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New syntheses of unsymmetrical thiepins and their selenium analogues

Hamid Shirani, Jan Bergman, Tomasz Janosik *

Unit for Organic Chemistry, Department of Biosciences and Nutrition, Karolinska Institute, Novum Research Park, SE-141 57 Huddinge, Sweden

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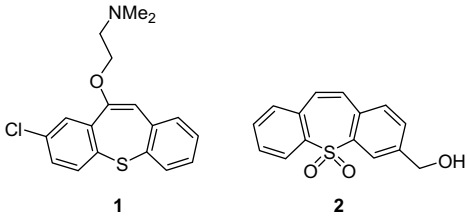
ABSTRACT

New routes toward fused thiepins and their selenium analogues are described, wherein initial cleavage of suitable diaryl disulfides or selenides bearing masked aldehyde functionalities with an *N*-protected and metalated indole-3-carbaldehyde acetal or a lithiated 2-bromobenzaldehyde acetal derivative gave a set of unsymmetrical diacetals. Subsequent deacetalization, followed by McMurry coupling, afforded the target unsymmetrical thiepins and selenepins.

1. Introduction

Cycloheptatrienes incorporating a heteroatom, such as the thiepins and selenepins, have attracted extensive attention due to the pharmacological and structural properties.[1–3] Numerous biological studies have demonstrated in particular that several dibenzo[*b*,*f*]thiepin derivatives exhibit potent biological effects.[1] For example, the system **1** (Fig. 1) has been ascribed antipsychotic properties,[4] while the oxygenated thiepin derivative **2** has been evaluated as a prostaglandin antagonist.[5] The most commonly used routes to dibenzo[*b*,*f*]thiepins rely on Friedel–Crafts-type annulation of 2(2-arylthiophenyl)acetic acid derivatives, followed by subsequent functionalization of the resulting 10,11-dihydrodibenzo[*b*,*f*]thiepin-10-ones,[6] or alternatively, reactions of bis(aryl) sulfides with chloroacetyl chloride mediated by $AlCl_3$.[7] As such previous approaches require rather complex starting materials and numerous steps, it was envisaged that more convenient access to unsymmetrical thiepin systems could be gained using a new route based on our previous work in this field, which resulted in syntheses of new symmetrical thiepins,[8] as well as some novel related cycloheptatrienes featuring other heteroatoms, namely selenium, silicon, and germanium.[9]

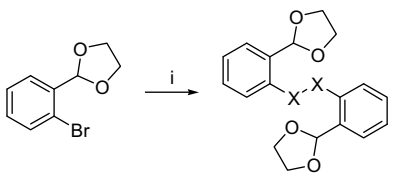


1 **2**

Figure 1.

2. Results and discussion

We now wish to describe an efficient approach toward the synthesis of unsymmetrical thiepins and the corresponding selenepins, starting from the protected diaryl sulfide **3** and the known diaryl diselenide **4**, following a variation of the concept used in our previous studies.[8,9] The only available approach to compound **4** is based on the metalation of 2-bromobenzaldehyde acetal (**5**)[10,11] using *n*-BuLi, followed by introduction of elemental selenium, but this gave only a very low yield of product (20%).[12] In order to improve the yields of compounds **3** and **4**, a modified procedure was used instead, wherein the solvent was changed from THF to diethyl ether, and an oxidative workup step was introduced (Scheme 1). This resulted in formation of **3** and **4** in somewhat better yields, 33% in both cases. Despite the fact that the yields were still rather low, the syntheses of **3** and **4** are quite useful, as only readily available and inexpensive reagents are involved, and the reactions can be conveniently carried out on multigram scale, providing sufficient amounts of material for further chemistry.



5

3 X= S (33%)
4 X= Se (33%)

Scheme 1. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 1 h, then S_8 or Se, −78 °C to rt, 16 h, then aq $K_3Fe(CN)_6$, rt, 1 h.

* Corresponding author. Tel.: +46 8 6089206; fax: +46 8 6081501.
E-mail address: tomasz.janosik@ki.se (T. Janosik).

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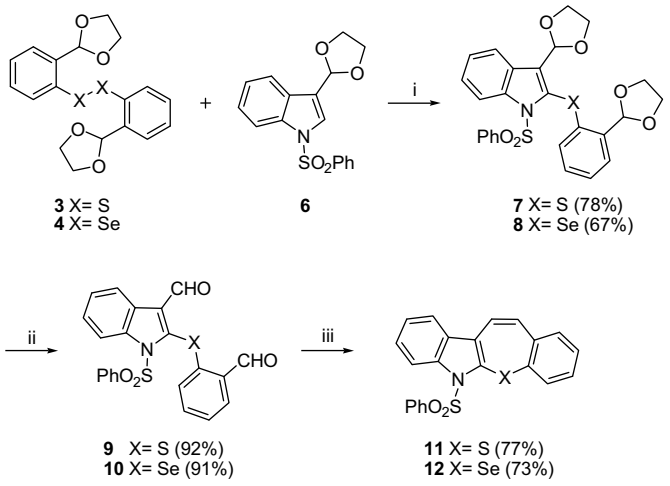
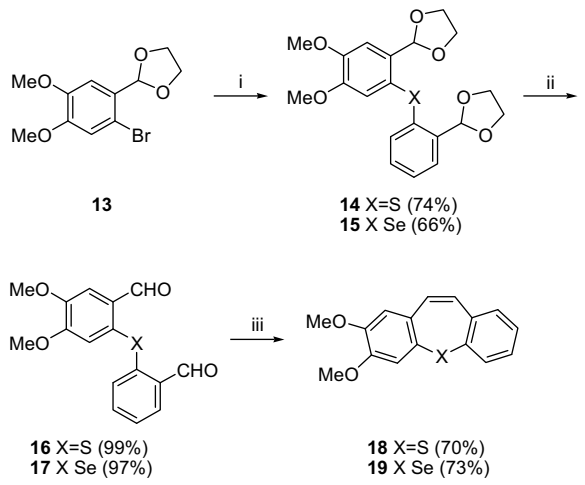
Having access to useful amounts of the disulfide **3** and diselenide **4**, experiments toward a first set of the target seven-membered ring systems were undertaken. Directed metalation[13–15] of the masked indole-3-carbaldehyde **6** as described previously,[16] followed by exposure of the resulting lithio-derivative to either the disulfide **3** or the diselenide **4**, gave the diacetals **7** and **8** in good yields (Scheme 2). As expected, the ensuing cleavage of the acetal units in acidic medium proceeded smoothly, affording the dialdehydes **9** and **10** in excellent yields. These products finally served as substrates for McMurry reactions,[17,18] leading to the desired systems **11** and **12**.



Scheme 2. Reagents and conditions: (i) LDA, THF, −78 °C, 0.5 h, then **3** or **4**, −78 °C to rt, 16 h; (ii) aq $HClO_4$, H_2O, acetone, rt, 4 h; (iii) $TiCl_4$, Zn, pyridine, THF, reflux, 2.5 h; then **9** or **10**, rt, 16 h, then reflux, 4 h; then K_2CO_3, rt, 18 h.

Likewise, halogen–metal exchange involving the acetal **13**[19] was followed by quenching with the disulfide **3** or the diselenide **4**, providing the unsymmetrical diacetals **14** and **15** in fair yields (Scheme 3). As before, acid-induced deacetalization of **14** and **15** gave the dialdehydes **16** and **17**, which were subjected to intramolecular McMurry coupling, eventually affording the known thiepin **18**[20] and its selenium analogue **19** in good overall yields.



Scheme 3. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 1 h, then **3** or **4**, −78 °C to rt, 16 h; (ii) aq $HClO_4$, H_2O, acetone, rt, 5 h; (iii) $TiCl_4$, Zn, pyridine, THF, reflux, 2.5 h; then **16** or **17**, rt, 16 h; then reflux, 4 h; then K_2CO_3, rt, 18 h.

In conclusion, we have demonstrated that diaryl disulfides or diselenides having masked aldehyde groups may be converted to unsymmetrically substituted diaryl sulfides or selenides, which can easily be deprotected, and finally annulated to unsymmetrical thiepins or selenepins using the McMurry reaction, providing a new route to this type of ring systems. It is plausible that many other heterocyclic or carbocyclic substrates may be subjected to such chemistry, allowing access to further derivatives.

3. Experimental

3.1. General information

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 instrument operating at 300.1 MHz for ^1H and 75.5 MHz for ^{13}C, respectively, using the residual solvent resonances as reference, unless otherwise stated. The IR spectra were performed on an Avatar 330 FT-IR spectrometer (Thermo Nicolet). The elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. All chemicals originated from commercial sources, and were used as received, except THF, which was distilled from sodium and benzophenone. Chromatography was performed using silica gel (particle size 40–63 μm).

3.2. General procedure for synthesis of disulfide 3 and diselenide 4

To a solution of 2-bromobenzaldehyde diethylene acetal[10,11] (6.9 g, 30 mmol) in anhydrous Et_2O (130 mL) was added *n*-BuLi (1.6 M in hexanes, 20.6 mL, 33 mmol) over 15 min under N_2 atmosphere at −78 °C. The solution was stirred for 1 h at −78 °C, resulting in the formation of a white precipitate. To this mixture was added elemental selenium or sulfur (30 mmol) in one portion, and the reaction mixture was allowed to warm to rt over 16 h. The mixture was poured into water (150 mL) containing $K_3Fe(CN)_6$ (13 g), and stirred at rt for 1 h. The layers were separated, and the aqueous phase was extracted with EtOAc (3×40 mL). The combined organic layers were washed with water (2×40 mL), brine (40 mL), and dried over Na_2SO_4. Evaporation of the solvents gave the crude products, which were treated as indicated below.

*3.2.1. 1,2-Bis[2-(1,3-dioxolan-2-yl)phenyl]disulfane (**3**).* The crude material (yellowish oil) was subjected to column chromatography using *n*-heptane/EtOAc (4:1→3:1) to give compound **3** (3.60 g, 33%) as a white solid, mp 74–75.5 °C; IR (neat) 2884, 1592, 1464, 1439, 1394, 1377, 1213, 1128, 1086, 1051, 1035, 1021, 967, 937, 863, 754, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72–7.69 (m, 2H), 7.57–7.54 (m, 2H), 7.35–7.24 (m, 4H), 6.12 (s, 2H), 4.19–4.06 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 136.5, 136.2, 130.2, 128.9, 127.2, 127.0, 101.9, 65.6. Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.01. Found: C, 59.73; H, 5.07.

*3.2.2. 1,2-Bis[2-(1,3-dioxolan-2-yl)phenyl]diselane (**4**).* The crude product was triturated with Et_2O, giving **4** (4.50 g, 33%) as a white solid, mp 117–119.5 °C (lit.[12] mp 108–110 °C). All other data were in agreement with those given previously.[12]

3.3. General procedure for synthesis of diacetals 7 and 8

To a solution of anhydrous diisopropylamine (1.3 mL, 8.8 mmol) in dry THF (20 mL) was added *t*-BuLi (1.7 M in pentane, 5.2 mL, 8.8 mmol) at −78 °C under N_2 atmosphere. After stirring at −78 °C for 1 h, 1-(phenylsulfonyl)indole-3-carbaldehyde diethylene acetal (**5**)[16] (2.64 g, 8 mmol) dissolved in dry THF (20 mL) was added for 15 min. The mixture was stirred for 40 min at −78 °C, followed by addition of **3** or **4** (8 mmol) in THF (20 mL) for 15 min. The reaction mixture was allowed to warm to room temperature overnight (16 h). A solution of satd NH_4Cl (40 mL) was added, followed by addition of Et_2O (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (30 mL). The combined

organic phases were washed with water (2×40 mL), brine (40 mL), and dried over $MgSO_4$. The solvents were evaporated, and the residue purified as indicated below, giving compound **7** or **8**.

*3.3.1. 2-[2-(1,3-Dioxolan-2-yl)phenylthio]-3-(1,3-dioxolan-2-yl)-1-(phenylsulfonyl)-1H-indole (**7**).* Purification by column chromatography using *n*-heptane/EtOAc (3:1→2:1) gave compound **7** (3.20 g, 78%) as a white solid, mp 142–144.5 °C; IR (neat) 1356, 1224, 1184, 1143, 1087, 1066, 1025, 985, 937, 768, 747, 725 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.28–8.26 (d, J=8.5 Hz, 1H), 7.87–7.80 (m, 3H), 7.66–7.13 (m, 8H), 6.64–6.61 (m, 1H), 6.19 (s, 1H), 6.02 (s, 1H), 4.19–3.39 (m, 8H); ^{13}C NMR (DMSO-d_6) δ 137.7, 137.5, 135.0, 134.8, 134.8, 129.7, 129.7, 129.5, 127.2, 127.0, 126.7, 126.7, 126.5, 126.1, 126.0, 124.1, 121.6, 114.9, 100.8, 98.9, 65.3, 64.9. Anal. Calcd for $C_{26}H_{23}NO_6S_2$: C, 61.28; H, 4.55; N, 2.75. Found: C, 61.37; H, 4.66; N, 2.61.

*3.3.2. 2-[2-(1,3-Dioxolan-2-yl)phenylselanyl]-3-(1,3-dioxolan-2-yl)-1-(phenylsulfonyl)-1H-indole (**8**).* Purification by column chromatography using *n*-heptane/EtOAc (3:1→2:1) gave compound **8** (3.00 g, 67%) as a white solid, mp 154–156 °C; IR (neat) 1355, 1220, 1182, 1173, 1137, 1086, 1063, 1024, 981, 936, 768, 748, 725 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.30–8.27 (m, 1H), 7.84–7.78 (m, 3H), 7.63–7.43 (m, 5H), 7.38–7.33 (m, 1H), 7.22–7.17 (m, 1H), 7.08–7.02 (m, 1H), 6.63 (dd, J=7.9, 1.0 Hz, 1H), 6.00 (s, 2H), 4.18–3.93 (m, 8H); ^{13}C NMR (DMSO-d_6) δ 138.2, 137.6, 135.6, 134.6, 132.1, 129.8, 129.6, 129.1, 128.9, 127.3, 126.7, 126.6, 126.5, 126.2, 123.8, 123.7, 121.5, 114.8, 102.4, 100.4, 65.2, 64.8. Anal. Calcd for $C_{26}H_{23}NO_6SSe$: C, 56.12; H, 4.17; N, 2.52. Found: C, 56.01; H, 4.26; N, 2.31.

3.4. General procedure for synthesis of diacetals 14 and 15

A solution of *n*-BuLi (1.6 M in hexanes, 4.1 mL, 6.6 mmol) was added dropwise to a solution of the acetal **13**[19] (1.73 g, 6.0 mmol) in anhydrous THF (40 mL) at −78 °C under N_2 atmosphere. The mixture was stirred for 1 h at −78 °C, followed by addition of a solution of compound **3** or **4** (2.74 g, 6.0 mmol) in THF (20 mL) for 15 min at −78 °C. The resulting mixture was allowed to warm to rt over 16–18 h, and was thereafter treated with satd aq NH_4Cl (30 mL), and extracted with Et_2O (2×30 mL). The combined organic extracts were washed with water (2×30 mL), brine (30 mL), and dried over $MgSO_4$. Evaporation of the solvents gave the crude product, which was purified as indicated below, giving the diacetal **14** or **15**.

*3.4.1. 2-{2-[2-(1,3-Dioxolan-2-yl)-4,5-dimethoxyphenylthio]phenyl}-1,3-dioxolane (**14**).* Purification by column chromatography using *n*-hexane/EtOAc (2:1→1:1) gave compound **14** (1.74 g, 74%) as a white solid, mp 125–127 °C; IR (neat) 1505, 1458, 1437, 1401, 1386, 1266, 1250, 1200, 1164, 1124, 1080, 1054, 1027, 991, 941, 877, 854, 840, 753, 723 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.53–7.50 (m, 1H), 7.28–7.18 (m, 2H), 7.13 (s, 1H), 6.92 (s, 1H), 6.83–6.80 (m, 1H), 6.09 (s, 1H), 6.01 (s, 1H), 4.12–3.88 (m, 8H), 3.81 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 149.8, 149.6, 137.1, 135.3, 133.2, 129.8, 128.7, 126.6, 125.8, 122.5, 117.9, 110.0, 100.6, 100.4, 64.9, 64.9, 55.7, 55.6. Anal. Calcd for $C_{20}H_{22}O_6S\cdot 1/8H_2O$: C, 61.17; H, 5.71. Found: C, 61.04; H, 5.73.

*3.4.2. 2-{2-[2-(1,3-Dioxolan-2-yl)-4,5-dimethoxyphenylselanyl]-phenyl}-1,3-dioxolane (**15**).* Purification by column chromatography using *n*-hexane/EtOAc (2:1→1:1) gave compound **15** (1.72 g, 66%) as a white solid, mp 126–128.5 °C; IR (neat) 1504, 1395, 1385, 1266, 1255, 1205, 1166, 1080, 1046, 1021, 983, 965, 939, 872, 755 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.51–7.48 (m, 1H), 7.28–7.18 (m, 2H), 7.13 (s, 1H), 6.99–6.96 (m, 2H), 5.97 (s, 1H), 5.95 (s, 1H), 4.11–3.88 (m, 8H), 3.80 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 149.7, 149.4, 136.7, 133.0, 132.9, 131.4, 129.9, 127.1, 126.4, 119.5, 119.2, 110.1, 102.6, 102.2, 64.9, 64.9, 55.6, 55.5. Anal. Calcd for $C_{20}H_{22}O_6Se$: C, 54.93; H, 5.07. Found: C, 54.85; H, 5.13.

3.5. General procedure for synthesis of dialdehydes 9,10 and 16,17

A solution of aqueous $HClO_4$ (70%, 0.45 mL) in H_2O (3 mL) was added to a solution of the appropriate acetal (**7**, **8**, **14**, or **15**) (1.5 mmol) in acetone (25 mL) at rt. The mixture was stirred at rt for 5 h, and was thereafter treated with satd aq $NaHCO_3$ (20 mL). The resulting mixture was extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were washed with water (30 mL), brine (30 mL), dried ($MgSO_4$), and the solvents were thereafter evaporated. The residue was triturated with Et_2O to provide the dialdehydes **9**,**10** or **16**,**17**.

*3.5.1. 2-(2-Formylphenylthio)-1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (**9**).* White solid (580 mg, 92%), mp 188–190.5 °C; IR (neat) 1675, 1561, 1436, 1375, 1367, 1218, 1192, 1167, 1144, 1110, 1085, 980, 859, 847, 751, 742, 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.33 (s, 1H), 10.25 (s, 1H), 8.48–8.42 (m, 2H), 8.00–7.97 (m, 2H), 7.91–7.86 (m, 1H), 7.61–7.35 (m, 7H), 6.78–6.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 192.0, 188.2, 140.6, 138.4, 138.2, 137.8, 135.1, 134.9, 134.5, 132.2, 129.6, 127.9, 127.9, 127.8, 127.7, 126.2, 125.8, 125.8, 122.5, 115.2. Anal. Calcd for $C_{22}H_{15}NO_4S_2$: C, 62.69; H, 3.59; N, 3.32. Found: C, 62.46; H, 3.71; N, 3.16.

*3.5.2. 2-(2-Formylphenylselanyl)-1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (**10**).* White solid (640 mg, 91%), mp 200–203 °C; IR (neat) 1667, 1385, 1209, 1194, 1176, 1083, 975, 752, 744, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.30 (s, 1H), 10.17 (d, J=0.7 Hz, 1H), 8.52–8.45 (m, 2H), 8.01–7.98 (m, 2H), 7.88 (dd, J=7.5, 1.6 Hz, 1H), 7.57–7.23 (m, 7H), 6.73 (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 192.2, 189.8, 139.1, 139.0, 138.4, 135.8, 135.1, 134.8, 134.7, 133.2, 129.8, 129.5, 128.0, 127.8, 127.5, 126.3, 126.3, 125.5, 122.4, 115.1. Anal. Calcd for $C_{22}H_{15}NO_4SSe$: C, 56.41; H, 3.23; N, 2.99. Found: C, 56.04; H, 3.34; N, 2.82.

*3.5.3. 2-(2-Formylphenylthio)-4,5-dimethoxybenzaldehyde (**16**).* White solid (450 mg, 99%), mp 149.5–152 °C; IR (neat) 1671, 1580, 1498, 1446, 1386, 1267, 1217, 1197, 1161, 1047, 844, 752, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.34 (s, 1H), 10.28 (s, 1H), 7.90–7.86 (m, 1H), 7.57 (s, 1H), 741–7.27 (m, 2H), 7.01 (s, 1H), 6.80–6.77 (m, 1H), 4.00 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 191.7, 190.8, 154.7, 150.7, 142.6, 134.5, 134.2, 132.7, 131.5, 129.0, 128.1, 125.8, 118.4, 110.7, 56.6, 56.5. Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67. Found: C, 63.49; H, 4.67.

*3.5.4. 2-(2-Formylphenylselanyl)-4,5-dimethoxybenzaldehyde (**17**).* White solid (530 mg, 97%), mp 157–159 °C; IR (neat) 1668, 1577, 1504, 1445, 1380, 1262, 1215, 1201, 1157, 1039, 1024, 866, 842, 751, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.25 (s, 1H), 10.19 (s, 1H), 7.90–7.87 (m, 1H), 7.59 (s, 1H), 7.40–7.28 (m, 2H), 7.15 (s, 1H), 6.90–6.85 (m, 1H), 4.01 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.0, 192.8, 154.5, 150.6, 139.1, 135.6, 134.5, 134.0, 131.6, 130.2, 126.3, 126.2, 120.1, 111.0, 56.6, 55.4. Anal. Calcd for $C_{16}H_{14}O_4Se\cdot 1/8H_2O$: C, 54.67; H, 4.09. Found: C, 54.53; H, 4.11.

3.6. General procedure for synthesis of thiepins and selenepins 11,12 and 18,19

$TiCl_4$ (2.7 mL, 25 mmol) was added cautiously for 10 min to dry THF (100 mL) at −78 °C under argon atmosphere and the resulting solution was stirred for 5 min. The mixture was allowed to warm to rt, followed by addition of zinc powder (3.3 g, 50 mmol) and pyridine (0.5 mL). This suspension was heated at reflux for

2.5 h. The appropriate dialdehyde (**9**,**10** or **16**,**17**) (1.0 mmol) was added slowly as a dilute solution in dry THF (100 mL) over 4 h. After complete addition, the reaction mixture was allowed to stir at rt for 16 h, and was thereafter heated at reflux for an additional period of 4 h. After cooling to rt, a 50% aqueous solution of K_2CO_3 (50 mL) was added. The resulting mixture was stirred vigorously for 18 h and thereafter passed through a pad of Celite, which was washed with EtOAc (40 mL). The layers were separated and the aqueous phase was extracted with EtOAc (50 mL). The combined organic layers were washed with water (2×50 mL), brine (50 mL), and dried (Na_2SO_4). Evaporation of the solvents, followed by purification of the residue as indicated below, yielded compounds **11**,**12** or **18**,**19**.

*3.6.1. 6-(Phenylsulfonyl)-[1]benzothiepino[2,3-b]indole (**11**).* Purification by column chromatography using *n*-hexane/EtOAc (6:1) gave compound **11** (300 mg, 77%) as a white solid, mp 192.5–195 °C; IR (neat) 1439, 1356, 1229, 1167, 1150, 1112, 1084, 973, 786, 763, 746, 723 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.21–8.18 (m, 1H), 8.09–8.06 (m, 2H), 7.76–7.61 (m, 4H), 7.46–7.13 (m, 8H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 141.2, 137.8, 136.8, 134.8, 134.1, 132.4, 130.3, 130.0, 130.0, 129.7, 129.2, 126.9, 126.8, 125.8, 125.2, 124.0, 123.8, 123.4, 119.0, 114.2. Anal. Calcd for $C_{22}H_{15}NO_2S_2$: C, 67.84; H, 3.88; N, 3.60. Found: C, 67.96; H, 3.95; N, 3.44.

*3.6.2. 6-(Phenylsulfonyl)-[1]benzoselenepino[2,3-b]indole (**12**).* Purification by column chromatography using *n*-hexane/EtOAc (6:1→4:1) gave compound **12** (320 mg, 73%) as a white solid, mp 177–179.5 °C; IR (neat) 1437, 1356, 1228, 1165, 1150, 1106, 1081, 973, 787, 762, 749, 722 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.19–8.10 (m, 3H), 7.74–7.59 (m, 4H), 7.45–7.31 (m, 6H), 7.21 (d, J=12.1 Hz, 1H), 7.10 (d, J=12.1 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 141.4, 137.4, 137.2, 134.8, 134.5, 133.7, 130.3, 129.9, 129.9, 129.0, 128.1, 126.9, 126.7, 125.4, 124.0, 123.9, 123.8, 120.8 118.8, 114.1. Anal. Calcd for $C_{22}H_{15}NO_2SSe$: C, 60.55; H, 3.46; N, 3.21. Found: C, 60.36; H, 3.52; N, 3.06.

*3.6.3. 2,3-Dimethoxydibenzo[b,f]thiepin (**18**).* Purification by column chromatography using *n*-hexane/EtOAc (7:1) gave compound **18** (190 mg, 70%) as a white solid, mp 107–112 °C (lit.[20] mp 123–124 °C); IR (neat) 1588, 1497, 1466, 1435, 1413, 1355, 1341, 1249, 1230, 1204, 1178, 1150, 1049, 1026, 973, 865, 855, 803, 776, 751 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.45–7.41 (m, 1H), 7.36–7.32 (m, 3H), 7.00–6.97 (m, 4H), 3.77 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 149.8, 148.8, 140.0, 133.7, 133.6, 132.7, 132.2, 132.0, 129.3, 129.3, 128.4, 124.2, 115.1, 112.4, 55.7, 55.6. Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.15; H, 5.23.

*3.6.4. 2,3-Dimethoxydibenzo[b,f]selenepin (**19**).* Purification by column chromatography using *n*-hexane/EtOAc (7:1) gave compound **19** (230 mg, 73%) as a white solid, mp 117–120 °C; IR (neat) 1589, 1503, 1463, 1433, 1354, 1339, 1250, 1229, 1206, 1175, 1150, 1041, 1025, 864, 794, 778, 746 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.57–7.54 (m, 1H), 7.34–7.25 (m, 3H), 7.10 (s, 1H), 6.96–6.95 (m, 3H), 3.76 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 149.8, 148.8, 140.2, 134.2, 133.4, 132.9, 132.7, 129.5, 129.3, 129.2, 128.3, 119.6, 116.4, 112.7, 55.6, 55.5. Anal. Calcd for $C_{16}H_{14}O_2Se$: C, 60.58; H, 4.45. Found: C, 60.37; H, 4.50.

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