Fluorinated and Trifluoromethylated Corannulenes

Bernd M. Schmidt,[a, c] Berit Topolinski,[a, c] Mihoko Yamada,[a, b] Shuhei Higashibayashi,[c] Mitsuhiko Shionoya,[b] Hidehiro Sakurai,[c] and Dieter Lentz*[a]

Introduction

Geodesic polyarenes, also called buckybowls, became the focus of attention not only because they can be considered as substructures of fullerenes with three-dimensional bowl shape or as the polar end caps of carbon nanotubes, but also because of their own chemical and physical properties. Corannulene (C_{20}H_{10}) and sumanene (C_{21}H_{12}) are the best-studied buckybowl compounds (Scheme 1). Corannulene has been known for more than four decades,[1] whereas sumanene was first synthesized in 2003 by Sakurai and co-workers.[2]

The chemistry of corannulenes is manifold and includes modification of the peripheral substituents leading to complex stereochemical, optical and electrochemical properties.[3] Other derivatives include bioconjugates,[4] push–pull systems,[5] supramolecular oligomers[6] and even curved radicals,[7] depending on the attached substituents. Rich organo-metallic coordination chemistry was revealed.[8] The η^6 coordination of the curved carbon surface of corannulene, which was achieved in ruthenium[9] and osmium[9d] complexes, is accompanied by flattening of the corannulene bowl, so that two ruthenium complex ions can be coordinated.[9c] Other metal complexes include those with η^2 coordination (generating 1D infinite chains)[10] and mono-,[11] di-,[11,12] tetra-,[12] and penta-[12] η^3-bonded complexes. These were obtained from the corresponding halogenated precursors by insertion. Cyclopalladated corannulenes were synthesized and their expanded η^4 systems and columnar self-assembly in the solid state investigated.[13a]

Corannulene was also shown to be a precursor to further η^4-extended polycyclic aromatic hydrocarbons, such as the family of indenocorannulenes.[14] Starting from the symmetrical pentachlorocorannulene,[15] a short [5,5] single-walled carbon nanotube (C_{10}H_{10}) was synthesized by stepwise chemical methods with a final flash vacuum pyrolysis step.[16]

In contrast, despite some earlier attempts[17] and theoretical studies,[18] research on sumanene only began with its first successful synthesis in 2003.[2a] Subsequently its solid-state packing,[19] the formation of benzylic anions,[19a] bowl-to-bowl contacts[19b], and crystal packing of a trifluoromethylated corannulene was determined by single-crystal X-ray analysis and compared with those known brominated and trifluoromethylated corannulenes. The general electron-acceptor properties of corannulenes bearing substituents introduced in particular positions by liquid-phase synthesis are discussed together with published computational results.

Abstract: The syntheses and properties of corannulenes carrying electron-withdrawing groups (F, CF₃, C₆F₅) are reported. Direct fluorination of corannulene (C_{20}H_{10}) was carried out with xenon difluoride, and the crystal structure of the product was confirmed by the X-ray analysis. Novel trifluromethylated corannulenes, including the versatile 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene, were obtained by various established ring-closing reactions. Besides the use of hexafluorobutylene for the construction of fluoranthenes by Diels–Alder reaction as precursor molecules to form 1,2-disubstituted corannulenes, bis(pentafluorophenyl)acetylene was employed as dienophile. The molecular structure and crystal packing of a trifluoromethylated corannulene was determined by single-crystal X-ray analysis and compared with those known brominated and trifluoromethylated corannulenes. The general electron-acceptor properties of corannulenes bearing substituents introduced in particular positions by liquid-phase synthesis are discussed together with published computational results.
www.chemeurj.org

Results and Discussion

In principal, three options can be considered for introducing fluorine into buckybowls: 1) substitution of an aromatic hydrogen atom at the rim of the bowl with a fluorine atom; 2) introduction of side chains or rings bearing electron-withdrawing fluorine atoms; 3) in sumanene, the benzylic CH₂ groups are also suitable for introduction of fluorine. We recently reported the synthesis of hexafluorosumanene and its congeners, therefore, its discussion is omitted here.

Syntheses: Despite the success of halogen exchange (halex) reactions in industry at high reaction temperatures and Pd-mediated formation of aryl fluorides, the synthesis of fluorinated aromatics is still challenging. For instance, reactions involving an arylene intermediate lead to the formation of regioisomers, and the corresponding hydrogen compounds (proto-dehalogenated) are commonly observed by-products in many cases. We opted to use the commercially available xenon difluoride, because it allows direct introduction of a fluorine substituent even in unactivated aromatic compounds.

Xenon difluoride was added to corannulene (1) at low temperature in dichloromethane and the reaction mixture slowly warmed to room temperature, at which the reaction occurs after some latency time. The crude reaction product consisted of a mixture of unconsumed corannulene, the desired monofluorocorannulene and traces of di- and trisubstituted compounds. Monofluorocorannulene (2) was separated from the crude reaction product by reverse-phase HPLC, because it could not be separated from 1 by column chromatography or recycling HPLC. Because of the overall simplicity of the fluorination reaction (despite the purification issues), we made several attempts to obtain higher fluorinated corannulenes. ³¹F NMR spectroscopy revealed that difluorinated corannulenes were also obtained, as indicated by a series of doublets between −116 and −119 ppm exhibiting J/F/H coupling constants of approximately 13 Hz. However, efforts to separate the difluorinated corannulenes by silica-gel column chromatography and normal-phase HPLC (Buckyprep column) failed.

Subsequent fluorination reactions of 2 or those starting from 1 suffered from severely decreased amounts of recovered material, most likely due to polymerization of the compounds. The substitution of up to three hydrogen atoms by fluorine could be observed by mass spectrometry, but isolation was not possible. Fluorination is assumed to have a weaker effect on the electron-acceptor properties than trifluoromethylation and even chlorination, as is discussed below.

Recently, we reported on the syntheses and properties of trifluoromethylated corannulenes from corannulene and obtained monotrifluoromethylcorannulene (3) by a direct reaction using Togni’s reagent (1-
trifluoromethyl-1,2-benzodioxol-3-(1H)-one, now also called Togni Reagent I) in the presence of methyltrioxorhenium,[30] although the yield is rather poor, monosubstituted derivative 3 can be purified simply by column chromatography.

To avoid the formation of positional isomers when converting a monofunctionalized corannulene to a disubstituted compound, it is feasible to introduce the desired substituent in an earlier stage of the synthesis. It seemed reasonable to introduce two trifluoromethyl groups into a precursor molecule of the corresponding corannulene for successive construction of the target molecule. Corannulene is prepared usually by a ring-closing reaction after obtaining a corresponding fluoranthene. Scott et al. [30c] and Rabideau, Sygula et al. [33b] used norbornadiene as dienophile for the construction of the tetramethylfluoranthene after subsequent CO loss and Retro-Diels–Alder reaction. Siegel and co-workers showed that dimethyl acetylenedicarboxylate can be used to synthesize the respective fluoranthene with two methyldiacylacrylate groups in ortho positions[33c] and this method was later taken up again.[33d] We therefore reasoned that hexafluorobutene should also be applicable, since it is a particularly electrophilic acetylene and hence a potent dienophile, and may circumvent the formation of regioisomers by a regioselective reaction. After work-up by column chromatography, the desired 1,6,7,10-tetramethyl-8,9-bis(trifluoromethyl)fluoranthene (4) could be isolated in 76% yield and converted to the desired 1,2-bis(trifluoromethyl)corannulene (10) in 22% yield.[33e]

The synthesis of a tris(trifluoromethylated)corannulene was pursued as follows. Because of the mirror plane, fluoranthene 4 has two positions in which trifluoromethylation according to the Togni protocol can occur. The sterically demanding methyl group may inhibit ortho attack and, indeed, after slight modification of the reaction conditions, 1,6,7,10-tetramethyl-3,8,9-tris(trifluoromethyl)fluoranthene (5) could be isolated from the reaction mixture by column chromatography on silica gel in 36% yield in high purity (Scheme 3).

The corresponding tris(trifluoromethyl)corannulene 11 was again obtained, in 16% yield, but so far no single crystals suitable for X-ray analysis could be grown.

To obtain further and higher trifluoromethylated corannulenes, the fluoranthene 5 can be treated again by the aforementioned trifluoromethylation protocol (Scheme 4). In this case, however, a mixture of trifluoromethylated products was obtained in a 6:2:1 ratio (5: asym-6: sym-6), which could be separated by recycling HPLC giving sym-6, asym-6 and 5 (in order of elution). Judging from the 19F NMR spectrum in a ratio of 1:1) sym-6 were unambiguously identified. Both fluoranthenes were accumulated and subjected to the ring-closing protocol, which yielded the desired corannulene only in the case of sym-6, to form 1,2,6,7-tetras(trifluoromethyl)corannulene (12).

Probably due to severe molecular strain (as apparent (di) bromination of the sterically highly stressed methyl groups might be unfavourable), fluoranthene asym-6 did not undergo the desired ring-closing reaction, whereas sym-6 did, albeit with very low yield.

To obtain access to functionalized trifluoromethylated corannulenes, the sodium hydroxide mediated ring-closing conditions of Sygula, Rabideau et al.[32a,b] were applied successfully. Like tetrabromocorannulene, the insolubility of 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene (8) in common organic solvents prohibited the acquisition of 13C NMR data,[32h] but the compound can be identified from 1H and 19F NMR data due its C2 symmetry. A broad singlet for the six equivalent fluorine atoms is observed in the 19F NMR spectrum at −49.96 ppm, and a singlet for the hydrogen atoms in ortho positions to the bromine atoms and an AB-type pattern for the remaining hydrogen atoms on the corannulene molecule in the 1H NMR spectrum.

Instead of hexafluorobutene or cyclic maleimides,[26c,34] bis(pentafluorophenyl)acetylene (14)[35] can be prepared and was used in the same manner to synthesize ortho-bis(pentafluorophenylated) fluoranthene 7 in 54% yield. Depending on the choice of reaction conditions, as described previously, 1,2-bis(pentafluorophenyl)corannulene (13) or 4,9-dibromo-1,2-bis(pentafluorophenyl)corannulene (9) can be obtained in 36 or 52% yield, respectively. Dibromocorannulene 9 can, for example, be methylated[30b,32c] to yield 4,9-dimethyl-1,2-bis(pentafluorophenyl)corannulene (15), the improved solubility of which in comparison to the brominated starting material gave access to satisfactory 13C NMR data. The rota-

Scheme 3. Synthesis of substituted fluoranthenes 4 and 5. a) Pentan-3-one (5.5 equiv), KOH (1.65 equiv), MeOH, 1 h, RT, then hexafluorobutene (3.9 equiv), Ac2O, 60°C, 48 h; b) 1-trifluoromethyl-1,2-benzodioxol-3-(1H)-one (Togni’s acid reagent, 1.75 equiv), methyltrioxorhenium (0.1 equiv), 1,2-dichloroethane, 80°C, 12 h.

Scheme 4. Subsequent trifluoromethylation of 5 yields two regioisomers in a ratio of 2:3:1 (asym-6:sym-6). a) 1-1-Trifluoromethyl-1,2-benzodioxol-3-(1H)-one (Togni’s acid reagent, 1.75 equiv), methyltrioxorhenium (0.1 equiv), 1,2-dichloroethane, 80°C; 8 h, total yield 44%.
tion of the pentafluorophenyl groups is fast and unrestricted on the NMR timescale at room temperature for all three studied compounds, and in each case in an AA'BB'C'-type \(^{19}\)F NMR spectrum results. The chemical shift is not dependent on other substituents attached to the corannulene bowl, and for all pentafluorophenyl rings multiplets at \(-137, -152\) and \(-160 \text{ ppm}\) are observed in CDCl\(_3\), corresponding to the ortho-, para- and meta-fluorine atoms, respectively.

**Crystal structures:** A surprising discovery was made during the purification of 2, namely, its co-crystallization with pristine corannulene 1. Mixtures containing variable amounts of 1 and 2 have a needle-like appearance after removal of the solvent, whereas pure corannulene appears as block-like crystals. Satisfactory X-ray data could not be obtained for mixed crystals due to severe disorder. This finding, however, is in accord with the results of Scott et al., who showed that several corannulenes undergo complexation reactions with equimolar quantities of perfluoro-ortho-phenylene to yield extended binary stacks in which the molecules alternate.[36]

Slow evaporation of a pentane/dichloromethane solution furnished pale needle-like crystals of pure 2, which could be solved in the monoclinic space group \(P_2_1/c\), whereby the fluorine atom is disordered over two positions in the solid state (1.4-positions). Crystallographic data of 2 are listed in Table 1. The bowl depth of 2 is only slightly shallower (0.87 Å) than that of corannulene (0.88 Å)[39] and consequently deeper than that of 8 (0.79 Å). The solid state structure is drastically changed upon introduction of the strongly electron withdrawing fluorine atom on the corannulene rim. Within one strand, along the crystallographic \(c\) axis, the bowl direction is the same, but the molecular bowls are not only displaced, but also twisted by 180°, so that an overall slipped stacking motif results (see Figure 1).[40] A short CH-\(\pi\) interaction[41] of 2.86 Å can be observed from one of the CH rim atoms to the centre of a proximate six-membered ring of the corannulene pointing in the same direction. This occurs within unidirectional columns, whereas the opposing columns participate predominantly by an intermolecular F-\(\cdots\)HC interaction[42,43] of 2.66 Å yielding the overall solid-state alignment. The shortest centroid-to-centroid distances within one strand are 3.84 Å for two opposing six-membered rings and 3.75 Å for a six-membered ring in contact with a central five-membered ring.

For comparison, the homologous monochlorocorannulene (16) was also investigated by X-ray crystallography. The solid-state structure of a needle-like crystal of 16 shows an almost identical packing structure, despite a change of the space group (orthorhombic space group \(Pnma\)) and again disorder of the chlorine atoms at the 1- and 4-positions.[43] Therefore, it can be concluded that the packing structure is formed mainly because of electrostatic interactions and not due to F-\(\cdots\)HC interactions. Crystallographic data of 16 are listed in Table 1.

Slow evaporation of a pentane/dichloromethane solution furnished pale yellow needle-like crystals of 4,9-dibromo,1,2-bis(trifluoromethyl)corannulene (8) that were suitable for X-ray analysis, the structure of which was solved in the monoclinic space group \(P_2_1/c\) (Figure 2). Crystallographic data of 8 are listed in Table 1. The increased substitution along the corannulene rim flattens the bowl to 0.79 Å (0.88 Å in the case of ten hydrogen atoms on the corannulene rim and 0.82 Å for the bis-trifluoromethylated 10 and decreases the intermolecular \(\pi-\pi\) stacking distance further to 3.67 Å (hub-to-hub centroid distance of 3.73 Å for the unbranminated 10). Within one strand along the crystallographic \(c\) axis, the bowl direction is the same and the molecular bowls are slightly tilted with respect to the stacking axis by 6.9° (the angle between the hub plane and the \(ab\) plane).
The bowls are not superimposed, the central five-membered ring deviates slightly by approximately 13° and the substituents are rotated by about 140°, probably to maximize both the electrostatic interactions between two stacked bowls and intercolumnar hydrogen bonding.

The antiparallel molecular strands are engaged in a few CH⋯F contacts of about 2.73 Å, and no rotational disorder of the trifluoromethyl group is observed. The hydrogen bonding in this crystal is dominated by CH⋯F contacts and no rotational disorder is observed for the trifluoromethyl group. Through selective substitution in specific positions deviations are apparent. This may not be attributed to inaccurate calculations, but to a significant dependence of the electron affinities on the substitution pattern on the corannulene rim. The calculated substitution patterns are given in the legend to Figure 3. Probably, 10 is a stronger electron acceptor than 1,5-bis(trifluoromethyl)corannulene and maybe even the strongest electron acceptor of all bis-trifluoromethylated corannulenes, because the two trifluoromethyl groups in immediate proximity lead to a highly polarized π system. In general, after the introduction of one trifluoromethyl group in 3, the $E_{1/2}$ value of the reduction is shifted by 0.28 V towards higher potentials relative to corannulene 1. For pentakis(trifluoromethyl)corannulene, Petrukhina and co-workers observed a shift of 0.95 V which roughly corresponds to a shift of 0.19 V per trifluoromethyl group. Through selective substitution in specific positions and the resulting lower symmetry, this shift can be increased to 0.25 V per trifluoromethyl group on average. Because of the different substitution pattern, no strictly linear increase of the electron accepting ability can be expected. For corannulene 11 with three trifluoromethyl groups, and for 12 with four, shifts of 0.82 and 1.0 V are observed relative to 1; these shifts surpass that of pentakis(trifluoromethyl)corannulene (0.95 V).

The influence of pentafluorophenyl groups was not considered before. In the case of 13, the effect of the pentafluorophenyl substituent on the electron affinity is less pronounced than that of trifluoromethyl groups but still superior to that of a chloro substituent. In general, the influence on electron affinity of the studied substituents follow the rough order of $CF_3 > CF_2Cl > Cl > F$, which is surprising at first sight. Fluorine, having the highest electronegativity of all elements, induces a strongly polarized C–F single bond and thus results in a dipole moment along the C–F bond axis. Fluorine is a strong σ acceptor and, to some extent, a π donor. The trifluoromethyl substituent is both a strong σ and π acceptor and induces a stronger dipole moment than...
just one fluorine atom.\textsuperscript{[47]} For $\alpha,\beta$-unsaturated systems, this phenomenon is known (negative hyperconjugation), and it may be a possibility to explain the experimentally obtained values as well.

Fluorine atoms have a much smaller effect than CF$_3$ groups and a smaller effect than chlorine atoms, contrary to the results for C$_6$F$_5$ versus C$_6$(CF$_3$)$_3$.\textsuperscript{[48]} The difference may be due to the different substituents on sp$^2$ carbon atoms in conjugation with an extensive $\pi$ system in corannulene and substituents on sp$^3$ carbon atoms, like in fluorinated fullerences. Density functional calculations further revealed that addition patterns with double bonds in five-membered rings having two sp$^2$ neighbours result in the strongest electron acceptors.\textsuperscript{[48]} This offers an explanation of why the studied corannulenes bearing two trifluoromethyl groups in ortho positions are even stronger electron-acceptor molecules than the isomers used in calculations,\textsuperscript{[49]} despite a possible solvent effect.

The earlier reported cyclic imides were added to Figure 3 with a substituent count of two on the corannulene rim and show the strongest change. However, the first reduction wave to the monoanion is expected to take place at the extended node of the molecules, which would be the highly conjugated five-membered imide ring and not the corannulene framework itself.

### Conclusion

Fluorinated and trifluoromethylated corannulenes have been prepared by liquid-phase synthesis. Corannulenes with up to four trifluoromethyl groups or one fluoro substituent have been isolated and characterized. X-ray crystallographic analyses revealed a columnar packing for the dibrominated and bis-trifluoromethylated corannulene and a slipped stacking motif for fluorocorannulene. Deeper understanding of the intrinsic properties of corannulenes bearing electron-withdrawing groups were obtained by analyzing their electrochemical behaviour in THF solution. A strong dependence on the substitution pattern is suggested to explain the difference between calculated and experimentally observed electron acceptor strength.

### Experimental Section

#### Techniques: All experiments were carried out by standard Schlenk methods under argon atmosphere or by working in an argon-filled MBraun glove box model LABmaster SP or a nitrogen-filled MBraun glove box model UNILab 2000.

#### Chemicals: Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to use and further purified by trap-to-trap distillation for electrochemical use, 1,2-dichloroethane and N,N-dimethylformamide (NDF) from ABCR, methyltrioxorhenium (MTO) from the elements, 2,2′-azobisisobutyronitrile (AIBN) from Aldrich, Diiodobenzene (DIBO) from TCI and Diazabicyclicoctadeca-1,11-diene (DBDO) from Sigma-Aldrich. Diazafullerenes (DBDO) and bis(pentafluorophenyl)acetylene (BPA) were synthesized by literature procedures. Compounds 14, 17 and Togni’s Reagent should be handled with special care due to their toxicity and explosive nature.\textsuperscript{[50]}

### Instrumentation: Melting points were determined on a Gallenkamp Melting Point Apparatus or Stanford Research Systems MPA100 and are uncorrected. IR spectra were recorded on a Nicolet 5 SX FTIR spectrometer equipped with a DTGS detector or a JASCO FT IR-4100 spectrometer. 1H, 13C and 19F NMR spectra were measured on a JEOL ECS 500/500 spectrometer or on a Bruker Instruments AVIII 700 at 23°C. CDCl$_3$ and CD$_2$Cl$_2$ were used as solvents, if not stated otherwise, and the residual solvent peak was taken as internal standard (1H NMR: CDCl$_3$, 7.26 ppm, CD$_2$Cl$_2$ 5.30 ppm; 13C NMR: CDCl$_3$, 77.0 ppm, CD$_2$Cl$_2$ 54.0 ppm). Chemical shifts are reported in parts per million (δ) relative to TMS. 19F NMR spectra were referenced against external CF$_3$Cl, Mass spectra were measured on a MAT CH7A (EI, 80 eV, 3 kV) at the given temperature for each sample or on a JEOL JMS-777V.

High-resolution masses were determined by peak-match method against perfluorokerosene. Gel permeation chromatography (GPC) was performed on JAI/VEL CHROMATEC LC-900W and chloroform as eluent. HPLC analysis and separation were performed with a JASCO LC-2000 HPLC using Cosmous Buckyprep columns, TLC ( precoated) analysis and PTLC ( precoated and self-made) was performed using Merck silica gel 60 F$_{254}$ or Wako Wako gel B-5F. Some reactions were carried out in parallel in different glass reactors (EYELA Chemistation series) and low-temperature reactors (EYELA PSL series).

The structure determination was performed on a Bruker SMART 1000 fitted with a CCD; the crystal of compound 8 was studied on a Bruker D8 QUEST. Data collection, reduction and empirical absorption correction were performed with the SMART, SAINT and SADABS programs, respectively.\textsuperscript{[51]} the SHELX program package\textsuperscript{[52]} was used for structure solution and refinement.

### Monofluorocorannulene (2): Corannulene ($\mathrm{C}_{20}$H$_{10}$; 1.0 equiv) was dissolved in dichloromethane (5 mL) and the solution cooled to −78°C. Solid xenon difluoride (92.0 mg, 0.54 mmol, 1.38 equiv) was added at once and the flask was sealed. The mixture was allowed to warm to room temperature over 3 h. The green slurry was diluted with 30 mL of dichloromethane and silica gel was added. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/ethyl acetate 20:1) to yield 2 together with unconverted corannulene and small amounts of the regiosomers of C$_{20}$(F)$_{13}$ (as indicated by a series of doublets between −116 and −119 ppm exhibiting 2J(C,F) coupling constants of 131−133 Hz) as an amorphous powder (34% conversion by crude NMR). Compound 2 was further purified by RP-HPLC to give analytically pure 2 (Gemini C18, methanol/water 9/1) at a flow rate of 1 mL min$^{-1}$ and 148 bar with an R$_{f}$ value of 10.9 min. Mw: 226 3C$_4$H$_8$ NMR (400 MHz, CDCl$_3$), δ = 7.39 (d, 3J(1F,1H) = 13 Hz, 1H), 7.76−7.88 (m, 7H), 7.96 (d, 3J(1F,1H) = 8.8 Hz, 1H), 3J(1F,1H) 101 MHz, CDCl$_3$), δ = 160.00 (d, 3J(C,F) = 260 Hz, 1C, CF), 125.53 (d, 3J(C,F) = 260 Hz, 1C, CF), 136.21 (s, C$_{\text{h}}$(C,F)$^2$), 135.38 (1C, C$_{\text{h}}$(C,F)$^2$), 134.80 (d, J(C,F) = 5 Hz, 1C, C$_{\text{h}}$(C,F)$^2$), 132.70 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 132.16 (d, 3J(C,F) = 10 Hz, 1C, C$_{\text{h}}$(C,F)$^2$), 131.11 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 130.87 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 130.28 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 127.85 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 127.78 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 127.51 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 127.26 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 127.02 (s, 1C, C$_{\text{h}}$(C,F)$^2$), 126.71 (d, 3J(C,F) = 13 Hz, 1C, C$_{\text{h}}$(C,F)$^2$).
1H NMR (400 MHz, CDCl3): δ = 8.46 (s, 1H), 7.83 (s, 1H), 2.82 (s, 3H), 2.74–2.75 ppm (m, 2H), 3.14–3.17 ppm (m, 2H), 2.20 ppm (s, 3H, CHF), 5.26 ppm (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ = 131.36 (s, 2C), 131.50 (s, 2C), 118.64 (s, 1C), 24.04 (s, 2C, CH2), 22.99 ppm (s, 2C, CHF), the corresponding CCF3 could not be observed due to strong coupling with large coupling constants and the consequent low S/N ratios; 19F NMR (376 MHz, CDCl3): δ = -52.88 (m, 6F), -50.08 ppm (s, 6F); IR: ν = 2921 (m), 2906 (w), 1762, 1710 (s), 1496 (s), 1453 (s), 1386 (m), 1331 (m), 1307 (m), 1180 (s), 1045 (s), 745 (m), 724 cm⁻¹ (m); MS (EI): m/z: 530 [M]+ (50%) [M − CF3]2; 461 (25) [M − CF2]+; HRMS (EI): m/z calc for C28H46F12: 530.0904; found: 530.0906.

Data for 1,2,6,7-tetrafluorobenzylidene (corannulene (12)): Yield: 36%; m.p. 271°C; 1H NMR (400 MHz, CDCl3): δ = 8.79 (s, 2H), 7.83–7.85 ppm (m, 6F); 13C NMR (100 MHz, CDCl3): δ = 131.36 (s, 2C), 131.50 (s, 2C), 118.64 (s, 1C), 24.04 (s, 2C, CH2), 22.99 ppm (s, 2C, CHF), the corresponding CCF3 could not be observed due to strong coupling with large coupling constants and the consequent low S/N ratios; 19F NMR (376 MHz, CDCl3): δ = -52.88 (m, 6F), -50.08 ppm (s, 6F); IR: ν = 2921 (m), 2906 (w), 1762, 1710 (s), 1496 (s), 1453 (s), 1386 (m), 1331 (m), 1307 (m), 1180 (s), 1045 (s), 745 (m), 724 cm⁻¹ (m); MS (EI): m/z: 530 [M]+ (50%) [M − CF3]2; 461 (25) [M − CF2]+; HRMS (EI): m/z calc for C28H46F12: 530.0904; found: 530.0906.
Fluorinated and Trifluoromethylated Corannulenes


Acknowledgements

This work was supported by MEXT, JST (ACT-C), JSPS and the DFG (GRK 1582/1). We thank M.Sc. Alma Jaeger for help with the preparation of 7. We are indebted to Dr. Holger Ott, Bruker-AXS for the data collection of compounds 2 and Dr. Katrin Niedermann for valuable discussions.