Palladium−Copper Catalyzed Synthesis of Benzofused Heterocycles with Two Heteroatoms: Novel and Highly Regio- and Stereoselective Syntheses of (*E*)-2-(2-Arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles and (*E*)-2-Alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzothiazines

Nitya G. Kundu* and Bidisha Nandi

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India

ocngk@mahendra.iacs.res.in

Received December 26, 2000

A highly novel, general, and convenient palladium and copper-catalyzed procedure has been developed for the synthesis of (*E*)-2-(2-arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles **28**−**40**. 3-(2-Aminophenylthio)prop-1-yne **1** reacts with aryl iodides **2**−**14** under palladium−copper catalysis to yield the disubstituted alkynes **15**−**27** which after tosylation undergo a novel cyclization with CuI in the presence of triethylamine in THF to (*E*)-2-(2-arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles **28**−**40** rather than to the expected 3-alkylidene-4-tosyl-3,4-dihydro-2*H*-1,4-benzothiazines **41**. The reaction is highly regio- and stereoselective. The synthesis of 2-(2-arylethyl)-3-tosylbenzothiazolines **42**−**47**, 2-(2-arylvinyl)benzothiazoles **48**−**54**, and a novel 5-substituted uracil derivative **55** of potential biological importance is also being reported. Similarly, the palladium−copper-catalyzed arylation of *S*-[2-(*N*-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate **58** with aryl iodides yields the disubstituted alkynes **59** which on cyclization with KOH in methanol leads to (*E*)-2-(2-aryl)methylidene-3,4-dihydro-2*H*-1,4-benzothiazines **61**. The reaction of the diiodo compounds **12**−**14a**, however, with **58** under palladium−copper-catalyzed reactions involves the participation of only one of the iodo groups in the heteroannulation process giving compounds **61i** and **61j**. These are amenable to further palladium-catalyzed reactions and afford polyunsaturated heteroaromatic compounds **62** and **63**.

1,3-Benzothiazoles, benzothiazolines (2,3-dihydro-1,3-benzothiazoles),[1] and 1,4-benzothiazines[2] have been of considerable interest because of their profound biological activities.[3,4] Thus, the syntheses of benzothiazoles and benzothiazines have attracted the attention of many organic and medicinal chemists for decades.[1,2,5,6] But to our knowledge, there have been only one report[7] on the synthesis of these interesting heterocyclic structures through palladium-catalyzed reactions. Palladium-catalyzed arylation of olefins (Heck's reaction)[8] and cross-coupling reactions[9] have been of immense value for C−C bond formation. Intense activities in these areas have resulted in many elegant syntheses of various carbocyclic[10] and heterocyclic structures.[11]

We have been interested in the synthesis of various heterocyclic structures because they are the integral part of many naturally occurring and biologically active compounds. With that objective, recently we have adopted palladium-catalyzed reactions of terminal alkynes and aryl halides[12] with a nucleophilic group in the ortho-position for the syntheses of a number of benzofused heterocyclic structures with one heteroatom only, e.g., benzofurans,[13] phthalides,[14] quinolines and quinolones,[15] isoindolinones,[16] and flavones and flavanones.[17] In an alternative strategy, we have utilized the reactions of mono-prop-2-ynyloxy or mono-prop-2-ynylamino aromatic compounds with a nucleophilic group (OH, NH-Ts, CO_2H) in the ortho-position and aryl halides under palladium−copper-catalyzed conditions for the synthesis of benzofused heterocyclic structures with two heteroatoms, e.g. 1,4-benzodioxans,[18] 1,4-benzoxazines,[19] 1,4-benzodioxepinones,[20] and 4,1-benzoxazepinones.[20] In an extension of this reaction, we recently reacted 3-(2-aminophenylthio)-prop-1-yne **1** with aryl iodides **2**−**14** under palladium−copper catalysis to get the disubstituted alkynes **15**−**27** which, after tosylation, surprisingly cyclized to 2-substituted benzothiazolines **28**−**40** instead of the expected 3-alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzothiazines **41** (Scheme 1, Table 1).[21] In this report we describe the detailed studies on the synthesis of the benzothiazolines, their conversion to benzothiazoles, and a novel palladium−copper-catalyzed procedure for the synthesis of 1,4-benzothiazines.

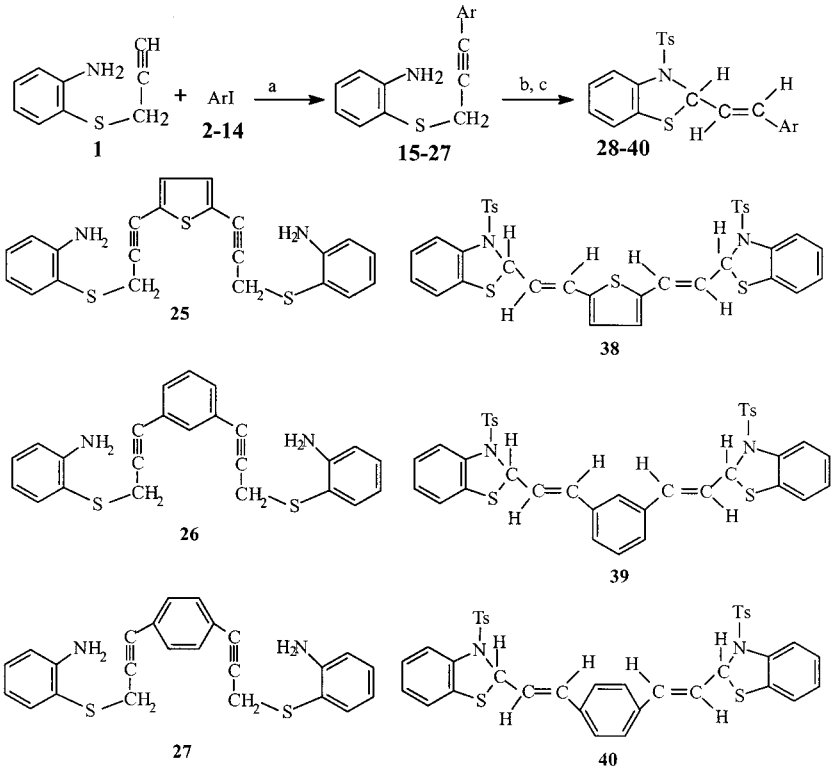
* Corresponding author. Fax: +91-33-473-2805.

(1) For general discussion on benzothiazoles and benzothiazolines, see (a) Campbell, M. M. Five-membered Ring Systems. In *Comprehensive Organic Chemistry, Vol. 4, Heterocyclic Compounds*; Barton, D., Ollis, W. D., Eds., Pergamon Press: Oxford, 1979; Part 20, pp 976−993. (b) Metzger, J. V. Thiazoles and their Benzo derivatives. In *Comprehensive Heterocyclic Chemistry*; Katrizky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 6, pp 235−331.

(2) For discussions on benzothiazines, see (a) Landquist, J. K. Six-membered Ring Systems. In *Comprehensive Organic Chemistry*; *Heterocyclic Compounds*; Barton, D., Ollis, W. D., Sammes, P. G., Eds.; Pergamon Press: Oxford, 1979; Vol. 4, pp 1092−1102. (b) Brown, C.; Davidson, R. M. 1,4-Benzothiazines, dihydro-1,4-benzothiazines and related compounds. *Adv. Heterocycl. Chem.* **1985**, *38*, 135−176. (c) Gupta, R. R., Ed. Phenothiazines and 1,4-Benzothiazines: Chemical and Biomedical Aspects. In *Bioactive Molecules*; Elsevier: Amsterdam, Neth, 1988; Vol. 4. (d) Sainsbury, M. 1,4-Thiazines, 1,4-Benzothiazines, Phenothiazines and Related Compounds. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Publisher: Elsevier: Amsterdam, Neth, 1998; Vol. 4 (Part G (partial)/Part H), pp 575−608.

10.1021/jo001783+ CCC: $20.00
Published on Web 06/06/2001

Scheme 1. Synthesis of (*E*)-2-(2-Arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles[a]



[a] Reaction conditions: (a) $(PPh_3)_2PdCl_2$ (3 mol %), CuI (6 mol %), Et_3N, CH_3CN, rt, 24 h; (b) *p*-TsCl, py, CH_2Cl_2, rt, 10 h; (c) CuI (40 mol %), Et_3N, THF, reflux, 36 h.

Table 1. Reaction of 3-(2-Aminophenylthio)prop-1-yne 1 with Aryl Iodides 2−14 in the Presence of Palladium Catalyst, Copper(I) Iodide, and Triethylamine and Subsequent Cyclization of the Disubstituted Alkynes 15−27 to (*E*)-2-(2-Arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles 28−40 (Scheme 1)[a]

entry	aryl iodides (ArI) Ar	disubstituted alkynes, (yield %)[b]	(*E*)-2-(2-arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles (yield %)[c]
1	C_6H_5 **2**	**15** (73)	**28** (67)
2	1-naphthyl **3**	**16** (68)	**29** (63)
3	2-naphthyl **4**	**17** (76)	**30** (74)
4	3-ClC_6H_4 **5**	**18** (78)	**31** (76)
5	2-MeC_6H_4 **6**	**19** (77)	**32** (69)
6	4-MeC_6H_4 **7**	**20** (76)	**33** (80)
7	4-$MeOC_6H_4$ **8**	**21** (69)	**34** (66)
8	2-$MeOCOC_6H_4$ **9**	**22** (80)	**35** (70)
9	2-thienyl **10**	**23** (71)	**36** (75)
10	2,4-dimethoxy-pyrimidin-5-yl **11**	**24** (73)	**37** (80)
11	5-iodo-2-thienyl **12**	**25** (59)	**38** (76)
12	3-iodophenyl **13**	**26** (57)	**39** (63)
13	4-iodophenyl **14**	**27** (56)	**40** (77)

[a] In all cases, $(PPh_3)_2PdCl_2$ (3 mol %) and CuI (6 mol %) were used. [b] Yields are based on **1**. [c] Yields are based on tosylates of the disubstituted alkynes.

Results and Discussion

3-(2-Aminophenylthio)prop-1-yne **1** was synthesized by the propargylation of 2-aminothiophenol with propargyl bromide in the presence of potassium carbonate. The reaction of **1** with various aryl iodides **2**−**14** took place under very mild conditions (25−30 °C, 24 h) in the presence of $(PPh_3)_2PdCl_2$ (3 mol %) as a catalyst, cuprous iodide (6 mol %) as a cocatalyst, and triethylamine (4 equiv) as a base in acetonitrile. Under the reaction conditions, the normal C-arylation of the terminal alkyne **1** took place yielding the disubstituted alkynes **15**−**27** in good yields (68−77%) (Scheme 1 and Table 1).

We have found that for C-arylation of the terminal alkyne **1**, both bis(triphenylphosphine)palladium(II) chlo-

(3) Benzothiazoles and benzothiazolines (a) as anticonvulsant, vasodilators, and blood platelet aggregation inhibitors: Santen Pharmaceutical Co. Ltd. *Jpn. Kokai, Tokyo Koho*, JP 5967,27 [8467,276]; *Chem. Abstr.* **1985**, *102*, 6464a. Ucar, H.; Vanderpoorten, K.; Cacciaguerra, S.; Spampinato, S.; Stables, J. P.; Deprovere, P.; Isa, M.; Masareel, B.; Delarge, J.; Poupaert, J. H. *J. Med. Chem.* **1998**, *41*, 1138−1145. (b) For treatment of airway diseases: Bounert, R. V.; Brown, R. C.; Chapman, D.; Cheshire, D. R.; Dixon, J.; Ince, F.; Kinchin, E. C.; Lyons, A. J.; Davis, A. M.; Hallam, C.; Harper, S. T.; Unitt, J. F.; Dougall, I. G.; Jackson, D. M.; Mckechnie, K.; Young, A.; Simpson, W. T. *J. Med. Chem.* **1998**, *41*, 4915−4917. (c) As histamine H-3 antagonists: Walczynski, K.; Guryn, R.; Zuiderveld, P.; Timmerman, H. *Arch. Pham.* **1999**, *332*, 389−398. (d) As antihypertensive, anticoagulant, and calcium agonist: Iwao, J.; Iso, I.; Oya, M. *Jpn. Kokai Tokyo Koho* JP 6183,175, *Chem. Abstr.* **1986**, *105*, 208865e. Yamamoto, K.; Fujita, K.; Tabasi, K.; Kawashima, Y.; Kato, E.; Oya, M.; Iso, T.; Iwao, J. *J. Med. Chem.* **1988**, *31*, 919−930. (e) For antipsychotic properties: Taverne, T.; Diouf, O.; Depreuse, P.; Poupaert, J. H.; Lesieur, D.; Guardiola-Lemaitre, B.; Renard, P.; Rettari, M.-C.; Caignard, D.-H.; Pfiffer, B. *J. Med. Chem.* **1998**, *41*, 2010−2018. (f) For analgesic activity: Coudert, P.; Couquelet, J.; Sudre, O.; Bastide, J. *J. Pharm. Belg.* **1988**, *43*, 258−262. (g) For antileukemic activity against lymphocytic leukemia P 388: Holbova, E. Czech CS 236,603; *Chem. Abstr.* **1988**, *109*, 6501e. (h) For antitubercular activity: Bhusari, K. P.; Khedekar, P. B.; Umathe, S. N.; Bahekar, R. H.; Rao, A. R. R. *Indian J. Hetero. Chem.* **2000**, *9*, 213−216. (i) For antitumour activity: Kawakami, M.; Suzuki, M.; Kawai, H.; Ogawa, K.; Shishido, T. *Tetrahedron Lett.* **1998**, *39*, 1763−1766; Chua, M. S.; Shi, D.-F.; Wringly, S.; Bradshaw, T. D.; Hutchinson, I.; Shaw, P. N.; Barrett, D. A.; Stanley, L. A.; Stevens, M. F. G. *J. Med. Chem.* **1999**, *42*, 381−392; Bradshaw, T. D.; Diana, P.; Seaton, A.; Shi, D. F.; Westwell, A. D.; Stevens, M. F. G. *Bioorg. Med. Chem. Lett.* **2000**,*10*, 513−515. (j) As antifungal agents: Singh, R. V. *Main Group Metal Chem.* **1990**, *13*, 55−64; *Chem. Abstr.* **1992**, *116*, 2555. Kanoongo, N.; Singh, R. V.; Tandan, J. P. *Indian J. Chem. Sect. A* **1990**, *29A*, 560−563; *Chem. Abstr.* **1990**, *113*, 164355x. (k) As herbicides: Machitani, K.; Miura, Y.; Nishioka, H.; Hiradate, S.; Yanai, I. *Japan Kokai Tokyo Koho*, JP 03,47,180 (1991); *Chem. Abstr.* **1991**, 92264h.

ride and cuprous iodide were essential as catalyst and cocatalyst, respectively. The amount of the catalyst was usually around 3 mol % of **1** whereas the cocatalyst was used in amount of 6 mol %. With other palladium-catalysts we used, e.g., tetrakistriphenylphosphine palladium (entry 2, Table 2) and palladium acetate (entry 3, Table 2), a much lower yield of the C-arylated product **15** was obtained. Cuprous iodide is an essential cocatalyst. In its absence the yield of **15** was much lower (37%, entry 4, Table 2). Again, with cuprous iodide alone (no palladium catalyst, entry 6, Table 2), a poor yield (12%) of the diarylated alkyne **15** was obtained. Similarly, studies with other bases, e.g., sodium acetate (entry 7) and potassium carbonate (entry 8) revealed that Et_3N is the best base for the palladium-catalyzed arylation reactions. Acetonitrile was found to be the best solvent for C-arylation reaction. The use of triethylamine both as the solvent and the base led to poorer yields due to incomplete solubility of some starting materials in Et_3N. The use of DMF as the solvent led to the formation of colored materials and some polymerization of the reaction mixture. The reactions were carried out at room temperature and a reaction period of 24 h was found to be the optimum. Various substituted aryl iodides were used for the C-arylation reaction under palladium−copper catalysis, and it was observed that substituents in the aromatic ring did not affect the yields considerably. However, in the case of the diiodo compounds, yields of the diynes **25**−**27** (Scheme 1, Table 1) were much lower from the loss of the starting material **1** due to polymerization. It is essential to use the free amine **1** for the success of the arylation reaction. The use of the corresponding tosylate with aryl iodides under normal palladium−copper catalysis conditions did not give any disubstituted alkyne. However, the use of excess of CuI (40 mol %) in the arylation reaction of the tosylate of **1** led to depropargylation and concurrent S-arylation.[22] Although in the case of the synthesis of (*Z*)-2-alkyl(aryl)idene-2,3-dihydrobenzodioxins,[18] we have observed that the arylation of the terminal alkyne and subsequent cyclization did take place in a single step, in the case of the attempted synthesis of the corresponding benzothiazines the cyclization of the disubstituted alkynes **15**−**27** did not take place in a single step under palladium−copper catalysis. Also we failed to cyclize the free amines **15**−**27** under

Table 2. Dependence of the Yield of 3-(2-Aminophenylthio)-1-phenylprop-1-yne 15 on a Catalyst, a Cocatalyst, and a Base

entry	catalyst (mol %)	cocatalyst (mol %)	base (equiv)	yield (%)
1	$(PPh_3)_2PdCl_2$ (3)	CuI (6)	Et_3N (4)	74
2	$(PPh_3)_4Pd$ ()	CuI (6)	Et_3N (4)	20
3	$Pd(OAc)_2$ (3)	CuI (6) PPh_3 (6)	Et_3N (4)	28
4	$(PPh_3)_2PdCl_2$ (3)	-	Et_3N (4)	37
5	-	CuI (6)	Et_3N (4)	0
6	-	CuI (20)	Et_3N (4)	12
7	$(PPh_3)_2PdCl_2$ (3)	CuI (6)	NaOAc (4)	0
8	$(PPh_3)_2PdCl_2$ (3)	CuI (6)	K_2CO_3 (4)	15

(4) ,4-Benzothiazines (a) as antiinflammatory agents: Lombardino, J. G.; Wiseman, E. H. *Med. Res. Rev*. **1982**, *2*, 127−152; Krapcho, J.; Turk, C. F. *J. Med. Chem*. **1973**, *16*, 776−779. (b) As antihypertensive agents: Prasad, R. N. *J. Med. Chem*. **1969**, *12*, 290−294; Cecchetti, V.; Fravolini, A.; Schiaffella, F.; DeRegis, M.; Orzalesi, G.; Volpato, I. *Farmaco. Ed. Sci*. **1983**, *38*, 35−44. (c) As anticancer agents: (a) Gupta, R. R.; Dev, P. K.; Sharma, M. L.; Rajoria, C. M.; Gupta, A.; Nyati, M. *Anticancer Drugs* **1993**, *4*, 589−592. (b) Todorov, D. K.; Ilarionova, M. V.; Gupta, R. R.; Molnar, J.; Motohashi, N. *Heterocycl. Commun*. **1995**, *1*, 153−155.

(5) Synthesis of benzothiazoles and benzothiazolines: (a) Dryanska, V.; Ivanov, Chr. *Synthesis* **1976**, 37−38. (b) Boger, D. L. *J. Org. Chem*. **1978**, *43*, 2296−2297. (c) Yates, P. C.; McCall, C. J.; Stevens, M. F. G. *Tetrahedron* **1991**, *47*, 6493−6502. (d) Bowman, W. R.; Heaney, H.; Jordan, B. M. *Tetrahedron* **1991**, *47*, 10119−10128. (e) Ares, J. J. *Synth. Commun*. **1991**, *21*, 625−633. (f) Leardini, R.; Nanni, D.; Santori, M.; Zanardi, G. *Tetrahedron* **1992**, *48*, 3961−3970. (g) Takahashi, M.; Ohba, M. *Heterocycles* **1995**, *41(3)*, 455−460. (h) Ohba, S.; Kosaka, T.; Wakabayashi, T. *Synth. Commun*. **1995**, *25*, 3421−3426. (i) Nivalkar, K. R.; Mashraqui, S. H. *Synth. Commun*. **1996**, *26*, 3535−3542. (j) Ben-Alloum, A.; Bakkas, S.; Soufiaoui, M. *Tetrahedron Lett*. **1997**, *38*, 6395−6396.

(6) Some recent syntheses of 1,4-benzothiazines: (a) Babudri, F.; DiNunno, L.; Florio, S. *Tetrahedron* **1982**, *38*, 3059−3065. (b) Babudri, F.; DiNunno, L.; Florio, S. *Synthesis* **1983**, 230−231. (c) Huang, X.; Chan, C.-C. *Synthesis* **1984**, 851−853. (d) Marfat, A.; Carta, M. P. *Synthesis* **1987**, 515−517. (e) Trapani, G.; Latrofa, A.; Reho, A.; Liso, G. *J. Heterocycl. Chem*. **1989**, *26*, 721−724. (f) Singh, H.; Singh, D. J.; Kumar, S. *Indian J. Chem. Sect. B*. **1992**, *31B*, 217−222. (g) Rai, D.; Gupta, V.; Gupta, R. R. *Heterocycl. Commun*. **1996**, *2*, 273−274.

(7) Perry, R. J.; Wilson, B. D. *Organometallics* **1994**, *13*, 3(*8*), 3346−3350.

(8) (a) Heck, R. F. *J. Am. Chem. Soc*. **1968**, *90*, 5518−5526, 5526−5531, 5531−5535, 5535−5538, 5538−5542, 5542−5546, 5546−5548. (b) Heck, R. F. *Org. React*. **1982**, *27*, 345−350. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985. (d) Daves, G. D., Jr.; Hallberg, A. *Chem. Rev*. **1989**, *89*, 1433−1445.

(9) (a) Negishi, E.-i. *Acc. Chem. Res*. **1982**, *15*, 340−350. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 508−524. (c) Kalinin, V. N. *Synthesis* **1992**, 413−432. (d) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457−2483. (e) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, 1995. (f) Larock, R. C. *J. Organomet. Chem*. **1999**, *576*, 111−124.

(10) Selected references: (a) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc*. **1993**, *115*, 12491−124509. (b) Balme, G.; Bouyssi, D. *Tetrahedron* **1994**, *50*, 403−414. (c) Negishi, E.; Coperet, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev*. **1996**, *96*, 365−393. (d) Larock, R. C.; Tian, Q. *J. Org. Chem*. **1998**, *63*, 2002−2009. (e) Larock, R. C.; Tian, Q.; Pletnev, A. A. *J. Am. Chem. Soc*. **1999**, *121*, 3238−3239.

(11) Selected references: (a) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl*. **1988**, *27*, 1113−1126. (b) Bouyssi, D.; Gore, J.; Balme, G.; Louis, D.; Wallach, J. *Tetrahedron Lett*. **1993**, *34*, 3129−3130. (c) Andersson, P. G.; Backvall, J. E. *J. Am. Chem. Soc*. **1992**, *114*, 8696−8698. (d) Trost, B. M.; McIntosh, M. C. *J. Am. Chem. Soc*. **1995**, *117*, 7255−7256. (e) Cavicchioli, M.; Decortiat, S.; Bouyssi, D.; Gore, J.; Balme, G. *Tetrahedron* **1996**, *52*, 11463−11478. (f) Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem*. **1998**, *63*, 7652−7662. (g) Zenner, J. M.; Larock, R. C. *J. Org. Chem*. **1999**, *64*, 7312−732. (h) Roesch, K. R.; Larock, R. C. *Org. Lett*. **1999**, *1*, 1551−1553.

(12) (a) Cassar, L. *J. Organomet. Chem*. **1975**, *93*, 253−257. (b) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem*. **1975**, *93*, 259−263. (c) Sonogashira, K.; Tohda, Y.; Hagihara, V. *Tetrahedron Lett*. **1975**, 4467−4469. (d) Torri, S.; Xu, L. H.; Okumoto, H. *Synlett* **1992**, 515−516. (e) Lu, X.; Huang, X.; Ma, S. *Tetrahedron Lett*. **1993**, *34*, 5963−5966. (f) Pal, M.; Kundu, N. G. *J. Chem. Soc., Perkin Trans. 1* **1996**, 449−451.

(13) (a) Kundu, N. G.; Pal, M.; Mahanty, J. S.; Dasgupta, S. K. *J. Chem. Soc., Chem. Commun*. **1992**, 41−42. (b) Kundu, N. G.; Pal, M.; Mahanty, J. S.; De, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2815−2820.

(14) (a) Kundu, N. G.; Pal, M. *J. Chem. Soc., Chem. Commun*. **1993**, 86−88. (b) Kundu, N. G.; Pal, M.; Nandi, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 561−568.

(15) (a) Kundu, N. G.; Mahanty, J. S.; Das, P.; Das, B. *Tetrahedron Lett*. **1993**, *34*, 1625−1628. (b) Mahanty, J. S.; De, M.; Das, P.; Kundu, N. G. *Tetrahedron* **1997**, *53*, 13397−13418.

(16) (a) Khan, M. W.; Kundu, N. G. *Synlett* **1997**, 1435−1437. (b) Kundu, N. G.; Khan, M. W.; Mahanty, J. S. *J. Chem. Res. (S)* **1999**, 460−461; *J. Chem. Res. (M)* **1999**, 1901−1918. (c) Kundu, N. G.; Khan, M. W.; Mukhopadhyay, R. *Tetrahedron* **1999**, *55*, 12361−12376. (d) Kundu, N. G.; Khan, M. W. *Tetrahedron* **2000**, *56*, 4777−4792.

(17) De, M.; Majumdar, D. P.; Kundu, N. G. *J. Indian Chem. Soc*. **1999**, *76*, 665−674.

(18) (a) Chowdhury, C.; Kundu, N. G. *J. Chem. Soc., Chem. Commun*. **1996**, 1067−1068. (b) Chowdhury, C.; Chaudhuri, G.; Guha, S.; Mukherjee, A. K.; Kundu, N. G. *J. Org. Chem*. **1998**, *63*, 1863−1871.

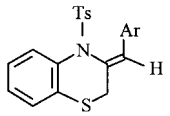
(19) (a) Chaudhuri, G.; Chowdhury, C.; Kundu, N. G. *Synlett* **1998**, 1273−1275. (b) Kundu, N. G.; Chaudhuri, G.; Upadhyay, A. *J. Org. Chem*. **2001**, *66*, 20−29.

(20) Chaudhuri, G.; Kundu, N. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 775−779.

(21) A preliminary account has appeared: Nandi, B.; Kundu, N. G. *Org. Lett*. **2000**, *2*, 235−238.

(22) Nandi, B.; Das, K.; Kundu, N. G. *Tetrahedron Lett*. **2000**, *41*, 7259−7262.

various conditions, e.g., (i) $Pd(OAc)_2$ (5 mol %), LiCl (0.7 mmol), K_2CO_3 (1.8 mmol), 80 °C, 24 h[23], (ii) NaOEt (2.5 equiv) in EtOH, reflux, 30 h,[20] (iii) NaH in THF, reflux, 20 h. However, the corresponding tosylates of **15**−**27**, which were obtained in high yields (88−96%), could be easily cyclized by refluxing for 36 h in THF in the presence of CuI (40 mol %) and Et_3N (4 equiv) in fairly good yields (63−80%, Table 1). Other cyclizing agents, e.g., (i) K_2CO_3 (2 equiv) in acetone, reflux for 24 h, (ii) KOH (10 equiv) in MeOH, reflux, 30 h, and (iii) NaOEt in EtOH, reflux for 36 h, yielded either the starting material or the detosylated material. Use of other agents, like NaH (2 equiv) in THF or CH_3CN and $PdCl_2$ (10 mol %) in CH_3CN in the presence of Et_3N (4 equiv), reflux, 30 h, led to the formation of polymeric materials. We noticed that for the cyclization step, considerable amount of CuI (40 mol %) was needed. In the absence of CuI, with Et_3N in THF alone 5% yield of cyclic product **28** was obtained—similarly, 6 mol % of CuI gave 10% yield, 20 mol % gave 30% yield, 30 mol % gave 45% yield, and 40 mol % gave 67% yield of **28**. Higher percentage of CuI led to a decline in yield. Also for cyclization, Et_3N plays a significant role since no cyclization was observed in the absence of Et_3N. The use of K_2CO_3 or NaOAc in place of Et_3N did not give any products. THF was found to be the best solvent for cyclization. The use of other solvents such as CH_3CN or DMF led to some polymeric materials. In contrast to our observations in the case of the synthesis of 2-alkyl(aryl)idene-2,3-dihydro-1,4-benzodioxins[18] and 2-alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzoxazines,[19] cyclization did not lead to the expected 3-alkyl(aryl)idene-1,4-benzothiazines **41** but to the (*E*)-2-(2-arylvinyl)-3-tosyl-1,3-benzothiazolines (**28**−**40**).

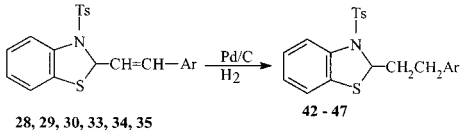


41

The structures of the products **28**−**40** follow from (1) the absence of a propargylic CH_2 signal both in ^1H NMR and ^{13}C NMR spectra, (2) the presence of −CH−CH=CH− signals in ^1H NMR spectra, (3) subsequent conversion of 2-(2-arylvinyl)-3-tosylbenzothiazolines to 2-(2-arylvinyl)benzothiazoles (see discussion below and Experimental Section), (4) conversion of 2-[2-(*m*-chlorophenyl)-vinyl]benzothiazoline **31** to *m*-chlorocinnamaldehyde by treatment with silver nitrate in Et_3N−phosphate buffer according to the procedure of Corey and Boger,[24] and (5) X-ray diffraction studies on **29**.[25] The configuration of the double bond was established from the splitting constants between two vinylic hydrogens at δ 6.25 and 6.69 (J = 15 Hz). Mechanistically[21] the formation of the benzothiazolines can be explained on the basis of (i) the usual Pd^0-mediated C-arylation[12c] leading to the disubstituted alkynes **15**−**27** and (ii) subsequent isomerization of the propargylic tosylates to allenic intermediates[21,26] which then undergo cyclization[27] to (*E*)-2-(2-arylvinyl)-3-tosyl benzothiazolines **28**−**40**.

Scope of the Reaction. We have shown the utility of our reaction in the synthesis of a number of (*E*)-2-(2-arylvinyl)-3-tosylbenzothiazolines **28**−**37** through palladium−copper-catalyzed reactions using readily available starting materials and under very mild conditions. Also, the synthesis of the bis-benzothiazoline derivatives, e.g., **38**−**40** (Table 1) adds in applicability of our synthetic protocol. To extend the scope, compounds **28**−**30**, **33**−**35** could be hydrogenated with Pd/C (10%) and hydrogen to the corresponding saturated derivatives, e.g., 2-(2-aryl)ethyl-3-tosylbenzothiazolines **42**−**47** (See Scheme 2, Table 3).

Scheme 2



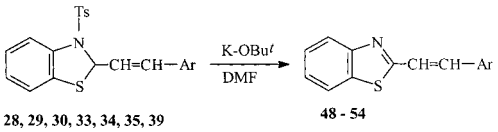
28, 29, 30, 33, 34, 35 **42 - 47**

Ar = **28, 42,** C_6H_5; **29, 43,** 1-naphthyl; **30, 44,** 2-naphthyl; **33, 45,** 4-MeC_6H_4; **34, 46,** 4-$MeOC_6H_4$; **35, 47,** 2-$MeOCOC_6H_4$

Table 3. Synthesis of 2-(2-Arylethyl)-3-tosylbenzothiazolines 42−47 (Scheme 2)

entry	2-(2-arylvinyl)-3-tosyl-benzothiazolines (Ar)	2-(2-arylethyl)-3-tosyl-benzothiazolines	yield (%)
1	**28**, C_6H_5	**42**	96
2	**29**, 1-naphthyl	**43**	98
3	**30**, 2-naphthyl	**44**	97
4	**33**, 4-MeC_6H_4	**45**	91
5	**34**, 4-$MeOC_6H_4$	**46**	95
6	**35**, 2-$MeOCOC_6H_4$	**47**	97

Scheme 3



28, 29, 30, 33, 34, 35, 39 **48 - 54**

Ar = **28, 48,** C_6H_5; **29, 49,** 1-naphthyl; **30, 50,** 2-naphthyl; **33,51,** 4-MeC_6H_4; **34, 52,** 4-$MeOC_6H_4$; **35, 53,** 2-$MeOCOC_6H_4$; **39,54,** 3-iodophenyl.

Another important outcome has been the synthesis of 2-(2-arylvinyl)benzothiazoles **48**−**54** which were easily obtained by dehydrotosylation of 2-(2-arylvinyl)-3-tosylbenzothiazolines **28**−**30**, **33**−**35**, **39** with potassium *tert*-butoxide in DMF at room temperature for 2 h in excellent yields (Scheme 3, Table 4).

A very significant aspect of our synthetic protocol is the generation of a number of 2-arylvinyl-substituted benzothiazolines, benzothiazoles, and bis-benzothiazoline

(23) Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689−6690.

(24) Corey, E. J.; Boger, D. L. *Tetrahedron Lett.* **1978**, 5−8.

(25) Maiti, S.; Mukherjee, M.; Nandi, B.; Helliwell, M.; Kundu, N. G. *Acta Crystallogr.* **2000**, *C56*, 992−994.

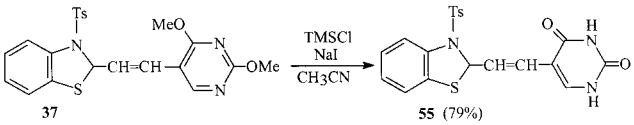
(26) Inspite of our best efforts, we could not isolate any allenic intermediates. They seem to be extremely reactive and undergo rapid cyclization to the benzothiazolines **28**−**40**. For propargyl to allenic isomerization, see, (a) Garratt, P. J.; Neoh, S. B. *J. Am. Chem. Soc.* **1975**, *97*, 3255−3256. (b) Midland, M. M. *J. Org. Chem.* **1977**, *42*, 2650−2657. (c) Flood, T.; Peterson, P. E. *J. Org. Chem.* **1980**, *45*, 5006−5007. (d) Brandsma, L.; Verkruijsee, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1980. (e) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805−2827. (f) Tsuji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 731−734. (g) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550−5555.

(27) For nucleophilic additions to allenes, see (a) Nixon, N. S.; Scheinmann, F. *Tetrahedron Lett.* **1983**, *24*, 597−600. (b) Tanaka, H.; Kamayema, Y.; Sumida, S.-i.; Yamada, T.; Tokumaru, Y.; Shiroi, T.; Sasaoka, M.; Taniguchi, M.; Torii, S. *Synlett.* **1991**, 888−890. (c) Kant, J.; Roth, J. A.; Fuller, C. E.; Walker, D. G.; Benigni, D. A.; Farina, V. *J. Org. Chem.* **1994**, *59*, 4956−4966. (d) Su, C.-C.; Chen, J.-T.; Leu, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 4999−5000. (e) Marshall, J. A.; Sehon, C. A. *J. Org. Chem.* **1995**, *60*, 5966−5968. (f) Marshall, J. A.; Wolf, M. A.; Wallace, E. *J. Org. Chem.* **1997**, *62*, 367−371. (g) Larock, R. C.; Tu, C.; Pace, P. *J. Org. Chem.* **1998**, *63*, 6859−6866. (h) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100* (*8*), 3067−3125.

Table 4. Synthesis of 2-(2-Arylvinyl)benzothiazoles 48−54 (Scheme 3)

entry	2-(2-arylvinyl)-3-tosyl-benzothiazolines (Ar)	2-(2-arylvinyl)-benzothiazoles	yield (%)
1	**28**, C_6H_5	**48**	74
2	**29**, 1-naphthyl	**49**	70
3	**30**, 2-naphthyl	**50**	78
4	**33**, 4-MeC_6H_4	**51**	75
5	**34**, 4-$MeOC_6H_4$	**52**	76
6	**35**, 2-$MeOCOC_6H_4$	**53**	73
7	**39**, 3-iodophenyl	**54**	71

Scheme 4

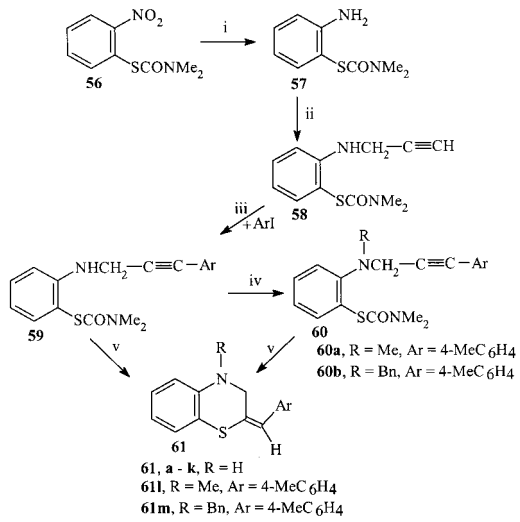


derivatives. Since benzothiazoles and benzothiazolines are of biological importance, we believe some of the compounds we have synthesized could have some biological activities and studies are in progress in this area. Also, we have converted **37** by treatment with TMSCl and NaI[28] in acetonitrile to 2-[2-(uracil-5-yl)vinyl]-3-tosylbenzothiazoline **55**, a uracil derivative with a novel substituent in the 5-position of the uracil ring (Scheme 4). Since 5-substituted uracil compounds[29] are of importance as anticancer and antiviral agents, **55** and the analogous nucleosides could be biologically important.

Synthesis of 2-Alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzothiazines. The synthesis of 2-alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzothiazines **61** was accomplished through the palladium−copper-catalyzed reactions of *S*-[2-(*N*-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate **58** with aryl iodides leading to the disubstituted alkynes **59** and the subsequent cyclization of the later with KOH in methanol (Scheme 5 and Table 5).

Since direct propargylation of 2-aminothiophenol leads to almost exclusive substitution at the thiol group, we utilized *S*-(2-nitrophenyl)-*N*,*N*-dimethylthiocarbamate[30] **56** as the starting material. The dimethyl carbamoyl group was found to be very suitable as a thiol protecting group[31] since it could be easily removed by alkaline hydrolysis during the subsequent cyclization step (Scheme 5, step v). Compound **56** was reduced with iron powder in acetic acid to *S*-(2-aminophenyl)-*N*,*N*-dimethyl thiocarbamate **57** in excellent yield (89%). This on usual propargylation with propargyl bromide in acetone in the presence of potassium carbonate yielded *S*-[2-(*N*-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate **58**. Compound **58** underwent C-arylation with aryl iodides in the presence of bis(triphenylphosphine) palladium(II) chloride (3.3−3.5 mol %) as a catalyst, cuprous iodide (6 mol %) as a cocatalyst, and triethylamine as a base in acetonitrile under very mild conditions (stirring at room temperature for 24 h) yielding the disubstituted alkynes, *S*-[2-(*N*-3′-aryl-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamates **59**, in excellent yields (Scheme 5, Table 5). The use of bis-triphenylphosphine palladium(II) dichloride as a catalyst was found to give the optimum yield (95%) (entry 1, Table 6). When tetrakistriphenylphosphine palladium(0) was used as the catalyst (entry 2, Table 6), the yield was much lower (23%). The cuprous iodide was found to be an essential cocatalyst. In its absence (entry 3, Table 6), 28% of the disubstituted alkyne was obtained whereas in the absence of the palladium catalyst but in the presence of CuI alone, 7% of **59a** (entry 4, Table 6) was obtained. Et_3N was found to be essential as a base for the coupling reaction. In its absence, no coupled products were obtained. The use of others bases, e.g., NaOAc or K_2CO_3, gave a very poor yield

Scheme 5[a]



[a] Reaction conditions: (i) Fe in AcOH; (ii) propargyl bromide, K_2CO_3 in acetone; (iii) $(PPh_3)_2PdCl_2$, CuI, Et_3N in CH_3CN at room temperature, 24 h; (iv) RX, K_2CO_3, acetone, reflux, 10 h; (v) KOH in MeOH, reflux, 24 h.

Table 5. Reaction of *S*-[2-(*N*-Prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethyl Thiocarbamate 58 with Aryl Iodides under Palladium−Copper Catalysis To Form Disubstituted Alkynes 59 and Their Subsequent Cyclization to 2-Alkyl(aryl)idene-3,4-dihydro-2*H*-1,4-benzothiazines 61 (Scheme 5)

entry	aryl iodides (ArI) Ar	disubstituted alkynes, **59** and **60** (%)[a]	2-alkylidene benzothiazines **61**(%)[b]
1	C_6H_5 **2**	**59a** (95)	**61a** (70)
2	1-naphthyl **3**	**59b** (90)	**61b** (74)
3	2-naphthyl **4**	**59c** (91)	**61c** (75)
4	3-ClC_6H_4 **5**	**59d** (93)	**61d** (76)
5	2-MeC_6H_4 **6**	**59e** (92)	**61e** (79)
6	4-MeC_6H_4 **7**	**59f** (92)	**61f** (81)
7	4-$MeOC_6H_4$ **8**	**59g** (95)	**61g** (77)
8	2-thienyl **10**	**59h** (90)	**61h** (82)
9	5-iodo-2-thienyl **12**	**59i** (59)	**61i** (75)
10	4-iodophenyl **14**	**59j** (65)	**61j** (79)
11	2-iodophenyl **14a**	**59k** (68)	**61k** (69)
12[c,e]		**60a** (96)	**61l** (95)
13[d,e]		**60b** (88)	**61m** (90)

[a] Yields are based on **58**. [b] Yields are based on disubstituted alkynes **59** or **60**. [c] **60a** was obtained by methylation of **59f** with MeI, K_2CO_3 in acetone, reflux, 10 h. [d] **60b** was obtained by benzylation of **59f** with BnBr, K_2CO_3 in acetone, reflux, 15 h. [e] Yields of **60a** and **60b** are based on **59f**.

(28) Morita, J.; Okamoto, Y.; Sakurai, H. *J. Chem. Soc., Chem. Commun*. **1978**, 874−875.

(29) (a) Heidelberger, C. *Pyrimidine and Pyrimidine Anti-metabolites in Cancer Medicine*; Holland, J. F.; Frei, E., Eds.; Lea and Febiger: Philadelphia, PA, 1984; pp 801−824. (b) De Clercq, E. *J. Med. Chem*. **1995**, *38*, 2491−2517. (c) Kundu, N. G.; Das, B.; Spears, C. P.; Majumdar, A.; Kang, S. I. *J. Med. Chem*. **1990**, *33*, 1975−1979. (d) Kundu, N. G.; Mahanty, J. S.; Chowdhury, C.; Dasgupta, S. K.; Das, B.; Spears, C. P.; Balzarini, J.; De Clercq, E. *Eur. J. Med. Chem*. **1999**, *34*, 389−398 and references therein.

(30) Newman, M.; Karens, H. A. *J. Org. Chem*. **1966**, *31*, 3980−3984.

(31) Thanks are due to Professor Asish De of our department for bringing this to our attention.

Table 6. Dependence of the Yield of *S*-[2-(*N*-3′-Arylprop-2′-ynyl)aminophenyl]-*N*,*N*-dimethyl Thiocarbamate 59a on a Catalyst, a Cocatalyst, and a Base

entry	catalyst	cocatalyst	base	yield (%)
1	$(PPh_3)_2PdCl_2$	CuI	Et_3N	95
2	$(PPh_3)_4Pd$	CuI	Et_3N	23
3	$(PPh_3)_2PdCl_2$	-	Et_3N	28
4	-	CuI	Et_3N	7
5	$(PPh_3)_2PdCl_2$	CuI	K_2CO_3	14

The amount of a catalyst used was 3.4−3.5 mol %, cocatalyst (6 mol %) except in case of entry 4 where 10 mol % of CuI was used, and the amount of base used was 4 equiv. The reactions were carried in CH_3CN at room temperature for 24 h.

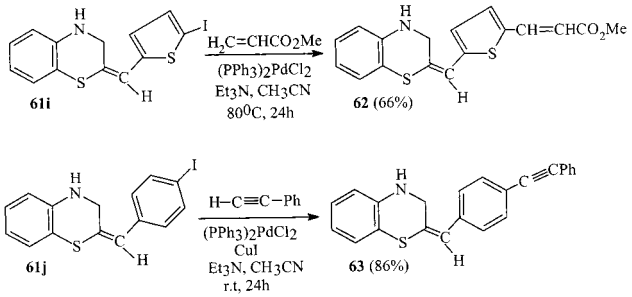
of **59a** (entry 5, Table 6). CH_3CN was found to be the best solvent for C-arylation reaction. The use of DMF gave rise to some polymeric materials, lowering the yield considerably. Also, due to insolubility of the starting material **58** in Et_3N, it could not be used as a solvent.

The C-arylation reaction was found to give excellent yields (90−95%) of the disubstituted alkynes **59a**−**59h** when monoiodo aromatic compounds were used as aryl iodides (entries 1−8, Table 5). The reaction was tolerant to various substituents in the aromatic ring. When diiodo compounds were used, the yields were somewhat lower (entries 9−11, Table 5). It was observed that only one of the iodide group entered the C-arylation reactions of **58**.

The cyclization of the disubstituted alkynes **59** was carried out by refluxing them with excess of KOH (10 equiv) in methanol. The use of lesser amount of KOH led to poorer yields. The use of other bases, e.g., NaOEt in EtOH, KOBu-*t* in *t*-BuOH, DMF or CH_3CN did not yield the cyclized materials. It was noticed that the presence of an alkyl or benzyl substituent on the N-atom (entries 12 and 13, Table 5) improves the yield (90−95%) of the cyclized products.

The structures of the cyclized products as 2-alkylidene-3,4-dihydro-2*H*-1,4-benzothiazines **61** follow from their analytical and spectroscopic (IR, ^{1}H NMR, and ^{13}C NMR) data. Particularly, in the ^{1}H NMR spectra, the presence of singlets at δ 3.69−4.01 (NCH_2) and δ 6.16−6.81 (C═CH) and in the ^{13}C NMR absorptions at δ 49.3−56.3 (NCH_2) and 113.9−120.1 (═CH) confirm the 2-alkylidene-3,4-dihydro-2*H*-1,4-benzothiazine structures. We have not observed the formation of any seven-membered ring compounds or any five-membered ring compounds, thus pointing to the regiospecificity of the cyclization reaction. The compounds were assigned the *E*-configuration on the basis of the chemical shift (δ 6.16−6.81) values of the vinylic hydrogen which is considerably shifted downfield due to deshielding effect[32] of the sulfur atom in the thiazine ring compared to the chemical shift of the vinylic hydrogens of (*Z*)-2-alkylidene-3,4-dihydro-2*H*-1,4-benzoxazines (δ 5.32−6.03)[19] and for the vinylic hydrogens of (*Z*)-2-alkylidene-2,3-dihydrobenzodioxins (δ 5.52−5.92).[18] Also, the $^3J_{CH}$ values between the vinylic proton and the methylenic carbon (NCH_2) of the heterocyclic ring confirmed the E-configuration of the exocyclic double bond. The $^3J_{CH}$ values of more than 7 Hz or less than 5 Hz have been attributed to *E*- and *Z*-isomers, respectively.[33,18,19] In our case, the $^3J_{CH}$ values were found to be 7.5 Hz for compounds **61a**, **61b**, **61d**, **61e**, and **61f**.

Scheme 6



Mechanism. Mechanistically, the terminal alkyne **58** undergoes the usual C-arylation catalyzed by Pd^0 generated from bis(triphenylphosphine)palladium(II) dichloride, as suggested by Sonogashira and co-workers,[12c] leading to the disubstituted alkynes **59**. The disubstituted alkynes then on hydrolysis cyclized to **61**. Interestingly, the cyclization of the disubstituted alkynes **59** led to 2-alkylidene benzothiazines **61** of *E*-configuration in contrast to the formation of (*Z*)-2-alkylidene-2,3-dihydro-1,4-benzodioxins[18] and (*Z*)-2-alkylidene-3,4-dihydro-2*H*-benzoxazines[19] in analogous cyclization reactions. No compounds with *Z*-configuration were observed. This could be explained by syn-addition[34] caused by an exo-dig attack on the alkyne moiety of the thiol group resulting from the hydrolysis of the dimethylthiocarbamoyl group.

Scope and Limitations. The (*E*)-2-alkylidene-3,4-dihydro-2*H*-1,4-benzothiazines **61** were found to decompose slowly in solution in $CHCl_3$, diethyl ether, ethyl acetate, and petroleum ether. Hence, various attempts to grow single crystals of **61** for X-ray diffraction studies by slow crystallization failed. Also, during hydrogenation over palladium on charcoal in solvents such as ethyl acetate, MeOH, glacial AcOH, compounds **61** were broken down into a number of unidentified components. Thus, we could not synthesize the corresponding saturated compounds, 2-alkyl-3,4-dihydro-2*H*-1,4-benzothiazines. We have also observed that the reactions of diiodo-aromatic compounds led to compounds **61i**, **61j**, and **61k**. Interestingly, these iodo-substituted benzothiazines **61i**−**k** could undergo further palladium-catalyzed reactions giving rise to variously substituted heteroaromatic compounds (Scheme 6).

Conclusion

Starting from 2-aminothiophenol, a readily available starting material, we have developed a highly general method for the synthesis of (*E*)-2-(2-arylvinyl)-3-tosyl-2,3-dihydro-1,3-benzothiazoles. The method involves two metal-catalyzed reactions, e.g., (i) a palladium−copper-catalyzed C-arylation of terminal alkynes giving rise to the disubstituted alkynes **15**−**27**, (ii) a unique copper-catalyzed cyclization which presumably involves a propargyl−allenic rearrangement[21,26] and subsequently a nucleophilic attack by the tosylamide group on the

(32) (a) Jager, V.; Gunther, H. J. *Tetrahedron Lett.* **1977**, 2543−2546. (b) Yamamoto, M. *J. Chem. Soc., Chem. Commun.* **1978**, 649−650. (c) Arcadi, A.; Burini, A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietrohi, B. R. *J. Org. Chem.* **1992**, *57*, 976−982.

(33) (a)Vogeli, U.; van Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617−627. (b) Cabiddu, S.; Floris, C.; Melis, S.; Sotgiu, F.; Cerioni, G. *J. Heterocycl. Chem.* **1986**, *23*, 1815−1820.

(34) The syn-addition to triple bond has been authenticated in the literature: (a) Bailey, W. F.; Ovaska, T. V. *Tetrahdron Lett.* **1990**, *31*, 627−630. (b) Weingarten, M. D.; Padwa, A. *Tetrahedron Lett.* **1995**, *36*, 4717−4720. Another explanation could be that during cyclization, compounds of *Z* configuration were formed which immediately got isomerised to benzothiazines having *E* configuration.

terminal carbon of the allenic moiety.[21,27] The process is highly regio- and stereoselective—only five-membered ring formation took place leading to the benzothiazolines. No six-membered compounds, e.g., the expected benzothiazines, or seven-membered ring heterocycles were obtained. The method not only requires cheap readily available starting materials and reagents, but is also carried out under mild reaction conditions. A number of (*E*)-2-(2-arylvinyl)-3-tosylbenzothiazolines **28**−**40**, their saturated derivatives, e.g., 2-(2-arylethyl)-3-tosylbenzothiazolines **42**−**47**, and also 2-arylvinylbenzothiazoles **48**−**54** could be accessed by our procedure. An uracil derivative **55** with a 2-(3-tosyl-2,3-dihydro-1,3-benzothiazol-2-yl) substituent at C-5 of the uracil ring and of potential biological significance has been synthesized. We have also described a novel procedure for the synthesis of 2-alkylidene-1,4-benzothiazines **61** where a palladium−copper-catalyzed arylation of terminal alkynes played a crucial role in the synthetic sequence. Interestingly, the 2-alkylidene benzothiazines were of the *E*-configuration instead of the expected *Z*-configuration.

Experimental Section

Melting points are uncorrected. Reactions were performed under argon atmosphere. Bis(triphenylphosphine)palladium(II) dichloride was obtained from Aldrich Chemical Co., Milwaukee, WI. Light petroleum used was the fraction boiling between 60 and 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.[35a] 2-Iodothiophene,[35b] 2,5-diiodothiophene,[35b] and 5-iodo-2,4-dimethoxypyrimidine[35c] were synthesized according to the known procedures. ^{1}H NMR spectra in $CDCl_3$ solutions were recorded at 300 MHz and that in CCl_4 solutions at 60 MHz. ^{13}C NMR spectra were recorded at 75 MHz. $^3J_{CH}$ values were obtained, performing ^{13}C NMR experiments under proton-coupled mode.

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-cooling, and the reaction mixture was heated under reflux for 15 h. After removal of acetone, the residue was diluted with H_2O and extracted with $CHCl_3$. The organic layer was washed with H_2O and dried (anhyd 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 eluent. Compound **1** was obtained as a light yellow oil (960 mg, 74%). IR (liquid film) 3460, 3360, 3290, 1608 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.06 (t, J = 3 Hz, 1H), 3.33 (d, J = 3 Hz, 2H), 4.2 (s, 2H), 6.53−6.69 (m, 2H), 6.92−7.46 (m, 2H). 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.

Typical Procedure for the Synthesis of 3-(2-Aminophenylthio)-1-phenylprop-1-yne (15). 3-(2-Aminophenylthio)prop-1-yne **1** (600 mg, 3.67 mmol) and iodobenzene **2** (730 mg, 3.67 mmol) were stirred in the presence of $(PPh_3)_2PdCl_2$ (90 mg, 0.13 mmol), CuI (42 mg, 0.22 mmol), and triethylamine (1.45 g, 14.33 mmol) in acetonitrile (10 mL) at room temperature under argon atmosphere for 24 h. After removal of the solvent under reduced pressure, the residue was treated with H_2O and extracted with $CHCl_3$. The organic layer was washed with H_2O and dried (anhyd Na_2SO_4) and solvent was distilled off to yield a brown gum which was purified by column chromatography on silica gel (60−120 mesh), the eluent being light petroleum/ethyl acetate (95/5, V/V) to afford **15** as a light yellow oil; IR (liquid film) 3460, 3370, 1605, 1480 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 2H), 4.27 (brs, 2H), 6.42−6.69 (m, 2H), 7.12 (td, J = 9, 1.5 Hz, 1H), 7.21−7.25 (m, 3H), 7.29−7.34 (m, 2H), 7.48 (dd, J = 7.8, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 84.3, 86.2, 115.4, 116.9, 118.9, 123.6, 128.6, 128.7, 131.2, 132.1, 137.6, 149.3; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 24.2 (inverted), 115.1, 118.6, 128.3, 128.4, 130.9, 131.8, 137.3. Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.34; H, 5.45; N, 5.71.

Tosylate of 15 was synthesized by stirring the alkyne **15** (400 mg, 1.79 mmol) in CH_2Cl_2 (20 mL) with *p*-TsCl (340 mg, 1.79 mmol) and pyridine (430 mg, 5.44 mmol) at room temperature for 10 h. Pyridine and dichloromethane were then removed under vacuum, and the residue was diluted with water followed by extraction with $CHCl_3$. The organic layer was washed with water and dried, and solvent was distilled off. Purification of the crude product by column chromatography on silica gel (60−120 mesh), the eluent being light petroleum/ethyl acetate (90/10, V/V), afforded the tosylate as a white solid; mp 85 °C; IR 3250, 1600, 1585, 1580, 1475 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.43 (s, 2H), 7.04 (td, J = 7.5, 1.2 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.25−7.34 (m, 6H), 7.55 (dd, J = 7.8, 1.5 Hz, 1H), 7.66 (d, J = 8.1 Hz, 3H), 7.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 26.2, 84.6, 85.2, 120.6, 122.9, 123.8, 125.3, 127.6, 128.7, 128.8, 130, 131.2, 132, 136.5, 137.2, 139.8, 144.4. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 25.9 (inverted), 120.3, 125, 127.3, 128.4, 128.5, 129.8, 130.9, 131.7, 136.9. Anal. Calcd for $C_{22}H_{19}NO_2S_2$: C, 67.15; H, 4.86; N, 3.56. Found: C, 66.95; H, 4.96; N, 3.54.

Compound **16**−**27** and their tosylates were synthesized following the procedure for **15** and the corresponding tosylate.

3-(2-Aminophenylthio)-1-(1-naphthyl)prop-1-yne (16): light brown oil; IR (liquid film) 3460, 3360, 1605, 1585, 1500, 1480 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 3.72 (s, 2H), 4.10 (brs, 2H), 6.46−7.03 (m, 3H), 7.13−7.79 (m, 7H), 8.00−8.16 (m, 1H). Anal. Calcd for $C_{19}H_{15}NS$: C, 78.83; H, 5.25; N, 4.83. Found: C, 78.71; H, 5.16; N, 4.72.

Tosylate of 16: light brown gum. IR (liquid film) 3280, 1600, 1485 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.36 (s, 2H), 6.92−7.10 (m, 3H), 7.29−7.53 (m, 6H), 7.59−7.82 (m, 6H), 7.89 (s, 1H). Anal. Calcd for $C_{26}H_{21}NO_2S_2$ C, 70.42; H,4.77; N,3.15. Found: C, 70.60; H, 4.81; N, 3.23.

3-(2-Aminophenylthio)-1-(2-naphthyl)prop-1-yne (17): white solid; mp 71 °C; IR 3470, 3365, 1600, 1580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 2H), 4.41 (brs, 2H), 6.71 (d, J = 7.2 Hz, 2H), 7.18 (t, J = 7.8 Hz, 1H), 7.35−7.44 (m, 3H), 7.53 (d, J = 7.8 Hz, 1H), 7.68−7.76 (m, 3H), 7.84 (s, 1H). Anal. Calcd for $C_{19}H_{15}NS$: C, 78.83; H, 5.25; N, 4.83. Found: C, 78.91; H, 5.40; N, 4.81.

Tosylate of 17: white solid; mp 91 °C; IR 3250, 1590, 1470 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.19 (s, 3H), 3.43 (s, 2H), 6.82−7.43 (m, 8H), 7.56−7.76 (m, 7H), 7.95 (s, 1H). Anal. Calcd for $C_{26}H_{21}NO_2S_2$: C, 70.39; H, 4.77; N, 3.15. Found: C, 70.51; H, 4.65; N, 3.05.

3-(2-Aminophenylthio)-1-(3-chlorophenyl)prop-1-yne (18): light yellow oil; IR (liquid film) 3440, 3360, 1600, 1590 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 3.56 (s, 2H), 4.23 (brs, 2H), 6.46−6.72 (m, 2H), 6.92−7.53 (m, 6H). Anal. Calcd for $C_{15}H_{12}ClNS$: C, 65.79; H, 4.41; N, 5.11. Found: C, 65.86; H, 4.37; N, 5.16.

Tosylate of 18: pale yellow gum; IR (liquid film) 3280, 1595, 1580 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.39 (s, 2H), 6.83−7.46 (m, 9H), 7.59−7.72 (m, 3H), 7.89 (s, 1H). Anal. Calcd for $C_{22}H_{18}ClNO_2S_2$: C, 61.73; H, 4.24; N, 3.27. Found: C, 61.66; H, 4.21: N, 3.32.

3-(2-Aminophenylthio)-1-(2-methylphenyl)prop-1-yne (19): light brown oil; IR (liquid film) 3460, 3360, 1600, 1560 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.30 (s, 3H), 3.66 (s, 2H), 4.33 (brs, 2H), 6.46−6.82 (m, 2H), 6.96−7.59 (m, 6H). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.91; H, 5.99; N. 5.48.

Tosylate of 19: pale yellow gum; IR (liquid film) 3260, 1600, 1580 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 2.33 (s, 6H), 3.36 (s,

(35) (a) Vogel, A. I. *A Text Book of Practical Organic Chemistry*, 4th ed.; ELBS, Longman Group Limited: London, 1978; pp 695−696. (b) Barker, J. M.; Huddlestone, P. R.; Wood M. L. *Synth. Commun.* **1975**, *5*, 59−64. (c) Das, B.; Kundu, N. G. *Synth. Commun.* **1988**, 855−867.

2H), 6.82−7.39 (m, 8H), 7.53−7.85 (m, 4H), 7.92 (s, 1H). Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.54; H, 4.98; N, 3.26.

3-(2-Aminophenylthio)-1-(4-methylphenyl)prop-1-yne (20): light yellow oil; IR (liquid film) 3450, 3360, 1600, 1505, 1475 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.65 (s, 2H), 4.38 (brs, 2H), 6.66−6.73 (m, 2H), 7.06 (d, J = 8.1 Hz, 2H), 7.13 (td, J = 8.1, 1.5 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 7.5, 1.2 Hz, 1H). ^{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, 75.60; H, 6.35; N, 5.28.

Tosylate of 20: white solid; mp 69 °C; IR 3280, 1597, 1575, 1520, 1470 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 3.43 (s, 2H), 7.04−7.32 (m, 8H), 7.54 (dd, J = 7.8, 1.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 3H), 7.95 (s, 1H). ^{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, 129.6, 130.5, 131.4, 136.4, 136.8, 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-Aminophenylthio)-1-(4-methoxyphenyl)prop-1-yne (21): pale yellow solid; mp 58 °C; IR 3450, 3360, 1605, 1565, 1500 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.56 (s, 2H), 3.73 (s, 3H), 4.39 (brs, 2H), 6.46−6.86 (m, 2H), 6.96−7.56 (m, 6H). Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20. Found: C, 71.38; H, 5.76; N, 5.47.

Tosylate of 21: white solid; mp 86 °C; IR 3265, 1600, 1585 cm^{-1}. ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.36 (s, 2H), 3.72 (s, 3H), 6.62−6.82 (m, 2H), 6.92−7.43 (m, 6H), 7.49−7.79 (m, 4H), 7.82 (s, 1H). Anal. Calcd for $C_{23}H_{21}NO_3S_2$: C, 65.22; H, 4.99; N, 3.30. Found: C, 65.28; H, 4.97; N, 3.47.

3-(2-Aminophenylthio)-1-(2-carbomethoxyphenyl)prop-1-yne (22): light yellow oil; IR (liquid film) 3460, 3360, 1720, 1605, 1565 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.82 (s, 2H), 3.96 (s, 3H), 4.49 (brs, 2H), 6.63−6.82 (m, 2H), 7.03−7.66 (m, 4H), 7.82−8.1 (m, 2H). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.7. Found: C, 68.79; H, 5.17; N, 4.61.

Tosylate of 22: yellow oil; IR (liquid film) 3270, 1720, 1609, 1570 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.46 (s, 2H), 3.86 (s, 3H), 7.03−7.49 (m, 8H), 7.06−7.79 (m, 3H), 7.86−8.00 (m, 2H). Anal. Calcd for $C_{24}H_{21}NO_4S_2$: C, 63.83; H, 4.68; N, 3.10. Found: C, 63.77; H, 4.68; N, 3.17.

3-(2-Aminophenylthio)-1-(2-thienyl)prop-1-yne (23): light brown oil; IR (liquid film) 3470, 3370, 1607, 1480 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.62 (s, 2H), 4.39 (brs, 2H), 6.49−7.26 (m, 5H), 7.33−7.49 (m, 2H). Anal. Calcd for $C_{13}H_{11}NS_2$: C, 63.63; H, 4.52; N, 5.7. Found: C, 63.79; H, 4.66; N, 5.82.

Tosylate of 23: white solid; mp 104 °C; IR 3250, 1595, 1575 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.39 (s, 2H), 6.49−7.00 (m, 7H), 7.43−7.76 (m, 4H), 7.89 (s, 1H). Anal. Calcd for $C_{20}H_{17}NO_2S_3$: C, 60.12; H, 4.28; N, 3.50. Found: C, 60.34; H, 4.51; N, 3.32.

3-(2-Aminophenylthio)-1-(2,4-dimethoxypyrimidin-5-yl)prop-1-yne (24): light brown oil; IR (liquid film) 3450, 3360, 1590, 1545 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.62 (s, 2H), 4.00 (s, 3H), 4.06 (s, 3H), 4.49 (brs, 2H), 6.49−6.79 (m, 2H), 7.00−7.50 (m, 2H), 8.03 (s, 1H). Anal. Calcd for $C_{15}H_{15}N_3O_3S$: C, 59.78; H, 5.01; N, 13.93. Found: C, 59.53; H, 4.81; N, 13.86.

Tosylate of 24: white solid; mp 121 °C. IR 3220, 1595, 1565 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 3H), 3.46 (s, 2H), 3.92 (s, 3H), 4.09 (s, 3H), 6.92−7.33 (m, 4H), 7.43−7.76 (m, 4H), 7.79 (s, 1H), 8.06 (s, 1H). Anal. Calcd for $C_{22}H_{21}N_3O_4S_2$: C, 58.00; H, 4.64; N, 9.22. Found: C, 53.73; H, 4.51; N, 9.07.

Syntheses of Substituted Dialkynes 25−27. The substituted dialkynes were synthesized according to the same procedure as for the disubstituted alkynes using diiodo aryl compounds (**12**−**14**) instead of the aryl iodides.

2,5-Bis[3-(2-aminophenylthio)prop-1-ynyl]thiophene (25): light brown oil; IR (liquid film) 3460, 3360, 1590, 1475 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.59 (s, 4H), 4.26 (brs, 4H), 6.53−6.82 (m, 4H), 6.89 (s, 2H), 7.03−7.56 (m, 4H). Anal. Calcd for $C_{22}H_{18}N_2S_3$: C, 64.99; H, 4.46; N, 6.88. Found: C, 65.21; H, 4.33; N, 6.75.

Tosylate of 25: light brown gum; IR (liquid film) 3260, 1590, 1465 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 6H), 3.39 (s, 4H), 6.92−7.36 (m, 10H), 7.43−7.76 (m, 10H). Anal. Calcd for $C_{36}H_{30}N_2O_4S_5$: C, 60.47; H, 4.23; N, 3.91. Found: C, 60.66; H, 4.17; N, 3.75.

1,3-Bis[3-(2-aminophenylthio)prop-1-ynyl]benzene (26): light brown oil. IR (liquid film) 3450, 3340, 1600, 1580 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.36 (s, 4H), 4.26 (brs, 4H), 6.50−6.69 (m, 4H), 6.91−7.56 (m, 7H), 7.72 (s, 1H). Analysis could not be performed since this compound was contaminated with the starting material. These two compounds have the same R_f value (TLC), so it could not be purified properly. In the tosylation step, the disubstituted alkyne was separated from the starting material.

Tosylate of 26: light yellow gum; IR (liquid film) 3270, 1595, 1582, 1545 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.33 (s, 6H), 3.39 (s, 4H), 6.95−7.33 (m, 10H), 7.43−7.59 (m, 9H), 7.76 (s, 1H), 7.92 (s, 2H). Anal. Calcd for $C_{38}H_{32}N_2O_4S_4$: C, 64.38; H, 4.55; N, 3.95. Found: C, 64.11; H, 4.62; N, 4.08.

1,4-Bis[3-(2-aminophenylthio)prop-1-ynyl]benzene (27): white solid; mp 117 °C; IR 3420, 3300, 1600, 1560, 1470 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 4H), 4.44 (brs, 4H), 6.71−6.77 (m, 4H), 7.11−7.24 (m, 6H), 7.50 (dd, J = 7.8, 1.5 Hz, 2H). Anal. Calcd for $C_{24}H_{20}N_2S_2$: C, 71.96; H, 5.03; N, 6.99. Found: C, 72.05; H, 4.98; N, 6.92.

Tosylate of 27: white solid; mp 120 °C; IR 3220, 1595, 1580, 1540 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 3.44 (s, 4H), 7.08 (td, J = 6, 1.5 Hz, 2H), 7.17−7.26 (m, 8H), 7.34 (td, J = 6, 1.5 Hz, 2H), 7.54 (dd, J = 7.8, 1.5 Hz, 2H), 7.66 (dd, J = 8.1, 1.5 Hz, 6H), 7.94 (s, 2H). 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.

Typical Procedure for the Synthesis of (*E*)-2-Styryl-3-tosylbenzothiazoline (28). The tosylate of the disubstituted alkyne **15** (0.3 g, 0.76 mmol) was refluxed with CuI (0.057 g, 0.3 mmol, 40 mol %) and triethylamine (0.31 g, 30.6 mmol) in THF (10 mL) for 36 h in an argon atmosphere. After removal of the solvent, the residue was treated with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extracts were combined, washed with H_2O, and dried (anhyd Na_2SO_4). The solvent was removed and the residue obtained was chromatographed on silica gel (60−120 mesh), eluent being light petroleum (60−80 °C)/ethyl acetate (95/5, V/V), furnishing the benzothiazoline **28** (0.2 g, 67%) as a white solid. This was crystallized from $CHCl_3$/light petroleum (60−80 °C); mp 154 °C; IR 1600, 1560, 1480, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.20 (dd, J = 15, 6 Hz, 1H), 6.25 (d, J = 6 Hz, 1H), 6.69 (d, J = 15 Hz, 1H), 7.02−7.30 (m, 10H), 7.46 (d, J = 9 Hz, 2H), 7.72 (d, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 68.9, 120.9, 122.6, 125.3, 125.6, 126.6, 126.9, 127.3, 128, 128.4, 129.3, 130.6, 132.5, 134.5, 136.9, 144.2; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 69.2, 121.1, 122.8, 125.5, 126.9, 127.1, 127.6, 128.3, 128.6, 129.6, 130.9. Anal. Calcd for $C_{22}H_{19}NO_2S_2$: C, 67.15; H, 4.86; N, 3.56. Found: C, 67.46; H, 5.07; N, 3.58.

Compounds **29**−**40** were synthesized according to the procedure as for the synthesis of **28**.

(*E*)-2-[2-(1-Naphthyl)vinyl]-3-tosylbenzothiazoline (29): white solid; mp 184 °C; IR 1600, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 6.24 (dd, J = 15, 6 Hz, 1H), 6.37 (d, J = 6 Hz, 1H), 7.06−7.18 (m, 5H), 7.36 (d, J = 15 Hz, 1H), 7.45−7.53 (m, 6H), 7.72−7.81 (m, 3H), 7.99 (d, J = 6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 69.5, 121.4, 123.3, 124.1, 124.6, 125.8, 125.9, 126.2, 126.6, 127.5, 127.9, 128.4, 128.9, 129.9, 130., 131.6, 133.1., 133.7, 133.9, 135, 137.4, 144.9; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.8, 69.2, 121.1, 123, 123.8, 124.3, 125.5, 125.6, 125.9, 126.4, 127.2, 127.6, 128.1, 128.6, 129.7, 129.7. Anal. Calcd for $C_{26}H_{21}NO_2S_2$: C, 70.42; H, 4.77; N, 3.15. Found: C, 70.36; H, 4.71; N, 3.09.

(*E*)-2-[2-(2-Naphthyl)vinyl]-3-tosylbenzothiazoline (30): white solid; mp 144 °C; IR 1590, 1445 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.32 (dd, J = 15, 6 Hz, 1H), 6.36 (d, J = 6 Hz, 1H), 6.87 (td, J = 15, 3.6 Hz, 1H), 7.04−7.17 (m, 5H), 7.4−7.51 (m, 5H), 7.7−7.78 (m, 5H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 22, 69.5, 121.4, 123.2, 124.1, 125.9, 126.5, 126.7, 127.5, 127.8, 127.9, 128, 128.5, 128.6, 129.9, 131.3, 133.1, 133.6, 133.6, 133.8, 134.9, 137.4, 144.9; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 69.3, 121.1, 122.9, 123.8, 125.6, 126.3, 126.4, 127.2, 127.5, 127.6, 127.7, 128.2, 128.3, 129.7, 131.01. Anal. Calcd for $C_{26}H_{21}NO_2S_2$: C, 70.40; H, 4.77; N, 3.15. Found: C, 70.36; H, 4.71; N, 3.09.

(*E*)-2-[2-(*m*-Chloro)styryl]-3-tosylbenzothiazoline (31): white solid; mp 147 °C; IR 1595, 1560, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.17 (dd, *J* = 15, 6 Hz, 1H), 6.24 (d, *J* = 6 Hz, 1H), 6.64 (d, *J* = 15 Hz, 1H), 7.02−7.18 (m, 8H), 7.31 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 69.1, 121.4, 123.2, 125.6, 125.9, 127.2, 127.5, 127.9, 128.6, 128.5, 129.8, 129.9, 130.1, 132.8, 134.9, 137.3, 138, 144.9; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.7, 68.8, 121.1, 122.9, 125.3, 125.7, 126.9, 127.2, 127.6, 128.3, 128.2, 129.5, 129.6, 129.8. Anal. Calcd for $C_{22}H_{18}ClNO_2S_2$: C, 61.73; H, 4.24; N, 3.27. Found: C, 61.56; H, 4.18; N, 3.03.

(*E*)-2-[2-(*o*-Tolyl)vinyl]-3-tosylbenzothiazoline (32): white solid; mp 86 °C; IR 1596, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.35 (s, 3H), 6.06 (dd, *J* = 15, 6 Hz, 1H), 6.25 (d, *J* = 6 Hz, 1H), 6.82 (d, *J* = 15 Hz, 1H), 7.06−7.25 (m, 9H), 7.45 (d, *J* = 9 Hz, 2H), 7.75 (d, *J* = 9 Hz, 1H). Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.85; H, 5.26; N, 3.61.

(*E*)-2-[2-(*p*-Tolyl)vinyl]-3-tosylbenzothiazoline (33): white solid; mp 109 °C; IR 1595, 1455, 1360 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.32 (s, 3H), 6.16 (dd, *J* = 15, 6 Hz, 1H), 6.25 (d, *J* = 6 Hz, 1H), 6.67 (d, *J* = 15 Hz, 1H), 7.01−7.22 (m, 9H), 7.47 (d, *J* = 9 Hz, 2H), 7.72 (d, *J* = 9 Hz, 1H); ^{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, 127.4, 129.2, 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.

(*E*)-2-[2-(4-Methoxyphenyl)vinyl]-3-tosylbenzothiazoline (34): white solid; mp 143 °C; IR 1600, 1570, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.76 (s, 3H), 6.07 (dd, *J* = 15, 6 Hz, 1H), 6.23 (dd, *J* = 6, 0.9 Hz, 1H), 6.65 (d, *J* = 15 Hz, 1H), 6.79 (d, *J* = 9 Hz, 2H), 7.02−7.14 (m, 5H), 7.26 (d, *J* = 9 Hz, 2H), 7.47 (d, *J* = 9 Hz, 2H), 7.72 (d, *J* = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 55.6, 69.7, 114.3, 121.4, 123.1, 125, 125.8, 127.4, 127.8, 128.6, 129.9, 130.7, 133.2, 133.8, 135.1, 137.4, 144.8, 160.1; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 55.3, 69.4, 114, 121.1, 122.8, 124.7, 125.5, 127.1, 127.6, 128.3, 129.6, 130.4. Anal. Calcd for $C_{23}H_{21}NO_3S_2$: C, 65.22; H, 4.99; N, 3.3. Found: C, 65.41; H, 4.96; N, 3.19.

(*E*)-2-[2-(2-Carbomethoxyphenyl)vinyl]-3-tosylbenzothiazoline (35): white solid; mp 153 °C; IR 1720, 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.83 (s, 3H), 6.07 (dd, *J* = 15, 6 Hz, 1H), 6.26 (d, *J* = 6 Hz, 1H), 7.00−7.13 (m, 5H), 7.23−7.51 (m, 6H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 52.6, 69.4, 121.3, 123.1, 125.8, 127.8, 128, 128.1, 129.4, 129.6, 129.9, 130.4, 132.4, 133, 135, 137.4, 137.8, 144.8, 168; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 52.2, 69.1, 121, 122.8, 125.5, 127.1, 127.7, 127.8, 129.3, 129.6, 130.1, 130.7, 132.1. Anal. Calcd for $C_{24}H_{21}NO_4S_2$: C, 63.83; H, 4.68; N, 3.10. Found: C, 63.67; H, 4.79; N, 3.19.

(E)-2-[2-(2-Thienyl)vinyl]-3-tosylbenzothiazoline (36): white solid; mp 143 °C; IR 1625, 1590, 1490, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.02 (dd, *J* = 15, 6 Hz, 1H), 6.22 (dd, *J* = 6, 0.9 Hz, 1H), 6.81−6.94 (m, 3H), 7.00−7.15 (m, 6H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 69.1, 121.4, 123.2, 124.5, 125.6, 125.9, 126.5, 127.5, 127.7, 127.9, 129.9, 133, 134.9, 137.3, 141, 144.9; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.8, 68.8, 121.1, 122.9, 124.2, 125.3, 125.6, 126.2, 127.2, 127.4, 127.6, 129.6. Anal. Calcd for $C_{20}H_{17}NO_2S_3$: C, 60.12; H, 4.29; N, 3.50. Found: C, 59.93; H, 4.40; N, 3.39.

(*E*)-2-[2-(2,4-Dimethoxypyrimidin-5-yl)vinyl]-3-tosylbenzothiazoline (37): white solid; mp 127 °C; IR 1590, 1550, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.90, 3.93 (2s, 6H), 6.15 (d, *J* = 6 Hz, 1H), 6.29 (dd, *J* = 15.6, 6 Hz, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.95−7.09 (m, 6H), 7.4 (d, *J* = 8.1 Hz, 2H), 8.12 (s, 1H); Anal. Calcd for $C_{22}H_{21}N_3S_2O_4$: C, 58.00; H, 4.64; N, 9.22. Found: C, 57.89; H, 4.51; N, 9.08.

2,5-Bis[(*E*)-2-(3′-tosyl-2′-benzothiazolinyl)vinyl]-thiophene (38): light yellow solid; mp 112 °C; IR 1625, 1590, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 5.91 (dd, *J* = 15, 6 Hz, 2H), 6.17 (d, *J* = 6 Hz, 2H), 6.69−6.76 (m, 4H), 7.00−7.13 (m, 10H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.69 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 69, 121.4, 123.2, 124.3, 125.9, 126.9, 127.5, 127.6, 127.8, 128.2, 129.9, 132.9, 134.9, 137.3, 140.8, 144.8; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 68.7, 121.1, 122.9, 124, 125.6, 126.6, 127.2, 127.4, 127.6, 127.9, 129.6. Anal. Calcd for $C_{36}H_{30}N_2O_4S_5$: C, 60.47; H, 4.23; N, 3.91. Found: C, 60.35; H, 4.22; N, 3.80.

1,3-Bis[(*E*)-2-(3′-tosyl-2′-benzothiazolinyl)vinyl]benzene (39): white solid; mp 125 °C; IR 1600, 1550 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 6H), 6.18 (dd, *J* = 15, 6 Hz, 2H), 6.24 (d, *J* = 6 Hz, 2H), 6.6 (d, *J* = 15 Hz, 2H), 6.99−7.4 (m, 13H), 7.46−7.54 (m, 4H), 7.67 (s, 1H), 7.73 (dd, *J* = 7.5, 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 69.1, 121.3, 123.2, 125.9 126.7, 127.5, 127.8, 128.5, 129.5, 129.9, 130.6, 132.8, 134.8, 136.1, 137.3, 137.3, 138.3, 145; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.8, 68.8, 121.1, 122.9, 125.7, 126.4, 127.3, 127.6, 128.2, 129.3, 129.7, 130.3, 135.7, 127.1. Anal. Calcd for $C_{38}H_{32}N_2O_4S_4$: C, 64.38; H, 4.55; N, 3.95. Found: C, 64.68; H, 4.69; N, 3.99.

1,4-Bis[(*E*)-2-(3′-tosyl-2′-benzothiazolinyl)vinyl]benzene (40): white solid; mp 148−149 °C; IR 1595, 1570, 1550 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H), 6.23 (dd, *J* = 15, 6 Hz, 2H), 6.27 (d, *J* = 6 Hz, 2H), 6.65 (d, *J* = 15 Hz, 2H), 7.05−7.15 (m, 10H), 7.5 (d, *J* = 8.1 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.75 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 69.2, 121.4, 123.2, 125.9, 127.6, 127.8, 127.9, 129.1, 130, 132.9, 134.7, 135.6, 137.3, 138, 145; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.8, 68.9, 121.1, 122.9, 125.6, 127.3, 127.7, 127.7, 128.8, 129.7, 137.7. Anal. Calcd for $C_{38}H_{32}N_2O_4S_4$: C, 64.38; H, 4.55; N, 3.95. Found: C, 64.08; H, 4.64; N, 3.95.

Typical Procedure for the Synthesis of 2-(2-Phenylethyl)-3-tosylbenzothiazoline (42). (*E*)-2-(2-Phenylvinyl)-3-tosylbenzothiazoline **28** (300 mg, 0.76 mmol) was hydrogenated in the presence of 10% Pd on activated charcoal (100 mg) in dry ethyl acetate (25 mL) at atmospheric pressure for 2 days (48 h.). After completion of the reaction, the catalyst was removed by filtration and washed with ethyl acetate. The solvent was distilled off, and the residue was chromatographed on silica gel (60−120 mesh) with the eluent being light petroleum/ethyl acetate (95/5, V/V) to afford **42** as a white solid; mp 130 °C; IR 1590, 1490 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.00−2.12 (m, 1H), 2.20−2.30 (m, 1H), 2.34 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 5.56 (t, *J* = 6.9 Hz, 1H), 7.00−7.25 (m, 10H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 31.7, 41.4, 69.2, 121.9, 122.9, 125.6, 126.5, 127.4, 127.9, 128.8, 128.9, 129.8, 134.2, 134.7, 137.3, 141, 144.7; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 31.5 (inverted), 41.1 (inverted), 68.9, 121.7, 122.7, 125.3, 126.2, 127.2, 127.6, 128.5, 128.6, 129.5. Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.80; H, 5.35; N, 3.54. Found: C, 66.69; H, 5.22; N, 3.47.

Similar procedure was followed for the synthesis of **43**−**47**.

2-[2-(1-Naphthyl)ethyl]-3-tosylbenzothiazoline (43): white solid; mp 162 °C; IR 1596.2, 1510.3, 1495.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.15−2.26 (m, 1H), 2.30−2.41 (m, 4H), 3.21−3.38 (m, 2H), 5.70 (t, *J* = 9 Hz, 1H), 7.04−7.14 (m, 5H), 7.36−7.47 (m, 6H), 7.68−7.84 (m, 3H), 8.01 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 28.9, 40.7, 69.5, 122, 123, 124, 125.7, 125.9, 126, 126.4, 126.5, 127.3, 127.5, 127.9, 129.1, 129.8, 134.2, 134.3, 134.7, 137.2, 137.3, 144.8. ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.8, 28.6 (inverted), 40.5 (inverted), 69.2, 121.7, 122.7, 123.7, 125.4, 125.6, 126.1, 126.2, 127, 127.2, 127.6, 128.9, 129.5. Anal. Calcd for $C_{26}H_{23}NO_2S_2$: C, 70.08; H, 5.20; N, 3.14. Found: C, 69.95; H, 5.22; N, 3.17.

2-[2-(2-Naphthyl)ethyl]-3-tosylbenzothiazoline (44): white solid; mp 123 °C; IR 1595, 1506.3, 1490.9, 1454.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03−2.15 (m, 1H), 2.23−2.36 (m, 4H), 2.95 (t, *J* = 9 Hz, 2H), 5.54 (t, *J* = 9 Hz, 1H), 6.98−

7.06 (m, 5H), 7.27−7.37 (m, 5H), 7.58−7.70 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22, 31.9, 41.3, 69.2, 122, 123, 125.6, 125.7, 126.3, 127, 127.5, 127.7, 128, 128.4, 129.8, 132.5, 134, 134.7, 137.3, 138.5, 144.7. ^{13}C NMR (300 MHz, $CDCl_3$, DEPT 135) δ 21.7, 31.6 (inverted), 40.9 (inverted), 69, 121.7, 122.7, 125.4, 126, 126.7, 127.2, 127.4, 127.6, 127.7, 128.1, 129.5. Anal. Calcd for $C_{26}H_{23}NO_2S_2$: C, 70.08; H, 5.2; N, 3.14. Found: C, 70.1; H, 4.99; N, 3.15.

2-(2-*p*-Tolylethyl)-3-tosylbenzothazoline (45): white solid; mp 84 °C; IR 1600, 1580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89−2.01 (m, 1H), 2.09−2.19 (m, 1H), 2.21 (s, 3H), 2.24 (s, 3H), 2.70 (t, J = 7.8 Hz, 2H), 5.48 (t, J = 7.2 Hz, 1H), 6.91−7.07 (m, 9H), 7.29 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22, 31.3, 41.5, 69.3, 121.9, 123, 125.6, 127.4, 127.9, 128.8, 129.5, 129.8, 134.2, 134.8, 135.8, 137.3, 137.9, 144.7; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.7, 31 (inverted), 41.3 (inverted), 69, 121.7, 122.7, 125.3, 127.2, 127.6, 128.5, 129.2, 129.5. Anal. Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.44; H, 5.66; N, 3.41. Found: C, 67.53; H; 5.36; N, 3.14.

2-[2-(4-Methoxyphenyl)ethyl]-3-tosylbenzothiazoline (46): colorless oil; IR (liquid film) 1596.7, 1580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94−1.99 (m, 1H), 2.09−2.19 (m, 1H), 2.27 (s, 3H), 2.70 (t, J = 9 Hz, 2H), 3.70 (s, 3H), 5.48 (t, J = 9 Hz, 1H), 6.74 (dd, J = 6, 3 Hz, 2H), 6.95−7.08, (m, 7H), 7.3 (d, J = 9 Hz, 2H), 7.62 (dd, J = 9, 3 Hz, 1H). Anal. Calcd for $C_{23}H_{23}NO_3S_2$: C, 64.91; H, 5.44; N, 3.29. Found: C, 64.87; H, 5.43; N, 3.31.

2-[2-(2-Carbomethoxyphenyl)ethyl]-3-tosylbenzothiazoline (47): white solid; mp 79 °C; IR 1716.5, 1595.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98−2.17 (m, 2H), 2.28 (s, 3H), 3.09 (t, J = 9 Hz, 2H), 3.79 (s, 3H), 5.56 (t, J = 9 Hz, 1H), 6.95−7.05 (m, 5H), 7.16−7.21 (m, 2H), 7.30−7.35 (m, 3H), 7.63 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.03, 30.9, 41.6, 52.4, 69.5, 121.9, 122.9, 125.5, 126.6, 127.4, 127.8, 129.8, 129.9, 131.3, 131.5, 132.5, 134.3, 134.8, 137.3, 143, 144.7, 168.3. ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 21.7, 30.6 (inverted), 41.3 (inverted), 52.1, 69.2, 121.6, 122.6, 125.3, 126.3, 127.1, 127.6, 129.5, 131, 131.2, 132.2. Anal. Calcd for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.08. Found: C, 63.76; H, 4.98; N, 3.24.

Typical Procedure for the Synthesis of (*E*)-2-(2-Phenylvinyl)benzothiazole (48). (*E*)-2-(2-Phenylvinyl)-3-tosylbenzothiazoline **28** (180 mg, 0.46 mmol) was added to KOBu^t (made from K = 60 mg, 1.38 mmol) in dry DMF (5 mL) at 0 °C. This reaction mixture was stirred at room temperature for 3 h. Ethyl acetate (10 mL) and saturated NaCl solution (5 mL) were added, and ethyl acetate layer was separated. The aqueous layer was further extracted with ethyl acetate. The combined organic layer was washed with H_2O and dried over anhyd Na_2SO_4. After removal of the solvent under reduced pressure, a light brown solid was obtained which on crystallization [$CHCl_3$/petroleum spirit (60−80 °C)] afforded **48** as a white solid; mp 112 °C (lit[36] mp: 112 °C); IR 1625, 1480 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.47 (m, 7H), 7.53 (dd, J = 9, 3 Hz, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.9, 122.5, 123.4, 125.7, 126.7, 127.8, 129.3, 129.8, 134.7, 135.8, 138, 154.3, 167.2; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT 135) δ 121.6, 122.2, 123.1, 125.4, 126.4, 127.5, 129, 129.5, 137.7. Anal. Calcd for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90. Found: C, 75.82; H, 4.59; N, 5.77.

Compounds **49**−**54** were synthesized by following the above procedure for **48**.

(*E*)-2-[2-(1-Naphthyl)vinyl]benzothiazole (49): white solid; mp 116 °C; IR 1618.2, 1583.4, 1554.5, 1485.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (t, J = 7.8 Hz,1H), 7.45−7.62 (m, 6H), 7.84−7.96 (m, 4H), 8.03 (d, J = 8.1 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H). Anal. Calcd for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; N, 4.87. Found: C, 79.68; H, 4.50; N, 4.86.

(*E*)-2-[2-(2-Naphthyl)vinyl]benzothiazole (50): white solid; mp 160 °C; IR 1620.5, 1582, 1550.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (t, J = 7.5 Hz, 1H), 7.45−7.54 (m, 4H), 7.65−7.76 (m, 2H), 7.81−7.88 (m, 4H), 7.94 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.9, 122.7, 123.4, 123.6, 125.8, 126.7, 127.1, 127.3, 128.2, 128.8, 129.1, 129.2, 133.3, 133.9, 134.2, 138.2, 154.3. Anal. Calcd for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; N, 4.87. Found: C, 79.6; H, 4.58; N, 4.88.

(*E*)-2-[2-(*p*-Tolyl)vinyl]benzothiazole (51): light yellow solid; mp 130 °C; IR 1625.9, 1602.7, 1569.9, 1515.9, 1479.3 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.15 (d, J = 7.8 Hz, 2H), 7.24−7.49 (m, 6H), 7.79 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.1, 121.5, 121.9, 123.2, 125.6, 127.7, 129.8, 130.1, 133.1, 138.2, 140.1, 154.2, 167.9. Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.66; H, 5.27; N, 5.42.

(*E*)-2-[2-(4-Methoxyphenyl)vinyl]benzothiazole (52): white solid; mp 142 °C; IR 1625.9, 1602.7, 1575.7, 1514 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.93 (d, J = 8.7 Hz, 2H), 7.24−7.38 (m, 2H), 7.43−7.54 (m, 4H), 7.84 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.7, 114.8, 120.3, 121.8, 123.1, 125.5, 126.6, 128.5, 129.3, 134.6, 137.8, 154.3, 161.1, 167.8. Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.23. Found: C, 72.10; H, 4.88; N, 5.31.

(*E*)-2-[2-(2-Carbomethoxyphenyl)vinyl]benzothiazole (53): white solid; mp 110 °C; IR 1714.6, 1628.3, 1600, 1580.2, 1494.7 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.18−7.39 (m, 4H), 7.46 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.1 Hz, 2H), 8.33 (d, J = 15 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.2, 120.4, 122.1, 123.8, 124.4, 125.2, 126.2, 127.6, 127.8, 129.9, 131.4, 135.7, 136.2, 152.8, 166.1. Anal. Calcd for $C_{17}H_{13}NO_2S$: C, 69.13; H, 4.43; N, 4.74. Found: C, 69.06; H, 4.35; N, 4.79.

1,3-Bis[(*E*)-2-(2′-benzothiazolyl)vinyl]benzene (54): pale yellow solid; mp 120 °C; IR 1625.9, 1583.4, 1554.5, 1485.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (t, J = 7.8 Hz, 2H), 7.36−7.55 (m, 7H), 7.68 (d, J = 7.5 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.93 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.9, 123.5, 123.7, 125.9, 126.8, 126.8, 130.9, 136, 136.7, 138, 138.5, 154.2, 166.6. Anal. Calcd for $C_{24}H_{16}N_2S_2$: C, 72.69; H, 4.07; N, 7.06. Found: C, 72.58; H, 4.11; N, 7.13.

(*E*)-2-[2-(Uracil-5-yl)vinyl]-3-tosylbenzothiazoline (55). Compound **37** (70 mg, 0.15 mmol) in acetonitrile (3 mL) was stirred with anhydrous sodium iodide (70 mg, 0.46 mmol) and chlorotrimethylsilane (50 mg, 0.46 mmol) at room temperature for 24 h in an argon atmosphere. After removal of solvent under reduced pressure the residue was treated with saturated sodium metabisulfite solution (0.5 mL) and then with water (2 mL). This was filtered and dried to yield a pale yellow solid which was crystallized from MeOH−H_2O to afford a white solid; mp >250 °C. IR 3242.1, 3184.2, 1712.7, 1678, 1596.9 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.34 (s, 3H), 6.20 (d, J = 6 Hz, 1H), 6.33 (dd, J = 15.6, 6 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 7.00−7.14 (m, 6H), 7.44 (d, J = 8.1 Hz, 2H), 8.16 (s, 1H), 11.14 (s, 1H), 11.35 (s, 1H). Anal. Calcd for $C_{20}H_{17}N_3S_2O_4$: C, 56.19; H, 4.00; N, 9.82. Found: C, 57.95; H, 3.98; N, 9.71.

Conversion of (*E*)-2-[2-(*m*-Chlorophenyl)vinyl]-3-tosylbenzothiazoline 31 to *m*-Chlorocinnamaldehyde. To a DMF solution (25 mL) of (*E*)-2-[2-(*m*-chlorophenyl)vinyl]-3-tosylbenzothiazoline **31** (280 mg, 0.65 mmol) was added phosphate buffer (0.05 M, pH = 7, 2 mL) at room temperature followed by the addition of $AgNO_3$ solution (180 mg, 1.05 mmol in 1.75 mL of H_2O). After a few minutes, a curdy white precipitate appeared and more $AgNO_3$ solution (180 mg, 1.05 mmol in 1.75 mL H_2O) was added. After stirring the reaction mixture for 10 min, Et_3N (71 mg, 0.0.7 mmol) was added and stirred for 2 h. The reaction mixture was filtered through Celite bed and washed throughly with ether. The ether layer was washed with H_2O and dried (anhydrous Na_2SO_4), and the solvent was removed. A light yellow oil, *m*-chlorocinnamaldehyde, (80 mg, 73%) was obtained after purification through neutral alumina (eluent being light petroleum/ethyl acetate: 80/20, V/V);yield: 80 mg, 73.29%. IR (liquid film) 1675, 1630, 1600, 1560 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (dd, J = 15.9, 7.5 Hz, 1H), 7.28−7.44 (m, 5H), 8.61 (d, J = 7.5 Hz, 1H). Anal. Calcd for C_9H_7ClO: C, 64.86; H, 4.23. Found: C, 64.62; H, 4.18.

(36) Brown, D. M.; Kon, G. A. R. *J. Chem. Soc.* **1948**, *70*, 2147−2154.

***S*-(2-Aminophenyl)-*N*,*N*-dimethylthiocarbamate (57).** To a mechanically stirred solution of *S*-(2-Nitrophenyl)-*N*,*N*-dimethylthiocarbamate[30] **56** (5.8 g, 27.3 mmol) in a mixture of glacial acetic acid (60 mL) and water (20 mL), iron powder (8 g, 136.5 mmol) was added slowly under ice-cold bath, and the reaction mixture was then stirred at room temperature for 8 h. This was neutralized with solid $NaHCO_3$ and filtered through a sintered-bed funnel, and the filtrate was extracted with $CHCl_3$. The organic layer was washed with H_2O and dried (anhyd Na_2SO_4), and the solvent was distilled off. The crude compound obtained was purified by column chromatography on silica gel (60−120 mesh) with the eluent being light petroleum/ethyl acetate (80/20, V/V) to yield **57** as a light yellow oil in 89% yield (4.47 g); IR (liquid film) 3442.7, 3334.7, 1660.6, 1614.3, 1587.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.01 (s, 3H), 3.12 (s, 3H), 3.75 (brs, 2H), 6.69−6.76 (m, 2H), 7.19 (dd, J = 7.5, 1.8 Hz, 1H), 7.28 (dd, J = 7.8, 1.5 Hz, 1H). Anal. Calcd for $C_9H_{12}N_2OS$: C, 55.07; H; 6.16; N, 14.26. Found: C, 54.88; H, 5.96; N, 14.51.

***S*-[2-(*N*-Prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (58).** Compound **57** (1 g, 5.09 mmol) was stirred at room temperature with K_2CO_3 (0.7 g, 5.09 mmol) in acetone (20 mL) in an argon atmosphere for 5 h. Propargyl bromide (0.6 g, 5.09 mmol) was added slowly, and the reaction mixture was heated under reflux for 16 h. Solvent was removed under reduced pressure, and the residue was diluted with H_2O. This was extracted with $CHCl_3$, washed with H_2O, and dried (anhyd Na_2SO_4). The residue obtained after removal of solvent was purified by column chromatography on silica gel (60−120 mesh), using light petroleum/ethyl acetate (80/20, V/V) as eluent to yield **58** as a white solid (0.8 g, 84%), mp 127 °C. IR 3374, 3277, 1667.7, 1592.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.19 (t, J = 3 Hz, 1H), 3.00, 3.12 (2s, 6H), 3.96 (d, J = 3 Hz, 2H), 4.81 (brs, 1H), 6.72−6.79 (m, 2H), 7.30−7.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.8, 37.4, 81, 96.5, 111.9, 112.8, 118.6, 132.1, 138.5, 149.3, 166; ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.5 (inverted), 37.1, 80.8, 111.6, 118.3, 131.8, 138.2. Anal. Calcd for $C_{12}H_{14}N_2OS$: C, 61.51; H, 6.02; N, 11.95. Found: C, 61.77; H, 5.71; N, 12.00.

Typical Procedure for the Synthesis of *S*-[2-(*N*-3′-Phenylprop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (59a). A mixture of **58** (300 mg, 1.27 mmol), iodobenzene (340 mg, 1.65 mmol), $(PPh_3)_2PdCl_2$ (30 mg, 0.43 mmol, 3.38 mol), copper(I) iodide (15 mg, 0.076 mmol, 6 mol %), and triethylamine (610 mg, 5.08 mmol) in acetonitrile (5 mL) was stirred at room temperature for 24 h in an argon atmosphere. Solvent was removed under reduced pressure, and the residue was diluted with H_2O. This was extracted with $CHCl_3$, and the organic layer was washed with H_2O. This was dried (anhyd Na_2SO_4), and the solvent was removed to furnish a brown gum which was purified by column chromatography on silica gel (60−120 mesh) using light petroleum/ethyl acetate (80/20, V/V) as eluent to yield **59a** as a pale yellow oil. IR (liquid film) 3338.3, 1666.2, 1590.4, 1567.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.97, 3.09 (2s, 6H), 4.18 (s, 2H), 4.98 (brs, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 7.22−7.26 (m, 3H), 7.34−7.4 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.8, 37.4, 83.7, 86.6, 112.1, 112.8, 118.5, 123.3, 128.7, 132.1, 138.3, 149.6, 166.2. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 34.5 (inverted), 37.2 111.8, 118.2, 128.4, 131.9, 138.2. Anal. Calcd for $C_{18}H_{18}N_2OS$: C, 69.65; H, 5.84; N, 9.02. Found: C, 69.81; H, 5.66; N, 8.97.

Compounds **59b**−**k** were synthesized by following the procedure for **59a**.

***S*-[2-{*N*-3′-(1-Naphthyl)prop-2′-ynyl}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59b):** white solid; mp 84 °C; IR 3347.4, 1667.9, 1591.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.00, 3.12 (2s, 6H), 4.25 (s, 2H), 5.03 (brs, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 7.30−7.48 (m, 5H), 7.59 (d, J = 7.2 Hz, 1H), 7.75 (t, J = 7.5 Hz, 2H), 8.19 (d, J = 7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.4, 37, 83.5, 86.4, 111.6, 112.3, 118.1, 120.1, 126.4, 126.5, 127.6, 127.8, 128.85, 131.5, 131.7, 132.7, 132.8, 138.1, 149.1, 165.8. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 34.6 (inverted), 37.2 111.8, 118.3, 126.6, 126.7, 127.8, 128, 128.6, 131.7, 131.9, 138.3. Anal. Calcd for $C_{22}H_{20}N_2OS$: C, 73.30; H, 5.59; N, 7.76. Found: C, 73.16; H, 5.49; N, 7.85.

***S*-[2-{*N*-3′-(2-Naphthyl)prop-2′-ynyl}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59c):** white solid; mp 104 °C; IR 3347.4, 1667.9, 1591.1, 1504.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.00, 3.12 (2s, 6H), 4.25 (s, 2H), 5.03 (brs, 1H), 6.78 (td, J = 7.8, 0.9 Hz, 1H), 6.90 (dd, J = 7.8, 0.9 Hz, 1H), 7.34−7.47 (m, 5H), 7.72−7.49 (m, 3H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.4, 37, 83.5, 86.4, 111.6, 112.3, 118.1, 120.1, 126.4, 126.5, 127.6, 127.8, 128.4, 131.5, 131.7, 132.7, 132.8, 138.1, 149.2, 165.8; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 34.6 (inverted), 37.2, 111.8, 118.3, 126.6, 126.7, 127.8, 128, 128.6, 131.7, 131.9, 138.3. Anal. Calcd for $C_{22}H_{20}N_2OS$: C, 73.30; H, 5.59; N, 7.76. Found: C, 73.21; H, 5.63; N, 7.81.

***S*-[2-(*N*-3′-*m*-chlorophenyl-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (59d):** white solid; mp 117 °C; IR 3346.3, 1668.3, 1587.3, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.97, 3.12 (2s, 6H), 4.18 (s, 2H), 4.96 (brs, 1H), 6.79 (td, J = 7.5, 1.2 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 7.17−7.38 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.7, 37.4, 82.3, 87.94, 112, 112.9, 118.6, 125, 129, 129.8, 130.3, 132.1, 134.5, 138.8, 149.5, 166.1; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 34.4 (inverted), 37.2 111.8, 118.4, 128.6, 129.5, 130 131.8, 138.3. Anal. Calcd for $C_{18}H_{17}ClN_2OS$: C, 62.68; H, 4.97, N, 8.12. Found: C, 62.76; H, 5.09; N, 7.91.

***S*-[2-(*N*-3′-*o*-Tolylprop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (59e):** pale yellow solid; mp 88 °C; IR 3350.2, 1671.9, 1616, 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.95, 3.12 (2s, 6H), 4.16 (s, 2H), 5.01 (brs, 1H), 6.73 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 7.08−7.35 (m, 5H), 7.49 (d, J = 7.8 Hz, 1H). Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.56; H, 5.99; N, 8.42.

S-[2-(*N*-3′-*p*-Tolylprop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (59f): white solid; mp 100 °C; IR 3355.9, 1672.2, 1618, 1591 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.00, 3.13 (2s, 6H), 4.17 (s, 2H), 4.95 (brs, 1H), 6.74 (td, J = 7.8, 1.2 Hz, 1H), 6.82 (dd, J = 7.8, 0.9 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.24−7.36 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 34.8, 37.4, 83.8, 85.7, 112.1, 112.6, 118.4, 120.3, 129.3, 132.1, 138.5, 149.6, 166.2; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.6, 34.5 (inverted), 37.1, 111.8, 118.1, 129.1, 131.7, 138.2. Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.41; H, 6.18; N, 8.55.

***S*-[2-{*N*-3′-(4-Methoxyphenyl)prop-2′-ynyl}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59g):** white solid; mp 85 °C; IR 3371, 1664, 1591, 1510 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.00, 3.12 (2s, 6H), 3.78 (s, 3H), 4.17 (s, 2H), 6.72−6.85 (m, 4H), 7.27−7.36 (m, 4H). Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.22. Found: C, 66.89; H, 6.03; N, 8.19.

***S*-[2-{*N*-3′-(2-Thienyl)prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (59h):** white solid; mp 103 °C; IR 3348.5, 1668.3, 1510.8, 1504.8 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.00 (s, 6H), 4.25 (s, 2H), 5.01 (brs, 1H), 6.66−6.89 (m, 3H), 7.03−7.43 (m, 4H). Anal. Calcd for $C_{16}H_{16}N_2OS_2$: C, 60.73; H, 5.09; N, 8.85. Found: C, 60.91; H, 4.99; N, 8.68.

***S*-[2-{*N*-3′-(5-Iodo-2-thienyl)prop-2′-ynyl)}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59i):** light yellow solid; mp 113 °C; IR 3346.3, 1666.4, 1591.2, 1502.4 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.06 (s, 6H), 4.26 (s, 2H), 4.89 (brs, 1H), 6.6−6.85 (m, 3H), 7.03−7.49 (m, 3H). Anal. Calcd for $C_{16}H_{15}IN_2S_2$: C, 43.44; H, 3.41; N, 6.33. Found: C, 43.49; N, 3.65; N, 6.08.

***S*-[2-{*N*-3′-(4-Iodophenyl)prop-2′-ynyl)}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59j):** white solid; mp 127 °C; IR 3390.6, 1668.3, 1591.2, 1500.5 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.03 (s, 6H), 4.16 (s, 2H), 4.86 (brs, 1H), 6.66−6.86 (m, 2H), 7.06−7.39 (m, 4H), 7.56−7.22 (m, 2H). Anal. Calcd for $C_{18}H_{17}IN_2OS$: C, 49.55; H, 3.92; N, 6.41. Found: C, 49.76; H, 3.79; N, 6.62.

***S*-[2-{*N*-3′-(2-Iodophenyl)prop-2′-ynyl)}aminophenyl]-*N*,*N*-dimethylthiocarbamate (59k):** white solid; mp 87 °C; IR 3391.3, 1667.39, 1590.8, 1501.2 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.09 (s, 6H), 4.2 (s, 2H), 5.00 (brs, 1H), 6.59−7.03 (m, 3H), 7.13−7.33 (m, 3H), 7.59−7.76 (m, 2H). Anal. Calcd for

$C_{18}H_{17}IN_2OS$: C, 49.55; H, 3.92; N, 6.41. Found: C, 49.59; H, 3.85; N, 6.36.

***S*-[2-(*N*-Methyl-*N*-3′-*p*-tolyl-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (60a).** A mixture of compound **59f** (100 mg, 0.3 mmol), anhyd K_2CO_3 (83 mg, 0.6 mmol), and methyl iodide (130 mg, 0.91 mmol) in acetone (10 mL) was treated under reflux for 10 h in an argon atmosphere. After usual workup, the crude product was purified by column chromatography on silica gel (60−120 mesh) using light petroleum/ethyl acetate mixture (95/5, V/V) as eluent affording **60a** as a colorless oil; IR (liquid film) 1673, 1583, 1509 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.30 (s, 3H), 2.89 (s, 3H), 3.00 (s, 6H), 4.00 (s, 2H), 6.95−7.13 (m, 3H), 7.23−7.56 (m, 5H). Anal. Calcd for $C_{20}H_{22}N_2OS$: C, 70.97; H, 6.55; N, 8.27. Found: C, 70.89; H, 6.50; N, 8.16.

***S*-[2-(*N*-Benzyl-*N*-3′-*p*-tolyl-prop-2′-ynyl)aminophenyl]-*N*,*N*-dimethylthiocarbamate (60b):** compound **59f** (200 mg, 0.6 mmol) and $PhCH_2Br$ (120 mg, 0.7 mmol) were refluxed with anhyd K_2CO_3 (165 mg, 1.2 mmol) for 15 h. After usual workup, the crude product was purified by column chromatography on silica gel (60−120 mesh) the eluent being light petroleum/ethyl acetate (90/10, V/V) furnishing **60b** as a colorless oil; IR (liquid film) 1667.5, 1584.1, 1509 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.02 (s, 6H), 3.72 (s, 2H), 4.28 (s, 2H), 6.72 (t, J = 6 Hz, 1H), 6.8 (d, J = 6 Hz, 1H), 7.1−7.44 (m, 10H), 7.5 (d, J = 9 Hz, 1H). Anal. Calcd for $C_{26}H_{26}N_2OS$: C, 75.33; H, 6.32; N, 6.75. Found: C,75.28;H, 6.29; N, 6.74.

Typical Reaction Procedure for the Synthesis of (*E*)-2-Benzylidene-3,4-dihydro-2*H*-1,4-benzothiazine (61a). A methanolic KOH solution [KOH (360 mg, 6.5 mmol) dissolved in 10 mL of methanol and 5 mL of H_2O] of compound **59a** (200 mg, 0.65 mmol) was heated under reflux in an argon atmosphere for 24 h. The solvent was removed under reduced pressure and diluted with water followed by extraction with $CHCl_3$. The organic layer was washed with H_2O and dried (anhyd Na_2SO_4), and the solvent was distilled off. The crude product obtained was purified by column chromatography on silica gel (60−120 mesh), the eluent being light petroleum/ethyl acetate (19/1, V/V) to yield **61a** as a white solid; mp 148 °C; IR 3382.9, 1608.5, 1585.4, 1487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 2H), 6.36 (s, 1H), 6.61 (dd, J = 8.1, 1.2 Hz, 1H), 6.76 (td, J = 8, 1.2 Hz, 1H), 6.94 (td, J = 7.5, 1.5 Hz, 1H), 7.10 (dd, J = 7.8, 1.2 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.4 ($^3J_{CH}$ = 7.5 Hz) 116.8, 119.1, 120.5, 122.4, 126.1, 126.7, 127.3, 129, 129.5, 131.8, 136.6, 144.3; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 50.1 (inverted), 116.5, 120.2, 122.1, 125.8, 126.4, 127, 128.5, 128.9. Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.07; H, 5.36; N, 5.61.

Compounds **61b**−**m** were synthesized by following the procedure for **61a**.

(*E*)-2-[(1-Naphthyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61b): white solid; mp 185 °C; IR 3349.4, 1603.9, 1586.9, 1484.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.03 (s, 2H), 6.56 (dd, J = 8.1, 1.2 Hz, 1H), 6.64 (td, J = 7.6, 1.2 Hz, 1H), 6.81 (s, 1H), 6.84 (dd, J = 7.8, 1.5 Hz, 1H), 6.91 (td, J = 7.8, 1.5 Hz, 1H), 7.34−7.44 (m, 3H), 7.61 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.75−7.79 (m, 1H), 7.91−7.95 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.9 ($^3J_{CH}$ = 7.5 Hz), 116.8, 119.3, 119.8, 120.5, 124.9, 125.7, 126, 126.3, 126.4, 126.7, 127.1, 128.4, 129, 131.9, 133.3, 134.1, 134.6, 144.1; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 49.6 (inverted), 116.5, 119.6, 120.2, 124.6, 125.4, 125.7, 126, 126.2, 126.4, 126.8, 128.1, 128.7. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.9; H, 5.22; N, 4.84. Found: C, 78.83; H, 5.24; N, 4.80.

(*E*)-2-[(2-Naphthyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61c): white solid; mp 204 °C; ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ 4.01 (s, 2H), 5.39 (s, 1H), 6.54 (s, 1H), 6.75 (d, J = 9 Hz, 2H), 6.96 (t, J = 6 Hz, 1H), 7.10 (d, J = 6 Hz, 1H), 7.47 (d, J = 3 Hz, 2H), 7.62 (t, J = 9 Hz, 1H), 7.84 (t, J = 9 Hz, 3H), 7.99 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 53.4, 120.1, 121.4, 123.1, 125.1, 129.7, 130, 130.8, 131.1, 131.3, 131.5, 131.7, 135.7, 136.3, 137, 137.6, 148.5; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 54.6 (inverted), 121.2, 124.2, 126.2, 130.9, 131.2, 132, 132.3, 132.4, 132.6, 132.9; Anal. Calcd for $C_{19}H_{15}NS$: C, 78.85; H, 5.22; N, 4.83. Found: C, 79.00; H, 4.96; N, 4.69.

(*E*)-2-[(*m*-Chlorophenyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61d): white solid; mp 138 °C; IR 3383.9, 1611.5, 1585.9, 1555.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 2H), 4.09 (brs, 1H), 6.20 (s, 1H), 6.56 (dd, J = 7.8, 1.2 Hz, 1H), 6.70 (td, J = 7.5, 1.2 Hz, 1H), 6.89 (td, J = 7.5, 1.2 Hz, 1H), 7.04 (dd, J = 7.8, 1.2 Hz, 1H), 7.09−7.13 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.32 (dd, J = 7.8, 1.2 Hz, 1H), 7.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50 ($^3J_{CH}$ = 7.5 Hz), 116.5, 118.3, 120.2, 120.5, 126, 126.4, 126.9, 128.7, 129.6, 133.4, 134.2, 138, 143.9; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 50.1 (inverted), 116.6, 120.3, 120.6, 126.1, 126.5, 127, 128.8, 129.7. Anal. Calcd for $C_{15}H_{12}ClNS$: C, 65.79; H, 4.41; N, 5.11. Found: C, 66.06; H, 4.47; N, 5.01.

(*E*)-2-(*o*-Tolylmethylidene)-3,4-dihydro-2*H*-1,4-benzothiazine (61e): white solid; mp 124 °C; IR 3360.1, 1609.8, 1587.8, 1482.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3H), 3.89 (s, 2H), 6.34 (s, 1H), 6.53 (dd, J = 7.5, 0.9 Hz, 1H), 6.65 (td, J = 7.5, 0.9 Hz, 1H), 6.85 (td, J = 7.2, 1.2 Hz, 1H), 6.94 (dd, J = 7.8, 1.2 Hz, 1H), 7.09−7.17 (m, 3H), 7.45 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 49.4 ($^3J_{CH}$ = 7.5 Hz), 116.3, 118.8, 120, 120.5, 125.5, 125.6, 126.2, 127.4, 128.6, 130.1, 132.3, 134.9, 136.3, 143.7; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 20.1, 49.6 (inverted), 116.5, 120.2, 120.7, 125.9, 125.8, 126.4, 127.6, 128.8, 130.3. Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.52. Found: C, 75.78; H, 5.83; N, 5.63.

(*E*)-2-(*p*-Tolylmethylidene)-3,4-dihydro-2*H*-1,4-benzothiazine (61f): white solid; mp 206 °C; IR 3362.8, 1584.1, 1492.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.90 (s, 2H), 4.05 (brs, 1H), 6.29 (s, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.5 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 50.4 ($^3J_{CH}$ = 7.5 Hz), 116.8, 119.2, 120.5, 122.5, 126, 126.7, 129.1, 129.4, 130.6, 133.8, 137, 144.2; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.4, 50.1 (inverted), 116.5, 120.2, 122.2, 125.7, 126.4, 128.8, 129.1. Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.52. Found: C, 75.75; H, 5.99; N, 5.76.

(*E*)-2-[(4-Methoxyphenyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61g): white solid; mp 186 °C; IR 3376.3, 1603, 1586.7, 1508.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.94 (s, 2H), 6.32 (s, 1H), 6.61 (d, J = 7.8 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 6.88−6.96 (m, 3H), 7.08 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.3, 55.6, 114.2, 114.5, 116.8, 119.1, 120.5, 122.2, 126, 126.7, 129.3, 130.5, 131.2, 144.2; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 50 (inverted), 55.3, 113.9, 116.5, 120.1, 121.9, 125.7, 126.4,130.2. Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.19. Found: C, 71.1; H, 5.60; N, 4.94.

(*E*)-2-[(2-Thienyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61h): white solid; mp 219 °C; IR 3380.08, 1604.8, 1583.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.99 (s, 2H), 4.18 (brs, 1H), 6.61 (s, 1H), 6.66 (d, J = 8.1 Hz, 1H), 6.80 (td, J = 8.1, 1.2 Hz, 1H), 6.99 (td, J = 8.1, 1.2 Hz, 1H), 7.03−7.06 (m, 1H), 7.15−7.2 (m, 2H), 7.33 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.3, 115.3, 116.4, 118.3, 120.1, 125.6, 125.8, 126.5, 126.8, 127.2, 128.9, 139.4, 143.3; ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.5 (inverted), 115.5, 116.6, 120.3, 125.8, 126, 126.7, 127.1, 127.4. Anal. Calcd for $C_{13}H_{11}NS_2$: C, 63.63; H, 4.52; N, 5.7. Found: C, 63.64; H, 4.41; N, 5.52.

(*E*)-2-[(5-Iodothienyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61i): white solid; mp 132 °C; IR 3365.5, 1600.4, 1595.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 2H), 4.19 (brs, 1H), 6.54 (s, 1H), 6.65 (dd, J = 8.1, 1.2 Hz, 1H), 6.76−6.82 (m, 2H), 6.99 (td, J = 7.8, 1.2 Hz, 1H), 7.15−7.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.6, 115.3, 117, 118.3, 120.6, 126.5, 126.9, 127.4, 128.9, 130.4, 137, 143.7, 146; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 49.3 (inverted), 115, 116.7, 120.3, 126.2, 126.7, 128.6, 136.8. Anal. Calcd for $C_{13}H_{10}INS_2$: C, 42.05; H, 2.71; N, 3.77. Found: C, 42.09; H, 2.62; N, 3.67.

(*E*)-2-[(4-Iodophenyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61j): white solid; mp 202 °C; IR 3369.3,

1608.5, 1583, 1481.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 2H), 6.29 (s, 1H), 6.66 (dd, J = 8.1, 0.9 Hz, 1H), 6.79 (td, J = 7.5, 1.2 Hz, 1H), 6.99 (td, J = 7.8, 1.2 Hz, 1H), 7.11 (dd, J = 7.8, 1.5 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.9, 115.4, 119.12, 119.8, 120, 122.8, 124.9, 126.1, 129.5, 131.7, 136.4, 142.8; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 50.1 (inverted), 116.6, 120.5, 120.9, 126, 126.5, 130.7, 137.5. Anal. Calcd for $C_{15}H_{12}INS$: C, 49.32; H, 3.31; N, 3.83. Found: C, 49.54; H, 3.21; N, 3.96.

(*E*)-2-[(2-Iodophenyl)methylidene]-3,4-dihydro-2*H*-1,4-benzothiazine (61k): white solid; mp 104 °C; IR 3377.1, 1606.6, 1585.4, 1508.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 2H), 6.30 (s, 1H), 6.58 (d, J = 6 Hz, 1H), 6.69 (t, J = 6 Hz, 1H), 6.82−6.98 (m, 3H), 7.30 (td, J = 7.5, 0.9 Hz, 1H), 7.37 (dd, J = 7.8, 1.2 Hz, 1H), 7.58 (d, J = 6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.7, 114.2, 116.8, 120.4, 122.2, 125.9, 126, 126.2, 126.7, 128.4, 129.2, 130, 130.5, 139.6, 144.1. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 49.4 (inverted), 113.9, 116.6, 120.3, 125.6, 125.9, 126.4, 128.1, 129.7, 130.3. Anal. Calcd for $C_{15}H_{12}INS$: C, 49.32; H, 3.31; N, 3.83. Found: C, 49.50; N, 3.37; N, 3.78.

(*E*)-4-Methyl-2-(*p*-tolylmethylidene)-3,4-dihydro-2*H*-1,4-benzothiazine (61l): white solid; mp 92 °C; IR 1604.6, 1585.6, 1511.61, 1488.51 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.88 (s, 3H), 3.70 (s, 2H), 6.25 (s, 1H), 6.72 (t, J = 7. Hz, 2H), 7.01 (td, J = 7.8, 1.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 3H), 7.33 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 39.8, 58.8, 113.9, 119.7, 120.8, 121.2, 126, 126.1, 128.6, 128.9, 131, 133.4, 136.5, 146.9; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.4, 40, 59 (inverted), 114.1, 120, 121.4, 126.2, 126.4, 128.8, 129.2. Anal. Calcd for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.23. Found: C, 76.45; H, 6.19; N, 5.16.

(*E*)-4-Benzyl-2-(*p*-tolylmethylidene)-3,4-dihydro-2*H*-1,4-benzothiazine (61m): white solid; mp 110 °C; IR 1604.1, 1579.9, 1484.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.78 (s, 2H), 4.43 (s, 2H), 6.16 (s, 1H), 6.82 (q, J = 8.1 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.2 Hz, 3H), 7.25−7.41 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 55.4, 56.1, 116.5, 120.1, 121.4, 121.7, 125.8, 126.3, 127.2, 127.7, 128.6, 129, 129.9, 133.4, 136.5, 137.9, 146.2; ^{13}C NMR (75 MHz, $CDCl_3$, DEPT 135) δ 21.4, 55.6 (inverted), 56.3 (inverted), 116.7, 120.3, 121.9, 126, 126.5, 127.5, 127.9, 128.8, 129.2. Anal. Calcd for $C_{23}H_{21}NS$: C, 80.42; H, 6.16; N, 4.07. Found: C, 80.39; H, 6.18; N, 4.16.

(*E*)-2-[5-(2-Carbomethoxyvinyl)thienyl]methylidene-3,4-dihydro-2*H*-1,4-benzothiazine (62). A mixture of compound **61i** (60 mg, 0.16 mmol), methyl acrylate (40 mg, 0.46 mmol), bis(triphenylphosphine)palladium(II) dichloride (4 mg, 0.006 mmol, 3 mol %) and triethylamine (65 mg, 0.64 mmol) in acetonitrile (5 mL) was heated at 80 °C (bath temperature) for 15 h in an argon atmosphere. After removal of the solvent and usual workup, 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 (19:1; V/V) afforded **62** as a light yellow solid; mp 150 °C; IR 3361.7, 1710.7, 1618.2, 1598.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.93 (s, 2H), 6.18 (d, J = 15.6 Hz, 1H), 6.50 (s, 1H), 6.62 (d, J = 8.1 Hz, 1H), 6.76 (t, J = 7.8 Hz, 1H), 6.89−6.98 (m, 2H), 7.10−7.15 (m, 2H), 7.70 (d, J = 15.6 Hz, 1H). Anal. Calcd for $C_{17}H_{15}NO_2S_2$: C, 61.98; H, 4.59; N, 4.25. Found: C, 61.92; H, 4.63; N, 4.26.

(*E*)-2-[4-(2-Phenylethynyl)phenyl]methylidene-3,4-dihydro-2*H*-1,4-benzothiazine (63). Compound **61j** (70 mg, 0.19 mmol) in acetonitrile (5 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 (77 mg, 0.76 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 usual workup, crude product was purified by column chromatography on silica gel (60−120 mesh) with the eluent being light petroleum/ethylacetate (19/1, V/V) to afford **63** as a light yellow solid; mp 210 °C; IR 3361.7, 1585.8, 1487.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.01(s, 2H), 6.38 (s, 1H), 6.67 (d, J = 7.8 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.34−7.37 (m, 3H), 7.52−7.57 (m, 6H). Anal. Calcd for $C_{23}H_{17}NS$: C, 81.38; H, 5.04; N, 4.12. Found: C, 81.19; H, 4.98; N, 4.16.

Acknowledgment. Thanks are due to Dr. S. A. Imam of Huntington Medical Research Institute, Pasadena, CA, for a gift of $(PPh_3)_2PdCl_2$ which was very helpful for the investigations reported in this paper. Grateful acknowledgment is also made of a Royal Society of Chemistry Journals Grants for International Authors to N.G.K. which made his visit to various research institutes and universities in the U.K and Europe possible.

Supporting Information Available: Copies of ^1H NMR and ^{13}C NMR spectra of compounds **28**, **29**, **33**, **42**, **45**, **52**, **61b**, **61e**, **61h**, **61l**. This material is available free of charge via the Internet at http://pubs.acs.org

JO001783+