Electronic Supplementary Information

Highly Efficient C-C Cross Coupling for Installing Thiophene Rings into π-Conjugated Systems

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**General Information**

All reactions were carried out using pre-dried glassware. DMF was purified by distillation under reduced pressure with Calcium hydride. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and naphthalene was added as internal standard. High Resolution mass spectrometry (HRMS) data report were performed on Waters Micromass GCT Premier, ionization mode: EI$^+$ and IonSpec 4.7 Tesla FTMS. $^1$H and $^{13}$C NMR data were recorded with Varian Mercury (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively. All solvents were dried and distilled before use according to the standard methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification.
Experimental Details

The preparation of Pd(OAc)$_2$ solution.

To an oven-dried 25 mL round bottom flask, 5.6 mg Pd(OAc)$_2$ was added under nitrogen atmosphere followed by 5 mL DMF. The solution was dissolved in an ultrasonic cleaner and 1.12 mg/mL of Pd(OAc)$_2$ solution was obtained.

Typical procedure for the preparation of 2-phenylthiophene.

Phenylboronic acid (73.2 mg, 0.6 mmol) and K$_2$CO$_3$ (138 mg, 1.0 mmol) were placed in a Schlenck tube, which was filled with nitrogen by using standard Schlenk techniques. 2-Bromothiophene (81.5 mg, 0.5 mmol), Pd(OAc)$_2$ solution in DMF (0.024 mg, 0.00010 mmol) and DMF (1.0 mL), were consequently added to the reaction tube. The reaction mixture was stirred at 120 °C for 12 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3*5 mL), the organic layers were combined, dried over sodium sulfate and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel (petroleum : ethyl acetate = 200:1)

Typical procedure for the preparation of 2,5-bis(4-tert-butylphenyl)thiophene.

4-tert-butylphenylboronic acid (106.8 mg, 0.6 mmol) and K$_2$CO$_3$ (138 mg, 1.0 mmol) were placed in a Schlenck tube, which was filled with nitrogen by using standard
Schlenk techniques. 2,5-dibromothiophene (60.5 mg, 0.25 mmol), Pd(OAc)$_2$ solution in DMF (0.0224 mg, 0.00010 mmol) and DMF (1.0 mL), were consequently added to the reaction tube. The reaction mixture was stirred at 120 °C for 14 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3*5 mL), the organic layers were combined, dried over sodium sulfate and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel (petroleum : ethyl acetate = 100:1).

**Typical procedure for the preparation of 5,5'-diphenyl-2,2'-bithiophene.**

Phenylboronic acid (73.2 mg, 0.6 mmol) and K$_2$CO$_3$ (138 mg, 1.0 mmol) were placed in a Schlenck tube, which was filled with nitrogen by using standard Schlenk techniques. 5,5'-dibromo-2,2'-bithiophene (81 mg, 0.25 mmol), Pd(OAc)$_2$ solution in DMF (0.0224 mg, 0.00010 mmol) and DMF (1.0 mL), were consequently added to the reaction tube. The reaction mixture was stirred at 120 °C for 14 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3*5 mL), the organic layers were combined, dried over sodium sulfate and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel (petroleum: dichloromethane = 20:1).
Characterization Data

\[
\begin{align*}
\text{S} & \quad \text{OMe} & \quad \text{2-(4-methoxyphenyl)thiophene (3a)} & \quad \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.54 \\
 & & & (d, J = 8.8 \, \text{Hz}, 2\text{H}), 7.24 - 7.16 \, \text{m,} \, 2\text{H}, 7.10 - 7.00 \, \text{m,} \, 1\text{H}, 6.91 \, (d, J = 8.8 \, \text{Hz}, 2\text{H}), 3.83 \, (s, 3\text{H}).
\end{align*}
\]

\[\begin{align*}
\text{S} & \quad \text{CHO} & \quad \text{4-(thiophen-2-yl)benzaldehyde (3b)} & \quad \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 9.98 \\
 & & & (s, 1\text{H}), 7.93 - 7.79 \, \text{m,} \, 2\text{H}, 7.74 \, (d, J = 8.3 \, \text{Hz}, 2\text{H}), 7.45 \, (dd, J = 3.7, 1.0 \, \text{Hz}, 1\text{H}), 7.38 \, (dd, J = 5.1, 1.0 \, \text{Hz}, 1\text{H}), 7.12 \, (dd, J = 5.0, 3.7 \, \text{Hz}, 1\text{H}). \\
& & & \text{H NMR (101 MHz, CDCl}_3\text{) } \delta 191.4, 142.6, 140.0, 134.9, 130.4, 128.4, 126.9, 125.9, 125.0.
\end{align*}
\]

\[\begin{align*}
\text{S} & \quad \text{CN} & \quad \text{4-(thiophen-2-yl)benzonitrile (3c)} & \quad \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.68 \, (q, J = 8.3 \, \text{Hz}, 4\text{H}), 7.42 \, (dd, J = 8.9, 4.4 \, \text{Hz}, 2\text{H}), 7.16 - 7.11 \, (m, 1\text{H}). \\
 & & & \text{H NMR (101 MHz, CDCl}_3\text{) } \delta 141.9, 138.5, 132.6, 128.4, 126.9, 125.9, 125.0, 118.7, 110.4.
\end{align*}\]

\[\begin{align*}
\text{C}_8\text{H}_{17}\text{C}_8\text{H}_{17} & \quad \text{S} & \quad \text{2-(9,9-dioctyl-9H-fluoren-2-yl)thiophene (3d)} & \quad \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.69 \, (dd, J = 7.3, 3.3 \, \text{Hz}, 2\text{H}), 7.59 \, (dd, J = 13.7, 5.8 \, \text{Hz}, 2\text{H}), 7.44 - 7.26 \, (m, 5\text{H}), 7.11 \, (dd, J = 5.0, 3.6 \, \text{Hz}, 1\text{H}), 2.14 - 1.84 \, (m, 4\text{H}), 1.22 - 0.95 \, (m, 20\text{H}), 0.80 \, (t, J = 7.0 \, \text{Hz}, 6\text{H}), 0.64 \, (d, J = 7.3 \, \text{Hz}, 4\text{H}). \\
 & & & \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 151.5, 150.9, 145.3, 140.7, 133.2, 128.1, 127.1, 126.8, 124.9, 124.5, 122.9, 120.1, 119.7, 55.2, 40.4, 31.8, 30.1, 29.3, 23.8, 22.6, 14.1.
\end{align*}\]

\[\begin{align*}
\text{S} & \quad \text{2-(naphthalen-2-yl)thiophene (3e)} & \quad \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.05 \, (d, J = 1.2 \, \text{Hz}, 1\text{H}), 7.89 - 7.79 \, (m, 3\text{H}), 7.75 \, (dd, J = 8.5, 1.8 \, \text{Hz}, 1\text{H}), 7.53 -
\end{align*}\]
7.39 (m, 3H), 7.32 (dd, \( J = 5.1, 1.1 \text{ Hz}, 1\text{H} \)), 7.13 (dd, \( J = 5.1, 3.6 \text{ Hz}, 1\text{H} \)). \(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 132.6, 131.7, 128.5, 128.0, 127.6, 126.5, 125.9, 125.0, 124.4, 124.1, 123.4.

![2-(naphthalen-1-yl)thiophene](image)

2-(naphtalen-1-yl)thiophene (3f): \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 8.26 - 8.17 \text{ (m, 1H)}, 7.89 - 7.80 \text{ (m, 2H)}, 7.55 (d, \( J = 7.1 \text{ Hz}, 1\text{H} \)), 7.46 (dt, \( J = 9.1, 4.3 \text{ Hz}, 3\text{H} \)), 7.39 (dd, \( J = 5.1, 1.2 \text{ Hz}, 1\text{H} \)), 7.23 (d, \( J = 3.5 \text{ Hz}, 1\text{H} \)), 7.16 (dd, \( J = 5.1, 3.5 \text{ Hz}, 1\text{H} \)). \(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 141.6, 133.7, 132.3, 131.7, 128.4 - 128.0, 127.2, 126.3, 125.9, 125.6, 125.1.

![2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dithiophene](image)

2,2’-(9,9-dioctyl-9H-fluorene-2,7-diyl)dithiophene (3g): \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.67 (d, \( J = 7.9 \text{ Hz}, 2\text{H} \)), 7.63 - 7.58 (m, 2H), 7.56 (d, \( J = 1.2 \text{ Hz}, 2\text{H} \)), 7.38 (dd, \( J = 3.6, 1.1 \text{ Hz}, 2\text{H} \)), 7.33 - 7.24 (m, 2H), 7.14 - 7.06 (m, 2H), 2.16 - 1.88 (m, 4H), 1.21 - 0.97 (m, 20H), 0.81 (dt, \( J = 14.1, 5.5 \text{ Hz}, 6\text{H} \)), 0.73 - 0.59 (m, 4H). \(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 151.7, 145.2, 140.3, 133.3, 128.1, 125.0, 124.6, 122.9, 120.2, 55.3, 40.5, 31.9, 30.0, 29.8, 29.3, 23.8, 22.7, 14.2.

![methyl 4-(thiophen-2-yl)benzoate](image)

methyl 4-(thiophen-2-yl)benzoate (3h): \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 8.10 - 7.98 \text{ (m, 2H)}, 7.72 - 7.63 \text{ (m, 2H)}, 7.42 (dd, \( J = 3.6, 1.1 \text{ Hz}, 1\text{H} \)), 7.36 (dd, \( J = 5.1, 1.1 \text{ Hz}, 1\text{H} \)), 7.12 (dd, \( J = 5.1, 3.7 \text{ Hz}, 1\text{H} \)), 3.93 (s, 3H). \(^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 166.7, 143.0, 138.6, 130.2, 128.7, 128.3, 126.3, 125.5, 124.5, 52.1.

![3-methyl-2-p-tolylthiophene](image)

3-methyl-2-p-tolylthiophene (3i): \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.35 (d, \( J = 7.7 \text{ Hz}, 2\text{H} \)), 7.19 (dd, \( J = 15.4, 6.5 \text{ Hz}, 3\text{H} \)), 6.91 (d, \( J = 5.1 \text{ Hz}, 1\text{H} \)), 2.38 (s,
3H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.8, 136.8, 132.6, 131.7, 130.9, 129.0, 128.7, 122.8, 21.0, 14.7.

![9-phenyl-3-(thiophen-2-yl)-9H-carbazole (3j): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, $J$ = 1.5 Hz, 1H), 8.17 (d, $J$ = 7.7 Hz, 1H), 7.66 (dd, $J$ = 8.5, 1.8 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.47 (dd, $J$ = 11.5, 4.3 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.32 – 7.24 (m, 2H), 7.10 (dd, $J$ = 5.1, 3.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.4, 140.2, 139.2, 136.3, 128.8, 126.9, 125.9, 125.6, 125.2, 123.4, 122.7, 122.2, 122.1, 121.1, 119.4, 119.0, 116.7, 109.0, 108.8; HRMS (EI): calcd. for C$_{23}$H$_{23}$NS [M$^+$] 325.0920; found 325.0919.](image)

![2-(2-chlorophenyl)thiophene (3k)$^{10}$: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.50 (m, 1H), 7.46 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29 – 7.20 (m, 2H), 7.14 – 7.07 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.0, 133.0, 132.2, 131.3, 130.3, 128.5, 127.5, 126.9, 126.0.](image)

![2,5-diphenylthiophene (5a)$^{11}$: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, $J$ = 7.6 Hz, 4H), 7.39 (t, $J$ = 7.8 Hz, 4H), 7.32 – 7.25 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.5, 134.2, 128.8, 127.4, 125.5, 123.9.](image)

![2,5-bis(4-fluorophenyl)thiophene (5b)$^{12}$: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.53 (m, 4H), 7.20 (s, 2H), 7.13 – 7.04 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.5, 161.0, 142.4, 130.4, 127.2, 127.2, 123.9, 116.0, 115.7.](image)
2,5-di(naphthalen-2-yl)thiophene (5c): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (s, 2H), 7.83 (ddd, $J = 12.4, 10.3, 5.1$ Hz, 8H), 7.58 – 7.41 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.8, 133.6, 132.7, 131.6, 128.5, 128.0, 127.7, 126.6, 126.0, 124.5, 123.9, 123.9.

After being dried, the product was found with poor solubility in the usual deuterated solvents.

2,5-bis(4-methylnaphthalen-1-yl)thiophene (5d): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 – 8.34 (m, 2H), 8.12 – 8.03 (m, 2H), 7.63 – 7.50 (m, 6H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.27 (d, $J = 13.7$ Hz, 2H), 2.74 (d, $J = 10.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.8, 134.5, 132.6, 131.5, 130.4, 127.6, 127.2, 126.2, 125.8, 125.6, 124.2, 19.4.

HRMS (EI): calcd. for C$_{26}$H$_{20}$S [M$^+$] 364.1278; found 364.1280.

5-bis(4-tert-butylphenyl)thiophene (5e): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, $J = 8.4$ Hz, 4H), 7.40 (d, $J = 8.4$ Hz, 4H), 7.24 (s, 2H), 1.34 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.5, 143.1, 131.6, 125.7, 125.3, 123.5, 123.3, 34.6, 31.2.

2,5-bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene (5f): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J = 7.7$ Hz, 4H), 7.69 (dd, $J = 7.9, 1.3$ Hz, 2H), 7.64 (s, 2H), 7.42 (s, 2H), 7.41 – 7.30 (m, 6H), 2.16 – 1.93 (m, 8H), 1.27 – 1.01 (m, 40H), 0.84 (t, $J = 7.1$ Hz, 12H), 0.70 (d, $J = 7.5$ Hz, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.6, 150.9, 144.1, 140.7, 133.2, 127.2, 126.9, 124.5, 123.8, 122.9, 120.1, 119.8, 55.2, 40.5, 31.9, 30.1, 29.3, 23.8, 22.7, 14.2; HRMS (EI): calcd. for C$_{62}$H$_{84}$S [M$^+$] 860.6276; found 860.6288.
**5,5'-diphenyl-2,2'-bithiophene (7a)**\textsuperscript{11}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.61 (d, J = 7.5 Hz, 4H), 7.39 (t, J = 7.6 Hz, 4H), 7.30 (d, J = 7.3 Hz, 2H), 7.24 (s, 2H), 7.18 (d, J = 3.7 Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 143.0, 136.6, 133.9, 128.9, 127.6, 125.5, 124.47, 123.7.

After being dried, the product was found with poor solubility in the usual deuterated solvents.

**4,4'-(2,2'-bithiophene-5,5'-diyl)dibenzonitrile (7b)**\textsuperscript{15}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.10 (d, J = 7.1 Hz, 2H), 7.69 (d, J = 0.8 Hz, 8H), 7.38 (d, J = 3.9 Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 141.2, 138.2, 138.0, 132.8, 126.0, 125.7, 125.4, 118.7, 110.7.

After being dried, the product was found with poor solubility in the usual deuterated solvents.

**5,5'-bis(3,5-difluorophenyl)-2,2'-bithiophene (7c)**: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.25 (d, J = 3.9 Hz, 2H), 7.18 (d, J = 3.8 Hz, 2H), 7.13 – 7.07 (m, 4H), 6.74 (tt, J = 8.8, 2.2 Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 164.6, 164.4, 162.1, 162.0, 140.8, 137.4, 136.8, 125.3, 124.9, 108.5, 108.4, 108.3, 108.2, 103.0, 102.8, 102.5; HRMS (EI): calcd. for C\textsubscript{20}H\textsubscript{20}F\textsubscript{4}S\textsubscript{2} [M\textsuperscript{+}] 390.0155; found 390.0154.

After being dried, the product was found with poor solubility in the usual deuterated solvents.
4,4′-(2,2′-bithiophene-5,5′-diyl)dibenzaldehyde (7d): ¹H NMR (400 MHz, CDCl₃) δ 10.02 (s, 2H), 8.10 (d, J = 6.9 Hz, 2H), 7.91 (d, J = 8.2 Hz, 4H), 7.77 (d, J = 8.2 Hz, 4H), 7.43 (d, J = 3.9 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 191.3, 141.8, 139.4, 138.2, 135.1, 130.5, 125.9, 125.7, 125.3; HRMS (EI): calcd. for C₃₂H₁₄O₂S₂ [M⁺] 374.0436; found 374.0429.

After being dried, the product was found with poor solubility in the usual deuterated solvents.

5,5′-bis(9,9-dioctyl-9H-fluoren-2-yl)-2,2′-bithiophene (7e): ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.65 (m, 4H), 7.64 – 7.49 (m, 4H), 7.33 (dd, J = 4.6, 3.5 Hz, 8H), 7.23 (d, J = 3.8 Hz, 2H), 2.07 – 1.93 (m, 8H), 1.11 (dd, J = 29.6, 21.6 Hz, 40H), 0.81 (t, J = 7.1 Hz, 12H), 0.65 (d, J = 7.4 Hz, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 151.6, 150.9, 143.9, 140.9, 140.6, 136.5, 132.8, 127.2, 126.9, 124.5, 123.6, 122.9, 120.1, 119.8, 55.2, 40.4, 31.8, 30.1, 29.8, 29.3, 23.8, 22.7, 14.1; HRMS (EI): calcd. for C₆₆H₈₆S₂ [M⁺] 942.6164; found 942.6165.

5,5′-bis(9-phenyl-9H-carbazol-3-yl)-2,2′-bithiophene (7f): ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 1.5 Hz, 2H), 8.20 (d, J = 7.7 Hz, 2H), 7.70 – 7.57 (m, 10H), 7.46 (dt, J = 13.8, 7.8 Hz, 8H), 7.36 – 7.29 (m, 4H), 7.23 (d, J = 3.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 141.3, 140.4, 137.4, 135.9, 129.9, 127.6, 127.0, 126.4, 126.3, 124.2, 124.1, 123.8, 123.2, 122.8, 120.4, 120.2, 117.4, 110.1, 109.9; HRMS (EI): calcd. for C₄₄H₃₈N₂S₂ [M⁺] 648.1692; found 648.1688.

After being dried, the product was found with poor solubility in the usual deuterated solvents.
References

Copies of Product $^1$H NMR and $^{13}$C NMR

![Chemical structures and NMR spectra](image)