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[4 + 2] Cycloaromatization of 4-Bis(methylthio)-3-buten-2-one with Active Methylene Ketones: A Simple and Facile Phenol Annulation

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Abstract: A new method for β-phenol annulation involving base-induced [4C + 2C] cycloaromatization of readily available 4-bis(methylthio)-3-buten-2-one with a variety of cyclic and acyclic active methylene ketones has been reported. Appropriate choice of ketones allows synthesis of diverse frameworks such as dihydroindan, tetrahydronaphthalenes, their higher homologues, dihydro/octahydrophenanthrenes, anthracene, and heteroannulated analogue in high yields with regiocontrol of phenolic functionality.

Substituted and fused phenols constitute structural subunit of several important natural products such as 7-hydroxycalamenene,[1a,b] ferruginol,[1c] hinokiol,[1d] 9,10-dihydrophenanthrenes such as juncusol,[2] and effusol displaying interesting microbial and cytotoxic properties.[3] Classical approaches to these complex subunits invariably exploit readily available phenolic precursors as an aromatic template on which the remaining molecular framework or substituents are introduced in the subsequent steps, which rely heavily on the conventional electrophilic, nucleophilic substitutions[4a−e] or metalation−functionalization reactions.[4f,g] However, these methods suffer from serious regiochemical ambiguities and require long multistep reactions resulting in lower yields of the target compounds. Important modern methods for regiospecific elaboration of substituted phenols involve highly convergent annulation reactions[5] in which the aromatic system is assembled from acyclic precursors and the substitution pattern of the product phenols is dictated by the structures and functionalities of the starting materials. Particularly noteworthy aromatic annulation reactions leading to substituted phenols developed recently include methods based on Diels−Alder reaction of suitably functionalized dienes and dienophiles,[6] Robinson annulation,[7] Dotz reaction of Fischer carbene complexes,[8a,b] transition-metal-catalyzed [2 + 2 + 2][8c] and [4 + 2] cycloaddition,[8d] thermal and photochemical electrocyclization of dienylketene intermediates,[9] carbonyl condensations,[10] and other related reactions.[11] Our continued interest in the development of new aromatic annulation strategies relies upon utilization of α-oxoketene dithioacetals as three carbon 1,3-bielectrophilic components in a [3C + 3C] cyclocondensation with various 1,3-binucleophilic species yielding a variety of regiospecifically substituted and fused aromatic and heteroaromatic structural frameworks.[12,13] These studies prompted us to investigate new methods for construction of substituted phenolic ring utilizing these precursors, and we now report a versatile phenol annulation capable of broad application, which unlike our earlier [3C + 3C] cycloaromatization process is based upon [4C + 2C] Robinson aromatic annulation of readily accessible 4-bis(methylthio)-3-buten-2-one (**2**) with various active methylene ketones.

The utility of Robinson annulation[7] for regiospecific phenol annulation has been recognized in a few instances. Thus, Boger's method[14] employs 2-(phenylsulfinyl)cyclo-

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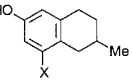
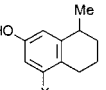
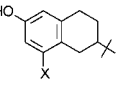
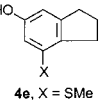
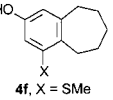
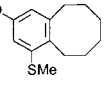
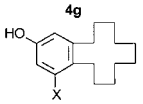
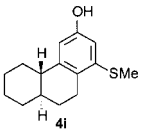
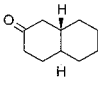
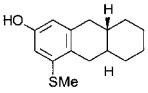
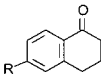
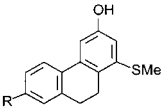
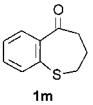
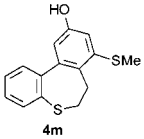
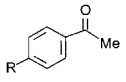
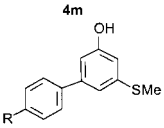
hexanone with an α-eliminating group that on cyclocondensation with a few substituted buten-3-ones (Michael acceptors) under basic conditions directly affords the phenol-annulated cyclohexanones in moderate yields. On the other hand, Takaki has utilized 3-(phenylthio)-3-buten-2-one with an α-eliminating group as a Michael acceptor in Robinson annulation with few cycloalkanones.[15] The initially formed Michael adducts or the ketols were transformed into the corresponding phenols either by oxidative elimination or under acidic/basic conditions. The 3-(phenylthio)-3-buten-2-one is, however, shown to undergo dimerization under alkaline conditions requiring milder conditions and care for successful Robinson annulation. Recently, 1-acetoxy-3-buten-2- one and the corresponding 1,4-diacetoxy-2-butanone are shown to undergo Robinson-type annulation with pyrrolidine enamines yielding pyrrolidino-substituted benzene derivatives in moderate yields.[16]

We became interested in examining 4-bis(methylthio)-3-buten-2-one (**2**), a stable readily available analogue of methylvinyl ketone with two leaving groups at the *β*-position, as a potential 4-carbon Michael acceptor component in Robinson-type phenol annulation. We first investigated annulation of **2** with aliphatic cyclic ketones (Table 1). When equimolar quantities of cyclohexanone and **2** in the presence of sodium hydride were stirred in DMF at room temperature for 6 h (method A), workup, and column chromatography of the reaction mixture furnished a white solid (78%), which was characterized as 7-hydroxy-5-methylthio-1,2,3,4-tetrahydronaphthalene (**4a**) on the basis of its spectral and analytical data. Thus, the entire reaction sequence, i.e., formation of conjugate addition−elimination adduct **3** followed by intramolecular Aldol condensation and cycloaromatization proceeds under surprisingly mild conditions affording the annulated phenol **4a** directly without isolation of the adduct (Scheme 1). This novel phenol annulation was found to be equally facile with other cyclic aliphatic ketones such as 4-methyl-, 2-methyl-, and 4-*tert*-butylcyclohexanones, cyclopentanone, cycloheptanone, cyclooctanone, and cyclododecanone (Table 1, entries 2−8), yielding 3-methylthio-4,5-annulated phenols **4b**−**h** in 68−89% overall yields (Table 1). Similarly, when the corresponding 1- and 2-*trans*-decalones **1i** and **1j** were subjected to phenol annulation under the identical conditions, the corresponding 3-hydroxyoctahydrophenanthrene (**4i**) and 2-hydroxyoctahydroanthracene (**4j**) were obtained in 77% and 87% yields respectively (Table 1, entries 9 and 10). A few of the annulated phenols (**4d**−**f**,**h**) were desulfurized with Raney Ni (W2) to give the corresponding dethiomethylated products **5d**−**f**,**h** in high yields. Alternatively, the

TABLE 1. *β*-Phenol Annulation of Various Ketones

Entry	Ketone	Method	Product	% Yield
1	 **1a**	A	 **4a**, X = SMe	78
2	 **1b**	A	 **4b**, X = SMe	85
3	 **1c**	A	 **4c**, X = SMe	72
4	 **1d**	A	 **4d**, X = SMe **5d**, X = H	73 88 [a] (63) [b]
5	 **1e**	A	 **4e**, X = SMe **5e**, X = H	78 74 [a]
6	 **1f**	A	 **4f**, X = SMe **5f**, X = H	88 83 [a] (62) [b]
7	 **1g**	A	 **4g**	72
8	 **1h**	A	 **4h**, X = SMe **5h**, X = H	89 89 [a] (64) [b]
9	 **1i**	A	 **4i**	77
10	 **1j**	A	 **4j**	87
11	 **1k**, R = H	B	 **4k**, R = H	64
12	**1l**, R = OMe	B	**4l**, R = OMe	71
13	 **1m**	B	 **4m**	62
14	 **1n**, R = H	B	 **4n**, R = H	64
15	**1o**, R = OMe	B	**4o**, R = OMe	63

[a] Yields of Raney Ni desulfurization. [b] Yields by cycloannulation with **6** (method A).

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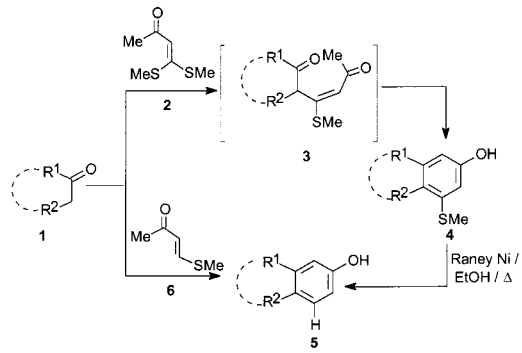
SCHEME 1



synthesis of sulfur-free annulated phenols **5d**,**f**,**h** could also be accomplished in good yields by cycloannulation of the respective ketones with β-methylthiomethylene-acetone **6** prepared by our earlier reported procedure through partial reductive dethiomethylation of **2** with nickel boride.[17]

The phenol annulation studies were further extended to benzocyclic ketones such as 1-tetralone (**1k**), which gave a mixture of conjugate adduct and 3-hydroxy-1-(methylthio)-9,10-dihydrophenanthrene (**4k**) in a ratio of 2:1 when exposed to **2** in the presence of sodium hydride/DMF at room temperature (method a). Treatment of the reaction mixture with *p*-toluenesulfonic acid in refluxing benzene (5 h) furnished **4k** in a total yield of 64% (method B). The corresponding 6-methoxytetralone **1l** and the benzothiepinone **1m** also underwent smooth two steps addition−cycloaromatization protocol (method B) with **2** to afford the respective annulated phenols **4l** and **4m** in good yields (Table 1). Versatility of the methodology was further demonstrated when the substituted acetophenones **1n**−**o** are employed as acyclic annulation partners affording 3-hydroxybiphenyls **4n**−**o** in reasonably good yields (Table 1, entries 14 and 15).

Conclusion

In summary, the work described in this paper provides a simple and efficient method for β-phenol annulation of both cyclic and acyclic ketones by making use of readily available 4-bis(methylthio)-3-buten-2-one (**2**) as 4-carbon component. Appropriate choice of ketones allows synthesis of diverse frameworks such as dihydroindane, tetrahydronaphthalenes, their higher homologues, dihydro/octahydrophenanthranenes, anthracene, and heteroannulated analogue in good yields with regiocontrol of phenolic functionality. The simplicity of the sequence and mild reaction conditions indicate that this process could be capable of broad application for elaboration of more complex and highly functionalized carbon ring systems, which is now underway in our laboratory.

Experimental Section

General Methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$, and TMS was used as 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 glass plates coated with silica gel containing 13% calcium sulfate as 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.

All the chemically pure solvents, i.e., DMF and ethanol, were purchased from standard firms and further dried whenever needed by standard procedures. Cyclopentanone, cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 4-*tert*-butylcyclohexanone, cycloheptanone, cyclooctanone, cyclododecanone, 1-tetralone, 6-methoxytetralone, acetophenone, and 4-methoxyacetophenone were purchased from a commercial supplier and used as such. 4-Bis(methylthio)-3-buten-2-one[18] and 3,4-dihydro-1-benzothiepin-5(2*H*)-one[19] were prepared according to the reported procedures.

General Procedure for the Cycloaromatization of 4-Bis-(methylthio)-3-buten-2-one (2) with Cyclic Aliphatic Ketones: **Synthesis of 4a**−**j (Method A).** A solution of ketone (6 mmol) and 4-bis(methylthio)-3-buten-2-one (1.0 g, 6 mmol) in DMF (20 mL) was added dropwise to a stirring suspension of sodium hydride (0.75 g, 12.5 mmol, 40%) in DMF (15 mL) at 0 °C over a period of 45 min. The reaction mixture was brought to room temperature, and the stirring was further continued for 5−8 h (monitored by TLC). It was then poured into an aqueous saturated solution of ammonium chloride (50 mL) and extracted with benzene (2 × 50 mL). The combined benzene extracts were washed with water (2 × 25 mL), dried (Na_2SO_4), and evaporated to give the crude products that were purified by column chromatography using hexanes−ethyl acetate (25:4) as eluent.

General Procedure for Two-Step Reaction of 4-Bis-(methylthio)-3-buten-2-one with Ketones: Synthesis of 4k−**o (Method B).** A solution of crude residue obtained after workup (method A) and dry PTSA (0.95 g, 5.0 mmol) in dry benzene (30 mL) was refluxed with stirring for 3 h (monitored by TLC). The reaction mixture was then cooled to room temparature and poured into water (50 mL), and the organic layer was separated, washed with water (4 × 50 mL), dried (Na_2SO_4), and evaporated to give a crude product that was purified by column chromatography over silica gel using hexanes−ethyl acetate (24:1) as eluent.

7-Hydroxy-5-(methylthio)-1,2,3,4-tetrahydronaphthalene (4a): yield 78% (0.90 g); white solid (chloroform−hexane); mp 68−69 °C; R_f 0.20 (9:1 hexanes−EtOAc); IR (KBr) 3356, 2928, 1590, 1449 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69−1.75 (m, 2H, CH_2), 1.77−1.83 (m, 2H, CH_2), 2.40 (s, 3H, SCH_3), 2.57 (t, J = 6.0 Hz, 2H, CH_2), 2.68 (t, J = 6.0 Hz, 2H, CH_2), 5.09 (brs, 1H, OH), 6.33 (d, J = 1.9 Hz, 1H, ArH), 6.48 (d, J = 1.9 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 22.7, 23.2, 25.9, 30.1, 108.7, 111.8, 126.4, 138.7, 139.3, 153.4; MS (*m*/*z*) 194 (M^+, 96.5), 176 (100). Anal. Calcd for $C_{11}H_{14}OS$ (194.30): C, 67.99; H, 7.26. Found: C, 68.11; H, 7.34.

7-Hydroxy-3-methyl-5-(methylthio)-1,2,3,4-tetrahydronaphthalene (4b): yield 85% (1.0 g); white solid (chloroform−hexane); mp 76 °C; R_f 0.20 (9:1 hexanes−EtOAc); IR (KBr) 3370, 2916, 1581, 1451 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, J = 6.3 Hz, 3H, CH_3), 1.26−1.36 (m, 1H, CH_2), 1.76−1.82 (m, 2H, CH_2), 2.00−2.07 (m, 1H, CH_2), 2.39 (S, 3H, SCH_3), 2.68−2.80 (m, 3H, CH_2), 5.22 (brs, 1H, OH), 6.34 (d, J = 1.96 Hz, 1H, ArH), 6.48 (d, J = 2.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 22.2, 29.4, 30.0, 30.9, 34.5, 108.7, 111.6, 126.4, 138.3, 139.1, 153.4; MS (*m*/*z*) 208 (M^+, 100), 193 (97). Anal. Calcd for $C_{12}H_{16}OS$ (208.33): C, 69.18; H, 7.74. Found: C, 69.48; H, 7.92.

7-Hydroxy-5-(methylthio)-3-(*tert*-butyl)-1,2,3,4-tetrahydronaphthalene (4d): yield 73% (1.0 g); white solid (chloroform−hexane); mp 145−146 °C; R_f 0.24 (9:1 hexanes−EtOAc); IR (KBr) 3285, 2956, 1580, 1457 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 9H, CH_3), 1.08−1.30 (m, 1H, CH), 1.38−1.46 (m, 1H, CH), 1.90−1.95 (m, 1H, CH), 2.13−2.20 (m, 2H, CH_2), 2.39 (s, 3H, SCH_3), 2.65−2.76 (m, 2H, CH_2), 5.23 (s, 1H, OH), 6.34 (d, J = 1.9 Hz, 1H, ArH), 6.48 (d, J = 1.9 Hz, 1H, ArH); ^{13}C NMR

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(100 MHz, $CDCl_3$) δ 14.8, 24.0, 27.2, 27.55, 27.56, 27.57, 31.2, 32.5, 45.0, 108.6, 111.3, 126.7, 138.6, 139.5, 153.4; MS (*m*/*z*) 250 (M^+, 100), 236 (7.8). Anal. Calcd for $C_{15}H_{22}OS$ (250.41): C, 71.95; H, 8.85. Found: C, 72.16; H, 8.98.

6-Hydroxy-4-(methylthio)Indane (4e): yield 78% (0.84 g); white solid (chloroform−hexane); mp 64−65 °C; R_f 0.21 (9:1 hexanes−EtOAc); IR (KBr) 3270, 2493, 1710, 1580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02−2.09 (m, 2H, CH_2), 2.38 (s, 3H, SCH_3), 2.74 (t, J = 7.5 Hz, 2H, CH_2), 2.83 (t, J = 7.5 Hz, 2H, CH_2), 5.22 (brs, 1H, OH), 6.46 (s, 1H, ArH), 6.47 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 25.0, 30.7, 33.2, 108.0, 109.0, 133.8, 135.0, 145.8, 154.9; MS (*m*/*z*) 180 (M^+, 52.7), 165 (100). Anal. Calcd for $C_{10}H_{12}OS$ (180.27): C, 66.63; H, 6.71. Found: C, 66.86; H, 6.89.

3-Hydroxy-1-(methylthio)-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (4f): yield 88% (1.0 g); white solid (chloroform−hexane); mp 95−96 °C; R_f 0.23 (9:1 hexanes−EtOAc); IR (KBr) 3307, 2917, 1595, 1449 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53−1.62 (m, 4H, CH_2), 1.76−1.80 (m, 2H, CH_2), 2.34 (s, 3H, SCH_3), 2.68 (t, J = 5.3 Hz, 2H, CH_2), 2.88 (t, J = 5.3 Hz, 2H, CH_2), 5.36 (brs, 1H, OH), 6.41 (d, J = 2.2 Hz, 1H, ArH), 6.54 (d, J = 2.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 27.3, 28.0, 29.9, 32.4, 36.5, 110.4, 113.5, 133.6, 137.4, 145.7, 153.3; MS (*m*/*z*) 208 (M^+, 100), 193 (50.9). Anal. Calcd for $C_{12}H_{16}OS$ (208.33): C, 69.18; H, 7.74. Found: C, 69.30; H, 7.92.

3-Hydroxy-1-(methylthio)-5,6,7,8,9,10,11,12,13,14-decahydrobenzododecene (4h): Yield 89% (1.48 g); white solid (chloroform−hexane); mp 133−134 °C; R_f 0.25 (9:1 hexanes−EtOAc); IR (KBr) 3477, 3377, 1573, 1439 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40−1.45 (m, 6H, CH_2), 1.47−1.57 (m, 6H, CH_2), 1.67−1.71 (m, 4H, CH_2), 2.40 (s, 3H, SCH_3), 2.56 (t, J = 8.5 Hz, 2H, CH_2), 2.74 (t, J = 7.8 Hz, 2H, CH_2), 4.85 (brs, 1H, OH), 6.48 (d, J = 2.4 Hz, 1H, ArH), 6.53 (d, J = 2.5 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 22.2, 23.0, 25.7, 26.7, 26.8, 27.0, 27.5, 27.6, 29.5, 30.6, 109.9, 113.0, 130.7, 139.6, 143.1, 153.5; MS (*m*/*z*) 278 (M^+, 100), 263 (18.8). Anal. Calcd for $C_{17}H_{26}OS$ (278.47): C, 73.33; H, 9.41. Found: C, 73.12; H, 9.60.

3-Hydroxy-1-(methylthio)-4a,5,6,7,8,8a,9,10-octahydrophenanthrene (4i): yield 77% (1.14 g); white solid (chloroform−hexane); mp 158−159 °C; R_f 0.22 (9:1 hexanes−EtOAc); IR (KBr) 3360, 1581, 1450, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83−0.89 (m, 1H, CH), 1.35−1.93 (m, 6H, CH_2), 1.94−2.07 (m, 2H, CH), 2.42 (s, 3H, SCH_3), 2.48−2.78 (m, 5H, CH_2), 4.64 (brs, 1H, OH), 6.33 (d, J = 2.2 Hz, 1H, ArH), 6.48 (d, J = 2.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 22.7, 23.9, 28.3, 28.6, 29.4, 33.3, 33.4, 33.8, 108.5, 111.8, 125.0, 137.1, 139.3, 153.4; MS (*m*/*z*) 248 (M^+, 100), 233 (50). Anal. Calcd for $C_{15}H_{20}OS$ (248.40): C, 72.53; H, 8.11. Found: C, 72.78; H, 8.34.

3-Hydroxy-1-(methylthio)-5,6,7,8,8a,9,10,10a-octahydroanthracene (4j): white solid (chloroform−hexane); mp 162−163 °C; yield 87% (1.29 g); R_f 0.23 (9:1 hexanes−EtOAc); IR (KBr) 3365, 2920, 1563, 1444 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08−1.17 (m, 2H, CH_2), 1.21−1.32 (m, 1H, CH), 1.36−1.46 (m, 3H, CH), 1.75−1.90 (m, 4H, CH), 2.20−2.34 (m, 2H, CH_2), 2.40 (s, 3H, SCH_3), 2.45−2.58 (m, 1H, CH), 2.72−2.77 (m, 1H, CH), 3.58 (brs, 1H, OH), 6.51 (d, J = 2.2 Hz, 1H, ArH), 6.59 (d, J = 1.75 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 26.1, 26.6, 26.9, 30.6, 31.2, 34.2, 39.8, 44.0, 108.5, 108.8, 126.4, 139.1, 142.4, 153.7; MS (*m*/*z*) 248 (M^+, 100), 233 (41.3). Anal. Calcd for $C_{15}H_{20}OS$ (248.40): C, 72.53; H, 8.11. Found: C, 72.64; H, 8.28.

3-Hydroxy-1-(methylthio)-9,10-dihydrophenanthrene (4k): red viscous liquid; yield 64% (0.93 g); R_f 0.24 (9:1 hexanes−EtOAc); IR (CCl_4) 3017, 2926, 1597, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H, SCH_3), 2.85 (s, 4H, CH_2), 5.14 (brs, 1H, OH), 6.68 (d, J = 2.2 Hz, 1H, ArH), 7.05 (d, J = 2.2 Hz, 1H, ArH), 7.23−7.29 (m, 3H, ArH), 7.63 (d, J = 7.3 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 24.4, 28.8, 107.8, 111.6, 124.1, 126.9, 127.5, 127.7, 127.9, 134.0, 136.0, 137.4, 138.2, 154.6; MS (*m*/*z*) 242 (M^+, 100), 227 (78). Anal. Calcd for $C_{15}H_{14}OS$ (242.35): C, 74.34; H, 5.82. Found: C, 74.58; H, 5.95.

10-Hydroxy-8-(methylthio)-6,7-dihydrodibenz[*b*,*d*]thiepin (4m): yield 62% (1.02 g); red viscous liquid; R_f 0.26 (9:1 hexanes−EtOAc); IR (CCl_4) 3357, 2928, 1593, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H, SCH_3), 2.84 (s, 4H, CH_2), 5.38 (brs, 1H, OH), 6.68 (d, J = 2.4 Hz, 1H, ArH), 7.05 (d, J = 2.4 Hz, 1H, ArH), 7.22−7.29 (m, 3H, ArH), 7.62 (d, J = 7.3 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 24.3, 28.8, 107.8, 111.5, 124.1, 126.9, 127.4, 127.7, 127.9, 134.0, 136.0, 137.4, 138.2, 154.6; MS (*m*/*z*) 274 (M^+, 0.5), 242 (95), 227 (75). Anal. Calcd for $C_{15}H_{14}OS_2$ (274.41): C, 65.64; H, 5.14. Found: C, 65.79; H, 5.36.

5-Hydroxy-3-(methylthio)biphenyl (4n): yield 64% (0.83 g); red viscous liquid; R_f 0.24 (9:1 hexanes−EtOAc); IR (CCl_4) 3340, 3055, 2926, 1672, 1587 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H, SCH_3), 5.75 (brs, 1H, OH), 6.74 (t, J = 1.2 Hz, 1H, ArH), 6.83 (t, J = 2 Hz, 1H, ArH), 7.01 (t, J = 1.2 Hz, 1H, ArH), 7.31−7.42 (m, 3H, ArH), 7.51−7.53 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 111.2, 113.0, 117.6, 127.1, 127.6, 128.4, 140.4, 143.2, 155.4; MS (*m*/*z*) 216 (M^+, 100), 201 (5). Anal. Calcd for $C_{13}H_{12}OS$ (216.30): C, 72.18; H, 5.58. Found: C, 72.24; H, 5.68.

General Procedure for the Raney-Ni Desulfurization of Phenols: Synthesis of 5d−f,h. To a solution of the appropriate thiomethylphenol (5 mmol) in absolute ethanol (10 mL) was added Raney-Ni (W2) (∼3 g), and the reaction mixture was refluxed with stirring for 6−7 h (monitored by TLC). It was then filtered through a sintered glass funnel and washed with hot ethanol and the filtrate concentrated to afford crude phenol, which was purified by column chromatography over silica gel using hexanes−ethyl acetate (24:1) as eluent.

General Procedure for Cycloaromatization of 4-(Methylthio)-3-buten-2-one (6) with Ketones 1d,f,h: Synthesis of Phenols 5d,f,h. The previous procedure (method A) was followed using ketone (6 mmol), NaH (0.75 g, 12.5 mmol, 40%), and **6** (0.69 g, 6 mmol) in 20 mL of DMF. Workup and column chromatography (method A) yielded pure phenols **5d**, **5f**, and **5h**.

6-Hydroxy-2-(*tert*-butyl)-1,2,3,4-tetrahydronaphthalene (5d): yield 88% (0.89 g, with Raney Ni), 63% (0.77 g, from **6**); white solid (chloroform−hexane); mp 92−93 °C; R_f 0.30 (9:1 hexanes−EtOAc); IR (KBr) 2957, 1501, 1451, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (s, 9H, CH_3), 1.16−1.24 (m, 1H, CH), 1.27−1.34 (m, 1H, CH), 1.82−1.87 (m, 1H, CH), 2.31−2.38 (m, 1H, CH), 2.59−2.67 (m, 3H, CH), 4.98 (brs, 1H, OH), 6.45 (d, J = 2.4 Hz, 1H, ArH), 6.50 (dd, J = 2.4, 8.0 Hz, 1H, ArH), 6.83 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 27.2, 30.1, 30.6, 32.4, 45.0, 112.9, 114.8, 129.7, 130.3, 138.4, 152.9; MS (*m*/*z*) 205 ($M^+ + 1$, 18), 204 (M^+, 86). Anal. Calcd for $C_{14}H_{20}O$ (204.31): C, 82.30; H, 9.86. Found: C, 82.52; H, 9.93.

5-Hydroxy-2,3-dihydro-1*H*-indene (5e): yield 74% (0.49 g, with Raney Ni); red viscous liquid; R_f 0.31 (9:1 hexanes−EtOAc); IR (CCl_4) 3356, 2915, 1489, 1263 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95−1.98 (m, 2H, CH_2), 2.69−2.74 (m, 4H, CH_2), 5.83 (brs, 1H, OH), 6.52 (d, J = 8.0 Hz, 1H, ArH), 6.62 (s, 1H, ArH), 6.94 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 31.9, 32.9, 111.4, 113.0, 124.8, 136.2, 145.9, 154.0; MS (*m*/*z*) 133 ($M^+ - 1$, 2), 115 (3). Anal. Calcd for $C_9H_{10}O$ (134.18): C, 80.56; H, 7.51. Found: C, 80.77; H, 7.68.

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Supporting Information Available: Characterization data for products **4c**, **4g**, **4l**, **4o**, **5f**, and **5h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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