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Synthesis, structure, and one-electron redox reactions of 4,7-disubstituted benzotrichalcogenoles containing sulfur and/or selenium atoms

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Abstract

Stable 4,7-disubstituted benzotrichalcogenoles containing sulfur and/or selenium atoms in the five-membered ring were systematically and selectively prepared in good yields by reaction of the corresponding benzodichalcogenastannoles, a synthetic equivalent of benzenedichalcogenols, with an S_1 or Se_1 source. Characterization of these new trichalcogenole frameworks was performed by multi-nuclear NMR studies and X-ray crystallographic analyses. The cyclic voltammograms of the trichalcogenoles showed well-defined reversible electrochemical redox couples with low oxidation potential. Novel radical ions were isolated in quantitative yields in the one-electron oxidation of the trichalcogenoles with one equivalent of $NOPF_6$ as a one-electron oxidant. The structures of the radical cation salts were analyzed by ^{31}P-NMR and EPR spectroscopies, and elemental analyses. The salts underwent one-electron reduction on treatment with one equivalent of samarium(II) iodide to give the neutral starting trichalcogenoles quantitatively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sulfur heterocycles; Selenium heterocycles; X-ray crystal structures; Voltammetry; Electron transfer; Redox reactions; Radical ions

1. Introduction

The chemistry of five-membered heterocycles containing multi-chalcogen linkages has blossomed since the discovery of isolable radical cation salts with a 7π carbon–sulfur [1] or carbon–selenium [2] framework. Our interest in the design of novel one-electron redox systems between neutral trichalcogenoles and their radical cations based on a stable 7π ring system has focused on the systematic synthesis of benzotrichalcogenoles. Such benzotrichalcogenoles, however, have received little attention due to their lower stability. Indeed, while there have been a few reports on trithioles [3], triselenoles [3d, 4], only one example of trichalcogenole containing both sulfur and selenium atoms in the five-membered ring [3d] has been described. Recently, we reported a preliminary communication of a new efficient method for the synthesis of benzotrichalcogenoles fused to a benzene ring [5]. This paper describes the first systematic synthesis, structural characterization and one-electron redox reactions of novel benzotrichalcogenoles containing sulfur and/or selenium atoms, which have the isopropyl, ethyl and methoxy groups at the 4- and 7-positions of the benzene ring serving as efficient stabilization substituents for the five-membered trichalcogenide ring.

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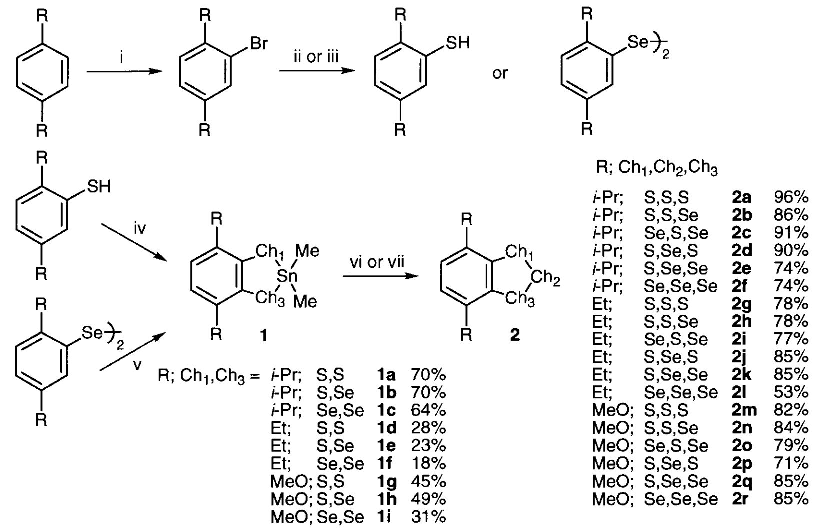


i, Br_2-Fe, CCl_4; ii, (a) Mg, Et_2O (b) S (c) H^+/H_2O; iii, (a) Mg, Et_2O (b) Se (c) H^+/H_2O (d) [O];
iv, (a) TMEDA, n-BuLi, n-hexane (b) S or Se (c) Me_2SnCl_2;
v, (a) $LiAlH_4$, THF (b) H^+/H_2O (c) TMEDA, *n*-BuLi, n-hexane (d) S or Se (e) Me_2SnCl_2;
vi, (a)$SOCl_2$, THF (b) NaI-$HClO_4$, THF/H_2O;
vii, (a) $SeOCl_2$, THF (b) TMSOTf, THF (c) SmI_2, THF

Scheme 1.

2. Results and discussion

2.1. Synthesis of dichalcogenastannoles **1a–i** and trichalcogenoles **2a–r**

4,7-Disubstituted 2,2-dimethyl-1,3,2-benzodichalcogenastannoles **1a–i**, a synthetic equivalent of unstable ortho benzenedichalcogenols, were prepared in moderate yields by a sequence of bromination [6], Grignard reaction-chalcogenation [7], ortho lithiation-chalcogenation [8] and dimethyltin protection [9]. Synthetic intermediates, bromides, thiols and diselenide derivatives, were obtained in quantitative yields. Transformation into trichalcogenoles **2a–r** was successfully carried out by following our original method, namely, by the reaction of stannoles with electrophiles containing one sulfur or selenium unit. Introduction of a sulfur atom at the 2-position was performed by the reaction of stannoles with thionyl chloride, followed by reduction with sodium iodide under acidic conditions in good yields. Introduction of a selenium atom at the 2-position was performed by sequential treatment of stannoles with selenium oxychloride, trimethylsilyl trifluoromethanesulfonate and samarium(II) iodide in good yields. These results are shown in Scheme 1.

2.2. Multi-nuclear NMR studies

Selenium has one and tin has two NMR-active spin 1/2 nuclei of relatively high natural abundance; ^{77}Se, ^{119}Sn and ^{117}Sn. Therefore, the ^{77}Se- and ^{119}Sn-NMR spectra provided pertinent information on the new five-membered frameworks of dichalcogenastannoles **1a–i** (Table 1) and trichalcogenoles **2a–r** (Table 2). The ^{77}Se-NMR spectra of dichalcogenastannoles containing selenium atom(s) showed the signals with ^{119}Sn and ^{117}Sn satellites, which were in accordance with the existence of a selenium atom or atoms neighboring a tin atom in the ring. The ^{119}Sn-NMR spectra also showed ^{77}Se satellites. The ^{77}Se-NMR spectra of trichalcogenoles containing one selenium atom indicated that each five-membered ring has a selenium atom at an appropriate position. The spectra of thiadiselenoles with two selenium atoms consisted of two equally intense signals, each with ^{77}Se satellites, and those of

Table 1
Multi-nuclear NMR data for stannoles **1a–i**

Compound	^{119}Sn [a] δ (ppm)	^{77}Se [b] δ (ppm)	$J_{^{117}Sn-^{77}Se}$, $J_{^{119}Sn-^{77}Se}$ (Hz)
1a	174.3	–	–
1b	121.4	27.2	1089, 1139
1c	62.9	83.2	1061, 1110
1d	177.9	–	–
1e	122.4	22.4	1086, 1136
1f	69.6	75.8	1052, 1101
1g	202.2	–	–
1h	147.3	21.7	1043, 1093
1i	90.7	72.0	1013, 1061

[a] Relative to neat Me_4Sn.
[b] Relative to neat Me_2Se.

Table 2
^{77}Se-NMR data for trichalcogenoles **2a–r**

Compound	^{77}Se ^{a} δ (ppm)	$J_{77Se-77Se}$ (Hz)	Compound	^{77}Se ^{a} δ (ppm)	$J_{77Se-77Se}$ (Hz)	Compound	^{77}Se ^{a} δ (ppm)	$J_{77Se-77Se}$ (Hz)
2a	–	–	**2g**	–	–	**2m**	–	–
2b	628.0	–	**2h**	620.8	–	**2n**	633.0	–
2c	653.9	–	**2i**	646.0	–	**2o**	651.0	–
2d	696.6	–	**2j**	702.8	–	**2p**	712.8	–
2e	509.2		**2k**	500.8		**2q**	504.1	
	575.1	275		583.0	281		579.5	313
2f	440.9		**2l**	450.1		**2r**	434.7	
	547.0	258		537.5	262		532.9	296

[a] Relative to neat Me_2Se.

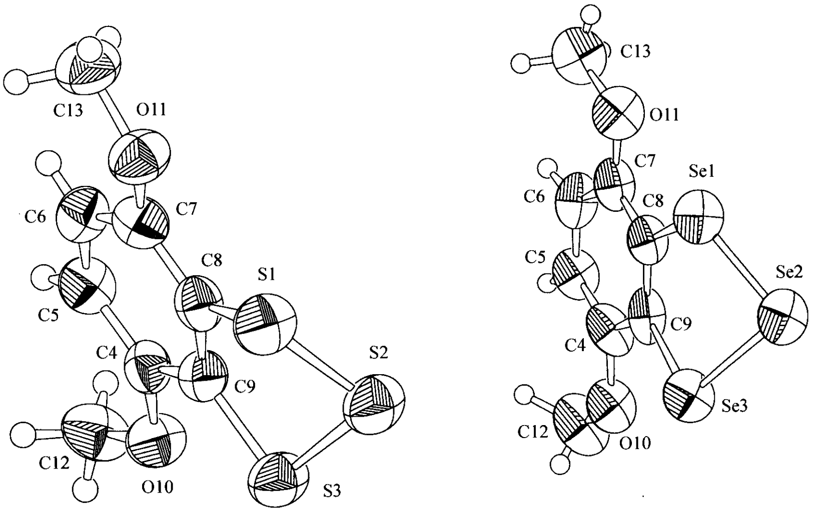


Fig. 1. ORTEP drawings of **2m** (left) and **2r** (right), showing atom numbering.

triselenoles consisted of two unequally intense signals, each with ^{77}Se satellites, which could be assigned to the number of selenium–selenium bonding in the ring.

2.3. X-ray crystallographic analysis

The crystal structures of trithiole **2m** and triselenole **2r** were confirmed by X-ray crystallographic analyses (Fig. 1, Table 3). Two chalcogen atoms at the 1- and 3-positions are almost coplanar with the benzene ring, while the chalcogen atoms at the 2-position lie out of this plane (Ch–Ch–Ch–C torsion angles are ca. 40°). The unique distorted geometry of the five-membered trichalcogenole rings implies the presence of lone pair–lone pair repulsion of three divalent chalcogen atoms. The sulfur–sulfur bond lengths of **2m** are similar to those in S_8, and the sulfur–carbon(sp^2) bond lengths are marginally longer than those of the general sulfur–carbon(sp^2) single bond lengths (1.75 Å). The bond lengths, bond angles, and torsion angles are similar to those for 4-nitro-6-trifluoromethylbenzotrithiole [3a,b], the only benzene fused trithiole for which the crystal structure is reported. On the other hand, the angles around the selenium atoms of **2r** are slightly narrower than those in literature, whereas the selenium–selenium bond lengths, selenium–carbon(sp^2) bond lengths are similar to those of acyclic selenium compounds previously reported [10].

2.4. Electrochemical studies

The solution redox properties of the trichalcogenoles **2a**–**2r** were studied by cyclic voltammetry technique, since little has been known about the electrochemical behavior of polychalcogenide ring systems. Cyclic voltammograms were measured in acetonitrile (MeCN) containing 0.1M n-$Bu_4N^+ClO_4^-$ as a supporting electrolyte using a glassy–carbon working electrode and Ag/0.01M $AgNO_3$ couple in MeCN as a reference electrode at 20°C. Interestingly, all trichalcogenoles exhibited one reversible one-electron step with low oxidation potential. The peak potentials of the first oxidation peak (E_P) and half-wave ($E_{1/2}$) have been found to be governed by the atom present at the 2-position of the chalcogen ring. It is a well-known fact that increasing selenium substitution normally leads to the lowering of

Table 3
Selected bond lengths (Å) and angles (°) [a]

Trithiole **2m**		Triselenole **2r**	
Bond lengths			
S1–S2	2.064(3)	Se1–Se2	2.340(3)
S2–S3	2.062(3)	Se2–Se3	2.339(3)
S1–C8	1.770(6)	Se1–C8	1.91(1)
S3–C9	1.768(6)	Se3–C9	1.89(1)
C8–C9	1.390(9)	C8–C9	1.44(2)
Bond angles			
S1–S2–S3	95.5(1)	Se1–Se2–Se3	91.88(9)
S2–S1–C8	93.4(2)	Se2–Se1–C8	93.6(5)
S2–S3–C9	93.7(2)	Se2–Se3–C9	92.9(5)
S1–C8–C9	117.7(5)	Se1–C8–C9	119(1)
S3–C9–C8	118.4(5)	Se3–C9–C8	120.7(9)
S1–S2–S3–C9	39.1(3)	Se1–Se2–Se3–C9	39.0(4)
S3–S2–S1–C8	−40.3(2)	Se3–Se2–Se1–C8	−37.2(5)
S1–C8–C9–S3	-2.9(8)	Se1–C8–C9–Se3	5(1)
S1–C8–C7–C6	−173.2(6)	Se1–C8–C7–C6	−179(1)
S1–C8–C9–C4	175.6(5)	Se1–C8–C9–C4	−179(1)
S3–C9–C8–C7	−179.6(6)	Se3–C9–C8–C7	-177(1)
S3–C9–C4–C5	178.0(6)	S3–C9–C4–C5	176(1)

[a] Values in parentheses are the greater of the range or the estimated S.D.

the oxidation potential of a donor. As expected, with increasing selenium substitution, lowered oxidation peaks were obtained (Table 4). Thus, the present results suggest that the desired stable one-electron oxidized species, benzotrichalcogenolium radical cations, may be generated during the electrochemical or chemical oxidation. In fact, the cyclic voltammograms of the isolated radical cation salts, which are described in the next section, also displayed reversible redox profiles with the same redox potentials observed in trichalcogenoles (Fig. 2).

2.5. Radical cations and EPR spectra

The results of the reversibility observed in cyclic voltammetry described above clearly indicate that the trichalcogenoles provide stable radical cations even at room temperature. Several novel trichalcogenolium radical cation salts were readily isolated in the one-electron oxidation of trichalcogenoles with one equivalent of $NOPF_6$ in ether–MeCN (Scheme 2). The dark-blue or purple salts were stable, and the structures of radical ions in solution were analyzed by ^{31}P-NMR and EPR spectroscopies. Each salt dissolved readily in THF or MeCN to give a red–purple solution. The EPR spectra of the solution showed the presence of triplet peaks (trithiolium), and a broad singlet peak (thiadiselenolium and triselenolium) attributable to trichalcogenolium radical cations (Fig. 3, Table 5). The aH splitting (triplet) suggests a partially spin delocalized system over both the benzene and trichalcogenole rings. Interestingly, the radical cation salts undergo one-electron reduction to give trichalcogenoles quantitatively on treatment with samarium(II) iodide (Scheme 2) [11].

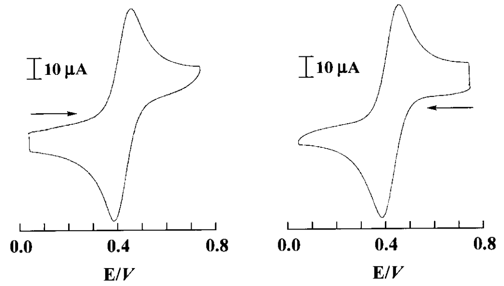
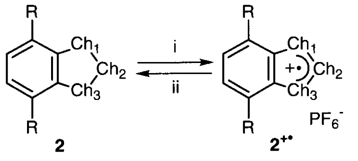


Fig. 2. Cyclic voltammetry waves on **2r** (left) and **2r**$^{+\bullet}$ (right), scan rate 100 mV s^{-1}.



i, $NOPF_6$, Et_2O/MeCN; ii, SmI_2, THF

condition i		condition ii	
2a$^{+\bullet}$	95%	**2a**	92%
2c$^{+\bullet}$	92%	**2c**	quant.
2f$^{+\bullet}$	99%	**2f**	94%
2g$^{+\bullet}$	quant.	**2g**	quant.
2i$^{+\bullet}$	quant.	**2i**	quant.
2l$^{+\bullet}$	97%	**2l**	quant.
2m$^{+\bullet}$	94%	**2m**	94%
2o$^{+\bullet}$	quant.	**2o**	quant.
2r$^{+\bullet}$	99%	**2r**	94%

Scheme 2.

Thus, the facile interconversion in the redox reactions of trichalcogenoles and their radical cations is ascribed to the destabilization of the distorted neutral trichalcogenide framework by lone pair–lone pair repulsion and the unusual stabilization of the oxidized radical cation by the 7π electron framework.

Table 4
Redox potentials (*V*) of trichalcogenoles **2a**–**r** [a]

Compound	E_{pa}	E_{pc}	$E_{1/2}$	Compound	E_{pa}	E_{pc}	$E_{1/2}$	Compound	E_{pa}	E_{pc}	$E_{1/2}$
2a	0.77	0.67	0.72	**2g**	0.77	0.66	0.71	**2m**	0.75	0.65	0.70
2b	0.75	0.64	0.70	**2h**	0.73	0.63	0.68	**2n**	0.69	0.62	0.65
2c	0.71	0.61	0.66	**2i**	0.68	0.59	0.64	**2o**	0.61	0.53	0.57
2d	0.64	0.56	0.60	**2j**	0.64	0.54	0.59	**2p**	0.59	0.51	0.55
2e	0.63	0.54	0.59	**2k**	0.59	0.49	0.54	**2q**	0.50	0.43	0.47
2f	0.60	0.52	0.56	**2l**	0.52	0.43	0.48	**2m**	0.47	0.39	0.43

[a] Concentration, 2 mM sample MeCN/0.1 M *n*-$Bu_4N^+ClO_4^-$; working electrode, glassy–carbon; reference electrode, Ag/0.01 M $AgNO_3$; counter electrode, Pt; scan rate 100 mV s^{-1}.

3. Experimental

3.1. General procedures

Melting points were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H- (400 MHz), ^{13}C- (101 MHz), ^{31}P- (162 MHz), ^{77}Se- (76 MHz) and ^{119}Sn- (149 MHz) NMR spectra are recorded on a Bruker AC-400 instrument; $CDCl_3$ was used as solvent if not mentioned otherwise. Mass spectra were recorded on a Hitachi M-2000 or JEOL JMS-SX 102 spectrometer. IR spectra were obtained on a JASCO FT-7300 spectrometer. Silica gel used for column chromatography was Wakogel C-200. Preparative HPLC was performed on a JAI LC-908. Elemental analyses were obtained using Yanaco MT-5 apparatus at the Elemental Analysis Division of Iwate University. Cyclic volmammetric experiments were performed by employing a Cypress Systems CS-1090. A three-electrode system was used, consisting of a glassy–carbon working electrode, a platinum wire auxiliary electrode and Ag/0.01 M $AgNO_3$ reference electrode. The measurements were carried out in MeCN solution with 0.1 M n-Bu_4NClO_4 as supporting electrolyte with scan rates 50–500 mV s^{-1} at 20°C. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.05 V. EPR data were taken in a JEOL RE 2X spectrometer working in the X-band with DPPH and Mn^{2+} on MgO as field markers.

3.2. Materials

THF and diethyl ether were distilled from sodium benzophenone ketyl. CH_2Cl_2 and acetonitrile were distilled from CaH_2. TMEDA (*N*,*N*,*N*,*N*,-tetramethyl-1,2-ethylene diamine) was distilled under argon. All reagents except for the solvent given above were purchased from commercial suppliers and used without further purification.

3.3. General procedure for the synthesis of 4,7-disubstituted 2,2-dimethyl-1,3,2-benzodichalcogenastannoles (*1a–i*)

A typical synthetic procedure of the 4,7-disubstituted 2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**2a**–**i**) is as follows. To a stirred solution of 2,5-diisopropylthiophenol (2.93 g, 15.1 mmol) in TMEDA (9.5 ml, 62.9 mmol) was slowly added dropwise 1.60 M n-BuLi (38.4 ml, 61.4 mmol; n-hexane solution) at 0°C under an N_2 atmosphere. The reaction mixture was refluxed for 2 h and cooled to 0°C. Elemental sulfur (2.41 g, 75.2 mmol atom) was slowly added to the mixture at 0°C. After having been stirred for 6 h at room temperature (r.t.), the solvent was removed under reduced pressure. The residue was dissolved in anhydrous THF (50 ml) and treated with $LiAlH_4$ (2.85 g, 75.1 mmol) under reflux for 3 h. After treatment with ice-water (100 ml) the mixture was treated with dimethyltin dichloride (3.96 g, 18.0 mmol) in H_2O (10 ml) and stirred for 30 min at r.t. The whole mixture was extracted with CH_2Cl_2 (3 × 20 ml), the extract was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, CCl_4–$CHCl_3$ = 1/1) to give 3.90 g of 2,2-isopropyl-1,3,2-benzodithiastannole (**1a**) in 70% yield.

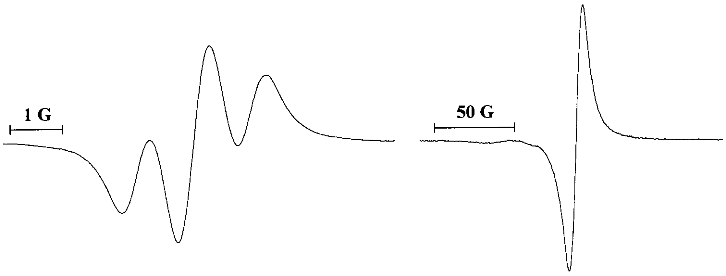


Fig. 3. X-band EPR spectra of **2g**$^{+\bullet}$ at −40°C (left) and **2o**$^{+\bullet}$ at 10°C (right) in acetonitrile.

Table 5
g-Value and hfc of several benzotricalcogenolium radical cations in acetonitrile[a]

Compound	g	hfc (*Hz*)	Compound	g	hfc (*Hz*)	Compound	g	hfc (*Hz*)
2a$^{+\bullet}$	2.012	0.106	**2g**$^{+\bullet}$	2.012	0.109	**2m**$^{+\bullet}$	2.012	0.081
2c$^{+\bullet}$	2.033	–	**2i**$^{+\bullet}$	2.033	–	**2o**$^{+\bullet}$	2.032	–
2f$^{+\bullet}$	2.058	–	**2l**$^{+\bullet}$	2.055	–	**2r**$^{+\bullet}$	2.057	–

[a] Observed at the range from −40 to 20°C. Data for **2a**$^{+\bullet}$, **2f**$^{+\bullet}$ and **2m**$^{+\bullet}$ were collected in THF solution.

3.3.1. Compound **1a**

Colorless plates; m.p. 168.0–169.0°C; ^{1}H-NMR $\delta =$ 0.97 (s, 6H, $SnCH_3$), 1.26 (d, $J = 6.8$ Hz, 12H, CH_3), 3.57 (sept, $J = 6.8$ Hz, 2H, CH), 6.97 (s, 2H, ArH); ^{13}C-NMR $\delta = 1.9$, 23.0, 34.0, 121.6. 137.4, 146.0; IR (KBr) 2961, 2925, 2869, 1465, 1423, 1385, 1368, 1314, 813 and 767 cm^{-1}; MS m/z 374 (M^+); Anal. Found: C, 44.85; H, 6.01. Calc. for $C_{14}H_{22}S_2Sn$: C,45.06; H, 5.94%.

3.3.2. Compound **1b**

Colorless plates; m.p. 158.0–159.0°C; ^{1}H-NMR $\delta =$ 1.01 (s, 6H, $SnCH_3$), 1.26 (d, $J = 6.8$ Hz, 6H, CH_3), 1.27 (d, $J = 6.8$ Hz, 6H, CH_3), 3.45 (sept, $J = 6.8$ Hz, 1H, CH), 3.63 (sept, $J = 6.8$ Hz, 1H, CH), 6.97 (d, $J = 8.2$ Hz, 1H, ArH), 7.03 (d, $J = 8.2$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 1.6$, 23.2, 23.4, 34.7, 37.1, 122.0, 122.8, 135.9, 139.9, 146.7, 147.7; IR (KBr) 2960, 2925, 2868, 1465, 1422, 1385, 1368, 1077, and 814 cm^{-1}; MS m/z 420 (M^+); Anal. Found: C, 39.82; H, 5.30. Calc. for $C_{14}H_{22}SSeSn$: C, 40.03; H, 5.28%.

3.3.3. Compound **1c**

Colorless plates; m.p. 160.5–162.0°C; ^{1}H-NMR $\delta =$ 1.06 (s, 6H, $SnCH_3$), 1.27 (d, 12H, $J = 6.8$ Hz, CH_3), 3.51 (sept, $J = 6.8$ Hz, 2H, CH_3), 7.04 (s, 2H, ArH); ^{13}C-NMR $\delta = 1.0$, 23.4, 37.6, 122.9, 138.5, 148.3; IR (KBr) 2963, 2867, 1872, 1694, 1385, 1363, 1183, 1158, 902 and 816 cm^{-1}; MS m/z 468 (M^+); Anal. Found: C, 35.85; H, 4.78. Calc. for $C_{14}H_{22}Se_2Sn$: C, 36.01; H, 4.75%.

3.3.4. Compound **1d**

Colorless needles; m.p. 106.0–107.0°C; ^{1}H-NMR $\delta = 0.97$ (s, 6H, $SnCH_3$), 1.27 (t, $J = 7.5$ Hz, 6H, CH_3), 2.83 (q, $J = 7.5$ Hz, 4H, CH_2), 6.85 (s, 2H, ArH); ^{13}C-NMR $\delta = 2.0$, 13.9, 30.6, 124.3, 137.9, 141.5; IR (KBr) 2962, 2926, 2868, 1431, 1366, 1197, 1092, 865, 818, 780 and 757 cm^{-1}; MS m/z 346 (M^+); Anal. Found: C, 41.53; H, 5.29. Calc. for $C_{12}H_{18}S_2Sn$: C, 41.77; H, 5.26%.

3.3.5. Compound **1e**

Colorless needles; m.p. 110.0–112.0°C (dec.); ^{1}H-NMR $\delta = 1.01$ (s, 6H, $SnCH_3$), 1.26 (t, $J = 7.5$ Hz, 3H, CH_3), 1.28 (t, $J = 7.5$ Hz, 3H, CH_3), 2.82 (q, $J = 7.5$ Hz, 2H, CH_2), 2.87 (q, $J = 7.5$ Hz, 2H, CH_2), 6.85 (d, $J = 7.6$ Hz, 1H, ArH), 6.91 (d, $J = 7.6$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 1.6$, 13.9, 14.1, 31.2, 32.8, 124.4, 125.3, 136.0, 140.4, 141.9, 143.1; IR (KBr) 2965, 2929, 2869, 1462, 1432, 1367, 1196, 1086, 1061, 857 and 769 cm^{-1}; MS m/z 392 (M^+); Anal. Found: C, 36.90; H, 4.64. Calc. for $C_{12}H_{18}SSeSn$: C, 36.77; H, 4.63%.

3.3.6. Compound **1f**

Colorless needles; m.p. 123.5–124.5 °C; ^{1}H-NMR $\delta = 1.06$ (s, 6H, $SnCH_3$), 1.27 (t, $J = 7.5$ Hz, 6H, CH_3), 2.87 (q, $J = 7.5$Hz, 4H, CH_2), 6.91 (s, 2H, ArH); ^{13}C-NMR $\delta = 1.2$, 14.2, 33.5, 125.4, 138.8, 143.5; IR (KBr) 2963, 2927, 2866, 1459, 1428, 1365, 1059, 819 and 760 cm^{-1}; MS m/z 440 (M^+); Anal. Found: C, 33.02; H, 4.24. Calc. for $C_{12}H_{18}Se_2Sn$: C, 32.84; H, 4.13%.

3.3.7. Compound **1g**

Colorless needles; m.p. 203.5°C (dec.); ^{1}H-NMR $\delta =$ 1.00 (s, 6H, $SnCH_3$), 3.87 (s, 6H, OCH_3), 6.58 (s, 2H, ArH); ^{13}C-NMR $\delta = 2.6$, 56.5, 107.0, 129.0, 152.7; IR (KBr) 3002, 2950, 2830, 1567, 1457, 1426, 1376, 1252, 1190, 1109, 1042 and 785 cm^{-1}; MS m/z 350 (M^+); Anal. Found: C, 34.35; H, 4.20. Calc. for $C_{10}H_{14}O_2S_2Sn$: C, 34.41; H, 4.04%.

3.3.8. Compound **1h**

Pale yellow needles; m.p. 192.5–193.0°C (dec.); ^{1}H-NMR $\delta = 1.02$ (s, 6H, $SnCH_3$), 3.85 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.55 (d, $J = 8.8$ Hz, 1H, ArH), 6.64 (d, $J = 8.8$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 2.2$, 56.5, 56.5, 106.8, 108.0, 125.8, 131.4, 153.0, 153.1; IR (KBr) 2948, 2830, 1566, 1456, 1426, 1376, 1243, 1021, 786 and 760 cm^{-1}; MS m/z 396 (M^+); Anal. Found: C, 30.24; H, 3.48. Calc. for $C_{10}H_{14}O_2SSeSn$: C, 30.33; H, 3.56%.

3.3.9. Compound **1i**

Colorless needles; m.p. 205.0–206.5°C (dec.); ^{1}H-NMR $\delta = 1.06$ (s, 6H, $SnCH_3$), 3.85 (s, 6H, OCH_3), 6.63 (s, 2H, ArH); ^{13}C-NMR $\delta = 1.7$, 56.7, 108.0, 128.6, 153.8; IR (KBr) 2997, 2933, 2828, 1565, 1455, 1421, 1250, 1187, 1095 and 1038 cm^{-1}; MS m/z 444 (M^+); Anal. Found: C, 27.13; H, 3.40. Calc. for $C_{10}H_{14}O_2Se_2Sn$: C, 27.12; H, 3.19%.

3.4. General procedure for the synthesis of 4,7-disubstituted benzotrichalcogenoles (**2a–r**)

A typical synthetic procedure of the 4,7-disubstituted benzotrichalcogenoles **2a–r** is as follows. 4,7-diisopropyl-1,3,2-benzodithiastannole (**1a**) (373 mg, 1.0 mmol) in anhydrous THF (30 ml) was treated with 1.2 equivalents of thionyl chloride (0.09 ml, 1.2 mmol) at 0°C under an N_2 atmosphere. The mixture was stirred at 0°C for 2 h and extracted with CH_2Cl_2 (3 × 30 ml). After removing the solvent, the crude product was purified by column chromatography (silica gel; eluent, CCl_4–$CHCl_3 = 1/1$) to give 272 mg of the corresponding 2-oxide (100%). Subsequently, a mixture of the 2-oxide (272 mg, 1.0 mmol) and five equivalents. of sodium iodide (750 mg, 5.0 mmol) in THF–H_2O (40 ml/5 ml) at 0°C was treated with 60% $HClO_4$ (5.2 ml, 51.7 mmol) and was stirred at r.t. for 3 h and extracted with CH_2Cl_2 (3 × 30 ml). After removing the solvent, the crude product was purified by column chromatography (silica gel; eluent, CCl_4) to give 245 mg of **2a** in 96% yield. To a stirred solution of dithiastannole (**1a**) (373 mg, 1.0 mmol) in THF (20 ml) was added selenium oxychloride (0.68 ml, 1.0 mmol) in THF (10 ml) under an Ar atmosphere at -78°C. After stirring for 15 min, the mixture was treated successively with trimethylsilyl trifluoromethanesulfonate (0.18 ml, 1.0 mmol) in THF (10 ml) and 0.1 M samarium(II) iodide (20.0 ml, 2.0 mmol) in THF at -78°C under an Ar atmosphere. The whole mixture was stirred at -78°C for 15 min and then at r.t. for 30 min. After hydrolysis, treatment with aqueous sodium hydrogensulfite and extraction with *n*-hexane (3×30 ml), the extract was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, *n*-hexane) to give 273 mg of dithiaselenole **2d** in 90% yield.

*3.4.1. Compound **2a***

Orange oil; ^{1}H-NMR $\delta = 1.24$ (d, $J = 6.8$ Hz, 12H, CH_3), 3.00 (sept, $J = 6.8$ Hz, 2H, CH), 6.99 (s, 2H, ArH); ^{13}C-NMR $\delta = 22.9$, 35.6, 124.4, 139.8, 142.7; IR (oil) 2961, 2868, 1470, 1387, 1373, 1063, 918, 819 and 758 cm^{-1}; Anal. Found: 256.0391 (M^+). Calc. for $C_{12}H_{16}S_3$: 256.0414 (M^+). Anal. Found: C, 56.02; H, 6.35. Calc. for $C_{12}H_{16}S_3$: C, 56.20; H, 6.29%.

*3.4.2. Compound **2b***

Dark red oil; ^{1}H-NMR $\delta = 1.23$ (d, $J = 6.8$ Hz, 6H, CH_3), 1.25 (d, $J = 6.8$ Hz, 6H, CH_3), 2.79 (sept, $J = 6.8$ Hz, 1H, CH), 3.07 (sept, $J = 6.8$ Hz, 1H, CH), 7.04 (d, $J = 6.9$ Hz, 1H, ArH), 7.06 (d, $J = 6.9$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 23.1$, 23.2, 35.8, 38.8, 124.6, 124.8, 139.7, 141.1, 143.6, 144.6; IR (oil) 2960, 2867, 2358, 1887, 1642, 1467, 1386 and 819 cm^{-1}; Anal. Found: 303.9799 (M^+). Calc. for $C_{12}H_{16}S_2Se$: 303.9858 (M^+). Anal. Found: C, 47.41; H, 5.45. Calc. for $C_{12}H_{16}S_2Se$: C, 47.51; H, 5.32%.

*3.4.3. Compound **2c***

Reddish–brown crystals; m.p. 45.0–46.0°C; ^{1}H-NMR $\delta = 1.24$ (d, $J = 6.8$ Hz, 12H, CH_3), 2.88 (sept, $J = 6.8$ Hz, 2H, CH), 7.09 (s, 2H, ArH); ^{13}C-NMR $\delta = 23.4$, 38.9, 125.0, 140.7, 141.3; IR (KBr) 2959, 2925, 2865, 1631, 1582, 1457, 1363, 1316, 824 and 781 cm^{-1}; Anal. Found: 351.9345 (M^+). Calc. for $C_{12}H_{16}SSe_2$: 351.9304 (M^+); Anal. Found: C, 41.22; H, 4.77. Calc. for $C_{12}H_{16}SSe_2$: C, 41.15; H, 4.60%.

*3.4.4. Compound **2d***

Red oil; ^{1}H-NMR $\delta = 1.24$ (d, $J = 6.8$ Hz, 12H, CH_3), 3.15 (sept. $J = 6.8$ Hz, 2H, CH), 6.94 (s, 2H, ArH); ^{13}C-NMR $\delta = 23.0$, 35.4, 124.4, 141.1, 143.7; IR (oil) 2965, 2870, 1469, 1388, 1373, 1265, 1162, 1062, 896, 822 and 738 cm^{-1}; Anal. Found: 303.9822 (M^+). Calc. for $C_{12}H_{16}S_2Se$: 303.9858 (M^+).

*3.4.5. Compound **2e***

Reddish–brown oil; ^{1}H-NMR $\delta = 1.23$ (d, $J = 6.8$ Hz, 6H, CH_3), 1.24 (d, $J = 6.8$ Hz, 6H, CH_3), 2.93 (sept, $J = 6.8$ Hz, 1H, CH), 3.21 (sept, $J = 6.8$ Hz, 1H, CH), 6.98 (d, $J = 8.0$ Hz, 1H, ArH), 7.00 (d, $J = 8.0$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 23.1$, 23.3, 35.6, 38.6, 124.6, 124.9, 140.4, 142.1, 144.7, 145.3; IR (oil) 2959, 2924, 2363, 1884, 1696, 1634, 1464, 1385 and 818 cm^{-1}; Anal. Found: 351.9270 (M^+). Calc. for $C_{12}H_{16}SSe_2$: 351.9304 (M^+).

*3.4.6. Compound **2f***

Reddish–brown oil; ^{1}H-NMR $\delta = 1.24$ (d, $J = 6.8$ Hz, 12H, CH_3), 3.02 (sept, $J = 6.8$ Hz, 2H, CH), 7.05 (s, 2H, ArH); ^{13}C-NMR $\delta = 23.4$, 38.7, 125.0, 141.5, 146.3; IR (oil) 2958, 2865, 1885, 1754, 1462, 1385, 1367, 1323, 1160, 1104, 906 and 820 cm^{-1}; Anal. Found: 397.8743 (M^+, 100%), 399.8682 (84.5%). Calc. for $C_{12}H_{16}Se_3$: 397.8761 (M^+, 100%), 399.8753 (84.5%).

*3.4.7. Compound **2g***

Orange oil; ^{1}H-NMR $\delta = 1.21$ (t, $J = 7.6$ Hz, 6H, CH_3), 2.66 (q, $J = 7.6$ Hz, 4H, CH_2), 6.89 (s, 2H, ArH); ^{13}C-NMR $\delta = 14.5$, 30.3, 127.2, 138.1, 140.2; IR (oil) 2964, 2928, 2868, 1466, 1369, 1319, 1059, 876 and 823 cm^{-1}; MS m/z 228 (M^+); Anal. Found: C, 52.51; H, 5.39. Calc. for $C_{10}H_{12}S_3$: C, 52.59; H, 5.30%.

*3.4.8. Compound **2h***

Dark red oil; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.6$ Hz, 3H, CH_3), 1.20 (t, $J = 7.6$ Hz, 3H, CH_3), 2.62 (q, $J = 7.6$ Hz, 2H, CH_2), 2.70 (q, $J = 7.6$ Hz, 2H, CH_2), 6.91 (d, $J = 7.8$ Hz, 1H, ArH), 6.94 (d, $J = 7.8$Hz, 1H, ArH); ^{13}C-NMR $\delta = 14.6$, 14.7, 30.7, 32.8, 127.3, 127.7, 138.8, 139.9, 140.0, 141.6; IR (oil) 2963, 2927, 2867, 1461, 1365, 1317, 1061, 866 and 823 cm^{-1}; Anal. Found: 275.9536 (M^+). Calc. for $C_{10}H_{12}S_2Se$: 275.9545 (M^+).

*3.4.9. Compound **2i***

Orange oil; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.6$ Hz, 6H, CH_3), 2.67 (q, $J = 7.6$ Hz, 4H, CH_2), 6.97 (s, 2H, ArH); ^{13}C-NMR $\delta = 14.9$, 33.1, 127.8, 140.7, 141.3; IR (oil) 2961, 2925, 2866, 1582, 1457, 1363 and 823 cm^{-1}; MS m/z 324 (M^+); Anal. Found: C, 37.10; H, 3.99. Calc. for $C_{10}H_{12}SSe_2$: C, 37.28; H, 3.75%.

*3.4.10. Compound **2j***

Red oil; ^{1}H-NMR $\delta = 1.21$ (t, $J = 7.5$ Hz, 6H, CH_3), 2.69 (q, $J = 7.5$ Hz, 4H, CH_2), 6.81 (s, 2H, ArH); ^{13}C-NMR $\delta = 14.5$, 30.4, 127.2, 139.1, 141.4; IR (oil) 2963, 2927, 2867, 1460, 1369, 1059 and 923 cm^{-1}; Anal. Found: 275.9546 (M^+). Calc. for $C_{10}H_{12}S_2Se$: 275.9545 (M^+).

3.4.11. Compound **2k**

Reddish–brown oil; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.6$ Hz, 6H, CH$_3$), 2.66 (q, $J = 7.6$ Hz, 2H, CH$_2$), 2.73 (q, $J = 7.6$ Hz, 2H, CH$_2$), 6.84 (d, $J = 7.8$ Hz, 1H, ArH), 6.88 (d, $J = 7.8$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 14.6$, 14.7, 30.8, 32.8, 127.3, 127.7, 139.8, 140.5, 140.7, 142.6; IR (oil) 2962, 2926, 2866, 2359, 1579, 1457, 1365, 1318, 1061, 864 and 824 cm^{-1}; MS m/z 324 (M$^+$); Anal. Found: C, 36.96; H, 3.89. Calc. for $C_{10}H_{12}SSe_2$: C, 37.28; H, 3.75%.

3.4.12. Compound **2l**

Reddish–brown oil; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.6$ Hz, 6H, CH$_3$), 2.71 (q, $J = 7.6$ Hz, 4H, CH$_2$), 6.92 (s, 2H, ArH); ^{13}C-NMR $\delta = 14.9$, 33.2, 127.8, 141.5, 141.7; IR (oil) 2960, 2925, 2866, 1453, 1363, 1317 and 823 cm^{-1}; MS m/z 370 (M$^+$); Anal. Found: C, 32.53; H, 3.29. Calc. for $C_{10}H_{12}Se_3$: C, 32.54; H, 3.28%.

3.4.13. Compound **2m**

Orange needles; m.p. 95.0–96.0°C; ^{1}H-NMR $\delta =$ 3.82 (s, 6H, OCH$_3$), 6.61 (s, 2H, ArH); ^{13}C-NMR $\delta = 56.5$, 110.9, 130.7, 150.0; IR (KBr) 2936, 2831, 1589, 1476, 1260, 1042 and 785 cm^{-1}; MS m/z 232 (M$^+$); Anal. Found: C, 41.23; H, 3.34. Calc. for $C_8H_8O_2S_3$: C, 41.35; H, 3.47%.

3.4.14. Compound **2n**

Orange needles; m.p. 96.0–97.0°C (dec.); ^{1}H-NMR $\delta = 3.79$ (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 6.60 (d, $J = 8.8$ Hz, 1H, ArH), 6.64 (d, $J = 8.8$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 56.4$, 56.5, 110.5, 111.1, 128.7, 131.9, 150.6, 151.0; IR (KBr) 2993, 2934, 2829, 1585, 1562, 1471, 1428, 1256, 1106, 1044, 1036 and 786 cm^{-1}; MS m/z 280 (M$^+$); Anal. Found: C, 34.29; H, 2.87. Calc. for $C_8H_8O_2S_2Se$: C, 34.41; H, 2.89%.

3.4.15. Compound **2o**

Orange needles; m.p. 107.0–108.0°C (dec.); ^{1}H-NMR $\delta = 3.80$ (s, 6H, OCH$_3$), 6.65 (s, 2H, ArH); ^{13}C-NMR $\delta = 56.5$, 110.9, 130.3, 151.8; IR (KBr) 2996, 2935, 2829, 1468, 1428, 1256, 1100 and 1033 cm^{-1}; MS m/z 328 (M$^+$); Anal. Found: C, 29.51; H, 2.47. Calc. for $C_8H_8O_2SSe_2$: C, 29.46; H, 2.47%.

3.4.16. Compound **2p**

Reddish–brown needles; m.p. 105.0°C (dec.); ^{1}H-NMR $\delta = 3.82$ (s, 6H, OCH$_3$), 6.56 (s, 2H, ArH); ^{13}C-NMR $\delta = 56.5$, 110.8, 132.0, 150.7; IR (KBr) 2938, 2830, 1583, 1563, 1471, 1428, 1260, 1041 and 784 cm^{-1}; MS m/z 280 (M$^+$); Anal. Found: C, 34.26; H, 2.81. Calc. for $C_8H_8O_2S_2Se$: C, 34.41; H, 2.89%.

3.4.17. Compound **2q**

Brown needles; m.p. 119.0–120.0°C (dec.); ^{1}H-NMR $\delta = 3.80$ (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 6.57 (d, $J = 8.6$ Hz, 1H, ArH), 6.62 (d, $J = 8.6$ Hz, 1H, ArH); ^{13}C-NMR $\delta = 56.5$, 56.6, 110.5, 111.2, 129.5, 133.2, 151.5, 151.6; IR (KBr) 2994, 2937, 2829, 1467, 1427, 1257, 1104, 1034 and 784 cm^{-1}; MS m/z 328 (M$^+$); Anal. Found: C, 29.57; H, 2.45. Calc. for $C_8H_8O_2SSe_2$: C, 29.46; H, 2.48%.

3.4.18. Compound **2r**

Dark red prisms; m.p. 122.5–124.0°C; ^{1}H-NMR $\delta =$ 3.80 (s, 6H, OCH$_3$), 6.63 (s, 2H, ArH); ^{13}C-NMR $\delta = 55.6$, 110.9, 130.9, 152.4; IR (KBr) 2934, 2827, 1180, 1097, 1033 and 785 cm^{-1}; MS m/z 374 (M$^+$); Anal. Found: C, 25.94; H, 2.14. Calc. for $C_8H_8O_2Se_3$: C, 25.76; H, 2.16%.

3.5. X-ray crystal structure analyses of **2m** and **2r**

3.5.1. Crystal data for **2m**

$M = 232.33$, $C_8H_8O_2S_3$, orthorhombic, space group $P2_12_12_1$, $a = 16.628(1)$, $b = 16.958(1)$, $c = 6.965(3)$ Å, $V = 1963.9(5)$ Å^3, $Z = 8$, $D_{calc} = 1.571$ g cm^{-3}. An orange prismatic crystal of dimensions $0.10 \times 0.07 \times 0.80$ mm was used for measurements at 293 K on a Rigaku AFC7R diffractometer employing Cu–K$_\alpha$ ($\lambda = 1.54178$ Å) radiation using a ω/2θ scan technique. The structure was solved by direct methods (SIR88) and expanded using Fourier techniques (DIRDIF92). All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The final cycle of full-matrix least-squares refinement was based on 1410 observed reflections ($I > 3.00\sigma(I)$) and 300 variable parameters with R (R_w) = 0.050 (0.060). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre (ref. code: TIYGEN).

3.5.2. Crystal data for **2r**

$M = 373.03$, $C_8H_8O_2Se_3$, monoclinic, space group $P2_1/c$, $a = 17.453(3)$, $b = 6.923(3)$, $c = 18.767(2)$, $\beta =$ 114.172(8)°, $V = 2068.6(7)$ Å^3, $Z = 8$, $D_{calc} = 2.395$ g cm^{-3}. A dark red prismatic crystal of dimensions $0.20 \times 0.14 \times 0.48$ mm was used for measurements at 293 K on a Rigaku AFC7R diffractometer employing Cu–K$_\alpha$ ($\lambda = 1.54178$ Å) radiation using ω/2θ scan technique. The structure was solved by heavy-atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF92). All calculations were performed using the TEXSAN crystallographic software package. The final cycle of full-matrix least-square refinement was based on 2095 observed reflections ($I > 3.00\sigma(I)$) and 300 variable parameters with $R = 0.066$, $R_w =$ 0.076. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre (ref. code: TUPZEJ).

3.6. General procedure for the synthesis of radical ions

All manipulations were carried out under argon with common Schlenk techniques or in drybox. A typical synthetic procedure of the 4,7-disubstituted 1,2,3-benzotrichalcogenoliun hexafluorophosphates (**2**$^{+\bullet}$) is as follows. A solution of nitorosonium tetrafluorophosphate (44 mg, 0.25 mmol) in dry acetonitrile (1 ml) was added dropwise to a solution of 4,7-diisopropyl-1,2,3-benzotrithiole **2a** (64 mg, 0.25 mmol) in dry ether (10 ml) at −50°C. The mixture was stirred and allowed to warm slowly to r.t.. After removing the solvent ether (10 ml) added to the residue. The residual solid so produced was filtered off, washed with ether (4 × 6 ml) and dried under vacuum to afford dark purple solid of 4,7-diisopropyl-1,2,3-benzotrithiole **2a**$^{+\bullet}$ (95 mg, 95%).

3.6.1. Compound 2a$^{+\bullet}$

Dark-purple powder; m.p. 89.0–90.5°C (dec.); ^{31}P-NMR (THF-d_8, relative to H_3PO_4) $\delta = -145.3$ (sept, $^1J_{PF} = 711$ Hz); Anal. Found: C, 36.02; H, 3.74. Calc. for $C_{12}H_{16}S_3PF_6$: C, 35.91; H, 4.02%.

3.6.2. Compound 2c$^{+\bullet}$

Dark-blue powder; m.p. 90.5–95.5°C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.6$ (sept, $^1J_{PF} = 706$ Hz). The agreement between the calculated and found values has not yet been within the usual limit of variation of elemental analysis.

3.6.3. Compound 2f$^{+\bullet}$

Dark-blue powder; m.p.166.0–172.0°C (dec.); ^{31}P-NMR (THF-d_8, relative to H_3PO_4) $\delta = -144.0$ (sept, $^1J_{PF} = 706$ Hz); Anal. Found: C, 26.78; H, 3.29. Calc. for $C_{12}H_{16}Se_3PF_6$: C, 26.59; H, 2.97%.

3.6.4. Compound 2g$^{+\bullet}$

Dark-blue powder; m.p. 156.0–159.0°C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.4$ (sept, $^1J_{PF} = 706$ Hz); Anal. Found: C, 32.21; H, 3.36. Calc. for $C_{10}H_{12}S_3PF_6$: C, 32.17; H, 3.24%.

3.6.5. Compound 2i$^{+\bullet}$

Dark-blue powder; m.p. 159.0–164.0°C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.6$ (sept, $^1J_{PF} = 707$ Hz); Anal. Found: C, 26.09; H, 2.74. Calc. for $C_{10}H_{12}SSe_2PF_6$: C, 25.71; H, 2.59%.

3.6.6. Compound 2l$^{+\bullet}$

Dark-blue powder; m.p. 182.0–187.0°C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.6$ (sept, $^1J_{PF} = 707$ Hz); Anal. Found: C, 23.47; H, 2.50. Calc. for $C_{10}H_{12}Se_3PF_6$: C, 23.37; H, 2.50%.

3.6.7. Compound 2m$^{+\bullet}$

Dark-purple powder; m.p. 161.0–162.5°C (dec.); ^{31}P-NMR (THF-d_8, relative to H_3PO_4) $\delta = -145.1$ (sept, $^1J_{PF} = 711$ Hz); Anal. Found: C, 25.82; H, 2.07. Calc. for $C_8H_8O_2S_3PF_6$: C, 25.47; H, 2.14%.

3.6.8. Compound 2o$^{+\bullet}$

Dark-purple powder; m.p. 162.5–167.0°C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.7$ (sept, $^1J_{PF} = 706$ Hz); Anal. Found: C, 20.24; H, 1.85. Calc. for $C_8H_8O_2SSe_2PF_6$: C, 20.40; H, 1.71%.

3.6.9. Compound 2r$^{+\bullet}$

Dark-purple powder; m.p. 208.0–212.0 °C (dec.); ^{31}P-NMR (CD_3CN, relative to H_3PO_4) $\delta = -143.7$ (sept, $^1J_{PF} = 707$ Hz); Anal. Found: C, 18.84; H, 1.51. Calc. for $C_8H_8O_2Se_3PF_6$: C, 18.55; H, 1.56%.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. TIYGEN and TUPZEJ. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) T.S. Cameron, R.C. Haddon, S.M. Mattar, S. Parsons, J. Passmore, A.P. Ramirez, J. Chem. Soc. Chem. Commun. (1991) 358. (b) T.S. Cameron, R.C. Haddon, S.M. Mattar, S. Parsons, J. Passmore, A.P. Ramirez, J. Chem. Soc. Dalton Trans. (1992) 1563.

[2] G. Wolmershäuser, G. Heckmann, Angew. Chem. Int. Ed. Engl. 31 (1992) 779.

[3] (a) K. Rasheed, J.D. Warkentin, J. Org. Chem. 45 (1980) 4806. (b) B.L. Chenard, R.L. Harlow, A.L. Johnson, S.A. Vladuchick, J. Am. Chem. Soc. 107 (1985) 3871. (c) M.J. Plater, C.W. Rees, J. Chem. Soc. Perkin Trans. 1 (1991) 317. (d) N. Tokitoh, H. Ishizuka, W. Ando, Chem. Lett. (1988) 657.

[4] (a) R.E. Humphries, A.G. Massey, Phosphorus Sulfur 36 (1988) 135. (b) M.J. Earle, K.R. Griffiths, A.G. Massey, Polyhedron 11 (1992) 395.

[5] (a) S. Ogawa, T. Kikuchi, S. Niizuma, R. Sato, J. Chem. Soc. Chem. Commun. (1994) 1593. (b) S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, R. Sato, Tetrahedron Lett. 35 (1994) 5469. (c) S. Ogawa, S. Saito, T. Kikuchi, Y. Kawai, S. Niizuma, R. Sato, Chem. Lett. (1995) 321. (d) S. Ogawa, T. Ohmiya, T. Kikuchi, Y. Kawai, S. Niizuma, R. Sato, Heterocycles 43 (1995) 1843.

[6] B.L. Patel, C.B. Ziegler, N.A. Cortese, J.E. Plevyak, T.C. Zebovitz, M. Terpko, R.F. Heck, J. Org. Chem. 42 (1977) 3903.

[7] D.G. Foster, Org. Synth. Coll. 3 (1955) 771.

[8] (a) G.D. Figuly, C.K. Loop, J.C. Martin, J. Am. Chem. Soc. 111 (1989) 654. (b) E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 658. (c) K. Smith, C.M. Lindsay, G.J. Pritchard, J. Am. Chem. Soc. 111 (1989) 665.

[9] (a) R.C. Poller, J.A. Spillman, J. Chem. Soc. A (1966) 958. (b) K. Grätz, F. Huber, A. Silvestri, G. Alonzo, R. Barbieri, J. Organomet. Chem. 290 (1985) 41.

[10] (a) M. Iwaoka, S. Tomoda, Phosphorus Sulfur Silicon 67 (1992) 125. (b) J.J. Ellison, K. Ruhlandt-Senge, H.H. Hope, P.P. Power, Inorg. Chem. 34 (1995) 49. (c) P.J. Barrie, R.J.H. Clark, Phosphorus Sulfur Silicon, 34 (1995) 4299. (d) M.J. Potrzebowski, M. Michalska, J. Blaszczyk, M.W. Wieczorek, W. Ciesielski, S. Kazmierski, J. Pluskowski, J. Org. Chem. 60 (1995) 3139.

[11] (a) P. Girard, J.L. Namy, H.B. Kagan, J. Am. Chem. Soc. 102 (1980) 2693. (b) J.A. Soderquist, Aldrichim. Acta 24 (1991) 15.