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A step toward direct fullerene synthesis: C_{60} fullerene precursors with fluorine in key positions

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ABSTRACT

Several fluorine containing polycyclic aromatic hydrocarbons with exact carbon atom topology of the C_{60} fullerene have been synthesized. Different numbers of fluorine atoms were introduced in the key positions, as needed for an efficient intramolecular condensation to the fullerene molecule. The polycyclic aromatic compounds obtained represent attractive precursors for rational, high-yield fullerene synthesis by flash vacuum pyrolysis.

1. Introduction

Direct synthesis of fullerenes is of considerable interest as a method to access new fullerenes, which cannot be obtained in the uncontrolled process of graphite evaporation or forms in low yields as a hard-to-isolate mixture. The general strategy of the direct approach to fullerenes is based on the synthesis of polycyclic aromatic hydrocarbons (PAH) that already contain the required carbon framework. Such 'unrolled' molecules can be 'rolled up' to form fullerenes under flash vacuum pyrolysis (FVP) conditions.[1–5] The presence of chlorine or bromine in the initial precursor has been found to be essential for effective cyclization via free radical mechanism.[1–5] Although the FVP approach has proven to be prolific for the synthesis of many small non-planar PAHs, high-yield synthesis of isomerically pure fullerenes has remained a challenge. The possibility of selective fullerene cage formation through FVP has been demonstrated by the examples of C_{60},[6–10] C_{78},[11] and C_{84}.[12] However, the rates of conversion to the target molecules have remained disappointingly low because of lack of efficient promoters of intramolecular condensation. The usually employed bromine or chlorine functionalizations reach their limits in the case of large molecules due to decomposition of such halogenated precursors during sublimation. The molar masses will generally be high, since the large numbers of new C–C bonds that need to be formed in the fullerene precursor necessitate the introduction of a considerable number of promoter groups. Moreover, the radical nature of the condensation drastically affects the selectivity of the process. Recently we reported on an efficient intramolecular fluorine promoted ring closure in benzo[*c*]phenanthrenes under FVP conditions via HF elimination, and have shown that HF elimination is a synchronous process leading directly to the target molecule without any intermediates, thus producing no side products.[13,14] The small size and low molecular weight of fluorine, as well as high thermostability of the C–F bond, make fluorine a 'perfect' activating group for rational fullerene synthesis. Here we present the synthesis of several C_{60} fullerene precursors containing fluorine atoms in the key positions.

2. Results and discussion

Two general strategies were found to be effective for the synthesis of fullerene-related PAHs. The first route starts from heptacyclic hydrocarbon truxene, the trianione of which can be alkylated by treatment with bromomethyl-bromoarene. The corresponding trialkylated truxene can be converted to the fullerene-related PAH by intramolecular palladium-catalyzed arylation via HBr elimination.[15,16] An alternative approach is based on the acid catalyzed head-to-tail cyclotrimerization of cyclic ketones,[17,18] which leads directly to the precursor molecule. In the present work we have examined both approaches for the synthesis of C_{60} fullerene precursors containing a various number of fluorine atoms in the key positions.

2.1. Synthesis on the base of truxene

The starting fluorinated truxenes can be obtained in one-step synthesis by acid catalyzed aldol cyclotrimerization of corresponding

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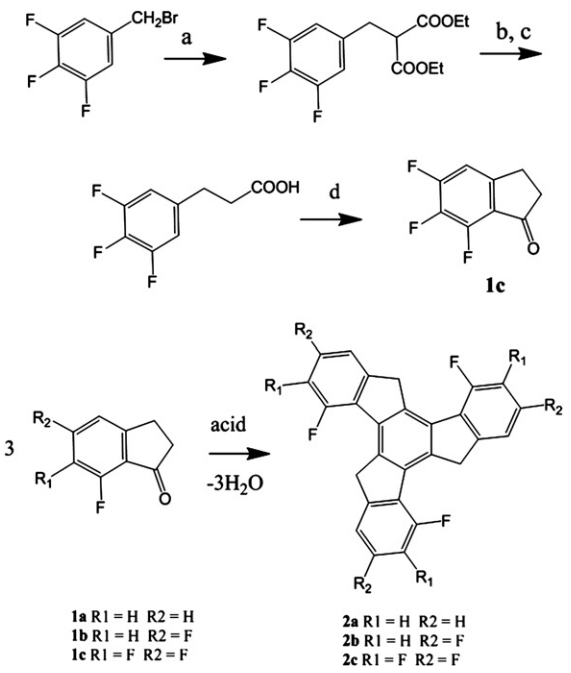
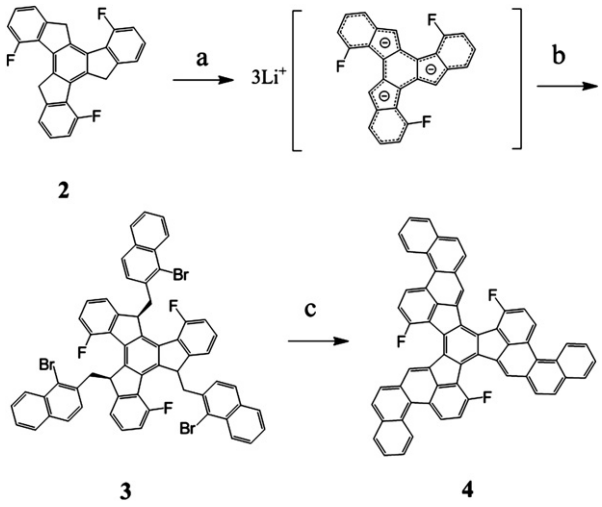
fluoroindanones (**1a**, **1b**, **1c**) as it is presented on Scheme 1. Indanone **1c** (5,6,7-trifluoro-1-indanone) was prepared in several steps from 3,4,5-trifluorobenzyl bromide. 3,4,5-Trifluoro-hydrocinnamic acid was synthesized analogously to the known procedure for hydrocinnamic acid.[19] On the final step, the trifluoro-hydrocinnamic acid was brought into direct cyclization by heating in polyphosphoric acid (PPA) (Scheme 1).[20]



Scheme 1. Synthetic route to 5,6,7-trifluoro-1-indanone (a) NaOEt/EtOH; (b) KOH; (c) H_2SO_4 (overall yield 32%); (d) PPA 80 °C (40%). Synthesis of fluorinated truxenes by aldol cyclotrimerization (**2a**: 27%, **2b**: 31%, **2c**: 45%).

6,11,16-Trifluorotruxene (compound **2a**) was prepared in 27% yield by the classical route consisting in refluxing of 7-fluoro-1-indanone (**1a**) in a 1:2 mixture of concentrated HCl and acetic acid (HOAc).[21] All attempts to trimerize **1b** and **1c** under the same conditions failed. Condensation of 5,7-difluoro-indanone (**1b**) in a HCl/HOAc mixture e.g., results in the formation of the pure dimer (2-(2,3-dihydro-4,6-difluoro-1*H*-inden-1-ylidene)-2,3-dihydro-4,6-difluoro-1*H*-Inden-1-one) with 44% yield. The reaction probably stops after dimerization because of the low solubility of the dimer, which precipitates out of the reaction mixture as soon as it is formed. Sterical reasons can be excluded since the trifluorotruxene **2a** containing three fluorine atoms in sterically hampered regions readily forms by trimerization of fluoroindanone **1a**. Applying the improved protocol for aldol trimerization (*p*-toluenesulfonic acid (TsOH)) in *o*-dichlorobenzene (ODCB),[17] gave the desired truxene **2b**, but the product is contaminated by the dimer and tetramer, according to MS data. Pure **2b** can be obtained after recrystallization from boiling *o*-xylene or 1,2-dichlorobenzene with an overall yield of about 30%. However, condensation of **1b** in aprotonic medium, using $TiCl_4$ in ODCB,[18] gave the pure product with more than 50% yield. Introducing a third fluorine atom in the indanone molecule additionally reduces the ability to undergo aldol trimerization. Thus, whereas difluoro-indanone **1b** trimerizes to hexafluorotruxene **2b** in fair yield using TsOH/ODCB system under relative mild conditions (110 °C), the trifluoro-indanone **1c** gives no more than traces of the trimer, in a wide range of temperatures. In contrast, the condensation of **1c** in ODCB in presence of $TiCl_4$ gave truxene **2c** with moderate yield (45%).

The fluorinated truxenes represent useful building blocks for synthesis of different fluorine-containing fullerene precursors. Thus a C_{60} precursor containing three fluorine atoms in the fjord positions (compound **4**) has been obtained in just two steps starting from trifluorinated truxene **1a** (Scheme 2) analogously to the previously reported procedure.[15] On the first step 1-bromo-2-bromomethylnaphthalene was added to trifluorinated truxene trianion, which was generated in situ by treatment of **2** with 3 equiv of *n*-BuLi. Compound **3** was obtained as a mixture of *syn* and *anti* isomers. Interestingly, both *syn* and *anti* isomers show good solubility in common organic solvents, whereas the *syn* isomer of nonfluorinated analog is a highly insoluble compound.[22] As a final step, palladium-catalyzed intramolecular arylation of the *anti*/*syn* mixture of **3** and the subsequent sublimation gave the compound **4**. It is easy to see that additional fluorine atoms can be introduced in all other key positions by using appropriately fluorinated bromomethyl arenes. For instance, the C_{60} fullerene precursor in which all six fjord regions are activated can be obtained starting from **2a** and 1-bromo-8-fluoro-2-bromomethylnaphthalene. The possibility of adding fluorinated bromomethyl arenes to the truxene trianione was previously demonstrated.[23]



Scheme 2. The synthetic route to the trifluorinated C_{60} precursor—$C_{60}H_{27}F_3$. (a) *n*-BuLi/THF, −78 °C; (b) 1-bromo-2-bromomethylnaphthalene (61%); (c) $Pd(OAc)_2$, DMA, Cs_2CO_3, Me_3BzNBr, 140 °C (67%).

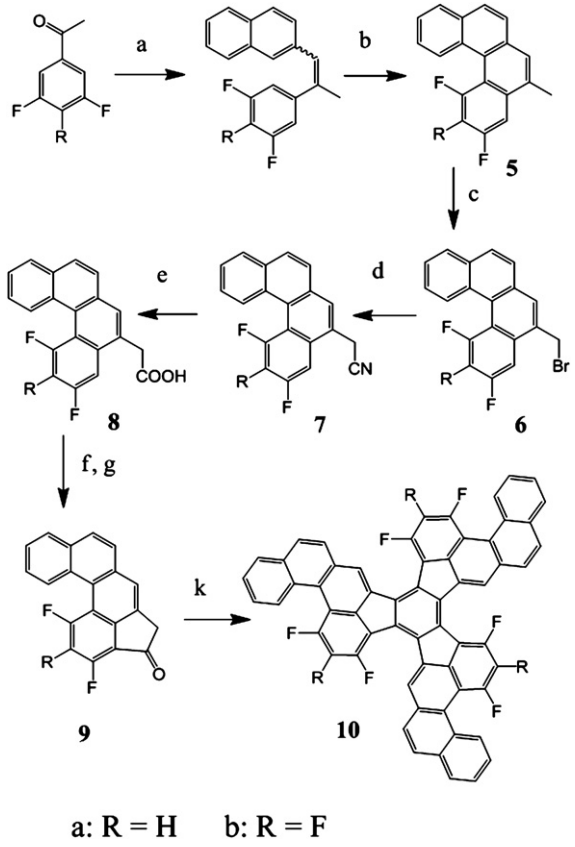
Hexa- and nona-fluorinated truxenes represent alternative building blocks for synthesis of multi-fluorinated precursors. However, all attempts to synthesize hexa- and nona-fluorinated precursor starting from truxenes **2b** and **2c** failed on the alkylation step. This is probably because of low stability of the corresponding truxene trianione and/or enhanced acidity of protons neighboring to fluorine. The reaction of 1-bromo,2-bromomethylnaphthalene with the corresponding fluorinated truxene trianion results in a complex mixture, which is difficult to analyze.

2.2. Aldol trimerization route

An alternative way to fullerene-related PAHs is based on the aldol trimerization of cyclic ketones. Although this reaction was discovered more than 100 years ago, it only recently became a powerful method for the synthesis of large molecules. It was demonstrated that large PAHs can be obtained effectively via aldol trimerization of cyclic ketones using TsOH in ODCB,[24,25] or $TiCl_4$ in ODCB.[6,8,18] In this work, both methods have been examined for synthesis of fluorinated precursors.

The synthetic route to hexa- and nona-fluorinated precursors is summarized on Scheme 3. Fluorinated methylbenzo[*c*]phenanthrenes (**5a** and **5b**) were synthesized by standard Wittig olefination of correspondingly fluorinated acetophenones with subsequent Mallory photocyclization using Katz improvement.[26] Benzylic

bromination with *N*-bromosuccinimide (NBS) and subsequent treatment with aqueous ethanolic sodium cyanide gave cyanomethylbenzophenanthrenes (**7a**, **7b**), which were hydrolyzed into acid (**8a**, **8b**). Ketones **9a** and **9b** were obtained after transforming the acids (**8a**, **8b**) to the corresponding acid chlorides with subsequent intramolecular Friedel–Crafts acylation in the presence of $AlCl_3$.



Scheme 3. The synthetic route to the hexa- and nona-fluorinated C_{60} precursors. (a) $Ph_3PCH_2Ph^+$ Br^-, NaOEt/EtOH; (b) *hv*, I_2, propylene oxide (**5a**: 67%; **5b**: 65%); (c) NBS, DBPO,CCl_4 (**6a**: 68%; **6b**: 72%); (d) NaCN, EtOH/H_2O (**7a**: 75%; **7b**: 85%); (e) H_2SO_4, H_2O, HOAc (**8a**: 90%; **8b**: 84%); (f) $SOCl_2$; (g) $AlCl_3$/DCM (**9a**: 30%; **9b**: 23%); (k) $TiCl_4$/ODCB (**10a**: 57%; **10b**: 85%).

Despite the quite smooth trimerization conditions needed for indanones **1b** and **1c**, the condensation scenario changes drastically in the case of structurally related benzacephenanthrylenones **9a** and **9b**. Thus, the condensation of **9a** in ODCB in presence of TsOH at 100–140 °C gave a complex mixture containing mainly dimer, tetramer, and hexamer according to MS data. Interestingly only a trace amount of trimer and pentamer were detected in MS. Condensation at 160 °C gave a highly insoluble product, which shows three groups of signals at 858.3, 856.3, and 854.3 *m*/*z* (Fig. 1).

The sample was purified by sublimation and analyzed. MS analyses have shown almost exclusively the ion peak at 854.2 *m*/*z*, which is 4 Da less than the mass of the expected trimer (Fig. 1). However, for the targeted structure a respective hydrogen elimination cannot take place since all possible condensation ways are blocked by the fluorine atoms (formation of new C–C bond requires HF elimination). The elimination of hydrogen atoms would have only become possible if one of the benzophenanthrene fragments is 'wrongly' oriented, as it shown in Fig. 1. Indeed, the analysis of intermediate products confirms this supposition. A more detailed MS analysis of the reaction mixture shows the presence of a dimer containing two carbonyl groups confirming the possibility of **9a** for atypical tail-to-tail dimerization. More information about the mechanism can be obtained by analysis of reaction products obtained at mild

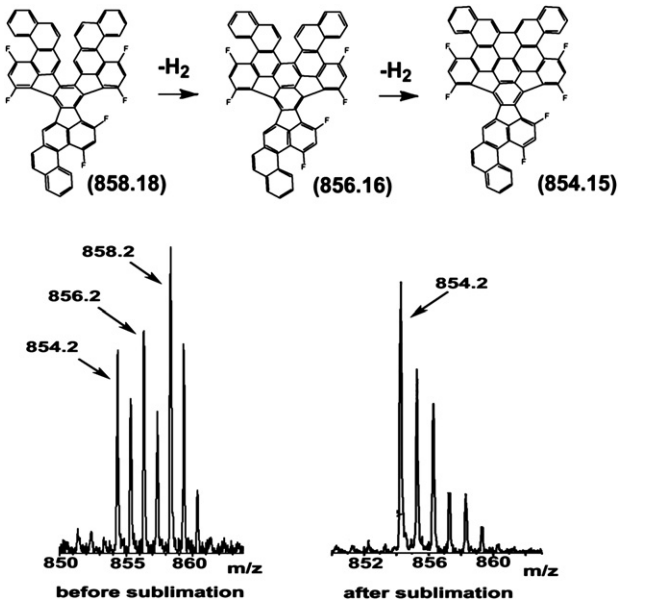


Fig. 1. The MS spectra of condensation products of **9a** in TsOH/ODCB system (the full MS spectra can be found in Supplementary data).

conditions (HCl/AcOH, 100 °C or TsOH/ODCB, 100 °C). In this case all intermediates can be easily detected in the MS spectra. According to MS data the reaction mixture contains the dimer and several products of its subsequent condensation. The molecular masses of trimer, tetramer, and pentamer are slightly less than expected which additionally confirms the presence of 'wrongly' connected benzacephenanthrylenone fragments (for details see Supplementary data). Although the mechanism of condensation is not fully clear, it obviously involves unusual tail-to-tail ketone condensation and is probably accompanied by numerous redox processes.

On the other hand the condensation of **9a** and **9b** in an aprotonic medium, using $TiCl_4$ in ODCB, gave the desired products with good yields (60–80%), and in high purity. The optimal conditions for this reaction are given in the Experimental section. In both cases, the MS analyses shows the single ion peaks at 858.2 *m*/*z* for the hexa-fluorinated precursor (**10a**) and 912.2 *m*/*z* for nona-fluorinated precursor (**10b**), which corresponds to the expected structures. Both compounds show poor solubility and cannot be analyzed by NMR spectroscopy. However, MS and MS/MS analyses have provided sufficient structural information. Thus, applying a higher ionization energy causes partial condensation of the precursor exclusively by HF elimination. No loss of two hydrogen atoms under high energy ionization confirms the expected structure (absence of 'wrongly' oriented benzophenanthrene fragments), because only in this case there is no possibility for intramolecular condensation via H_2 elimination. In the MS/MS experiment the monoisotopic precursor ions were selected and subjected to collision-induced dissociation with argon. The respective analyses show that H_2 elimination is a main fragmentation process for the non-substituted precursor $C_{60}H_{30}$,[27] which is a result of intramolecular condensation in the fjord regions. In the case of the trifluorinated precursor (**4**), the intramolecular condensation is accompanied by elimination of HF and H_2 molecules, which is in good agreement with the structure of the precursor. The hexa-fluorinated precursor (**10a**) is not able to undergo intramolecular condensation via H_2 elimination, since all fjord regions contain fluorine atoms. Therefore no $[M-H_2]^+$ ions are observed in the respective MS/MS spectra. Interestingly, the cyclization via HF elimination results in the formation of a new fjord region and H_2 elimination as a subsequent step become possible. Indeed, the corresponding ion peak ($[M-HF-H_2]^+$) was detected in the MS/MS spectra of **10a** (Fig. 2). In contrast, the nona-fluorinated

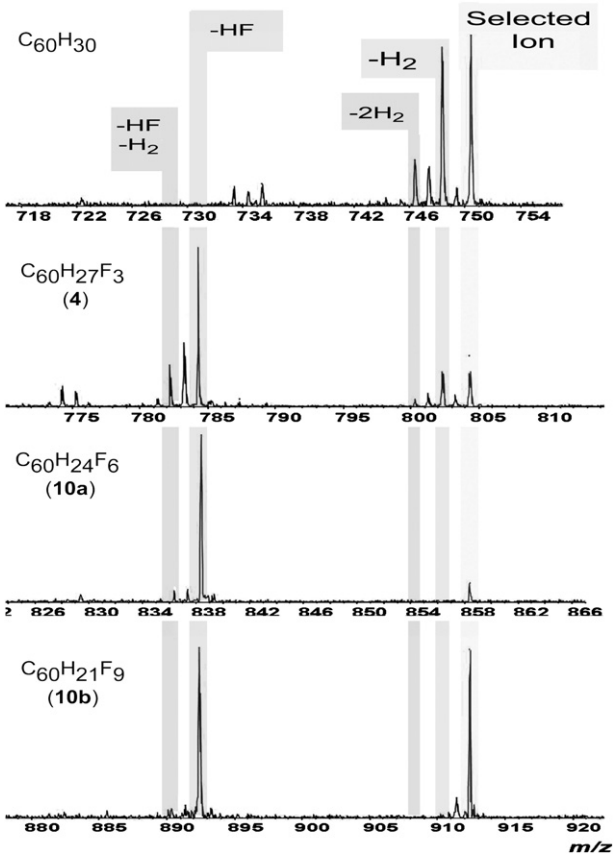


Fig. 2. MS/MS spectra of precursors **4**, **10a**, **10b**, and $C_{60}H_{30}$.

precursor (**10b**) does not show any H_2 elimination since the new fjord region which forms after HF elimination still contains a fluorine atom. The MS/MS patterns obtained indicate that all fjord regions in **10a** and **10b** contain fluorine atoms, which confirm the absence of 'wrongly' orientated benzophenanthrene fragments in the structure. Additionally, the comparison of UV spectra of nona-fluorinated (**10b**), hexa-fluorinated (**10a**), trifluorinated (**4**) precursors with well characterized $C_{60}H_{30}$ precursor,[27] reveals the similarity of π-system for all four compounds (Fig. 3.)

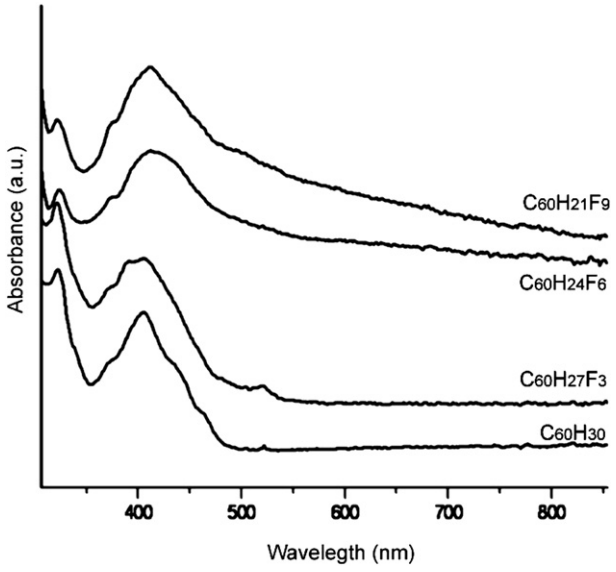


Fig. 3. UV/vis spectra of C_{60} fullerene precursors: $C_{60}H_{30}$, **4** ($C_{60}H_{27}F_3$), **10a** ($C_{60}H_{24}F_6$), and **10b** ($C_{60}H_{21}F_9$) (1,2,4-trichlorobenzene).

3. Conclusion

Several C_{60} fullerene-related structures containing a various number of fluorine atoms in the key positions have been synthesized. It has been shown that trifluorinated truxene is a promising starting block for the synthesis of fluorine-containing fullerene precursors. Alternatively, the aldol cyclotrimerization of cyclic ketones can be used as well for the synthesis of C_3 symmetrical fluorine containing precursors. In contrast to chlorine, the fluorine can be introduced quite easily into the sterically hampered fjord regions of the precursor molecules as a result of the small size of fluorine atom. The aldol condensation of fluorinated cyclic ketones in aprotonic medium using $TiCl_4$/ODCB was found to be an effective route for the synthesis of fluorine containing PAHs, whereas the condensation using TsOH/ODCB, which is the best route for the synthesis of related chlorinated PAHs completely failed.

The fluorinated PAHs obtained represent attractive precursor molecules for rational fullerene synthesis by flash vacuum pyrolysis. Taking into consideration that fluorine can promote the ring closure only if hydrogen is placed in a neighboring position in the precursor structure it appears to be possible to fully control the direction of the process. Moreover, the highly efficient intramolecular condensation to geodesic PAHs via homo-HF elimination is expected to occur.[14] Using fluorine as an activating group could solve the problem of selectivity in FVP and should provide an effective conversion of the planar PAH precursors to the desired fullerene cage. In contrast to the catalytic dehydrogenation of hydrocarbon analogues on the Pt surface,[28] the FVP technique should provide access to bulk amounts of new fullerenes.

4. Experimental section

4.1. General

LDI-mass spectra were recorded on a Shimadzu/Kratos (Columbia, MD) AXIMA CFR mass spectrometer. R_f were determined on TLC-PET sheets coated with silica gel with fluorescent indicator 254 nm (layer thickness 0.25 mm, medium pore diameter 60 Å), Fluka. Chromatographic purifications were carried out with flash grade silica gel Kieselgel 60 (0.06–0.2 mm), Roth.

4.1.1. 3-(3,4,5-Trifluoro) propionic acid. Yield 1.0 g (44 mmol) of metallic sodium were dissolved in 50 mL of absolute ethanol. 7.13 g (45 mmol) of diethylmalonate were added to the stirred solution of sodium ethoxide obtained. After gradual addition of 10.0 g (44.4 mmol) of the ntrifluorobenzylbromide the mixture was reflux for 2 h and cooled down. The sodium bromide was filtered out and the major part of ethanol was removed in vacuo. The residue was distilled under reduced pressure. The colorless oil obtained was mixed with aqueous KOH (5 g KOH in 10 mL H_2O) and reflux for 3 h. Afterward the ethanol formed was removed under diminished pressure, 5 mL of H_2O and 25 mL of 5 M H_2SO_4 were added additionally and the resulting mixture was reflux for 5 h. After cooling the mixture was diluted with 50 mL of water, three times extracted with Et_2O, dried over $MgSO_4$, and evaporated. The yellowish oil had crystallized during cooling. The product was filtered, washed with hexane, and dried. White crystalline powder (3.1 g, 32% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=2.5–2.6 (m, 2H), 2.8–2.9 (m, 2H), 6.7–6.8 (m, 2H). R_f=0.29 (DCM).

4.1.2. 5,6,7-Trifluoro-1-indanone. Yield 2.8 g (12.8 mmol) of 3-(3,4, 5-trifluoro) propionic acid and 25 mL of polyphosphoric acid were stirred for 24 h at 80 °C. After cooling down the mixture was diluted with 50 mL of water and extracted with DCM. Extract was dried over $MgSO_4$ and evaporated. The crude product was purified chromatographically using DCM as an eluent. White solid (1.0 g, 40% yield). R_f=0.40 (DCM). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=2.68 (t, J=6.1, 2H), 3.05

(t, J=5.7, 2H), 7.00 (t, J=6.8, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=25.76, 37.11, 110.08 (dd, J_1=4.5, J_2=18.1). LDI-TOF MS: m/z=186.03 $[M]^+$ (Exact mass: 186.0292).

*4.1.3. 6,11,16-Trifluorotruxene (**2a**).* Yield 4.5 g (30 mmol) of 7-fluoro-1-indanone were added to a mixture of 20 mL of acetic acid and 10 mL of concentrated (34%) HCl and stirred for 36 h at 100 °C. After cooling down the mixture was poured into ice. The solid was filtered, washed with water, acetone, and DCM to give a white powder. White solid (1.1 g, 27% yield). ^{1}H NMR ($C_2Cl_4D_2$, 300 MHz) δ=4.37 (s, 6H), 7.03 (t, J=10.6, 3H), 7.17–7.3 (m, 3H), 7.3–7.45 (m, 3H). ^{19}F NMR (C_2 Cl_4D_2, 235 MHz) δ=−112.5 (sex, J=6.01). LDI-TOF MS: m/z=395.04 $[M-H]^-$ (Exact mass: 395.1048).

*4.1.4. 6,8,11,13,16,18-Hexafluorotruxene (**2b**). Route* 1. A mixture of 5,7-difluoro-1-indanone (1 g, 5.95 mmol), *p*-toluenesulfonic acid monohydrate (3.45 g, 20.8 mmol), propionic acid (1.54 mL, 20.55 mmol), and *o*-dichlorobenzene (5 mL) was transferred in round-bottom flask. The mixture was heated at 110 °C for 16 h. After cooling down the mixture was poured into 50 mL of methanol containing aqueous KOH. The precipitate was filtrated, washed with methanol, H_2O, acetone, DCM, and petroleum ether resulting in a greenish powder (0.52 g). Recrystallization from boiling *o*-xylene gave a product as a white powder (0.28 g, 31% yield).

Route 2. 5,7-Trifluoro-1-indanone (200 mg), 6 mL of *o*-dichlorobenzene and 0.72 mL of $TiCl_4$ (6 M equiv) were transferred in a glass ampoule. The ampoule was evacuated and sealed by melting while the reaction mixture was frozen by liquid nitrogen to prevent the solvent from evaporation. The ampoule was heated at 180 °C for 20 h. After cooling down the ampoule was opened and the mixture was poured into 50 mL of acetone. The precipitate was filtrated, washed with acetone, DCM, and petroleum ether. Pink crystals (92 mg, 52% yield). ^{1}H NMR ($C_2Cl_4D_2$, 250 MHz, 120 °C) δ=4.38 (d, J=5.75, 6H), 6.81 (t, J=10.25, 3H), 7.10 (d, J=7.25, 3H). ^{19}F NMR ($C_2Cl_4D_2$, 235 MHz, 120 °C) δ=−112.04 (q, J=7.29), δ=−109.2 (sex, J=5.88). LDI-TOF MS: m/z=449.07 $[M-H]^-$ (Exact mass: 449.0765).

*4.1.5. 6,8,9,11,12,13,16,17,18-Nonafluorotruxene (**2c**).* Compound **2c** was synthesized analogously to **2b** (route 2) starting from 5,6,7-trifluoro-1-indanone. The mixture was heated at 170 °C for 16 h. Pink crystals (50 mg, 45%). ^{1}H NMR ($C_2Cl_4D_2$, 250 MHz, 120 °C) δ=4.35 (d, J=5.75, 6H), 7.19 (t, J=7.25, 3H). ^{19}F NMR ($C_2Cl_4D_2$, 235 MHz, 120 °C) δ=−166.57 (td, J_1=6.03, J_2=19.6), δ=−152–(−141) (m). LDI-TOF MS: m/z=503.03 $[M-H]^-$ (Exact mass: 503.0482).

4.1.6. 2-(2,3-Dihydro-4,6-difluoro-1H-inden-1-ylidene)-2,3-dihydro-4,6-difluoro-1H-inden-1-one. Yield 5.0 g (29.7 mmol) of 5,7-difluoro-1-indanone were added to a mixture of 20 mL of acetic acid and 10 mL of concentrated HCl. The mixture was stirred for 72 h at 100 °C, cooled down, and poured into ice. The solid precipitate was filtered, washed with water, acetone, and DCM to give a white powder (2.1 g, 44% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=3.01 (t, J=6.28, 2H), 3.5 (t, J=6.1, 2H), 3.95 (d, J=5.35, 2H), 6.6–6.8 (m, 2H), 6.88 (d, J=7.6, 1H), 6.94 (d, J=6.25, 1H). ^{19}F NMR ($C_2Cl_4D_2$, 235 MHz, 120 °C) δ=−112.8 (dd, J_1=9.6, J_2=2.6), δ=−105.3 (q, J=8.9), δ=−100.5 (7, J=5.2), δ=−100.1 (dt, J_1=8.9, J_2=12), LDI-TOF MS: m/z=319.06 $[M+H]^+$ (Exact mass: 319.2783).

*4.1.7. Compound $C_{60}H_{27}F_3$ (**4**).* THF was refluxed over KOH and distilled over metallic sodium. THF was degassed using 'freeze-thaw-pump' technique and additionally distilled under reduced pressure before use. All follow-up manipulations were carried out under argon atmosphere using Schlenk technique. 100 mg (0.25 mmol) of **2a** were suspended in 10 mL of THF. 0.5 mL of 1.6 M *n*-BuLi in hexane (0.8 mmol) were slowly added to the mixture at −78 °C. After stirring for about 40 min, the mixture was slowly warmed to 0 °C. After 1 h the solution of 1-bromo-2-bromomethylnaphthalene 250 mg (0.83 mmol) in THF (15 mL) was dropwise added to the red solution of truxene trianione. The resulting mixture was stirred for 2 h and diluted with EtOAc, washed with saturated aqueous NaCl solution, dried over Na_2SO_4, and concentrated. The product was precipitated through addition of hexane, filtered, and dried, resulting in compound **3**, which was used without additional purification (mixture of *syn*/*anti* isomers). White powder (162 mg, 61%). ^{1}H NMR aliphatic/aromatic proton ratio 1/3. R_{f1}=0.21, R_{f2}=0.30 (CCl_4/hexane 1:1). The mixture of 150 mg of **3**, $Pd(OAc)_2$ (45 mg), trimethylbenzylammoniumbromide (70 mg), Cs_2CO_3 (500 mg) and 10 mL of dimethylacetamide was stirred at 140 °C for 72 h. The mixture was cooled and solid was filtered off, washed with DCM, acetone, and water. The solid obtained was suspended in aqueous NaCN and stirred for 3 h, filtered off, and washed with water, acetone, and DCM to give **4** as yellow solid (83 mg, 67%). LDI-TOF MS: m/z=804.2 $[M]^+$ (Exact mass: 804.20648). UV: λ_{max} (1,2,4-trichlorobenyene)/[nm] 322, 371, 390, 408, 521. Mp>300 °C.

*4.1.8. 1,3 Difluoro 5-methylbenzo[c]phenanthrene (**5a**).* Yield 8.0 g (28.6 mmol) of naphthalene, 2-[2-(3,5-difluorophenyl)-1-ethyl-ethenyl] as a mixture of *cis*/*trans* isomers were dissolved in 350 mL of cyclohexane. The resulting solution was placed in a 500 W water cooled quartz photochemical reactor and 8.0 g (31.4 mmol) of iodine were then added. Argon was bubbled through the stirred solution for 15 min before excess of propylene oxide (40 mL) was added. After irradiation for 20–30 h the color of iodine had disappeared. The mixture was washed with aqueous $Na_2S_2O_3$ to remove residual iodine traces, concentrated in vacuo, and then purified by flash chromatography on silica gel. The mixture of light petroleum and DCM 1:1 was used as an eluent. The targeted compound was obtained with 67% yield as a white solid (5.2 g). R_f=0.17 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=2.68 (s, 2H), 7.08–7.2 (m, 1H), 7.48–7.7 (m, 5H), 7.82–7.95 (m, 2H), 8.08–8.22 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=19.83, 102.37 (t, J=28.2), 104.89 (dd, J_1=3.5, J_2=21), 124.97 (d, J=2.86), 125.44, 125.8, 127.48, 128.37, 128.96, 129.11, 129.34.

*4.1.9. 1,2,3 Trifluoro 5-methylbenzo[c]phenanthrene (**5b**).* Compound **2c** was synthesized analogously to **2b** starting from 5.25 g (17.86 mmol) of naphthalene, 2-[2-(3,4,5-trifluorophenyl)-1-ethyl-ethenyl]. Compound **2c** was obtained with 65% yield as a white solid (3.25 g). R_f=0.45 (hexane/DCM, 2:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=2.66 (s, 3H), 7.48–7.72 (m, 5H), 7.86–7.94 (m, 2H), 8.07–8.2 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=19.65, 106.02 (dd, J_1=3.7, J_2=17.3), 125.29 (d, J=2.9), 125.97, 127.56, 128.3 (broad), 128.66, 128.89, 128.93.

*4.1.10. 1,3 Difluoro 5-(bromomethyl) benzo[c]phenanthrene (**6a**).* Yield 4.65 g (16.7 mmol) of **5a** and 2.98 g (16.7 mmol) of NBS with catalytic amount of dibenzoyl peroxide (5 mg) were dissolved in 70 mL of CCl_4 and refluxed until the reaction had gone to completions as monitored by TLC (2–6 h). The reaction mixture was then allowed to cool, washed twice with water, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified chromatographically on silica gel using petrol ether as an eluent. Grayish solid (4.1 g, 68% yield). R_f (hexane/DCM, 1:1)=0.76. ^{1}H NMR ($CDCl_3$, 300 MHz) δ=4.9 (s, 2H), 7.1–7.22 (m, 1H), 7.48–7.6 (m, 2H), 7.63–7.74 (m, 2H), 7.82–7.95 (m, 3H), 8.08–8.22 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=31.36, 103.14 (t, J=27.8), 105 (dd, J_1=3.8, J_2=21.4), 125.31 (d, J=3.02), 125.44, 126.63, 127.56, 128.84, 129.34, 129.59, 130.56, 133.28.

*4.1.11. 1,2,3 Trifluoro 5-(bromomethyl) benzo[c]phenanthrene (**6b**).* Compound **6b** was synthesized analogously to **6a** starting from 3.2 g (11.0 mmol) of **5b**.

Yellowish solid (2.9 g, 72% yield). R_f (hexane/DCM, 2:1)=0.40. ^{1}H NMR ($CDCl_3$, 300 MHz) δ=4.87 (s, 2H), 7.49–7.6 (m, 2H), 7.68 (d,

J=8.5, 2H), 7.76–7.86 (m, 2H), 7.87–7.94 (m, 2H), 8.03–8.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=30.99, 106.23 (dd, J_1=3.6, J_2=18) 125.43, 125.63 (d, J=2.9), 126.8, 127.65 (d, J=1.1), 128.91, 129.14, 129.40, 129.83, 130.9 (broad), 133.19.

*4.1.12. 1,3 Difluoro benzo[c]phenanthrene-5-acetonitrile (**7a**).* Yield 3.85 g (11 mmol) of **6a** were dissolved in mixture of 200 mL of EtOH and 20 mL of H_2O. NaCN (600 mg, 12 mmol) was added and the solution was refluxed for 24 h, diluted with H_2O, and extracted with DCM. The extract was washed with H_2O, dried over Na_2SO_4, and evaporated in vacuo resulting in an orange oil. The oil was purified by chromatography using a mixture of DCM and petroleum 1:1 as eluent. Yellow solid (2.5 g, 75% yield). R_f (hexane/DCM, 1:1)=0.20. ^{1}H NMR (DMSO, 300 MHz) δ=4.51 (s, 2H), 7.6–7.7 (m, 2H), 7.7–7.81 (m, 1H), 7.88–7.97 (m, 1H), 7.99–8.05 (m, 1H), 8.06–8.22 (m, 4H). ^{13}C NMR (DMSO, 75 MHz) δ=21.17, 103.71 (t, J=28.1), 105.30 (dd, J_1=3.7, J_2=22.1), 118.76, 125.64 (d, J=2.88), 126.43 (dd, J_1=3.1, J_2=7.8), 126.77, 127.78, 128.81 (d, J=3.2), 128.93, 129.11, 129.15, 129.26, 130.38, 132.82.

*4.1.13. 1,2,3 Trifluoro benzo[c]phenanthrene-5-acetonitrile (**7b**).* Compound **7b** was synthesized analogously to 7**a** starting from 2.7 g (7.2 mmol) of 6**b**. White solid (1.95 g, 85% yield). R_f=0.16 (hexane/DCM, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=4.10 (s, 2H), 7.49–7.61 (m, 3H), 7.71–7.79 (m, 1H), 7.90–8.0 (m, 3H), 8.08–8.20 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=22.07, 104.74 (d, J=3.47), 104.88 (d, J=3.84), 106.65, 116.70, 125.4, 125.71, 125.83, 126.85, 127.71, 128.8, 128.93, 129.02, 129.7, 130.87, 133.16.

*4.1.14. 1,3 Difluoro benzo[c]phenanthrene-5-acetic acid (**8a**).* Yield 2.5 g (8 mmol) of **7a** were dissolved in mixture of acetic acid (60 mL), H_2SO_4 (40 mL), and water (40 mL). The mixture was heated under stirring at 120 °C for 24 h. After cooling down, 100 mL of H_2O were added and the product was filtrated, washed with H_2O, and dried. Purification of the crude product was performed by dissolution in DCM, addition of active carbon followed by filtration. The product was precipitated by addition of hexane, filtered, and dried. Gray solid (2.3 g, 90% yield). R_f=0.36 (EtOAc/DCM, 1:2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ=4.06 (s, 2H), 7.08–7.18 (m, 1H), 7.48–7.58 (m, 3H), 7.68–7.75 (m, 2H), 7.88–7.95 (m, 2H), 8.09–8.2 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=38.71, 125.14, 125.18, 125.42, 126.32, 127.53, 128.70, 129.3, 129.52, 131.12.

*4.1.15. 1,2,3 Trifluoro benzo[c]phenanthrene-5-acetic acid (**8b**).* Compound **8b** was synthesized analogously to **8a** starting from 1.95 g (6.07 mmol) of 7**b**. Gray solid (1.73 g, 84% yield). R_f=0.33 (EtOAc/DCM, 1:2). ^{1}H NMR (DMSO-d_6, 300 MHz) δ=3.38 (s, 2H), 6.78–6.89 (m, 2H), 7.1–7.19 (m, 2H), 7.2–7.48 (m, 4H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ=39.02, 107.91 (d, J=18.3), 126.32, 127.16, 128.36, 129.13, 129.35, 129.94, 130.59, 131.15, 131.9, 133.11, 172.9.

*4.1.16. 10,12 Difluoro benz[l]acephenanthrylen-9(8H)-one (**9a**).* Yield 2.3 g (7.2 mmol) of **8a** were stirred with more than 10 times excess of $SOCl_2$ (10 mL) for 2 h at 65 °C. After cooling down $SOCl_2$ was evaporated and a yellow-brown oil was obtained. The oil was dissolved in DCM (20 mL) and 1.43 g of $AlCl_3$ (11 mmol) were added in small portions while stirring. A black solution obtained was stirred for 3 h and then poured into ice resulting in an orange mass. After extraction with DCM the solution was dried over Na_2SO_4 and evaporated. The crude product was purified by chromatography using DCM as eluent. White solid (0.66 g, yield 30%). R_f (DCM)=0.53. ^{1}H NMR ($CDCl_3$, 300 MHz) δ=3.88 (s, 2H), 7.21–7.29 (m, 1H), 7.57–7.68 (m, 2H), 7.78–7.84 (m, 2H), 7.91–8.02 (m, 2H), 8.25–8.4 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=42.08, 124.75, 125.64 (d, J=2.88), 126.62, 127.74, 128.89, 129.14, 129.2.

*4.1.17. 10,11,12 Trifluoro benz[l]acephenanthrylen-9(8H)-one (**9b**).* Compound **9b** was synthesized analogously to 9**a** starting from 1.38 g (3.85 mmol) of 8**b**. Cream solid (0.3 g, 23% yield). R_f (DCM)=0.47. ^{1}H NMR ($CDCl_3$, 300 MHz) δ=3.87 (s, 1H), 7.58–7.67 (m, 2H), 7.72–7.82 (m, 2H), 7.91–8.2 (m, 2H), 8.22–8.39 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=41.58, 124.08, 125.96, 126.63, 126.80, 127.86, 128.48, 129.78.

*4.1.18. Compound $C_{60}H_{27}F_6$ (**10a**).* Yield 20 mg of indanone **9a**, 1.5 mL of *o*-dichlorobenzene, and 0.045 mL of $TiCl_4$ (6 M equiv) were transferred in a glass ampoule and sealed. The ampoule was heated at 180 °C for 20 h. After cooling down the glass ampoule was opened and the mixture was poured into 50 mL of acetone. The precipitate was filtered, washed with acetone, DCM, and petroleum ether resulting in orange-brown solid (12 mg, 57% yield.). LDI-TOF MS: m/z=858.2 $[M]^+$ (Exact mass: 858.1782). UV: λ_{max} (1,2,4-trichlorobenzene)/[nm] 324, 373, 415. Mp>300 °C.

*4.1.19. Compound $C_{60}H_{21}F9$ (**10b**).* Compound **10b** was synthesized analogously to **10a** starting from 20 mg of 9**b**. Orange solid (16 mg, 85% yield.). LDI-TOF MS: m/z=912.2 $[M]^+$ (Exact mass: 912.14995). UV: λ_{max} (1,2,4-trichlorobenzene)/[nm] 322, 374, 410. Mp>300 °C.

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Supplementary data

The supplementary data contains MS, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for all new compounds. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2010.09.055.

References and notes

1. Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325–13370.
2. Plater, M. J.; Praveen, M.; Schmidt, D. M. *Fullerene Sci. Technol.* **1997**, *5*, 781–800.
3. Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291–300.
4. Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994–5007.
5. Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.
6. Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, T. *Science* **2001**, *294*, 828–831.
7. Gomez-Lor, B.; Koper, C.; Fokkens, R. H.; Vlietstra, E. J.; Cleij, T. J.; Jenneskens, L. W.; Nibbering, N. M. M.; Echavarren, A. M. *Chem. Commun.* **2002**, *4*, 370–371.
8. Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500–1503.
9. Amsharov, K. Y.; Jansen, M. *Z. Naturforsch., B: Chem. Sci.* **2007**, *62*, 1497–1508.
10. Amsharov, K. Y.; Simeonov, K.; Jansen, M. *Carbon* **2007**, *45*, 337–343.
11. Amsharov, K. Y.; Jansen, M. *J. Org. Chem.* **2008**, *73*, 2931–2934.
12. Amsharov, K. Y.; Jansen, M. *Chem. Commun.* **2009**, *19*, 2691–2693.
13. Amsharov, K. Y.; Kabdulov, M.; Jansen, M. *Eur. J. Org. Chem.* **2009**, *36*, 6328–6335.
14. Amsharov, K. Y.; Kabdulov, M.; Jansen, M. *Chem.—Eur. J.* **2010**, *16*, 5868–5871.
15. (a) de Frutos, O.; Gomez-Lor, B.; Granier, T.; Monge, M. A.; Gutierrez-Puebla, E.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 204–207; (b) Gomez-Lor, B.; de Frutos, O.; Echavarren, A. M. *Chem. Commun.* **1999**, *23*, 2431–2432.
16. Echavarren, A. M.; Gomez-Lor, B.; Gonzalez, J. J.; de Frutos, O. *Synlett* **2003**, *5*, 585–597 and references cited herein.
17. Amick, A. W.; Scott, L. T. *J. Org. Chem.* **2007**, *72*, 3412–3418.
18. Boorum, M. M.; Scott, L. T. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 20–31; and references cited herein.
19. Vogel, A. I. A. *Textbook of Practical Organic Chemistry*, 3rd ed;; Wiley: New York, N.Y., 1956; p 768.
20. Panetta, C. A.; Sha, D.; Torres, E.; He, Z.; Hussey, C. L.; Fang, Z.; Heimer, N. E. *Synthesis* **1997**, 1085–1090.
21. Dehmkow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021–2031.
22. Soxhlet extraction of pure *syn*-5,10,15 tris(1-bromo-2-naphtylmethyl)truxene with toluene for 20 h shows no remarkable solubility of the material.
23. de Frutos, O.; Granier, T.; Gómez-Lor, B.; Jiménez-Barbero, J.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Chem.—Eur. J.* **2002**, *8*, 2879–2890.
24. Hill, T. J.; Hughes, R. K.; Scott, L. T. *Tetrahedron* **2008**, *64*, 11360–11369.

25. Mueller, A.; Amsharov, K. Yu.; Jansen, M. *Tetrahedron Lett.* **2010**, *51*, 3221–3225.
26. Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769–3775.
27. The $C_{60}H_{30}$ precursor used in this work was synthesized previously according Ref. 15.
28. Otero, G.; Biddau, G.; Sanchez-Sanchez, C.; Caillard, R.; Lopez, M. F.; Rogero, C.; Palomares, F. J.; Cabello, N.; Basanta, M. A.; Ortega, J.; Mendez, J.; Echavarren, A. M.; Perez, R.; Gomez-Lor, B.; Martin-Gago, J. A. *Nature* **2008**, *454*, 865–868.