Supplementary material

Palladium-Catalyzed Direct Arylation of Thiophenes Tolerant to Silyl Groups

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Table A Influence of the reaction conditions for palladium-catalysed direct 5-arylation of 2-(trimethylsilyl)thiophene with 4-bromobenzonitrile (Scheme 2)

Entry	Solvent	Base	Catalyst	Temp (°C)	Time (h)	Conv (%)	Ratio **2a**:**2b**:**2c**:**2d**
1	DMF	KOAc	$PdCl(C_3H_5)(dppb)$	120	16	15	10:2:3:0
2	NMP	KOAc	$PdCl(C_3H_5)(dppb)$	120	16	95	8:51:7:0
3	DMAc	KOAc	$PdCl(C_3H_5)(dppb)$	120	18	98	46:6:7:27
4	DMAc	CsOAc	$PdCl(C_3H_5)(dppb)$	120	16	100	8:81:6:2
5	DMAc	K_2CO_3	$PdCl(C_3H_5)(dppb)$	120	18	82	39:14:22:1
6	DMAc	Na_2OAc	$PdCl(C_3H_5)(dppb)$	120	16	20	4:1:13:0
7	DMAc	Cs_2CO_3	$PdCl(C_3H_5)(dppb)$	120	16	27	2:17:6:0
8	DMAc	KOAc	$Pd(OAc)_2$	120	16	69	28:37:3:0
9	DMAc	KOAc	½ $[PdCl(C_3H_5)]_2$	120	15	5	0:1:0:0
10	DMAc	KOAc	$PdCl(C_3H_5)(dppb)$	110	18	3	nd
11	DMAc	KOAc	$Pd(OAc)_2$ / 2 PCy_3	120	5	71	58:4:4:0
12	DMAc	KOAc	$Pd(OAc)_2$ / 2 PCy_3	120	10	100	69:24:7:0
13	DMAc	KOAc	$Pd(OAc)_2$ / dppb	120	5	100	**79:12:9:0**
14	DMAc	KOAc	$Pd(OAc)_2$ / dppm	120	5	98	66:24:8:0
15	DMAc	KOAc	$Pd(OAc)_2$ / dppb	120	17	100	11:78:11:0

Conditions: catalyst: [Pd] (0.004 mmol), 4-bromobenzonitrile (1 mmol), 2-(trimethylsilyl)thiophene (2 mmol), base (2 mmol), under argon, GC and NMR conversions of 4-bromobenzonitrile.

General procedure

As a typical experiment, the reaction of the aryl bromide (1 mmol), 2-(trimethylsilyl)thiophene (2 mmol) and KOAc (0.196 g, 2 mmol) at 120-150 °C during 1-18 h in DMAc (4 mL) in the presence of

$Pd(OAc)_2$ / dppb under argon affords the coupling product after addition of water (20 mL), extraction with dichloromethane (20 mL), drying on $MgSO_4$, evaporation and purification on silica gel (pentane/ether). The separation of silylated thiophenes and traces of desilylated thiophenes was easy, as the silylated thiophenes elute first.

4-Benzothiophen-2-ylbenzonitrile (1b)[1]

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)benzothiophene (0.412 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 5 h affords the product **1b** in 12% (0.028 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.88-7.80 (m, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.65 (s, 1H), 7.40-7.35 (m, 2H).

Synthesis of 4-(5-trimethylsilanylthiophen-2-yl)-benzonitrile (2a) using $Pd(OAc)_2$ / dppb as the catalyst (Table 1, entry 7 or Table A, entry 13).

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 5 h affords the product **2a** in 65% (0.167 g) isolated yield as a white solid (mp 110 °C).

4-Thiophen-2-ylbenzonitrile (2b) was also isolated in 8% yield (0.015 g) as a white solid (mp 178 °C). When the reaction was stopped after 17 h (Table 1, entry 9 or Table A, entry 15), **2a** was isolated in 8% yield (0.021 g), and **2b** was isolated in 70% yield (0.130 g).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 3.4 Hz, 1H), 7.28 (d, J = 3.4 Hz, 1H), 0.34 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.0, 143.1, 138.6, 135.2, 132.7, 126.2, 126.1, 118.9, 110.4, -.02. elemental analysis: calcd (%) for $C_{14}H_{15}NSSi$ (257.43): C

65.32, H 5.87; found: C 65.40, H 5.98. IR (neat) ν 759, 2225, 2922 cm^{-1}.

4-Thiophen-2-ylbenzonitrile (2b) ^{1}H NMR (200 MHz, $CDCl_3$): ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.50-7.35 (m, 2H), 7.10 (t, *J* = 4.0 Hz, 1H).

2,5-Di(4-cyanophenyl)-thiophene (2c) was also isolated ^{1}H NMR (500 MHz, $CDCl_3$): 7.74 (d, *J* = 8.2 Hz, 4H), 7.71 (d, *J* = 8.2 Hz, 4H), 7.46 (s, 2H).

Biphenyl-4,4'-dicarbonitrile (2d) was also isolated ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 4H).

Synthesis of 4-(5-trimethylsilanylthiophen-2-yl)-benzonitrile (2a) using $Pd(OAc)_2$ as the catalyst (Table 1, entry 2 or Table A, entry 8).

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 18 h affords the product **2a** in 22% (0.057 g) yield. Product **2b** was also isolated in 31% (0.058 g) yield.

Synthesis of 4-(5-trimethylsilanylthiophen-2-yl)-benzonitrile (2a) using $Pd(OAc)_2$ / 2 PCy_3 as the catalyst (Table 1, entry 6 or Table A, entry 12).

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and PCy_3 (23 mg, 0.08 mmol) in DMAc (5 mL) at 120°C during 18 h affords the product **2a** in 59% (0.152 g) yield. Product **2b** was also isolated in 18% (0.033 g) yield.

Synthesis of 4-(5-trimethylsilanylthiophen-2-yl)-benzonitrile (2a) using $Pd(OAc)_2$ / dppm as the catalyst (Table 1, entry 8 or Table A, entry 14).

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and bis(diphenylphosphino)methane (dppm) (15 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 5 h affords the product **2a** in 55% (0.141 g) yield. Product **2b** was also isolated in 18% (0.033 g) yield.

4-(5-Trimethylsilanylthiophen-2-yl)-propiophenone (3)

The reaction of 4-bromopropiophenone (0.213 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 7 h affords the product **3** in 75% (0.216 g) isolated yield as a white solid (mp 79 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 3.4 Hz, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.0, 148.0, 142.0, 138.5, 135.4, 135.1, 128.7, 125.7, 125.6, 31.7, 8.2, -0.2. elemental analysis: calcd (%) for $C_{16}H_{20}OSSi$ (288.48): C 66.61, H 6.99; found: C 66.78, H 7.14. IR (neat) ν 793, 1676, 2968 cm^{-1}.

4-(5-Trimethylsilanylthiophen-2-yl)-acetophenone (4)

The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 6 h affords the product **4** in 70% (0.192 g) isolated yield as a white solid (mp 94 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 3.4 Hz, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 2.61 (s, 3H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 197.5, 148.1, 142.4, 138.9, 135.8, 135.3, 129.2, 125.9, 125.8, 26.7, 0.0. elemental analysis: calcd (%) for $C_{15}H_{18}OSSi$ (274.45): C 65.64, H 6.61; found: C 65.57, H 6.73. IR (neat) ν 806, 1674, 2959 cm^{-1}.

4-(5-Trimethylsilanylthiophen-2-yl)-benzaldehyde (5)

The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 6 h affords the product **5** in 72% (0.187 g) isolated yield as a green solid (mp 95 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 10.0 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 3.4 Hz, 1H), 7.27 (d, *J* = 3.4 Hz, 1H), 0.38 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.4, 147.7, 142.8, 140.0, 135.2, 135.0, 130.4, 126.2, 126.1, -0.2. elemental analysis: calcd (%) for $C_{14}H_{16}OSSi$ (260.43): C 64.57, H 6.19; found: C 64.68, H 6.20. IR (neat) ν 804, 1694, 2960 cm^{-1}.

Methyl 4-(5-trimethylsilanyl-thiophen-2-yl)-benzoate (6)

The reaction of methyl 4-bromobenzoate (0.215 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 5 h affords the product **6** in 79% (0.229 g) isolated yield as a yellow solid (mp 76 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 3.4 Hz, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 3.92 (s, 3H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.7, 148.1, 141.9, 138.6, 135.1, 130.2, 128.7, 125.7, 125.6, 52.1, -0.1. elemental analysis: calcd (%) for $C_{15}H_{18}O_2SSi$ (290.45): C 62.03, H 6.25; found: C 62.10, H 6.47. IR (neat) ν 1109, 1276, 1715, 2950 cm^{-1}.

Trimethyl-[5-(4-trifluoromethylphenyl)-thiophen-2-yl]-silane (7)

The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 11 h affords the product **7** in 52% (0.156 g) isolated yield as a yellow solid (mp 56 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 3.4 Hz, 1H), 7.24 (d, *J* = 3.4 Hz, 1H), 0.38 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 147.6, 141.9, 137.7, 135.1, 129.1 (q, *J* = 32.5 Hz), 126.0, 125.8 (q, *J* = 3.8 Hz), 125.6, 124.9 (q, *J* = 273.0 Hz), -0.1. elemental analysis: calcd (%) for $C_{14}H_{15}F_3SSi$ (300.42): C 55.97, H 5.03; found: C 56.14, H 5.01. IR (neat) ν 829, 2959 cm^{-1}.

[5-(4-Chlorophenyl)-thiophen-2-yl]-trimethyl-silane (8)

The reaction of 4-chlorobromobenzene (0.191 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 4 h affords the product **8** in 78% (0.208 g) isolated yield as a pale blue solid (mp 78 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.38-7.30 (m, 3H), 7.21 (d, *J* = 3.4 Hz, 1H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.2, 140.6, 135.0, 133.1, 132.9, 128.9, 127.1, 124.7, -.01. elemental analysis: calcd (%) for $C_{13}H_{15}ClSSi$ (266.86): C 58.51, H 5.67; found: C 58.60, H 5.80. IR (neat) ν 754, 2955 cm^{-1}.

Trimethyl-(5-*p*-tolylthiophen-2-yl)-silane (9)[2]

The reaction of 4-bromotoluene (0.171 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 150°C during 23 h affords the product **9** in 40% (0.099 g) isolated yield as a blue oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.38-7.20 (m, 3H), 2.38 (s, 3H), 0.35 (s, 9H).

3-(5-Trimethylsilanylthiophen-2-yl)-benzonitrile (10)

The reaction of 3-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 5 h affords the product **10** in 64% (0.165 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.85 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.60-7.40 (m, 2H), 7.34 (d, J = 3.4 Hz, 1H), 7.23 (d, J = 3.4 Hz, 1H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 146.5, 142.1, 135.6, 135.2, 130.4, 129.9, 129.6, 129.1, 125.6, 118.5, 113.0, -0.1. elemental analysis: calcd (%) for $C_{14}H_{15}NSSi$ (257.43): C 65.32, H 5.87; found: C 65.18, H 5.80. IR (neat) ν 759, 2225, 2922 cm^{-1}.

2-(5-Trimethylsilanylthiophen-2-yl)-benzonitrile (11)

The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 7 h affords the product **11** in 73% (0.188 g) isolated yield as a colourless oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.80-7.50 (m, 4H), 7.34 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 3.4 Hz, 1H), 0.36 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 144.5, 143.3, 137.7, 135.2, 134.4, 133.0, 129.8, 128.8, 127.5, 119.0, 109.8, 0.0. elemental analysis: calcd (%) for $C_{14}H_{15}NSSi$ (257.43): C 65.32, H 5.87; found: C 65.24, H 5.84. IR (neat) ν 754, 2224, 2953 cm^{-1}.

2-(5-Trimethylsilanylthiophen-2-yl)-benzaldehyde (12)

The reaction of 2-bromobenzaldehyde (0.185 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 7 h affords the product **12** in 84% (0.219 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 10.2 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 3.4 Hz, 1H), 7.14 (d, J = 3.4 Hz, 1H), 0.39 (s, 9H).

^{13}C NMR (50 MHz, CDCl$_3$): δ 192.2, 143.9, 143.2, 138.2, 134.5, 133.9, 133.5, 131.2, 130.8, 128.1, 127.7, -0.1. elemental analysis: calcd (%) for $C_{14}H_{16}OSSi$ (260.43): C 64.57, H 6.19; found: C 64.40, H 6.14. IR (neat) ν 757, 1689, 2953 cm^{-1}.

2-(5-Trimethylsilanylthiophen-2-yl)-benzotrifluoride (13)

The reaction of 2-trifluoromethylbromobenzene (0.225 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 150°C during 16 h affords the product **13** in 70% (0.210 g) isolated yield as a colourless oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.60-7.45 (m, 3H), 7.20-7.15 (m, 2H), 0.37 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 144.8, 141.5, 133.9, 133.0, 131.2, 129.0 (q, *J* = 2.6 Hz), 128.6 (q, *J* = 29.9 Hz), 127.8, 126.4 (q, *J* = 5.5 Hz), 124.0 (q, *J* = 273.4 Hz), -0.1. elemental analysis: calcd (%) for $C_{14}H_{15}F_3SSi$ (300.42): C 55.97, H 5.03; found: C 56.04, H 5.19. IR (neat) ν 815, 2957 cm^{-1}.

Trimethyl-(5-naphthalen-2-ylthiophen-2-yl)-silane (14)

The reaction of 2-bromonaphthalene (0.207 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 15 h affords the product **14** in 63% (0.178 g) isolated yield as a yellow solid (mp 86 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 8.11 (s, 1H), 7.90-7.70 (m, 4H), 7.55-7.40 (m, 3H), 7.25 (d, *J* = 3.4 Hz, 1H), 0.45 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 149.6, 140.3, 135.1, 133.6, 132.7, 131.8, 128.4, 128.0, 127.7, 126.5, 125.9, 124.7, 124.5, 124.3, -0.1. elemental analysis: calcd (%) for $C_{17}H_{18}SSi$ (282.48): C 72.28, H 6.42; found: C 72.34, H 6.31. IR (neat) ν 752, 2955 cm^{-1}.

Trimethyl-(5-*o*-tolylthiophen-2-yl)-silane (15)

The reaction of 2-bromotoluene (0.171 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 48 h affords the product **15** in 55% (0.135 g) isolated yield as a colourless oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.50-7.40 (d, *J* = 8.2 Hz, 1H), 7.30-7.17 (m, 4H), 7.15 (d, *J* = 3.4 Hz, 1H), 2.47 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.5, 140.1, 135.8, 134.3, 134.0, 130.7, 130.3, 127.7, 127.6, 125.8, 21.2, 0.0. elemental analysis: calcd (%) for $C_{14}H_{18}SSi$ (246.44): C 68.23, H 7.36; found: C 68.279, H 7.21. IR (neat) ν 834, 2953 cm^{-1}.

Trimethyl-(5-naphthalen-1-ylthiophen-2-yl)-silane (16)

The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 23 h affords the product **16** in 80% (0.226 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, CDCl$_3$): δ 8.40-8.30 (m, 1H), 7.95-7.90 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.70-7.25 (m, 6H), 0.42 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 147.1, 140.7, 134.2, 133.8, 132.6, 131.6, 128.7, 128.3, 128.2, 127.9, 126.3, 125.9, 125.8, 125.2, 0.0. elemental analysis: calcd (%) for $C_{17}H_{18}SSi$ (282.48): C 72.28, H 6.42; found: C 72.41, H 6.31. IR (neat) ν 834, 2953 cm^{-1}.

3-(5-Trimethylsilanylthiophen-2-yl)-pyridine (17)

The reaction of 3-bromopyridine (0.158 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.312 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 15 h affords the product **17** in 77% (0.180 g) isolated yield as a yellow solid (mp 55 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 8.91 (s, 1H), 8.53 (d, *J* = 4.0 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 3.4 Hz, 1H), 7.33 (m, 1H), 7.27 (d, *J* = 3.4 Hz, 1H), 0.37 (s, 9H). ^{13}C NMR (50 MHz, CDCl$_3$):

δ 148.4, 147.0, 145.4, 141.7, 135.1, 133.0, 130.4, 125.4, 123.6, -0.1. elemental analysis: calcd (%) for $C_{12}H_{15}NSSi$ (233.41): C 61.75, H 6.48; found: C 61.89, H 6.34. IR (neat) ν 837, 1245, 2954 cm^{-1}.

1,4-Bis(5-trimethylsilanylthiophen-2-yl)-benzene (18)

The reaction of 1,4-dibromobenzene (0.234 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.624 g, 4 mmol) and KOAc (0.392 g, 4 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 1 h affords the product **18** in 70% (0.270 g) isolated yield as a pale green solid (mp 146 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (s, 4H), 7.42 (d, *J* = 3.4 Hz, 2H), 7.28 (d, *J* = 3.4 Hz, 2H), 0.42 (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.1, 140.1, 135.0, 133.4, 126.3, 124.3, -0.1. elemental analysis: calcd (%) for $C_{20}H_{26}S_2Si_2$ (386.72): C 62.12, H 6.78; found: C 62.20, H 6.74. IR (neat) ν 800, 2955 cm^{-1}.

1,3-Bis(5-trimethylsilanylthiophen-2-yl)-benzene (19)

The reaction of 1,3-dibromobenzene (0.234 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.624 g, 4 mmol) and KOAc (0.392 g, 4 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 3 h affords the product **19** in 81% (0.313 g) isolated yield as a white solid (mp 74 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.46 (d, *J* = 3.5 Hz, 2H), 7.38 (t, *J* = 3.5 Hz, 1H), 0.42 (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.2, 140.3, 135.0, 134.9, 129.3, 125.1, 124.7, 123.6, 0.1. elemental analysis: calcd (%) for $C_{20}H_{26}S_2Si_2$ (386.72): C 62.12, H 6.78; found: C 62.22, H 6.61. IR (neat) ν 830, 2955 cm^{-1}.

2,7-Bis-(5-trimethylsilanyl-thiophen-2-yl)-fluoren-9-one (20)

The reaction of 2,7-dibromofluoren-9-one (0.338 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.624 g, 4 mmol) and KOAc (0.392 g, 4 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 10 h affords the product **20** in 69% (0.337 g) isolated yield as a red solid (mp 188 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.92 (s, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 3.3 Hz, 2H), 7.22 (d, *J* = 3.3 Hz, 2H), 0.38 (s, 18H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 193.5, 148.3, 142.9, 141.2, 135.5, 135.3, 135.2, 132.0, 125.1, 121.8, 120.9, 0.0. elemental analysis: calcd (%) for $C_{27}H_{28}OS_2Si$ (488.81): C 66.34, H 5.77; found: C 66.30, H 5.51. IR (neat) ν 833, 1703, 1714, 2950 cm^{-1}.

1,4'-Bis(5-trimethylsilanylthiophen-2-yl)-biphenyl (21)

The reaction of 1,4'-dibromobiphenyl (0.310 g, 1 mmol), 2-(trimethylsilyl)thiophene (0.468 g, 3 mmol) and KOAc (0.392 g, 4 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 7 h affords the product **21** in 37% (0.171 g) isolated yield as a pale green solid (mp 226 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.71 (d, *J* = 8.1 Hz, 4H), 7.63 (d, *J* = 8.1 Hz, 4H), 7.41 (d, *J* = 2.7 Hz, 2H), 7.23 (d, *J* = 2.7 Hz, 2H), 0.36 (s, 18H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 149.1, 140.2, 139.3, 135.1, 133.5, 127.2, 126.4, 124.4, -0.1. elemental analysis: calcd (%) for $C_{26}H_{30}S_2Si_2$ (462.82): C 67.47, H 6.53; found: C 67.29, H 6.59. IR (neat) ν 832, 2953 cm^{-1}.

4-[5-(Dimethylthiophen-2-yl-silanyl)-thiophen-2-yl]-benzonitrile (22)

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), dimethyl-dithiophen-2-ylsilane (0.448 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd(OAc)$_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 1 h affords the product **22** in 58% (0.189 g) isolated yield as a yellow solid (mp 78 °C).

^{1}H NMR (200 MHz, CDCl$_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.68-7.65 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.35 (d, *J* = 3.5 Hz, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.23 (dd, *J* = 3.4 and 3.5 Hz, 1H), 0.67 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.9, 140.3, 138.4, 136.6, 136.4, 135.6, 132.7, 131.6, 128.4, 126.3, 126.2, 118.8, 110.6, -.03. elemental analysis: calcd (%) for $C_{17}H_{15}NS_2Si$ (325.53): C 62.72, H 4.64; found: C 62.81, H 4.52. IR (neat) ν 820, 2223, 2923 cm^{-1}.

4-(2-Methyl-5-trimethylsilanylthiophen-3-yl)-benzaldehyde (23)

The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol), 2-(trimethylsilyl)-5-methylthiophene (0.340 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 120°C during 12 h affords the product **23** in 28% (0.077 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 2.55 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.9, 143.2, 141.5, 139.0, 137.3, 135.8, 134.5, 130.0, 129.1, 14.4, -0.1. elemental analysis: calcd (%) for $C_{15}H_{18}OSSi$ (274.45): C 65.64, H 6.61; found: C 65.51, H 6.40. IR (neat) ν 800, 1691, 2953 cm^{-1}.

4-(2-Methyl-5-trimethylsilanylthiophen-3-yl)-benzonitrile (24)

The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 2-(trimethylsilyl)-5-methylthiophene (0.340 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in DMAc (5 mL) at 130°C during 12 h affords the product **24** in 31% (0.084 g) isolated yield as a yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 2.55 (s, 3H), 0.35 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.5, 138.3, 137.5, 136.5, 135.5, 132.2, 129.1, 119.0, 110.1, 14.3, -.01. elemental analysis: calcd (%) for $C_{15}H_{17}NSSi$ (271.45): C 66.37, H 6.31; found: C 66.50, H 6.24. IR (neat) ν 800, 2223, 2953 cm^{-1}.

2-Bromo-5-naphthalen-1-yl-thiophene (25)[3]

The reaction of trimethyl-(5-naphthalen-1-ylthiophen-2-yl)-silane **16** (0.282 g, 1 mmol) and N-bromosuccinimide (0.187, 1.05 mmol) in THF (5 mL) at 25°C during 16 h affords **25** in 92% (0.266 g) isolated yield after addition of water (20 mL), extraction with dichloromethane (20 mL), drying on $MgSO_4$, evaporation and purification on silica gel (pentane).

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