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A Route to Regioselectively Functionalized Carbazoles, Dibenzofurans, and Dibenzothiophenes through Anionic Cyclization of Benzyne-Tethered Aryllithiums

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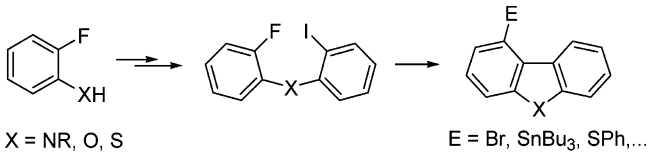

The treatment of 2-fluorophenyl 2-iodophenylamines, ether, and thioether, easily prepared from commercially available products, with 3.3 equiv of *t*-BuLi and further reaction with selected electrophiles gives rise to functionalized carbazole, dibenzofuran, and dibenzothiophene derivatives in a direct and regioselective manner. The process involves an anionic cyclization on a benzyne-tethered aryllithium intermediate.

Chemistry of arynes provides a robust tool for synthetic design and methodology.[1] The recent reports concerned with formation,[2] synthetic applications,[3] and in particular transition-metal-catalyzed[4] reactions of arynes illustrate the continued interest in this area. Some of the most productive applications of benzyne chemistry are their reactions with nucleophiles bearing neighboring electrophiles to afford overall aryne insertion products[5] and the construction of benzo-fused polycyclic systems by the addition of a nucleophile that is part of an aryne side chain. This last procedure, often called the benzyne cyclization,[6] has been extensively used for making four-, five-, and six-membered rings. In this field, while intramolecular additions of heteroatomic nucleophiles[7] or stabilized carbanions[8] to a benzyne is a well-developed synthetic procedure, the generation and cyclization of benzyne-tethered organolithiums remains a largely unexplored area and only few examples with alkyllithiums have been reported.[9] In this area, we have described the intramolecular anionic cyclization of benzyne-tethered vinyllithiums and its application to the synthesis of 4-functionalized indole derivatives.[10] In this context, we envisaged that if we were able to prepare a *o*-lithiophenyl *o*-benzyne amine, ether, or thioether, the subsequent intramolecular cyclization and further treatment with electrophiles would provide the corresponding regioselectively functionalized carbazole, dibenzofuran, or dibenzothiophene derivative (Scheme 1). This approach would represent an efficient strategy for simultaneous formation and regioselective functionalization of dibenzo-fused five-membered heterocycles.

Carbazoles, in view of incorporating an indole nucleus in their moieties, are the core structures of numerous biologically active compounds,[11] and several carbazole derivatives are also widely used as organic materials, due to their optical, electronic, and charge-transport properties.[12] Thus, a wide range of substituted carbazoles have been prepared by different approaches, mainly reductive cyclization of 2-nitrobiphenyls[13] and Pd-catalyzed

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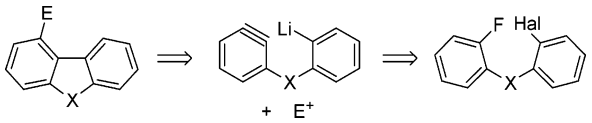
SCHEME 1. Retrosynthetic Analysis of Functionalized Dibenzo-Fused Five-Membered Heterocycles

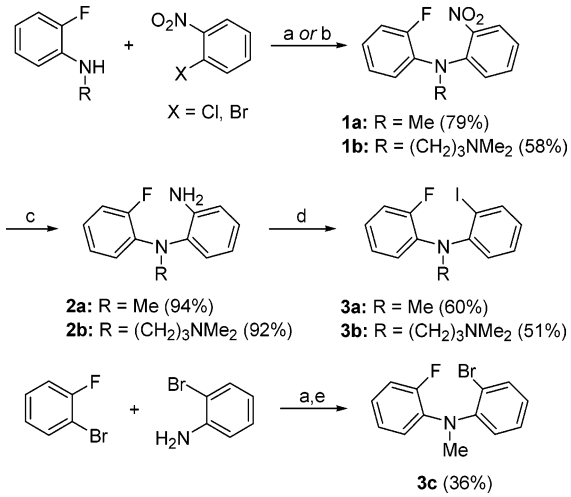


reactions, such as intramolecular arylation of *N*,*N*-diarylamines,[14] cyclization of 2-arylacetanilides,[15] oxidative cyclization of 3-(3′-alkenyl)indoles,[16] or double N-arylation of primary amines.[17] Oxygen and sulfur analogues of carbazoles, such as dibenzofurans[18] and dibenzothiophenes,[19] are also biologically interesting due to their occurrence in a wide variety of pharmaceutical and natural products possessing useful biological activities. This has prompted the development of versatile and regioselective synthetic routes to these compounds[20] with functional groups at specific positions, as well as interesting synthetic transformations that use these substrates as starting materials.[21]

In this paper, we wish to report a novel synthesis of selectively functionalized carbazole, dibenzofuran, and dibenzothiophene derivatives by anionic cyclization of benzyne-tethered aryllithiums.

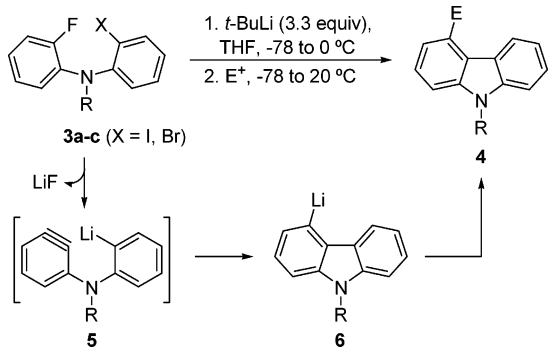
To develop a route to prepare functionalized carbazoles according to our retrosynthetic analysis (Scheme 1), we needed to synthesize 2-fluorophenyl 2-halophenylamines **3**. Thus, the starting compounds **3a**,**b** were easily prepared from commercially available *o*-halonitrobenzenes and 2-fluoroaniline in a three-step sequence, as shown in Scheme 2. First, Pd/BINAP-catalyzed amination[22] of *o*-bromonitrobenzene with *N*-methyl-2-fluoroaniline using cesium carbonate as base gave rise in good yield to tertiary amine **1a** (Scheme 2). Amine **1b** was prepared by deprotonation of *N*-(3-dimethylaminopropyl)-2-fluoroaniline with *n*-BuLi in THF and subsequent alkylation with *o*-chloronitrobenzene.[23] In a second step, reduction of the nitro group into an amino group yielded diamines **2a**,**b** in high yields. This process was carried out with potassium borohydride in the presence of copper(I) chloride.[24] In the last step, diazotation and further displacement by iodide[25] afforded the desired iodo

SCHEME 2. Preparation of 2-Fluorophenyl 2-Halophenyl Amines 3a−c[a]



[a] Reagents and conditions: (a) Cs_2CO_3 (1.4 equiv), $Pd_2(dba)_3$ (3 mol %), BINAP (4.5 mol %), 1-Br-2-$NO_2C_6H_4$ (1 equiv), toluene, 100 °C, 16 h; (b) (1) *n*-BuLi (1 equiv), THF, −50 to 20 °C, 1 h; (2) 1-Cl-2-$NO_2C_6H_4$ (1.5 equiv), THF, −78 to reflux, 12 h; (c) KBH_4 (7 equiv), CuCl (3 equiv), MeOH, 20 °C, 30 min; (d) (1) $NaNO_2$ (1.1 equiv), H_2SO_4, 0 °C, 30 min; (2) KI (1.3 equiv), 0 °C to reflux, 30 min; (e) (1) NaH (1.5 equiv), DMF, 0 °C, 30 min; (2) MeI (1.3 equiv), DMF, 0 to 20 °C, 1 h.

SCHEME 3. Synthesis of 4-Functionalized Carbazoles 4



derivatives **3a**,**b** in moderate to good yields (Scheme 2). Alternatively, related *N*-(2-bromophenyl)-*N*-(2-fluorophenyl)-methylamine **3c** could be prepared in two steps from commercially available 2-bromoaniline and 2-bromofluorobenzene. Their Pd/BINAP-catalyzed coupling in the same conditions as above[22] afforded *N*-(2-bromophenyl)-2-fluoroaniline though in a modest yield. This diarylamine was easily alkylated in almost quantitative yield with NaH/MeI in DMF (Scheme 2). On the basis of the starting materials, we obtained comparable overall yields from both routes.

Once we had prepared amines **3**, we investigated the best conditions to generate the targeted benzyne-tethered aryllithium. We found that treatment of **3a** or **3c** with 3.3 equiv of *t*-BuLi in THF at low temperature and further warming to 0 °C afforded after hydrolysis 9-methyl-9*H*-carbazole **4a** in good yield (Scheme 3 and Table 1). We have also observed that the addition of only 2 equiv of *t*-BuLi gave rise to selectively iodine− or bromine−lithium exchange. The formation of the carbazole skeleton could be explained through an intramolecular anionic 5-*exo*-*dig*

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TABLE 1. Preparation of Functionalized Carbazoles 4 from Amines 3a−c

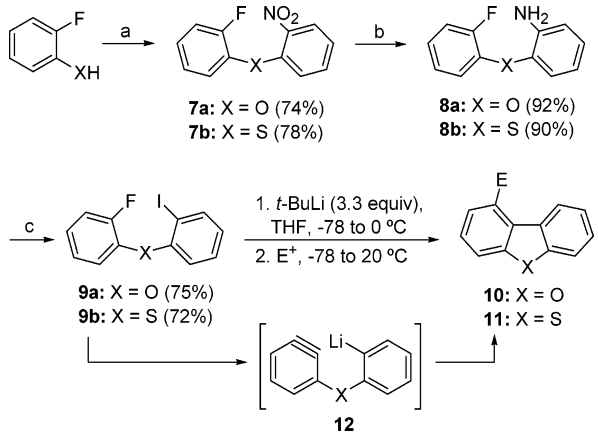
entry	amine	R	E^+	product	E	yield[a] (%)
1	**3a**	Me	MeOH	**4a**	H	79
2	**3a**	Me	Ph_2S_2	**4b**	SPh	64
3	**3a**	Me	$Br(CH_2)_2Br$	**4c**	Br	70
4	**3c**	Me	PhNCO	**4d**	CONHPh	71
5	**3c**	Me	Et_2CO	**4e**	$Et_2C(OH)$	74
6	**3b**	$(CH_2)_3NMe_2$	MeOH	**4f**	H	70
7	**3b**	$(CH_2)_3NMe_2$	Bu_3SnCl	**4g**	$SnBu_3$	61
8	**3b**	$(CH_2)_3NMe_2$	*p*-TolCHO	**4h**	*p*-TolC(H)OH	58

[a] Isolated yield based on starting amines **3**.

cyclization on the benzynic intermediate **5**, which is generated by consecutive halogen−lithium exchange, abstraction of the proton *ortho* to the fluorine atom, and elimination of lithium fluoride, affording in this way a regioselectively lithiated carbazole derivative **6** (Scheme 3).[26] The intermediacy of **6** was confirmed by its quenching with selected electrophiles and isolation of 4-functionalized carbazoles **4b**−**e** (Scheme 3 and Table 1, entries 2−5). With the starting amine **3b**, we found that its double lithiation took place under the same reaction conditions as the parent amines **3a**,**c**. It is interesting to note that even the occurrence of a potentially metalating directing group, such as the dimethylamino, did not represent any difficulty and, in fact, a good yield of the desired product was obtained. So, treatment of **3b** with 3.3 equiv of *t*-BuLi from −78 to 0 °C and further addition of electrophiles afforded the corresponding 4-functionalized carbazoles **4f**−**h** in similar yields as those reported for carbazoles obtained from **3a**,**c** (Scheme 3 and Table 1, entries 6−8). The easy preparation of *N*-(3-dimethylaminopropyl)carbazole derivatives **4f**−**h** following this methodology should be remarked as compounds with related structures are very useful products in medicinal chemistry.[27] Using this anionic benzyne cyclization methodology, it has been possible to further functionalize the cyclized product by reaction with electrophilic reagents, and so the introduction at C4 of a bromine (**4c**) or a tri-*n*-butylstannyl group (**4g**) is particularly useful for, for example, further transformations via Pd-catalyzed coupling reactions. Moreover, the most reactive positions for electrophilic substitution in carbazoles are the 3 and 6 positions, *para* to the nitrogen atom, and to a lesser extent, the 1 and 8 positions,[28] and therefore, the regioselective introduction of substituents at the 4 position still remains an attractive objective in carbazole chemistry.[29]

After the synthesis of carbazoles by the described method, we turned our attention to the possibility of applying this methodology for the preparation of related dibenzofurans and dibenzothiophenes starting from the corresponding 2-fluorophenyl ether **9a** and thioether **9b**. The synthesis of these compounds is shown in Scheme 4, and so, treatment of *o*-chloronitrobenzene

SCHEME 4. Synthesis of 1-Functionalized Dibenzofurans 10 and Dibenzothiophenes 11[a]



[a] Reagents and conditions: (a) *o*-$ClC_6H_4NO_2$ (1.5 equiv), Cu_2O (1.5 equiv), pyridine, 20 °C to reflux, 12 h; (b) Fe (3 equiv), HCl/EtOH, reflux, 6 h; (c) (1) $NaNO_2$ (1.1 equiv), H_2SO_4, 0 °C, 30 min; (2) KI (1.3 equiv), 0 °C to reflux, 30 min.

TABLE 2. Preparation of Functionalized Dibenzofurans 10 and Dibenzothiophenes 11

entry	starting product	E^+	product	E	yield[a] (%)
1	**9a**	$ClCO_2Et$	**10a**	CO_2Et	67
2	**9a**	Ph_2S_2	**10b**	SPh	61
3	**9a**	*p*-TolCN	**10c**	*p*-TolCO	62
4	**9a**	PhNCO	**10d**	CONHPh	63
5	**9a**	Et_2CO	**10e**	$Et_2C(OH)$	55
6	**9b**	MeOH	**11a**	H	79
7	**9b**	Ph_2S_2	**11b**	SPh	78
8	**9b**	$Br(CH_2)_2Br$	**11c**	Br	76
9	**9b**	*p*-TolCHO	**11d**	*p*-TolC(H)OH	75

[a] Isolated yield based on starting products **9**.

with 2-fluorophenol or 2-fluorothiophenol, respectively, in the presence of copper(I) oxide and pyridine[30] afforded diaryl ether **7a** and thioether **7b** in good yields (Scheme 4). The reduction of the nitro groups was carried out with Fe in HCl giving rise to the corresponding amino derivatives **8a**,**b**. Finally, their diazotation and further displacement by iodide[25] allowed the preparation of the required compounds **9a**,**b** in overall good yields (Scheme 4). Reaction of **9a**,**b** in the same conditions as described above for amines **3**, that is, addition of 3.3 equiv of *t*-BuLi at −78 °C, warming to 0 °C, and trapping with selected electrophiles, afforded 1-functionalized dibenzofurans **10** and dibenzothiophenes **11** in good yields (Scheme 4 and Table 2). Again, a benzyne-tethered aryllithium **12** accounts for the regioselective functionalization of the final heterocycles. These results illustrate the usefulness of this methodology for the synthesis of dibenzofurans and dibenzothiophenes functionalized at C1, which are difficult to prepare in isomerically pure form using classical organic chemistry.

In summary, we have developed a practical and efficient route to regioselectively functionalized carbazoles and related dibenzofurans and dibenzothiophenes. The starting materials (2-fluoroanilines, 2-fluorophenol, 2-fluorothiophenol, and *o*-halonitrobenzenes) are commercially available or can be easily made. The key step is the selective formation of a benzyne-

(26) Treatment of *N*-(2-bromophenyl)-2-fluoroaniline with 4.3 equiv of *t*-BuLi only gave rise to deprotonation and bromine−lithium exchange. Subsequent cyclization was not observed.

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tethered aryllithium followed by an intramolecular anionic cyclization and further trapping of the resulting organolithium with several electrophiles. This strategy allows the synthesis of carbazoles, dibenzofurans, and dibenzothiophenes substituted at positions which are difficult to functionalize by traditional methods. We believe that this methodology constitutes a synthetically competitive alternative to the existing strategies for the construction of this kind of regioselectively substituted dibenzo-fused heterocycles.

Experimental Section

General Procedure for the Synthesis of 4-Functionalized Carbazoles 4, 1-Functionalized Dibenzofurans 10, and Dibenzothiophenes 11. Synthesis of 4-Bromo-9-methyl-9*H*-carbazole (4c; Table 1, Entry 3). *t*-BuLi (2.2 mL of a 1.5 M solution in pentane, 3.3 mmol) was added to a solution of amine **3a** (0.327 g, 1 mmol) in THF (8 mL) at −78 °C. The resulting solution was stirred for 20 min at this temperature, and then, the reaction mixture was allowed to warm to 0 °C and stirred for 30 min. After cooling to −78 °C, 1,2-dibromoethane (0.225 g, 1.2 mmol) was added dropwise, and stirring continued at low temperature for further 30 min. The reaction mixture was then allowed to warm to room temperature, quenched with water, and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: hexane) on silica gel to afford **4c** (0.182 g, 70%) as a white solid: mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 8.0 Hz, 1H), 7.56−7.52 (m, 1H), 7.41−7.29 (m, 5H), 3.80 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.9 (C), 140.9 (C), 126.2 (CH), 126.0 (CH), 122.9 (CH), 122.5 (CH), 122.2 (C), 121.3 (C), 118.9 (CH), 116.6 (C), 108.2 (CH), 107.2 (CH), 29.0 (CH_3); EI-LRMS m/z 261 (M^+ + 2, 100), 259 (M^+, 100); IR (KBr) 2924, 1600, 1464 cm^{-1}. HRMS calcd for $C_{13}H_{10}BrN$, 258.9997; found, 259.9989. Anal. Calcd for $C_{13}H_{10}BrN$: C, 60.02; H, 3.87; N, 5.38. Found: C, 60.13; H, 3.88; N, 5.36.

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Supporting Information Available: Typical experimental procedures and spectroscopic details for all compounds and a copy of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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