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A NEW PREPARATIVE METHOD OF ARYL SULFONATE ESTERS BY USING CYCLIC ORGANOBISMUTH REAGENTS

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Dedicated to Prof. Dr. Ekkehard Winterfeldt on the occasion of his 75th birthday

Abstract – A new method for the preparation of aryl sulfonate esters by using a cyclic pentavalent bismuth is described. Aryl sulfonate esters are formed in good to high yields by treating 10-arylphenothiabismine 5,5-dioxides, *m*-chloroperoxybenzoic acid (*m*-CPBA) and various sulfonic acids in dichloromethane.

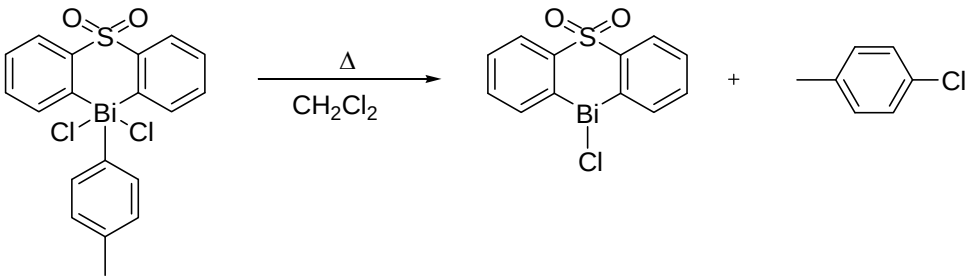
INTRODUCTION

Syntheses and reactions of organobismuth reagents were intensively studied by Barton et al. in 1980−90,[1] and in recent years, pentavalent organobismuth reagents are reported effective for N-arylation of pyridin-2(1*H*)-ones,[2] O-phenylation of tertiary alcohols[3] and oxidative coupling reaction of carbonyl compounds[4] from our laboratory. Among these reactions, a ligand coupling reaction of pentavalent organobismuth reagents is a very fundamental one, for example aryl halides or acetates were obtained by the ligand coupling of triaryl bismuth dihalides or diacetates (Scheme 1).[5] On the other hand, Suzuki et al. also reported that the cyclic pentavalent bismuth dichloride such as 10-dichloro-10-(4'-methylphenyl)phenothia-10$^{\lambda}$5-bismine 5,5-dioxide is quite unstable for refluxing CH_2Cl_2 to give 4-chlorotoluene quantitatively via reductive elimination whereas cyclic bismuth part remained unchanged (Scheme 2).[6] Although there are hardly any ligand coupling reactions of pentavalent bismuth disulfonates reported, an example of a coupling reaction of cyclic pentavalent organobismuth ditosylates in situ to form aryl tosylates was very recently reported from our laboratory.[7]

Aryl sulfonate esters are ubiquitous in the field of organic synthesis and are very attractive both as the protected phenolic hydroxyl group[8] and as the key intermediates of various synthetic reactions. For example, aryl triflates are often used in transition-metal-catalyzed cross-coupling reactions and alkoxycarbonylation,[9] and even tosylates or mesylates are recently shown to be applicable to those reactions.[10]

Aryl sulfonate esters are prepared generally by treating phenols with the corresponding sulfonyl chlorides or sulfonic anhydrides in the presence of organic bases such as pyridine or triethylamine.[11] It is also known that aryl triflates or mesylates are prepared after thermal decomposition of arenediazonium salts in the corresponding sulfonic acids.[12] However, these aryl triflates or mesylates were obtained by the reaction carried out in a sulfonic acids solvent under harsh reaction conditions. To the best of our knowledge, no general procedures for preparing the aryl arenesulfonates by using the corresponding sulfonic acids have been reported yet. In this paper, we would like to describe the extended scope and limitation of the present synthetic method.

Scheme 1



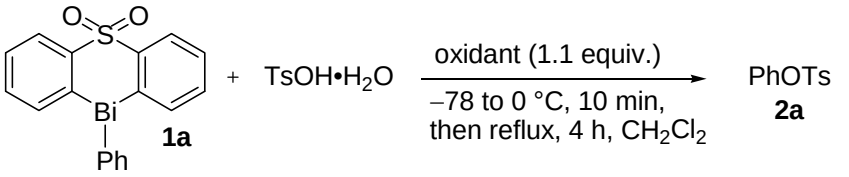
Scheme 2

RESULTS AND DISCUSSION

In the first place, the effects of oxidants and reaction conditions were examined. A model reaction was carried out by using 10-phenylphenothiabismine 5,5-dioxide (**1a**) and 1.1 equiv. of oxidants in the presence of *p*-toluenesulfonic acid in CH_2Cl_2, whose results are summarized in Table 1. When *tert*-butyl hydroperoxide or benzoyl peroxide was used as an oxidant, the expected phenyl tosylate was not obtained (Entries 1 and 2). On the other hand, the desired phenyl tosylate was obtained in 49 or 87% yields respectively when an oxidant such as peracetic acid or *m*-CPBA was used (Entries 3 and 4) and the reaction proceeded sluggishly at room temperature (Entry 5). When the amount of $TsOH \cdot H_2O$ was reduced to 1.1 equiv., the yield of **2a** decreased to 63% yield (Entry 6). Therefore, it was found that the

amount of $TsOH \cdot H_2O$ should be needed more than 2 equiv., and the best result was obtained when 2.8 equiv. of $TsOH \cdot H_2O$ was used (Entry 7). On the other hand, **2a** was not obtained at all when sodium *p*-toluenesulfonate was used (Entry 8).

Table 1. Reactions of **1a** with various oxidants



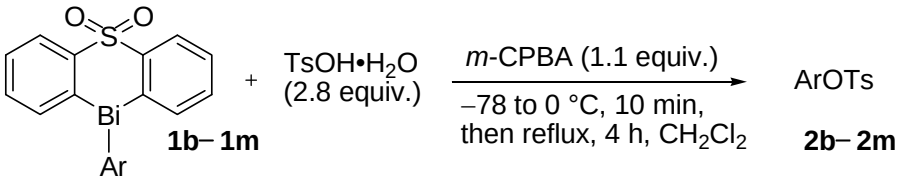
Entry	Equiv. of $TsOH \cdot H_2O$	Oxidant	Yield / %
1	2.2	^{t}BuOOH	ND[b]
2	2.2	$(PhCOO)_2$	ND
3	2.2	CH_3COOOH	49
4	2.2	*m*-CPBA	87
5[a]	2.2	*m*-CPBA	48
6	1.1	*m*-CPBA	63
7	2.8	*m*-CPBA	91
8	2.8[c]	*m*-CPBA	ND

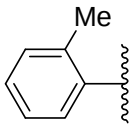
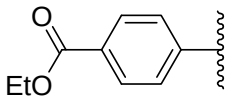
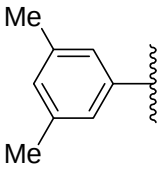
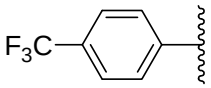
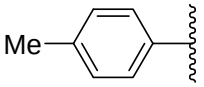
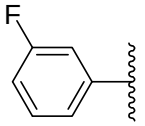
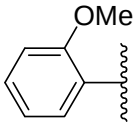
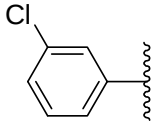
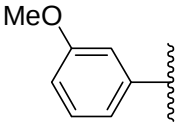
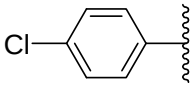
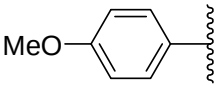
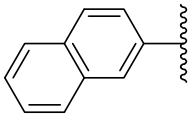
[a]Reaction was carried out at rt for 30 h. [b]Not Detected.
[c]Sodium *p*-toluenesulfonate was used.

Various aryl tosylates were prepared next by using the corresponding 10-arylphenothiabismine 5,5-dioxides under optimized conditions and the results are summarized in Table 2. Trivalent bismuth compounds (**1b**−**1m**) were synthesized by way of substitution reaction of aryl Grignard reagents with 10-iodophenothiabismine 5,5-dioxide. Bismuth compounds, **1b**−**1d**, having methylphenyl groups gave the corresponding aryl tosylates over 80% yields regardless of the substituents' position (Entries 1−3). In the cases of bismuth compounds, **1e**−**1g**, having methoxyphenyl groups, *m*-methoxyphenyl bismuth (**1f**) gave *m*-methoxyphenyl tosylate in 85% yield (Entry 5). However, those with *o*- and *p*-methoxyphenyl groups (**1e** and **1g**) gave *o*-methoxyphenyl tosylate in 5% and *p*-methoxyphenyl tosylate in 32% yields respectively. It was assumed that the intramolecular coordination of oxygen atom of *o*-methoxy group in particular retarded the ligand coupling reaction.[13] When the reaction was tried in refluxing $CHCl_3$, *o*-methoxyphenyl tosylate and *p*-methoxyphenyl tosylate were obtained in 52 and 76% yields, respectively. These increases in the yields were caused by the reaction temperature in $CHCl_3$ that was higher than CH_2Cl_2 (Entries 4 and 6). On the other hand, electron-poor aryl groups having ethoxycarbonyl, trifluoromethyl or halide substituents were tolerated to afford the expected aryl tosylates (**2h**−**2l**) in moderate to good yields (Entries 7−11), and 2-naphthyl tosylate (**2m**) was also obtained in 86% yield (Entry 12). In addition, it was found that the alkylbismuth derivative such as

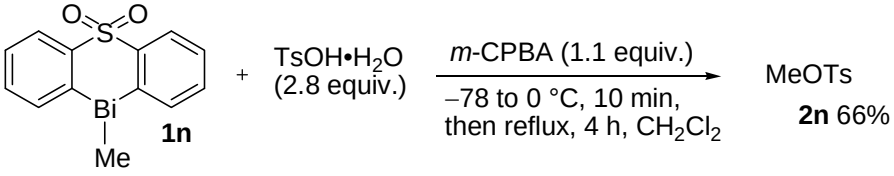
10-methylphenothiabismine 5,5-dioxide (**1n**) gave methyl tosylate in moderate yield under these conditions (Scheme 3).

Table 2. Synthesis of aryl tosylates by using optimized conditions



Entry		Ar	Product	Yield / %[a]	Entry		Ar	Product	Yield / %[a]
1	**1b**		**2b**	81	7	**1h**		**2h**	76
2	**1c**		**2c**	88	8[b]	**1i**		**2i**	79
3	**1d**		**2d**	83	9[b]	**1j**		**2j**	72
4[b]	**1e**		**2e**	5(52[c])	10[b]	**1k**		**2k**	73
5	**1f**		**2f**	85	11[b]	**1l**		**2l**	53
6[b]	**1g**		**2g**	32(76[c])	12	**1m**		**2m**	86

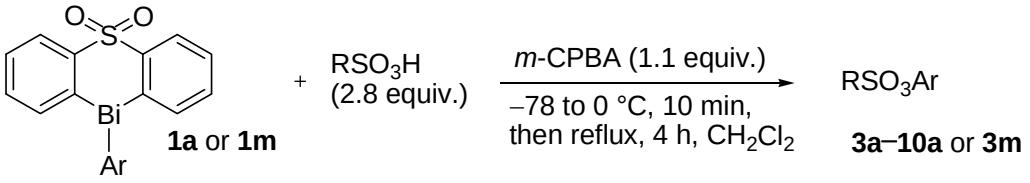
[a]Isolated yield. [b]Reflux for 8–12 h. [c]$CHCl_3$ was used as a solvent (see experimental section for detailed procedure).

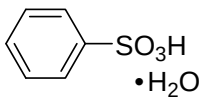
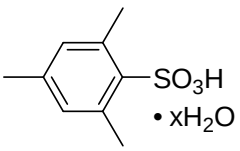
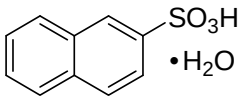
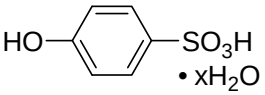
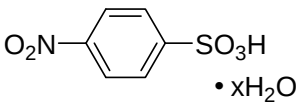
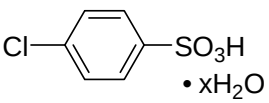


Scheme 3

In order to examine the generality of this reaction, various sulfonic acids were employed next by using 10-phenylphenothiabismine 5,5-dioxide (**1a**) or 10-(2-naphthyl)phenothiabismine 5,5-dioxide (**1m**) under optimized conditions (Table 3). Unsubstituted aromatic sulfonic acids such as benzenesulfonic acid or 2-naphthalenesulfonic acid and those having electron withdrawing substituents such as 4-nitro or 4-chloro group are applicable to this reaction to afford the desired phenyl sulfonate esters in good yields (Entries 1−4). Moreover, the aromatic sulfonic acid having bulky electron donating substituent such as 2,4,6-trimethyl group gave the expected sulfonate ester in sufficient yield (Entry 5). Although a phenyl sulfonate ester having a free phenolic hydroxyl group (**8a**) is considered to be difficult to synthesize by the conventional methods, the desired **8a** was obtained in moderate yields by this method (Entry 6). With respect to alkyl sulfonic acids, methane or ethanesulfonic acid gave the corresponding phenyl sulfonate esters in good yields while trifluoromethanesulfonic acid gave expected 2-naphthyl triflate in moderate yield due to an undesirable decomposition of bismuth compound by TfOH (Entries 7−9).

Table 3. Synthesis of aryl sulfonate esters



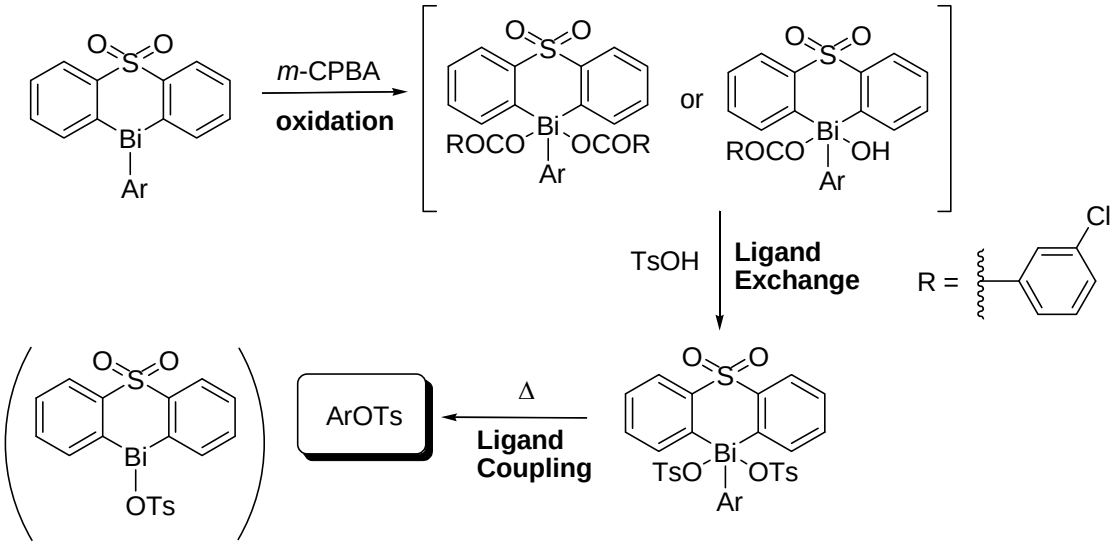
Entry	RSO_3H	Product	Yield / %[a]	Entry	RSO_3H	Product	Yield / %[a]
1		**3a**	86	5		**7a**	80
2		**4a**	83	6[b]		**8a**	48
3		**5a**	79	7	$MeSO_3H$	**9a**	89
				8	$EtSO_3H$	**10a**	84
4		**6a**	89	9	CF_3SO_3H	**3m**	50

[a]Isolated yield. [b]Reflux 8 h

3a–**10a**; Ar = Ph, **3m**; Ar = 2-naphthyl

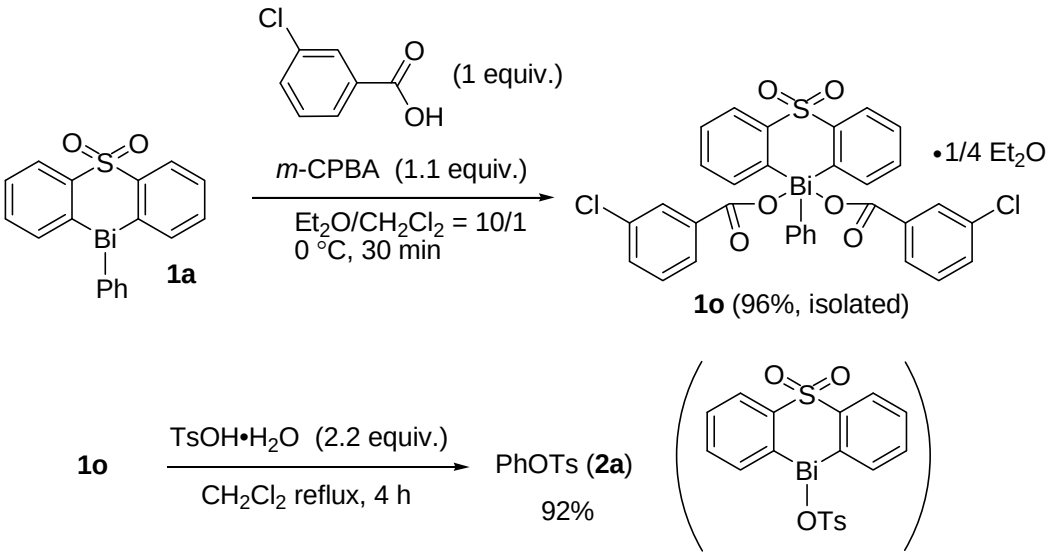
The mechanism of this reaction and the reactivity of bismuth compounds are shown below. The reaction started with the oxidation of trivalent bismuth by *m*-CPBA to form the corresponding pentavalent bismuth dicarboxylate or hydroxy-carboxylate, and then the ligands were exchanged for sulfonic acids to afford

pentavalent bismuth disulfonate. Finally, aryl sulfonate esters were formed by lingand coupling reaction of the disulfonates (Scheme 4).



Scheme 4. Plausible mechanism for the formation of the aryl sulfonate esters.

In order to clarify this mechanism, isolation of pentavalent bismuth compounds was tried, and the pentavalent bismuth dicarboxylate (**1o**) was isolated as 1/4 etherate. Preparation of phenyl tosylate was additionally demonstrated by using **1o** and $TsOH \cdot H_2O$ in CH_2Cl_2, and PhOTs was obtained in 92% yield (Scheme 5). Although the trivalent bismuth tosylate was not isolated in this reaction, PhOTs was apparently formed by the ligand coupling reaction of the pentavalent bismuth ditosylate since the exchange of ligands from carboxylate to sulfonate would take place easily in the reaction of sulfonic acids

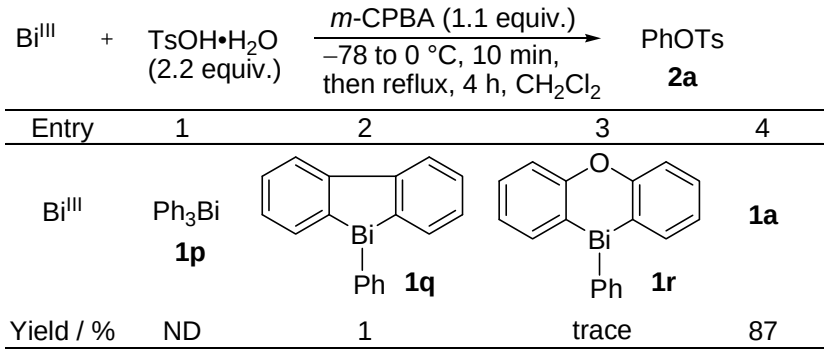


Scheme 5

and pentavalent bismuth dicarboxylate.[1g,14] Thus, it was almost proved that formation of aryl sulfonate esters by using cyclic organobismuth compounds proceeded as described in Scheme 4.

Further, it is very interesting to note that the cyclic bismuth compound having sulfone functionality gave aryl sulfonate esters exclusively (see Table 4). When the reactions were carried out by using other bismuth compounds such as triphenylbismuthane (**1p**), phenylbiphenyl-2,2'-ylenebismuthane (**1q**) or 10-phenylphenoxabismine (**1r**), the expected phenyl tosylate was hardly obtained under in any of the three cases (Entries 1−3). Concerning these three bismuth compounds, it was therefore assumed that the key step of the final ligand coupling did not proceed effectively though the oxidation with *m*-CPBA and subsequent ligand exchange that formed their disulfonate took place. This unique reactivity of **1a** might be caused by transannular interaction of **1a** between bismuth and the sulfonyl oxygen atom as was indicated by Suzuki's group.[6]

Table 4. Effect of organobismuth reagents



Entry	1	2	3	4
Bi^{III}	Ph_3Bi **1p**	**1q**	**1r**	**1a**
Yield / %	ND	1	trace	87

In conclusion, a synthesis of aryl sulfonate esters by using a novel ligand coupling between aryl group and sulfonyloxy group on the pentavalent bismuth reagents was established. It was easy to carry out these reactions since there was no need to isolate the less stable pentavalent bismuth reagents compared with trivalent ones which are able to be purified regardless of temperature and moisture. Further, this coupling reaction is considered as an alternative of the conventional method for preparing aryl sulfonate esters because no preparations of sulfonyl chlorides and phenols in advance are needed. In regard to organobismuth chemistry, it is interesting to note that the transannular interaction between bismuth and the sulfonyl oxygen atom of 10-arylphenothiabismine 5,5-dioxides brought about extremely unique ligand coupling reaction and that the cyclic pentavalent bismuth dicarboxylate (**1o**) was isolated in high yield for the first time.

EXPERIMENTAL

General.

Melting points were measured on a micro melting point apparatus (Yanaco MP-S3) and remain

uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer (KBr or neat) or a Thermo Electron Nicolet Avatar 370 spectrometer (ATR). ^{1}H NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz) spectrometer. Chemical shifts (δ_H) in $CDCl_3$ are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts (δ_C) in $CDCl_3$ are reported in ppm relative to TMS using the solvent resonance ($CDCl_3$: δ_C 77.0 ppm) as an internal standard. HRMS spectra were recorded on a JEOL JMS-700V (EI positive) and Agilent 6890 series GC system. Analytical TLC was performed on Merck TLC plates coated with silica gel (60 F_{254}, 0.25 mm). Preparative TLC was carried out on glass plates coated with silica gel (Wakogel B-5F). Anhydrous THF, Et_2O, CH_2Cl_2, $CHCl_3$ were purchased from Kanto Chemical Co., Inc.. Other solvents were distilled after dehydrated by using appropriate drying agents. *m*-CPBA (contents > 65 %, remainder 3-chloro benzoic acid and water) and Ph_3Bi were purchased from Tokyo Kasei Kogyo (TCI) and used without further purification. Hydrate formed sulfonic acids were also purchased from TCI, and used without further purification. Commercially available bismuth (III) chloride was activated by refluxing with thionyl dichloride before use. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical Co., Inc., Wako Pure Chemical Industry or Aldrich.

Preparation of organobismuth(III) reagents.

Organobismuth reagents such as 10-arylphenothiabismine 5,5-dioxides (**1a**−**1m**), 10-methylphenothiabismine (**1n**), phenylbiphenyl-2,2'-ylenebismuthane (**1q**) and 10-phenylphenoxabismine (**1r**) were prepared by modified method of the reported procedures, and described below in detail. All the new organobismuth reagents were identified by elemental analysis.

10-Phenylphenothiabismine 5,5-dioxide (1a)[11]

Dichlorophenylbismuthine (16.1 g, 45 mmol) was prepared as insoluble precipitate by the reaction of triphenylbismuthine (6.6 g, 15 mmol) and bismuth (III) chloride (9.5 g, 30 mmol) in Et_2O (50 mL) for 2 h at rt, and 100 mL of THF was added just before proceeding next step. To a solution of 2,2'-dilithiodiphenyl sulfone generated from diphenyl sulfone (9.8 g, 45 mmol) and *n*-butyllithium (36 mL of 2.6 M in hexane, 95 mmol) in Et_2O (450 mL) was added dropwise a homogeneous solution of dichlorophenylbismuthine in Et_2O/THF (150 mL, 50/100) at −78 °C, and resulting mixture was stirred for overnight, during which time the temperature was gradually raised to rt. The reaction mixture was quenched with cold water, and AcOEt was added. Upper organic layer was separated, and concentrated under reduced pressure to leave oily residue, and aqueous layer was extracted with CH_2Cl_2 (3 times). Combined CH_2Cl_2 layer was mixed with that oily residue, then washed with water and brine, dried with

$MgSO_4$, and filtered through Celite. The filtrate was concentrated, and purified by column chromatography (silica gel, hexane/AcOEt = 10/1 to 4/1) to afford almost pure product, and washed with hot EtOH to afford pure product **1a** as white solid (10.5 g, 46%).

IR (ATR, cm^{-1}) 1297, 1286, 1149, 1087, 1074, 766 ,742, 726, 719, 692; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.38 (d, J = 7.3 Hz, 2H), 7.86 (d, J = 7.0 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.45−7.31 (m, 7H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 165.3, 158.3, 141.4, 138.4, 137.3, 133.2, 130.6, 128.3, 127.9, 126.8.

10-Iodophenothiabismine 5,5-dioxide[11]

To a solution of compound **1a** (12.5 g, 25.0 mmol) in Et_2O (100 mL) was added dropwise Et_2O solution (120 mL) of I_2 (6.6 g, 26.3 mmol), and resulting mixture stirred for 1 h at rt. Yellow powder was filtered off, washed with CH_2Cl_2 and Et_2O to afford 10-iodophenothiabismine 5,5-dioxide as yellow solid (12.7 g, 92%).

IR (ATR, cm^{-1}) 1287, 1250, 1136, 1114, 1084, 1086, 1008, 754, 739, 713, 700; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 9.22 (d, J = 7.3 Hz, 2H), 8.30 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 163.5, 140.2, 139.9, 135.8, 128.6, 127.5.

10-(2-Methylphenyl)phenothiabismine 5,5-dioxide (**1b**)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 2-methylphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred 3 h, during which time the temperature was gradually raised to rt. The reaction mixture was quenched with cold water and THF was removed under reduced pressure, and aqueous layer was extracted with CH_2Cl_2 (3 times). Combined organic layer was washed with water and brine, dried with $MgSO_4$ and concentrated to leave crude solid, which was recrystallized from AcOEt/hexane to afford **1b** as white solid (990 mg, 77%).

mp 239−241 ºC; IR (ATR, cm^{-1}) 1300, 1287, 1151, 1134, 1118, 1088, 1074, 767, 739, 713; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.37 (dd, J = 7.6 , 1.1 Hz, 2H), 7.87 (d, J = 7.0 Hz, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.45−7.30 (m, 6H), 7.06 (t, J = 7.3 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 166.9, 157.6, 144.2, 141.5, 140.9, 137.7, 133.2, 130.2, 129.2, 128.7, 128.1, 126.9, 26.5; Anal. Calcd for $C_{19}H_{15}BiO_2S$: C, 44.19; H, 2.93%. Found: C, 44.10; H, 2.83%.

10-(3,5-Dimethylphenyl)phenothiabismine 5,5-dioxide (**1c**)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 3,5-dimethylphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1c** as white solid (745 mg, 56%).

mp 248−249 ºC; IR (ATR, cm^{-1}) 1285, 1249, 1140, 1124, 1086, 1073, 836, 758, 739, 714, 704, 688; ^{1}H

NMR (270 MHz, $CDCl_3$) δ = 8.38 (dd, J = 7.6, 1.9 Hz, 2H), 7.88 (dd, J = 7.0 , 1.4 Hz, 2H), 7.43−7.31 (m, 6H), 7.00 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 165.0, 158.2, 141.5, 140.0, 137.5, 135.9, 133.2, 130.3, 128.0, 126.9, 21.5; Anal. Calcd for $C_{20}H_{17}BiO_2S$: C, 45.29; H, 3.23%. Found: C, 45.19; H, 3.26%.

10-(4-Methylphenyl)phenothiabismine 5,5-dioxide (1d)[11]

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 4-methylphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1d** as white solid (798 mg, 62%).

IR (ATR, cm^{-1}) 1438, 1295, 1284, 1149, 1121, 1105, 1085, 1074, 789, 763, 739, 716; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.37 (dd, J = 1.6, 7.6 Hz, 2H), 7.87 (dd, J = 1.6, 7.3 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H), 7.40 (td, J = 7.6, 1.6 Hz, 2H), 7.33 (td, J = 7.6, 1.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 162.0, 158.1, 141.4, 138.5, 138.3, 137.3, 133.1, 131.5, 127.9, 126.8, 21.6.

10-(2-Methoxyphenyl)phenothiabismine 5,5-dioxide (1e)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 2-methoxyphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1e** as white solid (870 mg, 65%).

mp 173−177 ºC; IR (ATR, cm^{-1}) 1567, 1424, 1286, 1233, 1150, 1117, 1048, 1021, 755, 738, 713; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.35 (dd, J =1.9, 7.3 Hz, 2H), 7.90 (dd, J =1.9, 7.0 Hz, 2H), 7.55 (dd, J = 1.6, 7.3 Hz, 1H), 7.41−7.30 (m, 5H), 7.17 (d, J = 8.1 Hz, 1H), 6.89 (t, J = 7.3 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 162.2, 157.7, 152.6, 141.6, 139.3, 137.5, 132.9, 129.9, 127.7, 126.7, 124.7, 109.9, 55.6; Anal. Calcd for $C_{20}H_{17}BiO_2S$: C, 42.87; H, 2.84%. Found: C, 42.81; H, 2.77%.

10-(3-Methoxyphenyl)phenothiabismine 5,5-dioxide (1f)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 3-methoxyphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1f** as white solid (702 mg, 53%).

mp 180−183 ºC; IR (ATR, cm^{-1}) 1579, 1564, 1470, 1298, 1283, 1241, 1226, 1148, 1120, 1087, 1072, 1029, 762, 739, 715; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.38 (d, J = 7.3 Hz, 2H), 7.89 (d, J = 6.5 Hz, 2H), 7.43−7.32 (m, 7H), 6.88 (d, J = 7.9 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 166.2, 161.7,

158.5, 141.5, 137.4, 133.3, 131.7, 130.5, 128.1, 127.0, 124.1, 113.9, 55.2; Anal. Calcd for $C_{20}H_{17}BiO_2S$: C, 42.87; H, 2.84%. Found: C, 42.97; H, 3.06%.

10-(4-Methoxyphenyl)phenothiabismine 5,5-dioxide (1g)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 4-methoxyphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from CH_2Cl_2/hexane to afford **1g** as white solid (989 mg, 74%).

mp 227−230 ºC; IR (ATR, cm^{-1}) 1579, 1564, 1487, 1429, 1283, 1241, 1226, 1148, 808, 764, 739, 716; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.36 (dd, J =1.6, 7.6 Hz, 2H), 7.86 (dd, J =1.6, 7.0 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.42−7.30 (m, 4H), 6.92 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 159.7, 158.2, 156.6, 141.5, 140.1, 137.4, 133.2, 128.0, 126.8, 116.6, 55.1; Anal. Calcd for $C_{20}H_{17}BiO_2S$: C, 42.87; H, 2.84%. Found: C, 42.55; H, 2.68%.

10-(4-Ethoxycarbonylphenyl)phenothiabismine 5,5-dioxide (1h)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 4-ethoxycarbonylphenylmagnesium bromide (prepared by method B). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1h** as white solid (517 mg, 36%).

mp 183−186 ºC; IR (ATR, cm^{-1}) 1171, 1583, 1384, 1305, 1279, 1179, 1151, 1101, 1088, 1050, 1010, 842, 739, 714; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.39 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H), 7.84 (t, J = 7.3 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.0 Hz, 2H), 4.37 (q, J = 7.3 Hz, 2H), 1.38 (t, J = 7.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 171.3, 166.4, 158.6, 141.4, 138.5, 137.2, 133.4, 131.1, 130.3, 128.1, 127.0, 61.0, 14.3; Anal. Calcd for $C_{21}H_{17}BiO_4S$: C, 43.91; H, 2.98%. Found: C, 43.88; H, 3.12%.

10-(4-Trifluoromethylphenyl)phenothiabismine 5,5-dioxide (1i)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 4-trifluoromethylphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from Et_2O/hexane to afford **1i** as white solid (751 mg, 53%).

mp 187−190 ºC; IR (ATR, cm^{-1}) 1592, 1387, 1322, 1304, 1283, 1152, 1114, 1073, 1040, 1008, 823, 760, 739, 715, 673; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.40 (dd J = 7.6, 1.6 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.83 (dd, J = 7.6, 1.6 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.47−7.34 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 169.7, 158.7, 141.4, 138.9, 137.2, 133.5, 130.3 (q, $J_{C\text{-}C\text{-}F}$ = 39 Hz), 128.2, 127.1, 127.0 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4 Hz), 124.0 (q, $J_{C\text{-}F}$ = 271 Hz); Anal. Calcd for $C_{19}H_{12}BiF_3O_2S$: C, 40.01; H, 2.12%. Found: C, 39.8; H,

2.18%.

10-(3-Fluorophenyl)phenothiabismine 5,5-dioxide (1j)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 3-fluorophenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1j** as white solid (911 mg, 70%).

mp 193−195 ºC; IR (ATR, cm^{-1}) 1573, 1409, 1297, 1254, 1198, 1151, 1086, 785, 768, 741, 717, 681; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.39 (dd, J = 7.6, 2.2 Hz, 2H), 7.86 (dd, J = 6.8, 1.4 Hz, 2H), 7.56 (d, J = 7.3 Hz, 1H), 7.51−7.34 (m, 6H), 7.02 (td, J = 8.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 166.8, 165.2 (d, $J_{C\text{-}F}$ = 252 Hz), 158.6, 141.3, 137.2, 133.7 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3 Hz), 133.4, 131.9 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6 Hz), 128.1, 127.0, 125.1 (d, $J_{C\text{-}C\text{-}F}$ = 19 Hz), 115.6 (d, $J_{C\text{-}C\text{-}F}$ = 20 Hz); Anal. Calcd for $C_{18}H_{12}BiFO_2S$: C, 41.55; H, 2.32%. Found: C, 41.48; H, 2.24%.

10-(3-Chlorophenyl)phenothiabismine 5,5-dioxide (1k)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0°C was added dropwise a solution of 3-chlorophenylmagnesium bromide (prepared by method B). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1k** as white solid (577 mg, 43%).

mp 212−215 ºC; IR (ATR, cm^{-1}) 1564, 1426, 1285, 1249, 1149, 1086, 1073, 1014, 836, 758, 739, 714, 688; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.39 (dd, J = 7.3, 1.6 Hz, 2H), 7.86 (dd, J = 6.8, 1.1 Hz, 2H), 7.77 (s, 1H), 7.61 (d, J = 7.3 Hz, 1H), 7.46−7.30 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 166.6, 158.8, 141.4, 138.0, 137.4, 137.3, 136.4, 133.5, 132.0, 128.7, 128.3, 127.2; Anal. Calcd for $C_{19}H_{12}BiClO_2S$: C, 40.28; H, 2.25%. Found: C, 40.10; H, 2.08%.

10-(4-Chlorophenyl)phenothiabismine 5,5-dioxide (1l)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 4-chlorophenylmagnesium bromide (prepared by method B). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1l** as white solid (638 mg, 48%).

mp 209−211 ºC; IR (ATR, cm^{-1}) 1557, 1470, 1429, 1377, 1299, 1287, 1151, 1087, 766, 740, 715; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.38 (d, J = 7.0 Hz, 2H), 7.85 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.44−7.34 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 163.4, 158.6, 141.5, 140.1, 137.3, 134.7, 133.4, 130.9, 128.2, 127.1; Anal. Calcd for $C_{19}H_{12}BiClO_2S$: C, 40.28; H, 2.25%. Found: C, 40.15; H, 2.41%.

10-(2-Naphthyl)phenothiabismine 5,5-dioxide (**1m**)

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of 2-naphtylphenylmagnesium bromide (prepared by method A). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from CH_2Cl_2/hexane to afford **1m** as white solid (785 mg, 57%).

mp 230−233 ºC; IR (ATR, cm^{-1}) 1564, 1284, 1250, 1149, 1107, 1087, 1072, 1013, 860, 814, 762, 742, 715; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.43−8.39 (m, 3H), 7.86 (dd, J = 7.3, 1.1 Hz, 2H), 7.82−7.77 (m, 3H), 7.62 (dd, J = 8.1, 1.1 Hz, 1H), 7.57−7.47 (m, 2H), 7.41 (td, J = 7.3, 1.1 Hz, 2H) 7.31 (td, J = 7.6, 1.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 162.8, 158.3, 141.6, 138.3, 137.5, 135.6, 134.8, 133.3, 133.0, 130.5, 128.1, 127.9, 127.6, 127.0, 126.4, 126.3; Anal. Calcd for $C_{22}H_{15}BiO_2S$: C, 47.83; H, 2.74%. Found: C, 47.51; H, 2.85%.

10-Methylphenothiabismine 5,5-dioxide (**1n**)[11]

To a suspension of 10-iodophenothiabismine 5,5-dioxide (1.38 g, 2.5 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of methylmagnesium bromide (3 mL, ca. 1 mol/l in THF solution). Resulting mixture was stirred overnight, during which time the temperature was gradually raised to rt. Usual work-up, and crude solid was recrystallized from AcOEt/hexane to afford **1n** as white solid (610 mg, 55%).

IR (ATR, cm^{-1}) 1560, 1428, 1290, 1144, 1072, 1014, 764, 717; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.30 (dd, J = 7.0, 1.6 Hz, 2H), 8.04 (dd, J = 7.0, 1.6 Hz, 2H), 7.45−7.34 (m, 4H), 1.41 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 150.6, 141.4, 136.2, 132.9, 128.0, 126.7, 19.7.

Preparation of Grignard reagent.

Method A: To a solution of Mg turnings (73 mg, 0.3 mmol) in THF (2.5 mL) was added ArBr (2. 75 mmol). When the reaction started, the temperature was raised and the color of solution was changed to black, and the mixture was stirred until the solution was cooled to rt.

Method B: To a solution of ArI (2. 75 mmol) in THF (7.5 mL) was added isopropyl magnesium bromide (3.3 mL, ca. 1 mol/l in THF solution) at −45 to −35 ºC, and stirred at −45 to −35 ºC for 1 h.

Phenylbiphenyl-2,2'-ylenebismuthane (**1q**)[15]

To a solution of 2,2'-dilithiodiphenyl−TMEDA (TMEDA = *N*,*N*,*N*,*N*-tetramethylethylenediamine) generated from biphenyl (6.17 g, 40 mmol), TMEDA (13.3 ml, 88 mmol) and *n*-butyllithium (34 mL of 2.6 M in hexane, 88 mmol) was added dropwise a solution of dichlorophenylbismuthine (16.1 g, 45 mmol, as described above) at −78 °C, and resulting mixture was stirred for overnight, during which time the

temperature was gradually raised to rt. The reaction mixture was quenched with cold water, and AcOEt was added. Upper organic layer was separated, and concentrated under reduced pressure to leave oily residue. Aqueous layer was extracted with CH_2Cl_2 (3 times). Combined CH_2Cl_2 layer was mixed with that oily residue, then washed with water and brine, dried with $MgSO_4$, and filtered through Celite. The filtrate was concentrated, and purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 10/1 to 4/1) to afford almost pure product. The crude solid was washed with hot EtOH, and recrystallized from AcOEt/hexane to afford **1q** as white solid (5.34 g, 30%).

IR (ATR, cm^{-1}) 3049, 1564, 1425, 742, 726; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.6 Hz, 2H), 7.75−7.67 (m, 4H), 7.43−7.36 (m, 4H), 7.19−7.15 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 163.6, 157.8, 152.0, 137.1, 136.8, 130.0, 128.2, 127.6, 127.2, 126.3.

10-Phenylphenoxabismine (1r)[11]

To a solution of 2,2'-dilithiodiphenylether generated from diphenyl ether (3.57 g, 21 mmol) and *n*-butyllithium (17.8 mL of 2.6 M in hexane, 46 mmol) in Et_2O/THF (200 mL, 110/90) was added dropwise a solution of dichlorophenylbismuthine (7.5 g, 21 mmol, as described above) at −78 °C, and resulting mixture was stirred for overnight, during which time the temperature was gradually raised to rt. The reaction mixture was quenched with cold water, and AcOEt was added. Upper organic layer was separated, and aqueous layer was extracted with AcOEt (2 times). Combined AcOEt layer was washed with water and brine, dried with $MgSO_4$, and filtered through Celite. The filtrate was concentrated, and purified by column chromatography (silica gel, hexane/AcOEt = 10/1) to afford almost pure product. The crude solid was recrystallized from AcOEt-hexane to afford **1r** as white solid (1.5 g, 16%).

IR (ATR, cm^{-1}) 3051, 1568, 1421, 1259, 1207, 1108, 872, 792, 754, 694; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.81−7.74 (m, 4H), 7.63 (d, J = 8.1 Hz, 2H), 7.31−7.22 (m, 5H), 7.07 (t, J = 7.0 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 156.9, 152.3, 137.5, 137.1, 134.2, 130.2, 130.1, 127.7, 125.4, 119.4; Anal. Calcd for $C_{18}H_{13}BiO$: C, 47.59; H, 2.88%. Found: C, 47.44; H, 2.89%.

Typical procedure for the formation of phenyl tosylate (2a)

To a solution of *m*-CPBA (65% content, 87.6 mg, 0.33 mmol) and $TsOH·H_2O$ (159.8 mg, 0.84 mmol) in CH_2Cl_2 (2 mL) was added **1a** at −78 °C (when the reaction was carried out in $CHCl_3$, initial bath temperature was maintained at −55 to −60 °C). The resulting mixture was stirred in an ice-water bath for 10 min. The color of the solution changed to yellow during this time. Following that, reaction mixture was stirred under reflux for 4 h. After CH_2Cl_2 was removed from the reaction mixture under reduced pressure, then Et_2O was added, and the precipitate was filtered off. The filtrate was dried with $MgSO_4$, filtered and concentrated. The resulting residue was purified by preparative TLC (silica gel, hexane/CH_2Cl_2 = 1/1) to afford the desired phenyl tosylate **2a** as white solid.

Phenyl tosylate (**2a**)[4b]: White solid; IR (ATR, cm^{-1}) 1486, 1373, 1195, 1171, 1147, 1091, 855, 815, 804, 775, 724, 687, 657; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.1 Hz, 2H), 7.31−7.20 (m, 5H), 6.98 (dd, J = 8.1, 1.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.5, 145.2, 132.2, 129.6, 129.5, 128.4, 126.9, 122.3, 21.8.

2-Methylphenyl tosylate (**2b**)[4b]: White solid; IR (ATR, cm^{-1}) 1371, 1193, 1179, 1153, 1088, 871, 786, 777, 731, 710, 699, 659; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.73 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.15−7.08 (m, 3H), 7.00−6.97 (m, 1H), 2.45 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 148.2, 145.1, 133.0, 131.4(131.44), 131.4(131.41), 129.6, 128.2, 126.8, 126.7, 122.2, 21.8, 16.3.

3,5-Dimethylphenyl tosylate (**2c**)[16]: White solid; IR (ATR, cm^{-1}) 1593, 1368, 1188, 1176, 1123, 1093, 1018, 942, 854, 806, 770, 668; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 6.60 (s, 2H), 2.45 (s, 3H), 2.23 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.3, 145.0, 139.3, 132.6, 129.5, 128.6, 128.4, 119.7, 21.7, 21.2; HRMS (EI positive) Calcd. for $C_{15}H_{16}O_3S$: $[M+\cdot]^+$ 276.0820, Found: m/z 276.0815.

4-Methylphenyl tosylate (**2d**)[4b]: White solid; IR (ATR, cm^{-1}) 1596, 1503, 1372, 1198, 11174, 1155, 1093, 859, 829, 818, 786, 724, 693, 653; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 147.3, 145.1, 136.8, 132.3, 129.9, 129.6, 128.4, 121.9, 21.7, 20.9;

2-Methoxylphenyl tosylate (**2e**)[17]: Colorless oil; IR (ATR, cm^{-1}) 1600, 1498, 1368, 1258, 1179, 1157, 1090, 866, 758, 659; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.74 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.22−7.12 (m, 2H), 6.90−6.82 (m, 2H), 3.55 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 151.6, 144.8, 138.3, 133.1, 129.2, 128.4, 127.9, 123.9, 120.5, 112.6, 55.5, 21.7; HRMS (EI positive) Calcd. for $C_{14}H_{14}O_4S$: $[M+\cdot]^+$ 278.0613, Found: m/z 278.0613.

3-Methoxylphenyl tosylate (**2f**)[18] : Colorless oil; IR (ATR, cm^{-1}) 1606, 1588, 1485, 1369, 1191, 1177, 1121, 1090, 1039, 939, 926, 803, 786, 718, 684, 661; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.16 (td, J = 7.3, 1.4 Hz, 1H), 6.80−6.76 (m, 1H), 6.56−6.52 (m, 2H), 3.72 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 160.2, 150.3, 145.2, 132.3, 129.7, 129.6, 128.4, 114.2, 112.9, 108.1, 55.4, 21.7; HRMS (EI positive) Calcd. for $C_{14}H_{14}O_4S$: $[M+\cdot]^+$ 278.0613, Found: m/z 278.0610.

4-Methoxylphenyl tosylate (**2g**)[19]: Colorless oil; IR (ATR, cm^{-1}) 1596, 1500, 1368, 1250, 1168, 1092, 837, 786, 695; ^1H NMR (270 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.87 (td, J = 2.2, 9.2 Hz, 2H), 6.76 (td, J = 2.2, 8.9 Hz, 2H), 3.76 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 158, 145.1, 142.9, 132.2, 129.6, 128.4, 123.2, 114.4, 55.6, 21.8; HRMS (EI positive) Calcd. for $C_{14}H_{14}O_4S$: $[M+\cdot]^+$ 278.0613, Found: m/z 278.0615.

Ethyl (4-tosyloxy)benzoate (**2h**)[20]: Colorless oil; IR (ATR, cm^{-1}) 1719, 1371, 1287, 1175, 1154, 1119,

1090, 1021, 866, 839, 814, 774, 731, 692, 667; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 4.36 (q, J = 7.0 Hz, 2H), 2.45 (s, 3H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 165.2, 152.6, 145.5, 131.9, 131.0, 129.7, 129.1, 128.3, 122.1, 61.2, 21.7, 14.3; HRMS (EI positive) Calcd. for $C_{16}H_{16}O_5S$: $[M+\cdot]^+$ 320.0718, Found: m/z 320.0710.

4-Trifluoromethylphenyl tosylate (**2i**)[3d]: White solid; IR (ATR, cm^{-1}) 1378, 1322, 1202, 1175, 1159, 1124, 1102, 1065, 1017, 859, 853, 815, 776, 716, 664; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 151.7, 145.8, 131.8, 129.8, 129.2 (q, $J_{C\text{-}C\text{-}F}$ = 33 Hz), 128.3, 126.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4 Hz) 123.4 (q, $J_{C\text{-}F}$ = 272 Hz), 122.8, 21.7; HRMS (EI positive) Calcd. for $C_{14}H_{11}O_3F_3S$: $[M+\cdot]^+$ 316.0381, Found: m/z 316.0380.

3-Fluorophenyl tosylate (**2j**)[21]: Colorless oil; IR (ATR, cm^{-1}) 1600, 1482, 1373, 1901, 1178, 1111, 1091, 948, 803, 789, 719, 679, 660; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.27−7.21 (m, 1H), 6.97 (td, J = 8.1, 2.4 Hz, 1H), 6.82−6.72 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 162.4 (d, $J_{C\text{-}F}$ = 248 Hz), 150.0 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 11 Hz) , 145.5, 131.9, 130.2 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 9 Hz), 129.8, 128.4, 118.1 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3 Hz), 114.2 (d, $J_{C\text{-}C\text{-}F}$ = 20 Hz), 110.4 (d, $J_{C\text{-}C\text{-}F}$ = 24 Hz), 21.8; HRMS (EI positive) Calcd. for $C_{13}H_{11}O_3FS$: $[M+\cdot]^+$ 266.0413, Found: m/z 266.0409.

3-Chlorophenyl tosylate (**2k**)[3c]: Pale yellow solid; IR (ATR, cm^{-1}) 1585, 1468, 1373, 1197, 1170, 1087, 893, 786, 751, 676, 659; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.27−7.21 (m, 2H), 7.04−7.02 (m, 1H), 6.91−6.86 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.7, 145.6, 134.7, 131.9, 130.2, 129.8, 128.4, 127.3, 122.9, 120.6, 21.8; HRMS (EI positive) Calcd. for $C_{13}H_{11}O_3ClS$: $[M+\cdot]^+$ 282.0117, Found: m/z 282.0113.

4-Chlorophenyl tosylate (**2l**)[1c]: White solid; IR (ATR, cm^{-1}) 1596, 1484, 1373, 1201, 1171, 1089, 863, 840, 748, 671; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 147.9, 145.5, 132.6, 131.9, 129.7, 129.6, 128.4, 128.7, 21.8; HRMS (EI positive) Calcd. for $C_{13}H_{11}O_3ClS$: $[M+\cdot]^+$ 282.0117, Found: m/z 282.0122.

2-Naphthyl tosylate (**2m**)[1c]: White solid; IR (ATR, cm^{-1}) 1596, 1374, 1190, 1175, 1145, 1090, 958, 906, 863, 818, 785, 750, 707, 660; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.82−7,70 (m, 5H), 7.51−7.44 (m, 3H), 7.28 (d, J = 8.1 Hz, 2H), 7.09 (dd, J = 8.9, 2.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 147.0, 145.2, 133.3, 132.3, 131.7, 129.6(129.64), 129.6(129.61), 128.4, 127.7, 127.6, 126.7, 126.2, 121.0, 119.8, 21.8; HRMS (EI positive) Calcd. for $C_{17}H_{14}O_3S$: $[M+\cdot]^+$ 298.0664, Found: m/z 298.0667.

Methyl tosylate (**2n**)[22]: Colorless oil; IR (ATR, cm^{-1}) 1598, 1453, 1356, 1173, 1096, 986, 813, 759, 658; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.74 (s, 3H), 2.45 (s,

3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 144.7, 132.1, 129.7, 127.9, 56.1, 21.6.

Phenyl benzenesulfonate (**3a**)[23]: Colorless oil; IR (ATR, cm^{-1}) 1589, 1485, 1372, 1198, 1172, 1091, 857, 740, 685; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.82 (dd, J = 8.4, 1.1 Hz, 2H), 7.66 (t, J = 7.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31−7.21 (m, 3H), 6.97 (dd, J = 7.6, 1.4 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.4, 135.2, 134.1, 129.5, 129.0, 128.3, 127.0, 122.2.

Phenyl naphthalene-2-sulfonate (**4a**)[24]: White solid; IR (ATR, cm^{-1}) 1585, 1486, 1372, 1189, 1145, 1074, 915, 862, 780, 726; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 7.97−7.80 (m, 4H), 7.69−7.56 (m, 2H), 7.27−7.16 (m, 3H), 6.98 (dd, J = 8.1, 2.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.4, 135.2, 132.0, 131.6, 130.3, 129.5, 129.4, 129.3, 129.2, 127.8, 127.7, 127.0, 122.7, 122.2; HRMS (EI positive) Calcd. for $C_{16}H_{12}O_3S$: $[M+\cdot]^+$ 284.0507, Found: m/z 284.0500.

Phenyl 4-nitrobenzenesulfonate (**5a**)[23]: Pale yellow solid; IR (ATR, cm^{-1}) 3108, 1524, 1485, 1372, 1349, 1194, 1141, 1090, 854, 780, 684; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.37 (d, J = 8.9 Hz, 2H), 8.03 (d, J = 8.9 Hz, 2H), 7.37−7.29 (m, 3H), 6.99 (dd, J = 8.1, 2.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 150.8, 149.1, 140.9, 129.9, 129.8, 127.6, 124.2, 122.0; HRMS (EI positive) Calcd. for $C_{12}H_9O_5NS$: $[M+\cdot]^+$ 279.0201, Found: m/z 279.0199.

Phenyl 4-chlorobenzenesulfonate (**6a**)[23]: White solid; IR (ATR, cm^{-1}) 1585, 1477, 1377, 1283, 1172, 1146, 1087, 855, 823, 780, 759, 687; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.76 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.34−7.23 (m, 3H), 6.98 (dd, J = 8.6, 1.9 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.3, 140.8, 133.7, 129.8, 129.6, 129.4, 127.2, 122.2; HRMS (EI positive) Calcd. for $C_{12}H_9O_3ClS$: $[M+\cdot]^+$ 267.9961, Found: m/z 267.9962.

Phenyl 2,4,6-trimethylbenzenesulfonate (**7a**)[25]: White solid; IR (ATR, cm^{-1}) 1485, 1455, 1362, 1195, 1145, 851, 785, 731, 691; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.29−7.21 (m, 3H), 6.97−6.94 (m, 4H), 2.54 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.3, 143.7, 140.3, 131.6, 130.4, 129.4, 126.8, 122.1, 22.8, 21.2; HRMS (EI positive) Calcd. for $C_{15}H_{16}O_3S$: $[M+\cdot]^+$ 276.0820, Found: m/z 276.0823.

Phenyl 4-hydroxybenzenesulfonate (**8a**)[26]: Pale yellow solid; IR (ATR, cm^{-1}) 3432, 1585, 1486, 1357, 1194, 1149, 1091, 860, 837, 786, 733; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.69 (d, J = 8.6 Hz, 2H), 7.31−7.21 (m, 3H), 6.98 (dd, J = 7.6, 1.9 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.17 (br s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 160.9, 149.4, 130.9, 129.5, 127.1, 126.3, 122.3, 115.9; HRMS (EI positive) Calcd. for $C_{12}H_{10}O_4S$: $[M+\cdot]^+$ 250.0300, Found: m/z 250.0296.

Phenyl mesylate (**9a**)[5b]: White solid; IR (ATR, cm^{-1}) 1588, 1485, 1353, 1168, 1139, 967, 858, 793, 767, 688; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.46−7.26 (m, 5H), 3.13 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.1, 129.9, 127.3, 121.9, 37.4.

Phenyl ethanesulfonate (**10a**)[27]: Colorless oil; IR (ATR, cm^{-1}) 1588, 1487, 1360, 1141, 858, 779, 749, 688; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.44−7.26 (m, 5H), 3.27 (q, J = 7.6 Hz, 2H), 1.53 (t, J = 7.6 Hz,

3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 149.0, 129.8, 127.1, 121.9, 45.0, 8.3; HRMS (EI positive) Calcd. for $C_8H_{10}O_3S$: $[M+\cdot]^+$ 186.0351, Found: m/z 186.0347.

2-Naphthyl triflate (**3m**)[28]: Colorless oil; IR (ATR, cm^{-1}) 1511, 1420, 1202, 1136, 1106, 955, 912, 832; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.91−7.83 (m, 3H), 7.74 (d, J = 2.2 Hz, 1H), 7.59−7.52 (m, 2H), 7.36 (dd, J = 9.2, 2.4 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 147.0, 133.2, 132.3, 130.5, 127.9, 127.8, 127.5, 127.1, 119.4, 119.1, 118.8 (q, $J_{C\text{-}F}$ = 320 Hz).

Preparation of pentavalent bismuth(V) dicarboxylate;

10,10-Di(3-chlorobenzenecarboxy)-10-(4-methylphenyl)phenothia-10$^{\lambda}$5-bismine 5,5-dioxide 1/4 etherate (**1o**)

To a suspension of **1a** (1.51 g, 3 mmol) in Et_2O (6 mL) at 0 °C was added dropwise a solution of 3-chlorobenzoic acid (0.47 g, 3 mmol) in Et_2O (7 mL) and then a solution of *m*-CPBA (65% content, 0.88 g, 3.3 mmol) in Et_2O (7 mL) was added dropwise. CH_2Cl_2 (2 mL) was added and the reaction mixture was stirred at 0 °C for 30 min. Yellow precipitate was filtered off and washed with CH_2Cl_2/Et_2O = 1/10 to afford **1o** as yellow solid (2.35 g, 96%).

mp 129−132 ºC; IR (ATR, cm^{-1}) 1597, 1545, 1467, 1426, 1321, 1152, 981, 743; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 8.50 (dd, J = 7.6, 1.1 Hz, 2H), 8.40 (d, J = 7.6 Hz, 2H), 8.17 (d, J = 7.8 Hz, 2H), 7.97 (s, 2H), 7.87 (d, J = 7.8 Hz, 2H), 7.73 (td, J = 7.6, 1.4 Hz, 2H), 7.64−7.42 (m, 7H), 7.30 (d, J = 7.8 Hz, 2H), 3.48 (q, J = 7.0 Hz, 1H), 1.21 (t, J = 7.0 Hz, 1.5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 172.7, 168.1, 163.4, 147.9, 135.1, 134.9, 134.1, 133.0, 132.4, 132.1, 131.6, 131.4, 130.9, 130.3, 129.3, 128.4, 127.9, 65.8, 15.3; Anal. Calcd for $C_{32}H_{21}BiCl_2O_6S.1/4Et_2O$: C, 47.64; H, 2.85%. Found: C, 47.46; H, 2.90%.

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