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The [Cu]-catalyzed S_NAR reactions: direct amination of electron deficient aryl halides with sodium azide and the synthesis of arylthioethers under Cu(II)–ascorbate redox system

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ABSTRACT

A one pot [Cu]-promoted S_NAr reaction of electron-deficient halobenzenes with sodium azide and the reduction of the intermediate aryl azides under the same Cu(II)–ascorbate redox conditions leading to anilines has been documented. Control experiments revealed that both ascorbate and proline play important role in the reaction path way. Further, the use of this catalytic Cu(II)–ascorbate redox system has been explored for the synthesis of arylthioethers.

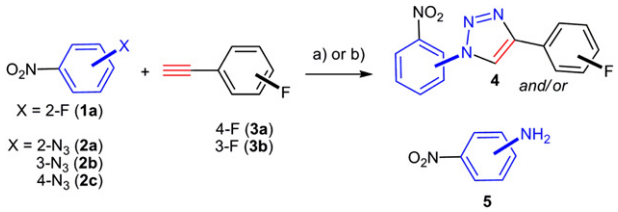
1. Introduction

The recent discovery of the Meldal[1] and Sharpless[2] groups revealing the dramatic rate acceleration of the azide-alkyne cycloaddition[3] under copper(I) catalysis (CuAAC) has extended this reaction to many branches of chemistry ranging from bio- to materials and polymers and is often referred as 'the click reaction'.[4] The inaugural protocol that employ the Cu(II) salts with ascorbate is the method of choice for preparative synthesis of 1,2,3-triazoles,[1] though there are several other mild alternatives that have been disclosed especially dealing with the bio-conjugations.[5] In recent publications, we showed that under the classical Cu(II)–ascorbate redox system, the 1,4-diaryltriazoles can be prepared in one-pot from S_NAr of *o*- and *p*-fluoronitrobenzenes with NaN_3 and subsequent Huisgen [3+2] cycloaddition of intermediate aryl azides with various alkynes, being both the S_NAr and [3+2] cycloaddition are promoted by Cu(II)–ascorbate redox system.[6] In this manuscript we document the direct amination of the electron deficient aryl halides using sodium azide as the amine source[7] and also the thiolation[8] with alkyl/aryl/heteroaryl thiols under the classical Cu (II)–ascorbate redox system, the first one being an unintended observation.

2. Results and discussion

2.1. Amination employing azide as ammonia surrogate

As a part of our ongoing studies dealing with the synthesis and structural analysis of isomeric halo-nitro derivatives of diphenyl-1,2,3-triazoles,[6b] the S_NAr–click reaction of *o*-/*p*-nitrofluorobenzenes with 4-fluorophenyacetylene (**3a**) was attempted (Scheme 1). Interestingly, the 2-aminonitrobenzene (**5a**) was obtained as the major product. This might be resulting from the competitive reduction of the intermediate aryl azide.[9] Intrigued by this, the three isomeric fluoronitrobenzenes (**1a**–**c**) were subjected to these conditions. The S_NAr followed by azide reduction was found to be facile with the 2- and 4-fluoronitrobenzenes (**1a** and **1c**) and the 3-fluoronitrobenzene (**1b**) was intact under these conditions. When the corresponding three isomeric azidonitrobenzenes (**2a**–**c**)



Scheme 1. Reagents and conditions: (a) 1.2 equiv NaN_3, $CuSO_4$ (20 mol %), Na–ascorbate (15 mol %), L-proline (20 mol %), Na_2CO_3 (20 mol %), DMSO/H_2O (9:1), 65–70 °C, 24 h; (b) for entries **2a**–**d** conditions are same as above without NaN_3.

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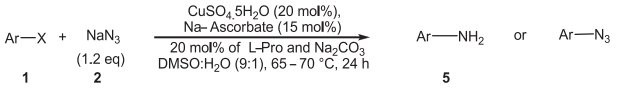
Entry	Reactants		Conditions	Yield	
				Triazole **4**	Aniline **5** (%)
1	**1a**	**3b**	a	—	55
2	**1a**	**3a**	a	—	57
3	**2a**	**3b**	b	—	57
4	**2a**	**3a**	b	—	63
5	**2b**	**3b**	b	23%	52
6	**2c**	**3a**	b	13%	65
7	**2a**	–	a	–	67%
8	**2b**	–	a	–	61%
9	**2c**	–	a	–	68%

were employed, all the three isomers gave the corresponding nitroanilines in good yields. This indicated that a nominal deactivation is required for the azide reduction when compared to that of S_NAr. As a control, the simple aryl halides were subjected for the one pot 'S_NAr–azide reduction'. The F-/Cl-/Br-benzenes were intact under these conditions and the iodobenzene was smoothly converted to azidobenzene (71%).[10] Under similar conditions, the *o*-chloronitrobenzene, *p*-bromo nitrobenzene, and also the corresponding iodonitrobenzenes gave the corresponding nitroanilines in comparable yields (Table 1, entries 1–5).[7]

Table 1
The scope of one-pot amination reaction of aryl halide with NaN_3 under Cu(II)–ascorbate redox system



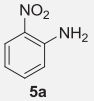
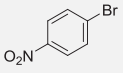
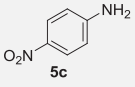
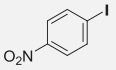
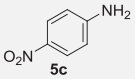
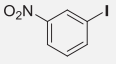
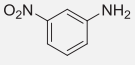
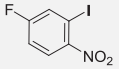
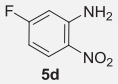
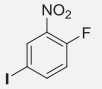
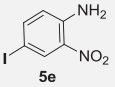
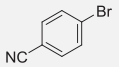
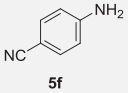
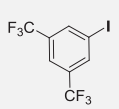
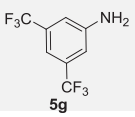
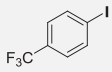
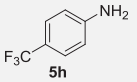
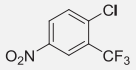
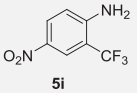
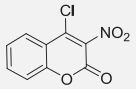
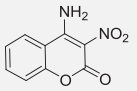
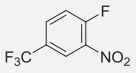
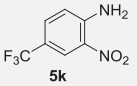
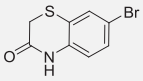
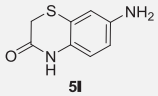
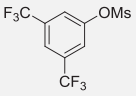
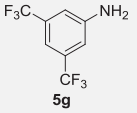
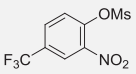
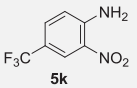
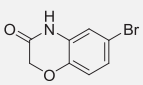
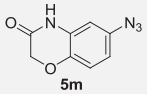
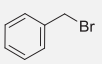
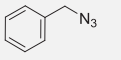
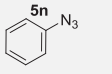
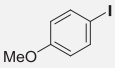
Entry	Substrate	Product	Yield (%)
1		 **5a**	74
2		 **5a**	76
3		 **5c**	76
4		 **5c**	86
5		 **5b**	77
6		 **5d**	67
7		 **5e**	69
8		 **5f**	54
9		 **5g**	68

Table 1 (*continued*)

Entry	Substrate	Product	Yield (%)
10		 **5h**	57
11		 **5i**	72
12		 **5j**	76
13		 **5k**	78
14		 **5l**	73
15		 **5g**	24
16		 **5k**	42
17		 **5m**	68
18		 **5n**	49
19		 **5o**	71
20		**5p**	53
21		**5q**	71
22		**5r**	28
23		No reaction	—
24		No reaction	—
25			32
26		No reaction	—

A literature search has revealed a recent report on azide to amine conversion under the Cu(II)–ascorbate redox system.[11] Peng and co-workers observed the reduction of a triazolyl azide during the CuAAC reaction [sodium ascorbate (0.5 equiv) and copper sulfate (0.15 equiv) in THF/water and heating at 70 °C (oil bath)]. The reduction in general was dictated by the azide positioning. Since both the azidation and the reduction are promoted under the similar conditions we have intended to further extend our observation in the direction of synthesis of anilines using sodium azide as amine source.[12,13a,13b]

Initial experiments on the reduction of 4-azidonitrobenzene employing all the components individually have revealed that the ascorbate could facilitate the reduction alone albeit it was required in stoichiometric amounts (1 equiv ascorbate, 2 h, 99% conversion, 94% isolated yield, Fig. 1a). Next we studied the azide reduction with ascorbate in the presence of $CuSO_4$ (1–20 mol % of each, Fig. 1b). The reduction was sluggish and the reactions were incomplete even after 24 h heating. Next we have introduced a fixed amount of base and concentrations of Cu(II)–ascorbate salt were varied. As it can be seen from the Figure 1c, there was an improvement however is not substantial. The role of proline has been examined subsequently. The reactions were carried out with varying concentrations of Cu(II)–sodium ascorbate with fixed concentrations of base and proline (20 mol % each). The results were exciting even with 1 mol % of Cu (II)–ascorbate redox system, the reactions were close to completion within 12 h (99% conversion 84% isolated yield). Thus these experiments revealed that presence of ascorbate is essential and that the rate of the reaction is enhanced by the presence of the Cu (II)–salt and proline and that proline is playing an important role. The stabilization of Cu(I)–species by proline has been proposed in the mechanism given for the CuAAC reactions.[14]

The scope of the one pot azidation–reduction reaction was examined employing a wide range of deactivated aryl halides. Table 1 shows the generality of the present amination and also the limitations, where the reactions were unsuccessful (Table 1, entries 23, 24, and 26) or resulted in azides (Table 1, entries 17–20) or sometimes even dehalogenation (Table1, entry 25).

The reactions are facile when the electron withdrawing groups (nitro or $-CF_3$) are placed either *ortho*- or *para*- to the leaving halo group. For example, the amination of 3-nitro-4-fluoroiodobenzene selectively occurred at *ortho*-position to the nitro group via fluorine displacement (Table 1, entry 7), whereas 2-nitro-4-fluoroiodobenzene gave mainly the 2-nitro-4-fluoroaniline with a net displacement of iodo group (Table 1, entry 6). The 'S_NAr–azide reduction' is also facile with hetero-aromatic halides, such as 4-chloro-3-nitro-coumarin and 7-bromo-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (Table 1, entries 12 and 14). With 6-bromo-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one, the corresponding azide was isolated in good yields (Table 1, entry 17). With regard to the reaction of benzyl halides under these conditions—benzyl bromide gave exclusively the benzyl azide (57%), 4-nitrobenzyl bromide gave the 4-nitrobenzaldehyde (32%) and unidentified complex mixture indicating the competitive halide hydrolysis and subsequent oxidation (Table 1, entries18 and 22). The *O*-mesylates were found to be hydrolyzed under these conditions (Table 1, entry 21).

The isolation of the intact aryl azides from iodobenzene (Table 1, entry 19) and from *p*-alkoxy substituted derivatives (Table 1, entries 17 and 20) indicate that the Cu(I)-mediated decomposition of the azide group depends upon relative electrophilicity of the azide group, which is controlled by the nature of the aryl substituent.[15] It has been proposed earlier that aryl azides exist in two octet resonance structures of the azide group—forms I and II (Fig. 2), amongst which the former is predominant when the *p*-substituent is an electronic withdrawing group.[16] Therefore, with the available information, we propose that under the present conditions, a preferential azide decomposition occurs via form I, where the doublebond character of the fissile $N-N_2$ bond is decreased and the entropy of activation for the rupture of this bond is lowered with the electron withdrawing substituents.[15] Further studies to understand the detailed mechanism of the reaction are in progress.

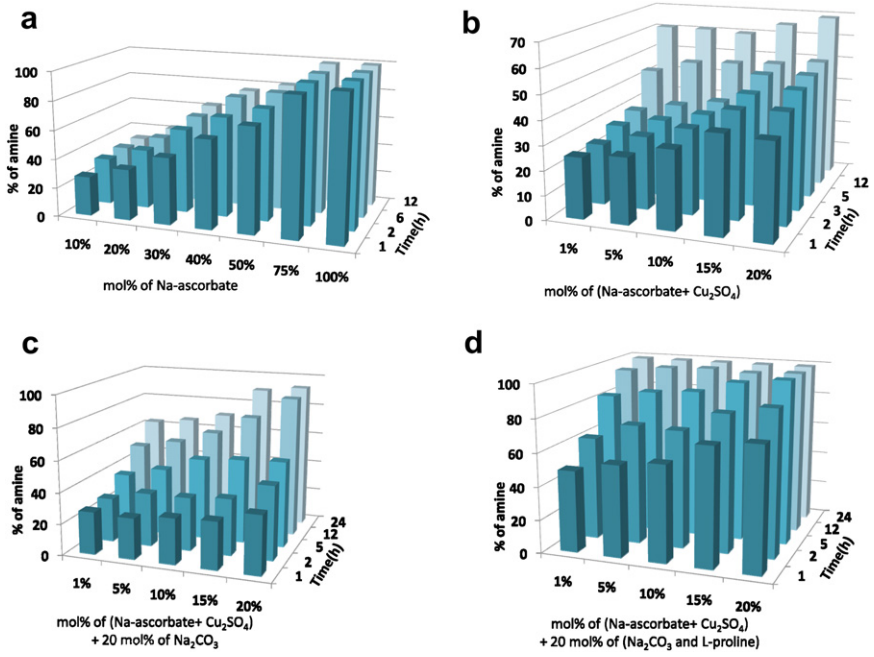


Figure 1. Control experiments revealing the effect of various additives on the outcome of the 4-azidonitrobenze reduction (conversion to nitroaniline estimated by GC).

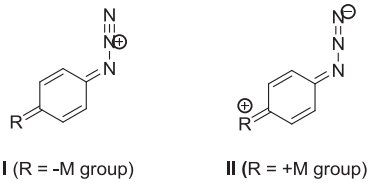


Figure 2. Two canonical forms of the aryl azides.

2.2. Synthesis of diaryl and alkyl aryl sulfides under classical 'click reaction' conditions

Encouraged by our observation of the rate enhancement of S_NAr with azide nucleophile under the classical Cu(II)–ascorbate redox system at ambient temperatures and the possibility of azidation–cycloaddition and azidation–reduction in one pot, we were further interested in expanding the scope of this 'click reaction' catalyst system for the synthesis of the arylthioethers via the S_NAr reaction. The C(aryl)–S bond formation of electron deficient aryl halides in the presence of strong bases is well documented.[17] On the other hand, various transition metal complexes have been explored for the C(aryl)–S bond formation employing the aryl iodides[18] or boronic acids[19] as the coupling partners. However, the use of metal catalysts in the C(aryl)–S bond formation via S_NAr is a much less studied transformation.[20]

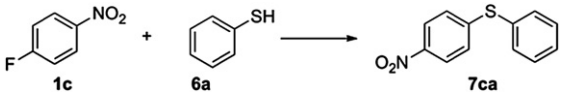
The thiophenol has been employed as the nucleophile for the initial exploratory experiments. Under the standard conditions used for the azidation (20 mol % of each Na_2CO_3, $CuSO_4$, L-proline and 15 mol % of ascorbate in DMSO at 65–70 °C for 24 h), the reaction of thiophenol with 4-nitrofluorobenzene gave the corresponding diarylthioether in moderate yields. Formation of substantial amounts of the diphenyl disulphide was noticed. Optimization of the reaction conditions has been carried out by varying the concentrations of additives and temperature (Table 2). These experiments revealed that the concentration of the base has a substantial effect on the outcome of the reaction. Use of 5 equiv of base was found to be optimal. The optimized reaction conditions employ 1.1 equiv of thiol, 5 equiv of base, 10 mol % of each ascorbate, Cu(II), and L-proline in DMSO to give the desired thioether in excellent yields (99% by GC/97% isolated). Further control experiments revealed that the absence of the ascorbate and L-proline has no substantial effect on the reaction time and on the product yield. These experiments indicated that the thiol is also acting as a reducing agent for the in situ generation of the active Cu(I)-species.[21] Next the effect of reaction temperature was examined. The lowering of the temperature was detrimental and the disulphide formation was found to be a competing reaction.

The scope of the Cu(I)-promoted thioether synthesis was examined by employing a set of four aryl halides (**1a** and **1c**–**e**) and four representative aryl-, heteroaryl-, and alkylthiols (**6a**–**d**). The results are given in Table 3. Table 4 presents the thioether synthesis employing randomly selected aryl and benzyl halides. The reactions in general are smooth and the corresponding diaryl thioethers are obtained in good to excellent yields. Remarkably, sterically demanding *ortho*-substituted aryl halides also give good results without any difficulty (Table 3, entries 1–4 and 13–16). The reaction of aryl halide containing deactivating groups like $-NO_2$, $-CF_3$,–CN with aryl and alkyl thiol afford the cross-coupling product in 91–96% yield in 10–18 h (Table 4). Under these conditions, *p*-nitrobenzyl bromide is highly reactive and promotes the desired thioether within 10 min (Table 4, entries 5 and 6). In addition, the reaction of pyridine-2-thiol and benzo[*d*]thiazole-2-thiol with aryl fluorides were successfully performed to afford the heteroaryl thioethers in good yields (Table 4, entries 7 and 8). As seen with the azidation, cross coupling reactions between the deactivated aryl halides and thiols resulted in good to excellent yields. In contrast the reaction of *p*-methoxy iodobenzene gave the coupling product in poor yields (entry 9, Table 4) and the diaryl disulfide was isolated as the major product. As noticed earlier with the azidation, the attempted S_NAr reaction of the 3-fluoronitrobenzene (**1b**) with thiophenol (**6a**) was unsuccessful under these conditions and the disulphide was obtained as the main product.

3. Conclusion

We document the S_NAr reaction of deactivated aryl halides with azide and thiol for the Cu(II)–ascorbate redox system. We found that the intermediate azides are reduced under the same catalytic conditions and afford the corresponding anilines. One-pot 'S_NAr–azide reduction' has been generalized as a simple tool for the direct amination of deactivated aryl halides under the Cu(II)–ascorbate catalytic system. Control experiments revealed the essential role of ascorbate and proline in the present reaction and the course of the reaction as S_NAr with azide proceeding with an in situ reduction of azidobenzene intermediates. Coming to the thioethers synthesis for

Table 2
Control experiments for coupling of 4-nitrofluorobenzene with thiophenol

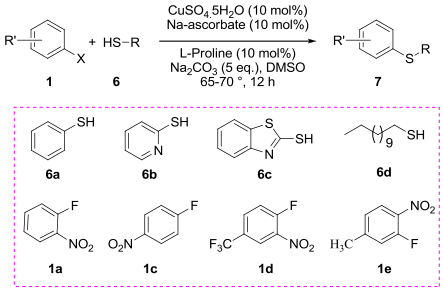


1c 6a 7ca

NO.	$CuSO_4$ (mol %)	Na–ascorbate (mol %)	L-Proline (mol %)	Na_2Co_3 (equiv)	Temp.	Yield (%)
1	10	10	10	2	65–70 °C	78[a]
2	10	10	10	5	rt	71[a]
3	10	10	10	5	65–70 °C	97[b]
4	—	—	—	5	65–70 °C	62[a]
5	10	—	—	5	65–70 °C	97[a]
6	10	10	—	5	65–70 °C	85[a]
7	5	5	—	5	65–70 °C	98[a]
8	5	5	5	5	65–70 °C	97[a]

[a] Based on GC.
[b] Isolated yield.

Table 3
Scope of Cu(I)-catalyzed thioether synthesis and the synthesized 4×4 thioether compounds library



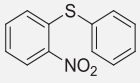
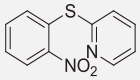
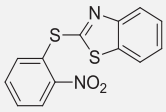
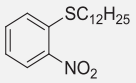
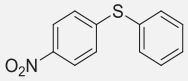
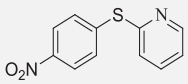
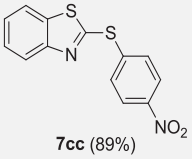
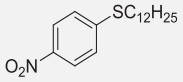
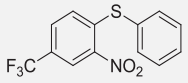
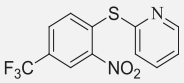
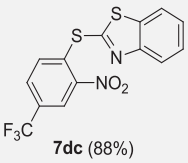
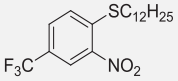
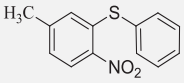
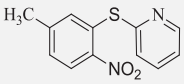
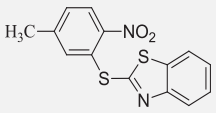
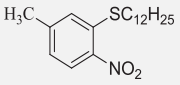
Entry	Haloderivative	Thiol	Product
1	**1a**	**6a**	 **7aa** (93%)
2	**1a**	**6b**	 **7ab** (91%)
3	**1a**	**6c**	 **7ac** (87%)
4	**1a**	**6d**	 **7ad** (89%)
5	**1c**	**6a**	 **7ca** (97%)
6	**1c**	**6b**	 **7cb** (91%)
7	**1c**	**6c**	 **7cc** (89%)
8	**1c**	**6d**	 **7cd** (87%)
9	**1d**	**6a**	 **7da** (97%)

Table 3 (*continued*)

Entry	Haloderivative	Thiol	Product
10	**1d**	**6b**	 **7db** (86%)
11	**1d**	**6c**	 **7dc** (88%)
12	**1d**	**6d**	 **7dd** (92%)
13	**1e**	**6a**	 **7ea** (93%)
14	**1e**	**6b**	 **7eb** (89%)
15	**1e**	**6c**	 **7ec** (86%)
16	**1e**	**6d**	 **7ed** (88%)

the Cu(II)–ascorbate catalytic system, the deactivated aryl halides underwent S_NAr smoothly in case of all the four different thiols employed. Control experiments reveal that the reaction works smoothly without ascorbate and L-proline. The thioether formation with the elector rich aromatic halides was found to be sluggish.

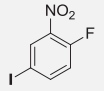
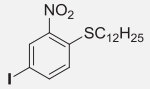
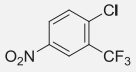
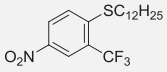
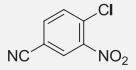
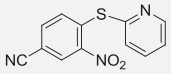
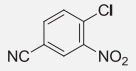
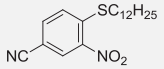
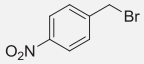
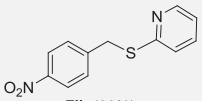
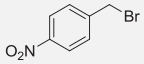
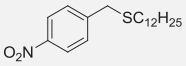
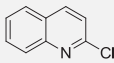
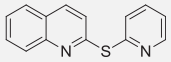
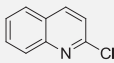
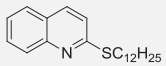
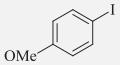
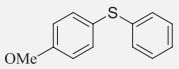
Since that the S_NAr reaction of deactivated aryl halides with azide or thiol are promoted under the same Cu(II)–ascorbate redox system, and that the azide-alkyne cycloaddition and amine reduction are also feasible under these catalytic conditions, we believe that the integration of all these possibilities on designed substrates with complementary functional groups will provide a platform for developing multi-component reactions—simple means of molecular complexity generation and small molecules library synthesis.

4. Experimental

4.1. General methods

Commercial reagents and solvents were used without purification. Column chromatography was carried out by using Spectrochem silica gel (100–200 mesh). ^1H and ^{13}C NMR spectroscopy

Table 4
Scope of the Cu(I) catalyzed thioether synthesis

Entry	Haloderivative	Thiol	Product
1		$C_{12}H_{25}SH$	 **7fd** (91%)
2		$C_{12}H_{25}SH$	 **7gd** (96%)
3			 **7hb** (91%)
4		$C_{12}H_{25}SH$	 **7hd** (94%)
5			 **7ib** (89%)
6		$C_{12}H_{25}SH$	 **7id** (87%)
7			 **7jb** (71%)
8		$C_{12}H_{25}SH$	 **7jd** (79%)
9			 **7ka** (27%)

measurements were carried out on Bruker AC 200 MHz or Bruker DRX 400 MHz spectrometers and TMS was used as an internal standard. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used to designate signal multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. The multiplicity of ^{13}C NMR signals was assigned with the help of DEPT spectra and the abbreviations used: s=singlet, d=doublet, t=triplet, q=quartet, represent C (quaternary), CH, CH_2, and CH_3, respectively. GC analyses were carried out on Agilent Technologies 7890. Mass spectra were recorded on API QStar Pulsar (Hybrid Quadrupole-TOF LC/MS/MS) spectrometer or on Applied Biosystems Voyager-DE STR 4383 (MALDI-TOF). Elemental analysis data were obtained on a Thermo Finnigan Flash EA 1112 Series CHNS Analyzer.

4.2. General procedure for azidation–reductions

To a solution of halobenzene (1 equiv) in DMSO/H_2O (9:1, 10 mL for 1 mmol substrate) were added L-proline (0.2 equiv), Na_2CO_3 (0.2 equiv), NaN_3 (1.2 equiv), sodium ascorbate (0.15 equiv), and $CuSO_4 \cdot 5H_2O$ (0.2 equiv). The mixture was stirred for 24 h at 70 °C (oil bath temperature) and then the mixture was poured into 30 mL of ice-cold water. The solid products were filtered and crystallized from appropriate solvent systems to procure the anilines/azides. Liquid products were purified by column chromatography.

*4.2.1. 2-Nitroaniline (**5a**).* Yellow solid; R_f (30% EtOAc/pet. ether) 0.5; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.06 (br s, 2H), 6.7 (dt, *J*=1.3, 8.4 Hz, 1H), 6.80 (dd, *J*=1.2, 8.4 Hz, 1H), 7.35 (dt, *J*=1.5, 8.4 Hz, 1H), 8.1 (dd, *J*=1.5, 8.6 Hz, 1H) ppm.

*4.2.2. 3-Nitroaniline (**5b**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.2; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.98 (br s, 2H), 6.92 (ddd, *J*=0.9, 2.3, 8.0 Hz, 1H), 7.25 (m, 1H), 7.46 (t, *J*=2.2 Hz, 1H), 7.55 (ddd, *J*=0.9, 2.2, 8.1 Hz, 1H) ppm.

*4.2.3. 4-Nitroaniline (**5c**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.2; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.41(br s, 2H), 6.57–6.65(m, 2H), 8.01–8.09 (m, 2H) ppm.

*4.2.4. 5-Fluoro-2-nitroaniline (**5d**).* Yellow solid; R_f (30% EtOAc/pet. ether) 0.4; mp: 74–75 °C; IR (Nujol) ν: 3488, 3348, 1641, 1463, 1377, 1259, 845, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.2 (s, 2H), 6.4–6.5 (m, 2H), 8.2 (dd, *J*=5.9, 9.3 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 103.6 (d, *J*=26.0 Hz), 105.7 (d, *J*=24.7 Hz), 129.3 (d, *J*=12.1 Hz), 146.7 (q, *J*=13.3 Hz), 164.3 (q), 169.4 (q) ppm; ESIMS (*m*/*z*) 157.2353 [17% $(M+1)^+$], 179.1590 [96% $(M+Na)^+$], 197.2501 [10% $(M+K)^+$].

*4.2.5. 4-Iodo-2-nitroaniline (**5e**).* Yellow solid; R_f (30% EtOAc/pet. ether) 0.4; mp: 118–119 °C; IR (Nujol) ν: 3520, 3398, 3019, 1619, 1508, 1215, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.1 (s, 2H), 6.6 (d, *J*=8.8 Hz, 1H), 7.6 (dd, *J*=2.1, 8.8 Hz, 1H), 8.4 (d, *J*=2.1 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 75.8 (q), 120.6 (d), 133.0 (q), 134.2 (d), 143.7 (d), 144.0 (q) ppm.

*4.2.6. 4-Aminobenzonitrile (**5f**).* Yellow solid; R_f (30% EtOAc/pet. ether) 0.2; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.21 (br s, 2H), 6.61–6.68 (m, 2H), 7.38–7.44 (m, 2H) ppm.

*4.2.7. 3,5-Bis(trifluoromethyl)aniline (**5g**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.2; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.27 (s, 2H), 7.43 (s, 2H), 7.64 (m, 1H) ppm.

*4.2.8. 4-(Trifluoromethyl)aniline (**5h**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.2; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.93 (br s, 2H), 6.66–6.70 (m, 2H), 7.36–7.40 (2H) ppm.

*4.2.9. 4-Nitro-2-(trifluoromethyl)aniline (**5i**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.3; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.95 (s, 2H), 6.76 (d, *J*=9.0 Hz, 1H), 8.17 (dd, *J*=2.6, 9.0 Hz, 1H), 8.38 (d, *J*=2.5 Hz, 1H) ppm.

*4.2.10. 4-Amino-3-nitro-2H-chromen-2-one (**5j**).* R_f (40% EtOAc/pet. ether) 0.2; mp: 248–249 °C; IR (Nujol) ν: 3389, 3294, 1715, 1633, 1462, 1377, 1271, 1107, 769 cm^{-1}; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.2 (dd, *J*=1.0, 8.3 Hz 1H), 7.3 (dd, *J*=1.0, 8.2 Hz 1H), 7.6 (dt, *J*=1.2, 7.2 Hz 1H), 8.3 (d, *J*=8.2 Hz 1H), 9.5 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6, 50 MHz): δ 112.9 (q), 117.0 (d), 124.2 (d), 125.1 (d), 134.9 (d), 151.8 (q), 153.2 (q), 170.2 (q) ppm; ESIMS (*m*/*z*) 207.1113 [6% $(M+1)^+$], 229.0860 [100% $(M+Na)^+$].

*4.2.11. 2-Nitro-4-(trifluoromethyl)aniline (**5k**).* Yellow solid; R_f (20% EtOAc/pet. ether) 0.3; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.38 (s, 2H), 6.91 (d, *J*=8.8 Hz, 1H), 7.56 (dd, *J*=2.1, 8.8 Hz, 1H), 8.44 (s, 1H) ppm.

*4.2.12. 7-Amino-2H-benzo[b][1,4]thiazin-3(4H)-one (**5l**).* R_f (40% EtOAc/pet. ether) 0.2; mp: 156–157 °C; IR (Nujol) ν: 3403, 3196,

1673, 1608, 1462, 1377, 1245, 814 cm^{-1}; ^1H NMR (DMSO-d_6, 200 MHz): δ 3.22 (s, 2H), 4.02 (s, 2H), 6.4 (dd, J=2.5, 8.5 Hz, 1H), 6.5 (d, J=2.4 Hz, 1H), 6.7 (d, J=8.5 1H), 9.8 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 50 MHz): δ 29.6 (t), 112.6 (d), 113.3 (d), 117.9 (d), 119.8 (q), 127.9 (q), 142.7 (q), 164.4 (q) ppm; ESIMS (m/z) 181.1051 [100% $(M+1)^+$], 203.1070 [31% $(M+Na)^+$], 219.1430 [12% $(M+K)^+$].

*4.2.13. 6-Azido-2H-benzo[b][1,4]oxazin-3(4H)-one (**5m**).* R_f (40% EtOAc/pet. ether) 0.5; mp: 213–215 °C; IR (Nujol) ν: 2923, 2854, 2111, 1683, 1598, 1461, 1377, 1219, 802 cm^{-1}; ^1H NMR (DMSO-d_6, 200 MHz): δ 4.6 (s, 2H),6.8 (d, J=8.6 Hz, 1H), 6.9 (d, J=2.2 Hz, 1H), 7.1 (dd, J=2.2, 8.6 Hz, 1H), 8.6 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 50 MHz): δ 67.1 (t), 114.6 (q), 118.3 (d), 118.8 (d), 126.9 (d), 142.8 (q), 165.6 (q) ppm.

4.3. General procedure for S_NAr with thiols

A suspension of halobenzene (1 equiv), L-proline (10 mol %), Na_2CO_3 (5 equiv), sodium ascorbate (10 mol %), and $CuSO_4 \cdot 5H_2O$ (10 mol %) in DMSO/H_2O (9:1, 10 mL for 1 mmol substrate) was added neat RSH (1.2 equiv) and contents were heated at 70 °C (oil bath temperature) with vigorous stirring for 12 h. The reaction mixture was cooled and partitioned between ethyl acetate and water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. Combined organic layer was washed with water, brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by either crystallization or by silica gel column chromatography.

*4.3.1. 2-Nitrophenyl phenyl sulfide (**7aa**)[22a].* Yellow solid; R_f (100% pet. ether) 0.3; mp: 73–74 °C; IR ($CHCl_3$) ν: 1591, 1517, 1474, 1452, 1336, 1304, 1250, 1106, 1042, 853, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 6.85 (dd, J=1.4, 8.1 Hz, 1H), 7.15–7.24 (m, 1H), 7.29–7.37 (m, 1H), 7.44–7.60 (m, 5H), 8.22 (dd, J=1.6, 8.2 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 124.9 (d), 125.7 (d), 128.2 (d), 130.0 (d), 130.1 (d, 2C), 130.9 (s), 133.4 (d), 135.9 (d, 2C), 139.4 (s), 144.9 (s) ppm; MALDI–MS (m/z): 232.0417 $[M+1]^+$.

*4.3.2. 2-[(2-Nitrophenyl)sulfanyl]pyridine (**7ab**).* Yellow solid; R_f (15% EtOAc/pet. ether) 0.2; mp: 74–75 °C; IR ($CHCl_3$) ν: 1592, 1562, 1463, 1377, 1150, 968, 722 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.25–7.31 (m, 2H), 7.35–7.47 (m, 1H), 7.41 (dd, J=1.7, 6.9 Hz, 1H), 7.52 (dt, J=1.0, 7.9 Hz, 1H), 7.73 (dt, J=1.9, 7.7 Hz, 1H), 8.15 (d, J=1.7, 8.0 Hz, 1H), 8.59–8.62 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 122.9 (d), 125.4 (d), 126.8 (d), 127.6 (d), 131.6 (d), 133.1 (d), 133.4 (s), 137.6 (d), 147.6 (s), 150.7 (d), 155.4 (s) ppm; ESIMS (m/z): 255.2525 $[M+Na]^+$.

*4.3.3. 2-(2-Nitrophenylthio)benzo[d]thiazole (**7ac**)[22b].* Yellow solid; R_f (100% pet. ether) 0.2; mp: 108–109 °C (lit. 111–113 °C); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.35–7.46 (m, 3H), 7.48–7.59 (m, 2H), 7.85–7.90 (m, 1H), 8.06–8.11 (m, 1H), 8.20–8.25 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 121.6 (d), 123.7 (d), 125.7 (d), 126.3 (d), 126.8 (d), 127.5 (d), 130.7 (d), 133.2 (s), 133.9 (d), 137.6 (s), 146.6 (s), 153.6 (s), 160.9 (s) ppm; MALDI–MS (m/z): 289.0117 $[M+1]^+$.

*4.3.4. 1-Dodecylthio-2-nitrobenzene (**7ad**).* Yellow solid; R_f (100% pet. ether) 0.2; mp: 35–36 °C; IR ($CHCl_3$) ν: 1582, 1460, 1376, 1338, 1091, 852, 722, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J=6.5 Hz, 3H), 1.26 (m, 16H), 1.42–1.48 (m, 2H), 1.67–1.78 (m, 2H), 2.95 (t, J=7.4, 2H), 7.19 (m, 1H), 7.39–7.43 (m, 1H), 7.51–7.60 (m, 1H), 8.20 (dd, J=1.4, 8.3 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 27.8 (t), 29.1 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2c), 31.9 (t), 32.3 (t), 124.2 (d), 126.1 (d), 126.5 (d), 133.3 (d), 138.3 (s), 145.9 (s) ppm; MALDI–MS (m/z): 346.1821 $[M+Na]^+$. Anal. Calcd for $C_{18}H_{29}NO_2S$: C, 66.83; H, 9.04; N, 4.33. Found: C, 66.79; H, 9.11; N, 4.26.

*4.3.5. 4-Nitrophenyl phenyl sulfide (**7ca**)[22c].* Brown solid; R_f (100% pet. ether) 0.2; mp: 52–53 °C (lit. 54–55 °C); IR ($CHCl_3$) ν: 1593, 1575, 1475, 1338, 1111, 1083, 1024, 852, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.12–7.19 (m, 2H), 7.43–7.56 (m, 5H), 8.02–8.09 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 124.0 (d, 2C), 126.6 (d, 2C), 129.7 (d), 130.0 (d, 2C), 130.3 (s), 134.7 (d, 2C), 145.3 (s), 148.5 (s) ppm; MALDI–MS (m/z): 232.0432 $[M+1]^+$.

*4.3.6. 2-[(4-Nitrophenyl)sulfanyl]pyridine (**7cb**)[22d].* Brown solid; R_f (15% EtOAc/pet. ether) 0.4; mp: 83–84 °C (lit. 84–85 °C); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.18 (ddd, J=1.1, 4.9, 7.5 Hz, 1H), 7.29 (dt, J=0.9, 8.0 Hz, 1H), 7.54–7.67 (m, 3H), 8.13–8.20 (m, 2H), 8.50 (d, J=4.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 121.9 (d), 124.0 (d, 2C), 124.8 (d), 131.6 (d, 2C), 137.3 (d), 142.3 (s), 146.7 (s), 150.3 (d), 156.9 (s) ppm; ESIMS (m/z): 233.1128 $[M+1]^+$.

*4.3.7. 2-(4-Nitrophenylthio)benzo[d]thiazole (**7cc**)[22b].* Yellow solid; R_f (100% pet. ether) 0.2; mp: 94–95 °C (lit. 95–96 °C); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.34–7.38 (m, 1H), 7.43 (dd, J=1.5, 5.6 Hz, 1H), 7.48–7.53 (m, 1H), 7.75–7.80 (m, 2H), 7.94–7.99 (m, 1H), 8.21–8.28 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 121.2 (d), 122.8 (d), 124.5 (d, 2C), 125.5 (d), 126.6 (d), 132.6 (d, 2C), 136.2 (s), 140.0 (s), 147.8 (s), 153.4 (s), 162.7 (s) ppm; MALDI–MS (m/z): 289.0096 $[M+1]^+$.

*4.3.8. 1-Dodecylthio-4-nitrobenzene (**7cd**)[17e].* Yellow solid; R_f (100% pet. ether) 0.2; mp: 48–49 °C (lit. 49.5–50.5 °C); IR ($CHCl_3$) ν: 1595, 1582, 1519, 1460, 1376, 1338, 1182, 1091, 972, 852, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.86 (t, J=6.4 Hz, 3H), 1.24 (br s, 16H), 1.37–1.47 (m, 2H), 1.63–1.74 (m, 2H), 3.0 (t, J=7.3 Hz, 2H), 7.25–7.33 (m, 2H), 8.07–8.14 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 28.4 (t), 28.8 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t, 2C), 123.9 (d, 2C), 125.9 (d, 2C), 144.8 (s), 148.2 (s) ppm; MALDI–MS (m/z): 324.1980 $[M+1]^+$.

*4.3.9. 2-Nitro-4-trifluoromethylphenyl phenyl sulfide (**7da**)[18g].* Yellow solid; R_f (100% pet. ether) 0.3; mp: 67–68 °C; IR ($CHCl_3$) ν: 1620, 1562, 1530, 1478, 1441, 1325, 1159, 1086, 910, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 6.96 (d, J=8.7 Hz, 1H), 7.52–7.63 (m, 6H), 8.55 (d, J=1.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 122.9 (d, J=272.2 Hz), 123.1 (q, J=4.0 Hz), 127.3 (d, J=34.5 Hz), 128.9 (d), 129.4 (q, J=3.4 Hz), 129.7 (s), 130.5 (d, 2C), 130.7 (d), 136.0 (d, 2C), 144.2 (s), 144.6 (s) ppm; ESIMS (m/z): 330.2256 $[M+1]^+$. Anal. Calcd for $C_{19}H_{28}F_3NO_2S$: C, 58.29; H, 7.21; N, 3.58. Found: C, 58.21; H, 7.26; N, 3.53.

*4.3.10. 2-Nitro-4-trifluoromethylphenyl 2-pyridinyl sulfide (**7db**)[18g].* Yellow solid; R_f (15% EtOAc/pet. ether) 0.3; mp: 91–92 °C (lit. 90–92 °C); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.30–7.39 (m, 2H), 7.59–7.65 (m, 2H), 7.79 (dt, J=1.9, 7.7 Hz, 1H), 8.43 (d, J=1.7 Hz, 1H), 8.64–8.67 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 122.8 (d, J=272.3 Hz), 122.9 (q, J=4.0 Hz), 123.8 (d), 128.7 (d, J=34.4 Hz), 128.9 (d), 129.3 (q, J=3.5 Hz), 131.1 (d), 138.1 (d), 146.2 (s), 151.3 (d), 153.8 (s) ppm; MALDI–MS (m/z): 301.0262 $[M+1]^+$.

*4.3.11. 2-((2-Nitro-4-(trifluoromethyl)phenyl)thio)benzo[d]thiazole (**7dc**)[22e].* White solid; R_f (100% pet. ether) 0.3; mp: 80–81 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.50–7.54 (m, 2H), 7.57–7.61 (m, 1H), 7.67 (dd, J=1.7, 8.6 Hz, 1H), 7.93 (br dd, J=1.2, 8.1 Hz, 1H), 8.13 (br d, J=8.3 Hz, 1H), 8.52 (d, J=1.1 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 121.2 (s, CF_3), 121.7 (d), 123.1 (q, J=3.9 Hz), 124.0 (d), 126.8 (d), 127.1 (d), 129.4 (d, J=34.7 Hz), 130.1 (q, J=3.3 Hz), 130.3 (d), 137.8 (s),

139.2 (s), 145.3 (s), 153.7 (s), 158.5 (s) ppm; MALDI–MS (*m*/*z*): 356.9994 $[M+1]^+$.

*4.3.12. 1-Dodecylthio-2-Nitro-4-trifluoromethylbenzene (**7dd**).* Yellow solid; R_f (100% pet. ether) 0.3; mp: 47–48 °C; IR ($CHCl_3$) ν: 1620, 1561, 1527, 1467, 1329, 1295, 1248, 1181, 1136, 1089, 1056, 911, 828, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.86 (t, J=6.5 Hz, 3H), 1.25 (br s, 16H), 1.42–1.52 (m, 2H), 1.68–1.83 (m, 2H), 2.98 (t, J=7.4 Hz, 2H), 7.51 (d, J=6.6 Hz, 1H), 7.72–7.77 (m, 1H), 8.48 (br s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.7 (t), 27.6 (t), 29.0 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t), 32.4 (t), 123.0 (d, J=272.2 Hz), 123.5 (q, J=4.0 Hz), 126.6 (d, J=34.7 Hz), 127.0 (d), 129.4 (q, J=3.3 Hz), 143.6 (s), 145.2 (s) ppm; ESIMS (*m*/*z*): 392.1818 $[M+1]^+$. Anal. Calcd for $C_{19}H_{28}F_3NO_2S$: C, 58.29; H, 7.21; N, 3.58. Found: C, 58.21; H, 7.26; N, 3.53.

*4.3.13. 5-Methyl-2-nitrophenyl phenyl sulfide (**7ea**).* Yellow solid; R_f (100% pet. ether) 0.3; mp: 89–90 °C; IR ($CHCl_3$) ν: 1577, 1460, 1377, 1217, 1158, 1018, 824, 722 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.19 (s, 3H), 6.59 (d, J=1.6 Hz, 1H), 6.98 (dd, J=1.5, 8.5 Hz, 1H), 7.44–7.60 (m, 5H), 8.12 (d, J=8.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6 (q), 125.8 (d), 125.9 (d), 128.3 (d), 129.9 (d), 130.0 (d, 2C), 131.0 (s), 135.8 (d, 2C), 139.4 (s), 142.1 (s), 144.8 (s) ppm; ESIMS (*m*/*z*): 268.0926 $[M+Na]^+$. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.57; H, 4.49; N, 5.67.

*4.3.14. 5-Methyl-2-nitrophenyl 2-pyridinyl sulfide (**7eb**).* Brown solid; R_f (15% EtOAc/pet. ether) 0.2; mp: 62–63 °C; IR ($CHCl_3$) ν: 1574, 1520, 1451, 1338, 1216, 1116, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.30 (s, 3H), 7.11–7.16 (m, 1H), 7.24–7.31 (m, 1H), 7.52 (dt, J=1.0, 7.8 Hz, 1H), 7.61–7.64 (m, 1H), 7.72 (dt, J=1.9, 7.7 Hz, 1H), 8.06 (d, J=8.4 Hz, 1H), 8.59–8.63 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.9 (q), 121.1 (d), 122.7 (d), 125.6 (d), 127.6 (d), 127.8 (d), 137.6 (d), 144.5 (s), 145.6 (s), 150.7 (d), 155.8 (s), 158.9 (s) ppm; ESIMS (*m*/*z*): 269.0455 $[M+Na]^+$. Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.46; H, 4.17; N, 11.24.

*4.3.15. 2-(5-Methyl-2-nitrophenylthio)benzo[d]thiazole (**7ec**).* Yellow solid; R_f (100% pet. ether) 0.3; mp: 118–119 °C; IR ($CHCl_3$) ν: 1712, 1582, 1464, 1377, 1166, 1075, 975, 723 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.30 (s, 3H), 7.15–7.21 (m, 2H), 7.42–7.59 (m, 2H), 7.85–7.90 (m, 1H), 8.07–8.15 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.7 (q), 121.5 (d), 123.6 (d), 125.8 (d), 126.1 (d), 126.7 (d), 128.4 (d), 130.8 (d), 132.9 (s), 137.5 (s), 144.5 (s), 145.5 (s), 153.6 (s), 161.2 (s) ppm; ESIMS (*m*/*z*): 324.99 $[M+Na]^+$. Anal. Calcd for $C_{14}H_{10}N_2O_2S_2$: C, 55.61; H, 3.33; N, 9.26. Found: C, 55.53; H, 3.26; N, 9.19.

*4.3.16. 1-Dodecylthio-5-methyl-2-nitrobenzene (**7ed**).* Yellow solid; R_f (100% pet. ether) 0.2; mp: 51–52 °C; IR ($CHCl_3$) ν: 1596, 1513, 1459, 1377, 1335, 1219, 1114, 823, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.87 (t, J=6.5 Hz, 3H), 1.25 (br s, 16H), 1.42–1.52 (m, 2H), 1.66–1.77 (m, 2H), 2.42 (s, 3H), 2.93 (d, J=7.3 Hz, 2H), 7.0 (dd, J=1.6, 8.5 Hz, 1H), 7.14 (br s, 1H), 8.11 (d, J=8.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 21.7 (q), 22.7 (t), 27.8 (t), 29.1 (t), 29.2 (t), 29.3 (t), 29.44 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t), 32.3 (t), 125.2 (d), 126.2 (d), 126.6 (d), 138.5 (s), 143.9 (s), 144.6 (s) ppm; ESIMS (*m*/*z*): 360.14 $[M+Na]^+$. Anal. Calcd for $C_{19}H_{31}NO_2S$: C, 67.61; H, 9.26; N, 4.15. Found: C, 67.53; H, 9.31; N, 4.06.

*4.3.17. 1-Dodecylthio-4-iodo-2-nitrobenzene (**7fd**).* Yellow solid; R_f (100% pet. ether) 0.3; mp: 60–61 °C; IR ($CHCl_3$) ν: 1580, 1538, 1463, 1377, 1333, 1249, 1168, 1054, 812, 718 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.87 (t, J=6.5 Hz, 3H), 1.24 (br s, 16H), 1.39–1.49 (m, 2H), 1.64–1.75 (m, 2H), 2.91 (t, J=7.4 Hz, 2H), 7.11 (d, J=8.6 Hz, 1H), 7.78 (dd, J=2.0, 8.6 Hz, 1H), 8.48 (d, J=2.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 27.6 (t), 29.0 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t), 32.3 (t), 86.4 (s), 128.0 (d), 134.5 (d), 138.5 (s), 141.9 (d), 146.2 (s) ppm. Anal. Calcd for $C_{18}H_{28}INO_2S$: C, 48.11; H, 6.28; N, 3.12. Found: C, 48.03; H, 6.36; N, 3.06.

*4.3.18. 1-Dodecylthio-4-nitro-2-trifluoromethylbenzene (**7gd**).* Yellow solid; R_f (100% pet. ether) 0.2; mp: 40–41 °C; IR ($CHCl_3$) ν: 1605, 1584, 1523, 1465, 1349, 1283, 1174, 1039, 917, 890, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.86 (t, J=6.5 Hz, 3H), 1.24 (br s, 16H), 1.43–1.50 (m, 2H), 1.67–1.78 (m, 2H), 3.06 (t, J=7.4 Hz, 2H), 7.46 (d, J=8.9 Hz, 1H), 8.27 (dd, J=2.5, 8.9 Hz, 1H), 8.45 (d, J=2.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.7 (t), 28.0 (t), 28.8 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t), 32.6 (t), 122.6 (d, J=274.5 Hz), 122.3 (q, J=6.0 Hz), 126.2 (d), 126.8 (d), 128.0 (d, J=32.4 Hz), 144.0 (s), 148.0 (s) ppm; ESIMS (*m*/*z*): 392.1891 $[M+1]^+$. Anal. Calcd for $C_{19}H_{28}F_3NO_2S$: C, 58.29; H, 7.21; N, 3.58. Found: C, 58.23; H, 7.28; N, 3.51.

*4.3.19. 3-Nitro-4-(pyridin-2-ylthio)benzonitrile (**7hb**).* Yellow solid; R_f (15% EtOAc/pet. ether) 0.2; mp: 131–132 °C; IR ($CHCl_3$) ν: 2233, 1716, 1573, 1512, 1458, 1377, 1291, 1155, 1051, 904, 767 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.30 (d, J=8.6 Hz, 1H), 7.42 (ddd, J=1.2, 4.8, 7.5 Hz, 1H), 7.60–7.70 (m, 2H), 7.85 (dt, J=1.9, 7.7 Hz, 1H), 8.49 (d, J=1.8 Hz, 1H), 8.68–8.72 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 109.7 (s), 116.5(s), 124.2 (d), 129.3 (d), 129.4 (d), 130.8 (d), 135.1 (d), 138.3 (d), 142.1 (s), 145.8 (s), 151.5 (d), 153.0 (s) ppm; ESIMS (*m*/*z*): 330.2256 $[M+1]^+$. Anal. Calcd for $C_{12}H_7N_3O_2S$: C, 56.02; H, 2.74; N, 16.33. Found: C, 55.91; H, 2.79; N, 16.21.

*4.3.20. 4-(n-Dodecylthio)-3-nitrobenzonitrile (**7hd**).* Yellow solid; R_f (5% EtOAc/pet. ether) 0.2; mp: 108–109 °C; IR ($CHCl_3$) ν: 2234, 1715, 1520, 1463, 1377, 1346, 1269, 1112, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.86 (t, J=6.5 Hz, 3H), 1.25 (br s, 16H), 1.40–1.52 (m, 2H), 1.68–1.80 (m, 2H), 2.98 (t, J=7.4 Hz, 2H), 7.49 (d, J=8.6 Hz, 1H), 7.75 (dd, J=1.9, 8.5 Hz, 1H), 8.51 (d, J=1.9 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.7 (t), 27.4 (t), 29.0 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.9 (t), 32.4 (t), 107.7 (s), 116.8 (s), 127.1 (d), 129.9 (d), 135.2 (d), 145.5 (s) ppm; ESIMS (*m*/*z*): 349.07 $[M+1]^+$. Anal. Calcd for $C_{19}H_{28}N_2O_2S$: C, 65.48; H, 8.10; N, 8.04. Found: C, 65.51; H, 8.01; N, 7.93.

*4.3.21. 2-[(4-Nitrobenzyl)sulfanyl]pyridine (**7ib**)[22d].* Yellow solid; R_f (15% EtOAc/pet. ether) 0.3; mp: 63–64 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 4.49 (s, 2H), 7.0 (ddd, J=1.1, 5.0, 7.3 Hz, 1H), 7.15 (dt, J=1.0, 8.1 Hz, 1H), 7.47 (ddd, J=1.9, 7.4, 9.3 Hz, 1H), 7.52–7.59 (m, 2H), 8.08–8.15 (m, 2H), 8.41–8.45 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 33.2 (t), 120.0 (d), 122.3 (d), 123.6 (d, 2C), 129.8 (d, 2C), 136.1 (d), 146.6 (s), 146.9 (s), 149.4 (d), 157.1 (s) ppm; ESIMS (*m*/*z*): 247.3450 $[M+1]^+$. Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.43; H, 4.13; N, 11.29.

*4.3.22. n-Dodecyl p-nitrobenzyl sulfide (**7id**)[22h].* White solid; R_f (100% pet. ether) 0.2; mp: 38–39°C(lit. 31–33 °C); IR ($CHCl_3$) ν: 1606, 1526, 1459, 1376, 1346, 1109, 858, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.86 (t, J=6.5 Hz, 3H), 1.23 (br s, 18H), 1.40–1.53 (m, 2H), 2.35–2.45 (m, 2H), 3.75 (s, 2H), 7.43–7.50 (m, 2H), 8.13–8.20 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 28.8 (t), 29.7 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2C), 31.6 (t), 31.9 (t), 35.8 (d), 123.7 (d, 2C), 129.6 (d, 2C), 146.6 (s) ppm. Anal. Calcd for $C_{19}H_{31}NO_2S$: C, 67.61; H, 9.26; N, 4.15. Found: C, 67.53; H, 9.31; N, 4.06.

*4.3.23. 2-(2-Pyridyl)quinoline (**7jb**)[22f].* Colorless oil; R_f (10% EtOAc/pet. ether) 0.2; IR ($CHCl_3$) ν: 1615, 1588, 1572, 1556, 1448, 1418, 1295, 1120, 1095, 941, 818, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.18 (ddd, J=2.0, 4.9, 6.8 Hz, 1H), 7.40 (d, J=8.6 Hz, 1H), 7.48 (ddd, J=1.2, 7.0, 8.1 Hz, 1H), 7.57–7.71 (m, 3H), 7.74 (d, J=1.3, 8.0 Hz, 1H),

7.96–8.02 (m, 2H), 8.53–8.57 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 122.0 (d), 122.7 (d), 126.4 (d), 126.5 (d), 126.7 (d), 127.5 (d), 128.7 (d), 129.9 (d), 136.6 (d), 137.0 (d), 148.3 (s), 150.2 (d), 156.3 (s), 157.6 (s) ppm; MALDI–MS (m/z): 239.0616 $[M+1]^+$. Anal. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.76. Found: C, 70.61; H, 4.16; N, 11.68.

*4.3.24. 2-[n-Dodecylmercapto]-quinoline (**7jd**)*[22g]. Colorless oil; R_f (100% pet. ether) 0.3; IR ($CHCl_3$) ν: 1614, 1594, 1497, 1465, 1376, 1294, 1137, 1088, 814, 779, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J=6.5 Hz, 3H), 1.25 (br s, 16H), 1.41–1.51 (m, 2H), 1.70–1.81 (m, 2H), 3.33 (t, J=7.3 Hz, 2H), 7.18 (d, J=8.7 Hz, 1H), 7.38 (ddd, J=1.2, 7.1, 8.1 Hz, 1H), 7.57–7.69 (m, 2H), 7.82 (d, J=8.7 Hz, 1H), 7.90–7.94 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 29.0 (t), 29.2 (t), 29.3 (t, 2C), 29.5 (t), 29.6 (t, 2C), 29.6 (t), 29.7 (t), 31.9 (t), 121.0 (d), 125.0 (d), 125.8 (s), 127.5 (d), 128.0 (d), 129.4 (d), 135.0 (d), 148.3 (s), 159.6 (s) ppm; MALDI–MS (m/z): 330.2256 $[M+1]^+$. Anal. Calcd for $C_{21}H_{31}NS$: C, 76.54; H, 9.48; N, 4.25. Found: C, 76.61; H, 9.43; N, 4.17.

*4.3.25. 4-Methoxyphenyl phenyl sulfide (**7ka**).* Colorless oil; R_f (100% pet. ether) 0.3; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.82 (s, 3H), 6.86–6.93 (m, 2H), 7.09–7.28 (m, 5H), 7.38–7.46 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): δ 55.3 (q), 115.0 (d, 2C), 124.2 (s), 125.7 (d), 128.2 (d, 2C), 128.9 (d, 2C), 135.4 (d, 2C), 138.6 (s), 159.8 (s) ppm.

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Supplementary data

Supporting information available: NMR spectra of representative compounds. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.07.032. These data include MOL files and InChIKeys of the most important compounds described in this article.

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