

Synthesis of Saddle-Shape Octaaminotetraphenylene Octahydrochloride

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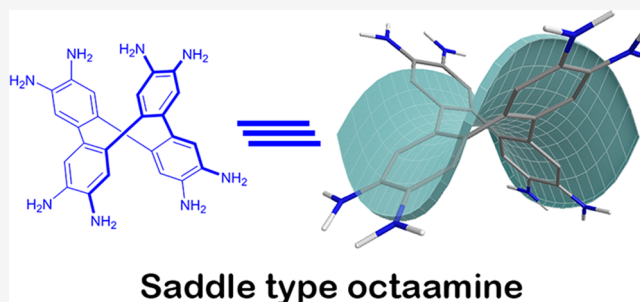


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ABSTRACT: Apart from being experimentally and theoretically interesting, tetraphenylene has potential applications in different fields, including supramolecular chemistry, material science, and asymmetric catalysis. Although a wide range of substituted tetraphenylenes have been reported, octaamine-based tetraphenylene derivatives have not been reported because of their instability. Here, stable octaaminotetraphenylene octahydrochloride is synthesized from the bromination of tetraphenylene to octabromotetraphenylene, which is subsequently aminated into octaiminotetraphenylene. Finally, the imino derivative is deprotected to yield octaaminotetraphenylene octahydrochloride.



INTRODUCTION

The material science experienced a significant revolution after the discovery of carbon allotropes such as zero-dimensional fullerene, one-dimensional carbon nanotubes, and two-dimensional graphene.^{1–4} In 1991, Mackay and Terrones proposed a new allotropic form - three-dimensional (3D) periodic carbon crystal with negative Gaussian curvature. These crystals formed triply regular trivalent networks with eight- and six-membered rings.^{5–8} Afterward, there were tremendous efforts to develop polyaromatic structures containing eight-membered rings.^{9–11} Generally, two approaches can be taken: constructing an octagonal structure at the late stage of synthesis or starting the synthesis from eight-membered building units to develop polyaromatics containing octagonal structures.^{12–18}

The development of nonplanar polyarenes has been one of the hotspot synthetic goals of the past few decades because of their unique molecular and electronic properties, which originate from their distorted structure.¹⁶ Their nonplanarity generally results from the insertion of nonhexagonal rings into the framework. Tetraphenylene is a nonplanar molecule with a saddle-shape conformation,¹⁹ containing four benzene rings attached to a rigid central octahedral ring due to ortho-annulation.²⁰ Each pair of phenyl rings are arranged alternately above and below the average plane of the molecule.²¹ Tetraphenylene fits the D_{2d} symmetry point group.²² This exceptional geometry promotes unique 3D platforms suitable for unique molecular clathrates,²³ supramolecular chemistry,^{24,25} materials science,²⁶ asymmetric catalysis,^{27,28} helical π -system,²⁹ and self-assembly building units.³⁰ Because of their rigid conformations, tetraphenylenes have unique molecular structures. However, despite their distinctive architectures,

[8]circulenes have yet to attain serious consideration, likely because synthetic protocols to produce functionalized derivatives are scarce.¹⁶ The functionalization of these compounds furnishes a large variety of new building blocks.³¹

For example, functionalization of the phenyl ring in tetraphenylene results in a large variety of unprecedented precursor molecules that can be employed in the design of different structures. Heterocyclic compounds, and specifically nitrogen-containing structures, are vital because of their diverse and exciting pharmaceutical functions.³² The formation of C–N bonds, and especially aromatic compounds containing nitrogen atoms, is crucial as it unlocks the window for inserting nitrogen in organic compounds.

Despite remarkable developments in this field, organic chemists still face challenges constructing C–N bonds, because in many cases, it involves a tedious multistep synthesis and difficult reaction conditions.³² Therefore, it is vital to find more appropriate and milder procedures for incorporating the amino groups into the C–H bonds.³³ The synthesis of arylamines has become increasingly important in pharmaceutical and material research communities.³⁴ *ortho*-Phenylenediamine (*o*-phenylenediamine), as a subdivision of arylamines, has emerged as an essential chemical building block for the synthesis of a wide variety of aromatic compounds such as benzotriazole, 70

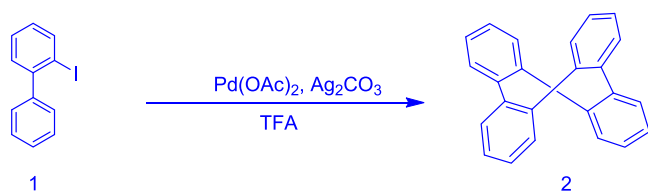
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71 benzimidazole, and pyrazine derivatives.^{35,36} Tetraphenylene
 72 with an *o*-diamine in each benzene ring could be an essential
 73 building block for further modifications. For example, a variety
 74 of organic frameworks³⁵ and heterocyclic functionalities can be
 75 synthesized by double-condensing *o*-phenylenediamine com-
 76 ponents with 1,2-dicarbonyl-containing moieties.³¹
 77 The obstacle to using molecules containing *o*-phenylenedi-
 78 amine is their sensitivity toward moisture and air.³⁷ Molecules
 79 containing *o*-diamine must be treated in an inert atmosphere or
 80 used immediately after the reduction of the *o*-dinitro
 81 precursors. An efficient and facile synthetic route to overcome
 82 this hurdle is highly desired. Here, we report a facile, air-stable,
 83 and high-yield synthetic route for octaaminotetraphenylene
 84 octahydrochloride.

85 ■ RESULTS AND DISCUSSION

86 Currently, there are four main synthetic routes to constructing
 87 a tetraphenylene (2) skeleton.^{38,39} In this work, tetraphenylene
 88 was conveniently synthesized by the palladium-catalyzed
 89 homocoupling of 2-iodobiphenyl following a literature-
 90 reported procedure (Scheme 1).

Scheme 1. Synthesis of Tetraphenylene as a Precursor for Saddle-Shape Octaaminotetraphenylene Octahydrochloride

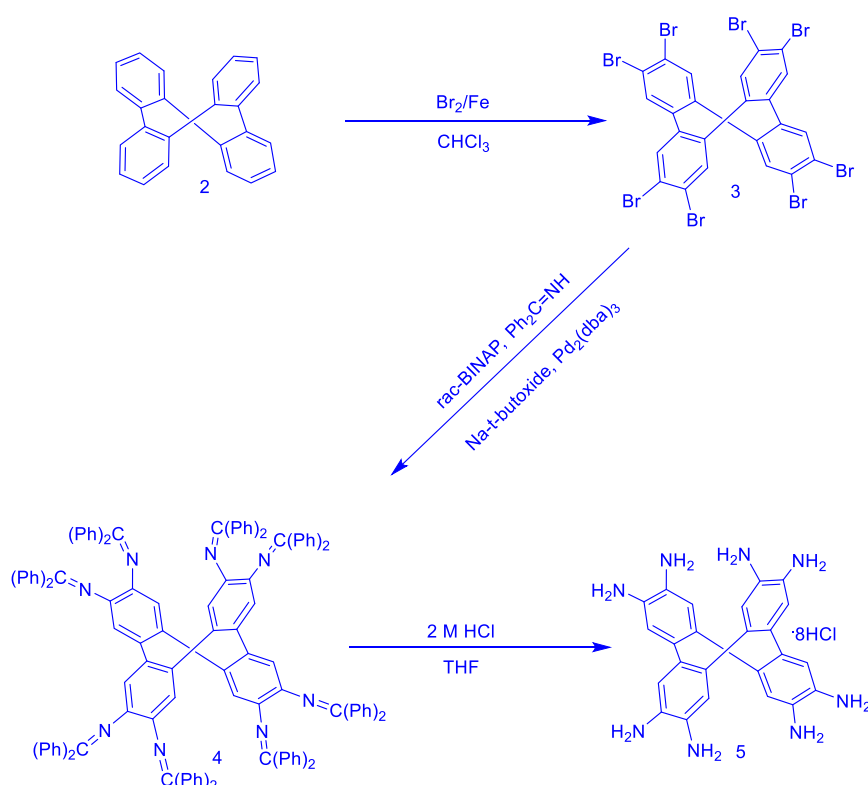


Given the exciting properties of tetraphenylene and its
 92 derivatives, the *o*-diamino derivative of tetraphenylene was
 93 designed and synthesized in four-step reactions (Scheme 2).
 94 s2

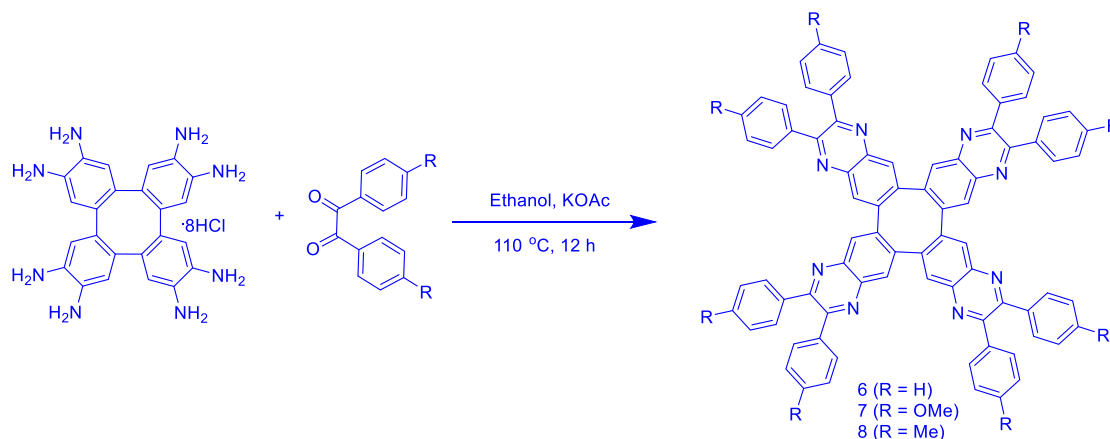
This saddle-shape tetraphenylene with cofacial benzene rings
 94 was subjected to electrophilic bromination with bromine in the
 95 presence of iron powder as a catalyst in chloroform at 80 °C,
 96 resulting in a quantitative yield of octabromotetraphenylene
 97 (3) (Figures S1–S3). Then, the palladium-catalyzed coupling
 98 reaction of compound 3 with benzophenone imine in toluene
 99 solution at 110 °C resulted in a high yield of (tetraphenylene-
 100 2,3,6,7,10,11,14,15-octyl)octakis(1,1-diphenylmethanimine)
 101 (4) (Figures S4–S6). Finally, the imine moiety was
 102 deprotected using an aqueous HCl (2 M) solution, resulting
 103 in a high yield of saddle-shape octaaminotetraphenylene
 104 octahydrochloride (5), which is an air-stable product allowing
 105 single-crystal study (*vide infra*) (Figures S7–S9).
 106

To gain more insight into the molecular geometry of
 107 compound 5 and examine its solid-state packing, brownish
 108 needle-like crystals of compound 5 were grown by passing dry
 109 HCl gas through the compound 5 solution. The crystal growth
 110 was quite challenging due to color change in common organic
 111 solvents or water without HCl. Because of color change, the
 112 recovery of the materials was difficult. Furthermore, the
 113 heating of compound 5 in solvents makes it more difficult to
 114 grow crystals. Compound 5 shows better stability in acidic
 115 conditions, so we opted to grow the crystal in concentrated
 116 HCl. Compound 5 (500 mg) was dissolved in deionized water
 117 (5 mL), filtered through a polytetrafluoroethylene (PTFE)
 118 membrane (0.45 μm) to remove dust particles, if any, and
 119 concentrated HCl (45 mL) was added. Freshly prepared dry
 120 HCl was passed through the solution for about 20 min, and the
 121 vial was tightly sealed and placed in the freezer (−20 °C) until
 122 crystals developed; it takes about a week. The brown crystals
 123

Scheme 2. Synthesis Route for Air-Stable Saddle-Shape Octaaminotetraphenylene Octahydrochloride



Scheme 3. Synthesis of Phenazine Derivatives of Octaaminotetraphenylene Octahydrochloride



124 were collected on a PTFE membrane, washed excessively with
 125 dichloromethane and hexane, and dried in the vacuum oven.
 126 The crystal structure was further confirmed by single-crystal X-
 127 ray crystallography. Compound **5** crystallizes in the ortho-
 128 rhombic form and belongs to the *Pmnn* space group ($a =$
 129 13.04 \AA , $b = 17.83 \text{ \AA}$, $c = 8.98 \text{ \AA}$) with two molecules per unit
 130 cell. The crystal structure exhibited a saddle-shape geometry
 131 with two phenyl rings oriented above and two others below the
 132 plane of the molecule with a dihedral angle of 122.9° .
 133 Protonated amine groups of the phenyl rings showed
 134 hydrogen-bonding interactions (both strong and weak) with
 135 different chlorine atoms. The N(1) atom of protonated amine
 136 has hydrogen-bonding interactions with four chlorine atoms,
 137 whereas the N(2) atom of the other protonated amine
 138 possesses hydrogen-bonding interactions with two chlorine
 139 atoms. Also, chlorine atoms possess strong anionic- π
 140 interactions with the phenyl groups of compound **5** (Table
 141 S5). The molecular structure and crystal packing of compound
 142 **5** are shown in Figures S10 and S11. The crystallographic data
 143 and refinement results are provided in Tables S1–S5.

144 The synthesis of saddle-shape octaaminotetraphenylene
 145 octahydrochloride is a facile and productive method with
 146 practical viability. The most important aspect of this synthesis
 147 is the crystal formation of air-stable octaaminotetraphenylene
 148 octahydrochloride salt. Because of its suitable synthetic route,
 149 saddle-shape octaaminotetraphenylene octahydrochloride (**5**)
 150 is a promising building block for various applications, including
 151 dendritic macromolecules and supramolecular structures, 3D
 152 covalent organic network structures, and rotaxanes. Specifi-
 153 cally, it opens the possibility of generating porous negative
 154 curvature materials.

155 For concept verification, compound **5** was reacted with 1,2-
 156 diketone compounds, such as 4,4-dimethylbenzil, 4,4-dime-
 157 thoxybenzil, and benzil in ethanol to produce compounds **6–8**
 158 (Scheme 3). The resultant compounds were analyzed by
 159 different characterization techniques (Figures S12–S20). The
 160 results demonstrate that a variety of materials can be
 161 synthesized by utilizing this stable saddle-shape octaaminote-
 162 traphenylene octahydrochloride (**5**) as a precursor.

163 CONCLUSIONS

164 In this study, we demonstrated a facile and efficient route for
 165 the synthesis of octaaminotetraphenylene octahydrochloride.
 166 This *ortho*-diamine-containing tetraphenylene derivative
 167 showed excellent stability, allowing purification using column

168 chromatography. It was used as a versatile building block for
 169 the synthesis of functional heterocyclic derivatives. More
 170 importantly, it can be a potential building block for the
 171 bottom-up synthesis of well-defined negative curvature
 172 structures.

173 EXPERIMENTAL SECTION

174 **Characterization Methods.** All chemicals, including solvents and
 175 reagents, were purchased from Aldrich Chemical, Inc. unless
 176 otherwise stated. 2-Iodobiphenyl was purchased from Alfa Aesar.
 177 Tetraphenylene was synthesized following the literature procedure.⁴⁰
 178 Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR)
 179 studies were performed on an AVANCE III HD 400 MHz FT-NMR
 180 (Bruker) spectrometer. Melting point analysis was performed with a
 181 KSPIN automatic melting point meter (A. Kriess Optronic GmbH,
 182 Germany). Elemental analysis (EA) was conducted on a Thermo
 183 Scientific Flash 2000 Analyzer. High-resolution mass spectra (HR-
 184 MS) analyses were carried out using JEOL/JMS-700 (2) and
 185 AccuTOF 4G+ DART.

186 **Single-Crystal Structure Analyses.** A crystal of octaaminote-
 187 traphenylene octahydrochloride was coated with parabar oil, and the
 188 diffraction data were measured at 100 K with synchrotron radiation (λ
 189 $= 0.80000 \text{ \AA}$) on a Rayonix MX225SHS detector at BL2D-SMC with
 190 silicon (111) double crystal monochromator (DCM) at the Pohang
 191 Accelerator Laboratory, Korea. The PAL BL2D-SMDC program⁴¹
 192 was used for data collection, and HKL3000sm⁴² was used for cell
 193 refinement, reduction, and absorption correction. The crystal
 194 structure of octaaminotetraphenylene octahydrochloride was solved
 195 by the SHELX structure solution program⁴³ and refined by full-matrix
 196 least-squares calculations with the SHELXL.⁴⁴

197 **Synthesis of 2,3,7,10,11,14,15-Octabromotetraphenylene**
 198 (**3**). A solution of tetraphenylene (0.5 g, 1.64 mmol) in distilled
 199 chloroform (60 mL) and iron powder (67 mg, 1.20 mmol, catalytic
 200 amount) were charged into a three-necked round-bottom flask (500
 201 mL), and bromine (3 mL, 59.04 mmol) was slowly added to the
 202 reaction flask and refluxed in an oil bath for 3 h. After completion, the
 203 solvent was concentrated by a rotary evaporator. Finally, the crude
 204 product was purified by column chromatography using pure hexane as
 205 an eluent to give a white solid (0.92 g, 60% yield). mp $220.5 \text{ }^\circ\text{C}$. ^1H
 206 NMR (400 MHz, CDCl_3) δ 7.42 (s, 8H) (Figure S1). $^{13}\text{C}\{^1\text{H}\}$ NMR
 207 (77.1 MHz, CDCl_3) δ 139.1, 133.9, 125.3 (Figure S2). Anal. calcd for
 208 $\text{C}_{24}\text{H}_8\text{Br}_8$: C, 30.81; H, 0.86; Br, 68.33. Found C, 30.07; H, 0.93; Br
 209 (estimated), 69.00. HRMS (DART⁺) m/z : Calcd for $\text{C}_{24}\text{H}_8\text{Br}_8$:
 210 927.4093. Found: 935.4008 ($[\text{M}^{79}\text{Br}_4^{81}\text{Br}_4]^+$ based on the relative
 211 mass abundance of bromine (79; 50.686% and 81; 49.314%); this
 212 value matches well the structure (Figure S3).

213 **Synthesis of (Tetraphenylene-2,3,6,7,10,11,14,15-octayl)-**
 214 **octakis(1,1-diphenylmethanimine) (4).** A toluene solution (85
 215 mL) of *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP,
 216 1.3 g, 2.07 mmol) and tris(dibenzylideneacetone) dipalladium(0) (1 g, 216

217 1.09 mmol) was charged into a three-necked round-bottom flask (500
218 mL) and stirred at 110 °C for 0.5 h under reflux conditions in
219 nitrogen atmosphere. After cooling, 2,3,7,10,11,14,15-octabromote-
220 traphenylene (3.0 g, 3.19 mmol), benzophenone imine (5.8 mL, 34.86
221 mmol), and sodium *tert*-butoxide (3.28 g, 35.0 mmol) were added
222 into the reaction flask and further stirred in an oil bath at 110 °C for
223 15 h. After cooling, the reaction mixture was diluted with
224 dichloromethane, filtered by passing through a pad of Celite to
225 remove metallic impurities, and the filtrate was condensed on a rotary
226 evaporator. Finally, the residue was purified through column
227 chromatography (silica gel, hexane/ethyl acetate, 8/2, v/v) as an
228 eluent to give a yellow solid (4.50 g, 80%). Mp 213.5 °C. ¹H NMR
229 (400 MHz, CDCl₃) δ 7.79–7.81 (d, *J* = 8 Hz, 32H), 7.57–7.60 (t, *J* =
230 12 Hz, 16H), 7.47–7.49 (t, *J* = 12 Hz, 32H) 7.26 (s, 8H singlet
231 merged with solvent peak) (Figure S4). ¹³C{¹H} NMR (77.1 MHz,
232 CDCl₃) δ 167.1, 140.5, 139.3, 136.7, 136.6, 130.1, 129.8, 129.3, 128.5,
233 127.9, 121.7 (Figure S5). Anal. calcd for C₁₂₈H₈₈N₈: C, 88.45; H,
234 5.10; N, 6.45. Found C, 88.02; H, 4.90; N, 6.26. HRMS (MALDI-
235 TOF) *m/z*: [M + H]⁺ calcd for C₁₂₈H₈₈N₈: 1737.7209. Found:
236 1737.735 (Figure S6).

Synthesis of Tetraphenylene-2,3,6,7,10,11,14,15-octaamine
238 (5). Aqueous HCl (2M, 5 mL) was added dropwise into a three-
239 necked round-bottom flask containing compound 4 (0.22 g, 0.12
240 mmol) solution in tetrahydrofuran (THF) over 2 h, and the reaction
241 mixture was stirred at room temperature for 6 h. Then, the mixture
242 was diluted with CH₂Cl₂, and the product was collected by solvent
243 extraction and dried under reduced pressure (0.05 mmHg). Finally,
244 the crude product was recrystallized from an aqueous HCl solution to
245 give brown crystals (0.075 g, 83% yield); mp becomes dark at 265 °C
246 before melting. ¹H NMR (400 MHz, D₂O-*d*₆) δ 6.93 (s, 8H) (Figure
247 S7). ¹³C{¹H} NMR (D₂O-*d*₆) δ 136.4, 128.0, 121.7 (Figure S8). Anal.
248 calcd for C₂₄H₃₂N₈Cl₈: C, 40.25; H, 4.50; N, 15.65; Cl, 39.60. Found
249 C, 44.24; H, 5.12; N, 13.35; Cl (estimated) 37.29. HRMS (EI) *m/z*:
250 Calcd for C₂₄H₃₂N₈: 424.2123. Found: 424.2130 (Figure S9).

Synthesis of (2,3,8,9,14,15,20,21-Octaphenylcycloocta)-
252 **tetraquinoxaline (6).** Compound 5 (150 mg, 0.21 mmol) and
253 benzil (222 mg, 1.05 mmol) solution in ethanol (15 mL) were added
254 into a three-necked round-bottom flask (50 mL), and the reaction
255 mixture was heated in an oil bath to 110 °C overnight. After
256 completion, the crude product was poured into ice cold water.
257 Precipitate was collected by suction filtration and air-dried. The
258 product was purified by column chromatography (silica gel, hexane/
259 EtOAc, 9/1, v/v) and further recrystallized from acetone/hexane (9/
260 1, v/v) mixture to give a pale yellow solid (152 mg, 64% yield). Mp
261 >360 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 8H), 7.51–7.49 (d,
262 *J* = 8 Hz, 16H), 7.35–7.33 (m, 8H), 7.32–7.29 (m, 16H) (Figure
263 S12). ¹³C{¹H} NMR (77.1 MHz, CDCl₃) δ 154.3, 142.7, 140.8,
264 138.9, 129.9, 129.3, 129.0, 128.4 (Figure S13). Anal. calcd for
265 C₈₀H₄₈N₈: C, 85.69; H, 4.31; N, 9.99. Found C, 85.64; H, 4.81; N,
266 8.95. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₈₀H₄₈N₈: 1121.4079.
267 Found: 1121.4073 (Figure S14).

Synthesis of (2,3,8,9,14,15,20,21-Octakis(4-
269 **methoxyphenyl)cycloocta)tetraquinoxaline (7).** Compound 5
270 (150 mg, 0.21 mmol), anisil (285.4 mg, 1.05 mmol), and potassium
271 acetate (165 mg, 1.5 mmol) were charged into a three-necked round-
272 bottom flask (50 mL), and then ethanol (15 mL) was added into the
273 reaction mixture under nitrogen. The reaction flask was stirred in an
274 oil bath at 110 °C for 12 h. After cooling, ice cold water was poured
275 into the reaction flask to precipitate out the resulting product, which
276 was purified through column chromatography (silica gel, hexane/
277 EtOAc, 8/2, v/v) to acquire product, which was further recrystallized
278 from acetone to give an off-white solid (187 mg, 65% yield). Mp >360
279 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 8H), 7.46–7.44 (d, *J* = 8
280 Hz, 16H), 6.85–6.83 (d, *J* = 8 Hz, 16H), 3.81 (s, 24H) (Figure S15).
281 ¹³C{¹H} NMR (77.1 MHz, CDCl₃) δ 160.3, 153.7, 142.5, 140.6,
282 139.1, 131.6, 129.0, 113.8, 55.4 (Figure S16). Anal. calcd for
283 C₈₈H₆₄N₈O₈: C, 77.63; H, 4.74; N, 8.23; O 9.40. Found: C, 77.76;
284 H, 5.57; N, 7.11; O 10.67. HRMS (ESI) *m/z*: [M + Na]⁺ calcd for
285 C₈₈H₆₄N₈O₈: 1383.4745. Found: 1383.4751 (Figure S17).

Synthesis of (2,3,8,9,14,15,20,21-Octa-*p*-tolylcycloocta) tetra-
286 **quinoxaline (8).** Compound 5 (150 mg, 0.21 mmol), 4,4-dimethyl
287 benzil (255 mg, 1.05 mmol) and potassium acetate (165 mg, 1.60
288 mmol) were placed into a three-necked round-bottom flask (50 mL),
289 and then ethanol (15 mL) was poured into the reaction flask under
290 nitrogen and stirred at 110 °C in an oil bath for 12 h. After cooling,
291 the reaction mixture was slowly poured into ice cold water to
292 precipitate out the resulting product, which was purified by column
293 chromatography (silica gel, hexane/EtOAc, 9/1, v/v) to afford an off-
294 white powder (178 mg, 69% yield). Mp >360 °C. ¹H NMR (400
295 MHz, CDCl₃) δ 8.13 (s, 8H), 7.39–7.37 (d, *J* = 8 Hz, 16H), 7.12–
296 7.10 (d, *J* = 8 Hz, 16H), 2.35 (s, 24H) (Figure S18). ¹³C{¹H} NMR
297 (77.1 MHz, CDCl₃) δ 154.3, 142.6, 140.7, 139.0, 136.3, 129.8, 129.2,
298 129.0, 21.50 (Figure S19). Anal. calcd for C₈₈H₆₄N₈: C, 85.69; H,
299 5.23; N, 9.08. Found: C, 84.14; H, 5.21; N, 8.11. HRMS (ESI) *m/z*:
300 [M + H]⁺ calcd for C₈₈H₆₄N₈: 1233.5331. Found: 1233.5341 (Figure
301 S20). 302

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/10.1021/acs.joc.1c01127>.

Proton/carbon NMR and HRMS of new compounds.
Single-crystal structure and crystal packing of compound
5. Crystal data and structure refinement results of
compound 5 (PDF)

Accession Codes

CCDC 2083485 contains the supplementary crystallographic
data for this paper. These data can be obtained free of charge
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354 Notes

355 The authors declare no competing financial interest.

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