Cycloaddition of (*E*)-*N*-[2-([2.2]paracyclophan-4-yl)ethylidene] methylamine-*N*-oxide with 2,3-diphenylcyclopropenones and dibenzoyl acetylene; synthesis of new paracyclophanylpyrroles

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When *N*-[2-([2.2]paracyclophan-4-yl)ethylidene]methylamine-*N*-oxide (**1**) is treated with cyclopropenones **6a–c**, the [2.2]paracyclophane-based pyrrole(-2-one, -thione and -ylidene malnonitrile) **7a–c** are formed in good yields via formal [3π + 3π]cycloaddition. The reaction of **1** with dibenzoyl acetylene (**12**) afforded, via a Michael-type reaction, the stereoisomeric pyrrole **13**. The reaction mechanism described the products formation is discussed.

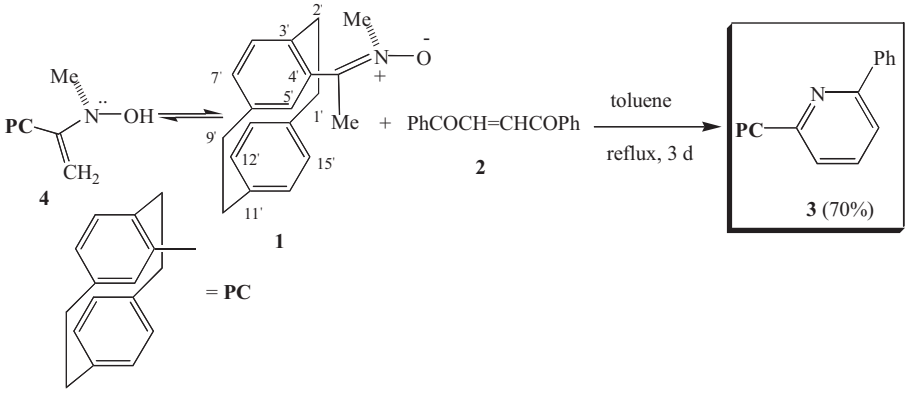
Keywords: paracyclophanyl-nitrone, cyclopropenones, dibenzoyl acetylene, pyrroles

Chiral paracyclophanyl substitutents are growing in importance as ligands and auxiliaries in asymmetric synthesis,[1] derivatives of this class of layered compounds reported in the literature is increasing rapidly.[2,3] For a long time, paracyclophanyl derivatives were mostly studied because of their unusual geometry, their steric, transannular, and ring strain effects as well as the electronic interaction between their aromatic rings.[4,5] Recently, the stereochemical properties of these systems especially their planar chirality have been the focus of studies in this field. In particular, paracyclophanyl derivatives carrying a nitrogen atom in the 4-position are of growing interest as auxiliaries.[6,7] These derivatives having substituted amino functions have also been shown to be useful as effective photoconductive components.[8] Cycloaddition reactions still play an important part in the synthesis of various classes of polycyclic and/or heterocyclic compounds derived and/or fused to the [2.2]paracyclophane moiety.[9] Our initial studies on the chemistry of **(***E***)**-*N*-[2-([2.2]paracyclophan-4-yl)ethylidene]methylamine-*N*-oxide (**1**) were studied towards dibenzoylethylene (**2**) and the corresponding paracyclophanyl-phenylpyridine **3** was obtained.[10] Furthermore, aldehydic nitrone as in *N*[2.2(paracyclophan-4-yl)methylylene]methylamine-*N*-oxide yielded various classes of five-member heterocyclic rings (imidazole, isoxazole and pyrrole derivatives of PC), when it was allowed to react with various dipolarophiles.[11] It has been shown that the use of cyclopropenone chemistry is of systematic interest in constructing a wide variety of heterocycles.[12] Recently, Aly *et al.* has reported on the synthesis of pyridazinethiones and [1,2,4]triazolo[4,3-*b*]pyridazinethiones from the reaction of thiosemicarbazides with 2,3-diphenylcyclopropenone.[13] On the basis that the reactivity of the target nitrone **1** is varied from one dipolarophile to another,[9b,10,11] we decided to reinvestigate its chemical behaviour with other types of dipolarophiles such as cyclopropenones and dibenzoyl acetylene.

Results and discussion

Nitrones are a well-studied class of 1,3-dipoles that react with numerous unsaturated systems,[14] among them 1,2-dibenzoylacetylene,[15] to yield the corresponding isoxazolidine derivatives, usually under mild conditions and in good yield. Diphenylcyclopropenone has been found to react with a wide range of imines and other compounds containing the C=N moiety, usually to form azacyclopentenones (pyrrolinones) *via* a formal [2π + 3π]cycloaddition reactions.[16-18] In view of our previous results,[10] we expected another pyridine skeleton from the reaction between **1** and cyclopropenones **6a**–**c**. To our surprise, on heating the two compounds together, we in fact obtained 1,5-dimethyl-3,4-diphenyl-5-([2.2]paracyclophan-4-yl)-1,5-dihydropyrrol-2-(one, thione or propenylidene malnonitrile) **7a**–**c** in good yields along with diphenyl acetylene (**8**) (Scheme 2). The structure elucidation of these unusual adducts rests primarily on their ^{1}H and ^{13}C NMR spectra, which were fully assigned by the techniques mentioned above.

During the course of reaction, thin layer analyses indicated that the reaction was completed when one equivalent of **1** reacted with two equivalents from **6a**–**c** (Scheme 2). The proton signals of the paracyclophanyl moiety were analysed by COSY H H, C H and NOE experiments. The points of attachment of the paracyclophanyl and pyrrole follow from the cross-peaks in the COSY H H and C H spectra. NOE experiments were done between the two methyl groups along with the methyl protons in position 5 and H-5' of the paracyclophanyl moiety.



Scheme 1

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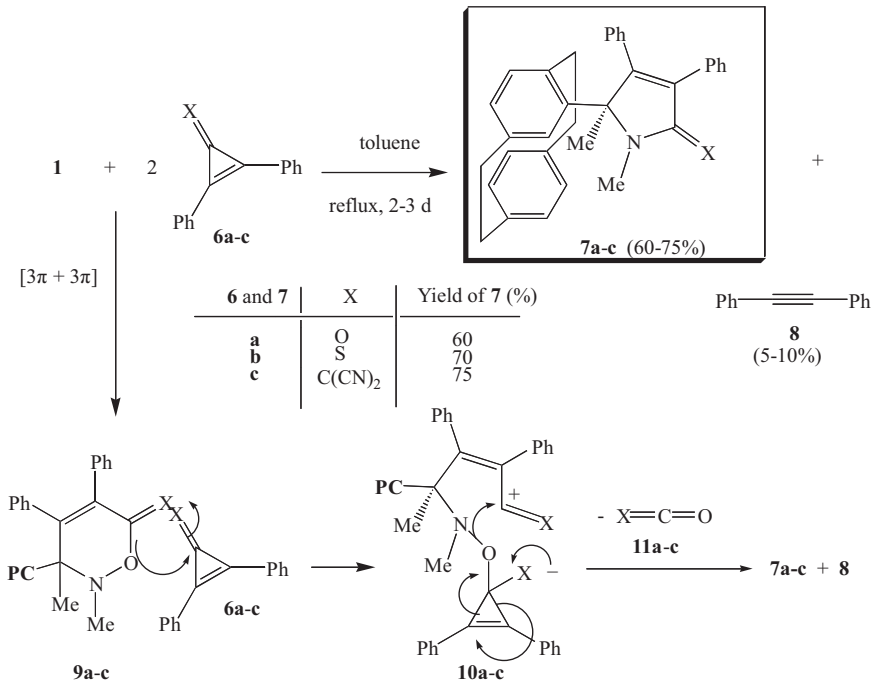


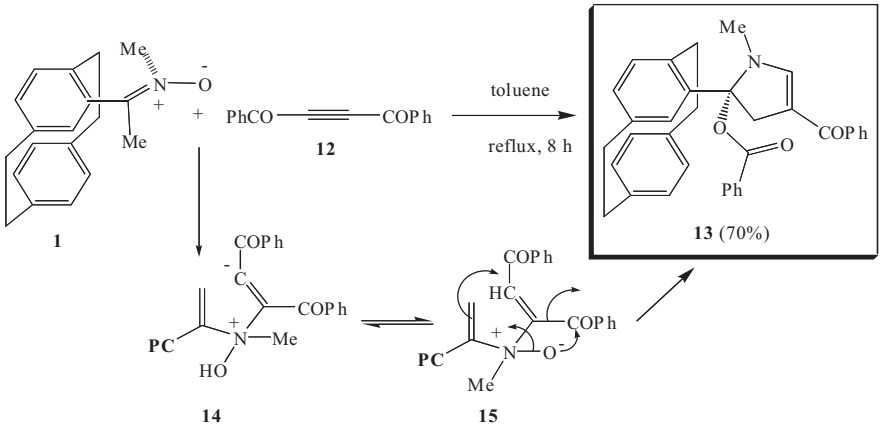
Scheme 2

Logically, it can be expected the formation of [3 + 3] cycloadducts **9a–c** as a formal step from the reaction of **1** with **6a–c** (Scheme 2). In the next step of the sequence, the oxygen with its bond electrons in **9a–c** could then attack the C = X of another molecule of **6a–c** forming the salt **10a–c** (Scheme 2). Intramolecular cyclisation process then occurred accompanied by loss of the X-C=O **11a–c**, thus generating the two isolated products **7a–c** and diphenyl acetylene (**8**) as shown in Scheme 2.

In a different manner, the reaction of nitrone **1** with dibenzoyl acetylene (**12**) in refluxing toluene produced the stereoisomeric pyrrole **13** in 70% yield (Scheme 3). Mass spectra and elemental analysis established the molecular formula of **13** as $C_{35}H_{31}NO_3$. The IR spectrum of **13** did not indicate the absorption of any hydroxyl or amino group (see the experimental). However, a broad band at ν = 1710–1685 cm^{-1} was assigned to the carbonyl groups. The ^1H NMR spectrum showed a singlet at δ = 3.64 assigned to the NMe protons. The other methyl protons present in the main nitrone **1** disappeared and a singlet at δ = 4.20 related to the presence of the CH_2-pyrrole protons. NOE experiments confirmed the proposed structure, since saturation of the CH_2 of pyrrole protons causes an enhancement of the ethano-bridge protons, which are also enhanced during irradiation of the NMe protons. COSY C H showed that the CH_2 protons have a correlation with *C*-5 (δ = 80.0) and *C*-3 (δ = 141.4). The carbonyl carbon signals resonated in the ^{13}C NMR spectrum of **13** at two different values (δ = 176.7 and 191.4). For the mechanism of the formation of **13**, we propose that the tautomer **4** initially attacks the activated triple bond of the dipolarophile **12** in a Michael-type reaction, thus resulting in the formation of the salt **14**. That intermediate would be found in tautomerism as in **15** (Scheme 3). In previous consequences[9b] of similar reactions such as the reaction between **1** and dimethyl acetylenedicarboxylate, the final step involves elimination of water. In our case, the reaction of **1** with dibenzoyl ethylene proceeds by the regioselective rearrangement of benzoate anion by the pathway shown in Scheme 3.

Conclusion

Nitrones derived from paracyclophanyl group still show new chemistry towards various dipolarophiles in a different reactivity compared to the classical aromatic system. Therefore much work has to be done for more investigation of the reactivity of nitrone **1** towards another diepolarophiles.



Scheme 3

Experimental

General procedure

Melting points: Kofler hot stage, uncorrected. NMR: Bruker AM-400, solvent: $CDCl_3$, internal standards: TMS (δ = 0.00) for 1H, $CDCl_3$ (δ = 77.05) for 13C. The results of NOE difference experiments are given in the form: irradiated signal→ enhanced signal. The spin systems of both CH_2CH_2 bridges in compounds **7a–c** and **13** were also fully analysed. Chromatography columns were packed with silica gel 7714 (Merck). For preparative layer chromatography (PLC), glass plates (20 cm x 48 cm) were covered with a slurry of silica gel Merck PF_{254} and the solvents listed for development and air-dried. Zones were detected by the quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were performed at the Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig. MS: Finnigan MAT 8430 spectrometer at 70 eV. IR: Nicolet 320 FT-IR with KBr pellets and paraffin films. (*E*)-*N*-[2-([2.2]Paracyclophan-4-yl)ethylidene]methylamine-*N*-oxide (**1**) was synthesised by the procedure mentioned in ref. 9a. 2,3-Diphenylcyclopropenone (**6a**) was bought from Fluka. 2,3-Diphenylcyclopropen-1-thione (**6b**) and 2-(2,3-diphenylcycloprop-2-enylidene)-malononitrile (**6c**) were prepared according to ref. 19, whereas dibenzoyl acetylene (**12**) was prepared according to ref. 20.

Reaction of nitrone **1** *with cyclopropenones* **6a–c**

(6): A mixture of **1** (279 mg, 1 mmol) and cyclopropenones **6a–c** (2 mmol) was heated at reflux in toluene (100 ml) for 2–3 d (the reaction was followed by TLC analysis). The solvent was evaporated in vacuo and the residue was column chromatographed on silica gel with toluene to give **7a–c** as the slowest migrating zones and **8** as the fastest migrating zones. The products **7a–c** were recrystallised from the stated solvents.

1,5-Dimethyl-3,4-diphenyl-5-([2.2]paracyclophan-4-yl)-1,5-dihydropyrrol-2-one **(7a):** (0.20 g, 60%), obtained as colourless crystals, R_f = 0.3 (toluene), m.p. 240°C; ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR: δ = 1.62 (s, 3 H, 5-*Me*), 2.62 (s, 3 H, N*Me*), 2.80 (ddd, 1 H, 2'-Ha, ethano bridge), 2.85 (ddd, 1 H, 1'-H_a, ethano bridge), 2.92 (ddd, 1 H, 9'-H_s, ethano bridge), 3.20 (ddd, 1 H, 10'-H_a, ethano bridge), 3.10-3.14 (ddd, 1 H, 1'-H_s, ethano bridge), 3.13 (ddd, 1 H, 10'-H_s, ethano bridge), 3.22-3.24 (m, 1 H, 9'-H_a, ethano bridge), 3.32 (ddd, 1 H, 2'-H_s, ethano bridge), 6.35 (dd, 1 H, 12'-H, PC–H), 6.52 (dd, 1 H, 13'-H, PC–H), 6.60 (m, 2 H, 7'-, 15'-H, PC–H), 6.73 (dd, 1 H, 16'-H, PC–H), 6.85 (d, 1 H, 5'-H, PC–H), 7.03–7.08 (m, 1 H, 8'-H, PC–H), 7.05 (td, 2 H, Ph–H), 7.10–7.13 (m, 2 H, Ph–H), 7.34 (dd, 2 H, Ph–H, *J* = 8.0, 1.2 Hz, Ph–H), 7.35–7.40 (m, 2 H, Ph–H), 7.47–7.54 (m, 2 H, Ph–H); J_{HH} in the paracyclophane fragment: $J_{5',7'}$ = 1.7, $J_{7',8'}$ = 8.0, $J_{12',13'}$ = 8.0, $J_{12',16'}$ = 2.1, $J_{13',15'}$ = 2.0, $J_{15',16'}$ = 7.8, $J_{1a',1s'}$ = –13.1, $J_{1a',2a}$ = 10.4, $J_{1a',2s'}$ = 3.9, $J_{1s',2a'}$ = 4.1, $J_{1s',2s'}$ = 10.2, $J_{2a',2s'}$ = –13.6, $J_{9a',9s'}$ = –13.4, $J_{9a',10a'}$ = 10.6, $J_{9a',10s'}$ = 3.0, $J_{9s',10a'}$ = 5.2, $J_{9s',10s'}$ = 10.5, $J_{10a',10s'}$ = –13.2 Hz; ^{13}C NMR: δ = 25.4 (q, 5-*Me*), 26.6 (q, *C*-2'), 29.4 (q, 1-N*Me*), 33.2 (t, *C*-9'), 34.9 (t, *C*-10'), 35.4 (t, *C*-1'), 73.8 (s, *C*-5), 108.6 (s, *C*-3), 125.0, 127.9 (d, *para* Ph–H), 128.1, 128.5 (d, *meta*-2 Ph–CH), 129.2, 129.3 (d, *ortho*-2 Ph–CH), 131.4 (d, *C*-5'), 131.6 (d, *C*-7'), 132.6 (d, *C*-12'), 133.0 (d, *C*-16'), 133.7 (d, *C*-13'), 134.6 (d, *C*-15'), 136.8 (*C*-4), 138.1 (s, *C*-4'), 138.8 (d, *C*-8'), 139.4, 139.8 (Ph–*C*), 140.0 (s, *C*-6'), 140.4 (s, *C*-11'), 140.6 (s, *C*-14'), 140.8 (s, *C*-3'), 171.2 (*C*-2); IR ν_{max} (KBr): 3060–3000 cm^{-1} (Ar-CH, s), 2960–2860 (aliph.-CH, m), 1685 (C=O, vs), 1610, 1130 (N–O, s); UV (CH_3CN): λ_{max} (log ε) 350 nm (3.2); *m/z* (%): 469 [M$^+$] (86), 440 (12), 365 (50), 336 (8) 308 (10) 293 (14), 261 (12), 218 (74), 202 (10), 178 (16), 158 (20), 144 (24), 118 (100), 91 (22), 77 (42), 44 (28). Anal. Calcd for $C_{34}H_{31}NO$ (469.63): C, 86.96; H, 6.65; N, 2.98. Found: C, 86.80; H, 6.50; N, 3.05.

1,5-Dimethyl-3,4-diphenyl-5-([2.2]paracyclophan-4-yl)-1,5-dihydropyrrol-2-thione **(7b): O**btained (0.32 g, 66%) as pale yellow crystals (ethanol), R_f = 0.6, toluene, m.p. 280°C; ^{1}H NMR: δ = 1.60 (s, 3 H, 5-*Me*), 2.70 (s, 3 H, N*Me*), 2.69 (ddd, 1 H, 2'-Ha, ethano bridge), 2.80 (ddd, 1 H, 1'-H_a, ethano bridge), 2.90 (ddd, 1 H, 9'-H_s, ethano bridge), 3.20 (ddd, 1 H, 10'-H_a, ethano bridge), 3.30 (ddd, 1 H, 1'-H_s, ethano bridge), 3.13 (ddd, 1 H, 10'-H_s, ethano bridge), 3.22–3.24 (m, 1 H, 9'-H_a, ethano bridge), 3.32 (ddd, 1 H, 2'-H_s, ethano bridge), 6.30 (dd, 1 H, 12'-H, PC–H), 6.50 (dd, 1 H, 13'-H, PC–H), 6.54 (dd, 1 H, 7'-H, PC–H), 6.65 (m, 1 H, 15'-H, PC–H), 6.70 (dd, 1 H, 16'-H, PC–H), 6.83 (d, 1 H, 5'-H, PC–H), 7.03–7.08 (m, 1 H, 8'-H, PC–H), 7.10 (td, 2 H, Ph–H), 7.15–7.18 (m, 2 H, Ph–H), 7.36 (dd, 2 H, Ph–H, *J* = 8.0, 1.2 Hz, Ph–H), 7.40–7.50 (m, 2 H, Ph–H), 7.52–7.56 (m, 2 H, Ph–H); J_{HH} in the paracyclophane fragment: $J_{5',7'}$ = 1.6, $J_{7',8'}$ = 7.8, $J_{12',13'}$ = 8.0, $J_{12',16'}$ = 2.1, $J_{13',15'}$ = 1.8, $J_{15',16'}$ = 7.8, $J_{1a',1s'}$ = –12.8, $J_{1a',2a}$ = 10.6, $J_{1a',2s'}$ = 4.0, $J_{1s',2a'}$ = 4.0, $J_{1s',2s'}$ = 10.2, $J_{2a',2s'}$ = –13.5, $J_{9a',9s'}$ = –13.6, $J_{9a',10a'}$ = 10.8, $J_{9a',10s'}$ = 3.0, $J_{9s',10a'}$ = 5.0, $J_{9s',10s'}$ = 10.5, $J_{10a',10s'}$ = –13.0 Hz; ^{13}C NMR: δ = 25.8 (q, 5-*Me*), 27.4 (q, *C*-2'), 29.8 (q, 1-N*Me*), 33.4 (t, *C*-9'), 34.6 (t, *C*-10'), 35.0 (t, *C*-1'), 74.2 (s, *C*-5), 109.0 (s, *C*-3), 125.8, 127.4 (d, *para* Ph–H), 128.0, 128.2 (d, *meta*-2 Ph–CH), 129.0, 129.6 (d, *ortho*-2 Ph–CH), 131.2 (d, *C*-5'), 131.5 (d, *C*-7'), 132.0 (d, *C*-12'), 133.2 (d, *C*-16'), 133.6 (d, *C*-13'), 134.4 (d, *C*-15'), 136.7 (*C*-4), 138.0 (s, *C*-4'), 138.5 (d, *C*-8'), 139.0, 139.6 (Ph–C), 140.0 (s, *C*-6'), 140.2 (s, *C*-11'), 140.6 (s, *C*-14'), 141.8 (s, *C*-3'), 182.0 (*C*-2); IR ν_{max} (KBr): 3050–3008 cm^{-1} (Ar-CH, s), 2940–2860 (aliph.-CH, m), 1315, 1100 (s, C=S), 1610, 1130 (N–O, s); UV (CH3CN): λ_{max} (log ε) 380 nm (3.8); *m/z* (%): 485 [M$^+$] (100), 470 (16), 455 (18), 380 (22), 205 (40) 178 (22), 158 (20), 142 (24), 118 (60), 91 (20), 77 (40), 44 (32). Anal. Calcd for $C_{34}H_{31}NS$ (485.70): C, 84.08; H, 6.43; N, 2.88; S, 6.60 Found: C, 84.20; H, 6.40; N, 2.95; S, 6.52.

[1,5-Dimethyl-3,4-diphenyl-5-([2.2]paracyclophan-4-yl)-1,5-dihydropyrrol-2-ylidene]malononitrile **(7c):** (0.31 g, 75%) obtained as yellow crystals (methanol), R_f = 0.2 (toluene), m.p. 200°C; ^{1}H NMR: δ = 1.52 (s, 3 H, 5-*Me*), 2.80 (s, 3 H, N*Me*), 2.90 (ddd, 1 H, 2'-Ha, ethano bridge), 3.00 (ddd, 1 H, 1'-H_a, ethano bridge), 3.10 (ddd, 1 H, 9'-H_s, ethano bridge), 3.18 (ddd, 1 H, 10'-H_a, ethano bridge), 3.20-3.25 (m, 2 H, 1'-H_s, 10'-H, ethano bridge), 3.32-3.36 (m, 1 H, 9'-H_a, ethano bridge) 3.40 (ddd, 1 H, 2'-H_s, ethano bridge), 6.38 (dd, 1 H, 12'-H, PC–H), 6.52 (dd, 1 H, 13'-H, PC–H), 6.60–6.66 (m, 3 H, 7'-, 15'-, 16'-H, PC–H), 6.75 (d, 1 H, 5'-H, PC–H), 6.90–7.00 (m, 1 H, 8'-H, PC–H), 7.08–7.16 (m, 5 H, Ph–H), 7.40-7.48 (m, 3 H, Ph–H), 7.60–7.66 (m, 2 H, Ph–H); J_{HH} in the paracyclophane fragment: $J_{5',7'}$ = 1.8, $J_{7',8'}$ = 8.0, $J_{12',13'}$ = 8.2, $J_{12',16'}$ = 2.1, $J_{13',15'}$ = 2.0, $J_{15',16'}$ = 8.0, $J_{1a',1s'}$ = –13.0, $J_{1a',2a}$ = 10.5, $J_{1a',2s'}$ = 3.9, $J_{1s',2a'}$ = 4.0, $J_{1s',2s'}$ = 10.0, $J_{2a',2s'}$ = –13.4, $J_{9a',9s'}$ = –13.6, $J_{9a',10a'}$ = 10.4, $J_{9a',10s'}$ = 3.0, $J_{9s',10a'}$ = 5.0, $J_{9s',10s'}$ = 10.6, $J_{10a',10s'}$ = –13.2 Hz; ^{13}C NMR: δ = 25.4 (q, 2-*Me*), 26.6 (q, *C*-2'), 32.4 (q, 1-N*Me*), 33.2 (t, *C*-9'), 34.9 (t, *C*-10'), 35.4 (t, *C*-1'), 48.0 (q, =$C(CN)_2$), 73.8 (s, *C*-5), 113.0, 113.6 (q, CN), 118.0 (s, *C*-3), 127.0, 128.0 (d, *para* Ph–H), 128.3, 128.7 (d, *meta*-2 Ph–CH), 129.6, 129.8 (d, *ortho*-2 Ph–CH), 131.0 (d, *C*-5'), 131.4 (d, *C*-7'), 132.4 (d, *C*-12'), 133.2 (d, *C*-16'), 133.6 (d, *C*-13'), 134.0 (d, *C*-15'), 134.6 (*C*-4), 138.1 (s, *C*-4'), 138.8 (d, *C*-8'), 139.4, 139.8 (Ph–C), 140.0 (s, *C*-6'), 140.4 (s, *C*-11'), 140.5 (s, *C*-14'), 140.4 (s, *C*-3'), 185.0 (*C*-2); IR ν_{max} (KBr): 3090–3015 cm^{-1} (Ar–CH, s), 2960–2820 (aliph.-CH, m), 2220-2210 (CN, vs), 1612, 1120 (N–O, s); UV (CH_3CN): λ_{max} (log ε) 300 nm (3.2); *m/z* (%): 518 [M + 1] (26), 517 [M$^+$] (80), 502 (14), 488 (22), 413 [M-$C(CN)_2$] (100), 282 (34), 260 (22), 218 (50), 178 (36), 144 (20), 118 (20), 91 (32), 77 (62). Anal. Calcd for $C_{37}H_{31}N_3$ (517.68): C, 85.85; H, 6.04; N, 8.12. Found: C, 86.00; H, 6.10; N, 8.08.

Reaction of nitrone 1 with dibenzoyl acetylene **(12):** A mixture of **1** (279 mg, 1 mmol) and **12** (234 mg, 1 mmol) was heated at reflux in toluene (300 ml) for 8 h. The solvent was evaporated *in vacuo* and the residue was applied on palates chromatography (silica gel) with dichloromethane to give **13**.

4-Benzoyl-1-methyl-2-([2.2]paracyclophan-4-yl)-2,3-dihydropyrrol-2-yl benzoate **(13):** (0.36 g, 70%) obtained as colourless needles (ethanol), R_f = 0.3, (dichloromethane), mp 290°C; ^{1}H NMR: δ = 2.70 (ddd, 1 H, 2'-Ha, ethano bridge), 2.83–2.90 (m, 2 H, 9'-H_s, 1'-H_a, ethano bridge), 3.10–3.16 (m, 2 H, 1'-H_s, 10'-H_a, ethano bridge), 3.20–3.26 (m, 2 H, 9'-H_a, 10'-H_s, ethano bridge), 3.35 (ddd, 1 H, 2'-H_s, ethano bridge), 3.64 (s, 3 H, N*Me*), 4.20 (s, 2 H, CH_2-pyrrole), 6.400 (m, 1 H, 12'-H, PC–H), 6.52 (d, 4 H, 13'-, 7'-, 15'-, 16'-H, PC–H), 6.73 (dd, 1 H, 8'-H, PC–H), 6.78 (d, 1 H, 5'-H, PC–H), 7.20–7.25 (m, 2 H, Ph-*meta*-H), 7.27-7.32 (m, 4 H, Ph–H), 7.37 (s, 1 H, pyrrole-2-H), 7.50–7.55 (m, 2 H, Ph-*ortho*-H), 7.82–7.85 (m, 2 H, Ph-*ortho*-H); ^{13}C NMR: δ = 27.2 (t, *C*-2'), 33.2 (t, *C*-9'), 34.9 (t, *C*-10'), 35.4 (t, *C*-1'), 45.3 (q, N*Me*), 48.5 (*C*H_2-2), 80.0 (s, *C*-5), 112.1 (d, *C*-3), 125.0, 127.9 (d, *para* Ph–H), 128.1, 128.5 (d, *meta*-2 Ph–CH), 129.2, 129.3 (d, *ortho*-2 Ph–CH), 131.4 (d, *C*-5'), 131.6 (d, *C*-7'), 132.6 (d, *C*-12'), 133.0 (d, *C*-16'), 133.7 (d, *C*-13'), 134.6 (d, *C*-15'), 138.1 (s, *C*-4'), 138.8 (d, *C*-8'), 139.4, 139.8 (Ph-*C*), 140.0 (s, *C*-6'), 140.4 (s, *C*-11'), 140.6 (s, *C*-14'), 141.4 (s, *C*-3'), 142.7 (s, *C*-2), 176.7 (O*C*OPh), 191.4 (*C*OPh); IR ν_{max} (KBr): 3060–3000 cm^{-1} (Ar-CH, s), 2960–2860 (aliph.-CH, m), 1710–1685 (C=O, vs), 1610 (C=N, s); UV (CH_3CN): λ_{max} (log ε) 270 nm (2.8); *m/z* (%): 513 [M$^+$] (100), 495 (14), 466 (8), 408 (14), 390 (16), 363 (14), 303 (10), 286 (12), 133 (20), 105 (60), 91 (18), 77 (40), 57 (18). Anal. Calcd for $C_{35}H_{31}NO_3$ (513.64): C, 81.84; H, 6.08; N, 2.73. Found: C, 81.70; H, 6.18; N, 2.70.

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