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Photoinduced Cyclization of 3-Acyl-2-halo-1-[(ω-phenylethynyl)alkyl]indoles to Azaheterocyclo[1,2,3-*lm*]-Fused Benzo[*c*]carbazoles

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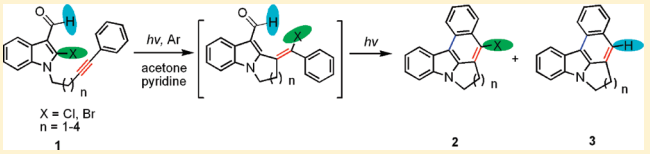
Supporting Information

ABSTRACT:



A one-pot synthesis of azaheterocyclo[1,2,3-*lm*]-fused benzo[*c*]carbazoles (**2** and **3**) has been developed by photocyclization of 3-acyl-2-halo-1-[(ω-phenylethynyl)alkyl] indoles (**1**) in good to excellent yields. All products are formed from **1** via two sequential photocyclization reactions. Two products, 9-chloro-7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (**2a**−**h**) and 7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (**3a**−**h**), are produced in the photocyclization of 2-halo-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes (**1a**−**h**). In contrast, only products **2a**−**h** are produced in the photocyclization of 3-acetyl-2-chloro-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes (**1o**−**t**). The 9-H in **3a**−**h** (n = 2) does originate from the formyl group in **1a**−**h** via 1,5-hydrogen shift. The structures of three new products, 9-bromo-7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (**2b**), 9-chloro-10-methyl-7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (**3h**) and 12-chloro-7,8-dihydro-6*H*-benzo[*c*]pyrido-[1,2,3-*lm*]carbazole (**2w**), have been corroborated by single-crystal X-ray structural analyses.

INTRODUCTION

Photoinduced coupling of aryl halides to alkenes[1] or alkynes[2] offers a convenient access for the formation of aryl−alkyl bonds under mild conditions, via fragmentation of an Ar−X bond and addition of a trappable intermediate (e.g., an aryl radical or a cation) to double or triple bonds. It is of interest that new heterocyclic rings could be formed from halogenated heteroarenes via the intramolecular coupling reactions with alkenes or alkynes.[1i−k] In general, two possible processes have been postulated for the photocoupling reaction. One is initiated by photoinduced homolytic or photoinduced electron-transfer promoted cleavage of an Ar−X bond to generate aryl radicals and the addition of aryl radicals to double bonds. The other involves photoinduced heterolytic cleavage of an Ar−X bond to produce aryl cations and the addition of aryl cations to double bonds. Another route for the addition of the C−X bond of 2-chloroindole-3-carbaldehyde (**Ia**) to the double bond could be one analogous to the stepwise transfer mechanism proposed by us earlier[1j] (Scheme 1) in analogy to the addition of aryl C−S bonds to activated C═C double bonds as proposed by Winkler (Scheme 2).[3]

In this paper, we report a new synthesis of azaheterocyclo-[1,2,3-*lm*]-fused benzo[*c*]carbazoles by the photocyclization of 2-chloro-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes **1** as shown in Scheme 3. Differently from the chlorine-atom transfer photocyclization of 2-chloro-1-(ω-alkenyl)indole-3-carbaldehydes, both chlorine-substituted benzo[*c*]azaheterocyclo-[1,2,3-*lm*]carbazole (**2**) and benzo[*c*]azaheterocyclo[1,2,3-*lm*]-carbazole (**3**) were obtained in excellent total yields.

Obviously, the two products **2** and **3** were all derived from two sequential cyclization reactions. The first cyclization was an intramolecular coupling reaction of 2-chloroindole-3-carbaldehyde to the tethered phenylacetylene and the second was initiated by a deformylation. In the two products, the dechlorination product **3** was unexpected and the formation of which was further approved to be derived from a hydrogen-shift reaction as shown in Scheme 4, eq 2. Few methods have been reported for the synthesis of azaheterocyclo[1,2,3-*lm*]-fused benzo[*c*]carbazoles, for example, palladium-catalyzed sequential migration/alkyne insertion/arylation of 3-(2-iodophenyl)-1-(5-phenylpent-4-ynyl)indole[4a] and palladium-catalyzed intramolecular annulation of 3-phenyl-2-iodo-1-(5-phenylpent-4-ynyl)indole.[4b] However, these reactions required the use of a transition metal catalyst, and the yield was not satisfactory. Therefore, a metal-free process was felt desirable.

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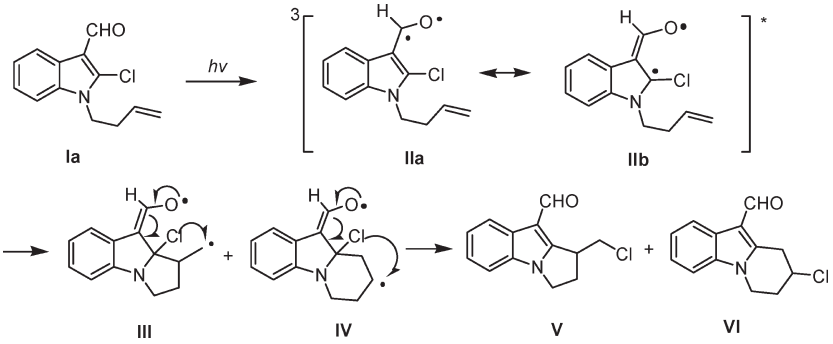
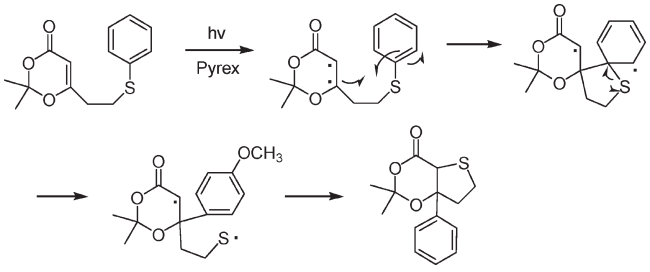
Scheme 1. Photocyclization of 2-Chloro-1-(3-butenyl)indole-3-carbaldehydes



Scheme 2. Photoinduced Sulfur-Transfer Cyclization of Aromatic Sulfides to Tethered Dioxenone According to Winkler[3]



RESULTS AND DISCUSSION

The photoreaction of 2-chloro-1-(4-phenylbut-3-ynyl)indole-3-carbaldehyde (**1a**) was chosen as representative for the investigation of reaction conditions. It was found that **1a** could be reacted in all selected solvents to afford two cyclization products **2a** and **3a** in different yields and ratio (Table 1). Comparatively, the reaction was more efficient in acetone than in DCM (Table 1, entry 2). This result may be derived from the sensitization effect of acetone to **1a** because the triplet energy of acetone (E_T = 326 kJ mol^{-1} [5a,b]) is higher than that of indole-3-carbaldehyde (E_T = 275 kJ mol^{-1} [5c]). The addition of pyridine to the reaction solutions (Table 1, entries 3 and 4) increased both the conversion of **1a** and the total yield of **2a** and **3a** probably because of the neutralization of pyridine to the produced HCl. The best result (99% conversion and 96% total yield) was obtained when **1a** was irradiated in acetone in the presence of pyridine (Table 1, entry 4).

In view of these results, we extended the study to other substrates **1b**−**n** with variation of halogen, substituents on the phenyl group, and N-tether length under the best condition (Table 2). Similarly to **1a**, the photoreactions of **1b** and **1d**−**n** except **1c** all gave a mixture of two products **2** and **3** in high total yields. As shown in Table 2, the reactivity of **1a**−**n** and the ratio of the products **2** and **3** were influenced greatly by the substituents on aromatic rings and the length of tethers. In general,the substrates **1d**−**g** bearing an electron-donating substituent (methyl or methoxyl group) on the phenyl ring were more reactive and afforded higher fraction of chlorine-retanined products **2d**−**g** than these substrates having no substituent (**1a**−**c**) or 4-Cl on the phenyl ring (**1h**). On the other hand, the substrates having a 2-substituted chlorine on the indole ring (**1a**, **1d**, **1f**, **1i**, **1k**, and **1 m**) were more reactive and produced a higher fraction of chlorine-retained products than the substrates bearing a 2-substituted bromine on the indole ring (**1b**, **1e**, **1g**, **1j**, **1l**, and **1n**). For the least reactive substrate **1c** bearing a 2-substituted iodine on the indole ring, the photoreaction gave only the dechlorination product **3c** (Table 2, entry 3). Furthermore, the substrates **1a**−**j** with the short tethers (n = 1−2) were more reactive than the substrates **1k**−**n** with the long tethers (n = 3−4). Apparently, the five- and six-membered rings (**2a**−**j** and **3a**−**i**) were more easily formed than the seven- and eight-membered rings (**2k**−**n** and **3k**−**m**). The structures of all products were determined by ^{1}H and ^{13}C NMR and HRMS, and the structures of **2b** (CCDC 770239) and **3h** (CCDC 784302) were further confirmed by single-crystal X-ray structure analyses (Figure 1) (see Supporting Information).

To evaluate the selectivity of photoreaction of **1** to **2** or **3**, the acetyl group-substituted substrates **1o**−**t** were also examined under the same conditions (Table 3). Irradiation of **1o**−**t** led to cyclization products **2a**−**k** as single products in excellent yields. It was noticeable that no dechlorination products were formed as the formyl group in **1a**−**n** was replaced by acetyl group.

Thus, it could be inferred that the chlorine-retained product **2** and the dechlorinated product **3** were formed by two different routes. To clarify the mechanism of dechlorination, we examined the source of the 9-hydrogen in product **3a** by deuterium-labeling experiments. First, **1a** was irradiated in acetone-d_6 with addition of pyridine, but it was found that no deuterated product except the normal products **2a** (41%) and **3a** (56%) was detected. This result indicated that the 9-hydrogen was not from the solvent. Then another substrate **1u** (Scheme 4, eq 1) with a deuterated phenyl group was prepared and irradiated under the same conditions. The result showed that only normal photocyclization products **2u** (56%) and **3u** (38%) were obtained and no deuterium-shifted product was detected. We next examined another substrate **1v** (Scheme 4, eq 2) with a deuterium-labeled formyl group and found that a deuterium-shifted product **3v** (51%) which corresponded to dechlorination cyclization product **3a** was obtained in addition to the chlorine-retained product **2a** (43%).

This result indicated that the 9-hydrogen in dehalogenation products **3a**−**g** came from the formyl group in **1a**−**n** via hydrogen shift from formyl group to vinylic carbon, and this result also gave an explanation to why no dechlorination product was formed in the photoreactions of 3-acetyl-2-chloro-1-(ω-phenylalkynyl)indole (**1o**−**t**), because no hydrogen shift could take place from the acetyl group in **1o**−**t**. In fact, photoinduced 1,5-hydrogen shift of a formyl hydrogen to a vinylic carbon in *o*-vinylbenzaldehydes or 5-phenyl-2,4-pentadienaldehydes to give a ketene methide intermediate was

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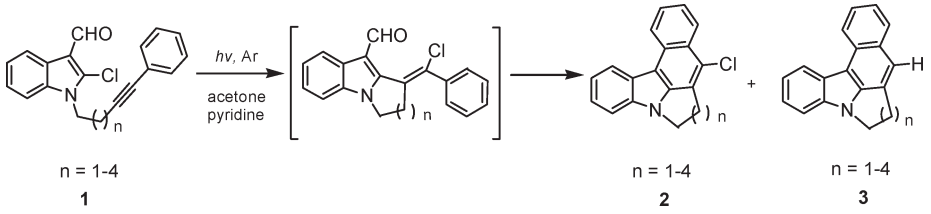
Scheme 3. Photocyclization of 2-Chloro-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes



Scheme 4. Photocyclization of the Deuterium-Labeled Substrates

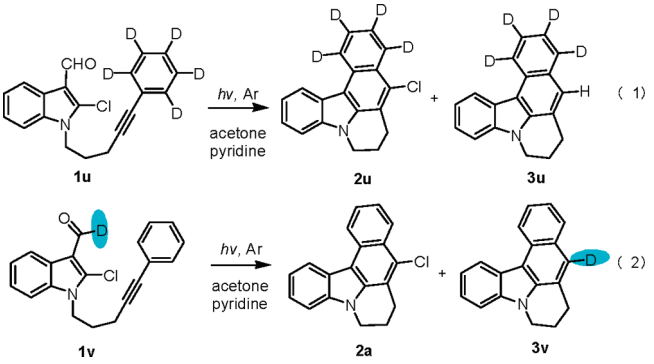
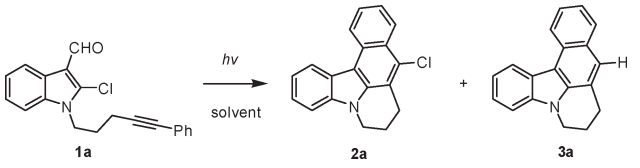


Table 1. Photocyclization of 1a under Various Conditions [a]

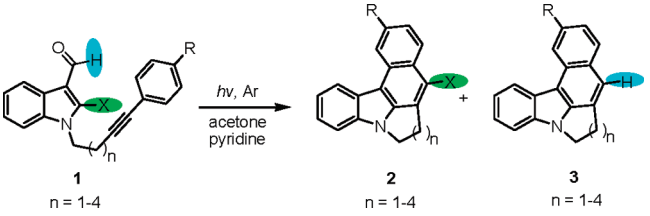


				yield(%)[c]	
entry	solvent	time (h)	convn (%)[b]	2a	3a
1	CH_2Cl_2	8	81	58	25
2	Me_2CO	8	92	46	42
3	CH_2Cl_2–pyridine	8	90	59	29
4	Me_2CO–pyridine	8	99	42	54
5	MeCN–pyridine	8	88	16	67

[a] 0.3 mmol **1a** was dissolved in different anhydrous solvents (20 mL). The solution was irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) under argon atmosphere at ambient temperature. [b] Conversion was calculated based on **1a**. [c] Yield of isolated product based on consumed **1a**.

reported by several authors.[6] Thus, we could deduce that the formation of the dehalogenation product **3a**–**m**, **3u**, and **3v** might involve the formation of a 2,4-pentadienaldehyde structure and subsequent 1,5-hydrogen shift of a formyl hydrogen to a vinylic carbon. In order to confirm this guess, we monitored the reaction solution of **1a** from the beginning to the end to find an intermediate containing a 2,4-pentadienaldehyde structure, but no intermediates were detected by ^{1}H NMR besides the reactant **1a** and the products **2a** and **3a**. We next examined the photoreaction of **1w** (Scheme 5) in the hope to retard the deformylation.

Table 2. Photocyclization of 2-Halo-1-[(ω-phenylethynyl)alkyl)]indole-3-carbaldehydes[a]



entry	substrate	R	X	*n*	time (h)	convn (%)[b]	yield (%)[c]			
1	**1a**	H	Cl	2	8	99	**2a**	42	**3a**	54
2	**1b**	H	Br	2	8	92	**2b**	58	**3a**	36
3	**1c**	H	I	2	16	86	**2c**	0	**3a**	80
4	**1d**	CH_3	Cl	2	6	99	**2d**	60	**3d**	36
5	**1e**	CH_3	Br	2	6	95	**2e**	64	**3d**	31
6	**1f**	OCH_3	Cl	2	4	99	**2f**	78	**3f**	20
7	**1g**	OCH_3	Br	2	4	96	**2g**	82	**3f**	16
8	**1h**	Cl	Cl	2	8	97	**2h**	32	**3h**	64
9	**1i**	H	Cl	1	8	98	**2i**	72	**3i**	23
10	**1j**	H	Br	1	10	92	**2j**	78	**3i**	18
11	**1k**	H	Cl	3	12	95	**2k**	44	**3k**	48
12	**1l**	H	Br	3	24	81	**2l**	62	**3k**	32
13	**1m**	H	Cl	4	24	90	**2m**	43	**3m**	46
14	**1n**	H	Br	4	30	78	**2n**	54	**3m**	34

[a] 0.3 mmol **1a**–**n** was dissolved in anhydrous acetone (20 mL) containing pyridine (0.1 mL). The solution was irradiated at $\lambda > 300$ nm with a high-pressure mercury lamp (500 W) under argon atmosphere at ambient temperature. [b] Conversion was calculated based on substrate. [c] Yield of isolated product based on consumed substrate.

In this case, a product **4** (obtained in 81% yield and the configuration was determined by NOE) could be isolated besides the normal products **2w** (6%) and **3w** (11%) within 1 h of irradiation. Compound **4** could be further converted to **2w** (31%) and **3w** (60%) after longer irradiation. These results indicated that the dechlorination products **3a**–**m** and **3u**–**w** really did originate from the cyclization of intermediates containing a 2,4-pentadienal structure via 1,5-hydrogen shift. Structure **2w** was further confirmed by single-crystal X-ray structure analysis (CCDC 804083, Figure 2).

Because a ketene structure was formed after the 1,5-hydrogen shift of the formyl hydrogen to the vinylic carbon in photoreaction of **1a**–**n** and **1u**–**w**, the photoreaction of **4** in methanol was carried out in order to capture the ketenes. It was found that a product **5** (82%) (Scheme 6) containing a methyl ester group, which was apparently derived from the addition reactions of methanol to ketene, was really produced. This result confirmed

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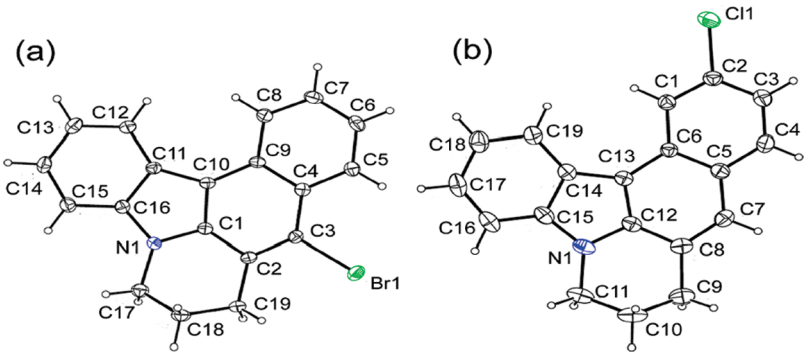
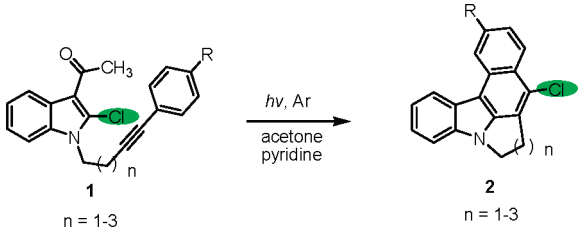


Figure 1. Molecular structure of (a) **2b** and (b) **3h** in the crystal.

Table 3. Photocyclization of 3-Acetyl-2-chloro-1-[(ω-phenylethynyl)alkyl)]indoles[a]



entry	substrate	R	*n*	time (h)	convn (%)[b]	yield (%)[c]	
1	**1o**	H	1	10	93	**2i**	86
2	**1p**	H	2	8	96	**2a**	96
3	**1q**	CH_3	2	8	97	**2d**	94
4	**1r**	OCH_3	2	8	99	**2f**	97
5	**1s**	Cl	2	8	93	**2h**	92
6	**1t**	H	3	8	89	**2k**	84

[a] 0.3 mmol **1o**−**t** was dissolved in anhydrous acetone (20 mL) containing pyridine (0.1 mL). The solution was irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) under argon atmosphere at ambient temperature. [b] Conversion was calculated based on substrate. [c] Yield of isolated product based on consumed substrate.

the presence of a ketene intermediate formed from the 1,5-hydrogen shift of the formyl hydrogen to the vinylic carbon in photoreactions of both **1a**−**n** and **1u**−**w.**

From the above discussion, two plausible mechanistic rationales to account for the formation of **2a** and **3a** are presented in Scheme 7. First, the chlorine atom transfer cyclization occurred from triplet 3-acyl-2-chloro-1-(4-phenyl-1-butynyl)indoles (**1a** or **1p**) to give the intermediate product **6a** or **6p**, which was similar to our earlier report of photocyclization of 3-acyl-2-chloro-1-(pent-4-enyl)indoles;[1j] then a 1,5-hydrogen shift of the formyl hydrogen to the vinylic carbon in **6** occurred to give the ketene methide intermediate **8**, which could eject carbon monoxide to produce a carbene.[6c,d] The electrophilic addition of the carbene center to the phenyl group and a subsequent elimination of HCl could afford the dechlorinative cyclization product **3a** (Scheme 7, route a); on the other hand, a photochemical isomerization of (*Z*)-**6a**,**p** to (*E*)-**6a**,**p** and subsequent electrocyclic ring closure of the latter to **9a**,**p**, in turn undergoing a Norrish I type elimination of formaldehyde or acetaldehyde, respectively, could form **2a** (Scheme 7, route b).

CONCLUSIONS

In summary, a one-pot synthesis of five-, six-, seven-, and eight-membered azaheterocyclo[1,2,3-*lm*]-fused benzo[*c*]carbazoles was achieved by the photocyclization of 2-halo-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes (**1a**−**n**) and 3-acetyl-2-chloro-1-[(ω-phenylethynyl)alkyl]indoles (**1o**−**t**) in excellent yields in acetone. Both 9-chloro-7,8-dihydro-6*H*-benzo[*c*]pyrido-[1,2,3-*lm*]carbazole (**2a**−**h**) and 7,8-dihydro-6*H*-benzo[*c*]pyrido-[1,2,3-*lm*]carbazole (**3a**−**h**) were formed in the photoreactions of 2-halo-1-[(ω-phenylethynyl)alkyl]indole-3-carbaldehydes (**1a**−**h**). The formation of the dehalogenated products **3** from **1a**−**n** were proved to proceed via photoinduced halogen-transfer addition of 2-haloindole-3-carbaldehydes to tethered phenylacetylene and a subsequent 1,5-hydrogen shift of the formyl hydrogen to a vinylic carbon, ejection of carbon monooxide, the cycloaddition reaction of a carbene center to the phenyl ring, and an elimination of HCl. In contrast, the halogen-retained product **2** was formed by the chlorine atom-transfer cyclization and a subsequent deformylative 6π electric cyclization. The ratio of the halogen-retained products **2** and dehalogenated products **3** was influenced by electronic or steric effects.

EXPERIMENTAL SECTION

2-Bromo-1*H*-indole-3-carbaldehyde.[7]. To a solution of dimethylformamide (3.6 mL, 46 mmol) in dichloromethane (12 mL) was added dropwise a solution of $POBr_3$ (11.1 g, 36.6 mmol) in dichloromethane (20 mL) at 0 °C. The white, thick mixture was refluxed during 15 min, and then oxindole (2.053 g, 15.42 mmol) was added portionwise. Next the mixture was stirred under reflux within 1 h. The reaction was quenched by addition of crushed ice to the media. The mixture was stirred for 20 min, and the two layers were separated. The aqueous layer was neutralized with solid potassium carbonate. The pale yellow precipitate was washed with cold water and cold dichloromethane, respectively, and was triturated with acetone. After evaporation of solvent, pure 2- bromo-1*H*-indole-3-carbaldehyde was obtained (3.44 g, 98%) as a pale yellow solid, mp 181−182 °C (lit. 186−187 °C[7]).

3-Acetyl-2-chloroindole[8]. To a solution of dimethylacetamide (5.7 mL) and $CHCl_3$ (20 mL) was added $POCl_3$ (5.51 mL) at 0 °C under stirring. Then a solution of oxindole (2.7 g; 18 mmol) in $CHCl_3$ (20 mL) was added portionwise. Next the white, thick mixture was heated under reflux for 5 h, and the solution was cooled and poured onto ice−water. The organic layer was extracted with ethyl acetate, and the pH of the aqueous layer was adjusted to pH 7 with sodium acetate. The mixture was left at room temperature overnight, and then the solid was collected by filtration and washed with water to give the product, 2.75 g, 79%, mp 237−238 °C (lit. 240−242 °C[8]).

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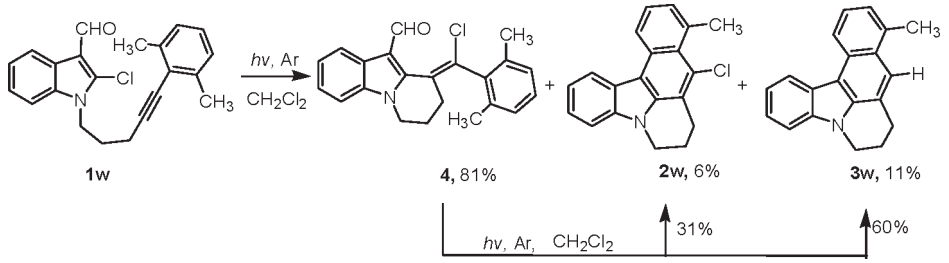
Scheme 5. Photocyclization of 2-Chloro-1-(5-dimethylphenyl-4-propynyl)indole-3-carbaldehyde



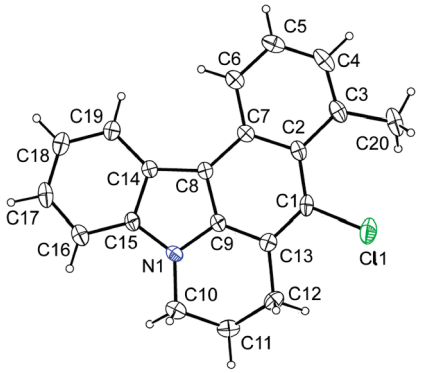
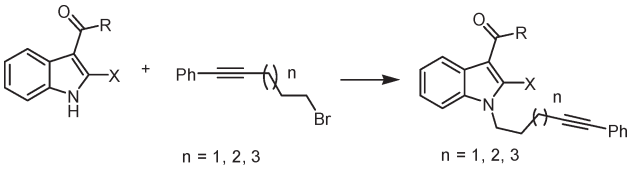


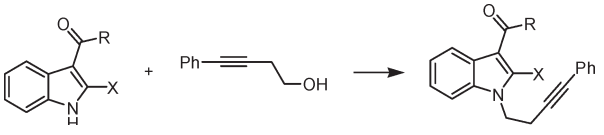
Figure 2. Molecular structure of **2w** in the crystal.

2-Chloro-1*H*-indole-3-carbaldehyde. This compound was obtained by the modificated preparation of 3-acetyl-2-chloroindole.[7] $POCl_3$ (5.51 mL) was added to a mixture of DMF (5.7 mL) and $CHCl_3$ (20 mL) under stirring at 0 °C. Then a solution of oxindole (2.7 g; 18 mmol) in $CHCl_3$ (20 mL) was added. After the mixture was heated under reflux for 18 h, the solution was cooled and poured onto water. The pH of the mixture was adjusted to pH 7 with sodium carbonate. Then the whole mixture was extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The mixture was separated by column chromatography (silica gel, hexane−acetone, 10:1) to afford the title compound, 2.1 g (65% mp 214−215 °C).

General Procedure for the Preparation of *N*-Alkyl-2-halo-3-acylindole Derivatives.



Method A:[9]. Potassium carbonate (3 mmol) was added to a solution of 3-acyl-2-haloindole (1 mmol) and the alkynyl halide (2 mmol) in acetone (25 mL). The mixture was heated to reflux for 10 h. When the starting materials were consumed completely monitored by TLC, the reaction mixture was concentrated by vacuum and then the product was isolated by silica gel column chromatography. The identity and purity of the product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.



Method B:[10]. To a mixture of 3-acyl-2-haloindole (0.5 mmol), the alkynyl alcohol (0.6 mmol), and PPh_3 (0.75 mmol) in CH_2Cl_2 (8 mL) was added diethyl azodicarboxylate (0.75 mmol) at 0 °C. The resulting mixture was flushed with Ar and stirred at room temperature for 24 h. The mixture was concentrated, and the residue was purified by chromatography on a silica gel column. The identity and purity of the product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

Photochemical Reactions. General Procedure. A sample of **1a** (0.096 g, 0.3 mmol) was dissolved in 25 mL of dry acetone containing 0.1 mL of pyridine. The solution was deaerated by bubbling Ar for 30 min and irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature. The progress of reaction was monitored by TLC at regular intervals. After the solvent was removed under reduced pressure, the residue was separated by column chromatography on silica gel eluted by hexane−ethyl acetate 20: 1 (v/v) to afford products **2a** and **3a**. The solid was further purified by recrystallization from ethyl acetate.

Analytical Data for Compounds 2a−5. *9-Chloro-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole* (***2a***). Colorless solid, mp 104−105 °C; R_f = 0.37 (3.3% petroleum ether in acetone); ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.67 (d, J = 8.0 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.45−7.49 (m, 2H), 7.36 (td, J = 5.6 Hz, 2.4 Hz, 1H), 4.26 (t, J = 6.0 Hz, 2H), 3.25 (t, J = 6.0 Hz, 2H), 2.33−2.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 135.4, 129.4, 126.6, 126.5, 126.4, 125.5, 124.0, 123.3, 123.2, 123.1, 122.0, 121.1, 119.9, 111.7, 108.9, 40.7, 24.1, 22.1; MS m/z (relative intensity, %): 293 (32.3), 291 (100), 254 (30.8), 228 (11.2), 146 (8.9), 127 (13.6), 99 (6.4), 75 (8.9); ESI-HRMS: m/z Calcd for $C_{19}H_{14}ClN + H^+$: 292.0888, found 292.0891; Anal. Calcd for $C_{19}H_{14}ClN$: C, 78.21; H, 4.84; N, 4.80. Found: C, 78.25; H, 4.81; N, 4.79.

7,8-Dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***3a***). Colorless solid, mp 93−94 °C; R_f = 0.29 (3.3% petroleum ether in acetone); ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.66 (d, J = 8.0 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.44−7.46 (m, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.33−7.38 (m, 1H), 4.23 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 6.0 Hz, 2H), 2.24−2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.6, 135.9, 129.49, 129.0, 128.8, 125.7, 123.6, 123.5, 123.2, 122.94, 122.90, 122.4, 122.0, 119.5, 112.6, 108.8, 41.1, 25.5, 22.5; MS m/z (relative intensity, %):, 257 (100), 241 (7.0), 228 (9.1), 128 (16.9), 114 (7.6), 100 (6.9), 39 (9.5); ESI-HRMS: m/z Calcd for $C_{19}H_{15}N + H^+$: 258.1277, found 258.1276; Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.74; H, 5.84; N, 5.42.

9-Bromo-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***2b***). Colorless solid, mp 138−139 °C; R_f = 0.46 (3.3% petroleum ether in acetone); ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.66 (d, J = 8.4 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.48−7.53 (m, 3H), 7.36 (td, J = 8.0 Hz, 4.0 Hz, 1H), 4.24 (t, J = 6.0 Hz, 2H), 3.23 (t, J = 6.0 Hz, 2H), 2.33−2.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.6, 135.6, 129.6, 128.2, 127.4, 126.5, 124.1, 123.7,

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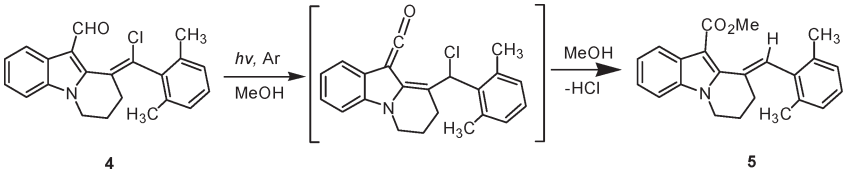
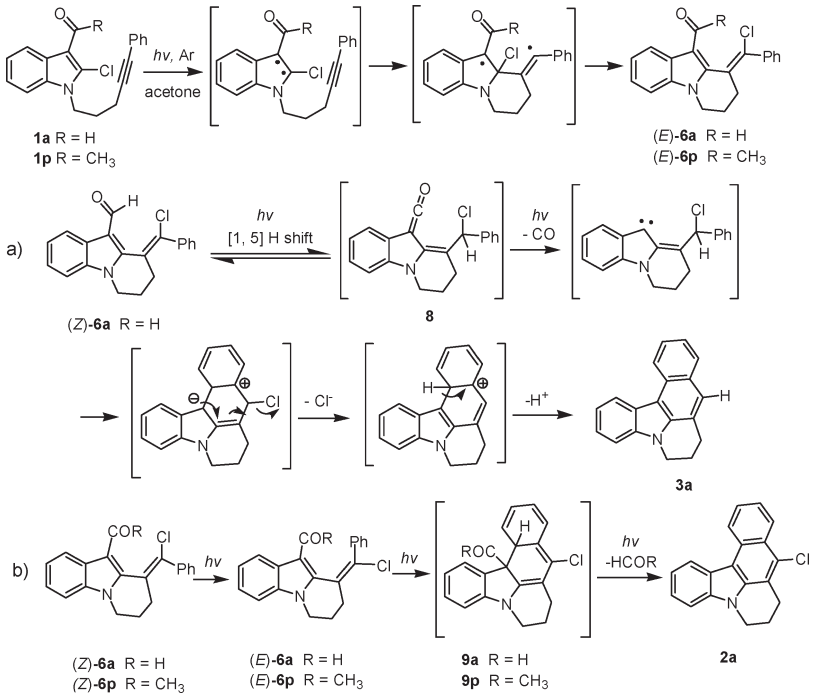
Scheme 6. Photoreaction of 4 in Methanol



4 5

Scheme 7. A Plausible Rationale for the Formation of 2a and 3a



123.5, 123.2, 123.0, 122.1, 119.9, 119.8, 112.4, 109.0, 40.8, 27.1, 22.3; MS *m*/*z* (relative intensity, %): 337 (93.0), 335 (100), 254 (38.1), 228 (16.1), 127 (22.8), 100 (12.4), 63 (8.9); ESI-HRMS: *m*/*z* Calcd for $C_{19}H_{14}BrN + H^+$: 336.0383, found 336.0380; Anal. Calcd for $C_{19}H_{14}BrN$: C, 67.87; H, 4.20; N, 4.17. Found: C, 67.95; H, 4.15; N, 4.14.

9-Chloro-7,8-dihydro-12-methyl-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***2d***). Colorless solid, mp 164−165 °C; R_f = 0.39 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.47 (d, *J* = 8.0 Hz, 1H), 8.41 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 2H), 7.32−7.37 (m, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 3.21 (t, *J* = 6.0 Hz, 2H), 2.64 (s, 3H), 2.30−2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 136.3, 135.6, 129.6, 126.6, 125.3, 125.3, 124.5, 123.8, 123.2, 122.7, 121.9, 120.0, 119.7, 111.3, 108.8, 40.7, 24.0, 22.1, 21.9; MS *m*/*z* (relative intensity, %): 307 (35.6), 305 (100), 271 (69.6), 254 (34.3), 127 (54.8), 40 (64.6); ESI-HRMS: *m*/*z* Calcd for $C_{20}H_{16}ClN + H^+$: 306.1044, found 306.1048; Anal. Calcd for $C_{20}H_{16}ClN$: C, 78.55; H, 5.27; N, 4.58. Found: C, 78.61; H, 5.24; N, 4.55.

7,8-Dihydro-12-methyl-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***3d***). Colorless solid, mp 133−134 °C; R_f = 0.36 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.55 (d, *J* = 8.0 Hz, 1H), 8.45 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.44−7.52 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 5.6 Hz, 1H), 4.32 (t, *J* = 6.0 Hz, 2H), 3.17 (t, *J* = 6.0 Hz, 2H), 2.65 (s, 3H), 2.32−2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 136.1, 135.5, 129.2, 128.6, 127.5, 124.5, 123.6, 123.5, 123.1, 122.5, 122.0, 121.8, 119.4, 112.3, 108.7, 41.3, 25.5, 22.6, 22.2; MS *m*/*z* (relative intensity, %): 271 (100), 254 (22.9), 149 (21.2), 121 (24.4), 40 (55.7); ESI-HRMS: *m*/*z* Calcd for $C_{20}H_{17}N + H^+$: 272.1444, found 272.1442; Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.59; H, 6.28; N, 5.12.

9-Bromo-7,8-dihydro-12-methyl-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***2e***). Colorless solid, mp 179−180 °C; R_f = 0.35 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.49 (d, *J* = 8.0 Hz, 1H), 8.48 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 4.0 Hz, 2H), 7.31−7.38 (m, 2H), 4.23 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 6.0 Hz, 2H), 2.65 (s, 3H), 2.32−2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.6, 136.4, 135.8, 129.8, 128.0, 125.6, 125.5, 123.9, 123.1, 122.7, 122.6, 122.1, 119.85, 119.84, 112.0, 108.9, 40.8, 27.0, 22.4, 21.9; MS *m*/*z* (relative intensity, %): 351 (100), 349 (99.6), 268 (47.4), 254 (38.3), 127 (62.8), 40 (68.1); ESI-HRMS: *m*/*z* Calcd for $C_{20}H_{16}BrN + H^+$: 350.0539, found 350.0543; Anal. Calcd for $C_{20}H_{16}BrN$: C, 68.58; H, 4.60; N, 4.00. Found: C, 68.64; H, 4.62; N, 3.90.

9-Chloro-7,8-dihydro-12-methoxy-6H-benzo[c]pyrido[1,2,3-lm]carbazole (***2f***). Colorless solid, mp 136−137 °C; R_f = 0.27 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.34 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 7.90 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.34 (td, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.13 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 4.19 (t, *J* = 6.0 Hz, 2H), 4.04 (s, 3H), 3.17 (t, *J* = 6.0 Hz, 2H), 2.28−2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.4, 138.7, 135.9, 130.5, 127.1, 126.6, 123.7, 123.2, 121.5, 121.3, 119.7, 118.4, 114.1, 111.2, 108.8, 103.4, 55.4, 40.7, 23.8, 22.1; MS *m*/*z* (relative

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intensity, %): 323 (19.2), 321 (51.6), 287 (27.7), 243 (18.5), 149 (43.5), 57 (56.1), 40 (100); ESI-HRMS: *m/z* Calcd for $C_{20}H_{16}ClNO + H^+$: 322.0993, found 322.0995; Anal. Calcd for $C_{20}H_{16}ClNO$: C, 74.65; H, 5.01; N, 4.35. Found: C, 74.69; H, 5.00; N, 4.32.

7,8-Dihydro-12-methoxy-6H-benzo[c]pyrido[1,2,3-lm]carbazole (**3f**). Colorless solid, mp 146−148 °C; R_f = 0.17 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.45 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.45−7.51 (m, 3H), 7.36 (t, *J* = 6.8 Hz, 1H), 7.08 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 4.31 (t, *J* = 6.0 Hz, 2H), 4.06 (s, 3H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.30−2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.9, 138.7, 136.4, 130.2, 130.0, 124.3, 123.6, 123.4, 123.1, 121.6, 120.2, 119.4, 113.5, 112.2, 108.7, 103.2, 55.3, 41.2, 25.3, 22.6; MS *m/z* (relative intensity, %): 287 (100), 244 (44.7), 143 (20.8), 120 (14.9), 39 (4.2); ESI-HRMS: *m/z* Calcd for $C_{20}H_{17}NO + H^+$: 288.1383, found 288.1381; Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.67; H, 5.91; N, 4.84.

9-Bromo-7,8-dihydro-12-methoxy-6H-benzo[c]pyrido[1,2,3-lm]carbazole (**2g**). Colorless solid, mp 128−129 °C; R_f = 0.35 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.34 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 9.6 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.44−7.46 (m, 2H), 7.34 (td, *J* = 6.0 Hz, 2.4 Hz, 1H), 7.12 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 4.04 (s, 3H), 3.16 (t, *J* = 6.0 Hz, 2H), 2.28−2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.4, 138.6, 136.1, 130.6, 129.7, 123.8, 123.0, 122.3, 121.6, 120.9, 119.8, 119.7, 114.4, 111.8, 108.9, 103.3, 55.4, 40.7, 26.8, 22.3; MS *m/z* (relative intensity, %): 367 (52.7), 365 (51.9), 287 (57.4), 244 (35.1), 129 (49.9), 57 (51.0), 40 (100); ESI-HRMS: *m/z* Calcd for $C_{20}H_{16}BrNO + H^+$: 366.0488, found 366.0485; Anal. Calcd for $C_{20}H_{16}BrNO$: C, 65.59; H, 4.40; N, 3.82. Found: C, 65.64; H, 4.38; N, 3.79.

9,12-Dichloro-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole (**2h**). Colorless solid, mp 150−151 °C; R_f = 0.37 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.51 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 7.45−7.51 (m, 2H), 7.40 (td, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.37 (td, *J* = 6.0 Hz, 2.4 Hz, 1H), 4.21 (t, *J* = 6.0 Hz, 2H), 3.19 (t, *J* = 6.0 Hz, 2H), 2.30−2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 135.8, 132.6, 129.9, 127.0, 126.4, 124.6, 124.3, 123.8, 122.7, 122.2, 121.7, 121.3, 120.2, 110.9, 109.1, 40.7, 24.0, 21.9; MS *m/z* (relative intensity, %): 329 (11.2), 327 (65.0), 325 (100), 254 (37.9), 126 (38.3), 43 (55.5); ESI-HRMS: *m/z* Calcd for $C_{19}H_{13}Cl_2N + H^+$: 326.0498, found 326.0497; Anal. Calcd for $C_{19}H_{13}Cl_2N$: C, 69.95; H, 4.02; N, 4.29. Found: C, 69.99; H, 4.00; N, 4.27.

12-Chloro-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole (**3h**). Colorless solid, mp 124−126 °C; R_f = 0.23 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.57 (d, *J* = 2.0 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.47−7.48 (m, 3H), 7.38 (td, *J* = 4.8 Hz, 3.2 Hz, 1H), 7.34 (td, *J* = 8.8 Hz, 2.0 Hz, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.13 (t, *J* = 6.0 Hz, 2H), 2.28−2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 136.3, 131.5, 130.1, 129.6, 127.6, 124.0, 123.17, 123.16, 123.0, 122.9, 122.1, 121.8, 119.8, 111.9, 108.9, 41.2, 25.4, 22.4; MS *m/z* (relative intensity, %): 293 (33.5), 291 (100), 254 (17.9), 227 (7.6), 146 (11.6), 127 (24.3), 57 (17.0), 43 (26.2); ESI-HRMS: *m/z* Calcd for $C_{19}H_{14}ClN + H^+$: 292.0888, found 292.0886; Anal. Calcd for $C_{19}H_{14}ClN$: C, 78.21; H, 4.84; N, 4.80. Found: C, 78.28; H, 4.81; N, 4.76.

8-Chloro-6,7-dihydrobenzo[c]pyrrolo[1,2,3-lm]carbazole (**2i**). Colorless solid, mp 146−147 °C; R_f = 0.28 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.44 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40−7.46 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 4.59 (t, *J* = 7.2 Hz, 2H), 3.91 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.7, 138.3, 130.8, 128.8, 128.1, 126.6, 125.6, 124.4, 123.59, 123.58, 123.5, 122.9, 122.4, 119.7, 110.6, 106.6, 47.5, 33.4; MS *m/z* (relative intensity, %): 279 (28.9), 277 (100), 241 (43.7), 213 (9.3), 120 (18.9), 106 (10.9); ESI-HRMS: *m/z* Calcd for $C_{18}H_{12}ClN + H^+$: 278.0731, found 278.0733; Anal. Calcd for $C_{18}H_{12}ClN$: C, 77.84; H, 4.35; N, 5.04. Found: C, 77.88; H, 4.34; N, 5.01.

6,7-Dihydrobenzo[c]pyrrolo[1,2,3-lm]carbazole (**3i**). Colorless solid, mp 157−158 °C; R_f = 0.23 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.45 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.60 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.36−7.46 (m, 4H), 7.32 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 4.51 (t, *J* = 7.2 Hz, 2H), 3.83 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.6, 138.2, 132.3, 129.7, 129.6, 128.5, 125.9, 125.8, 123.26, 123.25, 122.5, 122.2, 120.5, 119.3, 110.5, 107.5, 47.6, 33.2; MS *m/z* (relative intensity, %): 243 (100), 213 (5.5), 120 (19.2), 106 (8.6), 93 (4.6), 51 (4.2); ESI-HRMS: *m/z* Calcd for $C_{18}H_{13}N + H^+$: 244.1121, found 244.1125; Anal. Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.89; H, 5.40; N, 5.72.

8-Bromo-6,7-Dihydrobenzo[c]pyrrolo[1,2,3-lm]carbazole (**2j**). Colorless solid, mp 155−156 °C; R_f = 0.24 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.41 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.49 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.43 (d, *J* = 4.4 Hz, 2H), 7.34 (td, *J* = 7.2 Hz, 3.6 Hz, 1H), 4.55 (t, *J* = 7.2 Hz, 2H), 3.83 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.5, 138.3, 130.8, 129.6, 128.06, 128.05, 127.8, 126.6, 123.7, 123.6, 123.1, 122.5, 119.8, 114.1, 110.7, 107.1, 47.2, 35.1; MS *m/z* (relative intensity, %): 323 (100), 321 (93.8), 241 (86.2), 213 (19.5), 120 (39.1), 106 (18.9), 93 (11.5); ESI-HRMS: *m/z* Calcd for $C_{18}H_{12}BrN + H^+$: 322.0226, found 322.0225; Anal. Calcd for $C_{18}H_{12}BrN$: C, 67.10; H, 3.75; N, 4.35. Found: C, 67.16; H, 3.73; N, 4.31.

10-Chloro-6,7,8,9-tetrahydrobenzo[c]azepino[1,2,3-lm]carbazole (**2k**). Colorless solid, mp 138−140 °C; R_f = 0.42 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.74 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.66 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.52 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.45−7.48 (m, 2H), 7.34 (td, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.20−2.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 140.6, 139.3, 129.3, 128.5, 126.8, 126.6, 126.06, 126.01, 124.2, 123.7, 123.2, 123.1, 121.9, 120.0, 114.4, 109.5, 43.3, 27.4, 27.3, 25.0; MS *m/z* (relative intensity, %): 307 (36.2), 305 (100), 254 (18.4), 241 (19.1), 127 (13.6), 121 (10.8); ESI-HRMS: *m/z* Calcd for $C_{20}H_{16}ClN + H^+$: 306.1044, found 306.1047; Anal. Calcd for $C_{20}H_{16}ClN$: C, 78.55; H, 5.27; N, 4.58. Found: C, 78.60; H, 5.25; N, 4.55.

6,7,8,9-Tetrahydrobenzo[c]azepino[1,2,3-lm]carbazole (**3k**). Colorless solid, mp 123−125 °C; R_f = 0.25 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.74 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.63 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.53−7.56 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 4.55 (t, *J* = 5.2 Hz, 2H), 3.36 (t, *J* = 5.2 Hz, 2H), 2.21−2.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 140.3, 139.4, 129.3, 128.8, 128.3, 128.0, 126.02, 126.01, 123.8, 123.7, 122.9, 122.8, 122.0, 119.6, 115.6, 109.3, 43.6, 31.8, 27.9, 26.2; MS *m/z* (relative intensity, %): 271 (100), 254 (12.2), 242 (13.8), 136 (14.1), 127 (13.1), 41 (16.7); ESI-HRMS: *m/z* Calcd for $C_{20}H_{17}N + H^+$: 272.1434, found 272.1432; Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.59; H, 6.28; N, 5.12.

10-Bromo-6,7,8,9-tetrahydrobenzo[c]azepino[1,2,3-lm]carbazole (**2l**). Colorless solid, mp 137−138 °C; R_f = 0.47 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.74 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.66 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.48−7.54 (m, 3H), 7.36 (td, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.56 (t, *J* = 6.0 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.21−2.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 140.6, 139.3, 129.5, 129.0, 128.2, 128.0, 126.6, 124.4, 124.0, 123.1, 123.0, 122.4, 122.1, 120.0, 115.0, 109.5, 43.4, 31.0, 27.2, 24.9; MS *m/z* (relative intensity, %): 351 (100), 349

(94.7), 271 (26.9), 254 (35.5), 241 (42.3), 127 (38.1), 121 (23.7); ESI-HRMS: m/z Calcd for $C_{20}H_{16}BrN + H^+$: 350.0539, found 350.0538; Anal. Calcd for $C_{20}H_{16}BrN$: C, 68.58; H, 4.60; N, 4.00. Found: C, 68.64; H, 4.58; N, 3.96.

*11-Chloro-6,7,8,9-tetrahydro-10H-benzo[c]azocino[1,2,3-lm]carbazole (**2m**).* Colorless solid, mp 195−196 °C; R_f = 0.46 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.82 (d, J = 8.4 Hz, 1H), 8.59 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 7.69 (td, J = 7.6 Hz, 0.8 Hz, 1H), 7.46−7.55 (m, 3H), 7.37 (td, J = 7.2 Hz, 0.8 Hz, 1H), 4.86 (br, 2H), 3.84 (br, 2H), 2.01−2.08 (m, 4H), 1.35 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 139.6, 139.0, 130.0, 129.3, 126.7, 126.5, 126.1, 124.2, 124.1, 123.6, 123.1, 122.7, 122.0, 119.9, 113.6, 108.8, 43.3, 29.8, 28.8, 27.4, 21.4; MS m/z (relative intensity, %): 321 (30.0), 319 (100), 254 (20.1), 228 (10.9), 120 (9.5), 55 (8.5); ESI-HRMS: m/z Calcd for $C_{21}H_{18}ClN + H^+$: 320.1201, found 320.1204; Anal. Calcd for $C_{21}H_{18}ClN$: C, 78.86; H, 5.67; N, 4.38. Found: C, 78.92; H, 5.65; N, 4.34.

*6,7,8,9-Tetrahydro-10H-benzo[c]azocino[1,2,3-lm]carbazole (**3m**).* Colorless solid, mp 162−163 °C; R_f = 0.43 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.81 (d, J = 8.4 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.66 (td, J = 8.0 Hz, 0.8 Hz, 1H), 7.57 (s, 1H), 7.44−7.55 (m, 3H), 7.39 (t, J = 6.8 Hz, 1H), 4.82 (br, 2H), 3.51 (br, 2H), 2.01−2.09 (m, 4H), 1.41 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 139.4, 139.1, 129.2, 129.1, 128.3, 128.2, 126.1, 126.0, 123.7, 123.2, 122.8, 122.7, 121.9, 119.5, 114.6, 108.5, 43.0, 33.4, 29.77, 29.73, 21.5; MS m/z (relative intensity, %): 285 (100), 254 (12.8), 241 (8.4), 230 (12.7), 127 (5.5); ESI-HRMS: m/z Calcd for $C_{21}H_{19}N + H^+$: 286.1590, found 286.1593; Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.45; H, 6.67; N, 4.88.

*11-Bromo-6,7,8,9-tetrahydro-10H-benzo[c]azocino[1,2,3-lm]carbazole (**2n**).* Colorless solid, mp 173−174 °C; R_f = 0.41 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.84 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.48−7.60 (m, 3H), 7.38 (t, J = 8.0 Hz, 1H), 4.93 (br, 2H), 3.94 (t, J = 7.2 Hz, 2H), 2.05−2.11 (m, 4H), 1.38 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 139.6, 139.1, 129.5, 129.1, 127.9, 126.7, 126.49, 126.48, 124.4, 123.9, 123.1, 122.7, 122.1, 120.1, 114.4, 108.9, 43.5, 32.5, 29.9, 27.2, 21.4; MS m/z (relative intensity, %): 365 (99.4), 363 (100), 254 (61.6), 127 (27.2), 55 (82.1), 41 (90.5); ESI-HRMS: m/z Calcd for $C_{21}H_{18}BrN + H^+$: 364.0696, found 364.0694; Anal. Calcd for $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found: C, 69.28; H, 4.97; N, 3.82.

*9-Chloro-7,8-dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole-10,1,1,12,13-d_4 (**2u**).* Colorless solid, mp 108−109 °C; R_f = 0.33 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.48 (d, J = 8.0 Hz, 1H), 7.47−7.50 (m, 2H), 7.37 (td, J = 5.6 Hz, 2.4 Hz, 1H), 4.26 (t, J = 6.0 Hz, 2H), 3.25 (t, J = 6.0 Hz, 2H), 2.33−2.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.8, 135.4, 129.3, 126.6, 126.4, 124.0, 123.1, 121.9, 121.1, 119.9, 111.8, 108.9, 40.7, 24.1, 22.1; MS m/z (relative intensity, %): 297 (33.5), 295 (100), 261 (50.9), 149 (35.0), 129 (64.4), 83 (41.2), 43 (41.4); ESI-HRMS: m/z Calcd for $C_{19}H_{10}D_4ClN + H^+$: 296.1139, found 296.1137; Anal. Calcd for $C_{19}H_{10}D_4ClN$: C, 77.15; H, 6.13; N, 4.74. Found: C, 77.22; H, 6.10; N, 4.70.

*7,8-Dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole-10,1,1,12,13-d_4 (**3u**).* Colorless solid, mp 92−93 °C; R_f = 0.35 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.51 (d, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.43−7.48 (m, 2H), 7.35 (td, J = 6.0 Hz, 2.4 Hz, 1H), 4.26 (t, J = 6.0 Hz, 2H), 3.13 (t, J = 6.0 Hz, 2H), 2.27−2.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 135.9, 129.4, 128.9, 123.6, 123.5, 123.2, 122.8, 122.0, 119.5, 112.7, 108.8, 41.2, 25.5, 22.6; MS m/z (relative intensity, %): 261 (100), 258 (16.7), 149 (8.6), 129 (19.1), 40 (86.5); ESI-HRMS: m/z Calcd for $C_{19}H_{11}D_4N + H^+$: 262.1529, found 262.1527; Anal. Calcd for $C_{19}H_{11}D_4N$: C, 87.32; H, 7.32; N, 5.33. Found: C, 87.40; H, 7.30; N, 5.27.

*7,8-Dihydro-6H-benzo[c]pyrido[1,2,3-lm]carbazole-9-d (**3v**).* Colorless solid, mp 93−94 °C; R_f = 0.37 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.67 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.63 (td, J = 8.0 Hz, 0.8 Hz, 1H), 7.45−7.52 (m, 2H), 7.35−7.43 (m, 2H), 4.32 (t, J = 6.0 Hz, 2H), 3.18 (t, J = 6.0 Hz, 2H), 2.32−2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.7, 135.9, 129.4, 129.0, 128.7, 125.8, 123.6, 123.5, 122.9, 122.8, 122.5, 122.0, 119.5, 112.7, 108.8, 41.2, 25.5, 22.6; MS m/z (relative intensity, %): 258 (100), 257 (50.6), 242 (12.9), 149 (11.9), 127 (33.1), 40 (78.9); ESI-HRMS: m/z Calcd for $C_{19}H_{14}DN + H^+$: 259.1340, found 259.1342; Anal. Calcd for $C_{19}H_{14}DN$: C, 88.34; H, 6.24; N, 5.42. Found: C, 88.39; H, 6.22; N, 5.39.

*9-Chloro-7,8-dihydro-10-methyl-6H-benzo[c]pyrido[1,2,3-lm]carbazole (**2w**).* Colorless solid, mp 162−163 °C; R_f = 0.27 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.65 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.46−7.53 (m, 3H), 7.36 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 4.28 (t, J = 6.4 Hz, 2H), 3.26 (t, J = 6.0 Hz, 2H), 3.17 (s, 3H), 2.37−2.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 139.0, 136.2, 135.2, 131.2, 128.1, 127.2, 126.0, 125.9, 124.0, 123.2, 122.4, 122.2, 122.1, 119.9, 112.5, 109.0, 40.6, 27.2, 24.7, 22.3; MS m/z (relative intensity, %): 307 (33.3), 305 (100), 254 (12.9), 149 (11.9), 127 (33.1), 40 (78.9); ESI-HRMS: m/z Calcd for $C_{20}H_{16}ClN + H^+$: 306.1044, found 306.1041; Anal. Calcd for $C_{20}H_{16}ClN$: C, 78.55; H, 5.27; N, 4.58. Found: C, 78.62; H, 5.23; N, 4.55.

*7,8-Dihydro-10-methyl-6H-benzo[c]pyrido[1,2,3-l,m]carbazole (**3w**).* Colorless solid, mp 192−194 °C; R_f = 0.22 (3.3% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.59 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 7.6 Hz, 1H), 7.76 (s, 1H), 7.45−7.54 (m, 3H), 7.35 (td, J = 7.2 Hz, 1.2 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 4.33 (t, J = 6.0 Hz, 2H), 3.22 (t, J = 6.0 Hz, 2H), 2.77 (s, 3H), 2.33−2.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 138.8, 135.7, 134.9, 129.1, 128.2, 125.4, 123.84, 123.83, 123.6, 122.4, 122.2, 121.4, 119.47, 119.43, 113.2, 108.7, 41.2, 25.8, 22.7, 20.6; MS m/z (relative intensity, %): 271 (100), 257 (50.6), 242 (19.8), 149 (56.), 127 (45.6), 40 (92.1); ESI-HRMS: m/z Calcd for $C_{20}H_{17}N + H^+$: 272.1434, found 272.1438, Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.61; H, 6.28; N, 5.10.

*(Z)-9-((2,6-Dimethylphenyl)chloromethylenyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-10-carbaldehyde (**4**).* Colorless solid, mp 175−176 °C; R_f = 0.22 (10.0% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.38 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.20−7.34 (m, 3H), 7.09 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 2H), 4.17 (t, J = 6.4 Hz, 2H), 3.13 (t, J = 6.4 Hz, 2H), 2.24−2.30 (m, 2H), 2.12 (s, 6H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 184.7, 142.6, 136.6, 136.3, 135.1, 129.1, 128.3, 128.1, 128.0, 125.2, 123.8, 123.0, 122.6, 112.9, 109.0, 42.3, 30.9, 23.5, 20.3; MS m/z (relative intensity, %): 351 (33.4), 349 (100), 314 (68.4), 254 (20.1), 228 (10.9), 120 (9.5), 55 (8.5); ESI-HRMS: m/z Calcd for $C_{22}H_{20}ClNO + H^+$: 350.1306, found 350.1309, Anal. Calcd for $C_{22}H_{20}ClNO$: C, 75.53; H, 5.76; N, 4.00. Found: C, 75.59; H, 5.72; N, 3.88.

*(E)-Methyl 9-(2,6-Dimethylbenzylidenyl)-6,7,8,9-tetrahydropyrido[1,2-a]indole-10-carboxylate (**5**).* Colorless solid, mp 147−148 °C; R_f = 0.32 (10.0% petroleum ether in acetone); ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.83 (d, J = 8.0 Hz, 1H), 7.21−7.31 (m, 2H), 7.16 (td, J = 8.0 Hz, 0.8 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 7.2 Hz, 2H), 6.62 (s, 1H), 4.24 (t, J = 6.8 Hz, 2H), 3.33 (s, 3H), 2.86 (t, J = 6.8 Hz, 2H), 2.37−2.43 (m, 2H), 1.96 (s, 6H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 165.1, 139.3, 136.2, 135.9, 135.7, 129.6, 129.4, 127.6, 126.9, 126.6, 122.6, 121.5, 121.4, 108.9, 105.5, 50.4, 42.6, 33.1, 25.2, 20.1; MS m/z (relative intensity, %): 345 (100), 254 (50.6), 178 (19.9), 127 (26.1), 71 (52.3), 43 (62.1); ESI-HRMS: m/z Calcd for $C_{23}H_{23}NO_2 + H^+$: 346.1802, found 346.1806; Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 80.06; H, 6.67; N, 4.00.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, solubility data, spectroscopic data, and ^{1}H and ^{13}C NMR spectra for

all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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