 60:40). White crystals were isolated in 84% yield (471.9 mg, 1.59 mmol). ^{1}H NMR (CCl_3D) δ 6.41 (1H, s), 6.73 (1H, m), 6.87 (1H, dd, $^1J = 8.2$ Hz, $^2J = 1.5$ Hz), 7.10 (1H, m), 7.52 (5H, m), 7.72 (1H, dd, $^1J = 7.4$ Hz, $^2J = 1.5$ Hz), 7.92 (1H, m), 8.05 (1H, m). ^{13}C NMR (CCl_3D) δ 111.21, 115.46, 119.77, 120.19, 122.32, 124.94, 125.93, 126.20, 126.34, 128.20, 128.53, 129.14, 132.77, 134.78, 137.25, 143.13. GC-MS (*m*/*z*) 299 ($M^+ + 2$, 34), 298 (6), 297 (M^+, 35), 219 (11), 218 (79), 217 (100), 216 (26), 109 (67), 94 (13). Mp 74.0−75.0 °C. HR MS (EI) calcd for $C_{16}H_{12}BrN$ 297.0153, found 297.0147.

***N*-(2-(1*H*-Pyrrol-1-yl)phenyl)-2-bromobenzenamine (18d).** The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (60:40). Colorless oil was isolated in 88% yield (551.9 mg, 1.77 mmol). ^{1}H NMR (CCl_3D) δ 5.97 (1H, s), 6.37 (2H, t, $J = 2.2$ Hz), 6.81 (1H, td, $^1J = 7.9$ Hz, $^2J = 1.6$ Hz), 6.88 (2H, t, $J = 2.2$ Hz), 7.04 (1H, td, $^1J = 7.5$ Hz, $^2J = 1.4$ Hz), 7.21 (1H, m), 7.33 (4H, m), 7.52 (1H, dd, $^1J = 7.9$ Hz, $^2J = 1.4$ Hz). ^{13}C NMR (CCl_3D) δ 109.95, 114.22, 117.68, 118.23, 121.73, 121.77, 122.32, 127.51, 128.05, 128.21, 131.38, 133.17, 137.63, 140.23. GC-MS (*m*/*z*) 314 ($M^+ + 2$, 8), 313 (9), 312 (M^+, 8), 234 (17), 233 (100), 232 (20), 231 (10), 204 (11), 116 (31). HR MS (EI) calcd for $C_{16}H_{13}BrN_2$ 312.0262, found 312.0256.

***N*-(2-Bromophenyl)biphenyl-2-amine (18e).** The product was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (75:25). Yellow pale oil was isolated in 78% yield (502.4 mg, 1.55 mmol). ^{1}H NMR (CCl_3D) δ 6.07 (1H, s br), 6.72 (1H, t, $J = 7.5$ Hz), 7.09 (1H, t, $J = 7.5$ Hz), 7.16 (1H, t, $J = 7.6$ Hz), 7.38 (10H, m). ^{13}C NMR (CCl_3D) δ 112.90, 116.12, 119.57, 121.05, 122.54, 127.58, 128.05, 128.21, 128.82, 129.14, 131.02, 132.98, 133.45, 138.72, 138.78, 141.40. GC-MS (*m*/*z*) 326 (13), 325 ($M^+ + 2$, 70), 324 (18), 323 (M^+, 70), 245 (18), 244 (100), 243 (43), 242 (26), 241 (24), 167 (21), 166 (16), 122 (38), 121 (24). HR MS (EI) calcd for $C_{18}H_{14}BrN$ 323.0310, found 323.0292.

***N*^{4},*N*$^{4'}$-Bis(2-bromophenyl)biphenyl-4,4′-diamine (18f).** The crude was extracted with ethyl acetate (3 × 50 mL). The organic extract was dried with anhydrous $MgSO_4$. The product was detected by TLC and HPLC and purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether (75:25). Yellow crystals were isolated in 45% yield (210.8 mg, 0.427 to 0.95 mmol). ^{1}H NMR (CCl_3D) δ 6.15 (2H, s), 6.77 (2H, m), 7.21 (6H, m), 7.32 (2H, dd, $^1J = 8.3$ Hz, $^2J = 1.5$ Hz), 7.56 (6H, m). ^{13}C NMR (CCl_3D) δ 112.34, 116.05, 120.39, 121.06, 127.61, 128.17, 133.05, 135.02, 140.63, 141.29. MS direct injection (*m*/*z*) 497 (20), 496 (70), 495 (78), 494 (M^+, 100), 493 (99), 492 (84), 491 (82), 490 (28), 414 (18), 413 (18), 412 (15), 411 (13), 333 (11), 332 (15), 331 (12), 330 (9), 329 (6), 247 (14), 246 (11), 245 (6), 244 (7), 243 (24), 242 (20), 241 (17), 240 (13), 168 (10), 167 (37), 166 (38), 165 (35), 164 (15), 76 (9), 75 (9), 63 (10). Mp 173.0−175.0 °C. HR MS (EI) calcd for $C_{24}H_{18}Br_2N_2$ 491.9837, found 491.9830.

Representative Procedure for Photostimulated Reactions: Preparation of 9*H*-Carbazole (4) in Liquid Ammonia. The following procedure is representative of all these reactions. Liquid ammonia (150 mL), previously dried over Na metal, was distilled into a 250 mL three-necked, round-bottomed flask equipped with a coldfinger condenser and a magnetic stirrer under a nitrogen atmosphere. The base *t*-BuOK (2.0 equiv, 49.4 mg) and then the substrate 2-bromo-*N*-phenylbenzenamine (**18a**) (1 equiv, 40.7 mg) were added to the liquid ammonia and the solution was irradiated for 30 min. The reaction was quenched with an excess of ammonium nitrate and the liquid ammonia was allowed to evaporate. Water was added to the residue and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic extract was dried over anhydrous $MgSO_4$ then filtered, and the solvent was removed to leave the crude products. The products were separated and isolated by radial thin-layer chromatography on silica gel. In other similar experiments the products were quantified by GC by using the internal standard method. The yield of halide ions in the aqueous solution was determined potentiometrically.

Photostimulated Reaction of *N*-(2-Bromophenyl)naphthalen-1-amine (18c) in DMSO. The reaction was carried out in a Schlenk tube equipped with a nitrogen inlet and magnetic stirrer at room temperature. DMSO (10 mL) was dried and deoxygenated, then *t*-BuOK (2.0 equiv, 44.8 mg) was added and after 5 min **18c** (1 equiv, 59.4 mg) was added and the reaction mixture was irradiated for 60 min. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with CH_2Cl_2 (3 × 50 mL) and the organic extract was washed with water and dried with anhydrous $MgSO_4$.

The same procedure was carried out when THF was used as a solvent. THF was dried over Na metal and benzophenone.

9*H*-Carbazole (4). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (50:50) and then it was sublimated. White crystals were isolated in 93% yield (46.7 mg, 0.28 to 0.3 mmol). ^{1}H NMR (CCl_3D) δ 7.25 (2H, m), 7.43 (4H, m), 8.05 (1H, s), 8.10 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (CCl_3D) δ 110.53, 119.41, 120.30, 123.33, 125.80, 139.44. GC-MS (*m*/*z*) 168 ($M^+ + 1$, 13), 167 (M^+, 100), 166 (22), 140 (9), 139 (12), 84 (15), 69 (8). Mp 245.3−247.0 °C (lit.[37] mp 246 °C).

3-Phenyl-9*H*-carbazole (8).[38] The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (70:30 → 50:50). White crystals were isolated in 86% yield (55.8 mg, 0.23 to 0.268 mmol). ^{1}H NMR (CCl_3D) δ 7.28 (1H, m), 7.37 (1H, m), 7.49 (5H, m), 7.70 (1H, dd, $^1J = 8.4$ Hz, $^2J = 1.9$ Hz), 7.74 (2H, m), 8.10 (1H, s), 8.15 (1H, dd, $^1J = 7.8$ Hz, $^2J = 0.4$ Hz), 8.32 (1H, m). ^{13}C NMR (CCl_3D) δ 142.09, 139.93, 138.92, 133.03, 128.74, 127.31, 126.48, 126.03, 125.44, 123.88, 123.46,

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120.38, 119.59, 118.85, 110.76, 110.71. GC-MS (*m*/*z*) 244 (M^+ + 1, 20), 243 (M^+, 100), 242 (22), 241 (21), 122 (15), 121 (14). Mp 222.8−224.1 °C.

3-*tert*-Butyl-9*H*-carbazole (9). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (75:25). White crystals were isolated in 94% yield (48.2 mg, 0.216 to 0.23 mmol). ^{1}H NMR (CCl_3D) δ 1.44 (9H, s), 7.21 (1H, m), 7.35 (3H, m), 7.48 (1H, dd, ^1J = 8.5 Hz, ^2J = 1.9 Hz), 7.85 (1H, s), 8.08 (2H, m). ^{13}C NMR (CCl_3D) δ 31.96, 34.65, 110.03, 110.52, 116.31, 119.16, 120.09, 123.00, 123.55, 123.79, 125.51, 137.53, 139.86, 142.44. GC-MS (*m*/*z*) 224 (M^+ + 1, 6), 223 (M^+, 36), 209 (16), 208 (100), 180 (14), 168 (13), 167 (21), 90 (27). Mp 147.1−148.1 °C (lit.[39] mp 151.0−152.0 °C).

7*H*-Benzo[*c*]carbazole (10). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (75:25). ^{1}H NMR (CD_3COCD_3) δ 7.34 (1H, m), 7.44 (2H, m), 7.69 (2H, m), 7.78 (1H, d, J = 8.7 Hz), 7.90 (1H, d, J = 8.8 Hz), 8.03 (1H, d, J = 8.1 Hz), 8.60 (1H, d, J = 8.1 Hz), 8.83 (1H, d, J = 8.3 Hz), 10.82 (1H, br s). ^{13}C NMR (CD_3COCD_3) δ 111.49, 113.20, 114.79, 119.73, 121.70, 122.64, 123.04, 123.70, 124.06, 126.72, 127.07, 129.16, 129.20, 130.05, 137.75, 139.10. GC-MS (*m*/*z*) 219 (2), 218 (M^+ + 1, 17), 217 (M^+, 100), 216 (18), 189 (10), 109 (15), 94 (15). Mp 135.0−137.0 °C (lit.[40] mp 133−134 °C).

13*H*-13-Aza-indeno[1,2-*l*]phenanthrene (15). The product was purified by column chromatography on silica gel eluting with petroleum ether/acetone (90:10). Yellow crystals were isolated in 90% yield (48.1 mg, 0.18 mmol). ^{1}H NMR (CCl_3D) δ 7.44 (2H, m), 7.65 (4H, m), 7.78 (1H, m), 8.09 (1H, m), 8.56 (1H, d, J = 7.8 Hz), 8.81 (4H, m). ^{13}C NMR (CCl_3D) δ 111.30, 112.80, 120.56, 120.65, 121.73, 122.23, 123.54, 123.64, 123.70, 123.85, 123.90, 124.71, 126.14, 126.58, 126.88, 127.25, 129.88, 129.92, 133.64, 138.06. GC-MS (*m*/*z*) 268 (M^+ + 1, 21), 267 (M^+, 100), 266 (15), 265 (10), 134 (19), 133 (14). Mp 191−192 °C (lit.[41] mp 191−193).

3-Methoxy-9*H*-carbazole (19). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (93:7). White crystals were isolated in 80% yield (31.5 mg, 0.16 to 0.20 mmol). ^{1}H NMR (CCl_3D) δ 3.95 (3H, s), 7.08 (1H, dd, ^1J = 8.7 Hz, ^2J = 2.6 Hz), 7.23 (1H, m), 7.33 (1H, d, J = 8.7 Hz), 7.41 (2H, m), 7.58 (1H, d, J = 2.6 Hz), 7.90 (1H, s), 8.05 (1H, dd, ^1J = 7.8 Hz, ^2J = 0.6 Hz). ^{13}C NMR (CCl_3D) δ 56.06, 103.17, 110.71, 111.27, 115.05, 119.03, 120.22, 123.34, 123.77, 125.78, 134.35, 140.26, 153.89. GC-MS (*m*/*z*) 198 (M^+ + 1, 12), 197 (M^+, 88), 183 (13), 182 (100), 154 (40), 153 (12), 128 (12), 127 (14). Mp 149.1−150.8 °C (lit. mp146−148 °C[11b] and 152−153 °C[11f]).

11*H*-Benzo[*a*]carbazole (20). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10 → 70:30) and then it was sublimated. White crystals were isolated in 85% yield (37.1 mg, 0.17 to 0.20 mmol). ^{1}H NMR (CCl_3D) δ 7.34 (1H, m), 7.47 (1H, m), 7.58 (3H, m), 7.69 (1H, d, J = 8.6 Hz), 8.04 (1H, d, J = 7.7 Hz), 8.12 (1H, d, J = 8.1 Hz), 8.16 (2H, m), 8.74 (1H, s). ^{13}C NMR (CCl_3D) δ 110.99, 118.40, 119.28, 119.87, 119.95, 120.18, 120.41, 121.03, 124.15, 124.83, 125.17, 125.50, 129.00, 132.38, 134.81, 138.41. GC-MS (*m*/*z*) 218 (M^+ + 1, 17), 217 (M^+, 100), 216 (26), 109 (22), 94 (15). Mp 234.7−236.1 °C (lit.[42] mp 227−228 °C).

1-(1*H*-Pyrrol-1-yl)-9*H*-carbazole (21). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10). White crystals were isolated in 91% yield (51.0 mg, 0.22 to 0.24 mmol). ^{1}H NMR (CCl_3D) δ 6.50 (2H, t, J = 2.1 Hz), 7.16 (2H, t, J = 2.1 Hz), 7.30 (2H, m), 7.45 (3H, m), 8.06 (1H, d, J = 7.7 Hz), 8.13 (1H, d, J = 7.8 Hz), 8.27 (1H, s). ^{13}C NMR (CCl_3D) δ 110.15, 110.93, 118.85, 119.77, 119.96, 120.55, 120.78, 121.11, 123.35, 125.22, 125.50, 126.43, 133.76, 139.43. GC-MS (*m*/*z*) 233 (M^+ + 1, 17), 232 (M^+, 100), 231 (24), 205 (10), 204 (39), 116 (14), 102 (16). Mp 99.0−100.2 °C. HR MS (EI) calcd for $C_{16}H_{12}N_2$ 232.1000, found 232.0994.

1-Phenyl-9*H*-carbazole (22).[43] The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (80:20 → 60:40). White crystals were isolated in 40% yield (19.2 mg, 0.08 to 0.2 mmol). ^{1}H NMR (CCl_3D) δ 7.24 (1H, m), 7.31 (1H, t, J = 7.6 Hz), 7.42 (4H, m), 7.54 (2H, m), 7.68 (2H, m), 8.08 (2H, m), 8.29 (1H, s br). ^{13}C NMR (CCl_3D) δ 110.71, 119.52, 119.58, 119.94, 120.50, 123.57, 123.72, 125.06, 125.77, 125.98, 127.58, 128.41, 129.29, 137.28, 139.10, 139.49. GC-MS (*m*/*z*) 245 (M^+ + 2, 2), 244 (M^+ + 1, 20), 243 (M^+, 100), 242 (30), 241 (28), 121 (15). Mp 132.5−134.0 °C.

9*H*-Tribenz[*b*,*d*,*f*]azepine (23).[44] The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 (80:20 → 60:40). White crystals were isolated in 52% yield (25.3 mg, 0.104 to 0.2 mmol). ^{1}H NMR (CCl_3D) δ 5.18 (1H, s br), 6.88 (2H, d, J = 8.2 Hz), 7.11 (2H, t, J = 7.6 Hz), 7.20 (2H, t, J = 7.6 Hz), 7.45 (6H, m). ^{13}C NMR (CCl_3D) δ 119.77, 124.16, 127.79, 128.49, 130.13, 130.20, 132.68, 139.37, 150.98. GC-MS (*m*/*z*) 245 (2), 244 (M^+ + 1, 20), 243 (M^+, 100), 242 (21), 241 (19), 216 (11), 215 (14), 122 (12), 121 (13), 94 (10). Mp 232.0−233.0 °C.

3,3′-Bi(9*H*-Carbazole) (24).[45] The residue was dissolved with water and then extracted with ethyl acetate (3 × 50 mL). The product was purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether (60:40 → 0:100). A brown light solid was isolated in 68% yield (55.5 mg, 0.167 to 0.25 mmol). ^{1}H NMR (d_6-DMSO) δ 7.18 (2H, t, J = 7.7 Hz), 7.40 (2H, m), 7.51 (2H, d, J = 8.0 Hz), 7.58 (2H, d, J = 8.4 Hz), 7.81 (2H, dd, ^1J = 8.4 Hz, ^2J = 1.7 Hz), 8.24 (2H, d, J = 7.7 Hz), 8.51 (2H, s), 11.29 (2H, s). ^{13}C NMR (d_6-DMSO) δ 110.97, 111.16, 118.08, 118.45, 120.36, 122.64, 123.09, 124.91, 125.53, 132.28, 138.68, 140.19. MS direct injection (*m*/*z*) 334 (9), 333 (37), 332 (M^+, 83), 331 (100), 330 (34), 329 (16), 166 (11), 165 (10). Mp 375.0 °C dec.

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Supporting Information Available: General methods and ^{1}H NMR and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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