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Synthesis of Dibenzothiophenes and Carbazoles by Sequential 'Tetra-Fold Heck/6π-Electrocyclization/Dehydrogenation' Reactions of Tetrabromothiophene and Tetrabromo-*N*-methylpyrrole

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Abstract: Dibenzothiophenes and carbazoles were prepared by tetrafold Heck reactions of tetrabromothiophene and *N*-methyltetrabromopyrrole and subsequent 6π-electrocyclization and dehydrogenation. A number of reactions could be successfully carried out as domino reactions in only one synthetic step.

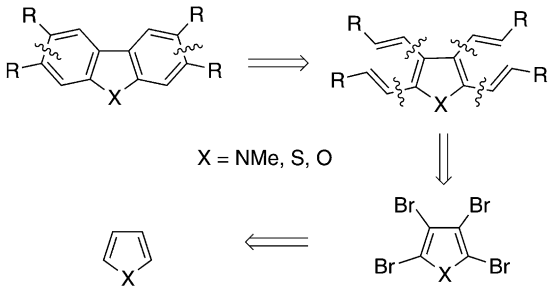
Keywords: cyclizations; domino reactions; Heck reaction; heterocycles; palladium

Introduction

The parent dibenzothiophene occurs in the phenanthrene fraction of coal tar and was first isolated by Kruber.[1] Dibenzothiophene and its alkylated derivatives represent one of the most abundant types of sulfur-containing compounds in crude oil.[2] It has been shown that dibenzothiophene derivatives, such as 4,6-dimethyldibenzothiophene, exhibit estrogenic activity.[3] Many dibenzothiophenes have been reported to show antitumor,[4] genotoxic,[5] antiprotozoal,[6] antidiabetic,[7] and antimicrobial[8] activity. The carbazole (dibenzopyrrole) system is found in many pharmacologically relevant natural products. Examples include clausenapine,[9] 3-methylcarbazole,[10] mukonidine[11] and koenoline.[12] The carbazole moiety occurs in several clinically used drugs. For example, caprofen has been used for the treatment of arthritis in man and in animals and carvedilol has been used for the treatment of hypertension.[13] Carbazoles have attracted much attention because of their antibiotic, antiviral, anti-inflammatory and antimalarial activity.[14] Thiophene-containing molecules are also important in material sciences, due to their electronic properties, such as luminescence, fluorescence, redox activity, non-linear optical chromism and electron transport.[15] This includes, for example, dibenzothiophenes,[15j] [2,2′;5′,2″]terthiophenes,[15k–n] and thienyl-diynes.[15o–q]

Dibenzothiophene was first synthesized in 1870 by heating of diphenyl sulfide in the presence of iron nails.[16] Later, a large number of methods for the synthesis of dibenzothiophenes by various methods have been reported.[17] For example, Nielsen and co-workers recently reported an efficient three-step protocol for the synthesis of functionalized dibenzothiophenes based on palladium-catalyzed carbon-carbon and carbon-sulfur bond formations.[18] The carbazole system was first synthesized by the method of Graebe and Ullmann based on the reaction of *o*-aminodiphenylamine with nitrous acid to give 1-phenyl-1*H*-benzo[*d*][1,2,3]triazole and subsequent loss of nitrogen upon heating.[19] Carbazoles have been also prepared from cyclohexanone phenylhydrazone using the Fischer indole synthesis.[20] Several other methods for the synthesis of carbazoles have been reported.[21] Recently, Ackermann et al. reported an efficient synthesis of carbazoles by a new palladium-catalyzed domino 'N–H/C–H activation' reaction of anilines with 1,2-dihaloalkenes.[22]

Some years ago, de Meijere and co-workers reported the synthesis of benzene derivatives by two-fold Heck reactions of 1,2-dibromoalkenes and subsequent 6π-electrocyclization.[23] This work has been applied to the synthesis of heterocycles.[23c–e] Following a retrosynthetic analysis (Scheme 1), we considered that carbazoles, dibenzothiophenes and dibenzofurans might



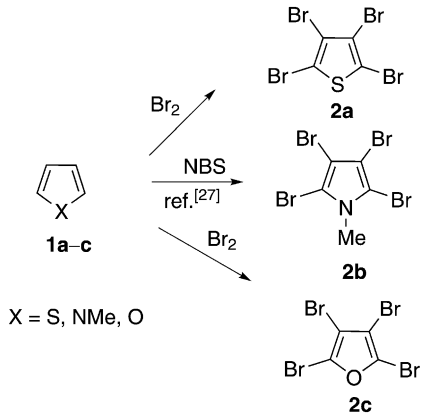
Scheme 1. Retrosynthetic analysis.

be prepared by a similar strategy starting with pyrrole, thiophene and furan, respectively. Herein, we report the synthesis of functionalized dibenzothiophenes and carbazoles by tetra-fold Heck reactions of tetrabromothiophene and tetrabromo-*N*-methylpyrrole and subsequent 6π-electrocyclization and dehydrogenation. Suzuki–Miyaura and Sonogashira reactions of tetrabromothiophene,[24] tetrabromo-*N*-methylpyrrole,[25] and tetrabromofuran[26] have been previously reported. In contrast, Heck reactions of these interesting, highly brominated substrates are, to the best of our knowledge, unknown to date. We also studied the photophysical properties of the products (absorption and fluorescence).

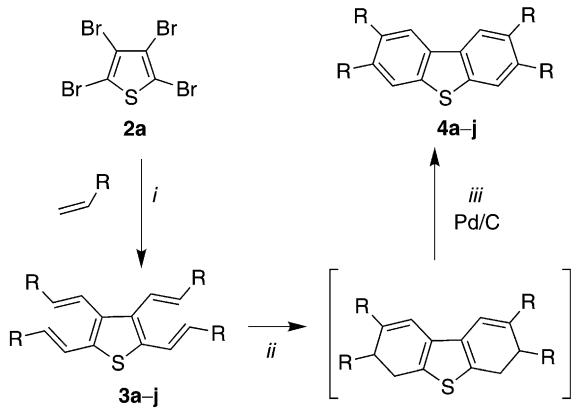
Results and Discussion

Tetrabromothiophene (**2a**), tetrabromo-*N*-methylpyrrole (**2b**) and tetrabromofuran (**2c**) were prepared in good yields according to procedures reported in the literature (Scheme 2).[27]

The Heck cross-coupling reaction of tetrabromothiophene (**2a**) with 5.0 equiv. of alkenes **2a–j** (90 °C, 12 h) afforded the tetra(alkenyl)thiophenes **3a–j** (Scheme 3, Table 1). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (3 mol%) in the presence of PCy_3 (5 mol%) as the catalyst and Na_2CO_3 as the base. The use of triethylamine resulted in partial reduction of **2a** (replacement of bromine by hydrogen atoms). Heating of a diphenyl ether solution of **3a–j** for 24 h at 200 °C and subsequent addition of Pd/C and heating for further 48 h at 200 °C afforded dibenzothiophenes **4a–j** in good yields (Scheme 2, Table 1). The reactions proceeded by 6π-electrocyclization and subsequent Pd/C-catalyzed dehydrogenation. Low yields were obtained when the reactions were carried out at 140 instead of 200 °C. The use of acrylonitrile or nitroethene instead of acrylates or styrenes proved to be unsuccessful (formation of a complex mixture).



Scheme 2. Synthesis of **2a–c** (see ref.[27]).



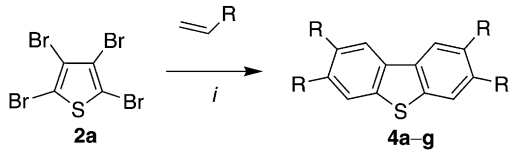
Scheme 3. Synthesis of **3a–j** and **4a–j**. *Reagents and conditions: i,* **2a** (1 equiv.), alkenes (5.0 equiv.), $Pd(OAc)_2$ (3 mol%), PCy_3 (5 mol%), Na_2CO_3, DMF, 90 °C, 12 h; *ii*, diphenyl ether, 200 °C, 24 h; *iii*, Pd/C (10 mol%), diphenyl ether, 200 °C, 48 h.

Table 1. Synthesis of **3a–j** and **4a–j**.

3, **4**	R	Yield [%] (**3**)[a]	Yield [%] (**4**)[a]
a	CO_2Me	71	60
b	CO_2Et	54	51
c	CO_2-*n*-Bu	51	59
d	CO_2-*i*-Bu	68	62
e	CO_2(2-ethylhexyl)	52	70
f	CO_2-*n*-hexyl	63	73
g	Ph	80	74
h	4-*t*-Bu-C_6H_4	72	63
i	4-MeO-C_6H_4	62	67
j	4-Me-C_6H_4	78	59

[a] Yields of isolated products.

During the optimization, the temperature also proved to be an important parameter. Interestingly, products **4a–g** could be prepared from **2a** in only one synthetic step when the reactions were carried out at 140 °C (Scheme 4). This is interesting because the thermal transformation of isolated tetra(alkenyl)thiophenes **3** into dibenzothiophenes **4** (*vide*



Scheme 4. Synthesis of **4a–g**. *Reagents and conditions*: *i*, **2a** (1 equiv.), alkenes (5.0 equiv.), $Pd(OAc)_2$ (3 mol%), $P(Cy)_3$ (5 mol%), Na_2CO_3, DMF, 140 °C, 24 h.

supra) required 200 °C and the yields decreased when the reactions were carried out at 140 °C. Therefore, we believe that, in the case of the domino reaction, the cyclization proceeds by a Pd-catalyzed mechanism. The products were formed by a domino 'tetrafold Heck/6π-electrocyclization/dehydrogenation' reaction. The yields of the domino reactions (in the range 36–52%) were comparable to the combined yields of the sequential syntheses (Scheme 3, Table 2). Although Suzuki–Miyaura reactions of **2a** have been reported to proceed with very good regioselectivity in favour of positions 2 and 5,[24] all attempts to induce regioselective Heck reactions of **2a**, using 2.0 equivalents of the alkene, failed.

The base plays also a very important role in the reaction (Table 3). The use of triethylamine resulted in the formation of a mixture of mono-, di- and tri-(alkenyl)thiophenes, but not of the desired tetra-(alkenyl)thiophenes. The use of Na_2CO_3 gave better yields than K_2CO_3. The use of DMF as the solvent proved to be important. Not even trace amounts of product were observed when the reactions carried out in toluene and xylene.

The Heck reaction of tetrabromo-*N*-methylpyrrole (**2b**) with acrylates **2** (5.0 equiv.) afforded the tetra-(alkenyl)pyrroles **5a–g** in 52–75% yield (Scheme 5, Table 4). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol%) as the catalyst in the presence of tricyclohexylphosphine (PCy_3, 10 mol%) or SPhos (10 mol%) (Table 5). In the reactions PCy_3 was employed, due to its lower price as compared to SPhos. During the optimization,

Table 2. Synthesis of **4a–g**.

4	R	Base	Solvent	*T* [°C]	*t* [h]	Yield [%] (**4**)[a]
a	CO_2Me	Na_2CO_3	DMF	140	24	43
b	CO_2Et	Na_2CO_3	DMF	140	24	38
c	CO_2-*n*-Bu	K_2CO_3	DMF	120	24	40
d	CO_2-*i*-Bu	Na_2CO_3	DMF	140	24	52
e	CO_2(2-ethylhexyl)	Na_2CO_3	DMF	120	24	36
f	CO_2-*n*-hexyl	Na_2CO_3	DMF	140	24	40
g	Ph	Na_2CO_3	DMF	140	36	48

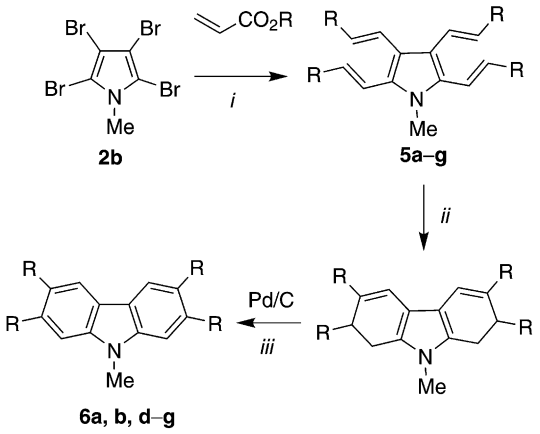
[a] Yields of isolated products.

Table 3. Optimization of the reaction conditions.

R	Base	Solvent	*T* [°C]	*t* [h]	Yield [%] (**4**)[a]
CO_2-*i*-Bu	Na_2CO_3	DMF	140	24	52
CO_2-*i*-Bu	Na_2CO_3	DMF	120	24	31
CO_2-*i*-Bu	Na_2CO_3	DMF	90	24	–[b]
CO_2-*n*-Bu	K_2CO_3	DMF	120	24	40
CO_2-*n*-Bu	K_2CO_3	DMF	140	24	26
CO_2-*n*-Bu	K_2CO_3	DMF	90	24	–[b]
CO_2-*i*-Bu	Et_3N	DMF	120	12	0
CO_2-*i*-Bu	Et_3N	DMF	140	24	0
CO_2-*n*-Bu	Et_3N	DMF	90	24	0
CO_2-*n*-Bu	Na_2CO_3	toluene	110	24	traces
CO_2(2-ethylhexyl)	Na_2CO_3	xylene	150	12	traces
CO_2-*i*-Bu	K_3PO_4	DMF	140	24	traces

[a] Isolated yields; tetra(alkenyl)thiophenes **3** were not isolated.

[b] Tetra(alkenyl)thiophenes **3** were isolated.



Scheme 5. Synthesis of **5a–g** and **6a**, **b**, **d–g**. *Reagents and conditions*: *i*, **2b** (1 equiv.), acrylates (5.0 equiv.), $Pd(OAc)_2$ (5 mol%), $P(Cy)_3$ (10 mol%), Et_3N, DMF, 90 °C, 12 h; *ii*, diphenyl ether, 200 °C, 24 h; *iii*, Pd/C (10 mol%), diphenyl ether, 200 °C, 48 h.

the temperature also proved to be an important parameter. A clean transformation was observed when the reaction was carried out at 90 °C. We have mentioned above that the use of triethylamine resulted in failure of the Heck reaction in the case of tetrabromothiophene because of reduction. In contrast, in the case of tetrabromo-*N*-methylpyrrole the employment of triethylamine gave better yields of Heck products than the use of sodium carbonate. This might be explained by the fact that pyrroles are more electron-rich than thiophenes and thus less prone to reduction. The employment of styrene instead of acrylates proved to be unsuccessful, due to decomposition under the reaction conditions employed. Tetra-(alkenyl)-*N*-methylpyrroles **5a–g** were transformed

Table 4. Synthesis of **5a–g** and **6a**, **b**, **d–g**.

5, 6	R	Yield [%] (**5**)[a]	Yield [%] (**6**)[a]
a	CO_2-*n*-Bu	65	75
b	CO_2-*i*-Bu	55	89
c	CO_2-*t*-Bu	71	–[b]
d	CO_2-*n*-hexyl	73	80
e	CO_2Me	52	69
f	CO_2Et	69	63
g	CO_2(2-ethylhexyl)	75	82
h	Ph	–[b]	–[c]

[a] Yields of isolated products.
[b] Complex mixture.
[c] Experiment was not carried out

into carbazoles **6a**, **b**, **d–g** by heating in diphenyl ether for 24 h at 200 °C and subsequent addition of Pd/C and heating for further 48 h at 200 °C (63–89% yield). The reactions proceeded by 6π-electrocyclization and subsequent Pd/C-catalyzed dehydrogenation. Low yields were observed when the reactions were carried out at 140 °C for 96 h instead of 200 °C for 72 h (Table 6). The Heck reaction of **2b** with acrylates, carried out at 140 instead of 90 °C, resulted in the formation of complex mixtures. The formation of carbazoles by a domino reaction proved to be not possible. Similar to substrate **2a**, all attempts to induce regioselective Suzuki–Miyaura reactions of **2b** failed.

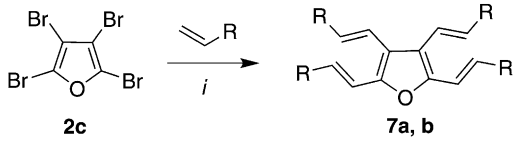
The Heck reaction of tetrabromofuran (**2c**) with 5.0 equiv. of alkenes **2** (90–100 °C, 8 h) afforded the tetra(alkenyl)furans **7a**, **b** (Scheme 6, Table 7) in low yield. The reactions were carried out under the same conditions as in the case of tetrabromothiophene (**2a**). Despite much efforts, the yields could not be optimized by variation of the conditions. The yields were low because of the unstable nature of the products and losses (due to decomposition) during the conditions of their formation and during chromatography. Heating of (slightly impure) **7a**, **b** in the presence of Pd/C at 120–200 °C for 12–36 h in diphenyl ether resulted in the formation of complex mixtures, due to decomposition.

The UV-Vis spectra of tetra(alkenyl)thiophenes **3d**, **g** and of dibenzothiophenes **4d**, **g**, containing an ester

Table 6. Influence of the temperature on the 6π-electrocyclization.

T [°C]	*t* [h]	Yield [%] (**6a**)[a]	Yield [%] (**6f**)[a]
140	96	21	12
200	72	75	63

[a] Yields of isolated products.



2c **7a, b**

Scheme 6. Synthesis of **7a**, **b**. *Reagents and conditions*: *i*, **2c** (1.0 equiv.), acrylate (5.0 equiv.), $Pd(OAc)_2$ (3 mol%), $P(Cy)_3$ (5 mol%), Na_2CO_3, DMF, 90 °C, 8 h.

Table 7. Synthesis of **7a**, **b**.

7	R	Base	Solvent	*T* [°C]	*t* [h]	% (**7**)[a]
a	CO_2-*i*-Bu	Na_2CO_3	DMF	90	8	27
b	CO_2Me	Na_2CO_3	DMF	100	8	19
c	CO_2-*i*-Bu	Na_2CO_3	DMF	140	8	traces
d	CO_2-*i*-Bu	Et_3N	DMF	90	12	traces

[a] Yields of isolated products.

Table 8. General overview of the UV-Vis data of selected compounds **3** and **4** (in CH_2Cl_2).

Compound	λ_{max} [nm]	Sh1 [nm]
4a	258	338
4d	264	342
4f	265	346
4g	270	313
4i	278	323
4j	274	316
3c	290	354
3d	287	343
3e	289	343
3g	340	401
3j	342	416

Table 5. Optimization of the reaction conditions for the synthesis **5a** and **5e**.

Catalyst	*T* [°C]	Yield [%] (**5a**)[a]	Yield [%] (**5e**)[a]
5 mol% $Pd(OAc)_2$, 10 mol% $P(Cy)_3$	90	65	52
5 mol% $Pd(OAc)_2$, 10 mol% SPhos	90	71	55
5 mol% $Pd(OAc)_2$, 10 mol% SPhos	120	48	–[b]
5 mol% $Pd(OAc)_2$, 10 mol% $P(Cy)_3$	120	21	–[b]
5 mol% $Pd(OAc)_2$, 10 mol% $P(Cy)_3$	140	13	–[b]

[a] Yields of isolated products; carbazoles **6** were not isolated.
[b] Experiment was not carried out

Table 9. Structure and λ_{max} values of compounds **3g**, **3h** and **3i**.

Compound	R	$\lambda_{max,\ emission}$ [nm]
3g	Ph	465
3h	4-*t*-Bu-C_6H_4	480
3i	4-MeO-C_6H_4	490

Table 10. λ_{max} values of compounds **4a**, **4d** and **4i**.

Compound	R	$\lambda_{max,\ emission}$ [nm]
4a	CO_2Me	365
4d	CO_2-*i*-Bu	395
4i	4-MeO-C_6H_4	370

Table 11. Emission wavelengths of **4a**, **4d**, **4i**, **3g**, **3h**, **3i** and **3j**.

Compound	$\lambda_{max,\ emission}$ [nm]
4a	365
4d	395
4i	370
3g	465
3h	480
3i	490
3j	480

group (**3d**, **4d**) or a phenyl group (**3g**, **4g**), are shown in Table 8. Compounds **3d**, **4g** and **4d** show λ_{max} values in the range of 260–290 nm, while the λ_{max} value of **3g** is shifted about 80 nm to higher wavelengths. The transition with the lowest energies $S_1 \leftarrow S_0$ belongs to the tetra(styryl)thiophenes (as shown for **3g**). The tetra(alkenyl)thiophenes generally show absorptions at lower energies than the corresponding dibenzothiophene derivatives. This can be explained by the presence of a 1,3,5-hexatriene system in the case of the tetra(alkenyl)thiophenes. Substituents located at the tetraaryldibenzothiophenes (**4g**, **4i** and **4j**) have a low impact on the absorption spectra. The presence of donor substituents located at the phenyl group results in a small bathochromic shift of λ_{max} (Table 8).

Products **3** and **4** exhibit fluorescence properties. The fluorescence spectra were recorded in dichloromethane ($c \approx 10^{-3}$–10^{-4} mol/L; excitation wavelength: 250 nm). Table 9 shows the fluorescence spectra of three tetra(styryl)thiophenes (**3g**, **3h** and **3i**). The compounds show emissions in the range of 465–490 nm. The presence of donor substituents located at the 4-position of the phenyl group leads to a bathochromic shift of the emission.

Dibenzothiophenes **4a**, **4d** and **4i** show emissions in the range of 365–395 nm (Table 10). Surprisingly, the type of ester group seems to have an influence on the emission (products **4a** and **4d**). This is unusual because the alkyl substituents of the ester group possess no π- or n-electrons. Thus, the red shift of compound **4d** presumably has steric reasons (maybe due to orthogonal twisting of the ester group with regard to the π-system.

A strong bathochromic shift (about 120 nm) is observed for the emission of tetra(alkenyl)thiophene **3i** as compared to dibenzothiophene **4i** (Table 11). This is a general trend which might be explained by the presence of a 1,3,5-hexatriene system in case of the tetra(alkenyl)thiophene (Table 11).

Conclusions

We have reported the synthesis of tetra(alkenyl)thiophenes, tetra(alkenyl)-*N*-methylpyrroles and tetra(alkenyl)furans by palladium(0)-catalyzed tetra-fold Heck cross-coupling reactions of tetrabrominated thiophene, *N*-methypyrrole and furan, respectively. The tetra(alkenyl)thiophenes and tetra(alkenyl)-*N*-methylpyrroles were transformed, by Pd/C-catalyzed electrocyclization and dehydrogenation, into the corresponding dibenzothiophenes and carbazoles, respectively. The absorption and fluorescence properties of the products were studied.

Experimental Section

General Procedure A for the Synthesis of 2,3,4,5-Tetra(alkenyl)thiophenes and 2,3,4,5-tetra(alkenyl)-furans

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 3 mol%) and $P(Cy)_3$ (7 mg, 0,025 mmol, 5 mol%) in DMF (5 mL) was purged with argon and stirred at 20 °C to give a yellowish clear solution. To the stirred solution were added **2a** or **2c** (0.5 mmol), Na_2CO_3 (216 mg, 4.0 mmol) and the alkene (1.25 equiv. per bromine atom of the substrate). The reaction mixture was stirred at 90–100 °C for 12 h. The solution was poured into H_2O, brine, and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3×25 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane-EtOAc).

(2*E*,2′*E*,2″*E*,2‴*E*)-Tetramethyl 3,3′,3″,3‴-(thiophene-2,3,4,5-tetrayl)tetraacrylate (3a): Starting with **2a** (200 mg, 0.5 mmol), methyl acrylate (0.23 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), $P(Cy)_3$ (7 mg, 5 mol%), Na_2CO_3 (216 mg, 4.0 mmol), and DMF (5 mL) (90 °C, 12 h) according to general procedure A, product **3a** was prepared as a yellowish solid; yield: 149 mg (71%), mp 80–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (s, 6H, $2OCH_3$), 3.77 (s, 6H, $2OCH_3$), 6.04 (d, 2H, $J = 16.0$ Hz, 2CH), 6.28 (d, 2H, $J =$

15.7 Hz, 2CH), 7.61 (d, 2H, $J=16.0$ Hz, 2CH), 7.76 (d, 2H, $J=15.7$ Hz, 2CH); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta=52.0$ ($2OCH_3$), 52.1 ($2OCH_3$), 121.1 (2CH), 125.8 (2CH), 133.8 (2CH), 135.4 (2CH), 138.3 (2C), 139.0 (2C), 166.0 (2CO), 166.2 (2CO); IR (KBr): $\nu=3000$, 2952, 2921, 2848 (w), 1710 (s), 1615, 1432, 1306 (m), 1267, 1192, 1164 (s), 1081, 1018 (m), 964 (s), 919, 852, 801, 735, 701, 657, 575 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 420 (28) $[M]^+$, 389 (12), 361 (25), 360 (33), 331 (10), 330 (18), 329 (100), 327 (16), 302 (10), 301 (20), 297 (15), 285 (30), 270 (10), 269 (29), 242 (16), 211 (23), 198 (11), 184 (29), 183 (12), 139 (11), 59 (18); HR-MS (EI, 70 eV): $m/z=420.08705$,calcd. for $C_{20}H_{20}O_8S$ $[M]^+$: 420.08734.

General Procedure B for the One-Pot Synthesis of Dibenzothiophenes (4)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (3.4 mg, 3 mol%) and $P(Cy)_3$ (7 mg, 0,025 mmol, 5 mol%) in DMF (5 mL) was purged with argon and stirred at 20 °C to give a yellowish clear solution. To the stirred solution were added **2a** (200 mg, 0.5 mmol), Na_2CO_3 (216 mg, 4.0 mmol) and the alkene or styrene (5.0 equiv. per bromine atom of the substrate). The reaction mixture was stirred at 140 °C for 24–36 h. The solution was poured into H_2O, brine and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3×25 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane-EtOAc).

General Procedure C for the Synthesis of Dibenzothiophenes (4)

A diphenyl ether solution (3 mL) of **3a–j** was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol%) was added. The solution was stirred at 200 °C for 48 h under an argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by chromatography (flash silica gel, eluent: heptanes-EtOAc).

Tetramethyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (4a): Product **4a** was prepared starting with **3a** (100 mg, 0.24 mmol), following general procedure C, as a white solid; yield: 59 mg (60%), mp. = 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.90$ (s, 6H, $2CH_3O$), 3.92 (s, 6H, $2CH_3O$), 8.15 (s, 2H, ArH), 8.54 (s, 2H, ArH); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta=51.9$ ($2CH_3O$), 52.0 ($2CH_3O$), 122.4 (2CH), 122.8 (2CH), 127.5 (2C), 130.6 (2C), 134.9 (2C), 142.3 (2C), 166.4 (2CO), 166.7 (2CO); IR (KBr): $\nu=2999$, 2951, 2923, 2850 (w), 1716 (s), 1600, 1548, 1465 (w), 1431 (m), 1351, 1316 (w), 1270, 1243 (m), 1191 (m), 1123, 1094 (s), 1012, 962, 896, 881, 820, 781, 746 (m), 609, 575 cm^{-1} (w); GC-MS (EI, 70 eV): m/z (%) = 416 (57) $[M]^+$, 386 (21), 385 (100), 339 (11), 268 (13); HR-MS (EI, 70 eV): $m/z=$ 416.05600, calcd. for $C_{20}H_{16}O_8S$ $[M]^+$: 416.05604.

Tetrabutyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (4c): Product **4c** was prepared starting with **2a** (200 mg, 0.5 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), $P(Cy)_3$ (7 mg, 5 mol%), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) (140 °C, 24 h) according to general procedure B as a brownish oil; yield: 117 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.91$ (t, 6H, $J=7.3$ Hz, $2CH_3$), 0.92 (t, 6H, $J=7.4$ Hz, $2CH_3$), 1.35–1.45 (m, 8H, $4CH_2$), 1.64–1.75 (m, 8H, $4CH_2$), 4.30 (t, 4H, $J=6.7$ Hz, $2CH_2O$), 4.31 (t, 4H, $J=6.7$ Hz, $2CH_2O$), 8.15 (s, 2H, ArH), 8.52 (s, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 12.7 ($4CH_3$), 18.2 ($4CH_2$), 29.5 ($2CH_2$), 29.6 ($2CH_2$), 64.9 ($2CH_2O$), 65.0 ($2CH_2O$), 122.3 (2CH), 122.7 (2CH), 128.1 (2C), 130.9 (2C), 134.9 (2C), 142.0 (2C), 166.2 (2CO), 166.3 (2CO); IR (KBr): $\nu=2953$, 2925, 2856 (m), 1716 (s), 1608, 1547, 1466, 1379 (m), 1268, 1240, 1119, 1097 (s), 991, 897, 781 (m), 746, 600, 542 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 584 (39) $[M]^+$, 528 (10), 457 (10), 456 (31), 457 (100), 399 (50), 360 (17), 343 (27), 342 (12), 325 (27), 254 (12), 57 (14), 44 (16), 41 (21); HR-MS (ESI): $m/z=585.2517$, calcd. for $C_{32}H_{41}O_8S$ $[M+H]^+$: 585.2516.

General Procedure D for the Synthesis of 2,3,4,5-Tetraalkenyl-*N*-methylpyrroles (5)

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol%) and $P(Cy)_3$ (28 mg, 0,1 mmol, 10 mol%) in DMF (5 mL) was purged with argon and stirred at 20 °C to give a yellowish or brownish transparent solution. To the stirred solution were added the brominated pyrrole **2b** (1.0 mmol), NEt_3 (1.1 mL, 8.0 mmol) and the alkene (1.25 equiv. per Br). The reaction mixture was stirred at 90 °C for 12 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

(2*E*,2′*E*,2″*E*,2‴*E*)-Tetrabutyl-3,3′,3″,3‴-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetraacrylate (5a): Product **5a** was prepared starting with **2b** (392 mg, 1.0 mmol), *n*-butyl acrylate (0.72 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%) , $P(Cy)_3$ (28 mg, 10 mol%), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) (90 °C, 12 h) following general procedure D as a brownish oil; yield: 380 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 0.89 (t, 12H, $J=7.4$ Hz, $4CH_3$), 1.30–1.40 (m, 8H, $4CH_2$), 1.58–1.65 (m, 8H, $4CH_2$), 3.71 (s, 3H, NCH_3), 4.14 (t, 4H, $J=6.7$ Hz, $2CH_2O$), 4.16 (t, 4H, $J=6.7$ Hz, $2CH_2O$), 6.02 (d, 2H, $J=16.0$ Hz, 2CH), 6.12 (d, 2H, $J=16.1$ Hz, 2CH), 7.58 (d, 2H, $J=16.1$ Hz, 2CH), 7.65 (d, 2H, $J=16.0$ Hz, 2CH); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta=13.7$ ($2CH_3$), 13.8 ($2CH_3$), 19.1 ($2CH_2$), 19.2 ($2CH_2$), 30.6 ($2CH_2$), 30.7 ($2CH_2$), 34.2 (NCH_3), 64.5 ($2CH_2O$), 64.8 ($2CH_2O$), 121.9 (2CH), 122.2 (2C), 122.5 (2CH), 130.5 (2CH), 132.8 (2C), 135.7 (2CH), 166.4 (2CO), 166.6 (2CO); IR (KBr): $\nu=$ 2957, 2933 (m), 2872 (w), 1705 (s), 1618 (m), 1453, 1383 (w), 1278, 1247 (m), 1161 (s), 1062, 1023, 964, 858, 735 (m), 653, 611 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 585 (44) $[M]^+$, 512 (12), 484 (21), 428 (12), 410 (100), 354 (14), 310 (30), 254 (22), 252 (15), 226 (17), 182 (17), 173 (11), 57 (23), 41 (17); HR-MS (EI, 70 eV): $m/z=585.32935$, calcd. for $C_{33}H_{47}NO_8$ $[M^+]$: 585.32962.

General Procedure E for the Synthesis of Carbazoles (6)

A diphenyl ether solution (3 mL) of **5a–g** (0.25 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol%) was added. The solution was stirred at 200 °C for 48 h under an argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by chromatography (flash silica gel, eluent: heptanes/EtOAc).

Tetrabutyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (6a): Compound **6a** was synthesized starting with **5a** (100 mg, 0.17 mmol), following general procedure E, as a brownish oil; yield: 74 mg (75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, 6H, $J = 7.4$ Hz, $2CH_3$), 0.92 (t, 6H, $J = 7.3$ Hz, $2CH_3$), 1.33–1.48 (m, 8H, $4CH_2$), 1.64–1.75 (m, 8H, $4CH_2$), 3.86 (s, 3H, NCH_3), 4.28 (t, 4H, $J = 6.7$ Hz, $2CH_2O$), 4.30 (t, 4H, $J = 6.7$ Hz, $2CH_2O$), 7.62 (s, 2H, ArH), 8.50 (s, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.7$ ($2CH_3$), 13.8 ($2CH_3$), 19.2 ($2CH_2$), 19.3 ($2CH_2$), 29.8 (NCH_3), 30.6 ($2CH_2$), 30.8 ($2CH_2$), 65.5 ($2CH_2O$), 65.9 ($2CH_2O$), 109.7 (2CH), 123.0 (2CH), 123.1 (4C), 132.6 (2C), 142.8 (2C), 167.3 (2CO), 168.8 (2CO); IR (KBr): $\nu = 2957$, 2932 (m), 2872 (w), 1712 (s), 1634, 1601, 1563 (w), 1457 (m), 1384, 1340 (w), 1254, 1230, 1107, 1084, 1074 (s), 1018, 961, 784 (m), 681, 603 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 581 (100) $[M]^+$, 525 (12), 453 (23), 422 (85), 396 (21), 340 (11), 322 (25), 173 (11); HR-MS (ESI): $m/z = 582.3064$, calcd. for $C_{33}H_{44}NO_8$ $[M+H]^+$: 582.3061.

Synthesis of Tetra(alkenyl)furans (7)

(2*E*,2′*E*,2″*E*,2‴*E*)-Tetrabutyl-3,3′,3″,3‴-(furan-2,3,4,5-tetrayl)tetraacrylate (7a): Product **7a** was prepared starting with **2c** (200 mg, 0.5 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), $P(Cy)_3$ (7 mg, 5 mol%), Na_2CO_3 (216 mg, 4.0 mmol), and DMF (5 mL) (90 °C, 8 h) according to general procedure A as a brownish oil; yield: 77 mg (27%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, 12H, $J = 7.3$ Hz, $4CH_3$), 1.33–1.40 (m, 8H, $4CH_2$), 1.58–1.67 (m, 8H, $4CH_2$), 4.16 (t, 4H, $J = 6.6$ Hz, $2CH_2O$), 6.15 (d, 2H, $J = 16.0$ Hz, 2CH), 6.52 (d, 2H, $J = 15.6$ Hz, 2CH), 7.47 (d, 2H, $J = 16.0$ Hz, 2CH), 7.55 (d, 2H, $J = 16.1$ Hz, 2CH); ^{13}C NMR (62 MHz, $CDCl_3$): $\delta = 13.7$ ($4CH_3$), 19.1 ($4CH_2$), 30.5 ($2CH_2$), 30.6 ($2CH_2$), 64.8 ($2CH_2O$), 64.9 ($2CH_2O$), 121.1 (2CH), 124.3 (2C), 124.7 (2CH), 126.9 (2CH), 132.1 (2CH), 150.5 (2C), 165.8 (2CO), 166.2 (2CO); IR (KBr): $\nu = 2956$, 2939, 2870 (w), 1707 (s), 1618 (m), 1393 (w), 1308 (m), 1161 (s), 1061, 1023, 855 (m), 730, 576 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 572 (90) $[M]^+$, 499 (20), 470 (27), 415 (15), 413 (11), 397 (64), 341 (24), 313 (17), 297 (67), 285 (15), 269 (11), 241 (73), 239 (21), 213 (20), 195 (60), 169 (19), 57 (100), 55 (15), 44 (30), 41 (63); HR-MS (ESI): $m/z = 595.28691$, calcd. for $C_{32}H_{44}NaO_9$ $[M+Na]^+$: 595.28775.

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