Synthesis and reactivity of chiral pentavalent bismuth derivatives

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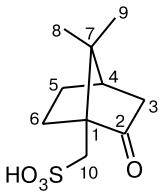
Eight new pentavalent organobismuth derivatives were synthesized by the reactions of triphenylbismuth or phenyl-2,2′-biphenylenebismuth with chiral (1*R*)-(−)-camphor-10-sulfonic, (−)-menthyloxyacetic, or (*R*)-3-phenylbutyric acids. Enantioselective *C*-arylation of enolizable substrates with organobismuth reagents was carried out for the first time. Unlike iodine, sulfur, and selenium derivatives, which contain a five-membered heterocycle including the 2,2′-biphenylene fragment, phenyl-2,2′-biphenylene organobismuth analogs enter into *C*-arylation reactions accompanied by the selective transfer exclusively of the phenyl group to the organic substrate.

Key words: *C*-arylation, triphenylbismuth, phenyl-2,2′-biphenylenebismuth, enantioselectivity.

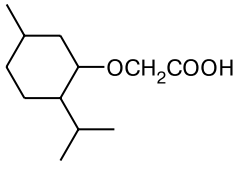
In the last two decades, aryl derivatives of boron, lead, sulfur, bismuth, and iodine have found application in organic synthesis as efficient *C*-, *O*-, *N*-, and *S*-arylating reagents.[1—6] Among these reactions, *C*-arylation with aryl derivatives of main-group elements along with methods based on metal-complex catalysis[7] are of considerable interest for the synthesis of chiral biaryls or for stereoselective arylation of enolizable substrates. However, data on the possibility of performing stereoselective arylation of organic substrates by reductive cross-coupling are scarce. For example, homochiral sulfoxides serve as efficient reagents in the synthesis of asymmetric 1,1′-binaphthyl derivatives with high enantioselectivity.[8] Optically active iodonium salts can be used for stereoselective arylation of ketones.[9] Only a few studies were devoted to diastereoselective arylation with aryllead triacetates.[2] The use of aryl derivatives of lead containing an auxiliary chiral group for arylation of β-keto esters results in only insignificant enantioselectivity.[10] However, the application of the $ArPb(OAc)_3$—BuLi—chiral base—4 Å molecular sieves reagent system allows one to increase the enantioselectivity of arylation of phenols and anilines to 90—95%.[11] Finally, the only study has dealt with stereoselective arylation with organobismuth reagents, where the diastereoselectivity of phenylation of α-nitro esters with Ph_3BiCl_2 has been demonstrated to depend on the nature of the base used.[12]

In the present study, new pentavalent bismuth derivatives containing chiral fragments were synthesized and the reactivities of these compounds in *C*-arylation were examined. The synthesis of organobismuth derivatives attracted interest because these compounds serve as mild regioselective and, in most cases, regiospecific arylating reagents (*C*-arylation in the presence of bases; *O*- and *N*-arylation in the presence of catalytic amounts of copper salts), which are resistant to atmospheric oxygen and moisture.[1—3] In addition, in spite of the fact that bismuth is the most heavy of all nonradioactive elements, aryl derivatives of bismuth possess low toxicity,[13] due to which this class of arylating reagents is particularly attractive for functionalization of a broad spectrum of physiologically active molecules.[14]

We synthesized eight new Bi^V derivatives based on triphenylbismuth (**1**), phenyl-2,2′-biphenylene-



3 (CSAH)



4 (MAAH)

MeCH(Ph)CH_2COOH

5 (PBAH)

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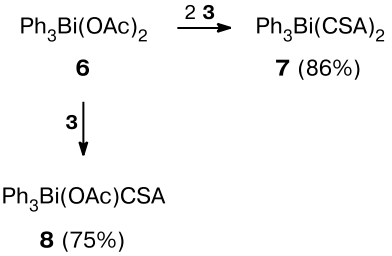
bismuth (**2**), and a series of optically active acids, such as (1*R*)-(−)-camphor-10-sulfonic (**3**) (CSAH), menthyloxyacetic (**4**, MAAH), and (*R*)-3-phenylbutyric (**5**, PBAH) acids.

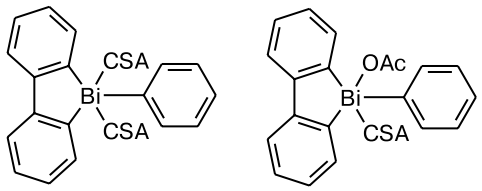
Triphenylbismuth dicamphorsulfonate **7** was synthesized using the ligand exchange method[15] by the reaction of triphenylbismuth diacetate[16] **6** with camphorsulfonic acid (molar ratio was 1 : 2) in acetonitrile (Scheme 1). The reaction with the use of equimolar amounts of the reagents produced triphenylbismuth acetoxycamphorsulfonate **8**.

Scheme 1



It should be noted that triphenylbismuth acetoxycamphorsulfonate (**8**) was also prepared by stirring equimolar amounts of triphenylbismuth diacetate **6** and dicamphorsulfonate analog **7** in CH_2Cl_2 for 15 min.

Analogously, dicamphorsulfonate **10** and acetoxycamphorsulfonate **11** of the bridged organobismuth derivative were synthesized starting from phenyl-2,2′-biphenylenebismuth diacetate **9**.[17]



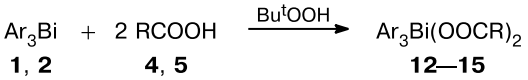
10 **11**

Chiral bis(menthyloxyacetates) (**12**, **14**) and bis(3-phenylbutyrates) (**13**, **15**) of triphenylbismuth (**12**, **13**) and phenyl-2,2′-biphenylenebismuth (**14**, **15**) were synthesized by the reactions of Bi^{III} derivatives **1** and **2** with the corresponding optically active acids in the presence of *tert*-butyl hydroperoxide[18] (Scheme 2).

Compounds **7**, **8**, **10**—**15** were identified by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Besides, the specific rotation of these compounds in CH_2Cl_2 was determined.

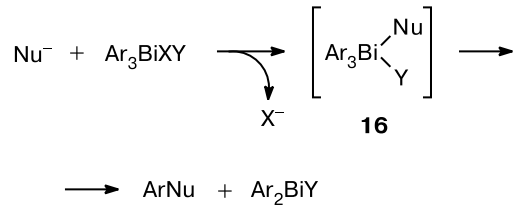
Organobismuth derivatives **7**, **8**, **10**, and **11** were tested in *C*-arylation reactions in the presence of bases. The mechanism of these reactions involves the following two steps (Scheme 3): the nucleophilic substitution in the coordination sphere of the metal atom giving rise to unstable covalent intermediate **16** and cross-coupling resulting in coupling of two ligands and a decrease in the valence of bismuth.[1,2] The role of the base is to activate the substrate (to ionize the substrate or to shift the equilibrium toward the enol form).[1,2] In addition, the base—metal coordination interactions in intermediate **16** can control the stereoselectivity of arylation.[8—12]

Scheme 2

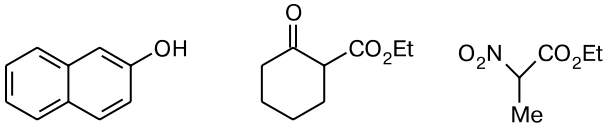


Starting compounds		Product	Yield (%)
1	**4**	**12**	69
	5	**13**	44
2	**4**	**14**	54
	5	**15**	57

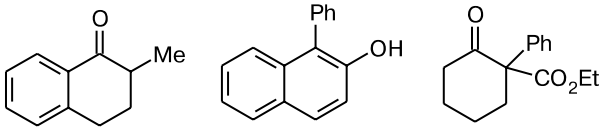
Scheme 3



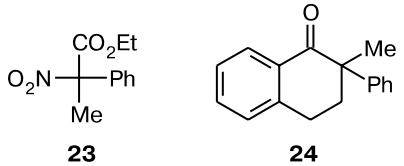
We used the following four organic derivatives as substrates: 2-naphthol (**17**), ethyl 2-oxocyclohexanecarboxylate (**18**), ethyl 2-nitropropanoate (**19**), and 2-methyltetralone (**20**).



17 **18** **19**



20 **21** **22**

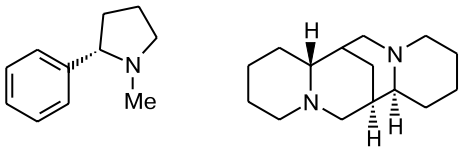


23 **24**

In spite of the fact that the steric factors can substantially decrease the reactivity of organobismuth reagents,[19]

all derivatives **7**, **8**, **10**, and **11** containing the bulky camphorsulfonate fragments react with phenol **17** in the presence of *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG, **25**) to give 1-phenyl-2-naphthol (**21**) in nearly quantitative yields (87, 88, 81, and 83%, respectively).

To examine the possibility of enantioselective arylation, the reactions with β-keto ester **18** and β-nitro ester **19** were carried out in the presence of bases, such as TMG (**25**), (−)-nicotine (**26**), (−)-sparteine (**27**), and brucine (**28**).



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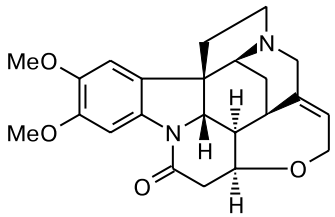

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In the case of derivative **18**, the highest yields of phenylation product **22** were obtained in the reactions with bis(camphor-10-sulfonate) derivatives of bismuth **7** and **10** (Table 1). Their acetoxycamphorsulfonate analogs **8** and **11** exhibit lower reactivity. This fact is consistent with the pubished data providing evidence that an increase in the electron-withdrawing ability of the leaving group in Bi^V derivatives (for example, in the reagents of the Ar_3BiX_2 or Ar_4BiX types) leads, as a rule, to a substantial increase in the arylating ability of these compounds.[20] Triphenylbismuth derivative **7** proved to be a more efficient phenylating reagent compared to compound **10** containing the five-membered metallocycle, which is in agreement with the published data on the reactivities of their diacetate analogs **6** and **9**.[17]

The application of various bases **25**—**27** has virtually no effect on the yields of the *C*-arylation products (see Table 1). It should be noted that brucine **28**, which has found use in asymmetric cross-coupling involving aryl derivatives of lead,[11] appeared to be absolutely inefficient in the reactions with organobismuth derivatives **7**, **8**, **10**, and **11**. In no case was the use of achiral base **25** lead to enantioselective phenylation of keto ester **18**. Apparently, the fact that the nearest chiral center of the auxiliary chiral group is remote from the metal center as well as the ease of pseudorotation in the coordination sphere of the bismuth atom[21] (despite the presence of the bulky camphorsulfonate substituents) are responsible for the fact that enantioselective phenylation does not occur in the absence of a chiral base. Actually, the reactions of β-keto ester **18** with dicamphorsulfonate **7** with the use of nicotine **26** or sparteine **27** as chiral bases proceeded with low enantioselectivity (see Table 1). The reactions with the use of bridged dicamphorsulfonate **10** as well as of acetoxycamphorsulfonates **8** and **11** in the presence of compounds **26** and **27** occurred enantioselectively. An analogous situation was observed in the case of arylation of β-nitro ester **19** (Table 2). Although good yields of phenylation product **23** were obtained in the reactions with all four organobismuth reagents (**7**, **8**, **10**, and **11**), low enantioselectivity was achieved only in the reaction with dicamphorsulfonate **7** in the presence of nicotine **26**.

Table 1. *C*-Phenylation of ethyl 2-oxocyclohexanecarboxylate (**19**) with Bi^V derivatives **7**, **8**, **10**, and **11** in the presence of TMG (**25**),* (−)-nicotine (**26**),** and (−)-sparteine (**27**)** giving rise to ethyl 1-phenyl-2-oxocyclohexanecarboxylate (**20**)***

Bismuth derivative	**25**			**26**			**27**		
	Conditions		Yield (%)	Conditions		Yield (%)	Conditions		Yield (%)
	τ/h	*T*/°C		τ/h	*T*/°C		τ/h	*T*/°C	
7	3, 17	40, 25	95	17	25	95 (7 *ee*)	19	25	95 (5 *ee*)
8	3, 15	40, 25	77	15	25	71	20	25	69
10	20, 15	60, 25	82	20, 17	60, 25	81	18, 19	60, 25	80
11	92	25	70	2, 15	50, 25	75	3, 5	50, 25	65

* The reaction was carried out with the use of 1.2 equiv. of the base with respect to the substrate.
** The reaction was carried out with the use of 3.0 equiv. of the base with respect to the substrate.
*** All reactions were carried out in THF.

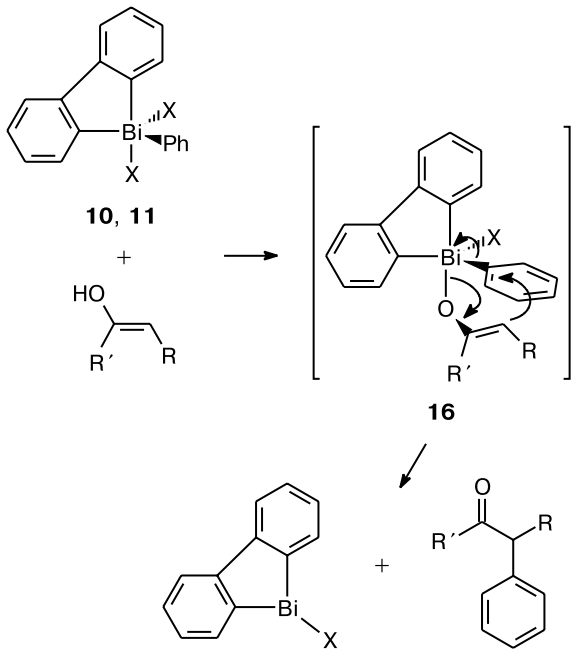
Table 2. *C*-Phenylation of ethyl 2-nitropropanoate (**19**) with Bi^V derivatives **7**, **8**, **10**, and **11** in the presence of TMG (**25**),* (−)-nicotine (**26**),** and (−)-sparteine (**27**)** giving rise to ethyl 2-phenyl-2-nitropropionate (**22**)***

Bismuth derivative	**25**			**26**			**27**		
	Conditions		Yield (%)	Conditions		Yield (%)	Conditions		Yield (%)
	τ/h	*T*/°C		τ/h	*T*/°C		τ/h	*T*/°C	
7	3, 15	50, 25	78	5, 15	50, 25	80 (5 *ee*)	5, 15	50, 25	76
8	3, 15	50, 25	61	4, 15	50, 25	60	— —	— —	— —
10	10, 15	65, 25	71	10, 15	65, 25	72	10, 15	65, 25	69
11	8, 15	Reflux, 25	57	6, 13	Reflux, 25	59	— —	— —	— —

* The reaction was carried out with the use of 1.2 equiv. of the base with respect to the substrate.
** The reaction was carried out with the use of 3.0 equiv. of the base with respect to the substrate.
*** All reactions were carried out in THF.

It should be noted that, unlike phenyl-2,2′-biphenyleneiodonium,[4] -sulfonium,[22] and -selenonium[23] salts, which enter into arylation reactions with various nucleophiles giving rise to mixtures of cross-coupling products (for example, cross-coupling accompanied by the transfer of the phenyl group and the biphenyl fragment), the reactions with bridging bismuth derivatives **10** and **11** proceeded selectively to give *ipso*-phenylation products. The reactions with sulfonium and selenonium salts are likely to proceed through the formation of four-coordinate sulfur and selenium intermediates, in which three aryl—heteroatom bonds are geometrically and energetically similar, which is responsible for a substantial decrease in selectivity of cross-coupling reactions.[22,23] This assumption was proved by NMR spectroscopic studies.[24] Therefore, the selectivity of the reactions involving compounds **10** and **11** indicates that the bismuth atom in intermediate **16** is in a distorted trigonal-bipyramidal rather than tetragonal-pyramidal environment with the biphenylene fragment in the apical position. One of the phenyl groups of the biphenylene fragment forms an equatorial bond, and the second phenyl group forms the axial bond. In the course of cross-coupling, the third phenyl group can occupy the equatorial position and adopts a conformation ideal for interactions between two π systems of the substrate and the phenyl group (Scheme 4), which is responsible for selective coupling of the substrate exclusively with the phenyl fragment.

Scheme 4

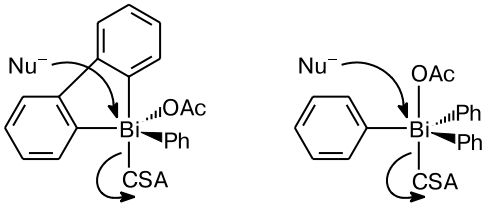


Taking into account the presence of one phenyl group that is transferred to the substrate as well as hindered pseudorotation in the coordination sphere of the bismuth atom in compound **10** compared to acyclic analog **7**, *C*-arylation with a bridged derivative would be expected to occur with higher stereoselectivity. The lack of enantioselectivity in the reactions with this compound can be explained assuming the trigonal-bipyramidal environment of the bismuth atom in the starting reagent. Apparently, the nucleophilic species can displace both the axially and equatorially arranged leaving groups resulting in the loss of selectivity of the attack of the phenyl group on the prochiral atom of the enolate from the *Re* or *Si* side of the π system of the substrate.

In *C*-arylation with acetoxycamphorsulfonates **8** and **11**, the nucleophilic attack occurs, apparently, from the least sterically hindered side and is accompanied by elimination of the bulky camphorsulfonate fragment. In

this case, the organobismuth intermediate loses the chirality element and cross-coupling occurs nonstereoselectively (Scheme 5).

Scheme 5



2-Methyltetralone **20** was used as the fourth substrate. Arylation of this substrate with organobismuth reagents **7**, **8**, **10**, and **11** in the presence of nitrogen-containing bases **25**—**28** does not occur. The reactions in the presence of a stronger base, *viz.*, Bu^{t}OK, with the use of dicamphorsulfonate **7** and acetoxycamphorsulfonate **8** as the phenylating reagents afforded product **24** in 38 and 93% yields, respectively. The reactions with the use of bridged bismuth derivatives **10** and **11** as the arylating reagents produced compound **24** only in trace amounts.

To summarize, enantioselective *C*-arylation with organobismuth reagents was carried out for the first time. In spite of the low enantioselectivity observed in the present reactions, the use of appropriate chiral ligand—chiral base combinations will, undoubtedly, lead to high enantioselectivity of arylation of enolizable substrates according to this method. In addition, the use of phenyl-2,2′-biphenylene derivatives of bismuth containing the five-membered metallocycle leads to the selective transfer exclusively of the phenyl group to the substrate, the bridging biphenylene fragment remaining intact.

Experimental

The NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13 MHz (^{1}H NMR) and 50.32 MHz (^{13}C NMR). The chemical shifts are given in the δ scale relative to Me_4Si. The specific rotation was determined on a Perkin—Elmer 341 polarimeter. The enantiomeric excesses were analyzed using europium trifluorohydroxymethylene-D-camphorate as the chiral shift reagent.

Commercially available (Aldrich) triphenylbismuth, (1*R*)-(−)-camphor-10-sulfonic acid, menthyloxyacetic acid, and (*R*)-3-phenylbutyric acid were used. Phenyl-2,2′-biphenylenebismuth,[17] triphenylbismuth diacetate,[16] and phenyl-2,2′-biphenylenebismuth diacetate[17] were synthesized according to known procedures.

Triphenylbismuth bis[(1*R*)-(−)-camphor-10-sulfonate] (7). A solution of (1*R*)-(−)-camphor-10-sulfonic acid **3** (0.49 g, 2.1 mmol) in MeCN (10 mL) was added to a solution of triphenylbismuth diacetate[16] (0.56 g, 1.0 mmol) in MeCN (15 mL). The reaction solution was refluxed with stirring for 1 h and then filtered. The solvent was removed under reduced pressure and the solid product was recrystallized from a CH_2Cl_2—Et_2O—pentane mixture. Compound **7** was isolated in a yield of 0.77 g (86%) as colorless crystals, m.p. 195—196 °C, $[\alpha]_D^{20}$ −40.0 (*c* 2.09, CH_2Cl_2). Found (%): C, 50.53; H, 5.05. $C_{38}H_{45}BiO_8S_2$. Calculated (%): C, 50.55; H, 5.02. ^{1}H NMR ($CDCl_3$), δ: 0.63 (s, 6 H, C(8)H_3 or C(9)H_3); 0.91 (s, 6 H, C(8)H_3 or C(9)H_3); 1.19—1.38 (m, 4 H, C(5)H_2); 1.72 (d, 2 H, *exo*-C(3)H_2, *J* = 18.3 Hz); 1.83—1.94 (m, 2 H, C(6)H_2); 1.89—1.98 (m, 2 H, C(4)H); 2.22 (d, 2 H, *endo*-C(3)H_2, *J* = 18.4 Hz); 2.31—2.43 (m, 2 H, C(6)H_2); 2.46 (d, 2 H, C(10)H_2, *J* = 13.7 Hz); 2.96 (d, 2 H, C(10)H_2, *J* = 13.9 Hz); 7.58 (t, 3 H, ArH(4′), *J* = 7.4 Hz); 7.71—7.81 (m, 6 H, ArH(3′), ArH(5′)); 8.30 (d, 6 H, H(2′) and H(6′), J_1 = 7.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.4 and 19.6 (C(8) and C(9)); 24.3 (C(5)); 26.6 (C(6)); 42.8 (C(4)); 42.9 (C(3)); 47.5 (C(7)); 48.4 (C(10)); 57.9 (C(1)); 132.2 (C(3′) and C(5′)); 134.8 (C(2′) and C(6′)); 132.2 (C(4′)); 157.8 (C(1′)); 215.4 (C(2)).

Acetoxytriphenylbismuth (1*R*)-(−)-camphor-10-sulfonate (8) was synthesized according to the above-described procedure starting from triphenylbismuth diacetate[16] (0.56 g, 1.0 mmol) and (1*R*)-(−)-camphor-10-sulfonic acid (**3**) (0.24 g, 1.05 mmol). The reaction product was recrystallized from a CH_2Cl_2—Et_2O—pentane—hexane mixture. Compound **8** was isolated in a yield of 0.55 g (75%) as colorless crystals, m.p. 135 °C, $[\alpha]_D^{20}$ −21.6 (*c* 2.17, CH_2Cl_2). Found (%): C, 48.13; H, 4.70. $C_{30}H_{35}BiO_7S$. Calculated (%): C, 48.13; H, 4.71. ^{1}H NMR ($CDCl_3$), δ: 0.59 (s, 3 H, C(8)H_3 or C(9)H_3); 0.90 (s, 3 H, C(8)H_3 or C(9)H_3); 1.13—1.27 (m, 2 H, C(5)H_2); 1.8 (d, 1 H, *exo*-C(3)H_2, *J* = 18.2 Hz); 1.75—1.93 (m, 5 H, CO(O)C$\underline{Me}_3$, C(12)H_3, *exo*-C(6)H_3, and *exo*-C(4)H_3); 2.07—2.43 (m, 3 H, *endo*-C(3)H_2, *endo*-C(6)H_2, and 1 H, C(10)H_2); 2.80 (d, 1 H, C(10)H_2, *J* = 14.8 Hz); 7.49 (t, 3 H, H(4′), *J* = 7.2 Hz); 7.55—7.69 (m, 6 H, H(3′) and H(5′); 8.18 (d, 6 H, H(2′) and H(6′), *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.4 and 19.7 (C(8) and C(9)); 21.4 (CO(O)$\underline{Me}$); 24.2 (C(5)); 26.6 (C(6)); 42.4 (C(4) and C(3)); 47.3 (C(7)); 47.9 (C(10)); 58.0 (C(1)); 131.5 (C(3′), C(4′), and C(5′); 134.5 (C(2′) and C(6′)); 157.8 (C(1′)); 177.4 ($\underline{C}$O(O)Me); 215.7 (C(2)).

Compound **8** was also prepared by stirring triphenylbismuth diacetate (0.28 g, 0.50 mmol) and triphenylbismuth bis[(1*R*)-(−)-camphor-10-sulfonate] **7** (0.45 g, 0.50 mmol) in CH_2Cl_2 (3 mL) at ~20 °C for 15 min. The solvent was removed under reduced pressure and the solid residue was recrystallized from a CH_2Cl_2—Et_2O—pentane—hexane mixture. Compound **8** was isolated in a yield of 0.56 g (77%).

Phenyl-2,2′-biphenylenebismuth bis[(1*R*)-(−)-camphor-10-sulfonate] (10) was synthesized according to the above-described procedure starting from phenyl-2,2′-biphenylenebismuth diacetate **9** [17] (0.56 g, 1.0 mmol) and (1*R*)-(−)-camphor-10-sulfonic acid **3** (0.49 g, 2.10 mmol). The reaction product was recrystallized from a CH_2Cl_2—Et_2O—pentane mixture. Compound **10** was isolated in a yield of 0.70 g (78%) as yellow crystals, m.p. 165 °C, $[\alpha]_D^{20}$ −52.6 (*c* 0.96, CH_2Cl_2). Found (%): C, 50.39; H, 4.94. $C_{38}H_{43}BiO_8S_2$. Calculated (%): C, 50.67; H, 4.81. ^{1}H NMR ($CDCl_3$), δ: 0.58 (s, 6 H, C(8)H_3 or C(9)H_3); 0.84 (s, 6 H, C(8)H_3 or C(9)H_3); 1.15—1.32 (m, 4 H, C(5)H_2); 1.67 (d, 2 H, *exo*-C(3)H_2, *J* = 18.3 Hz); 1.80—1.96 (m, 4 H, *exo*-C(6)H_2 and *exo*-C(4)H_2); 2.15—2.26 (m, 6 H, *endo*-C(3)H_2, *endo*-C(6)H_2, and 1 H, C(10)H_2); 2.69 (d, 2 H, C(10)H_2, *J* = 14.8 Hz); 7.68—7.93 (m, 7 H, ArH); 8.20—8.39 (m, 4 H, ArH);

8.58 (d, 2 H, ArH, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.3 and 19.5 (C(8) and C(9)); 24.3 (C(5)); 25.5 (C(6)); 42.3 (C(4)); 42.4 (C(3)); 47.5 (C(7)); 47.9 (C(10)); 58.0 (C(1)); 126.1, 132.0, 132.4, 132.6, 132.9, 133.0, and 133.3 (C(2′), C(3′), C(4′), C(5′), C(6′), C(8′), C(9′), C(10′), C(11′), C(12′), C(13′), C(14′), and C(15′)); 139.3 (C(17′) and C(18′)); 155.8 (C(1′); 166.2 (C(7′) and C(16′)); 216.4 (C(2)).

Acetoxyphenyl-2,2′-biphenylenebismuth (1*R*)-(−)-camphor-10-sulfonate (11) was synthesized according to the above-described procedure starting from phenyl-2-2′-biphenylenebismuth diacetate **9** [17] (0.50 g, 0.89 mmol) and (1*R*)-(−)-camphor-10-sulfonic acid **3** (0.22 g, 0.94 mmol). The reaction product was recrystallized from a CH_2Cl_2—Et_2O—pentane mixture. Compound **11** was isolated in a yield of 0.46 g (71%) as yellow crystals, m.p. 128 °C, $[\alpha]_D^{20}$ −19.6 (*c* 1.83, CH_2Cl_2). Found (%): C, 49.45; H, 4.27. $C_{30}H_{41}BiO_6S$. Calculated (%): C, 49.45; H, 4.29. ^{1}H NMR ($CDCl_3$), δ: 0.57 (s, 3 H, C(8)H_3 or C(9)H_3); 0.85 (s, 3 H, C(8)H_3 or C(9)H_3); 1.08—1.29 (m, 2 H, C(5)H_2); 1.68 (d, 1 H, *exo*-C(3)H_2, J = 18.3 Hz); 1.74—1.97 (m, 5 H, CO(O)Me, *exo*-C(6)H_2, and *exo*-C(4)H_2); 2.10—2.38 (m, 3 H, *endo*-C(3)H_2 and *endo*-C(6)H_2, 1 H, C(10)H_2); 2.64 (d, 1 H, C(10)H_2, J = 14.8 Hz); 7.50—7.86 (m, 7 H, ArH); 8.13—8.32 (m, 4 H, ArH); 8.42 (d, 2 H, ArH, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.3 and 19.6 (C(8) and C(9)); 20.6 (CO(O)Me); 24.3 (C(5)); 26.5 (C(6)); 42.3 (C(3) and C(4)); 47.4 (C(7)); 47.6 (C(10)); 58.1 (C(1)); 125.6, 131.6, 131.7, 132,6 132.3, 132.7, and 133.3 (C(2′), C(3′), C(4′), C(5′), C(6′), C(8′), C(9′), C(10′), C(11′), C(12′), C(13′), C(14′), and C(15′)); 138.8 (C(17′) and C(18′)); 155.2 (C(1′)); 166.8 (C(7′) and C(16′)); 177.5 (CO(O)Me); 216.4 (C(2)).

Triphenylbismuth bis[(−)-menthyloxyacetate] (12). A 98% Bu^{t}OOH solution (0.17 g, 1.90 mmol) in anhydrous Et_2O (3 mL) was slowly added with stirring and cooling (ice bath) to a mixture of triphenylbismuth **1** (0.72 g, 1.60 mmol) and (−)-menthyloxyacetic acid **4** (0.71 g, 3.30 mmol) in anhydrous Et_2O (10 mL). The reaction mixture was stirred at ~20 °C for 48 h under nitrogen. After completion of the reaction, volatile products were removed under reduced pressure. The solid residue was recrystallized from a CH_2Cl_2—Et_2O—pentane mixture. Compound **12** was isolated in a yield of 0.95 g (69%) as colorless crystals, m.p. 134 °C, $[\alpha]_D^{20}$ −47.1 (*c* 2.08, CH_2Cl_2). Found (%): C, 58.07; H, 6.65. $C_{42}H_{57}BiO_6$. Calculated (%): C, 58.19; H, 6.63. ^{1}H NMR ($CDCl_3$), δ: 0.61 (d, 6 H, C(9)H_3, J = 6.9 Hz); 0.73—0.85 (m, 18 H, C(11)H_3 and C(12)H_3, C(6)H_2 and C(10)H); 1.10—1.25 (m, 4 H, C(5)H_2); 1.43—1.59 (m, 4 H, C(8)H_2); 1.72—1.84 (m, 2 H, C(7)H); 2.12—2.25 (m, 2 H, C(4)H); 2.85 (dt, 2 H, C(3)H, J = 10.4 Hz, J = 4.0 Hz) Hz; 3.83 (s, 4 H, C(2)H_2); 7.38—7.61 (m, 9 H, ArH, C(3′)H, C(4′)H, and C(5′)H); 8.16 (d, 6 H, ArH, C(2′)H, and C(6′)H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 16.1, 20.7, and 22.1 (C(9), C(11), and C(12)); 22.0 (C(6)); 25.2 (C(10)); 31.2 (C(7)); 34.2 (C(5)); 39.9 (C(8)); 47.7 (C(4)); 67.2 (C(2)); 79.8 (C(3)); 130.6 (C(4′)); 130.9 (C(3′) and C(5′)); 134.0 (C(2′) and C(6′)); 159.9 (C(1′)); 176.8 (CO).

Triphenylbismuth bis[(*R*)-3-phenylbutanoate] (13). A solution of 98% Bu^{t}OOH (0.12 g, 1.30 mmol) in anhydrous Et_2O (2 mL) was slowly added with stirring and cooling (ice bath) to a mixture of triphenylbismuth **1** (0.53 g, 1.20 mmol) and (*R*)-3-phenylbutyric acid **5** (0.41 g, 2.50 mmol) in anhydrous Et_2O (10 mL). The reaction mixture was stirred at ~20 °C for 72 h under nitrogen. After completion of the reaction, volatile products were removed under reduced pressure. The solid residue was recrystallized from a CH_2Cl_2—Et_2O—pentane mixture. Compound **13** was isolated in a yield of 0.40 g (44%) as colorless crystals, m.p. 99—100 °C, $[\alpha]_D^{20}$ +10.5 (*c* 1.46, CH_2Cl_2). Found (%): C, 59.47; H, 4.87. $C_{38}H_{37}BiO_4$. Calculated (%): C, 59.53; H, 4.86. ^{1}H NMR ($CDCl_3$), δ: 0.93 (d, 6 H, Me, J = 7.0 Hz); 2.30 (dd, 2 H, C(2)H_2, J = 14.6 Hz, J = 8.2 Hz); 2.37 (dd, 2 H, C(2)H_2, J = 14.6 Hz, J = 6.9 Hz); 2.95—3.15 (m, 2 H, C(3)H); 7.01—7.21 (m, 10 H, ArH); 7.28—7.51 (m, 9 H, ArH); 7.95—8.03 (m, 6 H, ArH). ^{13}C NMR ($CDCl_3$), δ: 21.9 (Me); 36.8 (C(3)); 42.9 (C(2)); 126.0 (C(8)); 126.5 and 128.2 (C(6), C(7), C(9), and C(10)); 131.9 ((C3′) and (C(5′)); 133.7 (C(2′) and C(6′)); 145.5 (C(5)); 155.7 (C(1′); 178.5 (CO).

Phenyl-2,2′-biphenylenebismuth bis[(−)-menthyloxyacetate] (14). A solution of 98% Bu^{t}OOH (0.12 g, 1.30 mmol) in anhydrous benzene (3 mL) was slowly added with stirring and cooling (ice bath) to a mixture of phenyl-2,2′-biphenylenebismuth **2** (0.51 g, 1.20 mmol) and (−)-menthyloxyacetic acid **4** (0.50 g, 2.70 mmol) in anhydrous benzene (7 mL). The reaction mixture was stirred at ~20 °C for 35 h under nitrogen. After completion of the reaction, volatile products were removed under reduced pressure. The solid residue was recrystallized from an Et_2O—pentane mixture. Compound **14** was isolated in a yield of 0.54 g (54%) as yellow crystals, m.p. 74 °C, $[\alpha]_D^{20}$ −39.0 (*c* 1.96, CH_2Cl_2). Found (%): C, 58.33; H, 6.50. $C_{42}H_{55}BiO_6$. Calculated (%): C, 58.33; H, 6.41. ^{1}H NMR ($CDCl_3$), δ: 0.55 (d, 6 H, C(9)H_3, J = 6.8 Hz); 0.62—0.88 (m, 18 H, C(11)H_3 and C(12)H_3, C(6)H_2 and C(10)H); 1.08—1.20 (m, 4 H, C(5)H_2); 1.43—1.56 (m, 4 H, C(8)H_2); 1.70—1.81 (m, 2 H, C(7)H); 2.03—2.17 (m, 2 H, C(4)H); 2.84 (dt, 2 H, C(3)H, J = 10.4 Hz, J = 3.8 Hz); 3.86 (s, 4 H, C(2)H_2); 7.42—7.73 (m, 7 H, ArH); 8.10—8.27 (m, 6 H, ArH). ^{1}H NMR ($CDCl_3$), δ: 15.8, 20.7, and 22.1 (C(9), C(11), and C(12)); 22.9 (C(6)); 25.1 (C(10)); 31.2 (C(7)); 34.1 (C(5)); 39.6 (C(8)); 47.6 (C(4)); 66.6 (C(2)); 79.8 (C(3)); 124.7, 130.8, 131,0, 131.1, 131.2, 131.9, and 133.1 (C(2′), C(3′), C(4′), C(5′), C(6′), C(8′), C(9′), C(10′), C(11′), C(12′), C(13′), C(14′), and C(15′)); 137.8 (C(17′) and C(18′)); 155.6 (C(1′)); 179.2 (CO); signals for the quaternary carbon atoms bound to the bismuth atom (C(7′) and C(16′)) are not observed in the spectrum.

Phenyl-2,2′-biphenylenebismuth bis[(*R*)-3-phenylbutanoate] (15). A solution of 98% Bu^{t}OOH (0.16 g, 1.76 mmol) in anhydrous Et_2O (3 mL) was slowly added with stirring and cooling (ice bath) to a mixture of phenyl-2,2′-biphenylenebismuth **2** (0.70 g, 1.60 mmol) and (*R*)-3-phenylbutyric acid **5** (0.54 g, 3.30 mmol) in anhydrous benzene (10 mL). The reaction mixture was stirred at ~20 °C for 60 h under nitrogen. After completion of the reaction, volatile products were removed under reduced pressure. The solid residue was recrystallized from an Et_2O—pentane mixture. Compound **15** was isolated in a yield of 0.70 g (57%) as colorless crystals, m.p. 111—112 °C, $[\alpha]_D^{20}$ +0.36 (*c* 2.75, CH_2Cl_2). Found (%): C, 59.60; H, 4.70. $C_{38}H_{35}BiO_4$. Calculated (%): C, 59.69; H, 4.61. ^{1}H NMR ($CDCl_3$), δ: 0.94 (d, 6 H, Me, J = 6.9 Hz); 2.29 (dd, 2 H, C(2)H_2, J = 17.5 Hz, J = 8.4 Hz); 2.38 (dd, 2 H, C(2)H_2, J = 15.8 Hz, J = 6.8 Hz); 3.06—3.18 (m, 2 H, C(3)H); 6.93—7.21 (m, 10 H, ArH); 7.34—7.49 (m, 7 H, ArH); 7.85—8.15 (m, 4 H, ArH); 8.16—8.25 (m, 2 H, ArH). ^{1}H NMR ($CDCl_3$), δ: 21.5 (Me); 36.7 (C(3)); 42.5 (C(2)); 125.8 (C(8)); 126.5 and 128.1 (C(6), C(7), C(9), and C(10)); 124.6, 130.6, 130.7, 130.9, 131.8, 132.6, and 137.5 (C(2′), C(3′) C(4′), C(5′), C(6′), C(8′), C(9′), C(10′), C(11′),

C(12′), C(13′), C(14′), and C(15′)); 137.5 (C(17′) and C(18′)); 146.1 (C(5)); 156.0 (C(1)); 181.1 (CO); signals for the quaternary carbon atoms bound to the bismuth atom (C(7′) and C(16′)) are not observed in the spectrum.

***C*-Arylation with organobismuth reagents in the presence of bases (general procedure).** A mixture of the substrate (0.25—0.50 mmol, 1 equiv.) and a base (1.2—3.0 equiv.) in freshly distilled THF was stirred at ~20 °C for 10 min. Then the organobismuth reagent was added and the mixture was stirred as described below (see also Tables 1 and 2). After completion of the reaction, the solvent was removed under reduced pressure. *C*-Arylation products were isolated by column chromatography on SiO_2 as described below.

Synthesis of 1-phenyl-2-naphthol (21) by the reaction of 2-naphthol (17) with organobismuth derivatives 7, 8, 10, and 11 in the presence of TMG (1.2 equiv.). Reaction conditions: ~20 °C; column chromatography on SiO_2 (pentane—Et_2O, 7 : 3, as the eluent).

Derivative	τ/h	Yield of **21** (%)
7	17	87 *
8	15	88
10	1.5	81
11	1.5	83

* Colorless crystals were prepared, m.p. 84 °C (*cf.* lit. data[20]: m.p. 84 °C).

Synthesis of ethyl 1-phenyl-2-oxocyclohexanecarboxylate (22)[25] by the reaction of ethyl 2-oxocyclohexanecarboxylate with derivative 7 in the presence of TMG (1.2 equiv.) (general procedure). Reaction conditions: 3 h, 40 °C; 17 h, ~20 °C, column chromatography on SiO_2 (pentane—Et_2O, 7 : 3, as the eluent). A colorless oil was obtained[25] in 95% yield.

Synthesis of ethyl 2-nitro-2-phenylpropanoate (23)[26] by the reaction of ethyl 2-nitropropanoate (19) with derivative 7 in the presence of TMG (1.2 equiv.) (general procedure). Reaction conditions: 3 h, 50 °C, 15 h, ~20 °C; column chromatography on SiO_2 (pentane—Et_2O, 7 : 3, as the eluent). A colorless oil was obtained[26] in 78% yield.

Synthesis of 2-methyl-2-phenyltetralone (24)[27] using derivative 7. Potassium *tert*-butoxide (0.05 g, 0.45 mmol) was added to a solution of 2-methyltetralone **20** (0.06 g, 0.38 mmol) in THF (15 mL). The reaction solution was stirred at ~20 °C for 10 min. Then derivative **7** (0.41 g, 0.45 mmol) was added, the mixture was stirred at 50 °C for 30 h under argon, compound **7** (0.3 g, 0.33 mmol) was added, and the mixture was stirred at 50 °C for 20 h. After removal of the solvent, the product was purified by column chromatography on SiO_2 (pentane—Et_2O, 4 : 1, as the eluent). Compound **24** was isolated as a pale-yellow oil in a yield of 0.034 g (38%).[27]

Synthesis of 2-methyl-2-phenyltetralone (24)[27] using derivative 8. Potassium *tert*-butoxide (0.05 g, 0.45 mmol) was added to a solution of 2-methyltetralone **20** (0.06 g, 0.38 mmol) in THF (15 mL). The reaction solution was stirred at ~20 °C for 10 min. Then derivative **8** (0.33 g, 0.45 mmol) was added, the mixture was stirred at 50 °C for 72 h under argon, 35% HCl (2 mL) was added, the solvent was removed, and the product was purified by column chromatography on SiO_2 (pentane—Et_2O, 4 : 1, as the eluent). Compound **24** was isolated as a pale-yellow oil in a yield of 0.084 g (93%).[27]

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