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Regioselective Synthesis of Substituted 1-Methyl- and 2-Methylnaphthalenes

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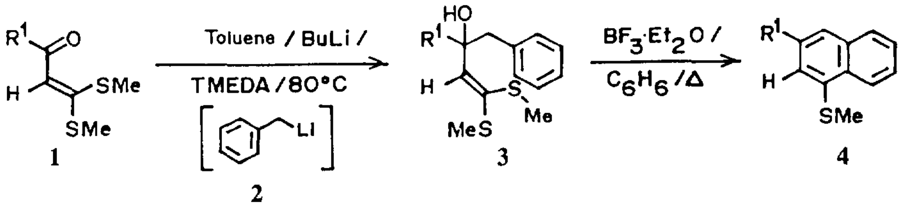
Abstract: Regiospecifically substituted 1-methyl- and 2-methylnaphthalenes, 5-methyl- and 6-methyl-1,2,3,4-tetrahydroanthracenes have been synthesized in good yields through 1,2- addition of the corresponding α-lithio- *o*- or *m*-xylenes onto α-oxoketene dithioacetals or their dihydro derivatives followed by cyclodehydration of the resulting carbinols in the presence of borontrifluoride etherate.

Development of new methods for regiocontrolled synthesis of substituted aromatic compounds has received considerable attention in recent years.[1] Modern methods for the synthesis of these compounds involve annulation reactions in which substitution pattern of the aromatic ring is governed by the functionalities and the structure of the starting materials. These methods are usually convergent involving shorter routes and provide substitution not easily attained by classical electrophilic and nucleophilic aromatic substitutions. Few of the recent annulation methods are the use of Fischer vinyl carbenes,[1d] ring expansion of cyclobutenones[2,3] and cycloaddition of quinodimethane intermediates.[4] We have earlier reported in a series of papers,[5] annulation of substituted benzene, naphthalene and phenanthrene rings to active methylene ketones *via* α-oxoketene dithioacetals. The overall strategy consists of [3+3] annulation approach[6] involving condensation of α-oxoketene dithioacetals (as 3 carbon 1,3-electrophilic species) with 1,3-anionic species like allyl, 2-methacryl, propargyl, benzyl and 1- and 2-(naphthylmethyl) Grignard reagents. The success of these annulation reactions, however, depends on effective utilization of the two electrophilic centres of α-oxoketene dithioacetals for sequential C-C bond formation in highly regioselective fashion. Thus, although allyl, propargyl and 1-(naphthylmethyl) Grignard reagents underwent regioselective 1,2-addition to α-oxoketene dithioacetals, the addition of benzylmagnesium halide to these intermediates resulted in sequential 1,4- and 1,2- addition yielding cycloaromatized products with undesirable benzylic side chain.[5c] This problem was subsequently circumvented by utilizing ß-oxodithioacetals as 1,3-electrophilic species, obtained by 1,4-conjugate reduction of α-oxoketene dithioacetals with sodium borohydride in acetic acid.[7] These studies further encouraged us to apply this methodology for regiocontrolled synthesis of substituted 1- and 2-methylnaphthalenes and the corresponding tetrahydroanthracene analogs by employing monolithiated *o*- and *m*-xylene as 1,3-anionic species in annulation reactions with α-oxoketene dithioacetals or their dihydro derivatives. The results of these studies are reported in this paper.

Results and Discussions

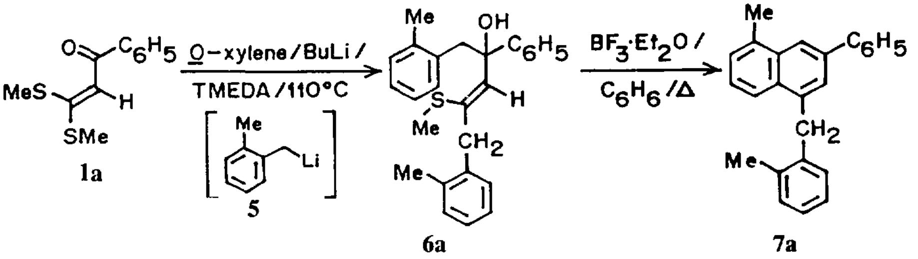
We first concentrated our studies on the addition of benzyllithium to α-oxoketene dithioacetals since earlier cycloaromatization studies on these intermediates mostly involved corresponding Grignard reagents as 1,3-anionic species.[5c,5e] It has been demonstrated that α-carbon of benzyllithium has substantial sp^3 character and the extent of charge localization being dependent upon Lewis acidity of the solvated cation.[8] We therefore anticipated that benzyllithium, unlike its Grignard counterpart should undergo charge controlled 1,2-addition with α-oxoketene dithioacetals. Indeed, when **1a** was treated with benzyllithium (generated by heating toluene and butyllithium-TMEDA at 80°C), the carbinol **3a** was formed exclusively. Cyclodehydration of **3a** in the presence of $BF_3.Et_2O/C_6H_6$ yielded the corresponding 1-(methylthio)-3-phenylnaphthalene (**4a**) in 90% yield (Scheme 1). Similarly the corresponding 3-(4-chlorophenyl)-1-methylthionaphthalene (**4b**) was obtained in high yield under the identical conditions.



1,3,4a, $R^1 = C_6H_5$
b, $R^1 = 4\text{-}ClC_6H_4$

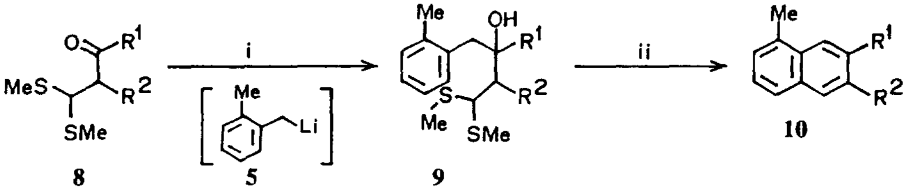
Scheme 1

Mono and dilithiated *o*- and *m*-xylene have been generated by metallation of respective xylenes with butyllithium-TMEDA at room temperature.[9] In a modified procedure, *o*-xylyllithium **5** was generated by heating a solution of n-butyllithium (15% solution in ether, 10 mmol), TMEDA (10 mmol) and *o*-xylene (in excess) at 110°C. Treatment of **5** with α-oxoketene dithioacetal **1a** at room temperature followed by work up afforded carbinol **6a** formed by sequential 1,4- and 1,2-addition of **5** on **1a**, as was evident from its cycloaromatized product **7a** (Scheme 2) formed in the presence of $BF_3.Et_2O/C_6H_6$. We therefore selected ß-oxodithioacetals **8a,8c-d** as annulation partners instead of



Scheme 2

oxoketene dithioacetals with a view to avoid 1,4-addition of **5**. Thus treatment of **5** with ß-oxodithioacetals **8a** and **8c** followed by cationic cyclization of the corresponding carbinols **9a** and **9c** ($BF_3.Et_2O/C_6H_6$) afforded 1-methyl-7-phenyl (**10a**) and 1,7-dimethylnaphthalenes (**10c**) in 73% and 80%yields respectively. Similarly Eudalene (**10d**), a naphthalene hydrocarbon obtained in the rearrangements of few sesquiterpenes[10] was also synthesized from the ß-oxodithioacetal **8d** in 87% yield under the identical conditions (Scheme 3).

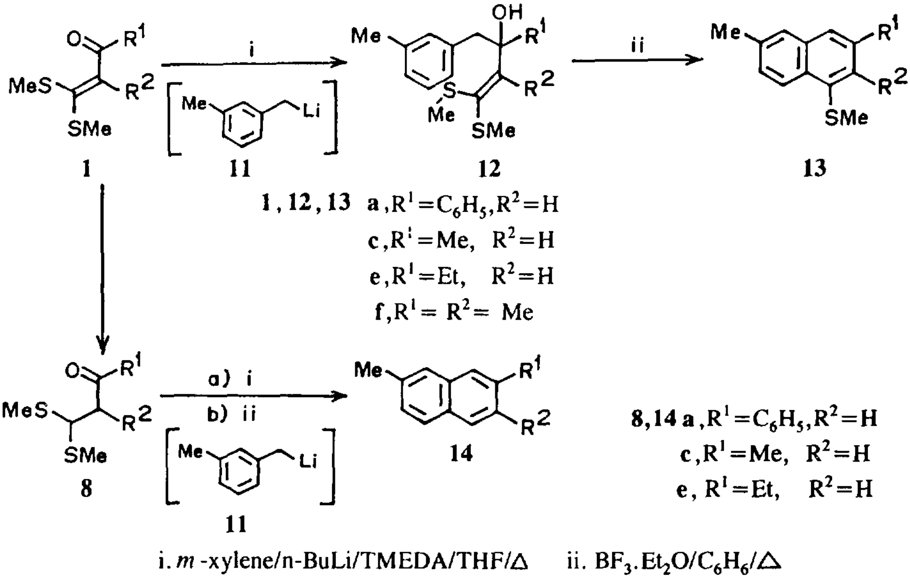


8, 9, 10 a, $R^1=C_6H_5, R^2=H$
c, $R^1=Me$, $R^2=H$
d, $R^1=i\text{-}Pr$, $R^2=H$

i. *o*-xylene/n-BuLi/TMEDA/110°C ii. $BF_3.Et_2O/C_6H_6/\Delta$

Scheme 3

Reactivity profile of *m*-xylyllithium **11** with α-oxoketene dithioacetals was next investigated. Interestingly, treatment of a solution of **11** (generated by heating a solution of n-BuLi,TMEDA and *m*-xylene in THF) with α-oxoketene dithioacetal **1a** yielded only the carbinol **12a** through exclusive 1,2-addition (Scheme 4). Borontrifluoride etherate induced cyclodehydration of the carbinol **12a**



1, 12, 13 a, $R^1=C_6H_5, R^2=H$
c, $R^1=Me$, $R^2=H$
e, $R^1=Et$, $R^2=H$
f, $R^1=R^2=Me$

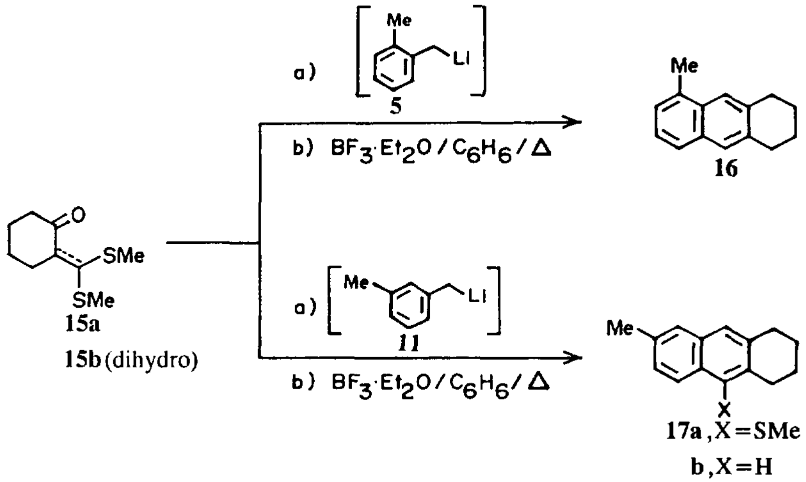
8, 14 a, $R^1=C_6H_5, R^2=H$
c, $R^1=Me$, $R^2=H$
e, $R^1=Et$, $R^2=H$

i. *m*-xylene/n-BuLi/TMEDA/THF/Δ ii. $BF_3.Et_2O/C_6H_6/\Delta$

Scheme 4

afforded 1-(methylthio)-6-methyl-3-phenylnaphthalene (**13a**) in 85% yield. Similarly the other ketenedithioacetals **1c**,**1e-f** underwent regioselective 1,2-addition followed by cyclization under the reported conditions to give substituted 3,6-dimethyl- (**13c**), 3-ethyl-6-methyl- (**13e**) and 2,3,6-trimethyl- (**13f**) 1- methylthionaphthalenes in 65-82% overall yields. Corresponding dethiomethylated naphthalenes (**14a**, **14c** and **14e**) were similarly obtained in good yields from the respective β-oxodithioacetals (**8a**,**8c** and **8e**) and **11** under the identical conditions (Scheme 4).

The methodology was further extended to cyclic ketenedithioacetals **15a** and its dihydro derivative **15b** with a view to synthesize 5- and 6-methyltetrahydroanthracenes in highly regiocontrolled fashion. Thus treatment of *o*-xylyllithium **5** with **15b** followed by cycloaromatization with $BF_3.Et_2O/C_6H_6$ yielded 5-methyl-1,2,3,4-tetrahydroanthracene **16** in 76% yield. Similarly the corresponding 6-methyl derivative **17a** was obtained in good yield under the identical conditions by reaction of oxoketenedithioacetal **15a** and *m*-xylyllithium **11** (Scheme 5) whereas the dethiomethylated product **17b** was formed on treatment of **15b** with **11**.



Scheme 5

In summary, a simple method for regiocontrolled synthesis of substituted 1-Methyl- and 2-methylnaphthalenes and the corresponding anthracene analogs from readily available starting materials has been described. Published procedures for alkylnaphthalenes with substituents occupying well defined positions usually involve multistep introduction of substituents into naphthalene ring *via* Friedel-Crafts or cycloaddition reactions.[11] These methods do not always give satisfactory results and are complicated by formation of isomeric mixtures necessitating laborious separation. Thus 1,7- and 2,7-dimethylnaphthalenes[12] and the corresponding 7-phenyl-[13] and 7-ethyl derivatives[14] have been prepared *via* multistep synthesis following general pattern of Haworth synthesis. Similarly Eudalene has been synthesized in multistep process starting from *o*-cresol or by succinoylation of bromobenzene.[15] Recently 1,7-and 2,7-dimethylnaphthalenes have been synthesized by cyclization of ylidenemalononitrile or the acetate[16] and by annulation of 3-methylbenzylmagnesium chloride and 4,4-dimethoxy-butan-2-one.[17] The latter process although similar to our approach involves not easily accessible β-oxodimethylacetal[18] and requires prior conversion of *m*-xylene to 3-methylbenzyl halide.

Corresponding 1-methyl and 2-methyl anthracenes have also been synthesized through circuitous route *via* reduction of 1-methyl- and 2-methylanthraquinones.[19]

Experimental Section

General: Melting points were determined in a capillary tube on a Thomas Hoover apparatus and are uncorrected. IR Spectra were recorded on a Perkin Elmer 297 spectrophotometer. ^{1}H NMR (90 MHz, Varian EM-390) spectra were taken in $CDCl_3$ or CCl_4 solution with TMS as the internal reference and chemical shifts are reported on the δ-scale relative to TMS. Elemental analyses were carried out on a Heraeus CHN-O-RAPID instrument. Mass sprectras were recorded on a Jeol JMS-D 300 mass spectrometer. Column chromatography was carried out on silica gel (60-120 mesh ACME'S), while TLC was performed on ACME'S silica gel containing 13% calcium sulfate as binder. Purification of the reagents and solvents was effected according to the standard procedures. Prior to concentration all the extracts were dried over anhydrous Na_2SO_4.

General Procedure for Reaction of Benzyllithium with α-Oxoketene dithioacetals 1a-b: Synthesis of 1-(Methylthio)-3-phenylnaphthalenes 4a-b:Butyllithium (15% solution in ether, 13 ml, 30 mmol) was added rapidly to a solution of TMEDA (4.5 ml, 30 mmol) in 30 ml of toluene under nitrogen atmosphere. The resulting yellow solution was heated at 80°C with stirring for 0.5 hr. During this period, bright yellow solid of benzyllithium-TMEDA complex was precipitated from the solution. The reaction mixture was cooled to room temperature and a solution of ketene dithioacetal **1a-b** (10 mmol) in 20 ml of toluene was added followed by further stirring at room temperature for 2 hr. It was then quenched with saturated ammonium chloride solution and extracted with chloroform. The organic layer was dried (Na_2SO_4) and the solvent was removed under low pressure to give crude carbinols **3a-b** in quantative yields. The carbinols were dissolved in benzene (100 ml) and treated with $BF_3.Et_2O$ (3.7 ml, 30 mmol) and refluxed for 30 min. After cooling to room temperature it was worked up with saturated sodium bicarbonate solution,the benzene layer was separated,washed thoroughly with water and dried over Na_2SO_4. After removing the solvent, crude product was purified by column chromatography over silica gel using hexane as eluent.

1-(Methylthio)-3-phenylnaphthalene (4a) : Yellow crystalline solid; m.p. 64-65°C; yield 90%; IR (CCl_4) 1630, 1581, 1563, 1544, 1449, 1399 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.57 (s, 3H, SCH_3), 7.4-7.97(m, 10H, ArH), 8.37 (m, 1H, H-8); (Anal. Calcd. for $C_{17}H_{14}S$: C, 81.56; H, 5.64%. Found: C, 81.78; H, 5.72%).

3-(4-Chlorophenyl)-1-methylthionaphthalene (4b): Yellow crystalline solid; m.p. 78-79°C, yield 85%; IR (KBr) 1565, 1490, 1420, 1295, 820, 725 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.55 (s, 3H, SCH_3); 7.20-8.17 (m, 9H ,ArH);8.42 (m, 1H, H-8); (Anal. Calcd. for $C_{17}H_{13}ClS$: C, 71.69; H, 4.6%. Found : C, 71.90; H, 4.74%).

General Procedure for Generation of *o* - and *m*-Xylyllithium and Their Reaction with α-Oxoketene dithioacetals and Their Dihydro Analogs: Synthesis of Substituted 1-Methyl- (7a, 10a,10c-d) and 2-Methyl-(13a,13c,13e-f,14a,14c,14e) naphthalenes, 5-Methyl- (16) and 6-Methyl- (17a-b) 1,2,3,4-tetrahydroanthracenes:Butyllithium (15% solution in ether, 8.5 ml, 20 mmol) was added rapidly to a solution of TMEDA (3 ml, 20 mmol) and *m*-xylene (2.5 ml, 20 mmol) in dry THF (70 ml) under nitrogen atmosphere. The resulting yellow solution was stirred at room temperature and then it was refluxed for 45 min. After cooling down to room temperature (25-30°C) the respective α-oxoketene dithioacetals or their dihydro derivatives (10 mmol) in 30 ml of dry THF was added rapidly. The red colored reaction mixture was stirred at room temperature for 4-6 hr (monitored by TLC), quenched with saturated ammonium chloride solution and extracted with chloroform. The organic layer was dried (Na_2SO_4) and evaporated on water bath to give crude carbinols in nearly quantitative yield.

The crude carbinols were dissolved in dry benzene (100 ml) and $BF_3.Et_2O$ (2.5 ml, 20 mmol) was added at a time. The reaction mixture was refluxed for 0.5 hr and worked up as described above to give crude naphthalenes which were purified by column chromatography over silica gel using hexane as eluent.

For the generation of *o*-xylyllithium, same procedure as described for *m*-xylyllithium was followed except that THF was replaced by excess *o*-xylene and the reaction mixture (*o*-xylene, n-BuLi and TMEDA) were heated at 110°C for 45 min.

1-(2 -Methylbenzyl)-3-phenyl-5-methylnaphthalene (7a): Yellow crystalline solid; m.p. 130-131°C; yield 85%; IR(KBr) 2900, 1460, 1395, 1265 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.33 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 4.40 (s, 2H, $ArCH_2$-), 6.83-7.92 (m, 13H, ArH), 8.13 (brs, 1H, H-4); (Anal. Calcd. for $C_{25}H_{22}$: C, 93.12; H, 6.88%. Found: C, 93.08, H, 6.82%).

1-Methyl-7-phenylnaphthalene (10a) [13a]: Low melting solid; m.p. 32-33°C; Yield 73% ; IR (CCl_4) 3040, 1605, 1500, 1445, 1388, 1070 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.65 (s, 3H, CH_3), 6.91-7.93 (m, 10H, ArH), 8.20 (brs, 1H, H-8); (Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47%. Found: C, 93.72; H, 6.62%).

1,7-Dimethylnaphthalene (10c) [16b] : Viscous liquid; yield 80%; IR (CCl_4) 3055, 2973, 2944, 2919, 1635, 1425 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.52 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 7.2-7.4 (m, 3H, ArH), 7.6-7.8 (m, 3H, ArH); (Anal. Calcd. for $C_{12}H_{12}$: C, 92.26; H, 7.74%. Found: C, 92.08; H, 7.84%).

1-Methyl-7-(isopropyl)naphthalene (Eudalene) (10d): Viscous liquid; picrate m.p. 90-91°C (lit. 93-94°C)[15a]; yield 87%; IR (CCl_4) 2915, 1920, 1610, 1515, 1460, 1390, 1070 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 1.32 [d, 6H, J=7Hz, $(CH_3)_2CH$], 2.68 (s, 3H, CH_3), 3.01 [sept, 1H, $CH(CH_3)_2$], 7.01-7.93 (m, 6H, ArH); (Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75%. Found: C, 91.43; H, 8.86%).

1-(Methylthio)-6-methyl-3-phenylnaphthalene (13a): Yellow crystalline solid; m.p. 115-116°C; yield 85%; IR (KBr) 1590, 1485, 1135, 970, 875, 790 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.45 (s, 3H, CH_3), 2.56 (s, 3H, SCH_3), 6.84-7.73 (m, 9H, ArH), 7.80- 8.28 (m, 1H, ArH); (Anal. Calcd. for $C_{18}H_{16}S$: C, 81.77; H, 6.10%. Found: C, 81.96; H, 6.22%).

3,6-Dimethyl-1-methylthionaphthalene (13c): Colorless crystalline solid; m.p. 55-57°C; yield 82%; IR (KBr) 1650, 1570, 1510, 1425, 885, 830, 805 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 2.50 (brs, 9H, two CH_3 and SCH_3), 7.19 (brd, 1H, J=9Hz, ArH), 7.31 (brs, 2H, ArH), 7.46 (brs, 1H, ArH), 8.16 (d, 1H, J=9Hz, H-8); (Anal. Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.98%. Found: C, 77.39; H, 7.04%).

3-Ethyl-6-methyl-1-methylthionaphthalene (13e): Yellow crystalline solid; m.p. 110-111°C; yield 82%; IR (KBr) 2940, 1510, 1430, 1270, 860, 810 cm^{-1}; ^{1}H NMR (90MHz, CCl_4) δ 1.24 (t, 3H, J=7Hz, CH_2CH_3), 2.41 (s, 3H, CH_3), 2.45 (s, 3H, SCH_3), 2.72 (q, 2H, J=7Hz, CH_2CH_3), 7.18-7.44 (m, 4H, ArH), 8.20 (d, 1H, J=8.5 Hz, H-8); (Anal. Calcd. for $C_{14}H_{16}S$: C, 77.72; H, 7.46%. Found: C, 77.56; H, 7.58%).

2,3,6-Trimethyl-1-methylthionaphthalene (13f): Yellow crystalline solid; m.p. 122-123°C; yield 65%; IR

(KBr) 3255, 3169, 3013, 2950, 2910, 2850 cm^{-1}; ^{1}H NMR (90MHz, CCl$_4$) δ 2.28 (s, 3H, CH$_3$), 2.42 (s, 3H, CH$_3$), 2.50 (s, 3H, CH$_3$), 2.71 (s, 3H, SCH$_3$), 7.38 (d, 1H, *J*=9Hz, ArH), 7.53 (brs, 2H, ArH), 8.61 (d, *J*=9Hz, 1H, H-8); (Anal. Calcd. for C$_{14}$H$_{16}$S: C, 77.72; H, 7.46%. Found: C, 77.88; H, 7.56%).

2-Methyl-7-phenylnaphthalene (14a) : Colorless crystalline solid; m.p. 123°C; yield 85%; IR (KBr) 1605, 1060, 910, 850, 835, 750 cm^{-1}; ^{1}H NMR (90 MHz, CCl$_4$) δ 2.50 (s, 3H, CH$_3$), 7.20-7.50(m, 5H, ArH), 7.60-8.22(m, 6H, ArH); (Anal. Calcd. for C$_{17}$H$_{14}$: C, 93.54; H, 6.47%. Found: C, 93.68; H, 6.57%).

2,7-Dimethylnaphthalene (14c) [16a,17]: Colorless crystalline solid; m.p. 94-95°C; (lit. m.p.96-97°C); yield 85%; IR (CCl$_4$) 1350, 1327, 1289, 1287, 1192, 1127, 1108 cm^{-1}; ^{1}H NMR (90MHz, CCl$_4$) δ 2.50 (s, 6H, CH$_3$), 7.12-7.78(m, 6H, ArH); (Anal. Calcd. for C$_{12}$H$_{12}$: C, 92.26; H, 7.74%. Found: C, 92.42; H, 7.62%).

2-Ethyl-7-methylnaphthalene (14e) [20]: Viscous liquid; yield 73%; IR (CCl$_4$) 3025, 1580, 1440, 920, 835, 791 cm^{-1}; ^{1}H NMR (90 MHz, CCl$_4$) δ 1.30 (t, 3H, *J*=7Hz, CH$_2$C*H*$_3$), 2.45 (s, 3H, CH$_3$), 2.70 (q, 2H, *J*=7Hz, C*H*$_2$CH$_3$), 7.10-7.85 (m, 6H, ArH); (Anal. Calcd. for C$_{13}$H$_{14}$: C, 91.71; H, 8.29%. Found: C, 91.67; H, 8.44%).

5-Methyl-1,2,3,4-tetrahydroanthracene (16) : Colorless crystalline solid; m.p. 137-138°C; yield 76%; IR (KBr) 2940, 1545, 1445, 1255, 1005, 870 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.53-2.10 [m, 4H, (CH$_2$)$_2$], 2.63 (s, 3H, CH$_3$), 2.77-3.50 [m, 4H, (CH$_2$)$_2$], 6.97-7.80(m, 5H, ArH); (Anal. Calcd. for C$_{15}$H$_{16}$: C, 91.78; H, 8.22%. Found: C, 91.96; H, 8.34%).

6-Methyl-9-methylthio-1,2,3,4-tetrahydroanthracene (17a) : Colorless crystalline solid; m.p. 47-48 °C ; Yield 69%; IR (CCl$_4$) 1566, 1503, 1465, 1265, 980, 900 cm^{-1}; ^{1}H NMR (90 MHz, CCl$_4$) δ 1.65-2.00 [m, 4H, (CH$_2$)$_2$], 2.14 (s, 3H, CH$_3$), 2.24 (s, 3H, SCH$_3$), 2.89 (brs, 2H, CH$_2$), 3.28 (brs, 2H, CH$_2$), 7.25-7.68 (m, 3H, ArH), 8.66 (d, 1H, *J*=9Hz, H-8); (Anal. Calcd. for C$_{16}$H$_{18}$S : C, 79.29; H, 7.47%. Found : C, 79.12; H, 7.58%).

6-Methyl-1,2,3,4-tetrahydroanthracene(17b) : Colorless crystalline solid; m.p.59-60°C; yield 75%; IR (CCl$_4$) 2920, 1620, 1460, 1385, 1255 cm^{-1}; ^{1}H NMR (90 MHz, CCl$_4$) δ 1.57-2.00[(m, 4H, (CH$_2$)$_2$], 2.40 (s, 3H, CH$_3$), 2.72-3.00 [m, 4H, (CH$_2$)$_2$], 6.70-7.60(m, 5H, ArH); (Anal. Calcd. for C$_{15}$H$_{16}$: C, 91.78%; H, 8.22%. Found: C, 91.94; H, 8.30%).

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