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Arylation

Programmed Site-Selective Palladium-Catalyzed Arylation of Thieno[3,2-*b*]thiophene

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Abstract: Mono-, di-, tri-, and tetraarylated thieno[3,2-*b*]thiophenes were synthesized by direct site-selective Pd-catalyzed C–H activation reactions with various aryl bromides in the presence of a phosphine-free $Pd(OAc)_2$/KOAc catalyst system in *N*,*N*-dimethylacetamide (DMAc). The arylation of 2-arylthieno[3,2-*b*]thiophene took place at the C3 position if the 2-aryl substituents possessed electron-withdrawing groups and at the C5 position if they were bulky and possessed electron-donating groups.

Introduction

Recently, the direct palladium-catalyzed arylation of arenes and heteroarenes by C–H bond activation by using aryl halides has been extensively developed.[1,2] It has become a powerful method[2] for the rapid construction and diversification of highly functionalized molecules. Until now, the palladium-catalyzed arylation method has found successful applications in the synthesis of bioactive natural products, drugs, and fine chemicals. In addition, it plays an essential role in the agrochemical industry and in materials science. Relative to classical cross-coupling reactions (e.g., Stille, Suzuki–Miyaura, Negishi, Kumada, etc.),[3–6] palladium-catalyzed C–H functionalization has several advantages concerning the unnecessary prefunctionalization of the substrates and the preparation of organometallic reagents. In this context, direct C–H bond activation has proved to be a straightforward and efficient tool for chemists in terms of atom economy, the production of less waste, and more environmentally friendly reaction conditions.

In recent decades, research related to the employment of functionalized thieno[3,2-*b*]thiophene as a basic building block has rapidly gained attention. Thieno[3,2-*b*]thiophene is known as an important building block in the structures of semiconductor polymers, molecular electronics, and electronic devices.[7,8] Because of intermolecular sulfur–sulfur interactions, organic materials containing the thieno[3,2-*b*]thiophene moiety may have increased electronic transport between neighboring molecules. In addition, the electronic properties, the solubility, and the molecular packing of various materials can be significantly changed if substituents are introduced into the core structure of the materials.[7,8]

For the purpose of fine-tuning the electronic and physical properties of thieno[3,2-*b*]thiophene-containing materials, many synthetic methods have been developed, especially those involving the use of conventional Pd-catalyzed cross-coupling reactions. The liquid-crystalline semiconducting polymers pBTTT and pQT[9–11] (Scheme 1) were reported to show valuable high charge-carrier mobility for transistor performance. Semiconductive polymers containing the thieno[3,2-*b*]thiophene unit (i.e., pBTTT and pQT) were prepared by palladium-catalyzed Stille cross-coupling reactions between 2,5-dibromothieno[3,2-*b*]thiophene and various substituted 2-thienylstannanes. Similarly, isoindigo-based low-band-gap conjugated polymers for application in photovoltaic devices were synthesized by the Stille cross-coupling reaction of 2,5-bis(tri-

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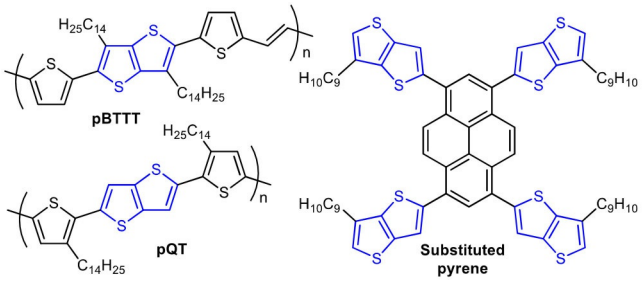

Scheme 1. Structures of polymers (pBTTT and pQT) and a pyrene-based organic semiconductor containing the thieno[3,2-*b*]thiophene building block.

methylstannyl)thieno[3,2-*b*]thiophene and 6,6′-dibromoisoindigo.[12] The star-shaped organic semiconductor 1,3,6,8-tetera(-thieno[3,2-*b*]thien-2-yl)pyrene[13] obtained from the Stille cross-coupling reaction of 1,3,6,8-tetrabromopyrene and tributyl(6-nonylthieno[3,2-*b*]thien-2-yl)stannane was successfully applied in the development of new organic light-emitting diodes (OLEDs). Several well-soluble thieno[3,2-*b*]thiophene-based oligomers[14] and 2,5-di(2-azulenyl)thieno[3,2-*b*]thiophenes,[15] which were constructed by Suzuki–Miyaura cross-coupling reactions of 2,5-disubstituted thieno[3,2-*b*]thiophenyl pinacolato boronic ester and 2-iodoazulene or 2-bromo- or 2,5-dibromothieno[3,2-*b*]thiophene, showed high hole mobilities, small transition energies, and high-order orientations in the crystalline state. These p-channel organic field-effect transistors (OFETs) demonstrated promising performance owing to the presence of the thieno[3,2-*b*]thiophene moiety.[7,16,17] Fluorescent boron–nitrogen heteroacenes[18] containing the thieno[3,2-*b*]thiophene building block were constructed by the Suzuki–Miyaura cross-coupling reaction of dibromothieno[3,2-*b*]thiophene isomers and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine, followed by the insertion of boron atoms with phenyldicholorborane.

Clearly, functionalization of the thieno[3,2-*b*]thiophene building block plays a remarkable role in the development of novel organic materials with promising electronic properties. In 2010, Knochel and Kunz reported the full functionalization of all four positions of thieno[3,2-*b*]thiophene by selective multiple magnesiation of 2,5-dichlorothieno[3,2-*b*]thiophene.[19] Very recently, Miura and co-workers[20] published a study on the convenient palladium-catalyzed direct alkenylation of thieno[3,2-*b*]thiophene. This protocol provided a facile route for the regioselective synthesis of mono- and dialkenylated thieno[3,2-*b*]thiophenes at the C-2 and/or C-5 positions. Multiarylated thieno[3,2-*b*]thiophenes prepared by sequential Suzuki–Miyaura cross-coupling reactions between tetrabromothieno[3,2-*b*]thiophene and various arylboronic acids were reported in our recent work.[21] In this context, the direct arylation of thieno[3,2-*b*]thiophene by site-selective C–H bond activation is straightforward, as it provides a more environmentally friendly and atom-economical approach to multiarylated thieno[3,2-*b*]thiophene without the employment of halogenated thieno[3,2-*b*]thiophenes or the preparation of the corresponding organometallic reagents.

Herein, we wish to report a new and efficient route for the synthesis of mono-, di-, tri-, and tetraarylated thieno[3,2-*b*]thiophenes with controllable site selectivity by the palladium-catalyzed direct arylation of thieno[3,2-*b*]thiophene with aryl bromides by using a low catalyst loading.

Results and Discussion

First, the starting material, thieno[3,2-*b*]thiophene (**1**) was synthesized by using Fuller's procedure.[22] Pioneering work reported by Ohta et al.[23] in 1990 for the direct arylation of thiophene, furan, and thiazole gave medium-to-good yields by using 5 mol% $Pd(PPh_3)_4$ as the catalyst. Since this high-impact discovery, the direct arylation of heterocycles has been studied thoroughly and has been proven to be a powerful tool for the construction of (hetero)biaryl frameworks.[24,25] Noticeably, Doucet and co-workers recently described a method for the efficient phosphine-free palladium-catalyzed functionalization of thiophene.[26–29] Their catalytic system, composed of $Pd(OAc)_2$ as the catalyst and a base (K_2CO_3, KOAc, or Cs_2CO_3) in an organic solvent [*N*,*N*-dimethylacetamide (DMAc), DMF, etc.], was efficient for the direct site-selective arylation of functionalized thiophenes.

In principle, the reactivities of thiophene and thieno[3,2-*b*]thiophene are similar. Therefore, we applied Doucet's protocol for the direct arylation of thieno[3,2-*b*]thiophene with various aryl bromides. As expected, the arylation of **1** was successfully conducted with various commercially available bromoarenes in the presence of $Pd(OAc)_2$/KOAc as the catalyst/base in DMAc.

The C–H arylation of **1** (2.0 equiv.) with various aryl bromides (1.0 equiv.) resulted in the site-selective formation of 2-arylthieno[3,2-*b*]thiophenes **3a**–**q** in moderate to good yields (35–75%, Table 1). After extensive screening with regard to the temperature, solvent, base, and water additive, $Pd(OAc)_2$ without a ligand was found to be an efficient catalyst for the direct arylation of thieno[3,2-*b*]thiophene. All reactions were performed at 120–150 °C (Table 1, also see the Supporting Information). The optimized reaction conditions were compatible with a wide range of functional groups, such as nitro, dialkylamino, ester, cyano, and heterocyclic substituents. Generally, the arylation reaction gave better yields with aryl bromides **2e**, **2h**, **2k**, **2n**, and **2q** bearing electron-withdrawing groups than with aryl bromides **2i** and **2o** bearing electron-donating groups. However, 9-bromoanthracene (**2f**) and 3-bromonaphthalene (**2g**) also afforded corresponding 2-substituted thieno[3,2-*b*]thiophene **3f** and **3g** in good yields. For the synthesis of compounds **3m** and **3q**, the 1,4-bis(diphenylphosphino)butane (dppb) ligand was employed, because aryl bromides **2m** and **2p** did not work well under the phosphine-free palladium-catalyzed reaction conditions.[30]

To perform a second arylation of the 2-arylated thieno[3,2-*b*]thiophenes, the C–H activation of 2-aryl^1-thieno[3,2-*b*]thiophenes **3f** and **3m** (1.0 equiv.) with aryl halides **2c**, **2g**, **2h**, 2**k**, and **2l** (1.1 equiv.) resulted in the highly site-selective formation of unsymmetrical 2-aryl^1-5-aryl^2-thieno[3,2-*b*]thiophenes **4a**–**f** in acceptable yields (41–60%, Table 2).

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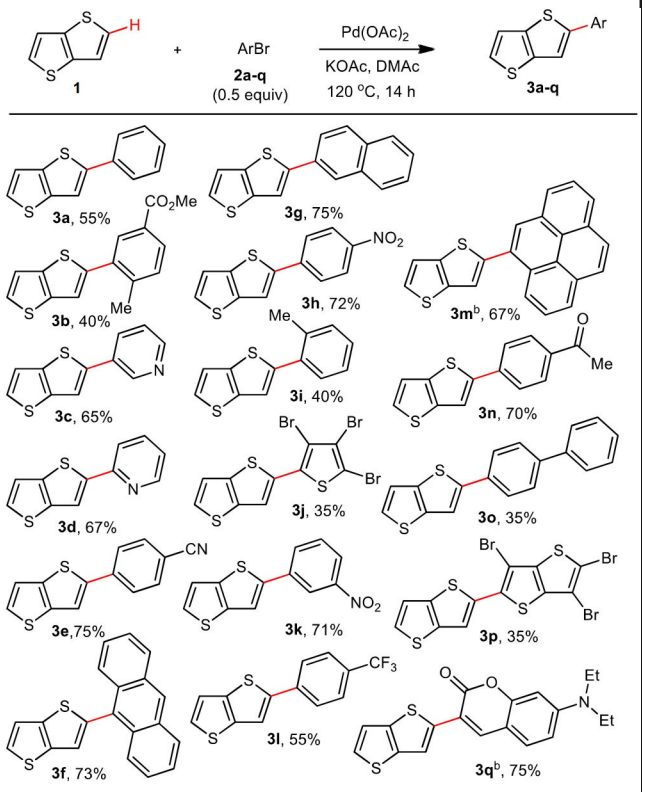
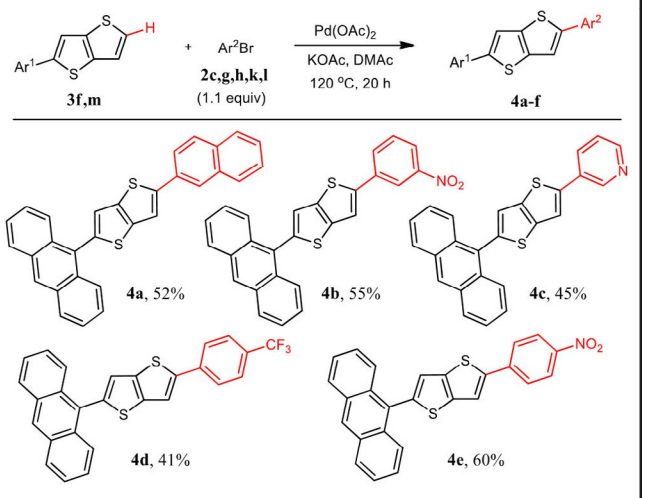
Table 1. Pd-catalyzed arylation of thieno[3,2-*b*]thiophene (**1**) with aryl bromides **2a**--**q**.[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), $Pd(OAc)_2$ (1 mol%), KOAc (0.2 mmol), DMAc (2 mL); yields of isolated products are given. [b] $PdCl(C_3H_5)$dppb was used.

Table 2. Pd-catalyzed arylation of 2-arylthieno[3,2-*b*]thiophenes **3f** and **3m** with aryl bromides.[a]



[a] Reaction conditions: **3f** or **3m** (0.1 mmol), **2** (0.11 mmol), $Pd(OAc)_2$ (1 mol%), KOAc (0.1 mmol), DMAc (1.5 mL); yields of isolated products are given.

To confirm the site selectivity at the C-2 and C-5 positions of thieno[3,2-*b*]thiophene in our arylation reaction, the structure of **4a** was well characterized by ^1H NMR and ^{13}C NMR spectroscopy in combination with X-ray crystal-structure analysis (Figure 1).

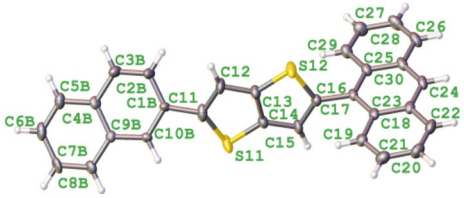
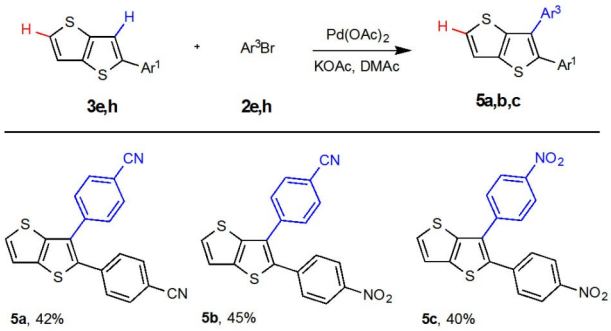


Figure 1. X-ray crystal structure of **4a**.[38]

The similar site selectivity in the direct arylation of thiophene and thieno[3,2-*b*]thiophene is predictable, as they share analogous structural characteristics.

Interestingly, the direct C–H arylation of 2-aryl[1]-thieno[3,2-*b*]thiophenes **3e** and **3h** (1.0 equiv.) with aryl halides **2e** and **2h** (1.1 equiv.) resulted in the abnormal site-selective formation of 2-aryl[1]-3-aryl[2]-thieno[3,2-*b*]thiophenes **5a–c** in 40–45% yield (Table 3). In an attempt to investigate the structures as well as the site selectivity in the direct arylation of **3e** and **3h**, the structure of **5c** was elucidated by NMR spectroscopy and X-ray crystal-structure analysis (Figure 2).

Table 3. Synthesis of 2,3-diarylthieno[3,2-*b*]thiophenes **5a–c** from 2-arylthieno[3,2-*b*]thiophenes **3e** and **3h** and aryl bromides **2e** and **2h**.[a]



[a] Reaction conditions: **3e** or **3h** (0.2 mmol), **2** (0.22 mmol), $Pd(OAc)_2$ (1 mol%), KOAc (0.2 mmol), DMAc (2.5 mL); yields of isolated products are given.

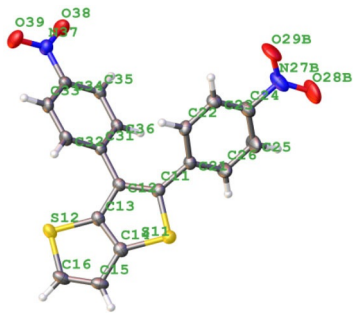


Figure 2. X-ray crystal structure of **5c**.[38]

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To investigate the abnormal site selectivity of the direct arylation of 2-substituted thieno[3,2-*b*]thiophenes further, we conducted the diarylation of thieno[3,2-*b*]thiophene (**1**) (1.0 equiv.) with **2h** and **2n** (3.0 equiv.) (Figure 3). To our expectation, the two corresponding 2,3-diarylthieno[3,2-*b*]thiophenes, **5c** and **5d**, were also obtained in yields of 40 and 35%, respectively. In these reactions, the more-reactive catalyst $PdCl(C_3H_5)(dppb)$ was employed instead of $Pd(OAc)_2$, as the latter showed sluggish conversion. Under these phosphine-supported conditions, the same site selectivity at the C-2 and C-3 positions was observed.

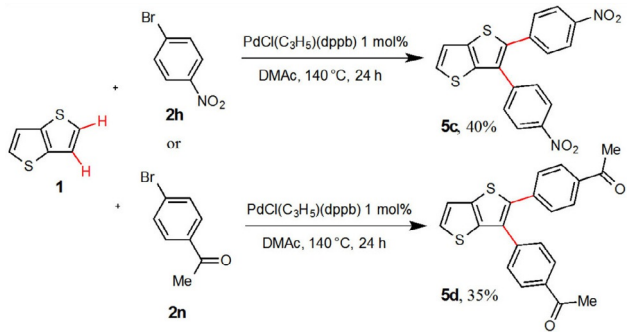

Figure 3. Synthesis of 2,3-diarylthieno[3,2-*b*]thiophenes **5c** and **5d** from **1** and aryl bromides **2**.

Considering the mechanism of the direct arylation by C–H bond activation, three potential pathways have been proposed for the C–C cross-coupling reactions.[25,31,32] In our catalytic system, the essential role of the base, KOAc, would support the concerted metalation deprotonation (CMD) pathway. This CMD mechanism has been thoroughly studied and can be applied in reactions of similar aromatic compounds.[33,34] In an aromatic ring, the most acidic proton is normally activated.[35]

To obtain insight into the site selectivity of the arylation of thieno[3,2-*b*]thiophene, the resonances of the related protons on the thieno[3,2-*b*]thiophene moiety of several 2-arylthieno[3,2-*b*]thiophene were compared (Table 4). In the scaffolds of the 2-arylated thieno[3,2-*b*]thiophenes, the electronic effect of a strong electron-withdrawing group (EWG) on the C-2 atom may have a significant influence on the proton in the adjacent position, that is, the C-3 atom.

Table 4. Resonances of the C-3, C-5, and C-6 protons of several 2-arylthieno[3,2-*b*]thiophenes.[a]

Compound	δ [ppm]		
	H3	H5	H6
3e	7.60	7.44	7.27
3f	7.35	7.36	7.47
3l	7.56	7.40	7.25
3n	7.63	7.43	7.28
3g	7.61	7.36	7.27
3h	7.66	7.46	7.28
3k	7.62	7.44	7.28

[a] See the Supporting Information for more details.

Indeed, the acidity of the proton at the C-3 position is higher than that of the proton at the C-5 position, as indicated by the NMR spectroscopy data. Table 4 shows that if the 2-aryl substituent of a 2-arylthieno[3,2-*b*]thiophene possesses an electron-withdrawing group, such as a cyano (as in **3e**), nitro (as in **3k** and **3h**), trifluoromethyl (as in **3l**), or acetyl (as in **3n**) group, especially in the *para* position, the resonance of the C-3 proton is noticeably higher than that of the C-5 proton. Clearly, this evidence reveals that the acidity of the C-3 proton in the 2-(EWG-aryl)thieno[3,2-*b*]thiophenes is increased. Hence, the subsequent direct arylation takes place more favorably at the C-3 position (Figure 4).

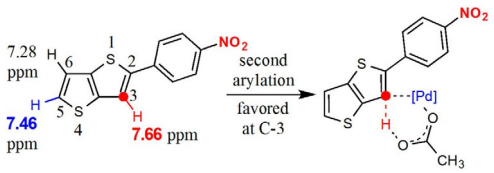

Figure 4. Possible interpretation of the selective formation of 2,3-diarylthieno[3,2-*b*]thiophenes.

Interestingly, the site selectivities of the second and third direct arylation reactions of 2-arylthieno[3,2-*b*]thiophenes **3f** and **3g** were again observed at the C-5 and C-6 positions on the other sites of the thieno[3,2-*b*]thiophene scaffold. The more reactive sites in these cases are still in good agreement with the CMD mechanism.[25] In fact, the arylation reactions of **3f** and **3g** (1.0 equiv.) with **2h** and **2l** (3.0 equiv.) furnished the two corresponding 2-aryl^1-5,6-(aryl^2)$_2$thieno[3,2-*b*]thiophenes, **6a** and **6b**, in yields of 20 and 32%, respectively (Figure 5). In

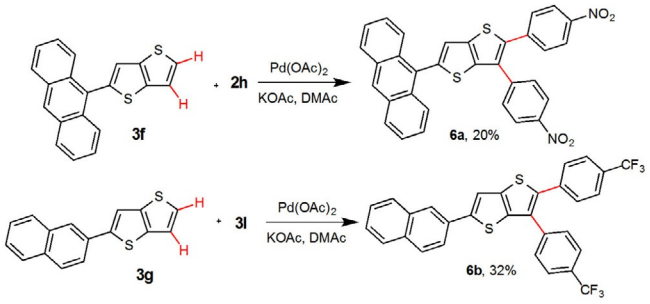

Figure 5. Synthesis of 2,3,5-triarylthieno[3,2-*b*]thiophenes **6a** and **6b** from 2-arylthieno[3,2-*b*]thiophenes **3f** and **3g** and aryl bromides **2h** and **2l**.

these cases, the site selectivity of the third arylation results from the increased acidity of the C-6 proton as a result of the EWG at the C-5 position. In addition, the steric hindrance caused by the fused aromatic ring systems at the C-2 position, namely, the anthracene and the naphthalene substituents, also contributes to the observed site selectivity. The structure of **6a** was confirmed by X-ray analysis (Figure 6).

2,3,5-Triarylthieno[3,2-*b*]thiophenes **6c** and **6d** were also directly synthesized from the arylation of thieno[3,2-*b*]thiophene in yields of 50 and 46%, respectively (Figure 7).

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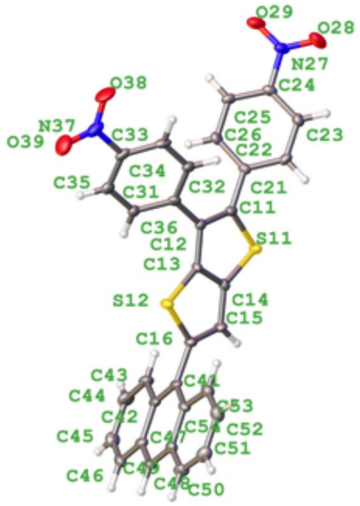

Figure 6. X-ray crystal structure of **6a**.[38]

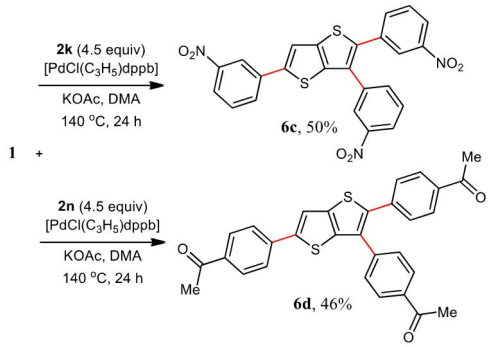

Figure 7. Synthesis of 2,3,5-triarylthieno[3,2-*b*]thiophenes **6c** and **6d** from thieno[3,2-*b*]thiophene (**1**) and aryl bromides **2k** and **2n**, respectively.

In summary, if the 2-aryl substituent bears an EWG, the sequential direct arylations take place first at the C-3 position, then at the C-5 position, and finally at the C-6 position owing to activation of the corresponding C–H bonds (Figure 8).

The one-pot synthesis of 2,3,5,6-tetraarylthieno[3,2-*b*]thiophene **7** could be achieved from the direct arylation of thieno[3,2-*b*]thiophene (**1**) with aryl bromide **2n** in 25% yield (Figure 9).

Conclusions

In conclusion, we developed an efficient and straightforward method for the direct site-selective palladium-catalyzed arylation of simple thieno[3,2-*b*]thiophene. This versatile method allows the synthesis of a large number of mono-, di-, tri-, and tetraarylated thieno[3,2-*b*]thiophenes under phosphine-free conditions with controllable site selectivity. Interestingly, the sequential arylation of 2-arylthieno[3,2-*b*]thiophenes took place at predictable positions, either at the C-3 or at the C-5 position of the thieno[3,2-*b*]thiophene skeleton, depending on the nature and the size of the 2-aryl substituents. In terms of a low catalyst loading, simple reaction conditions, and wide functional group tolerance, to our opinion, this current procedure is convenient and useful for further applications in materials science.

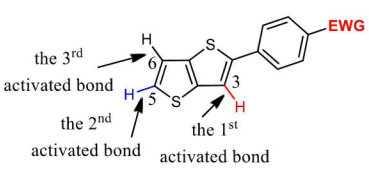

Figure 8. Sequential direct arylation of 2-arylthieno[3,2-*b*]thiophenes.

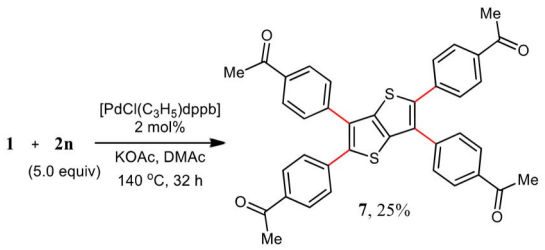

Figure 9. Synthesis of 2,3,5,6-tetra(4-acetylphenyl)thieno[3,2-*b*]thiophene (**7**) from **1** and 4-bromoacetophenone (**2n**).

Experimental Section

General methods

NMR spectra were recorded with a Bruker Avance spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). MS measurements were conducted with a Q-TOF Micro WATERS instrument by using electrospray ionization (ESI) in the positive method. The X-ray structure data of **4a**, **5c**, and **6a** were collected with a D8 QUEST Bruker (Germany) instrument at 100 K with MoK_{α} radiation ($\lambda = 0.71073$ Å) by using a TRIUMPH monochromator. Melting points were measured with a Stuart-Scientific SMP3 apparatus. THF was dried and distilled over sodium benzophenone ketyl just before used. Anhydrous DMAc and other commercially available reagents were used without further purification. All C–H activation reactions were performed under an argon atmosphere.

Syntheses

General procedure for the synthesis of 2-arylthieno[3,2-b]thiophenes 3a–q

Procedure A: Thieno[3,2-*b*]thiophene (**1**, 2.0 equiv.), KOAc (2.0 equiv.), aryl bromide **2** (1.0 equiv.), and $Pd(OAc)_2$ (0.01 equiv.) were dissolved in DMAc, which was saturated with argon. The resulting mixture was heated at 120–150 °C under an argon atmosphere until TLC (*n*-hexane/ethyl acetate) showed complete consumption of the starting material. The mixture was cooled to room temperature and was filtered to remove insoluble impurities. The filtrate was diluted with ethyl acetate, washed with water (3×), dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate) to give the C–H activation cross-coupling product.

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Procedure B: Procedure B was similar to procedure A except that the phosphine-based [PdCl(C_3H_5)dppb] (0.01 equiv.) complex was used as the catalyst instead of $Pd(OAc)_2$.[30,36,37]

2-(4-Nitrophenyl)thieno[3,2-*b*]thiophene (**3h**): Following procedure A, from thieno[3,2-*b*]thiophene (28 mg, 0.2 mmol, 2.0 equiv.), 1-bromo-4-nitrobenzene (20 mg, 0.1 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.5 mg, 0.02 mmol, 0.01 equiv.), KOAc (19.6 mg, 0.2 mmol, 2.0 equiv.), and DMAc (2.0 mL), **3h** was obtained as pale-yellow needles (18.8 mg, 72%); m.p. 110–112 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (2H, d, J = 8.5 Hz), 7.75 (2H, d, J = 8.5 Hz), 7.66 (1H, s), 7.47 (1H, d, J = 5.0 Hz), 7.29 ppm (1H, d, J = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.8, 143.1, 141.0, 140.4, 128.9, 125.9, 124.5, 119.7, 117.9 ppm. HRMS (ESI): *m/z*: calcd for $C_{12}H_7NO_2S_2Na$: 283.9816 $[M+Na]^+$; found: 283.9833.

7-Diethylaminocoumarin-3-ylthieno[3,2-*b*]thiophene (**3q**): Following procedure B, from **1** (70 mg, 0.5 mmol, 2.0 equiv.) and 7-diethylaminocoumarin-3-yl bromide (**2q**; 74 mg, 0.25 mmol, 1.0 equiv.), **3q** was isolated as orange crystals (66 mg, 75%); m.p. 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (1H, s), 7.82 (1H, s), 7.35 (1H, d, J = 5.5 Hz), 7.30 (1H, d, J = 9.0 Hz), 7.22 (1 H d, J = 5.0 Hz), 6.59 (1H, dd, J = 9.0, 2.5 Hz), 6.50 (1H, d, J = 2.5 Hz), 3.40 (4H, q, J = 7.0 Hz), 1.22 ppm (6H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.1, 155.5, 150.6, 140.0, 139.8, 138.7, 136.8, 128.9, 127.3, 119.4, 117.8, 114.8, 109.3, 108.7, 97.0, 44.8, 12.5 ppm; HRMS (ESI): *m/z*: calcd for $C_{19}H_{18}NO_2S_2$ 356.0778 $[M+H]^+$; found: 356.0789.

3a: White solid (23.7 mg, 55%); m.p. 68–70 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (2H, d, J = 8.0 Hz), 7.48 (1H, s), 7.39 (2H, t, J = 8.0 Hz), 7.35 (1H, d, J = 5.5 Hz), 7.28 (1H, t, J = 8.0 Hz), 7.24 ppm (1H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.3, 143.0, 138.5, 131.0, 128.9, 127.8, 126.8, 125.8, 119.6, 115.3 ppm.

3b: Colorless liquid (23 mg, 40%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (1H, d, J = 2.0 Hz), 7.93 (1H, dd, J = 8.0, 2.0 Hz), 7.38 (1H, d, J = 5.0 Hz), 7.37 (1H, d, J = 8.0 Hz), 7.28 (1H, d, J = 5.0 Hz), 7.25 ppm (1H, d, J = 6.0 Hz, overlapped by $CHCl_3$ residue).

3c: Yellow solid (28.4 mg, 65%); m.p. 87–89 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (1H, d, J = 2.0 Hz), 8.24 (1H, dd, J = 5.0, 1.5 Hz), 7.59 (1H, dt, J = 7.5, 2.0 Hz), 7.12 (1H, d, J = 5.5 Hz), 7.04 (1H, d, J = 8.0, 5.0 Hz), 6.99 (1H, s), 6.98 ppm (1H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.7, 146.8, 142.1, 140.1, 139.2, 132.8, 130.8, 127.8, 123.7, 119.5, 116.4 ppm. Structure of **3c** was independently determined by X-ray analysis (data not shown).

3d: Yellow solid (29 mg, 67%); m.p. 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (1H, dt, J = 5.0, 1.5 Hz), 7.78 (1H, s), 7.69 (2H, m), 7.41 (1H, d, J = 5.5 Hz), 7.28 (1H, d, J = 5.5 Hz), 7.16 ppm (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8, 149.7, 146.7, 140.7, 139.8, 136.6, 128.1, 122.9, 119.9, 118.7, 116.8 ppm; HRMS (ESI): *m/z*: calcd for $C_{11}H_8NS_2$ 218.0098 $[M+H]^+$; found: 218.0109.

3e:[39] White solid (36.2 mg, 75%); m.p. 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (2H, d, J = 8.0 Hz), 7.65 (2H, d, J = 8.5 Hz), 7.59 (1H, s), 7.45 (1H, d, J = 5.5 Hz), 7.27 ppm (1H, d, J = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 140.2, 139.9, 139.1, 132.8, 128.6, 125.9, 119.6, 118.8, 117.3; 110.8 ppm; HRMS (ESI): *m/z*: calcd for $C_{13}H_7NS_2Na$ 263.9918 $[M+Na]^+$; found: 263.9926.

3f:[39] White solid (46.1 mg, 75%); m.p. 133–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (1H, s), 8.03 (2H, d, J = 8.5 Hz), 7.97 (2H, d, J = 8.5 Hz), 7.47 (3H, m), 7.41 (2H, m), 7.35 ppm (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.0, 140.4, 139.2, 131.8, 131.2, 128.5, 128.4, 128.3, 126.7, 126.5, 126.1, 125.3, 121.6, 119.5 ppm.

3g:[39] White solid (40 mg, 75%); m.p. 115–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (1H, d, J = 1.0 Hz), 7.85 (2H, d, J = 8.0 Hz), 7.82 (1H, d, J = 7.5 Hz), 7.75 (1H, dd, J = 8.5, 2.0 Hz), 7.61 (1H, s), 7.47 (2H, m), 7.37 (1H, d, J = 5.0 Hz), 7.27 ppm (1H, d, J = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 140.2, 138.7, 133.6, 132.9, 132.2, 128.7, 128.1, 127.8, 127.0, 126.7, 126.1, 124.2, 124.1, 119.6, 115.7 ppm.

3i: White solid (18.4 mg, 40%); m.p. 52–53 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (1H, d, J = 8.0 Hz), 7.36 (1H, d, J = 5.0 Hz), 7.27 (2H, m), 7.23 (1H, dd, J = 7.0, 2.0 Hz), 7.21 ppm (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.1, 139.3, 136.3, 134.4, 131.2, 130.8, 130.6, 128.2, 126.4, 125.9, 119.4, 118.6, 21.1 ppm.

3j: White solid (31.8 mg, 35%); m.p. 147–148 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (1H, s), 7.47 (1H, d, J = 5.5 Hz), 7.30 ppm (1H, d, J = 5.0 Hz).

3k: Pale-yellow solid (37 mg, 71%); m.p. 122–123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (1H, m), 8.13 (1H, dq, J = 8.5, 1.5 Hz), 7.91 (1H, dq, J = 8.0, 1.0 Hz), 7.62 (1H, s), 7.56 (1H, t, J = 8.0 Hz), 7.44 (1H, d, J = 5.5 Hz), 7.28 ppm (1H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.8, 143.0, 140.1, 139.5, 136.5, 131.3, 129.9, 128.3, 122.1, 120.3, 119.6, 117.1 ppm; HRMS (ESI): *m/z*: calcd for $C_{12}H_7NO_2S_2Na$ 283.9816 $[M+Na]^+$; found: 283.9832.

3l:[39] White solid (31.2 mg, 55%); m.p. 136–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (2H, d, J = 8.5 Hz), 7.64 (2H, d, J = 8.5 Hz), 7.56 (1H, s), 7.41 (1H, d, J = 5.5 Hz), 7.26 ppm (1H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.3, 140.1, 139.4, 138.2, 129.4 (q, J = 32.6 Hz, C-CF_3), 127.9, 126.0 (q, J = 3.3 Hz, C-C-CF_3), 125.9, 124.1 (q, J = 270.5 Hz, CF_3), 119.6, 116.7 ppm.

3m: Yellow solid (45.6 mg, 67%); m.p. 184–185 °C; ^{1}H NMR (500 MHz, CDCl3): δ = 8.54 (1H, d, J = 9.0 Hz), 8.09 (8H, m), 7.52 (1H, s), 7.43 (1H, d, J = 5.0 Hz), 7.35 ppm (1H, d, J = 5.0 Hz).

3n: Yellow solid (36.2 mg, 70%); m.p. 116–117 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (2H, d, J = 8.0 Hz), 7.72 (2H, d, J = 8.5 Hz), 7.63 (1H, s), 7.43 (1H, d, J = 5.0 Hz), 7.28 (1H, d, J = 5.0 Hz), 2.62 ppm (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2, 144.7, 140.2, 139.6, 139.2, 136.0, 129.2, 128.1, 125.6, 119.6, 116.8, 26.5 ppm.

3o: White solid (20.5 mg, 35%); m.p. 65–66 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (2H, d, J = 8.0 Hz), 7.60 (4H, m), 7.51 (1H, s), 7.42 (2H, t, J = 7.5 Hz), 7.34 (2H, d, J = 5.0 Hz), 7.24 ppm (1H, d, J = 5.5 Hz).

3p: Yellow solid (35.8 mg, 35%); m.p. 142–143 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (1H, s), 7.36 (1H, d, J = 5.5 Hz), 7.23 ppm (1H, d, J = 5.0 Hz).

General procedure for the synthesis of 2,5-diarylthieno[3,2-b]thiophenes 4a–e

The procedure for the synthesis of 2,5-diarylthieno[3,2-*b*]thiophenes **4a–e** was similar to that for the synthesis of 2-arylthieno[3,2-*b*]thiophenes **3**: from thieno[3,2-*b*]thiophene (**1**, 1.0 equiv.), aryl bromide **2** (3.0 equiv.), $Pd(OAc)_2$ (0.02 equiv.), and KOAc (4.0 equiv.) or from 2-arylthieno[3,2-*b*]thiophene **3** (1.0 equiv.), aryl bromide **2** (1.1 equiv.), $Pd(OAc)_2$ (0.01 equiv.), and KOAc (1.0 equiv.).

2-(Anthracene-9-yl)-5-(4-nitrophenyl)thieno[3,2-*b*]thiophene (**4e**): From 2-(anthracene-9-yl)thieno[3,2-*b*]thiophene (**3f**; 31.6 mg, 0.10 mmol, 1.0 equiv.), 1-bromo-4-nitrobenzene (**2h**; 22.1 mg, 0.11 mmol, 1.1 equiv.), and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.01 equiv.), **4e** was isolated as an orange solid (26 mg, 60%); m.p. 178–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (1H, s), 8.29 (2H, d, J = 8.5 Hz), 8.06 (2H, d, J = 8.0 Hz), 7.95 (2H, d, J = 8.5 Hz), 7.83 (2H, d, J = 9.0 Hz), 7.77 (1H, s), 7.49 (2H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz), 7.38 ppm (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 142.8, 142.4, 141.3, 140.9, 140.2, 131.6, 131.0, 128.6, 128.3, 127.6, 126.2, 126.1, 125.8, 125.3, 124.4, 121.2, 118.0 ppm; HRMS (ESI): *m/z*: calcd for $C_{26}H_{15}NO_2S_2Na$ 460.0442 $[M+Na]^+$; found: 460.0438.

4a: White solid (23 mg, 52%); m.p. 184–185 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (1H, s), 8.14 (1H, s), 8.05 (2H, d, J = 8.5 Hz), 8.01 (2H, d, J = 8.5 Hz), 7.90 (2H, d, J = 8.5 Hz), 7.83 (2H, t, J = 8.0 Hz), 7.72 (1H, s), 7.45 (6H, m), 7.37 ppm (1H, s); ^{13}C NMR (125 MHz,

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$CDCl_3$): δ = 145.9, 141.3, 140.8, 138.6, 133.7, 132.9, 132.3, 131.9, 131.2, 128.7, 128.5, 128.4, 128.5, 127.8, 126.7, 126.5, 126.2, 126.1, 125.3, 124.3, 124.2, 121.9, 115.8 ppm.

4b: Orange solid (24 mg, 55%); m.p. 154–155 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (1H, s), 8.54 (1H, d, J = 2.0 Hz), 8.16 (1H, dt, J = 8.0, 1.0 Hz), 8.06 (2H, d, J = 8.5 Hz), 8.00 (1H, dt, J = 7.5, 1.0 Hz), 7.95 (2H, d, J = 8.0 Hz), 7.74 (1H, s), 7.62 (1H, t, J = 8.0 Hz), 7.49 (2H, t, J = 8.0 Hz), 7.44 (2H, t, J = 7.5 Hz), 7.38 ppm (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.8, 148.9, 142.4, 142.2, 141.2, 139.3, 136.5, 137.1, 131.3, 131.1, 130.8, 130.0, 128.7, 128.6, 128.3, 127.8, 126.3, 126.2, 126.0, 125.3, 122.1. 121.7, 120.3, 117.2 ppm.

4c: Orange solid (17.7 mg, 45%); m.p. 142–143 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.98 (1H, s), 8.56 (2H, m), 8.04 (2H, d, J = 8.5 Hz), 7.96 (2H, d, J = 8.5 Hz), 7.92 (2H, dt, J = 8.0, 1.5 Hz), 7.62 (1H, s), 7.49 (2H, t, J = 7.0 Hz), 7.44 (2H, t, J = 6.5 Hz), 7.35 ppm (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.7, 146.9, 141.7, 141.5, 141.2, 139.1, 132.9, 131.8, 131.1, 130.9, 128.6, 128.4, 128.0, 126.4, 126.2, 125.4, 123.8, 121.8, 116.6 ppm.

4d: White solid (18.9 mg, 41%); m.p. 166–167 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (1H, s), 8.05 (2H, d, J = 8.0 Hz), 7.97 (2H, d, J = 8.5 Hz), 7.79 (2H, d, J = 8.0 Hz), 7.68 (2H, m), 7.62 (1H, s), 7.49 (2H, t, J = 8.0 Hz), 7.43 (2H, t, J = 8.0 Hz), 7.36 ppm (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 141.9, 141.2, 139.3, 138.2, 131.8, 131.2, 129.5 (q, J = 35.7 Hz, C-CF_3), 128.6, 128.3, 126.4, 126.2, 126.0 (q, J = 35.7 Hz, C-C-CF_3), 125.9, 125.4, 121.8, 116.9 ppm.

General procedure for the synthesis of 2,3-diarylthieno[3,2-b]thiophenes 5a–d

The procedure for the synthesis of 2,3-diarylthieno[3,2-*b*]thiophenes **5a–d** was similar to that for the synthesis of 2-arylthieno[3,2-*b*]thiophenes **3**: from thieno[3,2-*b*]thiophene (**1**, 1.0 equiv.), 4-EWG-aryl bromide **2** (3.0 equiv.), [PdCl(C_3H_5)dppb] (0.01 equiv.), and KOAc (4.0 equiv.) or from 2-(4-EWG-aryl)thieno[3,2-*b*]thiophene **3** (1.0 equiv.), aryl bromide **2** (1.1 equiv.), $Pd(OAc)_2$ (0.01 equiv.), and KOAc (2.0 equiv.).

2-(4-Nitrophenyl)-3-(4-cyanophenyl)thieno[3,2-*b*]thiophene (**5b**): From 2-(4-nitrophenyl)thieno[3,2-*b*]thiophene (**3h**; 52.2 mg, 0.20 mmol, 1.0 equiv.) and 1-bromo-4-cyanobenzene (**2e**; 40 mg, 0.22 mmol, 1.1 equiv.), **5b** was isolated as a white solid (32.5 mg, 45%); m.p. 187–189 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (2H, d, J = 9.0 Hz), 7.70 (2H, d, J = 8.5 Hz), 7.54 (2H, d, J = 8.0 Hz), 7.49 (1H, d, J = 5.0 Hz), 7.45 (2H, d, J = 9.0 Hz), 7.35 ppm (2H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.2, 140.6, 139.4, 138.8, 138.4, 132.9, 132.6, 130.4, 129.9, 129.8, 129.7, 128.3, 128.1, 124.4, 124.1, 119.9, 118.3, 112.1 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{10}N_2O_2S_2Na$ 385.0081 $[M+Na]^+$; found: 385.0095.

2,5-Di(4-acetylphenyl)thieno[3,2-*b*]thiophene (**5d**): From thieno[3,2-*b*]thiophene (**1**; 70.0 mg, 0.5 mmol, 1.0 equiv.), 4-bromoacetophenone (**2n**; 297 mg, 1.5 mmol, 3.0 equiv.), and [PdCl(C_3H_5)dppb] (3 mg, 0.05 mmol, 0.01 equiv.), **5d** was isolated as a pale-yellow solid (65.8 mg, 35%); m.p. 166–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (2H, d, J = 8.5 Hz), 7.88 (2H, d, J = 8.0 Hz), 7.54 (2H, d, J = 8.0 Hz), 7.45 (1H, d, J = 5.0 Hz), 7.41 (2H, d, J = 8.5 Hz), 7.34 (1H, d, J = 5.0 Hz), 2.63 (3H, s), 2.59 ppm (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 197.5, 139.9, 139.1, 137.7, 136.3, 136.1, 130.6, 130.4, 129.4, 129.2, 129.0, 128.7, 127.5, 119.9, 26.7, 26.5 ppm; HRMS (ESI): m/z: calcd for $C_{22}H_{17}O_2S_2$ 377.0670 $[M+H]^+$; found: 377.0668.

5a: White solid (28.7 mg, 42%); m.p. 134–135 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (2H, d, J = 8.5 Hz), 7.58 (2H, d, J = 8.5 Hz), 7.53 (2H, d, J = 8.5 Hz), 7.46 (1H, d, J = 5.5 Hz), 7.38 (2H, d, J = 8.5 Hz), 7.34 ppm (1H, d, J = 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.1, 145.9, 141.3, 139.3, 138.6, 138.2, 132.9, 132.6, 129.8, 129.7, 128.0, 119.9, 118.4, 111.9, 111.7 ppm; HRMS (ESI): m/z: calcd for $C_{20}H_{10}N_2S_2Na$ 365.0183 $[M+Na]^+$; found: 365.0198.

5c: Yellow solid (30.6 mg, 40%); m.p. 192–193 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (2H, d, J = 9.0 Hz), 8.17 (2H, d, J = 9.0 Hz), 7.60 (2H, d, J = 9.0 Hz), 7.50 (1H, d, J = 5.0 Hz), 7.45 (2H, d, J = 9.0 Hz), 7.37 ppm (1H, d, J = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.3, 138.5, 130.0, 129.9, 129.8, 128.4, 124.5, 124.2, 120.0 ppm.

General procedure for the synthesis of 2,3,5-triarylthieno[3,2-b]thiophenes 6a–d

The procedure for the synthesis of 2,3,5-triarylthieno[3,2-*b*]thiophenes **6a–d** was similar to that for the synthesis of 2-arylthieno[3,2-*b*]thiophenes **3**: from thieno[3,2-*b*]thiophene (**1**, 1.0 equiv.), aryl bromide **2** (4.5 equiv.), [PdCl(C_3H_5)dppb] (0.02 equiv.), and KOAc (6.0 equiv.) or from 2-arylthieno[3,2-*b*]thiophene **3** (1.0 equiv.), aryl bromide **2** (3.0 equiv.), $Pd(OAc)_2$ (0.02 equiv.), and KOAc (4.0 equiv.).

2-(Anthracene-9-yl)-5,6-di(4-nitrophenyl)thieno[3,2-*b*]thiophene (**6a**): From 2-(anthracene-9-yl)thieno[3,2-*b*]thiophene (**3f**; 63.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-4-nitrobenzene (**2h**; 120.5 mg, 0.60 mmol, 3.0 equiv.), and $Pd(OAc)_2$ (0.9 mg, 0.004 mmol, 0.02 equiv.), **6a** was obtained as a pale-yellow solid (22.3 mg, 20%); m.p. 195–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.59 (1H, s), 8.25 (2H, d, J = 9.0 Hz), 8.22 (2H, d, J = 8.5 Hz), 8.07 (2H, d, J = 8.0 Hz), 7.94 (2H, d, J = 8.5 Hz), 7.68 (2H, d, J = 9.0 Hz), 7.54 (2H, d, J = 9.0 Hz), 7.50 (2H, t, J = 7.0 Hz), 7.45 (1H, s), 7.43 ppm (2H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.4, 147.3, 142.5, 142.3, 141.3, 140.5, 138.6, 138.4, 134.3, 131.7, 131.1, 130.2, 130.0, 129.9, 129.5, 128.9, 128.5, 127.3, 126.4, 126.1, 125.4, 124.5, 124.3, 122.1, 114.1 ppm; HRMS (ESI): m/z: calcd for $C_{32}H_{18}N_2O_4S_2Na$ 581.0600 $[M+Na]^+$; found: 581.1100.

2,3,5-Tri(4-acetylphenyl)thieno[3,2-*b*]thiophene (**6d**): From thieno[3,2-*b*]thiophene (**1**; 70.0 mg, 0.5 mmol, 1.0 equiv.), 4-bromoacetophenone (**2n**; 445.5 mg, 2.25 mmol, 4.5 equiv.), and [PdCl(C_3H_5)dppb] (6.1 mg, 0.01 mmol, 0.02 equiv.), **6d** was obtained as a pale-yellow solid (113.6 mg, 46%); m.p. 178–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (4H, d, J = 8.5 Hz), 7.88 (2H, d, J = 8.5 Hz), 7.72 (2H, d, J = 8.0 Hz), 7.67 (1H, s), 7.56 (2H, d, J = 8.0 Hz), 7.42 (2H, d, J = 8.5 Hz), 2.64 (3H, s), 2.63 (3H, s), 2.60 ppm (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.4, 197.3, 197.1, 144.6, 141.7, 140.5, 139.5, 138.6, 138.5, 136.6, 136.3, 129.4, 129.3, 129.2, 129.1, 128.8, 125.6, 117.1, 26.6, 26.5 ppm (br); HRMS (ESI): m/z: calcd for $C_{30}H_{23}O_3S_2$ 495.1089 $[M+H]^+$; found: 495.1053.

6b: Pale-yellow solid (35.5 mg, 32%); m.p. 184–185 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (1H, s), 7.91 (1H, d, J = 9.0 Hz), 7.87 (2H, t, J = 6.5 Hz), 7.79 (1H, dd, J = 8.5, 2.0 Hz), 7.71 (2H, m), 7.62 (2H, d, J = 8.5 Hz), 7.59 (2H, d, J = 8.5 Hz), 7.53 (1H, d, J = 9.0 Hz), 7.51 (1H, d, J = 9.0 Hz), 7.47 ppm (2H, d, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 140.6, 138.9, 138.5, 133.5, 133.0, 131.6, 130.1, 129.5, 129.3, 128.8, 128.1, 127.8, 126.9, 126.4, 126.0 (q, J = 3.75 Hz, C-C-CF_3), 125.7 (q, J = 3.75 Hz, C-C-CF_3), 124.4, 123.8, 115.9 ppm.

6c: Pale-yellow solid (125.8 mg, 46%); m.p. 201–202 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.49 (1H, d, J = 1.5 Hz), 8.34 (1H, s), 8.25 (1H, d, J = 9.0 Hz), 8.21 (1H, s), 8.18 (2H, d, J = 8.5 Hz), 7.94 (1H, d, J = 8.0 Hz), 7.74 (1H, d, J = 7.5 Hz), 7.71 (1H, s), 7.61 (3H, m), 7.50 ppm (1H, t, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 148.8, 148.6, 143.6, 141.0, 139.3, 138.6, 135.8, 135.2, 135.0, 134.9, 131.4, 130.3, 130.2, 130.0, 129.4, 124.0, 123.7, 123.3, 123.1, 122.7, 120.5, 117.4 ppm.

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Procedure for the synthesis of 2,3,5,6-tetra(4-acetylphenyl)-thieno[3,2-b]thiophene (7)

Thieno[3,2-*b*]thiophene (**1**; 70.0 mg, 0.5 mmol, 1.0 equiv.), KOAc (294 mg, 3.0 mmol, 6.0 equiv.), and 4-bromoacetophenone (**2n**; 495 mg, 2.5 mmol, 5.0 equiv.) were dissolved in DMAc (5.0 mL), which was saturated with argon. $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol, 0.02 equiv.) was added to the resulting solution. The mixture was heated at 140 °C under an argon atmosphere until TLC (*n*-hexane/ethyl acetate, 95:5 *v/v*) showed nearly complete consumption of the starting material (32 h). The mixture was cooled to room temperature and filtered to remove insoluble impurities. The filtrate was diluted with ethyl acetate, washed with water (3×), dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 98:2 *v/v*) to give **7** as a pale-yellow solid (76.5 mg, 25%); m.p. 221–223 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (2H, d, J = 8.0 Hz), 7.88 (2H, d, J = 8.5 Hz), 7.56 (2H, d, J = 8.0 Hz), 7.41 (2H, d, J = 8.0 Hz), 2.64 (3H, s), 2.59 ppm (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.4, 197.3, 139.8, 139.6, 139.2, 138.5, 136.6, 136.4, 130.8, 129.3, 129.2, 129.1, 128.8, 26.7, 26.6 ppm; HRMS (ESI): *m/z*: calcd for $C_{38}H_{29}O_4S_2$ 613.1507 $[M+H]^+$; found: 613.1547.

Compound **7** was also synthesized from 2,3,5-tri(4-acetylphenyl)thieno[3,2-*b*]thiophene (**6d**) and 4-bromoacetophenone (**2n**) in a comparable yield on the basis of the same procedure as that outlined for 2-arylthieno[3,2-*b*]thiophenes **3**.

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Conflict of interest

The authors declare no conflict of interest.

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[39] For further arylations, these compounds were synthesized on a large high scale and were obtained in yields similar to those obtained on a small scale. In particular, the scale of **3e** was 0.28 g, that of **3g** was 0.3 g, that of **3l** was 0.45 mg, and that of **3f** was 0.5 mg.

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