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Selective Multiple Magnesiations of the Thieno[3,2-*b*]thiophene Scaffold

Thomas Kunz and Paul Knochel*[a]

Abstract: A full functionalization of all four positions of the thieno[3,2-*b*]thiophene scaffold was achieved. Starting from 2,5-dichlorothieno[3,2-*b*]thiophene, magnesiation of the 3- and 6-position using tmpMgCl·LiCl furnishes, after trapping with various electrophiles, 3,6-difunctionalized dichlorothieno[3,2-*b*]thiophenes. Subsequent dechlorination and regioselective metalation or regioselective magnesium insertion into the C–Cl bond provides fully functionalized thieno[3,2-*b*]thiophenes. Furthermore, new condensed heterocycles and small oligomers of these compounds with potential applications in material chemistry have been prepared.

Keywords: C–H activation · cross-coupling · magnesium · metalation · regioselectivity

Introduction

In the research field of materials chemistry, molecular electronics and electronic devices have rapidly gained interest. Besides organic light-emitting diodes (OLEDs)[1] and organic field-effect transistors (FETs),[2] organic photovoltaics[3] have attracted considerable attention in the search for a reliable alternative energy supply. The different approaches to construct organic solar cells are based on bulk heterojunction, small-molecule, or nanorod systems,[4] consisting of various donor–acceptor interactions.[5] Improvement of these donor–acceptor systems depends on advances in the morphology of the materials as well as in their molecular structure.[6] Among the donor polymers, functional oligothiophenes or fused S-heterocycles are predominant.[7] More recently thienothiophenes, in particular the thieno[3,2-*b*]thiophene scaffold, have attracted considerable attention, as these moieties comprise some significant advantages, such as centrosymmetry and higher rigidity, over the universally employed thiophene building block.[8]

Direct lithiations are known for all positions of the fused thienothiophene ring, although selective lithiations on the 3- and 6-positions are only possible by halogen–lithium exchange and therefore require low temperatures. Furthermore, organolithium reagents are not compatible with several important functional groups, such as aldehydes, ketones, or esters.[9] Direct magnesiation of this scaffold as an alternative strategy has to the best of our knowledge, not been explored.[10] Directed magnesiations of aromatic and heteroaromatic substrates using the recently developed Mg/Li–amide tmpMgCl·LiCl (**1**; tmp = 2,2,6,6-tetramethylpiperidyl) have shown broad applicability and exceptional functional group tolerance.[11]

Herein, we report the full functionalization of the thieno[3,2-*b*]thiophene ring starting from readily available 2,5-dichlorothieno[3,2-*b*]thiophene[12] (**2**) using the tmpMgCl·LiCl base (**1**). This allows the incorporation of sensitive functional groups that are tolerated in further modifications leading to highly diverse compounds that were so far inaccessible. In a general reaction sequence, the thienothiophene **2** is metalated sequentially at the 3- and 6-position with base **1** and leads, after quenching with various electrophiles, to substituted thienothiophenes of type **5**. After the reductive cleavage of the C–Cl bonds, the intermediate **6** is then regioselectively deprotonated at the 2- and 5-position, again using tmpMgCl·LiCl (**1**), leading to fully functionalized thieno[3,2-*b*]thiophenes of type **8** (Scheme 1).

Results and Discussion

Preparation of 3,6-disubstituted 2,5-dichlorothieno[3,2-*b*]-thiophenes of type 5: The reaction of 2,5-dichlorothieno[3,2-*b*]thiophene (**2**) with tmpMgCl·LiCl (**1**; 1.1 equiv, 25 °C, 45 min) leads to the corresponding 3-magnesiated thienothiophene **3**, which can be trapped with $PhSO_2SMe$ to give

[a] M. Sc. T. Kunz, Prof. Dr. P. Knochel
Department Chemie, Ludwig-Maximilians-Universtät München
Butenandtstrasse 5–13, 81377 München (Germany)
Fax: (+49) 89-2180-77680
E-mail: paul.knochel@cup.uni-muenchen.de

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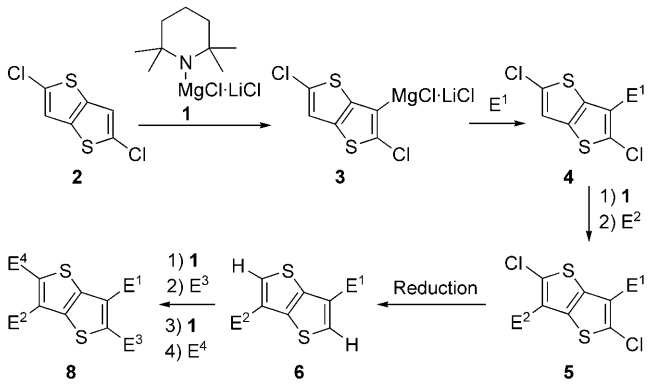


Scheme 1. Reaction sequence allowing the conversion of 2,5-dichlorothieno-[3,2-*b*]thiophene (**2**) to fully functionalized thieno[3,2-*b*]thiophenes of type **8**.

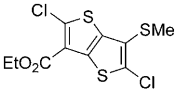
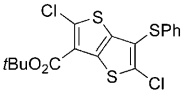
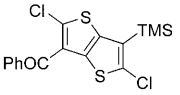
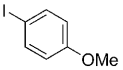
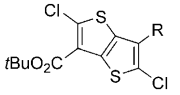
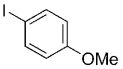
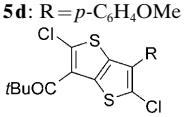
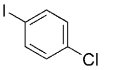
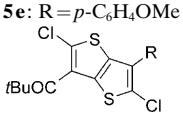
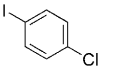
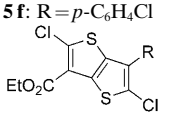
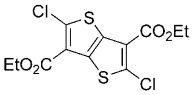
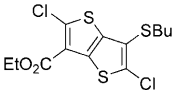
the thiomethylated thienothiophene **4a**[13] in 96% yield. A subsequent deprotonation of **4a** using base **1** (25°C, 45 min) yields the ester **5a** in 89% yield after reaction with ethyl cyanoformate (entry 1, Table 1). Similarly, treatment of intermediate **3** with $PhSO_2SPh$ provides the thioether **4b** in 85% yield. A further deprotonation of **4b** (25°C, 45 min) and quenching with di-*tert*-butyl dicarbonate gives the ester **5b** in 70% yield (entry 2, Table 1). The reaction of the 3-magnesiated thienothiophene **3** with TMSCN affords compound **4c** in 85% yield. Metalation of **4c** (25°C, 45 min) followed by a Cu^I-catalyzed acylation[14] with benzoyl chloride gives the difunctionalized thienothiophene **5c** in 95% yield (entry 3, Table 1). A Pd-catalyzed cross-coupling reaction[15] of **3** with 1-iodo-4-methoxybenzene or 1-chloro-4-iodobenzene (3 mol% $[Pd(dba)_2]$, 6 mol% tfp, tfp = tri-(2-furyl)-phosphine) leads to thienothiophenes **4d** and **4f** in 71–91% yield (entries 4–7, Table 1). After metalation of **4d** (25°C, 1 h), the magnesiated intermediate reacts directly with Boc_2O giving product **5d** in 73% yield (entry 4, Table 1). Alternatively, a Cu^I-catalyzed acylation reaction with pivaloyl chloride leads to ketone **5e** in 85% yield (entry 5, Table 1). Similarly, the deprotonation of **4f** (25°C, 45 min) affords after subsequent acylation with pivaloyl choride **5f** in 75% yield (entry 6, Table 1). The reaction with ethyl cyanoformate as second electrophile gives **5g** in 81% yield (entry 7, Table 1). The ester **4h** is obtained in 92% yield (entry 8, Table 1) by trapping the 3-magnesiated thienothiophene **3** with ethyl cyanoformate. After a successive metalation (−20°C, 20 min) and quenching again with ethyl cyanoformate the diester **5h** is isolated in 81% yield. Treatment of intermediate **3** with $PhSO_2SBu$ yields thioether **4i** in 94% yield. A subsequent deprotonation (25°C, 45 min) and trapping with ethyl cyanoformate provides the ester **5i** in 83% yield (entry 9).

Preparation of 3,6-disubstituted thieno[3,2-*b*]thiophenes of type 6: The best method for the reductive cleavage of a C–Cl bond was the reduction developed by Schlosser and coworkers using Pd/C and ammonium formate.[16] As conventional heating leads to a sluggish reaction, microwave irradiation (100 W, 120°C) was used. This enhances the reaction rate, so that the reduction of the dichlorothieno[3,2-*b*]thiophene **5a** is complete within 6 h, yielding **6a** in 77% yield.

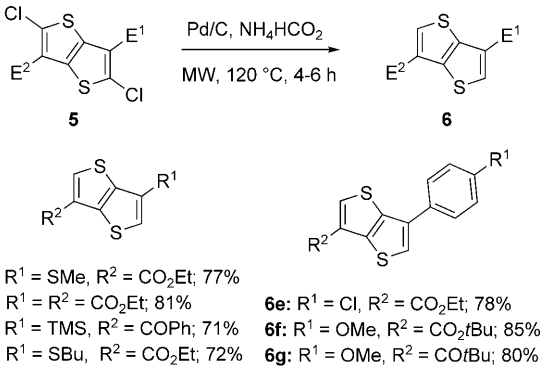
This procedure has also been used for the reduction of the dichlorothienothiophenes **5b–g** (4-6 h, 100 W, 120°C), furnishing the dechlorinated products **6b–g** in 71–85% yield (Scheme 2). Remarkably, this reduction is compatible with other aromatic C–Cl bonds (see Scheme 2, compound **6e**).

Preparation of fully functionalized thieno[3,2-*b*]thiophenes of type 8: A further deprotonation of the dechlorinated thienothiophenes of type **6** is achieved with complete regioselectivity. When treating the thienothiophene **6a** with tmpMgCl·LiCl (**1**; 1.1 equiv, −20°C, 40 min), the ester

Table 1. Synthesis of 3,6-disubstituted thienothiophenes of type **5**.

Entry	E^1 (Yield)[a]	E^2 (Yield)[a]	Product
1	$PhSO_2SMe$	$NCCO_2Et$	
	(96%)	(89%)	**5a**
2	$PhSO_2SPh$	Boc_2O	
	(85%)	(70%)	**5b**
3	TMSCN	PhCOCl	
	(85%)	(95%)[c]	**5c**
4		Boc_2O	
	(71%)[b]	(73%)	**5d**: R = *p*-C_6H_4OMe
5		*t*BuCOCl	
	(71%)[b]	(85%)[c]	**5e**: R = *p*-C_6H_4OMe
6		*t*BuCOCl	
	(91%)[b]	(75%)[c]	**5f**: R = *p*-C_6H_4Cl
7		$NCCO_2Et$	
	(91%)[b]	(81%)	**5g**: R = *p*-C_6H_4Cl
8	$NCCO_2Et$	$NCCO_2Et$	
	(92%)	(81%)	**5h**
9	$PhSO_2SBu$	$NCCO_2Et$	
	(94%)	(83%)	**5i**

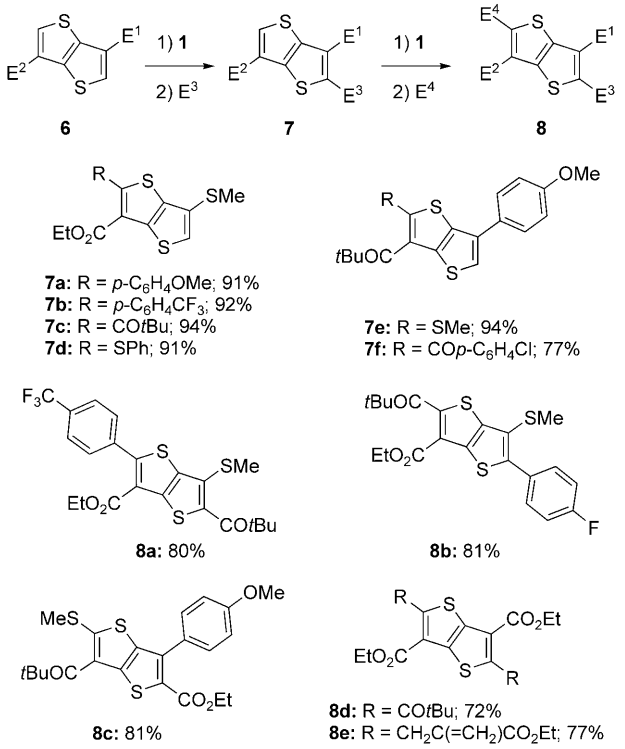
[a] Yield of isolated analytically pure product. [b] After transmetalation using $ZnCl_2$ (1.1 equiv) and a cross-coupling reaction ($[Pd(dba)_2]$ 3 mol%, tfp 6 mol%). [c] After transmetalation using CuCN·2 LiCl (20 mol%).



Scheme 2. Synthesis of thienothiophenes of type **6** using Pd/C and NH_4HCO_2 under microwave irradiation.

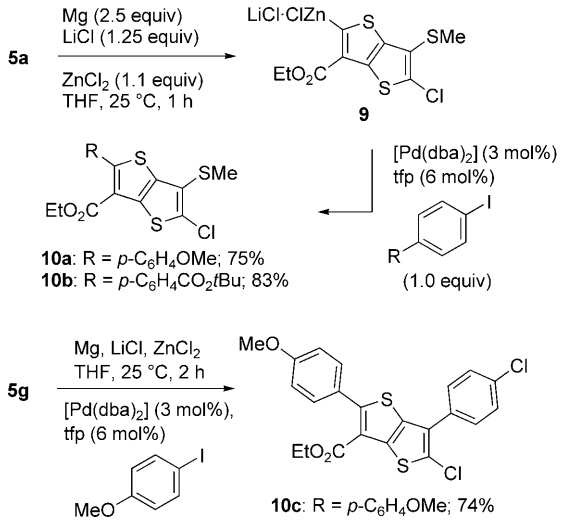
moiety acts as a directing group[17] and magnesiation occurs regioselectively on the adjacent carbon atom (Scheme 3). Pd-catalyzed cross-coupling reactions with 4-iodoanisole or 4-iodobenzotrifluoride, Cu^I-catalyzed acylation reactions with pivaloyl chloride, or quenching with $PhSO_2SPh$ afford the expected products **7a–d** in 77–94% yield. Similarly, a ketone proved to be an efficient directing group. After deprotonation of **6g** (−50°C, 20 min), thioether **7e** is isolated in 94% yield after trapping with $PhSO_2SMe$, and product **7f** is obtained in 77% yield after an acylation with 4-chlorobenzoyl chloride.

The remaining 5-position can again be metalated with tmpMgCl·LiCl (**1**). Deprotonation of **7b** (−20°C, 40 min) followed by a Cu^I-catalyzed acylation using pivaloyl chloride gives compound **8a** in 80% yield. After metalation of **7c** (−40°C, 15 min) and a Pd-catalyzed cross-coupling reaction with 1-fluoro-4-iodobenzene, the fully functionalized thieno[3,2-*b*]thiophene **8b** is isolated in 81% yield. Similarly, product **8c** is obtained in 81% yield after deprotonating thienothiophene **7e** (0°C, 90 min) and trapping the resulting magnesiated reagent with ethyl cyanoformate. The treatment of the diester **6b** with tmpMgCl·LiCl (**1**) directly leads to a bismagnesiated intermediate (2.2 equiv, −40°C, 20 min), which could be acylated with pivaloyl chloride in 72% yield (**8d**) or allylated with ethyl 2-(bromomethyl)acrylate in 77% yield (**8e**, Scheme 3).



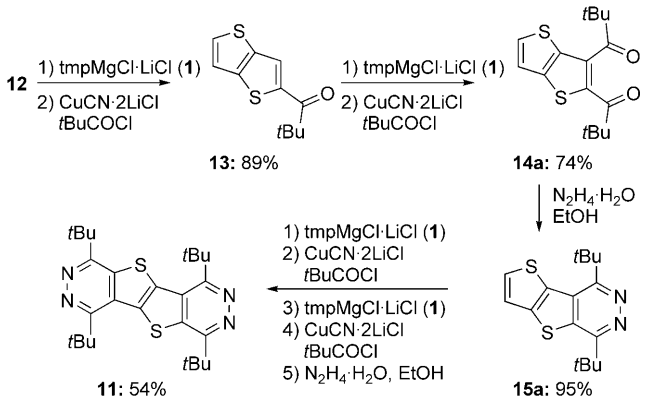
Scheme 3. Synthesis of fully substituted thienothiophenes of type **8**.

Direct magnesium insertion for the preparation of thieno[3,2-*b*]thiophenes of type 10: Recently, we have reported a LiCl-mediated magnesium insertion into aryl chlorides and bromides under mild and convenient conditions.[18] By using this method, the dichlorothienothiophenes of type **5** can also be directly magnesiated. Thus, the addition of the dichlorothienothiophene **5a** to Mg turnings (2.5 equiv), LiCl (1.25 equiv), and $ZnCl_2$ (1.1 equiv) in THF regioselectively gives the zincated intermediate **9** (25°C, 1 h), which can be arylated by a Pd-catalyzed cross-coupling reaction with 4-iodoanisole or *tert*-butyl 4-iodobenzoate, leading to the arylated products **10a** and **10b** in 75–83% yield. After a similar insertion/cross-coupling sequence, compound **5g** affords the arylated thienothiophene **10c** in 74% yield (Scheme 4).



Scheme 4. Magnesium insertion into dichlorothienothiophenes of type **5**.

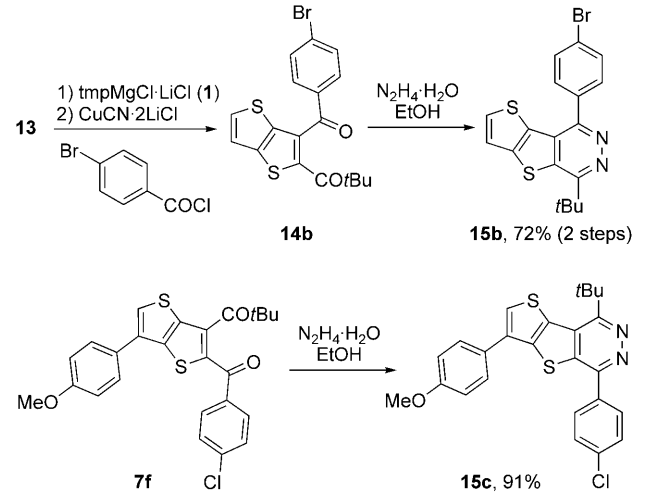
Preparation of condensed pyridazines: Furthermore, we have prepared a new class of condensed heterocycles of type **11**. The metalation of unsubstituted thieno[3,2-*b*]thiophene[19] (**12**) with tmpMgCl·LiCl (**1**, 25°C, 1 h) followed by a of Cu^I-catalyzed acylation reaction gives the ketone **13** in 89% yield (Scheme 5). When treating this compound again with tmpMgCl·LiCl (**1**, −50°C, 30 min), the keto group acts as a directing group[17] and magnesiation occurs regioselec-



Scheme 5. Synthesis of new condensed pyridazine heterocycles.

tively at the *ortho* position. A further acylation affords the diketone **14a** in 74% yield, which can be condensed with hydrazine hydrate to give the pyridazine **15a** in 95% yield. Repetition of this reaction sequence leads to the pyridazinopyridazine **11** in 54% yield.

In an analogous reaction sequence, the diketone **14b** is obtained from **13** after metalation with tmpMgCl·LiCl (**1**, −50 °C, 30 min) and acylation with 4-chlorobenzoyl chloride. The crude product is directly condensed with hydrazine hydrate to give the pyridazine **15b** in 72% yield (over two steps). Similarly, the functionalized thienothiophene **7f** is converted to the pyridazine **15c** in 91% yield (Scheme 6). These compounds represent an interesting scaffold as tailored building blocks for material applications.



Scheme 6. Synthesis of condensed pyridazine heterocycles of type **15**.

Preparation of thieno[3,2-*b*]thiophene oligomers: Finally, we have assembled small oligomers of these functionalized thienothiophenes (Scheme 7). The trimer **21** is obtained in 43% yield after metalation of **16** with tmpMgCl·LiCl (**1**, 25 °C, 1 h) followed by a Pd-catalyzed cross-coupling reaction[15] with dibromothienothiophene[12] **20** using $Pd(OAc)_2$ (2.5 mol%) and SPhos (5 mol%, SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl). A Br/Mg exchange (*i*PrMgCl·LiCl, −50 °C, 20 min) on the bromothienothiophenes **17** and **18** affords the oligomers **22** and **23** after a PEPPSI-*i*Pr-catalyzed cross-coupling reaction[20] in 48–51% yield (PEPPSI-*i*Pr = [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride). Deprotonation of **19** using tmpMgCl·LiCl (**1**, 25 °C, 1 h) and a PEPPSI-*i*Pr-catalyzed cross-coupling reaction with dibromothienothiophene **20** gives the trimer **24** in 47% yield. The oligomer **25** is isolated in 43% yield after a double Br/Li exchange on compound **20** and cross-coupling with the thienothiophene **7g**. The effect of ring fusion on the electronic absorption and emission properties of oligothiophenes has been reported in the literature.[21] In agreement with these results, the compounds **21**–**25** show similar absorption maxima (λ_{max} = 413–416 nm). However, the stability of the trimers varies widely. While the compounds **22**–**24** are very sensitive towards light and air, the trimeric species of **21** and **25** were found to be stable in air at room temperature over several weeks. This confirms that the appropriate functionalization of the thieno[3,2-*b*]thiophene scaffold allows the preparation of tailored building blocks with specifically tuned properties for use in material synthesis. Further elaboration of polyfunctional thienothiophenes for material applications is underway in our laboratories.

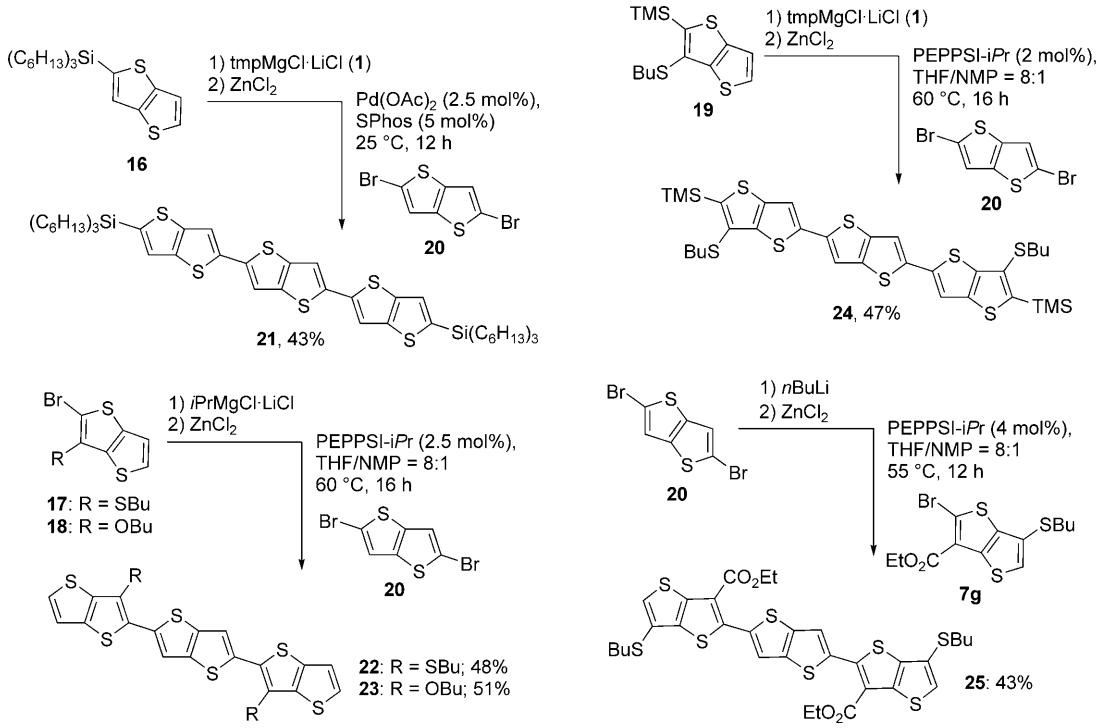
Conclusion

Direct metalation using tmpMgCl·LiCl (**1**) or magnesium insertion in the presence of zinc chloride and lithium chloride allow a full and regioselective functionalization of the thieno[3,2-*b*]thiophene scaffold. A large variety of functional groups can be introduced as substituents, affording various highly functionalized thienothiophenes that so far have not been accessible. This may allow one to fine-tune material properties of such heterocycles (e.g absorption band, overlap of frontier orbitals) by introducing specific side chains in monomeric building blocks, as could be shown in the oligomer synthesis (**21**–**25**). The condensation reaction of diketones with hydrazine hydrate leads to fused pyridazines (**15b** and **15c**) and pyridazinopyridazines (**11**). These compounds represent a new class of sulfur- and nitrogen-containing heterocycles that should also be of interest as new materials.

Experimental Section

For the complete experimental procedures, analytical data, and NMR spectra see the Supporting Information.

Metalation of thienothiophenes using tmpMgCl·LiCl (1): ethyl 2,5-dichlorothieno[3,2-*b*]thiophene-3-carboxylate (4h): A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer and a septum was charged with 2,5-dichlorothieno[3,2-*b*]thiophene (**2**; 6.27 g, 30.0 mmol) and THF (30 mL). tmpMgCl·LiCl (28.7 mL, 1.15 M in THF, 33.0 mmol)



Scheme 7. Synthesis of functionalized oligomers.

was added at 25 °C and the reaction mixture was stirred for 45 min (the completion of the reaction was checked by GC analysis of reaction aliquots quenched with a solution of I_2 in THF). Ethyl cyanoformate (3.57 g, 24.0 mmol) was added at −40 °C and the reaction mixture stirred for 1 h while warming to room temperature. The reaction was quenched with half-concentrated aqueous NH_4Cl solution, extracted three times with Et_2O, dried ($MgSO_4$), and concentrated in vacuo. Flash column chromatographic purification on silica gel (pentane/CH_2Cl_2 3:1) afforded **4h** (7.73 g, 92%) as a white solid. M.p. 115.3–117.0 °C; ^{1}H NMR (C_6D_6, 400 MHz): δ = 6.17 (s, 1H), 3.99 (q, J = 7.13 Hz, 2H), 0.97 ppm (t, J = 7.13 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz): δ = 160.1, 137.6, 135.7, 133.1, 131.3, 122.7, 118.2, 61.3, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 3087 (m), 1715 (vs), 1500 (m), 1468 (s), 1224 (vs), 1174 (w), 1078 (s), 1021 (m), 1010 (m), 868 (m), 842 (m), 772 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 280 (94) [M^+], 252 (100), 235 (44), 207 (18), 103 (19); HRMS (EI) for $C_9H_6O_2{}^{35}L_2{}^{32}S_2$ (279.9186): 279.9172.

Dechlorination of 3,6-disubstituted-2,5-dichlorothieno[3,2-*b*]thiophenes of type 5: diethyl thieno[3,2-*b*]thiophene-3,6-dicarboxylate (6b): A microwave vial equipped with a stirring bar was charged with the 2,5-dichlorothienothiophene **5h** (5.51 g, 15.6 mmol) in EtOH (30 mL). NH_4HCO_2 (2.95 g, 46.8 mmol) and Pd/C (664 mg, 2 mol%) were added, and the reaction mixture was heated by using a Biotage Initiatior 2.5 system (100 W, 120 °C) for 1 h. The mixture was allowed to cool to 25 °C, another portion of Pd/C was added, and the mixture was again heated. This procedure was repeated for a total of four reaction cycles. The mixture was allowed to cool to 25 °C and filtered through Celite. Flash column chromatographic purification on silica gel (pentane/CH_2Cl_2 2:1) afforded **6b** (3.61 g, 81%) as a pale yellow solid. M.p. 119.5–121.5 °C; ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.77 (s, 2H), 4.06 (q, J = 7.13 Hz, 4H), 1.01 ppm (t, J = 7.13 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz): δ = 161.5, 140.2, 139.0, 134.5, 127.2, 126.2, 125.5, 61.0, 16.9, 14.2 ppm; IR (ATR): $\tilde{\nu}$ = 3107 (w), 2989 (w), 1711 (vs), 1678 (m), 1499 (s), 1472 (m), 1452 (w), 1388 (w), 1377 (w), 1355 (w), 1230 (vs), 1159 (m), 1141 (m), 1117 (m), 1026 (s), 1003 (m), 876 (s), 849 (m), 831 (m), 821 (m), 725 (vs), 696 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 284 (100) [M^+], 256 (20), 239 (78), 211 (74), 183 (27), 69 (19); HRMS (EI) for $C_{12}H_{12}O_4{}^{32}S_2$ (284.0177): 284.0176.

Magnesium insertion in 3,6-disubstituted-2,5-dichlorothieno[3,2-*b*]thiophenes of type 5: ethyl 5-chloro-2-(4-methoxyphenyl)-6-(methylthio)thieno[3,2-*b*]thiophene-3-carboxylate (10a): A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer and a septum was charged with LiCl (160 mg, 3.75 mmol) and magnesium turnings (182 mg, 7.5 mmol), and was dried under vacuum. $ZnCl_2$ solution (3.3 mL, 3.3 mmol) and THF (6 mL) were added and the magnesium was activated with DIBAL-H (0.3 mL, 0.1 m in THF, 0.03 mmol). After the mixture had been stirred for 5 min, 2,5-dichlorothieno[3,2-*b*]thiophene (**5a**; 982 mg, 3.0 mmol) was added in one portion at room temperature. The reaction mixture was stirred for 1 h and then canulated to a new Schlenk flask. A cross-coupling reaction was performed by using 4-iodoanisole (702 mg, 3.0 mmol), $[Pd(dba)_2]$ (34 mg, 3%), and tfp (28 mg, 6%) over 3 h at 25 °C. The reaction mixture was quenched with half-concentrated aqueous NH_4Cl solution, extracted three times with Et_2O, dried (Na_2SO_4), and concentrated in vacuo. Flash column chromatographic purification on silica gel (pentane/CH_2Cl_2 2:1) afforded **10a** (898 mg, 75%) as a yellow solid. M.p. 108.7–109.9 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.51 (m, 2H), 6.95 (m, 2H), 4.30 (q, J = 7.13 Hz, 2H), 3.86 (s, 3H), 2.48 (s, 3H), 1.31 ppm (t, J = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 161.8, 160.6, 152.7, 137.1, 135.2, 133.6, 131.5, 125.3, 122.8, 120.7, 113.6, 61.2, 55.5, 17.6, 14.2 ppm; IR (ATR): $\tilde{\nu}$ = 2983 (w), 2925 (w), 2831 (w), 1716 (vs), 1671 (w), 1607 (m), 1572 (w), 1525 (m), 1487 (s), 1458 (m), 1439 (m), 1431 (m), 1414 (w), 1391 (m), 1365 (w), 1298 (m), 1267 (s), 1252 (vs), 1190 (s), 1172 (vs), 1113 (m), 1085 (w), 1061 (m), 1045 (m), 1031 (s), 1015 (s), 976 (w), 963 (w), 951 (w), 943 (w), 912 (m), 873 (w), 834 (s), 827 (m), 822 (m), 811 (m), 802 (w), 795 (m), 778 (s), 752 (w), 740 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 398 (100) [M^+], 370 (20), 355 (15), 185 (4); HRMS (EI) for $C_{17}H_{15}O_3{}^{35}L_1{}^{32}S_3$ (397.9872): 397.9857.

Preparation of fused pyridazines by condensation reactions with hydrazine hydrate: 5,8-di-tert-butylthieno[2′,3′:4,5]thieno[2,3-*d*]pyridazine (15a): A dry and argon-flushed Schlenk flask, equipped with a magnetic stirrer and a septum was charged with **13** (1.57 g, 7.0 mmol) and THF (7.0 mL). tmpMgCl·LiCl (6.70 mL, 1.15 m in THF, 7.7 mmol) was added at −50 °C and the reaction mixture was stirred for 30 min (the completion of the reaction was checked by GC analysis of reaction aliquots quenched with a solution of I_2 in THF). An acylation reaction was per-

fomed by using CuCN·2 LiCl (1.4 mL, 1 m in THF, 20 mol %) and pivaloyl chloride (1.01 g, 8.4 mmol) at −40 °C over 2 h. The reaction was quenched with half-concentrated aqueous NH_4Cl solution, extracted three times with Et_2O, dried ($MgSO_4$), and concentrated in vacuo. The crude product **14a** (1.83 g, 87 % purity by ^1H NMR, 74 %) was obtained as a white solid, which was used in the next step without further purification. Compound **14a** (1.54 g, 5.0 mmol) was dissolved in ethanol (20 mL). Hydrazine hydrate (751 mg, 64 %, 15.0 mmol) was added and the reaction mixture stirred for 12 h at 25 °C. The solvent was evaporated and the reaction was quenched with half-concentrated aqueous NH_4Cl solution, extracted three times with CH_2Cl_2, dried ($MgSO_4$), and concentrated in vacuo. Flash column chromatographic purification on silica gel (CH_2Cl_2) afforded **15a** (1.45 g, 95 %) as a light yellow solid. M.p. 198.2–200.9 °C; ^1H NMR (C_6D_6, 400 MHz): $\delta = 6.99$ (d, $J = 5.37$ Hz, 1H), 6.73 (d, $J = 5.37$ Hz, 1H), 1.78 (s, 9H), 1.68 ppm (s, 9H); ^{13}C NMR (C_6D_6, 150 MHz): $\delta = 162.7$, 159.9, 141.5, 140.6, 133.0, 132.7, 129.7, 119.1, 38.8, 38.5, 29.4, 29.3 ppm; IR (ATR): $\tilde{\nu} = 3052$ (m), 2966 (m), 2928 (m), 2904 (w), 2900 (w), 2868 (w), 1637 (m), 1497 (m), 1476 (m), 1418 (vs), 1399 (m), 1365 (s), 1348 (m), 1334 (m), 1278 (w), 1252 (w), 1220 (s), 1196 (s), 1160 (s), 1154 (s), 1109 (w), 1101 (w), 1075 (m), 1024 (w), 930 (m), 913 (vs), 883 (w), 858 (w), 835 (w), 803 (m), 797 (m), 785 (w), 767 (m), 749 (w), 738 (vs), 733 (vs), 710 (w), 702 (w), 690 (s), 674 (w), 669 (w), 666 (w), 658 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%): 304 (9) [M^+], 289 (29), 262 (100), 246 (13), 191 (7), 41 (5); HRMS (EI) for $C_{16}H_{20}N_2{}^{32}S_2$ (304.1068): 304.1043.

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