Tetrahedron 69 (2013) 11191–11196

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Building block synthesis of predominantly (*E*) symmetrical and unsymmetrical 1,2-difluorostilbenes from 1,2-dibromo-1,2-difluoroethene

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ARTICLE INFO

Article history:
Received 31 August 2013
Received in revised form 12 October 2013
Accepted 23 October 2013
Available online 28 October 2013

Keywords:
1,2-Difluorostilbenes
Palladium
Cross-coupling
Catalysis
Building block

ABSTRACT

An efficient synthesis of predominantly (*E*) symmetrical or unsymmetrical 1,2-difluorostilbenes based on the Suzuki–Miyaura palladium-catalyzed cross-coupling reaction of arylboronic acids with predominantly (*E*)-1,2-dibromo-1,2-difluoroethene in the presence of Cs_2CO_3 in toluene is described. The reaction preserved the stereochemistry of the building block and performed in good yield independently of the electron-withdrawing or electron-donating character of the substituents.

1. Introduction

Introducing a fluorine atom in an organic compound very often brings different properties either for biological or in material science applications. The special properties of fluorine, such as strong electronegativity, small size (comparable to hydrogen) and low polarizability of the C–F bond are responsible for these effects. Indeed, an increasing number of drugs or photoelectronic devices contain fluorine, the presence of which often is of major importance to their activity. There are by far fewer reports in the literature on disubstituted-1,2-difluorinated olefins when compared to disubstituted monofluorinated olefins, which have found numerous applications, especially in biology. Analogues of combrestatin, a natural oxygenated stilbene bearing two fluorine-atoms on the central double bond, have been synthesized as tubulin aggregation inhibitors. In most of the cases, the difluorinated analogues were shown to be as efficient for tubulin aggregation inhibition as their unfluorinated counterpart but proved to be by far less toxic.[1a] Very recently, Dalvit and Vulpetti proposed 1,2-difluoroethene as an amide (O=C–NH) structural analogue for building peptidomimetics by a QSAR approach based on ^{19}F NMR displacement.[1b] On the other hand, the photochemistry of 1,2-difluorostilbenes has received much attention: they isomerize very efficiently in the *Z* isomer by photo-irradiation, as their non-fluorinated analogues but with little halogen elimination, unlike others halogens, especially Br and I.[2a,2b] (*Z*) 1,2-Difluoristilbenes are also less prone under irradiation to phenantrene formation and are thermally more stable than their non-fluorinated analogues.[2c,2d] These properties led to the introduction of difluoroethene bridges in many conjugated molecules or materials designed to have opto-electronic properties. Substituted difluorostilbenes resulted in nematic crystals, the properties of which can be optimized.[3a] For example, (*E*)-1-(*trans*-4-alkylcyclohexyl)-2-(4-chlorophenyl)-difluoroethylene has been shown to grow into nematic crystals that show great promise for super twisted nematic displays due to their high contrast and rapid response time, but also due to their improved UV stability.[3b-e] Substituted 1,4-bis(1,2-difluoro-2-phenylethenyl)-benzene show electro-optical properties.[4a] Due to their enhanced stability they have found applications as sensors.[4b] Cyanin dyes linked by a perfluorinated polymethine chain, which implies the 1,2-difluroethene bridge, have been synthesized.[5] Theoretical calculations have shown that 1,2-bis-(3-thienyl)-1,2-difluoroethene derivatives exhibit non-linear optical properties and can act as photoswitches like their non-fluorinated analogues with modulated properties.[6] (*E*)-1,2-Difluoro-1,2-di-2-thienylethene, (*E*)-1,2-difluoro-1,2-bis(5-

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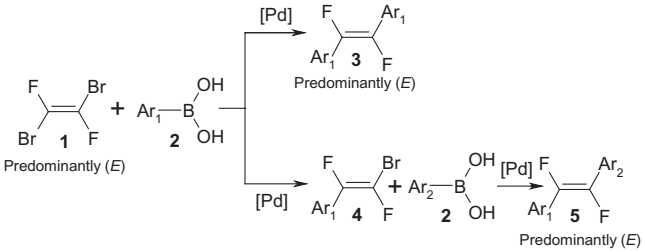
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.10.067

trimethylsilyl-2-thienyl)ethene and (*E*)-1,2-difluoro-1,2-bis(4-methoxy-5-trimethylsilyl-2-thienyl)-ethene monomers were prepared and polymerized under controlled oxidation.[7a,7b] The introduction of fluorine-atoms in the vinylene units yields a blue optical band gap in the obtained thin films.[7c,7d] Poly[5,5-(5′,6′-dioctyloxy-4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)-*alt*-1,2-difluorovinylene]polymer have been synthesized and exhibited also a higher band gap. This material have found applications in polymer solar cells.[8] Difluorinated olefins have also been used as bridging ligands between organometallic centers.[9]

These various applications push us to report a novel synthesis of 1,2-difluorostilbenes, symmetrical **3** and unsymmetrical **5** from the 1,2-dibromo-1,2-difluoroethene **1** building block. The cross-coupling reaction of predominantly (*E*) 1,2-dibromo-1,2-difluoroethene with arylboronic acids **2** using palladium(0) as the catalyst in toluene and cesium carbonate as a base affords, following the protocol established for synthesizing monofluoroolefins from 1,1-bromofluorolefins by Burton group[10] and our group[11] (for reviews see Ref. 12), the expected 1,2-difluorostilbenes either symmetrical or unsymmetrical in good yield (Scheme 1).



Scheme 1. Synthesis of 1,2-difluorostilbenes.

2. Results and discussion

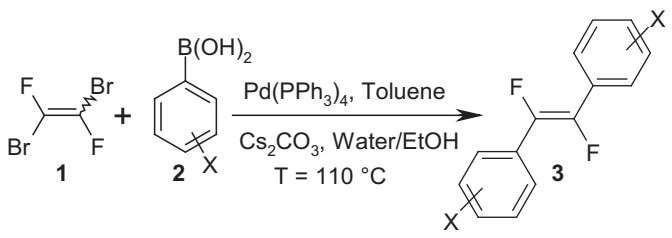
In the literature only a few studies have described the synthesis of 1,2-difluoroolefins in a simple, versatile, and stereoselective manner. The most important syntheses are summarized below. Dixon first reported the preparation of symmetrical (*E*)-1,2-difluorostilbenes via the reaction of tetrafluoroethene with phenyllithium in ether at −60 °C.[13] Unsymmetrical (*E*)-1,2-difluorostilbenes have been obtained via the reaction of trifluorostyrenes and aryllithiums in hexane at −80 °C.[14] Trifluorostyrene precursors were obtained by treatment of iodobenzenes with tetrafluoethylene in the presence of *n*-butyl lithium in a mixture of *n*-hexane and diethyl ether at −80 °C. Recently, trifluorostyrenes have been obtained by the reaction of phenyl boronic acids with chloro- or bromotrifluoroethylene catalyzed by palladium.[15] The Dixon synthesis has been employed for the synthesis of opto-electronic materials and in the polymer field.[7b,16]

Shimizu and Kuroboshi et al. have developed a highly stereoselective synthesis of (*E*) and (*Z*) β-bromo-α,β-difluorostyrene (ArCF=CFBr) from $ArCH(OH)CFBr_2$.[17] The treatment of tribromofluoromethane (CBr_3F) with BuLi in a mixture of THF and Et_2O at −130 °C afforded dibromofluoromethyl lithium, which was reacted with an aldehyde to give the fluorinated alcohol ($ArCH(OH)CFBr_2$). This alcohol was stereoselectively converted to pure (*E*)-1-bromo-1,2-difluoroolefin via fluorination with Et_2NSF_3, followed by dehydrobromination with lithium 2,2,6,6-tetramethylpiperidide (LiTMP), in THF at −98 °C for 10 min. The use of less crowded organic bases or superbases (DBU, $Bu_4N^+OH^-$, BEMP) on the same intermediate led to a mixture that was predominantly (*Z*). The obtained (*E*)-1-bromo-1,2-difluoroolefines (RCF=CFBr) were coupled with silanes, stannanes or boronic acids under palladium catalysis to afford in good yield (*Z*) difluoroolefins (RCF=CFR) with a complete retention of the geometry of the double bond. The obtained (*E*)-1-bromo-1,2-difluoroolefines (RCF=CFBr) could also been transformed in lithium reagents (RCF=CFLi) by treatment with butyllithium in THF/Et_2O at −130 °C, then condensed with electrophiles at the same temperature, with preservation of the double bond geometry. Recently Giannini et al. used this method to prepare (*Z*)-difluorocombretatastin analogues by coupling conveniently substituted (*E*)-β-bromo-α,β-difluorostyrenes with 3,4,5-trimethoxybenzenboronic acid in presence of palladium.[1a]

Burton et al. developed several methods for the preparation of symmetrical or unsymmetrical (*E*) (and, recently, (*Z*)) 1,2-difluorostilbenes. The key compounds in their approach of (*E*) isomers are (*Z*)-(1,2-difluoroethenyl)-tributylstannane (HFC=$CFSnBu_3$) and (*E*)-(1,2-difluoro-1,2-ethenediyl)-bis-[tributylstannane], which are obtained in three or four steps. In the first step chlorotrifluoroethylene (F_2C=CFCl) was metalated by *n*-butyl lithium in THF at −80 °C, then reacted with chlorotrimethylsilane to afford (1,2,2-trifluoroethenyl)-trimethylsilane (F_2C=$CFSiMe_3$), which was not isolated. In the second step (1,2,2-trifluoroethenyl)-trimethylsilane was reduced in situ by $LiAlH_4$ in THF to afford a mixture containing predominantly (*Z*)-(1,2-difluoroethenyl)-trimethylsilane (HFC=$CFSiMe_3$) (*Z*:*E*, 91:9), which was isolated by flash distillation. Then (1,2-difluoroethenyl)-trimethylsilane was reacted in THF with bis(tributyltin)oxide ($Bu_3SnOSnBu_3$) in the presence of a catalytic amount of tetrabutylammonium fluoride to give the desired, predominantly (*Z*), (1,2-difluoroethenyl)-tributylstannane (HFC=$CFSnBu_3$), which could be further purified by chromatography. Finally (*E*)-(1,2-difluoro-1,2-ethenediyl)-bis-[tributylstannane] (Bu_3SnFC=$CFSnBu_3$) was obtained by metalating the monostannane by lithium, 2,2,6,6-tetramethylpiperidide (LiTMP) in THF at −90 °C and trapping the intermediate with tributyltin chloride.[18a] Symmetrical (*E*)-1,2-difluorostilbenes were readily obtained via stereospecific Pd(0) coupling of (*E*)-(1,2-difluoro-1,2-ethenediyl)-bis-[tributylstannane] (Bu_3SnFC=$CFSnBu_3$) with aryliodides using $Pd(PPh_3)_4$/CuI as a catalyst in Stille–Liebeskind conditions.[18b] Unfortunately (*Z*)-(1,2-difluoro-1,2-ethenediyl)-bis-[tributylstannane] stereoisomers afforded no coupling products in the same conditions. Nevertheless, unsymmetrical (*Z*)-1,2-distilbenes were obtained using a combination of the previously described protocols. First, (*E*)-(1,2-difluoroethenyl)-trimethylsilane, obtained by the photoisomerization of the (*Z*) isomer by UV light in presence of a catalytic amount of phenyldisulfide. (*E*)-(1,2-Difluoroethenyl)-trimethylsilane was converted into (*E*)-1,2-difluorovinyliodide (HFC=CFI) by iodine at room temperature.[18c] (*E*)-1,2-difluorovinyliodide (HFC=CFI) was treated with zinc and coupled with aryliodide using palladium catalysis affording (*Z*)-α,β-difluorostyrene (PhFC=CHF). In turn (*Z*)-α,β-difluorostyrene was transformed into (*E*)-1,2-difluoro-2-aryl-tributylstannylethenes by metalation by lithium 2,2,6,6-tetramethylpiperidide (LiTMP) and trapping at −78 °C with tributyltin chloride.[18d] Then (*E*)-1,2-difluoro-2-aryl-tributylstannylethenes were coupled with the second aryliodide in the Stille–Liebeskind conditions described above to afford (*Z*)-1,2-difluorostilbenes.[18e]

We described here an original method for the stereoselective synthesis of (*E*)-1,2-difluorostilbenes in only two steps for unsymmetrical 1,2-difluorostilbenes and in a single step for symmetrical 1,2-difluorostilbenes. The starting reagent **1** 1,2-dibromo-1,2-difluoroethene is a non-volatile liquid product (boiling point about 85 °C), which is perfectly stable and which is commercially available as a mixture of stereoisomers (*E*/*Z*: 85/15). When 1,2-dibromo-1,2-difluoroethene **1** was reacted with 2.3 equiv of phenyl boronic acids using tetrakis(triphenylphosphine)palladium(0) as the catalyst in toluene and cesium carbonate (Cs_2CO_3) as a base in ethanol/water at 110 °C during 3 h, symmetrical 1,2-

difluorostilbenes **3** predominantly (*E*) were obtained in good yield (Scheme 2 and Table 1, entries a–e).[17,19]



Scheme 2. Synthesis of symmetrical 1,2-difluorostilbenes **3** predominantly (*E*) from 1,2-dibromo-1,2-difluoroethene **1** (*E*/*Z*: 85/15).

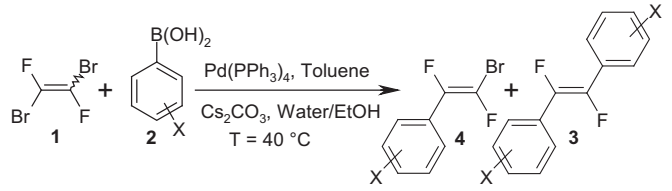
Table 1
Synthesis of symmetrical 1,2-difluorostilbenes **3** from 1,2-dibromo-1,2-difluoroethene **1** (*E*/*Z*: 85/15)

Entry	Substituent	**3** Yield (%)[a]	**3** (*E*/*Z*)[b]
a	*p*-NMe_2	84	83/17
b	*p*-Br	79	80/20
c	3,4-MeO	68	85/15
d	*m*-NO_2	72	79/21
e	*p*-NO_2	74	86/14

[a] Isolated yield.
[b] From ^{19}F NMR.

The yields are largely independent of the electron-acceptor or electron-donor character of the substituents. The stereochemistry of the starting material was always preserved in the obtained symmetrical 1,2-difluorostilbenes **3**. These results prove that the starting reagent **1** did not isomerize under our coupling conditions, contrary to the results we found in the stereoconvergent formylation of (*E*/*Z*)-β-bromo-β-fluorostyrenes mixture to (*Z*)-α-fluorocinnamic aldehydes.[11f]

In order to prepare asymmetrical 1,2-difluorostilbenes using the same methodology we needed to stop the reaction after the substitution of only one bromine. We studied the preparation of 1-bromo-1,2-difluorostyrenes **4** by varying the ratio of the reagents. When phenyl boronic acids **2** were reacted with 1,2-dibromo-1,2-difluoroethene **1** in excess in the same catalysis conditions as before, but at lower temperature we formed the expected 1-bromo-1,2-difluorostyrenes **4** but also the disubstituted product **3**. After careful optimization, in the best conditions (3 equiv of **1**, 40 °C, 4 h) the monosubstituted product **4** was formed predominantly, but the disubstituted product **3** could not be totally avoided (Scheme 3). Both products **3** and **4** were separated by chromatography on silica using ethyl acetate/petroleum ether (5/95) as an eluent. Table 2 summarizes the results for various substituents. The reaction conditions are robust and do not need optimization in function of the electron-withdrawing or electron-donating character of the substituents.



Scheme 3. Synthesis of 1-bromo-1,2-difluorostyrenes **4** predominantly (*Z*) from 1,2-dibromo-1,2-difluoroethene **1** (*E*/*Z*: 85/15).

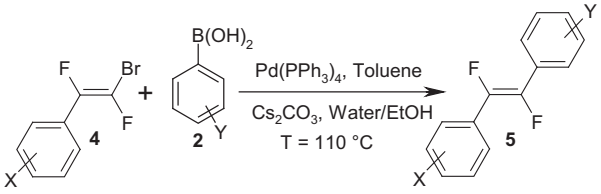
Table 2
Synthesis of 1-bromo-1,2-difluorostyrenes **4** from 1,2-dibromo-1,2-difluoroethene **1** (*E*/*Z*: 85/15)

Entry	Substituent	**4** yield (%)[a]	**4**/**3**	**4** (*Z*/*E*)[b]	**3** (*E*/*Z*)[b]
a	*p*-NMe_2	62	79/21	82/18	85/15
b	*p*-Br	60	78/22	87/13	85/15
c	3,4-MeO	58	80/20	90/10	88/12
d	*m*-NO_2	65	83/17	85/15	80/20
e	*p*-NO_2	68	81/19	84/16	82/18

[a] Isolated yield.
[b] From ^{19}F NMR.

Here also the obtained yields were good (Table 2, entries a–e). Burton and collaborators have shown that the (*E*)-1,1-bromofluorostyrene isomer reacts faster than the (*Z*) isomer in palladium catalysis.[10h,10i] We observed the same effect although smaller in the copper stereoselective cyanation of β-bromo-β-fluorostyrenes.[11g] No such effect is observed here. Despite the excess of 1,2-dibromo-1,2-difluoroethene **1** the 1-bromo-1,2-difluorostyrenes **4** almost kept the stereochemistry of the starting material (*Z*/*E*: 85/15) indicating that both stereoisomers reacted similarly.

The synthesis of unsymmetrical 1,2-difluorostilbenes **5** from 1-bromo-1,2-difluorostyrenes **4** was straightforward. 1-Bromo-1,2-difluorostyrenes **4** as *E*/*Z* mixture roughly 85/15 obtained in the previous reaction were heated in presence of phenyl boronic acids **2** with the same catalytic system as previously (tetrakis-(triphenylphosphine)palladium(0) as the catalyst in toluene and cesium carbonate (Cs_2CO_3) as a base in ethanol/water) at 110 °C during 3 h (Scheme 4). Table 3 summarizes the results. Here also the stereochemistry of the starting 1-bromo-1,2-difluorostyrenes **4** is preserved. Table 3 shows that the electron-donating or electron-withdrawing substituents can be introduced in any order. Neither the yield nor the stereoselectivity are modified.



Scheme 4. Synthesis of unsymmetrical 1,2-difluorostilbenes **5** predominantly (*E*) from 1-bromo-1,2-difluorostyrenes **4**.

Table 3
Synthesis of unsymmetrical 1,2-difluorostilbenes **5** from 1-bromo-1,2-difluorostyrenes **4** (*Z*/*E* ~ 85/15)

Entry	**4**	X	Y	**5** yield (%)[a]	**5** (*E*/*Z*)[b]
a	**a**	*p*-NMe_2	*p*-NO_2	85	81/19
b	**b**	*p*-Br	*p*-CHO	79	85/15
c	**e**	*p*-NO_2	*p*-NMe_2	78	83/17

[a] Isolated yield.
[b] From ^{19}F NMR.

We demonstrated in a previous paper that a phenyl bearing a phenol function protected by a methoxymethyl (MOM) ether group behaves similarly to methoxy groups during Suzuki–Miyaura palladium-catalyzed cross-coupling reaction with arylboronic acids and may be deprotected without loss of a fluorine atom in the vinylic position in the resveratrol series.[11d] Therefore, this synthesis paves the way to the synthesis of difluorinated resveratrol, pterostilbene and more complex structures, such as viniferin.

3. Conclusion

In conclusion, the cross-coupling reaction of arylboronic acids with predominantly (*E*)-1,2-dibromo-1,2-difluoroethene,

which is commercially available, was achieved using tetrakis-(triphenylphosphine)palladium(0) as the catalyst in toluene and cesium carbonate as a base to afford symmetrical or unsymmetrical difluorostilbenes in good yields with the same geometry as the starting building block. The method was applied to a variety of boronic acids, which opens the route to a general synthesis of 1,2-diflurostilbenes bearing reactive substituents like phenol groups. The 1-bromo-1,2-difluorostilbene intermediate may be potentially transformed into (*E*)-α,β-difluorocinnamaldehydes by formylation with carbon monoxide and sodium formate catalyzed by palladium, or with cyanide to afford (*E*)-α,β-difluorocinnamonitrile or coupled with itself to give (1*E*,3*E*)-1,2,3,4-tetrafluoro-1,4-diphenyl-buta-1,3-dienes.[11g,11e] Therefore, this general synthesis of (*E*)-difluorostilbenes opens the way to access new families of potentially active compounds. Work is in progress in our laboratory to produce (*Z*)-1,2-dibromo-1,2-difluoroethene in order to obtain compounds with opposite stereochemistry by the same method.

4. Experimental

4.1. General

1,2-Dibromo-1,2-difluoroethene was obtained from ABCR (Karlsruhe, Germany) as as a mixture of stereoisomers (*E*/*Z*: 85/15). All other commercially available products were purchased from Aldrich (Saint-Quentin Fallavier, France) and used as received. Deuterated solvents (99.9% or better) were purchased from Eurisо-Top (Saint-Aubin, France). For flash chromatography, Merck silica gel 60 (230–400 mesh ASTM) was used. NMR spectra were recorded on a Bruker (Wissembourg, France) AM 300 spectrometer (300, 282, and 75 MHz, for ^{1}H, ^{19}F, and ^{13}C, respectively) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts and *J* values are given in parts per million and Hertz, respectively.

4.2. General procedure for the preparation of symmetrical 1,2-difluorostilbenes

A 50 mL two neck flask equipped with a stir bar, water condenser, rubber septum, and argon inlet adapter was charged sequentially with (2.3 equiv, 1.2 mmol) of arylboronic acid, (1 equiv, 0.5 mmol) of dibromodifluoroethene, (3 equiv, 1.5 mmol) of anhydrous cesium carbonate, 6 mL of toluene, 2 mL of water and 2 mL of ethanol. The mixture was treated with 5% of tetrakis-(triphenylphosphine) palladium (0). The solution was heated at 110 °C for 3 h. The reaction mixture was transferred to a 50 mL separatory funnel and partitioned between 20 mL of diethyl ether and 10 mL H_2O. The aqueous layer was extracted with 10 mL of diethyl ether. The organic layer combined dried over $MgSO_4$ and concentrated by rotary evaporation. The solvent was evaporated and the residue was purified by flash column chromatography on silica gel using a mixture of ethyl acetate/petroleum ether (5/95) as eluent, to give the desired product.

4.2.1. 4-(1,2-Difluoroethenediyl)bis-N,N-dimethylbenzenamine ***3a***. Isomer *E* ^{19}F NMR ($CDCl_3$): δ=−141.7 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=2.95 (s, 6H, $N(CH_3)_2$), 7.41 (d, $^3J_{HH}$=8.2 Hz, 4 H), 7.53 (d, $^3J_{HH}$=8.4 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ=42.8, 115.6, 121.8 (t, J_{CF}=9.4 Hz), 125.5 (t, J_{CF}=8.1 Hz), 146.5. Isomer *Z* ^{19}F NMR ($CDCl_3$): −130.6 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=3.02 (s, 6H, $N(CH_3)_2$), 7.56 (d, $^3J_{HH}$=8.3 Hz, 4H), 7.82 (d, $^3J_{HH}$=8.4 Hz, 4H).

4.2.2. 1,1′-(1,2-Difluoro-1,2-ethenediyl)bis[4-bromo-benzene ***3b***. Isomer *E* ^{19}F NMR ($CDCl_3$): δ=−151.0 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=7.51 (d, $^3J_{HH}$=8.3 Hz, 4H), 7.65 (d, $^3J_{HH}$=8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ=121.8, 122.8, 123.2 (t, J_{CF}=9.2 Hz), 127.2 (t, J_{CF}=8.5 Hz), 147.6. Isomer *Z* ^{19}F NMR (300 MHz, $CDCl_3$): −127.5 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=7.6 (d, $^3J_{HH}$=8.2 Hz, 4H), 7.80 (d, $^3J_{HH}$=8.2 Hz, 4H).

4.2.3. 1,1′-(1,2-Difluoro-1,2-ethenediyl)bis[3,4-dimethoxy-benzene] ***3c***. Isomer *E* ^{19}F NMR ($CDCl_3$): δ=−138.3 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=3.96 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.95 (d, $^3J_{HH}$=8.1 Hz, 2H), 7.10 (s, 2H), 7.23 (d, $^3J_{HH}$=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=123.4, 124.9 (t, J_{CF}=8.0 Hz), 126.4 (t, J_{CF}=9.2 Hz), 125.4 (t, J_{CF}=8.4 Hz), 146.7, 146.9, 156.4, 159.3. Isomer *Z* ^{19}F NMR (300 MHz, $CDCl_3$): −124.3 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=3.94 (s, 3H, OMe), 3.97 (s, 3H, OMe), 7.02 (d, $^3J_{HH}$=8.3 Hz, 2H), 7.18 (s, 2H), 7.36 (d, $^3J_{HH}$=8.2 Hz, 2H).

4.2.4. 1,1′-(1,2-Difluoro-1,2-ethenediyl)bis[3-nitro-benzene] ***3d***. Isomer *E* ^{19}F NMR ($CDCl_3$): −149.6 (s, 2F). ^{1}H NMR ($CDCl_3$): 7.63 (m, 1H), 8.05 (d, $^3J_{HH}$=7.9 Hz, 1H), 8.23 (d, $^3J_{HH}$=8.2 Hz, 1H), 8.60 (s, 1H). ^{13}C NMR ($CDCl_3$): 115.0, 118.2 (t, J_{CF}=8.3 Hz), 123.2 (t, J_{CF}=9.2 Hz), 128.3, 132.2 (t, *J*=8.5 Hz), 145.7, 147.5. Isomer *Z* ^{19}F NMR ($CDCl_3$): −128.3 (s, 2F). ^{1}H NMR ($CDCl_3$): 7.72 (m, 1H), 8.12 (d, $^3J_{HH}$=8.0 Hz, 1H), 8.40 (d, $^3J_{HH}$=8.1 Hz, 1H), 8.60 (s, 1H).

4.2.5. 1,1′-(1,2-Difluoro-1,2-ethenediyl)bis[4-nitro-benzene] ***3e***. Isomer *E* ^{19}F NMR ($CDCl_3$): δ=−155.6 (s, 2F). ^{1}H NMR ($CDCl_3$): δ=7.55 (d, $^3J_{HH}$=8.7 Hz, 4H), 8.21 (d, $^3J_{HH}$=8.3 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ=125.4 (t, J_{CF}=9.2 Hz), 125.1, 129.2 (t, J_{CF}=8.4 Hz), 146.9, 147.8. Isomer *Z* ^{19}F NMR (300 MHz, $CDCl_3$): −124.0 (s, 2F). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.71 (d, $^3J_{HH}$=8.5 Hz, 4H), 8.30 (d, $^3J_{HH}$=8.4 Hz, 4H).

4.3. General procedure for the preparation of 1-bromo-1,2-difluorostyrenes

A 50 mL two neck flask equipped with a stir bar, water condenser, rubber septum, and argon inlet adapter was charged sequentially with (1 equiv, 0.5 mmol) of arylboronic acid (3 equiv, 1.5 mmol) of dibromodifluoroethene (3 equiv, 1.5 mmol) of anhydrous cesium carbonate, 6 mL of toluene, 2 mL of water and 2 mL of ethanol. The mixture was treated with 5% of tetrakis(triphenylphosphine) palladium (0). The solution was heated at 40 °C for 4 h. The reaction mixture was transferred to a 50 mL separatory funnel and partitioned between 20 mL of diethyl ether and 10 mL H_2O. The aqueous layer was extracted with 10 mL of diethyl ether. The organic layer combined dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel using a mixture of ethyl acetate/petroleum ether (5/95) as eluent, to give the desired product.

4.3.1. 4-(2-Bromo-1,2-difluoroethenyl)-N,N-dimethylbenzenamine ***4a***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−104.4 (d, $^3J_{FF}$=8.2 Hz, 1F), −120.2 (d, $^3J_{FF}$=8.6 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=2.87 (s, 6H, $N(CH_3)_2$), 6.67 (d, $^3J_{HH}$=8.1 Hz, 2H), 7.17 (d, $^3J_{HH}$=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=44.4, 112.7, 116.7, 124.3 (dd, $^3J_{CF}$=4.0, $^4J_{CF}$=3.4 Hz), 126.8 (d, $^2J_{CF}$=25.4 Hz), 135.9 (dd, $^1J_{CF}$=312.4 Hz, $^2J_{CF}$=28.5 Hz), 146.2 (dd, $^1J_{CF}$=257.6 Hz, $^2J_{CF}$=14.5 Hz). Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−121.9 (d, $^3J_{FF}$=132.6 Hz, 1F), −141.4 (d, $^3J_{FF}$=132.6 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=2.93 (s, 6H, $N(CH_3)_2$), 7.24 (d, $^3J_{HH}$=7.16 Hz, 2H), 7.38 (d, $^3J_{HH}$=8.4 Hz, 2H).

4.3.2. 4-(2-Bromo-1,2-difluoroethenyl)-1-bromo-benzene ***4b***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−98.8 (d, $^3J_{FF}$=11.1 Hz, 1F), −122.6 (d, $^3J_{FF}$=11.1 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.32 (d, $^3J_{HH}$=8.2 Hz, 2H), 7.61 (d, $^3J_{HH}$=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=128.3 (dd, $^3J_{CF}$=$^4J_{CF}$=3.8 Hz), 130.7 (d, $^2J_{CF}$=25.4 Hz), 131.8, 132.2, 137.9 (dd, $^1J_{CF}$=315.3 Hz, $^2J_{CF}$=26.8 Hz), 147.6 (dd, $^1J_{CF}$=263.4 Hz, $^2J_{CF}$=15.4 Hz). Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−114.4 (d,

$^3J_{FF}$=133.4 Hz, 1F), −142.2 (d, $^3J_{FF}$=133.4 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.41 (d, $^3J_{HH}$=8.7 Hz, 2H), 7.53 (d, $^3J_{HH}$=8.5 Hz, 2H).

4.3.3. 4-(2-Bromo-1,2-difluoroethenyl)-1,2-dimethoxy-benzene ***4c***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−106.1 (d, $^3J_{FF}$=6.3 Hz, 1F), −116.9 (d, $^3J_{FF}$=6.3 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=3.89 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.90 (d, $^3J_{HH}$=7.4 Hz, 1H), 6.97 (s, 1H), 7.0 (d, $^3J_{HH}$=7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=110.8, 112.3, 126.5, 128.8 (d, $^2J_{CF}$=25.2 Hz), 137.3 (dd, $^1J_{CF}$=318.5 Hz, $^2J_{CF}$=24.1 Hz), 147.3 (dd, $^1J_{CF}$=284.5 Hz, $^2J_{CF}$=16.5 Hz), 156.4, 157.8. Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−121.1 (d, $^3J_{FF}$=139.8 Hz, 1F), −132.3 (d, $^3J_{FF}$=139.8 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=3.89 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.92 (d, $^3J_{HH}$=7.4 Hz, 1H), 6.94 (s, 1H), 7.23 (d, $^3J_{HH}$=8.1 Hz, 1H).

4.3.4. 4-(2-Bromo-1,2-difluoroethenyl)-2-nitro-benzene ***4d***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−95.3 (d, $^3J_{FF}$=11.3 Hz, 1F), −123.8 (d, $^3J_{FF}$=11.4 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.34 (m, 2H), 8.12 (d, $^3J_{HH}$=8.1 Hz, 1H), 8.33 (d, $^3J_{HH}$=7.9 Hz, 1H), 8.74 (s, 1H). ^{13}C NMR ($CDCl_3$): δ=124.3, 126.9, 127.4, 128.5, 131.8 (d, $^2J_{CF}$=24.6 Hz), 138.7 (dd, $^1J_{CF}$=320.8 Hz, $^2J_{CF}$=25.3 Hz), 145.8, 148.9 (dd, $^1J_{CF}$=272.5 Hz, $^2J_{CF}$=16.2 Hz). Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−112.2 (d, $^3J_{FF}$=133.7 Hz, 1F), −142.6 (d; $^3J_{FF}$=133.6 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.21 (m, 2H), 8.05 (d, $^3J_{HH}$=7.9 Hz, 1H), 8.23 (d, $^3J_{HH}$=8.5 Hz, 1H), 8.60 (s, 1H).

4.3.5. 4-(2-Bromo-1,2-difluoroethenyl)-1-nitro-benzene ***4e***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−109.5 (d, $^3J_{FF}$=8.6 Hz, 1F), −124.5 (d, $^3J_{FF}$=8.7 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.85 (d, $^3J_{HH}$=8.3 Hz, 2H), 8.04 (d, $^3J_{HH}$=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=126.4, 127.2 (dd, $^3J_{CF}$=$^4J_{CF}$=3.4 Hz), 128.3 (d, $^2J_{CF}$=25.4 Hz), 138.6 (dd, $^1J_{CF}$=314.6 Hz, $^2J_{CF}$=27.6 Hz), 147.0 (dd, $^1J_{CF}$=259.6 Hz, $^2J_{CF}$=15.5 Hz), 147.8. Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−109.85 (d, $^3J_{FF}$=131.8 Hz, 1F), −142.30 (d, $^3J_{FF}$=131.8 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.63 (d, $^3J_{HH}$=8.1 Hz, 4H), 8.02 (d, $^3J_{HH}$=8.4 Hz, 4H).

4.4. General procedure for the preparation of unsymmetrical 1,2-difluorostilbenes

A 50 mL two neck flask equipped with a stir bar, water condenser, rubber septum, and argon inlet adapter was charged sequentially with 1.2 equiv of arylboronic acid, 1 equiv of 1-bromo-1,2-difluorostyrene, 3 equiv of anhydrous cesium carbonate, 4 mL of toluene, 1 mL of water and 1 mL of ethanol. The mixture was treated with 5% of tetrakis(triphenylphosphine)palladium(0). The solution was heated at 110 °C for 3 h. The reaction mixture was transferred to a 50 mL separatory funnel and partitioned between 15 mL of diethyl ether and 10 mL of H_2O. The aqueous layer was extracted with 10 mL of diethyl ether. The combined organic layer dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel using a mixture of ethyl acetate/petroleum ether (5/95) as eluent, to give the desired product.

4.4.1. 4-[1,2-Difluoro-2-(4-nitrophenyl)ethenyl]-N,N-dimethylbenzenamine ***5a*** *(identical with* ***5c****)*. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−157.9 (d, $^3J_{FF}$=136.4 Hz, 1F), −144.1 (d, $^3J_{FF}$=136.4 Hz, 1F) ppm. ^{1}H NMR ($CDCl_3$): δ=3.02 (s, 6H, $N(CH_3)_2$), 6.70 (d, $^3J_{HH}$=8.5 Hz, 2H), 7.63 (d, $^3J_{HH}$=8.8 Hz, 2H), 7.78 (d, $^3J_{HH}$=8.6 Hz, 2H), 8.24 (d, $^3J_{HH}$=8.2 Hz, 2H) ppm. ^{13}C NMR: δ=43.7, 115.8, 116.2, 120.4 (d, $^2J_{CF}$=23.1 Hz), 127.3 (dd, $^3J_{CF}$=$^4J_{CF}$=3.9 Hz), 129.5 (dd, $^3J_{CF}$=$^4J_{CF}$=2.6 Hz), 130.7, 134.7 (d, $^2J_{CF}$=24.5 Hz), 148.2 (dd, $^1J_{CF}$=246.5 Hz, $^2J_{CF}$=22.8 Hz), 150.3, 151.4 (dd, $^1J_{CF}$=253.7 Hz, $^2J_{CF}$=21.2 Hz). Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−138.1 (d, $^3J_{FF}$=17.1 Hz, 1F), −114.3 (d, $^3J_{FF}$=17.1 Hz, 1F) ppm. ^{1}H NMR ($CDCl_3$): δ=3.08 (s, 6H, $N(CH_3)_2$), 6.62 (d, $^3J_{HH}$=8.6 Hz, 2H), 7.23 (d, $^3J_{HH}$=8.8 Hz, 2H), 7.44 (d, $^3J_{HH}$=8.7 Hz, 2H), 8.02 (d, $^3J_{HH}$=8.3 Hz, 2H) ppm.

4.4.2. 4-[1,2-Difluoro-2-(4-bromophenyl)ethenyl]benzaldehyde ***5b***. Isomer *E*: ^{19}F NMR ($CDCl_3$): δ=−114.4 (d, $^3J_{FF}$=133.4 Hz, 1F), −142.2 (d, $^3J_{FF}$=133.4 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.30 (d, $^3J_{HH}$=8.4 Hz, 2H), 7.45 (d, $^3J_{HH}$=8.3 Hz, 2H), 7.82 (d, $^3J_{HH}$=8.4 Hz, 2H), 7.95 (d, $^3J_{HH}$=8.3 Hz, 2H), 9.98 (s, 1H, CHO) ppm. ^{13}C NMR: δ=123.42, 125.4, 126.8 (d, $^2J_{CF}$=23.1 Hz), 130.2 (dd, $^3J_{CF}$=$^4J_{CF}$=4.0 Hz), 131.5 (dd, $^3J_{CF}$=$^4J_{CF}$=2.8 Hz), 132.7, 134.7 (d, $^2J_{CF}$=24.5 Hz), 149.7 (dd, $^1J_{CF}$=247.3 Hz, $^2J_{CF}$=22.3 Hz), 152.3 (dd, $^1J_{CF}$=252.8 Hz, $^2J_{CF}$=22.1 Hz), 164.5. Isomer *Z*: ^{19}F NMR ($CDCl_3$): δ=−98.8 (d, $^3J_{FF}$=11.1 Hz, 1F), −122.6 (d, $^3J_{CF}$=11.1 Hz, 1F). ^{1}H NMR ($CDCl_3$): δ=7.23 (d, $^3J_{HH}$=8.2 Hz, 2H), 7.50 (d, $^3J_{HH}$=8.3 Hz, 2H), 7.74 (d, $^3J_{HH}$=8.4 Hz, 2H), 7.92 (d, $^3J_{HH}$=8.3 Hz, 2H), 9.92 (s, 1H, CHO) ppm.

Acknowledgements

This work was supported by the Conseil Régional Nord, Pas-de-Calais, France. The NMR and Mass Spectrometry facilities used in this study were funded by the European Community (FEDER), the Région Nord-Pas de Calais (France), the CNRS, and the Université de Lille 1, Sciences et Technologies. S.E. thanks the Université Cadi Ayyad, Faculté des Sciences et Techniques Guéliz, Marrakech, Morocco, for a sabbatical leave funded by the Erasmus Mundus Al Fihri program. This work was performed in the frame of the CNRST-CNRS Action Concertée Chimie 08/09 'Synthèse de sondes fluorescentes spécifiques des glyco et phopshopeptides pour l'analyse protéomique'. The authors thank Tarik Legdali, Abdelhamid Iuiry and Rachid Chbelti for performing some of the experiments during their Master's degree from Université Cadi Ayyad. The authors thank Dr. Maria van Agthoven for correcting the manuscript and the Referees for their careful reading.

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