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# Highly Regioselective 1,2-Addition of Alkoxybenzyl Grignard Reagents to α-Oxoketene Dithioacetals: A Facile Regiocontrolled Synthesis of Alkoxynaphthalenes and their Condensed Analogs *via* Aromatic Annelation

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***Abstract***: 4-Methoxybenzyl- (**A**), 3,4-dimethoxybenzyl- (**B**) and 3,4-methylenedioxybenzyl- (**C**) Grignard reagents are shown to undergo regioselective 1,2-addition with various acyclic and cyclic α-oxoketene dithioacetals to afford carbinol dithioacetals which on $BF_3.Et_2O$ catalyzed cyclization yield alkoxynaphthalenes and their condensed derivatives in a highly regiocontrolled manner. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: Ketene dithioacetals, Grignard reagents, aromatic annelation, alkoxynaphthalenes.

We have previously reported that the reaction of benzyl Grignard reagent with α-oxoketene dithioacetals followed a sequential 1,4- and 1,2-addition mode to yield the corresponding carbinol thioacetals in excellent yields.[1] Apparently two equivalents of benzyl Grignard reagent per mole of α-oxoketene dithioacetal were consumed in these reactions. The carbinol thioacetals thus obtained were subsequently cyclized in the presence of Lewis acid to yield only the corresponding benzyl substituted naphthalenes.[1] Alternatively, the benzyl Grignard reagent was also reacted with β-oxodithioacetals which followed exclusive 1,2-addition mode to yield the corresponding naphthalenes free from both benzyl and methylthio groups.[2] The required β-oxodithioacetals were obtained in good yields by subjecting α-oxoketene dithioacetals to sodium borohydride reduction in the presence of acetic acid as reported in our earlier paper.[3] In continuation of these studies, we further considered of interest to extend our aromatic annelation methodology[4] for the synthesis of alkoxy substituted naphthalenes and their condensed variants by reacting alkoxybenzyl Grignard reagents either with α-oxoketene dithioacetals or with β-oxodithioacetals. These oxygenated naphthalenes are important since they occur widely in nature as lignan lactones, naphthoquinones and anthracyclines with important biological properties, which have attracted the attention of many synthetic organic chemists in recent years.[5,6] The reported methods for the synthesis of substituted naphthalenes can broadly be classified into two categories: (a) derivatization of preconstructed naphthalenes through electrophilic or nucleophilic substitution or functional group transformation (b) annelation methods based on creation of regiospecifically substituted naphthalene ring from open chain precursors.[6] The former method however suffers from serious limitations due to the restriction on fixed aromatic orientation displayed by


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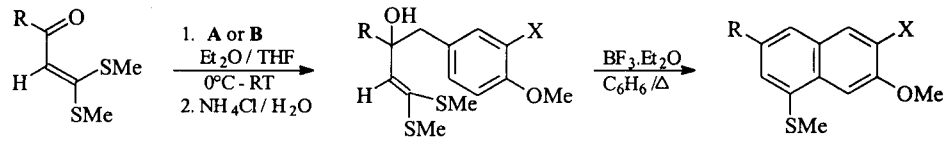
substituted naphthalenes in substitution reactions. On the other hand, annelation methods based on open chain precursors enjoy freedom of placing the appropriate substituents which will essentially become the part of product naphthalenes. Thus the reaction of oxygenated benzyl Grignard reagents with α-oxoketene dithioacetals should provide greater flexibility for regiocontrolled synthesis of substituted and annelated alkoxynaphthalenes. The results of these studies have been reported in this paper.

## Results and discussion

### (a) Reaction of 4-Methoxybenzyl- (A) and 3,4-Dimethoxybenzyl- (B) Grignard Reagents with α-Oxoketene Dithioacetals

The required (4-methoxybenzyl)- (**A**) and (3,4-dimethoxybenzyl)- (**B**) Grignard reagents were prepared according to the reported method.[7a] Generally the preparation of these Grignard reagents required careful reaction conditions including temperature, solvent combination and dilution for optimal yields. Any variation in these parameters resulted in the formation of coupling products instead of the desired Grignard reagents. In a typical experiment, **A** was prepared in the presence of a large excess of $Et_2O$:THF (1:1) and reacted with **1a** at 0°C. The reaction mixture was allowed to come to room temperature (1h) and after work-up yielded the corresponding carbinol thioacetal **2a** in nearly quantitative yield. The crude **2a** was then refluxed with $BF_3.Et_2O$ in dry benzene (40 ml) to afford after work-up, the corresponding naphthalene **3a** in 58% yield. The other mono- or dimethoxy substituted naphthalenes **3b-c** and **5a-b** (Scheme 1) were similarly prepared by reacting either **A** or **B** with **1b-c** in 59-75% overall yields under the described reaction conditions. In all these reactions examined, both anions **A** and **B** followed exclusive 1,2-addition mode with α-oxoketene dithioacetals to afford the respective naphthalenes **3a-c, 5a-b** and the corresponding 1,4- addition products however were not detected in the reaction mixture. Two of the (methylthio)naphthalenes **3b** and **3c** were subjected to Raney Ni desulphurization when the corresponding sulphur free methoxy naphthalenes **6b** and **6c** were obtained in 88% and 90% yields respectively. The benzyl Grignard reagents **A** and **B** were




**1**

**1a**, R = $CH_3$
**b**, R = $C_6H_5$
**c**, R = 4-$MeC_6H_4$

**2,4**

**2,3a**, R = $CH_3$, X = H (58%)
**b**, R = $C_6H_5$, X = H (75%)
**c**, R = 4-$MeC_6H_4$, X = H (72%)
**4,5a**, R = $CH_3$, X = OMe (71%)
**b**, R = $C_6H_5$, X = OMe (59%)

**3,5**

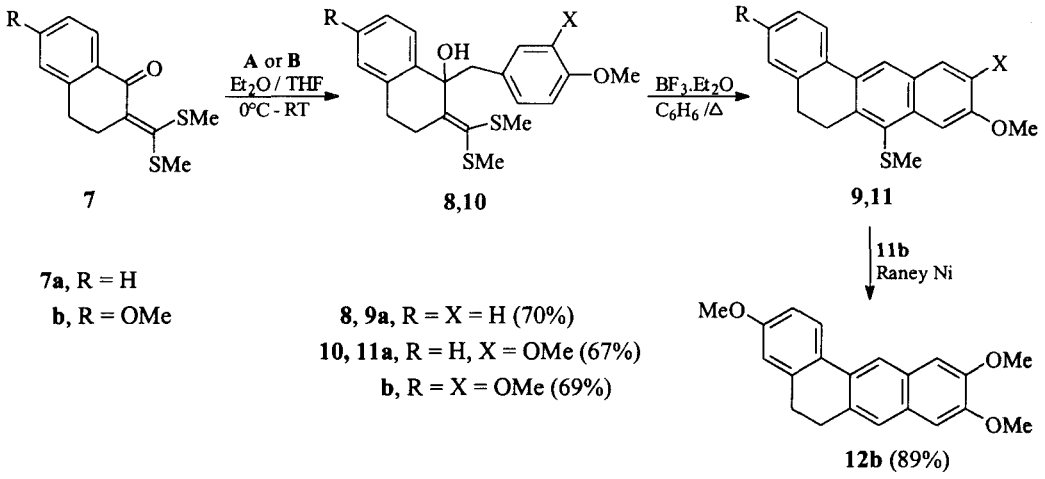
**6**

**6b**, R = $C_6H_5$ (88%)
**c**, R = 4-$MeC_6H_4$ (90%)

**Scheme 1**

similarly reacted with α-oxoketene dithioacetals **7a-b** derived from tetralone which also followed 1,2-addition mode. Thus 4-methoxybenzyl Grignard reagent **A** reacted with **7a** to afford the corresponding

dihydrobenzanthracene **9a** in 70% yield under similar reaction conditions. Similarly 3,4-dimethoxybenzyl Grignard reagent **B** was reacted with both **7a-b** to afford the corresponding methoxy substituted benzanthracenes **11a-b** in 67% and 69% yields respectively. One of the products **11b** was desulphurized in the presence of Raney Nickel to afford the corresponding dimethoxydihydrobenzanthracene **12b** in 89% yield (Scheme 2). However the reaction of cyclic ketene dithioacetal **21** from cyclohexanone with either 4-methoxybenzyl (**A**) or 3,4-dimethoxybenzyl (**B**) Grignard reagent under the described reaction conditions gave only complex product mixture from which no identifiable product could be isolated.




**7** **8,10** **9,11**

**7a**, R = H
**b**, R = OMe

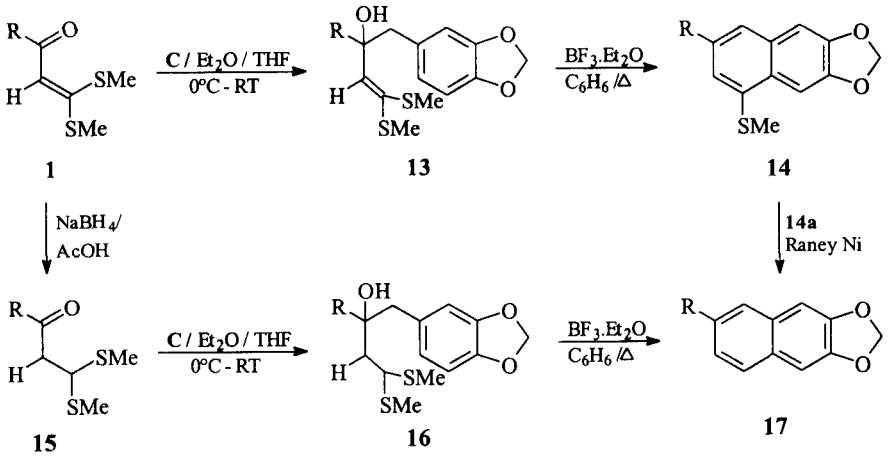
**8, 9a**, R = X = H (70%)
**10, 11a**, R = H, X = OMe (67%)
**b**, R = X = OMe (69%)

**12b** (89%)

**Scheme 2**

**(b) Reaction of 3,4-Methylenedioxybenzyl Grignard Reagent C with α-Oxoketene Dithioacetals**

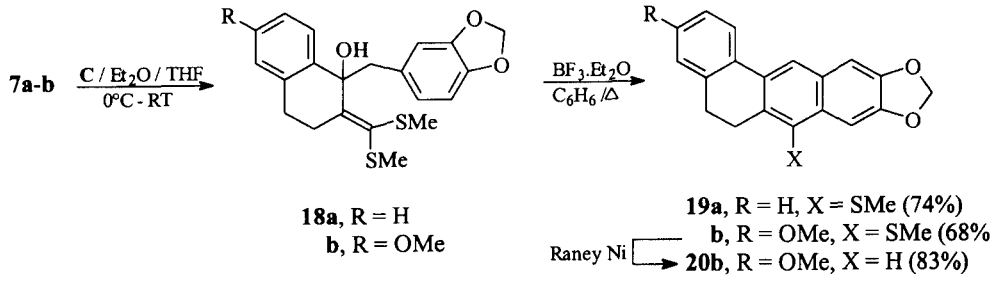
The addition reactions of 3,4-methylenedioxybenzyl Grignard reagent **C** with α-oxoketene dithioacetals were found to be very facile in all the cases examined. The reaction followed exclusive 1,2- addition mode (except in **21**) to yield the corresponding methylenedioxy substituted naphthalenes in good yields after cycloaromatization. Thus the acyclic ketene dithioacetals **1a-d** underwent smooth 1,2-addition with **C** to afford the respective carbinol thioacetals **13a-d** in nearly quantitative yields which on cyclization in the presence of $BF_3.Et_2O$ in refluxing benzene gave the corresponding 2-substituted 4-methylthio-6,7-(methylenedioxy)naphthalenes **14a-d** in 60-66% overall yields (Scheme 3). Raney Ni desulphurization of **14a** yielded the sulphur free naphthalene **17a** in 86% yield. Alternatively, the naphthalenes **17a-b** could also be obtained by the addition of **C** to β-oxodithioacetals **15a-b** initially to afford the corresponding carbinols **16a-b** followed by $BF_3.Et_2O$ cyclization as described earlier. The ketene dithioacetals **7a-b** from α-tetralone similarly reacted with **C** to afford the corresponding methylenedioxy substituted benzanthracenes **19a-b** in high yields (Scheme 4). One of the products **19b** was subjected to Raney Ni desulphurization to afford the corresponding benzanthracene **20b** in good yield. Interestingly the cyclohexanone marcaptal **21** reacted with **C** following the sequential 1,4- and 1,2- addition pathway to yield the corresponding tetrahydromethylenedioxyanthracene **23** carrying (3,4-methylenedioxybenzyl) side chain at 9-position. However the desired 9-unsubstituted-6,7-(methylenedioxy)tetrahydroanthracene **26** could be obtained in 67% yield by reacting β-oxodithioacetal **24** with **C** followed by cyclization as discussed above (Scheme 5).




**1, 13, 14a**, R = $CH_3$ (61%)
**b**, R = $C_6H_5$ (60%)
**c**, R = 4-$MeC_6H_4$ (66%)
**d**, R = 4-$ClC_6H_4$ (63%)

**15, 16, 17a**, R = $CH_3$ (67%)(86% from **14a**)
**b**, R = $C_6H_5$ (74%)

**Scheme 3**

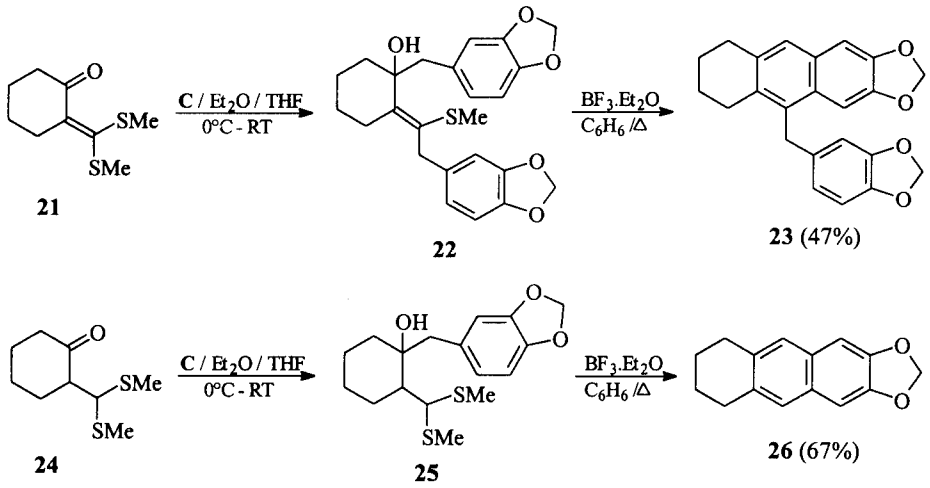



**18a**, R = H
**b**, R = OMe

**19a**, R = H, X = SMe (74%)
**b**, R = OMe, X = SMe (68%
**20b**, R = OMe, X = H (83%)

**Scheme 4**

In summary, the results described above have demonstrated high degree of 1,2-regioselectivity in the addition of alkoxy substituted benzyl Grignard reagents to α-oxoketene dithioacetals. Aromatic annelation of alkoxy substituted benzyl Grignard reagents with α-oxoketene dithioacetals *via* 1,2-addition-$BF_3.Et_2O$ cyclization sequence provides a general, simple and efficient protocol for regiospecific construction of novel alkoxy substituted naphthalenes, anthracenes and benzanthracenes. An attractive feature of this methodology is that by appropriate choice of α-oxoketene dithioacetals as well as alkoxy substituted benzyl halides, it makes readily available a wide range of alkoxynaphthalenes and its condensed analogs. The scope and application of this methodology for the synthesis of biologically important natural products are under investigation.




**Scheme 5**

## Experimental section

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer 297 and 983 spectrophotometer. $^{1}H$ NMR (300 MHz), $^{13}C$ NMR (75.43 MHz) spectra were recorded on Bruker ACF-300 Spectrometer. A few $^{1}H$ NMR spectra were recorded on Varian EM-390 (90 MHz) spectrometer. The chemical shifts were reported in $\delta$ (ppm) relative to TMS and the coupling constant ($J$) are given in Hertz (Hz). Mass spectra were obtained on a Jeol JMS-D-300 Mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer.

All the reactions were obtained in oven dried (120°C) glassware under dry argon or nitrogen atmosphere. All reactions were monitored by analytical TLC on glass plate coated silica gel (Acme's) containing 13% calcium sulfate as binder and visualization of spot was accomplished by exposure to iodine vapour or by spraying acidic potassium permanganate solution. Column chromatography was carried out using silica gel (Acme's, 60-120 mesh) and eluted with mixture of hexane and ethyl acetate.

Diethyl ether was dried by keeping over fused calcium chloride and then over sodium wire. THF was freshly distilled from benzophenone ketyl prior to use. Magnesium turnings (Sisco), Sodium borohydride (Aldrich) were used as supplied. The alkoxybenzyl chlorides were prepared from their corresponding alkoxy benzaldehydes as per the reported methods.

Raney Nickel (W2) was prepared according to the literature procedure.

**General Procedure for Reaction of α-Oxoketene Dithioacetals and β-Oxodithioacetals with 4-methoxy- (A), 3,4-dimethoxy- (B), 3,4-methylenedioxy- (C) benzylmagnesium chlorides.**

To a well stirred suspension of magnesium turnings (1g, 0.042 mol) in dry ether (100 ml), appropriate benzyl halide (0.03 mol) dissolved in dry $Et_2O$:THF (1:1, 100 ml) was added dropwise at ice cooled temperature under nitrogen atmosphere. The reaction mixture was stirred for 45 min at room temperature to ensure the complete formation of the Grignard reagent. The desired α-oxoketene dithioacetal (0.015mol) in THF

(30 ml) was then added drop wise at 0°C and the reaction mixture was further stirred for 1.5 h at room temperature. It was then poured into saturated solution of $NH_4Cl$ (200 ml), extracted with benzene (2×100 ml), dried ($Na_2SO_4$) and evaporated under reduced pressure to give the crude carbinol thioacetals which were found to be unstable on keeping at room temperature and used as such for cycloaromatization without any further purification. **2b**: IR (neat): 3418 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): 2.03 (s, $SCH_3$), 2.23 (s, $SCH_3$), 3.05 (s, benzylic), 3.75 (s, $OCH_3$), 4.81 (s, OH), 6.47 (s, olefinic), 6.65-7.30 (m, ArH).

**General Procedure for $BF_3.Et_2O$ Induced Cycloaromatization of Carbinol thioacetals: Synthesis of Alkoxy Substituted Naphthalenes and their Condensed Analogs.**

To a well stirred solution of crude carbinol thioacetal in dry benzene (50 ml), $BF_3.Et_2O$ (1.5 g) was added and the reaction mixture was refluxed for 45 min. It was cooled, poured into ice cooled saturated $NaHCO_3$ solution (200 ml), extracted with benzene (2×100 ml). The combined organic extracts were washed with water (2×100 ml), dried ($Na_2SO_4$) and evaporated under reduced pressure to afford crude alkoxynaphthalenes which were purified by column chromatography over silica gel using hexane-ethyl acetate as the eluent. The spectral and analytical data of all the new compounds are given below.

**7-Methoxy-3-methyl-1-(methylthio)naphthalene (3a).** Colorless crystals (ether); mp 55-56°C; yield 58%; IR (KBr): 1620, 1522, 1450, 1250, 1180 $cm^{-1}$; $^1H$ NMR (90 MHz, $CCl_4$): δ 2.43 (s, 3H, $CH_3$), 2.50 (s, 3H, $SCH_3$), 3.93 (s, 3H, $OCH_3$), 7.00-7.76 (m, 5H, ArH); Anal. Calcd for $C_{13}H_{14}OS$ (218.32): C, 71.52; H, 6.79%. Found: C, 71.74; H, 6.72%.

**7-Methoxy-1-methylthio-3-phenylnaphthalene (3b).** Light yellow crystals (ether); mp 84-85°C; yield 75%; IR (KBr): 1600, 1500, 1438, 1260, 1165, 1020 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.60 (s, 3H, $SCH_3$), 3.95 (s, 3H, $OCH_3$), 7.16-7.79 (m, 10H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 16.57, 55.38, 102.77, 119.29, 123.92, 124.59, 127.21, 128.84, 129.16, 130.38, 132.17, 134.45, 136.27, 140.96, 158.11; MS (*m/z*, %): 280 ($M^+$,100); Anal. Calcd for $C_{18}H_{16}OS$ (280.39): C, 77.11; H, 5.75%. Found; C, 77.32; H, 5.68%.

**7-Methoxy-3-(4'-methylphenyl)-1-(methylthio)naphthalene (3c).** Colorless crystals (ether); mp 95-96°C; yield 72%; IR (KBr): 1621, 1490, 1253, 1163, 1026 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, $CH_3$), 2.60 (s, 3H, $SCH_3$), 3.95 (s, 3H, $OCH_3$), 7.16 (dd, $J$ = 2, 10 Hz, 1H, H-6), 7.26 (d, $J$ = 10 Hz, 1H, ArH), 7.55-7.63 (m, 4H, ArH), 7.74-7.77 (m, 2H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 16.59, 21.10, 55.36, 102.77, 119.21, 123.62, 124.66, 127.01, 129.21, 129.56, 130.31, 132.05, 134.32, 136.21, 137.00, 138.04, 158.00; MS (*m/z*, %): 294 ($M^+$, 100); Anal. Calcd for $C_{19}H_{18}OS$ (294.42): C, 77.51; H, 6.16%. Found: C, 77.34; H, 6.24%.

**6,7-Dimethoxy-3-methyl-1-(methylthio)naphthalene (5a).** Colorless needles (ether); mp 62-63°C; yield 71%; IR (KBr): 1502, 1429, 1251, 1233, 1143, 1041 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H, $CH_3$), 2.54 (s, 3H, $SCH_3$), 3.96 (s, 3H, $OCH_3$), 4.01 (s, 3H, $OCH_3$), 7.01 (s, 1H, ArH), 7.13 (brs, 1H, ArH), 7.30 (brs, 1H, ArH), 7.50 (s, 1H, ArH); Anal. Calcd for $C_{14}H_{16}O_2S$ (248.34): C, 67.71; H, 6.49%. Found: C, 67.52; H, 6.56%.

**6,7-Dimethoxy-1-(methylthio)-3-phenylnaphthalene (5b).** Colorless crystals (ether); mp 65-66°C; yield 59%; IR (KBr): 1577, 1490, 1454, 1376, 1260, 1110, 1061 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.61 (s, 3H, $SCH_3$), 4.01 (s, 3H, $OCH_3$), 4.05 (s, 3H, $OCH_3$), 7.16 (s, 1H, ArH), 7.33-7.55 (m, 5H, ArH), 7.65-7.68 (d, $J$ = 2 Hz, 2H, ArH), 7.71 (s, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 16.69, 55.78, 55.86, 96.08, 103.30, 107.09, 122.70, 122.76, 126.80, 127.17, 128.75, 129.60, 134.10, 137.00, 141.12, 149.74, MS (*m/z*, %): 310 ($M^+$, 100), 295 (31). Anal. Calcd for $C_{19}H_{18}O_2S$ (310.42): C, 73.52; H, 5.84%. Found: C, 73.68; H, 5.74%.

**5,6-Dihydro-9-methoxy-7-(methylthio)benz[*a*]anthracene (9a)**. Colorless crystals (ether); mp 109°C; yield 70%; IR (KBr): 1620, 1500, 1390, 1260, 1220, 1030 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2,27 (s, 3H, $SCH_3$), 2.88 (t, $J$ = 7.2 Hz , 2H, $CH_2$), 3.46 (t, $J$ = 7.2 Hz, 2H, $CH_2$), 3.96 (s, 3H, $OCH_3$), 6.99-7.29 (m, 4H, ArH), 7.73 (d, $J$ = 8.5 Hz, 1H, ArH), 7.81 (d, $J$ = 8.5 Hz, 1H, ArH), 8.03 (brs, 1H, ArH), 8.07 (s, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): 12.83, 28.17, 29.21, 55.28, 105.03, 113.86, 118.25, 123.99, 128.77, 124.17, 126.97, 127.28, 128.48, 128.77, 132.09, 134.85, 135.79, 137.65, 141.62, 158.69; MS (*m/z*, %): 306 ($M^+$, 100), 258 (54), 215 (46). Anal. Calcd for $C_{20}H_{18}OS$ (306.43): C, 78.39; H, 5.92%. Found: C, 78.53; H, 5.87%.

**5,6-Dihydro-9,10-dimethoxy-7-(methylthio)benz[*a*]anthracene (11a)**. Colorless crystals (ether); mp 134-136°C; yield 67%; IR (KBr): 1621, 1497, 1462, 1421, 1260, 1251, 1236, 1150, 1016 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H, $SCH_3$), 2.90 (t, $J$ = 7 Hz, 2H, $CH_2$), 3.45 (t, $J$ = 7 Hz, 2H, $CH_2$), 4.02 (s, 3H, $OCH_3$), 4.08 (s, 3H, $OCH_3$), 7.18 (s, 1H, ArH), 7.25-7.36 (m, 3H, ArH), 7.84 (d, $J$ = 7.76 Hz, 1H, ArH), 8.06 (s, 2H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 19.00, 27.90, 29.35, 55.91, 55.99, 105.67, 107.13, 122.78, 124.19, 126.97, 127.34, 127.92, 128.63, 129.84, 130.58, 131.93, 135.02, 137.85, 139.22, 149.23, 150.28; MS (*m/z*, %); 336 ($M^+$, 100); Anal. Calcd for $C_{21}H_{20}O_2S$ (336.45): C, 74.97; H, 5.99%. Found: C, 74.76; H, 5.87%.

**5,6-Dihydro-7-methylthio-3,9,10-trimethoxybenz[*a*]anthracene (11b).** Colorless crystals (ether); mp 144-146°C; yield 69%; IR (KBr): 1498, 1256, 1239, 1155 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$): δ 2.28 (s, 3H, $SCH_3$), 2.86 (t, $J$ = 7.5 Hz, 2H, $CH_2$). 3.42 (t, $J$ = 7.5 Hz, 2H, $CH_2$), 3.83 (s, 3H, $OCH_3$), 4.00 (s, 3H, $OCH_3$), 4.06 (s, 3H, $OCH_3$), 6.80 (d, $J$ = 2 Hz, 1H, H-4 ), 6.86 (dd, $J$ = 2, 9.5 Hz, 1H, H-2), 7.14 (s, 1H, H-8, ArH), 7.75 (d, $J$ = 10 Hz, 1H, H-1), 7.95 (s, 1H, H-11), 8.03 (s, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): 18.96, 27.93, 29.72, 55.27, 55.87, 55.94, 105.67, 106.97, 112.65, 112.96, 121.74, 125.44, 127.87, 128.71, 129.71, 129.71, 129.98, 131.87, 138.69, 139.41, 149.17, 149.96, 159.06; MS (m/z, %); 366 ($M^+$, 100), 318 (47). Anal. Calcd for $C_{22}H_{22}O_3S$ (366.48): C, 72.10; H, 6.29%. Found: C, 72.38; H, 6.23%.

**3-Methyl-6,7-methylenedioxy-1-(methylthio)naphthalene (14a)**. Colorless crystals (ether); mp 103-105°C; yield 61%; IR (KBr): 1603, 1492, 1458, 1241, 1231, 1040 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$): δ 2.43 (s, 3H, $CH_3$), 2.56 (s, 3H, $SCH_3$), 6.03 (s, 2H, $OCH_2O$), 7.01 (s, 1H, ArH), 7.21 (brs, 1H, ArH), 7.32 (brs, 1H, ArH), 7.66 (s, 1H, ArH); MS (*m/z*, %): 232 ($M^+$, 100), 217 (50), 187 (38); Anal. Calcd for $C_{13}H_{12}O_2S$ (232.30): C, 67.22; H, 5.21%. Found: C, 67.38; H, 5.31%.

**6,7-Methylenedioxy-1-methylthio-3-phenylnaphthalene (14b)**. Colorless crystals (ether); mp 118-119°C; yield 60%; IR (KBr): 1605, 1510, 1465, 1240, 1046 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.57 (s, 3H, $SCH_3$), 6.05 (s, 2H, $OCH_2O$), 7.12 (s, 1H, ArH), 7.31-7.46 (m, 3H, ArH), 7.54 (brs, 1H, ArH), 7.63-7.65 (brs, 4H, ArH): $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 16.95, 101.11, 101.24, 104.57, 123.53, 123.60, 127.15, 127.19, 128.34, 128.72, 131.03, 134.72, 137.16, 140.87, 147.93, 148.10; MS (*m/z*, %): 294 ($M^+$, 100); 279 (68); Anal. Calcd for $C_{18}H_{14}O_2S$ (294.37): C, 73.44; H, 4.79%. Found: C, 73.58; H, 4.86%.

**6,7-Methylenedioxy-3-(4'-methylphenyl)-1-(methylthio)naphthalene (14c)**. Colorless crystals (ether); mp 148-149°C; yield 66%; IR (KBr): 1608, 1488, 1459, 1233, 1181, 1163 $cm^{-1}$; $^1H$ NMR (90 MHz, $CCl_4$): δ 2.40 (s, 3H, $CH_3$), 2.53 (s, 3H, $SCH_3$), 6.03(s, 2H, $OCH_2O$), 7.02-7.43 (m, 3H, ArH), 7.48-7.85 (m, 5H, ArH); Anal. Calcd for $C_{19}H_{16}O_2S$ (308.40): C, 74.00; H, 5.23. Found: C, 73.74; H, 5.29%.

**3-(4'-Chlorophenyl)-6,7-methylenedioxy-1-(methylthio)naphthalene (14d)**. Colorless crystals (ether); mp 148-149°C; yield 63%; IR (KBr): 1483, 1457, 1439, 1233, 1038 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.58

(s, 3H, $SCH_3$), 6.07 (s, 2H, $OCH_2O$), 7.14 (s, 1H, ArH), 7.41(d, $J$ = 10 Hz, 2H, ArH), 7.48 (s, 1H, ArH), 7.57 (d, $J$ = 10 Hz, 2H, ArH), 7.63 (brs, 2H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 16.91, 101.21, 101.36, 101.63, 122.90, 123.46, 128.40, 128.96, 130.99, 133.36, 135.04, 135.89, 139.31, 148.13, 148.35; MS (*m/z*, %): 328 ($M^+$, 100); Anal. Calcd for $C_{18}H_{13}ClO_2S$ (328.82): C, 65.75; H, 3.98%. Found: C, 65.94; H, 3.88%.

**6-Methyl-2,3-methylenedioxynaphthalene (17a)**. Colorless crystals (ether); mp 99-101°C; yield 67%; IR (KBr): 1630, 1480, 1330, 1260, 1190, 1050 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H, $CH_3$), 5.96 (s, 2H, $OCH_2O$), 6.93 (s, 1H, ArH ), 6.97 (s, 1H, ArH), 7.05 (brd, $J$ = 9.5 Hz, 1H, ArH), 7.33 (brs, 1H, ArH), 7.45 (d, $J$ = 9.5 Hz, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 21.30, 100.19, 103.09, 103.46, 125.99, 126.09, 126.55, 128.24, 130.42, 132.93, 146.55, 147.20. Anal. Calcd for $C_{12}H_{10}O_2$ (186.21): C, 77.40; H, 5.41%. Found: C, 77.68; H, 5.54%.

**2,3-Methylenedioxy-6-phenylnaphthalene (17b)**.Colorless needles (ether); mp 124-126°C; yield 74%; IR (KBr): 1630, 1480, 1250, 1170, 1050 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 5.99 (s, 2H, $OCH_2O$), 7.10 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.31-7.46 (m, 3H, ArH ), 7.55 (dd, $J$ = 2, 10 Hz, 1H, ArH), 7.64-7.70 (m, 3H, ArH), 7.82 (brs, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 101.02, 103.62, 104.09, 123.93, 125.02, 127.08, 127.19, 127.41, 128.77, 129.62, 130.72, 137.12, 141.12, 147.63, 147.87. Anal. Calcd for $C_{17}H_{12}O_2$ (248.28): C, 82.24; H, 4.87 %. Found: C, 82.47: H, 4.94%.

**5,6-Dihydro-9,10-methylenedioxy-7-(methylthio)benz[*a*]anthracene (19a)**. Colorless crystals (ether); mp 153°C; yield 74%; IR (KBr): 1480, 1260, 1048 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H, $SCH_3$), 2.86 (t, $J$ = 7.1 Hz, 2H, $CH_2$), 3.40 (t, $J$ = 7.1 Hz, 2H, $CH_2$), 6.00 (s, 2H, $OCH_2O$), 7.08 (s, 1H, ArH), 7.21-7.24 (m, 3H, ArH), 7.79 (d, $J$ = 8 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 8.03 (s, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 19.12, 27.88, 29.27, 101.13, 103.39, 104.50, 123.41, 124.17, 126.95, 127.41, 127.89, 129.99, 130. 56, 132.00, 132.14, 134.80, 137.84, 139.47, 147.21, 148.75; MS (*m/z*, %): 320 ($M^+$, 100), 272 (72); Anal. Calcd for $C_{20}H_{16}O_2S$ (320.41): C, 74.97; H, 5.03 %. Found: C, 74.71; H, 5.11%.

**5,6-Dihydro-3-methoxy-9,10-methylenedioxy-7-(methylthio)benz[*a*]anthracene (19b).** Light yellow crystals (ether); mp 113-115°C; yield 68%; IR (KBr): 1608, 1494, 1481, 1464, 1253, 1237, 1041 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H, $SCH_3$), 2.80 (t, $J$ = 7.1 Hz, 2H, $CH_2$), 3.37 (t, $J$ = 7.1 Hz, 2H, $CH_2$), 3.79 (s, 3H, $OCH_3$), 5.96 (s, 2H, $OCH_2O$), 6.75 (d, $J$ = 1.5 Hz, 1H, ArH), 6.81 (dd, $J$ = 1.5, 10 Hz, 1H, ArH), 7.03 (s, 1H, ArH), 7.66 (d, $J$ = 8.8 Hz, 1H, ArH), 7.82 (s, 1H, ArH), 8.01 (s, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 19.12, 27.94, 29.65, 55.24, 101.09, 103.37, 104.35, 112.62, 112.99, 122.41, 125.46, 127.63, 130.08, 130.43, 131.95, 131.99, 139.41, 138.92, 147.15, 148.44, 159.10; MS (*m/z*, %) : 350 ($M^+$, 13.1), 135 (100), 302 (23), 270 (35); Anal. Calcd for $C_{21}H_{18}O_3S$ (350.44): C, 71.98; H, 5.18%. Found: C, 71.71; H, 5.27%.

**6,7-Methylenedioxy-9-(3,4-methylenedioxybenzyl)-1,2,3,4-tetrahydroanthracene (23)**. Colorless crystals (ether); mp 135-137°C; yield 47%; IR (KBr): 1520, 1470, 1260, 1050 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$): δ 1.54-2.06 (m, 4H, -$(CH_2)_2$-), 2.70-3.17 (m, 4H, -$(CH_2)_2$-), 4.26 (s, 2H, $CH_2$), 5.91 (s, 2H, $OCH_2O$), 6.00 (s, 2H, $OCH_2O$), 6.43-6.91 (m, 3H, ArH), 7.10 (s, 1H, ArH), 7.28 (s, 1H, ArH), 7.49 (s, 1H, ArH); MS (*m/z*, %): 360 ($M^+$, 47.4), 306 (16.9), 272 (88), 135 (100); Anal. Calcd for $C_{23}H_{20}O_4$ (360.41): C, 76.65; H, 5.59%. Found: C, 76.79; H, 5.46%.

**6,7-Methylenedioxy-1,2,3,4-tetrahydroanthracene (26)**. Colorless crystals; mp 156-158°C; yield 67%; IR (KBr): 1530, 1310, 1265, 1109, 1005 $cm^{-1}$; $^1H$ NMR (90 MHz, $CCl_4$): δ 1.75 (m, 4H, -$(CH_2)_2$-), 2.89 (m, 4H, -$(CH_2)_2$-), 5.97 (s, 2H, $OCH_2O$), 6.98 (s, 2H, ArH), 7.34 (s, 2H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 23.45,

29.52, 100.66, 102.94, 126.09, 128.85, 134.34, 146.86; MS (*m/z*, %): 226 ($M^+$, 100). Anal. Calcd for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24%. Found: C, 79.42; H, 6.33%.

**General Procedure for the Dethiomethylation of 3b-c, 11b, 14a and 19b.** To a solution of corresponding methylthio substituted compound (2 mmol) in ethanol (25 ml), Raney Ni (W2, 4 times by weight) was added and the reaction mixture was stirred for 8h at room temp. It was then filtered through G-3 sintered funnel and the residue was washed with ethanol (20 ml). Ethanol was removed under vacuum and the residue was dissolved in chloroform (100 ml). The chloroform solution was washed with water (2×100 mL), dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure to give the crude products. Analytically pure compounds were obtained by passing through a short length silica gel column using hexane as eluent.

**2-Methoxy-6-phenylnaphthalene (6b).** Colorless crystals (ether); mp 124-126°C; yield 88%; IR (KBr): 1653, 1506, 1268, 1244, 1176 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H, $OCH_3$), 7.13 (s, 1H, ArH), 7.16 (dd, $J$ = 2, 9.5 Hz, 1H, ArH), 7.30-7.47 (m, 3H, ArH), 7.66-7.79 (m, 5H, ArH), 7.94 (brs, 1H, ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 55.24, 105.46, 119.12, 125.58, 125.98, 127.00, 127.18, 128.76, 129.12, 129.65, 133.71, 136.33, 141.16, 157.69. Anal. Calcd for $C_{17}H_{14}O$ (234.30): C, 87.15; H, 6.02%. Found: C, 87.43; H, 5.93 %.

**2-Methoxy-6-(4-methylphenyl)naphthalene (6c).** Colorless crystals (ether); mp 83-84°C; yield 90%; IR (KBr): 1653, 1505, 1269, 1245, 1177, 1025 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H, $CH_3$), 3.85 (s, 3H, $OCH_3$), 7.07 (s, 1H, ArH), 7.09 (dd, $J$ = 10, 2 Hz, 1H, ArH), 7.19 (d, $J$ = 9.5 Hz, 2H, ArH), 7.51 (d, $J$ = 9.5 Hz, 2H, ArH), 7.60-7.72 (m, 3H, ArH), 7.87 (s, 1H, ArH); Anal. Calcd for $C_{18}H_{16}O$ (248.32): C, 87.06; H, 6.49%. Found: C, 87.27; H, 6.56%.

**5,6-Dihydro-3,9,10-trimethoxybenz[*a*]anthracene (12b).** Colorless crystals (ether); mp 144-146°C; yield 89%; IR (KBr): 1601, 1493, 1385, 1249, 1205, 1166, 1030 $cm^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$): δ 2.70-3.03 (brs, 4H, $-CH_2CH_2-$), 3.86 (s, 3H, $OCH_3$), 4.00 (brs, 6H, 2 $OCH_3$), 6.79 (s, 1H, ArH), 6.90 (dd, $J$ = 1.5, 10 Hz, 1H, ArH), 7.03(s, 1H, ArH), 7.11 (s, 1H, ArH), 7.41 (s, 1H, ArH), 7.88 (d, $J$ = 10 Hz, 1H, ArH), 7.96 (s, 1H, ArH). Anal. Calcd for $C_{21}H_{20}O_3$ (320.39): C, 78.73; H, 6.29%. Found: C,78.88; H, 6.24%.

**5,6-Dihydro-3-methoxy-9,10-methylenedioxybenz[*a*]anthracene (20b).** Pale yellow crystals; mp 144-145°C; yield 83%; IR (KBr): 1640, 1580, 1528, 1498, 1337, 1300, 1180, 1100 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.83-2.96 (m, 4H, $-(CH_2)_2-$), 3.82 (s, 3H, $OCH_3$), 5.97 (s, 2H, $-OCH_2O-$), 6.75 (d, $J$ = 2 Hz, 1H, ArH), 6.84 (dd, $J$ = 2, 8.5 Hz, 1H, ArH), 7.00 (s, 1H, ArH), 7.08 (s, 1H, ArH), 7.42 (s, 1H, ArH), 7.75 (d, $J$ = 8.5 Hz, 1H, ArH), 7.87 (s, 1H , ArH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 29.48, 29.83, 55,22, 100.80, 103.24, 103.87, 112.58, 113.43, 120.75, 125.17, 127.51, 129.42, 129.86, 131.53, 133.77, 139.29, 147.16, 147.36, 158.97. Anal. Calcd for $C_{20}H_{16}O_3$ (304.34): C, 78.93; H, 5.30%. Found: C, 78.76; H, 5.43 %.

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