Sulfur Heterocyclization and 1,3-Migration of Silicon in Reaction of 1,3-Diynes with Sodium Triisopropylsilanethiolate: One-Pot Synthesis of 2,5-Disubstituted 3-(Triisopropylsilyl)thiophenes

Jialiang Tang, Ling Ming, Xiaoming Zhao*

Department of Chemistry, State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Siping Road 1239, Shanghai 200092, P. R. of China
Fax +86(21)65981376; E-mail: xmzhao08@mail.tongji.edu.cn

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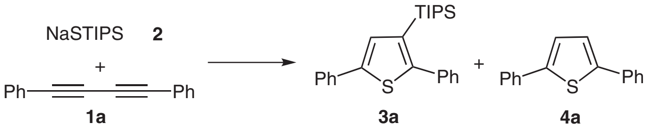
Abstract: Sulfur heterocyclization and 1,3-migration of silicon have been realized in the reactions of a range of 1,3-diynes with sodium triisopropylsilanethiolate in *N*,*N*-dimethylformamide. These provided 40–72% yields of 2,5-disubstituted 3-(triisopropylsilyl)thiophenes and up to 50% yield of 2,5-disubstituted thiophenes.

Key words: 1,3-diynes, cyclizations, 1,3-migration of silicon, thiophene, sulfur heterocycles

Silylated heteroaromatics are very important functionalities in materials displaying optical properties.[1] Thiophenes with a silyl group (SiR_3) can undergo significant transformations for the preparation of functionalized thiophenes.[2] Transition-metal-catalyzed heterocyclization of 1,3-diynes has also received great attention in the past decades.[3] In particular, five-membered heterocycles have found various applications in medicine,[4] agriculture,[5] and materials chemistry.[6] Conventional methods for the synthesis of silylated thiophenes require a metal catalyst, thiophene, and silicon reagent.[6c,7] Recently Nakamura and co-workers reported a gold-catalyzed intramolecular cyclization and a [1,3]-migration of a silyl group of (*o*-alkynylphenylsulfanyl)silanes, producing silylated thiophenes.[8] To date, metal-free cyclization and 1,3-migration of silicon in the reaction between a 1,3-diyne and a sulfur nucleophile has not been explored. In this paper, we report the first one-pot synthesis of 2,5-disubstituted 3-(triisopropylsilyl)thiophenes by means of sulfur heterocyclization and a 1,3-migration of triisopropylsilyl in the reactions of various 1,3-diynes with sodium triisopropylsilanethiolate (NaSTIPS; **2**).

We began with the investigation of the reaction between 1,4-diphenylbuta-1,3-diyne (**1a**) and sodium triisopropylsilanethiolate (**2**) to form a silylated thiophene (Table 1). First, the reaction of **1a** with sodium triisopropylsilanethiolate (**2**) in the absence of transition metal[7] in *N*,*N*-dimethylformamide was tested at room temperature under an air atmosphere; this led to the formation of a trace amount of 2,5-diphenylthiophene (**4a**)[9] (entry 1). When the temperature was increased to 50 °C, the yield of this reaction improved slightly (entry 2). Various solvents such as dimethyl sulfoxide, acetonitrile, toluene, tetrahydrofuran, and nitrobenzene were also screened (entries 3–7).

Table 1 Optimization of Metal-Free Sulfur Heterocyclization of 1,4-Diphenylbuta-1,3-diyne (**1a**) with Sodium Triisopropylsilanethiolate (**2**)[a]



Entry	Solvent	Ratio **1a**/**2**	Temp (°C)	Time (h)	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	DMF	1:1.2	25	18	–	trace
2	DMF	1:1.2	50	18	–	10
3	DMSO	1:1.2	50	18	–	13[c]
4	MeCN	1:1.2	50	18	–	trace
5	toluene	1:1.2	50	18	–	–
6	THF	1:1.2	50	18	–	–
7	$PhNO_2$	1:1.2	50	18	–	–
8	DMF	1:1.2	75	18	–	11
9	DMF	1:1.2	100	18	3	14
10	DMF	1:1.2	125	18	15	29
11	DMF	1:1.2	150	18	25	32
12	DMF	1:2	150	1	44	55
13	DMF	1:3	150	1	30	69
14	DMF	2:1	125	18	18	33
15[d]	DMF	1:2	150	1	52	46
16[e]	DMF	1:2	150	1	–	–

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2–0.6 mmol), solvent (2.0 mL), under air.
[b] Isolated yield.
[c] Two other byproducts were obtained.
[d] Under argon.
[e] HSTIPS was used instead of NaSTIPS under argon.

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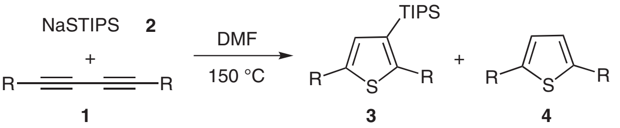
We found that *N*,*N*-dimethylformamide and dimethyl sulfoxide both gave **4a** in 10–13% yield, and dimethyl sulfoxide gave some byproducts, whereas other solvents were ineffective for this reaction (Table 1, entries 4–7). To study the influence of temperature on this reaction, we performed this reaction at a range of temperatures, from 50 to 150 °C (entries 2, 8–12). When the reaction temperature was increased from 75 to 100 °C, 2,5-diphenyl-3-(triisopropylsilyl)thiophene (**3a**)[10] was also observed (entry 9). These results suggested that a [1,3]-migration of triisopropylsilyl occurred during the course of the reaction.[8a] When the reaction was carried out at 150 °C, 25% yield of **3a** and 32% yield of **4a** were obtained upon completion of the reaction (entry 11). Variation of the ratio of **1a**/**2** has a considerable influence on the efficiency of this reaction. Excess of **2** led to improvement in the formation of **4a** (entries 12, 13). Two equivalents of **2** resulted in a superior yield of **3a** and a 55% yield of **4a** (entry 12). Notably, when the same reaction was carried out under argon, a 52% yield of **3a** and 46% yield of **4a** were obtained (entry 15). These results indicated that moisture has a considerable influence on the formation of **4a** (entry 12 vs. 15). We found that it is difficult to suppress the formation of **4a** during the reaction. A control experiment revealed that **3a** cannot be converted into **4a** under the identical reaction conditions. However, both **3a** and **4a** are of great importance in material chemistry.[1,2] This reaction completely failed when triisopropylsilanethiol was used as a nucleophile instead of sodium triisopropylsilanethiolate (entry 16).[11] Moreover, different silanethiolates, such as sodium triphenylsilanethiolate, were also explored under the same conditions, and only **4a** was obtained.

The scope of the sulfur heterocyclization and 1,3-migration of triisopropylsilyl in the reactions of various 1,3-diynes **1** with sodium triisopropylsilanethiolate (**2**) was then studied. As shown in Table 2, the reactions of 1,3-diynes **1a**–**g** with electron-donating (e.g., 3-methyl, 4-methyl, 4-pentyl, and 4-phenyl) or electron-withdrawing (e.g., 4-bromo and 4-fluoro) groups on the phenyl ring furnished 2,5-disubstituted 3-(triisopropylsilyl)thiophenes **3a**–**g** in 43–69% yields; trace to 50% yields of **4a**–**g** were also obtained (entries 1–7). Compound **4d** may find application as a liquid crystal.[6b] Both **3f** and **4f** contain the 4-bromophenyl group, which could be used in palladium-mediated couplings. The steric factor at the 4-position of aryl-substituted 1,3-diynes has a great influence on the chemoselectivity of this reaction. For example, **1e** bearing a phenyl group at the 4-position of the phenyl ring gave the corresponding **3e** as the major product (69% yield) along with a trace amount of **4e** (entry 5). When 1,4-bis(2-thienyl)-substituted **1h** was utilized as the substrate, it gave rise to 72% yield of **3h** and 21% yield of **4h** (entry 8). In contrast, the reaction of 1,4-bis(3-thienyl)-substituted **1i** gave 40% yield of **3i** along with 34% yield of **4i** (entry 9). It is noteworthy that either **3** or **4** may display fluorescence.[9,10]

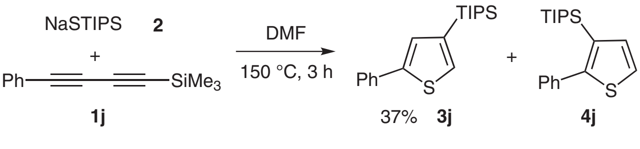
Table 2 Sulfur Heterocyclization and 1,3-Migration of Triisopropylsilyl of 1,3-Diynes **1** with Sodium Triisopropylsilanethiolate (**2**)[a]



Entry	R	Time (h)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	Ph	1	**3a**, 52	**4a**, 46
2	3-MeC$_6$H$_4$	1	**3b**, 55	**4b**, 44
3	4-MeC$_6$H$_4$	2	**3c**, 43	**4c**, 46
4	4-Me(CH$_2$)$_4$C$_6$H$_4$	2	**3d**, 49	**4d**, 50
5	4-PhC$_6$H$_4$	1	**3e**, 69	**4e**, trace
6	4-BrC$_6$H$_4$	1	**3f**, 53	**4f**, 46
7	4-FC$_6$H$_4$	1	**3g**, 53	**4g**, 45
8	2-thienyl	1	**3h**, 72	**4h**, 21
9	3-thienyl	1	**3i**, 40	**4i**, 34

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), DMF (2.0 mL), 150 °C, under argon.
[b] Isolated yield.

An unsymmetrical 1,3-diyne was also investigated as a substrate in this reaction and a representative example is demonstrated in Scheme 1. The reaction of 1-phenyl-4-(trimethylsilyl)buta-1,3-diyne (**1j**)[12] with sodium triisopropylsilanethiolate (**2**) under the optimized conditions afforded 2-phenyl-4-(triisopropylsilyl)thiophene (**3j**) in 37% yield (Scheme 1). Favorable attack of sodium triisopropylsilanethiolate at the 4-position of **1j** depends on the nature of the polarized conjugated system of **1j**. Removal of trimethylsilyl from either the thiophene ring or **1j** may occur in this case, possibly resulting from the use of an excess of sodium triisopropylsilanethiolate.[13] Experimental evidence supporting this hypothesis is that the reaction between buta-1,3-diynylbenzene (generated by desilylation of **1j** with KOH/MeOH under reflux) and sodium triisopropylsilanethiolate (**2**) under the optimized conditions gave **3j**, but in 8% yield. Indeed, no 2-phenyl-3-(triisopropylsilyl)thiophene (**4j**) was obtained in this case (Scheme 1).



Scheme 1 Sulfur heterocyclization and 1,3-migration of triisopropylsilyl of **1j** with sodium triisopropylsilanethiolate (**2**)

The possible application of these compounds in the area of materials was investigated. The photophysical properties of **3a**, **3d**, **3g**, and **3h** were studied by using UV-vis and photoluminescence (PL) spectroscopy. The results are shown in Figures 1 and 2. The λ_{max} values of both **3d** and **3g** blue-shifted by at least 17 nm compared with that of **3a**. These results reveal that the introduction of either fluoro or *n*-pentyl in the phenyl ring considerably reduce the conjugation effect of **3a**. Maximum absorption wavelength ($\lambda_{abs(max)}$) values, emission maximum ($\lambda_{em(max)}$), and Stokes shift of **3a**, **3d**, **3g**, and **3h** are listed in Table 3. In comparison with that of the known **4h** (λ_{max} = 354 nm),[14] the λ_{max} value of **3h** blue-shifted by 53 nm, which results from the introduction of a triisopropylsilyl group to the thiophene ring (Figure 1 and Table 3).

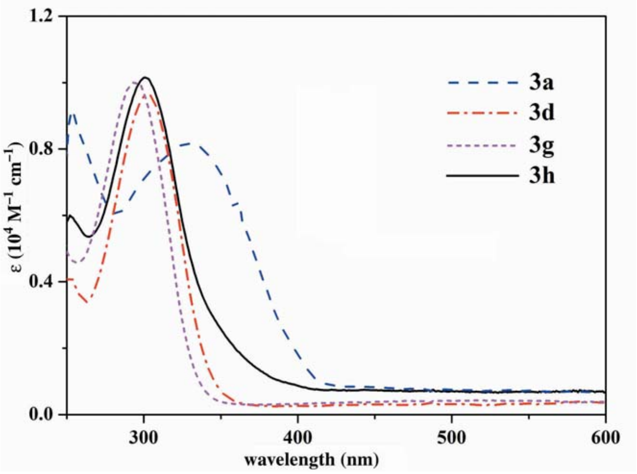


Figure 1 UV-vis spectra of **3a**, **3d**, **3g**, and **3h** in ethyl acetate

Table 3 Optical Absorption Wavelength [$\lambda_{abs(max)}$], Fluorescence Emission Wavelength [$\lambda_{em(max)}$], and Stokes Shifts for **3a**, **3d**, **3g**, and **3h**

Compound	$\lambda_{abs(max)}$, nm	$\lambda_{em(max)}$, nm	Stokes shift,[a] nm
3a	350	439	89
3d	333	405	72
3g	293	395	102
3h	301	397	96

[a] The Stokes shift is the difference between $\lambda_{abs(max)}$ and $\lambda_{em(max)}$.

The fluorescence emission wavelength ($\lambda_{em(max)}$) data of **3a**, **3d**, **3g**, and **3h** (Figure 2 and Table 3) showed a similar trend to that of the absorption wavelength ($\lambda_{abs(max)}$) data of these compounds. Compound **3a** exhibited the highest $\lambda_{em(max)}$ value and **3g** showed the largest Stokes shift (Table 3).

In summary, we have developed a convenient method for the preparation of 2,5-disubstituted 3-(triisopropylsilyl)thiophenes by sulfur heterocyclization and 1,3-migration of silicon during the reactions of various 1,3-diynes with sodium triisopropylsilanethiolate. To the best of our knowledge, this is the first reported method for the synthesis of 2,5-disubstituted 3-(triisopropylsilyl)thiophenes from 1,3-diynes.

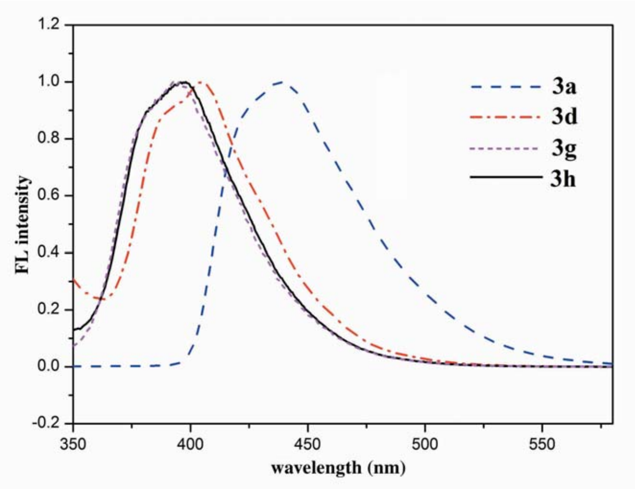


Figure 2 Fluorescence spectra of **3a**, **3d**, **3g**, and **3h** in ethyl acetate

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-400 spectrometer; samples were prepared in $CDCl_3$ with TMS as an internal standard. ^{19}F NMR spectra were obtained at 376 MHz, and CF_3CO_2H was used as internal standard. Mass spectra were obtained on an Agilent 5973N spectrometer. Melting points were recorded by using a WRS-2A micro-melting-point apparatus and are uncorrected. A Nicolet AVATAR 360 FT-IR spectrophotometer was used for IR spectra. UV-vis spectra were recorded on an Agilent 8453 spectrometer at r.t.; samples were prepared as diluted EtOAc solns. Photoluminescence spectra were recorded on a Hituchi F-2700 luminescence spectrometer; samples were diluted EtOAc solns. Analytical TLC was performed on glass plates precoated with GF 254 silica gel impregnated with fluorescent indicator. All manipulations were carried out under an argon atmosphere and by using standard Schlenk techniques, unless stated otherwise. All glassware was oven- or flame-dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

Thiophenes 3a–j and 4a–i; General Procedure

The appropriate 1,3-diyne **1** (0.2 mmol) and NaSTIPS (**2**; 0.4 mmol) were dissolved in DMF (2 mL) in a dry Schlenk tube filled with argon. The reaction mixture was stirred at 150 °C for 1–2 h. After completion of the reaction, as indicated by TLC, the mixture was quenched by the addition of brine (20 mL), and then extracted with Et_2O (3 × 5 mL). The combined organic layer was dried (Na_2SO_4). The solvent was evaporated and the crude product was purified by column chromatography (silica gel, PE); this gave thiophenes **3** and **4** as products. The 1,3-diynes[15] and NaSTIPS[16] were prepared according to known procedures.

2,5-Diphenyl-3-(triisopropylsilyl)thiophene (3a)

Yield: 41.1 mg (52%); colorless oil.

IR (KBr): 513, 639, 669, 705, 741, 762, 1143, 1264, 1457, 2849, 2877, 2973 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 7.2 Hz, 18 H), 1.11–1.17 (m, 3 H), 7.24–7.39 (m, 7 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.60 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3, 18.9, 125.9, 127.2, 127.5, 128.1, 128.8, 130.4, 130.7, 133.9, 134.4, 136.6, 143.2, 151.2.

ESI-MS: *m*/*z* = 392 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{25}H_{32}SSi$: 392.1994; found: 392.1990.

2,5-Di(*m*-tolyl)-3-(triisopropylsilyl)thiophene (3b)
Yield: 46.3 mg (55%); colorless oil.

IR (KBr): 668, 706, 741, 789, 1264, 1653, 2878 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.00 (d, *J* = 7.2 Hz, 18 H), 1.10–1.19 (m, 3 H), 2.36 (s, 3 H), 2.39 (s, 3 H), 7.07 (d, *J* = 7.6 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.20–7.31 (m, 5 H), 7.41 (s, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3, 18.9, 21.3, 21.4, 123.1, 126.7, 127.4, 127.4, 128.0, 128.7, 128.8, 130.6, 131.1, 133.6, 134.4, 136.5, 137.0, 138.4, 143.1, 151.3.

ESI-MS: *m*/*z* = 420 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{27}H_{36}SSi$: 420.2307; found: 420.2306.

2,5-Di(*p*-tolyl)-3-(triisopropylsilyl)thiophene (3c)
Yield: 36.2 mg (43%); mp 101–103 °C.

IR (KBr): 453, 518, 1507, 1540, 1559, 1636, 1653, 1683 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.00 (d, *J* = 7.2 Hz, 18 H), 1.10–1.19 (m, 3 H), 2.36 (s, 3 H), 2.39 (s, 3 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.24 (s, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3, 18.9, 21.2, 21.3, 125.8, 128.2, 129.5, 130.2, 131.7, 133.4, 133.7, 136.9, 137.8, 143.1, 150.9.

ESI-MS: *m*/*z* = 420 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{27}H_{36}SSi$: 420.2307; found: 420.2303.

2,5-Bis(4-pentylphenyl)-3-(triisopropylsilyl)thiophene (3d)
Yield: 52.2 mg (49%); colorless oil.

IR (KBr): 787, 1559, 1636, 2863, 2959 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.90 (t, *J* = 6.8 Hz, 6 H), 0.99 (d, *J* = 7.2 Hz, 18 H), 1.13–1.16 (m, 3 H), 1.30–1.34 (m, 8 H), 1.61–1.66 (m, 4 H), 2.59–2.66 (m, 4 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.24 (s, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3, 13.4, 13.5, 14.0, 14.0, 18.1, 18.3, 18.9, 31.0, 31.1, 31.3, 31.5, 125.8, 127.5, 128.8, 130.2, 130.2, 131.9, 133.6, 133.9, 142.0, 142.9, 143.0, 150.9.

ESI-MS: *m*/*z* = 532 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{35}H_{52}SSi$: 532.3559; found: 532.3553.

2,5-Bis(biphenyl-4-yl)-3-(triisopropylsilyl)thiophene (3e)
Yield: 75.2 mg (69%); mp 170–172 °C.

IR (KBr): 442, 516, 738, 1264, 1507, 1521, 1541, 1559, 1636, 2053 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.03 (d, *J* = 7.2 Hz, 18 H), 1.16–1.23 (m, 3 H), 7.33–7.39 (m, 3 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 2 H), 7.56–7.63 (m, 8 H), 7.67 (d, *J* = 7.2 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.4, 19.0, 126.2, 126.3, 126.9, 127.0, 127.3, 127.5, 127.5, 128.8, 128.8, 130.7, 130.9, 133.4, 134.2, 135.6, 140.0, 140.5, 140.6, 140.8, 142.9, 150.9.

ESI-MS: *m*/*z* = 544 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{37}H_{40}SSi$: 544.2620; found: 544.2618.

2,5-Bis(4-bromophenyl)-3-(triisopropylsilyl)thiophene (3f)
Yield: 58.4 mg (53%); mp 136–137 °C.

IR (KBr): 655, 669, 1345, 1612, 1631, 1641, 1659, 2342, 2360 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.00 (d, *J* = 6.8 Hz, 18 H), 1.11–1.18 (m, 3 H), 7.26 (s, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.8 Hz, 2 H); 7.47–7.51 (m, 4 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3, 18.9, 121.2, 122.6, 127.4, 130.8, 131.2, 131.8, 132.0, 133.1, 134.7, 135.4, 142.4, 149.9.

ESI-MS: *m*/*z* = 550 [M + 2]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{25}H_{30}Br_2SSi$: 548.0204; found: 548.0209.

2,5-Bis(4-fluorophenyl)-3-(triisopropylsilyl)thiophene (3g)
Yield: 45.4 mg (53%); mp 107–108 °C.

IR (KBr): 516, 624, 678, 1234, 1385, 1457, 1496, 1507, 1559, 1636, 2050 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.00 (d, *J* = 7.6 Hz, 18 H), 1.08–1.16 (m, 3 H), 7.01–7.09 (m, 4 H), 7.20 (s, 1 H), 7.42–7.46 (m, 2 H), 7.53–7.56 (m, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.2, 18.9, 114.5 ($J_{\text{C-F}}$ = 21 Hz), 115.8 ($J_{\text{C-F}}$ = 21 Hz), 127.5, 127.6, 130.5, 130.6, 132.0, 132.1, 132.4, 132.5, 134.5, 142.3, 149.7, 162.2 ($J_{\text{C-F}}$ = 246 Hz), 162.8 ($J_{\text{C-F}}$ = 246 Hz).

^{19}F NMR (376 MHz, CDCl$_3$): δ = –113.55, –114.84.

ESI-MS: *m*/*z* = 428 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{25}H_{30}F_2SSi$: 428.1806; found: 428.1807.

2,5-Bis(2-thienyl)-3-(triisopropylsilyl)thiophene (3h)
Yield: 58.3 mg (72%); colorless oil.

IR (KBr): 563, 740, 824, 1019, 1130, 1263, 1472, 1541, 1653, 2877, 2978 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.04 (d, *J* = 7.2 Hz, 18 H), 1.20–1.29 (m, 3 H), 6.99 (d, *J* = 4.0 Hz, 1 H), 7.01 (d, *J* = 4.0 Hz, 1 H), 7.13–7.14 (m, 2 H), 7.15 (s, 1 H), 7.20 (d, *J* = 6.0 Hz, 1 H), 7.32 (d, *J* = 6.0 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.4, 19.0, 123.9, 124.3, 126.6, 127.8, 128.8, 131.4, 136.8, 136.8, 136.9, 137.5, 141.4.

ESI-MS: *m*/*z* = 404 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{28}S_3Si$: 404.1122; found: 404.1127.

2,5-Bis(3-thienyl)-3-(triisopropylsilyl)thiophene (3i)
Yield: 32.4 mg (40%); mp 84–86 °C.

IR (KBr): 514, 654, 676, 706, 740, 773, 839, 1141, 1264, 1636, 2069, 2864, 2944 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.02 (d, *J* = 7.2 Hz, 18 H), 1.13–1.22 (m, 3 H), 7.16–7.17 (m, 2 H), 7.27–7.35 (m, 5 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3, 18.9, 119.4, 124.6, 124.8, 126.2, 126.2, 130.1, 130.7, 134.4, 135.4, 136.4, 138.0, 144.0.

ESI-MS: *m*/*z* = 404 [M]$^+$.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{28}S_3Si$: 404.1122; found: 404.1125.

2-Phenyl-4-(triisopropylsilyl)thiophene (3j)
Yield: 23.4 mg (37%); colorless oil.

IR (KBr): 487, 668, 691, 717, 731, 766, 1154, 1237, 1492, 2861, 2884, 2948 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.10 (d, *J* = 7.2 Hz, 18 H), 1.31–1.39 (m, 3 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.33–7.39 (m, 4 H), 7.62 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 11.4, 18.7, 126.2, 127.2, 128.8, 128.9, 132.4, 134.6, 137.1, 144.3.

ESI-MS: *m*/*z* = 316 [M]$^+$.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{19}H_{28}SSi$: 316.1681; found: 316.1684.

2,5-Diphenylthiophene (4a)[17]
Yield: 21.7 mg (46%); mp 148–150 °C.

IR (KBr): 685, 749, 804, 903, 944, 1079, 1326, 1457, 1640, 1873, 1934, 2847, 2914, 2956 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 7.6, 7.2 Hz, 2 H), 7.31 (s, 2 H), 7.41 (dd, *J* = 8.0, 7.2 Hz, 4 H), 7.65 (d, *J* = 8.0 Hz, 4 H).

2,5-Di(*m*-tolyl)thiophene (4b)[18]
Yield: 23.3 mg (44%); mp 83–85 °C.

IR (KBr): 592, 685, 778, 813, 1454, 1582, 1604, 2844, 2917, 2962 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 6 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 7.28 (dd, *J* = 9.2, 6.8 Hz, 2 H), 7.27 (s, 2 H), 7.44 (d, *J* = 7.6 Hz, 2 H), 7.45 (s, 2 H).

2,5-Di(*p*-tolyl)thiophene (4c)[19]
Yield: 24.3 mg (46%); mp 170–172 °C.

IR (KBr): 467, 797, 826, 938, 1066, 1130, 1454, 1556, 1649, 1771, 1899, 2853, 2914, 2966 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6 H), 7.18 (d, *J* = 8.0 Hz, 4 H), 7.22 (s, 2 H), 7.51 (d, *J* = 8.0 Hz, 4 H).

2,5-Bis(4-pentylphenyl)thiophene (4d)[20]
Yield: 37.6 mg (50%); mp 132–134 °C.

IR (KBr): 514, 745, 796, 835, 889, 937, 1011, 1081, 1120, 1261, 1415, 1450, 1498, 1540, 2850, 2930, 2955, 3052 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.4 Hz, 6 H), 1.29–1.41 (m, 8 H), 1.57–1.70 (m, 4 H), 2.61 (t, *J* = 7.6 Hz, 4 H), 7.19 (d, *J* = 8.0 Hz, 4 H), 7.23 (s, 2 H), 7.53 (d, *J* = 8.0 Hz, 4 H).

2,5-Bis(4-bromophenyl)thiophene (4f)[21]
Yield: 36.2 mg (46%); mp 202–203 °C.

IR (KBr): 467, 746, 791, 826, 935, 1117, 1262, 1332, 1399, 1447, 1559, 1627, 1652, 1774, 1899 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 2 H), 7.47 (d, *J* = 8.8 Hz, 4 H), 7.51 (d, *J* = 8.4 Hz, 4 H).

2,5-Bis(4-fluorophenyl)thiophene (4g)[22]
Yield: 24.5 mg (45%); mp 159–160 °C.

IR (KBr): 493, 551, 707, 733, 794, 836, 896, 938, 1101, 1265, 1300, 1412, 1457, 1502, 1521, 1652, 1764, 1886, 2847, 2917, 2988, 3052, 3078 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.06–7.11 (m, 4 H), 7.20 (s, 2 H), 7.55–7.59 (m, 4 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –114.30.

2,5-Bis(2-thienyl)thiophene (4h)[23]
Yield: 10.4 mg (21%); mp 120–121 °C.

IR (KBr): 468, 703, 738, 807, 822, 843, 1264, 1636, 1653, 2363 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 3.6 Hz, 1 H), 7.03 (d, *J* = 4.0 Hz, 1 H), 7.08 (s, 2 H), 7.17 (d, *J* = 0.8 Hz, 1 H), 7.18 (d, *J* = 0.8 Hz, 1 H), 7.21 (d, *J* = 0.8 Hz, 1 H), 7.22 (d, *J* = 1.2 Hz, 1 H).

2,5-Bis(3-thienyl)thiophene (4i)[24]
Yield: 16.9 mg (34%); mp 189–190 °C.

IR (KBr): 462, 714, 753, 827, 834, 851, 1189, 1574, 1683, 2257, 2386 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.12 (s, 2 H), 7.31 (d, *J* = 5.2 Hz, 1 H), 7.32 (d, *J* = 5.2 Hz, 1 H), 7.34–7.38 (m, 4 H).

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