Fast Synthesis and Redox Switching of Di- and Tetra-substituted Bisthioxanthylidene Overcrowded Alkenes

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1 General comments

All reagents and solvents were purchased from Sigma Aldrich, TCI Europe, Acros Organics, Fluorochem or Alfa Aesar and were used without further purification. Dry solvents were obtained from an MBraun SPS-800 solvent purification system. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise noted. Flash column chromatography was performed on silica gel (Merck, type 9385, 230-400 mesh). NMR spectra (¹H and ¹³C) were recorded on a Varian Mercury-Plus 400 spectrometer or a Bruker Avance 600 NMR spectrometer at 298K (referenced to residual solvent signal: for ¹H detection, δ = 7.26 ppm ; for ¹³C detection, δ = 77.16 ppm for CDCl₃). High resolution mass spectroscopy (HRMS) was performed on a LTQ Orbitrap XL spectrometer with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) as ionization technique. Cyclic voltammograms were recorded using a three-electrode setup on a CHI600C electrochemical workstation (CH Instruments) or a VSP-300 Potentiostat/Galvanostat (Biologic Science Instruments) using a saturated calomel electrode (SCE) reference electrode, a freshly polished glassy carbon (3 mm diameter) disc working electrode, and a platinum wire as counter electrode. All CVs were recorded with a scan speed of 0.010 Vs⁻¹ at room temperature with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in CH_2CI_2 , unless otherwise stated.

2 Synthesis

2.1 General methods



General method A – Ullmann thioether synthesis

In a pressure tube, the appropriate 2-halogenated benzoic acid **4** (1.00 equiv.), the appropriate benzene thiol **5** (1.05 equiv.), K_2CO_3 (3 equiv.) and Cu powder (5%) were suspended in DMF (0.3 M). The reaction mixture was degassed with Ar by bubbling for 15 min and the tube was closed. The reaction mixture was heated at reflux for 16 h. Afterwards, the mixture was allowed to cool to room temperature and was diluted with H₂O. Aqueous HCI (6 M) was added to precipitate the thioether-benzoic acid product, which was subsequently filtered off and used without further purification.

General method B – Friedel Crafts acylation

The appropriate thioether-benzoic acid was added portion wise to stirring concentrated sulfuric acid. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was carefully quenched by pouring it into an ice/water mixture. The product was extracted with CH_2CI_2 and washed with saturated NaCl (aq) solution. The thioxanthone products were purified by flash column chromatography (silica gel, EtOAc/*n*-pentane or CH_2CI_2/n -pentane).

General method C – Thionation

The appropriate thioxanthone **3** (1.0 equiv.) and P_2S_5 (2.0 equiv.) were dissolved in toluene (0.1 M) and heated at reflux until full conversion of the ketone **3** (approximately 3 h). The crude reaction mixture was filtered over a short pad of silica and flushed with CH_2Cl_2 . Volatiles were removed under reduced pressure and the product was purified by flash column chromatography (silica gel, EtOAc/*n*-pentane or CH_2Cl_2/n -pentane) and used directly for the dimerization procedure.

General method D - Dimerization

The appropriate thicketone 2 (1.0 equiv.) was dissolved in dry THF (0.05 M). 0.5 equivalent of the thioketone solution was added to a separate Schlenk flask. The mixture was cooled to -78 °C and TMSCHN₂ (0.55 equiv., 2.0 M in Et₂O) was added. Immediately after addition, the mixture was allowed to warm up to room temperature. The typical thicketone color fades and gas evolution can sometimes be observed. When the color change is complete, the remaining thioketone solution is added and the mixture was stirred at room temperature for 10 min. There should be no remaining thicketone color in the reaction mixture; full conversion of the chromatographic additionally confirmed by thin-layer thioketone was analysis. Tetrabutylammonium fluoride (2.0 equiv., 1.0 M in THF) was added to the mixture and followed by stirring at room temperature for 5 min. Volatiles were removed under reduced pressure and the product was purified by flash column chromatography (silica gel, CH₂Cl₂/n-pentane in ratios 1:50 to 1:1). If necessary, the products were triturated with cold *n*-pentane.

2.2 Data of bisthioxanthylidenes



2,2'-dimethyl-9,9'-bisthioxanthylidene (1a). Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.48, 15% CH₂Cl₂/*n*-pentane) on a 1.26 mmol scale as a white solid in 70% yield (183 mg, 0.44 mmol), 61:39 major/minor ratio. ¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.51 (m, 2H_{maj} + 2H_{min}), 7.43 – 7.39 (m, 2H_{maj} + 2H_{min}), 7.14 – 7.09 (m, 2H_{maj} + 2H_{min}), 6.98 – 6.93 (m, 2H_{maj} + 2H_{min}), 6.92 – 6.87 (m, 2H_{maj} + 2H_{min}), 6.82 – 6.79 (m, 2H_{maj} + 2H_{min}), 6.61 – 6.57 (m, 2H_{maj} + 2H_{min}), 2.02 (s, 6H_{maj}), 2.01 (s, 6H_{min}). ¹³C NMR (151 MHz, CDCl₃) δ 136.3, 136.2, 136.0, 135.9, 135.9, 135.8, 135.6, 135.4, 133.6, 132.2, 130.6, 130.6, 130.0, 130.0, 127.7, 127.7, 127.2, 127.1, 126.9, 126.8, 126.8, 126.7, 125.8, 125.5, 21.0, 20.9. HRMS (ESI Pos) for [C₂₈H₂₀S₂]+ calcd. m/z = 420.1001, found 420.0997.



3,3'-dimethyl-9,9'-bisthioxanthylidene (1b) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.37, 15% CH₂Cl₂/*n*-pentane) on a 1.07 mmol scale as a white solid in 56% yield (127 mg, 0.30 mmol), 72:28 major/minor ratio. ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H_{maj} + 2H_{min}), 7.35 (s, 2H_{maj} + 2H_{min}), 7.13 – 7.07 (m, 2H_{maj} + 2H_{min}), 6.93 – 6.82 (m, 2H_{maj} + 4H_{min}), 6.81 – 6.77 (m, 2H_{maj}), 6.74 (d, *J* = 1.4 Hz, 4H_{maj}), 6.70 (dd, *J* = 8.3, 7.9 Hz, 4H_{min}), 2.30 (s, 6H_{maj}), 2.29 (s, 6H_{min}). ¹³C NMR, major isomer (101 MHz, CDCl₃) δ 136.7, 136.5, 135.8, 135.5, 133.5, 133.2, 130.1, 129.7, 127.7, 127.2, 127.0, 126.7, 125.7, 21.3. HRMS (ESI Pos) for [C₂₈H₂₀S₂] calcd. m/z = 420.1001, found 420.0993.



4,4'-dimethyl-9,9'-bisthioxanthylidene (1c) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.44, 15% CH₂Cl₂/*n*-pentane) on a 0.77 mmol scale as a pale brown solid in 52% yield (84 mg, 0.20 mmol), *E/Z*-isomers are non-distinguishable by ¹H-NMR spectroscopy, a number of ¹³C signals do appear as two separate, overlapping signals. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 7.8, 3.4 Hz, 2H), 7.16 – 7.08 (m, 2H), 7.04 – 6.96 (m, 2H), 6.94 – 6.86 (m, 2H), 6.85 – 6.75 (m, 4H), 6.65 (dd, *J* = 11.4, 7.7 Hz, 2H), 2.51 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 136.4, 135.9, 135.7, 135. 6, 135.2, 134.1, 129.9, 128.0, 127.7, 127.4, 126.7, 125.9, 125.5, 20.8. HRMS (ESI Pos) for [C₂₈H₂₀S₂]⁺ calcd. m/z = 420.1001, found 420.0996.



2,2'-dimethoxy-9,9'-bisthioxanthylidene (1d) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.17, 15% CH₂Cl₂/*n*-pentane) on a 1.16 mmol scale as a yellow solid in 91% yield (240 mg, 0.53 mmol), 59:41 major/minor ratio. ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.51 (m, 2H_{maj} + 2H_{min}), 7.45 – 7.39 (m, 2H_{maj} + 2H_{min}), 7.17 – 7.10 (m, 2H_{maj} + 2H_{min}), 6.99 – 6.86 (m, 2H_{maj} + 4H_{min}), 6.81 (dd, *J* = 7.8, 1.4 Hz, 2H_{maj}), 6.78 – 6.70 (m, 2H_{maj} + 2H_{min}), 6.40 (d, *J* = 2.7 Hz, 2H_{maj}), 6.33 (d, *J* = 2.7 Hz, 2H_{min}), 3.39 (s, 6H_{maj}), 3.35 (s, 6H_{min}). ¹³C NMR (151 MHz, CDCl₃) δ 158.1, 158.0, 137.2, 137.1, 136.3, 136.2, 135.9, 135.8, 133.8, 130.1, 129.9, 128.1, 128.1, 127.2, 127.2, 126.9, 126.9, 126.8, 126.7, 125.8, 125.8, 115.2, 115.2, 114.2, 113.9, 55.4, 55.2. HRMS (ESI Pos) for [C₂₈H₂₀O₂S₂]⁺ calcd. m/z = 452.0899, found 452.0891.



3,3'-dimethoxy-9,9'-bisthioxanthylidene (1e) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.24, 15% CH₂Cl₂/*n*-pentane) on a 0.18 mmol scale as a pale yellow solid in 90% yield (37 mg, 0.08 mmol), 51:49 major/minor ratio. ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H_{maj} + 2H_{min}), 7.14 – 7.08 (m, 2H_{maj} + 2H_{min}), 7.07 – 7.03 (m, 2H_{maj} + 2H_{min}), 6.94 (t, *J* = 7.5 Hz, 2H_{maj}), 6.91 – 6.84 (m, 2H_{maj} + 2H_{min}), 6.80 – 6.76 (m, 4H_{min}), 6.70 (d, *J* = 8.6 Hz, 2H_{maj}), 6.52 (dd, *J* = 8.6, 2.6 Hz, 2H_{min}), 6.47 (dd, *J* = 8.6, 2.6 Hz, 2H_{maj}), 3.79 (s, 6H_{maj}). ¹³C NMR (151 MHz, CDCl₃) δ 158.3, 158.2, 137.1, 137.0, 136.8, 136.8, 135.5, 135.4, 132.5, 132.5, 131.1, 131.0, 130.1, 130.0, 128.9, 128.9, 127.2, 126.7, 126.6, 125.9, 125.8, 55.5 (2C). HRMS (ESI Pos) for [C₂₈H₂₀O₂S₂]⁺ calcd. m/z = 452.0899, found 452.0893.



4,4'-dimethoxy-9,9'-bisthioxanthylidene (1f) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.24, 15% CH₂Cl₂/*n*-pentane) on a 0.30 mmol scale as a pale-yellow solid in 53% yield (36 mg, 0.08 mmol), *E/Z*-isomers are non-distinguishable by ¹H-NMR spectroscopy. ¹H NMR (600 MHz, CDCl₃) δ 7.57 (ddd, *J* = 7.8, 4.4, 1.2 Hz, 2H_{maj} + 2H_{min}), 7.12 (dd, *J* = 7.5, 7.5 Hz, 2H_{maj} + 2H_{min}), 6.93 – 6.85 (m, 4H_{maj} + 4H_{min}), 6.81 (d, *J* = 7.9 Hz, 2H_{maj} + 2H_{min}), 6.70 (d, *J* = 8.0 Hz, 2H_{maj} + 2H_{min}), 6.45 (ddd, *J* = 7.8, 4.2, 1.1 Hz, 2H_{maj} + 2H_{min}), 3.97 (s, 6H_{maj} + 6H_{min}). ¹³C NMR (151 MHz, CDCl₃) δ 155.8, 155.7, 137.2, 137.1, 136.1, 136.0, 135.6, 135.5, 133.5 (2C), 129.9, 129.9, 127.4, 127.4, 126.8, 126.8, 126.3, 126.3, 125.9, 125.8, 124.2, 124.1, 122.6, 122.5, 108.3 (2C), 56.2 (2C). HRMS (ESI Pos) for [C₂₈H₂₀O₂S₂]⁺ calcd. m/z = 452.0899, found 452.0894.



2,2'-dibromo-9,9'-bisthioxanthylidene (1g) Obtained as a mixture of E/Z isomers via general method D (Rf = 0.57, 15% CH₂Cl₂/*n*-pentane) on a 0.49 mmol scale as an off-white solid in 96% yield (130 mg, 0.24 mmol), 56:44 major/minor ratio. ¹H NMR (600 MHz, CDCl₃)

δ 7.57 – 7.51 (m, 2H_{maj} + 2H_{min}), 7.44 – 7.38 (m, 2H_{maj} + 2H_{min}), 7.33 (dd, *J* = 8.3, 2.1 Hz, 2H_{maj}), 7.27 – 7.25 (m, 2H_{min}), 7.21 (d, *J* = 7.4 Hz, 2H_{min}), 7.16 (d, *J* = 7.4 Hz, 2H_{maj}), 7.01 (d, *J* = 7.6 Hz, 2H_{min}), 6.93 (d, *J* = 7.8 Hz, 2H_{maj}), 6.89 (d, *J* = 2.1 Hz, 2H_{maj}), 6.87 (d, *J* = 2.1 Hz, 2H_{min}), 6.81 – 6.79 (m, 2H_{maj}), 6.79 – 6.78 (m, 2H_{min}). ¹³C NMR signals of the separate isomers are non-distinguishable. ¹³C NMR (101 MHz, CDCl₃) δ 137.5 (2C), 137.0 (2C), 135.3, 135.3, 135.1, 134.8, 134.8, 134.7, 133.2 (2C), 132.6, 132.5, 130.1, 130.0, 129.9, 129.8, 128.5, 128.5, 127.6, 127.4, 127.4, 127.3, 126.2, 126.2, 119.6. HRMS (ESI Pos): for [C₂₆H₁₄Br₂S₂]⁺ calcd. m/z = 549.8878, found 549.8860.



3,3'-dibromo-9,9'-bisthioxanthylidene (1h) Obtained as a mixture of *E/Z* isomers via general method D (Rf = 0.60, 15% CH₂Cl₂/*n*-pentane) on a 0.29 mmol scale as a yellow solid in 51% yield (40 mg, 0.07 mmol), 50:50 ratio, labelled as isomer 1 and isomer 2. ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.68 (m, 2H_{isomer1} + 2H_{isomer2}), 7.56 – 7.51 (m, 2H_{isomer1} + 2H_{isomer2}), 7.21 – 7.12 (m, 2H_{isomer1} + 2H_{isomer2}), 7.09 (dd, *J* = 8.3, 2.0 Hz, 2H_{isomer1}), 7.03 (dd, *J* = 8.3, 2.0 Hz, 2H_{isomer2}), 6.98 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H_{isomer1}), 6.93 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H_{isomer2}), 6.84 – 6.76 (m, 2H_{isomer1} + 2H_{isomer2}), 6.70 – 6.62 (m, 2H_{isomer1} + 2H_{isomer2}). ¹³C NMR signals of the separate isomers are non-distinguishable. ¹³C NMR (101 MHz, CDCl₃) δ 138.0, 138.0, 135.6, 135.5, 135.1, 135.1, 135.0, 134.8, 133.2 (2C), 131.1, 131.0, 130.1, 130.0 (2C), 129.9, 129.3, 129.1, 127.5, 127.4, 127.3, 127.3, 126.5, 126.3, 120.8, 120.8. HRMS (ESI Pos): for [C₂₆H₁₄Br₂S₂]⁺ calcd. m/z = 549.8878, found 549.8862.



4,4',5,5'-tetramethyl-9,9'-bisthioxanthylidene (1i) Obtained via general method D on a 0.30 mmol scale, purified by flash column chromatography (silica gel, $CH_2Cl_2/Toluene$, gradient 0:1 to 1:1) and trituration from Et_2O to obtain the title product as a white solid in 20% yield (27 mg, 0.06 mmol), ¹H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, J = 7.4 Hz, 4H), 6.81 (dd, J = 7.6, 7.6 Hz, 4H), 6.63 (d, J = 7.8 Hz, 4H), 2.54 (s, 12r Not sufficiently soluble for ¹³C NMR. HRMS (ESI Pos): for [$C_{30}H_{24}S_2$]⁺ calcd. m/z = 448.1314, found 448.1311.



4,4',5,5'-tetramethoxy-9,9'-bisthioxanthylidene (1j) Obtained via general method on a 0.35 mmol scale, purified by flash column chromatography (silica gel, CH₂Cl₂/Toluene, gradient 0:1 to 1:1) and trituration from Et₂O as a pale-yellow solid in 20% yield (18 mg, 0.04 mmol), ¹H NMR (600 MHz, CDCl₃) δ 6.86 (dd, *J* = 7.9, 7.9 Hz, 4H), 6.67 (dd, *J* = 8.1, 1.1 Hz, 4H), 6.44 – 6.40 (m, 4H), 3.95 (s, 12H). Not sufficiently soluble for ¹³C NMR. HRMS (ESI Pos): for [C₃₀H₂₄O₄S₂]⁺ calcd. m/z = 512.1111, found 512.1103.



2,2'-diphenyl-9,9'-bisthioxanthylidene (1k) Obtained as a mixture of *E/Z* isomers via general method D on a 0.84 mmol scale as a white solid in 96% yield (219 mg, 0.40 mmol), 60:40 major/minor ratio. ¹H NMR (600 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 2H_{maj}), 7.65 – 7.63 (m, 2H_{min}), 7.61 (d, *J* = 8.1 Hz, 2H_{min}), 7.58 – 7.56 (m, 2H_{maj}), 7.40 – 7.36 (m, 2H_{maj} + 2H_{min}), 7.31 – 7.27 (m, 2H_{maj} + 2H_{min}), 7.24 – 7.18 (m, 4H_{maj} + 4H_{min}), 7.16 (ddd, *J* = 7.8, 7.2, 1.4 Hz, 4H_{min}), 7.12 (d, *J* = 1.9 Hz, 2H_{maj}), 7.08 (d, *J* = 1.9 Hz, 2H_{min}), 7.05 – 7.02 (m, 4H_{min}), 7.02 – 6.99 (m, 4H_{maj}), 6.99 – 6.92 (m, 4H_{maj} + 2H_{min}), 6.89 – 6.86 (m, 2H_{maj}). ¹³C NMR (151 MHz, CDCl₃) δ 140.50, 140.49, 139.51, 139.02, 136.25, 136.12, 135.89, 135.83, 135.79, 135.63, 134.72, 134.57, 133.85, 133.82, 130.08, 129.99, 129.06, 128.79, 128.70, 128.62, 127.66, 127.51, 127.45, 127.31, 127.21, 127.05, 127.02, 126.96, 126.16, 125.99, 125.88, 125.83. HRMS (ESI Pos) for [C₃₈H₂₅S₂]⁺ calcd. m/z = 545.1392, found 545.1385 and for [C₃₈H₂₄S₂]⁺ calcd. m/z = 544.1314, found 544.1299.



12-(9H-thioxanthen-9-ylidene)-12H-benzo[a]thioxanthene (11) (9H-thioxanthen-9vlidene)hydrazine (152 mg, 0.67 mmol) was dissolved in 5 mL dry CH₂Cl₂, cooled to 0 °C and MnO₂ (289 mg, 3.33 mmol) was added. After full conversion (30 min, confirmed by TLC) the mixture was filtered over a pad of silica gel under N₂ flow and flushed with 5 mL dry CH₂Cl₂. The diazo solution was added to a solution of 12H-benzo[a]thioxanthene-12-thione (152 mg, 0.55 mmol) in 5 mL dry CH₂Cl₂ and stirred for 16 h at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in 8 mL dry toluene and tris(dimethylamino)phosphine (0.24 mL, 1.32 mmol) was added and the mixture was heated at reflux for 16 h. Volatiles were removed under reduced pressure and the product was purified by flash column chromatography using silica gel and CH_2Cl_2/n -pentane (1:9) as eluent. The product was obtained as a white solid in 23% yield (55 mg, 0.12 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.5 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.57 (dd, J = 7.7, 0.7 Hz, 1H), 7.41 - 7.36 (m, 1H), 7.21 - 7.10 (m, 3H), 7.07 - 6.97 (m, 3H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 6.84 – 6.74 (m, 2H), 6.45 – 6.36 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 137.3, 136.8, 136.3, 136.1, 135.5, 134.8, 134.7, 134.4, 132.5, 131.8, 131.7, 130.2, 129.4, 129.2, 128.6, 127.7, 127.4, 127.1, 126.9, 126.9, 126.9, 126.7, 126.6, 126.3, 126.2, 125.8, 125.5, 125.2, 125.1, 125.0. HRMS (ESI Pos) for $[C_{30}H_{18}S]^+$ calcd. m/z = 442.0844, found m/z = 442.0837.

2.3 Data of thioxanthenones (3a – 3l)



All spectroscopic data of known compounds was in agreement with literature. **3a**[1], **3b**[2], **3c**[3], **3d**[4], **3e**[4], **3f**[1], **3g**[5], **3h**[6], **3j**[7], **3l**[5].



4,5-dimethylthioxanthone (3i) Obtained via general method A and B on a 4.95 mmol scale as a white solid in 39% yield over 2 steps (464 mg, 1.93 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 7.3 Hz, 2H), 7.42 (dd, J = 7.7, 7.7 Hz, 2H), 2.59 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.1, 136.2, 134.4, 133.6, 129.3, 127.7, 125.9, 19.7. HRMS (ESI Pos) for [C₁₅H₁₃OS]⁺ calcd. m/z = 241.0682, found m/z = 241.0682.



2-phenylthioxanthone (3k) A sealed tube was charged with 2-bromothioxanthone (**3g**) (407 mg, 1.4 mmol), $Pd(PPh_3)_4$ (81 mg, 0.07 mmol), K_2CO_3 (580 mg, 4.2 mmol), and a mixture of toluene:ethanol:water, 5:3:1 (14 mL). N₂ was bubbled through the solution for 10 min and the tube was sealed. The reaction mixture was heated at 130 °C for 16 h. The reaction mixture was allowed to cool to room temperature, taken up in CH_2Cl_2 and washed with water and saturated NaCl (aq) and dried over MgSO₄. Volatiles were removed under reduced pressure and the product was purified by flash column chromatography (silica gel, CH_2Cl_2/n -pentane, 1:9) and obtained as a yellow solid (348 mg, 1.21 mmol, 86% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.88 (d, *J* = 2.1 Hz, 1H), 8.68 – 8.63 (m, 1H), 7.89 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.69 – 7.65 (m, 1H), 7.65 – 7.58 (m, 2H), 7.54 – 7.46 (m, 3H), 7.43 – 7.37 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 139.7, 139.5, 137.3, 136.2, 132.5, 131.2, 130.1, 129.6, 129.4, 129.2, 128.0, 128.0, 127.3, 126.7, 126.5, 126.2. HRMS (APCI Pos) for [C₁₉H₁₃OS]⁺ calcd. m/z = 298.06816, found m/z = 289.06938.

2.4 Data for dicationic species



2,2'-dimethyl-[9,9'-bithioxanthene]-10,10'-diium (1 a^{2+}). Obtained by oxidation of 1a in CD₃CN with an excess of ceric ammonium nitrate. ¹H NMR (500 MHz, CD₃CN) δ 9.03 (d, *J* = 8.6 Hz, 2H), 8.98 (d, *J* = 8.8 Hz, 2H), 8.39 (dd, *J* = 7.8, 7.7 Hz, 2H), 8.35 – 8.27 (m, 2H), 7.84 (dd, *J* = 8.7, 7.5 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.52 (s, 2H), 2.35 (s, 6H). HRMS (ESI Pos) for [C₂₈H₂₀S₂]²⁺ calcd. m/z = 210.04977, found m/z = 210.04972.

2.5 Coupling of two distinct thioketones



2-methyl-2'-methoxy bisthioxanthylidene (ESI1). 2-methoxythioxanthene-thione (30 mg, 1.0 equiv.) was dissolved in THF (1.5 mL) and cooled to -78 °C. TMSCHN₂ (60 μ L, 1.05 equiv.) was added and the mixture was allowed to slowly warm up to room temperature. When the color of the thioketone had faded, a THF (1.5 mL) solution of 2-methylthioxanthene-thione (28 mg, 1.0 equiv.) was added to the mixture. After the color of the second thioketone had faded, TBAF (1.0 M in Et₂O, 0.20 mL, 2.0 equiv.) was added and the mixture was stirred at room

temperature for 5 min. Volatiles were removed under reduced pressure and the product was purified by flash column chromatography (silica, CH_2CI_2/n -pentane). The product was obtained as an off-white solid in 9% yield (5.0 mg, 0.01 mmol). The product was obtained as an *E/Z*-mixture in 53:47 ratio (major/minor). ¹H NMR (600 MHz, CDCI₃) δ 7.55 – 7.51 (m, 2H_{maj} + 2H_{min}), 7.45 – 7.38 (m, 2H_{maj} + 2H_{min}), 7.16 – 7.09 (m, 2H_{maj} + 2H_{min}), 6.98 – 6.93 (m, 3H_{maj}), 6.93 – 6.86 (m, 1H_{maj} + 3H_{min}), 6.82 – 6.78 (m, 2H_{maj} + 1H_{min}), 6.73 (ddd, *J* = 11.7, 8.5, 2.7 Hz, 2H_{min}), 6.66 (s, 1H_{maj}), 6.59 (s, 1H_{min}), 6.32 (dd, *J* = 8.4, 2.7 Hz, 1H_{maj} + 1H_{min}), 3.35 (s, 3H_{maj}), 3.34 (s, 3H_{min}), 2.05 (s, 3H_{maj}), 2.01 (s, 3H_{min}). ¹³C NMR (151 MHz, CDCI₃) δ 158.0, 157.9, 137.3, 137.1, 136.2, 136.2, 136.2, 136.1, 136.0, 136.0, 135.9, 135.8, 135.8, 135.8, 135.7, 135.7, 133.8, 133.8, 133.7, 133.6, 132.3, 132.1, 130.8, 130.5, 130.1, 130.0, 130.0, 129.9, 128.1, 128.0, 127.8, 127.2, 127.2, 127.2, 127.1, 126.9, 126.9, 126.9, 126.9, 126.8, 126.8, 126.8, 125.9, 125.8, 125.8, 125.5, 115.1, 115.1, 114.0, 114.0, 55.3, 55.2, 21.0, 21.0. HRMS (ESI Pos): for [C₂₈H₂₀OS]⁺ calcd. m/z = 436.0950, found m/z = 436.0954.

From this reaction, **1a** was obtained in 24% isolated yield and **1d** was obtained in 42% isolated yield.

3 Electrochemistry



Cyclic voltammograms of 1a - 1I. Glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode. 1.0 mM 1 in CH₂Cl₂ with 0.1 M TBAPF₆ as supporting electrolyte. Measured at room temperature under diffusion limited conditions.

In our experimental setup, diffusion is limited, but not wholly excluded in some cases; therefore, the reduction signal can be of lower intensity than the oxidation signal.











1c



1d



1e





1g



1h





1j









4 ¹H- and ¹³C-NMR Spectra

(400 or 600 MHz for $^1\text{H},\,101$ or 151 MHz for $^{13}\text{C},\,\text{CDCl}_3)$

1a



1b



17

1c





1e



00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 f1 (ppm)





1g



22

1h







1j



1k





Top to bottom ¹H-NMR spectra (500 MHz, CD_3CN) of: **1a**; **1a**²⁺ obtained by oxidation with an excess of ceric ammonium nitrate; **1a** obtained by reduction with an excess of cobaltocene.







Combined ¹H NMR (CD₃CN, 500 MHz) spectrum of the chemical oxidation and subsequent reduction procedure. a) 1a, b) $1a^{2+}$, c) 1a.

The sample in a), which is the full ¹H-NMR spectrum of Figure 3, is an unequal stereoisomeric (*E/Z*) mixture and the resulting sample in c) is an equal stereoisomeric (*E/Z*) mixture. From the signal at 7.04 ppm in a), it can be seen that a small amount of the stereoisomer is present, albeit in a smaller amount. After the oxidation–reduction procedure this is an equal mixture of stereoisomers. While the oxidation of both isomers of **1a** give the same dication **1a**²⁺ (as a mixture of atropisomers), the reduction of this dication is not selective towards either the *E*- or *Z*-isomer. Included here is an inset of the methyl region of the ¹H-NMR spectra of a) and c), where it could be more clearly observed.



ESI1



5 DFT calculations

The calculations were performed with the Gaussian16 software package[8] on the Peregrine HPC cluster.

1e

Anti-folded. DFT B3LYP/6-31G**. 0 imaginary frequencies.

Energy= -2025.8603749

Zero-point correction=	0.401615 (Hartree/Particle)
Thermal correction to Gibbs Free Ener	rgy= 0.345309
Sum of electronic and zero-point Ener	gies= -2025.458760
Sum of electronic and thermal Energie	es= -2025.432566
Sum of electronic and thermal Enthalp	ies= -2025.431621
Sum of electronic and thermal Free Er	nergies= -2025.515066

C -4.5934304021 0.7553327616 -0.637151681 C -4.8677754587 -0.3633360088 0.0919710293 C -3.226394017 1.13418818 -1.0924999307 C -6.2348690492 -0.7421590314 0.5471525588 C -3.8277645661 -1.3424051717 0.5238222792 C -4.0620107026 -2.7192035824 0.3416109969 S -5.5996457656 -3.2752609388 -0.3806459722 C -6.6835945297 -2.068057494 0.3685561955 C -2.7776685537 2.4600893726 -0.9139196819 S -3.8615433765 3.6672579148 -0.1645556459 C -5.3992597334 3.1111926656 -0.8866349803 C -5.6335048624 1.7343942695 -1.0688431034 C -2.3685681771 0.2490060989 -1.7567550459 C -1.0892880048 0.6245669164 -2.1621419118 C -0.6430877706 1.9296569038 -1.9164906362 C -1.5007591678 2.8525801494 -1.3056526879 C -6.3544282065 4.0598387344 -1.2683980606 C -7.5427664632 3.6471174602 -1.8657046927 C -7.7634776192 2.2891202557 -2.1099855989 C -6.8150564253 1.3473795306 -1.7219253805 C -7.9605715777 -2.4605028435 0.7601122106 C -8.8183248296 -1.5375259972 1.3707566246 C -8.3721531213 -0.2324194598 1.6163744177 C -7.0928021047 0.1430963638 1.2111680776 C -2.646343614 -0.9554156524 1.1771597646

C -1.698007776 -1.8971695272 1.5653951378 C -1.9186855613 -3.2551619015 1.3210596679 C -3.1069258538 -3.6678646634 0.7235479796 H -2.7056525541 -0.7636613283 -1.949215511 H -1.1612748658 3.8738790368 -1.1727225471 H -6.1507297208 5.1156452422 -1.1188643589 H -8.2795531558 4.3858369117 -2.1669142819 H -8.672416604 1.9642117553 -2.6071377388 H -6.987895666 0.2937682214 -1.9115553159 H -8.3000582735 -3.481800091 0.6271754809 H -9.0024928338 0.4900981291 2.1197467407 H -6.7557419738 1.1557820819 1.4035820983 H -2.4735338446 0.0981878086 1.3668519571 H -1.1819693514 -3.9938931951 1.6224126473 H -3.3106252876 -4.7236694031 0.5740031111 H -0.4590277192 -0.0979009738 -2.6656850148 H -0.7891646325 -1.5722757044 2.0627320941 O 0.5873603384 2.4082757068 -2.2590273841 O -10.048839258 -2.0161001935 1.713117037 C -10.9501205761 -1.1405153715 2.3736540544 H -11.1958623322 -0.2690279235 1.7537532526 H -11.8562876654 -1.7210583432 2.551646766 H -10.5482863225 -0.7952214581 3.334609442 C 1.4885532665 1.5327447479 -2.91975624 H 2.3946850322 2.1133116 -3.0978508879 H 1.7344013011 0.6612219934 -2.2999473379 H 1.0865779588 1.1875051551 -3.8806722233

1e²⁺

Orthogonal dication. DFT B3LYP/6-31G**. 0 imaginary frequencies.

Energy= -2025.3448905

Zero-point correction=	0.403209 (Hartree/Particle)
Thermal correction to Gibbs Free Ene	rgy= 0.346209
Sum of electronic and zero-point Ener	gies= -2024.941681
Sum of electronic and thermal Energie	es= -2024.915179
Sum of electronic and thermal Enthalp	bies= -2024.914235
Sum of electronic and thermal Free Er	nergies= -2024.998682

C -0.065365673 0.7570836406 -0.0573724399 C -0.0362199757 -0.7566991457 -0.0449951865 C 0.8175213437 1.4370395457 0.8386476182 C 0.8670190881 2.8659642825 0.9122439006 S -0.1193697275 3.9128450924 -0.0593624883 C -1.0785255235 2.833675634 -1.0242853097 C -0.9613955799 1.3940375589 -0.9358065598 C -0.9210069235 -1.4219643929 0.8601321662 C -0.9706834648 -2.8494993824 0.9569229455 S 0.0177326544 -3.9120723103 0.0046028602 C 0.9789367087 -2.8487693658 -0.9757726812 C 0.861648543 -1.4078814911 -0.911032237 C 1.8792878924 -3.4604515264 -1.8370261226 C 2.7060219359 -2.6914948769 -2.6691627611 C 2.6154073573 -1.2654349594 -2.630183244 C 1.7272705967 -0.6631264812 -1.7843934263 C -1.7950855014 -0.6813986752 1.7144479637 C -2.6475679304 -1.3102945861 2.5917082762 C -2.6759548733 -2.7192112282 2.6635909038 C -1.8488508859 -3.4795441766 1.8565676893 C 1.6897830235 0.7105226339 1.7067715721 C 2.5404255074 1.3536590436 2.575451573 C 2.5686870898 2.7635612656 2.6244006611 C 1.7433000338 3.5106150062 1.8033400214 C -1.977052573 3.4312124478 -1.8972937048 C -2.8020432198 2.6487703946 -2.7185182929 C -2.7115307372 1.2235376638 -2.6560965932 C -1.8251865178 0.6351208464 -1.7987271351 O -3.6246234038 3.31211656 -3.5103464954 O 3.5302527047 -3.3676548104 -3.4483351689 C 4.4410353371 -2.6944952607 -4.3474263336 C -4.5335053944 2.6243654877 -4.4002710252 H 1.9692025636 -4.5406657313 -1.8860227103 H 3.2482455026 -0.6599323979 -3.2667421714 H 1.6787326721 -0.3719462652 1.681985518 H -1.7839655458 0.4005220817 1.6720304973 H -3.2987030568 -0.7239661249 3.2306420386 H -3.3491210417 -3.2132798239 3.3565794259 H -1.8732377202 -4.5632215413 1.9166140536 H 1.6774150016 0.4186586383 -1.771293432 H 3.1902009232 0.7778417957 3.2252367537

H 3.2404002462 3.2688794582 3.3106546346 H 1.767579858 4.5951280822 1.8457521599 H -2.0668482266 4.5104821144 -1.9640901697 H -3.3430355632 0.6077214471 -3.2840271465 H -1.7753748181 -0.446305782 -1.7678805951 H 4.98458263 -3.4938697307 -4.8464026289 H 3.8866663015 -2.1060893742 -5.083132693 H 5.1368218877 -2.0655764279 -3.7861065572 H -5.0759773799 3.4154852674 -4.9133735357 H -3.9775856204 2.024046169 -5.1251021075 H -5.2304941154 2.004675091 -3.8302460804

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