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Cycloaddition Reactions of Benzo[b]thiophene S-Oxides

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***Abstract**:2-Substituted benzo[b]thiophene S-oxides have been prepared from the respective benzo[b]thiophenes by oxidation with meta-chloroperoxybenzoic acid in the presence of $BF_3{\cdot}Et_2O$ and have been submitted to cycloaddition reactions with alkenes and alkynes.*

***Keywords:** benzo[b[thiophene, benzo[b]thiophene S-oxide, Diels-Alder reaction, cycloaddition*

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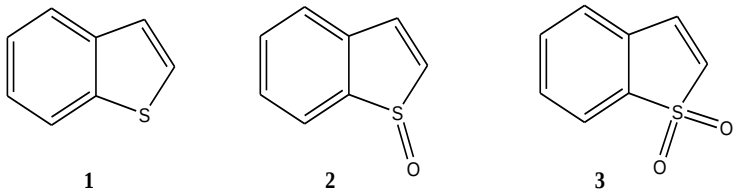
I. Introduction

Benzo[*b*]thiophene *S*-oxides **2** [1] (Fig. 1) have elicited attention in their role as intermediates in the biodegradation of benzo[*b*]thiophenes **1** in oil-contaminated soils [2] and in their role in the deposit formation in engine induction systems [3]. Benzo[*b*]thiophene *S*-oxides have been used as intermediates in the synthesis of substituted benzo[*b*]thiophenes [4], including 3-substituted benzo[*b*]thiophenes [5]. Furthermore, they have been forwarded as interesting products in their own right, such as as anti-inflammatory agents, due to their action as inhibitors of the adhesion of neutrophiles to the vascular endothelium [6]. Interestingly, 3-phenylbenzo[*b*]thiophene *S*-oxides have also been patented as pesticides (acaricides) [7]. In cycloaddition reactions, benzo[*b*]thiophene *S*-oxides have been found to react as the ene-component in [3+2]-cycloadditions with 1,3-dipoles such as mesitonitrile oxide [8], in Diels-Alder type [4+2]-cycloadditions, just as benzo[*b*]thiophene *S*,*S*-dioxides **3** [9], and photochemically in [2+2]-cycloadditions [10]. In [4+2]-cycloaddition reactions, benzo[*b*]thiophene *S*-oxides can act as diene component, also, as is shown by the dimerization of the unsubstituted benzo[*b*]thiophene *S*-oxide with itself [11]. In the following, the viability of 2-substituted benzo[*b*]thiophene *S*-oxides as dienes in [4+2]-cycloaddition is examined.



1 **2** **3**

Fig. 1. Structure of benzo[*b*]thiophene **1**, benzo[*b*]thiophene *S*-oxide **2**, and benzo[*b*]thiophene *S*,*S*-dioxide **3**

II. Experimental

General. – Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). The assignment in the 13C-NMR spectra was aided by DEPT experiments (DEPT = distortionless enhancement by polarization transfer), where (+) denotes methyl, (-) secondary carbon, (+, CH) tertiary carbon and (C_{quat}) a quaternary carbon. Mass spectra were measured with a JMS-01-SG-2 spectrometer. Column chromatography was carried out on Wakogel 300. Elemental analysis was carried out at Kyushu University, Hakozaki Campus, Fukuoka, Japan.

Chemicals. – Dimethyl acetylenedicarboxylate (**8a**) (Wako), ethyl propiolate (**8c**) (Wako), *N*-phenylmaleimide (**10**) (TCI), 2-methylbenzo[*b*]thiophene (**6d**) (TCI), benzo[*b*]thiophene (**1**) (TCI), 4-bromoanisole (**5b**) (TCI), 4-bromotoluene (**5a**) (TCI), and 1-bromo-4-nitrobenzene (**5c**) (TCI) were acquired commercially. Dibenzoylacetylene (**8b**) was prepared by bromination of (*E*)-dibenzoylethylene (Br_2, AcOH) with subsequent

double dehydrobromination (Et_3N, benzene [12]). 2-Methylbenzo[*b*]thiophene *S*-oxide (**7d**) was prepared according to the literature [13].

2-Benzo[*b*]thiopheneboronic acid (**4**) (Scheme 1). – To benzo[*b*]thiophene (**1**, 2.0 g, 14.9 mmol) in dry THF (30 mL), cooled to -78 °C, *n*-butyllithium (*n*-BuLi) (5.73 mL, 14.9 mmol, 2.6 M) was added gradually. The resulting solution was warmed to rt and stirred for 3h. Then, the solution was recooled to -78 °C, and trimethylborate (1.55 g, 14.9 mmol) was added slowly. Thereafter, the mixture was warmed to rt, and stirred for 12h. Then, it was poured into 10w% aq, HCl (100 mL). The resulting mixture was extracted with CH_2Cl_2 (100 mL) and othe organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The product was washed with hexane (3 X 50 mL) and dried *in vacuo* to give **4** (2.05 g, 11.5 mmol, 77%) as a colorless solid, mp. 235.0 – 237.5 °C [Lit. > 200 °C{14}]). IR (KBr) *v* 3052, 1516, 1354, 1176, 747, 703 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.71-3.80 (2H, bs), 7.40-7.51 (2H, m), 7.94-8.03 (2H, m), 8.34 (1H, bs); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 122.6, 124.3, 124.4, 125.0, 133.1, 140.5, 143.2, 145.0.

2-(*p*-Tolyl)benzo[*b*]thiophene (**6a**). A solution of 2-benzothiopheneboronic acid (**4**, 1.0 g, 5.6 mmol) and *p*-bromotoluene (**5a**, 1.15 g, 6.7 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in toluene (20 mL) and 2N aq. $CsCO_3$ (11.2 mL) was heated at 120 °C for 36h. Afterwards, the reaction mixture was poured into conc. aq. $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic phase was dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was separated by column chromatography on silica gel (hexane/ether: 1:1) to give 2(*p*-tolyl)benzo[*b*]thiophene (**6a**, 184 mg, 15%) as a colorless solid, mp. 162 °C [Lit. 162-163 °C{15}]; IR (neat) ν 3050, 2915, 1500, 1455, 810, 740, 725 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 7.22 (2H, d, ^3J = 8.0 Hz), 7.29 – 7.33 (2H, m), 7.49 (1H, s), 7.60 (2H, d, ^3J = 8.0 Hz), 7.70 – 7.80 (2H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.2 (CH_3), 118.8, 122.2, 123.4, 124.1, 124.4, 126.4, 129.6, 131.5, 138.3, 139.3, 140.8, 144.4; MS (EI, 70 eV) *m/z* (%) 224 (M^+, 37). HRMS Found: 224.0665. Calcd. for $C_{15}H_{12}S$: 224.0660.

2-(*p*-Tolyl)benzo[*b*]thiophene *S*-oxide (**7a**). – A solution of **6a** (132 mg, 0.59 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0 °C and $BF_3{\cdot}Et_2O$ (4.9 g, 33.7 mmol) was added to it. Then, a solution of *m*-CPBA (123 mg, 0.71 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to the solution, and the resulting mixture was stirred for 4h at rt. Thereafter, the reaction mixture was poured into conc. aq. $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic phase was washed with water (100 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was submitted to column chromatography on silica gel (ether) to give **7a** (109 mg, 0.45 mmol, 77%) as a colorless solid, mp. 73°C; IR (neat) ν 3026, 2918, 2854, 1582, 1505, 1448, 1063, 1025, 812, 756, 502 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.42 (3H, s, CH_3), 7.17-7.34 (3H, m). 7.35-7.52 (3H, m), 7.62 (2H, d, ^3J = 8.0 Hz), 7.86 (1H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.4 (CH_3), 124.3, 125.6, 126.3, 127.0, 128.0, 128.1, 129.9, 132.2, 138.0, 139.8, 144.0, 152.4; MS (EI, 70 eV) *m/z* (%) 240 (M^+, 21). HRMS Found: 240.0607. Calcd. for $C_{15}H_{12}OS$: 240.0609.

2-(4-Methoxyphenyl)benzo[*b*]thiophene (**6b**). – A mixture of 2-benzo[*b*]thiopheneboronic acid (**4**, 1.00 g, 5.6 mmol), *p*-iodoanisole (1.57 g, 6.7 mmol), and $Pd(PPh_3)_4$ (348 mg, 0.3 mmol), in 2N aq. Na_2CO_3 (5.6 mL) and toluene (20 mL) was heated under stirring at 100 °C for 12h. Thereafter, the cooled reaction mixture was poured into conc. aq. Na_2CO_3 (100 mL) and extracted with CH_2Cl_2 (50 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ethyl acetate 2:1) to give **6b** (618 mg, 2.58 mmol, 46%) as colorless prisms, mp. 200 °C [Lit. 200-201 °C{16}]; IR (neat) ν 3060, 2940, 1600, 1495, 1250, 1020, 825, 735, 700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.85 (3H, s, OCH_3), 6.96 (2H, d, ^3J = 8.6 Hz), 7.25 – 7.36 (2H, m), 7.42 (1H, s), 7.65 (2H, d, ^3J = 8.6 Hz), 7.72 (1H, d, ^3J = 7.9 Hz), 7.84 (1H, d, ^3J = 8.2 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 55.4, 114.3, 118.1, 122.1, 123.2, 123.9, 124.4, 127.7, 128.2, 139.8, 140.8, 144.1, 159.7; MS (EI, 70 eV) *m/z* (%) 240 (M^+, 100). HRMS Found: 240.0606. Calcd. for $C_{15}H_{12}OS$: 240.0609.

(2-(4-Methoxyphenyl)benzo[*b*]thiophene *S*-oxide (**7b**). – To a solution of **6b** (300 mg, 1.24 mmol) in dry CH_2Cl_2 (15 mL), cooled to -18 °C, $BF_3{\cdot}Et_2O$ complex (4.9 g, 33.7 mmol) was added. Then, a solution of *m*-CPBA (700 mg, 4.1 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to the solution at 0 °C, and the resulting mixture was stirred for 24h at 0 °C. Then, the reaction mixture was poured into conc. aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic phase was washed with water and brine, was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CH_2Cl_2:ether 2:1) to give **7b** (187 mg, 0.73 mmol, 59%) as light yellow prisms, mp. 145 °C; IR (KBr) ν 3054, 3002, 2958, 2832, 1603, 1530, 1498, 1433, 1290, 1254, 1245, 1178, 1029, 820 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.98 (2H, d, ^3J = 8.6 Hz), 7.13 (1H, s), 7.35 – 7.52 (3H, m), 7.74 (2H, d, ^3J = 8.6 Hz), 7.90 (1H, d, ^3J = 8.2 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 55.4, 114.6, 123.4, 124.4, 126.3, 127.9, 128.4, 128.8, 132.2, 138.1,

143.7, 151.9, 160.6; MS (EI, 70 eV) *m/z* (%) 256 (M^+, 89). HRMS Found: 256.0556. Calcd. for $C_{15}H_{12}O_2S$: 256.0558.

2-(4-Nitrophenyl)benzo[*b*]thiophene (**6c**). – A solution of 2-benzo[*b*]thiopheneboronic acid (**4,** 1.00 g, 5.6 mmol), 4-bromonitrobenzene (1.24 g, 6.2 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in a mixed solution of aq. Na_2CO_3 (11.2 mL) and toluene (20 mL) was heated at 100 °C for 12h. Afterwards, the reaction mixture was poured into conc. aq. $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2 (3 X 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether 1:1) to give **6c** (1.04 g, 4.1 mmol, 73%) as a yellow solid, mp. 200 °C (sublimation), [Lit. 201 ° {17}]); IR (neat) ν 3310 (bs, OH), 2968, 1524, 1484, 1374, 1302, 1257, 1195, 1144, 1048, 1027, 973, 948, 932 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.34 – 7.48 (2H, m), 7.73(1H, s), 7.81 – 7.91 (4H, m), 8.30 (2H, d, ^3J = 9.0 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 122.4, 124.3, 124.4, 125.0, 125.5, 126.7, 130.0, 132.6, 140.1, 140.5, 141.1, 147.1; MS (EI, 70 eV) *m/z* (%) 255 (M^+, 100).

2-(4-Nitrophenyl)benzo[*b*]thiophene *S*-oxide (**7c**). – To a solution of **6c** (300 mg, 1.24 mmol) in dry CH_2Cl_2 (15 mL), cooled to -15 °C, was added $BF_3{\cdot}Et_2O$ complex (880 mg, 6.2 mmol). To the ensuing mixture, warmed to 0 °C, was added dropwise a solution of *m*-CPBA (257 mg, 1.5 mmol) in dry CH_2Cl_2 (5 mL). The resulting reaction mixture was stirred for 8h at 0 °C. Thereafter, it was poured into conc. aq. NaHCO3 (50 mL) and extracted with CH_2Cl_2 (2 X 25 mL). The organic phase was washed with water (50 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($Et_2O/CHCl_3$ 2:1) to give **7c** (187 mg, 0.73 mmol, 59%) as a yellow solid, mp. 145 °C; IR (neat) ν 3382 (bs, OH), 2972, 2928, 1633, 1603, 1490, 1454, 1354, 1204, 1122, 1058, 998, 970, 843, 782 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.47 – 7.68 (4H, m), 7.94 – 8.09 (3H, m), 8.38 (2H, d, ^3J = 9.0 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 124.4, 125.3, 126.6, 127.3, 127.6, 129.5, 130.3, 132.7, 136.9, 144.8, 147.8, 149.8; MS (EI, 70 eV) *m/z* (%) 271 (M^+, 100). HRMS Found: 271.0303. Calcd. for $C_{14}H_9O_3NS$: 271.0303.

Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (7d) to dimethyl acetylenedicarboxylate (8a): Dimethyl 3-methylnaphthalene-1,2-dicarboxylate (9a) [13]. – A solution of **7d** (82 mg, 0.55 mmol) and dimethyl acetylenedicarboxylate (**8a**, 172 mg, 1.0 mmol) in benzene (2 mL) was held at 80 °C for 34h. The reaction mixture was concentrated *in vacuo* and submitted to column chromatography on silica gel (hexane/ether 3:1) to give 2-methylbenzo[*b*]thiophene (**6d**, 50 mg, 62%) and dimethyl 3-methylnaphthalene-1,2-dicarboxylate (**9a**, 45 mg, 32%) as a slowly crystallizing, colorless oil; IR (neat) ν 2950, 2924, 2850, 1732, 1438, 1276, 1236, 1203, 1179, 1136, 1068 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.56 (3H, s, CH_3), 3.94, (3H, s, CO_2Me), 3.99 (3H, s, CO_2Me), 7.51 – 7.56 (2H, m), 7.77 (1H, s), 8.07 – 8.12 (2H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 20.5 (+, CH_3), 52.5 (+, $CO_2\underline{Me}$), 52.7 (+, $CO_2\underline{Me}$), 125.7 (+, CH), 127.1 (+, CH), 127.5 (+, CH). 127.7 (+, CH), 128.2 (C_{quat}), 132.6 (CH), 134.1 (C_{quat}), 135.9 (C_{quat}), 168.4 (C_{quat}, CO), 168.7 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 258 (M^+, 60), 227 (96), 226 (96), 168 (100).

Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (7d) to dibenzoylacetylene (8b): 1,2-Dibenzoyl-3-methylnapthalene (9b). – A solution of 2-methylbenzo[*b*]thiophene *S*-oxide (**7d**, 100 mg, 0.61 mmol) and dibenzoylacetylene (**8b**, 142 mg, 0.61 mmol) in benzene (1 mL) was held at reflux for 34h. Then, the cooled reaction mixture was concentrated *in vacuo* and submitted to column chromatography on silica gel to give 2-methylbenzo[*b*]thiophene (**6d**, 19 mg, 21%) and 1,2-dibenzoyl-3-methylnapththalene (**9b** 89 mg, 42%) as a yellow solid, mp. 145 °C; IR (neat) ν 3060, 3022, 2962, 2924, 1666, 1596, 1449, 1265, 1232, 890, 755, 701 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.26 (3H, s, CH_3), 7.27 (4H, m), 7.41 – 7.50 (5H, m), 7.60 – 7.64 (4H, m), 7.76 (1H, s), 7.81 (1H, d, ^3J = 8.2 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 20.2 (+, CH_3), 126.0 (+, CH), 126.6 (+, CH), 127.2 (C_{quat}), 127.6 (+, CH), 128.4 (+, CH), 128.5 (+, CH), 129.8 (+, CH), 130.1(5) (+, CH), 130.2 (+, CH), 131.9 (C_{quat}), 133.6 (+, CH), 133.6(5) (+, CH), 136.3 (C_{quat}), 137.4(5) (C_{quat}), 137.5 (C_{quat}), 138.0 (C_{quat}), 198.3 (C_{quat}, CO), 198.5 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 350 (M^+, 100), 273 (M^+-C_6H_5, 75), 245 (M+-C_6H_5CO, 64), 215 (59), 202 (58), 105 (80), 77 (59). HRMS Found: 350.1307. Calcd. for $C_{25}H_{18}O_2$: 350.1307.

Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (7d) to ethyl propiolate (8c): ethyl 3-methylnaphthalene-1-carboxylate (9c) [18]. – A solution of 2-methylbenzo[*b*]thiophene *S*-oxide (**7d**, 100 mg, 0.61 mmol) and ethyl propiolate (**8c**, 180 mg, 1.83 mmol) in benzene (1 mL) was held at 80 °C for 72h. Column chromatography of the reaction mixture on silica gel (hexane/ether 5:1) gave 2-methylbenzo[*b*]thiophene (**6d**, 12 mg, 13%) and ethyl 3-methylnaphthalene-1-carboxylate (**9c**, 15 mg, 12%) as a colorless oil; IR (neat) ν 2922, 1714, 1509, 1291, 1244, 1190, 1151, 1042, 1028, 794 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.47 (3H, t, ^3J = 7.2 Hz),2.54 (3H, s, CH_3), 4.47 (2H, q, ^3J = 7.2 Hz), 7.45 – 7.54 (2H, m), 7.77 – 7.79 (2H, m), 8.02 (1H, d, ^4J = 1.6

Hz), 8.82 (1H, d, ^3J = 8.0 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 14.4 (+, CH_3), 19.4 (+, CH_3), 61.0 (-), 125.6 (+, CH), 126.2 (+, CH), 126.7 (+, CH), 127.4 (C_{quat}), 127.9 (+, CH), 129.5 (C_{quat}), 132.2 (+, CH), 134.1 (C_{quat}), 134.2 (C_{quat}), 167.7 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 214 (M^+, 38), 186 (19), 169 (75), 141 (85), 139 (49), 115 (100). HRMS Found: 214.0992. Calcd. For $C_{14}H_{14}O_2$: 214.0994.

Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (7d) to *N*-phenylmaleimide (10): 4-Methyl-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (9d) [19]. - A solution of 2-methylbenzo[*b*]thiophene *S*-oxide (**7d**, 100 mg, 0.61 mmol) and *N*-phenylmaleimide (**10**, 105 mg, 0.61 mmol) in toluene (1 mL) was held at 110 °C for 72h. The reaction mixture was concentrated *in vacuo*, and the reside was submitted to column chromatography on silica gel (hexane/ether 2:1) to give 2-methylbenzo[*b*]thiophene (**6d**, 10 mg, 11%) and 4-methyl-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (**9d**, 30 mg, 17%) as a pale yellow solid; mp. 183 – 185 °C; IR (KBr) ν 2920, 1712, 1459, 1376, 1113, 765; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.86 (3H, s, CH_3), 7.38 – 7.55 (5H, m), 7.68 (2H, m), 7.88 (1H, m), 7.96 (1H, s), 8.98 (1H, d. ^3J = 6.6 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 18.2 (CH_3), 123.4 (+, 2C), 125.1 (+, CH), 126.8 (+, 2 CH), 127.9 (+, 2 CH), 128.8 (+, CH), 129.8 (C_{quat}), 130.7 (C_{quat}), 134.1 (C_{quat}), 134.7 (C_{quat}), 136.0 (+, 2 CH), 138.2 (C_{quat}), 140.1 (C_{quat}), 174.9 (C_{quat}, CO), 175.5 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 287 (M+, 100), 259 (42), 243 (29), 139 (31). HRMS Found: 287.0946. Calcd. for $C_{19}H_{13}O_2N$: 287.0946.

Cycloaddition of 2-(4-methoxyphenyl)benzo[*b*]thiophene *S*-oxide (7b) to dimethyl acetylenedicarboxylate (8a). – A solution of 2-(4-methoxyphenyl)benzo[*b*]thiophene *S*-oxide (**7b**, 37.5 mg, 0.15 mmol) and dimethyl acetylenedicarboxylate (85 mg, 0.60 mmol) in toluene (1 mL) was heated at 110 °C for 48h. Thereafter, the solution was concentrated *in vacuo* and subjected to column chromatography on silica gel (hexane/ether 2:1) to give 2-(4-methoxyphenyl)benzo[*b*]thiophene (**6b**, 5 mg, 13%) and dimethyl 3-(4-methoxyphenyl)naphthalene-1,2-dicarboxylate (**11a**, 22 mg, 42%) as a colorless oil; IR (neat) ν 2918, 1722, 1689, 1511, 1277, 1219, 1036 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.67 (3H, s, OMe), 3.86 (CO_2Me), 4.01 (3H, s, CO_2Me), 6.96 (2H, d, ^3J = 8.6 Hz), 7.34 (2H, d, ^3J = 8.6 Hz), 7.58 (2H, m), 7.88 (1H, m), 7.92 (1H, s), 8.15 (1H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 52.5 ($CO_2\underline{Me}$), 52.9 ($CO_2\underline{Me}$), 55.3 (OCH_3), 113.8 (+, CH, 2C), 125.6 (+, CH), 127.8 (+, CH), 127.9 (+, CH), 128.3 (+, CH), 128.8 (C_{quat}), 129.6 (+, CH, 2C), 130.1 (C_{quat}), 130.9 (C_{quat}), 131.6 (+, CH), 132.5 (C_{quat}), 133.7 (C_{quat}). 136.7 (C_{quat}), 159.2 (C_{quat}), 168.2 (C_{quat}, 2C, CO); MS (EI, 70 eV) *m/z* (%) 350 (M^+, 100), 319 (24), 189 (23). HRMS Found: 350.1152. Calcd. for $C_{21}H_{18}O_5$: 350.1154.

Cycloaddition of 2-(4-nitrophenyl)benzo[*b*]thiophene *S*-oxide (7c) to dibenzoylacetylene (8b): 1,2-Dibenzoyl-3-(4-nitrophenyl)naphthalene (**11b**). – A solution of **7c** (54 mg, 0.20 mmol) and dibenzoylacetylene (**8b**, 95 mg, 0.4 mmol) in toluene (1 mL) was heated at 110 °C for 48h. Thereafter, the solvent was removed *in vacuo* and the residue was subjected to column chromatography on silica gel (ether) to give **11b** (40 mg, 44%) as a yellow solid, mp. 187 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.26 – 7.28 (4H, m), 7.41 – 7.50 (5H, m), 7.60 – 7.64 (4H, m), 7.74 (2H, d, ^3J = 8.2 Hz), 7.81 (1H, d, ^3J = 8.2 Hz), 7.95 (1H, s), 8.28 (2H, d, ^3J = 8.9 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 126.0 (+, CH), 126.6 (+, CH), 127.2 (C_{quat}), 127.6 (+, CH), 128.1 (+, 2C, CH), 128.4 (+, CH), 128.5 (+, CH), 129.8 (+, CH), 130.1(5) (+, CH), 130.2 (+, CH), 130.4 (+, 2CH), 130.8 (C_{quat}), 132.9 (C_{quat}),133.6 (+, CH), 133.6(5) (+, CH), 136.3 (C_{quat}), 137.4(5) (C_{quat}), 137.5 (C_{quat}), 138.0 (C_{quat}), 142.1 (C_{quat}), 198.3 (C_{quat}, CO), 198.5 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 457 (M^+, 44). HRMS Found: 457.1316. Calcd. for $C_{30}H_{19}O_4N$: 457.1314.

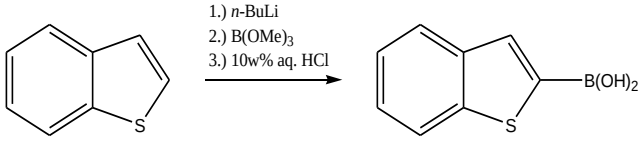
Cycloaddition of 2-(4-methoxyphenyl)benzo[*b*]thiophene *S*-oxide (7b) to *N*-phenylmaleimide (10): – A solution of **7b** (53 mg, 0.21 mmol) and *N*-phenylmaleimide (**10**, 72 mg, 0.42 mmol) in toluene (1 mL) was held at 110 °C for 48h. Thereafter, the solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ether 1:1) to give 4-(4-methoxyphenyl)-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (**12a**, 6 mg, 8%) as a pale yellow solid; mp. 141 °C; IR (KBr) ν 2924, 2850, 1714, 1512, 1378, 1263, 1181, 1030 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.86 (3H, s, OCH_3), 6.96 (2H, d, ^3J = 8.9 Hz), 7.26 – 7.89 (9H, m), 7.43 (1H, s), 7.64 (2H, d, ^3J = 7.9 Hz); MS (EI, 70 eV) *m/z* 379 (M^+, 100), 232 (9), 189 (14). HRMS Found: 379.1215. Calcd. for $C_{25}H_{17}O_3N$: 379.1208, and 3a,9b-dihydro-4-(4-methoxyphenyl)-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (**12b**, 32 mg, 40%) as a yellow solid; mp. 125 °C; IR (KBr) ν 3070, 2930, 2836, 1714, 1607, 1515, 1379, 1273, 1253, 1183, 1033, 911, 731 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.76 (3H, s, OCH_3), 4.48 (2H, s), 6.79 (1H, s), 6.87 (2H, d, ^3J = 8.9 Hz), 7.09 – 7.36 (6H, m), 7.31 (2H, d, ^3J = 7.9 Hz), 7.54 (2H, d, ^3J = 8.9 Hz), 7.69 (1H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 44.6 (+, CH), 45.1 (+, CH), 56.3 (OCH_3), 114.8 (+, CH, 2C), 125.5 (+, CH), 126.6 (C_{quat}), 127.2 (+, CH, 2C), 128.5 (+, CH, 2C), 128.8 (+, CH), 129.2 (+, CH, 2C), 129.4 (+, CH), 129.5 (+, CH), 129.9 (+, 2C, CH), 131.3 (C_{quat}), 132.4 (C_{quat}), 132.8 (C_{quat}), 133.1 (C_{quat}), 160.5 (C_{quat}), 176.3 (C_{quat}, NCO), 177.3 (Cquat, NCO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 382 (MH^+, 7), 381 (M^+, 8). HRMS Found: 382.1446. Calcd. for $C_{25}H_{20}O_3N$: 382.1443 (MH^+, FAB).

Cycloaddition of 2-(4-nitrophenyl)benzo[*b*]thiophene *S*-oxide (7c) to *N*-phenylmaleimide (10). – A solution of 2-(4-nitrophenyl)benzo[*b*]thiophene *S*-oxide (**7c**, 56 mg, 0.21 mmol) and *N*-phenylmaleimide (**10**, 72 mg, 0.42 mmol) in toluene (1 mL) was held at 110 °C for 48h. Thereafter, the solvent was evaporated *in vacuo* and the residue was submitted to column chromatography on silica gel (ether/hexane 2:1) to give 3a,9b-dihydro-4-(4-nitrophenyl)-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (**12c**, 44 mg, 52%) as a yellow solid; mp. 124 °C; IR (KBr) ν 3070, 2930, 2836, 1714, 1607, 1515, 1379, 1273, 1253, 1183, 1033, 911, 731 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.63 (2H, s), 7.06 (1H, s), 7.22 – 7.45 (8H, m), 7.80 – 7.83 (3H, m), 8.26 (2H, d, ^3J = 8.9 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 43.1 (+, CH), 43.8 (+, CH), 123.8 (+, CH, 2C), 126.1 (+, CH, 2C), 127.1 (+, CH, 2C), 128.3 (+, CH), 128.7 (+, CH), 128.9 (+, CH, C_{quat}, [2C]), 129.1 (+, CH, 2C), 129.2 (+, CH), 129.4 (+, CH), 129.7 (+, CH), 130.9 (C_{quat}), 131.5 (C_{quat}), 145.5 (C_{quat}), 147.1 (C_{quat}), 174.9 (C_{quat}, N<u>C</u>O), 175.7 (C_{quat}, N<u>C</u>O); MS (EI, 70 eV) *m/z* 397 (M^+, 5), 307 (39), 289 (17), 154 (100), 136 (53). HRMS Found: 397.1182. Calcd. for $C_{24}H_{17}O_4N_2$: 397.1188.

Cycloaddition of 3-methylthiophene *S*-oxide prepared *in situ* to *N*-phenylmaleimide (10). – To a solution of 3-methylthiophene (**13**, 980 mg, 10 mmol) and *N*-phenylmaleimide (**10**, 3.46 g, 20 mmol) in CH_2Cl_2 (2 mL) was added dropwise a solution of *m*-CPBA (4.9 g, 50w%, 15 mmol) in CH_2Cl_2 (10 mL) within 45 min. at 0 °C. After the mixture was stirred for 8h at rt, it was poured into $NaHCO_3$ (150 mL) and extracted with CH_2Cl_2 (3 X 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether) to give *N*-phenyl-5-methyl-7-thiabicyclo[2.2.1]hept-5-ene-2,3-carboximide 7-oxide (**14a**, 430 mg, 15%) as a colorless solid, mp. 165-166 °C; IR (KBr) ν 3056, 2970, 2912, 1711, 1496, 1194, 1080, 698, 624 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.93 (3H, s, CH_3), 4.12 (1H, m), 4.20 (2H, m), 4.21 (1H, m), 5.91 (1H, m), 7.13 (2H, m), 7.46 (3H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 18.2, 44.6, 45.8, 64.4, 67.8, 120.3, 126.5, 129.1, 129.3, 131.5, 140.0, 174.3, 174.5; MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 288 (MH^+, 81). HRMS Found: 288.0688. Calcd. for $C_{15}H_{13}NO_3S$: 288.0694 (MH^+).

Cycloaddition of 2,3,4-tribromo-4-methylthiophene *S*-oxide prepared *in situ* to *N*-phenylmaleimide (10). – A mixture of 2,3,4-tribromo-4-methylthiophene (**15**, 1.10 g, 3.3 mmol), *N*-phenylmaleimide (1.14 g, 6.6 mmol) and *m*-CPBA (1.70 g, 4.9 mmol) in CH_2Cl_2 (20 mL) was heated under reflux for 46h. Thereafter, the cooled reaction mixture was poured into aq. Na_2CO_3 (50 mL) and extracted with ether (2 X 20 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Addition of ether (20 mL) led to a precipitation (150 mg), which was filtered off. The residue was subjected to column chromatography on silica gel (hexane/ether 5:1 → hexane/ether 2.5:1) to give 3,4,5-tribromo-6-methylphthalimide (**14b**, 280 mg, 18%) as colorless needles, mp. 196-198 °C; IR (KBr) ν 1718, 1503, 1385, 1283, 1124, 750, 686 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.92 (3H, s, CH_3), 7.38 – 7.55 (5H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 19.4, 120.0, 126.7, 128.5, 128.8, 129.2, 129.2[5], 131.1, 137.0, 140.0, 141.4, 163.3, 163.9; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 476 ([$^{81}Br_3$]MH^+, 31), 474 ([$^{81}Br_2{}^{79}Br$]MH+, 100), 472 ([$^{81}Br^{79}Br_2$]MH^+, 95), 470 ([$^{79}Br_3$]MH^+, 32), 448 ([$^{81}Br_3$]MH^+-CO, 9), 446 ([$^{81}Br_2{}^{79}Br$]MH^+-CO, 28), 444 ([$^{81}Br^{79}Br_2$]MH^+-CO, 27), 442 ([$^{79}Br_3$]MH^+-CO, 9), 430 ([$^{81}Br_2{}^{79}Br$]MH^+-CO-CH_2, 11), 426 [$^{81}Br^{79}Br_2$]MH^+-$COCH_2$, 11), 367 ([$^{81}Br_2$]MH^+-CO-HBr, 6), 365 ([$^{81}Br^{79}Br$]MH^+-CO-HBr, 11), 363 ([$^{79}Br_2$]MH^+-CO-HBr, 6), and *N*-phenyl-1,4,5-tribromo-6-methyl-7-thiabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide 7-oxide (**14c**, 30 mg, 2%) as colorless crystals, mp. 206-207 °C; IR (KBr) ν 3066, 2982, 2924, 2852, 1711, 1498, 1381, 1195, 1116, 1097, 912, 729, 694 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.94 (3H, s, CH_3), 3.94 (1H, d, ^3J = 8.0 Hz), 3.94 (1H, d, ^3J = 8.0 Hz), 7.17 (3H, m), 7.46 (3H, m); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 15.6, 51.1, 53.4, 76.5, 79.8, 123.5, 125.0, 126.5, 128.3, 136.2, 142.3, 169.8, 171.0; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 528 [$^{81}Br_3$]MH^+, 1), 526 ([$^{81}Br_2{}^{79}Br$]MH^+, 3), 524 ([$^{81}Br^{79}Br_2$]MH^+, 3), 522 ([^{79}Br]$_3MH^+$, 1).

III. Results and Discussion

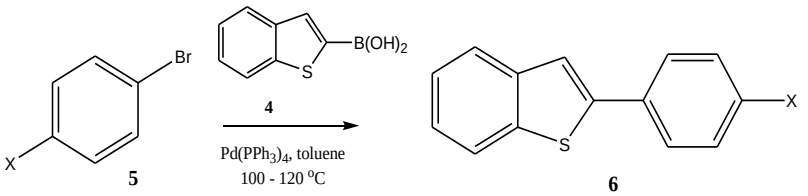


1 **4** (77%)

Scheme 1. Preparation of benzo[*b*]thienyl-2-boronic acid (**4**)

2-Substituted benzo[*b*]thiophenes **6** were synthesized by Suzuki-Miyaura reaction of benzo[*b*]thienyl-2-boronic acid (**4**) and bromoarenes **5** (Scheme 2). The preparation of benzo[*b*]thiophene *S*-oxides **7** from the respective benzo[b]thiophenes **6** followed an established route. Mostly, benzo[*b*]thiophene *S*-oxides have been prepared

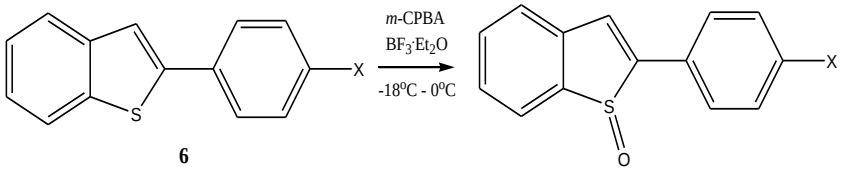
from benzo[*b*]thiophenes by oxidation, where it is important to avoid over-oxidation to the respective benzo[*b*]thiophene *S*,*S*-dioxides. This can be achieved by using the oxidizing reagents H_2O_2 - CF_3CO_2H [4,20], H_2O_2 – AcOH [6], H_2O_2 – SeO_2[6], dimethyldioxirane (DMD, albeit in low yields), oxaziridines [6], Bu^tOCl – MeOH [21,22] or by using enzymatic oxidation (*P. putida* UV4) [23]. In the present case, the benzo[*b*]thiophenes **6** were oxidized to the benzo[*b*]thiophene *S*-oxides **7** with *m*-CPBA-$BF_3{\cdot}Et_2O$ (Scheme 3), under conditions also used by our group to oxidize thiophenes to thiophene *S*-oxides [24,25]. 2-Methylbenzo[*b*]thiophene *S*-oxide (**7d**), 2-(4-nitrophenyl)benzo[*b*]thiophene *S*-oxide (**7c**), 2-(4-tolylbenzo[*b*]thiophene *S*-oxide (**7a**) and 2-(4-methoxyphenyl)benzo[*b*]thiophene *S*-oxide (**7b**) could be obtained in acceptable yield. The benzo[*b*]thiophene *S*-oxides **7** are solids and stable over an extended period of time. They should kept away from light, because as is in the case of thiophene *S*-oxides [26], photoirradiation can lead to deoxygenation to revert the compounds back to the benzo[*b*]thiophenes **6**.



X = CH_3 (**5a**), OCH_3 (**5b**), NO_2 (**5c**)

X = CH_3 (**6a**, 15%), OCH_3 (**6b**, 46%), NO_2 (**6c**, 73%)

Scheme 2. Preparation of 2-arylbenzo[*b*]thiophenes **6** by Suzuki-Miyaura reaction

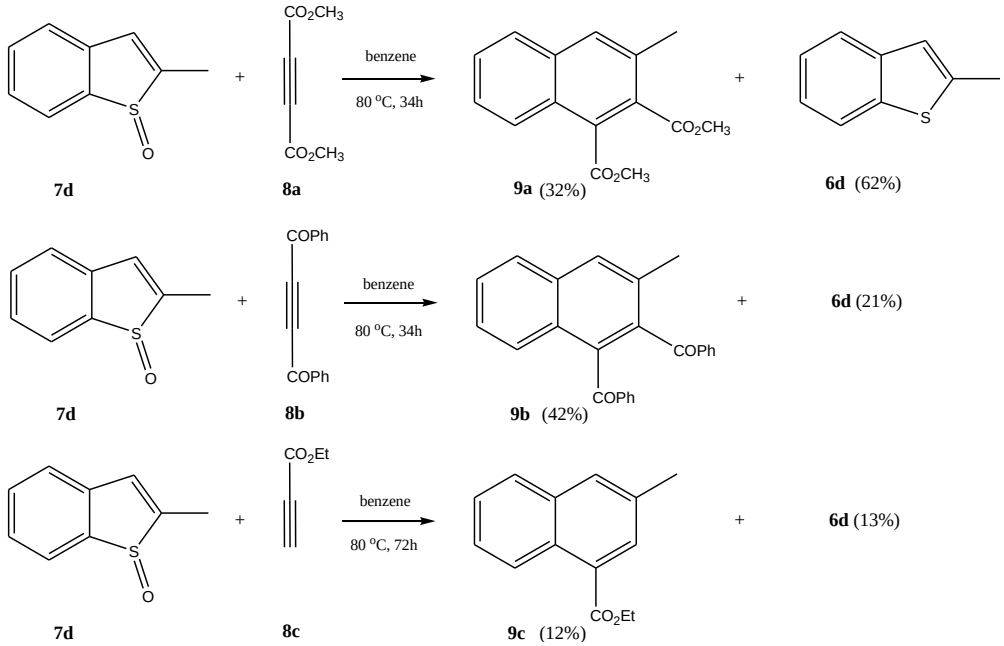


X = CH_3 (**6a**), OCH_3 (**6b**), NO_2 (**6c**)

X = CH_3 (**7a**, 77%), OCH_3 (**7b**, 59%), NO_2 (**7c**, 59%)

Scheme3. Oxidation 2-arylbenzo[*b*]thiophenes **6** to 2-arylbenzo[*b*]thiophene S-oxides **7**

The benzo[*b*]thiophene *S*-oxides **7**, thus prepared, were subjected to formal Diels-Alder type [4+2]-cycloaddition reactions with the electron-poor alkynes dibenzoylacetylene (**8b**), dimethyl acetylenedicarboxylate (**8b**), and ethylpropioplate (**8c**) and with alkene *N*-phenylmaleimide (**10**). The reaction with alkynes leads to substituted naphthalenes **9**, the reaction with N-phenylmaleimide (**10**) to either 3a,9b-dihydro-2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-diones (**12b**/**12c**) alone or in a mixture of 2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-diones such as **12a**, albeit only in fair yield. Here, the driving force of the extrusion of the SO-bridge formed in the primary cycloadduct is the reformation of the aromatic system in **12**. This stands in juxtaposition to the cycloaddition of other-wise substituted thiophene *S*-oxides where the 7-thiabicyclo[2.2.1]heptane *S*-oxides, eg/ **14a** and **14c**, formed as primary cycloadducts, are quite stable [24,25]. Two formerly unpublished examples are shown here, albeit where the thiophene *S*-oxide is produced *in situ*. Therefore, the yields of the cycloadducts are low, however, it can be seen that in the case of the thiophene *S*-oxides electron withdrawing substituents seem to facilitate SO extrusion from the primary cycloadduct. For comparison, benzo[*b*]thiophene *S*,*S*-dioxides such as the benzo[*b*]thiophene *S*,*S*-dioxide are worse dienes, preferring their role as enes in Diels-Alder- [9,27] and [3+2]-cycloaddition reactions [28].

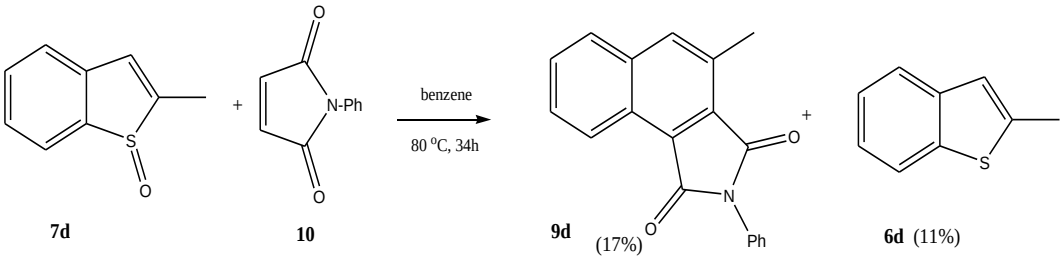


7d **8a** **9a** (32%) **6d** (62%)

7d **8b** **9b** (42%) **6d** (21%)

7d **8c** **9c** (12%) **6d** (13%)

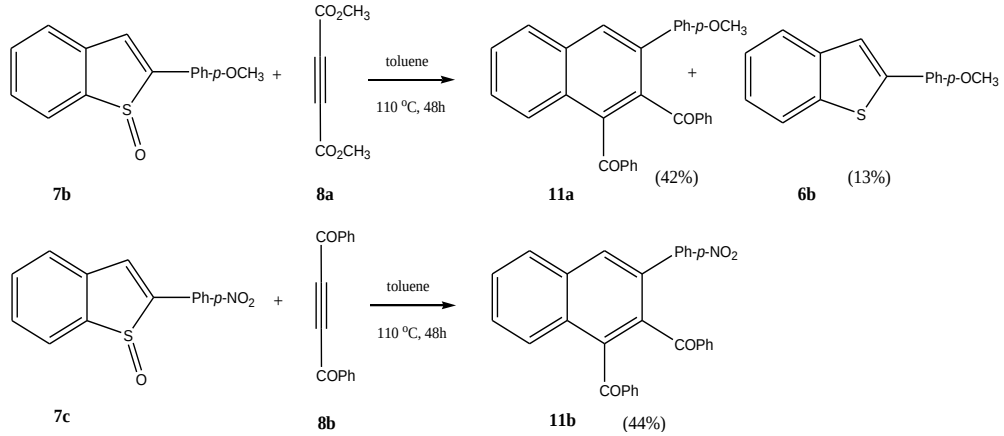
Scheme4. Cycloaddition of 2-methylbenzo[*b*]thiophene *S*-oxide (**7d**) to alkynes **8**



7d **10** **9d** (17%) **6d** (11%)

Scheme5. Cycloaddition of 2-methylbenzo[*b*]hiophene *S*-oxide (**7d**) with N-phenylmaleimide (**10**)

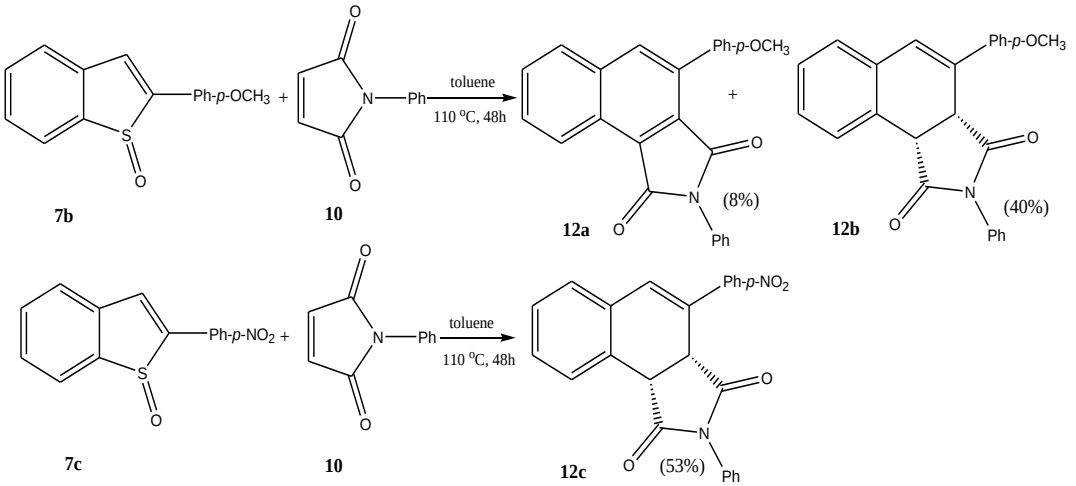
Lastly, in the aromatization of **12b** to **12a** the released "SO" species may play a role [29] to abstract two H-atoms to form the equally transient and reasonably reactive "H_2SO" [30]. The yields in the cycloaddition reactions above are fair, with the deoxygenated benzo[*b*]thiophene often in evidence. In the case of the reaction of **7d** with ethyl propiolate (**8c**), only one regioisomeric cycloadduct could be detected, namely ethyl 3-methylnaphthalene-1-carboxylate (**9c**), the identity could be ascertained by comparison in the literature [18], with **9c** prepared via a different route. One reason for the regioselectivity could be secondary pi-pi interactions between the ester functionality of the ethyl propiolate and the aromatic system of the benzo[*b*]thiophene *S*-oxide.



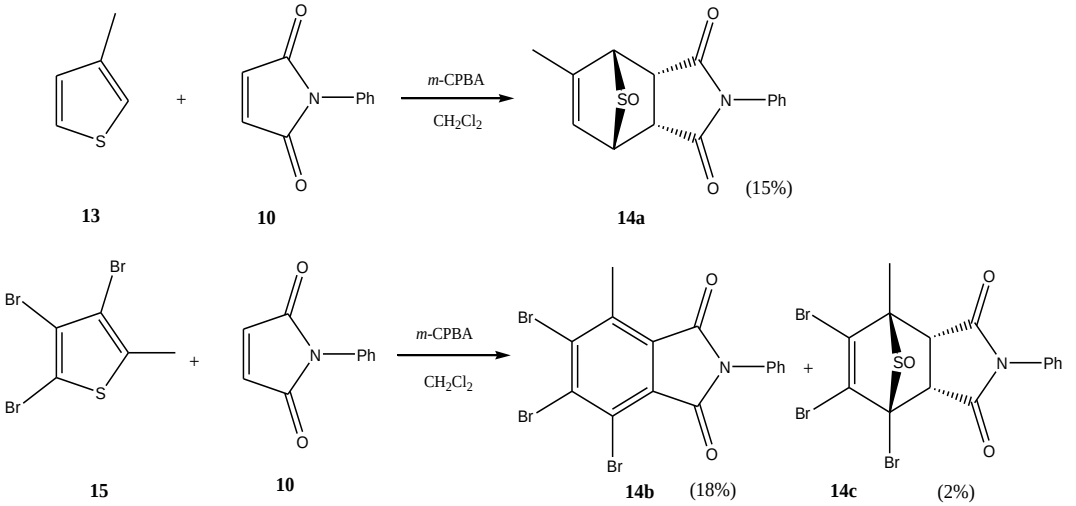
7b **8a** **11a** (42%) **6b** (13%)

7c **8b** **11b** (44%)

Scheme6. Cycloaddition of 2-arylbenzo[*b*]thiophene *S*-oxides **7** to alkynes **8**



Scheme7. Cycloaddition of 2-arylbenzo[*b*]thiophene *S*-oxides **7** to *N*-phenylmaleimide **(10)**



Schem8. Cycloaddition of thiophene *S*-oxides prepared in situ to *N*-phenylmaleimide (**10**).

IV. Conclusion

A number of 2-substituted benzo[*b*]thiophenes **6** were prepared by Suzuki-Miyaura reaction, with benzo[*b*]thienyl-2-boronic acid (**4**) as reagent. The 2-substituted benzo[*b*]thiophenes **6** were oxidized to the respective benzo[*b*]thiophene *S*-oxides **7** with *m*-CPBA·BF_3. Formal [4+2]-cycloaddition of the benzo[*b*]thiophene *S*-oxides **7** with alkynes **8** and with *N*-phenylmaleimide (**10**) gave substituted naphthalenes **9** and 2-phenyl-1*H*-benz[*e*]isoindole-1,3(2*H*)-diones **12**, respectively.

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