

Attempted cycloaromatization of α -arylmethyl sulfones with 2-bis(methylthio)methylene-1-tetralone: unexpected formation of 2-aryl-3-(methylthio)-4,5-dihydronaphtho[1,2-*b*]furans

Sukumar Nandi, Sarvesh Kumar, Hiriyakkanavar Ila* and Hiriyakkanavar Junjappa

Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India

E-mail: hila@iitk.ac.in

Dedicated to Prof. Franklin A. Davis on his 70th birthday

DOI: <http://dx.doi.org/10.3998/ark.5550190.0011.603>

Abstract

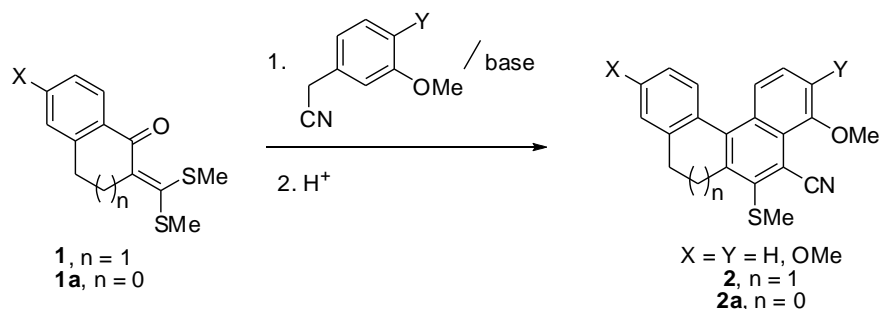
Base-induced conjugate addition-elimination of α -arylmethyl sulfones to α -oxoketene dithioacetal **1** followed by acid-induced cyclization affords 2-phenyl-3-(methylthio)-4,5-dihydronaphtho[1,2-*b*]furans which could be converted to parent aromatized products by DDQ dehydrogenation followed by Raney-Ni dethiomethylation. The approach was found to be amenable to a variety of sulfone components.

Keywords: α -Oxoketene dithioacetal, benzylaryl sulfones, conjugate addition-elimination, cyclization, DDQ, Raney-Ni, naphtho[1,2-*b*]furans.

Introduction

During the course of our aromatic and heteroaromatic annulation studies involving [3+3] cyclocondensation of α -oxoketene dithioacetals (1,3-bielectrophilic components),¹ with various allyl and heteroallyl anions (1,3-binucleophilic components),¹ we have earlier developed efficient and highly regioselective routes for benzo-, naphtho- and phenanthro-annulation^{2,3,1c} of active methylene ketones *via* these intermediates. In subsequent studies, we have further demonstrated that the stabilized carbanions derived from 3-(cyanomethyl)indole,⁴ 2-(cyanomethyl)pyrrole,⁵ and 2-/3-(cyanomethyl)thiophenes,⁶ and 5-(cyanomethyl)pyrazole⁷ add to α -oxoketene dithioacetals in exclusive 1,4-addition-elimination fashion to give conjugate adduct which upon subsequent acid-induced aromatization lead to the formation of angularly substituted/annulated benzoheterocycles such as substituted carbazoles,⁴ indoles,⁵ benzothiophenes,⁶ and indazoles,⁷ respectively. We have also extrapolated this strategy for the synthesis of few angularly-fused polycyclic hydrocarbons such as benzo[*c*]phenanthrene,

benzo[*c*]fluorene, and other potentially carcinogenic PAH's such as 11-methylcyclopenta[*a*]phenanthrene, 5-methylchrysene and 1,4-dimethylphenanthrene (Scheme 1).⁸ The cyano substituent present in these compounds is useful as latent functional group for amide, carboxylic acid, aldehydes as well as a methyl group, besides it can also be removed under drastic acidic or alkaline conditions.^{3b,7}



Scheme 1

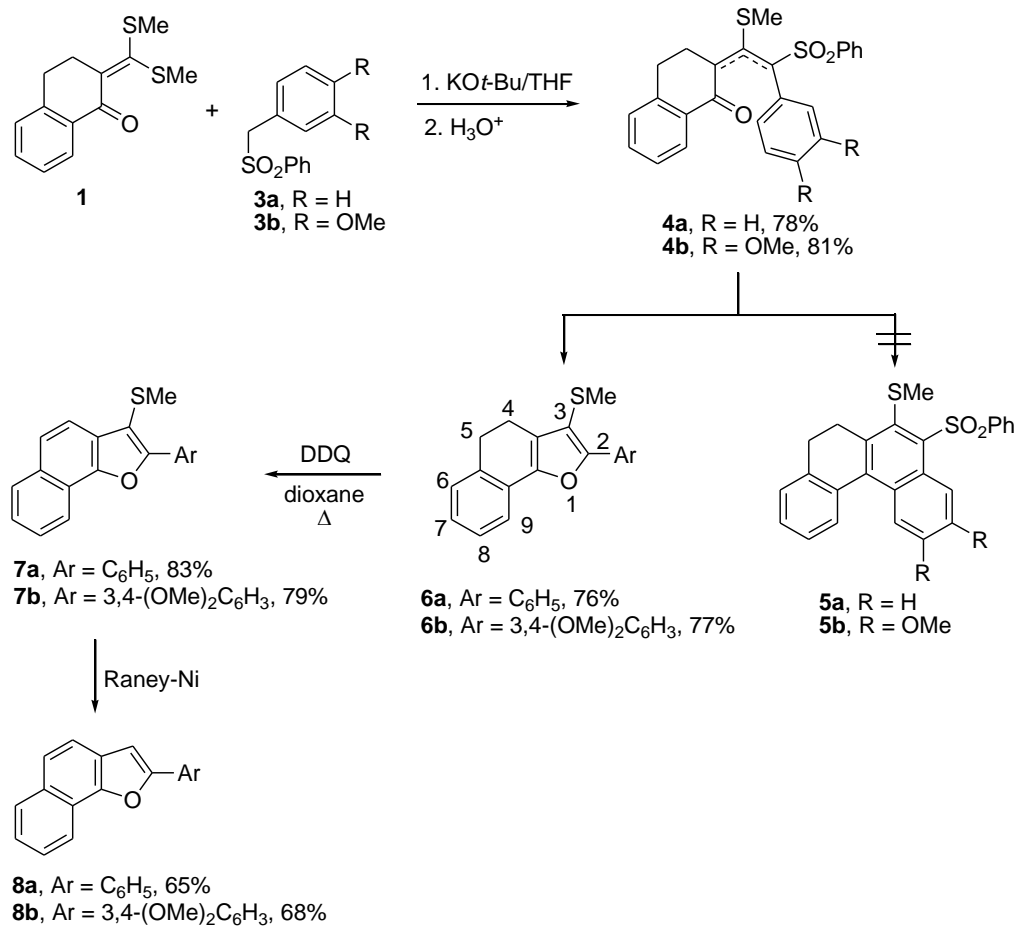
We further considered of interest at this juncture to use arylmethylsulfones (with sulfone as activating group) instead of arylacetonitriles in these cycloaromatizations since aryl sulfones can be more easily removed from the cycloaromatized products under milder conditions, unlike its nitrile counterpart. We have therefore investigated base-induced conjugate addition of few arylmethylsulfones such as **3a-b**, **9** and **14** (Schemes 2-4) with α -oxo ketene dithioacetal **1**, leading to the conjugate adducts **4a-b**, **10** and **15**, respectively, in excellent yields (Schemes 2-4). However, attempted acid-induced cyclization of these adducts yielded the unexpected naphthofuran derivatives instead of the desired angularly cycloaromatized products. The results of these studies are presented in this paper.

Results and Discussion

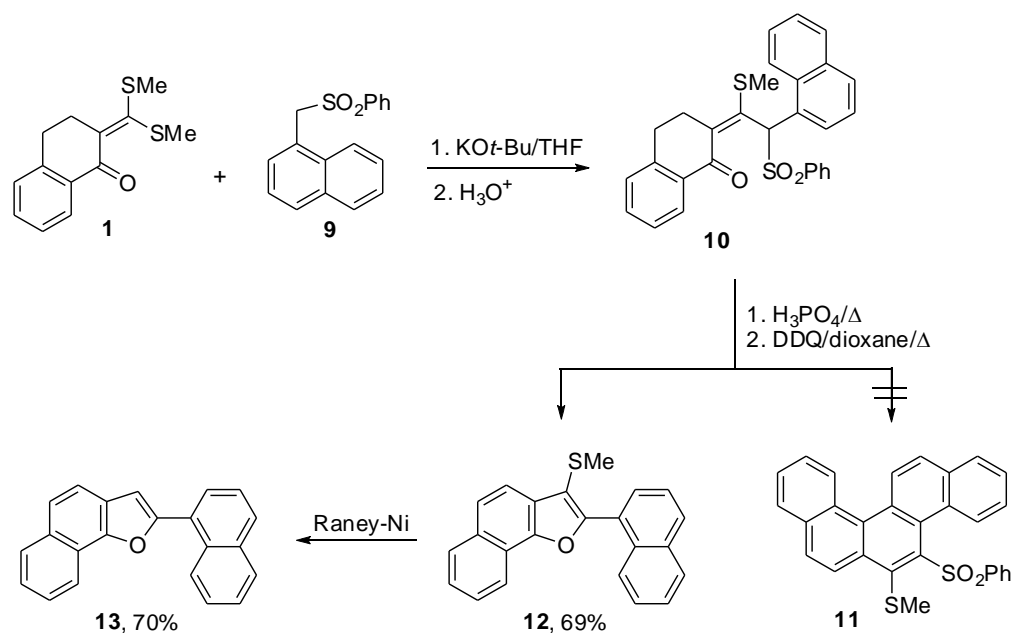
Benzylphenylsulfone **3a** was reacted with 2-bis(methylthio)methylene-1-tetralone **1** in the presence of a number of bases (NaH, LDA, KO*t*-Bu) with a view to obtain 1,4-addition-elimination adduct **4a** (Scheme 2).⁹ Best results were obtained with KO*t*-Bu in THF at -78 °C when the corresponding 1,4-adduct **4a** was obtained in 78% yield. Our various attempts to cyclize **4a** to benzo[*c*]phenanthrene **5a** in the presence of wide range of protic and Lewis acids were not successful yielding only either unreacted starting material or intractable reaction mixture. On the other hand, the reaction proceeded smoothly in the presence of hot H₃PO₄ (85%) yielding only one product (76%) which was not the expected dihydrobenzo[*c*]phenanthrene **5a** but was characterized as 3-(methylthio)-2-phenyl-4,5-dihydronaphtho[1,2-*b*]furan **6a** on the basis of its spectral and analytical data (Scheme 2). The corresponding 3,4-dimethoxybenzylsulfone **3b** similarly underwent base-induced conjugate addition-elimination

with **1** to give the adduct **4b** which upon cyclization in the presence of H₃PO₄ afforded the 2-[(3,4-dimethoxyphenyl)]-3-methylthio)dihydronaphthofuran **6b** in 77% yield (Scheme 2). The dihydronaphthofurans **6a-b** were subjected to DDQ mediated dehydrogenation furnishing the fully aromatized naphthofurans **7a-b** in excellent yields (Scheme 2). Subsequent Raney-Ni desulfurization of **7a-b** yielded the corresponding 2-aryl-3-unsubstituted naphtho[1,2-*b*]furans **8a-b** in overall high yields (Scheme 2). The structures of naphthofurans **8a-b** were further supported by the presence of the characteristic singlets near δ 7.0 for H-3 proton in their ¹H NMR spectra.¹⁰ Besides ¹³C NMR spectra of **8a-b** displayed signals near δ 102 due to C-3 proton.¹⁰ The adduct **10** derived from the 1-(naphthylmethyl)sulfone **9** also followed the similar reactivity pattern when subjected to two-step sequential H₃PO₄ induced cyclization-DDQ mediated dehydrogenation (without isolation of the corresponding 4,5-dihydronaphthofuran intermediate) under earlier described conditions yielding the 3-(methylthio)-2-(1-naphthyl)naphtho[1,2-*b*]furan **12** in 69% yield instead of the desired naphtho[*c*]phenanthrene **11** (Scheme 3). Subsequent dethiomethylation of **12** with Raney-Ni in refluxing ethanol provided the corresponding 3-unsubstituted 2-(1-naphthyl)naphthofuran **13** in good yield (Scheme 3). Similarly, the 1,4-adduct **15** derived from **1** and 2-(naphthylmethyl)sulfone **14** also yielded only the 3-(methylthio)-2-(2-naphthyl)naphtho[1,2-*b*]furan **17** (64%) when subjected to sequential H₃PO₄ mediated cyclization and dehydrogenation with DDQ and no trace of the desired helical pentacene **16** could be detected from the reaction mixture (Scheme 4).

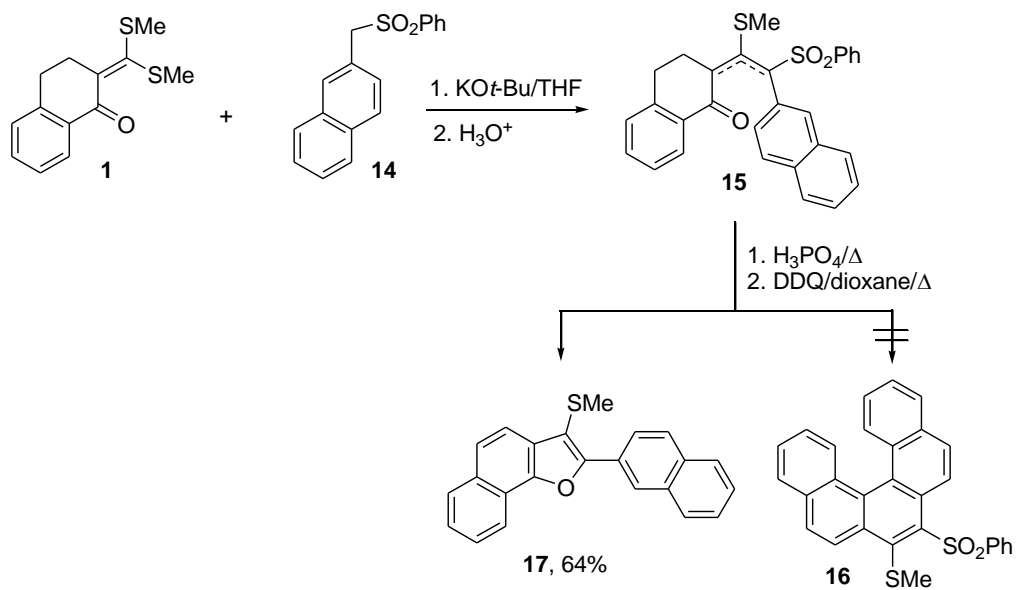
The probable mechanism for the formation of the unexpected naphthofurans from the conjugate adducts is depicted in the Scheme 5. It appears that the highly acidic benzylic proton of adducts **4**, **10**, and **15** rapidly tautomerizes in acidic medium to the enol **18** which undergoes intramolecular cyclization and elimination of phenyl sulfinic acid to afford the observed dihydronaphthofuran products **6a** (Scheme 5).¹¹ However, the expected pathway leading to benzo[*c*]phenanthrene **5** (or **11**, **16**) through intramolecular cyclodehydration on carbonyl group *via* participation of aromatic ring appears to be hindered due to steric crowding in the cyclization intermediate (or transition state) **19** due to the presence of two adjacent bulkier aryl sulfonyl and methylthio groups.



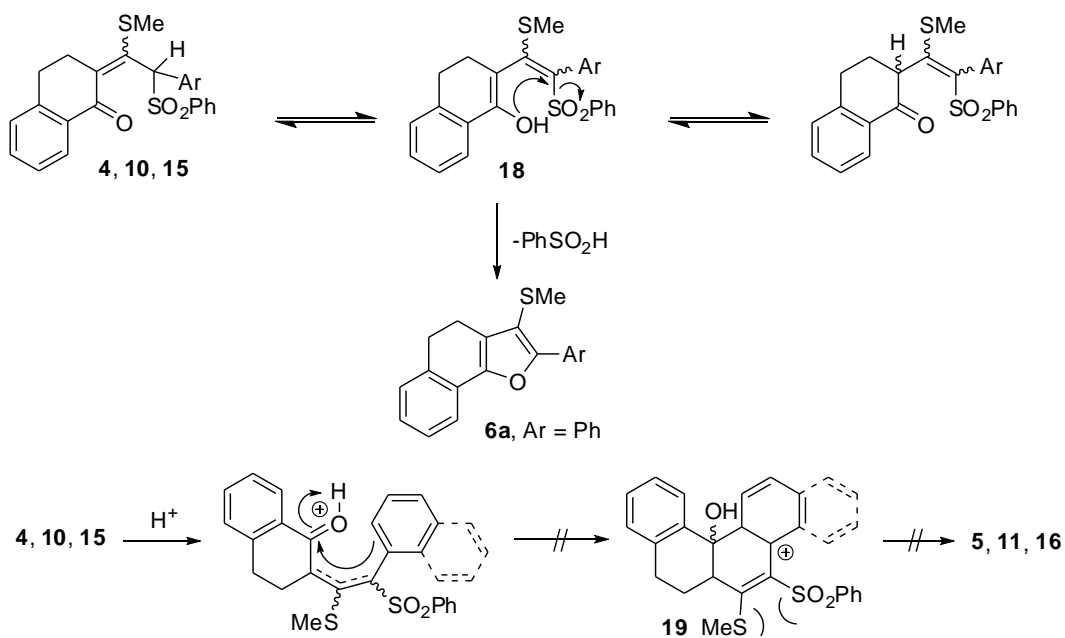
Scheme 2



Scheme 3



Scheme 4



Scheme 5

Conclusions

In conclusion, we have described unexpected results for regioselective assembling of 2-aryl-3-(methylthio)-4,5-dihydronaphtho[1,2-*b*]furans from 2-bis(methylthio)methylene-1-tetralone involving base induced addition of α -arylmethyl sulfones followed by acid-induced elimination-cyclization of the resulting adducts. A few examples of such kind of [4+1] protocol for substituted/annulated furans are described in the literature.¹² The easy availability of the requisite starting materials renders this approach remarkably fascinating.

Experimental Section

General. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on Jeol JNM Lambda Spectrometer with CDCl₃ as the solvent and TMS as an internal standard. Melting points were measured using Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1320 spectrometer. Mass spectra (FAB) were recorded on Jeol SX 102/DA-6000 Mass Spectrometer/Data system. Elemental analyses were carried out on Elementar Vario EL III analyzer. Column chromatography was carried out using silica gel (100-200 mesh). THF and dioxane were distilled over sodium benzophenone ketyl prior to use. KO*t*-Bu, H₃PO₄ and DDQ were purchased from standard firms. Raney Ni (W₂) was prepared according to the reported procedure.¹³ 2-Bis(methylthio)methylene-1-tetralone was prepared according to earlier reported procedure.¹⁴ The corresponding benzylphenyl sulfone, (3,4-dimethoxy)benzylphenyl sulfone, (1-naphthyl)benzylphenyl sulfone, and (2-naphthyl)benzylphenylsulfone were prepared according to the reported procedure.¹⁵

General procedure for the preparation of conjugate adducts (4a-b, 10, 15)

To a stirring solution of potassium *tert*-butoxide (0.78 g, 7 mmol) in THF (20 mL) at -78 °C, a solution of arylbenzylsulfone (5 mmol) in THF (20 mL) was added under nitrogen atmosphere followed by further stirring for 45 min at the same temperature. A solution of tetralone *S,S*-acetal **1** (1.25 g, 5 mmol) in THF (10 mL) was added at -78 °C and the reaction mixture was further stirred for three hours at the same temperature. It was then brought to room temperature during 45 min and stirred at room temperature overnight. The reaction mixture was then poured into ice-cold saturated solution of NH₄Cl (20 mL), extracted with CHCl₃ (3x50 mL) and the combined organic extracts were washed with water (3x50 mL), dried (Na₂SO₄) and concentrated to give adduct (TLC single spot) which were used as such for further acid-induced cyclization. The adduct **10** from 1-(naphthylmethyl)sulfone could be obtained in pure form after column chromatography over silica gel and its spectral and analytical data is given below.

General procedure for the cyclization of adducts 4a-b, 10 and 15 with orthophosphoric acid: synthesis of 2-aryl-3-(methylthio)-4,5-dihydronaphtho[1,2-*b*]furans

The crude adducts (5 mmol) obtained from the previous experiments were dissolved in H₃PO₄ (20 mL, 85%) and the reaction mixture was heated with stirring at 80-100 °C for 5-6 h (monitored by TLC). It was then cooled, poured into ice-cold water (150 mL), extracted with CHCl₃ (3x50 mL) and the combined organic layer was washed with water (3x50 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to give crude products which were purified by column chromatography over silica-gel using hexane-ethyl acetate (97:3) as eluent.

3-(Methylthio)-2-phenyl-4,5-dihydronaphtho[1,2-*b*]furan (6a). White crystalline solid (chloroform-hexane); yield 76%; mp 90-91 °C; IR (KBr): 1479, 1280, 1096, 951 cm⁻¹; ¹H NMR (CDCl₃): δ 2.28 (s, 3H, SCH₃), 2.80 (t, 2H, *J* = 7.8 Hz, CH₂), 3.01 (t, 2H, *J* = 7.8 Hz, CH₂), 7.11-7.32 (m, 4H, ArH), 7.41-7.45 (m, 2H, ArH), 7.53 (dd, 1H, *J* = 8.0, 1.8 Hz, ArH), 8.16 (dd, 2H, *J* = 8.0, 1.8 Hz, ArH); ¹³C NMR (CDCl₃): δ 18.8, 19.7, 28.8, 114.4, 119.3, 124.6, 125.8, 126.8, 127.5, 127.6, 128.0, 128.41, 128.42, 130.8, 134.8, 148.7, 152.4; MS (*m/z*): 292 (M⁺, 100%). Anal. calcd for C₁₉H₁₆OS (292.40): C, 78.05; H, 5.52%. Found: C, 78.14%, H, 5.36%.

2-(3,4-Dimethoxyphenyl)-3-(methylthio)-4,5-dihydronaphtho[1,2-*b*]furan (6b). White crystalline solid (chloroform-hexane); yield 77%; mp 103-104 °C; IR (KBr): 1538, 1493, 1446, 1270, 1254, 1223, 1174, 1142, 1096 cm⁻¹; ¹H NMR (CDCl₃): δ 2.29 (s, 3H, SCH₃), 2.80 (t, 2H, *J* = 7.2 Hz, CH₂), 3.02 (t, 2H, *J* = 7.2 Hz, CH₂), 3.93 (s, 3H, OCH₃), 3.98 (s, 3H, OCH₃), 6.94 (d, 1H, *J* = 8.8 Hz, ArH), 7.11-7.15 (m, 1H, ArH), 7.19-7.26 (m, 2H, ArH), 7.53 (d, 1H, *J* = 7.0 Hz, ArH), 7.73 (dd, 1H, *J* = 8.8, 2.0 Hz, ArH), 7.80 (d, 1H, *J* = 1.6 Hz, ArH); ¹³C NMR (CDCl₃): δ 18.8, 19.8, 28.8, 55.8, 55.9, 109.1, 111.0, 112.9, 118.9, 119.1, 123.9, 124.7, 126.6, 126.7, 127.6, 128.0, 134.7, 148.2, 148.70, 148.73, 152.5; MS (*m/z*): 352 (M⁺, 48%), 351 (100%). Anal. calcd for C₂₁H₂₀O₃S (352.45): C, 71.56; H, 5.72%. Found: C, 71.41%, H, 5.68%.

General procedure for the dehydrogenation of dihydronaphthofurans with DDQ

The suspension of dihydronaphthofuran (5 mmol) and DDQ (7 mmol) in dioxane (50 mL) was refluxed with stirring for 6-8 h (monitored by TLC). The solvent was evaporated under reduced pressure and the concentrated solution was poured into water (100 mL), extracted with CHCl₃ (3x50 mL), dried (Na₂SO₄) and evaporated to give crude product which was purified by column chromatography over silica-gel using hexane-ethyl acetate (98:2) as eluent.

3-(Methylthio)-2-phenylnaphtho[1,2-*b*]furan (7a). White crystalline solid (chloroform-hexane); yield 83%; mp 80-81 °C; IR (KBr): 1519, 1483, 1378, 1181, 1093, 1047, 951 cm⁻¹; ¹H NMR (CDCl₃): δ 2.40 (s, 3H, SCH₃), 7.39 (t, 1H, *J* = 7.2 Hz, ArH), 7.46-7.52 (m, 3H, ArH), 7.59 (t, 1H, *J* = 7.2 Hz, ArH), 7.70 (d, 1H, *J* = 8.0 Hz, ArH), 7.77 (d, 1H, *J* = 8.0 Hz, ArH), 7.92 (d, 1H, *J* = 8.0 Hz, ArH), 8.35 (br d, 3H, *J* = 8.0 Hz, ArH); ¹³C NMR (CDCl₃): δ 18.8, 110.4, 118.2, 120.0, 121.2, 123.9, 125.4, 126.5, 127.0, 128.46, 128.54, 128.57, 128.63, 130.5, 131.9, 149.1, 154.6; MS (*m/z*): 290 (M⁺, 25%), 289 (100%). Anal. calcd for C₁₉H₁₄OS (290.38): C, 78.59; H, 4.85%. Found: C, 78.81%, H, 4.87%.

2-(3,4-Dimethoxyphenyl)-3-(methylthio)benzo[1,2-*b*]furan (7b). White crystalline solid (chloroform-hexane); yield 79%; mp 94-95 °C; IR (KBr): 1545, 1499, 1457, 1264, 1226, 1143, 1094 cm⁻¹; ¹H NMR (CDCl₃): δ 2.42 (s, 3H, SCH₃), 3.97 (s, 3H, OCH₃), 4.03 (s, 3H, OCH₃), 7.02 (d, 1H, *J* = 8.5 Hz, ArH), 7.51 (t, 1H, *J* = 8.0 Hz, ArH), 7.60 (t, 1H, *J* = 8.0 Hz, ArH), 7.73 (d, 1H, *J* = 8.4 Hz, ArH), 7.78 (d, 1H, *J* = 8.5 Hz, ArH), 7.94 (dd, 2H, *J* = 8.0, 2.0 Hz, ArH), 8.02 (d, 1H, *J* = 2.0 Hz, ArH), 8.36 (d, 1H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃): δ 18.7, 55.9, 56.0, 108.8, 110.0, 111.0, 118.1, 119.8, 120.1, 121.1, 123.5, 123.8, 125.2, 126.4, 127.0, 128.5, 131.7, 148.86, 148.90, 149.5, 154.7; MS (m/z): 350 (M⁺, 23%), 349 (100%). Anal. calcd for C₂₁H₁₈OS₂ (350.43): C, 71.98; H, 5.18%. Found: C, 71.87%, H, 5.23%.

3-(Methylthio)-2-(naphthalen-1-yl)naphtho[1,2-*b*]furan (12). White crystalline solid (chloroform-hexane); yield 69%; mp 138-139 °C; IR (KBr): 1509, 1377, 1265, 1090 cm⁻¹; ¹H NMR (CDCl₃): δ 2.26 (s, 3H, SCH₃), 7.48-7.61 (m, 5H, ArH), 7.78 (d, 1H, *J* = 8.4 Hz, ArH), 7.82-7.86 (m, 2H, ArH), 7.91-7.98 (m, 3H, ArH), 8.09 (dd, 1H, *J* = 8.0, 2.0 Hz, ArH), 8.32 (d, 1H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃): δ 18.7, 113.3, 118.4, 120.0, 121.4, 124.0, 125.0, 125.5, 125.8, 126.0, 126.2, 126.6, 126.7, 127.4, 128.4, 128.5, 129.7, 130.0, 131.8, 132.1, 133.8, 150.1, 155.8; MS (m/z): 340 (M⁺, 88%), 339 (100). Anal. calcd for C₂₃H₁₆OS (340.44): C, 81.14; H, 4.74. Found: C, 81.19, H, 4.68.

3-(Methylthio)-2-(naphthalen-2-yl)naphtho[1,2-*b*]furan (17). White crystalline solid (chloroform-hexane); yield 64%; mp 145-146 °C; IR (KBr): 1456, 1371, 1260, 1081, cm⁻¹; ¹H NMR (CDCl₃): δ 2.45 (s, 3H, SCH₃), 7.49-7.55 (m, 3H, ArH), 7.62 (t, 1H, *J* = 7.0 Hz, ArH), 7.74 (d, 1H, *J* = 8.4 Hz, ArH), 7.81 (d, 1H, *J* = 8.4 Hz, ArH), 7.86 (dd, 1H, *J* = 8.0, 2.2 Hz, ArH), 7.94-7.99 (m, 3H, ArH), 8.43 (d, 1H, *J* = 8.0 Hz, ArH), 8.53 (dd, 1H, *J* = 8.0, 2.0 Hz, ArH), 8.82 (s, 1H, ArH); ¹³C NMR (CDCl₃): δ 18.9, 110.9, 118.3, 120.1, 121.2, 124.0, 124.3, 125.5, 126.45, 126.49, 126.53, 126.7, 127.1, 127.7, 128.0, 128.2, 128.5, 128.7, 132.0, 133.2, 133.3, 149.3, 154.7; MS (m/z): 340 (M⁺, 50%), 339 (100%), 324 (82%). Anal. calcd for C₂₃H₁₆OS (340.44): C, 81.14; H, 4.74. Found: C, 81.28, H, 4.67.

General procedure for Raney-Ni dethiomethylation of 2-aryl-3-(methylthio)naphthofurans (7a-b, 12)

A suspension of appropriate methylthiofuran **7a-b** or **12** (2 mmol) and Raney-Ni (W₂, 0.8 g) in absolute ethanol (25 mL) was refluxed with stirring for 6-7 h (monitored by TLC). The reaction mixture was then cooled, filtered through a sintered funnel and the residue was washed with ethanol. The combined filtrate was evaporated under reduced pressure and the residue was dissolved in chloroform (50 mL), washed with water (2x50 mL), dried (Na₂SO₄) and evaporated to give crude product which was purified by column chromatography over silica-gel using hexane-ethyl acetate (97:3) as eluent.

2-Phenylnaphtho[1,2-*b*]furan (8a). White crystalline solid (chloroform-hexane); yield 65%; mp 107-108 °C; IR (KBr): 1568, 1529, 1488 cm⁻¹; ¹H NMR (CDCl₃): δ 7.00 (s, 1H, ArH), 7.25 (t, 1H, *J* = 8.0 Hz, ArH), 7.35-7.41 (m, 3H, ArH), 7.49-7.57 (m, 3H, ArH), 7.82-7.85 (m, 3H, ArH), 8.30 (d, 1H, *J* = 8.0 Hz, ArH); ¹³C NMR (CDCl₃): δ 102.4, 119.5, 120.0, 121.3, 123.6, 124.9,

125.0, 126.3, 128.38, 128.40, 128.80, 128.82, 130.7, 131.5, 150.3, 155.3; MS (m/z): 244 (M^+ , 100%). Anal. calcd for $C_{18}H_{12}O$ (244.29): C, 88.50; H, 4.95%. Found: C, 88.53%, H, 5.03%.

2-(3,4-Dimethoxyphenyl)naphtho[1,2-*b*]furan (8b). White crystalline solid (chloroform-hexane); yield 68%; mp 131-132 °C; IR (KBr): 1561, 1467, 1453 cm^{-1} ; 1H NMR ($CDCl_3$): δ 3.93 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 6.95 (d, 1H, $J = 8.0$ Hz, ArH), 7.02 (s, 1H, ArH), 7.43-7.52 (m, 3H, ArH), 7.57-7.66 (m, 3H, ArH), 7.92 (d, 1H, $J = 8.0$ Hz, ArH), 8.38 (d, 1H, $J = 8.0$ Hz, ArH); ^{13}C NMR ($CDCl_3$): δ 55.97, 55.99, 102.2, 107.8, 111.4, 117.6, 119.4, 119.9, 121.2, 123.5, 123.8, 124.8, 125.0, 126.2, 128.4, 131.2, 149.2, 149.3, 149.9, 155.4; MS (m/z): 304 (M^+ , 52%), 303 (100%). Anal. calcd for $C_{20}H_{16}O_3$ (304.34): C, 78.93; H, 5.30%. Found: C, 78.74%, H, 5.40%.

2-(1-Naphthyl)naphtho[1,2-*b*]furan (13). White crystalline solid (chloroform-hexane); yield 70%; mp 121-122 °C; IR (KBr): 1501, 1498, 1403, 1201 cm^{-1} ; 1H NMR ($CDCl_3$): δ 7.20 (s, 1H, ArH), 7.47-7.68 (m, 5H, ArH), 7.68-7.73 (m, 2H, ArH), 7.89-7.96 (m, 4H, ArH), 8.41 (d, 1H, $J = 8.0$ Hz, ArH), 8.57 (d, 1H, $J = 8.0$ Hz, ArH); ^{13}C NMR ($CDCl_3$): δ 107.0, 119.6, 120.1, 121.4, 123.6, 124.6, 125.1, 125.3, 125.5, 126.0, 126.4, 126.9, 127.20, 127.25, 128.4, 128.6, 129.3, 130.6, 131.5, 134.0, 150.5, 155.0; MS (m/z): 294 (M^+ , 100%). Anal. calcd for $C_{22}H_{14}O$ (294.35): C, 89.77; H, 4.79. Found: C, 89.93, H, 4.91.

2-(1-(Methylthio)-2-(naphthalen-1-yl)-2-(phenylsulfonyl)ethylidene)-3,4-

dihydronaphthalen-1(2*H*)-one (10). Thick viscous liquid; yield 88%; IR (neat): 1702, 1596, 1455, 1380 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.74 (s, 3H, SCH_3), 2.84-3.03 (m, 4H, CH_2), 3.70 (br s, 1H, CH), 7.02 (t, 1H, $J = 7.6$ Hz, ArH), 7.10-7.18 (m, 3H, ArH), 7.31 (t, 1H, $J = 7.6$ Hz, ArH), 7.39-7.57 (m, 3H, ArH), 7.59 (t, 1H, $J = 8.0$ Hz, ArH), 7.76-7.86 (m, 4H, ArH), 7.95 (d, 1H, $J = 8.0$ Hz, ArH), 8.47 (d, 1H, $J = 8.4$ Hz, ArH), 8.70 (d, 1H, $J = 8.0$ Hz, ArH); ^{13}C NMR ($CDCl_3$): δ 20.0, 30.0, 33.8, 65.2, 123.3, 124.9, 125.4, 126.8, 127.1, 128.1, 128.3, 128.7, 128.9, 129.2, 130.4, 132.7, 133.1, 133.36, 133.40, 133.5, 133.7, 137.9, 139.5, 143.4, 148.9, 189.2; MS (m/z): 484 (M^+ , 100). Anal. calcd for $C_{29}H_{24}O_3S_2$ (484.63): C, 71.87; H, 4.99. Found: C, 71.93, H, 4.94.

References

1. Reviews: (a) Ila, H.; Junjappa, H.; Mohanta, P. K. In *Progress in Heterocyclic Chemistry*; Gribble, G. W., Gilchrist, T. L., Eds.; Pergamon: Oxford 2001; Vol 13, chapter 1, pp 1-24. (b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423. (c) Ila, H.; Junjappa, H.; Barun, O. *J. Organomet. Chem.* **2001**, *624*, 34. (d) Junjappa, H.; Ila, H. *Phosphorous, Sulfur Silicon Relat. Elem.* **1994**, *95*, 35.
2. (a) Singh, G.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1984**, *25*, 5095. (b) Balu, M. P.; Singh, G.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1986**, *27*, 117. (c) Rao, C. S.; Balu, M. P.; Ila, H.; Junjappa, H. *Tetrahedron* **1991**, *47*, 3499. (d) Mehta, B. K.; Nandi, S.; Ila, H.; Junjappa, H. *Tetrahedron* **1999**, *55*, 12843.

3. For recent papers: (a) Nandi, S.; Syam Kumar, U. K.; Ila, H.; Junjappa, H. *J. Org. Chem.* **2002**, *67*, 4916. (b) Panda, K.; Venkatesh, C.; Ila, H.; Junjappa, H. *Eur. J. Org. Chem.* **2005**, 2045. (c) Kumar, S.; Ila, H.; Junjappa, H. *Tetrahedron* **2007**, *63*, 10067.
4. Patra, P. K.; Suresh, J. R.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1997**, *38*, 3119.
5. Suresh, J. R.; Patra, P. K.; Ila, H.; Junjappa, H. *Tetrahedron* **1997**, *53*, 14737.
6. Suresh, J. R.; Barun, O.; Ila, H.; Junjappa, H. *Tetrahedron* **2000**, *56*, 8153.
7. Peruncheralathan, S.; Khan, T. A.; Ila, H.; Junjappa, H. *Tetrahedron* **2004**, *60*, 3457.
8. Nandi, S.; Panda, K.; Suresh, J. R.; Ila, H.; Junjappa, H. *Tetrahedron* **2004**, *60*, 3663.
9. The ^1H and ^{13}C NMR spectra of adducts **4a-b** and **15** showed them to be complex mixture of various tautomeric forms and geometrical isomers. However, the adduct **10** from (1-naphthylmethyl)phenylsulfone could be isolated in pure form by column chromatography over silica gel and could be characterized by its ^1H and ^{13}C NMR spectra and analytical data.
10. Csekei, M.; Novak, Z.; Kotschy, A. *Tetrahedron* **2008**, *64*, 8992.
11. For similar kind of “carbenoid” behavior (nucleophilic and then electrophilic) of methylsulfones, see: (a) Review: El-Awa, A.; Noshi, M. N.; du Jourdan, X. M.; Fuchs, P. L. *Chem. Rev.* **2009**, *109*, 2315 and references therein. (b) Pearlman, B. A.; Putt, S. R.; Fleming, J. A. *J. Org. Chem.* **2006**, *71*, 5646.
12. (a) Garst, M. E.; Spencer, T. A. *J. Am. Chem. Soc.* **1973**, *95*, 250. (b) Okazaki, R.; Negishi, Y.; Inamoto, N. *J. Org. Chem.* **1984**, *49*, 3819.
13. Furness, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R.; Vogel's Textbook of Practical Organic Chemistry, 5th Ed.; ELBS Longman, New York, 1989, p 450.
14. Chauhan, S. M. S.; Junjappa, H. *Tetrahedron* **1976**, *32*, 1779.
15. Sun, X.; Wang, L.; Zhang, Y. *Synth. Commun.* **1998**, *28*, 1785.