Pseudo Five-Component Synthesis of 3-(Hetero)arylmethyl-2,5-di(hetero)-aryl-Substituted Thiophenes via Sonogashira–Glaser Cyclization Sequence

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Received: 04.07.2014; Accepted after revision: 13.08.2014

Abstract: The Sonogashira–Glaser sequence combined with a microwave-assisted cyclization is a powerful tool to synthesize unsymmetrically substituted conjugated thiophenes. A variety of 3-(hetero)arylmethyl-2,5-di(hetero)aryl-substituted thiophenes could be synthesized in moderate to excellent yields using a single Pd/Cu catalyst system. The presented method is strikingly simple to perform using commercially available starting materials. The obtained trisubstituted oligothiophene derivatives are interesting molecules for materials science.

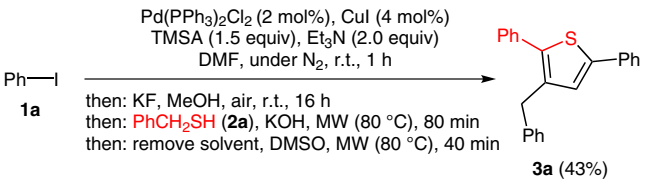
Key words: copper, cross-coupling, heterocycles, multicomponent reactions, palladium, thiols

Thiophenes have attracted remarkable interest over the past years. Most frequently, this compound class has been applied for the synthesis of π-conjugated materials such as oligomers or polymers for their use in electronic devices.[1] For achieving good processability these compounds are often substituted with benzyl or alkyl substituents in 3-position, since unsubstituted oligothiophenes are only poorly soluble. In addition they have found increasingly entry as scaffolds for active pharmaceutical ingredients.[2] In particular, unsymmetrically substituted arylthiophene systems can be of crucial importance.[3] Simultaneously addressing various positions of the thiophene core is advantageous in the development of new structural entities.

The most common de novo synthetic route to thiophenes is the Paal–Knorr reaction of diketones.[4] However, this process is a complicated and time-consuming synthetic pathway. In contrast, palladium-catalyzed processes offer the possibility to directly functionalize the heterocyclic core.[5] Especially the Suzuki coupling has extensively been employed in the synthesis of aryl-substituted thiophenes.[6] Yet, most syntheses only address monofunctionalization of thiophene and they are rarely used to synthesize unsymmetrically substituted arylthiophenes.

Multicomponent reactions (MCRs)[7] possibly can solve these shortcomings since they are conceptually considered to be diversity-oriented syntheses (DOS).[8] Fostered by our interest in Pd/Cu catalysis-initiated MCRs[9] we have paved a straightforward pathway to symmetrically substituted butadiynes from (hetero)aryl iodides.[10] Recently, this concept was employed to one-pot syntheses of 2,5-aryl-substituted thiophenes[11] and furans.[12] Here, we report the development of a novel multicomponent method leading to unsymmetrically substituted conjugated thiophenes by concomitantly introducing a benzyl group in the 3-position.

Based upon our one-pot synthesis of 2,5-substituted thiophenes we set out to employ iodobenzene (**1a**) and trimethylsilylacetylene (TMSA), and benzylmercaptan (**2a**), instead of sodium sulfide as sulfur source, for the cyclization step (Scheme 1).[11] In our first attempt, only the addition of the thiol and no subsequent cyclization was observed. For employing the superbase conditions of Freeman et al.,[13] the solvent had to be exchanged from DMF to DMSO and then the cyclization step was performed in a microwave reactor. The desired thiophene **3a** was isolated in moderate yield by this stepwise pathway.



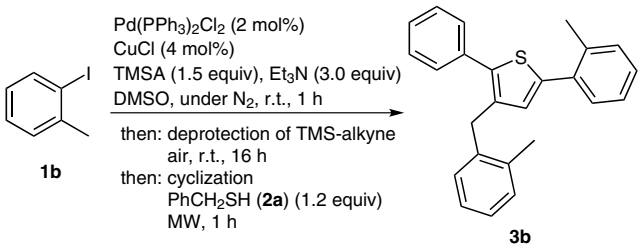
Scheme 1 Stepwise synthesis of 3-benzyl-2,5-diphenylthiophene (**3a**) with solvent exchange in the last step

The solvent DMSO proved to be crucial for the formation of the superbase system in the final cyclization step.[14] To circumvent the solvent exchange and to conduct a one-pot sequence it was necessary to perform the whole sequence in DMSO, including the Sonogashira–Glaser sequence. Therefore, *o*-iodotoluene (**1b**), TMSA, and benzylmercaptan (**2a**) were employed in an optimization study of the one-pot sequence (Table 1).

The catalyst system worked equally well in DMSO and no additional cosolvent was needed to increase the solubility of the fluoride source.[12] In an initial experiment, a Schlenk tube was used instead of a microwave vessel (Table 1, entry 1). For obtaining a real one-pot process in situ, the whole sequence was carried out in a microwave vessel; however, surprisingly no homocoupling product was formed (Table 1, entry 2). We reasoned that the gas flow through the solvent was hampered. Upon decreasing the amount of solvent and increasing the stirring speed the expected product **3b** was obtained in good yield (Table 1, entry 3). Lowering of the reaction temperature in the mi-

SYNTHESIS 2014, 46, 3415–3422
Advanced online publication: 17.09.2014
DOI: 10.1055/s-0034-1379074; Art ID: ss-2014-t0422-op

Table 1 Optimization of the One-Pot Sonogashira–Glaser Thiolation/Cyclization Sequence[a]



Entry	Deprotection	Cyclization	Temp (°C)	Yield of **3b** (%)[a]
1[b]	TBAF (1.5 equiv)	DMSO/KOH	150	70
2[c]	KF	DMSO/KOH	150	–
3[d]	KF	DMSO/KOH	150	76
4[d]	KF	DMSO/KOH	90	69
5[d,e]	KF/MeOH	DMSO/*t*-BuOK	90	44
6[d]	**KF**	**DMSO/KOH**	**130**	**75**

[a] Isolated yield after chromatography on silica gel.
[b] Performed in a Schlenk tube in DMSO (2 mL).
[c] Performed in a microwave tube in DMSO (2 mL).
[d] Performed in a microwave tube in DMSO (1 mL) under fast stirring.
[e] THF as a cosolvent.

crowave reactor gave lower yield (Table 1, entry 4). Performing the reaction in THF with further addition of DMSO and the cyclization with *t*-BuOK gave rise to lower isolated yield (Table 1, entry 5). The optimized conditions for this pseudo five-component reaction were finally obtained by increasing the reaction temperature to 130 °C in the microwave reactor (Table 1, entry 6).

With these conditions in hand, the substrate scope of (hetero)aryl iodides **1** and (hetero)arylmethanethiols **2** to give 3-(hetero)arylmethyl-2,5-di(hetero)aryl-substituted thiophenes **3** was studied (Scheme 2). All reactions were carried out in a 2 mmol scale. The structural assignments of all thiophenes **3** were unambiguously supported by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and combustion analysis and/or HRMS.

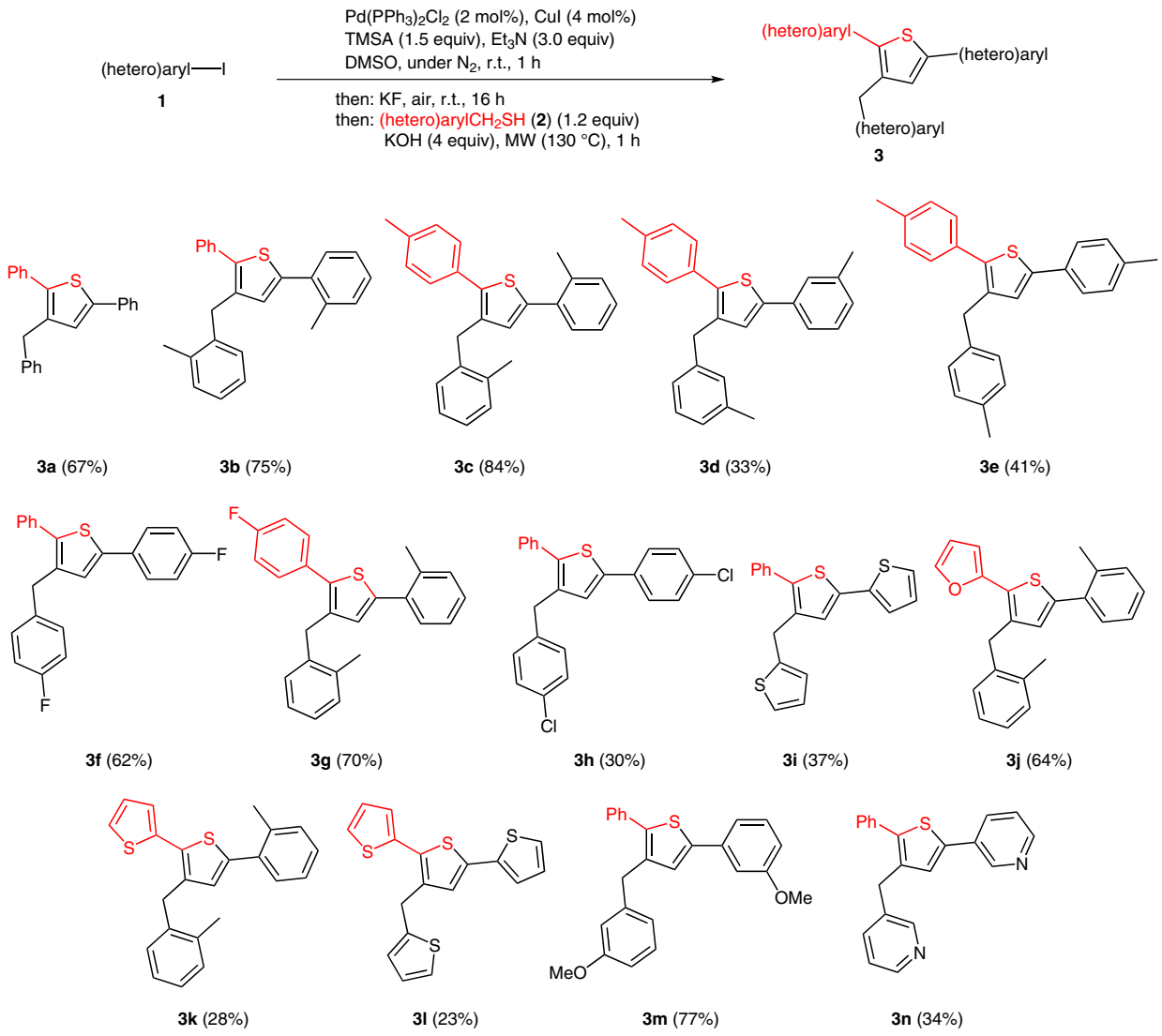
The scope of the possible (hetero)aryl iodides **1** and (hetero)arylmethanethiols **2** is fairly broad with respect to the employed superbase system DMSO/KOH and the isolated yields of the obtained 3-(hetero)arylmethyl-2,5-di(hetero)aryl-substituted thiophenes **3** are moderate to excellent. The employed (hetero)aryl iodides can be electron-neutral (**3a**), electron-rich (**3b–e**, **3g**, **3i**, **3j**, **3k**, **3l**, **3m**), and electron-poor (**3h**, **3n**). Substituents in *ortho*- (**3b**, **3c**, **3g**, **3j**, **3k**), *meta*- (**3d**, **3m**), and *para*-positions (**3e**, **3f**, **3h**) are well tolerated. The employed (hetero)arylmethanethiols **2** can be electron-neutral (**3a**, **3b**, **3f**, **3h**, **3i**, **3m**, **3n**) and electron-rich (**3c**, **3d**, **3e**, **3j**, **3k**, **3l**). Compounds **3k** and **3l** were synthesized from the corresponding thiophene precursor. All compounds were purified by column chromatography on silica gel.

This preparatively useful sequence is straightforward to perform, but using a superbase system sets some limitations to the scope of base sensitive starting materials. It is not required to conduct the sequence in anhydrous DMSO as the competing formation of a furan[12] was never detected and cyclization can even be performed under aerobic conditions. In comparison to the 2,5-diarylthiophenes or 2,5-diarylfurans, the solubility of the products **3** is relatively good. The greatest benefit of this sequence is the generation of unsymmetrically substituted conjugated thiophenes from symmetrically substituted butadiyne intermediates. Alternative syntheses of the same compounds require multi-step syntheses using successive cross-coupling reactions or even elaborated precursors.

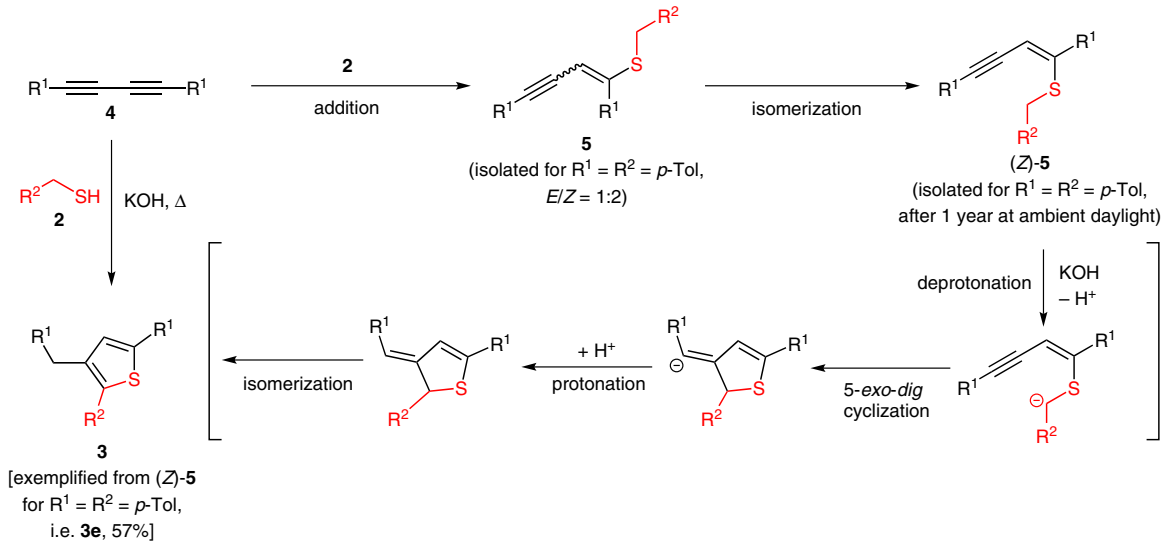
The mechanistic rationale of the cyclization of butadiynes and benzyl mercaptanes to thiophenes was first proposed by Freeman et al. in 1992 (Scheme 3).[13] Accordingly, the addition of the thiol anion to the butadiyne **4** should always furnish the regioisomer with the best resonance stabilization of the anion. Interestingly, in the absence of the superbase system, the addition product **5** ($R^1 = R^2 = p$-Tol) was formed in a 1:2 mixture of *E*/*Z*-diastereomers according to NMR analysis. For steric reasons it can be assumed that only the isomer (*Z*)-**5** will undergo the cyclization to give the thiophene. On exposure of this mixture **5** to indirect daylight for a long time (1 year on the shelf), a complete isomerization in the solid state to isomer (*Z*)-**5** was observed. Subsequent base-catalyzed cyclization of (*Z*)-**5** afforded the thiophene **3** ($R^1 = R^2 = p$-Tol, i.e., **3e**) in 57% isolated yield. Therefore, we assume that the equilibration of the initially formed *E*/*Z*-mixture of **5** occurs quite rapidly at elevated temperature (microwave reactor) and under superbasic conditions.

For accessing branched molecules, bisthiols had to be employed as substrates. However, the first attempt to synthesize expanded structures with 1,4-phenylenedimethanethiol (**6**) as a substrate failed and 2,5-diphenylthiophene (**7**) was obtained as the sole product (Scheme 4). Presumably, the superbase system initiates a hydrogen sulfide elimination to furnish the sulfide source for the cyclization to 2,5-diphenylthiophene (**7**). Interestingly, the *meta*-substituted di- and trimethanethiols **8** and **10** do not show this behavior and the desired products **9** and **11** were isolated in moderate to good yields (Scheme 5).

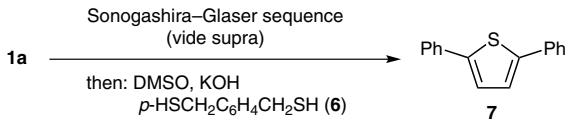
In summary, we have disclosed a concise and efficient microwave-assisted pseudo five-component synthesis of unsymmetrically substituted conjugated of 3-(hetero)arylmethyl-2,5-di(hetero)aryl-substituted thiophenes in a one-pot fashion. All starting materials are often commercially available or easily accessible. Also *meta*-substituted di- and trimethanethiols were successfully implemented in the one-pot sequence. Studies on the suitability of the obtained materials for organic devices are currently underway.



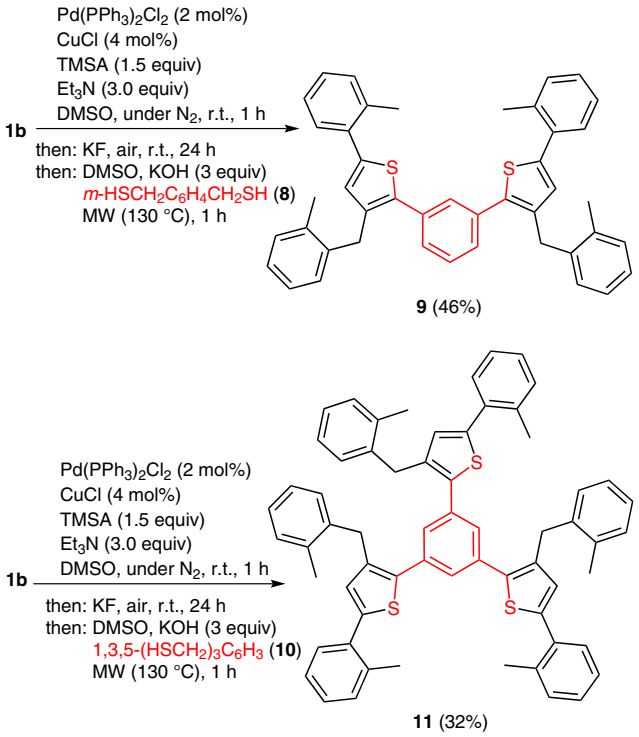
Scheme 2 Pseudo five-component Sonogashira–Glaser cyclization of 3-(hetero)arylmethyl-2,5-di(hetero)aryl-substituted thiophenes **3**



Scheme 3 Mechanistic rationale of the formation of **3** from butadiyne **4** and thiol **2** according to the formation and isolation of **5** and (*Z*)-**5**



Scheme 4 First attempt to implement 1,4-phenylenedimethanethiol (**4**)



Scheme 5 One-pot Sonogashira–Glaser cyclization/syntheses of branched di- and trithiophenes **9** and **11**

All cross-coupling reactions were carried out in oven-dried 80 mL microwave vessels (CEM Corporation) by using septa and syringes under N_2 atmosphere. Commercial-grade reagents were used as supplied without further purification and were purchased from Sigma-Aldrich, ABCR, Alfa Aesar, and Merck Serono. The purification of products was performed on silica gel 60 (0.015–0.040 mm) from Macherey-Nagel (Düren) by using the flash technique under a pressure of 1.5 bar. The crude mixtures were adsorbed on Celite 545 (0.02–0.10 mm) from Merck Serono (Darmstadt) before chromatographic purification. The reaction progress was monitored qualitatively by TLC silica gel 60 F254 aluminum sheets obtained by Merck Serono (Darmstadt). The spots were detected with UV light at 254 nm and by using aq $KMnO_4$.

^1H, ^{13}C, and 135-DEPT NMR spectra were recorded on a Bruker Avance III 600 or a Bruker Avance III 300 spectrometer. $CDCl_3$ was used as the deuterated solvent. The resonances of the residues of nondeuterated solvent were locked as internal standards ($CDCl_3$: ^1H, δ = 7.26, ^{13}C, δ = 7.2). Standard abbreviations were used to denote multiplicities of the signals. The type of carbon atoms was determined on the basis of 135-DEPT NMR spectra. EI mass spectra were recorded on Finnigan MAT 8200 or Shimadzu GC-2010/QP-2010 spectrometer. GC mass spectra were recorded on Shimadzu-GC-2010 spectrometer. IR spectra were recorded on Bruker Vector 22 FT–IR spectrophotometer. Standard abbreviations were used to denote the intensity of signals. The melting points (uncorrected) were measured on a Büchi Melting Point B-540 apparatus. Combustion analyses were carried out on Perkin-Elmer Series II Analyzer 2400 or Vario Micro Cube in the microanalytical laboratory of the Institut für Pharmazeutische and Medizinische Chemie at Heinrich Heine-Universität Düsseldorf. The UV/Vis spectra were recorded with a PerkinElmer Spectrometer (Lambda 19).

One-Pot Sonogashira–Glaser Cyclization/Synthesis of Thiophenes; General Procedure

A mixture of a (hetero)aryl iodide **1** (2.00 mmol), $Pd(PPh_3)_2Cl_2$ (28.1 mg, 0.04 mmol, 2 mol%), and CuCl (7.92 mg, 0.08 mmol, 4 mol%) was dissolved in DMSO (1.00 mL) in a 8 mL microwave vessel equipped with a stirring bar and a septum and was degassed with N_2 for 5 min. After the addition of TMSA (0.42 mL, 3.00 mmol) and anhydrous Et_3N (0.55 mL, 4.00 mmol), the solution was stirred at r.t. for 1 h. Then, KF (232 mg, 4.00 mmol) was added and the reaction mixture was vigorously stirred under air in the open reaction vessel at r.t. for 16 h. After the addition of the methanethiol **2** (or **6**, **8**) (1.20 mmol, 0.6 equiv), KOH (224 mg, 4 mmol), and DMSO (1.00 mL), the mixture was heated in the microwave cavity at 130 °C for 1 h. After cooling to r.t., the solvents were removed under reduced pressure. The residue was absorbed on Celite and purified by column chromatography on silica gel with *n*-hexane or *n*-hexane–THF (100:1) as eluent. The experimental details are shown in Table 2.

3-Benzyl-2,5-diphenylthiophene (3a)[13]

Colorless solid; mp 86 °C (Lit.[13] mp 94–95 °C); R_f = 0.25 (*n*-hexane).

IR (KBr): 3659 (w), 3022 (w), 2988 (w), 2916 (w), 1597 (m), 1489 (m), 1452 (m), 1254 (w), 1200 (w), 1072 (m), 1028 (m), 1005 (w), 910 (w), 851 (w), 760 (s), 746 (m), 700 (s), 692 (s), 699 (m), 638 (w), 621 cm^{-1} (w).

^1H NMR ($CDCl_3$, 600 MHz): δ = 4.10 (s, 2 H), 7.13 (s, 1 H), 7.24–7.32 (m, 4 H), 7.35 (t, ^3J = 7.6 Hz, 2 H), 7.40 (t, ^3J = 7.7 Hz, 3 H), 7.45 (t, ^3J = 7.6 Hz, 2 H), 7.54 (d, ^3J = 7.2 Hz, 2 H), 7.62 (d, ^3J = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 34.9 (CH_2), 125.7 (CH), 126.3 (CH), 126.5 (CH), 127.6 (CH), 127.7 (CH), 128.7 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 129.3 (CH), 134.4 (C_{quat}), 134.4 (C_{quat}), 137.2 (C_{quat}), 138.8 (C_{quat}), 141.0 (C_{quat}), 142.6 (C_{quat}).

GC-MS: *m*/*z* (%) = 326 (M^+, 100), 249 [$(M - C_6H_5)^+$, 46], 215 (15), 202 (6), 135 [$(C_8H_6S)^+$, 17], 121.0 [$(C_7H_5S)^+$, 7], 91 [$(C_7H_7)^+$, 6], 77 [$(C_6H_5)^+$, 3].

Anal. Calcd for $C_{23}H_{18}S$ (326.5): C, 84.62; H, 5.56. Found: C, 84.44; H, 5.45.

3-(2-Methylbenzyl)-2-phenyl-5-(*o*-tolyl)thiophene (3b)

Colorless solid; mp 83 °C; R_f = 0.30 (*n*-hexane).

IR (KBr): 3059 (w), 3017 (w), 2968 (w), 2951 (w), 2920 (s), 2857 (w), 1599 (w), 1485 (m), 1460 (m), 1443 (m), 1379 (w), 1194 (w), 1157 (w), 1076 (w), 1051 (w), 1034 (w), 849 (w), 756 (s), 741 (s), 727 (s), 698 (s), 638 cm^{-1} (w).

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.22 (s, 3 H), 2.45 (s, 3 H), 4.02 (s, 2 H), 6.74 (s, 1 H), 7.11–7.25 (m, 7 H), 7.34 (t, ^3J = 7.4 Hz, 1 H), 7.42 (q, ^3J = 8.4 Hz, ^3J = 7.8 Hz, 3 H), 7.50 (d, ^3J = 7.4 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 19.6 (CH_3), 21.3 (CH_3), 32.9 (CH_2), 125.9 (CH), 126.1 (CH), 126.3 (CH), 127.4 (CH), 127.7 (CH), 128.6 (CH), 128.8 (CH), 129.0 (CH), 129.8 (CH), 130.1 (CH), 130.8 (CH), 134.1 (C_{quat}), 134.4 (C_{quat}), 135.7 (C_{quat}), 135.9 (C_{quat}), 136.3 (C_{quat}), 138.7 (C_{quat}), 139.2 (C_{quat}), 141.3 (C_{quat}).

GC-MS: *m*/*z* (%) = 354 (M^+, 100), 263 [$(M - C_7H_7)^+$, 16], 249 [$(M - C_8H_9)^+$, 29], 228 (7), 215 (9), 135 [$(C_8H_7S)^+$, 12], 121.0 [$(C_7H_5S)^+$, 5], 115 (35), 105 [$(C_8H_9)^+$, 20], 91 [$(C_7H_7)^+$, 7].

Anal. Calcd for $C_{25}H_{22}S$ (354.1): C, 84.70; H, 6.26. Found: C, 84.76; H, 6.20.

Table 2 Experimental Data for the One-Pot Sonogashira–Glaser Cyclization/Synthesis of Thiophenes **3**

Entry	(Hetero)aryl iodide **1**	Methanethiol **2**	Thiophene (yield %)
1	iodobenzene (**1a**): 408 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3a**: 219 mg (67)
2	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3b**: 266 mg (75)
3	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	*p*-tolylmethanethiol (**2b**):[15] 166 mg (1.20 mmol)	**3c**: 310 mg (84)
4	*m*-iodotoluene (**1c**): 437 mg (2.00 mmol)	*p*-tolylmethanethiol (**2b**):[15] 166 mg (1.20 mmol)	**3d**: 121 mg (33)
5	*p*-iodotoluene (**1d**): 437 mg (2.00 mmol)	*p*-tolylmethanethiol (**2b**):[15] 166 mg (1.20 mmol)	**3e**: 151 mg (41)
6	1-fluoro-4-iodobenzene (**1e**): 444 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3f**: 210 mg (58)
7	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	4-fluorobenzylmercaptan (**2c**): 171 mg (1.20 mmol)	**3g**: 262 mg (70)
8	1-chloro-4-iodobenzene (**1f**): 477 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3h**: 119 mg (30)
9	2-iodothiophene (**1g**): 420 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3i**: 125 mg (37)
10	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	furan-2-ylmethanethiol (**2d**): 137 mg (1.20 mmol)	**3j**: 220 mg (64)
11	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	1,2-bis(thiophen-2-ylmethyl)disulfane (**2e**):[16] 155 mg (0.60 mmol)	**3k**: 102 mg (28)
12	2-iodothiophene (**1g**) 420 mg (2.00 mmol)	1,2-bis(thiophen-2-ylmethyl)disulfane (**2e**):[16] 155 mg (0.60 mmol)	**3l**: 80.0 mg (23)
13	3-iodoanisole (**1h**): 468 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3m**: 297 mg (77)
14	3-iodopyridine (**1i**): 410 mg (2.00 mmol)	benzylmercaptan (**2a**): 149 mg (1.20 mmol)	**3n**: 114 mg (34)
15	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	1,3-phenylenedimethanethiol (**8**):[17] 102 mg (0.60 mmol)	**9**: 147 mg (46)
16	*o*-iodotoluene (**1b**): 437 mg (2.00 mmol)	1,3,5-phenylenetrimethanethiol (**10**):[18] 86 mg (0.40 mmol)	**11**: 52.0 mg (32)

3-(2-Methylbenzyl)-5-(*o*-tolyl)-2-(*p*-tolyl)thiophene (3c)
Colorless solid; mp 76 °C; R_f = 0.19 (*n*-hexane).

IR (KBr): 3059 (w), 3018 (w), 2918 (w), 1908 (w), 1714 (w), 1601 (w), 1514 (w), 1489 (m), 1460 (m), 1379 (w), 1217 (w), 1186 (w), 1111 (w), 1096 (w), 1051 (w), 1034 (w), 993 (w), 941 (m), 941 (w), 849 (w), 816 (s), 758 (s), 740 (s), 727 (m), 682 (w), 665 (w), 650 (w), 617 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.10 (s, 3 H), 2.28 (s, 3 H), 2.33 (s, 3 H), 3.89 (s, 2 H), 6.60 (s, 1 H), 7.04–7.14 (m, 10 H), 7.29–7.33 (m, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.7 (CH_3), 21.4 (CH_3), 21.4 (CH_3), 33.0 (CH_2), 126.0 (CH), 126.2 (CH), 126.4 (CH), 127.7 (CH), 129.0 (CH), 129.0 (CH), 129.5 (CH), 129.8 (CH), 130.2 (CH), 130.9 (CH), 131.6 (C_{quat}), 134.3 (C_{quat}), 135.5 (C_{quat}), 136.0 (C_{quat}), 136.4 (C_{quat}), 137.4 (C_{quat}), 138.9 (C_{quat}), 139.4 (C_{quat}), 141.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 368 (M^+, 41), 265 [$(M - C_8H_7)^+$, 5], 263 [$(M - C_8H_9)^+$, 13], 254 (21), 164 (29), 152 (15), 148 [$(C_9H_8S)^+$, 18], 135 [$(C_8H_7S)^+$, 7], 134 (20), 115 (9), 105 [$(C_8H_9)^+$, 100], 91 [$(C_7H_7)^+$, 7], 77 (8), 57 [$(C_2HS)^+$, 7], 39 (3).

Anal. Calcd for $C_{26}H_{24}S$ (368.2): C, 84.70; H, 6.56; S, 8.70. Found: C, 84.73; H, 6.44; S, 8.81.

3-(3-Methylbenzyl)-5-(*m*-tolyl)-2-(*p*-tolyl)thiophene (3d)
Yellow oil; R_f = 0.47 (*n*-hexane).

IR (KBr): 3021 (w), 2918 (w), 2859 (w), 1603 (m), 1584 (w), 1557 (w), 1489 (m), 1456 (w), 1377 (w), 1308 (w), 1167 (w), 1092 (w), 1038 (w), 962 (w), 874 (w), 839 (m), 816 (s), 779 (s), 746 (m), 691 (s), 658 (w), 615 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.33 (s, 3 H), 2.37 (s, 3 H), 2.40 (s, 3 H) 4.01 (s, 2 H), 6.99–7.09 (m, 5 H), 7.17–7.23 (m, 4 H), 7.38–7.40 (m, 4 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 21.6 (CH_3), 21.6 (CH_3), 34.9 (CH_2), 122.8 (CH), 125.8 (CH), 126.4 (CH), 127.0 (CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 129.1 (CH), 129.5 (CH), 131.6 (C_{quat}), 134.4 (C_{quat}), 136.9 (C_{quat}), 137.5 (C_{quat}), 138.2 (C_{quat}), 138.6 (C_{quat}), 138.7 (C_{quat}), 141.1 (C_{quat}), 142.3 (C_{quat}).

GC-MS: *m*/*z* (%) = 368 (M^+, 4), 254 (38), 150 [$(C_9H_{10}S)^+$, 1], 135 [$(C_8H_7S)^+$, 2], 105 [$(C_8H_9)^+$, 100], 91 [$(C_7H_7)^+$, 2], 77 (6), 57 [$(C_2HS)^+$, 7].

Anal. Calcd for $C_{26}H_{24}S$ (368.5): C, 84.70; H, 6.56; S, 8.70. Found: C, 85.09; H, 6.88; S, 8.29.

3-(4-Methylbenzyl)-2,5-di-*p*-tolylthiophene (3e)
Yellow oil; R_f = 0.37 (*n*-hexane).

IR (KBr): 3048 (w), 3021 (w), 2918 (w), 2305 (w), 1892 (w), 1506 (m), 1481 (w), 1435 (w), 1379 (w), 1312 (w), 1184 (w), 1111 (w), 1040 (w), 1020 (w), 1006 (w), 947 (w), 905 (w), 854 (w), 821 (m), 810 (s), 788 (m), 748 (w), 725 (w), 678 (w), 621 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.36 (s, 3 H), 2.37 (s, 3 H), 2.41 (s, 3 H), 4.02 (s, 2 H), 7.05 (s, 1 H), 7.12–7.25 (m, 8 H), 7.41 (d, ^3J = 8.1 Hz, 2 H), 7.48 (d, ^3J = 8.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.0 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 34.4 (CH_2), 125.4 (CH), 125.8 (CH), 128.4 (CH), 129.0 (CH), 129.2 (CH), 129.3 (CH), 129.5 (CH), 131.5 (C_{quat}), 131.6 (C_{quat}), 135.5 (C_{quat}), 136.9 (C_{quat}), 137.2 (C_{quat}), 137.3 (C_{quat}), 137.9 (C_{quat}), 138.0 (C_{quat}), 142.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 368 (M^+, 1), 254 (35), 150 [$(C_9H_{10}S)^+$, 2], 135 [$(C_8H_7S)^+$, 2], 105 [$(C_8H_9)^+$, 100], 91 [$(C_7H_7)^+$, 3], 77 (6), 57 [$(C_2HS)^+$, 3].

Anal. Calcd for $C_{26}H_{24}S$ (368.5): C, 84.74; H, 6.56; S, 8.70. Found: C, 84.95; H, 6.79; S, 8.40.

3-(4-Fluorobenzyl)-5-(4-fluorophenyl)-2-phenylthiophene (3f)
Yellow oil; R_f = 0.36 (*n*-hexane).

IR (KBr): 3066 (w), 2953 (w), 2922 (w), 2852 (w), 1685 (w), 1597 (m), 1557 (w), 1508 (s), 1491 (m), 1460 (w), 1445 (w), 1433 (w), 1410 (w), 1371 (w), 1296 (w), 1229 (s), 1153 (m), 1130 (w), 1096 (w), 1016 (w), 1005 (w), 955 (w), 901 (w), 849 (w), 826 (s), 802 (s), 768 (m), 752 (s), 729 (w), 698 (s), 664 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.00 (s, 2 H), 6.95–7.15 (m, 7 H), 7.34–7.54 (m, 7 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.0 (CH_2), 115.3 (d, ^2J = 21.2 Hz, CH), 115.8 (d, ^2J = 21.8 Hz, CH), 126.0 (d, ^4J = 2.0 Hz, CH), 127.2 (d, ^3J = 8.0 Hz, CH), 127.8 (CH), 128.7 (CH), 129.1 (CH), 129.9 (d, ^3J = 7.8 Hz, CH), 130.4 (d, ^4J = 3.4 Hz, C_{quat}), 134.0 (C_{quat}), 136.4 (d, ^5J = 1.7 Hz, C_{quat}), 137.0 (C_{quat}), 138.6 (d, ^5J = 0.7 Hz, C_{quat}), 141.5 (C_{quat}), 161.4 (d, ^1J = 242.6 Hz, C_{quat}), 162.3 (d, ^1J = 245.7 Hz, C_{quat}).

GC-MS: *m*/*z* (%) = 362 (M^+, 100), 285 [$(M - C_6H_5)^+$, 10], 265 [$(M - C_6H_4F)^+$, 10], 233 (8), 139 [$(C_4H_4FS)^+$, 5], 121 [$(C_7H_5S)^+$, 5], 109 [$(C_7H_6F)^+$, 3], 57 [$(C_2HS)^+$, 2].

Anal. Calcd for $C_{23}H_{16}F_2S$ (362.1): C, 76.22, H, 4.45; S, 8.85. Found: C, 76.26; H, 4.60; S, 8.90.

2-(4-Fluorophenyl)-3-(2-methylbenzyl)-5-(*o*-tolyl)thiophene (3g)
Yellow oil; R_f = 0.21 (*n*-hexane).

IR (KBr): 3061 (w), 3016 (w), 2922 (w), 1686 (w), 1601 (w), 1555 (w), 1510 (m), 1489 (m), 1491 (m), 1460 (m), 1379 (w), 1221 (m), 1157 (m), 1096 (w), 1049 (w), 1033 (w), 935 (w), 833 (m), 812 (w), 758 (m), 743 (s), 727 (m), 668 (w), 650 (m), 615 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 2.20 (s, 3 H), 2.43 (s, 3 H), 3.96 (s, 2 H), 6.73 (s, 1 H), 7.06–7.24 (m, 9 H), 7.40–7.45 (m, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.7 (CH_3), 21.4 (CH_3), 32.9 (CH_2), 115.7 (d, ^2J = 21.5 Hz, CH), 126.1 (CH), 126.3 (CH), 126.5 (CH), 127.9 (CH), 128.9 (CH), 129.8 (CH), 130.3 (d, ^4J = 5.0 Hz, CH), 130.5 (d, ^4J = 3.4 Hz, C_{quat}), 130.8 (CH), 130.9 (d, ^3J = 7.7 Hz, CH), 134.1 (C_{quat}), 135.9 (C_{quat}), 136.0 (C_{quat}), 136.4 (C_{quat}), 137.6 (C_{quat}), 139.2 (C_{quat}), 141.5 (C_{quat}), 162.4 (d, J = 247.4 Hz, C_{quat}).

GC-MS: *m*/*z* (%) = 372 (M^+, 37), 281 [$(M - C_7H_7)^+$, 7], 267 [$(M - C_8H_9)^+$, 12], 140 (7), 115 (7), 109 (100), 97 (11), 95 [$(C_6H_4F)^+$, 10], 85 [$(C_4H_5S)^+$, 11], 83 (17), 71 (15), 69 (12), 57 [$(C_2HS)^+$, 24], 55 (12).

Anal. Calcd for $C_{25}H_{21}FS$ (372.1): C, 80.61; H, 5.68. Found: C, 80.63; H, 5.68.

3-(4-Chlorobenzyl)-5-(4-chlorophenyl)-2-phenylthiophene (3h)
Colorless solid; mp 150 °C; R_f = 0.36 (*n*-hexane).

IR (KBr): 3061 (w), 3026 (w), 2920 (w), 2358 (w), 1894 (w), 1595 (w), 1487 (s), 1456 (w), 1431 (w) 1402 (w), 1254 (w), 1179 (w), 1157 (w), 1090 (s), 1013 (m), 961 (w), 935 (w), 907 (w), 849 (w), 822 (s), 802 (s), 762 (s), 721 (m), 694 (s), 669 (w), 629 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.01 (s, 2 H), 7.02 (s, 1 H), 7.11 (d, ^3J = 8.5 Hz, 2 H), 7.27–7.52 (m, 11 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.3 (CH_2), 126.4 (CH), 126.8 (CH), 128.0 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 129.2 (CH), 130.0 (CH), 132.1 (C_{quat}), 132.7 (C_{quat}), 133.4 (C_{quat}), 134.0 (C_{quat}), 136.8 (C_{quat}), 139.3 (C_{quat}), 139.4 (C_{quat}), 141.5 (C_{quat}).

GC-MS: *m*/*z* (%) = 394 (M^+, 6), 262 (17), 260 (46), 170 [$(C_8H_7ClS)^+$, 4], 155 [$(C_7H_4ClS)^+$, 4], 150 [$(C_9H_7Cl)^+$, 3], 139 (10), 133 [$(C_8H_5S)^+$, 13], 125.0 [$(C_7H_6Cl)^+$, 6], 91 (100), 89 [$(C_7H_5)^+$, 7], 77 [$(C_6H_5)^+$, 5], 39 (2).

Anal. Calcd for $C_{23}H_{16}Cl_2S$ (394.0): C, 69.87; H, 4.08; S, 8.11. Found: C, 69.69; H, 4.13; S, 7.93.

5-Phenyl-4-(thiophen-2-ylmethyl)-2,2′-bithiophene (3i)[13]
Light green solid; mp 74 °C (Lit.[13] mp 70–71 °C); R_f = 0.43 (*n*-hexane).

IR (KBr): 3098 (w), 3063 (w), 2922 (w), 2851 (w), 1595 (w), 1487 (w), 1464 (w), 1352 (w), 1242 (w), 1231 (w), 1113 (w), 1074 (w), 1034 (w), 839 (m), 818 (m), 752 (s), 689 (s), 644 cm^{-1} (m).

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.19 (s, 2 H), 6.85–6.86 (m, 1 H), 6.98 (dd, ^3J = 5.1 Hz, ^4J = 3.4 Hz, 1 H), 7.04 (dd, ^3J = 5.1 Hz, ^4J = 3.6 Hz, 1 H), 7.19–7.25 (m, 3 H), 7.38–7.54 (m, 5 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.4 (CH_2), 123.8 (CH), 124.0 (CH), 124.5 (CH), 125.1 (CH), 126.6 (CH), 127.0 (CH), 127.9 (CH), 128.8 (CH), 129.3 (CH), 133.8 (C_{quat}), 136.0 (C_{quat}), 136.3 (C_{quat}), 137.4 (C_{quat}), 138.3 (C_{quat}), 143.9 (C_{quat}).

GC-MS: *m*/*z* (%) = 338 (M^+, 100), 305 (10), 271 (7), 253 (18), 227 (8), 221 (20), 152 (14), 127 [$(C_5H_3S_2)^+$, 28], 121 (26), 97 [$(C_5H_5S)^+$, 39], 84 (46), 77 [$(C_6H_5)^+$, 29], 69 (26), 58 [$(C_2H_2S)^+$, 25], 53 (23), 51 (23).

Anal. Calcd for $C_{19}H_{14}S_3$ (338.5): C, 67.41; H, 4.17; S, 28.42. Found: C, 67.67; H, 4.30; S, 28.31.

2-[3-(2-Methylbenzyl)-5-(*o*-tolyl)thiophen-2-yl]furan (3j)
Green oil; R_f = 0.26 (*n*-hexane).

IR (KBr): 3061 (w), 3015 (w), 2969 (w), 2951 (w), 2860 (w), 1601 (w), 1489 (m), 1456 (m), 1379 (w), 1152 (w), 1026 (w), 1003 (w), 876 (w), 851 (w), 758 (s), 725 cm^{-1} (s).

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.30 (s, 3 H), 2.40 (s, 3 H), 4.11 (s, 2 H), 6.38 (d, J = 3.3 Hz, 1 H), 6.48 (dd, J = 3.3 Hz, 1.8 Hz, 1 H), 6.60 (s, 1 H), 7.10–7.25 (m, J = 87.2 Hz, 7 H), 7.39 (d, J = 6.8 Hz, 1 H), 7.47 (d, J = 1.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 19.7 (CH_3), 21.3 (CH_3), 33.7 (CH_2), 106.8 (CH), 111.8 (CH), 126.1 (CH), 126.3 (CH), 126.6 (CH), 128.0 (C_{quat}), 128.1 (CH), 129.1 (CH), 129.8 (CH), 130.2 (CH), 130.3 (CH), 131.0 (C_{quat}), 133.9 (C_{quat}), 136.0 (C_{quat}), 136.4 (C_{quat}), 136.6 (C_{quat}), 138.4 (C_{quat}), 141.1 (C_{quat}), 141.7 (CH), 149.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 344 (M^+, 100), 315 (13), 240 (28), 165 (14), 115 (19).

Anal. Calcd for $C_{23}H_{20}OS$ (344.5): C, 80.19; H, 5.85; S, 9.31. Found: C, 79.98; H, 5.85; S, 9.49.

3-(2-Methylbenzyl)-5-(*o*-tolyl)-2,2′-bithiophene (3k)
Yellow oil; R_f = 0.33 (*n*-hexane).

IR (KBr): 3063 (w), 3015 (w), 2949 (w), 2920 (w), 2860 (w), 1601 (w), 1498 (m), 1456 (m), 1379 (m), 1219 (w), 1159 (w), 1051 (m), 988 (w), 939 (w), 843 (m), 824 (m), 758 (s), 741 (s), 727 (s), 692 cm^{-1} (s).

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.88 (s, 3 H), 3.02 (s, 3 H), 4.70 (s, 2 H), 7.63–7.86 (m, 10 H), 7.90 (d, ^3J = 5.1 Hz, 1 H), 8.00 (d, ^3J = 7.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 19.7 (CH_3), 21.4 (CH_3), 33.4 (CH_2), 125.6 (CH), 125.9 (CH), 126.1 (CH), 126.3 (CH), 126.6 (CH), 127.7 (CH), 127.9 (CH), 129.0 (CH), 130.0 (CH), 130.2 (CH), 130.3 (CH), 131.0 (C_{quat}), 131.5 (C_{quat}), 133.8 (C_{quat}), 136.0 (C_{quat}), 136.0 (C_{quat}), 136.5 (C_{quat}), 136.7 (C_{quat}), 138.8 (C_{quat}), 141.3 (C_{quat}).

GC-MS: *m*/*z* (%) = 360 (M^+, 100), 269 (14), 256 (26), 221 (10), 148 (6), 127 (15), 115 (14), 91 (17).

Anal. Calcd for $C_{23}H_{20}S_2$ (360.5): C, 76.62; H, 5.59; S, 17.79. Found: C, 76.77; H, 5.81; S, 17.49.

3′-(Thiophen-2-ylmethyl)-2,2′:5′,2″-terthiophene (3l)[13]
Yellow oil; R_f = 0.56 (*n*-hexane).

IR (KBr): 3103 (w), 3067 (w), 2901 (w), 2843 (w), 1790 (w), 1503 (w), 1429 (m), 1418 (m), 1294 (m), 1227 (m), 1107 (m), 1076 (m), 1038 (m), 818 (s), 685 cm^{-1} (s).

^1H NMR ($CDCl_3$, 600 MHz): δ = 4.26 (s, 2 H), 6.83 (d, ^3J = 3.3 Hz, 1 H), 6.95 (dd, ^3J = 5.0 Hz, ^4J = 3.5 Hz, 1 H), 7.01 (dd, ^3J = 5.0 Hz, ^4J = 3.7 Hz, 1 H), 7.03 (s, 1 H), 7.07 (dd, ^3J = 5.1 Hz, ^4J = 3.7 Hz, 1 H), 7.15 (d, ^4J = 3.5 Hz, 1 H), 7.17 (t, ^3J = 4.4 Hz, 2 H), 7.21 (d, ^3J = 5.1 Hz, 1 H), 7.32 (d, ^3J = 5.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 29.7 (CH_2), 124.0 (CH), 124.1 (CH), 124.7 (CH), 125.2 (CH), 126.0 (CH), 126.5 (CH), 126.8 (CH), 127.0 (CH), 127.8 (CH), 128.0 (CH), 130.8 (C_{quat}), 135.2 (C_{quat}), 135.9 (C_{quat}), 137.0 (C_{quat}), 137.2 (C_{quat}), 143.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 344 (M^+, 100), 311 (17), 272 (17), 227 (19), 127 [$(C_5H_3S_2)^+$, 27], 97 (18), 69 (17).

Anal. Calcd for $C_{17}H_{12}S_4$ (344.5): C, 59.26; H, 3.51; S, 37.23. Found: C, 59.52; H, 3.67; S, 37.19.

3-(3-Methoxybenzyl)-5-(3-methoxyphenyl)-2-phenylthiophene (3m)
Yellow oil; R_f = 0.43 (*n*-hexane).

IR (KBr): 3053 (w), 3022 (w), 2999 (w), 2935 (w), 2833 (w), 1597 (s), 1580 (m), 1485(s), 1464 (m), 1454 (m), 1433 (m), 1314 (w), 1288 (m), 1258 (s), 1198 (m), 1165 (s), 1078 (w), 1074 (s), 1009 (w), 995 (w), 964 (w), 924 (w), 839 (m), 773 (s), 760 (s), 748 (s), 799 (s), 640 (w), 623 cm^{-1} (w).

^1H NMR ($CDCl_3$, 600 MHz): δ = 3.78 (d, ^5J = 1.3 Hz, 3 H), 3.85 (d, ^5J = 1.3 Hz, 3 H), 4.04 (s, 2 H), 6.72–6.85 (m, 4 H), 7.11 (d, ^3J = 10.8 Hz, 2 H), 7.19 (d, ^3J = 7.6 Hz, 1 H), 7.23 (t, ^3J = 7.4 Hz, 1 H), 7.28 (t, ^3J = 8.0 Hz, 1 H), 7.35 (t, ^3J = 7.9 Hz, 1 H), 7.42 (t, ^3J = 7.5 Hz, 2 H), 7.50 (d, ^3J = 8.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 34.9 (CH_2), 55.3 (CH_3), 55.5 (CH_3), 111.3 (CH), 111.4 (CH), 113.1 (CH), 114.6 (CH), 118.3 (CH), 121.1 (CH), 126.6 (CH), 127.8 (CH), 128.8 (CH), 129.3 (CH), 129.6 (CH), 130.0 (CH), 134.4 (C_{quat}), 135.7 (C_{quat}), 136.9 (C_{quat}), 138.9 (C_{quat}), 142.4 (C_{quat}), 142.6 (C_{quat}), 159.9 (C_{quat}), 160.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 386 (M^+, 85), 294 (60), 279 [$(M - C_7H_7O)^+$, 22], 266 (100), 235 [$(M - C_8H_7OS)^+$, 17], 226 (26), 183 (44), 151 [$(C_8H_7OS)^+$, 6], 121 [$(C_7H_5S)^+$, 19], 91 (75), 77 [$(C_6H_5)^+$, 11], 51 (6).

Anal. Calcd for $C_{25}H_{22}O_2S$ (386.1): C, 77.69; H, 5.74. Found: C, 77.66; H, 5.85.

3-[5-Phenyl-4-(pyridin-3-ylmethyl)thiophen-2-yl]pyridine (3n)
Brown oil; R_f = 0.15 (*n*-hexane–EtOAc, 1:1).

IR (KBr): 3034 (w), 2930 (w), 2904 (w), 1715 (w), 1597 (w), 1572 (w), 1557 (w), 1456 (m), 1460 (w), 1337 (w), 1290 (w), 1221 (m), 1167 (w), 1099 (w), 1047 (w), 1026 (m), 1004 (w), 949 (w), 872 (w), 806 (m), 764 (s), 733 (w), 700 (s), 660 (w), 629 (m), 617 cm^{-1} (w).

^1H NMR ($CDCl_3$, 300 MHz): δ = 4.22 (s, 2 H), 7.32–7.70 (m, 9 H), 7.99 (dt, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 1 H), 8.60–8.70 (m, 3 H), 9.00 (d, ^4J = 1.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 32.2 (CH_2), 123.7 (CH), 123.8 (CH), 126.9 (CH), 128.3 (CH), 129.0 (CH), 129.3 (CH), 130.2 (C_{quat}), 132.7, 133.6 (C_{quat}), 136.1, 136.2 (C_{quat}), 136.2 (C_{quat}), 139.1 (C_{quat}), 140.5 (C_{quat}), 146.8 (CH), 147.9 (CH), 148.7 (CH), 150.0 (CH).

MS-EI: *m*/*z* (%) = 328 (M^+, 100), 250 [$(M - C_5H_4N)^+$, 29], 238 (11), 164 (4), 139 (14), 135 149 (6), 120 (12), 45 [$(CHS)^+$, 7].

HRMS: *m*/*z* calcd for $C_{21}H_{16}N_2S^+$: 329.1107; found: 329.1105.

1,3-Bis[3-(2-methylbenzyl)-5-(*o*-tolyl)thiophen-2-yl]benzene (9)
Colorless solid; R_f = 0.27 (*n*-hexane).

IR (KBr): 3059 (w), 3015 (w), 2918 (w), 1712 (m), 1593 (m), 1491 (m), 1479 (m), 1456 (m), 1379 (m), 1378 (m), 1219 (m), 1094 (m), 1051 (m), 936 (m), 903 (m), 851 (m), 791 (m), 760 (s), 741 (s), 723 (s), 698 cm^{-1} (s).

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.30 (s, 6 H), 2.40 (s, 6 H), 4.11 (s, 4 H), 6.38 (d, ^4J = 3.3 Hz, 2 H), 6.48 (dd, ^4J = 3.3 Hz, ^5J = 1.8 Hz, 2 H), 6.60 (s, 2 H), 7.06–7.25 (m, 12 H), 7.39 (dd, ^3J = 7.8 Hz, ^5J = 1.5 Hz, 2 H), 7.47 (d, ^5J = 1.7 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 19.7 (CH_3), 21.3 (CH_3), 33.7 (CH_2), 106.8 (CH), 111.8 (CH), 126.1 (CH), 126.3 (CH), 126.6 (CH), 128.0 (CH), 128.1 (C_{quat}), 129.1 (CH), 129.8 (CH), 130.2 (CH), 130.3 (CH), 131.0 (CH), 133.9 (C_{quat}), 136.0 (C_{quat}), 136.4 (C_{quat}), 136.6 (C_{quat}), 138.4 (C_{quat}), 141.1 (C_{quat}), 141.7 (CH), 149.1 (C_{quat}).

GC-MS: *m*/*z* (%) = 630 (M^+, 10), 426 (100), 335 (11), 322 (40), 17 (105).

HRMS: *m*/*z* calcd for $C_{44}H_{39}S_2^+$: 631.2487; found: 631.2484.

1,3,5-Tris[3-(2-methylbenzyl)-5-(*o*-tolyl)thiophen-2-yl]benzene (11)
Yellow oil; R_f = 0.56 (*n*-hexane).

IR (KBr): 3061 (w), 3017 (w), 2951 (w), 2922 (w), 2866 (w), 2359 (s), 2338 (s), 1586 (w), 1498 (w), 1456 (m), 907 (m), 729 (s), 648 cm^{-1} (m).

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.17 (s, 9 H), 2.46 (s, 9 H), 3.98 (s, 6 H), 6.74 (s, 3 H), 7.15 (m, 14 H), 7.12–7.18 (m, 7 H), 7.25–7.29 (d, ^3J = 8.0 Hz, 3 H), 7.60 (s, 3 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 9.7 (CH_3), 21.4 (CH_3), 33.2 (CH_2), 126.1 (CH), 126.2 (CH), 126.5 (CH), 127.9 (CH), 128.2 (CH), 129.0 (CH), 130.0 (CH), 130.2 (CH), 130.3 (CH), 131.0 (CH), 134.0 (C_{quat}), 135.3 (C_{quat}), 136.0 (C_{quat}), 136.4 (C_{quat}), 136.5 (C_{quat}), 137.8 (C_{quat}), 139.1 (C_{quat}), 142.0 (C_{quat}).

MS-EI: *m*/*z* (%) = 907 (M^+, 100), 802 (16), 644 (65), 540 (14), 439 (13), 315 (14), 275 (16), 229 (17), 135 (33), 119 (49), 105 (70), 91 (29).

HRMS: *m*/*z* calcd for $C_{63}H_{54}NaS_3^+$: 929.3280; found: 929.3274.

(*E*/*Z*)-(1,4-Di-*p*-tolylbut-1-en-3-yn-1-yl)(4-methylbenzyl)sulfane [(*E*/*Z*)-5]
The synthesis was carried out according to the general procedure (in the absence of KOH) with *p*-iodotoluene (**1d**; 437 mg, 2.00 mmol) and *p*-tolylmethanethiol[15] (**2b**; 166 mg, 1.20 mmol). The crude product was absorbed onto Celite and purified by column chromatography on silica gel with *n*-hexane as an eluent to give of (*E*/*Z*)-**5** (2:1); yield: 214.0 mg (58%); brown solid; mp 83 °C; R_f = 0.33 (*n*-hexane).

IR (KBr): 3023 (w), 2916 (w), 1501 (m), 1180 (w), 1107 (m), 1038 (m), 1020 (m), 812 (s), 748 (w), 723 (w), 667 cm^{-1} (w).

MS-EI: *m*/*z* (%) = 368 (M^+, 95), 277 [$(C_{19}H_{17}S)^+$, 33], 248 (41), 219 (18), 135 (15), 105 [$(C_8H_9)^+$, 100].

Anal. Calcd for $C_{26}H_{24}S$ (368.5): C, 84.74; H, 6.56; S, 8.70. Found: C, 84.87; H, 6.52; S, 8.65.

(*Z*)-(1,4-Di-*p*-tolylbut-1-en-3-yn-1-yl)(4-methylbenzyl)sulfane [(*Z*)-5]
(*Z*)-(1,4-Di-*p*-tolylbut-1-en-3-yn-1-yl)(4-methylbenzyl)sulfane [(*Z*)-**5**] was obtained by keeping the *E*/*Z* mixture of **5** under daylight for one year; brown solid.

^1H NMR ($CDCl_3$, 600 MHz): δ = 2.30 (s, 3 H), 2.36 (s, 3 H), 2.38 (s, 3 H), 3.87 (s, 2 H), 6.03 (s, 1 H), 7.04 (d, ^3J = 7.9 Hz, 2 H), 7.09 (d, ^3J = 7.9 Hz, 2 H), 7.14 (d, ^3J = 7.9 Hz, 2 H), 7.18 (d, ^3J = 7.9 Hz, 2 H), 7.38 (dd, ^3J = 7.9 Hz, ^4J = 3.2 Hz, 5 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 21.1 (CH_3), 21.3 (CH_3), 21.5 (CH_3), 37.2 (CH_2), 87.3 (C_{quat}), 97.6 (C_{quat}), 109.7 (CH), 120.6 (C_{quat}), 127.9 (CH), 128.8 (CH), 129.0 (CH), 129.2 (CH), 131.3 (CH), 134.7 (C_{quat}), 136.2 (C_{quat}), 136.6 (C_{quat}), 138.3 (C_{quat}), 138.7 (C_{quat}), 148.7 (C_{quat}).

Acknowledgment

The authors cordially thank the Fonds der Chemischen Industrie for support.

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