

Protective group	Method of preparation	Yield [%]	NMR	Elementary analysis	Yield Suzuki-coupling [%]
acetyl (1a)	D	80	$\delta = 7.53$ (2H, m, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 9$ Hz); 7.26 (2H, m, H-2, H-6); 2.42 (3H, s).	calc. [%] C 41.38 H 3.24 Br 34.57 found [%] C 41.58 H 3.28 Br 34.63	0.7 ± 0.1
pivaloyl (1b)	D	32	$\delta = 7.53$ (2H, m, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 8$ Hz); 7.25 (2H, m, H-2, H-6); 1.31 (9H, s).	calc. [%] C 48.39 H 4.84 Br 29.15 found [%] C 48.36 H 4.80 Br 29.25	35 ± 2
trichloroacetyl (1c)	A	76	$\delta = 7.44$ (2H, m, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 9$ Hz); 7.34 (2H, m, H-2, H-6).		0
benzoyl (1d)	A	64	$\delta = 8.02$ (2H, m, H-2', H-6'), 7.51 (7H, m, H-3', H-4', H-5', H-2, H-3, H-5, H-6).	calc. [%] C 53.43 H 3.35 Br 27.25 found [%] C 53.37 H 3.36 Br 26.98	0
ferrocenoyl (1e)	C	78	$\delta = 7.57$ (2H, AA'BB'-spectrum, H-3, H-5, -C ₆ H ₄ -, $^3J_{2-3} = ^3J_{5-6} = 9$ Hz), 7.35 (2H, AA'BB'-spectrum, H-2, H-6, -C ₆ H ₄ -), 4.92 (2H, t, H-2', H-5', subst. Cp-ring, $^3J_{2-3'} = ^3J_{4-5'} = 2$ Hz), 4.54 (2H, t, H-3', H-4', subst. Cp-ring), 4.28 (5H, s, unsubst. Cp-ring).	calc. [%] C 50.91 H 3.27 Br 19.92 found [%] C 50.92 H 3.54 Br 18.74	0
2,4,6-triisopropylbenzoyl (1f)	C	64	$\delta = 7.60$ (2H, AA'BB'-spectrum, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 9$ Hz), 7.39 (2H, AA'BB'-spectrum, H-2, H-6); 7.04 (2H, s, H-3', H-5'); 3.00 (3H, 2 x heptett in 2:1 ratio, CH(CH ₃) ₂ , $^3J = 7$ Hz); 1.25 (18H, 2 x d in 2:1 ratio, CH(CH ₃) ₂ , $^3J = 7$ Hz).	calc. [%] C 63.00 H 6.48 Br 19.05 found [%] C 63.56 H 6.74 Br 18.07	0
dimethylphenylacetyl (1g)	A	65	$\delta = 7.50$ (2H, AA'BB'-spectrum, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 8$ Hz), 7.38 (5H, m, arom. H), 7.18 (2H, AA'BB'-spectrum, H-2, H-6 arom. H), 1.68 (6H, s, CH ₃).	calc. C 57.32 H 4.56 Br 23.83 found C 57.25 H 4.62 Br 23.78	0
2-methoxyisobutyryl (1h)	C	49	$\delta = 7.61$ (2H, m, H-3, H-5), 7.55 (2H, m, H-2, H-6), 7.47 (4H, m, H-3', H-5', H-2', H-6'), 3.43 (3H, s, OCH ₃), 1.47 (6H, s, CH ₃).	calc. C 45.69 H 4.53 Br 27.63 found C 45.60 H 4.83 Br 27.86	74 ± 19 , 55 (isolated)
tert-butoxycarbonyl (1i)	B	75	$\delta = 7.50$ (2H, AA'BB'-spectrum, H-3, H-5, $^3J_{2-3} = ^3J_{5-6} = 9$ Hz), 7.37 (2H, AA'BB'-spectrum, H-2, H-6), 1.50 (9H, s, -CCH ₃).	calc. [%] C 45.69 H 4.53 Br 27.67 found [%] C 45.75 H 4.61 Br 27.60	1.0 ± 0.1

All reactions were carried out under nitrogen using dried solvents.

Method A

Imidazole (170 mg, 2.5 mmol) was added to a solution of 4-bromothiophenol (190 mg, 1.0 mmol) in CH_2Cl_2 (25 ml). When the imidazole was completely dissolved, the acid chloride (1.5 mmol) was added and then heated under reflux for 16 h. The solvent was removed and the crude product was purified by column chromatography with petroleum ether/ethyl acetate as solvent.

Method B

4-Bromothiophenol (190 mg, 1.0 mmol) and K_2CO_3 (210 mg, 1.5 mmol) in THF (1.5 ml) were cooled to 0°C . Di-*tert*-butylpyrocarbonate (240 mg, 1.1 mmol) and catalytic amounts of 18-crown-6-ether were added to the mixture, which was stirred for 16 h at room temperature. The organic layer was washed with brine and the solvent was removed. The crude product was purified by column chromatography with petroleum ether/ethyl acetate as solvent.

Method C

NaH (24 mg, 1.0 mmol) was added to a solution of 4-bromothiophenol (190 mg, 1.0 mmol) in THF (6 ml) and stirred for 15 minutes at room temperature. The acid chloride (1.1 mmol) in THF (20 ml) was added and the solution was stirred for 40 hours under reflux. CH_3COOH (0.1 ml) was added to the solution and the solvent was removed. The crude product was purified by column chromatography with petroleum ether/ethyl acetate as solvent.

Method D

Catalytic amounts of CoCl_2 in dried CH_3CN (0.2 ml) were added to a solution of 4-bromothiophenol (190 mg, 1.0 mmol) and acid chloride (1.1 mmol) in CH_3CN (0.8 ml). This solution was stirred under reflux over night. After removal of the solvent the crude product was solved in Et_2O and washed with H_2O , saturated sodium carbonate soln and again with

H₂O. The solvent of the organic layer was removed and the crude product was purified by column chromatography with CH₂Cl₂/ethyl acetate as solvent.

Suzuki coupling

The protected 4-bromothiophenol (1.0 mmol), tolylboronic acid anhydride (130 mg, 0.37 mmol), dried K₃PO₄ (320 mg, 1.5 mmol), and Pd(PPh₃)₄ (58 mg, 50 μmol) were dissolved in DME (3.5 ml) and this solution was heated to reflux for 16 h. NaOH (1.6 g, 40 mmol) in H₂O (3.5 ml) was saturated with N₂ and added to the reaction mixture. After stirring at 60°C for 3 ½ hours, citric acid (4.8 g, 25 mmol) was added and the stirring was continued for 30 minutes. 15 minutes after the stirrer was turned off a phase separation took place. A sample of the organic layer was taken to determine the yield of the reaction by gas chromatography.

Gas chromatography was carried out using a Perkin Elmer 8420 Capillary Gas-Chromatograph and a crosslinked methyl silicone gum capillary column (l = 25m, 0.25 mm outer diam.). Starting from 60°C, the temperature was raised by 10°C/min to 300°C, and held at this temperature for 10 min. Retention times of relevant substances were: 6.5 min (4-bromothiophenol), 14.0 min (4'-methylbiphenylthiol), 17.2 min (p-terphenyl), 17.5 min (PPh₃, form catalyst).