MoV-Mediated Synthesis of Non-Symmetric Diaryl and Aryl Alkyl Chalcogenides

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Supporting Information

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General remarks

All reagents were used of analytical grades. Solvents were desiccated if necessary by standard methods. Flash chromatography was performed on silica gel (40–60 μm, Merck, Darmstadt, Germany) by using mixtures of cyclohexane with ethyl acetate or n-heptane as eluents. For thin-layer chromatography, silica gel 60 sheets (F²₅₄, Merck, Darmstadt, Germany) were applied. Novel compounds were characterized by \(^1\)H NMR and \(^{13}\)C NMR, in addition to high resolution mass spectrometry. Copies of the \(^1\)H and \(^{13}\)C NMR are attached. \(^1\)H and \(^{13}\)C NMR spectra were recorded at 25 °C using a Bruker Avance III HD 300 or Avance II 400 instrument (Analytische Messtechnik, Karlsruhe, Germany). All \(^1\)H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were referenced to the signal for residual chloroform (7.26 ppm), d₁-dichloromethane (5.32 ppm) or d₂-acetonitrile (1.94 ppm) in the deuterated solvent. All \(^{13}\)C NMR spectra are reported in ppm relative d₁-chloroform (77.16 ppm), d₂-dichloromethane (53.84 ppm) or d₃-acetonitrile (1.32 ppm) and were obtained by \(^1\)H decoupling. The deuterated solvents were employed as purchased without further purification or drying. Melting points were measured by using a Stuart Scientific SMP 3 (Bibby Scientific, Stone, UK) and are uncorrected. FD mass spectra were performed on a MAT 95 (Thermo Finnigan, Bremen, Germany) apparatus and GC-MS mass spectra were measured with a GC-2010 gas chromatograph combined with a GCMS-QP2010 mass analyzer (Shimadzu, Kyoto, Japan). ESI high resolution mass spectra were obtained by using a QTof Ultima 3 (Waters, Milford, Massachusetts) instrument and APCI high resolution mass spectra were carried out using a Thermo QExact (Thermo Fisher Scientific, Waltham, Massachusetts).
Synthesis and characterization of the products

**Bis(2,4-dimethylphenyl)disulfide 5a**

According to the protocol for the disulfide synthesis (A), 2,4-dimethylthiophenol (5.11 g, 37.0 mmol) was treated with iodine (6.19 g, 24.4 mmol) in pyridine (85 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5a as a slightly yellow oil. (4.04 g, 79%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ = 7.36 (d, $J$ = 7.9 Hz, 2H), 7.04 (d, $J$ = 1.3 Hz, 2H), 6.95 (dd, $J$ = 7.9, 1.3 Hz, 2H), 2.32 (s, 6H), 2.25 (s, 6H). GCMS (EI+) m/z = 274.

All analytic data match to the reported data.\(^3\)

**Bis(4-methylphenyl)disulfide 5b**

According to the protocol for the disulfide synthesis (A), 4-methylthiophenol (2.00 g, 12.1 mmol) was treated with iodine (2.70 g, 7.97 mmol) in pyridine (55 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5b as a slightly yellow solid. (1.70 g, 85%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.46 (d, $J$ = 8.1 Hz, 4H), 7.16 (d, $J$ = 8.1 Hz, 4H), 2.38 (s, 6H). GCMS (EI+) m/z = 246.

All analytic data match to the reported data.\(^4\)

**Diphenyldisulfide 5c**

According to the protocol for the disulfide synthesis (A), thiophenol (1.20 g, 10.9 mmol) was treated with iodine (1.82 g, 7.19 mmol) in pyridine (35 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5c as a colorless solid. (1.11 g, 93%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ = 7.54–7.51 (m, 4H), 7.37–7.32 (m, 4H), 7.30–7.25 (m, 2H). GCMS (EI+) m/z = 218.

All analytic data match to the reported data.\(^4\)

**Dinaphth-2-yldisulfide 5d**

According to the protocol for the disulfide synthesis (A), 2-thionaphthol (1.20 g, 7.49 mmol) was treated with iodine (1.25 g, 4.94 mmol) in pyridine (20 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5d as a colorless solid. (1.11 g, 93%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 8.01 (m, 2H), 7.82–7.73 (m, 6H), 7.64 (dd, $J$ = 8.7, 2.0 Hz, 2H), 7.50–7.44 (m, 4H). GCMS (EI+) m/z = 318.
All analytic data match to the reported data.¹

**Bis(4-iodophenyl)disulfide 5e**

According to the protocol for the disulfide synthesis (A), 4-iodothiophenol (0.50 g, 2.12 mmol) was treated with iodine (0.36 g, 1.40 mmol) in pyridine (20 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5e as a colorless solid (0.44 g, 88%).

¹H NMR (400 MHz, CDCl₃): δ = 7.65–7.62 (m, 4H), 7.25–7.21 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ = 138.7, 137.2, 93.0. HRMS (APCI+) m/z calcd for C₁₂H₈I₂S₂ [M⁺] 469.8151, found 469.8160.

**Bis(4-fluorophenyl)disulfide 5f**

According to the protocol for the disulfide synthesis (A), 4-fluorothiophenol (1.00 g, 7.80 mmol) was treated with iodine (1.31 g, 5.15 mmol) in pyridine (25 mL) for 30 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5f as a slightly yellow oil (0.76 g, 76%).

¹H NMR (400 MHz, CDCl₃): δ = 7.48–7.43 (m, 4H), 7.05–6.99 (m, 4H). GCMS (EI⁺) m/z = 254.

All analytic data match to the reported data.¹

**Diphenyldiselenide 5g** was purchased from Tokyo Chemical Industries (Tokyo, Japan).

**Di(n-octyl)disulfide 5h**

According to the protocol for the disulfide synthesis (A), 1-octylthiol (1.26 g, 8.64 mmol) was treated with iodine (1.45 g, 5.70 mmol) in pyridine (25 mL) for 15 min. The crude product was filtered through a pad of silica (eluent: cyclohexane/ethyl acetate, 9:1) to yield compound 5h as a colorless oil (1.14 g, 91%).

¹H NMR (400 MHz, CDCl₃): δ = 2.68 (t, J = 7.3 Hz, 4H), 1.67 (p, J = 7.3 Hz, 4H), 1.40–1.27 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H). GCMS (EI⁺) m/z = 290.

All analytic data match to the reported data.¹

**2,4-Dimethylphenyl-2',4',6'-trimethoxyphenylsulfide 6a**

According to the protocol for the oxidative coupling reaction (B), bis(2,4-dimethylphenyl)disulfide 5a (0.25 g, 0.91 mmol) was treated with MoCl₅ (0.75 g, 2.73 mmol) and TiCl₄ (0.57 g, 3.00 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.77 g, 4.56 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography.
(eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6a as a colorless solid. (0.33 g, 60%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta = 6.95$ (m, 1H), 6.78–6.76 (m, 1H) 6.43 (d, $J = 8.0$ Hz, 1H), 6.30 (s, 2H), 3.85 (s, 3H), 3.74 (s, 6H), 2.33 (s, 3H), 2.20 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$CN): $\delta = 164.1, 163.6, 135.3, 135.3, 134.9, 131.6, 127.8, 125.9, 98.9, 92.4, 56.8, 56.3, 20.7, 19.9$. HRMS (ESI+) $m/z$ calcld for C$_{17}$H$_{20}$O$_3$S [M+Na]$^+$ 327.1031, found 327.1028. m.p.: 147.8–149.4 °C.

**4-Methylphenyl-2',4',6'-trimethoxyphenylsulfide 6b**

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.15 g, 0.61 mmol) was treated with MoCl$_5$ (0.50 g, 1.83 mmol) and TiCl$_4$ (0.38 g, 2.01 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.51 g, 3.04 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6b as a colorless solid. (0.23 g, 64%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta = 7.01–6.99$ (m, 2H), 6.85–6.82 (m, 2H), 6.30 (s, 2H), 3.85 (s, 3H), 3.75 (s, 6H). GCMS (EI+) $m/z$ = 290. m.p.: 118.2–120.9 °C.

All analytic data match to the reported data.$^5$

**Phenyl-2,4,6-trimethoxyphenylsulfide 6c**

According to the protocol for the oxidative coupling reaction (B), diphenyl disulfide 5c (0.15 g, 0.69 mmol) was treated with MoCl$_5$ (0.56 g, 2.06 mmol) and TiCl$_4$ (0.43 g, 2.27 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.58 g, 3.44 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6c as a colorless solid. (0.20 g, 51%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta = 7.20–7.15$ (m, 2H), 7.07–7.03 (m, 2H), 6.94–6.91 (m, 2H), 6.31 (s, 2H), 3.86 (s, 3H), 3.76 (s, 6H). GCMS (EI+) $m/z$ = 276. m.p.: 122.7–124.4 °C.

All analytic data match to the reported data.$^5$

**Naphth-2-yl-2',4',6'-trimethoxyphenylsulfide 6d**

According to the protocol for the oxidative coupling reaction (B), dinaphthyl disulfide 5d (0.20 g, 0.63 mmol) was treated with MoCl$_5$ (0.52 g, 1.89 mmol) and TiCl$_4$ (0.39 g, 2.07 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.53 g, 3.14 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6d as a colorless solid. (0.18 g, 47%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta = 7.09–7.06$ (m, 3H), 7.00–6.90 (m, 3H), 6.91–6.88 (m, 2H), 6.30 (s, 2H), 3.86 (s, 3H), 3.76 (s, 6H). GCMS (EI+) $m/z$ = 302. m.p.: 137.2–139.4 °C.

All analytic data match to the reported data.$^5$
cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6d as a colorless solid. (0.17 g, 41%).

1H NMR (400 MHz, CDCl3): δ = 7.74 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.41–7.31 (m, 3H), 7.17 (dd, J = 8.6, 1.9 Hz, 1H), 6.27 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H). GCMS (EI+) m/z = 326. m.p.: 110.0–111.1 °C.

All analytic data match to the reported data.5

4-Iodophenyl-2',4',6'-trimethoxyphenylsulfide 6e

According to the protocol for the oxidative coupling reaction (B), bis(4-iodophenyl)disulfide 5e (0.25 g, 0.53 mmol) was treated with MoCl5 (0.44 g, 1.60 mmol) and TiCl4 (0.33 g, 1.78 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.45 g, 2.66 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6e as a colorless solid. (0.25 g, 55%).

1H NMR (400 MHz, CD3CN): δ = 7.50–7.47 (m, 2H), 6.73–6.69 (m, 2H), 6.30 (s, 2H), 3.85 (s, 3H), 3.75 (s, 6H). 13C NMR (101 MHz, CD3CN): δ = 164.6, 163.5, 140.8, 138.4, 128.0, 92.4, 88.5, 56.9, 56.3. HRMS (APCI+) m/z calcd for C15H15IS [M+H]+ 402.9865, found 402.9850. m.p.: 134.5–135.5 °C.

All analytic data match to the reported data.5

4-Fluorophenyl-2',4',6'-trimethoxyphenylsulfide 6f

According to the protocol for the oxidative coupling reaction (B), bis(4-fluorophenyl)disulfide 5f (0.15 g, 0.59 mmol) was treated with MoCl5 (0.48 g, 1.77 mmol) and TiCl4 (0.37 g, 1.95 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.50 g, 2.95 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6f as a colorless solid. (0.22 g, 67%).

1H NMR (400 MHz, CD3CN): δ = 7.00–6.91 (m, 4H), 6.30 (s, 2H), 3.85 (s, 3H), 3.76 (s, 6H). GCMS (EI+) m/z = 294. m.p.: 87.3–88.7 °C.

All analytic data match to the reported data.5

Phenyl-2,4,6-trimethoxyphenylselenide 6g

a) According to the protocol for the oxidative coupling reaction (B), diphenyldiselenide 5g (0.15 g, 0.48 mmol) was treated with MoCl5 (0.39 g, 1.44 mmol) and TiCl4 (0.30 g, 1.59 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.40 g, 2.40 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 60 min. After the described workup, the crude product was purified by flash column chromatography (eluent:
cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6g as a colorless solid. (0.08 g, 26%).

b) According to the protocol for the oxidative coupling reaction (B), diphenyldiselenide 5g (0.20 g, 0.64 mmol) was treated with MoCl₅(HFIP)₂ (1.03 g, 1.92 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 1,3,5-trimethoxybenzene 4 (0.54 g, 3.20 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 60 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 9:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 6g as a colorless solid. (0.19 g, 45%).

1H NMR (400 MHz, CD₃CN): δ = 7.18–7.08 (m, 5H), 6.30 (s, 2H), 3.85 (s, 3H), 3.74 (s, 6H). GCMS (EI+) m/z = 324. m.p.: 107.8–108.9 °C.

All analytic data match to the reported data.⁵

n-Octyl-2,4,6-trimethylphenylsulfide 6h

According to the protocol for the oxidative coupling reaction (B), bis(n-octyl)disulfide 5h (0.20 g, 0.69 mmol) was treated with MoCl₅ (0.56 g, 2.07 mmol) and TiCl₄ (0.43 g, 2.27 mmol) in anhydrous dichloromethane (20 mL). Subsequently, mesitylene 7b (0.41 g, 3.44 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: n-heptane) to yield compound 6h as a colorless oil. (0.16 g, 45%).

1H NMR (400 MHz, CDCl₃): δ = 6.94 (s, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.52 (s, 6H), 2.27 (s, 3H), 1.58–1.50 (m, 2H), 1.42–1.35 (m, 2H), 1.32–1.27 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 143.0, 137.9, 130.7, 129.0, 35.7, 32.0, 30.0, 29.4, 29.1, 22.8, 22.1, 21.1, 14.2. HRMS (APCI+) m/z calcd for C₁₇H₂₀S [M+H]+ 265.1984, found 265.1986.

4-Methoxyphenyl-4’-methylphenylsulfide and 2-Methoxyphenyl-4’-methylphenylsulfide 8a

According to the protocol for the oxidative coupling reaction (B), bis(4-methoxyphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, anisole 7a (0.44 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 15 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) to yield compound mixture 8a as a yellow oil. (0.25 g, 67%).

1H NMR (400 MHz, CDCl₃): para-8a: δ = 7.39–7.35 (m, 2H), 7.16–7.13 (m, 2H), 7.08–7.06 (m, 2H), 6.90–6.86 (m, 2H), 3.81 (s, 3H), 2.31 (s, 3H). ortho-8a: δ = 7.34–7.32 (m, 2H), 7.21–7.17 (m, 3H), 6.95 (dd, J = 7.7, 1.7 Hz, 1H), 6.87–6.82 (m, 2H), 3.90 (s, 3H), 2.37 (s, 3H). GCMS (EI+) m/z = 230.

All analytic data match to the reported data.⁶
4-Methylphenyl-2',4',6'-trimethylphenylsulfide 8b

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl$_5$ (0.66 g, 2.44 mmol) and TiCl$_4$ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, mesitylene 7b (0.49 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) and recrystallized from methanol (approx. 15 mL, 65 → 4 °C) to yield compound 8b as a colorless solid. (0.24 g, 62%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.01–6.98 (m, 4H), 6.85–6.81 (m, 2H), 2.39 (s, 6H), 2.32 (s, 3H), 2.27 (s, 3H). GCMS (EI+) m/z = 242. m.p.: 89.4–90.3 °C.

All analytic data match to the reported data.$^7$

Bis(4-methylphenyl)sulfide 8c

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl$_5$ (0.66 g, 2.44 mmol) and TiCl$_4$ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, toluene 7c (0.37 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) to yield compound 8c as a colorless solid. (0.10 g, 30%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.26–7.23 (m, 4H), 7.12–7.09 (m, 4H), 2.33 (s, 6H). GCMS (EI+) m/z = 214.

All analytic data match to the reported data.$^6$

4-Methylphenyl-5’-(1,1-dimethylethyl)-2’-methoxyphenylsulfide 8d

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl$_5$ (0.66 g, 2.44 mmol) and TiCl$_4$ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 4-(1,1-dimethylethyl)-anisole 7d (0.67 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 10 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/toluene, 3:1) to yield compound 8d as a colorless oil. (0.21 g, 44%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ = 7.29 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.21–7.16 (m, 4H), 7.10 (d, $J$ = 2.5 Hz, 1H), 6.92 (d, $J$ = 8.6 Hz, 1H), 3.79 (s, 3H), 2.32 (s, 3H), 1.18 (s, 9H). $^{13}$C NMR (101 MHz, CD$_3$CN): $\delta$ = 156.2, 144.8, 138.2, 132.2, 132.0, 130.9, 129.5, 126.2, 124.1, 111.8, 56.5, 34.7, 31.6, 21.1. HRMS (ESI+) m/z calcd for C$_{18}$H$_{22}$OS [M+Na]$^+$ 309.1289, found 309.1285.

p8
4-Methylphenyl-4’-methoxy-2’-methyl-5’-(tris(1-methylethyl)silyloxy)phenylsulfide 8e

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 5-methyl-2-(triisopropylsilyloxy)anisole 7e (1.20 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 10 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) to yield compound 8e as a colorless solid (0.25 g, 36%).

¹H NMR (400 MHz, CDCl₃): δ = 7.06–7.01 (m, 4H), 6.85 (s, 1H), 6.73 (s, 1H), 3.80 (s, 3H), 2.30 (s, 6H), 1.20–1.11 (m, 3H), 1.04–1.03 (m, 18H). ¹³C NMR (101 MHz, CDCl₃): δ = 151.1, 143.9, 135.8, 134.0, 133.9, 129.8, 128.9, 126.0, 123.8, 114.4, 55.8, 21.1, 20.4, 18.0, 12.9. HRMS (ESI+) m/z calcd for C₄₂H₃₅O₃Si [M+H]+ 417.2284, found 417.2299. m.p.: 68.8–69.7 °C.

4-Methylphenyl-5’-bromo-2’-iodo-4’-methoxyphenylsulfide 8f

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 2-bromo-5-iodoanisole 7f (1.27 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 15 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) and recrystallized from methanol (approx. 15 mL, 65–4 °C) to yield compound 8f as a colorless solid (0.37 g, 52%).

¹H NMR (400 MHz, CD₂Cl₂): δ = 7.38 (s, 1H), 7.32 (s, 1H), 7.32–7.20 (m, 2H), 7.18–7.16 (m, 2H), 3.87 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CD₂Cl₂): δ = 155.8, 138.7, 135.5, 134.5, 131.9, 131.9, 130.9, 123.5, 113.1, 101.4, 57.3, 21.4. HRMS (ESI+) m/z calcd for C₁₄H₁₂OS²BrI [M+H]+ 434.8915, found 434.8924. m.p.: 135.2–136.7 °C.

3-(4-Methylphenylsulfanyl)-2-phenylbenzo[b]furan 8g

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 2-phenylbenzo[b]furan 7g (0.79 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: n-heptane) to yield compound 8g as a colorless solid (0.15 g, 30%).

¹H NMR (400 MHz, CD₃CN): δ = 8.22–8.20 (m, 2H), 7.62 (dt, J = 8.2, 0.8 Hz, 1H), 7.54–7.44 (m, 4H), 7.39 (ddd, J = 8.3, 7.3, 1.4 Hz, 1H), 7.27 (ddd, J = 8.1, 7.3, 1.0 Hz, 1H), 7.13–7.10 (m, 2H), 7.07–7.04 (m, 2H), 2.24 (s, 3H). GCMS (EI+) m/z = 316.

All analytic data match to the reported data.⁸
According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, N-(methylphenylsulfonyl)indole 7h (1.10 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 30 min. After the described workup, the crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 19:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 8h as a colorless solid. (0.25 g, 39%).

**1H NMR (400 MHz, CD₃CN):** δ = 8.01–7.98 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.87–7.82 (m, 2H), 7.38–7.30 (m, 4H) 7.23–7.19 (m, 1H), 7.06–7.00 (m, 4H), 2.32 (s, 3H), 2.23 (s, 3H).

**13C NMR (101 MHz, CD₃CN):** δ = 147.0, 137.3, 136.2, 135.1, 132.9, 131.9, 131.1, 130.7, 129.1, 127.8, 126.5, 125.0, 121.0, 114.8, 113.8, 21.6, 20.9.

**HRMS (ESI+) m/z calcd for C₂₂H₁₉NO₂S₂ [M+H]+ 394.0935, found 394.0940. m.p.: 96.6–98.1 °C.**

According to the protocol for the oxidative coupling reaction (B), bis(4-methylphenyl)disulfide 5b (0.20 g, 0.81 mmol) was treated with MoCl₅ (0.66 g, 2.44 mmol) and TiCl₄ (0.51 g, 2.68 mmol) in anhydrous dichloromethane (20 mL). Subsequently, 5-methoxy-N-(methylsulfonyl)indole 7i (0.91 g, 4.06 mmol) in anhydrous dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred for 15 min. In contrast to the general protocol, the reaction mixture was filtered through a pad of silica using dichloromethane as an eluent and subsequently the solvent was evaporated. The crude product was purified by flash column chromatography (eluent: cyclohexane/ethyl acetate, 3:1) and recrystallized from methanol (approx. 15 mL, 65→4 °C) to yield compound 8i as a colorless solid. (0.12 g, 20%).

**1H NMR (400 MHz, CD₃CN):** δ = 7.80 (d, J = 9.0 Hz, 1H), 7.72 (s, 1H), 7.20–7.17 (m, 2H), 7.09–7.07 (m, 2H), 7.01 (dd, J = 9.0, 2.5 Hz, 1H), 6.91 (d, J = 2.5 Hz, 1H).

**13C NMR (101 MHz, CD₃CN):** δ = 157.9, 137.4, 133.1, 132.9, 132.3, 130.9, 130.8, 129.2, 115.3, 115.3, 112.2, 103.2, 56.3, 41.7, 20.9.

**HRMS (ESI+) m/z calcd for C₁₇H₁₇NO₂S₂ [M+Na]+ 370.0548, found 370.0547. m.p.: 108.7–109.2 °C.**
NMR spectra

$^1$H NMR, 400 MHz, CD$_3$CN

$^1$H NMR, 300 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CD$_3$CN

$^1$H NMR, 400 MHz, CD$_2$Cl$_2$
$^{13}$C NMR, 101 MHz, CD$_3$CN

$^1$H NMR, 400 MHz, CD$_3$CN
$^1$H NMR, 400 MHz, CDCl$_3$

8b

$^1$H NMR, 400 MHz, CDCl$_3$

8c
$^{13}$C NMR, 101 MHz, CD$_3$CN

8h
Molecular structures

2,4-Dimethylphenyl-2′,4′,6′-trimethoxyphenylsulfide 6a

Cambridge Database: CCDC 1520078

The single crystals of compound 6a were prepared as described on page 4/5.

Phenyl-2,4,6-trimethoxyphenylselenide 6g

Cambridge Database: CCDC 1520079

The single crystals of compound 6g were prepared as described on page 6/7.
4-Methylphenyl-5'-bromo-2'-iodo-4'-methoxyphenylsulfide 8f
Cambridge Database: CCDC 1520081
The single crystals of compound 8f were prepared as described on page 9.

3-(4-Methylphenylsulfanyl)-N-(methylphenylsulfonyl)indole 8h
Cambridge Database: CCDC 1520080
The single crystals of compound 8h were prepared as described on page 10.
5-Methoxy-3-(4-Methylphenylsulfanyl)-N-(methylsulfonyl)indole 8i

Cambridge Database: CCDC 1520082

The single crystals of compound 8i were prepared as described on page 10.

The comparison of the indole derivatives (8h and 8i) is highly considerable. While the tosyl group from product 8h is arranged almost planar to the 4-methylphenyl group due to possible π interactions, the mesyl group from product 8i is pointing in the opposite direction.

References