Retraction

Cross coupling in water: Suzuki–Miyaura vinylation and difluorovinylation of arylboronic acids

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Green Chem., 2010, **12**, 636 (DOI: 10.1039/b924772f).

We, the named authors, hereby wholly retract this Green Chemistry article.

Signed: Jan Pschierer, Natalie Peschek and Herbert Plenio, Germany, September 2010.

Retraction endorsed by Sarah Ruthven, Editor.
Retraction published 15th September 2010

Cross coupling in water: Suzuki–Miyaura vinylation and difluorovinylation of arylboronic acids†

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Received 24th November 2009, Accepted 6th January 2010
First published as an Advance Article on the web 8th February 2010
DOI: 10.1039/b924772f

A general and efficient protocol for the Suzuki–Miyaura coupling of aryl boronic acids with vinylmesylate or difluorovinylmesylate or $Cl_2C{=}CF_2$ in water or water/*n*-butanol is reported, utilizing Na_2PdCl_4 (1 mol%) and a highly water-soluble fluorenylphosphine (CataCXium F sulf).

Various substituted styrenes are important monomers for polymerization reactions,[1] and are also applied in Mizoroki–Heck coupling,[2] (asymmetric) hydrosilylation,[3] hydroformylation,[4] hydroamination[5] or olefin-metathesis reactions.[6,7] The classic routes to vinylarenes rely on the elimination of activated leaving groups, the carbonyl olefination or the partial reduction of terminal alkynes. Recently two methods based on cross-coupling methodology using either the reaction of a vinylmetallic donor and an aryl halide (or pseudohalide) or the reaction of an arylmetallic donor and a vinyl halide (or pseudohalide) have seen great progress and subsequently the palladium- (and nickel-) catalyzed vinylation of aryl halides was reviewed by Denmark and Butler.[8]

The better developed approach to the synthesis of styrenes utilizes nucleophilic vinyl transfer reagents *via* Heck (ethene),[8] Kumada (vinyl-MgR),[9,10] Stille (vinyl-SnR_3),[11] Suzuki–Miyaura (vinyl-BR_2),[12-14] and Hiyama (vinyl-SiR_3) reactions.[15] The electronically inverse reaction of vinyl electrophiles with arylmetallic donors is less often applied,[16-19] which is probably also due to the lack of suitable vinyl transfer reagents. Significant progress was recently reported by Skrydstrup *et al.*, who introduced vinyl tosylate as a convenient and stable transfer reagent in palladium catalyzed reactions with various boronic acids and esters—albeit the desired products are formed in less than quantitative yields, despite the use of high catalyst loading (5 mol%).[20]

We recently reported that a water-soluble disulfonated fluorenylphosphine/palladium complex displays excellent activities in Suzuki–Miyaura reactions of various aryl chlorides when using water[21,22] or water/*n*-butanol[23,24] as solvents.[25] This protocol appears to be especially efficient for substrates containing difficult (potentially palladium coordinating) functional groups and unreactive C–X bonds.

We report here a simple coupling protocol utilizing Na_2PdCl_4 and the water-soluble and commercially available fluorenylphosphine (cataCXium F sulf)[26] in vinylation reactions of aryl boronic acids utilizing vinyl mesylate, 2,2-difluorovinylmesylate or 1,1-dichloro-2,2-difluoroethene.

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† Electronic supplementary information (ESI) available: Contains spectra of all newly synthesized compounds. See DOI: 10.1039/b924772f

Different phosphine ligands (see Fig. 2) were tested as well as different bases, Pd-sources and solvents (Table 1). As reported in a previous publication[19] the CataCXium F sulf ligand (Fig. 1) used in a Pd/ligand ratio of 1 : 2 in pure water turned out to be the most active catalyst (Table 1, entry 3).

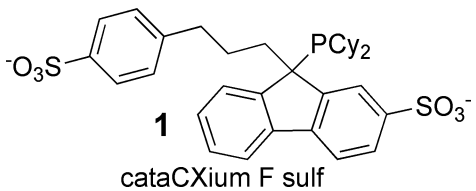
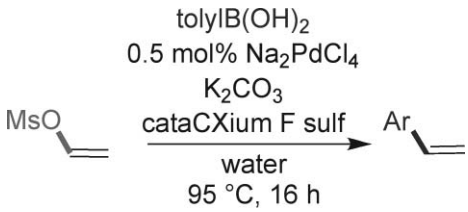


Fig. 1 CataCXium F sulf.

Initially, we tested the coupling reactions of vinyl tosylate with tolylboronic acid and the sterically hindered 2-naphthylboronic acid under the specified conditions (Table 2, entries 1, 2, 4, 6–8) at 0.5 mol% [Pd] loading. The respective vinylarenes

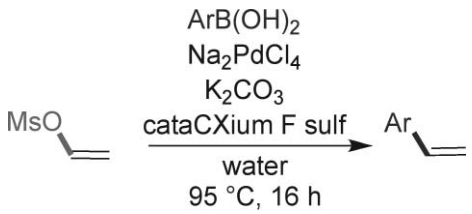
Table 1 Optimization of reaction conditions for vinyl transfer using vinyl mesylate (mesylate or methanesulfonate = Ms)

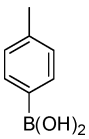
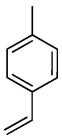
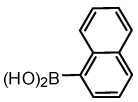
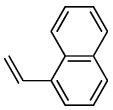
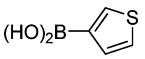
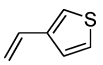
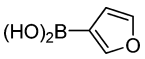
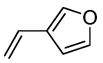
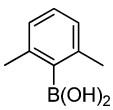
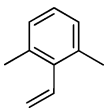
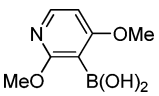
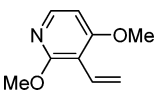
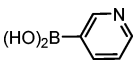
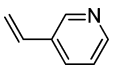


Entry	Ligand	Ratio Pd/ligand	Pd source	Base	Conversion[a]
1	**2**	1 : 2	Na_2PdCl_4	K_2CO_3	71%[b]
2	**2**	1 : 2	$PdCl_2$	K_2CO_3	12%[b]
3	**1**	1 : 2	Na_2PdCl_4	K_2CO_3	99%[b]
4	**3**	1 : 2	Na_2PdCl_4	Cs_2CO_3	87%[c]
5	**1**	1 : 1	Na_2PdCl_4	K_2CO_3	27%[b]
6	**1**	no ligand	Na_2PdCl_4	K_2CO_3	0%[b]
7	**1**	1 : 2	$PdCl_2$	K_2CO_3	46%[b]
8	**1**	1 : 2	Na_2PdCl_4	NaOH	93%[b]
9	**1**	1 : 2	Na_2PdCl_4	K_2CO_3	99%[d]
10	**2**	1 : 1	Na_2PdCl_4	K_2CO_3	11%[b]
11	**2**	1 : 2	Na_2PdCl_4	NaOH	67%[b]

[a] Determined *via* gas chromatography (heptadecane, internal standard), average of two runs. [b] Solvent water. [c] Solvent dioxane. [d] Solvent *n*-butanol/water 3/1.

Table 2 Suzuki–Miyaura coupling of vinyl mesylate with Pd/cataCXium F sulf



Entry	Boronic acid	Product	Mol % catalyst	Isolated yield [%]
1			1.0 0.5[a] 0.5 0.25	99 99 99 87
2			1.0 0.5[a] 0.5 0.25	99 99 99 83
3			1.0 0.5 0.25	99 84 42
4	$FcB(OH)_2$		1.0 1.0[a] 0.5 0.25	90 99 76 21
5			1.0	49% (99%)[b]
6			1.0 0.5 0.5[a] 0.25	99 81 95 49
7			1.0 0.5 0.5[a] 0.25	99 79 91 49
8			1.0 0.5 0.5[a]	99 84 94

Conditions: 1.0 mmol vinyl mesylate, 1.2 mmol boronic acid, 2.5 mmol K_2CO_3, degassed water (5.0 mL), 95 °C, reaction time: 16 h, catalyst stock solution in water (*c* (Pd) = 1.0 mol %/mL, Na_2PdCl_4/cataCXium F sulf 1 : 2. Fc = ferrocenyl.[a] Vinyl tosylate was used. [b] Quantitative formation of vinylfuran, but due to the low b.p. (86 °C) the isolated yield is modest for the small scale reactions performed. Yields correspond to isolated material after chromatography (silica), pentane–CH_2Cl_2 = 9/ 1.

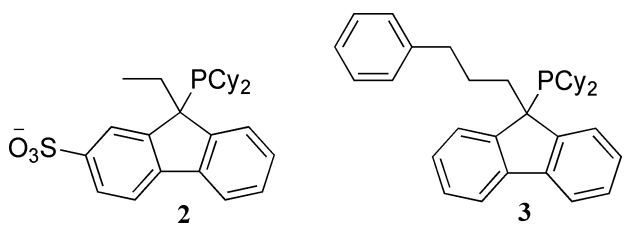
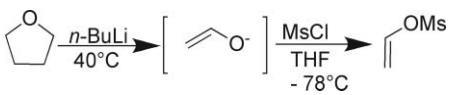


Fig. 2 Phosphine ligands.

were isolated in virtually quantitative yields, which compares favorably with the 5 mol% loading of a ferrocenyl palladium phosphine complex employed previously.[20]

With a view to the high catalytic efficiency of the Pd/cataCXium F sulf system we decided to use the even less reactive, but more atom-economical vinyl mesylate as the vinyl transfer reagent instead of the vinyl tosylates.[27] Vinyl mesylate was prepared in 78% yield on a multigram scale analogous to the synthesis of vinyl tosylate,[20] using THF and freshly distilled mesylchloride (Scheme 1).



Scheme 1 Synthesis of vinyl mesylate.

We next examined the Suzuki coupling of various aryl- and heteroarylboronic acids with vinyl mesylate in more detail (Table 1). Catalyst loadings of between 0.5–1 mol% are sufficient to effect quantitative conversion of the boronic acids tested. Due to the lower reactivity of vinyl mesylate (compared to vinyl tosylate) this substrate requires *ca.* twice the catalyst loading. All reactions were carried out in water as the only solvent. The use of water/*n*-butanol 1/3 as the reaction solvent gives the same cross coupling yields, since the small boronic acids as well as the vinyl mesylate employed here, appear to have sufficient water solubility. In the aqueous reaction mixtures the nature of the base does not have much influence on the reaction outcome and we therefore always used the cheap K_2CO_3. Sterically hindered (Table 1, entries 2, 6, 7) and heterocyclic boronic acids (Table 1, entries 3, 5, 7, 8) require 1 mol% [Pd] loading. For unhindered boronic acids 0.5 mol% are sufficient, while for a few substrates as little as 0.25 mol% give excellent results (Table 1, entries 1, 2). For the coupling reactions reported here we also optimized the amount of boronic acid. The present reaction protocol requires only a modest excess (1.2 equiv.) of the boronic acid to achieve full conversion of vinyl mesylate, while less boronic acid leads to significantly decreased coupling yields. Nonetheless, even for the Suzuki coupling of thiophene and furanboronic acid, which are both prone to hydrodeboronation reactions, the same amount of boronic acid as for the hydrolytically stable acids is sufficient. Despite using a small excess of boronic acid, we have not experienced purification problems caused by deboronated products.[28]

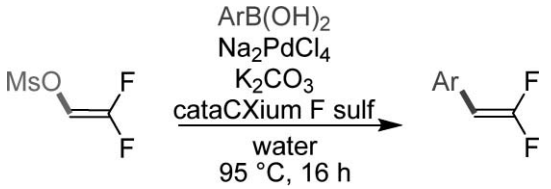
Rather than minimizing catalyst loading it is more useful, from a practical point of view, to avoid time and solvent consuming chromatographic purifications of the reaction products. This can be achieved here by applying a slightly higher catalyst loading—1 mol% of water-soluble Na_2PdCl_4 and 2 mol% of cataCXium F sulf—to effect the quantitative vinylation of the boronic acids for all entries in Table 1. The reaction products are then simply extracted with *n*-butanol or MTBE from the aqueous reaction phase, since the various salts and excess boronic acid remain dissolved in water. The evaporation of the solvent used for extraction under reduced pressure normally affords pure (> 99% purity) cross coupling products.

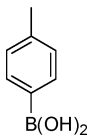
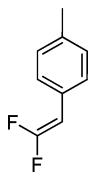
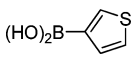
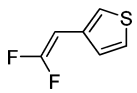
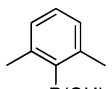
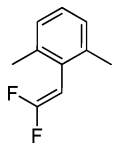
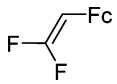
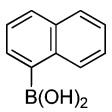
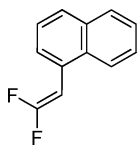
Notable in the present set of substrates is the facile synthesis of vinylferrocene (Table 1, entry 4) in good yields according to the reaction protocol reported here, as compared to the classical synthesis *via* acetylferrocene[29] or more recently *via* ethynylferrocene.[30] Vinylferrocenes are important precursors for polymers with variable electronic properties;[31,32] the protocol reported here provides a simple one step synthesis.

The reaction conditions used in the Suzuki–Miyaura coupling of vinyl mesylate were extended to difluorovinyl mesylate. The introduction of a fluorinated (vinyl) group is of significant interest for pharmaceutical and agrochemical products.[33,34] Excellent cross coupling yields were achieved using 1.0 mol % [Pd] catalyst for activated boronic acids (Table 3, entry 1), heteroaryl boronic acids (Table 3, entry 2) and sterically demanding boronic acids (Table 3, entry 3, 5).

Due to the facile difluorovinyl-group transfer reactions we became interested in testing other fluorinated building blocks as useful substrates for the Suzuki–Miyaura coupling and 1,1-dichloro-2,2-difluoroethene (R-1112a) is one of many

Table 3 Suzuki–Miyaura coupling of difluorovinyl mesylate with Pd/cataCXium F sulf



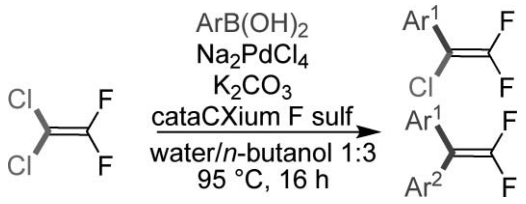
Entry	Boronic acid	Product	Mol % catalyst	Isolated yield [%]
1			1.0 0.5	99 65
2			1.0 0.5	89 27
3			1.0 0.5	81 43
4	$FcB(OH)_2$		1.0 0.5	89 67
5			1.0 0.5	93 73

Conditions: 1.0 mmol difluorovinyl mesylate, 1.2 mmol boronic acid, 2.5 mmol K_2CO_3, degassed water (5.0 mL), 95 °C, reaction time: 16 h, catalyst stock solution in water (c (Pd) = 1.0 mol %/mL, Na_2PdCl_4/cataCXium F sulf 1 : 2. Fc = ferrocenyl, Yields correspond to isolated material after chromatography (silica), pentane–CH_2Cl_2= 5/1.

commercially available chlorofluoroolefins.[35] The pioneering work of Burton on CF_2 transfer reagents[36] also established Negishi and Suzuki coupling *via* CF_2=CClZnCl for the synthesis of Ar,Ar′C=CF_2 type species under strictly anhydrous conditions.[37]

The reagent F_2C=CCl_2 used here is very volatile (bp 19 °C), but easy to handle after preparing a stock solution in cold *n*-butanol. Almost the same reaction protocol as described for the vinyl mesylates was utilized for Cl_2C=CF_2. However, with the poorly water-soluble alkene the coupling reactions need to be carried out in water/*n*-butanol mixtures instead of water to obtain good results. Excellent substrate conversions were achieved using 1 mol % [Pd] catalyst for a variety of activated boronic acids (Table 4, entry 1), sterically demanding boronic acids (Table 4, entry 2, 3) and heteroboronic acids (Table 4, entry 4). Using 1.2 equiv. of boronic acid it is possible to

Table 4 Suzuki–Miyaura coupling of $Cl_2C{=}CF_2$ with aryl boronic acids



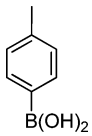
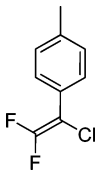
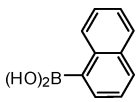
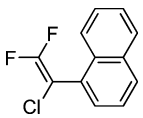
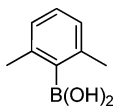
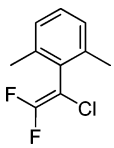
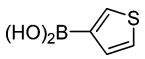
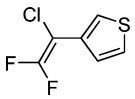
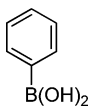
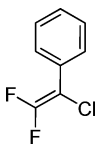
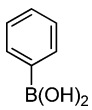
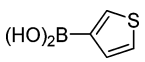
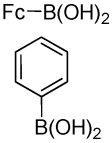
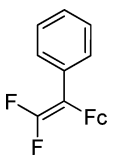
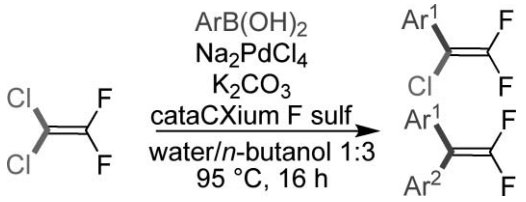
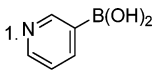
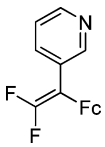
Entry	Boronic acid	Product	Mol % catalyst	Isolated yield [%]
1			1.0 0.5	99 67
2			1.0 0.5	99 64
3			1.0 0.5	89 56
4			1.0 0.5	96 37
5			1.0 0.5 0.25	99 89 70
6			1.0[a] 0.5[a]	99 64
7			1.0[a] 0.5[a]	99 65
8	1. Fc–B(OH)2 2. 		1.0	87

Table 4 *(Contd.)*



Entry	Boronic acid	Product	Mol % catalyst	Isolated yield [%]
9	1.  2. Fc–B(OH)2		1.0	84

Conditions: 1.0 mmol $Cl_2C{=}CF_2$, 1.2 mmol boronic acid, 2.5 mmol K_2CO_3, degassed water (1.5 mL), *n*-butanol (4.5 mL), 95 °C, reaction time: 16 h, catalyst stock solution in water (*c* (Pd) = 1.0 mol %/mL, Na_2PdCl_4/cataCXium F sulf 1 : 2. Fc = ferrocenyl, Yields correspond to isolated material after chromatography (silica), pentane–CH_2Cl_2= 5/1.[a] 2.2 equiv. boronic acid.

selectively introduce a single aryl group (Table 4, entries 1–5), while in the presence of 2.2 equiv. of boronic acid two identical aryl groups are introduced (Table 4, entries 6, 7) in a single reaction step. A second and different aryl group can be easily added by repeating the coupling protocol with the isolated and purified monarylated alkenes $ArClC{=}CF_2$. The respective $ArAr'C{=}CF_2$ products are isolated in excellent yields over the two steps (Table 4, entries 8, 9).

In conclusion, we have developed a simple Suzuki protocol for the aqueous coupling of vinyl mesylate, difluorovinyl mesylate and 1,1-dichloro-2,2-difluoroethene with various arylboronic acids. Catalyst loadings between 0.25 and 1 mol % Na_2PdCl_4 and twice as much of the disulfonated fluorenylphosphine (cataCXium F sulf) in water or *n*-butanol/water using a simple base (K_2CO_3) afford the respective cross-coupling products in excellent yields.

Experimental section

General experimental

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. Used solvents (water, *n*-butanol; all technical grade) were deaerated *via* freeze and thaw technique (3×). For cross coupling reactions under anhydrous conditions, *n*-butanol (technical grade, dried over molecular sieves, 4 Å) was used. Potassium carbonate, used in cross coupling reactions, was technical grade. All "phosphines" in this publication were used in the form of their air stable phosphonium salts and deprotonated *in situ* during the catalyst preparation. All experiments were carried out under an argon atmosphere, unless otherwise noted.

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on Bruker ARX 300 at 300 MHz respectively 75 Hz or on Bruker DRX 500 at 500 MHz, 125.75 MHz respectively, at 293 K. The chemical shifts are

given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (0 ppm). Melting points were recorded on an uncorrected Stuart SMP10 instrument. Mass spectra were recorded on a Finnigan MAT 95 magnetic sector spectrometer. Thin layer chromatography (TLC) was performed using Fluka silica gel 60 F 254 (0.2 mm) on alumina plates. Silica gel columns for chromatography were prepared with E. Merck silica gel 60 (0.063–0.20 mesh ASTM). GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB (l = 15 m, d_i = 0.25 mm, d_F = 1.0 μm), N2 (flow: 17 cm s^{-1}; split 1 : 50); Injector-temperature: 270 °C, detector temperature: 350 °C. Temperature program: isotherm 150 °C for 5 min, heating to 300 °C with 25 °C min^{-1}, isotherm for 15 min.

Synthesis of vinyl mesylate

A solution of 2.5 M *n*-butyllithium in hexane (39 mL, 98.5 mmol, 1.3 equiv.) was added to 150 mL THF and stirred for 3 h at 35 °C in a 500 mL Schlenk flask. Then the bright yellow reaction mixture was cooled to −78 °C. A solution of mesylchloride (8.55 g, 75 mmol, 1 equiv.) in THF was added dropwise with a syringe over a period of 20 min. Then the reaction mixture was stirred for 30 min at −78 °C. Afterwards it was allowed to warm to room temperature and stirred for another 1 h. The reaction solution was poured into 200 mL MTBE and 100 mL of iced, saturated sodium hydrocarbonate was added under vigorous stirring. The aqueous phase was extracted with MTBE (3 × 50 mL) and the combined organic phase was washed with brine (2 × 50 mL) and dried over sodium sulfate. After concentration *in vacuo* the crude product was purified by chromatography on silica gel using pentane/ethylacetate (40 : 1) as eluent. This afforded 7.8 g of the title compound (85%) as bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (dd, J = 5.9, 13.5, 1H), 5.14–4.89 (m, 2 H), 2.76 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.9, 129.9, 40.9. HRMS (m/z): calcd for $C_3H_6O_3S$: 122.0032; found: 122.00322. Viscous oil.

Synthesis of 2,2,2-trifluorethylmesylate

2,2,2-Trifluorethylmesylate was prepared according to the procedure reported by Vastra and Saint-Jalmes[38] in 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (dd, 3H, J = 14.1, 6.0 Hz), 2.47 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7 (q, J_{CF} = 260.8 Hz), 64.5 (q, J_{CF} = 64.2 Hz), 46.2. HRMS (m/z): calcd for $C_3H_5F_3O_3S$: 177.9934; found: 177.99453. Viscous oil.

Synthesis of 2,2-difluorovinyl mesylate

2,2,2-Trifluorethylmesylate (5.0 g, 28.0 mmol, 1.0 equiv.) was dissolved in dry THF (50 mL) and cooled to −78 °C. A solution of 2.5 M *n*-BuLi in hexane (18.0 mL, 46.0 mmol, 2.3 equiv.) was added drop wise with a syringe over a period of 10 min. The dark brown solution was stirred for 45 min at −78 °C. Hereafter it was quenched with a mixture of water–THF (1 : 1, 100 mL). The organic phase was extracted with ethyl acetate (3 × 150 mL). The combined organic phase was washed with brine (2 × 150 mL) and dried over sodium sulfate. After concentration *in vacuo* the crude product was purified by chromatography on silica gel using pentane–ethyl acetate (9 : 1) as eluent. This afforded 2.3 g of the title compound (58%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (dd, 1H, J = 12.6, 4.1 Hz), 2.47 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.9 (dd, J_{CF} = 256.4, 266.2 Hz), 100.8 (q, J_{CF} = 63.2 Hz), 30.3. HRMS (m/z): calcd for $C_3H_4F_2O_3S$: 157.9845; found: 157.98693. Viscous oil.

Suzuki–Miyaura coupling of vinyl tosylates/-mesylates or difluorovinyl mesylates with Pd/cataCXium F sulf

Preparation of the catalyst stock solution. [Na_2PdCl_4] (14.7 mg, 0.05 mmol), phosphine ligand (0.1 mmol) and K_2CO_3 (56 mg, 0.4 mmol) were placed in a Schlenk tube under argon, evacuated and backfilled with Ar thrice. Degassed water (5.0 mL) was added and the mixture was stirred at 45 °C for 3 h. This stock solution had a Pd concentration of 0.01 mol L^{-1}.

General procedure for cross coupling reaction

Boronic acid (1.2 mmol), vinyl tosylate or -mesylate (1.0 mmol) and K_2CO_3 (345 mg, 2.5 mmol) were placed in a 25 mL Schlenk tube and evacuated and backfilled with Ar thrice. Degassed water (5.0 mL) was added together with the appropriate volume of catalyst stock solution (*e.g.*, 1 mL of the solution prepared above was added to obtain a catalyst loading of 1 mol %).

The reaction mixture was stirred for 16 h at 100 °C and then cooled to room temperature. The reaction mixture was extracted with methyl *tert*-butyl ether (5.0 mL) twice. The combined organic layers were dried with brine and $MgSO_4$. Conversion was determined by product isolation: the organic layer was concentrated *in vacuo* and the residue was purified by column chromatography (CH_2Cl_2–pentane = 1/9 as eluent) to afford the pure corresponding cross coupling product.

Suzuki–Miyaura coupling of dichlorodifluoroethylene with Pd/cataCXium F sulf

Preparation of the catalyst stock solution. [Na_2PdCl_4] (14.7 mg, 0.05 mmol), phosphine ligand (0.1 mmol) and K_2CO_3 (56 mg, 0.4 mmol) were placed in a Schlenk tube under argon. Degassed water (5.0 mL) was added and the mixture was stirred at 45 °C for 3 h. This stock solution had a Pd concentration of 0.01 mol L^{-1}.

General procedure for cross coupling reaction

Boronic acid (1.2 mmol), $Cl_2C{=}CF_2$ (1.0 mmol) and K_2CO_3 (345 mg, 2.5 mmol) were placed in a 25 mL Schlenk tube and evacuated and backfilled with Ar thrice. Degassed water (1.5 mL) and degassed *n*-butanol (4.5 mL) were then added together with the appropriate volume of catalyst stock solution (*e.g.*, 1 mL of the solution prepared above was added to obtain a catalyst loading of 1 mol %). The reaction mixture was stirred for 16 h at 95 °C and then cooled to room temperature. The combined organic layers were dried with brine and $MgSO_4$. Conversion was determined by product isolation: the organic layer was concentrated *in vacuo* and the residue was purified by column chromatography (CH_2Cl_2–pentane = 1/9 as eluent) to afford the pure corresponding cross coupling product.

For analytical approach, the aqueous layer was extracted with *n*-butanol (5.0 mL) twice. Methyl *tert*-butyl ether was used to extract products with a low boiling point, for example 3-vinylfuran.

$Cl_2C{=}CF_2$ was used in liquid form as a stock solution in ice cooled *n*-butanol. Therefore a specified volume of the gaseous compound was injected (and dissolved) into a Schlenk tube with cooled *n*-butanol using a syringe. When stored in a fridge (4 °C), this stock-solution is usable for many days.

Analytical data of the coupling products

4-Methylstyrene (Table 2, entry 1). HRMS calcd for C_9H_{10}: 118.0801; found: 118.08250. liquid, b. p.: 170.5 °C.

1-Vinylnaphthalene (Table 2, entry 2). NMR spectra are in accord to those reported in literature.[15] HRMS calcd for $C_{12}H_{10}$: 154.0804; found: 154.08250. m. p.: 65 °C.

3-Vinylthiophene (Table 2, entry 3). ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.27 (d, $^3J = 7.4$ Hz, 2H) 6.55 (dd, $J = 16.9$, 10.4 Hz, 1H), 4.80 (dd, $J = 16.9$, 1.2 Hz, 1H), 4.59 (dd, $J = 17.0$, 10.4 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6, 131.8, 129.9, 127.8, 124.2, 115.5. HRMS calcd for $C_6H_6S_1$: 110.0244; found: 110.02431. liquid, b. p.: 160 °C.

Vinylferrocene (Table 2, entry 4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (dd, $J = 16.6$, 11.0 Hz, 1H), 4.81 (dd, $J = 17.3$, 1.2 Hz, 1H), 4.61 (dd, $J = 10.2$, 1.2 Hz, 1H), 4.18 (s, 2H), 4.12 (s, 2H), 4.09 (s, 5H). ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 135.1, 111.4, 83.9, 69.6, 69.1, 67.1. HRMS calcd for $C_{12}H_{12}Fe_1$: 212.0302; found: 212.03082. m. p.: 54 °C.

3-Vinylfuran (Table 2, entry 5). ^{1}H NMR (300 MHz, $CDCl_3$) 7.77 (s, 1H), 7.35 (d, $^3J = 7.6$ Hz, 2H), 6.60 (dd, $J = 17.3$, 1.3 Hz, 1H), 4.88 (dd, $J = 17.3$, 1.2 Hz, 1H), 4.67 (dd, $J = 11.6$, 1.3 Hz, 1H). ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 145.4, 141.7, 124.7, 122.3, 113.6, 102.7. HRMS (*m*/*z*): calcd for $C_6H_6O_1$: 94.0433; found: 94.04471. liquid, b. p.: 86 °C.

2,6-Dimethyl-1-vinylbenzene (Table 2, entry 6). NMR spectra are in accord to those reported in literature.[39] HRMS (*m*/*z*): calcd for $C_{10}H_{12}$: 132.0929; found: 132.08952. liquid, b. p.: 66 °C (10 Torr).

2,4-Dimethoxy-3-vinylpyridine (Table 2, entry 7). ^{1}H NMR (300 MHz, $CDCl_3$) 7.78 (d, $^3J = 8.1$ Hz, 1H), 7.34 (d, $^3J = 7.9$ Hz, 1H), 6.59 (dd, $J = 17.7$, 11.0 Hz, 1H), 4.87 (dd, $J = 17.6$, 1.4 Hz, 1H), 4.68 (dd, $J = 11.3$, 1.4 Hz, 1H), 3.91 (s, 6H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.2, 145.4, 140.9, 132.6, 106.4, 102.7, 101.1, 53.4. HRMS calcd for $C_9H_{11}N_1O_2$: 165.0841; found: 165.08760. m. p.: 121 °C.

3-Vinylpyridine (Table 2, entry 8). NMR spectra are in accord to those reported in literature.[40] HRMS calcd for $C_7H_7N_1$: 105.0625; found: 105.06390. liquid, m. p.: 126 °C.

1-(4-Tolyl)-2,2-difluoroethene (Table 3, entry 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d,$^3J = 7.1$ Hz, 1H), 7.30 (d, $^3J = 6.9$ Hz, 1H), 6.00 (dd, $J = 23.4$, 3.7 Hz, 1H), 2.23(s, 3H). ^{13}C {^{1}H} NMR (75 MHz $CDCl_3$) δ 161.0 (dd, $J_{CF} = 287.1$, 277.0 Hz), 146.3, 131.4, 130.2, 128.3 (t, $J_{CF} = 9$ Hz), 101.5 (dd, $J_{CF} = 29.8$, 12.2 Hz), 21.9. HRMS (*m*/*z*): calcd for $C_9H_8F_2$: 154.0611; found: 154.06300. liquid, boiling point: 60 °C (12 Torr).

1-(3-Thiophenyl)-2,2-difluoroethene (Table 3, entry 2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d,$^3J = 7.3$ Hz, 1H), 7.31 (d, $^3J = 7.2$ Hz, 1H), 7.18–6.93 (m, 1H), 6.01 (dd, $J = 25.1$, 4.1 Hz, 1H). ^{13}C {^{1}H} NMR (125.8 MHz $CDCl_3$) δ 159.8 (dd, $J_{CF} = 290.0$, 281.3 Hz), 139.1 (t, $J_{CF} = 6.7$ Hz), 134.4, 129.3, 127.6 (t, $J_{CF} = 17.8$ Hz), 99.8 (dd, $J_{CF} = 27.2$ Hz, 4.9 Hz). HRMS (*m*/*z*): calcd for $C_6H_4F_2S$: 146.0026; found: 126.00543. liquid.

1-(1-m-Xylyl)-2,2-difluoroethene (Table 3, entry 3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d,$^3J = 7.4$ Hz, 2H), 7.29 (d, $^3J = 7.3$ Hz, 2H), 6.00(dd, $J = 24.6$ Hz, $J = 3.9$ Hz, 1H), 2.39 (s, 5H). ^{13}C {^{1}H} NMR (75 MHz $CDCl_3$) δ 159.8 (dd, $J_{CF} = 271.0$, 262.5 Hz), 145.0 (d, $J_{CF} = 4.4$ Hz), 129.1 (t, $J_{CF} = 7.1$ Hz), 126.6, 125.1, 88.7 (dd, $J_{CF} = 28.3$ Hz, 4.4 Hz), 23.82. HRMS (*m*/*z*): calcd for $C_{10}H_{10}F_2$: 168.0848; found: 168.08812. viscous oil.

1-Ferrocenyl-2,2-difluoroethene (Table 3, entry 4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (dd, $J = 24.9$ Hz, $J = 3.9$ Hz, 1H), 4.38 (s, 2H), 4.35 (s, 2H), 4.33 (s, 5H). ^{13}C {^{1}H} NMR (125.8 MHz $CDCl_3$) δ 160.9 (t, $J_{CF} = 215.4$ Hz), 86.3 (dd, $J_{CF} = 19.3$, 4.6 Hz), 82.7, 68.2, 67.8, 66.9. HRMS (*m*/*z*): calcd for $C_{12}H_{10}Fe_1F_2$: 248.0122; found: 248.01301. viscous oil.

1-(1-Naphthyl, 2,2-difluoroethene (Table 3, entry 5). NMR spectra are in accord to those reported in literature.[41] HRMS (*m*/*z*): calcd for $C_{10}H_8F_2$: 190.0627; found: 190.06763. viscous oil.

1-(4-Tolyl)-l-chloro-2,2-difluoroethene (Table 4, entry 1). NMR spectra are in accord to those reported in literature.[42] HRMS (*m*/*z*): calcd for $C_9H_7Cl_1F_2$: 188.0230; found: 188.02291; viscous oil.

1-Chloro-1-naphthyl-2,2-difluoroethene (Table 4, entry 2). NMR spectra are in accord to those reported in literature.[43]

HRMS (*m*/*z*): calcd for $C_{12}H_7Cl_1F_2$: 224.0283; found: 224.02912. viscous oil.

1-(2,6-Dimethylphenyl)-1-chloro-2,2-difluoroethene (Table 4, entry 3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05–7.02 (m, 1H), 6.88 (d, $^3J = 7.9$ Hz, 2H), 2.21 (s, 6H). ^{13}C {^{1}H} NMR (75 MHz $CDCl_3$) δ 161.5 (dd, $J_{CF} = 278.2$, 267.0 Hz), 137.9, 127.3 (d, $J_{CF} = 4.4$ Hz), 125.6 (d, $J_{CF} = 3.9$ Hz), 93.5, 92.1 (d, $J_{CF} = 4.5$ Hz), 18.0. HRMS (*m*/*z*): calcd for $C_{10}H_9Cl_1F_2$: 202.0441; found 202.04633; viscous oil.

1-(3-Thiophenyl)-1-chloro-2,2-difluoroethene (Table 4, entry 4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (dd, $^3J = 8.4$ Hz, $J = 4.1$ Hz, 1H), 7.27–7.26 (m, 2H). ^{13}C {^{1}H} NMR (75 MHz $CDCl_3$) δ 157.4 (dd, $J_{CF} = 292.0$, 281.8 Hz), 138.3, 132.0 (t, $J_{CF} = 18.1$ Hz), 125.2, 122.6, 105.7 (t, $J_{CF} = 26.6$ Hz). HRMS (*m*/*z*): calcd for $C_6H_3Cl_1F_2S_1$: 179.9693; found 179.96753; viscous oil.

1-Phenyl-1-chloro-2,2-difluoroethene (Table 4, entry 5). NMR spectra are in accord to those reported in literature.[44] HRMS (*m*/*z*): calcd for $C_8H_5Cl_1F_2$: 174.0026; found 174.00092; viscous oil.

1,1-Diphenyl-2,2-difluoroethene (Table 4, entry 6). NMR spectra are in accord to those reported in literature.[41] HRMS (*m*/*z*): calcd for $C_{14}H_{10}F_2$: 216.0845; found 216.08366. m. p. 177 °C.

1,1-Di(3-thiophenyl)-2,2-difluoroethene (Table 4, entry 7). NMR spectra are in accord to those reported in literature.[38]

HRMS (m/z): calcd for $C_{10}H_6F_2S_2$: 227.9921; found 227.99159. m. p. 168 °C.

1-Phenyl-1-ferrocenyl-2,2-difluoroethene (Table 4, entry 8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.22 (m, 5H), 4.57 (s, 2H), 4.46 (s, 2H), 4.11 (s, 5H). ^{13}C {^{1}H} NMR (125.8 MHz $CDCl_3$) δ 152.4 (dd, J_{CF} = 301.3, 291.5 Hz), 130.6 (d, J_{CF} = 3.1 Hz), 127.6, 127.2 (d, J_{CF} = 2.9 Hz), 126.4 (d, J_{CF} = 2.9 Hz), 91.7 (t, J_{CF} = 12.0 Hz), 81.3, 73.3, 72.1, 67.6. HRMS (m/z): calcd for $C_{18}H_{14}F_2Fe_1$: 324.0466; found 324.04721. m. p. 146 °C.

1-(3-Pyridyl)-1-ferrocenyl-2,2-difluoroethene (Table 4, entry 9). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, ^3J = 8.7 Hz, 1H), 8.67 (s, 1H), 7.86–7.84 (m, 1H), 7.41 (d, ^3J = 8.3 Hz, 1H) 4.45 (s, 2H), 4.29 (s, 2H), 4.03 (s, 5H). ^{13}C {^{1}H} NMR (125.8 MHz $CDCl_3$) δ 149.9 (dd, J_{CF} = 267.0, 256.2 Hz), 133.1 (d, J_{CF} = 1.6 Hz), 131.8 (d, J_{CF} = 1.8 Hz), 130.1, 129.5 (d, J_{CF} = 2.0 Hz), 129.1 (d, J_{CF} = 1.6 Hz), 90.2 (t, J_{CF} = 19.3 Hz), 86.5, 75.7, 74.5, 70.1. HRMS (m/z): calcd for $C_{17}H_{13}F_2Fe_1N_1$: 325.0401; found 325.04430. m. p. 152–153 °C.

Acknowledgements

This work was supported by the DFG and the Fonds der Chemischen Industrie.

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