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Insertion of Benzyne into a Bi−S Bond: A New Synthetic Route to *ortho*-Functionalized Bismuthanes and Its Application to the Synthesis of Dibenzothiophene

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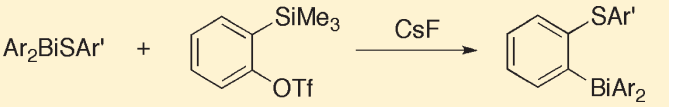
Supporting Information

ABSTRACT: *ortho*-Arylthio triarylbismuthanes $[2\text{-}(Ar'S)C_6H_4]_nBiAr_{3-n}$ have been conveniently synthesized by insertion of benzyne into the bismuth−sulfur bond of $(Ar'S)_nBiAr_{3-n}$ (n = 1, 2). A similar insertion takes place when a homologous antimony congener is used, but no reaction is observed with its phosphorus analogue. This suggests a clear difference in the bond strength between pnictogen−sulfur bonds. The carbon−bismuth bond of $[2\text{-}(2\text{-}BrC_6H_4S)C_6H_4]_nBiAr_{3-n}$ undergoes Pd-catalyzed intramolecular cross-coupling to produce dibenzothiophene in good yield. An X-ray crystallographic study of $2\text{-}(2\text{-}BrC_6H_4S)C_6H_4BiTol_2$ (Tol = 4-MeC_6H_4) reveals that this molecule is present in a dimeric structure, where the six heteroatoms including bismuth, sulfur, and bromine are linked through the nonbonded intramolecular bismuth−sulfur and intermolecular sulfur−bromine and bromine−bromine interactions.



INTRODUCTION

The insertion of benzyne into an element−element σ bond is a powerful synthetic route to diverse polysubstituted arenes.[1] Various σ bonds have been demonstrated to react with benzyne. However, only a limited number of examples has been reported on the insertion of arynes into a metal−element bond.[2] During the course of our studies on the antifungal activity[3a,b] and phosphorescence[3c] of sulfur-functionalized organobismuth compounds, we became interested in the possibility of applying the reaction of benzyne to the construction of triarylbismuthanes.[4] The most common method for preparing triarylbismuthanes is the reaction of bismuth(III) halides with aryl-Grignard or aryllithium reagents through halogen−metal exchange or *ortho*-lithiation of the parent arenes.[5] However, the design and synthesis of functionalized triarylbismuthanes is sometimes limited by the compatibility of functional groups with reactive organometallic reagents or lengthy synthesis of the parent haloarenes. Since a bismuth−element σ bond is reactive, insertion of benzyne into this bond would be a new synthesis of *ortho*-functionalized triarylbismuthanes. Herein, we describe the insertion of benzyne into a bismuth−sulfur bond, which provides a convenient synthetic method for triarylbismuthanes that carry an arylthio functional group *ortho* to the bismuth atom. Furthermore, this strategy is applied to the convenient and facile synthesis of dibenzothiophene by combination with an intramolecular cross-coupling reaction based on the synthetic utility of triarylbismuthanes.

RESULTS AND DISCUSSION

Synthesis of (Arylthio)bismuthanes and Their Reaction with Benzyne. In order to investigate the reactivity of the bismuth−sulfur bond toward benzyne, $PhSBiTol_2$ **1a** was synthesized from tris(4-methylphenyl)bismuthane (Tol_3Bi) and thiophenol in accordance with Scheme 1 (71% yield). We then examined its reaction with benzyne, which was generated from precursor **2**[6] using a reported procedure[2e] (eq 1 and Table 1). Initially, using 4 equiv of CsF to generate benzyne in THF did not give adduct **3a** (entry 1). However, when the solvent was changed from THF to acetonitrile, we found that **3a** was formed in low yield (entry 2). Furthermore, increasing the amount of CsF (5 equiv) dramatically improved the yield of **3a** (entry 3). The reaction was accelerated by further increasing the amount of CsF to 6 equiv (entry 4), but a longer reaction time significantly lowered the yield of **3a**, probably due to its decomposition by CsF (entry 5). These results indicate that the yield of **3a** was sensitive to the amount of CsF as well as to the nature of the solvent employed. In contrast, an attempted reaction of Tol_3Bi with benzyne under similar conditions did not proceed. It is known that triphenylphosphine reacts with benzyne to afford tetraphenylphosphonium triflate.[7]

Following the successful formation of **3a** from **1a** in moderate yield, substituted analogues **1** and **4** were synthesized in accordance

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Scheme 1

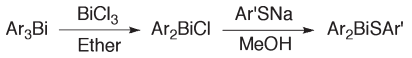
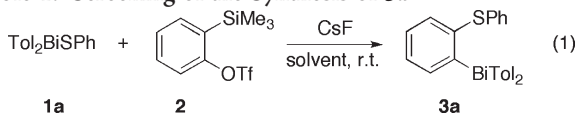


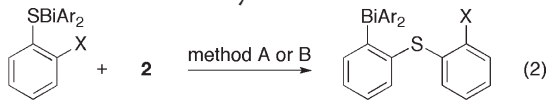
Table 1. Screening of the Synthesis of 3a



1a **2** **3a**

entry	CsF (equiv)	**2** (equiv)	solvent	time (h)	**3a** yield (%)
1	4	2	THF	24	0
2	4	2	MeCN	24	15
3	5	2	MeCN	24	58
4	6	2	MeCN	4	60
5	6	2	MeCN	24	20

Table 2. Reaction of Benzyne with 1 or 4



1: X = H
4: X = Br

a: Ar = Tol
b: Ar = Ph
c: Ar = 4-ClC$_6$H$_4$

3: X = H
5: X = Br

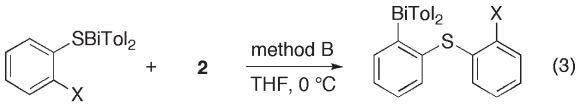
entry	**2** (equiv)	substrate	product	yield (%) method A[a]/ B[b]
1	2	**1a**	**3a**	58/60
2	2	**1b**	**3b**	59/67
3	2	**1c**	**3c**	59/65
4	2	**4a**	**5a**	38/46
5	2	**4b**	**5b**	41/43
6	2	**4c**	**5c**	35/43

[a] CsF (5 equiv), MeCN, rt, 24 h. [b] KF (3 equiv), 18-crown-6 (3 equiv), THF, 0 °C, 12 h.

with Scheme 1, and the substituent effect was studied through their reaction with benzyne, which was generated using two different methods (eq 2 and Table 2). The yields of the adducts **3** and **5** were improved by using KF and 18-crown-6 (method B), compared to CsF (method A). The *p*-substituent of the aryl group attached to the bismuth atom did not affect the yields of **3** and **5**. In contrast, the bromo substituent adjacent to the sulfur atom lowered the yield of **5** relative to **3**. Although the yields of **5** are modest, it should be noted that **5** is easily obtained in one simple step via benzyne. In contrast, its conventional synthesis using an organolithium method requires not only the preparation of the parent 2,2′-dibromodiphenyl sulfide but also control the sulfide's subsequent regioselective halogen−metal exchange.[8] Bismuthanes **5a**−**c** are considered to be highly useful as synthetic precursors for the synthesis of dibenzothiophene by a Pd-catalyzed cross-coupling reaction.[4c,9]

In order to understand the effect of the arylthio group's *ortho*-substituent on its reactivity with benzyne, **6a**, which bears a methyl substituent, was synthesized. Unlike **1a** and **4a**, **6a** was less stable and slowly decomposed by a redistribution reaction to form Tol$_3$Bi. Comparison of the reactivity between **1a**, **4a**, and **6a** revealed that the methyl substituent promotes the insertion of

Table 3. Effect of the *ortho*-Substituent

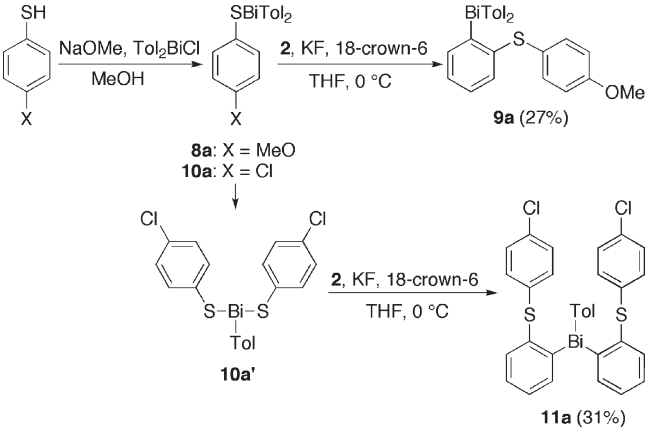


1a: X = H
4a: X = Br
6a: X = Me

3a: X = H
5a: X = Br
7a: X = Me

entry	substrate	**2** (equiv)	time (h)	product	yield (%)
1	**1a**	2	4	**3a**	29
2	**1a**	2	12	**3a**	60
3	**4a**	2	4	**5a**	28
4	**4a**	2	12	**5a**	46
5	**6a**	2	4	**7a**	62
6	**6a**	2	12	**7a**	79

Scheme 2



benzyne and that the reactivity of these compounds decreases in the order of the substituent Me > H > Br (eq 3 and Table 3). These results may be accounted for by the difference in the electronic effect between the electron-donating and -withdrawing nature of the methyl and bromo substituents, respectively. In addition, the greater steric bulk of the bromo substituent or its intramolecular interaction with the bismuth atom[10] may also block the approach of benzyne to the bismuth−sulfur bond.

On this basis, the effect of the *p*-substituent on the arylthio group was examined by synthesizing analogues **8a** and **10a**, which bear an electron-donating and an electron-withdrawing substituent, respectively (Scheme 2). Bismuthane **8a** was highly reactive, and it underwent a redistribution reaction to give Tol$_3$Bi. Although **8a** could not be isolated in pure form, the reaction with benzyne successfully afforded **9a**. On the other hand, **10a** easily underwent a redistribution reaction to afford **10a′** along with Tol$_3$Bi. This is in contrast to the stability of **4a**, which bears an analogous bromo substituent at the *ortho*-position. Recently, aromatic compounds persubstituted with sulfur ligands have attracted much attention owing to their interesting physical organic properties.[11] In this context, benzyne inserted into both of the bismuth−sulfur bonds of **10a′** to afford disulfurated bismuthane **11a**. Furthermore, application of this insertion reaction to **12a**, **14a**, and **16a** prepared from TolBiCl$_2$ gave **13a**, **15a**, and **17a**, respectively (Scheme 3). The conjugated system of the 2-phenylthiophenyl group in these derivatives is isoelectronic with that

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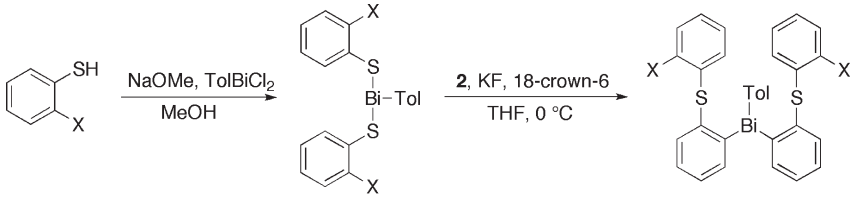
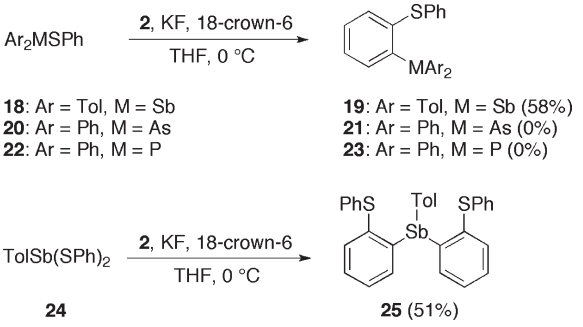
Scheme 3



12a: X = H
14a: X = Br
16a: X = Me

13a: X = H (30%)
15a: X = Br (32%)
17a: X = Me (52%)

Scheme 4



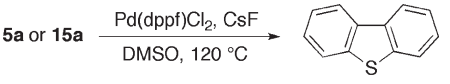
18: Ar = Tol, M = Sb
20: Ar = Ph, M = As
22: Ar = Ph, M = P

19: Ar = Tol, M = Sb (58%)
21: Ar = Ph, M = As (0%)
23: Ar = Ph, M = P (0%)

24

25 (51%)

Scheme 5



81% (from **5a**)
54% (from **15a**)

of the styrylphenyl scaffold of the phosphorescent triarylbismuthane bearing an (*E*)-4-(4-*tert*-butylstyryl)phenyl group.[12]

To compare the difference in the reactivity between **1a** and its pnictogen counterparts, **18**, **20**, and **22** were synthesized and the insertion of benzyne into the Sb−S, As−S, and P−S bonds was examined (Scheme 4). Stibine **18** underwent insertion with benzyne in a similar manner to **1a** to give **19**. However, when arylthioarsine **20**[13a,b] and arylthiophosphine **22**[13d] were submitted to the same reaction conditions, the corresponding adducts **21** and **23** were not formed. Such difference in reactivity reflects the stronger bond energy of the As−S and P−S bonds compared to the Bi−S and Sb−S bonds.[14] Stibine **24**, which bears two reaction sites, smoothly underwent insertion with benzyne to give **25**.

Cross-Coupling Reaction. Dibenzothiophenes have found numerous applications as dyes, pharmaceuticals, and conducting polymers.[15] Recent growing interests in the synthetic utility of triarylbismuthanes in palladium-catalyzed cross-coupling reactions[4c,9] led us to synthesize dibenzothiophene from **5a** and **15a** via an intramolecular cross-coupling reaction (Scheme 5). The reaction proceeded smoothly to afford dibenzothiophene in 81% and 54% yields, respectively. Although many methods have been reported for the synthesis of dibenzothiophene,[15,16] we expect this to provide one of the most efficient synthetic routes, because of the convenience and simplicity of the procedure.

X-ray Crystallographic Study of 5a. The molecular structure of a benzyne adduct was revealed by the X-ray crystallography of **5a** (Figure 1 and Table 4). The S(1) atom is adjacent to both Bi(1) and Br(1) atoms, and the S(1)−C(21) bond is disposed in a *trans* fashion toward the Bi(1)−C(8) bond. The intramolecular atomic distances of S(1)···Bi(1) [3.397(2) Å] and S(1)···Br(1) [3.174(2) Å] are within the sum of the van der Waals radii (4.2 and 3.7 Å, respectively),[10a] which indicates that the bismuth atom forms a distorted tetrahedron[10a] through the intramolecular interaction with the sulfur atom. An intramolecular interaction of this type between the bismuth and sulfur atoms may be responsible for the unique and unexpected effect, stabilizing the bismuth−methyl bond of heterocyclic 10-methylphenothiabismine [−Bi(Me)$C_6H_4SC_6H_4$−] enough to make this compound isolable and stable in air.[8] Furthermore, the bromine atom is in close proximity to the sulfur atom and appears to sterically block the insertion of benzyne into the Bi−S bond of **4a**. The crystal packing of **5a** is also unusual (see Supporting Information): the intermolecular atomic distances between the bromine atoms (3.646 Å) and between the bromine and sulfur atoms (3.621 Å) are both within the sum of the van der Waals radii (3.8 and 3.7 Å, respectively), suggesting the existence of a weak interaction. These interactions between molecules of **5a** produce a dimeric structure, where the heteroatoms are coplanar with the phenylene ring to which they are attached. Thus, the six heteroatoms, including bismuth, sulfur, and bromine, are linked through weak interactions. This kind of unusual interaction has been observed in *ortho*-disubstituted benzenes and *peri*-substituted naphthalene and anthracene.[17] Intermolecular CH−π interactions are present between the H(9) and one of the tolyl groups [C(8)−C(14)] at the bismuth atom. This is reflected in the C(1)−Bi(1)−C(8) bond angle [96.28(9)°], which is forced to be larger than the other bond angles around the bismuth atom.

In summary, the present method provides a novel approach to the synthesis of sulfur-functionalized bismuthanes and stibines. Furthermore, it is expected that this methodology will be applicable to the synthesis of functionalized bismuthanes that are heteroatom-substituted at the *ortho*-position from precursors bearing a bismuth−heteroatom σ bond. Further studies on the synthetic application of this strategy are currently underway.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out under argon unless otherwise noted. Acetonitrile, diethyl ether, methanol, and tetrahydrofuran were distilled from calcium hydride before use. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance 400S spectrometer with TMS as an internal standard.

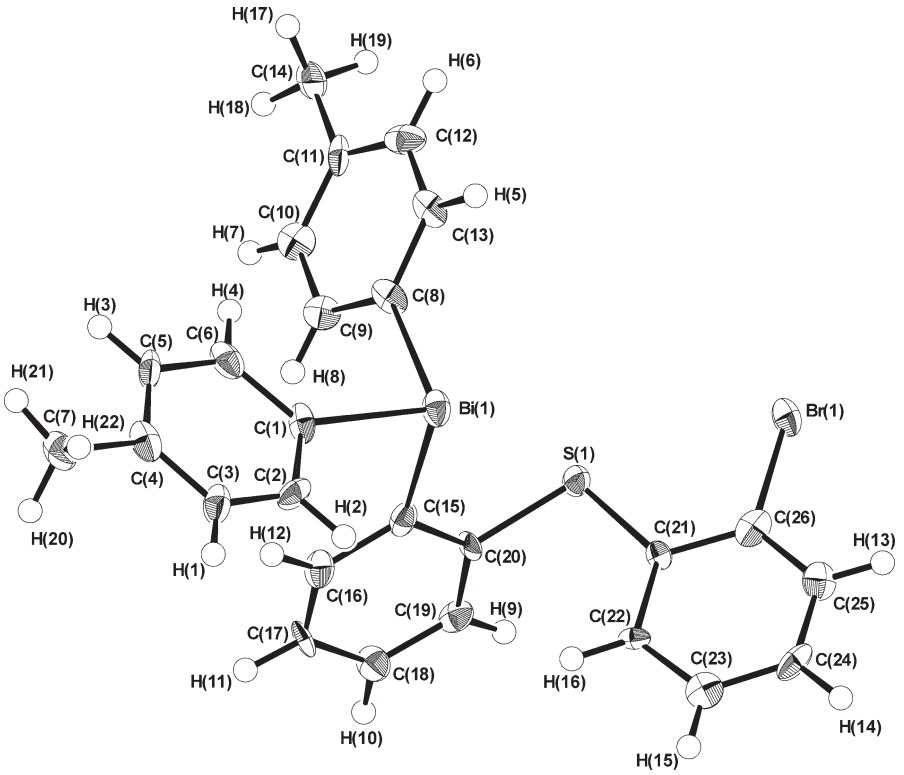


Figure 1. ORTEP drawing of the molecular structure of **5a** with 50% probability ellipsoids.

Table 4. Selected Bond Lengths or Atomic Distances (Å) and Angles (deg) for 5a

Bond Lengths		Intramolecular Atomic Distances	
Bi(1)−C(1)	2.261(2)	Bi(1)•••S(1)	3.397(2)
Bi(1)−C(8)	2.247(3)	Br(1)•••S(1)	3.174(2)
Bi(1)−C(15)	2.283(2)		
Br(1)−C(26)	1.913(3)	Intermolecular Atomic Distances	
S(1)−C(20)	1.800(3)	Br(1)•••S(1)	3.621
S(1)−C(21)	1.767(3)	Br(1)•••Br(1)	3.646
C(15)−C(16)	1.394(3)		
C(15)−C(20)	1.406(3)	Bond Angles	
C(19)−C(20)	1.376(4)	C(1)−Bi(1)−C(8)	96.28(9)
C(21)−C(22)	1.399(4)	C(1)−Bi(1)−C(15)	94.02(8)
C(21)−C(26)	1.390(3)	C(8)−Bi(1)−C(15)	92.97(9)
C(25)−C(26)	1.381(4)	C(20)−S(1)−C(21)	103.3(1)
		C(20)−C(15)−Bi(1)	119.5(2)
		S(1)−C(20)−C(15)	118.9(2)
		C(26)−C(21)−S(1)	117.9(2)

Synthesis of Diaryl(arylthio)bismuthanes. General Procedure. A typical example is exemplified by the synthesis of **1a**. To a solution of thiophenol (3 mmol) in methanol (3 mL) was added sodium methoxide (3.6 mmol) at room temperature, and the resulting solution was stirred for 30 min. To this solution thus obtained was added dropwise a suspension of chlorobis(4-methylphenyl)bismuthane (3 mmol), prepared from tris(4-methylphenyl)bismuthane (2 mmol) and bismuth(III) chloride (1 mmol) in diethyl ether (10 mL) by stirring for 1 h at room temperature, and the reaction mixture was stirred for 2 h at room temperature. The reaction was quenched with brine (10 mL), and the mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (5:1) to give the product.

Bis(4-methylphenyl)(phenylthio)bismuthane (1a): yellow solid; yield 71%; mp 108−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 7.08 (1H, t, J = 7.2 Hz), 7.15 (2H, t, J = 7.2 Hz), 7.36 (4H, d, J = 7.6 Hz), 7.36 (2H, d, J = 7.2 Hz), 7.96 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 126.3, 128.5, 132.2, 134.6, 135.9, 137.3, 138.2, 163.7. Anal. Calcd for $C_{20}H_{19}BiS$: C, 48.00; H, 3.83. Found: C, 47.70; H, 3.86.

Diphenyl(phenylthio)bismuthane (1b): yellow solid; yield 70%; mp 83−84 °C (lit.[4b] 91.7−92.7 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (1H, t, J = 7.2 Hz), 7.16 (2H, t, J = 7.2 Hz), 7.34−7.39 (4H, m), 7.56 (4H, t, J = 7.6 Hz), 8.08 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.4, 128.4, 128.5, 131.4, 134.7, 135.5, 137.2, 167.2. Anal. Calcd for $C_{18}H_{15}BiS$: C, 45.77; H, 3.20. Found: C, 45.80; H, 2.90.

Bis(4-chlorophenyl)(phenylthio)bismuthane (1c): yellow solid; yield 66%; mp 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (1H, t, J = 7.2 Hz), 7.17 (2H, t, J = 7.2 Hz), 7.32 (2H, d, J = 7.2 Hz), 7.49 (4H, d, J = 8.4 Hz), 7.96 (4H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.7, 130.9, 131.7, 134.5, 134.8, 138.6, 138.8, 152.8. Anal. Calcd for $C_{18}H_{13}BiCl_2S$: C, 39.94; H, 2.42. Found: C, 39.78; H, 2.34.

Bis(4-methylphenyl)(2-bromophenylthio)bismuthane (4a): yellow solid; yield 57%; mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 6.95 (1H, dt, J = 1.6, 7.6 Hz), 7.08 (1H, dt, J = 1.6, 7.6 Hz), 7.37 (4H, d, J = 7.6 Hz), 7.48 (1H, dd, J = 1.6, 7.6 Hz), 7.56 (1H, dd, J = 1.6, 7.6 Hz), 7.99 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.2, 126.7, 127.3, 131.2, 132.4, 133.1, 136.0, 136.8, 137.4, 138.9, 152.5. Anal. Calcd for $C_{20}H_{18}BiBrS$: C, 41.47; H, 3.13. Found: C, 41.76; H, 3.13.

Diphenyl(2-bromophenylthio)bismuthane (4b): yellow solid; yield 52%; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (1H, dt, J = 1.6, 7.6 Hz), 7.09 (1H, dt, J = 1.6, 7.6 Hz), 7.36 (2H, t, J = 7.6 Hz),

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7.49 (1H, dd, J = 1.6, 7.6 Hz), 7.56 (4H, t, J = 7.6 Hz), 7.57 (1H, dd, J = 1.6, 7.6 Hz), 8.11 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 126.5, 127.6, 127.7, 128.6, 131.1, 132.6, 135.7, 137.7, 140.6, 173.5. Anal. Calcd for $C_{20}H_{14}BiBrS$: C, 39.22; H, 2.56. Found: C, 39.19; H, 2.41.

Bis(4-chlorophenyl)(2-bromophenylthio)bismuthane (4c): yellow solid; yield 40%; mp 101−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (1H, dt, J = 1.6, 7.6 Hz), 7.11 (1H, dt, J = 1.6, 7.6 Hz), 7.47 (1H, dd, J = 1.6, 7.6 Hz), 7.49 (4H, d, J = 8.4 Hz), 7.57 (1H, dd, J = 1.6, 7.6 Hz), 7.99 (4H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.4, 128.4, 130.9, 131.7, 133.0, 134.9, 136.3, 137.0, 138.8, 165.5. Anal. Calcd for $C_{18}H_{12}BiBrCl_2S$: C, 34.86; H, 1.95. Found: C, 34.82; H, 1.85.

Bis(4-methylphenyl)(2-methylphenylthio)bismuthane (6a). yellow solid; yield 69%; mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 2.42 (3H, s), 6.97−7.04 (2H, m), 7.14 (1H, dd, J = 1.2, 7.6 Hz), 7.35 (4H, d, J = 7.6 Hz), 7.35 (1H, dd, J = 1.2, 7.6 Hz), 7.95 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.3, 126.0, 126.8, 130.0, 132.2, 135.2, 136.1, 137.3, 138.2, 141.6, 163.4. Anal. Calcd for $C_{21}H_{21}BiS$: C, 49.03; H, 4.11. Found: C, 48.82; H, 4.10.

Reaction of Diaryl(arylthio)bismuthanes with Benzyne. General Procedure. Method A: To a solution of diaryl(arylthio)-bismuthane (0.3 mmol) in acetonitrile (3 mL) were added benzyne precursor **2** (0.6 mmol) and CsF (1.5 mmol) at room temperature. The reaction mixture was allowed to react at this temperature for 24 h. The reaction was quenched with brine (5 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give the product. Method B: To a solution of diaryl(arylthio)bismuthane (0.3 mmol) in THF (3 mL) were added benzyne precursor **2** (0.6 mmol), KF (0.9 mmol), and 18-crown-6 (0.9 mmol) at 0 °C. The reaction mixture was allowed to react at this temperature for 1 h and then at room temperature for 11 h. The reaction was quenched with brine (5 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give the product.

Bis(4-methylphenyl)[2-(phenylthio)phenyl]bismuthane (3a): colorless solid; yield 60%; mp 74−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (6H, s), 7.08−7.11 (3H, m), 7.16 (2H, d, J = 7.4 Hz), 7.17 (4H, d, J = 7.2 Hz) 7.24 (1H, dt, J = 1.2, 7.4 Hz), 7.31 (1H, dt, J = 1.2, 7.4 Hz), 7.57 (4H, d, J = 7.2 Hz), 7.57 (1H, dd, J = 1.2, 7.4 Hz), 7.80 (1H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 125.9, 128.5, 128.9, 129.0, 131.1, 131.3, 135.2, 137.2, 137.6, 138.0, 139.0, 140.7, 154.1, 163.5. Anal. Calcd for $C_{26}H_{23}BiS$: C, 54.17; H, 4.02. Found: C, 54.27; H, 4.05.

Diphenyl[2-(phenylthio)phenyl]bismuthane (3b): colorless solid; yield 67%; mp 65−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09−7.13 (3H, m), 7.19 (2H, t, J = 7.2 Hz), 7.28−7.40 (8H, m), 7.60 (1H, dd, J = 1.2, 7.4 Hz), 7.69 (4H, d, J = 7.2 Hz), 7.79 (1H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.1, 127.6, 128.6, 129.0, 129.3, 130.5, 131.3, 135.4, 137.7, 137.9, 139.1, 140.8, 158.1, 164.1. Anal. Calcd for $C_{24}H_{19}BiS$: C, 52.56; H, 3.49. Found: C, 52.45; H, 3.45.

Bis(4-chlorophenyl)[2-(phenylthio)phenyl]bismuthane (3c): colorless solid, yield 65%; mp 60−61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (2H, d, J = 7.4 Hz), 7.12 (1H, t, J = 7.4 Hz), 7.18 (2H, t, J = 7.4 Hz), 7.32 (4H, d, J = 8.0 Hz), 7.33−7.40 (2H, m), 7.57 (4H, d, J = 8.0 Hz), 7.63 (1H, dd, J = 1.2, 7.4 Hz), 7.74 (1H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.2, 128.3, 129.1, 129.6, 130.8, 131.6, 134.0, 135.8, 137.4, 138.7, 139.0, 140.4, 155.7, 164.1. Anal. Calcd for $C_{24}H_{17}BiCl_2S$: C, 46.69; H, 2.78. Found: C, 46.39; H, 2.77.

Bis(4-methylphenyl)[2-(2-bromophenylthio)phenyl]bis-muthane (5a): colorless solid; yield 46%; mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (6H, s), 6.59 (1H, dd, J = 1.6, 7.6 Hz), 6.92 (1H, dt, J = 1.6, 7.6 Hz), 6.96 (1H, dt, J = 1.6, 7.6 Hz), 7.16 (4H, d, J = 7.6 Hz), 7.34 (1H, dt, J = 1.6, 7.6 Hz), 7.39 (1H, dt, J = 1.6, 7.6 Hz), 7.48 (1H, dd, J = 1.6, 7.6 Hz), 7.55 (4H, d, J = 7.6 Hz), 7.63 (1H, dd, J = 1.6, 7.6 Hz), 7.88 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 121.2, 126.4, 127.6, 128.1, 129.4, 131.3, 131.9, 132.7, 136.4, 137.2, 137.6, 138.9, 139.4, 139.8, 154.5, 165.0. Anal. Calcd for $C_{26}H_{22}BiBrS$: C, 47.65; H, 3.38. Found: C, 48.02; H, 3.44.

Diphenyl[2-(2-bromophenylthio)phenyl]bismuthane (5b): colorless solid; yield 43%; mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (1H, dd, J = 1.6, 7.6 Hz), 6.93 (1H, dt, J = 1.6, 7.6 Hz), 6.96 (1H, dt, J = 1.6, 7.6 Hz), 7.29 (2H, t, J = 7.6 Hz), 7.36 (4H, t, J = 7.6 Hz), 7.36 (1H, dt, J = 1.6, 7.6 Hz), 7.41 (1H, dt, J = 1.6, 7.6 Hz), 7.48 (1H, dd, J = 1.6, 7.6 Hz), 7.66 (1H, dd, J = 1.6, 7.6 Hz), 7.67 (4H, d, J = 7.6 Hz), 7.87 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2, 126.5, 127.6 (×2), 128.2, 129.5, 130.5, 132.0, 132.7, 136.5, 137.5, 139.0, 139.5, 139.6, 158.4, 165.5. Anal. Calcd for $C_{24}H_{18}BiBrS$: C, 45.95; H, 2.89. Found: C, 46.06; H, 2.88.

Bis(4-chlorophenyl)[2-(2-bromophenylthio)phenyl]bis-muthane (5c): colorless solid; yield 43%; mp 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51−6.54 (1H, m), 6.91−6.97 (2H, m), 7.29 (4H, d, J = 8.0 Hz), 7.35−7.47 (3H, m), 7.55 (4H, d, J = 8.0 Hz), 7.68 (1H, dd, J = 1.6, 7.6 Hz), 7.81 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2, 126.7, 127.7, 128.0, 129.8, 130.6, 132.3, 132.8, 134.0, 137.0, 138.8, 138.9, 139.1, 139.2, 156.0, 165.4. Anal. Calcd for $C_{24}H_{16}BiBrCl_2S$: C, 41.40; H, 2.32. Found: C, 41.79; H, 2.41.

Bis(4-methylphenyl)[2-(2-methylphenylthio)phenyl]bis-muthane (7a): colorless solid; yield 79%; mp 111−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (6H, s), 2.33 (3H, s), 6.89 (1H, dd, J = 1.2, 7.6 Hz), 6.99 (1H, dt, J = 1.2, 7.6 Hz), 7.07 (1H, dt, J = 1.2, 7.6 Hz), 7.16 (1H, dd, J = 1.2, 7.6 Hz), 7.17 (4H, d, J = 7.6 Hz), 7.23 (1H, dt, J = 1.6, 7.6 Hz), 7.30 (1H, dt, J = 1.6, 7.6 Hz), 7.43 (1H, dd, J = 1.6, 7.6 Hz), 7.57 (4H, d, J = 7.6 Hz), 7.79 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.5, 126.3, 126.6, 129.1, 129.3, 130.2, 130.6, 131.3, 134.2, 136.7, 137.0, 137.2, 137.6, 139.1, 141.0, 154.0, 162.5. Anal. Calcd for $C_{27}H_{25}BiS$: C, 54.91; H, 4.27. Found: C, 54.99; H, 4.34.

Bis(4-methylphenyl)[2-(4-methoxyphenylthio)phenyl]bis-muthane (9a): colorless solid; yield 27% based on the starting 4-methoxythiophenol (0.2 mmol); mp 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 3.77 (3H, s), 6.77 (2H, d, J = 9.2 Hz), 7.16−7.20 (3H, m), 7.20 (4H, d, J = 8.0 Hz), 7.27 (1H, dt, J = 1.6, 7.6 Hz), 7.44 (1H, dd, J = 1.6, 7.6 Hz), 7.60 (4H, d, J = 8.0 Hz), 7.74 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 55.3, 114.7, 127.5, 128.9, 130.1, 131.2, 131.3, 132.5, 133.1, 137.2, 137.5, 137.7, 138.7, 143.4, 158.9. Anal. Calcd for $C_{27}H_{25}BiOS$: C, 53.47; H, 4.15. Found: C, 53.39; H, 4.21.

Synthesis of Arylbis(arylthio)bismuthanes. General Procedure. A typical example is exemplified by the synthesis of **12a**. To a solution of thiophenol (6 mmol) in methanol (5 mL) was added sodium methoxide (7.2 mmol) at room temperature, and the resulting solution was stirred for 30 min. To this solution thus obtained was added dropwise a suspension of dichloro(4-methyllphenyl)bismuthane (3 mmol), prepared from tris(4-methylphenyl)bismuthane (1 mmol) and bismuth(III) chloride (2 mmol) in diethyl ether (10 mL) by stirring for 1 h at room temperature, and the reaction mixture was stirred for 2 h at room temperature. The reaction was quenched with brine (10 mL), and the mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was recrystallized from methanol to give **12a**.

(4-Methylphenyl)bis(phenylthio)bismuthane (12a): yellow solid; yield 47%; mp 158−159 °C (lit.[18] 155 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 7.11 (2H, t, J = 7.2 Hz), 7.20 (4H, t, J = 7.2 Hz), 7.33 (4H, d, J = 7.2 Hz), 7.55 (2H, d, J = 7.2 Hz), 8.28 (2H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.5, 125.3, 128.2, 133.0, 134.3, 137.0, 138.0, 138.6, 190.9. Anal. Calcd for $C_{19}H_{17}BiS_2$: C, 44.02; H, 3.31. Found: C, 43.79; H, 3.33.

Bis(2-bromophenylthio)(4-methylphenyl)bismuthane (14a): yellow solid; yield 46%; mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 6.96 (1H, dt, J = 1.2, 7.2 Hz), 7.15 (1H, dt, J = 1.2, 7.2 Hz), 7.55−7.59 (6H, m), 8.47 (2H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.6, 126.8, 127.3, 129.1, 132.4, 133.1, 136.0, 137.3, 138.9, 140.0, 191.9. Anal. Calcd for $C_{19}H_{15}BiBr_2S_2$: C, 33.75; H, 2.24. Found: C, 33.57; H, 2.18.

(4-Methylphenyl)bis(2-methylphenylthio)bismuthane (16a): yellow solid; yield 61%; mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 2.46 (6H, s), 7.00−7.06 (4H, m), 7.17−7.20 (2H, m), 7.28−7.31 (2H, m), 7.55 (2H, d, J = 7.2 Hz), 8.32 (2H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.6, 22.2, 125.7 (×2), 129.5, 132.9, 135.3, 137.1, 137.3, 138.6, 140.9, 190.5. Anal. Calcd for $C_{21}H_{21}BiS_2$: C, 46.15; H, 3.87. Found: C, 45.75; H, 3.82.

Reaction of Arylbis(arylthio)bismuthanes with Benzyne. General Procedure. A typical example is exemplified by the reaction of **12a**. To a solution of **12a** (0.3 mmol) in THF (3 mL) were added benzyne precursor **2** (0.9 mmol), KF (1.8 mmol), and 18-crown-6 (1.8 mmol) at 0 °C under argon. The reaction mixture was allowed to react at this temperature for 1 h and then at room temperature for 23 h. The reaction was quenched with brine (5 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give **13a**.

Bis[2-(phenylthio)phenyl](4-methylphenyl)bismuthane (13a): colorless solid; yield 30%; mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 7.06−7.10 (6H, m), 7.13−7.18 (6H, m), 7.26 (2H, dt, J = 1.2, 7.4 Hz), 7.34 (2H, dt, J = 1.2, 7.4 Hz), 7.53 (2H, d, J = 7.6 Hz), 7.58 (2H, dd, J = 1.2, 7.4 Hz), 7.75 (2H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 125.9, 128.4, 128.9, 129.1, 131.3, 131.5, 135.5, 137.1, 137.7, 137.9, 139.2, 140.5, 157.2, 166.8. Anal. Calcd for $C_{31}H_{25}BiS_2$: C, 55.52; H, 3.76. Found: C, 55.80; H, 4.04.

Bis[2-(4-chlorophenylthio)phenyl](4-methylphenyl)bismuthane (11a): colorless solid; yield 31%; mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (3H, s), 6.94 (4H, d, J = 8.4 Hz), 7.08 (4H, d, J = 8.4 Hz), 7.17 (2H, d, J = 7.2 Hz), 7.29 (2H, dt, J = 1.2, 7.4 Hz), 7.36 (2H, dt, J = 1.2, 7.4 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.60 (2H, dd, J = 1.2, 7.4 Hz), 7.74 (2H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 129.0, 129.3, 129.4, 131.5, 131.7, 131.8, 135.8, 136.5, 137.4, 137.6, 139.3, 140.0, 157.0, 166.8. Anal. Calcd for $C_{31}H_{23}BiCl_2S_2$: C, 50.35; H, 3.13. Found: C, 50.34; H, 3.25.

Bis[2-(2-bromophenylthio)phenyl](4-methylphenyl)bismuthane (15a): colorless solid; yield 32%; mp 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 6.62 (2H, dd, J = 1.2, 7.6 Hz), 6.90 (2H, dt, J = 1.2, 7.6 Hz), 6.96 (2H, dt, J = 1.2, 7.6 Hz), 7.15 (2H, d, J = 7.6 Hz), 7.33 (2H, dt, J = 1.2, 7.4 Hz), 7.39 (2H, dt, J = 1.2, 7.4 Hz), 7.45 (2H, dd, J = 1.2, 7.6 Hz), 7.50 (2H, d, J = 7.6 Hz), 7.61 (2H, dd, J = 1.2, 7.4 Hz), 7.81 (2H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 121.2, 126.5, 127.7, 128.2, 129.4, 131.5, 132.1, 132.7, 136.6, 137.1, 137.6, 139.0, 139.5, 139.7, 157.8, 168.2. Anal. Calcd for $C_{31}H_{23}BiBr_2S_2$: C, 44.95; H, 2.80. Found: C, 45.17; H, 2.96.

Bis[2-(2-methylphenylthio)phenyl](4-methylphenyl)bismuthane (17a): colorless solid; yield 52%; mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (6H, s), 2.32 (3H, s), 6.87 (2H, dd, J = 1.2, 7.6 Hz), 6.94 (2H, dt, J = 1.2, 7.6 Hz), 7.03 (2H, dt, J = 1.2, 7.6 Hz), 7.12 (2H, d, J = 7.6 Hz), 7.18 (2H, d, J = 7.6 Hz), 7.24 (2H, dt, J = 1.2, 7.4 Hz), 7.31 (2H, dt, J = 1.2, 7.4 Hz), 7.43 (2H, dd, J = 1.2, 7.4 Hz), 7.53 (2H, d, J = 7.6 Hz), 7.76 (2H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.5, 126.2, 126.5, 129.1, 129.2, 130.2, 130.8, 131.5, 134.5, 136.5, 136.7, 136.8, 137.1, 137.7, 139.3, 140.9, 157.0, 165.6. Anal. Calcd for $C_{33}H_{29}BiS_2$: C, 56.73; H, 4.18. Found: C, 56.51; H, 4.27.

Synthesis of Bis(4-methylphenyl)(phenylthio)stibine (18). To a solution of thiophenol (3 mmol) in methanol (3 mL) was added sodium methoxide (3.6 mmol) at room temperature, and the mixture was stirred for 30 min. Chlorobis(4-methylphenyl)stibine (3 mmol) was prepared by stirring tris(4-methylphenyl)stibine (2 mmol) and antimony(III) chloride (1 mmol) for 5 h at 80 °C under neat conditions. Then, the stibine thus obtained was diluted with diethyl ether (10 mL), and the resulting solution was added dropwise to the solution of sodium thiophenoxide at room temperature. After the reaction mixture was stirred for 2 h at room temperature, the reaction was quenched with brine (10 mL) and the mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (8:1) to give **18**.

Bis(4-methylphenyl)(phenylthio)stibine (18): colorless solid; yield 27%; mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (6H, s), 7.16−7.19 (3H, m), 7.21 (4H, d, J = 7.6 Hz), 7.41−7.43 (2H, m), 7.54 (4H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 126.4, 128.8, 129.9, 133.7, 135.0, 135.3, 136.9, 139.2. Anal. Calcd for $C_{20}H_{19}SSb$: C, 58.14; H, 4.63. Found: C, 57.97; H, 4.50.

Reaction of 18 with Benzyne. To a solution of **18** (0.3 mmol) in THF (3 mL) were added benzyne precursor **2** (0.6 mmol), KF (0.9 mmol), and 18-crown-6 (0.9 mmol) at 0 °C under argon. The reaction mixture was stirred at this temperature for 1 h and then at room temperature for 17 h. The reaction was quenched with brine (5 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give **19**.

Bis(4-methylphenyl)[2-(phenylthio)phenyl]stibine (19): colorless solid; yield 58%; mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s), 7.10−7.14 (7H, m), 7.17−7.20 (4H, m), 7.28 (4H, d, J = 7.6 Hz), 7.27−7.32 (1H, m), 7.47 (1H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 126.1, 128.8, 128.9 (×2), 129.7, 129.8, 134.5, 135.5, 136.3, 136.6, 137.5, 138.2, 141.2, 146.8. Anal. Calcd for $C_{26}H_{23}SSb$: C, 63.82; H, 4.74. Found: C, 63.93; H, 4.86.

Synthesis of 20. To a solution of thiophenol (0.31 mL, 3 mmol) in methanol (3 mL) was added sodium methoxide (194 mg, 3.6 mmol) at room temperature, and the mixture was stirred for 30 min. To this solution thus obtained was added dropwise a suspension of diphenylchlorarsine[13c] (3 mmol), prepared from phenylmagnesium chloride (6 mmol) and arsenic(III) chloride (3 mmol) in THF (10 mL) by stirring for 2 h at 0 °C, and the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched with brine (10 mL), and the mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (10:1) to give the product.

Diphenyl(phenylthio)arsine (20): colorless solid; yield 49%; mp 39−40 °C (lit.[13b] 40−42 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, t, J = 7.4 Hz), 7.28−7.36 (12H, m), 7.51 (2H, d, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.1, 127.5, 128.4, 128.6, 129.0, 133.7, 137.0, 139.6.

Synthesis of 24. To a solution of thiophenol (6 mmol) in methanol (5 mL) was added sodium methoxide (7.2 mmol) at room temperature, and the mixture was stirred for 30 min. Dichloro(4-methylphenyl)stibine (3 mmol) was prepared by stirring tris(4-methylphenyl)stibine (1 mmol) and antimony(III) chloride (2 mmol) for 5 h at 80 °C under neat conditions. Then, the stibine thus obtained was diluted with diethyl ether (10 mL), and the resulting solution was added dropwise to the solution of sodium thiophenoxide. After the reaction mixture was stirred for 2 h at room temperature, the reaction was quenched with brine (10 mL) and the mixture was extracted with ethyl acetate (10 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was recrystallized from methanol to give **24**.

(4-Methylphenyl)bis(phenylthio)stibine (24): colorless solid; yield 53%; mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 7.18−7.21 (6H, m), 7.26 (2H, d, J = 7.6 Hz), 7.39−7.42 (4H, m), 7.65 (2H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 127.1, 128.9, 130.1, 133.3, 134.5, 134.7, 138.5, 140.1. Anal. Calcd for $C_{19}H_{17}S_2Sb$: C, 52.92; H, 3.97. Found: C, 53.01; H, 3.99.

Reaction of 24 with Benzyne. To a solution of **24** (0.3 mmol) in THF (3 mL) were added benzyne precursor **2** (0.9 mmol), KF (1.8 mmol), and 18-crown-6 (1.8 mmol) at 0 °C under argon. The reaction mixture was allowed to react at this temperature for 1 h and then at room temperature for 29 h. The reaction was quenched with brine (5 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give **25**.

(4-Methylphenyl)bis[2-(phenylthio)phenyl]stibine (25): colorless solid; yield 51%; mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (3H, s), 7.07−7.11 (8H, m), 7.14−7.16 (6H, m), 7.19 (2H, dt, J = 1.2, 7.4 Hz), 7.24 (2H, d, J = 7.6 Hz), 7.30 (2H, dt, J = 1.2, 7.4 Hz), 7.48 (2H, dd, J = 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 126.1, 128.8, 128.9 (×2), 129.7, 129.8, 134.6, 136.3, 136.5, 136.8, 137.5, 138.1, 141.1, 148.1. Anal. Calcd for $C_{31}H_{25}S_2Sb$: C, 63.82; H, 4.32. Found: C, 63.86; H, 4.37.

Coupling Reaction. To a solution of **5a** (0.1 mmol) or **15a** (0.1 mmol) in DMSO (2 mL) were added Pd(dppf)Cl_2 (3 mol %) and CsF (0.75 mmol) at 120 °C under argon. The mixture was stirred for 20 h (in the case of **5a**) or 10 h (in the case of **15a**) at this temperature. The reaction was quenched with water (5 mL) after being cooled to room temperature, and then the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−ethyl acetate (15:1) to give dibenzothiophene.

Dibenzothiophene: colorless solid; yield 81% from **5a** and 54% from **15a**; mp 99−100 °C (lit.[16b] 100−102 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.49 (4H, m), 7.84−7.89 (2H, m), 8.15−8.19 (2H, m).

X-ray Crystallography. All measurements were made with a Rigaku Mercury CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of −100 ± 1 °C to a maximum 2θ value of 55.0°. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and not refined. All calculations were performed using the CrystalStructure crystallographic software package. Details of crystal data, data collection summary, and refinement parameters of compound **5a** are given in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information. Crystal data for compound **5a** and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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