Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 101–110

TETRAHEDRON

Double thioalkylation/arylation of nitroarenes with the reduction of nitro- to amino group

Zbigniew Wróbel

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01-224 Warsaw, Poland

Received 12 August 2002; revised 14 October 2002; accepted 7 November 2002

Abstract—Some active bicyclic nitroarenes readily react with an excess of alkyl/arylthiols in the presence of DBU and bis-trimethylsilylacetamide (BSA) in DMF solution, to give dithioalkyl/aryl substituted anilines in moderate to good yields via displacement of *ortho*- and *para*-hydrogen atoms with simultaneous reduction of the nitro- to amino-group.

1. Introduction

Sulfur-based anions are known as good nucleophiles in the aromatic nucleophilic substitution in nitroarenes containing the leaving group in the *ortho*-, *para*-[1–3] and even (in the case of polynitroarenes) *meta*-position.[4,5] However, there are a very few reports about the direct nucleophilic substitution of hydrogen by thioanions, and even in these cases due to low yields, the reaction was often not of synthetic value.[1,6] Recently it was reported that nitroquinolines react with alkanethiolate anions to give products of oxidative nucleophilic substitution of hydrogen by thiolates in moderate but preparative yields.[6] Nitroarenes as well as oxygen in the air were found to be involved in the oxidation process.

2. Results and discussion

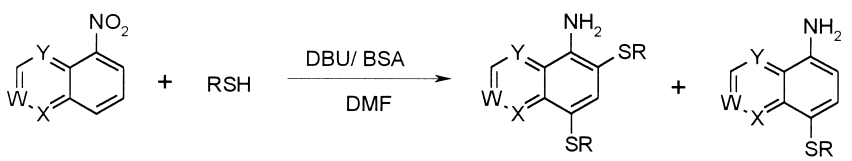
Continuing our investigations into reactions of aromatic nitro compounds with different nucleophilic agents in the presence of Lewis acids,[7–12] we observed a new kind of transformation of nitroarenes under action of thiols leading to dithioalkylated amines. Substitution of two hydrogen atoms with a sulfur nucleophile was accompanied by the reduction of a nitro-group to an amine.

Thus, treatment of nitronaphthalene **1a** (X=Y=Z=CH; 1 mmol) with an excess of 1,1-dimethylethylthiol **2a** (R=*t*-Bu; 5 mmol), DBU (7.5 mmol) and BSA (2.5 mmol) in DMF (5 mL) solution gave, after 10 days of stirring at room temperature, 2′,4′-di-(1,1-dimethylethylthio)-1-naphthylamine **3aa** in 87% yield (Scheme 1).

Investigation of the reaction in different conditions (Table 1) revealed that it proceeded without BSA, although the yield was much less. Other Lewis acids did not improve the yield of product **3aa**. Protic solvents, which can sometimes be complementary to base/Lewis acid/aprotic solvent system,[10] were less effective in this case.

The reaction was found to be general character for different alkyl or aryl thiols, and active bicyclic nitroarenes provided they possess two hydrogen atoms (to be replaced by two thiolate substituents) accessible for nucleophilic displacement (Table 2).

Reactions proceeded smoothly with hindered tertiary and



1a - d **2a - h** **3aa - dc** **4ab - dc**

Scheme 1.

Keywords: bicyclic aromatic compounds; thiols; substitution; reduction; amines.
E-mail: wrobel@icho.edu.pl

0040–4020/03/$ - see front matter
PII: S0040-4020(02)01454-0

Table 1. Reaction of nitronaphthalene **1a** with *t*-butylthiol **2a** in various conditions

Entry	Base	Lewis acid (LA)	LA (equiv.)	Solvent	Temperature (°C)	Time[a]	Yield[b] (%)
1	DBU	BSA	2.5	DMF	Room temperature	10	87
2	DBU	–	–	DMF	Room temperature	20	23
3	DBU	–	–	DMF	70	4	43
4	DBU	*t*-BuMe$_2$SiCl	2.5	DMF	Room temperature	30	38
5	DBU	$MgCl_2$	0.625	DMF	Room temperature	60	41
6	Et_3N	Me_3SiCl	5.0	DMF	60	4	49
7	Et_3N	Ti(O-*i*-Pr)$_4$	2.5	MeCN	Room temperature	6	–
8	DBU	$MgCl_2$	0.625	DMSO	Room temperature	14	45
9	NaOH	–	–	MeOH	Room temperature	10	59

[a] Days.
[b] Isolated.

Table 2. Reactions of bicyclic nitroarenes **1** with thiols **2** in DBU/BSA/DMF system

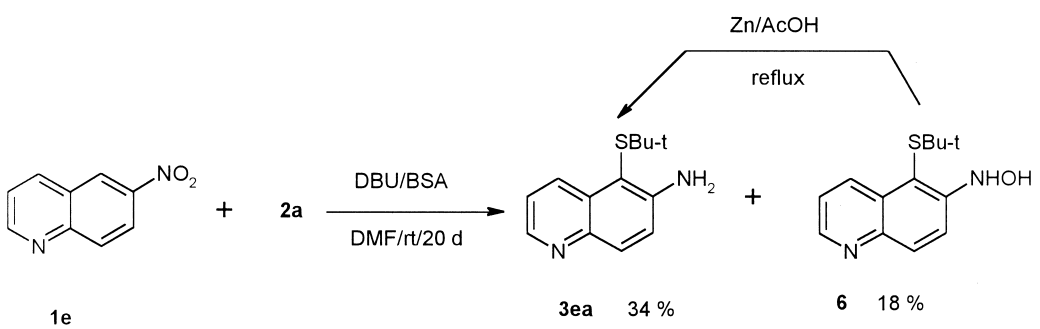
Entry	Reactants	X	Y	W	R	Time[a]	Products			
							3	Yield[b] (%)	**4**	Yield[b] (%)
1	**1a**+**2a**	CH	CH	CH	*t*-Bu	10	**3aa**	87	–	–
2	**1a**+**2b**	CH	CH	CH	*i*-Bu	10	**3ab**	65	**4ab**	Tr
3	**1a**+**2c**	CH	CH	CH	*n*-Bu	6	**3ac**	52	**4ac**	19
4	**1a**+**2d**	CH	CH	CH	Et	14	**3ad**	22	**4ad**	37
5	**1a**+**2e**	CH	CH	CH	Allyl	14	**3ae**	22	**4ae**	60
6	**1a**+**2f**	CH	CH	CH	4-ClC_6H_4	20	**3af**	59	–	–[c]
7	**1a**+**2g**	CH	CH	CH	4-MeC_6H_4	14	**3ag**	80	–	–[c]
8	**1a**+**2h**	CH	CH	CH	PhCH_2	30	**3ah**	25	**4ah**	27[c]
9	**1b**+**2a**	N	CH	CH	*t*-Bu	4	**3ba**	96	–	–
10	**1b**+**2b**	N	CH	CH	*i*-Bu	4	**3bb**	77	**4bb**	Tr
11	**1b**+**2c**	N	CH	CH	*n*-Bu	6	**3bc**	32	**4bc**	33
12	**1b**+**2e**	N	CH	CH	Allyl	3	**3be**	28	**4be**	47
13	**1b**+**2f**	N	CH	CH	4-ClC_6H_4	12	**3bf**	64	–	–[c]
14	**1c**+**2a**	CH	N	CH	*t*-Bu	2	**3ca**	54	–	–
15	**1d**+**2a**	CH	CH	N	*t*-Bu	6	**3da**	50	–	–
16	**1d**+**2c**	CH	CH	N	*n*-Bu	30	**3dc**	24	**4dc**	16

[a] Days.
[b] Isolated.
[c] Corresponding disulphide **5** isolated as a byproduct.

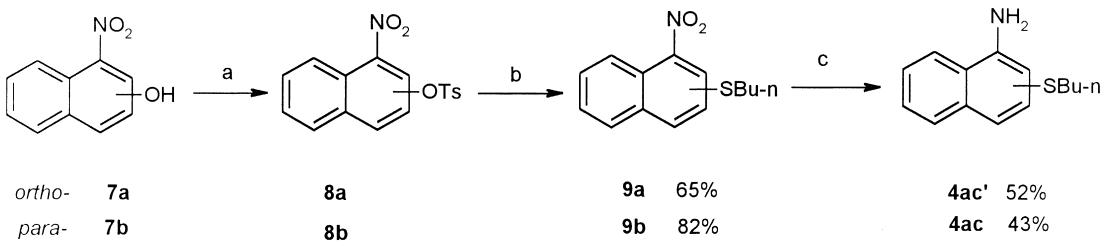
secondary alkylthiols or arylthiols. Interestingly, with less hindered primary alkylthiols it led to a mixture of di- (**3**) and mono- (**4**) thioalkylated products. The latter ones were comparatively unstable and darkened very quickly so in some cases correct elemental analysis was impossible to obtain. Reaction of **2a** with 6-nitroquinoline which has only one hydrogen atom (in position 5-) susceptible to aromatic nucleophilic substitution led to a mixture of amine **4ea** and hydroxylamine **6** (Scheme 2).

The position of the thioalkyl substituent in **4ac** was unambiguously elucidated by independent synthesis of **4ac** and its *ortho*-analog **4ac′** (Scheme 3).

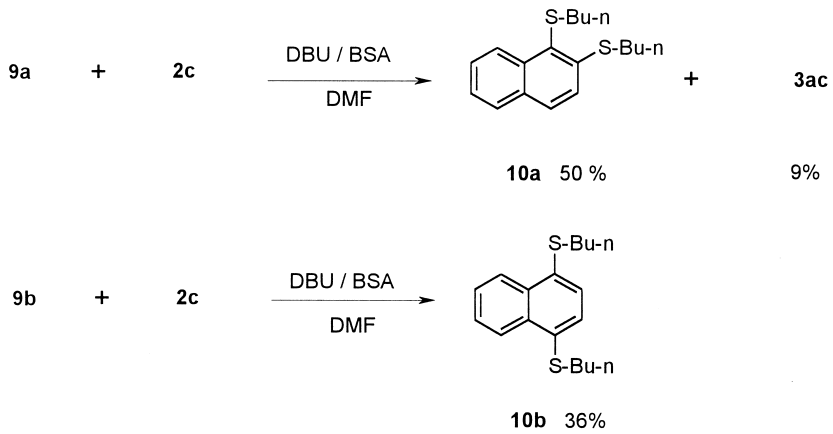
For other aminothiols **4**, the position of the thioalkyl substituent was assumed to be *para*- as in the case of **4ac**. The mechanism of the reaction was not clear. Kawakami and Suzuki showed that direct oxidative thioalkylation and dithioalkylation of various nitroquinolines with alkyl thiols in NaH/THF/−10°C system were very fast processes.[6] Thus, one could expect a similar pathway in our DBU/BSA/DMF/room temperature system with the modification that,



Scheme 2.



Scheme 3. (a) TsCI/DIPEA/DCM; (b) *n*-BuSH/K_2CO_3/DMF; (c) $SnCI_2$/AcOEt-EtOH.



Scheme 4.

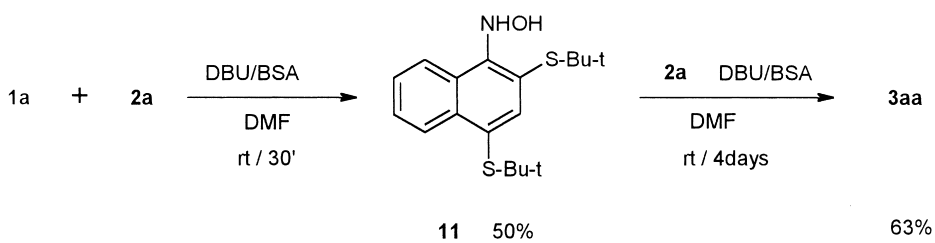
in the presence of an excess of the thiolate anion, reduction of the nitro-group to the amine could occur, thus terminating the reaction. This possibility was ruled by in experiment in which 1-butylthio-4-nitronaphthalenes **9a** and **9b** were allowed to react with thiol **2c** in standard reaction conditions (Scheme 4).

Neither **3ac** nor **4ac** were detected among the reaction products for **9b** as a substrate whereas for **9a** only small amount of **3ac** was isolated. The main products in both cases were bissulphides **10a** and **10b** resulting from the substitution of the nitro group with the *n*-butylthiolate anion. Such type of nitro-thiolate replacement although not completely clear has already been found.[6]

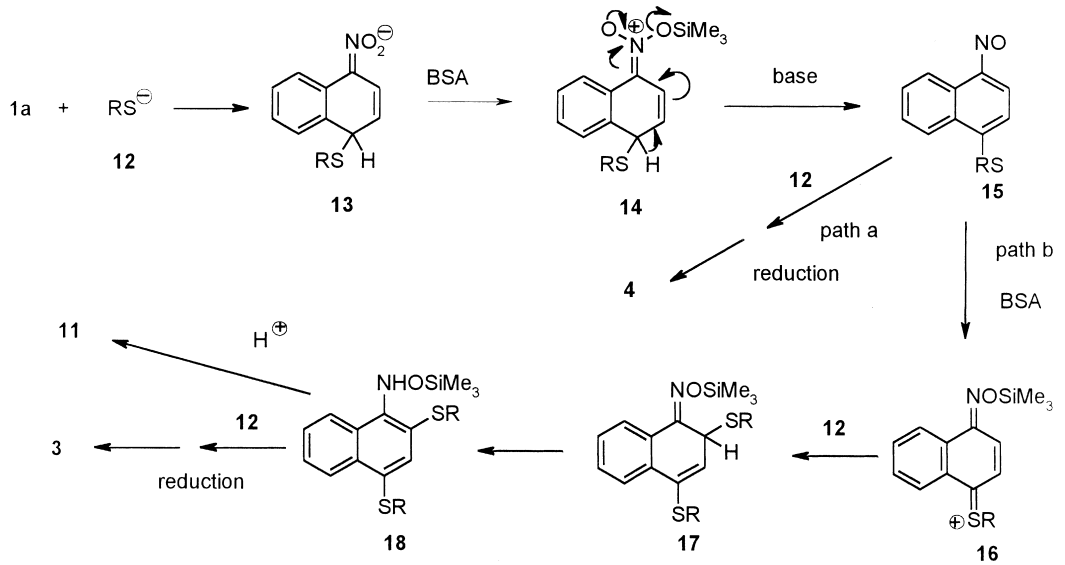
Following of the progress of the reaction of **1a** with **2a** carefully, revealed comparatively fast disappearance of the substrate **1a**, but rather slow formation of the terminal product **3aa**. Tlc analysis showed formation of an intermediate slightly more polar than **1a** in hexane–ethyl acetate (8:1) solvent system. This intermediate underwent destruction during column chromatography. It was isolated via crystallisation from the reaction mixture in about 50% yield when the reaction was arrested after 30 min, and turned out to be 2′,4′-di-(1,1-dimethyletylthio)-1-hydroxyl-aminonaphthalene **11**. This in turn could be converted to **3aa** under standard reaction conditions (Scheme 5).

These results can be rationalized on the basis of the reaction pathway shown in Scheme 6.

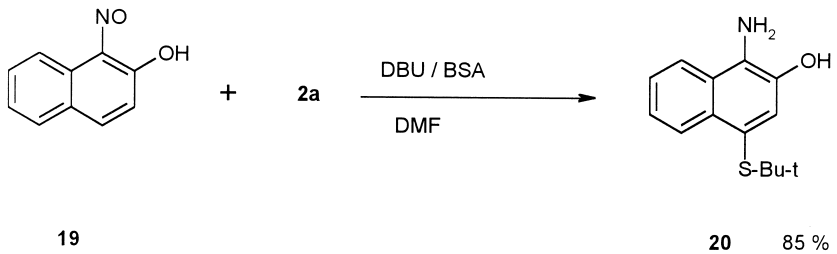
The thiolate anion **12** and nitroarene **1** form the Meisenheimer complex **13** directly, or via an electron transfer-recombination of a radical/anion two step sequence.[6] Adduct **13** is converted to the nitroso compound **15** probably via sililated derivative **14**.[7–12] Nitroso compound **15** can be reduced to **4** in a multistage way, including formation of *N*-hydroxysulfenamide and thiolytic cleavage of the N–S bond[13] (path a). In some cases, disulphides **5** were isolated from reaction mixtures. Alternatively nitroso compound **15** can be converted to a strongly electrophilic sulfenamide cation[13] which may rearrange to **3**, but more probably under action of silylating agent **15** is converted to quinoid-type oxime derivative **16**. This in turn undergoes



Scheme 5.



Scheme 6.



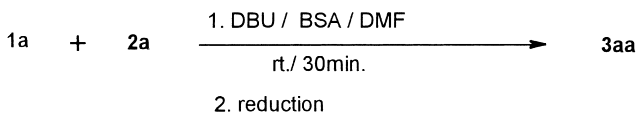
Scheme 7.

the second addition of **12** to form adduct **17** which, after silylation isomerises to hydroxylamine derivative **18** (isolated after quenching with water as deprotected **11**).

Instead of addition to the aromatic ring to form **16** and ultimately **3**, the nitroso derivative **15** can be reduced to amine **4**. It seems that addition prevailed in the case of tertiary thiolates, whereas less hindered primary ones cause the reduction as well.

It should be mentioned that the initial addition of anion **12** to the nitro compound **1** could occur both on *ortho*- and *para*-position. For clarity, only *para*-pathway was shown, leading to isomers *para*- of **13**, **14**, **15** and **16**. It seems obvious that **4** could be formed only from para- substituted nitroso compound **15**. On the other hand bis-substituted **3** could be formed by successive addition of two thiolates to *ortho*- then to *para*-position or vice versa.

Hypothesis of the presence of nitroso compound as an intermediate was supported by the reaction of stable commercial 1-nitroso-2-naphthol **19** with thiol **2a** under standard reaction conditions, in which 1′-amino-2′-hydroxy-4′-(1,1-dimethylethylthio)naphthalene was formed in 85% yield (Scheme 7).



Scheme 8. *Reduction conditions*: (a) $Na_2S_2O_4$ (10 eq.)/aq. $NaHCO_3$/60°C/3h 56%; (b) Zn (10 eq.)/AcOH/reflux/30′ 54%.

It appears to be analogous to the known reaction of **19** with sodium hydrogen sulphite, leading to sodium 1-amino-2-hydroxy-4-sulphonate[14–16] via substitution of hydrogen and reduction steps and most probably via an *ortho*-benzoquinone oxime intermediate.[17]

Reduction steps terminating the sequence and leading to amine **3** are rather vague. They may consist of silylation and electron transfer processes with thiolate anion **12** as an electron donor.[1]

In order to improve the yield of **3aa** and economize on the reaction time, some other 'external' reducing agents were tried to convert the crude reaction mixture after formation of **18** (or **11**) to final product **3aa** (Scheme 8).

In both cases, reaction can be completed very quickly but the yields were substantially lower when compared with the standard procedure.

3. Experimental

Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 400 MHz in $CDCl_3$ solution unless otherwise stated in reference to TMS. Chemical shifts were expressed in ppm, coupling constants

in hertz. Mass spectra were obtained on ADM-604. IR spectra were done on Spectrum 2000. Column chromatography was performed on silica gel 240–400 mesh with hexane-ethyl acetate mixtures as eluants. Nitronaphthalene, 5-, 8-nitroquinolines, 5-nitroisoquinoline and all thiols were commercially available.

3.1. Reactions of nitroarenes 1 with thiols 2 in the presence of Lewis acid: standard procedure

Nitroarene **1** (2.5 mmol), thiol **2** (12.5 mmol), and Lewis acid (for BSA: 1.6 mL; 6.25 mmol) were placed in 50 mL flask and dissolved in dry DMF (20 mL). The flask was immersed in a cold water bath and DBU (2.8 mL; 18.75 mmol) was added. After stoppering the flask the mixture was stirred at room temperature for the time indicated in Tables 1 and 2. The progress of the reaction was followed by tlc. After completion of the reaction the mixture was treated with satd aq. $NaHCO_3$ solution (20 mL), and argon was bubbled through the mixture (outlet connected to the bubbler with aq. chloramine T solution) to remove most odour and volatile substances. The residue was diluted with satd $NaHCO_3$ solution (100 mL) and extracted with ethyl acetate (3×50 mL), extracts were dried ($MgSO_4$), concentrated and the residue chromatographed using hexane–ethyl acetate mixtures as eluants. Products isolated are referred in Table 2 and Scheme 2.

3.1.1. Reaction of nitronaphthalene 1a with 1,1-dimethylethylthiol 2a (entry 1). Amino-2′,4′-di-(1,1-dimethylethylthio)naphthalene; **3aa**: 694 mg (87%). Yellow crystals; mp 98–100°C (AcOEt–hexane); δ_H=1.28 (s, 9H), 1.36 (s, 9H), 5.32 (broad s, 2H), 7.52 (ddd, *J*=8.4, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J*=8.4, 6.8, 1.4 Hz, 1H), 7.81 (ddd, *J*=8.4, 1.4, 0.6 Hz, 1H), 7.85 (s, 1H), 8.70 (ddd, *J*=8.4, 1.4, 0.6 Hz, 1H); δ_C=148.6, 147.3, 137.9, 128.2, 127.0, 125.2, 123.4, 121.8, 117.8, 109.5, 48.8, 47.3, 31.2, 31.1; ν_{max} (KBr): 3449.7, 3340.2, 2967.3, 1597.9, 1416.5, 1360.8, 1167.4, 756.8; *m/z* (%): 320 (5.2), 319 (24.1), 263 (14.7), 209 (9.5), 208 (13.9), 207 (100.0), 206 (15.9), 175 (6.2), 174 (33.4). Anal. calcd for $C_{18}H_{25}NS_2$ [319.53]: C, 67.66; H, 7.89; N, 4.35%; found: C, 67.81; H, 8.13; N, 4.36%.

3.1.2. Reaction of nitronaphthalene 1a with 1-methylpropylthiol 2a (entry 2). Amino-2′,4′-di-(1-methylpropylthio)naphthalene; **3ab**: 520 mg (65%). yellow oil. δ_H= 0.99–1.04 (m, 6H), 1.17–1.20 (m, 3H), 1.22–1.24 (d, *J*= 6.8 Hz, 3H), 1.44–1.56 (m, 2H), 1.58–1.70 (m, 2H), 2.95–3.01 (m, 1H), 3.02–3.09 (m, 1H), 5.10 (broad s, 2H), 7.47–7.52 (m, 1H), 7.55–7.59 (m, 1H), 7.76–7.83 (m, 2H), 7.81 (s, 1H), 8.54–8.59 (m, 1H); ν_{max} (KBr): 3469.5, 3361.3, 2964.1, 2922.9, 2873.6, 1601.7, 1496.9, 1453.1, 1416.1, 1377.7, 1362.8, 1224.8, 1147.9, 757.5; *m/z* (%): 321 (10.8), 320 (21.3), 319 (100.0), 318 (6.7), 317 (27.4), 288 (15.4), 263 (27.8), 262 (36.9), 260 (6.2), 232 (12.2), 231 (6.8), 208 (6.5), 207 (20.6), 206 (25.4). Anal. calcd for $C_{18}H_{25}NS_2$ [319.53]: C, 67.66; H, 7.89; N, 4.38; S, 20.01%; found: C, 67.65; H, 7.59; N, 4.64; S, 20.0%. Traces (11 mg; <1%) of amino-4′-(1-methylpropylthio)naphthalene; **4ab**: yellow oil. δ_H=0.99 (t, *J*=7.4 Hz, 3H), 1.19 (d, *J*=6.8 Hz, 3H), 1.43–1.53 (m, 2H), 1.58–1.68 (m, 2H), 2.98 (m, 1H), 4.25 (broad s, 2H), 6.72 (d, *J*=7.8 Hz, 1H), 7.48 (ddd, *J*=8.2, 6.8, 1.3 Hz, 1H), 7.56 (ddd, *J*=8.4, 6.8, 1.3 Hz, 1H), 7.59 (d, *J*=7.8 Hz, 1H), 7.82 (ddd, *J*=8.2, 1.3, 0.7 Hz, 1H), 8.61 (ddd, *J*=8.4, 1.3, 0.7 Hz, 1H); δ_C=143.1, 136.0, 135.8, 127.2, 126.5, 125.0, 124.2, 121.1, 120.6, 109.3, 46.3, 29.6, 20.4, 11.4; ν_{max} (KBr): 3468.1, 3379.7, 3233.7, 2963.5, 2923.5, 2873.0, 1621.9, 1584.2, 1511.5, 1456.4, 1386.4, 1358.2, 1338.2, 1279.8, 824.1, 758.3; *m/z* (%): 232 (9.3), 231 (59.9), 177 (4.5), 176 (13.1), 175 (100.0), 174 (50.1), 143 (22.1), 130 (21.2); HRMS calcd for $C_{14}H_{17}NS$: [231.1082]; found: 231.1080.

3.1.3. Reaction of nitronaphthalene1a with *n*-butylthiol 2c (entry 3). Amino-2′,4′-di-(1-butylthio)-naphthalene; **3ac**: 415 mg (52%). Dark yellow oil. δ_H=0.87 (t, *J*= 7.3 Hz, 3H), 0.88 (t, *J*=7.3 Hz, 3H), 1.36–1.46 (m, 4H), 1.50–1.58 (m, 4H), 2.76–2.81 (m, 4H), 5.1 (broad s, 2H), 7.50 (ddd, *J*=8.3, 6.8, 1.3 Hz, 1H), 7.57 (ddd, *J*=8.3, 6.8, 1.3 Hz, 1H), 7.78 (s, 1H), 7.83 (ddd, *J*=8.3, 1.3, 0.6 Hz, 1H), 8.51 (ddd, *J*=8.3, 1.3, 0.6 Hz, 1H); δ_C=145.3, 139.6, 134.9, 126.9, 126.7, 125.4, 123.7, 121.8, 120.7, 111.8, 36.0, 35.2, 31.9, 31.6, 21.8, 21.7, 13.7, 13.6; ν_{max} (film): 3467.8, 3358.7, 2957.3, 2928.4, 2871.1, 1602.1, 1415.5, 1378.5, 1363.4; *m/z* (%): 320 (18.1), 319 (85.5), 264 (10.8), 263 (23.4), 262 (100.0), 206 (39.0), 174 (15.9). Anal. calcd for $C_{18}H_{25}NS_2$ [319.53]: C, 67.66; H, 7.89; N, 4.38%; found: C, 67.52; H, 7.75; N, 4.39%. Amino-4′-(1-butylthio)-naphthalene; **4ac**: 110 mg (19%). Dark yellow oil. δ_H= 0.86 (t, *J*=7.2 Hz, 3H), 1.36–1.45 (m, 2H), 1.49–1.57 (m, 2H), 2.79 (t, *J*=7.2 Hz, 2H), 4.21 (broad s, 2H), 6.72 (d, *J*=7.9 Hz, 1H), 7.49 (ddd, *J*=8.3, 6.8, 1.4 Hz, 1H), 7.55 (ddd, *J*=8.3, 6.8, 1.4 Hz, 1H), 7.56 (d, *J*=7.9 Hz, 1H), 7.81 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H), 8.55 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H); δ_C=142.7, 135.0, 133.7, 126.7, 126.5, 125.0, 124.3, 121.6, 121.2, 109.4, 36.1, 31.6, 21.8, 13.7; ν_{max} (film): 3466.4, 3378.7, 2957.0, 2928.5, 2870.6, 1621.8, 1584.3, 1511.6, 1456.4, 1435.0, 1338.5, 1278.9, 823.0, 758.0; *m/z* (%): 232 (9.7), 231 (59.5), 175 (27.7), 174 (100.0), 143 (13.7), 130 (19.6); HRMS: calcd for $C_{14}H_{17}NS$: [231.1082]; found: 231.1076.

3.1.4. Reaction of nitronaphthalene 1a with ethylthiol 2d (entry 4). Amino-2′,4′-diethylthionaphthalene; **3ad**: 145 mg (22%); Dark yellow oil. δ_H=1.21 (t, *J*=7.3 Hz, 3H), 1.23 (t, *J*=7.3 Hz, 3H), 2.78–2.84 (m, 4H), 5.20 (broad s, 1H), 7.48–7.52 (m, 1H), 7.55–7.59 (m, 1H), 7.80 (s, 1H), 7.82 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H), 8.51 (ddd, *J*=8.2, 1.3, 0.6 Hz, 1H); ^{13}C: δ=145.6, 140.0 135.0, 127.0, 126.7, 125.5, 123.7, 121.8, 120.2, 111.3, 30.2, 29.5, 15.1, 14.7; ν_{max} (film): 3464.7, 3356.8, 2972.0, 2924.0, 2867.4, 1602.3, 1497.1, 1415.5, 1377.5, 1363.8, 1259.8, 756.1; *m/z* (%): 265 (6.8), 264 (11.8), 263 (71.6), 236 (9.4), 235 (14.8), 234 (100.0), 206 (11.5), 205 (8.0), 203 (10.3), 202 (17.9), 201 (3.9), 200 (5.6), 190 (9.4), 174 (14.0), 173 (4.3). Anal. calcd for $C_{14}H_{17}NS_2$: [263.43]: C, 63.83; H, 6.50; N, 5.32; S, 24.35%; found: C, 63.97; H, 6.66; N, 5.34; S, 24.27%. Amino-4′-ethylthionaphthalene; **4ad**: 188 mg (37%). Dark yellow oil; δ_H=1.19 (t, *J*=7.4 Hz, 3H), 2.80 (q, *J*=7.4 Hz, 2H), 4.20 (broad s, 2H), 6.70 (d, *J*=7.8 Hz, 1H), 7.45–7.49 (m, 1H), 7.53–7.58 (m, 1H), 7.57 (d, *J*=7.8 Hz, 1H), 7.81 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H), 8.54 (ddd, *J*=8.6, 1.3, 0.6 Hz, 1H); δ_C=142.9, 135.1, 134.0, 126.7, 126.5, 125.0, 124.2, 121.2, 121.0, 109.3, 30.2, 14.8; ν_{max} (film): 3461.6, 3374.8, 2971.8, 2924.2, 2866.5, 1622.0, 1584.5, 1511.6, 1435.2, 1359.0, 1338.6, 1280.7, 1259.4, 823.7, 757.4; *m/z* (%): 203

(8.5), 174 (15.0), 144 (10.7), 143 (100.0), 142 (4.9), 116 (17.4), 115 (30.4); HRMS: calcd for $C_{12}H_{13}NS$: [203.0769]; found: 203.0769.

3.1.5. Reaction of nitronaphthalene 1a with allylthiol 2e (entry 5). Amino-2′,4′-diallylthionaphthalene; **3ae**: 158 mg (22%). Dark yellow oil. δ_H=3.38–3.42 (m, 4H), 4.81–4.95 (m, 4H), 5.12 (broad s, 2H), 5.78–5.90 (m, 2H), 7.48–7.52 (m, 1H), 7.56–7.60 (m, 1H), 7.74 (s, 1H), 7.80–7.83 (m, 1H), 8.50–8.52 (m, 1H); ν_{max} (film): 3467.6, 3359.6, 3078.0, 2977.6, 2914.9, 1602.5, 1497.3, 1416.4, 1379.0, 1364.2, 1225.1, 987.4, 917.8, 756.4; *m/z* (%): 289 (5.4), 288 (9.8), 287 (56.8), 248 (8.9), 247 (16.5), 256 (100.0), 214 (8.9), 213 (56.2), 212 (5.2), 207 (5.0), 206 (8.5), 205 (51.4), 204 (5.1), 200 (12.7), 199 (6.8), 180 (11.3), 161 (21.4). Anal. calcd for $C_{16}H_{17}NS_2$ [287.45]: C, 66.86; H, 5.96; N, 4.87; S, 22.31%; found: C, 66.81; N, 6.12; N, 5.01; S, 22.19%. Amino-4′-allylthionaphthalene; **4ae**: 320 mg (60%). Dark yellow oil. δ_H=3.40 (ddd, *J*=7.3, 1.4, 0.9 Hz, 2H), 4.24 (broad s, 2H), 4.83 (ddt, *J*=17.0, 2.8, 1.4 Hz, 1H), 4.91 (ddt, *J*=9.9, 2.8, 0.9 Hz, 1H), 5.85 (ddt, *J*=17.0, 9.9, 7.3 Hz, 1H), 6.70 (d, *J*=7.7 Hz, 1H), 7.47–7.51 (m, 1H), 7.54–7.59 (m, 1H), 7.55 (d, *J*=7.7 Hz, 1H), 7.81 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H), 8.55 (dd, *J*=8.4, 1.3, 0.6 Hz, 1H); δ_C=143.1, 135.2, 134.8, 134.2, 126.7, 126.6, 125.0, 124.2, 121.2, 120.4, 117.0, 109.3, 39.6; ν_{max} (film): 3465.9, 3379.0, 3233.5, 3079.2, 2912.4, 1621.7, 1583.9, 1511.3, 1456.4, 1434.7, 1387.2, 1359.4, 1280.8, 918.7, 822.4, 757.7; *m/z* (%): 216 (3.3), 251 (23.0), 176 (4.2), 175 (10.6), 174 (100.0); HRMS: calcd for $C_{13}H_{13}NS$: [215.0769]; found: 215.0761.

3.1.6. Reaction of nitronaphthalene 1a with 4-chlorothiophenol 2f (entry 6). Amino-2′,4′-di-(4”-chlorophenylthio)naphthalene; **3af**: 631 mg (59%). Yellow crystals; mp 135–138°C (AcOEt). δ_H=5.27 (broad s, 2H), 6.94 (AA′ part of the 1st AA′XX′ system, 2H), 7.02 (AA′ part of the 2nd AA′XX′ system, 2H), 7.11 (XX′ part of the 1st AA′XX′ system, 2H), 7.18 (XX′ part of the 2nd AA′XX′ system, 2H), 7.52–7.59 (m, 2H), 7.85–7.87 (m, 1H), 7.93 (s, 1H), 8.32–8.35 (m, 1H); δ_C=147.9, 143.1, 137.6, 135.8, 134.9, 131.6, 130.9, 129.2, 128.9, 128.5, 127.7, 127.6, 126.9, 126.1, 123.7, 122.0, 116.9, 107.5; ν_{max} (KBr): 3480.1, 3366.6, 1601.3, 1494.3, 1473.7, 1420.1, 1381.5, 1364.5, 1089.9, 1008.1, 812.2, 757.7; *m/z* (%): 430 (18.1), 430 (18.8), 429 (75.3), 428 (26.2), 427 (100.0), 286 (33.2), 285 (21.4), 284 (90.6), 283 (12.3), 249 (21.8), 240 (27.5). Anal. calcd for $C_{22}H_{15}NS_2Cl_2$ [428.29]: C, 61.75; H, 3.53; N, 3.27%; found: C, 61.54; H, 3.49; N, 3.13%. 4-Chlorophenyl disulphide; **5f** (300 mg) also isolated and identified by means of ms spectrum: *m/z* (%): 290 (10.0), 289 (6.3), 288 (49.4), 287 (8.9), 286 (70.0), 224 (6.2), 222 (9.6), 145 (37.9), 144 (13.2), 143 (100.0); HRMS: calcd for $C_{12}H_8^{35}Cl_2S_2$: [285.9445]; found: 285.9457.

3.1.7. Reaction of nitronaphthalene 1a with 4-methylthiophenol 2g (entry 7). Amino-2′,4′-di-(4″-methylphenylthio)naphthalene; **3ag**: 770 mg (80%). light pink solid; mp 107–110°C (AcOEt–hexane). δ_H=2.24 (s, 3H), 2.29 (s, 3H), 6.98 (s, 4H), 7.04 (s, 4H), 7.47–7.55 (m, 2H), 7.81–7.85 (m, 1H), 7.94 (s 1H), 8.38–8.40 (m, 1H); δ_C=147.2, 142.7, 135.7, 135.6, 135.3, 134.9, 132.8, 129.8, 129.6, 127.9, 127.1, 127.0, 126.9, 125.8, 123.8, 121.8, 117.9, 108.9, 20.9, 20.8; ν_{max} (KBr): 3468.4, 3352.7, 3016.6, 2914.7, 1603.0, 1491.1, 1418.8, 1364.9, 1981.9, 1013.9, 801.6, 757.0, 676.7; *m/z* (%): 389 (11.8), 388 (24.7), 387 (100.0), 266 (3.8), 265 (12.6), 264 (63.5), 263 (11.1), 262 (4.2), 221 (4.2), 220 (16.7). Anal. calcd for $C_{24}H_{21}NS_2$: [387.57]: C, 74.38; H, 5.46; N, 3.61; S, 16.55%; found: C, 74.22; H, 5.27; N, 3.61; S, 16.46%; first fraction from column chromatography contained excess of **2g** together with its dimer 4-methylphenyldisulphide **5g**: *m/z* (%): 248 (9.2), 247 (14.9), 246 (92.7), 182 (11.1), 125 (5.5), 124 (17.4), 123 (100.0), 122 (7.6), 121 (8.2).

3.1.8. Reaction of nitronaphthalene 1a with benzylthiol 2h (entry 8). Amino-2′,4′-di-(phenylmethylthio)naphthalene; **3ah**: 240 mg (25%). yellow oil; δ_H=3.80 (s, 2H), 3.88 (s, 2H), 4.92 (broad s, 2H), 7.05–7.11 (m, 4H), 7.15–7.22 (m, 6H), 7.45–7.50 (m, 1H), 7.46 (s, 1H), 7.52–7.57 (m, 1H), 7.75 (ddd, *J*=8.2, 1.3, 0.6 Hz, 1H), 8.46 (ddd, *J*=8.4, 1.3, 0.6 Hz, 1H); δ_C=146.4, 141.2, 138.2, 138.2, 135.2, 129.0, 128.8, 128.4, 128.3, 127.2, 127.1, 126.9, 126.6, 125.4, 123.5, 121.9, 119.8, 110.9, 41.2, 40.4; ν_{max} (KBr): 3416.8, 3332.2 3025.0, 2927.2, 1601.2, 1492.6, 1450.8, 1410.5, 1373.8, 1225.4, 1026.9, 772.4, 757.6, 696.9; *m/z* (%): 389 (4.1), 388 (9.7), 397 (34.9), 298 (6.9), 297 (13.3), 296 (62.0), 205 (3.9), 91 (100.0). Anal. calcd for $C_{24}H_{21}NS_2$: [387.57]: C, 74.38; H, 5.46; N, 3.61; S, 16.55%; found: C, 73.83; H, 5.47; N, 3.61; S, 16.33%. Amino-4′-phenylmethylthionaphthalene; **4ah**: 179 mg (27%). Dark yellow oil. δ_H=3.94 (s, 2H), 4.23 (broad s, 2H), 6.63 (d, *J*=7.8 Hz, 1H), 7.07–7.10 (m, 2H), 7.14–7.22 (m, 3H), 7.37 (d, *J*=7.8 Hz, 1H), 7.48 (ddd, *J*=8.2, 6.7, 1.4 Hz, 1H), 7.54 (ddd, *J*=8.4, 6.7, 1.4 Hz, 1H), 7.82 (ddd, *J*=8.2, 1.4, 0.6 Hz, 1H), 8.53 (ddd, *J*=8.4, 1.4, 0.6 Hz, 1H); δ_C=143.2, 138.4, 135.1, 134.9, 128.9, 128.3, 126.8, 126.7, 126.6, 125.0, 124.2, 121.2, 120.6, 109.3, 41.3; ν_{max} (film):3468.0, 3381.7, 3233.1, 3059.2, 3027.5, 2920.5, 1621.5, 1583.2, 1511.3, 1454.7, 1434.9, 1387.2, 1359.8, 1339.2, 1281.2, 822.5, 757.7, 699.1; *m/z* (%): 266 (6.5), 265 (32.6), 176 (5.6), 175 (12.3), 174 (100.0), 165 (7.0), 164 (9.1), 131 (5.0), 130 (17.2), 121 (8.2); HRMS: calcd for $C_{17}H_{15}NS$: [265.0925]; found: 265.0934; first fractions from column chromatography (257 mg) consisted with mixture of benzyl mercaptan **2h** and its dimer benzyl disulphide **5h**: *m/z* (%): 247 (1.3), 246 (7.7), 214 (3.7), 181 (5.46), 92 (9.6), 91 (100.0); HRMS: calcd for $C_{14}H_{14}S_2$: [246.0537]; found: 246.0547.

3.1.9. Reaction of 5-nitroquinoline 1b with 1,1-dimethylethylthiol 2a (entry 9). 5′-Amino-6′,8′-di-(1,1-dimethylethylthio)quinoline; **3ba**: 768 mg (96%). yellow crystals; mp 149–156°C (EtOH). δ_H=1.31 (s, 9H), 1.38 (s, 9H), 5.40 (broad s, 2H), 7.39 (dd, *J*=8.5, 4.2 Hz, 1H), 8.09 (s, 1H), 8.20 (dd, *J*=8.5, 1.7 Hz, 1H), 9.06 (dd, *J*=4.2, 1.7 Hz, 1H); δ_C=151.0, 150.2, 148.7, 130.5, 120.0, 119.8, 118.5, 110.2, 49.1, 47.2, 31.2, 31.1; *m/z* (%): 320 (17.7), 264 (18.4), 210 (10.0), 209 (15.0), 208 (100.0), 207 (13.4), 175 (20.2), 163 (10.7); ν_{max} (KBr): 3328.7, 2957.5, 1618.1, 1558.1, 1362.3, 1341.4, 1162.7, 782.8. Anal. calcd for $C_{17}H_{24}N_2S_2$ [320.52]: C, 63.70, H, 7.55; N, 8.74; S, 20.01%; found: C, 63.53; H, 7.55; N, 8.65; S, 20.33%.

3.1.10. Reaction of 5-nitroquinoline 1b with 2-methylpropylthiol 2a (entry 10). 5′-Amino-6′,8′-di-(1-methylpropylthio)quinoline; **3bb**: 619 mg (77%). Light green solid;

mp 79–81°C (aq. EtOH); (main rotamer). δ_H=1.02 (t, J=7.3 Hz, 3H), 1.04 (t, J=7.3 Hz, 3H), 1.25 (d, J=6.8 Hz, 3H), 1.30 (dd, J=6.8, 1.6 Hz, 3H), 1.50–1.80 (m, 4H), 3.01–3.11 (m, 1H), 3.39–3.57 (m, 1H), 5.04 (broad s, 2H), 7.40 (dd, J=8.4, 4.0 Hz, 1H), 7.75 (d, J=0.9 Hz, 1H), 8.16 (dd, J=8.4, 1.7 Hz, 1H), 8.97 (dd, J=4.0, 1.7 Hz, 1H); ν_{max} (KBr): 3409.1, 3295.0, 3172.8, 2961.8, 2921.9, 1624.5, 1592.8, 1561.6, 1486.7, 1448.0, 1373.0, 1346.1, 857.9, 773.8; *m/z* (%): 322 (5.0), 321 (9.5), 320 (44.6), 319 (4.8), 318 (17.3), 289 (9.5), 288 (21.0), 287 (100.0), 286 (8.9), 285 (43.4), 264 (15.0), 263 (5.1), 234 (4.3), 233 (21.9), 232 (7.7), 231 (21.6), 230 (8.2), 229 (3.4), 209 (8.8), 208 (53.7), 207 (27.6), 201 (5.4), 177 (4.8), 176 (24.3), 175 (43.0), 174 (9.1), 173 (6.4), 163 (26.4). Anal. calcd for $C_{17}H_{24}N_2S_2$: [320.52]: C, 63.70; H, 7.55; N, 8.74; S, 20.01%; found: C, 63.63; H, 7.33; N, 8.62; S, 19.73%. 5′-Amino-8′-(1-methylpropylthio)quinoline; **4bb**: 12 mg (<1%). Dark yellow oil. δ_H=1.02 (t, J=7.4 Hz, 3H), 1.30 (d, J=6.6 Hz, 3H), 1.52–1.62 (m, 1H), 1.70–1.78 (m, 1H), 3.40–3.48 (m, 1H), 6.79 (d, J=7.9 Hz, 1H), 7.39 (dd, J=8.5, 4.2 Hz, 1H), 7.55 (d, J=7.9 Hz, 1H), 8.17 (dd, J=8.5, 1.6 Hz, 1H), 8.98 (dd, J=4.2, 1.6 Hz, 1H); δ_C=149.7, 147.9, 141.2, 131.9, 129.9, 124.7, 119.8, 119.5, 119.2, 42.7, 29.4, 20.0, 11.4; ν_{max} (KBr): 3341.0, 3232.6, 2963.7, 2926.0, 2872.6, 1630.5, 1598.5, 1586.9, 1562.3, 1505.7, 1458.5, 1419.4, 1378.5, 1323.0, 1017.5, 813.7, 779.6; *m/z* (%): 233 (5.8), 232 (34.0), 271 (3.4), 203 (5.6), 200 (10.1), 199 (69.4), 178 (4.9), 177 (13.2), 176 (100.0), 175 (23.7), 144 (31.9); HRMS: calcd for $C_{13}H_{16}N_2S$: [232.1034]; found: 232.1042.

3.1.11. Reaction of 5-nitroquinoline 1b with *n*-butylthiol 2c (entry 11). 5′-Amino-6′,8′-di-(1-butylthio)quinoline; **3bc**: 256 mg (32%). Yellow oil. δ_H=0.88 (q as a superposition of two t, J=7.3 Hz, 6H), 1.37–1.45 (m, 4H), 1.50–1.60 (m, 4H), 2.81–2.87 (m, 4H), 5.07 (broad s, 2H), 7.55 (dd, J=6.0, 1.0 Hz, 1H), 7.80 (s, 1H), 8.57 (d, J=6.0 Hz, 1H), 9.83 (d, J=1.0 Hz, 1H); δ_H=149.7, 146.9, 142.9, 134.5, 130.4, 125.5, 120.3, 118.9, 113.3, 35.3, 32.2, 31.9, 30.8, 22.1, 21.8, 13.7, 13.6; ν_{max} (film): 3438.4, 3339.1, 2957.1, 2928.6, 2870.9, 1608.3, 1561.9, 1484.1, 1450.8, 1401.5, 1387.1, 1353.4, 1222.1, 779.0; *m/z* (%): 322 (4.4), 321 (9.0), 320 (40.5), 291 (8.2), 289 (5.9), 288 (20.4), 287 (100.0), 264 (9.2), 246 (4.6), 245 (23.9), 231 (5.3), 230 (17.2), 208 (3.7), 207 (10.2), 189 (8.0), 188 (5.3). Anal. calcd for $C_{17}H_{24}N_2S_2$ [320.52]: C, 63.70, H, 7.55; N, 8.74; S, 20.01%; found: C, 63.6; H, 7.52; N, 8.68; S, 20.05%. 5′-Amino-8′-(1-butylthio)quinoline; **4bc**: 191 mg (33%). Dark yellow crystals; mp 98–100°C (AcOEt–hexane). δ_H=0.92 (t, J=7.4 Hz, 3H), 1.45–1.54 (m, 2H), 1.65–1.74 (m, 2H), 3.00 (t, J=7.4 Hz, 2H), 4.11 (broad s, 2H), 6.79 (d, J=7.9 Hz, 1H), 7.39 (dd, J=8.5, 4.2 Hz, 1H), 7.42 (d, J=7.9 Hz, 1H), 8.17 (dd, J=8.5, 1.7 Hz, 1H), 8.96 (dd, J=4.2, 1.7 Hz, 1H); δ_C=149.5, 146.9, 140.3, 129.9, 128.4, 126.3, 120.0, 119.6, 110.4, 32.1, 30.8, 22.2, 13.7; ν_{max} (KBr): 3441.7, 3335.5, 3216.8, 2950.0, 2920.2, 2852.2, 1629.8, 1602.8, 1589.5, 1460.5, 1416.4, 1382.8, 1358.0, 1319.1, 1258.1, 1017.8, 806.4, 798.9, 776.9, 645.2; *m/z* (%): 233 (6.3), 232 (35.6), 203 (14.5), 200 (15.0), 199 (100.0), 189 (13.4), 188 (7.9), 17.7 (4.1), 176 (26.5), 175 (18.4); HRMS: calcd for $C_{13}H_{16}N_2S$ [232.1034]: found: 232.1037.

3.1.12. Reaction of 5-nitroquinoline 1b with allylthiol 2e (entry 12). 5′-Amino-6′,8′-di-(allylthio)quinoline; **3be**: 202 mg (28%). Yellow oil. δ_H=3.41 (dt, J=7.3, 0.9 Hz, 2H), 3.67 (dt, J=6.9, 0.9 Hz, 2H), 4.88–5.10 (m, 4H), 4.99 (broad s, 1H), 5.79–5.97 (m, 2H), 7.43 (dd, J=8.5, 4.2 Hz, 1H), 7.68 (s, 1H), 8.16 (dd, J=8.5, 1.6 Hz, 1H), 8.98 (dd, J=4.2, 1.6 Hz, 1H); δ_C=150.0, 147.5, 144.2, 137.7, 133.9, 133.6, 130.5, 123.5, 120.2, 118.8, 117.8, 117.4, 111.9, 38.6, 36.3; ν_{max} (film): 3438.6, 3342.4, 3212.9, 3078.7, 2977.0, 2914.6, 1607.5, 1563.4, 1484.8, 1402.4, 1353.3, 1224.3, 988.0, 918.2, 779.0; *m/z* (%): 290 (3.3), 289 (5.6), 288 (31.4), 257 (3.8), 256 (11.0), 255 (68.5), 247 (17.5), 216 (6.2), 215 (18.8), 214 (100.0), 213 (32.9), 206 (15.1), 182 (31.9), 181 (28.5). Anal. calcd for $C_{15}H_{16}N_2S_2$ [288.44]: C, 62.44; H, 5.59; N, 9.71; S, 22.23%; found: C, 62.35; H, 5.61; N, 9.80; S, 22.12%. 5′-Amino-8′-allylthioquinoline; **4be**: 254 mg (47%). Yellow solid; mp 80–82°C (AcOEt–hexane). δ_H=3.66 (dt, J=6.8, 1.2 Hz, 2H), 4.17 (broad s, 2H), 5.00 (ddt, J=10.1, 1.7, 1.2 Hz, 1H), 5.06 (ddt, J=17.1, 1.7, 1.2 Hz, 1H), 5.92 (ddt, J=17.1, 10.1, 6.8 Hz, 1H), 6.77 (d, J=7.9 Hz, 1H), 7.39 (dd, J=8.4, 4.0 Hz, 1H), 7.51 (d, J=7.9 Hz, 1H), 8.17 (dd, J=8.4, 1.7 Hz, 1H), 8.98 (dd, J=4.0, 1.7 Hz, 1H); δ_C=149.7, 147.4, 141.2, 134.0, 131.1, 130.0, 124.4, 119.9, 119.5, 117.3, 110.1, 36.4; ν_{max} (film from $CHCl_3$): 3438.2, 3344.2, 3232.3, 1632.9, 1600.0, 1587.4, 1563.2, 1459.6, 1419.1, 1381.2, 1357.9, 1322.7, 919.1, 811.8, 778.5; *m/z* (%): 216 (16.9), 184 (13.9), 183 (100.0), 182 (9.4), 181 (3.5), 176 (8.9), 175 (37.9), 169 (8.1), 157 (10.1); HRMS: calcd for $C_{12}H_{12}N_2S$: [216.0721]; found: 216.0723.

3.1.13. Reaction of 5-nitroquinoline 1b with 4-chlorothiophenol 2f (entry 13). 5′-Amino-6′,8′-di-(4″-chlorophenylthio)quinoline; **3bf**: 686 mg (64%). Yellow solid; mp 156–159°C (AcOEt). δ_H=5.06 (broad s, 2H), 7.00 (AA′ part of the 1st AA′XX′ system, 2H), 7.17–7.35 (m, 6H), 7.47 (dd, J=8.4, 4.2 Hz, 1H), 7.54 (s, 1H), 8.20 (dd, J=8.4, 1.4 Hz, 1H), 9.01 (dd, J=4.2, 1.7 Hz, 1H); ν_{max} (KBr): 3478.8, 3359.5, 3072.3, 1604.8, 1559.1, 1474.4, 1406.8, 1350.7, 1090.2, 101.2, 812.5, 772.4; *m/z* (%): 432 (17.6), 431 (20.0), 430 (75.6), 429 (29.4), 428 (100.0), 287 (30.3), 286 (20.7), 285 (82.4), 284 (16.5), 254 (10.7), 252 (32.4), 250 (37.3). Anal. calcd for $C_{21}H_{14}N_2S_2Cl_2$ [429.27]: C, 58.76; H, 3.29; N, 6.53%; found: C, 58.68; H, 3.58; N, 6.51%.

3.1.14. Reaction of 8-nitroquinoline 1c with 1,1-dimethylethylthiol 2a (entry 14). 8′-Amino-5′,7′-di-(1,1-dimethylethylthio)quinoline; **3ca**: 433 mg (54%). Yellow solid. δ_H=1.26 (s, 9H), 1.38 (s, 9H), 6.11 (broad s, 2H), 7.46 (dd, J=8.5, 4.2 Hz, 1H), 7.83 (s, 1H), 8.75 (dd, J=4.2, 1.7 Hz, 1H), 8.90 (dd, J=8.5, 1.7 Hz, 1H); δ_C=150.4, 148.0, 147.3, 138.2, 135.8, 132.8, 122.2, 114.3, 109.5, 48.9, 47.3, 31.3, 31.1; ν_{max} (KBr): 3459.0, 3339.1, 2962.1, 1600.4, 1580.8, 1481.7, 1451.0, 1166.4, 789.2; *m/z* (%): 320 (25.9), 264 (16.6), 209 (13.3), 208 (100.0), 207 (16.8), 175 (37.3). Anal. calcd for $C_{17}H_{24}N_2S_2$ [320.52]: C, 63.70, H, 7.55; N, 8.74; S, 20.01%; found: C, 63.71; H, 7.45; N, 8.69; S, 20.11%.

3.1.15. Reaction of 5-nitroisoquinoline 1d with 1,1-dimethylethylthiol 2a (entry 15). 5′-Amino-2′,4′-di-(1,1-dimethylethylthio)isoquinoline; **3da**: 400 mg (50%). Yellow solid; mp 167–171°C (AcOEt–hexane). δ_H=1.30 (s, 9H), 1.38 (s, 9H), 5.40 (broad s, 2H), 7.56 (dd, J=5.9,

0.9 Hz, 1H), 8.56 (d, J=5.9 Hz, 1H), 10.01 (d, J=0.9 Hz, 1H); δ_C=153.1, 148.4, 147.5, 142.7, 131.8, 126.2, 117.8, 114.3, 113.5, 49.4, 47.4, 31.3, 31.1; ν_{max} (KBr): 3426.4, 3311.5, 3205.4, 3168.3, 2957.5, 1627.8, 1551.8, 1474.4, 1429.9, 1362.7, 1162.8, 823.8; *m/z* (%): 320 (15.8), 264 (14.9), 210 (9.0), 209 (13.4), 208 (100.0), 175 (23.7). Anal. calcd for $C_{17}H_{24}N_2S_2$ [320.52]: C, 63.70, H, 7.55; N, 8.74; S, 20.01%; found: C, 63.70; H, 7.55; N, 8.74%.

3.1.16. Reaction of 5-nitroisoquinoline 1d with *n*-butylthiol 2c (entry 16). 5′-Amino-2′,4′-di-(1-butylthio)isoquinoline; **3dc**: 188 mg (24%). Dark yellow oil. δ_H=0.88 (q as a result of superposition of two t, J=7.1 Hz, 6H), 1.39–1.46 (m, 4H), 1.51–1.59 (m, 4H), 2.81–2.87 (m, 4H), 7.55 (dd, J=6.0, 0.9 Hz, 1H), 7.80 (s, 1H), 8.56 (d, J=6.0 Hz, 1H), 9.82 (d, J=0.9 Hz, 1H); δ_C=151.8, 143.9, 143.2, 140.0, 129.2, 126.8, 121.6, 116.6, 114.6, 36.7, 35.1, 32.1, 31.8, 22.1, 22.0, 13.9, 13.8; ν_{max} (film): 3432.3, 3323.4, 3297.7, 2957.6, 2928.6, 2871.4, 1621.5, 1600.0, 1554.2, 1478.7, 1464.1, 1366.5, 1223.8, 1049.1, 821.4; *m/z* (%): 322 (10.7), 321 (20.9), 320 (100.0), 265 (7.7), 264 (21.2), 263 (58.2), 208 (10.4), 207 (31.4), 176 (5.7), 175 (12.0). Anal. calcd for $C_{17}H_{24}N_2S_2$ [320.52]: C, 63.70, H, 7.55; N, 8.74; S, 20.01%; found: C, 63.66; H, 7.47; N, 8.49; S, 19.91%. 5′-Amino-8′-(1-butylthioisoquinoline; **4dc**: 73 mg (13%). Dark yellow oil. δ_H=0.87 (t, J=7.4 Hz, 3H), 1.36–1.45 (m, 2H), 1.50–1.58 (m, 2H), 2.83 (t, J=7.4 Hz, 2H), 4.31 (broad s, 2H), 6.89 (d, J=7.8 Hz, 1H), 7.57 (dd, J=5.9, 0.8 Hz, 1H), 7.60 (d, J=7.8 Hz, 1H), 8.55 (d, J=5.9 Hz, 1H), 9.87 (d, J=0.8 Hz, 1H); δ_C=151.6, 142.3, 141.7, 134.6, 129.4, 127.1, 122.2, 114.0, 112.7, 38.5, 31.5, 21.8, 13.6; ν_{max} (film): 3345.5, 3209.3, 2957.4, 2928.6, 2871.0, 1640.8, 1605.4, 1583.2, 1494.4, 1448.5, 1381.5, 1360.8, 1330.6, 1282.6, 1055.5, 820.8; *m/z* (%): 234 (5.7), 233 (15.6), 232 (100.0), 189 (3.1), 178 (13.5), 177 (13.5), 176 (93.5), 175 (86.5), 174 (5.5); HRMS: calcd for $C_{13}H_{16}N_2S$: [232.1034]; found: 232.1033.

3.1.17. Reaction of 6-nitroisoquinoline 1e with 1,1-dimethylethylthiol 2a (Scheme 2): chromatography performed with $CHCl_3$–MeOH (10:1) as eluant. 6′-Amino-5′-(1,1-dimethylethylthio)isoquinoline; **4ea**: 197 mg. Brown solid; mp 49–51°C. δ_H=1.32 (s, 9H), 4.91 (broad s, 2H), 7.23 (d, J=9.0 Hz, 1H), 7.35 (dd, J=8.4, 4.2 Hz, 1H), 7.93 (dd, J=9.0, 0.7 Hz, 1H), 8.62 (dd, J=4.2, 1.6 Hz, 1H), 8.78 (ddd, J=8.4, 1.6, 0.7 Hz, 1H): ν_{max} (KBr): 3434.6, 3275.9, 3140.9, 2955.1, 1618.5, 1553.5, 1494.8, 1418.8, 1359.4, 1164.2, 1149.7, 827.5, 808.7; *m/z* (%): 232 (7.7), 177 (11.3), 176 (100.0), 175 (7.4), 149 (6.1), 148 (6.7), 144 (5.9), 132 (4.8), 132 (6.2). Anal. calcd for $C_{13}H_{16}N_2S$ [232.35]: C, 67.20; H, 6.94; N, 12.06; S, 13.80%; found: C, 66.97; H, 7.04; N, 11.78; S, 13.56%. Additionally 114 mg of brown solid was isolated which gave unresolvable ^{1}H NMR but was judged to be 6′-hydroxylamino-5′-(1,1-dimethylethylthio)isoquinoline; **6** on the basis of its ms spectrum: mp 177–179°C; *m/z* (%): 248 (10.6), 232 (2.6), 193 (3.8), 192 (31.7), 191 (3.2), 177 (8.4), 176 (41.4), 175 (100.0), 174 (5.6), 173 (7.8), 148 (9.1), 147 (4.0), 131 (8.6), 129 (5.9); HRMS: calcd for $C_{13}H_{16}N_2SO$: [248.0983]; found: 248.0991; ν_{max} (film): 3272.2, 3117.4, 2815.5 (broad), 1602.5, 1585.3, 1500.9, 1461.8, 1412.1, 1352.9, 1164.5, 1145.9, 1125.6, 987.8, 836.5, 807.9. The sample of **6** was converted to **4ae** on heating to reflux in Zn/AcOH system.

3.2. Independent synthesis of 1′-amino 2′/4′ butylthionaphthalenes 2ac and 2ac′ (Scheme 3)

3.2.1. Step a. *1′-Nitro 2′ and 4′ tosyloxynaphthalenes* **8a** *and* **8b**. 2′ or 4′ hydroxy-1′-nitronaphthalene[18] (**7a** or **7b**; 1.89 g, 10 mmol) were dissolved in dry DMF (25 mL) with diisopropylethylamine (2.2 mL, 12.5 mmol). The reaction flask was immersed in a cooling bath (cold water) and solid tosyl chloride (2.4 g, 12.5 mmol) was added. The reaction mixture was stirred overnight at room temperature. After pouring onto water (150 mL), the mixture was extracted with AcOEt (3×50 mL), the combined extracts washed with water, dried ($MgSO_4$), the solvent evaporated and the residue chromatographed to give products **8a** (2.68 g; 78%) or **8b** (2.16 g; 63%).

1′-Nitro-2′-Tosyloxynaphthalene **8a**. Yellow crystals; mp 135–137°C (AcOEt–hexane). δ_H=2.47 (s, 3H), 7.34–7.37 (AA′ part of AA′BB′ system, 2H), 7.61–7.67 (m, 2H), 7.66 (d, J=9.0 Hz, 1H), 7.70–7.72 (m, 1H), 7.79–7.81 (part BB′ of AA′BB′ system, 2H), 7.91–7.93 (m, 1H), 8.04 (d, J=9.0 Hz, 1H); δ_C=146.4, 138.5, 132.2, 131.8, 131.6, 130.1, 129.4, 128.6, 128.2, 127.7, 125.0, 121.8, 120.9, 21.8; ν_{max} (KBr): 1643.6, 1596.3, 1533.3, 1508.7, 1357.6, 1225.6, 1214.5, 1192.6, 1175.6, 1090.2, 1028.3, 965.8, 869.7, 813.3, 768.7, 678.9; *m/z* (%): 344 (4.1), 343 (20.7), 157 (4.0), 156 (6.9), 155 (80.2), 139 (3.5), 130 (5.0), 114 (5.6), 92 (7.4), 91 (100.0). Anal. calcd for $C_{17}H_{13}NO_5S$ [343.36]: C, 59.47; H, 3.82; N, 4.08; S, 9.34%; found: C, 59.52; H, 3.93; N, 4.16; S, 9.24%.

1′-Nitro-4′-tosyloxynaphthalene **8b**. Yellow crystals; mp 138–141°C (AcOEt–hexane). δ_H=2.44 (s, 2H), 7.31–7.35 (part AA′ of AA′BB′ system 2H), 7.36 (d, J=8.4 Hz, 1H), 7.58 (ddd, J=8.6, 6.9, 1.1 Hz, 1H), 7.72 (ddd, J=8.8, 6.9, 1.3 Hz, 1H), 7.80–7.81 (BB′ part of AA′BB′ system, 2H), 8.04 (ddd, J=8.6, 1.3, 0.8 Hz, 1H), 8.18 (d, J=8.4 Hz, 1H), 8.54 (dt, J=8.8, 0.8 Hz, 1H); δ_C=149.6, 146.2, 144.7, 132.1, 130.2, 130.1, 128.5, 128.1, 127.9, 126.6, 124.1, 123.2, 122.5, 116.5, 21.7; ν_{max} (KBr): 1632.2, 1595.8, 1569.6, 1522.8, 1507.4, 1425.3, 1367.4, 1348.8, 1260.7, 1226.1, 1188.9, 1175.2, 1090.8, 1042.6, 984.1, 848.1, 815.4, 803.5, 769.2, 733.5, 708.9, 681.8; *m/z* (%): 344 (4.5), 343 (22.1), 157 (5.7), 156 (8.8), 155 (100.0), 114 (5.1). Anal. calcd for $C_{17}H_{13}NO_5S$ [343.36]: C, 59.47; H, 3.82; N, 4.08; S, 9.34%; found: C, 59.46; H, 4.02; N, 4.14; S, 9.26%.

3.2.2. Step b. Tosylate **7a** or **7b** (972 mg, 3.84 mmol) was dissolved in dry DMF (20 mL), *n*-BuSH (470 μL, 4.4 mmol) was added, followed by addition of solid K_2CO_3 (830 mg, 6 mmol). The mixture was stirred overnight at room temperature. After pouring onto satd aq. $NaHCO_3$ solution (100 mL), extraction with AcOEt (3×50 mL) and column chromatography the product **9a** (480 mg, 65%) or **9b** (604 mg, 82%) was isolated.

2′-(1-Butylthio)-1′-nitronaphthalene **9a**. Yellow solid; mp 49–51°C (hexane). δ_H=0.91 (t, J=7.4 Hz, 3H), 1.40–1.49 (m, 2H), 1.59–1.66 (m, 2H), 3.02 (t, J=7.4 Hz, 2H), 7.54–7.58 (m, 1H), 7.57 (d, J=8.7 Hz, 1H), 7.60–7.65 (m, 1H), 7.73–7.76 (m, 1H), 7.86–.88 (m, 1H), 7.90 (d, J=8.7 Hz, 1H); δ_C=148.8, 132.1, 130.7, 129.0, 128.1, 128.0, 127.2, 126.8, 125.1, 121.4, 34.3, 31.3, 21.7, 13.5; *m/z* (%): 262

(5.8), 261 (35.4), 232 (23.3), 214 (5.8), 205 (16.0), 198 (3.6), 197 (21.6), 196 (7.0), 190 (4.9), 189 (9.3), 188 (59.3), 182 (36.6), 172 (11.7); ν_{max} (KBr): 2962.9, 2928.4, 2861.2, 1624.9, 1584.3, 1515.9, 1334.2, 1229.0, 1129.6, 1097.6, 861.1, 804.5, 793.3. Anal. calcd for $C_{14}H_{15}NO_2S$ [261.34]: C, 64.34; H, 5.78; N, 5.36; S, 12.27%; found: C, 64.41; H, 5.67; N, 5.37; S, 12.23%.

4′-(1-*Butylthio*)-1′-*nitronaphthalene* **9b**. Yellow solid; mp 56–58°C (hexane). δ_H=0.98 (t, *J*=7.3 Hz, 3H), 1.50–1.59 (m, 2H), 1.76–1.84 (m, 2H), 3.13 (t, *J*=6.7 Hz, 2H), 7.35 (d, *J*=8.3 Hz, 1H), 7.60–7.66 (m, 1H), 7.71–7.76 (m, 1H), 8.21 (d, *J*=8.3 Hz, 1H), 8.37 (ddd, *J*=8.4, 1.1, 0.6 Hz, 1H), 8.69 (ddd, *J*=8.8, 1.1, 0.6 Hz, 1H); δ_C=145.7, 143.4, 131.6, 129.7, 127.2, 125.3, 124.6, 124.1, 123.9, 119.9, 32.0, 30.3, 22.2, 13.6; ν_{max} (KBr): 2964.6, 2926.1, 2864.3, 1559.3, 1503.8, 1418.2, 1322.3, 1304.1, 1260.1, 1197.8, 1164.1, 933.3, 776.5, 766.2; *m/z* (%): 263 (6.3), 262 (17.2), 261 (100.0), 207 (3.2), 206 (7.6), 205 (59.3), 204 (5.3), 201 (8.1), 188 (3.9), 175 (14.5), 171 (12.9), 159 (14.7), 158 (10.5). Anal. calcd for $C_{14}H_{15}NO_2S$ [261.34]: C, 64.34; H, 5.78; N, 5.36; S, 12.27%; found: C, 64.61; H, 5.58; N, 5.52; S, 12.33%.

3.2.3. Step c. (1) Sulphide **9a** (65 mg, 0.25 mmol) was dissolved in EtOH (15 mL). $SnCl_2{\cdot}2H_2O$ (680 mg, 3 mmol) was added and the mixture stirred and refluxed for 20 h. After pouring onto satd aq. $NaHCO_3$ solution (20 mL), the solid material was filtered off and washed with AcOEt, and the filtrate was extracted with AcOEt. The combined organic solutions were washed with water, dried with $MgSO_4$, concentrated and chromatographed to yield 1′-amino-2′-(1-butylthio)naphthalene **4ac′** (304 mg, 53%) as a yellow oil. δ_H=0.88 (t, *J*=7.4 Hz, 3H), 1.35–1.45 (m, 2H), 1.50–1.60 (m, 2H), 2.79 (t, *J*=6.6 Hz, 2H), 5.01 (broad s, 2H), 7.21 (dd, *J*=8.6, 0.4 Hz, 1H), 7.44–7.50 (m, 3H), 7.74–7.78 (m, 1H), 7.79–7.83 (m, 1H); ν_{max} (film): 3464.7, 3357.7, 3053.0, 2957.2, 2928.4, 2971.0, 1602.5, 1503.7, 1403.7, 1376.4, 858.5, 796.6, 738.3; *m/z* (%): 233 (3.8), 232 (12.0), 231 (69.6), 176 (10.6), 175 (58.2), 174 (100.0), 147 (10.1), 144 (4.4), 143 (23.5); HRMS: calcd for $C_{14}H_{17}NS$: [231.1082]; found: 231.1084.

(2) Sulphide **9b** (22 mg, 0.08 mmol) was dissolved in AcOEt (3 mL) and treated with $SnCl_2{\cdot}2H_2O$ (90 mg, 0.4 mmol). After stirring at room temperature overnight, the reaction mixture was diluted with AcOEt (30 mL), and washed with satd aq. $NaHCO_3$ solution (10 mL). Column chromatography afforded 8 mg (43%) of product with both MS and ^{1}H NMR spectra superimposable with those of 1′-amino-4′-(1-butylthio)naphthalene **4ac**.

3.3. Reaction of 2′ and 4′ 1-nitronaphthalenes with *n*-butylthiol 2c (Scheme4)

3.3.1. Reaction of 2′-butylthio-1′-nitronaphthalene 9a with *n*-butylthiol 2c. Nitroarene **9a** (262 mg, 1 mmol) was dissolved in dry DMF (20 mL) and treated with BSA (640 μL, 2.5 mmol), *n*-butylthiol **2c** (560 μL, 5 mmol) and DBU (500 μL, 3.75 mmol). The mixture was stirred at room temperature for 15 days. After standard work up followed by column chromatography 1′,2′-di-(1-butylthio)naphthalene **10a** (152 mg, 50%) and amine **3ac** (28 mg, 9%) were obtained. Compound **10a**: off white solid; mp 109–111°C. δ_H=0.87 (t, *J*=7.3 Hz, 3H), 0.98 (t, *J*=7.3 Hz, 3H), 1.40–1.46 (m, 2H), 1.50–1.60 (m, 4H), 1.72–1.80 (m, 2H), 2.85 (t, *J*=7.5 Hz, 2H), 3.02 (t, *J*=7.5 Hz, 2H),.39 (d, *J*=7.8 Hz, 1H), 7.43 (ddd, *J*=8.0, 6.8, 1.2 Hz, 1H), 7.55 (ddd, *J*=8.4, 6.8, 1.2 Hz, 1H), 7.77–7.80 (m, 2H), 8.61–8.63 (m, 1H); δ_C=143.7, 136.0, 131.4, 129.4, 128.3, 128.0, 127.3, 125.7, 125.0, 122.8, 35.8, 32.4, 32.1, 31.3, 31.1, 33.5, 22.4, 114.0, 13.9; ν_{max} (KBr): 3051.8, 2956.2, 2924.3, 2870.3, 2856.5, 1614.9, 1578.7, 1496.5, 1463.4, 1434.6, 1420.9, 1375.9, 1223.3, 1118.9, 979.4, 857.8, 809.4, 797.3, 771.0, 747.6; *m/z* (%): 306 (8.1), 305 (16.7), 304 (77.8), 250 (9.7), 249 (17.0), 248 (100.0), 215 (5.3), 214 (10.3), 194 (7.3), 193 (12.1), 192 (80.4), 191 (31.3), 190 (29.8), 172 (7.0), 171 (12.4). Anal. calcd for $C_{18}H_{24}S_2$ [304.52]: C, 71.00; H, 7.94; S, 21.06%; found: C, 70.82; H, 8.01; S, 21.04%.

3.3.2. Reaction of 4′-butylthio-1′-nitronaphthalene 9b with *n*-butylthiol 2c. Nitroarene **9b** (130 mg, 0.5 mmol) was dissolved in dry DMF (10 mL) and treated with BTMSA (320 μL, 1.25 mmol), *n*-butylthiol **2c** (280 μL, 2.5 mmol) and DBU (500 μL, 3.75 mmol). The mixture was stirred at room temperature for 21 days. After standard work up followed by column chromatography, 1′,4′-di-(1-butylthio)naphthalene **10b** (55 mg, 36%) was obtained as the only isolable product. Compound **10b**: δ_H=0.92 (t, *J*=7.4 Hz, 6H), 1.44–1.52 (m, 4H), 1.61–169 (m, 4H), 2.95 (t, *J*=7.4 Hz, 4H), 7.48 (s, 2H), 7.57 (AA′ part of AA′XX′ system, 2H), 8.43 (XX′ part of AA′XX′ system, 2H); δ_C=133.2, 133.0, 127.3, 126.5, 125.7, 34.0, 31.2, 22.0, 13.7; ν_{max} (film): 3469.4, 2957.5, 2929.3, 2871.3, 1567.1, 1463.9, 1367.5, 1192.2, 992.3, 820.3, 758.6; *m/z* (%): 306 (10.6), 305 (20.5), 304 (100.0), 249 (5.3), 248 (19.2), 247 (28.3), 193 (5.0), 192 (19.2), 191 (33.8), 190 (4.6). Anal. calcd for $C_{18}H_{24}S_2$ [304.52]: C, 71.00; H, 7.94; S, 21.06%; found: C, 71.05; H, 7.87; S, 21.26%.

3.4. Reaction of 1a with 2a arrested on the stage of 2′,4′-di-(1,1-dimethyletylthio)-1′-hydroxylaminonaphthalene 11 (Scheme 5)

Reaction was performed according to the general procedure. After 30 min of stirring at room temperature the mixture was quenched with 50 mL of satd aq. NH_4Cl solution. A stream of Ar was bubbled through the mixture for 1 h to remove the excess of mercaptan and other volatile substances. The mixture was then extracted with AcOEt (3×50 mL) and dried over $MgSO_4$. Evaporation of the solvent followed by recrystallisation of the residue from hexane gave product **11** (425 mg, 50%), as unstable light yellow crystals containing small amounts of impurities; ^{1}H NMR spectra both in $CDCl_3$ and benzene-d_6 exhibited broadened signals because of the presence of dynamic system: δ_H ($CDCl_3$)=1.30 (s, 9H), 1.37 (s, 9H), 5.49 (s, 1H), 7.51–7.65 (m, 2H), 7.95 (s, 1H), 8.40–8.48 (m, 1H), 8.66 (s, 1H), 8.68–8.80 (m, 2H); δ_H (C_6D_6)=1.17 (s, 9H), 1.19 (s, 9H), 5.85 (s, 1H), 7.35–7.43 (m, 2H), 8.19 (s, 1H), 8.59 (d, *J*=7.6 Hz, 1H), 8.70 (s, 1H), 8.96 (d, *J*=8.6 Hz, 1H); ν_{max} (film): 3341.4, 3210.3, 3065.6, 2967.4, 2897.3, 2862.4, 1557.8, 1493.6, 1457.9, 1364.4, 1166.0, 1105.2, 1048.4, 875.3, 763.8, 670.6; *m/z* (%): 335 (<1), 320 (5.6), 319 (24.4), 263 (13.3), 221 (5.8), 220 (11.1), 209 (9.5), 208 (15.8), 207 (100.0), 206 (23.0), 205 (8.4), 175 (5.5), 174

(32.7); LSIMS: 335 (M^+), 319, 307, 289, 278, 262; LSIMS HR: calcd for $C_{18}H_{25}ONS_2$: [335.1378]; found: 335.1371.

Product **11** treated with BSA (2.5 equiv.) and DBU (5 equiv.) in DMF solution for 4 days at room temperature according to the general procedure afforded **3aa** in a 63% yield.

3.5. Reactions of 1a with 2a terminated with external reducing agents (Scheme 8)

The first stage of reaction was performed as in Section 3.4 on a 1 mmol scale but the reaction was quenched after 30 min with aq. satd $NaHCO_3$ (10 mL).

Procedure a. At this point $Na_2S_2O_4$ (870 mg, 5 mmol) and the mixture stirred at 60°C for 3 h. Usual work up followed by chromatography yielded **3aa** (168 mg, 53%).

Procedure b. The mixture was extracted with AcOEt extract evaporated, the residue dissolved in AcOH (10 mL). Zn dust (650 mg, 10 mmol) was added and the mixture was refluxed with stirring for 30 min. Work up followed by column chromatography yielded **3aa** (180 mg, 55%).

3.6. Reaction of 1-nitroso-2-naphthol 19 with 1,1-dimethylethylthiol 2a (Scheme 7)

To a stirred solution of 1-nitroso-2-naphthol **19** (173 mg, 1 mmol), *t*-BuSH **2a** (550 μL, 5 mmol) in DMF (15 mL), BSA (640 μL, 2.5 mmol) and DBU (1 mL, 7.5 mmol) were added. After stirring for 3 days at room temperature the reaction mixture was worked up according to standard procedure. Column chromatography gave product **20** (211 mg, 85%).

1′-Amino-4′-(1,1-dimethylethylthio)-2′-hydroxynaphthalene 20. δ_H (DMSO-d_6)=1.20 (s, 9H), 5.31 (broad s, 2H), 7.27–7.34 (m, 2H), 7.39 (s, 1H), 8.00–8.03 (m, 1H), 8.43–8.46 (m, 1H), 9.13 (broad s, 1H); δ_C=137.8, 131.8, 131.6, 128.3, 126.9, 123.7, 123.6, 123.0, 121.8, 114.4, 46.7, 30.8; ν_{max} (KBr): 3354.3, 3287.8, 3064.3, 2984.4, 1619.6, 1605.3, 1562.9, 1507.7, 1434.5, 1362.6, 1348.3, 1270.2, 1246.4, 1168.4, 1029.2, 958.2, 940.6, 888.3, 861.1, 759.0; *m/z*: 248 (3.5), 247 (21.6), 193 (5.5), 192 (12.6), 191 (100.0), 190 (11.6), 162 (6.7), 159 (13.3), 158 (5.0), 146 (15.1). Anal. calcd for $C_{14}H_{17}NOS$ [247.36]: C, 67.98; H, 6.93; N, 5.66; S, 12.96%; found: C, 68.12; H, 6.92; N, 5.91; S, 13.22%.

Acknowledgements

This study was funded by the State Committee of Scientific Research Grant No. PBZ 6.01.

References

1. Paradisi, C.; Scorrano, G. *Acc. Chem. Res.* **1999**, *32*, 958–968.
2. Chupakhin, O. N.; Charushin, V. N.; van der Plas, H. C. *Nucleophilic Aromatic Substitution of Hydrogen*. Academic: San Diego, 1994.
3. Terrier, F. *Nucleophilic Aromatic Displacement*. VCH: New York, 1991.
4. Zlotin, S. G.; Kislitsin, P. G.; Samet, A. V.; Serebriakov, E. A.; Konyushkin, L. D.; Semenov, V. V. *J. Org. Chem.* **2000**, *65*, 8430–8438.
5. Serushkina, O. V.; Dutov, M. D.; Shevelev, S. A. *Russ. Chem. Bull.* **2001**, *50*, 261–264.
6. Kawakami, T.; Suzuki, H. *J. Chem. Soc. Perkin Trans. 1* **2000**, 3640–3644.
7. Wróbel, Z. *Tetrahedron Lett.* **1997**, *38*, 4913–4916.
8. Wróbel, Z. *Tetrahedron* **1998**, *54*, 2607–2618.
9. Wróbel, Z.; Eur, *J. Org. Chem.* **2000**, 521–525.
10. It was found that 4-chloronotrobenzene reacts with phenylacetonitrile in NaOH/aq. MeOH solution to form 3-phenyl-2,1-benzisoxazole via replacement of *ortho*-hydrogen atom followed by further steps, whereas in DBU/DMF system only 4′-(1-cyano-1-phenylmethyl)nitrobenzene resulted from substitution of chlorine was detected. After adition of $MgCl_2$ to the later system only 3-phenyl-2,1-benzisoxazole was isolated Wróbel, Z. *Pol. J. Chem.* **1998**, *72*, 2384–2388.
11. Wróbel, Z. *Tetrahedron Lett.* **2000**, *41*, 7365–7366.
12. Wróbel, Z. *Tetrahedron* **2001**, *57*, 7899–7907.
13. Eyer, P.; Gallemann, D. Reactions of Nitrosoarenes with SH Groups. In *The Chemistry of Amino, Nitroso, Nitro and Related Groups*. Patai, S., Ed.; Wiley: New York, 1996; pp 999–1039 Supplement F2.
14. Schmidt, M. *J. Prakt. Chem.* **1890**, *42*, 156–158.
15. Schmidt, M. *J. Prakt. Chem.* **1891**, *44*, 522–523.
16. Boeniger, M. *Chem. Ber.* **1894**, *27*, 23–25.
17. Andersen, K. K. Sulphonic Acid and Their Derivatives. In *The Synthesis and Reactions of Organic Compounds*. *Comprehensive Organic Chemistry*, Sir Barton, D., Ed.; Pergamon: Oxford, 1979; p 336.
18. Mąkosza, M.; Sienkiewicz, K. *J. Org. Chem.* **1998**, *63*, 4199–4208.