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Synthesis of carbazoles and dibenzofurans via cross-coupling of *o*-iodoanilines and *o*-iodophenols with silylaryl triflates and subsequent Pd-catalyzed cyclization

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Abstract—An efficient route to a variety of carbazoles and dibenzofurans has been developed. It involves the reaction of *o*-iodoanilines or *o*-iodophenols with silylaryl triflates in the presence of CsF to afford the *N*- or *O*-arylated products, which are subsequently cyclized using a Pd catalyst to carbazoles and dibenzofurans in good to excellent yields. By using this methodology, the carbazole alkaloid, mukonine has been synthesized in 76% overall yield in three steps.

1. Introduction

Heterocycles are a very important class of organic compounds, because of their wide application in medicine, agriculture, and technology.[1] Among nitrogen heterocycles, carbazole alkaloids are a growing class of natural products, which display a wide variety of biological activities, such as antitumor, antibacterial, antimicrobial and anti-inflammatory activities.[2] Recently, a number of carbazole derivatives have been used as organic materials, due to their well-known photoconducting[3] and semiconducting properties,[4] and their charge-transport and high thermal properties.[5] Dibenzofurans and their derivatives have also attracted the attention of organic chemists for many years due to their occurrence in a wide variety of pharmaceuticals and natural products possessing useful biological activities.[6] Considerable effort has been devoted to the development of efficient methods for the synthesis of a wide range of substituted carbazoles, including the reductive cyclization of 2-nitrobiphenyl derivatives by suitable organophosphorus reagents[7] and the classical Fisher–Borsche synthesis starting with appropriate cyclohexanone arylhydrazones.[8] Recently, transition metal catalysts have also been widely used to construct these ring systems. For example, the palladium-mediated oxidative cyclization of *N*,*N*-diarylamines to carbazoles[9] and diaryl ethers to dibenzofurans,[10] and the palladium-catalyzed double N-arylation of primary amines with 2,2-dihalobiphenyls[11] have been employed to prepare carbazoles and dibenzofurans. Quite recently, Wu et al. have utilized anionic cycloaromatization to synthesize 5-substituted dibenzofurans and carbazoles.[12] Despite these significant recent improvements, there are still limitations in the present methods. For example, (a) stoichiometric amounts of palladium are needed in the oxidative cyclization reaction, (b) harsh reaction conditions are usually needed and some processes cannot tolerate many functional groups, and (c) the yields usually are not very good. One simple, new, efficient and general method to synthesize both the carbazole and dibenzofuran ring systems would be quite attractive because of the growing interest in these compounds.[13]

Although arynes have historically received much attention from organic chemists, their use as reagents in synthetic organic chemistry has been somewhat limited due to the harsh reaction conditions needed to generate arynes and the often uncontrolled reactivity exhibited by these species.[14] Recently, silylaryl triflate **1a**[15] has been employed in the presence of CsF to generate benzyne under very mild reaction conditions. The resulting aryne readily undergoes a variety of electrophilic and nucleophilic reactions,[16] several novel insertion reactions,[17] and even Pd-catalyzed annulation reactions.[18] We have reported that silylaryl triflates can react with a variety of nucleophiles, such as anilines and phenols to generate very high yields of the corresponding *N*- and *O*-arylated products and even more important is the fact that halides, such as iodides and bromides, are readily tolerated by the reaction conditions.[16c,d] We have taken advantage of this methodology to develop a simple, economical, and efficient one-pot, two-step procedure to synthesize the carbazole and dibenzofuran ring systems in good to excellent yields through the cross-coupling of *o*-iodoanilines or *o*-iodophenols with silylaryl triflates in the presence of CsF, followed by palladium-catalyzed intramolecular cyclization.[19] Herein, we wish to provide a full account of the

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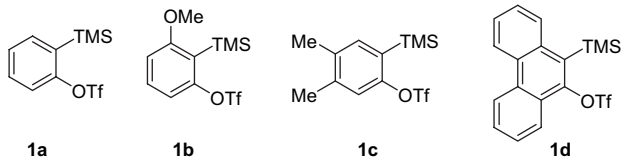
scope and limitations of this chemistry. We have also applied this chemistry to the high yield three-step synthesis of an interesting carbazole alkaloid, mukonine.

2. Results and discussion

2.1. Preparation of the aryne precursors

The arynes **1a–d** were selected as substrates for our experiments. Aryne precursor **1a** was selected as the simplest and most readily available aryne to study the scope of this chemistry, since it is commercially available. Aryne precursor **1b** was selected to study the regioselectivity of the palladium-catalyzed cyclization step. The synthesis of silylaryl triflates **1a**,[15] **1b**,[20] **1c**,[21] and **1d**[22] have previously been reported.



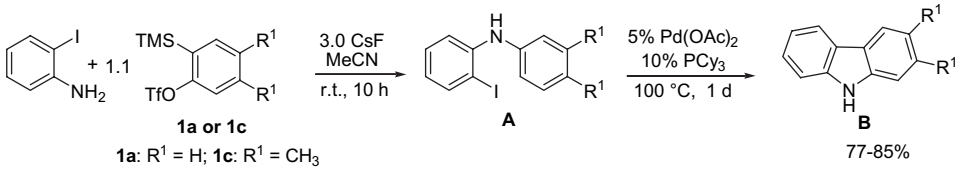
1a **1b** **1c** **1d**

2.2. Synthesis of carbazoles and analogs

The essential elements of our approach to the carbazole ring system are shown in Scheme 1. *o*-Iodoaniline is first allowed to react with the silylaryl triflate under very mild reaction conditions to afford the *N*-arylated *o*-iodoanilines **A**,[16c] which subsequently undergo intramolecular palladium-catalyzed arylation in the same pot to produce the carbazole derivatives **B** in good yields.

Our initial studies were directed toward achieving the optimal reaction conditions for the palladium-catalyzed intramolecular arylation step (**A**→**B**) (Scheme 1). A range of palladium catalysts were employed. We found that $Pd(OAc)_2$ was the best catalyst. All other palladium catalysts [$PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, $Pd(dba)_2$] examined afforded either comparable or lower yields. The ligand added to the reaction did not make much difference. Thus, the ligands dppe, dppm, and PCy_3 (Cy=cyclohexyl) all worked well in our system. However, the solvent had a big effect on this cross-coupling reaction; DMF and toluene both gave very low yields of the carbazole products, while MeCN proved to be the best solvent for this process. The first step in this sequence had already been optimized during some of our earlier work on the N-arylation of amines.[16c] After our optimization work was complete, we settled on the following standard two-step procedure. The iodoaniline (0.25 mmol), silylaryl triflate (1.1 equiv) and CsF (3.0 equiv) were allowed to react at room temperature for 10 h in acetonitrile (4.0 mL) under air. Then $Pd(OAc)_2$ (3.1 mg, 5 mol %) and PCy_3 (7.0 mg, 10 mol %) were added and the reaction heated to 100 °C for 1 d under argon.

We next studied the scope and limitations of this two-step cross-coupling process by allowing a wide variety of iodoanilines and their derivatives to react with silylaryl triflates **1a–d**. The results are summarized in Table 1. A variety of *o*-iodoanilines react with silylaryl triflates **1a**, **1b** or **1c** to afford, after Pd-catalyzed cyclization, high yields of the desired carbazoles (Table 1, entries 1–9). When a slight excess (1.1 equiv) of silylaryl triflate **1a** was allowed to react with *o*-iodoaniline (entry 1), the desired carbazole was obtained in a 77% yield under our standard reaction conditions. When 2.4 equiv of silylaryl triflate **1a** was allowed to react with *o*-iodoaniline, *N*-phenylcarbazole was isolated in only a 66% yield (entry 2). *o*-Iodoaniline also reacts with the methoxy-substituted silylaryl triflate **1b**, followed by palladium-catalyzed cyclization, to afford two carbazole derivatives **4** and **5** in a 5:1 ratio (entry 3). The fact that carbazole **4** is the major product can be easily explained by a steric effect during the Pd-catalyzed cyclization. The Pd-catalyzed cyclization is occurring at the less hindered position away from the methoxy group. When silylaryl triflate **1c** was employed with 2-iodo-4-methylaniline, we obtained the desired product in a 68% yield (entry 4). Approximately a 4% yield of the isomeric product 1,2,6-trimethylcarbazole was also observed as detected by GC/MS. Again the Pd-catalyzed cyclization is occurring with high regioselectivity for the less hindered position away from the methyl group. When substituted iodoanilines were allowed to react with silylaryl triflate **1a**, the corresponding carbazole derivatives could be obtained in good to excellent yields (entries 5–8). Similarly, 2,4-dichloro-6-iodoaniline reacts with 1.1 equiv of silylaryl triflate **1c** to afford the desired product in an 85% yield. Approximately a 5% yield of the isomeric product 6,8-dichloro-1,2-dimethylcarbazole was also observed as detected by GC/MS (entry 9). The presence of a chlorine in the starting anilines does not appear to interfere with the overall process (entries 7–9). *N*-Methylcarbazole is also readily obtained in an 82% yield when *N*-methyl-2-iodoaniline was employed as the substrate (entry 10). *N*-Phenylcarbazole was obtained in a slightly higher yield by this cross-coupling procedure, when *N*-phenyl-2-iodoaniline was employed, instead of 2-iodoaniline, in the presence of an excess of the aryne (compare entries 2 and 12). *N*-(2-Iodophenyl)methanesulfonamide and ethyl 2-iodophenylcarbamate and their derivatives also react well with silylaryl triflate **1a** or **1c** to afford high yields of the corresponding products (entries 13–18); again, only about 5% of a product isomeric with the products shown in entries 16 and 18 was observed by GC/MS analysis. Interestingly, when silylaryl triflate **1d** was allowed to react with *N*-(2-iodophenyl)-methanesulfonamide, we did not obtain the expected

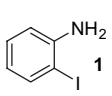
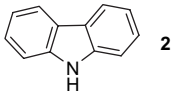
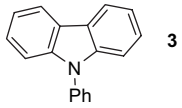
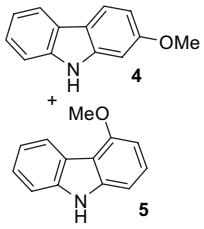
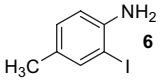
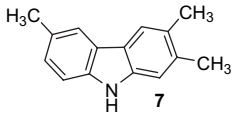
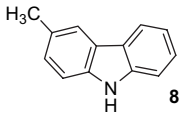
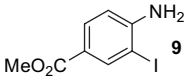
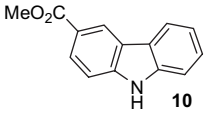
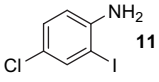
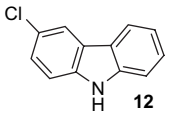
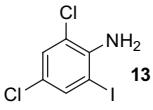
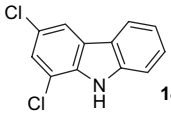
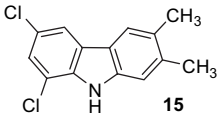
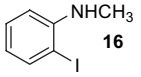
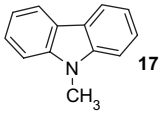
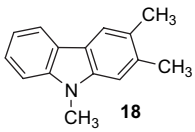


1a or 1c

1a: R^1 = H; **1c**: R^1 = CH_3

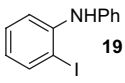
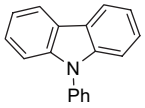
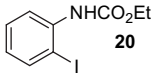
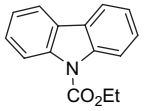
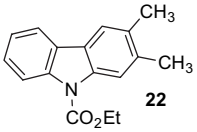
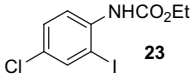
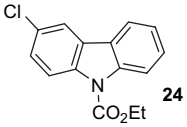
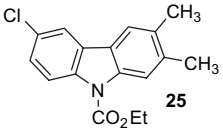
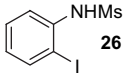
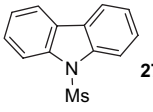
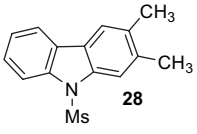
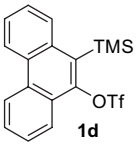
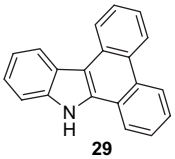
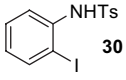
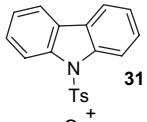
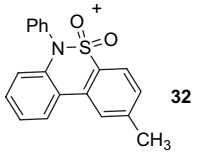
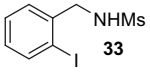
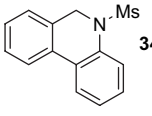
Scheme 1.

Table 1. Synthesis of carbazoles and analogs[a]

Entry	Substrate	Aryl triflate	CsF (equiv)	Product	Isolated yield (%)
1	 **1**	**1a**	3.0	 **2**	77
2	**1**	**1a**	5.0	 **3**	66[b]
3	**1**	**1b**	3.0	 **4** + **5**	61 (5:1)
4	 **6**	**1c**	3.0	 **7**	68
5	**6**	**1a**	3.0	 **8**	69
6	 **9**	**1a**	3.0	 **10**	68
7	 **11**	**1a**	3.0	 **12**	72
8	 **13**	**1a**	3.0	 **14**	87
9	**13**	**1c**	3.0	 **15**	85
10	 **16**	**1a**	3.0	 **17**	82
11	**16**	**1c**	3.0	 **18**	71

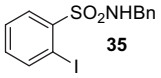
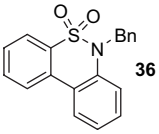
(*continued*)

Table 1. (*continued*)

Entry	Substrate	Aryl triflate	CsF (equiv)	Product	Isolated yield (%)
12	 **19**	**1a**	3.0	 **3**	76[c]
13	 **20**	**1a**	3.0	 **21**	85
14	**20**	**1c**	3.0	 **22**	85
15	 **23**	**1a**	3.0	 **24**	86
16	**23**	**1c**	3.0	 **25**	85
17	 **26**	**1a**	3.0	 **27**	85
18	**26**	**1c**	3.0	 **28**	85
19	**26**	 **1d**	3.0	 **29**	62
20	 **30**	**1a**	3.0	 **31**  **32**	83 (1:1)
21	 **33**	**1a**	3.0	 **34**	66

(*continued*)

Table 1. (*continued*)

Entry	Substrate	Aryl triflate	CsF (equiv)	Product	Isolated yield (%)
22	 **35**	**1a**	3.0	 **36**	62

[a] Reaction conditions: 0.25 mmol of aryl iodide is allowed to react with 1.1 equiv of aryl triflate and the number of equiv of CsF shown in table in 4.0 mL of MeCN as the solvent at room temperature for 10 h, followed by the addition of 5 mol % $Pd(OAc)_2$ and 10 mol % PCy_3 and heating for 1 d at 100 °C.
[b] Aryl triflate (2.4 equiv) was employed and the reaction was run at room temperature for 2 d, followed by the addition of 5 mol % $Pd(OAc)_2$ and 10 mol % PCy_3 and heating for 1 d at 100 °C.
[c] The reaction was run at room temperature for 1.5 d, followed by the addition of 5 mol % $Pd(OAc)_2$ and 10 mol % PCy_3 and heating for 1 d at 100 °C.

product, but rather the deprotected dibenzo[*a*,*c*]carbazole in a 62% yield (entry 19). Apparently the extended π-conjugation of the dibenzo[*a*,*c*]carbazole facilitates loss of the methanesulfonyl group. It is interesting that the reaction of *N*-tosyl-2-iodoaniline and silylaryl triflate **1a** afforded a 1:1 ratio of compounds **31** and **32** in an 83% overall yield (entry 20). It seems rather surprising that the Pd-catalyzed cyclization onto the tosyl group competes so effectively with cyclization onto the phenyl ring. One can also start with *N*-(2-iodobenzyl)methanesulfonamide or *N*-benzyl-2-iodobenzenesulfonamide and silylaryl triflate **1a** and produce the corresponding six-membered ring products in good yields (entries 21 and 22). None of the product from cyclization onto the benzyl group in entry 22 is observed, possibly because this would involve formation of a seven-membered ring.

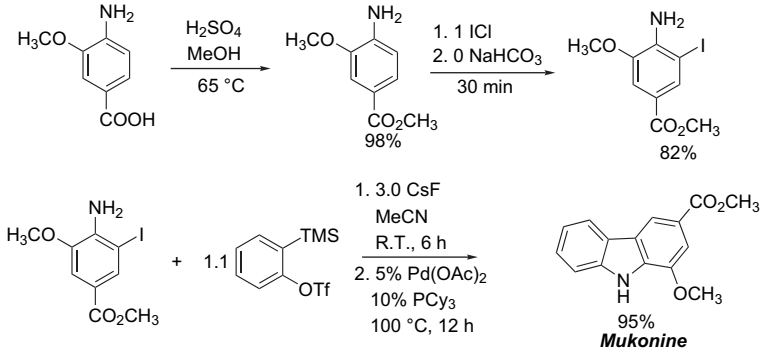
Although there are numerous examples in the literature of analogous palladium-catalyzed intramolecular cyclizations, the exact mechanism for this process is not well established at this time. Nevertheless, it seems clear that oxidative addition of the aryl halide to Pd(0) generates an arylpalladium species, which cyclizes to form a palladium(II)cycle, which in turn undergoes reductive elimination to the heterocycle while regenerating the Pd(0) catalyst.[23]

2.3. Synthesis of mukonine

Mukonine [1-methoxy-3-(methoxycarbonyl)carbazole] is an alkaloid obtained from the Indian curry-leaf tree (*Murraya koenigii*).[24] Mukonine has been synthesized by several different methods.[25] By employing our procedure, mukonine can be obtained in a 76% overall yield in three steps from commercially available 4-amino-3-methoxybenzoic acid (Scheme 2). 3-Methoxy-4-aminobenzoic acid reacts with methanol to afford methyl 3-methoxy-4-aminobenzoate in a 98% yield. Iodination using ICl in dichloromethane affords methyl 4-amino-3-iodo-5-methoxybenzoate in an 82% yield. Employing our standard reaction conditions on methyl 4-amino-3-iodo-5-methoxybenzoate, mukonine can be obtained in a 95% yield in only one additional step.

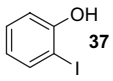
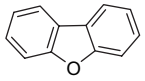
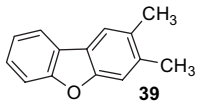
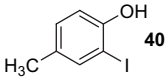
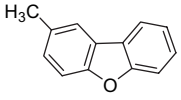
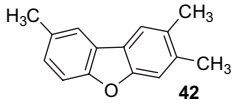
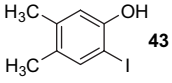
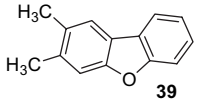
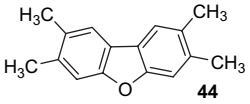
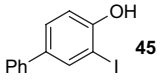
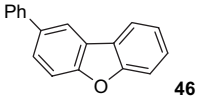
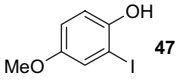
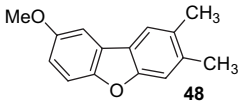
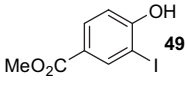
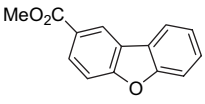
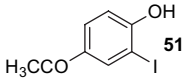
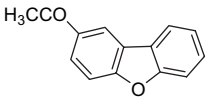
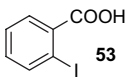
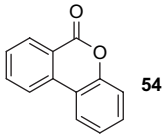
2.4. Synthesis of dibenzofurans and analogs

Since some effort has been devoted to the synthesis of carbazoles and related compounds, it seemed natural for us to extend this chemistry to the synthesis of dibenzofurans and related compounds by using *o*-iodophenol and its derivatives. Indeed, we have also investigated the use of *o*-iodophenols in this process. Here, we needed to use 1.2 equiv of silylaryl triflates **1a** or **1c** and 3.5 equiv of CsF to get the yields specified. The results are summarized in Table 2. *o*-Iodophenol reacts with silylaryl triflate **1a** or **1c** to afford, after Pd-catalyzed cyclization, the corresponding dibenzofurans in 70 and 67% yields, respectively (entries 1 and 2). A variety of substituted iodophenols have also been employed in this process; most of them work quite well and afford the desired compounds in modest to good yields (entries 3–10). Similar to our carbazole results, when silylaryl triflate **1c** was used in this cross-coupling process, approximately 4–5% yields of the expected isomeric products were observed as detected by GC/MS (entries 2, 4–6, and 8). It is noteworthy that the presence of an electron-withdrawing ester or ketone moiety on the phenol presents no difficulties and, in fact, these substrates gave slightly higher yields of the desired products (entries 9 and 10). In



Scheme 2.

Table 2. Synthesis of dibenzofurans and analogs[a]

Entry	Substrate	Aryl triflate	CsF (equiv)	Product	Isolated yield (%)
1	 **37**	**1a**	3.5	 **38**	70
2	**37**	**1c**	3.5	 **39**	67[b]
3	 **40**	**1a**	3.5	 **41**	68
4	**40**	**1c**	3.5	 **42**	68[b]
5	 **43**	**1a**	3.5	 **39**	63
6	**43**	**1c**	3.5	 **44**	61[b]
7	 **45**	**1a**	3.5	 **46**	63
8	 **47**	**1c**	3.5	 **48**	77[b,c]
9	 **49**	**1a**	3.5	 **50**	80
10	 **51**	**1a**	3.5	 **52**	76
11	 **53**	**1a**	4.0	 **54**	46[d]

[a] Reaction conditions: 0.25 mmol of aryl iodide is allowed to react with 1.2 equiv of aryl triflate and the number of equiv of CsF shown in the table in 4.0 mL of MeCN as the solvent at room temperature for 10 h, followed by the addition of 5 mol % $Pd(OAc)_2$ and 10 mol % PCy_3 and heating for 1 d at 100 °C.
[b] About 4% of the isomeric product was detected by GC/MS.
[c] In this reaction, 10 mol % $Pd(OAc)_2$ and 20 mol % PCy_3 were used.
[d] Aryl triflate (1.5 equiv) was used.

this process, one can also start with 2-iodobenzoic acid and allow it to react with silylaryl triflate **1a**. Cyclization produces the desired six-membered ring product benzo[*c*]coumarin in a 46% yield (entry 11).

3. Conclusions

In summary, we have developed a simple and efficient one-pot, two-step procedure to synthesize the carbazole and

dibenzofuran ring systems and related compounds. This process involves the reaction of *o*-iodoanilines or *o*-iodophenols with silylaryl triflates in the presence of CsF to afford the *N*- or *O*-arylated products, which are subsequently cyclized to carbazoles and dibenzofurans in situ using a Pd catalyst. The starting materials are commercially available or can be easily prepared using known chemistry. The yields are of good to excellent. Several new and multisubstituted carbazoles and dibenzofurans have been synthesized using this chemistry. By using this methodology, the carbazole alkaloid, mukonine has been synthesized in 76% overall yield in three steps from a commercially available starting material.

4. Experimental section

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz, respectively. All melting points are uncorrected. High-resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported represent an average of at least two independent runs. Silylaryl triflate **1a** is commercially available. The product characterization data, and ^{1}H and ^{13}C NMR spectra for compounds **2**, **14**, **15**, **17**, **21**, **22**, **27**, **33**, **34**, **38**, and **50** can be found in the supporting information of our previous communication.[19]

4.1.1. Preparation of methyl 4-amino-3-iodo-5-methoxybenzoate. To a solution of 0.905 g of methyl 4-amino-3-methoxybenzoate (5 mmol) and 0.84 g of $NaHCO_3$ (10 mmol) in 15 mL of CH_2Cl_2 at room temperature was added 0.893 g of ICl (5.5 mmol) in 5 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 30 min. The resulting solution was washed with saturated $NaHCO_3$ (20 mL) solution and extracted with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford 1.25 g of the desired product (82% yield) as a white solid: mp 93–94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.89 (s, 3H), 4.69 (s, 2H), 7.39 (d, J=1.8 Hz, 1H), 8.00 (d, J=1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 56.2, 80.7, 110.7, 120.5, 133.3, 142.0, 145.3, 166.3; IR ($CDCl_3$, cm^{-1}) 3495, 3391, 3001, 2949, 2838, 1694, 1268; HRMS *m/z* 306.9701 (calcd $C_9H_{10}INO_3$, 306.9705).

4.2. General procedure for the synthesis of carbazoles and related compounds

In a 4 dram vial, silylaryl triflate (0.275 mmol) and CsF (0.75 mmol) were added to a solution of *o*-iodoaniline (0.25 mmol) in acetonitrile (4 mL). The reaction mixture was allowed to stir at room temperature for 10 h under air. The vial was then flushed with argon and $Pd(OAc)_2$ (5 mol %, 3.1 mg) and PCy_3 (10 mol %, 7.0 mg) were added to the reaction, which was heated to 100 °C for 1 d. The resulting solution was washed with brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product. Schlenk tube techniques are not necessary.

4.2.1. 2,3,6-Trimethylcarbazole (7). The indicated compound was obtained in a 68% yield as a white solid: mp 208–209 °C (lit.[26] 211–211.5 °C); ^{1}H NMR (300 MHz, acetone-d_6) δ 2.38 (s, 6H), 2.47 (s, 3H), 7.15 (dd, J=8.4, 1.5 Hz, 1H), 7.25 (s, 1H), 7.33 (d, J=8.4 Hz, 1H), 7.81 (s, 1H), 9.89 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 19.4, 29.1, 20.8, 110.6, 111.6, 119.7, 120.5, 121.4, 123.5, 126.3, 126.9, 127.5, 134.4, 138.6, 139.6; IR ($CDCl_3$, cm^{-1}) 3393, 2963, 2934, 2852, 1464; HRMS *m/z* 209.1209 (calcd $C_{15}H_{15}N$, 209.1204).

4.2.2. 2,3,9-Trimethylcarbazole (18). The indicated compound was obtained in a 71% yield as a light yellow solid: mp 88–89 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 2.43 (s, 3H), 2.46 (s, 3H), 3.78 (s, 3H), 7.15–7.23 (m, 2H), 7.33 (d, J=8.1 Hz, 1H), 7.41 (td, J=6.9, 0.9 Hz, 1H), 7.83 (s, 1H), 8.02 (d, J=7.8 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 19.3, 20.3, 38.3, 114.6, 115.2, 120.2, 120.9, 124.1, 124.3, 126.5, 127.0, 132.9, 136.9, 137.4, 138.7; IR ($CDCl_3$, cm^{-1}) 3016, 2961, 2935, 2899, 1601; HRMS *m/z* 209.1209 (calcd $C_{15}H_{15}N$, 209.1204).

4.2.3. Ethyl 3-chlorocarbazole-9-carboxylate (24). The indicated compound was obtained in an 85% yield as a white solid: mp 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (t, J=7.2 Hz, 3H), 4.57 (q, J=7.2 Hz, 2H), 7.24–7.50 (m, 3H), 7.84–7.88 (m, 2H), 8.18 (d, J=9.0 Hz, 1H), 8.24 (d, J=9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.7, 63.5, 116.6, 117.5, 119.6, 120.0, 123.7, 124.9, 127.3, 127.4, 128.1, 129.1, 136.8, 138.8, 152.3; IR ($CDCl_3$, cm^{-1}) 3128, 3064, 2981, 2919, 1723, 1441; HRMS *m/z* 273.0560 (calcd $C_{15}H_{12}ClNO_2$, 273.0556).

4.2.4. Ethyl 6-chloro-2,3-dimethylcarbazole-9-carboxylate (25). The indicated compound was obtained in an 85% yield as a yellow solid: mp 125–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (t, J=7.2 Hz, 3H), 2.37 (s, 3H), 2.40 (s, 3H), 4.56 (q, J=7.2 Hz, 2H), 7.33 (dd, J=8.7, 2.1 Hz, 1H), 7.59 (s, 1H), 7.80 (d, J=2.1 Hz, 1H), 8.02 (s, 1H), 8.13 (d, J=9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.7, 20.2, 21.2, 63.4, 117.2, 117.5, 119.2, 120.4, 122.9, 126.5, 127.6, 128.9, 132.4, 136.7, 137.3, 137.6, 152.4; IR ($CDCl_3$, cm^{-1}) 2980, 2920, 2860, 1727, 1476; HRMS *m/z* 301.0873 (calcd $C_{17}H_{16}ClNO_2$, 301.0869).

4.2.5. 2,3-Dimethyl-9-(methanesulfonyl)carbazole (28). The indicated compound was obtained in an 85% yield as white solid: mp 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.43 (s, 3H), 2.93 (s, 3H), 7.38–7.45 (m, 2H), 7.74 (s, 1H), 7.91–7.94 (m, 2H), 8.12 (dd, J=7.2, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 21.1, 38.4, 115.0, 115.5, 120.0, 120.8, 124.3, 124.5, 126.8, 127.1, 133.2, 137.2, 137.3, 138.6; IR ($CDCl_3$, cm^{-1}) 3061, 3032, 3012, 2930, 2856, 1471; HRMS *m/z* 273.0829 (calcd $C_{15}H_{15}NO_2S$, 273.0823).

4.2.6. 9-Tosylcarbazole (31). The indicated compound was obtained in a 41% yield as a white solid: mp 129–130 °C

(lit.[27] 128.5–130 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 7.22 (dd, J=8.7, 0.6 Hz, 2H), 7.42 (td, J=7.5, 0.9 Hz, 2H), 7.57 (td, J=7.5, 1.2 Hz, 2H), 7.77 (dt, J=8.4, 1.8 Hz, 2H), 8.05–8.08 (m, 2H), 8.36 (dt, J=8.4, 0.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 115.2, 120.5, 124.4, 126.6, 126.7, 127.8, 130.1, 134.9, 138.5, 145.8; IR ($CDCl_3$, cm^{-1}) 3109, 3067, 2902, 1595, 1452; HRMS *m*/*z* 321.0827 (calcd $C_{19}H_{15}NO_2S$, 321.0823).

4.2.7. 2-Methyl-5,5-dioxide-6-phenyldibenzo[*c*,*e*][1,2]-thiazine (32). The indicated compound was obtained in a 42% yield as a white solid: mp 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 6.98–7.01 (m, 1H), 7.22–7.25 (m, 2H), 7.33–7.40 (m, 6H), 7.83 (s, 1H), 7.84 (d, J=8.0 Hz, 1H), 8.03–8.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 123.4, 123.8, 125.4, 125.5, 125.7, 126.4, 128.3, 128.6, 129.5, 129.7, 132.4, 132.7, 138.4, 140.4, 143.5; IR ($CDCl_3$, cm^{-1}) 3067, 2925, 2853, 2253, 1600, 1492; HRMS *m*/*z* 321.0827 (calcd $C_{19}H_{15}NO_2S$, 321.0823).

4.2.8. 6-Benzyl-5,5-dioxidedibenzo[*c*,*e*][1,2]thiazine (36). The indicated compound was obtained in a 62% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 2H), 7.18 (s, 5H), 7.23 (dd, J=8.0, 1.6 Hz, 1H), 7.28 (td, J=8.0, 1.2 Hz, 1H), 7.33 (td, J=8.0, 1.2 Hz, 1H), 7.54 (td, J=7.6, 1.2 Hz, 1H), 7.65 (td, J=8.0, 1.2 Hz, 1H), 7.85 (d, J=8.0 Hz, 1H), 7.93 (dd, J=7.6, 1.6 Hz, 1H), 7.99 (dd, J=7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.9, 122.2, 122.7, 125.6, 125.7, 125.7, 125.8, 127.7, 127.9, 128.4, 128.8, 130.4, 132.5, 132.7, 135.4, 135.9, 138.8; IR ($CDCl_3$, cm^{-1}) 3064, 3030, 2923, 2851, 1601, 1477; HRMS *m*/*z* 321.0827 (calcd $C_{19}H_{15}NO_2S$, 321.0823).

4.3. General procedure for the synthesis of dibenzofurans and related compounds

In a 4 dram vial, silylaryl triflate (0.3 mmol) and CsF (0.875 mmol) were added to a solution of *o*-iodophenol (0.25 mmol) in acetonitrile (4 mL). The rest of the procedure is the same as that used in the synthesis of the carbazoles. Schlenk tube techniques are not necessary.

4.3.1. 2,3-Dimethyldibenzofuran (39). The indicated compound was obtained in a 67% yield as a white solid: mp 90–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.40 (s, 3H), 7.34–7.42 (m, 3H), 7.52 (d, J=7.5 Hz, 1H), 7.68 (s, 1H), 7.87 (dd, J=7.5, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 20.9, 111.7, 112.4, 120.4, 121.1, 122.1, 122.6, 124.6, 126.6, 131.4, 136.6, 155.3, 156.4; IR ($CDCl_3$, cm^{-1}) 3046, 2968, 2941, 2922, 1448; HRMS *m*/*z* 196.0890 (calcd $C_{14}H_{12}O$, 196.0888).

4.3.2. 3-Methyldibenzofuran (41). The indicated compound was obtained in a 68% yield as a white solid: mp 42–43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.22–7.25 (m, 1H), 7.31 (td, J=7.6, 1.2 Hz, 1H), 7.40–7.45 (m, 2H), 7.54 (d, J=8.0 Hz, 1H), 7.73 (t, J=0.8 Hz, 1H), 7.90 (dd, J=8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 111.4, 111.9, 120.8, 120.9, 122.7, 124.4, 124.5, 127.2, 128.4, 132.4, 154.7, 156.7; IR ($CDCl_3$, cm^{-1}) 3026, 2978, 2941, 2921, 1446; HRMS *m*/*z* 182.0734 (calcd $C_{13}H_{10}O$, 182.0731).

4.3.3. 2,3,6-Trimethyldibenzofuran (42). The indicated compound was obtained in a 68% yield as a white solid: mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.36 (s, 3H), 2.46 (s, 3H), 7.17 (dd, J=8.4, 1.2 Hz, 1H), 7.28 (s, 1H), 7.37 (d, J=8.4 Hz, 1H), 7.61 (s, 1H), 7.63 (d, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.0, 21.6, 111.2, 112.4, 120.5, 121.0, 122.1, 124.6, 127.6, 131.2, 132.1, 136.4, 154.7, 155.6; IR ($CDCl_3$, cm^{-1}) 3014, 2970, 2940, 2921, 1454; HRMS *m*/*z* 210.1048 (calcd $C_{15}H_{14}O$, 210.1044).

4.3.4. 2,3,6,7-Tetramethyldibenzofuran (44). The indicated compound was obtained in a 61% yield as a white solid: mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 6H), 2.41 (s, 6H), 7.32 (s, 2H), 7.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 20.9, 112.3, 120.8, 122.3, 131.0, 135.7, 155.3; IR ($CDCl_3$, cm^{-1}) 3026, 2971, 2919, 2856, 1454; HRMS *m*/*z* 224.1204 (calcd $C_{16}H_{16}O$, 224.1201).

4.3.5. 3-Phenyldibenzofuran (46). The indicated compound was obtained in a 63% yield as a white solid: mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.37 (m, 2H), 7.43–7.48 (m, 3H), 7.55–7.66 (m, 5H), 7.96 (dd, J=7.6, 0.8 Hz, 1H), 8.11 (d, J=1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.0, 119.4, 120.9, 123.1, 124.5, 124.9, 126.9, 127.3, 127.6, 127.7, 129.1, 136.6, 141.6, 156.0, 156.9; IR ($CDCl_3$, cm^{-1}) 3057, 3032, 2920, 1601, 1470; HRMS *m*/*z* 280.0892 (calcd $C_{18}H_{12}O$, 280.0888).

4.3.6. 6-Methoxy-2,3-dimethyldibenzofuran (48). The indicated compound was obtained in a 67% yield as a white solid: mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.39 (s, 3H), 3.88 (s, 3H), 6.90 (dd, J=8.4, 2.4 Hz, 1H), 7.05 (d, J=2.4 Hz, 1H), 7.29 (s, 1H), 7.59 (s, 1H), 7.73 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 20.8, 55.9, 96.8, 110.7, 112.2, 117.8, 120.4, 120.7, 122.2, 131.3, 135.0, 155.4, 157.7, 159.6; IR ($CDCl_3$, cm^{-1}) 3015, 2999, 2979, 2939, 1590; HRMS *m*/*z* 226.0996 (calcd $C_{15}H_{14}O_2$, 226.0993).

4.3.7. 3-Acetyldibenzofuran (52). The indicated compound was obtained in a 76% yield as a white solid: mp 69–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.71 (s, 3H), 7.38 (td, J=7.5, 1.2 Hz, 1H), 7.70 (td, J=7.5, 1.2 Hz, 1H), 7.57 (s, 1H), 7.60 (s, 1H), 7.99 (dd, J=7.5, 0.6 Hz, 1H), 8.10 (dd, J=8.7, 1.8 Hz, 1H), 8.57 (d, J=1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 111.8, 112.2, 121.2, 121.8, 123.6, 123.9, 124.8, 128.2, 128.3, 132.7, 157.1, 159.1, 197.5; IR ($CDCl_3$, cm^{-1}) 3063, 3002, 2922, 2849, 1678, 1598; HRMS *m*/*z* 210.0683 (calcd $C_{14}H_{10}O_2$, 210.0680).

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