Supporting Information
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PALLADIUM-CATALYZED DIRECT ARYULATION OF 2,5-DISUBSTITUTED IMIDAZO[2,1-b][1,3,4]THIADIAZOLES

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General Methods. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX 250 MHz or 400 MHz instrument using CDCl$_3$ or DMSO-$d_6$. The chemical shifts are reported in parts per million ($\delta$ scale) and all coupling constant ($J$) values are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and dd (doublet doublet). Melting points are uncorrected. IR absorption spectra were obtained on a Perkin Elmer PARAGON 1000 PC and values were reported in cm$^{-1}$. HRMS were recorded on a Bruker maXis mass spectrometer by the "Fédération de Recherche" ICOA/CBM (FR2708) platform. Monitoring of the reactions was performed using silica gel TLC plates (silica Merck 60 F$_{254}$). Spots were visualized by UV light at 254 nm and 356 nm. Column chromatographies were performed using silica gel 60 (0.063-0.200 mm, Merck). The bromo-aryles were purchased from Sigma-Aldrich.

General Procedure. A solution of 2,6-disubstituted-imidazo[2,1-b][1,3,4]thiadiazole derivative (1.0 eq.), cesium carbonate (3.0 eq.) and bromo-(Het)Aryl (1.5 eq.) in dry 1,4-dioxane or toluene (3 mL for 80 mg) was degassed by argon bubbling for 15 min. Xantphos (0.2 eq.) and Pd(OAc)$_2$ (0.1 eq.) was then added and the mixture was heated to 150 °C for 60 min under microwave irradiations. After removing the solvent in vacuo, the crude product was purified by flash chromatography on silica gel.
2-(4-Methylphenyl)-5-phenyl-6-(4-nitrophenyl)-imidazo[2,1-b][1,3,4]thiadiazole (2).

The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and bromobenzene (37 µL, 0.36 mmol, 1.5 eq.) in dioxane (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 2/8 to 0/1) to afford 2 as a yellow solid (90 mg, 91%). Rf (PE/CH2Cl2, 2/8): 0.36 ; mp > 260 °C ; IR (ATR diamond): ν (cm⁻¹) 1593, 1505, 1481, 1338, 1324, 1108, 1084, 971, 856, 816, 739, 708, 681 ; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.16 (d, J = 8.7 Hz, 2H, 2xHₐr), 7.83 (d, J = 8.7 Hz, 2H, 2xHₐr), 7.77 (d, J = 8.1 Hz, 2H, 2xHₐr), 7.65 (dd, J = 7.6, 1.5 Hz, 2H, 2xHₐr), 7.56-7.44 (m, 3H, 3xHₐr), 7.30 (d, J = 8.1 Hz, 2H, 2xHₐr), 2.46 (s, 3H, CH₃) ; ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 162.6 (C₂), 146.8 (C₂), 145.3 (C₂), 142.8 (C₂), 141.4 (C₂), 140.0 (C₂), 130.1 (2xCH₂), 129.6 (2xCH₂), 129.3 (CH₃), 129.2 (2xCH₂), 128.5 (C₂), 128.0 (2xCH₂), 127.5 (C₂), 127.0 (2xCH₂), 126.0 (C₂), 124.0 (2xCH₂), 21.8 (CH₃) ; HRMS (EI-MS) m/z calcd for C₂₃H₁₆N₄O₂S: 413.1067 [M+H]⁺, found: 413.10692.
2-(4-Methoxy-phenyl)-5-(4-nitro-phenyl)-6-(4-methylphenyl)-imidazo[2,1-b][1,3,4]thiadiazole (7). The reaction was carried out as described in general procedure using B (80 mg, 0.25 mmol, 1.0 eq.) and 4-nitro-bromobenzene (75 mg, 0.37 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 7 as a yellow solid (88 mg, 80%). Rf (CH₂Cl₂): 0.47 ; mp = 256-258 °C ; IR (ATR diamond): ν (cm⁻¹) 1598, 1511, 1458, 1343, 1302, 1257, 1206, 1176, 1107, 1023, 976, 827, 741 ; ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.25 (d, J = 8.9 Hz, 2H, 2xH Ar), 7.90 (d, J = 8.9 Hz, 2H, 2xH Ar), 7.84 (d, J = 8.8 Hz, 2H, 2xH Ar), 7.50 (d, J = 8.0 Hz, 2H, 2xH Ar), 7.19 (d, J = 8.0 Hz, 2H, 2xH Ar), 7.02 (d, J = 8.8 Hz, 2H, 2xH Ar), 3.89 (s, 3H, OCH₃), 2.39 (s, 3H, CH₃) ; ¹³C NMR (63 MHz, CDCl₃): δ (ppm) 162.7 (C q), 162.0 (C q), 146.7 (C q), 145.9 (C q), 145.3 (C q), 138.4 (C q), 136.0 (C q), 131.3 (C q), 129.6 (2xCH₃Ar), 128.9 (2xCH₃Ar), 128.7 (2xCH₃Ar), 128.4 (2xCH₃Ar), 124.0 (2xCH₃Ar), 122.7 (C q), 121.5 (C q), 114.9 (2xCH₃Ar), 55.3 (OCH₃), 21.5 (CH₃) ; HRMS (EI-MS) m/z calcd for C₂₄H₁₈N₄O₃S: 443.11724 [M+H]⁺, found: 443.11732.
2-(4-Methylphenyl)-5,6-bis(4-nitrophenyl)imidazo[2,1-b][1,3,4]thiadiazole (8). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 4-nitro-bromobenzene (72 mg, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 2/8 to 0/1) to afford 6 as a yellow solid (98 mg, 90 %). Rf (CH2Cl2): 0.69 ; mp > 260 °C ; IR (ATR diamond): ν (cm⁻¹) 1595, 1513, 1472, 1339, 1212, 1108, 975, 855, 816, 744, 712 ; ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.34 (d, J = 9.0 Hz, 2H, 2xH₆), 8.23 (d, J = 9.0 Hz, 2H, 2xH₆), 7.91-7.76 (m, 6H, 6xH₆), 7.34 (d, J = 8.0 Hz, 2H, 2xH₆), 2.46 (s, 3H, CH₃) ; ¹³C NMR (63 MHz, CDCl₃): δ (ppm) 165.0 (C₆), 163.6 (C₆), 147.6 (C₆), 147.4 (C₆), 146.6 (C₆), 143.4 (C₆), 142.1 (C₆), 140.6 (C₆), 134.9 (C₆), 130.3 (2xCH₆), 129.7 (2xCH₆), 128.7 (2xCH₆), 127.1 (2xCH₆), 124.4 (2xCH₆), 124.2 (2xCH₆), 123.4 (C₆), 21.8 (CH₃) ; HRMS (EI-MS) m/z calcd for C₂₃H₁₅N₅O₄S: 458.09175 [M+H]+, found: 458.09174.
2-(4-Methylphenyl)-5-(4-benzaldehyde)-6-(4-nitrophenyl)-imidazo[2,1-b][1,3,4]thiadiazole (9). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 4-bromobenzaldehyde (66 mg, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7) to afford 9 as a yellow solid (88 mg, 81%). Rf (PE/CH2Cl2, 2/8): 0.26; mp > 260 °C; IR (ATR diamond): ν (cm⁻¹) 1703, 1594, 1508, 1477, 1337, 1209, 1106, 973, 856, 815, 756, 711; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.09 (s, 1H, CHO), 8.20 (d, J = 8.9 Hz, 2H, 2xH Ar), 8.00 (d, J = 8.3 Hz, 2H, 2xH Ar), 7.91-7.76 (m, 6H, 6xH Ar), 7.32 (d, J = 8.0 Hz, 2H, 2xH Ar), 2.45 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 191.5 (CHO), 163.3 (C₆), 147.2 (C₆), 146.3 (C₆), 143.2 (C₆), 141.6 (C₆), 140.9 (C₆), 136.2 (C₆), 134.4 (C₆), 130.4 (2xCH₂Ar), 130.2 (2xCH₂Ar), 129.7 (2xCH₂Ar), 128.5 (2x CH₂Ar), 127.2 (C₆), 127.1 (2xCH₂Ar), 124.5 (C₆), 124.1 (2xCH₂Ar), 21.8 (CH₃); HRMS (EI-MS) m/z calcd for C₂₄H₁₆N₄O₃S: 441.10159 [M+H]+, found: 441.10172.
2-(4-Methylphenyl)-5-(3-benzaldehyde)-6-(4-nitrophenyl)imidazo[2,1-b][1,3,4]thiadiazole (10). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 3-bromobenzaldehyde (42 µL, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 10 as a yellow solid (84 mg, 79 %). Rf (PE/CH2Cl2, 2/8): 0.20 ; mp = 258-260 °C ; IR (ATR diamond): ν (cm⁻¹) 1699, 1596, 1509, 1476, 1338, 1175, 1109, 974, 855, 809, 755, 709 ; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.08 (s, 1H, CHO), 8.23 (s, 1H, H₆), 8.18 (d, J = 8.9 Hz, 2H, 2xH₆), 7.99 (d, J = 7.7 Hz, 1H, H₆), 7.88 (d, J = 7.7 Hz, 1H, H₆), 7.81 (d, J = 8.9 Hz, 2H, 2xH₆), 7.77 (d, J = 8.2 Hz, 2H, 2xH₆), 7.67 (t, J = 7.7 Hz, 1H, H₆), 7.31 (d, J = 8.2 Hz, 2H, 2xH₆), 2.44 (s, 3H, CH₃) ; ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 191.7 (CHO), 163.2 (C₆), 147.0 (C₆), 145.8 (C₆), 143.1 (C₆), 140.9 (C₆), 140.8 (C₆), 137.3 (C₆), 135.2 (CH₆), 130.7 (CH₆), 130.2 (2xCH₆), 130.0 (CH₆), 129.9 (CH₆), 129.7 (C₆), 128.1 (2xCH₆), 127.2 (C₆), 127.1 (2xCH₆), 124.3 (C₆), 124.1 (2xCH₆), 21.8 (CH₃) ; HRMS (EI-MS) m/z calcd for C₂₄H₁₆N₄O₃S: 441.10159 [M+H]+, found: 441.10207.
2-(4-Methylphenyl)-5-(2-benzaldehyde)-6-(4-nitrophenyl)imidazo[2,1-b][1,3,4]thiadiazole (11). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 2-bromobenzaldehyde (42 µL, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 11 as a yellow solid (83 mg, 78 %). Rf (PE/CH2Cl2, 2/8): 0.17 ; mp = 254-256 °C ; IR (ATR diamond): ν (cm⁻¹) 1688, 1595, 1472, 1340, 1209, 1108, 974, 855, 815, 755, 708 ; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.95 (s, 1H, CHO), 8.17 (dd, J = 7.6, 1.2 Hz, 1H, Hₐ), 8.13 (d, J = 8.9 Hz, 2H, 2xHₐ), 7.81-7.67 (m, 7H, 7xHₐ), 7.59 (dd, J = 7.6, 1.2 Hz, 1H, Hₐ), 7.27 (d, J = 8.2 Hz, 2H, 2xHₐ), 2.42 (s, 3H, CH₃) ; ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 190.6 (CHO), 163.6 (Cₐ), 146.9 (Cₐ), 145.8 (Cₐ), 143.1 (Cₐ), 142.0 (Cₐ), 140.2 (Cₐ), 143.7 (CHₐ), 134.7 (Cₐ), 132.4 (CHₐ), 131.1 (Cₐ), 130.4 (CHₐ), 130.1 (2xCHₐ), 129.6 (CHₐ), 127.6 (2xCHₐ), 127.1 (Cₐ), 127.0 (2xCHₐ), 124.1 (2xCHₐ), 121.9 (Cₐ), 21.8 (CH₃) ; HRMS (EI-MS) m/z calcd for C₂₄H₁₆N₄O₃S: 441.10159 [M+H]⁺, found: 441.10222.
2-(4-Methylphenyl)-5-(4-fluorophenyl)-6-(4-nitrophenyl)-imidazo[2,1-b][1,3,4]thiadiazole (12). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 1-bromo-4-fluorobenzene (40 µL, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 12 as a yellow solid (87 mg, 84 %). Rf (CH2Cl2): 0.57; mp > 260 °C; IR (ATR diamond): ν (cm⁻¹) 1593, 1512, 1474, 1338, 1225, 1106, 974, 857, 814, 755, 711; 1H NMR (250 MHz, CDCl3): δ (ppm) 8.15 (d, J = 8.9 Hz, 2H, 2xHAr), 7.81 (d, J = 8.9 Hz, 2H, 2xHAr), 7.77 (d, J = 8.0 Hz, 2H, 2xHAr), 7.69-7.57 (m, 2H, 2xHAr), 7.30 (d, J = 8.0 Hz, 2H, 2xHAr), 7.18 (t, J = 8.6 Hz, 2H, 2xHAr), 2.41 (s, 3H, CH3); 13C NMR (101 MHz, CDCl3): δ (ppm) 163.5 (d, J = 157.0 Hz, Cq-F), 146.8 (Cq), 145.3 (Cq), 143.0 (Cq), 141.2 (Cq), 140.1 (Cq), 131.6 (d, J = 8.5 Hz, 2xCHAr), 130.2 (2xCHAr), 129.6 (Cq), 129.2 (Cq), 127.9 (2xCHAr), 127.4 (Cq), 127.0 (2xCHAr), 124.9 (Cq), 124.0 (2xCHAr), 116.8 (d, J = 21.8 Hz, 2xCHAr), 21.8 (CH3); HRMS (EI-MS) m/z calcd for C23H15FN4O2S: 431.09725 [M+H]+, found: 431.09789.
2-(4-Methylphenyl)-5-(4-benzonitrile)-6-(4-nitrophenyl)-imidazo[2,1-b][1,3,4]thiadiazole (13). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 4-bromobenzonitrile (66 mg, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 13 as a yellow solid (85 mg, 81 %). Rf (CH2Cl2): 0.58 ; mp > 260 °C ; IR (ATR diamond): ν (cm⁻¹) 2225, 1598, 1508, 1475, 1340, 1215, 1184, 1108, 1083, 977, 864, 839, 751, 708 ; ¹H NMR (400 MHz, CDCl3): δ (ppm) 8.23 (d, J = 8.9 Hz, 2H, 2×H Ar), 7.86-7.76 (m, 8H, 8×H Ar), 7.34 (d, J = 8.0 Hz, 2H, 2×H Ar), 2.47 (s, 3H, CH3) ; ¹³C NMR (101 MHz, CDCl3): δ (ppm) 163.5 (Cq), 147.3 (Cq), 146.4 (Cq), 143.3 (Cq), 141.7 (Cq), 140.7 (Cq), 133.1 (Cq), 132.9 (2×CH₃), 130.3 (2×CH₃), 129.6 (2×CH₃), 128.6 (2×CH₃), 127.1 (2×CH₃), 124.2 (2×CH₃), 123.7 (Cq), 118.6 (Cq), 112.4 (CN), 21.8 (CH3) ; HRMS (EI-MS) m/z calcd for C24H15N5O2S: 438.10192 [M+H]+, found: 438.10177.
2-(4-Methylphenyl)-5-(4-trifluoromethyl-phenyl)-6-(4-nitro-phenyl)-imidazo[2,1-b][1,3,4]thiadiazole (14). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 1-bromo-4-(trifluoromethyl)benzene (50 µL, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 14 as a yellow solid (91 mg, 80 %). Rf (CH2Cl2): 0.64; mp > 260 °C; IR (ATR diamond): ν (cm⁻¹) 1596, 1513, 1465, 1339, 1324, 1161, 1126, 1106, 1066, 1020, 974, 815, 711; H NMR (250 MHz, CDCl3): δ (ppm) 8.21 (d, J = 9.0 Hz, 2H, 2xHAr), 7.86-7.73 (m, 8H, 8xHAr), 7.32 (d, J = 8.5 Hz, 2H, 2xHAr), 2.45 (s, 3H, CH3); 13C DEPT 135 NMR (101 MHz, CDCl3): δ (ppm) 130.0 (2xCHAr), 129.5 (2xCHAr), 128.2 (2xCHAr), 126.9 (2xCHAr), 125.9 (q, J = 3.7 Hz, 2xCHAr), 124.0 (2xCHAr), 21.6 (CH3); HRMS (EI-MS) m/z calcd for C24H15F3N4O2S: 481.09410 [M+H]+, found: 481.09399.
2-(4-Methylphenyl)-5-(4-acetophenone)-6-(4-nitro-phenyl)-imidazo[2,1-b][1,3,4]thiadiazole (15). The reaction was carried out as described in general procedure using 1 (80 mg, 0.24 mmol, 1.0 eq.) and 4'-bromoacetophenone (77 mg, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 4/6 to 2/8) to afford 15 as a yellow solid (84 mg, 78%). Rf (CH2Cl2): 0.53; mp > 260 °C; IR (ATR diamond): ν (cm−1) 1721, 1596, 1464, 1338, 1273, 1183, 1105, 973, 862, 815, 752, 711; 1H NMR (250 MHz, CDCl3): δ (ppm) 8.26-8.09 (m, 4H, 4xH Ar), 7.89-7.69 (m, 6H, 6xH Ar), 7.31 (d, J = 8.0 Hz, 2H, 2xH Ar), 3.97 (s, 3H, COCH3), 2.44 (s, 3H, CH3); 13C NMR (101 MHz, CDCl3): δ (ppm) 166.4 (C=O), 153.1 (Cq), 147.1 (Cq), 146.0 (Cq), 143.1 (Cq), 141.1 (Cq), 132.9 (Cq), 130.4 (Cq), 130.3 (2xCHAr), 130.2 (2xCHAr), 129.2 (2xCHAr), 128.3 (2xCHAr), 127.3 (Cq), 127.0 (2xCHAr), 124.8 (Cq), 124.1 (2xCHAr), 52.5 (COCH3), 21.8 (CH3); HRMS (EI-MS) m/z calcd for C25H18N4O3S: 471.11215 [M+H]+, found: 471.11234.
2,6-bis-(4-Methoxy-phenyl)-5-(4-nitro-phenyl)-imidazo[2,1-b][1,3,4]thiadiazole (16). The reaction was carried out as described in general procedure using B (80 mg, 0.24 mmol, 1.0 eq.) and 4-nitro-bromobenzene (72 mg, 0.36 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 2/8 to 0/1) to afford 16 as a yellow solid (88 mg, 81%). 

Rf (CH2Cl2): 0.26; mp = 236-238 °C; IR (ATR diamond): ν (cm⁻¹) 2929, 2836, 1602, 1508, 1466, 1342, 1304, 1286, 1178, 1108, 1024, 973, 831, 802, 779; ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.26 (d, J = 8.8 Hz, 2H, 2xHAr), 7.91 (d, J = 8.8 Hz, 2H, 2xHAr), 7.84 (d, J = 8.6 Hz, 2H, 2xHAr), 7.54 (d, J = 8.6 Hz, 2H, 2xHAr), 7.02 (d, J = 8.7 Hz, 2H, 2xHAr), 6.92 (d, J = 8.7 Hz, 2H, 2xHAr), 3.89 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃); ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 162.7 (C₉), 161.9 (C₉), 159.9 (C₉), 146.6 (C₉), 145.9 (C₉), 145.1 (C₉), 136.1 (C₉), 129.8 (2xCHAr), 128.7 (2xCHAr), 128.6 (2xCHAr), 126.7 (C₉), 124.1 (2xCHAr), 122.7 (C₉), 121.2 (C₉), 114.9 (2xCHAr), 114.4 (2xCHAr), 55.7 (OCH₃), 55.5 (OCH₃); HRMS (EI-MS) m/z calcd for C₂₄H₁₈N₄O₄S: 459.11215 [M+H]+, found: 459.11229.
2-(4-Methoxy-phenyl)-5-(4-nitro-phenyl)-6-(4-methylphenyl)-imidazo[2,1-b][1,3,4]thiadiazole (17). The reaction was carried out as described in general procedure using B (80 mg, 0.25 mmol, 1.0 eq.) and 4-nitro-bromobenzene (75 mg, 0.37 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 3/7 to 0/1) to afford 17 as a yellow solid (88 mg, 80 %). Rf (CH2Cl2): 0.47 ; mp = 256-258 °C ; IR (ATR diamond): ν (cm⁻¹) 1598, 1511, 1458, 1343, 1302, 1257, 1206, 1176, 1107, 1023, 976, 827, 741 ; ¹H NMR (250 MHz, CDCl3): δ (ppm) 8.25 (d, J = 8.9 Hz, 2H, 2xH ar), 7.90 (d, J = 8.9 Hz, 2H, 2xH ar), 7.84 (d, J = 8.8 Hz, 2H, 2xH ar), 7.50 (d, J = 8.0 Hz, 2H, 2xH ar), 7.19 (d, J = 8.0 Hz, 2H, 2xH ar), 7.02 (d, J = 8.8 Hz, 2H, 2xH ar), 3.89 (s, 3H, OCH3), 2.39 (s, 3H, CH3) ; ¹3C NMR (63 MHz, CDCl3): δ (ppm) 162.7 (C q), 162.0 (C q), 146.7 (C q), 145.9 (C q), 145.3 (C q), 138.4 (C q), 136.0 (C q), 131.3 (C q), 129.6 (2xCh ar), 128.9 (2xCh ar), 128.7 (2xCh ar), 128.4 (2xCh ar), 124.0 (2xCh ar), 122.7 (C q), 121.5 (C q), 114.9 (2xCh ar), 55.3 (OCH3), 21.5 (CH3) ; HRMS (El-MS) m/z calcd for C24H18N4O3S: 443.11724 [M+H]+, found: 443.11732.
2,5-Bis(4-nitrophenyl)-6-(4-methoxyphenyl)imidazo[2,1-b][1,3,4]thiadiazole (18). The reaction was carried out as described in general procedure using B (50 mg, 0.14 mmol, 1.0 eq.) and 1-bromo-4-
nitrobenzene (43 mg, 0.21 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 2/8 to 0/1) to afford 18 as an orange solid (34 mg, 51%). Rf (CH2Cl2): 0.25; mp > 260 °C; IR (ATR diamond): ν (cm⁻¹) 1595, 1512, 1337, 1246, 1170, 1107, 1030, 979, 851, 748, 686; ¹H NMR (250 MHz, CDCl3): δ (ppm) 8.39 (d, J = 8.8 Hz, 2H, 2xHAr), 8.30 (d, J = 8.9 Hz, 2H, 2xHAr), 8.10 (d, J = 8.8 Hz, 2H, 2xHAr), 7.90 (d, J = 8.9 Hz, 2H, 2xHAr), 7.55 (d, J = 8.7 Hz, 2H, 2xHAr), 6.93 (d, J = 8.7 Hz, 2H, 2xHAr), 3.86 (s, 3H, OCH3); ¹³C DEPT 135 NMR (101 MHz, CDCl3): δ (ppm) 129.6 (2xCHAr), 128.8 (2xCHAr), 127.7 (2xCHAr), 124.7 (2xCHAr), 124.1 (2xCHAr), 114.3 (2xCHAr), 55.3 (OCH3); HRMS (EI-MS) m/z calcd for C23H15N5O5S: 474.08667 [M+H]+, found: 474.08645.
2,5-Bis(4-nitrophenyl)-6-(4-methylphenyl)imidazo[2,1-b][1,3,4]thiadiazole (19). The reaction was carried out as described in general procedure using B (50 mg, 0.15 mmol, 1.0 eq.) and 4-nitro-bromobenzene (45 mg, 0.22 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (petroleum ether/dichloromethane, 2/8 to 0/1) to afford 19 as a yellow solid (26 mg, 38 %). Rf (CH2Cl2): 0.47 ; mp > 260 °C ; IR (ATR diamond): ν (cm⁻¹) 1595, 1516, 1472, 1338, 1282, 1200, 1110, 1081, 977, 852, 825, 744, 687 ; ¹H NMR (250 MHz, CDCl3): δ (ppm) 8.40 (d, J = 8.7 Hz, 2H, 2xHAr), 8.30 (d, J = 8.7 Hz, 2H, 2xHAr), 8.09 (d, J = 8.7 Hz, 2H, 2xHAr), 7.90 (d, J = 8.7 Hz, 2H, 2xHAr), 7.51 (d, J = 8.0 Hz, 2H, 2xHAr), 7.30 (d, J = 8.0 Hz, 2H, 2xHAr), 7.20 (d, J = 8.0 Hz, 2H, 2xHAr), 2.41 (s, 3H, CH3) ; ¹³C NMR (101 MHz, CDCl3): δ (ppm) 159.3 (Cq), 149.7 (Cq), 147.1 (Cq), 146.3 (Cq), 145.8 (Cq), 138.9 (Cq), 135.7 (Cq), 135.5 (Cq), 130.8 (Cq), 129.7 (2xCHAr), 129.1 (2xCHAr), 128.4 (2xCHAr), 127.8 (2xCHAr), 124.8 (2xCHAr), 124.2 (2xCHAr), 121.9 (Cq), 21.5 (CH3) ; HRMS (EI-MS) m/z calcd for C23H15N5O4S: 458.09175 [M+H]⁺, found: 458.09150.
2-(4-Methoxyphenyl)-5-(4-nitrophenyl)imidazo[2,1-b][1,3,4]thiadiazole (20). The reaction was carried out as described in general procedure using B (120 mg, 0.52 mmol, 1.0 eq.) and 4-nitro-
bromobenzene (157 mg, 0.78 mmol, 1.5 eq.) in toluene (3 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane/methanol, 99/1) to afford 20 as a yellow solid (168 mg, 92 %). Rf (CH2Cl2/MeOH, 95/5): 0.66 ; mp = 222-224 °C ; IR (ATR diamond): ν (cm⁻¹) 1598, 1507, 1442, 1336, 1254, 1179, 1117, 1030, 749, 690 ; ¹H NMR (250 MHz, CDCl3): δ (ppm) 8.32 (d, J = 8.9 Hz, 2H, 2xH₆), 8.18 (d, J = 8.9 Hz, 2H, 2xH₆), 7.88 (d, J = 8.8 Hz, 2H, 2xH₆), 7.77 (s, 1H, H₆), 7.05 (d, J = 8.8 Hz, 2H, 2xH₆), 3.91 (s, 3H, OCH₃) ; ¹³C NMR (63 MHz, CDCl3): δ (ppm) 163.1 (C₉), 162.9 (C₉), 147.6 (C₉), 146.3 (C₉), 134.9 (C₉), 133.2 (H₆), 128.7 (2xCH₂), 126.0 (C₉), 124.7 (2xCH₂), 124.5 (2xCH₂), 122.5 (C₉), 114.9 (2xCH₂), 55.7 (OCH₃) ; HRMS (EI-MS) m/z calcd for C₁₇H₁₂N₄O₃S: 353.07029 [M+H]^+, found: 353.07022.