Highly Efficient Synthesis of Linear Pyrrole Oligomers by Twofold Heck Reactions

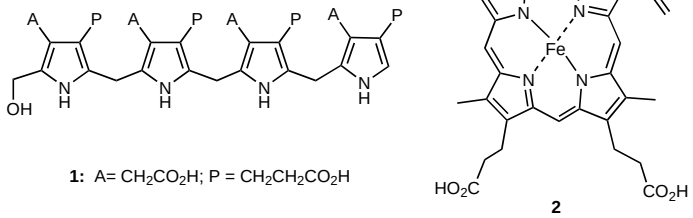
Lutz F. Tietze,* Georg Kettschau, Ulrich Heuschert, and Gero Nordmann[a]

Abstract: The twofold Heck reaction of the vinylpyrroles **3a** and **3b** with the iodobenzenes **4a–c** led to the linear pyrrole oligomers **5**, **6**, and **7**. The synthesis of both symmetrical and unsymmetrical oligomers, such as **10a** and **10b**, was also accomplished by a Heck reaction of **8** and **9** and by a Heck reaction of **3a** and **11** followed by a Wittig reaction and a second Heck reaction with **8**. The pentacyclic oligomers **14** and **19** were prepared by a twofold Heck reaction of **13** with **4** and by a twofold Heck reaction of **15** with **16** followed by a Wittig reaction and a twofold Heck reaction with **8**.

Keywords: Heck reactions · palladium · polypyrroles · pyrroles · Wittig reactions

Introduction

Linear oligomeric pyrroles are key building blocks in biosynthesis[1] and are also of interest for the synthesis of novel macrocycles.[2] This may be exemplified by the linear tetrameric pyrromethane hydroxymethylbilane **1** being the precursor of the porphyrins such as heme **2** (Scheme 1), the chlorophylls and vitamin B_{12}.[1]



1: A= CH_2CO_2H; P = $CH_2CH_2CO_2H$

2

Scheme 1. Hydroxymethylbilane **1** and heme **2**.

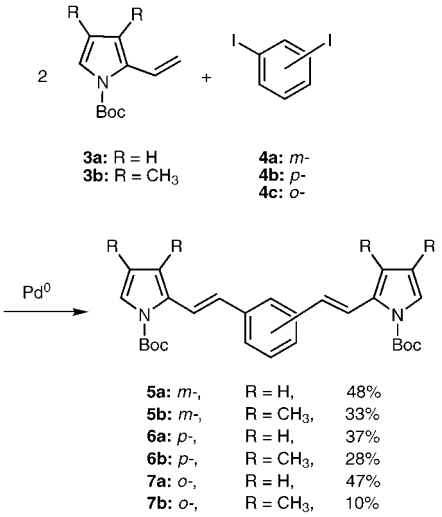
Further, polypyrroles in their oxidized form are of interest as organic conductors and LED materials.[3] In recent years π-conjugated oligomers of defined structure gained more and more interest due to their inherent electronic and optical properties.[4] Today this class of compounds represents a research field of its own. While there has been substantial progress in the synthesis of other types of π-conjugated oligomers,[5] straightforward synthesis of higher linear oligomers of pyrrole remains challenging.[6] Recently we reported on novel linear oligopyrroles.[7] Herein we describe the efficient synthesis of oligopyrroles **5**, **6**, **7**, **10**, **14**, and **19** being connected by divinylbenzene units using twofold Heck reactions.[8]

Results and Discussion

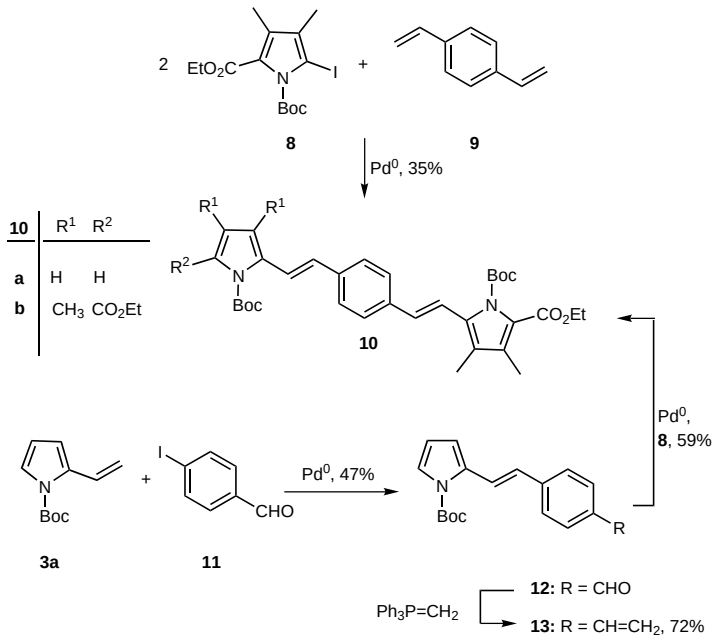
For the synthesis of the linear 2-divinylbenzene-1,3-bispyrroles **5**, **6** and **7**, *N*-Boc-vinylpyrroles **3a** and **3b**[7] were treated with *meta*-[9], *para*-, and *ortho*-diiodobenzene in the presence of catalytic amounts of palladium (see Scheme 2). A major problem in the transformations of **3b** was the control of regioselectivity at the vinyl group. Thus, reaction of **3b** under the usual reaction conditions gave a mixture of constitutional isomers. However, by employing silver acetate as base only the linear products were obtained. Silver phosphate and silver carbonate proved to be less effective for this purpose. Reaction of **3b** with *m*-diiodobenzene **4a** provided **5b** with 33% yield, reaction of **3b** with *p*-diiodobenzene **4b** gave **6b** with 28% yield and that of **3b** with *o*-diiodobenzene **4c** led to **7b** in only 10% yield. The lower yield of the reaction of **4c** with *o*-substitution is in accord with the increased steric hindrance at the reaction centers compared with **4a** and **4b**. In the transformations of **3a** the linear oligomers were obtained in the absence of a silver salt. Moreover, for these reactions it was in some cases appropriate to use triethylamine as solvent to obtain good results. Reaction of **3a** with **4a** gave **5a** in 48%

[a] Prof. Dr. Dr. h.c. L. F. Tietze, Dr. G. Kettschau, Dipl. Chem. U. Heuschert, Dipl. Chem. G. Nordmann
Institut für Organische Chemie
Georg-August-Universität Göttingen
Tammannstraße 2, 37077 Göttingen (Germany)
Fax: (+49) 551-399476
E-mail: ltietze@gwdg.de

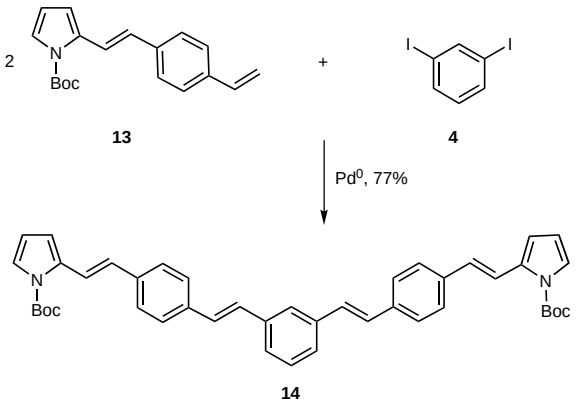
0947-6539/01/0702-0368 $ 17.50+.50/0



Scheme 2. Synthesis of the tricyclic compounds **5**–**7**.



Scheme 3. Synthesis of the tricyclic compounds **10a** and **10b**.



Scheme 4. Synthesis of **14**.

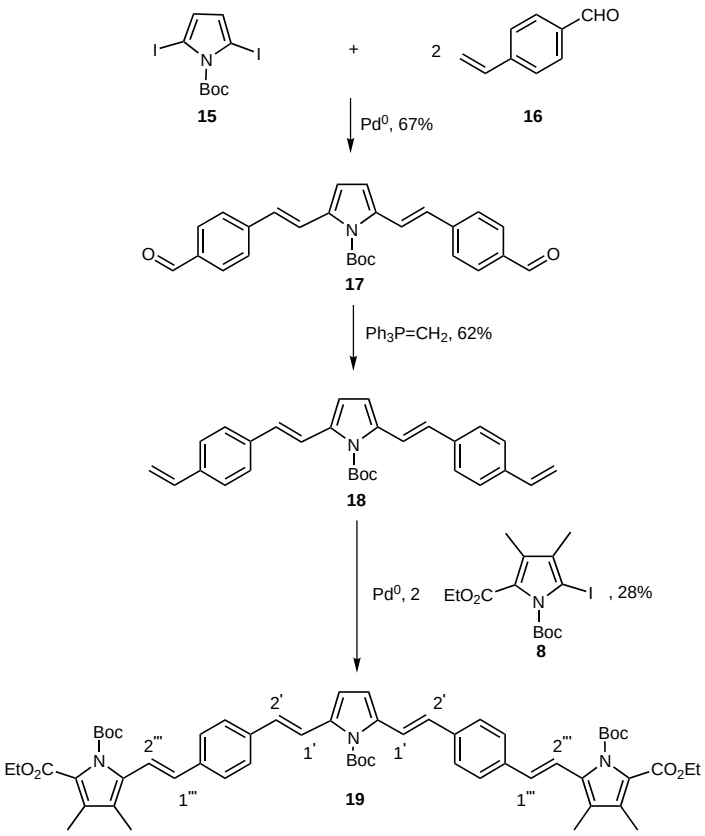
yield, that of **3a** with **4b** oligomer **6a** in 37% yield and that of **3a** with **4c** compound **7a** in 47% yield. The decreased regioselectivity under normal conditions and the lower yield in the reaction of **3b** is probably due to a strong 1,3-allylic strain[10] in the transition state leading to **5**–**7** due to the methyl group at C-3 of the pyrrole moiety of **3b**. Such a 1,3-allylic strain has recently been shown by us to be of importance in the cyclisation of hydroxymethylbilane.[1f] The improvement of the regioselectivity in the reaction of **3b** by addition of silver salt can be explained by the intermediate formation of a Pd^+ species which would generally increase the reactivity and also lower the steric interaction of the Pd attacked to α-position of the vinyl group in **3b**. However, electronic effects may also have some influence. Thus, Hallberg and others[11] showed that electron rich palladium species favor an α-arylation.

For the formation of oligomers of type **5**–**7** a second approach is also feasible, namely the use of a divinylbenzene and an iodopyrrole. This is exemplified by the preparation of the *p*-substituted system **10b** (see Scheme 3) from **8**[12] and **9**.[13] Reaction of **8** and **9** in the presence of catalytic amounts of palladium led to **10b** in 35% yield. Here and in some other reactions, especially when using iodopyrroles, the presence of triphenylphosphane is not suitable since decomposition may occur. This effect has been recognized by us for several different transformations. For the preparation of unsymmetrical oligomers we have also developed a stepwise approach in which first a Pd-catalyzed reaction of a vinylpyrrole **3a** with *p*-iodobenzaldehyde (**11**)[14] leads to the pyrrole derivative **12**. Wittig reaction gives the corresponding vinylbenzenepyrrole **13**, which now can react in a second Heck reaction with the iodopyrrole **8** to give **10** in 20% yield over three steps.

The vinyl derivative **13** could also be subjected to a twofold Heck reaction with *m*-diiodobenzene (**4**). This transformation gave the pentacyclic oligomer **14** in 77% yield which contains two pyrrole and three divinylbenzene moieties (Scheme 4).

Of particular interest for the synthesis of higher linear oligomeric pyrroles is the 2,5-diiodopyrrole derivative **15**, which is easily accessible from the corresponding dibromo derivative by halogen metal exchange with *n*BuLi and quenching with iodine.[15] The 2,5-dibromopyrrole can be obtained from pyrrole itself through bromination followed by protection with di-*tert*-butyldicarbonate according to the protocol of Cava[15] in 83% yield. While the 2,5-dibromopyrrole derivative is usually not sufficiently reactive in Heck reactions, **15** undergoes Pd-catalyzed C–C bond formation with several acceptor substituted alkenes, for example acrylic acid esters or *p*-vinylbenzaldehyde (**16**) (Scheme 5).[16] Twofold Heck reaction of **15** with **16** led to the pyrrole derivative **17**, which gave the bisvinyl derivative **18** using a twofold Wittig reaction. Compound **18** reacts with the iodopyrrole **8** again in a twofold Heck reaction to give the red pentacyclic oligomer **19** in 28% yield.

The structures of the newly formed oligopyrroles were determined mainly by NMR spectroscopy. The spectra are rather simple due to the symmetry of the molecules. As an example the ^1H NMR spectrum of **19** is discussed in detail. The hydrogens at the four double bonds resonate as a doublet



Scheme 5. Synthesis of **19**.

at $\delta = 6.79$ with $J = 16.5$ Hz for the 1‴-H, at $\delta = 6.93$ with $J = 16.0$ Hz for the 2′-H, at $\delta = 7.65$ with $J = 16.5$ Hz for the 2‴-H and at $\delta = 7.86$ with $J = 16.0$ Hz for the 1′-H. The large coupling constants of $J = 16.0$ and 16.5 Hz confirm that all double bonds have an (*E*)-configuration. The hydrogens at the central pyrrole unit and the arenes resonate as singlets at $\delta = 6.55$ and $\delta = 7.40$, respectively. For the methyl groups at the pyrrole units singlets at $\delta = 1.93$ and 2.20 are observed. The UV/Vis spectrum documents the extended π-conjugated system with $\lambda_{max} = 431$ nm and $\log \varepsilon = 4.858$.

Conclusion

The combination of several Heck reactions as well as of Wittig and Heck reactions allows a simple and highly efficient access to linear π-conjugated oligomeric pyrrole derivatives. Here the synthesis of defined oligomers with up to five arene and pyrrole units connected by C=C-double bonds is described. However, the approach could also be employed for the synthesis of higher oligomers.

Experimental Section

All reactions were performed under nitrogen or argon atmosphere in flame-dried flasks, and the reactants were introduced by syringe. All solvents were dried by standard methods. Solvents used in Pd-catalyzed reactions were degassed by pump and freeze methodology. All reagents obtained from commercial sources were used without further purification. TLC chromatography was performed on aluminum precoated silica gel SIL G/UV$_{254}$ plates (Macherey–Nagel GmbH), and silica gel 32–63 (0.032–0.064 mm) (Macherey–Nagel GmbH) was used for column chromatography(eluent 1: light petroleum/EtOAc 15:1; eluent 2: 10:1; eluent 3: 4:1; eluent 4: 15:1 + 1% NEt_3; eluent 5: 10:1 + 1% NEt_3; eluent 6: 4:1 + 1% NEt_3). UV/Vis spectra (λ_{max} [nm], log ε) were recorded in CH_3CN on a Mettler Lambda 2 spectrometer. IR spectra were recorded as KBr pellets or as films on a Bruker IFS 25 or Vector 22 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 200, VXR 200, and VXR 500 or a Bruker AM 300 with tetramethylsilane (TMS) as internal standard in $CDCl_3$ or [D_6]benzene. Multiplicities of ^{13}C NMR peaks were determined with the APT pulse sequence. Mass spectra were measured at 70 eV on a Varian MAT 311A, high-resolution mass spectra on a Varian MAT 731 instrument. Melting points are measured on a Mettler FP 61.

General procedure I. Wittig reaction: *n*BuLi (1.1 mol equiv, 2.1M solution in *n*-hexane) was added dropwise at 0 °C to a stirred suspension of methyl triphenylphosphonium iodide (1.2 mol equiv) in THF (10 mL per mmol aldehyde). Stirring was continued for 2 h at 0 °C and the aldehyde (1.0 equiv) in THF was added dropwise to the solution at −78 °C. After stirring for 15 min at this temperature the solution was warmed to room temperature and stirred for additional 30 min. The reaction was quenched by adding water, then the organic layer was separated and the aqueous layer extracted with Et_2O (3 ×). The combined organic layers were washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The obtained crude product was purified by column chromatography.

General procedure II. Heck reaction with pyrroles

Variant a: A stirred suspension of potassium acetate (4.0 mol equiv) and tetrapropylammonium bromide (1.0 mol equiv) in DMF (20 mL per mmol substrate) was degassed by freeze and pump methodology. Palladium acetate (5 mol%), triphenylphosphane (10 mol%) and the substrates were added. The vigorously stirred reaction mixture was slowly heated to the indicated temperature. After complete transformation (TLC) the reaction mixture was cooled to room temperature and water (20 mL per mmol substrate) and Et_2O (40 mL per mmol substrate) were added. The aqueous layer was extracted with Et_2O (3 ×). The combined organic phases were washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The obtained crude products were purified by column chromatography.

Variant b: The reaction was performed in the absence of triphenylphosphane.

Variant c: The reaction was performed in the presence of silver acetate (4.0 mol equiv) instead of potassium acetate and tetrapropylammonium bromide.

Variant d: The reaction was performed in the presence of triethylamine instead of potassium acetate and tetrapropylammonium bromide. For this purpose triethylamine was degassed in a pressure flask by bubbling argon through for 0.5 h and after addition of palladium acetate (5 mol%), triphenylphosphane (10 mol%) and the substrates the reaction mixture was degassed for another 10 min.

(*E*,*E*)-1,3-Bis-[2′-(1″-*tert*-butoxycarbonyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (5a): According to general procedure IId the vinylpyrrole **3a** (293 mg, 1.50 mmol, 1.3 equiv) was reacted with 1,3-diiodobenzene **4a** (165 mg, 500 μmol, 1.0 equiv) for 24 h at 90 °C. Column chromatography (20 g silica gel, eluent 2) afforded **5a** (111 mg, 241 μmol, 48%) as a yellow oil. $t_R = 0.40$ (eluent 2); IR (KBr): $\tilde{\nu} = 3004$, 2978, 2932 (C–H), 1742 (C=O), 1624, 1594, 1552 (C=C), 958 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} ($\log \varepsilon$) = 237.5 (4.280), 330.0 nm (4.574); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.29$ (s, 18H, $C(CH_3)_3$), 6.13 (t, $J = 3.5$ Hz, 2H, 4″-H), 6.53 (ddd, $J = 3.5$, 2.0, 1.0 Hz, 2H, 3″-H), 6.93 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.11 (t, $J = 7.5$ Hz, 1H, 5-H), 7.33 (dd, $J = 7.5$, 2.0 Hz, 2H, 4-H, 6-H), 7.37 (dd, $J = 3.5$, 2.0 Hz, 2H, 5″-H), 7.67 (br s, 1H, 2-H), 8.14 (d, $J = 16.5$ Hz, 2H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.0$ ($C(CH_3)_3$), 83.8 ($C(CH_3)_3$), 110.8 (C-4″), 111.1 (C-3″), 119.8 (C-2′), 122.2 (C-5″), 124.5 (C-2), 125.2 (C-4, C-6), 128.0 (C-1′), 128.8 (C-5), 134.3 (C-2″), 137.9 (C-1, C-3), 149.4 (C=O); MS (70 eV): *m*/*z* (%): 460 (37) $[M]^+$, 360 (15) $[M - CO_2C_4H_8]^+$, 348 (28) $[M - 2 \times C_4H_8]^+$, 304 (41) $[M - CO_2C_4H_8 - C_4H_8]^+$, 260 (100) $[M - 2 \times CO_2C_4H_8]^+$, 57 (13) $[C_4H_9]^+$; $C_{28}H_{32}N_2O_4$ (460.6): calcd C 73.02, H 7.00; found C 73.06, H 6.97.

(*E*,*E*)-1,3-Bis-[2′-(1″-*tert*-butoxycarbonyl-3″,4″-dimethyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (5b): According to general procedure IIc the vinylpyrrole **3b** (277 mg, 1.25 mmol, 1.3 equiv) was treated with 1,3-diiodobenzene **4a** (165 mg, 500 μmol, 1.0 equiv) for 4 h at 90 °C. Column chromatog-

0947-6539/01/0702-0370 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 2

raphy (10 g silica gel, eluent 1) afforded **5b** (85.0 mg, 165 μmol, 33 %) as a pale yellow oil. $t_R = 0.48$ (eluent 1); IR (KBr): $\tilde{\nu} = 2978, 2932$ (C–H), 1734 (C=O), 1626, 1594, 1578, 1520 (C=C), 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 242.5 (4.314), 327.5 nm (4.527); ^1H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.53$ (s, 18H, $C(CH_3)_3$), 1.96 (s, 6H, 4-CH_3), 2.10 (s, 6H, 3-CH_3), 6.64 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.07 (s, 2H, 5″-H), 7.31–7.42 (m, 3H, 4-H, 5-H, 6-H), 7.53 (d, $J = 16.5$ Hz, 2H, 2′-H), 7.61 (br s, 1H, 2-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.38, 11.38$ (3-CH_3, 4-CH_3), 28.11 ($C(CH_3)_3$), 82.97 ($C(CH_3)_3$), 118.4 (C-5″), 120.7 (C-2′), 122.2, 122.7 (C-3″, C-4″), 124.3 (C-2), 124.8 (C-4, C-6), 128.8 (C-5), 129.4 (C-2″), 129.7 (C-1′), 138.2 (C-1, C-3), 149.5 (C=O); MS (70 eV): *m*/*z* (%): 516 (23) $[M]^+$, 416 (16) $[M - CO_2C_4H_8]^+$, 316 (100) $[M - 2 \times CO_2C_4H_8]^+$, 57 (41) $[C_4H_9]^+$; $C_{32}H_{40}N_2O_4$ (516.7): HMRS calcd 516.2988; found 516.2988.

(*E*,*E*)-1,4-Bis-[2′-(1″-*tert*-butoxycarbonyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (6a): According to general procedure IIa the vinylpyrrole **3a** (483 mg, 2.50 mmol, 1.3 equiv) was reacted with 1,4-diiodobenzene (**4b**, 330 mg, 1.00 mmol, 1.0 equiv) for 20 h at 70 °C. Column chromatography (40 g silica gel, eluent 2) afforded **6a** (170 mg, 369 μmol, 37 %) as yellow crystals. M.p. > 180 °C (dec); $t_R = 0.40$ (eluent 2); IR (KBr): $\tilde{\nu} = 3004, 2980, 2932$ (C–H), 1738 (C=O), 1620, 1652, 1510 (C=C), 958 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 197.0 (4.532), 244.5 (4.138), 377.0 nm (4.685); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.63$ (s, 18H, $C(CH_3)_3$), 6.19 (t, $J = 3.5$ Hz, 2H, 4″-H), 6.56 (m, 2H, 3″-H), 6.87 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.28 (dd, $J = 3.5$, 1.5 Hz, 2H, 5′-H), 7.44 (s, 4H, Ph-H), 7.75 (d, $J = 16.5$ Hz, 2H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.0$ ($C(CH_3)_3$), 83.8 ($C(CH_3)_3$), 110.7 (C-4″), 111.1 (C-3″), 119.3 (C-2′), 122.2 (C-5″), 126.6 (C-2, C-3, C-5, C-6), 127.8 (C-1′), 134.4 (C-2″), 136.7 (C-1, C-4), 149.4 (C=O); MS (70 eV): *m*/*z* (%): 460 (30) $[M]^+$, 404 (8) $[M - C_4H_8]^+$, 360 (12) $[M - CO_2C_4H_8]^+$, 348 (100) $[M - 2 \times C_4H_8]^+$, 304 (37) $[M - CO_2C_4H_8 - C_4H_8]^+$, 259 (31) $[M - CO_2C_4H_8 - CO_2C_4H_9]^+$, 57 (13) $[C_4H_9]^+$; $C_{28}H_{32}N_2O_4$ (460.6): calcd C 73.02, H 7.00; found C 73.08, H 7.04.

(*E*,*E*)-1,4-Bis-[2′-(1″-*tert*-butoxycarbonyl-3″,4″-dimethyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (6b): According to general procedure IIc vinylpyrrole **3b** (277 mg, 1.25 mmol, 1.3 equiv) was treated with 1,4-diiodobenzene (**4b**, 165 mg, 500 μmol, 1.0 equiv) for 4 h at 90 °C. Column chromatography (eluent 2) afforded **6b** (72.3 mg, 139 μmol, 28 %) as yellow crystals. M.p. > 200 °C (dec); $t_r = 0.49$ (eluent 1); IR (KBr): $\tilde{\nu} = 3002, 2974, 2926$ (C–H), 1720 (C=O), 1628, 1566, 1506 (C=C), 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_2Cl_2): λ_{max} (log ε) = 251.0 (4.122), 372.5 nm (4.536); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.58$ (s, 18H, $C(CH_3)_3$), 2.00 (s, 6H, 4″-CH_3), 2.15 (s, 6H, 3″-CH_3), 6.59 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.04 (s, 2H, 5′-H), 7.44 (s, 4H, Ph-H), 7.56 (d, $J = 16.5$ Hz, 2H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.37, 11.36$ (3″-CH_3, 4″-CH_3), 28.16 ($C(CH_3)_3$), 83.00 ($C(CH_3)_3$), 118.4 (C-5″), 120.1 (C-2′), 122.2, 122.7 (C-3, C-4), 126.3 (C-2, C-3, C-5, C-6), 129.4 (C-1′), 129.4 (C-2″), 136.9 (C-1, C-4), 149.5 (C=O); MS (70 eV): *m*/*z* (%): 516 (72) $[M]^+$, 404 (99) $[M - 2 \times C_4H_8]^+$, 315 (100) $[M - CO_2C_4H_8 - CO_2C_4H_9]^+$, 57 (13) $[C_4H_9]^+$; $C_{32}H_{40}N_2O_4$ (516.7): HMRS calcd 516.2988; found 516.2988.

(*E*,*E*)-1,2-Bis-[2′-(1″-*tert*-butoxycarbonyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (7a): According to general procedure IId the vinylpyrrole **3a** (483 mg, 2.50 mmol, 1.3 equiv) was treated with 1,2-diiodobenzene (**4c**, 330 mg, 1.00 mmol, 1.0 equiv) for 20 h at 90 °C. Column chromatography (eluent 2) afforded **7a** (216 mg, 469 μmol, 47 %) as a yellow oil. $t_R = 0.39$ (eluent 2); IR (neat): $\tilde{\nu} = 2978, 2932, 2866$ (C–H), 1742 (C=O), 1616, 1548 (C=C), 958 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 311.0 nm (3.981); ^1H NMR (200 MHz, C_6D_6): $\delta = 1.29$ (s, 18H, $C(CH_3)_3$), 6.08 (t, $J = 3.5$ Hz, 2H, 4″-H), 6.50 (m, 2H, 3″-H), 7.05 (dd, $J = 6.0$, 3.5 Hz, 2H, 4-H, 5-H), 7.34 (dd, $J = 3.5$, 1.5 Hz, 2H, 5″-H), 7.48 (d, $J = 16.0$ Hz, 2H, 1′-H), 7.65 (dd, $J = 6.0$, 3.5 Hz, 2H, 3-H, 6-H), 8.03 (d, $J = 16.0$ Hz, 2H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.02$ ($C(CH_3)_3$), 83.84 ($C(CH_3)_3$), 110.9, 111.0 (C-3″, C-4″), 121.8 (C-2′), 122.2 (C-5″), 125.9, 126.4, 127.4 (C-3, C-4, C-5, C-6, C-1′), 134.6, 135.8 (C-1, C-2, C-2″), 149.4 (C=O); MS (70 eV): *m*/*z* (%): 460 (44) $[M]^+$, 404 (11) $[M - C_4H_8]^+$, 348 (36) $[M - 2 \times C_4H_8]^+$, 304 (17) $[M - CO_2C_4H_8 - C_4H_8]^+$, 259 (26) $[M - CO_2C_4H_8 - CO_2C_4H_9]^+$, 193 (27), 180 (32), 57 (13) $[C_4H_9]$; $C_{28}H_{32}N_2O_4$ (460.6): calcd C 73.02, H 7.00; found C 73.00, H 7.00.

(*E*,*E*)-1,2-Bis-[2′-(1″-*tert*-butoxycarbonyl-3″,4″-dimethyl-[1″*H*]-pyrrol-2″-yl)-vinyl]-benzene (7b): According to general procedure IIc vinyl pyrrole **3b** (553 mg, 2.50 mmol, 1.3 equiv) was treated with 1,2-diiodobenzene (**4c**, 330 mg, 1.00 mmol, 1.0 equiv) for 5 h at 90 °C. Column chromatography (10 g silica gel, eluent 1) afforded **7b** (52.4 mg, 101 μmol, 10 %) as a yellow oil. $t_R = 0.48$ (eluent 1); IR (KBr): $\tilde{\nu} = 2980, 2930, 2862$ (C–H), 1732 (C=O), 1600, 1524 (C=C), 962 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 251.0 nm (4.202), 313.0 (4.345), 341.0 (4.284); ^1H NMR (200 MHz, C_6D_6): $\delta = 1.32$ (s, 18H, $C(CH_3)_3$), 1.85 (s, 6H, 4″-CH_3), 2.07 (s, 6H, 3″-CH_3), 7.09 (dd, $J = 6.0$, 3.5 Hz, 2H, 4-H, 5-H), 7.20 (s, 2H, 5″-H), 7.27 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.82 (dd, $J = 6.0$, 3.5 Hz, 2H, 3-H, 6-H), 7.95 (d, $J = 16.5$ Hz, 2H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.36, 11.46$ (3″-CH_3, 4″-CH_3), 28.09 ($C(CH_3)_3$), 82.96 ($C(CH_3)_3$), 118.3 (C-5″), 122.1 (C-3″), 122.3 (C-2′), 122.5 (C-4″), 125.9, 127.1, 127.2 (C-3, C-4, C-5, C-6, C-1′), 129.7 (C-2″), 135.9 (C-1, C-2), 149.4 (C=O); MS (70 eV): *m*/*z* (%): 516 (41) $[M]^+$, 416 (14) $[M - CO_2C_4H_8]^+$, 315 (46) $[M - CO_2C_4H_8 - CO_2C_4H_9]^+$, 123 (40) $[C_8H_{13}N]^+$, 57 (100) $[C_4H_9]^+$; $C_{32}H_{40}N_2O_4$ (516.7): HMRS calcd 516.2988; found 516.2988.

(*E*,*E*)-1,4-Bis-[2′-(1″-*tert*-butoxycarbonyl-3″,4″-dimethyl-5″-ethoxycarbonyl-[1*H*]-pyrrol-2″-yl)-vinyl]-benzene (10b): According to general procedure IIb the iodopyrrole **8** (708 mg, 1.80 mmol, 1.5 equiv) was treated with 1,4-divinylbenzene (**9**, 78.4 mg, 600 μmol, 1.0 equiv) for 2 h at 75 °C. Column chromatography (10 g silica gel, eluent 5) afforded **10b** (137 mg, 207 μmol, 35 %) as yellow crystals. M.p. 170 °C; $t_R = 0.47$ (eluent 3); IR (KBr): $\tilde{\nu} = 2980, 2936, 2906$ (C–H), 1746 (carbamate-C=O), 1692 (ester-C=O), 1564, 1512 (C=C), 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 191.0 (4.481), 227.0 (4.144), 377.5 (4.688), 379.5 nm (4.688); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.37$ (t, $J = 7.0$ Hz, 6H, $CO_2CH_2CH_3$), 1.58 (s, 18H, $C(CH_3)_3$), 2.16 (s, 6H, 4-CH_3), 2.23 (s, 6H, 3-CH_3), 4.33 (q, $J = 7.0$ Hz, 4H, $CO_2CH_2CH_3$), 6.76 (d, $J = 17.0$ Hz, 2H, 1′-H), 7.31 (d, $J = 17.0$ Hz, 2H, 2′-H), 7.45 (s, 4H, Ph-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.4$ (3″-CH_3), 11.0 (4″-CH_3), 14.4 ($CO_2CH_2CH_3$), 27.7 ($C(CH_3)_3$), 60.5 ($CO_2CH_2CH_3$), 84.5 ($C(CH_3)_3$), 117.9 (C-2′), 120.4, 121.7 (C-3″, C-4″), 126.7 (C-2, C-3, C-5, C-6), 130.2 (C-5″), 132.3 (C-1′), 132.8 (C-2″); 136.8 (C-1, C-6), 149.9 (carbamate-C=O), 161.7 (ester-C=O); MS (70 eV): *m*/*z* (%): 661 (2) $[M]^+$, 561 (7) $[M - CO_2C_4H_8]^+$, 460 (100) $[M - CO_2C_4H_8 - CO_2C_4H_9]^+$, 413 (12) $[M - 2 \times CO_2C_4H_9 - OC_2H_5]^+$; $C_{38}H_{48}N_2O_8$ (660.8): calcd C 69.07, H 7.32; found C 68.90, H 7.25.

2-[(*E*)-2′-(4″-Formylphenyl)-vinyl]-[1*H*]-1-*N*-*tert*-butyloxycarbonyl-pyrrol (12): According to general procedure IIa the vinylpyrrole **3a** (212 mg, 1.10 mmol, 1.1 equiv) was treated with 4-iodobenzaldehyde (**11**, 232 mg, 1.00 mmol, 1.0 equiv) for 4 h at 90 °C. Column chromatography (20 g silica gel, eluent 2) afforded **12** (140 mg, 471 μmol, 47 %) as a yellow oil. $t_R = 0.34$ (eluent 2); IR (neat): $\tilde{\nu} = 2980, 2934, 2842, 2732$ (C–H), 1742 (carbamate-C=O), 1696 (aldehyde-C=O), 1598, 1564 (C=C), 962 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 194.0 (4.472), 251.5 (4.042), 360.5 nm (4.346); ^1H NMR (200 MHz, C_6D_6): $\delta = 1.29$ (s, 9H, $C(CH_3)_3$), 6.10 (t, $J = 3.5$ Hz, 1H, 4-H), 6.52 (m, 1H, 3-H), 6.77 (d, $J = 16.5$ Hz, 1H, 2′-H), 7.26 (d, $J = 8.5$ Hz, 2H, 2″-H, 6″-H), 7.32 (dd, $J = 3.5$, 1.5 Hz, 1H, 5-H), 7.52 (d, $J = 8.5$ Hz, 2H, 3″-H, 5″-H), 8.17 (d, $J = 16.5$ Hz, 1H, 1′-H), 9.66 (s, 1H, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 27.84$ ($C(CH_3)_3$), 83.97 ($C(CH_3)_3$), 111.2, 111.8 (C-3, C-4), 122.8 (C-1′), 122.9 (C-5), 126.2 (C-2′), 126.4 (C-2″, C-6″), 129.9 (C-3″, C-5″), 133.5, 134.8 (C-2, C-4″), 143.6 (C-1″), 149.1 (carbamate-C=O), 191.2 (aldehyde-C=O); MS (70 eV): *m*/*z* (%): 297 (24) $[M]^+$, 241 (100) $[M - C_4H_8]^+$, 197 (61) $[M - CO_2C_4H_8]^+$, 168 (33) $[M - CO_2C_4H_8 - CHO]^+$, 57 (78) $[C_4H_9]^+$; $C_{18}H_{19}NO_3$ (297.4): calcd C 72.71, H 6.44; found C 72.84, H 6.55.

2-[(*E*)-2′-(4″-Vinylphenyl)-vinyl]-[1*H*]-1-*N*-*tert*-butyloxycarbonyl-pyrrol (13): According to general procedure I aldehyde **12** (2.12 g, 7.13 mmol) was subjected to a Wittig reaction. Column chromatography (100 g silica gel, eluent 4) afforded compound **13** (1.51 g, 5.11 mmol, 72 %) as a pale yellow solid. M.p. 77 °C; $t_R = 0.57$ (eluent 2); IR (KBr): $\tilde{\nu} = 3040, 3002, 2976, 2932$ (C–H), 1744 (C=O), 1622, 1602, 1550, 1508 (C=C), 966 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 197.0 (4.502), 240.5 (4.019), 344.5 nm (4.494); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.62$ (s, 9H, $C(CH_3)_3$), 5.23 (dd, $J = 11.0$, 1.0 Hz, 1H, *trans*=CH_2), 5.74 (dd, $J = 18.0$, 1.0 Hz, 1H, *cis*=CH_2), 6.19 (t, $J = 3.5$ Hz, 1H, 4-H), 6.56 (m, 1H, 3-H), 6.70 (dd, $J = 18.0$, 11.0 Hz, 1H, $CH=CH_2$), 6.87 (d, $J = 16.5$ Hz, 1H, 2′-H), 7.28 (dd, $J = 3.5$, 1.5 Hz, 1H, 5-H), 7.37, 7.43 (AA′BB′-system, $J = 8.0$ Hz, 4H, Ph-H), 7.76 (d, $J = 16.5$ Hz, 1H, 1′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.0$ ($C(CH_3)_3$), 83.8 ($C(CH_3)_3$), 110.7 (C-4), 111.1 (C-3), 113.4 ($CH=CH_2$), 119.7 (C-1′), 122.3 (C-5), 126.4 (C-2″, C-3″, C-5″, C-6″), 127.7 (C-2′), 134.3 (C-2), 136.4 ($CH=CH_2$), 137.2 (C-1″, C-4″), 149.4 (C=O); MS (70 eV): *m*/*z* (%): 295 (16) $[M]^+$, 239 (100) $[M - C_4H_8]^+$, 195 (42) $[M - CO_2C_4H_8]^+$, 57 (32) $[C_4H_9]^+$; $C_{19}H_{21}NO_2$ (295.4): HMRS calcd 295.1572; found 295.1572.

1-[(*E*)-2′-(1″-*tert*-Butoxycarbonyl-3″,4″-dimethyl-5″-ethoxycarbonyl-[1″*H*]-pyrrol-2-yl)-vinyl]-4-[(*E*)-2‴-(1‴″-*tert*-butoxycarbonyl-[1‴″*H*]-pyrrol-2‴″-yl)-vinyl]-benzene (10a): According to general procedure IIa the compound **13** (118 mg, 400 μmol, 1.0 equiv) was treated with the iodopyrrole (**8**, 189 mg, 480 μmol, 1.2 equiv) for 2.5 h at 90 °C. Column chromatography (10 g silica gel, eluent 5) afforded **10a** (133 mg, 237 μmol, 59 %) as a yellow solid. M.p. 131 °C; $t_R = 0.31$ (eluent 2); IR (KBr): $\tilde{\nu} = 3002$, 2976, 2932 (C–H), 1744 (carbamate-C=O), 1668 (ester-C=O), 1624, 1596, 1546, 1512 (C=C), 972, 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 242.5 (4.169), 377.0 (4.732), 379.5 nm (4.722); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.37$ (t, $J = 7.0$ Hz, 3H, $CO_2CH_2CH_3$), 1.56 (s, 9H, $C(CH_3)_3$″), 1.63 (s, 9H, $C(CH_3)_3$‴″), 2.14 (s, 3H, 4″-CH_3), 2.21 (s, 3 H 3″-CH_3), 4.33 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 6.20 (t, $J = 3.5$ Hz, 1H, 4‴″-H), 6.57 (m, 1H, 3‴″-H), 6.76 (d, $J = 16.5$ Hz, 1H, 1′-H), 6.89 (d, $J = 16.5$ Hz, 1H, 1‴-H), 7.28 (d, $J = 16.5$ Hz, 1H, 2′-H), 7.29 (dd, $J = 3.5$, 1.5 Hz, 1H, 5‴″-H), 7.43, 7.46 (AA′BB′-system, $J = 8.5$ Hz, 4H, Ph-H), 7.78 (d, $J = 16.5$ Hz, 1H, 2‴-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.4$ (3″-CH_3), 11.0 (4″-CH_3), 14.4 ($CO_2CH_2CH_3$), 27.7 ($C(CH_3)_3$″), 28.1 ($C(CH_3)_3$‴″), 60.5 ($CO_2CH_2CH_3$), 83.9 ($C(CH_3)_3$‴″), 84.4 ($C(CH_3)_3$″), 110.8 (C-4‴″), 111.2 (C-3‴″), 117.5 (C-2′), 119.7 (C-2‴), 120.3, 121.6 (C-3″, C-4″), 122.3 (C-5‴″), 126.58, 126.63 (C-2, C-3, C-5, C-6), 127.6 (C-1‴), 130.2 (C-5″), 132.5 (C-1′), 132.9 (C-2″), 134.3 (C-2‴″), 136.2, 137.3 (C-1, C-4), 149.5 (1‴″-carbamate-C=O), 149.9 (1″-carbamate-C=O), 161.7 (ester-C=O); MS (70 eV): *m*/*z* (%): 561 (24) [*M*]$^+$, 461 (16) [$M - CO_2C_4H_8$]$^+$, 404 (9) [$M - CO_2C_4H_8 - C_4H_9$]$^+$, 360 (100) [$M - CO_2C_4H_8 - CO_2C_4H_9$]$^+$, 313 (40) [$M - 2 \times CO_2C_4H_9 - OC_2H_5$]$^+$, 56 (55) [$C_4H_8$]$^+$, 41 (87) [$C_3H_5$]$^+$; $C_{33}H_{40}N_2O_6$ (560.7): calcd C 70.69, H 7.19; found C 70.61, H 7.33.

(*E*,*E*)-1,3-Bis-[2′-(4″-((*E*)-2‴-(1‴″-*tert*-butoxycarbonyl-[1‴″*H*]-pyrrol-2‴″-yl)-vinyl)-phenyl)-vinyl]-benzene (14): According to general procedure IIb, **13** (443 mg, 1.50 mmol, 1.5 equiv) was treated with 1,3-diiodobenzene (**4**, 165 mg, 500 μmol, 1.0 equiv) for 3 h at 70 °C. Extraction was performed with CH_2Cl_2. Column filtration (silica gel, $CHCl_3$) of the poorly soluble residue gave an orange solid, which for further purification was absorbed on silica gel (40 g silica gel). After the silica gel was washed with light petroleum/EtOAc 10:1 to 1:1, **14** was eluated with warm $CHCl_3$ to give an orange solid (257 mg, 387 μmol, 77 %) after evaporation in vacuo. M.p. > 200 °C (dec); $t_R = 0.29$ (eluent 2); IR (KBr): $\tilde{\nu} = 3078$, 3024, 2978, 2932 (C–H), 1740 (C=O), 1618, 1590, 1510 (C=C), 960 cm^{-1}(C–H, (*E*)-alkene); UV (CH_2Cl_2): λ_{max} (log ε) = 246.0 (4.412), 377.5 (4.967), 379.5 nm (4.967); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.64$ (s, 18H, $C(CH_3)_3$), 6.20 (t, $J = 3.5$ Hz, 2H, 4‴″-H), 6.58 (ddd, $J = 3.5$, 1.5, 1.0 Hz, 2H, 3‴″-H), 6.90 (d, $J = 16.0$ Hz, 2H, 1‴-H), 7.14, 7.15 (AB-system, $J = 16.5$ Hz, 1′-H, 2′-H), 7.29 (dd, $J = 3.5$, 1.5 Hz, 5‴″-H), 7.36 (dd, $J = 8.0$, 6.5 Hz, 1H, 5-H), 7.41 – 7.44 (m, 2H, 4-H, 6-H), 7.49, 7.51 (AA′BB′-system, $J = 8.0$ Hz, 8H, Ph-H), 7.66 (s, 1H, 2-H), 7.79 (d, $J = 16.0$ Hz, 2H, 2‴-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 28.2$ ($C(CH_3)_3$), 83.9 ($C(CH_3)_3$), 110.9, 111.2 (C-3‴″, C-4‴″), 119.9 (C-2‴), 122.4 (C-5‴″), 124.8 (C-2), 125.7 (C-4, C-6), 126.8, 126.9 (C-2″, C-3″, C-5″, C-6″), 127.8, 128.3, 128.9 (C-1′, C-2′, C-1‴), 129.0 (C-5), 134.6 (C-2‴″), 136.5, 137.4, 138.0 (C-1, C-3, C-1″, C-4″); MS (DCI, NH_3): *m*/*z* (%): 666 (100) [*M*+H]$^+$, 667 (40) [*M*+2H]$^+$, 683 (4) [*M*+NH_4]$^+$; $C_{44}H_{44}N_2O_4$ (664.84): calcd C 79.49, H 6.67; found C 79.50, H 6.67.

(*E*,*E*)-2,5-Bis-[2′-(4″-formylphenyl)-vinyl]-[1*H*]-1-*N*-*tert*-butyloxycarbonyl-pyrrol (17): According to general procedure IIb 4-vinylbenzaldehyde **16** (792 mg, 6.0 mmol, 2.0 equiv) was treated with the diiodopyrrole **15** (692 mg, 1.50 mol, 1.0 equiv) for 2 h at 60 °C. Extraction was performed with CH_2Cl_2. Column filtration (15 g deactivated silica gel, CH_2Cl_2) of the crude reaction mixture was followed by recrystallisation from CH_2Cl_2/light petroleum to yield **17** (417 mg, 975 μmol, 67 %) as orange crystals. M.p. > 170 °C (dec); $t_R = 0.25$ (light petroleum/EtOAc 4:1); IR (KBr): $\tilde{\nu} = 3030$, 3004, 2974, 2934, 2822, 2728 (C–H), 1734 (carbamate-C=O), 1690 (aldehyde-C=O), 1592, 1562 (C=C), 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 195.0 (4.632), 264.0 (4.299), 419.0 nm (4.684); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.69$ (s, 9H, $C(CH_3)_3$), 6.67 (s, 2H, 3-H, 4-H), 6.93 (d, $J = 16.5$ Hz, 2H, 2′-H), 7.59 (d, $J = 8.0$ Hz, 4H, 2″-H, 6″-H), 7.73 (d, $J = 16.5$ Hz, 2H, 1′-H), 7.85 (d, $J = 8.0$ Hz, 4H, 3″-H, 5″-H), 9.99 (s, 2H, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.2$ ($C(CH_3)_3$), 85.3 ($C(CH_3)_3$), 112.2 (C-3, C-4), 123.0 (C-1′), 126.5 (C-2″, C-6″), 126.7 (C-2′), 130.2 (C-3″, C-5″), 135.0, 135.6 (C-2, C-5, C-4″), 143.5 (carbamate-C=O), 191.4 (aldehyde-C=O); MS (70 eV): *m*/*z* (%): 427 (24) [*M*]$^+$, 371 (100) [$M - C_4H_8$]$^+$, 327 (77) [$M - CO_2C_4H_8$]$^+$, 57 (21) [C_4H_9]$^+$; $C_{27}H_{25}NO_4$ (427.5): calcd C 75.86, H 5.89; found C 75.86, H 5.92.

(*E*,*E*)-2,5-Bis-[2′-(4″-vinylphenyl)-vinyl]-[1*H*]-1-*N*-*tert*-butyloxycarbonyl-pyrrol (18): According to general procedure I the dialdehyde **17** (480 mg, 1.12 mmol) was transformed to the corresponding divinyl compound. Due to the poor solubility of the substrate it was added as a solution in CH_2Cl_2. After warming to room temperature the reaction mixture was stirred for 1.5 h. Column chromatography (20 g silica gel, eluent 6) and subsequent crystallisation from light petroleum/EtOAc afforded **18** (294 mg, 694 μmol, 62 %) as an orange solid. M.p. 161 °C; $t_R = 0.66$ (eluent 2); IR (KBr): $\tilde{\nu} = 3078$, 3002, 2978, 2932 (C–H), 1746 (C=O), 1620, 1596, 1552, 1506 (C=C), 960 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 198.5 (4.701), 267.0 (4.355), 399.5 nm (4.722); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.66$ ($C(CH_3)_3$), 5.27 (dd, $J = 11.0$, 0.5 Hz, 2H, *trans*=CH_2), 5.75 (dd, $J = 17.5$, 0.5 Hz, 2H, *cis*=CH_2), 6.57 (s, 2H, 3-H, 4-H), 6.71 (dd, $J = 17.5$, 11.0 Hz, 2H, CH=CH_2), 6.86 (d, $J = 16.5$ Hz, 2H, 2′-H), 7.27 (AA′BB′-system, $J = 8.0$ Hz, 4H, Ph-H), 7.53 (d, $J = 16.5$ Hz, 2H, 1′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 28.2$ ($C(CH_3)_3$), 84.6 ($C(CH_3)_3$), 111.0 (C-3, C-4), 113.4 (CH=CH_2), 119.9 (C-1′), 126.3, 126.5 (C-2″, C-3″, C-5″, C-6″), 127.3 (C-2′), 135.6 (C-2, C-5), 136.4 (CH=CH_2), 136.5, 137.2 (C-1″, C-4″), 150.0 (C=O); MS (70 eV): *m*/*z* (%): 423 (26) [*M*]$^+$, 367 (100) [$M - C_4H_8$]$^+$, 323 (94) [$M - CO_2C_4H_8$]$^+$, 57 (24) [C_4H_9]$^+$; $C_{29}H_{29}NO_4$ (423.6): calcd C 82.24, H 6.90; found C 82.11, H 6.83.

(*E*,*E*)-2,5-Bis-[2′-(4″-((*E*)-2‴-(1‴″-*tert*-butoxycarbonyl-5‴″-ethoxycarbonyl-3‴″,4‴″-dimethyl-[1‴″*H*]-pyrrol-2‴″-yl)-vinyl)-phenyl)-vinyl]-[1*H*]-1-*N*-*tert*-butyloxycarbonyl-pyrrol (19): According to general procedure IIb the compound **18** (169 mg, 400 μmol, 1.0 equiv) was treated with the iodopyrrole **8** (472 mg, 400 μmol, 1.0 equiv) for 2 h at 75 °C. Column chromatography (10 g silica gel, eluent 5) and recrystallisation from Et_2O afforded **19** (107 mg, 112 mol, 28 %) as red crystals. M.p. 163 °C; $t_R = 0.41$ (eluent 3); IR (KBr): $\tilde{\nu} = 3076$, 2978, 2934 (C–H), 1742 (carbamate-C=O), 1704 (ester-C=O), 1618, 1594, 1556, 1510 (C=C), 954 cm^{-1} (C–H, (*E*)-alkene); UV (CH_3CN): λ_{max} (log ε) = 197.0 (4.657), 251.0 (4.282), 328.0 (4.265), 431.0 nm (4.858); ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.08$ (t, $J = 7.0$ Hz, 6H, $CO_2CH_2CH_3$), 1.34 (s, 9H, $C(CH_3)_3$, 1.46 (s, 18H, $C(CH_3)_3$‴″), 1.93 (s, 6H, 4‴″-CH_3), 2.20 (s, 6H, 3‴″-CH_3), 4.17 (q, $J = 7.0$ Hz, 4H, $CO_2CH_2CH_3$), 6.55 (s, 2H, 3-H, 4-H), 6.79 (d, $J = 16.5$ Hz, 2H, 1‴-H), 6.93 (d, $J = 16.0$ Hz, 2H, 2′-H), 7.40 (s, 8H, Ph-H), 7.65 (d, $J = 16.5$ Hz, 2H, 2‴-H), 7.86 (d, $J = 16.0$ Hz, 2H, 1′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 10.44$ (3‴″-CH_3), 10.97 (4‴″-CH_3), 14.42 ($CO_2CH_2CH_3$), 27.66 ($C(CH_3)_3$‴″), 28.23 ($C(CH_3)_3$), 60.49 ($CO_2CH_2CH_3$), 84.45 ($C(CH_3)_3$‴″), 84.75 ($C(CH_3)_3$), 111.1 (C-3, C-4), 117.6 (C-2‴), 120.0 (C-1′), 120.4, 121.6 (C-3‴″, C-4‴″), 126.6, 126.7 (C-2″, C-3″, C-5″, C-6″), 127.3 (C-2′), 130.3 (C-5‴″), 132.5 (C-1‴), 133.0 (C-2‴″), 135.7 (C-2, C-5), 136.3, 137.3 (C-1″, C-4″), 149.4 (1‴″-carbamate-C=O), 150.1 (1-carbamate-C=O), 161.7 (ester-C=O); MS (FAB, positive): *m*/*z* (%): 953 (100) [*M*]$^+$, 897 (8) [$M - C_4H_8$]$^+$, 854 (20) [$M - CO_2C_4H_8$+H]$^+$, 754 (13) [$M - 2 \times CO_2C_4H_8$+H]$^+$, 697 (7) [$M - 2 \times CO_2C_4H_8 - C_4H_8$]$^+$, 653 (93) [$M - 3 \times CO_2C_4H_8$]$^+$, 607 (14) [$M - 2 \times CO_2C_4H_8 - CO_2C_4H_9 - OC_2H_5$]$^+$, 560 (9) [$M - 3 \times CO_2C_4H_9 - 2 \times OC_2H_5$]$^+$; $C_{57}H_{67}N_3O_{10}$ (954.2): calcd C 71.75, H 7.08; found C 71.90, H 7.00.

Acknowledgement

This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the BASF AG, Bayer AG, Degussa-Hüls AG and the Wacker Chemie for the gift of chemicals.

[1] a) F. Blanche, B. Cameron, J. Crouzet, L. Debussche, D. Thibaut, M. Vuilhorgne, F. J. Leeper, A. R. Battersby, *Angew. Chem.* **1995**, *107*, 421; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 383; b) *The Biosynthesis of Tetrapyrrole Pigments*, Ciba Foundation Symposia, *Vol. 180* (Eds.: D. J. Chadwick, K. Ackrill), Wiley, Chichester, **1994**; c) *Biosynthesis of Tetrapyrroles* (Ed.: P. M. Jordan), Elsevier Publishers, Amsterdam, **1990**; d) A. I. Scott, *Tetrahedron* **1994**, *50*, 13315; e) L. F. Tietze, G. Schulz, *Chem. Eur. J.* **1997**, *3*, 523; f) L. F. Tietze, H. Geissler, G. Schulz, *Pure Appl. Chem.* **1994**, *66*, 2303; g) L. F. Tietze, H. Geissler, *Angew. Chem.* **1993**, *105*, 1087; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1038; h) L. F. Tietze, H.Geissler, *Angew. Chem.* **1993**, *105*, 1090; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1040.

[2] a) B. Franck, A. Nonn, *Angew. Chem.* **1995**, *107*, 1941; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1795; b) M. Bröring, H.-J. Dietrich, J. Dörr, G.

0947-6539/01/0702-0372 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 2

Hohlneicher, J. Lex, N. Jux, C. Pütz, M. Roeb, H. Schmickler, E. Vogel, *Angew. Chem.* **2000**, *112*, 1147; *Angew. Chem. Int. Ed.* **2000**, *39*, 1105; c) M. Bröring, J. Jendrny, L.Zander, H. Schmickler, J. Lex, Y.-D. Wu, M. Nendel, J. Chen, D. A. Plattner, K. N. Houk, E. Vogel, *Angew. Chem.* **1995**, *107*, 2709; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2515; d) J. L. Sessler, S. J. Weghorn, Y. Hiseada, V. Lynch, *Chem. Eur. J.* **1995**, *1*, 56; e) J. L. Sessler, A. K. Burrell, *Top. Curr. Chem.* **1991**, *161*, 177.

[3] a) A. C. Partridge, *Electrochim. Acta* **1995**, *40*, 1199; b) S. Martina, V. Enkelmann, A.-D. Schlüter, G. Wegner, G. Zotti, G. Zerbi, *Synth. Met.* **1993**, *55*, 1096; c) S. Nakamura, M. Maeda, *Nippon Joshi Daigaku Kiyo*, *Rigakubu* **1993**, *1*, 39; d) H. Lindenberger, D. Schäfer-Siebert, S. Roth, M. Hanack, *Synth. Met.* **1987**, *18*, 37; e) T. Kauffmann, H. Lexy, *Chem. Ber.* **1981**, *114*, 3674; see also: f) A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609; g) P. Delannoy, G. Horowitz, H. Bouchriha, F. Deloffre, J.-L. Fave, F. Garnier, R. Hajlaoui, A. Yassar, *Synth. Met.* **1994**, *67*, 197; h) P. Bäuerle, U. Segelbacher, K.-U. Gaudl, D. Huttenlocher, M. Mehring, *Angew. Chem.* **1993**, *105*, 125; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 76.

[4] *Electronic Materials*: *The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1997**.

[5] F. Diederich, R. E. Martin, *Angew.* Chem **1999**, *111*, 1440; *Angew. Chem. Int. Ed.* **1999**, *111*, 1350–1377.

[6] a) C. Pinchon, A. I. Scott, *Tetrahedron Lett.* **1994**, *35*, 4497; b) C. Pinchon, B. P. Atshaves, R. Danso-Danquah, N. J. Stolowich, A. I. Scott, *Bioorg. Med. Chem.* **1994**, *2*, 267; c) M. Xie, D. A. Lightner, *Tetrahedron* **1993**, *49*, 2185; d) W. M. Stark, G. J. Hart, A. R. Battersby, *J. Chem. Soc. Chem. Commun.* **1986**, 465; e) A. R. Battersby, C. J. R. Fookes, P. S. Pandey, *Tetrahedron* **1983**, *39*, 1919; f) A. R. Battersby, C. J. R. Fookes, K. E. Gustafson-Potter, E. McDonald, G. W. J. Matcham, *J. Chem. Soc. Perkin Trans. 1* **1982**, 2413; g) G. Bringmann, B. Franck, *Liebigs Ann. Chem.* **1982**, 1261.

[7] L. F. Tietze, G. Kettschau, K. Heitmann, *Synthesis* **1996**, *7*, 851.

[8] S. Bräse, A. de Meijere in *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, pp. 99–166.

[9] G. Félix, J. Dunoguès, F. Pisciotti, R. Calas, *Angew. Chem.* **1977**, *89*, 502; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 488.

[10] a) R. W. Hoffmann, *Chem. Rev.* **1989**, *89*, 1841; b) L. F. Tietze, G. Schulz, *Liebigs Ann. Chem.* **1996**, 1575.

[11] a) C.-M. Andersson, A. Hallberg, G. D. Daves, Jr., *J.Org. Chem.* **1987**, *52*, 3529; b) W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2 and references therein.

[12] J. L. Sessler, M. C. Hoehner, *Synlett* **1994**, 211.

[13] G. Wittig, H. Eggers, P. Duffner, *Liebigs Ann. Chem.* **1958**, *619*, 10.

[14] a) E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, *20*, 399; b) N. M. Yoon, C. S. Pak, H. C. Brown, S. Krishnamurthy, T. P. Stocky, *J. Org. Chem.* **1973**, *38*, 2786.

[15] W. Chen, M. P. Cava, *Tetrahedron Lett.* **1987**, *28*, 6025.

[16] Y. Le Bigot, M. Delmas, A. Gaset, *Synth. Commun.* **1983**, *13*, 177.

Received: May 16, 2000 [F2491]