Synthesis and (Non)linear Optical Properties of a Series of Donor−Oligopyrrole−Acceptor Molecules

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The Pd-catalyzed cross-coupling reaction involving organostannanes (Stille reaction) is applied to prepare a series of *N*-*t*-BOC-protected D−π−*A* oligopyrroles. After purification, oligomers with one to four pyrrole units inserted between a 4-nitrophenyl and a 4-methoxyphenyl group are isolated in yields between 20 and 47%. Only minor differences in the linear optical properties are observed for the four oligomers. The charge-transfer band around $\lambda_{max} = 365$ nm shows a small, unexpected, hypsochromic shift, while the π−π* band around $\lambda_{max} = 285$ nm shows a small, expected, bathochromic shift upon elongation of the molecule. Their nonlinear optical properties, however, show a surprising proceeding; going from the D−π−*A* oligomer with one pyrrole unit to that with three pyrrole units, the hyperpolarizability, as measured by hyper-Rayleigh scattering, increases additionally with the number of pyrrole units within the oligomer, up to 277×10^{-30} esu in case of the trimer. On the basis of the assumption that both transitions contribute to the hyperpolarizability, a better conjugated D−π−*A* oligomer with a bithienyl spacer inserted between a 2-(4-nitrophenyl)-5-pyrrolyl and a 2-(4-methoxyphenyl)-5-pyrrolyl group is prepared analogously. This molecule shows only one combined absorption at $\lambda_{max} = 378$ nm for both the charge transfer and the π−π* band, while the hyperpolarizability is as high as 440×10^{-30} esu. These data, showing a very favorable transparency−hyperpolarizability tradeoff, are explained in terms of the contribution of two transitions that are superimposed.

Introduction

Over the past 15 years there has been a growing interest in the design and synthesis of new organic molecules with large second-order molecular nonlinearities for applications in optical signal processing, optical computing, and telecommunications. These so-called nonlinear optical (NLO) materials, which possess the ability to double the frequency of light, are donor−acceptor substituted π-conjugated (D−π−*A*) molecules such as functionalized benzenes, stilbenes, azobenzenes, and acetylenes. Also extended π-conjugated systems such as oligo- and polyenes, -phenylenes and -(phenylene vinylene)s,[9] as well as aliphatic polymers with NLO chromophores in the side chains,[12,13] have been prepared and studied for their first-order hyperpolarizabilities (β). The observed tradeoff between the hyperpolarizability and transparancy in these systems is easily explained by a simple two-level model.

More recently, a number of concepts have been presented, by which the first hyperpolarizability of organic molecules is enhanced. The use of octupolar contributions[14,15] and the bond-length alternation concepts[10,16] are possible strategies to tune the hyperpolarizability

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of organic molecules. A number of these and other examples have been presented in which the two-level model is not appropriate to explain the hyperpolarizabilities found.[11,17] In the latter, we see a possibility to bypass the transparency−hyperpolarizability tradeoff.

A special class of NLO materials are heteroaromatic compounds.[20−22] Here, by far, most attention has been paid to oligo- and polythiophenes because of the availability of synthetic routes toward these systems.[23−29] Up to now, however, no experimental data have been reported on D−π−*A* molecules based on oligo- and/or polypyrroles, simply because the synthetic strategies toward these systems were not at hand. The only data known thus far are those of Morley, who reported on the calculated hyperpolarizabilities of oligo- and polythiophene, -furan, and -pyrrole derivatives; he predicted the largest values for polythiophenes, followed by polypyrroles and the smallest values for polyfurans.[30]

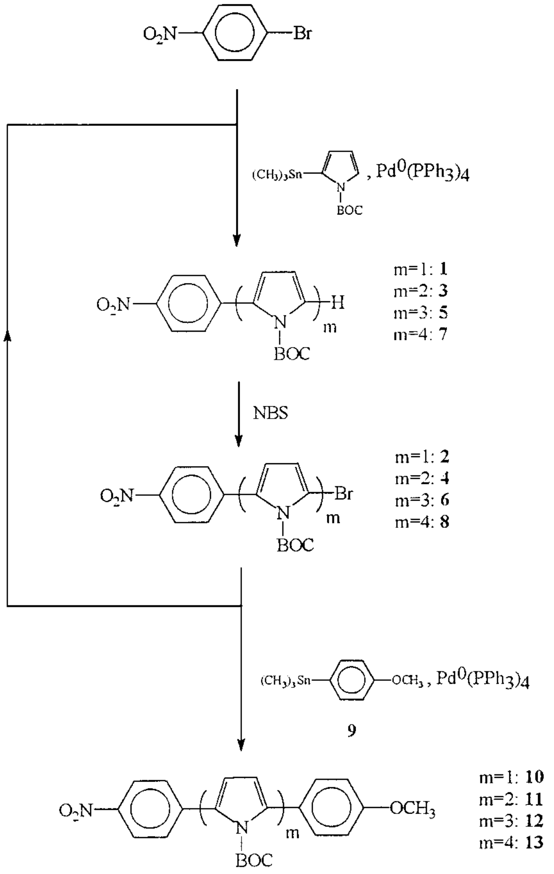
To study the (non)linear optical properties of NLO materials based on pyrrole, we have applied the Pd-catalyzed cross-coupling reaction involving organostannanes (Stille reaction) for the synthesis of the first series of D−π−*A* oligopyrroles. Performing a repetitive sequence of functionalization and Stille reactions, resulted in four different oligomers. These systems were subsequently studied by UV−vis spectroscopy and hyper-Rayleigh scattering (HRS) measurements. From these studies it appeared that the hyperpolarizability values of these systems are surprisingly high.

Results and Discussion

In the following section we first describe the synthesis and (non)linear optical properties of *N*-*t*-BOC protected D−π−*A* oligopyrroles with phenyl end groups. These results made it possible to design a special molecule that possesses an extremely favorable hyperpolarizability−transparency tradeoff. The synthesis and properties of that *t*-BOC-protected D−π−*A* pyrrole−thiophene oligomer is described in the second part.

Synthesis and Characterization of a Series of *N*-*t*-BOC-Protected D−π−*A* Oligopyrroles. The synthesis of D−π−*A* oligopyrroles is based on the Pd-catalyzed cross-coupling reaction between an organostannane and an aryl halide (Stille reaction).[31] Applying the knowledge that the reactivity of an aryl bromide increases with the introduction of an electron-withdrawing substituent, we used the reaction sequence as outlined in Scheme 1.

Scheme 1. Synthesis of Four D−π−A Oligopyrroles (10−13) by a Repetitive Sequence of Functionalization and Stille Reactions



N-*t*-BOC-2-(4-nitrophenyl)pyrrole (**1**) was prepared by the Stille reaction between 4-bromo-1-nitrobenzene and *N*-*t*-BOC-2-trimethylstannylpyrrole.[38] By performing this coupling reaction in the two-phase system of toluene and aqueous Na_2CO_3 (1 M) with 2 mol % of $Pd^0(PPh_3)_4$ as catalyst, **1** was isolated as a yellow solid in 53% yield. Bromination of **1** under standard conditions (NBS, THF, −70 °C)[38] resulted in *N*-*t*-BOC-2-bromo-5-(4-nitrophenyl)pyrrole (**2**) in quantitative yield. This compound was then coupled with *N*-*t*-BOC-2-trimethylstannylpyr-

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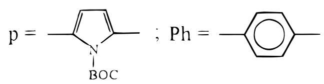
Table 1. Optical (λ_{max}) and Nonlinear Optical (β) Properties of Several D−π−*A* Oligopyrroles in $CHCl_3$ (nm = Not Measured)

	$\lambda_{max,2}$ (nm, ϵ)	$\lambda_{max,3}$ (nm, ϵ)	β (10^{-30} esu)	ϵ at 532 nm (L mol^{-1} cm^{-1})
O_2N−Ph−p (**1**)	245 (1.02 × 10^4)	345 (1.03 × 10^4)	55	0.010 × 10^4
O_2N−Ph−p−p (**3**)	255 (1.20 × 10^4)	364 (1.28 × 10^4)	60	0.027 × 10^4
O_2N−Ph−p−Ph−OCH_3 (**10**)	269 (1.42 × 10^4)	376 (1.29 × 10^4)	82	0.026 × 10^4
O_2N−Ph−p−p−Ph−OCH_3 (**11**)	286 (1.66 × 10^4)	366 (1.36 × 10^4)	177	0.056 × 10^4
O_2N−Ph−p−p−p−Ph−OCH_3 (**12**)	294 (1.84 × 10^4)	364 (1.24 × 10^4)	277	0.039 × 10^4
O_2N−Ph−p−p−p−p−Ph−OCH_3 (**13**)	297 (nm)	363 (nm)	nm	nm
p−Ph−OCH_3 (**14**)	275 (0.81 × 10^4)		<30	0.008 × 10^4



role using the same conditions as described for the synthesis of **1**. The resulting compound, *N*,*N*′-di-*t*-BOC-5-(4-nitrophenyl)-2,2′-bipyrrole (**3**, 53% yield), was subsequently brominated at the free α-pyrrolyl position, yielding *N*,*N*′-di-*t*-BOC-5-bromo-5′-(4-nitrophenyl)-2,2′-bipyrrole (**4**, 99% yield). Repetition of this sequence of Stille reaction−bromination steps gave the oligomers **5**−**8** (**5** 24%, **6** 98%, **7** 48%, **8** 92%). A final Stille reaction between the α-brominated species **2**, **4**, **6**, and **8** and 4-trimethylstannylanisole (**9**, prepared from 4-bromoanisole using *n*-BuLi and trimethylstannyl chloride) afforded the four D−π−*A* oligopyrroles **10**−**13**, which, after extensive purification (column chromatography and/or recrystallization), were isolated in moderate yields (20−47%). During these Stille reactions it was observed that the reactivity of the halide in the Stille reaction decreased by increasing the number of pyrrole units. This is due to the declining activating influence of the nitro substituent, resulting in longer reaction times. All compounds were fully characterized by NMR (^1H and ^{13}C), UV−vis, IR, and/or mass spectroscopy.

(Non)linear Optical Properties of a Series of *N*-*t*-BOC-Protected D−π−*A* Oligopyrroles. Table 1 shows the optical and nonlinear optical properties of the oligomers prepared above. The latter were measured by means of hyper-Rayleigh scattering (HRS) in chloroform with *p*-nitroaniline as reference. A Nd:YAG laser at λ = 1064 nm provided the fundamental beam, and the second harmonic (SH) was generated at λ = 532 nm, from which the molecular hyperpolarizability, β, was determined.

The four D−π−*A* oligomers **10**−**13** all show three absorption maxima in the UV−vis spectra (Figure 1). The first one, at ~240 nm, is a transition that is observed in every pyrrole derivative and that does not shift with the number of pyrrole units. The second absorption maximum ($\lambda_{max,2}$) is situated at ~285 nm and corresponds to the π−π* transition of the *N*-*t*-BOC-protected diphenyl-α-oligopyrrole part (Ph−p_n−Ph,[39] Figure 2). The third absorption maximum ($\lambda_{max,3}$), situated at ~365 nm, is most probably the charge-transfer (CT) transition of the oligomers.

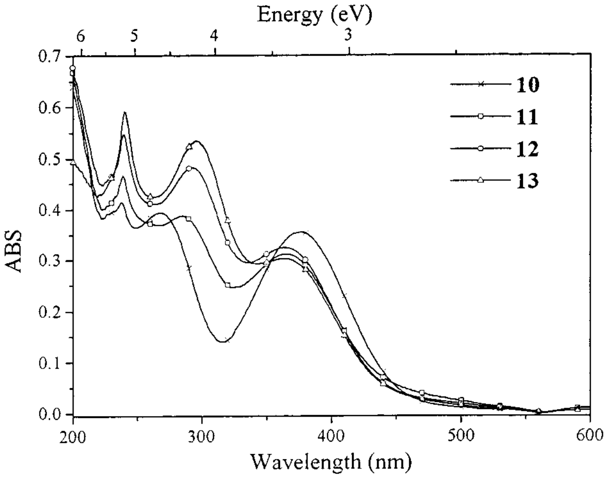


Figure 1. UV−vis absorption spectra of the *N*-*t*-BOC protected D−π−A oligopyrroles **10**−**13** recorded in $CHCl_3$.

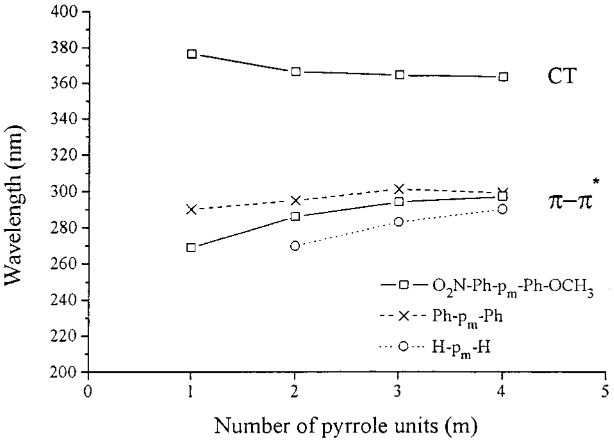


Figure 2. UV−vis absorption data of three series of *N*-*t*-BOC protected oligopyrroles, being O_2N−Ph−p_m−Ph−OCH_3 (*m* = 1−4), Ph−p_m−Ph (*m* = 1−4)[39a] and H−p_m−H (*m* = 2−4)[39b] (CT = charge-transfer transition).

Going to more extended oligomers, $\lambda_{max,2}$ shows a bathochromic shift of 28 nm, indicating that conjugation increases only slightly. This is due to the presence of the bulky *tert*-butoxycarbonyl groups, which prevent the molecules to become coplanar. $\lambda_{max,3}$ even undergoes a slightly hypsochromic shift (13 nm) going from **10** to **13** (Figure 2). The extinction coefficients (ϵ) of the π−π* transition increase going to higher oligomers, whereas those of the charge-transfer transition hardly change. Furthermore, the extinction coefficient at 532 nm, being the wavelength at which the second harmonic signal is measured, is very small and nearly constant in all four cases. At this wavelength, we also investigated the possible fluorescence that can influence our NLO mea-

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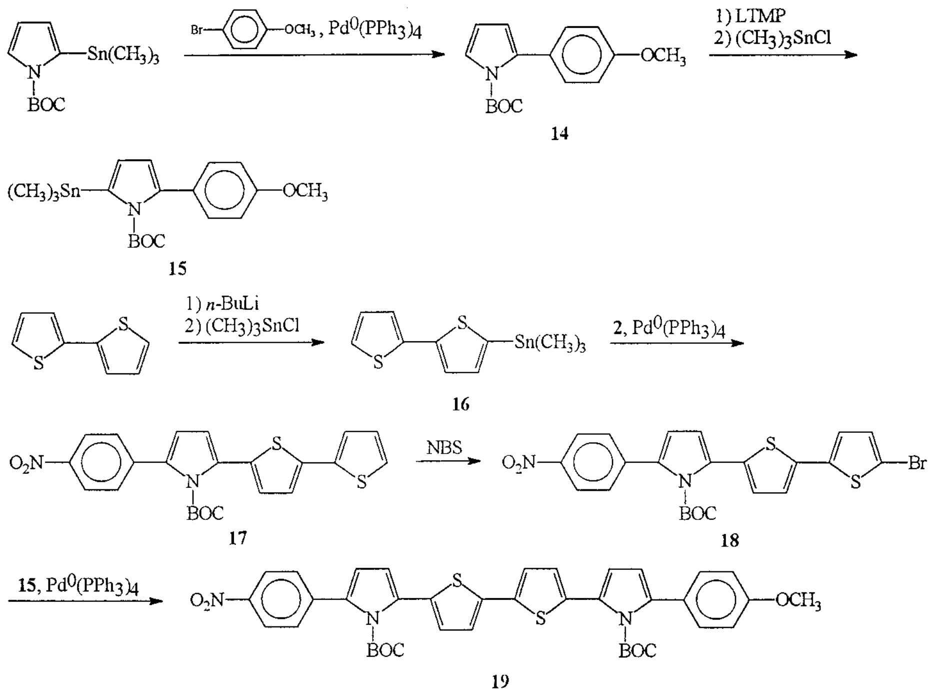
Scheme 2. Synthesis of D−π−A Oligopyrrole 19 by a Sequence of Functionalization and Stille Reactions



surements; no appreciable fluorescence is observed by using 532 nm as excitation wavelength.

HRS measurements reveal that although the linear optical data in this series of oligomers are quite similar, the hyperpolarizability (β) values increase significantly (82, 177, and 277 × 10^{-30} esu for **10**, **11**, and **12**, respectively). In the case of **13** we were not able to obtain a valid β value since the isolated amount of this oligomer was too small.

We suggest the following rationalization for this nonlinear optical behavior which was also, although far less pronounced, observed by Zyss et al. for a series of oligo-phenylenes,[11,17,18] and by Stiegman for a series of oligoacetylenes.[8] Surveying the experimental data in Table 1, it appears that only the π−π* transitions follow the increase of the hyperpolarizability values to some extent; the position of the absorption maximum slightly increases (25 nm going from **10** to **12**), while the corresponding extinction coefficients increase quite significantly (from 1.42 × 10^4 to 1.84 × 10^4 L mol^{-1} cm^{-1}). This observation leads to the assumption that it might not just be the highest wavelength transition (in this case the charge-transfer transition) which determines the value of the hyperpolarizability, but that lower wavelength transitions (in this case the π−π* transition of the conjugated part) also contribute substantially to this value. In other words, a simple two-level model to describe these nonlinear optical data is no longer sufficient; at least a combination of levels is required.

If this assumption is correct, it should be possible to increase the hyperpolarizability by shifting the π−π* transition to higher wavelength. To check this hypothesis, we designed and constructed a molecule that we expected to have a much higher π−π* transition. This D−π−*A* oligomer, 5-{*N*-*t*-BOC-2-[5-(4-methoxyphenyl)]-pyrrolyl}-5′-{*N*-*t*-BOC-2-[5-(4-nitrophenyl)]pyrrolyl}-2,2′-bithiophene (**19**), is more coplanar due to the bithienyl spacer and, therefore, should have a π−π* transition around 365 nm (the absorption maximum of the aromatic skeleton, being Ph−p−t_2−p−Ph,[39] is located at 364 nm in CH_3CN). It is expected that **19** shows only one absorption maximum, consisting of both transition, while its β value is significantly higher.

Synthesis and Characterization of 5-{*N-t*-BOC-2-[5-(4-methoxyphenyl)]pyrrolyl}-5′-{*N-t*-BOC-2-[5-(4-nitrophenyl)]pyrrolyl}-2,2′-bithiophene. Analogous to the four D−π−*A* oligopyrroles **10**−**13**, the Stille methodology was applied for the synthesis of 5-{*N*-*t*-BOC-2-[5-(4-methoxyphenyl)]pyrrolyl}-5′-{*N*-*t*-BOC-2-[5-(4-nitrophenyl)]pyrrolyl}-2,2′-bithiophene (**19**, Scheme 2).

First, *N*-*t*-BOC-2-(4-methoxyphenyl)pyrrole (**14**) was prepared from *N*-*t*-BOC-2-trimethylstannylpyrrole and 4-bromoanisole using standard Stille reaction conditions. After isolation by column chromatography (48% yield), **14** was directly stannylated at the free α-pyrrolyl position using LTMP and trimethylstannyl chloride, to give *N*-*t*-BOC-2-(4-methoxyphenyl)-5-trimethylstannylpyrrole (**15**) in 96% yield. The central part, 5-trimethylstannyl-2,2′-bithiophene (**16**), was prepared from 2,2-bithiophene using *n*-BuLi and trimethylstannyl chloride (66% yield). Subsequent coupling with *N*-*t*-BOC-2-(4-nitrophenyl)pyrrole (**2**) resulted in *N*-*t*-BOC-2-(5-[2,2′-bithienyl])-5-(4-nitrophenyl)pyrrole (**17**, 55% yield), which was then brominated with NBS in DMF at room temperature. Unfortunately, bromination occurred not only at the α-thienyl position but also at the β-position of the pyrrole unit; this is due to the high temperature at which **17** is brominated. However, after column chromatography and recrystallization, *N*-*t*-BOC-2-(5′-bromo-5-[2,2′-bithienyl])-5-(4-nitrophenyl)pyrrole (**18**) could be isolated in 43% yield. A final Stille reaction between **15** and **18** resulted in the desired D−π−*A*−oligopyrrole **19** (34% yield). All isolated compounds were fully characterized by NMR (^{1}H and ^{13}C), UV−vis, IR, and/or mass spectroscopy.

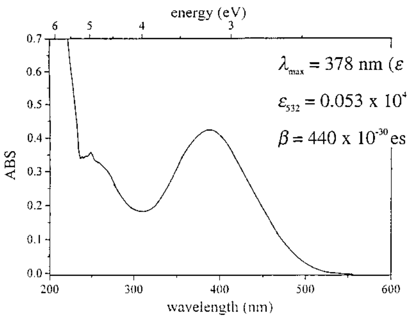


Figure 3. Optical and nonlinear optical properties of D–π–A oligomer **19** measured in $CHCl_3$.

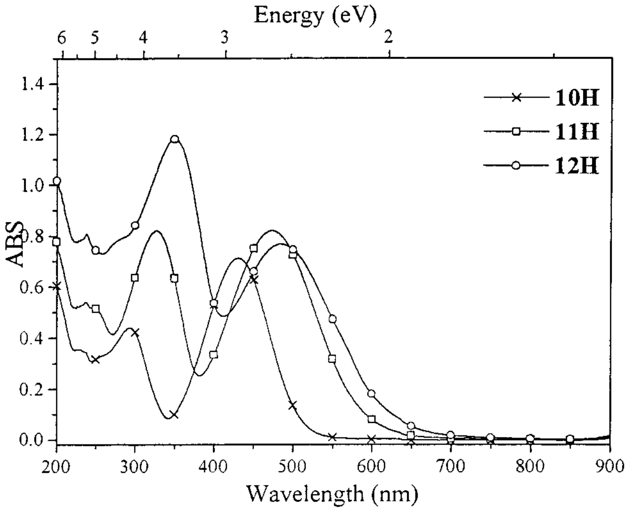


Figure 4. UV–vis absorption spectra of the deprotected D–π–A oligopyrroles **10H**–**12H** as measured in $CHCl_3$.

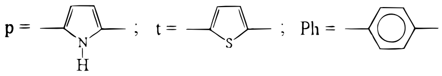
(Non)linear Optical Properties of 5-{*N*-*t*-BOC-2-[5-(4-methoxyphenyl)]pyrrolyl}-5′-{*N*-*t*-BOC-2-[5-(4-nitrophenyl)]pyrrolyl}-2,2′-bithiophene. Figure 3 shows the optical (λ) and nonlinear optical (β) properties of oligomer **19**. Only one absorption maximum with very large extinction coefficient is observed at 378 nm ($\epsilon = 3.11 \times 10^4$ L mol^{-1} cm^{-1}; $\epsilon_{532} = 0.053 \times 10^4$ L mol^{-1} cm^{-1}), indicating that the π–π* transition has indeed shifted underneath the charge-transfer transition. Furthermore, the β-value, 440×10^{-30} esu, is much higher than for all former molecules. This β value clearly indicates that the above-mentioned hypothesis, which states that both the π–π* and the charge-transfer transition contribute to the hyperpolarizability, is correct.

(Non)linear Optical Properties of Some Deprotected D–π–*A* Oligopyrroles. The *t*-BOC groups of some oligomers were thermally removed (heating for 20–30 min at 190 °C under inert atmosphere). The optical and nonlinear optical properties of the resulting deprotected analogues, which were measured by the same method and under the same conditions as applied for the *t*-BOC-protected derivatives, are listed in Table 2.

The UV–vis spectra of the deprotected oligomers show substantial red shifts for both the π–π* and the charge-transfer absorption maxima due to increased coplanarity and, thus, increased π-conjugation (Figure 4). Furthermore, the β values of **10H** and **11H** are much higher compared to their *N*-*t*-BOC-protected analogues.

Table 2. Optical (λ_{Max}) and Nonlinear Optical (β) Properties of Some Deprotected Oligomers in $CHCl_3$ (nm = Not Measured)

	$\lambda_{max,2}$ (nm)	$\lambda_{max,3}$ (nm)	β (10^{-30} esu)
O_2N–Ph–p (**1H**)	250	374	nm
O_2N–Ph–p–p (**3H**)	292	451	nm
O_2N–Ph–p–Ph–OCH_3 (**10H**)	295	431	450
O_2N–Ph–p–p–Ph–OCH_3 (**11H**)	328	479	1390
O_2N–Ph–p–p–p–Ph–OCH_3 (**12H**)	355	496	nm
O_2N–Ph–t–Ph–OCH_3[40]	295	400	320



This once more demonstrates the important contribution of conjugation to the hyperpolarizability. However, in the case of **11H** the extinction coefficient at 532 nm is quite significant, which results in a large resonance enhancement of β. In the case of **10H** the extinction coefficient at 532 nm has a value that is comparable with those of *N*-*t*-BOC-protected oligomers.

The availability of **10H** also opens the way to compare the optical and nonlinear optical properties of this compound with those of its thiophene analogue (O_2N–Ph–t–Ph–OCH_3).[40] The UV–vis data of the latter also show two absorption maxima in $CHCl_3$ (295 and 400 nm), while hyperpolarizability measurements, performed under exactly the same conditions, give a β value of 320×10^{-30} esu. This value is lower than for **10H**, which is in agreement with the optical data (π–π* transitions are identical, whereas the charge-transfer transition of **10H** is 31 nm higher). However, these observations seem to be in contradiction with the calculations of Morley, who predicted the highest β value for the thiophene derivative.[30]

Conclusions

The first series of D–π–*A* oligopyrroles has been prepared by a repetitive sequence of functionalization and Stille reactions. After tedious purification, oligomers with one to four pyrrole units inserted between a 4-methoxyphenyl donor and a 4-nitrophenyl acceptor side were isolated in moderate yields. Optical measurements showed two important absorption maxima for all four oligomers; the first one, situated at ~285 nm, corresponds to the π–π* transition of the *N*-*t*-BOC-protected diphenyl-α-oligopyrrole part (Ph–p_n–Ph), while the second one, situated at ~365 nm, was attributed to be the charge-transfer transition. Although the positions of both absorption maxima hardly shift going from small to larger oligomers, nonlinear optical measurements (obtained by hyper-Rayleigh scattering) do show a dramatic increase for the β values up to the trimer (82, 177, and 277 × 10^{-30} esu, respectively). These observations are explained by the assumption that it is not just the charge-transfer transition that determines the value of the hyperpolarizability, but that lower transitions (i.e., π–π* transition) also contribute significantly. The latter was checked by studying another D–π–*A* system, containing a bithienyl spacer between 2-(4-nitrophenyl)-5-pyrrolyl and a 2-(4-meth-

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(40) 2-(4-Methoxyphenyl)-5-(4-nitrophenyl)thiophene was kindly provided by W. ten Hoeve (Syncom, Groningen, The Netherlands).

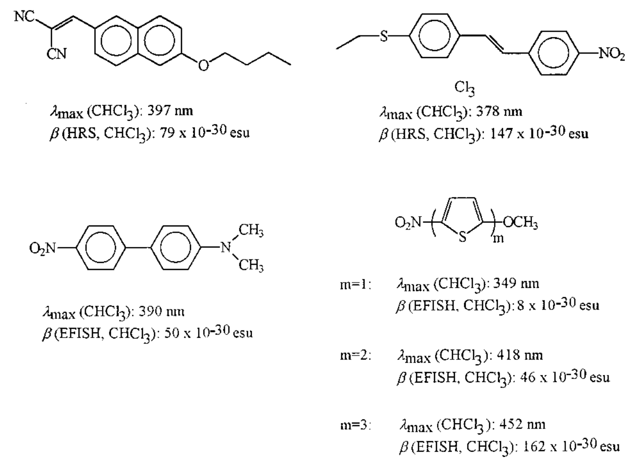

Figure 5. Some other NLO compounds with their specific (nonlinear) optical properties.[41]

oxy-phenyl)-5-pyrrolyl termini. This molecule showed only one absorption band at 378 nm with a high extrinction coefficient, indicating that the $\pi-\pi^*$ transition has shifted underneath the charge-transfer transition, while the β value was much higher (440×10^{-30} esu). If one compares this β value with that of other NLO molecules with similar linear optical properties, it appears that the β-value of this mixed system is significantly higher (Figure 5).[41] Furthermore, comparison with the D−π−*A* oligothiophenes as prepared by Effenberger *et al.*[29] shows large differences.

Some thermally deprotected D−π−*A* oligomers were also investigated. This resulted in substantial red shifts for both absorption maxima, while the β values increased dramatically. The latter is explained by increased π-conjugation and large resonance enhancement due to significant absorption at 532 nm.

Experimental Section

Materials. All materials and solvents were of p.a. quality and used as received. THF was distilled over sodium/benzophenone. For column chromatography Merck silica gel 60 (particle size 0.063−0.200 mm) and Merck aluminum oxide 90 (neutral; activity I) were used. The latter was deactivated before use by adding 7 wt % of distilled water. *N-t*-BOC-2-trimethylstannylpyrrole was prepared following literature procedures.[38] All deprotected oligomers were constantly kept under vigorously inert conditions.

Analyses and Spectroscopic Measurements. NMR spectra were run on a Bruker AM-400 spectrometer at frequencies of 400.1 and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively, with tetramethylsilane (TMS) as an internal standard. UV−vis spectra were taken on a Perkin-Elmer Lambda 3B UV−vis spectrophotometer with wavelengths between 190 and 900 nm. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer with wavenumbers between 4400 and 450 cm^{-1}. Mass data were obtained by high-resolution mass spectroscopy (HR-MS; measurements were performed at the University of Wageningen (The Netherlands)), or by field desorption mass spectroscopy (FD-MS; measurements were performed at the Max Planck Institute for Polymer Research in Mainz (Germany)). Hyper-Rayleigh scattering measurements were performed using a Nd:YAG laser (Spectra-Physics, DCR-3, 10 Hz) resulting in infrared laser pulses (1064 nm, 8 ns, 3−4 mJ).

***N-tert*-Butoxycarbonyl-2-(4-nitrophenyl)pyrrole (1).** A mixture of *N-t*-BOC-2-trimethylstannylpyrrole (9.03 g, 27.4 mmol), 1-bromo-4-nitrobenzene (5.24 g, 25.9 mmol), toluene (40 mL), and aqueous Na_2CO_3 (1 M, 40 mL) was deaerated and stored under argon. $Pd(PPh_3)_4$ (0.48 g, 0.42 mmol) was added and the reaction mixture was heated under reflux for 2 days. After this period, water and Et_2O (both 100 mL) were added. The two phases were separated and the aqueous phase was extracted twice with Et_2O (100 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and concentrated. The remaining dark solid was then recrystallized (hexane:CH_2Cl_2 (3:1)). The residue, remaining after evaporation of the filtrate, was purified by column chromatography (250 g of SiO_2, CH_2Cl_2:hexane (2:1), $R_f = 0.56$) and recrystallized. Both fractions gave **1** as a yellow solid (4.27 g, 14.8 mmol, 53%). Mp 120−121 °C. ^{1}H NMR ($CDCl_3$) δ 8.22 (d, J = 9.0 Hz, 2H, H-*meta*), 7.51 (d, J = 9.0 Hz, 2H, H-*ortho*), 7.41 (dd, J = 3.3 and 1.8 Hz, 1H, H-5), 6.32 (dd, J = 3.3 and 1.8 Hz, 1H, H-3), 6.28 (t, J = 3.3 Hz, 1H, H-4), 1.44 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 148.8 (C=O), 146.5 (C−NO_2), 140.6 (C-*ipso* (phenyl), 132.7 (C-2), 129.5 (C-*meta*), 124.3 (C-5), 122.9 (C-*ortho*), 116.5 (C-3), 111.1 (C-4), 84.4 (C-q (BOC)), 27.6 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 245 (1.02×10^4) and 345 (1.03×10^4) nm. IR (KBr) 3147, 2982, 2937, 1743, 1598, 1508, 1341, 1307, 1145, 976, 854, 772, 758 cm^{-1}.

1H. Thermal deprotection of the *t*-BOC groups was performed by heating neat **1** for 20−30 min at 190 °C under inert atmosphere. UV−vis ($CHCl_3$) 250 and 374 nm.

***N-tert*-Butoxycarbonyl-2-bromo-5-(4-nitrophenyl)pyrrole (2).** A mixture of *N-tert*-butoxycarbonyl-2-(4-nitrophenyl)pyrrole (**1**, 0.557 g, 1.93 mmol) and THF (20 mL) was cooled to −70 °C, blanketed by argon. *N*-Bromosuccinimide (NBS, 0.345 g, 1.94 mmol) was added, after which the mixture was stirred at −70 °C for 20 min. After this period it was allowed to warm to 3 °C at which temperature it was kept for another 18 h. Na_2SO_3 (0.5 g) was added, the mixture was stirred for 10 min and the solvent was evaporated. CCl_4 (40 mL) was added, the mixture was stirred for 5 min, filtered, and concentrated. A yellow solid remained, being pure **2** (0.700 g, 1.91 mmol, 99%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H, H-*meta*), 7.45 (d, J = 8.96 Hz, 2H, H-*ortho*), 6.37 (d, J = 3.6 Hz, 1H, H-3/H-4), 6.33 (d, J = 3.6 Hz, 1H, H-3/H-4), 1.43 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 148.0 (C=O), 146.5 (C−NO_2), 140.0 (C-*ipso* (phenyl)), 134.3 (C-5), 128.1 (C-*meta*), 123.4 (C-*ortho*), 115.6/114.9 (C-3/C-4), 104.6 (C-2), 86.0 (C-q (BOC)), 27.4 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 248 and 349 nm.

***N,N′*-Di-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2′-bipyrrole (3).** A Stille reaction between *N-t*-BOC-2-trimethylstannylpyrrole (2.06 g, 6.24 mmol) and **2** (2.28 g, 6.21 mmol) in toluene (10 mL) and aqueous Na_2CO_3 (1 M, 10 mL) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) was performed as described for **1**. After workup procedures a dark green liquid remained, which was purified by column chromatography (200 g of SiO_2, CH_2Cl_2:hexane (1:1), R_f = 0.12). Subsequent recrystallization from a mixture of CH_2Cl_2 and hexane gave **3** as a yellow solid (1.49 g, 3.29 mmol, 53%). Mp 122 °C. ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 9.0 Hz, 2H, H-*meta*), 7.48 (d, J = 8.8 Hz, 2H, H-*ortho*), 7.43 (dd, J = 3.3 and 1.9 Hz, 1H, H-5′), 6.36 (d, J = 3.4 Hz, 1H, H-4), 6.28−6.23 (m, 3H, H-3, H-3′, H-4′), 1.40 (s, 9H, H-methyl (BOC′)), 1.24 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 149.1 (C=O), 148.9 (C=O), 146.3 (C−NO_2), 140.8 (C-*ipso* (phenyl)), 134.1 (C-5), 129.8/125.3 (C-2/C-2′), 128.6 (C-*meta*), 123.2 (C-*ortho*), 122.2 (C-5′), 116.2/114.7/114.5/110.5 (C-3/C-4/C-3′/C-4′), 84.0 (C-q (BOC)), 83.6 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.3 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 255 (1.20×10^4) and 364 (1.28×10^4) nm. IR (KBr) 2986, 2936, 1750, 1596, 1515, 1333, 1312, 1259, 1155, 1110, 970, 852, 794, 733 cm^{-1}.

3H. Thermal deprotection of the *t*-BOC groups was performed as described for 1H. UV−vis ($CHCl_3$) 292 and 451 nm.

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(41) The naphthalene and stilbene derivatives (top of Figure 5) are unpublished results from the University of Leuven, which were measured with the same equipment and under the same conditions as the compounds described here. The biphenyl and oligothiophene derivatives (bottom of Figure 5) are examples from the literature which were measured with EFISH, refs 7 and 29, respectively.

***N,N*′-Di-*tert*-butoxycarbonyl-5′-bromo-5-(4-nitrophenyl)-2,2′-bipyrrole (4).** The bromination of **3** (0.252 g, 0.56 mmol) in THF (5 mL) with NBS (0.1033 g, 0.580 mmol) was performed as described for **2**. This finally resulted in pure **4** as a slightly red oil (0.295 g, 0.554 mmol, 99%). ^{1}H NMR ($CDCl_3$) δ 8.24 (d, $J = 8.9$ Hz, 2H, H-*meta*), 7.48 (d, $J = 8.8$ Hz, 2H, H-*ortho*), 6.37 ($2 \times$ d, $J = 3.6$ Hz, $2 \times$ 1H, H-4, H-4′), 6.25−6.22 (2 x d, $J = 3.5$ Hz, $2 \times$ 1H, H-3, H-3′), 1.41 (H-methyl (BOC′), 1.27 (H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 148.9 (C=O), 148.0 (C=O), 146.4 (C−NO_2), 140.6 (C-*ipso* (phenyl)), 134.5−127.7 (C-2, C-5, C-2′), 128.6 (C-*meta*), 123.3 (C-*ortho*), 115.7/115.6/115.0/114.8 (C-3/C-4/C-3′/C-4′), 102.6 (C-5′), 84.8 (C-q (BOC)), 84.7 (C-q (BOC)), 27.6 (C-methyl (BOC)), 27.4 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 255 and 358 nm.

***N,N*′*,N*″-Tri-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2′:5′,2″-terpyrrole (5).** A Stille reaction between *N*-*t*-BOC-2-trimethylstannylpyrrole (0.7187 g, 2.18 mmol) and **4** (1.154 g, 2.17 mmol) in toluene (3.5 mL) and aqueous Na_2CO_3 (1 M, 3.5 mL) in the presence of $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), was performed as described for **1**. The remaining dark liquid was purified by column chromatography (150 g of SiO_2, CH_2Cl_2:hexane (1:1), $R_f = 0.10$), which gave **5** as a reddish oil (0.322 g, 0.52 mmol, 24%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $J = 8.9$ Hz, 2H, H-*meta*), 7.49 (d, $J = 9.0$ Hz, 2H, H-*ortho*), 7.43 (dd, $J =$ 3.4 and 1.9 Hz, 1H, H-5″), 6.39 (d, $J = 3.4$ Hz, 1H, H-4), 6.26−6.19 (m, 4H, H-3, H-3′, H-4′, H-4″), 6.17 (dd, $J =$ 3.5 and 1.9 Hz, 1H, H-3″), 1.41 (s, 9H, H-methyl (BOC″)), 1.27 (s, 9H, H-methyl (BOC)), 1.26 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 149.0 (C=O), 148.9 (C=O), 148.8 (C=O), 146.2 (C−NO_2), 140.8 (C-*ipso* (phenyl)), 134.3/130.7/127.9/127.0/126.2 (C-2/C-5/C-2′/C-5′/C-2″), 128.5 (C-*meta*), 123.2 (C-*ortho*), 121.9 (C-5″), 115.4/115.1/114.3/113.8/110.3 (C-3/C-4/C-3′/C-4′/C-3″/C-4″), 84.3 (C-q (BOC)), 83.3 (C-q (BOC)), 82.9 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.5 (C-methyl (BOC)), 27.4 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 283 and 366 nm.

***N,N*′*,N*″-Tri-*tert*-butoxycarbonyl-5″-bromo-5-(4-nitrophenyl)-2,2′:5′,2″-terpyrrole (6).** The bromination of **5** (0.327 g, 0.527 mmol) in THF (5 mL) with NBS (0.0949 g, 0.533 mmol) was performed as described for **2**. This finally resulted in pure **6** as a red oil (0.320 g, 0.516 mmol, 98%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $J = 8.9$ Hz, 2H, H-*meta*), 7.50 (d, $J = 8.9$ Hz, 2H, H-*ortho*), 6.38 (d, $J = 3.4$ Hz, 1H, H-4/H-4″), 6.34 (d, $J = 3.4$ Hz, 1H, H-4/H-4″), 6.25−6.13 ($4 \times$ d, $J = 3.4$ Hz, $4 \times$ 1H, H-3, H-3′, H-3″, H-4′), 1.39 (s, 9H, H-methyl (BOC″)), 1.29 (H-methyl (BOC)), 1.25 (H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 148.9 (C=O), 148.7 (C=O), 148.1 (C=O), 146.3 (C−NO_2), 140.9 (C-*ipso* (phenyl)), 134.4/130.4/128.7/127.8/127.4 (C-2/C-5/C-2′/C-5′/C-2″), 128.6 (C-*meta*), 123.2 (C-*ortho*), 115.7/115.1/114.9/114.5/114.4/114.3 (C-3/C-4/C-3′/C-4′/C-3″/C-4″), 102.2 (C-5″), 84.6 (C-q (BOC)), 84.2 (C-q (BOC)), 83.6 (C-q (BOC)), 27.9 (C-methyl (BOC)), 27.7 (C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 283 and 361 nm.

***N,N*′*,N*″*,N*‴-Tetra-*tert*-butoxycarbonyl-5-(4-nitrophenyl)-2,2′:5′,2″:5″,2‴-quaterpyrrole (7).** A Stille reaction between *N*-*t*-BOC-2-trimethylstannylpyrrole (0.038 g, 0.115 mmol) and **6** (0.058 g, 0.083 mmol) in toluene (0.5 mL) and aqueous Na_2CO_3 (1 M, 0.5 mL) in the presence of $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) was performed as described for **1**. The remaining dark liquid was purified by column chromatography (6 g SiO_2, CH_2Cl_2:hexane (3:1), $R_f = 0.12$) yielding **7** as a red oil (31.6 mg, 0.040 mmol, 48%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $J = 8.9$ Hz, 2H, H-*meta*), 7.50 (d, $J = 8.9$ Hz, 2H, H-*ortho*), 7.40 (dd, $J =$ 3.2 and 1.9 Hz, 1H, H-5‴), 6.39 (d, $J = 3.5$ Hz, 1H, H-4), 6.27−6.16 (m, 7H, H-3, H-3′, H-3″, H-3‴, H-4′, H-4″, H-4‴), 1.41 (s, 9H, H-methyl (BOC‴)), 1.32 (s, 9H, H-methyl (BOC)), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 149.0 ($2 \times$ C=O), 148.9 (C=O), 148.8 (C=O), 146.3 (C−NO_2), 141.1 (C-*ipso* (phenyl)), 134.2/130.8/127.9/127.7/127.0/126.6 (C-2/C-5/C-2′/C-5′/C-2″/C-5″/C-2‴), 128.6 (C-*meta*), 123.2 (C-*ortho*), 121.9 (C-5‴), 115.4/115.2/114.5/114.5/113.9/110.2 (C-3/C-4/C-3′/C-4′/C-3″/C-4″/C-3‴/C-4‴), 84.2 (C-q (BOC)), 83.1 (C-q (BOC)), 82.7 ($2 \times$ C-q (BOC)), 27.8 (C-methyl (BOC)), 27.7 ($2 \times$ C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm.

***N,N*′*,N*″*,N*‴-Tetra-*tert*-butoxycarbonyl-5‴-bromo-5-(4-nitrophenyl)-2,2′:5′,2″:5″,2‴-quaterpyrrole (8).** The bromination of **7** (31.6 mg, 0.0403 mmol) in THF (3 mL) with NBS (7.2 mg, 0.0405 mmol) was performed as described for **2**. This finally gave pure **8** as a red oil (32.0 g, 0.037 mmol, 92%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $J = 8.8$ Hz, 2H, H-*meta*), 7.50 (d, $J = 8.8$ Hz, 2H, H-*ortho*), 6.38 (d, $J = 3.5$ Hz, 1H, H-4/H-4‴), 6.33 (d, $J = 3.6$ Hz, 1H, H-4/H-4‴), 6.28−6.14 (m, 6H, H-3, H-3′, H-3″, H-3‴, H-4′, H-4″), 1.40 (s, 9H, H-methyl (BOC‴)), 1.28 (s, 9H, H-methyl (BOC)), 1.27 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 149.0 (C=O), 148.8 (C=O), 148.6 (C=O), 148.2 (C=O), 146.3 (C−NO_2), 141.0 (C-*ipso* (phenyl)), 134.2/130.7/128.8/128.3/128.2/127.4/127.0 (C-2/C-5/C-2′/C-5′/C-2″/C-5″/C-2‴), 128.6 (C-*meta*), 123.2 (C-*ortho*), 115.6/115.1/114.8/114.6/114.5/114.3/114.0 (C-3/C-4/C-3′/C-4′/C-3″/C-4″/C-3‴/C-4‴), 102.1 (C-5‴), 84.4 (C-q (BOC)), 84.2 (C-q (BOC)), 83.4 (C-q (BOC)), 83.1 (C-q (BOC)), 27.7 (C-methyl (BOC)), 27.6 ($2 \times$ C-methyl (BOC)), 27.5 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 290 and 362 nm.

4-Trimethylstannylanisole (9). A two-necked flask containing 4-bromoanisole (0.561 g, 3.00 mmol) and THF (8 mL) was cooled to −70 °C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) was added over a 10 min period, after which the mixture was stirred at −70 °C for 1 h. Then a solution of trimethylstannyl chloride (0.63 g, 3.16 mmol) in THF (2 mL) was added, and the mixture was stirred at −70 °C for another 4 h. After this period the mixture was allowed to warm to room temperature. After 16 h at room temperature it was poured into water (15 mL) and extracted with Et_2O (3×10 mL). The combined organic fractions were dried ($MgSO_4$), filtered and concentrated resulting in **9** as a colorless liquid (0.80 g, 3.0 mmol, 98%). ^{1}H NMR ($CDCl_3$) δ 7.40 (d, $J = 8.5$ Hz, 2H, H-3), 6.91 (d, $J = 8.6$ Hz, 2H, H-2), 3.77 (s, 3H, H-methoxy), 0.27 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C NMR ($CDCl_3$) δ 159.8 (C-1), 137.3 (C-4), 137.0 (C-3), 113.9 (C-2), 54.9 (C-methoxy), −9.5 (C-methyl (stannyl)) ppm. IR (KBr) 2977, 2910, 2835, 1588, 1566, 1496, 1459, 1277, 1243, 1181, 1076, 1033, 809, 769, 528 cm^{-1}.

***N-tert*-Butoxycarbonyl-2-(4-methoxyphenyl)-5-(4-nitrophenyl)pyrrole (10).** A Stille reaction between **2** (0.94 g, 1.93 mmol) and **9** (0.565 g, 2.08 mmol) in toluene (5 mL) and aqueous Na_2CO_3 (1 M, 5 mL) in the presence of $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) was performed as described for **1**. This resulted in a red oil, which was purified by column chromatography (70 g of SiO_2, CH_2Cl_2:hexane (1:1), $R_f = 0.15$) and subsequent recrystallization (mixture of CH_2Cl_2 and hexane) to give **10** as a yellow solid (0.359 g, 0.910 mmol, 47%). ^{1}H NMR ($CDCl_3$) δ 8.24 (d, $J = 8.9$ Hz, 2H, H-*meta* (Ph−NO_2)), 7.54 (d, $J = 8.9$ Hz, 2H, H-*ortho* (Ph−NO_2)), 7.33 (d, $J = 8.8$ Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.94 (d, $J = 8.8$ Hz, 2H, H-*meta* (Ph−OCH_3)), 6.39 (d, $J = 3.4$ Hz, 1H, H-4), 6.22 (d, $J = 3.5$ Hz, 1H, H-3), 3.85 (s, 3H, H-methoxy), 1.21 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 159.3 (*C*-OCH_3), 149.5 (C=O), 146.2 (C−NO_2), 140.5 (C-*ipso* (Ph-NO_2)), 138.3/133.5 (C-2/C-5), 130.3 (C-*ortho* (Ph-OCH_3)), 128.5 (C-*meta* (Ph-NO_2)), 125.9 (C-*ipso* (Ph−OCH_3), 123.2 (C-*ortho* (Ph−NO_2)), 114.6 (C-4), 113.2 (C-*meta* (Ph−OCH_3)), 112.4 (C-3), 84.0 (C-q (BOC)), 55.2 (OCH_3), 27.1 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 269 (1.42×10^4) and 376 (1.29×10^4) nm. IR (KBr) 2979, 2938, 1739, 1597, 1514, 1496, 1340, 1305, 1243, 1175, 1143, 1109, 978, 850, 802, 749 cm^{-1}. HR-MS: mass calcd 394.1529; mass found 394.1525. GC-MS 394 (M^+), 338, 295, 294, 293, 279, 277, 57.

10H. Thermal deprotection of the *t*-BOC groups was performed as described for **1H**. ^{1}H NMR (THF-d_8) δ 10.63 (s, 1H, N−H), 8.19 (d, $J = 9.0$ Hz, 2H, H-*meta* (Ph−NO_2)), 7.81 (d, $J = 9.1$ Hz, 2H, H-*ortho* (Ph−NO_2)), 7.60 (d, $J = 9.0$ Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.95 (d, $J = 9.0$ Hz, 2H, H-*meta* (Ph−OCH_3)), 6.83 (dd, $J =$ 3.9 and 2.5 Hz, 1H, H-4), 6.50 (dd, $J =$ 3.8 and 2.5 Hz, 1H, H-3), 3.79 (s, 3H, H-methoxy) ppm. UV−vis ($CHCl_3$) 295 and 431 nm.

***N,N*′-Di-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5′-(4-nitrophenyl)-2,2′-bipyrrole (11).** A Stille reaction between **4** (0.266 g, 0.500 mmol) and **9** (0.148 g, 0.55 mmol) in toluene (3 mL) and aqueous Na_2CO_3 (1 M, 3 mL) in the presence of $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) was performed as described for **1**. This resulted in a dark liquid, which was purified by column chromatography (25 g of SiO_2, CH_2Cl_2:hexane (1:2), $R_f = 0.02$). Subsequent recrystallization from a mixture of CH_2Cl_2 and hexane, finally gave **11** as a yellow solid (0.102 g, 0.211 mmol, 42%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 8.9 Hz, 2H, H-*meta* (Ph−NO_2)), 7.50 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph−NO_2)), 7.29 (d, J = 8.7 Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.92 (d, J = 8.7 Hz, 2H, H-*meta* (Ph−OCH_3)), 6.41 (d, J = 3.4 Hz, 1H, H-4′), 6.32 (d, J = 3.4 Hz, 1H, H-3/H-3′), 6.26 (d, J = 3.4 Hz, 1H, H-3/H-3′), 6.19 (d, J = 3.4 Hz, 1H, H-4), 3.83 (s, 3H, H-methoxy), 1.32 (s, 9H, H-methyl (BOC)), 1.26 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 158.8 (*C*−OCH_3), 149.2 (C=O), 149.1 (C=O), 146.3 (C−NO_2), 140.8 (C-*ipso* (Ph−NO_2)), 136.6/134.3/130.3/126.9 (C-2/C-5/C-2′/C-5′), 129.6 (C-*ortho* (Ph−OCH_3)), 128.5 (C-*meta* (Ph−NO_2)), 126.8 (C-*ipso* (Ph−OCH_3)), 123.2 (C-*ortho* (Ph−NO_2)), 115.0/114.6/113.3/112.2 (C-3/C-4/C-3′/C-4′), 113.3 (C-*meta* (Ph−OCH_3)), 84.2 (C-q (BOC)), 83.4 (C-q (BOC)), 55.2 (OCH_3), 27.4 (C-methyl (BOC)), 27.3 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 286 (1.66×10^4) and 366 (1.36×10^4) nm. IR (KBr) 2980, 2934, 1745, 1597, 1515, 1369, 1344, 1307, 1248, 1152, 1032, 971, 850, 794, 750 cm^{-1}. HR-MS: mass calcd 559.2319; mass found 559.2319.

11H. Thermal deprotection of the *t*-BOC groups was performed as described for **1H**. ^{1}H NMR (THF-d_8) δ 10.61 (s, 1H, N−H′), 10.32 (s, 1H, N−H), 8.17 (d, J = 8.8 Hz, 2H, H-*meta* (Ph−NO_2)), 7.74 (d, J = 8.3 Hz, 2H, H-*ortho* (Ph−NO_2)), 7.51 (d, J = 8.4 Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.90 (d, J = 9.0 Hz, 2H, H-*meta* (Ph−OCH_3)), 6.81 (br s, 1H, H-4′), 6.45 (br s, 2H, H-3, H-3′), 6.39 (br s, 1H, H-4), 3.78 (s, 3H, H-methoxy) ppm. UV−vis ($CHCl_3$) 328 and 479 nm

***N*,*N*′,*N*″-Tri-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5″-(4-nitrophenyl)-2,2′:5′,2″-terpyrrole (12).** A Stille reaction between **6** (0.302 g, 0.432 mmol) and **9** (0.133 g, 0.491 mmol) in toluene (2 mL) and aqueous Na_2CO_3 (1 M, 2 mL) in the presence of $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), was performed as described for **1**. This resulted in a dark liquid, which was purified by column chromatography (15 g of SiO_2, CH_2Cl_2:hexane (1:1), $R_f = 0.06$), giving pure **12** as an oil (0.063 g, 0.087 mmol, 20%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H, H-*meta* (Ph−NO_2)), 7.51 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph−NO_2)), 7.29 (d, J = 8.9 Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.92 (d, J = 8.8 Hz, 2H, H-*meta* (Ph−OCH_3)), 6.39 (d, J = 3.5 Hz, 1H, H-4″), 6.27−6.18 (m, 5H, H-3, H-3′, H-3″, H-4, H-4′), 3.86 (s, 3H, H-methoxy), 1.33 (s, 9H, H-methyl (BOC)), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 158.7 (*C*−OCH_3), 149.3 (C=O), 149.0 (C=O), 148.9 (C=O), 146.3 (C−NO_2), 141.0 (C-*ipso* (Ph−NO_2)), 136.4/134.3/130.7/128.3/127.8/127.1 (C-*ipso* (Ph−OCH_3)/C-2/C-5/C-2′/C-5′/C-2″/C-5″), 129.5 (C-*ortho* (Ph−OCH_3)), 128.6 (C-*meta* (Ph−NO_2)), 123.2 (C-*ortho* (Ph−NO_2)), 115.2/114.4/114.4/114.3/113.9/112.3 (C-3/C-3′/C-3″/C-4/C-4′/C-4″), 113.3 (C-*meta* (Ph−OCH_3)), 84.2 (C-q (BOC)), 83.3 (C-q (BOC)), 83.1 (C-q (BOC)), 55.2 (OCH_3), 27.6 (C-methyl (BOC)), 27.5 (2 × C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 294 (1.84×10^4) and 364 (1.24×10^4) nm. IR (KBr) 2979, 1743, 1597, 1514, 1369, 1308, 1260, 1149, 1132, 1105, 1022, 849, 793 cm^{-1}. HR-MS: mass calcd 724.3108; mass found 724.3077.

12H. Thermal deprotection of the *t*-BOC groups was performed as described for **1H**. UV−vis ($CHCl_3$) 355 and 496 nm.

***N*,*N*′,*N*″,*N*‴-Tetra-*tert*-butoxycarbonyl-5-(4-methoxyphenyl)-5‴-(4-nitrophenyl)-2,2′:5′,2″:5″,2‴-quaterpyrrole (13).** A Stille reaction between **8** (33 mg, 0.038 mmol) and **9** (18.7 mg, 0.069 mmol) in toluene (1 mL) and aqueous Na_2CO_3 (1 M, 1 mL) in the presence of $Pd(PPh_3)_4$ (7.2 mg, 0.006 mmol), was performed as described for **1**. This resulted in a dark liquid, which was purified by column chromatography (6 g of SiO_2, CH_2Cl_2:hexane (3:1), $R_f = 0.33$) and gave pure **13** as an oil (8.6 mg, 0.010 mmol, 25%). ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J = 9.0 Hz, 2H, H-*meta* (Ph−NO_2)), 7.50 (d, J = 8.9 Hz, 2H, H-*ortho* (Ph−NO_2)), 7.28 (d, J = 8.8 Hz, 2H, H-*ortho* (Ph−OCH_3)), 6.91 (d, J = 8.8 Hz, 2H, H-*meta* (Ph−OCH_3)), 6.38 (d, J = 3.5 Hz, 1H, H-4‴), 6.28−6.16 (m, 7H, H-3, H-3′, H-3″, H-3‴, H-4, H-4′, H-4″), 3.86 (s, 3H, H-methoxy), 1.29 (s, 9H, H-methyl (BOC)), 1.28 (2 × s, 2 × 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 158.7 (*C*-OCH_3), 149.1 (2 × C=O), 148.8 (2 × C=O), 146.3 (C−NO_2), 141.1 (C-*ipso* (Ph−NO_2)), 136.3/134.2/130.8/128.1/128.0/127.2/127.0 (C-*ipso* (Ph-OCH_3)/C-2/C-5/C-2′/C-5′/C-2″/C-5″/C-2‴/C-5‴), 129.6 (C-*ortho* (Ph−OCH_3)), 128.6 (C-*meta* (Ph−NO_2)), 123.2 (C-*ortho*(Ph−NO_2)), 113.3 (C-*meta* (Ph−OCH_3)), 115.1/114.6/114.5/114.3/114.0/113.9/113.3/112.2 (C-3/C-4/C-3′/C-4′/C-3″/C-4″/C-3‴/C-4‴), 84.2 (C-q (BOC)), 83.2 (C-q (BOC)), 83.1 C-q (BOC)), 82.9 (C-q (BOC)), 55.2 (OCH_3), 27.7 (C-methyl (BOC)), 27.5 (C-methyl BOC)) ppm. UV−vis ($CHCl_3$) 297 and 363 nm. IR (KBr) 2963, 1738, 1598, 1515, 1395, 1369, 1311, 1260, 1092, 798, 698 cm^{-1}.

13H. Thermal deprotection of the *t*-BOC groups was performed as described for **1H**. UV−vis (CH_3CN) 360 and 474 nm.

***N*-*tert*-Butoxycarbonyl-2-(4-methoxyphenyl)pyrrole (14).** A Stille reaction between *N*-*t*-BOC-2-trimethylstannylpyrrole (0.60 g, 1.82 mmol) and 4-bromoanisole (0.34 g, 1.82 mmol) in toluene (5 mL) and aqueous Na_2CO_3 (1 M, 5 mL) in the presence of $Pd(PPh_3)_4$ (45 mg, 0.039 mmol) was performed as described for **1**. The resulting dark liquid was purified by column chromatography (25 g SiO_2, CH_2Cl_2:hexane (1:3), $R_f = 0.08$) giving **15** as a colorless oil (0.24 g, 0.88 mmol, 48%). ^{1}H NMR ($CDCl_3$) δ 7.32 (dd, J = 3.4 and 1.8 Hz, 1H, H-5), 7.27 (d, J = 8.8, 2H, H-*ortho*), 6.88 (d, J = 8.8 Hz, 2H, H-*meta*), 6.20 (t, J = 3.3 Hz, 1H, H-4), 6.13 (dd, J = 3.2 and 1.8 Hz, 1H, H-3), 3.82 (s, 3H, H-methoxy), 1.38 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR ($CDCl_3$) δ 158.8 (*C*−OCH_3), 149.4 (C=O), 134.8 (C-2), 130.3 (C-*ortho*), 126.8 (C-*ipso* (phenyl)), 122.1 (C-5), 113.9 (C-3), 113.0 (C-*meta*), 110.4 (C-4), 83.3 (C-q (BOC)), 55.2 (OCH_3), 27.6 (C-methyl (BOC)) ppm. UV−vis ($CHCl_3$) 275 (0.81×10^4) nm.

***N*-*tert*-Butoxycarbonyl-2-(4-methoxyphenyl)-5-trimethylstannylpyrrole (15).** A mixture of 2,2,6,6-tetramethylpiperidine (0.125 g, 0.887 mmol) in THF (3 mL) was cooled to −70 °C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 0.60 mL, 0.96 mmol) was slowly added, and the solution was stirred for 10 min at −70 °C. Then it was allowed to warm to 0 °C and again cooled to −70 °C. A mixture of **15** (0.222 g, 0.810 mmol) in THF (2 mL) was slowly added, and stirring was continued for 45 min at −70 °C. Then trimethylstannyl chloride (0.20 g, 1.00 mmol) in THF (1.5 mL) was slowly added, after which the mixture was stirred for 3 h at −70 °C and for another 16 h at room temperature. The solvent was evaporated and water (10 mL) was added. Extraction with Et_2O (3 × 10 mL) followed by drying ($MgSO_4$), filtration, and evaporation of the solvent finally resulted in pure **16** (0.339 g, 0.778 mmol, 96%). ^{1}H NMR ($CDCl_3$) δ 7.23 (d, J = 8.8 Hz, 2H, H-*ortho*), 6.87 (d, J = 8.8 Hz, 2H, H-*meta*), 6.37 (d, J = 3.1 Hz, 1H, H-4), 6.22 (d, J = 3.0 Hz, 1H, H-3), 3.82 (s, 3H, H-methoxy), 1.21 (s, 9H, H-methyl (BOC)), 0.27 (s, 9H, H-methyl (stannyl)) ppm. ^{13}C NMR ($CDCl_3$): δ 158.7 (*C*−OCH_3), 151.6 (C=O), 137.9/137.1 (C-2/C-5), 130.2 (C-*ortho*), 128.2 (C-*ipso* (phenyl)), 121.1 (C-4), 115.1 (C-3), 112.9 (C-*meta*), 83.2 (C-q (BOC)), 55.3 (OCH_3), 27.3 (C-methyl (BOC)), −7.5 (C-methyl (stannyl)) ppm.

5-Trimethylstannyl-2,2′-bithiophene (16). A solution of 2,2′-bithiophene (1.01 g, 6.02 mmol) in THF (15 mL) was cooled to 0 °C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 3.8 mL, 6.08 mmol) was slowly added, after which the mixture was stirred at room temperature for 1.5 h. Then it was cooled to −70 °C, and a solution of trimethylstannyl chloride (1.20 g, 6.02 mmol) in THF (5 mL) was slowly added. After this addition the mixture was stirred for 4 h at −70 °C and for another 12 h at room temperature. The dark mixture was concentrated, and water (30 mL) was added. After extraction with Et_2O (3 × 25 mL), the combined organic fractions were dried ($MgSO_4$). Filtration followed by evaporation of the solvent resulted in a dark oil. Purification by column chromatography (65 g Al_2O_3, hexane, $R_f = 0.34$) finally gave a colorless liquid (1.20 g, 3.65 mmol, 61%). ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 3.4 Hz, 1H, H-4), 7.16 (m, 2H, H-3′, H-5′), 7.07 (d, J = 3.3 Hz, 1H, H-3), 6.98 (dd, J = 3.5 and 1.9 Hz, 1H, H-4′), 0.37 (s, 9H, H-methyl (stannyl)) ppm. UV−vis (CHCl$_3$) 313 nm. IR (KBr) 3105−3050, 2981, 2913, 1413, 1195, 1050, 945, 796, 774, 692, 534 cm^{-1}.

***N-tert*-Butoxycarbonyl-2-(5-(2,2′-bithienyl))-5-(4-nitrophenyl)pyrrole (17).** A Stille reaction between **2** (0.735 g, 2.00 mmol) and **16** (0.675 g, 2.05 mmol) in toluene (5 mL) and aqueous Na$_2$CO$_3$ (1 M, 5 mL) in the presence of Pd(PPh$_3$)$_4$ (50 mg, 0.043 mmol) was performed as described for **1**. The resulting dark liquid was purified by column chromatography (60 g SiO$_2$, CH$_2$Cl$_2$:hexane (3:4), $R_f = 0.29$), which finally gave **17** as a red oil (0.497 g, 1.10 mmol, 55%). ^{1}H NMR (CDCl$_3$) δ 8.24 (d, $J = 8.9$ Hz, 2H, H-*meta*), 7.55 (d, $J = 8.9$ Hz, 2H, H-*ortho*), 7.24 (dd, $J = 5.1$ and 1.4 Hz, 1H, H-3′ (th)/H-5′ (th)), 7.20 (dd, $J = 5.1$ and 1.4 Hz, 1H, H-3′ (th)/H-5′ (th)), 7.13 (d, $J = 3.7$ Hz, 1H, H-3 (th)/H-4 (th)), 7.06 (d, $J = 3.7$ Hz, 1H, H-3 (th)/H-4 (th)), 7.03 (dd, $J = 5.0$ and 3.7 Hz, 1H, H-4′ (th)), 6.43 (d, $J = 3.5$ Hz, 1H, H-3 (pyr)/H-4 (pyr)), 6.40 (d, $J = 3.5$ Hz, 1H, H-3 (pyr)/H-4 (pyr)), 1.28 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR (CDCl$_3$) δ 149.1 (C═O), 146.4 (C−NO$_2$), 140.2 (C-*ipso* (phenyl)), 138.0, 136.9, 134.6, 132.5, 130.3, 128.7, 128.4 (C-*meta*), 127.8, 124.5, 123.7, 123.3, 123.3 (C-*ortho*), 114.7/114.6 (C-3/C-4), 85.2 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm. UV−vis (CHCl$_3$) 355 (1.69 × 10^4) nm.

***N-tert*-Butoxycarbonyl-2-(5′-bromo-5-(2,2′-bithienyl))-5-(4-nitrophenyl)pyrrole (18).** A solution of **17** (0.497 g, 1.10 mmol) in DMF (6 mL) was blanketed by argon. A solution of NBS (0.199 g, 1.12 mmol) in DMF (5 mL) was slowly added, and the mixture was stirred for 18 h at room temperature. Then the solution was poured into ice−water (30 mL) and extracted with Et$_2$O (3 × 25 mL). The combined organic fractions were dried (MgSO$_4$), filtered, and concentrated. Column chromatography (30 g SiO$_2$, CH$_2$Cl$_2$:hexane (1:1), $R_f = 0.40$) followed by recrystallization (hexane) finally gave **18** as an orange solid (0.251 g, 0.472 mmol, 43%). ^{1}H NMR (CDCl$_3$) δ 8.25 (d, $J = 8.8$ Hz, 2H, H-*meta*), 7.54 (d, $J = 8.9$ Hz, 2H, H-*ortho*), 7.06/6.99/6.93/6.93 (4 × d, $J = 3.8$ Hz, 4 × 1H, H-3/H-3′/H-4/H-4′ (th)), 6.42/6.39 (d, $J = 3.5$ Hz, 1H, H-3/H-4 (pyr)), 1.27 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR (CDCl$_3$) δ 149.0 (C═O), 146.5 (C−NO$_2$), 140.2 (C-*ipso* (phenyl)), 136.8, 134.7, 133.1, 130.6, 130.0, 128.9, 128.7, 128.5 (C-*meta*), 123.8, 123.6, 123.3 (C-*ortho*), 114.9/114.6 (C-3/C-4), 111.1 (C−Br), 85.3 (C-q (BOC)), 27.2 (C-methyl (BOC)) ppm.

5-{*N-t*-BOC-2-[5-(4-methoxyphenyl)]pyrrolyl}-5′-{*N-t*-BOC-2-[5-(4-nitrophenyl)]pyrrolyl}-2,2′-bithiophene (19). A Stille reaction between **16** (0.251 g, 0.472 mmol) and **18** (0.223 g, 0.512 mmol) in toluene (7 mL) and aqueous Na$_2$CO$_3$ (1 M, 7 mL) in the presence of Pd(PPh$_3$)$_4$ (55 mg, 0.048 mmol) was performed as described for **1**. The resulting dark liquid was purified by column chromatography (40 g SiO$_2$, CH$_2$Cl$_2$:hexane (1:1), $R_f = 0.16$). Subsequent recrystallization (hexane:CH$_2$Cl$_2$ (9:1)) gave **19** as an orange solid (0.116 g, 0.16 mmol, 34%). ^{1}H NMR (CDCl$_3$) δ 8.26 (d, $J = 8.8$ Hz, 2H, H-*meta* (Ph-NO$_2$)), 7.54 (d, $J = 9.0$ Hz, 2H, H-*ortho* (Ph-NO$_2$)), 7.32 (d, $J = 8.8$ Hz, 2H, H-*ortho* (Ph−OCH$_3$)), 7.13−7.02 (4 × d, $J = 3.7$ Hz, 4 × 1H, H-3, H-3′, H-4, H-4′ (th)), 6.90 (d, $J = 8.8$ Hz, 2H, H-*meta* (Ph−OCH$_3$)), 6.43−6.38 (3 × d, $J = 3.4$ Hz, 1H, H-3″, H-3‴, H-4‴ (pyr)), 6.19 (d, $J = 3.4$ Hz, 1H, H-4″ (pyr)), 3.86 (s, 3H, H-methoxy), 1.29 (s, 9H, H-methyl (BOC)), 1.25 (s, 9H, H-methyl (BOC)) ppm. ^{13}C NMR (CDCl$_3$) δ 159.1 (*C*-OCH$_3$), 149.7 (C═O), 149.2 (C═O), 146.5 (C−NO$_2$), 140.3 (C-*ipso* (Ph−NO$_2$)), 138.0, 136.9, 136.7, 134.7, 134.1, 132.5, 130.3, 129.8, 128.8, 128.5, 127.7, 127.6, 126.5, 123.5, 123.4, 123.2, 114.8, 114.6, 114.1, 113.4, 111.8, 85.4 (C-q (BOC)), 84.3 (C-q (BOC)), 55.3 (OCH$_3$), 27.3 (C-methyl (BOC)), 27.2 (C-methyl (BOC)) ppm. UV−vis (CHCl$_3$) 378 nm (3.10 × 10^4). IR (KBr) 2977, 1749, 1596, 1515, 1498, 1369, 1341, 1299, 1248, 1177, 1141, 1110, 1033, 842 cm^{-1}. Anal. Calcd N 5.81, C 64.71, H 5.15. Found: N 5.49, C 64.89, H 5.13. FD-MS calcd 723.87; found 723.4.

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