Substituent Effects on Vinyl Radical Cyclizations onto Aryl Rings

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Regioselective toluenesulfanyl radical addition to the C-1 carbon of propynyl benzyl ethers **2a**−**i** leads to vinyl radicals **3a**−**j** which mainly give methyl sulfides **9a**−**j** and methyl ethers **8a**−**j** through stereoselective 5-(π-endo)exo and 5-(π-exo)exo cyclization, respectively. Additionally, minor amounts of π-endo 6-membered cyclization products **5a**−**j** and hydrogen abstraction products **4a**−**j** are also formed. The role of steric and stereoelectronic factors in the 5-membered vs 6-membered and π-endo vs π-exo cyclization as well as the role of stabilization and polar factors has been studied. The substituent effect on the 5-(π-exo)exo cyclization has been estimated by the relative rate constants, k_R, calculated for several substituents in the 4- and 3-position. Results show that stabilization and polar factors slightly affect the rate of the vinyl radical cyclization onto arene rings, which appears to be rather unselective with respect to the nature of the substituent. The nature of polar effects indicates that vinyl radicals are slightly electrophilic in character.

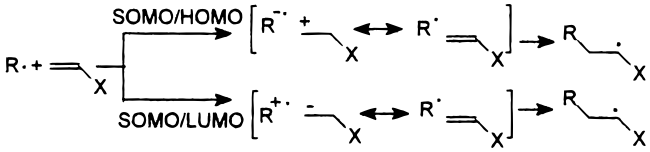
Carbon-centered radical additions to[1] (and radical cyclizations onto[2]) alkene and alkyne multiple bonds and aromatic rings are governed by several factors[3] (including steric, stereoelectronic,[4] polar, stabilization, and enthalpic factors) which exert different roles depending on the different nature of the radical and the radical acceptor.

Stabilization effects are determined by unpaired-electron delocalization in the radical adduct intermediate, while polar effects arise in the transition state by charge-transfer from/to the radical to/from the radical acceptor (Scheme 1). The direction of the charge transfer is determined by the frontier molecular orbital approach which can be controlled by either SOMO/HOMO or SOMO/LUMO interaction.[5,6]

These effects do not always play a determining role, especially when highly ergonic reactions are considered. In these cases the enthalpic factor predominates. When $\Delta H \ll 0$, the transition state is early and the reaction is fast and unselective, while when $\Delta H \gg 0$, the reaction is thermodynamically controlled and the rate of the radical addition is determined by the fate of the radical adduct.[3,5]

Polar and stabilization effects greatly depend on the nature of substituents present on both the radical and the radical acceptor.[4,5] Results reported for electrophilic

Scheme 1



substituted alkyl radicals indicate that the addition to alkene double bonds is dominated by SOMO/HOMO interaction and, therefore, is favored by alkene electron-releasing substituents.[7] In contrast, the addition to alkyne triple bonds appears to be either SOMO/HOMO- or SOMO/LUMO-controlled, depending on the nature of the alkyne substituent.[7d,8] Thus it is favored by both strong electron-releasing and strong electron-withdrawing (EWG) alkyne substituents.[7d] On the contrary, non-EWG-substituted alkyl radicals, which are nucleophilic in character, preferentially add to EWG-substituted alkenes[9] and alkynes.[10]

Both polar and stabilization factors play a little role in homolytic aromatic substitutions at benzene rings. Results reported in the 1960s by Hey et al.[11] provided evidence that the relative rates of para substitution by phenyl radicals is generally slightly enhanced by both

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EWG and electron-releasing substituents, while for the more electrophilic 4-cyano-, 4-chloro-, and 4-nitro-substituted phenyl radicals, a rate increase has been observed for electron-releasing substituents and a rate decrease for EWG substituents present on the benzene radical acceptor. This behavior can be explained by considering that EWG substituents are capable of accelerating the substitution rate by unpaired electron delocalization, but meanwhile, they exert unfavorable polar effects in these SOMO/HOMO controlled reactions. These unfavorable effects prevail for highly electrophilic aryl radicals, while stabilization effects prevail for weakly electrophilic phenyl radicals. On the other hand, k_{meta} values have been generally found to be higher than k_H for electron-releasing substituents and lower for EWG substituents, because the attack in the meta position is only governed by polar factors.

In contrast to the above homolytic aromatic substitutions, polar effects are dramatically important in the Minisci reaction, which provides a useful synthetic route to alkylated heterocycles through nucleophilic radical substitution at protonated heterocycles under oxidative conditions.[12]

At present, no data are available concerning the role of polar and stabilization factors for inter- or intramolecular vinyl radical homolytic aromatic substitutions. Therefore, in our interest for vinyl radical rearrangements and cyclizations,[13] we have undertaken a study to investigate the main factors affecting the rate of vinyl radical cyclizations onto aryl rings, with particular attention to the effect of the substituent present on the aromatic ring.

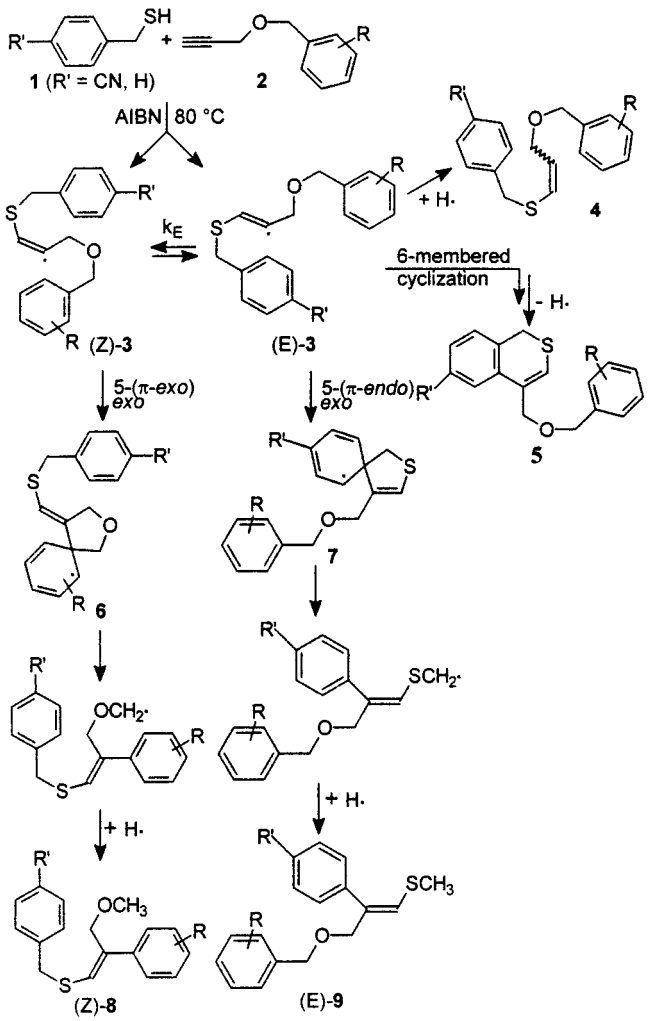
Results and Discussion

For our purpose we considered the fate of vinyl radicals **3a**−**i** generated by regioselective 4-cyanotoluenesulfanyl radical addition to a number of propynyl benzyl ethers **2a**−**i**. Sulfanyl radicals were produced from thiol **1**, R′ = CN, under thermal conditions in boiling benzene in the presence of 0.2 mol equiv of AIBN as initiator.

Chromatography of the reaction mixtures generally gave variable amounts of the 1,4-aryl migration products **9a**−**i** and **8a**−**i,** which were derived from vinyl radicals **3a**−**i** through 5-(*π*-endo)exo and 5-(*π*-exo)exo cyclization, respectively[14] (Scheme 2). The stereoselective *π*-endo cyclization led to spiro radicals **7a**−**i** from which (*E*)-methyl sulfides (*E*)-**9** arose through cleavage of the spiro ring. Similarly, the *π*-exo cyclization led to spiro radicals **6a**−**i** and then to 1,4-aryl migration products **8a**−**i**.

The *π*-exo cyclization onto aryl rings occurred in a highly stereoselective fashion, leading to configurationally pure ethers (*Z*)-**8a**−**i,** which were derived from radicals (*Z*)-**3a**−**i**. The actual configuration of (*Z*)-**8a**−**i** was established by NOE measurements. Irradiation on the vinyl proton signal caused an enhancement of the *S*-methylene group, but no enhancement of the *O*-methylene group was observed. Analogous stereoselectivity has been reported for *π*-exo vinyl radical cyclizations onto C−C double bonds. As previously suggested,[13a] the *π*-exo cyclization of (*E*)-vinyl radicals could be discouraged by steric repulsion occurring in the transition state between the radical acceptor moiety (alkene double bond or aromatic ring) and the *β*-substituent.

Scheme 2



a-**i**: R′ = CN; **a**: R = H; **b**: R= 4-OMe; **c**: R = 3-OMe;**d**: R = 4-Me; **e**: R = 3-Me; **f**: R = 4-Cl; **g**: R = 3-Cl; **h**: R = 4-CN; **i**: R = 3-CN **j**: R′ = R = H

In addition to products **9a**−**g** and **8a**−**g,** column chromatography generally separated minor amounts (ca. 10%) of (*E*)- and (*Z*)-adducts **4b**−**g** (40:60 *E*/*Z* ratio) resulting from radicals **3b**−**g** by hydrogen abstraction. Formation of small amounts of possible adducts **4a,h,i** was detected by ^{1}H NMR spectroscopy of the corresponding reaction mixtures, but subsequent column chromatography did not allow for the separation of these compounds.

The substituent effect on the vinyl radical cyclization onto aryl rings was estimated by comparison of the

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(14) We have previously shown that toluenesufanyl radical addition to terminal alkynes having radical acceptor moieties in the radical chain (terminal and styrene double bonds or aryl rings) leads to vinyl radicals which undergo *π*-exo cyclization onto the radical acceptor in competition with the 5-(*π*-endo) cyclization onto the aryl ring. See ref 13a.

Table 1. Relative Yields (%) of Products 9 and 8 from 5-(π-Endo)exo and 5-(π-Exo)exo Cyclizations of Radicals 3 and Relative Rate Values (k_R) for the π-Exo Cyclizations

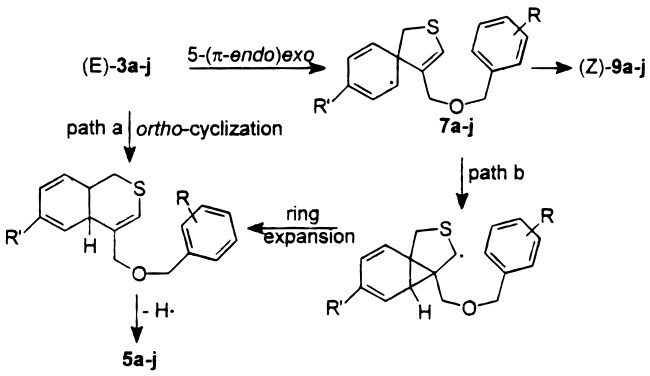
			(relative yields, %)		
entry	R′	R	sulfide **9**	ether **8**	k_R
1	CN	H	**9a** (87)	**8a** (13)	1.0
2	CN	4-OMe	**9b** (81)	**8b** (19)	1.57
3	CN	3-OMe	**9c** (86)	**8c** (14)	1.09
4	CN	4-Me	**9d** (82)	**8d** (18)	1.47
5	CN	3-Me	**9e** (83)	**8e** (17)	1.37
6	CN	4-Cl	**9f** (77)	**8f** (23)	2.0
7	CN	3-Cl	**9g** (83)	**8g** (17)	1.37
8	CN	4-CN	**9h** (57)	**8h** (43)	5.05
9	CN	3-CN	**9i** (87)	**8i** (13)	1.0
10	H	H	**9j** (57)	**8j** (43)	(1.0)

relative rate constants, k_R, obtained for the 5-(π-exo)exo cyclizations (Table 1). These values are referred to $k_H = 1$ and were calculated through the equation $k_R = ([\mathbf{9}]_H[\mathbf{8}]_R)/([\mathbf{8}]_H[\mathbf{9}]_R)$. The [**9**]/[**8**] ratios were obtained from direct ^{1}H NMR analyses of the corresponding reaction mixtures by measuring the integrals of the *S*-methyl singlet at 2.3 and the *O*-methyl singlet at 3.3. For this purpose the reaction mixtures were preliminarily worked up to eliminate unreacted thiol **1** and alkyne **2** (see Experimental Section).

From data reported in Table 1 it can be observed that both electron-releasing and EWG substituents in the 4-position activate the aromatic ring, although to a small extent ($k_{para} > 1$). Moreover, in all cases k_{para} values are slightly higher than the corresponding k_{meta} values. These findings indicate that stabilization effects prevail over polar effects. It is noteworthy that the cyano group presents the higher k_{para} value, as a consequence of its greater capability of delocalizing the unpaired electron, and the lower k_{meta} value, as a consequence of its strong electron-withdrawing effect. This trend suggests that vinyl radical cyclizations onto aryl rings are SOMO/HOMO-controlled, as expected from an electrophilic radical addition. It has been previously suggested[15] that vinyl radicals are electrophilic in character, even though no definite evidence has been reported yet.[16] The observed k_{Cl} and k_{CN} values (Table 1, entries 6−9) are quite similar to the partial rate factors reported in the literature for the phenylation of chlorobenzene[17] and benzonitrile[18] with benzoyl peroxide. This finding would suggest that vinyl and phenyl radicals have a comparable philicity, although the reported electronegativity of vinyl radicals ($\chi = (IP + EA)/2 = 4.63$ eV)[19] is rather lower than that of phenyl radicals ($\chi = 5.59$ eV).[20]

Nevertheless, it appears that both polar and stabilization effects do not play a great role. In fact, vinyl radical cyclizations onto aromatic rings are rather unselective, as evidenced by the finding that all k_R values lie in the range 1−5. On these bases it can be inferred that the enthalpic factor predominates, as expected from a highly exothermic reaction occurring through an early transition state.[21]

Scheme 3



In all cases, ^{1}H NMR analyses of the reaction mixtures showed the presence of small amounts of thiopyrans **5a**−**i** (see Scheme 2), which were characterized by methylene signals at 3.8 (CH_2S), 4.4 ($C{=}CCH_2O$), and 4.5 ($ArCH_2O$) and by the vinyl proton singlet at 6.6−6.7 in the ^{1}H NMR spectrum. The ratio between the methyl sulfides **9** and the corresponding thiopyrans **5**, irrespective of the nature of the R substituent, was found to be ca. 12−13:1. Unfortunately, complete characterization was only performed for the chloro derivative **5f**. In all the other cases it was not possible to obtain a suitable sample owing to the small amounts of these products.

Thiopyrans **5a**−**i** might in principle arise through two reaction pathways: a direct 6-membered π-endo cyclization (Scheme 3, path a), which would occur in competition with the 5-(π-endo)exo cyclization, and/or ring-expansion of the spiro radical **7** through three-membered cyclization followed by intraanular bond scission[22] (Scheme 3, path b). To clarify the actual mechanism, we carried out the reaction of benzenethiol **1**, R′ = H, with propynyl benzyl ether **2a**. From this reaction the expected products **9j** and **5j**, derived from the radical **3j** through formal 5- and 6-membered π-endo cyclizations, respectively, were obtained in a 2.5:1 ratio[23] in addition to the methyl ether **8j** and the adduct **4j**. The observed decrease of the [**9**]/[**5**] ratio from 12−13:1 to 2.5:1 on passing from R′ = 4-CN to R′ = H is in very good agreement with a mechanism involving competing 5- and 6-membered cyclizations.[24] In contrast, no change in the [**9**]/[**5**] ratio would be

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(16) Nevertheless, it should be stated that the "philicity" is a relative concept. In principle, a radical can behave as an electrophile or nucleophile, depending on the nature of the radical-acceptor counterpart. For example, reactions of vinyl radicals with olefins are usually dominated by SOMO−LUMO interaction; in this cases the vinyl radical behaves as a nucleophile and the olefin as an electrophile (see ref 6).

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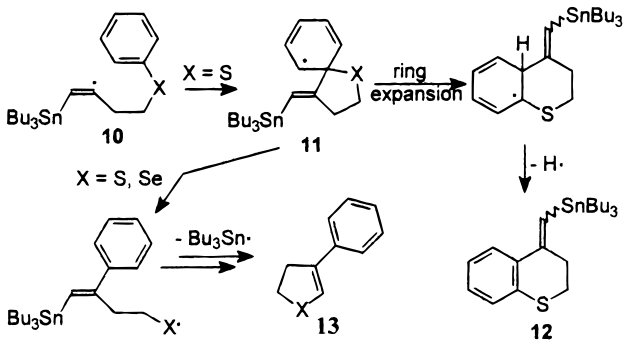
(21) This claim was been supported by semiempirical calculations (performed with a AM1 Spartan program) which gave ΔH = ca. −22 kcal/mol.

(22) Ring expansion of 5-exo to 6-endo radicals are well documented in cyclizations of β-multiply bonded alkyl or vinyl radicals. See: Beckwith A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. Jasperse, C. P.; Curran, D. P.; Fevig, D. L. *Chem. Rev.* **1991**, *91* 1237. Beckwith A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. Nanni, D.; Pareschi, P.; Tundo, A. *Tetrahedron Lett.* **1996**, *37*, 9337.

(23) A k_5/k_6 ratio = 6−7:1 has been reported for related π-endo vinyl radical cyclizations carried out at room temperature. See: Citterio, A.; Sebastiano, R.; Maronati A.; Santi, R.; Bergamini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1517.

(24) The cyano group do not affect the rate of vinyl radical cyclization in 3-position (see Table, entry 9) and thus the 6-membered ortho-cyclization reactions leading to **5h** and **5j**, respectively, would occur at the same rate. In contrast, the formation of sulfide **9j** should be 5.05 times slower than **9h** (see Table, entry 8). The calculated [**9h**]/[**5h**] = 5.05[**9j**]/[**5j**] = 12.75 ratio value is actually strictly closed to the observed [**9h**]/[**5h**] = 12−13.

Scheme 4



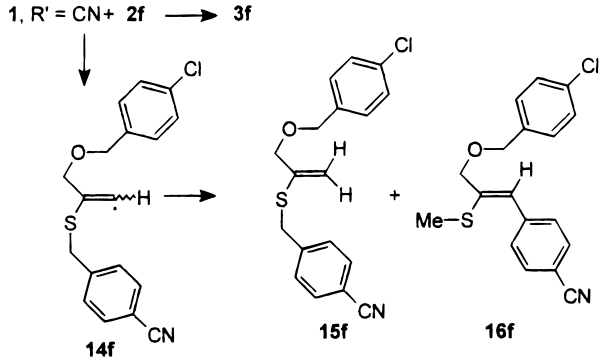
expected if the mechanism leading to both **5** and **9** occurred through intermediacy of the spiro radical **7**.

It is interesting to note that the same [**9**]/[**8**] ratio (57:43) was found in the cases of R = R′ = 4-CN and R = R′ = H (see Table, entries 8 and 10), as expected from cyclizations occurring from rapidly interconverting (*E*)- and (*Z*)-vinyl radicals **3**. This finding rules out the possibility that the sulfanyl radical addition to alkynes **2** preferentially leads to radicals (*Z*)-**3** from which π-endo cyclization might in principle occur in competition with the interconversion to the more stable radicals (*E*)-**3**.[25] In this case a higher [**9**]/[**8**] ratio should be expected for R = R′ = 4-CN, owing to the effect of the 4-cyano group. The observed slight preference for the 5-(π-endo) cyclization mode over the 5-(π-exo) one ([**9h,j**]/[**8h,j**] = $K_e k_{endo}/k_{exo} = 1.3$) might result from the fact that the more stable (*E*)-radicals could be preferred at the equilibrium ($K_e > 1$) (see Scheme 2), even though the role played by possible different stereoelectronic conditions cannot be valued.

Despite our efforts, no traces of any products derived from radicals **3a**−**j** through π-exo 6-membered ortho-cyclization were found, possibly as a consequence of unfavorable stereoelectronic conditions for this cyclization mode. This behavior parallels that exhibited by the related vinyl radicals **10**, X = S, Se, which have been previously found to undergo cyclization onto the phenyl ring only in a 5-(π-exo) mode.[26] The formal 6-(π-exo) cyclization product **12** has been suggested to arise from intermediate spiro radical **11**, X = S, through a ring-expansion process which competes with the C−S bond cleavage, eventually leading to **13**, X = S. A similar ring expansion was not provided by **11**, X = Se, owing to the lower C−Se bond energy (Scheme 4). In the case of spiro radicals **6a**−**j,** the ring expansion might be prevented by the more feasibile spiro-ring scission leading to stable α-oxymethyl radicals.

As mentioned above, radicals **3** arose from regioselective sulfanyl radical addition to the alkyne triple bond of **2**. Radical addition of thiols to terminal alkylacetylenes has been extensively studied and in all cases only formation of products derived from sulfanyl radical addition to the terminal C-1 carbon atom has been reported.[27] The regioselectivity is governed by steric effects; in fact, no stabilization can be provided by the

Scheme 5



β-alkyl substituent in these sp^2-hybridized vinyl radicals. However, a careful chromatographic analysis of the reaction mixture obtained from thiol **1**, R′ = CN, and alkyne **2f** allowed us to separate two products which were assigned the structure of the regioisomeric adduct **15f** and the methyl sulfide **16f**. ^{1}H NMR analysis showed a ca. 1:1 **15f**/**16f** ratio and a ca. 30:1 **9f**/**16f** ratio. Compounds **16f** and **15f** were clearly derived from the regioisomeric vinyl radical **14f** through hydrogen abstraction and 5-(π-exo)exo cyclization, respectively (Scheme 5). To our knowledge, the finding of products deriving from sulfanyl radical addition to the alkyl-substituted C-2 carbon atom is unprecedented.

Conclusions

In this work we have shown that toluenesulfanyl radical addition to the C-1 carbon of propynyl benzyl ethers **2** leads to vinyl radicals **3** which can undergo three kinds of cyclization, stereoselective 5-(π-endo)exo and 5-(π-exo)exo cyclization, eventually leading to the 1,4-aryl migration products **9** and **8**, respectively, and π-endo 6-membered cyclization, leading to thiopyrans **5**.

The rate of the vinyl radical cyclization onto aryl rings is determined by (a) steric factors which inhibit (*E*)-vinyl radicals from undergoing π-exo cyclization, (b) stereoelectronic factors which favor the 5-membered over the 6-membered cyclization [$k_{5(\pi-endo)}/k_{6(\pi-endo)} = 2.5$, $k_{5(\pi-exo)}/k_{6(\pi-exo)} \gg 1$], and (c) stabilization and polar factors determined by the presence of aryl ring substituents. The nature of the substituent effect would indicate that vinyl radicals are slightly electrophilic in character. However, vinyl radical cyclizations appear to be rather unselective with respect to the nature of the aryl substituent. This finding suggests that the enthalpic factor might play a major role.

Experimental Section

Starting Materials. Toluenethiol **1**, R′ = H, is commercially available. 4-Cyanotoluenethiol **1**, R′ = CN, was prepared as described in the literature.[13d] Propynyl benzyl ethers **2a**−**g,i** were obtained following a previously reported method.[13a] According to this procedure, a THF solution (50 mL) of sodium propargylate (50 mmol) (prepared from equimolar amounts of propargyl alcohol and sodium hydride in anhydrous THF) and the appropriate commercially available benzyl chloride (50 mmol) was heated in a sealed tube at 80 °C for 8 h. Subsequent work up and column chromatography gave ethers **2a**,[28] **2b**,[29] **2c** [^{1}H NMR 2.45 (1 H, t, J = 2.5 Hz),

(25) We have previously suggested that samarium diiodide-promoted vinyl radicals can undergo 5-exo cyclization onto C−C triple bonds in competition with the *E*/*Z* interconversion. (Capella, L.; Montevecchi, P. C.; Navacchia, M. L. *J. Org. Chem.* **1995**, *60*, 7424.)

(26) Capella, L.; Montevecchi, P. C.; Nanni, D. *J. Org. Chem.* **1994**, *59*, 3368.

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3.80 (3 h, s), 4.17 (2 H, d, J = 2.5 Hz), 4.6 (2 H, s), 6.8−7.3 (4 H, m); MS m/z (rel intensity) 176 (M^+, 30), 135 (30), 122 (100). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; O, 18.16. Found: C, 75.20; H, 6.90.], **2d**,[30] **2e**,[31] **2f** [^{1}H NMR 2.45 (1 H, t, J = 2.5 Hz), 4.15 (2 H, d, J = 2.5 Hz), 4.55 (2 H, s), 7.2−7.4 (4 H, m); MS m/z (rel intensity) 182, 180 (M^+, 20), 127, 125 (80), 77 (100). Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02; Cl, 19.63; O, 8.86. Found: C, 66.70; H, 5.0.], **2g** [^{1}H NMR 2.50 (1 H, t, J = 2.5 Hz), 4.20 (2 H, d, J = 2.5 Hz), 4.60 (2 H, s), 7.2−7.3 (4 H, m); MS m/z (rel intensity) 182, 178 (M^+, 4), 181, 179 (20), 141, 139 (80), 127, 125 (80), 77 (100). Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02; Cl, 19.63; O, 8.86. Found: C, 66.28; H, 5.05.], **2h**,[12a] and **2i** [^{1}H NMR 2.45 (1 H, t, J = 2.5 Hz), 4.20 (2 H, d, J = 2.5 Hz), 4.60 (2 H, s), 7.2−7.7 (4 H, m); MS m/z (rel intensity) 170 (M^+-1, 10), 132 (80), 130 (90), 117 (90), 116 (100). Anal. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18; O, 9.35. Found: C, 77.4; H, 5.27; N, 8.2.] in ca. 75−80% yield.

Reaction Products. Methyl sulfide **9h** and methyl ether **8h** have been previously reported.[13a] Structural assignments for the unknown sulfides **9a−g,i,j**, ethers **8a−g,i,j**, adducts **4b−g,j**, and thiopyran **5j** came from ^{1}H NMR and MS spectral data in addition to elemental analysis. Thiopyran **5f**, methyl sulfide **16f,** and adduct **15f** were characterized by GC−MS and ^{1}H NMR spectral analysis. Elemental analysis was not performed owing to the impossibility of obtaining a pure sample. Thiopyrans **5a−d,e−i** were not separated and thus not characterized. Their identification arose from ^{1}H NMR spectral analyses of the reaction mixtures by assignment of signals at ca. 3.8 (singlet, CH_2S), 4.5 (br singlet, HC=CCH_2O), 4.6 (singlet, OCH_2Ar), and 6.6 (br singlet, vinylic proton).

^{1}H NMR spectra were recorded at 200 (or 300 MHz) with Me_4Si as internal standard. Mass spectra were recorded with the electronic impact method.

Reactions of Thiols 1, R′ = H, CN with Propynyl Benzyl Ethers 2a−i. A benzene solution (50 mL) of the appropriate thiol **1**, R′ = H, CN (4 mmol), the appropriate ether **2a−i** (8 mmol), and AIBN (0.8 mmol) was refluxed for 3 h. The reaction mixture was washed twice with NaOH 10% and once with water, the organic layer was dried over Na_2SO_4, and the solvent evaporated off. The unreacted thiol **1**, R′ = H, CN, was generally recovered by acidification of the aqueous layer and extraction with diethyl ether in 45−50% yield. The organic residue was chromatographed on a Merck silica gel column (0.040−0.063 particle size). Elution with petroleum ether (bp 40−70 °C) (for the reaction of **1**, R′ = H, with ether **1a**) or gradual elution with light petroleum−diethyl ether (in all the other cases) separated the unreacted ether **2a−i** and a mixture of the appropriate sulfide **9a−j**, ether **8a−j**, thiopyran **5a−j**, and 1:1 adduct **4a−g,j** contaminated by small amounts of unidentified products (ca. 560−600 mg; ca. 80−85% overall yield based on reacted thiol **1**). These mixtures were analyzed by ^{1}H NMR to determine the relative ratios of products **5a−j**, **8a−j**, and **9a−j**. The relative yields of sulfides **9a−j** and ethers **8a−j** are reported in Table 1. The **9a−i**/**5a−i** ratios were found to be ca. 12−13:1. The **9j**/**5j** ratio was found to be 2.5:1. Subsequent repeated column chromatography of the above mixtures led to the separation of a head fraction (ca. 50 mg) containing unidentified products and fractions containing analytical samples of sulfides **9a−j**, ethers **8a−j** (60−65% overall yield), adducts **4b−g, j** (ca. 10%), and thiopyran **5j** (15%) [^{1}H NMR (300 MHz) 3.80 (2H, AB system, J_{AB} = 10 Hz, inner line separation = 2.5 Hz), 4.47 (2H, d, J = 1.0 Hz), 4.58 (2H, s), 6.55 (1H, t, J = 1.0 Hz), 7.1−7.5 (9H, m); MS m/z (rel intensity) 268 (M^+, 50), 161 (100), 128 (80), 115 (80), 91 (100). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01; O, 5.96; S, 11.95. Found: C, 76.35; H, 5.98; S, 12.0.]. The head fraction from the reaction of **1**, R = CN, with **2f** was subjected to a further chromatographic separation to give a ca. 2:1:1 mixture (30 mg) of thiopyran **5f**, methyl sulfide **16f** [^{1}H NMR (300 MHz) 2.40 (3H, s), 4.32 (2H, br s; irradiation at 6.62 caused a 6% enhancement), 4.55 (2H, s), 6.62 (1H, br s), 7.2−7.7 (aromatic protons); GC−MS m/z 329 (M^+).], and 1:1 adduct **15f** [^{1}H NMR (300 MHz) 3.95 (2H, s), 4.05 (2H, br s), 4.45 (2H, s), 5.0 (1H, t, J = 1.0 Hz, collapsing to singlet upon irradiation at 4.05), 5.35 (1H, t, J = 1 Hz, collapsing to singlet upon irradiation at 4.05), 7.2−7.7 (aromatic protons); GC−MS m/z 329 (M^+).]. A repeated column chromatography led to the separation of almost pure thiopyran **5f** (6 mg) [^{1}H NMR (300 MHz) 3.80 (2H, AB system, J_{AB} = 10 Hz, inner line separation 2.5 Hz), 4.40 (2H, s; irradiation at 6.72 caused a 5% enhancement), 4.47 (2H, s), 6.72 (1H, s), 7.2−7.7 (7H, m); GC-MS m/z (rel intensity) 329, 327 (M^+, 20), 186 (100)].

The following new methyl vinyl sulfides (*E*)-**9** were obtained as oily products. **9a**: ^{1}H NMR (200 MHz) 2.32 (3H, s), 4.28 (2H, s), 4.52 (2H, s), 6.46 (1H, s), 7.2−7.4 (5H, m), 7.6 (AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 295 (M^+, 15), 91 (100). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74; O, 5.42; S, 10.85. Found: C, 73.40; H, 5.82; N, 4.71; S, 10.88. **9b**: ^{1}H NMR (200 MHz) 2.35 (3 H, S), 3.80 (3H, s), 4.25 (2H, br s), 4.45 (2H, s), 6.45 (1H, br s), 6.90 (2H, d, J = 8.5 Hz), 7.20 (2H, d, J = 8.5 Hz), 7,6 (4H, AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 325 (M^+, 15), 121 (100). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 70.35; H, 5.90; N, 4.32; S, 9.82. **9c**: ^{1}H NMR (300 MHz) 2.32 (3 H, S), 3.78 (3H, s), 4.28 (2H, br s), 4.50 (2H, s), 6.45 (1H, br s), 6.8−6.90 (2H, m), 7.2−7.3 (2H, m), 7.6 (4H, AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 325 (M^+, 15), 122 (100), 121 (70). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 70.40; H, 5.9; N, 4.28; S, 9.88. **9d**: ^{1}H NMR (300 MHz) 2.35 (6H, s), 4.25 (2H, s), 4.46 (2H, s), 6.45 (1H, s), 7.1−7.7 (8H, m); MS m/z (rel intensity) 309 (M^+, 5), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 74.0; H, 6.15; N, 4.5; S, 10.3. **9e**: ^{1}H NMR (200 MHz) 2.32 (6H, s), 4.28 (2H, s), 4.48 (2H, s), 6.46 (1H, s), 7.0−7.3 (4H, m), 7.6 (4H, AB system, J = 8.5 Hz); MS m/z (rel intensity) 309 (M^+, 10), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 73.95; H, 6.22; N, 4.5; S, 10.32. **9f**: ^{1}H NMR (300 MHz) 2.35 (3 H, S), 4.28 (2H, s), 4.48 (2H, s), 6.45 (1H, s), 7.2−7.7 (8H, m); MS m/z (rel intensity) 331, 329 (M^+, 40), 127, 125 (70), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.75; H, 4.86; N, 4.23; S, 9.7. **9g**: ^{1}H NMR (300 MHz) 2.35 (3 H, S), 4.28 (2H, s), 4.48 (2H, s), 6.45 (1H, s), 7.2−7.7 (8H, m); MS m/z (rel intensity) 331, 329 (M^+, 40), 127, 125 (100), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.85; H, 4.92; N, 4.22; S, 9.66. **9i**: ^{1}H NMR (200 MHz) 2.35 (3 H, S), 4.30 (2H, s), 4.52 (2H, s), 6.48 (1H, s), 7.2−7.7 (8H, m); MS m/z (rel intensity) 320 (M^+, 4), 132 (60), 116 (100). Anal. Calcd for $C_{19}H_{16}N_2OS$: C, 71.22; H, 5.03; N, 8.74; O, 4.99; S, 10.01. Found: C, 71.0; H, 5.0; N, 8.7; S, 10.05. **9j**: ^{1}H NMR (300 MHz) 2.30 (3 H, S), 4.30 (2H, d, J = 1.1 Hz), 4.52 (2H, s), 6.30 (1H, t, J = 1.1 Hz), 7.2−7.4 (10 H, m); MS m/z (rel intensity) 270 (M^+, 20), 91 (100). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; O, 5.92; S, 11.86. Found: C, 75.25; H, 6.73; S, 11.83.

The following new methyl allyl ethers (*Z*)-**8** were obtained as oily products. **8a**: ^{1}H NMR (200 MHz) 3.30 (3H, s), 4.0 (2H, s), 4.30 (2H, s), 6.40 (1H, s), 7.2−7.4 (5H, m), 7.6 (AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 295 (M^+, 15), 91 (100). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74; O, 5.42; S, 10.85. Found: C, 73.4; H, 5.78; N, 4.76; S, 10.9. **8b**: ^{1}H NMR (200 MHz) 3.25 (3 H, S), 3.80 (3H, s), 3.95 (2H, s), 4.35 (2H, s), 6.32 (1H, s), 6.90 (2H, d, J = 8.5 Hz), 7.20 (2H, d, J = 8.5 Hz), 7,6 (4H, AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 325 (M^+, 15), 121 (100). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 70.35; H, 5.85; N, 4.28; S, 9.8. **8c**: ^{1}H NMR (200 MHz) 3.30 (3 H, S), 3.78 (3H, s), 4.0 (2H, s), 4.35 (2H, s), 6.41 (1H, s), 6.8−6.9 (2H, m), 7.2−7.3 (2H, m), 7.6 (4H, AB system, J_{AB} = 8.5 Hz); MS m/z (rel intensity) 325 (M^+, 15), 122 (100), 121 (70). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 69.95; H, 5.85; N, 4.32; S,

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9.88. **8d**: ^{1}H NMR (300 MHz) 2.33 (3H, s), 3.30 (3H, s), 3.96 (2H, s), 4.40 (2H, s), 6.37 (1H, s), 7.1−7.7 (8H, m); MS *m*/*z* (rel intensity) 309 (M^+, 5), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 74.05; H, 6.22; N, 4.5; S, 10.3. **8e**: ^{1}H NMR (300 MHz) 2.33 (3H, s), 3.30 (3H, s), 4.0 (2H, s), 4.35 (2H, s), 6.40 (1H, s), 7.0−7.3 (4H, m), 7.6 (4H, AB system, J_{AB} = 8.5 Hz); MS *m*/*z* (rel intensity) 309 (M^+, 5), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 73.95; H, 6.16; N, 4.5; S, 10.4. **8f**: ^{1}H NMR (200 MHz) 3.30 (3H, s), 4.0 (2H, s), 4.35 (2H, s), 6.40 (1H, s), 7.2−7.7 (8H, m); MS *m*/*z* (rel intensity) 331, 329 (M^+, 40), 127, 125 (100), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.85; H, 4.87; N, 4.22; S, 9.75. **8g**: ^{1}H NMR (200 MHz) 3.30 (3H, s), 4.0 (2H, s), 4.35 (2H, s), 6.45 (1H, s), 7.2−7.7 (8H, m); MS *m*/*z* (rel intensity) 331, 329 (M^+, 40), 127, 125 (100), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.8; H, 4.92; N, 4.27; S, 9.76. **8i**: ^{1}H NMR (200 MHz) 3.30 (3H, s), 4.05 (2H, s), 4.35 (2H, s), 6.52 (1H, s), 7.3−7.7 (8H, m); MS *m*/*z* (rel intensity) 320 (M^+, 4), 132 (70), 116 (100). Anal. Calcd for $C_{19}H_{16}N_2OS$: C, 71.22; H, 5.03; N, 8.74; O, 4.99; S, 10.01. Found: C, 71.0; H, 5.0; N, 8.7; S, 9.97. **8j**: ^{1}H NMR (300 MHz) 3.30 (3 H, S), 4.0 (2H, s), 4.40 (2H, s), 6.53 (1H, s), 7.2−7.4 (10H, m); MS *m*/*z* (rel intensity) 270 (M^+, 20), 91 (100). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; O, 5.92; S, 11.86. Found: C, 75.2; H, 6.73; S, 11.9.

The following new 1:1 adducts **4** were obtained as 60:40 Z/E mixtures. **4b**: ^{1}H $NMR_{Z-isomer}$ (200 MHz) 3.80 (3H, s), 3.85 (2H, s), 4.02 (2H, br d, J = 6.5 Hz; collapsing to br s upon irradiation at 5.75), 4.37 (2H, s), 5.75 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.05 (1H, br d, J = 10 Hz), 6.8−7.4 (8H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 3.80 (3H, s), 3.90 (2H, s), 3.92 (2H, br d, J = 6.5 Hz; collapsing to br s upon irradiation at 5.7), 4.37 (2H, s), 5.7 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, br d, J = 15 Hz), 6.8−7.4 (8H, m); MS *m*/*z* (rel intensity) 325 (M^+, 15), 121 (100). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 70.4; H, 5.85; N, 4.32; S, 9.88. **4c**: ^{1}H $NMR_{Z-isomer}$ (300 MHz) 3.78 (3H, s), 3.88 (2H, s), 4.09 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1.0 Hz upon irradiation at 5.70), 4.38 (2H, s), 5.7 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.06 (1H, dd, J_1 = 10 Hz, J_2 = 1.0 Hz), 6.8−6.9 (2H, m), 7.2−7.3 (2H, m), 7.,6 (4H, AB system, J_{AB} = 8.5 Hz); ^{1}H $NMR_{E-isomer}$ (200 MHz) 3.78 (3H, s), 3.92 (2H, s), 3.98 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1.0 Hz upon irradiation at 5.80), 4.38 (2H, s), 5.8 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, dd, J_1 = 15 Hz, J_2 = 1.0 Hz), 6.8−6.9 (2H, m), 7.2−7.3 (2H, m), 7.6 (4H, AB system, J_{AB} = 8.5 Hz); MS *m*/*z* (rel intensity) 325 (M^+, 15), 121 (100). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83; S, 9.85. Found: C, 70.45; H, 5.9; N, 4.33; S, 9.9. **4d**: ^{1}H $NMR_{Z-isomer}$ (200 MHz) 2.34 (3H, s), 3.88 (2H, s), 4.07 (2H, dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz; collapsing to d, J = 1.5 Hz upon irradiation at 5.78), 4.4 (2H, s), 5.78 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.05 (1H, dt, J_d = 10 Hz, J_t = 1.5 Hz), 7.1−7.7 (8H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 2.34 (3H, s), 3.92 (2H, s), 3.96 (2H, dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz; collapsing to d, J = 1.5 Hz upon irradiation at 5.70), 4.4 (2H, s), 5.7 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, dt, J_d = 15 Hz, J_t = 1.5 Hz), 7.1−7.7 (8H, m); MS *m*/*z* (rel intensity) 309 (M^+, 5), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 73.5; H, 6.16; N, 4.5; S, 10.3. **4e**: ^{1}H $NMR_{Z-isomer}$ (200 MHz) 2.3 (3H, s), 3.88 (2H, s), 4.10 (2H, dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz; collapsing to d, J = 1.5 Hz upon irradiation at 5.80), 4.38 (2H, s), 5.80 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.05 (1H, dt, J_d = 10 Hz, J_t = 1.5 Hz), 7.1−7.7 (8H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 2.3 (3H, s), 3.92 (2H, s), 3.95 (2H, dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz; collapsing to d, J = 1.5 Hz upon irradiation at 5.70), 4.38 (2H, s), 5.7 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, dt, J_d = 15 Hz, J_t = 1.5 Hz), 7.1−7.7 (8H, m); MS *m*/*z* (rel intensity) 309 (M^+, 5), 105 (100). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; O, 5.17; S, 10.36. Found: C, 73.55; H, 6.23; N, 4.5; S, 10.4. **4f**: ^{1}H $NMR_{Z-isomer}$ (200 MHz) 3.88 (2H, s), 4.08 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1 Hz upon irradiation at 5.77), 4.40 (2H, s), 5.77 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.08 (1H, dt, J_d = 10 Hz, J_t = 1 Hz), 7.2−7.7 (8H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 3.92 (2H, s), 3.97 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1 Hz upon irradiation at 5.68), 4.40 (2H, s), 5.68 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, dt, J_d = 15 Hz, J_t = 1 Hz), 7.2−7.7 (8H, m); MS *m*/*z* (rel intensity) 331, 329 (M^+, 40), 127, 125 (100), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.8; H, 4.92; N, 4.2; S, 9.75. **4g**: ^{1}H $NMR_{Z-isomer}$ (200 MHz) 3.90 (2H, s), 4.09 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1 Hz upon irradiation at 5.78), 4.42 (2H, s), 5.78 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.10 (1H, dt, J_d = 10 Hz, J_t = 1 Hz), 7.2−7.7 (8H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 3.93 (2H, s), 3.98 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1 Hz upon irradiation at 5.70), 4.42 (2H, s), 5.70 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.20 (1H, dt, J_d = 15 Hz, J_t = 1 Hz), 7.2−7.7 (8H, m); MS *m*/*z* (rel intensity) 331, 329 (M^+, 40), 127, 125 (70), 116 (100). Anal. Calcd for $C_{18}H_{16}ClNOS$: C, 65.54; H, 4.89; Cl, 10.75; N, 4.25; O, 4.85; S, 9.72. Found: C, 65.4; H, 4.87; N, 4.22; S, 9.75. **4j**: ^{1}H $NMR_{Z-isomer}$ (300 MHz) 3.87 (2H, s), 4.10 (2H, dd, J_1 = 6.5 Hz, J_2 = 1.1 Hz; collapsing to d, J = 1.1 Hz upon irradiation at 5.74), 4.45 (2H, s), 5.74 (1H, dt, J_d = 10 Hz, J_t = 6.5 Hz), 6.15 (1H, dt, J_d = 10 Hz, J_t = 1.1 Hz), 7.2−7.4 (10H, m); ^{1}H $NMR_{E-isomer}$ (200 MHz) 3.90 (2H, s), 3.98 (2H, dd, J_1 = 6.5 Hz, J_2 = 1 Hz; collapsing to d, J = 1.1 Hz upon irradiation at 5.70), 4.45 (2H, s), 5.70 (1H, dt, J_d = 15 Hz, J_t = 6.5 Hz), 6.24 (1H, dt, J_d = 15 Hz, J_t = 1.1 Hz), 7.2−7.4 (8H, m); MS *m*/*z* (rel intensity) 270 (M^+, 20), 91 (100). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; O, 5.92; S, 11.86. Found: C, 75.25; H, 6.7; S, 11.9.

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