Synthesis B. Wiredu et al. Paper

Synthesis of 2,24-Diene-12,13,15,16,34,35,37,38-octaphenyl[4.4]-triphenylparacyclophane

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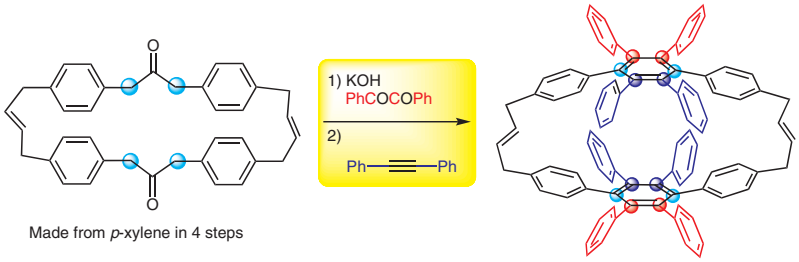

Received: 03.03.2021
Accepted after revision: 12.04.2021
Published online: 12.04.2021
DOI: 10.1055/a-1479-6611; Art ID: ss-2021-m0106-op

Abstract A new octaphenyl[4.4]triphenylparacyclophanediene was readily synthesized in six steps from *p*-xylene via the installment of bromine atoms, replacement with a vinyl group, carbonylative coupling, intermolecular followed by intramolecular double Grubbs olefin metathesis, Knoevenagel condensation, and Diels–Alder cycloaddition. The belt-shaped structure and *trans*-stereochemistry of the alkene moieties of the octaphenyl[4.4]triphenylparacyclophane and a synthetic intermediate, 2,21-dioxo-11,30-diene[3.4.3.4]paracyclophane, were determined by X-ray crystallography. The synthetic methodology leading to octaphenyl[4.4]triphenylparacyclophane is applicable for the synthesis of substituted triphenylparacyclophanes and possibly their corresponding bis-hexabenzocoronenylparacyclophanes via a Scholl–Mullen oxidative aryl-aryl coupling reaction.

Key words belt-shaped molecules, cyclophanes, octaphenyl[4.4]-triphenylparacyclophane, Grubbs olefin metathesis, Knoevenagel condensation, Diels–Alder cycloaddition, carbonylative coupling

Supramolecular chemistry[1] has led to the design of many fascinating molecules[2] possessing useful properties. In-plane aromaticity, magnetically induced currents, and photophysical and photochemical properties of belt-shaped molecules, assembled by fused benzene rings or carbon chains, have offered fascinating discoveries in the past few years. For example, liquid crystalline crown ether substituted phthalocyanines undergo self assembly to form molecular cables, consisting of a central electron wire surrounded by four ion channels.[3] A molecular tweezer, derived from a rigid bicyclic aromatic ring system, binds selectively to lysine and arginine residues of peptides, demonstrating a molecular recognition.[4] Planar chiral bis(thiourea)-[2.2]paracyclophanes serve as chiral catalysts for enantioselective Michael addition reaction.[5] Our interest in cyclophanes,[6,7] stemming from non-covalent π–π, π–cation, and hydrophobic interactions, may lead to self-assembled tubular molecules,[7,8] selective binding to guest molecules,[9] and unique bioactivity.[10] Herein, we described a short, effective synthesis of 2,24-diene-12,13,15,16,34,35,37,38-octaphenyl[4.4]triphenylparacyclophane (**1**) (Figure 1), which may serve as an intermediate for the construction of self-assembled cyclophanes and supramolecules. Triphenylparacyclophane **1**, a symmetrical molecule, possesses two alternated but-2-enyl-hexaphenylbenzene units. The but-2-ene moieties allow further functional group transformation and the phenyl units can be appended with substituents. Notably, substituted triphenylparacyclophane **1** may be used to produce a fragment of small and well-defined carbon nanotubes via an aryl-aryl dehydrogenative coupling reaction,[11] whose application in materials and biomaterials can be explored.

Various cyclophanes and belt-liked macrocycles have been synthesized by double Wittig reaction,[6,12] double Diels–Alder reaction,[13] titanium-mediated double coupling of 3,3′-(*Z*)-stilbenedicarbaldehyde,[14] cyclodimerization of cumulenes generated from 1,χ-elimination reaction,[15] double Suzuki coupling reaction of diiodoarenes and diarylboronates,[16] and 2nd generation Grubbs–$ZnCl_2$ catalyzed intramolecular metathesis of 1,1′-bis(but-3-enyl)-2,2′-bisbenzimidazole.[17] The latter reported only ten- and twelve-membered macrocycles and a 1:1 mixture of *E*- and *Z*-isomers were found in the twelve-membered ring system.[17] We envisioned that a short synthesis of cyclophane **1** could derive from biscyclopentadienylcyclophane **2**, which might obtain from diketocyclophane **3** as depicted in Figure 1. Diketocyclophane **3** could be made from a double Grubbs olefin metatheses of 1,3-diarylacetone **4**, which could readily be achieved from the carbonylation of 1-allyl-4-(bromomethyl)benzene (**5**). Synthesis of substituted hexaarylbenzenes has been reported via the carbonylation[18] followed by condensation with benzil and Diels–Alder

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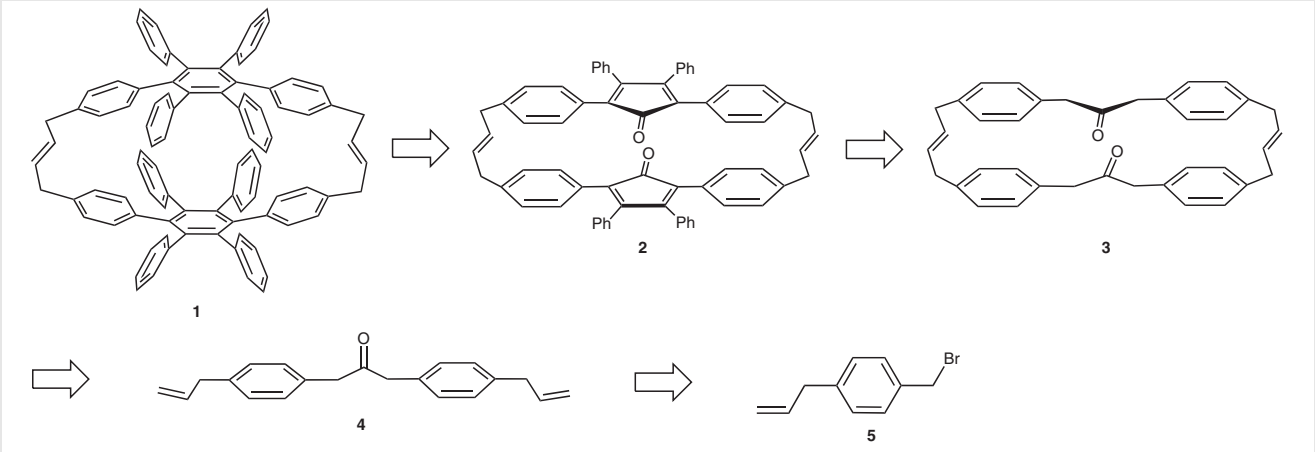
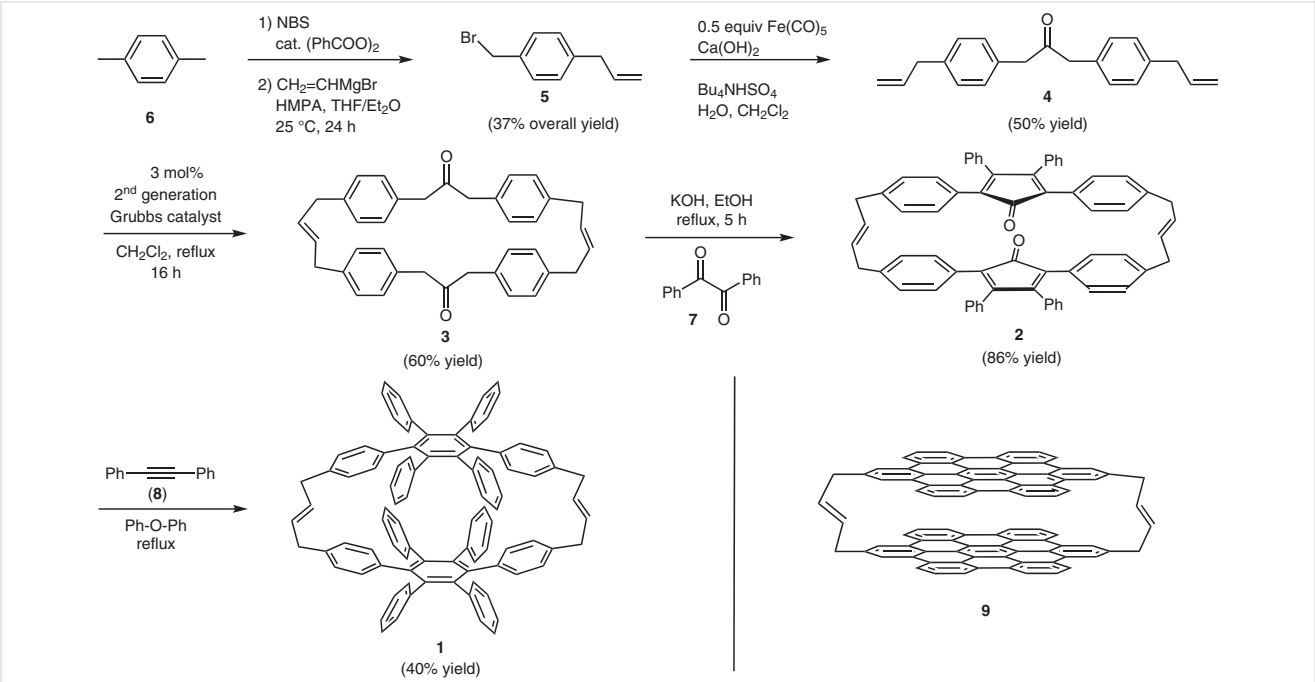


Figure 1 Retrosynthesis of cyclophane **1**

cycloaddition.[19] However, 1,3-bis(4-allylphenyl)propan-2-one (**4**) and its transformed cyclophanes **1**–**3** have not been reported previously.

1-Allyl-4-(bromomethyl)benzene (**5**) was synthesized from the dibromination of *p*-xylene (**6**) with 2 equiv of *N*-bromosuccinimide (NBS) and a catalytic amount of benzoyl peroxide followed by monosubstitution with 1 equiv of vinylmagnesium bromide and HMPA in diethyl ether and THF (1:1), in a 37% overall yield (Scheme 1). A reported carbonylative coupling reaction[18,19] was followed for the preparation of symmetrical diarylacetone **4**. Hence, treatment of benzyl bromide **5** with 0.5 equiv of $Fe(CO)_5$, calcium hydroxide, and a catalytic amount of phase-transfer reagent, tetrabutylammonium hydrogensulfate, in CH_2Cl_2/H_2O at 25 °C for 3 h gave a 50% yield of **4**. Using 3 mol% of 2nd generation Grubbs catalyst under refluxing dichloromethane for 16 h, diarylacetone **4** underwent homocoupling followed by ring-closing olefin metatheses to give a 60% yield of cyclophane **3**, whose structure was unambiguously determined by single-crystal X-ray analysis (Figure 2). The X-ray structure showed *trans* configuration[17] in both alkene moieties, indicating the Grubbs olefin metathesis is stereoselective under the reaction conditions. Double Knoevenagel condensation of diketone cyclophane **3** and 2 equiv of benzil



Scheme 1 Synthesis of 2,24-diene-12,13,15,16,34,35,37,38-octaphenyl[4.4]triphenylparacyclophane (**1**)

(**7**) under refluxing ethanol in the presence of potassium hydroxide afforded an 86% yield of bis-cyclopentadienone cyclophane **2**. Diels–Alder cycloaddition reaction of **2** and 2 equiv of diphenylacetylene (**8**) in refluxing diphenyl ether[19,20] with the concomitant of carbon monoxide furnished octaphenyl[4.4]triphenylparacyclophane **1** in 40% yield. An attempt to carry out the Diels–Alder reaction in refluxing 1,2-dichlorobenzene gave no desired product. The bulky cyclophane molecule **2** likely requires a higher activation energy for the intermolecular Diels–Alder reaction. The structure of molecule **1** was firmly established through a single-crystal X-ray analysis and the ORTEP drawing is depicted in Figure 3. The *trans*-stereochemistry of the two alkene moieties in **1** remains intact. The distance between the centers of the two central benzene rings of cyclophane **1** is 14.29 Å. It possesses a similar cavity as that of [8]cycloparaphenylene.[21] The two central phenyl rings, each attached to six aryl rings, are parallel, while the remaining twelve phenyl rings are slightly off from perpendicular, as found in the crystal structure (Figure 3).

Information of the two single-crystal X-ray structural analyses of molecules **3** and **1** are summarized in Table 1, including their formulas, crystal data, methods of collection, and methods of structural solutions and refinement.[22] Selected bond lengths and angles are listed in Figures 2 and 3.

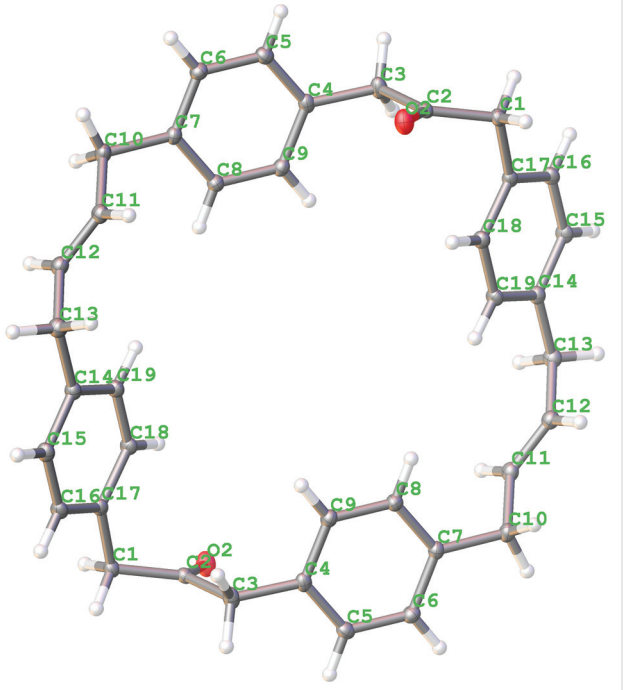


Figure 2 ORTEP drawing of the single-crystal X-ray analysis of diketone cyclophane **3**; CCDC 2065344. Selected bond lengths (Å) and angles (°): C1–C2 1.5171(14), C2–C3 1.5226(14), C2–O2 1.2090(12), C1–C17 1.5183(14), C7–C10 1.5182(14), C10–C11 1.5023(15), C11–C12 1.3336(15), C14–C15 1.3976(14); C1–C2–C3 116.51(8), C3–C4–C5 120.71(9), C1–C2–O2 122.15(9), C6–C7–C10 120.63(9), C7–C10–C11 112.66(9), C10–C11–C12 124.34(10), C11–C12–C13 124.88(10), C14–C15–C16 121.24(9).

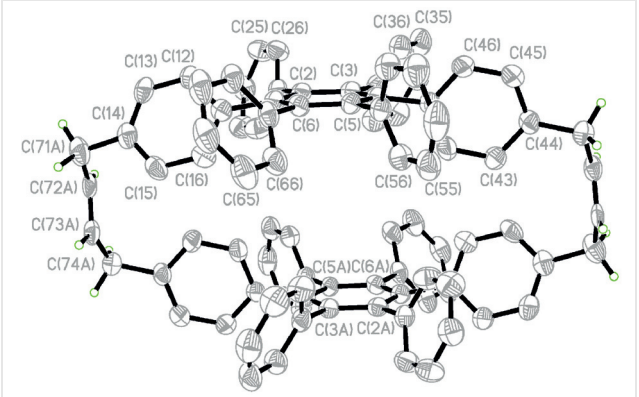


Figure 3 ORTEP drawing of the single-crystal X-ray analysis of triphenylparacyclophane **1**; CCDC 2065345. Selected bond lengths (Å) and angles (°): C4–C5 1.544(4), C8–C11 1.504(4), C11–C12 1.406(4), C11–C16 1.412(4), C13–C14 1.412(4), C14–C15 1.402(4), C14–C17 1.496(4), C15–C16 1.407(4), C20–C21 1.379(4), C1–C20 1.527(4), C1–C2 1.468(5), C2–C3 1.359(5), C3–C4 1.500(4); C13–C14–C15 120.3(2), C13–C14–C17 119.4(2), C6–C5–C10 117.8(3), C19–C20–C21 117.7(3), C18–C19–C20 121.5(3), C5–C10–C9 121.2(3), C1–C2–C3 125.0(3), C2–C3–C4 122.2(3).

Table 1 Formulas, Crystal Data, Method of Collection, and Methods of Structural Solutions and Refinement of X-ray Structures of **3** and **1**

Molecule	**3**[a]	**1**[b]
Formula	$C_{38}H_{36}O_2$	$C_{92}H_{68}$
FW	524.67	1170.28
T (K)	120(15)	120(15)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	*P*2(1)/*c*	*Pbca*
a (Å)	13.9091(5)	23.3936(11)
b (Å)	6.2647(2)	11.9225(5)
c (Å)	17.1630(6)	23.4018(11)
α (°)	90	90
β (°)	107.354(2)	90
γ (°)	90	90
V (Å^3)	1427.44(9)	6527.0(5)
Z	2 (molecules)	4 (molecules)
d_{calcd} (g/m^3)	1.221	1.191
Abs coeff (mm^{-1})	0.073	0.067
F(000)	560.0	2473.0
2θ range (°)	4.974–64.03	4.878–60.038
Reflns collected	31687	50637
Independent reflections/R_{int}	4967/0.0369	9131/0.0550
% Completeness /θ (°)	99.9/32.01	95.8/30.02

Molecule	**3**[a]	**1**[b]
Abs corr	none	none
Max, min transm	0.9891, 0.9783	0.9920, 0.9801
Least squares refinement method	full-matrix on F^2	full-matrix on F^2
Data/restraints/params	4967/0/181	9131/0/416
GOF (on F^2)	1.030	1.051
R_1 (obsd) wR_2 (all)[c]	0.0467 0.1250	0.0815 0.2272
Max/min residual electron density (e$^-$/Å^3)	0.53/–0.20	1.06/–0.37

[a] Bruker Platinum 135; Cu rotating anode/optical mirrors.
[b] Bruker APEX II; Mo sealed tube/monochromator.
[c] $R^1 = \Sigma[F_0 - F_c]/\Sigma[F_0]$; $wR^2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$.

Hexa-*peri*-hexabenzocoronene has been prepared from hexaphenylbenzene via a Scholl–Mullen oxidative aryl-aryl coupling reaction.[11,20,23] We have attempted to convert triphenylparacyclophane **1** into bishexabenzocoronenylparacyclophane **9** (Scheme 1) via the Scholl–Mullen reaction using various reagents in diluted solution including $FeCl_3$ in $MeNO_2$, $Cu(OTf)_2$ in CS_2, and $FeCl_3/Cu(OTf)_2$ in CS_2. In all cases, insoluble colored materials, consisting of purple or black, were obtained and the desired bishexabenzocoronenylparacyclophane **9** was not identifiable. Various organic and inorganic solvents were attempted to dissolve the crude products, including hexane, toluene, diethyl ether, ethyl acetate, chloroform, DMF, DMSO, H_2O, trifluoroacetic acid, THF/aqueous HCl or H_2SO_4 solution at room temperature or elevated temperature (~70 °C), but no detectable desired material was found in the solution. The but-2-enyl functions of octaphenyl[4.4]triphenylparacyclophane can be functionalized by the installation of alkyl chains or polar groups. Substituted aromatic ring systems, such as substituted benzils and diphenylacetylenes, can be used in the described synthetic scheme to generate substituted triphenylparacyclophane derivatives, which may afford the synthesis of solubilized substituted bis-hexabenzocoronenylparacyclophanes.

In summary, a facile synthesis of 2,24-diene-12,13,15,16,34,35,37,38-octaphenyl[4.4]triphenylparacyclophane was accomplished starting from *p*-xylene in six steps with a 3.8% overall yield and is amendable to large-scale synthesis. The key step involved a Grubbs ruthenium-catalyzed one-pot homocoupling olefin metathesis of 1,3-bis(4-allylphenyl)propan-2-one accompanied by ring-closing olefin metathesis to generate 2,21-dioxo-11,30-*trans*,*trans*-diene[3.4.3.4]paracyclophane. Only *trans*-stereochemistry was found in the paracyclophane product, suggesting both intermolecular and intramolecular Grubbs olefin metatheses in this system are stereoselective. The paracyclophane underwent condensation with two moles of benzil and subsequent Diels–Alder cycloaddition with diphenylacetylene furnished the targeted octaphenyl[4.4]triphenylparacyclophane.

Chemicals were purchased from Fisher Scientific and VWR international LLC. Solvents were dried over appropriated drying agent such as CaH_2 (for DMF, CH_2Cl_2, and MeCN), or Na/benzophenone (for THF and Et_2O) followed by distillation. Column chromatography was carried out on silica gel (200–400 mesh). ^{1}H NMR spectra (400 MHz and 200 MHz) and ^{13}C NMR spectra (100 MHz and 50 MHz) were recorded on Varian Unity plus 400 MHz and 200 MHz spectrometers, and measured from a solution in $CDCl_3$ unless otherwise mentioned. ^{1}H NMR were recorded relative to TMS (δ = 0) or $CHCl_3$ (δ = 7.26) and ^{13}C NMR relative to $CDCl_3$ (δ = 77.0). Mass spectra were obtained from an API 2000-triple quadrupole ESI-MS/MS mass spectrometer (Applied Biosystems). HRMS were obtained from a LCT Premier (Waters Corp., Milford MA) time of flight mass spectrometer at the University of Kansas. The instrument operated at 10,000 resolution (W mode) with dynamic range enhancement that attenuates large intensity signals. Mass correction for exact mass determinations was made automatically with the lock mass feature in the MassLynx data system. Single-crystal X-ray structures were obtained from a Siemens SMART 1000 low-temperature (LT-2A) single-crystal X-ray diffractometer.

1,4-Bis(bromomethyl)benzene

To a solution of *p*-xylene (**6**; 45 mL, 0.365 mol) in benzene (600 mL) under argon were added NBS (129 g, 0.731 mol) and benzoyl peroxide (3.38 g, 0.015 mol). The mixture was heated under reflux for 4 h. One half of the benzene of the reaction solution was removed using a rotary evaporator with a cold trap, and the resulting residue gradually cooled to 0 °C to obtain a white precipitate. The white solid was collected by filtration, washed several times with water, and dried under vacuum overnight to give 1,4-bis(bromomethyl)benzene as a white solid; yield: 58.0 g (60%); mp 141.0–144.0 °C (Lit.[24] 142–144 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.37 (s, 4 H, Ar-H), 4.48 (s, 4 H, CH_2-Br).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.2 (2 C), 129.7 (4 C), 33.0 (2 C).

The spectral data are in agreement with those reported.[25]

1-Allyl-4-(bromomethyl)benzene (5)

To a solution of 1,4-bis(bromomethyl)benzene (8.0 g, 30.3 mmol) in Et_2O/THF (1:1, 160 mL) under argon at 25 °C were added 1.0 M vinylmagnesium bromide in THF, 31 mL, 31 mmol) and freshly distilled HMPA (5.3 mL, 30.3 mmol). The mixture was stirred for 24 h, diluted with aq sat. NH_4Cl solution, and extracted with Et_2O (3 ×). The combined organic layers were washed with water and brine, dried (anhyd Na_2SO_4), concentrated, and column chromatographed (silica gel, gradient hexane/Et_2O) to give compound **5** (3.83 g, 62%) as an oil along with recovered 1,4-bis(bromomethyl)benzene (1.5 g, 19%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 6.00–5.90 (m, 1 H, =CH), 5.11–5.05 (m, 1 H, =CH_2), 5.04–4.90 (m, 1 H, =CH_2), 4.49 (s, 2 H, CH_2Br), 3.39 (d, *J* = 6.6 Hz, 2 H, CH_2C=).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.7, 137.2, 135.8, 129.4 (2 C), 129.3 (2 C), 116.4, 40.1, 33.8.

MS (ESI, MeOH): *m*/*z* (%) = 233.01 (100), 235.21 (97.3) (M + Na$^+$).

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{11}BrNa$: 232.9942; found: 233.1167.

The spectral data are in agreement with those reported.[26]

1,3-Bis(4-allylphenyl)propan-2-one (4)

To a mixture of $Ca(OH)_2$ (0.98 g, 13.3 mmol) and of Bu_4NHSO_4 (0.56 g, 1.66 mmol) under argon were added degassed water/CH_2Cl_2 (1:1, 60 mL); argon gas was bubbled into the solution for 5 min. To it was added $Fe(CO)_5$ (0.5 mL, 3.8 mmol) under vigorous stirring. A solution of

compound **5** (1.40 g, 6.63 mmol) in CH_2Cl_2 (5 mL) was added to the mixture via a cannula. After stirring at 25 °C for 3 h, air was bubbled into the reaction solution to destroy excess $Fe(CO)_5$, and the resulting mixture was filtered through a fritted funnel. The filtrate was diluted with 1 M HCl (10 mL) and extracted with EtOAc (3 ×). The combined organic layers were washed with aq $NaHCO_3$, water, and brine, dried (anhyd Na_2SO_4), filtered, and concentrated to dryness. The residue was subjected to column chromatography (silica gel, hexane/Et_2O 4:1) to give **4** as an oil; yield: 0.48 g (50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.4 Hz, 4 H), 7.09 (d, *J* = 8.4 Hz, 4 H), 6.02–5.92 (m, 2 H, =CH), 5.11 (dd, *J* = 12, 2 Hz, 2 H, =CH_2), 5.07 (dd, *J* = 9, 2 Hz, 2 H, =CH_2), 3.70 (s, 4 H), 3.39 (d, *J* = 6.6 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.2, 139.1 (2 C), 137.5 (2 C), 132.0 (2 C), 129.8 (4 C), 129.2 (4 C), 116.1 (2 C), 48.9 (2 C), 40.1 (2 C).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}O$: 291.1749; found: 291.1747.

2,21-Dioxo-11,30-diene[3.4.3.4]paracyclophane (3)

To a solution of ketone **4** (0.20 g, 0.69 mmol) in degassed CH_2Cl_2 (40 mL) under argon was added dropwise a solution of 2nd generation Grubbs catalyst (17.5 mg, 0.02 mmol) in degassed CH_2Cl_2 (10 mL) over a period of 30 min. After refluxing for 16 h, the mixture was cooled to 25 °C, diluted with water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with water and brine, dried ($MgSO_4$), concentrated, and column chromatographed (silica gel, gradient hexane/Et_2O) to give paracyclophane **3** as a white solid; yield: 0.108 g (60%); mp 61.0–62.0 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 7.0 Hz, 8 H), 7.03 (d, *J* = 7.0 Hz, 8 H), 5.63 (t, *J* = 6.8 Hz, 4 H), 3.68 (s, 8 H), 3.35 (d, *J* = 6.8 Hz, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 206.4, 139.5, 131.8, 130.6, 129.7 (8 C), 129.1 (8 C), 48.7, 38.6; a small amount of contaminants was found in the ^{13}C NMR spectrum.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{36}O_2Na$: 547.2613; found: 547.2629.

The compound crystallized (Et_2O) to give single crystals, whose structure was solved by X-ray analysis.

Paracyclophane 2

To a mixture of diketone **3** (58 mg, 0.109 mmol), KOH (15 mg, 0.27 mmol), and benzil (**7**; 57 mg, 0.271 mmol) under argon, was added distilled EtOH (5 mL), and the mixture was heated under reflux for 5 h. The mixture was cooled to 25 °C and concentrated on a rotary evaporator to remove EtOH. The residue was subjected to column chromatography (silica gel, gradient hexane/CH_2Cl_2) to afford compound **2** as a yellow solid; yield: 83 mg (86%); mp 85.0–87.0 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.25–6.83 (m, 36 H, Ar-H), 5.64 (t, *J* = 6.6 Hz, 4 H), 3.27 (d, *J* = 6.6 Hz, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 218.0, 153.4, 140.4, 139.5, 133.7, 131.2, 130.4, 129.5, 128.4, 128.2, 128.1, 125.1, 38.0.

HRMS-ESI: *m*/*z* [M + NH_4]$^+$ calcd for $C_{66}H_{48}O_2$ + NH_4^+: 890.3998; found: 890.4018; *m*/*z* [M + Na]$^+$ calcd for $C_{66}H_{48}O_2Na$: 895.3552; found: 895.3580.

2,24-Diene-12,13,15,16,34,35,37,38-octaphenyl[4.4]triphenylparacyclophane (1)

A solution of paracyclophane **2** (38 mg, 0.043 mmol) and diphenylacetylene (**8**; 39 mg, 0.22 mmol) in Ph_2O (1 mL) under argon was heated under reflux at 260 °C over a sand bath for 20 h. The purple color of compound **2** was discharged to give an off pale-yellowish colored solution. The solvent was removed by distillation under high vacuum and the residue was subjected to column chromatography (silica gel, gradient hexane/Et_2O) to yield compound **1** as a white solid; yield: 20 mg (40%); mp 76.0–77.0 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.20–6.25 (m, 56 H, ArH), 5.50–5.25 (br s, 4 H, =CH), 3.05–2.80 (br s, 8 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.7, 138.4, 137.7, 133.4, 131.7, 130.8, 129.9, 127.0, 126.6, 125.4, 38.1.

HRMS-ESI (micrOTOF-Q, electrospray): *m*/*z* [M + Na]$^+$ calcd for $C_{92}H_{68}Na$: 1195.5213; found: 1195.5183.

The compound crystallized (Et_2O) to give single crystals, whose structure was solved by X-ray analysis.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

Research reported in this publication was supported in part by the National Institute of General Medical Sciences of the National Institutes of Health under award number NIH R01GM128659 (to D.H.H.) and National Science Foundation (CHE-1662705). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. This material was based upon work in part supported by the National Science Foundation under 1826982 (to D.H.H.) for the purchase of an NMR spectrometer.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1479-6611.

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