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Domino Carbocationic Cyclization of Functionalized Cyclopropyl Ketones: Facile One-Pot Access to Peri- and Angularly Fused Polycyclic Aromatic and Heteroaromatic Frameworks†

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Conjugate adducts obtained by base-induced 1,4-addition−elimination of various aryl/heteroaryl acetonitriles with 1-(2-arylcyclopropyl)-3,3-(bismethylthio)-2-propen-1-ones have been shown to undergo facile acid-induced domino carbocationic rearrangement yielding a variety of substituted tricyclic aromatic and heteroaromatic frameworks in high yields in a one-pot operation. The methodology provides efficient, high-yield routes for synthesis of novel substituted dihydrophenalenes, dihydrobenzo[*d*,*e*]anthracene, cyclopenta[*a*]naphthalene, and fused heteroaromatics such as substituted 4,5-dihydrobenzo[*c*,*d*]indole, dihydronaphtho[1,8-*b*,*c*]thiophene, dihydroindeno[5,4-*b*]- and -[4,5-*b*]-thiophenes, cyclopenta[*a*]carbazole, and dihydrocyclopenta[*e*]indazol-3-one derivatives. The probable mechanism of this interesting domino process appears to involve stepwise or concomitant acid-induced ring opening and intramolecular cyclocondensation of cyclopropyl ketones to give benzo-fused arene (or heteroarene) intermediates bearing a reactive benzylic carbocation that is captured intramolecularly either by a preexisting aromatic (or heteroaromatic) ring or by a newly formed benzene ring to give either peri-fused or angularly fused products, respectively. Thus, the overall domino process entails formation of two C−C bonds, a substituted benzene ring along with a peri-fused cyclohexane or angularly fused cyclopentane ring in a single operation.

Introduction

The search for new and efficient methodologies that allow the rapid construction of polycyclic structures in a single operation is an important challenge today for synthetic organic chemists.[1] In this regard, formation of polycyclic ring systems based on cationic stitching of polyolefinic precursors has emerged as an extremely powerful synthetic method.[2,3] Cationic cyclizations also play an important role in acid-induced rearrangements of cyclopropyl ketones and carbinols.[4] The utility of cyclopropane in organic synthesis arises from the unique characteristic of the strained three-membered ring and the resemblance of its chemistry to that of carbon−carbon double bond. Depending on the functionality present, the carbocationic ring opening of cyclopropyl ketones and endocyclic trapping of the formal or incipient carbocation by a double bond or an aryl group represent an extremely useful method for the construction of carbon skeleton resulting in change of both the structure and the charge polarity of the product.[5] Our research interest in this regard has been concerned with the elaboration of domino reactions involving acid-induced rearrangements of 2-aryl (or styryl)-cyclopropyl-[bis(methylthio)alkylidene] ketones and carbinols leading to the formation of novel carbocyclic frameworks.[6] Thus, we have demonstrated in a series of papers that the acid-induced cyclopropyl ring opening of these compounds and subsequent intramolecular 5-exo-trig capture of the resulting carbocation initially produces

† Dedicated to Prof. Lutz F. Tietze on his 60th birthday.

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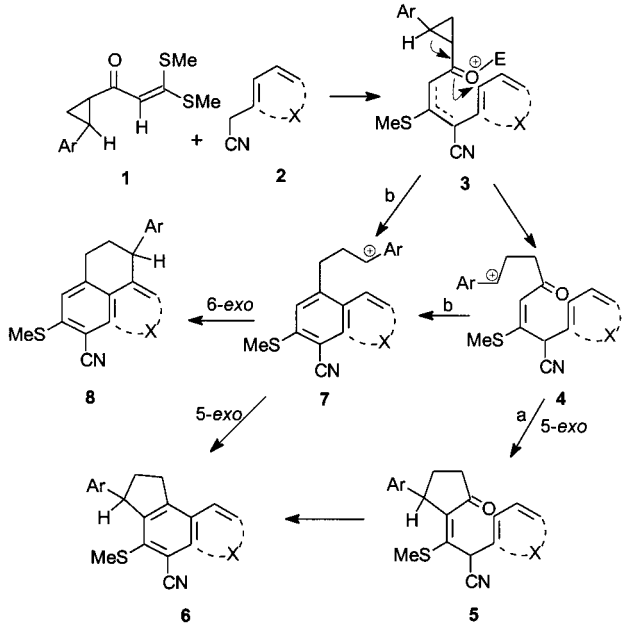
a cyclopentanoid ring bearing a reactive bis(methylthio)-methyl carbocation that can be further intercepted in a domino fashion by a pendant electron-rich arene or an olefinic double bond to furnish cyclopentanoindane,[7,8] diquinane,[8] or bicyclo[3.2.1]octene derivatives[9] in a highly stereoselective manner. Also, in a recent paper,[10] we have successfully elaborated another domino carbocationic process from strategically designed acyclic cyclopropyl carbinol precursors leading to the formation of a fused cyclopentane and a benzene ring in a cascade fashion to afford 1-arylindanes in good yields. This overall process combines our aromatic annelation protocol[11] and cyclopentane ring construction via oxoketene dithioacetals in a single one-pot synthetic operation. In continuation of these studies, we further considered it of interest to examine acid-induced cascade cyclization of cyclopropyl ketones of the general structure **3**, which were readily accessible in high yields via base-catalyzed conjugate addition−elimination of various aryl and heteroarylacetonitriles with [bis(methylthio)methylene]-arylcyclopropyl ketones **1**. It was envisaged that the initial acid-assisted ring opening of the cyclopropyl ketones **3** would furnish the stable benzylic carbocation **4**, which could be intercepted by the electron-rich (methylthio)methylene double bond via a 5-exo process followed by intramolecular cyclocondensation of the product cyclopentanones **5** to afford angularly fused benzo/heteroannelated indanes **6** (Scheme 1, pathway a). Alternatively, the cyclopropyl ketones **3** may undergo either stepwise or concomitant ring opening and intramolecular cyclocondensation to give benzo/heteroannelated arenes **7** with a pendant α-arylpropyl carbocationic side chain, which can be captured intramolecularly via 5- or 6-exo cyclization to yield either angularly fused indanes **6** or the novel pericyclized carbo- and heterocyclic ring systems **8** (pathway b). Indeed our studies revealed that both kind of products **6** and **8** are formed depending on the structure of the aryl/heteroaryl ring in the cyclopropyl ketones **3**. We report the results of this investigation in the present paper.

SCHEME 1



Results and Discussion

The adduct cyclopropyl ketones **3** were easily prepared in nearly quantitative yields by conjugate addition−elimination of the few selected aryl/heteroarylacetonitriles **2a**−**h** with 2-arylcyclopropyl-[bis(methylthio)-methylene] ketones **1a**−**c** in the presence of sodium hydride in DMF at room temperature. A few of the adducts were purified and characterized with the help of spectral and analytical data, whereas in the subsequent reactions, they were used as obtained for cyclization studies without further purification.[12] The adduct **3aa** was subjected to a detailed study for carbocationic ring opening and cyclization under the influence of various Lewis and protic acids ($SnCl_4/CH_3NO_2$, $SnCl_4/CH_2Cl_2$, $BF_3{\cdot}Et_2O/CH_3NO_2$, $BF_3{\cdot}Et_2O/CH_2Cl_2$, PTSA/$C_6H_6$, H_3PO_4), which showed the formation of only one product (TLC) in almost all cases, characterized as the 1-arylphenalene derivative **9a** on the basis of its spectral and analytical data (Scheme 3). The corresponding angularly fused cyclopenta[*a*]naphthalene structure **6** was ruled out on the basis of NOE studies between thiomethyl and H_a proton signals and also by Raney Ni (W2) dethiomethylation of **9a**, which furnished the 6-methylphenalene derivative **10a** in 78% yield. Apparently, the dethiomethylation is accompanied with concomitant exhaustive reduction of the nitrile functionality to a methyl group. The signals due to the aromatic protons (H_a and H_b) in the ^1H NMR spectra of **10a** appeared as sharp doublets at δ 6.96 ($J = 6.8$ Hz) and δ 7.11 ($J = 6.8$ Hz), respectively, whereas in the corresponding reduced cyclopenta[*a*]naphthalene derivative **11a**, all three aromatic protons (H_a, H_b, and H_c) are expected to appear as sharp singlets. The cationic cyclization of the adduct **3aa** to **9a** was found to be the most facile and clean (in terms of the yield and the workup) in H_3PO_4 (at 100 °C); therefore, all subsequent cyclizations were carried out in the presence of this acid. Thus, the cyclization of cyclopropyl ketones **3ba** and **3ca** in the presence of H_3-

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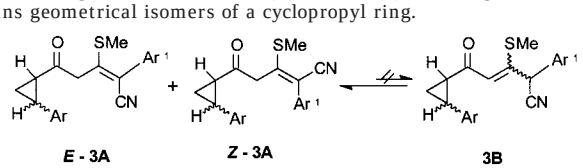
(12) ^1H and ^{13}C NMR spectra of adducts **3aa**, **3ca**, **3ab**, and **3ah** showed them to exist only in the tautomeric form **3A** as a complex mixture of geometrical isomers (*E*)-**3A** and (*Z*)-**3A** along with cis and trans geometrical isomers of a cyclopropyl ring.



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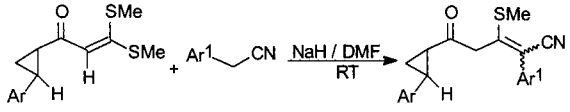
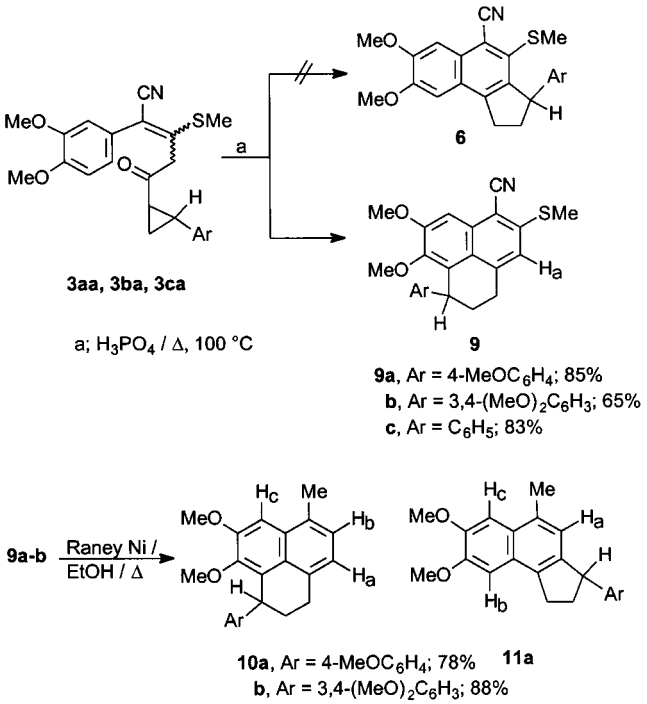
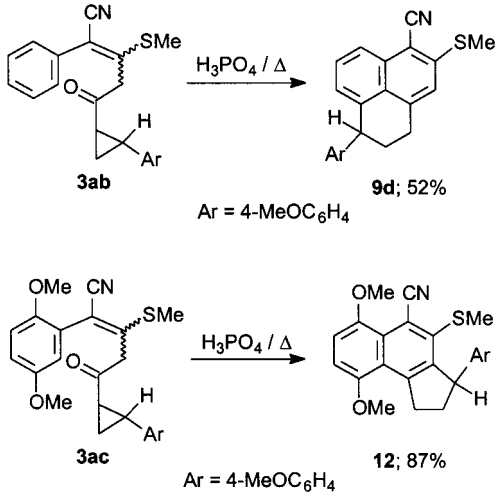


1	Ar	2	Ar^1	3
1a	4-MeOC$_6$H$_4$	**2a**	3,4-(MeO)$_2$C$_6$H$_3$	**3aa**
1b	3,4-(MeO)$_2$C$_6$H$_3$	**2a**	3,4-(MeO)$_2$C$_6$H$_3$	**3ba**
1c	C$_6$H$_5$	**2a**	3,4-(MeO)$_2$C$_6$H$_3$	**3ca**
1a	4-MeOC$_6$H$_4$	**2b**	C$_6$H$_5$	**3ab**
1a	4-MeOC$_6$H$_4$	**2c**	2,5-(MeO)$_2$C$_6$H$_3$	**3ac**
1b	3,4-(MeO)$_2$C$_6$H$_4$	**2d**	1-naphthyl	**3bd**
1a	4-MeOC$_6$H$_4$	**2e**		**3ae**
1a	4-MeOC$_6$H$_4$	**2f**	2-thienyl	**3af**
1a	4-MeOC$_6$H$_4$	**2g**	3-thienyl	**3ag**
1a	4-MeOC$_6$H$_4$	**2h**		**3ah**

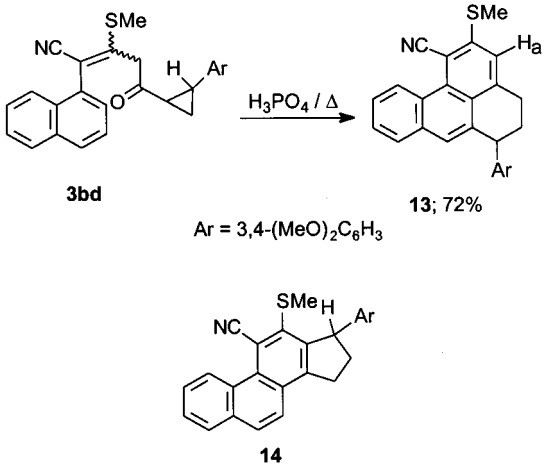
SCHEME 3



SCHEME 4



SCHEME 5



PO$_4$ also afforded the dihydrophenalenes **9b**−**c** in 65 and 83% yields, respectively. Both products **9b** and **9c** were characterized with the help of ^{1}H and ^{13}C NMR data and also by reductive desulfurization of **9b** to **10b** in 88% yield. The adduct **3ab** with an unsubstituted aryl group also yielded only the peri-bridged naphthalene derivative **9d** in 52% yield along with an intractable reaction mixture on prolonged heating (6 h) in H_3PO_4 (Scheme 4).

The domino carbocationic cyclization studies were next extended to cyclopropyl ketone adduct **3ac** from 2,5-dimethoxyphenylacetonitrile in which the peri cyclization pathway is blocked by the presence of a methoxy group, therefore deliberately steering the cyclization to another site. Indeed the adduct **3ac**, when heated in H_3PO_4, was efficiently transformed into a single product (87%), which was found to be the expected 3-arylcyclopenta[*a*]naphthalene derivative **12** on the basis of its spectral and analytical data. On the other hand, the corresponding adduct **3bd** from 1-naphthylacetonitrile yielded only the benzo[*d*,*e*]anthracene derivative **13** through peri cyclization under similar conditions with no trace of cyclopentanophenanthrene **14** (Scheme 5).

We next examined the acid-induced cyclization of the adduct cyclopropyl ketones (**3ae**−**ah**) obtained from conjugate addition of heteroarylacetonitriles to **1** as illustrated in Schemes 6−8, which followed a trend similar to that observed in the previous transformations. Thus, the adduct **3ae** from 1-methylpyrrole-2-acetonitrile yielded a single product (93%) in the presence of H_3PO_4, which was characterized as the tricyclic indole derivative **15** possessing the partial structural framework of several naturally occurring alkaloids[13] and biologically active

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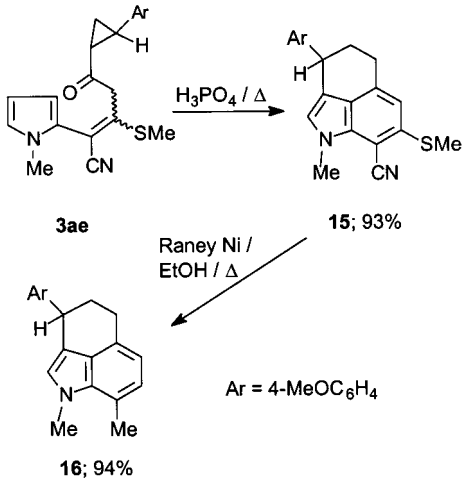
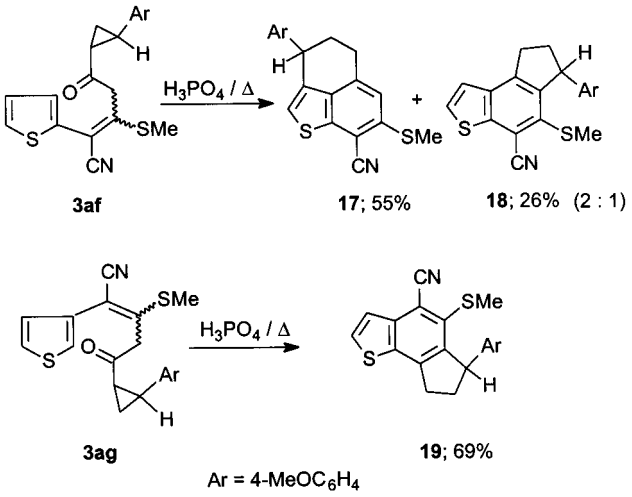
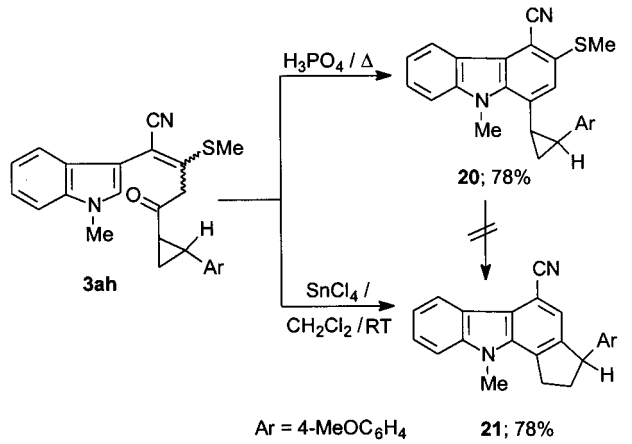
SCHEME 6



SCHEME 7

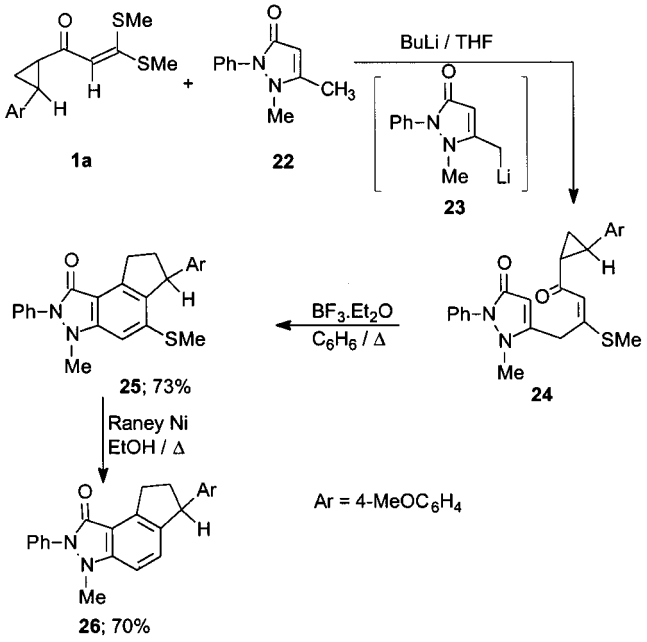


SCHEME 8



indole derivatives.[14] The regiochemistry of the cyclization was further supported by the structural assignment of the product **16** obtained from Raney Ni desulfurization

SCHEME 9



of **15** (Scheme 6). Interestingly, the cationic cyclization of the adduct **3af** from thiophene-2-acetonitrile under identical conditions provided a 2:1 mixture of two products, which were identified as the peri-annelated **17** and indeno[5,4-*b*]thiophene derivative **18** with the help of their spectral and analytical data (Scheme 7). The corresponding adduct **3ag** from thiophene-3-acetonitrile, in which the possibility of peri cyclization is blocked by the presence of a sulfur heteroatom, underwent the expected cycloaromatization−cyclopentane annelation sequence under identical conditions to furnish only the indeno[4,5-*b*]thiophene derivative **19** in 69% yield (Scheme 7). On the other hand, the carbocationic cyclization of the indole-3-acetonitrile adduct **3ah** in H_3PO_4 did not furnish the expected cyclopenta[*a*]carbazole **21**; the product isolated in 78% yield was characterized as the 1-(1-arylcycloprop-2-yl)carbazole **20** from its ^{1}H and ^{13}C NMR data (Scheme 8). Our attempts to transform the product **20** to **21** in the presence of various Lewis and protic acids were not successful. However, the adduct **3ah** could be transformed into the cyclopenta[*a*]carbazole **21** in 78% yield upon treatment with $SnCl_4$ in dichloromethane at room temperature (Scheme 8).

Finally, these cascade cationic cyclization studies were extended to the conjugate adduct **24** obtained from 3-lithiomethyl-2-methyl-1-phenylpyrazolin-5-one **23** and [bis(methylthio)methylene]cyclopropyl ketone **1a** (Scheme 9). We have shown in previous studies[15] that the anion **23** derived from antipyrine **22** undergoes 1,4-addition−elimination with various α-oxoketene dithioacetals followed by BF_3·Et_2O-assisted cycloaromatization to afford substituted and fused indazolones in high yields. Thus, the conjugate adduct **24** was obtained in good yield upon treatment of the oxoketene dithioacetal **1a** with the lithiomethyl anion **23** under the reported conditions.[15] The adduct **24** was smoothly transformed into the expected cyclopenta[*e*]indazolone derivative **25** under

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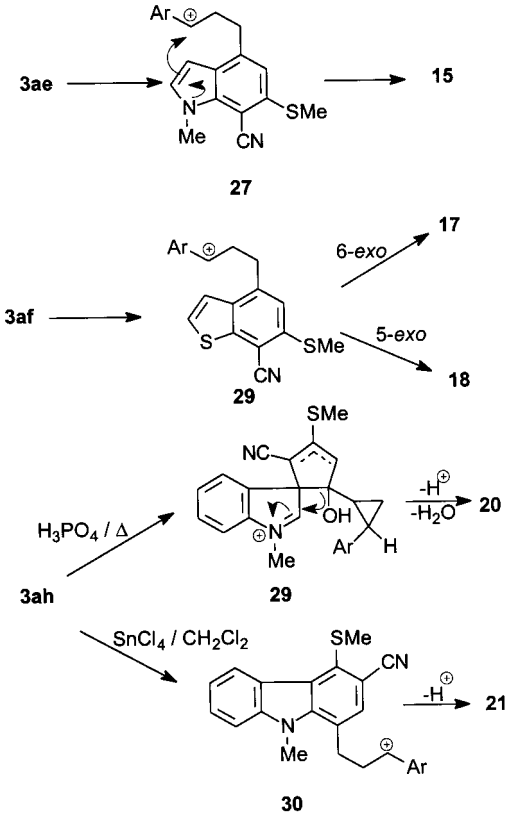
BF_3·Et_2O-induced cyclization in refluxing benzene (Scheme 9). The spectral and analytical data of **25** were found to be in conformity with the assigned structure, which was further corroborated by its conversion to the dethiomethylated product **26** in the presence of Raney Ni (W2) (Scheme 9).

The probable mechanism for the formation of various peri- and angularly fused products appears to be similar to that proposed in the Scheme 1 involving either stepwise or concomitant acid-induced ring opening and intramolecular cyclocondensation of the cyclopropyl ketones **3** to give the common carbocationic intermediate **7** (pathway b). The subsequent fate of the intermediate **7** of undergoing either 5- or 6-exo cyclization is governed by the size of the newly formed ring (six vs five members) and also by the nucleophilicity/availability of the site of cyclization. Thus, the intermediate carbocations **7** (X = CH=CH) derived from cyclopropyl ketones **3aa**, **3ba**, **3ca**, **3ab**, and **3bd** undergo more facile 6-exo cyclization[16] on the adjacent ring to afford the respective peri-fused naphthalenes (**9a**−**d**) and phenanthrene (**13**) (Schemes 3−5), whereas in the case of the ketone **3ac**, the site of 6-exo cyclization is blocked by a methoxy group, thus diverting the cyclization on the same ring to give cyclopenta[*a*]naphthalene derivative **12** (Scheme 4). Similarly, the 4-indolyl carbocation **27** from the ketone **3ae** also undergoes the preferred 6-exo cyclization at the highly electron-rich 3-position[17] of the indole ring to give exclusively the tricyclic indole derivative **15** in excellent yield. On the other hand, the adduct cyclopropyl ketone **3af** from thiophene 2-acetonitrile affords both peri- (**17**) and cyclopenta- (**18**) fused benzothiophenes (2:1) by intramolecular capture of the carbocation **28** at the C-3 and C-5 positions of the benzothiophene[18] (Scheme 10), whereas the adducts **3ag** from thiophene 3-acetonitrile yielded only the angularly fused benzothiophene **19** in the absence of the possible 6-exo cyclization. In the case of the conjugate adduct **3ah** derived from indole 3-acetonitrile, the intramolecular ring closure of the ketone appears to be faster than the cyclopropyl ring opening (in the presence of a weaker acid such as H_3PO_4) occurring first at the C-3 position of the indole to give the corresponding spiro-3*H*-indolium cation **29** (Scheme 10).[19] Subsequent rearrangement of **29** with concurrent dehydration and deprotonation affords the 1-(1-aryl-2-cyclopropyl)carbazole **20** as the sole product. However, in the presence of a stronger Lewis acid ($SnCl_4$), the reaction follows a pathway similar to that suggested for the other cyclopropyl ketones through concomitant ring opening and cyclization followed by intramolecular 5-exo trapping of the cation **30** to give only cyclopenta[*a*]-carbazole **21** (Scheme 10).

SCHEME 10



Conclusion

In summary, we have demonstrated that the easily accessible acyclic conjugate adducts **3** with an appropriately disposed cyclopropyl ketone functionality undergo an efficient acid-induced domino carbocationic cyclization to yield a range of novel functionalized tricyclic aromatic and heteroaromatic frameworks in high yields. These observations along with our earlier studies suggest that a wide range of domino sequence may be possible using carbocationic cyclization of strategically designed cyclopropyl ketone precursors. Our efforts in these directions are underway.

(16) Friedel−Crafts-type cyclization of *β*-(1-naphthyl)propionoic acid generally takes place at the peri position due to the formation of a six-membered ring; see: Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1996; Chapter 3, p 44. (b) Sethna, S. *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1964; Vol. 3, Chapter XXXV, p 920.

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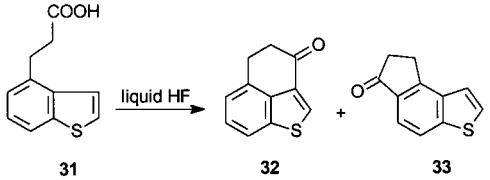
(18) Friedel−Crafts cyclization of *β*-(4-benzo[*b*]thienyl)propionoic acid **31** in the presence of hydrogen fluoride has been reported to give a mixture of isomeric ketones **32** and **33**; see: (a) Iddon, B.; Scrowston, R. M. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1970; Vol. 11, p 346. (b) Hawthorne, D. G.; Porter, Q. N. *Aust. J. Chem*. **1966**, *19*, 1909.



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Experimental Section

General. ^{1}H 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 done by column chromatography using 60−120 mesh silica gel. All reactions were monitored by TLC on a glass plate coated with silica gel containing 13% calcium sulfate as a binder, and visualization was effected with short-wavelength UV light (254 nm) or acidic $KMnO_4$ solution. All reagents were used directly as obtained commercially unless otherwise noted. DMF was distilled over CaH_2 and stored over molecular sieves. THF was distilled over sodium benzophenone ketyl prior to use. *n*-BuLi was purchased commercially.

The cyclopropyl ketones **1a**−**d** were prepared according to our earlier reported procedure.[6] All of the arylacetonitriles **2a**−**d**, *N*-methylpyrrole-2-acetontrile (**2e**), thiophene-2, 3-acetonitrile (**2f**,**g**), and antipyrine were purchased commercially, whereas indole-3-acetonitrile was prepared by the reported method.[20]

General Procedure for the Preparation of 1,4-Addition−Elimination Adducts 3aa−3ah. To a stirred suspension of NaH (0.60 gm, 40%, 10 mmol) in DMF (10 mL) at 0 °C was added a solution of aryl/heteroarylacetonitrile (5 mmol) in DMF (5 mL) dropwise over 15 min, and the reaction mixture was further stirred at 0 °C for 45 min. Appropriate aryl cyclopropyl ketone (5 mmol) in DMF (10 mL) was slowly added, and the reaction mixture was allowed to warm to room temperature with stirring over 8−10 h. The mixture was then poured into saturated NH_4Cl solution (200 mL) and extracted with chloroform (3 × 50 mL). The combined organic layer was washed with water (3 × 50 mL), dried (Na_2SO_4), and evaporated to give the crude 1,4-addition−elimination adducts, which were used as obtained for further cyclization. A few of the adducts were purified by column chromatography, and their spectral and analytical data are given below.

3-(3,4-Dimethoxyphenyl)-1-(2-Phenylcyclopropyl)-3-methylsulfanyl--2-propen-1-one (3ca): yield 80% (1.57 g); *E*:*Z* = 2.9:1; viscous liquid; R_f 0.46 (8:2 hexanes−EtOAc); IR (CCl_4) 2931, 2200, 1512, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (*E*, ddd, *J* = 9.4, 6.5, 3.8 Hz, 1H), 1.76 (*Z*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 1.84 (*E*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 2.16 (*Z*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 2.41 (*Z*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 2.27 (*Z*, s, 3H), 2.43 (*E*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 2.44 (*E*, s, 3H), 2.56 (*Z*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 2.62 (*E*, ddd, *J* = 9.4, 6.5, 3.9 Hz, 1H), 3.77−3.78 (*Z*, m, 2H), 3.79 (*Z*, s, 3H), 3.83 (*E*, s, 3H), 3.84 (*Z*, s, 3H), 3.86 (*E*, s, 3H), 4.12−4.19 (*E*, m, 1H), 6.75 (*E*, d, *J* = 5.9 Hz, 1H), 6.85 (*Z*, d, *J* = 8 Hz, 1H), 6.89 (*E*, s, 1H), 6.92 (*E*, d, *J* = 1.5 Hz, 1H), 7.05 (*Z*, d, *J* = 7.3 Hz, 1H), 7.13 (*E*, d, *J* = 7.3 Hz, 1H), 7.20−7.24 (*Z*, m, 5H), 7.26−7.31 (*E*, m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 (*E*), 15.4 (*Z*), 19.1 (*E*), 19.3 (*Z*), 30.3 (*E*), 30.0 (*Z*), 31.6 (*E*), 32.1 (*Z*), 49.6 (*E*), 47.3 (*Z*), 55.7 (*E*), 55.7 (*Z*), 55.8 (*E*), 55.8 (*Z*), 110.1 (*E*), 110.6 (*Z*), 111.0 (*E*), 111.2 (*Z*), 111.4 (*E*), 111.5 (*Z*), 111.6 (*E*), 111.2 (*Z*), 117.5 (*E*), 118.2 (*Z*), 121.9 (*E*), 121.2 (*Z*), 126.0 (*E*), 125.1 (*Z*), 126.7 (*E*), 126.8 (*Z*), 128.4 (*E*), 128.5 (*Z*), 139.2 (*E*), 139.4 (*Z*), 148.6 (*E*), 148.9 (*Z*), 149.3 (*E*), 149.2 (*Z*), 151.3 (*E*), 151.6 (*Z*), 202.2 (*E*), 203.1 (*Z*); MS (*m*/*z*, %) 393 (M$^+$, 63.3), 378 (32.8), 145 (100). Anal. Calcd for $C_{23}H_{23}NO_3S$ (393.51): C, 70.20; H, 5.89; N, 3.56. Found: C, 70.40; H, 5.80; N, 3.61.

General Procedure for the Cyclization of Adducts 3aa−ah with Orthophosphoric Acid. The crude adduct **3** (∼5 mmol) obtained from an earlier reaction was dissolved in H_3PO_4 (20 mL, 85%), and the reaction mixture was heated with stirring at 100 °C for 3−6 h (monitored by TLC). The mixture was then cooled, poured into ice-cold water (150 mL), and extracted with chloroform (3 × 50 mL), and the combined organic layer was washed with water (3 × 50 mL) and dried over Na_2SO_4. The solvent was distilled out to give a crude product that was purified by column chromatography over silica gel using 97:3 hexanes−ethyl acetate as an eluent.

4,5-Dimethoxy-1,2-dihydro-3-(4-methoxyphenyl)-8-methylsulfanyl-3*H*-phenalene-7-carbonitrile (9a): yield 85% (1.72 g); colorless crystals (chloroform−hexane); mp 144−145 °C; R_f 0.52 (97:3 hexanes−EtOAc); IR (KBr) 2924, 2208, 1508, 1261, 1242 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16−2.20 (m, 2H), 2.64 (s, 3H), 2.80 (ddd, *J* = 3.4, 7.4, 8.7 Hz, 1H), 2.92 (ddd, *J* = 3.4, 7.4, 8.7 Hz, 1H), 3.49 (s, 3H), 3.74 (s, 3H), 4.02 (s, 3H), 4.85 (dd, *J* = 3.1 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.09 (s, 1H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 25.8, 29.7, 37.7, 55.1, 55.7, 60.7, 102.8, 104.1, 113.5, 116.9, 120.2, 123.2, 128.8, 130.3, 131.9, 136.4, 141.9, 142.5, 145.9, 155.0, 157.9; MS (*m*/*z*, %) 405 (M$^+$, 100), 266 (31.1). Anal. Calcd for $C_{24}H_{23}NO_3S$ (405.52): C, 71.08; H, 5.72; N, 3.45. Found: C, 71.19; H, 5.70; N, 3.40.

6,9-Dimethoxy-3-(4-methoxyphenyl)-4-methylsulfanylcyclopenta[*a*]naphthalene-5-carbonitrile (12): yield 87% (1.77 g); colorless solid; mp 158−159 °C; R_f 0.52 (97:3 hexanes−EtOAc); IR (KBr) 2930, 2215, 1508, 1455, 1243 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (ddd, *J* = 9.6, 6.5, 3.9 Hz, 1H), 2.21 (s, 3H), 2.54−2.72 (m, 2H), 3.74 (ddd, *J* = 9.2, 6.4, 2.8 Hz, 1H), 3.75 (s, 3H), 3.90 (s, 3H), 4.00 (s, 3H), 4.80 (dd *J* = 7.6, 2.9 Hz, 1H), 6.76 (dd, *J* = 9.1, 2.8 Hz, 2H), 6.80 (d, *J* = 8.96 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.91 (dd, *J* = 9.1, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 34.2, 35.7, 50.5, 55.1, 55.6, 56.3, 106.0, 107.4, 110.8, 113.7, 118.1, 123.9, 127.2, 128.4, 137.9, 142.1, 145.4, 148.0, 148.5, 151.5, 157.8. MS (*m*/*z*, %) 407 (M$^+$, 100), 359 (7.6), 239 (15.6), 166 (29.10). Anal. Calcd for $C_{24}H_{23}NO_3S$ (405.52): C, 71.08; H, 5.72; N, 3.45. Found: C, 71.14; H, 5.62; N, 3.34.

6-(3,4-Dimethoxyphenyl)-2-methylsulfanyl-4,5-dihydro-6*H*-benzo[*d*,*e*]anthracene-1-carbonitrile (13): yield 72% (1.53 g); colorless crystals; mp 181−182 °C; R_f 0.62 (97:3 hexanes−EtOAc); IR (KBr) 2292, 2205, 1619, 1575, 1515 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (ddd, *J* = 8.7, 7.4, 3.4 Hz, 1H), 2.34 (ddd, *J* = 8.6, 6.4, 2.4 Hz, 1H), 2.69 (s, 3H), 3.18 (t, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 3.87 (s, 3H), 4.39 (dd, *J* = 7.6, 2.9 Hz, 1H), 6.56 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.71 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.35 (s, 1H), 7.59−7.65 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 9.80 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 30.0, 30.5, 46.2, 55.8, 55.8, 111.0, 111.3, 119.4, 120.7, 122.6, 125.2, 126.3, 127.2, 127.4, 127.7, 128.2, 128.2, 128.4, 131.8, 133.2, 135.8, 137.0, 142.2, 146.0, 147.7, 149.0; MS (*m*/*z*, %) 425 (M$^+$, 100), 394 (4.7), 287 (52), 240 (79.2). Anal. Calcd for $C_{27}H_{23}NO_2S$ (425.55): C, 76.20; H, 5.44; N, 3.29. Found: C, 76.09; H, 5.38; N, 3.28.

1-*N*-Methyl-3-(4-methoxyphenyl)-7-methylsulfanyl-4,5-dihydro-3*H*-benzo[*c*,*d*]indole-8-carbonitrile (15): yield 93% (1.58 g); colorless crystals; mp 141−142 °C; R_f 0.42 (97:3 hexanes−EtOAc); IR (KBr) 2939, 2210, 1609, 1511, 1453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (ddd, *J* = 8.9, 5.3, 4.0 Hz, 1H), 2.22 (ddd, *J* = 8.4, 6.3, 4.3 Hz, 1H), 2.60 (s, 3H), 2.97(m, 2H), 3.80 (s, 3H), 4.01 (s, 3H), 4.12 (dd, *J* = 7.2, 3.4 Hz, 1H), 6.50 (s, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 27.0, 33.3, 34.1, 38.7, 55.2, 92.2, 113.8, 117.1, 117.4, 125.7, 125.8, 127.4, 128.6, 133.9, 136.6, 138.0, 138.2, 158.2; MS (*m*/*z*, %) 348 (M$^+$, 100), 301 (48), 240 (34.2), 193 (40). Anal. Calcd for $C_{21}H_{20}N_2OS$ (348.46): C, 72.37; H, 5.79; N, 8.04. Found: C, 72.40; H, 5.70; N, 8.01.

3-(4-Methoxyphenyl)-7-methylsulfanyl-4,5-dihydro-3*H*-naphtho[1,8-*b*,*c*]thiophene-8-carbonitrile (17): yield 55% (0.96 g); white crystals; mp 110−112 °C; R_f 0.57 (97:3 hexanes−EtOAc); IR (KBr) 2922, 2212, 1609, 1573, 1511, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (ddd, *J* = 8.4, 6,3, 4.3 Hz, 1H), 2.22 (m, 1H), 2.57 (s, 3H), 2.96 (q, *J* = 8.1, 2H), 3.74 (s, 3H), 4.06 (dd, *J* = 7.3, 3.1 Hz, 1H), 6.71 (d, *J* = 1.2 Hz, 1H), 6.81 (dd, *J* = 6.6, 2.2 Hz, 2H), 7.05 (dd, *J* = 6.6, 2.0 Hz, 2H), 7.09 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 17.3, 28.0, 32.3, 42.8, 55.2, 113.8, 114.0, 115.6, 121.6, 121.6, 128.8, 129.0, 135.2, 138.8, 140.6, 143.7, 146.7, 158.6. Anal. Calcd for $C_{20}H_{17}NOS_2$ (351.49): C, 68.34; H, 4.88; N, 3.99. Found: C, 68.40; H, 4.89; N, 3.97.

6-(4-Methoxyphenyl)-4,5-dihydro-7-methylsulfanyl-6*H*-indeno[5,4-*b*]thiophene-8-carbonitrile (18): yield 26% (0.40 g); white crystals; mp 96−98 °C; R_f 0.58 (97:3 hexanes−EtOAc); IR (KBr) 2922, 2212, 1609, 1573, 1511, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.13 (m, 1H), 2.64 (ddd, J = 9.6, 6.5, 3.9 Hz, 1H), 3.19 (ddd, J = 9.6, 6.5, 3.9 Hz, 1H), 3.56 (ddd, J = 9.6, 6.5, 3.9 Hz, 1H), 3.69 (s, 3H), 4.71 (dd, J = 9, 3.3 Hz, 1H), 6.71 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 7.3 (d, J = 6.0 Hz, 1H), 7.56 (d, J = 6.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 19.4, 31.5, 34.8, 50.7, 55.1, 113.8, 114.1, 115.9, 121.6, 122.2, 128.5, 135.9, 137.8, 140.5, 140.9, 143.1, 146.9, 158.5; MS (*m*/*z*, %) 351 (M$^+$, 100), 336 (4.7), 303 (52), 186 (79.2). Anal. Calcd for $C_{20}H_{17}NOS_2$ (351.49): C, 68.34; H, 4.88; N, 3.99. Found: C, 68.41; H, 4.89; N, 3.98.

6-(4-Methoxyphenyl)-7,8-dihydro-5-methylsulfanyl-6*H*-indeno[4,5-*b*]thiophene-4-carbonitrile (19): yield 69% (1.21 g); white crystals; mp 139−140 °C; R_f 0.53 (97:3 hexanes−EtOAc); IR (KBr) 2920, 2211, 1608, 1509, 1429; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.21 (m, 1H), 2.71 (ddd, J = 9.6, 6.5, 3.9 Hz, 1H), 3.26 (ddd, J = 9.6, 6.5, 3.9 Hz, 1H), 3.44 (ddd, 2.5, 8.3, 16.5 Hz, 1H), 3.76 (s, 3H), 4.78 (dd, J = 9.0, 3.4 Hz, 1H), 6.78 (dd, J = 7.0, 2.0 Hz, 2H), 6.90 (dd, J = 9.0, 2.3 Hz, 2H), 7.36 (d, J = 5.3 Hz, 1H), 7.63 (d, J = 5.64 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 19.4, 31.5, 34.8, 50.7, 55.1, 110.4, 113.7, 113.8, 114.0, 116.7, 122.2, 128.3, 128.9, 136.4, 137.4, 143.7, 146.7, 158.0; MS (M/z, %) 351 (87.9, M$^+$), 336 (72.8), 303 (75.01), 196 (53.9). Anal. Calcd for $C_{20}H_{17}NOS_2$ (351.49): C, 68.40; H, 4.88; N, 3.99. Found: C, 68.44; H, 4.87; N, 4.00.

9-*N*-Methyl-1-[2-(4-methoxyphenyl)cyclopropyl]-3-methylsulfanyl-carbazole-4-carbonitrile (20): yield 78% (1.55 g); colorless crystals; mp 168−169 °C; R_f 0.40 (97:3 hexanes−EtOAc); IR (KBr) 2952, 2360, 2207, 1514, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (ddd, J = 8.0, 5.4, 3.7 Hz, 1H), 1.74 (ddd, J = 8.6, 5.3, 2.9 Hz, 1H), 2.19 (ddd, J = 7.9, 5.4, 3.3 Hz, 1H), 2.63 (s, 3H), 2.68 (ddd, J = 8.4, 4.9, 3.7 Hz, 1H), 3.82 (s, 3H), 3.9 (s, 3H), 6.90 (d, J = 8.5 Hz, 2H), 7.09 (dd, J = 8.8, 2.6 Hz, 2H), 7.26 (dd, J = 8.5, 2.6 Hz, 1H), 7.30−7.32 (m, 2H), 7.52 (t, J = 7.3 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 19.1, 25.7, 26.5, 32.4, 55.3, 104.6, 108.9, 114.2, 117.4, 119.9, 120.1, 121.1, 121.7, 124.6, 126.5, 127.5, 129.3, 132.0, 132.9, 138.9, 142.2, 158.1; MS (*m*/*z*, %) 398 (M$^+$, 34), 351 (47.5), 242 (18), 145 (100). Anal. Calcd for $C_{25}H_{22}N_2OS$ (398.52): C, 75.33; H, 5.57; N, 7.03. Found: C, 75.30; H, 5.55; N, 7.11.

Procedure for $SnCl_4$-Induced Cyclization of Cyclopropyl Ketone 3ah to 21. To a stirred solution of crude **3ah** (∼5 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added $SnCl_4$ (1.5 mL, 0.01 mol), and the reaction mixture was further stirred at room temperature for 3 h. The mixture was then poured into ice-cold aqueous $NaHCO_3$ solution (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried (Na_2SO_4), and evaporated to give a viscous residue that was purified by column chromatography using 9:1 hexanes−ethyl acetate as an eluent.

10-*N*-Methyl-3-(4-methoxyphenyl)-4-methylsulfanylcyclopenta[*a*]carbazole-5-carbonitrile (21): yield 78% (1.55 g); colorless crystals; mp 170−171 °C; R_f 0.33 (97:3 hexanes−EtOAc); IR (KBr) 2921, 2215, 1610, 1581, 1510, 1061 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.23 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 2.73 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.63 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.71 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.77 (s, 3H), 4.09 (s, 3H), 4.88 (dd, J = 8.0, 3.6 Hz, 1H), 6.77 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 8.0, 1H), 8.70 (d, J = 8.04 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 31.1, 31.2, 34.9, 50.2, 55.1, 108.7, 109.5, 113.7, 113.8, 117.9, 120.2, 120.5, 121.8, 127.4, 127.7, 128.3, 129.9, 136.5, 137.8, 141.9, 149.8, 157.9; MS (*m*/*z*, %) 398 (M$^+$, 65), 352 (100), 243 (41), 145 (55). Anal. Calcd for $C_{25}H_{22}N_2OS$ (398.52): C, 75.33; H, 5.57; N, 7.03. Found: C, 75.38; H, 5.50; N, 7.01.

Procedure for the Preparation of Adduct 24 and Its BF_3·Et_2O-Induced Cyclization to 25. To a stirring solution of diisopropylamine (2 mL, 14 mmol) in dry THF (10 mL) under a nitrogen atmosphere was added *n*-BuLi (6.25 mL, 10 mmol, 1.6 M) at 0 °C, and the reaction mixture was further stirred for 20 min. To the resulting solution of LDA at −78 °C was added a solution of **22** (0.96 g, 5 mmol) in dry THF (30 mL) followed by further stirring for 45 min. A solution of cyclopropyl ketone **1a** (1.45 g, 5 mmol) was added at −78 °C, and the reaction mixture was brought to room temperature over 45 min and left overnight with continuous stirring. The mixture was then poured into ice-cold saturated NH_4Cl solution (150 mL) and extracted with chloroform (3 × 50 mL), and the combined organic extracts were washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated to give crude adduct **24**, which was dissolved in benzene (40 mL) followed by addition of BF_3·Et_2O (1.2 mL, 6 mmol). The reaction mixture was refluxed for 1 h, cooled, poured into saturated $NaHCO_3$ solution (100 mL), and extracted with chloroform (3 × 50 mL), and the combined organic layer was washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated to give crude **25**, which was purified by column chromatography over silica gel using 19:1 hexanes−ethyl acetate as an eluent.

6-(4-Methoxyphenyl)-1-*N*-methyl-7-methylsulfanyl-2-*N*-phenyl-1,2-dihydro-3*H*-cyclopenta[*e*]indazol-3-one (25): yield 73% (1.51 g); colorless crystals; mp 193−194 °C; R_f 0.33 (97:1 hexanes−EtOAc); IR (KBr) 2923, 1674, 1608, 1506, 1442 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (ddd, J = 9.0, 7.4, 3.8 Hz, 1H), 2.38 (s, 3H), 2.64 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.13 (s, 3H), 3.39 (ddd, J = 9.0, 7.4, 3.76 Hz, 2H), 3.73 (s, 3H), 4.36 (dd, J = 7.0, 2.9 Hz, 1H), 6.79 (d, J = 7.8 Hz, 2H), 6.83 (s, 1H), 6.95 (d, J = 7.8 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.3 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 29.4, 36.3, 40.1, 48.7, 55.0, 104.7, 111.7, 113.7, 123.1, 128.3, 125.8, 128.9, 135.6, 136.6, 138.6, 142.3, 143.1, 152.9, 157.9, 162.5. MS (*m*/*z*, %) 416 (M$^+$, 100), 401 (37.2), 324 (31.4), 85 (24.3), 121 (62.9). Anal. Calcd for $C_{25}H_{24}N_2O_2S$ (416. 54): C, 72.09; H, 5.80; N, 6.72. Found: C, 72.01; H, 5.78; N, 6.61.

General Procedure for Dethiomethylation−Reduction of 9a, 9b, 15, and 25 with Raney Ni. To a solution of the appropriate thiomethyl compound (2 mmol) in absolute ethanol (25 mL) was added Raney Ni (W2, ∼0.8 g), and the suspension was refluxed with stirring for 6−7 h (monitored by TLC). The reaction mixture was then cooled and filtered through a sintered funnel, and the residue was washed with ethanol. The combined filtrate was evaporated under reduced pressure, and the residue was dissolved in chloroform (50 mL), washed with water (2 × 50 mL), dried (Na_2SO_4), and concentrated to give a crude product that was purified by column chromatography using 98:2 hexanes−ethyl acetate as an eluent.

4,5-Dimethoxy-1,2-dihydro-3-(4-methoxyphenyl)-7-methyl-3*H*-phenalene (10a): yield 78% (0.68 g); colorless crystals; mp 150 °C; R_f 0.65 (98:2 hexanes−EtOAc); IR (KBr) 2930, 1512, 1463, 1245 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (m, 2H), 2.57 (s, 3H), 2.67 (ddd, J = 8.9, 7.4, 3.5 Hz, 1H), 2.81 (ddd, J = 8.7, 7.4, 3.4 Hz, 1H), 3.41 (s, 3H), 3.63 (s, 3H), 3.90 (s, 3H), 4.79 (t, J = 3.5 Hz, 1H), 6.63 (dd, J = 7.8, 2.4 Hz, 1H), 6. 78 (dd, J = 7.3, 2.4 Hz, 2H), 6.96 (d, J = 6.8 Hz, 2H), 7.11 (d, J = 6.8 Hz, 1H), 7.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 25.1, 30.2, 38.1, 55.0, 55.3, 60.6, 102.5, 113.3, 122.3, 125.7, 125.8, 129.0, 129.8, 130.1, 130.4, 133.7, 137.7, 145.0, 151.2, 157.6. Anal. Calcd for $C_{23}H_{24}N_2O_3$: C, 79.28; H, 6.94. Found: C, 79.19; H, 6.90.

1-*N*-Methyl-3-(4-methoxyphenyl)-4,5-dihydro-3*H*-8-methylbenzo[*c*,*d*]indole (16): yield 94% (0.54 g); colorless crystals; mp 141−142 °C; R_f 0.51 (97:3 hexanes−EtOAc); IR (KBr) 2939, 1609, 1511, 1453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (ddd, J = 8.5, 4.5, 2.6 Hz, 1H), 2.22 (ddd, J = 8.5, 4.5, 2.6 Hz, 1H), 2.78 (s, 3H), 2.92 (m, 2H), 3.79 (s, 3H), 3.95 (s, 3H), 4.14 (dd, J = 9.5, 4.4 Hz, 1H), 6.39 (s, 1H), 6.72 (d, J = 7.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.17−7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 26.7, 34.2, 35.8, 39.4, 55.2, 113.6, 115.6, 116.3, 118.3, 124.2, 124.7, 128.1, 128.7, 129.8,

133.6, 138.0, 157.9; MS (*m*/*z*, %) 291 (M^+, 100), 276 (11), 232 (3.27), 184 (23). Anal. Calcd for $C_{20}H_{21}NO$ (291.40): C, 82.43; H, 7.26; N, 4.80. Found: C, 82.30; H, 7.20; N, 4.72.

6-(4-Methoxyphenyl)-1-*N*-methyl-2-*N*-phenyl-1,2-dihdro-3*H*-cyclopenta[*e*]indazol-3-one (26): yield 70% (0.518 g); colorless crystals; mp 146−147 °C; R_f 0.39 (9:1 hexanes−EtOAc); IR (KBr) 3065, 2927, 1680, 1596, 1506 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 2.56 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.19 (s, 3H), 3.2 (ddd, J = 9.0, 7.4, 3.7 Hz, 1H), 3.47 (ddd, J = 9.0, 7.3, 3.4 Hz, 1H), 3.76 (s, 3H), 4.25 (dd, J = 8.0, 3.1 Hz, 1H), 6.78 (dd, J = 7.3, 2.4 Hz, 2H), 6.96 (dd, J = 7.3, 2.4 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.3 Hz, 1H), 7.20 (t, J = 7.9 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.6, 37.0, 40.1, 49.8, 55.2, 110.6, 113.8, 113.9, 115.4, 123.3, 125.9, 128.8, 129.0, 129.3, 135.4, 137.5, 142.6, 151.7, 158.1, 162.5; MS (*m*/*z*, %) 370 (M^+, 100), 355 (8.68). Anal. Calcd for $C_{24}H_{22}N_2O$ (370.45): C, 77.81; H, 5.98; N, 7.56. Found: C, 77.68; H, 5.86; N, 7.50.

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Supporting Information Available: Full spectroscopic and analytical data for compounds **9b**−**d** and **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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