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Domino Carbocationic Rearrangement of Aryl-2-(1-*N*-methyl/benzyl-3-indolyl)cyclopropyl Ketones: A Serendipitous Route to 1*H*-Cyclopenta[*c*]carbazole Framework

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Abstract: Aryl-2-(*N*-methyl/benzyl-3-indolyl)cyclopropyl ketones **2a**−**m** are shown to undergo a novel unexpected domino carbocationic rearrangement in the presence of $SnCl_4$/CH_3NO_2 yielding 2-aroyl-3-aryl-1*H*-cyclopenta[*c*]carbazoles **3a**−**m** in good yields. The possible mechanistic pathway for this interesting transformation involves a series of cascade events, (a) electrophilic ring opening of cyclopropyl ketone, (b) intermolecular enol capture of the resulting zwitterionic intermediate, (c) electrophilic dimerization of indole moieties to give tetrahydrocarbazole intermediate and its subsequent aromatization by elimination of an indole moiety and dehydrogenation, and (d) intramolecular aldol condensation of the side chain to give a cyclopentene ring. The overall transformation involves formation of three carbon−carbon bonds along with a fused benzene and a substituted cyclopentene ring in one-pot operation from simple indole precursors.

Cationic olefinic cyclizations initiated by acid-induced ring opening of rigid or nonrigid cyclopropyl ketones followed by intramolecular participation of suitably disposed olefinic centers are shown to be useful synthetic transformations in organic chemistry.[1,2] The possibility of initiating a tandem or domino carbocationic cyclization involving olefinic participation and efficient trapping of the resulting carbocation by the enol generated via acylcyclopropane ring opening has also been demonstrated.[2c,3] This strategy has been successfully employed by Corey and co-workers in the synthesis of (±)-cedrene and (±)-cedrol.[4] Murphy has reported simple routes to 1-aryltetralones,[5] related lignans,[6] and other polycyclic carbon skeletons[7] via Lewis acid induced ring opening of arylcyclopropyl ketones and endocyclic capture of the resulting formal or incipient carbocation by an aryl group. Of particular interest are donor- and acceptor-substituted cyclopropyl ketones that undergo facile ring opening and cyclization by means of stabilized zwitterionic intermediates.[8] We have previously described in a series of papers a novel carbocationic domino process that relies upon initial electrophilic ring opening of 2-aryl(or styryl)-cyclopropyl[bis(methylthio)methylene]alkyl ketones or carbinols and subsequent intramolecular 5-*exo*-*trig* capture of the resulting carbocation by electron-rich bis-(methylthio)methylene double bond to give a cyclopentane ring bearing a stable bis(methylthio)methyl carbocationic side chain.[9] Subsequent trapping of this carbonium ion by electron-rich pendant arene or olefinic nucleophiles affords cyclopentanoindane,[10a,b] diquinane,[10b] bicyclo[3.2.1]octane,[10c] or 1-arylindane[10d] frameworks involving a series of rearrangement and termination events. We have also reported earlier the synthesis and Lewis acid induced rearrangement of novel push−pull cyclopropyl ketones derived from vinylogous oxoketene dithioacetals furnishing substituted and spirocyclopentenes in good yields.[11] Recently, we have developed a highly regio- and stereoselective synthesis of polyene esters via an interesting even number 1,4- to 1,12-reductive and alkylative carbonyl transposition strategy involving these novel push−pull cyclopropyl ketones.[12] In the course of these studies, we became interested in examining Lewis acid induced rearrangement of aryl 2-(*N*-methyl/benzyl-3-indolyl)cyclopropyl ketones of the general structure **2** that, to our surprise, yielded novel 2,3-substituted 1*H*-cyclopenta[*c*]carbazoles **3** in good yields (Scheme 1). We report in this paper the results of this new domino carbocationic process that entails a series of cascade events involving intermolecular trapping of zwitterionic intermediate with concomitant formation of three carbon−carbon bonds along with a fused benzene and substituted

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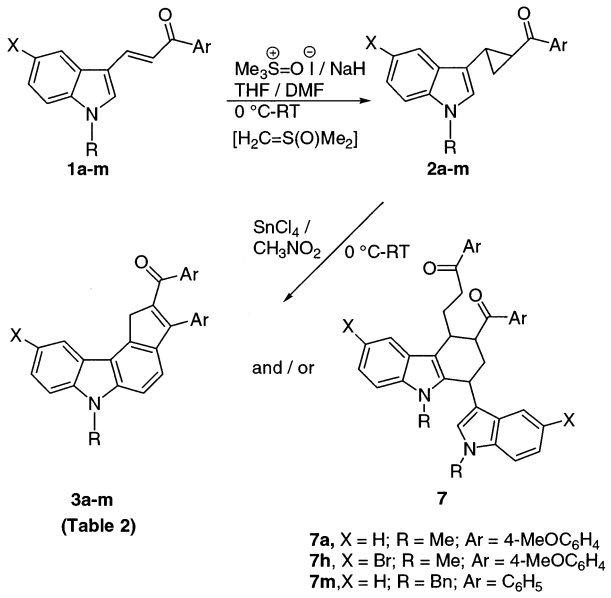
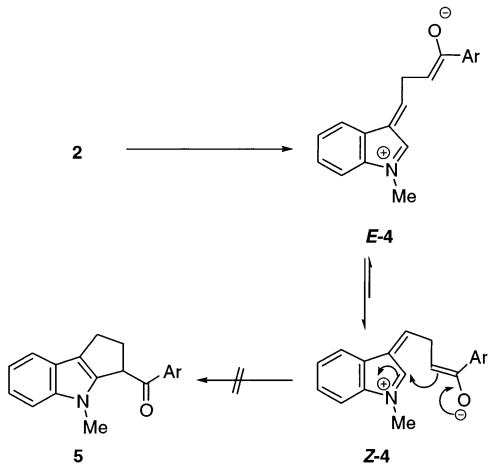
SCHEME 1



SCHEME 2



cyclopentene ring in a one-pot operation from simple indole precursors.

The desired aryl-2-(*N*-methyl/benzyl-3-indolyl)cyclopropyl ketones **2a**−**m** were readily obtained in nearly quantitative yields by cyclopropanation of the respective 1-aryl-3-(3-indolyl)-2-propen-1-ones **1a**−**m** with dimethylsulfoxonium methylide generated from the corresponding sulfonium salts in the presence of sodium hydride in THF/DMF (Scheme 1, Table 2). These cyclopropyl ketones were pure enough for their characterization by ^{1}H and ^{13}C NMR spectra and used as such for the further transformation.[13]

The ketone **2a** was subjected to electrophilic ring opening in the presence of common Lewis acids such as $TiCl_4$, $BF_3.Et_2O$ or $SnCl_4$ in various solvents. It was envisaged that Lewis acid induced ring opening of **2**, which is further assisted by indole nitrogen lone pair, should initially produce a stable zwitterionic intermediate **4**. If the dipolar intermediate **4** has longer lifetime enough to isomerize to *Z*-**4**, there exists possibility of its intramolecular interception by the enol moiety leading to the formation of cyclopentano[*b*]indole **5** (Scheme 2). However, no cyclopentano-fused derivative such as **5a** (Ar = 4-$MeOC_6H_4$)-was observed from **2a** under the influence of various Lewis acids.

The only product formed in varying yields under these conditions was characterized as 2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-6-*N*-methyl-1*H*-cyclopenta[*c*]carbazole (**3a**) (Scheme 1). The structure of **3a** was confirmed with the help of spectral, analytical, and X-ray crystallographic data. Under optimized conditions, the rearrangement of **2a** to **3a** was found to be most facile and clean (in terms of yield and workup) with $SnCl_4$ in nitromethane affording **3a** in 60% yield after 5 h (Table 1, entry 1). However, when the same reaction was run for a shorter reaction time (0.5 h), workup of the reaction mixture yielded different product identified as the dimeric tetrahydrocarbazole derivative **7a** (62%) on the basis of its spectral and analytical data (Table 1, entry 2). We therefore carried out a detailed study of the rearrangement of **2a** with $SnCl_4$ with a view to get more information on the role of solvent polarity and substrate to $SnCl_4$ ratio on the product profile. These results are presented in the Table 1.

TABLE 1. $SnCl_4$-Induced Rearrangement of the Cyclopropyl Ketone 2a

entry	substrate	$SnCl_4$ (equiv)	solvent	time[a] (h)	yield[b] (%) **3a**	yield[b] (%) **7a**
1	**2a**	1.5	CH_3NO_2	5.0	60	
2	**2a**	1.5	CH_3NO_2	0.5		62
3	**2a**	0.5	CH_3NO_2	5.0	15	71
4	**2a**	1.0	CH_3NO_2	5.0	35	44
5	**2a**	2.0	CH_3NO_2	5.0	61	
6	**2a**	1.5	CH_2Cl_2	6.0	47	8
7	**2a**	1.5	C_6H_6	6.0	5	83

[a] Reactions were carried out at room temperature. [b] Isolated yield.

It is apparent from the above studies that the dimeric tetrahydrocarbazole **7a** is an intermediate in the formation of cyclopenta[*c*]carbazole **3a** from the cyclopropyl ketone **2a**. To further show the generality of the reaction, the rearrangement studies were extended to other substituted indolylcyclopropyl ketones **2b**−**l**, which were also transformed smoothly into the corresponding substituted cyclopenta[*c*]carbazoles **3b**−**l** in 57−69% yield when exposed to $SnCl_4/CH_3NO_2$ for 3−5 h (Table 2). No attempts were made to isolate dimeric tetrahydrocarbazole intermediates **7b**−**l** from these reactions except from the cyclopropyl ketones **2h**, which also afforded the tetrahydrocarbazole **7h** (72%) when reacted with $SnCl_4/CH_3NO_2$ for a shorter reaction time (0.5 h).[14] The rearrangement of the corresponding *N*-benzylindolyl cyclopropyl ketone **2m** to cyclopenta[*c*]carbazole **3m** required prolonged time (8 h) under identical conditions, whereas workup after 3 h afforded only the tetrahydrocarbazole dimer **7m** in 72% yield (Scheme 1).

The possible mechanism for the formation of the observed products **3** is shown in Scheme 3. The Lewis acid assisted ring opening of cyclopropyl ketones **2** produces expected zwitterionic intermediate **4**, which is further stabilized by delocalization of positive charge on

(13) Most of the cyclopropyl ketones **2a**−**l** were obtained as viscous liquids, whereas the corresponding *N*-benzylcyclopropyl ketone **2m** could be purified by recrystallization from hexanes−ethyl acetate to give analytically pure sample.

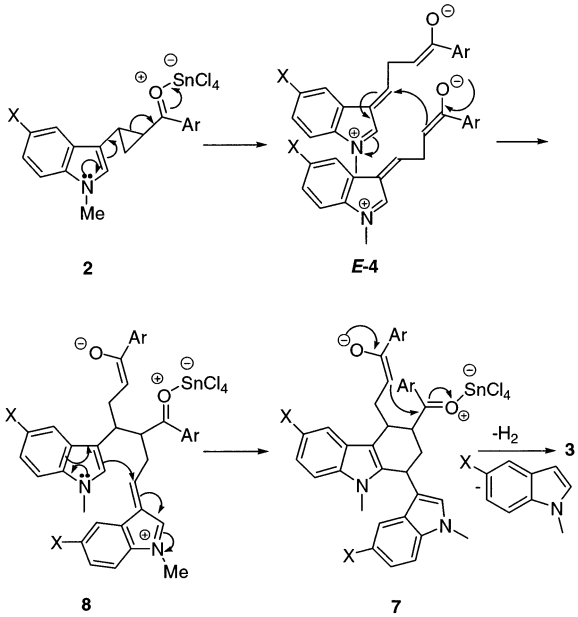
TABLE 2. 2,3-Substituted 1*H*-Cyclopenta[*c*]carbazole 3a−m

entry	1	2	X	Ar	R	3	time (h)	yield 3 (%)
1	**1a**	**2a**	H	4-$MeOC_6H_4$	Me	**3a**	5	60
2	**1b**	**2b**	H	C_6H_5	Me	**3b**	5	65
3	**1c**	**2c**	H	3,4-$(MeO)_2C_6H_3$	Me	**3c**	3	60
4	**1d**	**2d**	H	3,4-(methylenedioxy)C_6H_3	Me	**3d**	5	63
5	**1e**	**2e**	H	4-ClC_6H_5	Me	**3e**	3	61
6	**1f**	**2f**	H	2-thienyl	Me	**3f**	4	68
7	**1g**	**2g**	Br	C_6H_5	Me	**3g**	3	67
8	**1h**	**2h**	Br	4-$MeOC_6H_4$	Me	**3h**	5[a]	69
9	**1i**	**2i**	Br	3,4-(methylenedioxy)C_6H_3	Me	**3i**	5	68
10	**1j**	**2j**	MeO	C_6H_5	Me	**3j**	4	68
11	**1k**	**2k**	MeO	4-$MeOC_6H_4$	Me	**3k**	3	63
12	**1l**	**2l**	MeO	4-ClC_6H_5	Me	**3l**	5	57
13	**1m**	**2m**	H	C_6H_5	Bn	**3m**	8[b]	54

[a] Workup after 0.5 h gave tetrahydrocarbazole **7h** (72%). [b] Workup after 3 h gave only the tetrahydrocarbazole **7m** (72%).

indole ring. The intermediate **4** undergoes an interesting dimerization via intermolecular capture of one of the zwitterionic species by the enol functionality of the other affording the dimeric indole intermediate **8**.[15] Subsequent intramolecular trapping of the 3-indolylcarbinyl cation in the intermediate **8** by the electron-rich 2-position of the other indole ring leads to dimeric tetrahydrocarbazole intermediate **7**, which could be isolated in a few cases (**7a**, **7h**, and **7m**) under varying conditions (Table 2). The tetrahydrocarbazole intermediate **7** subsequently undergoes a series of events, i.e., (a) Lewis acid assisted elimination of indole,[16] (b) dehydrogenation of dihydrocarbazole, and (c) Lewis acid induced intramolecular Aldol condensation of suitably disposed carbonyl side chains leading to the formation of the observed cyclopenta[*c*]carbazoles **3**.[17]

SCHEME 3

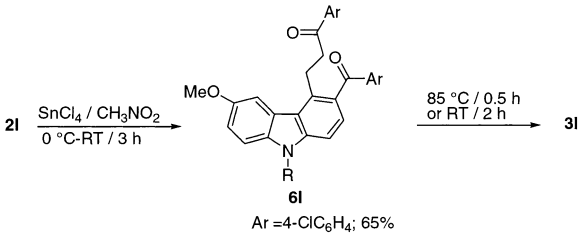


In summary, we have described a novel domino carbocationic rearrangement of aryl 2-(*N*-methyl/benzyl-3-indolyl)cyclopropyl ketones leading to unexpected formation of 2,3-substituted 1*H*-cyclopenta[*c*]carbazoles as most typical products in synthetically useful yields. Several interesting pathways are involved in the final disposition of the putative zwitterionic intermediate including an interesting intermolecular enol capture of zwitterionic intermediate, electrophilic dimerization along with the elimination of indole moiety and finally an intramolecular Aldol condensation to form an additional C−C bond and a cyclopentene ring. These observations suggest that a wide range of domino sequence[18] can be designed involving cationic ring opening and cyclization of appropriately substituted cyclopropyl ketones with diverse cationic olefinic trapping groups. Our efforts in this direction are underway and will be reported elsewhere.

Experimental Section

General Methods. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$, and TMS was used as an internal reference. Melting points are uncorrected. Chromatographic purification was conducted by column chromatography using 60−120 mesh silica gel obtained from Acme Synthetic Chemicals. X-ray crystallographic data was collected on a Stoe AED 2 diffractometer operating with graphite-monochromated Mo Kα (λ = 0.710 73 A) radiation using the $\omega - \theta$ scan technique. DMF was distilled over CaH_2 and stored over molecular sieves. THF was distilled over sodium/benzophenone prior to use. NaH (as 40% suspension in oil), $SnCl_4$ and nitromethane (AR grade) were purchased from standard firms and used directly. 1-*N*-Methylindole-3-aldehyde and the corresponding *N*-benzyl derivative were prepared according to a

(14) In one case, i.e., cyclopropyl ketone **2l**, workup of the reaction mixture after 3 h afforded the corresponding 3,4-disubstituted carbazole **6l** (65%), which is apparently formed by aromatization of the corresponding tetrahydrocarbazole dimer **7l** through dehydrogenation and elimination of the indole moiety. The carbazole **6l** was transformed into the corresponding cyclopenta[*c*]carbazole **3l** either by warming of the reaction mixture (85 °C, 0.5 h) or by further stirring (2 h) at room temperature.



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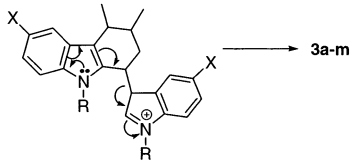
(16) In one case (**2k**), the 5-methoxyindole could be isolated in 10% yield. For acid induced elimination of indole: Stachel, S. J.; Nilges, M.; Van Vranken, D. L. *J. Org. Chem.* **1997**, *62*, 4756. The possible mechanism for elimination of indole can be shown as follows:



(17) The slower rate of the conversion of *N*-benzyltetrahydrocarbazole dimer **7m** to the corresponding cyclopenta[*c*]carbazole **3m** is probably due to bulkier *N*-benzyl group resisting elimination of *N*-benzylindole and intramolecular Aldol condensation steps.

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reported procedure.[19] The known[20] indole chalcones **1a**−**c**,**e** and the unknown **1d**,**1f**−**m** were prepared according to a literature procedure[21] in nearly quantitative yields.

General Procedure for the Preparation of Cyclopropyl Ketones (2a−m). A suspension of NaH (0.12 g, 2 mmol, 40%) and trimethylsulfoxonium iodide (0.26 g, 1.2 mmol) in THF/DMF (12 mL, 5:1) was stirred at 0 °C for 0.5 h under N_2 atmosphere. It was then brought to room temperature, and a solution of 1-aryl-3-(1-*N*-methyl/benzyl-3-indolyl)-2-propen-1-one **1** (1 mmol) in THF (2 mL) was added dropwise followed by further stirring for 15 min (monitored by TLC). The reaction mixture was poured into ice-cooled saturated NH_4Cl solution (20 mL) and extracted with chloroform (4 × 25 mL). The organic extracts were combined, washed with water (3 × 50 mL) and brine (1 × 25 mL), and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure to afford the crude cyclopropyl ketone **2**, which was pure enough for characterization by ^1H and ^{13}C NMR spectra.

1-Phenyl-2-(1-*N*-methyl-3-indolyl)cyclopropyl ketone (2b): yield 98% (0.27 g); viscous liquid; R_f 0.90 (9.5:0.5 benzene−EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (ddd, J = 7.8, 6.8, 3.7 Hz, 1H, CH), 1.93 (ddd, J = 8.9, 4.9, 3.6 Hz, 1H, CH), 2.79−2.81 (m, 1H, CH), 2.85 (ddd, J = 8.8, 4.6, 4.9 Hz, 1H, CH), 3.72 (s, 3H, NCH_3), 6.85 (s, 1H, ArH), 7.08 (t, J = 6.8 Hz, 1H, ArH), 7.21−7.29 (m, 2H, ArH), 7.43 (t, J = 7.3 Hz, 2H, ArH), 7.53 (t, J = 7.3 Hz, 1H, ArH), 7.59 (d, J = 8.0 Hz, 1H, ArH), 8.00−8.02 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 22.6, 27.9, 32.6, 109.3, 114.7, 118.9, 119.2, 121.9, 125.8, 127.9, 128.0, 128.5, 132.7, 137.0, 137.9, 199.2; MS (*m*/*z*) 275 (M^+, 11.2), 77 (100).

General Procedure for the $SnCl_4$-Induced Rearrangement of Cyclopropyl Ketones 2a−m to Cyclopenta[*c*]-carbazoles 3a−m and Tetrahydrocarbazoles 7a,h,m. To a solution of cyclopropyl ketone **2** (1 mmol) in nitromethane (25 mL) was added dropwise a solution of $SnCl_4$ (0.18 mL, 1.5 mmol) in nitromethane (5 mL) over a period of 0.5 h at 0 °C, and the reaction mixture was further stirred at ambient temperature for 3−8 h (monitored by TLC). It was then diluted with ice-cooled saturated $NaHCO_3$ solution (20 mL) and extracted with chloroform (4 × 25 mL). The organic extracts were combined, washed with water (3 × 25 mL) and brine (1 × 25 mL), and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure to afford crude products **3a**−**m** which were purified by passing through silica gel column using hexanes−ethyl acetate as eluent. The tetrahydrocarbazoles **7a**,**h**,**m** were isolated when the reactions were run for 0.5 h (for **7a** and **7h**) and 3 h (for **7m**), respectively. The cyclopropyl ketone **2l** gave the 3,4-disubstituted carbazole **6l** under the above conditions after 3 h, whereas the cyclopenta[*c*]carbazole **3l** was obtained by stirring the reaction mixture for 5 h or by warming the reaction mixture at 85 °C for 0.5 h.

2-(4-Methoxybenzoyl)-3-(4-methoxyphenyl)-6-*N*-methyl-1*H*-cyclopenta[*c*]carbazole (3a): yield 60% (0.14 g); yellow crystals; mp 219−220 °C; R_f 0.56 (9.5:0.5 benzene−EtOAc); IR (KBr) 3531, 3407, 1608, 1501, 1349, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.90 (s, 3H, NCH_3), 4.43 (s, 2H, CH_2), 6.62 (d, J = 8.6 Hz, 2H, ArH), 6.76 (d, J = 8.6 Hz, 2H, ArH), 7.27 (dd, J = 8.5, 3.2 Hz, 2H, ArH), 7.32−7.39 (m, 3H, ArH), 7.46 (d, J = 8.3 Hz, 1H, ArH), 7.54 (t, J = 7.1 Hz, 1H, ArH), 7.60 (dd, J = 6.5, 2.1 Hz, 2H, ArH), 8.19 (d, J = 7.9 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4, 39.6, 55.2, 55.3, 107.2, 108.6, 112.8, 113.5, 119.2, 119.5, 120.3, 122.0, 122.3, 125.8, 127.3, 130.9, 131.3, 131.6, 136.5, 136.9, 138.1, 141.1, 141.4, 150.7, 159.2, 162.2, 194.2; MS (*m*/*z*) 459 (M^+, 37.2), 326 (23.7), 325 (85.3), 135 (100). Anal. Calcd for $C_{31}H_{25}NO_3$ (459.51): C, 81.02; H, 5.48; N, 3.04. Found: C, 81.13; H, 5.75; N, 3.21.

9-Bromo-2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-6-*N*-methyl-1*H*-cyclopenta[*c*]carbazole (3h): yield 69% (0.19 g); yellow crystals; mp 230−231 °C; R_f 0.51 (3.0:1.0 hexanes−EtOAc); IR (KBr) 3064, 2927, 1600, 1471, 1350, 1245 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, NCH_3), 4.28 (s, 2H, CH_2), 6.59 (d, J = 8.5 Hz, 2H, ArH), 6.72 (d, J = 8.5 Hz, 2H, ArH), 7.22 (d, J = 8.6 Hz, 3H, ArH), 7.28 (d, J = 8.3 Hz, 1H, ArH), 7.53 (dd, J = 8.7, 1.7 Hz, 1H, ArH), 7.56 (d, J = 8.8 Hz, 3H, ArH), 8.15 (d, J = 1.7 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4, 39.5, 55.2, 55.3, 107.4, 109.9, 112.2, 112.9, 113.6, 118.1, 120.9, 123.8, 124.3, 127.1, 128.3, 130.8, 131.1, 131.5, 136.8, 137.0, 138.1, 139.9, 141.2, 150.3, 159.3, 162.2, 193.9; MS (*m*/*z*) 538 (M^+, 100). Anal. Calcd for $C_{31}H_{24}NO_3Br$ (538.41): C, 69.14; H, 4.49; N, 2.60. Found: C, 69.09; H, 4.57; N, 2.53.

2-(4-Chlorobenzoyl)-3-(4-chlorophenyl)-9-methoxy-6-*N*-methyl-1*H*-cyclopenta [*c*]carbazole (3l): yield 66% (0.15 g); yellow crystals; mp 224−225 °C; R_f 0.53 (8.5:1.5 hexanes−EtOAc); IR (KBr) 3074, 2934, 1597, 1483, 1342 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H, OCH_3), 3.98 (s, 3H, NCH_3), 4.43 (s, 2H, CH_2), 7.09 (d, J = 8.1 Hz, 2H, ArH), 7.18−7.20 (m, 5H, ArH), 7.34 (d, J = 8.5 Hz, 1H, ArH), 7.37 (d, J = 9.0 Hz, 1H, ArH), 7.45 (t, J = 8.8 Hz, 3H, ArH), 7.63 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5, 39.3, 56.3, 104.9, 107.7, 109.5, 115.1, 119.0, 120.3, 122.5, 127.8, 128.3, 130.4, 130.8, 133.1, 134.2, 135.3, 136.5, 137.0, 137.2, 137.6, 138.4, 142.0, 152.2, 154.2, 193.4; MS (*m*/*z*) 498 (M^+, 68). Anal. Calcd for $C_{30}H_{21}NO_2Cl_2$ (498.38): C, 72.29; H, 4.24; N, 2.81. Found: C, 72.37; H, 4.29; N, 2.78.

3-(4-Chlorobenzoyl)-6-methoxy-9-*N*-methyl-4-[2′-(4-chlorobenzoyl)-ethyl]carbazole (6l): yield 65% (0.17 g); yellow crystals; mp 186−187 °C; R_f 0.75 (3.0:1.0 hexanes−EtOAc); IR (KBr) 3068, 2924, 1676, 1642, 1582, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.61−3.72 (m, 4H, CH_2−CH_2), 3.87 (s, 3H, OCH_3), 3.88 (s, 3H, NCH_3), 7.18 (dd, J = 8.9, 2.4 Hz, 1H, ArH), 7.26 (d, J = 7.6 Hz, 1H, ArH), 7.38 (d, J = 9.0 Hz 1H, ArH), 7.41−7.47 (m, 5H, ArH), 7.77−7.79 (m, 3H, ArH), 8.01 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 29.3, 39.2, 56.0, 105.4, 105.5, 109.5, 115.5, 121.4, 122.5, 127.9, 128.4, 128.5, 128.9, 129.7, 131.8, 134.9, 136.4, 137.6, 138.4, 138.9, 139.5, 142.8, 154.4, 197.1, 198.9; MS (*m*/*z*) 516(M^+, 62), 515 (100). Anal. Calcd for $C_{30}H_{23}NO_3Cl_2$ (516.39): C, 69.77; H, 4.48; N, 2.71. Found: C, 69.74; H, 4.56; N, 2.83.

3-(4-Methoxybenzoyl)-9-*N*-methyl-1-(1-*N*-methyl-3-indolyl)-4-[2′-(4-methoxybenzoyl)ethyl]-1,2,3,4-tetrahydrocarbazole (7a): yield 62% (0.19 g); yellow crystals; mp 177−178 °C; R_f 0.50 (3.0:1.0 hexanes−EtOAc); IR (KBr) 3049, 2933, 1666, 1597, 1466, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.21 (ddd, J = 12.6, 12.3, 4.6 Hz, 1H, CH), 2.32−2.39 (m, 2H, CH_2), 2.64 (d, J = 12.7 Hz, 1H, CH), 2.69−2.84 (m, 2H, CH_2), 3.53 (s, 3H, OCH_3), 3.65−3.67 (m, 1H, CH), 3.70 (s, 3H, OCH_3), 3.75 (s, 3H, NCH_3), 3.81 (s, 3H, NCH_3), 4.03−4.08 (m, 1H, CH), 4.64 (t, J = 4.3 Hz, 1H, CH), 4.64 (brs, 1H, ArH), 6.51−6.55 (m, 3H, ArH), 6.77 (d, J = 8.8 Hz, 2H, ArH), 7.13 (dt, J = 7.8, 0.9 Hz, 2H, ArH), 7.21−7.25 (m, 1H, ArH), 7.29−7.34 (m, 1H, ArH), 7.39 (d, J = 8.3 Hz, 1H, ArH), 7.43 (d, J = 8.8 Hz, 2H, ArH), 7.60 (d, J = 8.1 Hz, 1H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH), 7.75 (d, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 29.2, 30.2, 32.8, 34.0, 34.7, 35.3, 43.4, 55.3, 55.4, 108.8, 109.5, 111.5, 113.4, 113.5, 116.0, 118.9, 119.1, 119.3, 119.7, 120.9, 122.0, 126.3, 126.5, 128.4, 129.0, 129.8, 130.2, 130.6, 137.1, 137.4, 137.6, 163.1, 163.2, 199.0, 200.7; MS (*m*/*z*) 611 (M^+, 100), 480 (42), 460 (90). Anal. Calcd for $C_{40}H_{38}N_2O_4$ (610.72): C, 78.66; H, 6.27; N, 4.58. Found: C, 78.60; H, 6.21; N, 4.62.

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Supporting Information Available: ^1H and ^{13}C NMR spectral data for compounds **2a**,**e**,**m**, **3b**−**g**,**i**−**k**,**m**, and **7h**,**m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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