

1 Inner-Bond Cleavage in Nanographenes: A 2 Constructive Destruction Strategy for Facile Access 3 to Molecules with Multiple Figure-Eight Structures

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21 **The elegant architectures of nonplanar π -systems, such as fullerene and corannulene,**
22 **exhibit distinctive functionalities that have played a significant role in advancing science**
23 **and technology. The current approach to synthesizing nonplanar π -systems heavily relies**
24 **on the stepwise formation of bonds between their constituent fragments, which is known**
25 **as the bottom-up approach. The limited number of synthetic pathways to nonplanar π -**
26 **systems inevitably results in impractical molecular frameworks. Herein, we demonstrate**
27 **that a constructive destruction approach, based on the oxidative cleavage of internal**
28 **double bonds of dibenzo[*g,p*]chrysene that immediately produces eightphenone: the first**
29 **readily available figure-eight molecule. Eightphenone adopts a D_2 -symmetric structure**

30 with excellent configurational stability and is a highly efficient emitter of circularly
31 polarized phosphorescence. The oxidative cleavage of internal double bonds is also
32 applicable to larger nanographene molecules, resulting in unprecedented structures with
33 multiple figure-eight units. This study introduces the concept of constructive destruction
34 as an alternative to conventional bottom-up approaches, paving the way for the design of
35 new materials.

36 The design of organic molecules is not only an academic curiosity for scientists but has
37 also contributed significantly to the evolution of science and technology. Nonplanar π -systems
38 with distinct three-dimensional shapes, such as bowls, waves, hoops, helices, and spheres,
39 represent an important class of molecules due to their beautiful structures and characteristic
40 functions.¹⁻⁶ To promote the use of such essential molecules in materials science, procedures
41 for their synthesis need to be scalable. Fullerenes,⁷ corannulenes,^{8,9} helicenes,^{10,11}
42 calix[*n*]arenes,¹² cycloparaphenylenes,^{13,14} and pillar[*n*]arenes¹⁵ meet this standard, and have
43 found diverse applications in organic electronics, optical materials, supramolecular assemblies,
44 and molecular recognition (Figure 1a).¹⁶⁻²¹ This wide range of applications highlights the
45 potential of readily available nonplanar π -systems to facilitate the creation of next-generation
46 materials. However, the current syntheses of nonplanar π -systems heavily rely on the stepwise
47 formation of bonds between their constituent fragments, which is known as the ‘bottom-up’
48 approach. The limited number of synthetic pathways to create nonplanar π -systems inevitably
49 results in impractical molecular frameworks.

50 Nonplanar conjugated macrocycles with a figure-eight conformation are topologically
51 different from conventional non-twisted cyclic molecules due to their characteristic 360°-
52 twisted macrocyclic conjugation (Figure 1b).²²⁻³⁷ This twisting leads to cross-linked
53 conjugation at the molecular center and the emergence of chirality. Consequently, figure-eight
54 molecules exhibit fascinating properties, such as efficient circularly polarized luminescence
55 (CPL)³⁵⁻³⁷ and unusual rearrangement reactions.^{33,34} However, to the best of our knowledge,
56 figure-eight molecules that can be easily synthesized remain unprecedented. This is most likely
57 due to a lack of alternative synthetic means to the conventional bottom-up approaches, which

58 often requires multistep transformations to avoid undesired side reactions.

59 In 1934, Suszko and Schillak reported that the treatment of dibenzo[*g,p*]chrysene (DBC;
60 **1a**) with sodium dichromate results in the oxidative cleavage of the inner double bond, yielding
61 tetrabenzocyclodecan-1,6-dione (**2a**) (Figure 1c).³⁸ In 1980, the X-ray crystal structure of **2a**
62 was reported.³⁹ However, the figure-eight structure of **2a** has arguably been under-appreciated
63 so far, and detailed, systematic investigations into its chemistry have not yet been
64 conducted.^{40,41}

65 In this study, we have revisited the chemistry of the oxidative cleavage of the inner double
66 bond of DBC and examined its utility with regard to the scope of the transformation and the
67 fundamental properties of the products of this reaction, thus establishing a constructive
68 destruction approach. Constructive destruction should be thought of as an internal-modification
69 strategy of conjugated π -systems in the same vein as molecular surgery,⁴² a research area which
70 also remains underexplored so far. We have also named tetrabenzocyclodecan-1,6-dione **2a**
71 ‘eightphenone’ in light of its beautiful figure-eight structure that consists of two benzophenone
72 subunits.

73 Eightphenone **2a** was synthesized via a modified literature procedure (Figure 2a).³⁸ A flask
74 was charged with **1a** (1.0 mmol), sodium dichromate dihydrate (Na₂Cr₂O₇•2H₂O), and acetic
75 acid, before the mixture was heated to reflux and stirred for 12 h. The subsequent addition of
76 water to the crude mixture furnished a white precipitate, which was collected by filtration.
77 Further purification using column chromatography on silica gel followed by recrystallization
78 from CH₂Cl₂/MeOH afforded eightphenone **2a** in 83% yield. This process can be scaled up by
79 omitting the column chromatography purification step, which afforded 23 g of **2a** (64% yield).

80 The reaction of 3,11-dibromo DBC (**1b**) under the same conditions also proceeded
81 smoothly to furnish 2,7-dibromoeightphenone (**2b**) in 82% yield. However, the reaction of
82 2,7,10,15-tetrabromo DBC (**1c**) under the same conditions was impeded by its low solubility.
83 Replacing acetic acid with propionic acid and increasing the reaction temperature promoted the
84 conversion, furnishing the corresponding tetrabrominated eightphenone (**2c**) in 69% yield.
85 1,8,9,16-Tetrabromo DBC (**1d**) was also reactive under these conditions, providing 4,5,12,13-

86 tetrabromoeightphenone (**2d**) in 43% yield. However, the reaction of 3,6,11,14-tetrabromo
87 DBC (**1e**) was significantly impeded by its poor solubility, affording 2,7,10,15-
88 tetrabromoeightphenone (**2e**) in merely 2% yield. Attempting the oxidative cleavage of **1e** in
89 refluxing butyric acid instead of propionic acid did not yield **2e**. These brominated
90 eightphenone derivatives can be expected to serve as useful precursors for the construction of
91 more elaborate frameworks.

92 The crystallization of racemic eightphenone **2a** from CH₂Cl₂/MeOH afforded a single
93 crystal suitable for X-ray diffraction analysis, which revealed that **2a** exhibits a figure-eight
94 structure identical to that reported by Cameron and Chan (Figure S52).³⁹ The strain energy of
95 **2a** has been estimated to be 15.5 kcal mol⁻¹, based on a hypothetical homodesmotic reaction
96 using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level (Figure S87).
97 The space group of the obtained single crystal is C222₁ (No. 20), which belongs to the Sohncke
98 group. We randomly chose four single crystals and determined their enantiomeric excesses to
99 be >99% ee (Figure S72). These results indicate that during the crystallization of **2a** it undergoes
100 a spontaneous resolution to afford a conglomerate, which is informative for the development of
101 a practical procedure that yields enantiopure **2a**.

102 The enantiomers of **2a** and those of its brominated derivative **2c** were separated using
103 high-performance liquid chromatography (HPLC) (Figures S64, S65). An X-ray diffraction
104 analysis revealed that the first fraction of **2c** is the (*M,M*)-enantiomer with a Flack parameter
105 of 0.002(7) (Figure S55). The palladium-catalyzed debromination of (*M,M*)-**2c** with
106 HCOOH/NEt₃ afforded (*M,M*)-**2a** (Scheme S1), which is identical to the first eluted fraction
107 from the HPLC resolution of **2a** (Figure S69). The activation barrier of the racemization process
108 of **2a** was evaluated by monitoring the decrease of the circular dichroism (CD) signals upon
109 heating. This analysis afforded an activation enthalpy (ΔH) of 29.8 kcal mol⁻¹ and an activation
110 entropy (ΔS) of -11 cal K⁻¹ mol⁻¹ (Figures S73, S74). These results indicate that **2a** is
111 configurationally stable at room temperature.

112 The process by which **2a** racemizes was simulated using DFT calculations (Figure 2b).
113 Figure-eight conformer **A** untwists to adopt the distorted ring conformation **B** with the two

114 carbonyl groups rotated inwards in opposite directions. While conformer **B** is chiral, it
115 isomerizes to achiral conformer **C** via a small activation barrier (1.9 kcal mol⁻¹). Further
116 isomerization finally affords an inverted figure-eight conformation. The overall activation
117 barrier for this process (33.7 kcal mol⁻¹) agrees closely with the experimentally determined
118 value. It is worth noting that we also found another possible isomerization route (Figure S88).
119 In this route, conformer **A** rotates the two carbonyl groups in the same direction to afford a
120 slightly unstable intermediate with a distorted ring structure ($\Delta E = 2.4$ kcal mol⁻¹) that retains
121 the chirality. However, the subsequent racemization of this structure requires a drastic activation
122 energy (51.7 kcal mol⁻¹), which renders this pathway implausible.

123 The UV/vis absorption of eightphenone **2a** in the range 300–380 nm is stronger than the
124 absorption of the n- π^* transition in benzophenone. This is due to the contribution of the π - π^*
125 transition in **2a** that arises from the π -extension along the biphenyl subunits (Figures S75, S83).
126 While **2a** is virtually non-emissive in CH₂Cl₂ at room temperature, phosphorescence with a
127 lifetime of 1.3×10^2 ms was observed in 2-methyltetrahydrofuran (2-MeTHF) at 77 K (Figure
128 S75). Transient absorption spectroscopy indicated that intersystem crossing proceeds rapidly
129 with a time constant of 3 ps (Figure S78). The CD and CPL spectra of (*M,M*)-**2a** and (*P,P*)-**2a**
130 are shown in Figure 2c. The CPL *g* values, $|g_{\text{CPL}}|$, reach 3.3×10^{-2} at 447 nm, which is higher
131 than those of previously reported organic molecules.⁴³

132 Next, we examined transformations of the carbonyl groups of eightphenone **2a** (Figure 3a).
133 Hydrogenation with sodium borohydride (NaBH₄) proceeded smoothly at room temperature to
134 afford diol **3** in 89% yield with a syn/anti ratio of 5:3. Treatment with 1.2 equiv of
135 triisopropylethynyllithium furnished the corresponding mono-adduct (**4**) in 96% yield. A Wittig
136 reaction with *in-situ*-generated methylenetriphenylphosphorane transformed the carbonyl
137 groups into *exo*-methylene groups, providing **5** in 4% yield. A single-crystal X-ray diffraction
138 analysis of **5** revealed a distorted ring conformation. The formation of this conformation is
139 likely due to the destabilization of the figure-eight conformation by the steric repulsion between
140 the *exo*-methylene units and the phenyl groups.

141 The functionalization of the peripheral sites of the benzene rings of **2a** is shown in Figure

142 3b. Bromination of **2a** with *N*-bromosuccinimide (NBS) furnished 2,7,10,15-
143 tetrabromoeightphenone (**2e**) in 15% yield. The low yield is due to the formation of byproducts
144 with three or five bromo groups. In contrast, iodination with *N*-iodosuccinimide (NIS)
145 proceeded selectively, affording **2e** in 58% yield. Brominated eightphenones **2c** and **2e** were
146 subsequently used in Suzuki–Miyaura cross-coupling reactions with 4-methylphenylboronic
147 acid, and furnished the corresponding *p*-tolylated derivatives **6** and **7** in 75% and 82% yield,
148 respectively. A single-crystal X-ray diffraction analysis of **7** revealed a π -extended figure-eight
149 structure (Figure S63).

150 2,7,10,15-Tetra(*p*-tolyl)eightphenone (**7**) exhibited fluorescence at 482 nm in CH₂Cl₂ with
151 a quantum yield of 2.7% and a lifetime of 6.4 ns (Figure S77). The enantiomers of **7** were
152 separated using HPLC (Figure S68). The CD and CPL spectra of the obtained fractions are
153 shown in Figure 3c, whilst the absolute configuration of the enantiomer has been determined
154 by the transformation of the corresponding enantiomerically pure brominated precursor whose
155 configuration has been confirmed by X-ray diffraction analysis (Figures S58, S71). Importantly,
156 these enantiomers display intense CPL with a high $|g_{\text{CPL}}|$ value of 1.4×10^{-2} . 3,6,11,14-Tetra(*p*-
157 tolyl)eightphenone (**6**) also showed CPL with a $|g_{\text{CPL}}|$ value of ca. 1×10^{-2} (Figure S76). These
158 g values are high and compare favorably with previously reported organic CPL emitters.^{44,45}
159 TD-DFT calculations on **6** and **7** revealed that their electric and magnetic transition dipole
160 moments adopt parallel arrangements due to their D_2 -symmetric structures, which is ideal for
161 archiving high g_{CPL} values.^{35–37}

162 To create more challenging structures that consist of two figure-eight subunits, we
163 subjected three nanographene molecules, tetrabenzo[*a,c,f,m*]phenanthro[9,10-*k*]tetraphene (**8**),
164 tetrabenzo[*a,c,f,k*]phenanthro[9,10-*m*]tetraphene (**9**), and hexabenzo[*a,c,fg,j,l,op*]tetracene
165 (**10**),⁴⁶ to constructive destruction (Figure 4a). Treatment of **8–10** with Na₂Cr₂O₇•2H₂O in
166 refluxing propionic acid cleaved the two inner double bonds of these molecules to furnish **11**,
167 **12**, and **13** in 50%, 38%, and 16% yield, respectively. The oxidatively cleaved C–C bonds are
168 identical to the local double bonds predicted by Clar's rule.⁴⁷ This empirical assumption was
169 corroborated using the harmonic oscillator model of aromaticity (HOMA)⁴⁸ values (Figure S86).

170 These results offer rational guidelines for predicting the selectivity of the oxidative cleavage of
171 the inner double bonds in such nanographene molecules.

172 X-ray diffraction analyses of **11**, **12**, and **13** revealed that they possess remarkably distorted
173 structures and that their local eightphenone subunits adopt figure-eight conformations (Figure
174 4b). In the structures of **11** and **12**, two eightphenone subunits share one benzene ring, which
175 results in the formation of S-shaped structures. Compound **11** is achiral because the two
176 eightphenone subunits are mirror images of each other, creating a rotatory reflection axis
177 orthogonal to the central benzene ring. Conversely, **12** is chiral because the two eightphenone
178 subunits adopt the same configuration. In the case of **13**, two eightphenone subunits with the
179 same configuration share a biphenyl unit, which affords a helical structure in which three
180 biphenyl segments are linked by carbonyl groups. The twisting angle between the two phenyl-
181 phenyl linkages at both ends is very large (270°) despite its short distance (6.2 \AA), thus creating
182 a short pitch (8.3 \AA). To the best of our knowledge, **11–13** are the first examples of nonplanar
183 π -systems that consist of more than two figure-eight subunits. These highly distorted structures
184 can be expected to be difficult to construct using conventional bottom-up approaches.

185 In summary, we have investigated the oxidative cleavage of the inner double bonds in
186 dibenzo[*g,p*]chrysene (DBC; **1a**) and we have developed four interesting strands of research in
187 this context. Firstly, we have shown that it is possible to scale this reaction up to yield 23 g of
188 eightphenone (**2a**) in one reaction. Secondly, we synthesized four brominated derivatives of **2a**
189 from brominated DBC precursors. It was then possible, using Suzuki–Miyaura cross-coupling
190 reactions of these building blocks, to readily obtain *p*-tolyl-derivatives that exhibit circularly
191 polarized luminescence with high g_{CPL} values of more than 1×10^{-2} . Thirdly, we investigated
192 the fundamental properties of **2a**, which revealed that (1) during crystallization, **2a** undergoes
193 spontaneous resolution to afford a conglomerate; (2) **2a** is configurationally stable with an
194 inversion barrier of 30 kcal mol^{-1} ; (3) the photoexcitation of **2a** creates a triplet state that emits
195 circularly polarized phosphorescence with a high g value of 3.3×10^{-2} ; and (4) the carbonyl
196 groups of **2a** can undergo conventional organic transformations, such as a hydride reduction,
197 nucleophilic alkynylation, and Wittig reactions. Finally, we synthesized three nonplanar π

198 systems that consist of two figure-eight subunits. These highly distorted structures can be
199 expected to be difficult to construct using conventional bottom-up approaches, and, to the best
200 of our knowledge, represent the first examples of nonplanar π -systems that consist of more than
201 two figure-eight subunits. The present results demonstrate a new synthetic strategy that we have
202 coined ‘constructive destruction’. Constructive destruction should be thought of as an internal-
203 modification strategy of conjugated π -systems and is a powerful strategy to create challenging
204 molecular fragments. This approach can be expected to become helpful in the design and
205 development of future materials.

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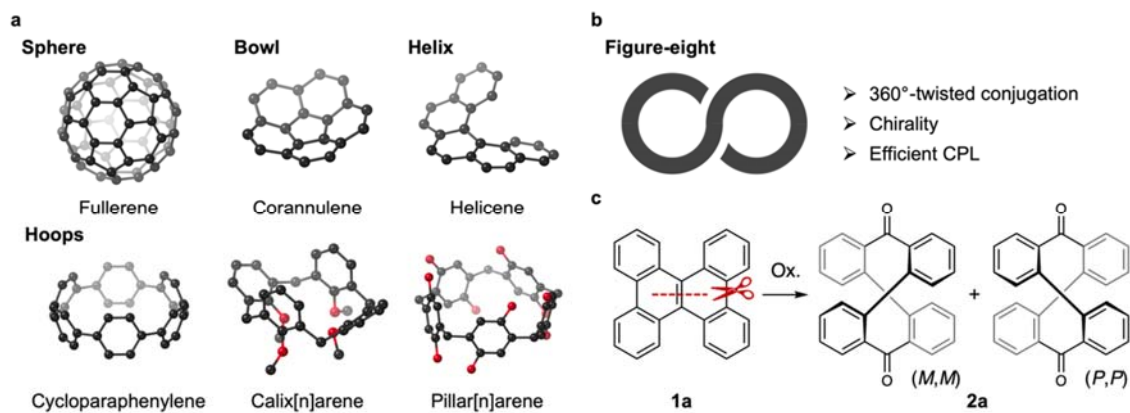
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297

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306



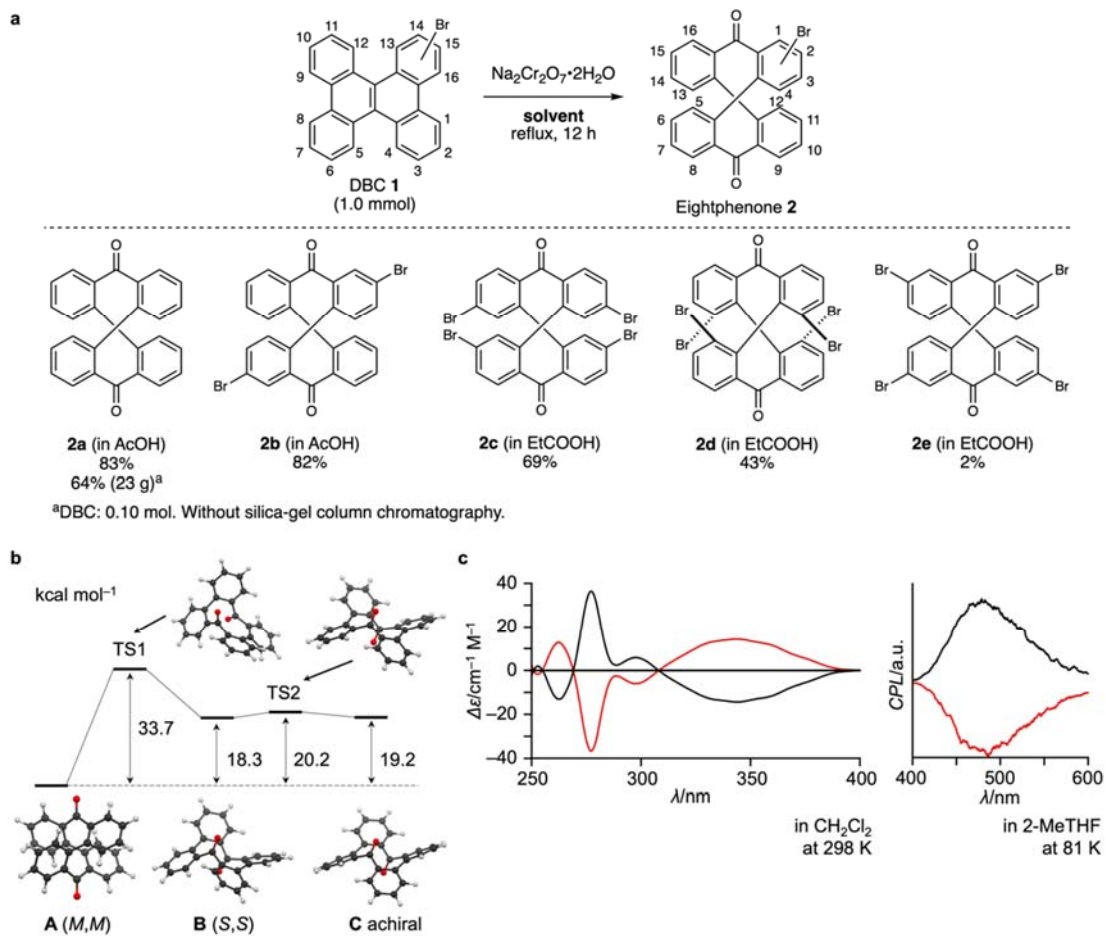
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308 **Fig. 1 Background information and focus of this study. a**, Widely known examples of

309 nonplanar π -systems. **b**, Properties of figure-eight π -systems. **c**, Synthesis of figure-eight

310 molecule **2a** via cleavage of the inner double bond of DBC **1a**.

311



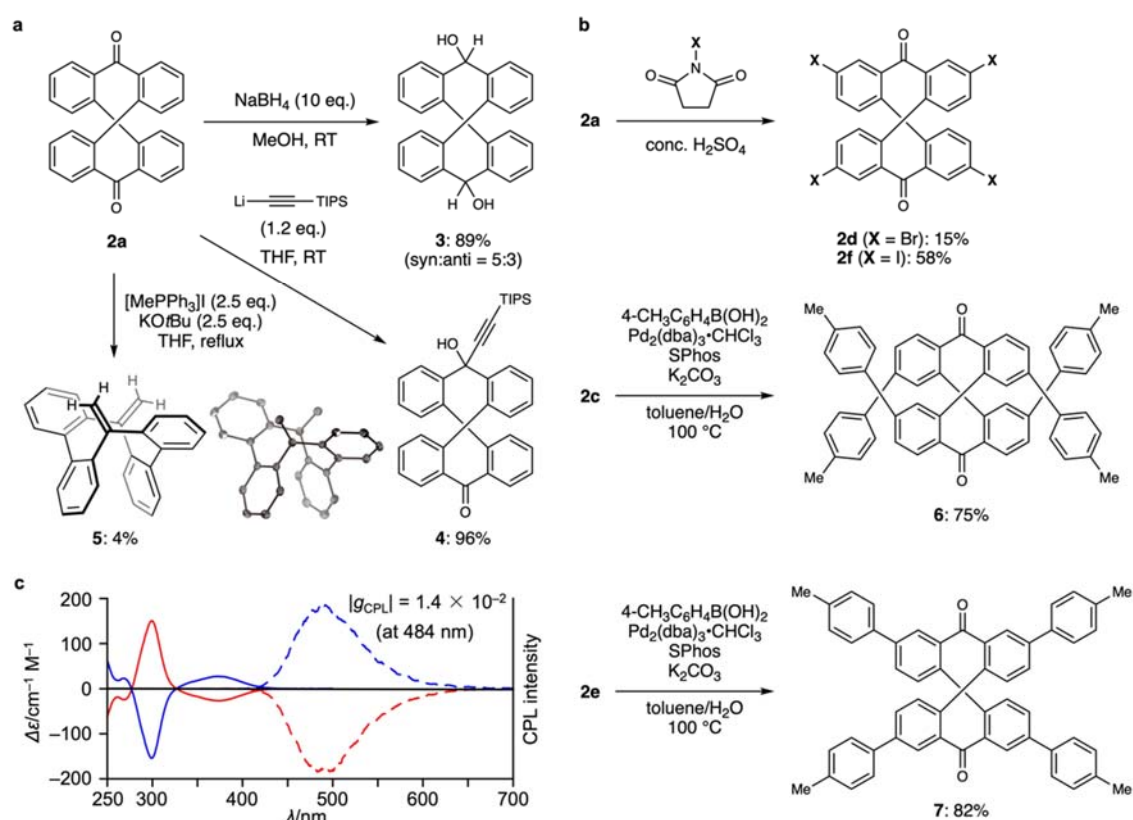
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313 **Fig. 2 Synthesis and properties of eightphenones (2).** a, Synthesis of eightphenone 2a and its

314 brominated derivatives (2b-2e). b, Simulated conformational dynamics of the racemization of

315 2a. c, CD (left) and CPL (right) spectra of (*M,M*)-2a (black) and (*P,P*)-2a (red).

316



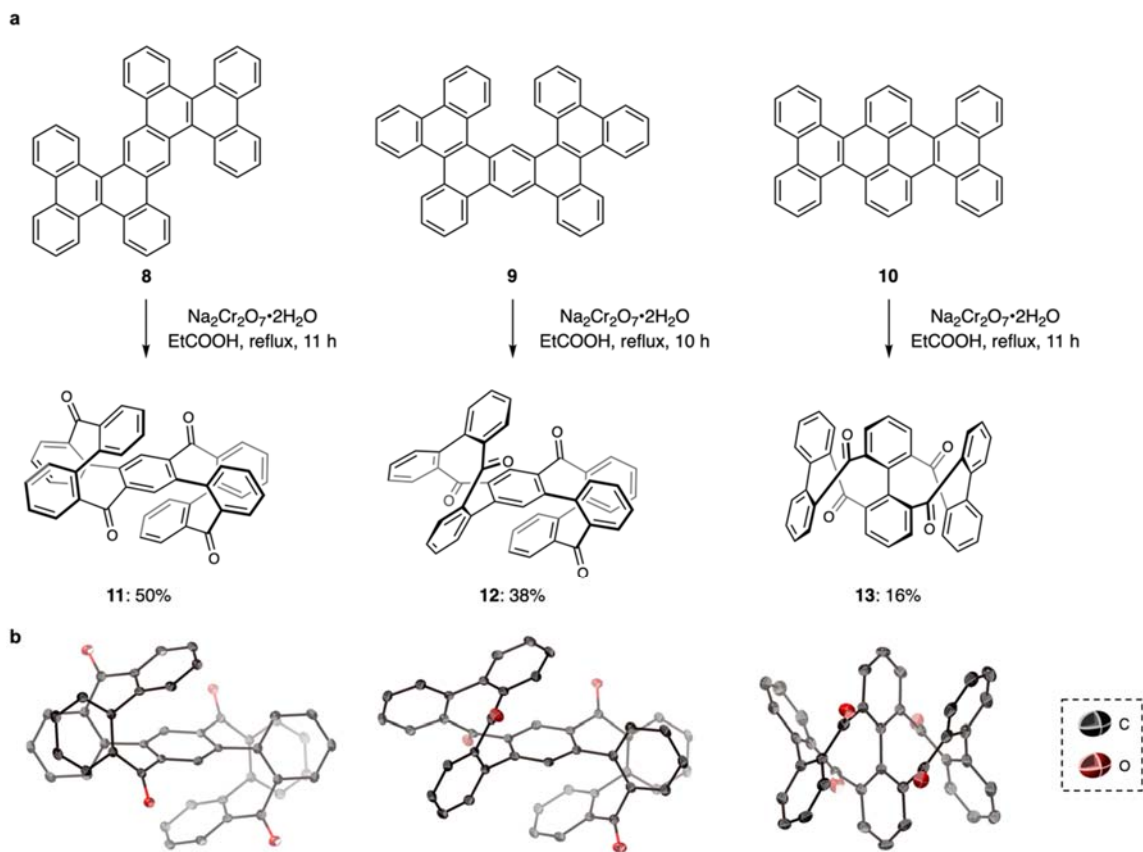
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318 **Fig. 3 Functionalization of the peripheral sites of eightphenone. a**, Transformations of the

319 carbonyl groups in **2a**. **b**, Functionalization of the benzene rings in **2a**, **2c**, and **2e**. **c**, CD (solid)

320 and CPL (dashed) spectra of (*M,M*)-**7** (red) and (*P,P*)-**7** (blue) in CH₂Cl₂.

321



322

323

Fig. 4 Constructive destruction of larger nanographene molecules. a, Oxidative bond

324

cleavage of the inner double bonds of nanographene molecules **8**, **9**, and **10**. **b,** X-ray crystal

325

structures of **11** (left), **12** (middle), and **13** (right).

326