Synthesis of polyfluorinated terphenyl and styrene derivatives by palladium catalysed C-F bond activation of polyfluoronitroaromatic substrates.

Jade M. Gadsby,[a] Christopher B. McPake,[a] Christopher B. Murray[b] and Graham Sandford[a*]

[a] *Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, U.K.*

[b] *AWE, Aldermaston, Reading, Berkshire, RG7 4PR, U.K.*

Corresponding Author E-mail : Graham.Sandford@durham.ac.uk

Abstract

Short series of polyfluorinated terphenyl and styrene derivatives were synthesised by palladium catalysed carbon-fluorine bond activation processes involving cross coupling reactions of polyfluorinated nitrobenzene and aryl- and vinyl-boron substrates respectively.

Keywords: carbon-fluorine activation, palladium catalysis, cross coupling reaction, perfluoroaromatic, pentafluoronitrobenzene.

1. Introduction

Transition metal catalysed carbon-fluorine activation processes that allow cross coupling reactions between highly fluorinated aromatic systems as the electrophilic partner are still relatively unusual compared to corresponding carbon-halogen or carbon-hydrogen activation processes for carbon-carbon bond formation. However, recently a range of carbon-fluorine activation reactions catalysed by a variety of transition metal catalysts (Pd, Rh, Ni, etc) have been reported to allow, for example, Stille, [1] Suzuki-Miyaura,[2] and borylation [3] processes for highly fluorinated aromatic substrates and the field has now been very comprehensively reviewed recently by Braun and co-workers.[4]

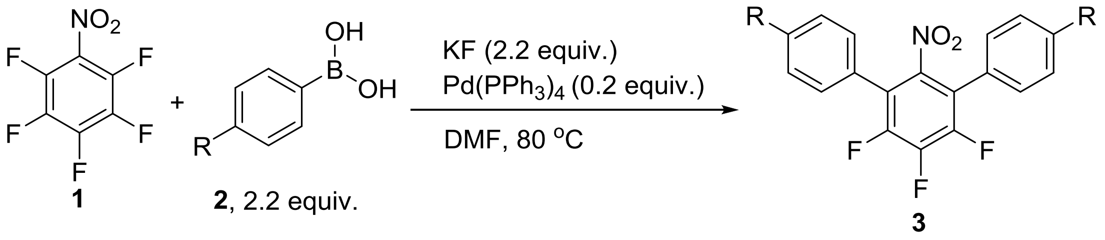
Previously, we demonstrated that highly fluorinated nitrobenzene derivatives could be used as substrates for C-F activation processes activated by inexpensive, commercially available $Pd(PPh_3)_4$ catalyst for the synthesis of various biphenyl [5] and aryl-alkynyl [6] derivatives by sp_2-sp_2 and sp_2-sp Suzuki-Miyaura type cross coupling processes respectively. In this paper, we present the synthesis of some terphenyl and styrene systems by Pd catalysed C-F activation processes involving polyfluorinated nitrobenzene precursors, further extending the use of transition metal catalysed carbon-fluorine bond activation processes. The use of various nickel and palladium catalysts for the cross coupling of highly fluorinated heteroaromatic systems, such as pentafluoro- and 2,3,5,6-tetrafluoro-pyridine, with vinyl-tin based reagents by Stille processes were discussed by Braun [1b, 4] but no analogous processes using vinyl boron derivatives have been reported for the synthesis of polyfluorinated styrene systems.

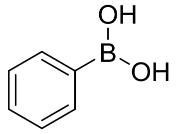
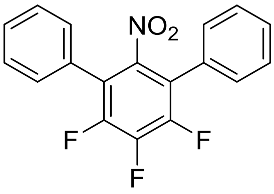
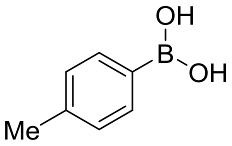
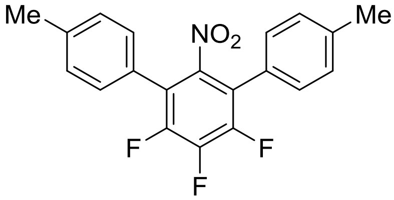
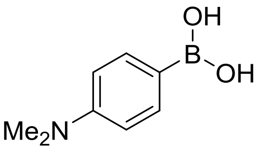
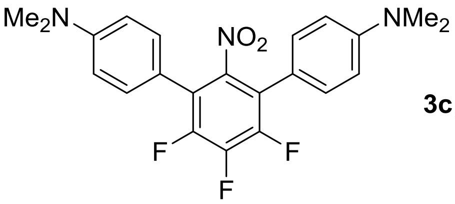
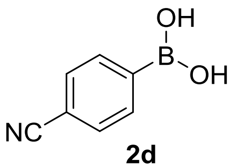
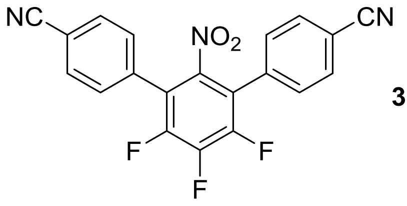
2. Results and discussion

Coupling of pentafluoronitrobenzene **1a** with one equivalent of an aryl boronic acid derivative **2** catalysed by $Pd(PPh_3)_4$ and KF in DMF at 80^oC gives the corresponding biphenyl product arising from substitution of the fluorine atom *ortho* to the activating nitro group as we described previously [5]. Analogous reaction of **1** with 2.2 equivalents gave the terphenyl systems **3** as the only fluoroaromatic products (Table 1). In all cases, activation of positions *ortho* to the nitro group occurs selectively, demonstrating the key role played by the nitro substituent in directing the approach of the palladium catalyst to activated *ortho* positions and subsequent insertion into the carbon-fluorine bond. The structures of **3a** and **3b** were confirmed by X-ray crystallography (Fig.1). The structure **3b** contains two independent molecules with different orientation of the substituents

(Fig 1c). Interestingly, no π…π interactions were found in both structures and the molecules in crystals **3a** and **3b** are linked together by a number of weak interactions of C-H…O and C-H…F type.

Table 1. Synthesis of terphenyl systems **3**



Aryl boronic acid	Terphenyl (Yield)	
 **2a**		**3a**, 52%
 **2b**		**3b**, 38%
 **2c**		**3c**, 36%
 **2d**		**3d**, 18%

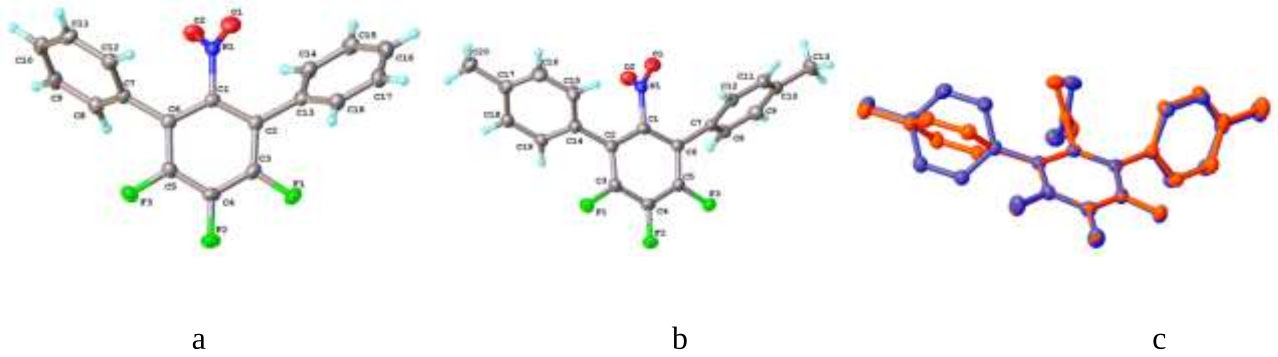
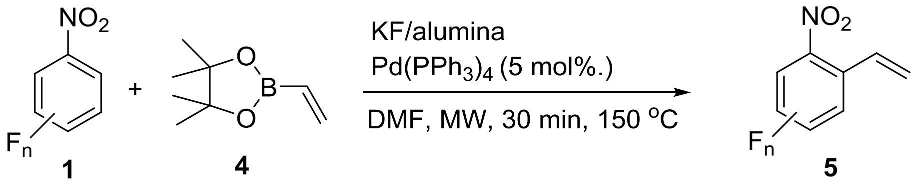
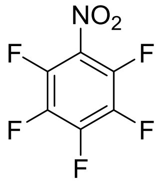
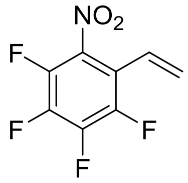
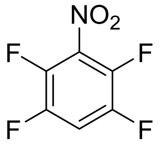
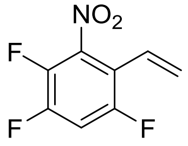
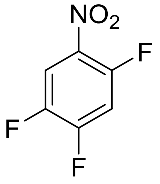
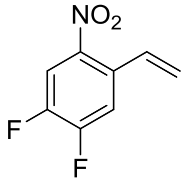
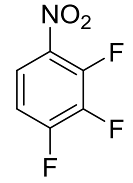
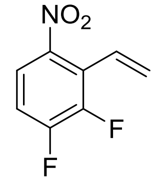
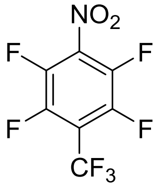
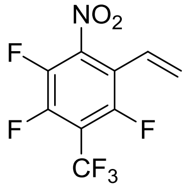


Fig.1. Molecular structures of terphenyl systems **3a** (a) and **3b** (b, one independent molecule is shown) and an overlay of two independent molecules in the structure **3b** (c, H-atoms are omitted for clarity) showing the different conformations of the substituent. All ellipsoids are shown at 50% probability level.

The synthesis of a short series of styrene derivatives **5** was achieved by analogous palladium catalysed cross coupling of fluorinated nitrobenzene derivatives **1** and vinyl borolane substrates **4** (Table 2). Again, in all cases fluorine attached to sites *ortho* to the nitro group were displaced by the vinyl group by Pd catalysed C-F activation following the mechanism we have previously described for related Suzuki-Miyaura processes [5].

Table 2. Synthesis of styrene derivatives **5**



Fluoronitrobenzene	Styrene (Yield)
 **1a**	 **5a**, 68%
 **1b**	 **5b**, 49%
 **1c**	 **5c**, 52%
 **1d**	 **5d**, 74%
 **1e**	 **5e**, 54%

Palladium catalysed C-F bond activation methods, therefore, allow further opportunities for the targeted synthesis of terphenyl **3** and styrene **5** derivatives where the central aryl ring bears several fluorine atom substituents.

3. Experimental

3.1 General

Analysis: Proton, carbon and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz or ^{1}H NMR, 700 MHz; ^{13}C NMR, 176 MHz; ^{19}F NMR, 658 MHz) using solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.36 ppm; ^{19}F NMR, $CFCl_3$ at 0.00 ppm). ^{1}H, ^{13}C and ^{19}F spectroscopic data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), and assignment. Melting points were measured at atmospheric pressure and are uncorrected.

X-ray crystallography: Single crystal X-ray data were collected at 120.0 K on a Bruker SMART CCD 6000 diffractometer (fine-focus sealed tube, graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, 0.3°ω-scan) equipped with a Cryostream (Oxford Cryosystem) cooling device. Both structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using SHELXTL [7] software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1428167 and 1428168.

Chemicals and Solvents: Unless otherwise stated, commercially available reagents were used without purification. MeCN, DMF, THF and Toluene were dried by colorimetric titration whilst anhydrous DMSO and 1,4-dioxane were purchased from Sigma Aldrich. Hexane and DCM were purchased from Fischer and used without further purification. All microwave irradiated reactions were carried out in a Biotage Initiator^{TM} Sixty microwave system (0-400 W at 2.45 GHz). Flash column chromatography was carried out using Fluorochem Silicagel LC60A (40-63 micron).

Synthesis of terphenyl derivatives 3 – General procedure

A flask was charged with phenylboronic acid **2**, potassium fluoride, tetrakis(triphenylphosphine), pentafluoronitrobenzene **1a** and degassed DMF under an atmosphere of dry argon. The reaction was stirred and heated at 80 ^{o}C until complete conversion was observed by ^{19}F NMR analysis. Upon cooling, ethyl acetate (150 mL) was added and the organic layer was washed with water (3 x 150 mL), dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel and further purified by recrystallisation if required to give the terphenyl derivative.

4’,5’,6’-Trifluoro-2’-nitro-1,1’:3’,1’’-terphenyl 3a

Phenylboronic acid **2a** (1.12 g, 9.2 mmol,), KF (0.59 g, 10.2 mmol), tetrakis(triphenylphosphine) (1.08 g, 0.93 mmol), pentafluoronitrobenzene **1a** (1.00 g, 4.7 mmol) and DMF (25 mL), after heating for 36 h and column chromatography on silica gel using hexane:ethyl acetate (4:1) as elutant and recrystallisation (hexane), gave *4’,5’,6’-trifluro-2’-nitro-1,1’:3’,1’’-terphenyl* **3a** (0.80 g, 52%) as a white solid; mp 107.7 - 108.3 ^{o}C (Found: C, 65.62; H, 3.08; N, 4.35. $C_{18}H_{10}F_3NO_2$ requires: C, 65.66; H, 3.06; N, 4.25%); ν_{max}/cm^{-1} 1541.7 and 1379.8 (NO_2); δ_H 7.36 (2H, m, H-2), 7.46 (3H, m, H-3,4); δ_C 120.8 (m, C-3’), 127.9 (d, $^3J_{CF}$ 3.0, C-1), 129.1 (s, C-2), 129.4 (s, C-4), 129.9 (s, C-3), 140.5 (dt $^1J_{CF}$ 256.0, $^2J_{CF}$ 13.6, C-5’), 145.6 (m, C-2’), 147.8 (ddd, $^1J_{CF}$ 256.0, $^2J_{CF}$ 13.6, $^3J_{CF}$ 3.0, C-4’); δ_F -133.15 (2F, d, $^3J_{FF}$ 22.0, F-4’), -154.44 (1F, t, $^3J_{FF}$ 22.0, F-5’); *m*/z (EI$^+$) 329 ([M]$^+$, 39%), 301 (52), 272 (100), 258 (48).

*Crystal data for **3a***: $C_{18}H_{10}F_3NO_2$, M = 329.27, orthorhombic, space group P $2_12_12_1$, a = 6.1320(3), b = 11.5715(5), c = 20.8846(9) Å, U = 2659.5(9) Å^3, F(000) = 968, Z = 4, D_c = 1.476 mg m^{-3}, μ = 0.122 mm^{-1}. 19681 reflections were collected yielding 4340 unique data (R_{merg} = 0.051). Final $wR_2(F^2)$ = 0.0759 for all data (257 refined parameters), conventional R_1 (F) = 0.0320 for 3644 reflections with I ≥ 2σ, GOF = 1.023.

***4',5',6'-Trifluoro-4,4''-dimethyl-2'-nitro-[1,1'; 3',1'']terphenyl* 3b**

4-Tolyboronic acid **2b** (1.38 g, 10.2 mmol), KF (0.60 g, 10.3 mmol), tetrakis(triphenylphosphine) (1.09 g, 0.94 mmol), pentafluoronitrobenzene **1a** (1.00 g, 4.7 mmol) and DMF (25 mL), after heating for 48 h and column chromatography on silica gel using hexane as elutant and recrystallisation (hexane), gave *4',5',6'-trifluoro-4,4''-dimethyl-2'-nitro-[1,1';3',1'']terphenyl* **3b** (0.64g, 38%) as a white solid; mp 124.7 - 125.5 °C (Found: C, 67.16; H, 3.99; N, 3.98. $C_{20}H_{14}F_3NO_2$ requires: C, 67.23; H, 3.95; N, 3.92%); ν_{max}/cm^{-1} 1543.2 and 1381.3 (NO_2); δ_H 2.40 (3H, s, CH_3), 7.20 – 7.30 (4H, m, ArH); δ_C 21.5 (s, CH_3) 120.8 (m, C-3'), 124.9 (d, $^3J_{CF}$ 3.0, C-1), 129.2 (s, C-2), 129.8 (s, C-4), 140.0 (s, C-3), 141.53 (dt, $^1J_{CF}$ 256.3, $^2J_{CF}$ 12.6, C-5'), 145.8 (m, C-2'), 147.7 (ddd, $^1J_{CF}$ 256.3, $^2J_{CF}$ 12.6, $^3J_{CF}$ 3.0, C-4'); δ_F -133.64 (2F, d, $^3J_{FF}$ 22.1, F-4'), -154.77 (1F, t, $^3J_{FF}$ 22.1, F-5'); *m*/z (EI$^+$) 357 ([M]$^+$, 100%), 288 (45), 286 (67), 275 (42), 234 (70).

*Crystal data for **3b***: $C_{20}H_{14}F_3NO_2$, M = 357.32, monoclinicic, space group P 2_1/c, a = 15.3539(4), b = 11.8568(3), c = 19.4111(5) Å, β = 106.91(1)°, U = 3380.98(15) Å^3, F(000) = 1472, Z = 8, D_c = 1.404 mg m^{-3}, μ = 0.113 mm^{-1}. 32819 reflections were collected yielding 8989 unique data (R_{merg} = 0.0267). Final $wR_2(F^2)$ = 0.1286 for all data (581 refined parameters), conventional R_1(F) = 0.0426 for 6729 reflections with I ≥ 2σ, GOF = 1.037.

***4',5',6'-Trifluoro-N^4,N^4,N^{4}'',N^4''-tetramethyl-2'-nitro-[1,1'; 3,1'']terphenyl-4,4''-diamine* 3c**

4-Dimethylaminophenylboronic acid **2c** (1.73 g, 10.5 mmol), KF (0.61 g, 10.4 mmol), tetrakis(triphenylphosphine) (0.55 g, 0.48 mmol), pentafluoronitrobenzene **1a** (1.00 g, 4.7 mmol) and DMF (25 mL), after heating for 43 h and column chromatography on silica gel using hexane: ethyl acetate (4:1) as elutant and recrystallisation (DCM), gave *4',5',6'-trifluoro-N^4,N^4,$N^{4''}$,$N^{4''}$-tetramethyl-2'-nitro-[1,1';3,1'']terphenyl-4,4''-diamine* **3c** (0.69 g, 36%) as a bright orange solid; mp 245.2 - 246.3 °C (Found: $[M]^+$, 415.1502. $C_{22}H_{20}N_3F_3O_2$ requires: $[M]^+$, 415.1503); δ_H 2.99 (12H, s, CH_3), 6.73 (4H, m, H-3''), 7.25 (4H, m, H-2''); δ_C 40.3 (s, CH_3) 112.2 (s, C-3) 114.9 (d, $^3J_{CF}$ 3.0, C-1), 120.9 (m, C-3'), 130.1 (s, C-2), 141.5 (dt, $^1J_{CF}$ 253.7, $^2J_{CF}$ 14.4, C-5'), 146.0 (m, C-2'), 147.3 (ddd, $^1J_{CF}$ 253.7, $^2J_{CF}$ 14.4, $^3J_{CF}$ 3.0, C-4'), 151.0 (s, C-4); δ_F -135.48 (2F, d, $^3J_{FF}$ 23.0, F-4'), -155.79 (1F, t, $^3J_{FF}$ 23.0, F-5'); *m*/z (EI^+) 415 ($[M]^+$, 100%), 184 (32).

4',5',6'-Trifluoro-2'-nitro-[1,1'; 3',1''] terphenyl-4,4''-dicarbonitrile 3d

4-Cyanophenylboronic acid **2d** (1.07 g, 7.3 mmol), KF (0.41 g, 7.1 mmol), tetrakis(triphenylphosphine) (0.39 g, 0.34 mmol), pentafluoronitrobenzene **1a** (0.70 g, 3.3 mmol) and DMF (25 mL), after heating for 48 h and column chromatography on silica gel using hexane as elutant and recrystallisation (DCM and hexane), gave *4',5',6'-trifluoro-2'-nitro-[1,1'; 3',1''] terphenyl-4,4''-dicarbonitrile* **3d** (0.33 g, 18%) as a pale yellow solid; mp 199.0 - 199.8 °C (Found, $[M]^+$, 379.0563. $C_{20}H_8N_3F_3O_2$ requires: $[M]^+$, 379.0562); δ_H 7.49 (4H, m, H-2''), 7.78 (4H, m, H-3''); δ_C 114.5 (s, C-4) 117.9 (s, CN), 119.6 (m, C-3'), 130.2 (s, C-2), 132.1 (s, C-3), 133.0 (s, C-1), 141.8 (dt, $^1J_{CF}$ 259.0, $^2J_{CF}$ 14.5, C-5'), 144.9 (m, C-2'), 148.2 (ddd, $^1J_{CF}$ 259.0, $^2J_{CF}$ 14.5, $^3J_{CF}$ 4.2, C-4'); δ_F -135.39 (2F, d, $^3J_{FF}$ 22.0, F-4'), -151.78 (1F, t, $^3J_{FF}$ 22.0, F-5'); *m*/z (EI^+) 379 ($[M]^+$, 38%), 322 (66), 299 (100), 283 (52), 207 (48), 204 (46).

Synthesis of styrene derivatives – General procedure

The polyfluorinated aromatic derivative **1**, KF/alumina and tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.024 mmol) were placed into a dry microwave vial (2–5 mL), which was then sealed and purged with argon. Degassed, dry DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** were added and the mixture irradiated at 150 ºC for 30 min. The reaction mixture was filtered through silica gel using acetone as the elutant and the organic extracts were evaporated to give the crude product. Purification by column chromatography on silica gel gave the desired styrene derivative **5**.

2-Ethenyl-3,4,5,6-tetrafluoronitrobenzene 5a

Pentafluoronitrobenzene **1a** (0.10 g, 0.5 mmol), KF/alumina (0.08 g, 1.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.02 mmol), DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** (0.09 mL, 0.52 mmol), after column chromatography on silica gel using a mixture of hexane : dichloromethane (4:1) as elutant, gave *2-ethenyl-3,4,5,6-tetrafluoronitrobenzene* **5a** (0.07 g, 68 %) as a pale yellow oil; (Found: $[MH]^+$, 222.0171. $C_8H_3F_4NO_2$ requires: $[MH]^+$, 222.0133); δ_H (400 MHz, $CDCl_3$) 5.80 (1H, d, $^3J_{HHcis}$ 11.7, $=CH_2$), 5.95 (1H, d, $^3J_{HHtrans}$ 17.8, $=CH_2$), 6.44 (1H, dd, $^3J_{HHtrans}$ 17.8, $^3J_{HHcis}$ 11.7, =CH); δ_C (176 MHz, $CDCl_3$) 116.8 (ddd, $^2J_{CF}$ 15.1, $^3J_{CF}$ 4.5, $^4J_{CF}$ 1.0, C-2), 122.0 (d, $^4J_{CF}$ 2.1, $=CH_2$), 126.3 (dd, $^3J_{CF}$ 8.9, $^4J_{CF}$ 1.3, =CH), 134.3 – 134.7 (m, C-1), 139.5 (dm, $^1J_{CF}$ 259.5, C-F), 140.7 (dddd, $^1J_{CF}$ 259.5, $^2J_{CF}$ 13.4, $^3J_{CF}$ 4.7, $^4J_{CF}$ 2.8, C-F), 142.5 (dddd, $^1J_{CF}$ 260.2, $^2J_{CF}$ 17.1, $^2J_{CF}$ 12.3, $^3J_{CF}$ 3.2, C-F), 145.2 (dddm, $^1J_{CF}$ 255.5, $^2J_{CF}$ 11.6, $^3J_{CF}$ 4.7, C-F); δ_F (376 MHz, $CDCl_3$) -139.0 (1F, ddd, $^3J_{FF}$ 21.7, $^4J_{FF}$ 3.9, $^5J_{FF}$ 11.3, F-3), -148.2 (1F, ddd, $^3J_{FF}$ 21.7, $^4J_{FF}$ 5.3, $^5J_{FF}$ 10.8, F-6), -150.4 (1F, td, $^3J_{FF}$ 20.6, $^4J_{FF}$ 5.3, F-4), -153.2 (1F, td, $^3J_{FF}$ 21.0, $^4J_{FF}$ 4.6, F-5); *m/z* (EI^+) 221 ($[M]^+$, 8 %), 204 (60), 191 (100), 176 (44).

2-Ethenyl-3,5,6-trifluoro-nitrobenzene 5b

2,3,5,6-Tetrafluoronitrobenzene **1b** (0.10 g, 0.5 mmol) KF/alumina (0.08 g, 1.4 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.03 mmol), DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** (0.09 mL, 0.56 mmol), after column chromatography on silica gel using hexane : dichloromethane (4:1) as the elutant, gave *2-ethenyl-3,5,6-trifluoro-nitrobenzene* **5b** (0.05 g, 49 %) as a pale yellow oil; (Found: $[M]^+$, 203.0183. $C_8H_4F_3NO_2$ requires:

$[M]^+$, 203.0194); δ_H (400 MHz, $CDCl_3$) 5.72 (1H, d, $^3J_{HHcis}$ 11.7, $=CH_2$), 5.90 (1H, d, $^3J_{HHtrans}$ 17.8, $=CH_2$), 6.42 (1H, dd, $^3J_{HHtrans}$ 17.8, $^3J_{HHcis}$ 11.7, =CH), 7.15 (1H, td, $^3J_{HF}$ 9.7, $^4J_{HF}$ 6.5, H-4); δ_C (176 MHz, $CDCl_3$) 108.0 (dd, $^2J_{CF}$ 28.8, $^2J_{CF}$ 20.8, C-4), 116.2 (ddd, $^2J_{CF}$ 18.7, $^3J_{CF}$ 4.8, $^4J_{CF}$ 1.9, C-2), 122.5 (s, $=CH_2$), 125.0 (dd, $^3J_{CF}$ 9.0, $^4J_{CF}$ 1.8, =CH), 139.6 (m, C-3), 139.8 (ddd, $^1J_{CF}$ 257.2, $^2J_{CF}$ 16.2, $^4J_{CF}$ 4.8, C-6), 148.8 (dm, $^1J_{CF}$ 256.5, C-5), 155.1 (ddd, $^1J_{CF}$ 253.7, $^3J_{CF}$ 9.7, $^4J_{CF}$ 3.5, C-3); δ_F (376 MHz, $CDCl_3$) -113.5 (1F, m, F-3), -131.0 (1F, m, F-5), -151.7 (1F, m, F-6); *m/z* (EI^+) 203 ($[M]^+$, 17 %), 186 (42), 174 (72), 158 (36), 145 (100).

***2-Ethenyl-4,5-difluoronitrobenzene* 5c**

2,4,5-Trifluoronitrobenzene **1c** (0.10 g, 0.6 mmol), KF/alumina (0.09 g, 1.5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.03 mmol), DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** (0.09 mL, 0.6 mmol), after column chromatography on silica gel using hexane : dichloromethane (4:1) as the elutant, gave *2-ethenyl-4,5-difluoronitrobenzene* **5c** (0.054 g, 52 %) as a pale yellow oil; (Found: $[M]^+$,185.0251. $C_8H_5F_2NO_2$ requires: $[M]^+$, 185.0288); δ_H (400 MHz, $CDCl_3$) 5.55 (1H, d, $^3J_{HHcis}$ 10.9, $=CH_2$), 5.70 (1H, d, $^3J_{HHtrans}$ 17.3, $=CH_2$), 7.18 (1H, ddm, $^3J_{HHtrans}$ 17.3, $^3J_{HHcis}$ 10.9, =CH), 7.42 (1H, dd, $^3J_{HF}$ 10.6, $^4J_{HF}$ 7.6, H-3), 7.90 (1H, dd, $^3J_{HF}$ 9.7, $^4J_{HF}$ 7.2, H-6); δ_C (176 MHz, $CDCl_3$) 115.1 (dd, $^2J_{CF}$ 21.8, $^3J_{CF}$ 2.2, C-3), 117.3 (d, $^3J_{CF}$ 9.6, C-2), 120.5 (s, $=CH_2$), 131.5 (s, =CH), 132.2 (dd, $^2J_{CF}$ 21.8, $^3J_{CF}$ 2.2, C-6), 142.8 – 143.2 (m, C-1), 149.1 (dd, $^1J_{CF}$ 254.8, $^2J_{CF}$ 14.0, C-4), 153.4 (dd, $^1J_{CF}$ 258.8, $^2J_{CF}$ 12.7, C-5); δ_F (376 MHz, $CDCl_3$) -127.9 (1F, ddd, $^3J_{FF}$ 21.3, $^3J_{FH}$ 10.4, $^4J_{FH}$ 7.4, F-4), -134.5 – -134.5 (1F, m, F-5); *m/z* (EI^+) 185 ($[M]^+$, 5 %), 168 (78), 156 (86), 140 (38%), 127 (88), 101 (100), 63 (94).

***2-Ethenyl-3,4-difluoronitrobenzene* 5d**

2,3,4-Trifluoronitrobenzene **1d** (0.10 g, 0.6 mmol), KF/alumina (0.09 g, 1.5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.03 mmol), DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** (0.09 mL, 0.56 mmol), after column chromatography on silica gel using hexane : dichloromethane (4:1) as the elutant, gave *2-ethenyl-3,4-difluoronitrobenzene* **5d** (0.077 g, 74 %) as a pale red oil; (Found: $[M]^+$, 185.0239. $C_8H_5F_2NO_2$

requires: [M]$^+$, 185.0288); δ_H (400 MHz, $CDCl_3$) 5.80 (1H, d, $^3J_{HHcis}$ 11.7, $=CH_2$), 5.86 (1H, dd, $^3J_{HHtrans}$ 17.8, $^3J_{HHcis}$ 11.7, $=CH_2$), 6.77 (1H, dd, $^3J_{HHtrans}$ 17.8, $^3J_{HHcis}$ 11.7, =CH), 7.20 (1H, dd, $^3J_{HF}$ 16.4, $^3J_{HH}$ 8.9, H-5), 7.77 (1H, ddd, $^3J_{HH}$ 8.9, $^4J_{HF}$ 4.5, $^5J_{HF}$ 2.1, H-6); δ_C (176 MHz, $CDCl_3$) 115.4 (d, $^2J_{CF}$ 19.0, C-2), 120.3 (s, $=CH_2$), 121.4 (dd, $^3J_{CF}$ 7.9, $^4J_{CF}$ 4.4, C-6), 127.5 (d, $^2J_{CF}$ 18.0, C-5), 133.7 (s, =CH), 140.1 – 141.0 (m, C-1), 147.2 (dd, $^1J_{CF}$ 252, $^2J_{CF}$ 13.8, C-4), 152.0 (dd, $^1J_{CF}$ 258, $^2J_{CF}$ 4.0, C-3); δ_F (376 MHz, $CDCl_3$) -127.5 (1F, ddd, $^3J_{FF}$ 20.0, $^3J_{FH}$ 8.5, $^4J_{FH}$ 4.5, F-4), -136.2 (1F, dd, $^3J_{FF}$ 20.0, $^4J_{FH}$ 4.5, F-3); *m/z* (EI$^+$) 185 ([M]$^+$, 5 %), 168 (64), 156 (80), 140 (46), 127 (74), 63 (100).

***2-Ethenyl-3,5,6-trifluoro-4-(trifluoromethyl)nitrobenzene* 5e**

2,3,5,6-Tetrafluoro-4-(trifluoromethyl)nitrobenzene **1e** (0.10 g, 0.4 mmol), KF/alumina (0.06 g, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (0.04 g, 0.04 mmol), DMF (2.0 mL) and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane **4** (0.06 g, 0.42 mmol), after column chromatography on silica gel using hexane : dichloromethane (19:1) as the elutant, gave *2-ethenyl-3,5,6-trifluoro-4-(trifluoromethyl)nitrobenzene* **5e** (0.06 g, 54 %) as a pale yellow oil; (Found: [M]$^+$, 271.1301. $C_9H_3F_6NO_2$ requires: [M]$^+$, 271.0068); δ_H (400 MHz, $CDCl_3$) 5.81 (1H, d, $^3J_{HHcis}$ 11.8, $=CH_2$), 5.94 (1H, d, $^3J_{HHtrans}$ 17.8, $=CH_2$), 6.44 (1H, dd, $^3J_{HHtrans}$ 17.8, $^3J_{HHcis}$ 11.8, =CH); δ_F (376 MHz, $CDCl_3$) -57.3 (3F, t, $^4J_{FF}$ 22.3, CF_3), -114.0 (1F, qd, $^3J_{FF}$ 22.4, $^4J_{FF}$ 13.8, F-5), -131.2 – -131.5 (1F, m, F-3), -149.1 (1F, m, F-6), *m/z* (EI$^+$) 271 ([M]$^+$, 2 %), 154 (44), 242 (86), 140 (38).

Acknowledgements

We thank AWE (studentship to C.B. McPake) and Durham University M. Chem. Undergraduate Degree Programme for funding and Prof. J.A.K. Howard and Dr. D.S. Yufit for X-ray crystallography.

References

[1] (a) T. Braun, R.N. Perutz, M.I. Sladek, M. I. Chem. Commun. (2001) 2254-2255; (b) T. Braun, J. Izundu, A. Steffen, B. Neumann, H.G. Stammler, J. Chem. Soc., Dalton Trans. (2006) 5118-5123.

[2] (a) A. Steffen, M.I. Sladek, T. Braun, B. Neumann, H.G. Stammler, Organometallics 24 (2005) 4057-4064; (b) T. Schaub, M. Backes, U. Radius, J. Am. Chem. Soc. 128 (2006) 15964-15965.

[3] (a) S.I. Kallaene, M. Teltewskoi, T. Braun, B. Braun, Organometallics 34 (2015) 1156-1169; (b) M. Teltewskoi, J.A. Panetier, S.A. MacGregor, T. Braun, Angew. Chem, 49 (2010) 3947-3951.

[4] T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, Chem. Rev., 115 (2015) 931-972.

[5] M.R. Cargill, G. Sandford, A.J. Tadeusiak, D.S. Yufit, J.A.K. Howard, P. Kilickiran, G. Nelles, J. Org. Chem. 75 (2010) 5860-5866.

[6] M.R. Cargill, G. Sandford, P. Kilickiran, G. Nelles, Tetrahedron 69 (2013) 512-516.

[7] G. M. Sheldrick, Acta Cryst., Sect. A, 64 (2008) 112-122.