# Synthesis of Hexa-*peri*-hexobenzocoronenes Carrying Linear or Branched Perfluoroalkylated Side Chains

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**Abstract:** Substituted disc-shaped perfluoroalkylated hexa-*peri*-hexabenzocoronenes (HBC), known to self-assemble into conducting ordered architectures, were synthesized and characterized. A systematic variation of the linear or branched perfluoroalkylated side chains was performed in order to screen the influence of the lateral chain on their one-dimensional self-aggregation.

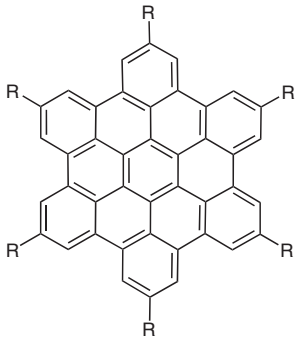
**Key words:** HBC, perfluoroalkylated substitutions, cross-coupling, cyclodehydrogenation, tandem Sonogashira



Self-assembling is emerging as a widely used strategy in supramolecular chemical synthesis, with the potential of generating nonbiological structures with dimensions of up to several hundred nanometers.[1] As example of involved intermolecular forces one could mention π-π interactions,[2] hydrogen bonding,[3] donor–acceptor interactions,[4] and reversible ligand–metal interactions.[5] Molecules that are promising self-assembling candidates with application in advanced functional materials include liquid crystal constituents,[6] block polymers,[7] hydrogen-bonded complexes,[8] and coordination polymers.[9]

Among supramolecular self-organizing systems, liquid crystals, formed of disc-shaped molecules, are of particular interest.[9a,10] They have great potential for incorporating desirable chemical functionalities in their periphery and the physical properties of the supramolecular structures they form may, therefore, be tuned at nanoscaled dimensions. An outstanding class of polycondensed aromatic hydrocarbons (PAH) are hexa-*peri*-hexabenzocoronene derivatives (HBC), which excel over their counterparts due to their high chemical and thermal stability and by their high charge carrier mobility measured in bulk.[11]

The replacement of purely alkyl chains by partially perfluoroalkylated chains should, in principle, not alter the electronic properties of these molecules, but should eventually prevent or reduce lateral aggregation of formed one-dimensional self-aggregated molecular wires. Promising results in this respect involving some perfluoroalkylated HBC derivatives have recently been reported.[12] In order to investigate the influence of the nature of the lateral chain, several derivatives have been systematically synthesized and characterized. The lateral substituents, either linear or branched, differ by the length of perfluoroalkyl chain and/or length of partitioning by the $CH_2$ spacer. The derivatives reported herein are shown in Figure 1.




| linear (**1**) | | | branched (**2**) | |
|---|---|---|---|---|
| R = | $Rf_{3,6}$ | **1a** | R = $(CH_2)_3CH[CH_2(CF_2)_4F]_2$ | **2a** |
| | $Rf_{3,8}$ | **1b** | $(CH_2)_3CH[(CH_2)_2(CF_2)_6F]_2$ | **2b** |
| | $Rf_{4,4}$ | **1c** | $(CH_2)_5CH[(CH_2)_2(CF_2)_6F]_2$ | **2c** |
| | $Rf_{4,10}$ | **1d** | | |
| | $Rf_{5,6}$ | **1e** | | |
| | $Rf_{6,8}$ | **1f** | | |
| | $Rf_{8,4}$ | **1g** | | |
| | $Rf_{8,6}$ | **1h** | | |
| | $Rf_{8,8}$ | **1i** | | |
| | $Rf_{5,8}$ | **1j** | | |

$Rf_{n,m} = (CH_2)_n(CF_2)_mF$

**Figure 1** Hexa-*peri*-hexabenzocoronene target molecules described in this paper

The most convenient way of synthesizing HBC derivatives consists of cyclodehydrogenation of the corresponding hexaphenylbenzene (HPB) under Kovacic conditions.[13] Among numerous variations of the Kovacic conditions, the mild iron(III) chloride reagent, which acts both as Lewis acid and as the oxidant, is superior to other alternative reagents, as, in most cases, the reaction goes to completion without unwanted chlorination. As the electron-withdrawing effect of a perfluorinated lateral chain prevents the final cyclodehydrogenation reaction, a minimum spacer of two $CH_2$ groups is required between the aromatic core and the perfluorinated part.[14]

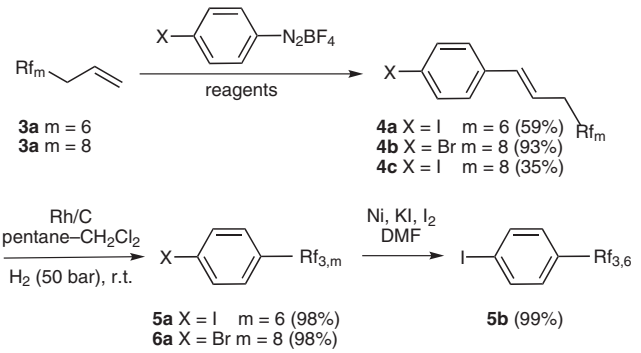
Symmetrical HPB derivatives are best prepared by cyclotrimerization of an alkyne species.[15] Although other transition metals, such as nickel and iron, or even silicon catalyze the cyclotrimerization of alkynes to arenes, co-

balt complexes such as $Co_2(CO)_8$ and $CpCo(CO)_2$ are among the most efficient.[16]

Cyclodehydrogenation, as well as cyclotrimerization, has been studied extensively in the past for the preparation of hexaalkyl-substituted HBC derivatives,[17] but, nevertheless, needed modification for the preparation of perfluorinated analogues.

The main challenge in preparing symmetrical perfluorinated HBC derivatives remains, therefore, in the preparation of correctly substituted tolane derivatives. These starting substituted tolanes, used in turn for cyclotrimerization, were found to be favorably made by tandem Sonogashira cross-couping[18] using the corresponding halogenated aryl species bearing the desired perfluorinated lateral chain. Mostly their preparation was very similar for derivatives with the same length $CH_2$ spacer, but varied greatly when the number of $CH_2$ groups changed.

The preparation of compounds **5a**,**b** and **6a** bearing a three $CH_2$ spacer between the phenyl ring and the perfluorinated tail has been reported involving a Wittig reaction of 4-bromobenzaldehyde and $[Ph_3PCH_2CH_2Rf_n]^+I^-$ (n = 6, 8, 10) and subsequent hydrogenation.[19] Nevertheless, we decided (Scheme 1) to use a different strategy due to easier access to the Heck starting compounds. The perfluorinated allyl derivatives **3a**,**b**, synthesized in two steps[20] are reacted with 4-bromo- or 4-iodobenzenediazonium tetrafluoroborate affording the desired cross-coupled products **4a–c** by palladium-catalyzed Heck reaction;[21] exclusively *E*-isomers were formed, as shown by $^1H$ NMR. The yield obtained from the iodinated diazonium salt is much lower than that from using the bromine analogue, because the iodinated diazonium salt undergoes partially a twofold Heck reaction forming a dialkylated product (up to 30%) which has to be separated by tedious column chromatography purification.

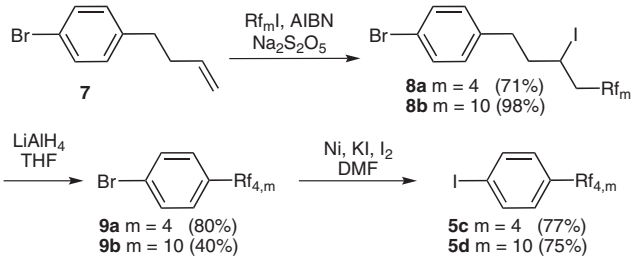



**Scheme 1** Preparation of perfluoroalkylated iodoaryl derivatives bearing a three-$CH_2$ spacer

Hydrogenation without halogen hydrogenolysis is best done by using the mild rhodium/carbon catalyst in pentane–dichloromethane (1:1). The reaction requires high hydrogen pressure (up to 60 bars) and a reaction time of around 12 hours to afford the hydrogenated compounds **5a** and **6a** quantitatively. Halogen exchange[22] on **6a** with potassium iodide using nickel as catalyst yields the more reactive iodinated compound **5b** for subsequent Sonogashira cross-coupling.

HBC derivatives bearing a four-$CH_2$ spacer were prepared by a slightly different method, in which the alkyl–aryl bond was formed prior to the attachment of the perfluorinated part to avoid any cross-coupling of perfluoroalkyl substituents. Heck reaction of an analogue of compound **3** bearing four nonfluorinated carbons was found inappropriate as many side products were formed.

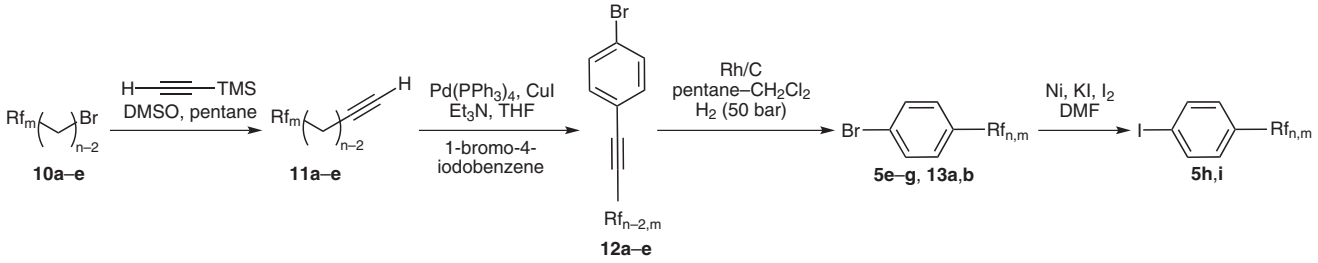
As illustrated in Scheme 2, compound **7**, formed by Wurtz-type coupling,[23] was reacted with the corresponding perfluoroalkyl iodide ($Rf_mI$) in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) to initiate the reaction and 30% aqueous sodium metabisulfite solution to reduce the formation of side products.[20a] Removal of the iodine group of the side chain in **8a**,**b** was achieved with lithium aluminum hydride[20c] affording the desired aryl bromides **9a**,**b** without cleavage of the aryl bromide. Even milder cleavage may be achieved using lauroyl peroxide in the presence of cyclohexane,[24] a procedure which afforded comparable yields in our case. Radical-mediated halogen exchange furnished, finally, the iodoaryl derivatives **5c**,**d**.




**Scheme 2** Three-step synthesis of the iodoaryl derivatives **5c**,**d**

The preparation of the key aryl derivatives **5h**,**i** is shown in Scheme 3 with yield data in Table 1. All polyfluoroalkyl bromides **10a–e** were obtained as colorless oils in very good yield according to a published procedure.[20c] The two-carbon elongation of the brominated alkynes was achieved by their treatment with lithium acetylide–ethylenediamine complex in dimethyl sulfoxide.[25] In order to improve the homogeneity of the reaction mixture, the starting bromides were diluted with pentane prior to the addition yielding the perfluoroalkynes **11a–e** as colorless, very volatile liquids in modest yield. The yields of the derivatives bearing an eight $CH_2$ spacer were, interestingly, much better than those of the corresponding shorter ones, probably due to lower volatility. An alternative way to produce semiperfluorinated alkynes has been reported for **11c**. Dimethylpropargyl alcohol was reacted with 6-bromohex-1-ene, which was subsequently transformed by addition of perfluorobutyl iodide. Reduction of the iodo group followed by deprotection of the alkyne yielded **11c**.[26]

The subsequent unfavorable Sonogashira cross-coupling (the alkyne bears an alkyl and not an aryl substituent) of **11a–e** was found to work best with $Pd(PPh_3)_4$ as the cata-




**Scheme 3** Preparation of the brominated bromoaryls **5e–g** and the iodoaryls **5h**,**i**

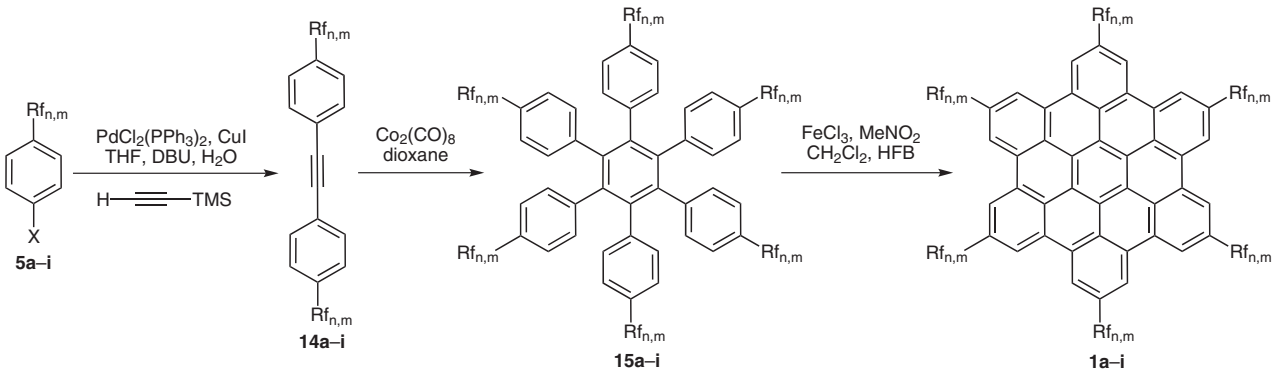
**Table 1** Yields of All Derivatives Shown in Scheme 3

| $Rf_{n,m}$ | | Starting compound | Derivative | Yield | Derivative | Yield | Derivative | Yield | Derivative | Yield |
|---|---|---|---|---|---|---|---|---|---|---|
| n | m | | | (%) | | (%) | | (%) | | (%) |
| 5 | 6 | **10a** | **11a** | 38 | **12a** | 38 | **5e** | 95 | | |
| 6 | 8 | **10b** | **11b** | 39 | **12b** | 36 | **5f** | 99 | | |
| 8 | 4 | **10c** | **11c** | 62 | **12c** | 78 | **5g** | 97 | | |
| 8 | 6 | **10d** | **11d** | 73 | **12d** | 35 | **13a** | 89 | **5h** | 88 |
| 8 | 8 | **10e** | **11e** | 44 | **12e** | 35 | **13b** | 93 | **5i** | 90 |

lyst with 1-bromo-4-iodobenzene. Even at elevated reaction temperatures (80 °C) no trace of any doubly alkylated product was found. The cross-coupling was repeated several times under various conditions in order to improve the yield, but the simplest conditions [$Pd(PPh_3)_4$, CuI, $Et_3N$] excel over more elaborated ones [such as $Pd(PPh_3)_4$, LDA, $ZnBr_2$] that involve in situ preformed zinc derivatives as active transmetalation species. Subsequent hydrogenation of the alkynes **12a–e** under 50 bar of hydrogen, afforded the reduced perfluorinated bromoaryl key products **5e–g** and **13a**,**b** in quantitative yield as colorless oils. Halogen exchange was only performed for two derivatives **13a**,**b** affording **5h**,**i**.

The tandem Sonogashira reaction (Scheme 4, Table 2) uses the standard $PdCl_2(PPh_3)_2$/CuI catalyst with trimethylsilylacetylene, tetrahydrofuran as solvent and 1,8-diazabicyclo[5.4.0]undec-7-ene–water as base to deprotect the formed TMS intermediate. This procedure allowed for total suppression of the homocoupled product. The only impurity found was the unreacted halogenated starting compound. It is noteworthy that the tandem Sonogashira reaction was also attempted with unsaturated compound **4a**. This reaction, however, afforded exclusively a tolane derivative, in which HF was eliminated from the side chain. We also attempted direct formation of tolane **14b** by twofold Kumada cross-coupling reaction between 11-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoroundecane and 1-bromo-4-[(4-bromophenyl)ethynyl]benzene, but this reaction gave, at best, the desired product in 19% yield. The Kumada cross-coupling reaction seems to be severely hampered due to the electron-withdrawing effect of the perfluorinated part, despite the three $CH_2$ spacer. In contrary, both tolanes **14a**,**b** were formed in good yield for a tandem reaction. For tolane **14c**, low yield was obtained since large quantities of unreacted starting material were recovered after the reaction. The high yield of **14d** was surprising, as extremely low solubility, due to the ten perfluorinated carbon tail, was expected to hamper the reaction resulting in a drop in the yield instead of an increase. In the case of the brominated precursors **5e**,**f**, the corresponding tolane **14e** was afforded in very low yield, only requiring separation from large amounts of recovered starting material, whereas **14f** was isolated in acceptable yield. Tandem Sonogashira reaction using brominated **5g** or iodinated **5h**,**i** yielded the tolanes **14g–i** in moderate to good yields. It appears that the influence of the more reactive iodo group as compared to bromine is negligible in the presence of bulky perfluoroalkylated chains.

Subsequent cobalt-mediated cyclotrimerization afforded most of the desired HPB derivatives **15a–i** in good yields. The very low solubility of the tolanes **14b** and **14d** as well as the corresponding HPB derivatives **15b** and **15d** prevented completion of the reaction on one hand, and severely hampered the purification of the obtained products on the other. To overcome these difficulties hexafluorobenzene (HFB) was added as co-solvent to prevent incomplete reaction due to co-precipitation of starting material with the even less soluble product. Purification was performed by filtration through a short silica gel plug using hot benzotrifluoride (α,α,α-trifluorotoluene, BTF) as solvent. It must be noted that HPB derivatives **15g** and **15h** bearing an eight $CH_2$ spacer terminated by a short perfluorinated part of four or six carbon atoms are the first HPBs with linear, partially fluorinated side chains that are oily instead of solid. This behavior was, to date, only reported for HPB derivatives bearing purely alkyl chains or branched lateral groups in their periphery.[15b] HPB **15i**, carrying eight perfluorinated carbon atoms, was again obtained as a powder.




**Scheme 4** Formation of HBC derivatives bearing linear perfluorinated side chains

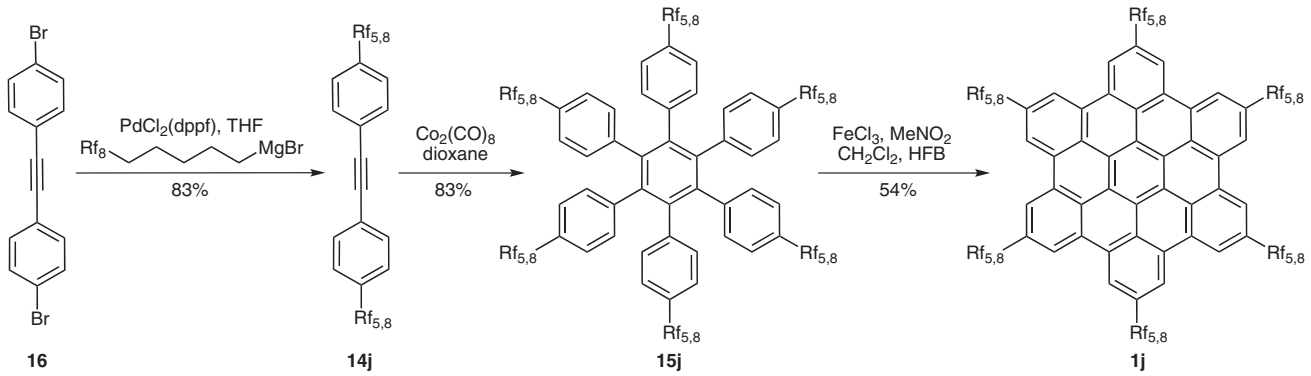
Cyclodehydrogenation of all HPB derivatives bearing linear perfluoralkylated chains **15a–i** afforded the corresponding HBC derivatives in moderate yields. HPB carrying short perfluorinated parts or long alkyl parts, normally well soluble in dichloromethane, were reacted using the standard iron(III) chloride/nitromethane protocol[27] whereas hexafluorobenzene was added as co-solvent for less soluble HPB derivatives as otherwise the transformation could not be completed. After the reaction the crude mixtures were quenched by the addition of methanol, which induced precipitation of the desired HBC derivatives, commonly as brown solids. Precipitation from common organic solvents ($Et_2O$, $CH_2Cl_2$, $MeNO_2$, and EtOH) and a fluorinated solvent such as benzotrifluoride or hexafluorobenzene yielded, after several suction filtrations over Millipore®, the desired HBCs as yellow solids. Interestingly, the four $CH_2$ spacer, independent on the length of the perfluoro part [4 $CF_2$ (**1c**), 6 $CF_2$,[27] 8 $CF_2$,[14] 10 $CF_2$ (**1d**)], proved to be ideal for purification as precipitation from benzotrifluoride and hexafluorobenzene afforded these products as very bright yellow solids.[27] Despite of the fact that HBCs **1g** and **1h**, bearing short perfluorinated parts, were even moderately soluble in common organic solvents, their purification proved to be more cumbersome. Due to moderate solubility of the later, silica gel filtration using hot benzotrifluoride, hot toluene, diethyl ether, or dichloromethane was attempted, but the HBC stuck irreversibly to the silica gel. Chromatography on preparative TLC plates afforded an observable migration, but it was impossible to recover the compound from the solid support. The usual solublilization/precipitation technique was therefore applied yielding HBC **1h** as a dark yellow solid whereas HBC **1g** remained a dark powder. MALDI-TOF analysis of **1g** revealed a mixture of chlorinated products (up to five chlorine substituents) of the target HBC. We assume that chlorination was provoked by the high solubility of the final product, since this chlorination occurred even at room temperature.

HBC **1i** with its eight perfluorinated carbons showed rather low solubility. Purification was, therefore, attempted by suspending **1i** in common organic solvents followed by suction filtration over Millipore®. Unfortunately the black impurity could not be removed in this way. Only repeated precipitation from refluxing 1,2,4-trichlorobenzene (TCB) afforded **1i** as dark yellow solid.

An alternative very short sequence to prepare symmetrically substituted tolane derivatives consists of a twofold Kumada cross-coupling reaction of a perfluorinated bromoalkane with 1-bromo-4-[(4-bromophenyl)ethynyl]ben-

**Table 2** Yields of All Derivatives Presented in Scheme 4

| $Rf_{n,m}$ | | X | Starting compound | Derivative | Yield | Derivative | Yield | Derivative | Yield |
|---|---|---|---|---|---|---|---|---|---|
| n | m | | | | (%) | | (%) | | (%) |
| 3 | 6 | I | **5a** | **14a** | 61 | **15a** | 86 | **1a** | 33 |
| 3 | 8 | I | **5b** | **14b** | 66 | **15b** | 84 | **1b** | 56 |
| 4 | 4 | I | **5c** | **14c** | 20 | **15c** | 95 | **1c** | 55 |
| 4 | 10 | I | **5d** | **14d** | 80 | **15d** | 85 | **1d** | 70 |
| 5 | 6 | Br | **5e** | **14e** | 6 | **15e** | 79 | **1e** | 60 |
| 6 | 8 | Br | **5f** | **14f** | 46 | **15f** | 64 | **1f** | 65 |
| 8 | 4 | Br | **5g** | **14g** | 50 | **15g** | 73 | **1g** | 46 |
| 8 | 6 | I | **5h** | **14h** | 21 | **15h** | 92 | **1h** | 64 |
| 8 | 8 | I | **5i** | **14i** | 21 | **15i** | 51 | **1i** | 40 |




**Scheme 5** Tolane preparation via Kumada cross-coupling followed by HBC formation

zene (**16**) (Scheme 5). Unfortunately the yield proved to be at best moderate and, in addition, not reproducible, the reason being, most probably, incomplete Grignard formation of the perfluorinated bromoalkyl hindered by micelle formation.[28] The very long reaction time (one week) of the subsequent Kumada cross-coupling, underlined these difficulties. Out of the large variety of different catalysts tested $PdCl_2(dppf)\cdot CH_2Cl_2$[29] proved to be the most promising, since with other catalysts, such as $Pd_2(dba)_3$ or $Pd(OAc)_2$[30] the reaction did not go to completion.

Only the use of highly pure tolane **14j** allowed the preparation of the desired HPB derivative **15j** in good yield as a white powder, as the remaining impurities of the Kumada cross-coupling catalyst appeared to poison the cobalt catalyst, preventing, therefore, the cyclotrimerization.

Oxidation of HPB **15j** was attempted first by using iron(III) chloride in nitromethane and dichloromethane as solvent. However, only starting material was recovered, presumably because the solubility was too low for the reaction to occur. Only by adding hexafluorobenzene as a co-solvent was the desired HBC **1j** obtained as slightly brown-yellow powder after several re-precipitations from benzotrifluoride and hexafluorobenzene solutions.

To further increasing the fluorine coat of the HBC columnar stacks, HBC derivatives carrying branched perfluorinated side chains were designed. One derivative **2a** was decorated with six branched chains each carrying two perfluorobutyl end groups. Modeling of the geometry of this side chain revealed a T-shaped arrangement of the perfluorinated end part with respect to the $CH_2$ spacer at the branching point. This geometry inherently imposes large steric hindrance on the π–π stacking. To reduce this steric hindrance two other derivatives were added, one with a longer $CH_2$ spacer after the branching point **2b** and a second derivative with an elongated $CH_2$ spacer before and after the branching point **2c**.

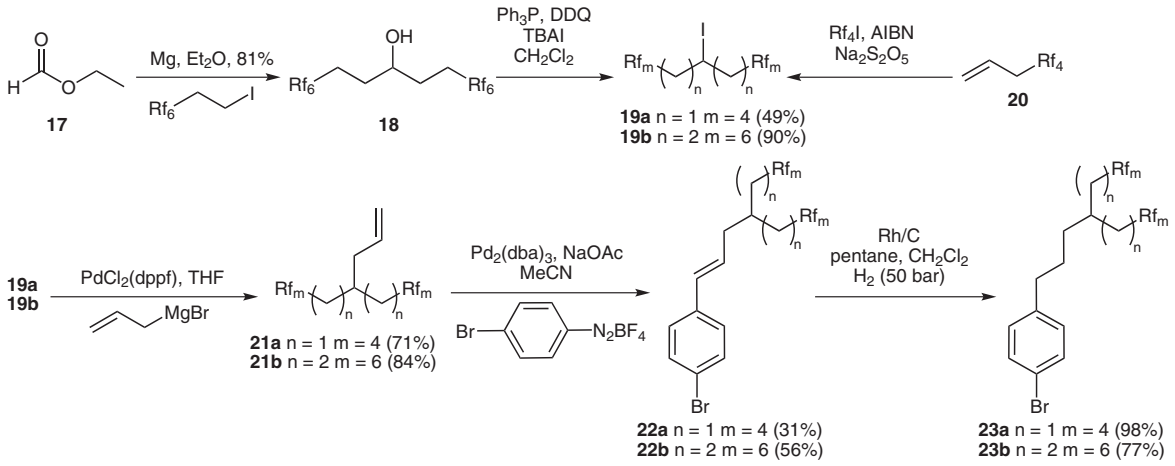
The addition of a second perfluorinated tail onto a perfluoroalkylated allyl derivative **20** proved to work smoothly, but required, in general, longer reaction times. Furthermore the addition of several portions of the radical initiator (AIBN) were needed to afford the desired branched iodide **19a** after distillation (Scheme 6). The analogue **19b** with a five-carbon spacer between the perfluorinated end tails was synthesized by twofold Grignard reaction on ethyl formate (**17**)[31] followed by iodination of the obtained alcohol **18**. Interestingly, all iodination attempts using hydrogen iodide and aliquat 336 as phase-transfer catalyst failed completely, most probably due to solubility problems. Only the use of tetrabutylammonium iodide in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and triphenylphosphine afforded the desired iodide **19b**.[32]

The subsequent Kumada reaction was found to be very tricky as the reaction was very sensitive to the applied conditions. It appeared crucial that the allylmagnesium bromide is added slowly over several hours at 0 °C as otherwise many side products are formed. Again $PdCl_2(dppf)\cdot CH_2Cl_2$ was found to be the most adapted catalyst to form selectively **21a**,**b**.

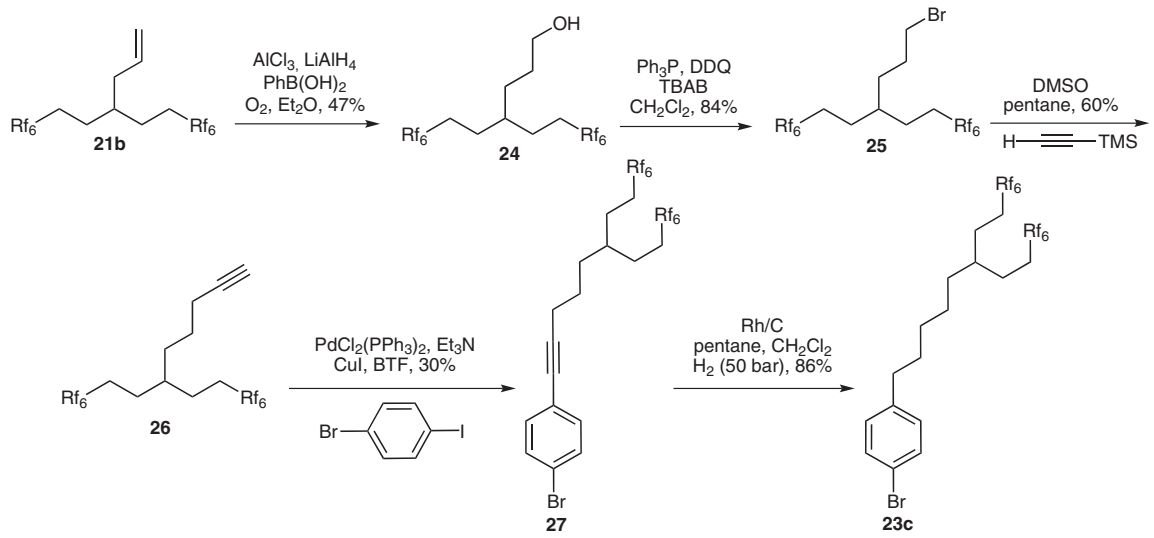
Heck reaction of the branched perfluorinated precursors **21a**,**b** with reactive 4-bromobenzenediazonium tetrafluoroborate did not work properly. Different catalytic systems were tested, from which $Pd(OAc)_2/CaCO_3$ and $Pd_2(dba)_3$/NaOAc excelled over all the others. Subsequent hydrogenation of **22a**,**b** afforded the desired aryl derivatives carrying branched perfluoroalkylated side chains **23a**,**b**.

Reaction of iodide **19b** with 5-bromopent-1-ene under Kumada cross-coupling conditions did not allow the direct preparation of the **21b** analogue. The Kumada cross-coupling worked only by using very reactive allylmagnesium bromide. Hence **21b** was oxidized[33] to the alcohol **24** which was, thereafter, converted into its brominated analogue **25** by using tetrabutylammonium bromide, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and triphenylphosphine. Subsequent acylation using lithium acetylide–ethylenediamine complex in a mixture of dimethyl sulfoxide and pentane afforded finally compound **26** (Scheme 7). Sonogashira cross-coupling of **26** gave the desired aryl derivative **27** in low yield. The low reactivity of the starting alkyne **26** was the reason that no traces of doubly coupled product were found. Hydrogenation of **27** using the already discussed rhodium/carbon conditions afforded the desired aryl bromide **23c** in good yield.

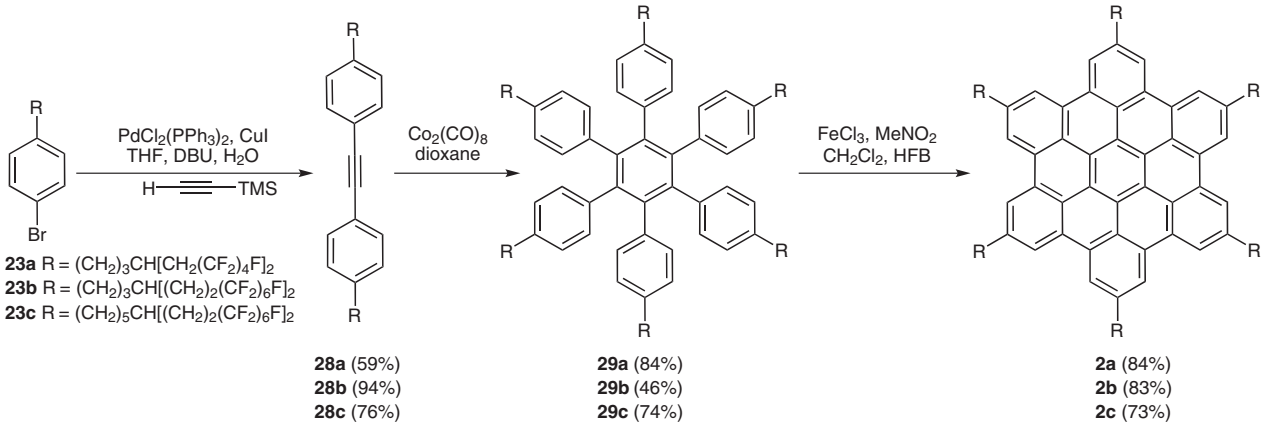
Conversion of the brominated aryl derivatives **23a**–**c** with their branched chains into the corresponding tolanes was




**Scheme 6** Formation of branched polyfluoroalkyl-substituted aryl bromides **23a**,**b**




**Scheme 7** Preparation of derivative **23c**




**Scheme 8** Formation of HBC derivatives **2a**–**c** bearing branched perfluoroalkylated side chains

performed by tandem Sonogashira reactions. Purification was achieved for all three derivatives by column chromatography over silica gel. The branched T-shaped lateral chain seems to impede considerably the π-π-aggregation of the central part as **28a**–**c** are the first reported tolanes that are obtained as oils instead of solids. The highly soluble tolanes afforded after $Co_2(CO)_8$-mediated cyclotrimerization the desired HPB derivatives **29a**–**c** in moderate to high yields (Scheme 8). These oily compounds had to be purified by column chromatography.

The oily consistence of HPB derivatives was already mentioned in literature for compounds that carry long linear (>$C_{12}$) or branched alkyl chains in their periphery.[34]

The oxidation of HPB **29a–c** was performed under mild iron(III) chloride conditions (Scheme 8). As a solvent dichloromethane was largely sufficient, since all starting materials were oils and, therefore, readily dissolved in dichloromethane. The purification of HBC **2a** was performed in the usual way by precipitation of the HBC from benzotrifluoride and hexafluorobenzene solution by the addition of diethyl ether, pentane, and methanol, which yielded finally the desired HBC **2a** as a yellow powder, whereas HBCs **2b**,**c** were obtained as dark powders.

All reagents and solvents were purchased from commercial sources and used without further purification. THF and $CH_2Cl_2$ were dried and deoxygenated by the Grubbs method.[35] All reactions were performed under inert atmosphere ($N_2$ or Ar). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 360 or a Bruker DRX 500 spectrometer, using $CDCl_3$ or HFB as solvent. Mass spectra were recorded on a Finnigan Thermo Quest GC/MS Voyager spectrometer, a Bruker 4.7 T BioAPEX II FT-ICR spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile) as matrix, or a Bruker Ultraflex II spectrometer. Analytical TLC was performed on Merck Kieselgel 60 F254 pre-coated glass plates and visualized by spraying with a $KMnO_4$ soln.

**2,5,8,11,14,17-Hexakis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1a); Typical Procedure**

In a 3-necked flask, HPB **15a** (0.2 g, 74 μmol) was dissolved in anhyd $CH_2Cl_2$ (15 mL) under an inert atmosphere. At the same time a soln of $FeCl_3$ (433 mg, 2.67 mmol, 3 equiv/H to be removed) was prepared in $MeNO_2$ (5 mL). The $FeCl_3$ soln was added to the soln of **15a** at 45 °C drop by drop with a syringe. Argon was bubbled through the mixture by a Teflon capillary during the entire reaction. After 6 h the mixture was quenched by the addition of MeOH (20 mL). The black precipitate was collected by suction filtration over Millipore® and was suspended in various common organic solvents ($CH_2Cl_2$, MeOH, $Et_2O$, and pentane). The suspensions formed were each treated in an ultrasonic bath for 30 min followed by reflux for 1 h. After 2 h of cooling in the refrigerator the suspensions were filtered over Millipore® to yield **1a** (62 mg, 33%) as a bright yellow powder.

$^1$H NMR (500 MHz, HFB, $CDCl_3$): δ = 8.69 (br s, 12 H, Ar), 3.55 (br s, 12 H), 2.74 (m, 24 H).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 2682.22 (100) ([$M^+$], calcd for $C_{96}H_{48}F_{78}$: 2682.25), 2336.20 (20).

UV/VIS (BTF, $10^{-5}$ M): λ (ε) = 344, 361 ($5.6 \times 10^3$), 386, 412 nm.

**2,5,8,11,14,17-Hexakis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1b)**

As described for **1a** using HPB **15b** (50 mg, 15 μmol), $FeCl_3$ (220 mg, 1.36 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (5 mL), $MeNO_2$ (4 mL), and HFB (5 mL) gave **1b** (28 mg, 56%).

$^1$H NMR (500 MHz, HFB, $CDCl_3$): δ = 8.95 (s, 12 H, Ar), 3.61 (br s, 12 H, $CH_2$), 2.73 (br s, 24 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3282.21 (100) ([$M^+$], calcd for $C_{108}H_{48}F_{102}$: 3282.21), 2836.20 (10).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 352, 369 ($1.5 \times 10^5$), 396 nm.

**2,5,8,11,14,17-Hexakis(5,5,6,6,7,7,8,8,8-nonafluorooctyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1c)**

As described for **1a** using HPB **15c** (0.2 g, 92 μmol), $FeCl_3$ (535 mg, 3.3 mmol, 3.0 equiv/H to be removed), $CH_2Cl_2$ (15 mL), and $MeNO_2$ (5 mL) gave **1c** (110 mg, 55%).

$^1$H NMR (500 MHz, HFB, $CDCl_3$): δ = 9.06 (s, 12 H, Ar), 3.57 (t, *J* = 7.8 Hz, 12 H, $CH_2$), 2.59–2.63 (m, 24 H, $CH_2$), 2.30 (quint, *J* = 7.8 Hz, 12 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 2166.36 (100) ([$M^+$], calcd for $C_{90}H_{60}F_{54}$: 2166.38), 1906.34 (20), 1644.28 (10), 1384.27 (5).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 343, 360 ($1.2 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1d)**

As described for **1a** using HPB **15d** (0.1 g, 25 μmol), $FeCl_3$ (366 mg, 2.26 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (10 mL), $MeNO_2$ (8 mL), and HFB (10 mL) gave **1d** (70 mg, 70%).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 9.12 (br s, 12 H, Ar), 3.58 (br s, 12 H, $CH_2$), 2.52 (br s, 24 H, $CH_2$), 2.37 (br s, 12 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3966.22 (100) ([$M^+$], calcd for $C_{126}H_{60}F_{126}$: 3966.27), 3405.01 (43).

UV/VIS (BTF, $10^{-5}$ M): λ (ε) = 364 nm ($4.2 \times 10^4$).

**2,5,8,11,14,17-Hexakis(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1e)**

As described for **1a** using HPB **15e** (0.1 g, 35 μmol), $FeCl_3$ (340 mg, 2.1 mmol, 5.0 equiv/H to be removed), $CH_2Cl_2$ (20 mL), and $MeNO_2$ (8 mL) gave **1e** (60 mg, 60%).

$^1$H NMR (360 MHz, HFB, $CDCl_3$): δ = 8.99 (br s, 12 H, Ar), 3.55 (br s, 12 H, $CH_2$), 2.50 (br s, 24 H, $CH_2$), 2.15 (br s, 24 H).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 2850.44 (100) ([$M^+$], calcd for $C_{108}H_{72}F_{78}$: 2850.44), 2476.40 (50), 2101.36 (15), 1725.33 (10).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 346, 360 ($2.8 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1f)**

As described for **1a** using HPB **15f** (0.2 g, 56 μmol), $FeCl_3$ (820 mg, 5.0 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (15 mL), $MeNO_2$ (12 mL), and HFB (15 mL) gave **1f** (130 mg, 65%).

$^1$H NMR (360 MHz, HFB, $CDCl_3$): δ = 8.83 (br s, 12 H, Ar), 3.48 (br s, 12 H, $CH_2$), 2.46 (br s, 24 H, $CH_2$), 2.10 (br s, 36 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3534.55 (100) ([$M^+$], calcd for $C_{126}H_{84}F_{102}$: 3534.49), 3046.68 (24).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 346, 360 ($2.5 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis(9,9,10,10,11,11,12,12,12-nonafluorododecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1g)**

As described for **1a** using HPB **15g** (1.0 g, 0.4 mmol), $FeCl_3$ (5.8 g, 36 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (80 mL), and $MeNO_2$ (20 mL) gave **1g** (0.46 g, 46%).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 2502.1 (100) ([$M^+$], calcd for $C_{114}H_{108}F_{54}$: 2502.76), 2536.1 (25) [M – H + Cl]$^+$, 2570.0 (16) [M – 2 H + 2 Cl]$^+$, 2604.0 (5) [M – 3 H + 3 Cl]$^+$, 2637.9 (2) [M – 4 H + 4 Cl]$^+$.

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 323, 372 ($5.2 \times 10^5$), 451 nm.

**2,5,8,11,14,17-Hexakis(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1h)**

As described for **1a** using HPB **15h** (0.1 g, 32 μmol), $FeCl_3$ (468 mg, 2.9 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (18 mL), and $MeNO_2$ (4 mL) gave **1h** (64 mg, 64%).

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 3103.4 (35) ([$M^+$], calcd for $C_{126}H_{108}F_{78}$: 3102.72), 1001.6 (100).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 371 nm ($9.2 \times 10^5$).

**2,5,8,11,14,17-Hexakis(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1i)**

As described for **1a** using HPB **15i** (0.2 g, 54 μmol), $FeCl_3$ (523 mg, 3.2 mmol, 5.0 equiv/H to be removed), $CH_2Cl_2$ (30 mL), $MeNO_2$ (12 mL), and HFB (10 mL) gave **1i** (80 mg, 40%).

$^1$H NMR (360 MHz, HFB, $CDCl_3$): δ = 9.00 (br s, 12 H, Ar), 3.51 (br s, 12 H, $CH_2$), 2.34 (br s, 24 H, $CH_2$), 1.88 (br s, 60 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3702.71 (100) ([$M^+$], calcd for $C_{138}H_{108}F_{102}$: 3702.68), 3186.87 (17), 2656.42 (12), 2139.37 (8).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 345, 360 ($1.5 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (1j)**

As described for **1a** using HPB **15j** (0.1 g, 28 μmol), $FeCl_3$ (423 mg, 2.6 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (10 mL), $MeNO_2$ (8 mL), and HFB (10 mL) gave **1j** (54 mg, 54%).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 9.06 (br s, 12 H, Ar), 3.60 (br s, 12 H, $CH_2$), 2.65 (br s, 24 H, $CH_2$), 2.20 (br s, 24 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3450.50 (100) ([$M^+$], calcd for $C_{120}H_{78}F_{102}$: 3450.40), 2976.34 (10).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 345, 360 ($1.9 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis[6,6,7,7,8,8,9,9,9-nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)nonyl]hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (2a)**

As described for **1a** using HPB **29a** (0.2 g, 55 μmol), $FeCl_3$ (800 mg, 4.9 mmol, 7.5 equiv/H to be removed), $CH_2Cl_2$ (10 mL), $MeNO_2$ (8 mL), and HFB (10 mL) gave **2a** (170 mg, 84%).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 9.29 (br s, 12 H, Ar), 3.67 (br s, 12 H, $CH_2$), 2.99 (br s, 6 H, CH), 2.44–2.71 (m, 36 H, $CH_2$), 2.54 (m, 12 H, $CH_2$).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3642.43 (100) ([$M^+$], calcd for $C_{126}H_{78}F_{108}$: 3642.44).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 346, 361 ($2.4 \times 10^5$), 391 nm.

**2,5,8,11,14,17-Hexakis[7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecyl]hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (2b)**

As described for **1a** using HPB **29b** (142 mg, 30 μmol), $FeCl_3$ (413 mg, 2.54 mmol, 7.0 equiv/H to be removed), $CH_2Cl_2$ (15 mL), and $MeNO_2$ (6 mL) gave **2b** (118 mg, 83%).

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 5011.66 (100) ([$M^+$], calcd for $C_{162}H_{102}F_{156}$: 5010.55).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 345, 361 ($3.5 \times 10^5$), 390 nm.

**2,5,8,11,14,17-Hexakis[9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradecyl]hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (2c)**

As described for **1a** using HPB **29c** (55 mg, 10 μmol), $FeCl_3$ (153 mg, 0.94 mmol, 7.8 equiv/H to be removed), $CH_2Cl_2$ (15 mL), and $MeNO_2$ (1.5 mL) gave **2c** (40 mg, 73%).

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 5180.04 (100) ([$M^+$], calcd for $C_{174}H_{126}F_{156}$: 5178.74).

UV/VIS (BTF, $10^{-6}$ M): λ (ε) = 345, 360 ($1.3 \times 10^5$), 390 nm.

**1-Iodo-4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononon-1-enyl)benzene (4a); Typical Procedure**

4-Iodobenzenediazonium tetrafluoroborate (9.7 g, 30.5 mmol), $Pd_2(dba)_3$ (508 mg, 0.56 mmol), and NaOAc (7.9 g, 97.0 mmol) were added to a 2-necked round-bottomed flask equipped with a reflux condenser under an inert atmosphere. Degassed MeCN (100 mL) was added. Compound **3a** (10 g, 27.8 mmol) was degassed in a separate flask and was diluted with MeCN (40 mL) and syringed into the reaction vessel. The inert gas entry was changed against a bubble counter. The mixture was stirred at r.t. for 4 h until the formation of $N_2$ had stopped. All volatiles were removed under reduced pressure yielding a dark brown solid that was dissolved in pentane (400 mL) and filtered through a plug of silica gel (pentane) under reduced pressure. After removing all volatiles, **4a** was recovered as slightly yellow solid which was further purified by column chromatography (pentane). Evaporating all volatiles from the desired fractions yielded **4a** (10.14 g, 59%) as a white solid; $R_f$ = 0.66 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.2 Hz, 2 H, Ar), 7.12 (d, *J* = 8.2 Hz, 2 H, Ar), 6.55 (d, *J* = 15.4 Hz, 1 H, CH), 6.15 (dt, *J* = 15.4, 7.5 Hz, 1 H, CH), 3.00 (dt, *J* = 17.9, 7.5 Hz, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 137.75, 136.22, 135.66, 128.17, 117.00 (t, *J* = 4.6 Hz), 105.70–120.02 (m, $Rf_6$), 93.57, 35.14 (t, *J* = 22.8 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 562.8 (7) [$M^+$], 116.0 (100).

**1-Bromo-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundec-1-enyl)benzene (4b)**

As described for **4a** using **3b** (13.0 g, 28.25 mmol), 4-bromobenzenediazonium tetrafluoroborate (8.4 g, 31.08 mmol), $Pd_2(dba)_3$ (440 mg, 0.42 mmol), NaOAc (8.1 g, 9.89 mmol), and MeCN (140 mL) gave **4b** (16.2 g, 93%); $R_f$ = 0.54 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.2 Hz, 2 H, Ar), 7.25 (d, *J* = 8.2 Hz, 2 H, Ar), 6.56 (d, *J* = 15.4 Hz, 1 H, CH), 6.13 (dt, *J* = 15.4, 7.5 Hz, 1 H, CH), 3.00 (dt, *J* = 17.7, 7.5 Hz, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 136.09, 135.09, 131.78, 127.96, 122.02, 116.89 (t, *J* = 4.3 Hz), 105.70–120.02 (m, $Rf_8$), 35.14 (t, *J* = 22.8 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 615.0 (7) [$M^+$], 535.8 (1), 168.9 (100).

**1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundec-1-enyl)-4-iodobenzene (4c)**

As described for **4a** using **3b** (6.0 g, 13.04 mmol), 4-iodobenzenediazonium tetrafluoroborate (4.14 g, 13.04 mmol), $Pd(OAc)_2$ (58 mg, 0.26 mmol), MeOH (20 mL), and THF (5 mL), NaOAc (8.1 g, 9.89 mmol), and MeCN (140 mL) at 40 °C for 18 h gave **4c** (3.0 g, 35%); $R_f$ = 0.54 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2 H, Ar), 7.12 (d, *J* = 8.4 Hz, 2 H, Ar), 6.55 (d, *J* = 15.4 Hz, 1 H, CH), 6.15 (dt, *J* = 15.4, 7.5 Hz, 1 H, CH), 3.00 (dt, *J* = 17.7, 7.5 Hz, 2 H, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 137.76, 136.22, 135.67, 128.17, 117.03 (t, *J* = 4.3 Hz), 105.70–120.02 (m, $Rf_8$), 93.56, 35.16 (t, *J* = 22.8 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 663.1 (7) [M$^+$], 535.8 (1), 115.7 (100).

**1-Iodo-4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)benzene (5a); Typical Procedure**

Iodoaryl **4a** (6.4 g, 11.4 mmol) was dissolved in $CH_2Cl_2$ (15 mL) and added to a 200-mL autoclave. After the addition of pentane (50 mL), argon was bubbled through the mixture for 10 min before Rh/C (5% Rh, 929 mg, 0.456 mmol) was added. The autoclave was then tightly closed and purged with $H_2$ (3 × 50 bar). The mixture was then stirred at r.t. under $H_2$ (60 bar) for 28 h. The suspension was filtered through a plug of silica gel (pentane); removal of all volatiles gave **5a** (6.3 g, 98%) as a white solid; $R_f$ = 0.66 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.2 Hz, 2 H, Ar), 6.96 (d, *J* = 8.2 Hz, 2 H, Ar), 2.67 (t, *J* = 7.5 Hz, 2 H, $CH_2$), 2.00–2.18 (m, 2 H, $CH_2$), 1.93 (quint, *J* = 7.5 Hz, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.20, 137.65, 130.40, 107.69–121.51 (m, $Rf_6$), 91.41, 34.49, 30.20 (t, *J* = 22.5 Hz), 21.66 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 564.8 (42) [M$^+$], 437.5 (1), 217.0 (100).

**1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-4-iodobenzene (5b); Typical Procedure**

Ni (6.2 g, 10.6 mmol), KI (7.0 g, 42.2 mmol), and $I_2$ (268 mg, 1.1 mmol) were charged into a Schlenk reaction vessel and suspended in DMF (30 mL) under an inert atmosphere. Compound **6a** (13.0 g, 21.0 mmol) was degassed in a separate flask, diluted with DMF (30 mL) and added to the mixture which was then heated to 150 °C for 27 h. The dark brown mixture was, after cooling to r.t., decanted off from the nickel residue. The crude product was extracted with pentane (3 × 100 mL) and the combined organic fractions were washed with $H_2O$ (100 mL), 3% HCl (50 mL), and $H_2O$ (100 mL), and dried ($Na_2SO_4$). Removal of all volatiles gave **5b** as a yellow crystalline solid. Purification was completed by filtration through a plug of silica gel (pentane) under reduced pressure to give **5b** (13.7 g, 99%) as a white crystalline solid; $R_f$ = 0.54 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 2 H, Ar), 6.94 (d, *J* = 8.2 Hz, 2 H, Ar), 2.65 (t, *J* = 7.5 Hz, 2 H, $CH_2$), 1.95–2.14 (m, 2 H, $CH_2$), 1.91 (quint, *J* = 7.5 Hz, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.22, 137.66, 130.40, 107.74–120.13 (m, $Rf_8$), 91.41, 34.51, 30.21 (t, *J* = 22.5 Hz), 21.68 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 665.1 (15) [M$^+$], 537.8 (1), 217.0 (100).

**1-Iodo-4-(5,5,6,6,7,7,8,8,8-nonafluorooctyl)benzene (5c)**

As described for **5b** using **9a** (5.5 g, 12.75 mmol), Ni (3.74 g, 63.78 mmol), KI (4.23 g, 25.51 mmol), $I_2$ (160 mg, 0.63 mmol), and DMF (35 mL) gave **5c** (4.71 g, 77%); $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.2 Hz, 2 H, Ar), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 2.59 (t, *J* = 7.3 Hz, 2 H, $CH_2$), 1.99–2.16 (m, 2 H, $CH_2$), 1.62–1.67 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.24, 137.47, 130.44, 108.55–122.20 (m, $Rf_4$), 90.98, 35.03, 30.58 (t, *J* = 22.5 Hz), 30.06, 19.72 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 478.6 (45) [M$^+$], 217.0 (100).

**1-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Henicosafluorotetradecyl)-4-iodobenzene (5d)**

As described for **5b** using **9b** (6.0 g, 8.2 mmol), Ni (2.4 g, 41.0 mmol), KI (2.7 g, 16.4 mmol), $I_2$ (104 mg, 0.4 mmol), and DMF (25 mL) gave **5d** (4.8 g, 75%); $R_f$ = 0.90 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.2 Hz, 2 H, Ar), 6.92 (d, *J* = 8.2 Hz, 2 H, Ar), 2.59 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.01–2.16 (m, 2 H, $CH_2$), 1.64–1.75 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.26, 137.50, 130.44, 107.79–121.91 (m, $Rf_{10}$), 90.98, 35.05, 30.67, 30.67 (t, *J* = 21.8 Hz), 19.77 (t, *J* = 3.5 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 777.9 (95) [M$^+$], 216.9 (100).

**1-Bromo-4-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundecyl)benzene (5e)**

As described for **5a** using alkyne **12a** (4.8 g, 8.9 mmol), Rh/C (300 mg), pentane (45 mL), and $CH_2Cl_2$ (15 mL) gave **5e** (4.61 g, 95%); $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.2 Hz, 2 H, Ar), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 2.58 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.97–2.11 (m, 2 H, $CH_2$), 1.60–1.68 (m, 4 H, $CH_2$), 1.36–1.43 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.06, 131.39, 130.12, 119.53, 105.33–118.80 (m, $Rf_6$), 35.01, 30.86, 30.79 (t, *J* = 22.5 Hz), 28.54, 19.99 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 544.9 (8) [M$^+$], 168.9 (100), 91.0 (27).

**1-Bromo-4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl)benzene (5f)**

As described for **5a** using alkyne **12b** (2.0 g, 3.1 mmol), Rh/C (100 mg), pentane (18 mL), and $CH_2Cl_2$ (6 mL) gave **5f** (2.0 g, 99%); $R_f$ = 0.65 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 2 H, Ar), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 2.56 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.96–2.11 (m, 2 H, $CH_2$), 1.56–1.65 (m, 4 H, $CH_2$), 1.34–1.42 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.39, 131.32, 130.12, 119.40, 107.69–118.71 (m, $Rf_8$), 35.19, 30.99, 30.83 (t, *J* = 22.5 Hz), 28.92, 28.72, 20.03 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 659.3 (6) [M$^+$], 168.9 (100), 91.0 (24).

**1-Bromo-4-(9,9,10,10,11,11,12,12,12-nonafluorododecyl)benzene (5g)**

As described for **5a** using alkyne **12c** (2.4 g, 4.96 mmol), Rh/C (150 mg), pentane (18 mL), and $CH_2Cl_2$ (6 mL) gave **5g** (2.34 g, 97%); $R_f$ = 0.91 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 2 H, Ar), 7.05 (d, *J* = 8.2 Hz, 2 H, Ar), 2.56 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.97–2.12 (m, 2 H, $CH_2$), 1.54–1.60 (m, 4 H, $CH_2$), 1.28–1.39 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.67, 131.26, 130.15, 119.29, 105.35–120.77 (m, $Rf_4$), 35.29, 31.26, 30.75 (t, *J* = 22.5 Hz), 29.02, 29.98, 29.15, 29.17, 20.03 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 488.7 (13) [M$^+$], 168.9 (100), 91.0 (41).

**1-Iodo-4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyl)benzene (5h)**

As described for **5b** using **13a** (2.1 g, 3.6 mmol), Ni (1.05 g, 17.9 mmol), KI (1.2 g, 7.15 mmol), $I_2$ (45 mg, 0.18 mmol), and DMF (15 mL) gave **5h** (2.0 g, 88%); $R_f$ = 0.90 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.2 Hz, 2 H, Ar), 6.92 (d, *J* = 8.2 Hz, 2 H, Ar), 2.54 (t, *J* = 7.3 Hz, 2 H, $CH_2$), 1.96–2.11 (m, 2 H, $CH_2$), 1.54–1.60 (m, 4 H, $CH_2$), 1.28–1.39 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 142.78, 137.67, 130.94, 90.94, 105.79–119.70 (m, $Rf_6$), 35.79, 31.60, 31.26 (t, *J* = 22.5 Hz), 29.45, 29.47, 29.50, 29.52, 20.47 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 635.2 (16) [M$^+$], 217.0 (100), 90.9 (29).

**1-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecyl)-4-iodobenzene (5i)**

As described for **5b** using **13b** (4.1 g, 5.9 mmol), Ni (1.75 g, 29.8 mmol), KI (2.0 g, 11.9 mmol), $I_2$ (76 mg, 0.30 mmol), and DMF (20 mL) gave **5i** (3.96 g, 90%); $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.2 Hz, 2 H, Ar), 6.92 (d, *J* = 8.2 Hz, 2 H, Ar), 2.54 (t, *J* = 7.3 Hz, 2 H, $CH_2$), 1.96–2.09 (m, 2 H, $CH_2$), 1.54–1.59 (m, 4 H, $CH_2$), 1.28–1.39 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 142.78, 137.67, 130.94, 105.79–119.70 (m, $Rf_8$), 90.94, 35.79, 31.61, 31.26 (t, *J* = 22.5 Hz), 29.45–29.52 (4C), 20.47 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 735.4 (8) [M$^+$], 217.0 (100), 91.0 (24).

**1-Bromo-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)benzene (6a)**

As described for **5a** using alkene **4b** (14.0 g, 23.0 mmol), Rh/C (702 mg), pentane (60 mL), and $CH_2Cl_2$ (20 mL) gave (13.9 g, 98%); $R_f$ = 0.54 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 2 H, Ar), 7.06 (d, *J* = 8.2 Hz, 2 H, Ar), 2.67 (t, *J* = 7.5 Hz, 2 H, $CH_2$), 2.0–2.14 (m, 2 H, $CH_2$), 1.92 (quint, *J* = 7.5 Hz, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 139.55, 131.68, 130.06, 120.13, 107.78–122.29 (m, $Rf_8$), 34.41, 30.21 (t, *J* = 22.5 Hz), 21.71 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 617.0 (15) [M$^+$], 537.8 (1), 170.8 (100).

**1-Bromo-4-(5,5,6,6,7,7,8,8,8-nonafluoro-3-iodooctyl)benzene (8a)**

1-Bromo-4-but-3-enylbenzene (**7**, 17 g, 80.53 mmol) was added to a round-bottomed flask and heated to 50 °C; 30% aq $Na_2S_2O_5$ soln (7.6 mL) and perfluorobutyl iodide (27 g, 78.45 mmol) were added. Under a positive stream of argon AIBN (230 mg, 1.39 mmol) was added and the mixture was heated to 80 °C for 2 h. The mixture was allowed to reach r.t. and then $H_2O$ (50 mL) was added. The obtained suspension was extracted with $Et_2O$ (3 × 100 mL). The combined organic phases were washed with $H_2O$ (50 mL) and dried ($Na_2SO_4$) and all volatiles were removed under reduced pressure to give **8a** (31.1 g, 71%) as a colorless oil; $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.6 Hz, 2 H, Ar), 7.09 (d, *J* = 8.6 Hz, 2 H, Ar), 4.23 (tt, *J* = 8.2, 5.0 Hz, 1 H, CH), 2.67–3.02 (m, 2 H, $CH_2$), 2.66 (t, *J* = 8.2 Hz, 2 H, $CH_2$), 2.02–2.16 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 138.76, 131.68, 130.22, 120.21, 108.40–122.40 (m, $Rf_4$), 41.57 (t, *J* = 22.5 Hz), 41.38, 35.12, 19.65 (t, *J* = 2.5 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 556.7 (8) [M$^+$], 429.5 (12), 168.9 (100).

**1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluoro-3-iodo-tetradecyl)benzene (8b)**

As described for **8a** using **7** (4.45 g, 21.1 mmol), perfluorodecyl iodide (15.0 g, 23.2 mmol), AIBN (70 mg, 0.42 mmol), and 30% $Na_2S_2O_5$ (5 mL) gave **8b** (17.7 g, 98%); $R_f$ = 0.91 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 2 H, Ar), 7.09 (d, *J* = 8.2 Hz, 2 H, Ar), 4.23 (tt, *J* = 8.6, 5.0 Hz, 1 H, CH), 2.65–3.04 (m, 2 H, $CH_2$), 2.65–2.73 (m, 2 H, $CH_2$), 2.05–2.12 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 138.78, 131.70, 130.24, 120.21, 108.37–121.10 (m, $Rf_{10}$), 41.71 (t, *J* = 21.1 Hz), 41.42, 35.14, 19.74.

MS (EI, 70 eV): *m*/*z* (%) = 857.5 (1) [M$^+$], 730.3 (4), 168.9 (100).

**1-Bromo-4-(5,5,6,6,7,7,8,8,8-nonafluorooctyl)benzene (9a); Typical Procedure**

$LiAlH_4$ (1.8 g, 47.4 mmol) was placed in a 500-mL 3-necked flask under inert atmosphere and THF (60 mL) was added by syringe. Compound **8a** (22 g, 39.5 mmol) was dissolved in THF (40 mL) and was carefully added to the $LiAlH_4$ slurry in such a rate to maintain the reaction medium at a gentle reflux. After 6 h at r.t. the mixture was quenched by the addition of $H_2O$ (5 mL), 15% NaOH (5 mL), and $H_2O$ (15 mL). The crude reaction product was extracted with $Et_2O$ (3 × 200 mL). The combined organic phases were filtered through a Büchner and the filtrate was washed with $H_2O$ (50 mL) and dried ($Na_2SO_4$) and all volatiles were removed under reduced pressure yielding **9a** (13.6 g, 80%) as a colorless oil; $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.6 Hz, 2 H, Ar), 7.04 (d, *J* = 8.6 Hz, 2 H, Ar), 2.58 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.00–2.13 (m, 2 H, $CH_2$), 1.58–1.69 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.53, 131.46, 130.05, 119.7, 107.19–121.07 (m, $Rf_4$), 35.11, 30.64, 30.54 (t, *J* = 22.5 Hz), 19.69 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 430.5 (12) [M$^+$], 168.9 (100).

**1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecyl)benzene (9b)**

As described for **9a** using aryl **8b** (18.0 g, 21.0 mmol), $LiAlH_4$ (797 mg, 21 mmol), and THF (50 mL) gave **9b** (6.2 g, 40%); $R_f$ = 0.80 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.2 Hz, 2 H, Ar), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 2.61 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.00–2.17 (m, 2 H, $CH_2$), 1.63–1.76 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.54, 131.48, 130.08, 119.72, 107.77–121.88 (m, $Rf_{10}$), 34.94, 30.69, 30.69 (t, *J* = 21.1 Hz), 19.75 (t, *J* = 4.0 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 731.8 (80) [M$^+$], 170.9 (100).

**6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundec-1-yne (11a); Typical Procedure**

Lithium acetylide–ethylenediamine complex (18.2 g, 0.20 mol) was suspended in DMSO (90 mL) in a round-bottomed flask under an inert atmosphere. To the brown-colored suspension 9-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononane (**10a**, 29 g, 65.7 mmol) dissolved in pentane (10 mL) was added at 8 °C. The black suspension was stirred at r.t. for 17 h and the mixture was quenched by the addition of $H_2O$ (30 mL). The resulting suspension was diluted with $CH_2Cl_2$ (100 mL), Büchner filtered, and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic phases were dried ($Na_2SO_4$) and all volatiles were removed under reduced pressure. The resulting black oily liquid was filtered over a plug of silica gel under reduced pressure (pentane). After removal of pentane the title compound (9.64 g, 38%) was obtained as colorless oil; $R_f$ = 0.95 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.33 (td, *J* = 6.8, 2.7 Hz, 2 H, $CH_2$), 2.16–2.28 (m, 2 H, $CH_2$), 2.02 (t, *J* = 2.7 Hz, 1 H, CH), 1.78–1.89 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108.10–121.18 (m, $Rf_6$), 82.27, 79.72, 29.83 (t, *J* = 22.5 Hz), 19.34 (t, *J* = 3.3 Hz), 17.91.

MS (EI, 70 eV): *m*/*z* (%) = 117.0 (15), 66.9 (100).

**7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluorotetradec-1-yne (11b)**

As described for **11a** using 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorododecane (**10b**, 15.0 g, 25.2 mmol), lithium acetylide–ethylenediamine complex (7.0 g, 75.6 mmol), DMSO (30 mL), and pentane (15 mL) gave **11b** (4.94 g, 39%); $R_f$ = 0.90 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.25 (td, *J* = 6.8, 2.7 Hz, 2 H, $CH_2$), 2.02–2.17 (m, 2 H, $CH_2$), 1.98 (t, *J* = 2.7 Hz, 1 H, CH), 1.71–1.80 (m, 2 H, $CH_2$), 1.59–1.67 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 107.43–121.94 (m, $Rf_8$), 83.27, 68.94, 30.44 (t, *J* = 22.5 Hz), 27.76, 19.34 (t, *J* = 3.3 Hz), 18.13.

MS (EI, 70 eV): *m*/*z* (%) = 500.8 (2) [M$^+$], 131.0 (42), 81.0 (100).

**9,9,10,10,11,11,12,12,12-Nonafluorododec-1-yne (11c)**

As described for **11a** using 10-bromo-1,1,1,2,2,3,3,4,4-nonafluorodecane (**10c**, 24.0 g, 62.6 mmol), lithium acetylide–ethylenediamine complex (17.3 g, 0.19 mol), DMSO (100 mL), and pentane (10 mL) gave **11c** (12.8 g, 62%); $R_f$ = 0.99 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.21 (td, *J* = 7.0, 2.7 Hz, 2 H, $CH_2$), 2.01–2.15 (m, 2 H, $CH_2$), 1.95 (t, *J* = 2.7 Hz, 1 H, CH), 1.59–1.67 (m, 2 H, $CH_2$), 1.52–1.59 (m, 2 H, Hz, $CH_2$), 1.39–1.52 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 106.03–123.20 (m, $Rf_4$), 84.27, 68.32, 30.71 (t, *J* = 22.5 Hz), 28.56, 28.24, 28.11, 19.97 (t, *J* = 3.3 Hz), 18.27.

MS (EI, 70 eV): *m*/*z* (%) = 95.0 (25), 81.4 (100), 67.0 (76).

**9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluorotetradec-1-yne (11d)**

As described for **11a** using 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorododecane (**10d**, 12.0 g, 24.8 mmol), lithium acetylide–ethylenediamine complex (16.9 g, 0.18 mol), DMSO (30 mL), and pentane (20 mL) gave **11d** (7.72 g, 73%); $R_f$ = 0.84 (silica gel, pentane, $KMnO_4$).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.21 (td, *J* = 7.0, 2.7 Hz, 2 H, $CH_2$), 2.00–2.15 (m, 2 H, $CH_2$), 1.96 (t, *J* = 2.7 Hz, 1 H, CH), 1.59–1.67 (m, 2 H, $CH_2$), 1.52–1.59 (m, 2 H, $CH_2$), 1.39–1.52 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 103.61–121.66 (m, $Rf_6$), 84.30, 68.34, 30.81 (t, *J* = 22.5 Hz), 28.56, 28.24, 28.11, 20.00 (t, *J* = 3.3 Hz), 18.28.

MS (EI, 70 eV): *m*/*z* (%) = 95.1 (33), 81.1 (100), 67.1 (36).

**9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadec-1-yne (11e)**

As described for **11a** using 14-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorotetradecane (**10e**, 14.1 g, 24.2 mmol), lithium acetylide ethylenediamine complex (6.7 g, 72.6 mmol), DMSO (40 mL), and pentane (30 mL) gave (5.6 g, 44%); $R_f$ = 0.80 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.21 (td, *J* = 7.0, 2.7 Hz, 2 H, $CH_2$), 2.00–2.15 (m, 2 H, $CH_2$), 1.95 (t, *J* = 2.7 Hz, 1 H, CH), 1.59–1.67 (m, 2 H, $CH_2$), 1.52–1.59 (m, 2 H, $CH_2$), 1.40–1.52 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 107.80–118.72 (m, $Rf_8$), 84.30, 68.34, 30.82 (t, *J* = 22.5 Hz), 28.56, 28.24, 28.11, 20.00 (t, *J* = 3.3 Hz), 18.28.

MS (EI, 70 eV): *m*/*z* (%) = 131.0 (43), 81.0 (100), 67.0 (30).

**1-Bromo-4-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundec-1-ynyl)benzene (12a); Typical Procedure**

$Pd(PPh_3)_4$ (1.65 g, 1.43 mmol), CuI (453 mg, 2.38 mmol), and 1-bromo-4-iodobenzene (6.74 g, 23.8 mmol) were dissolved in THF (110 mL) in a Schlenk reaction vessel under an inert atmosphere. Compound **11a** (9.2 g, 23.8 mmol) was degassed in a separate flask, diluted with THF (20 mL), and added into the Schlenk flask, and then $Et_3N$ (20.0 mL, 143 mmol) was added by syringe. The Schlenk tube was sealed and heated to 80 °C for 6 d. The cold mixture was then quenched by the addition of $H_2O$ (100 mL) and extracted with $Et_2O$ (3 × 100 mL). The combined organic fractions were washed with 10% HCl (150 mL) and $H_2O$ (100 mL) and dried ($Na_2SO_4$) and all volatiles were removed yielding a brown oil. Several filtrations through silica gel (pentane–$Et_2O$, 9:1 then pentane for successive filtrations) yielded **12a** (4.91 g, 38%) as a colorless oil; $R_f$ = 0.78 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.2 Hz, 2 H, Ar), 7.25 (d, *J* = 8.2 Hz, 2 H, Ar), 2.53 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.20–2.34 (m, 2 H, $CH_2$), 1.88–1.96 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 133.01, 131.51, 122.35, 122.06, 107.70–118.79 (m, $Rf_6$), 89.06, 81.00, 30.06 (t, *J* = 22.5 Hz), 19.58 (t, *J* = 3.3 Hz), 18.94.

MS (EI, 70 eV): *m*/*z* (%) = 540.9 (32) [M$^+$], 461.7 (8), 223.1 (17), 192.9 (100), 172.0 (45), 142 (63), 128.0 (63).

**1-Bromo-4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradec-1-ynyl)benzene (12b)**

As described for **12a** using alkyne **11b** (4.8 g, 9.6 mmol), $Pd(PPh_3)_4$ (670 mg, 0.57 mmol), CuI (183 mg, 0.96 mmol), 1-bromo-4-iodobenzene (2.7 g, 9.6 mmol), $Et_3N$ (8.0 mL, 57.6 mmol), and THF (50 mL) gave **12b** (2.27 g, 36%); $R_f$ = 0.62 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.2 Hz, 2 H, Ar), 7.24 (d, *J* = 8.2 Hz, 2 H, Ar), 2.46 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.06–2.20 (m, 2 H, $CH_2$), 1.75–1.84 (m, 2 H, $CH_2$), 1.66–1.74 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 132.99, 131.46, 122.65, 121.82, 107.74–119.07 (m, $Rf_8$), 90.16, 80.36, 30.45 (t, *J* = 22.5 Hz), 27.89, 19.50 (t, *J* = 3.3 Hz), 19.13.

MS (EI, 70 eV): *m*/*z* (%) = 655.2 (12) [M$^+$], 576.1 (16), 221.0 (27), 192.9 (90), 142 (100), 128.0 (83).

**1-Bromo-4-(9,9,10,10,11,11,12,12,12-nonafluorododec-1-ynyl)benzene (12c)**

As described for **12a** using alkyne **11c** (10.1 g, 30.7 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), CuI (470 mg, 2.5 mmol), 1-bromo-4-iodobenzene (8.7 g, 30.7 mmol), $Et_3N$ (25.6 mL, 0.18 mol), and THF (120 mL) gave **12c** (11.6 g, 78%); $R_f$ = 0.81 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.2 Hz, 2 H, Ar), 7.26 (d, *J* = 8.2 Hz, 2 H, Ar), 2.42 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.01–2.16 (m, 2 H, $CH_2$), 1.59–1.69 (m, 4 H, $CH_2$), 1.45–1.53 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 132.99, 131.42, 122.90, 121.64, 108.54–121.07 (m, $Rf_4$), 91.23, 79.82, 30.72 (t, *J* = 22.5 Hz), 28.61, 28.45, 28.27, 20.00 (t, *J* = 3.3 Hz), 19.31.

MS (EI, 70 eV): *m*/*z* (%) = 484.7 (9) [M$^+$], 237.1 (8), 223.1 (22), 209.0 (6), 194.9 (65), 181.8 (12), 168.9 (8), 142 (100).

**1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradec-1-ynyl)benzene (12d)**

As described for **12a** using alkyne **11d** (5.5 g, 12.8 mmol), $Pd(PPh_3)_4$ (890 mg, 0.77 mmol), CuI (245 mg, 1.28 mmol), 1-bromo-4-iodobenzene (3.6 g, 12.8 mmol), $Et_3N$ (10.75 mL, 77.0 mmol), and THF (65 mL) gave **12d** (2.63 g, 35%); $R_f$ = 0.86 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.2 Hz, 2 H, Ar), 7.26 (d, *J* = 8.2 Hz, 2 H, Ar), 2.42 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.01–2.16 (m, 2 H, $CH_2$), 1.59–1.70 (m, 4 H, $CH_2$), 1.45–1.55 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 132.99, 131.42, 122.90, 121.64, 107.22–119.17 (m, $Rf_6$), 91.23, 79.83, 30.83 (t, *J* = 22.5 Hz), 28.62, 28.45, 28.29, 20.03 (t, *J* = 3.3 Hz), 19.32.

MS (EI, 70 eV): *m*/*z* (%) = 584.9 (7) [M$^+$], 237.1 (8), 223.1 (35), 209.0 (6), 194.9 (84), 181.8 (12), 168.9 (18), 142 (100).

**1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadec-1-ynyl)benzene (12e)**

As described for **12a** using alkyne **11e** (5.5 g, 10.4 mmol), $Pd(PPh_3)_4$ (720 mg, 0.62 mmol), CuI (198 mg, 1.04 mmol), 1-bromo-4-iodobenzene (2.9 g, 10.4 mmol), $Et_3N$ (8.7 mL, 62.5 mmol), and THF (70 mL) gave **12e** (2.46 g, 35%); $R_f$ = 0.79 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.2 Hz, 2 H, Ar), 7.25 (d, *J* = 8.2 Hz, 2 H, Ar), 2.41 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.00–2.15 (m, 2 H, $CH_2$), 1.59–1.69 (m, 4 H, $CH_2$), 1.45–1.55 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 132.99, 131.42, 122.89, 121.64, 108.17–118.36 (m, $Rf_8$), 91.23, 79.82, 30.82 (t, *J* = 22.5 Hz), 28.62, 28.45, 28.27, 20.03 (t, *J* = 3.3 Hz), 19.31.

MS (EI, 70 eV): *m*/*z* (%) = 685.2 (7) [$M^+$], 237.1 (8), 223.1 (34), 209.0 (9), 194.9 (82), 181.8 (15), 168.9 (18), 142 (100).

**1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyl)benzene (13a)**

As described for **5a** using alkyne **12d** (2.5 g, 4.3 mmol), Rh/C (130 mg), pentane (24 mL), and $CH_2Cl_2$ (7 mL) gave **13a** (2.24 g, 89%); $R_f$ = 0.90 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 2 H, Ar), 7.05 (d, *J* = 8.2 Hz, 2 H, Ar), 2.56 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.98–2.13 (m, 2 H, $CH_2$), 1.56–1.60 (m, 4 H, $CH_2$), 1.27–1.38 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.67, 131.27, 130.15, 119.29, 105.35–120.77 (m, $Rf_6$), 35.30, 31.23, 30.85 (t, *J* = 22.5 Hz, 29.05, 29.08, 29.10, 29.11, 20.07 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 589.7 (9) [$M^+$], 170.9 (100), 90.9 (33).

**1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyl)benzene (13b)**

As described for **5a** using alkyne **12e** (4.5 g, 6.6 mmol), Rh/C (200 mg), pentane (21 mL), and $CH_2Cl_2$ (7 mL) gave **13b** (4.21 g, 93%); $R_f$ = 0.85 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 2 H, Ar), 7.05 (d, *J* = 8.2 Hz, 2 H, Ar), 2.56 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.98–2.13 (m, 2 H, $CH_2$), 1.56–1.60 (m, 4 H, $CH_2$), 1.27–1.39 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 142.08, 131.67, 130.55, 119.70, 106.40–118.86 (m, $Rf_8$), 35.70, 31.64, 31.26 (t, *J* = 22.5 Hz), 29.45, 29.49, 29.53, 29.58, 20.47 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 689.3 (9) [$M^+$], 170.8 (100), 90.9 (33).

**1-(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl)-4-{[4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)phenyl]ethynyl}benzene (14a); Typical Procedure**

CuI (209 mg, 1.1 mmol) and $PdCl_2(PPh_3)_2$ (463 mg, 0.66 mmol) were suspended in THF (10 mL) in an oven dried Schlenk reaction vessel under an inert atmosphere. Iodoaryl **5a** (6.2 g, 11.0 mmol) was dissolved in THF (10 mL) and degassed separately then added into the reaction vessel. Degassed DBU (9.9 mL, 65.9 mmol) was added via syringe into the Schlenk and the reaction medium was purged with argon. $H_2O$ (79 μL, 4.4 mmol) and cooled (4 °C) trimethylsilylacetylene (0.8 mL, 5.5 mmol) were added simultaneously with two syringes. The Schlenk was then covered with aluminum foil and heated to 75 °C. After 29 h, the black mixture was washed with $H_2O$ (2 × 100 mL), 10% HCl (50 mL), brine (50 mL), and $H_2O$ (50 mL). The combined organic fractions were purified by several precipitations ($Et_2O$–pentane–EtOH) to yield **14a** (3.0 g, 61%) as a white solid; $R_f$ = 0.42 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.2 Hz, 4 H, Ar), 7.17 (d, *J* = 8.2 Hz, 4 H, Ar), 2.73 (t, *J* = 7.3 Hz, 4 H, $CH_2$), 1.91–2.17 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.88, 131.81, 128.39, 121.32, 105.69–120.49 (m, $Rf_6$), 89.01, 34.90, 30.23 (t, *J* = 22.5 Hz), 21.63 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 900.0 (11) [$M^+$], 551.9 (100).

**1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-4-{[4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)phenyl]ethynyl}benzene (14b)**

As described for **14a** using iodoaryl **5b** (5.0 g, 7.7 mmol), $PdCl_2(PPh_3)_2$ (530 mg, 0.46 mmol), CuI (146 mg, 0.77 mmol), DBU (6.9 mL, 45.2 mmol), THF (40 mL), $H_2O$ (55 μL, 3.1 mmol), and trimethylsilylacetylene (0.56 mL, 3.8 mmol) gave **14b** (2.71 g, 66%); $R_f$ = 0.90 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.2 Hz, 4 H, Ar), 7.17 (d, *J* = 8.2 Hz, 4 H, Ar), 2.73 (t, *J* = 7.5 Hz, 4 H, $CH_2$), 1.95–2.14 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.87, 131.80, 128.39, 121.30, 107.74–120.13 (m, $Rf_8$), 89.01, 34.89, 30.23 (t, *J* = 22.5 Hz), 21.63 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 1349.27 (80) [M + DCTB]$^+$, 1098.10 (100) [$M^+$].

**1-(5,5,6,6,7,7,8,8,8-Nonafluorooctyl)-4-{[4-(5,5,6,6,7,7,8,8,8-nonafluorooctyl)phenyl]ethynyl}benzene (14c)**

As described for **14a** using iodoaryl **5c** (11.2 g, 26.0 mmol), $PdCl_2(PPh_3)_2$ (1.09 g, 1.56 mmol), CuI (496 mg, 2.6 mmol), DBU (23.3 mL, 156.2 mmol), THF (125 mL), $H_2O$ (190 μL, 10.4 mmol), and trimethylsilylacetylene (1.9 mL, 13.0 mmol) gave **14c** (1.9 g, 20%); $R_f$ = 0.82 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.67 (t, *J* = 7.3 Hz, 4 H, $CH_2$), 2.01–2.17 (m, 4 H, $CH_2$), 1.62–1.76 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.89, 131.64, 128.38, 110.50–125.52 (m, $Rf_4$), 120.94, 88.96, 35.44, 30.62, 30.62 (t, *J* = 22.5 Hz), 19.75 (t, *J* = 3.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 727.5 (20) [$M^+$], 465.7 (100).

**1-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Henicosafluorotetradecyl)-4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecyl)phenyl]ethynyl}benzene (14d)**

As described for **14a** using iodoaryl **5d** (3.25 g, 4.8 mmol), $PdCl_2(PPh_3)_2$ (203 mg, 0.29 mmol), CuI (92 mg, 0.48 mmol), DBU (4.3 mL, 29.0 mmol), THF (40 mL), $H_2O$ (35 μL, 1.9 mmol), and trimethylsilylacetylene (0.35 mL, 2.4 mmol) gave **14d** (2.15 g, 80%); $R_f$ = 0.60 (pentane–$Et_2O$, 1:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.7 Hz, 4 H, Ar), 7.15 (d, *J* = 7.7 Hz, 4 H, Ar), 2.67 (t, *J* = 6.8 Hz, 4 H, $CH_2$), 2.01–2.16 (m, 4 H, $CH_2$), 1.64–1.75 (m, 8 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 141.89, 131.73, 128.37, 121.28, 107.79–121.91 (m, $Rf_{10}$), 89.08, 35.47, 30.97 (t, *J* = 22.1 Hz), 30.59, 19.93.

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 1577.27 (85) [M + DCTB]$^+$, 1326.12 (100) [$M^+$].

**1-(6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundecyl)-4-{[4-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundecyl)phenyl]ethynyl}benzene (14e)**

As described for **14a** using bromoaryl **5e** (4.6 g, 8.4 mmol), $PdCl_2(PPh_3)_2$ (585 mg, 0.5 mmol), CuI (161 mg, 0.84 mmol), DBU (7.6 mL, 50.6 mmol), THF (50 mL), $H_2O$ (60 μL, 3.38 mmol), and trimethylsilylacetylene (0.74 mL, 5.1 mmol) gave **14e** (225 mg, 6%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.2 Hz, 4 H, Ar), 7.08 (d, *J* = 8.2 Hz, 4 H, Ar), 2.57 (t, *J* = 7.3 Hz, 4 H, $CH_2$), 1.90–2.09 (m, 4 H, $CH_2$), 1.56–1.64 (m, 8 H, $CH_2$), 1.30–1.38 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 142.45, 131.56, 128.40, 120.83, 108.10–118.79 (m, $Rf_6$), 88.93, 35.55, 30.79, 30.79 (t, *J* = 22.5 Hz), 28.59, 20.00 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m/z* (%) = 1205.34 (90) [M + DCTB]$^+$, 954.18 (100) [M$^+$].

**1-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluorotetradecyl)-4-{[4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl)phenyl]ethynyl}benzene (14f)**

As described for **14a** using bromoaryl **5f** (3.0 g, 4.6 mmol), $Pd(PPh_3)_4$ (316 mg, 0.27 mmol), CuI (87 mg, 0.46 mmol), DBU (4.08 mL, 27.3 mmol), THF (25 mL), $H_2O$ (32 μL, 27.3 mmol), and trimethylsilylacetylene (0.33 mL, 2.27 mmol) gave **14f** (1.2 g, 46%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.2 Hz, 4 H, Ar), 7.13 (d, *J* = 8.2 Hz, 4 H, Ar), 2.62 (t, *J* = 7.7 Hz, 4 H, $CH_2$), 1.99–2.10 (m, 4 H, $CH_2$), 1.57–1.67 (m, 8 H, $CH_2$), 1.36–1.40 (m, 8 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 142.76, 131.57, 128.40, 120.92, 109.13–121.02 (m, $Rf_8$), 89.00, 35.75, 31.00 (t, *J* = 22.5 Hz), 30.88, 28.99, 28.78, 20.13 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m/z* (%) = 1433.35 (45) [M + DCTB]$^+$, 1182.20 (100) [M$^+$].

**1-(9,9,10,10,11,11,12,12,12-Nonafluorododecyl)-4-{[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyl)phenyl]ethynyl}benzene (14g)**

As described for **14a** using bromoaryl **5g** (11.4 g, 23.4 mmol), $Pd(PPh_3)_4$ (1.62 g, 1.4 mmol), CuI (446 mg, 2.3 mmol), DBU (20.9 mL, 0.14 mol), THF (120 mL), $H_2O$ (150 μL, 9.4 mmol), and trimethylsilylacetylene (1.29 mL, 13.0 mmol) gave **14g** (4.8 g, 50%); $R_f$ = 0.52 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.61 (t, *J* = 7.3 Hz, 4 H, $CH_2$), 1.97–2.12 (m, 4 H, $CH_2$), 1.55–1.63 (m, 8 H, $CH_2$), 1.28–1.39 (m, 16 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 143.06, 131.48, 128.44, 120.65, 105.25–119.03 (m, $Rf_4$), 88.92, 35.85, 31.19, 30.77 (t, *J* = 22.5 Hz), 29.06, 29.11, 29.13, 29.22, 20.06 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m/z* (%) = 1089.44 (100) [M + DCTB]$^+$, 838.29 (63) [M$^+$].

**1-(9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluorotetradecyl)-4-{[4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyl)phenyl]ethynyl}benzene (14h)**

As described for **14a** using iodoaryl **5h** (2.0 g, 3.15 mmol), $Pd(PPh_3)_4$ (219 mg, 0.19 mmol), CuI (60 mg, 0.32 mmol), DBU (2.8 mL, 18.9 mmol), THF (20 mL), $H_2O$ (23 μL, 1.26 mmol), and trimethylsilylacetylene (0.23 mL, 1.57 mmol) gave **14h** (346 mg, 21%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.61 (t, *J* = 7.7 Hz, 4 H, $CH_2$), 1.97–2.12 (m, 4 H, $CH_2$), 1.55–1.61 (m, 8 H, $CH_2$), 1.28–1.39 (m, 16 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 143.45, 131.87, 128.83, 121.05, 104.64–122.38 (m, $Rf_6$), 89.31, 36.25, 31.57, 31.26 (t, *J* = 22.5 Hz), 29.46, 29.48, 29.51, 29.54, 20.47 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m/z* (%) = 1289.43 (100) [M + DCTB]$^+$, 1038.27 (91) [M$^+$].

**1-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecyl)-4-{[4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyl)phenyl]ethynyl}benzene (14i)**

As described for **14a** using iodoaryl **5i** (3.8 g, 5.2 mmol), $Pd(PPh_3)_4$ (360 mg, 0.31 mmol), CuI (98.5 mg, 0.52 mmol), DBU (4.6 mL, 31.05 mmol), THF (30 mL), $H_2O$ (30 μL, 2.07 mmol), and trimethylsilylacetylene (0.38 mL, 2.6 mmol) gave **14i** (680 mg, 21%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.61 (t, *J* = 7.7 Hz, 4 H, $CH_2$), 1.99–2.14 (m, 4 H, $CH_2$), 1.56–1.61 (m, 8 H, $CH_2$), 1.28–1.39 (m, 16 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, CDCl3): δ = 143.05, 131.46, 128.43, 120.64, 105.02–118.85 (m, $Rf_8$), 89.90, 35.84, 31.17, 30.86 (t, *J* = 22.5 Hz), 29.03, 29.05, 29.06, 29.08, 20.07 (t, *J* = 3.3 Hz).

MS (MALDI-ICR, DCTB): *m/z* (%) = 1489.41 (22) [M + DCTB]$^+$, 1238.26 (100) [M]$^+$.

**1-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluorotridecyl)-4-{[4-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyl)phenyl]ethynyl}benzene (14j)**

An oven dried Schlenk reaction vessel was charged with freshly activated Mg turning (87.5 mg, 3.6 mmol) under an inert atmosphere. The Mg was stirred under vacuum for 1 h and heated with a heat gun (3 ×). As soon as the reaction vessel reached r.t. THF (2 mL) was syringed in under argon. 13-Bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorotridecane (1.71 g, 3.0 mmol), dissolved in THF (2 mL) was syringed into the Mg suspension. The sealed Schlenk tube was heated to 75 °C for 12 h. In a second oven-dried Schlenk tube $PdCl_2(dppf)\cdot CH_2Cl_2$ (61.5 mg, 75 μmol) and 1-bromo-4-[(4-bromophenyl)ethynyl]benzene (252 mg, 0.74 mmol) were suspended under an inert atmosphere in THF (6 mL). The previously freshly prepared brownish Grignard soln was diluted with THF (3 mL) and added by syringe. The Schlenk tube was sealed and heated to 75 °C for 7 d and then the mixture was quenched by the addition of MeOH (20 mL). The formed precipitate was Büchner filtered and washed with MeOH and pentane. The obtained solid was dissolved in $CH_2Cl_2$ (50 mL) and was washed with $H_2O$ (3 × 50 mL). Removal of all volatiles of the organic fraction and precipitation ($Et_2O$–pentane) gave **14j** (720 mg, 83%); $R_f$ = 0.77 ($CH_2Cl_2$–cyclohexane, 3:7).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.64 (t, *J* = 7.7 Hz, 4 H, $CH_2$), 1.97–2.13 (m, 4 H, $CH_2$), 1.61–1.71 (m, 8 H, $CH_2$), 1.37–1.46 (m, 4 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 142.44, 131.54, 128.40, 120.80, 107.21–121.24 (m, $Rf_8$), 88.91, 35.53, 30.78 (t, *J* = 22.1 Hz), 30.78, 28.58, 19.99.

MS (EI, 70 eV): *m/z* (%) = 1154.14 (10) [M$^+$], 679.08 (100), 204.07 (70).

**Hexakis[4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)phenyl]benzene (15a); Typical Procedure**

A two necked round bottomed flask was charged with tolane **14a** (2.8 g, 3.1 mmol) under an inert atmosphere. Addition of deoxygenated dioxane (180 mL) followed by $Co_2(CO)_8$ (64 mg, 0.19 mmol) under a positive pressure of argon, afforded a dark brown soln which was refluxed for 60 h. Removal of the solvent under reduced pressure yielded the crude target compound as a grey solid, which was dissolved in pentane and agitated in an ultrasonic bath for 2 h. Collection of the solid by suction filtration over Millipore® afforded **15a** (2.4 g, 86%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.70 (d, *J* = 7.7 Hz, 12 H, Ar), 6.63 (d, *J* = 7.7 Hz, 12 H, Ar), 2.43 (t, *J* = 6.8 Hz, 12 H, $CH_2$), 1.71–1.83 (m, 24 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.10, 138.75, 137.11, 131.65, 126.53, 104.19–120.29 (m, $Rf_6$), 34.13, 29.71 (t, $J$ = 22.5 Hz), 21.45.

MS (MALDI-ICR, DCTB): $m/z$ (%) = 2695.34 (100) [M$^+$].

**Hexakis[4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)phenyl]benzene (15b)**
As described for **15a** using tolane **14b** (0.5 g, 0.45 mmol), $Co_2(CO)_8$ (12.4 mg, 36.4 µmol), dioxane (50 mL), and HFB (10mL) gave **15b** (0.42 g, 84%); $R_f$ = 0.43 (pentane–$Et_2O$, 1:1).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.74 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.66 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.45 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.81–1.91 (m, 12 H, $CH_2$), 1.70–1.77 (m, 12 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 140.30, 138.99, 137.32, 131.83, 126.65, 105.32–120.11 (m, $Rf_8$), 34.32, 30.14 (t, $J$ = 22.1 Hz), 21.63.

MS (MALDI-ICR, DCTB): $m/z$ (%) = 3294.22 (100) [M$^+$], 2858.20 (10).

**Hexakis[4-(5,5,6,6,7,7,8,8,8-nonafluorooctyl)phenyl]benzene (15c)**
As described for **15a** using tolane **14c** (1.8 g, 2.48 mmol), $Co_2(CO)_8$ (51.0 mg, 0.15 mmol), and dioxane (150 mL) gave **15c** (1.7 g, 95%); $R_f$ = 0.92 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.68 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.62 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.39 (t, $J$ = 6.8 Hz, 12 H, $CH_2$), 1.90–2.03 (m, 12 H, $CH_2$), 1.35–1.55 (m, 24 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.19, 138.52, 137.85, 131.58, 126.44, 105.63–121.06 (m, $Rf_4$), 34.61, 30.45 (t, $J$ = 22.5 Hz), 30.35, 18.94.

MS (MALDI-ICR, DCTB): $m/z$ (%) = 2179.48 (100) [M$^+$].

**Hexakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecyl)phenyl]benzene (15d)**
As described for **15a** using tolane **14d** (0.2 g, 0.15 mmol), $Co_2(CO)_8$ (4.1 mg, 12.0 µmol), dioxane (10 mL), and HFB (10mL) gave **15d** (164 mg, 85%); $R_f$ = 0.85 (BTF).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.66 (br d, $J$ = 8.2 Hz, 12 H, Ar), 6.60 (br d, $J$ = 8.2 Hz, 12 H, Ar), 2.33 (t, $J$ = 6.8 Hz, 12 H, $CH_2$), 1.97–2.08 (m, 12 H, $CH_2$), 1.54–1.60 (m, 12 H, $CH_2$), 1.36–1.42 (m, 12 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 140.33, 138.89, 138.44, 131.48, 126.43, 108.68–120.94 (m, $Rf_{10}$), 35.32, 31.12, 30.83 (t, $J$ = 22.0 Hz), 20.17.

MS (MALDI-ICR, DCTB): $m/z$ (%) = 3978.41 (100) [M$^+$].

**Hexakis[4-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundecyl)phenyl]benzene (15e)**
As described for **15a** using tolane **14e** (0.3 g, 0.31 mmol), $Co_2(CO)_8$ (8.6 mg, 25.0 µmol), and dioxane (20 mL) gave **15e** (238 mg, 79%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.68 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.61 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.36 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.90–2.04 (m, 12 H, $CH_2$), 1.47–1.55 (m, 12 H, $CH_2$), 1.41–1.45 (m, 12 H, $CH_2$), 1.17–1.21 (m, 12 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.20, 138.43, 138.39, 131.45, 126.42, 110.39–118.72 (m, $Rf_6$), 34.94, 30.79, 30.79 (t, $J$ = 22.5 Hz), 28.07, 19.87 (t, $J$ = 3.3 Hz).

MS (MALDI-ICR, DCTB): $m/z$ (%) = 2862.51 (100) [M$^+$].

**Hexakis[4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecyl)phenyl]benzene (15f)**
As described for **15a** using tolane **14f** (1.0 g, 0.85 mmol), $Co_2(CO)_8$ (17.4 mg, 51.0 µmol), and dioxane (75 mL) gave **15f** (0.64 g, 64%); $R_f$ = 0.98 (pentane–$Et_2O$, 9:1).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.67 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.60 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.34 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.95–2.06 (m, 12 H, $CH_2$), 1.49–1.56 (m, 12 H, $CH_2$), 1.38–1.45 (m, 12 H, $CH_2$), 1.27–1.33 (m, 12 H, $CH_2$), 1.11–1.17 (m, 12 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 140.31, 138.67, 138.48, 131.50, 126.43, 108.71–120.53 (m, $Rf_8$), 35.12, 30.98 (t, $J$ = 22.5 Hz), 30.85, 29.01, 28.34, 20.14 (t, $J$ = 3.3 Hz).

MS (MALDI-ICR, DCTB): $m/z$ (%) = 3546.64 (100) [M$^+$].

**Hexakis[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyl)phenyl]benzene (15g)**
As described for **15a** using tolane **14g** (2.5 g, 2.98 mmol), $Co_2(CO)_8$ (61 mg, 0.18 mmol), and dioxane (120 mL) gave **15g** (1.82 g, 73%); $R_f$ = 0.97 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.67 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.61 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.34 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.95–2.10 (m, 12 H, $CH_2$), 1.50–1.61 (m, 24 H, $CH_2$), 1.25–1.39 (m, 48 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.27, 138.85, 138.33, 131.42, 126.43, 107.63–122.18 (m, $Rf_4$), 35.29, 31.13, 30.77 (t, $J$ = 22.5 Hz, $CH_2$), 28.70. 28.93, 29.13, 29.24, 20.07 (t, $J$ = 3.3 Hz).

MS (MALDI-ICR, DCTB): $m/z$ (%) = 2514.85 (100) [M$^+$].

**Hexakis[4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyl)phenyl]benzene (15h)**
As described for **15a** using tolane **14h** (0.3 g, 0.29 mmol), $Co_2(CO)_8$ (5.9 mg, 17.0 µmol), and dioxane (25 mL) gave **15h** (275 mg, 92%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.67 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.61 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.34 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.95–2.10 (m, 12 H, $CH_2$), 1.50–1.61 (m, 24 H, $CH_2$), 1.21–1.41 (m, 48 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.27, 138.86, 138.33, 131.42, 126.44, 105.03–119.65 (m, $Rf_6$), 35.31, 31.15, 30.77 (t, $J$ = 22.5 Hz), 28.70, 28.95, 29.15, 29.27, 20.10 (t, $J$ = 3.3 Hz).

MS (MALDI-ICR, DCTB): $m/z$ (%) = 3114.82 (100) [M$^+$].

**Hexakis[4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyl)phenyl]benzene (15i)**
As described for **15a** using tolane **14i** (659 mg, 0.53 mmol), $Co_2(CO)_8$ (10.8 mg, 31.6 µmol), and dioxane (50 mL) gave **15i** (329 mg, 51%); $R_f$ = 0.95 (pentane–$Et_2O$, 9:1).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.66 (d, $J$ = 8.2 Hz, 12 H, Ar), 6.60 (d, $J$ = 8.2 Hz, 12 H, Ar), 2.33 (t, $J$ = 7.3 Hz, 12 H, $CH_2$), 1.97–2.08 (m, 12 H, $CH_2$), 1.54–1.60 (m, 12 H, $CH_2$), 1.35–1.42 (m, 12 H, $CH_2$), 1.30–1.35 (m, 12 H, $CH_2$), 1.09–1.28 (m, 36 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 140.33, 138.89, 138.44, 131.48, 126.43, 108.68–120.94 (m, $Rf_8$), 35.32, 31.12, 31.01 (t, $J$ = 22.5 Hz), 28.72, 28.96, 29.17, 29.24, 20.17 (t, $J$ = 3.3 Hz).

MS (MALDI-ICR, DCTB): $m/z$ (%) = 3714.72 (100) [M$^+$].

**Hexakis[4-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyl)phenyl]benzene (15j)**
As described for **15a** using tolane **14j** (231 mg, 0.20 mmol), $Co_2(CO)_8$ (10.7 mg, 31.2 µmol), and dioxane (75 mL) gave **15j** (191 g, 83%); $R_f$ = 0.95 (pentane–$Et_2O$, 5:1).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.69 (d, *J* = 8.2 Hz, 12 H, Ar), 6.61 (d, *J* = 8.2 Hz, 12 H, Ar), 2.36 (t, *J* = 7.3 Hz, 12 H, $CH_2$), 1.88–2.04 (m, 12 H, $CH_2$), 1.47–1.55 (m, 12 H, $CH_2$), 1.36–1.45 (m, 12 H, $CH_2$), 1.14–1.21 (m, 12 H, $CH_2$).

$^{13}$C NMR (125.77 MHz, $CDCl_3$): δ = 140.29, 138.55, 138.45, 131.54, 126.43, 108.67–120.49 (m, $Rf_8$), 34.97, 30.92 (t, *J* = 22.1 Hz), 30.78, 28.13, 19.96.

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3462.41 (100) [M$^+$], 2973.41 (10).

**1,1,1,2,2,3,3,4,4,5,5,6,6,12,12,13,13,14,14,15,15,16,16,17,17,17-Hexacosafluoroheptadecan-9-ol (18)**

To a stirred soln of the Grignard reagent prepared from 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (50 g, 102 mmol) and Mg (3.7 g, 152 mmol) in anhyd $Et_2O$ (150 mL) under argon at 25 °C was added dropwise a soln of ethyl formate (3.1 g, 42 mmol) in anhyd $Et_2O$ (6 mL). The mixture was stirred at r.t. overnight. It was then quenched by a slow addition of $H_2O$ (100 mL), extracted with $Et_2O$ (3 × 50 mL), washed with sat. NaCl (50 mL), dried ($Na_2SO_4$), and evaporated. The product was purified by filtration (silica gel, pentane). Elution with $Et_2O$ and evaporation of the solvent afforded the title compound (30.6 g, 81%); $R_f$ = 0.65 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 3.75 (m, 1 H, CH), 2.04–2.45 (m, 4 H, $CH_2$), 1.68–1.90 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108–122 (m, $Rf_6$), 69.62, 28.02, 27.22 (t, *J* = 22 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 707.7 (1), 377.3 (100), 357.3 (82).

**1,1,1,2,2,3,3,4,4,8,8,9,9,10,10,11,11,11-Octadecafluoro-6-iodoundecane (19a)**

As described for **8a** using 4,4,5,5,6,6,7,7,7-nonafluorohept-1-ene (**20**, 5.5 g, 21.14 mmol), perfluorobutyl iodide (7.67 g, 22.18 mmol), AIBN (170 mg, 1.05 mmol), and 30% aq $Na_2S_2O_5$ soln (3.5 mL) gave **19a** (6.36 mg, 49%); $R_f$ = 0.95 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 4.52 (quint, *J* = 6.8 Hz, 1 H, CH), 2.89–3.02 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 106.21–119.36 (m, $Rf_4$), 41.97 (t, *J* = 21.1 Hz), 0.00.

MS (EI, 70 eV): *m*/*z* (%) = 606.4 (5) [M$^+$], 479.4 (30), 459.4 (41), 245.2 (69), 195.1 (95), 69.0 (100).

**1,1,1,2,2,3,3,4,4,5,5,6,6,12,12,13,13,14,14,15,15,16,16,17,17,17-Hexacosafluoro-9-iodoheptadecane (19b)**

To a flask containing a stirring mixture of DDQ (3.76 g, 16.6 mmol), $Ph_3P$ (4.35 g, 16.6 mmol), and TBAI (6.1 g, 16.6 mmol) in $CH_2Cl_2$ (140 mL), **18** (10.0 g, 13.8 mmol) was added at r.t. and the mixture was stirred for 2 h. The yellow color of the mixture changed to red. The concentrated residue was filtered (silica gel, pentane) and evaporated to afford **19b** (10.6 g, 90%); $R_f$ = 0.92 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 4.04 (m, 1 H, CH), 2.06–2.6 (m, 4 H, $CH_2$), 2.06–2.3 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108–122 (m, $Rf_6$), 32.61, 31.58, 31.58 (t, *J* = 22 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 707.7 (46), 687.7 (20), 437.4 (24), 327.3 (100).

**6,6,7,7,8,8,9,9,9-Nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)non-1-ene (21a); Typical Procedure**

An oven-dried Schlenk tube was charged with Pd(dppf)$Cl_2$·$CH_2Cl_2$ (250 mg, 0.30 mmol) under an inert atmosphere. Compound **19a** (6.3 g, 10.4 mmol) was separately deoxygenated, diluted with THF (16 mL), and added by syringe to the Schlenk tube. The mixture was then cooled to 0 °C in an ice/NaCl bath. Allylmagnesium bromide (1 M in $Et_2O$; 14.6 mL, 14.6 mmol) was added slowly by syringe (2 h), yielding a yellow soln. The ice bath was removed after the addition was completed and the mixture (green) was stirred at r.t. for 16 h and quenched with MeOH (8 mL). All volatiles were removed under reduced pressure yielding a brown suspension that was filtered through a silica gel plug (pentane) under reduced pressure to give **21a** (3.86 g, 71%); $R_f$ = 0.95 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 5.72 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1 H, CH), 5.19 (d, *J* = 17.0 Hz, 1 H, $CH_2$), 5.14 (d, *J* = 10.0 Hz, 1 H, $CH_2$), 2.54 (sept, *J* = 6.8 Hz, 1 H, CH), 2.33 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.12–2.27 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 133.5, 119.40, 108.86–118.89 (m, $Rf_4$), 38.78, 33.53 (t, *J* = 21.1 Hz), 24.91.

MS (EI, 70 eV): *m*/*z* (%) = 520.5 (7) [M$^+$], 287.3 (100).

**7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodec-1-ene (21b)**

As described for **21a** using allyl **19b** (9.5 g, 11.4 mmol), Pd(dppf)$Cl_2$·$CH_2Cl_2$ (372 mg, 0.5 mmol), allylmagnesium bromide (1 M in $Et_2O$; 17.1 mL, 17.1 mmol), and THF (30 mL) gave **21b** (7.1 g, 84%); $R_f$ = 0.93 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 5.73 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1 H, CH), 5.11 (dd, *J* = 10.0, 1.4 Hz, 1 H, CH), 5.09 (dd, *J* = 16.8, 1.4 Hz, 1 H, CH), 2.10 (m, 6 H, $CH_2$), 1.61 (m, 5 H, $CH_2$, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 134.94, 108–122 (m, $Rf_6$), 117.79, 37.23, 36.29, 28.27 (t, *J* = 22 Hz), 23.33.

MS (EI, 70 eV): *m*/*z* (%) = 748.7 (2) [M$^+$], 720.7 (6), 706.6 (12), 401.4 (72), 387.3 (100).

**1-Bromo-4-[6,6,7,7,8,8,9,9,9-nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)non-1-enyl]benzene (22a); Typical Procedure**

As described for **4a** using **21a** (0.52 g, 1.0 mmol), 4-bromobenzenediazonium tetrafluoroborate (0.3 g, 1.1 mmol), $Pd_2(dba)_3$ (15.5 mg, 15 μmol), NaOAc (287 mg, 3.5 mmol), and MeCN (5 mL) gave **22a** (200 mg, 31%); $R_f$ = 0.71 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.2 Hz, 2 H, Ar), 7.22 (d, *J* = 8.2 Hz, 2 H, Ar), 6.42 (d, *J* = 15.8 Hz, 1 H, CH), 6.06 (dt, *J* = 15.8, 7.3 Hz, 1 H, CH), 2.63 (sept, *J* = 6.4 Hz, 1 H, CH), 2.48 (t, *J* = 7.3 Hz, 2 H, $CH_2$), 2.18–2.30 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 135.63, 133.31, 131.75, 127.70, 125.65, 121.45, 109.82–120.05 (m, $Rf_4$), 37.95, 33.69 (t, *J* = 21.1 Hz), 25.46.

MS (EI, 70 eV): *m*/*z* (%) = 674.6 (2) [M$^+$], 197.1 (30), 116.0 (100).

**1-Bromo-4-[7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodec-1-enyl]benzene (22b)**

As described for **22a** using **21b** (5.0 g, 6.7 mmol), 4-bromobenzenediazonium tetrafluoroborate (2.0 g, 7.4 mmol), $Pd_2(dba)_3$ (104 mg, 0.1 mmol), NaOAc (1.92 g, 23.5 mmol), and MeCN (40 mL) gave **22b** (3.8 g, 63%); $R_f$ = 0.78 (pentane).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.5 Hz, 2 H, Ar), 7.20 (d, *J* = 8.5 Hz, 2 H, Ar), 6.38 (d, *J* = 15.8 Hz, 1 H, CH), 6.11 (dt, *J* = 15.8, 7.4 Hz, 1 H, CH), 2.25 (m, 2 H, $CH_2$), 2.10 (m, 4 H, $CH_2$), 1.66 (m, 5 H, $CH_2$, CH).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 136.00, 131.76, 131.69, 127.58, 127.30, 121.26, 108–122 (m, $Rf_6$), 36.65, 36.37, 28.16 (t, *J* = 20.8 Hz), 23.35.

MS (EI, 70 eV): *m*/*z* (%) = 903.7 (74) [M$^+$], 805.0 (30), 475.5 (100).

**1-Bromo-4-[6,6,7,7,8,8,9,9,9-nonafluoro-4-(2,2,3,3,4,4,5,5,6,6,6-nonafluoropentyl)nonyl]benzene (23a)**

As described for **5a** using alkene **22a** (1.75 g, 2.6 mmol), Rh/C (100 mg), pentane (20 mL), and $CH_2Cl_2$ (10 mL) gave **23a** (1.75 g, 98%); $R_f$ = 0.81 (pentane).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.2 Hz, 2 H, Ar), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 2.59 (t, *J* = 7.0 Hz, 2 H, $CH_2$), 2.44 (sept, *J* = 5.9 Hz, 1 H, CH), 2.09–2.24 (m, 4 H, $CH_2$), 1.58–1.66 (m, 4 H, $CH_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 140.48, 131.50, 130.05, 119.78, 108.52–121.21 (m, $Rf_4$), 35.01, 34.24, 34.13 (t, *J* = 21.1 Hz), 27.76, 25.34.

MS (EI, 70 eV): *m*/*z* (%) = 676.6 (6) [M$^+$], 171.0 (100).

**1-Bromo-4-[7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecyl]benzene (23b)**

As described for **5a** using alkene **22b** (2.26 g, 2.5 mmol), Rh/C (250 mg), pentane (25 mL), and $CH_2Cl_2$ (25 mL) gave **23b** (1.75 g, 77%); $R_f$ = 0.87 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.5 Hz, 2 H, Ar), 7.05 (d, *J* = 8.5 Hz, 2 H, Ar), 2.58 (t, *J* = 7.5 Hz, 2 H, $CH_2$), 2.01 (m, 4 H, $CH_2$), 1.60 (m, 7 H, $CH_2$, CH), 1.32 (m, 2 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.95, 131.62, 130.21, 119.84, 108–122, 36.29, 35.45, 32.08, 28.12 (t, *J* = 21.1 Hz), 27.90, 23.24.

MS (EI, 70 eV): *m*/*z* (%) = 906.0 (100) [M$^+$], 826 (4), 373.3 (32).

**1-Bromo-4-[9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradecyl]benzene (23c)**

As described for **5a** using alkyne **27** (463 mg, 0.5 mmol), Rh/C (42 mg), pentane (5 mL), and $CH_2Cl_2$ (5 mL) gave **23c** (400 mg, 86%); $R_f$ = 0.79 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.6 Hz, 2 H, Ar), 7.04 (d, *J* = 8.6 Hz, 2 H, Ar), 2.56 (t, *J* = 7.3 Hz, 2 H, $CH_2$), 2.04 (m, 4 H, $CH_2$), 1.53–1.66 (m, 7 H, $CH_2$, CH), 1.30 (m, 6 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.61, 131.84, 130.29, 118.96, 108–122, 36.44, 35.41, 32.76, 31.34, 29.47, 28.18 (t, *J* = 21.1 Hz), 26.27, 23.30.

MS (EI, 70 eV): *m*/*z* (%) = 854.7 (12), 687.4 (10), 327.4 (100).

**7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecan-1-ol (24)**

To a 2-necked flask under argon with a stirred suspension of $AlCl_3$ (4.17 g, 31.2 mmol) in $Et_2O$ (12 mL) was added $LiAlH_4$ (0.4 g, 10.4 mmol) at 0 °C. After 15 min, $PhB(OH)_2$ (63 mg, 0.52 mmol), and **21b** (7.8 g, 10.4 mmol) were added. The resulting mixture was allowed to warm to r.t. and stirred at this temperature and then the inert gas protection was removed. Stirring was continued overnight under air. The mixture was quenched with 1 M HCl (10 mL), extracted with $Et_2O$ (3 × 25 mL), dried ($Na_2SO_4$), and concentrated. The product was purified by filtration (silica gel, pentane then $Et_2O$). Evaporation afforded **24** (3.73 g, 47%); $R_f$ = 0.72 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 3.67 (t, *J* = 6.1 Hz, 2 H, $CH_2$), 2.06 (m, 6 H, $CH_2$), 1.3–1.7 (m, 7 H, $CH_2$, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108–122 (m, $Rf_6$), 69.89, 36.30, 29.39, 28.91, 28.15 (t, *J* = 22 Hz), 23.33.

MS (EI, 70 eV): *m*/*z* (%) = 720.9 (10), 401.4 (100), 357.3 (82).

**9-(3-Bromopropyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,12,12,13,13,14,14,15,15,16,16,17,17,17-hexacosafluoroheptadecane (25)**

As described for **19b** using alcohol **24** (3.43 g, 4.48 mmol), DDQ (1.22 g, 5.38 mmol), $Ph_3P$ (1.41 g, 5.38 mmol), TBAB (1.74 g, 5.38 mmol), and $CH_2Cl_2$ (50 mL) gave **25** (3.13 g, 84%); $R_f$ = 0.87 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 3.42 (m, 2 H, $CH_2$), 2.08 (m, 4 H, $CH_2$), 1.87 (m, 2 H, $CH_2$), 1.4–1.8 (m, 7 H, $CH_2$, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108–122 (m, $Rf_6$), 35.88, 33.57, 31.16, 29.38, 28.12 (t, *J* = 22 Hz), 23.30.

MS (EI, 70 eV): *m*/*z* (%) = 749.9 (2), 481.4 (12), 401.5 (100).

**9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradec-1-yne (26)**

As described for **11a** using bromide **25** (3.0 g, 3.62 mmol), lithium acetylide–ethylenediamine complex (1.11 g, 10.85 mmol), DMSO (10 mL), and pentane (4 mL) gave **26** (1.67 g, 60%); $R_f$ = 0.84 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 2.22 (dt, *J* = 6.8, 2.3 Hz, 2 H, $CH_2$), 2.0–2.14 (m, 4 H, $CH_2$), 1.96 (t, *J* = 2.3 Hz, 1 H, CH), 1.77 (dt, *J* = 6.3, 2.3 Hz, 2 H, $CH_2$), 1.4–1.67 (m, 7 H, $CH_2$, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 108–122 (m, $Rf_6$), 83.89, 68.97, 36.02, 31.51, 28.15 (t, *J* = 22 Hz), 24.99, 23.31, 18.61.

MS (EI, 70 eV): *m*/*z* (%) = 441.5 (8), 427.5 (100).

**1-Bromo-4-[9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradec-1-ynyl]benzene (27)**

As described for **12a** using alkyne **26** (1.34 g, 1.74 mmol), $PdCl_2(PPh_3)_2$ (66 mg, 0.09 mmol), CuI (31 mg, 0.16 mmol), 1-bromo-4-iodobenzene (442 mg, 1.56 mmol), $Et_3N$ (12.0 mL, 86.4 mmol), and BTF (12 mL) gave **27** (463 mg, 30%); $R_f$ = 0.56 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.6 Hz, 2 H, Ar), 7.25 (d, *J* = 8.6 Hz, 2 H, Ar), 2.42 (t, *J* = 6.8 Hz, 2 H, $CH_2$), 2.08 (m, 4 H, $CH_2$), 1.48–1.64 (m, 9 H, $CH_2$, CH).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 133.08, 131.61, 122.75, 121.98, 108–122 (m, $Rf_6$), 90.71, 80.41, 36.09, 31.79, 28.18 (t, *J* = 20.8 Hz), 25.27, 23.33, 19.66.

MS (EI, 70 eV): *m*/*z* (%) = 760.0 (4), 581.6 (100), 516.6 (20).

**1-[6,6,7,7,8,8,9,9,9-Nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl) nonyl]-4-({4-[6,6,7,7,8,8,9,9,9-nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)nonyl]phenyl}ethynyl)benzene (28a)**

As described for **14a** using bromoaryl **23a** (1.0 g, 1.48 mmol), $Pd(PPh_3)_4$ (103 mg, 89 μmol), CuI (28 mg, 0.15 mmol), DBU (1.32 mL, 8.9 mmol), THF (10 mL), $H_2O$ (10 μL, 0.59 mmol), and trimethylsilylacetylene (0.11 mL, 0.74 mmol) gave **28a** (530 mg, 59%); $R_f$ = 0.15 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.2 Hz, 4 H, Ar), 7.15 (d, *J* = 8.2 Hz, 4 H, Ar), 2.65 (t, *J* = 7.1 Hz, 4 H, $CH_2$), 2.45 (sept, *J* = 6.0 Hz, 2 H, CH), 2.05–2.26 (m, 8 H, $CH_2$), 1.61–1.69 (m, 8 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 141.83, 131.66, 128.34, 121.06, 108.10–120.69 (m, $Rf_6$), 88.95, 35.52, 34.31, 34.16 (t, *J* = 21.1 Hz), 27.66, 25.37.

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 1469.33 (99) [M + DCTB]$^+$, 1218.18 (100) [M$^+$].

**1-[7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecyl]-4-({4-[7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecyl]phenyl}ethynyl)benzene (28b)**

As described for **14a** using bromoaryl **23b** (0.5 g, 0.52 mmol), $Pd(PPh_3)_4$ (36.4 mg, 30 µmol), CuI 9.9 mg, 50 µmol), DBU (0.48 mL, 3.12 mmol), THF (5 mL), $H_2O$ (3.7 µL, 0.21 mmol), and trimethylsilylacetylene (37.7 µL, 0.26 mmol) gave **28b** (410 mg, 94%); $R_f$ = 0.12 (pentane).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 4 H, Ar), 7.14 (d, *J* = 8.5 Hz, 4 H, Ar), 2.63 (t, *J* = 7.5 Hz, 4 H, $CH_2$), 2.01 (m, 8 H, $CH_2$), 1.60 (m, 14 H, $CH_2$, CH), 1.32 (m, 4 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 142.27, 131.76, 128.49, 108.13–122.98 (m, $Rf_6$), 121.15, 89.03, 36.29, 35.94, 32.06, 28.13 (t, *J* = 22.1 Hz), 27.76, 23.27.

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 1673.81 (100) [M$^+$].

**1-[9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradecyl]-4-({4-[9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradecyl]phenyl}ethynyl)benzene (28c)**

As described for **14a** using bromoaryl **23c** (289 mg, 0.31 mmol), $Pd(PPh_3)_4$ (22 mg, 20 µmol), CuI 6.0 mg, 30 µmol), DBU (0.28 mL, 1.86 mmol), THF (5 mL), $H_2O$ (3.0 µL, 0.12 mmol), and trimethylsilylacetylene (21.7 µL, 0.15 mmol) gave **28c** (203 mg, 76%); $R_f$ = 0.12 (pentane).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.2 Hz, 4 H, Ar), 7.14 (d, *J* = 8.2 Hz, 4 H, Ar), 2.62 (t, *J* = 7.6 Hz, 4 H, $CH_2$), 2.04 (m, 8 H, $CH_2$), 1.58 (m, 14 H, $CH_2$, CH), 1.31 (m, 12 H, $CH_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 142.65, 131.65, 128.57, 120.90, 108.05–120.83 (m, $Rf_6$), 89.06, 36.44, 35.93, 32.78, 31.23, 29.47, 28.22 (t, *J* = 21.1 Hz), 26.28, 23.35.

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 1729.98 (100) [M$^+$].

**Hexakis{4-[6,6,7,7,8,8,9,9,9-nonafluoro-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)nonyl]phenyl}benzene (29a)**

As described for **15a** using tolane **28a** (0.5 g, 0.41 mmol), $Co_2(CO)_8$ (11.2 mg, 33.0 µmol), and dioxane (50 mL) gave **29a** (0.42 g, 84%); $R_f$ = 0.21 (pentane–$Et_2O$, 99:1).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.70 (d, *J* = 8.2 Hz, 12 H, Ar), 6.61 (d, *J* = 8.2 Hz, 12 H, Ar), 2.34–2.36 (m, 18 H, CH and $CH_2$), 2.01–2.20 (m, 24 H, $CH_2$), 1.35–1.45 (m, 24 H, $CH_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 140.18, 138.60, 137.81, 131.57, 126.33, 106.14–120.41 (m, $Rf_4$), 34.74, 34.05 (t, *J* = 21.1 Hz), 33.81, 27.36, 25.15.

MS (MALDI-ICR, DCTB): *m*/*z* (%) = 3655.50 (100) [M$^+$].

**Hexakis{4-[7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)dodecyl]phenyl}benzene (29b)**

As described for **15a** using tolane **28b** (345 mg, 0.21 mmol), $Co_2(CO)_8$ (6 mg, 20.0 µmol), and dioxane (40 mL) gave **29b** (159 mg, 46%).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 6.71 (d, *J* = 8.3 Hz, 12 H, Ar), 6.61 (d, *J* = 8.3 Hz, 12 H, Ar), 2.35 (t, *J* = 7.1 Hz, 12 H, $CH_2$), 1.99 (m, 24 H, $CH_2$), 1.52 (m, 24 H, $CH_2$), 1.42 (m, 18 H, $CH_2$, CH), 1.13 (m, 12 H, $CH_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 140.48, 138.92, 138.40, 131.80, 126.48, 108.56–122.29 (m, $Rf_6$), 36.38, 35.38, 32.23, 28.38 (t, *J* = 22 Hz), 27.83, 23.48.

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 5023.98 (5) [M$^+$], 975.25 (100).

**Hexakis{4-[9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)tetradecyl]phenyl}benzene (29c)**

As described for **15a** using tolane **28c** (190 mg, 0.11 mmol), $Co_2(CO)_8$ (10 mg, 30.0 µmol), and dioxane (25 mL) gave **29c** (140 mg, 74%).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 6.66 (d, *J* = 8.2 Hz, 12 H, Ar), 6.59 (d, *J* = 8.2 Hz, 12 H, Ar), 2.34 (t, *J* = 7.3 Hz, 12 H, $CH_2$), 2.02 (m, 24 H, $CH_2$), 1.56 (m, 24 H, $CH_2$), 1.42 (m, 18 H, $CH_2$, CH), 1.10–1.32 (m, 36 H, $CH_2$).

$^{13}$C NMR (90.55 MHz, $CDCl_3$): δ = 140.35, 138.73, 138.53, 131.58, 126.52, 108.34–22.67 (m, $Rf_6$), 36.43, 35.33, 32.84, 31.16, 28.99, 28.08 (t, *J* = 21.1 Hz), 26.16, 23.22.

MS (MALDI-TOF, DCTB): *m*/*z* (%) = 5192.29 (100) [M$^+$], 3492.82 (8), 1731.95 (17).

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