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Depropargylation under palladium–copper catalysis: synthesis of diaryl sulfides

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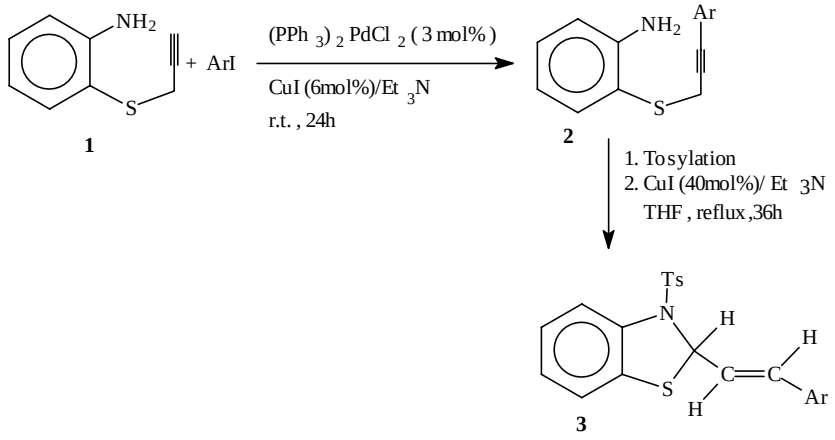
Abstract—3-[2-(*N*-*p*-Toluenesulfonyl)aminophenylthio]prop-1-yne, reacted with aryl iodides in the presence of Et_3N in THF solution with $(PPh_3)_2PdCl_2$ (3 mol%) and CuI (40 mol%) at room temperature for 8 h followed by reflux for 20 h to yield diaryl sulfides by a depropargylation and *S*-arylation reaction. © 2001 Elsevier Science Ltd. All rights reserved.

Palladium-catalysed reactions[1] have been of great significance for carbon–carbon bond formation and have been extremely useful for both carboannulation[2] and heteroannulation[3] processes. We have utilised palladium–copper catalysed reactions of terminal alkynes[4] for the synthesis of various heterocyclic structures of biological interest, e.g. benzofurans,[5] phthalides,[6] quinolines and quinolones,[7] isoindolinones,[8] flavanones,[9] benzodioxans,[10] benzodioxepinones,[11] benzoxazepinones,[11] and benzoxazines.[12] In that connection, we have recently developed[13] a novel method for the synthesis of benzothiazolines **3** by a two-step procedure, e.g. (i) carbon–carbon bond formation with bis(triphenylphosphine)palladium(II) chloride (3 mol%) and cuprous iodide (6 mol%) and (ii) cyclisation with copper(I) iodide (40 mol%) (Scheme 1).

In order to explore the possibility of the synthesis of benzothiazolines in a single-step operation, we reacted the tosylate **4** with various aryl iodides under palladium–copper catalysed conditions and were surprised to find that **4** underwent smooth depropargylation and concurrent *S*-arylation leading to a number of diaryl sulfides in excellent yields. In this report, we describe a detailed investigation on this unusual depropargylation reaction.[14]



Scheme 1.

Keywords: palladium–copper catalysis; depropargylation; *S*-arylation.

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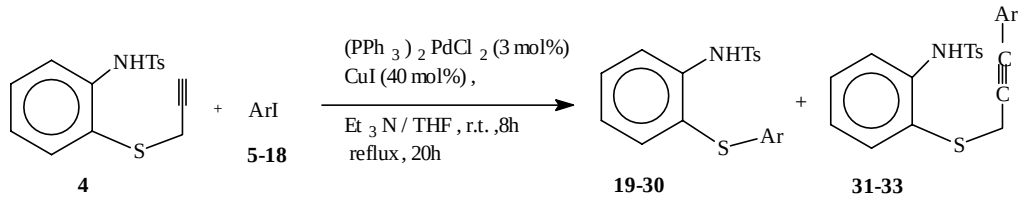
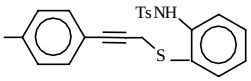


Ar

5, 19, C_6H_5
6, 20, C_6H_4Me-*p*
7, 21, C_6H_4Me-*o*
8, 22, 1-naphthyl
9, 23, 2-naphthyl
10, 24, C_6H_4Cl-*m*
11, 25, $C_6H_4CO_2Me$-*o*
12, 26, C_6H_4MeO-*o*
13, 27, 31, C_6H_4MeO-*p*
14, 28, 2, 4- dimethoxypyrimidin-5-yl
15, 32, 2-thienyl
16, 29, 5-iodothienyl
17, 30, 2-iodophenyl
18, 4-iodophenyl

33, Ar =



Scheme 2.

1. Results and discussion

The terminal alkyne, 3-[2-(*N*-*p*-toluenesulfonyl)amino-phenylthio]prop-1-yne, **4** reacted with the aryl iodides **5**–**18** in the presence of triethylamine in THF solution with 3 mol% of $(PPh_3)_2PdCl_2$ and 40 mol% of CuI at room temperature for 8 h followed by reflux for 20 h.

It was observed that instead of the expected *C*-arylation at the terminal alkyne group, carbon–sulfur bond scission took place followed by arylation at the sulfur atom leading to a number of substituted diaryl sulfides **19**–**30** in excellent yields (Scheme 2 and Table 1).

It is to be noticed from Table 1 that in most of the cases (entries 1–8, 10, 12 and 13), the diarylsulfides were the only products and the yields were very comparable (54–66%). However, when *p*-anisyliodide was used (entry 9) a mixture (3:1) of diaryl sulfide **27** and the disubstituted alkyne **31** was obtained. Again, with 2-iodothiophene 15 (entry 11) and 1,4-diiodobenzene (entry 14), no depropargylation was observed, only the expected *C*-arylated products **32** and **33** were obtained, respectively.

The reactions were usually carried out in THF as solvent when cleaner products were obtained. The use of CH_3CN as solvent led to lower yields (30%) whereas when DMF was used as the solvent, very poor yields (12%) of diarylsulfides were obtained due to the formation of considerable amounts of polymeric materials.

The optimum condition for the reaction was found to be stirring at room temperature for 8 h followed by 20 h of reflux. The reflux in THF was found to be essential since no diaryl sulfides were obtained when the reactions were carried out either at room temperature or at 60°C for 48 h.

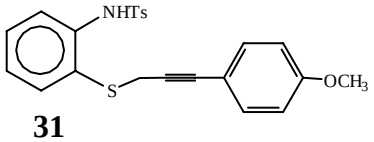
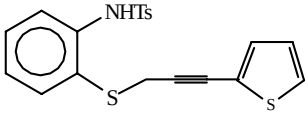
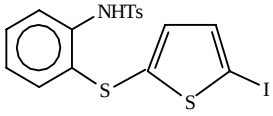
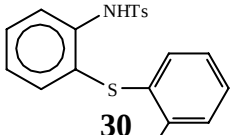
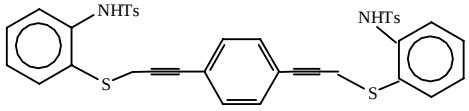
1.1. Role of catalyst, co-catalyst and base

Both bis(triphenylphosphine)palladium(II) chloride (3 mol%) and cuprous iodide (40 mol%) were found to be essential for the depropargylation reaction (Table 2). In the absence of either of these two, neither any depropargylation nor any *C*-arylation at the acetylenic moiety took place (entries 5 and 6), only the starting material was recovered. It was noticed that 40 mol% of CuI gave the optimum yield (entry 1, Table 2). The use of less CuI gave lower yields (entries 2–4, Table 2). We have also explored $(PPh_2)_4Pd$ (3 mol%) and $Pd(OAc)_2$ (3 mol%) with PPh_3 (6 mol%) as depropargylating agent, but got lower yields of the diaryl sulfides (entries 8 and 9). Similarly, Et_3N (4 equiv.) was found to be the base of choice. In its absence, no diaryl sulfides were obtained (entry 7). Also, the use of other bases, e.g. K_2CO_3 (4 equiv.) or NaOAc (4 equiv.) gave lower yields of the diaryl sulfides (entries 10 and 11).

1.2. Structural requirements in the propargyl compound 4

We have already shown that in the reaction of **4** with aryl iodides, in most of the cases, depropargylation took place (Table 1). We then explored the structural requirements in the S-propargylated compound **4** and the results are shown in Table 3. As can be seen from Table 3, the presence of a *N*-*p*-tosylamino group at the ortho-position to the S-propargyl group in the benzene ring is essential for the depropargylation reaction. The absence of the tosylamino group led to normal arylation at the terminal –C≡CH group (entry 1). Similarly, the presence of a free amino (entry 2), NH–Me (entry 4), and NH–Bn (entry 5) at *ortho*-position to the S-propargyl group led to normal arylation at the terminal alkyne moiety. It is interesting to note that when a non-terminal alkyne, e.g. compound **37** was treated with aryl iodide **12**, $(PPh_3)_2PdCl_2$ (3 mol%),

Table 1. Palladium–copper catalysed depropargylation of **4** with subsequent *S*-arylation leading to the diaryl sulfides **19**–**30** (Scheme 2)

Entry	Aryl iodides (ArI) Ar	Products	Yields (%)[a]
1	C_6H_5 (**5**)	**19**	61
2	C_6H_4Me-*p* (**6**)	**20**	56
3	C_6H_4Me-*o* (**7**)	**21**	62
4	1-Naphthyl (**8**)	**22**	63
5	2-Naphthyl (**9**)	**23**	54
6	C_6H_4Cl (m) (**10**)	**24**	62
7	$C_6H_4CO_2Me$-(*o*) (**11**)	**25**	64
8	C_6H_4OMe-(*o*) (**12**)	**26**	66
9	C_6H_4OMe-(*p*) (**13**)	**27** +  **31**	56(3:1)
10	2,4-Dimethoxypyrimidin-5-yl (**14**)	**28**	54
11	2-Thienyl (**15**)	 **32**	59
12	5-Iodothienyl (**16**)	 **29**	55
13	2-Iodophenyl (**17**)	 **30**	49
14	4-Iodophenyl (**18**)	 **33**	43

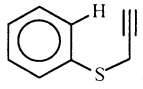
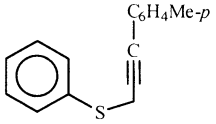
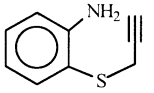
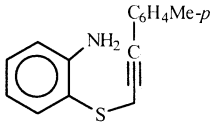
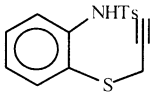
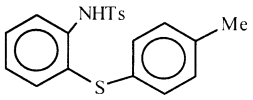
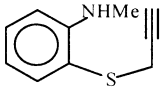
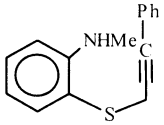
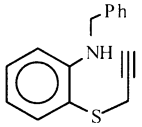
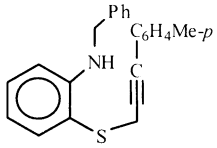
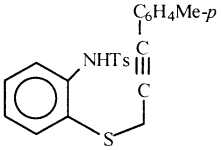
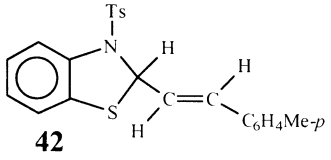
All reactions were carried out with $(PPh_3)_2PdCl_2$ (3 mol%), CuI (40 mol%) and Et_3N (4 equiv.) in THF at room temperature for 8 h followed by reflux for 20 h.
[a] Yields are based on **4**.

Table 2. Effects of catalyst, co-catalyst and base on the depropargylation and S-arylation of 4-iodotoluene **6** under palladium–copper catalysis leading to **20** (Scheme 2)

Entry	Pd cat.	CuI (mol%)	Base	Yield of diaryl sulfide 20 (%)
1	$(PPh_3)_2PdCl_2$ (3 mol%)	40	Et_3N (4 equiv.)	56
2	$(PPh_3)_2PdCl_2$ (3 mol%)	30	Et_3N (4 equiv.)	20
3	$(PPh_3)_2PdCl_2$ (3 mol%)	20	Et_3N (4 equiv.)	15
4	$(PPh_3)_2PdCl_2$ (3 mol%)	10	Et_3N (4 equiv.)	5
5	–	40	Et_3N (4 equiv.)	0
6	$(PPh_3)_2PdCl_2$ (3 mol%)	–	Et_3N (4 equiv.)	0
7	$(PPh_3)_2PdCl_2$ (3 mol%)	40	–	0
8	$(PPh_3)_4Pd$, (3mol%)	40	Et_3N (4 equiv.)	31
9	$Pd(OAc)_2$: (3 mol%) PPh_3: (6 mol%)	40	Et_3N (4 equiv.)	28
10	$(PPh_3)_2PdCl_2$ (3 mol%)	40	K_2CO_3 (4 equiv.)	15
11	$(PPh_3)_2PdCl_2$ (3 mol%)	40	NaOAc (4 equiv.)	10

Reactions were carried out in THF at room temperature for 8 h and then at reflux for 20 h.

Table 3. Effect of substituents present at the ortho position of the phenyl ring of S-propargylated compound **4** on the depropargylation reaction

Entry	Substrate	Aryl iodides (Ar)	Products	Yield (%)
1.	 **34**	*p*-Tolyl, **6**	 **38**	63
2.	 **1**	*p*-Tolyl, **6**	 **39**	59
3.	 **4**	*p*-Tolyl, **6**	 **20**	56
4.	 **35**	Phenyl, **5**	 **40**	68
5.	 **36**	*p*-Tolyl, **6**	 **41**	66
6.	 **37**	*o*-Anisyl, **12**	 **42**	63

Reactions were carried out with $(PPh_3)_2PdCl_2$ (3 mol%), CuI (40 mol%) and Et_3N (4 equiv.) in THF at room temperature for 8 h followed by reflux for 20 h.

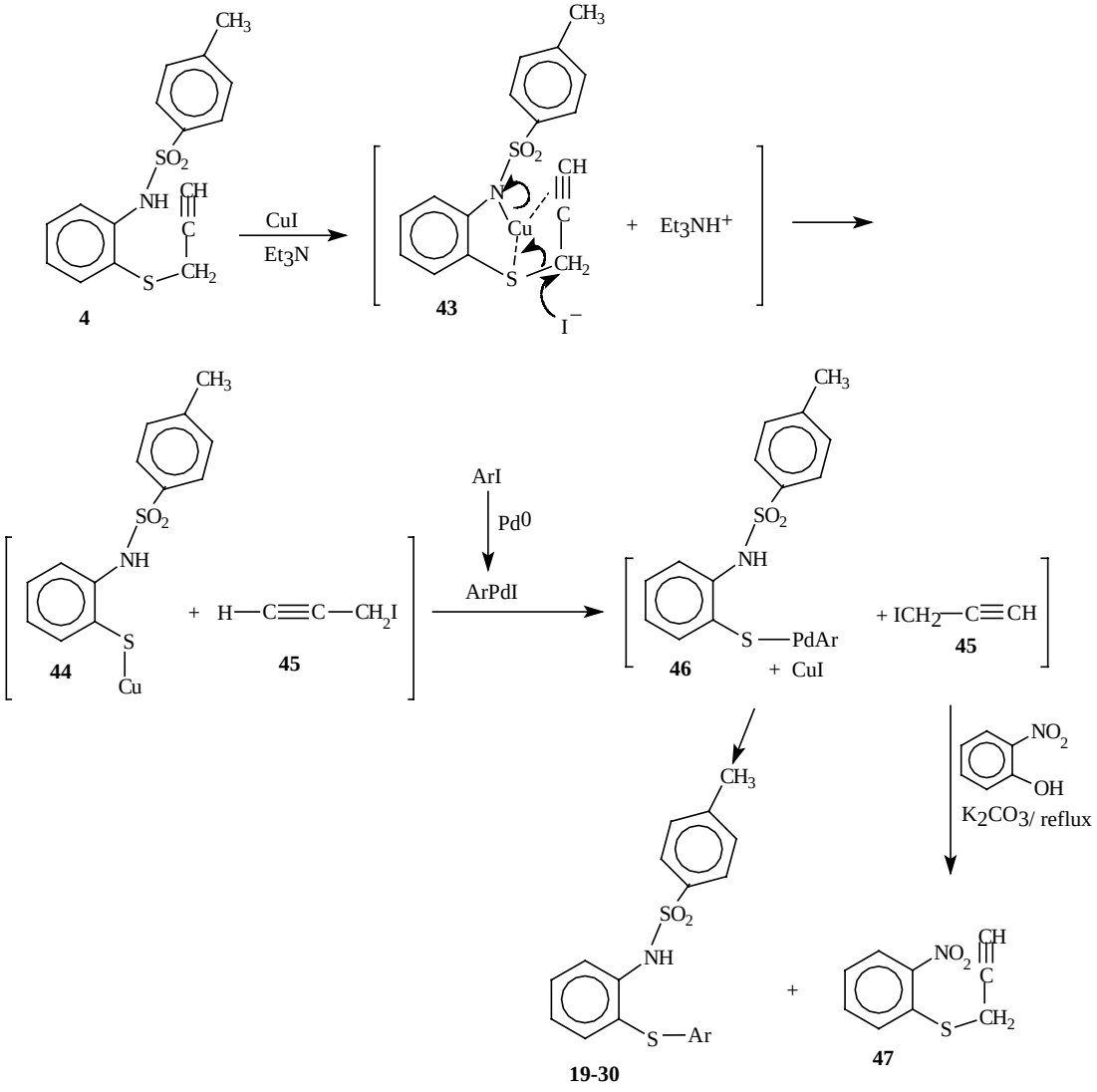
CuI (40 mol%) and Et_3N in THF under reflux, cyclisation leading to the thiazoline derivative **42** took place (entry 6, Table 3).[15]

1.3. Characterisation of products

The products were fully characterised from their IR, ^1H NMR, ^{13}C NMR (together with DEPT experiments) data and elementary analyses. Mass spectral analysis and X-ray diffraction experiment confirmed the structure of the product. IR absorption peaks at 3278.8 and 3236.3 cm^{-1} indicated the presence of a terminal acetylenic moiety and a –NH group in compound **4** whereas the absorption peaks corresponding to terminal acetylenic hydrogen (≡C–H) was absent in the IR spectra of the products **19**–**30**. In the ^1H NMR of compound **4**, a triplet at δ 2.19 (J=3 Hz) and a doublet at δ 3.17 (J=3 Hz) corresponded to C≡C*H* and S–CH_2 protons, respectively, whereas no signals corresponding to methylenic protons or for the C≡C*H* were observed in the products **19**–**30**. The methylenic carbon and acetylenic carbons of compound **4** appeared at δ 24.6, δ 72.42 and δ 78.85. These peaks were not observed in the ^{13}C NMR spectra of the products **19**–**30**. Mass spectral data of compound **20** [M^+ ion peak at 369.3] provided additional support in favour of the diaryl sulfide structure. Finally the X-ray diffraction experiment[16] carried out on **20** confirmed the structure of the product. The structures of compounds **31**, **32** and **33** were established from IR, ^1H–, ^{13}C NMR and elemental analyses (see Section 3).

1.4. Mechanism

It appears in the reaction of the alkyne **4** with aryl iodides in the presence of Pd-catalyst and CuI as co-catalyst, the normal *C*-arylation at the terminal alkyne does not take place due to either steric hindrance due to the tosyl amino group or because of complexation of CuI with the S-atom, N-atom and the triple bond giving rise to an intermediate **43** which could break down to **44** and the propargyl iodide **45** (Scheme 3). The transmetallation of **44** with ArPdI (generated from Pd-catalyst and ArI)[4] would lead to **46** which on



Scheme 3.

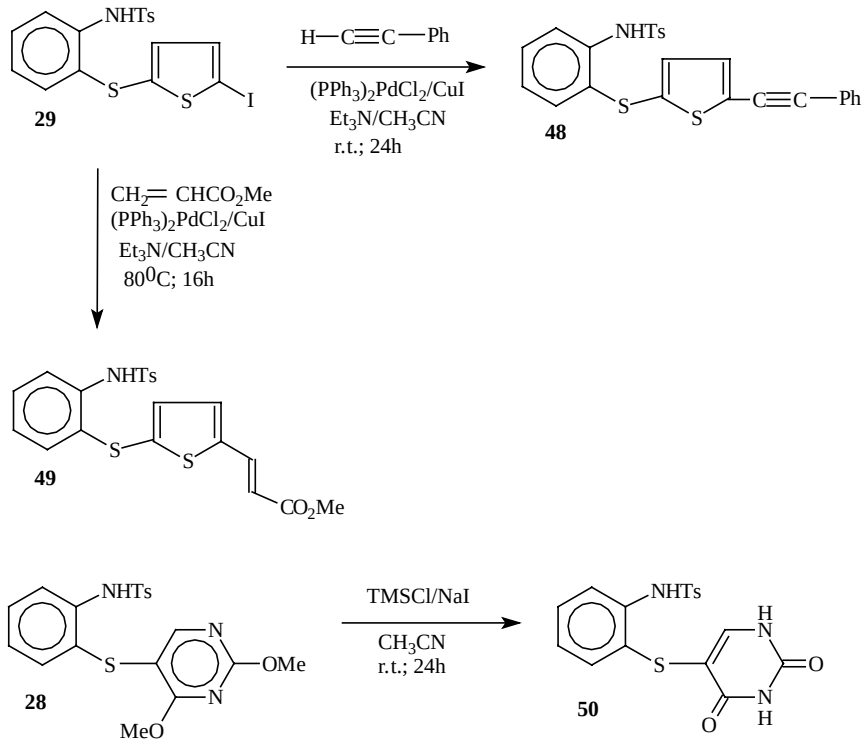
extrusion of Pd^{o} gives rise to the depropargylated-*S*-arylated products **19**–**30** The presence of propargyl iodide in the reaction mixture was established by the addition of *o*-nitrophenol and K_2CO_3 to it and the isolation of *o*-propargyloxynitrobenzene **47** (see Section 3).

1.5. Scope of the reaction

The substituted diaryl sulfides **19**–**30**, because of the presence of *o*-*p*-tosyl amino group are amenable to the synthesis of polyfused hetero aromatic compounds.[17] Also, the diarylsulfides derived from diiodoaromatic and heteroatomatic compounds contain an iodide group which could undergo further palladium-catalysed reactions. Thus, **29** could react with phenylacetylene or methyl acrylate under palladium-catalysed conditions leading to **48** and **49**, respectively (Scheme 4). Also, the pyrimidine derivative **28** could be demethylated with TMSCl and NaI in acetonitrile to yield a novel 5-substituted uracil **50** of possible biological significance.[18]

2. Conclusion

In this paper, we have reported an unusual cleavage of a C–S bond with concurrent *S*-arylation under palladium–copper catalysis which led to a number of substituted diarylsulfides. Although a number of methods for the preparation of diaryl sulfides[19] as well as the cleavage of the C–S bond are known,[20] ours is probably the first report of depropargylation and arylation in a single step operation with palladium–copper reagents. Also, the diaryl sulfides are formed in good yields from readily available starting materials under mild and easy to operate reaction conditions. Since the diaryl sulfides are extremely useful chemical intermediates in organic synthesis,[21] the procedure we have described here could be of considerable interest to many chemists from a synthetic view point. The diarylsulfides are also amenable to the synthesis of polynuclear sulfur heterocycles. Some of the diaryl sulfides could further undergo palladium-catalysed reactions leading to heteroaryl substituted alkynes and alkenes. The synthesis of a novel 5-substituted uracil derivative is also reported.



Scheme 4.

3. Experimental

3.1. General

Melting points are uncorrected. Reactions were performed in an argon atmosphere. Bis(triphenylphosphine)palladium(II)chloride was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, USA. Light petroleum used was the fraction boiling between 60–80°C. Column chromatography was performed on silica gel (60–120 mesh). TLC was done on 60F-254 precoated sheets. Aryl iodides were prepared according to the procedure given for the synthesis of iodobenzene.[22a] 2-Iodothiophene,[22b] 2,5-diiodothiophene,[22b] and 5-iodo-2,4-dimethoxypyrimidine[22c] were synthesised according to known procedure. ^{1}H NMR in $CDCl_3$ solutions were recorded at 300 MHz and that of CCl_4 solutions at 60 MHz. ^{13}C NMR spectra were recorded at 75 MHz.

3.1.1. Synthesis of 3-(2-aminophenylthio)prop-1-yne (1). 2-Aminothiophenol (1 g, 0.8 mmol) in dry acetone (15 mL) was stirred with anhydrous K_2CO_3 (1.12 g, 8 mmol) at room temperature for 4 h. Propargyl bromide (0.95 g, 8 mmol) was added under ice-cold condition and the reaction mixture was heated under reflux for 15 h. After removal of acetone, the residue was diluted with H_2O (10 mL) and extracted with $CHCl_3$ (3×50 mL). The organic layer was washed with H_2O (2×10 mL) and dried (anh. Na_2SO_4). After removal of the solvent, a brown residue was obtained which was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether/ethyl acetate mixture (95/5, v/v) as the eluent. Compound **1** was obtained as a light yellow oil (960 mg, 74%). IR (neat): ν_{max} 3460, 3360, 3290, 1608 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.06 (t, J=3 Hz, 1H, C≡CH), 3.33 (d, J=3 Hz, 2H, S–CH_2), 4.2 (s, 2H, NH_2), 6.53–6.69 (m, 2H, ArH), 6.92–7.46 (m, 2H, ArH). Anal. calcd for C_9H_9NS: C, 66.22; H, 5.56; N, 8.58. Found: C, 65.98; H, 5.57; N, 8.30.

3.1.2. Synthesis of 3-[2-(*N*-*p*-toluenesulfonyl)aminophenylthio]prop-1-yne (4). *S*-(2-Aminophenylthio)prop-1-yne **1** (1.87 g; 11.5 mmol) in dichloromethane (30 mL) was stirred with *p*-toluenesulfonyl chloride (2.19 g; 11.5 mmol) in the presence of pyridine (2 mL) at room temperature for 10 h. After the removal of the solvent, the residue was treated with H_2O (5 mL) and extracted thoroughly with $CHCl_3$ (3×20 mL). The organic layer was washed with H_2O (5 mL), dried (anh. Na_2SO_4) and the solvent was distilled off. The crude compound obtained after purification by column chromatography on silica gel (60–120 mesh) with the eluent being light petroleum–ethyl acetate (90/10; v/v) afforded **4** as a white solid; mp 91°C IR (KBr): ν_{max} 3280, 3240, 1585, 1575 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (t, J=3 Hz, 1H, C≡CH), 2.37 (s, 3H, $ArCH_3$), 3.17 (d, J=3 Hz, 2H, S–CH_2), 7.04 (t, J=6 Hz, 1H, ArH), 7.21 (d, J=9 Hz, 2H, ArH), 7.32 (t, J=9 Hz, 1H, ArH), 7.51 (d, J=6 Hz, 1H, ArH), 7.63–7.69 (m, 3H, ArH), 7.86 (s, 1H, NH). ^{13}C NMR (75 MHz) δ 21.5, 24.6, 72.7, 78.8,120, 123.1, 124.8, 127.1, 129.6, 130.7, 136, 136.4, 139.1, 144. Anal. calcd for $C_{16}H_{15}NO_2S_2$: C, 60.54; H, 4.76; N, 4.41. Found C, 60.51; H, 4.74; N, 4.37.

3.2. General method for the synthesis of diaryl sulfides

A THF solution (15 mL) of aryl iodide (0.82 mmol) was stirred at room temperature with $(PPh_3)_2PdCl_2$ (0.025 mmol, 3 mol%) and CuI (0.33 mmol, 40 mol%) in the presence of Et_3N (3.28 mmol) in an argon atmosphere

for 1/2 h. The acetylenic compound **4** (0.82 mmol) was added and the reaction mixture was stirred for 8 h at room temperature. This reaction mixture was heated under reflux for 20 h. After the removal of the solvent and Et_3N under reduced pressure, the residue was diluted with H_2O (10 mL) and extracted with $CHCl_3$ (3×25 mL). The organic layer was washed with H_2O (3×5 mL), dried (anh. Na_2SO_4) and the solvent was distilled off. Pure product was obtained through column chromatography on silica gel (60–120 mesh) with the eluent being light petroleum–ethylacetate (95:5; v/v).

3.2.1. (2-Phenylthio)-*p*-toluenesulfonanilide (19). White solid; mp 88°C. IR (KBr): ν_{max} 3310, 1585, 1573, 1473 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ δ 2.35 (s, 3H, $ArCH_3$), 6.86–6.88 (m, 2H, ArH), 7.04–7.16 (m, 6H, ArH), 7.36 (td, J_1=7.3 Hz, J_2=1.5 Hz, 1H, ArH), 7.45 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 1H, ArH), 7.54 (d, J=8.4 Hz, 2H, ArH), 7.73–7.76 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 119.4, 121.3, 124.8, 126.2, 127.2, 129.2, 129.5, 130.9, 135.4, 135.6, 137, 143.8. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.5, 119.6, 125, 126.4, 127.4, 129.4, 129.7, 131.1, 137.2. Anal. calcd for $C_{19}H_{17}NS_2O_2$: C, 64.19; H, 4.82; N, 3.94. Found: C, 63.94; H, 4.76; N, 3.92.

3.2.2. (2-*p*-Tolylthio)-*p*-toluenesulfonanilide (20). White solid, mp 85°C. IR (KBr) ν_{max} 3277.8, 1597.8, 1586.7, 1492.8 cm^{-1};^1H NMR (300 MHz, $CDCl_3$) δ 2.29, 2.35 (2s, 6H, $ArCH_3$), 6.81 (d, J=8.1 Hz, 2H, ArH), 6.96 (d, J=8.1 Hz, 2H, ArH), 7.02 (td, J_1=7.5 Hz, J_2=1.2 Hz, 1H, ArH), 7.1 (d, J=8.1 Hz, 2H, ArH), 7.31 (td, J_1=7.5 Hz, J_2=1.2 Hz, 2H, ArH), 7.39 (dd, J_1=7.5 Hz, J_2=1.2 Hz, 1H, ArH), 7.53 (d, J=8.4 Hz, 1H, ArH), 7.7 (dd, J_1=8.4 Hz, J_2=0.6 Hz, 2H, ArH, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22, 120, 123, 125.3, 127.7, 128.6, 129.9, 130.5, 131, 131.9, 136.2, 136.9, 139, 144.3; ^{13}C NMR (75 MHz; $CDCl_3$; DEPT 135) δ 21.1, 21.7, 119.8, 125, 127.4, 128.3, 129.7, 130.2, 130.7, 136.6. MS: *m/e* (rel. inten.) 369.3 (M^+, 95). Anal. calcd $C_{20}H_{19}NO_2S_2$: C, 65.00; H, 5.18; N, 3.79. Found: C, 65.02; H, 5.25; N, 3.74

3.2.3. 2-(*o*-Tolylthio)-*p*-toluenesulfonanilide (21). White solid; mp 121°C. IR (KBr): ν_{max} 3278.8, 1597.6, 1589.2, 1560, 1477.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.3 (s, 6H, $ArCH_3$), 6.87 (t, J=7.8 Hz, 1H, ArH), 7.06 (d, J=7.5 Hz, 2H, ArH), 7.1–7.17 (m, 3H, ArH), 7.31–7.36 (m, 2H), 7.56 (dd, J_1=6.9 Hz, J_2=1.5 Hz, 3H, ArH), 7.72 (d, J=7.5 Hz, 2H, ArH, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 21.9, 120.2, 122.2, 125.5, 126.7, 127.2, 127.6, 127.7, 130, 130.9, 131, 134.6, 136.2, 136.7, 136.7, 139.2, 144.3; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 20.2, 21.7, 120, 125.2, 126.4, 126.9, 127.3, 127.4, 129.7, 130.6, 136.4. Anal. calcd for $C_{20}H_{19}NO_2S_2$: C, 65.00; H, 5.18; N, 3.79. Found: C, 64.98; H, 5.17; N, 3.82.

3.2.4. [2-(1-Naphthyl)thio]-*p*-toluenesulfonanilide (22). White solid; mp 122°C. IR (KBr): ν_{max} 3246, 1596.9, 1587.3, 1569.9, 1502.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H, $ArCH_3$), 6.64 (d, J=7.5 Hz, 1H, ArH), 7.04–7.13 (m, 5H, ArH), 7.3–7.36 (m, 2H, ArH), 7.49–7.58 (m, 5H, ArH), 7.67 (d, J=8.1 Hz, 1H, ArH), 7.77 (d, J=8.1 Hz, 1H, ArH), 7.86 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 120.3, 122.4, 123.9, 125.3, 125.7, 126.6, 126.8, 127.2, 127.2, 128.6, 128.8, 129.5, 130.4, 131.3, 132, 133.8, 135.8, 136, 138.5, 143.9. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.5, 120.3, 123.9, 175.2, 126.7, 125, 126.6, 126.8, 127.2, 124.2, 128.6, 129.5, 130.4, 136. Anal. calcd for $C_{23}H_{19}NO_2S_2$: C, 68.11; H, 4.72; N, 3.45. Found: C, 68.29; H, 4.62; N, 3.55.

3.2.5. [2-(2-Naphthyl)thio]-*p*-toluenesulfonanilide (23). White solid; mp 95°C. IR (KBr): ν_{max} 3250, 1597, 1585.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H, $ArCH_3$), 6.69 (d, J=7.5 Hz, 1H, ArH), 7.2–7.31 (m, 4H, ArH), 7.36–7.45 (m, 3H, ArH), 7.51–7.59 (m, 5H, ArH), 7.69 (d, J=8.1 Hz, 1H, ArH), 7.76 (d, J=8.1 Hz, 1H, ArH), 7.89 (s, 1H, NH). Anal. calcd for $C_{23}H_{19}NO_2S_2$: C, 68.11; H, 4.72; N, 3.45. Found: C, 68.29; H, 4.62; N, 3.55.

3.2.6. 2-(*m*-Chlorophenylthio)-*p*-toluenesulfonanilide (24). White solid, mp 89°C. IR (KBr): ν_{max} 3277, 1590, 1580, 1562 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H, $ArCH_3$), 6.69 (s, 1H, ArH), 6.76–6.80 (m, 1H, ArH), 7.04–7.11 (m, 5H, ArH), 7.38–7.45 (m, 2H, ArH), 7.53 (d, J=9 Hz, 2H, ArH), 7.67 (s, 1H, NH), 7.76–7.79 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.51, 119.6, 119.9, 124.9, 125, 126.2, 126.3, 127, 129.6, 130.1, 131.5, 135, 135.5, 137.3, 137.7, 139.2, 144.1; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 119.8, 125, 125.2, 126.4, 126.5, 127.2, 129.8, 130.3, 131.7, 137.5. Anal. calcd for $C_{19}H_{16}ClNO_2S_2$: C, 58.51; H, 4.14; N, 3.59. Found: C, 58.68; H, 4.12; N, 3.67.

3.2.7. [2-(2-Carbomethoxyphenyl)thio]-*p*-toluenesulfonanilide (25). White solid; mp 97°C. IR (KBr): ν_{max} 3263.3, 1716.5, 1595, 1585.4, 1477.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H, $ArCH_3$), 3.88 (s, 3H, $-COOCH_3$), 6.91–7.06 (m, 6H, ArH), 7.29–7.38 (m, 2H, ArH), 7.49 (d, J=8.1 Hz, 2H, ArH), 7.7 (d, J=8.4 Hz, 1H, ArH), 7.76 (s, 1H, NH), 7.92 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 52.8, 119.3, 120.5, 125.2, 125.4, 126.4, 127, 127.6, 130, 131.9, 132.2, 133.2, 136.3, 138.5, 140.6, 141.7, 144.4, 167.1; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.6, 52.5, 119, 124.9, 125.1, 126.1, 127.3, 129.7, 131.6, 131.9, 132.9, 138.2. Anal. calcd for $C_{21}H_{19}NO_4S_2$: C, 60.99; H, 4.63; N, 3.38. Found: C, 61.12; H, 4.6; N, 3.43.

3.2.8. [2-(2-Methoxyphenyl)thio]-*p*-toluenesulfonanilide (26). Colorless gum. IR (neat): ν_{max} 3265.3, 1590, 1587.3, 1477.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.2 (s, 3H, $ArCH_3$) 3.8 (s, 3H, –OMe), 6.57–6.66 (m, 2H, ArH), 6.74 (d, J=8.1 Hz, 1H, ArH), 6.88 (td, J_1=7.5 Hz, J_2=1.2 Hz, 1H, ArH), 7.00 (d, J=8.4 Hz, 2H, ArH), 7.08 (td, J_1=7 Hz, J_2=1.4 Hz, 1H, ArH), 7.18 (td, J_1=7 Hz, J_2=1.5 Hz, 1H, ArH), 7.36 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 1H, ArH), 7.46 (d, J=8.1 Hz, 2H, ArH), 7.57 (dd, J_1=8.1 Hz, J_2=1.2 Hz, 1H, ArH), 8.12 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 56.4, 111.3, 120, 121.9, 122.9, 123.5, 125.2, 127.7, 129.1, 130, 131.2, 131.3, 136.2, 137.6, 140, 144.3, 157.3; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 56.1, 111, 119.7, 121.6, 125, 127.4, 128.8, 129.7, 130.9, 131, 137.3. Anal. calcd for $C_{20}H_{19}NO_3S_2$: C, 62.31; H, 4.96l N, 3.61. Found: C, 62.48; H, 4.99; N, 3.73.

3.2.9. 2-[(4-Methoxy)phenylthio]-*p*-toluenesulfonanilide

(27) and 1-(4-methoxyphenyl)-3-[2-(*p*-toluenesulfonyl)-aminophenylthio]prop-1-yne (31)Compound **27** could not be separated from the disubstituted alkyne **31** as the R_f value (TLC) of these two were same. The mixture of **27** and **31** was isolated as a light yellow gum. IR (neat): ν_{max} 3271, 1593.1, 1573.8, 1508.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31,2.34 (2s, $ArCH_3$), 3.43 (s, $S-CH_2$), 3.76, 3.77 (2s, $ArOCH_3$), 6.73 (d, J=8.7 Hz, 2H, ArH), 6.81 (d, J=8.7 Hz, ArH), 6.93–7.17 (m, ArH), 7.25–7.35(m, ArH), 7.55 (d, J=8.4 Hz, ArH), 7.67 (d, J=8.1 Hz, ArH),8.00 (s, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 21.5, 25.8, 55.2, 55.3, 82.7, 84.7, 113.8, 114.4, 114.9, 119.8, 120.1, 124.8, 124.9, 125, 127.1, 127.2, 129.5, 129.6, 129.9, 130.6,131, 133, 135.4, 135.7, 136.7, 137.9, 139.2, 143.8, 144, 159, 159.6; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 26 (inverted), 55.4, 55.5, 114, 115.2, 120, 120.3, 125.1, 127.4, 129.7, 129.8, 130.2, 130.8, 131.2, 133.2, 135.6, 136.9.

3.2.10. [2-(2,4-Dimethoxypyrimidin-5-yl)thio]-*p*-toluenesulfonanilide (28). White solid; mp 124°C. IR (KBr): ν_{max} 3236.3, 1598.9, 1575.2, 1562.2, 1477.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, $ArCH_3$), 3.96, 4.08 (2s, 6H, $ArCH_3$), 7.01 (d, J_1=7.8 Hz, J_2=1.2 Hz, 1H, ArH), 7.19 (d, J=8.4 Hz, 2H, ArH), 7.29 (td, J_1=7.8 Hz, J_2=1.5 Hz, 1H, ArH), 7.42 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 1H, ArH), 7.63 (d, J=8.4 Hz, 3H, ArH), 8.07 (s, 1H, ArH), 8.15 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 54.9, 55.1, 108.8, 120.7, 123.4, 125.1, 127.1, 129.5, 130.6, 135.8, 136.1, 138.8, 143.9, 161.8, 165.2, 169.1; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 55.1, 55.3, 120.9, 125.3, 127.3, 129.7, 130.8, 136.3, 162. Anal. calcd for $C_{19}H_{19}N_3O_4S_2$: C, 54.66; H, 4.59; N, 10.06. Found: C, 54.41; H, 4.41; N, 9.92.

3.2.11. [2-(5-Iodothienyl)thio]-*p*-toluenesulfonanilide (29). Synthetic procedure for compound **29** was same as for the synthesis of **19** using the diiodo compound **16** instead of the aryl iodides. White solid; mp 123°C. IR (KBr): ν_{max} 3276.8, 1585.4, 1475.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H, $ArCH_3$), 6.94–7.07 (m, 2H, ArH), 7.19 (d, J=8.1 Hz, 2H, ArH), 7.28 (td, J_1=7.2 Hz, J_2=1.2 Hz, 2H, ArH), 7.35 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 2H, ArH), 7.51 (s, 1H, NH), 7.57–7.62 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 121.1, 121.3, 125.6, 127.6, 130.2, 130.8, 132.6, 134.1, 134.4, 134.7, 136.2, 137.5, 137.9, 144.6; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.8, 120.8, 125.4, 127.9, 129.8, 130.5, 134.2, 134.4, 137.6. Anal. calcd for $C_{17}H_{14}INO_2S_3$: C, 41.89; H, 2.89; N, 2.87. Found: C, 41.97; H, 2.92; N, 2.94.

3.2.12. 2-[(2-Iodo)phenylthio]-*p*-toluenesulfonanilide (30). Light brown sticky gum. IR (neat): ν_{max} 3266.2, 1595.3, 1566.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 3H, $ArCH_3$), 6.75 (t, J=7.5 Hz, 1H, ArH), 6.86–7.12 (m, 6H, ArH), 7.36 (d, J=7.5 Hz, 2H, ArH), 7.51 (d, J=8.1 Hz, 2H, ArH), 7.6 (d, J=8.1 Hz, 2H, ArH, NH). Anal. calcd for $C_{19}H_{16}INO_2S_2$: C, 47.4; H, 3.35; N, 2.91. Found: C, 47.54; H, 3.41; N, 3.02.

3.2.13. 1-(2-Thienyl)-3-[2-(*p*-toluenesulfonyl)aminophenylthio]prop-1-yne (32). White solid; mp 104°C, IR (KBr): ν_{max} 3250, 1595, 1575 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H, $ArCH_3$), 3.39 (s, 2H, $S-CH_2$), 6.49–7.00 (m, 7H, ArH), 7.43–7.76 (m, 4H, ArH), 7.89 (s, 1H, NH). Anal. calcd for $C_{20}H_{17}NO_2S_3$: C, 60.12; H, 4.28; N, 3.5. Found: C, 60.34; H, 4.51; N, 3.32.

3.2.14. 1,4-Bis-[3-[2-(*p*-toluenesulfonyl)aminophenylthio]-prop-1-yne]benzene (33). White solid; mp 120°C. IR (KBr): ν_{max} 3220, 1595, 1580, 1540 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H, $ArCH_3$), 3.44 (s, 4H, $S-CH_2$), 7.08 (td, J_1=6 Hz, J_2=1.5 Hz, 2H,ArH), 7.17–7.26 (m, 8H, ArH), 7.34 (td, J_1=6 Hz, J_2=1.5 Hz, 2H, ArH), 7.54 (dd, J_1=7.8 Hz, J_2=1.5 Hz, 2H, ArH), 7.66 (dd, J_1=8.1 Hz, J_2=1.5 Hz, 6H, ArH), 7.94 (s, 2H, NH). Anal. calcd for $C_{38}H_{32}N_2O_4S_4$: C, 64.88; H, 4.55; N, 3.95. Found: C, 64.31; H, 4.59; N, 3.88.

3.2.15. Synthesis of 3-(phenylthio)prop-1-yne (34). A mixture of thiophenol (250 mg; 2.27 mmol), propargyl bromide (270 mg; 2.27 mmol) and K_2CO_3 (310 mg; 2.27 mmol) was refluxed in acetone (20 mL) for 16 h in an argon atmosphere. After the usual work-up, the crude product obtained was purified by column chromatography on silica gel with the eluent being light petroleum–$CHCl_3$ (8:2; v/v) furnishing **34** as a light brown oil. IR (neat): ν_{max} 3302, 2125, 1581 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.03 (t, J=3 Hz, 1H, C≡CH), 3.46 (d, J=3 Hz, 2H, $S-CH_2$), 7.03–7.49 (m, 5H, ArH). Anal. calcd for C_9H_8S: C, 72.9; H, 5.43. Found: C, 73.01; H, 5.55.

3.2.16. 3-[2-(*N*-Methyl)aminophenylthio]-prop-1-yne (35). *S*-(2-Aminophenylthio)prop-1-yne **1** (1 g; 6.12 mol) was refluxed with MeI (870 mg; 12.24 mmol) and K_2CO_3 (780 mg; 6.12 mol) in acetone (20 mL) in an argon atmosphere for 24 h. After the removal of the solvent, the residue was diluted with H_2O (1×5 mL) and extracted with $CHCl_3$ (3×25 mL). The organic layer was washed with H_2O (2×5 mL), dried (anh. Na_2SO_4) and the solvent was distilled off. The crude product obtained was purified by column chromatography on silica gel (60–120 mesh) with the eluent being light petroleum–ethyl acetate (95:5; v/v) to furnish **35** as a pale yellow oil in 92% yield. IR (neat): ν_{max} 3380, 3290, 1600, 1595 cm^{-1}; ^1H NMR (60 MHz, $CDCl_4$) δ 2.53 (t, J=3 Hz, 1H, C≡CH), 2.69 (s, 3H, NCH_3), 3.53 (d, J=3 Hz, 2H, $S-CH_2$), 6.92–7.33 (m, 4H, ArH). Anal. calcd for $C_{10}H_{11}NS$: C, 67.75; H, 6.25; N, 7.89. Found: C, 67.73; H, 6.21; N, 7.86.

3.2.17. 3-[2-(*N*-Benzyl)aminophenylthio]prop-1-yne (36). *S*-(2-Aminophenylthio)prop-1-yne (270 mg; 1.65 mmol) in acetone (10 mL) was stirred with K_2CO_3 (230 mg; 1.65 mmol) at room temperature for 12 h. Benzyl bromide (420 mg; 2.47 mmol) was added slowly and refluxed for 24 h. The solvent was removed and the residue was diluted with H_2O (10 mL) followed by extraction with $CHCl_3$ (3×20 mL). The organic layer was washed with H_2O (2×5 mL), dried (anh. Na_2SO_4) and the solvent was distilled off. The crude product after purification by column chromatography on silica gel (60–120 mesh) using light petroleum–ethyl acetate (95:5; v/v) mixture as the eluent, afforded **36** as a light yellow oil in 89% yield. IR (neat): ν_{max} 3394, 3290.3, 2115.8, 1600.8, 1577.7 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.23 (t, J=3 Hz, 1H, C≡CH), 3.69 (d, J=3 Hz, 2H, $S-CH_2$), 4.23 (s, 2H, CH_2Ph), 4.49 (s, 1H,

NH), 6.99–7.43 (m, 9H, ArH). Anal. calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.52. Found: C, 75.91; H, 6.0; N, 5.49.

3.2.18. 1-*p*-Tolyl-3-[2-(*p*-toluenesulfonyl)aminophenylthio]-prop-1-yne (37). White solid; mp 69°C; IR (KBr): ν_{max} 3280, 1597, 1575, 1520, 1470 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H, $ArCH_3$), 3.43 (s, 2H, S–CH_2), 7.04–7.32 (m, 8H, ArH), 7.54 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 1H, ArH), 7.67 (d, J=8.1 Hz, 3H, ArH), 7.95 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 25.7, 83.3, 84.9, 119.4, 120.1, 123.4, 124.7, 127.1, 128.9, 130.5, 131.4, 136.4, 138.3, 139.3, 143.7. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.6, 25.9 (inverted), 120.3, 124.9, 127.3, 129.1, 129.7, 130.7, 131.6, 136.8. Anal. calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.49; H, 5.30; N, 3.25.

3.2.19. Synthesis of 1-(*p*-tolyl)-3-(phenylthio)prop-1-yne (38). A mixture of *p*-iodotoluene, **6** (370 mg; 1.68 mmol), $(PPh_3)_2PdCl_2$ (35 mg; 0.05 mol; 3 mol%), CuI (130 mg; 0.67 mol; 40 mol%) and Et_3N (680 mg; 6.72 mmol) in THF (5 mL) was stirred for 1/2 h at room temperature in an argon atmosphere. 3-(Phenylthio)prop-1-yne **34** (250 mg; 1.68 mmol) was added and refluxed for 20 h. After the usual work up and purification by column chromatography on silica gel (60–120 mesh) with an eluent being light petroleum–ethyl acetate (95/5; v/v) the crude product furnished **38** as a light yellow oil. IR (neat): ν_{max} 2150, 1581.5, 1541 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.2 (s, 3H, $ArCH_3$), 3.71 (s, 2H, S–CH_2), 6.95 (d, J=8.1 Hz, 2H, ArH), 7.1–7.23 (m, 5H, ArH), 7.39 (d, J=7.5 Hz, 2H, ArH). Anal. calcd for $C_{16}H_{14}S$: C, 80.62; H, 5.92. Found: C, 80.55; H, 5.96.

3.2.20. Synthetic procedure for the compounds 39–42. Compounds **39**–**42** were synthesised according to the procedure for **38**.

3.2.21. 1-*p*-Tolyl-3-(2-aminophenylthio)-prop-1-yne (39). Light yellow oil. IR (neat) ν_{max} 3450, 3360, 1600, 1505, 1475 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H, $ArCH_3$), 3.65 (s, 2H, S–CH_2), 4.38 (brs, 2H, NH_2), 6.66–6.73 (m, 2H, ArH), 7.06 (d, J=8.1 Hz, 2H, ArH), 7.13 (td, J_1=8.1 Hz, J_2=1.5 Hz, 1H, ArH), 7.22 (d, J=8.1 Hz, 2H, ArH), 7.48 (dd, J_1=7.5 Hz, J_2=1.2 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 24.1, 83.8, 84.7, 114.8, 116.6, 118.4, 120, 128.9, 130.5, 131.4, 137, 138, 148.8 ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.4, 24.1 (inverted), 114.8, 118.4, 128.8, 130.5, 131.4, 137 Anal. calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.6; H, 6.35; N, 5.28.

3.2.22. 1-Phenyl-3-[2-(*N*-methyl)aminophenylthio]prop-1-yne (40). Light yellow oil. IR (neat): ν_{max} 3330, 1601, 1586 cm^{-1}. ^1H NMR (60 MHz, CCl_4) δ 2.76 (s, 3H, N–CH_3), 3.79 (s, 2H, S–CH_2), 6.92–7.03 (m, 4H, ArH), 7.2–7.36 (m, 5H, ArH). Anal. calcd for $C_{16}H_{15}NS$: C, 76.15; H, 5.96; N, 5.52. Found: C, 76.17; H, 5.93; N, 5.47.

3.2.23. 1-Phenyl-3-[2-(*N*-benzyl)aminophenylthio]prop-1-yne (41). Pale yellow oil. IR (neat): ν_{max} 3350, 1601, 1576.5 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.36 (s, 3H, $ArCH_3$), 3.89 (s, 2H, S–CH_2), 4.16 (s, 2H, CH_2Ph), 6.89–7.46 (m, 14H, ArH, NH). Anal. calcd for $C_{23}H_{21}NS$: C, 80.42; H, 6.16; N, 4.07. Found: C, 80.34; H, 6.19; N, 4.18.

3.2.24. (*E*)-2-[2-(*p*-Tolyl)vinyl]-3-tosyl benzothiazoline (42). White solid; mp 109°C. IR (KBr): ν_{max} 1595, 1455 1360 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H, $ArCH_3$), 2.32 (s, 3H, $ArCH_3$), 6.16 (q, J_1=15 Hz, J_2=6Hz, 1H, CH=CHAr), 6.25 (d, J=6 Hz, 1H, S–CH), 6.67 (d, J=15 Hz, 1H CH=CHAr), 7.01–7.22 (m, 9H, Ar), 7.47 (d, J=9 Hz, 2H, ArH), 7.72 (d, J=9 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.6, 69.2., 120.9, 122.7, 125.3, 125.7, 126.8, 127.4, 129.5, 130.6, 132.7, 132.8, 134.5, 136.9, 138, 144.4; ^{13}C NMR 75 MHz, $CDCl_3$, DEPT 135) 21.4, 21.7, 69.3, 121.1, 122.9, 125.5, 125.9, 127, 127.2, 127.6, 129.4, 129.6, 130.8. Anal. calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.87; H, 5.01; N, 3.13.

3.2.25. Isolation and characterisation of 3-(2-nitrophenylthio)prop-1-yne (47). A mixture of *p*-iodotoluene, **6** (360 mg; 1.64 mmol), $(PPh_3)_2PdCl_2$ (35 mg; 0.05 mmol; 3 mol%), CuI (125 mg; 0.65 mmol; 40 mol%) and Et_3N (660 mg; 6.56 mmol) was stirred in THF (15 mL) at room temperature for 1/2 h in an argon atmosphere. 3-[2-(*p*-Toluenesulfonyl)aminophenylthio]prop-1-yne **4** (500 mg; 1.64 mmol) was added and stirred for 8 h at room temperature. Then 2-nitrophenol (230 mg; 1.64 mmol) and K_2CO_3 (230 mg; 1.64 mmol) were added and the reaction mixture was then heated under reflux for 20 h. After the usual work-up and chromatographic purification (silica gel: (60–120 mesh); eluent: light petroleum–ethyl acetate (9:1; v/v)) of the crude product, 3-(2-nitrophenylthio)prop-1-yne **47** was isolated as a light yellow solid in 49% yield; mp 78°C; IR (KBr): ν_{max} 3299.1, 1601.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.5 (t, J=2.4 Hz, 1H, C≡CH), 4.76 (d, J=2.4 Hz, 2H, O–CH_2), 7.00 (td, J_1=7.8 Hz, J_2=1.2 Hz, 1H, ArH), 7.16 (dd, J_1=7.8 Hz, J_2=0.9 Hz, 1H, ArH), 7.46 (td, J_1=7.5 Hz, J_2=1.8 Hz, 1H, ArH), 7.75 (dd, J_1=8.1 Hz, J_2=1.8 Hz, 1H, ArH). Anal. calcd for $C_9H_7NO_3$: C, 61.02; H, 3.98; N, 7.9. Found: C, 60.99; H, 3.96; N, 7.88.

3.2.26. 2-(2′-Phenyl)ethynyl-5-(2′-*p*-tosylamino)phenylthio thiophene (48). Compound **29** (80 mg, 0.16 mmol) in acetonitrile (3 mL) was stirred with $(PPh_3)_2PdCl_2$ (4 mg, 0.006 mmol, 3 mol%), CuI (2 mg, 0.01 mmol, 6 mol%) and triethylamine (65 mg, 0.64 mmol) at room temperature for 1/2 h in an argon atmosphere. Phenylacetylene (40 mg, 0.39 mmol) was added and the reaction mixture was allowed to stir at room temperature for 24 h. After the usual work-up, the crude product was purified by column chromatography on silica gel (60–120 mesh) with the eluent being light petroleum–ethyl acetate (9:1; v/v) to afford **48** as a light yellow gum. IR (neat) ν_{max} 3278, 1603.2, 1596.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H, $ArCH_3$), 6.79–6.98 (m, 3H, ArH), 7.08–7.21 (m, 3H, ArH), 7.22–7.27 (m, 4H, ArH), 7.32–7.4 (m, 2H, ArH), 7.44–7.61 (m, 4H, ArH). Anal. calcd for $C_{25}H_{19}NO_2S_3$: C, 65.04; H, 4.15; N, 3.14. Found: C, 64.92; H, 4.21; N, 3.28.

3.2.27. 2-(2′-Carbomethoxy)vinyl-5-(2-*p*-tosylamino)-phenylthio thiophene (49). A mixture of compound **29** (80 mg, 0.16 mmol), methyl acrylate (30 mg, 0.35 mmol),

bis triphenylphosphone palladium(II) chloride (4 mg, 0.006 mmol) and triethylamine (65 mg, 0.64 mmol) in acetonitrile (5 mL) was heated at 80°C (bath temperature) for 15 h in an argom atmosphere. After the removal of the solvent and usual work-up, a brown gum was obtained which after purification through column chromatography on silica gel (60–120 mesh) with the eluent being light petroleum–ethyl acetate (9:1; v/v) furnished **49** as a light yellow oil in 68% yield. IR (neat) ν_{max} 3277.6, 1709.2, 1595, 1585.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H, $ArCH_3$), 3.72 (s, 3H, $COOCH_3$), 6.18 (d, J=15.4 Hz, 1H, C*H*=CO_2Me), 6.96–7.01 (m, 2H, ArH), 7.13 (d, J=8.1 Hz, 2H, ArH), 7.19–7.25 (m, 3H, ArH), 7.29 (dd, J_1=8.1 Hz, J_2=1.5 Hz, 1H, ArH), 7.43 (brs, 1H, NH), 7.5–7.59 (m, 3H, ArH), 7.8 (d, J=15.4 Hz, 1H, C*H*=$CHCO_2Me$). Anal. calcd for $C_{21}H_{19}NO_4S_3$: C, 56.6; H, 4.29; N, 3.14. Found: C, 56.52; H, 4.32; N, 3.22.

3.2.28. 5-(2-*p*-Tosylamino)phenylthio uracil (50). Compound **28** (100 mg, 0.25 mmol) in acetonitrile (5 mL) was stirred with TMSCl (80 mg, 0.75 mmol) and NaI (110 mg, 0.73 mmol) at room temperature for 24 h in an argon atmosphere. After the removal of the solvent under reduced pressure, the residue was treated with ice-cold water (2 mL) and allowed to stand at room temperature for 30 min. The resulting yellow solid was filtered, washed with saturated sodium metabisulfite solution (3 mL) and finally with H_2O (2×1 mL). This was dried to yield a pale yellow solid which was crystallised from MeOH–H_2O to afford **50** as a white solid (yield: 72%); mp >250°. IR(KBr) ν_{max} 3247.9, 3180, 3026, 1716.5, 1674.1, 1614.3, 1596.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H, $ArCH_3$), 6.85–6.91 (m, 2H, ArH), 7.08–7.11 (m, 2H, ArH), 7.33 (d, J=7.8 Hz, 2H, ArH), 7.61 (d, J=7.8 Hz, 2H, ArH), 8.05 (s, 1H, uracil-C_6 H), 9.71 (s, 1H, N*H*-Ts), 11.4 (brs, 1H, NH), 11.53 (s, 1H, NH). Anal. calcd for $C_{17}H_{15}N_3O_4S_2$: C, 52.43; H, 3.88; N, 10.78. Found: C, 52.15; H, 4.14; N, 10.81.

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