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One-Pot Synthesis of Fused Benzo[*c*]carbazoles by Photochemical Intramolecular Annulation of 3-Acyl-2-haloindoles with Tethered Styrenes

Shen-Ci Lu,[a] Shi-Chao Wei,[a] Wei-Xia Wang,[a] Wei Zhang,*[a] and Zhi-Feng Tu[a]

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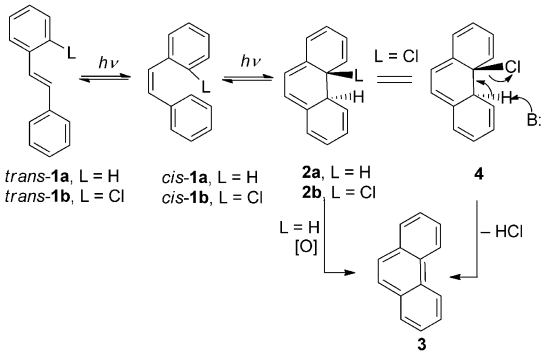
An efficient procedure for the synthesis of fused benzo[*c*]-carbazoles has been achieved in moderate to high yields by the one-pot photochemical annulation of 3-acyl-2-haloindoles with tethered styrenes by photoinduced electron-transfer coupling, electrocyclic reactions, and deacylative aromatization in the presence of pyridine. Fused furo[2,3-*c*]carbazoles were also synthesized under the same conditions. 5,6-Dihydrobenzo[*c*]pyrrolo[1,2,3-*lm*]carbazoles were oxidized by DDQ to afford aromatic benzo[*c*]pyrrolo[1,2,3-*lm*]carbazole products in moderate to high yields.

Introduction

The oxidative photocyclization of stilbenes (**1**) is the most useful and versatile synthesis of phenanthrenes.[1] In this reaction, the unstable intermediate dihydrophenanthrene (**2a**) can be produced by photochemically allowed conrotatory cyclization of (*Z*)-stilbene (**1a**) and then aromatized in situ by an oxidant, leading to phenanthrene (**3**) (Scheme 1). This reaction is equally useful for the synthesis of phenanthrenoids, the heterocyclic analogues of phenanthrenes.[2]



Scheme 1. Photocyclization of stilbenes.

The use of stilbenes containing a good leaving group at one of the *ortho* positions of the aryl substituents (**1b**) allows the operation of an interesting variant of the oxidative photocyclization of stilbenes for the synthesis of phenanthrenes. For example, the irradiation of stilbene (**1b**) leads to dihydrophenanthrene (**2b**), that can be aromatized by the action of a base (Scheme 1).[1,3]

Stilbenes are generally synthesized by several well-known methods such as the Wittig reaction,[4] Heck reaction,[5] and McMurry reaction.[6] Photochemical coupling of aryl halides with styrenes also supply another efficient route to stilbenes. For example, Arnold reported the photochemical coupling of 4-halobenzonitrile or 4-haloanisole with 1,1-diphenylethene to give 1-(4-cyanophenyl)-2,2-diphenylethene or 1-(4-methoxyphenyl)-2,2-diphenylethene;[7a] Albini reported the photochemical coupling of 4-bromo-*N*,*N*-dimethylaniline with 1,1-diphenylethene to give 1-[4-(dimethylamino)phenyl]-2,2-diphenylethene;[7b] D'Auria reported the photochemical coupling of 5-iodothiophene-2-carbaldehyde with styrene or 2-furylethene to afford 5-(2-phenylethenyl)thiophene-2-carbaldehyde or 5-[2-(2-furyl)ethenyl]-thiophene-2-carbaldehyde.[7c] In all these reported reactions, stilbenoids were generally formed by the deprotonation of the intermediate 1,2-diarylethyl cations derived from the photoinduced electron-transfer reaction between aryl halides with styrenes and the subsequent coupling of the aryl radicals and the styrene radical cations or from the addition of aryl cations to styrenes.

We have recently reported the photochemical coupling of 3-acyl-2-chloroindoles with styrenes and their subsequent electrocyclic reaction and aromatization by deacylation by a Norrish Type I reaction to afford benzo[*c*]carbazoles (Scheme 2)[8a] and the photochemical intramolecular chlorine atom transfer cyclization of 3-acyl-2-chloroindoles with tethered alkenes.[8b]

Continuing our studies on the photoreactions of 3-acyl-2-chloroheteroaromatics with olefins, especially the photocyclization of stilbenoids produced in photoreactions and the further aromatization of dihydrophenanthrenoids by deacylation, we report the combination of the above two reactions to synthesize several fused benzo[*c*]carbazoles (Scheme 3).

[a] State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Tianshui South Road 222, Lanzhou 730000, China
Fax: +86-931-8625657
E-mail: zhang_wei6275@yahoo.com

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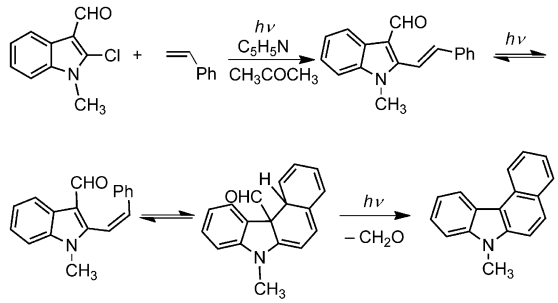
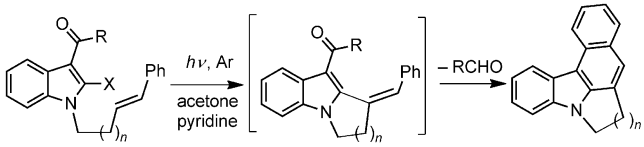


Scheme 2. Photochemical reaction of 2-chloroindole-3-carbaldehyde with styrene.

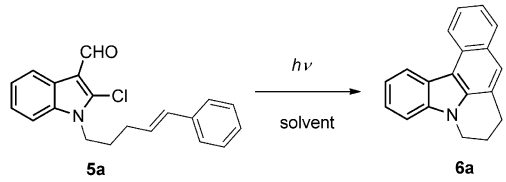


Scheme 3. Photochemical reactions of 3-acyl-2-halo-1-(ω-phenylalkenyl)indoles.

Results and Discussion

We first investigated the effect of solvents on the photoreaction of 2-chloro-1-(5-phenylpent-4-enyl)indole-3-carbaldehyde (**5a**, Table 1). It was found that **5a** could react in all selected solvents to afford the cyclization product **6a**. However, the conversion of **5a** and the yield of **6a** depended on the solvents. In CH_2Cl_2, the conversion of **5a** and the yield of **6a** were relatively low, because the solution became

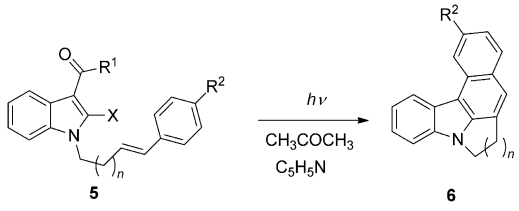
Table 1. Photoreaction of **5a** in different solvents and additives.[a]



Entry	Solvent	*t* [h]	Conversion [%][b]	Yield [%][c]
1	CH_2Cl_2	8	81	80
2	Me_2CO	8	92	85
3	CH_2Cl_2/pyridine	12	90	87
4	Me_2CO/pyridine	12	99	96
5	MeCN/pyridine	15	88	87

[a] **5a** (0.3 mmol) was dissolved in solvent (25 mL) or pyridine (0.1 mL). The solution was irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) under argon at ambient temperature. [b] Conversion was calculated on the basis of substrate. [c] Yield of isolated products based on consumed substrate.

Table 2. Photoreaction of 3-acyl-2-halo-1-(ω-phenylalkenyl)indoles.[a]



Entry	Substrate	X	*n*	R^1	R^2	*t* [h]	Conversion [%][b]	Product	Yield [%][c]
1	**5a**	Cl	2	H	H	12	99	**6a**	96
2	**5b**	Br	2	H	H	12	96	**6a**	95
3	**5c**	I	2	H	H	30	76	**6a**	92
4	**5d**	Cl	2	H	CH_3	12	96	**6d**	90
5	**5e**	Cl	2	H	OCH_3	12	94	**6e**	91
6	**5f**	Cl	2	H	Cl	12	98	**6f**	96
7	**5g**	Cl	2	H	F	12	98	**6g**	97
8	**5h**	Br	2	H	Cl	12	96	**6f**	95
9	**5i**	Cl	2	H	NO_2	24	0	**6i**	n.r.[d]
10	**5j**	Cl	2	CH_3	OCH_3	16	92	**6e**	91
11	**5k**	Cl	2	CH_3	Cl	16	94	**6f**	95
12	**5l**	Cl	2	CH_3	F	16	96	**6g**	92
13	**5m**	Cl	3	H	H	18	90	**6m**	89
14	**5n**	Cl	3	H	Cl	18	92	**6n**	91
15	**5o**	Cl	3	H	F	18	92	**6o**	93
16	**5p**	Cl	3	CH_3	F	24	92	**6o**	91
17	**5q**	Cl	4	H	H	48	90	**6q**	86
18	**5r**	Cl	1	H	H	12	94	**6r**	92
19	**5s**	Cl	1	CH_3	H	18	90	**6r**	90
20	**5t**	Cl	1	H	CH_3	18	92	**6t**	88
21	**5u**	Cl	1	CH_3	CH_3	24	90	**6t**	86
22	**5v**	Cl	1	H	OCH_3	36	92	**6v**	83
23	**5w**	Cl	1	CH_3	OCH_3	36	91	**6v**	81
24	**5x**	Cl	1	H	Cl	12	94	**6x**	91
25	**5y**	Cl	1	CH_3	Cl	16	92	**6x**	90

[a] **5a**–**y** (0.3 mmol) was dissolved in dry acetone (25 mL) containing pyridine (0.1 mL). The solution was irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) under argon at ambient temperature. [b] Conversion was calculated on the basis of substrate. [c] Yield of isolated products based on consumed substrate. [d] No reaction.

dark in a short time; whereas, in acetone a little improvement was observed. This result may be derived from the sensitization effect of acetone to **5a** because the E_T value of acetone is 326 kJ mol^{-1},[9a] which is higher than that of 2-chloroindole-3-carbaldehyde (E_T = 275 kJ mol^{-1}).[9b] However, the conversion of **5a** and the yield of **6a** were increased by the addition of base, such as pyridine, because the solution could be irradiated for a much longer time without becoming dark as pyridine retarded the oligomerization of indole derivatives induced by HCl and light. Comparatively, the reaction was more efficient in acetone with the addition of pyridine than in other solvents as shown in Table 1. Therefore, acetone with addition of pyridine was selected as the medium for the investigation of the photoreactions of all substrates.

In order to investigate the effects of the substrate structures on the photoreaction efficiency, other similar substrates **5b**–**y** with different substituents on both the indolyl and phenyl groups and tethers were synthesized and examined under the same photoreaction conditions. All of the substrates except **5i** gave the corresponding cyclization products **6** in moderate to high yields as shown in Table 2. It was found that the substituents on both the indolyl and phenyl rings and tethers all had a large influence on the photoreaction efficiency and the yields of product **6**. Comparatively, the conversion of the photoreaction of 2-chloro-1-(5-phenylpent-4-enyl)indole-3-carbaldehyde (**5a**), 2-bromo-1-(5-phenylpent-4-enyl)indole-3-carbaldehyde (**5b**) and 2-iodo-1-(5-phenylpent-4-enyl)indole-3-carbaldehyde (**5c**) decreased gradually within the same irradiation time. An electron-withdrawing group on the phenyl ring (e.g. Cl, F) in **5f**–**g** (Table 2, Entries 6 and 7) increased both the conversion of **5f**–**g** and the yields of **6f**–**g** compared to those with an electron-donating group on the phenyl ring (e.g. CH_3, OCH_3) in **5d** and **5e** (Table 2, Entries 4 and 5). However, for the substrate with an NO_2 group on the phenyl ring (Table 2, Entry 9) no desired product was obtained. The substrates with short tethers (**5r** and **5a**, n = 1 and 2, respectively) reacted more easily to form five- and six-membered rings (**6r** and **6a**) than those with long tethers (**5m** and **5q**, n = 3 and 4, respectively) to form seven- and eight-membered rings (**6m** and **6q**). Despite all these differences, the photoreactions of all these substrates gave fused benzo[*c*]carbazoles in high to excellent yields. The products were fully identified by ^{1}H and ^{13}C NMR spectroscopy and MS, and the structure of **6f** was further confirmed by X-ray crystallography (Figure 1).

Furthermore, to expand the scope of this reaction, we investigated the photoreaction of 3-acyl-2-halo-1-(ω-furylalkenyl)indoles. It was found that, under optimized conditions, **7a**–**d** were converted into the corresponding cyclization products **8a**–**c** in moderate to good yields as depicted in Table 3. Comparatively, the six-membered ring product **8c** was more easily formed than the five-membered compound **8a**. The conversion of the photoreaction of 3-formylindole derivatives (Table 3, Entries 1 and 3) was higher than that of 3-acetylindole derivatives (Table 3, Entries 2 and 4).

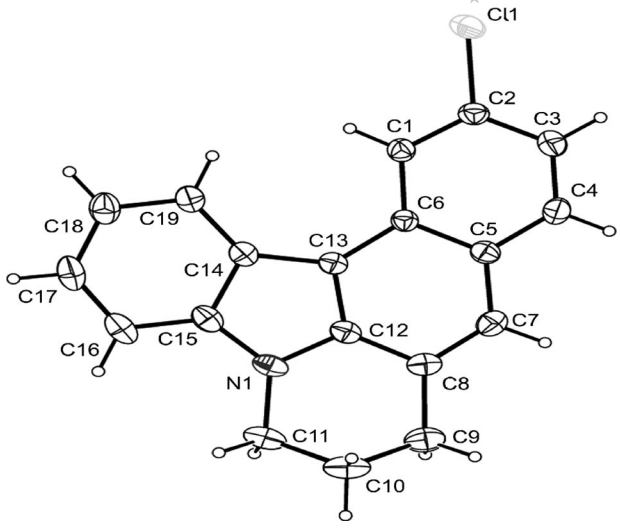
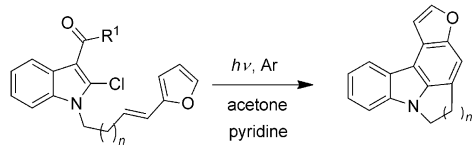


Figure 1. X-ray crystal structure of **6f**.

Table 3. Photoreaction of 3-acyl-2-chloro-1-(ω-furanylalkenyl)-indoles.[a]

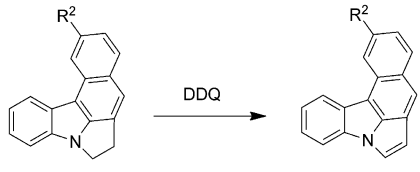


7 R^1 = H, CH_3; n = 1, 2 — **8** n = 1, 2

Entry	Substrate	n	R^1	t [h]	Conversion [%][b]	Product	Yield [%][c]
1	**7a**	1	H	48	89	**8a**	80
2	**7b**	1	CH_3	60	82	**8a**	65
3	**7c**	2	H	16	97	**8c**	95
4	**7d**	2	CH_3	24	92	**8c**	90

[a] **7a**–**d** (0.3 mmol) was dissolved in dry acetone (25 mL) containing pyridine (0.1 mL). The solution was irradiated at $\lambda > 300$ nm with a medium-pressure mercury lamp (500 W) under argon at ambient temperature. [b] Conversion was calculated on the basis of substrate. [c] Yield of isolated products based on consumed substrate.

Table 4. Aromatization of five-membered benzo[*c*]carbazoles **6r**, **6t**, and **6x**.[a]



Entry	Substrate	R^2	t [h]	Conversion [%][b]	Product	Yield [%][c]
1	**6r**	H	12	98	**9r**	96
2	**6t**	CH_3	12	82	**9t**	83
3	**6x**	Cl	12	96	**9x**	95

[a] **6r**–**x** (0.3 mmol) was dissolved in dry CH_2Cl_2 (25 mL), and the solution was stirred at room temperature. [b] Conversion was calculated on the basis of substrate. [c] Yield of isolated products based on consumed substrate.

We then tried the aromatization of the photoreaction products **6r**, **6t**, and **6x** by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The results showed that these five-membered ring-fused benzo[*c*]carbazoles were readily oxidized by DDQ at room temperature to afford aromatic products **9r**–**x** in moderate to high yields (Table 4).

Conclusions

An efficient procedure for the synthesis of fused benzo[*c*]carbazoles has been achieved in moderate to high yields by a one-pot intramolecular photochemical annulation of 3-acyl-2-haloindoles with tethered styrenes in the presence of pyridine. The fused benzo[*c*]carbazoles were formed by two sequential photocyclization reactions, namely, intramolecular photoinduced electron-transfer coupling of 3-acyl-2-haloindoles with styrenes and deacylative 6π-electrocyclic reactions.

Experimental Section

General Procedure for Photochemical Reactions: Substrate **5a** (0.097 g, 0.3 mmol) was dissolved in dry acetone (25 mL) containing pyridine (0.1 mL). 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 had been 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 product **6a**.

General Procedure for the DDQ Oxidation of Five-Membered Fused Benzo[*c*]carbazoles: To a solution of the substrate in CH_2Cl_2 (15 mL) was added DDQ, and the mixture was stirred at room temperature for 12 h. An aqueous saturated $NaHCO_3$ solution (10 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The reaction mixture was purified by flash chromatography (hexane/EtOAc) to afford the desired product.

7,8-Dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (6a): Colorless solid. M.p. 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, J = 8.0 Hz, 1 H), 8.51 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.67 (t, J = 8.0 Hz, 1 H), 7.51 (s, 1 H), 7.44–7.46 (m, 2 H), 7.40 (t, J = 7.2 Hz, 1 H), 7.33–7.38 (m, 1 H), 4.23 (t, J = 6.0 Hz, 2 H), 3.11 (t, J = 6.0 Hz, 2 H), 2.24–2.30 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 135.8, 129.4, 128.9, 128.7, 125.7, 123.6, 123.4, 123.2, 122.94, 122.90, 122.4, 122.0, 119.5, 112.6, 108.8, 41.1, 25.5, 22.5 ppm. MS: *m*/*z* (%) = 257 (100), 241 (7.0), 228 (9.1), 128 (16.9), 114 (7.6), 100 (6.9), 39 (9.5). ESI-HRMS: calcd. for $[C_{19}H_{15}N + H]^+$ 258.1277; found 258.1276. $C_{19}H_{15}N$ (257.33): calcd. C 88.68, H 5.88, N 5.44; found C 88.74, H 5.84, N 5.42.

7,8-Dihydro-12-methyl-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (6d): Colorless solid. M.p. 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 8.0 Hz, 1 H), 8.45 (s, 1 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.44–7.52 (m, 3 H), 7.36 (t, J = 7.2 Hz, 1 H), 7.25 (t, J = 5.6 Hz, 1 H), 4.32 (t, J = 6.0 Hz, 2 H), 3.17 (t, J = 6.0 Hz, 2 H), 2.65 (s, 3 H), 2.32–2.38 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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, 22.1 ppm. MS: *m*/*z* (%) = 271 (100), 254 (22.9), 149 (21.2), 121 (24.4), 40 (55.7). ESI-HRMS: calcd. for $[C_{20}H_{17}N + H]^+$ 272.1444; found 272.1442. $C_{20}H_{17}N$ (271.36): calcd. C 88.52, H 6.31, N 5.16; found C 88.59, H 6.28, N 5.12.

7,8-Dihydro-12-methoxy-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (6e): Colorless solid. M.p. 146–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.0 Hz, 1 H), 7.99 (d, J = 2.4 Hz, 1 H), 7.82 (d, J = 8.8 Hz, 1 H), 7.45–7.51 (m, 3 H), 7.36 (t, J = 6.8 Hz, 1 H), 7.08 (dd, J = 8.8, 2.4 Hz, 1 H), 4.31 (t, J = 6.0 Hz, 2 H), 4.06 (s, 3 H), 3.15 (t, J = 6.0 Hz, 2 H), 2.30–2.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 138.7, 136.4, 130.1, 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 ppm. MS: *m*/*z* (%) = 287 (100), 244 (44.7), 143 (20.8), 120 (14.9), 39 (4.2). ESI-HRMS: calcd. for $[C_{20}H_{17}NO + H]^+$ 288.1383; found 288.1381. $C_{20}H_{17}NO$ (287.36): calcd. C 83.59, H 5.96, N 4.87; found C 83.67, H 5.91, N 4.84.

12-Chloro-7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (6f): Colorless solid. M.p. 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 2.0 Hz, 1 H), 8.45 (d, J = 8.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.47–7.48 (m, 3 H), 7.38 (td, J = 4.8, 3.2 Hz, 1 H), 7.34 (td, J = 8.8, 2.0 Hz, 1 H), 4.27 (t, J = 6.0 Hz, 2 H), 3.13 (t, J = 6.0 Hz, 2 H), 2.28–2.34 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 136.3, 131.5, 130.1, 129.6, 127.6, 124.0, 123.1, 123.1, 123.04, 122.9, 122.1, 121.8, 119.8, 111.9, 108.9, 41.2, 25.4, 22.4 ppm. MS: *m*/*z* (%) = 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: calcd. for $[C_{19}H_{14}ClN + H]^+$ 292.0888; found 292.0886. $C_{19}H_{14}ClN$ (291.78): calcd. C 78.21, H 4.84, N 4.80; found C 78.28, H 4.81, N 4.76. CCDC-784302 (for **6f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

12-Fluoro-7,8-dihydro-6*H*-benzo[*c*]pyrido[1,2,3-*lm*]carbazole (6g): Colorless solid. M.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.0 Hz, 1 H), 8.25 (d, J = 8.4 Hz, 1 H), 7.89 (dd, J = 8.8, 6.4 Hz, 1 H), 7.47–7.54 (m, 3 H), 7.39 (td, J = 6.8, 1.6 Hz, 1 H), 7.17 (td, J = 8.8, 2.4 Hz, 1 H), 4.33 (t, J = 6.0 Hz, 2 H), 3.18 (t, J = 6.0 Hz, 2 H), 2.33–2.39 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (d, J = 243.0 Hz), 138.7, 136.4, 130.7 (d, J = 10.0 Hz), 129.7 (d, J = 9.0 Hz), 126.2, 123.8, 123.3, 123.1, 122.0 (d, J = 3.0 Hz), 121.6, 119.8, 112.4 (d, J = 5.0 Hz), 111.8 (d, J = 24.0 Hz), 108.9, 107.2 (d, J = 22.0 Hz), 41.3, 25.4, 22.5 ppm. MS: *m*/*z* (%) = 275 (100), 149 (8.4), 137 (14.3), 126 (7.8), 40 (40.9). ESI-HRMS: calcd. for $C_{19}H_{14}FN + H]^+$ 276.1183; found 276.1186. $C_{19}H_{14}FN$ (275.32): calcd. C 82.89, H 5.13, N 5.09; found C 82.85, H 5.15, N 5.12.

6,7,8,9-Tetrahydrobenzo[*c*]azepino[1,2,3-*lm*]carbazole (6m): Colorless solid. M.p. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 8.0 Hz, 1 H), 8.57 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.63 (td, J = 7.6, 0.8 Hz, 1 H), 7.53–7.56 (m, 2 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.42 (t, J = 7.2 Hz, 1 H), 7.36 (t, J = 7.2 Hz, 1 H), 4.55 (t, J = 5.2 Hz, 2 H), 3.36 (t, J = 5.2 Hz, 2 H), 2.21–2.30 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3, 139.4, 129.3, 128.9, 128.3, 128.1, 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 ppm. MS: *m*/*z* (%) = 271 (100), 254 (12.2), 242 (13.8), 136 (14.1), 127 (13.1), 41 (16.7). ESI-HRMS: calcd. for $[C_{20}H_{17}N + H]^+$ 272.1434; found 272.1432. $C_{20}H_{17}N$ (271.36): calcd. C 88.52, H 6.31, N 5.16; found C 88.59, H 6.28, N 5.12.

13-Chloro-6,7,8,9-tetrahydrobenzo[*c*]azepino[1,2,3-*lm*]carbazole (6n): Colorless solid. M.p. 92–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$):

δ = 8.66 (s, 1 H), 8.50 (d, J = 8.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.48–7.54 (m, 3 H), 7.34–7.39 (m, 2 H), 4.53 (t, J = 5.6 Hz, 2 H), 3.32 (t, J = 5.6 Hz, 2 H), 2.19–2.28 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 139.8, 131.7, 129.6, 129.4, 128.3, 127.5, 125.6, 124.1, 123.5, 123.3, 122.0, 121.7, 119.9, 114.8, 109.4, 43.5, 31.7, 27.8, 26.1 ppm. MS: *m*/*z* (%) = 307 (32.5), 305 (100), 254 (9.2), 241 (16.6), 152 (7.1), 127 (13.8), 41 (14.1). ESI-HRMS: calcd. for $[C_{20}H_{16}ClN + H]^+$ 306.1044; found 306.1047. $C_{20}H_{16}ClN$ (305.81): calcd. C 78.55, H 5.27, N 4.58; found C 78.52, H 5.28, N 4.55.

13-Fluoro-6,7,8,9-tetrahydrobenzo[*c*]azepino[1,2,3-*lm*]carbazole (6o): Colorless solid. M.p. 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.0 Hz, 1 H), 8.31 (dd, J = 11.2, 2.4 Hz, 1 H), 7.86 (dd, J = 8.8, 6.0 Hz, 1 H), 7.52–7.55 (m, 2 H), 7.49 (td, J = 7.2, 1.2 Hz, 1 H), 7.37 (td, J = 8.0, 0.8 Hz, 1 H), 7.18 (td, J = 8.4, 2.4 Hz, 1 H), 4.55 (t, J = 6.0 Hz, 2 H), 3.34 (t, J = 6.0 Hz, 2 H), 2.21–2.29 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (d, J = 243.0 Hz), 140.2, 139.9, 132.4 (d, J = 30.0 Hz), 130.3 (d, J = 9.0 Hz), 127.1, 126.1, 125.7, 124.0, 123.5, 121.5, 119.9, 113.4 (d, J = 5.0 Hz), 112.3 (d, J = 24.0 Hz), 109.4, 107.1 (d, J = 21.0 Hz), 43.6, 31.7, 27.9, 26.2 ppm. MS: *m*/*z* (%) = 289 (100), 274 (15.9), 149 (16.4), 127 (19.5), 40 (66.7). ESI-HRMS: calcd. for $[C_{20}H_{16}FN + H]^+$ 290.1340; found 290.1345. $C_{20}H_{16}FN$ (289.35): calcd. C 83.02, H 5.57, N 4.84; found C 83.05, H 5.56, N 4.81.

6,7,8,9-Tetrahydro-10*H*-benzo[*c*]azocino[1,2,3-*lm*]carbazole (6q): Colorless solid. M.p. 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 8.4 Hz, 1 H), 8.63 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.66 (td, J = 8.0, 0.8 Hz, 1 H), 7.57 (s, 1 H), 7.44–7.55 (m, 3 H), 7.39 (t, J = 6.8 Hz, 1 H), 4.82 (br., 2 H), 3.51 (br., 2 H), 2.01–2.09 (m, 4 H), 1.41 (br., 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 ppm. MS: *m*/*z* (%) = 285 (100), 254 (12.8), 241 (8.4), 230 (12.7), 127 (5.5). ESI-HRMS: calcd. for $[C_{21}H_{19}N + H]^+$: 286.1590; found 286.1593. $C_{21}H_{19}N$ (285.39): calcd. C 88.38, H 6.71, N 4.91; found C 88.45, H 6.67, N 4.88.

6,7-Dihydrobenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (6r): Colorless solid. M.p. 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.0 Hz, 1 H), 8.35 (d, J = 8.0 Hz, 1 H), 7.91 (d, J = 8.0 Hz, 1 H), 7.60 (td, J = 8.0, 1.2 Hz, 1 H), 7.36–7.46 (m, 4 H), 7.32 (td, J = 8.0, 1.2 Hz, 1 H), 4.51 (t, J = 7.2 Hz, 2 H), 3.83 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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, 110.56, 107.5, 47.6, 33.2 ppm. MS: *m*/*z* (%) = 243 (100), 213 (5.5), 120 (19.2), 106 (8.6), 93 (4.6), 51 (4.2). ESI-HRMS: calcd. for $[C_{18}H_{13}N + H]^+$ 244.1121; found 244.1125. $C_{18}H_{13}N$ (243.31): calcd. C 88.86, H 5.39, N 5.76; found C 88.89, H 5.40, N 5.72.

6,7-Dihydro-11-methylbenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (6t): Colorless solid. M.p. 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, J = 7.6 Hz, 1 H), 8.22 (s, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.43–7.45 (m, 2 H), 7.39 (td, J = 8.0, 1.2 Hz, 1 H), 7.32 (td, J = 8.0, 0.8 Hz, 1 H), 7.21 (dd, J = 8.4, 1.6 Hz, 1 H), 4.53 (t, J = 7.2 Hz, 2 H), 3.83 (t, J = 7.2 Hz, 2 H), 2.62 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 138.2, 135.6, 130.3, 129.8, 129.4, 128.6, 124.9, 124.1, 123.1, 122.9, 122.5, 120.4, 119.2, 110.4, 107.2, 47.7, 33.2, 21.9 ppm. MS: *m*/*z* (%) = 257 (100), 227 (35.5), 120 (49.6), 106 (10.6), 93 (24.3), 51 (4.2). ESI-HRMS: calcd. for $[C_{19}H_{15}N + H]^+$ 258.1277; found 258.1274. $C_{19}H_{15}N$ (257.33): calcd. C 88.68, H 5.88, N 5.44; found C 88.64, H 5.89, N 5.47.

6,7-Dihydro-11-methoxybenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (6v): Colorless solid. M.p. 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.0 Hz, 1 H), 7.83 (d, J = 9.2 Hz, 1 H), 7.81 (s, 1 H), 7.47–7.49 (m, 2 H), 7.41 (t, J = 7.2 Hz, 1 H), 7.33 (t, J = 7.2 Hz, 1 H), 7.05 (dd, J = 8.8, 2.4 Hz, 1 H), 4.61 (t, J = 7.2 Hz, 2 H), 4.05 (s, 3 H), 3.89 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 150.3, 138.3, 130.9, 130.8, 128.6, 127.0, 123.4, 123.1, 122.2, 120.5, 119.3, 112.6, 110.5, 107.3, 104.2, 55.4, 47.8, 33.1 ppm. MS: *m*/*z* (%) = 273 (100), 242 (85.7), 120 (29.2), 106 (8.6), 93 (14.6), 51 (9.2). ESI-HRMS: calcd. for $[C_{19}H_{15}NO + H]^+$ 274.1227; found 274.1229. $C_{19}H_{15}NO$ (273.33): calcd. C 83.49, H 5.53, N 5.12; found C 83.46, H 5.55, N 5.10.

11-Chloro-6,7-dihydrobenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (6x): Colorless solid. M.p. 165–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 2.0 Hz, 1 H), 8.30 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 1 H), 7.40–7.47 (m, 3 H), 7.30–7.36 (m, 2 H), 4.57 (t, J = 7.2 Hz, 2 H), 3.86 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 138.1, 131.6, 130.8, 130.4, 130.3, 128.1, 126.2, 123.6, 122.6, 122.42, 122.41, 120.2, 119.6, 110.6, 106.8, 47.7, 33.2 ppm. MS: *m*/*z* (%) = 279 (33.2), 277 (100), 242 (95.5), 120 (39.2), 106 (10.6), 51 (4.2). ESI-HRMS: calcd. for $[C_{18}H_{12}ClN + H]^+$ 278.0731; found 278.0735. $C_{18}H_{12}ClN$ (277.75): calcd. C 77.84, H 4.35, N 5.04; found C 77.86, H 4.37, N 5.01.

5,6-Dihydrofuro[2,3-*c*]pyrrolo[1,2,3-*lm*]carbazole (8a): Colorless solid. M.p. 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.0 Hz, 1 H); 7.76 (s, 1 H), 7.40–7.44 (m, 3 H), 7.25 (d, J = 9.6 Hz, 1 H), 7.17 (s, 1 H), 4.63 (t, J = 7.2 Hz, 2 H), 3.93 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 148.0, 144.3, 139.2, 127.4, 124.0, 122.4, 121.0, 119.0, 118.5, 110.3, 106.6, 105.6, 105.4, 48.3, 33.7 ppm. MS: *m*/*z* (%) = 233 (100), 204 (15.0), 176 (9.3), 149 (4.3), 108 (11.1), 39 (11.2). ESI-HRMS: calcd. for $[C_{16}H_{11}NO + H]^+$ 234.0914; found 234.0917. $C_{16}H_{11}NO$ (233.27): calcd. C 82.38, H 4.75, N 6.00; found C 82.35, H 4.76, N 6.03.

5,6-Dihydro-7*H*-furo[2,3-*c*]pyrido[1,2,3-*lm*]carbazole (8c): Colorless solid. M.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.0 Hz, 1 H); 7.75 (d, J = 2.0 Hz, 1 H), 7.43–7.48 (m, 2 H), 7.39 (s, 1 H), 7.24–7.29 (m, 2 H), 4.30 (t, J = 6.0 Hz, 2 H), 3.17 (t, J = 6.0 Hz, 2 H), 2.31–2.37 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 144.2, 139.3, 134.0, 124.4, 122.3, 121.4, 118.5, 118.4, 118.2, 111.9, 108.3, 107.2, 105.3, 41.2, 25.6, 22.7 ppm. MS: *m*/*z* (%) = 247 (100), 218 (15.0), 190 (7.3), 163 (7.3), 108 (11.1), 39 (11.2). ESI-HRMS: calcd. for $[C_{17}H_{13}NO + H]^+$ 248.1070; found 248.1074. $C_{17}H_{13}NO$ (247.30): calcd. C 82.57, H 5.30, N 5.66; found C 82.54, H 5.32, N 5.69.

Benzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (9r): Colorless solid. M.p. 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 8.4 Hz, 1 H), 8.42 (d, J = 7.6 Hz, 1 H), 8.28 (s, 1 H), 8.25 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 3.2 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.72 (td, J = 6.8, 1.2 Hz, 1 H), 7.54 (td, J = 6.8, 1.2 Hz, 1 H), 7.49 (td, J = 7.6, 1.2 Hz, 1 H), 7.42 (td, J = 7.6, 1.2 Hz, 1 H), 6.95 (d, J = 3.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 137.8, 133.0, 131.11, 131.10, 130.8, 127.8, 126.3, 126.1, 125.1, 123.9, 123.5, 122.8, 122.7, 122.0, 121.9, 111.5, 109.4 ppm. MS: *m*/*z* (%) = 241 (100), 225 (9.1), 128 (36.9), 114 (7.6), 100 (6.9), 39 (9.5). ESI-HRMS: calcd. for $[C_{18}H_{11}N + H]^+$ 242.0966; found 242.0968. $C_{18}H_{11}N$ (241.29): calcd. C 89.60, H 4.60, N 5.81; found C 89.64, H 4.59, N 5.78.

11-Methylbenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (9t): Colorless solid. M.p. 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 7.2 Hz, 1 H), 8.41 (s, 1 H), 8.24 (s, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 3.2 Hz, 1 H), 7.77 (d, J = 7.6 Hz, 1 H), 7.48 (td, J = 7.6, 1.2 Hz, 1 H), 7.42 (td, J = 7.6, 1.2 Hz, 1 H), 7.37 (dd, J = 8.4, 1.6 Hz, 1 H), 6.93 (d, J = 3.2 Hz, 1 H), 2.69 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 137.7, 136.1, 131.2, 130.8,

128.7, 128.1, 125.9, 125.1, 124.8, 123.5, 123.1, 122.0, 121.8, 121.7, 111.4, 110.8, 109.4, 22.2 ppm. MS: *m*/*z* (%) = 255 (100), 239 (11.1), 128 (46.9), 114 (9.6), 100 (12.9), 39 (11.5). ESI-HRMS: calcd. for $[C_{19}H_{13}N + H]^+$ 256.1121; found 256.1123. $C_{19}H_{13}N$ (255.32): calcd. C 89.38, H 5.13, N 5.49; found C 89.35, H 5.11, N 5.53.

11-Chlorobenzo[*c*]pyrrolo[1,2,3-*lm*]carbazole (9x): Colorless solid. M.p. 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 2.0 Hz, 1 H), 8.37 (d, J = 7.6 Hz, 1 H), 8.23 (s, 1 H), 8.15 (d, J = 8.8 Hz, 1 H), 7.91 (d, J = 3.2 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.41–7.52 (m, 3 H), 6.93 (d, J = 3.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 137.8, 132.3, 132.3, 132.0, 131.1, 130.3, 128.1, 126.6, 125.4, 123.6, 123.4, 122.9, 122.2, 121.8, 111.5, 110.9, 109.5 ppm. MS: *m*/*z* (%) = 277 (32.3), 275 (100), 128 (36.9), 114 (7.6), 100 (6.9), 39 (9.5). ESI-HRMS: calcd. for $[C_{18}H_{10}ClN + H]^+$ 276.0575; found 276.0578. $C_{18}H_{10}ClN$ (275.74): calcd. C 78.41, H 3.66, N 5.08; found C 78.44, H 3.63, N 5.05.

Supporting Information (see footnote on the first page of this article): General procedures for the preparation of the photoreaction substrates and copies of the ^{1}H and ^{13}C NMR spectra for all new compounds.

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