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"Transition-Metal Free" Synthesis of Carbazoles by Photostimulated Reactions of 2'-Halo-[1,1'-biphenyl]-2-amines

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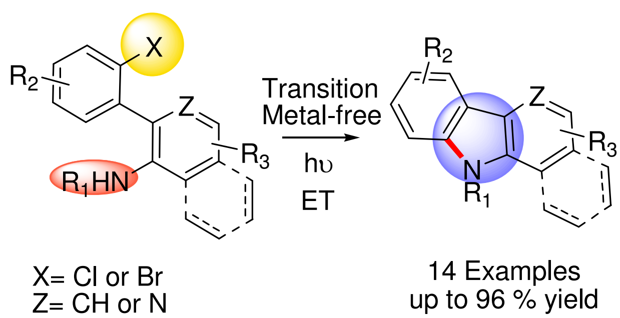


Abstract: An efficient and simple protocol for the preparation of a series of 9*H*-carbazoles by photostimulated $S_{RN}1$ substitution reactions is presented. Substituted 9*H*-carbazoles were synthesized from low to excellent yields (up to 96%) through an intramolecular C-N bond formation of 2'-halo-[1,1'-biphenyl]-2-amines by the photoinitiated $S_{RN}1$ mechanism under mild and "transition-metal free" conditions. The biphenyl amines used as substrates were obtained with isolated yields ranging from 21% to 84% by two approaches: A) the

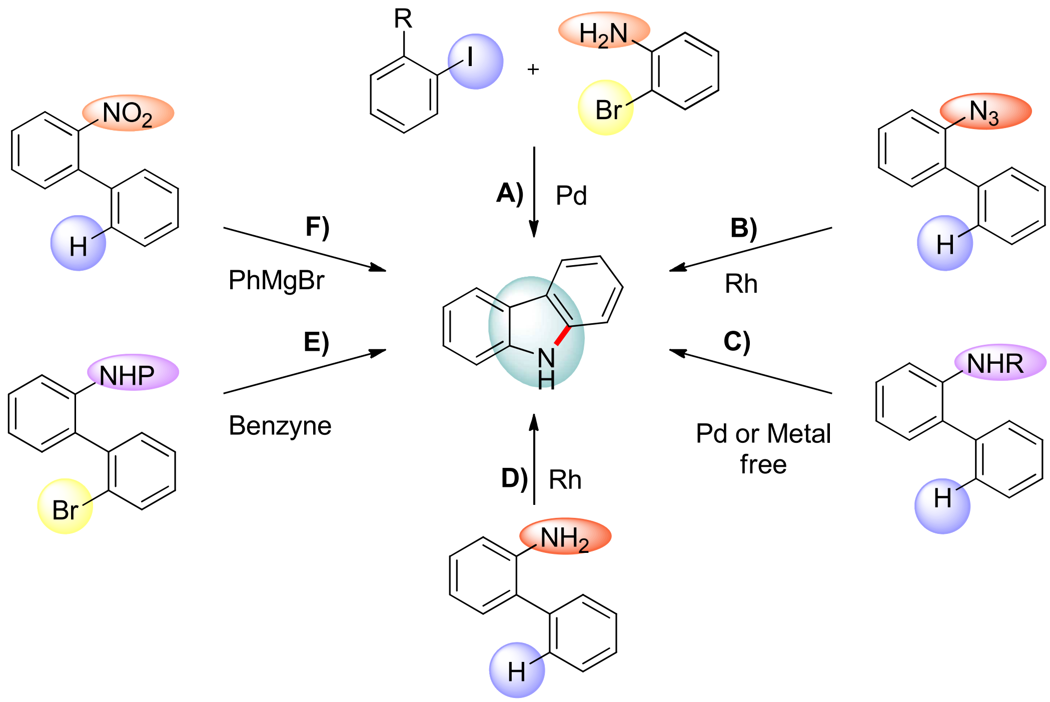
cross-coupling Suzuki-Miyaura reaction, and B) the radical arylation of anilines. Some key aspects of the proposed mechanism were evaluated at the B3LYP/6-311+G* level.

Introduction

Carbazole and its derivatives are an important type of nitrogen containing aromatic heterocycles with various pharmacological activities such as anticancer,[1,2] antimicrobial,[3] antipsychotic,[4] antimitotic[5] and antioxidant.[6] For example, the anti-inflammatory properties of carbazomycin B[7] and the antitumor properties of ellipticine derivatives[8] have been reported. Also, carvedilol[9] and carazolol[10] have been identified for their potential as multiple-action antihypertensive compounds. There are also many applications of these heteroaromatic compounds in materials science.[11]

Given the remarkable importance of functionalized carbazoles and their derivatives across many fields, the development of mild and efficient preparative protocols continues to be a challenging endeavor in synthetic organic chemistry.

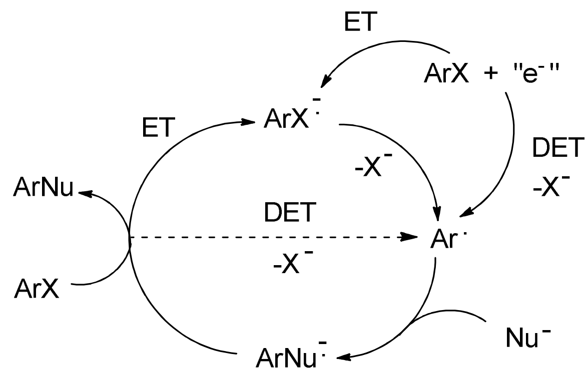
Representative synthetic protocols involving intramolecular C-N coupling are summarized in scheme 1 such as: A) Transition-metal-catalyzed sequential C-C and C-N bond formation using *N*-acetylated *o*-bromoanilines and *o*-substituted iodoarenes;[12] B) Rhodium-catalyzed carbazole formation from biaryl azides;[13] C) Metal catalyzed or transition-metal free intramolecular C-H amination of *N*-substituted aminobiphenyls;[14,15] D) One-pot Rh(III) catalyzed C-H amination of non-protected 2-aminobiaryls;[16] E) Benzyne-mediated cyclization of *N*-protected and halogenated diarylamines using magnesium bis(dialkyl amides) as a base;[17] F) Transition-metal free cyclization of 2-nitrobiaryls with PhMgBr.[18]



Scheme 1. Intramolecular C-N coupling strategies for the synthesis of carbazoles.

Despite the numerous useful synthetic procedures to prepare these compounds, several limitations still need to be overcome. Most of these procedures involve elevated temperatures, catalytic amounts of metal complexes (Pd or Rh), long reaction times, iodo- or bromo- arenes as starting material, or harsh reaction conditions. A practical, efficient and general route to carbazoles by C-N bond formation from chloro arenes would be desirable in view of the importance and applicability of these heterocycles.

The radical nucleophilic substitution mechanism ($S_{RN}1$) is a chain process that involves radicals and radical anions as intermediates as shown in scheme 2. The scope of this mechanism has increased considerably and nowadays serves as an important synthetic strategy.[19]



Scheme 2. The $S_{RN}1$ Mechanism.

The initiation step is an electron transfer (ET) from a suitable donor (e.g., the nucleophile or a base) to afford the radical anion of the substrate. This ET could also follow a concerted dissociative step to directly afford radicals and the anion of the leaving group (dissociative electron transfer or DET).[20] In some systems this ET is spontaneous, but in others light is required to induce the reaction. Electrons [(from dissolved alkali metals in liquid ammonia, or from a cathode) or inorganic salts (e.g., Fe(II) or SmI_2)] also can initiate the reaction.[19]

Several nucleophiles, such as carbanions and anions derived from heteroatoms can be used to form new C-C or C-heteroatom bonds in good yields; the reaction is also compatible with many substituents. An interesting feature is the possibility to obtain heterocycles by intramolecular ring closure of compounds bearing both the leaving group and the nucleophilic center in an adequate relative position.[19]

The intramolecular $S_{RN}1$ reaction has been used to synthesize by “C-C bond formation” 9*H*-carbazoles,[21] phenanthridines and benzophenanthridines,[22] carbolines,[23] bractazonine alkaloid,[24] 1-phenyl-indanes and tetralin derivatives,[25] and aporphine and homoaporphine alkaloids.[26] The cyclization of *N*-(2-halophenyl)phenyl acetamides to afford 1-methyl-3-phenylindolin-2-one has been performed under microwave (MW) heating.[27] The syntheses of benzo-fused heterocycles bearing from six- to nine-membered rings have been reported to proceed in good to excellent yields. This procedure involves as the key step the photostimulated $S_{RN}1$ reaction of ketone enolate anions linked by a bridge to a pendant haloarene.[28]

Furthermore, some examples of C-heteroatom bond formation were reported in cyclization reactions of aromatic amines with *ortho*-dihaloaromatic compounds.[29] Even though the intramolecular $S_{RN}1$ reaction has proved to be a successful tool to synthesize heterocycles, there are only a few reports of C-N bond formation within the intramolecular approach.[22a,30]

On this basis, we studied a new synthetic strategy that involved, first, the construction of compounds such as 2'-halo-[1,1'-biphenyl]-2-amines bearing both the leaving group and the precursor of the anion centre on nitrogen in the same molecule. In a second phase, the strategy includes as key step the formation of a new C-N bond by intramolecular "transition-metal free" photostimulated reaction, to give the 9*H*-carbazoles. Also, some relevant electronic and geometric factors of these reactions were examined by DFT calculations.

Results and Discussion

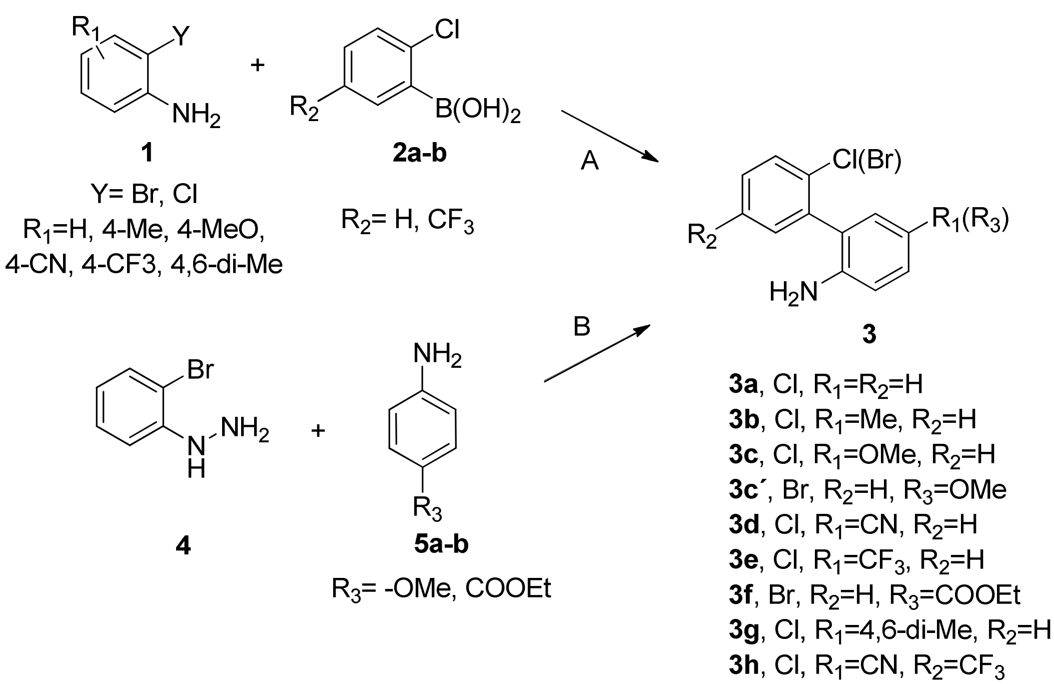
2'-Halo-[1,1'-biphenyl]-2-amines (**3**) used to achieve the synthesis of carbazoles were prepared by the cross-coupling Suzuki-Miyaura reaction[31] (method **A**), or by radical arylation of anilines **5** with arylhydrazines[32] **4** (method **B**) (Table 1). Most of the biphenylamines thus obtained have not been described in the literature.

The Pd-catalyzed reaction of 2-bromoaniline (**1a**) with 2-chlorophenylboronic acid (**2a**) under similar experimental conditions to those reported (method A),[33] afforded 2'-chloro-[1,1'-biphenyl]-2-amine (**3a**) in 84% isolated yield (entry 1, Table 1).

Following the same procedure, the reaction of different anilines with 2-phenylboronic acids afforded the corresponding mono and di-substituted 2'-chloro-[1,1'-biphenyl]-2-amines in 36-79% isolated yields (entries 2-3,5-6, 8-9, Table 1).

The substituted 2'-bromo-[1,1'-biphenyl]-2-amines (**3c´** and **f**) were obtained in low isolated yields (entries 4 and 7, Table 1) from 2-(bromophenyl)hydrazine (**4**) and 4-substituted anilines **5a-b** following the previously reported regioselective radical arylation of anilines with arylhydrazines (Table 1, method B).[32]

Tabla 1. Preparation of 2'-halo-[1,1'-biphenyl]-2-amines (**3a-h**).[a]

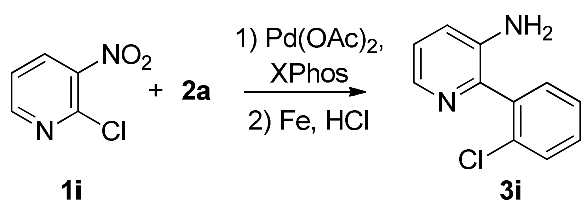


entry	substrate (**1** or **4**)	substrate (**2** or **5**)	method	product (%[b])

1	**1a** (Y=Br, R_1=H)	**2a** (R_2=H)	A	**3a** (84)
2	**1b** (Y=Br, R_1=4-Me)	**2a** (R_2=H)	A	**3b** (49)
3	**1c** (Y=Br, R_1=4-OMe)	**2a** (R_2=H)	A	**3c** (36)
4	**4**	**5a** (R_3=OMe)	B	**3c´** (31)
5	**1d** (Y=Br, R_1=4-CN)	**2a** (R_2=H)	A	**3d**(60)
6	**1e** (Y=Cl, R_1=4-CF_3)	**2a** (R_2=H)	A[c]	**3e**(17)
7	**4**	**5b** (R_3=COOEt)	B	**3f** (27)
8	**1g** (Y=Br, R_1=4,6-di-Me)	**2a** (R_2=H)	A	**3g** (79)
9	**1d** (Y=Br, R_1=4-CN)	**2b** (R_2=CF_3)	A	**3h**(39)

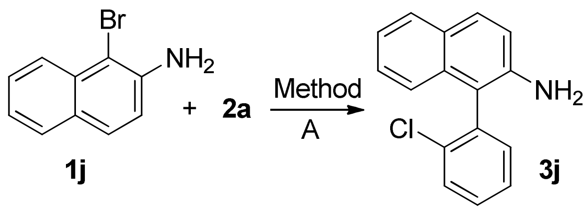
[a]**Method A**: 5 mol % $Pd(PPh_3)_2Cl_2$, 10 mol % PPh_3 as ligand, $NaHCO_3$ as base in DME-water (1:1) at 120°C for 3h. **Method B**: 15 equiv of aniline, 5 equiv of MnO_2 and $NaHCO_3$ as base (the latter when the hydrazine hydrochloride is used) in MeCN at rt for 2h. [b]Isolated yields. [c] 2 mol % $Pd(OAc)_2$, 4 mol % XPhos in dioxane at 80ºC for 18h.[34]

Utilizing the cross-coupling Suzuki-Miyaura reaction, 2-(2-chlorophenyl)pyridin-3-amine (**3i**) was prepared (30% isolated yield) by reaction of 2-chloro-3-nitro-pyridine (**1i**) with 2-chlorophenylboronic acid (**2a**) followed by chemical reduction[35] (scheme 3).



Scheme 3. Synthesis of 2-(2-chlorophenyl)pyridin-3-amine (**3i**).

The Pd-catalyzed reaction of polycyclic aromatic compounds to afford more complex precursors was also examined. Within this goal, 1-(2-chlorophenyl)naphthalen-2-amine (**3j**) was obtained (21% isolated yield, scheme 4).



Scheme 4. Synthesis of 1-(2-chlorophenyl)naphthalen-2-amine (**3j**).

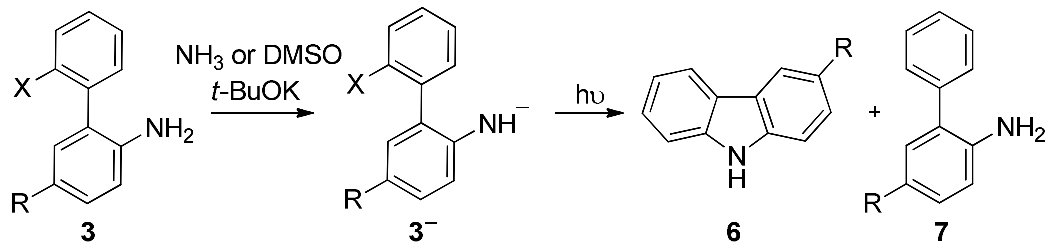
The scope of the $S_{RN}1$ reaction of the previously reported substrates (**3a-f**) to achieve the synthesis of various substituted carbazoles was further explored. The overall experimental details and the results obtained are presented in Table 2.

After 180 min of irradiation, the reaction of 2'-chloro-[1,1'-biphenyl]-2-amine (**3a**) in DMSO at 40 ºC with excess *t*-BuOK (2 equiv) afforded the 9*H*-carbazol (**6a**) in 57% yield, together with 13% of the reduced product [1,1'-biphenyl]-2-amine (**7a)** (entry 1, Table 2). Similar results were obtained in liquid ammonia as solvent at -33 ºC (entry 2, Table 2).

A similar yield of **6a** (43%) was obtained at shorter reaction times (60 min of irradiation, entry 3, Table 2). There was no reaction under dark conditions which excludes a benzyne mechanism (entry 4, Table 2). Besides, the photostimulated reaction was partially inhibited by *m*-dinitrobenzene (*m*-DNB), a strong electron-acceptor (entry 5, Table 2).[19c]

Also, the effect of the base was evaluated by carrying out the photostimulated reaction in the absence of *t*-BuOK (entry 6, Table 2). Under these conditions traces of **6a** were observed indicating the importance of the base to form the anion of the substrate and to initiate the reaction.

Table 2. Photostimulated reactions of 2'-halo-[1,1'-biphenyl]-2-amines (**3a-f**).



3a, X=Cl, R=H; **3b**, X=Cl, R=Me;
3c, X=Cl, R=OMe; **3c´**, X=Br, R=OMe;
3d, X=Cl, R=CN; **3e**, X=Cl, R=CF_3;
3f, X=Br, R=COOEt.

entry	biphenylamine			conditions[a]	products			
	3	R	recovered (%)		yields %[b]	**6**	**7**	Cl^- %[c]
1	**a**	H	---	hυ, 3h	**a**	57(41)	13(9)	90
2[d]	**a**	H	---	hυ, 3h	**a**	57(45)	9	95
3	**a**	H	12	hυ, 1h	**a**	43	18	80
4	**a**	H	84	dark, 1h	**a**	--	---	<10
5[e]	**a**	H	50	hυ, 1h	**a**	19	4	31
6[f]	**a**	H	92	hυ, 1h	**a**	<3	7	<10
7	**b**	Me	---	hυ, 3h	**b**	63(48)	9(<5)	93
8	**c**	OMe	---	hυ, 3h	**c**	(29)	(20)	90
9[g]	**c´**	OMe	---	hυ, 3h	**c**	34(30)	30(15)	83
10	**d**	CN	---	hυ, 3h	**d**	(79)	---	82
11	**e**	CF_3	---	hυ, 3h	**e**	83(72)	---	90
12[g]	**f**	COOEt	---	hυ, 3h	**f**	66(47)	---	90

[a] The reactions were run in 5 mL of DMSO (40 ºC) with 1 equiv of substrate and 2 equiv of *t*-BuOK and irradiated for the specific time. Irradiation was conducted in a photochemical reactor equipped with two Philips HPI-T 400 W lamps of metallic iodide (air and water refrigerated). [b]Yields were determined by CG (internal standard method). Isolated yields are given in parentheses. [c]Halide anions were determined potentiometrically. [d]The reaction was run in 200 ml of liquid ammonia (-33 ºC), with 1 equiv of substrate and 2 equiv of *t*-BuOK. [e]30 mol % of *m*-DNB with respect to the substrate was added. [f] In the absence of *t*-BuOK. [g]Bromide as leaving group.

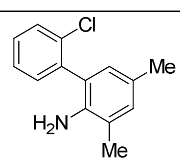
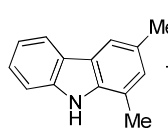
Low to very good yields of mono-substituted carbazoles were obtained by reaction of compounds **3b-f** (entries 7-12, Table 2). The anions of **3b**, **c** and **c´** afforded carbazoles **6b-c** in 34-63% together with the corresponding reduced products **7b-c** (entries 7-9, Table 2). Meanwhile, anions from **3d-f** gave specifically the carbazoles in higher yields (66-83%) (entries 10-12, Table 2).

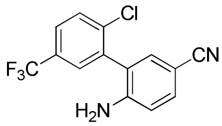
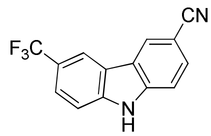
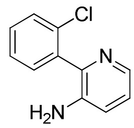
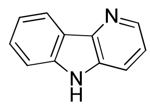
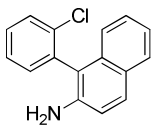
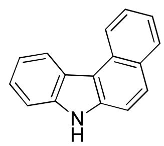
Extension of the procedure to synthesize more complex carbazoles and even δ-carboline is presented in Table 3. The reaction of the anion of **3g** and **3j** gave both, disubstituted carbazoles **6g, j** (49% and 53% yields, respectively) together with the reduced products **7g, j** (26%) (entries 1 and 4; Table 3).

On the other hand, $\mathbf{3h^-}$ gave only the carbazole **6h** (70% isolated yield, entry 2, Table 3). Moreover, the δ–carboline **6i** was obtained in 71% yields uncontaminated by the reduced product (entry 3, Table 3).

As can be seen in general, biphenylamines with electron donating group (EDG) like Me or OMe gave both, cyclized and reduced products, meanwhile biphenylamines containing electron-withdrawing groups (EWG) like CN, COOEt or CF_3 gave only the carbazole.

Table 3. Synthesis of di-susbstituted and polycyclic carbazoles (**6g-j**).[a]

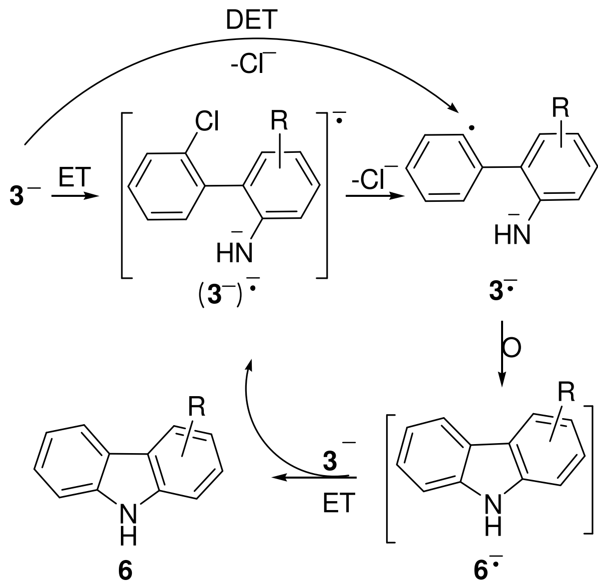
entry	biphenylamines[b]	products	yields %[c] **6**	yields %[c] **7**	Cl^- %[d]
1	 **3g**	 **6g** + **7g**	49 (44)	26 (15)	96

2	 **3h**	 **6h**	70		85
3	 **3i**	 **6i**	71 (58)		80
4	 **3j**	 **6j** + **7j**	53	26	95

[a]The reactions were run in 5 mL of DMSO (40 ºC), with 1 equiv of substrate and 2 equiv of *t*-BuOK and irradiated (180 min). Irradiation was conducted in a photochemical reactor equipped with two Philips HPI-T 400 W lamps of metallic iodide (air and water refrigerated). [b]In all cases conversion was complete. [c]Yields determined by CG (internal standard method). Isolated yields are in brackets. [d]Chloride anions were determined potentiometrically.

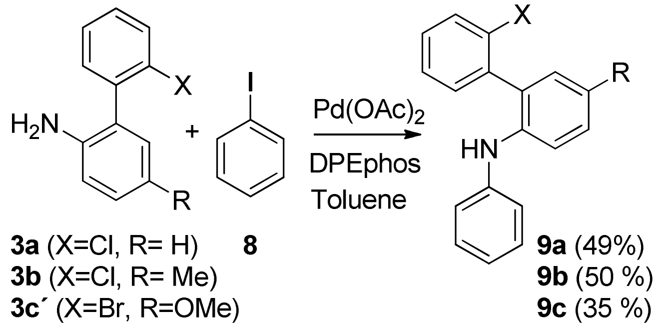
The partial inhibition of the irradiated reaction in the presence of *m*-DNB (Table 2, entry 5), and the lack of formation of **6a** (9*H*-carbazole) under dark conditions (Table 2, entry 4) provided evidence that the present cyclization could proceed via the $S_{RN}1$ mechanism.

We propose that in the presence of excess *t*-BuOK the anion $\mathbf{3}^{-}$ is formed. The initiation step of these reactions would be the photoinduced ET from an adequate electron source, such as *t*-BuOK,[36] to yield the respective radical dianions $(\mathbf{3}^{-})^{\bullet-}$ (scheme 5) which could dissociate to afford the distonic radical anion $\mathbf{3}^{\bullet-}$. Moreover, $\mathbf{3}^{\bullet-}$ could be formed by a concerted dissociative ET (DET). An additional ET from $\mathbf{6}^{\bullet-}$ to $\mathbf{3}^{-}$ will afford $\mathbf{6}^{-}$ and radical dianion $(\mathbf{3}^{-})^{\bullet-}$, which could propagate the reaction. Upon acidification of the reaction media and work up, product **6** was formed. Calculations supporting key steps of the proposed mechanism will be further discuss.



Scheme 5. Mechanism proposed for the formation of carbazole.

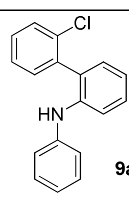
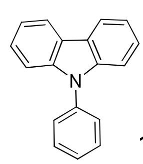
Based on the successful syntheses of substituted and polycyclic 9*H*-carbazoles and δ-carboline, via $S_{RN}1$ reactions of halo-biphenylamines, we explored the synthesis of *N*-phenyl-9*H*-carbazoles as possible future substrates. Within this goal the *N*-phenyl-[1,1'-biphenyl]-2-amines **9a-c** were prepared in low yields by reaction of iodobenzene (**8**) with the corresponding 2'-halo-[1,1'-biphenyl]-2-amines (**3a,b,c´**) under Buchwald-Hartwig conditions (scheme 6). [37,38] The synthesis of carbazoles from compounds **9a-c** is presented in Table 4.

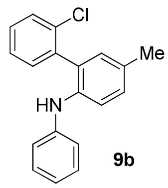
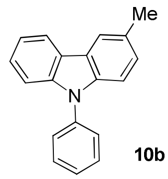
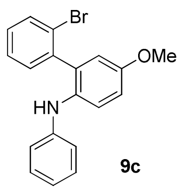
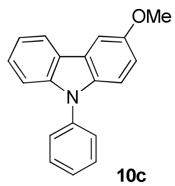


Scheme 6. Preparation of *N*-phenyl-[1,1'-biphenyl]-2-amines **9a-c**.

Excellent isolated yields of *N*-phenyl carbazoles **10a-c** (87 - 96%) were obtained by photostimulated reaction of **9a-c** either in liquid ammonia or DMSO (entries 1-4, Table 4). Interestingly, under the same experimental conditions a simple modification of the starting material (*N*-phenyl substitution) improved significantly the yield of the reaction. For example, **3a** afforded 9*H*-carbazole in 57% yield meanwhile its corresponding *N*-phenyl derivative **9a** gave the cyclic compound in 93% (entry 1, Table 1 vs. entry 2, Table 4). Also, it is important to notice that while **3a** afforded cyclization and reduction, cyclization was the only reaction obtained with **9a, b** and **c** (entries 1, 7 and 9, Table 1 vs. entries 2-4, Table 4).

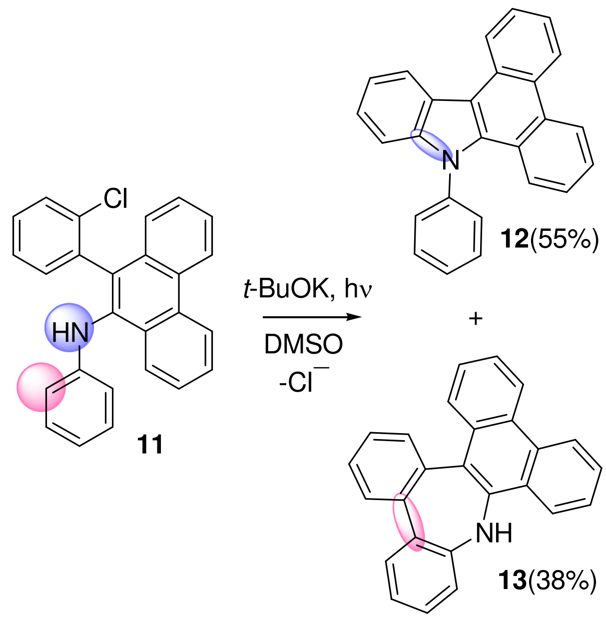
Table 4. Synthesis of *N*-phenyl-carbazoles (**9a-c**).[a]

entry	*N*-phenyl-biphenylamine	Product	Yield %[c]	Cl^-/Br^- %[d]
1[b]	 **9a**	 **10a**	96	95
2			93	97

3	 9b	 10b	87	90
4	 9c	 10c	87	87

[a] The reactions were run in 5 mL of DMSO (40 ºC), with 1 equiv of substrate and 2 equiv of *t*-BuOK and irradiated for 3 hours. Irradiation was conducted in a photochemical reactor equipped with two Philips HPI-T 400 W lamps of metallic iodide (air and water refrigerated). [b] The reaction was run in 200 ml of liquid ammonia (-33 ºC), with 1 equiv of substrate and 2 equiv of *t*-BuOK and irradiated for 3 hours. [c]Isolated yields. [d]Halide anions were determined potentiometrically.

To extend the application of the methodology developed to obtain *N*-phenyl-carbazoles, we evaluated the reactivity of a phenanthrene-9-amine in this system. When the photostimulated reaction was carried out with 10-(2-chlorophenyl)-*N*-phenylphenanthren-9-amine (**11**), 9-phenyl-9*H*-dibenzo[*a*,*c*]carbazole (**12**) was obtained in 55% yield together with 9*H*-dibenzo[*b,d*]phenanthro[9,10-*f*]azepine (**13**) in 38 % yield (scheme 7). It is important to notice that **13** is the product corresponding to the C-C coupling. This C-C coupling was not observed in the reactions of **9a-c** (entries 1-4, Table 4).



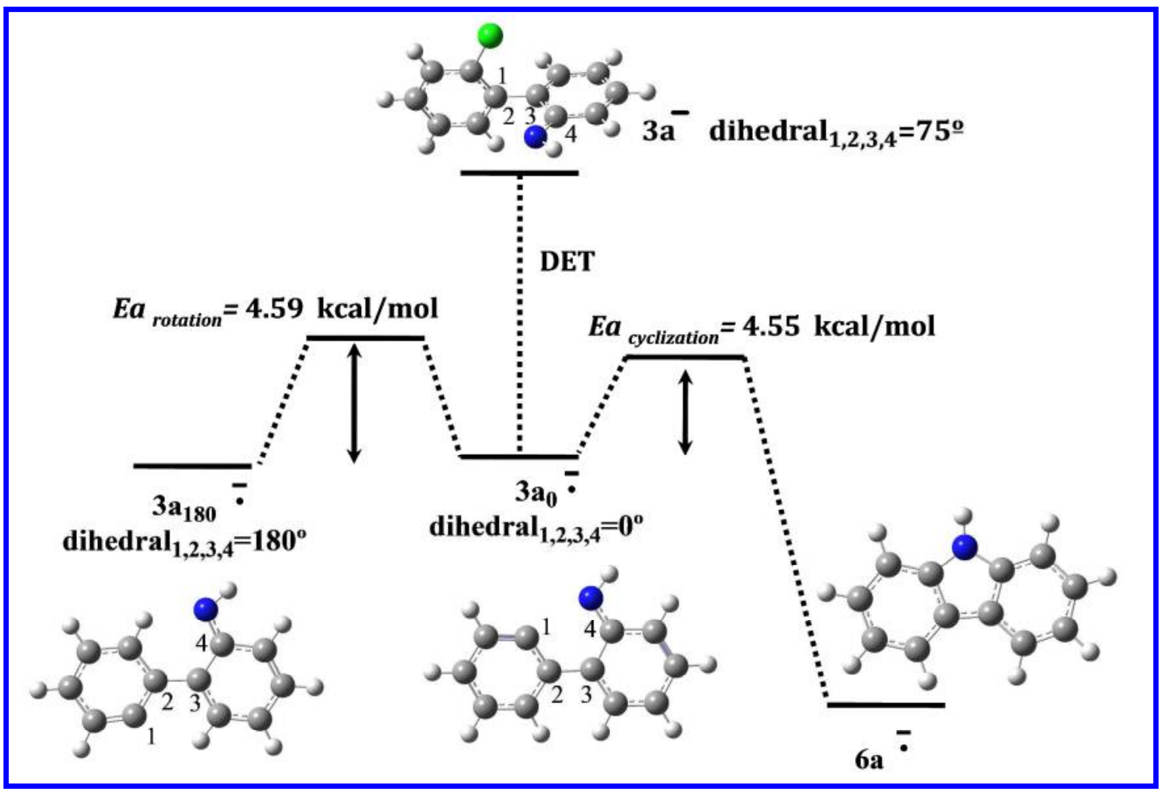
Scheme 7. Intramolecular photostimulated reactions of 10-(2-chlorophenyl)-*N*-phenylphenanthren-9-amine (**11**).

In order to rationalize our experimental results, a computational study with the B3LYP[39] DFT functional and the 6-311+G* basis set was carried out. The solvent effect was included with the continuum solvent model (PCM).[40] Key mechanistic intermediates and reactive pathways presented in Scheme 5 were studied for the anions of **3a**, **9a** and **11**.

In relation to the different initiation steps that could be in play,[19c] ET form *t*-BuO$^-$ to the substrate in its excited state has been proposed in other systems.[36] The thermodynamic of the ET from *t*-BuO$^-$ to the S_1 state of **3a**$^-$ was evaluated with TD-DFT as exothermic, indicating it is as a feasible initiation pathway under our experimental conditions (excess *t*-BuO$^-$). Another possibility being ET from S_1 to S_0 of **3a**$^-$ (see Supporting Information).[41]

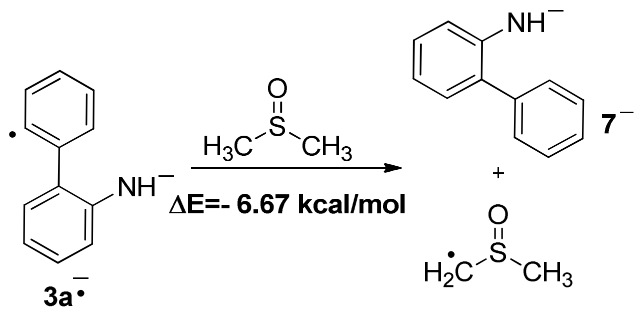
With respect to the species formed, the calculations failed to locate (**3**$^-$)$^{\bullet-}$ as a stationary species of the dianionic surface. This result indicates that, upon recipient of an electron, **3a**$^-$ dissociates into the distonic radical anion **3a**$^{\bullet-}$ and chloride anion (scheme 8).

The most stable conformer of the intermediate $\mathbf{3a_0}^{\bullet-}$ has a dihedral angle equal to 0 degrees between the two phenyl subunits. This high-energy intermediate may rotate around the C_{phenyl}-C_{phenyl} bond to give the less stable intermediate $\mathbf{3a_{180}}^{\bullet-}$ (dihedral=180 degree) with an activation energy of 4.59 kcal/mol. Based on the calculated energy difference between both conformers $\mathbf{3a_0}^{\bullet-}$ prevails (91%) under conformational equilibrium at 318 K. This conformer is responsible to follow the cyclization reactive pathway to afford the C-N cyclic radical anion $\mathbf{6a}^{\bullet-}$. This pathway is pursued by crossing a low activation energy barrier (*Ea*=4.55 kcal/mol).



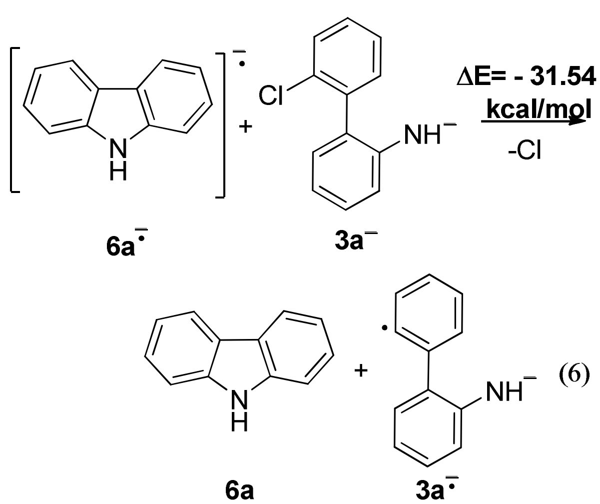
Scheme 8. Stationary points evaluated on the potential energy surface of C-N cyclization for $\mathbf{3a}^{-}$ by ET.

Cyclization of **3a**$_0^{\bullet -}$ as well as its reduction by hydrogen abstraction from the solvent (DMSO) (scheme 9) were calculated as exothermic processes in -36.92 and -6.67 kcal/mol, respectively; this meaning both reactions may occur under our experimental conditions.



Scheme 9. Hydrogen abstraction by **3a**$^{\bullet -}$from the solvent.

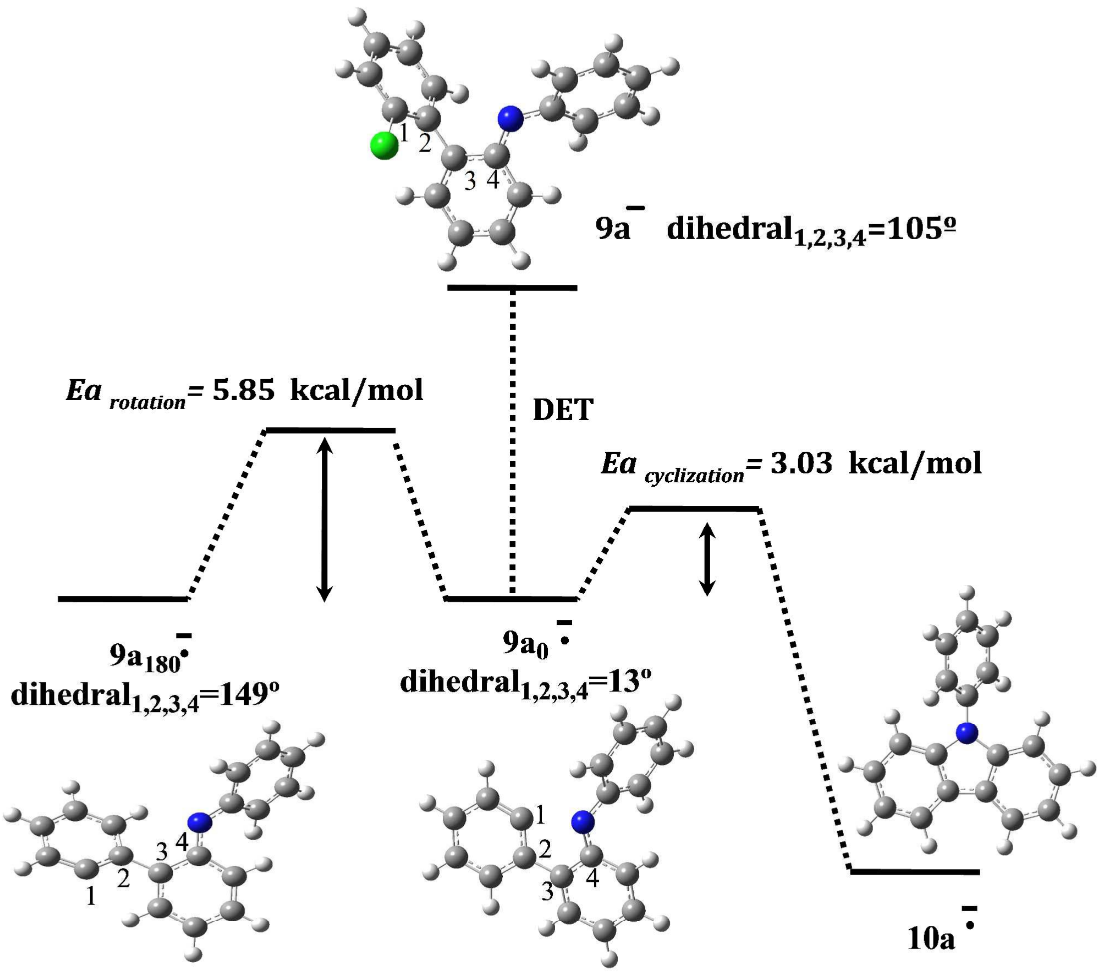
Important to point out is that the ET from **6a**$^{\bullet -}$ to **3a**$^{-}$ is calculated as exothermic by -31.54 kcal/mol (scheme 10). This exothermic reaction clearly demonstrated that the energetics for an efficient propagation of the proposed mechanistic cycle (scheme 5) are reasonable.



(6)

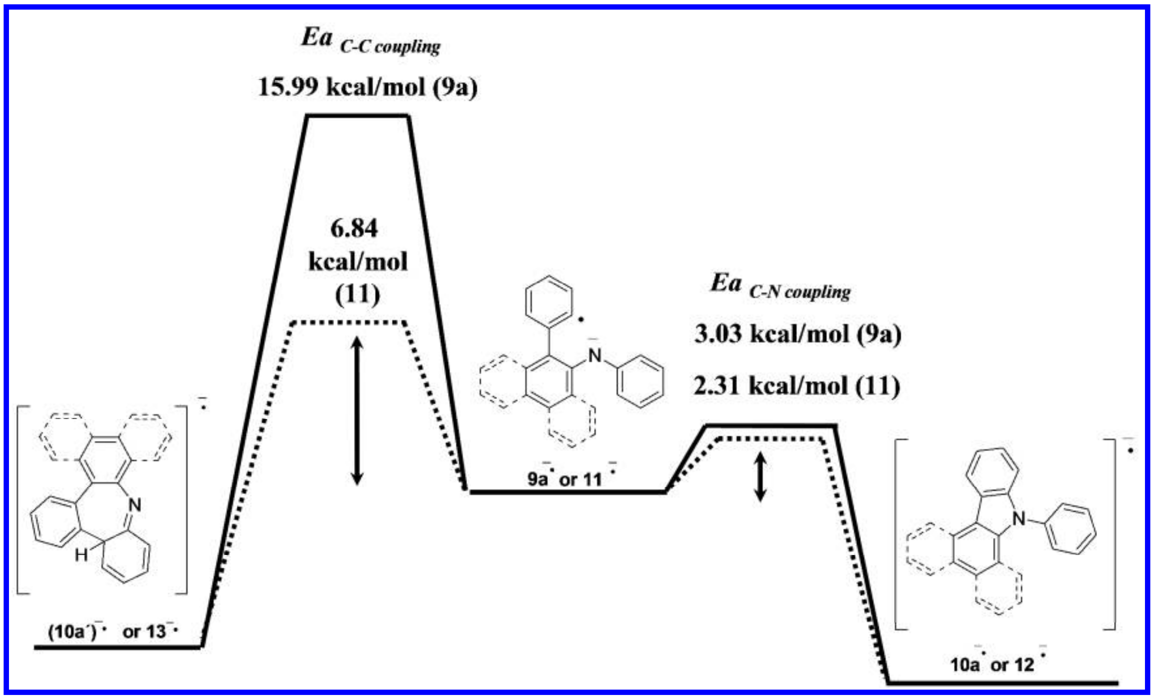
Scheme 10. ET from **6a**$^{\bullet -}$ to **3a**$^{-}$**.**

A similar energy profile was calculated for **9a**$^{-}$. This anion affords, after DET, the distonic radical anion $\mathbf{9a_0}^{\bullet -}$ (scheme 11). The $Ea_{cyclization}$ of $\mathbf{9a_0}^{\bullet -}$ was calculated to be 3.03 kcal/mol, which is 1.5 kcal/mol lower than $Ea_{cyclization}$ of $\mathbf{3a_0}^{\bullet -}$ (without *N*-phenyl substitution). Moreover, the activation energy for C_{aryl}-C_{phenyl} rotation of $\mathbf{9a_0}^{\bullet -}$ is higher than $Ea_{rotation}$ of $\mathbf{3a_0}^{\bullet -}$. Assuming $\mathbf{9a_0}^{\bullet -}$ and $\mathbf{3a_0}^{\bullet -}$ have similar *Ea* for hydrogen abstraction from the solvent, the lower $Ea_{cyclization}$ of $\mathbf{9a_0}^{\bullet -}$ indicates this is the preferred reaction path for **9a**$^{-}$ and thus explains the cyclization specificity observed experimentally for the *N*-phenyl substituted compounds.



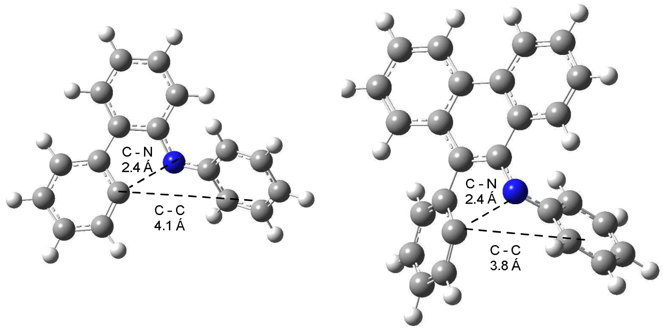
Scheme 11. Stationary points evaluated on the potential energy surface of C-N cyclization for **9a**$^{-}$ by ET.

The differences in C-N vs C-C regiochemistry in the cyclization of **9a**$^{-}$ and **11**$^{-}$ were also examined (scheme 12). As seen from the scheme, the C-N coupling of the reactive intermediates **9a**$^{\bullet-}$ and **11**$^{\bullet-}$ to form **10a**$^{\bullet-}$ and **12**$^{\bullet-}$ occurs with similar $Ea_{C\text{-}N\ cyclization}$. On the other hand, C-C cyclization is favored for **11**$^{\bullet-}$ with respect to **9a**$^{\bullet-}$ by ≈9 kcal/mol ($Ea_{C\text{-}C\ cyclization}$ (**11**$^{\bullet-}$)=6.84 kcal/mol; $Ea_{C\text{-}C\ cyclization}$ (**9a**$^{\bullet-}$)=15.99 kcal/mol).



Scheme 12. Evaluation of C-N vs. C-C cyclization for **9a**$^{\bullet-}$ and **11**$^{\bullet-}$ by ET.

Inspection of the minimum energy geometries of **9a**$^{\bullet-}$ and **11**$^{\bullet-}$ shows they bear a similar distance from N to the radical center ($C_{Radical\ Center}$-N distance=2.4Å, Figure 1). On the other hand, they differ in the distances of the radical center to the closest anionic carbon ($C_{Radical\ Center}$-$C_{ortho\text{-}N}$ distances being 4.1Å and 3.8Å for **9a**$^{\bullet-}$ and **11**$^{\bullet-}$, respectively, Figure 1). The greater proximity between the reactive centers in **11**$^{\bullet-}$ may be responsible for its lower activation energy to follow the C-C cyclization route and thus, to afford the corresponding observed azepine (C-C product). This product is other evidence that favors the proposed mechanism with radical anions intermediates, in which coupling between a radical and different positions of an anionic system can occur.



9a$^{\cdot-}$ **11**$^{\cdot-}$

Figure 1. Relevant C-N and C-C distances in energy-minimized conformers of **9a**$^{\cdot-}$ and **11**$^{\cdot-}$.

Conclusions

In summary, we report our studies on photostimulated intramolecular $S_{RN}1$ reactions using different 2'-halo-[1,1'-biphenyl]-2-amines as staring material. These reactions constitute a new, simple and efficient C–N protocol to obtain mono and di-substituted 9*H*-carbazoles and also 9-phenyl-9*H*-carbazoles. The approach does not involve the use of transition metals or drastic reaction conditions, and a variety of substituents are tolerated under the reaction conditions employed. The methodology compares fairly well with the approach based on C-C cyclization.[21] Moreover, we found that a simple modification of the starting material (*N*-phenyl substitution) under identical reaction conditions increased the yields significantly (87-96%). This is an interesting possibility not feasible with the C-C cyclization approach.

Considering the good yields, the low cost, availability and/or simplicity of starting materials, and the short time and mild reaction conditions of the procedures, we demonstrated that this can be a valuable alternative to access to 9*H*-carbazoles in a novel approach.

The computational calculations seem to be a successful approach to study the conformational equilibrium of anions and distonic radical anions as well as the energetic of their C-N cyclization. The calculations also explain the experimentally observed regiochemistry of C-C vs. C-N cyclization for the *N*-phenanthryl system.

Experimental Section

Computational Procedure. All calculations were performed with the Gaussian09 program. The conformers obtained were refined with complete geometry optimization within the B3LYP[39] DFT functional with the 6-311+G* basis set. The geometries thus found were used as starting points for the evaluation of the reaction profiles by using the distinguished coordinate scan. The effect of DMSO as solvent was evaluated through Tomasi's Polarized Continuum Model (PCM)[40] as implemented in Gaussian09. The inclusion of the solvent in the calculations is a requisite to evaluate valence radical anions. The B3LYP functional and the 6-311+G* basis set have been previously tested for similar systems.[42] The characterization of stationary points was done by Hessian matrix calculations. The energy informed for TSs, anions and radical anions includes zero-point corrections. The single excited stated (S_1) of anion **3a** was calculated with TD DTF the B3LYP functional and the 6-311+G* basis set. The energy of S_1 was calculated including the PCM contribution under the StateSpecific approach.

General Considerations. Gas chromatographic analyses were performed using a gas chromatograph with a flame ionization detector, and equipped with the following columns:

25 m x 0.20 mm x 0.25 µm column and 15 m × 0.25 mm × 0.25 µm column. ^{1}H NMR (400.16 MHz), ^{13}C NMR (100.63 MHz) spectra were obtained in DMSO-d_6 and $CDCl_3$ as solvents. Coupling constants are given in Hz and chemical shifts are reported in δ values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. Gas Chromatographic/Mass Spectrometer analyses were carried out on a GC/MS spectrometer equipped with a 30 m × 0.25 mm × 0.25 µm column. Irradiation was conducted in a reactor equipped with two Philips HPI-T 400 W lamps of metallic iodide (cooled with water). Potentiometric titration of halide ions where performed in a pHmeter using an Ag/Ag+ electrode. Melting points were performed with an electrical instrument. The high resolution mass (HRMS) of pure products were recorded on a TOF equipment, operated with an ESI source operated in (positive/negative) mode, using nitrogen as nebulizing and drying gas and sodium formiate 10 mM as internal calibrate instrument. Materials: 2-bromoaniline, 2-bromo-4-mtehyl-aniline, 2-bromo-4,6-*di*-methyl-aniline, 2-chloro-4-(trifluoromethyl)aniline, 2-chloro-3-nitropyridine, 4-methoxyaniline, ethyl 4-aminobenzoate, 2-(bromophenyl)hydrazine hydrochloride, (2-chlorophenyl)boronic acid, 2-chloro-5-(trifluoromethyl)phenylboronic acid, *t*-BuOK, *t*-BuONa, Cs_2CO_3, $Pd(PPh_3)_2Cl_2$, PPh_3, $NaHCO_3$, MnO_2, $Pd(OAc)_2$, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos), bis-[2-(diphenylphosphino)phenyl]ether (DPEphos), iodobenzene, 1,3-dinitrobenzene, iron powder (Fe(0)), were commercially available and used as received from the supplier. 4-Amino-3-bromobenzonitrile, 2-bromo-4-methoxyaniline, 1-bromonaphthalen-2-amine and 10-bromophenanthren-9-amine were obtained by reported methods.[43] DMSO was stored under molecular sieves (4 Å). Toluene, dimethoxyethane

(DME) and dioxane were distilled from Na-benzophenone and stored under N_2 atmosphere. All solvents were analytical grade. Silica gel (0.063–0.200 mm) was used in column chromatography.

Representative Procedure for synthesis of 2'-halo-[1,1'-biphenyl]-2-amines

Method A: The following procedure is representative for biphenylamines **3a-c, d-e, g-j**. A solution of 2-bromoaniline (86 mg, 0.5 mmol), 2-chlorophenylboronic acid (93.6 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and $NaHCO_3$ (126 mg, 1.5 mmol) in DME (2 mL) was stirred at room temperature for 5 min. H_2O (2 mL) was added, and the resulting mixture was slightly degassed, sealed, and stirred at 120ºC for 2 h. After being cooled to room temperature, the mixture was extracted with Et_2O or EtOAc. The extracts were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 80:20 %). Dark yellow crystals of *2'-chloro-[1,1'-biphenyl]-2-amine* (**3a**) was isolated in 84% yield (88 mg, 0.433 mmol), **m.p.**: 51-53 ºC (lit[33] 52-53ºC). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.52-7.49 (m, 1H), 7.35-7.29 (m, 3H), 7.21 (br. ddd, *J* = 7.2, 6.4, 1.6 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.55 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 143.9, 138.1, 134.0, 132.0, 130.5, 130.0, 129.3, 129.19, 127.3, 125.5, 118.5, 115.7. **GC-MS** (EI) *m/z* 205 (10), 203 (22) [M^+], 169 (14), 168 (98), 167 (100), 140 (6), 139 (11), 84 (25).

2'-Chloro-5-methyl-[1,1'-biphenyl]-2-amine (**3b**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 70:30 %). Dark yellow oil was obtained in 49% yield (53 mg, 0.245 mmol). **^{1}H**

NMR (400 MHz, *CDCl₃*): δ 7.47-7.50 (m, 1H), 7.27-7.33 (m, 3H), 7.00-7.03 (m, 1H), 6.87 (d, *J* = 1.6 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.43 (br.s, 2H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 141.3, 138.2, 133.8, 131.9, 130.8, 129.8, 129.7, 129.0, 127.6, 127.2, 125.5, 115.7, 20.4. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.47-7.50/129.8, 7.27-7.33/131.9, 7.27-7.33/129.0, 7.27-7.33/127.2, 7.00-7.05/129.7, 6.87/130.8, 6.70/115.7, 2.27/20.4. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.27-7.33/7.47-7.50, 6.87/7.00-7.03, 6.70-7.00-7.03. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.47-7.50/127.2, 7.27-7.33/138.2, 7.27-7.33/133.8, 7.27-7.33/131.9, 7.27-7.33/129.8, 7.27-7.33/129.0, 7.27-7.33/125.5, 6.87/141.3, 6.87/138.2, 6.70/127.6, 6.70/125.5, 2.27/130.8, 2.27/129.7, 2.27/127.6. **GC-MS** (EI) *m/z* 219 (10), 217 (55) [M^+], 183 (12), 182 (100), 181 (36), 180 (16), 167 (64), 90 (14), 77 (18), 76 (13). **HRMS** (TOF, ESI^+): calcd for $C_{13}H_{13}ClN$ $(M + H)^+$: 218.0737; Found: 218.0727.[44]

2'-Chloro-5-methoxy-[1,1'-biphenyl]-2-amine (**3c**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (50:50 → 0:100 %). Light brown oil was obtained in 39% yield (45.4 mg, 0.195 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.48-7.51 (m, 1H), 7.30-7.35 (m, 3H), 6.82 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 3.76 (s, 3H), 3.31 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 152.4, 137.9, 137.4, 133.7, 131.8, 129.9, 129.1, 127.2, 126.5, 116.9, 115.6, 115.1, 55.8. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.48-7.51/129.9, 7.30-7.35/131.8, 7.30-735/129.1, 7.30-735/127.2, 6.75/116.9, 6.65/115.6, 6.82/115.1, 3.76/55.8. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.30-735/7.48-7.51, 6.75/6.82, 6.65/6.82. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.48-7.51/127.2, 7.30-7.35/137.9, 7.30-7.35/133.7, 7.30-7.35/131.8, 7.30-7.35/129.9, 7.30-7.35/129.1, 7.30-7.35/126.5, 6.82/152.4, 6.82/137.4, 6.82/115.6, 6.75/152.4, 6.75/133.7, 6.65/152.4, 6.65/137.9, 6.65/137.4, 6.65/115.1. **GC-MS** (EI) *m/z*: 235 (28), 234 (23), 233 (85) [M^+], 220 (28), 218 (100), 198 (55), 183 (34), 182 (33), 155 (37), 154 (34). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_{13}ClNO$ $(M + H)^+$: 234.0686; Found 234.0691.

2'-Chloro-5-carbonitrile-[1,1'-biphenyl]-2-amine (**3d**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 60:40 %). White amorphous solid was obtained in 60% yield (68.4 mg, 0.3 mmol), **m.p.**: 90-91 ºC. **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.50-7.55 (m, 1H), 7.46 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.35-7.40 (m, 2H), 7.33 (d, *J* =2.0 Hz, 1H), 7.28-7.30 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.06 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 147.9, 135.5, 134.7, 133.8, 133.3, 131.7, 130.2, 123.0, 127.6, 124.8, 119.8, 115.0, 100.3. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.50-7.55/130.2, 7.46/133.3, 7.35-7.40/130.0, 7.35-7.40/127.6, 7.33/134.7, 7.28-7.30/131.7, 6.76/115.0. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.33/7.46, 7.28-7.30/7.50-7.55, 7.28-7.30/7.35-7.40, 6.76/7.46. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.50-7.55/135.5, 7.50-7.55/133.8, 7.50-7.55/127.6, 7.46/147.9, 7.46/134.7, 7.46/119.8, 7.35-7.40/135.5, 7.35-7.40/133.8, 7.35-7.40/131.7, 7.35-7.40/130.2, 7.33/147.9, 7.33/133.3, 7.33/119.8, 7.28-7.30/135.5, 7.28-7.30/133.8, 7.28-7.30/130.0, 7.28-7.30/124.8, 6.76/124.8, 6.76/100.3, 4.06/124.8, 4.06/115.0. **GC-MS** (EI) *m/z:* 228 (20) [M^+], 194 (12), 193 (100), 192 (46), 166 (10), 164 (13), 96 (10), 83 (12). **HRMS** (TOF, ESI$^+$): calcd for $C_{13}H_9ClN_2Na$ $(M + Na)^+$: 251.0346; Found 251.0353.

2'-Chloro-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (**3e**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 90:10 %). Colorless oil was obtained in 17% yield (23 mg, 0.09 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.50-7.54 (m, 1H), 7.30-7.39 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.00 (s, 1H), 3.73 (br.s, 2H). **^{13}C NMR** (100

MHz, *CDCl₃*): δ 144.2, 136.7, 133.6, 131.5, 131.3 (q, *J* = 32 Hz), 130.9, 130.1, 129.6, 128.1, 127.4, 124.1 (q, *J* = 271 Hz), 111.9 (q, *J* = 4 Hz), 111.7 (q, *J* = 4 Hz). **^{1}H-^{13}C HSQC NMR** ($CDCl_3$): δ_H/δ_C 7.50-7.54/130.1, 7.30-7.39/130.9, 7.30-7.39/129.6, 7.30-7.39/127.4, 7.15/130.9, 7.06/111.7, 7.00/111.9. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.30-7.39/7.50-7.54, 7.06/7.15, 7.00/7.06. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.50-7.54/136.7, 7.50-7.54/133.6, 7.50-7.54/127.4, 7.30-7.39/133.6, 7.30-7.39/131.5, 7.30-7.39/130.1, 7.30-7.39/129.6, 7.30-7.39/128.1, 7.15/144.2, 7.15/136.7, 7.15/131.2, 7.06/128.1, 7.06/111.9, 7.07/128.1, 7.07/124.1, 7.07/111.7. **^{19}F** (377 MHz, *$CDCl_3$*): δ_F -62.85. **GC-MS** (EI) *m/z* 271 (27) [M^+], 237 (18), 236 (100), 235 (31), 216 (37), 168 (11), 167 (64), 166 (14), 108 (12). **HRMS** (TOF, ESI^+): calcd for $C_{13}H_{10}ClF_3N$ $(M + H)^+$: 272.0448; Found 272.0458.

2'-Chloro-3,5-dimethyl-[1,1'-biphenyl]-2-amine (**3g**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (50:50 → 25:75 %). Light yellow crystals were obtained in 79% yield (91.3 mg, 0.395 mmol), **m.p.**: 90-91 ºC. **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.47-7.50 (m, 1H), 7.27-7.32 (m, 3H), 6.94 (br.s, 1H), 6.75 (br.s, 1H), 3.35 (br.s, 2H), 2.25 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 139.4, 138.5, 133.9, 132.0, 131.0, 129.9, 128.9, 128.5, 127.2, 127.0, 125.2, 122.6, 20.4, 17.8. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.47-7.50/129.9, 7.27-7.32/132.0, 7.27-7.32/128.9, 7.27-7.32/127.2, 6.94/131.0, 6.75/128.5, 2.25/20.4, 2.22/17.8. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.27-7.32/7.47-7.50, 6.75/6.94, 2.25/6.94, 2.25/6.75, 2.20/6.94, 2.20/6.75. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.47-7.50/127.2, 7.27-7.32/138.5, 7.27-7.32/133.9, 7.27-7.32/132.0, 7.27-7.32/129.9, 7.27-7.32/128.9, 7.27-7.32/125.2, 6.94/139.4, 6.94/128.5, 6.75/139.4, 6.75/131.0, 2.25/131.0, 2.25/128.5, 2.25/127.0, 2.20/139.4, 2.20/131.0, 2.20/122.6. **GC-MS** (EI) *m/z*: 233 (16), 232 (10), 231

(54) [M^+], 197 (13), 196 (100), 195 (38), 194 (24), 182 (11), 181 (76), 180 (40). **HRMS** (TOF, ESI^+): calcd for $C_{14}H_{15}ClN$ $(M + H)^+$: 232.0888; Found 232.0891.

2'-Chloro-5'-(trifluoromethyl)-5-carbonitrile-[1,1'-biphenyl]-2-amine (**3h**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (100:0 → 70:30 %). Colorless oil was obtained in 39% yield (57.8 mg, 0.195 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.63-7.69 (m, 2H), 7.59-7.60 (m, 1H), 7.50 (dd, *J*= 8.4, 2.0 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.04 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 147.7, 137.9, 136.4, 134.7, 133.8, 130.6, 130.2 (q, *J* = 33 Hz), 128.7 (q, *J* = 4 Hz), 126.8 (q, *J* = 4 Hz), 123.4 (q, *J* = 207 Hz), 123.2, 119.5, 115.3, 100.7. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.63-7.69/130.9, 7.63-7.69/126.8, 7.59-7.60/128.7, 7.50/133.8, 7.34/134.7, 6.79/115.3. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.59-7.60/7.63-7.69, 7.34/7.50, 6.79/7.50. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.63-7.69/137.9, 7.63-7.69/136.7, 7.63-7.69/130.2, 7.63-7.69/128.7, 7.63-7.69/123.4, 7.59-7.60/137.9, 7.59-7.60/126.8, 7.59-7.60/123.4, 7.59-7.60/123.2, 7.50/147.7, 7.50/134.7, 7.50/119.5, 7.34/137.9, 7.34/136.4, 7.34/133.8, 7.34/119.5, 6.79/136.4, 6.79/123.2, 6.79/110.7. **GC-MS** (EI) *m/z*: 298 (17), 296 (52) [M^+], 261 (87), 260 (26), 242 (13), 241 (100), 192 (71), 191 (19), 164 (18). **HRMS** (TOF, ESI^+): calcd for $C_{14}H_8ClF_3N_2Na$ $(M + Na)^+$: 319.0226; Found 319.0234.

2-(2-Chlorophenyl)pyridin-3-amine (**3i**). The compound was prepared in an oven-dried Schlenk tube charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and Xphos (10 mg, 0.02 mmol), evacuated, and filled with nitrogen. 1.4-Dioxane (2 mL) was added followed by 2-chloro-3-nitropyridine (**1h**) (79 mg, 0.5 mmol) to the flask via syringe. The resulting mixture was stirred at room temperature and 2-chlorophenylboronic acid (**2a**, 93.6 mg, 0.6 mmol) was added followed by Cs_2CO_3 (488 mg, 1.5 mmol), added in one portion. The solution was heated with stirring to 80ºC for 18 h. After being cooled to room temperature, the mixture was extracted with EtOAc. The resulting crude was chemically reduced in 2 ml of ethanol/water (5/2) with 1 equiv of Fe(0) in power and 2 equiv of HCl. The crude was filtrate over Celite and extracted with EtOAc. The extracts were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 50:50 %). Dark brown solid was obtained in 30% yield (31 mg, 0.15 mmol), **m.p.**: 122-123 ºC. **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 8.11 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.47-7.49 (m, 1H), 7.32-7.41 (m, 3H), 7.11 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.64 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 143.6, 140.5, 139.5, 137.1, 133.2, 131.5, 129.9, 129.8, 127.4, 123.8, 122.4. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 8.11/139.5, 7.47-7.49/129.9, 7.32-7.41/131.3, 7.32-7.41/129.8, 7.32-7.41/127.4, 7.11/123.81, 7.05/122.4. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.32-7.41/7.47-7.49, 7.11/8.11, 7.05/7.11, 7.05/7.11. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 8.11/143.6, 8.11/123.8, 8.11/122.4, 7.47-7.49/137.1, 7.47-7.49/133.2, 7.47-7.49/127.4, 7.32-7.41/143.6, 7.32-7.41/137.1, 7.32-7.41/133.2, 7.32-7.41/131.3, 7.32-7.41/129.9, 7.32-7.41/129.8, 7.11/140.5, 7.11/139.5, 7.05/143.6, 7.05/139.5. **CG-MS** (EI) *m/z*: 205 (10), 204 (23) [M^+], 203 (16), 170 (10), 169 (100), 168 (45), 115 (11), 102 (10). **HRMS** (TOF, ESI^+): calcd for $C_{11}H_{10}ClN_2$ $(M + H)^+$: 205.0533; Found 205.0527. [45]

1-(2-Chlorophenyl)naphthalen-2-amine (**3j**). Prepared by the general procedure **A** and purified by column chromatography on silica gel eluting with petroleum ether: EtOAc (100:0 → 70:30 %). Brown oil obtained in 21% yield (26.6 mg, 0.105 mmol). **^{1}H NMR**

(400 MHz, *CDCl$_3$*): δ 7.72-7.75 (m, 2H), 7.60-7.62 (m, 1H), 7.21-7.45 (m, 5H), 7.08 (d.br, J = 8.4 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 3.63 (br.s, 2H). **^{13}C NMR** (100 MHz, *CDCl$_3$*): δ 141.2, 135.8, 135.4, 133.3, 133.0, 130.3, 129.4, 129.4, 128.1, 127.9, 127.7, 126.6, 123.7, 122.3, 118.1, 117.1. **^{1}H-^{13}C HSQC NMR** (*CDCl$_3$*): δ_H/δ_C 7.72-7.75/129.4, 7.72-7.75/128.1, 7.60-7.62/130.3, 7.21-7.45/133.0, 7.21-7.45/129.4, 7.21-7.45/127.7, 7.21-7.45/126.6, 7.21-7.45/122.3, 7.08/123.7, 7.04/118.1. **^{1}H-^{1}H COSY NMR** (*CDCl$_3$*): δ_H/δ_H 7.21-7.45/7.60-7.62, 7.21-7.45/7.72-7.75, 7.08/7.21-7.45, 7.04/7.72-7.75. **^{1}H-^{13}C HMBC NMR** (*CDCl$_3$*): δ_H/δ_C 7.72-7.75/141.2, 7.72-7.75/133.3, 7.72-7.75/129.4, 7.72-7.75/128.1, 7.72-7.75/126.6, 7.60-7.62/135.8, 7.60-7.62/135.4, 7.60-7.62/127.7, 7.21-7.45/135.8, 7.21-7.45/135.4, 7.21-7.45/133.3, 7.21-7.45/133.0, 7.21-7.45/130.3, 7.21-7.45/129.4, 7.21-7.45/127.9, 7.21-7.45/127.7, 7.21-7.45/123.7, 7.21-7.45/117.1, 7.08/122.3, 7.04/117.1. **GC-MS** (EI) *m/z*: 255 (15), 253 (46) [M^+], 219 (12), 218 (76), 217 (100), 216 (18), 189 (23), 109 (40), 96 (16), 94 (29). **HRMS** (TOF, ESI$^+$): calcd for $C_{16}H_{13}ClN$ $(M + H)^+$: 254.0737; Found 254.0741.

Method B: The following procedure is representative of the biphenylamines **3c´** and **3f**. To a stirred suspension of the aniline derivative (1.65 g, 10.0 mmol), $NaHCO_3$ (210 mg, 2.5 mmol) and MnO_2 (217 mg, 2.5 mmol) in MeCN (2.5 mL) at rt was added the 2-bromophenylhydrazine hydrochloride (**4**, 111 mg, 0.5 mmol) in portions over a period of 10 to 30 min. After completion of the reaction, as monitored by TLC, the reaction mixture was filtered over Celite. The filter cake was further washed with ethyl acetate. The organic layer was washed with water (30 mL) and saturated aqueous NaCl and dried over Na_2SO_4. The solvent was removed under reduced pressure. The remaining aniline was recovered by Kugelrohr distillation and the resulting crude product was purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (100:0 → 80:20 %). Light brown oil of *2'-bromo-5-methoxy-[1,1'-biphenyl]-2-amine* (**3c´**) was obtained in 31% yield (43 mg, 0.155 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.69 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.39 (td, *J* = 7.2, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22-7.26 (m, 1H), 6.82 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.63 (d, *J* = 3.2 Hz, 1H), 3.76 (s, 3H), 3.29 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 152.3, 139.9, 137.2, 133.1, 131.7, 129.3, 128.2, 128.0, 124.0, 116.9, 115.4, 115.1, 55.7. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.69/133.1, 7.39/128.0, 7.33/131.7, 7.22-7.26/129.3, 6.82/115.1, 6.74/116.9, 6.63/115.4, 3.76/55.7. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.33/7.39, 7.22-7.26/7.69, 7.22-7.26/7.39, 6.74/6.82, 6.63/6.82. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.39/139.9, 7.69/127.8, 7.39/140.0, 7.39/133.1, 7.33/129.3, 7.33/124.0, 7.22-7.26/131.7, 7.22-7.26/124.0, 6.82/137.2, 6.82/115.4, 6.74/152.3, 6.74/128.2, 6.63/152.3, 6.63/139.9, 6.63/137.2, 6.63/115.1, 3.76/152.3. **GC-MS** (EI) *m/z*: 279 (79) [M^++2], 277 (70) [M^+], 264 (56), 262 (54), 198 (100), 183 (41), 182 (50), 167 (27), 155 (79), 154 (93), 77 (30). **HRMS** (TOF, ESI^+): calcd for $C_{13}H_{13}BrNO$ $(M + H)^+$: 278.0181; Found 278.0181.

Ethyl 6-amino-2'-bromo-[1,1'-biphenyl]-3-carboxylate (**3f**). Prepared by the general procedure **B** and purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 80:20 %). Light brown oil of was obtained in 27% yield (43 mg, 0.135 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24-7.29 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.94 (br.s, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 166.6, 147.9, 138.9, 133.2, 132.3, 131.9, 131.1, 129.6, 128.0, 125.8, 124.2, 119.9, 114.3, 60.4, 14.4. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.91/131.1, 7.74/132.3, 7.70/133.2, 7.41/128.0, 7.32/131.9, 7.24-7.29/129.6, 6.75/114.3, 4.32/60.4, 1.35/14.4. **^{1}H-^{1}H COSY NMR** (*CDCl$_3$*): δ_H/δ_H 7.74/7.91, 7.32/7.41, 7.24-7.29/7.70, 7.24-7.29/7.41, 6.75/7.91, 1.35/4.32. **^{1}H-^{13}C HMBC NMR** (*CDCl$_3$*): δ_H/δ_C 7.91/166.6, 7.91/147.9, 7.91/132.3, 7.74/166.6, 7.74/147.9, 7.74/138.9, 7.74/131.1, 7.70/138.9, 7.70/128.0, 7.41/138.9, 7.41/133.2, 7.32/129.6, 7.32/127.2, 7.24-7.29/131.9, 7.24-7.29/124.2, 6.75/125.8, 6.75/119.9. **GC-MS** (EI) *m/z*: 321 (28) [M^++2], 319 (24) [M^+], 276 (27), 274 (24), 240 (50), 168 (61), 167 (100), 166 (31), 139 (26), 83 (27). **HRMS** (TOF, ESI$^+$): calcd for $C_{15}H_{14}BrNNaO_2$ (M + Na)$^+$: 342.0106; Found 342.0116.

Representative Procedure for synthesis of *N*-phenyl-2'-halo-[1,1'-biphenyl]-2-amines (9a-c and 11). An oven-dried Schlenk tube was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and DPEphos (4 mg, 0.0075 mmol), evacuated, and filled with nitrogen. Toluene (2 mL) was added followed by 2'-chloro-[1,1'-biphenyl]-2-amine (**3a**) (122 mg, 0.6 mmol) and iodobenzene (102 mg, 0.5 mmol). The resulting mixture was stirred for 5 min at r.t., affording a dark yellow solution. The flask was opened, solid *t*-BuONa (62 mg, 0.65 mmol) was added in one portion. The reaction tube was purged for 3 min with nitrogen, and the mixture was heated with stirring to 100ºC overnight. After being cooled to r.t., the mixture was extracted with EtOAc. The extracts were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 90:10 %). Dark yellow crystals of *N-phenyl-2'-chloro-[1,1'-biphenyl]-2-amine* (**9a**) were isolated in 49% yield (68.4 mg, 0.245 mmol), **m.p.**: 51-53 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.51 (m, 1H), 7.37 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.27-7.35 (m, 4H), 7.20-7.25 (m, 2H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.99 (td, *J* =

7.6, 1.2 Hz, 1H), 6.90-6.94 (m, 1H), 5.31 (s, 1H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 143.0, 141.0, 137.7, 134.1, 132.0, 130.9, 129.9, 129.2, 129.2, 128.8, 127.2, 131.4, 120.5, 118.8, 116.8. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.48-7.51/129.9, 7.37/116.8, 7.27-7.35/132.0, 7.27-7.35/129.2, 7.27-7.35/128.8, 7.27-7.35/127.2, 7.20-7.25/129.2, 7.18/130.9, 7.03/118.8, 6.99/120.5, 6.90-6.94/121.4. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.37/7.48-7.51, 7.27-7.35/7.37, 7.18/7.27-7.35, 7.03/7.20-7.25, 6.99/7.37, 6.99/7.18, 6.90-6.94/7.20-7.25, 6.90-6.94/7.03. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.48-7.51/127.2, 7.37/128.8, 7.37/120.5, 7.27-7.35/141.0, 7.27-7.35/137.7, 7.27-7.35/134.1, 7.27-7.35/132.0, 7.27-7.35/130.9, 7.27-7.35/129.9, 7.20-7.25/143.0, 7.20-7.25/129.2, 7.20-7.25/118.8, 7.18/141.0, 7.18/137.7, 7.18/128.8, 7.03/129.2, 7.03/121.4, 7.03/118.8, 6.99/128.8, 6.99/116.8, 6.90-6.94/118.84. **GC-MS** (EI) *m/z*: 279 (30) [M^+], 245 (19), 244 (100), 243 (40), 242 (18), 241 (15), 167 (28), 166 (35), 139 (12), 121 (16), 120 (30). **HRMS** (TOF, ESI^+): calcd for $C_{18}H_{15}ClN$ (M + H)$^+$: 280.0893; Found 280.0910.

2'-Chloro-5-methyl-N-phenyl-[1,1'-biphenyl]-2-amine (**9b**). The compound was prepared by the general method above described and purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (100:0 → 90:10 %). Dark brown oil was obtained in 50% yield (73.3 mg, 0.25 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.45-7.48 (m, 1H), 7.28-7.32 (m, 4H), 7.17-7.22 (m, 2H), 7.11-7.13 (m, 1H), 7.00-7.01 (m, 1H), 6.94-6.96 (m, 2H), 6.83-6.88 (m, 1H), 5.22 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 143.8, 138.2, 137.9, 134.0, 131.9, 131.3, 130.5, 129.8, 129.4, 129.1, 129.0, 127.1, 120.6, 118.3, 117.7, 20.6. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.45-7.48/129.8, 7.32/131.3, 7.32/129.0, 7.32/127.1, 7.28-7.32/118.3, 7.17-7.22/129.1, 7.11-7.13/129.4, 7.00-7.01/131.9, 6.94-6.96/117.7, 6.83-6.88/120.6, 2.34/20.6. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.28-7.32/7.45-7.48, 7.11-7.13/7.28-7.32, 7.00-7.01/7.11-7.13, 6.94-6.96/7.17-7.22, 6.83-6.88/7.17-7.22,

6.83-6.88/6.94-6.96. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.45-7.48/127.1, 7.28-7.32/137.9, 7.28-7.32/134.0, 7.28-7.32/131.9, 7.28-7.32/130.5, 7.28-7.32/129.8, 7.28-7.32/129.0, 7.17-7.22/143.8, 7.17-7.22/129.1, 7.17-7.22/117.7, 7.11-7.13/138.2, 7.11-7.13/131.3, 7.00-7.01/138.2, 7.00-7.01/129.4, 6.94-6.96/120.6, 6.94-6.96/117.7, 6.83-6.88/117.7, 2.34/131.3, 2.34/130.5, 2.34/129.8. **GC-MS** (EI) *m/z*: 295 (19), 294 (11), 293 (57) [M^+], 259 (19), 258 (100), 257 (30), 256 (27), 243 (76), 180 (24), 127 (42), 121 (32). **HRMS** (TOF, ESI^+): calcd for $C_{19}H_{17}ClN$ $(M + H)^+$: 294.1050; Found 294.1054.

2'-Bromo-5-methoxy-N-phenyl-[1,1'-biphenyl]-2-amine (**9c**). The compound was prepared by the general method above described and purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (100:0 → 80:20 %). Dark brown oil was obtained in 35% yield (61.8 mg, 0.175 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.33 (td, *J* = 7.2, 1.2 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (ddd, *J* = 7.9, 7.3, 2.0 Hz, 1H), 7.13-7.18 (m, 2H), 6.91 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.84 (dd, *J* = 8.6, 0.8 Hz, 2H), 6.78-6.82 (m, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 5.09 (br.s, 1H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 154.7, 144.9, 139.8, 134.3, 133.5, 132.9, 131.6, 129.3, 129.1, 127.6, 124.0, 121.9, 119.7, 116.4, 115.8, 114.6, 55.6. **^{1}H-^{13}C HSQC NMR** (*$CDCl_3$*): δ_H/δ_C 7.66/132.9, 7.33/127.6, 7.33/121.9, 7.27/131.6, 7.21/129.3, 7.13-7.18/129.1, 6.91/114.6, 6.84/116.4, 6.78-6.82/119.7, 6.77/115.8, 3.81/55.6. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.33/7.66, 7.27/7.33, 7.21/7.66, 7.21/7.33, 7.21/7.27, 6.91/7.33, 6.84/7.13-7.18, 6.78-6.82/7.13-7.18, 6.78-6.82/6.84, 6.77/6.91. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 7.66/139.8, 7.66/127.6, 7.66/124.0, 7.33/154.7, 7.33/139.8, 7.33/134.3, 7.33/133.5, 7.33/132.9, 7.27/129.3, 7.27/124.0, 7.21/131.6, 7.21/124.0, 7.13-7.18/144.9, 7.13-7.18/129.1, 7.13-7.18/116.4, 6.91/154.7, 6.91/133.5, 6.91/115.8, 6.84/119.7, 6.84/116.4, 6.78-6.82/116.4, 6.77/154.7, 6.77/139.8, 6.77/133.5, 6.77/114.6. **GC-MS** (EI) *m/z*: 355 (61) [M^++2], 353 (52) [M^+], 340 (25), 338 (23), 274 (100), 259 (30), 258 (25), 243 (50), 231 (25), 230 (96), 137 (26), 130 (34), 115 (30). **HRMS** (TOF, ESI^+): calcd for $C_{19}H_{17}BrNO$ $(M + H)^+$: 354.0494; Found 354.0510.

10-(2-Chlorophenyl)-N-phenylphenanthren-9-amine (**11**). The compound was prepared as followed: a solution of 10-bromophenanthren-9-amine (135.5 mg, 0.5 mmol), 2-chlorophenylboronic acid (**2a**, 93.6 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and $NaHCO_3$ (126 mg, 1.5 mmol) in DME (2 mL) was stirred at room temperature for 5 min. H_2O (2 mL) was added, and the resulting mixture was slightly degassed, sealed, and stirred at 120ºC for 2 h. After being cooled to room temperature, the mixture was extracted with EtOAc. The extracts were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting mixture was used in the next step without purification. In an oven-dried Schlenk tube was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and DPEphos (4 mg, 0.0075 mmol), evacuated, and filled with nitrogen. Toluene (2 mL) was added followed by the crude of the Suzuki-reaction and iodobenzene (102 mg, 0.5 mmol). The resulting mixture was stirred for 5 min at r.t., affording a dark brown solution. The flask was opened, solid *t*-BuONa (62 mg, 0.65 mmol) was added in one portion. The reaction tube was purged for 3 min with nitrogen, and the mixture was heated with stirring to 100ºC overnight. After being cooled to r.t., the mixture was extracted with EtOAc. The extracts were combined, dried over Na_2SO_4, and filtered. After removal of volatile components from the filtrate, the resulting crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (100:0 → 90:10 %). Dark yellow oil was obtained in 30% yield (56.9 mg, 0.15 mmol). **^{1}H NMR** (400 MHz, *CD_3COCD_3*): δ 8.93 (d, *J* = 8.0 Hz, 1H), 8.91 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.71-7.75 (m, 1H), 7.65-7.69 (m, 1H), 7.50-7.58 (m, 3H), 7.42-7.46 (m, 1H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.25 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.98-7.02 (m, 2H), 6.63-6.65 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR** (100 MHz, *CD_3COCD_3*): δ 148.7, 137.3, 135.3, 135.2, 132.8, 132.7, 132.6, 132.4, 130.8, 130.4, 130.3, 130.1, 129.5, 128.0, 127.8, 127.6, 127.1, 127.1, 126.7, 124.0, 123.7, 119.0, 115.7. **^{1}H/^{13}C HSQC NMR** (*CD_3COCD_3*): δ_H/δ_C 8.93/124.0, 8.91/123.7, 8.10/126.7, 7.71-7.75/128.0, 7.65-7.69/127.1, 7.50-7.58/130.3, 7.50-7.58/127.8, 7.50-7.58/127.6, 7.42-7.46/130.4, 7.36/128.0, 7.32/132.7, 7.25/127.1, 6.98-7.02/129.5, 6.63-6.65/119.0, 6.52/115.7. **^{1}H/^{1}H COSY NMR** (*CD_3COCD_3*): δ_H/δ_H 7.71-7.75/8.93, 7.71-7.75/8.10, 7.65-7.69/8.91, 7.50-7.58/8.93, 7.50-7.58/8.91, 7.50-7.58/8.10, 7.50-7.58/7.71-7.75, 7.50-7.58/7.65-7.69, 7.36/7.50-7.58, 7.36/7.42-7.46, 7.32/7.42-7.46, 7.32/7.36, 7.25/7.65-6.69, 7.25/7.50-7.58, 6.63-6.65/6.98-7.02, 6.52/6.98-7.02, 6.52/6.63-6.65. **^{1}H/^{13}C HMBC NMR** (*CD_3COCD_3*): δ_H/δ_C 8.93/130.8, 8.93/127.8, 8.91/132.6, 8.91/127.6, 8.10/135.3, 8.10/132.6, 8.10/128.0, 7.71-7.75/132.4, 7.71-7.75/126.7, 7.65-7.69/130.1, 7.65-7.69/127.1, 7.50-7.58/137.3, 7.50-7.58/135.2, 7.50-7.58/132.6, 7.50-7.58/130.8, 7.50-7.58/128.0, 7.50-7.58/124.0, 7.50-7.58/123.7, 7.42-7.46/135.2, 7.42-7.46/132.7, 7.36/137.3, 7.36/130.3, 7.32/135.2, 7.32/130.4, 7.25/132.8, 7.25/130.1, 7.25/127.1, 6.98-7.02/148.7, 6.98-7.02/129.5, 6.63-6.65/115.7, 6.52/119.0, 6.52/115.7. **GC-MS** (EI) *m/z*: 282 (10), 381 (20), 380 (26), 379 (46) [M^+], 345 (29), 344 (88), 343 (100), 342 (25), 341 (25), 267 (44), 266 (22), 264 (9), 252 (10), 250 (10), 239 (14), 190 (10), 172 (12), 170 (24), 165 (24), 164 (30), 158 (11), 134 (25), 77 (12), 51 (11). **HRMS** (TOF, ESI^+): calcd for $C_{26}H_{19}ClN$ $(M + H)^+$: 380.1206; Found. 380.1232.

Representative Procedure for Photostimulated Reactions. Preparation of carbazole derivatives in Liquid Ammonia. Liquid ammonia (150 ml), previously dried over Na metal, was distilled into a 250 mL three-necked, round-bottomed flask equipped with a cold-finger condenser and a magnetic stirrer under a nitrogen atmosphere. The base *t*-BuOK (2.0 equiv, 45 mg, 0.4 mmol) and then the corresponding halo-biphenyl-amine (1 equiv, 0.2 mmol) was added to the liquid ammonia. In case the biphenyl-amine was an oil, it was added dissolved in dry ethyl ether. After 180 min of irradiation the reaction was quenched by addition of NH_4NO_3 in excess, and the ammonia was allowed to evaporate. Water (50 mL) was added to the residue and the mixture was extracted with methylene chloride or ethyl acetate (3 x 30 mL). The organic extract was dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to leave the crude products. The products were purified by chromatography on silica gel or quantified by GC using the internal standard method. The halide anions in the aqueous solution were determined potentiometrically.

Preparation of carbazole derivatives in DMSO. The following procedure is representative of all these reactions. The reaction was carried out in a Schlenk tube equipped with a nitrogen inlet and magnetic stirred at r.t. DMSO (5 ml) was dried and deoxygenated, then *t*-BuOK (2.0 equiv, 45 mg, 0.4 mmol) was added and after 5 min the corresponding biphenyl-amine (1 equiv, 0.2 mmol) was added and the reaction mixture was irradiated for 180 min. Also in case the biphenyl-amine was oil it was added dissolved in dry ethyl ether. The reaction was quenched with ammonium nitrate in excess. The residue was extracted with CH_2Cl_2 or ethyl acetate (3 x 30 ml) and the organic extracted was washed with water and dried with anhydrous Na_2SO_4.

Isolation and Identification of Products. *9H-carbazole* (**6a**). The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (100:0 → 25:75 %). White amorphous solid was obtained in 41% yield (14 mg, 0.082

mmol) **m.p.**: 245-246 (lit[21] 245-247ºC). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 8.07-8.09 (m, 2H), 8.04 (br.s, 1H), 7.39-7.44 (m, 4H), 7.22-7.26 (m, 2H). **^{13}C NMR** (400 MHz, *$CDCl_3$*): δ 139.5, 125.8, 123.4, 120.3, 119.4, 110.6. **GC-MS** (EI) *m/z*: 168 (11), 167 (100) [M^+], 166 (26), 140 (10), 139 (26), 89 (11), 84 (13), 70 (10).

[1,1'-Biphenyl]-2-amine (**7a**)**.**[46] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (100:0 → 25:75 %). Black solid was obtained in 9 % yield (3 mg, 0.018 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.34-7.45 (m, 5H), 7.12-7.15 (m, 2H), 6.74-6.84 (m, 2H), 3.74 (br.s, 2H). **GC-MS** (EI) *m/z*: 169 (56) [M^+], 168 (100), 167 (29), 141 (19), 116 (13), 115 (12), 84 (23), 78 (16), 62 (13), 57 (14).

3-Methyl-9H-carbazole (**6b**).[13] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40 %). White amorphous solid was obtained in 48% yield (17.4 mg, 0.096 mmol), **m.p.**: 208-209 ºC (lit[13] 204-205 ºC). **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.08 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.89 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.33-7.38 (m, 2H), 7.2 (d, J = 8.4 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 140.4, 138.4, 127.5, 127.2, 125.7, 123.0, 122.7, 120.4, 120.3, 118.7, 111.3, 111.1, 21.5. **GC-MS** (EI) *m/z*: 181 (81) [M^+], 180 (100), 179 (14), 90 (22), 76 (14), 77 (15), 90 (23).

5-Methyl-[1,1'-biphenyl]-2-amine (**7b**). The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40 %). Light brown oil was obtained with an approximate 5% yield (1.8 mg, 0.01mmol).**^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 6.95-6.98 (m, 5H), 6.69 (d, J = 8.0 Hz, 1H), 3.62 (br.s, 2H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 140.9, 139.7, 130.9, 129.1, 129.0, 127.8, 127.7, 127.0, 115.8, 20.4. **GC-MS** (EI) *m/z*: 184 (15), 183 (100), 182 (69), 167 (18), 109 (11), 85 (12), 71 (17), 69 (13).

3-Methoxy-9H-carbazole (**6c**).[13] The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100: 0→ 80:20 %). White crystals were isolated in 29% yield (11.4 mg, 0.058 mmol), **m.p.**: 150-151 ºC (lit[13] 147-148 ºC).**^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.03 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 153.4, 140.8, 135.0, 125.8, 123.2, 122.9, 120.7, 118.4, 115.2, 112.0, 111.4, 103.4, 56.1. **GC-MS** (EI) *m/z*: 183 (11), 182 (100) [M^+], 154 (40), 153 (13), 128 (10), 127 (18), 126 (10).

5-Methoxy-[1,1'-biphenyl]-2-amine (**7c**).[13] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (95:5 → 70:30 %). Light brown oil was obtained in 20% yield (8 mg, 0.04 mmol). **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.42-7.47 (m, 4H), 7.32-7.37 (m, 1H), 6.71-6.78 (m, 3H), 3.76 (s, 3H), 3.49 (br.s, 2H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 152.7, 139.5, 137.1, 129.0, 128.8, 128.7, 127.2, 116.9, 115.7, 114.4, 55.8. **GC-MS** (EI) *m/z*: 199 (74) [M^+], 185 (15), 184 (100), 156 (25), 128 (13), 77 (14).

3-Carbonitrile-9H-carbazole (**6d**).[47] The product was purified by column chromatography on silica gel eluting with petroleum ether/ethyl ether (100:0 → 60:40 %)). Light yellow crystals were obtained in 79% yield (31.1 mg, 0.158 mmol), **m.p.**: 189-190 ºC. **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.84 (br.s, 1H), 8.68 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45-7.49 (m, 1H), 7.22-7.26 (m, 1H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 142.1, 140.7, 129.0, 127.4, 126.0, 123.1, 122.1, 121.4, 121.0, 120.3, 112.5, 112.0, 100.7. **^{1}H-^{13}C HSQC NMR** (*CD_3SOCD_3*):

δ_H/δ_C 8.68/126.0, 8.22/121.4, 7.73/129.0, 7.61/112.5, 7.55/112.0, 7.45-7.49/127.4, 7.22-7.26/121.0. **^{1}H-^{1}H COSY NMR** (*CD_3SOCD_3*): δ_H/δ_H 7.61/7.73, 7.45-7.49/7.55, 7.22-7.26/8.22, 7.22-7.26/7.45-7.49. **^{1}H-^{13}C HMBC NMR** (*CD_3SOCD_3*): δ_H/δ_C 8.68/142.1, 8.68/129.0, 8.68/121.3, 8.22/140.7, 8.22/127.4, 8.22/123.1, 7.73/142.1, 7.73/126.0, 7.73/121.0, 7.61/123.1, 7.61/100.7, 7.55/122.1, 7.55/120.3, 7.45-7.49/140.7, 7.45-7.49/121.4, 7.22-7.26/122.0, 7.22-7.26/112.0. **GC-MS** (EI) *m/z*: 193 (14), 192 (100) [M^+], 191 (14), 165 (11), 164 (19), 96 (15). **HRMS** (TOF, ESI^+): calcd for $C_{13}H_9N_2$ $(M + H)^+$: 193.0766; Found. 193.0769.

3-(Trifluoromethyl)-9H-carbazole (**6e**).[1] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40 %). White amorphous solid was obtained in 72% yield (33.8 mg, 0.144 mmol), **m.p.**: 160-162 ºC (lit[13] 157-159 ºC). **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.64 (br.s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.22-7.26 (m, 1H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 141.3, 139.2, 129.6, 127.5, 126.1 (q, *J* = 31 Hz), 125.8, 125.5 (q, *J* = 270 Hz), 121.9, 121.5, 121.5, 119.8, 115.2 (q, *J* = 3 Hz), 112.0, 108.4 (q, *J* = 4 Hz, 1C). **^{19}F** (377 MHz, *CD_3SOCD_3*): δ_F -59.26. **GC-MS** (EI) *m/z*: 236 (14), 235 (100) [M^+], 234 (11), 216 (12), 166 (12), 117 (14), 93 (14).

Ethyl 9H-carbazole-3-carboxylate (**6f**).[48] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40%). White amorphous solid was obtained in 47% yield (22.5 mg, 0.094 mmol), **m.p.**: 168-169 ºC (lit[48] 164-165ºC). **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.71 (br.s, 1H), 8.78 (d, *J* = 1.6 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.53-7.57 (m, 2H), 7.45 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.23 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100.62 MHz, *CD_3SOCD_3*): δ 166.9, 143.0, 140.8, 127.1, 126.8, 122.9, 122.8, 122.7, 121.1, 120.6, 120.0, 111.8, 111.2, 60.7, 14.9. **GC-MS** (EI) *m/z*: 239 (43) [M^+], 224 (10), 211 (34), 195 (15), 194 (100), 166 (37), 139 (33).

1,3-Dimethyl-9H-carbazole (**6g**)**.**[49] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40 %). White amorphous solid was petroleum ether:ethyl ether (95:5 → 65:35 %). This solid was obtained in 44% yield (17.2 mg, 0.088 mmol), **m.p.**: 98-99 ºC. **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.03 (br.s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 2.51 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 140.5, 137.8, 127.9, 127.6, 125.6, 123.1, 122.6, 120.5, 120.2, 118.7, 117.8, 111.4, 21.5, 17.4. **GC-MS** (EI) *m/z*: 196 (10), 195 (100) [M^+], 194 (47), 180 (46), 90 (11), 84 (10).

3,5-Dimethyl-[1,1'-biphenyl]-2-amine (**7g**).[50] The product was purified by column chromatography on silica gel eluting with petroleum ether/1,2-dichloroethane (75:25 → 60:40 %). White amorphous solid was obtained in 15% yield (6 mg, 0.03 mmol), **m.p.**: 90-91 ºC. **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 7.43-7.44 (m, 4H), 7.31-7.36 (m, 1H), 6.91 (br.s, 1H), 6.84 (br.s, 1H), 3.58 (br.s, 2H), 2.26 (s, 3H), 2.2 (s, 3H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 139.9, 139.0, 130.4, 129.2, 128.7, 128.7, 127.6, 127.2, 127.0, 122.6, 20.3, 17.9. **GC-MS** (EI) *m/z*: 198 (14), 197 (61) [M^+], 196 (26), 182 (24), 181 (14), 86 (50), 84 (73), 51 (32), 49 (100).

6-(Trifluoromethyl)-9H-carbazole-3-carbonitrile (**6h**). The product was purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (95:5 → 70:30 %). Light yellow solid was obtained in 70% yield (36.4 mg, 0.14 mmol), **m.p.**: 221-223 ºC. **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 12.27 (s, 1H), 8.89 (s, 1H), 8.73 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 142.4, 142.1, 129.6, 126.4, 125.2 (q, *J* = 270 Hz), 123.4 (q, *J* = 4 Hz), 122.3, 121.4, 120.5 (q, *J* = 32 Hz), 120.2, 118.9 (q, *J* = 4 Hz), 112.6, 112.3, 101.3. **^{1}H-^{13}C HSQC NMR** (*CD_3SOCD_3*): δ_H/δ_C 8.89/126.4, 8.73/118.9, 7.84/129.6, 7.78/123.4, 7.75/112.3, 7.72/112.6. **^{1}H-^{1}H COSY NMR** (*CD_3SOCD_3*): δ_H/δ_H 7.84/8.89, 7.78/8.73, 7.75/7.78, 7.72/7.84. **^{1}H-^{13}C HMBC NMR** (*CD_3SOCD_3*): δ_H/δ_C 8.89/142.47, 8.89/129.6, 8.89/120.2, 8.73/142.1, 8.73/125.2, 8.73/123.4, 8.73/122.3, 7.84/142.4, 7.84/126.4, 7.84/120.2, 7.78/142.1, 7.78/118.9, 7.75/121.4, 7.75/120.5, 7.72/122.3, 7.72/101.3. **^{19}F** (377 MHz, *CD_3SOCD_3*): δ_F -58.5. **GC-MS** (EI) *m/z*: 260 (100) [M^+], 259 (12), 241 (12), 210 (14), 209 (10), 191 (10), 164 (10). **HRMS** (TOF, ESI^+): calcd for $C_{14}H_7F_3N_2Na$ $(M + Na)^+$: 283.0459; Found 283.0467.

5H-Pyrido[3,2-b]índole (**6i**). The product was purified by column chromatography on silica gel eluting with petroleum ether/acetone (75:25 → 50:50 %). Light yellow crystals were obtained in 58% yield (19.5 mg, 0.116 mmol), **m.p.**: 209-210 ºC (lit[23] 212-213 ºC). **^{1}H NMR** (400 MHz, *CD_3SOCD_3*): δ 11.44 (br.s, 1H), 8.46 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48-7.53 (m, 1H), 7.39 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.23-7.27 (m, 1H). **^{13}C NMR** (100 MHz, *CD_3SOCD_3*): δ 141.6, 141.0, 133.3, 127.8, 122.0, 120.6, 120.5, 119.8, 118.4, 112.2. **GC-MS** (EI) *m/z*: 169 (11), 168 (100) [M^+], 140 (14), 114 (10), 84 (11).

7H-Benzo[c]carbazole (**6j**). Compound **6j** was purified by column chromatography on silica gel (eluent: gradient petroleum ether: EtOAc (100:0 → 85:15 %). Colorless solid was obtained in 53% yield (21.5 mg, 0.099 mmol), **m.p.**: 135-136 ºC (lit[51] 133-134 ºC). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.33 (br.s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.76-7.71 (m, 1H), 7.57 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.39-7.55 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.4, 137.0, 129.9, 129.2, 127.4, 126.8, 124.3, 124.0, 123.2, 123.0, 122.0, 120.2, 115.4, 112.5, 111.1. **GC-MS** (EI) *m/z* 217 (100) [M^+], 216 (12), 189 (115), 94 (16).

1-Phenylnaphthalen-2-amine (**7j**).[52] Compound **7j** was purified by column chromatography on silica gel (eluent: gradient petroleum ether: EtOAc (100:0 → 85:15 %). Colorless solid was obtained in 26% yield (12.3 mg, 0.06 mmol), **m.p.**: 92-93 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.36-7.38 (m, 2H), 7.20-7.29 (m, 3H), 7.04 (d, *J* = 8.8 Hz, 1H), 3.72 (br.s, 2H).

9-Phenyl-9H-carbazole (**10a**).[49] The product was purified by column chromatography on silica gel eluting with petroleum ether/ EtOAc (100:0 → 85:15 %). Dark yellow oil was isolated in 96% yield (46.7 mg, 0.192 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.54-7.60 (m, 4H), 7.36-7.46 (m, 5H), 7.24-7.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.0, 137.8, 129.9, 127.5, 127.2, 126.0, 123.4, 120.3, 119.9, 109.8. **GC-MS** (EI) *m/z*: 244 (19), 243(100) [M^+], 242 (21), 241 (25), 120 (16), 51 (11).

3-Methyl-9-phenyl-9H-carbazole (**10b**).[49] The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0 → 95:5 %). Dark yellow oil was isolated in 87 % yield (44.7 mg, 0.17 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.93 (t, *J* = 0.8 Hz, 1H), 7.54-7.61 (m, 4H), 7.35-7.46 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.21-7.27 (m, 2H), 2.55 (m, 3H). ^{13}**C NMR** (100 MHz, *$CDCl_3$*): δ 141.1, 139.2, 138.0, 129.8, 129.2, 127.2, 127.0, 125.7, 123.5, 123.3, 120.2, 119.7, 109.7, 109.5, 21.4. **GC-MS** (EI) *m/z*: 258 (17), 257 (100) [M^+], 254 (14), 127 (22), 121 (13).

3-Methoxy-9-phenyl-9H-carbazole (**10c**).[49] The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0 → 95:5 %). Yellow oil was isolated in 87% yield (47.5 mg, 0.17 mmol). ^{1}**H NMR** (400 MHz, *$CDCl_3$*): δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 2.8 Hz, 1H), 7.52-7.59 (m, 4H), 7.37-7.44 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.22-7.26 (m, 1H), 7.04 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.94 (s, 3H). ^{13}**C NMR** (100 MHz, *$CDCl_3$*): δ 154.3, 141.3, 138.0, 135.9, 129.8, 127.2, 127.0, 125.9, 123.8, 123.3, 120.3, 119.5, 115.0, 110.6, 109.9, 103.2, 56.1. **GC-MS** (EI) *m/z*: 274 (15), 273 (71) [M^+], 259 (20), 258 (100), 230 (30), 228 (12), 137 (12), 114 (17).

9-Phenyl-9H-dibenzo[a,c]carbazole. (**12**). The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0 → 90:10 %). Yellow crystals were isolated in 55% yield (37.7 mg, 0.11 mmol), **m.p.**: 193-195 ºC (lit[53] 196-198 ºC). ^{1}**H NMR** (400 MHz, *$CDCl_3$*): δ 8.94 (d, *J* = 8.0 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 7.78-7.82 (m, 1H), 7.61-7.69 (m, 4H), 7.52-7.58 (m, 3H), 7.47-7.49 (m, 1H), 7.36-7.45 (m, 2H), 7.28-7.30 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H). ^{13}**C NMR** (100 MHz, *$CDCl_3$*): δ 142.1, 140.3, 134.6, 130.9, 130.2, 129.9, 129.1, 128.9, 128.8, 125.9, 125.7, 124.0, 124.0, 123.8, 123.8, 123.6, 123.03, 121.7, 121.1, 114.3, 111.0. ^{1}**H-**^{13}**C HSQC NMR** ($CDCl_3$): δ_H/δ_C 8.94/123.8, 8.81/123.8, 8.80/123.6, 8.65/121.7, 7.78-7.82/127.4, 7.61-7.69/130.2, 7.61-7.69/128.9, 7.61-7.69/124.0, 7.52-7.58/129.1, 7.52-7.58/125.7, 7.47-7.49/123.3, 7.36-7.45/124.0, 7.36-7.45/121.1, 7.28-7.30/125.9, 7.21/111.0. ^{1}**H-**^{1}**H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.78-7.82/8.94, 7.78-7.82/8.80, 7.61-7.69/8.94, 7.61-7.69/8.80, 7.61-7.69/7.78-7.82, 7.52-7.58/.8.81, 7.52-7.58/7.61-7.69, 7.47-7.49/7.52-7.58, 7.36-7.45/8.65, 7.28-7.30/8.81, 7.28-7.30/7.52-7.58, 7.28-7.30/7.47-7.49, 7.21/7.36-7.45. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 8.94/129.99, 8.94/128.8, 8.94/124.0, 8.94/114.3, 8.81/125.9, 8.81/123.3, 8.80/130.9, 8.80/129.9, 8.80/127.4, 8.65/142.1, 8.65/124.0, 8.65/114.3, 7.78-7.82/129.9, 7.78-7.82/123.6, 7.61-7.69/128.8, 7.61-7.69/123.8, 7.52-7.58/140.3, 7.52-7.58/130.9, 7.52-7.58/130.2, 7.52-7.58/129.1, 7.52-7.58/128.9, 7.52-7.58/123.3, 7.47-7.49/134.6, 7.47-7.49/130.9, 7.47-7.49/125.7, 7.36-7.45/142.1, 7.36-7.45/123.8, 7.36-7.45/121.7, 7.36-7.45/111.0, 7.28-7.30/123.8, 7.28-7.30/123.3, 7.21/123.8, 7.21/121.1. **GC-MS** (EI) *m/z*: 345 (9), 344 (28), 343 (100) [M^+], 342 (19), 341 (22), 265 (9); 264 (9), 171 (21), 170 (20), 164 (15), 86 (19), 51 (15), 49 (33). **HRMS** (TOF, ESI^+): calcd for $C_{26}H_{18}N$ $(M + H)^+$: 344.1439; Found 344.1462.

9H-Dibenzo[b,d]phenanthro[9,10-f]azepine (**13**). The product was purified by column chromatography on silica gel eluting with pentane/ EtOAc (100:0 → 0:100 %). Light yellow crystals were isolated in 38% yield (26.1 mg, 0.076 mmol), **m.p.**: 228-229 ºC. **^{1}H NMR** (400 MHz, *$CDCl_3$*): δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.53-8.55 (m, 1H), 8.31 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.94-7.99 (m, 2H), 7.74-7.78 (m, 1H), 7.64-7.69 (m, 3H), 7.57-7.62 (m, 3H), 7.45-7.47 (m, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 6.98 (td, *J* = 7.6, 1,2 Hz, 1H), 6.77 (dd, *J* = 7.6, 0.8 Hz, 1H). **^{13}C NMR** (100 MHz, *$CDCl_3$*): δ 141.0, 140.7, 138.4, 136.0, 135.3, 133.9, 132.1, 131.0, 130.3, 129.6, 129.5, 129.4, 129.0, 128.2, 128.1, 128.0, 127.8, 127.7, 127.7, 127.3, 125.1, 123.7, 122.5, 122.2, 111.4, 100.1. **^{1}H-^{13}C HSQC NMR** ($CDCl_3$): δ_H/δ_C 8.67/122.5, 8.53-8.55/122.2, 8.31/129.0, 7.94-7.99/132.1, 7.94-7.99/127.3, 7.74-7.78/128.0, 7.64-7.69/129.6, 7.64-7.69/128.1, 7.64-7.69/127.8, 7.57-7.62/130.3, 7.57-7.62/129.4, 7.57-7.62/127.7, 7.45-7.47/131.0, 7.15/127.7, 6.98/129.5, 6.77/128.2. **^{1}H-^{1}H COSY NMR** (*$CDCl_3$*): δ_H/δ_H 7.94-7.99/8.67. 7.94-7.99/8.53-8.55, 7.94-7.99/8.31, 7.74-7.78/8.67, 7.74-7.78/8.31, 7.74-7.78/7.94-7.99, 7.64-7.69/8.53-8.55, 7.64-7.69/7.94-7.99, 7.45-7.47/7.57-

7.62, 7.15/7.64-7.69, 6.98/7.64-7.69, 6.98/7.15, 6.77/7.15, 6.77/6.98. **^{1}H-^{13}C HMBC NMR** (*$CDCl_3$*): δ_H/δ_C 8.53-8.55/128.0, 8.53-8.55/125.1, 8.53-8.55/123.7, 8.31/133.9, 8.31/132.1, 8.31/100.1, 7.94-7.99/133.9, 7.94-7.99/129.0, 7.94-7.99/127.8, 7.94-7.99/123.7, 7.74-7.78/125.1, 7.74-7.78/122.5, 7.64-7.69/140.7, 7.64-7.69/138.4, 7.64-7.69/129.5, 7.64-7.69/127.3, 7.64-7.69/123.7, 7.64-7.69/122.2, 7.64-7.69/111.4, 7.57-7.62/141.0, 7.57-7.62/135.3, 7.57-7.62/131.0, 7.57-7.62/130.3, 7.57-7.62/129.4, 7.57-7.62/100.1, 7.45-7.47/135.3, 7.45-7.47/127.7, 7.15/136.0, 7.15/128.2, 6.98/138.4, 6.98/128.1, 6.77/141.0, 6.77/136.0, 6.77/127.7. **GC-MS** (EI) *m/z*: 345 (14), 344 (45), 343 (100) [M^+], 342 (28), 241 (14), 172 (15), 171 (33), 170 (32), 169 (12), 165 (18), 164 (18), 157 (13), 156 (10), 86 (28), 84 (38), 51 (17), 49 (46), 47 (12). **HRMS** (TOF, ESI^+): calcd for $C_{26}H_{18}N$ $(M + H)^+$: 344.1439; Found 344.1447.

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Supporting Information Available. Copies of ^{1}H NMR, ^{13}C NMR spectra for previously reported compounds, copies of ^{1}H NMR, ^{13}C NMR and 2D NMR spectra for new compounds and theoretical section (thermodynamic of possible initiation steps, schematic profile of the reaction steps calculated for **3a, 9a** and **11**, and xyz of stationary points) are available in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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