Synthesis of Thiophene/phenylene Co-oligomers. **III** [1]. Thienyl-capped Oligophenylenes

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The author reports the synthesis of thienyl-capped oligophenylenes *via* improved synthetic schemes. These schemes are based on either the Grignard or Suzuki coupling reaction and enable the author to obtain the target compounds at appreciably high yields. Regarding several of these compounds, their synthesis and characterization are believed to be reported for the first time. The resulting materials have been fully characterized through the nmr and ir spectroscopy. The ir analysis is particularly useful in characterizing the materials of higher molecular weight, since those materials are difficult to dissolve in organic solvents.

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Introduction.

Various oligothiophenes and oligophenylenes are currently synthesized and developed, since these materials are potentially useful as electroactive and/or photoactive organic semiconductors in thin film devices. Using the former materials, for instance, field-effect transistors have been proposed and fabricated [2,3]; the latter have been studied on electroluminescent devices [4,5].

In view of such promising aspects, Hotta and coworkers [6] and Samulski and coworkers [7] have most recently and independently developed thiophene/phenylene co-oligomers (*i.e.* the hybridized oligomers comprising thiophenes and phenylenes) in which the electronic structure and the extension of the π-conjugation can be tuned as desired. This can be done by changing the total ring number of the thiophenes and phenylenes and their mutual arrangement in the molecule [6]. Thus Hotta *et al*. have presented in previous papers [1,8] the syntheses and characterization of a variety of co-oligomers. Those include the phenyl-capped oligothiophenes and block and alternating co-oligomers. They have found out that these compounds exhibit unique molecular alignments in thin films [9].

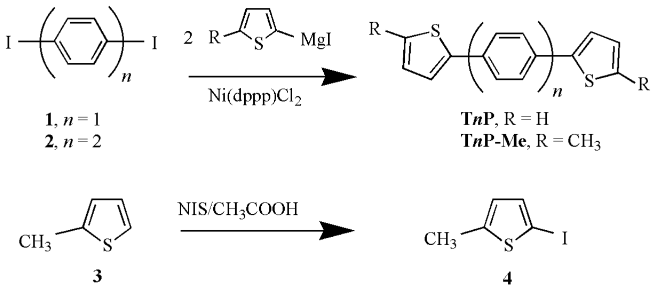
In this article the author reports syntheses of a series of thienyl-capped oligophenylenes **T*n*P** (*n* = 1–3) and **hT*n*P** (*n* = 2, 3), which comprise a specific class of thiophene/phenylene co-oligomers; see their molecular structure in Schemes 1–3. Of these, **hT*n*P** denote hemithienyl-capped compounds. A methyl derivative (**T2P-Me**) and an alternating co-oligomer (**12**) are also included. As compared with the phenyl-capped oligothiophenes, literature that deals with the syntheses of the co-oligomers possessing the oligophenylene sequence (*e.g.* biphenyl and terphenyl backbones) has been scarce up to this date. Most of the target compounds of the present studies are typical of such co-oligomers. Furthermore, some of them possess novel molecular structures that have not yet been reported.

Although **T2P** is a known compound, its synthetic yield was very low (8.7%) [10]. The author found out, however, that a combination of iodine compounds for the Grignard coupling reaction improved the yield of **T2P** (see EXPERIMENTAL). Regarding its methyl derivative (**T2P-Me**) neither the synthesis nor characterization has yet been presented.

Preparation of the Materials.

Scheme 1 shows synthetic routes of **T1P**, **T2P**, and **T2P-Me** based on the Grignard coupling reaction. All these compounds were synthesized in diethyl ether. In the case of the syntheses of **T2P** and **T2P-Me**, **2** was nearly insoluble in diethyl ether, however this compound gradually disappeared during overnight stirring, followed by the generation of strongly luminescent precipitates. Thus a yield of 22% (after purification through recrystallization) was attained for **T2P**. This is two and a half times as large as the previously reported yield [10]. This is perhaps due to the fact that iodine in **2** is more reducible in coexistence with 2-thienylmagnesium iodide than with 2-thienylmagnesium bromide [11]. Note that the combination of **2** with the latter reagent was adopted in the previous report [10].

Scheme 1



To synthesize *e.g.* alkyl derivatives of the target compounds intermediates like **4** are useful. For the purpose of the iodination of **3**, *N*-iodosuccinimide (NIS) can effectively be used in combination with glacial acetic acid *equimolar* to NIS [8]. The iodination takes place preferentially at the α-position of thiophene as in the bromination with *N*-bromosuccinimide [12] (see Scheme 1). This allows the author to avoid using toxic reagents such as mercury(II) oxide [13].

Schemes 2 and 3 utilize the Suzuki coupling reactions [14] that produce various thienyl-capped oligophenylenes. In these Schemes the boronic acid compounds **6**, **7**, and **11** are effectively coupled with bromides and iodides (**1**, **5a**,**b**, and **8**–**10**). In particular, **11** constitutes a co-oligomer itself and can be a useful building block of the co-oligomers. This boronic acid compound has been specially designed so that it can produce variations in the co-oligomer compounds. Its synthesis was carried out taking literature methods [15] into account. Regarding the target compounds **hT3P**, **T3P**, and **12**, to the best of my knowledge, their synthesis and characterization have been disclosed for the first time. Although the synthesis of **hT2P** was reported [16], its characterization remained insufficient.

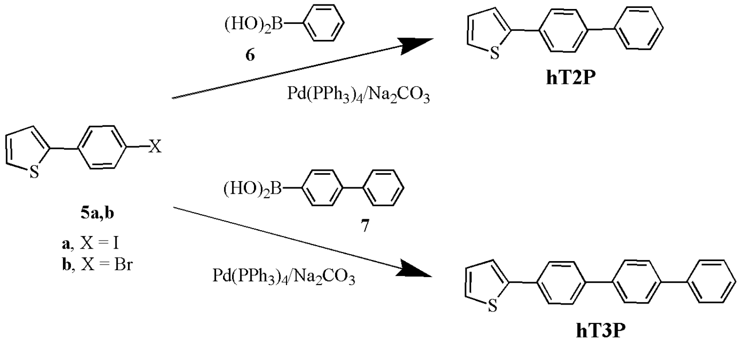
In all the cases represented in Schemes 2 and 3, the reaction solutions yield precipitates that are strongly luminescent blue to green. The as-precipitated crude materials were obtained nearly in a quantitative manner (88–100%). After purifying these the overall yields were moderately high (> 25%).

Spectroscopic Characterization of the Materials.

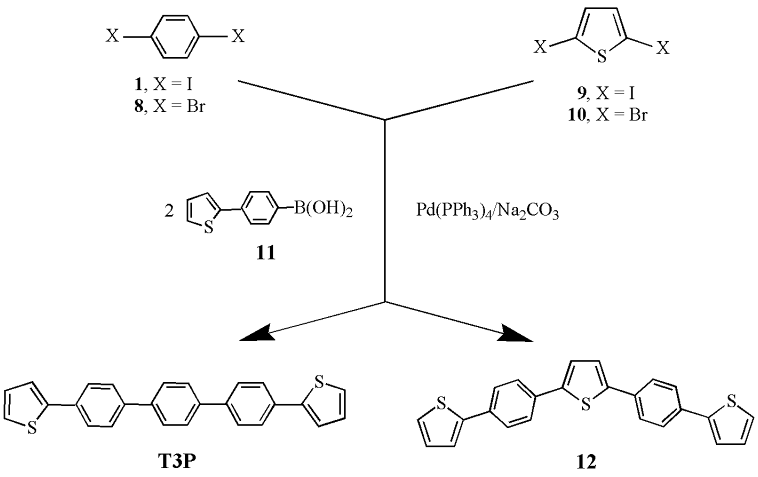
The compounds in which the total number of the thiophene and phenylene rings is up to four are sufficiently soluble in chloroform or acetone, and so their molecular structure can be determined by ^{1}H nmr. In addition to the routine assignments, the location of nmr lines provide interesting information about the local chemical environments in the vicinity of the individual hydrogen atoms. If the said chemical environments are closely related around those hydrogen atoms, the relevant lines also arise at closely related positions and sometimes coalesce. This is actually the case with **hT3P** and **T2P-Me** (see EXPERIMENTAL), and is also true of 1-(2-thienyl)-4-(5-phenylthiophen-2-yl)benzene, whose synthesis was reported previously [1]. Since a large number of co-oligomers are available, one expects that some of them will possess a suitable molecular structure such that specific hydrogen atoms show the coalesced lines in the spectra. Such spectroscopic features are important from a point of view of the conformational studies of molecules [17].

The five-ring compounds of **T3P** and **12** are extremely difficult to dissolve at room temperature in any common organic solvents. For their characterization, therefore, ir spectroscopy is a powerful tool instead of ^{1}H nmr. This is because the target compounds exhibit characteristic intense lines in the ir region around 1400–1500 and

Scheme 2



Scheme 3



700–800 cm^{-1} that result from the ring stretching and CH out-of-plane deformation vibrations, respectively. Furthermore, the locations of these vibrations unambiguously determine the substitution modes of the thiophenes and phenylenes [18,19].

A series of **T*n*P** (n = 1–3) exhibit closely related ir profiles. For these compounds distinct bands around 1490 and 1430 cm^{-1} are due to the 1,4-disubstituted benzene ring [18] and the 2-substituted thiophene ring [20], respectively. Sharply resolved peaks around 810 and 700 cm^{-1} are again assigned to the 1,4-disubstituted benzene [18] and the 2-substituted thiophene [21], respectively. The compound **12** additionally exhibits well-resolved bands at 1450 and 801 cm^{-1} characteristic of the 2,5-disubstituted thiophene [21,22]. On the basis of these assignments, the author concludes that the molecular structures of **T3P** and **12** are identical to those depicted in Scheme 3.

The compounds **hT*n*P** (n = 2, 3) indicate sharply resolved lines around 760 and 690 cm^{-1} that are attributed to the monosubstituted benzene [18], the latter line involving a thiophene-associated mode as a shoulder. A sharp line occurring at 1400–1410 cm^{-1} is specific to the 4-substituted biphenyl or *p*-terphenyl [1,23]. The CH out-of-plane deformation mode for the 2,5-disubstituted thiophene of **T2P-Me** is split into two at 799 and 792 cm^{-1}. The benzene-ring stretching mode of this compound is also split into two at 1506 and 1500 cm^{-1}. These splittings are probably showing the coexistence of two different kinds of conformers [17]. The major characteristic frequencies of the compounds are summarized in Table 1.

Thus the above-mentioned spectroscopic characteristics demonstrate that all the co-oligomers in the present studies possess the well-defined molecular structure, as represented in Schemes 1–3.

Conclusion.

The author has presented systematic synthetic methods for the thienyl-capped oligophenylenes that are based upon the Grignard coupling reaction and the Suzuki reaction. To improve the yield of **T2P** the author used 2-thienylmagnesium iodide in combination with 4,4'-diiodobiphenyl (**2**). The overall yield after purification turned out to be two and a half times higher than previously reported. To achieve further variations in syntheses, the author used three kinds of boronic acid compounds (**11**) one of which was purposely designed. These compounds were effectively coupled with bromides and iodides. The coupling reactions proceeded in a nearly quantitative manner to produce the purified target compounds in moderately high yields. All the materials prepared above have been satisfactorily characterized by ^{1}H nmr and ir spectroscopy.

EXPERIMENTAL

Melting points were measured on a Seiko Instruments DSC6200 thermal analysis system. The ^{1}H nmr spectra were recorded on a Varian Gemini 300BB spectrometer in deuteriochloroform solution and chemical shifts are reported in ppm (δ) relative to tetramethylsilane as an internal standard. As an exception the ^{1}H nmr spectrum of **11** was measured in a deuterioacetone solution to obtain good resolution. The ir spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrophotometer with finely pulverized particles dispersed and embedded in a potassium bromide matrix. Elemental analyses (for carbon, hydrogen, and sulfur) were carried out on a CEInstruments EA 1110 CHNS-O apparatus.

Dehydrated diethyl ether was purchased from Wako Pure Chemical and used without further purification or desiccation. Other chemical reagents were purchased from standard sources and used as received unless otherwise specified. The formation of the Grignard reagents and the subsequent Grignard coupling reaction were carried out in dry glassware and the reaction system was kept under dry nitrogen throughout.

1,4-Bis(2-thienyl)benzene (**T1P**).

Equimolar amounts of distilled 2-iodothiophene (9.51 g, 45.3 mmoles) and magnesium (1.101 g, 45.3 mmoles) were mixed in anhydrous diethyl ether (100 mL) to prepare a Grignard reagent. To the resulting Grignard reagent were added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride [abbreviated as Ni(dppp)Cl$_2$ in Scheme 1; 320 mg, 0.590 mmole] and **1** (5.98 g, 18.1 mmoles) successively. After stirring overnight at room temperature the reaction mixture was refluxed for 6 hours. When

Table 1

Infrared Band Positions (cm^{-1}) and Their Assignment of Various Thiophene/phenylene Co-oligomers

	CH stretching		Ring stretching		CH out-of-plane deformation	
Compound	Aromatic	Aliphatic	Phenyl(ene)	Thiophene	Phenyl(ene)	Thiophene
T1P	3067	—	1496	1428	815	699
T2P	3066	—	1488	1426	813	699
T2P-Me	3071	2914	1506 [a], 1500 [a]	1445	819	799 [a], 792 [a]
T3P	3067	—	1486	1429	811	697
hT2P	3065	—	1485, 1408	1427	820, 762, 687 [b]	—
hT3P	3066	—	1482, 1401	1427	817, 764, 688 [b]	—
12	3069	—	1493	1450, 1427	817	801, 697

[a] Split lines; [b] A thiophene-associated mode is involved as a shoulder.

cooled over an ice/water bath and subsequently hydrolyzed with 2 *N* hydrochloric acid (24 mL), the reaction mixture produced precipitates, which were collected by filtration and washed with cold methanol. The precipitates were recrystallized from methanol to give pale yellow solid **T1P**, yield 23%, mp 210°, lit [24] mp 202–204°, lit [13a] mp 204–206°; ^{1}H nmr: δ 7.10 (dd, 2H, thienyl protons, J = 5.3, 3.6 Hz), 7.30 (dd, 2H, thienyl protons, J = 5.3, 1.1 Hz), 7.34 (dd, 2H, thienyl protons, J = 3.6, 1.1 Hz), 7.63 ppm (s, 4H, phenylene protons).

Anal. Calcd. for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16; S, 26.46. Found: C, 69.36; H, 4.17; S, 26.31.

4,4'-Bis(2-thienyl)biphenyl (**T2P**).

The Grignard reagent was prepared using 2-iodothiophene (8.68 g, 41.3 mmoles) in the same manner as the synthesis of **T1P**. To the resulting Grignard reagent were added [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (320 mg, 0.590 mmole) and **2** (6.50 g, 16.0 mmoles) successively. The reaction mixture was then treated similarly to the case of the **T1P** synthesis. The resulting precipitates were recrystallized from toluene to give pale yellow solid **T2P**, yield 22%, mp 311°, lit [10] mp 310–315°; ^{1}H nmr: δ 7.11 (dd, 2H, thienyl protons, J = 5.2, 3.6 Hz), 7.31 (dd, 2H, thienyl protons, J = 5.2, 1.1 Hz), 7.37 (dd, 2H, thienyl protons, J = 3.6, 1.1 Hz), 7.65 (dd, 4H, phenylene protons, J = 8.6, 2.1 Hz), 7.71 ppm (dd, 4H, phenylene protons, J = 8.6, 2.1 Hz).

Anal. Calcd. for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.14. Found: C, 74.54; H, 4.29; S, 19.82.

4,4'-Bis(5-methylthiophen-2-yl)biphenyl (**T2P-Me**).

The Grignard reagent was prepared using 2-iodo-5-methylthiophene (1.03 g, 4.60 mmoles) in a manner similar to the synthesis of **T1P**. The same procedure as described for the **T2P** synthesis was applied afterward. The resulting precipitates were recrystallized from 2-butanone to give pale yellow solid **T2P-Me**, yield 17%, mp 305°; ^{1}H nmr: δ 2.53 (d, 6H, methyl protons, J = 1.1 Hz) [25], 6.75 (dd, 2H, thienylene protons, J = 3.6, 1.1 Hz) [25], 7.16 (d, 2H, thienylene protons, J = 3.6 Hz), 7.62 ppm (s, 8H, phenylene protons).

Anal. Calcd. for $C_{22}H_{18}S_2$: C, 76.26; H, 5.23; S, 18.51. Found: C, 76.08; H, 5.55; S, 18.35.

4-(2-Thienyl)biphenyl (**hT2P**).

2-(4-Bromophenyl)thiophene (**5b**) was synthesized following the literature method [1]. Of this, 246 mg (1.03 mmoles) was taken and dissolved in benzene (20 mL) together with benzeneboronic acid (**6**) of 244 mg (2.00 mmoles) and tetrakis(triphenylphosphine)palladium(0) [abbreviated as $Pd(PPh_3)_4$ in Schemes 2 and 3; 69.3 mg, 0.060 mmole]. Nitrogen was bubbled through this reaction solution for 30 minutes to remove dissolved oxygen. To the reaction solution was added 5 mL of an aqueous solution of sodium carbonate (424 mg, 4.00 mmoles), and then the solution was stirred for 20 hours at room temperature under nitrogen environment. The resulting solution was then cooled with an ice/water bath and oxidized with 1 mL of an aqueous solution of hydrogen peroxide (30%). This solution was washed in turn with water, saturated solution of aqueous sodium bicarbonate, and water and dried with anhydrous calcium chloride. White precipitates obtained after evaporating benzene were washed with cold methanol and recrystallized from hexane to give white solid **hT2P**, yield 26%, mp 172°; ^{1}H nmr: δ 7.11 (dd, 1H, a thienyl proton, J = 5.2, 3.6 Hz), 7.30 (dd, 1H, a thienyl proton, J = 5.2, 1.2 Hz), 7.36 (dd, 1H, a thienyl proton, J = 3.6, 1.2 Hz), 7.33–7.64 (m, 5H, phenyl protons), 7.62 (dd, 2H, phenylene protons, J = 8.9, 2.1 Hz), 7.70 ppm (dd, 2H, phenylene protons, J = 8.9, 2.4 Hz).

Anal. Calcd. for $C_{16}H_{12}S$: C, 81.31; H, 5.12; S, 13.57. Found: C, 81.32; H, 5.17; S, 12.79.

4-(2-Thienyl)-1,1':4',1"-terphenyl (**hT3P**).

The author applied the same procedure as the case of the **hT2P** synthesis, except for using 4-biphenylboronic acid (**7**) in place of **6**. The reaction mixture was then refluxed for 4 hours. The precipitates generated after the course of reaction were collected by filtration and washed with methanol. These precipitates underwent Soxhlet extraction with acetone and the extracted material was recrystallized from 2-butanone to give white solid **hT3P**, yield 43%, mp 298°; ^{1}H nmr: δ 7.11 (dd, 1H, a thienyl proton, J = 5.0, 3.5 Hz), 7.31 (dd, 1H, a thienyl proton, J = 5.0, 1.2 Hz), 7.38 (dd, 1H, a thienyl proton, J = 3.5, 1.2 Hz), 7.34–7.68 (m, 5H, phenyl protons), 7.67 (d, 2H, phenylene protons, J = 8.7 Hz), 7.70 (s, 4H, phenylene protons), 7.72 ppm (d, 2H, phenylene protons, J = 8.7 Hz).

Anal. Calcd. for $C_{22}H_{16}S$: C, 84.58; H, 5.16; S, 10.26. Found: C, 84.98; H, 5.30; S, 9.14.

4,4"-Bis(2-Thienyl)-1,1':4',1"-terphenyl (**T3P**).

1,4-Diiodobenzene **1** (247 mg, 0.75 mmole) and 4-(2-thienyl)benzeneboronic acid (**11**) of 612 mg (3.00 mmoles) as well as tetrakis(triphenylphosphine)palladium(0) (104 mg, 0.090 mmole) were dissolved in benzene (60 mL). Nitrogen was bubbled through this reaction solution for 30 minutes to remove dissolved oxygen. To the reaction solution was added 10 mL of an aqueous solution of sodium carbonate (636 mg, 6.00 mmoles), and then the solution was refluxed for 26 hours under nitrogen environment. The precipitates generated after the course of reaction were collected by filtration and washed by turns with methanol and acetone. These precipitates were recrystallized from 1,2,4-trichlorobenzene to give pale yellow solid of **T3P**, yield 38%, mp 387°.

Anal. Calcd. for $C_{26}H_{18}S_2$: C, 79.15; H, 4.60; S, 16.25. Found: C, 79.04; H, 4.56; S, 15.88.

2,5-Bis[4-(2-thienyl)phenyl]thiophene (**12**).

The author applied the same procedure as the case of the **T3P** synthesis, except for using 2,5-diiodothiophene (**9**) in place of **1**. The resulting precipitates were recrystallized from 1,2,4-trichlorobenzene to give yellow solid of **12**, yield 63%, mp 284°.

Anal. Calcd. for $C_{24}H_{16}S_3$: C, 71.96; H, 4.03; S, 24.01. Found: C, 72.14; H, 3.84; S, 23.39.

2-Iodo-5-methylthiophene (**4**).

2-Methylthiophene **3** (9.82 g, 0.10 mole) and *N*-iodosuccinimide (27.0 g, 0.12 mole) were dissolved in methanol (240 mL). To this solution was added acetic acid (6.87 mL, 0.12 mole), and the reaction solution was stirred for 3 hours over an ice/water bath, making the resulting solution dark orange. To this solution were added 240 mL water and 360 mL diethyl ether, the reaction products obtained above were transferred to the diethyl ether layer in a separating funnel. This layer was separated from the water layer and washed successively with water, 10% aqueous solution of sodium hydroxide (four times), and water (two times). The resulting diethyl ether solution was dried with anhydrous calcium chloride and diethyl ether was removed with a rotary evaporator to give 15.4 g of a pale yellow liquid (in a yield of 69%). This compound was distilled under reduced pressure to obtain a colorless liquid **4**; ^{1}H nmr: δ 2.46 (d, 3H, methyl protons, J = 1.1 Hz) [25], 6.45 (dd, H, a thienylene proton, J = 3.6 , 1.1 Hz) [25], 7.01 ppm (d, H, a thienylene proton, J = 3.6 Hz).

4-(2-Thienyl)benzeneboronic acid (**11**).

2-(4-Bromophenyl)thiophene (**5b**) was synthesized following the literature method [15a]. The crude product of this compound was purified by column chromatography on silica gel with hexane as eluent.

Equimolar amounts of the purified material of **5b** (40.0 g, 0.167 mole) and magnesium (4.07 g, 0.167 mole) were mixed in anhydrous diethyl ether (100 mL) to prepare a Grignard reagent. Meanwhile, trimethyl borate (17.4 g, 0.167 mole) was dissolved in anhydrous diethyl ether (100 mL) and kept at -78°. To this solution of trimethyl borate, the above Grignard reagent was added slowly, while stirring vigorously. After being stirred overnight at room temperature the reaction mixture was slowly poured into 10% sulfuric acid (150 mL) over an ice/water bath. The diethyl ether layer was separated from the water layer in a separating funnel. The former layer was washed with water, while the latter was extracted with diethyl ether. The combined diethyl ether layers were dried with anhydrous calcium chloride and diethyl ether was removed with a rotary evaporator to give a crude material.

This material was purified by column chromatography on silica gel with ethyl acetate-tetrahydrofuran (10:1, v/v) as eluent. The material obtained through evaporating the eluent was dissolved in refluxing ethyl acetate (five times the said material in weight) and the resulting solution was subsequently reprecipitated in hexane to yield pale gray powder. This was recrystallized from a mixture solvents methanol:water (2:1, v/v) to give colorless crystals **11**, yield 45%, mp 252°; ir: ν (OH) 3329, (CH) 3062, (CH) 822, 702 cm^{-1}; ^{1}H nmr: δ 7.14 (dd, 1H, a thienyl proton, J = 5.0, 3.7 Hz), 7.23 (s, 2H, hydroxyl protons) [26], 7.48 (dd, 1H, a thienyl proton, J = 5.0, 1.1 Hz), 7.52 (dd, 1H, a thienyl proton, J = 3.7, 1.1 Hz), 7.68 (dd, 2H, phenylene protons, J = 8.6, 2.1 Hz), 7.93 ppm (dd, 2H, phenylene protons, J = 8.6, 2.0 Hz).

Anal. Calcd. for $C_{10}H_9O_2SB$: C, 58.86; H, 4.45; S, 15.71. Found: C, 58.18; H, 4.37; S, 15.67.

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