New method for the synthesis of indenes

V. G. Nenajdenko, D. I. Denisenko, and E. S. Balenkova*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846. E-mail: nen@acylium.chem.msu.ru

A new two-step method was developed for the synthesis of 2-sulfonyl-substituted indenes from aromatic aldehydes. The reactions of 1-phenylsulfonyl-1-(trimethylsilyl)ethylene with *ortho*-lithiated derivatives of aromatic and heteroaromatic aldehydes afford conjugate addition products whose subsequent cyclization gives substituted 2-sulfonylindenes in preparative yields. The reactions of 2-(phenylsulfonyl)indenes with Grignard reagents were studied. It was shown that the sulfonyl group can be replaced in the presence of iron(III) acetylacetonate.

Key words: indene, transmetallation, 1-phenylsulfonyl-1-(trimethylsilyl)ethylene, aldehydes, Grignard reagents.

Substituted indenes are of particular interest for the organometallic chemistry of transition metals. This interest stems primarily from the fact that indene complexes of titanium and zirconium serve as the basis for the construction of highly efficient catalysts, which can induce polymerization of prochiral olefins, such as propylene, to form stereospecific polymers (isotactic, syndiotactic, and hemitactic polypropylenes).[1] In spite of the diversity of available procedures for the preparation of indenes, a general approach (applicable in all cases) to the synthesis of these compounds is lacking. Hence, the development of new procedures for the synthesis of indene systems is a topical problem.

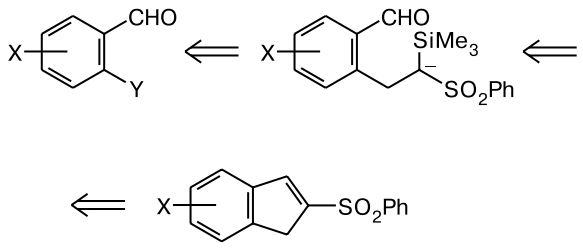
Among numerous methods for the synthesis of polysubstituted aromatic compounds, procedures with the use of organometallic compounds, which are prepared by the metal—halogen exchange and directed *ortho*-metallation,[2] are characterized by particularly high regioselectivity. In the directed *ortho*-metallation, α-amino alkoxides, which are formed in the *in situ* reactions of tertiary amides with organolithium compounds or in the reactions of aldehydes with *N*-lithiated secondary amides, are most often used as compounds containing protected aldehyde or ketone functional groups. Lithiated α-amino alkoxides allow one to selectively introduce various functional groups at the *ortho* position of aromatic and heteroaromatic aldehydes.[3—11]

The aim of the present study was to examine the reactions of lithiated α-amino alkoxides with 1-phenylsulfonyl-1-(trimethylsilyl)ethylene (**1**) and to develop a new procedure for the synthesis of 2-substituted indenes based on this reaction. Analysis of the published data demonstrated that substituted ethylene **1** is readily involved in the Michael reaction with organolithium compounds to give the corresponding products in good yields. However, the reactions of ethylene **1** with lithiated α-amino alkoxides have not been investigated.

Intramolecular cyclization of these reaction products proceeds as Peterson olefination. The reactions of α-silyl-α-sulfonyl-substituted carbanions with carbonyl compounds proceed readily to yield the corresponding vinyl sulfones in high yields. Thus, olefination of carbonyl compounds with α-silyl-α-sulfonyl-substituted carbanions has been successfully used previously.[12—15]

Taking these data into account, we chose 1-phenylsulfonyl-1-(trimethylsilyl)ethylene (**1**) as the "acceptor" in the Michael reaction for the synthesis of 2-substituted indenes. The method developed by us is based on the addition of lithiated α-amino alkoxides to vinyl sulfone **1** followed by cyclization under the action of a base (Bu^tOK). The retrosynthetic scheme of this approach can be represented as follows (Scheme 1).

Scheme 1



1-Phenylsulfonyl-1-(trimethylsilyl)ethylene (**1**) was synthesized from thiophenol (Scheme 2, the yields of the

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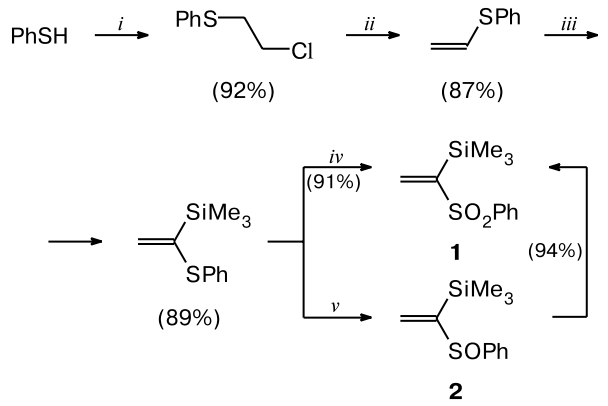
Scheme 2



Reagents and conditions: *i*. $Cl(CH_2)_2Cl$, NaOH; *ii*. NaOH; *iii*. LDA, Me_3SiCl, THF—hexane; *iv*. MCPBA; *v*. H_2O_2/AcOH.

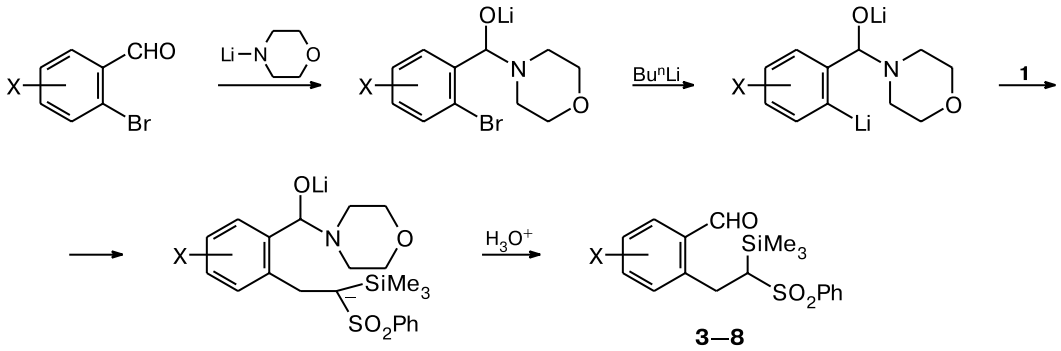
products are given in parentheses). The sulfide was oxidized by MCPBA or 50% H_2O_2 in AcOH. The intermediate formation of sulfoxide **2** was confirmed by ^1H NMR spectroscopy of the isolated product.

Lithiated α-amino alkoxides were prepared by the metal—halogen exchange with the use of substituted *o*-bromobenzaldehydes as the substrates (Scheme 3, Table 1).

The reactions of most of the aldehydes under study proceeded smoothly (the yields were 40—65%, see Table 1). However, these reactions with some substrates were more complicated. Thus, an attempt to prepare the addition products with lithiated α-amino alkoxides of the pyridine series failed.[16]

It appeared that the use of two equivalents of Bu^tOK in THF was optimum for cyclization of products **3—8**, which were prepared by the addition of ethylene **1** to lithiated α-amino alkoxides, as well as of 3-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]thiophene-2-carbaldehyde (**9**) (Scheme 4, Table 2). The use of this amount is required because 2-phenylsulfonylindenes that formed immediately reacted with the second equivalent of Bu^tOK to give the corresponding indenyl anions. Subsequent acidification of the reaction mixture afforded mixtures of two isomeric indenes in the reactions of aldehydes **4**, **5**, **7**, and **9** or gave one product in the reactions of aldehydes **3**,

Scheme 3



Scheme 4

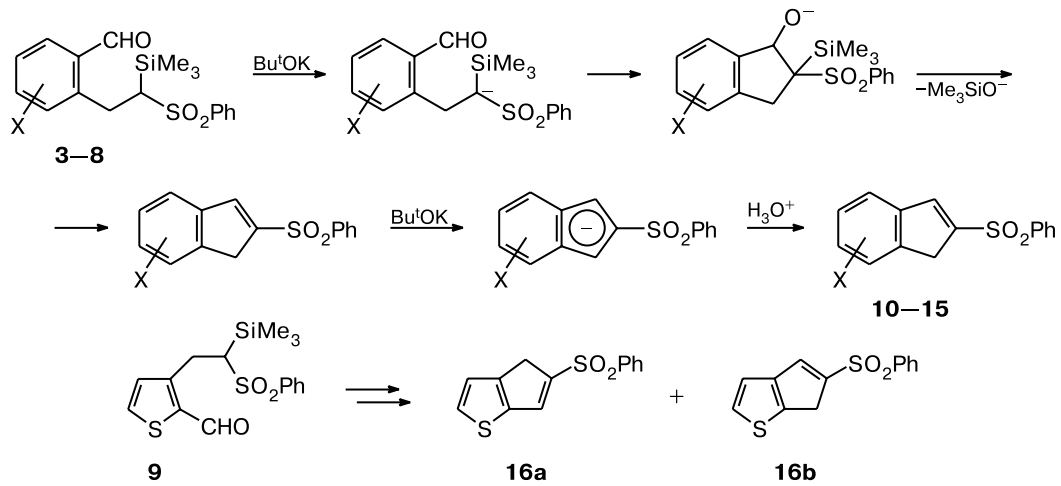


Table 1. Addition of sulfone **1** to lithiated α-amino alkoxides

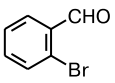
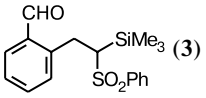
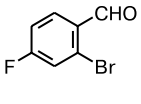
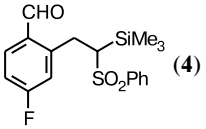
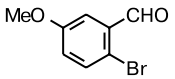
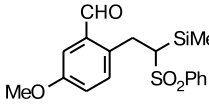
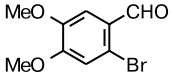
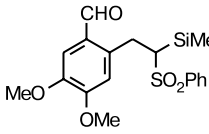
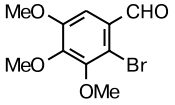
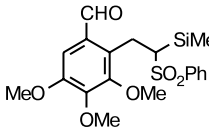
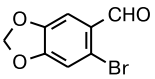
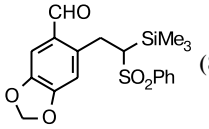
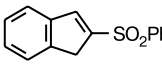
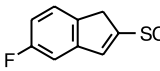
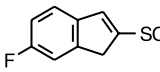
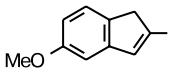
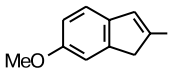
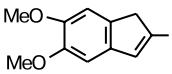
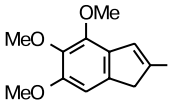
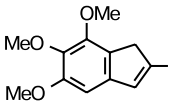
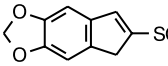
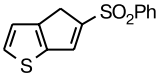
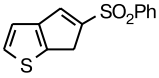
Starting aromatic aldehyde	Product	Yield (%)
	 (**3**)	65
	 (**4**)	61
	 (**5**)	45
	 (**6**)	46
	 (**7**)	40
	 (**8**)	44

Table 2. Cyclization of aldehydes **3—9**

Starting aldehyde	Product	Yield (%)*	**a** : **b****
3	 (**10**)	94	—
4	 (**11a**)	84	1 : 1.6
	 (**11b**)		
5	 (**12a**)	72	1 : 2.5
	 (**12b**)		
6	 (**13**)	71	—
7	 (**14a**)	70	1 : 1.4
	 (**14b**)		
8	 (**15**)	71	—
9	 (**16a**)	60	1.7 : 1
	 (**16b**)		

* For the reactions giving rise to compounds **11a,b**, **12a,b**, **14a,b**, and **16a,b**, the total yields of the mixtures of isomeric products are given.

** The ratio of the isomers **a** and **b** in the mixture.

6, and **8** (see Table 2). Unfortunately, we failed to perform cyclization without isolation of aldehydes **3—9** in pure form by decomposition of the reaction mixture, which was obtained after the addition of sulfonylethylene **1**, with the use of one equivalent of MeOH instead of acid.

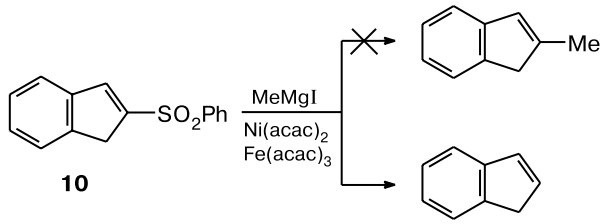
The isomer ratios of the sulfonylindenes were determined by ^{1}H NMR spectroscopy from the integral intensities of the signals of the CH_2 groups. These signals are characteristic of the compounds synthesized and are observed at δ 3.5—3.6. The signals for the protons at the double bond are also characteristic. The latter signals are observed at δ ~7.7 and occur generally as a triplet with the spin-spin coupling constant of ~2 Hz.

The resulting indenes contain the phenylsulfonyl group, which enables one to carry out their modifications. Several procedures are available for the replacement of the sulfonyl group in vinyl and aryl sulfones under the action of trialkylboranes[17] and lithium trialkylborohydrides.[18] It is more convenient to use Grignard reagents in the presence of nickel or iron catalysts (generally, nickel(II) or iron(III) acetylacetonates).[19—21] Hence, we employed this method in the study of the replacement of the phenylsulfonyl group in the indenes synthesized. 2-Phenylsulfonylindene **10** was used as the model substrate.

The reactions with MeMgI in the presence of both $Ni(acac)_2$ and $Fe(acac)_3$ did not afford the expected 2-methylindene; instead, these reactions gave rise only to indene, *viz.*, the desulfonylation product, (Scheme 5) in low yields (11 and 22%, respectively).

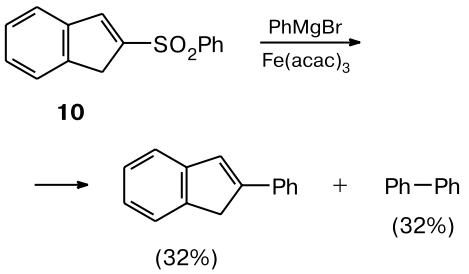
However, the reaction with PhMgBr produced the substitution product, *viz.*, 2-phenylindene, while the formation of indene was not observed. The reaction afforded

Scheme 5



the starting sulfone and biphenyl along with the target product (Scheme 6).

Scheme 6



The total yield of the isolated products (taking into account the conversion of the starting compound) was close to 100%, the ratio of 2-phenylindene to biphenyl being equal to 1 : 1. Apparently, the first equivalent of PhMgBr reacted with 2-phenylsulfonylindene to give the anion whose subsequent decomposition can proceed at any of the C—S bonds with approximately equal probabilities (Scheme 7).

Although the replacement of the sulfonyl group by the aryl substituent proceeded in low yield, we hope that the further search for the reaction conditions and catalysts will allow us to develop a universal procedure for the synthesis of 2-substituted indenes.

Hence, we devised a new procedure for the synthesis of 2-sulfonyl-substituted indenes from readily available aromatic aldehydes. The advantages of this procedure are that it has a general character (it can be applied to various *ortho*-metallated aldehydes) and involves a few steps. In addition, all steps can be carried out under basic conditions. This is also an advantage over other available procedures for the synthesis of indenes, which are generally prepared by dehydration of indanols in an acidic medium.

Experimental

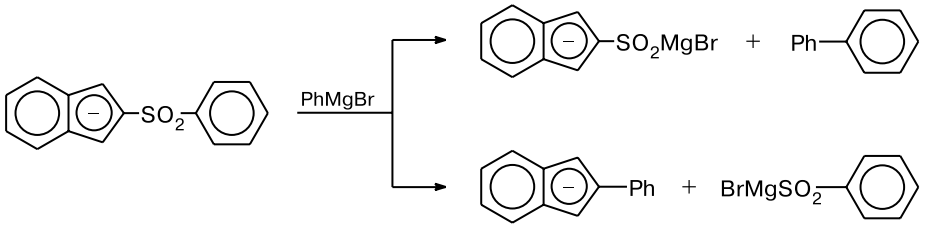
The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. The IR spectra were measured on a UR-20 spectrophotometer in thin films (for liquids) and Nujol mulls (for solids). The TLC analysis was carried out on Merck plates; visualization was performed with the use of an acidified solution of $KMnO_4$ or iodine vapor. Column chromatography was carried out with the use of silica gel (Merck, 60—200 mesh).

(2-Chloroethylthio)benzene,[22] (ethenylthio)benzene,[22] 1-phenylthio-1-(trimethylsilyl)ethylene,[23] 2-bromo-5-methoxybenzaldehyde,[24] 2-bromo-4,5-dimethoxybenzaldehyde,[24] 2-bromo-4,5-methylenedioxybenzaldehyde,[25] and 2-bromo-3,4,5-trimethoxybenzaldehyde[26] were prepared according to procedures described previously. Their spectroscopic characteristics were identical with those published in the literature.

1-Phenylsulfonyl-1-(trimethylsilyl)ethylene (1). ***A.*** A 55% MCPBA solution (70 g, 223 mmol) was added portionwise with vigorous stirring and cooling to a solution of 1-phenylthio-1-(trimethylsilyl)ethylene (23 g, 110 mmol) in CH_2Cl_2 (350 mL), the temperature being maintained at 20 °C. The reaction mixture was stirred at 20 °C for 5 h. The precipitate of *meta*-chlorobenzoic acid was filtered off and washed with CH_2Cl_2 (100 mL). The filtrate was successively washed with solutions of $KHCO_3$, $Na_2S_2O_3$, and $KHCO_3$ and then with water, dried with $CaCl_2$, and concentrated *in vacuo*. The residue was distilled. Sulfonylethylene **1** was obtained in a yield of 24 g (91%), b.p. 124—125 °C (1 Torr) (*cf.* lit. data[27]: b.p. 133 °C (2 Torr)). ^{1}H NMR, δ: 0.13 (s, 9 H, $SiMe_3$); 6.23 (s, 1 H, CH_2); 6.70 (s, 1 H, CH_2); 7.49—7.53 (m, 2 H, Ar); 7.56—7.61 (m, 1 H, Ar); 7.82—7.84 (m, 2 H, Ar).

B. A solution of 50% H_2O_2 (35 mL, 613 mmol) in glacial AcOH (50 mL) was added with stirring and cooling to a solution of 1-phenylthio-1-(trimethylsilyl)ethylene (40 g, 192 mmol) in glacial AcOH (70 mL) at 20—25 °C. The reaction mixture was stirred on a water bath at 20 °C for 1 h. Then the reaction mixture was heated at 30 °C for 12 h, water (500 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×150 mL). The extract was successively washed with solutions of $KHCO_3$, $Na_2S_2O_3$, and $KHCO_3$ and then with water, dried with $CaCl_2$, and concentrated *in vacuo*. The residue was distilled. Sulfonylethylene **1** was obtained in a yield of 43.4 g (94%), b.p. 124—125 °C (1 Torr). The ^{1}H NMR spectrum was identical

Scheme 7



with that of the sample synthesized according to the procedure ***A***.

1-Phenylsulfinyl-1-(trimethylsilyl)ethylene (2) was prepared according to the procedure ***B***. The reaction was carried out at 20 °C. The product was isolated analogously without distillation. ^{1}H NMR, δ: –0.09 (s, 9 H, $SiMe_3$); 6.16 (d, 1 H, CH_2, J = 0.7 Hz); 6.73 (d, 1 H, CH_2, J = 0.7 Hz); 7.36—7.43 (m, 3 H, Ar); 7.58—7.60 (m, 2 H, Ar).

Lithiation of *o*-bromobenzaldehydes and their reactions with 1-phenylsulfonyl-1-(trimethylsilyl)ethylene (1) (general procedure). A 1.6 *M* Bu^{n}Li solution in hexane (3.3 mL, 5.28 mmol) was added to a solution of morpholine (0.45 mL, 0.45 g, 5.17 mmol) in THF (5 mL) cooled to –40 °C. The reaction mixture was stirred at this temperature for 10 min and then cooled to –80 °C. A solution of the corresponding *o*-bromobenzaldehyde (5 mmol) in THF (5 mL) was added. The reaction mixture was stirred at –70 °C for 15 min and cooled to –80 °C, after which a 1.6 *M* Bu^{n}Li solution in hexane (3.3 mL, 5.28 mmol) was added and the reaction mixture was stirred at this temperature for 30 min. A solution of sulfonylethylene **1** (1.2 g, 5 mmol) in THF (10 mL) was added, the temperature being maintained below –70 °C. Then the temperature was increased to –10 °C and the reaction mixture was poured into 0.5 *M* hydrochloric acid (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (2×20 mL). The combined organic fractions were dried with $CaCl_2$ and concentrated *in vacuo*. The product was isolated from the residue by chromatography (CH_2Cl_2 as the eluent). Compounds **3—8** were obtained.

2-[2-Phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (3). The yield was 65%, colorless crystals, m.p. 110—111 °C. Found (%): C, 62.33; H, 6.33. $C_{18}H_{22}O_3SSi$. Calculated (%): C, 62.39; H, 6.40. IR, ν/cm^{-1}: 1700 (HC=O). ^{1}H NMR, δ: 0.35 (s, 9 H, $SiMe_3$); 3.26 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 10.4 Hz); 3.50 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 5.2 Hz); 3.63 (dd, 1 H, $CH_2C\underline{H}$, J = 10.4 Hz, J = 5.2 Hz); 7.13—7.17 (m, 2 H, Ar); 7.21—7.24 (m, 1 H, Ar); 7.26—7.32 (m, 3 H, Ar); 7.34 (br.s, 1 H, Ar); 7.36—7.39 (m, 2 H, Ar); 9.71 (s, CHO). ^{13}C NMR, δ: –0.80 ($SiMe_3$); 31.29 ($\underline{C}H_2CH$); 54.92 ($CH_2\underline{C}H$); 126.86; 127.17; 128.33; 131.83; 132.89; 133.36; 133.71; 135.23; 139.42; 142.35; 192.96 (CHO).

4-Fluoro-2-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (4). The yield was 61%, colorless crystals, m.p. 129—131 °C. Found (%): C, 59.50; H, 5.73. $C_{18}H_{21}FO_3SSi$. Calculated (%): C, 59.31; H, 5.81. IR, ν/cm^{-1}: 1693 (HC=O). ^{1}H NMR, δ: 0.38 (s, 9 H, $SiMe_3$); 3.22 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 11.0 Hz); 3.54 (dd, 1 H, C$\underline{H}_2$CH, J = 14.3 Hz, J = 4.4 Hz); 3.63 (dd, 1 H, $CH_2C\underline{H}$, J = 11.0 Hz, J = 4.4 Hz); 6.85 (ddd, 1 H, Ar, J = 8.2 Hz, J = 8.2 Hz, J = 2.7 Hz); 6.94 (dd, 1 H, Ar, J = 6.0 Hz, J = 2.7 Hz); 7.16—7.20 (m, 2 H, Ar); 7.27—7.31 (m, 1 H, Ar); 7.36 (dd, 1 H, Ar, J = 8.2 Hz, J = 6.0 Hz); 7.39—7.41 (m, 2 H, Ar); 9.68 (s, CHO). ^{13}C NMR, δ: –0.84 ($SiMe_3$); 31.13 ($\underline{C}H_2CH$); 54.69 ($CH_2\underline{C}H$); 114.09 (Ar, $^2J_{C,F}$ = 21.6 Hz); 120.21 (Ar, $^2J_{C,F}$ = 21.6 Hz); 126.71; 128.39; 130.28 (Ar, $^4J_{C,F}$ = 2.4 Hz); 132.01; 137.88 (Ar, $^3J_{C,F}$ = 9.6 Hz); 142.46; 143.05 (Ar, $^3J_{C,F}$ = 9.6 Hz); 164.99 (d, C(4), $^1J_{C,F}$ = 258.5 Hz); 191.30 (CHO).

5-Methoxy-2-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (5). The yield was 45%, colorless oil. IR, ν/cm^{-1}: 1700 (HC=O). ^{1}H NMR, δ: 0.34 (s, 9 H, $SiMe_3$); 3.21 (dd, 1 H, C$\underline{H}_2$CH, J = 14.5 Hz, J = 10.4 Hz); 3.42 (dd, 1 H, C$\underline{H}_2$CH, J = 14.5 Hz, J = 5.3 Hz); 3.56 (dd, 1 H, $CH_2C\underline{H}$, J = 10.4 Hz, J = 5.3 Hz); 3.77 (s, 3 H, MeO); 6.84—6.87 (m, 2 H, Ar); 7.14—7.16 (m, 1 H, Ar); 7.17—7.21 (m, 2 H, Ar); 7.30—7.35 (m, 1 H, Ar); 7.38—7.40 (m, 2 H, Ar); 9.70 (s, CHO). ^{13}C NMR, δ: –0.77 ($SiMe_3$); 30.26 ($\underline{C}H_2CH$); 55.44 ($CH_2\underline{C}H$); 119.12; 119.18; 126.87; 128.33; 131.46; 131.81; 133.98; 134.50; 142.43; 158.61; 192.45 (CHO).

4,5-Dimethoxy-2-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (6). The yield was 46%, colorless crystals, m.p. 130—132 °C. IR, ν/cm^{-1}: 1680 (HC=O). ^{1}H NMR, δ: 0.37 (s, 9 H, $SiMe_3$); 3.18 (dd, 1 H, C$\underline{H}_2$CH, J = 14.2 Hz, J = 10.7 Hz); 3.50 (dd, 1 H, C$\underline{H}_2$CH, J = 14.2 Hz, J = 4.8 Hz); 3.60 (dd, 1 H, $CH_2C\underline{H}$, J = 10.7 Hz, J = 4.8 Hz); 3.80 (s, 3 H, MeO); 3.94 (s, 3 H, MeO); 6.66 (s, 1 H, Ar); 6.83 (s, 1 H, Ar); 7.17—7.22 (m, 2 H, Ar); 7.28—7.32 (m, 1 H, Ar); 7.36—7.38 (m, 2 H, Ar); 9.67 (s, CHO). ^{13}C NMR, δ: –0.77 ($SiMe_3$); 30.63 ($\underline{C}H_2CH$); 55.54 ($CH_2\underline{C}H$); 56.02 (MeO); 56.47 (MeO); 110.43; 115.44; 126.56; 126.67; 128.20; 131.79; 134.45; 142.68; 147.53; 152.68; 190.57 (CHO).

3,4,5-Trimethoxy-2-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (7). The yield was 40%, colorless crystals, m.p. 165—167 °C. IR, ν/cm^{-1}: 1683 (HC=O). ^{1}H NMR, δ: 0.34 (s, 9 H, $SiMe_3$); 3.17 (dd, 1 H, C$\underline{H}_2$CH, J = 13.1 Hz, J = 3.5 Hz); 3.57 (dd, 1 H, C$\underline{H}_2$CH, J = 13.1 Hz, J = 10.2 Hz); 3.62 (dd, 1 H, $CH_2C\underline{H}$, J = 10.2 Hz, J = 3.5 Hz); 3.69 (s, 3 H, MeO); 3.72 (s, 3 H, MeO); 3.80 (s, 3 H, MeO); 6.94 (s, 1 H, Ar); 7.19—7.24 (m, 2 H, Ar); 7.31—7.36 (m, 1 H, Ar); 7.44—7.46 (m, 2 H, Ar); 10.17 (s, CHO). ^{13}C NMR, δ: –0.79 ($SiMe_3$); 21.86 ($\underline{C}H_2CH$); 55.29; 55.97; 60.53; 60.58; 107.44; 126.76; 127.90; 128.40; 129.80; 131.93; 142.53; 146.56; 151.81; 152.32; 190.13 (CHO).

4,5-Methylenedioxy-2-[2-phenylsulfonyl-2-(trimethylsilyl)ethyl]benzaldehyde (8). The yield was 44%, colorless crystals, m.p. 99—101 °C. Found (%): C, 58.36; H, 5.64. $C_{19}H_{29}O_5SSi$. Calculated (%): C, 58.43; H, 5.68. IR, ν/cm^{-1}: 1681 (HC=O). ^{1}H NMR, δ: 0.37 (s, 9 H, $SiMe_3$); 3.19 (dd, 1 H, C$\underline{H}_2$CH, J = 14.5 Hz, J = 10.4 Hz); 3.46 (dd, 1 H, C$\underline{H}_2$CH, J = 14.2 Hz, J = 4.5 Hz); 3.60 (dd, 1 H, $CH_2C\underline{H}$, J = 10.4 Hz, J = 4.5 Hz); 5.95 (s, 2 H, OCH_2O); 6.62 (s, 1 H, Ar); 6.81 (s, 1 H, Ar); 7.21—7.25 (m, 2 H, Ar); 7.33—7.37 (m, 1 H, Ar); 7.43—7.46 (m, 2 H, Ar); 9.64 (s, CHO). ^{13}C NMR, δ: –0.77 ($SiMe_3$); 30.59 ($\underline{C}H_2CH$); 55.71 ($CH_2\underline{C}H$); 102.01 (OCH_2O); 112.29; 112.57; 126.81; 128.16; 128.29; 131.87; 136.82; 142.56; 146.69; 151.46; 190.00 (CHO).

3-[2-Phenylsulfonyl-2-(trimethylsilyl)ethyl]thiophene-2-carbaldehyde (9). Tetrahydrofuran (5 mL) was added to a 1.6 *M* Bu^{n}Li solution in hexane (3.3 mL, 5.28 mmol) cooled to –30 °C. Then the reaction mixture was cooled to –80 °C and a solution of 2,3-dibromothiophene (1.21 g, 5 mmol) in THF (5 mL) was added. The reaction mixture was stirred at –70 °C for 30 min and cooled to –80 °C. Then a solution of anhydrous DMF (0.385 g, 5.28 mmol) in THF (5 mL) was added. The reaction was heated to –40 °C, stirred at this temperature for 5 min, and cooled to –80 °C, after which a solution of phenylsulfonylethylene **1** (1.2 g, 5 mmol) in THF (10 mL) was added, the temperature being maintained below –70 °C. Then the temperature was raised to –10 °C and the reaction mixture was poured into 0.5 *M* hydrochloric acid (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (2×20 mL). The combined organic fractions were dried with $CaCl_2$ and concentrated *in vacuo*. The product was isolated

from the residue by chromatography (CH_2Cl_2 as the eluent). The yield was 50%, colorless oil. Found (%): C, 54.75; H, 5.79. $C_{18}H_{22}O_3SSi$. Calculated (%): C, 54.51; H, 5.72. IR, ν/cm^{-1}: 1698 (HC=O). ^{1}H NMR, δ: 0.34 (s, 9 H, $SiMe_3$); 3.24 (dd, 1 H, C$\underline{H}_2$CH, J = 11.9 Hz, J = 1.3 Hz); 3.40 (dd, 1 H, CH$_2$C$\underline{H}$, J = 11.9 Hz, J = 8.8 Hz); 3.42 (dd, 1 H, C$\underline{H}_2$CH, J = 8.8 Hz, J = 1.3 Hz); 6.72 (d, 1 H, H of thiophene, J = 5.0 Hz); 7.26—7.31 (m, 2 H, Ar); 7.38 (d, 1 H, H of thiophene, J = 5.0 Hz); 7.39—7.43 (m, 1 H, Ar); 7.53—7.55 (m, 2 H, Ar); 9.70 (s, CHO). ^{13}C NMR, δ: –0.98 ($SiMe_3$); 26.05 (C$\underline{H}_2$CH); 55.88 (CH$_2$C$\underline{H}$); 126.95; 128.74; 130.85; 132.53; 134.07; 137.89; 141.59; 146.49; 181.66 (CHO).

Cyclization of aldehydes 3—9 (general procedure). A solution of the corresponding aldehyde (1 mmol) in THF (5 mL) was added to a solution of Bu^{t}OK (0.235 g, 2.1 mmol) in THF (10 mL). The course of the reaction was monitored by TLC. The reaction mixture was stirred for 5 min, poured into 0.5 *M* hydrochloric acid (20 mL), and extracted with ether (2×10 mL). The extract was dried with $CaCl_2$ and concentrated *in vacuo*. The product was purified by passing through a short column with silica gel (CH_2Cl_2—hexane, 3 : 1, as the eluent).

2-Phenylsulfonyl-1*H*-indene (10). The yield was 94%, colorless crystals, m.p. 121—122 °C (*cf.* lit. data[27]: m.p. 120—122 °C). ^{1}H NMR, δ: 3.63 (d, 2 H, CH$_2$, J = 1.7 Hz); 7.31—7.36 (m, 2 H); 7.42—7.44 (m, 1 H); 7.51—7.55 (m, 3 H); 7.58—7.62 (m, 1 H, Ar); 7.70 (t, 1 H, J = 1.7 Hz); 7.97—7.99 (m, 2 H, Ar). ^{13}C NMR, δ: 37.86 (CH$_2$); 124.00; 124.35; 127.39; 127.74; 128.28; 129.30; 133.35; 140.62; 140.86; 141.00; 144.30; 145.26.

A mixture of 5-fluoro-2-phenylsulfonyl-1*H*-indene (11a) and 6-fluoro-2-phenylsulfonyl-1*H*-indene (11b) (1 : 1.6). The yield was 84%, colorless crystals, m.p. 115—117 °C. Found (%): C, 65.90; H, 4.07. $C_{15}H_{11}FO_2S$. Calculated (%): C, 65.68; H, 4.04. ^{1}H NMR, δ: 3.60 (d, 2 H, CH$_2$ (**11a**), J = 1.1 Hz); 3.62 (br.s, 2 H, CH$_2$ (**11b**)); 7.00—7.07 (m, 2 H, H(6) (**11a**), H(5) (**11b**)); 7.13 (dd, 1 H, H(7) (**11b**), $^3J_{H,F}$ = 9.1 Hz, J = 1.9 Hz); 7.19 (dd, 1 H, H(4) (**11a**), $^3J_{H,F}$ = 8.5 Hz, J = 2.5 Hz); 7.36 (dd, 1 H, H(7) (**11a**), J = 8.2 Hz, $^4J_{H,F}$ = 4.9 Hz); 7.46 (dd, 1 H, H(4) (**11b**), J = 8.2 Hz, $^4J_{H,F}$ = 4.9 Hz); 7.52—7.56 (m, 4 H, Ph (**11a**), Ph (**11b**)); 7.58—7.62 (m, 3 H, H(3) (**11a**), Ph (**11a**), Ph (**11b**)); 7.64 (t, 1 H, H(3) (**11b**), J = 1.1 Hz); 7.96—7.99 (m, 4 H, Ph (**11a**), Ph (**11b**)). ^{13}C NMR, δ: 37.29 (CH$_2$ (**11a**)); 38.01 (d, CH$_2$ (**11b**), $^4J_{C,F}$ = 2.6 Hz); 110.80 (d, C(6) (**11a**), $^3J_{C,F}$ = 23.5 Hz); 112.09 (d, C(7) (**11b**), $^3J_{C,F}$ = 23.5 Hz); 114.87 (d, C(5) (**11b**), $^3J_{C,F}$ = 23.5 Hz); 115.37 (d, C(4) (**11a**), $^3J_{C,F}$ = 23.5 Hz); 125.10 (d, C(4) (**11b**), $^4J_{C,F}$ = 10.4 Hz); 125.38 (d, C(7) (**11a**), $^4J_{C,F}$ = 9.1 Hz); 127.72; 127.81; 129.34; 129.36; 133.42; 133.53; 140.10; 162.96 (d, C(5) (**11a**), $^1J_{C,F}$ = –217.8 Hz); 165.56 (d, C(6) (**11b**), $^1J_{C,F}$ = –242.6 Hz).

A mixture of 5-methoxy-2-phenylsulfonyl-1*H*-indene (12a) and 6-methoxy-2-phenylsulfonyl-1*H*-indene (12b) (1 : 2.5). The yield was 72%, colorless oil. ^{1}H NMR, δ: 3.56 (dd, 2 H, CH$_2$ (**12a**), J = 1.9 Hz, J = 0.6 Hz); 3.59 (d, 2 H, CH$_2$ (**12b**), J = 1.9 Hz); 3.81 (s, 6 H, MeO (**12b**), MeO (**12a**)); 6.86—6.90 (m, 2 H, H(4) (**12a**), H(5) (**12b**)); 7.03 (m, 1 H, H(6) (**12a**)); 7.30 (dd, 1 H, H(7) (**12a**), J = 8.3 Hz); 7.41 (d, 1 H, H(4) (**12b**), J = 8.6 Hz); 7.50—7.55 (m, 4 H, Ph (**12a**), Ph (**12b**)); 7.56—7.60 (m, 3 H, H(3) (**12a**), H$_p$, Ph (**12a**), H$_p$, Ph (**12b**)); 7.64 (t, 1 H, H(3) (**12b**), J = 1.9 Hz); 7.95—7.98 (m, 4 H, Ph (**12a**), Ph (**12b**)); 7.98 (d, 1 H, H(7) (**12b**), J = 1.8 Hz). ^{13}C NMR, δ: 37.19 (CH$_2$ (**12a**)); 37.91 (CH$_2$ (**12b**)); 55.10 (MeO (**12a**)); 55.55 (MeO (**12b**)); 108.69; 110.28; 113.62; 115.14; 124.78; 124.92; 127.61; 127.74; 128.10; 129.24; 129.28; 133.12; 133.31; 133.90; 134.48; 140.65; 140.90; 141.05; 142.43; 146.75; 160.55.

5,6-Dimethoxy-2-phenylsulfonyl-1*H*-indene (13). The yield was 71%, colorless crystals, m.p. 126—128 °C. Found (%): C, 64.54; H, 5.10. $C_{17}H_{16}O_4S$. Calculated (%): C, 64.40; H, 5.24. ^{1}H NMR, δ: 3.53 (d, 2 H, CH$_2$, J = 1.8 Hz); 3.85 (s, 6 H, 5- and 6-MeO); 6.95 (s, 1 H, H(7)); 6.99 (s, 1 H, H(4)); 7.46—7.50 (m, 2 H, Ph); 7.52—7.56 (m, 1 H, Ph); 7.60 (t, 1 H, H(3), J = 1.8 Hz); 7.91—7.94 (m, 2 H, Ph). ^{13}C NMR, δ: 38.04 (CH$_2$); 56.00 (MeO); 55.10 (MeO); 112.65; 115.25; 127.80; 129.75; 133.62; 140.90; 141.12; 141.82; 144.86; 146.28; 148.29; 153.36.

A mixture of 4,5,6-trimethoxy-2-phenylsulfonyl-1*H*-indene (14a) and 5,6,7-trimethoxy-2-phenylsulfonyl-1*H*-indene (14b) (1 : 1.4). The yield was 70%, colorless oil. Found (%): C, 62.41; H, 5.24. $C_{18}H_{18}O_5S$. Calculated (%): C, 62.52; H, 5.38. ^{1}H NMR, δ: 3.56 (dd, 2 H, CH$_2$ (**14a**), J = 1.8 Hz, J = 0.8 Hz); 3.58 (d, 2 H, CH$_2$ (**14b**), J = 1.8 Hz); 3.82, 3.83, 3.84, 3.85, 3.92, and 3.99 (all s, 3 H each, MeO); 6.75 (s, 1 H, H(7) (**14a**)); 6.82 (s, 1 H, H(4) (**14b**)); 7.48—7.53 (m, 4 H, Ph (**14a**), Ph (**14b**)); 7.54—7.59 (m, 3 H, H(3) (**14b**), Ph (**14a**), Ph (**14b**)); 7.78 (t, 1 H, H(3) (**14a**), J = 1.8 Hz); 7.93—7.96 (m, 4 H, Ph (**14a**), Ph (**14b**)). ^{13}C NMR, δ: 35.31 (CH$_2$ (**14a**)); 38.57 (CH$_2$ (**14b**)); 55.48; 56.84; 58.25; 59.10; 60.22; 60.81; 105.64; 107.32; 115.47; 118.44; 128.21; 128.52; 129.72; 129.85; 133.42; 133.64; 140.25; 140.67; 141.28; 141.56; 146.75; 147.14; 151.12; 151.27; 152.13; 152.53.

5,6-Methylenedioxy-2-phenylsulfonyl-1*H*-indene (15). The yield was 71%, colorless crystals, m.p. 176—178 °C. Found (%): C, 64.01; H, 4.12. $C_{16}H_{12}O_4S$. Calculated (%): C, 63.99; H, 4.03. ^{1}H NMR, δ: 3.52 (dd, 2 H, CH$_2$, J = 2.1 Hz, J = 0.8 Hz); 5.97 (s, 2 H, OCH$_2$O); 6.88 (s, 1 H, H(7)); 6.93 (s, 1 H, H(4)); 7.49—7.53 (m, 2 H, Ph); 7.55—7.59 (m, 2 H, H$_p$ (Ph), H(3)); 7.93—7.96 (m, 2 H, Ph). ^{13}C NMR, δ: 37.94 (CH$_2$); 102.58 (OCH$_2$O); 112.84; 113.45; 127.65; 129.36; 133.58; 141.05; 141.28; 141.67; 143.95; 145.93; 147.48; 151.22.

A mixture of 5-phenylsulfonyl-4*H*-cyclopenta[*b*]thiophene (16a) and 5-phenylsulfonyl-6*H*-cyclopenta[*b*]thiophene (16b) (1.7 : 1). The yield was 60%, colorless oil. Found (%): C, 59.52; H, 3.84. $C_{13}H_{10}O_2S_2$. Calculated (%): C, 59.60; H, 4.06. ^{1}H NMR, δ: 3.49 (d, 2 H, CH$_2$ (**16a**), J = 1.8 Hz); 3.62 (d, 2 H, CH$_2$ (**16b**), J = 1.8 Hz); 7.03 (d, 1 H, H of thiophene (**16a**), J = 4.8 Hz); 7.05 (d, 1 H, H of thiophene (**16b**), J = 5.2 Hz); 7.31 (d, 1 H, H of thiophene (**16b**), J = 5.2 Hz); 7.43 (d, 1 H, H of thiophene (**16a**), J = 4.8 Hz); 7.49—7.54 (m, 4 H, Ph (**16a**), Ph (**16b**)); 7.56—7.60 (m, 2 H, Ph (**16a**), Ph (**16b**)); 7.66 (t, 1 H, =CH (**16b**), J = 1.8 Hz); 7.70 (t, 1 H, =CH (**16a**), J = 1.8 Hz); 7.94—7.97 (m, 4 H, Ph (**16a**), Ph (**16b**)). ^{13}C NMR, δ: 35.27 (CH$_2$ (**16a**)); 35.87 (CH$_2$ (**16b**)); 120.11; 122.29; 127.52; 128.01; 129.28; 129.49; 131.33; 133.14; 136.39; 137.36; 141.20; 141.25; 141.56; 144.84; 145.96; 146.37; 147.83; 151.32.

Reaction of 2-phenylsulfonyl-1*H*-indene (10) with methylmagnesium iodide. A solution of MeI (0.93 mL, 2.12 g, 15 mmol) in THF (5 mL) was added dropwise with stirring to a suspension of Mg (0.73 g, 15 mmol) in anhydrous THF (5 mL) and the reaction mixture was refluxed for 30 min. Then Ni(acac)$_2$ (0.129 g, 0.5 mmol) or Fe(acac)$_3$ (0.177 g, 0.5 mmol) and a solution of indene **10** (1.28 g, 5 mmol) in THF (10 mL) were added. The reaction mixture was refluxed with stirring for 12 h, decomposed with hydrochloric acid, and extracted with ether (2×15 mL). The extract was dried with $CaCl_2$ and concentrated *in vacuo*. The product was isolated from the residue by passing

through a short column with silica gel (hexane as the eluent). The yield of the indene was 11% (with $Ni(acac)_2$) and 22% (with $Fe(acac)_3$). The ^1H NMR spectrum of the indene was identical with that published in the literature.[28]

Reaction of 2-phenylsulfonyl-1*H*-indene (10) with phenylmagnesium bromide. A solution of bromobenzene (1.28 mL, 2.36 g, 15 mmol) in THF (5 mL) was added dropwise with stirring to a suspension of Mg (0.73 g, 15 mmol) in anhydrous THF (5 mL) and the reaction mixture was refluxed for 30 min. Then $Fe(acac)_3$ (0.177 g, 0.5 mmol) and a solution of indene **10** (1.28 g, 5 mmol) in THF (10 mL) were added. The reaction mixture was refluxed with stirring for 24 h, decomposed with dilute hydrochloric acid, and extracted with ether (2×15 mL). The extract was dried with $CaCl_2$ and concentrated *in vacuo*. The product was isolated from the residue by passing through a short column with silica gel (hexane—CH_2Cl_2, 3 : 1, as the eluent). 2-Phenylsulfonyl-1*H*-indene, biphenyl, and 2-phenylindene were obtained in yields of 0.46 g (36%), 0.25 g (32%), and 0.31 g (32%), respectively. The ^1H NMR spectra of the products were identical with those published in the literature.[29]

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References

1. C. Janiak, in *Metallocenes*, Eds. A. Togni and R. L. Halterman, Wiley-VCH, Weinheim, 1998, **2**, 547.
2. V. Snieckus, *Chem. Rev.*, 1990, **90**, 879.
3. D. L. Comins, J. D. Brown, and N. B. Mantlo, *Tetrahedron Lett.*, 1982, **23**, 3979.
4. L. Barsky, H. W. Gschwend, J. McKenna, and H. R. Rodriguez, *J. Org. Chem.*, 1976, **41**, 3651.
5. J. Einhorn, J.-L. Luche, and P. Demerseman, *J. Chem. Soc., Chem. Commun.*, 1988, 1350.
6. N. P. Peet, J. R. McCarthy, S. Sunder, and J. McCowan, *Synth. Commun.*, 1986, **16**, 1551.
7. D. L. Comins, M. F. Baevsky, and H. Hong, *J. Am. Chem. Soc.*, 1992, **114**, 10971.
8. F. Denat, H. Gaspard-Iloughmane, and J. Dubac, *Synthesis*, 1992, 954.
9. T. R. Kelly and M. H. Kim, *J. Org. Chem.*, 1992, **57**, 1593.
10. A. Schoning and W. Friedrichsen, *Tetrahedron Lett.*, 1988, **29**, 1137.
11. A. K. Sinhababu and R. T. Borchardt, *J. Org. Chem.*, 1983, **48**, 2356.
12. D. Craig, S. V. Ley, N. S. Simpkins, G. H. Whitham, and M. J. Prior, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1949.
13. K. Schank and F. Schroeder, *Liebigs Ann. Chem.*, 1977, 1676.
14. D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, 1986, 183.
15. C. Palomo, J. M. Aizpurua, J. M. Garcia, I. Ganboa, F. P. Cossio, B. Lecea, and C. Lopez, *J. Org. Chem.*, 1990, **55**, 2498.
16. A. Numata, Y. Kondo, and T. Sakamoto, *Synthesis*, 1999, 306.
17. N. Miyamoto, D. Fukuoka, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 503.
18. H. C. Brown, S.-C. Kim, and S. Krishnamurthy, *Organometallics*, 1983, **2**, 779.
19. J.-L. Fabre, M. Julia, and J.-N. Verpeaux, *Tetrahedron Lett.*, 1982, **23**, 2469.
20. J.-L. Fabre, M. Julia, and J.-N. Verpeaux, *Bull. Soc. Chim. Fr.*, 1985, 763.
21. J.-L. Fabre, M. Julia, and J.-N. Verpeaux, *Bull. Soc. Chim. Fr.*, 1985, 772.
22. N. O. Brace, *J. Org. Chem.*, 1993, **58**, 4506.
23. B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 522.
24. R. Pschorr, *Liebigs Ann. Chem.*, 1912, 23.
25. A. I. Meyers, J. R. Flisak, and R. A. Aitken, *J. Am. Chem. Soc.*, 1987, **109**, 5446.
26. R. Brown, J.-P. Robin, and R. Dhal, *Tetrahedron*, 1982, **38**, 2569.
27. W. E. Truce and C. T. Goralski, *J. Org. Chem.*, 1970, **35**, 4221.
28. L. Stille, *J. Am. Chem. Soc.*, 1976, **98**, 5841.
29. T. Sugimoto, K. Teshima, N. Nakamura, M. Nojima, S. Kusabayashi, and K. J. McCullough, *J. Org. Chem.*, 1993, **58**, 135.

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