Supporting Information
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Supporting Information
for
Sequential Dual Electrophilic Trapping-Negishi Coupling with
Dilithiothiophenes in a Three-Component-One-Pot Process
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SUPPORTING INFORMATION
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The catalyses were performed in degassed THF which was dried using MBraun system MB-SPS-800. All reactions were carried out in oven-dried Schlenk glassware using septa and syringes under argon atmosphere. The purification of products was performed on silica gel 60 (0.015-0.040 mm) using flash technique and under pressure of 2 bar. The crude mixtures were adsorbed on Celite 545 (0.02-0.10 mm) before chromatographic purification. The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 500, Bruker DRX 300 and an Avance DRX 250 spectrometer. TMS was used as reference ($\delta$ 0.0) or the resonance of CDCl$_3$ was locked as internal standard ($^1$H: $\delta$ 7.24, $^{13}$C: $\delta$ 77.0).

The multiplicities of signals were abbreviated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet) and corresponding combinations. The type of carbon atoms (CH$_3$, CH$_2$, CH, C$_{quat}$) was determined on the basis of DEPT-135 NMR spectra. EI mass spectra were measured on Finnigan MAT 8200 spectrometer. IR spectra were obtained on a Bruker Vector 22 FT-IR. The solids were measured as KBr pellets and the oils in the form of films on KBr plates. The intensity of signals is abbreviated as s (strong), m (medium) and w (weak). Combustion analyses were carried out on a Perkin Elmer Series II Analyser 2400 in the microanalytical laboratory of the Institut für Pharmazeutische und Medizinische Chemie der Heinrich-Heine-Universität Düsseldorf.

Representative Procedure - Synthesis of (5-(3,5-dimethyl-phenyl)thiophen-2-yl)trimethylsilane (3b; Table 1, Entry 2)

In a flame-dried Schlenk flask under argon atmosphere $n$-butyllithium (1.6 M in $n$-hexane, 2.5 ml, 4.0 mmol) and TMEDA (0.6 ml, 4.0 mmol) were dissolved in anhydrous THF (80 ml) at -78 °C. 2,5-Dibromothiophene (I) (484 mg, 2.0 mmol) was added slowly to the solution, and the mixture was stirred for 30 min. Then, TMSCl (217 mg, 2.0 mmol) in anhydrous THF (20 ml) was added drop wise to the stirred solution over a period of 3 h. The reaction mixture was stirred for another 30 min and ZnBr$_2$ (496 mg, 2.2 mmol) in anhydrous THF (10 ml) was added. After stirring for 15 min the reaction mixture was allowed to warm to room temperature and stirred for another 20 min. 1-Iodo-3,5-dimethylbenzene (510 mg, 2.2 mmol) in anhydrous THF (5 ml) and Pd(PPh$_3$_4) (5 mol%) were added. The solution was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel ($n$-hexane) yielding 280 mg (54 %) of 3b as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$). $\delta$ 0.32 (s, 9 H), 2.33 (s, 6 H), 6.90 (s, 1 H), 7.18 (d, $^3$J = 3.3 Hz, 1 H), 7.23 (s, 2 H), 7.31 (d, $^3$J = 3.3 Hz, 1 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 0.1 (CH$_3$), 21.5 (CH$_3$), 124.2 (CH), 129.4 (CH), 134.5 (C$_{quat}$), 135.1 (C$_{quat}$), 138.5 (CH), 139.8 (C$_{quat}$), 150.2 (C$_{quat}$). EI MS (70 eV, m/z (%)): 260 ([M]+, 44), 245 ([C$_{14}$H$_{17}$SSi]$,^+$, 100), 215 ([C$_{12}$H$_{11}$SSi]$^+$, 5), 123 (9), 115 (43). IR (KBr):
\( \nu = 544 \text{ cm}^{-1} \) (w), 561 (w), 608 (w), 623 (w), 652 (w), 692 (m), 756 (m), 802 (s), 842 (s), 947 (w), 990 (s), 1055 (m), 1182 (w), 1212 (m), 1250 (s), 1323 (w), 1377 (w), 1438 (m), 1526 (w), 1601 (m), 1760 (w), 2858 (m), 2925 (m), 2956 (m). UV/Vis (CHCl\(_2\)): \( \lambda_{\text{max}} \) (ε) 294 nm (12700), 314 nm (21800).

Trimethyl(5-p-tolylthiophen-2-yl)silane (3a, Table 1, Entry 1)

\(^1\)H NMR (300 MHz, CDCl\(_3\)). \( \delta \) 0.33 (s, 9 H) 2.35 (s, 3 H), 7.18 (m, 3 H), 7.31 (d, \( \beta J = 3.4 \text{ Hz}, 1 \) H), 7.51 (d, \( \beta J = 8.2 \text{ Hz}, 2 \) H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) -0.4 (CH\(_3\)), 21.2 (CH\(_3\)), 123.9 (CH), 126.0 (CH), 129.5 (CH), 131.7 (CH), 133.8 (C\(_{\text{quat}}\)), 134.9 (C\(_{\text{quat}}\)), 137.3 (C\(_{\text{quat}}\)), 139.4 (C\(_{\text{quat}}\)). EI MS (70 eV, m/z (%)): 246 ([M]+, 61), 231 ([C\(_{14}\)H\(_{18}\)SSi]+, 100).

(5-(4-Methoxyphenyl)thiophen-2-yl)trimethylsilane (3c, Table 1, Entry 3)

\(^1\)H NMR (500 MHz, CDCl\(_3\)). \( \delta \) 0.32 (s, 9 H) 3.82 (s, 3 H), 6.89 (d, \( \beta J = 8.9 \text{ Hz}, 2 \) H), 7.17 (d, \( \beta J = 3.5 \text{ Hz}, 1 \) H), 7.24 (d, \( \beta J = 3.5 \text{ Hz}, 1 \) H), 7.53 (d, \( \beta J = 8.9 \text{ Hz}, 2 \) H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 0.1 (CH\(_3\)), 55.5 (CH\(_3\)), 114.3 (CH), 123.6 (CH), 127.4 (CH), 127.5 (C\(_{\text{quat}}\)), 135.1 (CH), 139.0 (C\(_{\text{quat}}\)), 149.7 (C\(_{\text{quat}}\)), 159.3 (C\(_{\text{quat}}\)). HR MS (C\(_{14}\)H\(_{18}\)OSSi): calc: 262.0848 found: 262.0847.

(5-(4-Chlorophenyl)thiophen-2-yl)trimethylsilane (3d, Table 1, Entry 4)

\(^1\)H NMR (500 MHz, CDCl\(_3\)). \( \delta \) 0.32 (s, 9 H) 7.18 (d, \( \beta J = 3.6 \text{ Hz}, 1 \) H), 7.31 (d, \( \beta J = 3.6 \text{ Hz}, 1 \) H), 7.32 (d, \( \beta J = 8.5 \text{ Hz}, 2 \) H), 7.52 (d, \( \beta J = 8.5 \text{ Hz}, 2 \) H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 0.2 (CH\(_3\)), 125.0 (CH), 127.5 (CH), 129.3 (CH), 133.3 (C\(_{\text{quat}}\)), 133.4 (C\(_{\text{quat}}\)), 135.4 (CH), 141.0 (C\(_{\text{quat}}\)), 148.5 (C\(_{\text{quat}}\)). EI MS (70 eV, m/z (%)): 266 ([M]+, 36), 251 ([C\(_{13}\)H\(_{15}\)ClSSi]+, 100), 126 (20), 115 (43). IR (KBr): \( \tilde{\nu} = 506 \text{ cm}^{-1} \) (w)626 (w), 731 (w), 755 (m), 804 (s), 817 (s), 947 (m), 995 (m), 1011 (w), 1076 (w), 1093 (m), 1114 (w), 1203 (w), 1251 (m), 1415 (w), 1402 (w), 1434 (w), 1459 (w), 1486 (m), 1509 (w), 1524 (w), 1543 (w), 1561 (w), 1626 (w), 1632 (w), 1655 (w), 1686 (w), 1701 (w), 1719 (w), 1751 (w), 1774 (w), 2356 (w), 2959 (m), 3449 (m). UV/Vis (CHCl\(_2\)): \( \lambda_{\text{max}} \) (ε) 296 nm (13500), 317 nm (7900). Anal. calcd. for C\(_{13}\)H\(_{15}\)ClSSi (266.9): C: 58.51, H: 5.67; found: C: 58.28, H: 5.54.
(5-(4-Fluorophenyl)thiophen-2-yl)trimethylsilane (3e, Table 1, Entry 5)

1H NMR (500 MHz, CDCl3). δ 0.34 (s, 9 H), 7.02-7.09 (m, 2 H), 7.20 (d, J = 3.4 Hz, 1 H), 7.29 (d, J = 3.4 Hz, 1 H), 7.53-7.61 (m, 2 H). 13C NMR (125 MHz, CDCl3): δ 0.12 (CH3), 116.0 (d, J = 21.8 Hz, CH), 124.6 (CH), 127.9 (d, J = 8.0 Hz, CH), 131.0 (Cquat), 135.2 (CH), 140.3 (Cquat), 148.7 (Cquat), 162.5 (d, J = 247.0 Hz, Cquat). EI MS (70 eV, m/z (%)): 250 ([M]+, 39), 235 ([C12H7FSSi]+, 100), 118 (16), 115 (22). IR (KBr): ν/combiningtildeaccent = 580 cm⁻¹ (w), 630 (w), 699 (w), 758 (m), 804 (s), 820 (w), 839 (s), 951 (m), 996 (m), 1013 (w), 1080 (w), 1100 (w), 1163 (w), 1228 (m), 1255 (m), 1301 (w), 1409 (w), 1436 (w), 1498 (m), 1509 (w), 1532 (m), 1560 (w), 1600 (w), 1638 (w), 1655 (w), 1686 (w), 1701 (w), 1719 (w), 1775 (w), 1887 (w), 2960 (m), 3448 (m). UV/Vis (CH2Cl2): λmax (ε) 290 nm (14800), 309 nm (10800). Anal. calcd. for C13H15FSSi (250.4): C: 62.35, H: 6.04; found: C: 62.41, H: 6.26.

Methyl 4-(5-(trimethylsilyl)thiophen-2-yl)benzoate (3f, Table 1, Entry 6)

1H NMR (500 MHz, CDCl3). δ 0.33 (s, 9 H), 3.90 (s, 3 H), 7.21 (d, J = 3.5 Hz, 1 H), 7.44 (d, J = 3.5 Hz, 1 H), 7.66 (d, J = 8.5 Hz, 3 H), 8.01 (d, J = 8.5 Hz, 2 H). 13C NMR (125 MHz, CDCl3): δ 0.1 (CH3), 52.3 (CH3), 125.8 (CH), 128.9 (Cquat), 130.5 (CH), 131.2 (CH), 137.9 (CH), 142.2 (Cquat), 148.3 (Cquat), 167.0 (Cquat).

4-(5-(Trimethylsilyl)thiophen-2-yl)benzonitrile (3g, Table 1, Entry 7)

1H NMR (500 MHz, CDCl3). δ 0.33 (s, 9 H), 7.22 (d, J = 3.4 Hz, 1 H), 7.44 (d, J = 3.4 Hz), 7.60 (d, J = 7.9 Hz, 2 H), 7.68 (d, J = 7.9 Hz, 2 H). 13C NMR (125 MHz, CDCl3): δ 0.0 (CH3), 110.6 (Cquat), 119.1 (Cquat), 126.3 (CH), 132.8 (CH), 132.9 (CH), 135.5 (CH), 138.8 (Cquat), 143.3 (Cquat), 147.9 (Cquat). EI MS (70 eV, m/z (%)): 257 ([M]+, 34), 242 ([C13H12NSSi]+, 100), 121 (10), 115 (16). IR (KBr): ν = 525 cm⁻¹ (w), 554 (w), 629 (w), 704 (w), 762 (m), 813 (s), 844 (s), 948 (m), 991 (s), 1075 (m), 1177 (m), 1201 (m), 1251 (s), 1317 (m), 1410 (m), 1492 (m), 1528 (m), 1602 (s), 2226 (s), 2962 (s), 3419 (m). UV/Vis (CH2Cl2): λmax (ε) 319 nm (26200), 337 (16600). Anal. calcd. for C14H15NSSi (257.4): C: 65.32, H: 5.87; N: 5.44; found: C: 65.15, H: 5.36; N: 5.36.

3-(5-(Trimethylsilyl)thiophen-2-yl)pyridine (3h, Table 1, Entry 8)

1H NMR (500 MHz, CDCl3). δ 0.33 (s, 9 H), 7.22 (d, J = 3.4 Hz, 1 H), 7.28 (dd, J = 7.9 Hz, 4.8 Hz, 1 H), 7.39 (d, J = 3.4 Hz, 1 H), 7.82-7.89 (m, 1 H), 8.48 (dd, J = 4.7 Hz, 1.2 Hz, 1 H), 8.87 (d,
Representative Procedure - Synthesis of 5,5″-bis(trimethylsilyl)-2,2‴:5′,2″-terthiophene (4a)

In a flame-dried Schlenk flask under argon atmosphere n-butyllithium (1.6 M in n-hexane, 2.5 ml, 4.0 mmol) and TMEDA (0.6 ml, 4.0 mmol) were dissolved in anhydrous THF (80 ml) at -78 °C. 2,5-Dibromothiophene (1, 484 mg, 2.0 mmol) was added slowly to the solution, and the mixture was stirred for 30 min. Then, TMSCl (217 mg, 2.0 mmol) in anhydrous THF (20 ml) was added drop wise to the stirred solution over a period of 3 h. The reaction mixture was stirred for another 30 min and ZnBr₂ (496 mg, 2.2 mmol) in anhydrous THF (10 ml) was added. After stirring for 15 min the reaction mixture was allowed to warm to room temperature and stirred for another 20 min. Finally 2,5-Diiodothiophene (269 mg, 0.8 mmol) and Pd(PPh₃)₄ (5 mol%) were added. The solution was stirred at room temperature for 16 h and afterwards the solvent removed under reduced pressure and the residue purified by flash chromatography on silica gel (n-hexane) yielding 200 mg (67 %) of 3a as a light yellow solid.

¹H NMR (500 MHz, CDCl₃). δ 0.32 (s, 18 H), 7.06 (s, 2 H), 7.12 (d, ³J = 3.4 Hz, 2 H), 7.20 (d, ³J = 3.4 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ 0.1 (CH₃), 124.6 (CH), 125.1 (CH), 135.0 (CH), 136.5 (C_quat), 140.2 (C_quat), 142.4 (C_quat). EI MS (70 eV, m/z (%)): 393 ([M⁺]⁺, 2.5), 320 (47), 305 (46), 261 (47), 215 (49), 203 (12), 184 (12), 171 (36), 137 (17), 115 (100), 109 (10).

1,4-Bis(5-(trimethylsilyl)thiophen-2-yl)benzene (4b)

¹H NMR (500 MHz, CDCl₃). δ 0.34 (s, 18 H), 7.20 (d, ³J = 3.4 Hz, 2 H), 7.37 (d, ³J = 3.4 Hz, 2 H), 7.61 (s, 4 H). ¹³C NMR (125 MHz, CDCl₃): δ 0.1 (CH₃), 124.6 (CH), 126.5 (CH), 133.7 (C_quat), 135.3 (CH), 140.4 (C_quat), 149.3 (C_quat). EI MS (70 eV, m/z (%)): 386 ([M⁺]⁺, 20), 317 ([C₁₉H₂₃SSi₂]⁺, 18), 115 (45), 91 (14), 73 (100). IR (KBr): v = 630 cm⁻¹ (w), 698 (w), 758 (m), 804 (s), 840 (s), 950 (m), 1001 (m), 1017 (w), 1047 (w), 1082 (w), 1206 (w), 1252 (m), 1320 (w), 1434 (w), 1491 (w), 1541 (w), 1637 (w), 2959 (m), 3424 (m). UV/Vis (CH₂Cl₂): λ_max (ε) 264 nm (5700), 336 (31400), 357 (20500). Anal. calcd. for C₂₀H₂₆SSi₂ (386.7): C: 62.12, H: 6.78; found: C: 62.22, H: 6.92.