Unsymmetrical Diaryl Sulfones Through Palladium Catalyzed Coupling of Aryl Boronic Acids and Arylsulfonyl Chlorides

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Supporting Information

General considerations: All reactions were carried out in acetone : water (3:1) under a nitrogen atmosphere. Palladium (II) chloride was purchased from Aldrich. Requisite boronic acids were prepared via literature procedures¹ or purchased from Across. All other chemicals were commercially available and were used without further purification. All solids were weighed in the air. All spectra were taken in CDCl₃. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ac 300 F (300 MHz) instrument with tetramethylsilane (TMS) as an internal standard. All yields reported in this paper refer to direct isolated yields of products estimated to be > 99% pure as determined by ¹H NMR and therefore further purification of products was not carried out.

General Procedure for the palladium-catalyzed coupling of Aryl/Heteroaryl Boronic Acids with Arylsulfonyl chlorides.

To a mixture of aryl/heteroaryl boronic acid (1 mmol), aryl sulfonyl chloride (1 mmol), K₂CO₃ (2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol) was added and stirring was continued at room temperature under N₂ atmosphere. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. Distilled water (10 ml) was added in the reaction mixture and the product was extracted with petroleum ether and washed with water (2 x 10 ml). The removal of solvent under reduced pressure yielded the product, which was found to be pure (TLC and ¹H NMR) and there was no need of further purification.

¹ (a) Brown, H.C.; Bhat, N.G.; Somayaji, R. *Organometallics*, **1992**, *11*, 652 (b) Brown, H.C.; Scouten, C.G.; Liotta, R. *J.Am.Chem.Soc.* **1979**, *101*, 96.

Diphenyl sulfone (Table 2, Entry 1). General Procedure was followed using phenyl boronic acid (121 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (206 mg, 94 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 127 °C (lit.² 128-129 °C); IR (KBr) : 1146, 1389, 1600, 2946, 3140 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.4–7.5 (m, 6 H, Ar-H), 7.75-7.82 (m, 4 H, Ar-H); Anal. Calcd. for $C_{12}H_{10}SO_2$ (218.27) : C, 66.03; H, 4.62; S, 14.69; Found : C, 66.07; H, 4.48; S, 14.52 %.

p-Methoxyphenyl phenyl sulfone (Table 2, Entry 2). General Procedure was followed using p-methoxyphenyl boronic acid (152 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (245 mg, 98 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 114 °C, IR (KBr) : 1182, 1273, 1602, 2836, 2916, 2964 cm^{-1} ; 1H NMR : δ 3.82 (s, 3 H, OCH_3), 6.90 (d, 2 H, $J = 8.7$ Hz, Ar-H), 7.4 (d, 2 H, $J = 8.7$ Hz, Ar-H), 7.44-7.46 (m, 5 H, Ar-H); Anal Calcd. for $C_{13}H_{12}SO_2$ (248.30): C, 62.89; H, 4.87; S, 12.91; Found : C, 61.72; H, 4.67; S, 12.84 %.

² Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X-Q.; Noyori, R. *Tetrahedron*, **2001**, 57, 2469.

p-Benzyloxyphenyl phenyl sulfone (Table 2, Entry 3). General Procedure was followed using p-benzyloxy- phenyl boronic acid (228 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (317.5 mg, 98 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 214 °C; I.R. (KBr) : 1024, 1115, 1225, 1596, 2849, 2910 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$); δ 5.10 (s, 2 H, OCH_2), 7.02 (m, 5 H, Ar-H), 7.1 (d, 2 H, $J = 7.9$ Hz, Ar-H), 7.8 (d, 2 H, $J = 7.9$ Hz, Ar-H), 7.85 (m, 3 H, Ar-H), 7.92 (m, 2 H, Ar-H); Anal. Calcd. for $C_{19}H_{16}SO_3$ (324.40) : C, 70.35; H, 4.97; S, 9.88; Found : C, 70.21; H, 4.90; S, 9.72 %.

Phenyl p-tolyl sulfone (Table 2, Entry 4). General Procedure was followed using of phenyl boronic acid (121 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (227 mg, 98 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 121 °C (lit.³ 119-122 °C); IR (KBr) : 1091, 1340, 1596, 2922, 3092 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$); δ 2.5 (s, 3 H, Ar- CH_3), 7.2 (d, 2 H, $J=8.7$ Hz, Ar-H), 7.4-7.43 (m, 5 H, Ar-H), 7.77 (d, 2 H, $J = 8.7$ Hz, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 21.5, 127.2, 127.5, 129.7, 129.9, 132.8, 138.5, 141.5, 143.7; Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 61.21; H, 5.21; S, 13.80; Found : C, 61.11; H, 5.26; S, 13.69 %.

³ Baarschers, W. H.; *Can. J. Chem.* **1976**, 54 (19), 3056.

p-Tolyl p-methoxyphenyl sulfone (Table 2, Entry 5). General Procedure was followed using p-methoxyphenyl boronic acid (152 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (256.7 mg, 98 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 101 °C (lit.⁴ 103 °C); IR (KBr) : 1128, 1219, 1280, 1346, 1590, 2855, 2916 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.50 (s, 3 H, Ar-CH₃), 3.83 (s, 3 H, OCH₃), 6.93 (d, 2 H, J = 8.7 Hz, Ar-H), 7.43 (d, 2 H, J = 8.3 Hz, Ar-H), 7.45 (d, 2 H, J = 8.7 Hz, Ar-H), 7.82 (d, 2 H, J = 8.3 Hz, Ar-H); Anal. Calcd. for C₁₄H₁₄SO₃ (262.33) : C, 64.10; H, 5.38; S, 12.22; Found : C, 64.01; H, 5.26; S, 12.15 %.

p-Tolyl p-benzyloxyphenyl sulfone (Table 2, Entry 6). General Procedure was followed using p-benzyloxyphenyl boronic acid (228 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (327.8 mg, 97 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 201 °C; IR (KBr) : 1024, 1219, 1128, 1352, 1584, 2855, 2922 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.51 (s, 3 H, CH₃), 5.10 (s, 2 H, OCH₂), 7.05 (m, 5 H, Ar-H), 7.15 (d, 2 H, J = 8.1 Hz, Ar-H), 7.45 (d, 2 H, J = 8.0 Hz, Ar-H), 7.6 (d, 2 H, J = 8.1 Hz, Ar-H), 7.83 (d, 2 H, J = 8.0 Hz, Ar-H); Anal. Calcd. for C₂₀H₁₈SO₃ (338.42) : C, 70.98; H, 5.36; S, 9.48; Found : C, 70.81; H, 5.31; S, 9.37 %.

⁴ Proctor, T.; *J. Chem. Soc.* **1957**, 2312

Bis-p-tolyl sulfone (Table 2, Entry 7). General Procedure was followed using p-methylphenyl boronic acid (136 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (236.1 mg, 96 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 158-159 °C (lit.⁵158); IR (KBr) : 1158, 1315, 2920 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : 2.38 (s, 6 H), 7.30 (d, 4 H, J = 8.5 Hz), 7.7 (d, 4 H, J = 8.5 Hz); Anal. Calcd. for $C_{14}H_{14}O_2S$ (246.32) : C, 68.26; H, 5.72; S, 13.01; Found : C, 68.23; H, 5.69; S, 13.01 %.

o-Methylphenyl phenyl sulfone (Table 3, Entry 1). General Procedure was followed using o-methylphenyl boronic acid (136 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (218 mg, 94 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 125-127 °C; IR (KBr) : 1150, 1325, 2925 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 3.3 (s, 3 H), 7.2-7.4 (m, 4 H) 7.65-7.75 (m, 5H, Ar-H); Anal Calcd. for $C_{13}H_{12}O_2S$ (232.30) : C, 67.21; H, 5.20; S, 13.80; Found : C, 67.20; H, 5.19; S, 13.78 %.

⁵ Meyer, H. Ann. **1923**, 433, 336.

o-Methylphenyl p-tolyl sulfone (Table 3, Entry 2). General Procedure was followed using o-methylphenyl boronic acid (136 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (228.7 mg, 93 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 105-107 °C; IR (KBr) : 1158, 1310, 2930 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.30 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 7.25-7.35 (m, 4 H, Ar-H), 7.70 (d, J = 8.1 Hz, 2 H, Ar-H), 7.85 (d, J = 8.1 Hz, 2 H, Ar-H); Anal. Calcd. for $C_{14}H_{14}O_2S$ (246.32) : C, 68.26; H, 5.72; S, 13.01; Found : C, 68.24; H, 5.70; S, 13.00 %.

o-Methoxyphenyl phenyl sulfone (Table 3, Entry 3). General Procedure was followed using o-methoxyphenyl boronic acid (152 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (216.5 mg, 91 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 75 °C; IR (KBr): 1152, 1315, 2935 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 3.80 (s, 3 H, OCH_3), 7.1-7.25 (s, 4 H, Ar-H), 7.4-7.6 (m, 5 H, Ar-H), Anal Calcd. for $C_{13}H_{12}O_3S$ (262.33); C, 62.89; H, 4.87; S, 12.91; Found: C, 62.69; H, 4.72; S, 12.80 %.

o-Methoxyphenyl p-tolyl sulfone (Table 3, entry 4). General Procedure was followed using o-methoxyphenyl boronic acid (152 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (216.4 mg, 88 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 80 °C; IR (KBr): 1151, 1318, 2938 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.32 (s, 3 H, Ar- CH_3), 3.84 (s, 3 H, OCH_3), 7.05-7.12 (m, 4 H, Ar-H), 7.4 (d, 2 H, $J = 8.3$ Hz, Ar-H), 7.8 (d, 2 H, $J = 8.3$ Hz, Ar-H); Anal Calcd. for $C_{14}H_{14}O_3S$ (262.33) : C, 64.10; H, 5.38; S, 12.22; Found : C, 64.00; H, 5.24; S, 12.08 %.

o-Fluorophenyl phenyl sulfone (Table 3, Entry 5). General Procedure was followed using o-fluorophenyl boronic acid (138 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone: water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (200.6 mg, 85 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 92-94 °C; IR (KBr): 1155, 1320, 2927 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 7.1-7.2 (m, 4 H, Ar-H), 7.4-7.5 (m, 5 H, Ar-H), Anal Calcd. for $C_{12}H_9FO_2S$ (236.26) : C, 61.00; H, 3.83; F, 8.04; S, 13.57; Found : C, 61.00; H, 3.82; F, 8.00; S, 13.55 %.

o-Fluorophenyl p-tolyl sulfone (Table 3, Entry 6). General Procedure was followed using o-fluorophenyl boronic acid (138 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium

chloride (3 mg, 0.016 mmol). The title compound (225 mg, 90 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 78-81 °C; IR (KBr): 1148, 1323, 2925 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.31 (s, 3 H, Ar-CH₃), 7.51-7.22 (m, 4 H, Ar-H), 7.6 (d, 2 H, J = 8.2 Hz, Ar-H), 7.83 (d, 2 H, J = 8.2 Hz, Ar-H); Anal Calcd. for C₁₃H₁₁FO₂S (250.29) : C, 62.38; H, 4.42; F, 7.59; S, 12.81; Found : C, 62.37; H, 4.40; F, 7.56; S, 12.77 %.

(5-Phenyl sulfonyl)-2-furfuraldehyde (Table 3, Entry 7). General Procedure was followed using 2-furfuraldehyde-5-boronic acid (140 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (193.5 mg, 82 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 130 °C; IR (KBr): 1150, 1320, 1690, 2322, 2720 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 7.15 (m, 5 H, Ar-H), 7.82 (d, 1 H, J = 7.2 Hz, Ar-H), 7.95 (d, 1 H, J = 7.2 Hz, Ar-H), 9.2 (s, 1 H, -CHO); Anal Calcd. for C₁₁H₈O₄S (236.24) : C, 55.92; H, 3.41; S, 13.57; Found : C, 55.90; H, 3.38; S, 13.51 %.

(5-Tolyl-4-sulfonyl)-2-furfuraldehyde (Table 3, entry 8). General Procedure was followed using 2-furfuraldehyde-5-boronic acid (140 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (200 mg, 80 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 155 °C; IR (KBr): 1153, 1326, 1692, 2328, 2725 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.34 (s, 3 H, Ar-CH₃), 7.25 (d, 2 H, J = 8.5 Hz, Ar-H), 7.40 (d, 2 H, J = 8.5 Hz, Ar-H), 7.85 (d, 1 H, J = 7.3 Hz, Ar-H), 7.97 (d, 1 H, J = 7.3 Hz, Ar-H), 9.25 (s, 1 H, -CHO); Anal Calcd. for C₁₂H₁₀O₄S (250.27) : C, 57.58; H, 4.02; S, 12.81; Found : C, 57.49; H, 4.00; S, 12.80 %.

2-(Phenylsulfonyl)-thiophene (Table 3 entry 9). General Procedure was followed using 2-thiophene boronic acid (129mg, 1 mmol), phenyl sulfonyl chloride (190mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (190.4 mg, 85 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 90 °C; IR (KBr): 1150, 1320, 2320 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 7.20 (dd, J = 5.0, 3.6 Hz, 1 H, Ar-H), 7.43 (m, 5 H, Ar-H), 7.9 (dd, J = 5.0, 1.4 Hz, 1 H, Ar-H), 8.2 (dd, J = 3.6, 1.4, 1 H, Ar-H); Anal. Calcd. for $C_{10}H_8O_2S_2$ (224.30) : C, 53.54; H, 3.59; S, 28.59; Found : C, 53.54; H, 3.56; S, 28.57 %

2-(Toluene-4-sulfonyl)-thiophene (Table 3 entry 10). General Procedure was followed using 2-thiophene boronic acid (129mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (207.6 mg, 87 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 118-120 °C (lit.⁶ 113-114 °C); IR (KBr): 1159, 1330, 2940 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.42 (s, 3 H, Ar- CH_3), 7.20 (dd, J = 5.1, 3.8 Hz, 1 H, Ar-H), 7.44 (d, J = 8.1 Hz, 2 H, Ar-H), 7.75 (dd, J = 3.8, 1.5 Hz, 1 H, Ar-H), 7.93 (d, J = 8.1 Hz, 2 H, Ar-H), 8.05 (dd, J = 5.1, 1.5 Hz, 1 H, Ar-H); Anal Calcd. for $C_{11}H_{10}O_2S_2$ (238.33) : C, 55.43; H, 4.22; S, 26.90; Found : C, 55.41; H, 4.22; S, 26.89 %.

⁶ Voronkor et al : *Chem. Heterocycle. Compd. (Eng. Trans)*, **1975**, *11*, 1131.

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Supporting Information

General considerations: All reactions were carried out in acetone : water (3:1) under a nitrogen atmosphere. Palladium (II) chloride was purchased from Aldrich. Requisite boronic acids were prepared via literature procedures¹ or purchased from Across. All other chemicals were commercially available and were used without further purification. All solids were weighed in the air. All spectra were taken in CDCl₃. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ac 300 F (300 MHz) instrument with tetramethylsilane (TMS) as an internal standard. All yields reported in this paper refer to direct isolated yields of products estimated to be > 99% pure as determined by ¹H NMR and therefore further purification of products was not carried out.

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Diphenyl Sulfone (Table 2, Entry 1). General Procedure was followed using phenyl boronic acid (121mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0°C, palladium chloride (3 mg, 0.016 mmol). The title compound (206 mg, 94 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60°C). M.P. 127°C (lit.² 128-129°C); IR (KBr) : 1146, 1389, 1600, 2946, 3140 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.4–7.5 (m, 6 H, Ar-H), 7.75-7.82 (m, 4 H, Ar-H); Anal. Calcd. for $C_{12}H_{10}SO_2$ (218.27) : C, 66.03; H, 4.62; S, 14.69; Found : C, 66.07; H, 4.48; S, 14.52 %.

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Phenyl p-tolyl sulfone (Table 2, Entry 4). General Procedure was followed using of phenyl boronic acid (121 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0°C, palladium chloride (3 mg, 0.016 mmol). The title compound (227 mg, 98 %) was obtained as a white solid in pure form after extraction (40-60°C). M.P. 121 °C (lit.³ 119-122°C); IR (KBr) : 1091, 1340, 1596, 2922, 3092 cm⁻¹; ¹H NMR (300 MHz, CDCl₃); δ 2.5 (s, 3 H, Ar-CH₃), 6.95 (d, 2 H, J=8.7 Hz, Ar-H), 7.4-7.43 (m, 5 H, Ar-H), 7.47 (d, 2 H, J = 8.7 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃); δ 21.5, 127.2, 127.5, 129.7, 129.9, 132.8, 138.5, 141.5, 143.7; Anal. Calcd. for C₁₃H₁₂O₂S : C, 61.21; H, 5.21; S, 13.80; Found : C, 61.11; H, 5.26; S, 13.69 %.

³ Baarschers, W. H.; *Can. J. Chem.* **1976**, 54 (19), 3056

p-Tolyl p-methoxyphenyl sulfone (Table 2, Entry 5). General Procedure was followed using p-methoxyphenyl boronic acid (152 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (256.7 mg, 98 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 101 °C (lit.⁴103 °C); IR (KBr) : 1128, 1219, 1280, 1346, 1590, 2855, 2916 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.50 (s, 3 H, Ar-CH₃), 3.83 (s, 3 H, OCH₃), 6.93 (d, 2 H, J = 8.7 Hz, Ar-H), 7.43 (d, 2 H, J = 8.3 Hz, Ar-H), 7.45 (d, 2 H, J = 8.7 Hz, Ar-H), 7.82 (d, 2 H, J = 8.3 Hz, Ar-H); Anal. Calcd. for C₁₄H₁₄SO₃ (262.33) : C, 64.10; H, 5.38; S, 12.22; Found : C, 64.01; H, 5.26; S, 12.15 %.

p-Tolyl p-benzyloxyphenyl sulfone (Table 2, Entry 6). General Procedure was followed using p-benzyloxyphenyl boronic acid (228 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C ,palladium chloride (3 mg, 0.016 mmol). The title compound (327.8 mg, 97 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 201 °C; IR (KBr) : 1024, 1219, 1128, 1352, 1584, 2855, 2922 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.51(s, 3 H, CH₃), 5.10 (s, 2 H, OCH₂), 7.05 (m, 5 H, Ar-H), 7.15 (d, 2 H, J= 8.1 Hz, Ar-H), 7.45 (d, 2 H, J = 8.0 Hz, Ar-H), 7.6 (d, 2 H, J= 8.1 Hz, Ar-H), 7.83 (d, 2 H, J= 8.0 Hz, Ar-H); Anal. Calcd. for C₂₀H₁₈SO₃ (338.42) : C, 70.98; H, 5.36; S, 9.48; Found : C, 70.81; H, 5.31; S, 9.37 %.

⁴ Proctor, T.; *J. Chem. Soc.* **1957**, 2312

Bis-p-tolyl sulfone (Table 2, Entry 7). General Procedure was followed using p-methylphenyl boronic acid (136 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (236.1 mg, 96 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 158-159 °C (lit.⁵158); IR (KBr) : 1158, 1315, 2920 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : 2.38 (s, 6 H), 7.30 (d, 4 H, J = 8.5 Hz), 7.7 (d, 4 H, J = 8.5 Hz); Anal. Calcd. for $C_{14}H_{14}O_2S$ (246.32) : C, 68.26; H, 5.72; S, 13.01; Found : C, 68.23; H, 5.69; S, 13.01 %.

o-Methylphenyl phenyl sulfone (Table 3, Entry 1). General Procedure was followed using o-methylphenyl boronic acid (136 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (218 mg, 94 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 125-127 °C; IR (KBr) : 1150, 1325, 2925 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 3.3 (s, 3 H), 7.2-7.4 (m, 4 H) 7.65-7.75 (m, 5H, Ar-H); Anal Calcd. for $C_{13}H_{12}O_2S$ (232.30) : C, 67.21; H, 5.20; S, 13.80; Found : C, 67.20; H, 5.19; S, 13.78 %.

⁵ Meyer, H. Ann. **1923**, 433, 336.

o-Methylphenyl p-tolyl sulfone (Table 3, Entry 2). General Procedure was followed using o-methylphenyl boronic acid (136 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (228.7 mg, 93 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 105-107 °C; IR (KBr) : 1158, 1310, 2930 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.30 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 7.25-7.35 (m, 4 H, Ar-H), 7.70 (d, J = 8.1 Hz, 2 H, Ar-H), 7.85 (d, J = 8.1 Hz, 2 H, Ar-H); Anal. Calcd. for $C_{14}H_{14}O_2S$ (246.32) : C, 68.26; H, 5.72; S, 13.01; Found : C, 68.24; H, 5.70; S, 13.00 %.

o-Methoxyphenyl phenyl sulfone (Table 3, Entry 3). General Procedure was followed using o-methoxyphenyl boronic acid (152 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (216.5 mg, 91 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 75 °C; IR (KBr): 1152, 1315, 2935 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 3.80 (s, 3 H, OCH_3), 7.1-7.25 (s, 4 H, Ar-H), 7.4-7.6 (m, 5 H, Ar-H), Anal Calcd. for $C_{13}H_{12}O_3S$ (262.33); C, 62.89; H, 4.87; S, 12.91; Found: C, 62.69; H, 4.72; S, 12.80 %.

o-Methoxyphenyl p-tolyl sulfone (Table 3, entry 4). General Procedure was followed using o-methoxyphenyl boronic acid (152 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (216.4 mg, 88 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 80 °C; IR (KBr): 1151, 1318, 2938 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.32 (s, 3 H, Ar- CH_3), 3.84 (s, 3 H, OCH_3), 7.05-7.12 (m, 4 H, Ar-H), 7.4 (d, 2 H, $J = 8.3$ Hz, Ar-H), 7.8 (d, 2 H, $J = 8.3$ Hz, Ar-H); Anal Calcd. for $C_{14}H_{14}O_3S$ (262.33) : C, 64.10; H, 5.38; S, 12.22; Found : C, 64.00; H, 5.24; S, 12.08 %.

o-Fluorophenyl phenyl sulfone (Table 3, Entry 5). General Procedure was followed using o-fluorophenyl boronic acid (138 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone: water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (200.6 mg, 85 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 92-94 °C; IR (KBr): 1155, 1320, 2927 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 7.1-7.2 (m, 4 H, Ar-H), 7.4-7.5 (m, 5 H, Ar-H), Anal Calcd. for $C_{12}H_9FO_2S$ (236.26) : C, 61.00; H, 3.83; F, 8.04; S, 13.57; Found : C, 61.00; H, 3.82; F, 8.00; S, 13.55 %.

o-Fluorophenyl p-tolyl sulfone (Table 3, Entry 6). General Procedure was followed using o-fluorophenyl boronic acid (138 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium

chloride (3 mg, 0.016 mmol). The title compound (225 mg, 90 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 78-81 °C; IR (KBr): 1148, 1323, 2925 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.31 (s, 3 H, Ar-CH₃), 7.51-7.22 (m, 4 H, Ar-H), 7.6 (d, 2 H, J = 8.2 Hz, Ar-H), 7.83 (d, 2 H, J = 8.2 Hz, Ar-H); Anal Calcd. for C₁₃H₁₁FO₂S (250.29) : C, 62.38; H, 4.42; F, 7.59; S, 12.81; Found : C, 62.37; H, 4.40; F, 7.56; S, 12.77 %.

(5-Phenyl sulfonyl)-2-furfuraldehyde (Table 3, Entry 7). General Procedure was followed using 2-furfuraldehyde-5-boronic acid (140 mg, 1 mmol), phenyl sulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (193.5 mg, 82 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 130 °C; IR (KBr): 1150, 1320, 1690, 2322, 2720 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 7.15 (m, 5 H, Ar-H), 7.82 (d, 1 H, J = 7.2 Hz, Ar-H), 7.95 (d, 1 H, J = 7.2 Hz, Ar-H), 9.2 (s, 1 H, -CHO); Anal Calcd. for C₁₁H₈O₄S (236.24) : C, 55.92; H, 3.41; S, 13.57; Found : C, 55.90; H, 3.38; S, 13.51 %.

(5-Tolyl-4-sulfonyl)-2-furfuraldehyde (Table 3, entry 8). General Procedure was followed using 2-furfuraldehyde-5-boronic acid (140 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K₂CO₃ (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (200 mg, 80 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 155 °C; IR (KBr): 1153, 1326, 1692, 2328, 2725 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) : δ 2.34 (s, 3 H, CH₃), 7.25 (d, 2 H, J = 8.5 Hz, Ar-H), 7.40 (d, 2 H, J = 8.5 Hz, Ar-H), 7.85 (d, 1 H, J = 7.3 Hz, Ar-H), 7.97 (d, 1 H, J = 7.3 Hz, Ar-H), 9.25 (s, 1 H, -CHO); Anal Calcd. for C₁₂H₁₀O₄S (250.27) : C, 57.58; H, 4.02; S, 12.81; Found : C, 57.49; H, 4.00; S, 12.80 %.

2-(Phenylsulfonyl)-thiophene (Table 3 entry 9). General Procedure was followed using 2-thiophene boronic acid (129 mg, 1 mmol), phenyl sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (190.4 mg, 85 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 90 °C; IR (KBr): 1150, 1320, 2320 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 7.20 (dd, J = 5.0, 3.6 Hz, 1 H, Ar-H), 7.43 (m, 5 H, Ar-H), 7.9 (dd, J = 5.0, 1.4 Hz, 1 H, Ar-H), 8.2 (dd, J = 3.6, 1.4 Hz, 1 H, Ar-H); Anal Calcd. for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}_2$ (224.30) : C, 53.54; H, 3.59; S, 28.59; Found : C, 53.54; H, 3.56; S, 28.57 %

2-(Toluene-4-sulfonyl)thiophene (Table 3 entry 10). General Procedure was followed using 2-thiophene boronic acid (129 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0°C, palladium chloride (3 mg, 0.016 mmol). The title compound (207.6 mg, 87 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60°C). M.P. 118-120 °C (lit.⁶ 113-114 °C); IR (KBr): 1159, 1330, 2940 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) : δ 2.42 (s, 3 H, Ar- CH_3), 7.20 (dd, J = 5.1, 3.8 Hz, 1 H, Ar-H), 7.44 (d, J = 8.1 Hz, 2 H, Ar-H), 7.75 (dd, J = 3.8, 1.5 Hz, 1 H, Ar-H), 7.93 (d, J = 8.1 Hz, 2 H, Ar-H), 8.05 (dd, J = 5.1, 1.5 Hz, 1 H, Ar-H); Anal Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}_2$ (238.33) : C, 55.43; H, 4.22; S, 26.90; Found : C, 55.41; H, 4.22; S, 26.89 %.

⁶ Voronkor et al : *Chem. Heterocycle. Compd. (Eng. Trans)*, **1975**, *11*, 1131.

Phenyl 3-pyridyl sulfone (Table 3 entry 11). General Procedure was followed using 3-pyridine boronic acid (123 mg, 1 mmol), phenylsulfonyl chloride (176 mg, 0.127 ml, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (192.7 mg, 88 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 125 °C; IR (KBr): 1148, 1335, 2930 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 7.6 (m, 5 H, Ar-H), 7.85 (m, 4 H, Ar-H), Anal. Calcd. for $C_{11}H_9O_2S$ (219.26) : C, 60.26; H, 4.13; S, 14.62; N, 6.38; Found : C, 60.17; H, 4.13; S, 14.70; N, 6.35 %.

3-Pyridyl-p-tolyl sulfone (Table 3 entry 12). General Procedure was followed using 3-pyridine boronic acid (123 mg, 1 mmol), p-toluene sulfonyl chloride (190 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) in acetone : water (3:1, 10 ml) at 0 °C, palladium chloride (3 mg, 0.016 mmol). The title compound (191 mg, 82 %) was obtained as a white solid in pure form after extraction with petroleum ether (40-60 °C). M.P. 160 °C; IR (KBr): 1157, 1325, 2325 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) : δ 2.35 (s, 3 H, Ar- CH_3), 7.4 (d, J = 8.4 Hz, 2 H, Ar-H), 7.75 (m, 4 H, Ar-H), 7.92 (d, J = 8.4 Hz, 2 H, Ar-H) Anal. calcd. for $C_{12}H_{11}NO_2S$ (233.28) : C, 61.78; H, 4.75; N, 6.00, S, 13.74; Found : C, 61.78; H, 4.75; N, 6.01; S, 13.74 %.