Electronic supplementary information

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

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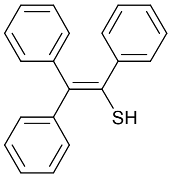
1. General Comments

All reactions were carried out under Ar atmosphere unless otherwise noted. Dimethyl sulfoxide (DMSO) was distilled from CaH_2 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. ^{1}H-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 Herts (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. ^{13}C-NMR spectra were recorded on JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from $^{13}CDCl_3$ (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.

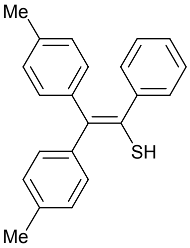
2. Synthesis of Starting Thioenols (1)

1,2,2-Triphenylethenethiol (1a)



To a mixture of triphenylvinyl bromide (10.0 g, 29.8 mmol) and magnesium (1.1 g, 44.7 mmol) in Et_2O (100 mL), a catalytic amount of diiodoethane was added and the mixture was heated under reflux for 6 h. Then, S_8 (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 NH_4Cl (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) to give **1a** (3.1 g, 36 %) as a pale yellow solid; mp: 107-110 °C (pale yellow needles from hexane-ethyl acetate, lit.[1)] mp 110-112 ºC); IR ν (film, cm^{-1}): 1597, 2563; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{20}H_{16}S$: 288.0973, Found: 288.0963.

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

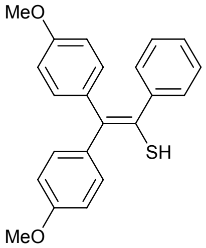


4-Methyphenylmagnesium bromide (0.96 M solution in THF, 25.0 mL, 24.0 mmol) was added to a solution of methyl phenylacetate (1.8 g, 12.0 mmol) in THF (10 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH_4Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase 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) to give 1,1-bis(4-methylphenyl)-2-phenylethanol (3.0 g, 82%) as a colorless solid; IR ν (film, cm^{-1}): 3558; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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. H_2O (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 $MgSO_4$. 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%); ^{1}H-NMR (400 MHz, $CDCl_3$) 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 $C_{22}H_{19}Br$: 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, S_8 (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 NH_4Cl (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) 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{20}S$: 316.1286, Found: 316.1274; *Anal.* Calcd for $C_{22}H_{20}S$: 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 NH_4Cl (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) 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 48.2, 55.2, 77.4, 113.2, 126.6, 127.3, 127.9, 130.8, 136.0, 139.0, 158.2.

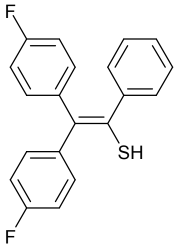
A mixture of the above obtained alcohol (1.5 g, 4.4 mmol) and *p*-TsOH-H_2O (0.35 g, 1.9 mmol) in benzene (14 mL) was heated under reflux for 1.5 h. H_2O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over $MgSO_4$. 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 oil; IR ν (neat, cm^{-1}): 1605; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{20}O_2$: 316.1463, Found: 316.1454.

To a solution of the above obtained ethylene (1.3 g, 4.2 mmol) in CCl_4 (20 mL), bromine (0.23 mL, 4.6 mmol) was added at 0 °C and stirred for 2 h at the same temperature. Et_3N (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 $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to give 2,2-bis(4-methoxyphenyl)-1-phenylvinyl bromide (quant.) as a yellow solid; IR ν (film, cm^{-1}): 1607; ^{1}H-NMR (400 MHz, $CDCl_3$) 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_4Cl (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 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.0, 55.1, 112.9, 113.2, 127.2, 127.9, 131.5, 131.7, 131.8, 135.2, 135.4, 135.8, 139.2, 142.1, 158.0, 158.4; MS *m/z* (relative intensity): 694 (M^+, 1.8), 346 (100); HRMS Calcd for $C_{44}H_{38}O_4S_2$: 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_4Cl 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 ºC); 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, 113.9, 127.2, 128.2, 128.6, 129.5, 131.1, 131.6, 134.5, 135.6, 136.6, 142.7, 157.7, 158.7; MS *m/z* (relative intensity): 348 (M^+, 100); HRMS Calcd for $C_{22}H_{20}O_2S$: 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_4Cl (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 (19:1)] to give 1,1-bis(4-fluorophenyl)-2-phenylethanol (4.4 g, 88%) as a colorless solid; 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).

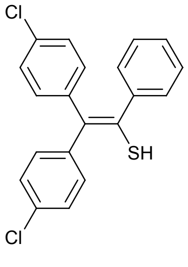
A mixture of the above obtained alcohol (4.1 g, 13.2 mmol) and *p*-TsOH-H_2O (1.1 g, 5.5 mmol) in toluene (40 mL) was heated under reflux for 4 h. H_2O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x

3). The combined organic layer was washed with brine (15 mL) and dried over $MgSO_4$. 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; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.88 (1H, s), 7.97 (6H, m), 7.11-7.17 (5H, m), 7.26 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 CCl_4 (45 mL), bromine (0.63 mL, 12.2 mmol) was added at room temperature and stirred for 2 h at 35 °C. Et_3N (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 $MgSO_4$. 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{20}H_{13}BrF_2$: 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, S_8 (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 NH_4Cl (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) 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{20}H_{14}F_2S$: 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 NH_4Cl (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 the crude alcohol.

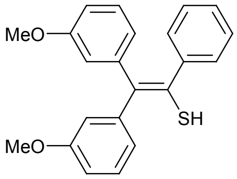
A mixture of the above obtained crude alcohol and *p*-TsOH-H_2O (1.6 g, 8.4 mmol) in toluene (50 mL) was heated under reflux for 4 h. H_2O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over $MgSO_4$. 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) as a pale yellow solid; ^{1}H-NMR (400 MHz, $CDCl_3$) 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 H_2O (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 (49:1)] to give 2,2-bis(4-chlorophenyl)-1-phenylvinyl bromide (3.2 g, 51%) as a colorless solid; ^{1}H-NMR (400 MHz, $CDCl_3$) 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 $C_{20}H_{13}BrCl_2$: 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, S_8 (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 NH_4Cl (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 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 $MgSO_4$. 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{20}H_{14}Cl_2S$: 356.0193, Found: 356.0171; *Anal.* Calcd for $C_{20}H_{14}Cl_2S$: C, 67.23; H, 3.95. found: C, 67.16; H, 4.04.

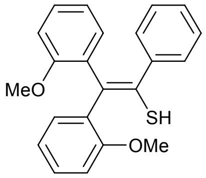
2,2-Bis(3-methoxyphenyl)-1-phenylethenethiol (1f)



A mixture of acetophenone (0.30 g, 2.5 mmol), 3-bromoanisole (1.4 g, 7.5 mmol), $Pd(OAc)_2$ (0.028 g, 0.13 mmol), PPh_3 (0.13 g, 0.50 mmol), and Cs_2CO_3 (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 $MgSO_4$. 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-phenylethanone (0.43 g, 51%) as a yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) 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 $C_{22}H_{20}O_3$: 332.1413, Found: 332.1395.

A mixture of the above obtained ketone (0.15 g, 0.35 mmol) and Lawessos'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 residure 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{20}O_2S$: 348.1184, Found: 348.1159.

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



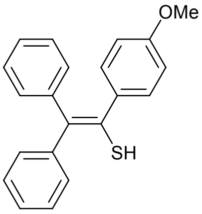
2-Methoxyphenylmagnesium bromide (1.3 M solution in THF, 20.0 mL, 26.6 mmol) was added to a solution of methyl phenylacetate (2.0 g, 13.3 mmol) in THF (26 mL) at 0 °C and stirred at room temperature for 90 min. Saturated aqueous NH_4Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous 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 (4:1)] to give 1,1-bis(2-methoxyphenyl)-2-phenylethanol (3.5 g, 78%) as a colorless solid; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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-H_2O (0.79 g, 4.2 mmol) in toluene (50 mL) was heated under reflux for 1.5 h. H_2O (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 $MgSO_4$. 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{20}O_2$: 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 CCl_4 (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). 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 2,2-bis(2-methoxyphenyl)-1-phenylvinyl bromide (0.28 g, 45%) as a colorless solid; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.5, 55.7, 111.3, 111.7, 120.4, 120.5, 126.4, 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 $C_{22}H_{19}BrO_2$: 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, S_8 (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 NH_4Cl (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 (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, $CDCl_3$) 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), 6.87-7.14 (6H, m), 7.24-7.33 (4H, m), 7.46 (1H, dd, J = 7.7, 1.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{20}O_2S$: 348.1184, Found: 348.1170.

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



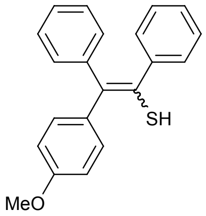
Phenylmagnesium bromide (1.8 M solution in THF, 16.0 mL, 28.0 mmol) was added to a solution of methyl 4-methoxyphenylacetate (2.5 g, 14.0 mmol) in THF (5 mL) at 0 °C and stirred at room temperature for 2.5 h. Saturated aqueous NH_4Cl (5 mL) was added to the reaction mixture at 0 °C and the aqueous phase 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 (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, $CDCl_3$) 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_2O (0.65 g, 3.4 mmol) in toluene (20 mL) was heated under reflux for 4 h. H_2O (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 $MgSO_4$. 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, $CDCl_3$) 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, $CDCl_3$) 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_3N (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 $MgSO_4$. 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, $CDCl_3$) δ (ppm): 3.73 (3H, s), 6.68 (2H, d, J = 9.2 Hz), 6.94-6.97 (2H, m), 7.04-7.08 (3H, m), 7.22-7.38 (7H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.2, 113.2, 122.3, 126.7, 127.3, 127.8, 128.1, 129.4, 130.2, 131.6, 133.3, 141.2, 142.5, 143.9, 158.9; MS *m/z* (relative intensity): 364 (M^+, 33.2), 285 (100); HRMS Calcd 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, S_8 (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 NH_4Cl (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 (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.[1)] mp 109 ºC); IR ν (film, cm^{-1}): 1605, 2561; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 NH_4Cl (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 1,2-diphenyl-1-(4-methoxypheny)ethanol, (4.5 g, 78%) as a colorless solid; IR ν (film, cm^{-1}): 1110, 1609, 3553; ^{1}H-NMR (400 MHz, $CDCl_3$) 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).

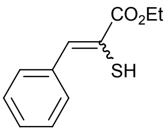
A mixture of the above obtained alcohol (0.070 g, 0.23 mmol) and *p*-TsOH-H_2O (0.018 g, 0.092 mmol) in toluene (1.5 mL) was heated under reflux for 1.5 h. H_2O (10 mL) was added and the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (15 mL) and dried over $MgSO_4$. 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 CCl_4 (1 mL), bromine (0.012 mL, 0.24 mmol) was added at 0 °C and stirred for 1 h at the same temperature. Et_3N (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 $MgSO_4$. 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 ν (film, cm^{-1}): 1508, 1605; MS *m/z* (relative intensity): 364 (M^+, 72.6), 285 (100); HRMS Calcd for $C_{21}H_{17}BrO$: 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, S_8 (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 NH_4Cl (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 (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 $MgSO_4$. 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, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{21}H_{18}OS$: 318.1078, Found: 318.1086.

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

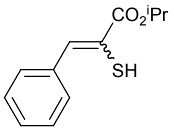


A mixture of benzaldehyde (0.9 g, 9.4 mmol), rhodanine (1.3 g, 9.4 mmol), and anhydrous sodium acetate (2.2 g, 28.2 mmol) in acetic acid (10 mL) was stirred at 100 °C for 1 h. The reaction mixture was cooled to room temperature and H_2O (10 mL) was added. The precipitate formed was filtered and washed with H_2O (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 H_2O (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, $CDCl_3$) 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 $MgSO_4$. 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, $CDCl_3$) 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 $MgSO_4$. The residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give **1j** (0.63 g, 77%) as an yellow oil; IR ν (neat, cm^{-1}): 1693, 2556; ^1H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{11}H_{12}O_2S$: 208.0558, Found: 208.0543.

Isopropyl 2-Mercapto-3-phenylacrylate (1k)



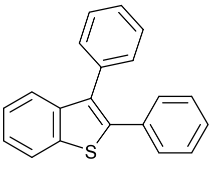
LiOH (0.14 g, 6.0 mmol) was added to a solution of the oxathiolanone (0.062 g, 0.30 mmol) in ^{i}PrOH (2.3 mL) at 0 °C and the mixture was stirred at the same temperature for 1 h, then acidified with 3 M HCl. The reaction mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layer was washed with brine (15 mL), then dried over $MgSO_4$. 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; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{12}H_{14}O_2S$: 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 $PdCl_2$(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 $MgSO_4$. 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)



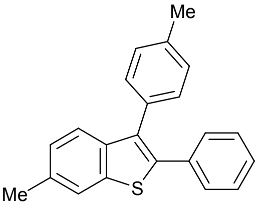
mp: 114-116 °C (colorless needles from hexane-ethyl acetate, lit.[2)] mp 117-118 ºC); IR ν (film, cm^{-1}): 1431, 1443, 1599; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21-7.24 (3H, m), 7.29-7.40 (9H, m), 7.57-7.59 (1H, m), 7.84-7.86 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 122.0, 123.3, 124.4, 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 $C_{20}H_{14}S$: 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 ºC); IR ν (film, cm^{-1}): 1443, 1491, 1597; ^{1}H-NMR (400 MHz, $CDCl_3$) 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); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{40}H_{30}S_2$: 574.1787, Found: 574.1774.

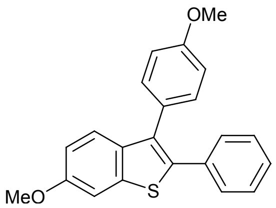
Analytical Data of Benzo[b]thiophenes

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



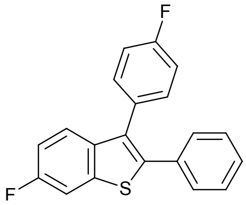
mp: 169-171 °C (pale yellow needles from hexane-ethyl acetate); IR ν (film, cm^{-1}): 1443, 1508, 1597; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.40 (3H, s), 2.48 (3H, s), 7.14 (1H, d, *J* = 8.2 Hz), 7.20-7.25, (7H, m), 7.30-7.33 (2H, m), 7.45 (1H, d, *J* = 8.2 Hz), 7.65 (1H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{18}S$: 314.1129, Found: 314.1112.

6-Methoxy-3-(4-methoxyphenyl)-2-phenylbenzo[*b*]thiophene (2c)



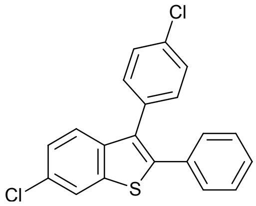
mp: 119-121 °C (pale yellow needles from hexane-ethyl acetate, lit.[4)] mp 143-145 ºC); IR ν (film, cm^{-1}): 1472, 1508, 1597; ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.84 (3H, s), 3.89 (3H, s), 6.92-6.97 (3H, m), 7.21-7.25 (5H, m), 7.29-7.7.32 (2H, m), 7.34 (1H, d, *J* = 1.8 Hz), 7.47 (1H, d, *J* = 8.5 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$) 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 $C_{22}H_{18}O_2S$: 346.1028, Found: 346.1025.

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



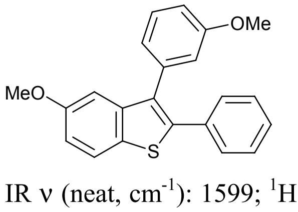
mp: 155-158 °C (yellow needles from hexane-ethyl acetate); IR ν (film, cm^{-1}): 1466, 1504, 1597; ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 7.05-7.14 (3H, m), 7.23-7.28 (7H, m), 7.47 (1H, dd, *J* = 8.7, 5.2 Hz), 7.53 (1H, dd, *J* = 8.7, 2.6 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$) δ (ppm): 108.2 (d, *J* = 25.5 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 $C_{20}H_{12}F_2S$: 322.0628, Found: 322.0619; *Anal.* Calcd for $C_{20}H_{12}F_2S$: C, 74.51; H, 4.01. found: C, 74.45; H, 4.01.

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



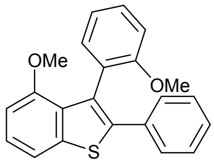
mp: 149-152 °C (colorless plates from hexane-ethyl acetate); IR ν (film, cm^{-1}): 1450, 1585; ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 7.22 (2H, dt, *J* = 8.7, 2.1 Hz), 7.24-7.31 (6H, m), 7.36 (2H, dt, *J* = 8.7, 2.1 Hz), 7.44 (1H, dd, *J* = 8.7, 0.7 Hz), 7.82 (1H, dd, *J* = 2.5, 0.7 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$) 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 $C_{20}H_{12}Cl_2S$: 354.0037, Found: 354.0044.

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



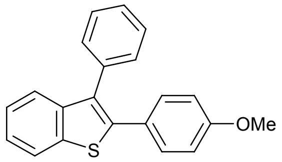
IR ν (neat, cm^{-1}): 1599; ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.63 (3H, s), 3.69 (3H, s), 6.77-6.84 (3H, m), 6.92 (1H, dd, *J* = 8.8, 2.4 Hz), 6.99 (1H, d, *J* = 2.4 Hz), 7.13-7.24 (6H, m), 7.63 (1H, d, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.2, 55.6, 105.7, 113.3, 114.5, 115.5, 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 $C_{22}H_{18}O_2S$: 346.1028, Found: 346.1000.

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



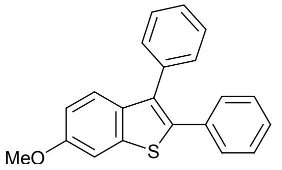
IR ν (neat, cm^{-1}): 1466, 1564; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.54 (3H, s), 3.65 (3H, s), 6.70 (1H, d, *J* = 7.7 Hz), 6.83 (1H, td, *J* = 7.7, 1.3 Hz), 6.89 (1H, d, *J* = 7.7 Hz), 7.04 (1H, dd, *J* = 7.7, 1.3 Hz), 7.17-7.29 (7H, m), 7.45 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{18}O_2S$: 346.1028, Found: 346.1013.

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



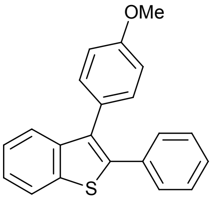
mp: 138-140 °C (colorless needles from hexane-ethyl acetate, lit.$^{5)}$ mp 119-120 ºC); IR ν (film, cm^{-1}): 1508, 1607; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.77 (3H, s), 6.77 (2H, dt, *J* = 8.8, 2.6 Hz), 7.24 (2H, dt, *J* = 8.8, 2.6 Hz), 7.28-7.42 (7H, m), 7.54-7.57 (1H, m), 7.83-7.86 (1H, m); ^{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)



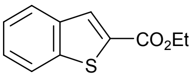
mp: 137-139 °C (colorless plates from hexane-ethyl acetate, lit.$^{6)}$ mp 136-137 °C); IR ν (film, cm^{-1}): 1472, 1595; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.89 (3H, s), 6.95 (1H, dd, *J* = 8.9, 2.8 Hz), 7.21-7.38 (11H, m), 7.46 (1H, d, *J* = 8.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 55.7, 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)



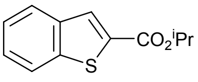
mp: 128-131 °C (colorless scales from hexane-ethyl acetate, lit.[5)] mp 123-124 °C); IR ν (film, cm^{-1}): 1508, 1611; ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.85 (3H, s), 6.94 (2H, d, *J* = 9.2 Hz), 7.22-7.28 (5H, m), 7.33-7.37 (4H, m), 7.58-7.61 (1H, m), 7.86-7.88 (1H, m); ^{13}C-NMR (100 MHz, CDCl$_3$) 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 $C_{21}H_{16}OS$: 316.0922, Found: 316.0913.

2-Ethoxycarbonylbenzo[*b*]thiophene (2j)



IR ν (neat, cm^{-1}): 1246, 1713; ^{1}H-NMR (400 MHz, CDCl$_3$) 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); ^{13}C-NMR (100 MHz, CDCl$_3$) 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 $C_{11}H_{10}O_2S$: 206.0402, Found: 206.0378.

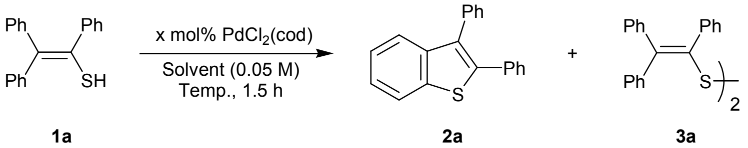
2-Isopropoxycarbonylbenzo[*b*]thiophene (2k)



IR ν (neat, cm^{-1}): 1713; ^{1}H-NMR (400 MHz, CDCl$_3$) 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); ^{13}C-NMR (100 MHz, CDCl$_3$) 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 $C_{12}H_{12}O_2S$: 220.0558, Found: 220.0544.

4. Detailed Results of Screening

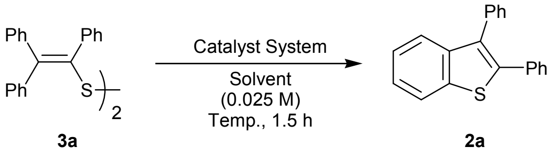
(a) Effect of Solvent, Temperature and Catalyst Loading (**1a** → **2a**)



Entry	x	Solvent	Temp. (ºC)	Yield of **2a** / **3a** / **1a** (%)[a]
1	10	DMF	120	13 / 6 / 53
2	10	DMSO-DMF (1:1)	120	60 / 16 / 0
3	10	DMSO-EtOH (1:1)	120	43 / 22 / 0
4	10	DMSO	120	85 / 2 / 0
5	10	DMSO	80	0 / 37 / 3
6	5[b]	DMSO	120	44 / 27 / 0

[a] Isolated yield. [b] $PdCl_2$ was used instead of $PdCl_2$(cod).

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



Entry	Catalyst System	Solvent	Temp. (ºC)	Yield of **2a** / **3a** (%)[a]
1	10 mol% $PdCl_2$	DMF	120	15 / 88
2	10 mol% $PdCl_2$ / 100 mol% $Cu(OAc)_2$	DMF	120	42 / 75
3	10 mol% $PdCl_2$	DMSO	120	127 / 0
4	10 mol% $PdCl_2$	DMSO	80	0 / 96
5	None	DMSO	120	0 / quant.

[a] Isolated yield.

5. References

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