Supplementary Information

Enhanced π-frustration in *carbo*-benzenic chromophores

Iaroslav Baglai,[a,b,c] Valérie Maraval,*[a,b] Christian Bijani,[a,b] Nathalie Saffon-Merceron,[b] Zoia Voitenko,[c] Yulian M. Volovenko[c] and Remi Chauvin*[a,b]

[a] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France. E-mail: vmaraval@lcc-toulouse.fr; chauvin@lcc-toulouse.fr; Fax: +33 (0)5 61 55 30 03; Tel: +33 (0)5 61 33 31 13.*

[b] *Université de Toulouse, UPS, INPT, F-31077 Toulouse, France.*

[c] *Kiev National Taras Shevchenko University, 60 Volodymlyrska St, 01033 Kiev, Ukraine.*

Experimental section.

General. THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane and dichloromethane over P_2O_5. All other reagents were used as commercially available. In particular, commercial solutions of *n*-BuLi were 2.5 M in hexane, solutions of ethylmagnesium bromide were 3 M in THF, solutions of HCl were 2 M in diethylether. Previously described procedures were used for the preparation of **2.**[4] All reactions were carried out under argon using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 P, 70-200 mm). Silica gel thin–layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20 %). The following analytical instruments were used. ^{1}H and ^{13}C NMR: Bruker DPX 300, Avance 300, Avance 400, Avance 400WB or Avance 500 spectrometers. Mass spectrometry: Quadrupolar Nermag R10-10H spectrometer. Most of the NMR spectra were recorded in $CDCl_3$ solutions. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants *J* are in Hz. UV: spectrometer Perkin-Elmer UV-Vis Win-Lab Lambda 35.

3-bromo-1-methyl-2-phenyl-1H-indole (**1**). To a solution of 1-ethyl-2-phenyl-1*H*-indole (1.0 g, 4.52 mmol) in $CHCl_3$ (50 mL) at 0 ˚C was added N-bromosuccinimide (0.845 g, 4.75 mmol) over 5 min in small portions. The mixture was stirred at the same temperature for 3 h. After evaporating the solvent, the residue was extracted with dichloromethane and washed with H_2O. The organic layer was separated and dried over $MgSO_4$ and the solvent was

removed under reduced pressure. After purification by chromatography over silica gel (acetone:pentane 5:95) pure **1** was isolated in 93 % yield (1.26 g). $R_f \approx 0.18$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 1 H, H_9-Ind), 7.53 (m, 5 H, *o*-,*m*-,*p*-Ph), 7.42 (d, J = 8.1 Hz, 1 H, H_6-Ind), 7.33 (t, J = 7.5 Hz, 1 H, H_7- or H_8-Ind), 7.27 (t, J = 7.2 Hz, 1 H, H_7- or H_8-Ind), 4.16 (q, J = 7.1 Hz, 2 H, CH_2), 1.27 (t, J = 7.1 Hz, 3 H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.6, 135.6 (C_2-, C_5- Ind), 130.8 (*i*-Ph), 130.6, 128.5(*m*-,*o*-Ph), 128.8 (*p*-Ph), 127.4 (C_4-Ind), 122.7, 120.5, 119.5 (C_7-, C_8-, C_9-Ind), 109.9 (C_6-Ind), 90.5 (C_3-Ind-Br), 39.5 (CH_2), 15.4 (CH_3). HRMS (DCI/CH_4): *m/z* calcd for $C_{16}H_{14}NBr$: 299.0310, found: 299.0320. M.p: 56 ˚C.

1-methyl-3-[10-(1-methyl-2-phenyl-1H-indol-3-yl)-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl]-2-phenyl-1H-indole (**4**). To a solution of 3-bromo-1-ethyl-2-phenyl-1H-indole **1** (168 mg, 0.56 mmol) in THF (15 mL) under stirring at -78 °C was added *n*-BuLi (192µl, 0.48 mmol). The reaction mixture was stirred during 1 hour at -78 °C before adding a solution of the [6]pericyclynedione **2** (136 mg, 0.2 mmol) in THF (3 mL). The temperature was allowed to increase slowly up to -20 °C over 3 h. After treatment with saturated aqueous NH_4Cl, the aqueous layer was extracted with diethylether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The obtained poorly stable [6]pericyclynediol **3** was directly used in the reduction step without further purification. The mixture was thus dissolved in DCM, before adding $SnCl_2$ (400 mg, 2.1 mmol) followed by a solution of HCl in diethylether (2.1 ml, 4.2 mmol) at – 78 °C. The reaction mixture was allowed to warm up to room temperature slowly, and the stirring was maintained for 30 min. before treatment with aqueous 1 M NaOH (4.4 mL, 4.4 mmol). After addition of brine, the aqueous layer was extracted with DCM. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography over silica gel (DCM:pentane 3:7) to give **4** as a green-gold solid in 3 % overall yield over two steps (6 mg).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.44 (d, J = 7.7 Hz, 2 H, H_9-Ind), 9.16 (d, J = 7.7 Hz, 8 H, *o*-Ph-C_{18}), 7.85 (m, 2 H, H_6-Ind), 7.83 (t, J = 7.7 Hz, 8 H, *m*-Ph-C_{18}), 7.73 (d, J = 7.0 Hz, 2 H, *o*-Ph-Ind), 7.65 (m, 6 H, *p*-Ph-C_{18}, H_7-Ind), 7.56 (t, J = 7.4 Hz, 2 H, H_8-Ind), 7.16 (m, 2 H, *p*-Ph-Ind), 7.10 (m, 4 H, *m*-Ph-Ind), 4.58 (q, J = 6.8 Hz, 4 H, CH_2), 1.63 (t, J = 6.8 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 142.0 (C_2-Ind), 140.1 (*i*-Ph-C_{18}), 139.8 (C_4-Ind), 137.5 (C_5-Ind), 131.9 (*o*-Ph-Ind), 130.7 (*i*-Ph-Ind), 130.0 (*o*-Ph-C_{18}), 129.4 (*m*-Ph-C_{18}), 129.1 (*p*-Ph-C_{18}), 128.9 (*m*-Ph-Ind), 128.5 (*p*-Ph-Ind), 123.7 (C_7-Ind), 121.9 (C_8-Ind), 120.2 (C_9-

Ind), 116.0 (C_3-Ind), 120.2, 117.26, 115.7, (C-*C*≡*C*-C, C=*C*=*C*=C), 110.6 (C_6-Ind), 102.5(*C*(C_{18})-Ph), 99.0 (*C*(C_{18})-Ind), 39.6 (*C*H_2), 15.3 (*C*H_3). MS (MALDI-TOF/DCTB): *m/z* = 964.3 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{74}H_{48}N_2$: 964.3817, found: 964.3875. UV-vis ($CHCl_3$): λ_{max} = 503 nm (ε = 40778 $L.mol^{-1}.cm^{-1}$), 242 nm. M.p. 264 °C.

1-ethyl-3-ethynyl-2-phenyl-1H-indole (5): three-step synthesis.

1) **1-ethyl-3-iodo-2-phenyl-1*H*-indole.**

To a solution of 1-ethyl-2-phenyl-1*H*-indole (0.5 g, 2.26 mmol) in $CHCl_3$ (30 mL) at 0 ˚C was added N-iodosuccinimide (0.535 g, 2.37 mmol) over 5 min in small portions. The mixture was stirred at the same temperature for 3 h. After evaporation of the solvent, the residue was extracted with dichloromethane and washed with H_2O. The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure. After purification by chromatography over silica gel (acetone:pentane 2:98), pure 1-ethyl-3-iodo-2-phenyl-1*H*-indole was isolated in 92 % yield (0.72 g).

^{1}H NMR ($CDCl_3$) δ 7.59 - 7.44 (m, 6 H, H_9-Ind, *o-,m-,p*-Ph), 7.39 - 7.22 (m, 3 H, H_6-, H_7-, H_8-Ind), 4.16 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.26 (t, *J* = 7.2 Hz, 3 H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4 (C_2-Ind), 136.5 (C_5-Ind), 132.0 (*i*-Ph), 130.8 (*m*-Ph), 130.6 (C_4-Ind), 128.9 (*p*-Ph), 128.5 (*o*-Ph), 122.8, 121.6, 120.6, (C_7-, C_8-, C_9-Ind), 110.0 (C_6-Ind), 59.5 (C_3-Ind-I), 39.9 (*C*H_2), 15.5 (*C*H_3). HRMS (DCI/CH_4): *m/z* calcd for $C_{16}H_{14}NI$: 347.0171, found: 347.0165. M.p. 93 ˚C.

2) **1-ethyl-2-phenyl-3-[2-(trimethylsilyl)ethynyl]-1*H*-indole**

CuI (42 mg, 0.21 mmol) and $Pd(PPh_3)_2Cl_2$ (60 mg, 0.09 mmol) were added to 1-ethyl-3-iodo-2-phenyl-1*H*-indole (1.04 g, 3.0 mmol) under Argon. Then, freshly distilled diisopropylamine (15 mL) was added and the mixture was stirred for 20 min before adding $Me_3SiC{\equiv}CH$ (1.0 ml, 6.52 mmol) and stirring the suspension for 60 h at room temperature before. Then, diethylether (20 mL) was added and the mixture was filtrated through Celite. The filtrate was evaporated and the residue was dissolved in Et_2O, washed with 10 % aqueous HCl, water, and $NaHCO_3$. The resulting organic solution was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the brown residue was purified by chromatography over silica gel (ether:pentane 1:99) to give 1-ethyl-2-phenyl-3-[2-(trimethylsilyl)ethynyl]-1*H*-indole in 56 % yield (0.53 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 1 H, H_9-Ind), 7.72 (d, *J* = 7.9 Hz, 2 H, *o*-Ph), 7.61- 7.33 (m, 6 H, H_6-, H_7-, H_8-Ind, *m-,p*-Ph), 4.26 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.38 (t, *J*

= 7.1 Hz, 3 H, CH_3), 0.34. (s, 9 H, TMS). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.3 (C_2-Ind), 135.9 (C_5-Ind), 131.1 (*i*-Ph), 130.2 (*m*-Ph), 129.4 (C_4-Ind), 128.6 (*p*-Ph), 128.4 (*o*-Ph), 122.9, 120.9, 120.3 (C_7-, C_8-, C_9-Ind), 110.2 (C_6-Ind), 100.0, 97.4, 96.4 (C_3-Ind, -*C*≡*C*-), 39.3 (*C*H_2), 15.3 (*C*H_3), 0.43 (Si(*C*H_3)$_3$). HRMS (DCI/CH_4): *m/z* calcd for $C_{21}H_{23}NSi$: 317.1600, found: 317.1614. M.p. 86 ˚C.

3) **1-ethyl-3-ethynyl-2-phenyl-1*H*-indole** (**5**)

K_2CO_3 (0.3 g, 2.16 mmol) was added to a solution of 1-ethyl-2-phenyl-3-[2-(trimethylsilyl)ethynyl]-1*H*-indole (0.23 g, 0.72 mmol) in methanol (20 mL) at room temperature. The resulting suspension was stirred 24 h, then saturated NH_4Cl (10 mL) was added and the mixture was concentrated under reduced pressure to remove methanol. After addition of diethyl ether (30 mL), the organic layer was washed with saturated NH_4Cl, brine, dried over $MgSO_4$ and concentrated to give pure **5** in 90 % yield (0.16 g).
^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1 H, H_9-Ind), 7.66 (d, *J* = 8.0 Hz, 2 H, *o*-Ph), 7.61-7.46 (m, 4 H, *m*-,*p*-Ph, H_6-Ind), 7.35 (dt, *J* = 20.3, 7.2 Hz, 2 H, H_7-, H_8-Ind), 4.22 (q, *J* = 7.1 Hz, 2 H, CH_2), 3.20 (s, 1 H, C≡C-*H*), 1.36 (t, *J* = 7.2 Hz, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.4 (C_2-Ind), 135.7 (C_5-Ind), 131.0 (*i*-Ph), 130.1 (*m*-Ph), 129.5 (C_4-Ind), 128.8 (*p*-Ph), 128.6 (*o*-Ph), 122.9, 120.9, 120.1, (C_7-, C_8-, C_9- Ind), 110.2 (C_6-Ind), 96.6 (C_3-Ind), 79.3 (≡*C*-H), 78.3 (≡*C*-Ind), 39.2 (*C*H_2), 15.3 (*C*H_3). HRMS (DCI/CH_4): *m/z* calcd for $C_{18}H_{15}N$: 245.1204, found: 245.1210. M.p.79 ˚C.

1,10-bis[2-(1-ethyl-2-phenyl-1*H*-indol-3-yl)ethynyl]-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (**6**).

n-BuLi (0.68 mL, 1.7 mmol) was added to a solution of HMDS (0.38 mL, 1.8 mmol) in THF (20 mL) under stirring at -78 °C. The mixture was stirred during 30 minutes at -78 °C before adding a solution of **5** (210 mg, 0.86 mmol) in THF (3 mL). The reaction mixture was stirred during 30 minutes at -78 °C before adding of [6]pericyclynedione **2** (194 mg, 0.29 mmol) in THF (5 mL). The temperature was slowly increased up to - 45°C over 1 hour before adding saturated aqueous NH_4Cl. The aqueous layer was extracted with diethylether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography over silica gel (EtOAc:pentane 4:6) to give the [6]pericyclynediol **6** as a light solid in 61 % yield (210 mg).
^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.20 (m, 38 H, *H*ar), 4.26- 4.18 (m, 4 H, CH_2), 3.73- 3.28 (m, 14 H, CH_3-O, O*H*), 1.41-1.28 (m, 6 H, CH_3-CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ

145.0 (C_2-Ind), 139.6 (*i*-Ph-C_{18}), 135.9 (C_5-Ind), 130.4 (*i*-Ph-Ind), 129.7, 129.2, 129.0, 128.8 (*o*-,*m*-,*p*-Ph-Ind), 128.5 (*m*-,*p*-Ph-C_{18}), 126.6 (*o*-Ph-C_{18}), 123.0, 121.1, 120.0 (C_7-, C_8-, C_9-Ind), 110.3 (C_6-Ind), 95.0 (C_3-Ind), 88.0, 85.2, 85.0, 84.4, 79.5 (-*C*≡*C*-), 71.9 (*C*-OMe), 55.0 (*C*-OH), 53.5 (O-CH_3), 39.3 (CH_2Me), 30.35, 15.27 (CH_3). HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{82}H_{62}N_2O_6Na$ $[MNa]^+$: 1193.4506, found: 1193.4419. M.p. 123 ˚C.

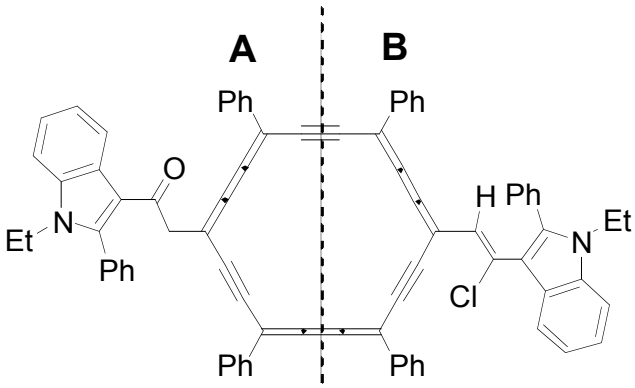
3-(1-chloro-2-{10-[2-chloro-2-(1-ethyl-2-phenyl-1*H*-indol-3-yl)ethenyl]-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}ethenyl)-1-ethyl-2-phenyl-1H-indole (8)

To a solution of **6** (110 mg, 0.1 mmol) in dry dichloromethane (30 mL) at -78 °C were added $SnCl_2$ (190 mg, 1.0 mmol) and then $HCl{\cdot}Et_2O$ (1.0 mL, 2.0 mmol). The temperature of the reaction mixture was slowly increased up to -10 °C in 3 hours. Then aqueous 1 M NaOH (2.2 mL, 2.2 mmol) was added. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography over silica gel (DCM:pentane 3:7) to give the three *carbo*-benzenic products **8**, **9** and **10** in 7 % global yield (based on **8**).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.41 (d, J = 7.2 Hz, 8 H, *o*-Ph-C_{18}), 8.47 (d, J = 6.9 Hz, 2 H, H_9-Ind), 8.39 (s, 2 H, (*H*C=C-Cl), 7.97-7.92 (m, 8 H, *m*-Ph-C_{18}), 7.89 (d, J = 7.0 Hz, 4 H, *o*-Ph-Ind), 7.75-7.70 (m, 4 H, *p*-Ph-C_{18}), 7.68 (d, J = 7.4 Hz, 2 H, H_6-Ind), 7.64-7.59 (m, 4 H, *m*-Ph-Ind), 7.52-7.48 (m, 6 H, H_7-, H_8-Ind, *p*-Ph-Ind), 4.36 (q, J = 7.0 Hz, 4 H, CH_2), 1.49 (t, J = 7.2 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 141.2 (C_2-Ind), 140.2 (*i*-Ph-C_{18}), 136.4 (C_4-Ind), 136.2 (C_5-Ind), 131.8 (HC=*C*-Cl) 131.6 (*i*-Ph-Ind),130.9 (*o*-Ph-Ind) 130.6 (*p*-Ph-Ind), 130.0 (*o*-Ph-C_{18}), 129.8 (*m*-Ph-C_{18}), 129.6 (*p*-Ph-C_{18}), 129.1 (*m*-Ph-Ind), 128.1 (H*C*=C-Cl), 122.9 (C_7-Ind), 121.3 (C_8-Ind), 120.6 (C_9-Ind), 120.0, 119.5, 118.7 (C-*C*≡*C*-C, C=*C*=*C*=C), 114.5 (C_3-Ind), 110.6 (C_6-Ind), 104.0 (*C*(C_{18})-Ph), 100.05 (*C*(C_{18})-CH=), 39.2 (CH_2), 15.2 (CH_3). UV-vis ($CHCl_3$): λ_{max} = 243, 514 nm. MS (MALDI-TOF/DCTB): *m/z*: 1084.4 $[M]^+$.

2-{10-[2-chloro-2-(1-ethyl-2-phenyl-1H-indol-3-yl)ethenyl]-4,7,13,16-tetraphenylcyclo-octadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}-1-(1-ethyl-2-phenyl-1H-indol-3-yl)ethan-1-one (**9**)

Isolated upon purification of **8** by chromatography over silica gel).



^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.48 (d, J = 7.8 Hz, 4 H, *o*-Ph-C_{18}B), 9.32 (d, J = 7.8 Hz, 4 H, *o*-Ph-C_{18}A), 9.15 (m, 1 H, H_9-IndA), 8.48 (m, 2 H, H_9-IndB, *H*C=C-Cl), 7.97(m, 4 H, *m*-Ph-C_{18}B), 7.96 (m, 2 H, *p*-Ph-C_{18}A), 7.90 (m, 4 H, *m*-Ph-C_{18}A) 7.89 (m, 2 H, *o*-Ph-IndB), 7.73 (m, 2 H, *p*-Ph-C_{18}B), 7.68 (m, 1 H, H_6-IndB), 7.63 (m, 2 H, *m*-Ph-IndB), 7.58 (m, 1 H, H_6-IndA), 7.57 (m, 1 H, H_8-IndA), 7.52 (m, 2 H, H_7-IndA, H_7-IndB), 7.50 (m, 1 H, *p*-Ph-IndB), 7.49 (m, 1 H, H_8-IndB), 7.32 (m, 2 H, *o*-Ph-IndA), 7.22 (m, 1 H, *p*-Ph-IndA), 7.13 (m, 2 H, *m*-Ph-IndA), 5.44 (s, 2 H, CH_2-C=O), 4.36 (q, J = 6.8 Hz, 2 H, CH_2-NB), 3.93 (q, J = 7.2 Hz, 2 H, CH_2-NA), 1.50 (t, J = 7.1 Hz, 3 H, CH_3B), 1.13 (t, J = 7.3 Hz, 3 H, CH_3A). ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ 191.6 (*C*=O), 147.3, C_2-IndA), 141.2 (C_2-IndB), 140.5 (*i*-Ph-C_{18}B), 140.2 (*i*-Ph-C_{18}A),136.3 (C_5-IndB), 136.2 (C_4-IndA), 135.9 (C_5-IndA), 135.0 (C_4-IndB) 131.6 (*i*-Ph-IndA, *i*-Ph-IndB), 130.8 (*o*-Ph-IndB), 130.5 (*p*-Ph-IndB), 130.4 (*p*-Ph-IndA), 130.2 (*o*-Ph-IndA), 130.1 (=*C*-Cl), 130.0 (*o*-Ph-C_{18}A), 129.9 (*o*-Ph-C_{18}B), 129.7 (*m*-Ph-C_{18}B), 129.6 (*m*-,*p*-Ph-C_{18}A), 129.4 (*p*-Ph-C_{18}B), 129.1 (*m*-Ph-IndB), 129.0 (*C*=C-Cl), 128.8 (*m*-Ph-IndA), 123.6 (C_7-IndA), 123.5 (C_9-IndA), 123.2 (C_8-IndA), 123.0 (C_7-IndB), 122.1 (C_3-IndA), 121.3 (C_8-IndB), 120.6 (C_9-IndB), 120.2, 119.0, 118.9, 117.6, 117.3, 117.0 (C-*C*≡*C*-C, C=*C*=*C*=C), 114.5 (C_3-IndB), 110.5 (C_6-IndB), 110.3 (C_6-IndA), 104.0 (*C*(C_{18}A)-Ph, *C*(C_{18}B)-Ph), 100.7 (*C*(C_{18})-CH_2), 100.0 (*C*(C_{18})-CH=), 51.2 (*C*H_2-CO), 39.3 (*C*H_2-N(B)), 39.1 (*C*H_2-N(A)), 15.2 (*C*H_3(B)), 15.0 (*C*H_3(A)). UV-vis ($CHCl_3$): λ_{max} = 242, 482 nm. MS (MALDI-TOF/DCTB): *m/z*: 1066.3 $[M]^+$.

1-(1-ethyl-2-phenyl-1H-indol-3-yl)-2-{10-[2-(1-ethyl-2-phenyl-1H-indol-3-yl)-2-oxoethyl]-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}ethan-1-one (**10**).

Isolated upon purification of **8** by chromatography over silica gel.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.38 (d, J = 7.2 Hz, 8 H, *o*-Ph-C_{18}), 9.15 (d, J = 6.9 Hz, 2 H, H_9-Ind), 7.91 (m, 8 H, *m*-Ph-C_{18}), 7.71 (m, 4 H, *p*-Ph-C_{18}), 7.58 (m, 2 H, H_8-Ind), 7.54 (m, 2 H, H_6-Ind), 7.52 (m, 2 H, H_7-Ind), 7.32 (m, 4 H, *o*-Ph-Ind), 7.21 (m, 2 H, *p*-Ph-Ind), 7.10 (m, 4 H, *m*-Ph-Ind), 5.56 (s, 4H, CH_2-CO), 3.93 (m, 4 H, CH_2-N), 1.19 (t, J = 7.2 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_2$) δ 191.6 (C=O), 147.2 (C_2-Ind), 139.5 (*i*-Ph-C_{18}), 136.1 (C_4-Ind), 136.0 (C_5-Ind), 130.3 (*i*-Ph-Ind), 130.2 (*o*-Ph-Ind), 130.1 (*p*-Ph-Ind), 130.0 (*o*-Ph-C_{18}), 129.7 (*m*-Ph-C_{18}), 129.5 (*p*-Ph-C_{18}), 128.8 (*m*-Ph-Ind), 123.7 (C_7-Ind), 123.3 (C_8-Ind), 123.2 (C_9-Ind), 122.0 (C_3-Ind), 119.2, 118.4, 115.8 (C-C≡C-C, C=C=C=C), 110.2 (C_6-Ind), 103.7 (C(C_{18})-Ph), 100.5 (C(C_{18})-CH_2), 51.3 (CH$_2$-CO), 39.1 (CH$_2$-N), 14.9 (CH$_3$). UV-vis ($CHCl_3$): λ_{max} = 241, 451 nm. MS (MALDI-TOF/DCTB): *m/z*: 1048.3 $[M]^+$.

Crystallographic data

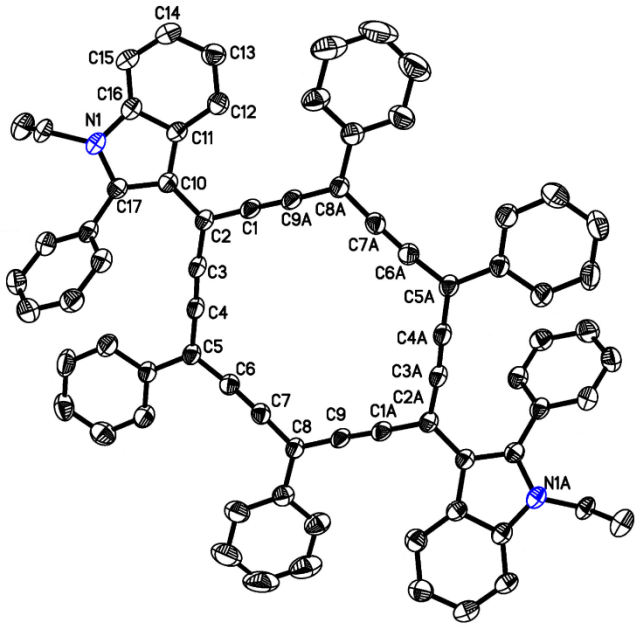
The data of the structures for compounds **4** and **8** were collected on a Bruker-AXS Quazar APEX II diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics at a temperature of 193(2)K, with MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[1,2] The structures were solved by direct methods, using SHELXS-97 and refined using the least–squares method on F^2.[3] All non-H atoms were treated anisotropically. All H atoms attached to C atoms were fixed geometrically and treated as riding on their parent atoms with C-H = 0.95 Å (aromatic), 0.98 Å (CH_3), 0.99 Å (CH_2) or 1.0 Å (CH) with U_{iso}(H) = 1.2U_{eq}(CH, CH_2) or U_{iso}(H) = 1.5U_{eq}(CH_3).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–936754 (**4**) and CCDC–936755 (**8**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[1] SAINT-NT; Bruker AXS Inc.:Madison, Wisconsin, 2000.
[2] SADABS, Program for data correction, Bruker−AXS.
[3] SHELXL−97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, Acta Crystallogr., Sect.A **2008**, *64*, 112-12.

Selected crystal data

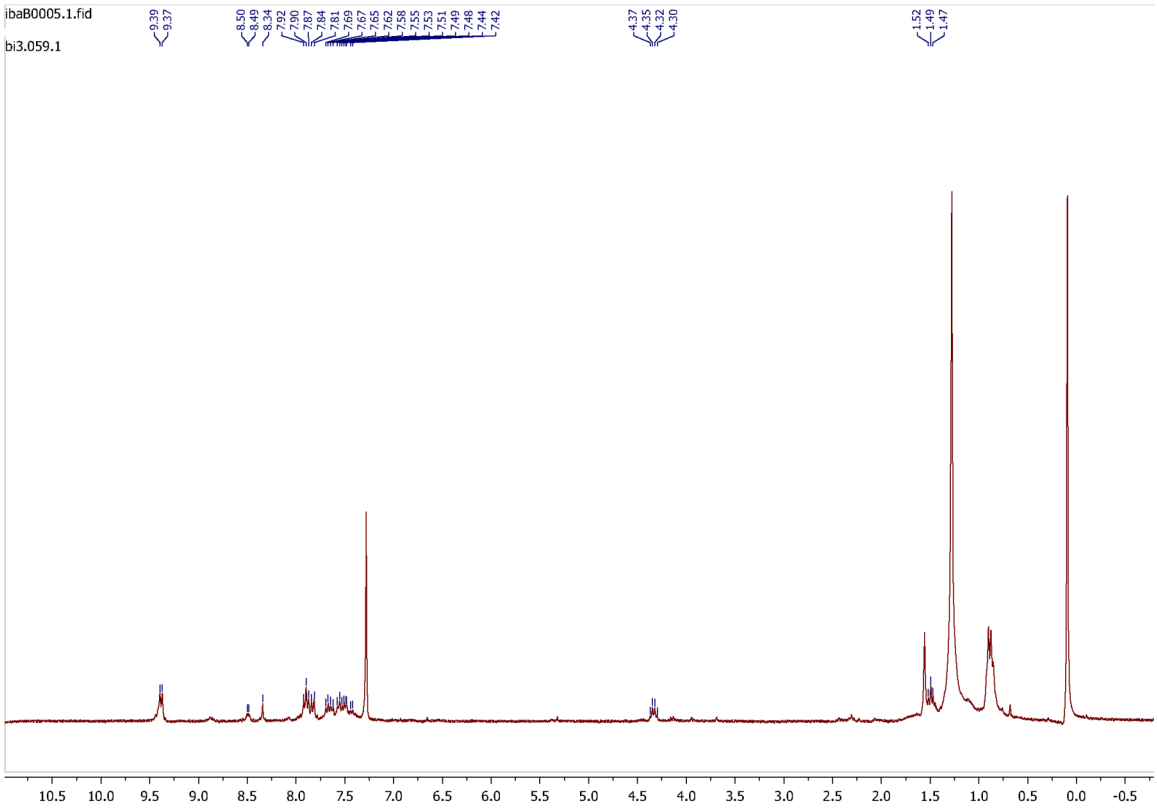
4 (CCDC–936754): $C_{74}H_{48}N_2$, M = 965.14, Monoclinic, space group P2(1)/c, a = 9.095(2) Å, b = 26.610(7) Å, c = 11.307(3) Å, V = 2565.3(12) Å^3, Z = 2, crystal size 0.26 x 0.20 x 0.02 mm^3, 41058 reflections collected (5197 independent, R_{int} = 0.1136), 344 parameters, 0 restraints, $R1[I>2\sigma(I)]$ = 0.0596, *wR2* [all data] = 0.1572, largest diff. peak and hole: 0.287 and -0.204 e.Å^{-3}. Detail of the molecular view shown in Fig. 2:



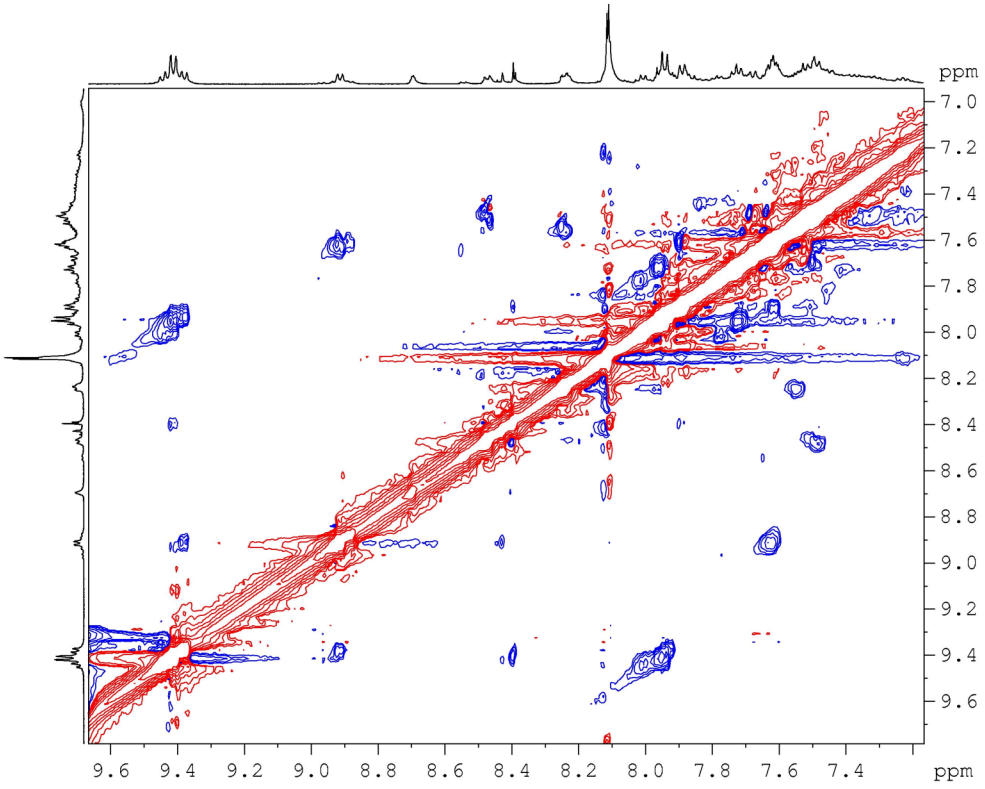
8 (CCDC–936755): $C_{79.50}H_{51.50}C_{l6.50}N_2$, M = 1265.15, Triclinic, space group P-1, a = 12.939(6) Å, b = 15.040(7) Å, c = 18.094(8) Å, V = 3301(3) Å^3, Z = 2, crystal size 0.22 x 0.03 x 0.02 mm^3, 63465 reflections collected (10737, R_{int} = 0.1520), 887 parameters, 157 restraints, $R1[I>2\sigma(I)]$ = 0.0884, *wR2* [all data] = 0.2965, largest diff. peak and hole: 0.809 and -0.373 e.Å^{-3}. Molecular view of **8**: see Fig. 3.

Selected NMR data

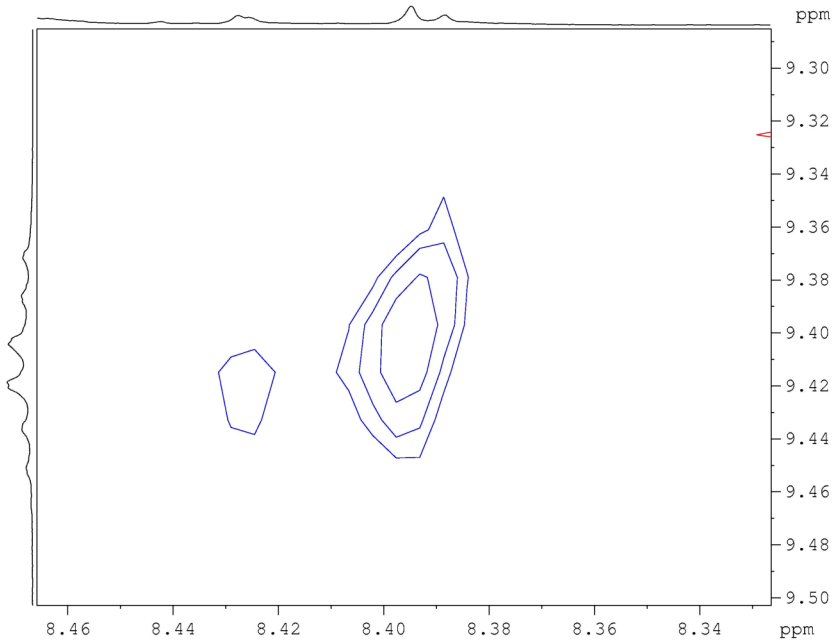
Full ^{1}H NMR spectrum of **8**:



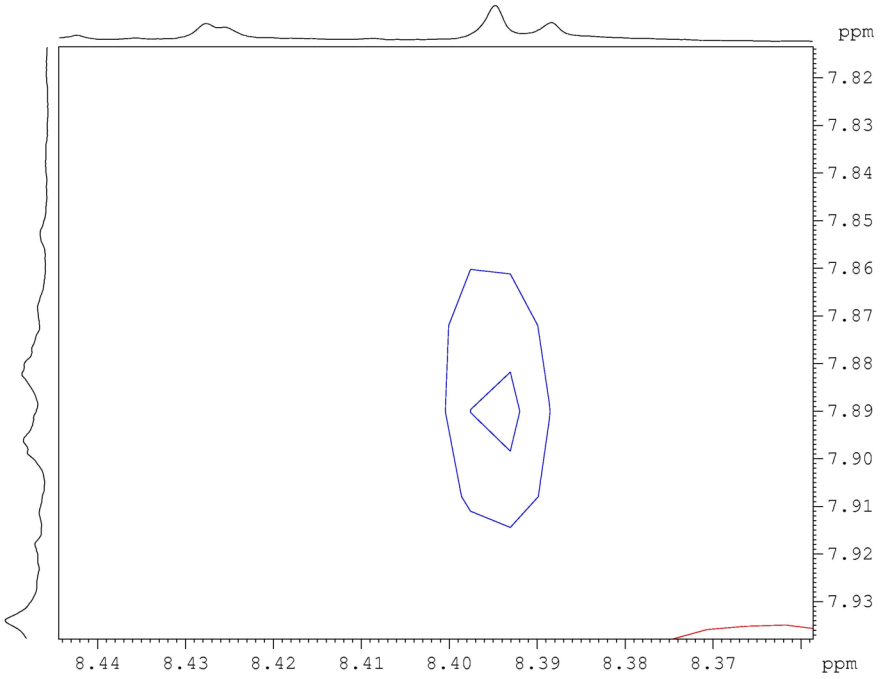
Global view of the aromatic region in the ROESY spectrum of **8**:



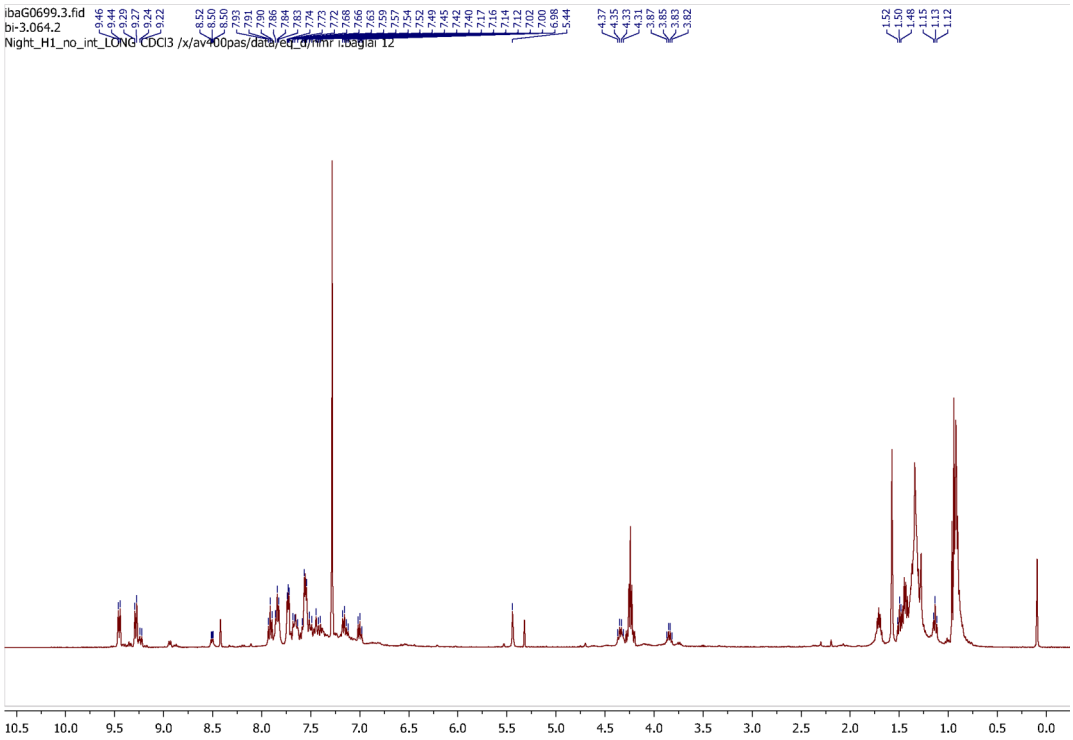
Detail of the ROESY spectrum of **8**: correlation between the ethylenic protons at 8.39 ppm and the *ortho* protons of the phenyl substituents of the macrocycle at 9.41 ppm:



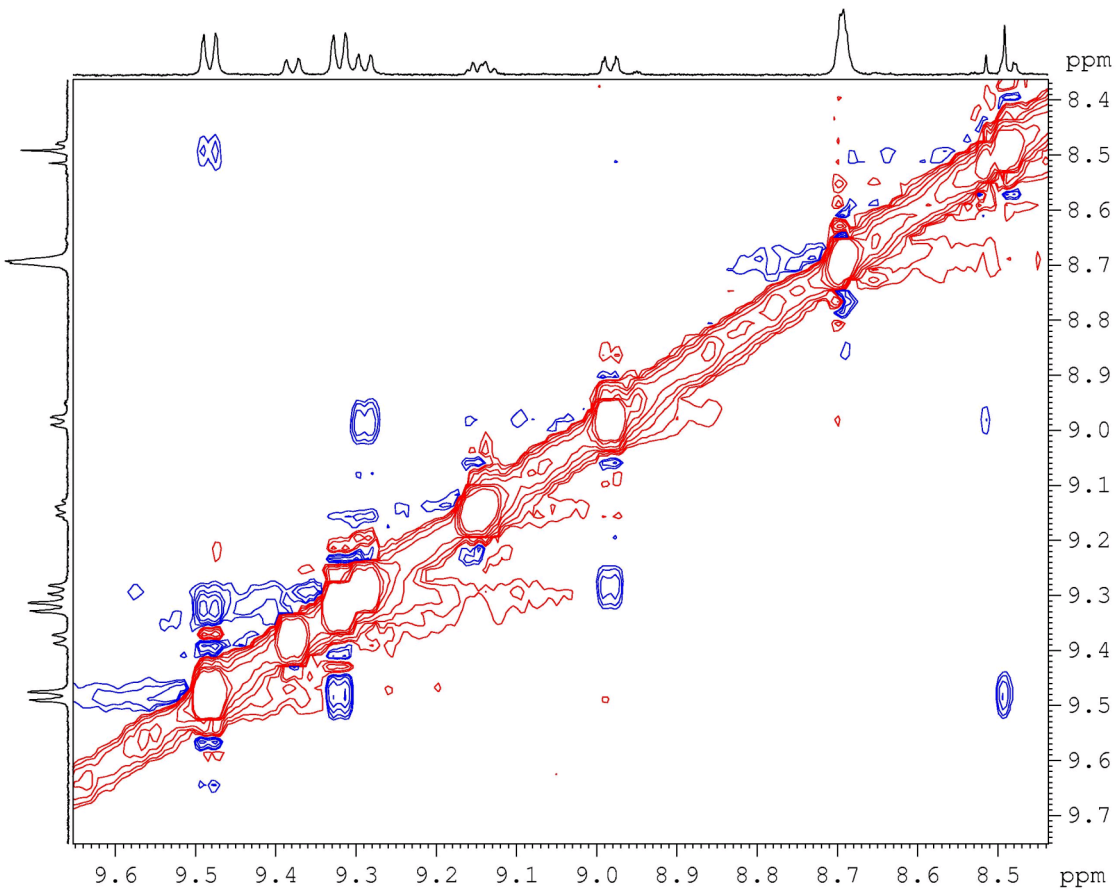
Detail of the ROESY spectrum of **8**: correlation between the ethylenic protons at 8.39 ppm and the *ortho* protons of the phenyl substituent at the C_2 position of the indole at 7.89 ppm:



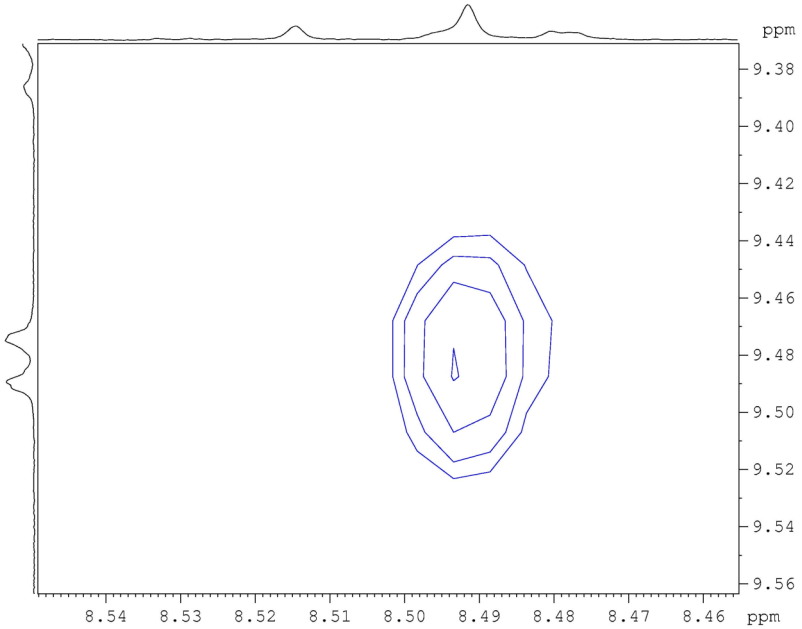
Full ^{1}H NMR spectrum of **9**:



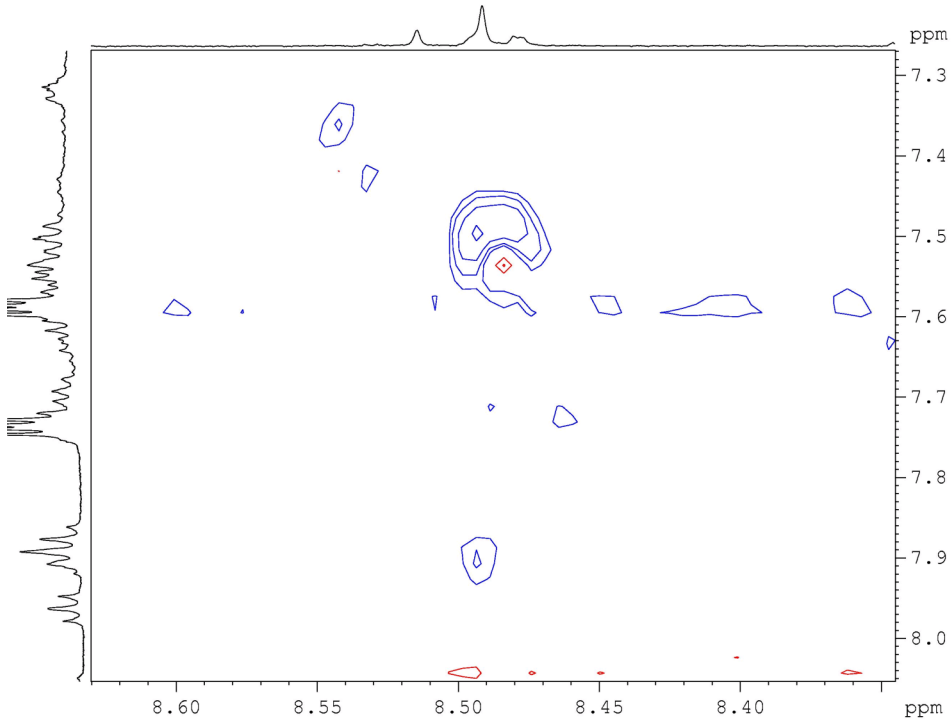
Global view of the aromatic region in the ROESY spectrum of **9**:



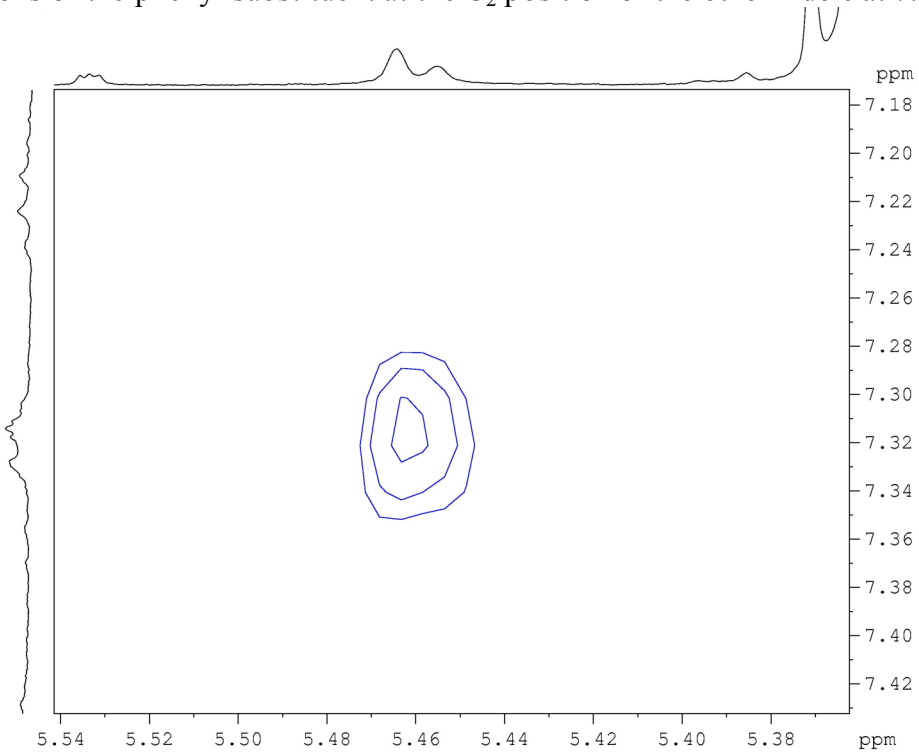
Detail of the ROESY spectrum of **9**: correlation between the ethylenic protons at 8.48 ppm and the *ortho* protons of the phenyl substituents of the macrocycle at 9.48 ppm:



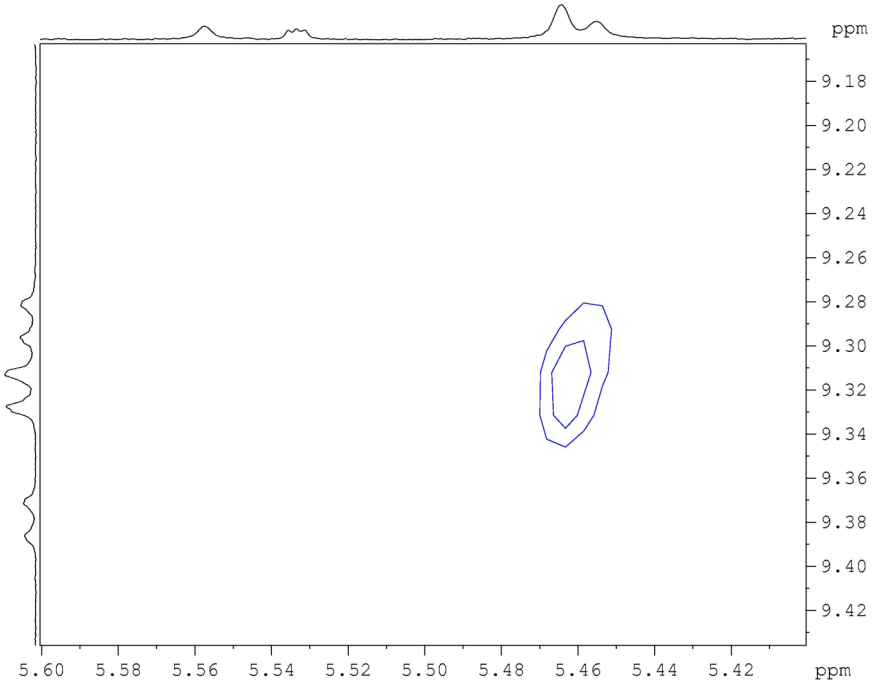
Detail of the ROESY spectrum of **9**: correlation between the ethylenic protons at 8.48 ppm and the *ortho* protons of the phenyl substituent at the C_2 position of the indole at 7.89 ppm:



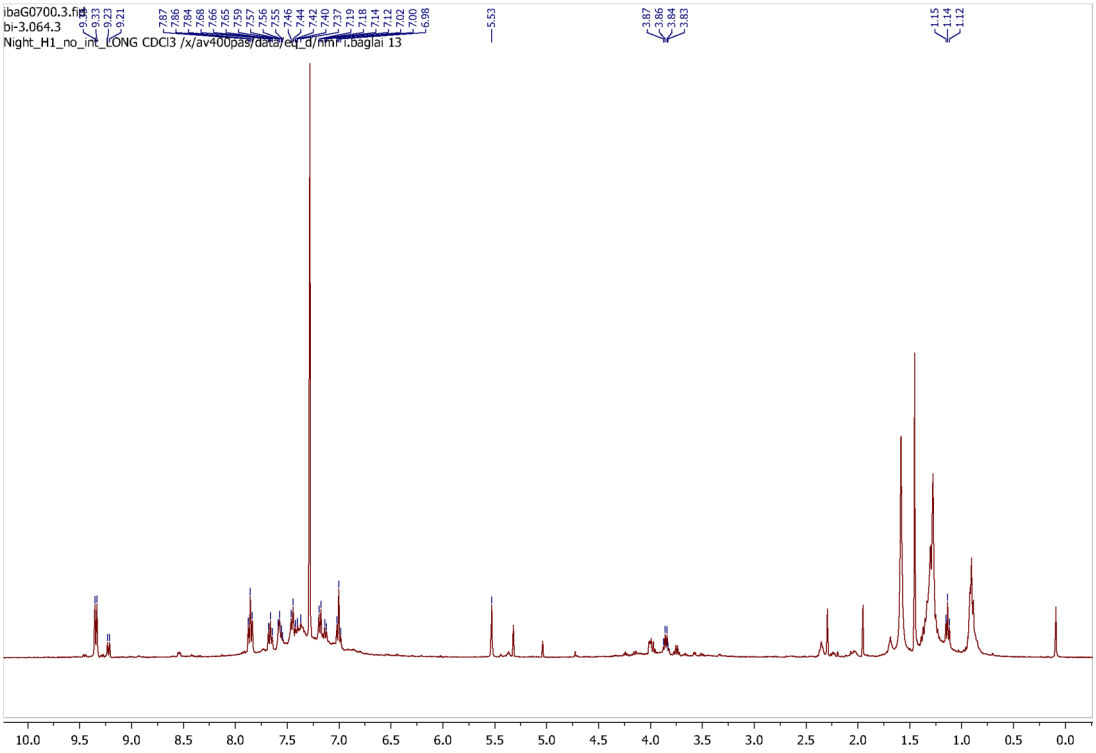
Detail of the ROESY spectrum of **9**: correlation between the CH_2-C=O at 5.44 ppm and the *ortho* protons of the phenyl substituent at the C_2 position of the other indole at 7.32 ppm:



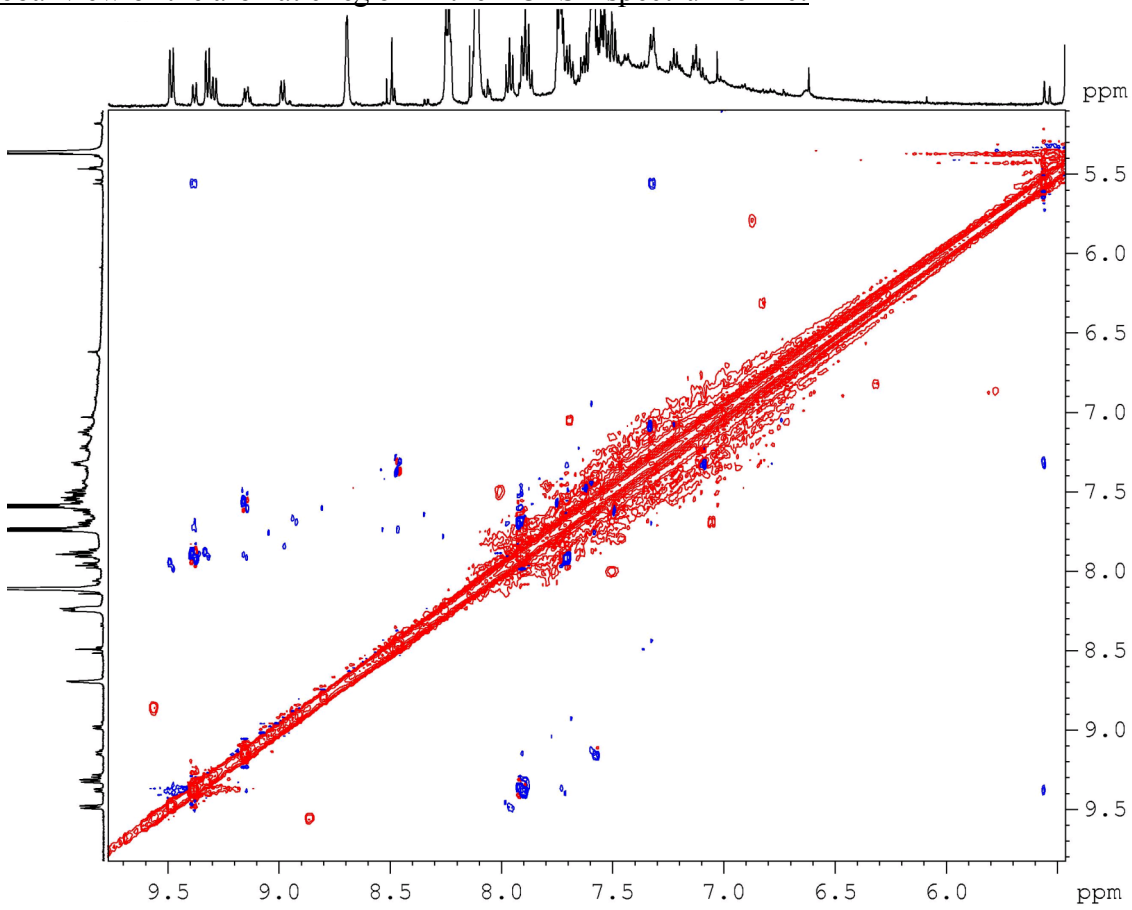
Detail of the ROESY spectrum of **9**: correlation between the CH_2-C=O at 5.44 ppm and the *ortho* protons of the phenyl substituents of the macrocycle at 9.32 ppm:



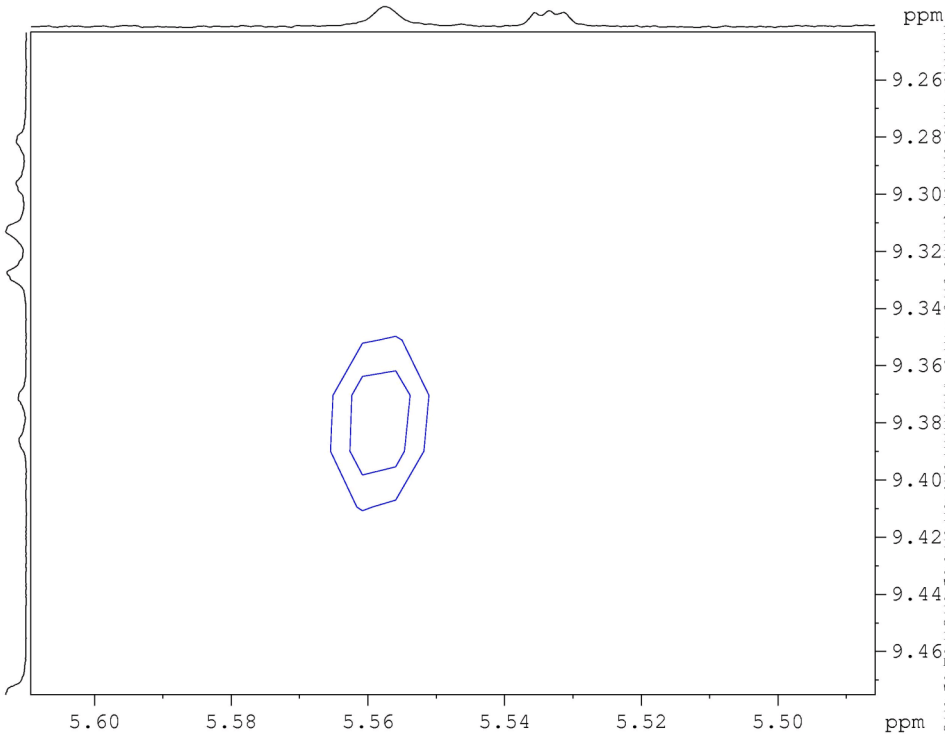
Full ^{1}H NMR spectrum of **10**:



Global view of the aromatic region in the ROESY spectrum of **10**:



Detail of the ROESY spectrum of **10**: correlation between the CH_2-C=O at 5.56 ppm and the *ortho* protons of the phenyl substituents of the macrocycle at 9.38 ppm:



Detail of the ROESY spectrum of **10**: correlation between the CH_2-C=O at 5.56 ppm and the *ortho* protons of the phenyl substituent at the C_2 position of the other indole at 7.32 ppm: