Electronic supplementary information

Palladium-catalysed direct synthesis of benzo[b]thiophenes from thioenols

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1. General Comments

All reactions were carried out under Ar atmosphere unless otherwise noted. Dimethyl sulfoxide (DMSO) was distilled from CaH₂ under Ar atmosphere. All other commercially available materials, including palladium salts, were used as received. Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400. ¹H-NMR spectra were recorded on JEOL JNM-AL400 (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = double doublet, dt = double triplet, td = triple doublet, tt = triple triplet, ddd = double double doublet, m = multiplet. ¹³C-NMR spectra were recorded on JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from ¹³CDCl₃ (77.0 ppm). Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 instruments, respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6.
2. Synthesis of Starting Thioenols (1)

1,2,2-Triphenylethenethiol (1a)

![Structure of 1a]

To a mixture of triphenylvinyl bromide (10.0 g, 29.8 mmol) and magnesium (1.1 g, 44.7 mmol) in Et₂O (100 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 6 h. Then, S₈ (0.98 g, 3.7 mmol) was added and the whole mixture was heated under reflux for additional 2 h. The reaction mixture was cooled to room temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 1a (3.1 g, 36 %) as a pale yellow solid; mp: 107-110 °C (pale yellow needles from hexane-ethyl acetate, lit. 11 mp 110-112 ºC); IR ν (film, cm⁻¹): 1597, 2563; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.28 (1H, s), 6.87-6.89 (2H, m), 6.99-7.02 (3H, m), 7.14-7.21 (3H, m), 7.28-7.33 (3H, m), 7.37-7.41 (4H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 126.1, 127.3, 127.4, 127.5, 128.1, 128.6, 129.5, 129.7, 130.3, 130.4, 137.2, 141.6, 142.2, 142.9; MS m/z (relative intensity): 288 (M⁺, 100); HRMS Calcd for C₂₀H₁₆S: 288.0973, Found: 288.0963.

2,2-Bis(4-methylphenyl)-1-phenylethenethiol (1b)

![Structure of 1b]

4-Methylphenylmagnesium bromide (0.96 M solution in THF, 25.0 mL, 24.0 mmol) was added to a solution of methyl phenylacetate (1.8 g, 12.0 mmol) in THF (10 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH₄Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 2,2-bis(4-methylphenyl)-1-phenylethanol (3.0 g, 82%) as a colorless solid; IR ν (film, cm⁻¹): 3558; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.23 (1H, s), 2.30 (6H, s), 3.59 (2H, s), 6.89-6.92 (2H, m), 7.08 (4H, d, J = 8.0 Hz), 7.13-7.15 (3H, m), 7.28 (4H, d, J = 8.0 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 21.0, 48.0, 77.7, 125.9, 126.6, 127.9, 128.6, 130.8, 136.0, 136.2, 143.8; MS m/z (relative intensity): 284 (M⁺-18, 2.3), 211 (100).

To a solution of the above obtained alcohol (2.5 g, 8.5 mmol) in AcOH (28 mL), bromine (0.65 mL, 12.7 mmol) was added at room temperature and stirred for 2 h at the same temperature. H₂O (5 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give crude 2,2-bis(4-methylphenyl)-1-phenylvinyl bromide. Recrystallization from hexane-ethyl acetate gave the pure product (pale yellow plates, 1.1 g, 36%); ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.20 (3H, s), 2.37 (3H, s), 6.82-6.87 (4H, m), 7.14-7.20 (5H, m), 7.24-7.26 (2H, m), 7.31 (2H, dt, J = 6.4, 1.9 Hz); MS m/z (relative intensity): 362 (M⁺, 67.2), 283 (100); HRMS Calcd for C₂₂H₁₉Br: 362.0670, Found: 362.0663.
To a mixture of the above vinyl bromide (0.50 g, 1.4 mmol) and magnesium (0.050 g, 2.1 mmol) in THF (5 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 2 h. Then, S₈ (0.046 g, 0.17 mmol) was added and the whole mixture was heated under reflux for additional 5 h. The reaction mixture was cooled to room temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 1b (0.21 g, 48 %) as a pale yellow solid; mp: 131-134 °C (pale yellow needles from hexane-ethyl acetate); IR ν (film, cm⁻¹): 2559; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.18 (3H, s), 2.37 (3H, s), 3.26 (1H, s), 6.75 (2H, d, J = 8.0 Hz), 6.80 (2H, d, J = 8.0 Hz), 7.13-7.33 (9H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 21.1, 21.4, 127.2, 128.12, 128.15, 129.2, 129.3, 129.5, 129.6, 130.2, 135.6, 136.9, 137.1, 138.8, 140.2, 142.5; MS m/z (relative intensity): 316 (M⁺, 100); HRMS Calcd for C₂₂H₂₀S: 316.1286, Found: 316.1274; Anal. Calcd for C₂₂H₂₀S: C, 83.50; H, 6.37. found: C, 83.45; H, 6.41.

2,2-Bis(4-methoxyphenyl)-1-phenylethenethiol (1c)

4-Methoxyphenylmagnesium bromide (0.60 M solution in THF, 40.0 mL, 23.9 mmol) was added to a solution of methyl phenylacetate (1.8 g, 12.0 mmol) in THF (10 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH₄Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 1,1-bis(4-methoxyphenyl)-2-phenylethanol (2.6 g, 65%) as a colorless solid; IR ν (film, cm⁻¹): 1508, 1609, 3547; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.23 (1H, s), 3.57 (2H, s), 3.77 (6H, s), 6.81 (4H, d, J = 8.6 Hz), 6.89 (2H, d, J = 3.6 Hz), 7.14-7.15 (3H, m), 7.29 (4H, d, J = 8.6 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 48.2, 55.2, 77.4, 113.2, 126.6, 127.3, 127.9, 130.8, 136.0, 139.0, 158.2.

A mixture of the above obtained alcohol (1.5 g, 4.4 mmol) and p-TsOH-H₂O (0.35 g, 1.9 mmol) in benzene (14 mL) was heated under reflux for 1.5 h. H₂O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 1,1-bis(4-methoxyphenyl)-2-phenylethylene (quant.) as a colorless solid; IR ν (neat, cm⁻¹): 1605; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.80 (3H, s), 3.81 (3H, s), 6.82-6.85 (5H, m), 7.02-7.11 (7H, m), 7.46 (2H, d, J = 8.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.2, 55.3, 113.5, 113.9, 126.1, 126.2, 127.8, 128.8, 129.3, 131.5, 132.6, 136.3, 137.8, 141.7, 158.8, 159.1; MS m/z (relative intensity): 316 (M⁺, 30.8), 214 (100); HRMS Calcd for C₂₂H₂₀O₂: 316.1463, Found: 316.1454.

To a solution of the above obtained ethylene (1.3 g, 4.2 mmol) in CCl₄ (20 mL), bromine (0.23 mL, 4.6 mmol) was added at 0 °C and stirred for 2 h at the same temperature. Et₃N (5 mL) was added at 0 °C and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 2,2-bis(4-methoxyphenyl)-1-phenylvinyl bromide (quant.) as a yellow solid; IR ν (film, cm⁻¹): 1607; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.68 (3H, s), 3.82 (3H, s), 6.58 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 3.82 (3H, s), 6.58 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 6.65 (2H, d, J = 8.8 Hz), 7.13-7.33 (9H, m); IR ν (film, cm⁻¹): 1607; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.68 (3H, s), 3.82 (3H, s), 6.58 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 7.13-7.33 (9H, m); IR ν (film, cm⁻¹): 1607; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.68 (3H, s), 3.82 (3H, s), 6.58 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 7.13-7.33 (9H, m); IR ν (film, cm⁻¹): 1607; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.68 (3H, s), 3.82 (3H, s), 6.58 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz),
6.89 (2H, d, J = 8.8 Hz), 7.12-7.19 (3H, m), 7.28-7.31 (4H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) δ (ppm): 55.1, 55.2, 113.1, 113.3, 120.3, 127.5, 127.9, 130.3, 130.9, 131.7, 133.6, 136.3, 141.5, 142.6, 158.3, 158.7.

To a mixture of the above vinyl bromide (0.50 g, 1.3 mmol) and magnesium (0.10 g, 4.1 mmol) in THF (5 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 1.5 h. Then, S\(_8\) (0.15 g, 0.56 mmol) was added and the whole mixture was heated under reflux for additional 15 h. The reaction mixture was cooled to room temperature and saturated aqueous NH\(_4\)Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO\(_4\). The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give disulfide (0.36 g, 80%) as a yellow solid; mp: 178-181 °C (yellow scales from hexane-ethyl acetate); IR ν (film, cm\(^{-1}\)): 1506, 1605; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) δ (ppm): 3.68 (3H, s), 3.78 (6H, s), 6.52 (4H, dt, J = 9.4, 2.5 Hz), 6.66 (4H, dt, J = 9.4, 2.5 Hz), 6.70 (4H, dt, J = 9.4, 2.5 Hz), 6.77 (4H, dt, J = 9.4, 2.5 Hz), 7.16-7.19 (4H, m), 7.22-7.25 (4H, m), 7.30-7.34 (4H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) δ (ppm): 55.0, 55.1, 112.9, 113.2, 127.2, 127.9, 131.5, 131.6, 134.5, 135.6, 136.6, 142.7, 157.7, 158.7; MS m/z (relative intensity): 694 (M\(^+\), 1.8), 346 (100); HRMS Calcd for C\(_{44}\)H\(_{38}\)O\(_4\)S\(_2\): 694.2212, Found: 694.2196.

To a solution of the above disulfide (0.36 g, 0.51 mmol) in THF (10 mL), NaBH\(_4\) (0.077 g, 2.0 mmol) was added and stirred at 40 °C for 17 h. The reaction mixture was neutralized with saturated aqueous NH\(_4\)Cl and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO\(_4\). The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 1c (0.077 g, 22%) as a pale yellow solid; mp: 99-103 °C (yellow needles from hexane-ethyl acetate, lit.4) mp 96-98 °C); IR ν (film, cm\(^{-1}\)): 1605, 2561; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) δ (ppm): 3.26 (1H, s), 3.68 (3H, s), 3.84 (3H, s), 6.54 (2H, d, J = 9.4 Hz), 6.77 (2H, d, J = 9.4 Hz), 6.92 (2H, d, J = 8.8 Hz), 7.13-7.22 (3H, m), 7.30-7.34 (4H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) δ (ppm): 55.0, 55.2, 112.9, 113.2, 127.2, 127.9, 131.5, 131.7, 131.8, 135.2, 135.4, 135.8, 139.2, 142.1, 158.0, 158.4; MS m/z (relative intensity): 348 (M\(^+\), 100); HRMS Calcd for C\(_{22}\)H\(_{20}\)O\(_2\)S: 348.1184, Found: 348.1184.

2,2-Bis(4-fluorophenyl)-1-phenylethenethiol (1d)

Benzylmagnesium chloride (1.5 M solution in THF, 10.7 mL, 16.1 mmol) was added to a solution of 4,4’-difluorobenzophenone (3.5 g, 16.0 mmol) in THF (20 ml) at 0 °C and stirred at room temperature for 2 h. Saturated aqueous NH\(_4\)Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO\(_4\). The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 1d (0.077 g, 22%) as a pale yellow solid; mp: 99-103 °C (yellow needles from hexane-ethyl acetate, lit.4) mp 96-98 °C); IR ν (film, cm\(^{-1}\)): 3553; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) δ (ppm): 2.29 (1H, s), 3.58 (2H, s), 6.86-6.88 (2H, m), 6.97 (4H, dd, J = 8.7, 6.9 Hz), 7.14-7.18 (3H, m), 7.34 (4H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) δ (ppm): 48.2, 77.3, 114.8 (d, J = 21.4 Hz), 126.9, 127.8 (d, J = 8.2 Hz), 128.1, 130.7, 135.2, 142.1 (d, J = 3.3 Hz), 161.6 (d, J = 244.2 Hz); MS m/z (relative intensity): 292 (M\(^+\)-18, 1.5), 219 (100). A mixture of the above obtained alcohol (4.1 g, 13.2 mmol) and p-TsOH-H\(_2\)O (1.1 g, 5.5 mmol) in toluene (40 mL) was heated under reflux for 4 h. H\(_2\)O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3)
The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 1,1-bis(4-fluorophenyl)-2-phenylethylene (3.2 g, 82%) as a colorless solid; IR ν (film, cm⁻¹): 1599; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.88 (1H, s), 7.97 (6H, m), 7.11-7.17 (5H, m), 7.26 (2H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 115.1 (d, J = 21.5 Hz), 115.7 (d, J = 20.6 Hz), 126.9, 128.0, 128.3, 129.1 (d, J = 7.5 Hz), 129.4, 132.0 (d, J = 7.4 Hz), 135.9 (d, J = 3.3 Hz), 137.0, 139.3 (d, J = 2.5 Hz), 140.4, 162.1 (d, J = 245.9 Hz), 162.3 (d, J = 245.9 Hz).

To a solution of the above obtained ethylene (3.0 g, 10.2 mmol) in CCl₄ (45 mL), bromine (0.63 mL, 12.2 mmol) was added at room temperature and stirred for 2 h at 35 °C. Et₃N (5 mL) was added at 0 °C and the reaction mixture was extracted with ethyl acetate (10 mL x 3) . The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 2,2-bis(4-fluorophenyl)-1-phenylvinyl bromide (3.3 g, 86 %) as a pale yellow solid; IR ν (film, cm⁻¹): 1601; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.75 (2H, tt, J = 9.0, 2.4 Hz), 6.86-6.91 (2H, m), 7.06 (2H, tt, J = 9.0, 2.4 Hz), 7.14-7.23 (3H, m), 7.27-7.34 (4H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 114.9 (d, J = 21.5 Hz), 115.2 (d, J = 21.5 Hz), 122.5, 128.1, 130.1, 131.3 (d, J = 8.3 Hz), 131.9 (d, J = 7.5 Hz), 136.8 (d, J = 3.3 Hz), 139.3 (d, J = 3.3 Hz), 140.7, 141.3, 161.5 (d, J = 245.9 Hz), 162.0 (d, J = 246.7 Hz); MS m/z (relative intensity): 370 (M⁺, 74.5), 291 (100); HRMS Calcd for C₂₀H₁₃BrF₂: 370.0169, Found: 370.0157.

To a mixture of the above vinyl bromide (0.50 g, 0.14 mmol) and magnesium (0.065 g, 2.7 mmol) in THF (20 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 1 h. Then, S₈ (0.054 g, 0.20 mmol) was added and the whole mixture was heated under reflux for additional 15 h. The reaction mixture was cooled to room temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 1d (0.29 g, 65 %) as a yellow solid; mp: 91-93 °C (yellow scales from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1601, 2565; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.24 (1H, s), 6.70 (2H, t, J = 8.7 Hz), 6.79-6.83 (2H, m), 7.09 (2H, t, J = 8.7 Hz), 7.16-7.30 (5H, m), 7.34-7.39 (2H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 114.5 (d, J = 21.4 Hz), 115.7 (d, J = 21.4 Hz), 127.6, 128.3, 129.3, 131.1, 131.6 (d, J = 8.3 Hz), 131.8 (d, J = 7.4 Hz), 135.1, 137.5 (d, J = 3.3 Hz), 138.5 (d, J = 3.3 Hz), 142.0, 161.0 (d, J = 245 Hz), 161.8 (d, J = 245.8 Hz); MS m/z (relative intensity): 324 (M⁺, 100); HRMS Calcd for C₂₀H₁₄F₂S: 324.0784, Found: 324.0770.

**2,2-Bis(4-chlorophenyl)-1-phenylethenethiol (1e)**

Benzylmagnesium chloride (2.0 M solution in THF, 15.0 mL, 30.0 mmol) was added to a solution of 4,4′-dichlorobenzophenone (7.5 g, 30.0 mmol) in THF (45 ml) at 0 °C and stirred at room temperature for 2 h. Saturated aqueous NH₄Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give the crude alcohol.

A mixture of the above obtained crude alcohol and p-TsOH-H₂O (1.6 g, 8.4 mmol) in toluene (50 mL) was heated under
reflux for 4 h. H₂O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (49:1)] to give 1,1-bis(4-chlorophenyl)-2-phenylethylene (7.1 g, 72% for 2 steps); ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.93 (1H, s), 7.02 (2H, d, J = 8.0 Hz), 7.09-7.18 (5H, m), 7.21 (2H, d, J = 8.0 Hz), 7.24-7.30 (4H, m).

A mixture of the above obtained ethylene (5.1 g, 15.6 mmol) and NBS (3.4 g, 18.7 mmol) in DMF (30 mL) was stirred at 50 °C for 1.5 h. The reaction mixture was cooled to room temperature and H₂O (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (49:1)] to give 2,2-bis(4-chlorophenyl)-1-phenylvinyl bromide (3.2 g, 51%) as a colorless solid; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.84 (2H, dt, J = 8.7, 2.2 Hz), 7.03 (2H, dt, J = 8.7, 2.2 Hz), 7.19-7.23 (3H, m), 7.27-7.30 (4H, m), 7.35 (2H, dt, J = 8.7, 2.2 Hz); MS m/z (relative intensity): 402 (M⁺, 30.1), 324 (100); HRMS Calcd for C₂₀H₁₃BrCl₂: 401.9578, Found: 401.9563.

To a mixture of the above vinyl bromide (2.3 g, 5.7 mmol) and magnesium (0.17 g, 6.8 mmol) in THF (30 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 1 h. Then, S₈ (0.23 g, 0.85 mmol) was added and the whole mixture was heated under reflux for additional 1 h. The reaction mixture was cooled to room temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated to give the crude disulfide.

A mixture of the above crude disulfide and Zn powder (0.70 g, 10.7 mmol) in AcOH (10 mL) was stirred at 50 °C for 1 h. The reaction mixture was filtered, neutralized with 3 M NaOH, and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (49:1)] to give 1e (0.85 g, 42% for 2 steps) as a pale red solid; mp: 127-129 °C (pale red plates from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1489, 2569; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.26 (1H, s), 6.76 (2H, dt, J = 8.9, 2.4 Hz), 6.98 (2H, dt, J = 8.9, 2.4 Hz), 7.19-7.38 (9H, m), 13C-NMR (100 MHz, CDCl₃) δ (ppm): 127.8, 128.4, 128.9, 129.3, 131.3, 131.6, 132.1, 133.3, 134.7, 139.7, 140.8, 141.8; MS m/z (relative intensity): 356 (M⁺, 19.6), 121 (100); HRMS Calcd for C₂₀H₁₄Cl₂S: 356.0193, Found: 356.0171; Anal. Calcd for C₂₀H₁₄Cl₂S: C, 67.23; H, 3.95. found: C, 67.16; H, 4.04.

2,2-Bis(3-methoxyphenyl)-1-phenylethenethiol (1f)

A mixture of acetonophene (0.30 g, 2.5 mmol), 3-bromoanisole (1.4 g, 7.5 mmol), Pd(OAc)₂ (0.028 g, 0.13 mmol), PPh₃ (0.13 g, 0.50 mmol), and Cs₂CO₃ (2.4 g, 7.5 mmol) in degassed DMF (12 mL) was stirred at 150 °C for 100 min. The reaction mixture was neutralized with 3 M HCl and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (29:1)] to give 2,2-bis(3-methoxyphenyl)-1-phenylethane (0.43 g, 51%) as a yellow oil; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.75 (6H, s), 5.96 (1H, s), 6.78 (2H, ddd, J = 7.8, 1.6, 1.6 Hz), 6.82 (2H, t, J = 1.6 Hz), 6.86 (2H, d, J = 7.8 Hz), 7.23 (2H, t, J = 7.8 Hz), 7.40 (2H, t, J = 7.8 Hz), 7.50 (1H, tt, J = 7.8, 1.6 Hz), 7.99 (2H, dd, J = 7.8, 1.6 Hz); MS m/z (relative intensity): 332 (M⁺, 25.1), 227 (100); HRMS Calcd for C₂₂H₂₅O₂: 332.1413, Found: 332.1395.
A mixture of the above obtained ketone (0.15 g, 0.35 mmol) and Lawesson’s reagent (0.085 g, 0.21 mmol) in toluene (3 mL) was heated under reflux for 23 h. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (29:1)] to give **1f** (0.025 g, 20%) as a yellow oil; IR ν (neat, cm⁻¹): 1595, 2561; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.32 (1H, s), 3.50 (3H, s), 3.82 (3H, s), 6.43 (1H, t, J = 2.0 Hz), 6.48 (1H, d, J = 7.8 Hz), 6.56 (1H, dd, J = 7.8, 2.0 Hz), 6.86 (1H, dd, J = 7.8, 2.0 Hz), 6.92-6.96 (2H, m), 6.99 (1H, d, J = 7.8 Hz), 7.17-7.24 (3H, m), 7.30-7.35 (3H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 54.9, 55.3, 112.3, 113.1, 115.2, 115.7, 122.1, 122.9, 127.5, 128.3, 128.4, 129.4, 129.7, 130.8, 136.9, 142.3, 142.7, 144.1, 158.7, 159.8; MS m/z (relative intensity): 348 (M⁺, 97.8), 346 (100); HRMS Calcd for C₂₂H₂₀O₂S: 348.1184, Found: 348.1159.

**2,2-Bis(2-methoxyphenyl)-1-phenylethenethiol (1g)**

SH
MeO
OMe

2-Methoxyphenylmagnesium bromide (1.3 M solution in THF, 20.0 mL, 26.6 mmol) was added to a solution of methyl phenylacetate (2.0 g, 13.3 mmol) in THF (26 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH₄Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give **1,1-bis(2-methoxyphenyl)-2-phenylethanol (3.5 g, 78%)** as a colorless solid; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.49 (6H, s), 3.74 (2H, s), 4.90 (1H, s), 6.79 (2H, d, J = 7.9 Hz), 6.87-6.91 (4H, m), 7.06-7.08 (3H, m), 7.17 (2H, t, J = 7.9 Hz), 7.43 (2H, dd, J = 7.9, 1.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 43.5, 55.6, 76.8, 112.1, 120.2, 125.6, 127.0, 127.72, 127.73, 130.9, 134.8, 137.6, 156.3.

A mixture of the above obtained alcohol (3.5 g, 10.4 mmol) and p-TsOH-H₂O (0.79 g, 4.2 mmol) in toluene (50 mL) was heated under reflux for 1.5 h. H₂O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give **1,1-bis(2-methoxyphenyl)-2-phenylethylene (quant.)** as a colorless solid; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.49 (3H, s), 3.64 (3H, s), 6.82-6.93 (5H, m), 7.02-7.12 (6H, m), 7.20-7.25 (3H, m), 7.27, 127.3, 130.9, 134.8, 137.6, 156.3; ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.5, 55.7, 111.5, 111.8, 120.4, 120.6, 126.5, 127.7, 128.2, 128.3, 128.8, 130.4, 130.6, 131.2, 131.6, 133.4, 136.2, 138.1, 157.1, 157.3; MS m/z (relative intensity): 316 (M⁺, 100); HRMS Calcd for C₂₂H₂₀O₂: 316.1463, Found: 316.1444.

A mixture of the above obtained ethylene (0.50 g, 1.6 mmol), NBS (0.29 g, 1.6 mmol), and benzoyl peroxide (0.0071 g, 0.029 mmol) in CCl₄ (10 mL) was heated under reflux for 1 h with irradiation of Hg lamp. The reaction mixture was filtered and the filtrate was extracted with ethyl acetate (10 mL x 3). A mixture of the above vinyl bromide (0.30 g, 0.76 mmol) and magnesium (0.024 g, 0.99 mmol) in THF (20 mL) was heated under reflux (1 h) with irradiation of Hg lamp. The reaction mixture was filtered and the filtrate was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give **2,2-bis(2-methoxyphenyl)-1-phenylvinyl bromide (0.28 g, 45%)** as a colorless solid; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.54 (3H, s), 3.80 (3H, s), 6.64 (1H, d, J = 7.7 Hz), 6.70 (1H, t, J = 7.7 Hz), 6.91 (1H, d, J = 7.7 Hz), 6.97 (1H, t, J = 7.7 Hz), 7.04-7.12 (5H, m), 7.25-7.33 (3H, m), 7.39 (1H, dd, J = 7.7, 1.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.5, 55.7, 111.3, 111.7, 120.4, 120.5, 124.6, 127.6, 128.2, 128.3, 128.7, 130.3, 130.5, 131.0, 131.5, 133.3, 136.1, 138.0, 156.9, 157.1; MS m/z (relative intensity): 394 (M⁺, 24.0), 300 (100); HRMS Calcd for C₂₂H₁₈BrO₂: 394.0568, Found: 394.0548.

To a mixture of the above vinyl bromide (0.30 g, 0.76 mmol) and magnesium (0.024 g, 0.99 mmol) in THF (20 mL), a
catalytic amount of diiodoethane was added and the mixture was heated under reflux for 30 min. Then, S8 (0.030 g, 0.11 mmol) was added and the whole mixture was heated under reflux for additional 1 h. The reaction mixture was cooled to room temperature and saturated aqueous NH4Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO4. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 1g (0.16 g, 56%) as a pale yellow solid; mp: 100-101 °C (pale yellow scales from hexane-ethyl acetate); IR ν (film, cm\(^{-1}\)): 1489, 1595, 2561; \(^1\)H-NMR (400 MHz, CDCl3) δ (ppm): 3.20 (1H, s), 3.52 (3H, s), 3.79 (3H, s), 6.60 (1H, d, \(J = 7.7\) Hz), 6.66 (1H, dt, \(J = 7.7, 1.4\) Hz), 7.24-7.33 (4H, m), 7.46 (1H, dd, \(J = 7.7, 1.4\) Hz); \(^13\)C-NMR (100 MHz, CDCl3) δ (ppm): 55.1, 55.8, 110.7, 111.8, 119.8, 120.7, 127.1, 127.5, 127.8, 128.7, 128.9, 131.2, 131.7, 142.0, 156.8; MS m/z (relative intensity): 348 (M\(^+\), 100); HRMS Calcd for C\(_{22}\)H\(_{20}\)O\(_2\)S: 348.1184, Found: 348.1170.

2,2-Diphenyl-1-(4-methoxyphenyl)ethenethiol (1h)

Phenylmagnesium bromide (1.8 M solution in THF, 16.0 mL, 28.0 mmol) was added to a solution of methyl 4-methoxyphenylacetate (2.5 g, 14.0 mmol) in THF (5 mL) at 0 °C and stirred at room temperature for 2.5 h. Saturated aqueous NH4Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO4. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give 1,1-diphenyl-2-(4-methoxyphenyl)ethanol (1.3 g, 29%) as a colorless solid; IR ν (film, cm\(^{-1}\)): 3539; \(^1\)H-NMR (400 MHz, CDCl3) δ (ppm): 2.31 (1H, s), 3.59 (2H, s), 3.78 (3H, s), 6.69 (2H, d, \(J = 8.6\) Hz), 6.80 (2H, d, \(J = 8.6\) Hz), 7.21 (2H, t, \(J = 7.5\) Hz), 7.29 (4H, t, \(J = 7.5\) Hz), 7.42 (4H, d, \(J = 7.5\) Hz); MS m/z (relative intensity): 286 (M\(^+\)-18, 11.0), 183 (100).

A mixture of the above obtained alcohol (2.6 g, 8.5 mmol) and p-TsOH-H\(_2\)O (0.65 g, 3.4 mmol) in toluene (20 mL) was heated under reflux for 4 h. H\(_2\)O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO4. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 2,2-diphenyl-1-(4-methoxyphenyl)ethylene (2.2 g, 88%) as a colorless oil; IR ν (neat, cm\(^{-1}\)): 1605; \(^1\)H-NMR (400 MHz, CDCl3) δ (ppm): 3.77 (3H, s), 6.67 (2H, dt, \(J = 9.5, 2.5\) Hz), 6.92 (1H, s), 6.95 (2H, d, \(J = 9.5\) Hz), 7.20-7.37 (10H, m); \(^13\)C-NMR (100 MHz, CDCl3) δ (ppm): 55.1, 113.3, 127.06, 127.14, 127.3, 127.5, 128.0, 128.6, 129.9, 130.3, 130.7, 140.4, 140.5, 143.4, 158.2; MS m/z (relative intensity): 286 (M\(^+\), 100); HRMS Calcd for C\(_{21}\)H\(_{18}\)O: 286.1358, Found: 286.1354.

To a solution of the above obtained ethylene (3.1 g, 10.8 mmol) in CCl\(_4\) (50 mL), bromine (0.78 mL, 15.1 mmol) was added at 0 °C and stirred at room temperature for 1 h. Et\(_3\)N (5 mL) was added at 0 °C and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO4. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 1-(4-methoxyphenyl)-2,2-diphenylvinyl bromide (2.4 g, 60 %) as a pale yellow solid; IR ν (film, cm\(^{-1}\)): 1605; \(^1\)H-NMR (400 MHz, CDCl3) δ (ppm): 3.77 (3H, s), 6.67 (2H, dt, \(J = 9.5, 2.5\) Hz), 6.92 (1H, s), 6.95 (2H, d, \(J = 9.5\) Hz), 7.20-7.37 (10H, m); \(^13\)C-NMR (100 MHz, CDCl3) δ (ppm): 55.1, 113.3, 127.06, 127.14, 127.3, 127.5, 128.0, 128.6, 129.9, 130.3, 130.7, 140.4, 140.5, 143.4, 158.2; MS m/z (relative intensity): 286 (M\(^+\), 100); HRMS Calcd for C\(_{22}\)H\(_{20}\)O\(_2\): 286.1358, Found: 286.1354.
for C_{21}H_{17}BrO: 364.0463, Found: 364.0449.

To a mixture of the above vinyl bromide (1.5 g, 4.1 mmol) and magnesium (0.15 g, 6.2 mmol) in THF (18 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 1.5 h. Then, S₈ (0.49 g, 1.8 mmol) was added and the whole mixture was heated under reflux for additional 3.5 h. The reaction mixture was cooled to room temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 1h (0.91 g, 70%) as a pale yellow solid; mp: 115-117 °C (pale yellow needles from hexane-ethyl acetate, lit. mp 109 °C); IR (film, cm⁻¹): 1605, 2561; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.27 (1H, s), 3.76 (3H, s), 6.72 (2H, d, J = 8.8 Hz), 6.87-6.90 (2H, m), 7.00-7.05 (3H, m), 7.23-7.31 (3H, m), 7.38-7.39 (4H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.2, 113.5, 125.9, 127.2, 127.5, 128.6, 129.8, 130.2, 130.3, 130.8, 134.3, 136.5, 141.9, 143.2, 158.7; MS m/z (relative intensity): 318 (M⁺, 69.1), 151 (100); HRMS Calcd for C_{21}H_{18}OS: 318.1078, Found: 318.1080.

1,2-Diphenyl-2-(4-methoxyphenyl)ethenethiol (1i)

Benzylmagnesium chloride (2.0 M solution in THF, 9.5 mL, 19.0 mmol) was added to a solution of 4-methoxybenzophenone (4.0 g, 18.8 mmol) in THF (30 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH₄Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 1,2-diphenyl-1-(4-methoxyphenyl)ethanol, (4.5 g, 78%) as a colorless solid; IR (film, cm⁻¹): 1110, 1609, 3553; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.25 (1H, s), 3.61 (2H, s), 3.78 (3H, s), 6.83 (2H, dt, J = 8.3, 2.5 Hz), 6.89 (2H, dd, J = 8.3, 2.5 Hz), 7.13-7.17 (3H, m), 7.21 (1H, t, J = 8.3 Hz), 7.28 (2H, t, J = 8.3 Hz), 7.33 (2H, dt, J = 8.3, 2.5 Hz), 7.39 (2H, d, J = 8.3 Hz).

A mixture of the above obtained alcohol (0.070 g, 0.23 mmol) and p-TsOH-H₂O (0.018 g, 0.092 mmol) in toluene (1.5 mL) was heated under reflux for 1.5 h. H₂O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (29:1)] to give crude 1,2-diphenyl-1-(4-methoxyphenyl)ethylene as a colorless oil.

To a solution of the above obtained crude ethylene (0.057 g, 0.20 mmol) in CCl₄ (1 mL), bromine (0.012 mL, 0.24 mmol) was added at 0 °C and stirred for 1 h at the same temperature. Et₃N (5 mL) was added at 0 °C and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (29:1)] to give 1,2-diphenyl-2-(4-methoxyphenyl)vinyl bromide (0.034 g, 44% for 2 steps, a mixture of two isomers) as a colorless solid; IR (film, cm⁻¹): 1508, 1605; MS m/z (relative intensity): 364 (M⁺, 72.6), 285 (100); HRMS Calcd for C_{21}H_{16}BrO: 364.0463, Found: 364.0452.

To a mixture of the above vinyl bromide (0.73 g, 2.0 mmol) and magnesium (0.063 g, 2.6 mmol) in THF (10 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 1 h. Then, S₈ (0.080 g, 0.30 mmol) was added and the mixture was heated under reflux for additional 6 h. The reaction mixture was cooled to room
temperature and saturated aqueous NH₄Cl (10 mL) was added. The aqueous phase was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give the crude disulfide.

A mixture of the above crude disulfide and Zn powder (0.26 g, 4.0 mmol) in AcOH (4 mL) was stirred at 90 °C for 3.5 h. The reaction mixture was filtered, neutralized with 3 M NaOH, and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (29:1)] to give 1i (0.38 g, 59%) as a mixture of the two isomers. Recrystallization gave the single isomer; mp: 125-128 °C (pale yellow needles from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1508, 1607, 2561; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.30 (1H, s), 3.83 (3H, s), 6.86-6.91 (2H, m), 6.92 (2H, dt, J = 8.7, 2.1 Hz), 6.99-7.03 (3H, m), 7.12-7.20 (3H, m), 7.30 (2H, dd, J = 8.7, 2.1 Hz), 7.33 (2H, dt, J = 8.7, 2.1 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.2, 113.9, 126.0, 127.3, 127.4, 128.1, 129.5, 129.9, 130.4, 131.1, 135.3, 136.9, 141.9, 142.4, 158.6; MS m/z (relative intensity): 318 (M⁺, 55.0), 316 (100); HRMS Calcd for C₂₁H₁₈OS: 318.1078, Found: 318.1086.

Ethyl 2-Mercapto-3-phenylacrylate (1j)

A mixture of benzaldehyde (0.9 g, 9.4 mmol), rhodanine (1.3 g, 9.4 mmol), and anhydrous sodium acetate (2.2 g, 28.2 mmol) in acetic acid (10 mL) was stirred at 100 °C for 1 h. The reaction mixture was cooled to room temperature and H₂O (10 mL) was added. The precipitate formed was filtered and washed with H₂O (10 mL x 3), then dried under reduced pressure. A solution of the above precipitate in 3 M NaOH (12 mL) was stirred at 75 °C for 2 h. After cooling, the reaction mixture was neutralized with 3 M HCl. The precipitate formed was filtered and washed with H₂O (10 mL x 3), then dried under reduced pressure. Recrystallization from hexane-ethyl acetate gave 2-mercapto-3-phenylacrylic acid (0.69 g, 40% for 2 steps); ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 4.65 (1H, s), 7.38 (1H, t, J = 7.4 Hz), 7.46 (2H, t, J = 7.4 Hz), 7.68 (2H, d, J = 7.4 Hz), 7.91 (1H, s).

A solution of the above obtained acid (0.25 g, 1.4 mmol) in acetic anhydride (1.4 mL) was stirred at 120 °C for 2 h. After cooling, the reaction mixture was concentrated and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over MgSO₄. The residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give 2-methylene-4-(1-phenylmethylidene)-1,3-oxathiolan-5-one (0.10 g, 36%) as an orange solid; IR ν (film, cm⁻¹): 1600, 1771; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 4.60 (1H, d, J = 3.8 Hz), 5.15 (1H, d, J = 3.8 Hz), 7.39-7.49 (5H, m), 7.67 (1H, s).

LiOH (0.19 g, 7.9 mmol) was added to a solution of the above obtained oxathiolanone (0.80 g, 3.9 mmol) in EtOH (30 mL) at 0 °C and the mixture was stirred at the same temperature for 2 h, then acidified with 3 M HCl. The reaction mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give 1j (0.63 g, 77%) as an yellow oil; IR ν (neat, cm⁻¹): 1693, 2556; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.27 (3H, t, J = 7.0 Hz), 4.23 (2H, q, J = 7.0 Hz), 4.64 (1H, s), 7.22 (1H, t, J = 7.5 Hz), 7.31 (2H, t, J = 7.5 Hz), 7.53 (2H, d, J = 7.5 Hz), 7.66 (1H, s); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 14.2, 62.6, 123.3, 128.4, 128.7, 129.7, 134.6, 134.9, 165.1; MS m/z (relative intensity): 208 (M⁺, 28.0), 134 (100); HRMS Calcd for C₁₁H₁₂O₂S: 208.0558, Found: 208.0543.
Isopropyl 2-Mercapto-3-phenylacrylate (1k)

LiOH (0.14 g, 6.0 mmol) was added to a solution of the oxathiolanone (0.062 g, 0.30 mmol) in iPrOH (2.3 mL) at 0 °C and the mixture was stirred at the same temperature for 1 h, then acidified with 3 M HCl. The reaction mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over MgSO₄. The residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 1k (0.018 g, 28%) as an yellow oil; IR ν (neat, cm⁻¹): 1699, 2554; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.37 (6H, d, J = 6.1 Hz), 4.74 (1H, s), 5.17 (1H, sept, J = 6.1 Hz), 7.33 (1H, t, J = 7.4 Hz), 7.43 (2H, t, J = 7.4 Hz), 7.64 (2H, d, J = 7.4 Hz), 7.74 (1H, s); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 21.9, 70.5, 123.8, 128.5, 128.7, 129.8, 134.5, 135.1, 164.7; MS m/z (relative intensity): 222 (M⁺, 21.1), 134 (100); HRMS Calcd for C₁₂H₁₄O₂S: 222.0715, Found: 222.0705.
3. Synthesis of Benzo[b]thiophenes

Typical Procedure for Pd-Catalysed Cyclisation of Thioenols for the Synthesis of Benzo[b]thiophene (Table 1, Entry 10)

A mixture of triphenylethenethiol 1a (0.050 g, 0.17 mmol) and PdCl₂(cod) (0.0049 g, 0.017 mmol) in DMSO (3.4 mL) was heated at 120 °C for 1.5 h in a sealed tube. The reaction mixture was extracted with ethyl acetate (5 mL x 3) and the combined organic layer was washed with brine (10 mL), then dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane) to give 2,3-diphenylbenzothiophene 2a (42.3 mg, 85%) along with disulfide 3a (2.1 mg, 2%).

2,3-Diphenylbenzo[b]thiophene (2a)


mp: 114-116 °C (colorless needles from hexane-ethyl acetate, lit.² mp 117-118 °C); IR ν (film, cm⁻¹): 1431, 1443, 1599; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.21-7.24 (3H, m), 7.29-7.40 (9H, m), 7.57-7.59 (1H, m), 7.84-7.86 (1H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 122.0, 123.3, 124.4, 124.5, 127.3, 127.6, 128.3, 128.6, 129.5, 130.4, 133.1, 134.1, 135.4, 138.7, 139.4, 140.8; MS m/z (relative intensity): 286 (M⁺, 100); HRMS Calcd for C₂₀H₁₄S: 286.0816, Found: 286.0825.

Disulfide (3a)


mp: 182-184 °C (pale yellow needles from hexane-ethyl acetate, lit.³ mp 179.5-180.5 °C); IR ν (film, cm⁻¹): 1443, 1491, 1597; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.74 (4H, dd, J = 6.5, 2.9 Hz), 6.81 (4H, dd, J = 6.5, 2.9 Hz), 6.97-6.99 (6H, m), 7.16-7.18 (10H, m), 7.24-7.27 (6H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 126.3, 126.8, 127.5, 127.8, 127.9, 130.0, 130.3, 131.6, 137.7, 138.3, 142.22, 142.24, 142.5; MS m/z (relative intensity): 574 (M⁺, 18.7); HRMS Calcd for C₄₀H₃₀S₂: 574.1787, Found: 574.1774.

Analytical Data of Benzo[b]thiophenes

6-Methyl-3-(4-methylphenyl)-2-phenylbenzo[b]thiophene (2b)


mp: 169-171 °C (pale yellow needles from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1443, 1508, 1597; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.40 (3H, s), 2.48 (3H, s), 7.14 (1H, d, J = 8.2 Hz), 7.20-7.25, (7H, m), 7.30-7.33 (2H, m), 7.45 (1H, d, J = 8.2 Hz), 7.65 (1H, s); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 21.3, 21.5, 121.9, 123.1, 126.1, 127.4, 128.3, 129.3, 129.5, 130.2, 132.6, 133.0, 134.5, 134.6, 136.9, 138.0, 138.9, 139.1; MS m/z (relative intensity): 314 (M⁺, 100); HRMS Calcd for C₂₂H₁₈S: 314.1129, Found: 314.1112.
6-Methoxy-3-(4-methoxyphenyl)-2-phenylbenzo[b]thiophene (2c)

mp: 119-121 °C (pale yellow needles from hexane-ethyl acetate, lit. mp 143-145 °C); IR ν (film, cm⁻¹): 1472, 1508, 1597;¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.84 (3H, s), 3.89 (3H, s), 6.92-6.97 (3H, m), 7.21-7.25 (5H, m), 7.29-7.32 (2H, m), 7.34 (1H, d, J = 1.8 Hz), 7.47 (1H, d, J = 8.5 Hz);¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.2, 55.7, 104.6, 114.1, 114.3, 124.1, 127.3, 127.9, 128.3, 129.4, 131.4, 132.5, 134.6, 135.3, 136.4, 140.1, 157.6, 158.9; MS m/z (relative intensity): 346 (M⁺, 100); HRMS Calcd for C₂₂H₁₈O₂S: 346.1028, Found: 346.1025.

6-Fluoro-3-(4-fluorophenyl)-2-phenylbenzo[b]thiophene (2d)

mp: 155-158 °C (yellow needles from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1466, 1504, 1597;¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.05-7.14 (3H, m), 7.23-7.28 (7H, m), 7.47 (1H, dd, J = 8.7, 5.2 Hz), 7.53 (1H, dd, J = 8.7, 2.6 Hz);¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 108.2 (d, J = 25.5 Hz), 113.4 (d, J = 24.0 Hz), 115.8 (d, J = 21.5 Hz), 124.1 (d, J = 9.1 Hz), 127.8, 128.4, 129.4, 131.0 (d, J = 3.3 Hz), 131.5, 131.9 (d, J = 8.4 Hz), 133.7, 139.3 (d, J = 4.1 Hz), 139.5 (d, J = 9.9 Hz), 160.5 (d, J = 243.4 Hz), 162.1 (d, J = 245.8 Hz); MS m/z (relative intensity): 322 (M⁺, 100); HRMS Calcd for C₂₀H₁₂F₂S: 322.0628, Found: 322.0619; Anal. Calcd for C₂₀H₁₂F₂S: C, 74.51; H, 4.01. found: C, 74.45; H, 4.01.

6-Chloro-3-(4-chlorophenyl)-2-phenylbenzo[b]thiophene (2e)

mp: 149-152 °C (colorless plates from hexane-ethyl acetate); IR ν (film, cm⁻¹): 1450, 1585;¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.22 (2H, dt, J = 8.7, 2.1 Hz), 7.24-7.31 (6H, m), 7.36 (2H, dt, J = 8.7, 2.1 Hz), 7.44 (1H, dd, J = 8.7, 0.7 Hz), 7.82 (1H, dd, J = 2.5, 0.7 Hz);¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 88.2, 90.3, 91.9, 94.6, 95.0, 95.5, 96.0, 97.2, 97.9, 98.1, 99.93, 99.95, 100.1, 105.4, 106.2, 107.0; MS m/z (relative intensity): 354 (M⁺, 100); HRMS Calcd for C₂₀H₁₂Cl₂S: 354.0037, Found: 354.0044.

5-Methoxy-3-(3-methoxyphenyl)-2-phenylbenzo[b]thiophene (2f)

IR ν (neat, cm⁻¹): 1599;¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.63 (3H, s), 3.69 (3H, s), 6.77-6.84 (3H, m), 6.92 (1H,
dd, $J = 8.8, 2.4$ Hz), 6.99 (1H, d, $J = 2.4$ Hz), 7.13-7.24 (6H, m), 7.63 (1H, d, $J = 8.8$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ (ppm): 55.2, 55.6, 105.7, 113.3, 114.5, 115.5, 122.69, 122.71, 127.6, 128.2, 129.4, 129.6, 131.2, 132.8, 134.2, 136.9, 140.9, 141.7, 157.7, 159.7; MS m/z (relative intensity): 346 (M$^+$, 100); HRMS Calcd for C$_{22}$H$_{18}$O$_2$S: 346.1028, Found: 346.1000.

4-Methoxy-3-(2-methoxyphenyl)-2-phenylbenzo[b]thiophene (2g)

O
O

IR ν (neat, cm$^{-1}$): 1466, 1564; $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.54 (3H, s), 3.65 (3H, s), 6.70 (1H, d, $J = 7.7$ Hz), 6.83 (1H, td, $J = 7.7$, 1.3 Hz), 6.89 (1H, d, $J = 7.7$ Hz), 7.04 (1H, dd, $J = 7.7$, 1.3 Hz), 7.17-7.29 (7H, m), 7.45 (1H, d, $J = 7.7$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ (ppm): 55.6, 55.7, 105.7, 107.8, 110.1, 114.7, 119.8, 124.9, 127.18, 127.21, 128.0, 128.2, 129.2, 129.3, 130.6, 131.5, 134.7, 140.3, 156.4, 158.4; MS m/z (relative intensity): 346 (M$^+$, 100); HRMS Calcd for C$_{22}$H$_{18}$O$_2$S: 346.1028, Found: 346.1013.

2-(4-Methoxyphenyl)-3-phenylbenzo[b]thiophene (2h)

mp: 138-140 °C (colorless needles from hexane-ethyl acetate, lit.$^5$) mp 119-120 °C); IR ν (film, cm$^{-1}$): 1508, 1607; $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.77 (3H, s), 6.77 (2H, dt, $J = 8.8$, 2.6 Hz), 7.24 (2H, dt, $J = 8.8$, 2.6 Hz), 7.28-7.42 (7H, m), 7.54-7.57 (1H, m), 7.83-7.86 (1H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ (ppm): 55.2, 113.8, 121.9, 123.0, 124.2, 124.3, 126.6, 127.2, 128.6, 130.4, 130.7, 132.2, 135.6, 138.4, 139.4, 140.9, 159.0; MS m/z (relative intensity): 316 (M$^+$, 100); HRMS Calcd for C$_{21}$H$_{16}$OS: 316.0922, Found: 316.0897; Anal. Calcd for C$_{21}$H$_{16}$OS: C, 79.71; H, 5.10. found: C, 79.63; H, 5.24.

2,3-Diphenyl-6-methoxybenzo[b]thiophene (2i-A)

mp: 137-139 °C (colorless plates from hexane-ethyl acetate, lit.$^6$) mp 136-137 °C); IR ν (film, cm$^{-1}$): 1472, 1595; $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.89 (3H, s), 6.95 (1H, dd, $J = 8.9$, 2.8 Hz), 7.21-7.38 (11H, m), 7.46 (1H, d, $J = 8.9$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ (ppm): 55.7, 104.5, 114.3, 124.0, 127.26, 127.31, 128.2, 128.6, 129.4, 130.3, 132.8, 134.3, 135.0, 135.6, 136.7, 140.1, 157.5; MS m/z (relative intensity): 316 (M$^+$, 100); HRMS Calcd for C$_{21}$H$_{16}$OS: 316.0922, Found: 316.0917.
3-(4-Methoxyphenyl)-2-phenylbenzo[b]thiophene (2i-B)

mp: 128-131 °C (colorless scales from hexane-ethyl acetate, lit.5) mp 123-124 °C); IR ν (film, cm⁻¹): 1508, 1611; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.85 (3H, s), 6.94 (2H, d, J = 9.2 Hz), 7.22-7.28 (5H, m), 7.33-7.37 (4H, m), 7.58-7.61 (1H, m), 7.86-7.88 (1H, m); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 55.3, 114.1, 122.0, 123.3, 124.3, 124.4, 127.5, 127.6, 128.3, 129.5, 131.4, 132.8, 134.3, 138.7, 139.0, 141.0, 158.8; MS m/z (relative intensity): 316 (M⁺, 100); HRMS Calcd for C₂₁H₁₆OS: 316.0922, Found: 316.0913.

2-Ethoxycarbonylbenzo[b]thiophene (2j)

IR ν (neat, cm⁻¹): 1246, 1713; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.42 (3H, t, J = 7.2 Hz), 4.41 (2H, q, J = 7.2 Hz), 7.40 (1H, t, J = 7.6 Hz), 7.45 (1H, td, J = 7.6, 1.5 Hz), 7.85-7.88 (2H, m), 8.06 (1H, s); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 14.3, 61.6, 122.7, 124.9, 125.5, 126.8, 130.3, 133.9, 138.8, 142.2, 162.8; MS m/z (relative intensity): 206 (M⁺, 82.2), 161 (100); HRMS Calcd for C₁₁H₁₀O₂S: 206.0402, Found: 206.0378.

2-Isopropoxycarbonylbenzo[b]thiophene (2k)

IR ν (neat, cm⁻¹): 1713; ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.40 (6H, d, J = 6.2 Hz), 5.26 (1H, sept, J = 6.2 Hz), 7.39 (1H, td, J = 7.5, 1.1 Hz), 7.42 (1H, td, J = 7.5, 1.1 Hz), 7.84-7.89 (2H, m), 8.03 (1H, s); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 22.0, 69.3, 122.6, 124.7, 125.3, 126.7, 130.0, 134.4, 138.6, 142.0, 162.2; MS m/z (relative intensity): 220 (M⁺, 54.0), 178 (100); HRMS Calcd for C₁₂H₁₂O₂S: 220.0558, Found: 220.0544.
4. Detailed Results of Screening

(a) Effect of Solvent, Temperature and Catalyst Loading (1a → 2a)

![Diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>x</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield of 2a / 3a / 1a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>1</td>
<td>10</td>
<td>DMF</td>
<td>120</td>
<td>13 / 6 / 53</td>
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<tr>
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<tr>
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<td>10</td>
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<td>80</td>
<td>0 / 37 / 3</td>
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<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>DMSO</td>
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<td>44 / 27 / 0</td>
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</table>

<sup>a</sup> Isolated yield.  
<sup>b</sup> PdCl<sub>2</sub> was used instead of PdCl<sub>2</sub>(cod).

(b) Effect of Solvent, Temperature and Catalyst System (3a → 2a)

![Diagram](image)

<table>
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<th>Entry</th>
<th>Catalyst System</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield of 2a / 3a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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</thead>
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<td>DMF</td>
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<tr>
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<td>10 mol% PdCl&lt;sub&gt;2&lt;/sub&gt; / 100 mol% Cu(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DMF</td>
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<td>42 / 75</td>
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<tr>
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<td>DMSO</td>
<td>120</td>
<td>127 / 0</td>
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<tr>
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<td>DMSO</td>
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<tr>
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<td>None</td>
<td>DMSO</td>
<td>120</td>
<td>0 / quant.</td>
</tr>
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<sup>a</sup> Isolated yield.
5. References