Domino Carbocationic Rearrangement of α-[Bis(methylthio)methylene]alkyl-2-aryl-cyclopropyl Carbinols: Facile Access to 1-Arylindanes

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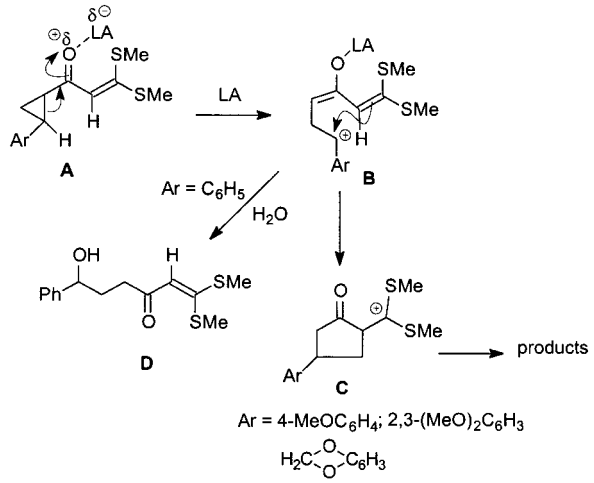
Domino or tandem processes occupy a central role in the syntheses of complex organic compounds and confer great strategic value in molecular construction.[1] These reactions typically entail the formation of multiple new bonds and rings in a single operation in high yields with good regio- and stereocontrol.[2] The carbocationic cyclization of polyolefinic precursors into fused polycyclic products exemplifies these reactions and has proven especially useful in the construction of six-membered rings.[3] Application of these carbocationic cyclizations to cyclopentanoid syntheses has also been reported.[4,5] We have previously described a new synthesis of substituted cyclopentanes via acid-induced rearrangement of 1-aryl-2-bis(methylthio)methylene cyclopropyl ketones and carbinols.[6] The overall transformation involves Lewis acid assisted cyclopropyl ring opening and intramolecular 5-*exo*-*trig* capture of the resulting carbocationic intermediate by the bis(methylthio)methylene double bond. These rearrangements can be regarded as modified Nazarov reactions in which one double bond of the pentadiene system is replaced by a cyclopropyl group.[4,7] We subsequently realized that this transformation is a potential candidate for domino process, since the initial cyclization results in the formation of a new carbon−carbon bond and cyclopentanoid ring while also producing a reactive bis(methylthio)methyl carbocationic intermediate. Thus, in the subsequent papers,[8] we demonstrated that a pendant electron rich arene or olefinic nucleophile can intercept this carbocation to furnish functionalized cyclopentanoindane and diquinane derivatives in highly stereoselective fashion. Also in a recent paper[9] we reported the unexpected formation of the bicyclo[3.2.1]-octane framework by domino carbocationic transformation of 1-styryl-2-bis(methylthio)methylene cyclopropyl carbinols through a series of rearrangement and termination events. In continuation of these studies, we now report further on our findings on one-pot domino carbocationic cyclization of the cyclopropyl carbinols with general structures **3**−**5** to substituted 1-arylindanes. The overall transformation entails the concomitant formation of two strategic carbon−carbon bonds leading to a substituted benzene and cyclopentane ring from acyclic precursors in one synthetic operation.

The carbinol substrates **3a**−**h**, **4a**,**b**, and **5a** were easily prepared by addition of the various allyl Grignard reagents **2a**−**c** to the cyclopropyl ketones[6b,c] **1a**−**h** under our earlier described standard reaction conditions.[10] We anticipated that the initially generated benzylic carbocation **18** in the presence of Lewis acid would be intercepted by a pendant bis(methylthio)methylene and allylic double bond in a domino fashion leading to concomitant formation of indane framework after subsequent aromatization (Scheme 3). Thus, with these carbinols in hand, common Lewis acids were surveyed and $BF_3{\cdot}Et_2O$ was found to cleanly effect the desired transformation. When the carbinol **3a** obtained from addition of methallyl Grignard reagent to **1a** was treated with $BF_3{\cdot}Et_2O$ in nitromethane at 0 °C for 12 h, a single new product was formed. After



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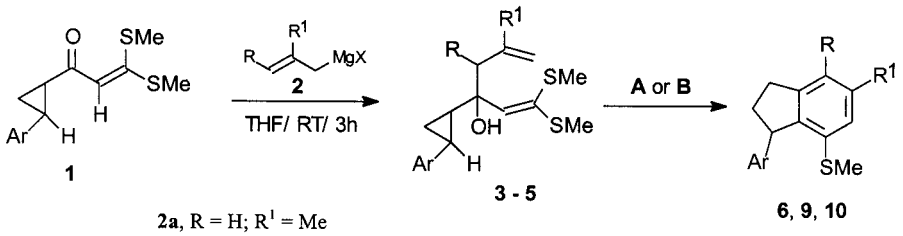
Scheme 1



2a, R = H; R^1 = Me

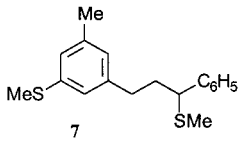
b, R = H; R^1 = H

c, R = Me; R^1 = H

Table 1. Synthesis of Substituted 1-Arylindanes

Entry	1	2	3,4,5	Conditions	Product	Ar	R	R^1	%Yield
1	1a	2a	3a	A	6a	4-$MeOC_6H_4$	H	Me	79
2	1b	2a	3b	A	6b	2-$MeOC_6H_4$	H	Me	75
3	1c	2a	3c	A	6c	3, 4-$(MeO)_2C_6H_3$	H	Me	78
4	1d	2a	3d	A	6d	3,4-H_2C(O)(O)C_6H_3	H	Me	80
5	1e	2a	3e	A	6e	3, 4,5-$(MeO)_3C_6H_2$	H	Me	82
6	1f	2a	3f	A	6f	2-thienyl	H	Me	60
7	1g	2a	3g	A	6g	4-MeC_6H_4	H	Me	68
8	1h	2a	3h	A	7	C_6H_5	H	Me	62
9	1a	2b	4a	B	9a	4-$MeOC_6H_4$	H	H	65
10	1b	2b	4b	B	9b	3, 4-$(MeO)_2C_6H_3$	H	H	69
11	1a	2c	5a	B	10a	4-$MeOC_6H_4$	Me	H	61

A: $BF_3.Et_2O$ / CH_3NO_2 / 0°C-RT / 12-15 h; B: $BF_3.Et_2O$ / C_6H_6 / Δ / 3-15 h.



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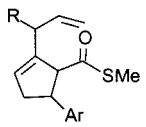


8a, R = H; Ar = 4-$MeOC_6H_4$ (45%)

11a, R = Me; Ar = 4-$MeOC_6H_4$ (65%)

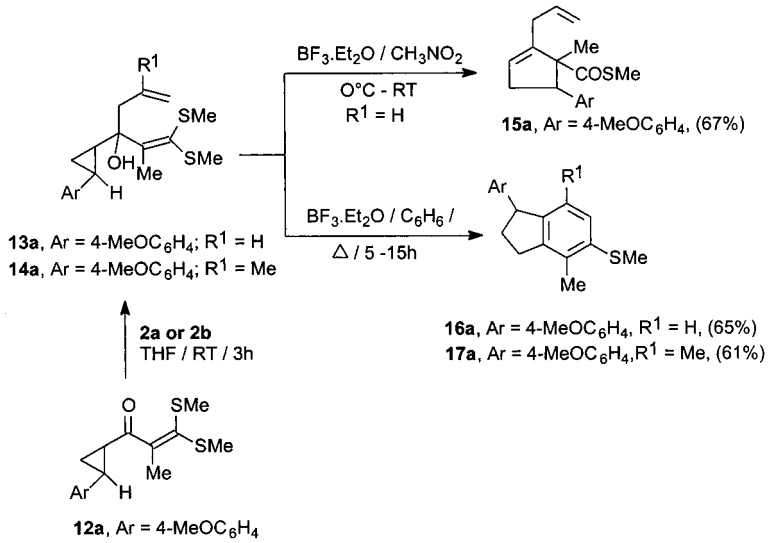
workup and isolation, the spectral analysis of the new product was found to be consistent with 1-(4-methoxyphenyl)-5-methyl-7-(methylthio)indane (**6a**) (Table 1). All the carbinols **3b**−**g** obtained by addition of methallyl Grignard reagents to **1b**−**g** were transformed into the corresponding 1-arylindanes **6b**−**g** (Scheme 1, Table 1) in facile manner, when subjected to the above reaction conditions (**A**). However, the corresponding phenyl-substituted carbinol **3h** did not yield the desired 1-phenylindane and the product isolated (62%) was characterized as the substituted benzene derivative **7**.

The carbinol **4a** formed by addition of allyl Grignard reagent to **1a** gave only the 2-allylcyclopentene carbothioate **8a**, when subjected to cyclization under the above reaction conditions (**A**). However, when **4a** was treated with BF_3·Et_2O in refluxing benzene (3 h) (**B**), the desired 1-(4-methoxylphenyl)-7-methlythioindane (**9a**) was obtained in 65% yield (Table 1, entry 9). Similarly, the dimethoxyphenylcyclopropyl carbinol **4b** was readily transformed into 1-arylindane **9b** in 69% yield under similar conditions (**B**). The carbinol **5a** from crotyl Grignard reagent also required refluxing conditions for domino transformation to 4-methyl-1-arylindane **10a**, whereas at room temperature (**A**) formation of only 2-(1-methallyl)cyclopentene carbothioate **11a** (65%) was observed.

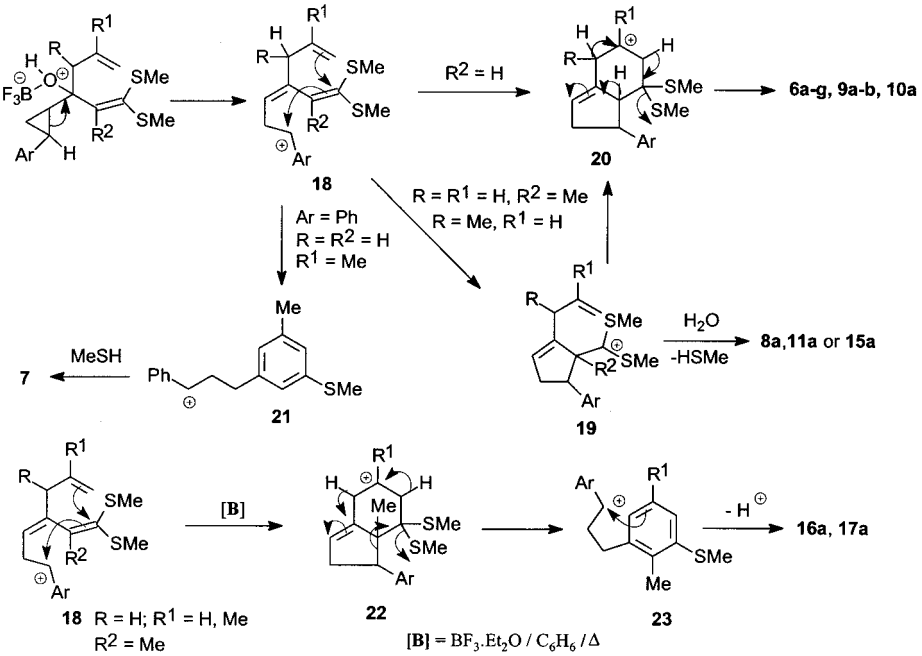
We next investigated the rearrangement of the carbinols **13a** and **14a** obtained by addition of allyl Grignard reagents to α-[bis(methylthio)methylene]ethyl arylcyclopropyl ketone **12a** with a view to examine the effect of an alkyl substituent in the carbinol side chain on product formation (Scheme 2). Thus, **13a** yielded only the 1-methyl-2-allylcyclopentene carbothioate **15a** under the influence of BF_3·Et_2O (**A**) whereas cyclization of **14a** under these conditions (**A**) resulted only in multiple products that cannot be characterized. Interestingly, in refluxing benzene (**B**), both the carbinols **13a** and **14a** were efficiently transformed to single products, which were found to be the isomeric 1-arylindanes **16a** and **17a**, respectively on the, basis of spectral and analytical data (Scheme 2).

The probable mechanism for the formation of various products is shown in Scheme 3. The initial Lewis acid assisted cleavage of the hydroxy group in all the carbinols followed by ring cleavage of the resulting cyclopropylcarbinyl carbocationic intermediate affords the new benzylic carbocation **18**. The cation **18** is then trapped

Scheme 2



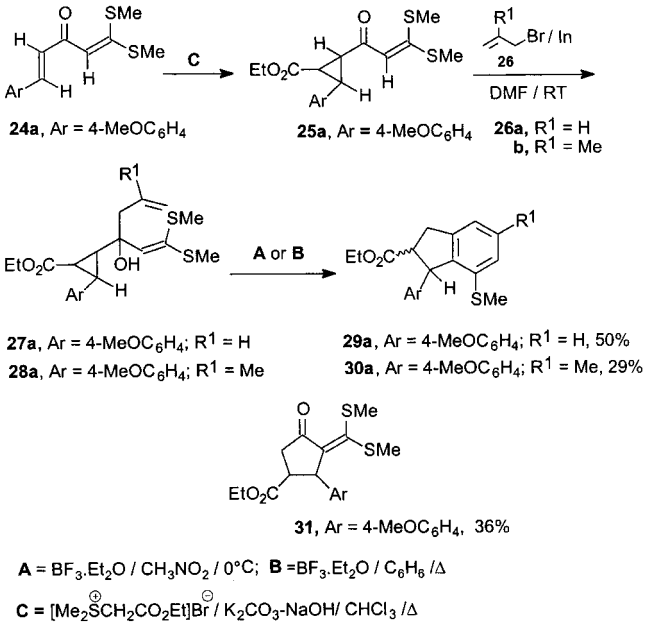
Scheme 3



intramolecularly by the bis(methylthio)methylene double bond in a 5-*exo*-cycilzation, establishing a new C−C bond and a highly stable tertiary bis(methylthio)methyl carbocation **19**, which is probably captured concomitantly by the pendant methallyl side chain (R = H, R^1 = Me) at room temperature in a 6-*endo* cyclization, leading to a new C−C bond and a six-membered carbocyclic ring in the tertiary carbocationic intermediate **20**, which undergoes subsequent aromatization under reaction conditions to afford 1-arylindanes in good yields. In the case of the carbinols with allyl or crotyl side chains (R = R^1 = H or R^1 = H, R = Me), the overall cyclization and aromatization process takes place only under refluxing conditions, whereas at room temperature, initially formed bis(methylthio)methyl cyclopentenyl carbocation **19** fails to undergo 6-*endo* cyclization due to the formation of less stable secondary carbocation **20** (R^1 = H) and yields only hydrolyzed carbothioates **8a** or **11a**. When Ar = C_6H_5, benzylic carbocation **18** is not stable enough to be intercepted by the bis(methylthio)methylene double bond via the 5-*exo*-*trig* process in line with our earlier observations,[6a,b] and furnishes only aromatized product **7** after quenching of carbocation **21** by methylmercaptan generated during the cycloaromatization process. In the case of carbinols **13a** and **14a** with a bis(methylthio)-propenyl side chain (R^2 = Me) (Scheme 2), we believe that carbocation **18** (R^1 = H or Me; R^2 = Me) undergoes concurrent 5-*exo* and 6-*endo* cyclizations under refluxing conditions (**B**) to yield the bicyclic carbocationic intermediate **22**. Subsequently, **22** rearranges itself to thermodynamically more stable aromatized intermediate **23** with a pendant carbocationic side chain, which is intercepted by electron rich benzene ring to afford the observed rearranged arylindanes **16a** or **17a** in good yields (Scheme 3).

In summary, a successful domino carbocationic process[11] has been demonstrated, leading to formation of a fused cyclopentane and a substituted benzene ring from cyclopropyl carbinol precursors. The overall process combines our aromatic annelation protocol[12] and cyclo-

Scheme 4



pentane ring construction via oxoketene dithioacetals in a single one-pot synthetic operation. The reaction provides facile access to substituted 1-arylindane frameworks. Alkyl-substituted arylindanes are shown to be highly valuable monomers for NLO polymeric materials,[13] whereas the 1,3-diarylidan-2-carboxylic acid motif has been identified as a useful scaffold to build new potent and selective non-peptide endothelin receptor antagonists.[14] Thus, in an effort toward constructing part of this structural motif involving our domino carbocationic process, we investigated possible rearrangement of the carbinols **27a** and **28a** to 1-aryl-2-carboethoxyindanes **29a** and **30a**, respectively (Scheme 4). The 2-carboethoxycyclopropyl ketone **25a** was prepared by addition of ethoxycarbonyl dimethylsulfonium methylide[15] to cinnamoyl ketenedithioacetal[6] **24a**. However, the desired carbinols **27a** and **28a** could not be obtained by direct addition of allyl and methallyl Grignard reagents to cyclopropyl ketone **25a** since the reaction was complicated by simultaneous addition to the ester carbonyl group, leading to complex product mixture. We therefore examined addition of allyl and 2-methallylindium[16] to **25a** for obtention of the carbinols **27a** and **28a**. Thus, the addition of allylindium to **25a** proceeded smoothly at room temperature to afford the corresponding carbinol **27a** exclusively, whereas with 2-methallylindium[16] only 40% conversion to carbinol **28a** was observed. Our effort to increase the yield of carbinol **28a** was not successful. When **27a** was refluxed with $BF_3{\cdot}Et_2O$ in benzene (**B**), the corresponding 1-aryl-2-carboethoxyindane **29a** was obtained in 50% yield. Treatment of the crude carbinol **28a** (along with **25a**) with $BF_3{\cdot}Et_2O$ at room temperature (**A**) furnished indane **30a** along with cyclopentanone derivative **31** which is evidently formed from the rearrangement of unreacted cyclopropyl ketone **25a**. These observations suggest that the present domino process could be applicable for the synthesis of more complex highly substituted arylindane targets. Additional studies of the scope of this reaction and further examples of synthetically useful transformations involving the ketene-dithioacetal moiety as terminator and initiator in the domino carbocationic process will be reported elsewhere.

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 conducted by column chromatography using 60−120 mesh silica gel obtained from Acme Synthetic Chemicals. THF, diethyl ether, and benzene were distilled over sodium/benzophenone and stored over sodium wire before use. All reagents were purchased commercially and used as such unless until stated otherwise.

All the bis(methylthio)methylene arylcyclopropyl ketones **1a**−**h** and **12** were prepared according to the earlier reported[6c] procedure.

General Procedure for the Addition of Allylic Grignard Reagents to Cyclopropyl Ketones. To a well-stirred suspension of metallic magnesium (0.21 g) in dry ether (30 mL) was added a solution of the appropriate allyl halide **2** (5 mmol) in dry ether (10 mL) at room temperature under a nitrogen atmosphere. After 1 h, a solution of cyclopropyl ketone (3.4 mmol) in dry THF (15 mL) was added dropwise and the resulting mixture was stirred at room temperature for 3 h (monitored by TLC). It was then diluted with saturated ammonium chloride solution and extracted with ether (3 × 30 mL). The organic extracts were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the respective carbinol, which was used as such for the next reaction.

All the carbinols **3a**−**h**, **4a**,**b**, **5a**, **13a**, **and 14a** were characterized by their IR and ^{1}H and ^{13}C NMR spectra. The spectral data for one of the representative carbinols, **3a**, is given below.

3-[2-(4-Methoxyphenyl)cyclopropan-1-yl]-5-methyl-1-bis-(methylthio)hexa-1,5-dien-3-ol (3a). Colorless oil: R_f = 0.5 (3:17; ethyl acetate:hexane); IR (neat) 3366, 2924, 1258, 739 cm^{-1}; ^{1}H NMR δ 6.91 (dd, J = 8.8, 3.0 Hz, 2H), 6.72 (dd, J = 8.8, 3.0 Hz, 2H), 6.0 (s, 1H), 4.93−4.44 (m, 2H), 3.68 (s, 3H), 3.50−3.36 (m, 1H), 3.18 (br s, 1H), 2.42−2.38 (m, 1H), 2.25 (s, 3H), 2.17 (s, 3H), 2.08−192 (m, 1H), 1.90−1.85 (m, 1H), 1.71−1.63 (m, 1H), 1.18 (s, 3H), 1.07−0.77 (m, 1H); ^{13}C NMR δ 157.6, 142.1, 139.5, 139.2, 135.0, 131.3, 127.2, 115.1, 113.7, 55.3, 50.3, 32.8, 29.7, 24.6, 18.3, 17.9, 16.9, 10.9.

General Procedure for the $BF_3{\cdot}Et_2O$-Induced Cyclization of Carbinols 3−5, 13a, and 14a: Synthesis of 1-Arylindanes and Cyclopentene Carbothioates: Reaction Conditions A. To a solution of crude carbinol (**3**−**5**, **13a**, **14a**) obtained from an earlier reaction in nitromethane (10 mL) was added $BF_3{\cdot}Et_2O$ (5 mmol, 0.65 mL) at 0 °C, and the reaction mixture was stirred at ambient temperature for 12−15 h (monitored by TLC). It was diluted with ice-cooled bicarbonate solution (15 mL) and extracted with ethyl acetate (3 × 30 mL). The organic extracts were combined, washed with water, and

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dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford arylindanes **6a**−**6g** or **7** or cyclopentene carbothioate **8a, 11a**, or **15a**, which was purified by column chromatography on silica gel using hexanes−ethyl acetate (97:3) as eluent to obtain analytically pure product.

Reaction Conditions B. To a solution of crude carbinol (**4a**,**b**, **5a**, **13a**, **14a**) obtained from an earlier reaction mixture in dry benzene (25 mL) was added $BF_3{\cdot}Et_2O$ (5 mmol, 0.65 mL) at room temperature, and the reaction mixture was refluxed for 3 h (for carbinols **4a**,**b**, **5a**) or 5 h (**13a**) or 15 h (for **14a**) (monitored by TLC). The reaction mixture was cooled to room temperature, poured into an ice-cooled bicarbonate solution (15 mL), and extracted with ethyl acetate (3 × 30 mL). The organic extracts were combined, washed with water, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford substituted arylindane, which was purified by column chromatography on silica gel using hexanes−ethyl acetate (97:3) as eluent to obtain analytically pure product.

1-(4-Methoxyphenyl)-5-methyl-7-(methylthio)indane (6a). Yield[17] 79% (0.76 g). Colorless needles (ether): mp 78−79 °C; R_f = 0.7 (3:17; ethyl acetate:hexane); IR (KBr) 2910, 1580, 1550, 1425 cm^{-1}; ^{1}H NMR δ 6.93 (dd, J = 6.8, 2.2 Hz, 2H), 6.90 (s, 1H), 6.79 (s, 1H), 6.77 (dd, J = 6.8, 2.2 Hz, 2H), 4.37 (dd, J = 8.8, 2.7 Hz, 1H), 3.74 (s, 3H), 3.04 (ddd, J = 15.9, 8.3, 8.8 Hz, 1H), 2.83 (ddd, J = 15.9, 9.4, 3.2 Hz, 1H), 2.53 (ddt, J = 18.0, 10.9, 7.1 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H), 1.97 (ddt, J = 18.1, 8.8, 8.0 Hz, 1H); ^{13}C NMR δ 157.8, 144.9, 140.7, 137.6, 137.3, 135.0, 128.4, 123.3, 121.7, 113.7, 55.1, 49.2, 36.1, 31.4, 21.4, 15.1; MS *m*/*e* 285 (M$^+$, 100), 270 (94), 237 (46). Anal. Calcd for $C_{18}H_{20}$-OS (284.43): C, 76.0; H, 7.08. Found: C, 76.22; H 7.19.

1-(2-Methoxyphenyl)-5-methyl-7-(methylthio)indane (6b). Yield 75% (0.73 g). Colorless oil: R_f = 0.7 (3:17; ethyl acetate:hexane); IR (neat) 2954, 1596, 1564, 1489, 1457 cm^{-1}; ^{1}H NMR δ 7.18−7.14 (m, 1H), 6.91 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.82 (s, 1H), 6.76−6.72 (m, 1H), 6.52 (d, J = 8.8 Hz, 1H), 4.76 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H), 2.95 (ddd, J = 16.1, 8.2, 8.8 Hz, 1H), 2.79 (ddd, J = 15.7, 8.8, 2.4 Hz, 1H), 2.50 (ddt, J = 18.1, 10.3, 8.8 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.94 (ddt, J = 12.7, 8.3, 2.4 Hz, 1H); ^{13}C NMR δ 156.9, 145.8, 140.2, 137.4, 134.9, 132.7, 127.2, 127.1, 123.2, 121.6, 120.2, 110.4, 55.5, 43.0, 34.3, 31.3, 21.5, 15.2; MS *m*/*e* 284 (M$^+$, 68.7), 269 (37.7), 237 (100). Anal. Calcd for $C_{18}H_{20}OS$ (284.43): C, 76.0; H, 7.08. Found: C, 76.29; H, 7.21.

3-[3-(Methylthio)-3-phenylpropyl]-5-(methylthio)toluene (7). Yield 62% (0.64 g). Yellow oil: R_f = 0.7 (1:10; ethyl acetate:hexane); IR (neat) 2916, 1579, 1490, 1449 cm^{-1}; ^{1}H NMR δ 7.26−7.13 (m, 5H), 6.80 (s, 1H), 6.74 (s, 1H), 6.63 (s, 1H), 3.54 (t, J = 6.8 Hz, 1H), 2.47 (t, J = 6.8 Hz, 2H), 2.35 (s, 3H), 2.19 (s, 3H), 2.14−2.0 (m, 2H); 1.75 (s, 3H); ^{13}C NMR δ 142.0, 141.9, 138.4, 138.0, 128.4, 127.8, 127.0, 126.1, 124.7, 123.6, 50.6, 37.2, 33.5, 21.2, 15.7, 14.1; MS *m*/*e* 302 (M$^+$, 43.8), 253 (35.8), 151 (100). Anal. Calcd for $C_{18}H_{22}S_2$ (302.50): C, 71.47; H, 7.33. Found: C, 71.59; H, 7.18.

1-(4-Methoxyphenyl)-7-(methylthio)Indane (9a). Yield 65% (0.60 g). Colorless crystals (ether): mp 68−69 °C; R_f = 0.65 (3:17; ethyl acetate:hexane); IR (KBr) 2949, 1512, 1454, 1438 cm^{-1}; ^{1}H NMR δ 7.26−7.21 (m, 1H), 7.11 (d, J = 7.4 Hz, 1H), 7. 01 (d, J = 7.8 Hz, 1H), 6.97 (dd, J = 8.8, 3.6 Hz, 2H), 6.81(dd, J = 8.8, 3.2 Hz, 2H), 4.42 (d, J = 9.0 Hz, 1H), 3.78 (s, 3H), 3.11 (ddd, J = 16.01, 8.4, 8.8 Hz, 1H), 2.90 (ddd, J = 15.8, 8.8, 2.2 Hz, 1H), 2.59 (ddt, J = 15.3, 10.4, 9.0 Hz), 2.33 (s, 3H), 2.0 (ddt, J = 16.3, 9.4, 2.9 Hz, 1H); ^{13}C NMR δ 157.8, 144.7, 143.5, 137.0, 135.5, 128.4, 127.8, 122.4, 120.8, 113.7, 55.1, 49.6, 35.8, 31.5, 15.1; MS *m*/*e* 270 (M$^+$, 100), 255 (85). Anal. Calcd for $C_{17}H_{18}OS$ (270.40): C, 75.51; H, 6.71. Found: C, 75.68; H, 6.97.

1-(3,4-Dimethoxyphenyl)-7-(methylthio)indane (9b). Yield 69% (0.7 g). Viscous liquid: R_f = 0.6 (3:17; ethyl acetate:hexane); IR (neat) 2984, 1589, 1573, 1441 cm^{-1}; ^{1}H NMR δ 7.27−7.22 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 2.0 Hz, 1H), 6.52 (dd, J = 8.0, 1.9 Hz, 1H), 4.42 (dd, J = 9.0, 2.9 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.12 (ddd, J = 15.9, 8.3, 8.7 Hz, 1H), 2.9 (ddd, J = 15.9, 9.4, 3.2 Hz, 1H), 2.60 ((ddt, J = 17.8, 10.8, 7.0 Hz, 1H), 2.34 (s, 3H), 2.04 (ddt, J = 18.1, 8.6, 3.0 Hz, 1H); ^{13}C NMR δ 148.8, 147.2, 144.7, 143.2, 137.4, 135.6, 127.9, 122.5, 120.8, 119.1, 111.1, 110.9, 55.7, 55.1, 50.1, 35.7, 31.5, 15.2; MS *m*/*e* 300.0 (M$^+$, 100), 253 (43.9), 162 (41.3). Anal. Calcd for $C_{18}H_{20}O_2S$ (300.43): C, 71.96; H, 6.71. Found: C, 72.13; H, 6.96.

1-(4-Methoxyphenyl)-4-methyl-7-(methylthio)indane (10a). Yield 61% (0.59 g). Colorless oil: R_f = 0.4 (1:9; ethyl acetate:hexane); IR (neat) 2949, 1509, 1458, 1437 cm^{-1}; ^{1}H NMR δ 7.05 (d, J = 8.3 Hz, 1H), 6.94 (br d, J = 8.8 Hz, 3H), 6.78 (d, J = 8.8 Hz, 2H), 4.44 (dd, J = 9.0, 2.7 Hz, 1H,), 3.74 (s, 3H), 2.97 (ddd, J = 16.1, 8.3, 8.5 Hz, 1H), 2.89 (ddd, J = 15.9, 9.4, 3.2 Hz, 1H), 2.58 (ddt, J = 15.9, 9.4, 3.2 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 2.0 (ddt, J = 17.1, 8.6, 8.0 Hz, 1H);); ^{13}C NMR δ 157.8, 143.8, 143.6, 137.4, 132.1, 130.5, 128.7, 128.4, 123.8, 113.7, 55.1, 50.0, 35.3, 30.3, 18.9, 15.7; MS *m*/*e* 285 (M$^+$, 100), 270 (94), 237(46). Anal. Calcd for $C_{18}H_{20}OS$ (284.43): C, 76.01; H, 7.08. Found: C, 76.18; H, 7.14.

***S*-Methyl 2-(But-1-ene-3-yl)-5-(4-methoxyphenyl)cyclopent-2-en-1-carbothioate (11a).** Yield 65% (0.67 g). Colorless oil: R_f = 0.55 (1:9; ethyl acetate:hexane); IR (neat) 2927, 1680, 1581, 1512, 1447 cm^{-1}; ^{1}H NMR δ 7.13−7.09 (m, 2H), 6.82 (dd, J = 8.8, 2.7 Hz, 2H), 5.93−5.59 (m, 2H), 5.06−4.95 (m, 2H), 3.77 (s, 3H), 3.75 (br s, 1H), 3.63−3.55 (m, 1H), 3.03−2.89 (m, 2H), 2.42 (br d, J = 14.2 Hz, 1H), 2.29 (s, 3H), 1.23 (dd, J = 6.8, 3.3 Hz, 3H); ^{13}C NMR δ 201.9, 158.2, 144.6, 141.3, 137.8, 127.7, 126.9, 114.4, 113.9, 69.4, 55.2, 48.4, 41.0, 38.3, 18.8, 11.7; MS *m*/*e* 302 (M$^+$, 35.7), 226 (100). Anal. Calcd for $C_{18}H_{22}O_2S$ (302.44): C, 71.49; H, 7.33. Found: C, 71.62; H, 7.16.

1-(4-Methoxyphenyl)-4-methyl-5-(methylthio)indane (16a). Yield 65% (0.63 g). Colorless crystals (pentane): mp 64−65 °C; R_f = 0.5 (1:9 ethyl acetate:hexane); IR (KBr) 2998, 1609, 1511, 1454 cm^{-1}; ^{1}H NMR δ 7.0 (dd, J = 8.8, 1.9 Hz, 2H), 6.92 (d, J = 7.8 Hz, 1H), 6.75 (dd, J = 8.4, 1.9 Hz, 2H), 6.67 (d, J = 7.8 Hz, 1H), 4.17 (d, J = 8.3 Hz, 1H), 3.68 (s, 3H), 2.90 ((ddd, J = 15.8, 9.1, 3.2 Hz, 1H), 2.74 (ddd, J = 16.1, 8.3, 8.5 Hz, 1H), 2.45 (ddt, J = 12.7, 10.0, 6.3 Hz, 1H)), 2.32 (s, 3H), 2.24 (s, 3H), 1.9 (ddt, J = 13.0, 9.6, 6.3 Hz, 1H); ^{13}C NMR δ 158.1, 144.3, 143.8, 137.6, 135.2, 132.1, 129.0, 124.7, 122.7, 113.8, 55.2, 50.9, 36.3, 30.8, 16.5, 16.4; MS *m*/*e* 284 (M$^+$, 100), 237 (63). Anal. Calcd for $C_{18}H_{20}OS$ (284.43): C, 76.01; H, 7.09. Found: C, 76.21; H, 7.18.

4,7-Dimethyl-1-(4-methoxyphenyl)-5-(methylthio)indane (17a). Yield 61% (0.62 g). Colorless oil: R_f = 0.45 (1:9; ethyl acetate:hexane); IR (neat) 2919, 1510, 1458, 1437 cm^{-1}; ^{1}H NMR δ 6.93 (dd, J = 6.6, 2.0 Hz, 2H), 6.85 (s, 1H), 6.78 (dd, J = 6.6, 2.0 Hz, 2H), 4.34 (dd, J = 8.8, 1.6 Hz, 1H), 3.77 (s, 3H), 3.93 (m, 1H), 2.86−2.79 (m, 1H), 2.53 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 2.94 (ddt, J = 12.7, 10.3, 6.6 Hz, 1H)), 1.92 (s, 3H); ^{13}C NMR δ 157.8, 143.9, 141.9, 138.0, 132.5, 129.5, 128.3, 127.5, 126.2, 113.8, 55.2, 49.6, 35.7, 30.7, 18.9, 16.4, 16.2; MS *m*/*e* 298 (M$^+$, 100), 250 (56.3). Anal. Calcd for $C_{19}H_{22}OS$ (298.45): C, 76.47; H, 7.43. Found: C, 76.34; H, 7.29.

Ethyl 2-{[Bis(methylthio)methylene]acetyl}-3-(4-methoxyphenyl)cyclopropanecarboxylate (25a). To a well-stirred solution of ethyl (dimethylsulfuranylidine)acetate (EDSA)[15] (15 mmol) in chloroform (50 mL) at 0 °C was injected cinnamoyl ketenedithioacetal **24a** (2.8 g, 10 mmol) in chloroform (20 mL), and the reaction mixture was stirred at room temperature for (2 h) and then refluxed for 30 h (monitored by TLC). It was then cooled and concentrated under reduced pressure to afford crude **25a**, which was purified by being passes through a silica gel column using hexanes−ethyl acetate (24:1) as eluent. Yellow oil: yield 71% (2.6 g); R_f = 0.5 (1:4; ethyl acetate:hexane); IR (neat) 2980, 1729, 1695, 1512, 1302, 1249 cm^{-1}; ^{1}H NMR δ 7.10 (d, J = 8.3 Hz, 2H), 6.73 (d, J = 8.3 Hz, 2H), 6.25 (s, 1H), 3.94−3.86 (q, J = 7.0 Hz, 2H), 3.70 (s, 3H), 3.04−3.01 (m, 1H), 2.93−2.90 (m, 1H), 2.58−2.56 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 1.01 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ 190.2, 169.3, 165.5, 158.5, 130.0, 127.1, 113.5, 112.4, 60.6, 55.1, 34.0, 33.7, 31.6, 17.2, 14.9, 14.1; MS *m*/*e* 366 (M$^+$, 25.5), 293 (49), 147 (100). Anal. Calcd for $C_{18}H_{22}O_4S_2$ (366.50): C, 58.99; H, 6.05. Found: C, 59.11; H, 6.27.

General Procedure for the Addition of Allylic Indium Reagents to 2-Carboethoxycyclopropyl Ketone (25a). To a suspension of indium powder (0.68 g) in dry DMF (5 mL) was injected allyl bromide (or methallyl bromide) (9.0 mmol) through a septum, and the reaction mixture was stirred for 1 h at room temperature. A solution of **25a** (3 mmol) in dry DMF (3 mL) was added, and the stirring was continued for 24−30 h (moni-

(17) The reported yields of all substituted arylindanes are the overall yields from their respective cyclopropyl ketones.

tored by TLC). The reaction mixture was poured into a saturated sodium chloride solution and extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to afford carbinol **27a** or **28a** (along with cyclopropyl ketone **25a**) which was characterized by IR and ^{1}H and ^{13}C NMR data and used as such for the next reaction.

2-Carboethoxy-1-(4-methoxyphenyl)-7-(methylthio)indane (29a). The title compound was obtained as a yellow oil by treatment of carbinol **27a** (2.4 mmol) with $BF_3{\cdot}Et_2O$ (0.65 mL, 5 mmol) in refluxing benzene (3 h) under reaction conditions **B**. Yield 50% (0.51 g). Chromatography (1:19; ethyl acetate:hexane), R_f = 0.5 (13:87; ethyl acetate:hexane): IR (neat) 2927, 1732, 1691, 1513, 1249 cm^{-1}; ^{1}H NMR δ 7.24 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.03−7.0 (m, 3H), 6.81 (dd, J = 8.6, 2.0 Hz, 2H), 4.75 (d, J = 4.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.32 (dd, J = 16.4, 9.0 Hz, 1H), 3.26 (dd, J = 16.4, 5.1 Hz, 1H), 3.14 (ddd, J = 9.0, 4.6, 6.6 Hz, 1H), 2.29 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C δ NMR 174.7, 158.2, 142.3, 141.3, 135.8, 128.7, 128.3, 128.2, 123.2, 120.6, 113.8, 60.8, 55.2, 53.1, 53.4, 35.0, 15.3, 14.2; MS *m/e* 342 (M^+, 100), 268 (90), 221 (81.5). Anal. Calcd for $C_{20}H_{22}O_3S$ (342.46): C, 70.15; H, 6.47. Found: C, 70.09; H, 6.28.

1-(4-Methoxyphenyl)-2-carboethoxy-5-methyl-7-methylthioindane (30a). The title compound **30a** was obtained along with **31** by treatment of the reaction mixture, resulting from addition of methallylindium reagent **26b** to **25a**, with $BF_3{\cdot}Et_2O$ (0.65 mL, 5 mmol) in nitromethane (12 h) under reaction conditions **A**. Yield 29% (0.31 g). Chromatography (1:19; ethyl acetate:hexane), R_f = 0.55 (13:87; ethyl acetate:hexane): IR (neat) 2926, 1731, 1610, 1579, 1302, 1250 cm^{-1}; [exists as a mixture of two isomers (3:1), NMR value of minor isomer is given inside bracket]; ^{1}H NMR δ 7.01[6.89] (d, J = 8.6 Hz, 2H), [6.93]6.88 (br s, 1H), 6.81−6.79[6.74−6.68] (m, 3H), 4.69 (d, J = 4.24 Hz, 1H) [4.66] (d, J = 9.3 Hz, 1H), 4.15[3.84] (q, J = 6.8 Hz, 2H), 3.76[3.71] (s, 3H), 3.30[3.77] (dd, J = 16.1, 9.0 Hz, 1H), 3.21[3.60] (dd, J = 16.0, 5.2 Hz, 1H), 3.15−3.09 (ddd, J = 9.0, 4.9, 4.8 Hz, 1H)[2.97] (dd, J = 15.9, 8.0 Hz), [2.35]2.34 (s, 3H), 2.27[2.26] (s, 3H), 1.25[1.06] (t, J = 6.2 Hz, 3H);^{13}C NMR δ 174.8-[172.3], 158.4[158.2], 142.6[142.3], [139.6]138.6, 138.1, 136.1-[134.7], 135.3, 131.5 [130.0], 129.7, 128.7 [128.6], 124.2[124.1], 121.7[121.0], 113.8[113.3], 60.7[60.3], 55.1[55.0], 53.7[51.8], 53.4-[50.2], [35.6]34.9, [21.5]21.4, 15.3[15.1], 14.3[14.0]; MS *m/e* 356 (M^+, 100), 341 (75.18), 282 (92.58), 235 (89.01), 135 (77.94). Anal. Calcd for $C_{21}H_{24}O_3S$ (356.49): C, 70.33; H, 6.79. Found: C, 70.16; H, 6.56.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectral data for compounds **6c**−**g**, **8a**, **15a**, and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

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