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Domino Carbocationic Rearrangement of α-[Bis(methylthio)methylene]alkyl-2-(3/2-indolyl) Cyclopropyl Ketones†

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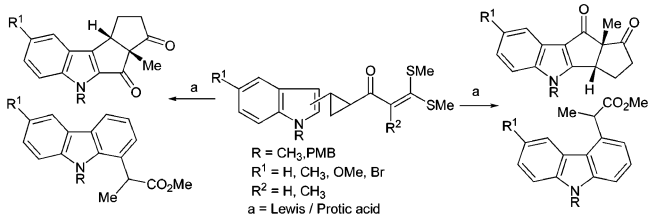
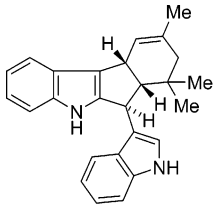


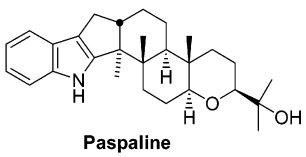
Domino carbocationic rearrangement of a number of substituted 3- and 2-indolylcyclopropyl ketones with an α-bis(methylthio)methylene group in the presence of various protic/Lewis acids yields a variety of products, mainly the pentaleno fused indoles and the carbazole derivatives.

Introduction

The cyclopenta[*b*]indole ring system occurs in a number of alkaloids,[1] notably the tremorgenic mycotoxins such as paxilline, the lolitrems, penitrems, janthitrems, and paspaline,[2] etc. Yuehchukene,[3] a monoterpenoid alkaloid containing a cyclopenta[*b*]indole ring system has been shown to exhibit mixed estrogenic and antiestrogenic activity as well as potent antiimplantation activity.[4] Recently, a cyclopenta[*b*]indole derivative has been identified as the promising prostaglandin D_2 (PGD_2) receptor antagonist in the alleviation of various allergic disorders.[5,6] Several syntheses of yuehchukene[7] and cyclopenta[*b*]-indole framework,[5,8] in general, have been reported in recent years. Our continued interest in the synthesis of indolo[*b*] fused



Yuehchukene



Paspaline

† Dedicated to Professor Lutz F. Tietze on his 65th birthday.

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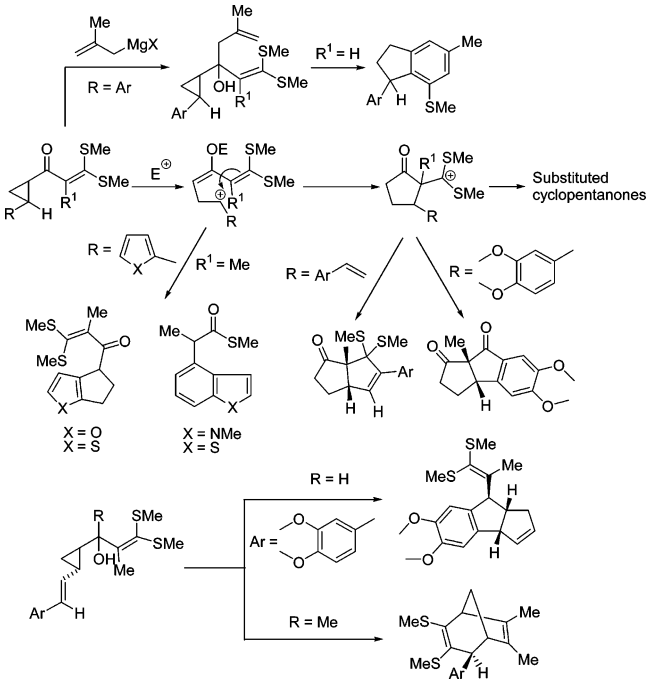
SCHEME 1

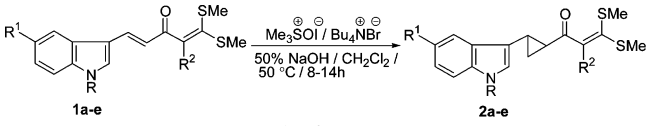


heterocycles[9] and the related natural products[9b,9d] prompted us to examine the possibility of constructing cyclopenta[*b*]indole and the related ring systems via domino carbocationic rearrangement of 3- and 2- indolylcyclopropyl ketones of the general structures **2** and **4** (Schemes 2 and 3). We have demonstrated in our earlier studies, in a series of papers,[10−12] the domino carbocationic rearrangements of a number of related aryl and heteroarylcyclopropyl ketones with an α-(bismethylthio)methylene functionality as the cationic cyclization terminator, yielding a wide variety of products such as substituted cyclopentanones,[10] cyclopenta[*b*]indanes,[11a−b] diquinanes,[11b] 1-arylindanes,[12a] bicyclo[3.2.1]octene,[11c] and other cyclopentano fused heterocycles[12b−c] (Scheme 1).In continuation of this work, we now report in this paper a detailed study of domino carbocationic rearrangement of 3- (and 2-) indolylcyclopropyl ketones of the type **2** and **4** in the presence of various Lewis/protic acids yielding a range of products, mainly the pentaleno fused indoles and the carbazole derivatives.

Results and Discussion

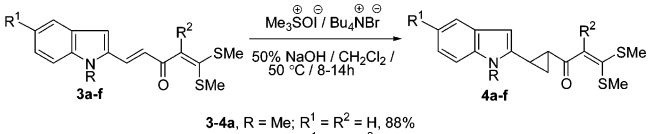
The starting α-[3/2-(indolyl)propenoyl]ketene dithioacetals **1a**−**e** and **3a**−**f** were prepared according to the earlier reported procedure via base catalyzed aldol condensation of indole 3- or 2-aldehydes with the appropriate acylketene dithioacetals.[13] The unsaturated ketene dithioacetals **1a**−**e** and **3a**−**f** were transformed into the corresponding cyclopropyl ketones **2a**−**e** and **4a**−**f** regioselectively in high yields by treatment with dimethyloxosulphonium methylide generated from the corresponding sulfonium salt in the presence of phase transfer catalyst (Schemes 2 and 3).[10c] The cyclopropyl ketones **2a**−**e** were found to be unstable when subjected to purification on silica gel column, yielding a mixture of several products. However, they were pure enough (>98%) to be characterized by their ^{1}H and ^{13}C NMR spectra and used as such for the further transformations. On the other hand, the corresponding (2-indolyl)-cyclopropyl ketones **4a**−**f** were stable and could be purified by column chromatography for the preparation of analytically pure compounds.

SCHEME 2



1-2a, R = Me; R^1 = R^2 = H, 94%
1-2b, R = Me; R^1 = H; R^2 = Me, 85%
1-2c, R = Me; R^1 = OMe; R^2 = Me, 90%
1-2d, R = Me; R^1 = Br; R^2 = Me, 93%
1-2e, R = PMB; R^1 = H; R^2 = Me, 88%

SCHEME 3



3-4a, R = Me; R^1 = R^2 = H, 88%
3-4b, R = Me; R^1 = Br; R^2 = H, 86%
3-4c, R = Me; R^1 = H; R^2 = Me, 87%
3-4d, R = Me; R^1 = Br; R^2 = Me, 91%
3-4e, R = Me; R^1 = R^2 = Me, 84%
3-4f, R = PMB; R^1 = H; R^2 = Me, 88%

Domino Carbocationic Rearrangement of 3-Indolylcyclopropyl Ketones 2a−**e.** Carbocationic rearrangement of the cyclopropyl ketone **2a** without the α-methyl group was first investigated in the presence of common Lewis/protic acids which have been successfully applied previously for the 5-*exo* cyclization of 2-arylcyclopropyl ketones with the similar structures.[10] Thus, under optimized reaction conditions ($SnCl_4$, C_6H_6, 0 °C), the cyclopropyl ketone **2a** could be transformed into the expected 3-(1-*N*-methyl-3-indolyl)-2-bis(methylthio)-methylenecyclopentanone **5a** in 63% yield (Scheme 4), whereas in the presence of other protic/Lewis acids (H_3PO_4, TFA, PTSA, CF_3SO_3H, $TiCl_4$), no identifiable product could be isolated. Exposure of **2a** with BF_3OEt_2 in CH_3NO_2 furnished the corresponding *β*-ketocarbothioate **6a** in 61% yield (Scheme 4).

Carbocationic rearrangements of 3-indolylcyclopopyl ketone **2b** with an α-methyl(bismethylthio)methylene moiety were next investigated under the influence of various Lewis/protic acids, and the results are presented in Scheme 5 (Table 1). We have demonstrated in the earlier studies that similar dialkoxyarylcyclopropyl ketones with α-methyl(bismethylthio)methylene functionality undergo double cyclopentanone annulation in domino

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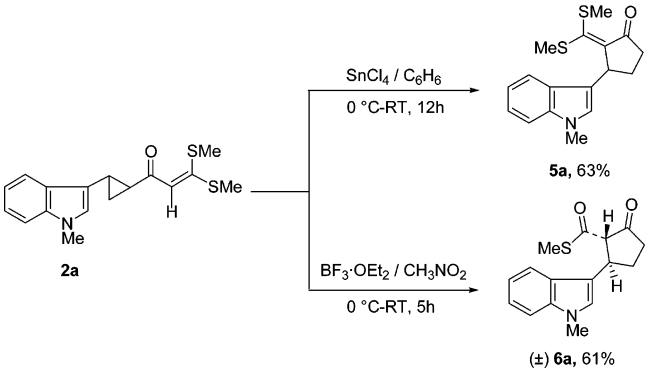
SCHEME 4



SCHEME 5

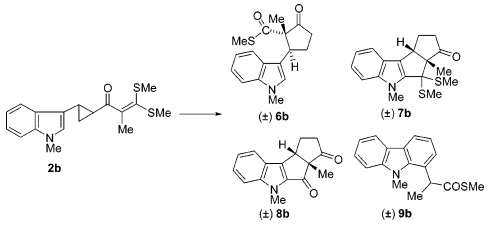


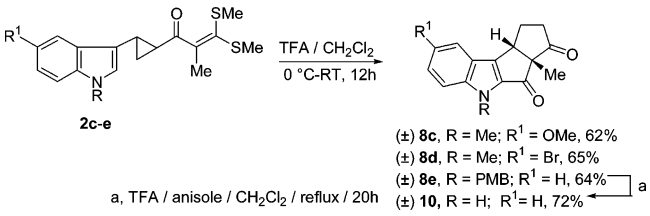
TABLE 1. Lewis/Protic Acid-Induced Rearrangement of the Cyclopropyl Ketone (2b)

entry	reaction conditions	time (h)	product (% yield) 6b	7b	8b	9b
1	silica gel column	48	32	–	–	–
2	BF_3·OEt_2/CH_3NO_2, 0 °C−RT	12	58	–	–	–
3	$SnCl_4$/CH_3NO_2, 0 °C−RT	12	–	56	–	–
4	H_3PO_4, RT	12	–	–	56	–
5	TFA/CH_2Cl_2, 0 °C−RT	12	–	–	60	–
6	TFA/$ClCH_2CH_2Cl$, 80 °C	12	–	–	63	–
7	PTSA/C_6H_6/reflux	12	–	–	–	51

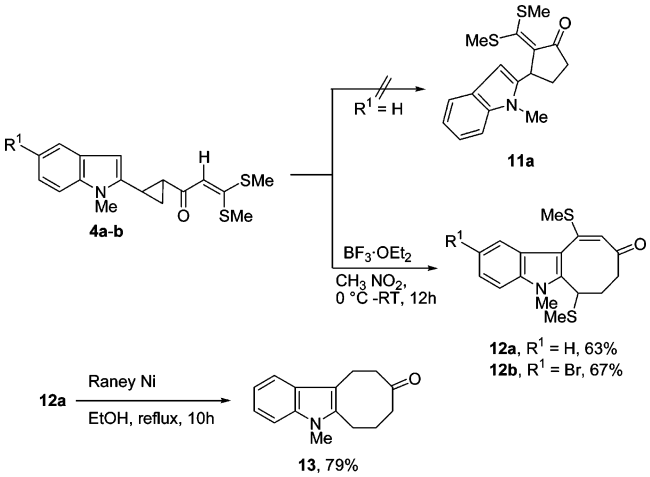
fashion to furnish cyclopenta[*b*]indanediones in good yields.[11a] Interestingly, in one of the experiments, during the attempted purification of cyclopropyl ketone **2b**, on silica gel, the carbothioate **6b** was isolated in 32% yield (Table 1, entry 1) when **2b** was left on the silica gel column for a prolonged time. The carbothioate **6b** was obtained in improved yield (58%) when the ketone **2b** was exposed to BF_3·OEt_2 in nitromethane for a prolonged time (Table 1, entry 2). However, when **2b** was reacted with $SnCl_4$ in nitromethane (12 h), workup of the product mixture furnished one product (56%) which was characterized as the pentaleno fused indole **7b** on the basis of its spectral and analytical data (Table 1, entry 3). Surprizingly, treatment of the cyclopropyl ketone **2b** with protic acids such as H_3PO_4 (entry 4) or TFA (entry 5) yielded a single product, the structure of which was established as the indolo fused diquinane diketone derivative **8b** formed by in situ dethioketalization of **7b**. The structure and stereochemistry of the tetracyclic diketone **8b** was further confirmed by its single-crystal X-ray crystallographic data. Our attempts to improve the yield of the diketone **8b** did not meet with much success, and at higher temperature with TFA in dichloroethane, **8b** was obtained only in 63% yield along with more intractable polymeric mixture.

Finally, when the cyclopropyl ketone **2b** was subjected to rearrangement in the presence of PTSA in refluxing benzene, the product isolated (entry 7) was found to be the methyl 2-(9-*N*-methyl-1-carbazolyl)propane carbothioate **9b** (51%) on the basis of its spectral and analytical data.

SCHEME 6



SCHEME 7



With optimized reaction conditions in hand for double cyclopentanone annulation of indole, the other substituted 3-indolylcyclopropyl ketones **2c**−**e** were also subjected to this unique domino carbocationic cyclization in the presence of TFA/CH_2Cl_2 affording the corresponding pentaleno fused indolodiketones **8c**−**e** in 62−65% overall yields (Scheme 6).

The deprotection of the corresponding *N*-(4-methoxybenzyl) pentaleno[*b*]indole **8e** in the presence of TFA/anisole in dichloromethane[14] furnished the 1-*N*-unsubstituted pentaleno-[*b*]indolodiketone **10** in 72% yield (Scheme 6).

Domino Carbocationic Rearrangement of 2-Indolylcyclopropyl Ketones 4a−**f.** The 2-(indolyl)cyclopropyl ketone **4a** without an α-methyl group on the bis(methylthio)methylene moiety was first subjected to rearrangement under standard reaction conditions in the presence of various Lewis/protic acids with a view to isolate 3-(2-indolyl)cyclopentanone derivatives such as **11a** formed by 5-*exo* trapping of the carbocation derived from acid induced ring opening of cyclopropyl ketone **4a**. However, our various attempts to isolate **11a** (or the products derived from it) under the influence of various Lewis/protic acids were not successful. Interestingly, treatment of **4a** with either $SnCl_4$ or BF_3·OEt_2 (in nitromethane) yielded one product in varying yields (40−51%) which was identified as the indolo fused cyclooctenone derivative **12a** on the basis of its spectral and analytical data (Scheme 7). Under optimized reaction conditions (BF_3·OEt_2/CH_3NO_2, 12 h), the product **12a** was obtained in improved yield (63%), and its structure was further confirmed from its X-ray diffraction data. The corresponding (5-bromo-2-indolyl)cyclopropyl ketone **4b** also furnished, similarly, the corresponding bromo substituted indolocyclooctenone **12b** in 67% yield under identical conditions (Scheme 7). Dethiomethylation of **12a** with Raney Ni afforded the corresponding indolocyclooctanone **13** in 79% yield (Scheme 7).

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SCHEME 8

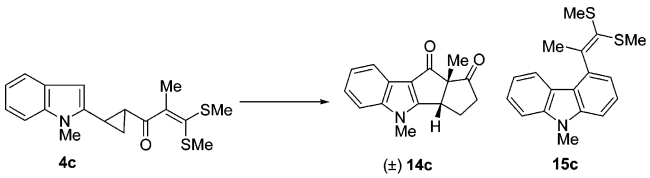
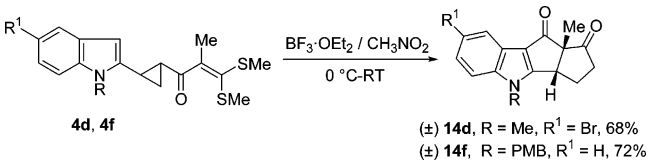


TABLE 2. Lewis/Protic Acid-Induced Rearrangement of the Cyclopropyl Ketone (4c)

entry	reaction conditions	time (h)	product (% yield) 14c	15c
1	BF_3·OEt_2/CH_3NO_2, 0 °C−RT	4	69	
2	BF_3·OEt_2/CH_3NO_2, 0 °C−RT	12	58	
3	TFA/CH_2Cl_2, 0 °C−RT	12	53	30
4	CF_3SO_3H/CH_2Cl_2, 0 °C−RT	6	58	−
5	$SnCl_4$/CH_3NO_2, 0 °C−RT	12	−	25
6	PTSA/C_6H_6/reflux	12	−	65

SCHEME 9



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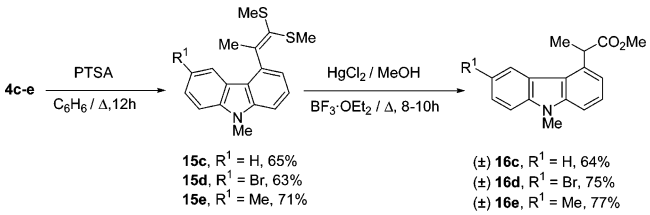

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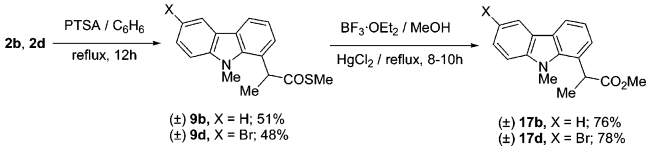
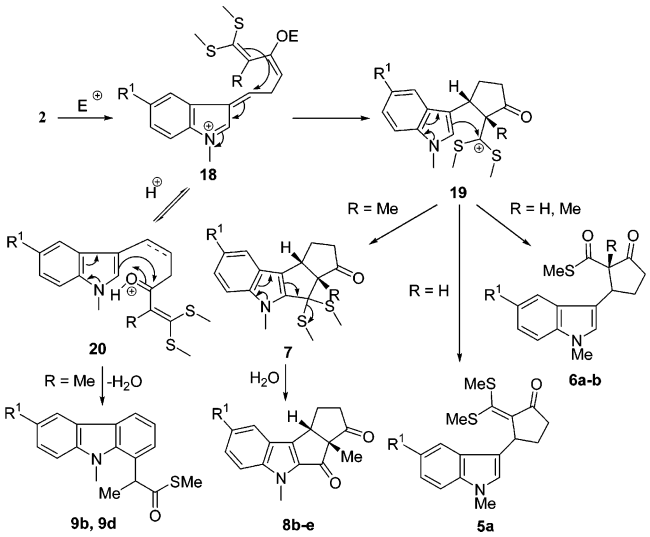


SCHEME 12



The (2-indolyl)cyclopropyl ketone **4c** with α-methyl(bismethylthio)methylene functionality was next subjected to treatment with various Lewis/protic acids and the results are shown in the Scheme 8 (Table 2). To our surprise, the desired pentaleno fused indolodiketone **14c** was obtained in 69% yield, when the ketone **4c** was reacted with BF_3·OEt_2 in nitromethane for 4 h (Table 2, entry 1). The yield of the diketone was reduced to 58% when the reaction was continued for prolonged time (12 h) (entry 2). In the presence of other protic acids (TFA, CF_3SO_3H), the diketone **14c** was obtained in varying yields (entries 3, 4). Treatment of **4c** with $SnCl_4$/CH_3NO_2 under standard reaction conditions afforded, on the other hand, the corresponding 4-[(bismethylthio)ethylidene]-*N*-methylcarbazole **15c** in low yield (entry 5), whereas in the presence of PTSA in refluxing benzene, **15c** was isolated in increased yield of 65% (Table 2, entry 6).

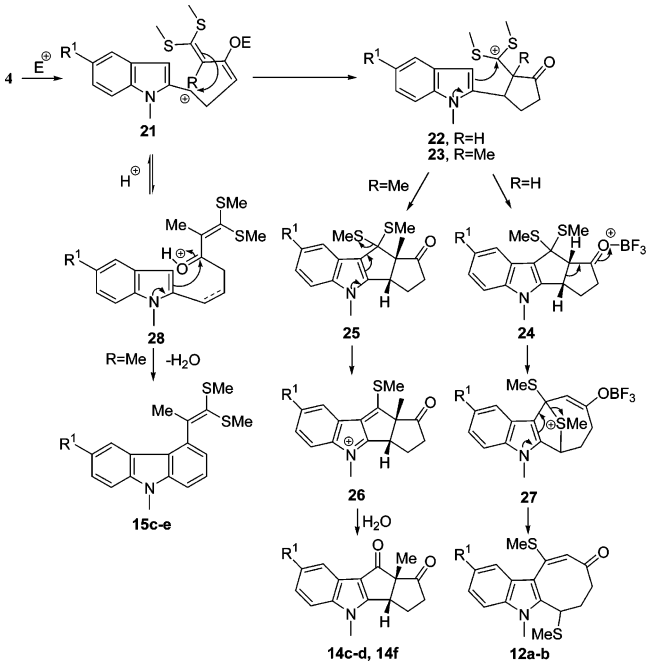
The generality of this unusually facile double cyclopentanone annulation of indole was further demonstrated by subjecting (2-indolyl)cyclopropyl ketones **4d** and **4f** to rearrangement under identical conditions affording the tetracyclic diketones **14d** and **14f** in 68% and 72% yields, respectively (Scheme 9). The structures of all the diketones (**14c**−**d, 14f**) were established with the help of spectral and analytical data and by X-ray diffraction data for **14c**.

The cyclopropyl ketones **4c**−**e** could also be converted to the carbazoles **15c**−**e** in synthetically useful yields (63−71%) in the presence of PTSA in refluxing benzene (Scheme 10). The 4-[(bismethylthio)ethylidene] functionality present in these carbazoles **15c**−**e** could be transformed to propanoates **16c**−**e** on methanolysis in the presence of BF_3·OEt_2 and $HgCl_2$ (Scheme 10). Attempts to convert **4c**−**e** directly to (4-carbazolyl)propanoates with BF_3·OEt_2/$HgCl_2$ in methanol gave only intractable polymeric mixture.

Similarly, the regioisomeric carbazole-1-propanoates **17b** and **17d** could also be prepared in good yield by BF_3·OEt_2 induced methanolysis of the corresponding carbazole-1-propane carbothioates **9b** and **9d** which were obtained in modest yields via intramolecular cyclocondensation of cyclopropyl ketones **2b** and **2d** on treatment with PTSA in refluxing benzene (Scheme 11).

The probable mechanism for the formation of various products from the acid induced rearrangements of cyclopropyl ketones **2** and **4** are shown in Schemes 12 and 13. Thus, the cationic ring opening of 3- indolylcyclopropyl ketones **2** (which is further assisted by the lone pair on indole nitrogen) affords the stabilized cationic intermediate **18** which on intramolecular 5-*exo* trapping by bis(methylthio)methylene double bond yields cyclopentanone intermediate **19** with a pendent bis(methylthio)-methyl carbocation (Scheme 12). Under kinetically controlled conditions, depending on the nature of acid catalyst and the reaction conditions, the carbocationic intermediate **19** undergoes either deprotonation or hydrolysis to give 3-(3-indolyl)cyclopentanone derivatives like **5a** or **6a**,**b** (R = H, Me). When R = Me, the major pathway involves nucleophilic trapping of the carbocation **19** by the 2-position of the indole ring furnishing the pentaleno fused indole derivative **7** (Scheme 5, Table 1, entry 3) or the corresponding diketone **8** (entries 4−6) formed by in situ hydrolysis of the thioketal moiety. On the other hand, in refluxing PTSA, the cationic intermediate **18** undergoes intramolecular cyclocondensation through the intermediate **20** to afford carbazole-1-propane carbothioates **9** directly by in situ hydrolysis of the bis(methylthio)ketal group in **20**.

SCHEME 13



The probable mechanism for the formation of various products from carbocationic rearrangement of 2- indolylcyclopropyl ketones **4** is shown in the Scheme 13. Thus, the carbocationic ring opening of **4** followed by intramolecular trapping of the resulting carbocation **21** by bis(methylthio)methylene double bond furnishes the intermediates **22** or **23** with a bis(methylthio)methyl cationic side chain, which are rapidly intercepted by the highly reactive 3-position of indole ring to give pentaleno fused indole derivatives **24** or **25**, respectively. None of the cyclopentanone products like **5**−**6** formed from the rearrangement of the cyclopropyl ketone **2** were isolated in this case. When R = Me, the intermediate thioketal **25** undergoes facile elimination of one of the methylmercapto groups assisted by the lone pair of indole nitrogen affording the cationic intermediate **26** which on subsequent hydrolysis gives the diketones **14c**,**d** and **14f** as the sole products from the cyclopropyl ketones **4c**,**d** and **4f**, respectively (Schemes 8 and 9). However, when R = H, the reaction takes an unexpected course, and the pentaleno fused indole intermediate **24** appears to undergo ring cleavage with concomitant migration of methylthio group through bridged sulfonium ion intermediate **27** yielding the rearranged indolocyclooctenone derivatives **12a**,**b** in reasonably good yields (Scheme 13). We are unable to give plausible explanation at this stage for the different reactivity pattern of the intermediates **24** and **25**, yielding the products **12** and **14**, respectively. The carbocation **21** undergoes intramolecular cyclocondensation at the 3-position of the indole ring through intermediate **28** in the presence of PTSA in refluxing benzene to give the 4-[bis(methylthio)ethylidene]-carbazoles **15c**−**e** (Scheme 13),[15] which could be transformed to the corresponding propanoate derivatives **16c**−**e** in synthetically useful yields under $BF_3{\cdot}OEt_2$ induced methanolysis (Scheme 10).

Conclusion

In summary, domino carbocationic rearrangements of 3- and 2-indolylcyclopropyl ketones **2** and **4** with bis(methylthio)-methylene functionality yield a variety of products depending on the nature of acid catalysts and reaction conditions. The facile cascade cationic cyclization of 3- and 2-indolylcyclopropyl ketones **2** and **4** to pentaleno[*b*]indole diketones **8** and **14**, respectively, provides an efficient new way of appending diquinane framework to indole ring in a single one-pot operation. Similarly, the PTSA induced intramolecular cyclocondensation of cyclopropyl ketones **2** and **4** provides a synthetically useful route to 1- and 4-substituted carbazole 2-propanoates **16**−**17** (Schemes 10 and 11) which are reported to display anti-inflammatory activity.[16] Further work to investigate the detailed mechanism and application of this new domino carbocationic process for construction of novel polycyclic heterocyclic scaffolds is in progress.

Experimental Section

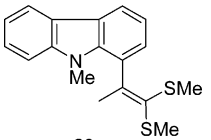
General Procedure for Preparation of 3/2-Indolylcyclopropyl Ketones 2a−e and 4a−f. A suspension of the appropriate α-oxoketene dithioacetal (10 mmol), trimethylsulfoxonium iodide (2.64 g, 12 mmol), tetrabutylammonium bromide (1.61 g, 5 mmol) in 50% NaOH solution (50 mL) and CH_2Cl_2 (50 mL) was heated with stirring at 50 °C for 8−14 h (monitored by TLC). The organic layer was separated, and the aqueous layer after dilution with H_2O (50 mL) was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude residue, which was diluted with EtOAc and filtered off to remove tetrabutylammonium bromide. The filtrate was evaporated to give crude 3/2-indolylcyclopropyl ketones **2a**−**e** and **4a**−**f**. The cyclopropyl ketones **2a**−**e** were found to be unstable when subjected to purification on silica gel column. The cyclopropyl ketones **4a**−**f** were purified by filtration through a small silica gel column using EtOAc−hexane as eluent.

3,3-Bis(methylthio)-1-[2-(1-*N*-methyl-3-indolyl)cyclopropyl]-2-propen-1-one (2a). Yield 94% (2.98 g); yellow solid; mp 118−120 °C; R_f 0.40 (3:2 hexane−EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.43 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.06 (s, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.36 (s, 1H), 3.63 (s, 3H), 2.42 (s, 3H), 2.35 (bs, 4H), 2.23 (ddd, J = 7.9 Hz, 4.2 Hz, 4.1 Hz, 1H), 1.40 (ddd, J = 8.7 Hz, 4.3 Hz, 4.3 Hz, 1H), 1.32−1.27 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.3, 161.2, 136.7, 127.4, 126.1, 121.4, 118.7, 118.5, 113.9, 113.2, 109.8, 32.3, 31.5, 20.2, 16.9, 16.6, 14.2.

3,3-Bis(methylthio)-2-methyl-1-[2-(1-*N*-methyl-3-indolyl)cyclopropyl]-2-propen-1-one (2b). Yield 85% (2.81 g); viscous oil; R_f 0.40 (4:1 hexane−EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.55 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.15 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.54−2.50 (m, 1H), 2.37−2.34 (m, 1H), 2.29 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 1.60 (ddd, J = 8.8 Hz, 4.4 Hz, 3.9 Hz, 1H), 1.56−1.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 203.7, 144.3, 136.7, 134.4, 127.4, 126.4, 126.3, 121.4, 118.7, 118.4, 113.3, 109.8, 32.3, 31.7, 22.5, 19.4, 18.0, 17.0, 16.1.

Procedure for Acid Induced Rearrangement of 3-Indolylcyclopropyl Ketone 2a. (a) With $SnCl_4$. To a solution of 3-indolyl-

(15) The similar product, i.e., 1-[bis(methylthio)ethylidene]-*N*-methylcarbazole **29** could not be isolated from 3-indolylcyclopropyl ketone **2b**, probably because of steric crowding.



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(16) Randall, L. O.; Baruth, H. *Arch. Int. Pharmacodyn. Ther.* **1976**, *220* (1), 94.

cyclopropyl ketone **2a** (0.317 g, 1 mmol) in C_6H_6 (15 mL), $SnCl_4$ (0.18 mL, 1.5 mmol) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h (monitored by TLC). It was then poured into cold saturated $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The organic extracts were washed with H_2O (2 × 50 mL), brine (50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude product **5a** which was purified by column chromatography over silica gel using EtOAc−hexane (1:6) as eluent.

2,2-Bis(methylthio)methylene-3-(1-*N*-methyl-3-indolyl)-1-cyclopentanone (5a). Yield 63% (0.2 g); viscous oil; R_f 0.45 (3:1 hexane−EtOAc); IR (CH_2Cl_2): 2923, 1680, 1515, 1477 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.0 Hz, 1H), 7.13 (t, J = 6.9 Hz, 1H), 6.57 (s, 1H), 4.75 (d, J = 6.8 Hz, 1H), 3.69 (s, 3H), 2.55−2.10 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 152.3, 138.2, 137.5, 126.5, 126.0, 121.7, 119.0, 118.8, 117.0, 109.4, 42.1, 38.3, 32.6, 27.8, 18.40, 18.39; MS (*m*/*z*, %): 317 (M^+, 80), 270 (90), 254 (100); HRMS (ES) *m*/*z* Calcd. for $C_{17}H_{19}NOS_2$: 317.0908; Found: 317.0906.

(b) With BF_3·OEt_2. To a solution of 3-indolylcyclopropyl ketone **2a** (0.317 g, 1 mmol) in CH_3NO_2 (15 mL) was added BF_3·OEt_2 (0.19 mL, 1.5 mmol) dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 5 h. It was then poured into cold saturated $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL), brine (50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude product **6a** which was purified by column chromatography over silica gel using EtOAc−hexane (1:4) as eluent.

Methyl *trans*-2-(1-*N*-Methyl-3-indolyl)-5-oxocyclopentane-*r*-1-carbothioate (6a). Yield 61% (0.18 g); colorless solid; mp 67−68 °C; R_f 0.62 (3:2 hexane−EtOAc); IR (CH_2Cl_2): 2926, 1746, 1666, 1473, 1118, 1017, 817, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.16 (brt, J = 7.3 Hz, 1H), 7.03 (t, J = 6.8 Hz, 1H), 6.83 (s, 1H), 4.09 (dt, J = 6.2 Hz, 10.4 Hz, 1H), 3.64 (s, 3H), 3.60 (d, J = 10.4 Hz, 1H), 2.54−2.38 (m, 3H), 2.23 (s, 3H), 2.06−1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 195.7, 137.2, 126.6, 125.3, 121.9, 119.10, 114.9, 109.4, 69.3, 38.9, 38.3, 32.6, 28.5, 12.0; MS (*m*/ *z*, %): 287 (M^+, 100); HRMS (EI) *m*/*z* Calcd. for $C_{16}H_{17}NO_2S$: 287.0981, Found 287.1025.

Silica Gel Induced Rearrangement of 3-Indolylcyclopropyl Ketone 2b to 6b. To a solution of 3-indolylcyclopropyl ketone **2b** (0.331 g, 1 mmol) in CH_2Cl_2 (10 mL) was added silica gel (2 g), and solvent was removed under reduced pressure. The slurry was kept at room temperature for 48 h. It was then loaded on silica gel column and eluted with EtOAc−hexane to give colorless crystals of carbothioate **6b.**

Procedure for Acid Induced Rearrangement of 3-Indolylcyclopropyl Ketone 2b. (a) With BF_3·OEt_2. General procedure described for 3-indolylcyclopropyl ketone **2a** was followed.

Cyclization of **2b** afforded **6b** (Table 1, entry 2).

Methyl *r*-2-(1-*N*-Methyl-3-indolyl)-*c*-1-methyl-5-oxo-1-cyclopentane Carbothioate (6b). Yield 58% (0.18 g); colorless crystals; mp 143−144 °C; R_f 0.27 (2:1 hexane−EtOAc); IR (KBr): 2924, 1741, 1638, 1477, 1376, 1196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 7.1 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.88 (s, 1H), 4.50 (dd, J = 9.3 Hz, 6.4 Hz, 1H), 3.77 (s, 3H), 2.64−2.59 (m, 2H), 2.38−2.32 (m, 1H), 2.33 (s, 3H), 2.23−2.15 (m, 1H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2, 201.9, 136.9, 127.8, 126.9, 121.9, 119.8, 119.1, 112.5, 109.2, 67.5, 43.1, 38.2, 32.8, 25.4, 14.9, 12.2; MS (*m*/*z*, %): 301 (M^+, 40), 254 (60), 226 (60); HRMS (ESI) *m*/*z* Calcd. for $C_{17}H_{19}NO_2SNa$: 324.10287; Found: 324.10263.

(b) With $SnCl_4$. General procedure described for 3-indolylcyclopropyl ketone **2a** was followed.

Cyclization of **2b** afforded **7b** (Table 1, entry 3).

5,6a-Dimethyl-6,6-bis(methylthio)-6,6a,7,8,9,9a-hexahydropentaleno[2,1-*b*]indol-7-one (7b): Yield 56% (0.19 g); colorless crystal; mp 96−97 °C; R_f 0.55 (2:1 hexane−EtOAc) IR (CH_2Cl_2): 2923, 1735, 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 3.93 (s, 3H), 3.54 (d, J = 6.4 Hz, 1H), 2.52−2.31 (m, 2H), 2.40 (dd, J = 15.0 Hz, 6.4 Hz, 1H), 2.38 (s, 3H), 1.98 (ddd, J = 15.0 Hz, 12.6 Hz, 6.4 Hz, 1H), 1.60 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.1, 142.9, 140.4, 122.3, 121.9, 120.6, 119.7, 119.0, 110.0, 69.8, 64.8, 49.0, 37.8, 30.2, 22.7, 21.5, 15.1, 13.4; MS (*m*/*z*, %): 331 (M^+, 10), 284 (100); HRMS (ES) *m*/*z* Calcd. for $C_{18}H_{22}NOS_2$ (M + H): 332.1143, Found: 332.1169.

(c) In H_3PO_4. A solution of 3-indolylcyclopropyl ketone **2b** (0.331 g, 1 mmol) in H_3PO_4 (88%, 10 mL) was stirred at room temperature for 12 h (Table 1, entry 4). It was then poured into cold saturated $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude product **8b** which was separated by column chromatography over silica gel using EtOAc−hexane (1:2) as eluent.

(d) General Procedure for Cyclization of 2b-e to 8b-e. (1) Cyclization of (2b−e) in TFA/Dichloromethane. To a solution of 3-indolylcyclopropyl ketones **2b**−**e** (1 mmol) in CH_2Cl_2 (15 mL) was added TFA (0.14 mL, 1.5 mmol) dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h (monitored by TLC). It was then poured into cold saturated $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude products **8b**−**e** which were purified by column chromatography over silica gel using EtOAc−hexane (1:2) as eluent.

(2) Cyclization of 2b in TFA/Dichloroethane. To a solution of 3-indolylcyclopropyl ketone **2b** (0.331 g, 1 mmol) in $ClCH_2$-CH_2Cl (15 mL) was added TFA (0.14 mL, 1.5 mmol) dropwise at room temperature, and the reaction mixture was stirred at 80 °C for 12 h (monitored by TLC). It was then poured into cold saturated $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). Work up of the reaction mixture as described above gave **8b** in 63% yield.

5,6a-Dimethyl-6,6a,7,8,9,9a-hexahydropentaleno[2,1-*b*]indol-6,7-dione (8b). Yield 60% (0.15 g); colorless crystals; mp 132−133 °C; R_f 0.24 (2:1 hexane−EtOAc); IR (CH_2Cl_2): 2933, 1729, 1674, 1453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.3 Hz, 1H), 7.46 (dt, J = 1.3 Hz, 6.8 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.23 (dt, J = 1.2 Hz, 7.5 Hz, 1H), 3.90 (s, 3H), 3.85 (d, J = 8.1 Hz, 1H), 2.49−2.25 (m, 4H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 188.2, 145.5, 144.4, 137.8, 127.3, 122.3, 121.6, 120.7, 111.4, 70.0, 44.0, 36.0, 30.3, 22.9, 17.4; MS (*m*/*z*, %): 253 (M^+, 20), 252 (85), 197 (100); HRMS (EI) *m*/*z* Calcd. for $C_{16}H_{15}NO_2$: 253.1103, Found: 253.1028.

(e) In PTSA. To a solution of 3-indolylcyclopropyl ketones **2b** and **2d** (1 mmol) in C_6H_6 (15 mL) was added PTSA (0.22 g, 1.1 mmol), and the reaction mixture was refluxed for 12 h. It was then poured into cold saturated $NaHCO_3$ solution (25 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O (2 × 50 mL), brine (50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude products which were purified by column chromatography over silica gel using EtOAc−hexane (1:99) as eluent to give **9b** (51%) and **9d** (48%).

Methyl 2-(9-*N*-Methyl-1-carbazolyl)propane Carbothioate (9b). Yield 51% (0.14 g); light yellow solid; mp 78−79 °C; R_f 0.37 (99:1 hexane−EtOAc); IR (KBr): 2927, 1663, 1462, 1328, 1112, 937, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 0.5H), 8.07−8.03 (m, 1H), 7.50−7.34 (m, 3.5H), 7.28−7.21 (m, 2H), 4.89 (distorted q, J = 7.2 Hz, 1H), 4.08 (s, 1.5H),

3.82 (s, 1.5H), 2.23 (s, 1.5H), 2.21 (s, 1.5H), 1.77 (d, $J = 7.2$ Hz, 1.5H), 1.73 (d, $J = 7.2$ Hz, 1.5H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 202.0, 201.4, 141.5, 141.0, 140.8, 138.4, 134.5, 126.1, 125.8, 125.5, 123.9, 123.0, 122.3, 121.9, 121.2, 120.0, 119.9, 119.6, 119.3, 119.1, 119.0, 117.9, 109.4, 109.2, 108.4; 50.5, 47.8, 32.8, 29.0, 19.1, 17.8, 11.4, 11.3; MS (*m/z*, %): 283 (M^+, 41), 208 (100); HRMS (ES) *m/z* Calcd. for $C_{17}H_{17}NOS$: 283.1031, Found: 283.1028.

Procedure for Acid Induced Rearrangement of 2-Indolylcyclopropyl Ketones (4a,b). (a) With BF_3·OEt_2. General procedure described for 3-indolylcyclopropyl ketone **2a** was followed.

Cyclization of **4a**,**b** afforded **12a**,**b**.

5-Methyl-6,11-bis(methylthio)-5,6,7,8-tetrahydro-cycloocta-[*b*]indol-9-one (12a). Yield 63% (0.20 g); light yellow solid; mp 129−130 °C; R_f 0.32 (7:1 hexane−EtOAc); IR (KBr): 2914, 1624, 1541, 1397, 1170, 1024, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.25−7.14 (m, 2H), 6.09 (s, 1H), 4.49 (dd, $J = 13.6$ Hz, 4.8 Hz, 1H), 3.99 (s, 3H), 2.51−2.39 (m, 1H), 2.36 (s, 3H), 2.29−2.18 (m, 2H), 2.05 (s, 3H), 2.04−1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 154.1, 138.5, 138.0, 125.2, 122.74, 122.70, 121.1, 120.9, 111.7, 109.3, 41.7, 39.2, 36.3, 32.1, 16.4, 16.2; MS (*m/z*, %): 318 (M + 1, 100), 317 (M^+, 49); HRMS (ES) *m/z* Calcd. for $C_{17}H_{19}NOS_2Na$: 340.0806, Found: 340.0800

Procedure for Acid Induced Rearrangement of 2-Indolylcyclopropyl Ketones 4c,d and 4f to 14c,d and 14f. (a) With BF_3·OEt_2. General procedure described for 3-indolylcyclopropyl ketone **2a** was followed.

Cyclization of **4c**,**d** and **4f** afforded **14c**,**d** and **14f** (Table 2, entries 1,2).

(b) In TFA. General procedure described for 3-indolylcyclopropyl ketone **2b** was followed.

Cyclization of **4c** afforded **14c** (Table 2, entry 3).

(c) In Triflic Acid. To a solution of 2- indolylcyclopropyl ketone **4c** (0.331 g, 1 mmol) in CH_2Cl_2 (15 mL), CF_3SO_3H (0.13 mL, 1.5 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h (monitored by TLC). Work up of the reaction mixture as described above gave **14c** in 58% yield.

4,9a-Dimethyl-1,2,3,3a,9,9a-hexahydropentaleno[1,2-*b*]indol-1,9-dione (14c). Yield 69% (0.18 g); colorless crystal; mp 196−197 °C; R_f 0.18 (3:2 hexane−EtOAc); IR (KBr): 2934, 1741, 1674, 1523, 1460, 1025, 896, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.35−7.22 (m, 3H), 3.84 (s, 3H), 3.74 (d, $J = 7.08$ Hz, 1H), 2.48−2.26 (m, 4H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 188.5, 166.9, 143.6, 124.1, 122.8, 121.3, 121.1, 118.3, 110.2, 69.8, 43.5, 35.9, 30.9, 22.2, 17.9; MS (*m/z*, %): 254 (M + 1, 100), 253 (M^+, 85); HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}NO_2Na$: 276.0995, Found: 276.09935.

(d) With $SnCl_4$. General procedure described for 3- indolylcyclopropyl ketone **2a** was followed.

Cyclization of **4c** afforded **15c** (Table 2, entry 5).

(e) In PTSA. General procedure described for 3-indolylcyclopropyl ketone **2b** was followed.

Cyclization of **4c**−**e** afforded **15c**−**e.**

9-*N*-Methyl-4-[1-methyl-2,2 bis(methylthiovinyl)]carbazole (15c). Yield 65% (0.20 g); viscous liquid; R_f 0.30 (99:1 hexane−EtOAc); IR (CH_2Cl_2): 2921, 1587, 1466, 1423, 1324, 751, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, $J = 7.8$ Hz, 1H), 7.40−7.35 (m, 2H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 7.3$ Hz, 1H), 3.77 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 141.1, 141.0, 139.0, 130.1, 125.48, 125.44, 122.1, 121.9, 118.92, 118.90, 118.0, 108.3, 107.0, 29.1, 23.7, 17.2, 16.7; MS (*m/z*, %): 313 (M^+, 100); HRMS (ES) *m/z* calcd. for $C_{18}H_{19}NS_2$: 313.0959, Found: 313.0957

BF_3·OEt_2 Catalyzed Methanolysis of 15c−e, 9b, and 9d. A suspension of **15c**−**e**, **9b**, and **9d** (0.5 mmol) and $HgCl_2$ (1.36 g, 5 mmol) in anhydrous MeOH (5 mL) was stirred at room temperature (10 min) followed by addition of BF_3·OEt_2 (0.5 mL, 3.9 mmol). The reaction mixture was refluxed (8−10 h), cooled, and filtered to remove mercury salts. The filtrate was poured into saturated $NaHCO_3$ solution (25 mL), followed by extraction with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with H_2O (2 × 25 mL) and brine (25 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford crude products **16c**−**e**, **17b**, and **17d** which were purified by passing through silica gel column using EtOAc−hexane (1:99) as eluent.

Methyl 2-(9-*N*-Methyl-4-carbazolyl)propanoate (16c). Yield 64% (0.09 g); viscous liquid; R_f 0.40 (99:1 hexane−EtOAc); IR (CH_2Cl_2): 2927, 1734, 1594, 1470, 1326, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, $J = 8.0$ Hz, 1H), 7.51−7.41 (m, 3H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 4.78 (q, $J = 7.1$ Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 1.70 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 141.3, 141.1, 135.9, 125.8, 125.4, 122.5, 122.0, 120.3, 119.0, 117.2, 108.5, 107.3, 52.1, 42.6, 29.1, 17.8; MS (*m/z*, %): 267 (M^+, 11), 266 (20), 265 (100); HRMS (ES) *m/z* Calcd. for $C_{17}H_{17}NO_2Na$: 290.1157, Found: 290.1137.

Methyl 2-(9-*N*-Methyl-1-carbazolyl)propanoate (17b). Yield 76% (0.10 g); viscous liquid; R_f 0.50 (99:1 hexane−EtOAc); IR (CH_2Cl_2): 2945, 1735, 1592, 1465, 1440, 1329, 1200, 1159, 1068, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (d, $J = 7.8$ Hz, 0.5H), 8.08 (d, $J = 7.8$ Hz, 0.5H), 8.02 (d, $J = 7.8$ Hz, 0.5H), 7.53−7.16 (m, 5.5H), 4.81 (distorted q, $J = 7.0$ Hz, 1H), 4.13 (s, 1.5H), 3.81 (s, 1.5H), 3.70 (s, 3H), 1.76 (d, $J = 7.0$ Hz, 1.5 H), 1.70 (d, $J = 7.0$ Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 141.9, 141.3, 141.0, 138.3, 135.9, 125.9, 125.8, 125.4, 125.0, 124.5, 123.7, 122.7, 122.4, 121.9, 120.3, 119.9, 119.4, 119.1, 119.0, 117.1, 108.6, 108.4, 107.3, 52.2, 52.1, 42.5, 39.7, 32.9, 29.0, 19.4, 17.7; MS (*m/z*, %): 267 (M^+, 100); HRMS (ES) *m/z* Calcd. for $C_{17}H_{18}NO_2$ (M + H): 268.1337, Found: 268.1337.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectral data for compounds and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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