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Very Important Publication

Concise Synthesis of Dithiophene Derivatives by a Palladium-Catalyzed Multiple C–S Cross Coupling/Cyclization Sequence

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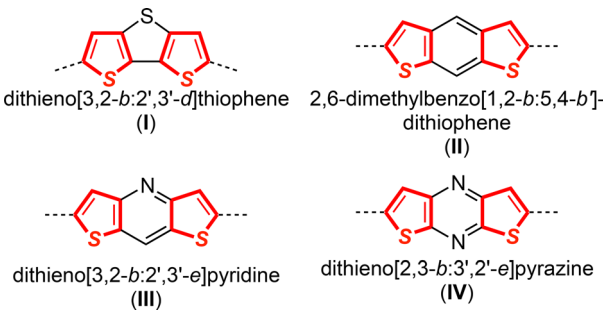
Abstract: The facile synthesis of new sulfur-containing fused heterocycles was achieved by a two-fold domino reaction consisting of a carbon-sulfur cross-coupling, followed by a 5-*endo*-dig cyclization. Using this strategy a series of benzo-, thiopheno-, pyridine- and pyrazino-dithienoacenes with electron-neutral (-C_6H_4-*n*-Hex), electron-rich (-C_6H_4-NPh_2) and electron-deficient (-$C_4H_3N_2$) substituents was synthesized in high yields. The developed method was applied in the efficient synthesis of a complex donor-acceptor molecule. The photophysical and electrochemical properties of the products were analyzed by UV-VIS/luminescence spectroscopy and cyclic voltammetry.

Keywords: carbon-sulfur cross-coupling; heteroacenes; luminescence; palladium; UV-vis spectroscopy

Introduction

Fused aromatic carbo- and heterocyclic compounds have attracted significant attention due to their potential uses as dyes or semiconducting materials[1] in organic solar cells[2] or organic light emitting devices.[3] In particular, sulfur-containing heterocycles have found application as semiconducting materials for organic field-effect transistors due to their transparency for visible light and their thermal and chemical stability.[4] Prominent examples for such thioacenes are dithieno[3,2-*b*:2′,3′-*d*]thiophene[5] (**I**), benzo[1,2-*b*:5,4-*b*′]dithiophene[6] (**II**) and derivatives (Scheme 1).[7]



Scheme 1. Thioacenes with different aromatic core structures.

The syntheses of these fused aromatic structures rely on cyclocondensation reactions,[8,9] 5-*endo*-dig cyclization of thiols or thioethers[10] or on the reductive dimerization of metallated thiophenes.[4b,11] The latter two strategies require the formation of an aromatic thio compound usually accessed through metallation (lithium/halide exchange or deprotonation with strong lithium bases) and subsequent reaction with sulfur electrophiles[4b,10b,12] or nucleophilic aromatic substitution at elevated temperatures.[13] Particularly, the nucleophilic substitution of halides in 2-haloalkynes by sodium sulfide and subsequent cyclization is an attractive method, since the haloalkynes are readily accessible.[13c,14] However, such conditions often interfere with reactive moieties in the molecule, for example, functional groups or electron-deficient heterocycles. As an alternative, transition metal-catalyzed cross-coupling reactions display excellent functional group tolerance combined with control of the chemoselectivity through the electrophile's nature. Transition metal-catalyzed C–S bond forming reactions using thiols or thiolates are well known[5j,15] but were only occasionally utilized in the *de novo* synthesis of sulfur-containing heterocycles. In that sense the application of hydrogen sufide surrogates,[15f,g,n,p,16] for example, thiourea or potassium thioacetate is a highly desirable alternative to thiols since handling and preparation of these malodorous and often air-sensi-

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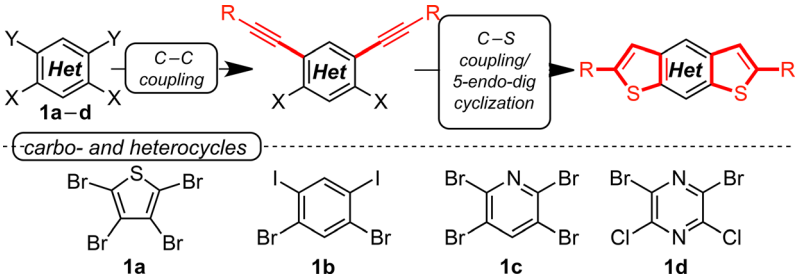


Scheme 2. Strategy for the synthesis of thioacenes.

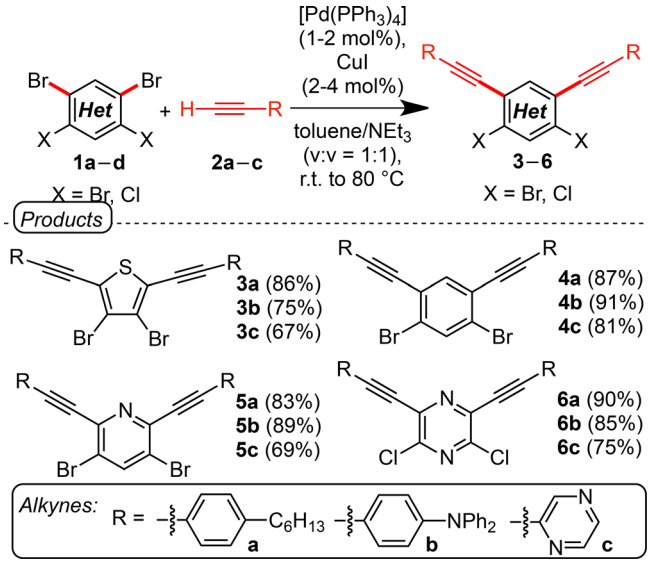
tive compounds is avoided. Recently, we utilized thiourea and potassium thioacetate[15p,q] as hydrogen sulfide surrogates for the construction of benzothiophene, thienothiophene and DTT derivatives through single C–S cross-coupling/cyclization and C–S coupling/C–H activation.[10a,17]

Herein we report the application of thioacetate as hydrogen sulfide surrogate for the unprecedented two-fold palladium-catalyzed C–S cross coupling/5-*endo*-dig cyclization to afford 2,6-disubstituted dithienoacenes (Scheme 2). This two-fold domino reaction[18] allows both the straightforward synthesis of novel BDT and DTT derivatives and so far largely unexplored dithienopyridines[19] (**III**) and dithienopyrazines[20] (**IV**).

Results and Discussion

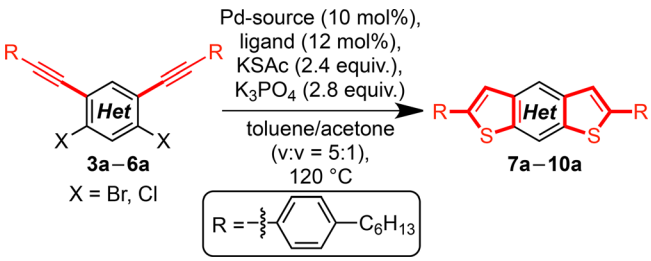
For the synthesis of the triple fused sulfur-containing heterocycles we selected the four benzo, thiopheno, pyridino and pyrazino aromatic cores **1a–d**. The cyclization precursors were obtained from the appropriately halogenated arenes **1a–d** through Sonogashira cross-coupling with the three alkynes **2a–c** bearing electron-neutral (**2a**), electron-rich (**2b**) and electron-deficient (**2c**) arenes (Scheme 3).

The corresponding twelve bisalkynes **3–6** were obtained in high to excellent yields with exclusive regioselective formation of the *meta*-substituted bisalkynes from tetrabromothiophene (**1a**), 1,5-dibromo-2,4-diiodobenzene (**1b**), tetrabromopyridine (**1c**) and 2,6-dibromo-3,5-dichloropyrazine (**1d**), respectively. Next we investigated the two-fold palladium-catalyzed carbon-sulfur cross-coupling/5-*endo*-dig cyclization of the bisalkynes with thioacetate[15p,q] as hydrogen sulfide surrogate. First, the *n*-hexylphenyl-derived bisalkyne **3a** was reacted with 2.4 equiv. thioacetate in the presence of the $Pd(OAc)_2$/dppf derived catalyst (Table 1, entry 1). The product of the double cyclization **7a** was obtained in 23% yield. The change of the palladium source to $Pd(dba)_2$ led to an increased yield of 36% (entry 2). Further optimization through change of the bisphosphine ligand to xantphos and dippf gave comparable yields of the dithienothio-



Scheme 3. Synthesis of the cyclization precursors.

Table 1. Optimization of the two-fold C–S cross-coupling/5-*endo*-dig cyclization.[a]



Entry	Halide	Pd Source	Ligand	Product	Yield [%]
1	**3a**	$Pd(OAc)_2$	dppf	**7a**	23
2	**3a**	$Pd(dba)_2$	dppf	**7a**	36
3	**3a**	$Pd(dba)_2$	xantphos	**7a**	62
4	**3a**	$Pd(dba)_2$	dippf	**7a**	65
5	**4a**	$Pd(dba)_2$	dippf	**8a**	64
6	**5a**	$Pd(dba)_2$	dippf	**9a**	69
7	**6a**	$Pd(dba)_2$	dippf	**10a**	41
8	**6a**	$\{Pd[P(o\text{-tol})_3]_2\}$	dippf	**10a**	67

[a] dba = dibenzylideneacetone; dppf = 1,1′-bis(diphenylphosphino)ferrocene; xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dippf = 1,1′-bis(diisopropylphosphino)ferrocene.

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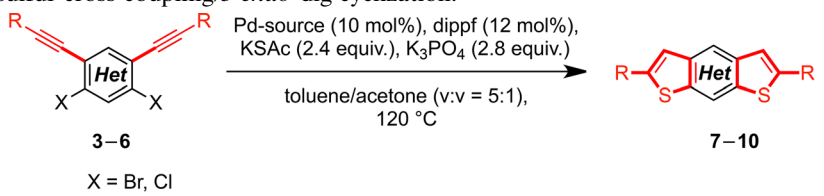
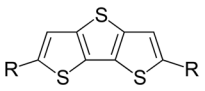
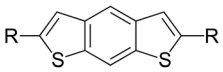
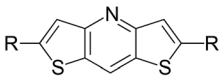
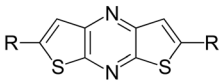
phene **7a** (62% and 65%, entries 3 and 4). In the course of the project we found that the dippf ligand proved to be more versatile compared to xantphos (entries 5–8). The benzodithiophene **8a** and the pyridinedithiophene **9a** were isolated in high yields of 64% and 69%, while the pyrazinedithiophene **10a** was obtained in 41% yield. However, the yield was significantly improved to 67% by the application of bis-[tris(2-tolyl)phosphine]palladium as a highly reactive palladium(0) source (entry 8). Since both the Sonogashira and the C–S cross-coupling are catalyzed by Pd(0) species, a one-pot reaction appears feasible. However, in our hands only traces of the monocyclization product were obtained using {Pd[P(*o*-tol)$_3$]$_2$}/CuI/dippf/KSAc as precatalyst, while other precatalysts were entirely ineffective. The generality of this methodology was demonstrated by subjection of the electronically modified bisalkynes **3–6** to the C–S cross-coupling/cyclization sequence (Table 2). Pleasingly, Pd(dba)$_2$ or {Pd[P(*o*-tol)$_3$]$_2$} in combination with dippf as supporting ligand proved to be viable catalysts for the synthesis of the peripheral electronically modified products **7–10** in high yields. However, the catalyst was ineffective for the synthesis of the pyrazinyl derivative **7c** although the two DTT derivatives **7a** and **7b** were obtained in good yields (entries 1–3). Good to high yields were achieved in the C–S cross-coupling/cyclization of benzo- and pyridine-derived dithiophenes **8a–8c** and **9a–9c** (entries 4–9). For these structures the products bearing electron-neutral and electron-releasing groups were isolated in high yields. The introduction of the electron-withdrawing pyrazinyl groups in **4c** and **5c** reduced the yields to 44% and 54% (entries 6 and 9). A similar trend was observed for the pyrazinedithiophenes **10a–c** using [Pd(P*o*tol$_3$)$_2$] as Pd(0) source (entries 10–12). Nevertheless, these electron-deficient structures were obtained in 47–76% yield. As a mechanistic proposal the catalytic reaction is initiated by the oxidative addition of the Pd(0) species into the C–Br bond followed by salt metathesis with KSAc leading to an aryl palladium sulfide species. Subsequent reductive elimination furnishes the corresponding *S*-acetyl thiophenol derivative, which is *in situ* deprotected by the combination of K_3PO_4/toluene/acetone.[15p,q] The liberated potassium thiolate readily undergoes 5-*endo*-dig cyclization to form the thiophene core. The dithiophenes **7–10** were characterized by NMR, UV-VIS/luminescence spectroscopy

Table 2. Domino carbon-sulfur cross-coupling/5-*endo*-dig cyclization.[a]



Entry	Halide	Core	R	Pd Source	Ligand	Product	Yield [%]
1	**3a**		C_6H_{13}	Pd(dba)$_2$	dippf	**7a**	55
2	**3b**		NPh_2	Pd(dba)$_2$	dippf	**7b**	59
3	**3c**			Pd(dba)$_2$	dippf	**7c**	0
4	**4a**		C_6H_{13}	Pd(dba)$_2$	dippf	**8a**	64
5	**4b**		NPh_2	[Pd[P(*o*-tol)$_3$]$_2$}	dippf	**8b**	72
6	**4c**			Pd(dba)$_2$	dippf	**8c**	44
7	**5a**		C_6H_{13}	Pd(dba)$_2$	dippf	**9a**	69
8	**5b**		NPh_2	Pd(dba)$_2$	dippf	**9b**	81
9	**5c**			Pd(dba)$_2$	dippf	**9c**	54
10	**6a**		C_6H_{13}	[Pd[P(*o*-tol)$_3$]$_2$}	dippf	**10a**	67
11	**6b**		NPh_2	[Pd[P(*o*-tol)$_3$]$_2$}	dippf	**10b**	76
12	**6c**			[Pd[P(*o*-tol)$_3$]$_2$}	dippf	**10c**	47

[a] dba = dibenzylidene acetone; dppf = 1,1′-bis(diphenylphosphino)ferrocene; xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dippf = 1,1′-bis(diisopropylphosphino)ferrocene

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(*vide infra*) and by mass spectrometric analysis. The molecular structures of the three NPh_2-substituted heteroacenes **7b**, **8b** and **9b** were unambiguously characterized by single crystal structure analyses confirming the *cis*-fusion of both thiophene entities (molecular structure representations are depicted in Figure 1).[21] The structures do not feature unusual structural deviations from their parent structures.[22] The electrochemical and photophysical properties of the dithienoacenes were characterized by cyclic voltammetry and by UV-VIS/luminescence spectroscopy (summarized in Table 3).[23] After we had demonstrated the efficiency of the methodology for the synthesis of peripheral electronically modified dithieno-derived heteroacens, we expanded the scope of the method to a complex donor-acceptor-donor molecule.[24] Thienothiophene-containing 2*H*-triazole polymers[25] were successfully applied as organic photovoltaic devices and are usually accessed by bisfunctionalized tin reagents. Long alkyl chains at the central 2*H*-triazole provided beneficial solubilizing properties and Ph_2N-C_6H_4-substituted DTT derivatives are known as strong donors. Consequently, we selected the synthesis of the 4,7-bisdithienothiophene-2*H*-benzotriazole **11** as a challenging and innovative target, which should be readily accessible through an eight-fold C–S bond forming reaction (Scheme 4).

The synthesis of **11** commenced with the palladium-catalyzed Sonogashira coupling of **1a** and **2b** (3:1 ratio) to produce the mono coupling product **12** in 70% yield. The 4,7-diethynyl-2*H*-benzo[*d*][1,2,3]tria-

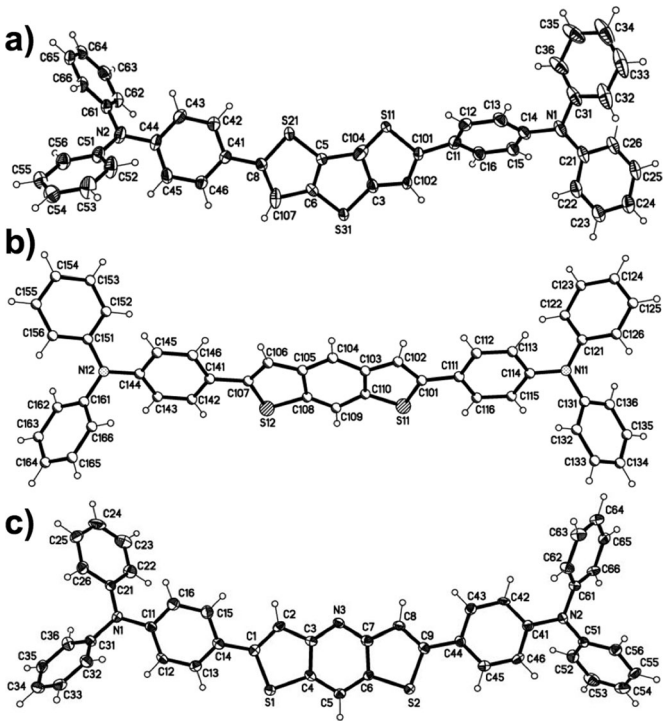
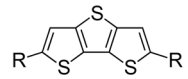
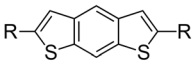
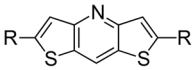
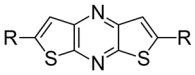


Figure 1. Molecular structure representations of the heteroacenes: a) **7b**, b) **8b** and c) **9b**.[21]

Table 3. Photophysical and electrophysical data for **7**–**10**.

Entry	Compound		Λ_{max} [nm]	Λ_{onset}[a] [nm]	Λ_{em}[b] [nm]	ΔE_{opt}[c] [eV]	$E_{1/2}$ *vs.* Fc/Fc$^+$ [V][d]	E_{HOMO}[e] [eV]	E_{LUMO}[f] [eV]
1		**7a**	373	412	412	3.02	0.51	–5.61	–2.59
2		**7b**	431	460	462	2.70	0.24	–5.34	–2.64
3		**8a**	315	380	376	3.27	0.72[i]	–5.82	–2.55
4		**8b**	378	414	422	3.00	0.42	–5.52	–2.52
5		**8c**	341	384	428	3.24	–2.07[j]	–6.27[g]	–3.03[h]
6		**9a**	373	389	385	3.20	0.96[i]	–6.06	–2.86
7		**9b**	417	442	450	2.81	0.40[i]	–5.50	–2.69
8		**9c**	383	395	392	3.15	–1.89	–6.36[g]	–3.21[h]
9		**10a**	396	416	413	2.98	–1.07[i]	–6.17	–3.19
10		**10b**	446	484	493	2.57	0.61	–5.71	–3.14
11		**10c**	398	407	403	3.05	–1.59[j]	–6.56[g]	–3.51

[a] Calculated from the cross point of the absorption onset with the base line.
[b] Maximum of emission.
[c] Calculated from $E = h \cdot c/\lambda_{onset}$.
[d] For oxidation wave if not indicated otherwise.
[e] $E_{HOMO} = -(eE_{1/2(substrate)} + 5.1\ eV)$ referenced to Fc/Fc$^+$ couple.
[f] $E_{LUMO} = E_{HOMO} + \Delta E_{opt.}$
[g] $E_{LUMO} = -(eE_{1/2(substrate)} + 5.1\ eV)$ referenced to Fc/Fc$^+$ couple.
[h] $E_{HOMO} = E_{LUMO} - \Delta E_{opt.}$
[i] Deduced from the onset of the oxidation wave.
[j] $E_{1/2}$ for reduction wave.

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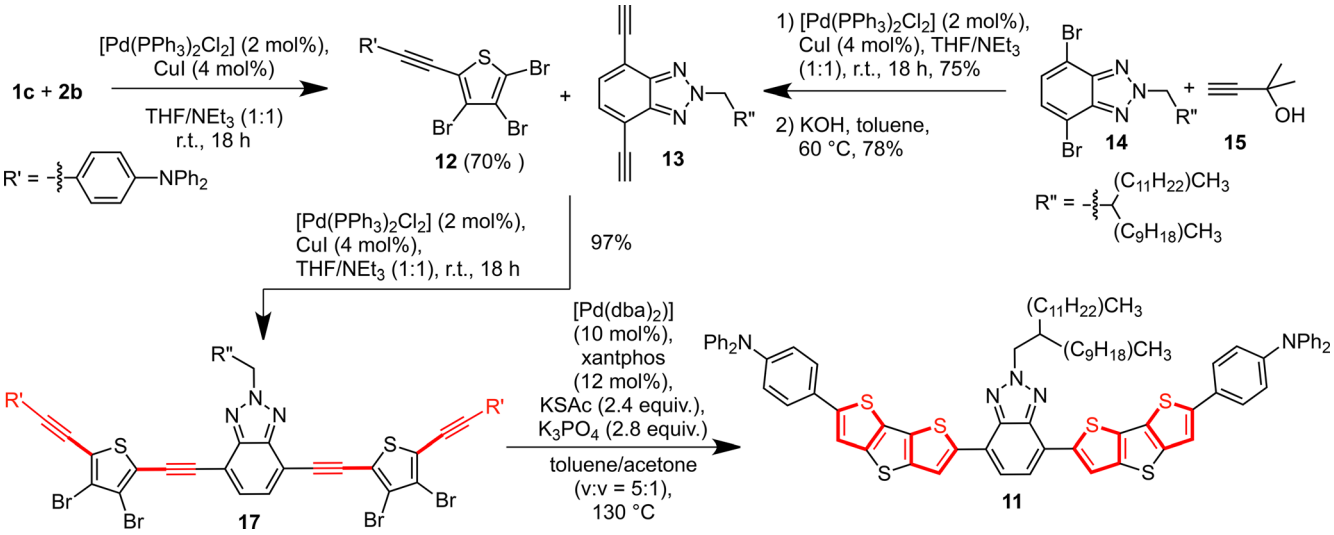

Scheme 4. Synthesis of the donor-acceptor-donor molecule **13** through four-fold C–S cross-coupling/5-*endo*-dig cyclization.

zole (**13**) was accessed by C–C coupling of 4,7-dibromo-2*H*-benzo[*d*][1,2,3]triazole (**14**) with 2,2-dimethylpropargyl alcohol (**15**) and subsequent deprotection in 59% yield over two steps. The Sonogashira coupling of two equivalents **12** with one equivalent bisalkyne **13** afforded the cyclization precursor **17** in excellent yield of 97%. The most challenging part in the synthesis of **11** was the four-fold C–S coupling/cyclization sequence. To our surprise, the catalyst consisting of $Pd(dba)_2$/dippf was ineffective in the double DTT formation. However, the xantphos ligand displayed comparable efficiency in the initial DTT synthesis (see Table 1, entry 3). Delightfully, the catalyst derived from $Pd(dba)_2$/xantphos generated the donor-acceptor-donor molecule **11** as a result of eight C–S bond-forming events in an excellent yield of 80%, which corresponds to 97% yield for each individual C–S bond formation. The UV-VIS spectrum of **11** revealed a broad absorption between 410 nm and 561 nm (λ_{max} = 492 nm) and emission between 522 nm to 702 nm in the luminescence spectrum (excitation at 487 nm, $\lambda_{max,\ em}$ = 558 nm, for further characterization see the Supporting Information). According to this synthesis the donor-acceptor-donor **11** was obtained in four linear steps in an overall yield of 45% as a bright red solid.

Conclusions

In conclusion, we have achieved the efficient two-step synthesis of a series of 2,6-donor- and acceptor-substituted dithioenoacenes bearing benzo, thiopheno, pyridino and pyrazino cores. Eleven heteroacenes were accessed by Sonogashira coupling followed by double domino carbon-sulfur cross-coupling/5-*endo*-dig cyclization to afford the products in good to excellent yields. The applicability of the elaborated heteroacene synthesis to complex heterocyclic structures was demonstrated by the highly efficient four-step synthesis of the donor-acceptor-donor dye **11** with an overall yield of 45%.

Experimental Section

General Procedure for the Two-Fold C–S Coupling/Cyclization Reaction

The respective halogenated bisalkyne (1.00 equiv.), potassium thioacetate (2.40 equiv.), potassium phosphate (2.80 equiv.), the respective palladium(0) precursor (10 mol%) and 1,1′-bis(di-isopropylphosphino)ferrocene (12 mol%) were dissolved in a mixture of degassed toluene and degassed acetone (v:v = 5:1; 20 mL mmol^{-1}) under argon and stirred for the given time at 120 °C (for the exact times see the Supporting Information). After cooling to room temperature, the mixture was poured onto a pad of Celite® which was rinsed with dichloromethane or boiling bromobenzene. The products were isolated either by precipitation and filtration or by column chromatography.

Acknowledgements

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[21] For further information see the Supporting Information. Full crystallographic data for **7b** and **9b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC 1486933 (**7b**) and CCDC 1486934 (**9b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (+44)-1223-1336-1033; e-mail: deposit@ccdc.cam.ac.uk). For **8b**: triclinic, space group P-1; only isotropic refinement was possible.

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[23] A short discussion of the physical properties can be found in the Supporting Information.

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8 Concise Synthesis of Dithiophene Derivatives by a Palladium-Catalyzed Multiple C–S Cross Coupling/Cyclization Sequence

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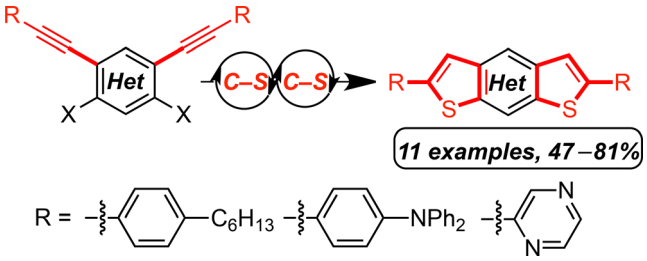

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