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Synthesis and photophysical properties of tetra- and pentaalkynylfluorobenzenes by Sonogashira reactions of novel iodofluorobenzenes

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ABSTRACT

1,2-Difluoro-3,4,5,6-tetraiodobenzene, 1,3-difluoro-2,4,5,6-tetraiodobenzene, 1,4-difluoro-2,3,5,6-tetraiodobenzene and 1-fluoro-2,3,4,5,6-pentaiodobenzene were prepared by oxidative iodination of fluorinated benzenes. Sonogashira cross-coupling reactions of these fluorinated periodobenzenes afforded fluorescent penta- and tetraalkynylfluorobenzenes in high yields.

1. Introduction

Polyalkynylated carbon rich molecules are of considerable importance as liquid crystals,[1] non-linear optical materials,[2] light-emitting materials[3] and building blocks for two-dimensional carbon networks.[1a,4] Light emitting materials have been applied in biological and material sciences, such as FET (field effect transistors), OLED (organic light emitting devices), photovoltaic cells and 3D-optical memory devices.[5] Extended π-systems of alkynes often give rise to extraordinary electronic and optical changes of the molecule.[6] In this context, star-shaped π-conjugated molecules with C_6 and C_3 symmetries have attracted considerable attention.[7] D_{6h}-symmetric hexaethynylbenzenes and related compounds have been used as core structures for dendritic materials,[8] and functional dyes.[9] Recently, hexaethynylbenzene derivatives have also been employed as building blocks for supramolecular architectures[10] and potential nonlinear optical materials for two-photon absorption (TPA) and third-order optical nonlinearity.[3,11] Functionalized hexa(arylethynyl)-benzenes have been synthesized by different synthetic approaches.[12] Hexaalkynylbenzenes of C_{2v} symmetry have been prepared by Diels–Alder reaction of tetraalkynylcyclopentadienones with alkynes.[13] A method for the synthesis of hexaalkynylbenzenes of D_{3h} symmetry was developed by Rubin.[14] Recently, Anthony et al. reported the synthesis of a D_{2h} symmetric hexaalkynylbenzene from tetrabromo-benzoquinone.[15] Vollhardt et al. reported the synthesis of hexaalkynylbenzenes and their application to the synthesis of archimedanes.[16]

The fluorine atom has a strong electronic influence on aromatic compounds. Despite the importance of fluorinated arenes in medicinal chemistry and material sciences,[17,18] peralkynylated fluorobenzenes have, to the best of our knowledge, not been reported so far. Herein, we report the synthesis of four novel hexahalobenzenes, i.e., 1,2-difluoro-3,4,5,6-tetraiodo-benzene, 1,3-difluoro-2,4,5,6-tetraiodobenzene, 1,4-difluoro-2,3,5,6-tetraiodobenzene and 1-fluoro-2,3,4,5,6-pentaiodobenzene. Despite their structural simplicity, only fluoropentaiodobenzene has been previously reported and fully characterized. Although all four compounds represent very interesting synthetic building blocks, their chemistry has, to the best of our knowledge, not been studied so far. Herein, we report Sonogashira reactions of these molecules, which allow for a convenient synthesis of hitherto unknown fluorescent tetra- and pentaalkynylfluorobenzenes.

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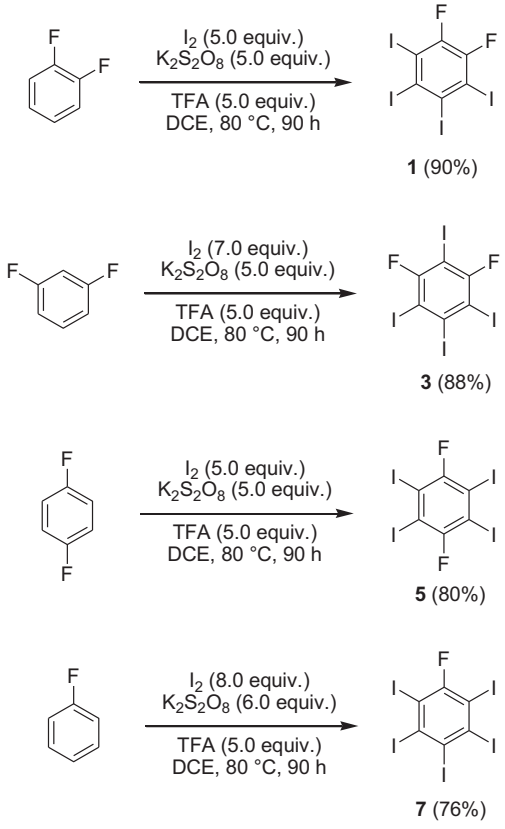
2. Results and discussion

1,2-Difluoro-3,4,5,6-tetraiodobenzene (**1**), 1,3-difluoro-2,4,5,6-tetraiodobenzene (**3**), 1,4-difluoro-2,3,5,6-tetraiodobenzene (**5**) and 1-fluoro-2,3,4,5,6-pentaiodobenzene (**7**) were prepared in very good yields by potassium persulfate mediated periodination of 1,2-difluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene and fluorobenzene, respectively (Scheme 1). The reactions were carried out using the method recently developed by Rahman et al.[19] The synthesis and characterization of **7** has been previously reported.[19] The synthesis of **5** was mentioned in a patent,[20] however, spectroscopic data were not enclosed. The synthesis of **1** and **3** has, to the best of our knowledge, not yet been reported. We have fully characterized all four derivatives and were also able to grow single crystals and to obtain X-ray crystal structure analyses for all molecules (Figs. 1–4).



Scheme 1. Synthesis of fluoroiodobenzenes **1**, **3**, **5** and **7**.

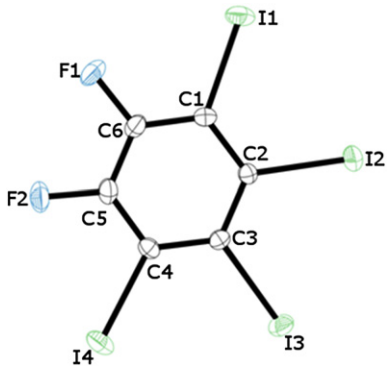


Fig. 1. The molecular structure of **1** in the crystal.

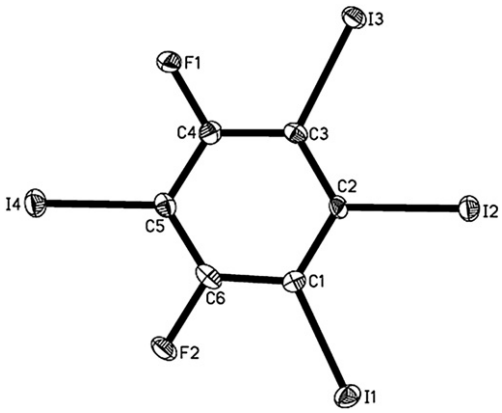


Fig. 2. The molecular structure of **3** in the crystal.

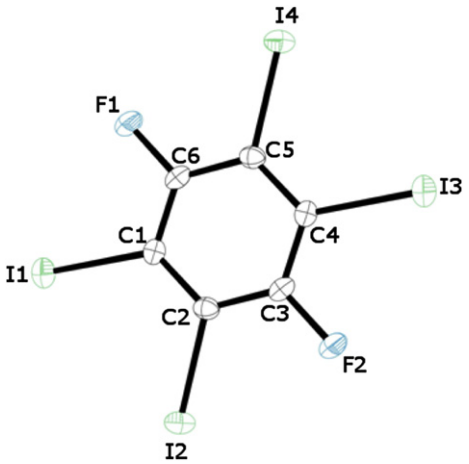


Fig. 3. The molecular structure of **5** in the crystal.

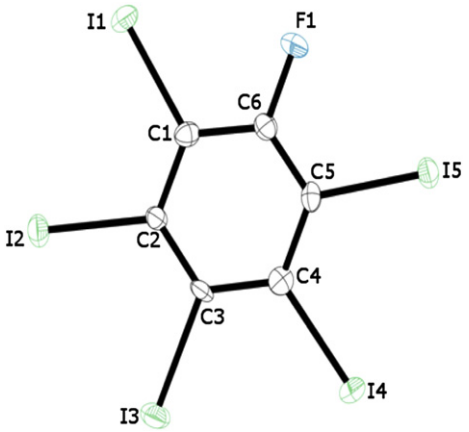
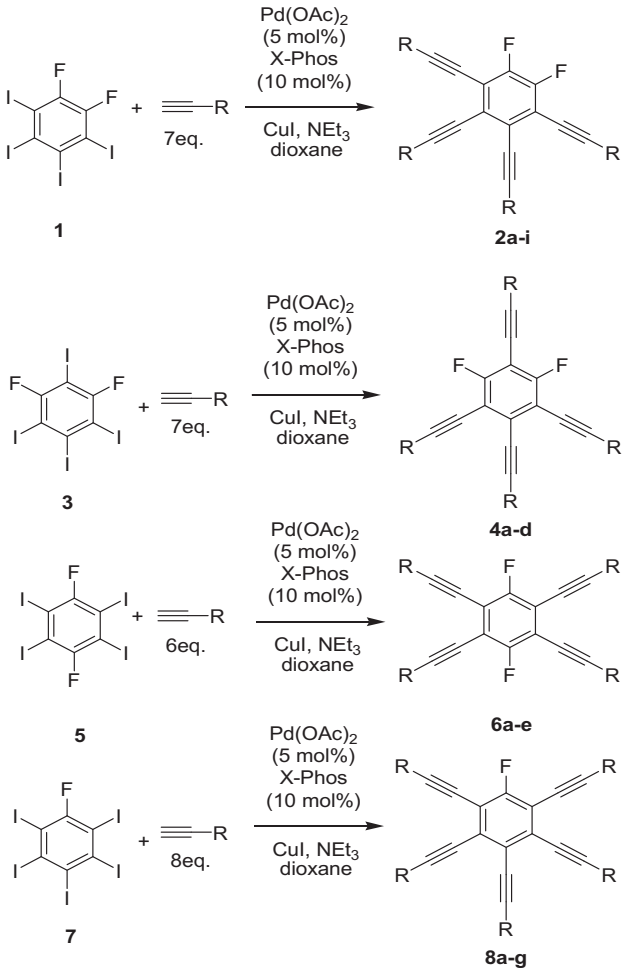


Fig. 4. The molecular structure of **7** in the crystal.

The ^{13}C NMR data reveal interesting structural properties. On the one hand, the iodo substituent has a strong anisotropic effect and results in a strong upfield shift of the signal of the carbon atom attached to the iodine atom. On the other hand, fluorine has a strong negative inductive effect and a strong downfield shift is generally observed for the signal of carbon atoms neighbouring to fluorine.

Due to the π-donating effect of fluorine, an upfield shift is observed for carbon atoms located *ortho* to a fluorine atom. In case of **1**, a significant upfield shift was observed for carbon atoms C3 and C6 (97.3 ppm), due to the anisotropic effect of the iodo substituent and the π-donating effect of the fluoro substituent in *ortho* position. For comparison, the signals of carbon atoms C4 and C5 located *meta* to the fluoro substituent appears at 115.3 ppm. Carbon atoms C1 and C2 resonate at 150.5 ppm. An upfield shift is observed with regard to products **3** and **5** (vide infra), due to the neighbourhood of the second fluoro substituent. The signal of carbon C2 of **3** is dramatically shifted upfield (70.7), due the neighbourhood of two fluoro substituents located in *ortho* position. For comparison, carbon atoms C4 and C6 (located *ortho* to one fluoro substituent) resonate at 91.6 ppm and carbon C5 appears at 124.2 ppm. Carbon atoms C2, C3, C4 and C5 of **5** are all located *ortho* to one fluoro substituent and the signal appears at 98.0 ppm. Carbon atoms C2/C6 of 1-fluoro-2,3,4,5,6-pentaiodobenzene resonate at 96.6 ppm, due to their location *ortho* to one fluoro substituent. Carbon atoms C3/5 appear at 117.8 ppm, while C4 is observed at 124.1 ppm. The discussion shows the strong influence and the additive character of the π-donating effect of the fluoro substituent on the electron distribution of the benzene ring.

The Sonogashira coupling of **1** with 7 equiv of phenylacetylene afforded 3,4,5,6-tetraalkynyl-1,2-difluorobenzene (**2a**) in up to 78% yield (Scheme 2). During the optimization (Table 1), the use of sterically demanding ligands, such as X-Phos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) or HP(^{t}Bu)$_3$BF$_4$, proved to be important.



Scheme 2. Synthesis of peralkynylated fluorobenzenes **2a**–**i**, **4a**–**d**, **6a**–**e** and **8a**–**g**.

Table 1
Optimization of the synthesis of **2a**

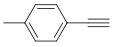
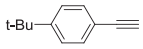
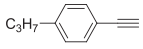
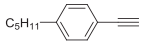
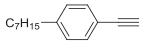
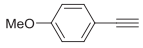
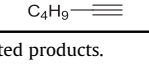
	Catalyst	Base	T [°C]	CuI [mol]	*t* [h]	Yield[a] [%]
1	$Pd(PPh_3)_4$ (5 mol %)	$HN(^iPr)_2$	20	5	20	Traces
2	$Pd(PPh_3)_4$ (5 mol %)	NEt_3	80	5	20	Traces
3	$Pd(PPh_3)_2Cl_2$ (5 mol %)	$HN(^iPr)_2$	80	5	12	48
4	$Pd(OAc)_2$/S-Phos (5 mol %)	NEt_3	80	5	12	60
5	$Pd(OAc)_2$/S-Phos (5 mol %)	Cs_2CO_3	80	—	12	30
6	$Pd(OAc)_2$ (5 mol %) X-Phos (10 mol %)/	NEt_3	100	1	12	78

[a] Yields of isolated products.

Four C–C bonds are formed in only one step, which refers to a nearly quantitative yield and less than 1 mol % of catalyst for each bond formation. The reaction of **1** with various alkynes, using our optimized procedure, afforded products **2a**–**i** in good yields (Table 2).

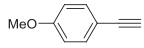
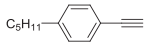
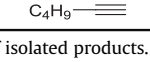
The Sonogashira reaction of **3**, **5** and **7** with various alkynes afforded, following our optimized procedure, the tetra- and pentaalkynylated fluorobenzenes **4a**–**d**, **6a**–**e** and **8a**–**g**, respectively (Scheme 2, Tables 3–5). The structures of all products were confirmed by spectroscopic methods. The structure of **6c** was independently confirmed by X-ray crystal structure analysis

Table 2
Synthesis of **2a**–**i**

2	Alkyne	*t* [h]	Yield[a] [%]
a		12	78
b		10	65
c		8	70
d		8	62
e		12	67
f		12	71
g		12	54
h		8	70
i		12	64

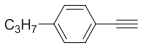
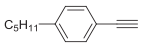
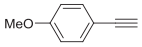
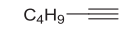
[a] Yields of isolated products.

Table 3
Synthesis of **4a**–**d**

4	Alkyne	*T* [°C]	*t* [h]	Yield[a] [%]
a		100	12	81
b		80	10	68
c		100	12	75
d		100	12	83

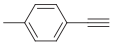
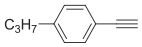
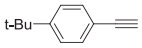
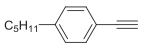
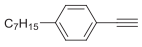
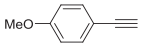
[a] Yields of isolated products.

Table 4
Synthesis of **6a**–**e**

6	Alkyne	T [°C]	t [h]	Yield[a] [%]
a		100	12	85
b		100	12	86
c		100	12	80
d		80	10	78
e		100	12	83

[a] Yields of isolated products.

Table 5
Synthesis of **8a**–**g**

8	Alkyne	T [°C]	t [h]	Yield[a] [%]
a		80	12	55
b		80	12	69
c		100	12	74
d		80	10	68
e		100	12	79
f		100	12	63
g		80	12	78

[a] Yields of isolated products.

(Fig. 5). The phenyl groups and the central benzene moiety are nearly in plane. Layers are formed in the crystal lattice.

Compounds **2**, **4**, **6** and **8** show fluorescence in the range of 352–454 nm (Fig. 6). Comparison of the spectra of derivatives **2h**, **4b**, **6d** and **8g**, all containing a *p*-methoxyphenyl group, reveals that the absorption and fluorescence depend on the type of core structure (Table 6). Product **8g**, containing five alkynyl groups, shows a bathochromic shift compared to the tetraalkynyl derivatives. Compound **2h** shows a bathochromic shift compared to

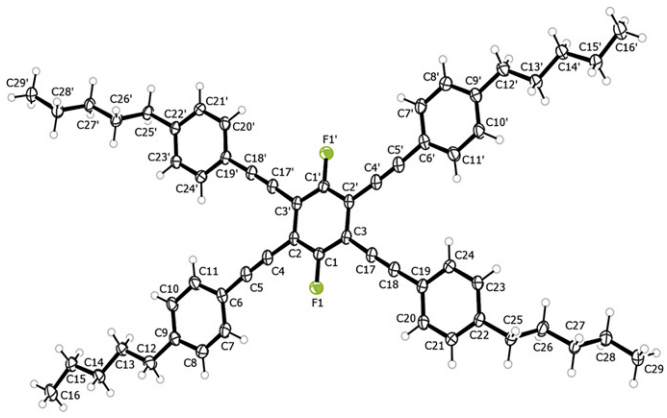


Fig. 5. The molecular structure of **6c** in the crystal.

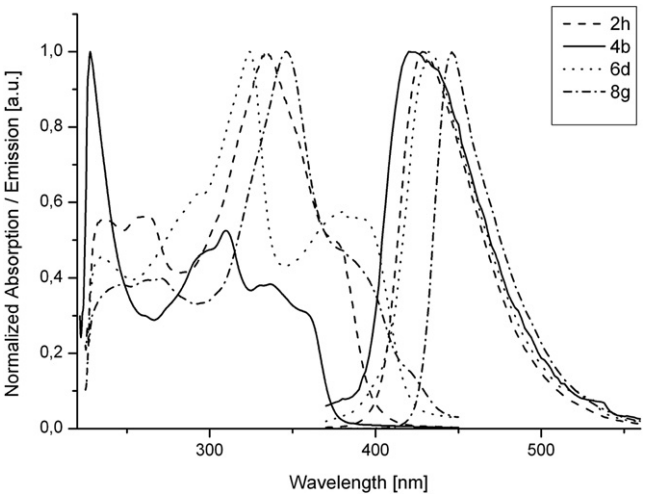


Fig. 6. Absorption and fluorescence of **2h**, **4b**, **6d** and **8g** (measurements in dichloromethane).

6d and **4b**, which might be again explained by the more extended π-system. Within a series of a specific core structure a bathochromic shift is observed for aryl- as compared to alkyl-substituted derivatives, due to the extended π-system. No clear trend was observed for the influence of different types of substituents attached to the phenyl group. Comparison of the absorption and emission of **8d** and **8g** with the known[21] non-fluorinated penta(alkynyl)benzene derivatives revealed a slight bathochromic shift in case of the fluorinated compounds. This might be explained by the electronic correspondence between the electron donating alkynyl groups and the electron-withdrawing fluoride substituent.

In conclusion, we have reported the synthesis of a variety of hitherto unknown fluorescent tetra- and pentaalkynylfluorobenzenes by Sonogashira reactions of novel hexahalobenzenes, i.e., 1,2-difluoro-3,4,5,6-tetraiodo-benzene (**1**), 1,3-difluoro-2,4,5,6-tetraiodo-benzene (**3**), 1,4-difluoro-2,3,5,6-tetraiodobenzene (**5**) and 1-fluoro-2,3,4,5,6-pentaiodobenzene (**7**). We believe that fluoroiodobenzenes **1**, **3**, **5** and **7** represent interesting building blocks for other synthetic transformations, which will be studied in the future.

Table 6
Photophysical properties of compounds **2a**–**i**, **4a**–**d** and **6a**–**e** and **8a**–**g** (measurements in dichloromethane)

Compd	λ_{abs} [nm] ([10^5 M^{-1} cm^{-1}])	λ^{fluo}_{max} [nm]	Stokes shift [nm]
2a	309	390	81
2b	309	424	115
2c	320	409	99
2d	229	352	123
2f	325	420	95
2g	325	420	95
2h	333	396	63
4a	305	400	95
4b	310	425	115
4c	314	410	96
4d	300	370	70
6a	313	409	96
6b	317	421	104
6c	316	419	103
6d	317	428	111
6e	258	360	102
8c	337	430	93
8d	336	454	108
8e	317	421	104
8f	337	440	103
8g	346	444	108

3. Experimental section

3.1. General

^{1}H NMR spectroscopy: Bruker: AM 250, Bruker ARX 300, Bruker ARX 500; δ=0.00 ppm for tetramethylsilane; δ=7.26 ppm for ($CDCl_3$); Characterization of the signal fragmentations: s=singlet, d=doublet, dd=double of doublet, t=triplet, q=quartet, m=multiplet, br=broadly. All coupling constants are indicated as (*J*). 2D NMR techniques (NOESY, COSY, HMQC and HMBC) were used for the confirmation of structure. ^{13}C NMR Spectroscopy: Bruker: AM 250, (62.9 MHz); Bruker: ARX 300, (75 MHz), Bruker: ARX 500, (125 MHz) Ref: 29.84±0.01 ppm and 206.26±0.13 ppm δ=77.00 ppm for $CDCl_3$. The multiplicity of the carbon atoms was determined by the DEPT 135 and APT technique (APT=Attached Proton Test) and quoted as CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms. Characterization of the signal fragmentations: quart=quartet the multiplicity of the signals was determined by the DEPT recording technology and/or the APT recording technology. Mass Spectroscopy: AMD MS40, Varian MAT CH 7, MAT 731 (EI, 70 eV), Intecta AMD 402 (EI, 70 eV and CI), Finnigan MAT 95 (CI, 200 eV). High Resolution mass spectroscopy: Finnigan MAT 95 or Varian MAT 311; Bruker FT CIR, AMD 402 (AMD Intectra). Infrared spectroscopy (IR): Bruker IFS 66 (FT-IR), Nicolet 205 FT-IR; Nicolet Protege 460, Nicolet 360 Smart Orbit (ATR); KBr, KAP, Nujol and ATR; Peaks are given following assignments: w=weak, m=medium, s=strong, br=broad. Elemental Analysis: LECO CHNS-932, Thermoquest Flash EA 1112. UV/vis and Fluorescence measurement: UV/vis spectra were recorded at 20 °C with a Lamda 5 (Perkin–Elmer) spectrometer with a solution concentration of 10^{-5}–10^{-6} mol L^{-1}, λ_{max} in nm. Fluorescence spectra were recorded with a Hitachi F-4010 fluorescence spectrophotometer using similar concentration solutions. Distilled dichloromethane was used as a solvent. Melting points: micro heating table HMK 67/1825 Kuestner (Büchi apparatus). Column chromatography: chromatography was performed over Merck silica gel 60 (0.063–0.200 mm, 70–230 mesh) as normal and/or over mesh silica gel 60 (0.040–0.063 mm, 200–400 mesh) as Flash Chromatography. All solvents were distilled before use. X-ray crystal structure analysis:[22] crystallographic data were collected on a Bruker X8Apex, Diffractometer with CCD-Kamera (MoKa und Graphit Monochromator=0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full matrix least-squares with SHELXL-97. SCHAKAL 99 program (Schakal 99. Keller, E.; University of Freiburg, Germany, 1999) is used for the molecular representation of crystal structures.

3.2. General procedure for the periodination

The arene (1.0 mmol), molecular iodine and $K_2S_2O_8$ were dissolved in dichloroethane (DCE) (10 mL). The reaction mixture was stirred at 0 °C for 5 min and then TFA (4 mL) and H_2SO_4 (concentrated, 0.18 mL, 1 mmol) were slowly added with stirring. The mixture was stirred at 0 °C for 10 min and at 20 °C for 15 min. Subsequently, the temperature of the mixture was slowly increased to the indicated temperature and the mixture was stirred until completion of the reaction. The mixture was cooled and poured into ice-cold H_2O (40–50 mL). The precipitated solid was filtered off, washed with H_2O (30–40 mL) and subsequently with CH_2Cl_2 (20–25 mL) to remove unreacted iodine.

*3.2.1. 1,2-Difluoro-3,4,5,6-tetraiodobenzene (**1**).* Starting with 1,2-difluorobenzene (1.00 g, 0.008 mol), $K_2S_2O_8$ (11.0 g, 0.044 mol), TFA (11.8 g, 0.044 mol) and I_2 (12.1 g, 0.048 mmol), **1** was isolated as a yellow crystalline solid (4.8 g, 90%). Mp 153–155 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−94.3. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ=97.3 (d, *J*=23.3 Hz, C), 115.3 (C), 150.3 (d, *J*=243.2 Hz, CF). IR (KBr): $\tilde{\nu}$=2635, 2366, 2340, 2188, 2043, 1979 (w), 1537 (m), 1408, 1402 (s), 1316, 1224, 1172, 1046, 876, 702 (m), 678, 656, 557 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=617 ($[M]^+$, 100), 490 (24), 237 (22), 127 (10), 110 (22). HRMS (EI) calcd for $C_6F_2I_4$ $[M]^+$: 617.61413 found 617.613808. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 11.68.

*3.2.2. 1,3-Difluoro-2,4,5,6-tetraiodobenzene (**3**).* Starting with 1,3-difluorobenzene (1.00 g, 0.008 mol), $K_2S_2O_8$ (11.0 g, 0.044 mol), TFA (11.8 g, 0.044 mol) and iodine (16.9 g, 0.067 mmol), **3** was isolated as a yellow crystalline solid (4.7 g, 88%). Mp 176–177 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−70.0. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ=70.7 (t, *J*=36.6 Hz, C), 91.6 (dd, *J*=31.9, 3.10 Hz, C), 124.2 (C), 161.0 (dd, *J*=241.1, 7.03 Hz, CF), 161.1 (dd, *J*=241.1, 7.03 Hz, CF). IR (KBr): $\tilde{\nu}$=2921 (w), 2764 (w), 2591 (w), 2412 (w), 2351 (w), 1667 (w), 1604 (w), 1474 (w), 1380 (w), 1355 (w), 1275 (w), 1238 (w), 1188 (w), 1079 (w), 1033 (w), 923 (w), 889 (w), 820 (w), 699 (w), 634 (w), 559 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=617 (100) $[M]^+$, 490 (2), 237 (22), 127 (10), 110 (22). HRMS (EI) calcd for $C_6F_2I_4$ $[M]^+$: 617.61413; found 617.61438. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 12.15.

*3.2.3. 1,4-Difluoro-2,3,5,6-tetraiodobenzene (**5**).* Starting with 1,4-difluorobenzene (1.00 g, 0.008 mol), $K_2S_2O_8$ (11.0 g, 0.044 mol), TFA (11.8 g, 0.044 mol) and I_2 (12.1 g, 0.048 mmol), **5** was isolated as a yellow crystalline solid (4.3 g, 80%). Mp 253–255 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−54.40. ^{13}C NMR (62.8 MHz, DMSO-d_6): δ=98.0 (dd, *J*=38.6, 4.74 Hz, C), 156.9 (dd, *J*=239.5, 4.5 Hz, C). IR (KBr): $\tilde{\nu}$=2773 (w), 2655 (w), 2515 (w), 1380 (w), 1311 (w), 1268 (w), 1222 (w), 1172 (w), 1099 (w), 1005 (w), 920 (w), 806 (w), 705 (w), 664 (w), 616 (w), 586 (w), 538 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)= 617 (100) $[M]^+$, 491 (17), 490 (11), 363 (31), 237 (14), 128 (13), 110 (17), 43 (14). HRMS (EI): calcd for $C_6F_2I_4$ $[M]^+$: 617.61413; found 617.614004. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 11.94.

*3.2.4. 1-Fluoro-2,3,4,5,6-pentaiodobenzene (**7**).* Starting with fluorobenzene (0.008 mol), $K_2S_2O_8$ (11.0 g, 0.044 mol), TFA (11.8 g, 0.044 mol) and I_2 (19.4 g, 0.077 mmol), **7** was isolated as a yellow crystalline solid (4.1 g, 76%). Mp 259–260 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−39.8. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ=96.6 (d, *J*=31.7 Hz, C), 117.8 (d, *J*=3.92 Hz, C), 124.1 (C), 158.8 (d, *J*=241.6 Hz, CF). IR (KBr): $\tilde{\nu}$=2924 (m), 2810 (m), 2778 (m), 2533 (m), 2477 (m), 2351 (m), 1693 (m), 1650 (m), 1587 (m), 1494 (m), 1471 (m), 1327 (s), 1274 (s), 1206 (m), 1150 (m), 1052 (m), 923 (m), 875 (s), 802 (m), 764 (m), 688 (m), 620 (s), 584 (s), 539 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%)=726 (30) $[M]^+$, 600 (100), 473 (25), 346 (22), 219 (16), 92 (19). HRMS (EI) calcd for C_6FI_5 $[M]^+$: 725.52319; found: 725.519725.

3.3. General procedure for Sonogashira coupling reactions

A suspension of tetraiodobenzenes (**1**, **3**, **5**, **7**), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), CuI (5 mol %), Cs_2CO_3 (5 equiv) in 1,4-dioxane or DMF was degassed three time in a pressure tube. The alkyne (1.2 equiv per bromine atom) was added using a syringe. The mixture was heated at the indicated temperature (60–100 °C) for 12–72 h. The reaction mixture was filtered and the residue was washed with CH_2Cl_2. The filtrate was washed with a saturated solution of ammonium chloride (2×25 mL), water (2×25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The product was purified by column chromatography on silica gel.

*3.3.1. 1,2-Difluoro-3,4,5,6-tetrakis(phenylethynyl)benzene (**2a**).* Starting with **1** (150 mg, 0.24 mmol), phenylacetylene (149 mg, 1.45 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2a** was isolated as a yellow solid (97 mg, 78%). Mp 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.27–7.34 (m, 10H, ArH), 7.52–7.57 (m, 10H, ArH). ^{13}C

NMR (75.4 MHz, $CDCl_3$): δ=80.8 (C≡C), 85.9 (C≡C), 98.5 (C≡C), 101.4 (C≡C), 116.1 (t, J=6.25 Hz, C), 122.6 (d, J=58.7 Hz, C), 125.1 (C), 128.2 (CH), 128.5 (CH), 129.1 (d, J=38.7 Hz, CH), 131.6 (CH), 131.7 (CH), 131.9 (CH), 150.1 (dd, J=256.2, 16.3 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.12. IR (ATR, cm^{-1}): $\tilde{\nu}$=3078 (w), 3052 (w), 3030 (w), 2928 (w), 2872 (w), 2714 (w), 2524 (w), 2435 (w), 2393 (w), 2207 (w), 1947 (w), 1872 (w), 1798 (w), 1744 (w), 1666 (w), 1584 (w), 1492 (m), 1453 (m), 1441 (m), 1409 (m), 1355 (w), 1327 (w), 1276 (w), 1235 (w), 1194 (w), 1174 (w), 1132 (w), 1093 (w), 1066 (m), 1023 (m), 998 (w), 966 (w), 934 (m), 910 (w), 871 (w), 835 (w), 771 (w), 748 (s), 682 (s), 622 (w), 577 (m), 528 (m). MS (EI, 70 eV); m/z (%)=514 (100) $[M]^+$, 513 (19), 512 (17), 492 (10), 436 (14), 385 (19), 384 (78), 369 (10), 198 (11). HRMS (EI) calcd for $C_{38}H_{20}F_2$ $[M]^+$: 514.15276; found 514.153109.

*3.3.2. 1,2-Difluoro-3,4,5,6-tetrakis(4-methylphenylethynyl)-benzene (**2b**).* Starting with **1** (150 mg, 0.24 mmol), 4-methylphenylacetylene (168 mg, 1.45 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2b** was isolated as a yellow solid (90 mg; 65%). Mp 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.33 (s, 12H, CH_3), 7.09–7.14 (m, 8H, ArH), 7.42–7.45 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.60, 21.63, 29.6 (CH_3), 80.5 (C≡C), 85.5 (C≡C), 98.5 (C≡C), 101.5 (C≡C), 115.9 (CH), 119.4 (C), 119.9 (C), 125.0 (C), 128.2 (CH), 129.5 (CH), 131.6 (CH), 139.1 (C), 139.6 (C), 159.8 (d, J_{CF}=247.6 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.78. IR (ATR, cm^{-1}): $\tilde{\nu}$=3051 (w), 3028 (w), 2960 (w), 2917 (w), 2849 (w), 2733 (w), 2204 (w), 1895 (w), 1739 (w), 1603 (m), 1581 (w), 1509 (m), 1450 (m), 1412 (w), 1378 (w), 1316 (w), 1280 (w), 1260 (w), 1212 (w), 1195 (w), 1177 (w), 1101 (m), 1076 (w), 1037 (w), 1019 (m), 941 (m), 869 (w), 810 (s), 728 (w), 659 (w), 646 (w). MS (EI, 70 eV); m/z (%)=6570 (41) $[M]^+$. HRMS (EI): calcd for $C_{42}H_{28}F_2$ $[M]^+$: 570.21536; found 570.213690.

*3.3.3. 1,2-Difluoro-3,4,5,6-tetra(3-methylphenylethynyl)-benzene (**2c**).* Starting with **1** (150 mg, 0.24 mmol), 3-methylphenylacetylene (139 mg, 1.20 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **2c** was isolated as an orange solid (98 mg; 70%). Mp 151–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.38 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 7.23–7.27 (m, 4H, ArH), 7.31 (q, J=15.1, 7.4 Hz, 4H, ArH), 7.48–7.52 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.2 ($2CH_3$), 21.3 ($2CH_3$), 80.8 (C≡C), 85.8 (C≡C), 98.7 (C≡C), 101.7 (C≡C), 116.1 (t, J=6.4 Hz, 2C), 122.3 (C), 122.8 (2C), 125.2 (t, J=2.8 Hz, C), 128.4 (d, J=2.2 Hz, 4C), 128.9 (4CH), 129.0 (4CH), 130.2 (4CH), 132.5 (d, J=4.4 Hz, 4C), 138.2 (C), 138.6 (C), 150.0 (d, J_{CF}=256.2 Hz, CF), 150.5 (d, J_{CF}=256.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.45 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2916 (w), 2202 (w), 1773 (w), 1577 (w), 1487 (w), 1452 (w), 1408 (w), 1293 (w), 1268 (w), 1152 (w), 1093 (w), 997 (w), 960 (w), 902 (w), 854 (w), 777 (w), 683 (w), 586 (w), 569 (w), 501 (w), 435 (w), 383 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 233, 255, 320, 362 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=409, 421 nm. MS (EI, 70 eV); m/z (%)=570 (100) $[M]^+$, 555 (20), 540 (14). HRMS (EI) calcd for $C_{42}H_{28}F_2$ $[M]^+$: 570.21536; found 570.216596. Anal. Calcd for $C_{42}H_{28}F_2$: C, 88.40. H, 4.95. Found: C, 88.45. H, 4.99.

*3.3.4. 1,2-Difluoro-3,4,5,6-tetrakis(4-tert-butylphenylethynyl)-benzene (**2d**).* Starting with **1** (100 mg, 0.16 mmol), 4-*tert*-butylphenylacetylene (153 mg, 0.97 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2d** was isolated as a yellow oil (74 mg; 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.27 (s, 18H, CH_3), 1.28 (s, 18H, CH_3), 7.19–7.35 (m, 8H, ArH), 7.47–7.50 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=31.2 [$(CH_3)_3C$], 34.9 ($C(CH_3)$), 80.5 (C≡C), 85.5 (C≡C), 98.5 (C≡C), 101.5 (C≡C), 119.5 (C), 120.0 (C), 125.04 (C), 125.5 (CH), 131.6 (CH), 131.7 (CH), 152.3 (C), 152.6 (C), 158.1 (d, J=242.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.77, −131.77. IR (ATR, cm^{-1}): $\tilde{\nu}$=3083 (w), 3035 (w), 2956 (m), 2901 (w), 2865 (w), 2710 (w), 2212 (w), 1912 (w), 1660 (w), 1607 (w), 1587 (w), 1552 (w), 1515 (w), 1455 (m), 1409 (w), 1391 (w), 1315 (w), 1267 (w), 1200 (w), 1182 (w), 1107 (m), 1079 (w), 1064 (w), 1015 (w), 943 (m), 830 (s), 784 (w), 735 (w), 697 (w), 656 (w), 620 (w), 559 (s), 528 (w). MS (EI, 70 eV); m/z (%)=728 (36) $[M]^+$, 617 (73), 364 (15), 237 (10), 128 (27), 110 (20), 57 (17), 44 (100). HRMS (EI) calcd for $C_{54}H_{52}F_2$ $[M]^+$: 738.40316; found 738.409188.

*3.3.5. 1,2-Difluoro-3,4,5,6-tetrakis(4-n-propyl-phenylethynyl)-benzene (**2e**).* Starting with **1** (100 mg, 0.16 mmol), 4-*n*-propyl-butylphenylacetylene (139 mg, 0.97 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2e** was isolated as a yellow oil (74 mg; 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, J=7.11 Hz, 12H, CH_3), 1.53–1.66 (sext, 8H, CH_2), 2.54 (t, J=7.4 Hz, 8H, CH_2), 7.09–7.13 (m, 8H, ArH), 7.44–7.47 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.8 ($2CH_3$), 24.3 ($2CH_2$), 38.0 ($2CH_2$), 80.5 (C≡C), 85.5 (C≡C), 98.6 (C≡C), 101.6 (C≡C), 119.7 (C), 120.2 (C), 125.0 (C), 128.6 (C), 128.7 (CH), 131.5 (CH), 131.8 (CH), 143.9 (C), 144.3 (C), 160.2 (dd, J=251.0, 13.6 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.76. IR (ATR, cm^{-1}): $\tilde{\nu}$=3400 (w), 3119 (w), 3078 (w), 2956 (m), 2927 (m), 2869 (m), 2732 (w), 2668 (w), 2206 (m), 1906 (w), 1787 (w), 1703 (w), 1666 (w), 1604 (w), 1553 (w), 1509 (m), 1454 (s), 1412 (m), 1338 (m), 1258 (m), 1178 (m), 1113 (m), 1079 (m), 1018 (m), 941 (m), 867 (m), 800 (s), 741 (m), 660 (m), 561 (m), 528 (m). MS (EI, 70 eV); m/z (%)=682 (91) $[M]^+$, 653 (11), 397 (17), 396 (78), 394 (20), 329 (12), 153 (10), 44 (100). HRMS (EI) calcd for $C_{50}H_{44}F_2$ $[M]^+$ 682.34056; found 682.339960.

*3.3.6. 1,2-Difluoro-3,4,5,6-tetra(4-n-pentylphenylethynyl)-benzene (**2f**).* Starting with **1** (150 mg, 0.24 mmol), 4-*n*-pentylphenylacetylene (206 mg, 1.20 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **2f** was isolated as a brown solid (137 mg; 71%). Mp 72–74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (m, 12H, CH_3), 1.23–1.26 (m, 16H, CH_2), 1.49–1.59 (m, 8H, CH_2), 2.54 (t, J=7.7 Hz, 8H, $CH_2CH_2CH_2CH_2CH_3$), 7.08 (dd, J=8.4, 5.9 Hz, 8H, ArH), 7.43 (dt, J=8.5, 1.0 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.0 ($4CH_3$), 22.6 ($4CH_2$), 30.9 ($4CH_2$), 31.5 ($4CH_2$), 36.0 ($4CH_2$), 80.6 (C≡C), 85.6 (C≡C), 98.6 (C≡C), 101.1 (C≡C), 116.0 (C), 116.3 (C), 119.7 (C), 120.2 (C), 125.0 (C), 125.3 (C), 126.6 (C), 128.6 (2C), 131.8 (d, J=8.3 Hz, 2CH), 144.4 (C), 150.0 (d, J_{CF}=256.8 Hz, CF), 150.5 (d, J_{CF}=256.8 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.89 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3030 (w), 2925 (m), 2854 (m), 2206 (w), 1901 (w), 1605 (w), 1511 (m), 1453 (s), 1376 (w), 1284 (w), 1200 (w), 1177 (w), 1115 (w), 1079 (w), 1018 (w), 941 (m), 849 (m), 806 (s), 729 (m), 688 (w), 644 (w), 527 (s), 479 (w), 428 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 229, 255, 325, 369 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=420 nm. MS (EI, 70 eV); m/z (%)=794 (100) $[M]^+$, 44 (28). HRMS (EI) calcd for $C_{58}H_{60}F_2$ $[M]^+$: 794.46576; found 794.465130. Anal. Calcd for $C_{58}H_{60}F_2$: C, 87.61. H, 7.61. Found: C, 87.64. H, 7.64.

*3.3.7. 1,2-Difluoro-3,4,5,6-tetra(n-heptylphenylethynyl)-benzene (**2g**).* Starting with **1** (150 mg, 0.24 mmol), *n*-heptylphenylacetylene (240 mg, 1.20 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **2g** was isolated as a yellow solid (120 mg, 54%). Mp 46–48 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, 12H, CH_3), 1.28–1.32 (m, 30H, CH_2), 1.56–1.65 (m, 10H, CH_2), 2.62 (t, J=7.6 Hz, 8H, CH_2), 7.17 (dd, J=8.3, 5.6 Hz, 8H, ArH), 7.52 (dt, J=8.35, 1.95 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.1 ($4CH_3$), 22.7 ($4CH_2$), 29.2 ($4CH_2$), 29.3 ($4CH_2$), 31.3 ($4CH_2$), 31.8 ($4CH_2$), 36.1 ($4CH_2$), 80.5 (C≡C), 85.6 (C≡C), 98.6 (C≡C), 101.6 (C≡C), 116.0 (2C), 116.6 (2C), 119.9 (2C), 120.2 (2C), 125.1 (2C), 128.6 (8CH), 131.8 (8CH), 144.1 (C), 149.8 (d, J_{CF}=257.9 Hz, CF), 150.0 (d, J_{CF}=257.9 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−131.90 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2954 (w), 2922 (s), 2852 (m), 2208 (w), 1605 (w), 1511 (w), 1455 (s), 1376 (w), 1178 (w), 1116

(w), 1018 (w), 942 (w), 805 (m), 724 (w), 526 (m) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 229, 255, 325, 368 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=420 nm. MS (EI, 70 eV); *m/z* (%)=907 (65) $[M]^+$, 906 (99), 57 (12), 44 (100), 43 (15). HRMS (EI) calcd for $C_{66}H_{77}F_2$ $[M]^+$: 907.59879; found 907.596555.

*3.3.8. 1,2-Difluoro-3,4,5,6-tetrakis(4-methoxylphenylethynyl)-benzene (**2h**).* Starting with **1** (150 mg, 0.24 mmol), 4-methoxyphenylacetylene (191 mg, 1.45 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2h** was isolated as a yellow solid (107 mg; 70%). Mp 151–153 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 6H, OCH_3), 3.76 (s, 6H, OCH_3), 6.79–6.83 (m, 8H, ArH), 7.44–7.48 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=55.4 ($2OCH_3$), 80.1 (C≡C), 85.1 (C≡C), 98.3 (C≡C), 101.4 (C≡C), 114.2 (CH), 114.6 (CH), 115.2 (C), 122.2 (C), 124.8 (C), 128.8 (CH), 130.9 (CH), 133.3 (CH), 133.5 (CH), 152.2 (d, *J*=258.0 Hz, CF), 160.1 (C), 167.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−132.35. IR (ATR, cm^{-1}): $\tilde{\nu}$=2957 (w), 2931 (w), 2838 (w), 2536 (w), 2206 (w), 2041 (w), 1907 (w), 1722 (w), 1660 (w), 1602 (m), 1565 (w), 1509 (s), 1455 (m), 1415 (w), 1389 (w), 1286 (m), 1244 (s), 1203 (w), 1177 (m), 1167 (s), 1103 (m), 1072 (w), 1022 (s), 939 (m), 832 (s), 795 (m), 743 (w), 705 (w), 651 (w), 642 (w), 636 (w), 533 (m). MS (EI, 70 eV); *m/z* (%)=634 (100) $[M]^+$. HRMS (EI) calcd for $C_{42}H_{28}O_4F_2$ $[M]^+$: 634.19502; found 634.195842.

*3.3.9. 1,2-Difluoro-3,4,5,6-tetrakis(4-n-butyl-ethynyl)benzene (**2i**).* Starting with **1** (100 mg, 0.16 mmol), 4-*n*-butyl-acetylene (80 mg, 0.97 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **2i** was isolated as a yellow oil (45 mg; 64%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, *J*=7.20 Hz, 12H, CH_3), 1.40–1.57 (m, 16H CH_2), 2.40–2.46 (sext, 8H, CH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.6 ($2CH_3$), 19.6 ($2CH_3$), 21.9 ($2CH_2$), 22.6 ($2CH_2$), 29.6 ($2CH_2$), 30.6 ($2CH_2$), 31.5 ($2CH_2$), 38.1 ($2CH_2$), 59.5 (C≡C), 72.3 (C≡C), 98.5 (C≡C), 102.1 (CC), 125.9 (C), 135.5 (C), 137.0 (C), 148.3 (C), 150.9 (dd, J_{CF}=246.8, 14.3 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−133.81. IR (ATR, cm^{-1}): $\tilde{\nu}$=3390 (w), 2956 (w), 2930 (w), 2871 (w), 2228 (w), 1714 (w), 1683 (w), 1608 (w), 1558 (w), 1509 (w), 1456 (m), 1378 (w), 1341 (w), 1246 (w), 1180 (w), 1119 (w), 1068 (w), 997 (w), 900 (w), 828 (w), 745 (w), 723 (w), 694 (w), 541 (m). MS (EI, 70 eV); *m/z* (%)=434 (36) $[M]^+$, 397 (33), 396 (94), 394 (36), 331 (11), 329 (21), 277 (15), 210 (15), 198 (11), 186 (16), 44 (100). HRMS (EI) calcd for $C_{30}H_{36}F_2$ $[M]^+$: 434.27786; found 434.278396.

*3.3.10. 1,3-Difluoro-2,4,5,6-tetra(phenylethynyl)benzene (**4a**).* Starting with **3** (100 mg, 0.16 mmol), phenylacetylene (83 mg, 0.81 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **4a** was isolated as orange solid (68 mg; 81%). Mp 155–157 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.51–7.56 (m, 12H, ArH), 7.27–7.33 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=75.5 (C≡C), 80.3 (C≡C), 86.2 (C≡C), 98.9 (C≡C), 101.3 (t, *J*=2.6 Hz, C), 101.4 (C), 111.3 (C), 111.5 (d, *J*=7.5 Hz, C), 122.2 (C), 122.6 (C), 122.7 (C), 128.5 (6CH), 128.6 (CH), 129.1 (CH), 129.4 (d, *J*=3.5 Hz, CH), 131.8 (2CH), 132.0 (CH), 161.5 (d, J_{CF}=260.4 Hz, CF), 161.7 (d, J_{CF}=260.4 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−100.42 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3051 (m), 2205 (m), 1887 (w), 1596 (m), 1489 (m), 1441 (m), 1352 (m), 1268 (w), 1214 (m), 1156 (w), 1094 (m), 1067 (m), 998 (w), 939 (m), 747 (s), 684 (s), 578 (m), 529 (m), 498 (m), 436 (m) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 255, 305, 345 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=400, 409 nm. MS (EI, 70 eV); *m/z* (%)=514 (75) $[M]^+$, 69 (29), 44 (100). HRMS (EI) calcd for $C_{38}H_{20}F_2$ $[M]^+$: 514.15276; found 514.154168. Anal. Calcd for $C_{38}H_{20}F_2$: C, 88.70. H, 3.92. Found: C, 88.75. H, 3.66.

*3.3.11. 1,3-Difluoro-2,4,5,6-tetrakis(4-methoxylphenylethynyl)-benzene (**4b**).* Starting with **3** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (128 mg, 0.97 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **4b** was isolated as a yellow solid (69 mg; 68%). Mp 124–126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.88–3.94 (m, 12H, OCH_3), 6.90–6.97 (m, 9H, ArH), 7.07 (d, *J*=8.5 Hz, 2H, ArH), 7.55–7.60 (m, 5H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−102.21. IR (ATR, cm^{-1}): $\tilde{\nu}$=2917 (w), 2542 (w), 2205 (w), 1644 (w), 1602 (w), 1567 (w), 1509 (w), 1447 (w), 1368 (w), 1289 (w), 1245 (w), 1169 (w), 1104 (w), 1028 (w), 955 (w), 913 (w), 868 (w), 828 (w), 766 (w), 708 (w), 679 (w), 615 (w), 532 (w). MS (EI, 70 eV); *m/z* (%)=634 (17) $[M]^+$, 397 (23), 396 (100), 394 (25), 329 (13), 210 (10), 186 (10), 153 (10), 152 (10). HRMS (EI) calcd for $C_{42}H_{28}O_4F_1$ $[M]^+$: 634.19502; found 634.197057.

*3.3.12. 1,3-Difluoro-2,4,5,6-tetra(4-n-pentylphenylethynyl)-benzene (**4c**).* Starting with **3** (100 mg, 0.16 mmol), 4-*n*-pentylphenylacetylene (137 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **4c** was isolated as a dark brown oil (97 mg, 75%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.79–0.84 (m, 12H, $4CH_3$), 1.23–1.26 (m, 16H, $8CH_2$), 1.47–1.57 (m, 8H, $2CH_2$), 2.54 (t, *J*=7.6 Hz, 8H, $4CH_2$), 7.06–7.12 (m, 8H, ArH), 7.40–7.45 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.1 ($4CH_3$), 22.6 ($4CH_2$), 30.9 (d, *J*=2.0 Hz, $4CH_2$), 31.5 ($4CH_2$), 36.3 (d, *J*=2.0 Hz, $4CH_2$), 76.2 (d, *J*=165.9 Hz, C≡C), 76.6 (C≡C), 80.0 (C≡C), 85.9 (t, *J*=4.8 Hz, C≡C), 99.0 (t, *J*=3.0 Hz, C), 101.4 (t, *J*=4.8 Hz, C), 101.6 (C), 103.1 (t, *J*=20.6 Hz, C), 111.2 (C), 111.5 (d, *J*=7.8 Hz, C), 119.4 (C), 119.9 (d, *J*=4.2 Hz, C), 128.6 (6CH), 128.6 (CH), 131.7 (3CH), 131.9 (CH), 132.0 (CH), 149.2 (C), 144.6 (d, *J*=2.0 Hz, C), 161.5 (d, J_{CF}=259.1 Hz, CF), 161.8 (d, J_{CF}=259.1 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−101.12 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3027 (w), 2955 (w), 2925 (m), 2854 (m), 2204 (w), 1905 (w), 1606 (w), 1509 (m), 1444 (s), 1377 (w), 1262 (w), 1178 (w), 1092 (m), 1019 (m), 904 (w), 809 (m), 727 (w), 661 (w), 551 (m), 459 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 262, 314, 355 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=410 nm. MS (EI, 70 eV); *m/z* (%)=794 (100) $[M]^+$, 737 (10), 625 (11), 338 (10), 285 (10), 284 (23), 44 (53), 43 (11), 41 (13) cm^{-1}. HRMS (EI) calcd for $C_{58}H_{60}F_2$ $[M]^+$: 794.46576; found 794.465446.

*3.3.13. 1,3-Difluoro-2,4,5,6-tetra(hex-1-ynyl)benzene (**4d**).* Starting with **3** (100 mg, 0.16 mmol), 1-hexyne (65 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **4d** was isolated as a dark brown oil (59 mg, 83%). ^1H NMR (300 MHz, $CDCl_3$): δ=0.79–0.91 (m, 12H, CH_3), 1.06–1.21 (m, 3H, CH_2), 1.38–1.58 (m, 15H, CH_2), 2.39–2.47 (m, 6H, CH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.6 (CH_3), 13.6 ($2CH_2$), 13.7 (CH_3), 19.5 ($2CH_2$), 19.6 (CH_2), 19.7 (CH_2), 21.8 ($3CH_2$), 21.9 (CH_2), 30.4 (CH_2), 30.6 ($2CH_2$), 30.7 (CH_2), 71.7 (C), 77.2 (C), 99.5 (2C), 99.6 (C≡C), 101.5 (C≡C), 102.4 (C≡C), 102.5 (C≡C), 162.0 (d, J_{CF}=255.7 Hz, CF), 162.3 (d, J_{CF}=255.7 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.9 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2957 (m), 2931 (m), 2871 (w), 2234 (w), 1718 (w), 1599 (w), 1445 (s), 1378 (w), 1318 (w), 1260 (w), 1168 (w), 1104 (w), 1025 (m), 876 (w), 801 (w), 725 (w), 555 (w). UV–vis (CH_2Cl_2) λ_{max}: 251, 260, 380, 300 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=359, 370 nm. MS (EI, 70 eV); *m/z* (%)=434 (100) $[M]^+$, 391 (10), 377 (14), 363 (10), 349 (19), 335 (25), 321 (19), 307 (15), 295 (11), 281 (14), 277 (10), 275 (13), 257 (10), 105 (13), 71 (12), 57 (22), 44 (19), 43 (26), 40 (21) cm^{-1}. HRMS (EI) calcd for $C_{30}H_{36}F_2$ $[M]^+$: 434.27796; found 434.278900.

*3.3.14. 1,4-Difluoro-2,3,5,6-tetra(3-methylphenylethynyl)-benzene (**6a**).* Starting with **5** (100 mg, 0.16 mmol), 3-methylphenylacetylene (92 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **6a** was isolated as a yellow solid (79 mg, 85%). Mp 198–200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.27 (s, 12H, CH_3), 7.12–7.21 (m, 8H, ArH), 7.30 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.2 ($4CH_3$), 80.8 (2C≡C), 101.4 (2C≡C), 114.9 (C), 115.1 (d, *J*=8.1 Hz, C), 122.3 (C),

128.4 (4CH), 129.0 (4CH), 130.2 (2CH), 132.6 (4CH), 138.2 (C), 158.3 (d, J_{CF}=253.5 Hz, CF), 158.6 (d, J_{CF}=253.5 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−108.69 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2917 (w), 2206 (w), 1769 (w), 1599 (w), 1485 (w), 1444 (w), 1408 (w), 1346 (w), 1273 (w), 1089 (w), 1038 (w), 961 (w), 874 (w), 774 (m), 683 (m), 587 (w), 537 (w), 441 (m), 394 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 313, 378 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=409 nm. MS (EI, 70 eV); *m*/*z* (%)=570 (100) [M]$^+$. HRMS (EI) calcd for $C_{42}H_{28}F_2$ [M]$^+$: 570.21536; found 570.21536. Anal. Calcd for $C_{42}H_{28}F_2$: C, 88.40. H, 4.95. Found: C, 88.36. H, 4.91.

*3.3.15. 1,4-Difluoro-2,3,5,6-tetra(4-n-propylphenylethynyl)-benzene (**6b**).* Starting with **5** (100 mg, 0.16 mmol), 4-*n*-propylphenylacetylene (115 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **6b** was isolated as yellow solid (96 mg, 86%). Mp 189–191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.85 (t, *J*=7.3 Hz, 12H, CH_3), 1.51–1.61 (m, 8H, CH_2), 2.52 (t, *J*=7.8 Hz, 8H, CH_2), 7.08 (dt, *J*=6.5, 2.0 Hz, 8H, ArH), 7.42 (dt, *J*=6.5, 2.0 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.8 (4CH_3), 24.4 (4CH_2), 38.4 (4CH_2), 80.6 (2C≡C), 101.4 (2C≡C), 114.8 (d, *J*=8.7 Hz, C), 114.9 (d, *J*=8.4 Hz, C), 128.7 (4CH), 131.9 (4CH), 144.3 (C), 158.4 (d, J_{CF}=253.6 Hz, CF), 158.7 (d, J_{CF}=253.6 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−108.88 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2957 (m), 2929 (m), 2868 (m), 2206 (m), 1904 (m), 1604 (m), 1510 (s), 1442 (s), 1376 (m), 1344 (m), 1266 (m), 1201 (m), 1112 (m), 1018 (m), 944 (s), 868 (m), 800 (s), 709 (m), 645 (m), 566 (s), 524 (s), 440 (m) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 317, 382 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=410, 421 nm. MS (EI, 70 eV); *m*/*z* (%)=682 (100) [M]$^+$, 284 (23). HRMS (EI) calcd for $C_{50}H_{44}F_2$ [M]$^+$: 682.34056; found 682.339721. Anal. Calcd for $C_{50}H_{44}F_2$: C, 87.94. H, 6.49. Found: C, 87.91. H, 6.45.

*3.3.16. 1,4-Difluoro-2,3,5,6-tetra(4-n-pentylphenylethynyl)-benzene (**6c**).* Starting with **5** (100 mg, 0.16 mmol), 4-*n*-pentylphenylacetylene (137 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **6c** was isolated as a yellow solid (103 mg, 80%). Mp 114–116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (t, *J*=6.6 Hz, 12H, CH_3), 1.24–1.27 (m, 14H, CH_2), 1.50–1.60 (m, 10H, CH_2), 2.56 (t, *J*=7.6 Hz, 8H, CH_2), 7.11 (dt, *J*=6.4, 1.9 Hz, 8H, ArH), 7.44 (dt, *J*=6.4, 1.9 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.1 (4CH_3), 22.6 (4CH_2), 30.9 (4CH_2), 31.5 (4CH_2), 36.2 (4CH_2), 80.6 (4C≡C), 101.4 (4C≡C), 114.7 (d, *J*=8.7 Hz, C), 114.9 (d, *J*=10.0 Hz, C), 119.7 (C), 128.6 (4CH), 131.9 (4CH), 144.6 (C), 158.3 (d, J_{CF}=253.9 Hz, CF), 158.7 (d, J_{CF}=253.9 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−108.90 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3029 (w), 2956 (m), 2926 (m), 2853 (m), 2205 (m), 1898 (w), 1686 (w), 1605 (w), 1512 (m), 1441 (m), 1375 (w), 1347 (m), 1270 (w), 1177 (w), 1114 (w), 1018 (w), 946 (m), 829 (m), 804 (m), 746 (w), 656 (w), 571 (w), 538 (m), 493 (w), 441 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 227, 316, 381 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=419 nm. MS (EI, 70 eV); *m*/*z* (%)=794 (100) [M]$^+$, 682 (10), 681 (20), 284 (20), 69 (10), 44 (48). HRMS (EI) calcd for $C_{58}H_{60}F_2$ [M]$^+$: 794.46576; found 794.465121.

*3.3.17. 1,4-Difluoro-2,3,5,6-tetrakis(4-methoxylphenylethynyl)-benzene (**6d**).* Starting with **5** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (128 mg, 0.97 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **6d** was isolated as a yellow solid (80 mg, 78%). Mp 179–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.78 (s, 12H, OCH_3), 6.83 (dt, *J*=9.00 Hz, 8H, ArH), 7.47 (dt, *J*=9.00 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=55.4 (OCH_3), 80.2 (C≡C), 101.1 (C≡C), 114.2 (CH), 114.7 (C), 132.2 (C), 133.5 (CH), 160.4 (C), 162.9 (d, J_{CF}=257.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.13. IR (ATR, cm^{-1}): $\tilde{\nu}$=2914 (w), 2847 (w), 2206 (w), 1604 (w), 1566 (w), 1513 (w), 1467 (w), 1413 (w), 1376 (w), 1343 (w), 1292 (w), 1249 (w), 1170 (w), 1105 (w), 1025 (w), 944 (w), 821 (w), 792 (w), 718 (w), 660 (w), 643 (w), 628 (w), 594 (w), 531 (m). MS (EI, 70 eV); *m*/*z* (%)=634 (70) [M]$^+$, 396 (15), 119 (25), 91 (25), 69 (10), 57 (14), 55 (11), 44 (100), 41 (15). HRMS (EI) calcd for $C_{42}H_{28}F_2O_4$ [M]$^+$: 634.19502; found 634.197451.

*3.3.18. 1,4-Difluoro-2,3,5,6-tetra(hex-1-ynyl)benzene (**6e**).* Starting with **5** (100 mg, 0.16 mmol), 1-hexyne (65 mg, 0.80 mmol), CuI (5 mol %), X-Phos (10 mol %), Pd(OAc)2 (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **6e** was isolated as a brown solid (59 mg, 83%). Mp 66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.87 (t, *J*=7.0 Hz, 12H, CH_3), 1.38–1.59 (m, 16H, CH_2), 2.43 (t, *J*=6.7 Hz, 8H, CH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.6 (4CH_3), 19.6 (4CH_2), 21.9 (4CH_2), 30.5 (4CH_2), 72.3 (t, *J*=2.0 Hz, 2C≡C), 101.9 (t, *J*=2.3 Hz, 2C≡C), 114.7 (d, *J*=8.8 Hz, C), 114.9 (d, *J*=9.2 Hz, C), 159.0 (d, J_{CF}=249.8 Hz, CF), 159.3 (d, J_{CF}=249.8 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−111.10 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=2952 (m), 2930 (m), 2865 (w), 2231 (w), 1707 (w), 1463 (m), 1441 (s), 1420 (m), 1374 (w), 1315 (w), 1265 (w), 1106 (w), 1029 (w), 974 (w), 926 (w), 888 (w), 840 (w), 740 (w), 688 (w), 553 (w), 518 (w), 446 (w), 419 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 227, 258, 301, 314, 333, 351 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$= 350 nm): λ_{max} (emission)=360, 380 nm. MS (EI, 70 eV); *m*/*z* (%)=434 (100) [M]$^+$, 377 (19), 349 (10), 277 (10), 275 (10), 265 (10). HRMS (EI) calcd for $C_{30}H_{36}F_2$ [M]$^+$: 434.27796; found 434.278389.

*3.3.19. 1-Fluoro-2,3,4,5,6-pentakis(2-methylphenylethynyl)-benzene (**8a**).* Starting with **7** (100 mg, 0.16 mmol), 2-methylphenylacetylene (95 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **8a** was isolated as a yellow solid (59 mg, 55%). Mp 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 2.39 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 7.04–7.17 (m, 15H, ArH), 7.21–7.49 (m, 5H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=20.8, 20.9, 21.0, 29.7 (CH_3), 85.2 (C≡C), 85.3 (C≡C), 90.7 (C≡C), 99.1 (C≡C), 122.4 (CH), 122.6 (CH), 125.5 (CH), 1125.6 (CH), 129.1 (d, *J*=3.85 Hz, C), 132.2 (C), 132.4 (C), 140.6 (C), 140.8 (C), 140.9 (C), 155.9 (C), 157.9 (d, *J*=233 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−102.35. MS (EI, 70 eV): *m*/*z* (%)=666 (100) [M]$^+$. HRMS (EI) calcd for $C_{51}H_{35}F$ [M]$^+$: 666.271173; found 666.271113.

*3.3.20. 1-Fluoro-2,3,4,5,6-pentakis(4-methylphenylethynyl)-benzene (**8b**).* Starting with **7** (100 mg, 0.14 mmol), 4-methylphenylacetylene (95 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **8b** was isolated as yellow solid (63 mg, 69%). Mp 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.32 (s, 15H, CH_3), 7.09–7.13 (m, 10H, ArH), 7.43–7.45 (m, 10H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.13. IR (ATR, cm^{-1}): $\tilde{\nu}$=3171 (w), 3077 (w), 3025 (w), 2952 (w), 2918 (w), 2856 (w), 2729 (w), 2204 (w), 1903 (w), 1726 (w), 1604 (w), 1115 (w), 1069 (w), 1019 (w), 985 (w), 961 (w), 945 (w), 932 (w), 811 (s), 741 (w), 721 (w), 706 (w), 690 (w), 659 (w), 645 (w), 526 (w). MS (EI, 70 eV); *m*/*z* (%)=666 (36) [M]$^+$, 397 (33), 396 (94), 394 (36), 331 (11), 329 (21), 277 (15), 210 (15), 198 (11), 186 (16), 44 (100). HRMS (EI) calcd for $C_{51}H_{35}F$ [M]$^+$: 666.27173; found 666.273441.

*3.3.21. 1-Fluoro-2,3,4,5,6-penta(4-n-propylphenylethynyl)-benzene (**8c**).* Starting with **7** (100 mg, 0.13 mmol), 4-*n*-propylphenylacetylene (112 mg, 0.78 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **8c** was isolated as a dark brown solid (83 mg, 74%). Mp 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (t, *J*=7.3 Hz, 15H, CH_3), 1.53–1.65 (m, 10H, CH_2), 2.54 (t, *J*=7.3 Hz, 10H, CH_2), 7.10 (dd, *J*=8.3, 4.0 Hz, 10H, ArH), 7.46 (dt, *J*=8.0, 3.3 Hz, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.8 (5CH_3), 24.4 (5CH_2), 38.1 (5CH_2), 80.9 (C≡C), 86.5 (C≡C), 86.6 (C≡C), 100.4 (C≡C), 100.6 (C≡C), 114.5 (C), 120.0 (C), 120.2 (C), 120.5 (C), 128.7 (d, *J*=2.0 Hz, 8CH), 143.7 (C), 144.1 (d, *J*=1.4 Hz, C),

163.5 (d, J_{CF}=255.6 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.17 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3025 (w), 2956 (w), 2868 (w), 2323 (w), 2205 (w), 1906 (w), 1671 (w), 1604 (m), 1509 (w), 1455 (s), 1376 (m), 1338 (w), 1257 (w), 1203 (w), 1178 (w), 1113 (w), 1090 (w), 1018 (w), 933 (w), 867 (w), 799 (w), 528 (w), 450 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 227, 337, 380 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=430 nm. MS (EI, 70 eV); *m*/*z* (%)=806 (42) $[M]^+$. HRMS (EI) calcd for $C_{62}H_{57}F$ $[M]^+$: 806.42823; found 806.425932. *: CF-group not resolved in ^{13}C NMR.

*3.3.22. 1-Fluoro-2,3,4,5,6-pentakis(4-tert-butylphenylethynyl)-benzene (**8d**).* Starting with **7** (100 mg, 0.16 mmol), 4-butylphenylacetylene (129 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **8d** was isolated as a yellow solid (96 mg, 68%). Mp 161–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.28 (s, 27H, CH_3), 1.29 (s, 9H, CH_3), 1.48 (s, 9H, CH_3), 7.31–7.35 (m, 10H, ArH), 7.48–7.51 (m, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=31.2 ((CH_3)$_3$C), 34.9 (C(CH_3)$_3$), 80.3 (C≡C), 80.9 (C≡C), 83.3 (C≡C), 86.2 (C≡C), 89.8 (C≡C), 100.3 (C≡C), 100.5 (C≡C), 119.8 (C), 120.1 (C), 125.5 (CH), 125.6 (CH), 131.5 (C), 131.6 (C), 131.7 (C), 152.0 (C), 152.4 (C).*^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.10. IR (ATR, cm^{-1}): $\tilde{\nu}$=3082 (w), 3033 (w), 2958 (w), 2902 (w), 2866 (w), 2205 (w), 1605 (w), 1513 (w), 1504 (w), 1462 (w), 1406 (w), 1361 (w), 1267 (w), 1201 (w), 1107 (w), 1016 (w), 934 (w), 876 (w), 831 (m), 736 (w), 665 (w), 614 (w), 559 (w). MS (EI, 70 eV); *m*/*z* (%)=876 (17) $[M]^+$, 207 (11), 97 (10), 69 (23), 44 (100). HRMS (EI): calcd for $C_{66}H_{65}F$ $[M]^+$: 876.50648; found 876.513743. Anal. Calcd for $C_{66}H_{65}F$: C, 90.37. H, 7.47. Found: C, 90.35. H, 6.70. *: CF-group not resolved in ^{13}C NMR.

*3.3.23. 1-Fluoro-2,3,4,5,6-penta(4-n-pentylphenylethynyl)-benzene (**8e**).* Starting with **7** (100 mg, 0.13 mmol), 4-*n*-pentylphenylacetylene (142 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **8e** was isolated as a dark brown oil (103 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, *J*=6.5 Hz, 15H, CH_3), 1.24–1.28 (m, 20H, CH_2), 1.53–1.61 (m, 10H, CH_2), 2.56 (t, *J*=7.7 Hz, 10H, CH_2), 7.10 (dd, *J*=8.3, 4.7 Hz, 10H, ArH), 7.46 (dt, *J*=8.0, 3.0 Hz, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.1 (5CH_3), 22.5 (CH_2), 30.9 (CH_2), 31.0 (CH_2), 36.3 (CH_2), 80.9 (C≡C), 86.1 (C≡C), 86.5 (C≡C), 86.6 (C≡C), 97.8 (C≡C), 100.4 (C), 100.5 (d, *J*=5.1 Hz, C), 114.2 (C), 114.4 (C), 120.0 (C), 120.2 (C), 120.5 (C), 128.6 (d, *J*=2.8 Hz, 8CH), 131.7 (4CH), 131.9 (d, *J*=3.3 Hz, 8CH), 144.0 (C), 144.3 (d, *J*=1.8 Hz, C), 161.1 (d, J_{CF}=256.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.17 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3025 (w), 2953 (w), 2924 (m), 2854 (m), 2206 (w), 1908 (w), 1679 (w), 1605 (w), 1510 (m), 1455 (m), 1376 (w), 1260 (w), 1178 (w), 1113 (w), 1070 (w), 1018 (w), 968 (w), 897 (w), 813 (m), 727 (w), 529 (m), 444 (w), 403 (w) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 260, 337, 378 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=440 nm. MS (EI, 70 eV); *m*/*z* (%)=946 (10) $[M]^+$, 448 (13), 432 (19), 403 (10), 69 (13), 44 (100). HRMS (EI) calcd for $C_{72}H_{77}F$ $[M]^+$: 946.58473; found 946.583714.

*3.3.24. 1-Fluoro-2,3,4,5,6-penta(4-n-heptylphenylethynyl)-benzene (**8f**).* Starting with **7** (100 mg, 0.13 mmol), 4-*n*-heptylphenylacetylene (165 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and 1,4-dioxane (5 mL), **8f** was isolated as a yellow-brown oil (95 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81 (t, *J*=6.6 Hz, 15H, CH_3), 1.21–1.26 (m, 30H, CH_2), 1.49–1.60 (m, 20H, CH_2), 2.56 (t, *J*=7.7 Hz, 10H, CH_2), 7.10 (d, *J*=255.6 Hz, 10H, ArH), 7.46 (dt, *J*=8.3, 3.0 Hz, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=14.1 (5CH_3), 22.7 (5CH_2), 29.2 (5CH_2), 31.3 (5CH_2), 31.8 (CH_2), 36.3 (CH_2), 80.9 (CH_2), 100.4 (C≡C), 100.6 (C≡C), 119.9 (C≡C), 120.2 (C≡C), 120.5 (C≡C), 128.0 (d, *J*=2.5 Hz, 8CH), 129.3 (C), 131.5 (2C), 131.6 (2C), 131.7 (4CH), 131.8 (d, *J*=2.5 Hz, 8CH), 134.5 (d, *J*=4.1 Hz, 2C), 142.8 (2C), 143.9 (2C), 144.4 (d, *J*=1.3 Hz, 4C), 158.0 (d, J_{CF}=249.9 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.2 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3025 (w), 2953 (w), 2922 (s), 2852 (m), 2205 (w), 1903 (w), 1690 (w), 1604 (w), 1510 (w), 1462 (w), 1425 (m), 1375 (w), 1261 (w), 1177 (w), 1115 (w), 1070 (w), 1018 (w), 933 (w), 839 (m), 806 (m), 725 (m), 527 (m), 400 (m) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}: 228, 259, 337, 378 nm. Fluorescence (CH_2Cl_2, $\lambda_{excitation}$=350 nm): λ_{max} (emission)=440 nm. MS (EI, 70 eV); *m*/*z* (%)=1086 (10) $[M]^+$, 612 (14), 610 (10). HRMS (EI) calcd for $C_{62}H_{57}F$ $[M]^+$ not possible: *CF-group not resolved in ^{13}C NMR. Anal. Calcd for $C_{62}H_{57}F$: C, 88.14. H, 9.90. Found: C, 88.18. H, 9.93.

*3.3.25. 1-Fluoro-2,3,4,5,6-pentakis(4-methoyphenylethynyl)-benzene (**8g**).* Starting with **7** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (108 mg, 0.82 mmol), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 equiv) and DMF (5 mL), **8g** was isolated as a yellow solid (94 mg, 78%). Mp 151–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 6H, OCH_3), 3.78 (s, 9H, OCH_3), 6.79–6.84 (m, 10H, ArH), 7.45–7.48 (m, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=55.4 (2OCH_3), 55.5 (2OCH_3), 80.5 (C≡C), 100.1 (C≡C), 100.2 (C≡C), 114.1 (CH), 114.2 (CH), 115.0 (C), 115.5 (C), 116.6 (C), 133.2 (CH), 133.3 (CH), 160.0 (C), 160.2 (C), 160.9*. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.84. IR (ATR, cm^{-1}): $\tilde{\nu}$=3045 (w), 2999 (w), 2954 (w), 2835 (w), 2536 (w), 2203 (w), 1715 (w), 1603 (m), 1565 (w), 1505 (s), 1455 (m), 1413 (w), 1361 (w), 1288 (m), 1243 (s), 1167 (s), 1104 (m), 1024 (m), 932 (m), 825 (s), 717 (w), 665 (w), 642 (w), 627 (w), 531 (m). MS (EI, 70 eV); *m*/*z* (%)=746 (100) $[M]^+$, 135 (10), 57 (15). HRMS (EI) calcd for $C_{51}H_{35}O_5F$ $[M]^+$: 746.24630; found 746.248188. *: CF-group not resolved in ^{13}C NMR.

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References and notes

1. (a) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107; (b) Diederich, F. *Nature* **1994**, *369*, 199.
2. (a) Ebert, M.; Jungbauer, D. A.; Kleppinger, R.; Wendorff, J. H.; Kohne, B.; Praefcke, K. *Liq. Cryst.* **1989**, *4*, 53; (b) Kumar, S.; Varshney, S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3140.
3. Kondo, K.; Yasuda, S.; Sakaguchi, T.; Miya, M. *J. Chem. Soc., Chem. Commun.* **1995**, 55.
4. (a) Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969; (b) Wan, W. B.; Brand, S. C.; Pak, J.; Haley, M. M. *Chem.—Eur. J.* **2000**, *6*, 2044 For recent reviews, see: (c) Haley, M. M. *Synlett* **1998**, 557; (d) Haley, M. M.; Wan, W. B. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI: New York, NY, 2000; Vol. 8, p 1.
5. (a) Gray, G. W.; Hird, M.; Toyne, K. *Liq. Cryst.* **1991**, *195*, 221; (b) Lincker, F.; Bourgun, P.; Masson, P.; Dider, P.; Guidoni, L.; Bigot, J. Y.; Nicoud, J. F.; Donnio, B.; Guillon, D. *Org. Lett.* **2005**, *7*, 1505; (c) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402; (d) Lo, S. C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097; (e) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571; (f) Funahashi, M.; Zhang, F.; Tamaoki, N. *Adv. Mater. (Weinheim, Ger.)* **2007**, *19*, 353; (g) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789; (h) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73.
6. Itami, K.; Yamazaki, D.; Yoshida, J.-I. *J. Am. Chem. Soc.* **2004**, *126*, 15396; (b) Lin, Y.-C.; Lai, C. K.; Chang; Liu, K. T. *Liq. Cryst.* **2002**, *29*, 237.
7. (a) Bryce, M. R.; Marshallsay, G. J.; Moore, A. J. *J. Org. Chem.* **1992**, *57*, 4859; (b) Fourmigué, M.; Johannsen, I.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Am. Chem. Soc.* **1993**, *115*, 3752; (c) Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3823; (d) Iyoda, M.; Fukuda, M.; Yoshida, M.; Sasaki, M. S. *Chem. Lett.* **1994**, 2369.
8. Kayser, B.; Altman, J.; Beck, W. *Chem.—Eur. J.* **1999**, *5*, 754.
9. Ito, S.; Inabe, H.; Morita, N.; Ohta, K.; Kitamura, T.; Imafuku, K. *J. Am. Chem. Soc.* **2003**, *125*, 1669.
10. Hasegawa, M.; Enozawa, H.; Kawabata, Y.; Iyoda, M. *J. Am. Chem. Soc.* **2007**, *129*, 3072.

11. (a) Kamada, K.; Antonov, L.; Yamada, S.; Ohta, K.; Yoshimura, T.; Tahara, K.; Inaba, A.; Sonoda, M.; Tobe, Y. *ChemPhysChem* **2007**, *8*, 2671; (b) Ha-Thi, M.-H.; Souchon, V.; Hamdi, A.; Métivier, A. R. V.; Nakatani, K. P.; Lacroix, G.; Genêt, J.-P.; Michelet, V.; Leray, I. *Chem.—Eur. J.* **2006**, *12*, 9056.
12. (a) Sonoda, M.; Inabe, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *3*, 2419; (b) Kobayashi, K.; Kobayashi, N. *J. Org. Chem.* **2004**, *69*, 2487.
13. (a) Tobe, Y.; Kubota, K.; Naemura, K. *J. Org. Chem.* **1997**, *62*, 3430; (b) Tovar, J. D.; Jux, N.; Jarrosson, T.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **1997**, *62*, 3432.
14. Anthony, J. E.; Khan, S. I.; Rubin, Y. *Tetrahedron Lett.* **1997**, *38*, 3499.
15. Bowls, D. M.; Palmer, G. J.; Landis, C. A.; Scott, J. L.; Anthony, J. E. *Tetrahedron* **2001**, *57*, 3753.
16. Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 268.
17. (a) *Fluorine in Bioorganic Chemistry*; Filler, R., Kobayasi, Y., Yagupolskii, L. M., Eds.; Elsevier: Amsterdam, 1993; (b) Filler, R. *Fluorine Containing Drugs in Organofluorine Chemicals and Their Industrial Application*; Pergamon: New York, NY, 1979, Chapter 6; (c) Hudlicky, M. *Chemistry of Organic Compounds*; Ellis Horwood: Chichester, UK, 1992; (d) Kirsch, P. *Modern Fluoroorganic Chemistry*; VCH: Weinheim, 2004; (e) Chambers, R. D. *Fluorine in Organic Chemistry*; Blackwell Publishing CRC: 2004; See also: (f) Ryckmanns, T.; Balancon, L.; Berton, O.; Genicot, C.; Lamberty, Y.; Lallemand, B.; Passau, P.; Pirlot, N.; Quéré, L.; Talaga, P. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 261; (g) Malamas, M. S.; Sredy, J.; Moxham, C.; Katz, A.; Xu, W.; McDevitt, R.; Adebayo, F. O.; Sawicki, D. R.; Seestaller, L.; Sullivan, D.; Taylor, J. R. *J. Med. Chem.* **2000**, *43*, 1293; (h) Ciha, A. J.; Ruminski, P. G. *J. Agric. Food Chem.* **1991**, *39*, 2072; (i) Albrecht, H. A.; Beskid, G.; Georgopapadakou, N. H.; Keith, D. D.; Konzelmann, F. M.; Pruess, D. L.; Rossman, P. L.; Wei, C. C.; Christenson, J. G. *J. Med. Chem.* **1991**, *34*, 2857; (j) Albrecht, H. A.; Beskid, G.; Christenson, J. G.; Deitcher, K. H.; Georgopapadakou, N. H.; Keith, D. D.; Konzelmann, F. M.; Pruess, D. L.; Wie, C. C. *J. Med. Chem.* **1994**, *37*, 400; (k) Song, C. W.; Lee, K. Y.; Kim, C. D.; Chang, T.-M.; Chey, W. Y. *J. Pharmacol. Exp. Ther.* **1997**, *281*, 1312; (l) De Voss, J. J.; Sui, Z.; DeCamp, D. L.; Salto, R.; Babe, L. M.; Craik, C. S.; Ortiz de Montellano, P. R. *J. Med. Chem.* **1994**, *37*, 665; (m) Anjaiah, S.; Chandrasekhar, S.; Gree, R. *Adv. Synth. Catal.* **2004**, *346*, 1329; (n) Iorio, M. A.; Paszkowska, R. T.; Frigeni, V. *J. Med. Chem.* **1987**, *30*, 1906; (o) Popp, J. L.; Musza, L. L.; Barrow, C. J.; Rudewicz, P. J.; Houck, D. R. *J. Antibiot.* **1994**, *47*, 411; (p) Chen, T. S.; Petuch, B.; MacConnell, J.; White, R.; Dezeny, G. *J. Antibiot.* **1994**, *47*, 1290; (q) Lam, K. S.; Schroeder, D. R.; Veitch, J. M.; Colson, K. L.; Matson, J. A.; Rose, W. C.; Doyle, T. W.; Forenza, S. *J. Antibiot.* **2001**, *54*, 1.
18. Reviews: (a) Tredwell, M.; Gouverneur, V. *Org. Biomol. Chem.* **2006**, *4*, 26; (b) Ma, J.-A.; Cahard, D. *Chem. Rev.* **2004**, *104*, 6119; (c) Singh, R. P.; Shreeve, J. M. *Synthesis* **2002**, *17*, 2561; (d) Taylor, S. D.; Kotoris, C. C.; Hum, G. *Tetrahedron* **1999**, *55*, 12431; (e) Purrington, S. T.; Kagen, B. S.; Patrick, T. B. *Chem. Rev.* **1986**, *86*, 997; (f) Nyffeler, P. T.; Duron, S. G.; Burkart, M. D.; Vincent, S. P.; Wong, C.-H. *Angew. Chem., Int. Ed.* **2005**, *44*, 192; (g) Singh, R. P.; Shreeve, J. M. *Acc. Chem. Res.* **2004**, *37*, 31.
19. Rahman, M. A.; Shito, F.; Kitamura, T. *Synthesis* **2010**, 27.
20. U.S. Patent 5,386,069, 31.1.1995.
21. Ehlers, P.; Neubauer, A.; Lochbrunner, S.; Villinger, A.; Langer, P. *Org. Lett.* **2011**, *13*, 1618.
22. CCDC-908403–908406 and CCDC-905527 contain all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.