Construction of Benzo[*c*]carbazoles and Their Anti-tumor Derivatives through the Diels-Alder Reaction of 2-Alkenylindoles and Arynes

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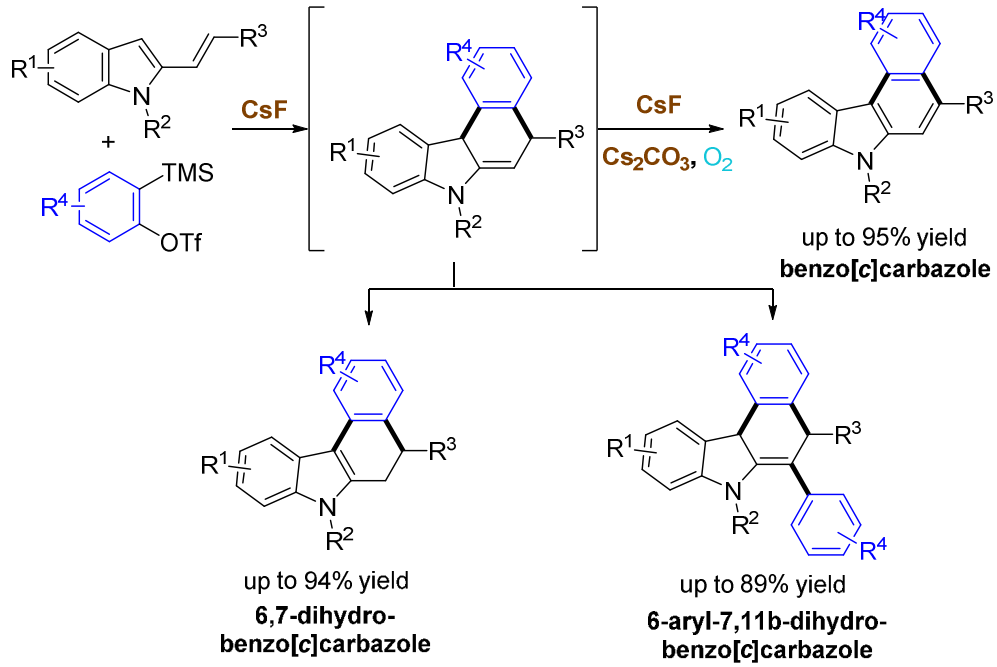
TOC Graphic



Abstract: The direct assembly of benzo[*c*]carbazole derivatives *via* the Diels-Alder reaction of arynes and easily accessible 2-alkenylidoles was reported. By employing different aryne precursor load, 6,7-dihydro-benzo[*c*]carbazoles or aryl substituted 7,11b-dihydro-benzo[*c*]carbazoles could be controllably generated in good to

excellent yields under nitrogen atmosphere. On the other hand, when the reaction was conducted under oxygen, oxidated/aromatized product benzo[*c*]carbazoles could be generated directly with high selectivity and efficiency in one step manner. Interestingly, the amidation derivatives benzo[*c*]carbazole-5-carboxamides of the above products showed good anti-tumor activities. The inhibitory effect of these molecules against cancer cells was also described.

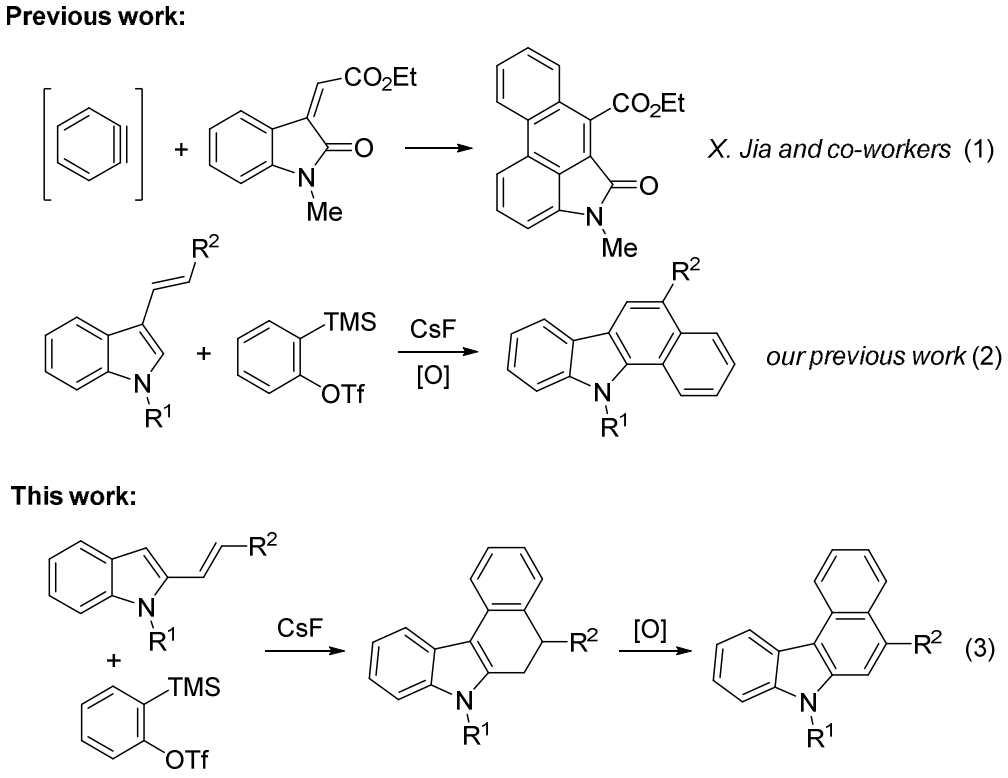
INTRODUCTION

The benzo[*c*]carbazole skeleton is a kind of privileged molecular scaffold of pharmaceuticals and natural products, and also a pivotal building block in material science.[1,2] Therefore, much effort has been devoted to develop the synthetic methods for the construction of benzo[*c*]carbazoles. However, most of the literature approaches involve harsh reaction conditions and lengthy procedures or low yields.[3] Thus, it is still of importance to develop direct and efficient routes to produce benzo[*c*]carbazole derivatives under mild and efficient conditions.

Arynes are highly reactive intermediates in organic synthesis and have received much attention during the past decades.[4] Due to their highly electrophilic character, arynes, *in situ* generated from 2-(trimethylsilyl)aryl triflates, have been widely applied in various procedures to afford aromatic compounds.[5] Especially, Diels-Alder reactions involving aryne[6] can lead to a variety of promising natural products and useful material skeletons. Recently, Jia and co-workers reported the Diels-Alder reaction of aryne with 3-methyleneindolin-2-one as the diene to furnishnaphtho[3,2,1-*cd*]indol-5(4*H*)-one (eq. 1, Scheme 1).[7] Very recently, our group

introduced vinyl indoles as dienes to react with arynes, and the reaction was successfully disclosed to generate useful benzo[*a*]carbazole derivatives in good-to-excellent yields (eq. 2).[8] On the basis of our previous study on arynes,[9] herein we wish to describe the direct and concise synthesis of benzo[*c*]carbazoles through the Diels-Alder reaction of 2-alkenylindoles and arynes as the ongoing research (eq. 3).

Scheme 1. Diels-Alder Reactions Involving Aryne

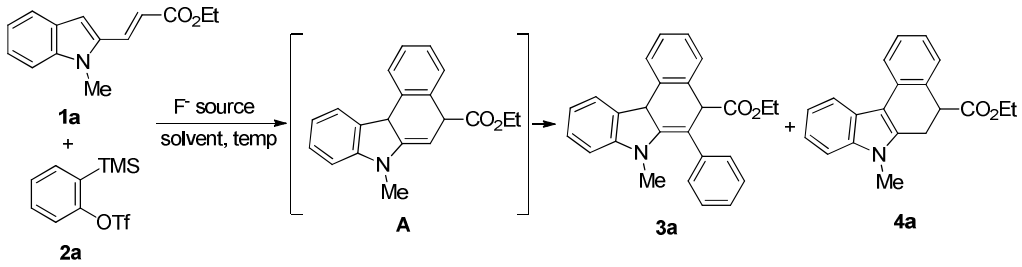


RESULTS AND DISCUSSION

Initially, the reaction of ethyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (**1a**) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) was carried out in the presence of TBAF in THF at room temperature under nitrogen atmosphere. However, neither desired [4+2] adduct 7,11b-dihydro-5*H*-benzo[*c*]carbazole-5-carboxylate **A**

nor its rearrangement product **4a** was observed (Table 1, entry 1). Instead, product **3a**, the adduct of intermediate **A** and another molecular of aryne, was isolated in 37% yield. When the reaction was conducted in the presence of KF/18-crown-6, the yield of **3a** was greatly increased to 64%, accompanied by a trace amount of **4a** isolated (entry 2). With the utilization of 3.0 equiv of **2a**, up to 95% of **3a** could be obtained (entry 3). By changing the fluoride source to CsF, the yield of **4a** was enhanced to 20% (entry 4). To our pleasure, with MeCN as solvent, the yield of **4a** was dramatically increased to 73% (entry 5). Enhancement of the reaction temperature to 60 ^{o}C led to a higher yield of **4a** (76% vs 73%, compare entry 6 with 5). Furthermore, toluene was added to slow down the generation rate of benzyne (Table 1, entries 7-12).[10] It is demonstrated that when the reaction was conducted in MeCN and toluene (v/v 1:4) at 80 ^{o}C, the yield of **4a** could be further improved to 92% (entry 9). Moreover, trials were conducted with the enhancement or reduction of the benzyne precursor (entries 11-13). It appeared that employment of 1.5 equiv of benzyne precursor resulted in **4a** in a higher yield. Thus, the optimal reaction conditions for the synthesis of **3a** and **4a** are settled as that described in entries 3 and 9, respectively.

Table 1. Optimization of the Reaction Conditions[a]



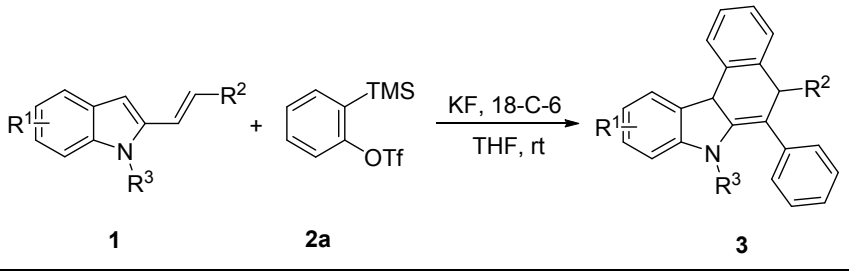
Entry	F^- source	**1a**/**2a** (mol)	Solvent (MeCN/toluene) (v/v)	Temp (^oC)	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	TABF	1:1.5	THF	rt	37	--
2	KF/18-C-6	1:1.5	THF	rt	64	trace
3	**KF/18-C-6**	**1:3**	**THF**	**rt**	**95**	**--**
4	CsF	1:1.5	THF	rt	5	20
5	CsF	1:1.5	MeCN	rt	12	73
6	CsF	1:1.5	MeCN	60	14	76
7	CsF	1:1.5	1/2	60	trace	84
8	CsF	1:1.5	1/2	80	--	86
9	**CsF**	**1:1.5**	**1/4**	**80**	**--**	**92**
10	CsF	1:1.5	1/6	80	--	53
11	CsF	1:1.3	1/4	80	--	88
12	CsF	1:1.7	1/4	80	19	73
13	CsF	1:2	1/4	80	31	55

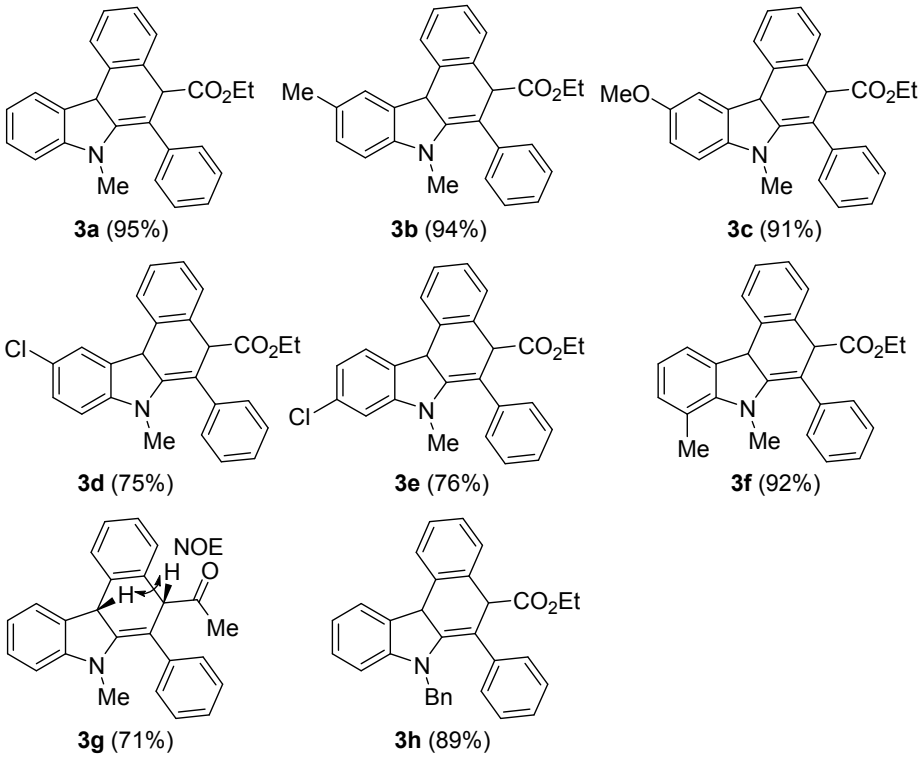
[a] Reaction conditions: 1.0 equiv of **1a** (0.3 mmol), 1.2-1.7 equiv of **2a**, 2.0 equiv of F^- source based on **2a** and 3.0 mL of solvent. [b] Isolated yield based on **1a**.

With the optimized conditions in hand, we then focused on the application scope of the reaction furnishing product **3**. As shown in Table 2, with the utilization of 5-, 6- or 7-substituted **1**, reactions all proceeded smoothly and generated corresponding substituted 7,11b-dihydro-5*H*-benzo[*c*]carbazoles **3a**-**f** in good-to-excellent yields.

When substrate **1** with chloro-substituted **1** was applied, the yields of **3d** and **3e** were slightly decreased. Moreover, **1** with acryl substituent as electron-withdrawing group furnished corresponding product **3g** in good yield. Benzyl group could also be applied as the *N*-protecting group, and 89% yield of product **3h** was obtained. In addition, the NOESY study of compound **3g** has been investigated, which demonstrated the *cis*-configuration of product **3g** (Table 2).

Table 2. Reaction of Substrates 1 with Benzyne Precursor 2a to Afford 3[a,b]

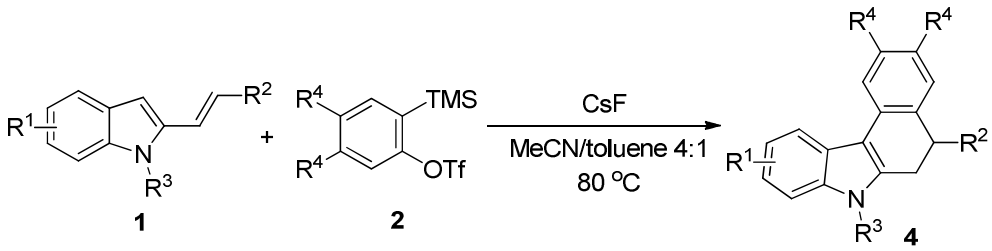




[a] Reaction conditions: 1.0 equiv of **1** (0.3 mmol), 3.0 equiv of **2a**, 6.0 equiv of KF, 5.0 equiv of 18-crown-6 in 3.0 mL of THF at room temperature. [b] Isolated yield of **3** based on **1**.

In addtion, we explored the substrate scope of this reaction with a series of substituted indole-2-acrylates **1** and aryne precursors **2** to afford product **4**. As shown in Table 3, various indole-2-acrylates **1** bearing both electron-withdrawing and -donating substituents on C5-C7 position were successfully applied to react with 2-(trimethylsilyl)phenyl triflate **2a**, dihydrobenzo[*c*]carbazoles **4c**-**f** were generated in good-to-excellent yields (80-93%, entries 3-6). It's worth noting that the reaction of ethyl (*E*)-3-(1,4-dimethyl-1*H*-indol-2-yl)acrylate (**1b**) with **2a** led to product **4b** in a relatively lower yield (55%, entry 2), which may lie in the steric hindrance between the C1-H and the C11-Me (Fig. 1). With the employment of different *N*-protecting groups on **1**, excellent yields were also observed (entries 7-8). Moreover, the annulation reaction could also be successfully realized by introducing acetyl group instead of ester moiety of **1i**, and led to the corresponding product **4i** in 71% yield (entry 9). Other than ester or acryl substituents, a phenyl group could also be introduced into (*E*)-1-methyl-2-styryl-1*H*-indole (**1j**). To our delight, the reaction was conducted successfully and afforded the desired product **4j** in 87% yield (entry 10). In addition, other substituted symmetric arynes (derived from precursors **2b** and **2c**) were also examined, with **4k** and **4l** furnished in good yields (entries 11-12).

Table 3. Reaction of Substrates 1 with Aryne Precursors 2 to Afford 4[a]



Entry	1				2		Product	Yield (%)[b]
	R^1	R^2	R^3		R^4		(**4**)	
1	H	CO_2Et	Me	(**1a**)	H	(**2a**)	**4a**	92
2	4-Me	CO_2Et	Me	(**1b**)		**2a**	**4b**	55
3	5-MeO	CO_2Et	Me	(**1c**)		**2a**	**4c**	80
4	5-Cl	CO_2Et	Me	(**1d**)		**2a**	**4d**	93
5	6-Cl	CO_2Et	Me	(**1e**)		**2a**	**4e**	84
6	7-Me	CO_2Et	Me	(**1f**)		**2a**	**4f**	90
7	H	CO_2Et	Ph	(**1g**)		**2a**	**4g**	93
8	H	CO_2Et	Boc	(**1h**)		**2a**	**4h**	94
9	H	COMe	Me	(**1i**)		**2a**	**4i**	71[c]
10	H	Ph	Me	(**1j**)		**2a**	**4j**	87[d]
11	H	CO_2Et	Me	(**1a**)	Me	(**2b**)	**4k**	77[e]
12	H	CO_2Et	Me	(**1a**)	F	(**2c**)	**4l**	73

[a] Reaction conditions: 1.0 equiv of **1** (0.3 mmol), 1.5 equiv of **2**, 3.0 equiv of CsF in 0.6 mL of MeCN and 2.4 mL of toluene at 80 °C under nitrogen atomosphere. [b] Isolated yields of **4** based on **1**. [c] The reaction was conducted at 100 °C. [d] The reaction was conducted at 100 °C using 2.5 equiv of **2** and 5.0 equiv of CsF. [e] The reaction was conducted with 2.0 equiv of **2**, 4.0 equiv of CsF.

Moreover, regioselectivity of this Diels-Alder reaction was examined by applying non-symmetric arynes. Reaction of **1a** and *ortho*-methyl-substituted aryne precursor **2d** was carried out (eq. 4). As expected, a mixture of regioisomers **4ma**[11] and **4mb** in a ratio of 79:21 was obtained (determined by ^{1}H NMR analysis). Similar

with the reaction of **1b** with **2a** (Fig. 1), steric hindrance among the C11-H atom and the methyl group of **4mb** may affect the selectivity, with **4ma** favored as the major isomer. When the reaction was carried out by using bulkier *t*-butyl benzyne (derived from precursor **2e**) and **1a**, only the sole regioisomer **4n** was isolated in 69% yield (eq. 5). Furthermore, introduction of *ortho*-methoxy aryne (derived from precursor **2f**) afforded regioisomer **4o** as the sole product in 83% yield (eq. 6). The structure of **4o** was further confirmed by the X-ray diffraction analysis.

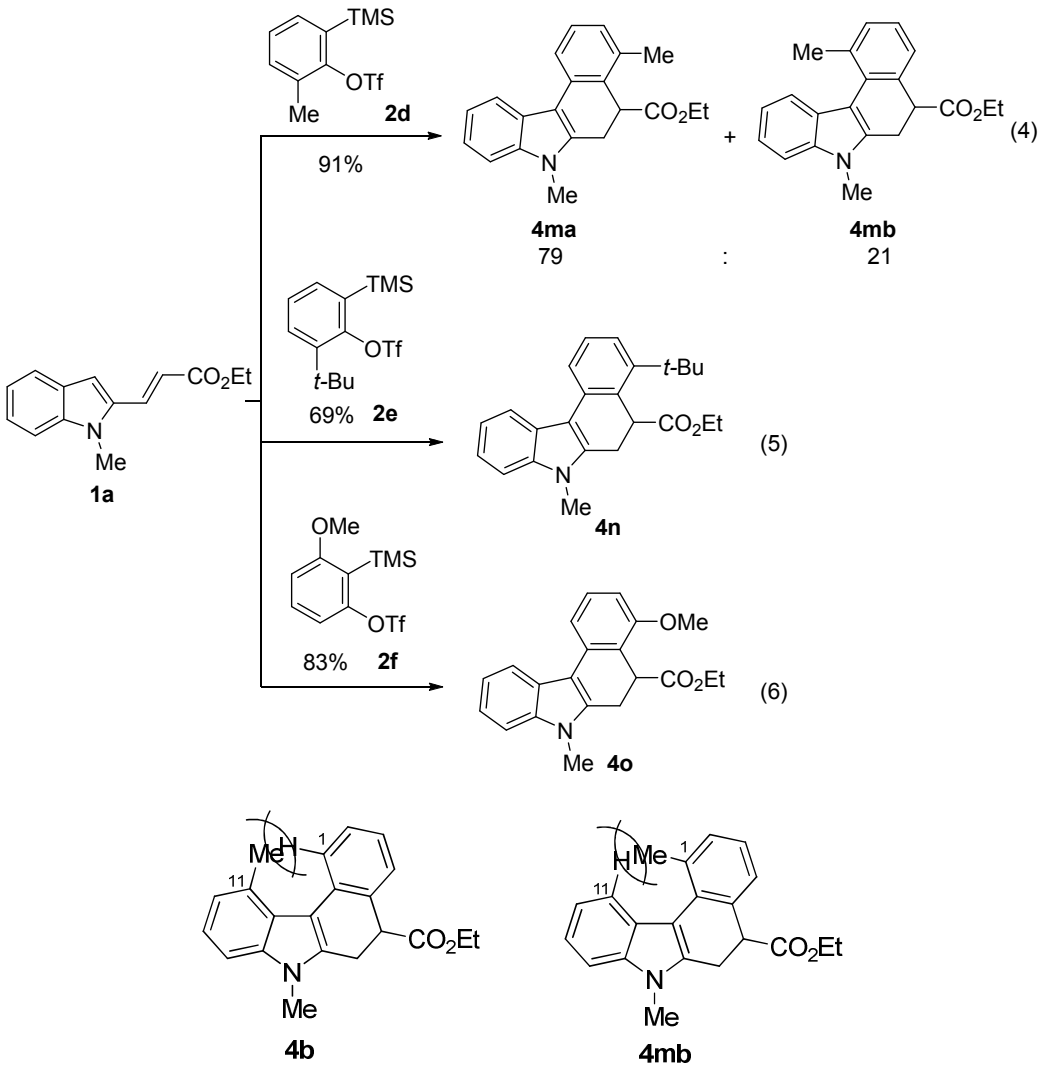
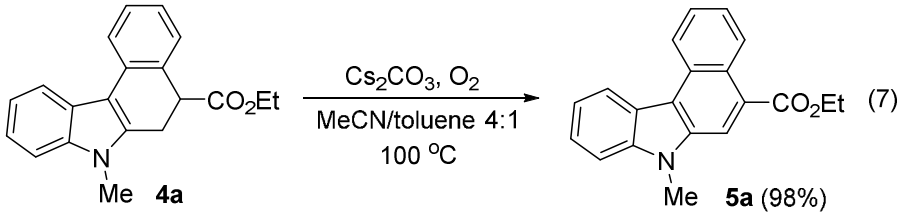


Figure 1. Effect of Steric Hindrance

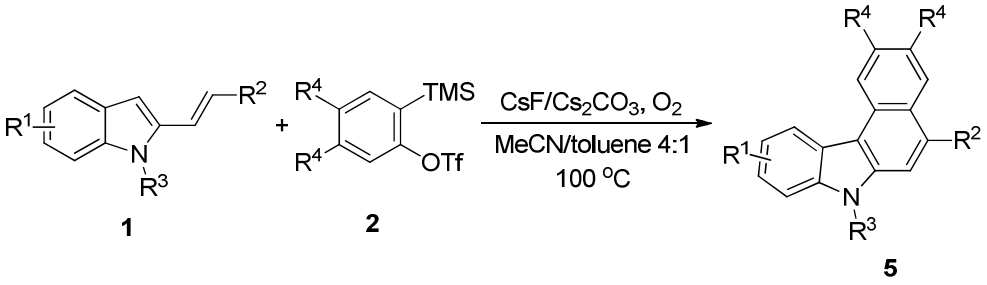
Considering that benzo[*c*]carbazoles are an important structural motif in medicinal and material science but rare in nature,[12] we tried to approach the benzo[*c*]carbazole skeleton *via* the oxidation-aromatization of **4**. As shown in eq. 7, benzo[*c*]carbazole **5a** could be smoothly afforded in 98% yield from **4a** in the presence of Cs_2CO_3 under oxygen atmosphere.

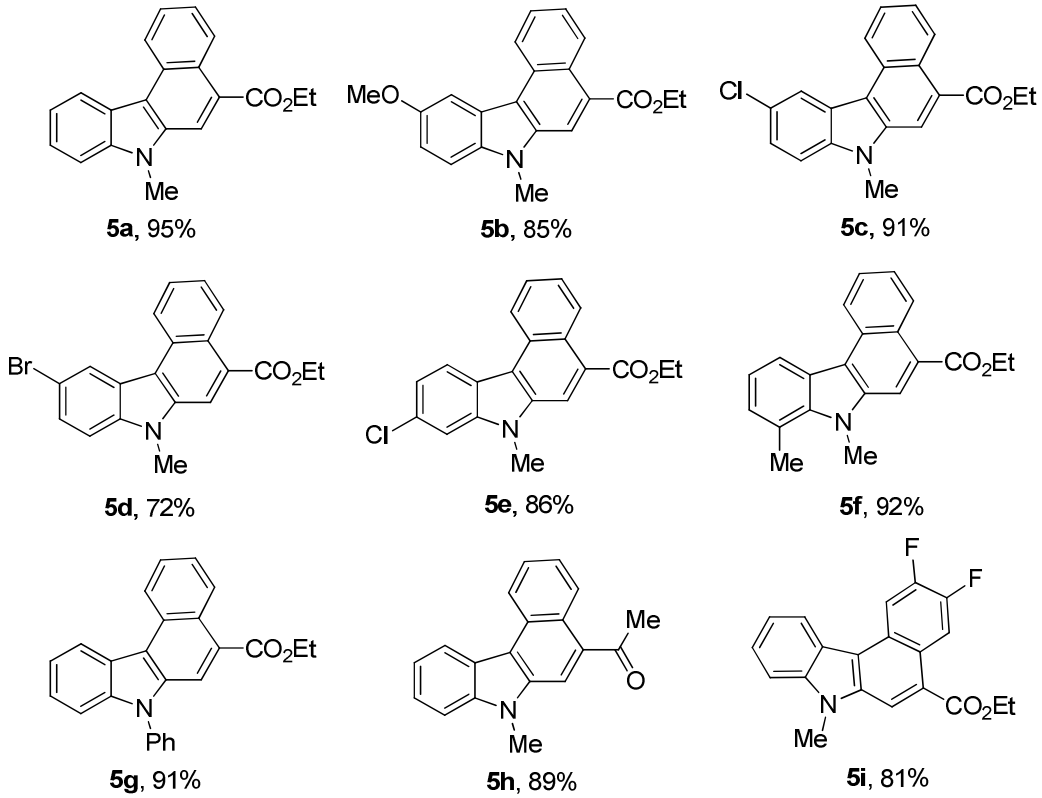


(7)

Inspired by the above result, we proposed to combine the Diels-Alder reaction and oxidative transformation in one step to explore a direct strategy for the synthesis of the useful benzo[*c*]carbazole skeleton. Therefore, the reaction of **1a** and **2a** was carried out in the presence of CsF and Cs_2CO_3 in MeCN and toluene at 100 °C under oxygen for 36 h. To our great pleasure, benzo[*c*]carbazole **5a** was furnished directly in up to 95% yield (Table 4). Further examination demonstrated that substituents such as halide, alkyl and alkoxyl group could be smoothly introduced, generating corresponding products **5b-h** in good-to-excellent yields (72-92%). Notably, when the reaction was conducted with difluorobenzyne (generated from **2c**), desired product **5i** was obtained in a slightly lower yield (81%), which may attribute to the higher reactivity of difluorobenzyne in side reactions.

Table 4. Reaction of Indole-2-acrylates 1 with Aryne Precursors 2 to Afford 5[a,b]



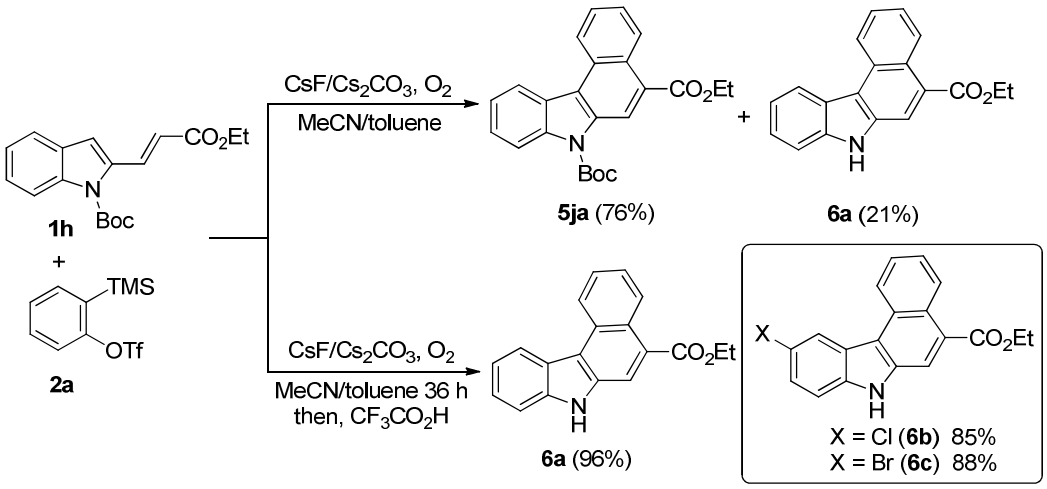


[a] Reaction conditions: 1.0 equiv of **1** (0.3 mmol), 1.5 equiv of **2**, 3.0 equiv of CsF in 0.6 mL of MeCN and 2.4 mL of toluene at 100 °C under O_2 atmosphere. [b] Isolated yields of **5** based on **1**.

7*H*-benzo[*c*]carbazole skeleton is of potential utility due to the facile further transformation of the free N-H bond. Therefore, an acyl group was employed as the *N*-protecting group instead of methyl or phenyl group for easier deacylation. Interestingly, employment of **1h** with the *N*-*t*-butoxycarbonyl group (*N*-Boc) **1h** led to

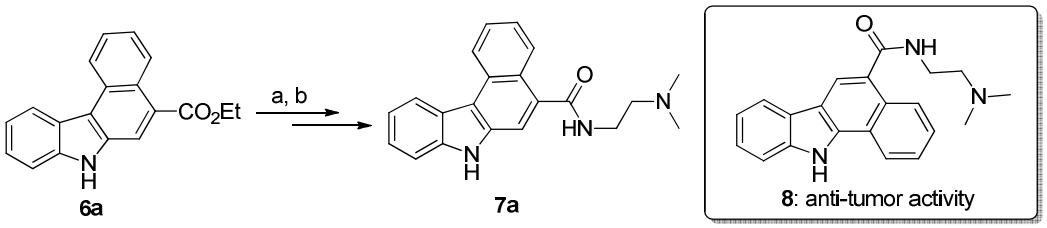
76% of **5ja** in 36 h accompanied with 21% of deprotected product **6a**, indicating a high overall conversion rate (Scheme 2). When the reaction mixture of **1h** and **2a** was treated with trifluoroacetic acid after 36 h, up to 96% yield of the product **6a** could be isolated. In addition, 5-Cl and 5-Br substituents were also tolerated, affording **6b** and **6c** in high yields.

Scheme 2. Synthesis of N-H Benzo[*c*]carbazoles 6

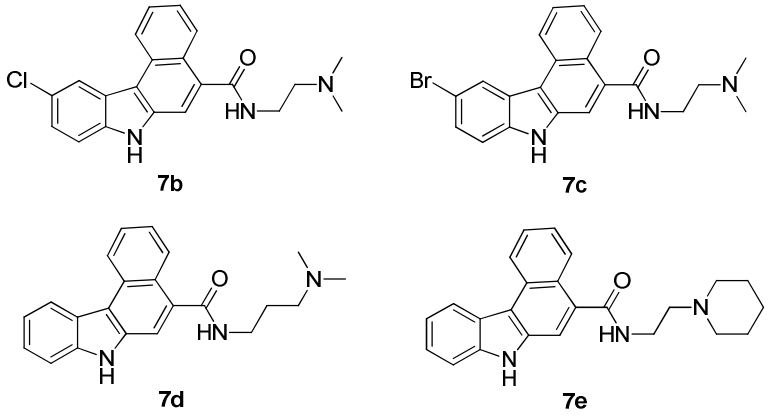


Notably, *N*-(2-(dimethylamino)ethyl)-11*H*-benzo[*a*]carbazole-5-carboxamide **8** can serve as the anti-tumor agent, which inspired us to synthesize its isomer **7a** starting from **6a**.[13] As demonstrated in Scheme 3, a series of benzo[*c*]carbazole amides **7a-e** were obtained with the previous product **6**. Pleasingly, benzo[*c*]carbazole amide **7** also revealed anti-tumor activity as demonstrated in Table 5.

Scheme 3. Synthesis of Benzo[*c*]carbazole Amides 7

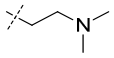
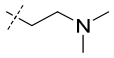
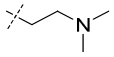
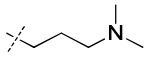
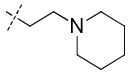


a: NaOH/EtOH/H_2O, reflux; *b*: $(COCl)_2$/THF, 0 °C; R-NH_2/THF, rt.



The compounds **7a-e** were evaluated against human lung cancer A549 cells and human colon cancer HCT-116 cells using the MTT (3-(4,5)-dimethylthiahiazo(-z-y1)-3,5-di-phenytetrazoliumromide) assay.[14] Fortunately, most of the compounds exhibited comparable potency against HCT-116 cell lines. First, we evaluated the effect on the inhibitory activity of substituent on the 8-position of the core structure among **7a-c**. Compounds **7b** and **7c** with halogen atom substituted were found to be more potent than **7a** in both A549 and HCT-116 cell lines (Table 5, entries 1-3). Furthermore, basic side chain (BSC) at 5-position was replaced with other amines (**7d** and **7e**). Increasing the length of the BSC (**7d**) improved the inhibitory activity of A549 slightly. The BSC with a piperidin-cycle (**7e**) is more preferable than the ones bearing *N*,*N*-dimethyl substituent in A549.

Table 5. Structures and Growth Inhibitory Activity (IC_{50}) of Compounds 7a-e

Entry	**7**		IC_{50} (μM) [a, b]	
	R^1	R^2	A549	HCT-116
1		H (**7a**)	41.3±1.2	36.4±1.7
2		Cl (**7b**)	32.2±1.1	34.3±1.5
3		Br (**7c**)	30.1±0.8	36.1±1.3
4		H (**7d**)	34.3±1.7	39.2±2.1
5		H (**7e**)	27.3±1.5	35.7±1.8

[a] Exposure time: 72 h. [b] The average IC_{50} values were determined by MTT assay.

CONCLUSION

In summary, a novel and direct methodology for the construction of benzo[*c*]carbazole skeleton has been realized *via* the Diels-Alder reaction of arynes and 2-alkenylindoles. With high selectivity, desired benzo[*c*]carbazole derivatives were obtained in good-to-excellent yields. By controlling the reaction conditions, dihydrobenzo[*c*]carbazoles and benzo[*c*]carbazoles could be obtained effectively in a one-pot manner. On the other hand, benzo[*c*]carbazole amide derivative **7** was synthesized, and exhibited comparable IC_{50} potency against both A549 and HCT-116 cell lines. Due to the high formation efficiency of the carbazole skeletons and the promising utilization of the benzo[*c*]carbazole derivative products, this methodology may be of high interest to organic and pharmaceutical chemistry.

EXPERIMENTAL SECTION

General Information. Anhydrous solvents were distilled prior to use: THF, Et_2O, and toluene were distilled from sodium-benzophenone; MeCN was distilled from P_2O_5; CH_2Cl_2 was distilled from CaH_2. Petroleum ether refers to the fraction with boiling point in the range of 60-90 °C. ^{1}H NMR and ^{13}C NMR spectra were measured on a 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz), using $CDCl_3$ or d_6-DMSO as the solvent at room temperature. Chemical shifts are expressed in ppm and J values are given in Hz. Melting points are uncorrected. High Resolution Mass Spectra (HRMS) were recorded on an electron spray ionization time-of-flight (ESI-TOF) mass spectrometer. IR spectra were measured on a FT-IR spectrometer. 2-(Trimethylsilyl)aryl triflates **2** were prepared according to the known methods.[15]

General Procedure for the Preparation of 2-Alkenylindoles (1a-c, 1f, 1i, 1j).

To a solution of indole (1.76 g, 15 mmol) and potassium hydroxide (4.20 g, 75 mmol) in anhydrous DMF (50 mL) was added iodomethane (1.9 mL, 30 mmol). The reaction mixture was stirred at room temperature for 20 min. The mixture was then filtered through a plug of silica gel and H_2O (200 mL) was added into the filtrate. The water layer was extracted by CH_2Cl_2 (50 mL × 2). The organic layer was combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford 1-methyl-1*H*-indole (1.93 g, 98%).

Under nitrogen atmosphere, to a solution of 1-methyl-1*H*-indole (1.31 g, 10 mmol) in anhydrous ether (15 mL) was added *n*-BuLi (1.2 M, 10.1 mL, 12 mmol)

dropwisely at room temperature. The mixture was heated to reflux for 3 h followed by the addition of DMF (3.0 mL, 15 mmol) dropwise. The mixture was then reflux for 5 h monitored by TLC and quenched by saturated solution of NH_4Cl at room temperature. The water layer was then extracted by ethyl acetate (30 mL × 3). The organic layer was combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford 1-methyl-1*H*-indole-2-carbaldehyde (1.24 g, 78%).

To a solution of 1-methyl-1*H*-indole-2-carbaldehyde (0.80 g, 5.0 mmol) in anhydrous EtOH (40 mL) was added phosphorus ylide (1.92 g, 5.5 mmol) in one portion and the reaction mixture was stirred at room temperature monitored by TLC. The mixture was then concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1) to give compound **1a** (0.75 g, 65%).

(*E*)-Ethyl 3-(1-methyl-1*H*-indol-2-yl)acrylate (1a). Yellow solid, mp 89-90 ^oC; ^1H NMR($CDCl_3$, 400MHz): δ 7.80 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.14-7.10 (m, 1H), 6.96 (s, 1H), 6.49 (d, J = 15.6 Hz, 1H), 4.29 (q, J = 6.8 Hz, 2H), 3.83 (s, 3H), 1.36 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 138.9, 134.8, 132.6, 127.3, 123.5, 121.3, 120.4, 118.1, 109.6, 103.6, 60.5, 29.9, 14.3; IR (neat): 2992, 2938, 1709, 1462, 1402, 1178, 960, 771, 751 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1106.

(*E*)-Ethyl 3-(1,4-dimethyl-1*H*-indol-2-yl)acrylate (1b). 64% yield (0.70 g), yellow solid, mp 105-106 ^oC; ^1H NMR($CDCl_3$, 400MHz): δ 7.78 (d, J = 15.6 Hz, 1H),

7.18-7.11 (m, 2H), 6.97 (s, 1H), 6.90 (d, J = 6.4 Hz, 1H), 6.49 (d, J = 15.6 Hz, 1H), 4.30-4.25 (m, 2H), 3.77 (s, 3H), 2.53 (s, 3H), 1.35 (td, J_1 = 2.0 Hz, J_2 = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 138.8, 134.3, 132.6, 130.9, 127.4, 123.7, 120.4, 117.7, 107.2, 102.3, 60.5, 30.1, 18.5, 14.3; IR (neat): 2988, 2938, 1709, 1635, 1354, 1304, 1167, 968, 759 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}NO_2$ 243.1259, found 243.1260.

(*E*)-Ethyl 3-(5-methoxy-1-methyl-1*H*-indol-2-yl)acrylate (1c). 68% yield (0.70 g), yellow solid, mp 121-122 °C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.75 (d, J = 16.0 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.92 (dd, J_1 = 2.4 Hz, J_2 = 9.2 Hz, 1H), 6.86 (s, 1H), 6.44 (d, J = 15.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 154.5, 135.1, 134.5, 132.5, 127.6, 117.6, 114.7, 110.4, 103.0, 101.6, 60.5, 55.6, 30.1, 14.3; IR (neat): 3005, 2951, 1699, 1634, 1300, 1166, 1026, 839, 798 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}NO_3$ 259.1208, found 259.1201.

(*E*)-Ethyl 3-(1,7-dimethyl-1*H*-indol-2-yl)acrylate (1f). 67% yield (0.74 g), yellow solid, mp 72-73 °C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.74 (d, J = 15.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 6.97-6.90 (m ,2H), 6.88 (s, 1H), 6.42 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 2.71 (s, 3H), 1.34 (td, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 138.0, 135.4, 132.7, 128.2, 126.5, 121.2, 120.4, 119.4, 118.2, 104.1, 60.4, 32.8, 20.4, 14.3; IR (neat): 2976, 2926, 1705, 1627, 1445, 1279, 1178, 1156, 1037, 743 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}NO_2$ 243.1259, found 243.1262.

(*E*)-4-(1-Methyl-1*H*-indol-2-yl)but-3-en-2-one (1i). 50% yield (0.50 g), yellow solid, mp 109-110 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.66-7.60 (m, 2H), 7.32-7.25 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 139.4, 134.9, 130.9, 127.4, 126.3, 123.9, 121.5, 120.5, 109.6, 104.2, 30.0, 28.3; IR (neat): 3054, 2926, 1661, 1594, 1348, 1250, 967, 747, 729 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0999.

NaH in mineral oil (200.0 mg, 60%, 5.0 mmol) was added to the suspension of $BnPh_3PCl$ (1.94 g, 5.0 mmol) in toluene (10 mL) at 0 ^{o}C. The mixture was stirred at room temperature for 30 min followed by the addition of 1-methyl-1*H*-indole-2-carbaldehyde (0.67 g, 4.2 mmol) in toluene (3 mL). Then the mixture was heated to 80 ^{o}C for 2 h monitored by TLC and quenched by saturated solution of NH_4Cl at room temperature. The water layer was then extracted by ethyl acetate (30 mL × 3). The organic layer was combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford (*E*)-1-methyl-2-styryl-1*H*-indole (**1j**, 0.55 g, 56% yield). Yellow solid, mp 112-113 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31-7.28 (m ,2H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.1, 137.2, 130.9, 128.8, 128.0, 127.8, 126.4, 121.8, 120.4, 119.9, 117.1, 109.1, 99.0, 29.9; IR (neat): 2921, 2847, 1594, 1463, 1396, 1346, 1319, 957, 748,690 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}N$ 233.1204, found 233.1209.

General Procedure for the Preparation of 2-Alkenylindoles (1g, 1h, 1d, 1e, 1k).

To a solution of ethyl 1*H*-indole-2-carboxylate (3.78 g, 20 mmol) in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (2.27 g, 60 mmol) in THF (20 mL) at 0 °C under nitrogen atmosphere. The solution was stirred for 30 min at 0 °C and quenched by H_2O carefully. The solution was then diluted with dichloromethane (40 mL) and the layers were separated. The water layer was extracted with dichloromethane (2 × 20 mL). The organic layer was combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 2:1) to afford (1*H*-indol-2-yl)methanol (2.10 g, 71% yield).

To a solution of (1*H*-indol-2-yl)methanol (1.47 g, 10 mmol) in MeCN (20 mL) was added acetic acid (0.69 mL, 12 mmol) and IBX (3.38 g, 12 mmol). The reaction mixture was stirred at room temperature monitored by TLC. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford 1*H*-indole-2-carbaldehyde (1.23 g, 85% yield).

To a solution of 1*H*-indole-2-carbaldehyde (0.73 g, 5.0 mmol) in anhydrous EtOH (40 mL) was added phosphorus ylide (1.92 g, 5.5 mmol) in one portion and the reaction mixture was stirred at room temperature monitored by TLC. The mixture was then concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 15:1) to give compound (*E*)-ethyl 3-(1*H*-indol-2-yl)acrylate (0.65 g, 60% yield).

Under nitrogen atmosphere, compound (*E*)-ethyl 3-(1*H*-indol-2-yl)acrylate (1.08 g, 5.0 mmol), Iodobenzene (1.22 g, 6.0 mmol), CuI (47.6 mg, 0.25 mmol), K_3PO_4 (2.20 g, 10 mmol) and cyclohexane-1,2-diamine (121 μL, 1.0 mmol) were added to a Schlenk tube equipped with a stir bar. Then 10 mL toluene was added. The reaction mixture was stirred at 90 ^oC for 24 h. The mixture was then cooled to ambient temperature, diluted with CH_2Cl_2 (10 mL), filtered through a plug of silica gel, eluting with additional CH_2Cl_2 (50 mL). The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to provide (*E*)-ethyl 3-(1-phenyl-1*H*-indol-2-yl)acrylate (**1g**, 1.06 g, 73% yield). Yellow solid, mp 69-70 ^oC; ^1H NMR($CDCl_3$, 400MHz): δ 7.66 (d, *J* = 7.2 Hz, 1H), 7.57-7.46 (m, 4H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.21-7.13 (m, 3H), 7.09 (s, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.19 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 139.7, 136.9, 135.3, 133.4, 129.7, 128.4, 128.2, 127.5, 124.0, 121.3, 121.1, 118.1, 110.7, 105.1, 60.4, 14.2; IR (neat): 3054, 2980, 1707, 1629, 1500, 1341, 1269, 1166, 1037, 977, 749 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NO_2$ 291.1259, found 291.1257.

To a solution of (*E*)-ethyl 3-(1*H*-indol-2-yl)acrylate (1.08 g, 5.0 mmol) in DCM (50 mL) was added DMAP (60.9 mg, 0.5 mmol) and triethylamine (0.9 mL, 6.5 mmol). Then $(Boc)_2O$ (1.41 g, 6.5 mmol) was added. The reaction mixture was stirred at room temperature monitored by TLC and quenched by saturated solution of NH_4Cl. The water layer was then extracted by ethyl acetate (30 mL × 3). The organic layer was combined and dried over Na_2SO_4. After filtration and evaporation, the residue

was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford (*E*)-tert-butyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-1*H*-indole-1-carboxylate (**1h**, 1.40 g, 89% yield). White solid, mp 85-86 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 8.26 (d, *J* = 16.0 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.94 (s, 1H), 6.36 (d, *J* = 15.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.70 (s, 9H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 150.0, 137.6, 136.4, 136.0, 128.6, 125.6, 123.3, 121.1, 119.2, 115.8, 110.1, 84.8, 60.5, 28.2, 14.3; IR (neat): 2980, 2938, 1735, 1712, 1626, 1371, 1328, 1161, 1093, 747 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{21}NO_4$ 315.1471, found 315.1478.

According to the above reported methylation procedure to furnish 1-methyl-1*H*-indole, 2-vinylindoles **1d**, **1e** and **1k** could be prepared from substituted (*E*)-ethyl 3-(1*H*-indol-2-yl)acrylate.

(*E*)-Ethyl 3-(5-chloro-1-methyl-1*H*-indol-2-yl)acrylate (1d). 99% yield (0.65 g), yellow solid, mp 71-72 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55 (s, 1H), 7.22-7.17 (m, 2H), 6.85 (s, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 137.2, 136.1, 132.0, 128.2, 126.0, 123.8, 120.4, 119.2, 110.6, 102.7, 60.7, 30.2, 14.3; IR (neat): 2976, 2930, 1706, 1632, 1467, 1306, 1285, 1180, 968, 789 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{14}{}^{35}ClNO_2$ 263.0713, found 263.0710.

(*E*)-Ethyl 3-(6-chloro-1-methyl-1*H*-indol-2-yl)acrylate (1e). 99% yield (0.73 g), yellow solid, mp 109-110 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.71 (d, *J* = 15.6 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.26 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 2.0

Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.73-3.72 (m, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 139.2, 135.6, 132.0, 129.4, 125.8, 122.1, 121.2, 118.7, 109.5, 103.5, 60.6, 30.1, 14.3; IR (neat): 2976, 2930, 1704, 1632, 1461, 1348, 1305, 1280, 1179, 970, 808 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{14}{}^{35}ClNO_2$ 263.0713, found 263.0708.

(*E*)-Ethyl 3-(5-bromo-1-methyl-1*H*-indol-2-yl)acrylate (1k). 99% yield (0.69 g), yellow solid, mp 82-83 ^{o}C; ^{1}H NMR($CDCl_3$, 400MHz): δ 7.78-7.72 (m, 2H), 7.33 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.18 (d, J = 9.2 Hz, 1H), 6.87 (s, 1H), 6.49 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 137.5, 136.0, 132.1, 128.9, 126.3, 123.6, 119.4, 113.6, 111.1, 102.6, 60.7, 30.2, 14.3; IR (neat): 2976, 2930, 1706, 1632, 1465, 1284, 1180, 1050, 966, 788 cm^{-1}; HRMS calcd for $C_{14}H_{15}{}^{79}BrNO_2$ $[M+H]^+$: 308.0286, found 308.0291.

General Procedure for the Synthesis of Products (3). Under the nitrogen atmosphere, 2-alkenylindole **1** (0.3 mmol), KF (104.6 mg, 1.8 mmol) and 18-crown-6 (396.5 mg, 1.5 mmol) were added to a 25 mL Schlenk tube equipped with a stir bar. Then 3.0 mL of THF and aryne precursor **2a** (268.6 mg, 0.9 mmol) were added. The reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the mixture was poured into water (10 mL), and the water layer was extracted by CH_2Cl_2 (10 mL × 3). The organic layer was combined and dried over Na_2SO_4. After evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford **3a-h**.

Ethyl 7-methyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3a). 95% yield (108.7 mg), white solid, mp 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.38-7.32 (m, 2H), 7.26-7.23 (m, 2H), 7.19-7.13 (m, 4H), 7.07-6.99 (m, 3H), 4.97 (d, J =0.8 Hz, 1H), 4.11-4.04 (m, 1H), 4.00-3.93 (m, 2H), 3.60 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 139.6, 138.7, 138.1, 133.4, 131.0, 128.8, 128.2, 127.9, 127.6, 127.1, 124.3, 124.3, 122.3, 121.4, 120.3, 120.0, 110.0, 109.5, 61.3, 54.4, 39.8, 29.4, 14.0; IR (neat): ν 1724, 1602, 1471, 1377, 1241, 1198, 1080, 749, 702 cm^{-1}; HRMS calcd for $C_{26}H_{24}NO_2$ $[M+H]^+$: 382.1807, found: 382.1810.

Ethyl 7,10-dimethyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3b). 94% yield (111.2 mg), pale yellow solid, mp 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.6 Hz, 1H), 7.91 (s, 1H), 7.37-7.32 (m, 1H), 7.22-7.10 (m, 5H), 7.09-6.97 (m, 4H), 4.95 (s, 1H), 4.09-4.02 (m, 1H), 3.99-3.92 (m, 2H), 3.49 (s, 3H), 2.53 (s, 3H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 139.7, 138.7, 136.5, 133.6, 131.0, 129.6, 128.7, 128.1, 127.8, 127.6, 127.1, 124.4, 124.1, 122.8, 122.2, 119.9, 109.5, 109.2, 61.2, 54.4, 39.8, 29.4, 21.7, 14.0; IR (neat): ν 2980, 2922, 1724, 1594, 1545, 1481, 1242, 1162, 748 cm^{-1}; HRMS calcd for $C_{27}H_{26}NO_2$ $[M+H]^+$: 396.1964, found: 396.1964.

Ethyl 10-methoxy-7-methyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3c). 91% yield (112.5 mg), white solid, mp 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.90 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H), 7.38-7.33 (m, 1H), 7.22-7.12 (m, 5H), 7.05-6.98 (m, 3H), 6.92-6.88 (m, 1H), 4.94 (s, 1H), 4.12-4.03 (m, 1H), 4.00-3.93 (m, 5H), 3.55 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 154.7, 139.6, 139.3, 133.5, 133.4, 131.1, 128.7, 128.1, 127.8, 127.6, 127.1, 124.5, 124.1, 121.9, 110.9, 110.1, 109.6, 102.8, 61.2, 56.1, 54.4, 39.8, 29.5, 13.9; IR (neat): ν 2934, 1724, 1602, 1480, 1233, 1159, 1030, 742 cm^{-1}; HRMS calcd for $C_{27}H_{25}NO_3Na$ $[M+Na]^+$: 434.1732, found: 434.1736.

Ethyl 10-chloro-7-methyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3d). 75% yield (93.6 mg), yellow solid, mp 230-231 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.38-7.33 (m, 1H), 7.23-7.13 (m, 6H), 7.07-7.03 (m, 1H), 7.00-6.97 (m, 2H), 4.93 (d, J = 0.8 Hz, 1H), 4.08-4.04 (m, 1H), 3.99-3.95 (m, 2H), 3.57 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 140.0, 139.3, 136.5, 132.7, 131.1, 128.8, 128.3, 127.9, 127.5, 127.3, 126.1, 125.0, 124.7, 122.2, 121.5, 119.5, 110.4, 109.6, 61.3, 54.2, 39.8, 29.6, 13.9; IR (neat): ν 2922, 1731, 1601, 1471, 1286, 1245, 1155, 1022, 805, 706 cm^{-1}; HRMS calcd for $C_{26}H_{22}{}^{35}ClNO_2Na$ $[M+Na]^+$: 438.1237, found: 438.1241.

Ethyl 9-chloro-7-methyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3e). 76% yield (94.4 mg), pale yellow solid, mp 159-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 1H), 7.91-7.87 (m, 1H), 7.38-7.31 (m, 2H), 7.22-7.15 (m, 5H), 7.09-7.04 (m, 1H), 7.00-6.97 (m, 2H), 4.94 (d, J = 6.0 Hz, 1H), 4.12-4.05 (m, 1H),

4.00-3.94 (m, 2H), 3.56 (d, J = 2.0 Hz, 3H), 1.13-1.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 139.3, 139.3, 138.6, 132.8, 131.1, 128.9, 128.2, 127.9, 127.5, 127.4, 127.3, 124.7, 122.7, 122.3, 120.8, 110.1, 109.6, 61.3, 54.3, 39.7, 29.5, 14.0; IR (neat): v 1725, 1602, 1494, 1472, 1240, 1198, 1060, 948, 742 cm^{-1}; HRMS calcd for $C_{26}H_{22}{}^{35}ClNO_2Na$ $[M+Na]^+$: 438.1237, found: 438.1234.

Ethyl 7,8-dimethyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3f). 92% yield (109.0 mg), pale yellow solid, mp 197-198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.20-7.07 (m, 5H), 7.05-6.98 (m, 3H), 6.93 (d, J = 6.8 Hz, 1H), 4.95 (s, 1H), 4.10-4.03 (m, 1H), 3.99-3.90 (m, 2H), 3.85 (s, 3H), 2.75 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 139.5, 139.1, 137.0, 133.4, 131.0, 128.7, 128.1, 128.0, 127.7, 127.1, 125.1, 124.6, 124.2, 122.3, 121.4, 120.3, 118.1, 110.2, 61.2, 54.5, 39.8, 32.6, 20.5, 14.0; IR (neat): v 2930, 1709, 1598, 1459, 1405, 1241, 1029, 742 cm^{-1}; HRMS calcd for $C_{27}H_{26}NO_2$ $[M+H]^+$: 396.1964, found: 396.1968.

1-(7-Methyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazol-5-yl)ethanone (3g). 71% yield (74.9 mg), white solid, mp 204-205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.08 (m, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.27-7.23 (m, 2H), 7.20 (d, J = 7.6 Hz, 1H), 7.14-7.05 (m, 4H), 6.97-6.94 (m, 2H), 5.03 (s, 1H), 3.79 (s, 1H), 3.59 (d, J = 0.8 Hz, 3H), 1.95 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 139.7, 139.6, 138.1, 133.8, 131.0, 128.7, 128.4, 127.6, 127.0, 124.5, 124.1, 122.6, 121.5, 120.4, 119.9, 109.8, 109.6, 62.8, 38.8, 29.4,

28.5; IR (neat): *v* 3050, 2918, 1705, 1599, 1541, 1472, 1377, 750 cm^{-1}; HRMS calcd for $C_{25}H_{21}NONa$ $[M+Na]^+$: 374.1521, found: 374.1518.

Ethyl 7-benzyl-6-phenyl-7,11b-dihydro-5H-benzo[c]carbazole-5-carboxylate (3h). 89% yield (122.4 mg), white solid, mp 132-133 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.40-7.35 (m, 1H), 7.26-7.18 (m, 7H), 7.12-7.00 (m, 6H),6.97-6.95 (m, 2H), 5.17 (dd, J_1 = 16.8 Hz, J_2 = 36.0 Hz, 2H), 4.87 (s, 1H), 3.99-3.93 (m, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 139.7, 138.5, 137.8, 136.9, 133.4, 130.9, 128.8, 128.6, 128.2, 128.0, 127.6, 127.3, 127.2, 126.3, 124.5, 124.5, 122.5, 121.7, 120.5, 120.2, 110.6, 110.2, 61.2, 54.5, 46.9, 40.2, 13.9; IR (neat): *v* 3059, 2976, 2926, 1726, 1599, 1495, 1463, 1195, 1026, 749 cm^{-1}; HRMS calcd for $C_{32}H_{27}NO_2Na$ $[M+Na]^+$: 480.1939, found: 480.1938.

General Procedure for the Synthesis of Products 4. Under the nitrogen atmosphere, 2-alkenylindole **1** (0.3 mmol) and CsF (136.7 mg, 0.9 mmol) were added to a 25 mL Schlenk tube equipped with a stir bar. Then 0.6 mL of MeCN, 2.4 mL of toluene and aryne precursor **2** (0.45 mmol) were added. The reaction mixture was stirred at 80 ^oC. When the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short column of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the residue, which was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford **4a-n**.

Ethyl 7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4a). 92%

yield (84.3 mg), white solid, mp 88-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01-7.99 (m, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.36-7.29 (m, 3H), 7.21-7.18 (m, 2H), 7.10 (td, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 4.12-4.00 (m, 2H), 3.96 (t, J = 6.0 Hz, 1H), 3.71 (s, 3H), 3.47 (dd, J_1 = 5.2 Hz, J_2 = 16.0 Hz, 1H), 3.08 (dd, J_1 = 6.4 Hz, J_2 = 16.4 Hz, 1H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 137.9, 137.1, 133.7, 129.8, 128.9, 128.0, 124.3, 124.1, 122.4, 121.0, 120.2, 119.4, 109.4, 109.2, 61.0, 45.3, 29.4, 23.3, 14.0; IR (neat): 3046, 2980, 2926, 1753, 1603, 1541, 1499, 1472, 1201, 1154, 766, 748 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{19}NO_2$ 305.1416, found 305.1418.

Ethyl 7,11-dimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4b). 55% yield (52.8 mg), oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 7.6 Hz, 1H), 7.33-7.26 (m, 2H), 7.18-7.08 (m, 3H), 6.97 (d, J = 6.8 Hz, 1H), 4.11-4.07 (m, 2H), 3.90 (t, J = 5.6 Hz, 1H), 3.72 (s, 3H), 3.41 (dd, J_1 = 6.0 Hz, J_2 = 16.0 Hz, 1H), 2.97 (dd, $_1$ = 6.0 Hz, J_2 = 15.6 Hz, 1H), 2.76 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 138.5, 138.3, 133.8, 131.5, 129.9, 128.1, 127.3, 126.3, 124.0, 123.8, 122.6, 121.2, 111.0, 106.8, 61.0, 46.0, 29.7, 23.9, 23.2, 14.1; IR (neat): 3038, 2919, 2851, 1730, 1494, 1416, 1186, 1150, 1021, 758 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}NO_2$ 319.1572, found 319.1573.

Ethyl 10-methoxy-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4c). 80% yield (80.7 mg), white solid, mp 120-121 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 9.2 Hz, 1H), 7.09 (td, J_1 = 0.8 Hz, J_2 = 7.2 Hz, 1H), 6.86 (dd, J_1 = 2.4 Hz, J_2 = 9.2 Hz, 1H), 4.13-4.00 (m, 2H), 3.94 (t, J = 5.8 Hz, 1H), 3.90 (s,

3H), 3.67 (s, 3H), 3.44 (dd, J_1 = 5.6 Hz, J_2 = 16.0 Hz, 1H), 3.05 (dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 137.6, 136.8, 133.6, 130.0, 128.8, 127.9, 125.2, 124.3, 124.0, 122.4, 121.2, 120.3, 117.5, 109.2, 61.1, 45.3, 32.7, 23.5, 20.5, 14.0; IR (neat): 2976, 2926, 2826, 1728, 1505, 1479, 1234, 1168, 1031, 757 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1516.

Ethyl 10-chloro-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4d). 93% yield (94.8 mg), white solid, mp 146-148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 1.6 Hz, 1H), 7.75 (d, J = 6.8 Hz, 1H), 7.35 (td, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.15-7.10 (m, 2H), 4.12-4.00 (m, 2H), 3.96 (t, J = 5.8 Hz, 1H), 3.70 (s, 3H), 3.45 (dd, J_1 = 5.2 Hz, J_2 = 16.0 Hz, 1H), 3.07 (dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 138.4, 136.2, 132.9, 129.7, 129.1, 128.0, 125.9, 125.0, 124.4, 122.2, 121.0, 118.8, 110.2, 108.8, 61.1, 45.0, 29.5, 23.2, 14.0; IR (neat): 2976, 2918, 2847, 1729, 1503, 1471, 1288, 1181, 1084, 1035, 757 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}{}^{35}ClNO_2$ 339.1026, found 339.1029.

Ethyl 9-chloro-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4e). 84% yield (85.8 mg), white solid, mp 155-156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.34-7.27 (m, 3H), 7.14-7.08 (m, 2H), 4.12-4.00 (m, 2H), 3.94 (t, J = 5.6 Hz, 1H), 3.65 (s, 3H), 3.43 (dd, J_1 = 5.2 Hz, J_2 = 16.0 Hz, 1H), 3.04 (dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 138.4, 137.7, 133.0, 129.9, 129.1, 128.0, 126.9,

124.5, 122.8, 122.3, 120.7, 120.1, 109.5, 109.3, 61.1, 45.1, 29.5, 23.2, 14.0; IR (neat): 2976, 2918, 2847, 1728, 1498, 1471, 1202, 951, 798, 740 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}{}^{35}ClNO_2$ 339.1026, found 339.1023.

Ethyl 7,8-dimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4f). 90% yield (86.2 mg), white solid, mp 137-139 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 6.8 Hz, 1H), 4.12-4.00 (m, 2H), 3.94 (s, 3H), 3.92 (t, J = 6.0 Hz, 1H), 3.42 (dd, J_1 = 5.6 Hz, J_2 = 16.0 Hz, 1H), 2.99 (dd, J_1 = 6.4 Hz, J_2 = 15.6 Hz, 1H), 2.75 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 154.7, 137.7, 133.7, 133.2, 129.8, 129.0, 128.0, 124.6, 123.9, 122.0, 110.4, 109.9, 108.8, 102.3, 61.1, 56.0, 45.3, 29.5, 23.4, 14.1; IR (neat): 3042, 2976, 2922, 2851, 1729, 1600, 1504, 1459, 1181, 1032, 779, 741 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}NO_2$ 319.1572, found 319.1573.

Ethyl 7-phenyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4g). 93% yield (102.5 mg), oil; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.45-7.36 (m, 4H), 7.32 (d, J = 7.6 Hz, 1H), 7.28-7.12 (m, 4H), 4.11-3.99 (m, 2H), 3.90 (t, J = 5.2 Hz, 1H), 3.38 (dd, J_1 = 5.2 Hz, J_2 = 16.0 Hz, 1H), 3.00 (dd, J_1 = 6.4 Hz, J_2 = 16.4 Hz, 1H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 138.3, 136.9, 133.4, 130.6, 129.6, 129.1, 128.0, 127.8, 127.4, 127.4, 124.6, 124.5, 122.7, 121.7, 121.0, 119.4, 110.6, 110.5, 61.0, 45.4, 23.9, 14.0; IR (neat): 3054, 2976, 2926, 2847, 1728, 1596, 1498, 1454, 1197, 1026, 765, 748 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{21}NO_2$ 367.1572, found 367.1575.

7-tert-Butyl 5-ethyl 5H-benzo[c]carbazole-5,7(6H)-dicarboxylate (4h). 94% yield (110.4 mg), oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (t, J = 3.8 Hz, 1H), 7.99 (d, J = 3.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.39-7.30 (m, 4H), 7.21 (t, J = 7.2 Hz, 1H), 4.08 (q, J = 6.8 Hz, 2H), 4.03-3.97 (m, 2H), 3.40 (dd, J_1 = 8.4 Hz, J_2 = 20.0 Hz, 1H), 1.70 (s, 9H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 150.2, 136.7, 136.1, 131.8, 131.3, 128.7, 127.8, 126.4, 125.9, 123.6, 123.3, 123.1, 119.4, 115.7, 115.5, 84.2, 61.0, 45.3, 28.2, 25.9, 14.0; IR (neat): 3052, 2976, 2930, 1753, 1454, 1359, 1301, 1152, 1121, 769, 744 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{25}NO_4$ 391.1784, found 391.1782.

1-(7-Methyl-6,7-dihydro-5H-benzo[c]carbazol-5-yl)ethan-1-one (4i). 71% yield (58.7 mg), white solid, mp 118-120 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99-7.97 (m, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.40-7.32 (m, 3H), 7.23-7.19 (m, 2H), 7.14 (t, J = 7.2 Hz, 1H), 3.75-3.73 (m, 4H), 3.60 (dd, J_1 = 2.0 Hz, J_2 = 15.6 Hz, 1H), 3.01 (dd, J_1 = 6.8 Hz, J_2 = 16.0 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.7, 138.1, 137.8, 134.0, 130.6, 129.8, 128.3, 124.2, 124.2, 122.6, 121.0, 120.3, 119.3, 109.4, 108.8, 53.1, 29.5, 28.4, 22.2; IR (neat): 3042, 2918, 2847, 1705, 1599, 1498, 1471, 1163, 766, 748 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NO$ 275.1310, found 275.1309.

7-Methyl-5-phenyl-6,7-dihydro-5H-benzo[c]carbazole (4j). 87% yield (80.5 mg), white solid, mp 209-210 ^{o}C; ^{1}H NMR (C_6D_6, 400 MHz): δ 8.20 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.34-7.25 (m, 3H), 7.14-6.98 (m, 8H), 4.12 (t, J = 8.0 Hz, 1H), 2.73 (d, J = 2.4 Hz, 1H), 2.71 (d, J = 1.2 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 144.8, 138.4, 137.4, 135.9, 134.8, 128.9, 128.8, 127.9, 127.7,

127.0, 125.2, 124.6, 122.8, 121.3, 120.8, 120.2, 110.3, 109.7, 46.1, 29.4, 28.5; IR (neat): 3041, 2913, 2847, 1597, 1494, 1450, 1138, 1081, 745 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{19}N$ 309.1517, found 309.1516.

Ethyl 2,3,7-trimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4k). 77% yield (77.4 mg), white solid, mp 137-138 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.01 (q, J = 2.8 Hz, 1H), 7.63 (s, 1H), 7.29 (q, J = 2.8 Hz, 1H), 7.18 (q, J = 2.8 Hz, 2H), 7.06 (s, 1H), 4.12-4.01 (m, 2H), 3.89 (t, J = 5.6 Hz, 1H), 3.67 (s, 3H), 3.42 (dd, J_1 = 5.6 Hz, J_2 = 16.0 Hz, 1H), 3.04 (dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 1.15 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 137.8, 136.5, 135.9, 132.1, 131.2, 130.1, 127.3, 124.3, 123.9, 120.8, 120.0, 119.4, 109.3, 109.1, 60.9, 44.9, 29.3, 23.5, 19.8, 19.5, 14.1; IR (neat): 2921, 2851, 1729, 1510, 1471, 1180, 739 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{23}NO_2$ 333.1729, found 333.1726.

Ethyl 2,3-difluoro-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4l). 73% yield (74.9 mg), white solid, mp 121-123 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.0 Hz, 1H), 7.55 (dd, J_1 = 8.0 Hz, J_2 = 11.6 Hz, 1H), 7.31 (d, J = 6.8 Hz, 1H), 7.24-7.18 (m, 2H), 7.11 (dd, J_1 = 8.0 Hz, J_2 = 10.4 Hz, 1H), 4.11-4.00 (m, 2H), 3.86 (t, J = 5.6 Hz, 1H), 3.69 (s, 3H), 3.47 (dd, J_1 = 4.8 Hz, J_2 = 16.4 Hz, 1H), 3.03 (dd, J_1 = 6.8 Hz, J_2 = 16.0 Hz, 1H), 1.14 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 151.3, 151.1, 148.8, 148.7, 148.0, 147.9, 145.6, 145.5, 137.8, 137.0, 130.7, 130.7, 130.6, 130.6, 126.0, 126.0, 126.0, 125.9, 123.8, 121.4, 120.6, 118.8, 118.2, 118.1, 110.9, 110.7, 109.6, 107.8, 61.4, 44.5, 29.4, 23.1, 14.0; IR (neat): 3042, 2913, 2851, 1731, 1608, 1514, 1472, 1383, 1180, 802, 740 cm^{-1}; HRMS (EI) calcd for

$C_{20}H_{17}F_2NO_2$ 341.1227, found 341.1229.

Ethyl 4,7-dimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4ma). 72% yield (69.0 mg), white solid, mp 95-96 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.01-7.99 (m, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.34-7.32 (m, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.23-7.17 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 4.16 (d, J = 6.4 Hz, 1H), 4.06-3.82 (m, 2H), 3.75 (s, 3H), 3.62 (dd, J_1 = 1.6 Hz, J_2 = 16.0 Hz, 1H), 3.03 (dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 2.44 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 137.9, 137.2, 136.8, 133.7, 128.8, 127.6, 126.6, 124.5, 120.9, 120.6, 120.1, 119.5, 109.7, 109.3, 61.0, 40.9, 29.4, 23.2, 20.4, 13.9; IR (neat): 3046, 2976, 2930, 1723, 1588, 1552, 1472, 1410, 1372, 1200, 1178, 784, 740 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}NO_2$ 319.1572, found 319.1573.

Ethyl 1,7-dimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate & ethyl 4,7-dimethyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4ma & 4mb). 91% yield (87.2 mg), oil; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.98 (m, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 0.27H), 7.32-7.08 (m, 5.62H), 6.98 (d, J = 7.6 Hz, 1H), 4.12 (d, J = 6.4 Hz, 1H), 4.04-3.77 (m, 2.81H), 3.75 (s, 0.81H), 3.69 (s, 3H), 3.58 (dd, J_1 = 1.6 Hz, J_2 = 16.0 Hz, 1H), 3.39 (dd, J_1 = 4.4 Hz, J_2 = 15.2 Hz, 0.27H), 3.00-2.94 (m, 1.27H), 2.60 (s, 0.81H), 2.42 (s, 3H), 1.04-0.97 (m, 3.81H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 172.7, 138.9, 137.9, 137.5, 137.2, 136.8, 133.8, 133.7, 133.0, 132.7, 131.0, 128.7, 127.6, 126.6, 126.1, 125.2, 124.5, 124.5, 121.5, 120.8, 120.6, 120.4, 120.1, 119.5, 119.3, 110.0, 109.6, 109.3, 109.1, 60.9, 60.8, 47.0, 40.8, 29.6, 29.4, 23.1, 23.1, 22.5, 20.3, 14.1, 13.9.

Ethyl 4-(tert-butyl)-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4n). 69% yield (74.7 mg), white solid, mp 77-78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05-7.98 (m, 2H), 7.96-7.90 (m, 1H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 2H), 4.69-4.61 (m, 1H), 3.96-3.81 (m, 2H), 3.73 (s, 3H), 3.68-3.61 (m, 1H), 3.07-2.97 (m, 1H), 1.26 (s, 9H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 149.7, 137.9, 137.5, 137.4, 127.9, 125.5, 124.3, 124.0, 122.0, 121.3, 120.5, 119.5, 109.8, 109.4, 61.0, 43.4, 35.7, 31.7, 29.7, 24.4, 13.9; IR (neat): 3039, 2978, 1698, 1574, 1409, 1385, 1193, 1086, 757 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{27}NO_2$ 361.2042, found 361.2045.

Ethyl 4-methoxy-7-methyl-6,7-dihydro-5H-benzo[c]carbazole-5-carboxylate (4o). 83% yield (83.5 mg), white solid, mp 106-107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01-7.99 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.35-7.31 (m, 2H), 7.22-7.18 (m, 2H), 6.74 (d, J = 8.0 Hz, 1H), 4.47 (dd, J_1 = 2.0 Hz, J_2 = 7.2 Hz, 1H), 4.06-3.86 (m, 5H), 3.73 (s, 3H), 3.61 (dd, J_1 = 2.0 Hz, J_2 = 16.0 Hz, 1H), 3.02 (dd, J_1 = 7.2 Hz, J_2 = 16.0 Hz, 1H), 1.05 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 157.3, 137.8, 137.3, 134.8, 128.6, 124.5, 120.9, 120.1, 119.5, 118.2, 115.5, 109.4, 109.3, 107.2, 60.8, 55.6, 37.5, 29.4, 23.1, 13.9; IR (neat): 3042, 2926, 2851, 1717, 1600, 1545, 1472, 1259, 1180, 1066, 744 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1522.

The procedure for the synthesis of 5a. Under the oxygen atmosphere, **4a** (0.3 mmol) and Cs_2CO_3 (107.5 mg, 0.33 mmol) were added to a 25 mL Schlenk tube equipped with a stir bar. Then 0.6 mL of MeCN and 2.4 mL of toluene were added.

The reaction mixture was stirred at 100 °C. When the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short column of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the residue, which was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford ethyl 7-methyl-7*H*-benzo[*c*]carbazole-5-carboxylate (**5a**, 89.2 mg, 98% yield). Yellow solid, mp 92-93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.04 (d, J = 8.4 Hz, 1H), 8.82 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.32 (s, 1H), 7.74-7.69 (m, 1H), 7.58-7.50 (m, 3H), 7.40-7.36 (m, 1H), 4.55 (q, J = 7.6 Hz, 2H), 3.95 (s, 3H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 140.9, 136.3, 130.2, 127.0, 126.8, 126.6, 125.6, 125.4, 124.0, 123.4, 122.7, 122.6, 120.1, 118.3, 114.9, 109.3, 61.2, 29.2, 14.5; IR (neat): 3428, 2926, 2511, 2142, 1798, 1701, 1476, 1338, 1032, 777, 748, 735, 685 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{17}NO_2$ 303.1259, found 303.1263.

General Procedure for the Synthesis of Products 5. Under the oxygen atmosphere, 2-alkenylindole **1** (0.3 mmol), CsF (136.7 mg, 0.9 mmol) and Cs_2CO_3 (107.5 mg, 0.33 mmol) were added to a 25 mL Schlenk tube equipped with a stir bar. Then 0.6 mL of MeCN, 2.4 mL of toluene and aryne precursor **2** (0.45 mmol) were added. The reaction mixture was stirred at 100 °C. When the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short column of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the residue, which was purified by silica gel chromatography (petroleum ether/ethyl acetate 20:1) to afford **5b-l**.

Ethyl 10-methoxy-7-methyl-7H-benzo[c]carbazole-5-carboxylate (5b). 85% yield (85.0 mg), yellow solid, mp 109-110 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.00 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.77 (d, J = 2.4 Hz, 1H), 7.63 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.08 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 4.51 (q, J = 7.6 Hz, 2H), 3.93 (s, 3H), 3.65 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 154.0, 136.4, 136.0, 130.1, 126.9, 126.5, 126.2, 125.0, 123.6, 123.0, 122.4, 117.6, 115.0, 114.8, 109.7, 104.8, 61.0, 55.9, 28.9, 14.4; IR (neat): 3415, 2936, 2839, 1720, 1490, 1320, 1262, 1182, 1151, 1033, 815, 748 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{19}NO_3$ 333.1365, found 333.1369.

Ethyl 10-chloro-7-methyl-7H-benzo[c]carbazole-5-carboxylate (5c). 91% yield (92.2 mg), yellow solid, mp 137-138 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 1.6 Hz, 1H), 7.97 (s, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.34 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 4.52 (q, J = 7.6 Hz, 2H), 3.64 (s, 3H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 138.9, 136.6, 129.7, 127.0, 126.9, 126.4, 126.1, 125.4, 125.2, 124.2, 123.1, 123.0, 121.8, 117.0, 114.6, 110.0, 61.2, 29.1, 14.5; IR (neat): 2918, 2507, 1794, 1705, 1557, 1477, 1288, 1234, 1182, 1149, 1035, 773 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}{}^{35}ClNO_2$ 337.0870, found 337.0872.

Ethyl 10-bromo-7-methyl-7H-benzo[c]carbazole-5-carboxylate (5d). 72% yield (82.6 mg), yellow solid, mp 150-151 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.97 (d, J = 8.4 Hz, 1H), 8.55-8.52 (m, 2H), 8.12 (s, 1H), 7.70-7.65 (m, 1H), 7.57-7.51 (m, 2H),

7.25 (d, J = 3.2 Hz, 1H), 4.54 (q, J = 7.6 Hz, 2H), 3.79 (s, 3H), 1.53 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 139.3, 136.6, 129.8, 127.9, 127.1, 127.0, 126.5, 126.4, 125.0, 124.3, 123.9, 123.1, 117.1, 114.6, 113.0, 110.6, 61.3, 29.2, 14.5; IR (neat): 2976, 2926, 1709, 1476, 1287, 1236, 1181, 1150, 1033, 777 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}{}^{79}BrNO_2$ 381.0364, found 381.0365.

Ethyl 9-chloro-7-methyl-7H-benzo[c]carbazole-5-carboxylate (5e). 86% yield (87.5 mg), yellow solid, mp 137-138 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95 (d, J = 8.8 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 7.58 (td, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.50 (td, J_1 = 1.2 Hz, J_2 = 6.8 Hz, 1H), 7.20 (d, J = 1.6 Hz, 1H), 7.14 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 4.52 (q, J = 7.2 Hz, 2H), 3.57 (s, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 141.0, 136.2, 131.0, 129.5, 126.9, 126.7, 126.5, 125.5, 124.1, 123.0, 123.0, 120.7, 120.2, 117.5, 114.4, 109.0, 61.1, 28.8, 14.4; IR (neat): 2934, 2893, 2511, 1702, 1614, 1555, 1477, 1384, 1238, 1149, 1037, 943, 740 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}{}^{35}ClNO_2$ 337.0870, found 337.0873.

Ethyl 7,8-dimethyl-7H-benzo[c]carbazole-5-carboxylate (5f). 92% yield (87.5 mg), yellow solid, mp 126-127 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.02 (d, J = 8.8 Hz, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 7.2 Hz, 1H), 4.50 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 2.69 (s, 3H), 1.49 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 139.6, 136.6, 129.9, 128.3, 126.9, 126.6, 126.5, 125.0, 123.8, 123.3, 123.2, 121.0, 120.6, 120.0, 118.0, 114.9, 61.0, 32.1, 20.6, 14.5; IR (neat):

2852, 2517, 1699, 1558, 1464, 1379, 1227, 1184, 1039, 781, 748 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{19}NO_2$ 317.1416, found 317.1419.

Ethyl 7-phenyl-7H-benzo[c]carbazole-5-carboxylate (5g). 91% yield (99.9 mg), yellow solid, mp 114-115 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.00 (d, J = 8.4 Hz, 1H), 8.91 (d, J = 8.4 Hz, 1H), 8.67 (d, J = 7.2 Hz, 1H), 8.22 (s, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.66-7.40 (m, 9H), 4.46 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 141.3, 136.8, 136.7, 130.3, 130.0, 128.2, 127.8, 127.1, 127.1, 127.0, 126.5, 125.7, 124.4, 123.7, 123.1, 122.7, 121.0, 118.9, 115.8, 110.7, 61.2, 14.4; IR (neat): 3417, 2980, 2897, 1720, 1598, 1504, 1463, 1381, 1288, 1219, 1043, 779, 736 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{19}NO_2$ 365.1416, found 365.1416.

1-(7-Methyl-7H-benzo[c]carbazol-5-yl)ethanone (5h). 89% yield (73.1 mg), yellow solid, mp 179-181 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.77 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.68 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.55-7.49 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.36 (t, = 8.0 Hz, 1H), 3.83 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 140.9, 136.0, 134.2, 130.2, 127.1, 127.0, 125.5, 125.3, 124.3, 123.3, 122.6, 122.5, 120.1, 117.9, 113.2, 109.3, 30.3, 29.1; IR (neat): 3407, 3046, 2930, 2519, 1659, 1615, 1558, 1476, 1384, 1339, 1235, 1015, 746 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1155.

Ethyl 2,3-difluoro-7-methyl-7H-benzo[c]carbazole-5-carboxylate (5i). 81% yield (82.6 mg), yellow solid, mp 164-165 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.84 (dd, J_1 = 8.8 Hz, J_2 = 14.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.06-8.01 (m, 2H), 7.50

(t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 4.49 (q, J = 7.2 Hz, 2H), 3.73 (s, 3H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 151.2, 151.1, 149.3, 149.1, 148.7, 148.6, 146.8, 146.7, 140.8, 135.9, 135.9, 126.8, 126.8, 126.7, 126.7, 125.8, 123.6, 123.6, 123.5, 123.5, 123.4, 123.3, 123.3, 123.3, 121.9, 121.6, 120.2, 117.7, 117.7, 117.6, 117.6, 115.2, 115.1, 114.1, 113.9, 109.4, 109.3, 109.3, 61.3, 29.0, 14.4; IR (neat): 3415, 3067, 2922, 2843, 1694, 1566, 1538, 1475, 1246, 1114, 873, 732 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{15}F_2NO_2$ 339.1071, found 339.1075.

7-tert-Butyl 5-ethyl 7H-benzo[c]carbazole-5,7-dicarboxylate (5ja). 76% yield (88.9 mg), yellow solid, mp 80-83 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24 (s, 1H), 9.06 (d, J = 8.4 Hz, 1H), 8.79 (d, J = 8.4 Hz, 1H), 8.52 (t, J = 6.8 Hz, 2H), 7.69 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 4.52 (q, J = 7.2 Hz, 2H), 1.82 (s, 9H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 150.6, 139.2, 134.7, 129.2, 128.4, 127.0, 127.0, 126.8, 126.4, 125.7, 125.4, 123.8, 123.6, 122.5, 122.2, 120.4, 116.4, 84.7, 61.2, 28.3, 14.4; IR (neat): 2926, 2511, 1735, 1699, 1557, 1453, 1127, 1049, 997, 781, 678 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{23}NO_4$ 389.1627, found 389.1633.

7-tert-butyl 5-ethyl 10-chloro-7H-benzo[c]carbazole-5,7-dicarboxylate (5ka). 58% yield (73.9 mg), yellow solid, mp 146-147 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17 (s, 1H), 9.03 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.46-8.42 (m, 2H), 7.71 (dt, J_1 = 1.2, J_2 = 8.0 Hz, 1H), 7.63 (dt, J_1 = 1.2, J_2 = 8.0 Hz, 1H), 7.49 (dd, J_1 =2.0, J_2 = 8.4 Hz, 1H), 4.53 (q, J = 7.2 Hz, 2H), 1.82 (s, 9H), 1.50 (t, J = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 150.3, 137.5, 135.2, 129.1, 128.9, 128.3, 127.3, 127.2, 126.9, 126.9, 126.5, 125.9, 123.5, 122.0, 121.0, 120.2, 117.4, 85.1, 61.3, 28.3, 14.4; IR (neat): 2963, 1734, 1631, 1464, 1317, 1220, 1135, 1083, 806 cm^{-1}; HRMS calcd for $C_{24}H_{23}{}^{35}ClNO_4$ $[M+H]^+$: 424.1316, found 424.1317.

7-tert-butyl 5-ethyl 10-bromo-7H-benzo[c]carbazole-5,7-dicarboxylate (5la). 76% yield (106.6 mg), yellow solid, mp 170-171 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.13 (s, 1H), 9.01 (d, J = 8.8 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 1.2 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 7.2 Hz, 1H), 7.63-7.59 (m,21H), 4.52 (q, J = 7.2 Hz, 2H), 1.82 (s, 9H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 150.2, 137.8, 135.0, 129.6, 128.9, 128.3, 127.3, 127.2, 126.9, 126.9, 125.9, 125.0, 123.4, 120.9, 120.2, 117.8, 116.8, 85.1, 61.3, 28.3, 14.4; IR (neat): 2971, 1739, 1706, 1631, 1457, 1320, 1219, 1134, 781cm^{-1}; HRMS calcd for $C_{24}H_{23}BrNO_4$ $[M+H]^+$: 468.0810, found 468.0815.

General Procedure for the Synthesis of Products 6. Compound **5ja**, **5ka** or **5la** (0.2 mmol) was dissolved in 2 mL CH_2Cl_2 in a 25 mL round flask in the open air. Then, CF_3COOH (1.0 mmol) was dropped at 0 ^{o}C. After The reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the mixture was then diluted with dichloromethane (10 mL) and quenched by saturated $NaHCO_3$ (aq) carefully. The organic layer was separated. The water layer was extracted with dichloromethane (2 × 10 mL). The organic layers were combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford **6a-c**.

Ethyl 7H-benzo[c]carbazole-5-carboxylate (6a). 99% yield (57.3 mg), yellow solid, mp 134-135 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.07 (d, J = 8.4 Hz, 1H), 8.84 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 7.6 Hz, 2H), 8.35 (d, J = 3.2 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.61-7.57 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 4.53 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 139.6, 135.1, 130.3, 127.0, 127.0, 126.9, 125.9, 125.6, 124.4, 123.6, 123.3, 122.7, 120.6, 119.1, 117.1, 111.5, 61.2, 14.4; IR (neat): 3319, 2980, 2922, 1683, 1620, 1468, 1369, 1223, 1030, 779, 696, 612 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1104.

Ethyl 10-chloro-7H-benzo[c]carbazole-5-carboxylate (6b). 99% yield (64.1 mg), yellow solid, mp 204-205 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.17 (s, 1H), 8.89-8.84 (m, 2H), 8.69 (d, J = 1.6 Hz, 1H), 8.38 (s, 1H), 7.77-7.72 (m, 2H), 7.61-7.59 (m, 1H), 7.53 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, 1H), 4.46 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.6 Hz, 3H); ^{13}C NMR (DMSO-d_6,100 MHz): δ 167.1, 138.2, 136.2, 129.5, 127.4, 126.5, 126.1, 125.8, 125.4, 124.6, 124.2, 123.6, 123.1, 121.5, 117.4, 116.6, 113.6, 61.0, 14.2; IR (neat): 3298, 1676, 1482, 1259, 1224, 1055, 804, 750 cm^{-1}; HRMS calcd for $C_{19}H_{15}{}^{35}ClNO_2$ $[M+H]^+$: 324.0791, found 324.0787.

Ethyl 10-bromo-7H-benzo[c]carbazole-5-carboxylate (6c). 99% yield (72.9 mg), yellow solid, mp 186-187 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.18 (s, 1H), 8.89-8.81 (m, 3H), 8.38 (s, 1H), 7.79-7.74 (m, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.64-7.57 (m, 2H), 4.46 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.6 Hz, 3H); ^{13}C NMR (DMSO-d_6,100 MHz): δ 167.0, 138.5, 136.0, 129.4, 127.9, 127.4, 126.5, 126.1,

125.8, 124.3, 124.3, 123.8, 123.6, 117.4, 116.5, 114.0, 112.4, 61.0, 14.2; IR (neat): 3303, 2959, 1676, 1618, 1479, 1400, 1224, 1047, 776 cm^{-1}; HRMS calcd for $C_{19}H_{15}{}^{79}BrNO_2$ $[M+H]^+$: 368.0286, found 368.0283.

General Procedure for the Synthesis of Products 7. Compound **6a** (191 mg, 0.6 mmol) was dissolved in 2 mL of ethanol, 3 M NaOH (1 ml) was added slowly to the mixture followed by heating to reflux for 2 h. The dilute hydrochloric acid was added dropwisely until the pH < 7. The water layer was then extracted by CH_2Cl_2 (5 mL × 3). The organic layer was combined and dried over Na_2SO_4. The solvent was removed under reduced pressure give the crude product without other purification. The above compound (78.4 mg, 0.3 mmol) was dissolved in 5 mL of anhydrous tetrahydrofuran (THF) then one drop of anhydrous *N*,*N*-dimethyl methanamide (DMF) was added. The mixture was cooled to 0 ^oC followed by adding 15 drops of oxalyl chloride then the mixture was warmed to room temperature and stirred for 30 min. The solvent was removed under reduced pressure to give acyl chloride as light yellow solid which was used directly without any purification. The freshly prepared acyl chloride was dissolved in 5 mL of anhydrous THF, *N*,*N*-dimethyl ethylenediamine (66.1 mg) was added drop wisely then the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure, and the residue was poured onto ice water, the solid was precipitated, filtrated, and dried over vacuum. Then the residue was purified by silica gel chromatography (petroleum ether/dichloromethane/ammonium hydroxide 100:10:1) to give **7a-e** as white solid.

N-(2-(Dimethylamino)ethyl)-7H-benzo[c]carbazole-5-carboxamide (7a). 86%

yield (85.3 mg), white solid, mp 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.33 (s, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.67 (s, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.35-7.23 (m, 3H), 6.24 (s, 1H), 3.41-3.36 (m, 2H), 2.42 (t, J = 6.0 Hz, 2H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 139.2, 135.5, 132.6, 130.0, 126.9, 126.3, 125.5, 124.7, 123.4, 123.3, 123.1, 122.0, 120.0, 116.5, 112.7, 111.6, 57.6, 44.7, 37.1; IR (neat): 3247, 2944, 2858, 2824, 2779, 1638, 1528, 1466, 1360, 1250, 909, 749 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{21}N_3O$ 331.1685, found 331.1680.

10-Chloro-N-(2-(dimethylamino)ethyl)-7H-benzo[c]carbazole-5-carboxamide (7b). 81% yield (88.6 mg), white solid, mp 190-191 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.11 (s, 1H), 8.81 (d, J= 6.8 Hz, 1H), 8.66-8.60 (m, 2H), 8.34 (d, J= 8.8 Hz, 1H), 7.82-7.70 (m, 3H), 7.52-7.47 (m, 2H), 3.48 (s, 2H), 2.51 (s, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.8, 137.6, 136.8, 134.9, 129.3, 127.4, 126.9, 125.4, 124.4, 124.3, 123.5, 123.4, 123.2, 121.0, 114.2, 113.3, 112.6, 58.2, 45.3, 37.4; IR (neat): 3411, 3241, 2918, 1612, 1458, 1352, 1285, 1010, 1055, 748 cm^{-1}; HRMS calcd for $C_{21}H_{21}ClN_3O$ $[M+H]^+$: 366.1373, found 366.1379.

10-Bromo-N-(2-(dimethylamino)ethyl)-7H-benzo[c]carbazole-5-carboxamide (7c). 82% yield (100.1 mg), white solid, mp 283 °C (dec.); ^{1}H NMR (400 MHz, CD_3OD): δ 8.58 (d, J= 8.0 Hz, 1H), 8.54 (s, 1H), 8.26 (d, J= 8.4 Hz, 1H), 7.88 (s, 1H), 7.65 (t, J= 8.0 Hz, 1H), 7.44-7.38 (m, 3H), 3.77 (t, J= 6.0 Hz, 2H), 3.34 (t, J= 6.0 Hz, 2H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 137.9, 136.6, 134.7, 129.3, 127.4, 127.0, 126.9, 125.4, 124.2, 123.9, 123.4, 123.3, 114.1, 113.8,

112.7, 112.1, 57.9, 44.9, 37.0; IR (neat): 3234, 2925, 2857, 1638, 1527, 1474, 1350, 1287, 1049, 800, 750 cm^{-1}; HRMS calcd for $C_{21}H_{21}BrN_3O$ $[M+H]^+$: 410.0868, found 410.0862.

N-(3-(Dimethylamino)propyl)-7H-benzo[c]carbazole-5-carboxamide (7d). 76% yield (78.9 mg), white solid, mp 186-187 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.83 (d, J = 8.0 Hz, 1H), 8.70-8.67 (m, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.76-7.68 (m, 2H), 7.52-7.44 (m, 2H), 7.36-7.31 (m, 1H), 3.43-3.38 (m, 2H), 2.37-2.33 (m, 2H), 2.18 (s, 6H), 1.79-1.72 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.0, 139.2, 135.9, 134.0, 129.6, 127.0, 126.8, 125.4, 124.5, 123.3, 123.0, 122.6, 121.9, 119.8, 114.9, 112.7, 111.8, 56.9, 45.3, 37.6, 27.2; IR (neat): 3399, 3253, 2913, 1610, 1358, 1261, 1103, 881, 764, 749 cm^{-1}; HRMS calcd for $C_{22}H_{24}N_3O$ $[M+H]^+$: 346.1919, found 346.1919.

N-(2-(Piperidin-1-yl)ethyl)-7H-benzo[c]carbazole-5-carboxamide (7e). 72% yield (80.2mg), white solid, mp 206-207 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.83 (d, J = 7.6 Hz, 1H), 8.61 (d, J = 7.2 Hz, 1H), 8.54 (s, 1H), 8.42 (d, J = 7.6 Hz, 1H), 7.81 (s, 1H), 7.74-7.67 (m, 2H), 7.49-7.46 (m, 2H), 7.36-7.33 (m, 1H), 3.50-3.49 (m, 2H), 2.54-2.44 (m, 6H), 1.55 (s, 4H), 1.42 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 139.2, 136.0, 134.2, 129.5, 127.1, 127.0, 125.4, 124.5, 123.1, 122.9, 122.6, 121.9, 119.8, 114.8, 112.6, 111.8, 57.7, 54.1, 36.8, 25.7, 24.1; IR (neat): 3270, 2927, 2854, 1670, 1458, 1275, 1261, 1091, 764, 750 cm^{-1}; HRMS calcd for $C_{24}H_{26}N_3O$ $[M+H]^+$: 372.2076, found 372.2074.

Supporting Information

The copies of ^{1}H NMR and ^{13}C NMR spectra for products **1** and **3-7**, the copies of 2D ^{1}H-^{1}H NOESY Spectra of **3g**, **4ma** and **4n**, the X-ray crystallographic data of **4o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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