ChemPubSoc Europe

DOI: 10.1002/ejoc.201600311

EurJOC European Journal of Organic Chemistry

Full Paper

Fullerenes

Synthesis of a Crushed Fullerene $C_{60}H_{24}$ through Sixfold Palladium-Catalyzed Arylation

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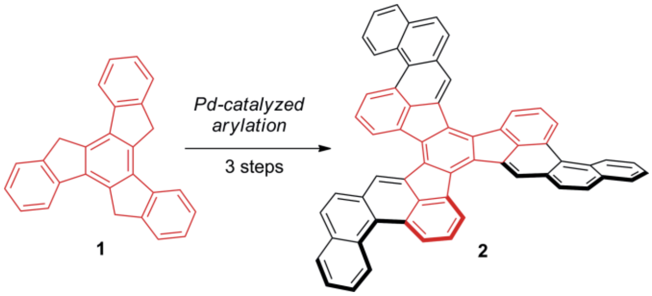
Dedicated to Professor Achille Umani-Ronchi in the occasion of his 80th birthday

Abstract: The synthesis of a new C_{3v}-symmetric crushed fullerene $C_{60}H_{24}$ (**5**) has been accomplished in three steps from truxene through sixfold palladium-catalyzed intramolecular arylation of a *syn*-trialkylated truxene precursor. Laser irradiation of **5** induces cyclodehydrogenation processes that result in the formation of C_{60}, as detected by LDI-MS.

Introduction

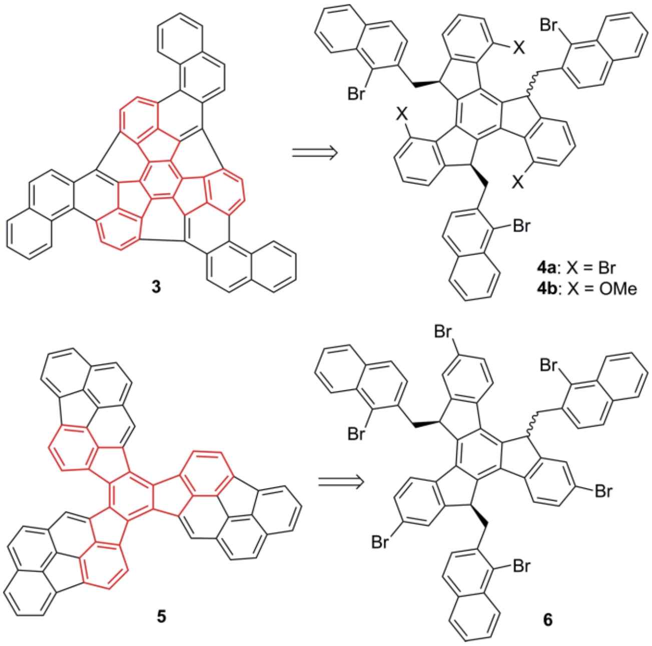
Truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorene) (**1**) is a useful platform for the threefold synthesis of crushed fullerene $C_{60}H_{30}$ (**2**) and other C_{3v}-symmetric molecules (Scheme 1),[1–3] as well as being an attractive building block for the preparation of new materials to be used in molecular electronics.[4] The laser-induced cyclodehydrogenation in the gas phase to form closed-shell C_{60} fullerene has been previously demonstrated for **2** ("crushed fullerene")[5] and other related functionalized compounds,[6] whereas flash-vacuum pyrolysis was used in the synthesis of fullerene C_{60} from $C_{60}H_{27}Cl_3$ as the precursor.[7]



Scheme 1. Synthesis of crushed fullerene $C_{60}H_{30}$ (**2**).

Fullerene C_{60} and triazafullererene $C_{57}N_3$ were also formed from **2** and $C_{57}H_{33}N_3$[8] precursors, respectively, by cyclodehydrogenation on a platinum surface.[9] STM images were obtained for deposited triangular fullerene precursors that, after annealing at 750 K, formed round-shaped C_{60}, indistinguishable from those images of authentic C_{60} fullerene, and ball-shaped heterofullerene $C_{57}N_3$, which was previously unknown.

We now report our efforts towards the synthesis of new crushed fullerenes already containing 78 of the 90 C–C bonds present in C_{60} fullerene. We envisioned two possible truxene-



Scheme 2. Retrosynthetic strategy for crushed fullerenes $C_{60}H_{24}$ **3** and **5**.

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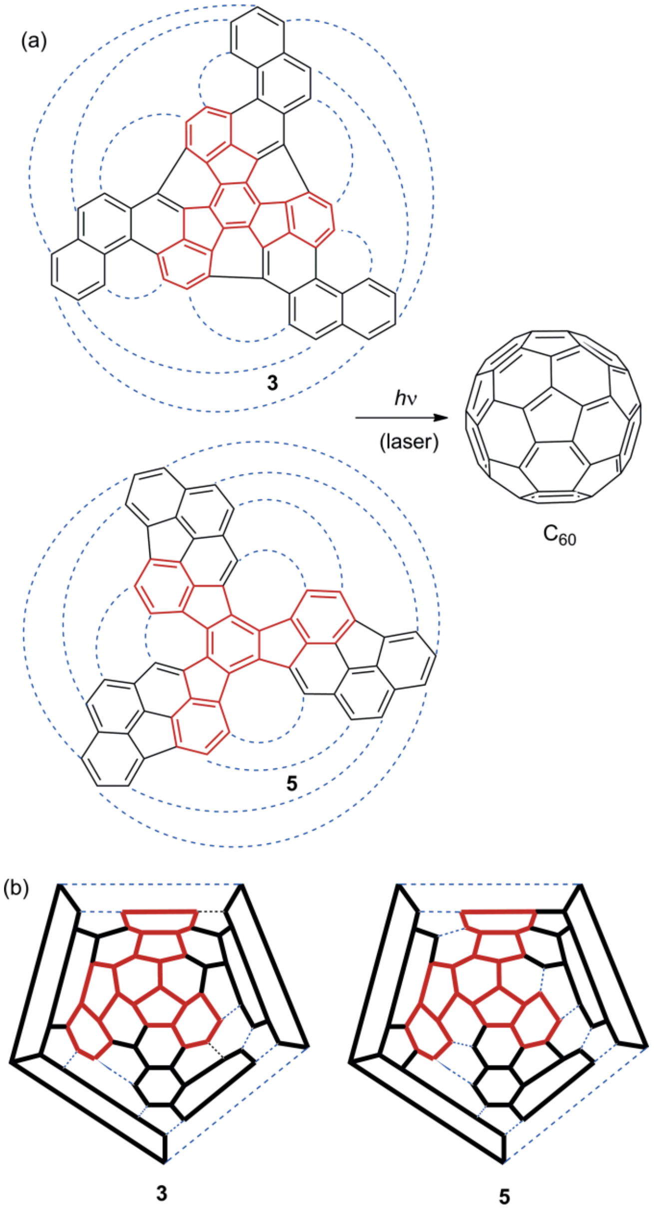
based $C_{60}H_{24}$ isomers **3** and **5**, which are more advanced crushed fullerenes than **2** and could be respectively accessed from the suitably functionalized trialkylated truxene precursors **4** and **6** by means of multiple Pd-catalyzed direct arylations (Scheme 2).[10] These π-expanded truxenes could also give rise to C_{60} by laser-promoted cyclodehydrogenation (Scheme 3). Interestingly, **5** was proposed to be a plausible intermediate in the formation of C_{60} fullerene,[11] although its synthesis and characterization have never been reported.

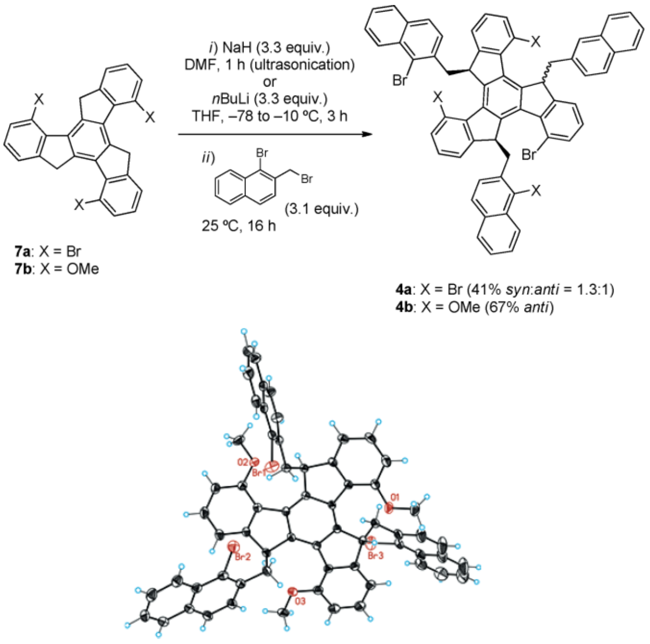


Scheme 3. (a) Laser-induced formation of C_{60} fullerene from **3** and **5**. (b) Schlegel projections of **3** and **5** onto C_{60}.

Although remarkable multiple intermolecular palladium-catalyzed arylations have been reported,[12] for the intramolecular palladium-catalyzed arylation reaction of bromoarenes, the formation of **5** from **6** would involve the highest order (sixfold) arylation of this type to date.[12a]

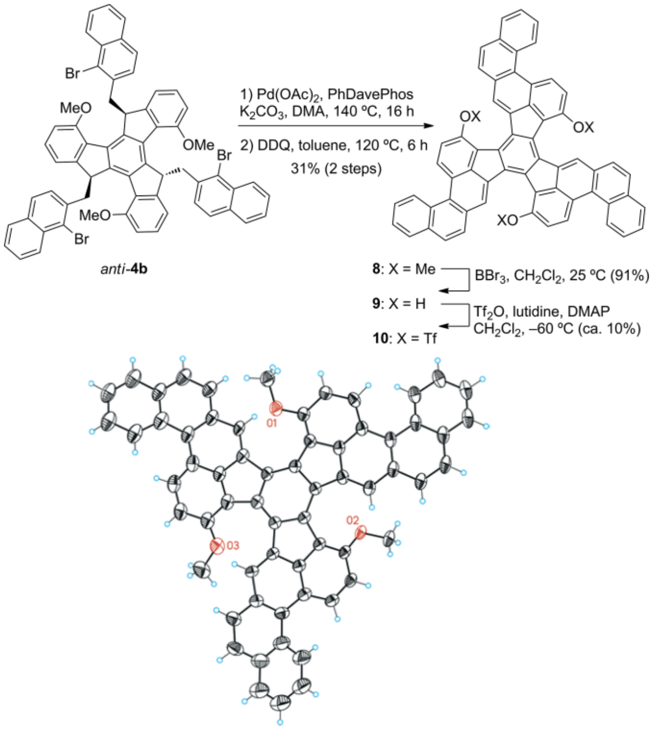
Results and Discussion

4,9,14-Trisubstituted truxenes **7** were prepared by acid-catalyzed trimerization of the corresponding 7-substituted 1-indanones.[1b] Triple alkylation of their lithium or sodium trianions afforded the expected products **4** as crude mixtures of *syn* and *anti* isomers, as determined from ^1H NMR spectra of the crude materials, which surprisingly could not be isomerized in the presence of base to form exclusively the *syn* isomer, as we had previously observed in the vast majority of cases.[1a] Thus, **4a** was obtained as a 1.3:1 mixture of *syn* and *anti* isomers after chromatographic purification, whereas in the case of **4b**, pure *anti* isomer was isolated after column chromatography and precipitation from mixtures of CH_2Cl_2 and pentane (Scheme 4). The structure of *anti*-**4b** was confirmed by X-ray diffraction analysis.[13]



Scheme 4. Synthesis of trialkylated precursors **4** and X-ray crystal structure of *anti*-**4b**.

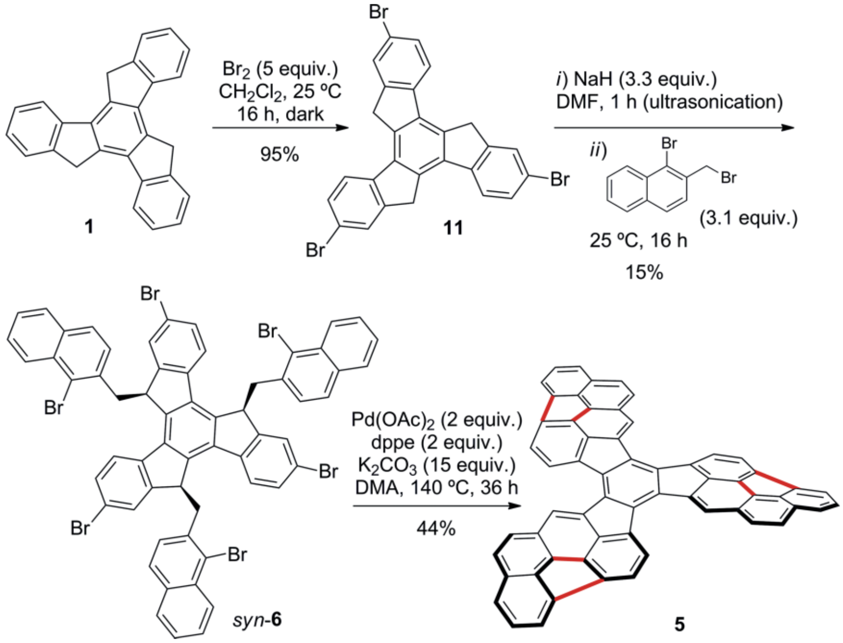
Given that all attempts to convert **4a** directly into crushed fullerene **3** by Pd-catalyzed intramolecular direct arylation afforded complex mixtures from which **3** could not be identified, we turned our attention to the cyclization of **4b**. It seemed clear to us that this cyclization could be sequentially carried out by initial triple Pd-catalyzed cyclization of **4b** to form **8** after dehydrogenation, followed by triple demethylation, formation of the corresponding tristriflate, and subsequent triple Pd-catalyzed intramolecular arylation (Scheme 5). After screening a range of reaction conditions, we found that the triple Pd-catalyzed cyclization of *anti*-**4b** proceeded in moderate yield in the presence of $Pd(OAc)_2$ and PhDavePhos. Treatment of the resulting mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) forced the triple dehydrogenation to afford **8** in 31 % yield over the two steps, the structure of which was confirmed by X-ray diffraction.[13] Demethylation of **8** was carried out with BBr_3 to form **9** as a poorly soluble solid in excellent yield. However, conversion of **9** into tristriflate **10** could only be achieved at low temperatures and in low yield. Furthermore, **10** turned out to be unstable under ambient conditions, and attempts to cyclize this tristriflate to form **3** in the presence of different Pd catalysts failed, providing complex mixtures, presumably due to its low stability.



Scheme 5. Synthesis tristriflate **10** from *anti*-**4b** and X-ray crystal structure of **8**.

Not discouraged by these results, we decided to focus our efforts on the synthesis of crushed fullerene **5**. Thus, tribromotruxene **11** was prepared by direct bromination of truxene,[1b] which can be readily obtained in a multigram scale from 1-indanone.[14] Triple alkylation of the corresponding sodium trianion with 1-bromo-2-(bromomethyl)naphthalene furnished the desired hexabrominated precursor **6**. The triple alkylation of **11** afforded mixtures of *anti* and *syn* isomers that, as happened in the case of **4**, could not be isomerized in the presence of base to form exclusively the *syn* isomer.[1a] Nevertheless, pure *syn* isomer could be obtained upon precipitation from mixtures of CH_2Cl_2 and pentane (Scheme 6). A conceivable alternative synthesis of **5** by the direct acid-catalyzed triannulation strategy[15] would require the development of a synthesis of unknown ketone indeno[4,3,2,1-*lmno*]acephenanthrylen-1(2*H*)-one or its regioisomer.[16]

Hexabromotruxene *syn*-**6** was next subjected to different palladium-catalyzed direct arylation reaction conditions. Due to the high insolubility of both *syn*-**6** and the product of this transformation, LDI-MS experiments were used as a tool to find the optimal conditions for the intramolecular arylation. When Pd(OAc)$_2$, BnMe$_3$NBr, and K$_2$CO$_3$[1g] were used under different reaction conditions, only complex mixtures were detected, and no clear formation of **5** was observed. The use of phosphine ligands such as Xantphos, 1,3-bis(diphenylphosphanyl)propane (dppp) or PhDavePhos did not result in any improvement. Fortunately, when ethylenebis(diphenylphosphine) (dppe) was used as the ligand, we were able to observe clear evidence for the formation of **5**. After extensive optimization of the reaction conditions, LDI experiments of the isolated solid in positive and negative modes showed a single peak at *m/z* 744 with an experimental isotopic pattern that was consistent with the theoretical distribution calculated for **5** (Figure 1). This peak corresponds to the target crushed fullerene, which could be isolated in 44 % yield as a highly insoluble orange solid. Formation of **5** from *syn*-**6** involves a remarkable sequence of nine reactions catalyzed by palladium: sixfold intramolecular arylation and a triple dehydrogenation process.



Scheme 6. Synthesis of crushed fullerene $C_{60}H_{24}$ (**5**).

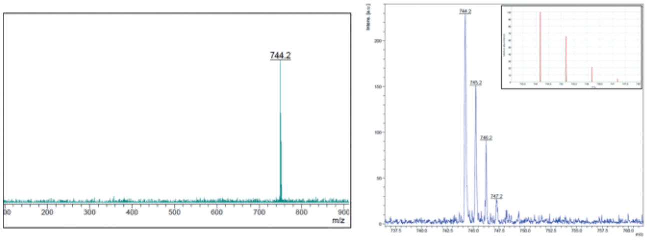


Figure 1. (left) LDI⁻ mass spectrum of crushed fullerene $C_{60}H_{24}$ (**5**). (right) Theoretical and experimental isotopic pattern for $C_{60}H_{24}$ (**5**).

To verify that **5** is a direct precursor of C_{60} fullerene, a sample of pure $C_{60}H_{24}$ was analyzed by MALDI and LDI-MS in positive and negative modes by using increasing laser powers, and the results in positive mode were compared to those arising from the analogous experiments on a sample of pure C_{60}. MALDI-MS analysis at the threshold of ion formation in negative mode using 2,5-dihydroxybenzoic acid (DHB) as the matrix showed exclusively the molecular ion of **3**, whereas at a higher laser power in the range of 129 µJ, this precursor ion underwent threefold H_2 loss giving $[C_{60}H_{22}]^{\cdot-}$, $[C_{60}H_{20}]^{\cdot-}$, and $[C_{60}H_{18}]^{\cdot-}$ (*m/z* 742, 740, and 738, respectively, Figure 2, a). On the other hand, when the sample was analyzed in positive mode by LDI-MS to avoid interferences derived from the matrix at a laser power in the range of 126 µJ, a peak at *m/z* 721 corresponding to the formation of $[C_{60} + H]^{\cdot+}$ could be identified, which underwent further C_2 fragmentations to give a series similar to that resulting from pure C_{60} fullerene (Figure 2, b).[5b]

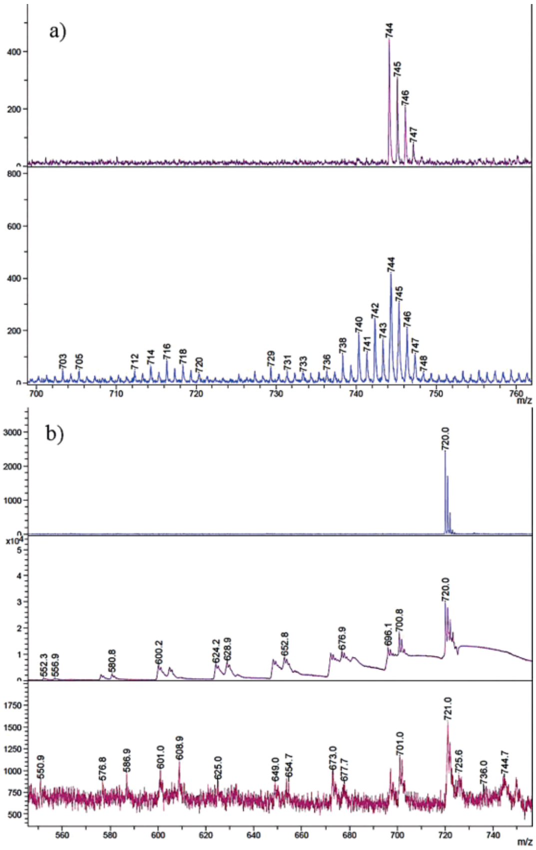


Figure 2. (a) (top) MALDI⁻ mass spectrum of **5** at the threshold of ion formation using DHB as the matrix. (bottom) MALDI⁻ mass spectrum of **5** at 129 µJ using DHB as the matrix. (b) (top) LDI⁺ mass spectrum of C_{60} fullerene at a laser power of 106 µJ. (center) LDI⁺ mass spectrum of C_{60} fullerene at a laser power of 115 µJ. (bottom) LDI⁺ mass spectrum of **5** at a laser power of 126 µJ.

Conclusions

A new, advanced crushed fullerene $C_{60}H_{24}$ has been synthesized by a sixfold palladium-catalyzed intramolecular arylation, which takes place in a remarkable 44 % yield, equivalent to an average 87 % yield per C–C bond formation, and subsequent in situ dehydrogenation. Open-shell C_{60} derivative **5** gives rise to C_{60} fullerene by applying high-power laser irradiation in LDI-MS experiments. On-surface cyclodehydrogenation experiments to form C_{60} are underway.

Experimental Section

General Procedures: Reactions were performed under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Thin-layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234). Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40–60 µm). NMR spectra were recorded at 25 °C with a Bruker Avance 300, 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus, or at 120 °C with a Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded with a MicroTOF Focus Bruker Daltonics mass spectrometer (ESI) or with an Autoflex Bruker Daltonics (MALDI and LDI) equipped with a nitrogen laser (337 nm) with a mean energy of 165.6 µJ per pulse and a beam dimension of 4 × 2.5 mm. Samples were measured at least four times under the same conditions and a minimum of 200 shots were accumulated per full spectrum. Melting points were determined with a Büchi melting point apparatus. Crystal structure determinations were carried out with a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with Mo-Kα radiation, Montel mirrors as monochromator and a Kryoflex low-temperature device (T = –173 °C). Full-sphere data collection was used with w and j scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved by using direct methods as implement in SHELXTL and visualized by using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

5,10,15-Tris[(1-bromonaphthalen-2-yl)methyl]-4,9,14-tribromo-10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorine (4a): A suspension of 4,9,14-tribromo-10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]-fluorene (360 mg, 0.62 mmol) in anhydrous DMF (5 mL) was added over a suspension of NaH (60 % in mineral oil, 82 mg, 2.04 mmol) in anhydrous DMF (5 mL) at 0 °C under Ar atmosphere. After ultrasonicating the resulting mixture for 50 min, a solution of 1-bromo-2-(bromomethyl)naphthalene (577 mg, 1.92 mmol) in anhydrous DMF (10 mL) was added and the mixture was stirred at room temperature for 16 h. H_2O (20 mL) was added and the precipitate formed was filtered off and dissolved in CH_2Cl_2 (50 mL). The resulting green solution was dried with $MgSO_4$, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (cyclohexane/CH_2Cl_2 8:2) gave a major fraction containing **4a** as a mixture of *syn* and *anti* isomers together with unidentified impurities. This fraction was partially dissolved in CH_2Cl_2 (10 mL) and precipitated with pentane (30 mL). The supernatant was removed and the solid was washed again with pentane (3 × 20 mL) and dried under reduced pressure giving the title compound, yield 331 mg (0.268 mmol, 41 %); pale-yellow solid; *syn*/*anti* = 1.3:1; m.p. 298–300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.16 (m, 4.9 H, *syn, anti*), 8.13 (d, *J* = 8.5 Hz, 2 H, *anti*), 7.80 (d, *J* = 9.6 Hz, 1 H, *anti*), 7.74–7.69 (m, 5.9 H, *syn, anti*), 7.68–7.63 (m, 5.9 H, *syn, anti*), 7.62–7.58 (m, 4.9 H, *syn, anti*), 7.57–7.47 (m, 10 H), 7.46–7.43 (m, 3.9 H, *syn*), 7.43–7.39 (m, 4.9 H, *syn, anti*), 7.36–7.33 (m, 3 H, *anti*), 7.26 (d, *J* = 8.4 Hz, 3.9 H, *syn*), 7.09 (t, *J* = 8.4 Hz, 1 H, *anti*), 6.96 (t, *J* = 7.6 Hz, 3.9 H, *syn*), 6.89 (dt, *J* = 7.4, 0.9 Hz, 3.9 H, *syn*), 6.87–6.84 (m, 1 H, *anti*), 6.81 (d, *J* = 7.6 Hz, 1 H, *anti*), 6.79–6.76 (m, 1 H, *anti*), 6.63 (t, *J* = 7.6 Hz, 1 H, *anti*), 6.44 (t, *J* = 7.5 Hz, 1 H, *anti*), 6.41–6.36 (m, 2 H, *anti*), 6.12 (dd, *J* = 8.5, 6.1 Hz, 3.9 H, *syn*), 5.99 (dd, *J* = 9.7, 5.9 Hz, 1 H, *anti*), 3.77–3.71 (m, 3.9 H, *syn*), 3.70–3.67 (m, 1 H, *anti*), 3.59 (dd, *J* = 13.8, 7.0 Hz, 1 H, *anti*), 3.49 (dd, *J* = 13.8, 6.6 Hz, 1 H, *anti*), 3.22 (dd, *J* = 13.8, 8.0 Hz, 1 H, *anti*), 3.16 (dd, *J* = 14.1, 8.6 Hz, 3.9 H, *syn*), 2.76 (dd, *J* = 13.9, 9.8 Hz, 1 H, *anti*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.66, 150.31, 149.54, 149.16, 144.95, 144.43, 142.51, 142.41, 141.14, 140.64, 139.30, 138.95, 137.65, 137.26, 137.23, 137.01, 136.87, 136.68, 136.30, 135.92, 133.31, 133.28, 133.24, 133.20, 133.15, 132.91, 132.85, 132.37, 132.24, 132.21, 132.20, 128.27, 128.18, 128.08, 128.02, 127.97, 127.94, 127.88, 127.86, 127.84, 127.79, 127.74, 127.68, 127.60, 127.40, 127.37, 127.24, 127.17, 127.14, 126.99, 126.87, 126.84, 126.25, 126.02, 125.99, 125.85, 125.80, 125.64, 125.52, 123.88, 123.79, 123.32, 123.30, 116.11, 115.99, 115.19, 52.49 (*anti*), 52.14 (*syn*), 50.45 (*anti*), 49.98 (*anti*), 42.12 (*anti*), 41.53 (*anti*), 39.95 (*anti*), 39.31 (*syn*) (aromatic peaks missing due to overlapping) ppm. HRMS ($MALDI^+$): *m/z* calcd. for $C_{60}H_{35}{}^{79}Br_3{}^{81}Br_3$ $[M - H]^+$ 1234.7772; found 1234.7785.

(5*R,10*S**,15*S**)-5,10,15-Tris[(1-bromonaphthalen-2-yl)methyl]-4,9,14-trimethoxy-10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorine (*anti*-4b):** To a mixture of 4,9,14-trimethoxy-10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorine (600 mg, 1.39 mmol) in anhydrous THF (55 mL) at –78 °C was added *n*BuLi (2.5 M in hexanes, 1.94 mL, 4.86 mmol) and the mixture was slowly warmed to –10 °C for 3 h. Then, 1-bromo-2-bromomethylnaphthalene (1.67 g, 5.56 mmol) in anhydrous THF (20 mL) was added and the mixture was warmed to room temperature. After 30 min at that temperature, the mixture was diluted with EtOAc and washed with saturated aqueous NaCl, dried with $MgSO_4$, and the volatiles evaporated. The residue was purified by chromatography (cyclohexane/CH_2Cl_2, 8:2 to 1:1) to give **4b** as a 3:1 mixture of *anti*/*syn* isomers together with unidentified impurities. After precipitation from CH_2Cl_2/pentane mixtures, pure *anti*-**4b** was obtained, yield 1.01 g (0.93 mmol, 67 %); m.p. 193–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (dt, *J* = 8.6, 1.0 Hz, 1 H), 8.22 (d, *J* = 8.6 Hz, 1 H), 8.18 (dd, *J* = 8.6, 1.0 Hz, 1 H), 7.78 (d, *J* = 7.0 Hz, 1 H), 7.73 (d, *J* = 7.0 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.61 (d, *J* = 5.5 Hz, 1 H), 7.59 (d, *J* = 6.2 Hz, 1 H), 7.55 (dt, *J* = 8.7, 1.6 Hz, 1 H), 7.51 (dd, *J* = 6.2, 1.4 Hz, 1 H), 7.49–7.41 (m, 5 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1 H), 7.14–7.09 (m, 1 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 7.6 Hz, 1 H), 6.94 (dd, *J* = 8.1, 7.4 Hz, 1 H), 6.86–6.76 (m, 4 H), 6.68 (dt, *J* = 7.4, 0.9 Hz, 1 H), 6.40 (dt, *J* = 7.4, 0.9 Hz, 1 H), 5.74 (dd, *J* = 8.3, 5.8 Hz, 1 H), 5.64 (t, *J* = 6.2 Hz, 1 H), 5.47 (dd, *J* = 9.5, 5.3 Hz, 1 H), 4.13 (s, 3 H), 4.08 (s, 3 H), 4.06 (s, 3 H), 4.04–4.00 (m, 1 H), 3.79 (dd, *J* = 14.0, 5.9 Hz, 1 H), 3.64 (dd, *J* = 13.8, 6.3 Hz, 1 H), 3.50 (dd, *J* = 14.2, 5.3 Hz, 1 H), 3.21 (dd, *J* = 14.0, 8.3 Hz, 1 H), 2.85 (dd, *J* = 14.1, 9.5 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.45, 154.30, 154.14, 150.07, 148.98, 142.91, 141.24, 141.09, 138.18, 137.74, 137.15, 136.21, 136.15, 135.88, 133.17, 133.11, 132.34, 132.29, 129.73, 128.55, 128.42, 128.21, 128.13, 128.02, 127.96, 127.87, 127.78, 127.76, 127.73, 127.57, 127.47, 126.99, 126.88, 126.77, 126.53, 126.50, 125.79, 125.72, 125.69, 125.61, 125.51, 125.28, 118.22, 117.73, 117.67, 110.04, 109.92, 109.84, 56.07, 55.96, 55.61, 50.97, 50.04, 49.56, 42.78, 41.68, 41.57 (peaks missing due to overlapping) ppm. HRMS (ESI^+): *m/z* calcd. for $C_{63}H_{45}Br_3NaO_3$ $[M + Na]^+$ 1109.0811; found 1109.0779.

3,13,23-Trimethoxybenzo[1,2-*e*:3,4-*e*′:5,6-*e*′′]tribenzo[*l*]acephenanthrylene (8): Compound *anti*-**4b** (400 mg, 0.37 mmol), $Pd(OAc)_2$ (82.4 mg, 0.37 mmol), PhDavePhos (70.6 mg, 0.19 mmol) and K_2CO_3 (102.3 mg, 0.74 mmol) were suspended in anhydrous DMA (1.9 mL, 0.2 M) in a sealed tube under Ar atmosphere, and the mixture was heated at 140 °C for 16 h. After cooling to room temperature, $CHCl_3$ (20 mL) was added and the mixture was washed with saturated aqueous NaCl (3 × 15 mL), dried with $MgSO_4$, and concentrated to dryness. The resulting crude material was dissolved in toluene (10 mL), then DDQ (840 mg, 3.7 mmol) was added and the reaction was stirred at 120 °C for 6 h. After cooling to room temperature, the solution was washed with 2 M solution of KOH (3 × 10 mL), dried with $MgSO_4$, and concentrated to a volume of ca. 2 mL (higher yields were obtained when the crude material was not taken to dryness). Purification by flash chromatography (cyclohexane/$CHCl_3$, 7:3 to 0:1) afforded the product as a brownish solid that became insoluble after drying, yield 96.5 mg (0.11 mmol, 31 % over two steps); m.p. >300 °C. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 9.24 (d, *J* = 8.4 Hz, 3 H), 9.10 (d, *J* = 9.1 Hz, 3 H), 8.42 (s, 3 H), 8.12 (dd, *J* = 8.0, 1.4 Hz, 3 H), 8.06 (d, *J* = 8.6 Hz, 3 H), 7.94 (d, *J* = 8.6 Hz, 3 H), 7.85 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 3 H), 7.74 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 3 H), 7.61 (d, *J* = 9.2 Hz, 3 H), 4.12 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ = 153.16, 136.34, 134.69, 133.49, 133.17, 131.87, 131.04, 130.06, 129.66, 128.72, 128.29, 128.15, 128.02, 126.57, 126.13, 126.08, 125.52, 121.55, 121.54, 113.70, 54.79 ppm. HRMS ($MALDI^+$): *m/z* calcd. for $C_{63}H_{36}O_3$ $[M]^+$ 840.2664; found 840.2673.

3,13,23-Trihydroxybenzo[1,2-*e*:3,4-*e*′:5,6-*e*′′]tribenzo[*l*]acephenanthrylene (9): To a mixture of **8** (70 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (10 mL) was added BBr_3 (1.0 M in CH_2Cl_2, 2.12 mL, 2.12 mmol) and the mixture was stirred at room temperature for 5 d. After cooling to 0 °C, H_2O (10 mL) was slowly added, the aqueous phase was extracted with CH_2Cl_2 (10 mL), the combined organic layers were dried with $MgSO_4$ and the volatiles evaporated. The solid was triturated with hexanes and EtOAc to obtain **9** as a brown solid with low solubility in organic solvents, yield 57.4 mg (0.07 mmol, 91 %); m.p. >300 °C. ^{1}H NMR (400 MHz, $[D_6]$acetone): δ = 10.00 (s, 3 H), 9.32 (d, *J* = 8.5 Hz, 3 H), 9.15 (d, *J* = 9.0 Hz, 3 H), 9.01 (s, 3 H), 8.24 (d, *J* = 8.6 Hz, 3 H), 8.16 (d, *J* = 7.9 Hz, 4 H), 8.02 (d, *J* = 8.6 Hz, 3 H), 7.88–7.83 (m, 3 H), 7.75–7.71 (m, 6 H) ppm. Full ^{13}C NMR spectroscopic data could not be recorded due to the low solubility of the product. HRMS (FAB^+): *m/z* calcd. for $C_{60}H_{30}O_3$ $[M]^+$ 798.2195; found 798.2194.

(5*S,10*S**,15*S**)-2,7,12-Tribromo-5,10,15-tris[(1-bromonaphthalen-2-yl)methyl]-10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorene (*syn*-6):** A suspension of **11** (360 mg, 0.62 mmol) in anhydrous DMF (5 mL) was added over a suspension of NaH (60 % in mineral oil, 82 mg, 2.04 mmol) in anhydrous DMF (5 mL) at 0 °C under Ar atmosphere. After ultrasonicating the resulting mixture for 50 min, a solution of 1-bromo-2-(bromomethyl)naphthalene (577 mg, 1.92 mmol) in anhydrous DMF (10 mL) was added and the mixture was stirred at room temperature for 16 h.

H_2O (20 mL) was added and the precipitate formed was filtered off and redissolved in CH_2Cl_2 (50 mL). The resulting green solution was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (cyclohexane/CH_2Cl_2, 8:2) gave a major fraction containing the desired *syn*-compound together with variable amounts of the *anti*-isomer and unidentified impurities. This fraction was partially dissolved in CH_2Cl_2 (10 mL) and precipitated with pentane (30 mL). The supernatant was removed and the solid was washed again with pentane (3 × 20 mL) and dried under reduced pressure to give the title compound, yield 121 mg (0.098 mmol, 15 %); pale-yellow solid; m.p. > 300 °C. ^1H NMR (500 MHz, $CDCl_2CDCl_2$, 120 °C): δ = 8.37 (d, J = 9.3 Hz, 3 H), 7.77 (d, J = 2.9 Hz, 3 H), 7.76 (d, J = 3.0 Hz, 3 H), 7.63 (ddd, J = 8.5, 6.9, 1.4 Hz, 3 H), 7.56–7.49 (m, 6 H), 7.37 (dd, J = 8.1, 1.9 Hz, 3 H), 7.05 (d, J = 1.9 Hz, 3 H), 6.86 (d, J = 8.3 Hz, 3 H), 4.72 (dd, J = 7.1, 7.1 Hz, 3 H), 3.79 (dd, J = 13.7, 6.4 Hz, 3 H), 3.34 (dd, J = 13.9, 8.2 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_2CDCl_2$, 120 °C): δ = 148.2, 140.1, 138.2, 135.6, 133.1, 132.1, 129.6, 128.1, 128.1, 127.4, 126.9, 126.9, 126.4, 125.7, 124.6, 122.8, 119.8, 46.1, 40.6 (one aromatic carbon missing due to overlapping) ppm. HRMS (MALDI$^+$): *m/z* calcd. for $C_{60}H_{35}{}^{79}Br_3{}^{81}Br_3$ [M – H]$^+$ 1234.7772; found 1234.7809.

Triindeno[4,3,2,1-*lmno*]acephenanthrylene (5): A mixture of *syn*-**6** (62.8 mg, 0.051 mmol), $Pd(OAc)_2$ (22.9 mg, 0.102 mmol), dppe (40.5 mg, 0.102 mmol), and K_2CO_3 (105.7 mg, 0.765 mmol) in anhydrous DMA (0.5 mL) under Ar atmosphere was heated at 140 °C in a sealed tube for 36 h. After cooling to room temperature, H_2O (5 mL) was added and the precipitated solid was filtered off and washed by centrifugation with H_2O (6 × 15 mL), acetone (6 × 15 mL), satd. aq. NaCN (3 × 15 mL), acetone (6 × 15 mL) and finally CH_2Cl_2 (5 × 15 mL) until the liquid phase remained colorless. After drying the remaining solid under reduced pressure, crushed fullerene $C_{60}H_{24}$ was obtained, yield 16.8 mg (0.023 mmol, 44 %); dark-orange highly insoluble solid; m.p. > 300 °C. NMR spectroscopic data could not be acquired due to the low solubility of the compound. HRMS (LDI$^-$): *m/z* calcd. for $C_{60}H_{24}$ [M]$^-$ 744.1883; found 744.1848.

Acknowledgments

The authors thank the Ministerio de Economía y Competitividad (MINECO) (Severo Ochoa Excellence Accreditation 2014–2018, SEV-2013-0319, project number CTQ2013-42106-P), the European Research Council (ERC) (Advanced Grant 321066), the Agència de Gestió d'Ajuts Universitaris (AGAUR) (2014 SGR 818), and the ICIQ Foundation.

Keywords: Fullerenes · Truxene · Palladium · Arylation · Mass spectrometry

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Received: March 14, 2016
Published Online: May 2, 2016