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Short Communication

Site-selective Sonogashira reactions of 1,2-dibromo-3,5-difluorobenzene

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ABSTRACT

A variety of mono- and diethynyl substituted fluorinated benzene derivatives was prepared by Sonogashira cross coupling reactions of 1,2-dibromo-3,5-difluorobenzene. The reactions proceed with very good site-selectivity in favor of position 1, due to electronic and steric reasons.

1. Introduction

The unique properties of fluorine-containing arenes and hetarenes are of considerable importance in organic, medicinal and agricultural chemistry and play an important role as lead compounds [1]. The fluorine atom combines high electronegativity with a small size. Hereby, the replacement of hydrogen by fluorine in organic molecules has often led to dramatic changes in their physico-chemical and biological properties [2]. This has a drastic effect on the overall electronic distribution within the molecule thereby affecting dipole moments and the acidity, basicity or activity of neighboring groups; any of which can affect molecular interactions with receptors or other interacting molecules [3]. Moreover, fluorinated arenes- and hetarenes are useful substrates in transition metal-catalyzed cross-coupling reactions [4]. Aryl fluorides are used as ligands [5] in catalytic reactions and as organocatalysts [6].

In recent years, a number of site-selective palladium(0)-catalyzed cross coupling reactions of polyhalogenated heterocycles have been developed. The site-selectivity of these reactions is generally influenced by electronic and steric parameters [7,8]. For example, our group has reported site-selective palladium(0)-catalyzed cross-coupling reactions of tetrachloropyrimidine, *N*-methyltetrabromo-pyrrole and tetrabromoselenophene [9]. Site-selective Suzuki–Miyaura reactions of 2,3,5-tribromoinden-1-one, tribromopyrazoles, tetrabrominated thiophene and of other polyhalogenated heterocycles have also been studied [10]. Site-selective Sonogashira reactions of dibromides, diiodides or bis(triflates) of fluorinated arenes have, to the best of our knowledge, not been reported to date. Herein, we report the results of our study related to site-selective Sonogashira reactions of 1,2-dibromo-3,5-difluorobenzene. These reactions provide a convenient approach to various fluorinated mono- and dialkynylbenzenes which have, to the best of our knowledge, not been previously prepared.

2. Results and discussion

The Sonogashira reaction of commercially available 1,2-dibromo-3,5-difluorobenzene **1** with different substituted acetylenes **2a-q** (1.0 equiv.) afforded the corresponding 1-alkynyl-substituted 2-bromo-3,5-difluorobenzene derivates **3a-q** in moderate to good yields (Scheme 1, Table 1). The best yields were obtained using 1.0 equivalent of the alkyne, $Pd(PPh_3)_4$ (3 mol%) as the catalyst and Et_3N (2.0 equiv) as the base (THF, 60 °C, 6 h). The formation of the opposite isomer was not observed. The yields depend on the type of acetylene **2** employed. No significant changes in yields could be observed for para-substituted electron-donating, electron-withdrawing, and *ortho*- and *meta*-substituted alkynes. The yield of compound **3o** decreased to 35% when hept-1-yne **2o** was employed (Table 1). However, the successful use of a broad range of different acetylenes in this kind of reaction was successfully shown.

The Sonogashira reaction of **1** with 2.1 equiv. of alkynes **2a-f,j,l,r** afforded the symmetrical *ortho*-substituted ethynylated fluorobenzenes **4a-i** (Scheme 2, Table 2). The best yields were obtained using

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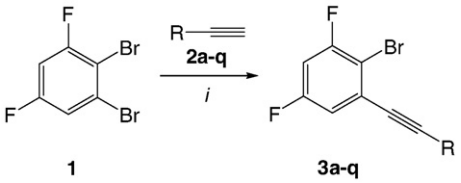
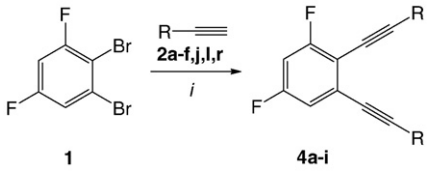


Scheme 1. Synthesis of **3a-q.** Conditions: (*i*): **1** (1.0 equiv), **2a-q** (1.0 equiv), Et_3N (2.0 equiv), $Pd(PPh_3)_4$ (3 mol %), CuI (3 mol %), THF, 60 °C, 6 h.



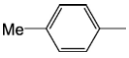
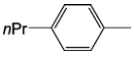
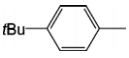
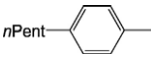
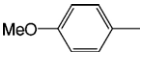
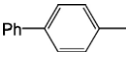
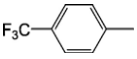
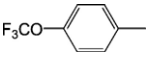
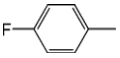
Scheme 2. Synthesis of **4a-i**. Conditions and reagents: (*i*): **1** (1.0 equiv), **2** (2.1 equiv), Et_3N (2.5 equiv), $Pd(PPh_3)_4$ (3 mol %), CuI (3 mol %), THF, 60 °C, 6 h.

2.1 equiv. of the alkyne, $Pd(PPh_3)_4$ (3 mol %) as the catalyst, CuI (3 mol %) and Et_3N (2.5 equiv) as the base (THF, 60 °C, 6 h). The yields of disubstituted ethynyl-fluorobenzenes **4** were not significantly influenced by the *para*-substituent of the acetylene, while *ortho*- and *meta*-substituents resulted in lower yields (Table 2).

The synthesis of unsymmetrical *ortho*-substituted ethynylated fluorobenzenes was next studied. The Sonogashira reaction of selected ethynyl-substituted 2-bromo-3,5-difluorobenzenes **3** with 1.1 equiv. of different substituted acetylenes **2** yielded *ortho*-substituted ethynyl-fluorobenzenes **5a-f** bearing different ethynyl moieties (Scheme 3, Table 3).

The structures of all products were confirmed by spectroscopic methods. In addition, high resolution ^{13}C NMR spectroscopy confirmed the site-selectivity of these reactions. Carbon atom C-7 of the alkyne moiety showed a long range coupling with the fluorine atom (F^1 and F^2) over four bonds with a coupling constant of $^4J_{C\text{-}F} = 4.0$ Hz which appear as two doublets. No coupling was observed for carbon atom C-8.

Table 1
Synthesis of **3a-q**.

2,3	R	% (3)[a]
a		70
b		69
c		67
d		66
e		72
f		66
g		75
h		56
i		59
j		69
k		63
l		61
m		42
n	CH_3COOCH_2—	47
o	*n*Pent—	35
p	$HO(CH_3)_2C$—	59
q	Me_3Si—	59

[a] Yields of isolated products.

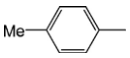
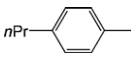
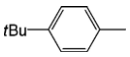
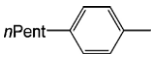
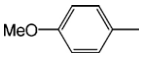
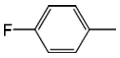
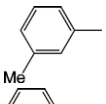
The opposite regioisomer with a long range coupling over three bonds for carbon atom C-7 in the range of 8.0 Hz and for carbon atom C-8 in the range of 3.0 Hz could not be detected. Carbon atom C-2 (C-Br) resonated as a doublet of doublet in the range of 128.0 ppm and showed a typical coupling to the fluorine atom F^2 with a coupling constant of $^2J_{C\text{-}F} = 22.0$ Hz and a coupling to the fluorine atom F^1 with a coupling constant of $^4J_{C\text{-}F} = 4.0$ Hz (Scheme 4).

The structure of **3a** is independently confirmed by X-ray crystal structure analysis which unambiguously proves the constitution of the molecule (Fig. 1) and shows a planar constitution of the mono-substituted ethynyl benzene [11].

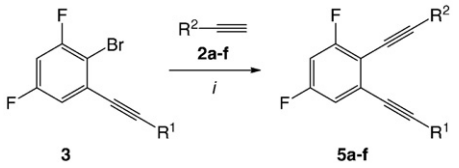
The site-selective formation of **3a-p** and **5a-f** can be explained by electronic and steric reasons. The first attack of palladium (0)-catalyzed cross-coupling reactions generally occurs at the more electronic deficient and sterically less hindered position [12,13]. Position 1 of 1,2-dibromo-3,5-difluorobenzene (**1**) is sterically less hindered because it is located next to a hydrogen and bromine atom, while position 2 is located next to a fluorine- and bromine atom (cf. Scheme 5). In addition, position 1 (located *meta* to the fluorine atom) is more electron deficient than position 2 (located *ortho* to the fluorine atom), due to the π-donating effect of the fluorine atom. The same observations were made for the synthesis of fluorinated terphenyls by site-selective Suzuki–Miyaura reactions of halogenated fluorobenzenes [14,15].

In addition, this assumption could be confirmed by Density Functional Theory calculations (DFT) at the B3LYP level of theory using a 6–31 G* basis set. In compound **1** the C-1–Br bond is lengthened by about 0.7 pm compared to the C-2—Br bond with the neighboured fluorine atom (189.7 pm vs. 189.0 pm). Of course, the lengthening indicates a weaker C-1—Br bond, which can be preferentially attacked

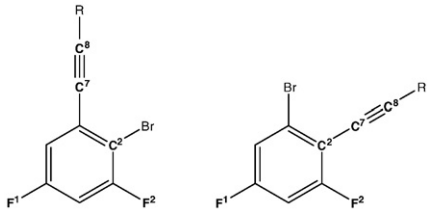
Table 2
Synthesis of **4a-i**.

4	2	R	% (4)[a]
a	**a**		56
b	**b**		53
c	**c**		62
d	**d**		56
e	**e**		56
f	**f**		57
g	**j**		69
h	**r**		42
i	**l**		43

[a] Yields of isolated products.



Scheme 3. Synthesis of **5a-f**. Conditions and reagents: (*i*): **3** (1.0 equiv), **2** (1.1 equiv), Et_3N (2.0 equiv), $Pd(PPh_3)_4$ (3 mol %), CuI (3 mol %), THF, 60 °C, 6 h.



Scheme 4. Numbering of compound **3** (left) and of the opposite regioisomer (*not* observed, right).

(cf. Fig. 2). Also the calculated natural charges from Natural Bond Orbital analysis (NBO) support this view (Fig. 3). The NBO-charges at the reactive centers in compound **1** indicate that carbon atom C-1 carries only half of the charge than the carbon atom C-2 (C-1 = −0.116 [a.u.] vs. C-2 = −0.227 [a.u.]). It is well known from literature that the less electronegative position which is the C-1 carbon in compound **1** will be attacked preferentially. Furthermore the NBO analysis shows that the higher charge at carbon C-2 is related to the charge transfer from the neighboured fluorine atom which strongly donates charge from its lone-pairs into the C-2—C anti-bond orbital. The charge transfer weakens the C-2—C bond but strengthens the neighboured C-2—Br bond leading to shorter bond length relative to that of the C-1—Br bond. Of course, this effect is stronger for the fluorine atoms located in *ortho/para* position (cf. Fig. 3). A crude estimate of the C—Br bond strength can be obtained from the calculated energy differences (isodesmic reaction) between 1-bromo-2,4-fluorobenzene and 1-bromo-3,5-fluorobenzene. The latter compound has a 5.0 kJ mol^{-1} lower energy explaining its higher reactivity empirically.

2.1. Conclusions

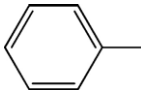
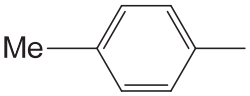
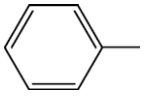
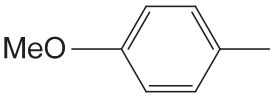
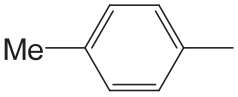
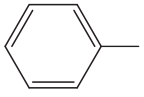
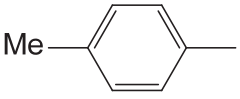
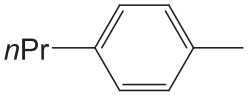
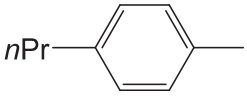
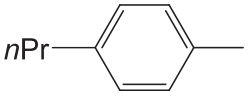
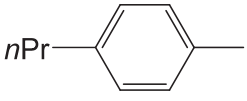
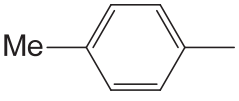
In conclusion, we demonstrated an easy and applicable route for the versatile synthesis of mono- and disubstituted ethynyl-fluorobenzenes by site-selective Sonogashira reactions of 1,2-dibromo-3,5-difluorobenzene. The site-selectivity in favor of position 1 can be explained by electronic and steric reasons and was confirmed by X-ray structure analysis, high resolution ^{13}C NMR spectroscopy and Density Functional Theory calculations (NBO, isodesmic reaction). The application of the concept outlined herein to other fluorinated arenes is currently studied in our laboratories.

3. Experimental section

3.1. General

All reactions were carried out in oven-dried reaction pressure tubes under Argon atmosphere. Tetrakis(triphenylphosphine)palladium(0) was purchased from a commercial source (ABCR). 1,2-Dibromo-3,5-difluorobenzene (TCI), copper iodide (Acros) and the corresponding alkynes (Acros, AlfaAesar, TCI) were purchased from a commercial source. Solvent (THF) was distilled and purged with argon before use. Triethylamine (Et_3N) was purchased from a commercial source (Acros) and purged with argon before use. Thin layer chromatography (TLC) was run on Merck precoated aluminium plates (Si 60F254). Column chromatography was performed using Merck Silicagel 60 (0.043–0.06 mm). NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers. ^{13}C- and ^{1}H-NMR spectra were referenced to signals of deutero solvents, respectively. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column using helium carrier gas. ESI HR-MS measurements were performed on an Agilent 1969A TOF mass-spectrometer.

Table 3
Synthesis of **5a-f**.

5	3	2	R^1	R^2	% (5)[a]
a	**a**	**b**			60
b	**a**	**f**			61
c	**b**	**a**			55
d	**b**	**c**			62
e	**c**	**a**			55
f	**c**	**b**			58

[a] Yields of isolated products.

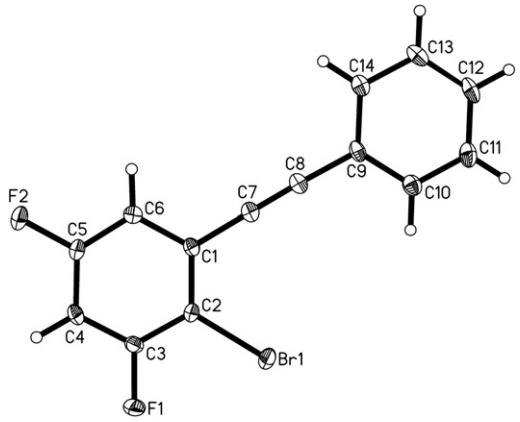


Fig. 1. ORTEP drawing of **3a**. Displacement ellipsoids are drawn at the 30% probability level.

X-ray crystal structure analysis of **3a**: Data were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F2 with the SHELXTL software package (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.). XP (Bruker AXS) was used for graphical representation. crystal data: C14H7BrF2, $M = 293.11$, triclinic, space group $P\bar{1}$, $a = 6.8718(4)$, $b = 7.3507(5)$, $c = 12.0591(8)$ Å, $\alpha = 80.181(5)$, $\beta = 79.038(5)$, $\gamma = 74.648(5)°$, $V = 572.02(6)$ Å3, $T = 150(2)$ K, $Z = 2$, $\mu = 3.59$ mm^{-1}, 9493 reflections measured, 2633 independent reflections (Rint = 0.0347), final R values ($I > 2\sigma(I)$): R1 = 0.028, wR2 = 0.0562, final R values (all data): R1 = 0.0398, wR2 = 0.0588, 154 refined parameters. CCDC^{-}… contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.2. Calculations

Geometry optimizations have been carried out using the Gaussian 03 programme package. We used the B3LYP method including the Becke-3-parameter gradient corrected exchange functional combined with the gradient-corrected correlation LYP functional by Lee, Yang and Parr to calculate the structures of the compounds. No imaginary frequencies were found indicating that all geometries represent at least local minimum structures on the potential energy surface. For all structures the calculations have been performed with 6–31 G* basis set implemented in Gaussian 03 [16]. Additionally we calculated the natural atomic charges by applying the NBO program as implemented in Gaussian 03. All calculations have been carried out on the HPPC-Cluster in Rostock.

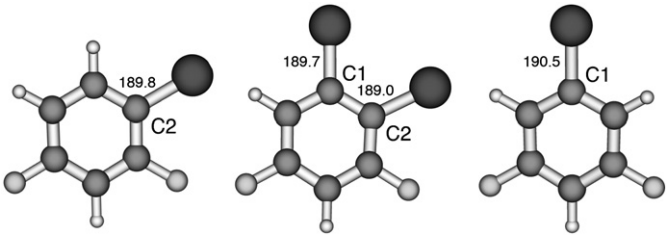


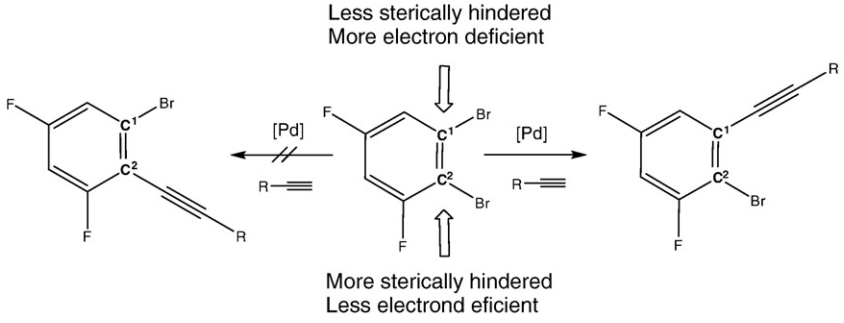
Fig. 2. B3LYP/ 6–31G* calculated structures. The bond lengths are given in ppm.

3.3. General procedure for the synthesis of 3a-q

A suspension of 1,2-dibromo-3,5-difluorobenzene **1**, $Pd(PPh_3)_4$ (3 mol %), CuI (3 mol %) in THF (3 mL/mmol **1**) was degassed by bubbling argon through the solution for 10 minutes in a oven dried pressure tube. The acetylene **2** (1.0 equiv.) and finally triethylamine (2.0 equiv.) were added by syringe. The mixture was heated at 60 °C for 6 h. After cooling to room temperature the organic and aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The product was purified by column chromatography (silica gel, EtOAc/heptane).

3.4. 2-bromo-3,5-difluorophenyl-1-ethynylbenzene (3a)

Starting with **1** (271.9 mg, 1.0 mmol), $Pd(PPh_3)_4$ (34.6 mg, 3 mol%), CuI (5.7 mg, 3 mol%), ethynylbenzene **2a** (0.11 mL, 1.0 mmol), Et_3N (0.28 mL, 2.0 mmol) and THF (3.0 mL), **3a** was isolated by column chromatography (heptane) as a colorless solid (0.203 g, 70%); mp = 71–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (d*t*, ^3J = 8.4 Hz, ^{4}J = 2.8 Hz, 1H, CH), 7.63–7.68 (ddd, $J = 1.5$ Hz, $^4J_{H\text{-}H}$ = 2.9 Hz, $^3J_{H\text{-}F} = 8.6$ Hz, $^5J_{H\text{-}F} = 1.5$ Hz, 1H, CH), 7.25–7.33 (m, 3H, CH_{Ph}), 7.46–7.52 (m, 2H, CH_{Ph}). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 86.2$ (dd, $^4J_{C\text{-}F} = 4.0$ Hz, C_{alkyne}), 96.1 (C_{alkyne}), 105.0 (*t*, $^3J_{C\text{-}F} = 26.0$ Hz, CH), 107.9 (dd, $^2J = 22.0$ Hz, $^4J_{C\text{-}F} = 4.0$ Hz, C-Br) 115.6 (dd, $^3J_{C\text{-}F}$ = 24.0 Hz, $^5J_{C\text{-}F} = 4.0$ Hz, CH), 122.0 (C_{Ph}), 128.0 (dd, $^4J_{CF} = 12.0$ Hz, $^4J_{C\text{-}F} = 12.0$ Hz, C) 128.5, 129.3, 131.9 (CH_{Ph}), 159.5 (dd, ^1J = 247.0 Hz, $^4J = 12.0$ Hz, C-F), 161.3 (dd, $^1J = 248.0$ Hz, $^4J = 13.0$ Hz, C-F). ^{19} F NMR (282.4 MHz, $CDCl_3$): $\delta = -99.19$ (F-2), -110.78 (F-1). IR (ATR, cm^{-1}): = 3084 (w), 3020 (w), 2918 (w), 2849 (w), 2209 (w), 1578 (s), 1489 (w), 1461 (w), 1440 (s), 1416 (s), 1356 (m), 1275 (w), 1228 (w), 1170 (w), 1122 (s), 996 (m), 980 (w), 913 (w), 857 (m), 835 (m), 750 (s), 685 (s), 599 (s), 566 (w), 524 (s). MS (EI, 70 eV): *m/z* (%) = 292 (M+, 100), 212 (38), 193 (21), 173 (4), 106 (7), 96 (3). HRMS (EI, 70 eV): calcd. for $C_{14}H_7BrF_2$ 291.96937, found 291.969201. Anal. calcd. for $C_{14}H_7BrF_2$ (293.11): C, 57.37; H, 2.41. Found: C, 57.34; H, 2.654.



Scheme 5. Possible explanation for the site-selectivity of cross-coupling reactions of **1**.

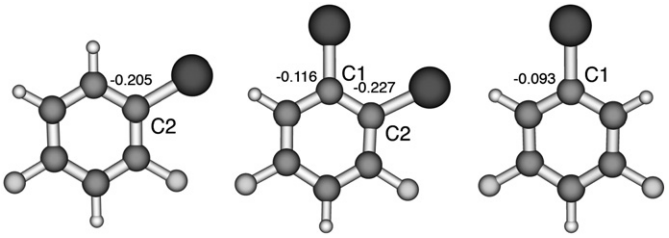


Fig. 3. NBO Natural Charges calculated on the B3LYP/6-31 G* optimized structures. The charges are given in units of e (elementary charge).

3.5. General procedure for the synthesis of 4a-i

A suspension of 1,2-dibromo-3,5-difluorobenzene **1**, $Pd(PPh_3)_4$ (3 mol%), CuI (3 mol%) in THF (3 mL/mmol **1**) was degassed by bubbling argon through the solution for 10 minutes in a oven dried pressure tube. The acetylene **2** (2.1 equiv.) and finally triethylamine (2.5 equiv.) were added by syringe. The mixture was heated at 60 °C for 6 h. After cooling to room temperature the organic and aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The product was purified by column chromatography (silica gel, EtOAc/heptane).

3.6. 3,5-difluoro-1,2-(phenylethynyl)benzene (4a)

Starting with **1** (271.9 mg, 1.0 mmol), $Pd(PPh_3)_4$ (34.6 mg, 3 mol-%), CuI (5.7 mg, 3 mol-%), ethynylbenzene **2a** (0.23 mL, 2.1 mmol), Et_3N (0.35 mL, 2.5 mmol) and THF (3.0 mL), **3a** was isolated by column chromatography (heptane) as a slightly yellowish oil (0.176 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 (d*t*, ^3J = 8.9 Hz, ^{4}J = 2.6 Hz, 1H, CH), 7.63–7.68 (ddd, J = 1.5 Hz, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{H\text{-}F}$ = 2.5 Hz, $^5J_{H\text{-}F}$ = 1.3 Hz, 1H, CH), 7.21–7.32 (m, 6H, CH_{Ph}), 7.43–7.52 (m, 4H, CH_{Ph}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.8 (*d*, ^5J = 1.5 Hz, C_{alkyne}), 86.3 (*t*, ^4J = 4.0 Hz, C_{alkyne}), 95.6 (C_{alkyne}), 98.3 (C_{alkyne}), 104.4 (*d*, $^2J_{CF}$ = 26.4 Hz, CH), 111.2 (*dd*, $^2J_{C\text{-}F}$ = 21.2 Hz, $^4J_{C\text{-}F}$ = 3.8 Hz, C), 114.0 (dd, $^2J_{C\text{-}F}$ = 24.1 Hz, $^4J_{C\text{-}F}$ = 3.5 Hz, CH), 122.4 (C), 122.8 (C), 128.4 (CH), 128.7 (C),128.5, 128.8, 129.6, 131.7, 131.8 (CH-Ar), 161.5 (dd, ^1J = 250.9 Hz, ^3J = 13.4 Hz, C-F), 162.9 (dd, ^1J = 252.9 Hz, ^3J = 14.1 Hz, C-F). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −103.87 (F-2), -107.45 (F-1). IR (ATR, cm^{-1}): = 3084 (w), 3020 (w), 2928 (w), 2213 (w), 1577 (s), 1490 (m), 1461 (w), 1441 (m), 1413 (s), 1357 (m), 1276 (w), 1229 (w), 1170 (w), 1121 (s), 1067 (w), 995 (m), 981 (m), 913 (w), 857 (m), 835 (m), 751 (s), 686 (s), 599 (s), 566 (m), 523 (m). MS (EI, 70 eV): *m/z* (%) = 314 (M+, 100), 294 (10), 288 (5), 273 (2), 236 (2), 156 (8). HRMS (EI, 70 eV): calcd. for $C_{22}H_{12}F_2$ 314.09016, found 314.089667.

3.7. General procedure for the synthesis of 5a-f

A suspension of substituted ethynyl-fluorobenzenes **3** (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol %), CuI (3 mol %) in THF (3 mL/mmol 3) was degassed by bubbling argon through the solution for 10 min in an oven-dried pressure tube. The acetylene **2** (1.1 equiv.) and finally triethylamine (2.0 equiv.) were added by syringe. The mixture was heated at 60 °C for 6 h. After cooling to room temperature the organic and aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The product was purified by column chromatography (silica gel, EtOAc/heptane).

3.8. 3,5-difluoro-1-(phenylethynyl)-2-(4-methylphenyl)-benzene (5a)

Starting with **3a** (293 mg, 1.0 mmol), $Pd(PPh_3)_4$ (34.6 mg, 3 mol-%), CuI (5.7 mg, 3 mol-%), 1-ethynyl-4-methybenzene **2b** (0.144 mL, 1.1 mmol), Et_3N (0.28 mL, 2.0 mmol) and THF (3.0 mL), **5a** was isolated by column chromatography (heptane) as a slightly yellowish oil (0.210 g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 6.76 (d*t*, $^3J_{HF}$ = 8.9 Hz, ^4J = 2.4 Hz, 1H, CH), 6.99 (ddd, $^3J_{H\text{-}F}$ = 8.9 Hz, $^4J_{H\text{-}H}$ = 2.4 Hz, $^5J_{H\text{-}F}$ = 1.3 Hz, 1H, CH), 7.07 (*d*, ^3J = 8.1 Hz, 7.05–7.11 (m, 2H, CH), 7.25–7.31 (m, 3H, CH) 7.38 (d, ^3J = 8.1 Hz, 2H, CH), 7.45–7.50. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 80.2 (d, ^5J = 1.7 Hz, C_{alkyne}), 86.4 (t, ^4J = 4.5 Hz, C_{alkyne}), 95.5 (C_{alkyne}), 98.6 (C_{alkyne}), 104.5 (d, $^2J_{CF}$ = 25.7 Hz, CH), 114.5 (dd, $^2J_{C\text{-}F}$ = 23.2 Hz, $^4J_{C\text{-}F}$ = 3.8 Hz, CH), 119.8, 122.4 (C), 128.5, 129.0, 129.1, 131.6, 131.8 (CH), 132.4, 139.0 (C), 161.5 (dd, ^1J = 250.8 Hz, ^3J = 13.3 Hz, C-F), 162.8 (dd, ^1J = 252.8 Hz, ^3J = 13.9 Hz, C-F). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −104.03 (F-2), -107.85 (F-1). IR (ATR, cm^{-1}): = 3082 (w), 3059 (w), 3028 (w), 2916 (w), 2854 (w), 2206 (m), 1608 (m), 1572 (s), 1511 (s), 1468 (m), 1430 (m), 1360 (m), 1283 (m), 1229 (s), 1168 (s), 1132 (w), 1114 (s), 1071 (w), 1007 (m), 930 (m), 857 (m), 830 (m), 818 (s), 756 (s), 729 (m), 690 (s), 603 (m), 568 (m), 531 (m), 461 (m). MS (EI, 70 eV): *m/z* (%) = 328 (M+, 100), 327 (25), 326 (11), 325 (27), 312 (22). HRMS (EI, 70 eV): calcd. for $C_{23}H_{14}F_2$ 328.35407, found 328.353998. Anal. calcd. for $C_{23}H_{14}F_2$ (328.35): C, 84.13; H, 4.30. Found: C, 84.19; H, 4.488.

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