Novel bis(tetrahydropyrrolo[3,4-*b*]carbazoles) linked with aliphatic chains: synthesis and structural aspects

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Syntheses of novel bis(tetrahydropyrrolo[3,4-*b*]carbazoles) by a [4+2]cycloaddition reaction are described. By variation of dienophiles bis(tetrahydropyrrolo[3,4-*b*]carbazoles) of varying aliphatic spacer length could be obtained in high yields. These conformationally highly flexible molecules represent an interesting class of compounds, believed to have an affinity towards DNA, as potential DNA ligands.

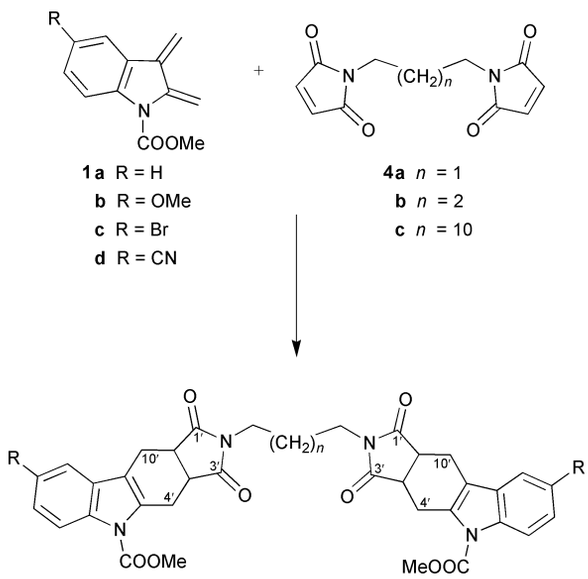
Introduction

Over the past decades many biologically active carbazole alkaloids have been obtained from terrestrial plants, marine sources, and streptomycetes.[1] Their isolation induced the development of novel strategies for the total synthesis of structurally unprecedented carbazole derivatives.[2] Often heterocyclic annelated carbazoles are of special pharmacological interest. The biological activity of such heterocyclic annelated carbazoles is mostly based on their special affinity to DNA. Therefore these compounds play a crucial role as potential leads for the discovery of antitumor active drugs.[3–5] Moreover, carbazole systems have been used as multifunctional material in supramolecular[6] and polymer chemistry (for example poly-*N*-vinylcarbazoles)[7] in the field of material science.

Thus on account of the growing importance of carbazole chemistry in the last year we have developed several synthetic concepts for a variety of carbazoles. On the basis of our investigations of pericyclic reactions giving rise to carbazole derivatives and carbazole alkaloids,[8–11] the Diels–Alder reaction of appropriate indole-2,3-quinodimethanes with the respective dienophiles has been established as a reliable synthetic method for special diaryl-linked bis(pyrrolo[3,4-*b*]carbazoles) as potential DNA ligands.[11] With the great structural varieties of DNA-ligands reported in the literature (ref. 5 and 13), the incorporation of a longer aliphatic chain between two carbazole moieties should give rise to the possibility of an orientated intercalative adaptation of chromophores towards the DNA. Additionally the aliphatic linker can interact with the grooves of the DNA by hydrophobic van der Waals, interactions.

The bis(tetrahydropyrrolo[3,4-*b*]carbazoles) and also the mono(tetrahydropyrrolo[3,4-*b*]carbazoles) could play an important role as potential DNA-ligands.

Synthetic developments and the structural chemistry of biscarbazoles linked generally with different types of spacers is rarely studied in the literature.[12,13] Thus, in continuation of our developments in pericyclic anellation reactions with indole derivatives,[8] we report here an access to a variety of new conformatively flexible mono- and bis-carbazoles linked with aliphatic chains of different length (Scheme 1). The starting compounds with twelve methylene groups have the same spacer length as Ditercalinium, which shows pronounced antitumor activity in procaryotes as well as in eucaryotes, and also Flexi-Di, which is only active in procaryotes.[15] We have varied the spacer length to four and three methylene groups and we have also varied the carbazole nucleus (Scheme 1), in order to establish approximate structure–affinity studies on DNA binding.



Scheme 1

Results and discussion

Synthetic aspects

The tetrahydropyrrolo[3,4-*b*]carbazoles **5a**–**l** were directly synthesised by a Diels–Alder reaction. The *N*-substituted indole-2,3-quinodimethanes **1a-d** were used as dienes and were readily generated *in situ* from their respective *N*-substituted 2,3-bis(bromomethylene)indoles **2** in the presence of sodium iodide[14] (Scheme 2). The *N*-substituted 2,3-bis(bromomethylene)indoles themselves were produced from their respective *N*-substituted 2,3-dimethylindoles **3** in the presence of *N*-bromosuccinimide (NBS). The bismaleimides **4a**–**c** were generated as described in ref. 19.

Finally, compounds **2a**–**d** and the dienophiles **4a**–**c** were added in a molar ratio 2 : 1 to give rise to the double Diels–Alder adducts **5a**–**l** with two pyrrolo[3,4-*b*]anellated carbazole structures in 65–90% yield (Scheme 1). This reaction constitutes

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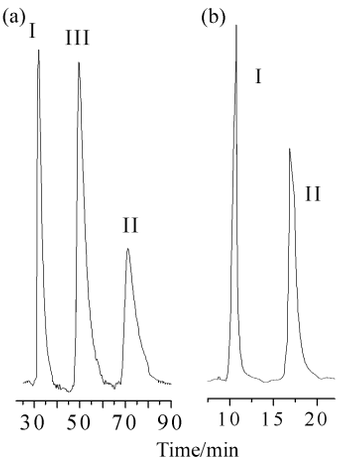
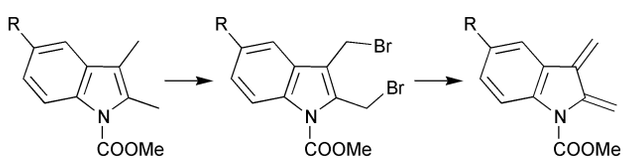
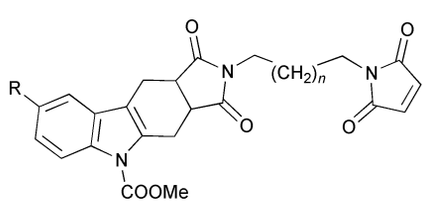


Fig. 1 HPLC-chromatograms of (a) compound **5i** and (b) **6a**. These chromatograms are representative of the bis(tetrahydropyrrolo-[3,4-*b*]carbazoles) **5**, as well as the mono(tetrahydropyrrolo[3,4-*b*]carbazoles) **6**. The only variable regarding the chromatograms is the retention time, but the order of the peaks remains the same. I, II: enantiomeric form, III: *meso*-form; column: (*S*,*S*)-Whelk O1, eluent: propan-2-ol–*n*-hexane (70 : 30), flow: 1.5 ml min^{-1}.



Scheme 2

a repetitive Diels–Alder reaction, since in several cases we were also able to isolate the mono-Diels–Alder products **6a**–**g**. These compounds could be also of interest as potential DNA-ligands.



In the double Diels–Alder products **5**, there are 4 stereocentres, which should lead theoretically to 16 different stereoisomeric species. However, we only obtained three different forms in all cases, since the Diels–Alder reaction itself is *cis*-selective. These three forms are a *meso*-form with C_S-symmetry and two diastereomeric forms with C_2-symmetry formed throughout in a ratio 2 : 1 : 1 (HPLC). The three stereoisomeric species of compounds **5** showed complete superposition of all NMR signals. A preparative separation of the isomers was not successful. The constitutional elucidation of compounds **5** and **6** was made by ^{1}H- and ^{13}C-NMR spectroscopy. The H,H-COSY as well the H,C-COSY spectroscopy were very useful in combination with several different NOE experiments.

However we were looking for a method to separate analytically the three stereoisomeric forms. This aim was finally achieved with chiral HPLC (Fig. 1).

With the HPLC-chromatograms we were able to show that the first and the third peaks represent the enantiomeric forms with C_2-symmetry, while the second peak represents the *meso*-form. Unfortunately, we have not yet been able to determine whether the first or the third peak (I, II) represents the (C-3a'-*R*, C-10a'-*S*)$_2$- or the (C-3a'-*S*, C-10a'-*R*)$_2$-form by analytical chiral HPLC.

The mono Diels–Alder educts **6a**–**g** exist as a racemate as expected. Hence, we obtained two different peaks in the chiral HPLC (Fig. 1b).

Conclusion

In summary, we have presented some new Diels–Alder adducts from the cycloaddition reactions of some indole-2,3-quinodimethanes with different bismaleimidoalkanes. The method described is useful for synthesis of a variety of selectively functionalized pyrrolo[3,4-*b*]anellated carbazoles with conformationally highly flexible linkers with potential antitumor activity in sufficiently high yields.

Experimental

General details

^{1}H- and ^{13}C-NMR spectra were recorded at room temperature on Bruker AC 300 spectrometers using Me_4Si as internal reference; *J* values are given in Hz. The EI (70 eV) mass spectra were recorded on a Varian MAT 311A spectrometer and FD mass spectra were measured on a Finnigan MAT95 spectrometer. Ionisation modes and ion fragment intensity percentages are indicated in parentheses. Elemental analyses were performed using a Heraeus CHN rapid apparatus. Melting points were determined in open capillaries with a Büchi melting point apparatus and are uncorrected. Column chromatography was performed on Merck 60 silica gel (particle size: 0.040–0.063 mm). HPLC was performed on a Merck Hitachi L-6200 instrument with a Whelk O1 (5 μm), 250 × 4 mm analytical column. Eluents are given in parentheses. All reactions were performed in highly pure, anhydrous solvents under argon atmosphere. The light petroleum used boiled in the range of 40–60 °C. *n*-Butyllithium is a 1.6 mol l^{-1} solution in *n*-hexane. The yields given refer to analytically pure compounds. The mono- and bis-carbazoles must be handled carefully because they can be carcinogenic and mutagenic

General procedure for the preparation of the compounds 3a–d

To a stirred solution of the appropriate 2,3-dimethylindole derivative (35 mmol) in Et_2O (200 ml) was added dropwise *n*-butyllithium (24.83 ml, 42 mmol) at 0 °C, followed by methyl chloroformate (3.26 ml, 42 mmol). After 1 h the mixture was poured into saturated aqueous $NaHCO_3$ (100 ml) and extracted with Et_2O (200 ml). The organic extract was dried (Na_2SO_4), and evaporated *in vacuo* to afford a dark brown oil. A further purification by recrystallisation from MeOH afforded **3a**–**d** in yellow crystals.

***N*-Methoxycarbonyl-2,3-dimethylindole 3a.** This compound was obtained from 2,3-dimethylindole[16] (5.08 g, 35 mmol). The crude product was purified by crystallisation from MeOH; yield 81% (5.76 g), mp 45–48 °C (from MeOH) (Found: C, 70.98; H, 6.42; N, 6.91. $C_{12}H_{13}NO_2$ requires C, 70.92; H, 6.48; N, 6.89%); δ_H (300 MHz, $CDCl_3$) 2.18 (s, 3H, CH_3, 1‴-H), 2.52 (s, 3H, CH_3, 1″-H), 4.01 (s, 3H, $COOCH_3$), 7.30 (m, 2H, CH, 5-H, 6-H), 7.42 (dd, 1H, *J* = 7.8, *J* = 3.9, CH, 4-H), 8.06 (dd, 1H, *J* = 8.2, *J* = 3.9, CH, 7-H); δ_C (75 MHz, $CDCl_3$) 8.7 (CH_3, C-1‴), 13.6 (CH_3, C-1″), 53.3 ($COOCH_3$), 114.5 (Cq), 115.4 (CH), 117.9 (CH), 122.7 (CH), 123.6 (CH), 131.1 (Cq), 132.8 (Cq), 135.5 (Cq), 152.9 (Cq, $COOCH_3$); *m*/*z* (EI) 202.9 ($M^{+\bullet}$, 18.75%), 144.0 (15.37), 143.0 (100), 87.0 (6.68), 69.0 (37.98).

***N*-Methoxycarbonyl-2,3-dimethyl-5-methoxyindole 3b.** This compound was obtained from 2,3-dimethyl-5-methoxyindole[17] (6.13 g, 35 mmol). The crude product was purified by crystallisation from MeOH; yield 76% (6.21 g), mp 62 °C (from MeOH) (Found: C, 67.01; H, 6.51; N, 6.02. $C_{13}H_{15}NO_3$ requires C, 66.94; H, 6.48; N, 6.00%); δ_H (300 MHz, $CDCl_3$) 2.15 (s, 3H, CH_3, 1‴-H), 2.51 (s, 3H, CH_3, 1″-H), 3.87 (s, 3H, OCH_3), 4.00 (s, 3H, $COOCH_3$), 6.86 (m, 2H, 5-H, 6-H), 7.42 (d, 1H, J = 8.6, 7-H); δ_C (75 MHz, $CDCl_3$) 8.8 (CH_3, C-1‴), 13.7 (CH_3, C-1″), 53.2 ($COOCH_3$), 55.7 (OCH_3), 101.1 (CH), 111.5 (CH), 114.3 (Cq), 116.1 (CH), 130.1 (Cq), 131.9 (Cq), 133.7 (Cq), 152.2 ($COOCH_3$), 156.0 (Cq, C-5); *m*/*z* (EI) 233.2 ($M^{\bullet+}$, 100%), 218.4 (25.44), 174.3 (33.48), 159.2 (17.97), 146.4 (25.82), 131.1 (37.55), 130.2 (16.29), 77.3 (17.08), 59.5 (26.57).

***N*-Methoxycarbonyl-5-bromo-2,3-dimethylindole 3c.** This compound was obtained from 5-bromo-2,3-dimethylindole[18] (7.84 g, 35 mmol). The crude product was purified by crystallisation from MeOH; yield 91% (9.00 g), mp 130 °C (from MeOH) (Found: C, 51.12; H, 4.31; N, 4.98. $C_{12}H_{12}BrNO_2$ requires C, 51.09; H, 4.29; N, 4.96%); δ_H (300 MHz, $CDCl_3$) 2.11 (s, 3H, CH_3, 1‴-H), 2.48 (s, 3H, CH_3, 1″-H), 4.00 (s, 3H, $COOCH_3$), 7.26 (dd, 1H, J = 6.9, J = 3.0, CH, 6-H), 7.48 (d, 1H, CH, 4-H), 7.88 (d, 1H, J = 8.3, CH, 7-H); δ_C (75 MHz, $CDCl_3$) 8.4 (CH_3, C-1‴), 11.7 (CH_3, C-1″), 53.4 ($COOCH_3$), 107.1 (Cq), 111.6 (CH), 112.3 (Cq), 120.7 (CH), 123.6 (CH), 131.34 (Cq), 132.4 (Cq), 133.9 (Cq), 152.9 ($COOCH_3$); *m*/*z* (EI) 283.2 (98.16%), 280.9 (M^+, 100), 238.0 (22.67), 236.2 (22.78), 223.9 (25.49), 222.1 (25.34), 202.1 (17.86), 143.1 (73.84), 115.0 (27.19), 101.9 (30.29).

***N*-Methoxycarbonyl-5-cyano-2,3-dimethylindole 3d.** This compound was obtained from 5-cyano-2,3-dimethylindole[18] (5.96 g, 35 mmol). The crude product was purified by crystallisation from MeOH; yield 71% (5.67 g), mp 132 °C (from MeOH) (Found: C, 68.38; H, 5.27; N, 12.23. $C_{13}H_{12}N_2O_2$ requires C, 68.41; H, 5.30; N, 12.27%); δ_H (300 MHz, $CDCl_3$) 2.18 (s, 3H, CH_3, 1‴-H), 2.53 (s, 3H, CH_3, 1″-H), 4.05 (s, 3H, $COOCH_3$), 7.47 (dd, 1H, J = 8.36, J = 1.65, CH, 6-H), 7.70 (d, 1H, J = 1.40, CH, 4-H), 8.13 (d, 1H, J = 8.04, CH, 7-H); δ_C (75 MHz, $CDCl_3$) 8.6 (CH_3, C-1‴), 13.7 (CH_3, C-1″), 53.8 ($COOCH_3$), 101.9 (Cq, C≡N), 106.0 (Cq), 114.2 (CH), 116.1 (Cq), 120.0 (CH), 122.6 (CH), 131.1 (Cq), 135.4 (Cq), 137.5 (Cq), 152.2 ($COOCH_3$); *m*/*z* (EI) 227.9 ($M^{\bullet+}$, 100%), 201.9 (36.42), 168.9 (27.56), 142.9 (19.45).

General procedure for the preparation of the compounds 2a–d

A solution of the appropriate compound **3a**–**d** (23 mmol) and *N*-bromosuccinimide (NBS) (8.3 g, 46 mmol) in CCl_4 (400 ml) was heated to reflux after which AIBN (200 mg) was carefully added. After 3 h the mixture was cooled to room temperature and the succinimide which resulted was filtered off and washed with CCl_4 (2 × 30 ml). The solvent was removed under reduced pressure to yield a red–brown solid. A further purification by recrystallisation from *n*-hexane afforded **2a**–**d** in off-white colored crystals.

***N*-Methoxycarbonyl-2,3-bis(bromomethyl)indole 2a.** This compound was obtained from **3a** (5.0 g, 23 mmol). The crude product was purified by crystallisation from *n*-hexane; yield 70% (8.0 g), mp 148 °C (from *n*-hexane); δ_H (300 MHz, $CDCl_3$) (s, 3H, $COOCH_3$), 4.68 (s, 2H, CH_2, 1‴-H), 5.05 (s, 2H, CH_2, 1″-H), 7.36 (m, 2H, 5-H, 6-H), 7.63 (dd, 1H), 8.10 (dd, 1H); δ_C (75 MHz, $CDCl_3$) 21.4 (CH_2, C-1‴), 22.7 (CH_2, C-1″), 54.2 ($COOCH_3$), 116.2 (CH), 119.2 (CH), 119.8 (Cq), 123.9 (CH), 126.4 (CH), 127.4 (Cq), 134.0 (Cq), 136.3 (Cq), 153.1 (Cq, $COOCH_3$); *m*/*z* (EI) 361.0 ($M^{\bullet+}$, 18.05%), 358.6 (10.67), 282.1 (94.26), 280.0 (100), 200.9 (57.51), 162.7 (8.63), 157.0 (41.80), 142.2 (59.10), 115.2 (33.94).

***N*-Methoxycarbonyl-2,3-bis(bromomethyl)-5-methoxyindole 2b.** This compound was obtained from **3b** (5.4 g, 23 mmol). The crude product was purified by crystallisation from *n*-hexane; yield 68% (6.1 g), mp 147 °C (from *n*-hexane); δ_H (300 MHz, $CDCl_3$) 3.78 (s, 3H, OCH_3), 4.00 (s, 3H, $COOCH_3$), 4.58 (s, 2H, CH_2, 1‴-H), 4.95 (s, 2H, CH_2, 1″-H), 6.88 (dd, 1H, J = 8.5, J = 2.6, 6-H), 7.11 (d, 1H, J = 2.24, 4-H), 7.89 (d, 1H, J = 9.0, 7-H); δ_C (75 MHz, $CDCl_3$) 21.7 (CH_2, C-1‴), 22.7 (CH_2, C-1″), 50.2 (OCH_3), 55.7 ($COOCH_3$), 101.3 (CH), 115.3 (CH), 117.0 (CH), 119.4 (Cq), 132.6 (Cq), 134.4 (Cq), 138.9 (Cq), 156.5 ($COOCH_3$), 159.9 (Cq, C-5); *m*/*z* (EI) 390.1 (M^+, 6.18%), 311.3 (33.07), 309.2 (33.86), 257.3 (18.26), 255.3 (50.90), 230.9 (41.42), 191.5 (13.71), 171.7 (27.06), 159.8 (38.32), 127.9 (52.66), 95.5 (20.89).

***N*-Methoxycarbonyl-5-bromo-2,3-bis(bromomethyl)indole 2c.** This compound was obtained from **3c** (6.5 g, 23 mmol). The crude product was purified by crystallisation from *n*-hexane; yield 91% (9.2 g), mp 154 °C (from *n*-hexane); δ_H (300 MHz, $CDCl_3$) 4.10 (s, 3H, $COOCH_3$), 4.61 (s, 2H, CH_2, 1‴-H), 5.00 (s, 2H, CH_2, 1″-H), 7.45 (dd, 1H, J = 7.6, J = 2.0, CH, 6-H), 7.73 (d, 1H, J = 1.4, CH, 4-H), 7.96 (d, 1H, J = 9.9, CH, 7-H); δ_C (75 MHz, $CDCl_3$) 21.7 (CH_2, C-1‴), 22.7 (CH_2, C-1″), 53.8 ($COOCH_3$), 106.0 (Cq), 114.2 (Cq), 116.1 (CH), 120.0 (Cq), 122.6 (CH), 126.8 (CH), 131.1 (Cq), 137.5 (Cq), 152.2 (Cq, $COOCH_3$); *m*/*z* (EI) 447.8 (4.63%), 445.5 (15.59), 443.1 (13.63), 440.9 ($M^{\bullet+}$, 4.71), 363.2 (55.68), 360.7 (100), 358.3 (57.36), 281.7 (38.13), 279.5 (37.84), 237.2 (18.66), 235.2 (18.11), 222.0 (27.77), 220.2 (31.48), 154.6 (20.72), 141.2 (64.60), 114.1 (21.35), 99.4 (19.74), 75.2 (11.91).

***N*-Methoxycarbonyl-5-cyano-2,3-bis(bromomethyl)indole 2d.** This compound was obtained from **3d** (5.3 g, 23 mmol). The crude product was purified by crystallisation from *n*-hexane; yield 76% (6.8 g), mp 133 °C (from *n*-hexane); δ_H (300 MHz, $CDCl_3$) 4.14 (s, 3H, $COOCH_3$), 4.64 (s, 2H, CH_2, 1‴-H), 5.00 (s, 2H, CH_2, 1″-H), 7.62 (dd, H, J = 8.86, J = 2.17, CH, 6-H), 7.97 (d, 1H, J = 1.86, CH, 4-H), 8.21 (d, 1H, J = 8.84, CH, 7-H); δ_C (75 MHz, $CDCl_3$) 20.2 (CH_2, C-1‴), 21.6 (CH_2, C-1″), 54.8 ($COOCH_3$), 101.4 (Cq, C≡N), 107.5 (Cq), 117.1 (CH), 119.2 (Cq), 124.1 (CH), 129.2 (CH), 131.6 (Cq), 136.2 (Cq), 138.9 (Cq), 150.0 ($COOCH_3$); *m*/*z* (EI) 386.4 (1.07%), 384.7 ($M^{\bullet+}$, 3.8), 382.9 (1.33), 305.9 (9.88), 304.0 (10.46), 225.5 (7.93), 181.6 (9.03), 166.8 (8.69), 106.8 (11.47), 98.5 (100), 56.7 (99.86).

General procedure for preparation of compounds 5a–l and 6a–f

To a preheated solution (55 °C) of the appropriate compound **2a**–**d** (2.8 mmol) and the appropriate bismaleimide[18] (1.4 mmol) in dimethylformamide was added powdered NaI (200 mg). After 2 h the solvent was removed under reduced pressure, the residue was taken up in CH_2Cl_2 (50 ml), washed with aqueous sodium thiosulfate (200 ml), and dried ($MgSO_4$). After removal of solvent under reduced pressure, the residue was purified by column chromatography (petroleum–ethyl acetate, 2 : 3) to afford yellow solids.

1,3-Bis(5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)propane 5a. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*′-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 87% (776 mg), mp 119 °C (from EtAc) (Found: C, 66.27; H, 5.12; N, 8.83. $C_{35}H_{32}N_4O_8$ requires C, 66.03; H, 5.07; N, 8.80%); δ_H (300 MHz, $CDCl_3$) 1.24 (q, 2H, CH_2, 2-H), 2.89–2.97 (m, 2H, 2 × CH_2-*H*, 2 × 10′-H), 3.24–3.30 (m, 6H), 3.31 (t, 4H, 2 × CH_2, 1-H, 3-H), 3.33 (m, 2H), 3.89 (dd, 2H, J = 16.91, J = 2.11, 2 × CH_2-*H*, 2 × 4′-H), 4.04 (s, 6H, 2 × $COOCH_3$), 7.21–7.27 (m, 4H, 4 × CH, 2 × 7′-H, 2 × 8′-H), 7.39 (dd, 2H, J = 6.46, J = 2.14, 2 × CH, 2 × 9′-H), 8.04 (dd, 2H, J = 6.65, J = 1.75, 2 × CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.5 (2CH_2, 2 × C-10′), 23.2 (2CH_2, 2 × C-4′), 24.3 (CH_2, C-2), 38.2 (2CH,

2 × C-10a′), 38.7 (2CH_2, C-1, C-4), 39.7 (2CH, 2 × C-3a′), 53.7 (2 × COO*C*H_3), 115.0 (2Cq), 115.6 (2CH), 117.0 (2CH), 123.2 (2CH), 124.4 (2CH), 128.4 (2Cq), 132.8 (2Cq), 135.9 (2Cq), 152.2 (2Cq, 2 × *C*OOCH$_3$), 179.2 (2Cq, 2 × C=O), 179.5 (2Cq, 2 × C=O); *m*/*z* (FD) 636.7 (100%).

2-(3-Maleimidopropanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6a. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*'-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 10% (61 mg), mp 168 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.21 (q, 2H, CH_2, 2″-H), 2.87–2.94 (m, 1H, CH_2-*H*, 10-H), 3.22–3.51 (m, 8H, 2CH_2-*H*, 2CH, 2CH_2, 4-H, 10-H, 3a-H, 10a-H, 1″-H, 3″-H), 3.71 (dd, 1H, *J* = 16.91, *J* = 2.03, CH_2-*H*, 4-H), 4.04 (s, 3H, COO*C*H_3), 6.67 (s, 2H, 2CH, 3‴-H, 4‴-H), 7.22–7.28 (m, 2H, 2CH, 7-H, 8-H), 7.39 (dd, 1H, *J* = 6.46, *J* = 2.14, CH, 9-H), 8.04 (dd, 1H, *J* = 6.65, *J* = 1.97, CH, 6′-H); δ_C (75 MHz, $CDCl_3$) 20.3 (CH_2, C-10), 23.2 (CH_2, C-4), 26.3 (CH_2, C-2″), 35.0 (CH_2), 36.4 (CH_2), 38.7 (CH, C-10a′), 39.6 (CH, C-3a′), 53.7 (COO*C*H_3), 115.1 (Cq), 115.6 (CH), 117.8 (CH), 123.1 (CH), 124.4 (CH), 128.4 (Cq), 132.7 (Cq), 134.1 (2CH, C-3‴, C-4‴), 136.0 (Cq), 152.2 (Cq, *C*OOCH$_3$), 170.8 (2C=O, C-2‴, C-5‴), 179.2 (Cq, C=O), 179.5 (Cq, C=O); *m*/*z* (EI) 434.9 ($M^{\bullet+}$, 84.33%), 376.3 (19.27), 200.5 (40.33), 193.4 (67.22), 166.8 (85.49), 143.9 (21.39), 139.7 (46.23), 109.5 (28.39), 97.2 (9.31), 81.8 (10.86).

1,4-Bis(5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)butane 5b. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*'-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 68% (619 mg), mp 197 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.17 (q, 4H, 2 × CH_2, 1-H, 4-H), 2.86–2.95 (m, 2H, 2 × CH_2-H, 2 × 10′-H), 3.18–3.28 (m, 6H), 3.31 (t, 4H, 2 × CH_2, 1-H, 4-H), 3.33 (m, 2H), 3.89 (dd, 2H, *J* = 16.91, *J* = 2.11, 2 × CH_2-H, 2 × 4′-H), 4.04 (s, 6H, 2 × $COOCH_3$), 7.22–7.26 (m, 4H, 4 × CH, 2 × 7′-H, 2 × 8′-H), 7.41 (dd, 2H, *J* = 6.46, *J* = 2.14, 2 × CH, 2 × 9′-H), 8.07 (dd, 2H, *J* = 6.65, *J* = 1.75, 2 × CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.5 (2CH_2, 2 × C-10′), 23.3 (2CH_2, 2 × C-4′), 24.3 (2CH_2, C-2, C-3), 38.2 (2CH, 2 × C-10a′), 38.7 (2CH_2, C-1, C-4), 39.7 (2CH, 2 × C-3a′), 53.7 (2 × COO*C*H_3), 115.0 (2Cq), 115.6 (2CH), 117.8 (2CH), 123.2 (2CH), 124.4 (2CH), 128.4 (2Cq), 132.8 (2Cq), 136.0 (2Cq), 152.2 (2Cq, 2 × *C*OOCH$_3$), 179.2 (2Cq, 2 × C=O), 179.5 (2Cq, 2 × C=O); *m*/*z* (FD) 650.7 (100%).

2-(4-Maleimidobutanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6b. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*'-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 20% (126 mg), mp 172 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.13–1.49 (m, 4H, 2CH_2, 1″-H, 4″-H), 2.86–2.95 (m, 1H, CH_2-*H*, 10-H), 3.16–3.33 (m, 8H, 2CH_2-*H*, 2CH, 2CH_2, 4-H, 10-H, 3a-H, 10a-H, 1″-H, 4″-H), 3.84 (dd, 1H, *J* = 16.84, *J* = 1.98, CH_2-*H*, 4-H), 4.01 (s, 3H, COO*C*H_3), 6.67 (s, 2H, 2CH, 3‴-H, 4‴-H), 7.22–7.26 (m, 2H, 2CH, 7-H, 8-H), 7.41 (dd, 1H, *J* = 6.46, *J* = 2.14, CH, 9-H), 8.07 (dd, 1H, *J* = 6.55, *J* = 1.87, CH, 6-H); δ_C (75 MHz, $CDCl_3$) 20.4 (CH_2, C-10), 23.3 (CH_2, C-4), 24.3 (CH_2), 24.7 (CH_2), 38.2 (CH, C-10a), 38.7 (CH_2), 39.1 (CH_2), 39.7 (CH, C-3a), 53.7 (COO*C*H_3), 115.0 (Cq), 115.6 (CH), 117.8 (CH), 123.2 (CH), 124.4 (CH), 128.4 (Cq), 132.8 (Cq), 134.2 (2CH, C-3‴, C-4‴), 136.0 (Cq), 152.2 (Cq, *C*OOCH$_3$), 171.0 (2Cq, 2C=O, C-2‴, C-5‴), 179.2 (Cq, C=O), 179.5 (Cq, C=O); *m*/*z* (EI) 449.1 ($M^{\bullet+}$, 37.36%), 389.9 (19.27), 295.7 (23.57), 251.2 (52.59), 226.8 (20.79), 193.5 (77.47), 167.6 (88.40), 156.9 (27.65), 143.6 (47.89), 129.7 (33.35), 114.5 (20.27), 109.5 (30.46), 84.4 (20.24).

1,12-Bis(5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)dodecane 5c. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*'-dodecamethylenedimaleimide (505 mg, 1.4 mmol); yield 53% (556 mg), mp 58 °C (from EtAc) (Found: C, 69.44; H, 6.69; N, 7.45. $C_{44}H_{50}N_4O_8$ requires C, 69.27; H, 6.61; N, 7.34%); δ_H (300 MHz, $CDCl_3$) 0.93–1.13 (m, 12H, 6 × CH_2), 1.21–1.29 (m, 4H, 2 × CH_2, 6-H, 7-H), 1.33–1.43 (q, 4H, 2 × CH_2, 2-H, 11-H), 2.88–2.95 (m, 2H, 2 × CH_2-*H*, 2 × 10′-H), 3.20–3.41 (m, 12H, 2 × CH_2, 4 × CH_2-*H*, 4 × CH, 1-H, 12-H, 2 × 10′-H, 2 × 4′-H, 10a′-H, 3a′-H), 3.93 (dd, 2H, *J* = 16.94, *J* = 2.13, 2 × CH_2-*H*, 2 × 4′-H), 4.04 (s, 6H, 2 × $COOCH_3$), 7.22–7.29 (m, 4H, 4 × CH, 2 × 7′-H, 2 × 8′-H), 7.42 (dd, 2H, *J* = 6.59, *J* = 1.98, 2 × CH, 2 × 9′-H), 8.09 (dd, 2H, *J* = 7.06, *J* = 1.50, 2 × CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.6 (2CH_2, 2 × C-10′), 23.4 (2CH_2, 2 × C-4′), 26.5 (2CH_2, C-3, C-10), 26.9 (2CH_2, C-2, C-11), 27.5 (2CH_2), 29.1 (2CH_2), 29.3 (2CH_2), 29.5 (2CH, 2 × C-10a′), 29.7 (2CH_2, C-1, C-12), 38.8 (2CH, 2 × C-3a′), 53.7 (2 × COO*C*H_3), 115.1 (2Cq), 115.6 (2CH), 117.8 (2CH), 123.2 (2CH), 124.4 (2CH), 128.4 (2Cq), 132.8 (2Cq), 136.0 (2Cq), 152.2 (2Cq, 2 × *C*OOCH$_3$), 179.4 (2Cq, 2 × C=O), 179.6 (2Cq, 2 × C=O); *m*/*z* (FD) 762.9 (100%).

2-(4-Maleimidododecanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6c. This compound was obtained from compound **2a** (1.0 g, 2.8 mmol) and *N*,*N*'-dodecamethylenedimaleimide (505 mg, 1.4 mmol); yield 31% (244 mg), mp 58 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 0.96–1.24 (m, 16H, 8 × CH_2), 1.36 (q, 2H, CH_2), 1.56 (q, 2H, CH_2), 2.91 (dd, 1H, *J* = 16.81, *J* = 7.40, CH_2-*H*), 3.16–3.51 (m, 8H, 2 × CH_2, 2 × CH_2-*H*, 2 × CH), 3.93 (dd, 1H, *J* = 16.99, *J* = 2.11, CH_2-*H*), 4.03 (s, 3H, COO*C*H_3), 6.66 (s, 2H, 2 × CH), 7.19–7.29 (m, 2H, 2 × CH), 7.41 (dd, 1H, *J* = 6.84, *J* = 2.36, CH), 8.08 (d, 1H, *J* = 6.88, *J* = 1.65, CH); δ_C (75 MHz, $CDCl_3$) 20.6 (CH_2, C-10), 23.4 (CH_2, C-4), 26.5 (CH_2), 26.8 (CH_2), 27.5 (CH_2), 28.6 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.5 (3CH_2), 38.0 (CH_2), 38.8 (CH, C-10a), 39.1 (CH_2), 39.8 (CH, C-3a), 53.7 (COO*C*H_3), 115.1 (Cq), 115.6 (CH), 117.8 (CH), 123.1 (CH), 124.4 (CH), 128.5 (Cq), 132.8 (Cq), 134.0 (2CH, C-3‴, C-4‴), 136.0 (Cq), 152.2 (Cq, *C*OOCH$_3$), 170.9 (2Cq, 2 × C=O), 179.4 (Cq, C=O), 179.6 (Cq, C=O); *m*/*z* (FD) 561.7 (100%).

1,3-Bis(8-methoxy-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)propane 5d. This compound was obtained from compound **2b** (1.1 g, 2.8 mmol) and *N*,*N*'-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 58% (566 mg), mp 88 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 0.80–0.90 (m, 2H, CH_2, 2-H), 3.20–3.37 (m, 14H [structure elements: CH, CH_2, CH_2-*H*], 2 × 10a′-H (2H), 2 × 4a′-H (2H), 1-H (2H), 3-H (2H), 2 × 10′-H (4H), 2 × 3′-H (2H)), 3.87 (dd, 2H, 2 × CH_2-*H*, 2 × 4′-H), 3.90 (s, 6H, 2 × OCH_3), 4.03 (s, 6H, 2 × $COOCH_3$), 6.83 (m, 2H, CH, 2 × 7′-H), 7.27 (m, 2H, 2CH, 2 × 9′-H), 8.03 (m, 2H, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 21.9 (2CH_2, 2 × C-10′), 23.5 (2CH_2, 2 × C-4′), 24.2 (CH_2, C-2), 38.0 (2CH_2, C-1, C-3), 39.1 (2CH, 2 × C-10a′), 39.3 (2CH, 2 × C-3a′), 54.9 (2 × COO*C*H_3), 57.3 (2 × OCH_3), 102.4 (2Cq), 109.4 (4CH, 2 × C-6′, 2 × C-9′), 114.7 (2CH, 2 × C-7′), 115.5 (2Cq), 120.3 (2Cq), 128.1 (2Cq), 135.4 (2Cq), 151.8 (2Cq, 2 × *C*OOCH$_3$), 179.2 (2Cq, 2 × C=O), 179.3 (2Cq, 2 × C=O); *m*/*z* (FD) 696.7 (100%).

1,4-Bis(8-methoxy-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)butane 5e. This compound was obtained from compound **2b** (1.1 g, 2.8 mmol) and *N*,*N*'-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 56% (557 mg), mp 138 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.19–1.27 (m, 4H, 2CH_2, 2-H, 3-H), 3.11–3.33 (m, 14H [structure elements: CH, CH_2, CH_2-*H*], 2 × 10a′-H (2H), 2 × 3a′-H (2H), 1-H (2H), 3-H (2H), 2 × 10′-H (4H), 2 × 4′-CH_2-*H* (2H)), 3.87 (dd, 2H, 2 × CH_2-*H*, 2 × 4′-CH_2-*H*), 3.90 (s, 6H, 2 × OCH_3), 4.03 (s, 6H, 2 × $COOCH_3$), 6.86 (dd, 2H,

$J = 9.12$, $J = 2.75$, 2CH, 2 × 7′-H), 7.27 (m, 2H, 2CH, 2 × 9′-H), 8.03 (m, 2H, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 21.9 ($2CH_2$, 2 × C-10′), 23.5 ($2CH_2$, 2 × C-4′), 24.3 ($2CH_2$, C-2, C-3), 38.1 ($2CH_2$, C-1, C-4), 39.0 (2CH, 2 × C-10a′), 39.3 (2CH, 2 × C-3a′), 53.9 (2 × COO*C*H_3), 57.3 (2 × OCH_3), 102.4 (2Cq), 109.4 (4CH, 2 × C-6′, 2 × C-9′), 114.6 (2CH, 2 × C-7′), 115.5 (2Cq), 120.3 (2Cq), 128.1 (2Cq), 135.4 (2Cq), 151.7 (2Cq, 2 × *C*$OOCH_3$), 179.2 (2Cq, 2 × C=O), 179.3 (2Cq, 2 × C=O); *m*/*z* (FD) 710.5 (100%).

1,12-Bis(8-methoxy-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)dodecane 5f. This compound was obtained from compound **2b** (1.1 g, 2.8 mmol) and *N*,*N*′-dodecamethylenedimaleimide (505 mg, 1.4 mmol); yield 59% (680 mg), mp 198 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 0.94–1.34 (m, 16H, $8CH_2$, 3-H, 10-H, 5-H, 8-H, 4-H, 9-H, 6-H, 7-H), 1.37 (q, 4H, $2CH_2$, 2-H, 11-H), 2.88–3.33 (m, 6H, $2CH_2$, $2CH_2$-*H*, 2 × 10′-H, 2 × 4′-CH_2-H), 3.37 (t, 4H, $2CH_2$, 1-H, 12-H), 3.66–3.92 (m, 12H, 2CH, $2CH_2$-*H*, $2OCH_3$, 2 × 10a′-H, 2 × 3a′-H, 2 × CH_2-*H*), 4.03 (s, 6H, $2COOCH_3$), 6.86 (m, 2H, 2CH, 2 × 7′-H), 7.28 (m, 2H, 2CH, 2 × 9′-H), 8.05 (m, 2H, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 22.1 ($2CH_2$, 2 × C-10′), 23.6 ($2CH_2$, 2 × C-4′), 26.4 ($2CH_2$, C-3, C-10), 27.5 ($2CH_2$, C-2, C-11), 29.0 ($2CH_2$), 29.9 ($2CH_2$), 39.1 (2CH, 2 × C-10a′), 39.1 ($2CH_2$, C-1, C-12), 39.4 (2CH, 2 × C-3a′), 53.9 (2 × COO*C*H_3), 57.3 (2 × OCH_3), 104.0 (2Cq), 109.3 (4CH, 2 × C-6′, 2 × C-9′), 115.0 (2CH, 2 × C-7′), 115.6 (2Cq), 120.4 (2Cq), 128.2 (2Cq), 138.2 (2Cq), 151.7 (2Cq, 2 × *C*$OOCH_3$), 179.2 (2Cq, 2 × C=O), 179.3 (2Cq, 2 × C=O); *m*/*z* (FD) 823.0 (100%).

1,3-Bis(8-bromo-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)propane 5g. This compound was obtained from compound **2c** (784 mg, 2.8 mmol) and *N*,*N*′-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 54% (601 mg), mp 128 °C (from EtAc) (Found: C, 53.07; H, 3.92; N, 7.13. $C_{35}H_{30}Br_2N_4O_8$ requires C, 52.92; H, 3.81; N, 7.05%); δ_H (300 MHz, $CDCl_3$) 1.71–1.79 (m, 2H, CH_2, 2-H), 2.88 (dd, 2H, $J = 16.01$, $J = 7.84$, 2 × CH_2-*H*, 2 × 10′-H), 3.13–3.37 (m, 12H [structure elements: CH, CH_2, CH_2-*H*], 2 × 10a′-H (2H), 2 × 3a′-H (2H), 1-H (2H), 3-H (2H), 2 × 10′-H (2H), 2 × 3′-H (2H)), 3.87 (dd, 2H, $J = 16.84$, $J = 2.34$, 2 × CH_2-*H*, 2 × 3′-H), 4.05 (s, 6H, 2 × $COOCH_3$), 7.32 (dd, 2H, $J = 8.84$, $J = 1.85$, 2 × 7′-H), 7.54 (d, 2H, $J = 1.9$, 2 × 9′-H), 7.96 (d, 2H, $J = 8.82$, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.1 ($2CH_2$, 2 × C-10′), 23.2 ($2CH_2$, 2 × C-4′), 25.1 (CH_2, C-2), 36.1 ($2CH_2$, C-1, C-3), 38.5 (2CH, 2 × C-10a′), 39.5 (2CH, 2 × C-4a′), 53.9 (2 × CO-O*C*H_3), 114.2 (2Cq), 116.6 (2Cq), 117.1 (2CH, 2 × C-6′), 120.7 (2CH, 2 × C-9′), 127.1 (2CH, 2 × C-7′), 130.2 (2Cq), 134.1 (2Cq), 134.7 (2Cq), 151.9 (2Cq, 2 × *C*$OOCH_3$), 179.0 (2Cq, 2 × C=O), 179.1 (2Cq, 2 × C=O); *m*/*z* (FD) 794.4 (100%).

8-Bromo-2-(4-maleimidopropanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6d. This compound was obtained from compound **2c** (784 mg, 2.8 mmol) and *N*,*N*′-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 38% (274 mg), mp 168 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.82 (q, 2H), 3.04 (dd, 1H, $J = 18.43$, $J = 8.71$), 3.22–3.44 (m, 8H), 3.92 (dd, 1H, $J = 17.43$, $J = 2.01$), 4.04 (s, 3H), 6.65 (s, 2H), 7.34 (dd, 1H, $J = 8.82$, $J = 2.20$), 7.54 (d, 1H, $J = 1.9$), 7.96 (d, 1H, $J = 9.03$); δ_C (75 MHz, $CDCl_3$) 20.17 (CH_2, C-10), 23.26 (CH_2, C-4), 26.29 (CH_2, C-2″), 35.03 (CH_2), 36.48 (CH_2), 38.61 (CH, C-10a), 39.53 (CH, C-3a), 53.92 (COO*C*H_3), 114.26 (Cq), 116.58 (Cq), 117.13 (CH, C-6), 120.67 (CH, C-7), 127.17 (CH, C-7), 130.15 (Cq), 134.07 (Cq), 134.15 (2CH, C-3‴, C-4‴), 134.76 (Cq), 151.93 (Cq, *C*$OOCH_3$), 170.53 (2Cq, 2C=O, C-2‴, C-5‴), 179.06 (Cq, C=O), 179.19 (Cq, C=O); *m*/*z* (EI) 513.6 (31.71%), 511.9 ($M^{\bullet+}$, 29.68), 431.7 (8.21), 331.0 (20.52), 328.8 (20.41), 224.6 (73.24), 166.8 (100), 154.9 (65.71), 139.8 (62.17), 109.5 (46.95), 106.7 (36.49), 90.7 (20.10).

1,4-Bis(8-bromo-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)butane 5h. This compound was obtained from compound **2c** (784 mg, 2.8 mmol) and *N*,*N*′-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 78% (883 mg), mp 219 °C (from EtAc) (Found: C, 53.68; H, 4.01; N, 6.99. $C_{36}H_{32}Br_2N_4O_8$ requires C, 53.48; H, 3.99; N, 6.93%); δ_H (300 MHz, $CDCl_3$) 1.63 (m, 4H, $2CH_2$, 2-H, 3-H), 2.88 (dd, 2H, $J = 15.96$, $J = 6.65$, 2 × CH_2-*H*, 2 × 10′-H), 2.95–3.36 (m, 12H, $2CH_2$, 4 × CH_2-*H*, 4CH, 1-H, 4-H, 2 × 10′-H, 2 × 4′-H, 2 × 10a′-H, 2 × 3a′), 3.89 (dd, 2H, $J = 17.23$, $J = 2.34$, 2 × CH_2-*H*, 2 × 4′-H), 4.05 (s, 6H, 2 × $COOCH_3$), 7.35 (dd, 2H, $J = 8.88$, $J = 1.85$, 2CH, 2 × 7′-H), 7.54 (d, 2H, $J = 1.90$, 2CH, 2 × 9′-H), 7.97 (d, 2H, $J = 8.84$, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.1 ($2CH_2$, 2 × C-10′), 23.2 ($2CH_2$, 2 × C-4′), 25.2 ($2CH_2$, C-2, C-3), 36.1 ($2CH_2$, C-1, C-4), 38.6 (2CH, 2 × C-10a′), 39.4 (2CH, 2 × C-4a′), 53.9 (2 × COO*C*H_3), 114.2 (2Cq), 116.6 (2Cq), 117.2 (2CH, 2 × C-6′), 120.6 (2CH, 2 × C-9′), 127.2 (2CH, 2 × C-7′), 130.2 (2Cq), 134.1 (2Cq), 134.7 (2Cq), 151.9 (2Cq, 2 × *C*$OOCH_3$), 179.0 (2Cq, 2 × C=O), 179.1 (2Cq, 2 × C=O); *m*/*z* (FD) 808.5 (100%).

8-Bromo-2-(4-maleimidododecanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6e. This compound was obtained from compound **2c** (784 mg, 2.8 mmol) and *N*,*N*′-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 18% (133 mg), mp 168 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.77–1.84 (m, 4H, $2CH_2$, C-2″, C-3″), 3.04 (dd, 1H, $J = 17.43$, $J = 8.71$, CH_2-*H*, C-10), 3.22–3.44 (m, 8H, $2CH_2$-*H*, $2CH_2$, 2CH, C-4, C-10, C-3a, C-10a, C-1″, C-4″), 3.92 (dd, 1H, $J = 17.43$, $J = 2.01$, CH_2-*H*, C-4), 4.04 (s, 3H, COO*C*H_3), 6.65 (s, 2H, 2CH, 3‴-H, 4‴-H), 7.34 (dd, 1H, $J = 8.82$, $J = 2.20$, CH, 7-H), 7.54 (d, 1H, $J = 1.9$, CH, 9-H), 7.96 (d, 1H, $J = 9.03$, CH, 6-H); δ_C (75 MHz, $CDCl_3$) 20.2 (CH_2, C-10), 23.3 (CH_2, C-4), 26.3 (CH_2), 35.0 (CH_2), 36.5 (CH_2), 36.7 (CH_2), 38.6 (CH, C-10a), 39.5 (CH, C-3a), 53.9 (COO*C*H_3), 114.3 (Cq), 116.6 (Cq), 117.1 (CH, C-6), 120.7 (CH, C-9), 127.2 (CH, C-7), 130.2 (Cq), 134.1 (Cq), 134.2 (2CH, C-3‴, C-4‴), 134.8 (Cq), 151.9 (Cq, *C*$OOCH_3$), 170.5 (2Cq, 2C=O, C-2‴, C-5‴), 179.1 (Cq, C=O), 179.2 (Cq, C=O); *m*/*z* (EI) 527.8 (25.51%), 525.5 ($M^{\bullet+}$, 24.08), 331.0 (20.34), 328.8 (20.52), 224.6 (73.24), 166.8 (58.82), 134.7 (24.09), 109.5 (33.78), 106.7 (27.82), 96.9 (21.02), 81.7 (17.71).

1,12-Bis(8-bromo-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)dodecane 5i. This compound was obtained from compound **2c** (784 mg, 2.8 mmol) and *N*,*N*′-dodecamethylenedimaleimide (505 mg, 1.4 mmol); yield 92% (1.19 g), mp 92 °C (from EtAc) (Found: C, 57.60; H, 5.30; N, 6.18. $C_{44}H_{48}Br_2N_4O_8$ requires C, 57.40; H, 5.25; N, 6.09%); δ_H (300 MHz, $CDCl_3$) 0.94–0.98 (m, 16H [structure elements: 8 × CH_2], 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H), 1.35 (q, 4H, $2CH_2$, 2-H, 11-H), 2.88–2.96 (dd, 2H, $2CH_2$-*H*, 2 × 10′-CH_2-*H*), 3.21–3.34 (m, 4H, $4CH_2$-*H*, 2 × 10′-CH_2-*H*, 2 × 4′-CH_2-*H*), 3.36–3.41 (m, 8H, $2CH_2$, 4CH, 1-H, 12-H, 2 × 10a′-H, 2 × 3a′-H), 3.95 (dd, 2H, $J = 17.40$, $J = 1.76$, $2CH_2$-*H*, 2 × 4′-CH_2-*H*), 4.08 (s, 6H, $2COOCH_3$), 7.52 (dd, 2H, $J = 8.65$, $J = 1.3$, 2CH, 2 × 7′-H), 8.02 (d, 2H, $J = 1.3$, 2CH, 2 × 9′-H), 8.19 (d, 2H, $J = 8.64$, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 17.7 ($2CH_2$, 2 × C-10′), 20.8 ($2CH_2$, 2 × C-4′), 23.8 ($2CH_2$, C-3, C-10), 24.8 ($2CH_2$, C-2, C-11), 26.3 ($2CH_2$), 26.7 ($2CH_2$), 26.8 ($2CH_2$), 35.9 (2CH, 2 × C-10a′), 36.5 ($2CH_2$, C-1, C-12), 36.9 (2CH, 2 × C-3a′), 51.7 (2 × COO*C*H_3), 104.1 (2Cq), 112.2 (2Cq), 113.8 (2CH, 2 × C-6′), 116.8 (2Cq), 119.8 (2CH, 2 × C-9′), 124.9 (2CH, 2 × C-7′), 125.9 (2Cq), 135.2 (2Cq), 149.0 (2Cq, 2 × *C*$OOCH_3$), 176.4 (2Cq, 2 × C=O), 176.5 (2Cq, 2 × C=O); *m*/*z* (FD) 920.7 (100%).

1,3-Bis(8-cyano-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)propane 5j. This

compound was obtained from compound **2d** (1.1 g, 2.8 mmol) and *N*,*N*'-trimethylenedimaleimide (324 mg, 1.4 mmol); yield 66% (634 mg), mp 178 °C (from EtAc) (Found: C, 57.60; H, 5.30; N, 6.18. $C_{44}H_{48}Br_2N_4O_8$ requires C, 57.40; H, 5.25; N, 6.09%); δ_H (300 MHz, $CDCl_3$) 1.22–1.27 (m, 2H, CH_2, 2–H), 2.88–2.97 (m, 2H, $2CH_2$-*H*, 2 × 10′-H), 3.18–3.39 (m, 12H [structure elements: CH_2, CH_2-*H*, CH], 1-H (2H), 3-H (2H), 2 × 10′-H (2H), 2 × 4′-H (2H), 2 × 10a′-H (2H), 2 × 3a′-H (2H)), 3.87 (dd, 2H, *J* = 17.44, $2CH_2$-*H*, 2 × 4′-H), 4.08 (s, 6H, 2 × $COOCH_3$), 7.53 (dd, 2H, *J* = 6.93, *J* = 1.43, 2CH, 2 × 7′-H), 7.74 (d, 2H, *J* = 1.89, 2CH, 2 × 9′-H), 8.18 (d, 2H, *J* = 8.66, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 17.3 ($2CH_2$, 2 × C-10′), 20.6 ($2CH_2$, 2 × C-4′), 22.4 (CH_2, C-2), 33.4 ($2CH_2$, C-1, C-3), 35.7 (2CH, 2 × C-10a′), 36.6 (2CH, 2 × C-3a′), 51.6 (2COO*C*H_3), 104.0 (2Cq, 2 × C≡N), 111.9 (2Cq), 113.8 (2CH, 2 × C-6′), 116.9 (2Cq), 119.9 (2CH, 2 × C-9′), 124.9 (2CH, 2 × C-7′), 125.9 (2Cq), 132.6 (2Cq), 135.7 (2Cq), 149.0 (2Cq, 2 × *C*$OOCH_3$), 176.17 (2Cq, 2 × C=O), 176.25 (2Cq, 2 × C=O); *m*/*z* (FD) 686.7 (100%).

1,4-Bis(8-cyano-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)butane 5k. This compound was obtained from compound **2d** (1.1 g, 2.8 mmol) and *N*,*N*'-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 53% (520 mg), mp 108 °C (from EtAc) (Found: C, 65.32; H, 4.63; N, 11.88. $C_{38}H_{32}N_6O_8$ requires C, 65.14; H, 4.60; N, 11.99%); δ_H (300 MHz, $CDCl_3$) 1.22–1.27 (m, 4H, $2CH_2$, 2-H, 3-H), 2.88–2.97 (m, 2H, $2CH_2$-*H*, 2 × 10′-H), 3.20–3.40 (m, 12H, $2CH_2$, $6CH_2$-*H*, 2CH, 1-H, 4-H, 2 × 10′CH_2-*H*, 2 × 4′CH_2-*H*, 2 × 10a′-H, 2 × 3a′-H), 3.90 (dd, 2H, $2CH_2$-*H*, 2 × 4′-CH_2-*H*), 4.08 (s, 6H, 2 × $COOCH_3$), 7.53 (dd, 2H, *J* = 7.46, *J* = 1.43, 2CH, 2 × 7′-H), 7.75 (d, 2H, *J* = 1.45, 2CH, 2 × 9′-H), 8.18 (d, 2H, *J* = 7.46, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 20.2 ($2CH_2$, 2 × C-10′), 23.3 ($2CH_2$, 2 × C-4′), 24.3 ($2CH_2$, C-2, C-3), 38.3 ($2CH_2$, C-1, C-4), 38.4 (2CH, 2 × C-10a′), 39.4 (2CH, 2 × C-3a′), 54.3 (2 × COO*C*H_3), 106.7 (2Cq, 2 × C≡N), 114.7 (2Cq), 116.5 (2CH, 2 × C-6′), 119.5 (2Cq), 122.6 (2CH, 2 × C-9′), 127.6 (2CH, 2 × C-7′), 128.6 (2Cq), 135.4 (2Cq), 137.9 (2Cq), 151.6 (2Cq, 2 × *C*$OOCH_3$), 178.9 (2Cq, 2 × C=O), 179.0 (2Cq, 2 × C=O); *m*/*z* (FD) 700.7 (100%).

8-Cyano-2-(4-maleimidobutanyl)-5-methoxycarbonyl-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazole-1,3-dione 6f. This compound was obtained from compound **2d** (1.1 g, 2.8 mmol) and *N*,*N*'-tetramethylenedimaleimide (347 mg, 1.4 mmol); yield 27% (179 mg), mp 92 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 1.34–1.48 (m, 4H, $2CH_2$, 1″-H, 4″-H), 3.04 (dd, 1H, *J* = 18.43, *J* = 8.35, CH_2-*H*, 10-H), 3.24–3.38 (m, 2H, $2CH_2$-*H*, 4-H, 10-H), 3.40–3.46 (m, 6H, 2CH, $2CH_2$, 10a-H, 3a-H, 1″-H, 4″-H), 3.92 (dd, 1H, *J* = 19.29, *J* = 2.10, CH_2-*H*, 4-H), 4.08 (s, 3H, COO*C*H_3), 6.64 (s, 2H, 2CH, 3‴-H, 4‴-H), 7.53 (dd, 1H, *J* = 8.70, *J* = 1.54, 7-H), 7.54 (d, 1H, *J* = 1.44, 9-H), 7.96 (d, 1H, *J* = 8.66, 6-H); δ_C (75 MHz, $CDCl_3$) 20.1 (CH_2, C-10), 23.2 (CH_2, C-4), 24.7 (CH_2), 26.3 (CH_2), 35.0 (CH_2), 36.48 (CH_2), 38.64 (CH, C-10a), 39.50 (CH, C-3a), 54.34 (COO*C*H_3), 106.9 (Cq, C≡N), 114.7 (Cq), 117.5 (CH, C-6), 119.5 (Cq), 121.9 (CH, C-9), 127.5 (CH, C-7), 128.6 (Cq), 134.1 (Cq), 134.2 (2CH, C-3‴, C-4‴), 134.8 (Cq), 151.7 (Cq, *C*$OOCH_3$), 170.4 (2Cq, C=O, C-2‴, C-5‴), 178.9 (Cq, C=O), 180.0 (Cq, C=O); *m*/*z* (EI) 474.5 ($M^{\bullet+}$, 4.79%), 319.2 (7.89), 276.5 (4.77), 250.5 (3.93), 218.5 (5.15), 205.6 (5.30), 168.8 (14.80), 148.6 (9.69), 98.6 (72.80), 69.3 (9.41).

1,12-Bis(8-cyano-5-methoxycarbonyl-1,3-dioxo-4,5,10,10a-tetrahydro-3a*H*-pyrrolo[3,4-*b*]carbazol-2-yl)dodecane 5l. This compound was obtained from compound **2d** (1.1 g, 2.8 mmol) and *N*,*N*'-dodecamethylenedimaleimide (505 mg, 1.4 mmol); yield 73% (831 mg), mp 82 °C (from EtAc); δ_H (300 MHz, $CDCl_3$) 0.94–1.02 (m, 16H [structure elements: 8 × CH_2], 3-H, 10-H, 5-H, 8-H, 4-H, 9-H, 6-H, 7-H), 1.35 (q, 4H, $2CH_2$, 2-H, 11-H), 2.88–2.96 (dd, 2H, 2 CH_2-*H*, 2 × 10′-CH_2-*H*), 3.21–3.34 (m, 4H, $4CH_2$-*H*, 2 × 10′-CH_2-*H*, 2 × 4′-CH_2-*H*), 3.31–3.41 (m, 8H, $2CH_2$, 4CH, 1-H, 12-H, 2 × 10a′-H, 2 × 3a′-H), 3.95 (dd, 2H, *J* = 17.40, *J* = 1.76, $2CH_2$-*H*, 2 × 4′-CH_2-*H*), 4.08 (s, 6H, $2COOCH_3$), 7.52 (dd, 2H, *J* = 8.65, *J* = 1.3, 2CH, 2 × 7′-H), 8.02 (d, 2H, *J* = 1.3, 2CH, 2 × 9′-H), 8.20 (d, 2H, *J* = 8.64, 2CH, 2 × 6′-H); δ_C (75 MHz, $CDCl_3$) 17.7 ($2CH_2$, 2 × C-10′), 20.9 ($2CH_2$, 2 × C-4′), 23.8 ($2CH_2$, C-3, C-10), 24.8 ($2CH_2$, C-2, C-11), 26.3 ($2CH_2$), 26.7 ($2CH_2$), 26.8 ($2CH_2$), 35.9 (2CH, 2 × C-10a′), 36.5 ($2CH_2$, C-1, C-12), 36.9 (2CH, 2 × C-3a′), 51.7 (2 × COO*C*H_3), 104.1 (2Cq, C≡N), 112.2 (2Cq), 113.8 (2CH, 2 × C-6′), 116.8 (2Cq), 119.8 (2CH, 2 × C-9′), 124.9 (2CH, 2 × C-7′), 125.9 (2Cq), 132.7 (2Cq), 135.2 (2Cq), 149.0 (2Cq, 2 × *C*$OOCH_3$), 176.35 (2Cq, 2 × C=O), 176.47 (2Cq, 2 × C=O); *m*/*z* (FD) 812.9 (100%).

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