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Relay Catalysis of Bismuth Trichloride and Byproduct Hydrogen Bromide Enables the Synthesis of Carbazole and Benzo[α]carbazoles from Indoles and α-Bromoacetaldehyde Acetals

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Abstract. Benzo[α]carbazoles were synthesized from 2-phenylindoles and α-bromoacetaldehyde using bismuth trichloride as a catalyst. The reaction was triggered by a bismuth trichloride-catalyzed Friedel–Crafts alkylation of these two precursors, which provided a tryptaldehyde intermediate that underwent intramolecular olefination to form the final product. Interestingly, the HBr byproduct generated in the upstream step of the reaction catalyzed the following downstream reaction steps, thus creating a byproduct-participated relay catalytic process. Motivated by this mechanism, we developed a three-component reaction of indole, α-bromoacetaldehyde acetal, and 1,3-dicarbonyl compounds. This study offers a straightforward method for synthesizing substituted carbazoles.

Keywords: Relay catalysis; Waste-mediated reaction; Carbazole; Benzo[α]carbazole; Acid catalysis

Introduction

Realization of simple and green synthetic procedures is an important goal in organic synthesis.[1] To combat the tedious operational procedure associated with multistep organic synthesis, synthetic chemists often use one-pot tandem reactions. In this context, some new catalysis concepts, such as single-catalyst-driven auto-tandem catalysis (ATC)[2] and relay catalysis of two distinctive catalysts[3] have emerged as significant means to facilitate studies of tandem reactions. ATC and relay catalysis can shorten reaction steps and minimize material and energy inputs. This also minimizes waste generation.[4] Tangentially, the concept of byproduct-induced (or waste-induced) relay catalysis was recently described.[5] However, this concept generally requires a judicious design of both the reaction and the catalytic systems, and successful examples of this type of catalysis are rare.[6]

Carbazoles and benzo[α]carbazoles are naturally occurring heterocycles. They are important and biologically active pharmaceuticals that are also widely used in the synthesis of optoelectronic materials because of their unique electrical and thermal properties.[7] Although there are many methods to prepare these privileged molecules and their derivatives,[8] current efforts focus on efficient synthetic methods using readily available chemicals under user-friendly conditions. In continuation of our research on aldo-X bifunctional building blocks in organic synthesis,[9, 10] we identified the α-haloacetaldehyde as an important reactant because it is readily available and inexpensive. In α-bromoacetaldehyde, for example, the presence of a carbonyl group and a bromo substituent makes this compound a 1,2-biselectrophile. Therefore, it has been widely used in organic synthesis.[11]

Here, we report for the first time the acid-catalyzed synthesis of benzo[α]carbazoles and carbazoles with α-bromoacetaldehyde acetals and indoles as substrates. The tryptaldehyde is formed in situ via Friedel–Crafts alkylation of α-bromoacetaldehyde acetal with indoles, but it is unstable in air. This is critical to selective synthesis reactions. The concomitantly formed byproduct hydrogen bromide generated in the first step of the reaction played an intriguing role as a catalyst in the second step. This established an interesting system involving byproduct-induced relay catalysis.

Results and Discussion

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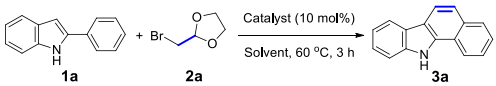
This work used 2-phenylindole **1a** and α-bromoacetaldehyde ethylene acetal **2a**. Initially, the reaction was performed in acetonitrile at 60 °C. Only unreacted starting materials were recovered in the absence of catalyst (**Table 1**, entry 1). Weak acids, such as LiBr and H_3BO_3, cannot initiate this reaction (entries 2 and 3). Then, some strong acids, such as $BF_3{\cdot}Et_2O$, $AlCl_3$, $Sc(OTf)_3$, and *para*-toluenesulfonic acid (PTSA) were examined. Although the expected product **3a** can be obtained, the yields were low (entries 4 to 7). When $Bi(OTf)_3$ was used, the yield of **3a** reached 30% after 3 h (entry 8). Encouraged by this promising result, other commercially available bismuth salts were then examined.

The reaction using $BiCl_3$ as the catalyst proceeded well, and **3a** can be isolated with 60% yield (entry 9). $BiBr_3$ and BiI_3 can also promote this reaction, but the yields were not comparable with those using $BiCl_3$ (entries 10 and 11). The effect of solvent was then investigated. Acetonitrile was the best solvent followed by nitromethane (entries 12 to 15). Notably, a small amount of **1a** remained unreacted after 3 h of heating at 60 °C. We also increased the reaction time, but no further increase in yield was noted (entry 16). However, a slight yield improvement was observed by performing the reaction at 80 °C (entry 17). Thereafter, the reaction was performed at 80 °C.

Table 1. Condition optimization for the reaction between **1a** and **2a**.[a]

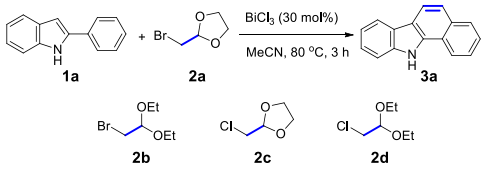


Entry	Catalyst	Solvent	Yield (%)
1	—	MeCN	0
2	LiBr	MeCN	Trace
3	H_3BO_3	MeCN	Trace
4	$BF_3{\cdot}Et_2O$	MeCN	8
5	$AlCl_3$	MeCN	10
6	$Sc(OTf)_3$	MeCN	12
7	PTSA	MeCN	6
8	$Bi(OTf)_3$	MeCN	30
9	$BiCl_3$	MeCN	60
10	$BiBr_3$	MeCN	45
11	BiI_3	MeCN	32
12	$BiCl_3$	$MeNO_2$	42
13	$BiCl_3$	DMSO	8
14	$BiCl_3$	Toluene	12
15	$BiCl_3$	1,4-Dioxane	15
16[b]	$BiCl_3$	MeCN	65
17[c]	$BiCl_3$	MeCN	70

[a] **1a**: 0.3 mmol, **2a:** 0.6 mmol, solvent: 1 mL, catalyst: 0.03 mmol, 60 °C, 3 h.
[b] 6 h.
[c] 80 °C.

Interestingly, the expected product **3a** can be isolated with 86% yield by increasing the amount of $BiCl_3$ to 30 mol% (**Table 2**, entry 1). Here, the ratio of **2a**/**1a** is 2/1. When the ratio decreased to 1/1, the yield dropped to 66% (entry 2). Species **3a** can also be formed when **2a** is replaced by an acyclic acetal **2b**. However, the yield only reached 64% (entry 3). Similarly, acetals of α-chloroacetaldehyde, **2c** and **2d**, can also react with **1a**. However, the yields of **3a** were slightly lower (entries 4 and 5). The results in **Table 2** also indicated higher yields with ethylene acetals than with diethyl acetals. This phenomenon can be explained by the reaction mechanism, which will be discussed in detail later. We also tried to use bromoacetaldehyde to replace acetal **2a**, but the reaction was nonselective, and an inseparable mixture was obtained. This indicated that the use of acetal is necessary for this reaction. The $BiCl_3$-promoted reaction of **1a** and **2a** can also be used for a gram-scale synthesis of **3a** (entry 6).

Table 2. Reactions of **1a** with different acetals.[a]



Entry	Acetal	Yield (%)
1	**2a**	86
2[b]	**2a**	66
3	**2b**	64
4	**2c**	72
5	**2d**	55
6[c]	**2a**	83

[a] **1a**: 0.3 mmol, acetal **2a**-**d**: 0.6 mmol, MeCN: 1 mL, catalyst: 0.09 mmol, 80 °C, 3 h.
[b] **2a**: 0.3 mmol.
[c] 10.0 mmol scale reaction.

With the optimized conditions in hand, we probed the scope of reaction with respect to the 2-arylindole component. **Scheme 1** shows that indoles with an electron-donating group at the C5-position readily participated in the reaction to produce the corresponding benzo[α]carbazoles in high yields (**3b** and **3c**). The existence of weak electron-withdrawing groups, such as fluoro or chloro substituents, in the indole ring showed no significant effect on the reaction yield (**3d** and **3e**). However, those containing strongly electron-withdrawing groups, such as ethyl 2-phenyl-1*H*-indole-5-carboxylate and 5-nitro-2-phenyl-1*H*-indole, failed to participate in the reaction. The reactions with 1-methyl-2-phenylindole and 1-ethyl-2-phenylindole proceeded rapidly under

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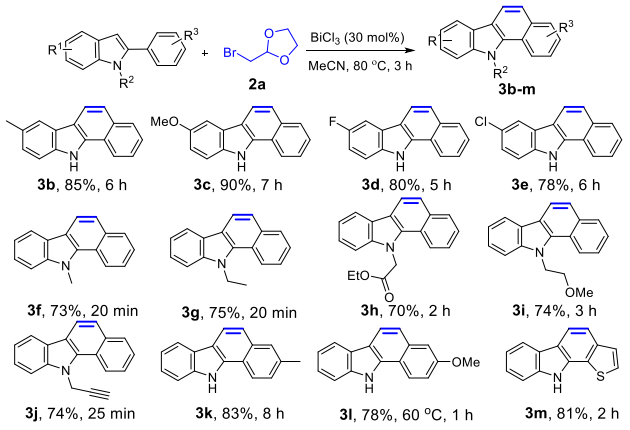
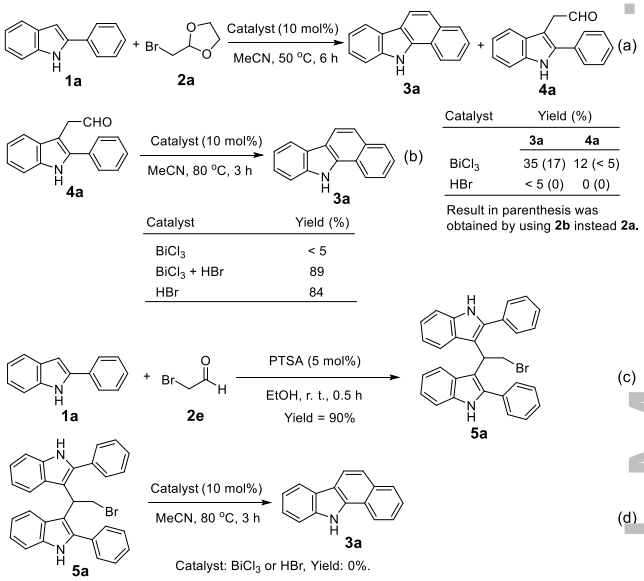
standard conditions, and the expected products formed with more than 70% yield within 20 min (**3f** and **3g**). Ester and ether groups and a C-C triple bond in the indole component can all be delivered into the benzo[α]carbazole products (**3h**, **3i**, and **3j**). The existence of an electron-donating group at the *para*-position of the C2-phenyl ring also favored this transformation (**3k** and **3l**). However, methyl 4-(1*H*-indol-2-yl)benzoate cannot participate in this reaction. Two 2-heteroarylindoles were also used in this reaction. The 2-(thiophen-2-yl)-1*H*-indole can be converted to 10*H*-thieno[2,3-*a*]carbazole in 81% yield via the $BiCl_3$ catalyst (**3m**). However, the reaction of 2-(furan-2-yl)-1*H*-indole and **2a** produced an inseparable mixture, possibly due to the susceptibility of the furan moiety to acids.



Scheme 1. Substrate scope of $BiCl_3$-catalyzed reaction between 2-arylindoles and **2a**.

The benzo[α]carbazoles are important building blocks for the synthesis of optoelectrical materials.[12] Many methods have been developed for synthesis of these compounds including one-pot oxidative condensation of α-tetralone and phenylhydrazine hydrochloride,[13] oxidative dehydrogenation of 1,2,3,4-tetrahydro-11*H*-benzo[α]carbazole with either dichlorodicyanoquinone[14] or oxygen over a palladium-based catalyst,[15] base-catalyzed intramolecular C−C bond formation of diarylamines by $S_{RN}1$ mechanism,[16] and iron- or platinum-catalyzed intramolecular C-H amination (see **Figure S1** in electronic supporting information).[17] However, most of these methods involve the use of expensive reagents or catalysts and also suffer from the lack of simplicity. In some cases, the yields and selectivities are far from satisfactory due to several side reactions. The $BiCl_3$-catalyzed reaction of **1a** and **2a** provides a cost-effective route for synthesis of benzo[α]carbazoles.

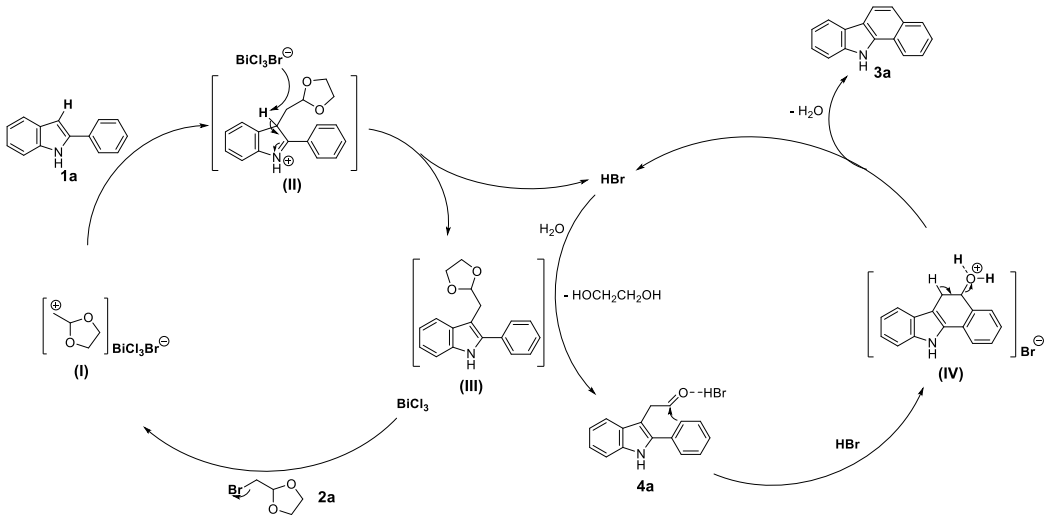
Additional experiments were performed to identify the mechanism of this reaction (**Scheme 2**). Performing the model reaction at 50 °C not only resulted in a yield drop of **3a** but also enabled us to isolate a tryptaldehyde-type product **4a**. Treatment of **4a** in the presence of a $BiCl_3$ catalyst did not produce **3a**. However, most of **4a** decomposed, and it could not be recovered. Interestingly, by adding 10 mol% of hydrogen bromide (an acetic acid solution of HBr, 40 wt%), **4a** can be readily converted to **3a** in acetonitrile. Further studies revealed that hydrogen bromide alone can effectively catalyze the transformation of **4a** to **3a**. However, hydrogen bromide cannot effectively catalyze the Friedel–Crafts-type reaction of **1a** and **2a**. Aldehydes can react with two molecules of indoles via an acid catalyst to form di(indolyl)methanes.[18] In the presence of PTSA, α-bromoacetaldehyde reacted with **1a** in an ethanol solution to yield a di(indolyl)methane derivative **5a**. However, this compound cannot be converted into **3a** via $BiCl_3$ or a HBr catalyst. This observation precluded the possibility of considering **5a** as an intermediate in the mechanism.



Scheme 2. Some control experiments.

A plausible mechanism was proposed based on these data (**Scheme 3**). The first step is the $BiCl_3$-catalyzed Friedel–Crafts alkylation of **2a**. This involved activation of **2a** and the following nucleophilic attack of **1a** to a carbocation intermediate (**I**). Although the bromomethyl and acetal sides are both reactive toward **1a** with a mild Lewis acid, the bismuth trichloride,[19] reaction occurred selectively on the bromomethyl side. This yielded an acetal intermediate (**III**) via the formation reaction of intermediate (**II**). This process simultaneously released one molecule of HBr.

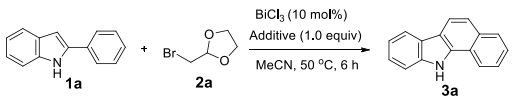
Some water exists in the reaction system because the reagents and solvents are not absolutely dry. Deacetalization of (**III**) under acidic conditions yielded **4a**. Finally, **3a** was formed via HBr-catalyzed intramolecular olefination of **4a**.[20] Although only one catalyst was added in the beginning of the reaction, this process involved relay catalysis of $BiCl_3$ and HBr. The latter is a byproduct of the first reaction. Although such concomitant byproduct-participated relay catalysis has been reported in the literature,[6, 21] this study is the first to establish relay



Scheme 3. Plausible mechanism of the model reaction.

catalysis of two different acid catalysts based on this concept. The high nucleophilicity of 2-phenylindole **1a** is conceivably the key for rendering the model reaction possible, and this enables rapid trapping of carbocation intermediate (**I**). Such trapping forms a tryptaldehyde-type intermediate (**III**). The cyclic acetal **2a** is relatively stable compared with acyclic acetal **2b**. With acetal **2a**, the acetal group can last for a longer time without decomposition. Thus, Friedel–Crafts alkylation of **2a** with **1a** smoothly proceeded via the $BiCl_3$ Lewis acid.

To support this relay catalysis-based mechanism, some hydrogen bromide scavengers, such as betaine, 1,8-bis(dimethylamino)naphthalene (proton sponge), and γ-butyrolactone, were added respectively in the reaction of **1a** and **2a**. Betaine can react with one equivalent of hydrogen bromide to form betaine hydrobromide.[22] Species **3a** was barely formed in the presence of betaine. A similar result was obtained with the proton sponge (**Scheme 4**). Betaine can hamper the acid catalyst, and the reaction was also studied in the presence of betaine hydrobromide. Here, **3a** formed slowly, and the yield reached 11% after 6 h of reaction. The γ-butyrolactone can react with hydrogen bromide to form 4-bromobutyric acid.[23] The presence of γ-butyrolactone imposed a negative effect on the reaction. As a result, the yield of **3a** decreased to 25%. 4-Bromobutyric acid can be detected by GC-MS analysis. These results imply that the concomitant byproduct, hydrogen bromide, ensured the success of synthesizing **3a** from **1a** and **2a**.



Additive	Yield (%)
Betaine	0
Proton sponges	trace
Betaine hydrobromide	11
γ-Butyrolactone	25

Scheme 4. Control experiments with HBr scavengers.

With this understanding of the relay catalysis-based mechanism, we next attempted to develop other tandem reactions of C3-unsubstituted indole and α-bromoacetaldehyde acetals. We primarily searched for a suitable reagent that could trap the generated tryptaldehyde-type intermediate. Tryptaldehyde is a commercially available compound. it is not stable and should be placed in a glovebox under nitrogen to prevent oxidization to acid.[24] The combination of the $BiCl_3$ catalyst and indole/**2a** thus offers an ideal method for generating *in situ* tryptaldehyde. Theoretically, tryptaldehyde possesses two reactive sites: (i) an aldehyde as an electrophilic center; and (ii) the C2 position of the indole ring as a nucleophilic site.[25] To meet this reactivity, a dual nucleophilic and electrophilic bifunctional building block should be used. The 1,3-dicarbonyl compounds may be feasibly used for such purpose because they are easily available and contain both nucleophilic and electrophilic sites.[26] Therefore, a three-component reaction of indole **1b**, **2a**, and ethyl acetoacetate **6a** was investigated. In this reaction, we expected **6a** to trap the generated tryptaldehyde to form a carbazole derivative **7a**.

Table 3 shows that no reaction occurred in the absence of catalyst (entry 1). The reaction over 15 mol% of the $BiCl_3$ catalyst proceeded very well and produced the expected carbazole **7a** in 92% yield (entry 2). By using HBr as the catalyst, **7a** was obtained with 5% yield (entry 3). Under identical conditions, the use of PTSA and $FeCl_3$ resulted in a significant yield drop due to the formation of considerable amounts of inseparable byproducts (entries 4 and 5). The reaction was also affected by the amount of $BiCl_3$ catalyst, ratio of substrate, reaction temperature, and running time (entries 6 to 9). Thus, the reaction conditions indicated in entry 2

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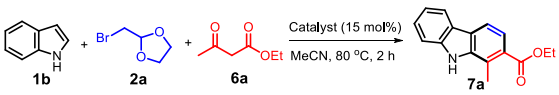
in **Table 3** appeared to be appropriate for this reaction.

When the reaction was performed at 50 °C, tryptaldehyde ethylene acetal **4b′** can be isolated in 8% yield (**Table 3**, entry 8). We therefore speculated that **7a** was formed via a tryptaldehyde-like intermediate. $BiCl_3$ can catalyze the Friedel–Crafts alkylation of an indole derivative and **2a**, thus, we mainly aimed to identify the actual catalyst in the benzoannulation reaction between this intermediate and **6a**. **Scheme 5** shows that $BiCl_3$ and HBr can both catalyze the reaction between tryptaldehyde **4b** and **6a** producing **7a** in 70% and 93% yields, respectively (equation (a)). However, a remarkable difference was observed when an acetal of **4b** was used. While the reaction of **4b′** and **6a** proceeded well via HBr as a catalyst, most of **4b′** remained unchanged with the $BiCl_3$ catalyst (equation (b)). These results imply that HBr played a key role in the deacetalization reaction of **4b′**.

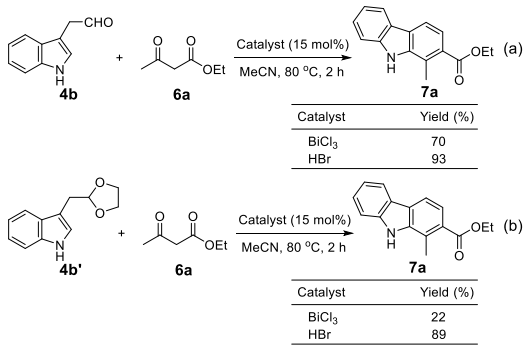
Table 3. Three-component reaction of **1b**, **2a**, and **6a**.[a]



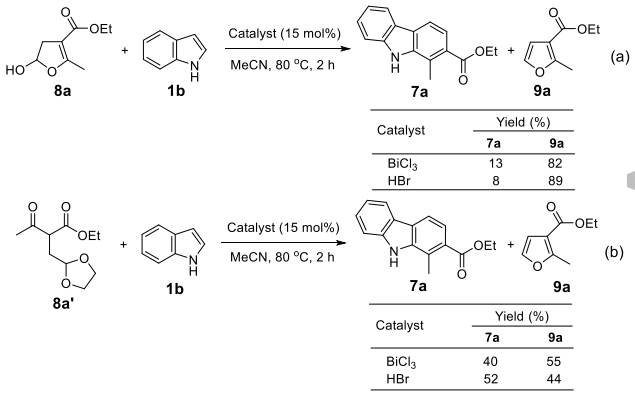
Entry	Catalyst	Yield (%)
1	—	0
2	$BiCl_3$	92
3	HBr (AcOH sol. 40 wt%)	5
4	PTSA	12
5	$FeCl_3$	8
6	$BiCl_3$ (10 mol%)	65
7[b]	$BiCl_3$	56
8[c]	$BiCl_3$	47 (8)[e]
9[d]	$BiCl_3$	69
10[f]	$BiCl_3$	42

[a] **1b**: 0.3 mmol, **2a**: 0.6 mmol, **6a**: 0.6 mmol, MeCN: 1.0 ml, 80 °C 2 h.
[b] Ratio of **1b**/**2a**/**6a**: 1/1/1.
[c] 50 °C.
[d] 1 h.
[e] yield of tryptaldehyde ethylene acetal **4b′**.
[f] γ-Butyrolactone (0.3 mmol) was added.

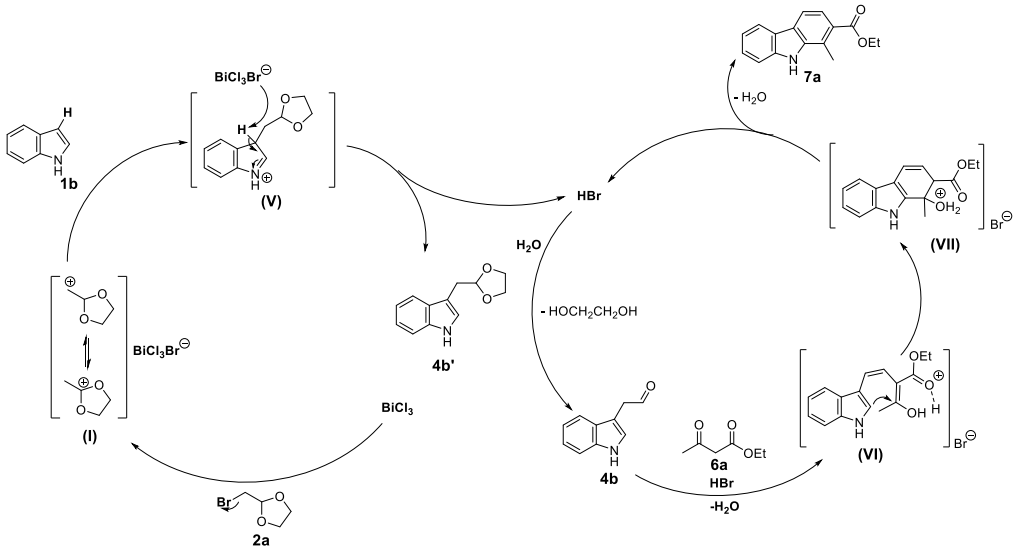
The 1,3-dicarbonyl compound **6a** is also an active nucleophile, and its reaction with **2a** will produce a substituted 1,3-dicarbonyl compound **8a′** (**Scheme 6**). The deacetalization product of this compound theoretically forms a cyclic dihydrofuran **8a**.[27] Although these compounds were barely detected in the reaction mixture, we also investigated the possibility of synthesizing **7a** via the benzoannulation reaction of **1b** and **8a** or **8a′**. As shown in **Scheme 6**, with the aid of either $BiCl_3$ or HBr catalyst, species **8a** and **8a′** can react with **1b** to yield **7a**. Impressively, in all these cases, formation of by-product **9a** is obvious. However, no **9a** can be detected in the reaction mixture of a $BiCl_3$-catalyzed three-component reaction of **1b**, **2a**, and **6a**. These results imply that proposing **8a** or **8a′** as the reaction intermediate might be inappropriate. The reaction should likely proceed via a mechanism involving tryptaldehyde and its acetal as intermediates. Therefore, this reaction is also mechanistically an example of byproduct HBr-participated relay catalysis. In the beginning of the reaction, Friedel–Crafts alkylation of **1b** and **2a** occurred via the $BiCl_3$ catalyst through the formation of an intermediate (**V**) (**Scheme 7**). This generated **4b′** as the reaction product and HBr as the byproduct. The HBr catalyzed deacetalization of **4b′**, affording **4b**. Finally, **7a** was generated through benzoannulation of **4b** and **6a**. Catalysis of HBr played a key role in the last two steps of the reaction. To obtain an indirect proof of the catalytic effect of HBr, one equivalent of γ-butyrolactone was added to the reaction system. In this case, the yield of **7a** dropped to 42% (**Table 3**, entry 10). The 4-bromobutyric acid can be detected by GC-MS analysis. This result verified that partial removal of hydrogen bromide has a detrimental effect on the reaction.



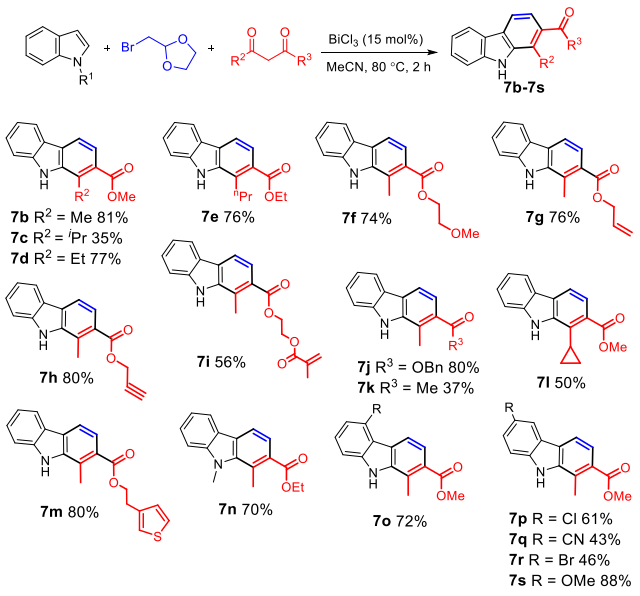
Scheme 5. Reaction of **4b**-type tryptaldehydes with **6a**.



Scheme 6. Benzoannulation of **8a** or **8a′** with **1b**.



Scheme 7. Plausible mechanism of the three-component reaction of indole, α-bromoacetaldehydes, and **6a**.



Scheme 8. Scope of three-component reactions of indoles, **2a**, and 1,3-dicarbonyl compounds.

Then, we probed the scope of reaction with respect to both 1,3-dicarbonyl and indole components. **Scheme 8** suggests that various β-ketoesters with an electron-donating β-acyl readily participated in this three-component reaction. This led to the expected carbazoles in generally good yields (**7b**–**e**, **7j**). However, the expected carbazoles cannot be formed when the β-ketoesters with electron-withdrawing β-acyl were used, i.e., ethyl trifluoroacetoacetate or ethyl benzoylacetate. Ether, double and triple bonds, and thiophene functionalities can all be delivered into the product molecules without structural damage (**7f**–**i**, **7m**). An acid-liable cyclopropyl-containing β-ketoester is also amenable to this three-component reaction affording the desired product **7l** in 50% yield. However, the reaction of the indole, **2a**, and acetylacetone proceeded sluggishly producing compound **7k** in 37% yield. The scope of the reaction with respect to the indole component was next investigated and found to be excellent. Indoles with different substituents smoothly reacted with **2a** and **6a**. Both electron-rich (**7n**, **7o** and **7s**) and moderately electron-poor (**7q** and **7r**) indoles readily participated in the reaction. However, the target compound cannot be formed when 6-nitro-1*H*-indole was used, perhaps due to the poor nucleophilicity. Notably, the similar substituted carbazoles have been synthesized with a Lewis acid-catalyzed benzoannulation protocol via 2-butoxy-2,3-dihydrofurans and indoles as substrates.[10e] However, a two-step method has to be used to synthesize 2-butoxy-2,3-dihydrofurans; this method also involves the use of Ru complex as catalyst.[28] The present three-component reaction was established based on relay catalysis of $BiCl_3$ and byproduct HBr. This offered a cost-effective route for accessing carbazole products.

Conclusion

Straightforward methods for the synthesis of benzo[α]carbazoles and carbazoles from indoles and α-bromoacetaldehyde acetal were developed via the $BiCl_3$ catalyst. The reaction mechanism involved a byproduct HBr-participated relay catalysis in which the $BiCl_3$ catalyst promoted a Friedel–Crafts alkylation reaction while eliminating the HBr byproduct. Intriguingly, the resulting HBr played the role of catalyst in the following steps, and generated benzo[α]carbazole and carbazole products. To the best of our knowledge, this study is the first to present this unique system of catalysis, although

similar concomitant waste acid-participated relay catalysis might already exist in some organic reactions. This method could be useful for developing other synthetic methodologies via byproducts generated in the upstream steps; we are actively working in this direction.

Experimental Section

General Procedure for synthesis of 3a

In a typical reaction, **1a** (0.3 mmol) and **2a** (0.6 mmol) were mixed with $BiCl_3$ (30 mol%) in MeCN (1.0 mL). The mixture was then stirred at 80 °C for 3 h. After the reaction, the mixture was cooled to room temperature, and the product **3a** was obtained by isolation with preparative TLC (56.0 mg, yield = 86%, eluting solvent: pertroleum ether/ethyl acetate = 20/1 (v/v)). Synthesis of the other compounds including carbazoles was performed by an analogous procedure.

The Procedure for Synthesis of 3a in large scale

The reaction was conducted in a 50.0 mL of bottomed flask equipped with magnetic stirring and a condenser. Compound **1a** (10.0 mmol) and **2a** (20.0 mmol) were mixed with $BiCl_3$ (3.3 mmol, 30 mol%) in MeCN (30.0 mL). The mixture was then stirred at 80 °C for 3 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (50.0 mL) and washed with brine (2 × 50.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **3a** was obtained by isolation with silica column chromatography (1.8 g, yield = 83%, eluting solvent: pertroleum ether/ethyl acetate = 20/1 (v/v)).

The Procedure for Synthesis of 4a

The reaction was conducted in a 50.0 mL of bottomed flask equipped with magnetic stirring. Compound **1a** (10.0 mmol) and **2a** (20.0 mmol) were mixed with catalyst (3.0 mmol, 10 mol%) in MeCN (30.0 mL). The mixture was then stirred at 50 °C for 6 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (50.0 mL) and washed with brine (2 × 50.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **4a** was obtained by isolation with silica column chromatography (0.3 g, yield = 12%, eluting solvent: pertroleum ether/ethyl acetate = 10/1 (v/v)).

The Procedure for Synthesis of 4b

A solution of tryptophol (5.0 mmol) in DMSO (10.0 mL) was added IBX (5.5 mmol, 1.1 equiv). The resulting suspension was stirred at 40 °C for 2 h. After the reaction, the mixture was cooled to room temperature, and filtered through a cotton plug. Then the filtrate washed with brine (30.0 mL) and diluted with ethyl acetate (2 × 20.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **4b** was obtained by isolation with silica column chromatography (0.6 g, yield = 78%, eluting solvent: pertroleum ether/ethyl acetate = 10/1 (v/v)).

The Procedure for Synthesis of 4b′

The reaction was conducted in 10.0 mL of V-type flask equipped with triangle magnetic stirring. Compound **4b** (2.0 mmol), ethylene glycol (4.0 mmol), and PTSA (20 mol%) were mixed in 1,2-dichloroethane (4.0 mL). The mixture was then stirred at 30 °C for 2 h. After the reaction, the mixture was cooled to room temperature, and diluted with 1,2-dichloroethane (10.0 mL) and washed with brine (2 × 30.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **4b′** was obtained by isolation with silica column chromatography (0.4 g, yield = 99%, eluting solvent: pertroleum ether/ethyl acetate = 50/1 (v/v)).

The Procedure for Synthesis of 5a

The reaction was conducted in 10 mL of V-type flask equipped with triangle magnetic stirring. Compound **1a** (2.0 mmol), **2e** (1.0 mmol, prepared from α-bromoacetaldehyde dimethyl acetal) and PTSA (5 mol%) in MeOH (4.0 mL). The mixture was then stirred at room temperature for 0.5 h. After the reaction, the mixture was diluted with ethyl acetate (15 mL) and washed with brine (20 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **5a** was obtained by isolation with silica column chromatography (441.0 mg, yield = 90%, elutent: pertroleum ether/ethyl acetate = 5/1 (v/v)).

The Procedure for Synthesis of 7a-s

In a typical reaction, **1b** (0.3 mmol), **2a** (0.6 mmol) and **6a** (0.6 mmol) were mixed with $BiCl_3$ (15 mol%) in MeCN (1.0 mL). The mixture was then stirred at 80 °C for 2 h. After the reaction, the mixture was cooled to room temperature, and the product **7a** was obtained by isolation with preparative TLC (69.8 mg, yield = 92%, eluting solvent: pertroleum ether/ethyl acetate = 10/1 (v/v)). Synthesis of the other compounds was performed by an analogous procedure.

The Procedure for Synthesis of 8a

The reaction was conducted in 50.0 mL of bottomed flask equipped with round magnetic stirring. In a typical reaction, ethyl 3-oxobutanoate (10.0 mmol) and α-chloroacetaldehyde (wt 40%, 11.0 mmol) were mixed with NaOH (10.0 mmol) in MeCN (30.0 mL). The mixture was then stirred at room temperature for 10 min. After the reaction, the mixture was diluted with ethyl acetate (60.0 mL) and washed with brine (2 × 50.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **8a** was obtained by isolation with silica column chromatography (1.55 g, yield = 90%, eluting solvent: pertroleum ether/ethyl acetate = 20/1 (v/v)).

The Procedure for Synthesis of 8a′

The reaction was conducted in 50.0 mL of bottomed flask equipped with round magnetic stirring. Ethyl 3-oxobutanoate (10.0 mmol) was added to a mixture of 1.09 g (8.0 mmol) of calcined potassium carbonate in 30.0 mL of DMSO. The mixture was stirred for 10 h at 80 °C. After the reaction, the mixture was cooled to room temperature and then water (80.0 mL) was added. The aqueous phase was extracted with ethyl acetate (2 × 50.0 mL). The acquired organic phase was then dried over anhydrous Na_2SO_4. After removing the volatile solvent, the product **8a′** was obtained by isolation with silica column chromatography (1.14 g, yield = 53%, eluting solvent: pertroleum ether/ethyl acetate = 10/1 (v/v)).

Spectroscopic data of compounds

11*H*-benzo[α]carbazole (3a):[14] 56.0 mg, 86%; white solid, mp: 223–224 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 7.31–7.35 (m, 1H), 7.44–7.48 (m, 1H), 7.53–7.62 (m, 3H), 7.68 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 8.11–8.17 (m, 3H), 8.78 ppm (s, 1H); ^{13}C (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 111.2, 118.6, 119.5, 120.0, 120.1, 120.4, 120.6, 121.2, 124.3, 125.0, 125.4, 125.7, 129.2, 132.6, 135.0, 138.6 ppm.

8-Methyl-11*H*-benzo[α]carbazole (3b):[29] 58.9 mg, 85%; white solid, mp: 258–259 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.50 (s, 3H), 7.23 (d, J = 8.0 Hz, 1H), 7.52–7.55 (m, 2H), 7.59–7.64 (m, 2H), 7.95 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 12.08 (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 21.2, 111.1, 117.0, 118.9, 119.4, 119.5, 121.3, 121.8, 123.4, 125.1, 125.4, 126.0, 127.8, 128.5, 131.8, 135.4, 137.0.

8-Methoxy-11*H*-benzo[α]carbazole (3c):[30] 66.7 mg, 90%; white solid, mp: 205–206 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 3.88 (s, 3H), 7.05 (dd, J = 2.4, 8.8 Hz, 1H), 7.51–7.64 (m, 4H), 7.73 (d, J = 2.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 12.03 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 55.6, 102.1, 112.0, 114.1, 117.3, 118.6, 119.7, 121.4, 121.7, 123.6, 125.1, 125.3, 128.5, 131.9, 133.6, 135.8, 153.5 ppm.

8-Fluoro-11*H*-benzo[α]carbazole (3d):[31] 56.4 mg, 80%; dark brown solid, 214–215 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 7.23–7.28 (m, 1H), 7.55–7.66 (m, 4H), 7.99–8.05 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H); 8.50 (d, J = 8.0 Hz, 1H), 12.30 ppm (s, 1H); ^{13}C (100 Hz, DMSO-d_6, 25 °C): δ = 105.1 ($J_{C\text{-}F}$ = 24.0 Hz), 112.2 ($J_{C\text{-}F}$ = 3.0 Hz), 112.4 ($J_{C\text{-}F}$ = 12.0 Hz), 117.2, 119.2, 119.7, 121.3, 121.9, 123.6 ($J_{C\text{-}F}$ = 10.0 Hz), 125.6 ($J_{C\text{-}F}$ = 12.0 Hz), 128.6, 132.1, 135.2, 136.5, 155.7, 158.0 ppm; ^{19}F (377 Hz, DMSO-d_6, 25 °C): δ = –124.3 (sextet, J = 3.8 Hz, 1F) ppm.

8-Chloro-11*H*-benzo[α]carbazole (3e):[32] 58.7 mg, 78%; white solid, mp: 208–209 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 7.41 (dd, J = 2.0, 7.2 Hz, 1H), 7.56–7.59 (m, 1H), 7.64–7.68 (m, 3H), 8.05 (d, J = 8.0 Hz, 1H), 8.23–8.29 (m, 2H), 8.51 (d, J = 8.0 Hz, 1H), 12.40 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 112.8, 116.6, 119.3, 119.6, 119.7, 121.2, 121.9, 123.6, 124.3, 124.5, 125.6, 125.7, 128.6, 132.2, 136.1, 137.1 ppm.

***N*-Methyl-11*H*-benzo[α]carbazole (3f):**[29] 50.6 mg, 73%; white solid, mp: 173–174 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 4.29 (s, 3H), 7.37–7.40 (m, 2H), 7.51–7.63 (m, 4H), 7.70 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.19–8.21 (m, 2H), 8.67 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 33.9, 109.0, 119.0, 119.2, 119.5, 119.7, 120.5, 122.1, 122.8, 123.0, 124.6, 124.7, 125.2, 129.5, 133.7, 135.5, 140.7ppm.

***N*-Ethyl-11*H*-benzo[α]carbazole (3g):**[33] 41.3 mg, 75%; white solid, mp: 157–158 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.71 (t, J = 7.2 Hz, 3H), 4.85 (q, J = 7.2 Hz, 2H), 7.43–7.46 (m, 1H), 7.60–7.66 (m, 3H), 7.69–7.73 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.27–8.29 (m, 2H), 8.59 ppm (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.1, 40.5, 108.9, 119.2, 119.3, 119.6, 119.7, 120.6, 121.9, 122.3, 123.2, 124.6, 124.8, 125.5, 129.7, 133.7, 134.4, 140.0 ppm.

Ethyl 2-(11*H*-benzo[α]carbazol-11-yl)acetate (3h): 63.6 mg, 70%; white solid, mp: 124–125 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 1.20 (t, J = 7.2 Hz, 3H), 4.20 (q, J = 7.2 Hz, 2H), 5.82 (s, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.47–7.51 (m, 1H), 7.54–7.64 (m, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 7.6 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.37 ppm (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 14.1, 47.7, 61.2, 109.8, 118.9, 119.2, 119.6, 120.0, 120.8, 121.3, 121.8, 122.5, 124.8, 125.0, 125.6, 129.4, 133.1, 134.3, 140.5, 169.3 ppm; IR: ν = 3363, 3114, 3047, 2978, 2923, 2851, 1938, 1869, 1796, 1743, 1558, 1526, 1469, 1444, 1409, 1390, 1333, 1288, 1210, 1163, 1130, 1095, 1051, 1018, 988, 913, 861, 801, 735, 630, 553, 509, 436 cm^{-1}; HRMS (EI): m/z: calcd for $C_{20}H_{17}NNaO_2$: 326.1151 [M + Na]$^+$; found: 326.1156.

***N*-(2-Methoxyethyl)-11*H*-benzo[α]carbazole (3i):** 61.1 mg, 74%; brown liquid; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 3.18 (s, 3H), 3.90 (t, J = 5.6 Hz, 2H), 5.03 (t, J = 5.6 Hz, 2H), 7.28 (t, J = 7.6Hz, 1H), 7.45-7.48 (m, 1H), 7.54–7.58 (m, 1H), 7.63–7.68 (m, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.63 ppm (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 45.2, 59.5, 71.1, 110.3, 118.8, 119.2, 119.4, 119.6, 120.5, 121.8, 122.1, 122.3, 124.7, 124.8, 125.6, 129.3, 133.1, 133.9, 140.8 ppm; IR: ν = 3362, 3053, 2924, 2890, 2815, 1888, 1747, 1660, 1615, 1558, 1528, 1468, 1407, 1383, 1331, 1289, 1189, 1159, 1056, 1015, 965, 914, 855, 808, 782, 743, 682, 599, 557, 510, 439 cm^{-1}; HRMS (EI): m/z: calcd for $C_{19}H_{17}NNaO$: 298.1202 [M + Na]$^+$; found: 298.1206.

***N*-(Prop-2-yn-1-yl)-11*H*-benzo[α]carbazole (3j):** 56.6 mg, 74%; white solid, mp: 165–166 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 3.42 (s,1H), 5.75 (d, J = 2.0 Hz, 2H), 7.31–7.35 (m,1H), 7.51–7.54 (m, 1H), 7.58–7.61 (m, 1H), 7.68–7.72 (m, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.24–8.30 (m, 2H), 8.80 ppm (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 35.6, 75.7, 79.8, 109.8, 118.9, 119.2, 119.7, 120.1, 120.9, 121.7, 122.5, 124.9, 125.1, 125.6, 129.1, 133.1, 133.8, 139.7 ppm; IR: ν = 3363, 3275, 3049, 2922, 2851, 2115, 1920, 1885, 1800, 1743, 1657, 1592, 1557, 1525, 1466, 1446, 1406, 1381, 1326, 1248, 1253, 1193, 1127, 1037, 924, 1088, 1037, 977, 924, 852, 806, 742, 729, 683, 648, 554, 506, 431 cm^{-1}; HRMS (EI): m/z: calcd for $C_{19}H_{13}NNa$: 278.0940 [M + Na]$^+$; found: 278.0945.

3-Methyl-11*H*-benzo[α]carbazole (3k):[34] 57.5 mg, 83%; white solid, mp: 195–196 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2,58 (s, 3H), 7.23–7.32 (m, 1H), 7.41–7.45 (m, 2H), 7.56–7.60 (m, 2H), 7.80 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.10–8.13 (m, 2H), 8.75 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 21.4, 111.0, 118.1, 119.7, 120.0, 120.1, 120.3, 122.1, 124.4, 124.6, 124.7, 125.4, 128.1, 132.2, 132.4, 134.9, 138.5 ppm.

3-Methoxy-11*H*-benzo[α]carbazole (3l):[34] 57.8 mg, 78%; white solid, mp: 243–244 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 3.91 (s, 3H), 7.18–7.22 (m, 1H), 7.30 (dd, J = 2.4, 8.8 Hz, 1H), 7.35–7.39 (m, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.54–7.61 (m, 2H), 8.11–8.16 ppm (m, 2H), 8.42 (d, J = 9.2 Hz, 1H), 12.08 (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 55.2, 107.9, 111.2, 115.9, 116.1, 117.0, 118.4, 119.0, 119.4, 120.0, 123.3, 123.4, 124.0, 133.5, 135.6, 138.6, 157.0 ppm.

10*H*-Thieno[2,3-α]carbazole (3m):[35] 54.2 mg, 81%; black solid, mp: 91–92 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 7.29 (t, J = 7.6 Hz, 1H), 7.42–7.44 (m, 2H), 7.51 (d, J = 5.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.35 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 111.1, 116.0, 117.4, 119.4, 120.2, 120.3, 122.6, 124.1, 124.3, 125.4, 125.7, 134.2, 139.1, 139.3 ppm.

2-(2-Phenyl-1*H*-indol-3-yl)acetaldehyde (4a):[24c] 0.3 g, 12%; plight green liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 3.86 (d, J = 1.6 Hz, 2H), 7.13–7.16 (m, 1H), 7.20–7.24 (m, 1H), 7.34–7.38 (m, 2H), 7.42–7.47 (m, 4H), 7.52 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H), 9.73 ppm (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 40.2, 103.1, 111.2, 118.8, 120.4, 122.9, 128.2, 128.4, 129.2, 132.2, 136.0, 136.9, 200.2 ppm.

2-(1*H*-Indol-3-yl)acetaldehyde (4b):[36] 0.6 g, 78%; brown liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 3.80 (d, J = 1.2 Hz, 2H), 7.13–7.17 (m, 2H), 7.20–7.25 9m, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 8.22 (s, 1H), 9.76 ppm (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 40.5, 106.2, 111.5, 118.6, 120.1, 122.7, 123.6, 127.5, 136.4, 199.8 ppm.

3-((1,3-Dioxolan-2-yl)methyl)-1*H*-indole (4b'):[37] 0.4 g, 99%; brown liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 3.11 (d, J = 4.8 Hz, 2H), 3.78–3.86 (m, 2H), 3.88–3.99 (m, 2H), 5.13–5.16 (m, 1H), 6.97 (d, J = 1.2, Hz, 1H), 7.08–7.19 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 8.03 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 30.6, 65.0, 104.5, 110.3, 111.2, 119.1, 119.4, 122.0, 123.1, 127.8, 136.2 ppm.

3,3'-(2-Bromoethane-1,1-diyl)bis(2-phenyl-1*H*-indole) (5a): 441.0 mg, 90%; white solid, mp: 178–179 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 4.46 (d, J = 8.0 Hz, 2H), 5.12 (t, J = 8.4 Hz, 1H), 6.95–6.99 (m, 2H), 7.12–7.15 (m, 2H), 7.22–7.25 (m, 6 H), 7.30–7.33 (m, 6H), 7.59 (d, J = 8.0 Hz, 2H), 8.06 ppm (s, 2H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 38.5, 65.2, 110.9, 112.5, 120.0, 120.9, 122.0, 128.0, 128.2, 128.5, 129.0, 133.4, 136.0, 136.5 ppm; IR: ν = 3552, 3396, 3289, 3056, 2966, 2925, 2854, 1886, 1663, 1605, 1549, 1487, 1452, 1425, 1367, 1335, 1309, 1261, 1243, 1184, 1158, 1047, 1018, 964, 922, 881, 845, 744, 700, 665, 609, 564, 537, 501, 436 cm^{-1}; HRMS (EI): m/z: calcd for $C_{30}H_{23}BrN_2Na$: 513.0937 [M + Na]$^+$; found: 513.0935.

Ethyl 1-methyl-9*H*-carbazole-2-carboxylate (7a):[10e] 69.8 mg, 92%; white solid, mp: 111–113 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.44 (t, J = 7.6 Hz, 3H), 2.82 (s, 3H), 4.41 (q, J = 7.6 Hz, 2H), 7.24–7.27 (m, 1H), 7.44–7.50 (m, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.25 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 14.6, 15.0, 60.9, 111.1, 117.4, 120.0, 121.2, 122.0, 122.7, 123.3, 125.6, 126.7, 127.0, 139.5, 140.6, 168.5 ppm.

Methyl 1-methyl-9*H*-carbazole-2-carboxylate (7b):[10e] 58.1 mg, 81%; colourless oil; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 2.80 (s, 3H), 3.94 (s, 3H), 7.22–7.26 (m, 1H), 7.43–7.47 (m, 2H), 7.82 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.0, 52.0, 111.1, 117.4, 120.0, 121.2, 122.0, 122.9, 123.2, 125.7, 126.2, 127.0, 139.5, 140.6, 169.0 ppm.

Methyl 1-isopropyl-9*H*-carbazole-2-carboxylate (7c):[10e] 28.1 mg, 35%; light yellow oil; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.55 (s, 3H), 1.57 (s, 3H), 3.95 (s, 3H), 4.01–4.07 (m, 1H), 7.23 (s, 1H), 7.45–7.57 9m, 3H), 7.94 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.24 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 22.0, 29.2, 52.4, 58.6, 99.9, 107.3, 111.1, 117.9, 119.9, 120.1, 121.3, 122.7, 127.1, 131.2, 137.3, 160.0, 169.4 ppm.

Methyl 1-ethyl-9*H*-carbazole-2-carboxylate (7d): 58.4 mg, 77%; light yellow liquid; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 1.28 (t, J = 7.2 Hz, 3H), 3.26 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 6.55 (s, 2H), 7.17–7.21 (m, 1H), 7.43–7.47 (m, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 11.50 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 14.9, 21.7, 51.8, 111.4, 117.5, 119.0, 120.6, 120.9, 122.0, 124.8, 125.1, 126.6, 128.9, 138.6, 140.9, 168.0 ppm; IR: ν = 3374, 3060, 2953, 2926, 2854, 1714, 1624, 1573, 1500, 1459, 1430, 1377, 1342, 1326, 1288, 1263, 1214, 1196, 1147, 1075, 1055, 1013, 891, 825, 799, 608, 499, 432 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{16}H_{15}O_2NNa$: 276.0995 [M + Na]$^+$; found: 276.0998.

Ethyl 1-propyl-9*H*-carbazole-2-carboxylate (7e):[10e] 64.3 mg, 76%; light yellow oil; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.09 (t, J = 7.6 Hz, 3H), 1.44 (t, J = 7.2 Hz, 3H), 1.75–1.84 (m, 2H), 3.22–3.26 (m, 2H), 4.01 (q, J = 7.2 Hz, 2H), 7.23–7.27 (m, 1H), 7.44–7.50 (m, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 8.26 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 14.4, 14.6, 23.6, 31.1, 60.8, 110.9, 117.5, 119.8, 121.0, 122.1, 123.2, 125.7, 126.4, 126.8, 127.4, 139.0, 140.4, 168.4 ppm.

2-Methoxyethyl 1-methyl-9*H*-carbazole-2-carboxylate (7f):[10e] 62.8 mg, 74%; white solid, mp: 156–157 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.79 (s, 1H), 3.33 (s, 1H), 3.68–3.70 (m, 2H), 4.40–4.42 (m, 2H), 7.18–7.22 (m, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 11.47 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 14.9, 58.1, 63.4, 69.9, 111.4, 117.3, 119.1, 120.6, 121.0, 122.0, 122.7, 124.6, 125.7, 126.7, 139.5, 140.9, 167.6 ppm.

Allyl 1-methyl-9*H*-carbazole-2-carboxylate (7g): 60.4 mg, 76%; light brown liquid; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.80 (s, 3H) 4.82 (d, J = 5.2 Hz, 2H), 5.29–5.32 (m, 1H), 5.41–5.46 (m, 1H), 6.05–6.15 (m, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 11.48 ppm (s, 1H);^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 15.0, 64.9, 111.4, 117.4, 117.9, 119.1, 120.5, 121.0, 122.0, 122.9, 124.7, 125.5, 126.7, 132.9, 139.5, 140.9, 167.2 ppm; IR: ν = 3363, 3060, 2955, 2925, 2853, 1711, 1625, 1576, 1501, 1459, 1422, 1378, 1360, 1327, 1286, 1257, 1214, 1194, 1147, 1094, 1048, 1026, 930, 819, 753, 708, 499, 440 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{17}H_{15}O_2NNa$: 288.0995 [M + Na]$^+$; found: 288.0990.

Prop-2-yn-1-yl 1-methyl-9*H*-carbazole-2-carboxylate (7h): 63.1 mg, 80%; light brown oil; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 2.53 (t, J = 2.0 Hz, 1H), 2.86 (s, 3H), 4.96 (d, J = 2.0 Hz, 2H), 7.26–7.30 (m, 1H), 7.46–7.54 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.21 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.0, 52.2, 74.9, 78.1, 111.0, 117.4, 120.0, 121.2, 122.2, 123.1, 123.3, 125.1, 125.9, 127.1, 139.3, 140.5, 167.3 ppm; IR: ν = 3381, 3309, 2955, 2925, 2854, 1717, 1624, 1573, 1500, 1460, 1376, 1328, 1287, 1252, 1215, 1193, 1144, 1050, 1016, 971, 823, 751, 675, 494 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{17}H_{13}NNaO_2$: 286.0838 [M + Na]$^+$; found: 286.0834.

2-(Methacryloyloxy)ethyl 1-methyl-9*H*-carbazole-2-carboxylate (7i): 56.6 mg, 56%; colourless oil; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.98 (s, 3H), 2.84 (s, 3H), 4.53–4.55 (m, 2H), 4.60–4.62 (m, 2H), 5.61 (s, 1H), 6.18 (s, 1H), 7.26–7.29 (m, 1H), 7.46–7.51 (m, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.20 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.0, 18.3, 62.5, 62.7, 111.1, 117.4, 120.0, 121.2, 122.1, 122.9, 123.1, 125.7, 125.8, 126.1, 127.0, 135.8, 139.6, 140.6, 167.2, 168.1 ppm; IR: ν = 3391, 2955, 2922, 2851, 1705, 1622, 1497, 1454, 1417, 1378, 1342, 1284, 1254, 1179, 1146, 1057, 1023, 938, 890, 846, 811, 787, 745, 730, 642, 594, 531, 451, 435 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_8H_{12}O_2Na$: 360.1206 [M + Na]$^+$; found: 360.1204.

Benzyl 1-methyl-9*H*-carbazole-2-carboxylate (7j):[39] 75.6 mg, 80%; yellow solid, mp: 145–146 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.81 (s, 3H), 5.37 (s, 2H), 7.18–7.24 (m, 1H), 7.31–7.38 (m, 1H), 7.41–7.52 (m, 5H), 7.57 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 H,z 1H), 11.48 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 15.0, 66.0, 111.4, 117.3, 119.0, 120.6, 121.0, 122.0, 123.0, 124.7, 125.4, 127.0, 128.0, 128.1, 128.5, 136.4, 140.0, 140.9, 167.4 ppm.

1-(1-Methyl-9*H*-carbazol-2-yl)ethanone (7k):[10e] 24.8 mg, 37%; yellow oil; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.70 (d, J = 0.8 Hz, 3H), 2.78 (s, 3H), 7.25–7.28 (m, 1H), 7.45–7.51 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.25 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 15.0, 30.2, 111.1, 117.4, 120.1, 121.0, 121.3, 123.3, 127.2, 132.4, 134.8, 139.8, 140.7, 141.5, 202.1 ppm.

Methyl 1-cyclopropyl-9*H*-carbazole-2-carboxylate (7l):[10e] 39.8 mg, 50%; light yellow oil; ^{1}H (400 Hz. $CDCl_3$, 25 °C, TMS): δ = 0.63–0.67 (m, 2H), 1,12–1,17 (m, 2H), 2.31–2.38 (m, 1H), 3.97 (s, 3H), 7.17–7.31 (m, 1H), 7.44–7.54 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 8.53 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 6.7, 10.8, 52.1, 110.9, 118.2, 119.7, 120.8, 121.0, 123.0, 125.3, 125.4, 126.8, 129.7, 140.0, 140.1, 169.5 ppm.

2-(Thiophen-3-yl)ethyl 1-methyl-9*H*-carbazole-2-carboxylate (7m): 80.4 mg, 80%; colourless liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 2.80 (s, 3H), 3.34 (t, J = 7.2 Hz, 2H), 4.58 (t, J = 7.2 Hz, 2H), 6.95–6.98 (m, 2H), 7.18–7.28 (m, 2H), 7.44–7.48 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 8.18 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.0, 29.7, 65.2, 111.1, 117.4, 120.1, 121.3, 122.2, 123.1, 123.3, 124.2, 125.8, 126.2, 127.1, 127.2, 139.5, 140.3, 140.6, 168.2 ppm; IR: ν = 3372, 3060, 2956, 2925, 2854, 1710, 1624, 1574, 1499, 1458, 1422, 1379, 1327, 1285, 1213, 1194, 1148, 1048, 1014, 971, 891, 850, 824, 788, 752, 734, 697, 576, 497, 435 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{20}H_{17}NO_2NaS$: 358.0872 [M + Na]$^+$; found: 358.0876.

Ethyl 1,9-dimethyl-9*H*-carbazole-2-carboxylate (7n):[40] 56.1 mg, 70%; white solid, mp: 112–113 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 1.35 (t, J = 7.2 Hz, 3H), 2.95 (s, 3H), 4.16 (s, 3H), 4.33 (q, J = 7.2 Hz, 2H), 7.21–7.25 (m,1 H), 7.48–7.65 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.17 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 Hz, DSMO-d_6, 25 °C): δ = 14.2, 16.3, 33.2, 60.7, 109.7, 117.5, 119.3, 120.2, 120.6, 121.3, 121.9, 125.0, 126.8, 129.5, 139.7, 142.7, 168.5 ppm.

Methyl 5-fluoro-1-methyl-9*H*-carbazole-2-carboxylate (7o):[10e] 55.5 mg, 72%; white solid, mp: 175–176 °C; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 2.84 (s, 3H), 3.97 (s, 3H), 6.91–6.96 (m, 1H), 7.26–7.28 (m, 1H), 7.37–7.42 (m, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.33 ppm (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 15.0, 52.2, 105.5, 105.7, 106.8 ($J_{C\text{-}F}$ = 3.7 Hz), 111.8, 112.0, 111.8 ($J_{C\text{-}F}$ = 3.1 Hz), 122.5, 123.0, 126.4, 127.6,

127.7, 138.9,142.4 (J_{C-F} = 10.1 Hz), 157.6, 160.1, 168.7 ppm; ^{19}F (377Hz, $CDCl_3$, 25 °C, TMS): δ = -118.5 ppm.
Methyl 5-chloro-1-methyl-9*H*-carbazole-2-carboxylate (7p): 50.0 mg, 61%; white solid, mp: 156–157 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.77 (s, 3H), 3.86 (s, 3H), 7.19 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.54 (d, *J* = 0.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 11.61 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C, TMS): δ = 14.9, 51.8, 110.9, 117.4, 120.9, 122.4, 121.0, 123.0, 124.0, 126.1, 131.1, 128.6, 139.8, 141.4, 167.9 ppm; IR: ν = 3368, 2953, 2854, 1716, 1698, 1625, 1575, 1500, 1459, 1411, 1378, 1339, 1287, 1259, 1230, 1202, 1149, 1095, 1055, 977, 871, 824, 802, 749, 646, 590, 433 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{15}H_{12}ClNaO_2$: 296.0449 [M + Na]$^+$; found: 296.0445.
Methyl 6-cyano-9*H*-carbazole-2-carboxylate (7q): 32.5 mg, 43%; colourless oil; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.79 (s, 3H), 3.88 (s, 3H), 7.67–7.74 (m, 2H), 7.81–7.83 (m, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.78 (s, 1H), 12.08 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 15.4, 52.5, 101.3, 113.0, 118.6, 122.1, 122.7, 123.8, 124.3, 125.4, 127.1, 130.0, 130.1, 140.6, 143.2, 168.3 ppm; IR: ν = 3337, 2954, 2924, 2853, 2213, 1746, 1718, 1622, 1580, 1498, 1462, 1433, 1337, 1307, 1289, 1261, 1214, 1199, 1147, 1129, 1092, 1055, 878, 823, 783, 740, 665, 612, 586, 535, 518, 485, 423 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{16}H_{12}N_2NaO_2$: 273.0634 [M + Na]$^+$; found: 273.0635.
Methyl 6-bromo-1-methyl-9*H*-carbazole-2-carboxylate (7r): 43.7 mg, 46%; white solid, mp: 172–173 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.77 (s, 3H), 3.87 (s, 3H), 7.50–7.52 (m, 1H), 7.56–7.59 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.42 (s, 1H), 11.65 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 14.9, 51.9, 111.1, 113.4, 117.8, 120.8, 123.0,123.5, 124.0, 126.4, 129.1, 139.5, 139.9, 168.0 ppm; IR: ν = 3444, 3225, 3191, 3102, 3064, 2995, 2951, 2915, 2853, 2673, 2253, 2126, 1711, 1622, 1571, 1501, 1454, 1436, 1409, 1382, 1337, 1298, 1266, 1202, 1152, 1056, 1008, 930, 881, 820, 787, 756, 735, 699, 627, 514, 483, 427 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{15}H_{12}BrNaO_2$: 339.9944 [M + Na]$^+$; found: 339.99470
Methyl 6-methoxy-1-methyl-9*H*-carbazole-2-carboxylate (7s): 71.1 mg, 88%; white solid, mp: 158–159 °C; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 2.82 (s, 3H), 3.93 (s, 3H), 3.95 (s, 3H), 7.12 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.06 ppm (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 15.0, 52.0, 56.2, 103.5, 111.9, 116.8, 117.3, 121.7, 123.1, 123.7, 125.6, 126.2, 135.5, 140.2, 154.3, 168.9 ppm; IR: ν = 3411, 2951, 2922, 2851, 1890, 1848, 1604, 1581, 1495, 1460, 1434, 1376, 1341, 1286, 1241, 1202, 1177, 1145, 1073, 1051, 1024, 974, 878, 846, 825, 802, 783, 747, 666, 610, 588, 519 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{16}H_{15}NNaO_3$: 292.0944 [M + Na]$^+$; found: 292.0949.
Ethyl 5-hydroxy-2-methyl-4,5-dihydrofuran-3-carboxylate (8a): 1.55 g, 90%; clourless liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.27 (t, *J* = 7.2 Hz, 3H), 2.20 (s, 3H), 2.84 (d, *J* = 2.0 Hz, 1H), 4.114.23 (m, 2H), 4.24–4.30 (m, 1H), 4.34–4.48 (m, 1H), 5.17–5.19 ppm (m, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 14.4, 14.5, 59.9, 73.0, 77.6, 107.0, 165.8, 172.0 ppm; IR: ν = 3363, 3192, 2957, 2925, 2853, 1706, 1660, 1636, 1465, 1410, 1379, 1336, 1222, 1141, 1083, 1026, 985, 922, 861, 800, 722, 634 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_8H_{12}O_2Na$: 195.0628 [M + Na]$^+$; found: 195.0624.
Ethyl 2-((1,3-dioxolan-2-yl)methyl)-3-oxobutanoate (8a'): 1.14 g, 53%; colourless liquid; ^{1}H (400 Hz, $CDCl_3$, 25 °C, TMS): δ = 1.26 (t, *J* = 7.2 Hz, 3H), 2.25 (s, 3H), 2.29–2.31 (m, 2H), 3.68 (t, *J* = 7.2 Hz, 1H), 3.81–3.87 (m, 2H), 3.88–3.94 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.95 ppm (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C, TMS): δ = 14.0, 29.0, 31.7, 54.2, 61.5, 65.0, 65.1, 102.0, 169.5, 202.4 ppm; IR: ν = 3425, 2982, 2829, 2755, 2658, 2255, 1742, 1717, 1644, 1473, 1430, 1393, 1362, 1300, 1268, 1182, 1142, 1095, 1025, 947, 866, 734, 703, 648, 511 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{10}H_{16}O_5Na$: 239.0890 [M + Na]$^+$; found: 239.0894.
Ethyl 2-methylfuran-3-carboxylate (9a):[38] yellow oil; ^{1}H (400 Hz, DMSO-d_6, 25 °C): δ = 1.28 (t, *J* = 7.2 Hz, 3H), 2.54 (s, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 2.0 Hz, 1H), 7.59 ppm (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 Hz, DMSO-d_6, 25 °C): δ = 13.8, 14.6, 60.2, 110.8, 113.5, 141.9, 159.0, 163.6 ppm.

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FULL PAPER

Relay Catalysis of Bismuth Trichloride and Byproduct Hydrogen Bromide Enables Synthesis of Carbazole and Benzo[α]carbazoles from Indoles and α-Bromoacetaldehyde Acetals

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