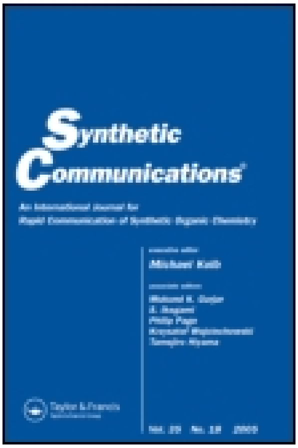

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A Convenient One-Pot Preparation of Benzo[b]-tellurophenes,-selenophenes, and -thiophenes from o-Bromoethynylbenzenes

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A CONVENIENT ONE-POT PREPARATION OF BENZO[b] -TELLUROPHENES, -SELENOPHENES, AND -THIOPHENES FROM *o*-BROMOETHYNYLBENZENES

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ABSTRACT: 2-Substituted and unsubstituted benzo[b]tellurophenes (**3Aa-e**) were synthesized in one-pot from *o*-bromoethynylbenzenes (**2**) *via* three steps in good yields. Similarly, benzo[b]-selenophenes (**3Ba-e**) and -thiophenes (**3Ca-e**) were also obtained.

Considerable attention[1] has been directed toward the synthesis and reactions of monocyclic and benzene ring fused heterocycles containing a chalcogen element (Te, Se, and S) because of their chemical reactivities and synthetic utilities. In particular, various synthetic methods for preparation of five-membered heterocycles, benzo[b] -thiophenes,[2] -selenophenes,[3] and -tellurophenes[4] have been provided. However, the synthetic techniques for these

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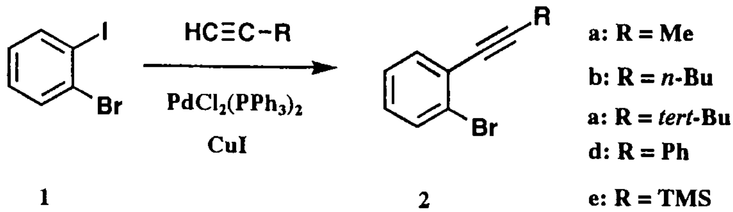
compounds have always been applied with limited success and generality in each case. We herein describe a versatile one-pot preparation of the five-membered title compounds from *o*-bromoethynylbenzenes (**2**) as common key starting materials.

The compounds **2** were readily obtained by palladium-catalyzed coupling reaction of *o*-bromoiodobenzene (**1**)[5] with 1-substituted acetylenes according to the reported method[6] in excellent yields, as shown in Scheme 1. They were lithiated with *tert*-butyllithium in anhydrous ether, followed by treatment with Te, Se, or S powder, and then ethanolyzed to afford the corresponding five-membered heterocycles (**3**) as a sole product in good yields in one-pot. The results are summarized in Table 1.

Trimethylsilyl (TMS) group is well known to be removed by treatment with alkali in alcohol or fluoride anion containing water. In the present case, reductive removal of TMS group was also effective. Thus treatment of 2-TMS derivatives (**3Ae-Ce**) with sodium borohydride in refluxing ethanol gave the corresponding 2-unsubstituted (**3Af-Cf**) in good yields, respectively. The ^{1}H-NMR spectral data for these compounds (**3**) are listed in Tables 2, 3 and 4. The high-resolution mass (MS) spectral and ^{13}C-NMR spectral data are shown in Tables 5, 6 and 7.

It has already been reported[7] and well known that the stereo-specific intermolecular *trans*-additions of unisolable phenyltelluroles and relatives to acetylenic compounds proceeded to afford the vinyl tellurides. In addition, we have previously presented the synthesis of novel seven-membered heterocyclic systems, 1-benzotellurepines and 1-benzoselenepines,[8] by an intramolecular ring closure of phenyl -telluroles and -selenoles generated by sodium borohydride reduction of the corresponding ditellurides and diselenides having a triple bond, respectively. These results clearly support that a possible mechanism for formation of **3** is that shown in Scheme 2.



Scheme 1

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and HR-MS were recorded on a JEOL JMS-DX300 instrument. NMR spectra were determined with a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as internal standard.

Preparation of *o*-bromoethynylbenzenes (2); General procedure:

In the literature,[6] this coupling reaction was carried out using diethylamine as a solvent . However, when a mixed solution of benzene and piperidine in stead of diethylamine was used, the product yields were remarkably elevated. To a mixture of alkyne (b: 1-hexyne, c: *tert*-butylacetylene, d: phenylacetylene, e: trimethylsilylacetylene, 0.11mol) and o-bromoiodobenzene (**1**, 28.3g, 0.1mol) in benzene (200ml) and piperidine (200ml) were added bis [triphenylphosphine] palladium dichloride (II) (702mg, 1mmol) and copper (I) iodide (400mg, 2.1mmol). The reaction mixture was heated at 80-90 °C with stirring until disappearance of starting material (about 10-15 h). After cooling, cold water (300ml) was added to the mixture, and the resulting aqueous mixture was

Table 1. Benzo[b]-tellurophenes(**3A**), -selenophenes(**3B**) and -thiophenes(**3C**)

Compd. No.	X	R	Yield (%)[a]	Appearance
3Aa	Te	Me	72	colorless prisms[b)] mp 55-57 °C (Lit.[4e] mp 58 °C)
3Ab	Te	*n*-Bu	70	pale yellow oil
3Ac	Te	*tert*-Bu	74	pale yellow oil
3Ad	Te	Ph	67	colorless prisms[c)] mp 123-125 °C
3Ae	Te	TMS	45	pale yellow oil
3Ba	Se	Me	67	colorless prisms[d)] mp 54-56 °C (Lit.[2b] mp 63 °C)
3Bb	Se	*n*-Bu	77	pale yellow oil
3Bc	Se	*tert*-Bu	64	colorless oil
3Bd	Se	Ph	78	colorless prisms[e)] mp 160 °C
3Be	Se	TMS	57	colorless oil
3Ca	S	Me	72	colorless prisms[b)] mp 51-52 °C (Lit.[2c] mp 50 °C)
3Cb	S	*n*-Bu	58	colorless oil
3Cc	S	*tert*-Bu	77	yellow oil
3Cd	S	Ph	68	colorless prisms [b)] mp 173-176 °C (Lit.[2c] mp 170-171 °C)
3Ce	S	TMS	70	yellow oil

a) isolated yields.
b) recrystallized from EtOH.
c) recrystallized from *n*-hexane.
d) recrystallized from MeOH.
e) recrystallized from *n*-hexane-EtOH.

Table 2. ^{1}H-NMR Spectral Data for the 3-Benzo[b]tellurophenes (**3A**)

Compd. No.	^{1}H-NMR (90 MHz, $CDCl_3$, J=Hz) 3-H	4-H	5-H	6-H	7-H	2-R
3Aa	7.43 (d) (J =1.0)	6.87-7.33 (2H, m, 5-H, 6-H) 7.60-7.88 (2H, m, 4-H, 7-H)				2.63 (3H, d, J=1.0) R=Me
3Ab	7.42 (s)	7.60 (d) (J=8.1)	7.00 (dd) (J=7.6, 8.1)	7.26 (dd) (J=7.3, 8.1)	7.77 (d) (J=8.1)	0.92, 1.35-1.65, 2.85 (3H, t, J=7.3, 4H, m, 2H, t, J=7.7) R=*n*-Bu
3Ac	7.43 (s)	7.61 (d) (J=8.1)	7.00 (dd) (J=7.6, 8.1)	7.27 (dd) (J=7.3, 7.6)	7.78 (d) (J=7.3)	1.37 (9H, s) R=*tert*-Bu
3Ad			7.12-8.03 (10H, m)			R=Ph
3Ae	7.93 (s)	7.54 (d) (J=8.4)	6.83 (dd) (J=7.3, 8.4)	7.08 (dd) (J=7.3, 7.7)	7.66 (d) (J=7.7)	0.07 (9H, s) R=TMS
3Af	7.96 (d) (J =7.0)	7.84 (d) (J=7.7)	7.14 (dd) (J=7.7, 8.1)	7.37 (d) (J=7.0, 8.1)	7.96 (d) (J=7.0)	8.70 (1H, d, J=7.3) 2-H

Table 3. ^{1}H-NMR Spectral Data for the Benzo[b]selenophenes (**3B**)

Compd. No.	^{1}H-NMR (90 MHz, $CDCl_3$, J=Hz)					
	3-H	4-H	5-H	6-H	7-H	2-R
3Ba	7.20 (d) (J=1.0)	7.12-7.30 (2H, m, 5-H, 6-H) 7.53-7.87 (2H, m, 4-H, 7-H)				2.63 (3H, d, J=1.0) R=Me
3Bb	7.15 (s)	7.63 (d) (J=7.7)	7.17 (dd) (J=7.0, 7.7)	7.29 (dd) (J=7.0, 7.0)	7.79 (d) (J=7.0)	0.95, 1.40-1.75, 2.93 (3H, t, J=7.3, 4H, m, 2H, t, J= 7.0) R=*n*-Bu
3Bc	7.13 (s)	7.59 (d) (J=7.7)	7.11 (dd) (J=7.3, 7.7)	7.24 (dd) (J=7.7, 8.1)	7.74 (d) (J=8.1)	1.38 (9H, s) R=*tert*-Bu
3Bd	7.69 (s)	7.76 (d) (J=7.7)	7.62-7.64 (2H, m, 5H, 6-H)		7.85 (d) (J=8.1)	7.21-7.41 (5H, m) R=Ph
3Be	7.71 (s)	7.77 (d) (J=7.7)	7.20 (dd) (J=7.3, 7.7)	7.32 (dd) (J=7.3, 7.7)	7.89 (d) (J=7.7)	0.35 (9H, s) R=TMS
3Bf	7.54 (d) (J=5.8)	7.18-8.07 (4H, m, 4H, 5-H, 6-H, 7-H)				7.93 (d, J=5.8) R=H

Table 4. [1] H-NMR Spectral Data for the Benzo[b]thiophenes (**3C**)

Compd. No.	^{1}H-NMR (90 MHz, $CDCl_3$, J=Hz) 3-H	4-H	5-H	6-H	7-H	2-R
3Ca	6.96 (d) (J=1.0)	7.03-7.37 (2H, m, 5-H, 6-H) 7.52-7.77 (2H, m, 4-H, 7-H)				2.50 (3H, d, J= 1.0) R=Me
3Cb	6.91 (s)	7.60 (d) (J=7.7)	7.18 (dd) (J=7.2, 7.7)	7.24 (dd) (J=7.2, 7.7)	7.70 (d) (J=7.7)	0.92, 1.33-1.72, 2.83 (3H, t, J=7.3, 4H, m, 2H, t, J= 7.0) R=*n*-Bu
3Cc	6.98 (s)	7.62 (d) (J=8.1)	7.19 (dd) (J=7.7, 8.1)	7.25 (dd) (J=7.3, 7.7)	7.71 (d) (J=7.3)	1.41 (9H, s) R=*tert*-Bu
3Cd	7.53 (s)	7.76 (d) (J=7.3)	7.59-7.72 (2H, m, 5-H, 6-H)		7.82 (d) (J=7.7)	7.28-7.43 (5H,m) R=Ph
3Ce	7.44 (s)	7.77 (d) (J=7.3)	7.26-7.30 (2H, m, 5-H, 6-H)		7.85 (d) (J=7.7)	0.36 (9H, s) R=TMS
3Cf	7.30 (d) (J=5.5)	7.23-7.30 (4H, m, 4-H, 5-H, 6-H, 7-H)				7.39 (1H, J=5.5) R=H

Table 5. Spectral Data for the 3-Benzo[b]tellurophenes (**3A**)

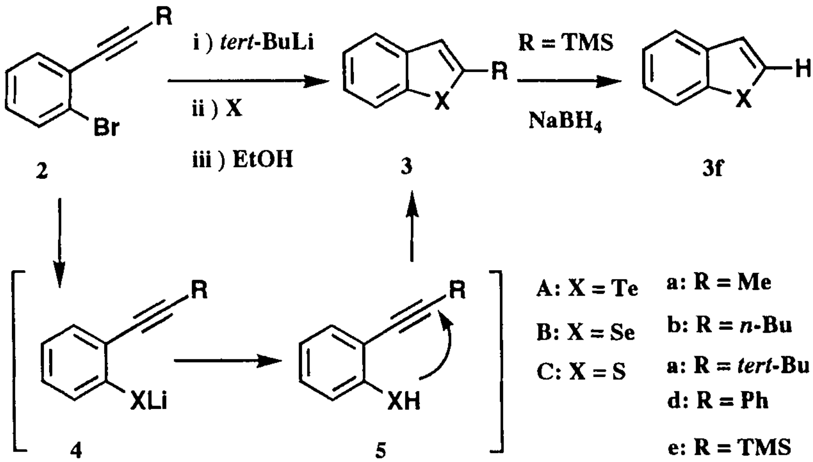
Compd. No.	HR-MS Formula Calcd (Found)	^{13}C-NMR (100 MHz, $CDCl_3$)
3Aa	C_9H_8Te 245.9689 (245.9687	23.18 (q), 123.77 (d), 125.30 (d), 126.54 (d), 132.07 (d), 132.65 (s), 134.54 (d), 138.07 (s), 144.66(s)
3Ab	$C_{12}H_{14}Te$ 288.0158 (288.0156)	13.83 (q), 22.08 (t), 35.67 (t), 36.94 (t), 123.51 (d), 125.05 (d), 126.49 (d), 131.56 (s), 131.88 (d), 132.51 (d), 146.68 (s), 148.21 (s)
3Ac	$C_{12}H_{14}Te$ 288.0158 (288.0160)	33.45 (q), 38.69 (s), 123.56 (d), 125.05 (d), 126.83 (d), 129.44 (d), 131.06 (s), 131.67 (d), 148.69 (s), 160.67 (s)
3Ad	$C_{14}H_{10}Te$ 307.9845 (307.9844)	124.54 (d), 125,66 (d), 127.59 (d), 127.83 (d), 128.18 (d), 129.07 (d), 131.95 (d), 140.38 (s), 143.30 (s), 144.93 (s), 149.30 (s)
3Ae	$C_{11}H_{14}SiTe$ 303.9927 (303.9883)	0.46 (q), 124.16 (d), 124.94 (d), 127.63 (d), 131.95 (d), 135.15 (s), 142.45 (s), 142.58 (d), 150.69 (s)
3Af	C_8H_6Te 231.9531 (231.9533)	120.55 (d), 124.27 (d), 125.12 (d), 127.64 (d), 132.08 (d), 132.71 (s), 136.81 (d), 148.15 (s)

Table 6. Spectral Data for the Benzo[b]selenophenes (**3B**)

Compd. No.	HR-MS Formula Calcd (Found)	^{13}C-NMR (100 MHz, $CDCl_3$)
3Ba	C_9H_8Se 195.9791 (195.9799)	18.72 (q), 123.63 (d), 124.23 (d), 124.41 (d), 125.31 (d), 125.37 (d), 141.29 (s), 142.81 (s), 144.50 (s)
3Bb	$C_{12}H_{14}Se$ 238.0261 (238.0252)	13.82 (q), 22.17 (t), 32.99 (t), 34.00 (t), 123.57 (d), 123.95 (d), 124.24 (d), 124.35 (d), 125.38 (d), 140.71 (s), 142.58 (s), 151.22 (s)
3Bc	$C_{12}H_{14}Se$ 238.0261 (238.0252)	32.65 (q), 36.56 (s), 121.03 (d), 123.62 (d), 124.30 (d), 124.58 (d), 125.22 (d), 140.18 (s), 142.58 (s), 163.30 (s)
3Bd	$C_{14}H_{10}Se$ 257.9948 (257.9944)	123.02 (d), 124.48 (d), 124.83 (d), 125.35 (d), 125.38 (d), 126.86 (d), 128.23 (d), 128.93 (d), 136.17 (s), 140.93 (s), 143.23 (s), 147.67 (s)
3Be	$C_{11}H_{14}SiSe$ 206.0586 (206.0590)	0.01 (q), 124.29 (d), 124.32 (d), 125.22 (d), 125.44 (d), 134.51 (d), 143.73 (s), 144.50 (s), 147.19 (s)
3Bf	C_8H_6Se 181.9635 (181.9633)	124.35 (d), 124.46 (d), 125.35 (d), 125.63 (d), 127.73 (d), 128.62 (d), 141.23 (s), 142.02 (s)

Table 7. Spectral Data for the Benzo[b]thiophenes (**3C**)

Compd. No.	HR-MS Formula Calcd (Found)	^{13}C-NMR (100 MHz, $CDCl_3$)
3Ca	C_9H_8S 148.0347 (148.0350)	reported in ref. 2c
3Cb	$C_{12}H_{14}S$ 190.0816 (190.0826)	13.76 (q), 22.51 (t), 30.40 (t), 33.16 (t), 120.32 (d), 122.01 (d), 122.57 (d), 123.24 (d), 123.91 (d), 139.26 (s), 140.18 (s), 146.65 (s)
3Cc	$C_{12}H_{14}S$ 190.0816 (190.0819)	32.12 (q), 34.83 (s), 117.63 (d), 122.04 (d), 122.83 (d), 123.37 (d), 123.92 (d), 138.87 (s), 140.02 (s), 158.08 (s)
3Cd	$C_{14}H_{10}S$ 210.0503 (210.0500)	reported in ref. 2c
3Ce	$C_{11}H_{14}SiS$ 206.0586 (206.0590)	0.00 (q), 122.17 (d), 123.38 (d), 123.97 (d), 124.11 (d), 130.81 (d), 141.07 (s), 142.17 (s), 143.52 (s)
3Cf	C_8H_6S 134.0190 (134.0185)	reported in ref. 2e



Scheme 2

extracted with benzene (200 x 3). The combined organic extract was washed with water (200 x 5), 5% H_2SO_4 (200 x 3), sat.$NaHCO_3$ (200 ml x 2) and brine (200 x 2), then dried over $MgSO_4$. Benzene was removed *in vacuo*. The red residual oil was purified by distillation under reduced pressure to give pure **2**. In the case of **2a**, a slow current of methylacetylene, which was prepared from 1,2-dibromopropane and KOH in refluxing *n*-butanol, was immediately passed through the reaction mixture without isolation.

2a: 93% yield, colorless oil, bp 104-108 °C (10mm Hg). IR (neat): 2232 (C≡C) cm^{-1}. ^{1}H-NMR (60 MHz) : 2.40 (3H, s, Me),7.02-7.97 (4H, m, Ar-H). HR-MS *m/z*;

M^+ Calcd for C_9H_7Br: 193.9731, 195.9711. Found: 193.9735, 195.9719.

2b: 78% yield, colorless oil, bp 135-138 °C (8mm Hg). IR (neat): 2236 (C≡C) cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.95, 1.37-1.63, 2.29

(3H, t, *J*=7 Hz, 4H, m, 2H, t, *J*=6 Hz, *n*-Bu), 6.85-8.00 (4H, m, Ar-H). HR-MS *m/z*; M^+ Calcd for $C_{12}H_{13}Br$: 236.0201, 238.0180. Found: 236.0202, 238.0188.

2c: 81% yield, colorless oil, bp 112-115 °C (9mm Hg). IR (neat): 2244 (C≡C) cm^{-1}. ^1H-NMR (60 MHz) δ : 1.33 (9H, s, *tert*-Bu), 6.92-7.62 (4H, m, Ar-H). HR-MS *m/z*; M^+ Calcd for $C_{12}H_{13}Br$: 236.0201, 238.0180. Found: 236.0206, 238.0189.

2d: 91% yield, colorless oil, bp 154-156 °C (3mm Hg). IR (neat): 2200 (C≡C) cm^{-1}. ^1H-NMR (60 MHz) δ : 7.00-7.75 (9H, m, Ar-H). HR-MS *m/z*; M^+ Calcd for $C_{14}H_9Br$: 255.9888, 257.9867. Found: 255.9873, 257.9849.

2e: 80% yield, colorless oil, bp 100-102 °C (5mm Hg). IR (neat): 2164 (C≡C) cm^{-1}. ^1H-NMR (60 MHz) δ : 0.28 (9H, s, TMS), 7.03-7.97 (4H, m, Ar-H). HR-MS *m/z*, M^+ Calcd for $C_{11}H_{13}BrSi$: 251.9970, 253.9949. Found: 251.9938, 253.9893.

Preparation of Benzo[b]tellurophenes (3A);

General procedure:

To a stirring solution of *o*-bromoethynylbenzenes (**2**; 5 mmol) in anhydrous ether (50 ml) at -80 °C under an argon atmosphere was slowly added *tert*-BuLi (1.5 mol in pentane solution, 3.5 ml, 5.2 mmol). The reaction mixture was stirred at same temperature for 1 h and then allowed warm to -30 °C for further 1 h. Powdered tellurium was added to the reaction mixture all at one portion, then the cooing bath was removed and the mixture was allowed to rise to room temperature during 1-2 h. Freshly distillated ethanol (10 ml) was added to the mixture. The resulting mixture was further stirred for 3 h under the same conditions, poured into ice-water, and extracted with ether (50 ml x 3). The etheral extract was washed with brine (50 ml x 2), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography using *n*-hexane as an eluent to give pure tellurophenes (**3**).

Benzo[b]selenophenes (**3B**) and benzo[b]thiophenes (**3C**) were prepared in an analogous manner using selenium or sulfur instead of tellurium.

Preparation of 2-Unsubstituted Benzo[b]-tellurophene (3Af), -Selenophene (3Bf), and -Thiophene (3Cf) from Corresponding 2-TMS derivatives (3Ae, 3Be, and 3Ce).

To a solution of 2-TMS compound (**3e**, 1mmol) in EtOH (30 ml) at room temperature under an argon atmosphere was added $NaBH_4$ (270 mg) in a small portions. The reaction mixture was heated at 80 °C with stirring for 12 h. After cooling, the mixture was poured into water and extracted with *n*-hexane (50 ml x 3). The organic layers were washed with brine (50 ml x 2), dried over $MgSO_4$ and evaporated. The resulting residues were chromatographed on silica gel using *n*-hexane as an eluent to give 2-unsubstituted derivatives (**3f**), which were recrystallized from *n*-pentane.

3Af: 172 mg, 74 % yield, colorless prisms, mp 67-68 °C (Lit.[4f] mp. 65-66 °C).

3Bf: 98 mg, 54 % yield, colorless prisms, mp 48-51 °C (Lit.[2b] mp. 51 °C).

3Cf: 48 mg, 36 % yield, colorless prisms, mp 29-32 °C

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5. This compound **1** is commercial available, but easily obtained from *o*-bromaniline *via* 3 steps (Bechanp reduction, diazotization, and iodination) in large scale.
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